Concise

Coordination Chemistry

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Preface

Coordination chemistry is an important and fascinating section of chemistry taught at all undergraduate and postgraduate courses in colleges and universities. Several important theories underlie this subject. During the last three decades, the industrial applications of metal complexes have gained significant importance, especially in the area of catalysis. The scope for further development of such applications is extensive. Several biological processes in the living cells involve metal complexes. Coordination chemistry is a subject which uniquely involves the applications of quantum mechanics, spectroscopy, kinetics, catalysis, biology and industrial chemistry in its delineation. Thus, a clear understanding of coordination chemistry has become a necessity for chemistry students. This book has been written keeping these important aspects of the subject in mind.

The principles of coordination chemistry have been presented in seventeen chapters in a simple fashion with a view to render easy understanding of the subject for the students. The book contains clear line drawings which will be easy for the students to comprehend and reproduce. The unique feature of this book is the inclusion of a chapter on Solved Spectral Problems in Coordination Chemistry, an aspect of this subject normally ignored while teaching in colleges. The Glossary at the end of the book is expected to provide the students a bird's eye-view of the subject by means of clear and simple definitions of the terms used in the chapters. A section on Preparation of Coordination Compounds can be adopted for laboratory work.

The exhaustive Question Bank with selected answers would help students prepare for their examinations. This book has been written in a simple language covering the syllabi prescribed in our colleges and universities for B Sc., B. Sc. (Hons) and M Sc. Courses in chemistry. Though several books are available in the market on this subject, we are convinced that this book is uniquely student-friendly and as such highly usable by the students .The teachers of this subject would find this book useful for teaching the same in a comprehensive manner.

Suggestions from the students and teachers for improving this book in its future editions are welcome and will be gratefully acknowledged.

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We place on record our appreciation to our spouses, Aruna Gopalan and Chandra Ramalingam and our children Rajeev Gopalan, Ganesh Ramalingam, Abirami Ganesh and Suganthi Ramalingam who happily tolerated our "aberration" of authoring books at the expense of domestic duties.

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Chapter 1 Introduction

Coordination chemistry is the study of a class of compounds formed by metals. For example, when an excess of aqueous potassium cyanide is added to aqueous ferrous sulphate; a yellow solution is formed; this reaction is denoted by the equation

$$Fe^{2+} + 6CN^- \longrightarrow [Fe(CN)_6]^{4-}$$

The product $[Fe(CN)_6]^{4-}$ is called a *metal complex ion*; it can be isolated as its potassium salt $K_4[Fe(CN)_6]$. This product is called a *coordination compound*. The formation of a coordination compound from a metal is called *complexation*. The part $[Fe(CN)_6]^{4-}$ in $K_4[Fe(CN)_6]$ is called the *complex species* or *complex entity*. The formula of the complex species is written within bracket [ ].

1.1 CHARACTERISTICS OF COORDINATION COMPOUNDS

1. A coordination compound is a compound of a metal with a certain number of species called ligands bound to the metal. In $[Fe(CN)_6]^{4-}$, the six CN^- groups are called the *ligands*. The word ligand means, 'that which binds or gets attached'. Ligands bind metals. In this example, the ligand is an anion. Many of the ligands are anions; for example CN^-, Cl^- SCN^-, etc. Neutral molecules such as H_2O, CO, NH_3, etc. can also behave as ligands. An organic molecule (such as ethylene diamine $H_2NCH_2CH_2NH_2$) or an organic ion, such as the oxalate ion, ($^-OOC-COO^-$) can also function as a ligand. Normally, a positive ion cannot function as a ligand, as the availability of an electron pair on the ligand for binding with the positive metal is the prime requirement for complex formation.

   A ligand is nucleophilic.

2. Complex species are of different types; cationic, neutral and anionic:

   $[Pt(NH_3)_4]^{2+}$ cationic

   $[Pt(NH_3)_2Cl_2]$ neutral

   $[PtCl_4]^{2-}$ anionic

3. Complexation of a metal ion usually increases the stability of the metallic species; thus the complex of a metal ion is more stable than the metal ion itself. However, different complexes of a metal have different stabilities.
4. Complex formation is often accompanied by striking changes in colour. For example, the complexation of the light yellow, aqueous Fe(III) with SCN^- produces a blood-red colour.
5. The molecules (or ions) of complexes have characteristic shapes such as tetrahedral, square-planar, octahedral, etc. depending on the number of ligands bonded to the central metal.
6. A complex may be diamagnetic or paramagnetic depending on the type of bonding in it.
7. A metal complex differs from an ordinary salt in some respects. When a simple salt such as $FeSO_4$ is dissolved in water, it produces its constituent simple ions, Fe^{2+} and SO_4^{2-}; but when a complex compound is dissolved in a solvent, it produces complex ions. For example, the complex $K_4[Fe(CN)_6]$ produces $[Fe(CN)_6]^{4-}$ on its dissolution in water. The ligands (CN^-) attached to the central metal ion are not easily ionized away from the metal ion. The species $[Fe(CN)_6]^{4-}$, though containing a metal, migrates to the positive electrode (anode) when its solution is electrolysed.
8. Some of the metal complexes are soluble in water whereas the others are insoluble. For example, $[Ag(NH_3)_2]^+$ is soluble whereas the complex of Ni(II) with dimethylglyoxime is insoluble in water. Some complexes are soluble in organic solvents; for example, bis(acetylacetonato)copper(II) is insoluble in water but soluble in organic solvents.

CHRONOLOGY OF COORDINATION CHEMISTRY

- Some metal complexes were prepared and used in the eighteenth century itself, though nothing about their structures was then known. Indian painters used a mixture of metal salts and vegetable extracts as paints for drawing on walls and fabrics. Presumably, the metal ions complexed with the constituents of the vegetable extracts and formed coloured complexes. The earliest well-documented metal complex was Prussian blue, $Fe_4[Fe(CN)_6]_3$. This was used in Germany as the artist's paint in the beginning of the eighteenth century. Then in 1798, Tassart discovered $COCl_3.6NH_3$ This discovery encouraged other chemists to discover many more metal complexes and thus the subject of coordination chemistry progressed. Though several coordination compounds were prepared and their properties studied in the nineteenth century (upto 1893), very little was understood about their structures and the bonding in them.
- In 1893, Werner proposed a theory on these compounds, which for the first time led to a clear understanding of the bonding in such compounds. The development of the quantum mechanical understanding of chemical bonds subsequently resulted in clearer knowledge about the structure and bonding in the coordination compounds.

- The crystal field theory developed in 1930 by the physicists, Van Vleck and Bethe helped understand clearly the magnetic and spectral properties and also the stability of complexes.
- Whatever deficiency existed in the understanding of coordination compounds was mostly removed by the application of the Molecular Orbital Theory and Pauling's Valence Bond Theory.
- The study of organometallic chemistry assumed great significance after the preparation of ferrocene in 1951 by Kealy and Paulson and establishment of its structure by Wilkinson and Fischer. Then, coordination chemistry assumed a vital significance with the development of bio-inorganic chemistry, which is mainly the chemistry of coordination compounds.
- The effectiveness of complexes as catalysts has dramatically improved the efficiency of several industrial processes. Several coordination compounds are now routinely used in industries to benefit mankind.
- The extensive kinetic study on reactions of metal complexes and the applications of several spectroscopic methods to establish their structures have further fine-tuned the understanding of this class of compounds.
- Today, the study of coordination chemistry has become an extensive field of research, with hundreds of research papers being published every month.

1.2 DOUBLE SALTS AND COORDINATION COMPOUNDS

Ferric alum $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$ is called a double salt because it is an addition compound of two stable compounds(ammonium sulphate and ferric sulphate). When crystals of ferric alum are dissolved in water, the solution shows the properties of NH_4^+, SO_4^{2-} and Fe^{3+} ions. The double salt on dissolution breaks down to its component simple ions. Such a salt exists only in the solid state.

Potassium ferrocyanide $K_4[Fe(CN)_6]$, on the other hand, does not break down to simple ions when dissolved in water; its solution consists of K^+ and $[Fe(CN)_6]^{4-}$, the latter being called a complex ion. This complex ion does not break down to Fe^{2+} and CN^- ions in solution. Therefore, $K_4[Fe(CN)_6]$ is called a coordination compound. A complex ion is denoted by writing its formula inside a bracket, [ ]. Metal ions, in particular the transition metal ions, form many complexes. The chemistry of these metal ions in solution is actually the chemistry of their complexes. In $[Fe(CN)_6]^{4-}$, the six CN^- ions are called the ligands and these ligands are said to be *coordinated* to the iron ion. In aqueous solution itself, several metal ions exist as coordinated ions, the H_2O molecules acting as ligands. For example, an aqueous solution of copper sulphate contains the complex ion $[Cu(H_2O)_6]^{2+}$

1.3 COORDINATION NUMBER

The total number of monodentate ligands attached to the central metal in a complex is called the *coordination number*. For example, in the complex ion $[Cu(NH_3)_4]^{2+}$, as four monodentate ligands are attached to the central metal, the coordination number is four. The coordination number equals the number of sigma bonds between the ligands and the central atom.

Coordination number from two to nine are known in complexes (Table 1.1). Of these, 4 and 6 are the common coordination numbers. The coordination number 3 is rare.

Table 1.1 Coordination numbers of some metal ions

Ion	Coordination number	Example
Ag^+	2	$[Ag(NH_3)_2]^+$
Au^+	2	$[AuCl_2]^-$
Tl^+	2	$[TlBr_2]^-$
Cu^+	2, 4	$[CuCl_2]^-$, $[Cu(CN)_4]^{3-}$
Hg^{2+}	3	$[HgI_3]^-$
Au^{3+}	4	$[AuCl_4]^-$
Zn^{2+}	4	$[Zn(CN)_4]^{2-}$
Pd^{2+}	4	$[PdCl_4]^{2-}$
Pt^{2+}	4	$PtCl_4^{2-}$
Al^{3+}	4, 6	$[Al(OH)_4]^-$, $[Al(H_2O)_6]^{3+}$
Cu^{2+}	4, 6	$[Cu(NH_3)_4]^{2+}$, $[Cu(H_2O)_6]^{2+}$
Co^{2+}	4, 6	$[CoCl_4]^{2-}$ $[Co(NH_3)_6]^{2+}$
Ni^{2+}	4, 6	$[Ni(CN)_4]^{2-}$ $[Ni(H_2O)_6]^{2+}$
Fe^0	5	$Fe(CO)_5$
Ca^{2+}	6	$[Ca(H_2O)_6]^{2+}$
Fe^{2+}	6	$[Fe(CN)_6]^{4-}$
Fe^{3+}	6	$[Fe(CN)_6]^{3-}$
Cr^{3+}	6	$[Cr(NH_3)_6]^{3+}$
Co^{3+}	6	$[Co(NH_3)_6]^{3+}$
Pt^{4+}	6	$[PtCl_6]^{2-}$
Pd^{4+}	6	$[PdF_6]^{2-}$
Tl^{3+}	6	$[TlCl_6]^{3-}$
Zr^{4+}	7	$[ZrF_7]^{3-}$
Mo^{4+}	8	$[Mo(CN)_8]^{4-}$
Re^{7+}	9	$[ReH_9]^{2-}$

1.4 OXIDATION NUMBER

This number denotes the charge, the central metal atom would have if all the ligands in the complex were removed along with their electron pairs that were shared with the central atom. It is represented by a Roman numeral. For example, if all the four Cl^- ligands are removed from $[NiCl_4]^{2-}$, then the central atom Ni would have a charge of +2. Then, the oxidation number of this metal in this complex is written as II:

$$\overset{II}{[NiCl_4]^{2-}}.$$

Complex	$[Co(NH_3)_6]^{3+}$	$[Fe(CO)_5]$	$[Zn(CN)_4]^{2-}$	$[Ag(CN)_2]^-$
Coordination number	6	5	4	2
Oxidation number	+3 (III)	0	+2 (II)	+1 (I)

1.5 TYPES OF LIGAND

A ligand is an ion, or a molecule capable of functioning as an electron-donor and therefore participates in the formation of a coordinate bond. The ligands are of different types:

a) A unidentate ligand is one which uses only one atom at a time as the donor atom; this fills only one coordination position of a given cation. The ligands such as Cl^-, Br^-, I^- etc. which contain only one atom each are necessarily unidentate or *monodentate*. The polyatomic ligands such as CN^-, SCN^-, NO_3^-, NO_2^-, etc. are also monodentate. The molecular ligands such as R_3N, pyridine, CO, H_2O etc. are also monodentate. Some unidentate ligands are listed in Table 1.2.

Table 1.2 Some unidentate ligands

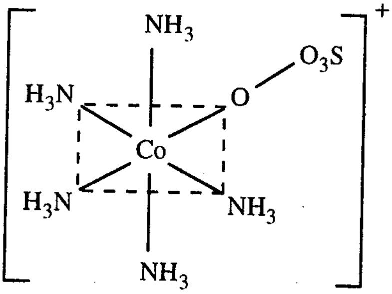
Formula	Name of the ligand
Neutral molecules	
H_2O	aqua
NH_3	ammine
CO	carbonyl
NO	nitrosyl
CH_3NH_2	methylamine
C_5H_5N	pyridine
PPh_3	triphenylphosphine
NH_2NH_2	hydrazine
Et_2O	diethyl ether
Anions	
F^-	fluoro
Cl^-	chloro
Br^-	bromo
I^-	iodo

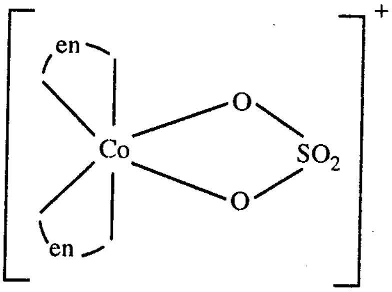
(Contd.,)

Other ambidentate ligands:

CN^-	cyano	$M-CN$
	isocyano	$M-NC$
$S_2O_3^{2-}$	thiosulphato – S	$M-SSO_3$
	thiosulphato – O	$M-OSO_2S$

e) A flexidentate ligand is a polydentate ligand which can bind to a metal with different numbers of its ligand sites. For example, EDTA, though normally functions as a hexadentate ligand, can sometimes function as a pentadentate or a tetradentate ligand; therefore, it is called a flexidentate ligand. Similarly, SO_4^{2-} can function as either a monodentate or a bidentate ligand:





EXERCISES

*1. Explain the following:
   a) $CrCl_3 \cdot 6H_2O$ on dissolving in water gives a white precipitate with $AgNO_3$ (aq). On filtering off the solid and warming the filtrate, the filtrate forms a further quantity of AgCl.
   b) The substance $CoBr_3 \cdot 4NH_3 \cdot 2H_2O$ behaves like a (3+ : 1–) electrolyte in solution; write its correct formula.

2. Rationalize the following:
   a) An aqueous solution of sodium hexaiodoplatinate (IV) is black.
   b) In forming a metal complex, the metal functions as a Lewis acid and the ligand functions as a Lewis base.
   c) Ionic coordination species of opposite charges can combine to form a new coordination species (salt).
   d) A double salt is not a coordination compound.

*3. Cite examples for low coordination numbered complexes.

*4. Arrange the following in the increasing order of molar conductivity:
   a) $Na[Cr(NH_3)_2Cl_4]$ b) $[Cr(NH_3)_3Cl_3]$ c) $Na_3[CrCl_6]$

*5. Match the following:

ion	characteristic coordination number
a) Cu(I)	(i) 4
b) Cu(II)	(ii) 6
c) Fe(III)	(iii) 2

*6. Write the oxidation state of the central metal in each of the following:

a) $[Co(NH_3)_4(NO_2)_2]^+$ b) $K_2[Ni(CN)_2]$

c) $[Fe(CO)_5]$ d) $K[CuBr_2]$

e) $[Cr(ox)_3]^{3-}$ f) $K_3[Co(ox)_2(SO_4)]$

g) $Na[Os(NH_3)_3Cl_3]$ h) $[Fe(en)_2(SCN)_2]Cl$

i) $[Tc(CO)_5]I$ j) $[Co(py)_3SO_4Cl]$

k) $[Pt(en)_3]Br_4$ l) $[Pt(NH_3)_4][PtCl_4]$

7. Write the structure of the ligand *o*-phenylene-bis (dimethylarsine).

8. What is the *denticity* of each of the following ligands?
   a) 1, 10 – phenanthroline
   b) 8 – quinolinate
   c) terpyridine
   d) nitrilotriacetate
   e) salicylaldiminate

* 9. NO_2^- can act as a bridging ligand; depict the different ways by which it can do so with two metal (M) atoms.

10. What is the characteristic coordination number for each of the following? Write a formula to illustrate it:

a) Ag^+ b) Al^{3+} c) Mo^{6+} d) Zn^{2+} e) Au^{3+}

*11. Explain the following:

a) A freshly prepared aqueous solution of $Pt(NH_3)_2Cl_2$ does not conduct electricity.

b) $[Co(NH_3)_6]Cl_3$ causes more freezing point depression than $[Co(NH_3)_5Cl]Cl_2$.

*12. A complex of the composition $PtCl_4(NH_3)_5$ has a molar conductance of 404 siemens. Based on this datum, guess its proper formula.

*13. 0.01 mole of each of the following is dissolved separately in 1000 ml of water; KNO_3, $[Co(NH_3)_6]Cl_3$, $Na_2[PtCl_6]$ and $[Cu(NH_3)_3]Cl_2$. Arrange these in the increasing order of their conductivity.

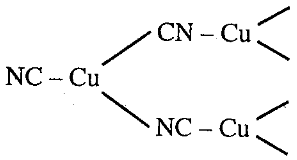
ANSWERS

1. (a) The complex should be $[Cr(H_2O)_5Cl]Cl_2H_2O$ or $[Cr(H_2O)_4Cl_2]Cl.2H_2O$. The Cl^- ions outside the coordination sphere produce AgCl initially. On warming, the H_2O replaces Cl^- from the coordination sphere, the replaced Cl^- forms further precipitate of AgCl.

   (b) $[Co(NH_3)_4(H_2O)_2]Br_3$

3. $[Ag(NH_3)_2]^+$: responsible for the dissolution of AgCl(s) in excess of NH_3 (aq)

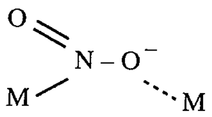
   $[Cu(CN)_2]^-$: exists in solid state in the salt $K[Cu(CN)_2]$; it forms polymers with three-coordinate copper atoms

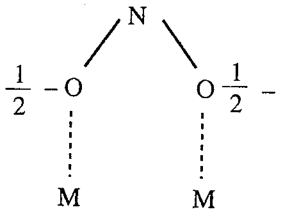


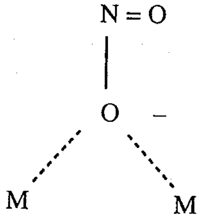
4. b < a < c

   The more the number of ions and the larger the charge on each, the larger is the conductivity.
5. a - iii, b - i, c - ii
6. a) + 3 b) 0 c) 0 d) + 1 e) + 3 f) + 3 g) + 2 h) + 3 i) + 1 j) + 3 k) + 4 l) + 2, + 2

9.







11. a) All the ligands in it are covalently linked; it has no ions in its structure; it does not dissociate into ions on dissolution.
    b) $[Co(NH_3)_6]Cl_3$ is constituted by four ions whereas $[Co(NH_3)_5Cl]Cl_2$ by only three ions; more the number of ions, more is the depression in freezing point.
12. An ion with unit charge has ionic conductance of 65 S at infinite dilution; a doubly charged ion has a conductance of about 130 S and a triply charged ion, 195 S. Based on these values, the ionic conducatnces of MX_1, MX_2 and MX_3 should be (65 + 65), (130 + 2 × 65) and (195 + 3 × 65) S respectively. As the conductnace value of the complex is close to that expected for MX_3, it may be formulated as $[PtCl(NH_3)_5]Cl_3$.
13. $[Cu(NH_3)_2Cl_2] < KNO_3 < Na_2[PtCl_6] < [Co(NH_3)_6]Cl_3$

Chapter 2

Nomenclature of Metal Complexes

The metal complexes are named based on certain rules. These rules were recommended by the International Union of Pure and Applied Chemistry (IUPAC). The names thus given to the complexes are called the *systematic names.*

2.1 COMPLEX CATIONS

a. The name of a complex cation has to begin with the number of ligands followed by the name of the ligand bonded to the central metal atom or ion:
b. This is followed by the name of the metal.
c. The oxidation number (Stock number) of the metal is indicated by Roman numeral in parenthesis.

For example $[Cr(NH_3)_6]^{3+}$ is named as hexaamminechromium(III) ion
a b c

No space should be left between the ligand name and the metal name; similarly, no space should be left between the metal name and the parenthesis. $[Cr(NH_3)_6]^{3+}$ is considered as a single entity similar to the Na^+ ion in NaCl:

NaCl	sodium	chloride
$[Cr(NH_3)_6]Cl_3$	hexaamminechromium(III)	chloride

$BaCl_2$ is named barium chloride and not barium dichloride because the divalency of barium is implied. Similarly, $[Cr(NH_3)_6]Cl_3$ is not named a trichloride but simply a chloride. The first part of the name of the complex, hexaamminechromium(III) automatically indicates that it is a trichloride.

Other examples

$[Cu(NH_3)_4]SO_4$	tetraamminecopper(II) sulphate
$[Fe(H_2O)_6]Cl_3$	hexaaquairon(III) chloride
$[CoSO_4(NH_3)_4]NO_3$	tetraamminesulphatocobalt(III) nitrate

For a metal in zero oxidation state, the symbol(O) is used:

$[Ni(CO)_4]$	tetracarbonylnickel(O)
$[Fe(CO)_5]$	pentacarbonyliron(O)

2.2 COMPLEX ANIONS

When the ligands attached to the metal ion produce a complex negative ion (e.g. $[Fe(CN)_6]^{4-}$, then the suffix *ate* is attached to the name of the metal:

$K_4[Fe(CN)_6]$	potassium hexacyanoferrate(II)
$Na_2[ZnCl_4]$	sodium tetrachlorozincate(II)
$[PtCl_6]^{2-}$	hexachloroplatinate(IV) ion

The names of some complex anions with different metals are given in Table 2.1.

However, complex positive ions or neutral molecules do not have such ending (*ate*):

$[Co(NH_3)_6]^{3+}$	hexaamminecobalt(III) ion
$[Co(NO_2)_3(NH_3)_3]$	trinitrotriamminecobalt(III)

The name of the complex is started with the name of the cation, whether the cation is a simple ion such as Na^+, K^+, etc., or is itself a complex cation such as $[Co(NH_3)_6]^{3+}$.

The complex ion is enclosed in a bracket, [ ]. This is one of the ions expected to be formed in solution when the complex is dissolved in a solvent:

$$[Co(NH_3)_6]Cl_3 \longrightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$$

Table 2.1 Names of complex anions containing metal atoms

Metal	Ending in the name of the complex anion
Ag	argentate
Au	aurate
Al	aluminate
Cr	chromate
Co	cobaltate
Cu	cuprate
Fe	ferrate
Pb	plumbate
Mn	manganate
Ni	nickelate
Sn	stannate
Os	osmate
W	tungstate
Zn	zincate
Pt	platinate
Mo	molybdate
V	vanadate
Ti	titanate

2.3 NAMING LIGANDS

2.3.1 Negative Ligands

The name of a negative ligand ends in - *o* (Table 2.2).

Table 2.2 Names of negative ligands

Formula	Name	Formula	Name	Formula	Name
F^-	fluoro	H^-	hydrido	HS^-	mercapto
Cl^-	chloro	HO^-	hydroxo	Br^-	bromo
O^{2-}	oxo	CN^-	cyano	I^-	iodo
O_2^{2-}	peroxo	NO_2^-	nitro	SO_4^{2-}	sulphato
^-SCN	thiocyanato	$S_2O_3^{2-}$	thiosulphato	CH_3COO^-	acetato
$C_2O_4^{2-}$	oxalato	H_2N^-	amido	HN^{2-}	imido

2.3.2 Neutral Ligands

The neutral ligands are named as such without any special name ending (Table 2.3).

Table 2.3 Names of neutral ligands

Formula	Name	Formula	Name
NH_3	ammine	O_2	dioxygen
H_2O	aqua	N_2	dinitrogen
CO	carbonyl	$H_2NCH_2CH_2NH_2$	ethylenediamine
NO	nitrosyl	C_5H_5N	pyridine

2.3.3 Positive Ligands

The positive ligands are named with an ending *-ium*:

$NH_2-NH_3^+$ hydrazinium

This ligand, though positive can bind through the uncharged nitrogen.

2.3.4 Order of Ligands

1. When a complex contains more than one type of ligand, then the ligands are named in the order, negative ligand, neutral ligand, and positive ligand.

   $[Co(NO_2)_3(NH_3)_3]$ trinitrotriamminecobalt(III).

   $[PtCl_2(H_2O)(NH_2NH_3)]^+$ dichloroaquahydraziniumplatinum(II) ion

   e.g. $\left[PtCl_2\left(Ph_2PH\right)(tu)\right]$
   dichlorodiphenylphosphinethioureaplatinum(II)

   $Na\left[PtBrCl\left(NO_2\right)(NH_3)\right]$
   sodium amminebromochloronitro-N-platinate(II)
2. When a complex contains more than one kind of ligands of similar charges (– ve, + ve, or o), then, the ligands are listed in the alphabetical order:

   $[CrCl_3(NO_2)_3]^{3-}$ trichlorotrinitrochromate(III) ion

   $[Cr(NH_3)_3(H_2O)_3]^{3+}$ triamminetriaquachromium(III) ion.

3. The prefixes, *di, tri, tetra, penta* and *hexa* are used to indicate the number of ligands of the same kind present in the complex:

$[Ag(NH_3)_2]^+$	diamminesilver(I) ion

However, when the name of the ligand itself has a prefix such as di, tri, tetra, etc. then to avoid confusion, prefixes such as *bis* (= di), *tris* (= tri) and *tetrakis* (= tetra) are used to indicate the number of such ligands present in the complex:

$[Cu(en)_2]SO_4$	*bis*(ethylenediamine)copper(II) sulphate
$[Cr(en)_3]Cl_3$	*tris*(ethylenediamine)chromium(III) chloride
$[Ni(PF_3)_4]$	*tetrakis*(phosphorustrifluoride)nickel(O)

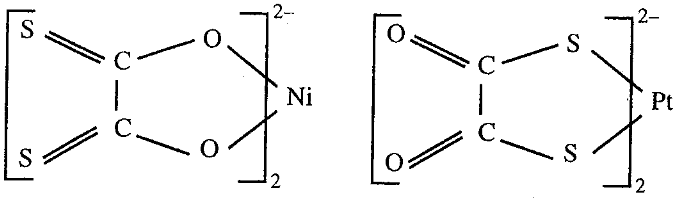
2.3.5 Naming Isomeric Ligands

A type of isomerism among complexes involves attachment of a ligand through different donor atoms of it to the metal. For example, the ligand NO_2^- may be linked to the metal M through N or O. Then, such differences in linkages are indicated by different ligand names:

$M - NO_2$	nitro (nitro–N–)
M – ONO	nitrito (nitro–O–)
M – SCN	thiocyanato (thiocyanato–S–)
M – NCS	isothiocyanato (thiocyanato–N–)

2.3.6 Designating the Ligating Atom in a Polydentate Ligand

A polydentate ligand has more than one donor site; some or all of which may be bonded to the metal. For example, dithiooxalato ligand can bind a metal through its two oxygen atoms or two sulphur atoms. The mode of binding is indicated by the atom symbols:



bis*(dithiooxalato – O,O')*
nickelate(II)

bis(dithiooxalato – S,S')
platinate(II)

Fig. 2.1

2.4 NONIONIC COMPLEXES

Nonionic or molecular complexes are given a one-word name:

$[Fe(NH_3)_3(CO)_3]$	triamminetricarbonyliron(O)
$[Co(NO_2)_3(NH_3)_3]$	trinitro-N-triamminecobalt(III)

2.5 POLYNUCLEAR COMPLEXES

A complex molecule formed with two or more metal ions per molecule is called a polynuclear complex. Usually, the two metal ions in it are bridged by ligands. Such bridging ligands are indicated by the prefix μ-:

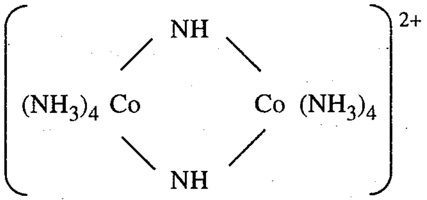


Fig. 2.2 *tetraamminecobalt(III)di-μ-imidotetraamminecobalt(III) ion.*

If there are two or more bridging ligands of the same type, this is indicated by di-μ, tri-μ, etc. If there are two or more bridging ligands of different types, then the prefix μ is used for each such bridging ligands which are listed in alphabetical order. For example, the complex denoted below is named as tetramminecobalt(III)- μ-amido-μ-hydroxo- tetramminecobalt(III) ion:

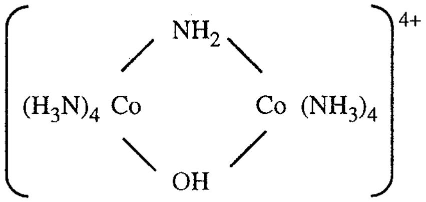
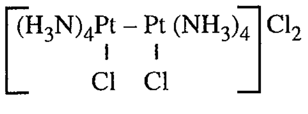


Fig. 2.3

2.5.1 Complexes with Metal-Metal Bond

In a complex containing a metal-metal bond, the prefix *bi-* (or *di-*) is introduced before the name of the metal involved in the metal-metal bond.

Examples:



$$\left[\begin{array}{c}(H_3N)_4\underset{\displaystyle Cl}{\underset{|}{Pt}} - \underset{\displaystyle Cl}{\underset{|}{Pt}}(NH_3)_4\end{array}\right]Cl_2$$

sym-dichlorooctaammine*bi*-platinum(II)

The metal-metal bonding in a complex may be indicated by italicised symbols of the metals;

$[Br_4ReReBr_4]^{2-}$	bis(tetrabromorhenate) (*Re-Re*)(2-)
$[Mn_2(CO)_{10}]$	bispentacarbonylmanganese (*Mn-Mn*) (decacarbonyldimanganese)

The symbols of the metal are enclosed in parenthesis, placed after the list of central atoms and before the ionic charge.

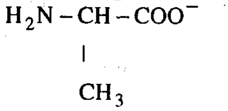
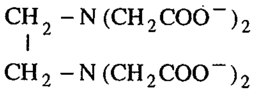
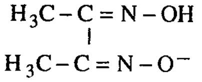
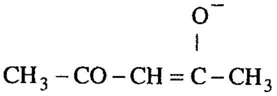
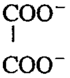
In the *Ewens – Bassett system of nomenclature*, the overall charge of the complex ion is indicated by Arabic numeral followed by the sign both within parenthesis.

e.g. : $K_3[Fe(CN)_6]$ potassium hexacyanoferrate (3–)

2.6 ABBREVIATIONS FOR LIGAND NAMES

Some of the ligands, especially those with long organic names are indicated by their abbreviated names for convenience (Table 2.4).

Table 2.4 Abbreviations for ligands

Name	Abbreviation	Formula
Ethylenediamine	en	$H_2N-CH_2-CH_2-NH_2$
Propylenediamine	pn	$CH_3-CH(NH_2)CH_2-NH_2$
Trimethylenediamine	tn	$H_2N-CH_2-CH_2-CH_2-NH_2$
Diethylenetriamine	dien	$H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH_2$
Glycinato	gly	$H_2N-CH_2-COO^-$
Alaninato	ala	 $\begin{array}{l} H_2N-CH-COO^- \\ \qquad \vert \\ \qquad CH_3 \end{array}$
Pyridine	py	C_5H_5N
Ethylenediamminetetra-acetato	EDTA	 $\begin{array}{l} CH_2-N(CH_2COO^-)_2 \\ \vert \\ CH_2-N(CH_2COO^-)_2 \end{array}$
Dimethylglyoximato	DMG	 $\begin{array}{l} H_3C-C=N-OH \\ \qquad \vert \\ H_3C-C=N-O^- \end{array}$
Thiourea	tu	$H_2N-CS-NH_2$
Triethylenetetramine	trien	$H_2N-C_2H_4-NH-C_2H_4-NH-C_2H_4-NH_2$
Acetato	Ac	CH_3COO^-
Cyclopentadienyl	cp	$C_5H_5^-$
Acetylacetonato ion	acac	 $\begin{array}{r} O^- \quad\ \\ \vert \quad\ \\ CH_3-CO-CH=C-CH_3 \end{array}$
Bipyridine	bipy	$(C_5H_4N)_2$
1,10 - Phenanthroline	*o*-phen	$C_{12}H_8N_2$
Oxalato	ox	 $\begin{array}{l} COO^- \\ \vert \\ COO^- \end{array}$
Triphenylphosphine	PPh_3	$(C_6H_5)_3P$
8-Hydroxyquinalinato	oxin	C_9H_6NO
Nitrilotriacetato	NTA	$N(CH_2COO^-)_3$

2.7 CHEMISTS' NAMES FOR COMPLEXES

Some of the metal complexes are named after the chemists who first prepared these (Table 2.5).

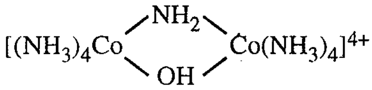
Table 2.5 Metal complexes named after chemists

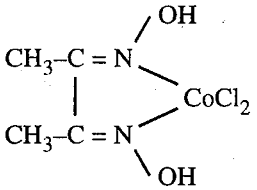
Name	Formula
Zeise's salt	$K[Pt(C_2H_4)Cl_3]$
Magnus green salt	$[Pt(NH_3)_4][PtCl_4]$
Edmann's salt	$K[Co(NH_3)_2(NO_2)_4]$
Reinecke's salt	$NH_4[Cr(NH_3)_2(NCS)_4]$
Vaska's complex	$[Ir(CO)(PPh_3)_2Cl]$
Wilkinson's catalyst	$[Rh(PPh_3)_3Cl]$

EXERCISES

1. Write the formula of the complex species formed in each of the following:
   a) metallic copper is dissolved in aqueous KCN
   b) metallic gold is dissolved in aqua regia
   c) con. HCl is added to $CuSO_4$ (aq)
   d) KCN (aq) is added to CuS (s)
   e) pyridine is added to $CuSO_4$ (aq)
2. a) Write the name of the complex $K_2Pb[Co(NO_2)_6]$
   b) What is the oxidation state of Co in this?
   c) How many types of ions would it produce on dissolving it in a suitable solvent?

*3. Name the following complexes:
   a) $[(NH_3)_5Cr-OH-Cr(NH_3)_5]Cl_2$
   b) $[(CO)_3Fe(CO)_3Fe(CO)_3]$
   c) $[Cr(EDTA)]^-$
   d) $[Ni(CO)_3py]$
   e) $(NH_4)_3[ZrF_7]$
   f) $[Ni(NH_3)_6]_3[Co(NO_2)_6]_2$

*4. Name the following complexes:
   a) $[Co(NH_3)_5CO_3]Cl$
   b) $[Pt(NH_2CH_2CH_2NH_2)_3]Br_4$
   c) $Na[B(NO_3)_4]$
   d) $[Cr(NCS)_4(NH_3)_2]^-$
   e) 
   $[(NH_3)_4Co\overset{NH_2}{\underset{OH}{\rightleftarrows}}Co(NH_3)_4]^{4+}$

f) 

*5. Draw the structure of the following:
trans – diamminetetraisothiocyanatochromate (III)

6. Write the names of the following complexes:
   - a) $[Rh(CO)H(PR_3)_2]$
   - b) $[CoCl_2(en)(NH_3)_4]^+$
   - c) $[AuCl(dien)]^{2+}$
   - d) $Nb_2Cl_6(PMe_3)_4$
   - e) $[Ru(C_4H_4)(CO)_3]$
   - f) $[VO(H_2O)_5]^{2+}$
   - g) $[NiI_2(PHPh_2)_2]$
   - h) $[Co(N_2H_4)_6]Cl_2$
   - i) $[Cr(NH_3)_6][Co(CN)_6]$
   - j) $[Pb\{SC(NH_2)_2\}_6]^{2+}$
   - k) $[Co(NH_3)_5CO_3]^+$

*7. Write the formula / structure of the following:
   - a) diammine*tetrakis*(isothiocyanato)chromate(III)
   - b) tris(ethylenediamine)rhodium(III) ion
   - c) bis(acetylacetone)ethylenedi-iminecopper(II)
   - d) sulphatopentamminecobalt(III) chloride

8. Write the formulae with the over-all electrical charge of the coordination complexes containing the following species:
   - a) Co(III) with one oxalate ligand, one NH_3 ligand and three NO_2^- ligands.
   - b) Pt(IV) with two NH_3 ligands, two H_2O ligands and two F^- ligands.
   - c) Co(0) with one H^- ligand and five CO ligands.

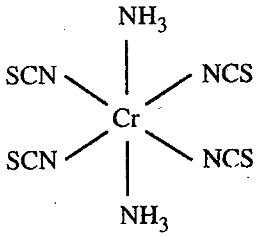
9. Write the structure of the metal complex formed between
   - a) Cu(II) and glycinate ions
   - b) Mg(II) and EDTA
   - c) Fe(II) and *o*-phen
   - d) Pb(II) and thiourea.

ANSWERS

3. a) µ-hydroxo-bis[pentamminechromium(III)] chloride
   - b) tri-µ-carbonyl-bis(tricarbonyliron)
   - c) ethylenediaminetetracetatochromate(III)
   - d) tricarbonylpyridinenickel(O)
   - e) ammonium heptafluorozirconate(IV)
   - f) hexamminenickel (II) hexanitrocobaltate(III)

4. a) pentamminecarbonatocobalt(III) chloride
   - b) tri(ethylenediamine)platinum (IV) bromide
   - c) sodium tetranitratoborate (III)
   - d) diamminetetrakis(isothiocyanato)chromate (III) ion
   - e) octa-ammine-µ-amido-µ-hydroxo-dicobalt (III) ion
   - f) dichlorodimethylglyoxime – N, N'-cobalt (II)

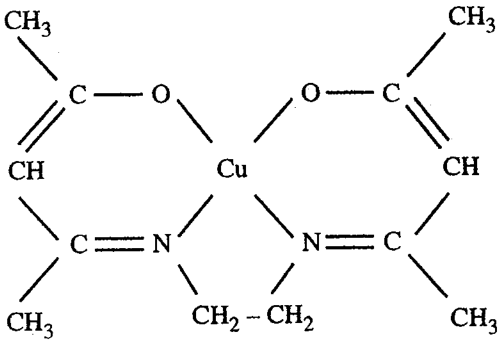
5.



7. a) $[Cr(NCS)_4(NH_3)_2]^-$

   b) $[Rh(en)_3]^{3+}$

   c)



   d) $[Co(NH_3)_5SO_4]Cl$

Chapter 3

Theories of Coordination Compounds I

The bonding between the metal and the ligands and also the properties of complexes are explained by some theories.

3.1 EARLY STRUCTURAL THEORIES

3.1.1 Blomstrand-Jorgensen's Chain Theory

This theory is only of historical importance. Blomstrand along with his student Jorgensen developed the chain theory in order to explain the existence of metal complexes. At that time, there was a belief that elements had only one kind of valence. Hence, considering $CoCl_3.6NH_3$ they proposed that there could be only three bonds to cobalt(III) in its complexes. As a consequence, a chain structure [Fig. 3.1(a)] was suggested to account for the additional six ammonia molecules in $CoCl_3.6NH_3$.

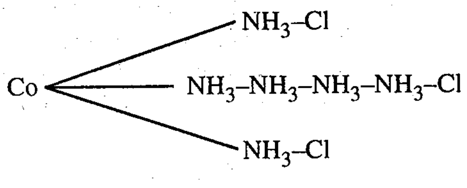


Fig. 3.1(a)

Since the three chlorides are separated by some distance from cobalt, they are assumed to be less tightly bound to cobalt. Hence all the three chlorides are readily precipitated as AgCl on the addition of $AgNO_3$ solution. This is in agreement with the experimental fact. On the basis of this theory, $CoCl_3.5NH_3$ [Fig. 3.1(b)] is represented as

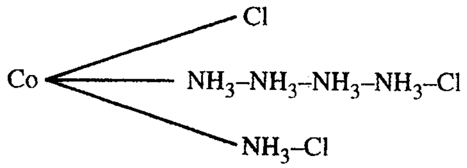


Fig. 3.1(b)

In this structure, the chloride which is directly attached to cobalt is very tightly bound to it. Hence only 2/3 of its chloride content should get precipitated as AgCl on treatment with $AgNO_3$ solution. This is also in agreement with the experimental fact. Structure [Fig. 3.1(c)] for $CoCl_3.4NH_3$ is also in accordance with experiments which show that two of the chlorides are more tightly held than the third one. They did not succeed in preparing the next member of this series, namely, $CoCl_3.3NH_3$. However, they were able to prepare the analogous iridium complex. $IrCl_3.3NH_3$ [Fig. 3.1(d)]. It was represented as

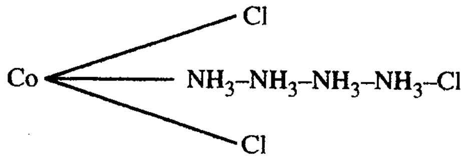


Fig. 3.1(c)

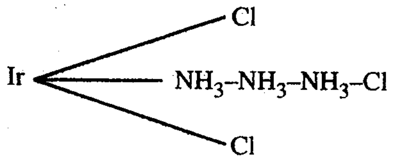


Fig. 3.1(d)

The chloride that is not directly linked to iridium should be less tightly bound to the central metal according to this theory. This means that 1/3 of its chloride content should be precipitated as AgCl on the addition of $AgNO_3$ solution. But a solution of this compound did not give any precipitate of AgCl. Thus, this chain theory was proved to be incorrect in this case and also in several other metal complexes.

3.1.2 Werner's Coordination Theory

In 1893, Alfred Werner, at the age of 26, proposed a theory which is now referred to as *Werner's Coordination Theory*. His theory is a guiding principle in the concept of valence in inorganic chemistry. The well-known concept of "primary" and "secondary" valencies in metal complexes has been developed by him.

ALFRED WERNER

Alfred Werner was a Swiss chemist (1866–1919). Though metal complexes were known to chemists even before his time, very little was known about the bonding in and structure of such compounds. Werner was the first in successfully explaining these aspects of complexes. His theory on coordination compounds, now called Werner's theory was proposed by him by applying the theory of electrolytic dissociation and the principles of structural chemistry ingeniously to these compounds. Werner's theory triggered the imagination of the other chemists, subsequent to his time, in proposing advanced theories on metal complexes. His theory and pioneering experimental work on metal complexes won for him the Nobel Prize for Chemistry in 1913. Werner was the first *inorganic* chemist to be awarded the Nobel Prize in chemistry.

Postulates of Werner's theory

(1) Generally, elements exhibit two types of valencies, namely *primary valence* and *secondary valence*. The primary valence is also known as *ionisable valence* and secondary valence is otherwise known as *nonionisable valence*. Anions can satisfy primary valence whereas anions or neutral molecules can satisfy secondary valence. In modern terms, the primary valence corresponds to the oxidation number and the secondary valence corresponds to the coordination number.

(2) All elements tend to satisfy both primary and secondary valences. But in every case the fulfilment of secondary valence appears to be more essential. For example, in $CoCl_3.4NH_3$, two of the three chloride ions are attached by secondary valence and hence it is represented as $[Co(NH_3)_4Cl_2]Cl$.

(3) The secondary valences are directed towards some fixed positions in space. For example, in 4-coordinated complexes the four valences are arranged in either a planar or a tetrahedral manner and in 6-coordinated complexes the 6 valences are directed towards the six corners of an octahedron.

Werner extensively studied the chloramminecobalt(III) complexes to substantiate his theory. The experimental observations collected by him on these complexes are tabulated in Table 3.1.

Table 3.1 Werner's cobalt complexes

Complex	No.of Cl^- ions precipitated as AgCl	Formula	No.of ions in solution	Molar conductivity (Ohm^{-1})
$CoCl_3.6NH_3$ **(A)**	3	$[Co(NH_3)_6]Cl_3$	4	~ 404
$CoCl_3.5NH_3$ **(B)**	2	$[Co(NH_3)_5Cl]Cl_2$	3	~ 229
$CoCl_3.4NH_3$ **(C)**	1	$[Co(NH_3)_4Cl_2]Cl$	2	~ 97
$CoCl_3.3NH_3$ **(D)**	0	$[Co(NH_3)_3Cl_3]$	0	0

Werner's theory predicts structure shown in Fig. 3.2(d) for the next member of the series, $CoCl_3.3NH_3$ and it is formulated as $[Co(NH_3)_3Cl_3]$. This theory also predicts that

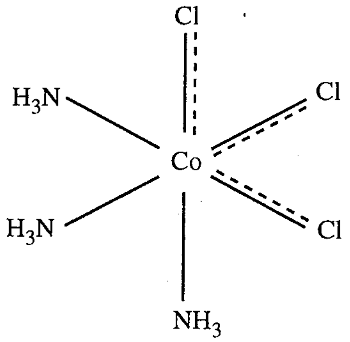


Fig. 3.2(d)

this complex will not yield any chloride ion in solution. Actually, no chloride ion is precipitated as AgCl on treating it with $AgNO_3$ solution. It is a non-electrolyte in solution because no ions are produced in solution.

Defects of Werner's theory

1. (1) Werner's theory describes the structures of many coordination compounds successfully; however, it does not explain the nature of bonding within the coordination sphere.
2. (2) More than 90% of the known complexes at Werner's time were either 4-coordinated or 6-coordinated. Werner's theory is unable to account for the preference for 4-and 6-coordination among complexes.
3. (3) Werner's theory fails to account for the fact that certain 4-coordinated complexes are square-planar whereas some others are tetrahedral.

3.1.3 Sidgwick's Electronic Concept of Coordination

Sidgwick in his theory used the Lewis concept of the covalent bond between two atoms in a molecule. He introduced a new concept of *coordinate bond*, also called *dative bond* or *semipolar bond*. According to him, the ligands donate electron pairs to the central metal ion to form coordination compounds. These ligands are known as the *donors* and the central metal ions are known as the *acceptors*. The bonds formed between the donors and acceptors are called *coordinate* or *dative* or *semipolar bonds*, which are not very different from a covalent bond. The coordinate bond formed is generally represented by an arrow starting from the donor pointing towards the acceptor as $L \rightarrow M$, where M is the acceptor and L is the donor of electrons. For example, the complex ion, $[Cr(NH_3)_6]^{3+}$ can be represented as:

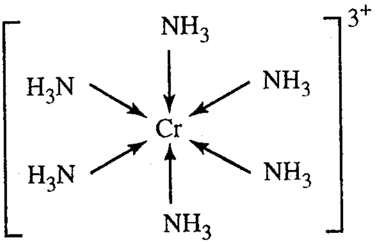


Fig. 3.3

Sidgwick's effective atomic number rule (EAN rule) The Effective Atomic Number rule is also known as the *18-electron rule* (or) *noble gas rule.* According to Sidgwick, the total number of electrons around the central metal ion, including those gained through coordination by the ligands is known as the *Effective Atomic Number* (EAN) of the central metal ion. In many cases this number is equal to the atomic number of the next higher inert gas. Such coordination compounds are said to obey the EAN rule.

EAN for a central metal ion is obtained as follows :

EAN = Atomic number of the central metal ± the number of electrons gained or lost in ion formation + the number of electrons gained through coordination.

Some examples of complexes that obey EAN rule are given in Table 3.2

Table 3.2 Complexes that obey EAN rule

Complex	Central metal M	At. No. of M	Oxidation number of M	Electrons gained through coordination	EAN	At. No. of the next higher inert gas
$[Ni(CO)_4]$	Ni	28	0	8	28 – 0 + 8 = 36	36
$[Fe(CO)_5]$	Fe	26	0	10	26 – 0 + 10 = 36	36
$[Fe(CN)_6]^{4-}$	Fe	26	2+	12	26 – 2 + 12 = 36	36
$[Co(NH_3)_6]^{3+}$	Co	27	3+	12	27 – 3 + 12 = 36	36
$[Zn(NH_3)_4]^{2+}$	Zn	30	2+	8	30 – 2 + 8 = 36	36
$[V(CO)_6]^-$	V	23	1–	12	23 + 1 + 12 = 36	36

There are exceptions to this rule. Some of these exceptions are given in Table 3.3

Table 3.3 Complexes that do not obey EAN rule

Complex	Central metal M	At. No. of M	Oxidation number of M	Electrons gained through coordination	EAN	At. No. of the next higher inert gas
$[V(CO)_6]$	V	23	0	12	23 – 0 + 12 = 35	36
$[Mn(CN)_4]^{2-}$	Mn	25	2+	8	25 – 2 + 8 = 31	36
$[Fe(CN)_6]^{3-}$	Fe	26	3+	12	26 – 3 + 12 = 35	36
$[Co(NH_3)_6]^{2+}$	Co	27	2+	12	27 – 2 + 12 = 37	36
$[Ni(NH_3)_6]^{2+}$	Ni	28	2+	12	28 – 2 + 12 = 38	36

Defects of Sidgwick's theory Sidgwick's electronic theory is also not free from defects. Some of the defects of this theory are listed below:

(1) The donation of electrons by the ligands to the central metal ion would cause an accumulation of unfavourable negative charge over the electropositive central metal. This will reduce the stability of the complex.

(2) The electron pair donated by H_2O, NH_3 etc. to the central metal ion is $2s^2$ pair of electrons. This $2s^2$ pair has no bonding characteristics. In order to make them useful for bonding purpose, these electrons should be promoted to higher energy level. This requires more energy than what is usually available in the bond formation.

(3) According to Sidgwick, coordination compounds must be covalent. But there are complexes which are predominantly ionic in nature. Hence, the forces acting between the central metal ion and the ligands may be regarded as essentially electrostatic.

3.2 LATER STRUCTURAL THEORIES

The structural theories, based on modern principles of bonding are

(i) The Valence Bond Theory
(ii) The Crystal Field Theory
(iii) The Molecular Orbital Theory

According to Werner's theory, it seemed reasonable that ligands donate electron pairs to metal ions or atoms to form coordinate linkages. This approach was first applied to coordination compounds by Linus Pauling and Slater (1935). Their theory is primarily concerned with the shapes and magnetic behaviour of metal complexes. This theory is called *Pauling's Theory of Complexes* or *Valence Bond Theory* (VBT). It is somewhat successful in describing and predicting some of the chemical and physical properties of complexes known at that time. But towards the end of 1950's, some facts which were not easily explained by this theory became known. At this stage another theory called the *Crystal Field Theory* (CFT) revived from the early work of J.H.Van Vleck and H.Bethe, both physicists was proposed. This theory is useful in describing metal-ligand interaction and is especially helpful in explaining the visible absorption spectra of metal complexes. During the same period, the *Molecular Orbital Theory* abbreviated as MOT was also developed.

Each theory has advantages and disadvantages. In principle, the MOT is the most exact one, but, calculations and predictions involved in it are difficult. Since more than 95% of the known complexes are either 4-coordinated with planar or tetrahedral configuration or 6-coordinated with octahedral configuration, these theories are usually discussed with reference to these complexes. The VBT is described in this chapter whereas the other two theories are described in the next chapter.

3.2.1 The Valence Bond Theory

This theory involves the following assumptions or postulates:

(1) The central metal makes available a number of vacant orbitals equal to its coordination number for the formation of covalent bonds with the ligand orbitals.

(2) A covalent bond is formed by the head-on overlap of a vacant metal orbital and a filled ligand orbital:

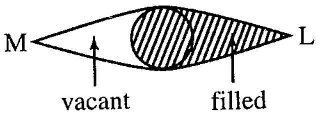


Fig. 3.4 *M – L σ bond formation*

(the unshaded orbital indicates that it is empty and the shaded orbital indicates that it is filled with two electrons). This head-on overlap leads to the formation of M-L, σ bond.

(3) In addition to the σ bond, there is the possibility of a π bond formation due to the side-ways overlapping of a filled metal orbital with a suitable vacant ligand orbital:

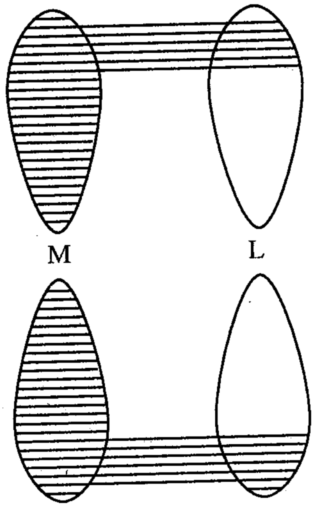


Fig. 3.5 *M-L, π bond formation*

(4) A strong covalent bond is formed only when the orbitals overlap to the maximum extent. This maximum overlapping is possible only when the metal vacant orbitals undergo a process called *hybridisation.* A hybridised orbital has a better directional characteristics than an unhybridised one.

Numerous combinations of *s,p* and *d* orbitals are possible for hybridisation giving rise to different spatial geometries. But in practice only a few are encountered in metal complexes. Table 3.4 gives the coordination number, orbital hybridisation, spatial geometry and examples for some of the more important geometries.

Table 3.4 Types of hybridisation in metal complexes

Coordination number	Type of hybridisation	Geometry	Example
2	sp	linear	$[Ag(NH_3)_2]^+$
3	sp^2	triangular planar	$[HgI_3]^-$
4	sp^3	tetrahedral	$[Ni(CO)_4]$
4	dsp^2	square-planar	$[Ni(CN)_4]^{2-}$
5	dsp^3	trigonal bipyramid	$[Fe(CO)_5]$
6	d^2sp^3	octahedral	$[Co(NH_3)_6]^{3+}$
6	sp^3d^2	octahedral	$[CoF_6]^{4-}$

VBT VIGNETTE

- According to VBT, complex formation essentially involves reaction between Lewis bases (ligands) and a Lewis acid (metal or metal ion).
- A coordinate-covalent bond is formed between the ligands and metal.
- The theory utilizes hybridisation of *s*, *p* and *d* orbitals of the metal to account for the observed structures and magnetic properties of complexes. The converse, namely, the geometry may be arrived at from the measured magnetic moment. This interrelationship is called the *magnetic criterion of bond type*.
- The theory helps predict the geometry of a four-coordiniate d^8 complex if its magnetic properties are known; diamagnetic implies square-planar; paramagnetic, tetrahedral.

Spin-only magnetic moment A species having at least one unpaired electron in it is said to be *paramagnetic*. It is attracted by an external magnetic field. Theoretically, the paramagnetic moment of an ion can be calculated from its number of unpaired electrons using the following *spin-only* formula (it does not take into account the orbital angular momentum):

$$\mu_s = \sqrt{n(n+2)}\ \text{BM}$$

where μ_s = spin-only magnetic moment
n = number of unpaired electrons

BM = Bohr magneton, the unit which expresses the magnetic moment.

When the species does not contain any unpaired electron, it is *diamagnetic*.

Some *spin-only* magnetic moments in BM and the corresponding number of unpaired electrons are given in Table 3.5.

Table 3.5 Spin-only magnetic moments of metal complexes

No.of unpaired electrons	Spin-only moment (BM)
1	$\sqrt{3} = 1.73$
2	$\sqrt{8} = 2.83$
3	$\sqrt{15} = 3.87$
4	$\sqrt{24} = 4.90$
5	$\sqrt{35} = 5.92$

The valence bond theory may now be applied to

(a) tetrahedral complexes,
(b) square-planar complexes and
(c) octahedral complexes.

(a) Tetrahedral complexes Considering the 4-coordinated complex ion, $[Ni(NH_3)_4]^{2+}$, it is found to be paramagnetic with a moment of 2.83 BM. The central metal ion in this complex is Ni^{2+}. To guess the shape of the complex, first the number of *d* electrons in the metal ion should be known. This is arrived at as follows:

No. of *d* electrons = At. No. of central metal – number of electrons lost in ion formation – At. No. of previous inert gas

This method is applicable for the first and second row transition elements. For the third row transition elements, in addition, the number fourteen should be subtracted.

Then, these *d* electrons are arranged in the *d* orbitals in such a way that the arrangement gives the number of unpaired electrons which accounts for the observed magnetic moment. From the electronic distribution, an idea about the available empty metal orbitals is obtained. For guessing the hybridisation, we have to use a number of empty metal orbitals equal to its coordination number. From the type of hybridisation we can predict its geometry or shape.

For Ni^{2+} in the complex $[Ni(NH_3)_4]^{2+}$, the number of *d* electrons is, 28 – 2 – 18 = 8. Hence Ni^{2+} belongs to the d^8 system. The observed magnetic moment of 2.83 BM corresponds to two unpaired electrons. Now these eight *d* electrons are arranged in the 3*d* orbitals in such a way that it gives two unpaired electrons:

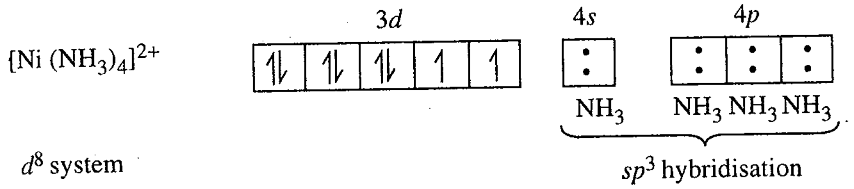


Fig. 3.6

This electronic distribution accounts for the observed magnetic moment (2.83 BM). Since the coordination number of nickel in this complex is four, the next four higher vacant orbitals are required for hybridisation. This corresponds to sp^3 hybridisation. Hence the geometry of the complex $[Ni(NH_3)_4]^{2+}$ is tetrahedral. In the VB diagram the single headed arrows (↿) represent metal *d* electrons and dots (:) represent electrons donated by NH_3 ligands.

The other examples of tetrahedral complex molecules and ions are given in Table 3.6.

Table 3.6 Tetrahedral (sp^3 hybridised) complexes

Complex	Magnetic character
$[Ni(CO)_4]$	diamagnetic
$[NiCl_4]^{2-}$	paramagnetic (2.83 BM)
$[MnCl_4]^{2-}$	paramagnetic (5.92 BM)
$[Zn(NH_3)_4]^{2+}$	diamagnetic
$[FeCl_4]^-$	paramagnetic (5.92 BM)
$[BeF_4]^{2-}$	diamagnetic
$[CoCl_4]^{2-}$	paramagnetic (3.87 BM)
$[Cu(py)_4]^+$	diamagnetic

(b) Square-planar complexes Another possible geometry for the 4-coordinated complex is the square-planar configuration involving dsp^2 hybridisation. The complex $[Ni(CN)_4]^{2-}$ is diamagnetic. Nickel is in its dipositive state in this complex ion. Hence the number of *d* electrons in Ni^{2+} will be, $28 - 2 - 18 = 8$. That is, it belongs to the d^8 system. The fact that it is diamagnetic clearly indicates that it contains no unpaired electrons. Now these eight *d* electrons are distributed within the 3*d* level in such a way that there are no unpaired electrons.

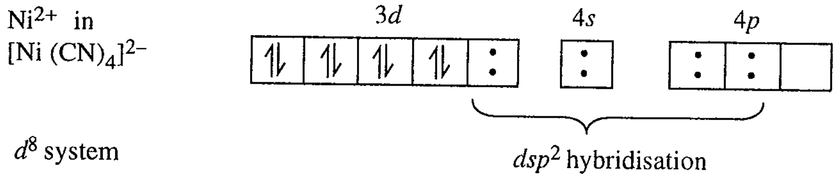


Fig. 3.7

Since the coordination number of nickel is four, the next higher four vacant orbitals are required for hybridisation. This corresponds to dsp^2 hybridisation. Hence the geometry of the complex $[Ni(CN)_4]^{2-}$ is square-planar. Other examples of square-planar complexes are given in Table 3.7.

Table 3.7 Square-planar (dsp^2 hybridized) complexes

Complex	Magnetic character
$[Pt(NH_3)_4]^{2+}$	diamagnetic
$[PtCl_4]^{2-}$	diamagnetic
$[Cu(NH_3)_4]^{2+}$	paramagnetic (1.73 BM)
$[AuCl_4]^-$	diamagnetic

(c) Octahedral complexes The ion $[Co(NH_3)_6]^{3+}$ is diamagnetic. The central metal cobalt is in the tripositive state. Hence the number of *d* electrons will be 27 – 3 – 18 = 6. The metal ion Co^{3+} belongs to the d^6 system. Since it is diamagnetic, no unpaired electron should be present in it. Now these six *d* electrons are arranged among the 3*d* levels in such a way that no unpaired electron is present. Since the coordination number of cobalt is six in this complex, the next six higher vacant orbitals are used for hybridisation.

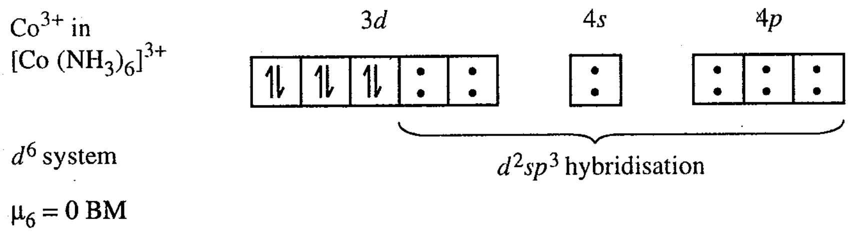


Fig. 3.8

This corresponds to d^2sp^3 hybridisation. Therefore, this complex species is an octahedral one. More specifically it is called as *inner-orbital octahedral complex* because it makes use of the inner *d* orbitals for hybridisation (The *d* orbitals do not belong to the shell to which *s* and *p* orbitals belong to). The hybridisation is (n-1) d^2 ns np^3 hybridisation. Another example for an inner orbital octahedral complex is $[Fe(CN)_6]^{4-}$ which is also diamagnetic.

However, the situation is different for the hexaaquairon(II) ion, which is paramagnetic with a magnetic moment of 4.90 BM. Here, iron is in the dipositive state and hence the number of *d* electrons is, 26 – 2 – 18 = 6. It is a d^6 -system. In order to account for the observed magnetic moment of 4.90 BM, these six *d* electrons have to be distributed among the 3*d* levels in such a way as to give four unpaired electrons. This electronic distribution is denoted below:

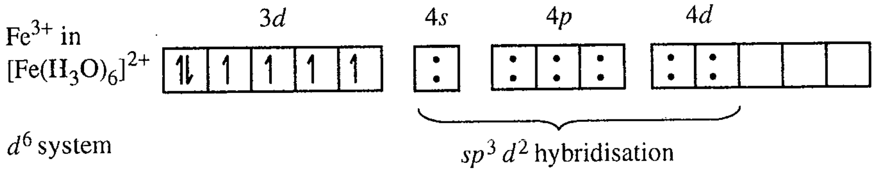


Fig. 3.9

All the 3*d* levels in this complex are occupied by metal electrons either doubly or singly. The coordination number for iron in this complex is six. So the next six higher vacant orbitals are required for hybridisation. This corresponds to sp^3d^2 hybridisation. Since it makes use of the outer *d* orbitals for hybridisation, it is called an outer-orbital octahedral complex. Another example of an outer-orbital octahedral complex is $[CoF_6]^{4-}$.

Defects of the valence bond theory Even though this theory is better than Werner's coordination theory, it is not free from defects. The major drawbacks of the valence bond theory are listed below:

1. The valence bond theory does not take into account the splittings of the metal's *d* energy levels.
2. It is unable to account for or predict the relative energies of the different alternative structures for a complex.
3. It is not helpful in the interpretation of the spectra of complexes.
4. It fails to explain the reaction rates and mechanisms of reactions with complexes.
5. It does not indicate why certain ligands form outer-orbital complexes whereas some others form inner-orbital complexes.
6. It does not explain why certain 4-coordinated complexes are tetrahedral whereas others are square-planar.
7. This theory does not account for the detailed magnetic properties of certain complexes. For these complexes, experimentally determined magnetic moments are slightly higher than the values theoretically calculated from the *spin-only* formula. This deviation is due to the orbital contribution to the magnetic moment, which is not explained by this theory.

EXERCISES

***I. Choose the best answer for each of the following:**

1. $[CoF_6]^{4-}$ is
   a) outer orbital and diamagnetic
   b) inner orbital and paramagnetic
   c) inner orbital and diamagnetic
   d) outer orbital and paramagnetic
2. An octahedral complex of a metal ion has a magnetic moment of 5.92 BM and another octahedral complex of the some metal ion in the same oxidation state has a magnetic moment of 1.75 BM. Which one of the following ions could it be?
   a) Fe^{2+}
   b) Co^{2+}
   c) Fe^{3+}
   d) Co^{3+}
3. A dipositive metal ion of first transition series forms an octahedral complex with magnetic moment of 4.9 BM and another octahedral complex which is diamagnetic. The metal ion is
   a) Fe^{2+}
   b) Co^{2+}
   c) Mn^{2+}
   d) Ni^{2+}
4. A metal ion from the first transition series forms a tetrahedral complex which has a magnetic moment of 2.83 BM and a square complex which is diamagnetic. The metal ion is
   a) Co^{2+}
   b) Ni^{2+}
   c) Fe^{2+}
   d) none of the above
5. $Ni(CO)_4$ is
   a) square planar and paramagnetic
   b) tetrahedral and diamagnetic
   c) square planar and diamagnetic
   d) tetrahedral and paramagnetic
6. $[NiCl_4]^{2-}$ is paramagnetic. Hence its geometry is
   a) square planar
   b) tetrahedral
   c) tetragonal
   d) none of the above
7. Pickout the complex whose aqueous solution (equal concentrations) is expected to have the highest molar conductivity.
   a) $Cr(NH_3)_6Br_3$
   b) $Cr(NH_3)_3Br_3$
   c) $Cr(NH_3)_5Br_3$
   d) $Cr(NH_3)_4Br_3$

8. The *d*-orbital used for dsp^2 hybridization in $[Ni(CN)_4]^{2-}$ ion is
   a) d_{z^2}
   b) $d_{x^2-y^2}$
   c) d_{xz}
   d) d_{yz}
9. Paramagnetic moment is expressed in
   a) Debye unit
   b) k Joules
   c) BM
   d) ergs
10. The instrument used to measure the magnitude of magnetic moment is
   a) Gouy balance
   b) Metler balance
   c) UV spectrometer
   d) none of the above
11. Which of the following is not diamagnetic?
   a) Sc^{3+}
   b) Cu^+
   c) Zn^{2+}
   d) Fe^{3+}
12. Which of the following is not paramagnetic?
   a) Cr^{2+}
   b) Ti^{3+}
   c) Ti^{4+}
   d) Mn^{3+}
13. Which of the following compounds is paramagnetic?
   a) $Cr(CO)_6$
   b) $V(CO)_6$
   c) $Ni(CO)_4$
   d) $Fe(CO)_5$
14. Which of the following is diamagnetic?
   a) $[Fe(CN)_6]^{4-}$
   b) $[Co(NH_3)_6]^{3+}$
   c) $Fe(CO)_5$
   d) all the above
15. Assuming that this complex obeys EAN rule, what is the fomula for a carbonyl complex of Mn, $(CO)_x Mn - Mn(CO)_x$ where there is a single covalent bond between the two Mn atoms.
   a) $Mn_2(CO)_{10}$
   b) $Mn_2(CO)_8$
   c) $Mn_2(CO)_{12}$
   d) none of the above

*II. Match the following:

1. $[CoCl_4]^{2-}$	a) tetrahedral and diamagnetic
2. $[Fe(H_2O)_6]^{2+}$	b) inner orbital and paramagnetic
3. $[Ni(CN)_4]^{2-}$	c) tetrahedral and paramagnetic
4. $[Cr(CN)_6]^{3-}$	d) inner orbital and diamagnetic
5. $[Cr(CO)_6]$	e) outer orbital and paramagnetic
6. $[Zn(NH_3)_4]^{2+}$	f) square planar and diamagnetic

III Explain the following statements:

1. $[Ni(CN)_4]^{2-}$ is diamagnetic whereas $[NiCl_4]^{2-}$ is paramagnetic.

*2. $[Ni(CO)_4]$ is tetrahedral and diamagnetic but $[Ni(CN)_4]^{2-}$ is square planar but diamagnetic.

*3. $[Fe(H_2O)_6]^{2+}$ is paramagnetic whereas $[Fe(CN)_6]^{4-}$ is diamagnetic even though both contain Fe^{2+}.

4. $MnBr_4^{2-}$ is paramagnetic with a moment of 5.92 BM.

*5. $[Zn(NH_3)_4]^{2+}$ cannot be square planar in shape.

6. $[CoF_6]^{3-}$ is paramagnetic whereas $[Co(NH_3)_6]^{3+}$ is diamagnetic even though both contain Co^{3+}.

*7. Though the normal oxidation state of Ni is +2, $[Ni(CO)_4]$ with Ni(0) is stable.

IV Answer the following:

*1. Mention the types of hybridisation and shapes of
   a) $Ni(CO)_4$
   b) $Fe(CO)_5$
   c) $Cr(CO)_6$
   d) $V(CO)_6$
   Also predict their magnetic behaviour.

*2. Assume that 0.01 mol of each of the following compounds is dissolved separately in 1 litre of water : KCl, $[Cd(NH_3)_2Cl_2]$, $[Co(NH_3)_6]Cl_3$ and $K_4[Fe(CN)_6]$. Arrange the resulting four solutions in decreasing order of conductivity.

*3. Is the complex, $[Co(NH_3)_6]Br_3$ paramagnetic or diamagnetic ?

*4. An octahedral complex of Fe^{2+} is diamagnetic . Is it an inner orbital or outer orbital octahedral complex?

*5. How is the paramagnetic moment of a substance related to the number of unpaired electrons? Calculate the "spin-only" magnetic moment for the following complexes.
   a) $[MnCl_4]^{2-}$ b) $[Fe(H_2O)_6]^{2+}$ c) $[Ni(CN)_4]^{2-}$ d) $[CoF_6]^{4-}$ e) $[Fe(CN)_6]^{4-}$

*6. Predict the formula for the following assuming that they obey EAN rule. nickel carbonyl, iron carbonyl, chromium carbonyl and ruthenium carbonyl.

7. Draw the VB diagram and indicate the type of hybridization you would expect for each of the following; Predict the shape of each of the following:
   a) $[Cr(NH_3)_6]^{3+}$ b) $[Ni(CN)_4]^{2-}$ c) $[CoCl_4]^{2-}$
   d) $[Fe(H_2O)_6]^{2+}$ e) $[MnBr_4]^{2-}$ f) $[Cr(CN)_6]^{3-}$

*8. The magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Is it a tetrahedral or square planar complex?

*9. Two different compounds of Cr(III) have the same empirical formula, $CrCl_3 \cdot 6H_2O$. One is green and the other is violet. When one mole of the green compound is dissolved in water and treated with excess $AgNO_3$ solution, it gave one mole of AgCl precipitate. The molar conductivity of a freshly prepared 0.001 M solution of that salt is 132 ohm^{-1} (value for 1 : 1 electrolyte). When it is dried in an oven at 110°C for several hours, it loses weight and the residue has the formula $CrCl_3 \cdot 4H_2O$. When a solution of the violet compound is mixed with excess $AgNO_3$ solution, three moles of AgCl are precipitated per mole of that salt. The molar conductivity of a freshly prepared 0.001 M solution of the violet compound is 437 ohm^{-1} (value for 3 : 1 electrolyte). When it is dried in an oven at 110°C for several hours, it loses no weight and still has the formula $CrCl_3 \cdot 6H_2O$. Arrive at the formula for the green and violet salts.

*10. 0.2664 g of Cr(III) aqua complex of composition $CrCl_3 \cdot 6H_2O$ gave 0.2867 g of silver chloride on treatment with slight excess of silver nitrate solution. Formulate its composition.

*11. $[NiCl_4]^{2-}$ is paramagnetic. Is it square planar or tetrahedral in shape?

12. What are the postulates of valence bond theory as applied to coordination compounds?

13. Bring out the defects of valence bond theory of coordination compounds.

14. What are the postulates of Werner's coordination theory? How is this theory applied to $CoCl_3 \cdot 4NH_3$? How does this account for the experimental observations of this compound?

15. What are the drawbacks of Werner's coordination theory?

16. The μ_{eff} for $[Ni(PEt_3)_2Cl_2]$ is 0.0. Based on this, describe the structure and bonding in it.

17. Why does NH_3 form coordination complexes whereas the isoelectronic species, CH_4 does not?

18. Dilute equimolar solutions of each of the following complexes are prepared. Arrange these complexes in the order of decreasing conductivity of their solutions.

a) $Na[Fe(EDTA)]$ b) $K_3[Fe(NO_2)_6]$ c) $[Pd(NH_3)_6]Cl_4$
d) $[Co(NH_3)_3Br_3]$ e) $[Cr(H_2O)_5Cl]Br_2$

19. A complex of Ni^{2+}, $[NiBr_2(PPh_3)_2]$ is paramagnetic whereas $[PdBr_2(PPh_3)_2]$ is diamagnetic. Predict the number of isomers that will exist for these complexes.

20. The complex $[Ni(CO)_4]$ is diamagnetic, $[Ni(CN)_4]^{2-}$ is diamagnetic and $[NiCl_4]^{2-}$ is paramagnetic with two unpaired electrons. Account for these observations and arrive at the structures of these complexes using the VBT.

*21. An aqueous solution of a complex of composition, $CrCl_3 \cdot 6H_2O$ containing 0.319 g of it is passed through a cation-exchange resin in the acid form and the acid liberated is titrated against a decinormal solution of NaOH. It required 35.9 ml. Formulate the complex.

*22. An aqueous solution of a complex of composition, $CrCl_3 \cdot 6H_2O$ containing 0.638 g of it was passed through a cation-exchange resin in the acid form and the acid liberated was titrated against a standard solution of NaOH of strength 0.12N. It required 39.9 ml of NaOH. What is the formula of the complex?

*23. $CrCl_3 \cdot 6H_2O$ solution containing 0.4785 g of it is passed through a cation-exchange resin in the acid form and the acid liberated is titrated against a NaOH solution of strength 0.125 N. It required 14.4 ml. Determine the correct formula of the complex.

24. The addition of PPh_2Et to $NiBr_2$ at – 80°C in CS_2 gives a red, diamagnetic complex with formula, $(PPh_2Et)_2NiBr_2$. This is converted into a green, paramagnetic (3.2 BM) complex of same composition on keeping at room temperature. Account for this observation.

25. There are five complex ions that can be prepared from Cr(III) using 'en' and Br^- as ligands. Arrive at their formulae and sketch their structures. Using Na^+ and Cl^- as counter ions to get neutral compounds, give their formulae and name them using IUPAC.

26. Cobalt carbonyl is a dimer, $(CO)_nCo\text{-}Co(CO)_n$. Each Co gets 36 as its EAN. Arrive at the value of n. The Co-Co bond is a normal two electron covalent bond. What is the formula for the dimer? Why does it not form a monomer? But it forms $[Co(NO)(CO)_3]$. Why?

*27. The empirical formula of a compound is $[Pd(NH_3)_2Cl_2]$. Its aqueous solution gives no AgCl on treatment with an excess $AgNO_3$ solution. Treatment with H_2SO_4 gives no HCl gas. NH_4^+ ions are not detected in the resulting solution. Its molar conductivity in dilute solutions corresponds to that of the bi-bivalent electrolyte. Its molecular weight is around 423. Arrive at the formula of the compound. Explain these observations.

ANSWERS

I. 1. (d)
2. (c)
3. (a)
4. (b)
5. (b)
6. (b)
7. (a)
8. (b)
9. (c)
10. (a)
11. (d)
12. (c)
13. (b)
14. (d)
15. (a)

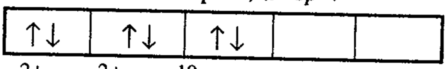
II 1. (c) 2. (e) 3. (f) 4. (b) 5. (d) 6. (a)

III 2. Ni in $Ni(CO)_4$ is Ni(0), d^{10}, all *d*-levels are doubly occupied by electrons, hence sp^3 hybridisation, it adopts tetrahedral geometry, and diamagnetic. But Ni in $[Ni(CN)_4]^{2-}$ is Ni^{2+}, d^8, four *d* levels are doubly occupied by metal electrons, hence dsp^2 hybridisation, it adopts square planar geometry and diamagnetic.

3. Fe^{2+} is d^6; water being weak field ligand does not force the electrons to get paired up; hence electron distribution in $[Fe(H_2O)_6]^{2+}$ is

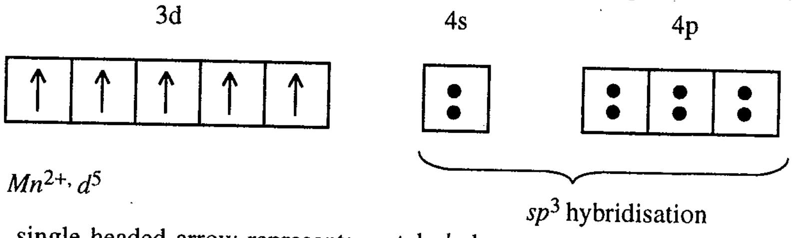
↑↓	↑	↑	↑	↑

It is an outer orbital octahedral complex, sp^3d^2, and paramagnetic.
But in $[Fe(CN)_6]^{4-}$, CN^- is a strong field ligand, hence it forces the metal electrons to get paired up leaving no unpaired electrons. Hence it is diamagnetic. It is inner orbital octahedral complex, d^2sp^3.



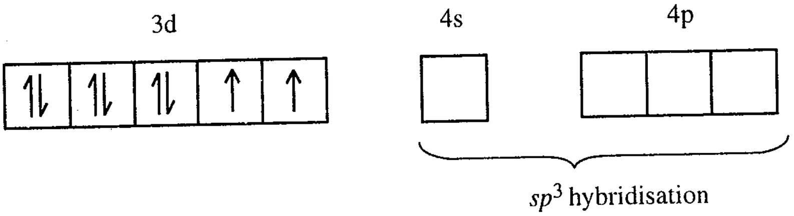
5. In $[Zn(NH_3)_4]^{2+}$, Zn^{2+} is d^{10} system. Hence all the five *d*-orbitals will be doubly occupied, hence it makes use of sp^3 hybridization. It is a tetrahedral complex. It cannot be square planar complex which requires one *d*-orbital for hybridization.
7. The carbon atom of CO has the ability to direct electrons strongly towards Ni even in its zero oxidation state because the negative charge added to the metal atom can be dissipated by back donation into the π orbitals of CO ligands.

IV 1. a) sp^3, tetrahedral, diamagnetic
   b) dsp^3, trigonal bipyramid, diamagnetic
   c) d^2sp^3, octahedral, diamagnetic
   d) d^2sp^3, octahedral, paramagnetic. 1.73 BM.
2. $[K_4Fe(CN)_6] > [Co(NH_3)_6]Cl_3 > KCl > [Cd(NH_3)_2Cl_2]$
3. diamagnetic
4. Fe^{2+}, d^6 ion, no unpaired electron, hence d^2sp^3 hybridization, inner orbital octahedral complex.
5. $\mu_s = \sqrt{n\,(n+2)}$ where n = number of unpaired electrons.
   a) d^5, 5 unpaired, $\mu_s = \sqrt{5\,(7)} = \sqrt{35} = 5.92$ BM
   b) d^6, weak field ,4 unpaired, $\mu_s = \sqrt{4\,(6)} = \sqrt{24} = 4.90$ BM
   c) d^8, square planar , dsp^2 hybridization, no unpaired, diamagnetic
   d) d^7, weak field, sp^3d^2, 3 unpaired, $\mu_s = \sqrt{3\,(5)} = \sqrt{15} = 3.87$ BM
   e) d^5, d^2sp^3, 1 unpaired, $\mu_s = \sqrt{1\,(3)} = \sqrt{3} = 1.73$ BM
6. $Ni(CO)_4$ $Fe(CO)_5$ $Cr(CO)_6$ $Ru(CO)_5$
8. Mn^{2+}, d^5 system. magnetic moment of 5.9 BM indicates the presence of 5 unpaired electrons. Hence the electron distribution among 3*d*-orbitals is,



single headed arrow represents metal *d* electron, : represents the electrons donated by the ligand, Br^-. Since no *d* orbital is available for hybridisation and since its coordination number is four, the next four vacant orbitals are used for hybridisation. Hence it involves sp^3 hybridisation which corresponds to a tetrahedral geometry.

9. Of the three Cl^- ions in green salt, only two are tightly bound because 1 mole of AgCl is precipitated per mole of that salt. Two of the six water molecules are not tightly bound to the Cr^{3+} because they are removed when the salt is heated to 110°C in an oven. So we can conclude that two Cl^- and 4 H_2O are tightly bound to Cr^{3+}. Therefore the complex cation is $[Cr(H_2O)_4Cl_2]^+$. The remaining one Cl^- and 2 H_2O are present in the second coordination sphere. So the formula of the green salt is $[Cr(H_2O)_4Cl_2]Cl.2H_2O$.
   Similarly, the violet salt must have all six water molecules tightly bound to Cr^{3+} because it loses no weight on drying and three Cl^- are not tightly bound to Cr^{3+} because all of them are precipitated as AgCl. Its molar conductivity corresponds to 3 : 1 electrolyte which gives four ions per formula unit. Therefore its formula is $[Cr(H_2O)_6]Cl_3$.
10. $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$
11. tetrahedral, Ni^{2+}, d^8



21. $[Cr(H_2O)_6]Cl_3$
22. $[Cr(H_2O)_5Cl]Cl_2.H_2O$
23. $[Cr(H_2O)_4Cl_2]Cl.2H_2O$
27. $[Pd(NH_3)_4][PdCl_4]$

Chapter 4

Theories of Coordination Compounds II

4.1 CRYSTAL FIELD THEORY (CFT)

This theory involves an electrostatic approach to the bonding in complexes. It was first applied to ionic-type crystalline substances. Therefore, it is very often called the crystal field theory (CFT). This theory considers the metal ion as being placed in an electrostatic field created by the surrounding molecules or ions. This electric field changes the energies of the *d* electrons in the case of transition metal ions. Many of the properties of the complexes are related to these energy changes. This theory considers the bonding in complexes to be entirely electrostatic. The crystal field theory was proposed a little earlier than the valence bond theory, but it took about twenty years for this theory to be used by chemists. In 1951 many theoretical chemists working independently, used the crystal field theory to interpret the spectra of complexes of the *d*-block elements.

4.1.1 Shapes of *d* Orbitals

In order to have a thorough understanding of the crystal field theory, it is essential to have a clear picture of the spatial orientation of the *d* orbitals (Fig. 4.1).

Three orbitals, namely, d_{xy}, d_{xz} and d_{yz} resemble one another in producing regions of electron density in between the three cartesian axes. The other two orbitals, namely, $d_{x^2-y^2}$ and d_{z^2}, differ from these three orbitals and also between them. The $d_{x^2-y^2}$ orbital has the regions of electron density along the *x*- and *y*-axes. The d_{z^2} orbital has most of its electron density along the *z*-axis with an annulus in the *xy* plane. The group of three *d* orbitals, namely, d_{xy}, d_{xz} and d_{yz} is referred to as t_{2g} or d_ϵ orbitals whereas the group of two *d* orbitals, namely, $d_{x^2-y^2}$ and d_{z^2} is referred to as e_g or d_γ orbitals.

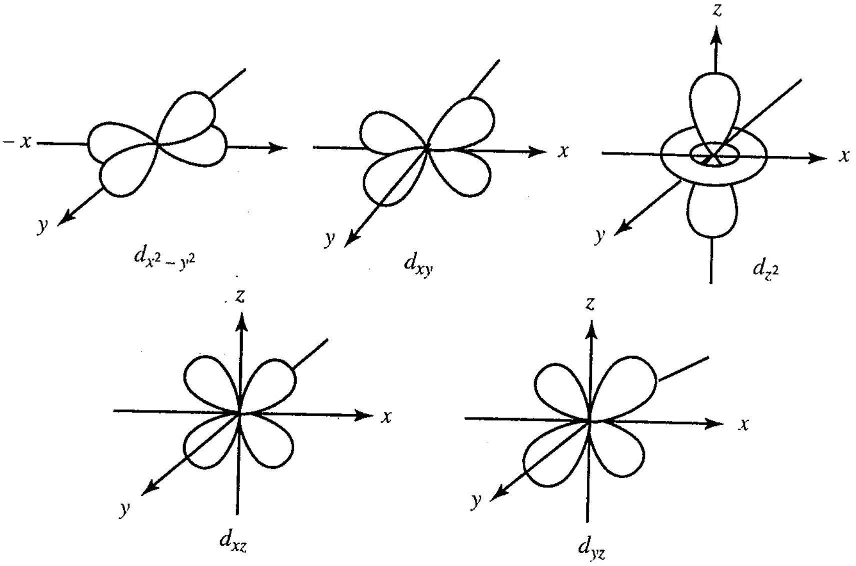


Fig. 4.1 Shapes of d orbitals

4.1.2 Assumptions of the Crystal Field Theory

In the crystal field theory the following assumptions are made:

(1) This theory considers a complex as a combination of a central ion surrounded by other ions or molecules with electrical dipoles called ligands. It regards these *ligands as point charges or as point dipoles.*

(2) The bonding between the metal cation and ligands arises due to the electrostatic attraction between the nucleus of the metal cation and the partial negative charge invariably present on the ligands. Thus the *bond between the metal and the ligand is purely ionic.*

(3) The interaction between the electrons of the cation and those of the ligands is entirely repulsive. These *repulsive forces are responsible for the splitting of the d orbitals of the metal cation.*

(4) In its simplest form, the crystal field theory *does not consider the overlapping between the metal orbitals and ligand orbitals.*

(5) The *d orbitals which are degenerate* (of equal energy) in a free metal ion have their *degeneracy destroyed by the approach of the ligands* during the formation of a complex.

4.1.3 Crystal Field Splitting of *d* Orbitals in Different Geometries; Splitting of *d* Orbitals in Octahedral Complexes

The five *d* orbitals in an isolated gaseous metal ion are degenerate. When a spherically symmetric field of negative charges is placed around the central metal ion, all the five orbitals will be raised in energy as a result of the repulsion between the negative

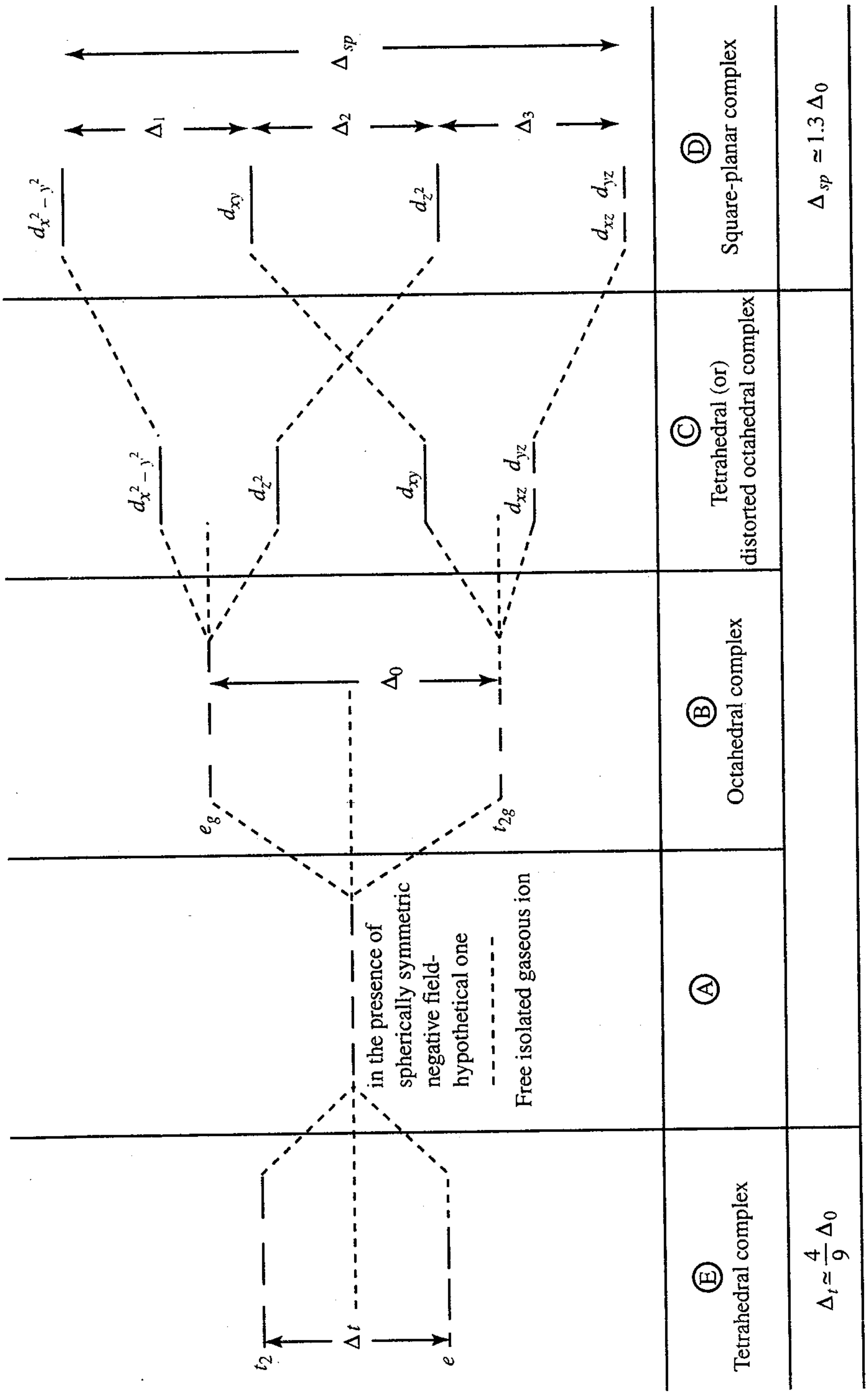


Fig. 4.2 Splitting of d orbitals in different geometries

field and the negative electrons of the metal ion. Although they still remain degenerate they will have higher energy than before (refer Section A of Fig. 4.2). This is only a hypothetical situation.

In an octahedral complex such as $[TiF_6]^{2-}$, the six fluoride ligands approach the central Ti^{4+} ion along the three cartesian axes, namely from the directions, $-x$, x, $-y$, y, $-z$, and z.

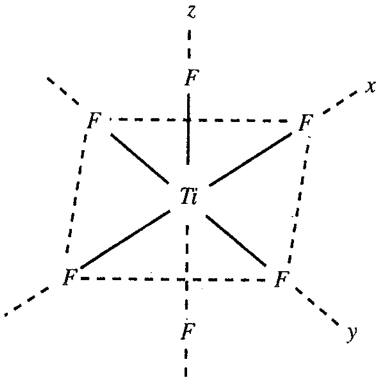


Fig. 4.3 The interaction of six flouride ligands with Ti^{4+}

Since the lobes of the two e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) point directly at the path of the approaching ligands (See Fig. 4.3), the electrons in these orbitals experience greater repulsion from the ligands than those in three t_{2g} orbitals (d_{xy}, d_{xz} and d_{yz}) whose lobes are directed in space in between the paths of the approaching ligands. Hence the energy of the e_g orbitals is increased and in order to maintain the barycentre, the energy of the t_{2g} orbitals is decreased. Thus the five *d* orbitals which were originally degenerate in the free metal ion are split into two levels under the influence of approaching ligands. The e_g level which is doubly degenerate is of higher energy and the t_{2g} level which is triply degenerate is of lower energy (Fig. 4.2 Section B). *The splitting of the five d orbitals into* e_g *and* t_{2g} *energy levels by the approaching ligands is called the crystal field splitting* which is the major feature of crystal field theory. The energy difference between e_g and t_{2g} levels is denoted by Δ_0 or $10\,D_q$ and is called *crystal field splitting energy* in octahedral geometry.

4.1.4 Crystal Field Stabilisation Energy (CFSE)

Now let us calculate the crystal field stabilisation energy in terms of Δ_0 or $10\,D_q$ due to the presence of electrons in t_{2g} and e_g levels of the octahedral complexes. It is assumed that the sum of the energies of the five *d* orbitals in the free state must be equal to the sum of the energies of the five *d* orbitals in the octahedral configuration. Splitting occurs in such a way that there is no net change in energy for the fully occupied orbitals. If we take the energy of the free state as zero, then equations (1), (2) and (3) apply:

$$E_{d_{xy}} + E_{d_{xz}} + E_{d_{yz}} + E_{d_{x^2-y^2}} + E_{d_{z^2}} = 0 = 5\,E(d\text{ free}) \qquad (1)$$

$$\therefore\ 3\,E_{d_{xy}} + 2\,E_{d_{z^2}} = 0 \qquad (2)$$

$$E_{d_{z^2}} - E_{d_{xy}} = \Delta_0 \qquad (3)$$

Multiply equation (3) by two and then subtract it from equation (2):

$$2\,E_{d_{z^2}} - 2E_{d_{xy}} = 2\,\Delta_0$$

$$5\,E_{d_{xy}} = -2\,\Delta_0$$

$$\therefore\ E_{d_{xy}} = -\frac{2}{5}\ \Delta_0 = -0.4\ \Delta_0\ (\text{or}) - 4\ D_q \quad (\because\ \Delta_0 = 10D_q)$$

Since t_{2g} levels are degenerate,

$$E_{d_{xy}} = E_{d_{xz}} = E_{d_{yz}} = -0.4\ \Delta_0\ (\text{or}) - 4\,D_q$$

On substituting the value of $E_{d_{xy}}$, namely $-0.4\ \Delta_0$ in equation (3),

$$E_{d_{z^2}} - (-0.4\ \Delta_0) = \Delta_0$$

$$\therefore\ E_{d_{z^2}} = \Delta_0 - 0.4\ \Delta_0 = 0.6\ \Delta_0$$

Since e_g orbitals are degenerate

$$E_{d_{z^2}} = E_{d_{x^2-y^2}} = 0.6\,\Delta_0\ (\text{or})\ 6D_q$$

This means that the presence of an electron in the t_{2g} level will stabilise the complex to the extent of $0.4\,\Delta_0$. This stabilisation energy is called the *crystal field stabilisation energy* (CFSE). The presence of an electron in e_g level will de-stabilise the complex to the extent of $0.6\,\Delta_0$.

For example, Δ_0 for $[Ti(H_2O)_6]^{3+}$ ion is found to be about 58 kcal/mole. Ti^{3+} is a d^1 system. This single electron occupies one of the three t_{2g} levels. Its CFSE = $0.4\,\Delta_0$. Thus the energy gained due to CFSE is $0.4\ \times\ 58 \simeq 23.2$ kcal/mole. This means that if all other things were the same, the Ti^{3+} ion in $[Ti(H_2O)_6]^{3+}$ should bind the water molecules 23.2 kcal/mole tighter than does the neighbouring d^0 ion, Sc^{3+} in $[Sc\,H_2O)_6]^{3+}$

4.1.5 Splitting of *d* Orbitals in Square-planar Complexes

The splitting of the energy levels in square-planar complexes may be justified in the same manner as discussed for the octahedral geometry.

Generally, we speak of the *xy* plane as the square plane. If the two trans ligands, lying on the *z*-axis of an octahedron are moved away from the central cation, then their distance from the metal cation is slightly greater than it is for the other four ligands lying in the *xy* plane. Now we get a tetragonally-distorted octahedron. Such a structure is referred to as a tetragonal structure. In order to consider the splitting of *d* orbitals in a tetragonal structure, we can start with the splitting in octahedral geometry. In a tetragonal structure, the distance of the two ligands on *z*-axis is increased by moving these ligands away from the central metal ion. Therefore, the *d* orbitals having *z* component, namely, d_{z^2}, d_{xz} and d_{yz} experience less repulsion from the ligands than they do in an octahedral geometry. The other two orbitals, namely, d_{xy} and $d_{x^2-y^2}$ experience a relatively greater repulsion from the ligands than they do in an octahedral environment. As a result, the energy of the orbitals experiencing greater repulsion increases whereas the energy of the orbitals experiencing lesser repulsion decreases (Fig. 4.2 Section C). The d_{xz} and d_{yz} orbitals are degenerate. Thus under the influence of ligands in a tetragonal complex, the order of increasing energy of various d-orbitals is,

$$d_{xz} = d_{yz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$$

If the two ligands on the z-axis are completely removed, we get a square-planar complex. This is accompanied by a further decrease in the energies of d_{z^2}, d_{xz} and d_{yz} orbitals and a further increase in the energies of d_{xy} and $d_{x^2-y^2}$ orbitals as shown in Fig. 4.2, Section D. Thus the order of increasing energies of d orbitals in a square-planar complex is

$$d_{xz} = d_{yz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$$

The difference in energy between the lowest d_{xz}, d_{yz} pair and the highest $d_{x^2-y^2}$ is called the *square-planar splitting energy* and is denoted by Δ_{sp}. The value of Δ_{sp} is larger than Δ_0. It has been found that Δ_{sp} is about 1.3 times Δ_0.

4.1.6 Splitting of *d* Orbitals in Tetrahedral Complexes

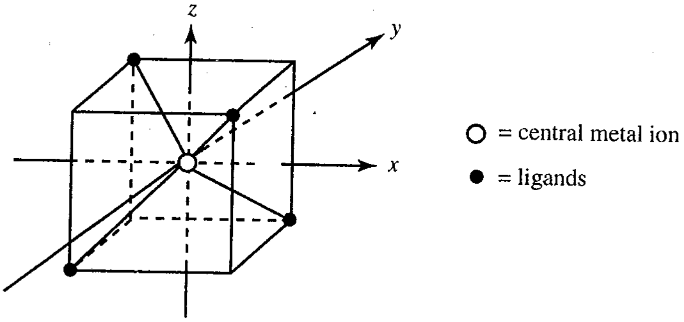


Fig. 4.4 Tetrahedron placed inside the cube

Imagine a tetrahedron placed inside a cube. The centre of the tetrahedron is at the centre of the cube. The four corners of the tetrahedron (indicated by dots in Fig. 4.4) are located at four of the eight corners of the cube (alternate corners of the cube). Insert the x, y and z axes in such a way that they pass through the centre of the cube and protrude from the centres of its six faces as shown in Fig. 4.4. Now begin to see the positions of the four ligands with respect to the d orbitals of the central metal ion.The d orbitals having their lobes oriented in between the axes, namely the d_{xz}, d_{yz} and d_{xy} (t_{2g} orbitals) orbitals are nearer to the four ligands whereas the two d orbitals having their lobes oriented in space along the cartesian axes, namely $d_{x^2-y^2}$ and d_{z^2}, (e_g orbitals) orbitals are away from the four ligands. Hence the t_{2g} orbitals interact with the ligand orbitals to a greater extent than do the e_g orbitals. Therefore, in a tetrahedral complex t_{2g} orbitals become the higher energy levels. (Fig. 4.2 Section E). Note that the mode of splitting of d orbitals in a tetrahedral complex is just the reverse of that in an octahedral complex. The difference in energy between the low energy e_g orbitals and high energy t_{2g} orbitals in a tetrahedral complex is called the *tetrahedral crystal field splitting energy* and is denoted by Δ_t. It has been found that $\Delta_t < \Delta_0$ $(\Delta_t \approx \frac{4}{9}\Delta_0)$.

4.1.7 Reasons for Smaller Δ_t Over Δ_0

The smaller Δ_t value over Δ_0 value is mainly attributed to the following two reasons:

1. There are only four ligands in a tetrahedral complex whereas in an octahedral complex there are six ligands. Hence one-third decrease in the number of ligands decreases the Δ_t value to some extent from the Δ_0 value.
2. The high energy t_{2g} orbitals in a tetrahedral complex, although nearer to the ligands, do not point directly at the ligands. Hence the extent of their interaction is less. But in an octahedral complex, the high energy e_g orbitals point directly at the ligands. Therefore, the extent of their interaction is more. Hence, Δ_0 is always greater than Δ_t.

4.1.8 Reasons for Inverted Mode of *d* Orbital Splitting in a Tetrahedral Complex when Compared with that in an Octahedral Complex

In an octahedral complex, the ligands are approaching the central metal ion along the three cartesian axes. Hence the orbitals having their lobes oriented in space along these axes, namely the e_g orbitals interact with ligand orbitals to a greater extent (Fig. 4.3) and thus e_g orbitals become the high energy orbitals in an octahedral complex. But in a tetrahedral complex, none of these orbitals is directly pointing at the ligands (Fig. 4.4). The t_{2g} orbitals are nearer to the ligands and hence they interact to a greater extent with the ligand orbitals. Therefore,the t_{2g} orbitals become the high energy orbitals in a tetrahedral complex. Thus, the mode of splitting of *d* orbitals in an octahedral complex is just the reverse of that observed in a tetrahedral complex.

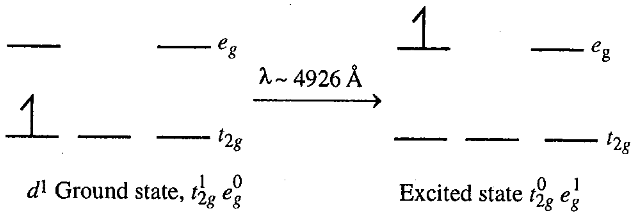
4.1.9 Measurement of Δ_0 or 10 D_q

The value of Δ_0 or 10 D_q can be estimated experimentally from the absorption spectra of the complex. When light of frequency Δ_0/h, (h = Planck's constant), is passed through the complex, it will be absorbed. Some of the *d* electrons from the low energy level will be promoted to the high energy level. This type of transition between the different *d* levels is called *d-d transition.*

For example, for the complex ion, $[Ti(H_2O)_6]^{3+}$, (d^1 system) there is a single absorption maximum at a wave length of 4926Å. This corresponds to the wave number $\bar{\nu} = 20,300\ cm^{-1}$ as shown below:

$$\bar{\nu} = \frac{1}{\lambda \text{ in cm}} = \frac{1}{4926\times10^{-8}\text{ cm}} = \frac{1}{4.296\times10^{-5}\text{ cm}}$$
$$= 0.2030\times10^{5}\ cm^{-1} = 20,300\ cm^{-1}$$

Since 349.75 cm^{-1} = 1 kcal/mole, this 20,300 cm^{-1} corresponds to 58.0 kcal/mole. Thus Δ_0 for $[Ti(H_2O)_6]^{3+}$ is 58.0 kcal/mole.



$$[\mathrm{Ti(H_2O)_6}]^{3+} \xrightarrow{\lambda = 4926\ \text{Å}} [\mathrm{Ti(H_2O)_6}]^{3+*} \text{ (excited state)}$$

Fig. 4.5 Depiction of electron promotion from t_{2g} to e_g level

This method of determination of Δ_0 is applicable only for one-electron systems; but difficulties are encountered when applied to many-electron systems. The reasons for the difficulties are (a) inter electronic repulsions and (b) overlapping of the electronic transitions.

4.1.10 Determination of Crystal Field Stabilisation Energy (CFSE)

The Δ_0 for the complex $[\mathrm{Ti(H_2O)_6}]^{3+}$ (d^1) is found to be 58.0 kcal/mole. The single electron occupies the lowest energy level possible, namely the t_{2g} orbital in an octahedral complex. CFSE for an electron in the t_{2g} level is 0.4 times Δ_0. Therefore, the CFSE in this case will be $0.4 \times 58.0 = 23.2$ kcal/mole.

4.1.11 Factors Affecting the Magnitude of Δ_0 or $10\,D_q$ Values

Some of the more important factors that affect the magnitude of Δ_0 or $10\,D_q$ are discussed below.

(a) Geometry of the complex The degree of splitting of *d* orbitals is affected by the geometry of the complex. We have already seen that $\Delta_{sp} > \Delta_0 > \Delta_t$. The reasons for this have been discussed under the mode of splitting of *d* orbitals in different geometries.

(b) Oxidation state of the central metal ion The charge of the central metal ion has a direct effect on the magnitude of Δ values. Greater the charge on the central metal ion greater is the attraction for the ligands. Hence the ligands are drawn in more closely by the central metal ion. So, they will have a greater effect in perturbing the metal *d* orbitals. This leads to higher Δ value. Theoretically, an increase from 2+ to 3+ ionic charge should result in an increase in value by 50%. But actually, it is only about a 40% increase; this is because of increased inter-electronic repulsions at closer distances. For example, Δ_0 for $[\mathrm{Co(NH_3)_6}]^{3+}$ is greater than that for $[\mathrm{Co(NH_3)_6}]^{2+}$, because in the former the charge on Co is higher than that in the latter.

(c) Principal quantum number of the d orbital Generally, the crystal field splitting is the greatest for complexes containing 5*d* electrons and the least for complexes containing 3*d* electrons. This is due to the fact that the 5*d* orbitals extend farther into space and hence interact more strongly with the ligands leading to an increase in the amount of splitting. For example, the Δ_0 values for $[Co(NH_3)_6]^{3+}$ (3*d*), $[Rh(NH_3)_6]^{3+}$ (4*d*) and $[Ir(NH_3)_6]^{3+}$ (5*d*) are around 23,000 cm^{-1}, 34,000 cm^{-1} and 41,000 cm^{-1} respectively. The increase in Δ_0 values is about 40–50% from 3*d* to 4*d* and about 20–30% from 4*d* to 5*d* ions. As a result of the high splitting values of second and third row transition elements (4*d* and 5*d* series), most of their complexes are exclusively low-spin (maximum pairing of electrons) compared to the large number of both low-spin and high-spin (maximum unpaired electrons) complexes of the first row transition elements.

(d) Nature of the ligands The nature of the ligands also affects the degree of splitting of *d* orbitals. The ligands having less splitting ability are called *weak field ligands* whereas those with greater splitting power are known as *strong field ligands*. The splitting abilities of various ligands are arrived at from the spectra of their complexes. The ligands are arranged in the order of their increasing splitting ability. This series is called the *spectrochemical series* (since the values of splitting ability are obtained from the spectra of their complexes), This series is given below:

$$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O$$

$$< NH_3 < en < bipy < o\text{-open} < NO_2^- < CN^- < CO$$

The first few ligands in the above series are known as weak field ligands. The last few ligands are called the strong field ligands. The intermediate ligands are termed as *intermediate field strength ligands*. This order of increasing field strength of common ligands is independent of the nature of the central metal ion and the geometry of the complex. Although this is the usual order, reversals occur, especially with ligands of about the same field strength.

If the splitting of *d* orbitals results from the effect of point charges, we would expect the anionic ligands to exert the greatest effect. But most of these anionic ligands lie on the weak field end of the spectrochemical series. Moreover, OH^- lies below the neutral H_2O molecule. Again NH_3 produces a stronger field than H_2O. But their dipole moments are in the reverse order. (μ for NH_3 = 1.47 D and that for H_2O = 1.85 D). Such results question the original assumption of purely electrostatic interaction between the central metal ion and ligands. In order to account for this observed characteristic, it is necessary to abandon a completely electrostatic model for the bonding in complexes and to realise that covalent interactions also exist. Adjusted crystal field theory (ACFT), which includes the possibility of covalent bonding is better known as *ligand field theory* (LFT). Qualitatively, it will account for the *d* orbital splitting caused by various ligands. The importance of covalent bonding or π bonding is indicated in the explanation for the order of some ligands in the spectrochemical series.

The ligand OH^- having more negative charge than H_2O gives a lower *d* orbital splitting. CN^-, bipy and NO_2^- produce unusually high splitting but they are weak bases. These observations may be understood qualitatively on the basis of the two types of π bonding, namely ligand-to-metal and metal-to-ligand π bonding. The $:\ddot{\underset{\cdot\cdot}{O}}-H^-$ having three unshared pairs of electrons would have a greater tendency to back donate electrons to the metal than water, having only two unshared electron pairs. When this occurs, the net effective positive charge on the metal ion would decrease and hence the extent of splitting of *d* orbitals would also decrease. Electronically unsaturated ligands such as CN^-, bipy, NO_2^-, CO etc. (Species having fairly low lying antibonding m.o., capable of accepting electrons, are said to be electronically unsaturated) form π-bonds of the other type, namely metal to ligand. Here the removal of electrons from the filled *d* orbitals of the metal leaves the metal ion with a higher positive charge. This increase in the positive charge on the metal ion causes a greater degree of *d* orbital splitting than the ligands which do not form a π-bond, such as ammonia and ethylenediamine. Thus, the splitting energy is highly dependent on the metal ion charge.

4.1.12 Consequences of Crystal Field Splitting

(i) Ionic radii of transition metal ions The variation in ionic radii of divalent cations of the metals of the first transition series in their crystalline compounds, MX_2 (metal halides), where each metal ion is octahedrally surrounded by six X^- ions, may be considered. In the absence of CFSE due to the *d* orbital splittings, the ionic radii of the transition metal ions should decrease gradually with increasing nuclear charge. Thus the ionic radii for M^{2+} ions are expected to decrease smoothly from Ca^{2+} to Zn^{2+} due to the increased nuclear charge. A plot of these radii is given in Fig. 4.6; but the change in size is not regular. A smooth dotted line is drawn through Ca^{2+}, Mn^{2+} and Zn^{2+}, which have d^0, d^5 and d^{10} configurations. In these cases, the *d* orbitals are empty, half full and full respectively. These configurations develop almost spherical field round the nucleus. They have zero CFSE.

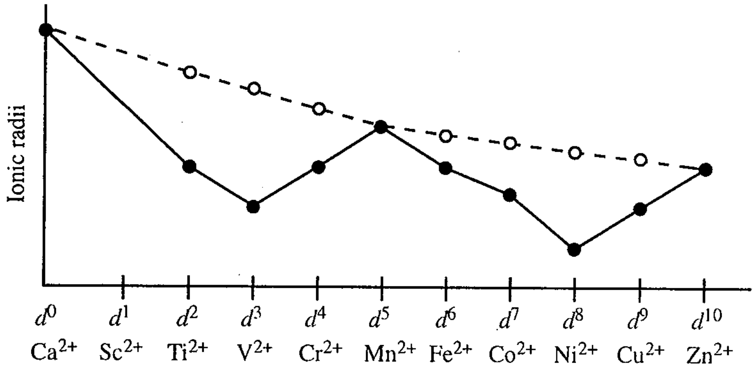


Fig. 4.6 *Variation of ionic radii with the number of d electrons*

In Ti^{2+} $(t_{2g}^2 e_g^0)$, the two *d* electrons occupy t_{2g} orbitals of lower energy, that is, the electrons occupy orbitals which are oriented in between the ligands. Thus there is no shielding of the nuclear charge and the ligands are drawn closer to the nucleus. As a result, its ionic radius is less than that expected, when there was no crystal field effect.

In V^{2+} $(t_{2g}^3 e_g^0)$, the effect of crystal field splitting is more prominent because now there are three t_{2g} electrons. The increased nuclear charge has an even greater effect with V^{2+}. Hence its ionic radius is less than that of Ti^{2+}.

In Cr^{2+} $(t_{2g}^3 e_g^1)$, the e_g level has one electron. This orbital is oriented in the direction of the ligand. Hence it provides good shielding to the ligands. Therefore, the ligands can no longer approach so closely and hence the ionic radius increases. The ionic radius of Cr^{2+} is more than that of V^{2+} ion. But it is still smaller than the value expected, if there were no crystal field effects.

For high spin Mn^{2+} $(t_{2g}^3 e_g^2)$, each *d* orbital has one electron. This results in a spherical distribution of charge around the nucleus. Hence the octahedral radius of high spin Mn^{2+} has the value as expected from the consideration of nuclear charge alone. Therefore, it falls on the smooth line joining Ca^{2+} and Zn^{2+}

The next three electrons enter the t_{2g} orbitals and hence the ionic radii again decrease for Fe^{2+} $(t_{2g}^4 e_g^2)$, Co^{2+} $(t_{2g}^5 e_g^2)$ and Ni^{2+} $(t_{2g}^6 e_g^2)$. In Cu^{2+}, the added electron goes to the e_g $(t_{2g}^6 e_g^3)$. Hence its ionic radius is greater than that of Ni^{2+} but smaller than that of Zn^{2+}.

Thus the shape of the curve is explained by the crystal field splitting. If there was no crystal field splitting, then a smooth curve (dotted line from Ca^{2+} to Zn^{2+} through Mn^{2+}) would have been obtained; but a curve with two humps is actually obtained.

(ii) Heats of hydration of bivalent ions of first transition series The heat of hydration is the heat evolved in the hydration process,

$$M^{2+}{}_{(g)} + 6H_2O_{(l)} \rightarrow [M(H_2O)_6]^{2+} + \text{heat of hydration}$$

The negative sign indicates that heat is evolved in the hydration process. (Generally six water molecules enter the coordination sphere to form an octahedral aqua complex).

We know that the ionic radii of divalent ions of the first row transition elements decrease from Ca^{2+} to Zn^{2+}. Hence the experimental values of heats of hydration of these ions should increase regularly from Ca^{2+} to Zn^{2+}. This is because the decrease in ionic radii values brings the ligand water molecules closer to the metal, M^{2+} ions resulting in the increased electrostatic attraction between the cation and water ligands; but this expected regular increase does not occur, as is evident from the graph shown in Fig. 4.7.

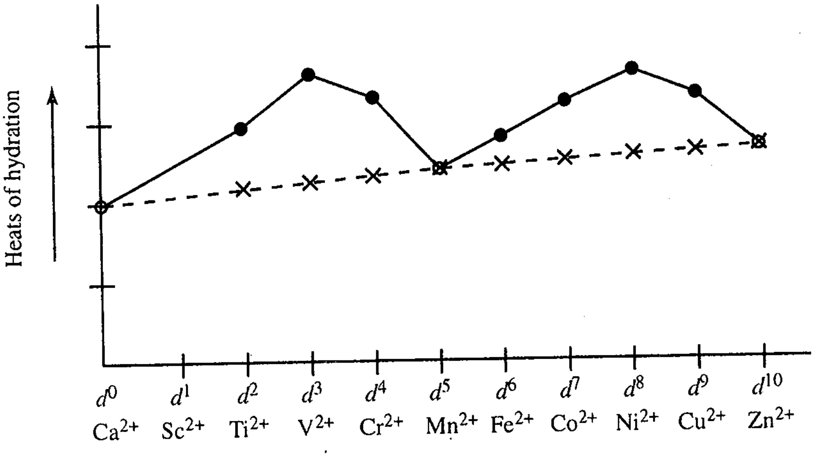


Fig. 4.7 Variation of heats of hydration with the number of d electrons

The ions Ca^{2+}, Mn^{2+} and Zn^{2+} have d^0, d^5 (high spin) and d^{10} configurations respectively. These ions which have zero CFSE fall almost on the straight line. The distance of the other points above this line corresponds to the CFSE. The experimental values, instead of increasing regularly, show maxima at V^{2+} $(t_{2g}^3e_g^0)$ and Ni^{2+} $(t_{2g}^6e_g^2)$ and minima at Ca^{2+} $(t_{2g}^0e_g^0)$, Mn^{2+} $(t_{2g}^3e_g^2)$ and Zn^{2+} $(t_{2g}^6e_g^4)$. These maxima and minima can be explained by the concept of CFSE. All the hexahydrate ions, $[M(H_2O)_6]^{2+}$ are high-spin octahedral complexes. For high-spin complexes, CFSE is minimum (zero) for d^0 (Ca^{2+}), d^5 (Mn^{2+}) and d^{10} (Zn^{2+}) ions. Hence they show minima in the graph. CFSE will be maximum ($1.2\ \Delta_0$) for d^3 (V^{2+}) and d^8 (Ni^{2+}) ions. Hence they correspond to maxima in the graph.

If the experimental values are corrected by subtracting the CFSE values calculated from the spectral data, then the resulting points (indicated by crosses in the graph (Fig. 4.7) fall almost on a straight line from Ca^{2+} to Zn^{2+} through Mn^{2+}.

Hence we conclude that if there was no crystal field splitting, then a smooth graph would have been obtained.

(iii) Lattice Energy and CFSEs Let us consider the difluorides of transition metals of the first transition series from CaF_2 to ZnF_2. In crystalline state, these fluorides possess an octahedral arrangement of F^- ions around the M^{2+} metal ions. Since the ionic radii of M^{2+} ions are expected to decrease gradually, their lattice energies should increase gradually. This is because, the lattice energy is inversely proportional to the inter-ionic distance. Since the radius of the anion is the same in all these compounds, the lattice energy should be inversely proportional to the ionic radius of the metal ion. This is actually the case as is evident from the plot of lattice energy against the number of *d* electrons (Fig. 4.8). An almost straight line could have been drawn through the points which indicates the lattice energies of CaF_2, MnF_2 and ZnF_2.

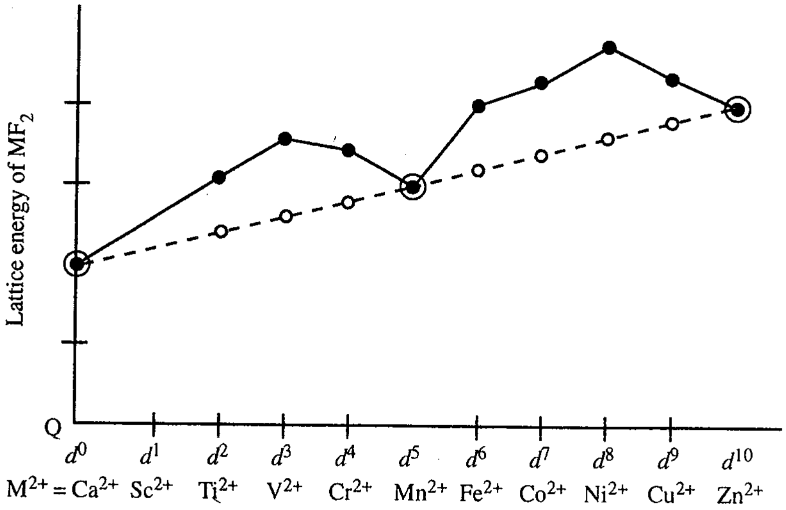


Fig. 4.8 *Variation of lattice energies with the number of d electrons*

However, the points showing the observed lattice energies of all the other bivalent metal fluorides of the series follow an irregular variation. The points showing the observed lattice energies of these fluorides lie above the points which show their theoretical lattice energies in the absence of any crystal field effects. The difference between the observed lattice energy and the theoretical lattice energy in the absence of crystal field effects gives the CFSE. From this CFSE, the crystal field splitting energy, Δ_0, can be calculated.

If there was no crystal field splitting of *d* orbitals, then a smooth graph would have been obtained.

4.1.13 Merits of Crystal Field Theory

1. This theory can be used to predict the most favourable geometry of a complex.
2. It accounts for the fact that certain four-coordinated complexes are square-planar whereas others are tetrahedral.
3. It also explains the fact that certain ligands form outer orbital octahedral complexes whereas others form inner orbital octahedral complexes. They in turn correspond to high-spin and low-spin complexes.
4. The greatest achievement of this theory is its success in interpreting the magnetic properties taking into consideration the orbital contributions also.
5. The colours of transition metal complexes can be readily interpreted using this theory.
6. Spectral properties of many transition metal complexes can be easily explained by this theory.
7. This theory helps predict site selection in spinel and antispinel structures.

Site selection in spinel and anti-spinel structures The mineral spinel is $MgAl_2O_4$. The spinel structure is found among a number of oxides of the type AB_2O_4 and also in a limited number of sulphides, selenides, fluorides and cyanides of similar composition. A^{2+} is a second group metal or a transition metal in 2+ state and B^{3+} is a third group metal or a transition metal in 3+ state.

The unit cell of this structure contains 32 oxide ions, that is, the unit cell is $A_8B_{16}O_{32}$. In this structure, the oxide ions are arranged as in cubic close packing with A^{2+} ions and B^{3+} ions in the tetrahedrally and octahedrally coordinated interstices respectively. Such structures are called *normal spinel* structures. They are represented as $(A)_t(B_2)_0O_4$ where, subscript *t* and 0 represent tetrahedral and octahedral sites respectively. Some examples of normal spinel structures are Mn_3O_4 and Co_3O_4.

However, some oxides of this composition, have an alternative *inversed structure*, also called *anti-spinel* structure. Some examples of oxides having inverse spinel structures are Fe_3O_4 and $NiAl_2O_4$. In these oxides, the pattern of sites in the structure and the distribution of the oxide ions are the same as in the normal spinel except the arrangement of the cations. To indicate this type of distribution, the formula for the inversed or antispinels may be written as $(B)_t(A,B)_0O_4$.

The adoption of normal or inverse spinel structure by an oxide of composition, AB_2O_4 can be explained using CFSEs. Since $\Delta_0 > \Delta_t$; octahedral site stabilisation energies are usually much greater than tetrahedral site stabilisation energies. Mn_3O_4 and Co_3O_4 adopt normal spinel structure whereas Fe_3O_4 and $NiAl_2O_4$ adopt inverse spinel or antispinel structure. CFT can easily explain this.

Generally the ion, which is crystal field stabilised, tends to occupy octahedral site (because of its higher stabilisation energy, that is $\Delta_0 > \Delta_t$). In Mn_3O_4, both Mn^{2+} and Mn^{3+} are present. Mn^{2+} is a d^5 system with zero CFSE (oxide ion is a weak field ligand), whereas Mn^{3+} is a d^4 system with some net CFSE. Hence Mn^{3+} which is crystal field stabilised, occupies the octahedral sites. Therefore, it is represented as $(Mn^{2+})_t(Mn_2^{3+})_0O_4$. Hence it adopts the *normal spinel structure.* In Co_3O_4, the Co^{3+} ions occupy octahedral sites as low-spin d^6 ions, providing maximum stabilisation. If the structure was to invert, half of the Co^{3+} ions should have been transferred to tetrahedral sites where they would probably become high-spin and lose high amount of crystal field stabilisation energy. Hence it adopts the *normal spinel structure.*

The situation is different in the case of Fe_3O_4 and $NiAl_2O_4$, which adopt antispinel structure. In Fe_3O_4, Fe^{2+} ions (d^6) are crystal field stabilised but Fe^{3+} ions (d^5) are not. Hence Fe^{2+} ions occupy octahedral sites while one half of Fe^{3+} ions occupy tetrahedral holes. It is then represented as $(Fe^{3+})_t(Fe^{2+}, Fe^{3+})_0O_4$. Therefore, it adopts an *antispinel structure*. Similarly, in $NiAl_2O_4$, only the Ni^{2+} ions are crystal field stabilised and therefore they occupy octahedral sites. Dipositive Ni(II) ions occupy octahedral holes which means, that $NiAl_2O_4$ adopts an *antispinel structure.*

4.1.14 Limitations of Crystal Field Theory

Although the crystal field theory readily explains many properties of metal complexes convincingly, and is a more satisfactory and general approach to the study of metal complexes than the valence bond theory, it is not free from defects. Some of its demerits are mentioned below:

1. Due to its emphasis on the orbitals and electrons of the central atom, this theory must necessarily become less accurate as delocalisation of ligand electrons and orbitals becomes more important. This means that as covalent bonding increases this theory becomes less accurate.
2. The point-charge model assumed by this theory does not exactly represent the actual situation of a metal ion in the field of the surrounding ligands.
3. This theory fails to account satisfactorily for the relative strengths of ligands. For example, it gives no explanation as to why negatively charged hydroxyl ion appears in the spectrochemical series as a weaker ligand than the neutral water.
4. In several complexes, the bonding strength and chemical properties cannot be explained solely on the basis of electrostatic attraction as emphasised by this theory.

4.1.15 Occupancy of *d* Orbitals by Electrons in Octahedral Complexes: Weak-field and Strong-field Cases; High-spin (Spin-free) and Low-spin (Spin-paired) Complexes

The distribution of *d*-electrons in t_{2g} and e_g orbitals depends on the relative values of the crystal field splitting energy, and electron pairing energy, E_p. Crystal field splitting energy depends on (a) charge of the central metal ion, (b) geometry of the complex, (c) principal quantum number of the *d*-orbital involved and (d) nature of the ligand. But the value of electron pairing energy depends only on the nature of the metal ion.

For d^1, d^2, d^3, d^8, d^9, and d^{10} systems in octahedral complexes, there is only one ground state for each system obtained on the basis of the fact that these electrons will occupy the lowest-energy state possible, without unnecessary pairing of electrons. The ground states for these systems are given in Fig. 4.9. Irrespective of the magnitude of the crystal field splitting, the same number of unpaired electrons will exist for these systems.

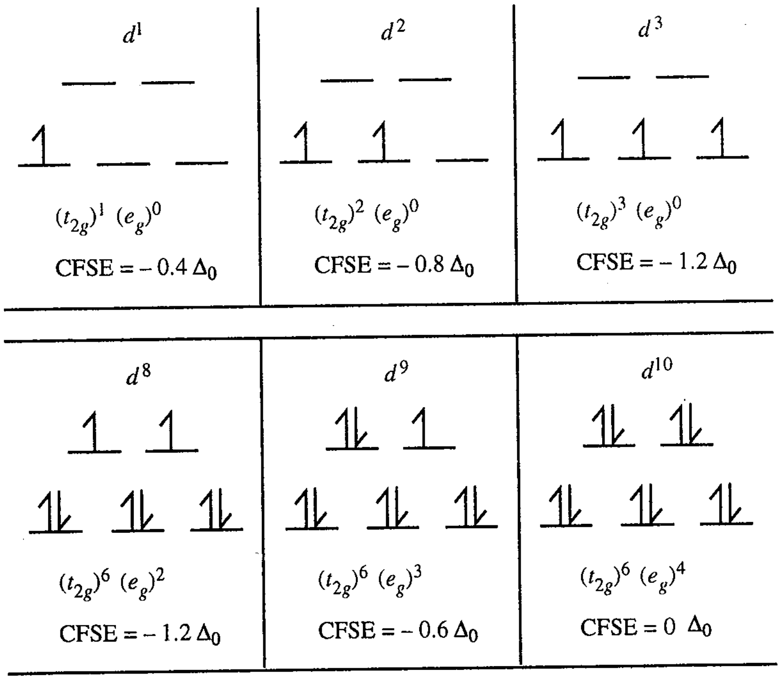
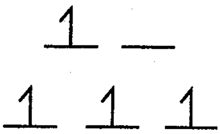


Fig. 4.9 Occupancy of d orbitals by electrons in octahedral complexes for d^1, d^2, d^3, d^8, d^9 *and* d^{10} *systems*

Except the d^{10}, the other systems gain different crystal field stabilisation energies over the d^0 system. Magnetically, the number of unpaired electrons per ion is the same as that expected in the valence bond theory and is in agreement with the observed magnetic moment.

All the other remaining systems, d^4, d^5, d^6 and d^7 possess two states, namely the high-spin (spin-free or weak-field case) and low-spin (spin-paired or strong-field case) as shown in Fig. 4.10.

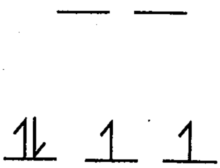
d^4



$\Delta_0 < E_p$

High-spin spin-free
weak-field case
4 *unpaired electrons*
$(t_{2g})^3\ (e_g)^1$
$CFSE = -0.6\ \Delta_0$

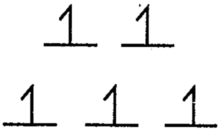
d^4



$\Delta_0 > E_p$

Low-spin spin-paired
strong-field case
2 *unpaired electrons*
$(t_{2g})^4\ (e_g)^0$
$CFSE = -\ 1.6\ \Delta_0 + \mathrm{E}_p$

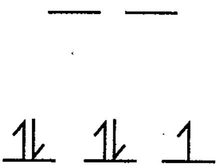
d^5



$\Delta_0 < E_p$

High-spin spin-free
weak-field case
5 *unpaired electrons*
$(t_{2g})^3\ (e_g)^2$
$CFSE = 0\,\Delta_0$

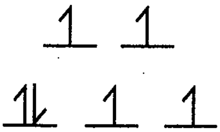
d^5



$\Delta_0 > E_p$

Low-spin spin-paired
strong-field case
1 *unpaired electron*
$(t_{2g})^5\ (e_g)^0$
$CFSE = -2.0\ \Delta_0 + 2\,\mathrm{E}_p$

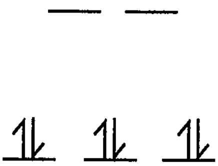
d^6



$\Delta_0 < E_p$

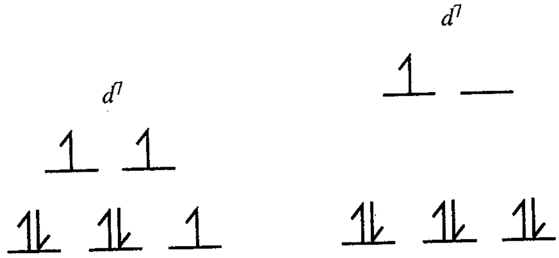
High-spin spin-free
weak-field case
4 *unpaired electrons*
$(t_{2g})^4\ (e_g)^2$
$CFSE = -\ 0.4\ \Delta_0 + 0$

d^6



$\Delta_0 > E_p$

Low-spin spin-paired
strong-field case
0 *unpaired electron*
$(t_{2g})^6\ (e_g)^0$
$CFSE = -\ 2.4\ \Delta_0 + 2\,\mathrm{E}_p$



$\Delta_0 < E_p$

High-spin spin-free
weak-field case
3 unpaired electrons
$(t_{2g})^5\ (e_g)^2$
$CFSE = -0.8\ \Delta_0 + 0$

$\Delta_0 > E_p$

Low-spin spin-paired
strong-field case
1 unpaired electron
$(t_{2g})^6\ (e_g)^1$
$CFSE = -1.8\ \Delta_0 + E_p$

Fig. 4.10 *Occupancy of* d *orbitals by electrons in octahedral complexes for* d^4, d^5, d^6 *and* d^7 *systems*

The high-spin states have the maximum number of unpaired electrons possible whereas the low-spin states have the minimum number of unpaired electrons. Either of the two states shown for d^4, d^5, d^6 and d^7 systems may be obtained. The crystal field splitting energy, Δ_0 and the electron pairing energy, E_p will decide which spin state would be found. If $\Delta_0 < E_p$, a high-spin state is found whereas when $\Delta_0 > E_p$, a low-spin state is obtained. This is well illustrated by the following examples: $[Mn(H_2O)_6]^{3+}$ is a high-spin complex because, Δ_0 for the H_2O ligand, (21,000 cm^{-1}) is less than the E_p for Mn^{3+} (28,000 cm^{-1}).

$[Mn(CN)_6]^{3-}$ is a low-spin complex, because Δ_0 for CN^- ligand (40,000 cm^{-1}) is greater than the E_p (28,000 cm^{-1}) of Mn^{3+}. These details are tabulated below:

Complex ion	E_p cm^{-1}	Δ_0 cm^{-1}	spin state	comment
$[Mn(H_2O)_6]^{3+}$	28,000	21,000	High-spin	$\Delta_0 < E_p$
$[Mn(CN)_6]^{3-}$	28,000	40,000	Low-spin	$\Delta_0 > E_p$

In these systems, high-spin states correspond to the outer orbital complexes of valence bond theory and the low-spin states correspond to the inner orbital complexes of valence bond theory.

4.1.16 Effect of Ligand Field Strength on the Colour of Complexes

The complexes of *s*- and *p*- block elements are almost colourless. But the transition metal complexes are generally coloured. Colour of a species is associated with the promotion of an electron from one energy state to another. The energy required to do this is obtained by absorbing the light of a particular wavelength. In transition elements, there are partially filled *d* levels. These *d* levels are split into different energy levels depending upon the geometry of the complex. Thus, there is the possibility of promoting one electron from one *d* level to another *d* level. This transition is known as *d-d* transition. This corresponds to a small energy difference resulting in absorption of light of higher wavelength in the visible region and the complex appear coloured.

In the cases of *s*- and *p*- block elements, there cannot be any *d-d* transition as all the *d* levels in them are doubly occupied. The energy required to promote an electron from the *s*- or *p*- level to a higher level in them is much greater. This may correspond to the ultraviolet region in which case the compound will not appear coloured.

The energy difference between the split *d* levels in a transition element depends on the nature of the ligand to a large extent. Depending upon this crystal field splitting energy, light of different wavelengths will be absorbed to effect *d-d* transitions and depending upon the wavelength of light absorbed, the complexes will have different colours. Thus the ligand field strength is related to the colour of the complex as illustrated below :

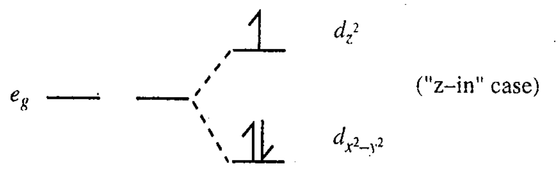
$[Cu(H_2O)_4]^{2+}$ light blue; $[Cu(NH_3)_4]^{2+}$ deep blue; $[CuCl_4]^{2-}$ yellow; $[Cu(en)_2]^{2+}$ violet; $[Cu(CN)_4]^{2-}$ colourless. [In all these complexes, copper is in the 2+ state, but the ligand field strengths differ. Hence they have different colours].

4.1.17 Jahn-Teller Effect; Jahn-Teller Theorem; Jahn-Teller Distortion

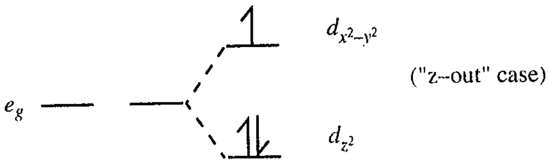
In 1937 Jahn and Teller proposed a theorem which states that *any nonlinear molecular system in a degenerate electronic state will be unstable and will undergo some kind of distortion which will lower its symmetry and energy and split the degenerate state.*

This simple theorem has great practical importance in understanding the chemistry of certain transition metal complexes. For example, let us consider an octahedrally coordinated Cu^{2+} ion [d^9 system $(t_{2g})^6\,(e_g)^3$]. There is one vacancy in the e_g orbitals, in either the $d_{x^2-y^2}$ or the d_{z^2} orbital. If the geometry is a regular octahedral one, then the two configurations, $d^2_{x^2-y^2}, d^1_{z^2}$ and $d^1_{x^2-y^2}, d^2_{z^2}$ are of equal energy. This is the reason why the electronic state of the Cu^{2+} ion is doubly degenerate. However, this is the state which cannot be stable according to this theorem. Therefore, the octahedron distorts in such a way that the two configurations mentioned above are of unequal energies.

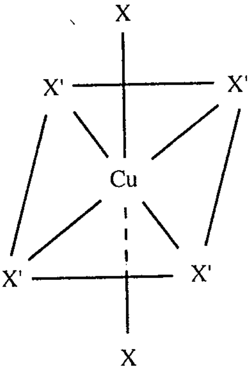
If the actual configuration in the e_g orbitals is $d^2_{x^2-y^2}, d^1_{z^2}$, the ligands in the *xy* plane are repelled to a greater extent than the ligands along the *z*-axis. Since the ligands in the *xy* plane move further away, the $d_{x^2-y^2}$ orbital becomes more stable than the d_{z^2} orbital, thus destroying the degeneracy as shown below:



If the actual configuration is $d^1_{x^2-y^2}$, $d^2_{z^2}$, a distortion of the opposite type results. The ligands along the z-axis are repelled to a greater extent than the ligands in the xy plane. Since the ligands along the z-axis move away, the d_{z^2} orbital becomes more stable than the $d_{x^2-y^2}$ orbital. Thus the degeneracy is removed as shown below:



It is very difficult to predict which situation actually occurs. Generally, elongation of two bonds along the z-axis is energetically more favourable than elongation of four bonds in the xy- plane. Hence *z-out case* is much more common than *z-in case*. This is well illustrated by the Cu^{2+} halides such as CuF_2, $CuCl_2$ and $CuBr_2$. In each case the Cu^{2+} ion has a coordination number of 6, with four near neighbours in the xy-plane and two remote ones along the z-axis as shown in Fig. 4.11.



Distances

Cu – X′	Cu – X
X′ = F, 1.93 Å	X = F, 2.27 Å
X′ = Cl, 2.30 Å	X = Cl, 2.95 Å
X′ = Br, 2.40 Å	X = Br, 3.18 Å

Fig. 4.11 *"Z-out" case*

The ions having an unsymmetrical electronic distribution in the e_g orbitals (1 or 3 electrons in e_g orbitals) are expected to have this type of distortion. Some examples where this may occur are $(t_{2g})^3(e_g)^1$ - high-spin, d^4 systems (Cr^{2+}, Mn^{3+}), $(t_{2g})^6(e_g)^1$ - low-spin, d^7 systems (Co^{2+}, Ni^{3+}) and $(t_{2g})^6(e_g)^3 - d^9$ system (Cu^{2+}).

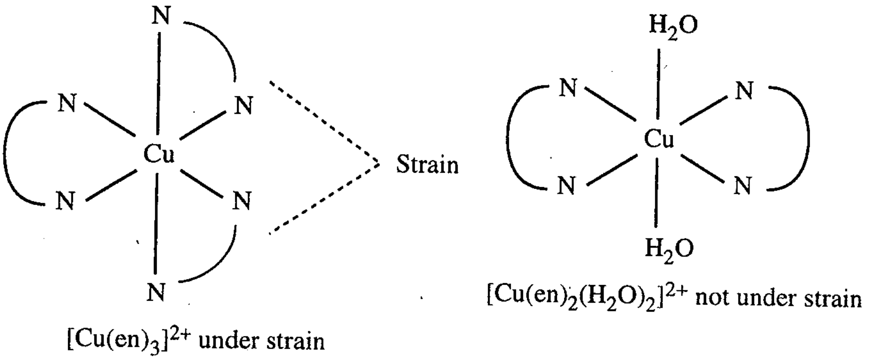
A similar but smaller effect is to be expected when the t_{2g} orbitals are unsymmetrically populated by electrons. Since these t_{2g} orbitals are not directly pointing at the ligands, in an octahedral complex, this distortion generally goes unnoticed.

For example, in CrF_2 solid, each Cr^{2+} has two F^- at 2.43 Å and four F^- at 2.00 Å. In CuF_2 solid, each Cu^{2+} has two F^- at 2.27 Å and four F^- at 1.93 Å. In these cases the electron density is higher in the d_{z^2} orbital, that is $(t_{2g})^6 d^2_{z^2} d^1_{x^2-y^2}$. But in MnF_2 and NiF_2, where the configurations of the cations are high spin d^5

(Mn^{2+}) and d^8 (Ni^{2+}) respectively, the environment of the cation is a regular octahedron. Distortion is not to be expected in these cases due to the symmetrical electronic distribution, $(t_{2g})^3(e_g)^2$ and $(t_{2g})^6(e_g)^2$ respectively.

4.1.18 Consequences of Jahn-Teller Distortion

1. 6-coordinated complexes are found to possess distorted octahedral structure due to this effect. For example, $[Cu(H_2O)_6]^{2+}$ has a distorted octahedral structure with four near H_2O molecules in *xy* plane and two remote ones along the *z*-axis.
2. Even though $[Cu(en)_3]^{2+}$ contains three chelate rings, it is less stable than $[Cu(en)_2(H_2O)_2]^{2+}$ which contains only two chelate rings. This is contrary to the general trend of chelation; greater the number of chelate rings greater will be the stability. But here the opposite trend is observed. In the former case, two chelate rings make use of two elongated bonds (due to *z*-out) along the *z*-axis. These rings are under strain; hence it is less stable (Fig. 4.12).

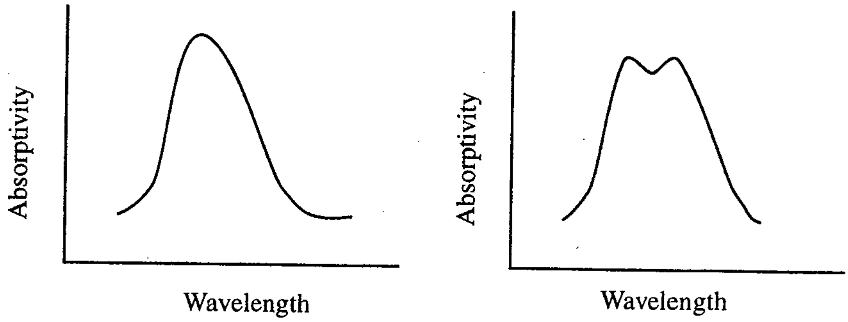


$[Cu(en)_3]^{2+}$ under strain

$[Cu(en)_2(H_2O)_2]^{2+}$ not under strain

Fig. 4.12 Chelate rings and ring strain

3. The absorption spectra of complexes having this distortion are different from the spectra of complexes having no distortion; instead of getting a single Gaussian curve, a curve with a shoulder as shown in Fig. 4.13 is obtained in the spectrum due to distortion.



(a) Gaussian curve (where there is no distortion)

(b) Gaussian curve with a shoulder (where there is distortion)

Fig. 4.13 Absorption spectra of complexes:
a) without J-T distortion b) with J-T distortion

4. This distortion also affects the reactivity of complexes. For example, $[Cu(H_2O)_6]^{2+}$ (d^9 system) exchanges two of its H_2O molecules on the elongated z-axis more rapidly than its four H_2O molecules in the xy-plane.

4.2 MOLECULAR ORBITAL THEORY (MOT)

The molecular orbital theory takes into account the covalent character of metal to ligand bond. The presence of M-L covalent bonding in metal complexes is proved by several spectroscopic studies as explained below:

(a) ESR spectra The most direct evidence for M→L π bonding is obtained from the ESR spectra of complexes. For example, $[IrCl_6]^{2-}$ gives hyperfine structure which can be explained by assuming that some of the iridium orbitals and some chloride ion orbitals overlap to such an extent that the single unpaired d-electron is not localised on the metal ion but is about 5% localised on each chloride ion. Similar results are found in many other complexes also.

(b) NMR studies NMR studies of the complexes $K[MnF_3]$ and $K[NiF_3]$ indicate that the metal t_{2g} and e_g electrons spend a fraction of time around the flourine nuclei confirming that M-L covalent bonding exists in such complexes.

(c) NQR spectra NQR spectra of some of the square-planar complexes of Pt(II) and Pd(II) such as $[PtX_4]^{2-}$ and $[PdX_4]^{2-}$ indicate that there is considerable amount of covalence in the M-L bonds.

Certain tetrahedral complexes such as $[CoCl_4]^{2-}$ give unusually large NQR absorption band intensities. This can be explained by considering the M-L bonds in them to have appreciable covalent character.

The covalent character of M-L bond in complexes may be explained in terms of the *molecular orbital theory (MOT)*. This theory begins with the idea that overlap of atomic orbitals of the central metal ion and the ligands occurs to some extent whenever the conditions of energy, overlap and symmetry permit. First, we have to find out which atomic orbitals of the central ion and ligands can be combined. This is done using the principles of group theory. The symbols used to represent the molecular orbitals such as A_{1g}, T_{1u}, E_g, T_{2g} are derived from the group theory. In Fig. 4.14 the letter A denotes an energy level which is singly degenerate, corresponding to a single orbital having the full symmetry of the system. In T_{1u} the letter T denotes a triply degenerate energy level of a set of three orbitals differing only in directional properties. They are equivalent in all respects except for their orientations in space. Similarly in E_g the letter E denotes an energy level which is doubly degenerate and corresponds to a pair of orbitals which are equivalent except for their spatial orientations. They differ only in directional properties.

The subscript numeral, if any, in the above-mentioned symbols denotes the symmetry of the set of orbitals; subscript one means that the wave functions do not change sign on rotation about the cartesian axes and subscript two, means that they do not change sign on rotation about axes diagonal to the cartesian axes. The subscripts *g* and *u* indicate whether the orbitals are centrosymmetric (*g* from the German *gerade* = even) or antisymmetric (*u* from *ungerade* = uneven).

The *s* orbital corresponds to a single degenerate energy level, a_{1g} , a set of three *p* orbitals corresponds to a triply degenerate energy level t_{1u}, a set of two $d_{x^2-y^2}$ and d_{z^2} orbitals corresponds to a doubly degenerate energy level e_g , and a set of three d_{xy} , d_{xz} and d_{yz} orbitals corresponds to a triply degenerate energy level, t_{2g} . The same symbols with capital letters are used for molecular orbitals. They are A_{1g} , T_{1u} , E_g and T_{2g} . Asterisks if any on these symbols denote that they are antibonding orbitals.

The fundamental assumption of molecular orbital theory is that the metal and ligand orbitals will overlap and combine to give molecular orbitals by the linear combination of atomic orbitals (LCAO) method. Only the valence orbitals are considered here and the combinations of metal and ligand orbitals of widely differing energies are neglected.

In an octahedral complex like $[Cr(NH_3)_6]^{3+}$, the metal has six σ orbitals, i.e., the (n+1)*s* orbital, three (n+1)*p* orbitals and the e_g pair orbital of the n*d* set. Each ligand i.e., NH_3 , has one σ orbital containing the lone pair of electrons. These six σ orbitals on the six NH_3 ligands are combined to give orbitals with the correct symmetry to overlap with the metal σ orbitals. The molecular orbital energy level diagram for this octahedral complex is given in Fig. 4.14. The six electron pairs from the ligands are accommodated in the six lowest molecular orbitals, namely, T_{1u} , A_{1g} and E_g . The nonbonding T_{2g} and the antibonding E_g^* are now available to accommodate the metal *d* electrons. The central portion of the energy level diagram is similar to the t_{2g} and e_g splitting explained in crystal field theory. It may be noted that the lower part of the energy level diagram emphasises the valence bond theory. Thus, in a sense molecular orbital theory incorporates both valence bond theory and crystal field theory. But here the E_g^* orbitals have some ligand character (due to overlap of e_g with ligand group orbitals) which implies that some covalent character is present in metal-ligand bonds.

Greater the energy difference between the metal atomic orbitals and the ligand group orbitals, greater will be the metal to ligand bond ionic character.

If the ligand possesses orbitals of σ as well as π symmetry, then the situation is altered due to the overlap of the metal t_{2g} orbitals with the ligand π orbitals. This type of π bonding occurs in metal complexes under two different situations. In one case the ligand π orbitals are empty and of higher energy than the metal t_{2g} ortibals. This results in an increase in Δ_0 value as shown in Fig. 4.15. This situation occurs in metal complexes with CO, CN^- , NO^+ etc. as ligands.

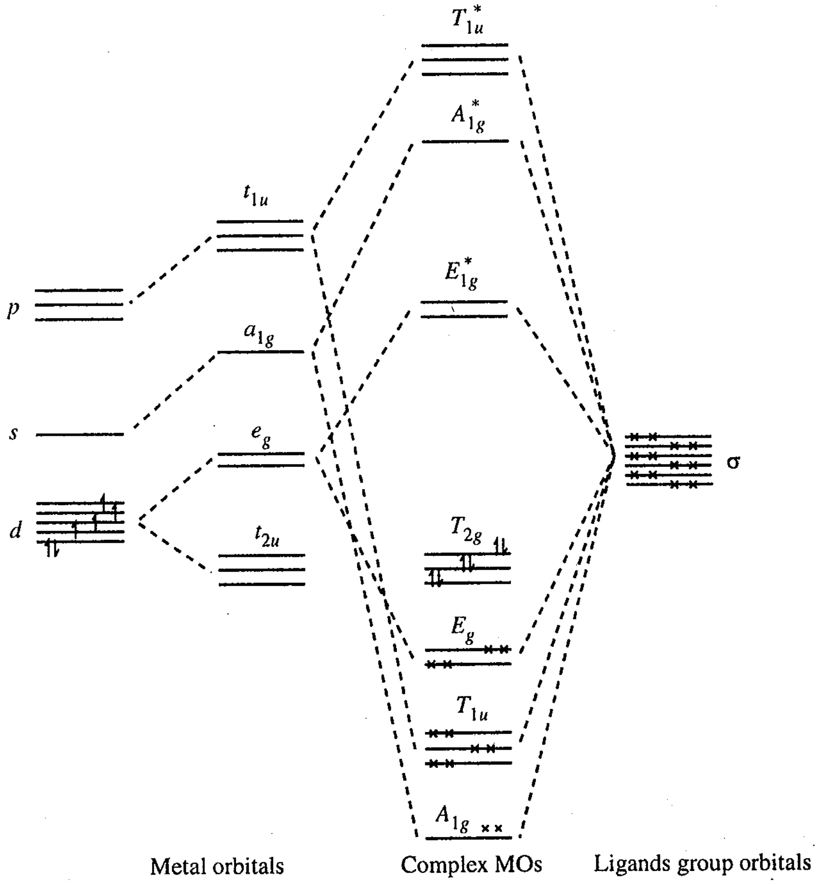


Fig. 4.14 *MO diagram for an octahedral complex having only σ interaction. xx represents ligand electron pairs and | represents metal d electrons*

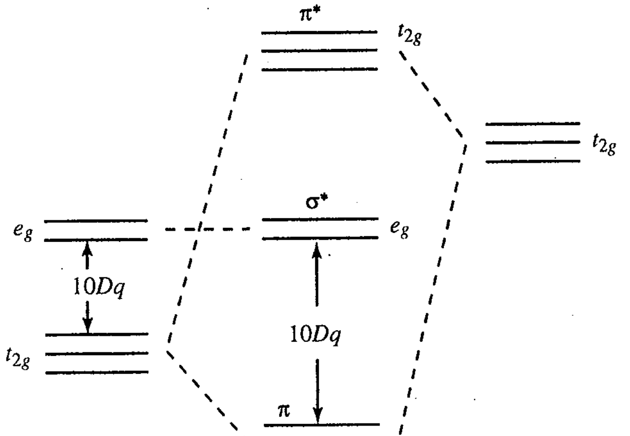


Fig. 4.15 *Energy level diagram for a pi system with an acceptor ligand such as CO, P or S*

[Increase in Δ_0 value due to π bonding when ligand π orbitals are empty and of higher energy than metal t_{2g} orbitals].

Another situation arises when the ligand π orbitals are filled and of less energy than the metal t_{2g} orbitals. This effect results in a decrease in Δ_0 value as shown in Fig. 4.16.

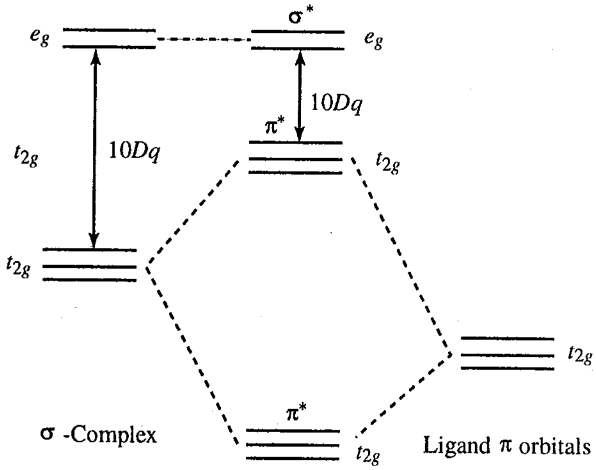


***Fig. 4.16** Energy level diagram for a pi system with donor ligand such as O, F etc.*

[Decrease in Δ_0 value due to π bonding when the ligand π orbitals are filled and of lesser energy than the metal t_{2g} orbitals].

This is probably the situation in complexes of metal ions in their normal oxidation states with ligand atoms, oxygen and fluorine. This type of covalence, called π bonding or *back bonding* gives explanation for the position of these ligands such as CO, CN^-, NO^+, O^{-2}, F^-, etc. in the spectrochemical series. Similar molecular orbital treatments are possible for other geometries such as square-planar and tetrahedral, but, they are somewhat more complicated.

EXERCISES

***I. Choose the best answer for each of the following:**

1. Fe^{3+} forms a high-spin octahedral complex; then its magnetic moment is
   a) 5.92 BM
   b) 0 BM
   c) 1.73 BM
   d) none of the above
2. The magnitude of Δ_0 value will depend upon,
   a) charge of the central metal ion
   b) nature of the ligand
   c) principal quantum number of the *d*-electron
   d) all the above
3. Which one of the following divalent ions is expected to have the minimum octahedral ionic radius?
   a) Ti^{2+}
   b) Cr^{2+}
   c) V^{2+}
   d) Mn^{2+}
4. The ion which is expected to have Jahn-Teller distortion in an octahedral field is
   a) Co^{3+} (strong field)
   b) Co^{2+} (low-spin)
   c) Ni^{2+}
   d) Mn^{2+} (weak field)
5. The complex ion developing the highest crystal field splitting energy is
   a) $[Co(NH_3)_6]^{2+}$
   b) $[Rh(NH_3)_6]^{3+}$
   c) $[Ir(NH_3)_6]^{3+}$
   d) $[Co(NH_3)_6]^{3+}$
6. E_p for Co^{3+} is 250 KJ mole^{-1} and Δ_0 for the complex ion $[Co(CN)_6]^{3-}$ is 345 KJ mole^{-1}. Then the complex ion is
   a) paramagnetic
   b) diamagnetic
   c) ferromagnetic
   d) none of the above
7. The oxide which adopts normal spinel structure is
   a) Co_3O_4
   b) Fe_3O_4
   c) $NiAl_2O_4$
   d) none of the above
8. The order of increasing energies of different *d*-orbitals in a square-planar geometry is
   a) $d_{xy} = d_{xz} = d_{yz} < d_{x^2-y^2} = d_z^2$
   b) $d_{x^2-y^2} = d_z^2 = d_{xy} = d_{xz} = d_{yz}$

c) $d_{xz} = d_{yz} = d_{xy} < d_{z}^{2} < d_{x^2-y^2}$

d) $d_{xz} = d_{yz} = d_{z}^{2} < d_{xy} < d_{x^2-y^2}$

9. CFSE for a high-spin system is zero. Its electronic distribution is
   a) $(t_{2g})^4(e_g)^0$
   b) $(t_{2g})^6(e_g)^3$
   c) $(t_{2g})^4(e_g)^2$
   d) $(t_{2g})^3(e_g)^2$
10. Which of the following cations is colourless in aqueous solution?
    a) Zn^{2+}
    b) Cu^{2+}
    c) Fe^{2+}
    d) Cr^{2+}
11. Which of the following cations is coloured in aqueous solution?
    a) Cu^{+}
    b) Zn^{2+}
    c) Ti^{4+}
    d) Ni^{2+}
12. The one with the largest Δ_0 value is
    a) $[Fe(H_2O)_6]^{2+}$
    b) $[Fe(NH_3)_6]^{3+}$
    c) $[Ru(CN)_6]^{3-}$
    d) $[Ru(H_2O)_6]^{2+}$
13. The CFSE for a high-spin octahedral complex of a d^6 ion is
    a) $-0.6\ \Delta_0$
    b) $1.2\ \Delta_0$
    c) $1.8\ \Delta_0$
    d) $-0.4\ \Delta_0$
14. The CFSE for a low-spin octahedral complex of a d^7 ion is
    a) $2.4\ \Delta_0$
    b) $-1.8\ \Delta_0$
    c) $1.2\ \Delta_0$
    d) $-0.6\ \Delta_0$

***II Match the following:**

1. MnF_2
2. Mn_3O_4
3. Fe_3O_4
4. $[Ti(H_2O)_6]^{3+}$
5. CrF_2
6. $[Zn(NH_3)_4]^{2+}$
7. $[Mn(H_2O)_6]^{2+}$
8. $[Mn(CN)_6]^{4-}$

a) spinel structure
b) coloured
c) regular shape
d) inverse spinel structure
e) colourless
f) distorted shape
g) low-spin
h) high-spin

III Account for the following:

*1. Octahedral field splitting energy, Δ_0 is always higher than tetrahedral field splitting energy, Δ_t, that is $\Delta_0 > \Delta_t$

*2. In the crystal of CuF_2, all Cu-F bond distances are not equal.

*3. Compounds of many transition elements are coloured.

4. Δ_0 increases in the order

$$[Co(H_2O)_6]^{2+} < [Co(H_2O)_6]^{3+} < [Rh(H_2O)_6]^{3+} < [Ir(H_2O)_6]^{3+}$$

5. Splitting energy of *d* orbitals by CN^- ligand is greater than that of F^- ligand.

*6. $[Mn(H_2O)_6]^{2+}$ is a high-spin complex whereas $[Mn(CN)_6]^{4-}$ is a low-spin complex.

7. $[Cu(NH_3)_6]^{2+}$ is deep-blue coloured whereas $[CuCl_4]^{2-}$ is yellow coloured eventhough both contain Cu^{2+} ion.

*8. Jahn-Teller distortion may lead either to "Z-out case" or to "Z-in case". Generally "Z-out case" is much more common than "Z-in case".

9. A number of tetrahedral Co(II) complexes, unlike tetrahedral Ni(II) complexes, are stable.

*10. The order of increasing Δ_0 is

$$[CrCl_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(CN)_6]^{3-}$$

IV Answer the following:

1. State and explain the Jahn-Teller Theorem. What are its consequences?

*2. Explain why Cu^{2+} does not form a regular octahedral complex whereas Ni^{2+} does.

*3. Why is CO (or CN^-) a blood poison?

4. Explain why Cr^{2+} does not form a regular octahedral complex with a weak field ligand whereas Mn^{2+} forms a regular octahedral complex with that ligand.

*5. Among the complex ions, $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$, which is expected to give greater splitting of *d* orbitals? Explain.

*6. Differentiate between high-spin and low-spin complexes with an example.

7. Calculate the CFSE values in terms of Δ_0 and E_p for d^4, d^5, d^6 and d^7 systems for both weak and strong-field cases of octahedral geometry.

*8. Amongst the two, $[Co(NO_2)_6]^{4-}$ ion and $[Co(NO_2)_6]^{3-}$ ion, which would absorb light of longer wavelength in the visible region?

*9. For $[Cr(H_2O)_6]^{2+}$ ion, $E_p = 23500\ cm^{-1}$ and $\Delta_0 = 13900\ cm^{-1}$. Will it be a high-spin or low-spin complex?

*10. What is spectrochemical series ? Why is it so called?

*11. List the different factors that affect the magnitude of *d*-orbital splitting values in an octahedral complex.

*12. An aqueous solution of zinc nitrate contains the ion, $[Zn(H_2O)_6]^{2+}$ and is colourless. What do you infer about the absorption spectrum of the $[Zn(H_2O)_6]^{2+}$ ion?

*13. Should the ion, $[Co(NO_2)_6]^{4-}$ be easy or difficult to oxidize to $[Co(NO_2)_6]^{3-}$. Explain your answer.

*14. From the following list, pick out the oxides that adopt normal spinel structure.

Mn_3O_4, Fe_3O_4, $MgAl_2O_4$, $NiAl_2O_4$, $MgFe_2O_4$ and Co_3O_4

*15. CN^- and NO_2^- complexes have high Δ values ; explain.

*16. Account for the fact that Cr^{3+} and Co^{3+} form generally inert octahedral complexes.

17. Fe^{3+} forms a high-spin octahedral complex. Calculate its spin-only magnetic moment.

*18. Why does H_2O ligand give higher Δ value than OH^- ion ?

*19. Account for : the mode of splitting of *d*-orbitals in an octahedral field is just the reverse of that in a tetrahedral field.

*20. Predict which of the following octahedral complexes should have the longest frequency of absorption in the visible spectrum : $[FeCl_6]^{3-}$, $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$

*21. A complex of a transition metal ion with a d^6 configuration is diamagnetic ; is it an octahedral or a tetrahedral one?

*22. Using CFT, show the orbital occupancies for both weak and strong octahedral fields for Mn^{2+}, Zn^{2+}, Fe^{2+} and Co^{2+}. Indicate the number of unpaired electrons in each case.

*23. $[Fe(CN)_6]^{4-}$ is diamagnetic. State whether the following statements are true or false. If false, give the correct statement.

a) It is an outer orbital complex
b) Its hybridization is sp^3d^2
c) It is a spin-paired complex
d) It is a high-spin complex
e) It obeys Hund's rule
f) Its geometry is planar hexagon.

24. Account for the fact that for the same metal ion and for the same ligands, the *d*-orbital splitting in a tetrahedral field is less than that in an octahedral field.

*25. Explain why octahedral coordination complexes with three and eight *d*-electrons on the central metal atom / ion are particularly stable. Under what condition would you expect a complex with six *d*-electrons on the central metal atom / ion to be particularly stable?

*26. F^-, inspite of being smallest in size, does not give the strongest field of all ligands; explain.

*27. An aqueous solution of $Fe(NO_3)_3$ is only pale in colour, but an aqueous solution of $K_3[Fe(CN)_6]$ is bright red.

a) Would you expect a solution of $K_3[FeF_6]$ to be pale or brightly coloured? Explain your answer.
b) Would you expect a solution of $Na_2[HgI_4]$ to be brightly coloured or pale or colourless ?

28. How many unpaired electrons are present in each of the following:

a) $[Co(en)_3]^{3+}$ (low-spin)
b) $[CoF_6]^{3-}$ (high-spin)
c) $[MnCl_6]^{4-}$ (high-spin)
d) $[Mn(CN)_6]^{3-}$ (low-spin)
e) $[Fe(H_2O)_6]^{2+}$ (high-spin)

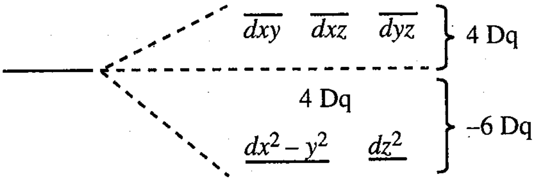
f) $[Ni(CN)_4]^{2-}$

g) $[MnBr_4]^{2-}$ (high-spin)

*29 For an octahedral Mn^{3+} complex, Δ_0 = 21150 cm^{-1} and electron pairing energy, $E_p = 27750\ cm^{-1}$. Will it be a high-spin complex or low-spin complex? Calculate its CFSE. Find out the "spin-only" magnetic moment of that complex ion.

*30. The octahedral complex ions, $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$ are paramagnetic but to different extent. Identify the *d*-electron configurations in these two octahedral complex ions. In which case the octahedral field splitting is greater? How does the crystal field stabilization energy differ between them ?

*31. The crystal field splitting in a tetrahedral complex is



a) All the tetrahedral complexes are high-spin. For which configuration will the value of CFSE be greatest?

b) Calculate the CFSE value for each of the following tetrahedral complexes: $[NiBr_4]^{2-}$, $[FeCl_4]^-$, $[CoCl_4]^{2-}$, $[MnBr_4]^{2-}$, $[Zn(OH)_4]^{2-}$

*32. $[Co(CN)_6]^{3-}$ is diamagnetic but $[CoF_6]^{3-}$ is paramagnetic with a moment of about 5.3 BM. Account for this difference in magnetic properties of these two octahedral complexes using CFT.

*33. The electron pairing energy of Co^{3+} ion is 250 kJ $mole^{-1}$. Δ_0 value for the complex ion, $[Co(NH_3)_6]^{3+}$ is 275 kJ $mole^{-1}$. Would you expect the ammine complex to be paramagnetic or diamagnetic? Explain. Also calculate its CFSE.

*34. Rationalize the following observations:

a) $[Fe(H_2O)_6]^{3+}$ is a stronger oxidizing agent than $[Fe(CN)_6]^{3-}$.

b) $[Fe(H_2O)_6]^{3+}$ is a weaker oxidizing agent than $[Fe(o\text{-}phen)_3]^{3+}$

*35. The nephelauxetic effect for ammonia is less than that for CN^- : explain.

36. $[Cu(H_2O)_6]^{2+}$ exchanges two of its water molecules more easily than the other four. Explain why?

37. What are spinels and antispinels (inverse spinels) ?

38. Pickout the species having greater Δ_0 value from the following pairs of complexes and give reason for your choice.

a) $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$

b) $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$

c) $[Co(NH_3)_6]^{2+}$ and $[Ir(NH_3)_6]^{2+}$

39. What are the postulates of crystal field theory ?

40. What are the limitations of crystal field theory ?

41. Define crystal field stabilization energy.

42. How do *d*-orbitals split in?

a) octahedral field
b) square-planar geometry and
c) tetrahedral field

43. Explain the method of finding out the crystal field splitting value for an octahedral complex with an example.

44. What are the factors that affect the magnitude of crystal field splitting energy? How do they affect?

45. The three complex ions, $[Ti(H_2O)_6]^{3+}$, $[TiF_6]^{3-}$ and $[Ti(CN)_6]^{3-}$ absorb light of wavelengths 4000 Å, 4920 Å and 5900 Å. Identify the complex ion with the wavelength of the light absorbed. Write an explanatory sentence.

46. Which of the two, $[CoCl_4]^{2-}$ and $[CoI_4]^{2-}$ is expected to have higher Δ_t and why?

*47. $[Ru(NH_3)_6]^{3+}$ behaves as a protonic acid. Rationalize this.

*48. Since NH_3 is in the middle of the spectrochemical series, some of its complexes are high-spin while others are low-spin. Illustrate.

49. $[Co(NH_3)_6]^{3+}$ is orange-yellow whereas $[CoF_6]^{3-}$ is blue, though both contain Co^{3+} ion. Account for this difference in colour qualitatively.

50. When excess aqueous HCl is added to an aqueous solution of copper sulphate, the colour changes from blue to green. Explain the observed colour change. Write balanced equation for the reaction that takes place.

*51. For which of the following metal ions are low-spin octahedral complexes impossible?
a) Cd^{2+} b) Co^{3+} c) Ti^{2+} d) Cu^+ e) Re^{3+} f) Fe^{2+}

*52. When excess NH_4OH is added to an aqueous solution of Ni^{2+}, the colour of the solution changes from bright green to blue-violet. Explain the change in colour. Write balanced equation for the reaction that occurs.

53. Calculate the spin-only magnetic moment for a d^7 ion in octahedral, (both strong-field and weak-field cases) tetrahedral and square-planar ligand fields.

*54. The four complex ions, a) $[Cr(H_2O)_6]^{3+}$, b) $[Cr(CN)_6]^{3-}$, c) $[CrCl_6]^{3-}$ and d) $[Cr(NH_3)_6]^{3+}$ show absorption. peaks at 13640 cm^{-1}, 17830 cm^{-1}, 21680 cm^{-1} and 26280 cm^{-1}. Identify the ion with the absorption peak.

*55. The three complex ions a) $[Co(NH_3)_6]^{3+}$, b) $[Rh(NH_3)_6]^{3+}$ and c) $[Ir(NH_3)_6]^{3+}$ have absorption peaks at 34000 cm^{-1}, 24800 cm^{-1} and 41000 cm^{-1}. Identify the complex ion with the absorption peak.

56. Pick out the complex species which has larger crystal field splitting in each pair. Account for your choice.
a) $[Mn(en)_3]^{3+}$ and $[MnF_6]^{3-}$
b) $[Co(H_2O)_6]^{3+}$ and $[Ir(H_2O)_6]^{3+}$
c) $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{2+}$
d) $[Fe(CN)_6]^{3-}$ and $[Fe(SCN)_6]^{3-}$

57. $[Ir(H_2O)_6]^{2+}$ and $[IrF_6]^{3-}$ approximately possess the same crystal field splitting energies. Is this consistent with the positions of these ligands ? If not, how is this similarity in Δ_0 values explained?

58. The Δ_0 value for $[Ir(H_2O)_6]^{3+}$ is greater than that for $[Co(NH_3)_6]^{3+}$ ion eventhough both contain tripositive central metal ion, same ligand and same geometry. Explain.

59. The Δ_0 values for the complexes $[Co(H_2O)_6]^{3+}$, $[Rh(H_2O)_6]^{3+}$ and $[Ir(H_2O)_6]^{3+}$ are 2.0×10^3, 3.2×10^3 and 4.0×10^3 m^{-1} respectively. What are these Δ_0 values expressed in kilocalories / mole.

60. Draw the energy level splitting diagrams and show the occupancy of the *d*-orbitals by electrons in the following cases.
    a) d^6 octahedral, high-spin
    b) d^7 octahedral, low-spin
    c) d^8 square-planar
    d) d^9 octahedral with tetragonal shortening
    e) d^9 octahedral with tetragonal elongation
    f) d^6 tetrahedral

*61. Calculate the crystal field stabilization energies in terms of Δ_0 for a d^8 system in octahedral and tetrahedral complexes. Which is more stable?

*62. Calculate the crystal field stabilization energy for the following cases. Indicate the electronic distributions using the crystal field theory.
    *a) d^3 high-spin (tet)
    b) d^4 high-spin (tet)
    *c) d^8 (oct)
    d) d^5 high-spin (oct)
    e) d^5 low-spin (oct)
    f) d^6 high-spin (oct)
    g) d^6 low-spin (oct)

63. Give the ground state *d* electron configuration, the number of unpaired electrons and the expected spin-only magnetic moment of the following ions. Predict the cases where there is a possibility of an orbital contribution to the magnetic moment. Calculate the magnitude of CFSE in terms of Δ_0.

    a) $[Rh(en)_3]^{2+}$ high-spin

    b) $[Cr(CN)_6]^{4-}$

    c) $[Co(C_2O_4)_3]^{3-}$ low-spin

    d) $[Mn(CN)_6]^{4-}$

    e) $[Mn(H_2O)_6]^{2+}$

ANSWERS

I 1. (a) 2. (d) 3. (c) 4. (b) 5. (c) 6. (b) 7. (a) 8. (d) 9. (d)
10. (a) 11. (d) 12. (c) 13. (d) 14. (b)

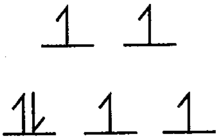
II 1. (c) 2. (a) 3. (d) 4. (b) 5. (f) 6. (e) 7. (h) 8. (g)

III

1. In octahedral complexes there are six ligands whereas in tetrahedral complexes there are only four ligands. Hence decrease in the number of ligands, decreases the amount of interaction between the ligands and metal *d*-orbitals. This is reflected in the degree of splitting. Moreover, in octahedral geometry the metal *d*-orbitals are directly pointing at the ligands whereas in tetrahedral geometry no orbital is directly pointing at the ligands, hence the amount of interaction is less. As a result of these two factors, $\Delta_0 > \Delta_t$.
2. In CuF_2, Cu is in the dipositive state, d^9, system which is subjected to Jahn-Teller distortion, due to unsymmetrical distribution of electrons in e_g levels. Hence all Cu-F distances are not equal.
3. Transition metal ions have incompletely filled *d*-orbitals, hence there is the possibility of d-d transitions. This involves less energy. Therefore light absorption occurs in the visible region; hence they are coloured.
6. In $[Mn(H_2O)_6]^{2+}$, $\Delta_0 < E_p$ hence high-spin state. But in $[Mn(CN)_6]^{4-}$ $\Delta_0 > E_p$, hence low-spin state.
8. In "Z-out case" only two bonds along Z-axis are elongated whereas in "Z-in case" four bonds in the xy-plane are elongated. Elongation of two bonds along the Z-axis is energetically more favourable than elongation of four bonds in the xy-plane. Hence "Z-out case" is more common than "Z-in case".
10. The ligand Cl^- with its negative charge is expected to produce greater Δ_0 than the neutral NH_3; however, the p π electrons of Cl^- and the d π electrons of Cr^{3+} repel each other decreasing the Δ_0 of Cl^-. Δ_0 for CN^- is very high due to back-bonding; the shift of electron density from the d π orbitals of Cr^{3+} to the antibonding π^* orbitals of CN^-; this interaction stabilizes the dπ orbitals and enhances Δ_0.

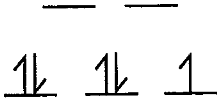
IV

2. Cu^{2+}, d^9 system, hence subjected to Jahn-Teller distortion. But Ni^{2+} is d^8 system which is not subjected to this distortion due to symmetrical distribution of electrons in the e_g level. Hence Ni^{2+} octahedral complexes are regular.
3. The sixth coordination position around iron in haemoglobin which is originally occupied by weak-field, H_2O ligand is occupied by this strong-field ligand CO or CN^-. Hence that position is not vacated for O_2. Therefore such haemoglobin loses its oxygen-carrying capacity. Thus it poisons the blood.
5. $[Fe(H_2O)_6]^{3+}$ is expected to have higher splitting energy for *d*-orbitals because of its higher charge. Greater the charge of the complex ion, greater is the amount of interaction leading to greater splitting energy.
6. Complexes having maximum number of unpaired electrons are called as high-spin complexes. For example $[Fe(H_2O)_6]^{2+}$, Fe^{2+}, d^6, H_2O is a weak field ligand. The electron distribution is, (High spin complexes are also called spin-free complexes.)



4 unpaired electrons

Complexes having minimum number of unpaired electrons are called low-spin complexes. For example, $[Fe(CN)_6]^{3-}$. Fe^{3+} d^5 system. CN^- is a strong field ligand. Hence the electron distribution is,

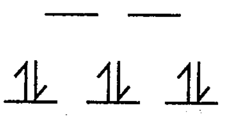


only one unpaired electrons

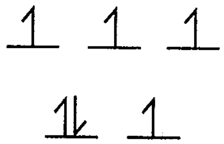
Low-spin complexes are also called spin-paired complexes.

8. $[Co(NO_2)_6]^{4-}$ ion absorbs light of longer wavelength because Co^{2+} in it develops less crystal field splitting energy. Lesser the energy, larger will be the wavelength of light absorbed.
9. It is high-spin complex because $E_p > \Delta_0$; hence electrons do not prefer to get paired, that is one e_g orbital is also filled by a single electron.
10. Spectrochemical series is the series of ligands where the ligands are arranged in the increasing order of their splitting ability for the metal *d*-orbitals. Since the splitting ability of various ligands are arrived at from the study of the absorption spectra of their complexes; the term spectrochemical series is used for such series.
11. (i) charge of the central metal ion
    (ii) geometry of the complex
    (iii) nature of the ligand and
    (iv) principal quantum number of the *d*-electron.
12. This ion does not absorb any significant amount of light in the visible region.
13. $[Co(NO_2)_6]^{4-}$ should be easier to oxidize to $[Co(NO_2)_6]^{3-}$ because the cobalt in $[Co(NO_2)_6]^{4-}$ has an electron in the upper e_g level.
14. Normal spinel structure: Mn_3O_4, Co_3O_4 and $MgAl_2O_4$
    Inverse structure: Fe_3O_4, $NiAl_2O_4$, $MgFe_2O_4$
15. This is due to $d\pi \rightarrow p\pi^*$ back bonding.
16. Cr^{3+} has half-filled $(t_{2g})^3$ levels and Co^{3+} has completely filled $(t_{2g})^6$ levels with strong field ligands. These configurations confer exceptional stability. The activated complex in a ligand substitution reaction is a configuration that includes both the ligand that is leaving and the ligand that will be bound to the metal in the product. There is a large loss in CFSE on formation of the activated complex for octahedral complexes with either the $(t_{2g})^3$ or $(t_{2g})^6$ configuration, and thus the activation energy is very large and the reaction occurs very slowly, that is they are inert generally.
18. In H_2O, there is only $p\pi$ lone pair orbital in contrast to two in OH^-; therefore, the $p\pi$-$d\pi$ repulsion is lesser with H_2O than with OH^-.

19. In an octahedral field, e_g, metal orbitals are directly pointing at the approaching ligands; hence e_g orbitals interact to a greater extent with the ligands. So e_g orbitals become high energy orbitals in octahedral complexes. But in a tetrahedral complex, the t_{2g} metal orbitals are closer to the approaching ligands hence t_{2g} orbitals interact to a greater extent with the ligand orbitals. So t_{2g} orbitals become high energy orbitals in a tetrahedral field.
20. CN^- is the strongest field ligand among Cl^-, H_2O and CN^-. Hence CN^- splits the d-orbitals by the greatest amount. Therefore the frequency of the light absorbed should be greatest for $[Fe(CN)_6]^{3-}$ ion. That is the wavelength of the light absorbed is the shortest for this ion.
21. It is octahedral because it gives no unpaired electron as shown below. But tetrahedral geometry has 4 unpaired electrons.

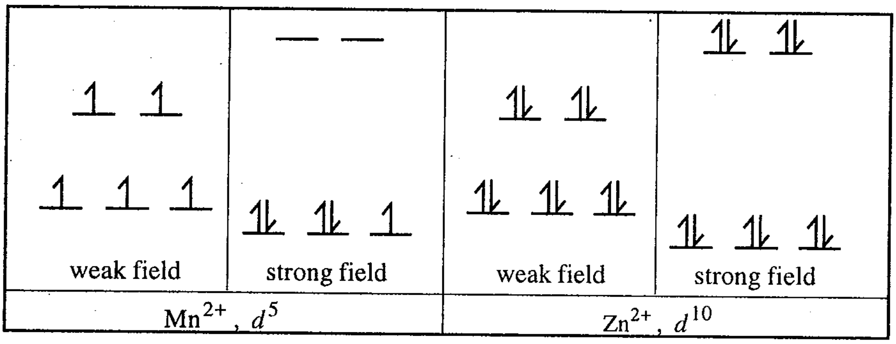


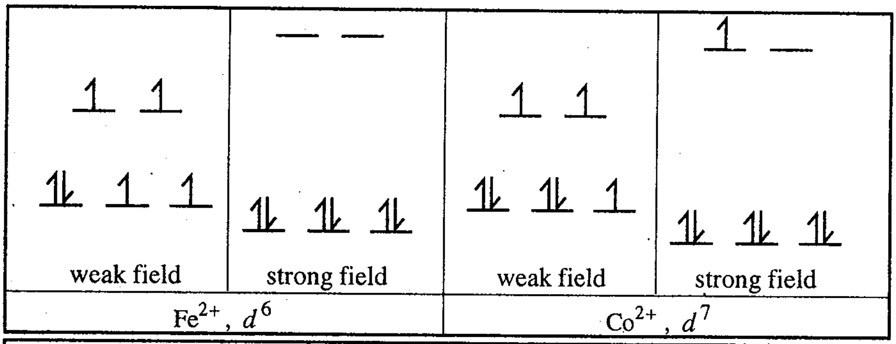
a) octahedral splitting
no unpaired electron, hence
diamagnetic.



b) tetrahedral splitting
it is paramagnetic due to
unpaired electrons

22.





No. of unpaired electrons	Mn^{2+}	Zn^{2+}	Fe^{2+}	Co^{2+}
weak field	5	0	4	3
strong field	1	0	0	1

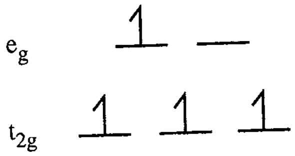
23. a) False : It is an inner orbital octahedral complex
    b) False : Its hybridisation is d^2sp^3
    c) True
    d) False : It is a low-spin complex
    e) False : It does not obey Hund's rule.
    f) False : Its geometry is octahedral

25. d^3 gives half-filled (t_{2g})and d^8 gives filled (t_{2g}) and half-filled (e_g) shells for metal atoms / ions in an octahedral field. d^6 will be particularly stable for a low-spin case since it gives filled subshell $(t_{2g})^6$.

26. With F^- ligand, there are pπ-dπ repulsions which reduce Δ values. These repulsions are responsible for the relatively low ligand fields (Δ values) for the halide ions.

27 (a) pale in colour because F^- is an even weaker field ligand than H_2O. Hence it is high-spin, d^5, half-filled shell, and absorbs only weakly.
   (b) colourless because, Hg^{2+} is a d^{10}, completely filled sublevel species.

29. Mn^{3+} is a d^4 system. Since $\Delta_0 < E_p$, it will be a high-spin complex. The electron distribution will be,



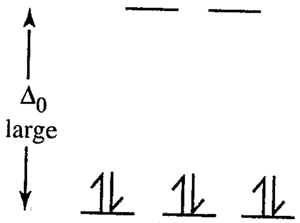
Its CFSE will be $-1.2\ \Delta_0 + 0.6\ \Delta_0 = -0.6\ \Delta_0$
$= -0.6 \times 21150 = -12690\ \text{cm}^{-1}$.
Its spin-only magnetic moment will be,
$\sqrt{n(n+2)} = \sqrt{4(6)} = \sqrt{24} = 4.90$ BM
It is paramagnetic with a moment of 4.90 BM.

30. Fe^{3+} has five d electrons. $[FeF_6]^{3-}$ is a high-spin complex hence it has 5 unpaired electrons $(t_{2g}^3 e_g^2)$. But $[Fe(CN)_6]^{3-}$ is a low-spin complex, hence it has only one unpaired electron $(t_{2g}^5 e_g^0)$. The splitting is greater for cyanide ion than for fluoride ion. The CFSE for $[FeF_6]^{3-}$ is zero, whereas it is $-2\ \Delta_0 + 2\ E_p$ where E_p is the electron pairing energy which has to be spent to pair the electrons in $[Fe(CN)_6]^{3-}$.

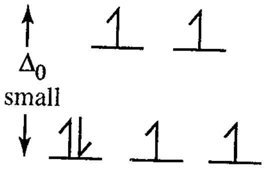
31. a) d^2 and d^7 configurations
    b)

Complex			*CFSE*
$[NiBr_4]^{2-}$	Ni^{2+}	d^8	$-8\ D_q$
$[FeCl_4]^-$	Fe^{3+}	d^5	$0\ D_q$
$[CoCl_4]^{2-}$	Co^{2+}	d^7	$-12\ D_q$
$[MnBr_4]^{2-}$	Mn^{2+}	d^5	$0\ D_q$
$[Zn(OH)_4]^{2-}$	Zn^{2+}	d^{10}	$0\ D_q$

32.



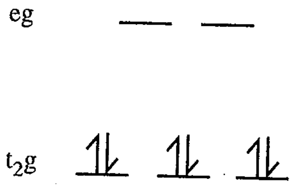
strong field low-spin case
$[Co(CN)_6]^{3-}$, $\mu = 0$



weak field high-spin case
$[CoF_6]^{3-}$, $\mu = 0$

"spin-only" magnetic moment for $[CoF_6]^{3-}$ is, $\sqrt{4(6)} = \sqrt{24} = 4.90$ BM. But the observed magnetic moment is slightly larger than 4.90 BM (the value predicted by "spin-only" formula) because of a small contribution from the orbital angular momentum of the electrons.

33. Co^{3+} is a d^6 system. Since $\Delta_0 > E_p$, it is a low-spin complex. The electron distribution for a low-spin case will be,



$\Delta_0 > E_p$
Co^{3+}, d^6 system

Since there is no unpaired electron, the ammine complex would be diamagnetic. Its CFSE will be, $-2.4\ \Delta_0 + 2\ E_p$
$= -2.4\ (275) + 2\ (250)$
$= -660 + 500$
$= -160$ kJ mole^{-1}

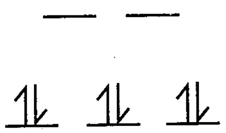
34. a) CN^- is a strong-field ligand and therefore it stabilizes Fe(III) in $[Fe(CN)_6]^{3-}$, reducing its oxidizing power.

b) The overall stability constant of $[Fe(o\text{-}phen)_3]^{2+}$ is greater than that of $[Fe(o\text{-}phen)_3]^{3+}$ as the former, unlike the latter is a low-spin complex. The increased stability of the Fe(II) complex is the driving force for the stronger oxidizing power of the Fe(III) complex,
E_0 : Fe(III) = +0.77 V
$E_0 : [Fe(phen)_3]^{3+} / [Fe(phen)_3]^{2+} = 1.14$

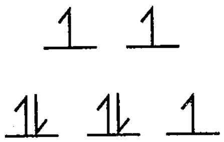
35. The extent of nephelauxetic effect depends on the degree of outlet provided by the ligands by which metal *d* electrons escape from the metal to some extent (the size of the *d* electron cloud is increased). CN^- can function as a π-acid unlike NH_3. It means that CN^- can form molecular orbitals with the metal e_g and t_{2g} orbitals leading to high cloud expansion. NH_3, which is not a π-acid can form molecular orbitals only with the metal e_g orbitals and hence its nephelauxetic ability is lesser than that of CN^-

47. The neutral ligand NH_3 cannot stabilize a higher oxidation state of a metal as much as a negative ligand does. Therefore, the hydrogen of NH_3 ligand of this complex tend to become positive (H^+) leading to the formation of NH_2^- ; this anion then stabilizes the complex.

48. $[Co(NH_3)_6]^{2+}$ is a paramagnetic, high-spin complex whereas $[Co(NH_3)_6]^{3+}$ is a diamagnetic, low-spin complex. This is because the higher charge on the Co^{3+} ion results in a greater value of Δ_0 for $[Co(NH_3)_6]^{3+}$ than for $[Co(NH_3)_6]^{2+}$. There are six *d* electrons for Co^{3+} and they fill the t_{2g} level of $[Co(NH_3)_6]^{3+}$, so that there are no unpaired electrons. But there are seven *d* electrons for Co^{2+} and since Δ_0 is less for $[Co(NH_3)_6]^{2+}$, these electrons occupy both t_{2g} and e_g levels giving rise to 3 unpaired electrons; hence $[Co(NH_3)_6]^{2+}$ is paramagnetic and high-spin complex.



$[Co(NH_3)_6]^{3+}$, d^6



$[Co(NH_3)_6]^{2+}$, d^7

a) Δ_0 is large due to larger charge on cobalt hence low-spin state no unpaired electrons hence diamagnetic.

b) Δ_0 is small due to smaller charge on cobalt hence high-spin state paramagnetic due to 3 unpaired electrons.

51. a, c, and d

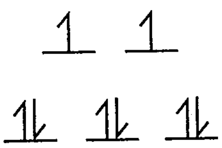
52. In aqueous solution, Ni^{2+} exists as $[Ni(H_2O)_6]^{2+}$ which transmits green whereas $[Ni(NH_3)_6]^{2+}$ in the presence of excess NH_4OH transmits blue violet.

$$[Ni(H_2O)_6]^{2+} + 6\,NH_4OH \rightleftharpoons [Ni(NH_3)_6]^{2+} + 12\ H_2O$$

54. a) 17830 cm^{-1} b) 26280 cm^{-1} c) 13640 cm^{-1} d) 21680 cm^{-1}

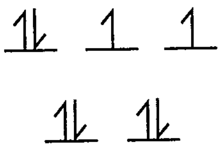
55. a) 24800 cm^{-1} b) 34000 cm^{-1} c) 41000 cm^{-1}

61.



d^8 octahedral

CFSE = $-1.2\,\Delta_0$



d^8 tetrahedral

CFSE = $-0.8\,\Delta_0 \times 0.45$

$= -0.36\ \Delta_0$

d^8, octahedral complex having greater stabilization energy will be more stable.

62. a) CFSE 0.8 Δ_t : $(e)^2(t_2)^1$

d) CFSE = 0 Δ_0 : $(t_{2g})^3(e_g)^2$

than one *d* electron, the interactions or couplings between the quantum numbers for the individual electrons must be considered in explaining the spectrum.

5.3.1 Quantum Numbers

An electron in a complex ion can initially be assigned a set of four quantum numbers:

1) *n* principal quantum number
2) *l* azimuthal or orbital angular momentum quantum number
3) m_l magnetic orbital quantum number
4) *s* spin quantum number.

In a two-electron system (d^2), then three types of electronic interactions are possible:

1) *Spin-spin coupling*, in which the spin angular momenta of the two electrons are coupled.
2) *Orbit-orbit coupling*, in which the orbital angular momenta of the two electrons are coupled.
3) *Spin-orbit coupling*, in which coupling of spin and orbital angular momenta on the same electron are coupled.

The coupling between the spin of one electron with the orbital angular momentum of a different electron is negligible and hence ignored.

These couplings are called the *Russell–Saunders couplings*; such couplings modify electron energies.

For elements of low atomic numbers, including those of first transition series.

spin-spin coupling > orbit-orbit coupling > spin-orbit coupling

Among elements beyond $Z = 30$, spin-orbit coupling becomes significant and therefore with heavy elements, a different system called *jj* coupling is used.

5.3.2 jj - Coupling for Heavy Elements

In this procedure, first the spin (*s*) and the orbital angular momentum (ℓ) of individual electrons are coupled to get the *j* value for the electron. Then the *j* values of all the electrons are coupled to get the resultant *j* values. However, as the atomic number of the system increases, the selection rules also progressively fail. Thus, with heavy atoms, the transitions between singlet and triplet states ($S = 0$ and $S = 1$), which are normally forbidden in lighter atoms, also become allowed.

5.3.3 Spin-Spin Coupling

The spin quantum number(*s*) of the individual electrons are coupled to give the *resultant spin quantum number (S)* of electrons:

$$S = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2), \ldots\ldots (s_1 - s_2)$$

(1) For two electrons, $S = 1$ or 0. When the spins of the two electrons are coupled parallel (↑↑), then $S = 1$.

(2) When they are coupled opposed (↑↓), then $S = 0$.

(3) For three electrons,
 a) the coupling $\uparrow\uparrow\uparrow$ gives $S = 3/2$;
 b) the coupling $\uparrow\uparrow\downarrow$ gives $S = 1/2$.

(4) For four electrons,
 a) the coupling $\uparrow\uparrow\uparrow\uparrow$ gives $S = 2$;
 b) the coupling $\uparrow\uparrow\uparrow\downarrow$ gives $S = 1$;
 c) the coupling $\uparrow\uparrow\downarrow\downarrow$ gives $S = 0$

5.3.4 Orbit-Orbit Coupling

The total angular momentum quantum number L for two electrons is obtained by adding vectorially their orbital angular momenta ℓ_1 and ℓ_2:

$$L = (\ell_1 + \ell_2), (\ell_1 + \ell_2 - 1), (\ell_1 + \ell_2 - 2), \ldots\ldots (\ell_1 - \ell_2)$$

For two p electrons,

$\ell_1 = 1$ and $\ell_2 = 1$.

Therefore $L = 2$, 1 and 0.

For two d electrons,

$\ell_1 = \ell_2 = 2$. Therefore, $L = 4,3,2,1,0$

For individual electrons ℓ values define their orbitals; $\ell = 0$ implies an s orbital, $\ell = 1$ implies a p orbital,etc. Similarly, L values define the quantum numbers or energy states for a system (group) of electrons. Such L values (*states*) are denoted by a set of capital letters called *term letters*:

L	0	1	2	3	4	5	6
Term letter	S	P	D	F	G	H	I

5.3.5 Spin-Orbit Coupling

The total angular momentum for a system of electrons is denoted by the letter J. It is obtained by coupling the resultant spin and angular momenta as per the relation

$$J = (L + S), (L + S - 1), (L + S - 2), \ldots\ldots\ldots (L - S)$$

Terms of different L values denote different energies. For given values of L and S, several levels close together are possible. The number of such possible levels is called the *multiplicity*. The multiplicity is arrived at by the formula $(2S + 1)$:

S	J	Multiplicity
0	L	1, singlet
½	$(L + ½), (L - ½)$	2, doublet
1	$(L + 1), L, (L - 1))$	3, triplet

When $L = 0$, the multiplicity can be only 1; that is, S terms can have only one value of J.

All these information pertaining to the system of electrons is usually conveyed in a single symbol called as a *term symbol*:

$$\text{term symbol} = {}^{(2S+1)}L_J$$

When $L = 2$ and $S = 1$, the term symbol becomes,

$${}^{(2\times1+1)}2_{3,2,\text{or}\,1} = {}^3\text{D}$$

as $J = (2 + 1 = 3), (2 + 1 - 1 = 2), (2 - 1 = 1)$

(D is the term letter for $L = 2$). The three states of the triplet are ${}^3\text{D}_3$, ${}^3\text{D}_2$ and ${}^3\text{D}_1$.

5.3.6 Terms for *d* Electron Systems

d^1 For d^1 system, there is only one electron and therefore, $L = \ell = 2$, $S = ½$ Therefore, there is only one term possible, that is ^{2}D.

d^2 For a d^2 system, $L = 4, 3, 2, 1$ and 0. Therefore, it gives G, F, D, P and S terms. multiplicities = 1 and 3

[as $S = 1$ or 0, $(2S + 1) = 3$ or 1]

Some of these terms violate Hund's rule and therefore are not allowed; only ${}^3P$, ${}^3F$, ${}^1S$, ${}^1D$ and ${}^1G$ are allowed. Then, the lowest-energy or ground term is identified by applying Hund's rules; according to these rules

(*a*) *The most stable state is that with maximum multiplicity*

(*b*) *For a group of terms with the same multiplicity, that with the largest L value has its lowest energy. Then, for the d^2 system, ${}^3F$ is the ground term.*

The Russell-Saunders coupling scheme for a d^2 ion is denoted in Fig. 5.1.

1. λ in this figure is called the *spin-orbit coupling constant*; the energy separations between levels produced by spin-orbit coupling are expressed in terms of λ.
2. The separation between the levels of J values, J and $(J + 1) = (J + 1)\ \lambda$.
3. For the ${}^3F$ term, $L = 3$ and $S = 1$; therefore, $J = (3 + 1)$, 3 and $(3 - 1)$; these correspond to the three states ${}^3F_4$, ${}^3F_3$ and ${}^3F_2$.
4. The separation between ${}^3F_4$ and ${}^3F_3$ is 4λ and that between ${}^3F_3$ and ${}^3F_2$ is 3λ.

On applying an external magnetic field to the electron system, a further splitting of energy level occurs (the Zeeman effect). Then, the J values are split into $(2J + 1)$; these split levels are equally spaced and their number corresponds to the number of values that can be assumed by the magnetic quantum number m. $(-J, \ldots\ldots 0, \ldots\ldots +J)$. The separation between these energy levels is $g\,\beta H$;

g is the Lande splitting factor

β is the Bohr magneton

H is the applied magnetic field strength

The Lande factor is given by the equation

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

This equation indicates that g varies between 1 and 2 as J varies between L ($S = 0$) and S ($L = 0$).

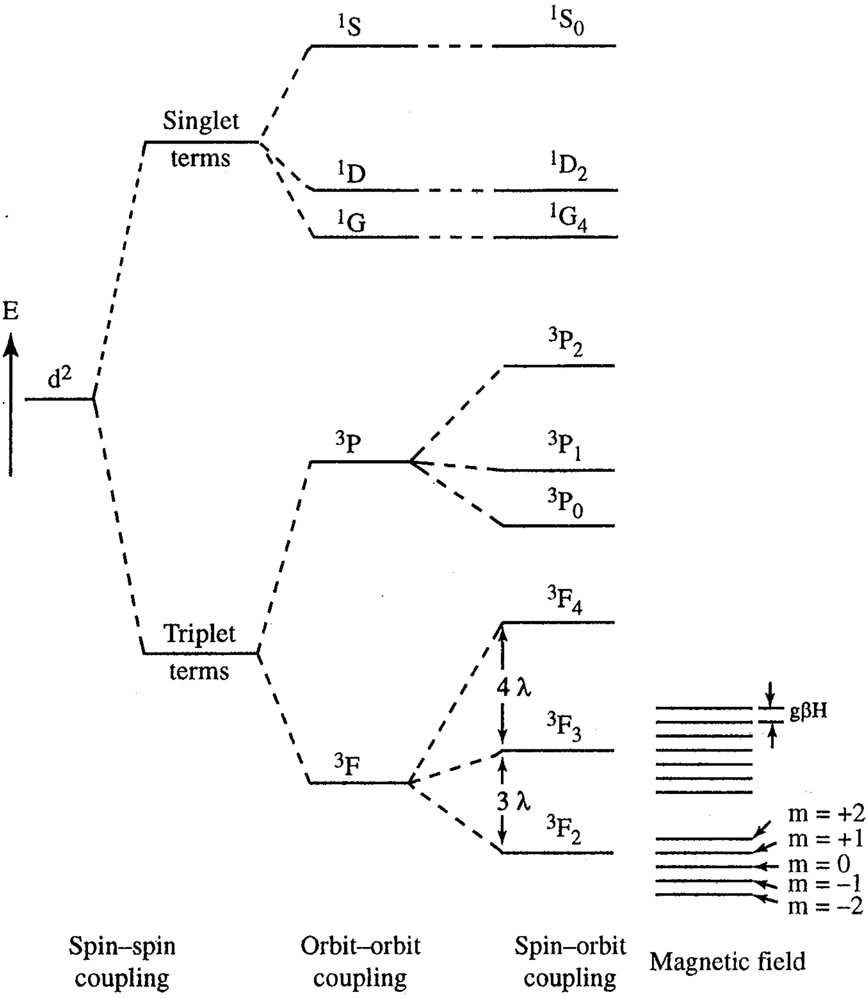


Fig. 5.1 The effect of Russell-Saunders coupling on d^2 configuration

5.3.7 Terms Resulting from d^n Configurations

The terms resulting from the other d^n configurations can be deduced similar to the procedure adopted for the d^2 configuration; then the Russell–Saunders coupling process applied to these terms. Such terms from d^3, d^4, d^5, d^6 and d^7 configurations are many; these are given in Table 5.2.

Table 5.2 Terms arising from the d^n configurations

Configuration	Terms
d^1, d^9	$^2\mathrm{D}$
d^2, d^8	$^3\mathrm{F}$, $^3\mathrm{P}$, $^1\mathrm{G}$, $^1\mathrm{D}$, $^1\mathrm{S}$
d^3, d^7	$^4\mathrm{F}$, $^4\mathrm{P}$, $^2\mathrm{H}$, $^2\mathrm{G}$, $^2\mathrm{F}$, $^2\mathrm{D}$ (2), $^2\mathrm{P}$
d^4, d^6	$^5\mathrm{D}$, $^3\mathrm{H}$, $^3\mathrm{G}$, $^3\mathrm{F}$ (2), $^3\mathrm{D}$, $^3\mathrm{P}$ (2), $^1\mathrm{I}$, $^1\mathrm{G}$ (2), $^1\mathrm{F}$, $^1\mathrm{D}$ (2), $^1\mathrm{S}$ (2)
d^5	$^6\mathrm{S}$, $^4\mathrm{G}$, $^4\mathrm{F}$, $^4\mathrm{D}$, $^4\mathrm{P}$, $^2\mathrm{I}$, $^2\mathrm{H}$, $^2\mathrm{G}$ (2), $^2\mathrm{F}$ (2), $^2\mathrm{D}$ (3), $^2\mathrm{P}$, $^2\mathrm{S}$

5.3.8 Ground Terms for d^n Configurations

A ground term is the one which describes that electronic arrangement which has the lowest energy. The action of crystal field on the ground term of the isolated transition metal ion is largely responsible for the observed spectra.

In understanding the electronic spectra of d^n species, identifying the ground term is useful. This is done as indicated below:

The ground term should have the largest value of S; using this as guidance, the multiplicity can be written. As there are five degenerate d orbitals in the free ion, pairing of spins can occur only after d^5. The multiplicities for the d^n ions are

d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
2	3	4	5	6	5	4	3	2

Applying the Pauli Exclusion Principle, the maximum value of M_L should be found out. The M_L values thus arrived at for the d^n ions are given in Table 5.3.

Table 5.3 Ground terms for d^n configurations

Configuration	m_l					M_L	S	Ground term	Example
	2	1	0	−1	−2				
d^1	↑					2	1/2	$^2\mathrm{D}$	Ti^{3+}
d^2	↑	↑				3	1	$^3\mathrm{F}$	V^{3+}
d^3	↑	↑	↑			3	3/2	$^4\mathrm{F}$	Cr^{3+}
d^4	↑	↑	↑	↑		2	2	$^5\mathrm{D}$	Cr^{2+}
d^5	↑	↑	↑	↑	↑	0	5/2	$^6\mathrm{S}$	Mn^{2+}
d^6	↑↓	↑	↑	↑	↑	2	2	$^5\mathrm{D}$	Fe^{2+}
d^7	↑↓	↑↓	↑	↑	↑	3	3/2	$^4\mathrm{F}$	Co^{2+}
d^8	↑↓	↑↓	↑↓	↑	↑	3	1	$^3\mathrm{F}$	Ni^{2+}
d^9	↑↓	↑↓	↑↓	↑↓	↑	2	1/2	$^2\mathrm{D}$	Cu^{2+}

The details in Table 5.3 indicate that the term arising from a d^n configuration is the same as that for the d^{10-n} configuration; this simplifies the treatment of spectral and magnetic data of d^n complexes.

5.4 SELECTION RULES FOR ELECTRONIC TRANSITIONS IN COMPLEXES

The electronic transitions in complexes are governed by two sets of rules:

5.4.1 Spin Selection Rule

Transitions between states of different multiplicity, S are forbidden.

The electromagnetic field of the incident radiation cannot change the relative orientations of the spins of the electrons in a complex. The antiparallel pair (↑↓) cannot be converted to a parallel pair (↑↑); a singlet ($S = 0$) cannot undergo a transition to a triplet ($S = 1$). Therefore, $\Delta S = 0$ for spin-allowed transitions.

The breakdown of the spin-selection rule The spin selection rule can be relaxed by the coupling of spin and orbital angular momenta leading to a transition. Such a transition is spin-forbidden transition ($\Delta S \neq 0$). These transitions are much weaker than spin-allowed transitions. The spin-orbit coupling depends on the charge on the nucleus and therefore it is greater for heavy atoms; consequently, the intensity of spin-forbidden bands increases with increasing atomic number. The breakdown of the spin selection rule due to spin-orbit coupling is called the *heavy-atom effect.* In the first transition series, with weak spin-orbit coupling, the spin-forbidden bands are weak; with second and third *d* series, these bands are significant.

5.4.2 The Laporte Selection Rule

This rule is related to the change in parity in an electronic transition:

The only allowed transitions in a centrosymmetric molecule or ion are those accompanied by a change in parity.

This rule implies that transitions between *g* (*gerade*) and *u* (*ungerade*) terms are permitted, but not between two *g* terms and between two *u* terms.

$$g \leftrightarrow u \qquad g \not\leftrightarrow g \qquad u \not\leftrightarrow u$$

Thus, $d \rightarrow d$ and $p - p$ transitions are forbidden but $s - p$ and $p - d$ transitions are allowed.

In a centrosymmetric complex, ligand-field *d-d* transitions are *g-g* and are therefore forbidden. Their forbidden nature accounts for the weakness of these transitions in octahedral complexes. As tetrahedral complexes have no centre of symmetry, the Laporte rule is not applicable to them and therefore, the *d-d* transitions in them are strong.

Why does a weak *d-d* transition occur, though the Laporte rule rules out such a transition? This question may be answered by considering four factors:

(a) The environment of the complex packed in a crystal may induce slight deviation in the perfect centrosymmetry of the complex species.

(b) The intrinsic asymmetry in the structure of the polyatomic ligands can render the complex species slightly asymmetric.

(c) An asymmetric vibration of the complex ion can cause destruction of its centre of inversion.

(d) In a complex, several normal modes of vibration occur; some of these are antisymmetric with respect to the inversion centre (*u*-type vibrations). On mixing the vibrational and electronic parts of the wave function (called *vibronic coupling*), the ground term may get mixed with a *g*-type vibration and the excited term with a *u*-type vibration. Then, the transition may become partly $g \rightarrow u$ (allowed) instead of being $g \rightarrow g$.

A Laporte-forbidden transition is usually stronger than a spin-forbidden transition. The charge-transfer transitions are stronger than *d-d* transitions.

The selection rules control the intensity of absorption bands. The molar absorption coefficient (ε) measures the absorption band intensities. The ε values for intensities of spectral bands for electronic transitions in 3*d* complexes are given in Table 5.4.

Table 5.4 Spectral band intensities in 3*d* complexes

Transition	$\varepsilon/\mathrm{M}^{-1}\mathrm{cm}^{-1}$
Spin-forbidden	< 1
Laporte-forbidden *d-d*	20 – 100
Laporte-allowed *d-d*	~ 250
Symmetry allowed	1,000 – 50,000

The weak absorptions by some oxy-anions such as NO_2^- and NO_3^- overlap with the *d-d* transition bands. Ions such as Cl^-, ClO_4^- and SO_4^{2-} do not absorb in this region and therefore are preferred as *counter-ions* to avoid complications when the spectra of complexes are recorded.

The intensities of absorption bands are experimentally measured in terms of the molar absorption coefficient ε. The term ε is related to the measured light intensities by the Beer-Lambert law:

$$\log \frac{I_o}{I} = \varepsilon c l$$

where I_0 = intensity of incident light
I = intensity of transmitted light
c = concentration of the absorbing species in gram-moles per litre
l = path length (cm) of light passing through the solution

$$\log \frac{I_o}{I} = \text{absorbance } A$$

Therefore, $A = \varepsilon c l$; $\varepsilon = \dfrac{A}{cl}$

The molar absorption coefficient is the absorbance of a 1 molar solution of thickness 1 cm.

5.5 WIDTH OF ABSORPTION SPECTRA

The widths of the absorption spectra of different complexes vary; some complexes produce sharp bands while others broad ones. For example, the single absorption band of $[Ti(H_2O)_6]^{3+}$ is quite broad, extending over several thousand wave numbers

($25{,}000\ cm^{-1} - 15000\ cm^{-1}$). This band breadth arises from non-rigid, non-static structure of the complex. The metal-ligand bonds in it constantly vibrate leading to molecules with slightly different structures. The ground state *d* electron energies in one structure are slightly different from those in another of the same complex and therefore Δ_0 varies for these structures. This precludes sharp, single-energy electron transition and therefore a broad band results in the spectrum. The metal-ligand vibration is accentuated by molecular collisions in solution.

Line broadening of an absorption spectrum of a complex may arise from

(i) metal-ligand bond vibrations
(ii) spin-orbit coupling
(iii) the Jahn-Teller effect.

Therefore, electronic spectral bands are usually very broad with band widths of the order $1000 cm^{-1} - 3000 cm^{-1}$

5.5.1 Jahn–Teller effect and Electronic Spectra

The electronic spectra of some complexes can be diagnostic of the Jahn–Teller distortions in them. The Jahn–Teller theorem is applicable to excited states also as it is to ground states. However, the effect on an excited state is complicated because of the short life of the excited state, which does not permit the attainment of a stable equilibrium configuration of the complex. To understand the Jahn-Teller effect on an excited state, the $[Ti(H_2O)_6]^{3+}$ can be considered. The presence of a single e_g electron in it leads to splitting of the excited state; such a splitting produces a broad, flat contour of the absorption spectrum for $[Ti(H_2O)_6]^{3+}$ (Fig. 5.2). In $[Fe(H_2O)_6]^{2+}$ and also in $[CoF_6]^{3-}$, the ground state has the configuration $t_{2g}^4e_g^2$ and the excited state $t_{2g}^3e_g^3$ with the same number of unpaired electrons. Therefore, the excited states of these complexes undergo Jahn-Teller splitting into two components; this splitting is reflected in their absorption spectra, each of which consists of two broad peaks. The spectrum of $[CoF_6]^{3-}$ is shown in Fig. 5.3.

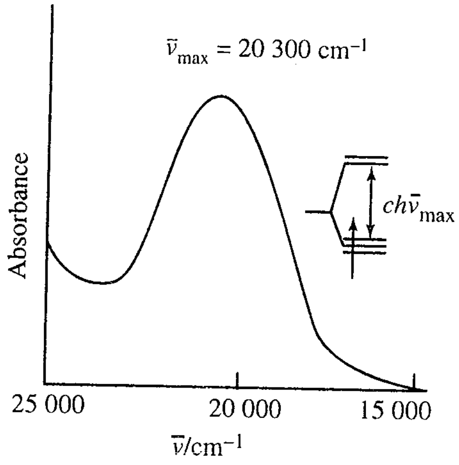


Fig. 5.2 The electronic spectrum of $[Ti(H_2O)_6]^{3+}$

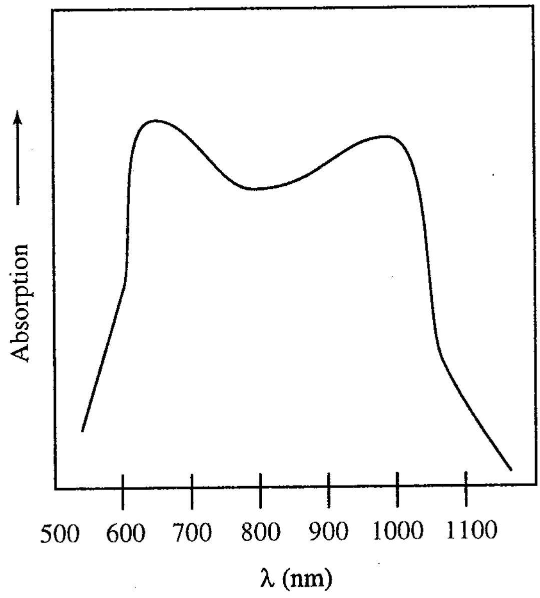


Fig. 5.3 The absorption spectrum of $[CoF_6]^{3-}$

5.6 TERMS GENERATED IN LIGAND FIELDS

The terms arising from free ions have been considered earlier. The ligand fields in a complex influence the Russell-Saunders couplings. The dengeneracy of the ground terms are lifted by the ligand fields and a number of component terms is produced. In addition to the spin multiplicity already explained, each of the ground terms of the d^n ions has an orbital multiplicity of $(2L + 1)$. (This is similar to the multiplicity $(2l + 1)$ for the number of atomic orbitals of a particular kind, *s*, *p*, *d* or *f*). Thus, the splittings of spectral terms for d^n configurations in an octahedral field are given in Table 5.5. These terms are called the *Mulliken symbols.*

Table 5.5 Terms arising from d^n configurations in octahedral and tetrahedral fields

Term	Degeneracy	States in octahedral field
S	1	A_1
P	3	T_1
D	5	$E + T_2$
F	7	$A_2 + T_1 + T_2$
G	9	$A_1 + E + T_1 + T_2$

These orbital degeneracies are depicted in Fig. 5.4a

A : orbitally non-degenerate term
E : doubly degenerate term
T : triply degenerate term

For simplicity the *g* (gerade) subscripts are omitted in the term symbols.

In each case, the spin multiplicity, which is the same for the component terms as for the parent term, is added as the left superscript (e.g., $^3T_2$)

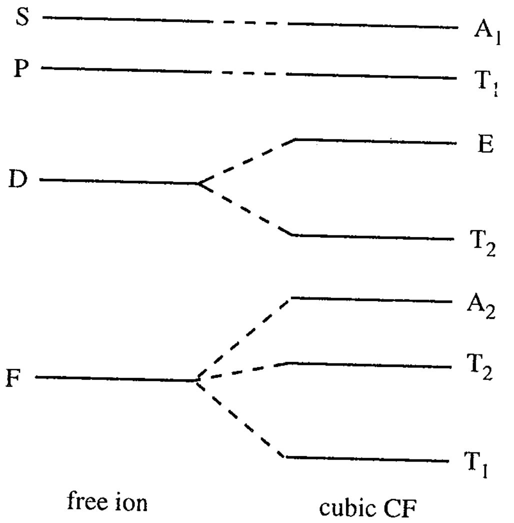
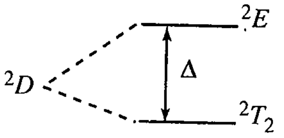


Fig. 5.4a The splitting of free-ion spectroscopic terms by a cubic crystal field

The splitting of the D and F terms under the influence of a cubic CF is not always as depicted in Figure 5.4a; it may be inverted. For the splitting of d orbitals, if the nature of the cubic CF (octahedral or tetrahedral) is known, then which orbital set t_{2g} or e_g lies lower can be known; but for D and F terms, in addition to this information, the number of electrons present should also be known to describe the splitting.

5.6.1 Correlation of Spectroscopic Ground Terms with Electron Configurations for d^n Ions in Octahedral CF

d^1 ion The ground configuration is t_{2g}^1. The single electron can occupy any of the three degenerate t_{2g} orbitals; therefore, it has an orbital degeneracy of 3, corresponding to a ground T term. When this electron is excited to an e_g orbital, then it has an orbital degeneracy of only 2; this excited e_g^1 configuration corresponds to an E term at an energy Δ above the T:



e^1 1 electron in 2 orbitals, degeneracy = 2

t_2^1 1 electron in 3 orbitals, degeneracy = 3

Fig. 5.4b

d^9 ion This has a ground configuration $t_{2g}^6e_g^3$; in this, the "positive hole" (absence of electron) can occupy either of the two degenerate e_g orbitals. Then, the orbital degeneracy is 2 corresponding to an E term. When a t_{2g} electron is excited to the e_g set, then the "hole" is effectively transferred to a t_{2g} orbital and has an orbital degeneracy of 3.

an electron from a t_{2g} orbital to an e_g orbital. The spectroscopic term for the ground state of gaseous Ti^{3+} ion is ^2D; the corresponding description of the $\left(t_{2g}^1\right)$ and (e_g^1) configurations are T_{2g} and E_g. The T_{2g} state lies 0.4 Δ_0 below, and E_g state 0.6 Δ_0 above the values of the energies of the five *d* orbitals in a spherical field. The energy for the electronic transition $E_g \leftarrow T_{2g}$ increases as Δ_0 increases. The emission is denoted as $E_g \rightarrow T_{2g}$. The energy level diagram for the d^1 ion is shown in Fig. 5.6.

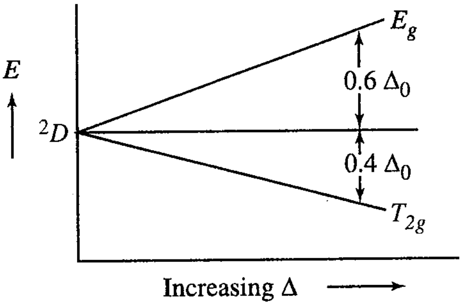


Fig. 5.6 *Energy level diagram for a d^1 ion (octahedral field)*

In several cases, the λ_{max} of the lowest frequency band in the visible or ultraviolet region arises from the promotion of an electron from a t_{2g} orbital to an e_g orbital. This band in the visible region results in characteristic colours for many transition metal complexes.

In $[Ti(H_2O)_6]^{3+}$, this transition corresponds to an energy absorption of 244 kJ $mole^{-1}$. In the free Ti^{3+}, such a transition is spectroscopically forbidden as according to the selection rule for electronic spectra $\Delta l = \pm 1$, where *l* is the second quantum number. However, it occurs in the complex due to the loss of the perfect octahedral symmetry by the vibrations of the ligand molecules (H_2O). This vibration causes also broadening of the absorption peak; in the absence of such vibrations, the spectral absorption should be sharp producing a line. The absorption in $\left[Ti(H_2O)_6\right]^{3+}$ is weak and therefore the complex has a pale colour.

The value of Δ_0 for the complex can be evaluated from its spectrum. For $[Ti(H_2O)_6]^{3+}$,

$$\Delta_0 = 20{,}400 \text{ cm}^{-1}$$

Therefore, 0.4 Δ_0 = 8160 cm^{-1} = 98 kJ

Thus, 0.4 Δ_0, the LFSE (ligand field stabilization energy) for this complex is 98 kJ.

The 0.4 Δ_0 values have been evaluated for several ligands from the spectral absorptions. The spectrochemical series is evolved based on such spectral data.

The magnitude of the splitting 0.4 Δ_0 depends on the nature of the ligands, and it affects the energy of the transition; this in turn influences the frequency of maximum absorption in the spectrum:

Complex species	$[TiCl_6]^{3-}$	$[TiF_6]^{3-}$	$[Ti(H_2O)_6]^{3+}$	$[Ti(CN)_6]^{3-}$
λ_{max} (cm^{-1})	13,000	18,900	20,400	22,300

In $[TiL_6]^{3+}$, the λ_{max} corresponds to Δ_0. The Δ_0 value is a function of the ligand and therefore it changes on changing *L*. When L is Cl^- (a weak field ligand),

Δ_0 should decrease and hence a *bathochromic shift* in the spectrum is observed (lesser λ_{max}). With a strong-field ligand, such as CN^-, Δ_0 should increase leading to a *hypsochromic shift* in the spectrum (higher λ_{max}).

For the complexes of the divalent first transition series metals, Δ_0 values are in the range 7500cm^{-1} – 12500 cm^{-1}; for those of trivalent metals, Δ_0 values are in the range 14000 cm^{-1} – 25000 cm^{-1}. On going from a metal in the first transition series to a metal in the same group in the second transition series (with the same charge on metals), Δ_0 value increases by 30 – 50%. Similarly, from the second to the third transition series, in the same family, it increases by another 30 – 50%.

Δ_t value is about 40 – 50% of Δ_0 value for complexes of a metal which differ only in their geometries.

Now a d^9 ion in the octahedral field may be considered. In this case, the Δ_0 value corresponds to the promotion of an electron from a t_{2g} orbital to an e_g orbital. In this case the energy of e_g state is less than that of t_{2g}. This reversal of relative energies is because for the d^9 system, the ground state $(t_{2g})^6(e_g)^3$ is doubly degenerate,

$$(t_{2g})^6(d_{x^2-y^2})^2(d_{z^2})^1 \quad \text{or} \quad (t_{2g})^6(d_{x^2-y^2})^1(d_{z^2})^2$$

and the excited state $(t_{2g})^5(e_g)^4$ is triply degenerate,

$$(d_{xy})^2(d_{yz})^2(d_{xz})^1(e_g)^4$$
$$(d_{xy})^2(d_{yz})^1(d_{xz})^2(e_g)^4$$
$$(d_{xy})^1(d_{yz})^2(d_{xz})^2(e_g)^4$$

The energy level diagram for the d^9 ion (Fig. 5.7) is therefore the inverted form of that for a d^1 ion.

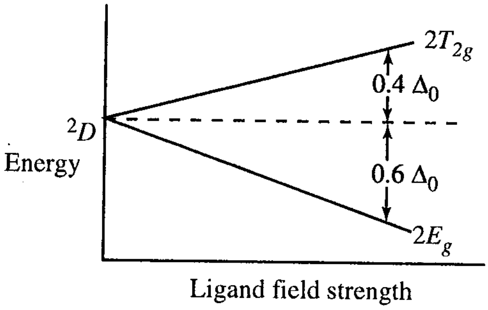


Fig. 5.7 *Energy level diagram for a d^9 ion*

Another way of depicting the d^9 system is to describe the e_g orbital in the ground state as an orbital with a *hole* and the t_{2g} orbital in the excited state as an orbital with a hole (because the e_g orbital lacks one electron for full occupancy in the ground state and the t_{2g} orbital loses one electron to the e_g orbital in the excited state).

On changing the geometry of the d^1 system from octahedral to tetrahedral, then also the energy level diagram is inverted (as a tetrahedral field is actually a negative octahedral field).

5.7 CORRELATION DIAGRAMS

5.7.1 Orgel Diagrams

The various aspects of energy levels of a d^n system may be represented in a diagram called the *Orgel diagram*. The Orgel diagram for a d^1 system is represented in Fig. 5.8.

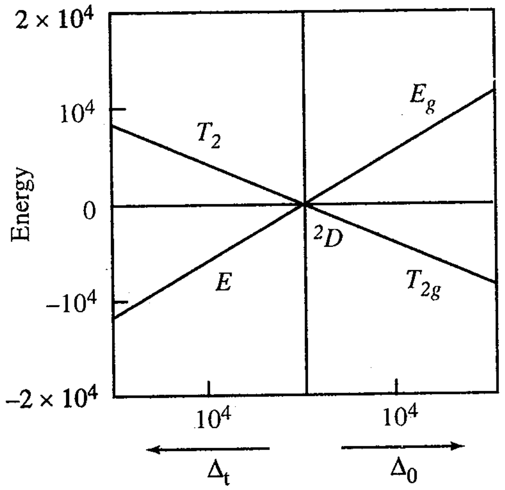


Fig. 5.8 Orgel diagram for octahedral and tetrahedral d^1 complexes

1. An Orgel diagram depicts the energies of states as a function of field strength.
2. In this depiction, for simplicity, the excited states of multiplicities different from those of the ground state are ignored.
3. The diagram is used only for weak field systems.
4. The Orgel diagrams are useful for predicting the number of spin-allowed absorption bands in an ultraviolet or a visible spectrum for a complex.

A generalised Orgel diagram can be drawn for d^1, d^4 (high-spin), d^6 (high-spin) and d^9 ions in octahedral and tetrahedral fields. (Fig. 5.9)

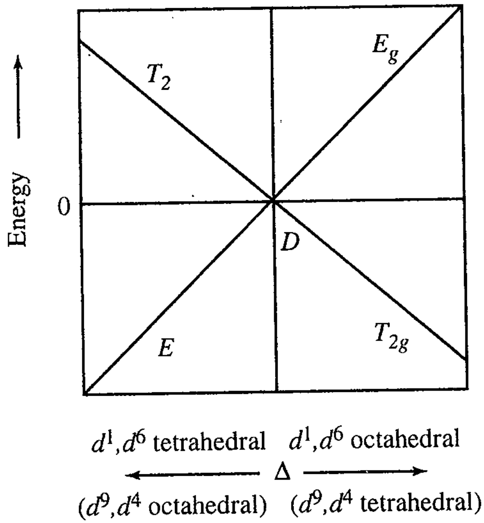


Fig. 5.9 Generalised Orgel diagram for d^1, d^4 (high spin), d^6 (high spin) and d^9 ions in an octahedral or a tetrahedral field

5.7.2 High-spin d^6 ion

The absorption spectrum for a high-spin d^6 ion $[(t_{2g})^4(e_g)^2]$ in an octahedral or a tetrahedral field is simple, containing a single band like that of a d^1 ion, $[Ti(H_2O)_6]^{3+}$. For example, the spectrum of $[Fe(H_2O)_6]^{2+}$ (high-spin d^6) has only one band (Fig. 5.5(f)). For this ion, only one allowed $d-d$ transition is possible, namely

$$(t_{2g})^4(e_g)^2 \rightarrow (t_{2g})^3(e_g)^3;$$
$$^5E_g \leftarrow {}^5T_{2g}$$

The frequency of the absorption maximum would then give the Δ_0 value.

5.7.3 High-spin d^4 ion

A high-spin d^4 ion in an octahedral or a tetrahedral field must be analogous to a d^1 ion in the same geometry; however, the Jahn-Teller effect in it complicates the absorption.

d^5 ion The correlation diagram for a d^5 ion is depicted in Fig. 5.10. The lowest energy term for the free ion is a ^6S; this splits in a weak octahedral field to produce

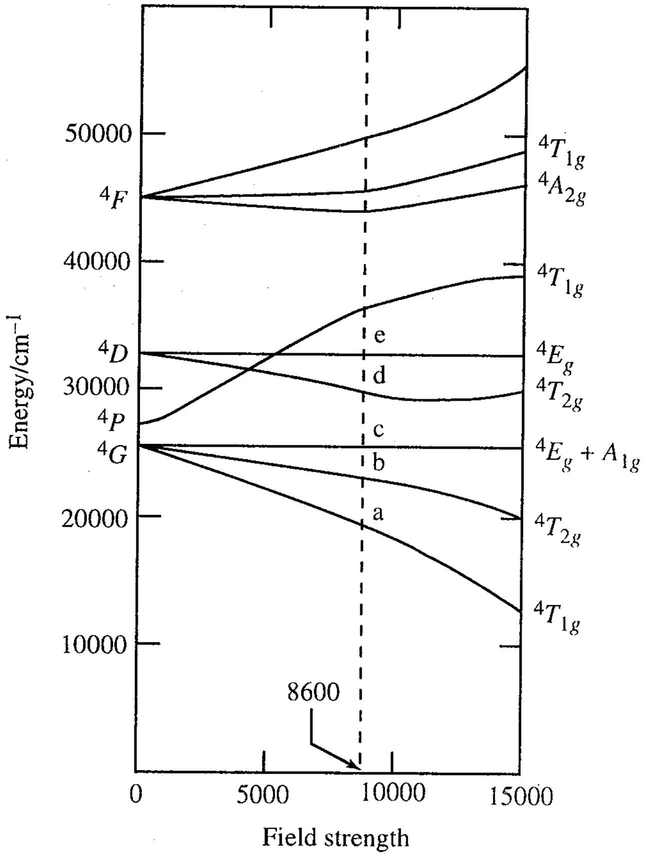


Fig. 5.10 Correlation diagram for d^5 ion (Mn^{2+})

${}^6A_{1g}$ ground state; this is the only state on the diagram with a multiplicity of six. This implies that for a d^5 octahedral complex, all transitions are not only Laporte-forbidden, but also spin-forbidden. Transitions which are doubly-forbidden produce extremely weak absorption bands; their extinction coefficients are several hundred times smaller than those for singly-forbidden transitions. This is evidenced by the colourlessness of dilute solutions of Mn^{2+} species; only at high concentrations, a faint pink colour is noticeable.

5.7.4 Comparison of the d^n Octahedral and d^n Tetrahedral Energy Level Diagrams

The comparison of the energy level diagrams for the d^n ions in octahedral and tetrahedral fields reveals the following:

(1) The energy level diagrams of a d^n system in octahedral field is the *inverse* of the diagram of the same ion in tetrahedral field (The order of levels arising from each free ion state is reversed; the diagram as a whole is not reversed). The components into which each Russell-Saunders state gets split are reversed in their energy order on changing the field from octahedral to tetrahedral.

(2) When the metal-ligand distance is kept constant, a purely electrostatic interaction between metal ion and ligands in a tetrahedral field will produce only 4/9 the splittings of octahedral field.

(3) The energy level diagrams of certain sets of the d^n systems have similarities; these similarities are caused by the combined effects of

  (i) reversals in the splitting patterns on changing from an octahedral to a tetrahedral field and

  (ii) changing from a d^n system to a d^{10-n} system.

  When a d^n ion in octahedral field is switched to a d^n ion in tetrahedral field, all splittings of the Russell-Saunders states are inverted. Interestingly, the same inversions are caused on changing from the d^n configuration from an octahedral field to the d^{10-n} configuration in an octahedral field; the same is true for the change d^n tetrahedral → d^{10-n} tetrahedral.

  (iii) For the free ions, the Russell-Saunders states of the pairs of d^n and d^{10-n} systems are identical in number, types and relative energies.

Thus, the various pairs of configuration – geometry combinations have qualitatively identical energy level diagrams in crystal fields; the difference lies only in splittings of the individual free ion states:

d^1_{oct} and d^9_{tet} : reverse of d^9_{oct} and d^1_{tet}

d^2_{oct} and d^8_{tet} : reverse of d^8_{oct} and d^2_{tet}

d^3_{oct} and d^7_{tet} : reverse of d^7_{oct} and d^3_{tet}

d^4_{oct} and d^6_{tet} : reverse of d^6_{oct} and d^4_{tet}

d^5_{oct} : same as d^5_{tet}

5.7.5 Racah Parameters

(1) Coloumbic repulsion exists among electrons in the molecular orbitals of the complex; therefore, different terms of a configuration have different energies. The repulsion energy of each term of a configuration is expressed as sums of three quantities. The three different sums of integrals are called the *Racah parameters*; these three parameters are denoted as *A*, *B* and *C*.

(2) These parameters represent *interelectronic repulsions.*

The energy of each term originating from a given configuration is expressed as linear combination of the three Racah parameters. Accurate evaluation of these parameters is not possible. These parameters are calculated from spectral data of free ions. For example, for a d^2 system, the energies of the possible terms are given below:

$$E(^1S) = A + 14B + 7C$$

$$E(^1G) = A + 4B + 2C$$

$$E(^1D) = A - 3B + 2C$$

$$E(^3P) = A + 7B$$

$$E(^3F) = A - 8B$$

The observed energies of the terms, obtained from spectral data, can be substituted in these expressions to evaluate *A*, *B* and *C*.

1. As the Racah parameters represent repulsions, all of these are positive. The parameter *B* is sufficient to evaluate the difference in energy between states of the same multiplicity.
2. As *A* is common to all the terms, it can be ignored, only if the relative energies of the terms need to be known. The relative energies of the triplet terms (^3P and ^3F) can be obtained without knowing the value of *C*.
3. The difference in energy between a free ion in ground state *F* term and an excited *P* term of the same spin multiplicity is 15 *B*.
4. For most of the transition metal ions, *B* values are about 1000cm^{-1} and $C \approx 4B$, as evaluated from spectral data. The actual values of *B* and *C* for these ions are given in Table 5.6.

Table 5.6 Values of B and C Racah Parameters (in cm^{-1}) for some transition metal free ions

Configuration	Ion	*B*	*C*
$3d^2$	Ti^{2+}	718	2629
	V^{3+}	861	4165
	Cr^{4+}	1039	4238
$3d^3$	Sc^{+}	480	
	V^{2+}	766	2855
	Cr^{3+}	918	3850
	Mn^{4+}	1064	
$3d^4$	Cr^{2+}	830	3430
	Mn^{3+}	1140	3675
$3d^5$	Mn^{2+}	960	3325
$3d^6$	Fe^{2+}	1058	3901
	Co^{3+}	1100	
$3d^7$	Co^{2+}	971	4366
$3d^8$	Ni^{2+}	1041	4831

5. In a Tanabe-Sugano diagram(*vide infra*), the energy E is expressed as E/B; the field strength is expressed as Δ/B.
6. The B value for a complex is always smaller than that for the corresponding free ion. This is attributed to the *nephelauxetic effect.* (This effect is the delocalization of the metal electrons over molecular orbitals that encompass both the metal and ligands). As a consequence of the nephelauxetic effect or "cloud expansion" effect, the average interelectronic repulsion is reduced to a value denoted as B' (the value of B' is less than that of B). The ratio $B'/B = \beta$ is called the *nephelauxetic ratio* and is always less than one (0.6 – 0.9). It decreases with increasing delocalization. The β value depends upon both the metal ion and the ligand. For a series of complexes of a particular metal ion with different ligands, the β values are in the order

$$I^- > Br^- > CN^- > Cl^- > HO^- > NH_3 > H_2O > F^-$$

This order denotes the order of tendency of the electrons of metal ions to shift to the ligands (delocalization); the mean distance of the d electrons from the nucleus increases with their increasing shift to the ligands.

A similar series (β values) has been derived for the cations.

$$Pt^{4+} > Pd^{4+} > Rh^{3+} > Co^{3+} > V^{3+} > Cr^{3+} > Fe^{3+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$$

Based on these two series, the extent of covalent bonding between the metal and ligands can be predicted. Thus, the electronic spectra provide evidence for electron delocalization in transition metal complexes.

5.7.6 Tanabe-Sugano Diagrams

A knowledge of the quantitative aspects of the transition from weak to strong fields is necessary for the interpretation of electronic spectra. All the energy levels of a d^n system in the presence of both interelectronic repulsions and crystal fields of medium strength can be calculated easily. This can be carried out only for certain relationships between the parameters of interelectronic repulsion. The results of such calculations are denoted in the form of graphs called Tanabe-Sugano diagrams.

1. The Tanabe-Sugano diagrams are actually elaborated versions of the simple correlation diagrams. They provide an alternative way of describing the variation of term energies with field strengths.
2. These diagrams were first proposed by the Japanese Chemists Tanabe and Sugano.
3. A Tanabe-Sugano diagram is obtained by plotting E/B against Δ_0/B.

   E = term energy
   B = Racah parameter
   Δ_0 = LFSE

   The term energies are expressed as E/B in this diagram; the ligand field splitting Δ_0 is similarly expressed as Δ_0/B. In these diagrams, the energies of the levels of a d^n system are plotted as the vertical coordinate in units of interelectronic repulsion parameter B; the crystal field strength is the horizontal coordinate.

4. The energy of the lowest term is taken as zero for drawing this diagram. The energies of the other states are plotted relative to this; therefore, the diagram is discontinuous (slope varies) when there is a change in the ground term i.e., when the ligand field becomes strong enough to produce electron pairing.
5. Some lines in these diagrams are non-linear because of the mixing of terms of the same symmetry type.
6. These diagrams indicate that if the increasing ligand field causes two weak field terms of the same symmetry to approach, they do not cross but bend apart from each other (Figure 5.11). This is called the *non-crossing rule*, originating from the mixing of the terms of the symmetry type.

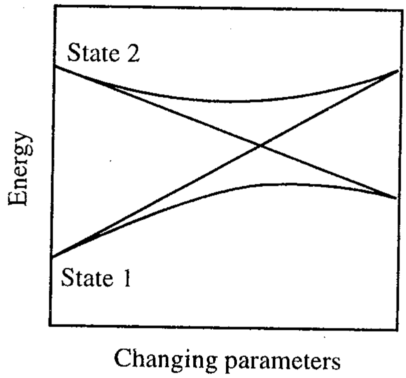


Fig. 5.11 Depiction of the non-crossing rule

7. The Tanabe-Sugano diagrams are more useful than the Orgel diagrams because these include both weak and strong fields.
8. The diagrams, though similar to correlation diagrams, provide more qualitative information on absorption spectra of complexes.
9. The Δ value for a complex can be evaluated by fitting the observed spectral data in the Tanabe-Sugano diagram of the ion.
10. From this diagram, the *interelectronic repulsion parameter B* can be obtained.

5.7.7 The Tanabe-Sugano Diagram for the d^3 Complex $[Cr(NH_3)_6]^{3+}$

The electronic spectrum of d^3, $[Cr(NH_3)_6]^{3+}$ in aqueous medium is represented in Fig. 5.12a. It covers the absorption range of 51000cm^{-1} (200 nm in the ultraviolet) to 10000cm^{-1} (1000 nm in the infrared). The spectrum consists of two prominent bands (*a*) and (*b*) and a very weak band (*c*):

The band (*a*) is a band with an intermediate intensity (log $\varepsilon \approx 1.8$; $\lambda_{max} = 370$nm) It arises from the transition

$$^4T_{1g} \leftarrow {}^4A_{2g}$$

The band (*b*) is a band also with intermediate intensity (log $\varepsilon \approx 1.7$; $\lambda_{max} = 470$ nm). It arises from the transition

$$^4T_{2g} \leftarrow {}^4A_{2g}$$

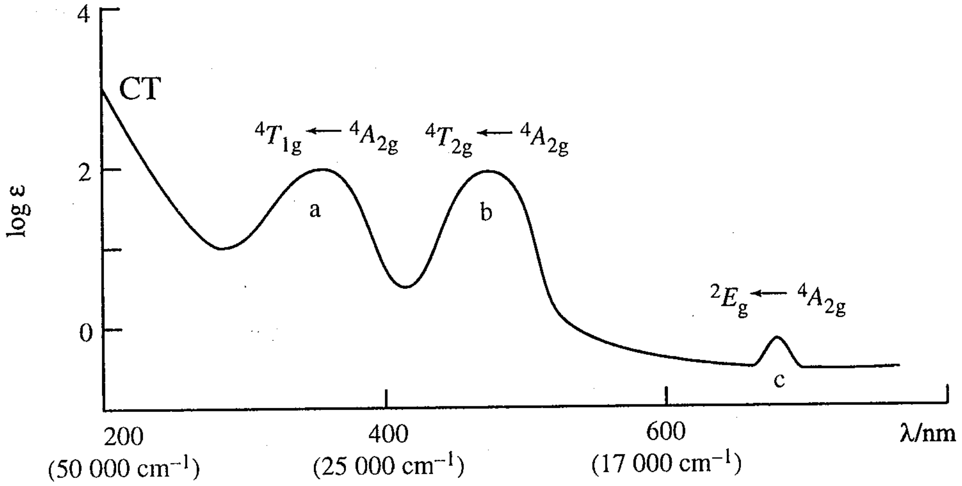


Fig. 5.12(a) *The absorption spectrum of* d^3 $[Cr(NH_3)_6]^{3+}$

These two bands denote the transitions between the t_{2g} (HOMO) and e_g (LUMO) orbitals of the complex; these orbitals are mainly derived from the metal *d* orbitals.

Both (a) and (b) bands correspond to an $e_g \leftarrow t_{2g}$ electron transition though they occur at different energies; they are actually split absorption of a band. This splitting is the net result of the electron-electron repulsions in the molecular orbitals.

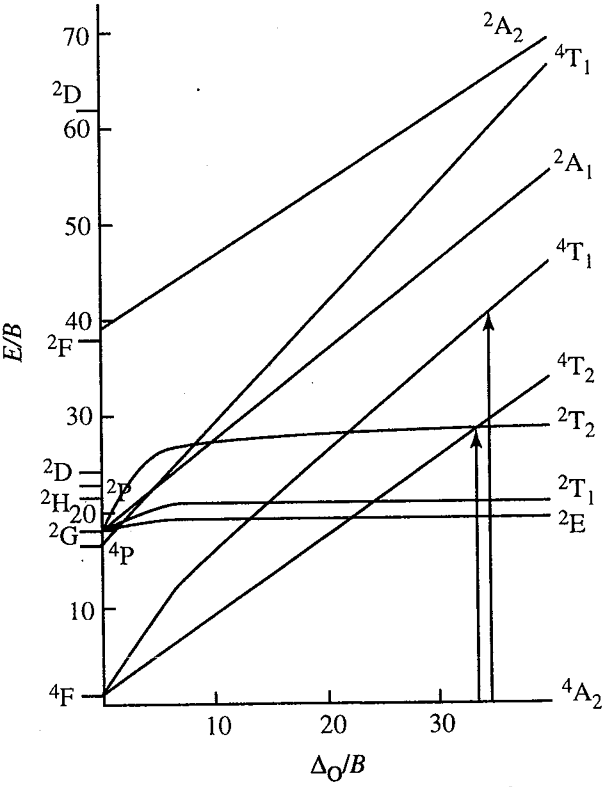


Fig. 5.12(b) *The Tanabe-Sugano diagram for the* d^3 *configuration*

(c) This is the band at the lowest energy; it is due to a spin-forbidden transition and hence very weak.

The Tanabe-Sugano diagram for the d^3 configuration (Figure 5.12b) can be used to interpret these spectral effects of $[Cr(NH_3)_6]^{3+}$.

The two ligand-field transitions (*a*) at $28{,}500 cm^{-1}$ ($^4T_{1g} \leftarrow {}^4A_{2g}$) and (*b*) at $21{,}550 cm^{-1}$ ($^4T_{2g} \leftarrow {}^4A_{2g}$) are evident (indicated by vertical arrows) from the diagram.

These two absorptions have the relative ratio $28{,}500 cm^{-1} / 21{,}550 cm^{-1} = 1.32$. The diagram shows that this ratio is valid only at one point on the far right of the lines. This point helps to evaluate values of Δ_0 and the Racah parameter *B*.

5.8 ELECTRONIC SPECTRA OF d^x COMPLEXES

The spectrum of d^1 $[Ti(H_2O)_6]^{3+}$ has already been discussed.

5.8.1 The Electronic Spectrum of the d^2 $[V(H_2O)_6]^{3+}$

This spectrum is given in Fig. 5.13a. The free ion ground term is ^3F (Fig. 5.13b); therefore, three main absorptions are expected corresponding to the transitions

$$^3T_{1g}(F) \rightarrow {}^3T_{2g} \qquad \nu_1 = 17250 cm^{-1}$$
$$^3T_{1g}(F) \rightarrow {}^3T_{1g}(P) \qquad \nu_2 = 25000 cm^{-1}$$
$$^3T_{1g}(F) \rightarrow {}^3A_{2g} \qquad \nu_3 = 35700 cm^{-1}$$

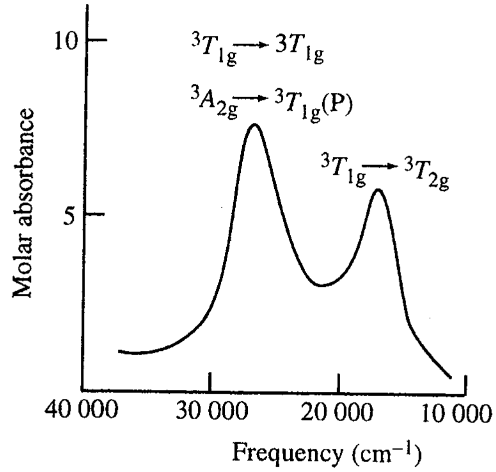


Fig. 5.13(a) The electronic absorption spectrum of d^2 $[V(H_2O)_6]^{3+}$

Only two bands are visible in the spectrum; these correspond to the first two spin-allowed transitions. The third band is obscured by charge transfer in the ultraviolet region. Calculations using the Racah parameters show that it should occur at $35700 cm^{-1}$. ν_3 has actually been observed with V^{3+} in corundum (Al_2O_3) in which no CT band is possible.

5.8.2 The Electronic Spectrum of the d^3 $[Cr(H_2O)_6]^{3+}$

This spectrum shows three absorption bands:

$$\nu_1 = 17400\ \text{cm}^{-1}$$
$$\nu_2 = 24500\ \text{cm}^{-1}$$
$$\nu_3 = 37800\ \text{cm}^{-1}$$

The Racah parameter B for complex can be calculated and compared with the B value of 1030cm^{-1} for the free d^3 ion.

The interelectronic repulsion parameter B can be obtained by fitting the ratio ν_1/ν_2 to the Tanabe-Sugano diagram for d^3 ion in an octahedral CF.

$$\nu_1/\nu_2 = 17400/24500 = 0.710$$

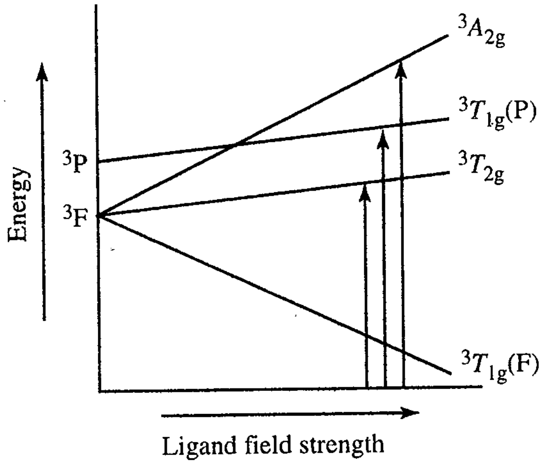


Fig. 5.13(b) Orgel diagram for a d^2 ion in an octahedral field

This fits the Tanabe-Sugano diagram at $D_q/B = 2.40$, when $\nu_1/B = 24$, $\nu_2/B = 34$ and $\nu_3/B = 52.0$

Then, $10\ D_q = \nu_1 = 17400\text{cm}^{-1}$

Therefore, $B = \dfrac{17400}{24.0} = 725\ \text{cm}^{-1}$

$\nu_3 = 52.0 \times 7.25 = 37700\text{cm}^{-1}$

The calculated B (725cm^{-1}) is less than the free ion B value (1030cm^{-1}); this must be due to expansion of d-electron charge in the complex. The decreased B for the complex indicates decreased interelectronic repulsions.

5.8.3 The Electronic Spectrum of the d^4 ion, $[Cr(H_2O)_6]^{2+}$

The free ion ground term for this system is ^5D; therefore one main absorption $t_{2g}^3e_g \rightarrow t_{2g}^2e_g^2$ in the spectrum is expected. This occurs at 14100cm^{-1} (Fig. 5.14). The blue colour of the complex is due to this absorption.

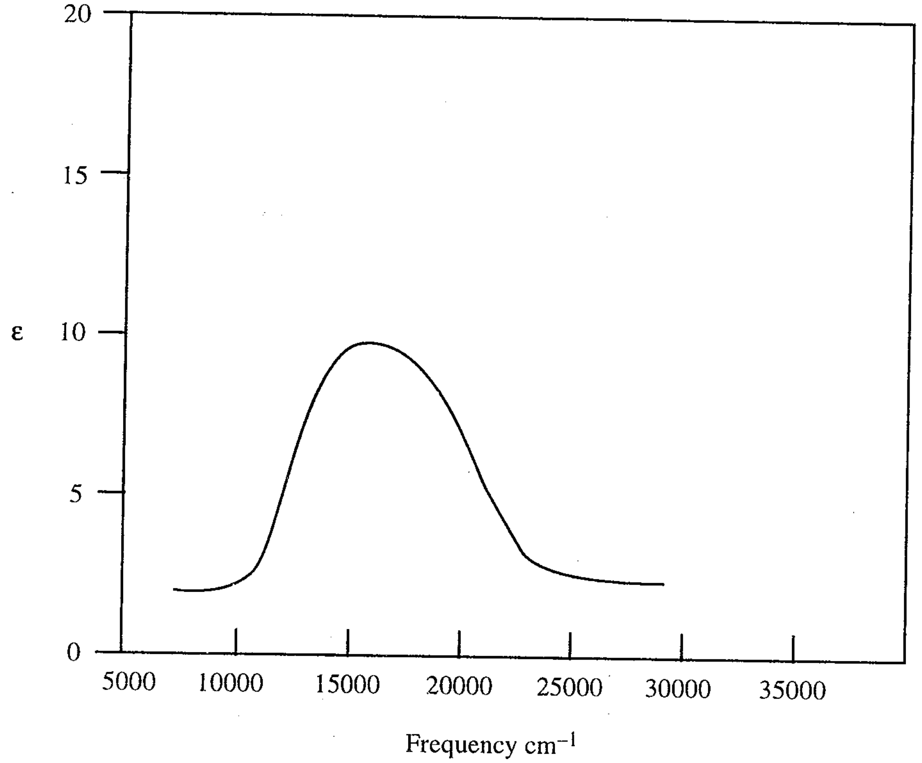


Fig. 5.14 *The absorption spectrum of* $[Cr(H_2O)_6]^{2+}$

5.8.4 The Electronic Spectrum of the d^5, $[Mn(H_2O)_6]^{2+}$

The free ion ground term is ^6S ; therefore, no spin-allowed absorptions are possible. Its spectrum (Fig. 5.15) consists of weak spin-forbidden bands compared to the spectra of other transition metal cations; this spectrum differs in three respects from the other spectra:

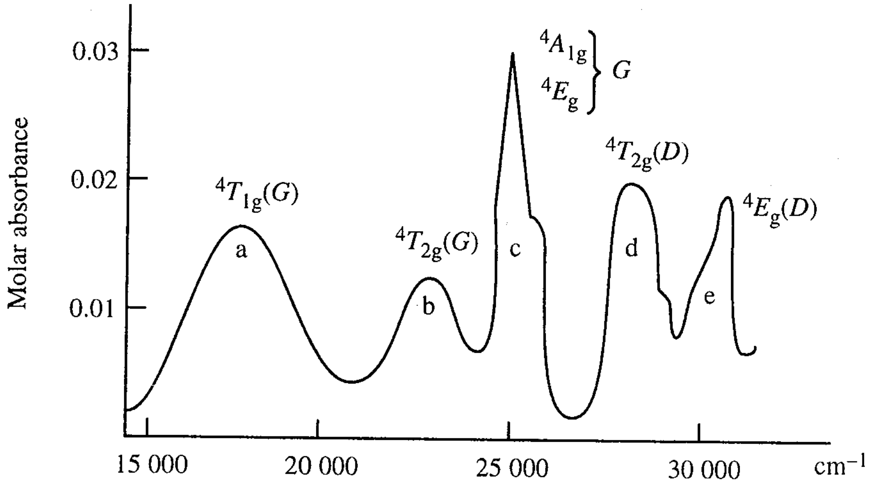


Fig. 5.15 *The electronic absorption spectrum of* $[Mn(H_2O)_6]^{2+}$

(i) the bands are extremely weak
(ii) there are more bands
(iii) some of the bands are sharp.

The electronic *d-d* transition from a high-spin d^5 configuration must necessarily involve the pairing of some electron spins; such transitions are both spin-forbidden and orbitally-forbidden; therefore the bands are weak.

There is only one possible way of arranging 5 electrons with parallel spins in five orbitals; however, there are many ways if two of these electrons are paired. This is the origin for the more number of bands in the spectrum.

Using the Orgel diagram, the bands are assigned to transitions as below:

$^6A_{1g} \rightarrow {}^4T_{1g}$	18900 cm^{-1}
$^6A_{1g} \rightarrow {}^4T_{2g}(G)$	23100 cm^{-1}
$^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$	24970, 25300 cm^{-1}
$^6A_{1g} \rightarrow {}^4T_{2g}$ (D)	28000 cm^{-1}
$^6A_{1g} \rightarrow {}^4E_g$ (D)	29700 cm^{-1}

5.8.5 The Electronic Spectrum of the d^6 Ion $[Fe(H_2O)_6]^{2+}$

The free-ion ground term for the d^6 ion is ^5D; therefore, only one absorption is expected (Fig 5.5). This occurs at 10500cm^{-1} (=Δ)

5.8.6 The Electronic Spectrum of the d^7 Ion $[Co(H_2O)_6]^{2+}$

The free ion ground term for this ion is ^4F; therefore, in a cubic field, three main allowed transitions are expected (because of the splitting of the free-ion ^4F term and the accompanying ^4P term). In an octahedral field, the splitting is the same as for the octahedral d^2 ion and therefore the spectrum can be interpreted by using the same Tanabe-Sugano diagram used for the d^2 (say V^{3+}) system. Its spectrum is shown in Figure 5.16.

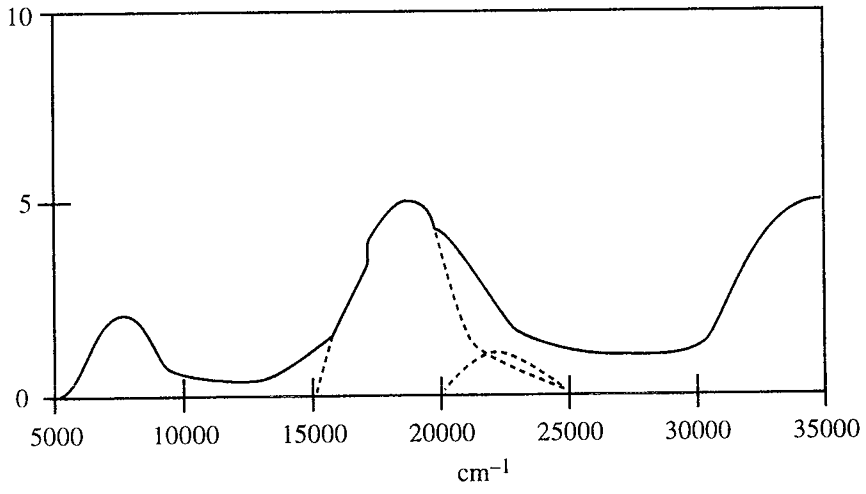


Fig. 5.16 The absorption spectrum of $[Co(H_2O)_6]^{2+}$

5.8.7 The Electronic Spectrum of the d^8, $[Ni(H_2O)_6]^{2+}$

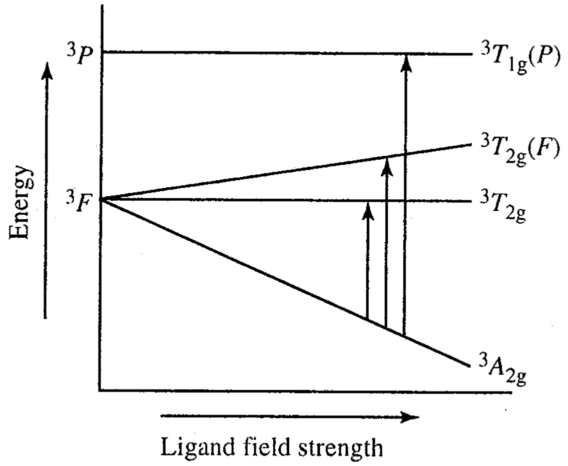
The spectrum of $[Ni(H_2O)_6]^{2+}$ is shown in Fig. 5.17. In a cubic field three spin-allowed transitions are possible, due to the splitting of the free ion, ground ^3F term and the presence of the ^3P term. In an octahedral field the splitting is the same as for the octahedral d^3 ion. The free-ion ground term is ^3F; therefore three main absorptions are expected. Accordingly, the spectrum consists of three bands corresponding to the transitions

$$(8500\ \text{cm}^{-1})\nu_1 = {}^3A_{2g}\ (F) \rightarrow {}^3T_{2g}\ (F) = 10\ D_q$$

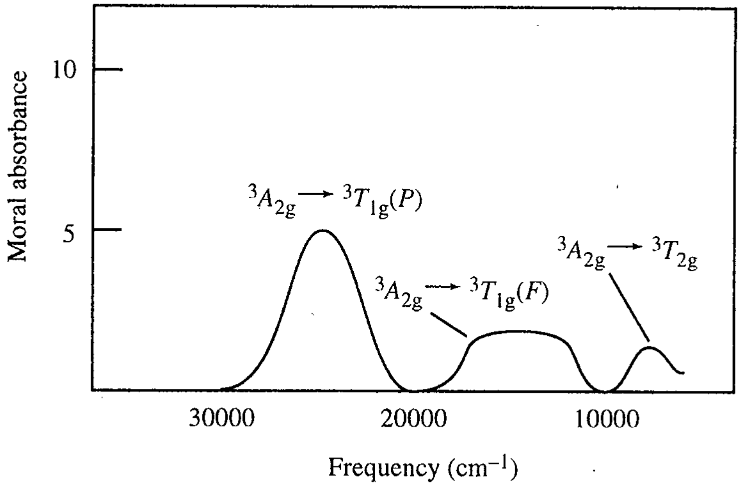
$$(13800\ \text{cm}^{-1})\nu_2 = {}^3A_{2g}\ (F) \rightarrow {}^3T_{1g}\ (F)$$

$$(25300\ \text{cm}^{-1})\nu_3 = {}^3A_{2g}\ (F) \rightarrow {}^3T_{1g}\ (P)$$

ν_1 directly gives the value of Δ (10 D_q); it is 8500cm^{-1}.



(*a*) *Energy level diagram for d^8 ion in an octahedral field*



(*b*) *The absorption spectrum of d^8 $[Ni(H_2O)_6]^{2+}$*

Fig. 5.17

5.8.8 The Absorption Spectrum of the d^9 $[Cu(H_2O)_6]^{2+}$

The free-ion ground term for Cu^{2+} is ^2D; therefore only one main absorption is expected. The spectrum of $[Cu(H_2O)_6]^{2+}$ is shown in Figure 5.18. As the d^9 system is considered to be an inversion of d^1, relatively a simple spectrum might be expected; this is actually so, the spectrum having a single broad band at 12500cm^{-1}. This band is unsymmetrical because of large distortions from octahedral symmtery expected in a d^9 system. The free-ion ground term ^2D should split in a crystal field in the same way as the ^5D term of the d^4 ion; therefore, the interpretation of the spectrum is similar to that of the d^4 complex.

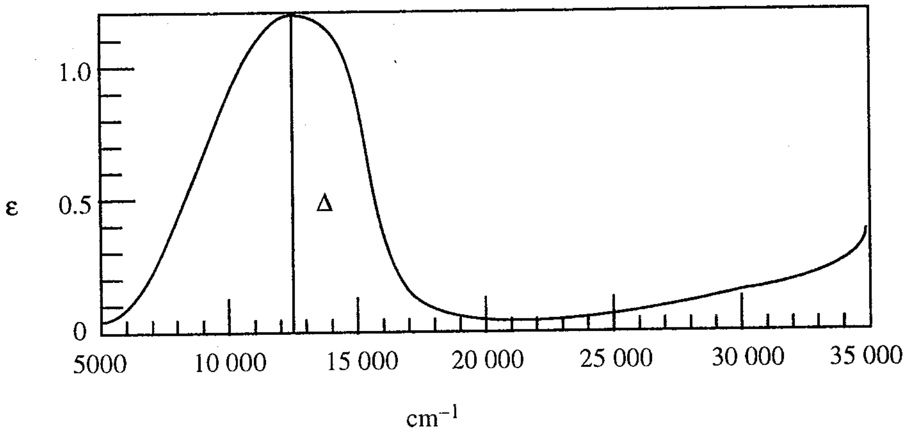


Fig. 5.18 The absorption spectrum of $[Cu(H_2O)_6]^{2+}$

5.9 CHARGE-TRANSFER SPECTRA

The absorption arising from the transfer of an electron either

a) from a ligand orbital to the metal orbital (L → M) or
b) from the metal orbital to a ligand orbital (M → L)

in a complex is called the *charge-transfer spectrum.*

5.9.1 Characteristics

(1) Charge-transfer (CT) transitions do not violate the usual selection rules. Charge-transfer transitions, unlike *d-d* transitions are normally neither multiplicity-forbidden nor Laporte-forbidden; therefore, they produce *strong* absorption bands. Such strong bands enable charge-transfer absorption to be distinguished from *d-d* transitions in a complex.

(2) The charge-transfer bands have extinction coefficients in the 500 – 2000 unit range (for $d-d$ transitions, the coefficients are below 100 unit).

(3) These bands mostly occur in the near ultraviolet region.

(4) In the spectra of some metal complexes, an overlap between the end of the charge-transfer band and a *d-d* absorption occurs. This makes recording clearly the full *d-d* spectrum of the complex impossible.

(5) A CT transition is an *intramolecular transition*; electronic transition from an orbital localized mainly on one atom to an orbital localized mainly on another atom occurs. This requires much higher energies than a *d-d* transition.

(6) The L → M transfer is exhibited by complexes containing the ligands O^{2-}, Cl^-, Br^- and I^-.

In d^0 complexes, there can be no *d-d* transitions and therefore Δ for these can be evaluated only from their charge-transfer absorption frequencies. For example, in MnO_4^-, the Mn^{7+} ion has no *d* electron. There is a low-energy (visible region) $O^{2-} \rightarrow Mn^{7+}$ (L → M) charge transfer in this tetrahedral species; this produces the purple colour for MnO_4^-.

The M → L charge-transfer occurs in complexes containing ligands which have stable but empty orbitals. Ligands such as NO, CO and CN^-, which are π-acceptor ligands, cause such M → L absorption bands. The organic ligands, pyridine, bipyridine and *o*-phenanthroline have empty π antibonding orbitals which favour M → L transfer.

The possible charge transfer transitions in an octahedral complex are depicted in Figure 5.19.

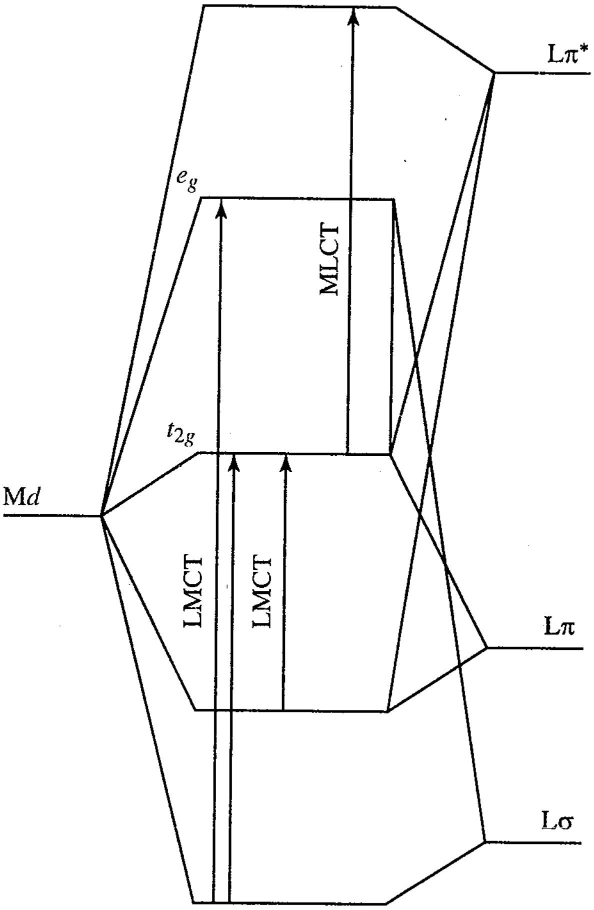


Fig. 5.19 The CT transitions in an octahedral complex

(7) A charge-transfer process is related to an oxidation–reduction reaction. In a complex containing a ligand of low electronegativity, the charge transfer L → M may be so easy that it may become a redox reaction. For example, the dark blue colour of $[CuCl_4]^{2-}$ arises from a strong charge-transfer ($Cl^- \rightarrow Cu^{2+}$) absorption. Bromine is less electronegative than chlorine and consequently Br^- transfers its charge to the metal more easily than a Cl^-; consequently the colour of the bromocomplex must be more intense. With I^-, the electronegativity being very low, an electron is entirely lost to an orbital on Cu^{2+}, with the result, Cu^{2+} is reduced to Cu^+ and I^- is oxidized to iodine:

$$4\,I^- + 2\,Cu^{2+} \rightarrow 2\,CuI + I_2$$

In this case, charge-transfer ends in a redox reaction. In a series of complexes of the formula $[Co(NH_3)_5X]^{2+}$, where X is halogen, absorption in the ultraviolet region occurs due to charge-transfer. However, the frequencies of absorption progressively increase in the order I^-, Br^-, Cl^-, F^-. This order denotes increasing difficulty in transferring an electron from the ligand to the metal; it is the easiest with I^- and therefore the least energy is involved (low frequency), and most difficult with F^- (highest energy and highest frequency). Thus, if the frequency of the charge-transfer is low, reduction of the metal occurs.

Predict whether the reduction of Fe(III) to Fe(II) would occur in the Fe(III) – thiocyanate complex.

(8) A majority of charge-transfer complexes of transition metals involves L → M transfer; this is expected from the availability of non-bonding or antibonding orbitals on the metal. In a few cases, the reverse, M → L transfer occurs. For example, in Fe(II)-dipyridyl complex, an electron transfer occurs from iron to dipyridyl. In this case, the metal is in its low oxidation state and it can pass on to its high oxidation state [Fe(III)] by M → L transfer. This transfer is aided by the presence of a low-lying antibonding orbital in the ligand. The situation with Fe(II) – *o*-phenanthroline complex is similar to that with the red Fe(II) – dipyridyl complex, leading to M → L transfer.

The metal-ligand combination can be modified to make ligand-to-metal electron transfer easy. A metal with high ionization energy has empty orbitals at low energies; for example, a transition or a post-transition metal in its high oxidation state. A ligand with low electron affinity, which would have high energy, filled orbitals and which would be easily oxidized (which can easily donate an electron); O^{2-}, Cl^-, Br^- and I^- are such ligands. In such a metal-ligand combination, the orbitals involved in LMCT would have very close energy and therefore the electron transfer would require very little energy; a photon in the visible or near-ultraviolet region can induce the electron transfer in such cases.

5.9.2 Charge-Transfer Spectrum of MnO_4^- (LMCT)

Favourable situations of CT mentioned above exist in MnO_4^-; manganese is in high oxidation state (+7) and the oxide ions have electrons in high energy orbitals.

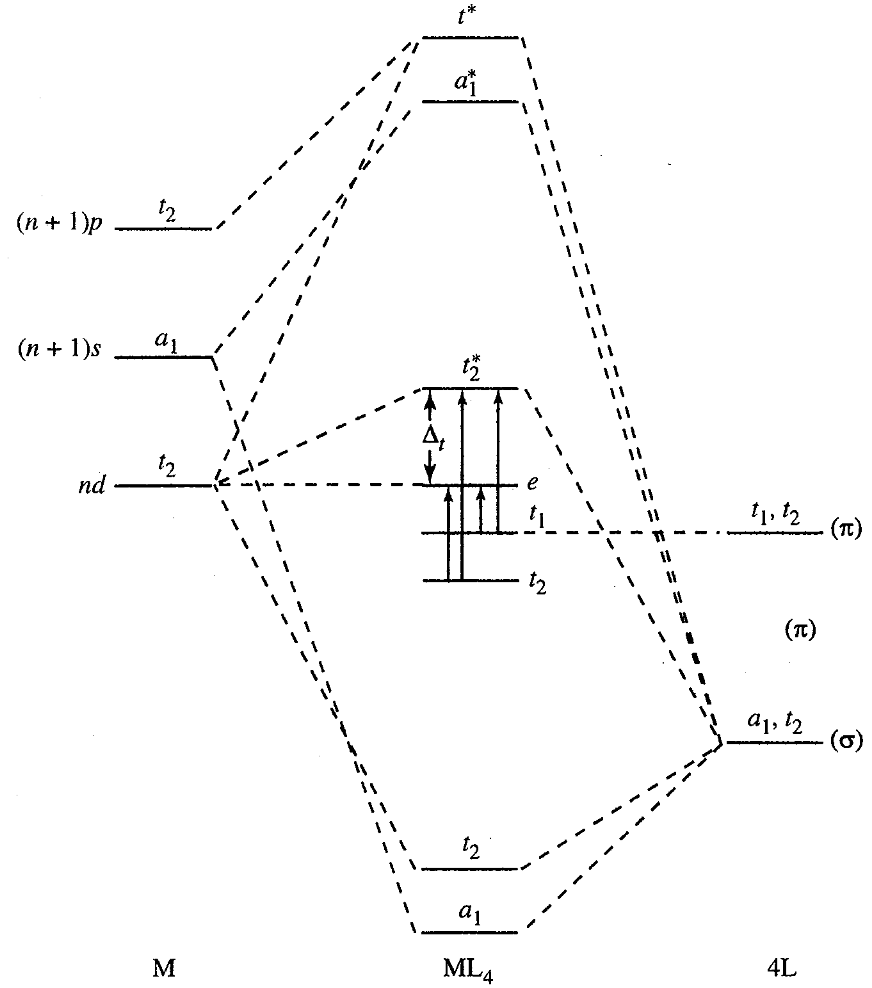


Fig. 5.20 The m.o.diagram for a tetrahedral complex indicating LMCT transitions

The molecular orbital diagram for a tetrahedral complex (such as MnO_4^-) is represented in Figure 5.20. This figure indicates that in MnO_4^-, four possible L → M (O^{2-} → Mn^{7+}) charge transfers can occur:

$t_1\ (\pi)$	→	$e\ (\pi^*)$	$17{,}700\ cm^{-1}$
$t_1\ (\pi)$	→	$t_2{}^*\ (\sigma^*)$	$29{,}500\ cm^{-1}$
$t_2\ (\pi)$	→	$e\ (\pi^*)$	$30{,}300\ cm^{-1}$
$t_2\ (\pi)$	→	$t_2{}^*\ (\pi^*)$	$44{,}400\ cm^{-1}$

Of these absorptions, only that at $17{,}700\ cm^{-1}$ is in the visible region and it imparts deep purple colour to MnO_4^-.

The Δ_t value ($26{,}900\ cm^{-1}$) for this species is obtained by the energy difference in the transition $e(\pi^*) \rightarrow t_2\ (\sigma^*, \pi^*)$

CT VERSUS *d*– *d*TRANSITIONS

- The CT transitions result in high molar extinction coefficients and therefore form the basis for most of the spectrophotometric estimations of trace quantities of metal ions. The *d-d* transitions are of little value for such estimations.
- The L → M charge transfer energies decrease as the ligands become more reducing in nature.
- The M → L charge transfer energies decrease as the ligand becomes more reducible in nature.
- For a fixed L, the M → L charge transfer energies decrease as the charge on the metal decreases.
- In a CT transition, the charges on the metal in the initial and final states are appreciably different.
- As a rule of thumb, charge-transfer transitions produce dark colours whereas *d-d* transitions produce pale colours.
- CT transitions may occur not only in metal complexes with incomplete *d* orbitals but also in species with d^{10} or d^0 electron spectrum; thus HgI_2 (d^{10}) is intensely coloured; MnO_4^- (d^0) is also intensely coloured).

5.9.3 Mixed-Valence Complexes

A mixed-valence complex consists of the ions of the same metal in two of its oxidation states. For example, ***Prussian blue*** [Potassiumiron(III)-hexacyanoferrate(II)], $K\overset{III}{Fe}[\overset{II}{Fe}(CN)_6]$ consists of Fe(II) andFe(III) species. For this complex, high-spin Fe(III) is octahedrally coordinated by the nitrogen atoms of six cyanide ions, and low-spin Fe(II) by six carbon atoms. On excitation of this molecule, the Fe(III) in it is reduced to Fe(II) and the Fe(II) in it is oxidized to Fe(III). The transfer of an electron from Fe(II) to Fe(III) in this complex is facilitated by the cyanide ligand; the π system in this ligand helps electron-transfer; it acts as the conduit for electron-transfer. This complex thus produces a charge-transfer spectrum in the visible region and it is intensely coloured. In a mixed-valence compound, one of the electrons is delocalized to produce two equivalent metal ions:

$$\text{Fe(II)} \ldots\ldots\ldots\ldots e^- \ldots\ldots\ldots\ldots \text{Fe(II)}$$

Such a compound is called an *intervalence compound*; the electronic transition in it is *intervalence transition*.

Another example for an intervalence complex is the *Creutz-Taube complex*:

$$K_5[(NH_3)_5\,Ru(pyrazine)\,Ru(NH_3)_5];$$

The pyrazine ligand, with its conjugated π-system is an efficient bridging ligand for favouring electron-transfer; consequently, its intervalence transition is strong.

5.10 ELECTRONIC SPECTRA OF LANTHANIDE COMPLEXES

(1) The *f* orbitals in Ln^{3+} species are deep inside the metal; therefore, the crystal field effects are very much smaller in the lanthanide complexes compared to those in the *d* series metals. The external fields split the various states arising from f^n configurations only to the extent of $100\,cm^{-1}$. The spectra of Ln(III)

ions in the presence of complexing agents are strikingly similar to those of simple aquated cations.

(2) The weak crystal field effects are incapable of distorting the symmetry of the lanthanide metal ions and therefore they cannot produce the relaxation of the selection rule as with *d* series metals. Consequently, Ln(III) complexes have less intense colours.

(3) In the heavy lanthanide ions, the spin-orbit coupling is more important than crystal field splitting.

(4) The relatively small crystal field effect in these complexes implies that the energies of the electronic states are affected only slightly by the nature of the ligands. In addition, these states are not appreciably affected by thermal vibrations of the bonds. These two factors make the absorption bands of the Ln(III) complexes much sharper than those of $d \rightarrow d$ transitions. All the bands in the visible or near ultraviolet spectra are line-like involving $f \rightarrow f$ transitions. Such sharp bands help identify and determine Ln(III) ions satisfactorily.

(5) The broad bands in some cases are due to excitation of *f* electrons to *d, s* or *p* orbitals.

(6) Inspite of low dependence of the transition energies on ligand fields, some of the band intensities of these complexes are influenced by the coordinated ligands in them.

(7) The crystal fields lift some of the $(2J + 1)$ degeneracy of the states of f^n ion [similar to the lifting of the orbital degeneracy $(2L + 1)$ of the terms of d^n ions]. This produces fine structure in some bands of lanthanide complexes.

(8) CT spectra are possible for some of these complexes; such spectra produce intense colours. The intense yellow colour of Ce(IV) complexes arises due to CT rather than $f-f$ transition.

(9) The colours of aqueous Ln(III) species are listed in Table 5.7. The colours of them depend on the number of *f* electrons; species with *nf* electrons have a similar colours to those with (14-*n*)*f* electrons; thus the colour sequence in the La-Gd series is repeated in the Lu-Gd series.

Table 5.7 Colours and electronic ground states of the Ln(III) ions

Ion	n in $4f^n$	Colour	Ion	n in $4f^n$	Colour
La(III)	0	colourless	Lu(III)	14	colourless
Ce(III)	1	colourless	Yb(III)	13	colourless
Pr(III)	2	green	Tm(III)	12	green
Nd(III)	3	blue-violet	Er(III)	11	pink
Pm(III)	4	rose	Ho(III)	10	yellow
Sm(III)	5	cream	Dy(III)	9	cream
Eu(III)	6	pale pink	Tb(III)	8	pale pink
Gd(III)	7	colourless	Gd(III)	7	colourless

5.11 ELECTRONIC SPECTRA OF ACTINIDE COMPLEXES

The electronic spectra of complexes of actinides originate from three types of transitions.

(1) *f* – *f* transitions Though these transitions are orbitally forbidden, the selection rule is partially relaxed by crystal field effects, which distort the symmetry of the metal ion. The bands are more intense than those for lanthanides as the 5*f* orbitals in these experience stronger ligand fields than the 4*f* orbitals. Thus the spectra of actinide species are sensitive to ligand environment. The bands are narrow, but not as narrow as those of lanthanide species; they are more complex than those of lanthanide complexes. These bands occur in the visible and ultraviolet regions. The hydrated actinide species are thus coloured.

(2) 5*f* – 6*d* transitions These are orbitally allowed and therefore produce bands more intense than the $f-f$ bands. These are broader compared to the $f-f$ bands. They occur at lower energies compared to $4f \rightarrow 5d$ bands of Ln(III) species. These bands occur in the ultraviolet region.

(3) M → L charge transfer These arise from fully allowed transitions. They produce broad, intense absorptions in the ultraviolet region; a few of the bands trail into the visible region. The M → L bands make the actinide complexes intensely coloured.

The spectra of trivalent actinides are of two types: (a) the spectra of Am^{3+} and heavier actinides resemble those of lanthanides (b) the spectra of Pu^{3+} and lighter actinides resemble those of lanthanides in some respects, but have broadening like the spectra of transition metals. This broadening is due to exposure of the 5*f* orbitals to their environment in the lighter actinides and consequent gretaer interaction of these orbitals with the ligands. In the heavy actinides, the 5*f* orbitals are more like the 4*f* orbitals in their feeble interaction with the ligands.

Spectra involving only one *f* electron are simple, consisting of only a single absorption corresponding to $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition.

In Cm^{3+} with f^7 configuration, the excited state has about 6×10^{-19} *J* above the ground level (large energy separation) so that this ion exhibits only CT absorption in the ultraviolet region.

The spectra of the actinide complexes are not useful for inferring stereochemistry because the spectra are complex. However, they are useful for "fingerprint" analysis and stability constant evaluation.

INSIGHT EMERGENT FROM ELECTRONIC SPECTRA

The energy, width and intensity of spectral bands provide valuable information on coordination compounds

- By assigning bands to the corresponding transitions by quantum-chemical calculations, the band positions provide quantitative information on the number and energy of transitions.
- The spectrum can furnish information on the electronic structure of the central metal atom.
- The ligand-field strength can be evaluated.
- The magnitude of ligand-field splitting (Δ) can be calculated
- The geometry of the complex can be inferred.
- Any distortion of the symmetry environment in the complex can be guessed.
- Certain bonding properties (charge-transfer bands) can be ascertained.
- With a set of complexes of analogous composition, their degree of covalency can be compared.

5.12 MAGNETIC PROPERTIES OF METAL COMPLEXES

5.12.1 Types of Magnetic Character

The way a substance interacts with an applied magnetic field is called its magnetic property. When a substance is subjected to a magnetic field H, a magnetization, I is induced in it. The ratio I / H is called the *volume susceptibility* (κ). The volume susceptibility is related to the *gram susceptibility* (χ) and the *molar susceptibility* (χ_M) as indicated below:

$$\chi = \frac{\kappa}{d} \qquad \chi_M = \frac{\kappa M}{d}$$

d is the density
M is molecular weight

For most substances, κ, χ and χ_M have negative values. (Table 5.8). Such substances are called *diamagnetic*. A diamagnetic substance is repelled by a magnetic field. Such a substance has no spin-free electron.

For some substances, κ, χ and χ_M have positive values; they are called *paramagnetic* substances. A paramagnetic substance is attracted into a magnetic field. Paramagnetism originates from the presence of spin-free electron.

Table 5.8 Molar magnetic susceptibilities of some substances

Substance	$\chi_M \times 10^6$ (cm^3 mol^{-1})
H_2O (l)	– 13
NH_3 (g)	– 18
$FeSO_4$ (s)	10,200
$MnSO_4.5H_2O$ (s)	14,700
$K_4[Fe(CN)_6]$	– 130
$K_3[Fe(CN)_6]$	2300

When a magnetic field is applied to a paramagnetic substance, the moments of the paramagnetic molecules or ions tend to align with the field; such orientations are however randomized by thermal agitation. Applying theoretical calculations, the actual susceptibility is given by

$$\chi_M^{\text{corr}} = \frac{N\mu^2}{3kT}$$

χ_M^{corr} = molar susceptibility which has been corrected both for diamagnetic contribution to the susceptibility (due to the non-paramagnetic atoms in the sample) and for small temperature–independent paramagnetism, arising from paramagnetic excited states of the system.
N = Avogadro's constant
k = Boltzmann constant
μ = *magnetic moment* of the molecule
T = absolute temperature

On substituting the actual values for *N* and *k*, the above equation becomes

$$\chi_M^{\text{corr}} = \frac{0.125\,\mu^2}{T}$$

Therefore, $\mu = 2.83\sqrt{\chi_M^{\text{corr}}\, T}$

The value of μ can be experimentally measured; also, it can be theoretically calculated. Any difference between the experimental value and the theoretical value in a compound is indicative of change in the nature of the bonding originally assumed; therefore, the μ values are helpful in characterizing certain compounds, especially metal complexes.

The spin and the orbital motions of the electron are the sources of magnetic moment. Thus μ is given by the expression

$$\mu_{S+L} = \sqrt{4\mathrm{S}\,(\mathrm{S}+1) + \mathrm{L}(\mathrm{L}+1)}$$

In several complexes, the ligand field almost completely quenches the orbital contribution; therefore, the magnetic moment (μ_s) for such complexes can be calculated by the following *spin-only formula*.

$$\mu_s = \sqrt{4S(S+1)} = 2\sqrt{S\,(S+1)}$$

Where S is the total spin of the complex. In the ground state S is one-half the number of unpaired electrons, n.

Therefore, $\mu_s = \sqrt{n\,(n+2)}$; this is called the *spin-only formula*.

The spin-only formula can thus be used to calculate the magnetic moment from the value the number of spin-free electrons in the complex.

For example, $[\mathrm{Cr}\,(\mathrm{H_2O})_6]\mathrm{SO_4}$ is a weak-field d^4 complex; it is expected to have 4 spin-free electrons; hence its μ_s should be

$$= \sqrt{4\,(4+2)} = \sqrt{24} = 4.9$$

This value agrees closely with that (5.1) determined experimentally.

Magnetic moment values are expressed in Bohr magneton unit (μ_B).

$$1\,\mu_\mathrm{B} = \frac{eh}{4\pi\, mc} = 0.9273\times 10^{-20} \text{ erg gauss}^{-1}$$

$$= 9.27\times 10^{-24} \text{ Joules Tesla}^{-1}. \text{ (SI unit)}$$

e = electronic charge
h = Planck's constant
m = electron mass
c = velocity of light

Predict the μ_s values for (a) $\mathrm{K_2[Mn(H_2O)_6](SO_4)_2}$ and (b) $\mathrm{K_4[Mn(CN)_6]}$.

The complex (a) is a d^5 weak field complex; therefore it should have $t_{2g}^3 e_g^2$ configuration with 5 spin-free electrons. Its μ_s should then be

$$\sqrt{5(5+2)} = 5.9$$

Complex (b), on the other hand is a strong-field complex; the configuration should be $t_{2g}^5 e_g^0$, with only one spin-free electron. Its μ_s should be

$$\sqrt{1(1+2)} = 1.7$$

5.12.2 Determination of Magnetic Susceptibility

The Gouy Method The apparent weight of a substance in air is greater in presence of an applied magnetic field than its weight in the absence of the field. The difference in weight denotes the force (F) acting on the sample to draw it into the field. This force is related to the volume susceptibility by the expression

$F = \frac{1}{2}(k_1 - k_2)(H_2^2 - H_1^2)\text{A}$

k_1 = volume susceptibility of the sample

k_2 = volume susceptibility of air

H_2 = applied magnetic field strength

H_1 = Earth's magnetic field strength

A = cross- sectional area of the sample

The expression for F is rewritten as

$F = \text{constant}\ \frac{1}{2}(k_1 - k_2)$ where constant $= (H_2^2 - H_1^2)\text{A}$

$F = \Delta w \times g$ where Δw is the difference in the weight of the sample between the presence and absence of magnetic field; g is the gravitational constant.

The constant is evaluated by measuring F for a standard substance of known volume susceptibility. Then, by measuring F for the test substance in the calibrated apparatus, k_1 is calculated. The mass susceptibility $\chi = k_1 / \rho$ where ρ is the density of the test substance. On multiplying χ by the molecular weight, the molar susceptibility χ_M is obtained.

The magnetic moment of the test substance is given by the expression

$$\mu = \sqrt{3RT\chi_M / N} = 2.83\sqrt{\chi_M T}$$

a) The experiment involves the determination of two weights, one out-of-field weight and the other in-field weight, using a balance (Gouy balance). The sample is suspended from one arm of the balance into a magnetic field. (Figure 5.21)

b) The sample tube (3 – 10 cm) is of pyrex glass, flat and closed at the bottom; it has uniform diameter.

c) The test substance is packed as a powder uniformly in the tube.

d) $CuSO_4 \cdot 5H_2O$ (s) or $Hg[Co(NCS)_4]$ can be used as a solid standard.

e) A liquid sample is also suitable for this method; then, $NiCl_2$ (aq) is used as the standard.

5.12.3 Magnetic Properties of Complex Ions

Some complex ions are paramagnetic while others are diamagnetic. The paramagnetic behaviour of a complex ion depends upon:

(i) the number of spin-free electrons present in it

(ii) the strength of the ligand field

(iii) the symmetry of the ligand field

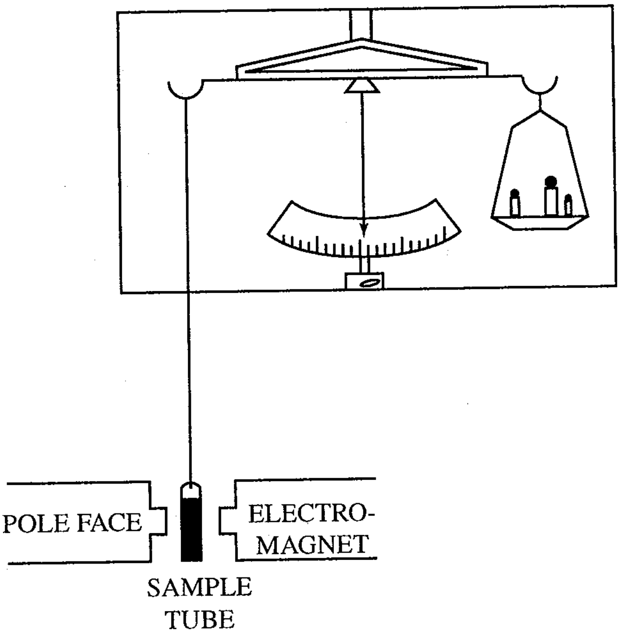


Fig. 5.21 *Gouy magnetic balance*

In terms of Paramagnetic behaviour, the complex ions can be classified into three groups

(i) Spin-only group For a complex of this group, the magnetic moment is correctly denoted by the spin-only formula. Complexes of *d* transition ions belong to this group. The orbital contribution to magnetic moment can be ignored in these cases. For the *d* electrons in these complexes, the orbital angular momentum is completely or largely quenched, as these electrons are not screened by any outer electrons.

(ii) Group with large multiplet separation In this group of complex ions, the spin-orbit coupling is significant unlike with the first group; the spin-free electrons in these lie deep inside the electron shell—shielded by overlying electrons—and therefore their orbital contributions are not quenched by their environment (ligands, solvent, etc.). In addition, the energy state next to that occupied by spin-free electrons is higher by more than kT (200 cm^{-1} / 2.3 kJ mole^{-1}); this precludes promotion and pairing of electrons. Their magnetic moments are given by the equation

$$\mu_J = \mu_{\text{eff}} = g\sqrt{J(J+1)}\ \text{BM}$$

The μ_J is independent of *magnetic dilution*, i.e., separation of the paramagnetic ions by the diamagnetic species present in the material. The lanthanide ions belong to this group in which their *f* electrons are well-shielded.

(iii) Group with small multiplet separation In complex ions belonging to this group, the orbital contribution is neither large nor insignificant to be ignored. In these cases, the orbital contribution is not totally quenched because of insufficient shielding of the spin-free electrons. Such behaviour is observed in a few 3*d* transition metal complexes; in such a case, the observed moment is higher than μ_s but not equal to μ_{S+L}; it is so with some Co(II) and Ni(II) complex species.

5.12.4 Magnetic Criterion of Bond Type in Complexes

The magnetic moment of a metal complex is an indication of the type of bond and configuration of the complex. This relationship can be illustrated with, say, complexes of Ni(II).

The complex $[Ni(CN)_4]^{2-}$ is *diamagnetic* indicating the absence of any spin-free electron in it. The diamagnetism of this complex can be rationalized by assuming dsp^2 hybridisation for Ni(II) and square-planar geometry for the complex:

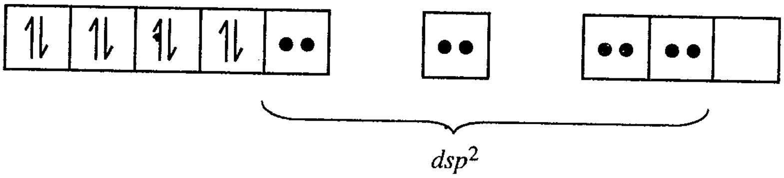


Fig. 5.22 dsp^2 *hybridisation*

The strong field CN^- ligands in this complex force the *d* electrons to pair. If it were tetrahedral, with sp^3 hybridisation, then it would be paramagnetic with two spin-free electrons in its *d* level.

On the other hand, $[NiCl_4]^{2-}$ is *paramagnetic* (μ = 3.1 BM), leading to the conclusion that it should be tetrahedral with sp^3 hybridisation. The Cl^- ligands, not being as strong as the CN^- ligands, do not effect pairing of the *d* electrons of Ni(II); the complex also has two spin-free electrons like the free Ni(II).

The magnitude of magnetism in certain complexes helps decide whether these complexes are *outer orbital* ones or *inner-orbital* ones. To understand this, the cyanide and fluoro complexes of Fe(III) can be considered. In the ground state of Fe^{3+} there are five spin-free electrons, one in each of its 3*d* orbitals. However, the measured magnetic susceptibility for $K_3[Fe(CN)_6]$ corresponds to only one spin-free electron. This is possible only if two of the 3*d* electrons of Fe^{3+} had paired with two other 3*d* electrons, leaving a single spin-free electron, and two vacant 3*d* orbitals. Then, d^2sp^3 hybridisation is possible in which the inner orbitals (the two vacant *d* orbitals below 4*s* and 4*p* levels) are involved in bonding with the six cyanide ligands. The complex then becomes a low-spin or inner-orbital complex. On the contrary, the measured magnetic moment of $K_3[FeF_6]$ indicates the existence of five spin-free electrons in it. Evidently, the five *d* electrons of Fe^{3+} remain spin-free in the complex also. Then, bonding in this complex should involve sp^3d^2 hybridisation, the complex being a high-spin outer-orbital complex. These complexes prove that the measured magnetic moments of complexes are useful for predicting the geometry and hybridisations (bond type) in complexes. More such examples are listed in Table.5.9.

Table 5.9 Magnetic moments of first row transition series complexes (octahedral, high-spin)

Complex of	Number of spin-free electrons	d level structure	Magnetic Moment (BM)	
			μ_s (calc) (spin-only)	μ(obsd)
Ti^{3+}	1	t_{2g}^1	1.73	1.7 - 1.8
V^{3+}	2	t_{2g}^2	2.83	2.8 - 3.1
Cr^{3+}	3	t_{2g}^3	3.87	3.7 - 3.9
Cr^{2+}	4	$t_{2g}^3 e_g^1$	4.90	4.8 - 4.9
Mn^{3+}	4	$t_{2g}^3 e_g^1$	4.90	4.8 - 4.9
Mn^{2+}	5	$t_{2g}^3 e_g^2$	5.92	5.7 - 6.0
Fe^{3+}	5	$t_{2g}^3 e_g^2$	5.92	5.7 - 6.0
Fe^{2+}	4	$t_{2g}^4 e_g^2$	4.90	5.0 - 5.6
Co^{2+}	3	$t_{2g}^5 e_g^2$	3.87	4.3 - 5.2
Ni^{2+}	2	$t_{2g}^6 e_g^2$	2.83	2.9 - 3.9
Cu^{2+}	1	$t_{2g}^6 e_g^3$	1.73	1.9 - 2.1

The measured magnetic monent of $[Mn(NCS)_6]^{4-}$ is 6.1 μ_B. Infer its electron configuration based on this datum.

This Mn(II) complex is a d^5 system. The two possible configurations are $t_{2g}^5 e_g^0$ with one spin-free electron and $t_{2g}^3 e_g^2$ with five spin-free electrons. The observed μ value is close to that expected (5.92) for five spin-free electrons. Therefore, the electronic configuration should be $t_{2g}^3 e_g^2$.

5.12.5 Orbital Contribution to Magnetic Moment

The observed moments of high-spin complexes of first row transition metals are in good agreement with the calculated spin only magnetic moments. However, such agreements are absent in a few cases. For example, for Co(II) complexes, the observed μ is *higher* than that calculated by the spin-only formula. This enhanced moment is due to orbital contribution to the magnetic moment. When it is possible to transform an orbital into an equivalent (degenerate) orbital by rotation, then an orbital angular momentum arises. For example, the t_{2g} orbitals (d_{xy}, d_{xz} and d_{yz}) by rotation through 90° can be interconverted; this is possible because these three orbitals have the same shape, though with different orientations in space. The e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) have different shapes and therefore they cannot be interconverted by rotation. However, if the t_{2g} orbitals are all singly occupied by an electron each, then the d_{xy} orbital cannot be transformed into d_{xy} or d_{yz}, since the latter two already contain an electron each with the same spin. Similarly,doubly occupied t_{2g} orbitals cannot be interconverted. Therefore, configurations with $(t_{2g})^3$ and $(t_{2g})^6$ have no orbital contribution.

In an octahedral geometry (high-spin) the following systems have orbital contribution:

$$(t_{2g})^1(e_g)^0,\ (t_{2g})^2(e_g)^0,\ (t_{2g})^4(e_g)^2,\ (t_{2g})^5(e_g)^2$$

In a tetrahedral geometry, the following systems have orbital contribution:

$$(e)^2(t_2)^1,\ (e)^2(t_2)^2,\ (e)^4(t_2)^4,\ (e)^4(t_2)^5$$

A Co(II) complex, with $(t_{2g})^5\ (e_g)^2$ configuration, therefore, has an orbital contribution; this leads to higher measured *magnetic moment* value for it.

5.12.6 Summarizing

- For an electron to have orbital angular momentum about an axis, the orbital which it occupies must be transformable into an equivalent and degenerate orbital by rotation about the axis in question.
- Orbital contribution is possible when an orbital exists which is similar in energy to that of the orbitals occupied by the unpaired spins. In such a case, the electrons can use degenerate orbitals to circulate themselves through the framework of the complex; this ability of electrons generates angular momentum and a magnetic moment contribution.
- The variations between the spin-only magnetic moments and the actual moments can be used to evaluate energy separations among orbitals and hence the degrees of distortion of orbitals and Δ values.
- The differences between μ_{obs} and μ_s are generally large for $3d^1$ and $3d^2$ and low-spin $3d^4$ and $3d^5$ complexes.

In the lanthanide elements, the spin free electrons are deep inside the electron shell (4*f* orbitals) and are protected by the outer electrons from interaction with the environment of the ions. Therefore, the orbital motions of such electrons are not quenched and their orbital contribution L must be included in the calculations. In some cases there is coupling between the spin contribution S and the orbital contribution L; this is called *spin-orbital coupling* or *Russell-Saunders coupling*. Such a coupling leads to a new quantum number J. Then, modified equations are used for calculating μ:

$$\mu = g\ \sqrt{\mathrm{J}\,(\mathrm{J}+1)}\cdot\mu_{\mathrm{B}}$$

$$\text{where } g = \frac{1+S\,(S+1)-L(L+1)+J\,(J+1)}{2J\,(J+1)}$$

For example, for the lanthanide ions, the use of modified equations gives calculated μ values close to the experimental values. Spin-orbit coupling produces fine structure in the absorption spectra of complexes of these ions.

5.12.7 Quenching of Orbital Contribution

The relationship

$$\mu_s = \sqrt{n\,(n+2)}$$

which ignores the orbital contribution holds good for several high-spin complexes. This is surprising as in these species the orbital contributions must be significant leading to high magnetic moment values. The absence of orbital contribution in these complexes is explained based on the concept of *quenching of orbital contribution*; quenching causes lowering of moment. This quenching is caused by restriction of the orbital motion of the electrons by the influence of strong ligand fields; the ligand field in these complexes is greater than the spin-orbit interaction.

5.12.8 Spin-orbit Coupling and Magnetic Moments

As indicated earlier, $[Co(H_2O)_6]^{2+}$ with $(t_{2g})^5\,(e_g)^2$ is an octahedral high-spin complex. There should be no quenching in this complex; however in $[CoCl_4]^{2-}$ with $(e)^4(t_2)^3$ configuration, there should be quenching and it should have low moment with no orbital moments compared to $[Co(H_2O)_6]^{2+}$. Experimentally, it is true.

$$\mu \text{ for } [Co(H_2O)_6]^{2+} = 5.0\text{ BM}$$
$$\mu \text{ for } [CoCl_4]^{2-} = 4.4\text{ BM}$$

However, the value for $[CoCl_4]^{2-}$ is above the spin-only value of 3.87. This indicates the involvement of one more factor in influencing μ values of complexes. This factor is called *spin-orbit coupling*. This factor *opposes* the quenching of orbital angular momentum by coupling it with spin angular momentum (the spin angular momentum is not directly influenced by the ligand field). Thus, the spin only moment μ_s is modified and this is denoted by the expression,

$$\mu = \mu_s\,(1 - \alpha \frac{\lambda}{\Delta})$$

where α is a constant denoting the spectroscopic state of the ion in the ligand field; *Δ is the separation energy between the ground level and the level being mixed in; λ is called the spin-orbit coupling constant per electron*. The value of λ can be obtained from the differences in energy between states of different J values.

5.12.9 Magnetic Character of Polynuclear Complexes: Bis(acetylacetonato)nickel(II)

$Ni(acac)_2$ is paramagnetic. Let it be assumed to be 4-coordinate and *square-planar*. Then, the hybridisation should be *dsp*^{2}

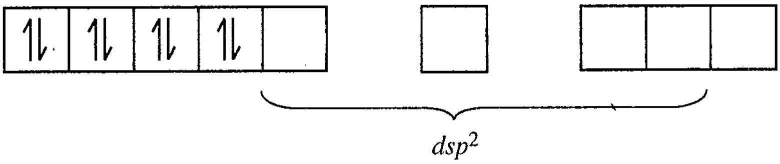


Fig. 22a

The eight electrons of Ni^{2+} should all be paired in the four *d* orbitals and the complex should be spin-paired and diamagnetic. The paramagnetism of it rules out the square-planar geometry. If it were *tetrahedral*, then the hybridisation should be *sp*^{3}:

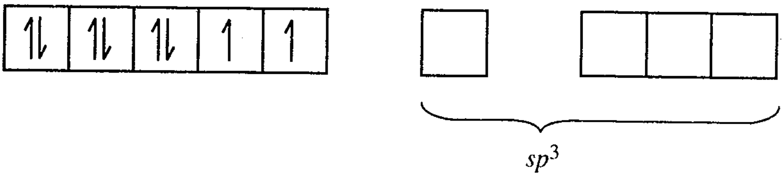
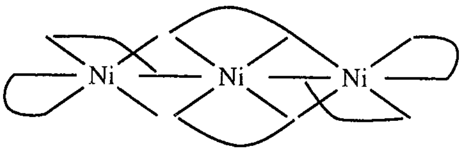


Fig. 22b

The two unpaired electrons in this geometry would account for the paramagnetism of the complex.

However, the X-ray analysis of this *solid* complex indicates a trimeric structure for it; each nickel is six-coordinated. Each molecule has two Ni-Ni bonds, each bond being formed involving a spin-free electron from each nickel:



$Ni_3\ (acac)_6$

This example indicates that the magnetic criterion of geometry based on the number of spin-free electrons is not absolute.

EXERCISES

1. The *d-d* transitions in metal complexes involve different energies; rationalize this observation.

*2. State whether each of the following is true or false:
   a) NMR can be used to study complexes with lifetimes larger than microseconds (10^{-6}s).
   b) Mass spectrometry is of no use for elucidating structures of metal complexes.
   c) Very short-lived complexes (of the order of nanoseconds, 10^{-9} s) can be studied by vibrational and electronic spectroscopy.
   d) The existence of metal-metal bonds in complexes cannot be established by infrared spectroscopy.

3. The ^1H – NMR signals for the protons bonded to metals such as Os in the complex $HOs(CO)(PPh_3)_3$ occur at very high field, corresponding to τ values in the range 15 – 50. Explain this.

*4. Complexes containing metal-metal bonds are intensely coloured. Rationalize this fact.

5. Why is an N-N infrared stretching absorption is expected of

   $[(NH_3)_5Os-N\equiv N-Os(NH_3)_5]^{5+}$?

*6. Account for the following:
   a) Hexaaquairon(III) ion is practically colourless, whereas $[CoF_6]^{3-}$ is coloured.

b) The Racah parameter B for $[Co(CN)_6]^{3-}$ is 460 cm^{-1}, whereas that for $[Co(NH_3)_6]^{3+}$ is 615 cm^{-1}.

c) The Racah paramater B for $[Ni(H_2O)_6]^{2+}$ is only about 70% of that for free Ni^{2+} ion.

*7. Explain why both the low-spin $[Fe(CN)_6]^{4-}$ and the high-spin $[Fe(H_2O)_6]^{2+}$ are colourless.

*8. What does the existence of infrared $\nu_{Cr\text{-}Cl}$ stretching vibration in $[Cr(NH_3)_4Cl_2]^+$ prove?

*9. The electronic absorption bands for $[Ni(en)_3]^{2+}$ occur at higher frequencies corresponding to the bands for $[Ni(H_2O)_6]^{2+}$; justify.

*10. In $[Co(NH_3)_5I]^{2+}$, the charge-transfer bands largely obscure the *d-d* bands: explain.

*11. An aqueous solution of Cr(III) is pale violet but an aqueous solution of CrO_4^{2-} is bright yellow. Explain this difference.

*12. Explain the following:

a) The two spin-allowed ligand field transitions of $[Cr(NCS)_6]^{3-}$ are at lower energy than those of $[Cr(NH_3)_6]^{3+}$.

b) The electronic spectrum of $[Cr(NCS)_6]^{3-}$ has an intense MLCT band unlike that of $[Cr(NH_3)_6]^{3+}$.

c) $[Mn(NCS)_4]^{2-}$ is tetrahedral whereas $[Mn(NCS)_6]^{4-}$ is octahedral; however, their molar magnetic susceptibilities at room temperature are the same.

d) $[Mn(NCS)_6]^{4-}$ is a low-spin complex.

e) $[Fe(H_2O)_6]^{2+}$ is paramagnetic whereas $[Fe(CN)_6]^{4-}$ is diamagnetic.

*13. The NO stretching vibration in the free NO occurs at 1876 cm^{-1} whereas it occurs at 2200 cm^{-1} in $NOBF_4$. Explain.

*14. Predict the number of infrared bands for the complex $[Os(py)_2(CO)_4]$.

*15. $[FeF_6]^{3-}$ is colourless whereas $[CoF_6]^{3-}$ is coloured. How can this difference be accounted for?

16. The species $[Fe(H_2O)_5NO]^{2+}$ is formed in the brown ring test for nitrates. The N-O stretching frequency for this species is 1745 cm^{-1} and $\mu_{eff} = 3.9$. Discuss the bonding in this.

*17. List the experimental methods which can measure back-bonding in a transition metal carbonyl.

18. Discuss the spectral consequences of the Jahn-Teller effect.

19. What is the interrelationship between spin-orbit coupling and the spectrum in a complex?

*20. The ^{19}F NMR spectrum of $[WF_6L]$ shows three lines of relative intensity 4 : 1 : 1. Account for this.

*21. What is the origin of the intense yellow colour of CrO_4^{2-}?

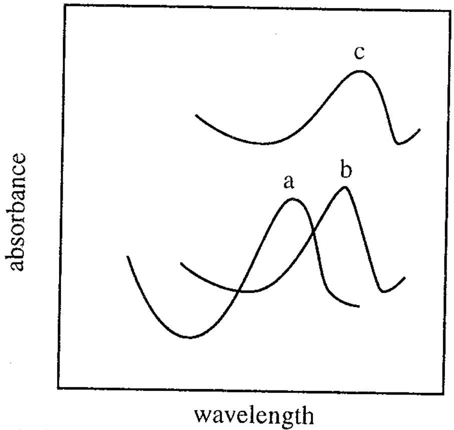
22. a) When are CT transitions in complexes favoured? b) The ^{13}C NMR spectrum of aqueous $[Mo(CN)_8]^{4-}$ has only one peak; how is this justified ?

23. Explain why the $[Mn(H_2O)_6]^{2+}$ ion has an extremely pale pink colour.

24. Predict the *d-d* absorption spectrum of $NiCl_4^{2-}$.
25. Though the ion CrO_4^{2-} is a d^0 system, it is coloured; how can this be rationalized?
26. Predict the number of spin-allowed ligand field transitions expected for
    (a) $[Zn(OH)_4]^{2-}$ (b) $[Ni(NH_3)_6]^{2+}$
27. The high-spin d^6, $[CoF_6]^{3-}$ shows two absorption bands in the visible spectral region; account for this.

*28. What is a redox spectrum?

29. Explain the charge-transfer spectrum of $[Co(NH_3)_5X]^{2+}$ depicted in the following figure.



a) $[Co(NH_3)_5Cl]^{2+}$
b) $[Co(NH_3)_5Br]^{2+}$
c) $[Co(NH_3)_5I]^{2+}$

*30. Match the following:

Complex species	**μ (BM)**
(a) $[Mn(CN)_6]^{3-}$	(i) 0.0
(b) $[Zn(CN)_4]^{2-}$	(ii) 5.9
(c) $[MnBr_4]^{2-}$	(iii) 2.8

31. $[IrCl_6]^{2-}$ has only one spin-free electron. Explain.

*32. Explain the following:
The magnetic moment of $K_3[Fe(CN)_6]$ is 2.3 μ_B, which is between spin-only values for one and two unpaired electrons (1.7 μ_B and 2.8 μ_B)

*33. $[NiBr_2(PEtPh_2)_2]$, on dissolution in chloroform has a magnetic moment value between that expected for planar, diamagnetic form ($\mu_B = 0$) and that expected for tetrahedral, paramagnetic form ($\mu_s = 3.2$ BM); explain.

*34. The observed magnetic moment of $[Mn(NCS)_6]^{4-}$ is 6.06 μ_B. Predict the electronic configuration.

*35. Calculate the magnetic moment for $[CoCl_4]^{2-}$ taking into account the fact that there is angular momentum contribution to the moment. ($\Delta = 3100 cm^{-1}$).

36. What is the magnetic consequence of the Jahn-Teller effect?

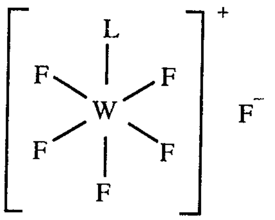
ANSWERS

2. a) True
   b) False
   c) True
   d) False
4. True. In such complexes fully allowed transitions of the type $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $\delta \rightarrow \delta^*$ are possible; such transitions occurring in the visible region render these complexes intensely coloured. (For example, $Mn_2(CO)_{10}$ is bright yellow and $Co_2(CO)_8$ is purple-black)
6. a) $[Fe(H_2O)_6]^{3+}$ has $t_{2g}^3 e_g^2$ configuration; therefore, it can take part only in spin-forbidden LF transition.
   $[CoF_6]^{3-}$ has $t_{2g}^4 e_g^2$ configuration; therefore, it can undergo spin-allowed $(5E_g \leftarrow 5T_{2g})$ transition.
   b) The B value is proportional to interelectronic repulsions in the metal. The lesser B value for the cyanide complex indicates lesser repulsion compared to the repulsion in the ammine complex. CN^- forms a more covalent bond than NH_3 with the metal reducing repulsion. The nephelauxetic effect by CN^- is more than that by NH_3.
   c) The considerably reduced B value for the complex compared to the B value for the free ion indicates a strong nephelauxetic effect in the complex. The nephelauxetic effect reduces electron repulsion.
7. The strong-field ligand CN^- makes the Δ value for the cyanide complex high. The LF transition, therefore occcurs at a high energy, in the ultraviolet region. The weak-field ligand H_2O makes the Δ value for the aqua complex very low; therefore, the LF transition in this complex occurs at a very low energy, in the infrared region. Hence, both the complexes are colourless.
8. Covalent bonding between the metal and the ligand.
9. This order is in accordance with the spectrochemical series; the splitting energy Δ is greater with *en* than with H_2O.
10. In $[Co(NH_3)_5I]^{2+}$, the L $\rightarrow$ M electron transfer is facile and occurs at low frequency. Thus this CT band obscures the weak *d-d* bands.
12. a) NCS^- induces a smaller Δ_0 in the d^3 Cr(III) ion than does NH_3.
    NCS^- has an empty but stable low-lying π^* orbital for MLCT; NH_3 does not have such an orbital.
13. The bond order in NO is 2.5. In $NOBF_4$, NO occurs as NO^+; in forming this, an antibonding electron is shifted to boron and therefore the bond order in NO^+ is 3. This increased bond order (decreased bond length) increases the NO stretching frequency.
14. This can exist in cis-trans isomeric forms. The trans form is expected to have a single band and the cis form four bands.
15. The Fe(III) in $[FeF_6]^{3-}$ has a d^5 configuration. In this octahedral complex, as F^- is a weak-field ligand; the *d* configuration is $t_{2g}^3 e_g^2$, with 5 spin-free electrons (high-spin). Its ground term is $^6A_{1g}$; there is no higher energy term

of the same multiplicity as the $^6A_{1g}$ term. Therefore, no spin-allowed transitions are possible in this complex; consequently it is colourless.

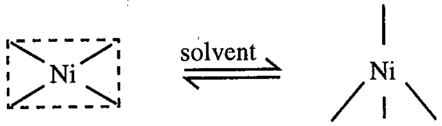
The ground term for Co(III) d^6 ($t_{2g}^4e_g^2$) system is $^5T_{2g}$. In this case, a spin-allowed transition $^5E_g \rightarrow ^5T_{2g}$ is possible; therefore, $[CoF_6]^{3-}$ is coloured.

17. a) IR spectroscopy (C-O stretching frequency)
    b) ^{13}C NMR (chemical shift)
    c) XRD (C-O or M-C bond distance)
    d) Electron diffraction (C-O or M-C bond distance)
    e) X-ray photoelectron spectroscopy, ESCA (electron binding energy).
20. The spectrum indicates that the six F^- ions in the complex are chemically non-equivalent. There are three types of F^- ions; this is not possible if the complex were 7-coordinate. A possible structure is



The four coplanar fluorines produce the most intense peak and the axial fluorine the second peak. The fluoride ion, outside the coordination sphere can account for the third absorption. (4 : 1 : 1)

21. The chromium in CrO_4^{2-} is in its +6 oxidation state with d^0 electron structure. This indicates that no ligand field transitions can occur in it. As the metal is in its high oxidation state in association with oxide ion, L → M charge transfer is possible in the chromate ion; this produces the yellow colour. The CT transitions are both spin-allowed and Laporte-allowed, and so the colour is intense.
28. Redox spectra refer to charge-transfer spectra because in charge-transfer process electrons are transferred involving redox reaction.
29. The wavelength of absorption energy is in the order $I^- > Br^- > Cl^-$. This indicates that the transition energy increases from I^- to Br^- to Cl^-. The least electronegative iodine, readily transfers its charge to the metal (L → M)
30. a. (iii) b. (i) c. (ii)
32. The deviation of the measured magnetic moment from the spin-only value is due to orbital contribution (an orbital similar in energy to that of the orbitals occupied by the unpaired electrons can contribute to μ_0. The electrons can make use of such an orbital to circulate themselves through the framework of the complex and hence generate angular momentum and a magnetic moment)
33. This "anomalous" behaviour is due to the existence of planar - tetrahedral equilibrium for the complex in solution:



brown, diamagnetic green, paramagnetic

Several $[Ni(PR_3)_2X_2]$ complexes behave like this. The diamagnetic planar form is favoured when R = alkyl, X = I and the paramagnetic tetrahedral form when R = aryl, X = Cl. If the complex is a mixed alkylaryl phosphate, *conformational isomerism* occurs; both the forms exist independently.

34. Mn in this complex is Mn(II), d^5. There are two possibilities of electron configuration for this octahedral species, namely low-spin t_{2g}^5 with one unpaired electron and $t_{2g}^3e_g^2$ with five unpaired electrons. The observed magnetic moment is close to the "spin-only" value, $\sqrt{5(5+2)} = 5.92\ \mu_B$. Therefore, the configuration should be $t_{2g}^3e_g^2$ (high-spin).

35. The spin-only formula is modified into

$$\mu = (1 - \frac{\lambda'}{\Delta}) \quad [n\,(n+2)]^{1/2}$$

when the angular momentum contribution to the moment occurs. In this expression, λ' is the spin-orbit coupling parameter. For Co(II), it is $-688\ \text{cm}^{-1}$

Then,
$$\mu = (1 + \frac{688}{3100})\ [3\,(3+2)]^{1/2}$$
$$= 4.73\ \text{BM}$$

Chapter 6

Stability of Coordination Compounds

The subject of stability of metal complexes is important in understanding the properties of complexes. Many variables associated with the central metal ion and the ligand greatly complicate the study of this subject. The reasonable approach to the study of stability of complexes is to maintain constant as many variables as possible and then examine a small area of the whole subject.

6.1 THERMODYNAMIC STABILITY AND KINETIC STABILITY

There are two types of stability viz. the *thermodynamic stability* and the *kinetic stability* for a molecule. If the term "stability" is used without any modification, then it refers to the thermodynamic stability. When we are interested in stability from the thermodynamic point of view, then we must deal with metal-to-ligand bond energies, stability constants and the thermodynamic variables derivable from them. From a thermodynamic point of view, it is more appropriate to speak of complexes as being stable or unstable. If we are interested in stability from the kinetic point of view, then we must deal with the rates and mechanisms of reactions and also with the energies involved in the formation of the activated complex. In the kinetic point of view, it will be more proper to speak of complexes as being *inert* or *labile* rather than stable or unstable. Very often these two groups of terms are used incorrectly. Stable complexes may be *inert* or *labile* and unstable complexes may be *labile* or *inert.*

For example, CN^- ion forms a very stable complex with Ni^{2+}:

$$[Ni(H_2O)_6]^{2+} + 4\,CN^- \longrightarrow [Ni(CN)_4]^{2-} + 6H_2O$$

Ni^{2+} prefers CN^- rather than H_2O as a ligand. Thus $[Ni(CN)_4]^{2-}$ is thermodynamically more stable than $[Ni(H_2O)_6]^{2+}$. However, when ^{14}C-labelled CN^- ($^{14}CN^-$) is added to the solution, it is almost instantaneously incorporated into the complex:

$$[Ni(CN)_4]^{2-} + 4\,{}^{14}CN^- \longrightarrow [Ni({}^{14}CN)_4]^{2-} + 4CN^-$$

This means that the complex, $[Ni(CN)_4]^{2-}$ is kinetically labile. Thus the stability of this complex does not ensure inertness.

$[Co(NH_3)_6]^{3+}$ is thermodynamically unstable in acid solutions. But it can be kept in acid solution for several days at room temperature without noticeable decomposition. This means that this complex is kinetically inert. Thus instability of a complex does not ensure lability.

$[Fe(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{3+}$ have roughly the same bond energy. This means that these two complexes are of equal stability from the thermodynamic point of view. But $[Fe(H_2O)_6]^{3+}$ is labile and exchanges its ligands with other ligands rapidly, whereas $[Cr(H_2O)_6]^{3+}$ is inert and hence exchanges its ligands very slowly. Many such examples may be given. Thus these two types of stability are related to two different phenomena.

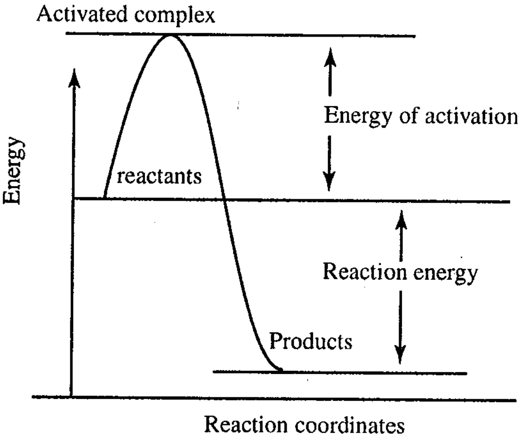


Fig. 6.1 The relative energies of products, reactants and activated complex of a reaction

The thermodynamic stability of a complex depends on the difference in energy between the reactants and the products, namely the *reaction energy* (Fig. 6.1). Greater this reaction energy, greater will be the thermodynamic stability. But the kinetic stability of a complex depends on the difference in energy between the reactants and the activated complex, namely the *activation energy*. Greater this activation energy lesser will be the reaction rate, implying that the complex is inert.

6.2 STEP-WISE STABILITY CONSTANTS AND OVERALL-STABILITY CONSTANT

Coordination compounds are assumed to be formed from their constituents in aqueous solution by a step-wise replacement of coordinated water molecules by ligand molecules or ions. The different steps involved in the formation of a complex may be represented as follows (for the sake of simplicity, the charges on the complex ions are ignored):

$$[M(H_2O)_n]+L \overset{K_1}{\rightleftharpoons} [M(H_2O)_{n-1}L]+H_2O$$

$$[M(H_2O)_{n-1}L]+L \overset{K_2}{\rightleftharpoons} [M(H_2O)_{n-2}L_2]+H_2O$$

$$[M(H_2O)_{n-2}L_2]+L \overset{K_3}{\rightleftharpoons} [M(H_2O)_{n-3}L_3]+H_2O$$

$$[M(H_2O)L_{n-1}]+L \overset{K_n}{\rightleftharpoons} [ML_n]+H_2O$$

For each step in the above process, there is an equilibrium constant, K_1, K_2, K_3, ... K_n. These equilibrium constants are called *step-wise stability constants* or *successive stability constants* of the system. The stability constant is also referred to as *formation constant.* They are called stability constants because the larger their values, the greater will be the stability of the system. $1/K$ is known as the *instability constant.*

If the reaction takes place in a single step, then the following equation applies:

$$[M(H_2O)_n]+nL \overset{\beta_n}{\rightleftharpoons} [ML_n]+nH_2O$$

This reaction is defined by the equilibrium constant, β_n, which is called the *over-all stability constant* or *over-all formation constant* for the nth stage product.

6.3 RELATIONSHIP BETWEEN STEP-WISE FORMATION CONSTANTS AND OVER-ALL FORMATION CONSTANT

Let us consider the first three steps in the formation of a complex from an aquated cation by step-wise replacement of the coordinated water molecules by ligand molecules or ions. These reactions are represented by the following equations:

$$[M(H_2O)_n]+L \rightleftharpoons [M(H_2O)_{n-1}L]+H_2O$$

$$[M(H_2O)_{n-1}L]+L \rightleftharpoons [M(H_2O)_{n-2}L_2]+H_2O$$

$$[M(H_2O)_{n-2}L_2]+L \rightleftharpoons [M(H_2O)_{n-3}L_3]+H_2O$$

On applying the Law of Mass Action to the above equilibria,

$$K_1 = \frac{[M(H_2O)_{n-1}L]}{[M(H_2O)_n][L]}$$

$$K_2 = \frac{[M(H_2O)_{n-2}L_2]}{[M(H_2O)_{n-1}L][L]} \quad \text{and}$$

$$K_3 = \frac{[M(H_2O)_{n-3}L_3]}{[M(H_2O)_{n-2}L_2][L]}$$

The activity of the water molecules involved in these reactions are not included in the equilibrium constants. By convention, the activity of pure water is defined as unity. Hence the activity of water is close to one in dilute solutions. If we assume that the third step product, $[M(H_2O)_{n-3}L_3]$, is formed in a single step,then the equation representing that reaction will be

$$[M(H_2O)_n] + 3L \underset{}{\overset{\beta_3}{\rightleftharpoons}} [M(H_2O)_{n-3}L_3] + 3H_2O$$

The equilibrium constant, β_3, (over-all stability constant for the third stage product) is defined by the following expression:

$$\beta_3 = \frac{[M(H_2O)_{n-3}L_3]}{[M(H_2O)_n][L]^3}$$

On multiplying both the numerator and denominator by $[M(H_2O)_{n-1}L]$ $[M(H_2O)_{n-2}L_2]$,

$$\beta_3 = \frac{[M(H_2O)_{n-3}L_3][M(H_2O)_{n-1}L][M(H_2O)_{n-2}L_2]}{[M(H_2O)_n][L]^3[M(H_2O)_{n-1}L][M(H_2O)_{n-2}L_2]}$$

On rearranging the above expression,

$$\beta_3 = \frac{[M(H_2O)_{n-1}L]}{[M(H_2O)_n][L]} \cdot \frac{[M(H_2O)_{n-2}L_2]}{[M(H_2O)_{n-1}L][L]} \cdot \frac{[M(H_2O)_{n-3}L_3]}{[M(H_2O)_{n-2}L_2][L]}$$

The first term on the right hand side of the above expression is equal to K_1, the second term is equal to K_2 and the third term is equal to K_3. Therefore $\beta_3 = K_1 \times K_2 \times K_3$. *Hence the over-all stability constant β_n is the product of the step-wise stability constants of the system.*

For a system having *n* steps

$$\beta_n = K_1 \times K_2 \times K_3 \times \dots K_n$$

The over-all stability constant is generally used as a guide to the stability of the complex. Values of the over-all stability constants may cover a very wide range. For extremely stable complexes such as $[Fe(CN)_6]^{4-}$, β_n is of the order of 10^{30} and for extremely unstable complexes β_n may even be less than unity. On account of this wide range, the values of the constants are frequently quoted on a logarithmic scale.

$$p\beta = \log_{10} \beta$$

$$\log_{10} \beta_n = \log_{10} K_1 + \log_{10} K_2 + \log_{10} K_3 + \dots + \log_{10} K_n$$

As a rough guide, a $p\beta$ value greater than 8 represents a "stable" complex.

6.4 TREND IN *K* VALUES

The *K* values generally decrease gradually with increasing substitution of H_2O by L. This gradual decrease in *K* values is attributed to three factors, namely, the *statistical factor, steric factor* and the *electrostatic factor.*

Statistical factor As the coordinated water molecules are replaced by ligand molecules or ions (L), the number of water molecules in the complex formed decreases. Hence the probability of replacing water molecules also decreases. As a result *K* values decrease gradually.

Steric factor This arises only when the incoming ligands are bulkier in size than the coordinated water molecules. As the small sized water molecules are replaced by bulkier ligands (L), the steric crowding around the central metal ion increases. As a result of these steric repulsions the subsequent steps are retarded; hence the *K* values gradually decrease.

Electrostatic factor In the first step of complex formation, one ligand (L) replaces one coordinated water molecule to give $[M(H_2O)_{n-1}L]$. In the second step, another ligand (L) of the same charge approaches the first stage product. Now there is an electrostatic repulsion between the incoming ligand and a similar ligand already present in the complex. As a result of this electrostatic repulsion between the ligands, the subsequent steps are retarded. Hence K values decrease gradually.

Therefore, the general trend in K values is $K_1 > K_2 > K_3 \ldots > K_n$. Some examples to illustrate such a trend are given in Table 6.1.

Table 6.1 Effect of ligand number on the stabilities of complexes

System	log K_1	log K_2	log K_3	log K_4	log β_4
Cu^{2+}/NH_3	4.15	3.50	2.89	2.13	12.67
Ni^{2+}/NH_3	2.80	2.24	1.73	1.19	7.96

There are a few exceptions to this general trend. Such exceptions are given in Table 6.2.

Table 6.2 Exceptions to the stability constant - number of ligands relationship

System	log K_1	log K_2	log K_3	log K_4	log β_4
Cd^{2+}/I^-	2.08	0.77	2.15	1.48	6.48
Cd^{2+}/Br^-	1.56	0.54	0.06	0.37	2.53

Any anomaly in the trend in K values suggests a major structural change. Generally, the aqua complexes are six-coordinated whereas the halo complexes are tetrahedral. For example, in Cd^{2+}/Br^- system, the reaction of the fourth Br^- group and the complex with three Br^- groups is,

$$\begin{array}{ccc} [CdBr_3(H_2O)_3]^- + Br^- & & [CdBr_4]^{2-} + 3H_2O \\ \text{(octahedral)} & \longrightarrow & \text{(tetrahedral)} \\ 1+1=2 \text{ particles} & & 1+3=4 \text{ particles} \end{array}$$

This reaction is accompanied by an increase in the number of particles and hence it is entropically favoured; this in turn results in an increase in K_4 value.

6.5 IRVING - WILLIAMS SERIES

Metal ions are empirically classified into three classes based on the stabilities of complexes formed by them with ligands having donor atoms from Groups V A, VI A or VII A.

Class a metal ions are those ions which form complexes of the greatest stability with the lightest element of each of these groups as the donor atom.

Examples of *class a* metal ions are

Li^+ Na^+ K^+

Be^{2+} Mg^{2+} Ca^{2+} Sr^{2+}

Al^{3+} Ga^{3+} Cr^{3+} Fe^{3+} Co^{3+} etc.

Class b metal ions are those which form least stable complexes with the lightest element of each group as donor atom.

Examples of *class b* metal ions are

Cu^+ Ag^+ Au^+ Tl^+

Hg^{2+} Pd^{2+} Pt^{2+} Tl^{3+}

Some metal ions form complexes whose stabilities cannot be predicted on the basis of the order which was observed for *class a* and *class b* metal ions. Those ions are classified as *border line class.*

Examples of border line class are Mn^{2+} Fe^{2+} Co^{2+} Ni^{2+} Cu^{2+} Zn^{2+} etc. For these metal ions, the stability of complexes with a given ligand is almost in the order

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

This order is known as the *Irving - Williams series.* This is illustrated for some ligands in Fig. 6.2.

Although the figure shows the trend in K_1 values, the Irving - Williams series generally holds good for K_2 and K_3 also.

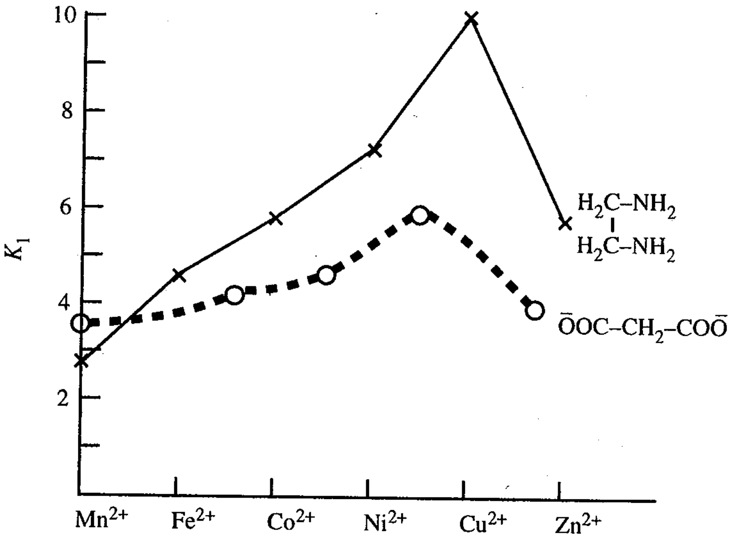


Fig. 6.2 Trend in K_1 values as M^{2+} is altered, illustrating the Irving-Williams series

6.6 FACTORS AFFECTING THE STABILITY OF COORDINATION COMPOUNDS

Stability constants vary over a very wide range of values even when we consider the reaction of a particular metal with a number of ligands or a particular ligand with a variety of metals. It is not possible to conclude that a particular ligand or a particular metal forms complexes of high or low stability. No single factor is expected to account for the relative stabilities of coordination compounds; they are affected by many physical and chemical factors. Some of these factors are discussed below.

The charge, size and outer electronic configuration of the central metal ion affect the stabilities of complexes.

6.6.1 Charge of the Central Metal Ion

The complex formation is essentially a reaction between a cation (central metal ion) and an anion or a dipole (ligand);therefore, the charge of the central metal ion is expected to be of importance in deciding the stability of the complex. Greater the positive oxidation state of the central metal ion greater will be its attraction for the ligands; hence greater will be the stability of the complex. Therefore, when a metal ion forms complexes with the same ligand in more than one oxidation state, the complexes of the higher oxidation states are always more stable than those of the lower oxidation states. Table 6.3 gives the stability constants (p*K*) of EDTA complexes with metals in two different oxidation states. The p*K* values of the complexes with the metals in their higher oxidation states are always higher.

Table 6.3 The pK values of EDTA complexes with certain metal ions in 2+ and 3+ oxidation states

V^{2+} 12.7	Fe^{2+} 14.3	Co^{2+} 16.2
V^{3+} 25.9	Fe^{3+} 25.1	Co^{3+} 36.0

6.6.2 Size of the Central Metal Ion

Keeping the charge constant, as the size of the central metal ion decreases, the specific charge per unit surface area increases. Hence the metal's attraction for the ligand increases. Generally, stabilities of complexes increase with decrease in size of the central metal ion. This is well illustrated by the gradual increase in stability of the tripositive lanthanide ion - EDTA complexes from La to Lu due to "lanthanide contraction". This contraction leads to a steady decrease in size of the central metal ion; hence the stability increases.(Table 6.4.)

Table 6.4 The pK values of the 3+ lanthanide-EDTA complexes $[Ln(EDTA)]^-$

Ion	pK
La^{3+}	15.50
Ce^{3+}	15.98
Gd^{3+}	17.37
Tb^{3+}	17.93
Ho^{3+}	18.74
Tm^{3+}	19.32
Yb^{3+}	19.51
Lu^{3+}	19.83

Within a group of the periodic table, say, the alkali group, where the charge remains constant but size increases down the group, the stability of the complex with a particular ligand decreases in the order,

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

The charge-to-radius ratio is called the *ionic potential.* As the charge increases and as the size decreases, the stability will increase. Therefore, as the ionic potential of the central metal ion increases the stability of the complexes with a particular ligand will also increase. The ionic potential decreases from Li^+ to Cs^+.

6.6.3 Outer Electronic Configuration of the Central Metal Ion

An apparent anomaly arises when we compare the stabilities of complexes formed by similarly charged and similarly sized metal ions belonging to two subgroups of the same periodic family (group). For example, K^+ and Cu^+ complexes with a particular type of ligand may be considered to explain this fact. Potassium is a non-transition element whereas copper is a transition element(*d*-block element). Cations of *d*-block elements invariably form more stable complexes than the cations of non-transition elements (both elements belonging to the same group of the periodic table). The reason for this difference in stabilities is traced to the fundamental electronic difference in these two type of metals. The cations of non-transition elements have inert gas configurations, $(n-1)s^2p^6$, in the outermost shell whereas the cations of transition elements have pseudo-inert gas configurations, $(n-1)s^2p^6d^{10}$, in the outermost shell. It is a well-known fact that the latter configuration is much poorer in shielding the excess positive charges located on the nucleus than the former configuration. Hence the effective nuclear charge is actually larger in Cu^+ than it is in K^+, that is Cu^+ will behave as if it possesses greater nuclear charge. So Cu^+ has a greater attraction for the electrons offered by the ligands. Consequently, Cu^+ forms the more stable complex than K^+ with a particular type of ligand.

Many factors associated with the ligands also affect the stability of complexes. Some of these factors are the nature of the ligand atom, the basicity of the ligand and the chelating ability of the ligand.

6.6.4 Nature of the Ligand Atom

The atoms which are bound directly to metal ions in complexes are those of the more electronegative elements on the right hand side of the periodic table (such as the halogens, oxygen, sulphur, arsenic, phosphorus, nitrogen etc.). The complexes formed by the halide ions have been widely studied. For most metals the order of stabilities follows the sequence $F^- > Cl^- > Br^- > I^-$. But this order is reversed for a few metals like $Pt^{2+}, Cu^+, Ag^+, Hg^{2+}$ and Tl^+, where back donation from metal to ligand occurs in addition to the transfer of electrons from the ligand to the metal. For this back donation from metal to ligand to occur, the ligand must possess vacant orbitals capable of receiving electrons. Iodine, being the least electronegative among the halogens, can easily accept the back donated electrons by the metal. Hence the order of stability is the reverse of that observed for most of the other metal ions.

6.6.5 Basicity of the Ligands

Basicity is a measure of electron pair donation. Greater the basicity of the ligand, greater will be the tendency to donate electron pairs. This means that the more basic ligands will form more stable complexes. Bjerrum studied the stabilities of the amine complexes of Ag^+ and Hg^{2+}, with reference to ligand basicities; he observed that other things being equal, the increase in basicity of the ligands increases the stability of their complexes. Table 6.5 gives the log K values for some Ag^+ - alkylamine complexes.

Table 6.5 Effect of ligand basicity on the stability of some Ag^+ complexes

Ligand	$10^4 K_b$	$\log K(Ag^+)$
CH_3-NH_2	4.4	3.34
$CH_3-CH_2-NH_2$	5.6	3.65
$CH_3-CH_2-CH_2-NH_2$	4.7	3.84

Similar linear relationships between base strength and coordinating ability of ligands are obtained for secondary and tertiary amines. In certain cases, the lower stability of the complexes of secondary and tertiary amines is attributed to steric hindrance between the ligands.

6.6.6 Chelating Ability of the Ligand

The stabilities of complexes are greatly increased by the coordination of polydentate ligands. Coordination of such ligands produces ring structures with the metal atom forming a part of the ring system. Such ring-structured complexes are called chelates. (in Greek *chela* means crab's claw). This process of chelate formation is called *chelation*. The ligand that forms a chelate is called *chelating agent*. Due to chelation, extra stability is conferred on the complex. This extra stability is termed as the *chelate effect*. The chelate effect may be regarded thermodynamically as due to the favourable entropy change of the reaction. When a solvated metal ~~ion in~~ solution reacts with a chelating agent, the solvent molecules in the coordination sphere of the metal ion are replaced by chelating agent. For example, when an aquated Ni^{2+} ion is treated with ethylenediamine (en), the coordinated water molecules are replaced by *en* molecules to form a chelate.

$$[Ni(H_2O)_6]^{2+} + 3en \longrightarrow [Ni(en)_3]^{2+} + 6H_2O$$

$$1+3=4 \text{ particles} \longrightarrow 1+6=7 \text{ particles}$$

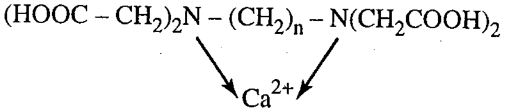
This chelation process results in an increase of three in the number of particles present ($4 \rightarrow 7$). The replacement of monodentate ligands by chelating agents must lead to this effect. This increase in the number of particles results in an increase of randomness in the system. This in turn, results in a positive entropy change of the process ($\Delta S°$)which adds to the negative $\Delta H°$ value to give a more negative $\Delta G°$. ($\Delta G° = -RT \ln K$). Hence, an increase in randomness causes greater complex stability. Thus chelate complexes have a greater probability of formation than the corresponding complexes with monodentate ligands. Table 6.6 shows the overall stability constants for a number of metalammines (non-chelates)and the corresponding ethylenediamine complexes (chelates).

Table 6.6 Overall stability constants for some metalammine complexes and the corresponding metal ethylenediamine chelate complexes

Cation	Coordination number	$p\beta(NH_3)$	$p\beta(en)$
Co^{2+}	6	5	14
Co^{3+}	6	34	49
Ni^{2+}	6	9	19
Cu^{2+}	4 (sq pl)	13	20
Zn^{2+}	4 (tet)	9	11

6.6.7 Chelate Ring Size

One factor of great importance in chelation is the size of the ring produced. When there is no double bond in the chelate ring, generally a 5-membered ring will be the most stable. When there are double bonds, a 6-membered ring is the most stable. Any ring containing less than 5 members or more than 6 members will be less stable generally. Table 6.7 shows the variation of the stability constants with ring size of the calcium complexes with a series of acids of general formula.



$$(HOOC-CH_2)_2N-(CH_2)_n-N(CH_2COOH)_2 \quad Ca^{2+}$$

When $n = 2$, a 5-membered ring is formed between two nitrogen atoms and the metal; when $n = 3$, a 6-membered ring is formed, and so on. The maximum stability is found when $n = 2$.

Table 6.7 Variation of stability constants with the ring size of chelates

n	Ring size	Stability constant log K
2	5	10.7
3	6	7.1
4	7	5.1
5	8	4.6

6.6.8 Number of Chelate Rings

Another factor of importance in chelation is the *number of chelate rings*. Greater the number of chelate rings, greater will be the stability of complex. This greater stability of complexes having more number of chelate rings is attributed to the greater increase in the positive entropy (entropy change) of the system. For example, in $[Co(en)(H_2O)_4]^{2+}$, there is one chelate ring. During its formation from aqueous solution there is an increase in the number of particles from 2 to 3 as shown below:

$$[Co(H_2O)_6]^{2+} + en \longrightarrow [Co(en)(H_2O)_4]^{2+} + 2H_2O$$

$$1+1=2\text{ particles} \longrightarrow 1+2=3\text{ particles}$$

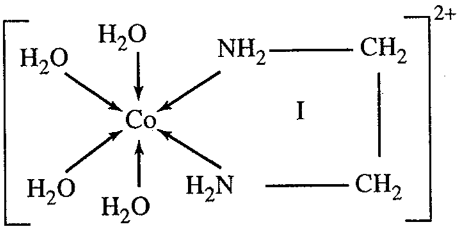
In $[Co(dien)(H_2O)_3]^{2+}$, there are two chelate rings and there is an increase of particles from 2 to 4 during its formation

$$[Co(H_2O)_6]^{2+} + dien \longrightarrow [Co(dien)(H_2O)_3]^{2+} + 3H_2O$$
$$1+1=2 \text{ particles} \longrightarrow 1+3=4 \text{ particles}$$

In $[Co(trien)(H_2O)_2]^{2+}$, there are three chelate rings and there is an increase of particles from 2 to 5.

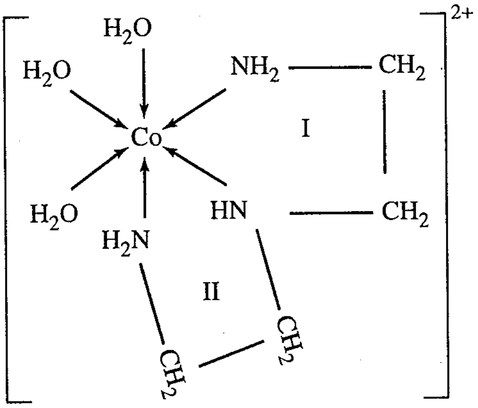
$$[Co(H_2O)_6]^{2+} + trien \longrightarrow [Co(trien)(H_2O)_2]^{2+} + 4H_2O$$
$$1+1=2 \text{ particles} \longrightarrow 1+4=5 \text{ particles}$$

The structures of these three complexes are denoted in Fig. 6.3.They contain 1,2 and 3 rings respectively.



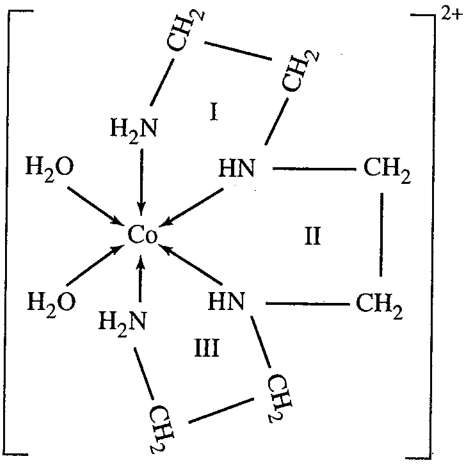
$[Co(en)(H_2O)_4]^{2+}$

(a)



$[Co(dien)(H_2O)_3]^{2+}$

(b)



$[Co(trien)(H_2O)_2]^{2+}$

(c)

Fig. 6.3 Chelate structures with different numbers of rings

Table 6.8 shows the influence of the number of chelate rings on the stability of complexes formed by Co^{2+} and Ni^{2+} with *en*, *dien* and *trien* as chelating agents.

Table 6.8 Effect of the number of chelate rings on the complex stability

Ligand	Change in the number of particles	Number of rings	$\log K_1(Co^{2+})$	$\log K_1(Ni^{2+})$
en	2 to 3	1	6.0	7.9
dien	2 to 4	2	8.1	10.7
trien	2 to 5	3	10.8	14.0

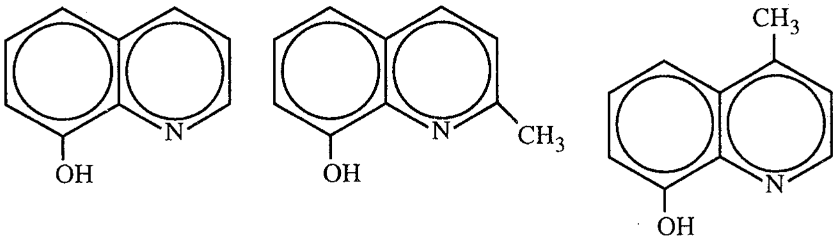
6.6.9 Steric Effect

One more factor of significance in chelation is the *steric factor*. This is associated with the presence of a bulky group,either attached to the donor atom or near enough to it to cause mutual repulsion between the ligands which results in the weakening of the metal to ligand bonds. This effect is illustrated in complexes formed by Ni^{2+} with ethylenediamine (*en*) and with N, N'- dimethylethylenediamine (N, N'-dime-*en*). The first step formation constant is higher (7.7) for the complex with N, N'-dime-*en* because of its higher basicity than that with *en*. But its second step stability constant is less (4.7) than that of the complex with *en*(6.5). A similar trend is shown by the third step stability constant values. These decreased values for the complexes with substituted ethylenediamine are attributed to the *steric repulsions* developed by the methyl substituents. Table 6.9 presents the observations made on Ni^{2+}-*en* complex and Ni^{2+}-N,N'-dime-*en* complex.

Table 6.9 Steric effect on stability constants of complexes

	Ni^{2+}-*en* complex	**Ni^{2+}-N,N'-dime-*en* complex**
$\log K_1$	7.6	7.7
$\log K_2$	6.5	4.7
$\log K_3$	5.0	1.5

The metal complexes of 2-methyl-8-hydroxyquinoline are less stable than those of either 8-hydroxyquinoline itself or its 4-methylderivative (Fig. 6.4).



(a) 8-hydroxyquinoline (oxine)

(b) 2-methyl derivative

(c) 4-methyl derivative

***Fig. 6.4** Oxines*

The $\log \beta_2$ values for some metal complexes with these three ligands are given in Table 6.10.

Table 6.10 Steric effect on stability contants of Ni(II) and Co(II)–oxine complexes

Substituent	**$\log \beta_2$ of Ni^{2+} complex**	**$\log \beta_2$ of Co^{2+} complex**
None	21.4	19.7
2-methyl	17.8	18.5
4-methyl	22.3	20.0

Among the three ligands considered in Table 6.10, the 2-methyl derivative is the most basic one and hence it is expected to form the most stable complex (greater basicity means greater complex stability). But actually, it forms the least stable complex. The least stability of this complex is attributed to the greater difficulty of chelation caused by the steric hindrance of the methyl group at position 2. Here, the bulky methyl group is near enough to the donor atom to cause mutual repulsion between the ligands. The 4-methyl derivative is more basic than oxine itself. Since the bulky methyl group in this ligand is too far away from the donor nitrogen to sterically affect the process of complex formation, it forms the most stable complex.

6.6.10 Stereochemical Requirements of Ligands

The stereochemical requirements of the ligands affect the stabilities of complexes. For example, *tren*, $N(CH_2-CH_2-NH_2)_3$ is unable to coordinate to four planar positions but it may do so to four tetrahedral positions.

But *trien*, $H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-NH_2$, is more suited to a planar arrangement than *for* a tetrahedral one. The common stereochemistry of Cu^{2+} is square-planar and hence it prefers *trien* over *tren*. On the other hand, Zn^{2+} prefers *tren* to *trien*, because its preferred stereochemistry is a tetrahedral one.

6.7 DETECTION OF COMPLEX FORMATION

Many methods are used to confirm the formation of complex compounds in a reaction. Some of the important methods are discussed below briefly.

6.7.1 Formation of Precipitate

When a neutral covalent complex is formed in a polar medium, it gets precipitated. Formation of the precipitate on the addition of a ligand indicates the formation of a neutral covalent complex. For example,

$$Ni^{2+} + 2\,HDMG \rightarrow [Ni(DMG)_2]\downarrow + 2H^+ \quad (pH > 8)$$

$$Al^{3+} + 3\,CH_3-CO-CH_2-CO-CH_3 + 3\,OH^- \rightarrow [Al(CH_3-CO-CHCOCH_3)_3]\downarrow + 3H_2O$$

6.7.2 Change in Chemical Behaviour

The altered reactivity of the metal ions in the presence of the ligands is still an useful indication of complex formation. For example, Fe^{3+} is not precipitated as $Fe(OH)_3$ by NH_4OH in the presence of tartaric acid. This indicates the formation of Fe^{3+}-tartrate complex. Similarly, H_2S fails to precipitate Cu^{2+} ions as CuS in the presence of CN^- ions due to the formation of $[Cu(CN)_4]^{3-}$ complex. Ag^+ does not give the precipitate of AgCl in the presence of NH_4OH indicating the formation of $[Ag(NH_3)_2]^+$ complex.

6.7.3 Dissolution of an Insoluble Compound in the Presence of Complexing Agents

Many water-insoluble substances dissolve readily in the presence of a reagent that forms soluble complex. For example, dissolution of AgCl in aqueous ammonia indicates the formation of a soluble complex, $[Ag(NH_3)_2]Cl$

$$\underset{\text{(insoluble)}}{AgCl} + 2\,NH_3 \rightarrow \underset{\text{(soluble)}}{[Ag(NH_3)_2]Cl}$$

Similarly, dissolution of scarlet red, HgI_2 in excess iodide solution indicates the formation of a soluble complex, $[HgI_4]^{2-}$

$$\underset{\text{(insoluble)}}{HgI_2} + 2\,I^- \rightarrow \underset{\text{(soluble)}}{[HgI_4]^{2-}}$$

6.7.4 Colour Change in Solution (Spectral Method)

A change in colour of the solution on the addition of another reagent indicates the formation of a new species. In many cases, the colour of the uncomplexed metal ion gets altered or intensified and in some cases, a totally new colour is produced. For example,

$$\underset{\text{pink}}{Co^{2+}} + 4\,Cl^- \rightleftharpoons \underset{\text{blue}}{[CoCl_4]^{2-}}$$

$$\underset{\text{light blue}}{Cu^{2+}} + 4\,Cl^- \rightleftharpoons \underset{\text{green}}{[CuCl_4]^{2-}}$$

$$\underset{\text{light blue}}{Cu^{2+}} + 4\,NH_3 \rightleftharpoons \underset{\text{deep blue}}{[Cu(NH_3)_4]^{2+}}$$

$$\underset{\text{green}}{Fe^{2+}} + 6\,CN^- \rightleftharpoons \underset{\text{yellow}}{[Fe(CN)_6]^{4-}}$$

6.7.5 pH Method

The addition of the ligand (HL) to a metal (M) in solution results in the release of protons as the complexes are formed. For example, Cu^{2+} ions are treated with salicylaldoxime (Hsal) to form the complex, $[Cu(sal)_2]$ with the release of protons.

$$Cu^{2+} + 2\,Hsal \rightarrow [Cu(sal)_2] + 2\,H^+$$

Due to the release of H^+, the pH of the solution gets lowered. Similarly, if an aqueous solution of NH_3 is added to a solution of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} or Cd^{2+} ions, ammine complexes of the type $[M(NH_3)_x]^{2+}$ are formed. Due to the consumption of ammonia, concentration of free ammonia reduces. This means that the pH of the solution gets lowered. Thus change in pH of the solution can be taken as an indication for the formation of complexes.

6.7.6 Conductivity Measurements

If the complex formation reaction involves changes in the number of ions, then there would be changes in the conductivity of the solution. For example, in the complexation reaction

$$M^{n+} + x\ Cl^- \rightarrow [MCl_x]^{n-x}$$

there is a decrease in the number of ions in solution. Hence conductivity of the solution decreases due to the formation of the complex. Similarly, if the complex formation involves the liberation or absorption of protons or hydroxyl ions, then the conductance of the solution changes abnormally. This is because of the abnormal conductivity of the protons and hydroxyl ions in aqueous solutions. This change in conductance can be used to detect the complex formation.

6.7.7 Magnetic Method

On complexation, frequently, the magnetic susceptibility of the metal ion is altered. As complexation changes the *d* electron configurations, susceptibility changes;

therefore, magnetic susceptibility can be a diagnostic of complexation. The following magnetic data illustrate this:

Species	Fe^{3+}	$[Fe(CN)_6]^{3-}$	Co^{3+}	$[Co(NH_3)_6]^{3+}$
Magnetic moment (BM)	5.9	1.7	4.9	0.0

Many other physical properties of the system, depending upon the nature of the species present in the solution, can be used to detect complex formations. Some of these useful methods are chromatography, polarography, NMR, X-ray analysis, ESR, mass spectrometry and ion-exchange.

6.8 DETERMINATION OF STABILITY CONSTANTS

Stability constants of complexes have been measured by different methods. The experimental determination of β is an important one but often a difficult task. Some of the difficulties encountered in the determination of stability constants of complexes are given below.

(i) Equilibrium constants depend on activities rather than on concentrations. Since activities and concentrations are numerically equal in very dilute solutions, concentrations of all species have to be kept low.

(ii) During measurement of equilibrium concentrations, the equilibrium may get disturbed.

(iii) A major problem in the determination of stability constants is the difficulty in identification of species which are actually present in the solution.

The selection of the best method to determine the stability constant of a complex is generally made on the basis of the experimenter's experience. Results of more than one method are generally compared to get maximum reliability of the data.

6.8.1 Solubility Method

If the metal ion forms a relatively insoluble salt whose solubility product is known, the stability constant of the more soluble complex may be determined by measuring the increased solubility of the salt due to the presence of the ligand. The reaction between AgOAc and OAc^- ion may now be considered. When a solution of AcONa of known high concentration is equilibrated at constant temperature with an excess of AcOAg, the equilibria given below (1) are obtained.

$$\begin{aligned} AgOAc &= Ag^+ + OAc^- \\ K_{sp} &= [Ag^+][OAc^-] \\ Ag^+ + 2OAc^- &= [Ag(OAc)_2^-] \\ \beta_2 &= \frac{[Ag(OAc)_2^-]}{[Ag^+][(OAc^-)]^2} \end{aligned} \tag{1}$$

After equilibration, the excess solid AcOAg is removed by filtration and the solution analysed for total silver content. Now the following relationship holds:

$$C_{Ag^+} = [Ag^+] + [Ag(OAc)_2^-] \tag{2}$$

where C_{Ag^+} is the Ag^+ concentration in solution. From the solubility product expression,

$$[Ag^+] = \frac{K_{sp}}{[OAc^-]}$$

and this becomes

$$[Ag^+] = \frac{K_{sp}}{C_{AcONa}} \tag{3}$$

considering the excess AcONa. Substitution of equations (2) and (3) in the stability constant equation (1) gives

$$\beta_2 = \frac{C_{Ag^+} - \left(\dfrac{K_{sp}}{C_{AcONa}}\right)}{\left(\dfrac{K_{sp}}{C_{AcONa}}\right)[C_{AcONa}]^2} \tag{4}$$

Since all the quantities on the right hand side of expression (4) are known, the overall stability constant, β_2 can be calculated. It is essential to vary the concentration of AcONa to check whether β_2 is really a constant. Further refinement of this method would take into account the hydrolysis of acetate ion which is almost negligible in basic medium.

6.8.2 Ion-exchange Method

An ion-exchange resin is an insoluble solid, organic polymer containing positive ions (cation exchange resin) or negative ions (anion exchange resin). These ions can be exchanged for some other ions of similar charge. If a cationic resin is in contact with a solution of Na^+ and Ca^{2+} ions, an equilibrium constant for such a system may be denoted as,

$$K_r = \frac{[Na^+]^2_{soln}\,[Ca^{2+}]_{resin}}{[Na^+]^2_{resin}\,[Ca^{2+}]_{soln}}$$

If the concentration of Na^+ is high in comparison to Ca^{2+} concentration, then the Na^+ concentrations in the two phases remain nearly constant and the following expression results:

$$K'_r = \frac{[Ca^{2+}]_{resin}}{[Ca^{2+}]_{soln}}$$

When a ligand such as citrate ion is added, calcium citrate is formed

$$Ca^{2+} + \text{citrate}^{3-} = [\text{Ca citrate}^-]$$

Then, the formation constant, K for the citrate is given by the expression

$$K = \frac{[\text{calcium citrate}^-]}{[Ca^{2+}]\,[\text{citrate}^{3-}]}$$

When citrate ion is added, the concentration of free Ca^{2+} decreases because of the formation of calcium citrate. Thus, the amount of Ca^{2+} in the resin decreases. The distribution quotient, D, is given by

$$D = \frac{[\mathrm{Ca}^{2+}]_{\mathrm{resin}}}{[\mathrm{Ca}^{2+}]_{\mathrm{soln}} + [\text{calcium citrate}^{-}]_{\mathrm{soln}}}$$

From these an useful equation is obtained as described below:

$$\frac{1}{D} = \frac{K[\text{citrate}^{3-}]}{Kr'} + \frac{1}{Kr'}$$

$$\frac{1}{D} = \frac{[\mathrm{Ca}^{2+}]_{\mathrm{soln}} + [\text{calcium citrate}^{-}]_{\mathrm{soln}}}{[\mathrm{Ca}^{2+}]_{\mathrm{resin}}}$$

$$= \frac{[\mathrm{Ca}^{2+}]_{\mathrm{soln}} + [\text{Ca citrate}^{-}]_{\mathrm{soln}}}{K'_r \cdot [\mathrm{Ca}^{2+}]_{\mathrm{soln}}}$$

$$= \frac{[\text{calcium citrate}^{-}]_{\mathrm{soln}}}{K'_r \cdot [\mathrm{Ca}^{2+}]_{\mathrm{soln}}} + \frac{[\mathrm{Ca}^{2+}]_{\mathrm{soln}}}{K'_r \cdot [\mathrm{Ca}^{2+}]_{\mathrm{soln}}}$$

$$= \frac{[\text{Ca citrate}^{-}]_{\mathrm{soln}}}{K'_r \cdot [\mathrm{Ca}^{2+}]_{\mathrm{soln}}} + \frac{1}{K'_r}$$

$$= \frac{K[\mathrm{Ca}^{2+}][\text{Citrate}^{3-}]}{K'_r \cdot [\mathrm{Ca}^{2+}]} + \frac{1}{K'_r}$$

$$\therefore \frac{1}{D} = \frac{K[\text{citrate}^{3-}]}{K'_r} + \frac{1}{K'_r}$$

Since D can be measured at various citrate ion concentrations and since this is an equation of the form, $y = mx + b$, a graph of $1/D$ against concentration of $[\text{citrate}^{3-}]$ produces a straight line with a slope of (K / K'_r) and an intercept of $(1 / K'_r)$. From the slope and intercept, K can be calculated:

$$K = \frac{\text{slope}}{\text{intercept}} = \frac{K}{K'_r} \times \frac{K'_r}{1} = K$$

This method of determining the stability constant is fast and easy. If the metal ion is radioactive, then the concentration of the metal ion in the resin phase and solution phase can be more conveniently determined by measuring its radioactivity. If a suitable radioactive metal ion is available, then this method is preferred over the other methods.

6.8.3 Electrochemical Method

J.Bjerrum determined the stability constants of a number of ammine complexes of metals by the electro-chemical method. This method makes use of the glass electrode. This electrode is the fundamental component of the common laboratory pH meter used to determine the activity of H^+ in solution. The equilibria studied with this device must involve changes in pH.

The ammonia concentration in a solution is related to the $[H^+]$ by the equilibrium constant for the acid dissociation of NH_4^+. In acidic solutions, the $[NH_4^+]$ is large with respect to $[NH_3]$.

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

$$K = \frac{[NH_3][H^+]}{[NH_4^+]}$$

$$\therefore\ [NH_3] = \frac{K[NH_4^+]}{[H^+]} \qquad (1)$$

The $[NH_4^+]$ is virtually unchanged as the $[H^+]$ is increased. In these acid solutions,

$$[NH_3] = \frac{K[NH_4^+]}{[H^+]} = K' \frac{1}{[H^+]}$$

Hence, under these conditions, the glass electrode that measures $[H^+]$ can also measure $[NH_3]$ directly.

The stability constants for $Ag^+ - NH_3$ systems were determined by this technique

$$Ag^+ + NH_3 \overset{K_1}{\rightleftharpoons} [Ag(NH_3)^+]$$

$$[Ag(NH_3)^+] + NH_3 \overset{K_2}{\rightleftharpoons} [Ag(NH_3)_2^+]$$

$$\therefore\ K_1 = \frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]} \text{ and}$$

$$K_2 = \frac{[Ag(NH_3)_2^+]}{[Ag(NH_3)^+][NH_3]}$$

The concentrations of complexed ammonia, uncomplexed ammonia and uncomplexed Ag^+ are obtained by the following method. On substituting these values in the above expressions, K_1 and K_2 can be evaluated.

All solutions, prepared at 30°C contained small but various concentrations of Ag^+ and NH_3 ($[Ag^+]_0$ and $[NH_3]_0$). The pH of each of these solutions is measured. The concentration of uncomplexed ammonia, $[NH_3]$ is calculated using equation(1). Some of the data obtained thus are presented in Table 6.11.

Table 6.11 Evaluation of stoichiometry of $Ag^+ - NH_3$ complexes

$[Ag]_0$	$[NH_3]_0$	pH	$[H^+]$	$[NH_3]$	$\bar{n}$
0.02	0.00502	4.970	10.7×10^{-6}	0.88×10^{-4}	0.246
0.02	0.01504	5.372	4.25×10^{-6}	2.21×10^{-4}	0.740
0.02	0.03012	5.793	1.61×10^{-6}	5.83×10^{-4}	1.477
0.02	0.05022	6.342	0.455×10^{-6}	20.60×10^{-4}	1.895

These data are recorded at 30°C in the presence of 2M NH_4NO_3. The average number ($\bar{n}$) of ammonia molecules bound per Ag^+ is determined from these experimental data using the equation given below:

$$\bar{n} = \frac{[NH_3]_0 - [NH_3]}{[Ag^+]}$$

A plot of $\bar{n}$ vs (NH_3] is shown in Fig. 6.5.

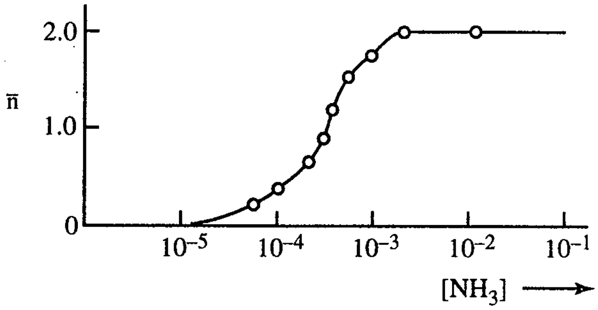


***Fig. 6.5** The average number of* NH_3 *molecules bound per* Ag^+ *in solutions containing various concentrations of free ammonia. These data apply to solutions at 30°C containing 2M* NH_4NO_3

This plot indicates that at concentrations of free ammonia greater than 10^{-2} M, $[Ag(NH_3)_2]^+$ is the predominant species, whereas at free ammonia concentrations below 10^{-4} M, Ag^+ is the predominant species in solution. The complex $[Ag(NH_3)]^+$ is present only within a small [NH_3] range. From these data, K_1 is calculated. Similarly, K_2 can also be evaluated. However, the calculations are rather tedious.

6.8.4 Polarographic Method

The half-wave potential ($E_{1/2}$) for the polarographic reduction of a metal ion is altered when the metal is complexed. Generally, the $E_{1/2}$ for the reduction of a metal complex is more negative than that for the reduction of the corresponding simple metal ion. This implies that the metal in the complexed state is less easily reduced than the free metal. Therefore, polarographic $E_{1/2}$ values can be used to determine the formation constants of complexes. This can be illustrated with a Pb(II) complex. For the reduction of simple Pb^{2+}, the equation is

$$Pb^{2+} + 2e^- \rightleftharpoons Pb$$

The Nernst equation for this reduction is

$$E = E^o_{Pb} - \frac{0.059}{n}\log\frac{[Pb]}{[Pb^{2+}]} \qquad (1)$$

Let the complex formation with ligand L be denoted as

$$Pb^{2+} + x\,L \rightleftharpoons PbL_x$$

(For simplicity, the charge on L is ignored).

Then, the formation constant is given by

$$K = \beta_x = \frac{[PbL_x]}{[Pb^{2+}][L]^x} \quad \text{or}$$

$$[Pb^{2+}] = \frac{[PbLx]}{K\,[L]^x} \qquad (2)$$

The activity of $[Pb^{2+}]$ decreases as the ligand concentration increases.

The effect of complexation on $(E_{1/2})_c$, the half-wave potential for the complex can be understood by combining equations (1) and (2) {substituting the value of $[Pb^{2+}]$ from (2) in (1)}:

$$E = E^{o}_{Pb} - \frac{0.059}{n}\log\frac{[Pb]}{[PbL_x]} - \frac{0.059}{n}\log K - \frac{0.059\,x}{n}\log[L]$$

Assuming that the complex is reversibly reduced, the values for [Pb] and $[PbL_x]$ can be obtained:

$$E = \left(E^{o}_{Pb} - \frac{0.059}{n}\log\frac{k}{k'}\right) - \left(\frac{0.059}{n}\log\frac{I}{I_d - I}\right) - \left(\frac{0.059}{n}\log K\right) - \left(\frac{0.059\,x}{n}\log[L]\right)$$

$$E_{1/2} = E^{o}_{Pb} - \frac{0.059}{2}\log\frac{k}{k'}$$

For simplicity, let *k* be assumed to remain the same for the complex as for the simple ion.

Then,

$$E = E_{1/2} - \frac{0.059}{n}\log\frac{I}{I_d - I} - \frac{0.059}{n}\log K - \frac{0.059\,x}{n}\log[L]$$

$E_{1/2}$ is the half-wave potential for the simple metal ion couple.

When $I = I_d/2$ for the complex, $E = (E_{1/2})_c$

$$\therefore\quad (E_{1/2})_c = E_{1/2} - \frac{0.059}{n}\log K - \frac{0.059\,x}{n}\log[L]$$

The half-wave potential shift due to complexation is $\Delta E_{1/2}$.

$$\Delta E_{1/2} = (E_{1/2})_c - E_{1/2}$$

$$\therefore\quad \Delta E_{1/2} = -\frac{0.059}{n}\log K - \frac{0.059\,x}{n}\log[L]$$

The equation indicates that a plot of $\Delta E_{1/2}$ versus log [L] will produce a straight line.

$$\text{slope} = -\frac{0.059\,x}{n}$$

Therefore, x, the number of ligands bonded to the metal can be known.

$$\text{intercept} = -\frac{0.059}{n}\log K$$

Therefore, the stability constant *K* of the complex can be calculated.

6.8.5 Spectrophotometric Method

This method of determining the stability constant of a complex can be considered with the example,

$$Fe^{3+}(aq) + NCS^{-} \rightleftharpoons [Fe(NCS)]^{2+}$$

The stability constant for this complex is given by

$$K = \frac{\left[[\mathrm{Fe(NCS)}]^{2+}\right]}{[\mathrm{Fe}^{3+}][\mathrm{NCS}^-]}$$

where the concentration terms represent the actual equilibrium concentrations.

Ferric ion and thiocyanate ion individually are almost colourless in aqueous solution; however, the complex $[[\mathrm{Fe(NCS)}]^{2+}]$ is bright-red. Its $\lambda_{\max}$ is 450 nm (Fig. 6.6).

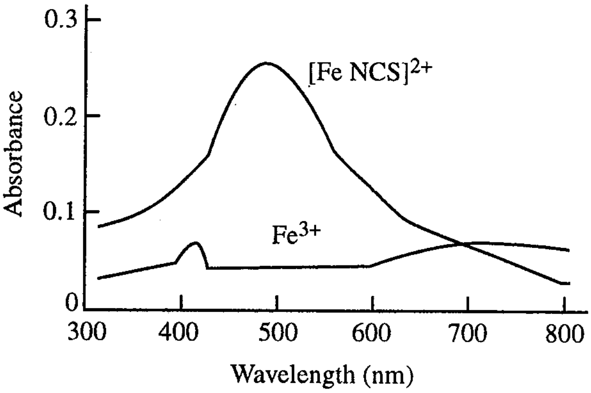


Fig. 6.6 *The absorption spectra of* Fe^{3+} *(aq) and* $[\mathrm{Fe\,NCS}]^{2+}$

Therefore, the concentration of this coloured complex can be estimated by measuring its absorbance in the visible region using a spectrophotometer. The absorbance A is directly proportional to the concentration of absorbing species as per the Beer Law:

$$A = \epsilon cl$$

ϵ = molar extinction coefficient
c = concentration of absorbing species
l = path length of the absorbing solution

The value of ϵ for $[[\mathrm{Fe(NCS)}]^{2+}]$ can be determined first by measuring the absorbance of a solution of the complex of known concentration (such a solution can be prepared by mixing a known amount of Fe^{3+} with a large excess of NCS^-, so that all the Fe^{3+} is converted to the complex).

For determining K, a solution of Fe^{3+} of known concentration $[\mathrm{Fe}^{3+}]_0$ is mixed with a solution of NCS^- of known concentration $[\mathrm{NCS}^-]_0$. The mixture in which the complex $[[\mathrm{Fe(NCS)}]^{2+}]$ has been formed is equilibrated. Its absorbance (A) at 450 nm is measured. Then K is evaluated as indicated below:

$$A = \epsilon l\ [[\mathrm{Fe(NCS)}]^{2+}]$$

Therefore, equilibrium concentration of complex,

$$[[\mathrm{Fe(NCS)}]^{2+}] = A/\epsilon l$$

$$[\mathrm{Fe}^{3+}]_0 = \underset{\text{uncomplexed } \mathrm{Fe}^{3+}}{[\mathrm{Fe}^{3+}]} + \underset{\text{complexed } \mathrm{Fe}^{3+}}{[[\mathrm{Fe(NCS)}]^{2+}]}$$

∴ equilibrium concentration of Fe^{3+},

$$[Fe^{3+}] = [Fe^{3+}]_0 - [[Fe(NCS)]^{2+}]$$

$$\underset{\text{}}{[NCS^-]_0} = \underset{\text{uncomplexed } NCS^-}{[NCS^-]} + \underset{\text{complexed } NCS^-}{[[Fe(NCS)]^{2+}]}$$

∴ equilibrium concentration of NCS^-,

$$[NCS^-] = [NCS^-]_0 - [[Fe(NCS)]^{2+}]$$

$$\text{Therefore, } K = \frac{[[Fe(NCS)]^{2+}]}{[Fe^{3+}][NCS^-]}$$

The experiment is then repeated with three or more different initial Fe^{3+} and NCS^- concentrations to check the constancy of K.

This method does not disturb the equilibrium during absorbance measurement and hence it is a reliable method of evaluating K value.

6.8.6 The Method of Continuous Variation (Job's Method)

This method is used for solutions where only one complex is formed.

Determination of formula If the sum of the total concentrations C of complexing agent C_x and metal ion C_M is held constant and only their ratio is varied, then

$$C_M + C_x = C$$

A wavelength of light is selected such that where the complex absorbs strongly and the ligand and metal ions do not.

A plot of the mole fraction of the ligand in the mixture X versus absorbance gives a triangular-shaped curve (Fig. 6.7).

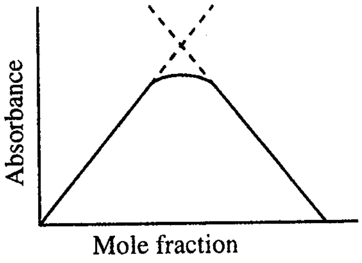


Fig. 6.7 Plot of absorbance versus mole fraction of ligand for complex formation

The mole fraction of the ligand in the mixture $X = C_x / C$

The mole fraction of the metal ion in the mixture $= C_M / C$

$$C_x / C + C_M / C = C / C$$

$$\therefore \quad 1 - X = C_M / C$$

The legs of the triangle are extrapolated until they cross. The mole fraction at the point of this intersection gives the formula of the complex, since at this point, for the complex MX_n,

$$n = C_x / C_M = X / 1 - X$$

At this point, the ligand and metal are in proper relative concentrations to give maximum complex formation. Performing the experiment at several different wavelengths and at several different values of C would indicate whether there is more than one complex formed in solution; in such cases n would not be constant.

The curve may be observed to deviate somewhat from the experimental intersecting lines. From the amount of this deviation, the stability constant of the complex can be determined.

Determination of stability constant For a 1 : 1 complex, the ratio of the true absorbance (A) to the extrapolated absorbance (A_{ext}) is the mole fraction of the complex actually formed.

$$\frac{A}{A_{ext}} = \frac{[\mathrm{MX}]}{C}$$

where C = total concentration of the metal or ligand, whichever is the limiting concentration at the point considered.

Then,

$$\begin{aligned}[\mathrm{MX}] &= (A / A_{ext})\, C \\ [\mathrm{M}] &= C_M - [\mathrm{MX}] \\ &= C_M - (A / A_{ext})\, C \\ [X] &= C_{\mathrm{x}} - [\mathrm{MX}] \\ &= C_{\mathrm{x}} - (A / A_{ext})\, C\end{aligned}$$

Therefore, $K = \dfrac{[\mathrm{MX}]}{[\mathrm{M}][\mathrm{X}]} = \dfrac{(A / A_{ext})\, C}{[C_M - (A / A_{ext})\, C][C_x - (A / A_{ext})\, C]}$

where K is the stability constant and C_M and C_x are the total concentrations of metal and ligand respectively.

EXERCISES

***I Choose the best answer for each of the following:**

1. Inertness of a complex depends on
   - a) reaction energy
   - b) activation energy
   - c) both (a) and (b)
   - d) none of the above
2. Thermodynamic stability of a complex depends on
   - a) reaction energy
   - b) activation energy
   - c) both (a) and (b)
   - d) none of the above
3. Generally, step-wise stability constants gradually decrease. This general trend is due to
   - a) statistical factor
   - b) steric factor

c) electrostatic factor
d) all the above

4. With a particular ligand, under identical conditions, which one of the following ions is expected to form the most stable complex?
   a) La^{3+}
   b) Gd^{3+}
   c) Lu^{3+}
   d) Dy^{3+}
5. With a particular ligand, which one of the following ions will form the least stable complex (keeping other factors constant)?
   a) K^+
   b) Na^+
   c) Rb^+
   d) Cs^+
6. Successive stability constants of 'en' complexes with a metal ion are: $\log K_1 = 2.5$, $\log K_2 = 1.7$ and $\log K_3 = 0.8$. Therefore, the over-all stability constant is
   a) 5
   b) 104.2
   c) 10^5
   d) none of the above

*II Match the following:

	complex		log (stability constant)
1.	Ni^{2+} - en	a)	4.8
2.	Ni^{2+} - trien	b)	7.9
3.	Ni^{2+} - dien	c)	14.0
4.	Ni^{2+} - penten	d)	10.7
5.	Ni^{2+} - ammonia	e)	19.3

III Account for the following

*1. $[Fe(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{3+}$ are equally stable thermodynamically but the former is labile whereas the latter is inert.

*2. As a general trend, the step-wise stability constants gradually decrease.

*3. For Cd^{2+}/Br^- system in aqueous medium, $\log K_1 = 1.56$, $\log K_2 = 0.54$, $\log K_3 = 0.06$ and $\log K_4 = 0.37$. General trend is observed upto third stage formation constant, but $\log K_4$ is greater than $\log K_3$. Why?

*4. Even though Cu^+ and K^+ have similar size and same charge, Cu^+ forms more stable complex than K^+ with a particular ligand.

*5. Because of its smaller size, Mg^{2+} is expected to form more stable complex than Ca^{2+}. But the EDTA complex of Mg^{2+} is less stable than that of Ca^{2+}

6. Generally chelate complex is more stable than non-chelated complex. But $[Ag(NH_3)_2]^+$ is more stable than $[Ag(en)]^+$

*7. $\log K_1$ for Ni^{2+} - en complex is less than that of Ni^{2+} - N, N'-dimethylethylenediamine complex but $\log K_2$ for the first complex is greater than that of the second complex.

*8. $[Co(en)_3]^{3+}$ is more stable than $[Co(NH_3)_6]^{3+}$.

*9. In alkaline solution, EDTA prevents the precipitation of Ba^{2+} as $BaSO_4$ on the addition of SO_4^{2-} ions.

10. Stability of complexes between Ag^+ and aliphatic amines increases in the order,

$$CH_3-NH_2 < CH_3-CH_2-\dot{N}H_2 < CH_3-CH_2-CH_2-NH_2$$

IV Answer the following:

1. Define, "step-wise stability constants" and "over-all stability constants". How are they related?

*2. For Cu^{2+}/NH_3 system, the log of the step-wise stability constants are $\log K_1 = 4.15$, $\log K_2 = 3.50$, $\log K_3 = 2.89$ and $\log K_4 = 2.13$. Calculate the over-all stability constant of $[Cu(NH_3)_4]^{2+}$ species.

*3. For Cd^{2+}/NH_3 system log K values are as follows:
$\log K_1 = 2.65$; $\log K_2 = 2.10$, $\log K_3 = 1.44$; $\log K_4 = 0.93$
For Cd^{2+}/CN^- system log K values are as follows:
$\log K_1 = 5.48$; $\log K_2 = 5.12$, $\log K_3 = 4.63$; $\log K_4 = 3.65$
Calculate the over-all stability constants for $[Cd(NH_3)_4]^{2+}$ and $[Cd(CN)_4]^{2-}$ ions. Which is more stable?

4. Ni^{2+} forms 1 : 2 complexes with each of the following ligands, oxine, 2-methyloxine and 4- methyloxine. Of these three complexes, which is expected to be the most stable. Explain your choice.

5. Sketch the structures of:
a) $[M(C_2O_4)_3]^{n-6}$ b) $[M(en)_3]^{n+}$ c) $[M(dien)_2]^{n+}$ d) $[M(trien)(H_2O)_2]^{n+}$

6. Rationalize the fact that stability increases in the order
$[Co(NH_3)_6]^{3+} < [Co(en)_3]^{3+} < [Co(dien)_2]^{3+}$

7. Why do the 8-electron shell ions give less stable complexes than 18-electron shell ions?

8. How do the π-bonding ligands help in the stabilization of metal complexes?

9. Why is the formation of $[Cu(en)_3]^{2+}$ not observed in solutions?

10. Differentiate between thermodynamic stability and kinetic stability of metal complexes.

11. How is ionic potential of a metal ion related to the stability of the complex of that metal ion?

12. Explain how the fluoride ion helps to stabilize higher oxidation states in metal complexes.

13. How do the stabilities of chelates differ with:
a) size of the chelate rings
b) number of chelate rings.

14. How are the complex formations detected?

15. Discuss the different methods of determining stability constants of complexes.

*16. How is the over-all stability constant of a complex related to its step-wise stability constants?

17. Differentiate between step-wise and over-all stability constants of a complex formation reactions.

*18. Describe the behaviour of a complex which is both thermodynamically stable and kinetically labile.

*19. The log β values of the two complex ions, $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ are 18.3 and 8.6. Identify the complex with the over-all stability constant. Write an explanatory sentence.

20. Differentiate between (a) stable and unstable and (b) labile and inert complexes.

*21. Explain why $p\beta_2$ for $[Ag(NH_3)_2]^+$ is 7.2 whereas $p\beta$ for $[Ag(en)]^+$ is only 6.0.

22. The formation constant for $[Fe(CN)_6]^{4-}$ is 1×10^{37} and that for $[Fe(CN)_6]^{3-}$ is 1×10^{44}. Is it consistent with the difference in CFSE between the two complexes? CN^- is a strong-field ligand in both complexes. What other feature can explain the difference in formation constant?

*23. Justify the following $p\beta$ values:

complex	$p\beta$
$[Cu(NH_2CH_2CH_2NH_2)_2]^{2+}$	10.7
$[Cu(MeNHCH_2CH_2NHMe)_2]^{2+}$	9.7
$[Cu(Me_2NCH_2CH_2NMe_2)_2]^{2+}$	7.2

*24. Explain the following:

a) CH_3NH_2 forms the more stable complex with $Cr^{2+}(aq)$ than does CH_3OH.

b) $[Ni(NBr_3)_2]^{2+}$ is a weaker complex than $[Ni(NH_3)_2]^{2+}$

25. Prove that for the formation of $[Cu(NH_3)_4]^{2+}$ from Cu^{2+} and NH_3, $\beta_4 = K_1 . K_2 . K_3 . K_4$

ANSWERS

I 1. (b) 2. (a) 3. (d) 4. (c) 5. (d) 6. (c)

II 1. (b) 2. (c) 3. (d) 4. (e) 5. (a)

III

1. Metal ions having one or more electrons in their e_g orbitals or less than 3 electrons in t_{2g} orbitals will form labile complexes whereas ions having no electron in their e_g orbitals or 3 electrons in their t_{2g} orbitals will form inert complexes. Hence, Fe^{3+} (d^5) in $[Fe(H_2O)_6]^{3+}$ has 2 electrons in its e_g orbitals; hence this complex is labile. But Cr^{3+} in $[Cr(H_2O)_6]^{3+}$ (d^3) has no electron in its e_g orbitals; hence this complex is inert.
2. decrease in step-wise stability constants is due to
   (i) electrostatic factor
   (ii) statistical factor
   (iii) steric factor

3. In aqueous medium, the reactions are represented as follows :

$$[Cd(H_2O)_6]^{2+} + Br^- \overset{K_1}{\rightleftharpoons} [Cd(H_2O)_5Br]^+ + H_2O$$

$$[Cd(H_2O)_5Br]^+ + Br^- \overset{K_2}{\rightleftharpoons} [Cd(H_2O)_4Br_2] + H_2O$$

$$[Cd(H_2O)_4Br_2] + Br^- \overset{K_3}{\rightleftharpoons} [Cd(H_2O)_3Br_3]^- + H_2O$$

Till the third stage product formation, the complex adopts octahedral geometry and the general trend namely gradual decrease in stepwise stability constants is observed. But the fourth stage complex formation involves a major structural change of the complex. Since Br^- is a bulky ligand when compared with H_2O ligand, 4th stage complex becomes a tetrahedral one as represented as below:

$$[Cd(H_2O)_3Br_3]^- + Br^- \overset{K_4}{\rightleftharpoons} [CdBr_4]^{2-} + 3H_2O$$

$$1 + 1 = 2 \text{ particles} \rightleftharpoons 1 + 3 = 4 \text{ particles}$$

Since this reaction is accompanied by an increase in the number of particles, this reaction is entropically favoured. Hence log K_4 is greater than log K_3, which is inconsistent with the general trend.

4. The electrons present in Cu^+ have lesser screening effect, hence the outer electrons are attracted more towards the nucleus; that is Cu^+ behaves as if it possesses greater nuclear charge; hence Cu^+ forms more stable complexes than K^+.
5. The space available at the centre of the EDTA ligand is too big to accommodate the small Mg^{2+} ion. But that space can just accommodate Ca^{2+} ; hence its complex with EDTA is more stable than Mg^{2+}-EDTA complex.
7. Ni^{2+}-en complex is less stable than the Ni^{2+}- N,N' dimethyl ethylenediamine because N, N'-dimethylethylenediamine is more basic than en. But [Ni^{2+}-$(en)_2$] is more stable than [Ni^{2+} - (N,N' dimethylethylenediamine)$_2$] because in the latter the two methyl groups sterically hinder the formation of the second stage product.
8. $[Co(en)_3]^{3+}$ is a chelate complex hence it is more stable than $[Co(NH_3)_6]^{3+}$ which is a nonchelated complex. The formation of $[Co(en)_3]^{3+}$ from aqueous solution is entropically favoured; hence it is more stable than $[Co(NH_3)_6]^{3+}$

$$[Co(H_2O)_6]^{3+} + 3\text{ en} \rightleftharpoons [Co(en)_3]^{3+} + 6\,H_2O$$

$$1 + 3 = 4 \text{ particles} \quad 1 + 6 = 7 \text{ particles}$$

Increase in the number of particles increases the positive entropy of the sytem; hence the resulting complex will be more stable.

9. In alkaline solutions, Ba^{2+} forms a very stable complex with EDTA of composition, $[Ba\text{-}EDTA]^{2-}$. The precipitant ion SO_4^{2-} is also an anion.

Hence there will not be any reaction between $[Ba-EDTA]^{2-}$ and SO_4^{2-} ; that is Ba^{2+} is not precipitated as $BaSO_4$ by the addition of SO_4^{2-} in the presence of EDTA.

IV

2. $$\log\beta_4 = \log K_1 + \log K_2 + \log K_3 + \log K_4$$
$$= 4.15 + 3.50 + 2.89 + 2.13 = 12.67$$

Therefore $\beta_4 = 4.677 \times 10^{12}$

3. For Cd^{2+}/NH_3 system, $\log\beta_4 = \log K_1 + \log K_2 + \log K_3 + \log K_4$
$$= 2.65 + 2.10 + 1.44 + 0.93 = 7.12$$

Therefore β_4 for $[Cd(NH_3)_4]^{2+} = 1.318 \times 10^7$

For Cd^{2+}/CN^- system, $\log\beta_4 = \log K_1 + \log K_2 + \log K_3 + \log K_4$
$$= 5.48 + 5.12 + 4.63 + 3.65 = 18.88$$

Therefore β_4 for $[Cd(CN)_4]^{2-} = 7.586 \times 10^{18}$

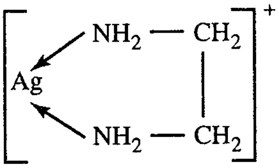
$[Cd(CN)_4]^{2-}$ having higher value for over-all stability constant is more stable than $[Cd(NH_3)_4]^{2+}$

16. $\beta_n = K_1 \times K_2 \times K_3 \times \ldots K_n$

18. Such a complex will persist in solution but will exchange its ligands with other ligands as is verified by isotopic labelling experiments.

19. $\log\beta$ of $[Ni(NH_3)_6]^{2+}$ is 8.6 and $\log\beta$ of $[Ni(en)_3]^{2+}$ is 18.3. The former is a non- chelate complex; hence it is less stable than the latter which is a chelate complex. Generally, formations of chelates are entropically favoured reactions. Therefore chelates are more stable than non-chelated complexes.

21. Ag^+ tends to form linear complexes; thus $[Ag(NH_2)_2]^+$ a linear complex is more stable than the chelate $[Ag(en)]^+$. In this chelate,



the five membered ring produces a ring strain reducing the stability.

23. The decreasing stability of the Cu(II) complexes is due to steric effect by the methyl groups.

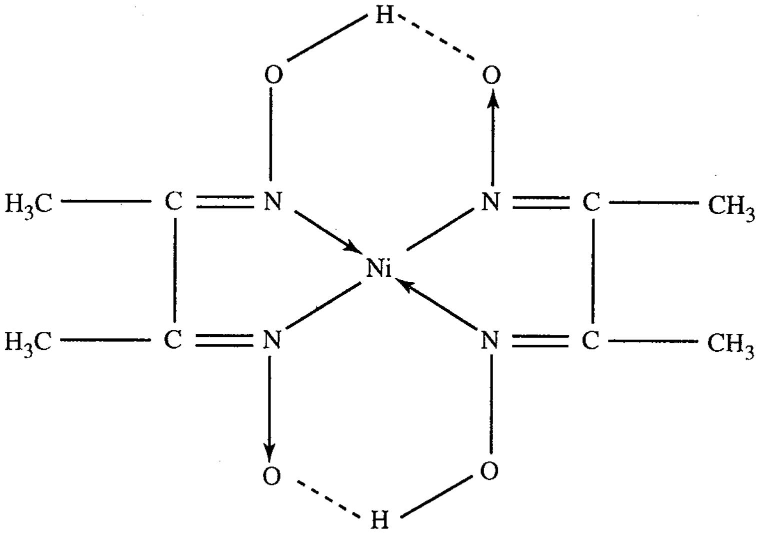
24. a) CH_3NH_2 is a stronger base than CH_3OH.

b) NBr_3 is a weaker lewis base than NH_3

Chapter 7 Chelates

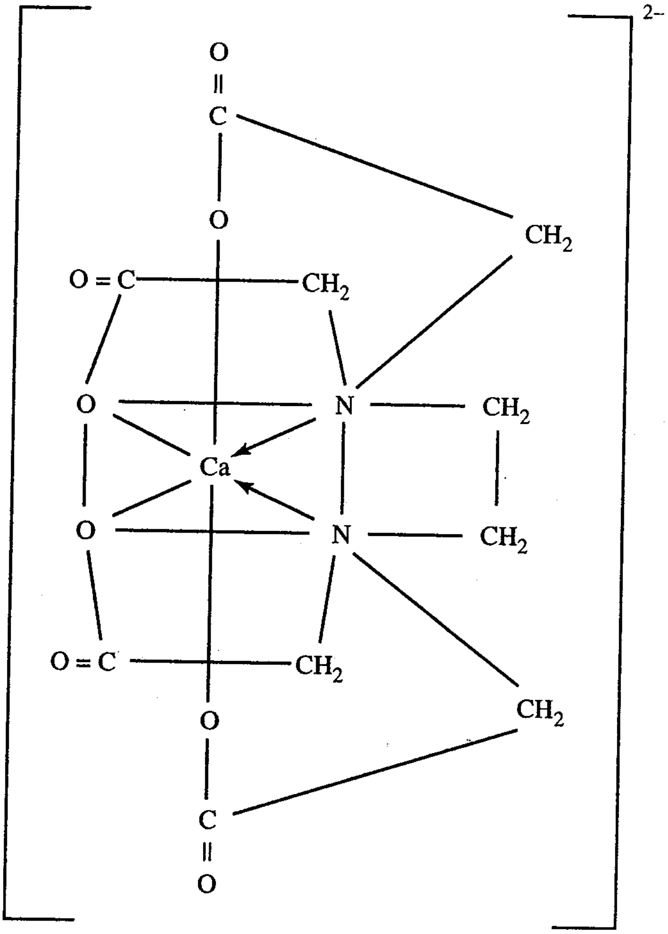
7.1 INTRODUCTION

A ligand having more than one point of attachment to the central metal ion in a complex is called a polydentate ligand. Examples of such polydentate ligands are ethylenediamine (en), diethylenetriamine (dien), triethylenetetramine (trien), dimethylglyoxime (DMG), ethylenediaminetetraacetate (EDTA), acetylacetonate (acac), etc. These polydentate ligands coordinate through their points of attachment to the same central metal ion to form complexes with ring structures. Such ring-structured metal complexes with the metal forming a part of the ring system are called the *chelates*. (From the Greek word *chela* that means crab's claw). Some examples of metal chelates are $[Cu(en)_2]^{2+}$, $[Ni(dien)_2]^{2+}$, $[Ni(DMG)_2]$, $[Ca\text{-}EDTA]^{2-}$, $[Cu(acac)_2]$ etc. The structures of these chelates are given in Fig 7.1.



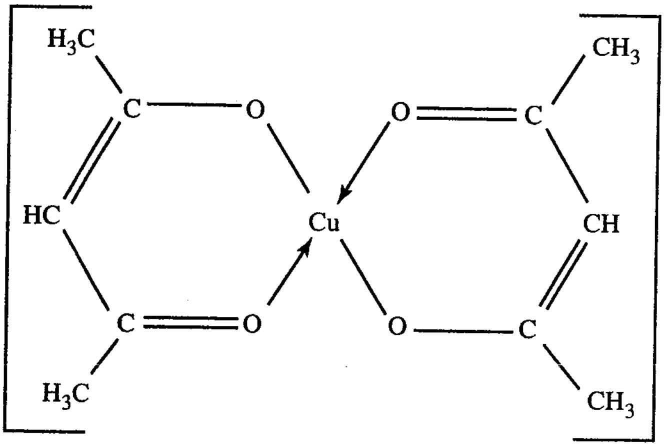
$[Ni(DMG)_2]$

(a)



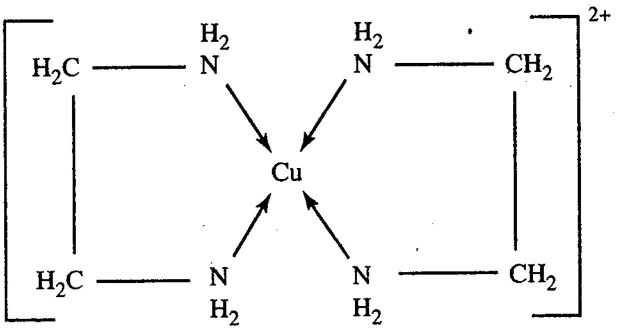
[Ca-EDTA]$^{2-}$

(b)



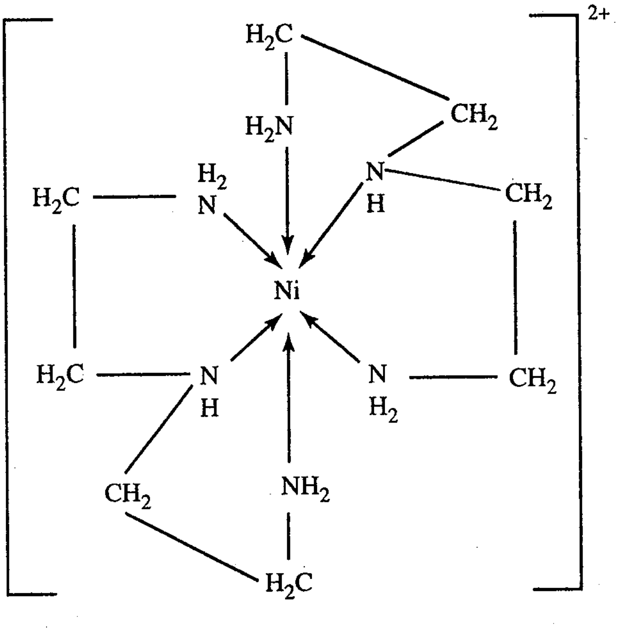
[Cu(acac)$_2$]

(c)



$[Cu(en)_2]^{2+}$

(d)



$[Ni(dien)_2]^{2+}$

(e)

Fig. 7.1 Structures of some chelates

The polydentate ligands that form the chelates are called the *chelating agents*. The process of chelate formation is known as *chelation*. Due to chelation the stability of the complex is enhanced. This extra stability conferred on a complex due to chelation is called the *chelate effect*.

7.2 CHELATE EFFECT

Thermodynamically, the chelate effect can be related to the entropy change of the reaction. When a solvated metal ion in solution reacts with a chelating agent, the solvent molecules in the coordination sphere of the metal ion are replaced by the chelating agent. For example,

$$[Ni(H_2O)_6]^{2+} + 3\,en \longrightarrow [Ni(en)_3]^{2+} + 6H_2O$$

$$1 + 3 \text{ particles} \longrightarrow 1 + 6 \text{ particles}$$

This chelation process results in an increase of three particles (7 – 4 = 3). The replacement of the monodentate ligands by chelating agents always has this effect. This increase in the number of particles results in an increase in randomness of the system. This in turn, results in a positive $\Delta S°$ which adds on to the already negative $\Delta H°$ to give more negative $\Delta G°$ ($\Delta G° = \Delta H° - T\,\Delta S°$). As, $-\Delta G° = RT\ln K$, the more negative is $\Delta G°$, the larger the formation constant or stability constant. Thus an increase in the degree of randomness of the system causes greater complex stability. As a general rule, stability of a chelate complex is higher than that of a non-chelate complex of the same metal ion.

Table 7.1 gives the overall stability constants for a number of metal ammines (non-chelates) and the corresponding ethylenediamine chelates.

Table 7.1 Stabilities of some chelated and non-chelated metal complexes

Cation	Coordination number	$p\beta(NH_3)$	$p\beta$(en)
Co^{2+}	6	5	14
Co^{3+}	6	34	49
Ni^{2+}	6	9	19
Cu^{2+}	4	13	20

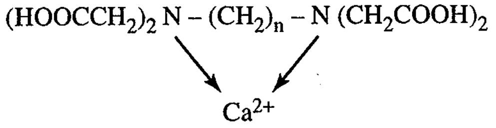
7.3 CONDITIONS FOR CHELATION

The chelating agents must possess at least two donor groups per molecule; i.e., the ligands should be polydentate. These donor groups must be so situated in the molecule in such a way that they permit the formation of a ring with the metal atom without any strain. The donor atoms should be sterically capable of coordinating to the same metal to form a chelate. Hydrazine ($H_2N - NH_2$), even though a polydentate ligand, does not form a stable chelate, because it does not satisfy the second condition pertaining to steric condition.

7.4 FACTORS AFFECTING STABILITY OF CHELATES

1. A factor of great importance in chelation is the size of the chelate ring produced. If there is no double bond in the chelate ring, then a 5-membered ring is the most stable. Chelate rings having more or less than 5-members are generally

less stable. Table 7.2 shows the variation of the stability constants with ring size of the calcium complexes with a series of acids of the general formula,



$$(HOOCCH_2)_2N-(CH_2)_n-N(CH_2COOH)_2 \quad \searrow Ca^{2+} \swarrow$$

which are bidentate ligands. When $n = 2$, a 5-membered ring is formed between the two nitrogen atoms and the metal; when $n = 3$, a 6-membered ring is formed and so on. The greatest stability for the chelate is found when $n = 2$.

Table 7.2 Variation of stability constants with the ring size of chelates

Value of *n*	Ring size	Stability constant (log K)
2	5	10.7
3	6	7.1
4	7	5.1
5	8	4.6

2. Another factor which determines chelate stability is the influence of the number of chelate rings in a chelate molecule. Greater the number of chelate rings greater will be the stability of the complex. As the number of donor atoms in a chelating agent increases, the stability increases. This is attributed to the increase in the number of chelate rings formed by such ligands.

Table 7.3 shows the increase in the stability constants of Ni^{2+} complexes with some polydentate ligands which give rise to different numbers of chelate rings.

Table 7.3 Variation of stability constants with increase in the number of rings

Ligand	log K_1 for Ni^{2+} complex	Increase in the number of particles due to chelation	Number of rings
en	7.9	2 to 3 (= 1)	1
dien	10.7	2 to 4 (= 2)	2
trien	14.0	2 to 5 (= 3)	3

$$\begin{aligned}
[Ni(H_2O)_6]^{2+} + en &\longrightarrow [Ni(H_2O)_4en]^{2+} + 2H_2O \\
1+1 &\longrightarrow 1+2 \text{ particles} \\
[Ni(H_2O)_6]^{2+} + dien &\longrightarrow [Ni(H_2O)_3dien]^{2+} + 3H_2O \\
1+1 &\longrightarrow 1+3 \text{ particles} \\
[Ni(H_2O)_6]^{2+} + trien &\longrightarrow [Ni(H_2O)_2trien]^{2+} + 4H_2O \\
1+1 &\longrightarrow 1+4 \text{ particles}
\end{aligned}$$

3. One more factor of significance in chelation is the steric factor. This arises due to the presence of a bulky group either attached to or near to a donor atom to cause mutual repulsion between the ligands and thereby weakening the metal-ligand bond. This leads to lesser stability. This is well illustrated by the stabilities of three complexes formed by Ni^{2+} with three different chelating agents such as 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline

and 4-methyl-8-hydroxyquinoline. The second stage formation constants for these complexes are given in Table 7.4.

Table 7.4 Variation of stability constants for unsubstituted and substituted oxine complexes of Ni^{2+}

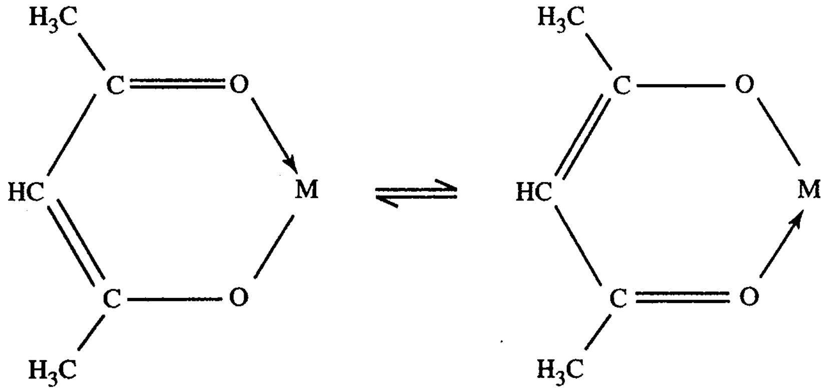
Substituent	$\log(K_1 K_2)$ for Ni^{2+} complex
none	21.4
2-methyl	17.8
4-methyl	22.3

The complex with 2-methyl-8-hydroxyquinoline is less stable (17.8) than those of either 8-hydroxyquinoline itself (21.4) or 4-methyl-8-hydroxyquinoline (22.3). Generally, the more basic ligands are expected to form more stable complexes. 2-Methyl- 8-hydroxyquinoline is the most basic among these three chelating agents; but it forms the least stable chelate. This is because in this ligand the bulky methyl group is present very near to the donor atom (nitrogen) to cause mutual repulsion between the ligands and thereby it decreases the stability of the chelate.

The 4-methyl derivative forms the most stable chelate. This is attributed to its more basic nature than 8-hydroxyquinoline. In this ligand, the bulky methyl group is far away from the donor nitrogen atom and hence it will not sterically hinder the approach of the second ligand. Hence it forms the most stable chelate among the three ligands. This is found to be true with many other metal ions such as Mn^{2+}, Co^{2+}, Zn^{2+}, etc.

7.4.1 Resonance and Chelation

Some chelating ligands are capable of experiencing resonance stabilisation of their molecules. This stabilisation is extended to the metal chelates formed by them. For example, acetylacetone can form a chelate with an M(III) ion, $[M(acac)_3]$. One ring of the structure of the complex is represented as two resonance forms:



M = Al(III), Cr(III) or Co(III)

Fig. 7.2 Resonance stabilisation of chelate

This, and also similar resonance in the other two rings stabilise the chelate. In these complexes, the ligand-metal pi bonding enhances the delocalisation of electrons compared to that in the free enolate ligand, producing some resonance stabilisation.

7.5 CLATHRO-CHELATE

Some polymeric, large-sized ligands encapsulate or encircle metal ions; these ligands form a three-dimensional cage about the metal. The chelate thus formed is called a *clathro-chelate* or a *cryptate*. One such ligand is $N(CH_2CH_2O\,CH_2CH_2O\,CH_2CH_2)_3N$; it complexes alkali metals forming exceptionally stable complexes. This ligand is known also as *football ligand* because the polyether bridges between the two nitrogen atoms resemble the seams of a football. The size of the "football" can be adjusted to fit the selected cation for chelation.

7.6 IMPORTANCE OF CHELATES IN BIOLOGY

In biology, many widely divergent chemical and biological processes are closely related to the formation of chelate rings. Many metals, which are essential for the normal growth and maintenance of life in both animals and plants are present in the form of their chelates in the organisms.

(1) Haemoglobin, which is the oxygen carrier in the blood is an iron chelate.
(2) Chlorophyll, which is essential for photosynthesis in plants is a magnesium chelate.
(3) Oxygen carriers in the blood of various invertebrates are the chelate compounds of the elements such as manganese and vanadium.
(4) Vitamin B_{12}, which is an anti-pernicious anaemia factor, is a cobalt chelate.
(5) Cytochromes, which are electron carriers are iron chelates.
(6) Plastocyanins, which are also electron carriers, are copper chelates.
(7) Metal poisoning due to lead, mercury, copper, etc. is attributed to the formation of very stable, toxic chelates of these metals with biologically important substances like adrenalin, citric acid, cortisone, etc. thereby affecting their normal metabolisms. Such metal poisoning can be treated by drinking an aqueous solution of EDTA. This chelating agent complexes with the poisonous lead, mercury, copper etc. and these toxic chelates are excreted in the urine. But unfortunately EDTA also complexes the essential calcium in the body and the complex is excreted in urine. This problem may be partly overcome by using Ca-EDTA complex as the antidote in the place of EDTA.

7.7 CHELATES IN ANALYTICAL CHEMISTRY

Chelates are of great importance in analytical chemistry.

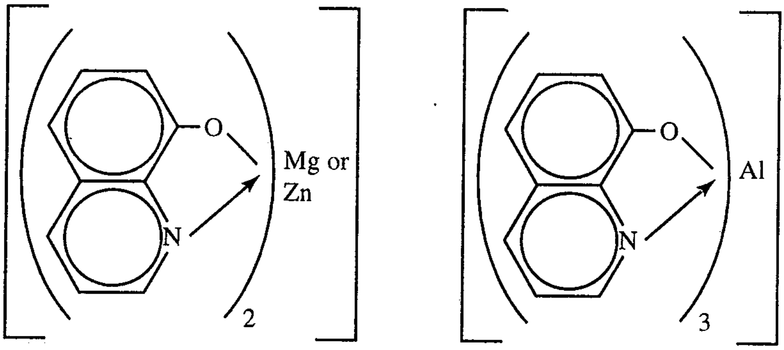
(1) In qualitative analysis, nickel can be readily identified as its DMG chelate which gets precipitated as a rosy red solid in ammoniacal medium.

(2) Magnesium, aluminium and zinc ions can also be identified as their stable and intensely coloured chelates.

(3) In gravimetric analysis, magnesium, aluminium, and zinc are precipitated quantitatively as their 8-hydroxyquinoline chelates called the *oxinates*.

(4) Ni^{2+} is quantitatively precipitated as its dimethylglyoxime chelate in ammoniacal medium.

(5) In volumetric analysis, certain metal chelates are used as indicators. For example $[Fe^{II}(o\text{-phen})_3]$ chelate, called ferroin, is used as the indicator in the titration of $Cr_2O_7^{2-}$, or Ce^{4+} with Fe^{2+}.



(a) *Mg or Zn oxinate chelate*

(b) *Al oxinate chelate*

Fig. 7.3

(6) The formation of Ca^{2+} and Mg^{2+} - EDTA chelates is used in the determination of the total hardness of water.

VERSATILE VERSENE

EDTA is known commercially as versene. It is a versatile chelating agent for a large number of metals. This extraordinary complexing ability is the origin for its another name *complexone*. It is an efficient sequesterent as it is able to reduce the concentration of simple (hydrated) metal ions in solution by forming stable complexes; therefore it is called also as *sequestrene*. Its applications include volumetry, gravimetry, water softening, industrial descaling, chelate therapy, analytical separations etc.

(7) In certain analytical separations, chelating agents are used as *masking agents*. A masking agent is defined as a substance that hides certain metal ions from other reagents with which their interactions are undesired. For example, in the gravimetric determination of Ni^{2+} as its DMG complex, the presence of Fe^{3+} gives $Fe(OH)_3$ precipitate. Thus Fe^{3+} interferes in this determination. To avoid the formation of $Fe(OH)_3$, before the addition of DMG and ammonium hydroxide, a slight excess of tartaric acid or citric acid is added as masking agent. Fe^{3+} forms a very stable, water soluble Fe^{3+}-tartrate or Fe^{3+}-citrate chelate complex in which iron forms a part of a complex anion. Hence, the reaction between OH^- and this complex anion is avoided. Thus the interference of Fe^{3+} is avoided.

(8) The formation of chelates is also used in the highly difficult separation of mixture of metals, such as zirconium and hafnium. These two metals chemically resemble each other very closely. The separation of these two metals was a difficult analytical task until it was discovered that the chelates of the two metals formed with thenoyltrifluoroacetone (Fig. 7.4) possess different solubilities in benzene. The distribution coefficients of the two chelates differ by a factor of 20, the zirconium chelate having greater tendency to be extracted into benzene. Consequently, it is now posible to effect a good separation of these metals by repeated extractions of these two ions with thenoyltrifluoroacetone in benzene.

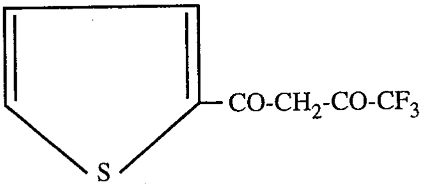


Fig. 7.4 *Thenoyltrifluoroacetone*

CHELATE CHRONICLE

The term "chelate" was first used in chemistry by G.T. Morgan and H.D.K.Drew in 1920 for "groups (ligands) which function as two associating units which fasten to the central metal atom to form heterocyclic rings." This word has been derived from the Greek word *chela* which means claw. Later, chelated structures of metal compounds were studied elaborately by Diehl. The Russian chemist Chugaev first noted that the chelating ligands are much less likely to be replaced from a complex than are monodentate ligands; this tendency is called the chelate effect. For a ligand which forms three or four bonds to a metal, Morgan suggested the name *tridentate* (three-toothed) ligand or *quadridentate* (four-toothed) ligand could be used.

EXERCISES

***I. Choose the best answer for each of the following:**

1. Pick-out the *odd* ligand from
   a) py
   b) bipy
   c) en
   d) dien
2. An antidote used in mercury poisoning is
   a) calomel
   b) cis-platin
   c) EDTA
   d) none of the above

3. A polydentate ligand that does not form a chelate is
   a) gly
   b) acac
   c) trien
   d) hydrazine
4. Citric acid acts as a ——— in the gravimetric determination of Ni^{2+} as its DMG complex in the presence of Fe^{3+}
   a) precipitating agent
   b) reducing agent
   c) masking agent
   d) none of the above
5. A bidentate ligand having one acidic and one coordinating group is
   a) en
   b) glycine
   c) $C_2O_4^{2-}$
   d) bipy
6. $[Ca\text{-}EDTA]^{2-}$ chelate complex has ——— 5-membered rings.
   a) three
   b) two
   c) four
   d) five
7. The coordination number of a central metal (M) in a 1 : 1 complex of the metal with EDTA is
   a) 6
   b) 5
   c) 4
   d) 3
8. Among the following, the most stable complex is
   a) $[Co(en)(H_2O)_4]^{3+}$
   b) $[Co(en)_2(H_2O)_2]^{3+}$
   c) $[Co(NH_3)_6]^{3+}$
   d) $[Co(en)_3]^{3+}$
9. The cation present in haemoglobin is
   a) Fe^{3+}
   b) Zn^{2+}
   c) Fe^{2+}
   d) Mg^{2+}
10. The metal present in the blood of various invertebrates is
    a) Fe
    b) Mn
    c) Co
    d) Zn

11. The metal present in Vitamin B_{12} is
    a) cobalt
    b) manganese
    c) iron
    d) magnesium
12. The metal present in chlorophyll is
    a) Mn
    b) Mg
    c) V
    d) Cu
13. Which of the following is not bidentate?
    a) oxalate
    b) glycine
    c) *o*-phen
    d) nitrilotriacetic acid
14. Which of the following has/have two acidic groups?
    a) oxalato
    b) sulphato
    c) carbanato
    d) all the above
15. Pickout the odd one from
    a) oxine
    b) en
    c) bipy
    d) *o*-phen
16. Which of the following compounds is not a chelate ?
    a) bis(dimethylglyoximato)nickel (II)
    b) potassium tetrachlorodinitrocobaltate(III)
    c) diglycinatoplatinum(II)
    d) tetraaquaethylenediaminechromium(III) chloride

***II Match the following:**

1. plastocyanins	a) anti-pernicious amaemia factor
2. cytochromes	b) $[\mathrm{Fe}(o\text{-phen})_3]^{2+}$
3. cyanocobalamin	c) copper chelates
4. EDTA	d) Zr, Hf separation
5. ferroin	e) iron chelates
6. thenoyltrifluoroacetone	f) lead poisoning

III Account for the following:

*1. $[\mathrm{Cu(en)_2(H_2O)_2}]^{2+}$, even though it contains only two chelate rings, is more stable than $[\mathrm{Cu(en)_3}]^{2+}$ which contains three chelate rings.

*2. log K_1 for Ni^{2+}- en complex is 7.9 whereas that for Ni^{2+}-trien complex is 14.0

*3. log (K_1K_2) for Ni^{2+}-oxine complex is 21.4, that for Ni^{2+}- 2 methyloxine is 17.8 and that for Ni^{2+}- 4 methyloxine is 22.3.

4. EDTA is used as an antidote for copper poisoning.
5. Gravimetric determination of Ni^{2+} as its DMG complex in the presence of Fe^{3+} is carried out using citric acid as masking agent.

IV Answer the following:

*1. What is a chelating agent?
*2. What is chelation?
*3. What is a chelate?
*4. What is a chelate effect?
5. How does the size of chelate rings affect stability of complexes?
6. How does the number of chelate rings affect the stability of complexes?
*7. What are the conditions to be satisfied by ligands to act as chelating agents?
8. How are chelate formations useful in
   a) qualitative analysis
   b) volumetric analysis and
   c) gravimetric analysis
9. Account for the chelate effect.
10. How can a mixture of zirconium and hafnium be separated using chelate formation?

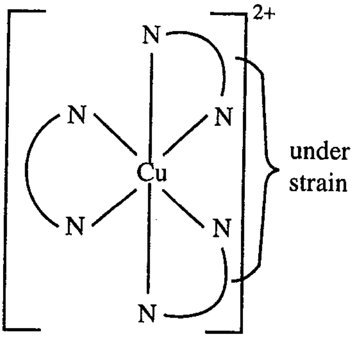
ANSWERS

I 1. (a) 2. (c) 3. (d) 4. (c) 5. (b) 6. (d) 7. (a) 8. (d) 9. (c) 10. (b) 11. (a) 12. (b) 13. (c) 14. (d) 15. (a) 16. (b)

II 1. (c) 2. (e) 3. (a) 4. (f) 5. (b) 6. (d)

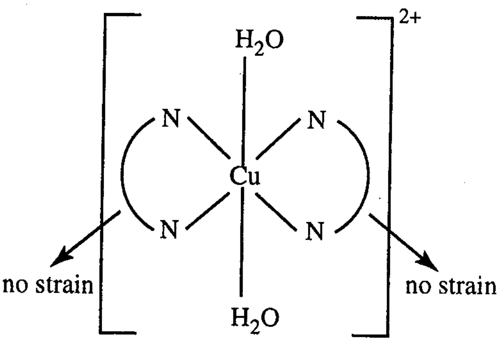
III

1. In these two complexes, copper is in its dipositive state, that is, d^9 system which is subjected to Jahn-Teller distortion. As a result, two bonds along the *z*-axis are elongated. Therefore, two out of three chelate rings in $[Cu(en)_3]^{2+}$ are under strain. Hence this complex is less stable than $[Cu(en)_2(H_2O)_2]^{2+}$ in which the two chelate rings are without any strain. These effects are depicted in diagrams (a) and (b).



$[Cu(en)_3]^{2+}$

(*a*)



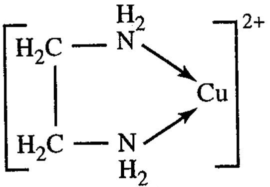
$[Cu(en)_2(H_2O)_2]^{2+}$.

(*b*)

2. log K_1 for Ni^{2+}-en complex is less (7.9) than that for Ni^{2+}- trien complex (14.0) because the former has only one chelate ring whereas the latter has three chelate rings. Generally greater the number of chelate rings greater will be the stability of complex.
3. log (K_1K_2) for Ni^{2+}-oxine complex (21.4) is greater than that for Ni^{2+}-2 methyl oxine complex (17.8) because the second stage complex formation is sterically hindered by the two methyl groups which are close to the donor atoms in the ligand of the latter complex. But log. (K_1K_2) for Ni^{2+}-4-methyloxine complex (22.3) is the highest among the three complexes because the ligand 4-methyloxine is more basic than oxine itself and the methyl group is far away from the donor atom so that it does not sterically hinder the second stage complex formation.

IV

1. The ligand which gives rise to a chelate complex is called a chelating agent. It will be a polydentate ligand with the donor atoms situated in the molecule in such a way as to form ring structured complexes without strain. Example: ethylenediamine.
2. The process of chelate formation is called chelation.
3. Ring-structured complex with the metal atom forming a part of the ring is called a chelate. For example, $[Cu(en)]^{2+}$



chelate ring

4. Due to chelation the stabilities of complexes will be enhanced. This extra stability conferred on a complex due to chelation is called chelate effect.
7. Two conditions are to be satisfied by a ligand to act as a chelating agent. They are,
   a) it should be a polydentate ligand
   b) the donor atoms should be situated in the molecule in such a way that they are sterically capable of coordinating with the same central metal without any strain.

Chapter 8

Isomerism of Metal Complexes

Isomerism is generally considered to be characteristic of organic compounds. Since isomerism is a phenomenon of position or arrangement of atoms or groups, it cannot be limited to the compounds of any one type or of any one element. Although many examples of isomerism are noted among various inorganic substances, the coordination compounds offer a variety of examples. This is because of the complicated formulae of complexes with different possible bond types and shapes.

Compounds having the same chemical formula but different physical and chemical properties due to the different structural arrangements are called isomers. This phenomenon is known as isomerism. Alfred Werner's classification of isomerism of metal complexes proposed nearly a century ago is still relevant and followed.

Coordination compounds exhibit two major types of isomerism, namely, ***(I) structural isomerism*** and ***(II) stereoisomerism (space isomerism)***. Each of these is further classified as shown below:

Isomerism

I. structural isomerism	II. stereoisomerism (space isomerism)
1) ionisation isomerism	1) Geometrical or cis-trans isomerism
2) solvate isomerism	2) optical or object-mirror image isomerism
3) linkage isomerism	
4) coordination isomerism	
5) ligand isomerism	
6) polymerisation isomerism	

8.1 STRUCTURAL ISOMERISM

8.1.1 Ionisation Isomerism

Coordination compounds having the same molecular formula but forming different ions in solution are called *ionisation isomers*. This property is known as ionisation isomerism. This type of isomerism is due to the exchange of groups between the complex ion and the ions present outside it. A classical example of this type of isomerism is furnished by the red-violet, $[Co(NH_3)_5Br]SO_4$ and red,

$[Co(NH_3)_5SO_4]Br$. The red-violet isomer yields sulfate ion and the red isomer furnishes bromide ion in solution. These two isomers could be differentiated by a simple test: an aqueous solution of the former gives a white precipitate of $BaSO_4$ with $BaCl_2$ solution whereas that of the latter does not give any precipitate. This confirms the presence of sulfate ions in the aqueous solution of the red-violet isomer. The aqueous solution of the red isomer gives a pale yellow precipitate of AgBr with a solution of $AgNO_3$, confirming the presence of bromide ions in its aqueous solution.

Another example for this isomerism is furnished by the two modifications of the composition $[Pt(NH_3)_4(OH)_2SO_4]$. One modification is a neutral compound which gives an immediate white precipitate with $BaCl_2$ solution and is formulated as $[Pt(NH_3)_4(OH)_2]SO_4$. The other isomer is a strong base and is formulated as $[Pt(NH_3)_4SO_4](OH)_2$. In ionisation isomers,clearly an interchange of negative groups between the coordination sphere and the ionisation sphere is involved. Some other examples of this type are,

$[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$
$[Co(NH_3)_4NO_2Cl]Cl$ and $[Co(NH_3)_4Cl_2]NO_2$
$[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$
$[Co(en)_2(NO_2)Cl]SCN$, $[Co(en)_2)(NO_2)(SCN)]Cl$ and
$[Co(en)_2(SCN)Cl]NO_2$

8.1.2 Solvate Isomerism

Solvate isomerism is somewhat analogous to ionisation isomerism but involves the interchange of a neutral solvent molecule with a negative ion. This type of isomerism is illustrated by the three modifications of the composition $CrCl_3 \cdot 6H_2O$. One modification does not lose water when stored over concentrated sulfuric acid (a dehydrating agent). Its molar conductance is of the same order as that of a ter-univalent salt indicating the presence of a tripositive complex ion and three mononegative chloride ions. All its chloride content is immediately precipitated as AgCl by $AgNO_3$ in cold solution.

These properties of this isomer indicate its formula to be

$$[Cr(H_2O)_6]Cl_3$$
(β-form, violet)

The second modification loses one mole of water per mole of it over concentrated sulfuric acid. Its molar conductance corresponds to that of a bi-univalent salt indicating the presence of a dipositive complex ion and two chloride ions. Only two-thirds of its chloride content is immediately precipitated as AgCl by $AgNO_3$ solution. These properties of this isomeric form correspond to the formula.

$$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$$
(γ-form, green)

The third modification, based on its properties, is formulated as

$$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$$
(α-form, green)

Other complexes illustrating the solvate isomerism include,

$[Co(py)_2Cl_2(H_2O)_2]Cl$ and $[Co(py)_2Cl_3(H_2O)]\cdot H_2O$

$[Co(NH_3)_3Cl(H_2O)_2]Br_2$ and $[Co(NH_3)_3(H_2O)(Cl)(Br)]BrH_2O$

When a negative group gets exchanged for water molecule as in the above cases, the isomerism is more specifically called the *hydrate isomerism*. An example involving both ionisation and hydrate isomerism is provided by the following pair of complexes

$[Co(NH_3)_4(H_2O)(Cl)]Br_2$ and $[Co(NH_3)_4Br_2]Cl\cdot H_2O$
(violet) (green)

An example of *ammoniate isomerism*, where a negative group gets exchanged for neutral ammonia molecule, is illustrated by the following complexes of composition, $PtCl_4 \cdot 6NH_3$:

$[Pt(NH_3)_6]Cl_4$
$[Pt(NH_3)_5Cl]Cl_3\cdot NH_3$
$[Pt(NH_3)_4Cl_2]Cl_2\cdot 2NH_3$
$[Pt(NH_3)_3Cl_3]Cl\cdot 3NH_3$ and
$[Pt(NH_3)_2Cl_4]4NH_3$

8.1.3 Linkage Isomerism

A ligand molecule containing more than one atom which could donate an electron pair is called an ambidentate ligand. For example, each of NO_2^-, SCN^-, CN^-, etc. contains more than one possible site of attachment. In the case of NO_2^-, for example, either the nitrogen or oxygen atom may act as the donor and hence there is the possibility of isomerism. Jorgensen prepared two pentamminecobalt(III) chlorides, each containing a single NO_2^- ligand. One isomer which is red in colour is easily decomposed by acids to give nitrous acid. The other isomer which is of yellowish-brown colour is stable to acids. This behaviour is analogous to the behaviour of organic nitrites, R-ONO and nitro compounds, R- NO_2. Hence, these two isomeric modifications are represented as follows:

$[Co(NH_3)_5(ONO)]Cl_2$	and	$[Co(NH_3)_5(NO_2)]Cl_2$
(red)		(yellowish-brown)
nitro-O-pentamminecobalt(III) chloride		nitro-N-pentamminecobalt(III) chloride

The linkage isomers are easily identified by means of infra-red spectroscopy. The symmetrical NO_2 stretching frequency is different in nitro and nitrito groups attached to a metal ion. These values are around 1315 cm^{-1} and 1060 cm^{-1} respectively for the pentamminecobalt(III) complexes.

The thiocyanate ion can attach itself to the metal through either the nitrogen , M–N=C=S or the sulfur, M–S–C≡N. Generally, the first-row transition elements are linked through nitrogen and the second and third row transition elements are linked through sulfur in their complexes. The following linkage isomers with thiocyanate ions have been prepared;

$[Mn(CO)_5SCN]$ and $[Mn(CO)_5NCS]$

These isomers could also be readily identified by infra-red spectroscopy. The C–S stretching frequency is much lower in M–S–C≡N (= 705 cm^{-1}) than in M–N=C=S (= 825 cm^{-1})

8.1.4 Coordination Isomerism

In a bimetallic complex both complex cation and complex anion may be present. In such a case the distribution of ligands between the two coordination spheres can vary, giving rise to isomers called the *coordination isomers.* This phenomenon is called coordination isomerism. This isomerism is illustrated by the following pairs of complexes where the complex cation and anion contain different metal centres.

$[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$
$[Cr(NH_3)_6][Co(CN)_6]$ and $[Co(NH_3)_6][Cr(CN)_6]$
$[Co(en)_3][Cr(C_2O_4)_3]$ and $[Cr(en)_3][Co(C_2O_4)_3]$

Such isomerism can also occur when both the cationic and anionic systems contain the same central metal. For example,

$[Co(NH_3)_6][Co(NO_2)_6]$ and $[Co(NH_3)_5(NO_2)][Co(NO_2)_5(NH_3)]$
$[Pt(NH_3)_4][PtCl_6]$ and $[Pt(NH_3)_4Cl_2][PtCl_4]$
$[Cr(NH_3)_6][Cr(SCN)_6]$ and $[Cr(NH_3)_4(SCN)_2][Cr(NH_3)_2(SCN)_4]$

A special type of coordination isomerism occurs due to the difference in the placement of ligands in a bridged complex. This special type of isomerism is called *coordination position isomerism.* The following illustrate this isomerism.

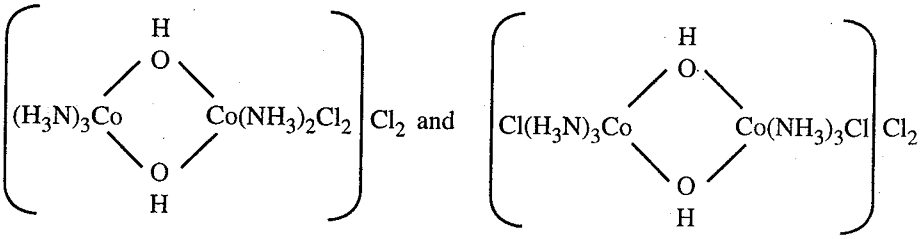


Fig. 8.1 Coordination position isomerism

8.1.5 Ligand Isomerism

Certain ligands can exist in isomeric forms. They can be so incorporated into complexes as to give rise to isomers, called *ligand isomers.* This phenomenon is called ligand isomerism. For example, there are two isomers of the composition, $C_3H_6(NH_2)_2$, namely, 1,2-diaminopropane (*pn*) and 1,3-diaminopropane also called trimethylenediamine(*tn*). These two bidentate ligands form isomeric complexes such as,

$[Co(pn)_2Cl_2]Cl$ and $[Co(tn)_2Cl_2]Cl$

Another example of this type of isomerism is illustrated by the three isomers with the molecular formula given below, corresponding to the use of ortho-, meta- and para-toluidine respectively.

$[Co(H_2N-CH_2-CH_2-NH_2)_2(H_3C-C_6H_4-NH_2)(Cl)]SO_4$

8.1.6 Polymerisation Isomerism

Certain complexes possess the same stoichiometric composition but different molecular compositions. Their actual molecular compositions are multiples of the simplest stoichiometric arrangement. Such complexes are said to be *polymerisation isomers* and this phenomenon is called polymerisation isomerism. In the true sense of the word, this is not a real isomerism, because it occurs between complexes having different molecular formulae but the same empirical formula. This type of isomerism is illustrated by the series of complexes based upon trichlorotriammine cobalt(III) and dinitrodiamminepalladium(II) as shown in Table 8.1.

Table 8.1 Polymerisation isomerism in cobalt and palladium complexes

No.of stoichio-metric groups	Cobalt series	Palladium series
1	$[Co(NH_3)_3Cl_3]$	$[Pd(NH_3)_2(NO_2)_2]$
2	$[Co(NH_3)_6][CoCl_6]$	$[Pd(NH_3)_4][Pd(NO_2)_4]$
3	$[Co(NH_3)_5Cl][Co(NH_3)_2Cl_4]_2$	$[Pd(NH_3)_4][Pd(NH_3)(NO_2)_3]_2$
4	$[Co(NH_3)_6][Co(NH_3)_2Cl_4]_3$	
5	$[Co(NH_3)_5Cl]_3[CoCl_6]_2$	

8.2 STEREOISOMERISM (SPACE ISOMERISM)

When two compounds contain the same ligands attached to the same central metal ion, but the arrangement of ligands in space about the central metal ion being different, then these two compounds are said to be stereoisomers and this phenomenon is known as stereoiosmerism or space isomerism. Stereoisomerism is of two different types, namely, (i) Geometrical isomerism and (ii) Optical isomerism

8.2.1 Geometrical or Cis-trans Isomerism

This type of isomerism is not possible in 2-coordinated complexes, 3-coordinated complexes and 4-coordinated tetrahedral complexes. This is because in 2-coordinated complexes there are no cis-positions. But in 3-coordinated complexes and in 4-coordinated tetrahedral complexes all the coordination positions are cis to each other; there are no trans positions. However, cis-trans isomerism is very common in many 4-coordinated square-planar complexes and 6-coordinated octahedral complexes.

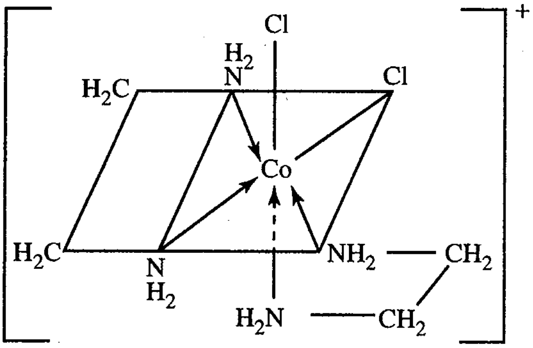
In a cis-isomer two identical or similar groups are adjacent to each other whereas in a trans-isomer they are diametrically opposite to each other.

Square-planar complexes of the type $[Ma_2b_2]^{n\pm}$, where a and b are monodentate ligands, exist as cis- and trans-isomers as shown below:

Specific examples of this type of complexes are $[Pt(NH_3)_2Cl_2]$ and $[Pd(NH_3)_2(NO_2)_2]$. The cis-trans isomers of these compounds are represented as

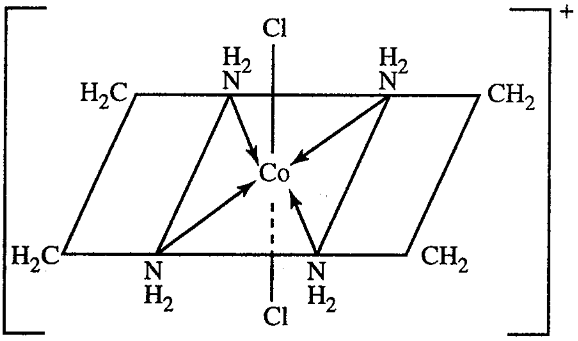
A specific example for such isomerism is $[Co(NH_3)_4Cl_2]^+$ which exists as two geometrical isomers.

The octahedral complexes are of the type $[M(AA)_2 a_2]^{n\pm}$ where (AA) is a symmetrical bidentate ligand such as ethylenediamine, $H_2N-CH_2-CH_2-NH_2$ and '*a*' a monodentate ligand. A specific example for this is $[Co(H_2N-CH_2-CH_2-NH_2)_2Cl_2]^+$



cis-isomer

(a)



trans-isomer

(b)

Fig. 8.8

The octahedral complexes of the type, $[Ma_3b_3]^{n\pm}$, where *a* and *b* are monodentate ligands also exist as geometrical isomers. For example, $[Rh(py)_3Cl_3]$ exists as cis-(1,2,3 trichlorocomplex) and trans- (1, 2, 6-trichlorocomplex) isomers as represented below.

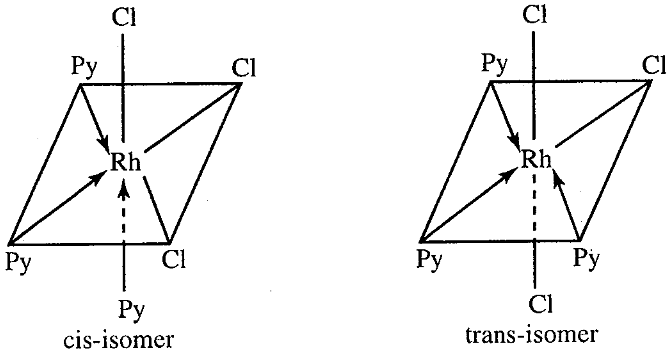


Fig. 8.9

8.2.2 Optical Isomerism

Solutions of certain complexes rotate the plane of plane polarised light either in the clock-wise direction or in the anticlock-wise direction. Such complexes are said to be optically active. They are known as *optical isomers* and this phenomenon is called *optical isomerism*. Optical isomers have similar physical and chemical properties. But they differ in the direction in which they rotate the plane of plane polarised light. They are related to one another as object and its mirror image. They are called either *dextro* or *laevo* (*d* or *l*) depending on whether they rotate the plane of plane polarised light in the clock-wise or anticlock-wise direction respectively.

Conditions to be satisfied by a compound to exhibit optical isomerism (i) The molecule should be asymmetric and (ii) the object and its mirror image should be non-superimposable over each other.

Optical isomerism is common in octahedral complexes. For example, cis-$[Co(en)_2Cl_2]^+$ exists as two optically active forms.

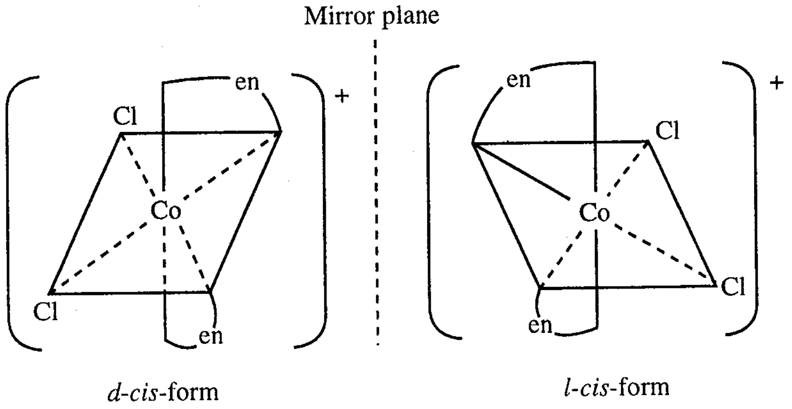


Fig. 8.10

The presence of three bidentate ligands also causes asymmetry and hence leads to optical isomerism. For example, tris(ethlene diamine)platinum(IV) ion, $[Pt(en)_3]^{4+}$ exists as *d*- and *l*-forms which are represented as follows:

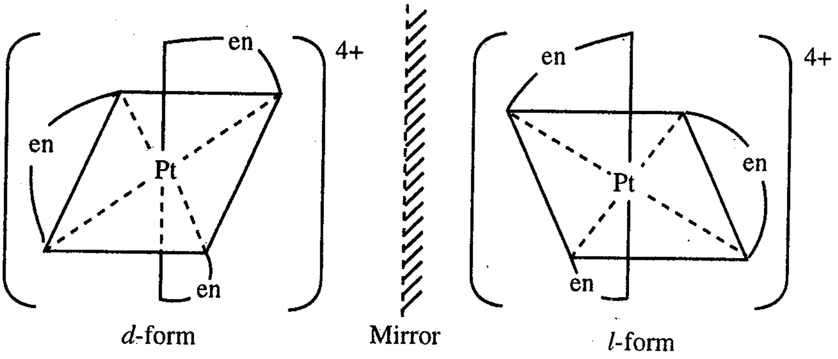


Fig. 8.11

The tetrahedral complexes of the type, [M*abcd*] where *a,b,c* and *d* are monodent ligands, exist as two optical isomers as shown below.

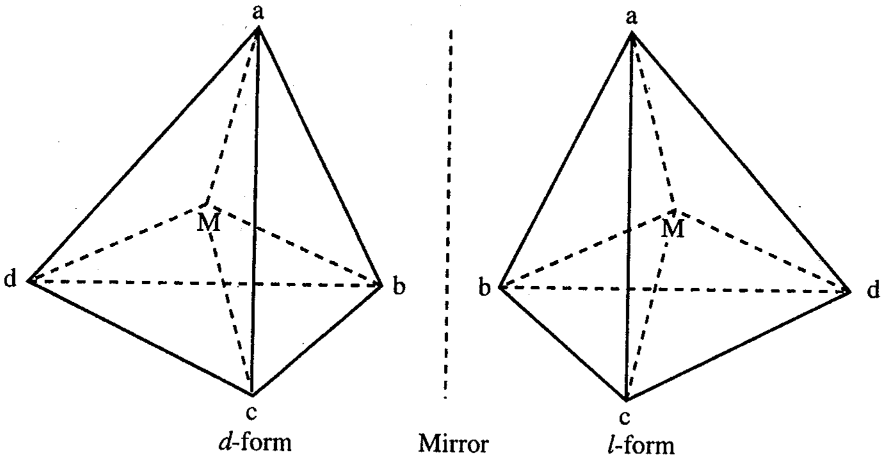


Fig. 8.12

Tetrahedral complexes of Be^{2+}. Zn^{2+} etc. with unsymmetrical bidentate ligands; have been prepared and have been resolved into two optically active forms; for example, bis(benzoylacetonato)zinc(II), which is a tetrahedral complex, exists as two optically active forms.

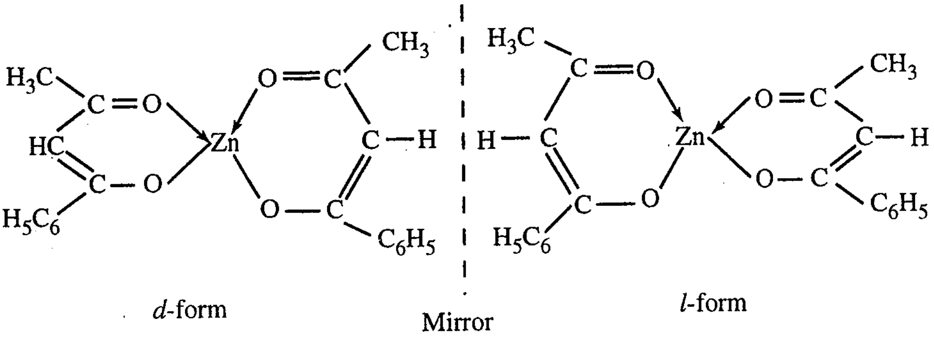


Fig. 8.13

For the isomers to be resolvable, the chelate must be unsymmetrical with respect to the two ends of the chelating molecule. [Zn(*acac*)$_2$] is not optically active because the two ends of the chelating molecule is symmetrical.

8.3 IDENTIFICATION OF ISOMERIC METAL COMPLEXES

8.3.1 By Conductivity Measurement

If the isomeric complexes consitute different numbers of ions, then they would have different molar conductances.

e.g. $[Cr(H_2O)_6]Cl_3$ (4 ions) and $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (3 ions)

If the charge on the ions produced on dissolving the isomers in water are different, then also the molar conductances of the complexes are different.

e.g. $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

8.3.2 By Electrolysis

If the isomers are hetero-bimetallic, one metallic ion constituting a cationic complex and the other an anionic complex, then by electrolysis the two isomers can be distinguished. e.g. (a) $[Co(NH_3)_6][Cr(NO_2)_6]$ is isomeric with (b) $[Cr(NH_3)_6]$ $[Co(NO_2)_6]$

On electrolysis of the aqueous solution of (a), the cobalt(III) species $[Co(NH_3)_6]^{3+}$ will migrate to the negative electrode where cobalt metal would be deposited; however, when the aqueous solution of (b) is electrolysed, the chromium species would migrate to the negative electrode and chromium gets deposited there.

8.3.3 By Freezing Point Depression

If the isomers are constituted by different numbers of ions, then they would produce different freezing point depressions for a solvent.

e.g. $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

8.3.4 By Infra-Red Spectroscopy

If the isomers contain the same ligand bonded differently to the metal, then some of the infra-red absorption frequencies would differ for the complexes.

e.g. $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$

In the nitro-complex, a metal-nitrogen bond is present whereas in the nitrito-complex a metal-oxygen bond is present, whose absorption frequencies in the infra-red region are different.

8.3.5 By X-ray Diffraction

The crystal structures are different for isomeric complexes, the positions of the ligands in space being different. Therefore, X-ray diffraction can be used to identify such isomers.

e.g. $[Co(NH_3)_6][Cr(NO_2)_6]$ and $[Cr(NH_3)_6][Co(NO_2)_6]$

8.3.6 By Dipole Moment

The cis-trans isomers can be distinguished by dipole moments as the trans-isomer has a low dipole moment and the cis-isomer a high dipole moment.

8.3.7 By N.M.R. Spectroscopy

The isomeric complexes containing hydrogen atoms in different chemical environments would produce different ^{1}H-NMR signals;

e.g. cis-$[Pt(NH_3)_4Cl_2]$ and trans-$[Pt(NH_3)_4Cl_2]$

8.3.8 By Mass Spectrometry

Mass spectrometry is not useful for distinguishing either geometric isomers or optical isomers. In two geometric isomers or in two optical isomers, all the atoms are attached (bonded) to each other identically. These isomers on fragmentation produce identical fragments. However, structural isomers such as

$$[Co(NH_3)_6][Cr(NO_2)_6]$$
$$[Cr(NH_3)_6][Co(NO_2)_6]$$

can be identified by this technique, as these isomers form different ions on fragmentation.

8.3.9 By Chemical Method: Grinberg's Method

The cis- and trans- isomers of a complex react with oxalic acid under identical conditions to give entirely different final products. Hence, by analysing the final product we can identify the isomer. For example, cis-$[PtCl_2(NH_3)_2]$ reacts with oxalic acid to give the final product of composition, $[Pt(NH_3)_2(C_2O_4)]$. This reaction is represented as follows:

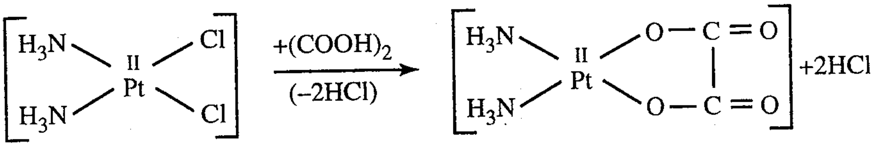


Fig. 8.14

But under similar conditions, the corresponding trans-isomer gives an entirely different product of composition, $[Pt(NH_3)_2(OOC-COOH)_2]$. This reaction is represented as follows:

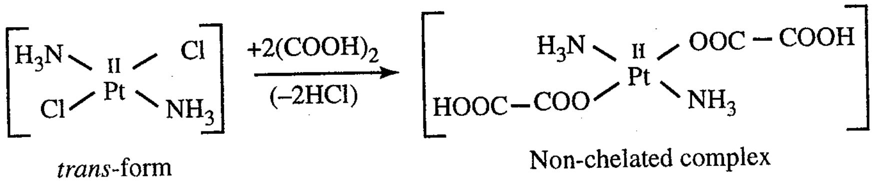


Fig. 8.15

This difference in the final products is attributed to the fact that the bidentate ligand (oxalic acid) can easily occupy the cis-positions and hence it behaves as a bidentate ligand. But the trans positions cannot be occupied by this bidentate ligand on stereochemical grounds. Hence, it behaves as a monodentate ligand with the trans-isomers.

EXERCISES

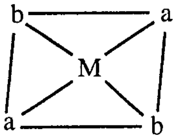
***I. Choose the best answer for each of the following:**

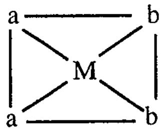
1. The number of isomers possible for a square-planar complex [Mabcd], is
   a) 2
   b) 3
   c) 4
   d) none of the above
2. Isomerism exhibited by the complex $[Co(NH_3)_5NO_2]SO_4$ is
   a) linkage isomerism
   b) ligand isomerism
   c) coordination isomerism
   d) optical isomerism
3. Which of the following can exhibit optical isomerism
   a) trans-$[CrCl_2(NH_3)_4]^+$
   b) cis-$[CrCl_2(NH_3)_4]^+$
   c) trans-$[Cr(NCS)_4(NH_3)]^-$
   d) none of the above
4. The kind of isomerism illustrated by complexes containing diaminopropane as one of the ligands is
   a) linkage isomerism
   b) polymerisation isomerism
   c) ionization isomerism
   d) ligand isomerism
5. $[Pt(NH_3)_4]^{2+}$ on treatment with Cl^- gives a product $[Pt(NH_3)_4Cl_2]$. It is
   a) cis-isomer
   b) mixture of cis- and trans-isomer
   c) trans-isomer
   d) optical isomer
6. The pair of complexes $[Cr(NH_3)_4(H_2O)Br]Cl_2$ and $[Cr(NH_3)_4Cl_2]Br.H_2O$, illustrates
   a) both ionization and hydrate isomerism
   b) ionization isomerism
   c) hydrate isomerism
   d) ligand isomerism.
7. Which one of the following complexes behaves as bi-univalent salt
   a) $[Cr(NH_3)_6]Cl_3$
   b) $[Cr(NH_3)_4Cl_2]Cl.2NH_3$
   c) $[Cr(NH_3)_5Cl]Cl_2.NH_3$
   d) $[Cr(NH_3)_3Cl_3].3NH_3$
8. Which of the following exhibits optical isomerism?
   a) cis-dichlorotetranitrochromate (III) ion
   b) trans-dichlorotetranitrochromate (III) ion

c) cis-diglycinatopalladium (II)
d) trans-diglycinatopalladium (II)

9. The instrument used to determine the optical activity of an optically active isomer is
   a) potentiometer
   b) polarimeter
   c) UV spectrometer
   d) Gouy balance

***II. Match the following:**

1. $[Co(NH_3)_3(NO_2)_3]$ and $[Co(NH_3)_6][Co(NO_2)_6]$
2. $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$
3. $[Cr(H_2O)_5Cl]Cl_2.H_2O$ and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$
4. $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$
5. $[Co(NH_3)_5ONO]Cl_2$ and $[Co(NH_3)_5NO_2]Cl_2$
6. $[Co(en)_2(Cl)(o\text{-toluidine})]SO_4$ and $[Co(en)_2(Cl)(m\text{-toluidine})]SO_4$
7. $[Ma_2b_2]$ square-planar
8. 

9. 

10. [Mabcd] tetrahedral

a) ionization isomers
b) linkage isomers
c) coordination isomers
d) ligand isomers
e) polymerization isomers
f) hydrate isomers
g) cis-iosmer
h) optical isomerism
i) trans - isomer
j) geometrical isomerism

III Account for the following:

1. complexes containing SCN^- ligand exhibit linkage isomerism.
2. $[Ma_2b_2]$ square-planar complex exists as two isomers whereas tetrahedral complex of the same composition does not.
3. Tetrahedral complex of composition [Mabcd], exhibits optical isomerism.
4. $[Pt(NH_3)_4SO_4](OH)_2$ and $[Pt(NH_3)_4(OH)_2]SO_4$ are said to be ionization isomers.

5. cis-$[Co(en)_2Cl_2]^+$ exhibits optical isomerim whereas the trans-form does not.
6. $[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Br_2]Cl.H_2O$ are said to illsutrate both ionization isomerism and solvate isomerism.

*7. In complexes of the type $[M(SCN)_4]^{2-}$ the ligands bond through their π - acceptor sulphur ends; however in the presence of stronger π - acceptor ligands such as PR_3 and AsR_3 they tend to bond through their nitrogen ends.

IV Answer the following:

*1. How many isomers are possible for the neutral complex $[Co(NH_3)_3Cl_3]$? Sketch them.
*2. Sketch the possible geometric isomers for $[Cr(NH_3)_2Cl_4]^-$. Which of these isomers will exhibit optical isomerism.
*3. Sketch the geometric isomers for the square-planar complex, $[Pt(NH_3)_2ClBr]$.
*4. Can the square-planar complex, $[Ni(en)Cl_2]$ exhibit geometrical isomerism? Explain your choice.
5. How are geometrical isomers distinguished?
6. What type of tetrahedral complexes can form optical isomers?
*7. A complex $[Ma_2b_2]$, where *a* and *b* are monodentate ligands, exists as two isomers. What do you infer about its shape?
*8. A complex [Mabcd] exists as two isomers. *a*, *b*, *c* and *d* are monodentate ligands. Predict its shape (geometry).
9. How will you distinguish between $[Pt(NH_3)_4SO_4](OH)_2$ and $[Pt(NH_3)_4(OH)_2]SO_4$? What type of isomerism is illustrated by this pair of complexes.
*10. A complex , [Mabcd] where *a*, *b*, *c* and *d* are monodentate ligands, exists as three isomers. Predict its shape. Sketch their shapes.
*11. The isomers of $[Cu(NH_3)_4Cl_2]$ are not separable; rationalize this observation.
12. Name and sketch the structures of the following complexes and indicate if any cis, trans and optical isomers.

    a) $[Pt(NH_3)_2(NO_2)_2]$ b) $[Zn(NH_3)(py)(I)(CN)]$ c) $[Cr(C_2O_4)_2Br_2]^{3-}$

    d) $[Ni(NH_3)_4Br_2]$ e) $[Co(en)_2Cl_2]^+$

*13. Is *all cis*-$[Cr(H_2O)_2(NH_3)_2Cl_2]^+$ optically active?
14. How many geometrical isomers are possible for the octahedral complex, $[Cr(NH_3)_3(NO_2)_3]$?
*15. Consider the formula $[CrCl_2(ox)_2]^{3-}$. Can it exhibit geometrical isomerism? If so, draw the isomeric geometries. Can it exhibit optical isomerism? Explain.
16. Sketch the isomers of $[Co(en)_2Cl_2]^+$ Identify them.
17. Draw the optical isomers of $[Zn-EDTA]^{2-}$
18. How are the following pairs of complexes differentiated?

    a) $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$

    b) $[Cr(NH_3)_5NO_3]Cl$ and $[Cr(NH_3)_5Cl]NO_3$

    c) $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

d) $[Pd(NH_3)_2(SCN)_2]$ and $[Pd(NH_3)_2(NSC)_2]$

e) $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

f) cis-$[PtCl_2(NH_3)_2]$ and trans-$[PtCl_2(NH_3)_2]$

g) $[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_4][PtCl_4]$

*19. Sketch all the possible isomers of a square-planar complex [Mabcd]

20. cis-$[Pt(NH_3)_2Cl_2]$, known as cis-platin is the anticancer drug. Only the cis-isomer is clinically active against tumours. But the trans-isomer is totally ineffective. Why?

*21. Sketch all possible isomers of $[Co(NH_3)_2(H_2O)_2Cl_2]^+$

*22. A coordination compound of empirical formula, $[PdCl_2(NH_3)_2]$, does not give NH_3 on treatment with HCl. Its molar conductance corresponds to 2 ions. Its aqueous solution gives no precipitate with $AgNO_3$. Its molecular weight is about 423. Give the formulae for two possible isomers of this compound. Name the isomerism illustrated by this compound.

*23. 0.2664 g of a compound of composition $CrCl_3.6H_2O$ was kept over con. H_2SO_4 in a closed vessel for about a week. After a week it was found to weigh 0.2484 g. Formulate the complex. What fraction of the total chloride content will get precipitated as AgCl on treatment with a slight excess of $AgNO_3$ solution? Name the type of isomerism illustrated by such a compound.

24. Soft metal ions such as Pd^{2+} and Hg^{2+} form sulphur – bonded thiocyanate complexes, whereas relatively hard metal ions such as Cr^{3+} and Fe^{2+} form nitrogen – bonded thiocyanate complexes. Explain.

25. Draw all the isomers of an octahedral complex which has six monodentate ligands, two of type X and four of type Y, $[MX_2Y_4]$

26. The diamminedifluorodiiodochromate (III) ion has six isomers. Sketch their structures and identify the enantiomers.

27. How many coordination isomers could be formed from $[Pt(NH_3)_4][PdCl_4]$?

28. Give the formulae for four polymerization isomers derived from $[Co(NH_3)_3Cl_3]$.

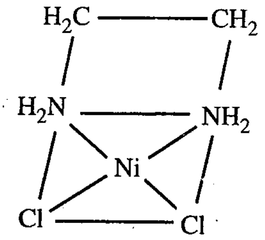
29. Write the formulae for two polymerization isomers derived from $[Pt(NH_3)_2(NO_2)_2]$.

*30. 0.3996 g of Cr(III) aqua complex of composition $CrCl_3.6H_2O$ gave 0.6452 g of AgCl on treatment with slight excess of $AgNO_3$ solution. Formulate its composition.

*31. 0.5328 g of a complex of composition $CrCl_3.6H_2O$ gave 0.5734 g of AgCl on treatment with a slight excess of $AgNO_3$ solution. Formulate the complex.

*32. 0.2664 g of Cr(III) aqua complex whose composition is $CrCl_3.6H_2O$, gave 0.1434 g of AgCl when treated with an excess of $AgNO_3$ solution. Formulate its composition.

*33. a) Aqueous solutions of equimolar concentrations of these complexes given in questions 30, 31 and 32 are prepared separately in very dilute conditions. Their molar conductivities are determined experimentally. Arrange them in the order of decreasing molar conductivities.



only cis-isomer

Fig. 8-g

7. Since coordination is four, it can be either square-planar or tetrahedral . It is a square-planar complex because geometrical isomerism is not possible for a tetrahedral arrangement.
8. It is tetrahedral in geometry which can exist as two optical isomers.

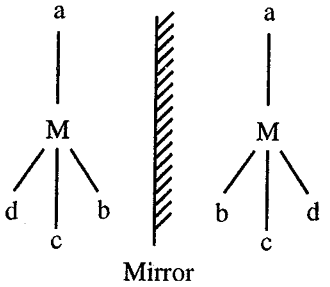
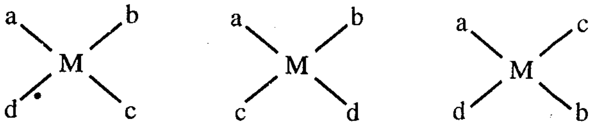


Fig. 8-h

10. Complex is 4-coordinated; either tetrahedral or square-planar. If tetrahedral, there could be only two isomers *d*- and *l*-forms. But it exists as three isomers. Hence it should be square-planar. They are,



(a) *(b)* *(c)*

Fig. 8-i

11. This Cu(II), d^9 complex can exist in cis-trans isomeric forms. The inability to separate these isomers indicates that the isomerization between them is rapid; the isomers are labile and rapid ligand substitution is possible.
13. Yes, because the object and its mirror image are not superimposable even after the former is rotated.

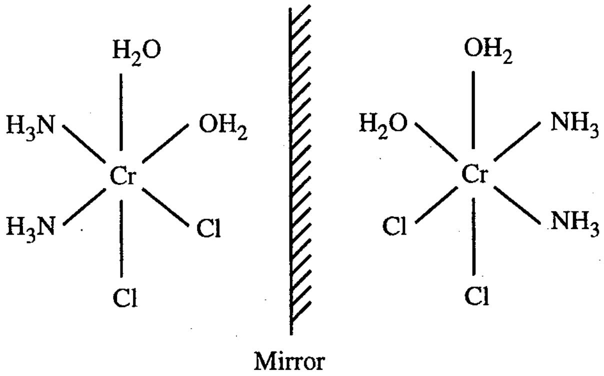


Fig. 8-j

15. This complex ion should be octahedral. It can exhibit geometrical isomerism:

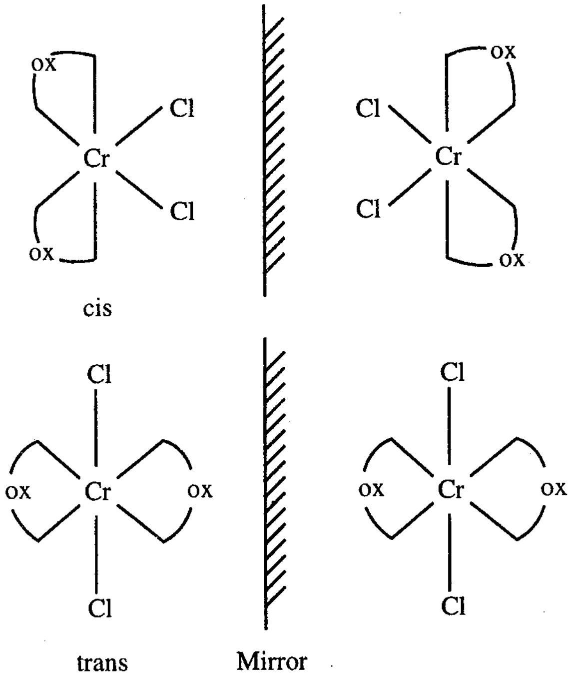


Fig. 8-k

The mirror image of the cis-isomer is not superimposable on the original structure. Therefore, this isomer is chiral and can exhibit optical isomerism. The enantiomers are dissymmetric. The mirror image of the trans-isomer is superimposable on the original structure; therefore it is achiral and cannot exhibit optical isomerism.

19. Three isomers are possible:

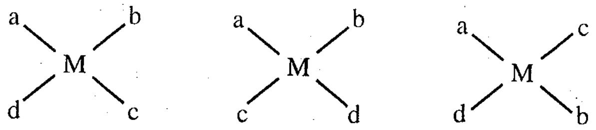


Fig. 8-l

21. This complex has a variety of geometrical isomers. Each ligand could be trans to one like it, as shown in Fig. (a)

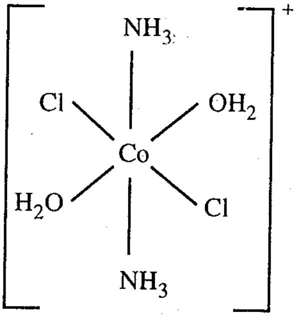


Fig. 8-m-a

or the NH_3 molecules could be trans to each other with two cis H_2O ligands and two cis Cl ligands as in Fig. (b).

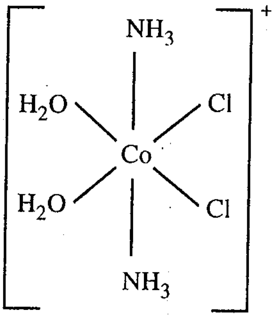


Fig. 8-m-b

Similarly, the H_2O molecules or the Cl ligands could be trans to each other while the other similar ligand pairs are cis (Fig. (c) and Fig. (d)).

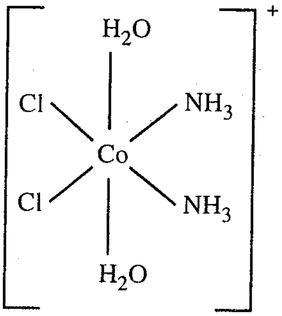


Fig. 8-m-c

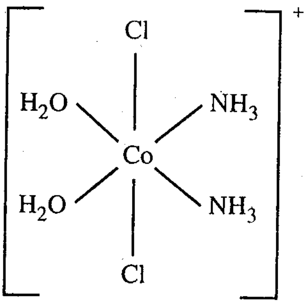
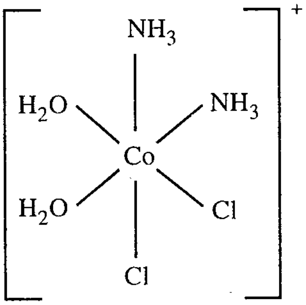


Fig. 8-m-d

Finally, every could be cis; in this case two different arrangements are possible, Fig. (e) and Fig. (f).



Mirror

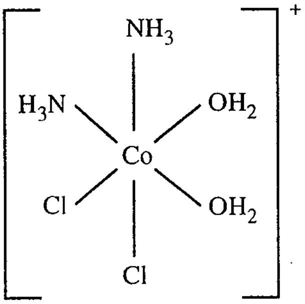


Fig. 8-m-e

Fig. 8-m-f

Thus, $[Co(NH_3)_2(H_2O)_2Cl_2]^+$ complex has a total of six geometrical isomers, the last two being pair of identical ligands a pair of optical isomers.

22. The complex formula is $[Pd(NH_3)_4][PdCl_4]$
The other isomer is $[Pd(NH_3)_3Cl][Pd(NH_3)Cl_3]$
They illsutrate coordination isomerism.

23. Formula of the complex is $[Cr(H_2O)_5Cl]Cl_2.H_2O$
Since two chloride groups are in the ionisation sphere, 2/3 of the total chloride content will get precipitated as AgCl on treatment with a slight excess of $AgNO_3$ solution.
1 g mole of the complex loses 1 g mole of water. Hence one H_2O is in the second coordination sphere as shown in the above formula.
Hydrate isomerism is illustrated by such a compound.

30. $[Cr(H_2O)_6Cl_3]$

31. $[Cr(H_2O)_5Cl]Cl_2.H_2O$

32. $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

33. a) $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2.H_2O$, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$
b) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ shows maximum weight loss.
$[Cr(H_2O)_6]Cl_3$ will not show any weight loss.
c) Hydrate isomersim.

34. a) A is $[Cr(H_2O)_3Cl_3].3H_2O$
B is $[Cr(H_2O)_5Cl]Cl_2.H_2O$
C is $[Cr(H_2O)_4Cl_2]Cl.2H_2O$
b) $[Cr(H_2O)_6Cl_3]$
c) $[Cr(H_2O)_3Cl_3].3H_2O$

35. When a complex of composition [Mabcd] exists as two isomers, it should be tetrahedral in geometry. If it exists as three isomers then its geometry should be square-planar.

39. a) and d)

Chapter 9

Reactions of Metal Complexes I

Metal complexes undergo a variety of reactions like other inorganic molecules. The reactivities of the complexes, however, are not equal. Some react fast and some others react very slow.

9.1 LABILE AND INERT COMPLEXES

A complex which reacts rapidly is called a *labile complex.* A complex which reacts slowly is an *inert complex.* The word *inert* used here indicates only slowness of reaction but not inability to react. These two terms, labile and inert relatively refer to rates of reactions and are not related to instability and stability. The term stability or instability refers to the thermodynamic character of the complex to exist under equilibrium conditions. For example, $[Hg(CN)_4]^{2-}$ is thermodynamically very stable. The thermodynamic stability of a complex is related to its formation constant; higher is its formation constant (β), greater the stability. Thus for $[Hg(CN)_4]^{2-}$, the formation constant is very high.

$$Hg^{2+} + 4CN^- \rightleftharpoons [Hg(CN)_4]^{2-}$$

$$\beta = 1 \times 10^{42}$$

The kinetic nature of this complex (lability or inertness) is not decided by its thermodynamic stability alone; it is influenced by other factors also, such as the nature of the other reactant, temperature, solvent, etc. Though $[Hg(CN)_4]^{2-}$ is thermodynamically stable, it can react fast with some reagents. For example, its exchange reaction with isotopically-labelled cyanide ion is extremely rapid:

$$[Hg(CN)_4]^{2-} + {}^*CN^- \longrightarrow [Hg(CN)_3\,{}^*CN]^{2-} + CN^-$$

On the other hand $[Co(NH_3)_6]^{3+}$ is thermodynamically unstable; it has a low β value.

$$Co^{3+} + 6\,NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$$

$$\beta = 1 \times 10^{-25}$$

However, $[Co(NH_3)_6]Cl_3$ can be prepared from aqueous medium and stored in the laboratory. This is possible because its reaction with H_2O in acid medium is very slow.

$$[Co(NH_3)_6]^{3+} + 6H_3O^+ \rightleftharpoons [Co(H_2O)_6]^{3+} + 6NH_4^+ \quad : \text{slow}$$

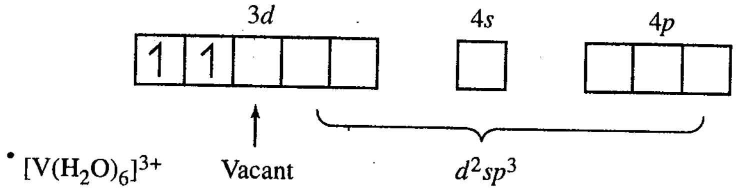
Thus, $[Hg(CN)_4]^{2-}$ is stable but labile; $[Co(NH_3)_6]^{2+}$ is thermodynamically unstable, but inert. Unlike these two complex ions, $[Fe(CN)_6]^{3-}$ is stable and inert.

> The terms "labile" and "inert" as applied to the reactivity of complexes are only relative. Generally, complexes (of 0.1 M) that react completely within about one minute should be considered labile and those that take longer time should be considered inert.

9.1.1 VBT Explanation of Lability and Inertness

According to the VBT, the octahedral complexes are of two types, namely, (i) outer orbital complexes which use sp^3d^2 hybridisation and (ii) inner orbital complexes which use d^2sp^3 hybridisation. Outer orbital complexes are generally labile. This lability is correlated with the weakness of the bonds of sp^3d^2 type as compared with d^2sp^3 bonds. For example, Mn^{2+} (d^5), Fe^{2+} (d^6), Fe^{3+} (d^5) and Co^{2+} (d^7), all high-spin complexes (outer orbital complexes), exchange their ligands rapidly and hence are labile.

In the inner orbital complexes, if all the three t_{2g} levels are filled either singly or doubly, then they are inert kinetically. If an inner orbital complex contains one or two electrons in the t_{2g} set, then at least one level will be vacant. For example, $[V(H_2O)_6]^{3+}$ contains two electrons in the $3d$ level. Two of the three t_{2g} levels are singly occupied. Hence the third level can be used to accept the electron pair donated by the incoming ligand to form a 7-coordinated intermediate which is less stable. To get itself stabilised, one of the original six ligands is expelled leading to a substitution product. This means that this complex, $[V(H_2O)_6]^{3+}$ is labile.



But in $[Cr(H_2O)_6]^{3+}$, there is no d level vacant to accept the electron pair donated by the incoming ligand; hence this complex is inert.

9.1.2 Taube's Explanation of Lability and Inertness

According to Taube, the degree of lability or inertness of a transition metal complex can be correlated with the d electronic configuration of the metal ion. If a complex contains electrons in the antibonding e_g^* orbitals, the ligands are expected to be relatively weakly bound and easily displaced; it is labile. If the metal contains an empty t_{2g} orbital, the four lobes of that orbital correspond to directions from which an incoming ligand, which is to displace one of the bound ligands, can approach the complex with relatively little electrostatic repulsion. *Therefore it may be concluded that a complex with one or more e_g^* electrons or with fewer than three d electrons* *should be relatively labile and that a complex with any other electronic configuration should be relatively inert.*

In Table 9.1, examples of octahedral complexes with all possible electronic configurations are listed and classified as labile or inert.

Table 9.1 The Taube's classification of labile and inert complexes

Complex	*d* Level structure	Labile/Inert
$[V(o\text{-phen})_3]^{3+}$	d^2	labile
$[V(H_2O)_6]^{2+}$	d^3	inert
$[Cr(H_2O)_6]^{2+}$	d^4 (high spin)	labile
$[Cr(CN)_6]^{4-}$	d^4 (low spin)	inert
$[Mn(H_2O)_6]^{2+}$	d^5 (high spin)	labile
$[Mn(CN)_6]^{3-}$	d^4 (low spin)	inert
$[Fe(H_2O)_6]^{2+}$	d^6 (high spin)	labile
$[Fe(CN)_6]^{3-}$	d^5 (low spin)	inert
$[Ni(en)_3]^{2+}$	d^8	labile

The reactions generally undergone by complexes can be classified into

1. Ligand substitution reactions
2. Electron transfer reactions
3. Reactions of coordinated ligands
4. Isomerisation reactions

9.2 LIGAND SUBSTITUTION REACTIONS

The substitution of one or more ligands in a complex by another ligand(s) is a ligand substitution reaction. This can be denoted as

$$[ML_5X]^{n+} + Y^- \longrightarrow [ML_5Y]^{n+} + X^-$$

In this reaction, the ligand X in the complex is substituted by another ligand Y^-

$$e.g.\ [Cr(H_2O)_6]^{3+} + CN^- \rightleftharpoons [Cr(H_2O)_5CN]^{2+} + H_2O$$

A ligand substitution reaction may proceed through S_N1 or S_N2 mechanism.

9.2.1 S_N1: Substitution, Nucleophilic, Unimolecular Mechanism (Dissociative Mechanism)

In this mechanism, first the reactant metal complex dissociates; the ligand to be replaced is lost from the complex. Then, the vacancy created in the coordination sphere is taken by the new ligand. This mechanism is depicted generally as

$$ML_n \rightarrow ML_{n-1} + L \quad : \text{slow dissociation}$$

$$ML_{n-1} + Y \rightarrow ML_{n-1}Y \quad : \text{fast}$$

Characteristics

1. Only one species (ML) is involved in the formation of the activated species (in the slow step).
2. In the second step, the activated species undergoes fast reaction with the incoming ligand Y.
3. The activation energy for the first step is high and that for the second step is low.
4. The rate of the over-all reaction depends upon $[ML_n]$, not upon [Y].
5. The reaction is first order with respect to ML_n; it is zero order with respect to Y.
6. In the formation of the activated complex in an S_N1 reaction, the coordination number of the metal is decreased by one (n to $n-1$).
7. The rate law for this substitution is

$$v = k_1 [ML_n]$$

where v is the rate and k_1 is the first order rate constant.

Example

$$\begin{tikzcd} {[Cr(H_2O)_6]^{3+}} \arrow[r, "\text{slow}"] & {[Cr(H_2O)_5]^{3+} + H_2O} \arrow[d, "+CN^-"', "\text{fast}"] \\ & {[Cr(H_2O)_5CN]^{2+}} \end{tikzcd}$$

five-coordinated intermediate

The rate law for this reaction is

$$v = k_1 [[Cr(H_2O)_6]^{3+}]$$

According to this mechanism, the rate of the reaction is directly proportional to the concentration of $[Cr(H_2O)_6]^{3+}$; it is independent of the concentration of CN^-

9.2.2 S_N2: Substitution, Nucleophilic, Bimolecular Mechanism (Associative Mechanism)

This mechanism is depicted in the general form as

$$ML_n + Y \rightarrow ML_nY \quad : \text{slow association}$$
$$ML_nY \rightarrow ML_{n-1}Y + L \quad : \text{fast}$$

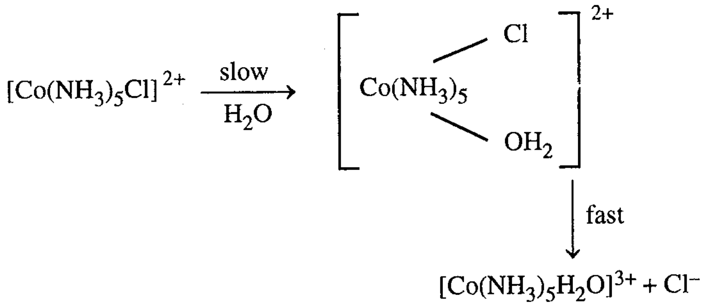
Characteristics

1. In this reaction, two species (ML_n and Y) are involved in the formation of the activated species; Y is added to the reactant complex to form the activated species.
2. In the second fast step, the activated complex loses a ligand (L) and the new ligand Y becomes a permanent part of the molecule.
3. The rate of the over-all reaction depends upon both $[ML_n]$ and [Y].

4. The reaction is first order with respect to ML_n and first order with respect to Y; it is over-all second order.
5. In the formation of the activated species, the coordination number of the metal is increased (n to n+1).
6. The general rate law for this reaction is

$$v = k_2\,[ML_n]\,[Y]$$

This mechanism may be illustrated with the hydrolysis of $[Co(NH_3)_5Cl]^{2+}$:



The rate of this reaction is proportional to the product of the concentrations of the two reactants:

$$v = k_2\left[[Co(NH_3)_5Cl]^{2+}\right][H_2O]$$

The expectation that a reaction would occur exclusively either by the S_N1 mechanism or by the S_N2 mechanism is not realistic. In a reaction, the attachment of Y to M and the release of L from M can be simultaneous. In addition, the activated species cannot be directly detected.

9.2.3 S_N1CB : Substitution Nucleophilic Unimolecular Conjugate Base Mechanism

Characteristics

1. In this mechanism, one of the ligands in the complex is converted into its conjugate base (CB) by the action of a base (normally OH^-). This first step is fast.
2. Then in the second step, which is rate-determining, the conjugate base dissociates releasing the ligand to be replaced.
3. Subsequently, the new ligand is added to the remaining part of the complex species, leading to the product.
4. This mechanism is called unimolecular because in the slow step only one molecule (ion as shown in the mechanism) is involved.
5. But the kinetics is second-order because the concentration of the complex and the concentration of the base (OH^-) are involved *upto* the slow step.
6. The rate of this reaction is denoted as

$$v = k_2\,[ML_n]\,[OH^-]$$

For this mechanism, the reacting complex should have at least one protonic hydrogen atom on a non-leaving ligand. This mechanism may be illustrated with the hydrolysis of $[Co(NH_3)_5Cl]^{2+}$:

$$[Co(NH_3)_5Cl]^{2+} + OH^- \rightleftharpoons \underset{\text{conjugate base}}{[Co(NH_3)_4NH_2Cl]^+ + H_2O}$$

$$[Co(NH_3)_4NH_2Cl]^+ \xrightarrow{\text{slow}} [Co(NH_3)_4NH_2]^{2+} + Cl^-$$

$$[Co(NH_3)_4NH_2]^{2+} + H^+OH^- \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{2+}$$

$$v = k_2\,[[Co(NH_3)_5Cl]^{2+}]\,[OH^-]$$

It is actually a hydrolytic reaction, Cl^- getting replaced by OH^-. For the hydrolysis of cobalt ammines, the reaction rates are about million times faster with base (pH > 10) compared to acid hydrolysis.

The rate constants for some substitution reactions are given in Table 9.2.

Table 9.2 Rate constants for some substitution reactions in metal complexes at 25°C.

Reaction	Rate constant
$[Co(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{3+} + Cl^-$	$k_1 = 6.7 \times 10^{-6}\ sec^{-1}$
$[Cr(H_2O)_5I]^{2+} + H_2O \longrightarrow [Cr(H_2O)_6]^{3+} + I^-$	$k_1 = 8.4 \times 10^{-5}\ sec^{-1}$
$[Co(NH_3)_5Br]^{2+} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + Br^-$	$k_2 = 7.5\ M^{-1}\ sec^{-1}$

9.2.4 Anation Reaction

This is a kind of ligand substitution reaction. In this reaction, one or more H_2O ligands in a complex are replaced by an anion:

$$[Co(CN)_5H_2O]^{2-} + CN^- \longrightarrow [Co(CN)_6]^{3-} + H_2O$$

Anation reactions follow second order kinetics, the rate being dependent on $[X^-]$ also. One of the mechanisms suggested for these reactions is depicted below.

$$[Co(NH_3)_5H_2O]^{3+} \underset{-H_2O}{\overset{\text{slow}}{\rightleftharpoons}} [Co(NH_3)_5]^{3+} \underset{+X^-}{\overset{\text{fast}}{\rightarrow}} [Co(NH_3)_5X]^{2+}$$

In this mechanism, an equilibrium between the aquacomplex $[Co(NH_3)_5H_2O]^{3+}$ and the five-coordinated intermediate is assumed to exist. As X^- is expected to compete with the solvent H_2O for the formation of the active intermediate, the rate of formation of $[Co(NH_3)_5X]^{2+}$ would be dependent on $[X^-]$. If $[X^-]$ is very high, then, the rate of replacement of H_2O would no longer be dependent on $[X^-]$;

at such high X^- concentrations, the rate of formation of $[Co(NH_3)_5X]^{2+}$ should be equal to the rate of formation of $[Co(NH_3)_5]^{3+}$.

A large number of negative ligands (X^-) effect anation reactions with complexes of Co(III) and Fe(III). The rate constants for some such reactions are listed in Table 9.3.

Table 9.3 Rate constants for some anation reactions at 25°C and $\mu = 0.5$

$[Co(NH_3)_5H_2O]^{3+} + X^- \rightarrow [Co(NH_3)_5X]^{2+} + H_2O$

X^-	$10^6 k_2 / M^{-1}s^{-1}$
Cl^-	2.1
Br^-	2.5
NO_3^-	2.3
NCS^-	1.3
SO_4^{2-}	15.0
$H_2PO_4^-$	2.0

9.3 ELECTRON-TRANSFER REACTIONS (REDOX REACTIONS)

In an electron-transfer reaction, an electron is transferred from one complex to another:

$$[Cr(H_2O)_6]^{2+} + [IrCl_6]^{2-} \longrightarrow [Cr(H_2O)_6]^{3+} + [IrCl_6]^{3-}$$

In the reaction given above, an electron has been transferred from the chromium complex to the iridium complex. Thus the chromium complex gets oxidised and the iridium complex gets reduced. This is a simple redox reaction. An electron-transfer can occur between two complexes of the same metal, the metal being present in two oxidation states in the two reactants:

$$[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$$

No net change in the stochiometry occurs in such an electron-transfer as all the concentrations *apparently* remain unchanged; there is no net chemical change. But this reaction involving electron-transfer, can be proved by labelling one of the reactants. For example, if labelled iron(II) is used, then, after the reaction, the labelled iron will be found in Fe(III) state also.

$$[Fe^*(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} \rightarrow [Fe^*(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$$

The kinetics of this reaction can be followed by estimation of Fe* either as Fe(III) or Fe(II). The energy of activation, for this reaction is 33 kJ mol^{-1}. An electron is transferred from a t_{2g} orbital of Fe(II) to a t_{2g} orbital of Fe(III). Table 9.4 gives the second-order rate constants for some electron transfer reactions.

An electron-transfer with no net chemical change is called an *electron-exchange* reaction. No net free energy change occurs in this reaction.

For this process, a sketch of the energy versus reaction coordinate is indicated in Fig. 9.1.

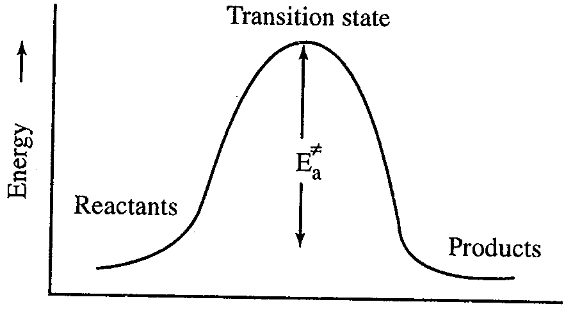


Fig. 9.1 *Profile of the energy versus reaction coordinate for an electron transfer reaction with identical reactants and products*

Table 9.4 Rate constants for some electron-transfer reactions

Reaction between	Temp(°C)	$k_2/M^{-1}sec^{-1}$
$[Fe(H_2O)_6]^{2+}$ — $[Fe(H_2O)_6]^{3+}$	0	0.87
$[Fe(CN)_6]^{4-}$ — $[Fe(CN)_6]^{3-}$	4	7.4×10^{-2}
$[Co(NH_3)_6]^{2+}$ — $[Co(NH_3)_6]^{3+}$	25	1.7×10^{-7}
$[Mo(CN)_8]^{4-}$ — $[Mo(CN)_8]^{3-}$	25	3.0×10^{4}
$[Fe(CN)_6]^{4-}$ — $[Mo(CN)_8]^{3-}$	25	1.0×10^{2}

Two types of mechanisms are known for electron-transfer reactions:

1. The outer-sphere mechanism
2. The inner-sphere mechanism

9.3.1 Outer-sphere Mechanism (OSM): Tunnelling Mechanism

1. In this mechanism, the electron hops across from the reductant to the oxidant. The coordination spheres remain unaffected. The ligands in the two reactants remain as such and bonds are neither made nor broken. The reduction of $[Co(NH_3)_6]^{3+}$ by $[Cr(H_2O)_6]^{2+}$ occurs through OSM:

   $$[Cr(H_2O)_6]^{2+} + [Co(NH_3)_6]^{3+} \rightarrow [Cr(H_2O)_6]^{3+} + [Co(NH_3)_6]^{2+}$$

   The electron is set to *tunnel through* the medium from the reductant to the oxidant.

2. As there is no movement of any ligand, the Franck-Condon activation barrier for this process is small.

   The energy $E_a^{\#}$ is constituted by three portions:

   (i) the electrostatic energy arising from repulsion between the species of like charge.

   (ii) the energy required to distort and reorient the two coordination spheres for easy flow of electron and

   (iii) the energy needed to modify the solvent structure about each reactant species.

3. This mechanism is expected of reactants which are not labile complexes. The ligands in the two reactants are so firmly attached that one complex does not form any bond with the other involving its ligands. Even if one of the reactants is labile, the other would not offer a suitable site for attachment of the metal ion of the labile complex; hence only OSM is possible. This is the case with $[Co(NH_3)_6]^{3+}$ — $[Cr(H_2O)_6]^{2+}$ pair; $[Cr(H_2O)_6]^{2+}$ is labile but not $[Co(NH_3)_6]^{3+}$. The firmly bound NH_3 ligands in the cobalt complex do not offer their unshared electron pairs for attachment to the Cr^{2+}.
4. Outer-sphere reactions are first order in each reactant, the over-all order being two.
5. These reactions are sensitive to the ionic strength of the medium and hence subjected to salt effects. This is understandable as the reaction involves transfer of electron (a charged entity) from the reactant to the oxidant through the medium.
6. An outer-sphere electron-transfer can be denoted by the following reaction scheme:
   (i) The oxidant (O) and the reductant (R) interact and form a *precursor complex.*

   $$O + R \rightarrow O - - - R$$

   (ii) In the second step, the precursor complex is activated, which is a prerequisite for reaction.

   $$O - - - R \rightarrow (O - - - R)^*$$

   The energy of activation can be acquired by $O - - - - R$ from other O and R molecules or from the solvent molecules.

   (iii) Then changes in the metal-ligand bond length occur, the molecular framework remaining intact (without bond breaking).

   $$(O - - - R)^* \rightarrow (\overset{-}{O} - - - - - - - \overset{+}{R})$$

   In this step, the electron from the reductant is displaced towards the oxidant, producing an ion pair.

   (iv) In the final step, the ion pair breaks into product ions.

   $$(\overset{-}{O} - - - - - - - \overset{+}{R}) \rightarrow \overset{-}{O} + \overset{+}{R}$$

Essential requisite for electron-transfer For easy electron-transfer, the reductant and oxidant should have similar structures. This is so with $[Fe(H_2O)]^{2+}$ and $[Fe(H_2O)_6]^{3+}$. The Franck-Condon principle assumes that an electron moves very quickly compared to an atom; therefore, during the electron-transfer, no rearrangement of atoms (which is slow) is possible. In addition, this principle prescribes equal energies for the participating electronic orbitals. In the $[Fe(H_2O)]^{2+}$ — $[Fe(H_2O)_6]^{3+}$ reaction, an electron is transferred from a t_{2g} orbital of Fe(II) to a t_{2g} orbital of Fe(III). The energies of these two orbitals are not equal and so is the case with the bonds in them.

If electron-transfer occurs as such without any energy input, then, the product Fe(II) complex would have bond lengths characteristic of Fe(III) and the Fe(III) complex product would have bond lengths characteristic of Fe(II). Since such a situation is unacceptable, energy input must *precede* electron-transfer. This energy input causes shortening of the bonds in Fe(II) reactant complex and lengthening of the bonds in Fe(III) reactant complex so that the participating orbitals are modified to have the same energy. After these readjustments of the bond lengths, the electron jump occurs. The energy involved in the readjustments of the bond lengths is small because the geometries of the two reactants are similar. Thus, the bond length adjustment is critical for ease of electron-transfer in OSM.

Explain the following OSM electron-transfer rate data:

System	$k_2 / M^{-1}s^{-1}$	Metal-N bond length difference (Å)
1. $[Ru(NH_3)_6]^{2+} / [Ru(NH_3)_6]^{3+}$	8.2×10^2	0.04
2. $[Co(NH_3)_6]^{2+} / [Co(NH_3)_6]^{3+}$	1.0×10^{-6}	0.178
3. $[Co(phen)_3]^{2+} / [Co(phen)_3]^{3+}$	40.0	0.178

In the first case, the bond length difference is very low and therefore only a minimum adjustment of length in the two reactants is needed; consequently, the rate is high. In the second case, the bond length difference, $(Co^{2+} - N) - (Co^{3+} - N)$ is large. Prior to electron-transfer, large readjustments of bond lengths have to occur, requiring a large energy of activation; therefore, this reaction has a low rate constant. In addition, electronic configurations in cobalt ions [$t_{2g}^5 e_g^2$ Co(II) and t_{2g}^6 Co(III)] being dissimilar inhibit the redox reaction. Reaction 3, on the basis of same argument should be slow; however, it is fast. This is explained based on the nature of the ligand in it. The *phen* ligand has a π electron system which permits easy passage of electron from the reductant to oxidant. Thus, the nature of the ligand greatly influences the speed of electron-transfer reactions.

Electron transfer and M.O. symmetry The highest occupied molecular orbital (HOMO) of the reductant is the donor orbital and the lowest unoccupied molecular orbital (LUMO) of the oxidant is the receptor orbital. If either of these molecular orbitals does not meet the symmetry requirements for effective electron-transfer, then higher chemical activation – involving strong deformation and electron configuration change – is necessary for reaction. This factor is a qualitative guide to guess the speed of electron-transfer reactions. Each of the following OS electron-transfers involves symmetric molecular orbitals.

				$k_2 / M^{-1}s^{-1}$
a)	$[Fe(H_2O)_6]^{2+}$	+	$[Fe(H_2O)_6]^{3+}$	4.0
	$(\pi^*)^4(\sigma^*)^2$		$(\pi^*)^3(\sigma^*)^2$	$\pi^* \rightarrow \pi^*$ transfer
b)	$[Fe(phen)_3]^{2+}$	+	$[Fe(phen)_3]^{3+}$	3.0×10^7
	$(\pi^*)^6$		$(\pi^*)^5$	$\pi^* \rightarrow \pi^*$ transfer
c)	$[Co(H_2O)_6]^{2+}$	+	$[Co(H_2O)_6]^{3+}$	5.0
	$(\pi^*)^5(\sigma^*)^2$		$(\pi^*)^6$	$\sigma^* \rightarrow \sigma^*$ transfer

FACTORS WHICH FAVOUR OUTER-SPHERE ELECTRON-TRANSFER REACTIONS

- similar structures / geometries for the reactants.
- equivalent energies of donor and recipient metal orbitals.
- equal bond lengths in the two metallic systems or only small difference in bond lengths.
- ligands with π electron systems.
- complexes which are not labile.

Cross reactions: Marcus-Hush principle Reactions between two completely different complex ions or molecules is a cross reaction.

Example $V^{2+} + [Ru(NH_3)_6]^{3+} \rightarrow$ products

A cross reaction involves large chemical activation; however, it is fast because the large $E_a^{\#}$ requirement is partly compensated by an attendant negative free energy change. For cross reactions, $\Delta G^{\#} < 0$; the products are more stable than reactants. The rate is maximum when the electron is transferred from a π^* to a π^* orbital (Table 9.5).

Table 9.5 Examples for cross reactions

Reductant	**Oxidant**	$E_a^{\#}$	**Electron transfer**	$k_2 / M^{-1}s^{-1}$
V^{2+}	$[Ru(NH_3)_6]^{3+}$	0	$\pi^* \rightarrow \pi^*$	80
V^{2+}	$[Co(NH_3)_6]^{3+}$	required	$\sigma^* \rightarrow \pi^*$	1.0×10^{-2}
Cr^{2+}	$[Co(NH_3)_6]^{3+}$	required	$\sigma^* \rightarrow \sigma^*$	1.0×10^{-2}

The rate constant of a cross reaction involving the OSM can be predicted by an equation proposed by Marcus and Hush:

$$k_{1,2} = (k_1 k_2 K_{1,2} f)^{1/2}$$

$k_{1,2}$ is the rate constant for the cross reaction

k_1 and k_2 each is the rate constant for electron-exchange species of the same metal.

$K_{1,2}$ is the equilibrium constant for the cross reaction

The term f is close to 1 and is given by

$$\log f = (\log K_{1,2})^2 \Big/ 4 \log \frac{k_1 k_2}{z^2}$$

z = measure of collision frequency

This equation, called *Marcus-Hush Equation* can now be applied to an example: The rate constant for the cross electron-transfer

$$[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \xrightarrow{k_{1,2}} [Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$$

can be predicted from the rate constants of the reactions

$$[Fe(CN)_6]^{4-} + [Fe^*(CN)_6]^{3-} \xrightarrow{k_1} [Fe^*(CN)_6]^{3-} + [Fe(CN)_6]^{4-}$$

$$[Mo(CN)_8]^{4-} + [Mo^*(CN)_8]^{3-} \xrightarrow{k_2} [Mo^*(CN)_8]^{3-} + [Mo(CN)_8]^{4-}$$

by substituting the *experimentally measured* k_1 and k_2 values in the Marcus-Hush equation.

Good agreement between the calculated $k_{1,2}$ values and the experimentally determined $k_{1,2}$ values has been noticed with several cross reactions. For example, the calculated $k_{1,2}$ is $1.6 \times 10^{-3} M^{-1} s^{-1}$ and the experimental $k_{1,2}$ is $1.0 \times 10^{-3} M^{-1} s^{-1}$ for the reaction,

$$Cr^{2+} + [Co(NH_3)_6]^{3+} \rightarrow \text{products}$$

Such agreements substantiate the validity of the Marcus-Hush principle.

9.3.2 Inner-sphere Mechanism (ISM)

Characteristics

1. In this mechanism, the oxidant and the reductant attach themselves to one another at some stage of the reaction. (In the OSM, at no stage of the reaction, the two reactants are attached to one another).
2. Activation is required for the two reactant molecules to orient themselves in proper configurations for reaction.
3. There should be atleast one ligand (in one reactant) capable of binding simultaneously to two metals, however transiently.
4. The attachment between O and R occurs through a bridging ligand (molecule, atom or ion).
5. In this mechanism, a ligand is shared between the reductant and oxidant in their inner (primary) coordination sphere.
6. This bridge helps the transfer of electron from the R to O, the electron presumably passing through the bridging ligand.
7. The intermediate formed in this reaction is binuclear.
8. Unlike with the OSM, here bonds are broken and made during reaction; therefore, this mechanism is more complicated than OSM.
9. The rate-determining step is the electron-transfer step and not the complex formation step.
10. One ligand of one reactant (usually the reductant) must be substitutionally labile; that is, it should be capable of getting replaced by a bridging ligand in an easy substitution process.

Example Taube's Reaction

Taube's reaction is the IS redox reaction between $[Cr(H_2O)_6]^{2+}$ and $[(NH_3)_5CoCl]^{2+}$:

$$\overset{\text{(II)}}{[Cr(H_2O)_6]^{2+}} + \overset{\text{(III)}}{[(NH_3)_5CoCl]^{2+}}$$

$$\downarrow$$

$$\underset{\text{bridged activated complex}}{[(H_2O)_5Cr.........Cl........Co(NH_3)_5]^{4+}} + H_2O$$

$$\downarrow \text{slow}$$

$$\overset{\text{(III)}}{[(H_2O)_5CrCl]^{2+}} + \overset{\text{(II)}}{[(NH_3)_5Co]^{2+}}$$

$$[Cr(II) \rightarrow Cr(III)] \;;\; [Co(III) \rightarrow Co(II)]$$

Proof for ISM The two important aspects of ISM are:

(i) The transfer of a particular ligand from one coordination sphere to another

(ii) The formation of a binuclear intermediate.

Therefore, the proof for this mechanism must prove these two facts.

At the end of the Cr(II) – Co(III) reaction, all the Cr(III) is found as $[Cr(H_2O)_5Cl]^{2+}$ and the Co(II) species without any Cl^- attached to it. This proves the transfer of Cl^- from the reactant Co(III) species to reactant Cr(II) species.

The formation of the bridged transition state is in accord with the following facts: The reactant Co(III) complex is not labile and therefore, the transfer of Cl^- is independent of bridge formation and electron-transfer is unlikely. When an electron is transferred from Cr(II) to Co(III), the Co-Cl bond becomes labile while the Cr-Cl bond becomes non-labile.

When the reaction is conducted in the presence of added radioactive Cl^- in solution, no radioactivity is incorporated in the product chromium complex. If Cl^- had dissociated from $[Co(NH_3)_5Cl]^{2+}$ and then the free Cl^- migrated to $[Cr(H_2O)_6]^{2+}$ through the solvent, then some added radioactive Cl^- would have been incorporated in the Cr(III) product. The absence of radioactivity in Cr(III) species proves that the chlorine is transferred direct from Co to Cr through the bridge in the redox reaction and not through the solvent.

Though the reaction pathway indicates the formation of the pentamminecobalt(II) complex, actually $[Cr(H_2O)_6]^{2+}$ is formed because the d^7 – Co(II) complex is so labile that it gets hydrolysed quickly to the aqua complex in an acidic medium.

Other redox reactions which follow this mechanism are listed in Table 9.6.

Table 9.6 Some inner-sphere electron-transfer reactions

Reductant : $[Cr(H_2O)_6]^{2+}$ Medium : Water Temperature : 25°C

Oxidant	$k_2 / M^{-1}s^{-1}$
$[Co(NH_3)_5Cl]^{2+}$	6×10^5
$[Co(NH_3)_5Br]^{2+}$	1.4×10^6
$[Co(NH_3)_5I]^{2+}$	3×10^6
$[Co(NH_3)_5N_3]^{2+}$	3×10^5
$[Co(NH_3)_5F]^{2+}$	2.5×10^5
$[Co(NH_3)_5H_2O]^{3+}$	0.5
$[Co(NH_3)_5OH]^{2+}$	1.5×10^6
$[Co(NH_3)_6]^{3+}$	8.9×10^{-5} (OSM)

The rate-accelerating role of the bridging ligand is obvious, as in its absence the complex $[Co(NH_3)_6]^{3+}$ undergoes a very slow (OSM) reaction.

The rates of electron-transfer from Fe(II) to various FeX^{2+} complexes (where $X = F^-, Cl^-, Br^-, I^-$) do not differ much.

As the rates do not differ much, the bridge mechanism is ruled out. The reactions are likely to follow OSM in which the X^- ligands do not play any significant role so as to affect the reaction rate.

The influence of the bridging ligand on IS electron-transfer The bridging ligand significantly influences the rates of inner-sphere electron-transfers. The ligands which provide the easiest path for electron-transfer cause the fastest reaction. For the halide ions, the k_2 increases with decreasing electronegativities of X. i.e., the ease with which X can part with an electron.

With the ISM, the order of effectiveness of common bridging ligands is

$$N_3^- >> I^- > Br^- > Cl^- > F^-$$

The observance of this order with a reactant complex couple can be diagnostic of the operation of the ISM in the chosen couple.

Rationalise the following observations For the reaction,

$$[Co(NH_3)_5X]^{2+} + [Cr(H_2O)_6]^{2+} \xrightarrow{H^+} [Co(H_2O)_6]^{2+} + [Cr(H_2O)_5X]^{2+} + 5\,NH_4^+$$

both OS and IS mechanisms operate simultaneously; however,

$$\frac{k_{os}(N_3^-)}{k_{os}(NCS^-)} \approx 1 \quad \text{and} \quad \frac{k_{IS}(N_3^-)}{k_{IS}(NCS^-)} >> 1$$

The nature of the ligand X on Co does not matter for the OSM as the electron presumably tunnels to the oxidant ; X has no role to play in this process. In the ISM, on the contrary, X forms a bridge between the reactants and promotes the electron-transfer. Therefore, the nature of X does matter in this mechanism. The N_3^- ligand, as a bridge in the intermediate produces a resonance structure, unlike NCS^-. This stabilises the intermediate (Fig. 9.2) and hence accelerates the reaction $[k_{IS}(N_3^-) > k_{IS}(NCS^-)]$.

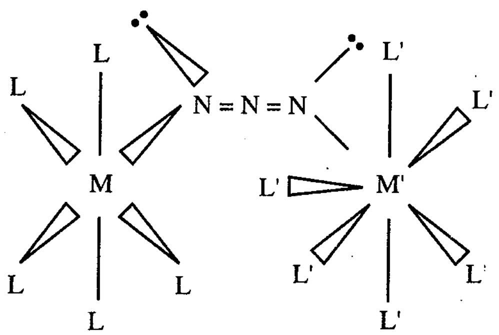
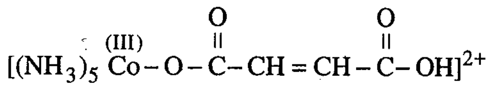
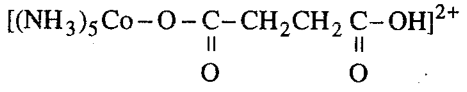


Fig. 9.2 Resonance-stabilised bridge intermediate

A conjugated ligand enables faster reaction than a nonconjugated one, as, in the former the conduction of electron over the conjugated system is easy. Thus

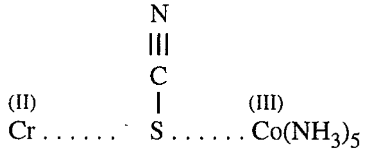

$$[(NH_3)_5\overset{(III)}{Co}-O-\overset{\overset{O}{\|}}{C}-CH=CH-\overset{\overset{O}{\|}}{C}-OH]^{2+}$$ is more rapidly reduced than


$$[(NH_3)_5Co-O-\underset{\underset{O}{\|}}{C}-CH_2CH_2\underset{\underset{O}{\|}}{C}-OH]^{2+}$$

Such an accelerated transfer of electrons with conjugated ligands is called *resonance transfer.*

When the bridging ligand is a single-atom ligand such as Cl^-, then such a ligand is necessarily bound to both the metals in the activated species. However, if it is a multi-atom ligand, such as CN^-, SCN^-, NO_2^-, etc, then the two metal atoms may not be bound to the same atom of the ligand; different atoms of the ligands may be bridging the two metals:

(a)



$$\overset{(II)}{Cr}\ldots\ldots\underset{}{\overset{\overset{N}{|||}\atop\overset{C}{|}}{S}}\ldots\ldots\overset{(III)}{Co}(NH_3)_5$$

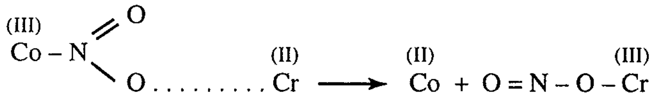
adjacent attack

(b) $\overset{(II)}{Cr}\ldots\ldots NCS\ldots\ldots\overset{(III)}{Co}(NH_3)_5$ remote attack

The adjacent attack (a) should produce $\overset{(III)}{Cr}-S-C\equiv N$ complex whereas the remote attack (b) should produce $\overset{(III)}{Cr}-N=C=S$ as products.

Actually, both the products are formed indicating that both adjacent attack and remote attack occur in the reaction. [Some reactant molecules take part in (a) and the others in (b)].

With $[\overset{(III)}{Co}(NH_3)_5NO_2]^{2+}$ oxidant only the remote attack is likely :



The Cr(III) product would be a nitrito complex. However, the kinetically-favoured nitrito complex quickly isomerizes to the thermodynamically-favoured nitro complex.

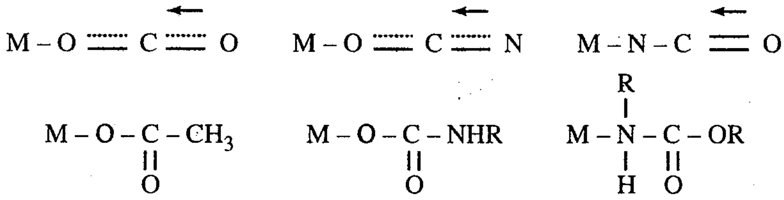
When a ligand such as ethyl carbamate (urethane) is bonded to $[Co(NH_3)_5]^{3+}$ through a nitrogen atom, the reduction rate is very high compared to a ligand bonded through an oxygen (Table 9.7.)

Table 9.7 Rates of reduction of $[Co(NH_3)_5X]^{n+}$ by Cr(II) at 25°C

X	$k / M^{-1}s^{-1}$
acetato	0.18
carbamic acid	9.1
urethane	400
imidazole	1×10^{-4}
pyridine	6×10^{-3}

The greater rate of reduction is related to the greater covalency of the metal-nitrogen bond compared to the metal-oxygen bond. Electron donation from Cr(II) into the e_g orbital of Co(III) is facilitated through the covalent (σ) bond. The rates for the acetato, carbamato and urethano complexes are accordingly in the ratio 1 : 50 : 2200.

The bonds for the bridging ligands may be denoted as



With the imidazole and pyridine complexes, involving the bond system N=C–N, the rates of reduction are found to be very low.

In rare cases of inner-sphere reaction, the binuclear bridged intermediate has been experimentally identified; this becomes possible because of the extra stability of the intermediate, arising from the strength of the M-L bond. This is the case when a ruthenium(III) complex is used as the oxidant.

Thus, the nature of the bridging ligand significantly influences the rate of electron-transfer in complexes.

The ISM k_2 value for the electron-transfer from $[Cr(H_2O)_6]^{2+}$ to $[(NH_3)_5\,Co\text{-}OCOX]$ is 7.2 $M^{-1}s^{-1}$ when $X = CH_3$ but $9.6 \times 10^{-3} M^{-1}s^{-1}$ when $X = (CH_3)_3C$. Explain.

Explanation The bridge formation should occur through the carbonyl oxygen of the carboxyl group. A severe steric strain, hindering the formation of the bridge is expected with $(CH_3)_3C$ group; this can explain the significantly reduced k_2 with this group.

ISM and electron configuration The electron orbitals of the metals in the reactants and products involved are important in determining whether a reaction proceeds by an ISM or an OSM. To substantiate this, the following examples can be considered:

(a) $[\overset{(II)}{V}(H_2O)_6]^{2+} + [\overset{(III)}{Co}(NH_3)_5H_2O]^{3+} \rightarrow$: OSM

(b) $[\overset{(II)}{V}(H_2O)_6]^{2+} + [\overset{(III)}{Co}(NH_3)_5(C_2O_4)H^-]^{2+} \rightarrow$: ISM

In (a), a t_{2g} electron from the V^{2+} is transferred, and its orbital overlaps an orbital on Co^{3+} facilitating easy tunelling of an electron (OSM). But in (b), the low-lying π orbital of the oxalato group can interact with the donor orbital of V^{2+}, which also has π symmetry, by an inner-sphere activated complex.

M.O. symmetry and IS rates The rates of IS electron-transfers in complexes are critically dependent on the symmetries of the M.O.'s involved. The rate is highest, among other conditions being identical, when the HOMO and LUMO are of σ^* type. (Table 9.8)

Table 9.8. Rates of IS electron-transfer and M.O. symmetry

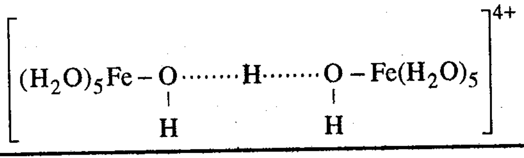
HOMO	LUMO	Example	~ $k_2 / M^{-1}s^{-1}$
σ^*	σ^*	Cr(II) / Co(III)	10^{10}
σ^*	π^*	Cr(II) / Ru(III)	10^2
π^*	σ^*	V(II) / Co(III)	10^4
π^*	π^*	V(II) / Ru(III)	No ISM; all by OSM

In σ^* to σ^* transfer, the bridging ligand is intimately involved with donor and receptor molecular orbitals and consequently the rate acceleration is maximum.

Electron-transfer with attendant H transfer In certain electron-transfer reactions involving aqua ions, hydrogen atoms are transferred. However, the evidence for this is only indirect. For example, the reaction between $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_5(OH)]^{2+}$ in H_2O is twice as fast as in D_2O. This rate ratio is normally observed in other reactions in which hydrogen atom must move.

$$\frac{k_H}{k_D} = 2$$

This reaction is believed to proceed through $Fe(OH)^{2+}$ ion via a symmetrical transition state :



$$\left[(H_2O)_5Fe-\underset{\underset{H}{|}}{O}\cdots\cdots H\cdots\cdots\underset{\underset{H}{|}}{O}-Fe(H_2O)_5\right]^{4+}$$

OSM VERSUS ISM

- The electron-transfer from $[Cr(H_2O)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$ cannot occur by the ISM. The bonded NH_3 ligand in the cobalt oxidant complex has no non-bonding electron pairs to donate (though this donation is temporary) to a second metal and form a bridge. The reaction therefore occurs through OSM. If a suitable ligand for bridging the two metals is not available, then an ISM is ruled out.
- The rate of inner-sphere reaction is always slower than the rate of exchange of the bridging ligand in the absence of a redox reaction. This is justifiable because the exchange of the ligand is an integral part of the ISM.
- If the electron-transfer is faster than ligand exchange in a complex, then an OSM is implied.
- Both OSM and ISM follow the same rate law, rate = k [oxidant] [reductant]; therefore, the rate law is of no use in distinguishing between these two.
- The bridging ligand is not transferred in all ISMs. This ligand may be left with its original metal after electron-transfer has occurred through it. Thus, ligand transfer, though common in inner-sphere reactions, is not a necessity. The ligand transfer is not favoured, if bridging ligand stabilised its original complex more than the product complex (where it is normally expected). This is illustrated by the following example:

expected : $[\overset{(III)}{Fe}(CN)_6]^{3-} + [\overset{(II)}{Co}(CN)_5]^{3-} \rightarrow$

$[\overset{(II)}{Fe}(CN)_5]^{3-} + [\overset{(III)}{Co}(CN)_5(NC)]^{3-}$

(NC, because of bridge Fe---CN---Co)

actual : $[\overset{(III)}{Fe}(CN)_6]^{3-} + [\overset{(II)}{Co}(CN)_5]^{3-} \rightarrow$

$[\overset{(II)}{Fe}(CN)_6]^{4-} + [\overset{(III)}{Co}(CN)_5]^{2-}$

The retention of the CN^- ligand in the Fe-complex is rationalised based on the fact that CN^- bonded to Fe through its C, stabilises the d^6 (Fe^{2+}) system of $[Fe(CN)_6]^{4-}$ more than the N-bound cyano group's stabilisation of d^6 (Co^{3+}) system in $[Co(CN)_5(NC)]^{3-}$.

- OSM is always possible in a redox system whereas the ISM requires certain facilitating features of the reactants. In some cases, the two mechanisms may operate simultaneously and competitively.

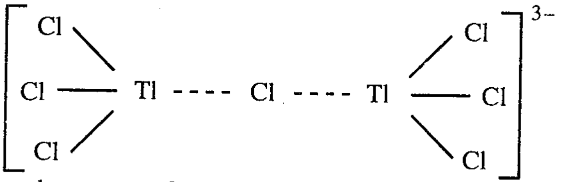
Henry Taube was awarded the Nobel Prize in Chemistry in 1983 for his extensive research on mechanisms of redox reactions of metal complexes.

9.3.3 Two-electron Transfers

Some elements exist in two stable oxidation states differing by two electrons, e.g., Tl^+ and Tl^{3+}, the oxidation state (Tl^{2+}) in between these two being unstable. Then, when a complex of Tl^+ reacts with a complex of Tl^{3+}, two electrons are transferred from the reductant to the oxidant. Such a reaction is called a two-electron transfer reaction. An example for such a reaction is

$$[TlCl_4]^- + [TlCl_3]^{2-} \rightleftharpoons [TlCl_3]^{2-} + [TlCl_4]^-$$

A mechanism involving an activated complex containing seven chloride ions has been suggested for this two-electron transfer.



Similarly, two-electron transfer reactions occur in some Pt(II) to Pt(IV) complexes.

9.3.4 Non-complementary Electron-transfer Reactions

In all the electron-transfer reactions considered so far, the oxidant and the reductant have undergone change in oxidation state by the same number.

(e.g., $Fe^{2+} \rightarrow Fe^{3+}$; $Fe^{3+} \rightarrow Fe^{2+}$). Such reactions are called *complementary reactions*. However, in the electron transfer reaction

$$2Fe^{2+} + Tl^{3+} = 2Fe^{3+} + Tl^+,$$

the reductant has changed its oxidation state by 1 unit (Fe^{2+} to Fe^{3+}) whereas the oxidant has changed its oxidation state by two units (Tl^{3+} to Tl^+). Such a reaction is called a *non-complementary reaction*. The non-complementary reactions are generally slower than complementary reactions because in the former termolecular collision is required; this is more difficult than the bimolecular collision in a complementary reaction.

9.4 REACTIONS OF THE COORDINATED LIGANDS

A ligand attached to the central metal ion may sometimes undergo a reaction. For example, one of the aqua ligands in $[Al(H_2O)_6]^{3+}$ can lose a proton by the action of a base(B):

$$[Al(H_2O)_6]^{3+} + B: \rightleftharpoons [Al(H_2O)_5OH]^{2+} + BH^+$$

In this reaction, the reaction site is the ligand. Another example for this type of reaction is

$$[Pt(NH_2C_2H_4OH)_2Cl_2] + OH^- \xrightarrow{\text{fast}} [Pt(NH_2C_2H_4OH)(NH_2C_2H_4O)Cl_2]^- + H_2O$$

Some ligands in a complex may get protonated; for example, CN^- in the following reaction:

$$[Fe(phen)_2(CN)_2] + H^+ \rightarrow [Fe(phen)_2(CN)(CNH)]^+$$

Another possibility of ligand reaction involves substitution reaction:

$$\underset{\text{Ferrocene}}{(\pi - C_5H_5)_2Fe} + CH_3COCl \xrightarrow{AlCl_3} [(\pi - C_5H_5)Fe(\pi - C_5H_4 - COCH_3)] + HCl$$

9.5 ISOMERISATION REACTIONS

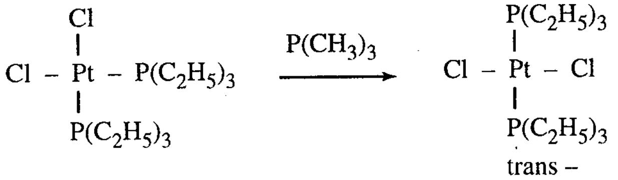
The isomerisation reactions with complexes are of two types:

(a) isomerisation involving geometrical isomers

(b) isomerisation involving optical isomers

9.5.1 Isomerisation Involving Geometrical Isomers

When cis-$[Pt\{P(C_2H_5)_3\}_2Cl_2]$ is treated with a catalytic quantity of $P(CH_3)_3$ in benzene solution, it isomerises to its trans isomer:



$$\begin{array}{c} Cl \\ | \\ Cl - Pt - P(C_2H_5)_3 \\ | \\ P(C_2H_5)_3 \end{array} \xrightarrow{P(CH_3)_3} \begin{array}{c} P(C_2H_5)_3 \\ | \\ Cl - Pt - Cl \\ | \\ P(C_2H_5)_3 \\ \text{trans} - \end{array}$$

cis-bis(triethylphosphine)dichloroplatinum(II).

Such cis-trans isomerisation occurs among octahedral complexes also. For example, a solution of cis-$K[Cr(C_2O_4)_2(H_2O)_2]$ isomerises to its trans form on slow evaporation.

9.5.2 Isomerisation Involving Optical Isomers

In this type of reaction, one optical form of an optically active metal complex forms its other form and gets racemised.

For example, when (+)-trisoxalatochromate(III) ion is placed in water, it racemises to its optically inactive form.

$$(+) - [Cr(C_2O_4)_3]^{3-} \longrightarrow (-) - [Cr(C_2O_4)_3]^{3-} \xrightarrow{(+) - \text{form}} \text{racemic mixture}$$

This racemisation has been proved to occur by an intramolecular mechanism.

The racemisation of (dextro)-cis-$[Co(en)_2(H_2O)_2]^{3+}$ occurs via the formation of its trans isomer:

$$\begin{array}{ccc} \text{(dextro)-cis-}[\mathrm{Co(en)_2(H_2O)_2}]^{3+} & \rightleftharpoons & \text{trans-}[\mathrm{Co(en)_2(H_2O)_2}]^{3+} \\ & & \uparrow\downarrow \\ & & \text{(laevo)-cis-}[\mathrm{Co(en)_2(H_2O)_2}]^{3+} \end{array}$$

UNIQUE COMPLEXATIONS

The following reaction is unique:

$$\underset{\text{yellow}}{\mathrm{K_2[\overset{(II)}{Ni}(CN)_4]+2K}} \xrightarrow{\text{liquid } \mathrm{NH_3}} \underset{\text{yellow}}{\mathrm{K_4[\overset{(0)}{Ni}(CN)_4]}}$$

This reaction involves the reduction of Ni(II) to Ni(O), the latter being an unusual low oxidation state of Ni in its complex.

Another unique reaction involving a complex is the formation of the Fe in its dinegative (2–) state through the reduction,

$$\underset{\text{yellow}}{\mathrm{Fe(CO)_5}} + 4\mathrm{KOH} \rightarrow \underset{\text{colourless}}{\mathrm{K_2[Fe(CO)_4]}} + \mathrm{K_2CO_3} + 2\,\mathrm{H_2O}$$

9.6 ELECTRON TRANSFER REACTIONS IN BIOLOGICAL SYSTEMS

Certain biological functions in living cells such as photosynthesis and respiration involve electron-transfer reactions.

1. Cytochrome *c*, a metalloprotein present in all cells, is an electron carrier for oxidative phosphorylation; it transfers electron to O_2. It is the Fe in it which combines with the electrons. The energy released in this transfer is used to synthesise adenosine triphosphate (ATP).
2. Several other cell proteins are electron-transfer agents; azurin and plastocyanin are two such proteins.

EXERCISES

*1. List the factors which influence the rates of substitution reactions in metal complexes.

2. For the reaction,

$$\mathrm{Ni^{2+} + 4CN^- \rightarrow [Ni(CN)_4]^{2-}}$$

$\Delta G = -126$ kJ mole^{-1}. Comment on the ease of this reaction.

3. The electronic configuration of the metal ion in the complex greatly influences the rate of substitution; explain this with examples.

*4. List the experimental methods which may be adopted for evaluating the rate constant of the reaction:

$$\mathrm{[Co(NH_3)_5Cl]^{2+} + H_2O \rightarrow \left[Co(NH_3)_5\,H_2O^-\right]^{3+} + Cl^-}$$

5. Justify the following observations :
   a) If a substitution reaction with an aqua complex is associative, it may be difficult to characterize such a complex as labile as inert.
   b) The "tunnelling" electron transfer process involves a very low chemical activation energy.

*6. The rate of substitution for the reaction

$$[Co(LL)_2Cl_2]^+ + H_2O \rightarrow [Co(LL)_2Cl(H_2O)]^{2+} + Cl^-$$

is found to increase with the size of the ligand LL (LL is chelating *en* derivative). Explain.

*7. The aquation of $[Co(NH_3)_4Cl_2]^+$ is 10^3 times faster than that of $[Co(NH_3)_5Cl]^{2+}$; explain.

8. Explain the following data for the reaction

$$[Co(NCS)en_2Cl]^+ + H_2O \rightarrow [Co(NCS)en_2H_2O]^{2+} + Cl^-$$

substrate	**k/s^{-1} at 298 K**	**$E_a^{\#}$/kJ mole^{-1}**	**% cis product**
cis – complex	1.1×10^{-5}	87	100
trans - complex	5.0×10^{-8}	127	~ 60

*9. The rate constants for the reactions

$$[Co(NH_3)_5H_2O]^{3+} + X \rightarrow [Co(NH_3)_5X]^{2+} + H_2O$$

$$(X = Cl^-, \quad Br^- \text{ or } N_3^-)$$

do not vary appreciably; explain this.

*10. The rate constants for the reactions

$$[Co(en)_2XCl]^+ + H_2O \rightarrow [Co(en)_2X(H_2O)]^{2+} + Cl^-$$

is in the order (X) $NH_2^- > OH^- > Cl^- > NCS^- > NO_2^-$; explain this.

11. Both S_N^1 CB and S_N^2 mechanisms in a ligand substitution reaction with a metal complex give second-order kinetics; justify this.

*12. The rate of outer-sphere electron transfer exchange from $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ is much faster than that from $[Co(NH_3)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$; comment on this.

13. Illustrate the use of radioisotopes in the study of electron transfer reactions.

14. What experimental method is useful for studying the rate of the reaction

$$[M(d\text{-pdta})] + l\text{-}H_4pdta \rightleftharpoons [M(l\text{-pdta})] + d\text{-}H_4pdta$$

(pdta = 1, 2 propylenediaminetetraacetic acid)

*15. The electron transfer from $[Co(NH_3)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$ is extremely slow; what is the reason?

*16. The electron transfer from $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ is very rapid; explain.

*17. The electron transfer between $[Co(NH_3)_5Cl]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ leads to quantitative transfer of the chloride ion from cobalt to chromium. What experiment could have proved this?

*18. Predict the products of electron transfer of the reaction between $[Fe(H_2O)_6]^{2+}$ and $[Co(NCS)(NH_3)_5]^{2+}$.

*19. The rate constant for the electron transfer between $[Fe(H_2O)_6]^{2+}$ and $[Fe(OH)(H_2O)_5]^{2+}$ is reduced by 50% on changing the reaction medium from H_2O to D_2O ; explain.

*20. The substitution reaction denoted by the equation

$$\begin{aligned} ML_n &\rightarrow ML_{n-1} + L \quad \text{(slow)} \\ ML_{n-1} + Y &\rightarrow ML_{n-1}Y \end{aligned}$$

is termed unimolecular. What is the order of the reaction with respect to Y ?

ANSWERS

1. (i) Charge on the metal
   (ii) Electronic configuration of the metal ion
   (iii) Geometry of the complex
   (iv) Nucleophilic reagent used
   (v) Solvent
   (vi) Effect of steric hindrances, if any

4. A free Cl^- is liberated into the solution; it can be determined volumetrically or gravimetrically.

   The reactant complex is purple while the product complex is pink. Thus, they absorb visible light of different wavelengths. Therefore, either the product or the reactant concentration (absorbance) can be monitored at suitable λ_{max}. As the reaction proceeds, conductance will increase; this can be measured periodically.

   The product complex functions as an acid and therefore, the pH of the reaction medium changes; hence the reaction can be followed by measuring the variation of pH with time.

6. The increasing bulk of LL leads to steric strain; ready dissociation of LL is favoured when it is bulky and a speedy dissociative process is possible. An alkyl substituted *en* ligand, in addition to steric effect may exert an inductive effect also; it can increase the electron intensity on the cobalt and facilitate the dissociation of the chloride ion and consequently favour the reaction.

7. The increase of charge on the complex is expected to strengthen the metal-ligand bond and hinder metal-ligand bond cleavage required for a dissociative process.

9. For reactions involving dissociative mechanism, the nature of the entering ligand does not appreciably influence rate constants (unlike for associative mechanism).

10. NH_2^- is the strongest base among the X ligands. It therefore tends to form π bonds with the metal by its strong basicity, that is by donating its pi electrons. Such a donation reduces the positive charge on the metal atom, facilitating the breakage of the Co-Cl bond. In addition, π bonding stabilizes the 5–coordinate intermediate that is formed in the reaction.

The basicity decreases in the order NH_2^-, OH^-, Cl^- and NCS^- and therefore, both π bonding and the stabilization of the intermediate weaken in the same order; thus the rates decrease.

With the electron attracting NO_2^- ligand, the reaction rate is the least.

12. Both the iron complexes are octahedral and low-spin. Electron exchange between such a pair requires very low activation energy and consequently the rate is high.

    Though both the cobalt complexes are octahedral, oxidation transforms the high-spin cobalt complex into a low-spin complex. Such a reaction requires high activation energy and results in low rate.

15. The complexes differ widely in their electronic structures; $[Co(NH_3)_6]^{3+}$ has the t_{2g}^6 ground state while $[Co(NH_3)_6]^{2+}$ has the $t_{2g}^5 e_g^2$ ground state. Changes in spatial arrangement as well as bond lengths must occur before electron transfer occurs in this pair.

16. The bond lengths in these two are not very different and therefore the reaction requires only a low activation energy.

17. The reaction could have been conducted with labelled Cl^- on cobalt and unlabelled Cl^- in solution. The chromium product contained only labelled chloride ion indicating that this ion had come only from the cobalt complex.

16. The Fe in the complex is in its +2 oxidation state; therefore, it should be the reducing agent transferring an electron and getting itself oxidized to Fe^{3+}. Co(III) in the reactant would get reduced to Co(II). Thus, the redox process is

$$[\overset{\text{II}}{\mathrm{Fe}}(H_2O)_6]^{2+} + [\overset{\text{III}}{\mathrm{Co}}(NCS)(NH_3)_5]^{2+} \rightarrow [\overset{\text{III}}{\mathrm{Fe}}(NCS)(H_2O)_5]+ + [\overset{\text{II}}{\mathrm{Co}}(NH_3)_5]^{2+}$$

    The NCS^- ligand is expected to favour inner-sphere mechanism with bridge formation [Co – (NCS) – Fe] and its subsequent transfer to Fe.

    The five-coordinate $[Co(NH_3)_5]^{2+}$ would rapidly pick up a water molecule to form $[Co(NH_3)_5H_2O]^{2+}$; then this is expected to form $[Cr(H_2O)_6]^{2+}$. Similarly, $[Fe(NCS)(H_2O)_5]^{2+}$ is labile and it hydrolyses to $[Fe(H_2O)_6]^{3+}$.

19. This directly indicates that the mechanism involves transfer of a hydrogen atom. When the reaction involves the movement of a hydrogen atom, the k_D / k_H for the reaction is usually ½.

20. The rate will depend not only on the nature of the aqua-complex but also on the nature of the incoming ligand.

    One species (ML_n) is involved in the formation of the activated complex (ML_{n-1}) with which further reaction occurs.

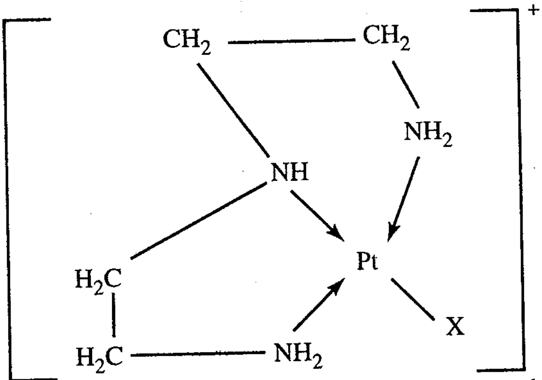
    Zero order, as the rate of the overall reaction depends upon $[ML_n]$ and not upon [Y]

Chapter 10

Reactions of Metal Complexes II

10.1 SUBSTITUTION REACTIONS OF SQUARE-PLANAR COMPLEXES

The Co(III) complexes are cited in octahedral substitution reactions. Similarly, for studying the general mechanism of square-planar substitution reactions, Pt(II)complexes are cited as model compounds.This is because of their stability, ease of preparation and slow reactions. Their substitution rate constants are close to those of Co(III) octahedral complexes. For substitution of a single ligand, a convenient model compound for study is $[Pt(dien)X]^+$, where X is a halide ion and *dien* is diethylenetriamine. This tridentate ligand locks up the other coordination sites.



It is now widely accepted that square planar-complexes undergo substitution reactions predominantly by an associated type, S_N2 mechanism.

10.1.1 Evidence for Associative Type S_N2 Mechanism

1. The rates (k/min at 25°C) of reactions for some Pt(II) complexes having different charges are shown below:

$$[PtCl_4]^{2-} + H_2O \longrightarrow [PtCl_3(H_2O)]^- + Cl^- : 300$$

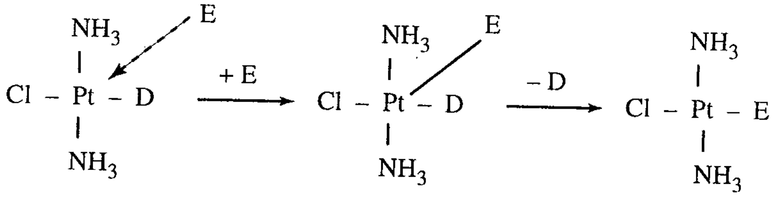
$$[PtCl_3NH_3]^- + H_2O \longrightarrow [PtCl_2(NH_3)(H_2O)] + Cl^- : 310$$

$$\text{cis}-[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]+\text{H}_2\text{O} \longrightarrow [\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})]^+ + \text{Cl}^-: 300$$

$$[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+ + \text{H}_2\text{O} \longrightarrow [\text{Pt}(\text{NH}_3)_3\text{H}_2\text{O}]^{2+} + \text{Cl}^-: 690$$

In the above series of complexes, the charge on the complex reactant changes from 2– to 1+. But the rate changes only by a factor of two which is a small effect. The rupture of the Pt-Cl bond should become more difficult as the charge on the complex becomes more positive. But the formation of a new bond should become easier. This small effect of the charge of the complex on reaction rate suggests that both bond making and bond breaking are important. This is characteristic of an associative type, S_N2 mechanism.

2. If the substitution in square-planar complexes follows dissociative type (S_N1 mechanism), then the change in the nature of departing group should affect the rate of bond breaking and hence appreciable changes in rate constants should be observed. But the rates of substitutions in square-planar complexes do not change appreciably with the changes in the nature of departing group (D). Hence, an S_N2 mechanism is likely in such substitutions.
3. It has been found that the rates of substitutions in square-planar complexes are greatly affected by the change in the nature of the entering group (E). This clearly indicates that the entering ligand, E, takes part in the rate determining step. This is another evidence for an associative type mechanism.
4. It has been observed that substitution in Pt(II) square-planar complexes occurs with retention of configuration, that is cis → cis and trans → trans. This is in agreement with a trigonal bipyramidal intermediate. This intermediate has a coordination number of 5. This is another evidence for associative type, S_N2 mechanism. If this reaction proceeds by a dissociative type mechanism, then a 3-coordinate intermediate would have been obtained. In this intermediate, the entering group (E) may lead to both cis and trans-isomers. Inversion of configuration would have taken place but actually this does not occur.



Trans reactant

trigonal bipyramidal intermediate

trans product

5. As the bulkiness of other ligands increases, the rate of substitution decreases. For example,

$$[\text{Pt}(\textit{dien})\text{Cl}]^+ + \text{NH}_3 \xrightarrow{k_a} [\text{Pt}(\textit{dien})(\text{NH}_3)]^{2+} + \text{Cl}^-$$

$$[\text{Pt}(\text{C-alkyl}\textit{dien})\text{Cl}]^+ + \text{NH}_3 \xrightarrow{k_b} [\text{Pt}(\text{C-alkyl}\textit{dien})(\text{NH}_3)]^{2+} + \text{Cl}^-$$

Comparing these two reactions, k_a is greater than k_b. The lesser value of k_b over k_a is attributed to the bulkiness of the C-alkyl*dien* ligand. This bulkier ligand prevents the entry of the entering group. Thus it retards the associative type, S_N2 mechanism.

If it proceeds by S_N1 mechanism, then as the bulkiness of the groups already present increases, the rate of substitution should increase; but actually this does not occur.

Of the various factors that affect the rates of substitution reactions in square-planar complexes, the most important factor is the nature of the trans ligand to the leaving ligand. This effect of the ligand trans to the leaving ligand on the rate of substitution reaction is called the *trans effect.* The stronger trans influencing ligand will facilitate the substitution of a ligand trans to it. The effects of trans ligands are usually higher than the effects of cis ligands. Hence the *cis effect* is not generally considered as important in these reactions.

10.1.2 Trans effect

Substitution reactions in square-planar complexes have been extensively studied using platinum(II) complexes. These studies revealed that substitutions in these complexes gave different geometrical isomers merely by changing the order of introduction of the ligands. Werner attributed this to the different tendencies of the ligands to direct the incoming ligands to their trans positions.

Various ligands having different trans directing influence are arranged in an increasing order of their trans effect. This series is known as the *trans effect series.* This series is based on some qualitative and quantitative observations. This series is,

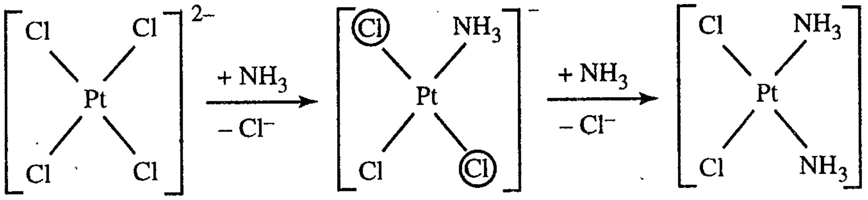
$$CN^- > C_2H_4 > CO > tu > NO_2^- > SCN^- > I^- > Br^- > Cl^- > py > NH_3 > OH^- > H_2O$$

(tu = thiourea; py = pyridine).

> Trans effect may be defined as the labilisation of ligands trans to other trans-directing ligands.

10.1.3 Applications of Trans effect

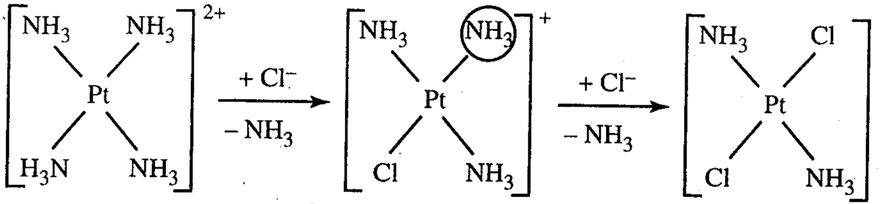
Making use of this trans effect, several geometrical isomers can be synthesised. For example, cis and trans-isomers of the composition, $[Pt(NH_3)_2Cl_2]$ can be prepared by the following sequence of reactions:



cis-dichlorodiammine platinum (II)

In the first step of the above reaction one Cl^- is replaced by NH_3 to give $[PtCl_3(NH_3)]^-$ ion. In this complex ion the more labile ions are circled. The Cl^- trans to NH_3 is not labile, because the trans effect of NH_3 is less than that of Cl^-. In the second step, the greater trans effect of Cl^- over NH_3 is made use of. One of the two circled Cl^- ions is replaced by NH_3 to give exclusively the cis-product.

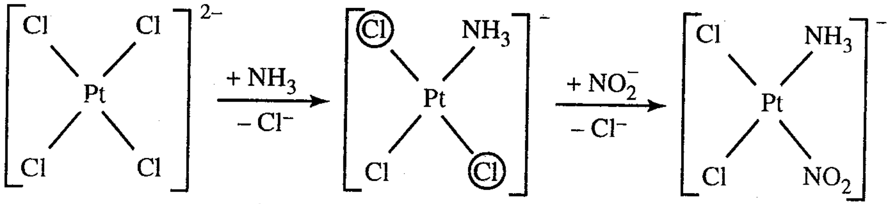
On the other hand, the displacement of NH_3 from $[Pt(NH_3)_4]^{2+}$ by Cl^- gives exclusively the trans-product:



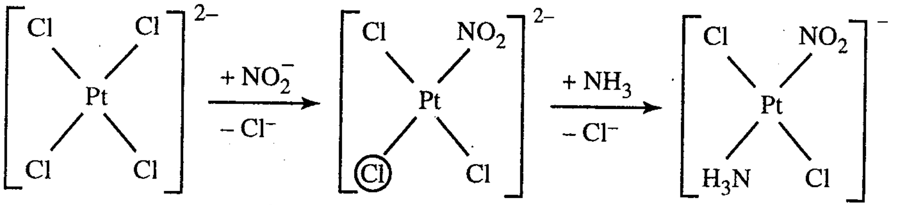
trans-dichlorodiammine platinum (II)

In the first step of the above reaction, one NH_3 is displaced by Cl^- to give $[Pt(NH_3)_3Cl]^+$ ion. In this complex ion the NH_3 trans to Cl^- is more labile (the circled one). This is because the trans-effect of Cl^- is greater than that of NH_3. In the second step, the greater transeffect of Cl^- over NH_3 is made use of to form the trans product.

The cis and trans-isomers of the type, $[PtCl_2(NH_3)NO_2]^-$ can be synthesised by the following sequence of reactions. Just by reversing the order of introduction of ligands, the two isomers can be produced. In each reaction the more labile group/groups is/are circled.



cis-dichloronitro-N-ammineplatinum (II) ion

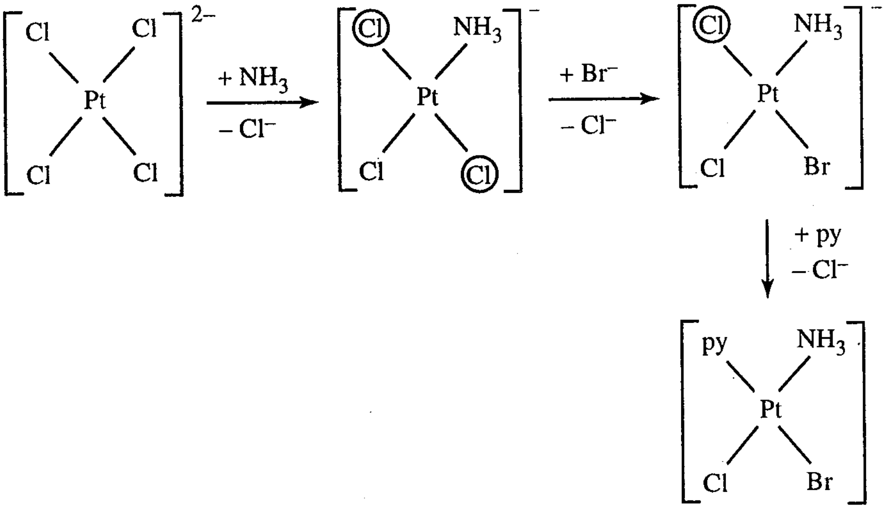


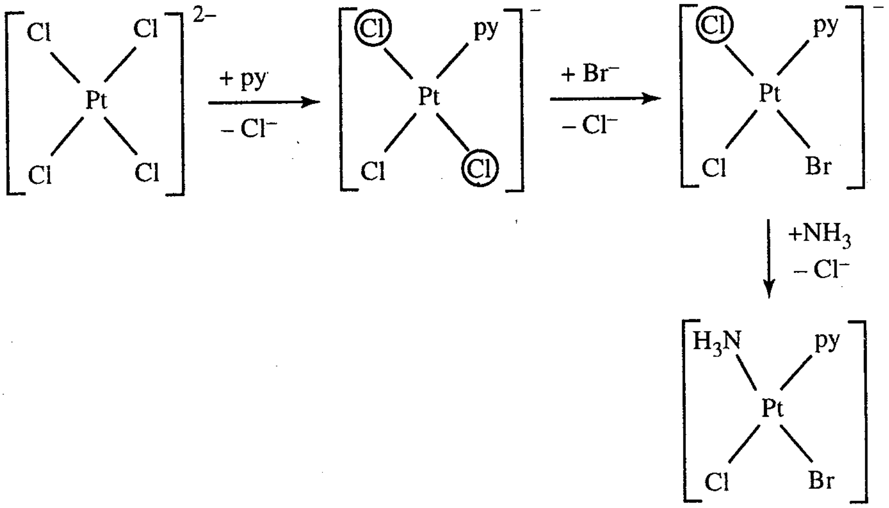
trans-dichloronitro-N-ammineplatinum (II) ion

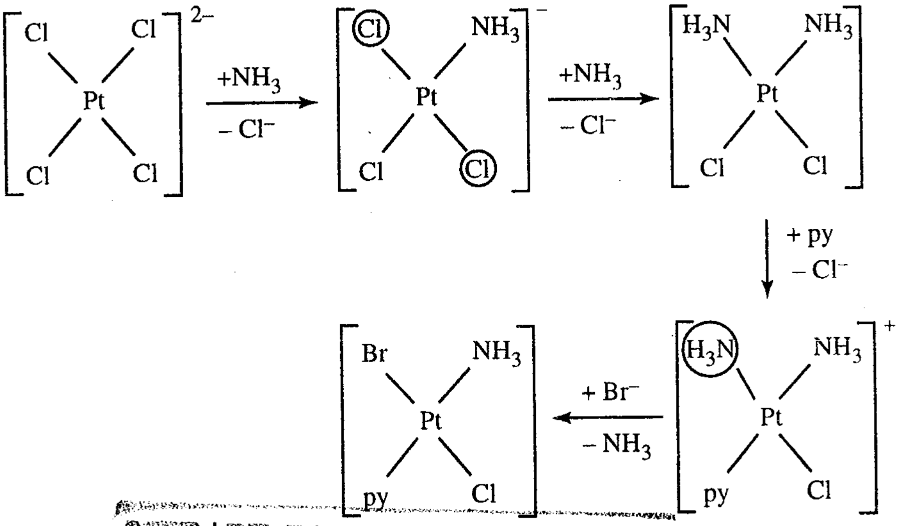
The trans-effect order, $NO_2^- > Cl^- > NH_3$ is made use of in these reactions.

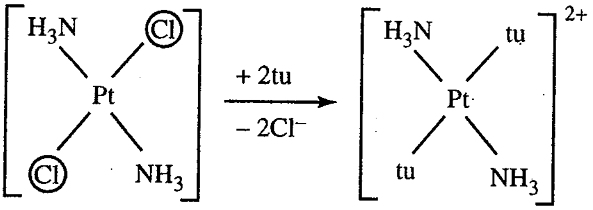
By utilising the knowledge of the trans effect, the following sequences of reactions have been suggested for the synthesis of the three isomers of bromochloroammine (pyridine)platinum(II), $[Pt(Cl)(Br)(NH_3)(py)]$. The order of introduction of ligands is changed.

Another interesting application of the trans-effect is in distinguishing the cis and trans-isomers,of the formula $[PtCl_2(NH_3)_2]$. Thiourea(*tu*) is used as the reagent for this. Addition of thiourea to the trans-isomer results in the replacement of the two trans chloride ions. The reaction stops at this stage because the trans ammonia molecules do not labilise each other.



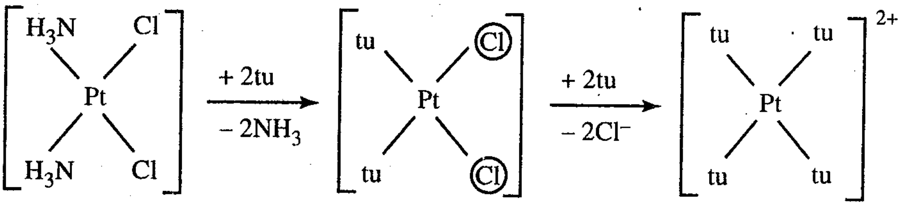






trans-

But the addition of thiourea to the cis-isomer results in the displacement of all the original ligands and gives $[Pt(tu)_4]^{2+}$ as the final product.



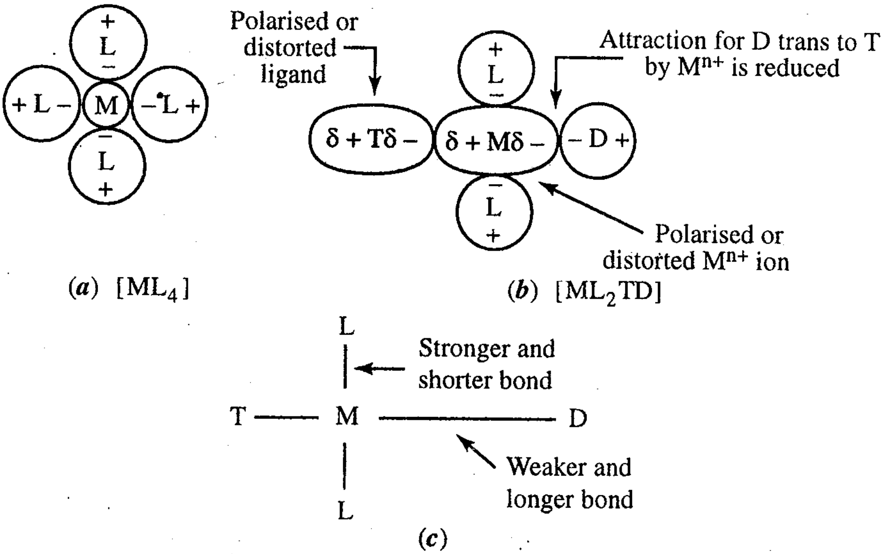
cis-

The trans effect of the ligands decreases in the order, tu > Cl^- > NH_3. This method of differentiating the geometrical isomers is called the *Kurnakov test.*

10.1.4 Theories of Trans Effect

Several theories have been proposed for the explanation of the trans effect. Only two theories representing different approaches are outlined here.

I. The polarisation theory This theory was proposed by Grinberg (1927) and is a thermodynamic approach (since it deals with M-D departing ligand bond weakening). He utilised Fajan's polarisation concept to explain the weakening of the M-D bond opposite to the trans-directing group(T). A pictorial representation of this concept is shown in Fig. 10.1 (a) and (b).



(*a*) $[ML_4]$

(*b*) $[ML_2TD]$

(*c*)

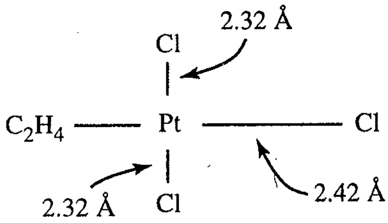
Fig. 10.1 Pictorial representation of polarisation theory of trans effect

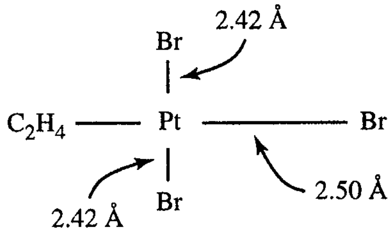
This figure represents the polarisation of metal ion induced by highly polarisable ligand T in ML_2TD(b) as compared to ML_4(a).

According to this theory, the primary positve charge of M^{n+} induces a dipole in all the 4 ligands. If all the 4 ligands are identical as in (a), then the dipoles induced by the metal ion cancel each other and the resultant dipole is zero.[Fig. (a)].Thus none of the 4 ligands shows trans effect. But if the 4 ligands are not identical as in Fig. (b), then the induced dipoles do not cancel each other. The two L ligands which are similar and trans to each other balance each other. But the other two trans ligands, T and D, which are not similar do not balance each other. T is large and has greater polarisability than D. Here the polarisation takes place in such a way that the positive charge of M^{n+} central ion at a point trans to T is reduced. Hence the attraction of D for M^{n+} is also reduced and the bond trans to T is weakened and consequently lengthened, i.e. the M-D bond trans to T is weaker and longer than M-L bonds cis to T. [Fig. (c)]. This facilitates the replacement of D by E (entering ligand) at a point trans to T.

Evidence in favour of the polarisation theory

1. This theory predicts that trans effect is important only when the central metal ion itself is polarisable and large in size. Actually, trans effect is observed predominantly in Pt(II) complexes than in Pd(II) or Ni(II) complexes. Hence the order of importance of trans effect is Pt(II) > Pd(II) > Ni(II). The size and polarisability decrease in the same order.
2. We have seen that if the ligand T is highly polarisable in [PtL_2TD] complex, then Pt-D bond trans to T is longer than Pt-L bond cis to T. The complex, $[Pt(C_2H_4)X_3]^-$ type, where $X^- = Cl^-$, Br^- and C_2H_4 has large trans effect. The Pt-Cl or Pt-Br bond trans to C_2H_4 is longer than that cis to C_2H_4.





Defect This electrostatic polarisation theory can explain well the trans effect of the ligands at the low end of the trans effect series like H_2O, OH^-, NH_3 etc. However, this theory cannot explain the high trans effect of the π-bonding ligands like C_2H_4, CN^-, CO etc., which lie at the other end of trans effect series.

II. The π -bonding theory This theory, which is due to Chatt, Duncanson and Venanzi (1955) and Orgel (1956), accounts well for the high trans effect of the π-bonding ligands like C_2H_4, CN^-, CO etc. The concept of π-bonding in metal complexes was first introduced by L. Pauling in order to account for the short Ni-C bond distance in [$Ni(CO)_4$] and also to account for the large stability of the cyano complexes of transition metals as compared to those of non-transition metals.

According to Chatt, Duncanson and Venanzi, the vacant π or π^* orbitals of the π-bonding ligands accept a pair of electrons from the filled d-orbitals of the met (d_{xz} or d_{yz}) to form metal-ligand π-bond (d_π - p_π or d_π - d_π).

In the case of Pt(II) square-planar complex, Pt L_2TD (T is the π-bonding ligand, D is the departing ligand trans to T) the filled orbital of Pt(II) overlaps with the empty orbital of the ligand T to form M-T π-bond. The formation of this π-bond increases the electron density in the direction of T and diminishes it in the direction of the ligand D trans to T.

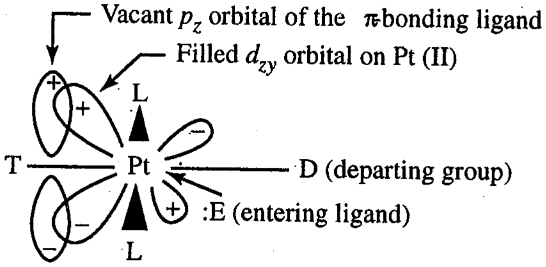
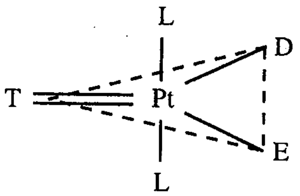
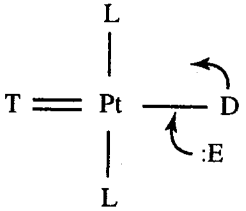


Fig. 10.2 *The formation of d_π - p_π bond between Pt(II) and the π-bonding ligand, T in the 5-coordinated transition complex*

This electron-shift towards T facilitates the approach of the entering ligand, :E with its lone pair in the direction of diminished electron density that is trans to T, to form 5-coordinated transition state, [PtL_2TDE] which on losing D, gives the substitution product, [PtL_2TE]. In this process, D trans to T is substituted by E. The removal of the electronic charge from Pt(II) by π-bonding of T enhances the addition of the entering group, E and favours more rapid substitution of D trans to T.

Orgel independently proposed essentially the same picture to account for the trans effect in square-planar complexes. He emphasised that the enhanced stability of the 5-coordinated transition state due to π-bonding rather than the ease of approach of the entering group (E) facilitates the substitution reactions. Since substitution reactions of Pt(II) complexes take place with retention of configuration, a distorted trigonal bipyramid structure was proposed as the transition state. Here the T, D and E are in equatorial plane with the two L groups (cis to T) in apical positions. This transition state results from an approach to E from one side to the plane with a compensating motion of D into the opposite side of the plane.





Thus, the lability of the trans ligand, D is attributed to the lowering of activation energy of the reaction. So greater the π-bonding character of T ligand, lesser will be the activation energy for the substitution reaction and hence greater will be its trans effect.

10.1.5 Cis Effect

Certain ligands such as thiocyanate and hydroxide ions greatly accelerate the hydrolysis of a complex when they are cis to the leaving group as compared to the analogous reaction in which the leaving group is trans to these ligands. For example, let us consider the hydrolysis of the following complex:

$$[\mathrm{Co(en)_2XCl}]^{n+} + \mathrm{H_2O} \rightarrow [\mathrm{Co(en)_2\,X(H_2O)}]^{(n+1)+} + \mathrm{Cl^-}$$

where X is a cis-activating ligand like OH^-, SCN^- etc. When the OH^- is cis to the leaving Cl^-, the reaction rate is about ten times as great as that when it is in the trans position.

The ligands that possess a strong cis effect are those that have unshared pairs of electrons in addition to the pair used in the sigma dative bond. It has been suggested that this electron pair is donated to the metal in a d_π - p_π pi bond. Such pi bonding by a cis-substituent can stabilise a square-pyramidal activated complex by lowering the positive charge on the metal. This also allows the reaction to proceed without extensive rearrangement and the product is 100% cis siomer. When these ligands are in the trans position, there is no orbital available for overlap unless the complex rearranges to a trigonal-bipyramidal structure. This raises the energy of activation and makes the substitution reactions more difficult. There are two types of ligands which fail to exhibit cis effect. They are (i) the ligands such as nitro group which are pi-acceptors. (They tend to withdraw electrons through pi bonding and therefore they cannot operate through the mechanism outlined above) and (ii) the ligands like ammonia, that do not have another lone pair to donate to the metal.

The cis effect is similar in origin to the trans effect. It has been shown that the ligands which weaken bonds trans to themselves also weaken cis M-L bonds, but not by as large an amount. Bond breaking in the transition state becomes somewhat easier for good cis directors and therefore the reaction rate increases; however, it is not as much as if this cis ligand were in the trans position.

EXERCISES

***I. Choose the best answer for each of the following:**

1. $[Pt(NH_3)_4]^{2+}$ on treatment with Cl^- gives a product of composition, $[PtCl_2(NH_3)_2]$. It is a
   a) trans-isomer
   b) cis-isomer
   c) mixture of cis- and trans- isomer
   d) none of the above
2. $[PtCl_4]^{2-}$ on treatment with NH_3 gives a product of composition, $[PtCl_2(NH_3)_2]$. It is a
   a) trans- isomer
   b) cis- isomer
   c) both (a) and (b)
   d) none of the above
3. $[PtCl_4]^{2-}$ on treatment with NH_3 followed by the action of NO_2^- gives a product of composition, $[PtCl_2(NH_3)(NO)_2]^-$. It is a
   a) trans- isomer
   b) cis- isomer
   c) mixture of cis- and trans-
   d) none of the above
4. $[PtCl_4]^{2-} + NO_2^- \rightarrow [PtCl_3(NO_2)]^{2-} + NH_3 \rightarrow [PtCl_2(NO_2)NH_3]^-$
   The final product is
   a) mixture of cis- and trans-
   b) cis- isomer
   c) trans- isomer
   d) none of the above
5. Cis-$[PtCl_2(NH_3)_2]$ is treated with thiourea (tu). The final product is
   a) $[Pt(tu)_4]^{2+}$
   b) $[PtCl_2(tu)_2]$
   c) $[Pt(NH_3)_2(tu)_2]^{2+}$
   d) none of the above
6. Trans- $[PtCl_2(NH_3)_2]$ is treated with thiourea (tu). The final product is
   a) $[Pt(tu)_4]^{2+}$
   b) $[Pt(NH_3)_2(tu)_2]^{2+}$
   c) $[PtCl_2(tu)_2]$
   d) none of the above
7. Which of the following complexes / ions is expected to be inert to ligand substitution reaction?
   a) $[Rh(NH_3)_6]^{3+}$
   b) $[Co(NO_2)_6]^{3-}$

c) $[Cr(NH_3)_6]^{3+}$

d) all the above

8. Which of the following complexes / ion is expected to be labile to ligand substitutions?

a) $[Ir(NH_3)_6]^{3+}$

b) $[Mo(NH_3)_6]^{3+}$

c) $[Ni(en)_3]^{2+}$

d) $[Co(NO_2)_6]^{3-}$

9. A complex that shows anti-tumour activity is

a) cis $[PtCl_2(NH_3)_2]$

b) trans $[PtCl_2(NH_3)_2]$

c) cis $[PdCl_2(NH_3)_2]$

d) trans $[PdCl_2(NH_3)_2]$

***II Match the following:**

1. labile complex
2. $[Pt(NH_3)_4]^{2+} + 2\,Cl^- \rightarrow$
3. Anti-cancer drug
4. $[PtCl_4]^{2-} + 2\,NH_3 \rightarrow$
5. inert complex
6. $[PtCl_4]^{2-} + NO_2^- \rightarrow$ product $\xrightarrow{NH_3}$
7. $[PtCl_4]^{2-} + NH_3 \rightarrow$ product $\xrightarrow{NO_2^-}$

a) cis- $[Pt(NH_3)(NO_2)Cl_2]^-$

b) trans- $[PtCl_2(NH_3)(NO_2)]^-$

c) cis $[PtCl_2(NH_3)_2]$

d) $[FeF_6]^{3-}$

e) trans $[PtCl_2(NH_3)_2]$

f) $[Cr(en)_3]^{3+}$

g) cis- platin

III Account for the following:

1. $[Cr(H_2O)_6]^{3+}$ is inert whereas $[Cr(H_2O)_6]^{2+}$ is labile to ligand substitution reactions.
2. Is $[Ni(en)_3]^{2+}$ labile or inert? Explain your choice .
3. The rate of aquation of $[Co(NH_3)_5Cl]^{2+}$ is much slower than the rate of aquation of either cis- or trans- $[Co(NH_3)_4Cl_2]^+$.
4. $[Pt(NH_3)_4]^{2+}$ on treatment with Cl^- gives trans- $[Pt(NH_3)_2Cl_2]$
5. $[PtCl_4]^{2-}$ on treatment with NH_3 gives cis-$[Pt(NH_3)_2Cl_2]$.
6. $[PtCl_4]^{2-}$ on treatment with NH_3 followed by the action of NO_2^- gives cis-$[PtCl_2(NH_3)(NO_2)]^-$ whereas the trans $[PtCl_2(NH_3)(NO_2)]^-$ product is obatined when the order of introduction of the ligands is reversed.

*7. When the yellow complex $[Ni(en)_2]Br_2$ is dissolved in pyridine, a blue coloured solution is formed.

IV Answer the following:

*1. Classify the following complex ions as labile or inert. Write an explanatory sentence on each:

a) $[V(o\text{-phen})_3]^{3+}$ b) $[V(H_2O)_6]^{2+}$ c) $[Cr(H_2O)_6]^{2+}$ d) $[Cr(CN)_6]^{4-}$
e) $[Mn(CN)_6]^{3-}$ f) $[Mn(CN)_6]^{3-}$ g) $[Fe(H_2O)_6]^{2+}$ h) $[Fe(CN)_6]^{3-}$
i) $[Ni(en)_3]^{2+}$ j) $[Fe(CN)_6]^{4-}$ k) $[Mn(CN)_6]^{4-}$ l) $[Cr(NH_3)_6]^{2+}$

2. How is trans effect useful in the synthesis of cis- and trans- $[PtCl_2(NH_3)_2]$ from the appropriate starting material?
3. How are cis- and trans- $[Pt(NH_3)(NO_2)Cl_2]^-$ synthesized from $[PtCl_4]^{2-}$?
4. Suggest suitable routes to cis- and trans-$[PtCl_2(NH_3)(PPh_3)]$ from $[PtCl_4]^{2-}$. For the three ligands under consideration, the increasing trans effect is in the order, $NH_3 < Cl^- < PPh_3$
5. How are the three isomers of $[PtBr(NH_3)(Cl)py]$ prepared from $[PtCl_4]^{2-}$?
6. Write a note on the applications of trans-effect.
7. Discuss the different theories proposed for explaining the trans-effect.
8. What is cis-effect?

ANSWERS

I 1. (a) 2. (b) 3. (b) 4. (c) 5. (a) 6. (b) 7. (d) 8. (c) 9. (a)
II 1. (d) 2. (e) 3. (g) 4. (c) 5. (f) 6. (b) 7. (a)
III

7. The planar complex $[Ni(en)_2]^{2+}$ interacts with py solvent molecules and forms the blue coloured, octahedral complex, $[Ni(en)_2(py)_2]Br_2$. In solution, actually the planar – octahedral equilibrium occurs.

IV 1. a) labile, d^2 b) inert, d^3 c) labile, d^4, high-spin d) inert, d^4, low-spin e) labile, d^5, high-spin f) inert, d^4, low-spin g) labile, d^6, high-spin h) inert, d^5, low-spin i) labile, d^8 j) inert, d^6, low-spin k) inert, d^5, low-spin l) labile, d^7, low-spin

Complexes of metal ions having one or more electrons in e_g level or less than three electrons in the t_{2g} level are generally labile.

Chapter 11

Organometallic Compounds

11.1 ORGANOMETALLIC COMPOUNDS — DEFINITION AND TYPES

The compounds formed between metals and organic compounds containing metal – carbon bond(s) are called organometallic compounds. The metal in such a compound is bonded *to carbon* of an organic molecule, radical or ion. For example, when methyl chloride is reacted with lithium in benzene solvent, an organometallic compound, methyllithium results.

$$CH_3Cl + 2\,Li \longrightarrow CH_3Li + LiCl$$

Actually, CH_3Li exists as a tetramer. The tetramer structure consist of 4 Li atoms constituting the corners of a tetrahedron, the methyl groups occupying spaces symmetrically in the four phases of the tetrahedron. The bonding in it involves electron-deficient 4-centre-2-electron bonds.

CH_3Li is not a coordination compound. Several other metals, such as Na, Ca, Zn, Al, etc. form such *organometallic compounds*. However, several transition metals or their compounds react with organic molecules forming organometallic compounds, which are actually coordination compounds. For example, $Fe(CO)_5$ forms an organometallic complex with butadiene.

$$Fe(CO)_5 + C_4H_4 \xrightarrow{80°C} C_4H_4Fe(CO)_3 + 2CO$$

11.1.1 Alkene Complexes (Olefin Complexes)

Certain metal ions, such as Cu^+, Ag^+, Hg^{2+} and Pb^{2+} form complexes with alkenes. For example, the formation of a silver-alkene complex is denoted as

$$Ag^+(aq) + \text{alkene} \longrightarrow Ag[\text{alkene}]^+(aq)$$

On thoroughly mixing $AgNO_3$ with cyclooctatetraene (C_8H_8), a complex of the composition $[Ag(C_8H_8)_2]^+ NO_3^-$ is formed.

11.1.2 Zeise's Salt

The first organometallic compound, an alkene complex with the formula $K[Pt(C_2H_4)Cl_3]\cdot H_2O$ was synthesised in 1827 by Zeise, a Danish pharmacist.

This was obtained by him as pale-yellow crystals by reacting ethyl alcohol with K_2PtCl_6. During his period, the theory of coordination chemistry was not developed and therefore, this compound remained a mystery. Later, with the development of the theories of coordination compounds, this compound was reinvestigated and its structure understood (Fig.11.1). It can be prepared also from K_2PtCl_4 and C_2H_4:

$$[PtCl_4]^{2-} + C_2H_4 \xrightarrow{\text{alcoholic HCl}} [Pt(C_2H_4)Cl_3]^- + Cl^-$$

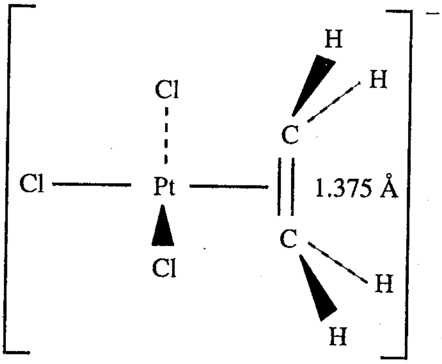


Fig. 11.1 The structure of the anion of Zeise's salt

11.1.3 Structural Features of Zeise's Salt

1. The platinum ion in the salt is 4-coordinated, with three sites occupied by the chloride ions and the fourth site by the ethylene molecule.
2. Its geometry is square-planar.
3. The π-electrons in ethylene are coordinated to the platinum metal. Overlap of the π-bonding orbital of the alkene with a vacant σ-type orbital of the Pt (a $[5d6s6p^2]$ hybrid) produces an L → M bond of σ-type. In addition, a π-bond originating from the overlap of a $[5d_{xz}6p_z]$ filled orbital of Pt atom with the empty *π-bonding* orbital of the alkene is formed.

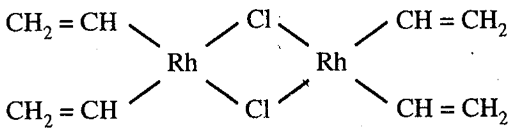
   The ethylene molecule is called a *π-bonding ligand.*
4. The length of the coordinated alkene C-C bond (1.375Å) is greater than the C=C bond length (1.337 Å) in the free ethylene molecule.
5. The C=C bond is perpendicular to the molecular plane.
6. The orginally planar ethylene becomes non-planar on bonding itself to platinum.
7. The metal is located above the plane of the alkene, symmetrically between the two skeletal carbon atoms.
8. The two carbon atoms are almost equidistant (non-bonded distance) from the platinum ion.
9. The water molecule present in the salt is not attached to the metal but is acommodated in the lattice as a solvent molecule of crystallisation.

The way in which the ethylene molecule is bonded in this complex remained unresolved for over a century. In 1954, crystal structure determination by X-ray method and I.R. and Raman spectral data solved the structure.

11.1.4 Rhodium-ethylene Complex

When rhodium chloride reacts with ethylene a binuclear complex is formed

$$RhCl_3(aq) + C_2H_4 \longrightarrow$$

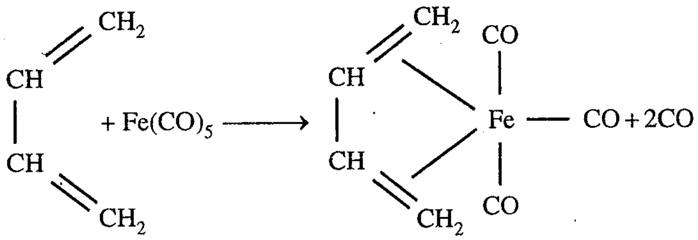


11.1.5 Other Metal-alkene Complexes

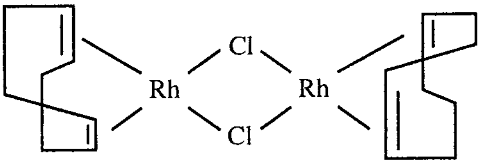
Several other alkenes similarly form complexes with metals, such as Pt, Rh, Fe, Cr, etc. Very stable complexes are formed when the ligand is a *diolefin.*

11.1.6 Iron-butadiene Complex

Iron pentacarbonyl reacts with 1,3-butadiene to form $[Fe(CO)_3C_4H_4]$



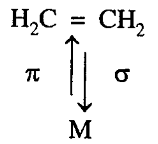
In this reaction, the weakly bound ligands (CO) are substituted by an alkene ligand. Diolefins, such as 1,3-butadiene and cyclo-octadiene form chelates and therefore such metal-olefin complexes are more stable than those formed with monolefins. Rh, for example forms a stable chelate with cyclo-octadiene.



11.1.7 Bonding in Metal-alkene Complexes

The bonding in metal-alkene complexes is different compared to that in other complexes.

1. In a metal-alkene complex, localised σ bonds between the metal atom and carbon do not exist. The π electrons of the alkenes are used to bind the ligand with the metal. Such a bond is called a μ-bond. The polarity of the μ-bond is $alkene^+ M^-$.
2. This primary π-electrons-metal bonding is strengthened by back-donation from a filled metal t_{2g} orbital to a π^* orbital of the alkene ligand.



3. The complex formation and the bonding satisfy the EAN rule; for example, in bis-(π-cyclopentadienyl)iron [Fe$(C_5H_5)_2$], the EAN = 26 + (2 × 5) = 36; and in bis-(benzene)chromium [Cr$(C_6H_6)_2$], the EAN = 24 + (2 × 6) = 36.
4. The length of the coordinated olefinic C-C bond is greater than the C-C bond in the free alkene. This is substantiated by the observed decrease (140–160 cm^{-1}) in C = C stretching frequency in the complex compared to the frequency in the free alkene.
5. The C=C bond of the ligand is perpendicular to the molecular plane in complexes of the type [L_3M(alkene)], such as $[Pt(C_2H_4)Cl_3]^-$, but it is in the molecular plane in complexes of the type $[M(alkene)L_2]_2$, such as [Pd (styrene) $Cl_2]_2$.
6. The number of electrons donated by the alkene to the metal depends on the nature of the alkene, particularly, the number of double bonds in it (Table 11.1).
7. A free alkene is susceptible to electrophilic attack; however, when it is bound to a metal, it becomes susceptible to nucleophilic attack, a reversal of its character. This reversal is due to the carbon atoms in the alkene becoming positive on getting coordinated to a metal.

Table 11.1 The number of electrons donated by the ligands in metal-alkene complexes

Alkene ligand	Number of electrons donated by the alkene	Example
ethylene	2	$K[Pt(C_2H_4)Cl_3]$
allyl	3	$(OC)_4Mn.C_3H_5$
cyclobutadiene	4	$C_4H_4Fe(CO)_3$
cyclopentadienyl anion	6	$Ni(C_5H_5)_2$
benzene	6	$Cr(C_6H_6)_2$
cycloheptatrienyl	7	$C_5H_5VC_7H_7$
cyclo-octatetraene	8	$Fe(CO)(C_8H_8)$

M.J.S.Dewar, in 1957 explained the bonding in alkene complexes such as Zeise's salt based on the M-O theory.The bonding in a metal-alkene complex is of two parts.

1. The electron pair in the filled π orbital on ethene overlaps with an empty hybrid orbital on the metal producing a dative σ bond (Fig. 11.2).
2. A filled metal *d* orbital overlaps with an empty antibonding orbital on ethene, by back-bonding (Fig. 11.3). The back-bonding is as important as the σ bonding for the formation of the molecule. The extent of back-bonding varies depending on the metal, the substituents on alkene and the other ligands on the metal. Only metal atoms in low oxidation states are sufficiently good π donors to stabilise alkene complexes (similar to carbonyl complexes).

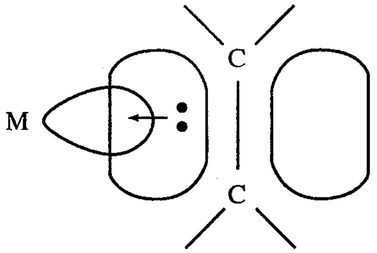


Fig. 11.2 *Electron-donation from the filled π orbitals to vacant metal orbital*

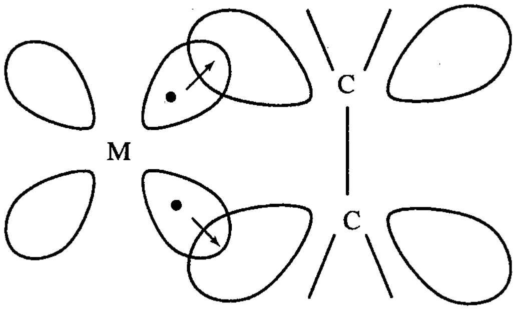


Fig. 11.3 *Back-bonding occurs from the filled metal orbital to acceptor π* orbitals*

Sc, though a transition metal does not form an alkene complex. Its *d* orbitals are not sufficiently populated (d^1) with electrons for the occurrence of back-bonding. In the absence of back-bonding, a stable Sc-olefin complex is not formed.

The bonding in a metal-butadiene complex may be understood by considering the two extreme situations denoted in Fig. 11.4.

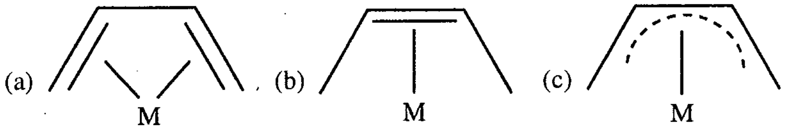


Fig. 11.4 *Modes of bonding between a metal and butadiene*

According to Fig. (a), the metal is bonded to the two π orbitals. According to Fig. (b), the metal and the olefin are involved in σ, σ, π interaction. These two are extreme situations of bonding. Fig. (c) probably denotes the reality according to which the bonding interaction between the metal and the olefin is delocalised π interaction.

11.1.8 Metal-butadiene Complexes

When butadiene is complexed with a transition metal, the bonding occurs through a combination of forward and back donation [Fig. 11.5(a)]. Butadiene has two

π-bonding and two π^*-antibonding orbitals [Fig 11.5(b)]. The antibonding orbital (3*) receives electron density by back-donation from the metal. This orbital has lobes which correspond to a double bond between the two central carbon atoms. As this orbital receives electron density, the central C – C bond is shortened. For example, in butadienetricarbonyliron (Fig. 11.6), the central bond is 1.45 Å long. (It is shortened from 1.48 Å in free butadiene). The terminal bonds are also of 1.45 Å long. The iron atom is 2.06 and 2.14 Å from the internal and terminal carbon atoms respectively.

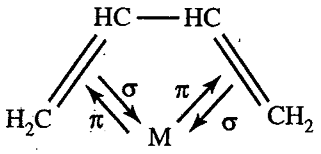


Fig. 11.5(a) Bonding between a metal and butadiene

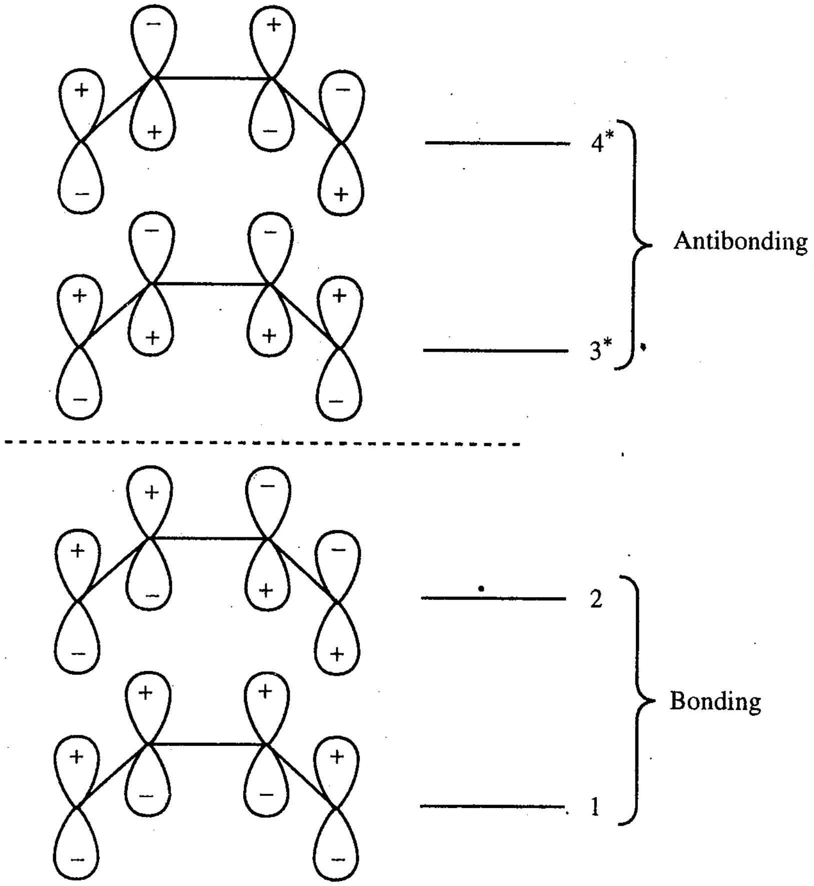


Fig. 11.5(b) Molecular orbitals of butadiene

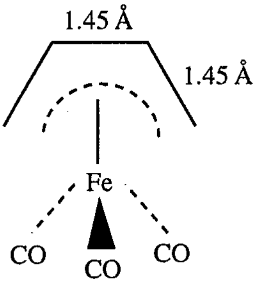


Fig. 11.6 Structure of butadienetricarbonyliron

11.1.9 The 18-electron Rule and the Organometallic Compounds

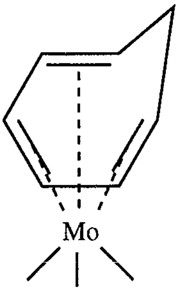
The 18-electron rule implies that in a metal complex, 18 electrons are made available to the metal through bonding and then the metal assumes the electron structure of the next noble gas. The 18 electrons are accommodated in the five (n-1)*d* orbitals (10 electrons), the three *np* orbitals (6 electrons) and the one *ns* orbital (2 electrons). These 18 electrons comprise the electrons of the metal together with the electrons contributed by the ligands. The attainment of the 18-electron configuration leads to stability of the complex. For example, in $Fe(CO)_5$, iron ($4s^2\ 3d^6$) provides 8 electrons and the five CO ligands 10 electrons, so that the 18-electron rule is satisfied. The 18-electron rule applies to several organometallic complexes also. Some examples of such complexes are indicated below:

$[Cr(\eta^6-C_6H_6)_2]$ Cr $4s^1\ 3d^5$: 6 electrons
C_6H_6 : 6 electrons
Total : 6 + (2 × 6) = 18 electrons.

[Ni(cyclo-octadiene)$_2$] Ni $4s^2\ 3d^8$: 10 electrons
cyclo-octadiene : 2 × 4 electrons
Total : 10 + (2 × 4) = 18 electrons.

$[Fe(\eta^5-C_5H_5)_2]$ 6 + (2 × 6) = 18 electrons

$[\eta^6-(C_7H_8)Mo(CO)_3]$ 6 + 6 + (3 × 2) = 18 electrons



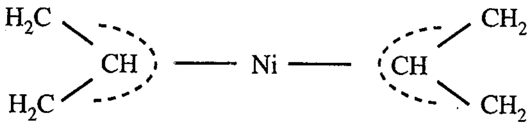
tricarbonylheptatrienemolybdenum

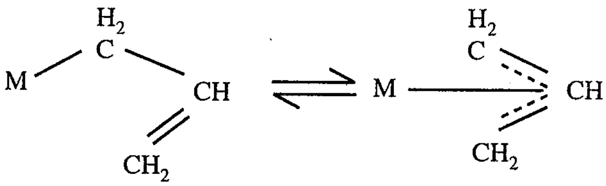
11.1.10 Metal-allyl Complexes

The allyl group, $CH_2 = CH - CH_2 -$ can function as a sigma ligand (*monohapto*) or as a sigma plus pi ligand (*trihapto*). For example, nickel chloride reacts with allyl magnesium bromide forming a π-allyl complex.

$$NiCl_2 + 2CH_2 = CH - CH_2 - MgBr \longrightarrow (\pi\text{-}CH_2CHCH_2)_2Ni + MgBr_2 + MgCl_2$$

Such a π-allyl complex has a three-carbon delocalised allylic system $CH_2 \underline{\cdots} CH \underline{\cdots} CH_2$ which acts as "half sandwich".

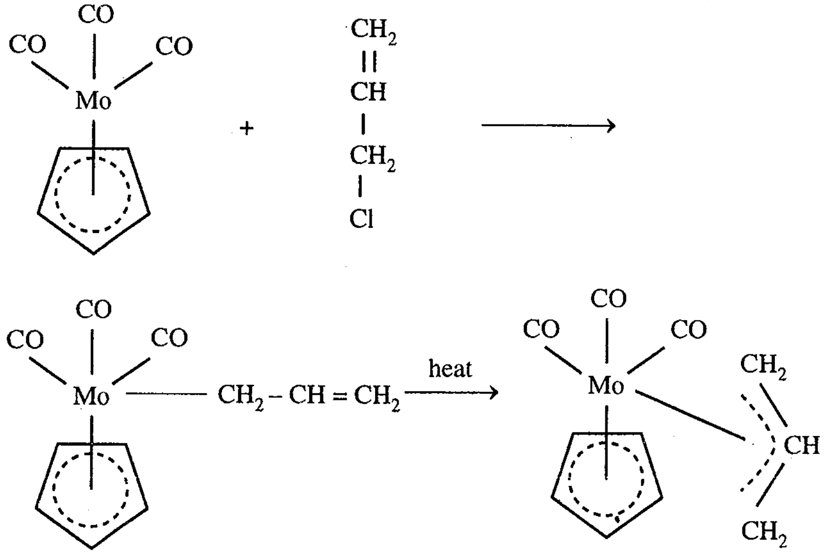




π-allyl (η^1) (monohaptoallyl) π-allyl (η^3) (trihaptoallyl)

The π-allyl complex is believed to be formed via the σ-bonded allyl derivative of the metal $[(CH_2 = CH - CH_2-)_2M]$. The σ-compound is transformed to the π-compound (η^3-allyl complex) by thermal or photochemical energy. Such a complex is called a *fluxional complex*; it isomerises with a little energy.

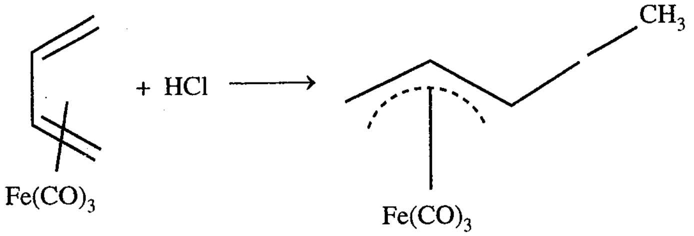
π-(Cyclopentadienyl)-molybdenum tricarbonyl reacts with allyl chloride to form first the σ-compound which on warming isomerises to the π-complex.



σ-compound, yellow oil π-complex, yellow solid

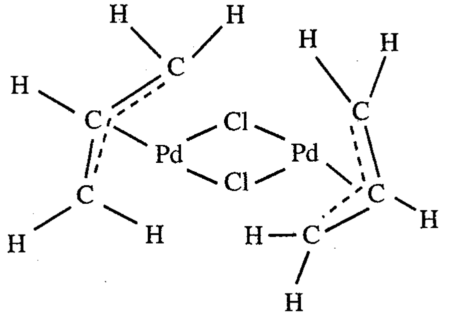
fluxional complexes

Some allyl complexes are obtained by protonation of butadiene complexes; the following is an example for such transformations:

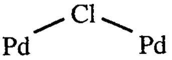


11.1.11 η^3 – Allylpalladium Chloride Dimer

The structure of this is denoted below:



The η^3 – allyl systems in it are related by a centre of symmetry in the molecule.

The C-C-C plane makes an angle of 111° with the  plane. All the C-C distances are 1.38 Å; the C-C-C angle is 120°. Each Pd atom is equidistant (2.11 Å) from all three carbon atoms of its respective allyl group.

11.1.12 Metal-acetylene Complexes

The metal-acetylene complexes are similar to the metal-olefin complexes in their formation and formulae. The alkynes also have π system that could be involved in bonding similar to that in metal-alkene complexes; however, the bonding in them is more complicated than that in olefin complexes, because there are more types of bonding possible with triple bonds. An example for an acetylene complex is the Pt-diphenylacetylene,

$[\mathrm{Pt}(C_6H_5C \equiv CC_6H_5)(PPh_3)_2]$. Its structure is denoted in Fig. 11.7.

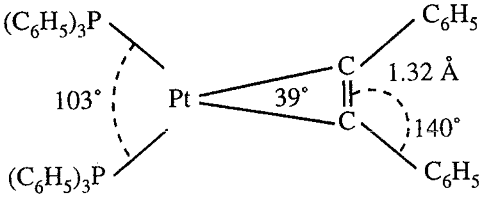
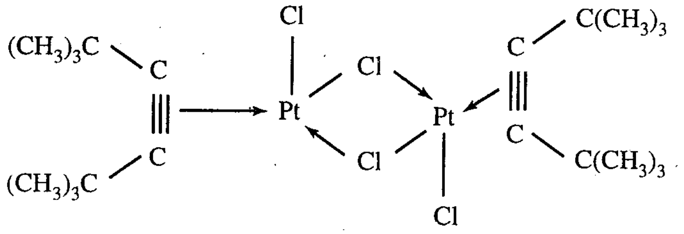


Fig. 11.7 Structure of bis(triphenylphosphine)-diphenylacetyleneplatinum(0)

The olefin unit lies almost in the plane of $Pt(PPh_3)_2$. The structure is approximately square-planar.

Another example for an alkyne complex is $[\{PtCl_2(t\text{-}BuC \equiv Ct\text{-}Bu)\}_2]$. It is a bisalkyne, binuclear complex. Its structure is denoted as

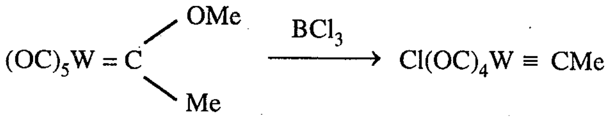


11.1.13 Carbyne Complexes (Alkylidynes)

A carbyne complex consists of a metal-carbon triple bond:

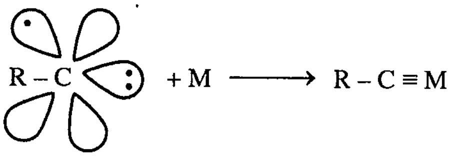
$$M \equiv C - R$$

The following reaction indicates the formation of such a complex.



$$(OC)_5W = C(OMe)(Me) \xrightarrow{BCl_3} Cl(OC)_4W \equiv CMe$$

The carbyne ligand is a three-electron donor (similar to NO), with a pair of electrons in an *sp* orbital and one electron in a *p* orbital. The *sp* electron pair forms a π bond, the *p* electron pairing with a metal electron forms a σ bond; the second π bond is formed by the donation of an electron pair from the metal atom to the empty *p* orbital of the ligand.

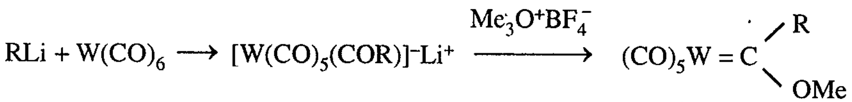


11.1.14 Carbene Complexes (Alkylidenes)

A carbene complex contains a metal-carbon double bond:

$$M = CR_2$$

•For example, the reaction between phenyl lithium (or methyl lithium) and hexacarbonyltungsten produces first an acyl anion, which on alkylation with $R_3O^+.BF_4^-$ (or CH_2N_2) forms the tungsten – carbene complex:



$$RLi + W(CO)_6 \longrightarrow [W(CO)_5(COR)]^-Li^+ \xrightarrow{Me_3O^+BF_4^-} (CO)_5W = C(R)(OMe)$$

Metal carbenes of this type, called *Fischer's carbenes* are characterised by

(i) a metal in a low oxidation state.
(ii) π-accepting auxiliary ligands.
(iii) substituents on the carbene carbon capable of donating π electron density.
(iv) electrophilic nature of the carbene carbon.

The short-lived carbenes, formed during certain organic reactions can be trapped with a transition metal, producing $M:CR_2$. A carbene , like a CO is a two-electron donor as it contains a lone pair of electrons, and its carbon atom is formally divalent.

11.1.15 Carbido Complexes

In a carbido complex, carbon is bound only to a metal atom. For example, $Fe_5(CO)_{15}C$ is a carbido complex.

11.1.16 Metal "Sandwich" Complexes

A sandwich metal complex consists of a metal sandwiched between two cyclic organic ligands. The first such complex prepared was bis-π-(cyclopentadienyl)iron, commonly called ferrocene. Its formula is $(\pi\text{-}C_5H_5)_2Fe$.

SCIENTIFIC SERENDIPITY

The word "serendipity" means making fortunate discoveries accidentally. This word was coined by Horace Walpole after his story *The Three Princes of Serendip.* The three princes of Serendip, according to this novel, made discoveries by accidents. The formation of ferrocene was a serendipity. In 1951, Kealy and Paulson attempted to prepare bicyclopentadienyl $(C_5H_5-C_5H_5)$ by reacting $FeCl_2$ and C_5H_5MgBr. Instead of the expected product, this reaction produced ferrocene.

$$2\,C_5H_5-Mg-Br+FeCl_2 \longrightarrow \underset{\text{Ferrocene}}{(\pi\text{-}C_5H_5)_2Fe}+MgBr_2+MgCl_2$$

Further study of this product was done by Wilkinson and Fischer.

Ferrocene may be regarded as the Fe^{2+} -derivative of the cyclopentadienyl anion, $C_5H_5^-$

$$2\,C_5H_5^- + Fe^{2+} \longrightarrow \pi\text{-}Fe(C_5H_5)_2$$

A method of preparing this complex involves the reaction between $FeCl_2$ and C_5H_6 in presence of a strong base, such as diethyl amine.

$$FeCl_2+2\,C_5H_6+2\,(C_2H_5)_2\,NH \longrightarrow (\pi\text{-}C_5H_5)_2Fe+2\,(C_2H_5)_2\,NH_2Cl$$

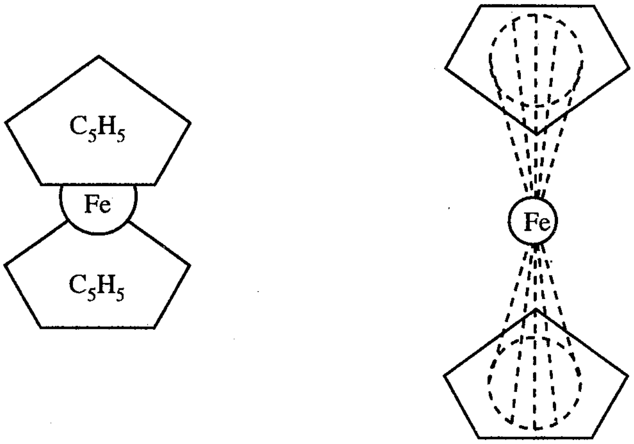
11.1.17 Structure of Ferrocene

The structure of ferrocene (Fig.11.8), has been determined by X-ray diffraction.

The important structural features of ferrocene are the following :

1. It has a *sandwich structure*, in which the two cyclopentadienyl groups are nearly eclipsed with respect to each other (the two planar rings are aligned in space in the same manner, parallel to each other).
2. The hydrogen atoms are slightly tilted towards the iron atom.
3. All the carbon atoms in it are equidistant from Fe; therefore the ring is assumed to have a hapticity η of 5, i.e., $\eta^5-C_5H_5$.
4. All the C-C distances are same (1.389 Å), a value close to 1.395 Å of benzene. The bond order is similar to that in benzene.

5. The two rings are separated by a distance of 3.25 Å.
6. The Fe-C distances are all equal (2.04 Å).
7. The energy barrier for rotation of the rings about the metal to ring axis is very small (4 kJ mol^{-1}).



(*a*) (*b*)

Fig. 11.8 *Structure of ferrocene*

11.1.18 Bonding in Ferrocene

The bonding in ferrocene can be understood by considering the molecule to be a combination of a ferrous ion with two $C_5H_5^-$ anions. Each $C_5H_5^-$ is planar with a symmetrical pentagonal shape. The entire ring is bonded uniformly to the metal atom. The bonding in it occurs by overlap of the sextet of π electrons of the ring with the 3*d* orbitals of the metal, thereby producing a *delocalised covalent bond* between the metal atom and the cyclopentadienyl ring as a whole. One such overlap is shown in Fig. 11.9.

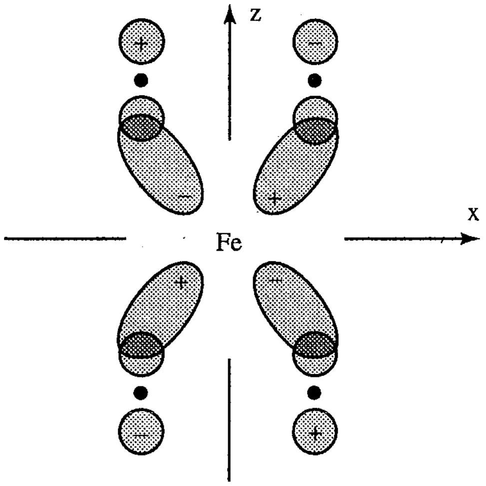


Fig. 11.9 *A sketch showing the overlap of a* d_{xz} *metal orbital with a ring* π *orbital to produce a metal-ring bond*

11.1.19 Properties of Ferrocene

1. Ferrocene is a crystalline orange solid, with a m.p. of 174°C.
2. It is insoluble in water but soluble in organic solvents.
3. It is thermally stable up to 500°C in the absence of air.
4. It is diamagnetic and non-polar.
5. Alkalis and acids do not attack this complex.
6. It gets oxidised to blue paramagnetic ferricinium ion $[\pi\text{-}(C_5H_5)_2Fe]^+$ by Ag^+. This ion can form salts with X^- ions. This oxidation is reversible.

$$[(\pi\text{-}C_5H_5)_2 \overset{(III)}{Fe}]^+ + e^- = [(\pi\text{-}(C_5H_5)_2)\overset{(II)}{Fe}] \quad E^\circ = 0.5\ V$$

7. Ferrocene undergoes electrophilic substitution reactions such as halogenation, acetylation and alkylation like an aromatic compound; Woodward named it ferrocene because of its aromatic character. This aromatic character is in accord with the Huckel rule which requires $(4n + 2)\ \pi$ electrons for aromatic character.
8. It cannot be catalytically hydrogenated, and it does not add on maleic anhydride. Thus, it does not show the unsaturated character of the parent reactant cyclopentadiene. This is justifiable as the π electrons of the rings are involved in the bonding with the Fe atom.

11.1.20 Bis(cyclopentadienyl)beryllium

$Be(C_5H_5)_2$ is prepared by metathesis of $BeCl_2$ with $Na[C_5H_5]$:

$$BeCl_2 + 2\ Na[C_5H_5] \rightarrow Be\ (C_5H_5)_2 + 2\ NaCl$$

In the gas phase, it has an antisymmetrical sandwich structure. It has pentahapto bonding (η^5), as all the C atoms of each C_5H_5 group are within bonding distance of the Be atom. In the solid phase, the structure corresponds to $\eta^5 - C_5H_5.\eta^1 - C_5H_5$; the hapticity for one of the C_5H_5 groups is reduced from 5 to 1.

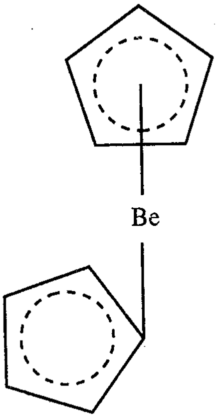


Fig. 11.10 Structure of solid bis(cyclopentadienyl) beryllium

11.1.21 Metallocenes

Several other 3*d* metals also form sandwich compounds similar to iron. Elements which form carbonyls generally also form π-cyclopentadienyls.These compounds and also ferrocene are commonly called *metallocenes*. The metallocenes are isostructural. Some of the metallocenes and their properties are summarised in Table 11.2. Ferrocene is the most stable of the metallocenes.

Table 11.2 Some bis-π-(cyclopentadienyl) metal complexes

Formula	Name	Colour	m.p.(°C)	Magnetic Property(BM)
$(\pi\text{-}C_5H_5)_2Ti$	titanocene	green	200	diamagnetic
$(\pi\text{-}C_5H_5)_2V$	vanadocene	violet	168	3.78
$(\pi\text{-}C_5H_5)_2Cr$	chromocene	scarlet	173	3.02
$(\pi\text{-}C_5H_5)_2Mn$	manganocene	brown	173	2.50 at 195°C
$(\pi\text{-}C_5H_5)_2Fe$	ferrocene	orange	174	diamagnetic
$(\pi\text{-}C_5H_5)_2Co$	cobaltocene	purple	174	1.76
$(\pi\text{-}C_5H_5)_2Ni$	nickelocene	green	173	2.86
$(\pi\text{-}C_5H_5)_2WH_2$	dihydridotungstocene	yellow	163	diamagnetic

Not all these metallocenes obey the 18-electron rule.

Among these, only ferrocene is thermally stable (upto 500°C) and unaffected by air. The 19-electron cobaltocene understandably gets easily oxidized to the 18-electron cobaltocenium ion, $[Co(\eta^5-C_5H_5)_2]^+$; this ion is remarkably stable.

Several cyclopentadienyl complexes containing other ligands such as carbonyl, nitrosyl and hydride are known. Some of these are isoelectronic. Assuming that each cyclopentadiene ring contributed all its π electrons to the molecular orbitals, an 18-electron valence shell is conferred on the central atom of most of these complexes (Table 11.3)

Table 11.3 Valence electron numbers in cyclopentadienyl complexes

Complex	Valence electron number
$[Ti(C_5H_5)_2]^{2+}$	$(2 \times 5) + 2 = 12$
$[V(C_5H_5)(CO)_4]$	$5 + 5 + (4 \times 2) = 18$
$[V(C_5H_5)_2]$	$(2 \times 5) + 5 = 15$
$[Cr(C_5H_5)_2]$	$(2 \times 5) + 6 = 16$
$[Cr(C_5H_5)(NO)_2]^+$	$5 + 5 + (2 \times 3) = 16$
$[Cr(C_5H_5)(CO)_2NO]$	$5 + 6 + (2 \times 2) + 3 = 18$
$[Cr(C_5H_5)(CO)_3H]$	$5 + 6 + (3 \times 2) + 1 = 18$
$[Mn(C_5H_5)(CO)_3]$	$7 + 5 + (3 \times 2) = 18$
$[Fe(C_5H_5)_2]$	$8 + (2 \times 5) = 18$
$[Fe(C_5H_5)(CO)_2]_2$	$8 + 5 + 1 + (2 \times 2) = 18$
$[Co(C_5H_5)_2]$	$9 + (2 \times 5) = 19$
$[Co(C_5H_5)_2]^+$	$8 + (2 \times 5) = 18$
$[Co(C_5H_5)(CO)_2]$	$9 + 5 + (2 \times 2) = 18$
$[Ni(C_5H_5)_2]$	$10 + (2 \times 5) = 20$
$[Mo(C_5H_5)(CO)_3]_2$	$6 + 5 + 1 + (3 \times 2) = 18$

COINCIDENTAL CHEMISTRY

The synthesis and characterisation of ferrocene was reported by G.Wilkinson at Imperial College, London, in 1951. This report was a great surprise to the chemists at that time as no other such compounds were then known; ferrocene, an iron-hydrocarbon derivative is a unique combination between a metal and an organic compound, producing a sandwich structure. The same discovery was made at the same time by E.O.Fischer in Munich (Germany). For the preparation and characterisation of ferrocene and other similar compounds, Wilkinson and Fischer were jointly awarded the Nobel Prize for chemistry in 1973. The preparation of ferrocene served as the trigger for synthesising a large number of organometallic compounds soon after 1951. Today, several organometallic compounds are well-known and many of these are used in several industrial processes.

11.1.22 Dibenzene Chromium

The formation of this metallocene was predicted by Fischer based on the 18-electron rule. It satisfies this rule (6*d*-electrons from Cr and 2 × 6 = 12 electrons from the two C_6H_6 groups). Later, it was synthesised through the reaction

$$3\,CrCl_3 + 2\,Al + AlCl_3 + 6\,C_6H_6 \rightarrow 3\,[Cr(\pi\text{-}C_6H_6)_2]^+\,[AlCl_4]^-$$

$$2\,[Cr((\pi\text{-}C_6H_6)_2]^+ + S_2O_4^{2-} + 4\,OH^- \rightarrow 2\,[Cr(\pi\text{-}C_6H_6)_2] + 2\,SO_3^{2-} + 2\,H_2O$$

It is a brown-black, crystalline solid. It melts at 285°C and decomposes at 300°C.

It can be sublimed in vacuum at 150°C. Its structure is a sandwich one, the Cr atom being between the two benzene rings. It is oxidized to $Cr(\pi\text{-}C_6H_6)_2^+$ by acids, similar to ferrocene.

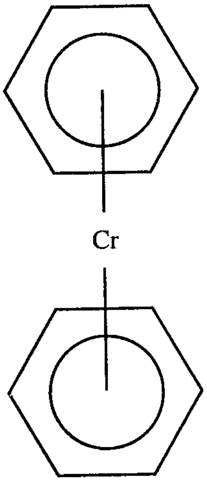
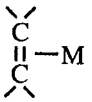
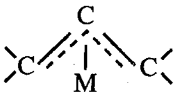
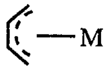
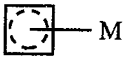
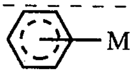
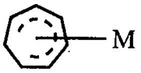
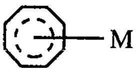


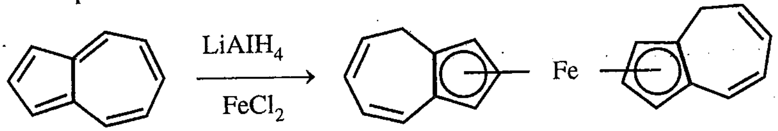
Fig. 11.11 Structure of dibenzenechromium

Table 11.4 gives the important bonding features for some organic ligands which form organometallic compounds.

Table 11.4 Some organic ligands which form organometallics

Ligand	Available electrons	Metal-ligand structure	Hapticity
Methyl, alkyl, CH_3, CH_2R	1	$M - CH_2R$	η^1
Alkylidene (carbene)	2	$M = CR_2$	η^1
Alkene $H_2C = CH_2$	2		η^2
π-Allyl C_3H_6	3		η^3
Alkylidyne (carbyne) C—R	3	$M \equiv CR$	η^1
1,4-Butadiene C_4H_8	4		η^4
Cyclobutadiene C_4H_4	4		η^4
Cyclopentadiene C_5H_5 (Cp)	5 (3) (1)		η^5 η^3 η^1
Benzene C_6H_6	6		η^6
Tropylium ion $C_7H_7^+$	6		η^7
Cycloheptatriene C_7H_8	6		η^6
Cyclooctatetraene C_8H_8 (cot)	8 (6) (4)		η^8 η^6 η^4

Azulene produces a metallocene on treatment with $FeCl_2$ and $LiAlH_4$:



The lanthanide and actinide elements form complexes with cyclo-octatetraene in which the ligand acts as a dianion, $C_8H_8^{2-}$. An example for such a product is uranocene.

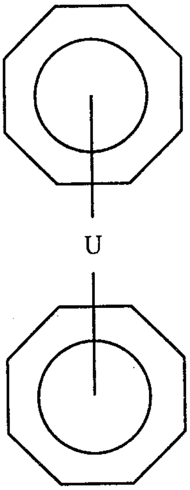


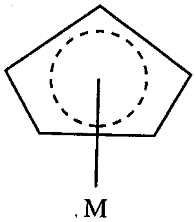
Fig. 11.12 *Structure of uranocene*

It is a sandwich molecule; the two rings are planar. All the C–C bond lengths in it are equal; 1.39 Å. The two rings in it are eclipsed. The bonding in it is similar to that in ferrocene, except that it involves the *f* orbital of *U*; *U* is formally in the +4 oxidation state.

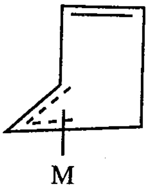
11.1.23 Notation in the Nomenclature of Metal-olefin Complexes

An olefin containing more than one π bond can bond with a metal in different ways; more than one carbon atom may be attached to the metal. Therefore, a systematic notation is used to designate the number of carbon atoms that are bound to the metal. This notation uses the Greek term *hapto*, which means *to fasten*. If only one carbon of the olefin is bonded to the metal, then the prefix *monohapto* (symbol η^1) is used for the name of the complex.The prefixes *bihapto* (η^2), *trihapto* (η^3), *tetrahapto* (η^4), *pentahapto* (η^5), etc. designate the other types of binding. In a η^5 complex, five carbon atoms are linked to the metal, [e.g. $(\eta^5 - (\pi - C_5H_5)_2 Fe)$].

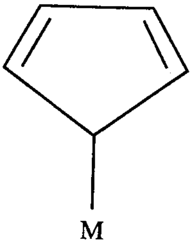
Allyl, for example, may attach itself to a metal through one of its carbon atoms (behaving like an alkyl ligand) or through all three carbon atoms via its π electron system. Ligands with a more extended π systems show a greater number of binding modes. For example, the cyclopentadienyl ligand may function as a penta, tri, or monohapto ligand:



η^5-C_5H_5



η^3-C_5H_5

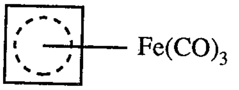


η^1-C_5H_5

11.1.24 Half-sandwich Compounds

In a *half-sandwich* compound, only one ring is coordinated to the metal along with other ligands. These can be prepared from the respective metal carbonyls. Cyclobutadieneiron tricarbonyl is such a complex. This complex is stable though cyclobutadiene itself is not. This is an example for stabilisation of a labile ring species by complexation.

The molecular orbital calculations indicate that there are effectively six pi electrons in the cyclobutadiene-metal system; it is said to be *metalloaromatic*.



UNIFICATION OF CHEMISTRY

The wrong idea that no organic compound could be prepared from inorganic compounds was called the *vital force theory*. The synthesis of an organic compound, urea from inorganic compounds for the first time by Wohler in 1828 disproved this theory and removed the water-tight distinction between organic chemistry and inorganic chemistry. Then, the synthesis of organometallic compounds provided a "bridge" between organic and inorganic chemistry. The use of such compounds now provides a unifying link between organic and inorganic chemists. Compounds of aluminium, boron, silicon, lithium, chromium, etc. and also metal complexes are extensively used in organic synthesis. Inorganic chemists use organic molecules as ligands for identifying and determining metals, stabilising low oxidation and high oxidation states of metals. These facts indicate that chemistry is actually unified and the terms "organic", "inorganic" and "organometallic" are simply labels used for the convenience of chemists.

11.1.25 Uses of Organometallic Compounds

The organometallic componds are used in several industrial and laboratory reactions. The following are some of such uses:

1. Ferrocene, when added to fuel oils promotes smokeless combustion of the oil.
2. $Pb(C_2H_5)_4$ is used as an antiknock agent in petrol.

3. Cyclopentadienylmanganese tricarbonyl is an effective antiknock agent for petrol; it is more effective than $Pb(C_2H_5)_4$.
4. A mixture of $(C_5H_5)_2TiCl_2$ and $Al(C_2H_5)_2Cl$ is used as a catalyst for the polymerisation of ethylene.
5. $Co_2(CO)_8$ is used as the catalyst in the manufacture of aldehydes and alcohols from olefins (oxo process).
6. $Fe(CO)_5$ acts as the catalyst in reactions of the type

$$CO + ROH + C_2H_2 \longrightarrow H_2C = HC\text{-}COOR$$

7. In the heterogeneous polymerisation of olefins with Ziegler- Natta catalyst, organometallic intermediates are involved.
8. In the hydrogenation of olefins, Wilkinson's catalyst, $[RhCl(PPh_3)_3]$ is used.

OUTLOOK ON ORGANOMETALLICS

These compounds are currently used as catalysts and reactants in the production of

- polymers
- pharmaceuticals
- agriculturals
- flavours
- fragrances
- semiconductors
- ceramic precursors
- fuels, fuel additives

An important outcome of using these catalysts in industrial processes is the reduction in chemical reactor operation temperatures; this implies a large saving of fuels; therefore, with increasing global energy crisis, this aspect of their use alone would render them a vital class of raw materials in chemical industries. In addition, the conversion of synthesis gas (derived from coal) into useful organic intermediates with the mediation of organometallic catalysts would become a significant process in view of the depleting world petroleum reserves.

EXERCISES

*1. The reaction between $(\pi\text{-}C_5H_5)_2TiCl_2$ and $AlEt_3$ gives as one of the products, a blue crystalline complex of composition $(\pi\text{-}C_5H_5)_2TiCl_2AlEt_2$. A solution of this product acts as Ziegler catalyst to polymerize ethene. Predict the structure of this catalyst.

*2. What hapticities are possible for benzene?

*3. The reaction of $NiBr_2$ with allyl magnesium bromide produces η^3-diallylnickel(0). Draw the possible structures for the product.

*4. What is "ring-whizzing" with reference to complexes of the type $\eta^1\text{-}(C_5H_5)\eta^5(C_5H_5)Fe(CO)_2$?

5. Does nickelocene $Ni(C_5H_5)_2$ obey the EAN rule?

6. Describe the bonding in nickelocene.

*7. **Match the following:**

a) monohapto	(i) π-allyl
b) dihapto	(ii) tropylium
c) trihapto	(iii) perfluoroethene
d) heptahapto	(iv) isocyanide

8. The stability of η^1 complexes of a metal is in the order for ligands alkyl < aryl < *o*-substituted aryl < ethynyl ; explain this.

9. In the structure of $[Pt(\eta^2\text{-}C_2H_4)Cl_3]^-$, the Pt-Cl distance trans to the C_2H_4 group is longer than the two cis-Pt-Cl distances by 3.8 pm; What causes this bond distance difference?

10. **Match the following:**

a) Dewar – Chatt – Duncanson	(i) first synthesis of ferrocene
b) Wilkinson	(ii) theory of metal – olefin bonding
c) Kealey – Paulson	(iii) structure of ferrocene

11. **Suggest a method of preparing each of the following:**

a) $[Pd(\eta^3-C_5H_5)_2]$

b) $[Fe(\eta^5-C_5H_5)(\eta^5-C_4H_4N)]$

c) $[M(\eta^6-C_6H_6)(CO)_3]$

12. **Explain the following statements:**

a) The fact that the C = C bond in the Zeise salt is perpendicular to the $PtCl_2$ plane can be established by neutron diffration method.

b) Back-donation alters the C – C bond distances in metal – alkene complexes.

c) Many η^3 – allyl complexes at room temeperature are fluxional.

*13. $[Fe(\eta^5-C_5H_5)_2]$ is more stable than $[Co(\eta^5-C_5H_5)_2]$ and $[Ni(\eta^5-C_5H_5)_2]$.

14. Predict and draw the structure of $\pi\text{-}C_5H_5MnC_2H_4(CO)_2$.
How many ^1H NMR signals are expected of this compound?

*15. On reacting $Mn(CO)_5^-$ with $ClCH_2-CH=CH_2$, a product *A* with a molar mass 236 is formed. *A* on irradiation with ultraviolet light forms *B* with a molar mass 180. Find out *A* and *B*.

14. Outline how X-ray diffraction is useful in determining the structures of π-bonded metal complexes.

17. Discuss the structure and bonding in $[(\pi\text{-}C_5H_5)Mn(CO)_3]$

*18. **Illustrate the following:**
   a) metallation
   b) methylenation

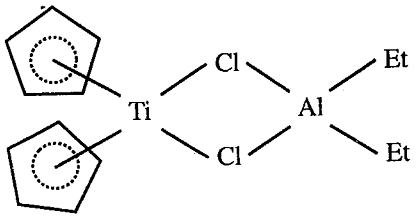
*19. Fe, Ru and Os form neutral 18-electron $(C_5H_5)_2M$ compounds; rationalize this.

*20. The IR spectrum of $[Ni(C_5H_5)_2(CO)_2]$ consists of two CO stretching bands at 1857 cm^{-1} and 1897 cm^{-1}. How can these be justified?

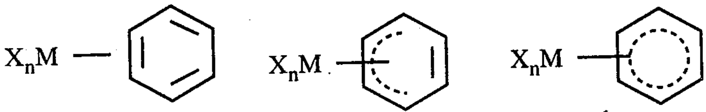
21. Arrive at the number of valence electrons surrounding the central metal in each of the following:
   a) $[HTc(CO)_5]$
   b) $[HMn(CO)_5]$
   c) $[Fe(C_5H_5)(CO)_2Cl]$
   d) $[Mn(C_5H_5)(C_6H_6)]$

ANSWERS

1.

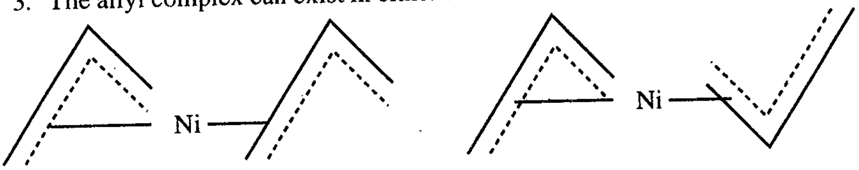


2.



η^2 η^4 η^6

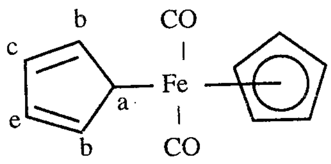
3. The allyl complex can exist in either the cis or trans form:



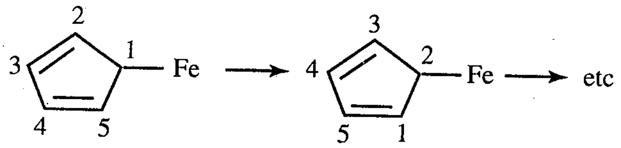
cis trans

The complex has fluxional character proved by ^1H NMR studies.

4. The structure of this complex is



The bonding of Fe with the $\eta^1-C_5H_5$ ring can change with respect to the ring carbon atoms. The π-bonded C_5H_5 can change its point of attachment to the Fe through 1, 2 shifts.



This kind of site change is called ring-whizzing. Due to ring-whizzing, all the protons of the σ-bonded ring become equivalent and produce a single ^1H NMR signal when the temperature is not very low.

7. a) (iv) b) (iii) c) (i) d) (ii)

13. The Fe complex is an 18-electron system whereas the Co complex is a 19-electron system and the Ni complex is a 20-electron system. The latter two are easily oxidized as they contain in their e_{1g} *, one extra electron and two extra electrons respectively than the EAN Fe system.

15. $Mn(CO)_5^- + ClCH_2-CH=CH_2 \rightarrow (CO)_5MnCH_2-CH=CH_2$ (A)
$\rightarrow (CO)_3Mn(\pi\text{-}C_3H_5)$ (B)

18. a) Metallation is hydrogen – metal exchange:
$$2\,C_5H_6 + 2\,Na \rightarrow 2\,C_5H_5Na + H_2$$
b) Methylenation is inserting methyl carbon atom next to a metal:
$$GeCl_4 + CH_2N_2 \xrightarrow[210\,K]{Cu\ catalyst} Cl\text{-}CH_2\text{-}GeCl_3 + N_2$$

19. Each C_5H_5 ligand contributes 5 electrons to the central metal. Therefore 10 electrons are contributed by the two ligand species. Fe, Ru and Os belong to the VIII group in the periodic table; therefore each has 8 electrons in its valence shell. Consequently the neutral $(C_5H_5)_2M$ complexes satisfy the 18-electron rule. These complexes are therefore stable.

20. For a terminal CO ligand ν_{CO} is normally greater than 1900 cm^{-1}. The absence of such an absorption in this case rules out the presence of any terminal CO group. Thus both CO groups must be of bridging type. The different ν values for these two indicate that the CO groups are nonequivalent; probably they are not collinear.

Chapter 12

Metal Carbonyls and Related Compounds

Metal carbonyls and their related compounds are most commonly formed by the metals in group VIII in the periodic table, and less commonly by the neighbouring transition elements in groups VII and VI, and still less commonly by certain elements in group V. They are formed by reactions involving CO and either free metals or metal salts, and are characterised as having CO groups directly bonded to the metal atoms through carbon. Transition metal carbonyls and related anions and cations are defined as complexes of the transition metal in zero or low positive or low negative oxidation state with CO.

A characteristic feature of the *d*-block elements is their ability to form complexes with a variety of neutral molecules such as CO, NO, pyridine, dipyridyl etc. In many of these complexes, the metal atoms are in either zero, or low positive, or low negative oxidation states. This is because these ligands stabilise the low oxidation states. This property of *d* block elements is associated with the fact that the donor atoms of these ligands possess vacant orbitals in addition to lone pairs. These vacant orbitals accept electron density from filled metal orbitals to form a type of π-bonding which supplements the σ -bonding arising from lone pair donation. The formation of an additional π-bond by the transference of charge from the metal provides the means for strengthening the original σ -bond by the removal of unfavourable charge separation induced by the donor σ -bond. The drift of metal electrons into CO orbitals will tend to make CO as a whole negative and hence it increases its basicity which accounts for the greater strength of σ -bond; at the same time, the drift of electrons to the metal in the σ -bond tends to make CO positive, thus enhancing the acceptor strength of the π-orbitals. The effects of σ -bond formation thus strengthen π-bonding and vice versa. This bonding mechanism is known as *synergic interaction* which accounts probably for a major part of the M-C bond strength in metal carbonyls and related compounds. For this interaction to occur, the metal atoms must have more electrons, that is, metal atoms should be in zero or low positive or low negative oxidation states.

- The first carbonyl to be known was $Ni(CO)_4$; it was prepared in 1888 by C. Langer in L. Mond's Laboratory.
- $Fe(CO)_5$ was the second carbonyl to be synthesised in 1891.
- L. Mond developed the industrial method of producing Ni through the carbonyl, $Ni(CO)_4$ in 1899.
- IR, ^{13}C NMR and Mössbauer spectroscopies provide unequivocal evidence for the bonding and structures in metal carbonyls.
- X-ray diffraction is useful in the geometry determination of carbonyls.

12.1 EAN RULE AND METAL CARBONYLS

The adherence of metal carbonyls and related compounds to the EAN rule is striking. In mononuclear metal carbonyls, $M(CO)_y$, the EAN of metal M is that of the next higher inert gas and is given by the relation,

$$\text{EAN} = m + 2y$$

where m is the atomic number of the metal, M. Each CO group adds two electrons. Examples for such carbonyls include, $Cr(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$, etc.

Atomic number of Cr	24
Oxidation state(0)	0
Electrons gained through coordination	$6 \times 2 = 12$
Total	36

which is the atomic number of the next higher inert gas, krypton. Thus many metal carbonyls obey the EAN rule.

For carbonyls of the type, $M_x(CO)_y$, the relation,

$$G - \left(\frac{xm + 2y}{x}\right) = x - 1$$

holds good. In the above equation, G is the atomic number of the next higher inert gas and m is the atomic number of the metal M. For example, manganese forms a binuclear carbonyl, $Mn_2(CO)_{10}$, which obeys this expression.

$$36 - \left(\frac{(2 \times 25) + (2 \times 10)}{2}\right) = 36 - 35 = x - 1$$

that is, $36 - 35 = 2 - 1 = 1$. Thus, $x = 2$.

This relation also applies to polynuclear compounds and most of the related carbonyl compounds. The EAN rule can only be used as a guiding principle and not as a strict inviolable rule. If the central metal in a complex is present as an ion, then the EAN of the metal is derived by deducting the number of electrons lost in ion formation from the atomic number of the metal, and then adding the number of electrons gained by coordination. In many cases the EAN so calculated is equal to the atomic number of the next higher inert gas element.

12.2 CLASSIFICATION OF METAL CARBONYLS

Metal carbonyls are broadly classified into two types, namely, *mononuclear* and *polynuclear metal carbonyls*. Mononuclear metal carbonyls are those which contain only one central metal atom. Examples for mononuclear metal carbonyls are $[V(CO)_6]$, $[Cr(CO)_6]$, $[Fe(CO)_5]$, $[Ni(CO)_4]$ etc. Polynuclear metal carbonyls are those which contain more than one central atom. Depending upon the number of central metal atoms polynuclear carbonyls are called binuclear, trinuclear, tetranuclear metal carbonyls. These polynuclear metal carbonyls are further classified into *homopolynuclear* and *heteropolynuclear metal carbonyls.* Homopolynuclear metal carbonyls are those which contain the same central metal atoms. For example, $[Mn_2(CO)_{10}]$, $[Fe_2(CO)_9]$, $[Fe_3(CO)_{12}]$, $[Co_2(CO)_8]$, $[Co_4(CO)_{12}]$, $[Co_6(CO)_{16}]$ etc. Heteropolynuclear metal carbonyls are those which contain more than one kind of central metal atom. For example, $[Mn_2Fe(CO)_{14}]$, $[CoMn(CO)_9]$, $[Fe_2Ru(CO)_{12}]$, $[FeRu_2(CO)_{12}]$ etc.

12.3 PREPARATION OF METAL CARBONYLS

Metal carbonyls can be prepared by the following methods.

12.3.1 Direct Combination

$$xM + yCO \rightarrow M_x(CO)_y$$

Metal carbonyls can be prepared by passing CO over finely divided metal at suitable temperature and pressure. $Ni(CO)_4$, $Fe(CO)_5$, $Co_2(CO)_8$, $Mo(CO)_6$, $Ru(CO)_5$, $Rh_2(CO)_8$, etc are such metal carbonyls prepared by this method. Pressure greater than one atmosphere is required in the preparation of all except $Ni(CO)_4$, and the yields are small except for the carbonyls of Fe and Ni. In general, the metal must be in a finely divided active state. In the case of nickel, the metal has been prepared by the reduction of the oxide using hydrogen at 400°C or of the oxalate at 300°C. The lower the temperature of reduction, the more active is the resulting metal for carbonyl formation. A very active metal has been prepared by electrolysing a solution of $NiSO_4$ with a mercury cathode and subsequent low temperature distillation of mercury.

For example, the iron pentacarbonyl is directly formed:

$$Fe + 5\,CO \xrightarrow[200\text{ atm}]{200^\circ C} Fe(CO)_5$$

12.3.2 High Pressure Synthesis

Almost all of the known metal carbonyls have been prepared by reactions between metallic halides or sulphides or oxides and CO under pressure. Such reactions are useful especially in cases where metallic compounds are largely covalent. Generally, some free metal must be present to act as an acceptor for the non-metal. For example, $Co_2(CO)_8$ is prepared as per the equation,

$$2\,CoS + 8\,CO + 4\,Cu \rightarrow Co_2(CO)_8 + 2\,Cu_2S$$

12.3.3 Disproportionation Reaction

Disproportionation reactions are reactions involving self-oxidation and reduction. One part of the reactant is oxidised at the expense of the other part which gets reduced.

For example, when nickel(I) cyanide is treated with carbon monoxide, $Ni(CO)_4$ and $Ni(CN)_2$ are formed.

$$2\overset{I}{Ni}CN + 4\,CO \rightarrow \overset{0}{Ni}(CO)_4 + \overset{II}{Ni}(CN)_2$$

A similar reaction takes place when a complex of univalent nickel is employed, an intermediate probably being formed.

$$K_2[\overset{I}{Ni}(CN)_3] + CO \rightarrow K_2[\overset{I}{Ni}(CN)_3CO]$$

$$2\,K_2[\overset{I}{Ni}(CN)_3CO] + 2\,CO \rightarrow \overset{0}{Ni}(CO)_4 + K_2[\overset{II}{Ni}(CN)_4] + 2KCN$$

12.3.4 Oxidation of Metal Carbonyl Hydrides

Oxidation of metal carbonyl hydrides by MnO_2 or H_2O_2 yields metal carbonyls. For example, oxidation of iron carbonyl hydride using H_2O_2 gives the trimeric tetracarbonyl of iron:

$$3H_2Fe(CO)_4 \xrightarrow[3(O)]{H_2O_2} [Fe(CO)_4]_3 + 3\,H_2O$$

12.3.5 Other Methods of Preparation

(a) By photolysis

$$2Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO$$

(b) By thermolysis

$$2\,Co_2(CO)_8 \xrightarrow{70^\circ C} Co_4CO_{12} + 4\,CO$$

(c) By reductive carbonylation

$$WCl_6 + 3\,Fe(CO)_5 \xrightarrow{100^\circ C} W(CO)_6 + 3\,FeCl_2 + 9\,CO$$

12.4 GENERAL PROPERTIES OF METAL CARBONYLS

i) Metal carbonyls are diamagnetic with the exception of $V(CO)_6$, which is paramagnetic.

ii) They are generally covalent. Their covalent characteristics are indicated not only by their volatility but also by the fact that they are insoluble in polar solvents but soluble in many nonpolar solvents.

iii) Most of the metal carbonyls are crystalline solids, except $Ni(CO)_4$ and $M(CO)_5$ (M = Fe,Ru,Os) which are liquids.

iv) Many are coloured, except $Ni(CO)_4$, which is colourless.

Table 12.1 Colourful Carbonyls

Carbonyl	Colour
$Fe(CO)_5$	yellow
$Fe_2(CO)_9$	orange
$Fe_3(CO)_{12}$	green
$Rh_4(CO)_{12}$	red

Carbonyl	Colour
$Ir_4(CO)_{12}$	yellow
$Co_2(CO)_8$	orange-red
$V(CO)_6$	blue-green
$Mn_2(CO)_{10}$	golden

v) Many are extremely toxic.

vi) They decompose on heating to their respective metals and CO.

$$Ni(CO)_4 \rightarrow Ni + 4\,CO$$

vii) In many reactions, their properties are those of the metal and CO. For example, $Ni(CO)_4$ gives $NiBr_2$ and CO with bromine and with Grignard reagents, its reactions are those of CO.

viii) Many metal carbonyls react with NO to form metal carbonyl nitrosyls where NO acts as a three-electron donor.

$$Fe(CO)_5 + 2\,NO \rightarrow Fe(CO)_2(NO)_2 + 3\,CO$$
$$Co_2(CO)_8 + 2\,NO \rightarrow 2\,Co(CO)_3NO + 2\,CO$$

ix) Metal carbonyls react with alkalis to form carbonylate anions which produce carbonyl hydrides on acidification.

$$Fe(CO)_5 + NaOH \rightarrow Na[HFe(CO)_4] + CO_2$$
$$Na[HFe(CO)_4] + HCl \rightarrow [H_2Fe(CO)_4] + NaCl$$

x) Many metal carbonyls combine directly with halogens to form metal carbonyl halides.

$$Fe(CO)_5 + X_2 \rightarrow [Fe(CO)_4X_2] + CO$$

xi) Some metal carbonyls are reduced by H_2 to form metal carbonyl hydrides.

$$Mn_2(CO)_{10} + H_2 \rightarrow 2\,HMn(CO)_5$$
$$Co_2(CO)_8 + H_2 \rightarrow 2\,HCo(CO)_4$$

12.5 USES OF METAL CARBONYLS

i) Purification of nickel by Mond's process makes use of the formation of nickel tetracarbonyl.

ii) The instability of iron pentacarbonyl in light has been used for the preparation of blueprints pertaining to building plans.

iii) Some are used in the preparation of carbonyl metals. For example, carbonyl nickel is used as an excellent hydrogenation catalyst. Carbonyl iron is soft, ductile and resistant to corrosion. The major use of carbonyl iron is in the making of magnetic core for electronic equipment. It is excellent for this purpose because of its uniform particle size, shape and structure as well as its purity.

iv) Some metal carbonyls are used in the preparation of metal oxides of industrial, use. For example, very finely divided iron oxide is obtained by heating iron carbonyl below 100°C under carefully controlled conditions. This oxide is suitable for use as a colouring agent, polishing powder and decarbonising agent for cast iron and steel.

v) Iron, cobalt and nickel carbonyls are used as antiknock agents in motor fuels instead of the less efficient lead tetraethyl.

12.6 NATURE OF BONDING IN METAL CARBONYLS

There are three kinds of bonds in metal carbonyls. They are

i) C-O bond in CO group
ii) M-C bond
iii) M-M bond in polynuclear metal carbonyls.

12.6.1 C-O bond

The idea that CO as such is in some way bound to the metal atom was postulated. The chemical evidence shows that CO is liberated in many reactions of the metal carbonyls and that the CO groups can be replaced step by step by other neutral ligands. The force constant of the CO group in metal carbonyls is not very different from that of the free CO molecule. This means that the bond character in the CO group is much the same as in the free CO molecule.

12.6.2 M-C bond

The metal atoms have nine valence orbitals [nd^5, $(n+1)s^1$ and $(n+1)p^3$], and in metal carbonyls and related compounds they show a strong tendency to utilise all of them in forming bonds. Thus in $Fe(CO)_5$, five orbitals are used for the Fe-C σ bonds, the electrons of which come from the CO groups. The remaining orbitals contain iron electrons which are used in π-bonding. The overlapping of the lone pair with the carbon atom with nd, $(n+1)s$ and $(n+1)p$ vacant metal orbitals may be regarded as forming a M-C σ bond. Because of the low basicity of CO, this is not sufficient to explain the stability of the carbonyls. Hence, further source of bonding should exist. In all metal carbonyls, there are filled non-bonding d orbitals of the metal, which are of the correct symmetry to overlap with fairly low lying π antibonding orbitals of CO to form a M-C π bond. This formation of an additional π bond by transfer of charge from the metal can be seen, not only as an additional bond, but also as a means of strengthening the original σ bond by the removal of the unfavourable charge separation induced by the donor σ bond. The drift of metal electrons into CO orbitals will tend to make CO as a whole negative and hence it increases its basicity, which accounts for the greater strength of σ bond; at the same time the drift of electrons to the metal in the σ bond tends to make CO positive, thus enhancing the acceptor strength of the π orbitals. The effects of σ bond formation thus strengthen the π bonding and vice versa. This bonding mechanism is known as *synergic interaction* which accounts for major part of the M-C bond strength in metal carbonyls and related compounds.

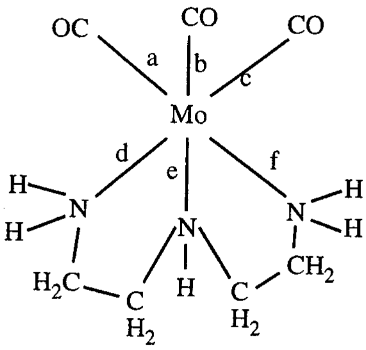
A major consequence of the presence of electrons in the π-antibonding orbitals of CO is the reduction in the bond order of the C-O bond. The C-O stretching frequency in CO itself is about 2155 cm^{-1} whereas the corresponding frequencies in terminal metal carbonyl groups lie at considerably lower values, and are generally around 2000 cm^{-1}. Any effect which decreases C-O bond order should necessarily increase M-C bond order because the two are roughly complementary to each other. This point is illustrated by the consideration of the three species $Ni(CO)_4$, $[Co(CO)_4]^-$ and $[Fe(CO)_4]^{2-}$. These are isostructural and isoelectronic. But there is a gradual increase in the excess negative charge on the metal. The excess charge will increase the extent of M-C back bonding and hence will raise the M-C bond order; consequently a corresponding decrease in the C-O bond order is expected. This decrease is reflected in the decrease of carbonyl stretching frequencies (Table 12.2).

Table 12.2 The bond orders and carbonyl stretching frequencies of isoelectronic $[Ni(CO)_4$, $[Co(CO)_4]^-$ and $[Fe(CO)_4]^{2-}$.

Species	C-O bond order	M-C bond order	Sum of bond orders	Carbonyl stretching frequency (cm^{-1})
$Ni(CO)_4$	2.64	1.33	3.97	~ 2060
$[Co(CO)_4]^-$	2.14	1.89	4.03	~ 1890
$[Fe(CO)_4]^{2-}$	1.85	2.16	4.01	~ 1790

Evidence for back bonding The main aspects of physical evidence confirming the multiple nature of the M-C bonds are *vibrational spectra* and *bond lengths*. It is possible to infer directly the extent of M-C bonding from the vibrational spectra of metal carbonyls. This is easily achieved by studying the carbonyl stretching frequencies. These give rise to strong sharp bands, well separated from all other vibrational modes of the molecules. The inferring of M-C bond orders from the behaviour of C-O vibrations depends on the assumption that the valence of carbon is constant, so that a given increase in the M-C bond order should cause an equal decrease in the C-O bond order; this will cause a drop in the carbonyl vibrational frequency. From the direct comparison of CO stretching frequencies in carbonyl molecules with the stretching frequency of free CO, certain useful qualitative conclusions can be drawn. The CO molecule has a stretching frequency of 2155 cm^{-1}; those of terminal CO groups in neutral metal carbonyls are found in the range 2125 – 1900 cm^{-1} showing the reduction in CO bond orders. When changes are made which would increase the extent of M-C back bonding, the carbonyl frequencies are shifted to even lower values. Thus if some CO groups are replaced by ligands with negligible back-accepting ability, then these CO groups remaining must accept metal π electrons to a greater extent in order to prevent unfavourable accumulation of negative charge on the metal atom. Thus, carbonyl stretching frequency for $Mo(CO)_6$ is $\approx$ 2000 cm^{-1}, whereas when three CO groups are replaced by *dien* (which has no ability to back accept), as in Mo(*dien*) $(CO)_3$, a band occurs at ~ 1760 cm^{-1} corresponding to the one found at ~ 2000 cm^{-1} in $Mo(CO)_6$. Thus the participation of the metal $d\pi$ electrons in M-C multiple bonding is demonstrated.

Evidence for M-C π-bonding can also be obtained from M-C bond length data. As the extent of back donation from M to CO increases, the M-C bond becomes stronger and the C-O bond becomes weaker. Thus multiple bonding is evidenced by shorter M-C bond and longer C-O bond as compared to M-C single bond and C-O triple bond respectively. In order to estimate the extent to which the M-C bonds are shortened, the lengths of M-C bonds are measured in a molecule in which some other bond M-Y exists, such that this bond must be single. Then, using the known covalent radius for Y, estimating the single bond covalent radius of C to be 0.70 Å when an *sp* hybrid orbital is used, the length for a single M-C bond in this molecule can be found out. This value, on comparison with the observed M-C bond length gives evidence for M-C multiple bonding. The data shown in Figure 12.1 illustrates this argument.



$a = b = c \ = \ 1.94\ \text{Å}$

$d = e = f \ = \ 2.32\ \text{Å}$

Fig. 12.1 *M-C multiple bonding*

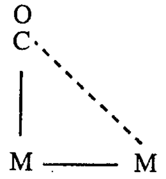
In Mo(*dien*)$(CO)_3$, the Mo-N bond length represents Mo-N single bond because the amine nitrogen atom has no orbitals available for π-bonding. When the covalent radius of sp^3-hybridised nitrogen (0.70 Å) is subtracted and the covalent radius of sp-hybridised carbon (0.70 Å) is added, the single bond length for Mo-C is obtained as 2.32 Å (= 2.32 – 0.70 + 0.70). But the observed bond length is only 1.94 Å. This large difference in bond length clearly indicates appreciable multiple bonding between metal and carbon in metal carbonyls.

In addition to the M-C bond outlined so far, many polynuclear metal carbonyls contain CO groups simultaneously bonded to 2 or 3 metal atoms. This type of bridging CO groups are not confined to metals of the first transition series. Many examples are known where 2 or 3 atoms of the second or the third transition metal series are bridged by CO groups. In structures where a CO group bridges two metal atoms, it is generally assumed that the CO group contributes one electron to each of the metal atoms to form localised σ bonds by pairing with metal electrons. The nature of π bonding with bridging CO groups is somewhat more complicated than terminal CO ligands. This is deduced from the lowered C-O bond order and observed CO stretching frequency around 1850 cm^{-1}. Although in many cases, each bridging CO group is symmetrically bound to two metal atoms, in some other cases it is asymmetrically bound to the two metal atoms. In $Rh_6(CO)_{16}$, CO groups bonded to 3 metal atoms have been identified. The CO stretching frequency in compounds where CO is bonded to 3 metal atoms is even lower (1742 cm^{-1}) than that of CO bridging only two metal atoms (1850 cm^{-1}).

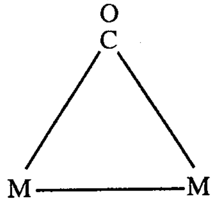
MODES OF LIGATION BY CO

There are four different modes of ligation by CO.

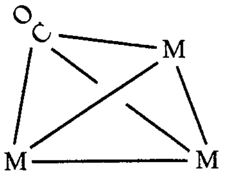
(a) terminal ligand



(b) unsymmetrical ligand (μ_2-CO)



(c) symmetrical ligand (μ_2-CO)



(d) triply bridging ligand (μ_3-CO)

Several substituted carbonyls of the formula $[M(CO)_5L]$ are known where M represents Fe, Co, Ni, W or V and L represents H^-, X^- or PX_3. In a series of complexes of the formula $[W(CO)_5L]$, the C-O stretching frequency is maximum where L is PF_3. The very high stretching frequency of the PF_3 complex indicates that this ligand is comparable to carbon monoxide itself in its π acidity. The inherent ligand π acidity influences the ν_{co} values in carbonyl complexes. The PF_3 ligand with its highly electronegative fluorine atoms withdraws electron density from W and suppresses M → L back bonding. This, in turn strengthens the C-O bond.

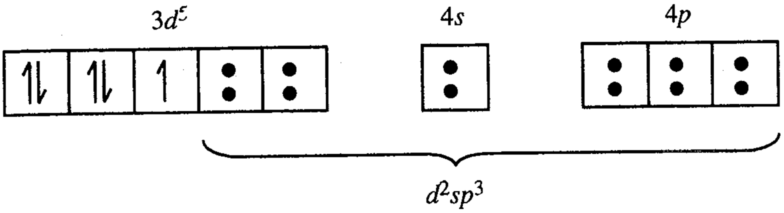
12.6.3 M-M bond

The other important type of bond present in metal carbonyls is the M-M bond. It is present either alone as in $Mn_2(CO)_{10}$ or in combination with the bridging CO groups as in $Fe_2(CO)_9$. When present with bridging CO groups, the M-M bond is used to explain the diamagnetism of the binuclear species. But such resultant diamagnetism does not require a strong M-M bond, but only a weak coupling of the unpaired spins. However, it is usual to take the M-M distance in such compounds as suggesting a direct M-M bond. In general, M-M bonding is assumed in order to satisfy the 18-electron rule for all metal atoms.

12.7 STRUCTURES AND SHAPES OF METAL CARBONYLS

12.7.1 Vanadium Group

$V(CO)_6$ is the only example of paramagnetic binary neutral metal carbonyl. Since it is short of a complete inert gas shell by one electron, it is considerably less stable than the hexacarbonyls of Cr,Mo and W. $V(CO)_6$ is assigned an octahedral structure based on X-ray and IR spectroscopies. In the VB diagram shown below, single-headed arrows represent metal electrons while dots represent the electrons donated by the CO ligands. The steric factors prevent the dimerisation of this carbonyl.



(a) VB diagram

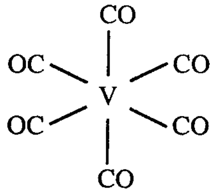


Fig. 12.2(b) *Structure of* $V(CO)_6$

The diamagnetic ion $[V(CO)_6]^-$, hexacarbonylvanadate (– I) ion, is more stable than the paramagnetic neutral carbonyl. The anions $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ have also been reported.

12.7.2 Chromium Group

IR, Raman, Electron diffraction and X-ray measurements of the hexacarbonyls of Cr, Mo and W are in agreement with a perfectly octahedral structure for each.

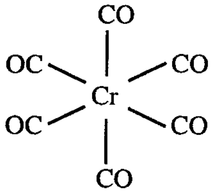


Fig. 12.3 *Structure of* $Cr(CO)_6$

In addition to these neutral carbonyls, many metal carbonyl anions have been prepared for this group of elements. The anions, $[M(CO)_5]^{2-}$, where M = Cr,Mo or W have been prepared as sodium salts by the action of metallic sodium on the hexacarbonyls in liquid ammonia. Thus $[Cr(CO)_5]^{2-}$ is isoelectronic with $Fe(CO)_5$ and hence it is quite reasonable to believe that this ion might have a trigonal bipyramidal structure as $Fe(CO)_5$. Reduction of the hexacarbonyls with $NaBH_4$ in liquid ammonia gives the anions $[M_2(CO)_{10}]^{2-}$ (M = Cr,Mo,W). The structure of each of these ions is likely to be the same as that of the neutral $M_2(CO)_{10}$ (M = Mn,Tc,Re) carbonyls of Group VII with which they are isoelectronic. The trimeric anions, $[M_3(CO)_{14}]^{2-}$ (M = Cr,Mo,W) are produced when $NaBH_4$ in tetrahydrofuran reacts with the hexacarbonyls of these metals. In these trimeric carbonyls, it is likely that two M-M bonds are present to give a linear structure $[(OC)_5M.M(CO)_4.M(CO)_5]^{2-}$ in which each M atom is essentially in an octahedral environment.

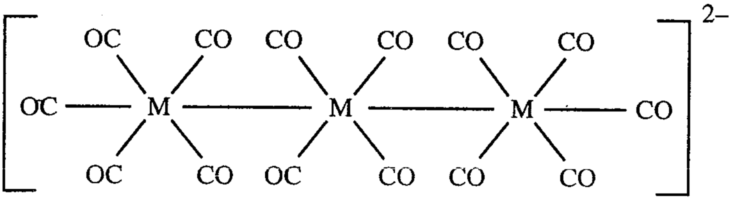


Fig. 12.4 *Structure of* $[M_3(CO)_{14}]^{2-}$

12.7.3 Manganese Group

Metal carbonyls of composition $M_2(CO)_{10}$ are known for Mn,Tc and Re. Structurally they are of interest in that they contain two square-pyramidal $M(CO)_5$ groups joined only by an M-M bond, giving each metal atom an octahedral arrangement. There is no help from bridging CO groups. This kind of linkage of the two halves of the metal carbonyl molecules by a single M-M bond occurs only in the Mn,Tc and Re compounds. In other binuclear metal carbonyls, the metal atoms are linked together not only by M-M bonds, but also by some carbonyl bridges as in $Fe_2(CO)_9$. The structure of $Mn_2(CO)_{10}$ is obtained from X-ray investigation. Its structure may be described as two staggered octahedra sharing one corner. In each of the octahedra, the four equatorial Mn-CO bonds are bent slightly inwards. This places the Mn atoms 0.12 Å out of the equatorial planes of carbon atoms. This distortion is attributed to crystal packing. The Mn atoms assume octahedral configuration with the *d* orbitals containing the unpaired electrons overlapping to give an Mn-Mn bond and a diamagnetic molecule.

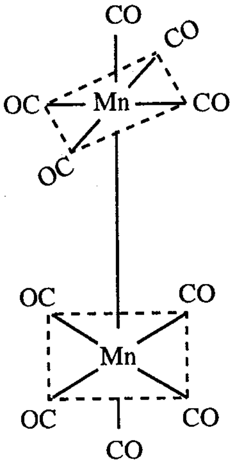


Fig. 12.5 Structure of $Mn_2(CO)_{10}$

The M-M bond in these carbonyls is larger than that expected for a single bond probably because of repulsions between neighbouring CO groups belonging to different metal atoms. The anion, $[Mn(CO)_5]^-$ is isoelectronic and hence isostructural with $Fe(CO)_5$; it posseses a trigonal bipyramidal structure. The cation, $[Mn(CO)_6]^+$ is isoelectronic with $Cr(CO)_6$ and is presumably a perfect octahedral. A novel anion whose structure has been elucidated by X-ray studies is $[Re_4(CO)_{16}]^{2-}$. In its structure the rhenium atom skeleton consists of two fused ,coplanar, approximately equilateral triangles as shown in Fig. 12.6.

Each of the the observed Re-Re bond lengths, 2.956 Å – 3.024 Å is close to the value 3.02 Å found for the Re-Re distance in $Re_2(CO)_{10}$. Each Re carries four terminal CO groups. Two of them are approximately axial and the other two are approximately equatorial. The two doubly bridging Re atoms are octahedrally coordinated. But the two triply bridging Re atoms are associated with a distorted pentagonal bipyramidal shape. In the polynuclear metal carbonyl structures, it is common to have metal atoms with different coordination numbers. Infact, even the assignment of coordination numbers to certain atoms in these structures is difficult.

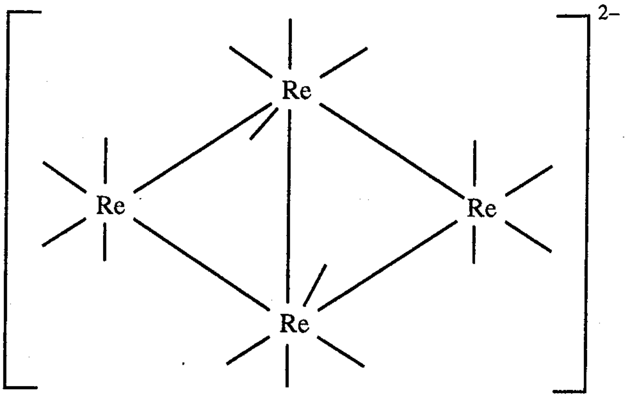


Fig. 12.6 Structure of $[Re_4(CO)_{16}]^{2-}$

12.7.4 Iron Group

The structure of $Fe(CO)_5$ molecule has been controversial for sometime. Combined IR and Raman spectral measurements have presented fairly conclusive evidence for a trigonal bipyramidal structure. Now this structure has been fully confirmed by a single crystal X-ray determination at low temperature. The electron diffraction studies suggest that the Fe-CO apical bond is slightly shorter than the equatorial one, the lengths being 1.806 Å and 1.833 Å respectively. Ruthenium and osmium form pentacarbonyls. But both of them are less stable than $Fe(CO)_5$, in accordance with a decreased tendency towards 5-coordination in the second and third series of transition elements.

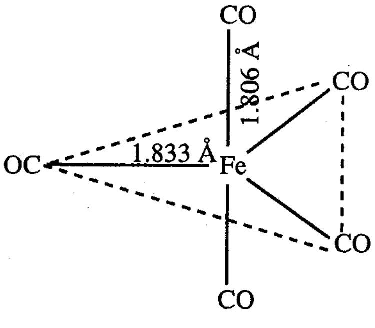


Fig. 12.7 Structure of $Fe(CO)_5$

They are likely to have trigonal pyramidal shape as $Fe(CO)_5$.

The structure of enneacarbonyldiiron, $Fe_2(CO)_9$, can be described in terms of two octahedra sharing a common face formed by the carbon atoms of the three bridging CO groups.

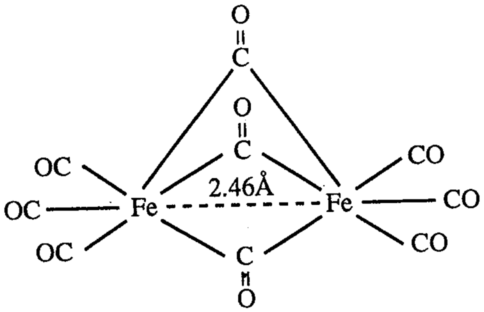


Fig. 12.8 *Structure of* $Fe_2(CO)_9$

Each iron carries three terminal CO groups. The remaining three CO groups form bridges between the two iron atoms. Fe-Fe bond is needed to account for the observed diamagnetic behaviour of the compound. The Fe-Fe distance is roughly 2.46 Å, the same as expected for a single bond.

The structure of $Fe_3(CO)_{12}$ has presented a difficult problem. A linear structure was first proposed on the basis of IR spectra and an incomplete X-ray analysis supported this. But later X-ray work required a cyclic structure. The crystal disorder prevented the location of the CO groups. More recently, Mossbauer spectra and further solid state IR studies were interpreted in favour of a cyclic structure as shown below:

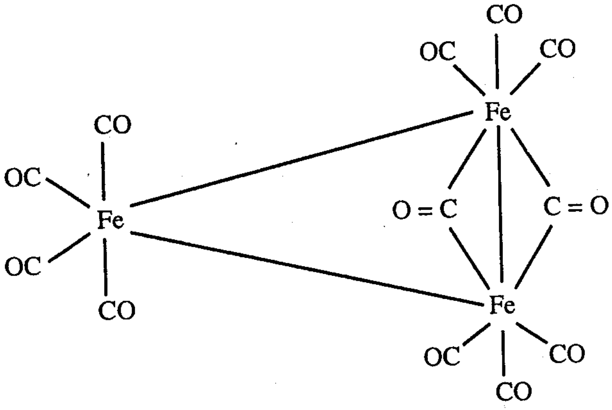


Fig. 12.9 *Structure of* $Fe_3(CO)_{12}$

This structure has been proposed on the basis of analogy with the known structure of the hydridocarbonylate anion, $[HFe_3(CO)_{11}]^-$. This structure satisfies the existing data. In this structure, the three iron atoms are at the corners of an isosceles triangle rather than an equilateral triangle. The two bridging CO groups are unsymmetrically placed. This structure for $Fe_3(CO)_{12}$ accommodates both the Mossbauer spectrum and the solid state IR spectrum.

Note: IR spectrum indicates the presence of bridging CO groups. Mossbauer spectrum reveals the presence of two different kinds of iron atoms in $Fe_3(CO)_{12}$.

The osmium and ruthenium dodecacarbonyls, $[M_3(CO)_{12}]$, are isomorphous and contain the three metal atoms linked by M-M bonds in an equilateral triangle without any help from bridging CO groups.

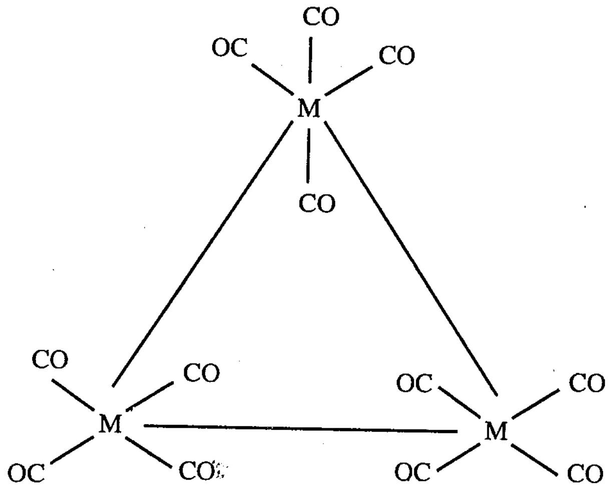
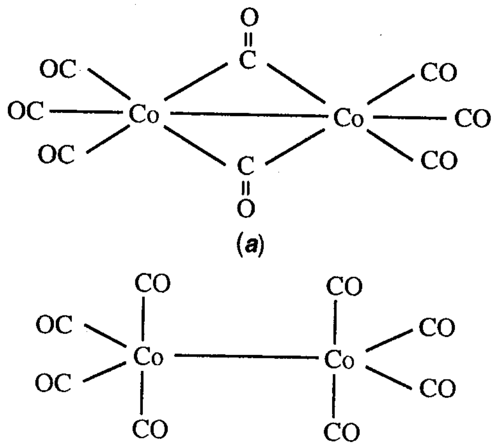


Fig. 12.10 *Structure of* $[M_3(CO)_{12}]$ *[M = Os or Ru]*

$[Fe(CO)_4]^{2-}$ is isoelectronic with $Ni(CO)_4$. Hence it is isostructural with $Ni(CO)_4$ which has a tetrahedral structure.

12.7.5 Cobalt Group

Cobalt forms three neutral carbonyls, namely $Co_2(CO)_8$, $Co_4(CO)_{12}$ and $Co_6(CO)_{16}$. In octacarbonyldicobalt, each of the cobalt atoms carries three terminal carbonyl groups. The remaining two carbonyl groups act as bridging groups between the two cobalt atoms. In addition, the two cobalt atoms are linked by a direct Co-Co



(*a*)

(*b*)

Fig. 12.11 *Structure of* $Co_2(CO)_8$ *(a) bridged and (b) non-bridged* bond. A non-bridged structure is also proposed. Both bridged and non-bridged structures are present in nearly equal proportions at room temperature.

In cobalt dodecacarbonyl, $Co_4(CO)_{12}$, the four cobalt atoms are located at the four corners of a tetrahedron in the solid state. The apical cobalt atom carries three terminal carbonyl groups. The three basal cobalt atoms carry two terminal carbonyl groups each. The apical cobalt atom is symmetrically bonded only by Co-Co bonds to the three basal cobalt atoms which are located at the three corners of an equilateral triangle. The three basal cobalt atoms are directly linked to one another not only by Co-Co bonds but also by three carbonyl groups bridged along the three sides of the equilateral triangle carrying the basal cobalt atoms. Its structure is thus considered as an icosohedron of twelve carbonyl groups encompassing the tetrahedron of four cobalt atoms.

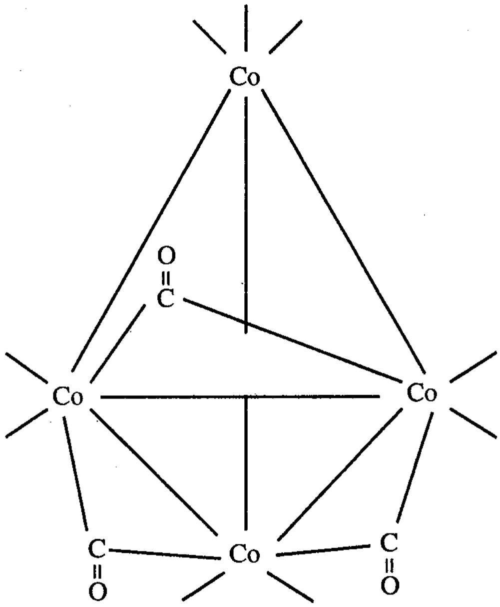


Fig. 12.12 *Solid state structure of* $Co_4(CO)_{12}$ *(terminal CO groups have been omitted for the sake of clarity)*

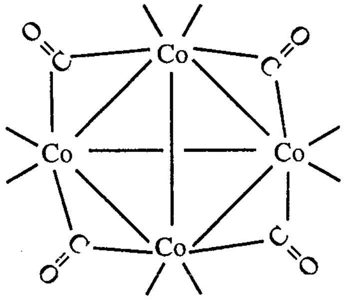


Fig. 12.13 *Structure of* $Co_4(CO)_{12}$ *in pentane solution*

But in pentane solution, IR study of this compound indicates a different structure. In this structure, each cobalt is directly linked to the other three cobalt atoms. In addition, each pair of two cobalt atoms is linked by one carbonyl bridge along the four sides of the square containing the four cobalt atoms at its corners.

The structure of $Co_6(CO)_{16}$ consists of an octahedron of six cobalt atoms with two terminal CO groups on each cobalt atom. Two CO groups out of the remaining four CO groups are present as triply-bridging CO groups, just above two opposite triangular faces above the equatorial plane of the Co_6 octahedron. The other two CO groups are also present as triply-bridging CO groups just above the other two opposite triangular faces below the equatorial plane of the Co_6 octahedron. This does not obey EAN rule. Probably multicentre bonding is involved in Co_6 octahedron.

The structures of $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ are similar to those of $Co_4(CO)_{12}$ and $Co_6(CO)_{16}$ respectively.

The structure of $[Rh_{12}(CO)_{30}]^{2-}$ is related to that of $Rh_6(CO)_{16}$ by substituting the two terminal CO groups on each Rh_6 octahedral cluster with two doubly-bridging CO groups. This carbonylate anion also does not obey the EAN rule. But the bonding could be satisfactorily accounted for, in molecular orbital terms.

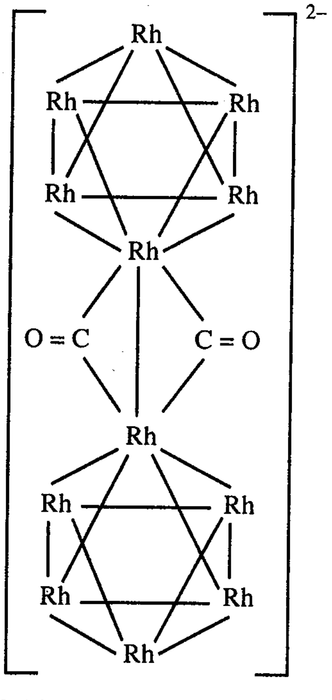


Fig. 12.14 Structure of $[Rh_{12}(CO)_{30}]^{2-}$

Iridium forms a carbonyl of composition $Ir_4(CO)_{12}$. In its structure, the tetrahedron of Ir_4 is stabilized without any help from bridging CO groups. All the twelve CO groups are present as terminal CO groups, three on each Ir atom. The twelve CO groups are in a cubo-octahedral arrangement around the tetrahedron of iridium atoms.

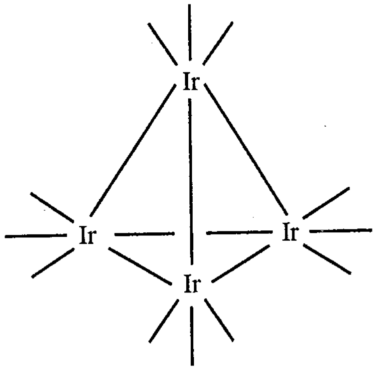


Fig. 12.15 Structure of $Ir_4(CO)_{12}$

In the cobalt subgroup, a structural change occurs between polynuclear carbonyls of similar compositions between second and third element. A similar change occurs in iron subgroup also, but between first and second element rather than between second and third.

12.7.6 Nickel Group

Nickel forms a tertacarbonyl, $Ni(CO)_4$ which is found to have a perfect tetrahedral shape from electron diffraction, X-ray and IR studies.

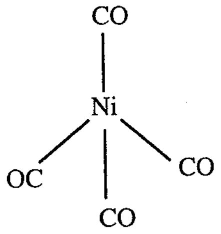


Fig. 12.16 Structure of $Ni(CO)_4$

In addition to the neutral tetracarbonyls of nickel, salts containing anions such as $[Ni_2(CO)_6]^{2-}$ and $[Ni_4(CO)_9]^{2-}$ have been prepared but the structures of these anions are not known.

12.8 HETEROPOLYNUCLEAR OR MIXED METAL CARBONYLS

Many metal carbonyls containing more than one kind of metal atom have been prepared. Some such examples are $CoMn(CO)_9$, $Mn_2Fe(CO)_{14}$, $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$, $HRe_2Mn(CO)_{14}$ and $[FeCo_3(CO)_{12}]^{2-}$. The structures of these *heteropolynuclear metal carbonyls* have been determined either by IR or by X-ray studies.

$CoMn(CO)_9$ is found to contain $Co(CO)_4$ group attached to $Mn(CO)_5$ group only by a metal-metal bond without any bridging CO group. Both Co and Mn obey the EAN rule.

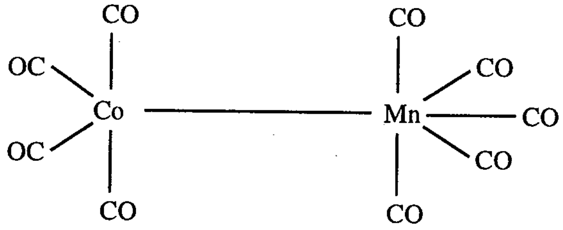


Fig. 12.17 Structure of $CoMn(CO)_9$

X-ray examination of the complex, $Mn_2Fe(CO)_{14}$ indicates a linear Mn-Fe-Mn arrangement. Each Mn carries five terminal CO groups and Fe carries four terminal CO groups. None of the CO ligands acts as bridging group.

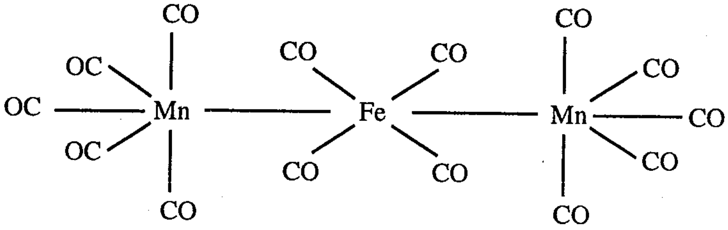


Fig. 12.18 Structure of $Mn_2Fe(CO)_{14}$

IR spectral analysis of $Fe_2Ru(CO)_{12}$ reveals a molecular structure similar to that of $Fe_3(CO)_{12}$

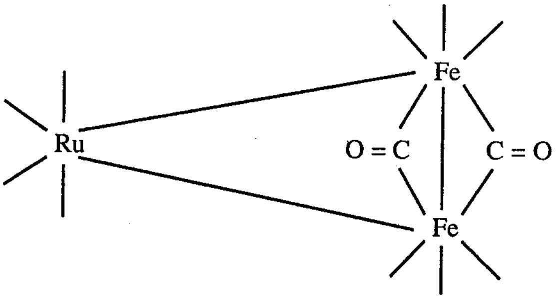


Fig. 12.19 Structure of $Fe_2Ru(CO)_{12}$

The IR spectrum of $FeRu_2(CO)_{12}$ suggests a structure similar to that of $Os_3(CO)_{12}$. The metal atoms carry four terminal CO groups each. There is no bridging CO ligand in this compound.

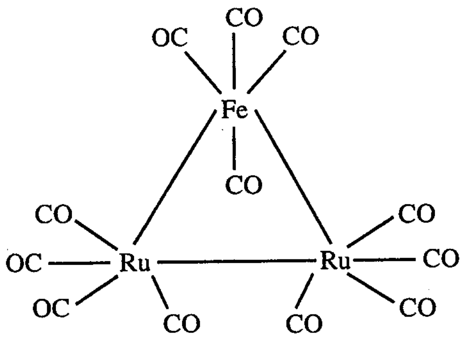


Fig. 12.20 Structure of $FeRu_2(CO)_{12}$

X-ray analysis of $HRe_2Mn(CO)_{14}$ shows that the Mn-Re bond distance is as expected on the basis of the M-M bond distances in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. But it also reveals that the Re-Re bond length is about 0.37 Å longer than expected for a simple σ bond. Therefore, it is logical to assume that the hydrogen atom is situated in between the two Re atoms. Assuming a linear symmetric arrangement as Re-H-Re, the observed Re-H bond distance of 1.696 Å is close to that found in K_2ReH_9, namely 1.680 Å by neutron diffraction studies.

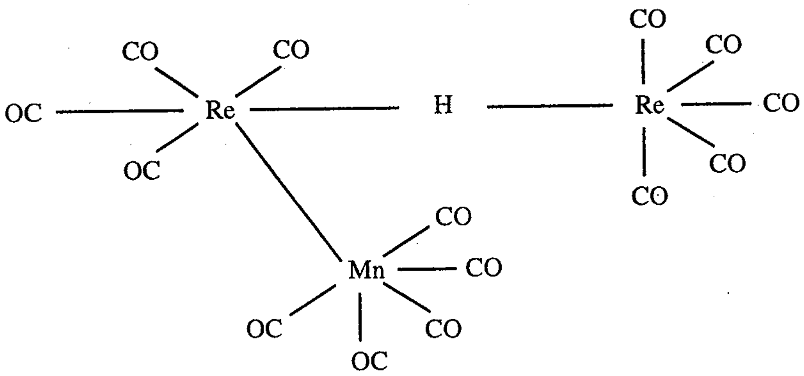


Fig. 12.21 Structure of $HRe_2Mn(CO)_{14}$

The structure of the anion, $[FeCo_3(CO)_{12}]^{2-}$ is believed to be similar to that proposed for $Co_4(CO)_{12}$, but one Co atom of the latter is replaced by one Fe atom.

12.9 METAL CARBONYL HALIDES

Metal carbonyl halides, $M_x(CO)_yX_z$ are known not only for most of the elements forming binary carbonyls but also for the elements like Pd, Pt and Au, which do not form binary carbonyls. The EAN rule is obeyed by assuming that each bridging halogen atoms acts as three electron donor. It coutributes one electron to the bond with one metal atom and forms a two electron coordinate link to the other.

12.9.1 Preparation of Metal Carbonyl Halides

(i) Metal carbonyl halides can be prepared by the direct interaction of metal halides with carbon monoxide, usually at high pressures.

$$AuCl_3 + CO \xrightarrow[\text{at } 120°C,\text{ pressure}]{C_2Cl_4 \text{ solution}} [Au(CO)Cl_3]$$

$$n\,RuI_3 + 2n\,CO \longrightarrow [Ru(CO)_2I_2]_n + \frac{n}{2}I_2$$

$$2PtCl_2 + 2CO \longrightarrow [Pt(CO)Cl_2]_2$$

(ii) They are also obtained by the action of halogens on metal carbonyls.

$$Fe(CO)_5 + I_2 \longrightarrow [Fe(CO)_4I_2] + CO$$

$$4\,Ru(CO)_5 + 4\,F_2 \longrightarrow [Ru(CO)_3F_2]_4 + 8\,CO$$

(iii) They are also prepared by cleaving the polynuclear metal carbonyls using halogens.

$$Mn_2(CO)_{10} + Br_2 \xrightarrow{40°C} 2\,[Mn(CO)_5Br] \xrightarrow{120°C} [Mn(CO)_4Br]_2$$

12.9.2 Properties of Metal Carbonyl Halides

(i) For metals like Pd, Pt, Cu, Au etc, which do not form metal carbonyls, the stability of metal carbonyl halides decreases in the order, $Cl^- > Br^- > I^-$; but for metals that form carbonyls the stability of metal carbonyl halides increases from chloride to iodide.

(ii) Substitution of PPh_3 for some of the CO groups greatly increases the stability of carbonyl halides. For example, $[Co(CO)_4I]$ is unstable, but $[(Ph_3P)(CO)_3CoI]$ is stable.

(iii) They are generally soluble in organic solvents and decomposed by water. For example,

$$[Fe(CO)_4I_2] + 6\,H_2O \longrightarrow [Fe(H_2O)_6]I_2 + 4\,CO$$

(iv) They readily undergo substitution of CO by Lewis bases such as *py*, *diarsine*, Ph_3P etc. For example,

$$[Fe(CO)_4I_2] + 2PPh_3 \longrightarrow [Fe(CO)_2(Ph_3P)_2I_2] + 2CO$$

(v) The halogen bridges in polynuclear complexes are broken by numerous donor ligands such as *py*, substituted phosphines etc. For example,

$$[Mn(CO)_4I]_2 + 2\,py \rightarrow 2\,[Mn(CO)_4Ipy] \xrightarrow{2\,py} 2\,[Mn(CO)_3I(py)_2] + 2\,CO$$

12.9.3 Structure of Metal Carbonyl Halides

When they are polymeric, the metal atoms are invariably bridged by the halogens but not by carbonyl groups. The structures of the following metal carbonyl halides have been established by X-ray analysis.

(i) $[Mn(CO)_4Br]_2$

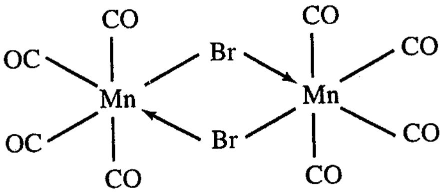


Fig. 12.22

(ii) $[Ru(CO)_3Br_2]_2$

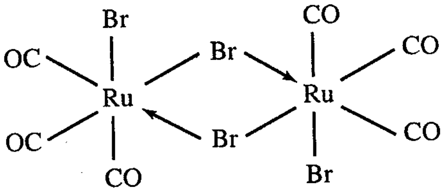


Fig. 12.23

(iii) $[Rh(CO)_2Cl]_2$

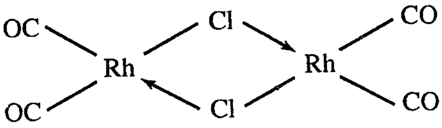


Fig. 12.24

(iv) $[Ru(CO)_4I_2]$

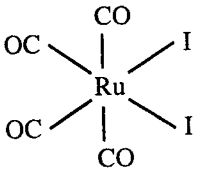


Fig. 12.25

(v) $[Pt(CO)Cl_2]_2$

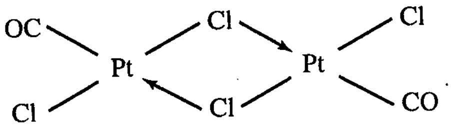


Fig. 12.26

(vi) $[Re(CO)_4I]_2$

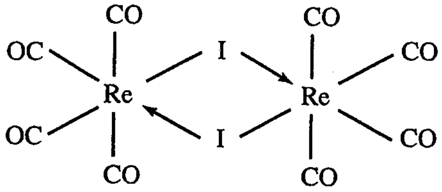


Fig. 12.27

(vii) $[Fe(CO)_2I]_2$

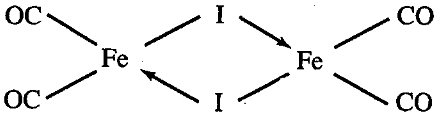


Fig. 12.28

(viii) $[Os(CO)_4I]_2$

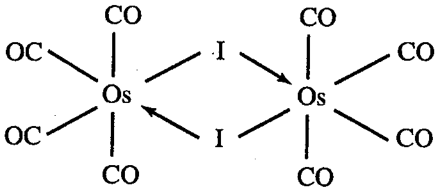


Fig. 12.29

(ix) $[Ru(CO)_3F_2]_4$

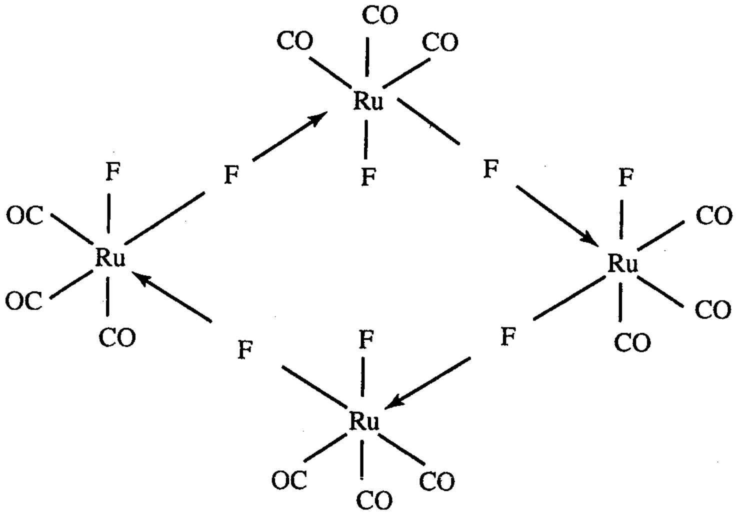


Fig. 12.30

12.10 METAL CARBONYL HYDRIDES

It was first shown by Hieber, who has made a lot of contributions to metal carbonyl chemistry, that when $Fe(CO)_5$ is treated with aqueous alkali it dissolves to give an initially yellow solution containing the ion, $[HFe(CO)_4]^-$. This alkaline solution on acidification gives thermally unstable gas, $H_2Fe(CO)_4$, iron carbonyl hydride. Many such carbonylate anions give metal carbonyl hydrides on acidification.

12.10.1 Preparation of Metal Carbonyl Hydrides

(i) Metal carbonyls on treatment with alkalis followed by acidification give metal carbonyl hydrides.

$$Fe(CO)_5 + 3\,NaOH \rightarrow Na[HFe(CO)_4] + Na_2CO_3 + H_2O$$

$$Na[HFe(CO)_4] + HCl \rightarrow NaCl + \underset{\text{iron carbonyl hydride}}{[H_2Fe(CO)_4]}$$

(ii) The reduction of metal carbonyls using sodium amalgam in tetrahydrofuran followed by the acidification of the solution gives metal carbonyl hydrides.

$$Co_2(CO)_8 + 2\,Na/Hg \xrightarrow{THF} 2Na[Co(CO)_4]$$

$$Na[Co(CO)_4] + HCl \rightarrow NaCl + \underset{\text{cobalt carbonyl hydride}}{[HCo(CO)_4]}$$

Other methods of their preparation include,

(iii) $$Mn_2(CO)_{10} + 2\,Li \xrightarrow{THF} 2\,Li[Mn(CO)_5] \xrightarrow{2\,HCl} 2\,LiCl + 2\,\underset{\text{manganese carbonyl-hydride}}{[HMn(CO)_5]}$$

(iv) $$Fe(CO)_4I_2 \xrightarrow[THF]{NaBH_4} [H_2Fe(CO)_4]$$

(v) $$Mn_2(CO)_{10} + H_2 \xrightarrow[200\,atm]{200°C} 2\,[HMn(CO)_5]$$

(vi) $$Co + 4\,CO + \tfrac{1}{2}H_2 \xrightarrow[50\,atm]{200°C} [HCo(CO)_4]$$

However, metal carbonyl hydrides corresponding to many known carbonylate anions are unstable and therefore have not been isolated.

12.10.2 Properties of Metal Carbonyl Hydrides

(i) Many of them are either colourless or pale yellow gases or liquids.
(ii) In general, the metal carbonyl hydrides are unstable.
(iii) They are readily oxidised by air.
(iv) They are not very soluble in water.
(v) One feature of some metal carbonyl hydrides [especially $HCo(CO)_4$], which distinguishes them from all other hydrido complexes is their acidity. It seems incorrect to formulate a compound which dissociates to give H^+ as a complex containing H^-; but the explanation lies in the great stability of the carbonylate anion which results upon acid dissociation.
(vi) Metal carbonyl hydrides undergo a variety of reactions in which they are added to a molecule or the hydrogen is transferred. Some examples are:

$$[\pi\text{-}C_5H_5Mo(CO)_3H] + CH_2N_2 \rightarrow [\pi\text{-}C_5H_5Mo(CO)_3CH_3] + N_2$$
$$[\pi\text{-}C_5H_5Mo(CO)_3H] + CCl_4 \rightarrow [\pi\text{-}C_5H_5Mo(CO)_3Cl] + CHCl_3$$

(vii) They can also add across multiple bonds to give compounds with metal-carbon σ-bonds. For example,

$$HCo(CO)_4 + R-CH=CH_2 \rightarrow R-CH_2-CH_2-Co(CO)_4$$

This is one of the steps in the oxo reaction of alkenes to give aldehydes.

12.10.3 Structure of Metal Carbonyl Hydrides

On the basis of electron diffraction studies, it was reported that for $H_2Fe(CO)_4$ and $HCo(CO)_4$, the $M(CO)_4$ groups are nearly tetrahedral. IR spectra also suggested that the $Mn(CO)_5$ in $HMn(CO)_5$ might be the same as that of $Fe(CO)_5$. But the question of where and how the hydrogen atoms are bound was a vexed one until recently. It was shown by later IR study that a suggestion that the hydrogen atoms are bound to oxygen or carbon is incorrect. The abnormally high field proton NMR lines indicated metal-hydrogen bonding. Moreover, the large separation in the acid dissociation constants for $H_2Fe(CO)_4$ strongly suggests that the hydrogen atoms must be bound to iron atom. Later it has been recognised that hydrogen can form an extensive series of hydrido complexes with transition elements.

In $HMn(CO)_5$, the five CO groups are located at approximately five of the six corners of an octahedron and it is assumed that the hydrogen atom lies at the sixth corner. Thus $HMn(CO)_5$ is to be considered as a hydrido complex, structurally related to other $XMn(CO)_5$ compounds where X = alkyl, acyl, halide etc.

It has also been suggested that $H_2Fe(CO)_4$ is an octahedral molecule with the two hydrogen atoms in cis positions. This is consistent with all available data though there is no direct proof and it incidentally implies that the electron diffraction study mentioned above is incorrect.

The structure of the metal carbonyl hydride anion, $[H_2Re_3(CO)_{12}]^{2-}$ has been elucidated by X-ray studies. The structure is based on three Re atoms forming an isosceles triangle. Each Re atom carries four terminal CO groups. Of these four terminal CO groups, two occupy axial positions and the other two occupy equatorial positions. Hydrogen atoms were not detected by the X-ray study. But there is evidence, that they form two Re-H-Re bridges in the Re_3 plane. The ^1H NMR spectrum shows a signal at $\tau = 27.2$.

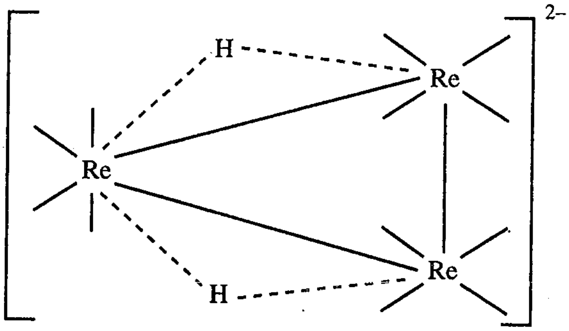


Fig. 12.31 *Structure of* $[H_2Re_3(CO)_{12}]^{2-}$

EXERCISES

***I Choose the best answer for each of the following:**

1. The molecular formula for mononuclear molybdenum carbonyl is
   a) $[Mo(CO)_6]$
   b) $[Mo(CO)_7]$
   c) $[Mo(CO)_5]$
   d) none of the above
2. The EAN for iron in $Fe(CO)_5$ is
   a) 35
   b) 37
   c) 36
   d) 34
3. The metal carbonyl that does not obey the EAN rule is
   a) $Ni(CO)_4$
   b) $V(CO)_6$
   c) $Cr(CO)_6$
   d) all the above
4. The simplest cobalt carbonyl is
   a) $Co(CO)_4$
   b) $Co_3(CO)_9$
   c) $Co_4(CO)_{10}$
   d) $Co_2(CO)_8$
5. In $Mn_2(CO)_y$ the Mn-Mn bond is a normal two-electron covalent bond; there is no bridging CO group. The value of y is
   a) 10
   b) 8
   c) 9
   d) 12
6. $2\,NiCN + 4\,CO \rightarrow Ni(CO)_4 + Ni(CN)_2$. This type of reaction is a/an
   a) disproportionation reaction
   b) oxidation reaction
   c) reduction reaction
   d) chelation
7. Which one of the following is paramagnetic?
   a) $Fe(CO)_5$
   b) $Cr(CO)_6$
   c) $Ni(CO)_4$
   d) $V(CO)_6$
8. Which one of the following metal carbonyls is not paramagnetic?
   a) $Ni(CO)_4$
   b) $Co_2(CO)_8$
   c) $W(CO)_6$
   d) all the above

9. The formula for cobalt carbonylnitrosyl is,
    a) $Co(CO)_2(NO)_2$
    b) $Co(CO)_3NO$
    c) $Co(CO)(NO)_2$
    d) $Co(CO)_2(NO)_3$
10. $Fe(CO)_5$ on treatment with NaOH gives,
    a) $Na_2[Fe(CO)_4]$
    b) $Na_2[Fe(CO)_4]H$
    c) $Na[HFe(CO)_4]$
    d) $Na_2[FeH(CO)_4]$
11. Mond's process makes use of the formation of
    a) $Ni(CO)_4$
    b) $Ni(CO)_5$
    c) $Cr(CO)_6$
    d) none of the above
12. The species that is isoelectronic with $Ni(CO)_4$ is
    a) $[Fe(CO)_4]^+$
    b) $[Co(CO)_4]^-$
    c) $[Fe(CO)_4]^-$
    d) all the above
13. The C-O stretching frequency in free CO is about
    a) 1700 cm^{-1}
    b) 1900 cm^{-1}
    c) 1850 cm^{-1}
    d) 2150 cm^{-1}
14. The formula for the tetranuclear cobalt carbonyl is
    a) $Co_4(CO)_{12}$
    b) $Co_4(CO)_{16}$
    c) $Co_4(CO)_{10}$
    d) none of the above
15. A polynuclear metal carbonyl which does not contain bridging carbonyl groups is
    a) $Fe_2(CO)_9$
    b) $Co_4(CO)_{12}$
    c) $Tc_2(CO)_{10}$
    d) all the above

***II Match the following:**

1. $V(CO)_6$
2. $Ni(CO)_4$
3. $Mn_2(CO)_{10}$
4. $Co_2(CO)_8$
5. $Cr(CO)_6$
6. $Fe(CO)_5$

a. Mond's process
b. bridging CO and metal-metal bond
c. paramagnetic
d. no bridging CO groups
e. blueprint
f. octahedral, diamagnetic

III Account for the following:

1. $V(CO)_6$ is paramagnetic.
2. $V(CO)_6$ does not dimerise to give diamagnetic $V_2(CO)_{12}$.
3. Cobalt does not form a mononuclear carbonyl but it forms a mononuclear carbonyl nitrosyl of composition $Co(CO)_3(NO)$.
4. Chromium forms a hexacarbonyl whereas iron forms a pentacarbonyl.
5. Iron forms a pentacarbonyl while nickel forms a tetracarbonyl.
6. The carbonyl stretching frequencies for $Ni(CO)_4$, $Co(CO)_4^-$ and $Fe(CO)_4^{2-}$ decrease gradually from 2060 cm^{-1} to 1790 cm^{-1}.
7. The carbonyl stretching frequency for $Mo(CO)_6$ is about 2000 cm^{-1} whereas it is about 1760 cm^{-1} for Mo(dien)$(CO)_3$.

*8. In a series of complexes of the formula $[W(CO)_5L]$, the C-O stretching frequency is maximum when L is PF_3.

IV Answer the following:

1. What are metal carbonyls? How are they classified? Give examples.
2. Explain the EAN rule as applied to metal carbonyls.

*3. Predict the stability of $Mo(CO)_7$.

4. Calculate the EAN for the central metal in each of the following metal carbonyls.
   a) $Mo(CO)_6$ b) $Fe_2(CO)_9$ c) $Co_2(CO)_8$ d) $Fe_3(CO)_{12}$ e) $Co_4(CO)_{12}$
5. How are metal carbonyls prepared ?
6. Discuss the properties of metal carbonyls.
7. What are the uses of metal carbonyls ?
8. Discuss the nature of M-C bonding in metal carbonyls.
9. Discuss in detail, the evidences in favour of back bonding in metal carbonyls.
10. Write a note on M-M bond in polynuclear metal carbonyls.
11. Predict the relative stabilities of $V(CO)_6$ and $V(CO)_6^-$.
12. Discuss the structures of a) $V(CO)_6$ b) $Cr(CO)_6$ c) $Mn_2(CO)_{10}$ d) $Fe(CO)_5$ e) $Fe_2(CO)_9$ f) $Fe_3(CO)_{12}$ g) $Co_2(CO)_8$h) $Co_4(CO)_{12}$ i) $Co_6(CO)_{16}$ j) $Ni(CO)_4$
13. What are heteropolynuclear metal carbonyls ? Give three examples.
14. Discuss the structures of the following mixed metal carbonyls.
    a) $CoMn(CO)_9$ b) $Mn_2Fe(CO)_{14}$ c) $Fe_2Ru(CO)_{12}$ and d) $FeRu_2(CO)_{12}$
15. What are metal carbonyl halides? Give three examples. How many electrons are contributed by bridging halogen atoms ?
16. Discuss the chemistry of metal carbonyl halides under the following headings:
    a) preparation b) properties c) structures
17. How are metal carbonyl hydrides prepared ? What are their properties ? Discuss the structures of any three such compounds ?

ANSWERS

I 1. (a) 2. (c) 3. (b) 4. (d) 5. (a) 6. (a) 7. (d) 8. (d) 9. (b) 10. (c) 11. (a) 12. (b) 13. (d) 14. (a) 15. (c)

II 1. (c) 2. (a) 3. (d) 4. (b) 5. (f) 6. (e)

III 8. The PF_3 ligand with its highly electronegative fluorine atoms withdraws electron density from W and suppresses M→ L back bonding. This, in turn, strengthens the C-O bond.

IV 3. The Mo atom being a member of Group VI contributes 6 electrons. Therefore, the EAN for this carbonyl is $6 + (7 \times 2) = 20$. This carbonyl is likely to be unstable as organometallic compounds with more than 18 valence electrons on the central metal are not stable.

Chapter 13

Industrial Applications of Organometallic Compounds

13.1 IMPORTANCE OF ORGANOMETALLIC COMPOUNDS AS CATALYSTS

Until the 1950s, organometallic chemistry was an unexplored area of chemistry. Tremendous interest in this field originated predominantly from the two discoveries of,

(i) Synthesis of ferrocene in 1952 and

(ii) The low pressure catalytic polymerisation of ethylene, discovered by Ziegler in 1952.

No area of chemistry has produced more surprises and challenges during the past few decades as organometallic chemistry. This field continues to be one of great excitement and research activity. Elegant and skilful synthetic programmes are being supplemented by an unusual number of chance discoveries.

Synthetic chemists take an intellectual approach. Structural chemists are able to press their various techniques in elucidating the structures of various products formed. Industrial chemists exploit and extent the results by developing numerous catalytic processes of great importance.

Some organometallic compounds of transition metals with both saturated and unsaturated organic systems are of great utility as catalysts in organic chemistry and also in some industrial processes. Examples include, $[RhCl(PPh_3)_3]$, Wilkinson's catalyst in the hydrogenation of olefins, $HCo(CO)_4$ in the hydroformylation of olefins, $TiCl_3$ - $Al(C_2H_5)_3$ in the polymerisation of olefins, $[Ni(acac)_2]$ in cyclo-oligomerisation of acetylenes etc.

A catalyst speeds up a reaction by replacing the high energy barrier of an uncatalysed process with a series of steps of much lower activation energy. Catalysts are of particular interest to industry because they speed up reactions as well as enabling them to occur with lower inputs of energy (both time and energy are costly).

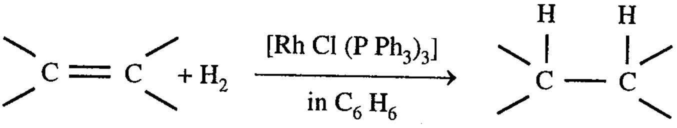
13.1.1 Conditions to be Satisfied by a Metal to Act as a Catalyst

1. Atleast two moderately stable oxidation states for the metal separated by two units should exist. Example, Rh^+ and Rh^{3+} in Wilkinson's catalyst.
2. It should be capable of forming complexes with a range of coordination numbers and of forming moderately stable coordinatively unsaturated species. Example, coordination numbers 3,4,5 and 6 for rhodium in Wilkinson's catalyst.
3. It must have the ability to match the substrate orbitals. For example, if the substrate is an alkene, then this means that the metal must have an empty orbital capable of accepting σ - donation from the alkene and a filled orbital capable of π - back donation to the alkene.

The metals Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Pt meet all of these requirements most effectively. As a consequence, the most versatile catalysts come from this group of metals.

13.1.2 Hydrogenation of Olefins

Hydrogenation of olefins is a reaction of major industrial importance, being used in the petrochemical industries and in the pharmaceutical industries where the preparation of drugs often involves the hydrogenation of specific double bonds. It is for the hydrogenation of specific double bonds in compounds containing several double bonds that the search for new, more efficient and above all more selective catalysts has been most vigorous. One very successful catalyst for this process is $[Rh(Cl)(PPh_3)_3]$, chlorotris(triphenylphosphine)rhodium(I). This is an effective homogeneous catalyst in solutions of aromatic hydrocarbons such as benzene and toluene. As it very often happens with important discoveries, this particular catalyst was discovered independently by two groups and now almost universally referred to as Wilkinson's catalyst. The net reaction is



13.1.3 Importance of Wilkinson's Catalyst

An ideal hydrogenation catalyst should be capable of catalysing hydrogenations at or near atmospheric pressure and room temperature. This is because it eliminates the need for expensive vessels capable of withstanding high pressure and high temperature. In this respect this catalyst is remarkably effective, because the hydrogenation of isolated double or triple bonds takes place at atmospheric pressure and at room temperature. The applications of Wilkinson's catalyst are important in pharmaceutical industries for making specific drugs inspite of the high cost of the catalyst.

13.1.4 Preparation of the Catalyst, [RhCl(PPh$_3$)$_3$]

This red-violet coloured compound is prepared by refluxing ethanolic $RhCl_3 . 3H_2O$ with an excess PPh_3.

13.1.5 Role of Rhodium Metal in the Catalytic Process

The role of the metal in the catalytic process is three-fold. Firstly, the metal provides a low energy path for cleaving the H-H bond in H_2. Secondly, the metal coordinates with the alkene, thereby weakening the bonding between the carbon atoms. Thirdly, the metal provides a mechanism for transferring the two hydrogen fragments to the alkene carbon atoms, yielding an alkane.

13.1.6 Mechanism of Hydrogenation of Olefins using Wilkinson's Catalyst

On passing hydrogen into a solution of the catalyst in benzene followed by the addition of olefin, the alkane is formed. The precise mechanism of this process is complicated and has been the subject of much speculation and controversy. But the following scheme is a simplified, but a reasonable one. For the sake of simplicity, PPh_3 is represented as L in the catalytic cycle. (Fig. 13.1)

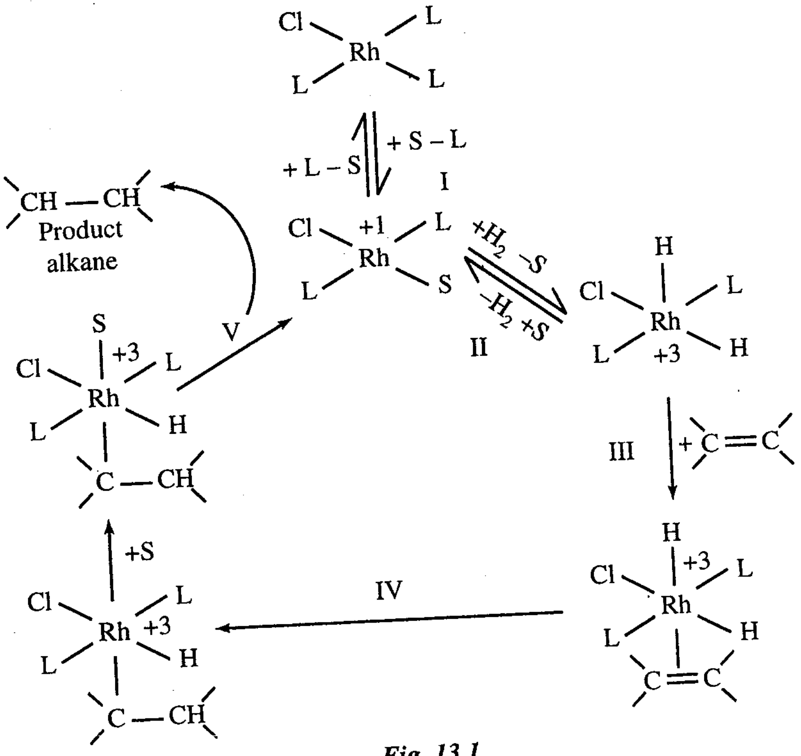


Fig. 13.1

Step I involves a reversible loss of one PPh_3. This is indicated by two lines of evidence:

1. In less sterically hindered phosphine complexes, the catalytic effect disappears. As small ligands do not readily dissociate, which is essential for catalysis, they render the catalyst ineffective.
2. In the corresponding iridium complex in which the metal-phosphorus bond is stronger (due to increased CFSE of the third over the second transition series element) apparently no dissociation takes place and hence catalytic behaviour disappears.

Step II is *oxidative addition* leading to the formation of a 5-coordinated species, $[RhCl(H)_2L_2]$, in which the oxidation state of Rh is + 3 (raised from +1 state). This step is an oxidation reaction. The coordination number of the central metal ion is increased from 4 to 5 in this step. Hence this step is also an addition reaction. Since this step involves both oxidation and addition, it is referred to as an oxidative addition reaction (or) *oxad* reaction. In this reaction, which is reversible, the first role of the catalyst, i.e., the cleavage of the H-H bond is accomplished. This is identified by NMR peaks characteristic of Rh-H bond.

The term oxidative addition was introduced by Vaska, who studied some addition reactions of the complex, trans-$[Ir(Cl)(CO)(PPh_3)_2]$, which is called as *Vaska's compound.*

$$[Ir(Cl)(CO)(PPh_3)_2]+O_2 \rightleftharpoons [Ir(Cl)(CO)(PPh_3)_2(O_2)]$$

Ir	oxidation number	+ 1	→	+ 3
	coordination number	4	→	6

Oxidative addition reaction involves an increase in the formal oxidation state and coordination number of the metal in the complex. The reaction,

$$[Ir(Cl)(CO)(PPh_3)_2]+Cl_2 \rightleftharpoons [Ir(Cl)_3(CO)(PPh_3)_2]$$

also involves oxidative addition. The reverse reaction is known as *reductive elimination*, which involves a decrease in the formal oxidation state and coordination number of the central metal in a complex.

Conditions to be satisfied for an oxidative addition reaction to take place are,

1. The metal should possess non-bonding electron density.
2. Two vacant coordination sites on the complex should be available to allow formation of two new bonds to the addendum (that is the complex should be coordinatively unsaturated) and
3. The metal should possess two stable oxidation states separated by two units.

Step III involves the coordination of the alkene to the potential vacant site on the 5-coordinate dihydrido complex to form the 6-coordinated species. In this step, the metal has not only weakened the alkene double bond by coordination, but has also brought the alkene and the hydrogen atoms into close proximity, where they react, probably in a two-step process (steps IV and V) to give an alkane (product) and $[RhClL_2S]$ which can restart the catalytic cycle. In this step the second role of the catalyst namely, the weakening of the bond between the two carbon atoms, is accomplished.

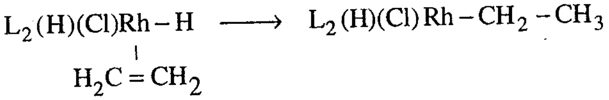
Step IV is an *insertion reaction.* It involves the insertion of olefin into metal–H bond to give metal – alkyl derivative.

The concept of "insertion" is of wide applicability in chemistry when defined as a reaction where an atom or a group of atoms is inserted between two atoms initially bound together. For example,

$$L_nM-X + YZ \rightarrow L_nM-(YZ)-X$$

Some representative examples are,

$$(CO)_5Mn-CH_3 + CO \rightarrow (CO)_5Mn-CO-CH_3$$



$$\underset{H_2C=CH_2}{L_2(H)(Cl)Rh-H} \longrightarrow L_2(H)(Cl)Rh-CH_2-CH_3$$

Carbonyl insertion into M-alkyl bond to give metal-acyl derivatives and olefin insertion into M-H bond to give metal-alkyl derivatives are the partial steps in most of the catalytic cycles in industrial processes. In addition, insertion into M-N and M-O bonds are also known.

Step V is the *reductive elimination step.* The metal is reduced from +3 state to +1 state and coordination number of the central metal is decreased from 6 to 4. In this step, the product, alkane is formed. The third role of the catalyst, namely, the transfer of hydrogen fragments to the alkene yielding the product alkane is achieved in steps IV and V.

In this reductive elimination reaction, two substrates, *X* and *Y* present in the catalyst system bonded to one or more metal centres combine to form a product, *XY*, which then leaves the coordination sphere of the metal. This is essentially the reverse of oxad reaction.

An example of reductive elimination is the elimination of acetyliodide in the Rh-catalysed carbonylation (insertion of CO into M-C bond) of methanol. One of the steps in the above reaction is

$$[Rh(I)_3(CO)_2(COCH_3)]^- \rightarrow [Rh(I)_2(CO)_2]^- + CH_3COI$$

Rh oxidation number +3 → +1
coordination number 6 → 4

This is a reductive elimination reaction.

Another example of reductive elimination is the elimination of an aldehyde in the cobalt catalysed hydroformylation of olefins (to be discussed later). One step in the process in which reductive elimination occurs is,

$$[Co(CO)_2(L)(H)_2(COR)] \rightarrow [Co(CO)_2(L)(H)] + RCHO$$

Co oxidation number +3 → +1
coordination number 6 → 4

Advantages

1. Compared with the older process which was likewise homogeneously catalysed and marked by high reaction temperature of about 250°C and by pressures around 750 atmospheres, this new process operates under considerably milder reaction conditions.
2. It is possible to selectively hydrogenate biologically active substrates such as steroids. The value of this catalyst is based upon the fact that the hydrogens are transferred specifically to the cis positions.

3. This catalyst is specific for the hydrogenation of terminal olefins due to steric reasons.

Disadvantages

1. Being a soluble catalyst, it cannot be removed easily at the end of the reaction by simple filtration. Due to this imperfect separation of alkane and rhodium complex at the end of the hydrogenation, rhodium is lost in practice although the catalytic cycle shows no loss of rhodium. The separation of the catalyst at the end of the reaction is a major problem and it is one of the reasons why industries have been unwilling to adopt homogeneous catalysts more widely.
2. Because of the high cost of rhodium and the high cost of converting it into Wilkinson's catalyst, this process is highly expensive.

13.1.7 Modification over the Original Catalyst

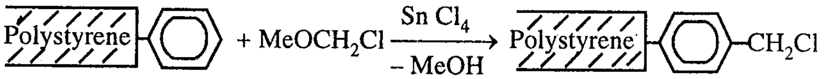
Removal of the catalyst at the end of the catalytic reaction is made easy by building the catalyst on an insoluble support. The types of support used are beads either of cross-linked polymers such as polystyrene or polyvinylchloride or of inorganic materials such as silica. The resulting *polymer-supported catalyst* is a solid and hence can be easily filtered off at the end of the catalytic process. This process of converting a homogeneous catalyst into a heterogeneous one is called *anchoring of catalysts*. In the anchored catalyst, all the rhodium atoms have identical coordination sites, leading to high selectivity, (which is one of the major advantages of the homogeneous catalysts). Thus the selectivity is retained in this modified process.

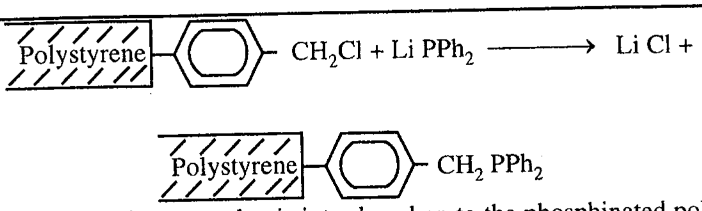
In recent years the discovery and utility of homogeneous hydrogenation, isomerisation, oligomerisation, carbonylation reactions etc. have expanded enormously. Commercial processes based on homogeneously catalysed routes are becoming increasingly important as evidenced by the Wacker process (to be discussed later) and others. However, homogeneous *catalysis* can exhibit the problems of product contamination and catalyst loss, where the products are not easily separated from the catalyst. Anchoring homogeneous catalysts to polymers or other supports effectively *heterogenise* them, allowing their use in fixed beds and simplifying catalyst recovery. Thus, the anchoring of homogeneous catalysts has become the objective of several groups of chemists.

When a homogeneous catalyst is heterogenised in such a way that it can react mechanistically in the same manner as its homogeneous counterpart, the greater selectivity and activity of the homogeneous catalyst are thus preserved.

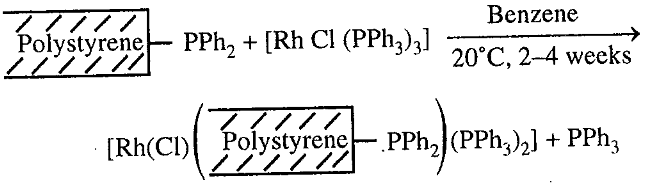
In general, polymer-bound catalysts appear to offer great promise for practical applications in specific and selective chemical transformations at comparatively mild conditions.

Polymer-supported Wilkinson's catalyst is prepared as follows. Phosphine groups are introduced on to the polymer support by the following series of reactions.





Then the rhodium complex is introduced on to the phosphinated polymer support by stirring them together at room temperature for several weeks.



The resulting polymer-supported catalyst is a solid and hence can be easily filtered at the conclusion of the catalytic process.

13.1.8 Hydroformylation of Olefins—The Oxo Process

The most important example of homogeneous catalysis involving an organometallic compound is the so-called hydroformylation reaction, which involves the addition of H_2 and CO (formally H and CHO) to a terminal alkene to yield an aldehyde. Thus the net reaction is,

$$R-CH=CH_2+H_2+CO \xrightarrow{\text{catalyst}} R-CH_2-CH_2-CHO$$

Since it is used to make oxygen-containing compounds from hydrocarbons, it is also known as the *oxo process*.

A kinetic study of the oxo reaction reveals that it is first order in olefin and approximately first order in the amount of the catalyst used. The reaction rate increases with increasing hydrogen pressure and decreases with increasing carbon monoxide pressure. The rate is virtually independent of the nature of the solvent used. It is faster for terminal olefins than for internal olefins. Since olefins are isomerised under the conditions of oxo reaction, a mixture of linear and branched aldehydes and ketones is often produced.

Importance of the Oxo process The technical importance of this reaction stems from the ease with which the primary oxo product, the aldehyde, can be converted into a multitude of industrially important secondary products, such as alcohols (by reduction), acids (by oxidation), or esters (by allowing the alcohols to react with acids formed by the reduction and oxidation of aldehydes respectively). Some of these secondary products are useful as plasticisers, detergents, lubricating oils and solvents.

13.1.9 Mechanism of Hydroformylation of Olefins Using the Original Catalyst, $HCo(CO)_4$

Here, the reactants are olefin, H_2, CO and $Co_2(CO)_8$; the last one forms the catalyst, $HCo(CO)_4$, by reaction with H_2, one of the reactants. The different steps involved in this catalytic process are depicted in Fig. 13.2.

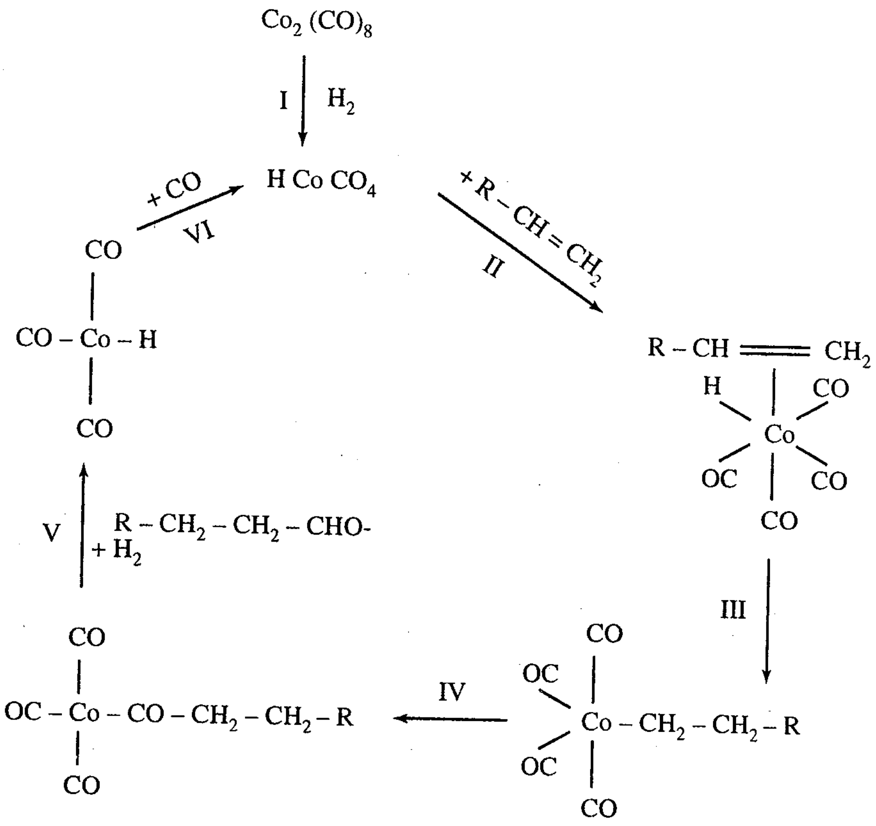


Fig. 13.2

Step I involves the generation of the active catalyst, $HCo(CO)_4$ from $Co_2(CO)_8$ and H_2.

Step II is the addition of olefin to the coordinatively unsaturated $HCo(CO)_4$ to form a coordinatively saturated 6-coordinated alkene π-complex.

Step III involves the insertion of alkene into the Co-H bond to give an alkyl intermediate.

Step IV is another insertion reaction, namely carbonyl insertion to give an acyl complex.

Step V is the reaction of gaseous hydrogen with the acyl complex to yield an aldehyde and $HCo(CO)_3$.

Step VI is the rapid absorption of CO molecule by $HCo(CO)_3$ to regenerate the active catalyst, $HCo(CO)_4$, which will restart the whole catalytic cycle.

Defects of this catalyst

1. This catalyst works well only at 150°C and at a pressure of about 200 – 400 atmospheres . This necessitates the use of vessels which can withstand this

high temperature and high pressure. This leads to a high plant cost for the industrial process.

2. This catalyst also catalyses hydrogenation of olefin under these conditions. Hence a part of the olefin is lost as alkane (lack of specificity).
3. Volatility of $HCo(CO)_4$ poses recovery problems.
4. Since the addition of $HCo(CO)_4$ to unsymmetrical olefins can occur in two directions and since $HCo(CO)_4$ can isomerise olefins under these conditions, it is not surprising that mixtures of linear and branched chain aldehydes and ketones are often obtained.

13.1.10 Modification over the Original Catalyst

Various modified catalysts have been described for increasing the yield of linear aldehydes. Tributylphosphine and triphenylphosphine substituted cobalt carbonyls and rhodium complexes have been tried. Of these modified catalysts, the most important is the rhodium catalyst of composition, $[Rh(H)(CO)(PPh_3)_3]$. This hydridocarbonyltris(triphenylphosphine)rhodium(I) was also discovered in Wilkinson's laboratories.

Advantages of the modified catalyst

1. This complex is catalytically active even at 25°C and one atmospheric pressure.
2. Due to steric reasons, it produces only linear aldehydes.

13.1.11 Mechanism of the Modified Catalysis

The different steps involved in this catalysis are represented in Fig. 13.3.

Step I is the reversible loss of one molecule of PPh_3 to yield 4-coordinated species **(A)**, the active catalyst.

Step II is the carbonyl addition to give 5-coordinated species **(B)**.

Step III is an associative attack of alkene on species **(B)** to give a 6-coordinated species **(C)**.

Step IV is the insertion of the alkene into the Rh-H bond to give an alkyl derivative **(D)**.

Step V is the carbonyl insertion to give an acyl complex **(E)**. This reaction is also considered as an alkyl migration reaction.

Step VI is the rate determining (slow) step which involves the oxidative addition of molecular hydrogen to yield the dihydridoacyl complex **(F)**.

Step VII involves another hydrogen transfer to the carbon atom of the acyl group followed by the loss of aldehyde and regeneration of the 4-coordinated species **(A)** which is used to restart the whole catalytic cycle again. This step is a reductive elimination step since it involves reduction of Rh^{3+} to Rh^+ and also a decrease in the coordination number of the central metal Rh from 6 to 4.

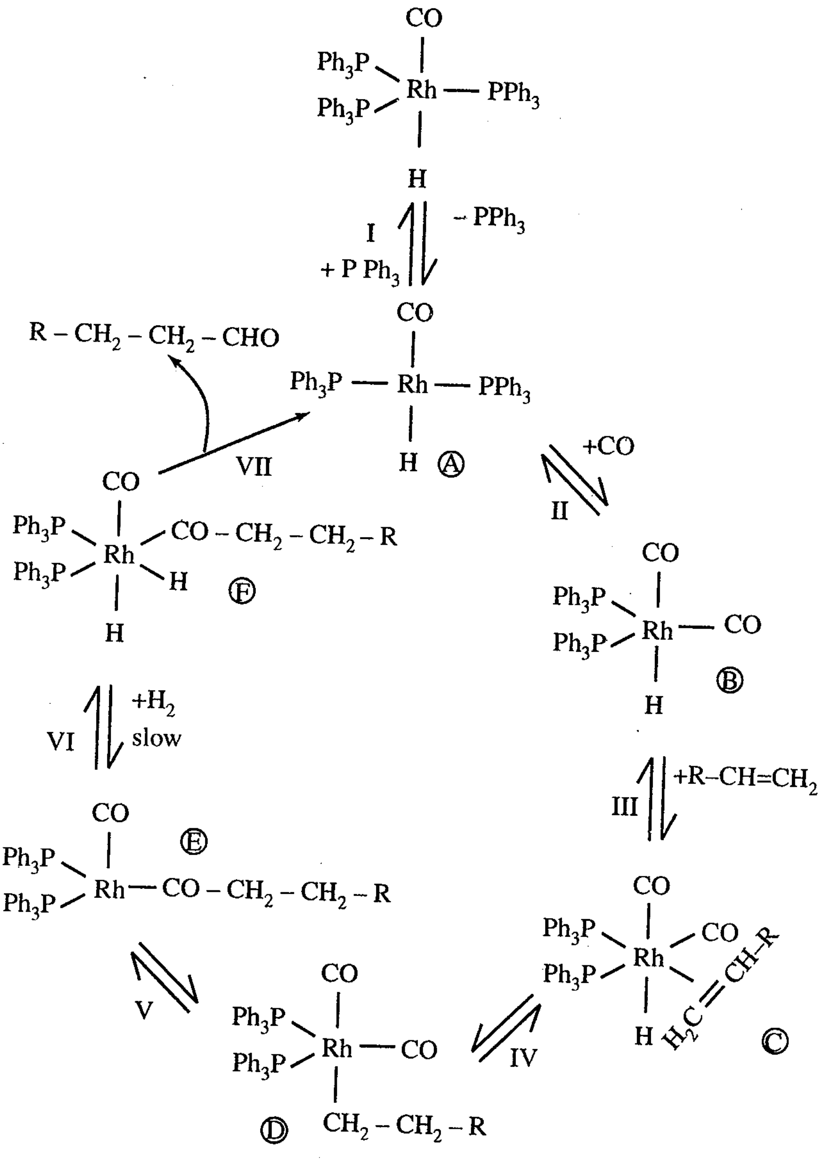


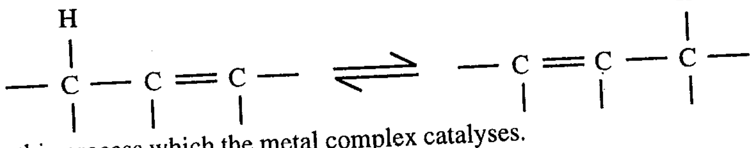
Fig. 13.3

13.1.12 Isomerisation of Olefins

One of the major reactions of transition metal salts with alkenes is isomerisation of the alkenes. There are many instances of the isomerisation of olefins or olefinic compounds under the influence of transition metal compounds as catalysts. Many transition metal complexes especially those of group VIII metals, promote double bond migration – that is isomerisation in alkenes to give the thermodynamically more stable isomeric mixture. Isomerisation is the process by which chemical bonds or groups are redistributed within a given molecule. Unlike hydrogenation and other catalysed reactions, this process affects only the molecular structure but not the chemical formula of the substrate. An example of olefin isomerisation reaction is,

$$\underset{\text{1-alkene}}{R-CH_2-CH=CH_2} \rightleftharpoons \underset{\text{2-alkene}}{R-CH=CH-CH_3}$$

Double bond migration essentially involves movement of a hydrogen from the alkyl group adjacent to the double bond, to the α-carbon of the double bond.



$$-\underset{|}{\overset{\overset{H}{|}}{C}}-\underset{|}{C}=\underset{|}{C}- \rightleftharpoons -\underset{|}{C}=\underset{|}{C}-\underset{|}{\overset{\overset{H}{|}}{C}}-$$

It is this process which the metal complex catalyses.

13.1.13 Mechanism of Olefin Isomerisation

The organometallic compound used as the catalyst in olefin isomerisation is $[Rh(H)(CO)(PPh_3)_3]$. The different steps involved in this process are represented in Fig. 13.4.

Step I is the reversible loss of one PPh_3 to give a 4-coordinated hydrido complex as the essential species in this catalytic process.

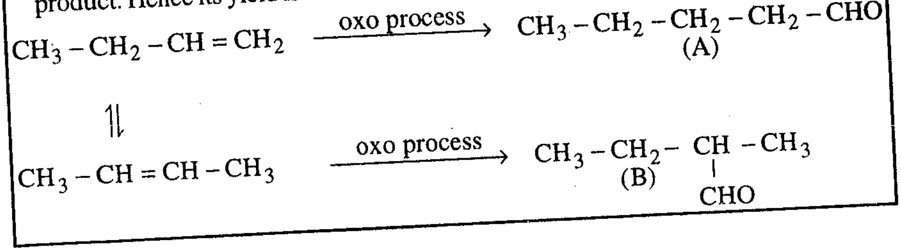
Step II is the associative attack of olefin on the active species to give a 5-coordinated species, which is a hydrido-alkene-metal complex.

Step III is a hydride ligand migration reaction to form a metal-alkyl species which is a 4-coordinated species. This migration probably occurs via a four-centred transition state.

In ***Step IV*** the metal-alkyl species undergoes a β-elimination reaction in which H abstraction occurs at a site other than that at which the initial H addition occurred. This results in a net migration of the double bond one position along the chain. This gives isomerised olefin-metal π-complex.

Step V involves the liberation of isomerised olefin from the π-complex followed by the regeneration of the 4-coordinated hydrido complex which is used to restart the whole catalytic cycle.

Isomerisation is an evil or devil in hydroformylation but not in hydrogenation. This is because an olefin and its isomerised product when subjected to hydroformylation reaction will give different oxo products. Hence yield of the expected aldehyde will be less. On the other hand, when an olefin and its isomerised product are subjected to hydrogenation they give the same final product. Hence its yield is not affected. These reactions are illustrated as follows:



$$CH_3-CH_2-CH=CH_2 \xrightarrow{\text{oxo process}} \underset{\text{(A)}}{CH_3-CH_2-CH_2-CH_2-CHO}$$

$$\upharpoonleft\downharpoonright$$

$$CH_3-CH=CH-CH_3 \xrightarrow{\text{oxo process}} \underset{\text{(B)}}{CH_3-CH_2-}\underset{\underset{CHO}{|}}{CH}-CH_3$$

Note that (**A**) and (**B**) are different products. But for the same reactants, the hydrogenation reactions are,

$$CH_3-CH_2-CH=CH_2 \xrightarrow{\text{hydrogenation}} \underset{(C)}{CH_3-CH_2-CH_2-CH_3}$$

$$\upharpoonleft\downharpoonright$$

$$CH_3-CH=CH-CH_3 \xrightarrow{\text{hydrogenation}} \underset{(D)}{CH_3-CH_2-CH_2-CH_3}$$

Note that (**C**) and (**D**) are same products.

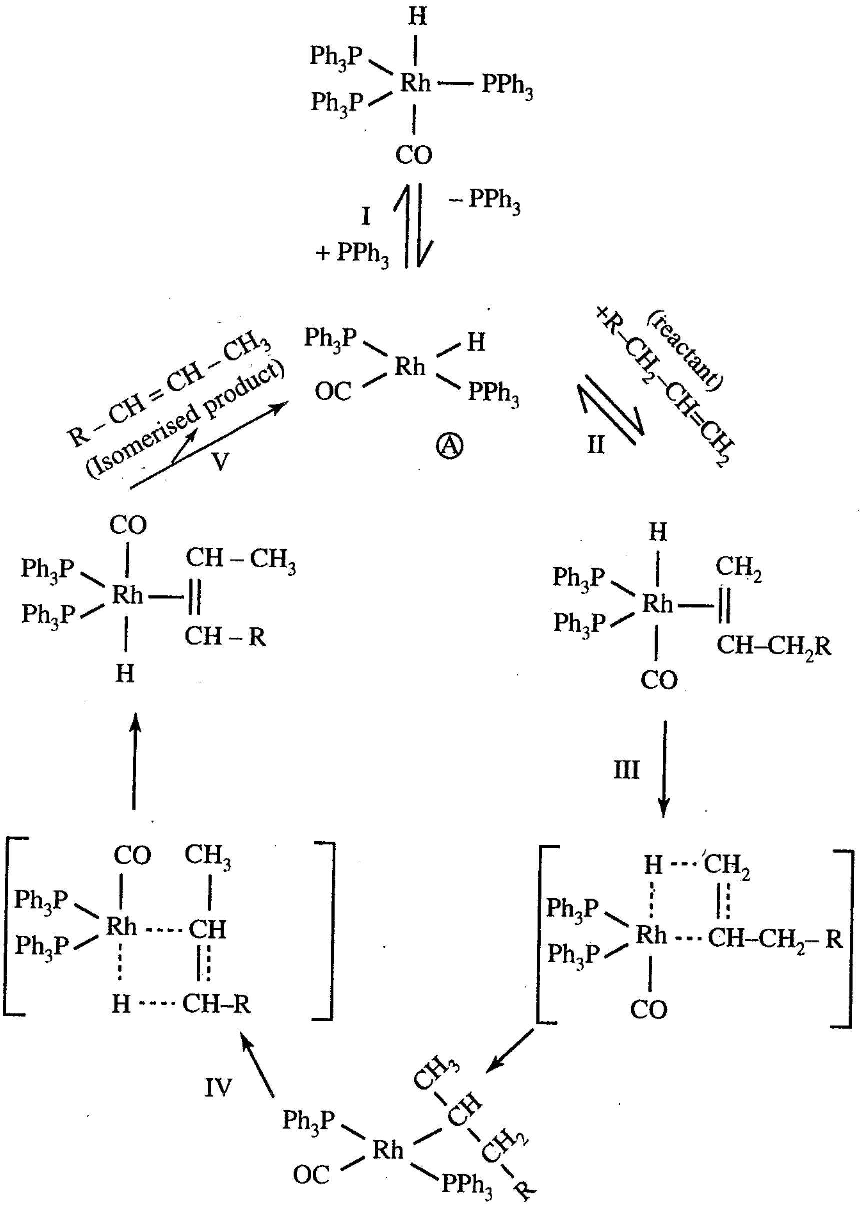


Fig. 13.4

13.1.14 Oxidation of Olefins—Wacker's Process

Acetaldehyde and vinyl acetate are important industrial intermediates. They may be produced in a variety of ways. But many of these methods suffer major disadvantages. For example, C_2H_2 is considerably more expensive than C_2H_4, but addition of H_2O to C_2H_2 to give CH_3CHO was found to be somewhat easier than production of CH_3CHO from C_2H_4.

The oxidation of ethylene to acetaldehyde with platinum group metals has been known since 1894. When ethylene is bubbled into a solution of K_2PtCl_4, the first product is Ziese's salt, $K[PtCl_3(C_2H_4)]$. Heating this compound in water results ultimately in the formation of acetaldehyde and metallic platinum.

$$[PtCl_3(C_2H_4)]^- + H_2O \xrightarrow{\text{heat}} CH_3CHO + Pt(0) + 3\,Cl^- + 2\,H^+$$

In contrast, palladium chloride does not give an isolable intermediate analogous to Ziese's salt, rather, the process moves rapidly to final products in the presence of oxygen.

$$C_2H_4 + \tfrac{1}{2}O_2 \xrightarrow[H_2O]{PdCl_4^{2-}} CH_3CHO$$

The palladium chloride – catalysed production of acetaldehyde from ethylene was first exploited commercially by Smidt at Wacker Chemie in Germany. (Hence the name Smidt reaction or Wacker's process). In this process copper(II) chloride is used as co-catalyst in the presence of dilute hydrochloric acid.

13.1.15 Steps Involved in Wacker's Process

1. In this process, ethylene is passed into a slightly acidic solution of Pd(II) chloride. Ethylene forms a complex with the palladium. Ethylene ligand is then attacked by OH^- ions. This attack leads to the formation of palladium metal and acetaldehyde.

   $$C_2H_4 + PdCl_4^{2-} + H_2O \rightarrow CH_3CHO + Pd(0) + 2\,HCl + 2\,Cl^-$$

   This is the product formation step in Wacker's process.

2. The palladium metal formed cannot be reused directly as the catalyst. It has to be reoxidised to Pt(II). The whole commercial use of this process is based on the ease with which this reoxidation can be carried out. Fortunately, it can be done using a Cu(II) salt as co-catalyst. Cu(II) is reduced to Cu(I) salt.

   $$Pd(0) + 2\,CuCl_2 + 2\,Cl^- \rightarrow PdCl_4^{2-} + 2\,CuCl$$

   This is the catalyst regeneration step.

3. If the solution is acidic, the Cu(I) salt produced can be reoxidised to Cu(II) salt by blowing in oxygen. This is the reason for operating this process at low pH.

   $$2\,CuCl + 2\,HCl + \tfrac{1}{2}O_2 \rightarrow 2\,CuCl_2 + H_2O$$

   This is the co-catalyst regeneration step.

Thus the net result is an overall catalytic process which may be written as,

$$C_2H_4 + \tfrac{1}{2}O_2 \xrightarrow[\text{dil.HCl}]{PdCl_4^{2-} + CuCl_2} CH_3CHO$$

13.1.16 Mechanism of Wacker's Process

The mechanism of the first step in the Wacker's process has attracted a great deal of attention. Kinetic studies in aqueous solution suggest the following rate law.

$$\frac{d\,[CH_3CHO]}{dt} = \frac{k\,[C_2H_4]\,[PdCl_4^{2-}]}{[H^+]\,[Cl^-]^2}$$

Thus there is a first order dependence on ethylene and the palladium halide, an inverse dependence on H^+ (an inhibition by H^+) and an inverse square dependence on Cl^-

The different steps involved in the oxidation of ethylene to acetaldehyde in the presence of $[PdCl_4^{2-}]$ are depicted in Fig. 13.5.

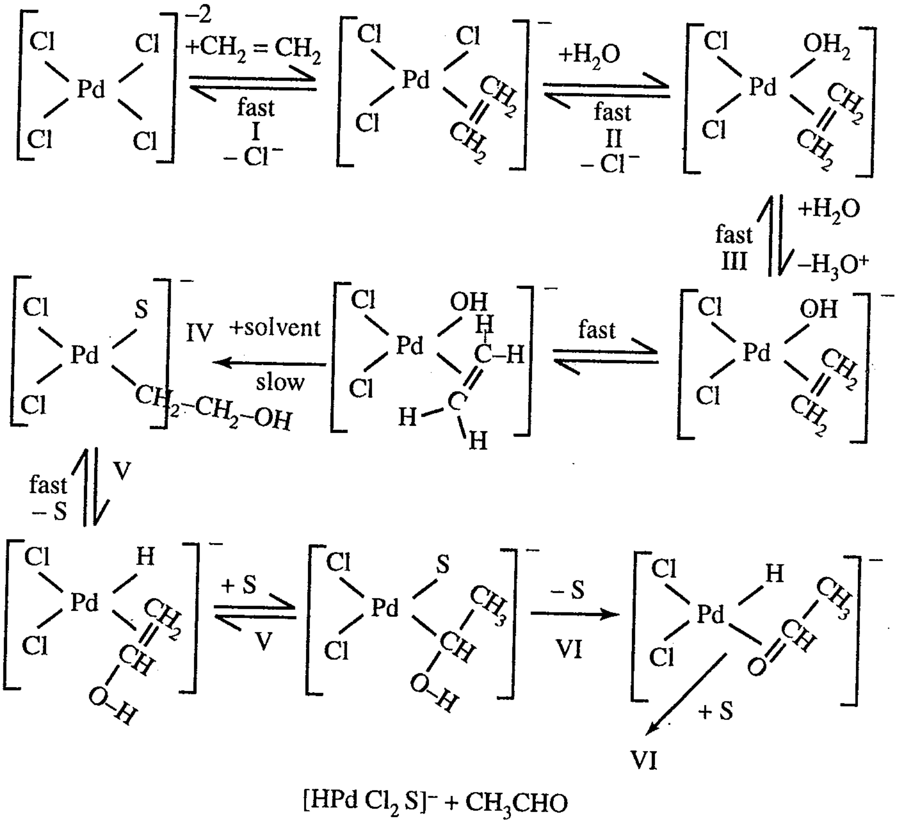


Fig. 13.5

Step I is the formation of a metal-olefin π-complex. It is a conventional alkene complex similar to Ziese's salt. This step is further supported by the observation that addition of Cl^- decreases the rate of oxidation.

Step II involves substitution of the second Cl^- by H_2O. Since Cl^- is eliminated in this step and the preceding one, this accounts for the inverse square dependence on chloride concentration. This gives cis-geometry in which the ligand oxygen atom is next to ethylene.

Step III is deprotonation step. This involves loss of H^+ to form a hydroxo-metal complex. It is this step that accounts for the inverse dependence of the process on H^+ concentration. All these three steps are rapidly established equilibria.

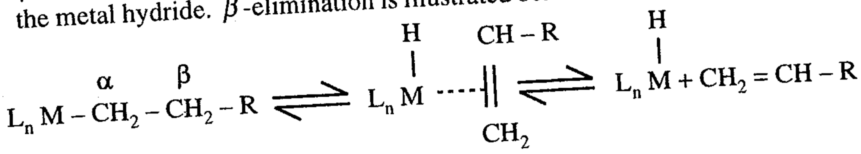
Step IV is the rate determining step. It involves the migration of the hydroxyl ligand to one carbon of the coordinated olefin and the other carbon adopts a σ donor arrangement with the palladium to give 2-hydroxyethylpalladium complex.

Step V is β-elimination to produce a π-vinyl alcohol complex, which then reinserts into the Pd-H bond in the opposite sense to form 1-hydroxyethylpalladium complex. During the conversion of 2-hydroxyethyl to 1-hydroxyethyl there is shifting of hydrogen atom on to the Pd and back.

Step VI is another β-elimination in which acetaldehyde is produced (the major product of Wacker's process). It is followed by a reductive elimination reaction of $[HPdCl_2S]^-$ to give Pd(0), HCl, Cl^- and S.

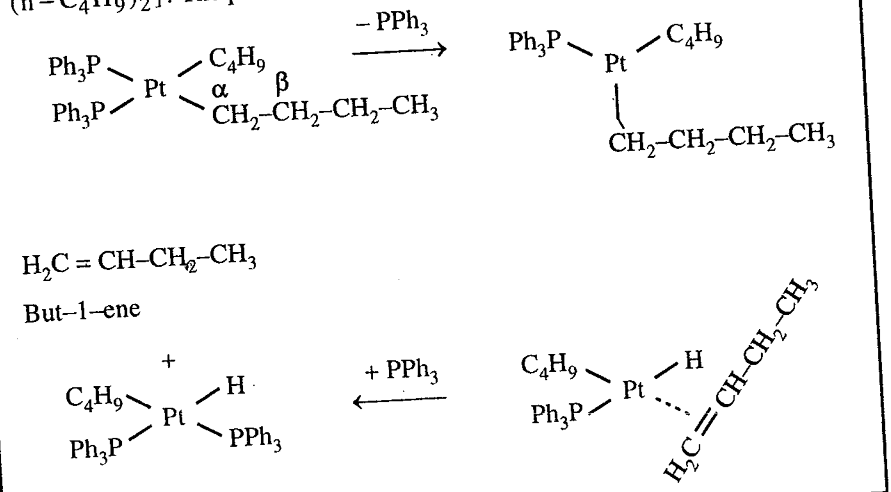
β-ELIMINATION

Many transition metal alkyl derivatives are especially unstable with respect to thermal decomposition. The reason for this is not that metal-carbon σ bonds are thermodynamically weak, but that one or more pathways for their decomposition are readily available. One such pathway is the so-called β-elimination which involves the elimination of olefin and the formation of the metal hydride. β-elimination is illustrated below:



$$L_nM-\overset{\alpha}{CH_2}-\overset{\beta}{CH_2}-R \rightleftharpoons L_n\overset{\overset{H}{|}}{M}\cdots\begin{matrix}CH-R\\ \|\\ CH_2\end{matrix} \rightleftharpoons L_n\overset{\overset{H}{|}}{M}+CH_2=CH-R$$

β-hydrogen elimination is generally an intramolecular β-hydrogen abstraction by the metal. The best studied example is, $[Pt(PPh_3)_2(n-C_4H_9)_2]$. The probable mechanism is,



This type of fragmentation process is facilitated by three conditions.

1. The metal should be capable of increasing its coordination number by one unit. That is, it should be capable of forming a coordinatively unsaturated complex.
2. A substituent attached to the β atom should be readily transferred to the metal centre and
3. The β atom should be able to form multiple bond with the α-carbon atom.

Factors retarding the β-elimination process

1. Metal alkyls having less bulky ligands will be coordinatively saturated. Hence they are expected to be more stable and do not undergo this fragmentation.
2. Fragmentation process may also be prevented by designing the alkyl in such a way that the transfer of a fragment group to the metal is no longer feasible. Since the transfer of groups other than hydrogen from the β carbon atom to the metal is very unlikely, alkyl groups having no β-hydrogens will retard this fragmentation process.
3. Multiple bonding between the α and β skeletal atoms may be prevented by the presence of a β-atom having no tendency to π-bond. For example, β-silicon atoms hardly ever participate in multiple bonds and when they have substituents methyl groups, no β-elimination occurs.

   Example, $Cr[CH_2-Si(CH_3)_3]_4$ does not decompose by this fragmentation.

α-Hydrogen abstraction in which an α-hydrogen of an alkyl ligand is abstracted to give an alkylidene or carbene complex, is much less recognised. A substantial amount of information indicates that this is also a significant decomposition mode for organometallic compounds.

13.1.17 Role of Palladium in Catalysing the Oxidation of Ethene to Ethanal

1. Palladium coordinates with alkene thereby weakening the C=C bond.
2. Palladium atom also coordinates with hydroxide ion (initially in the form of water which is subsequently deprotonated) thereby ensuring that the alkene and hydroxide ion are held close together and thus facilitating reaction between them.
3. The coordination of alkene to palladium removes more electron density from the π-bonding orbital of the alkene, than that goes into the π^* anti-bonding orbital, thereby rendering the alkene more susceptible to nucleophilic attack than in the uncoordinated state.

13.1.18 Polymerisation of Olefins: Ziegler – Natta Catalysis

Polymerisation deals with reactions in which two or more unsaturated organic molecules such as alkenes, conjugated dienes or alkynes combine with or without the transfer of hydrogen atoms to form C-C bonds. These reactions are catalysed by transition metal complexes. While investigating the multiple insertion of ethene into an Al-alkyl bond to give long chain Al-alkyls, K. Ziegler and his co-workers discovered that small amounts of Ni inhibit this polymerisation reaction. This stimulated an extensive study of the effect of the transition metals on the Al-alkyl polymerisation system. In the early 1950s, these studies led to the discovery that certain transition metal complexes in the presence of Al-alkyl compounds, will catalyse the polymerisation of ethene under mild reaction conditions to give a material of molecular weight in excess of 50,000. This discovery was of tremendous technical importance because previously ethene had been considered a very difficult molecule to polymerise, needing pressures of over 1000 atmospheres and temperature of the order of 200°C.

G. Natta extended Ziegler's work to the polymerisation of propene and higher α-olefins using Ziegler-type catalysts based on Ti. After these discoveries, many metal combinations have been found to be capable of catalysing alkene polymerisation and the definition extended to include any combination of alkyl, hydride or halide of Groups I – III with a transition metal salt or complex of Groups IV – VIII of the periodic table.

Ziegler and Natta were jointly awarded Nobel Prize for Chemistry in 1963.

The most familiar example is the original Ziegler catalyst formed from $TiCl_4$ and AlR_3.

In the inert hydrocarbon solvent used, an insoluble mixed halide-alkyl complex of Al and Ti is formed. This material is the active catalyst for the polymerisation of ethylene, presumably acting as a heterogeneous catalyst.

HETEROGENEOUS CATALYSIS AND HOMOGENEOUS CATALYSIS

In recent years, the utilities of homogeneous hydrogenation, isomerisation, oligomerisation, carbonylation reactions etc. have expanded enormously. Commercial processes based on homogeneously-catalysed routes are becoming increasingly important as evidenced by the Wacker's process and others. However, homogeneous catalysts can exhibit the problems of product contamination and catalyst loss, where the prodcuts are not readily separated from the catalyst.

Anchoring homogeneous catalysts to polymers or other compounds, effectively *heterogenises* them, allowing their use in fixed beds and simplifying catalyst recovery. Thus anchoring of homogeneous catalysts has assumed importance.

In the development and planning of new processes, it is very important to compare carefully the advantages and disadvantages of both the catalysts. A comparison of important aspects of the two types of catalysts is presented in Table 13.1.

Table 13.1 Comparison of homogeneous catalysis and heterogeneous catalysis

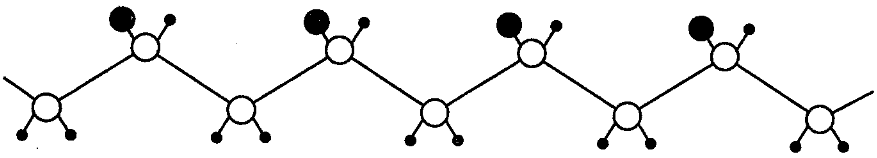
Aspect	Homogeneous	Heterogeneous
1. Active centres	all metal atoms	only surface atoms
2. Concentration	small	high
3. Diffusion problems	not present	present
4. Structure of catalyst	known	unknown
5. Stochiometry	known	unknown
6. Modification possibility	high	small
7. Reaction conditions for preparing the catalyst	mild	severe
8. Catalyst separation	not easy	easy
9. Applications	limited	wide
10. Catalyst contamination in the product	small	nil

The advantages of homogeneous catalysts outweigh the disadvantages because the greater variety of possible and specifically designed reactions promise a bright future with regard to homogeneous catalysis.

13.1.19 Importance of Ziegler-Natta Catalysis

The Ziegler-Natta catalysis of alkene polymerisation which operates at modest temperatures and pressures leads to the formation of stereoregular polymers. This is in direct contrast to the high temperature and high pressure polymerisation of alkenes. Stereoregularity often introduces some very desirable properties into the polymer. In this process, the alkenes polymerise in such a way as to yield long linear head-to-tail chains consisting of sequences of monomeric units having the same steric arrangement. These polymers are called *isotactic polymers.* The advantages of stereoregularity are that it conveys greater mechanical strength to the polymer enabling it to be used in making string and rope as well as more rigid articles such as industrial buckets. They possess higher melting points and are stronger than nylon.

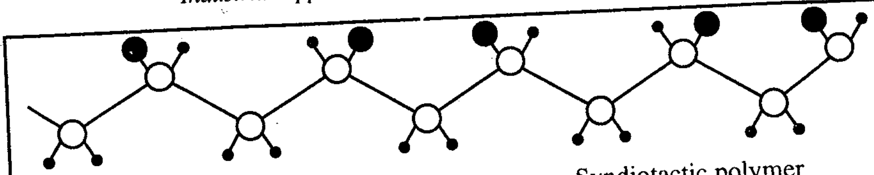
One of the features of organometallic polymerisation catalysts is that they produce stereoregular polymers. For example, propylene forms two stereoregular polymers namely, *isotactic* and *syndiotactic* polymers and one non-regular polymer namely *atactic* polymer. In isotactic polymer, the methyl groups always lie on the same side of the chain.



○ = C, ● = CH_3 • = H

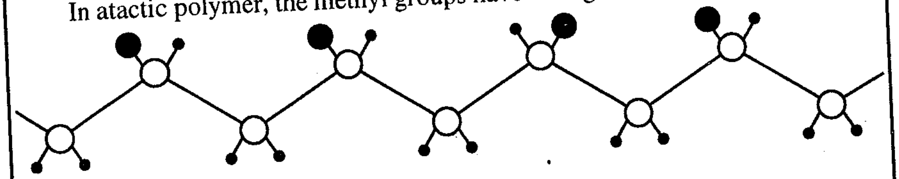
Isotactic polymer

In syndiotactic polymers methyl groups alternate along the chain.



Syndiotactic polymer

In atactic polymer, the methyl groups have no regularity along the chain.



Atactic polymer

When the double bond of the propylene attaches itself to Ti, the methyl group must always point away from the surface of the crystal simply because the reaction occurs on the surface. Thus when the molecule migrates and is inserted into the Ti-C bond, it always has the same orientation. This is called *cis-insertion* of the alkene and explains why the polymers produced are stereoregular.

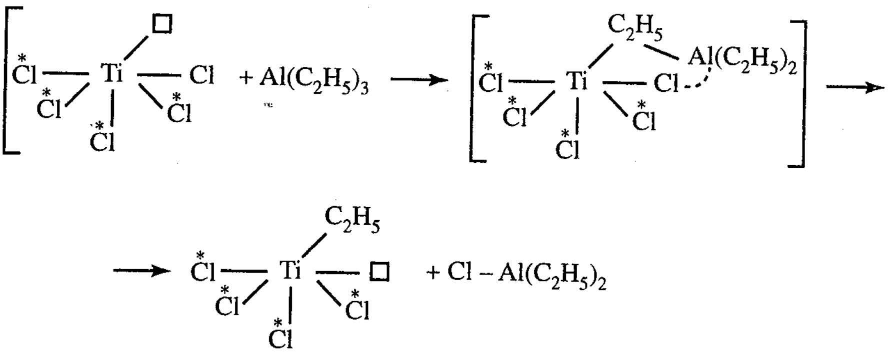
13.1.20 Mechanism of Ziegler-Natta Catalysis

The most familiar example of Ziegler-Natta catalyst is the one formed from $TiCl_4$ and $Al(C_2H_5)_3$. These components react in a way that is not completely understood but may involve the following steps.

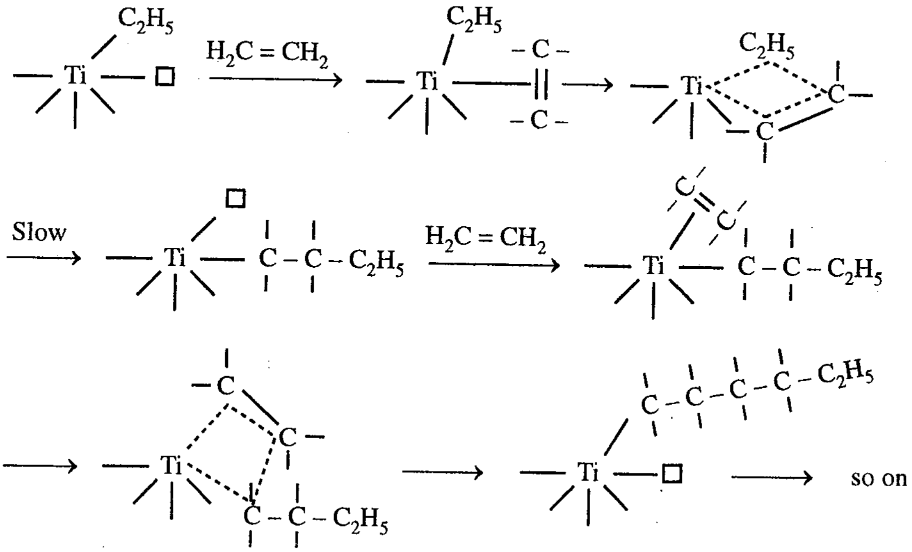
$$\begin{aligned} TiCl_4 + Al(C_2H_5)_3 &\rightarrow Al(C_2H_5)_2Cl + TiCl_3C_2H_5 \\ TiCl_3C_2H_5 &\rightarrow HCl + C_2H_4 + TiCl_2 \\ TiCl_3C_2H_5 + HCl &\rightarrow C_2H_6 + TiCl_4 \\ TiCl_2 + TiCl_4 &\rightarrow 2\,TiCl_3 \end{aligned}$$

Thus, if inert hydrocarbon solvent is used, an insoluble mixed halide-alkyl complex of Al and Ti of variable composition is formed. This is the active catalyst for the polymerisation of ethylene, presumably acting as a heterogeneous catalyst.

Several similar mechanisms have been proposed for this catalytic process. The most widely accepted of these is outlined below. To understand how the catalyst works, we must look at the crystal structure of $TiCl_3$. In solid $TiCl_3$, a Ti atom in the centre of the crystal is surrounded octahedrally by six chlorine atoms. Each Cl atom is further bound to a Ti atom (otherwise the formula would be $TiCl_6$ but not $TiCl_3$). However, if such a bonding is carried on indefinitely, it is apparent that, in order to make the crystal electrically neutral (that is to have the formula $TiCl_3$), some of the Ti atoms at the surface should have only 5 Cl atoms around them and so possess a vacant site, -□. On treating such a crystal of $TiCl_3$ with $Al(Et)_3$, this vacant site is alkylated. The starred Cl (Cl*) indicates a Cl bound to a second Ti and an unstarred Cl atoms lie on the surface of the crystal.

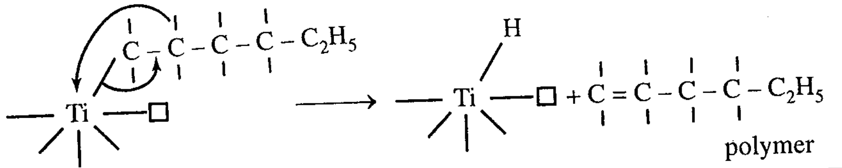


In the alkylated product, the vacancy in the coordination shell of the Ti atom is still present but in a fresh position. This vacant site is potentially capable of coordinating an alkene such as C_2H_4. The alkene coordinates to the Ti atom as a π-donor in its vacant coordination site. The electropositive nature of the Ti atom allows the electrons in the Ti-C_2H_5 bond to flow towards the C_2H_5 group. This weakens the bond which is labile and is cis to the newly arrived alkene π bond. When an alkene and an alkyl group are bound to adjacent sites on a metal atom, they react to give what is known as an insertion product through a concerted four-centre rearrangement.This step is assumed to be the rate-determining step. The alkyl group shifts to one carbon of the alkene double bond, while the other carbon develops a sigma bond to the Ti atom. When the rearrangement of the alkyl on to the alkene carbon is complete, a new coordination site is opened up on the Ti atom cis to the new longer alkyl group. This regeneration of the vacant site enables the process to be repeated. For the sake of clarity, the starred chlorine atoms have been omitted.



The presence of the vacant site enables the chain to continue growing by switching back and forth between the two sites.

Termination would occur by a reverse insertion reaction in which a hydride ion shifts to the metal.



Polyethylene produced by Ziegler-Natta catalysis is superior to that produced by free radical polymerisation. A comparative account of these two polymers is given in Table 13.2.

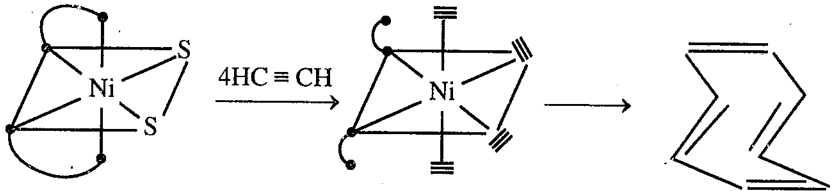
Table 13.2 Comparative account of polyethylenes produced by Zieglar-Natta catalysis and by free radical polymerisation

Polyethylene produced by Ziegler-Natta catalysis	Polyethylene produced by free radical polymerisation
1. Produced under milder reaction conditions	1. Produced under severe conditions of about 190° - 210°C and 1500 atmospheres of pressure
2. Has high density, 0.95 – 0.97 g/cc	2. Has lower density, 0.91 – 0.94 g/cc
3. Has higher melting point, 135°C	3. Has lower melting point, 115°C
4. Contains straight chains with very little branching	4. Consists of branched chains
5. Relatively hard and stiff	5. Relatively softer
6. Has higher molecular weight, 20,000 – 30,000	6. Has relatively lower molecular weight

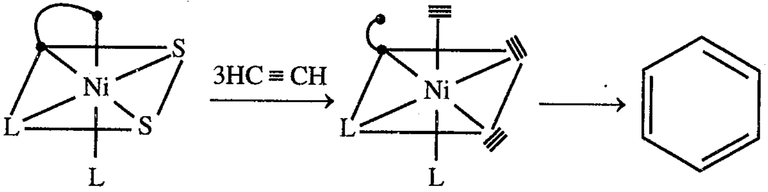
13.1.21 Cyclo–oligomerisation of Acetylenes—Reppe's Catalysis

When many monomer units combine to give a macromolecule, the process is called polymerisation. But when two to about nine or ten monomer units combine to give a single molecule then the process is referred to as oligomerisation. If oligomerisation process is accompanied by cyclisation (ring closure) then it is called cyclo–oligomerisation. The catalysts for alkyne cyclo–oligomerisation predominantly involve organometallic compounds of Group VIII transition elements. Among these, nickel compounds seem to be the most catalytically active. More typical of acetylene behaviour are the aromatic cyclisations catalysed by these transition metal complexes, discovered by Reppe. The classical examples, discovered by Reppe in 1940 involve Ni(II) salts with ligands such as acetylacetonate and salicylaldehyde. Such ligands can be partially displaced by the acetylene, the number of vacatable sites determining the type of product formed as shown below ((is a bidentate ligand, S is solvent and L is triphenyl phosphine (PPh_3))

1. If oxygen donor ligands such as acetylacetone or salicylaldehyde are employed in a solvent such as tetrahydrofuran or dioxan, 4-coordination sites are vacated or available, and cyclotetramerisation occurs to give mainly cyclooctatetraene (COT).

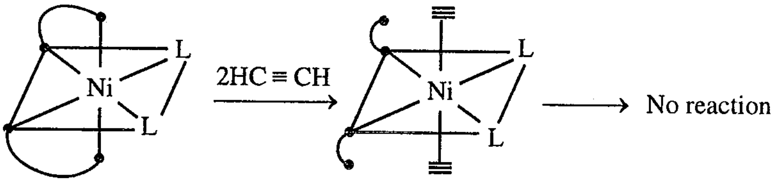


2. If a less labile ligand such as PPh_3 is incorporated, the coordination sites required for tetramerisation are not available and cyclotrimerisation to benzene predominates. Substituted benzene derivatives can be obtained from the appropriately substituted alkynes.



Benzene

3. If only the two trans positions are vacated, then there will be no reaction.



13.1.22 Fischer-Tropsch Synthesis

The Fischer-Tropsch synthesis was discovered in Germany in the 1920s and was used during the second world war to produce liquid hydrocarbon fuel from coal. The mixture of CO and H_2 is passed over certain transition metal surface. The basic reaction is given by the equations,

$$n\,CO + 2\,n\,H_2 \xrightarrow{\text{catalyst}} -(CH_2)_n - + n\,H_2O$$

$$\text{(or)}\ n\,CO + (2n+1)H_2 \xrightarrow{\text{catalyst}} C_n\,H_{2n+2} + n\,H_2O$$

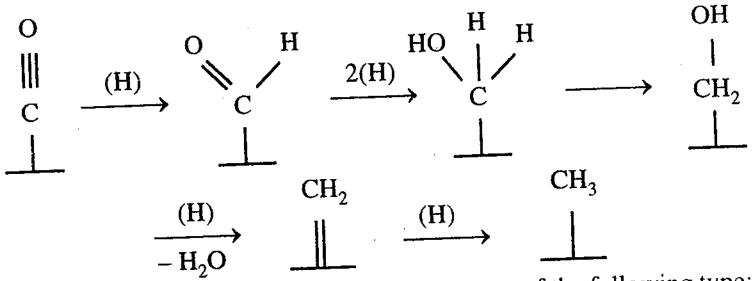
This equation is an oversimplification because oxygen-containing products such as alcohols, acids and esters are also formed apart from the hydrocarbons. The original process used CO and H_2 with 100 atmosphere pressure and temperature of about 400°C over an alkaline-doped iron heterogeneous catalyst. The process from then on has undergone considerable refinement and is currently being used in South Africa.

The mechanism of Fischer-Tropsch synthesis is complicated. Work has been carried out on heterogeneous and homogeneous systems, using mono and polynuclear metal complexes.

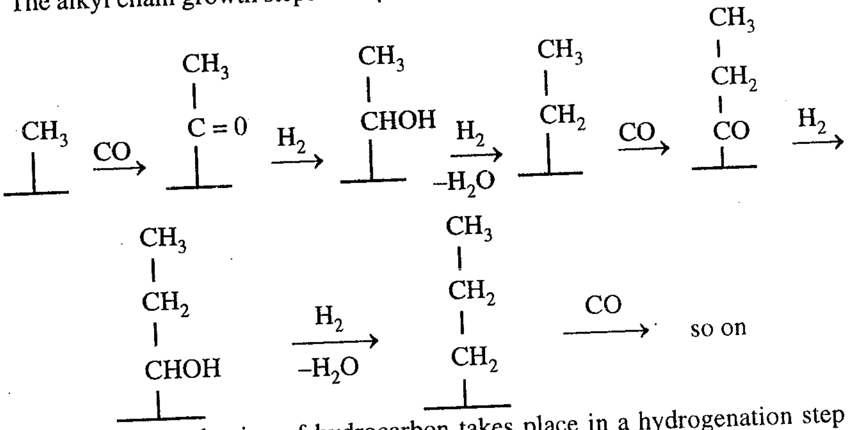
The rapid and at times drastic increase in the price of crude oil which has occurred over the last few decades coupled with the realisation that crude oil supplies whether limited by technical or political factors, are likely to fall short of potential demand has rekindled interest in coal both as a source of energy and as a feed-stock for the petrochemical industries. At the current rate of energy consumption, the known coal reserves are sufficient for more than 250 years. The most direct method of using coal as a primary energy source is combustion. However, if coal is to replace crude oil in the production of fuels and organic chemicals, it is necessary to develop efficient methods of converting coal into gas, liquid hydrocarbons and some organic chemicals. One method of atleast partially accomplishing these goals is the Fischer-Tropsch synthesis, where synthesis gas, namely a mixture of CO and H_2 obtained by burning coal in the presence of oxygen and steam, is converted into a number of hydrocarbon products.

13.1.23 Mechanism of Fischer-Tropsch Synthesis

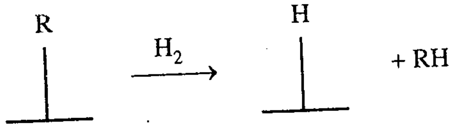
The widely accepted mechanism for this process involves the generation of a methyl group on the surface of the catalyst followed by a series of steps in which methylene groups are successively inserted between the metal and the alkyl group, thus building up a linear alkyl group. Then the linear alkyl group is severed from the metal in a hydrogenation step. Thus a product hydrocarbon molecule is released. The methyl group is assumed to be formed by the reaction of adsorbed hydrogen atoms formed by surface dissociation of H_2, with adsorbed CO in a sequence as shown below:



The alkyl chain growth steps in this mechanism are of the following type:



Finally, the production of hydrocarbon takes place in a hydrogenation step as shown below, where R is a long hydrocarbon chain and RH is the product hydrocarbon.



This mechanism derived some evidence from the fact that the various proposed intermediates have known analogues in homogeneous organometallic reactions.

13.1.24 Water Gas Shift Reaction

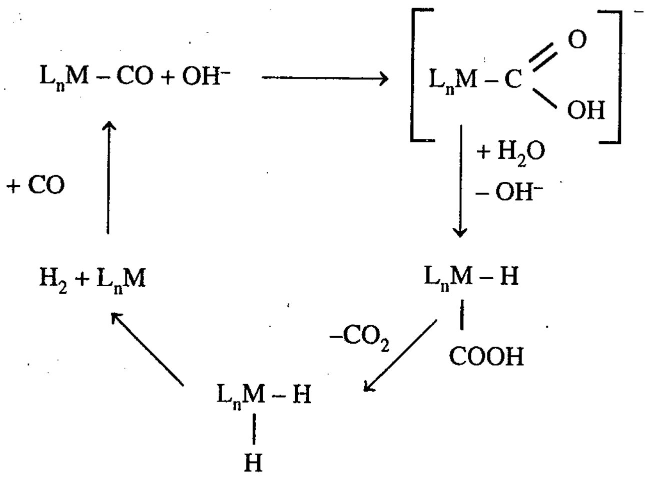
The water gas shift reaction,

$$H_2O + CO \rightleftharpoons CO_2 + H_2$$

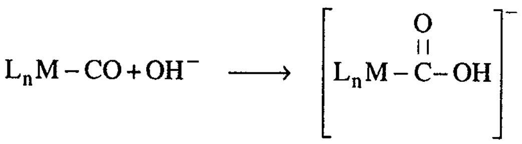
has received renewed attention because of the need to produce hydrogen from non petroleum sources such as coal. Commercially, the reaction is best carried out over solid metal oxide catalyst at elevated temperatures. However, the reaction can proceed homogeneously using alkaline solutions of various metal carbonyls.

13.1.25 Mechanism of Water Gas Shift Reaction

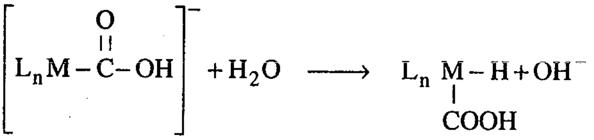
The proposed mechanism for homogeneous catalysis of this reaction is as follows:



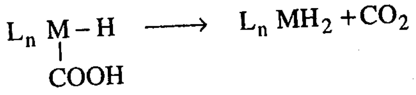
In this mechanism, ML_n might represent, for example, the $Fe(CO)_4$ group. The attack of OH^- on L_n MCO presumably forms an anionic carboxylic acid intermediate which in turn abstracts a proton from the solvent to form L_n MH(COOH). This species undergoes decarboxylation to form the dihydride, which reductively eliminates H_2 and adds to CO to reform L_n MCO, thus completing the cycle. This catalytic cycle can also be represented by the following equations:



$$L_nM-CO+OH^- \longrightarrow \left[L_nM-\overset{O}{\overset{\|}{C}}-OH\right]^-$$



$$\left[L_nM-\overset{O}{\overset{\|}{C}}-OH\right]^- + H_2O \longrightarrow L_n\underset{\underset{COOH}{|}}{M}-H+OH^-$$



$$L_n\underset{\text{COOH}}{\underset{|}{M}}-H \longrightarrow L_nMH_2 + CO_2$$

$$L_nMH_2 \longrightarrow L_nM + H_2$$

$$L_nM + CO \longrightarrow L_nM-CO$$

The net reaction is,

$$CO + H_2O \xrightarrow{L_nM-CO} CO_2 + H_2$$

EXERCISES

***I Choose the best answer for each of the following:**

1. Vaska's complex is
   a) $[Pt(Cl)(CO)(PPh_3)_2]$
   b) $[It(Cl)(CO)(PPh_3)_2]$
   c) $[It(Cl)(CO)(PEt_3)_2]$
   d) $[Pt(CO)(Cl)(PEt_3)_2]$
2. Wilkinson's catalyst is
   a) $[RhCl(PPh_3)_3]$
   b) $[Rh(PPh_3)_3]Cl$
   c) $[RhCl(PEt_3)_3]$
   d) none of the above
3. Condition to be satisfied by a metal to act as a catalyst is,
   a) it must have two moderately stable oxidation states,
   b) it must be capable of forming moderately stable coordinatively unsaturated complexes.
   c) it must have the ability to match the substrate orbitals.
   d) all the above
4. The role of rhodium metal in Wilkinson's catalysis is,
   a) it provides a low energy path for cleaving H-H bond in H_2
   b) it coordinates the alkene to weaken the C = C bond
   c) it provides a mechanism to transfer the two H atoms to the alkene carbon atoms.
   d) all the above
5. The reaction, $[RhC1L_2] + H_2 \rightleftharpoons [RhC1L_2(H)_2]$ is called
   a) reductive elimination
   b) insertion
   c) oxidative addition
   d) complementary reaction
6. The reaction $[Co(CO)_2(L)(H)_2(COR) \rightarrow [Co(CO_2)(L)(H)] + RCHO$ is called,
   a) oxoprocess
   b) reductive elimination

c) non-complementary reaction
d) none of the above

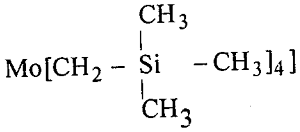
7. Wacker's process involves
   a) hydrogenation of olefins
   b) isomerization of olefins
   c) oxidation of olefins
   d) polymerization of olefins.
8. The function of Cu(II) salt in Wacker's process is
   a) co-catalyst
   b) catalyst
   c) reducing agent
   d) all the above
9. The reaction $L_nM-CH_2-CH_2-R \rightleftharpoons R-CH=CH_2+L_nMH$ is known as
   a) reduction
   b) elimination
   c) β-elimination
   d) none of the above
10. When the methyl groups in polypropene lie on the same side of the C-C chain, it is called as
    a) syndiotactic
    b) isotactic
    c) atactic
    d) stereo non-regular
11. Reppe's catalyst is used in the
    a) hydrogenation of olefins
    b) hydroformylation process
    c) polymerization process
    d) cyclooligomerization
12. The fischer – Tropsch synthesis involves,
    a) $n\,CO+(2n+1)\,H_2 \rightarrow C_nH_{2n+2}+n\,H_2O$
    b) $H_2O+CO \rightleftharpoons CO_2+H_2$
    c) $R-CH=CH_2+H_2+CO \rightleftharpoons R-CH_2-CH_2-CHO$
    d) none of the above

***II Match the following:**

1. non-complementary reaction	a) $[Rh(I)_3(CO)_2(COCH_3)]^- \rightarrow [Rh(I)_2(CO)_2]^- + CH_3COI$
2. complementary reaction	b) $L_nM\text{-}X+YZ \rightarrow L_nM\text{-}(YZ)-X$
3. oxad reaction	c) $2\,Fe^{3+}+Sn^{2+} \rightarrow 2\,Fe^{2+}+Sn^{4+}$
4. reductive elimination reaction	d) $[Pt(PPh_3)_2(C_4H_9)_2] \rightarrow C_4H_8 + [Pt(PPh_3)_2(C_4H_9)(H)]$
5. insertion reaction	e) $Ce^{4+}+Fe^{2+} \rightarrow 2\,Ce^{3+}+Fe^{3+}$
6. β-elimination reaction	f) $2\,Cu^{+} \rightarrow Cu^{0}+Cu^{2+}$

7. disproportionation reaction	g) $[Rh(Cl)L_2]+H_2 \quad [Rh(Cl)L_2(H)_2]$
8. Smidt reaction	h) $H_2O+CO \quad CO_2+H_2$
9. oxo-reaction	i) $n\,CO+(2n+1)H_2 \rightarrow C_nH_{2n+2}+n\,H_2O$
10. water gas shift reaction	j) $R-CH=CH_2+H_2+CO \rightarrow R-CH_2-CH_2-CH_2-CHO$
11. Fischer – Tropsch synthesis	k) $[PtCl_3(C_2H_4)]^- + H_2O \rightarrow CH_3CHO + Pt(0) + 3\,Cl^- + 2\,H^+$

III Account for the following:

1. $[RhL_2(Cl)]+H_2 \quad [RhL_2(Cl)(H)_2]$ is called an oxad reaction.
2. $[RhL_2(H)(Cl)(R)] \quad [RhL_2(Cl)]+RH$ is a reductive elimination reaction.
3. $[(OC)_5MnCH_3]+CO \quad [(OC)_5MnCOCH_3]$ is an insertion reaction.
4. $R-CH=CH_2+H_2+CO \rightarrow R-CH_2-CH_2-CHO$ is called hydroformylation reaction.
5. Isomerization is an evil in hydroformylation process but not in hydrogenation.
6. Wacker's process is carried out in the presence of Cu(II) salt.
7. 
$Mo[CH_2-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3]_4]$ does not undergo β - elimination reaction.
8. Polymers produced by Ziegler – Natta catalysis is generally stereoregular.
9. Generally heterogeneous catalysts are better than homogeneous catalysts.
10. In Wilkinson's catalyst, if Rh is replaced by Ir, catalytic behaviour disappears.

IV Answer the following:

1. What are the conditions to be satisfied by a metal to act as a catalyst?
2. What is Wilkinson's catalyst? How is it prepared? What is its use?
3. Bring out the importance of Wilkinson's catalyst.
4. Explain the part played by rhodium metal in Wilkinson's catalysis .
5. Discuss the mechanism of hydrogenation of olefins using Wilkinson's catalyst.
6. Define the following with examples:
   a) oxidative addition reactions
   b) reductive elimination reactions
   c) insertion reactions
   d) β-elimination reactions
7. What are the advantages and disadvantages of Wilkinson's catalyst? How are these defects overcome?
8. What is oxo-process? What is its importance? Discuss its mechanism using $HCo(CO)_4$ as catalyst.
9. Why is modification required over the original catalyst for the hydroformylation process?
10. Discuss the mechanism of hydroformylation of olefins using rhodium complex as catalyst.
11. What is an isomerization reaction? How is isomerization of alkenes brought about using rhodium complex as catalyst?

12. What is Wacker's process? Discuss its mechanistic aspects?
13. Explain the role of copper (II) salt in Wacker's process?
14. How is co-catalyst regenerated in the oxidation of ethene to ethanal?
15. Discuss the different factors that a) facilitate and b) retard, the β-elimination reactions.
16. What is the role of palladium in catalysing the oxidation of ethylene to acetaldehyde?
17. What is Ziegler-Natta catalyst? How does it catalyse the polymerization of olefins? What is its importance?
18. Write a note on stereo-regular polymers of propylene.
19. Compare and contrast between homogeneous and heterogeneous catalyses.
20. Compare the properties of polyethylene produced by Ziegler-Natta catalysis with those of polyethylene produced by free radical polymerization.
21. What is cyclooligomerization of acetylenes? How is it carried out? Name the catalyst used in such process.
22. What is Fischer – Tropsch synthesis? What is its importance? Discuss its mechanism.
23. Discuss the mechanism of water gas shift reaction.

ANSWERS

I 1. (b) 2. (a) 3. (d) 4. (d) 5. (c) 6. (b) 7. (c) 8. (a) 9. (c) 10. (b) 11. (d) 12. (a)

II 1. (c) 2. (e) 3. (g) 4. (a) 5. (b) 6. (d) 7. (f) 8. (k) 9. (j) 10. (h) 11. (i)

Chapter 14

Biological Coordination Compounds

Coordination compounds participate in many important biological processes in plants and animals. The following are some of such processes:

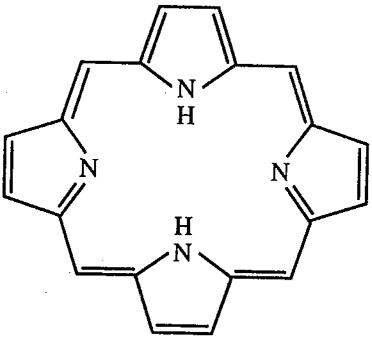
1. Transport and storage of oxygen
2. Electron transfer
3. Catalysis
4. Photosynthesis.

14.1 TRANSPORT AND STORAGE OF OXYGEN

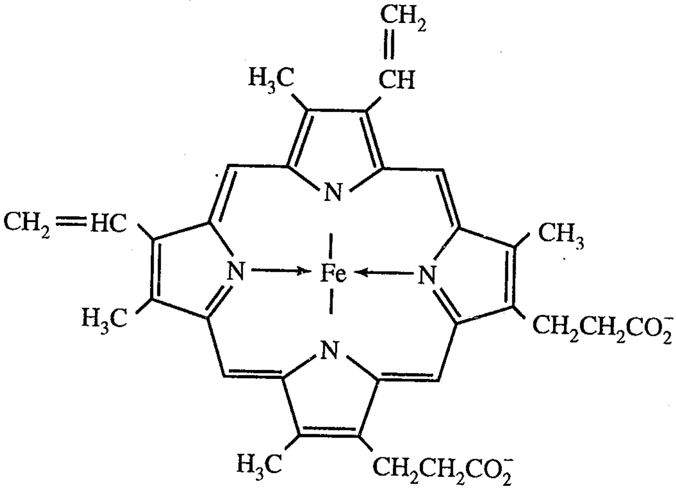
14.1.1 Haemoglobin

Haemoglobin, the red pigment in red blood cells carries oxygen from the lungs to the tissues. It is called the respiratory pigment. It delivers the oxygen molecule to the myoglobin in the tissues. Haemoglobin, a protein is an iron-porphyrin complex. Fig.14.1*a* denotes the structure of the ligand *porphine*. Its two H^+ ions bonded to nitrogen atoms are displaced upon coordination to iron. Complexes formed between porphine and metals are called metal porphyrins; the iron-porphyrin complex is called the heme group(prosthetic group), which is a part of haemoglobin(Fig.14.1*b*).

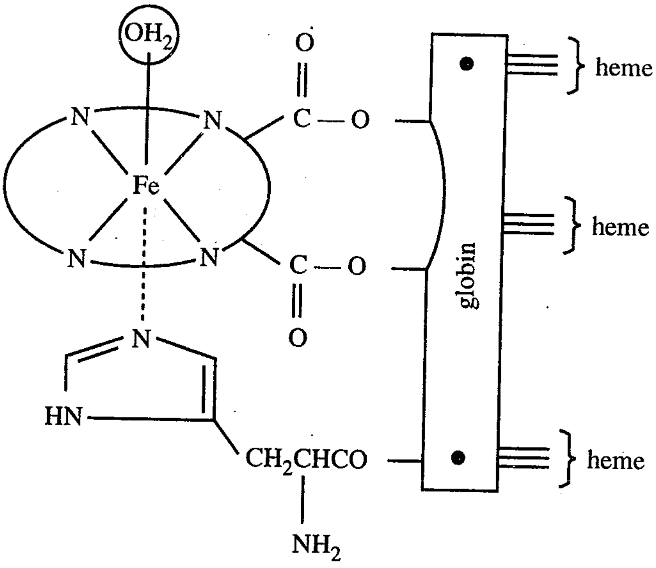
> Haemoglobin in the red blood cells combines with oxygen inhaled in the lungs and transports it to all the cells in the body. When the oxygen has been released for cell respiration, haemoglobin loses its bright red colour and becomes purple. It then combines with the waste carbon dioxide produced by the cells and deposits it in the lungs so that the gas can be exhaled.



(*a*) *Structure of phorphine ligand*



(*b*) *Heme group*



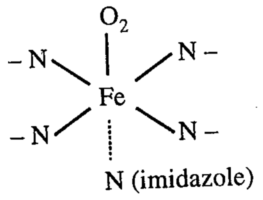
(*c*) *Haemoglobin sub-unit*

Fig. 14.1

14.1.2 Structural Features of Haemoglobin

1. Each haemoglobin molecule consists of four sub-units, each unit being a folded chain. A sub-unit consists of a protein unit, (globular protein, called globin), a heme group and a histidine unit (Fig. 14.1*c*).
2. The heme unit is a chelate of iron with porphine ligand.
3. Its molecular weight is about 65,000.
4. The four polypeptide chains of haemoglobin are wound in such a manner as to make the molecule spherical.
5. The iron in haemoglobin is in the Fe(II) state; it is coordinated to the four nitrogen atoms in the porphine group. Two more ligands, a histidine unit and a water molecule are also coordinated to Fe(II). The histidine ligand is the link between the heme group and the protein unit. The water molecule is denoted by a circle in the figure, because, the exact geometry of the bonding between H_2O and Fe(II) is not certain.
6. The complex is octahedral. The porphyrin ring is conjugated and planar. The charge transfer between stable and low-lying orbitals on the ring and iron is the origin for the red colour of the complex. The water ligand in haemoglobin can be readily replaced by molecular oxygen to form the red-coloured *oxyhaemoglobin*; this is present in the arterial blood. The water-coordinated complex is called deoxyhaemoglobin; it is blue, the colour characteristic of the venous blood. As each sub-unit can bind one O_2, each haemoglobin molecule can bind up to four O_2 molecules.
7. In oxyhaemoglobin, the Fe(II) is in the low-spin state and is diamagnetic; but in deoxyhaemoglobin, the Fe(II) is in the high-spin state and is paramagnetic. The size of Fe(II) is increased by about 30 per cent, when it changes from the diamagnetic to paramagnetic state. This increase in size distorts the bonds around Fe and also the shape of the complex. In oxyhaemoglobin, the Fe(II) is of the right size to get into the hole at the centre of the porphyrin ring; but in deoxyhaemoglobin, because of its enlargement, it is above the plane of the ring.

The O_2 molecule is bonded to the heme group as shown in Fig.14.2.



A portion of oxygenated haemoglobin

Fig. 14.2 The bonding of the oxygen molecule with the heme unit of haemoglobin

The arteries carry blood to the muscles in various parts of the body, where oxygen is required. In the muscles, the oxygen is transferred to a myoglobin molecule and stored, until it is required to produce energy from glucose. When haemoglobin loses its O_2, a water molecule is again coordinated to iron. Then, the protein part of it absorbs H^+. This indirectly helps remove CO_2 from the tissues; CO_2 is converted to HCO_3^- and H^+. HCO_3^- readily dissolves in blood and H^+ is absorbed by the protein unit of haemoglobin. The impure blood returns to the heart through the veins. Then, it is pumped to the lungs where HCO_3^- is converted to $CO_2(g)$ and exhaled. The blood once again, picks up O_2 in the lungs and the cycle is repeated.

The oxygen-carrying process by haemoglobin is reversible; the oxyhaemoglobin complex is not too stable to render the release of O_2 at the muscles difficult. The transfer of O_2 by haemoglobin involves only Fe(II) and not Fe(III). The oxidation of Fe(II) to Fe(III), which would be irreversible and ruinous for O_2 transport, is prevented by the protein unit.

14.1.3 Transport and Exchange of Gases

The iron in each heme unit of haemoglobin combines with one molecule of oxygen; thus each haemoglobin molecule can carry four molecules of oxygen. The oxygen molecules are added one at a time:

$$\begin{aligned} Hb_4 + O_2 &= Hb_4O_2 \\ Hb_4O_2 + O_2 &= Hb_4O_4 \\ Hb_4O_4 + O_2 &= Hb_4O_6 \\ Hb_4O_6 + O_2 &= Hb_4O_8 \end{aligned}$$

Combination of the first sub-unit (Hb) with O_2 increases the affinity of haemoglobin for the second O_2 and the combination of the second O_2 further increases the affinity for the third O_2 and so on. The combination of each O_2 with the pigment molecule brings the polypeptide chains of haemoglobin closer and closer leading to enhanced affinity for O_2. This enhanced affinity results in a sigmoid shape instead of a straight line for the curve relating the uptake of oxygen to P_{O_2} (Fig. 14.3). As the blood leaves the lungs, the haemoglobin is saturated with oxygen (P_{O_2} = 100 mm Hg). As the haemoglobin molecules travel through the tissue capillaries, the P_{O_2} drops, as O_2 bound to the haemoglobin is given to the muscle cells. At this stage P_{O_2} drops to 60 mm Hg.

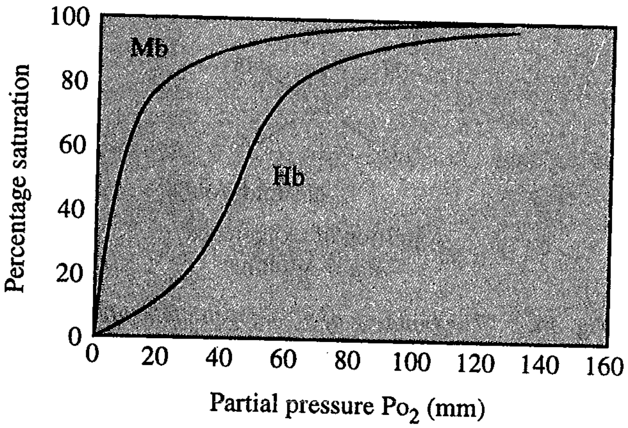


Fig. 14.3 The oxygen-binding curves for myoglobin (Mb) and haemoglobin (Hb)

As the blood returns from the tissue, it takes away CO_2. CO_2 is more soluble than O_2 in the blood, and a small amount of it is simply dissolved in the blood plasma. About another 25 per cent of CO_2 is bound to the amino groups of the haemoglobin molecule. However, most of the CO_2 (about 65%) is carried in the blood as HCO_3^-. The bicarbonate ion is produced in a two-stage reaction. First, CO_2 combines with water to form carbonic acid catalysed by the enzyme *carbonic anhydrase* present in red blood cells. Then H_2CO_3, a weak acid, dissociates to give HCO_3^-:

$$CO_2 + H_2O \overset{\text{carbonic anhydrase}}{\rightleftharpoons} H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

When CO_2-loaded blood reaches the lungs, CO_2 diffuses from the plasma into the alveoli (air pocket) and flows out of the lungs with the expired air.

When an oxygen molecule is bound to the iron atom in haemoglobin, it occupies a position opposite to the imidazole-nitrogen atom. The addition of this sixth ligand to Fe alters the strength of the ligand field. Thus an iron atom is transformed into a low-spin state in which the six d electrons occupy the d_{xy}, d_{yz} and d_{zx} orbitals. The $d_{x^2-y^2}$ orbital which was originally occupied by an electron is now empty and therefore, the repulsion which existed between the iron atom and the porphyrin nitrogen atoms vanishes. As a result of this, the iron atom slips into the centre of an approximately planar porphyrin ring and an octahedral complex is formed. (Fig. 14.4). This movement of iron atom in haemoglobin triggers extensive structural changes in the other sub-units and enhances the oxygen binding capability of the heme group.

CYANIDE POISON

The cyanide ion is a powerful poison; on consumption, it can kill a person quickly. The CN^- ions in the victim replace the O_2 ligands in the haemoglobin molecules; this stops oxygen supply to the body tissues leading to death of the victim. The coordination of CN^- to Fe(II) is irreversible. In addition, CN^- interferes with the cytochrome enzyme system, which is the main reason for its extreme toxicity; as with haemoglobin, CN^- strongly binds with the iron of cytochrome and paralyses the activity of cytochrome. Carbon monoxide, like the cyanide ion, can also occupy the oxygen site in haemoglobin and stop oxygen transfer.

CARBON MONOXIDE POISON

Carbon monoxide (CO) is similar to O_2 electronically and sterically. Therefore CO can bind to the sites in haemoglobin and metalloproteins where O_2 does in living cells. In fact, haemoglobin and myoglobin have a higher affinity for CO than for O_2. Therefore, if CO is inhaled by a person, it can bind to, and block the oxygen transport sites of haemoglobin, thus preventing oxygen from being distributed to various tissues of the body. The resulting oxygen deficiency in the tissues (*anoxia*) would cause unconsciousness (coma) and then death. The binding between CO and haemoglobin is very strong and the complex does not readily dissociate; this complex is brighter red than the normal haemoglobin.

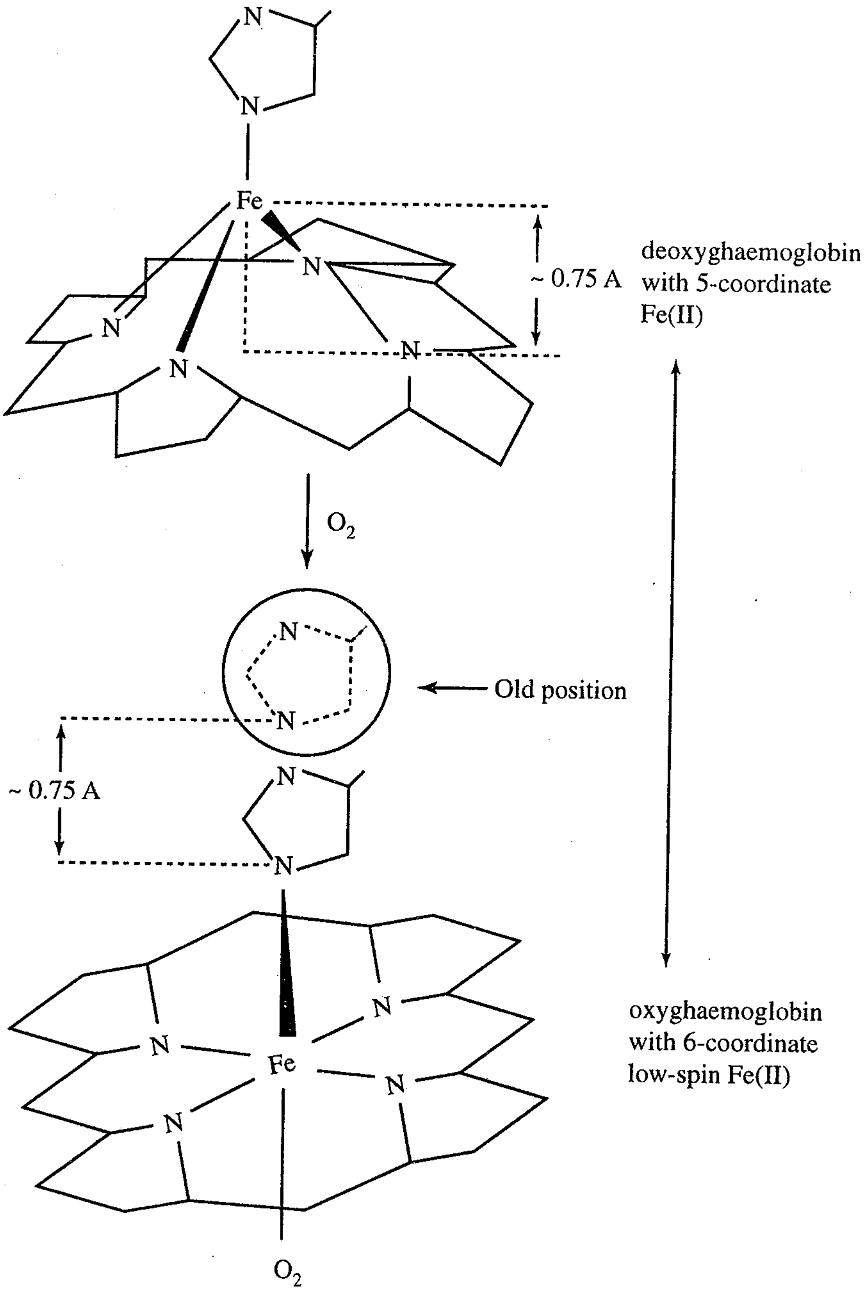


Fig. 14.4 The transformation from deoxyhaemoglobin to oxyhaemoglobin

14.1.4 Myoglobin

Myoglobin is a respiratory pigment present in skeletal muscle. Its structure is similar to a single sub-unit of the haemoglobin molecule; it contains only one iron ion and has a molecular weight of about 17,000. Its affinity for O_2 is greater than that of haemoglobin and therefore, it picks up oxygen from haemoglobin. It releases its oxygen only when the partial pressure P_{O_2} in the skeletal muscle falls below 20 mm Hg.

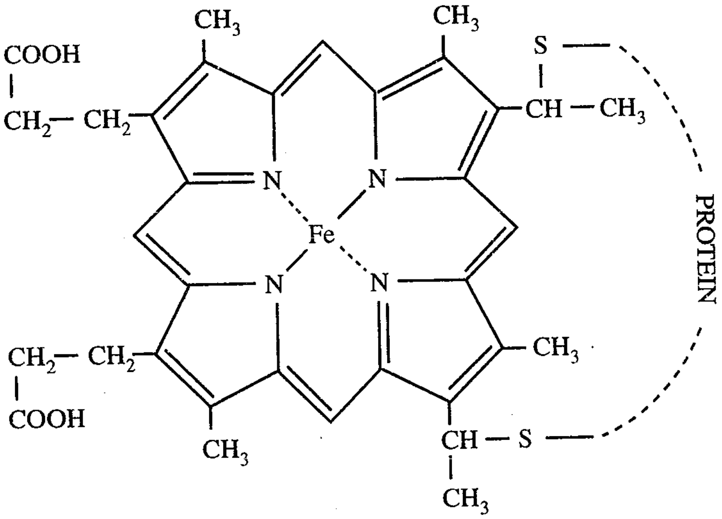
When the muscle is at rest or engaged in only moderate activity, the myoglobin holds on its oxygen. During rigorous exercise, when the muscle cells are using oxygen rapidly and the partial pressure of oxygen in the muscle drops to zero, myoglobin releases its oxygen. Thus, myoglobin provides an additional reserve of oxygen for active muscles.

14.2 ELECTRON TRANSFER

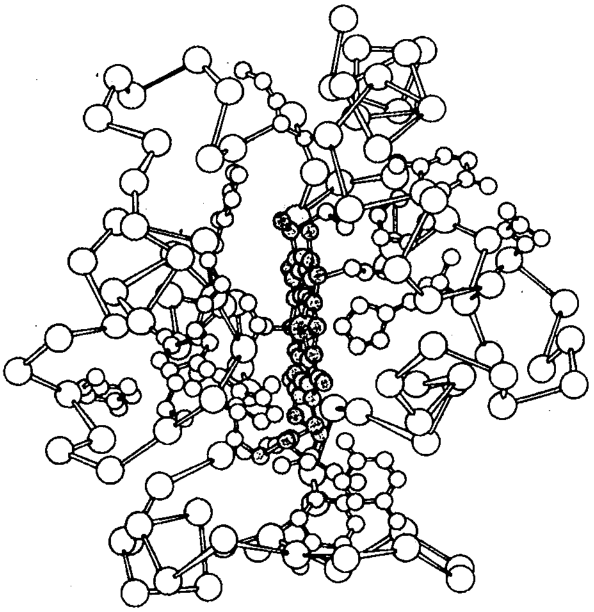
14.2.1 Cytochromes

The porphyrin ligand is very effective as a chelating agent; therefore, it is found in a number of biological systems. Cytochromes are another class of proteins, which are built up of the iron-heme complex.

There are three types of cytochromes, cytochrome *a*, cytochrome *b* and cytochrome *c*; they differ slightly in their structures. The prosthetic group in all cytochromes comprises four heme units. The molecular weight of a cytochrome is about 12,400. As in haemoglobin, in cytochrome, each Fe is bonded to four N atoms in each porphyrin ring and the fifth site is occupied by a N atom from the associated protein. The sixth site is occupied by a S atom of an amino acid, which is a part of a protein. Fig.14.5 denotes the structure of cytochrome *c*. In this, the ligands above and below the porphyrin ring are the methionine group and histidine group of the protein, respectively. The iron in this system forms an octahedral complex. Both the histidine and the methionine groups are firmly bonded to the metal ion unlike the water ligand in haemoglobin; therefore, these ligands cannot be displaced by oxygen or other ligands.



(*a*) *The heme group of cytochrome c. In the cytochromes, an atom of iron (Fe) is enclosed in a nitrogen-containing ring (a porphyrin ring)*



(*b*) *In the cytochrome c structure shown here, the heme group is in dark shade*

Fig. 14.5 *Cytochromes are molecules in which a heme group is held in an intricate protein structure*

The cytochromes act as electron carriers. The iron in them is in the low-spin state and undergoes rapid, reversible redox reaction:

$$Fe^{3+} + e^{-} = Fe^{2+}$$

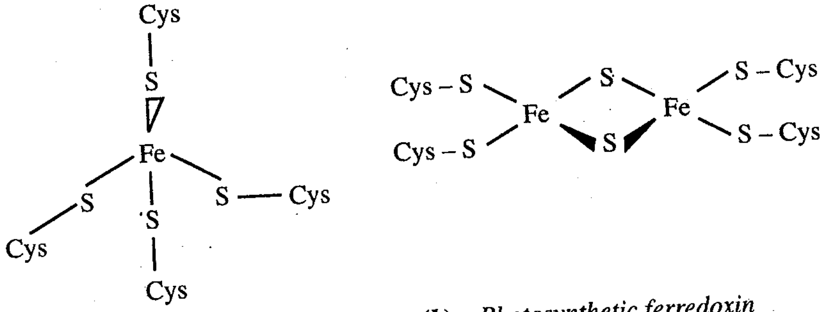
These reactions are coupled to the oxidation of carbohydrates. For example, energy is released by oxidizing glucose with molecular oxygen in the mitochondria in living cells, the cytochrome acting as the electron carrier. The iron atom of each cytochrome alternately accepts and releases an electron, passing it along to the next cytochrome at a slightly lower energy level; ultimately, at the end of the chain, the electrons, their energy spent, are accepted by oxygen, which then combines with protons from the solution to form water. The energy released in each step of the passage of electron is harnessed to form ATP molecules from ADP. This formation of ATP is called *oxidative phosphorylation.*

14.2.2 Rubredoxins

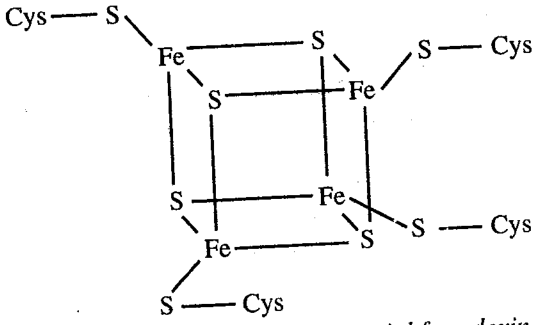
These are non-heme iron-sulphur proteins. They participate in several biological redox reactions, especially in anaerobic bacteria. The simplest bacterial rubredoxin contains $(Cys-S)_4Fe$ unit as a part of its structure (Fig 14.6*a*). It consists of a single peptide chain of 53 amino acid residues. The single iron species in this molecule is in the +3 state; it is coordinated by four sulphur atoms of cystein residues. This coordination is close to tetrahedral. The sulphur atoms in it are non-labile; they are not lost on treatment with an acid.

14.2.3 Ferredoxins

Ferredoxins are a group of non-heme iron proteins; these effect electron transfer in plants and bacteria. These are iron complexes and serve the same biological function that cytochromes do in animals. However, these have much lower molecular weights (6,000 – 12,000). A ferredoxin molecule may contain one, two, four or eight iron atoms. The simplest of these is bacterial rubredoxin, $(Cys\text{-}S)_4Fe$ (Fig. 14.6*a*). The ferredoxin, which helps photosynthesis in higher plants has a bridge structure (with Fe_2S_2 units) (Fig.14.6*b*). Another type of ferredoxin molecule found in certain bacteria has a cubane -like cluster of four iron atoms, four labile sulphur atoms and four cysteine ligands, (Fig 14.6*c*).



(*a*) *Bacterial rubredoxin* (*b*) *Photosynthetic ferredoxin*



(*c*) *Cubane - like unit in bacterial ferredoxin*

Fig. 14.6 *Fe-S Structual clusters in ferredoxins*

14.3 CATALYSIS

14.3.1 Catalase

It is an enzyme; each molecule contains four Fe(III)–heme groups. It is a ferriprotoporphyrin complex, with a molecular weight of about 2,48,000. It catalyses the decomposition of H_2O_2.

Catalase is a very powerful enzyme; one molecule of it can decompose 26,40,000 molecules of H_2O_2 per minute at 0°C. It occurs in the mammalian tissue and is believed to eliminate H_2O_2 produced by the flavo-protein oxidases in the tissue;

$$2\,H_2O_2 \xrightarrow{\text{catalase}} 2\,H_2O + O_2$$

The enzymes which catalyse the decomposition of H_2O_2 and also the oxidation of certain cell molecules by H_2O_2 are collectively called *catalases.*

14.3.2 Blue Copper Proteins

Stellacyanin, plastocyanin and *azurin* are called blue copper proteins. These Cu(II) complexes function as electron transfer redox systems. Each of these has pseudo-tetrahedral (between tetrahedral and square-planar) geometry. The Cu(I)/Cu(II) centre in these enzymes is ideally adapted for electron exchange, in that, no change in spin state occurs; therefore, there is no movement of the ligands during electron exchange.

The blue copper proteins occur in some bacteria known as cyanobacteria (also called blue-green algae). Some of these species are free-living, others live in close association with plants. Some are nitrogen-fixing; they directly convert the atmospheric nitrogen into nitrogen compounds. They reduce N_2 to NH_3, which then forms NH_4^+ in the soil; thus, certain plants can assimilate the atmospheric nitrogen through mediation by blue copper proteins of algae. These algae are photosynthetic also and fix carbon. *Anabaena cylindaica* is one such cyanobacterium.

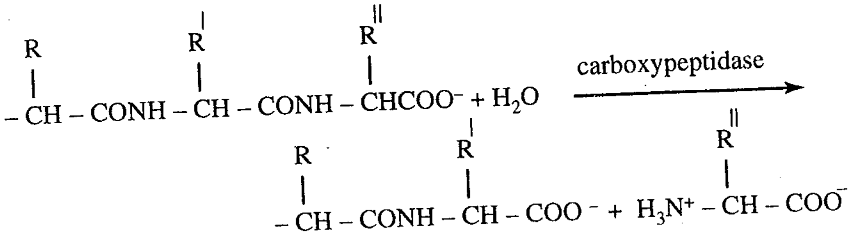
CYANO-BACTERIA – NATURE'S CURIOUS CREATURES

- The photosynthetic, nitrogen-fixing cyano-bacteria are among the most self-sufficient of organisms.
- Their nutritional requirements are the simplest of any living species, needing only nitrogen, carbon dioxide, a few minerals and water.
- They can colonize bare areas of rock and soil because of their nutritional independence.
- It is surmised that these bacteria were the first colonizers of land in the early period of biological evolution on earth.
- The metal chelate structure in them plays a vital role in the functioning of these bacteria.
- Different species of cyano-bacteria have different colours such as blue, golden-yellow, brown, red, emerald-green, violet and blue-black depending on the pigments present in them. The Red Sea is so named because of the dense concentrations of red-pigmented cyano-bacteria that float on its surface.

14.3.3 Metalloenzymes

Some enzyme molecules contain one or more metal ions in each of their molecules. These metal ions do not participate in the biological reaction but form a permanent part of the enzyme. They are bonded at or near the enzyme active site and enhance the activity of the enzyme. In the absence of such metal ions, the enzymes are rendered inactive. Such enzymes incorporated with metal ions in their structures are called *metalloenzymes*. Zn, Cu, Fe, Mn, Mo, etc. are metals found in metalloenzymes.

Carboxypeptidase is one such metalloenzyme. It contains one zinc ion per molecule and its molecular weight is about 34,000. It occurs in the pancreas of mammals and it catalyses the hydrolysis of the peptide bond at the carboxyl end of the peptide chain:



$$-\overset{\overset{\displaystyle R}{|}}{C}H-CONH-\overset{\overset{\displaystyle R'}{|}}{C}H-CONH-\overset{\overset{\displaystyle R''}{|}}{C}HCOO^- + H_2O \xrightarrow{\text{carboxypeptidase}} -\overset{\overset{\displaystyle R}{|}}{C}H-CONH-\overset{\overset{\displaystyle R'}{|}}{C}H-COO^- + H_3N^+-\overset{\overset{\displaystyle R''}{|}}{C}H-COO^-$$

The zinc ion in carboxypeptidase is bound in a distorted tetrahedral shape surrounded with two histidine–nitrogen atoms, one water molecule and one glutamate carboxyl oxygen atom as ligands.

The copper metalloenzymes are generally *oxidases*, i.e., they catalyse oxidations. For example, *cytochrome oxidase*, *ascorbic acid oxidase* and *tyrosinase* are copper-containing oxidising enzymes. Some metalloenzymes are called *nitrogenases*, as they promote the fixation of the atmospheric nitrogen under mild conditions. They are found to contain Mo and Fe. The Mo ion binds with the N_2 molecule and Fe supplies electrons for reducing the molecular nitrogen.

14.4 PHOTOSYNTHESIS

14.4.1 Chlorophyll

Chlorophyll is a magnesium-porphyrin complex. The magnesium is at the centre of the flat heterocyclic porphyrin ring system (Fig.14.7). The metal ion is bonded to four nitrogen atoms. This complex is the green pigment in plants.

There are several kinds of chlorophyll that vary slightly in their molecular structure. In plants, chlorophyll *a* is the pigment directly responsible for the transformation of light energy to chemical energy. Most photosynthetic cells contain a second type of chlorophyll also; in plants, it is chlorophyll *b*. This is able to absorb light at wavelengths different from those absorbed by chlorophyll *a*, and pass the energy on to chlorophyll *a*, thus extending the range of light available for photosynthesis.

Chlorophyll *a* is a large molecule with a central atom of magnesium attached to a porphyrin ring. An hydrophobic long carbon-hydrogen chain, attached to the ring, helps anchor the molecule in the internal membranes of chloroplast. Chlorophyll *b* differs from chlorophyll *a* in having an aldehyde (CHO) group in place of the CH_3 group (indicated by a circle in the figure). Chlorophyll can convert light energy into chemical energy only when it is associated with certain proteins and embedded in a specialised membrane. Photosynthesis requires, in addition to chlorophyll, the help of four other metal complexes, a manganese complex, two iron complexes (cytochromes and ferredoxins) and a copper complex (plastocyanin).

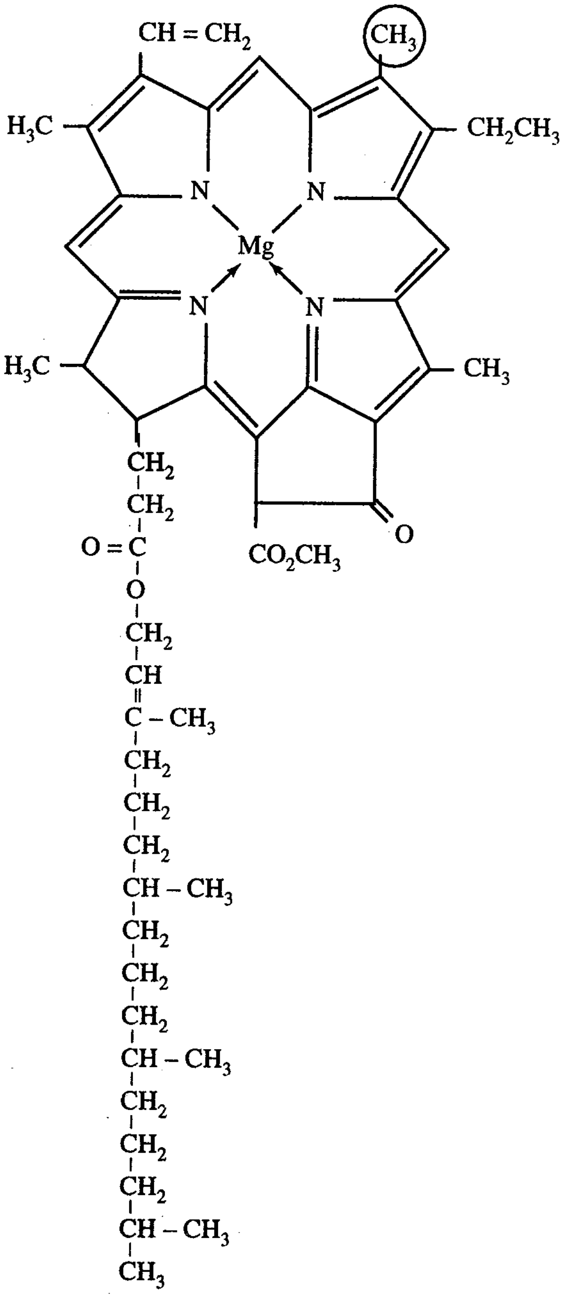


Fig. 14.7 Structure of chlorophyll

(Chlorophyll *a* is a large molecule with a central atom of magnesium held in a porphyrin ring. Attached to the ring is a long, hydrophobic carbon-hydrogen chain that may help to anchor the molecule in the internal membranes of the chloroplast.)

Chlorophyll *b* differs from chlorophyll *a* in having an aldehyde (CHO) group in place of the CH_3 group.

(i) Chlorophyll absorbs light in the red region (near 700 nm) from the sunlight and supplies the absorbed energy for photosynthesis; in this synthesis, CO_2 is converted into sugars.

$$x\,CO_2 + y\,H_2O \xrightarrow[\text{sunlight}]{\text{chlorophyll}} \underset{\text{carbohydrate}}{C_x(H_2O)_y} + x\,O_2$$

CO_2 is "fixed" and oxygen is a by-product in this process. Photosynthesis occurs not only in higher plants but also in algae and certain bacteria. It involves the conversion of light energy into chemical energy.

(ii) Many individual enzyme-catalysed reactions occur in photosynthesis. The process begins with the absorption of light by chlorophyll. The green colour of chlorophyll and, therefore, its capacity to absorb sunlight in the visible region, is primarily due to its extended conjugated system. Chlorophyll traps photons of sunlight and supplies these to the plant cells to reduce carbon dioxide to carbohydrates and to oxidise water to oxygen.

(iii) Magnesium in it makes the molecule rigid so that the energy absorbed is not lost thermally through molecular vibrations. In addition, it enhances the rate at which the short-lived excited state initially formed by photon absorption is transformed into the corresponding triplet state; the triplet state has a longer lifetime and therefore can transfer its excitation energy into the redox chain.

(iv) Photosynthesis involves a series of redox reactions. At the initial stage of the electron-transfer sequence, a manganese complex undergoes reversible redox reaction. At other stages, iron-containing cytochromes and ferredoxins, and copper-containing plastocyanin participate in redox reactions. The chain of these redox processes ultimately releases molecular oxygen.

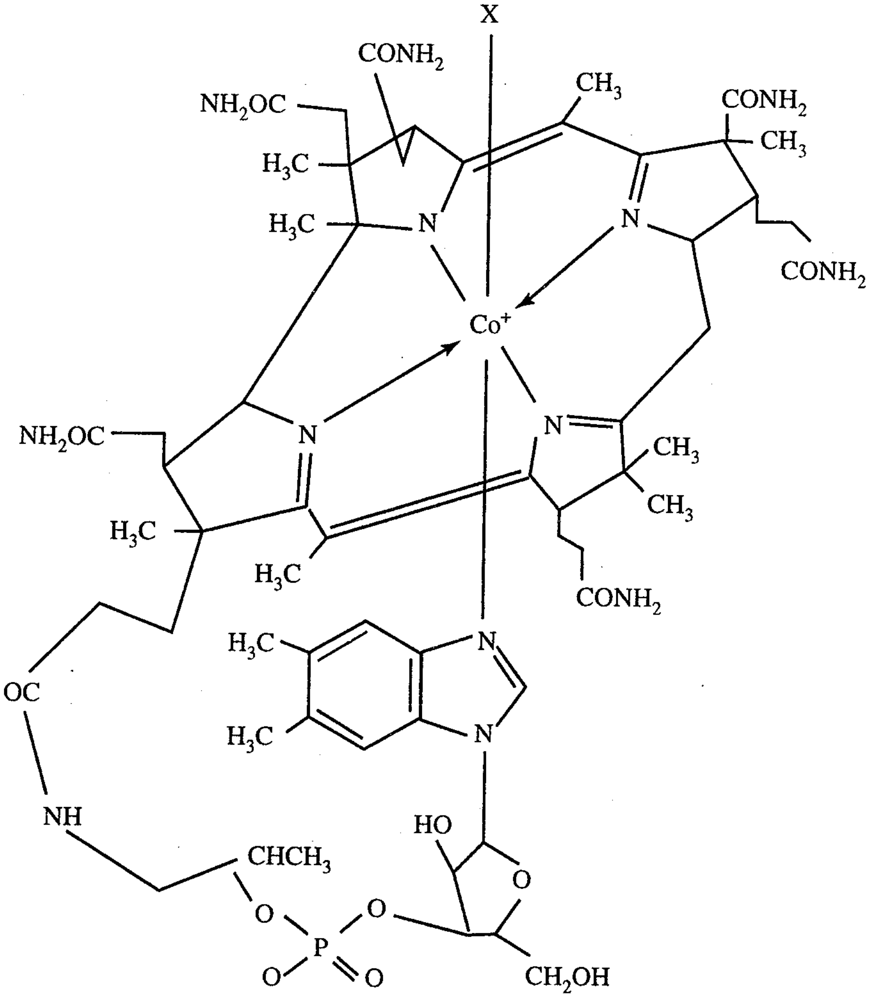
> The structure of chlorophyll-*a* was established by H.Fischer, R.Willstater and J.B. Conant. R.B. Woodward first synthesised chlorophyll from simple organic molecules in 1960. He was awarded the Nobel Prize in 1965 for his excellent contribution to synthetic organic chemistry.

14.5 VITAMIN B_{12} (CYANOCOBALAMIN)

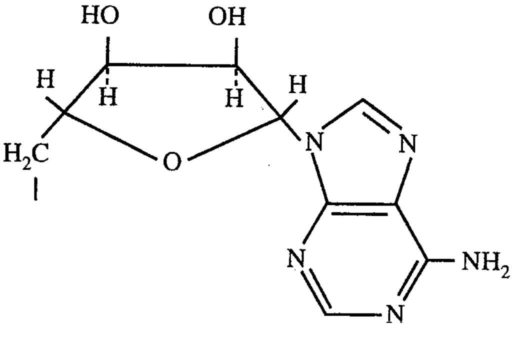
Vitamin B_{12} is a cobalt complex (Fig.14.8). It is a coenzyme and occurs in liver. It is tightly bound to several enzymes in the body. It was isolated from liver extract in 1948. In 1965, Dorothy Hodgkin (Nobel Laureate) determined its structure crystallographically.

The following are the important structural features of this vitamin:

1. The cobalt in it exists as Co(III).
2. Cobalt is located at the centre of a macrocyclic ring called corrin ring; this ring resembles the porphine ring. However, this ring is not conjugated like the porphyrin ring.
3. In addition, a complex organic portion consisting of a sugar, a phosphate group and an organic base are bonded in the molecule.



(*a*) *The structure of cobalamin*



(*b*) *The ligand 5'deoxyadenosyl group*

Fig. 14.8

4. Co(III) is octahedrally bonded by four N atoms of the corrin group, the organic base and the sixth ligand X. Vitamin B_{12} is cyanocobalamin, X being CN^-. Normally, X is H_2O.
5. Cobalamin refers to the structure without the ligand X.

$X = CN^-$: cyanocobalamin
$X = H_2O$: aquacobalamin
$X = CH_3$: methylcobalamin
X = 5'-deoxyadenosyl : coenzyme B_{12}.

Vitamin B_{12} is cyanocobalamin.

The exact role of vitamin B_{12} in the cell processes is not clear; however, it can act only in concert with a number of enzymes. The B_{12} coenzymes function in concert with a number of enzymes to effect several biological reactions. One such reaction is dehydration of diols by *dioldehydrases* assisted by a B_{12} coenzyme.

$$RCHOHCH_2OH \rightarrow RCH_2CHO + H_2O \quad (R = CH_3 \text{ or } H)$$

It is of critical importance in the metabolisms of carbohydrates, fats and proteins. In humans, deficiency of vitamin B_{12} causes pernicious anaemia. Methylcobalamin ($X = CH_3$) is responsible for the environmental conversion of Hg(II) to toxic CH_3Hg^+ through methane-producing bacteria. Similarly, it can transfer methyl groups to Tl(III), Pt(II) and Au(I).

14.5.1 Non-enzymic Chemistry of B_{12} Coenzymes

With a view to understanding the roles of these in biological systems, these complexes were studied in isolation (*in vivo*).

(i) The cobalamines undergo reduction in neutral or alkaline medium to give Co(II) and Co(I) species, called B_{12r} and B_{12s} respectively. B_{12s} is a powerful reducing agent; it reduces water to H_2 and forms B_{12r}.

(ii) When the cyano- or hydroxocobalamin is reduced, the ligand CN^- or OH^- is lost forming a 5-coordinate Co(I) complex. This product reacts with adenosine triphosphate in presence of a suitable enzyme to form the B_{12} coenzyme.

(iii) B_{12s} reacts with acetylene to form $Cb-CH=CH_2$, where Cb denotes the cobalamine group.

$$B_{12s} + CH \equiv CH \rightarrow Cb-CH=CH_2$$

(iv) B_{12s}, on treatment with BrCN affords cyanocobalamin:

$$B_{12s} + BrCN \rightarrow CN-Cb^+Br^-$$

14.6 IRON INVENTORY IN THE HUMAN BODY

Iron is present in the human body in several types of molecules (Table 14.1). Most of these molecules are chelates of iron. These chelates play vital roles in several physiological processes in the body cells.

Table 14.1 Iron-containing compounds of the human body

Compound	Physiological role
Haemoglobin	Oxygen transport
Myoglobin	Oxygen transport
Ferritin	Iron storage
Haemosiderin	Iron storage
Transferrin	Iron transport
Catalase	Iron transport
Peroxidase	Anti-microbial
Cytochromes	Electron transfer
Aconitase	Enzyme action
Aldehyde oxidase	Enzyme action
Xanthine oxidase	Enzyme action

14.6.1 Iron Storage in Human Body

The formation of erythrocytes (red blood cells) is called *erythropoiesis*. Every twenty four hours about 2×10^{11} of these cells are replaced by the red bone marrow. When the iron after digestion of food enters the plasma, it is attached to the specific iron binding protein transferrin, a β-globulin. This protein transports iron to and from various compartments, for example, from gut to bone marrow and from destroyed red cells back to the bone marrow. The iron binding capacity of transferrin is 300 μg/ 100 ml.

Iron which is not used for erythropoiesis is stored in the liver and reticuloendothelial cells. It constitutes a reserve, which may be used when there is an increased iron need, say after blood loss. Storage iron consists of *ferritin* and *haemosiderin*. Ferritin is a water soluble crystalline protein; it has 26 per cent of iron by mass. Haemosiderin consists of iron-rich water soluble granules.

EXERCISES

*1. Explain why *d*-metals such as Mn, Fe, Co and Cu are involved in redox enzymes in preference to Zn, Al and Ca?
*2. List the role of Fe, Mn, Mo and Zn in biological processes.
*3. How do Fe and Mg differ in their physiological roles?
4. Explain the relative affinity of O_2 for haemoglobin and myoglobin.
5. Outline how CO poisoning of the human system occurs.
6. Explain the characteristics of *nitrogenase* enzymes.

ANSWERS

1. The redox reactions in cells are catalysed by enzymes involved in cyclic oxidation and reduction of the metal ion; for example, in cytochromes cyclic transfer occurs with Fe [Fe(II) $\rightleftharpoons$ Fe(III)]. Such a cyclic process requires the ability for the metal to have at least two oxidation states. Fe, Mn, Co and Cu have this ability and therefore these metals are involved in redox enzymes. Zn, Al and Ca can have only stable oxidation state each and therefore they cannot be involved in physiological redox processes in living cells.

2. Fe : oxygen transport (haemoglobin and haemerythrin)
 : oxygen storage in tissue (myoglobin)
 : electron transfer (cytochromes, rubredoxin, ferredoxins)
 : oxygenation of hydrocarbons (cytochrome P-450)
Mn : oxidation of water to oxygen (photosystem II)
Mo : reduction of N_2 to NH_3 or nitrogen fixation (*nitrogenase*)
Cu : oxygen transport (haemocyanin)
electron transfer (blue copper proteins)
Zn : CO_2 to HCO_3^- conversion (*carbonic anhydrase*)
hydrolysis of peptide linkages (*carboxypeptidase*)
decarboxylation of oxaloacetic acid (*oxaloacetate decarboxylase*)

3. Fe, with its ability to exist in two stable oxidation states (Fe^{2+} and Fe^{3+}), helps redox reactions in physiological processes. For example, in a cytochrome Fe(II) is the source of an electron, as it changes its oxidation state to Fe(III). Such a role cannot be played by Mg as it is incapable of existing in more than one oxidation state. It is involved in the spatial orientation of the chlorophyll molecule relative to the other parts of the reaction centre, a necessity for reaction.

Chapter 15

Applications of Coordination Compounds

Coordination compounds are used in several areas of chemistry such as analytical chemistry, medicinal chemistry, industrial chemistry and agriculture.

15.1 METAL COMPLEXES IN ANALYTICAL CHEMISTRY

15.1.1 Inorganic Qualitative Analysis

Several principles of coordination chemistry are used in inorganic qualitative analysis. The formation of metal complexes is employed in the separation and identification of some of the metals.

Separation The principle of masking (sequesteration) is used in separating some metals from each other in qualitative analysis. For example, both Cu^{2+} and Cd^{2+} form insoluble sulphides in the II Group. These two metals are separated by complexing them with CN^-. Both form complexes but with a difference:

$$2\,CuS + 8\,CN^- \longrightarrow 2[Cu(CN)_4]^{3-} + S_2^{2-}$$

$$CdS + 4\,CN^- \longrightarrow [Cd(CN)_4]^{2-} + S^{2-}$$

The reaction of CN^- with CuS is an oxidation-reduction reaction coupled with complexation; Cu^{2+} is reduced to Cu^+ and then the latter is complexed to form soluble species. This complex species has high stability and therefore it does not form the sulphide of copper with H_2S. With Cd^{2+}, the reaction is only complexation and the colourless species $[Cd(CN)_4]^{2-}$ is not as stable as the copper complex and therefore it forms CdS on passing H_2S through its solution. Thus, the marked difference in the stabilities of the copper and cadmium cyano complexes is the basis for separating these two metals.

Reductive complexation When a ligand reduces a metal and then complexes the reduced metal ion, then that process is called *reductive complexation*. On adding KCN to aqueous copper sulphate, first Cu^{2+} is reduced and cuprous cyanide is formed. This reacts with excess CN^- to form a soluble species $[Cu(CN)_4]^{3-}$.

$$2Cu^{2+} + 4CN^- \longrightarrow 2CuCN + (CN)_2 \text{ cyanogen}$$
$$CuCN + 3CN^- \longrightarrow [Cu(CN)_4]^{3-}$$

$[Cu(CN)_4]^{3-}$ has a tetrahedral shape. The formation of stable $[Cu(CN)_4]^{3-}$ promotes the reduction of Cu^{2+} to Cu^+ by the cyanide ions.

Identification of metals Complex formation is used to identify several metals in qualitative analysis. The bright colours of the metal complexes render the process of identifying some metals easy and unequivocal. In some cases, the coloured complexes are insoluble in water; in some other cases, they dissolve in water and produce coloured solutions. The use of complex formation (spot tests) for confirming the presence of metals in qualitative analysis is summarised in Table 15.1.

Table 15.1 Complex formation in qualitative analysis

Metal ion	Complexing agent	Colour of the product	Formula
Ag^+	rhodamine	violet	–
Hg^+	dithizone	brick-red	–
Pb^{2+}	dithizone	brick-red precipitate	$Pb[Sc(NHC_6H_5)_2]_2$
Tl^+	sodium hexanitro-cobaltate (III)	red	$Tl_3[Co(NO_2)_6]$
Cu^{2+}	ammonia solution	deep blue solution	$[Cu(NH_3)_4]^{2+}$
Bi^{3+}	iodide	orange	$[BiI_4]^-$
Sb^{3+}	rhodamine	violet	–
Cu^{2+}	potassium hexacyanoferrate(II)	reddish-brown precipitate	$Cu_2[Fe(CN)_6]$
Fe^{2+}	potassium hexacyanoferrate(II)	white	$K_2Fe[Fe(CN)_6]$
Fe^{2+}	1,10-phenanthroline	red	$[Fe(o-phen)_3]^{2+}$
Fe^{2+}	potassium hexacyanoferrate(III)	dark-blue precipitate	$Fe_4[Fe(CN)_6]_3$ Turnbull's blue
Fe^{3+}	ammonium thiocyanate	deep-red solution	$Fe(SCN)_3$
Fe^{3+}	potassium hexacyanoferrate(II)	intense-blue precipitate	$Fe_4[Fe(CN)_6]_3$ Prussian blue
Fe^{3+}	cupferron	brown	$Fe[C_6H_5N(NO)O]_3$
Al^{3+}	alizarin-S	red lake	–
Al^{3+}	aluminon	red	–
Cr^{3+}	diphenylcarbazide	violet colouration	–
Co^{2+}	ammonium thiocyanate	blue colour	$[Co(SCN)_4]^{2-}$ Vogel reaction
Co^{2+}	potassium nitrite	yellow	$K_3[Co(NO_2)_6]$
Ni^{2+}	dimethylglyoxime	red precipitate	–
Zn^{2+}	potassium hexacyanoferrate(II)	white precipitate	$K_2Zn_3[Fe(CN)_6]_2$
Zn^{2+}	oxine	yellow	
Mg^{2+}	oxine	yellow precipitate	$Mg(C_9H_6ON)_2 4H_2C$
Mg^{2+}	quinalizarin	blue precipitate or colouration	–
Te^{4+}	iodide	red	$[TeI_6]^{2-}$
V^{5+}	hydrogen peroxide	red	–
Be^{2+}	quinalizarin	blue	–
Ti^{4+}	hydrogen peroxide	yellow	–

THE 'BROWN RING' TEST

In the test for a nitrate, the brown ring is constituted by a complex of iron. The formula of this brown complex is $[Fe(H_2O)_5NO]^{2+}$. The colour of the complex arises due to charge transfer. The complex is constituted by Fe(I) and NO^+

15.1.2 Complexometric Titrations

Certain metal ions react stoichiometrically (quantitatively) with certain ligand solutions and form stable metal complexes. For example Ag^+ reacts with CN^- quantitatively forming a stable, soluble complex ion.

$$Ag^+ + 2CN^- \longrightarrow [Ag(CN)_2]^-$$

This reaction can be used in volumetric estimation of Ag^+[CN^- (aq) is titrated with Ag^+(aq)]. As long as there is unreacted CN^- in the solution the contents of the reaction mixture remain clear. This is because the product is soluble. Immediately after the end point, the excess of Ag^+ added reacts with $[Ag(CN)_2]^-$ to form an insoluble product $Ag[Ag(CN)_2]$. This produces a turbidity in the reaction medium. Therefore, the appearance of turbidity signals the end point of the reaction. This titration is called as a *complexometric titration*.

A complexometric titration involves a metal ion and a ligand which react quantitatively to form a complex species.

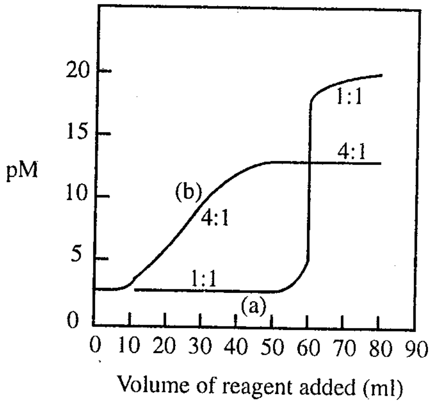
Chelates in complexometric titration The use of a chelating ligand instead of a monodentate ligand in a titration has the following advantages:

1. The formation of the product between the metal ion and the chelating ligand is usually a single-step process.
2. Chelates are much more stable than the complexes formed by monodentate ligands; therefore, the end points with chelating reactions are located precisely.
3. Polydentate ligands have high molecular weights and therefore, there is no compulsion of using very small quantities of the chelants(titrants). Using very small quantities of titrants requires expensive balance and more skill to avoid error in analysis.

To understand the advantage of employing a chelate, consider a metal ion M (charge ignored) reacting with a quadridentate ligand L:

$$M + L \longrightarrow ML$$

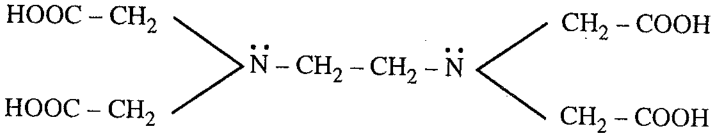
As the ligand solution is added to the metal ion solution, the concentration of the free metal ion in solution decreases. ($-\log[M] = pM$, which increases). The titration curve for this reaction is drawn by plotting pM values against [L] (Fig. 15.1). The equivalence point is indicated by a sharp change in the pattern of the curve; as the metal and the ligand combine in 1:1 ratio, the addition of even an extremely small excess of the ligand beyond the equivalence point produces a drastic change in the curve pattern. In this case, the change in the pM value at the equivalence point is large. When the metal (M) and an unidentate ligand (X) combine in 1:4 ratio (giving MX_4), this advantage of sharp change in pM is lost, because the change in the pM value at the equivalence point is not large. Then, the end point for the titration is not sharp.



(*a*) $M + L \rightarrow ML$; (quadridendate) (*b*) $M + 4X \rightarrow MX_4$; (monodendate)

Fig. 15.1 *Complexometric titration curves*

Titrations with ethylenediaminetetraacetic acid Ethylenediaminetetraacetic acid (EDTA) is a versatile ligand which reacts with several metal ions. It is a tetraprotic acid and for simplicity it can be denoted as H_4Y.



The ion Y^{4-} forms very stable one-to-one complexes with metals. A single ligand molecule coordinates through its several positions around a central metal ion and therefore only one-to-one metal-to-ligand complex is formed. This one-step complexation eliminates the problem encountered in the stepwise reactions involved between a metal and monodentate ligands wherein some steps may be slow and the others fast. The end point of the titration also would not be sharp in such a reaction. The metal-EDTA complex is a chelate and has five-membered rings in its structure. In such a five-membered ring, all the five atoms in the ring lie in a plane and this gives extra stability to the complex.

The reaction between the metal ion (M^{n+}) and EDTA may be written as

$$M^{n+} + Y^{4-} \longrightarrow M^{n-4}$$

Some of the metal ions which form stable EDTA complexes and which can be titrated with EDTA are listed in Table 15.2.

Table 15.2 Stability constants of metal-EDTA complexes

Metal ion	log K (25°C)	Metal ion	log K (25°C)
Al^{3+}	16.1	Fe^{3+}	25.1
Cd^{2+}	16.5	Mg^{2+}	8.69
Ca^{2+}	10.7	Ni^{2+}	18.6
Co^{2+}	16.3	Zn^{2+}	16.5
Cu^{2+}	18.8	Ag^{+}	7.30
Fe^{2+}	14.3		

The equilibrium constant K for the formation of several metal-EDTA complexes are very high and therefore such metals can be conveniently titrated with EDTA (Actually, the disodium salt of EDTA is used as the titrant because EDTA itself is not appreciably soluble in water). These titrations are performed in neutral or alkaline solution. In acidic solution, the complexes decompose. The end points in these titrations are signalled by using a *metallochromic indicator* such as Eriochrome black T or Calmagite.

The determination of water hardness The hardness of water is caused mainly by dissolved calcium and magnesium ions in it. It can be determined by an EDTA titration at the pH of 10.

15.1.3 Complexes in Colourimetry

Some of the metals can be colourimetrically estimated by forming their coloured complex species in solution, mostly aqueous solution. For adopting this method, the following conditions have to be satisfied:

(i) The metal ion should form a water-soluble coloured complex.
(ii) The complex species should have sufficient stability to impart a stable colour shade during the estimation.
(iii) The complex in solution should obey the Beer-Lambert law over a sufficient range of its concentration, especially for visual colourimetry.

Table 15.3 lists some information on such colourimetric estimations.

Table 15.3 Complexes in colourimetry

Metal ion estimated	Reagent	Colour of complex
Fe^{3+}	SCN^-	red
Ni^{2+}	DMG	rosy red
Cu^{2+}	NH_4OH	blue
Fe^{2+}	1,10-phenanthroline	red
Al^{3+}	aluminon	red
Bi^{3+}	thiourea	yellow
Ag^+	dithizone	yellow
$Cr_2O_7^{2-}$	s-diphenylcarbazide	violet
Ti^{4+}	H_2O_2	orange-red
V^{5+}	H_2O_2 / NaOH	yellow

15.1.4 Coordination Compounds in Gravimetry

The formation of a coordination compound serves as an excellent means for gravimetrically estimating certain metals, (Table 15.4). The ligand used for such estimations can be inorganic (as in the estimation of platinum with Cl^-, forming $Ag_2[PtCl_6]$) or organic (as in the estimation of nickel with DMG). However, complexing the metal with an organic ligand (*precipitant*) has certain advantages, especially when the product is a chelate:

1. The precipitate with an organic ligand is covalent and therefore highly insoluble in water; this insolubility renders the separation of the metal ion from the medium quantitative.

2. The precipitate has a high formula weight relative to the metal ion being separated, so that even a small weight of the metal being estimated gives a large precipitate weight. This imparts high accuracy to the estimation.
3. The metal-organic complex has large particle size (low density) and therefore is easily filtered and washed.
4. Organic precipitates are more easily dried than inorganic precipitates because of their lesser tendency to hold water.

The use of metal-organic ligand complexes in gravimetry is summarised in Table 15.4.

Table 15.4 Some metal complexes in gravimetry

Metal ion estimated	Complexing agent	Formula
Ni^{2+}	DMG	$Ni(C_4H_7O_2N_2)_2$
Mg^{2+}	oxine	$Mg(C_9H_6ON)_2$
Cu^{2+}	anthranilic acid	$Cu(C_7H_6O_2N)_2$
Cu^{2+}	cupferron	$Cu[C_6H_5N(NO)O]_2$
Cu^{2+}	salicylaldoxime	$Cu(C_7H_6O_2N)_2$
Cu^{2+}	quinaldic acid	$Cu(C_{10}H_6NO_2)_2\ H_2O$
Fe^{3+}	cupferron	$Fe[C_6H_5N(NO)O]_3$

15.1.5 Stabilisation of Oxidation States

Cobalt exists in two oxidation states, Co(II), and Co(III); of these Co(III) is unstable in aqueous medium. It is a strong oxidising agent, oxidising even water to O_2. This behaviour of Co(III) can be explained based on the standard electrode potential for the reduction of Co(III) to Co(II).

$$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq) \quad E° = +1.82V$$

The potential has a large positive value indicating the instability of Co^{3+} in aqueous medium. However, the stability of this is greatly increased by complexing it with certain ligands, say, NH_3.

$$[Co(NH_3)_6]^{3+} + e^- \longrightarrow [Co(NH_3)_6]^{2+} \quad E = 0.10V$$

The Co(III)- NH_3 complex has high stability ($K_f = 4.5 \times 10^{23}$) and it is stable in aqueous solution. This complex, because of its high stability, does not ionise in aqueous solution avoiding the formation of free Co^{3+} ions. Thus, complexation stabilises an oxidation state of a metal which is otherwise unstable.

Cr(II) is another example for stabilisation of an oxidation state by complexation. This oxidation state is unstable and easily oxidised by molecular oxygen.

$$Cr^{2+} \longrightarrow Cr^{3+} + e^- \quad E° = +0.41V$$

But it gets stabilised on complexing it with NH_3

$$\underset{\text{Unstable}}{Cr^{2+}} + 6NH_3 \longrightarrow \underset{\text{Stable}}{[Cr(NH_3)_6]^{2+}}$$

More examples of stabilisation of unusual oxidation states of some metals are listed in Table 15.5.

Table 15.5 Stabilisation of unusual oxidation states by complexation

Metal	Unusual oxidation state	Stabilised in the complex
V	0	$[V(CO)_6]$
V	–1	$[V(CO)_6]^-$
V	+1	$[V(o\text{-}phen)_3]^+$
Cr	0	$[Cr(CO)_6]$
Mo	0	$[Mo(CO)_5I]^-$
Mn	+1	$[Mn(R-CN)_6]^+$
Fe	0	$[Fe(CO)_4(PPh_3)]$
Fe	0	$[Fe(CO)_5]$
Co	0	$[CO(CO)_3(NO)]$
Ni	0	$[Ni(CN)_4]^{4-}$
Ni	0	$[Ni(PF_3)_4]$

15.1.6 Complexes in Separation of Metals

Some chelating agents are used for separating certain metallic mixtures. For example, the separation of Zr and Hf remained difficult until a method using the chelate theonyltrifluoroacetone was evolved. The chelates of these two metals with this ligand possess different solubilities in benzene. The distribution coefficient for the Zr chelate / Hf chelate in benzene is 20 / 1 (The Zr chelate, unlike the Hf chelate is thus highly soluble in benzene). Therefore, the separation of these two using chelation is now very easy.

15.2 METAL COMPLEXES IN MEDICINAL CHEMISTRY

15.2.1 Complexation in Food Poisoning

Lead is a poison to the human system. It can cause brain damage called *encephalopathy*. This disease can produce convulsion, coma, blindness, mental retardation or death. A person who has ingested lead is fed with $[Ca(EDTA)]^{2-}$. It reacts with Pb^{2+} in the victim to form $[Pb(EDTA)]^{2-}$.

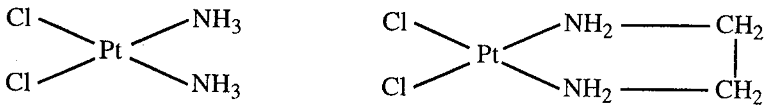
$$Pb^{2+} + [Ca(EDTA)]^{2-} \longrightarrow [Pb(EDTA)]^{2-} + Ca^{2+}$$

The complexed lead is excreted by the human body saving the victim from poisoning. The lead-EDTA complex is much more stable than the Ca-EDTA complex and therefore Pb^{2+} ions in the body are readily trapped by EDTA. Victims who have ingested radioactive metals are treated with EDTA for detoxification. This chelant helps quick elimination of the hazardous radioactive metals from the body.

Some of the enzymes in the human system have cysteine unit, $HOOC-CH(NH_2)-CH_2-SH$. The lead forms covalent bonds with the sulfhydryl (SH) group of cysteine and inhibits enzyme actions; this is the basis for lead poisoning. EDTA binds the lead atoms more strongly than cysteine does and consequently releases the enzyme for its normal physiological action.

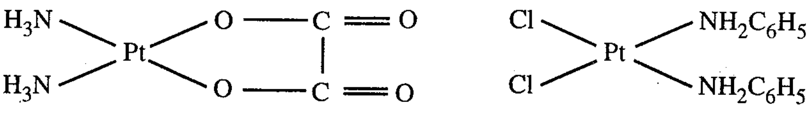
15.2.2 Metal Complexes in Therapy

Tumour therapy Some coordination compounds of platinum inhibit the growth of cancerous cells. Therefore these compounds are used in cancer therapy. The structures of these antitumour complexes are represented in Fig. 15.2.



(**a**) cis-diamminedichloroplatinum(II)

(**b**) cis-ethylenediaminedichloroplatinum(II)



(**c**) Oxalatodiammineplatinum(II)

(**d**) dichlorodiphenylamineplatinum(II)

Fig. 15.2 Anti-tumour platinum complexes

All these complexes have a common feature, namely, the cis arrangement of identical ligands. The trans isomers of these complexes do not have curative property. Therefore, the conclusion that chelation is involved in the mode of action of the antitumour agent with the cancer cells may be drawn. Probably, the two cis groups in the drug molecule are replaced by some other groups in the cancer cell, forming an association between the drug molecule and a species in the cancerous cell. Such an association may be the starting point for destroying cancerous cells. The replacement of the groups in the trans position by a chelating agent is not easy, and that is why the trans isomer of any of these complexes has no potency as a drug.

15.3 METAL COMPLEXES IN INDUSTRIAL PROCESSES

Several metal complexes are used in chemical industries as reactants, catalysts, and sequestering agents. Some examples are given below.

15.3.1 Heavy Metals-protein Complexes in the Raschig Process

This process is used for manufacturing hydrazine by reacting Cl_2, NaOH and NH_3:

$$2NaOH\,(aq) + Cl_2 + 2NH_3 \longrightarrow N_2H_4\,(aq) + 2NaCl\,(aq) + 2H_2O$$

The reaction involves the intermediate chloramine (NH_2Cl). This takes part in a side reaction,

$$2NH_2Cl\,(aq) + N_2H_4\,(aq) \xrightarrow{M^{2+}} 2NH_4Cl\,(aq) + N_2\,(g)$$

This side reaction decreases the yield of N_2H_4. It is catalysed by heavy metal ions such as Cu^{2+}

The raw material used in this process and water are usually contaminated with traces of such heavy metals; removing these metals from the raw materials is expensive. To solve this problem, a small amount of a protein (gelatin, albumin or glue) is added to the reaction mixture. The protein molecule strongly bonds with the Cu^{2+} ions rendering it ineffective in catalysing the side reaction; the Cu^{2+} ions are "masked".

15.3.2 The Ziegler-Natta Catalyst

The development of a catalyst for the low-pressure polymerisation of ethylene to polyethylene was a dramatic progress in the field of plastics. This polymerisation process has rendered the use of polythene products a common consumer practice at home and other places. The catalyst used in this polymerisation is a complex of the metals aluminium and titanium; this was developed by K.Ziegler of the Max Planck Institute, in Germany, and G.Natta of the University of Milan, in Italy. They were awarded the 1963 Nobel Prize in Chemistry for the formulation of this catalyst. Before the invention of the Ziegler-Natta catalyst, the polymerisation of ethylene required high pressure, which is an expensive reaction condition. In addition, the product polythene was less crystalline and had low melting point compared to the one formed with this catalyst.

This catalyst is prepared from titanium tetrachlorade ($TiCl_4$) and a trialkyl aluminium (R_3Al), say Et_3Al.

$$n\ CH_2 = CH_2 \xrightarrow[\text{ambient temp}]{\substack{\text{Ziegler-Natta catalyst} \\ \text{one atmosphere pressure}}} (C_2H_4)_n$$

15.3.3 Metal Complexes in Alkene Conversions

The conversions of alkenes to important products with metal complexes as catalysts are industrially vital processes. These are outlined below.

Hydroformylation or oxo reaction

$$R-CH=CH_2 + CO + H_2 \xrightarrow{\substack{CO_2(CO)_8,\ 150°C \\ 100\text{–}400\ \text{atm}}} R-CH_2-CH_2-CHO$$

Carboxylation reaction

$$R-CH=CH_2 + CO + ROH \xrightarrow{\substack{Ni(CO)_4, \\ 250°C,\ 200\ \text{atm}}} R-CH_2-CH_2-COOR$$

Hydrogenation reaction

$$R-CH=CH_2 + H_2 \xrightarrow[25°C, 1\,\text{atm}]{(Ph_3P)_3RhCl} R-CH_2-CH_3$$

$(Ph_3P)_3RhCl$ is called *Wilkinson's catalyst.*

Isomerisation reaction

$$CH_3-CH_2-CH=CH_2 \xrightarrow{Rh(CO)_2Cl_2, HCl} CH_3-CH=CH-CH_3$$

15.3.4 Complexation and Electroplating

Copper is usually electroplated on an object from a solution containing CN^-. In this electroplating, the object to be plated is made the cathode and a rod of copper metal is the anode. During electrolysis, the following reactions occur:

$$\text{Anode:} \quad Cu + 4CN^- \longrightarrow [Cu(CN)_4]^{3-} + e^-$$

$$\text{Cathode:} \quad [Cu(CN)_4]^{3-} + e^- \longrightarrow Cu + 4CN^-$$

The metal ion is transferred from the anode to the cathode; this transfer occurs through the formation, migration and decomposition of tetracynocuprate(I) complex ion. This mode of electroplating produces a smooth, tough and bright deposit on the object. In this electrolysis, one mole of Cu is obtained per faraday, as the reaction involves one-electron transfer. When the electroplating is done from Cu^{2+} solution, only ½ mole of Cu will be obtained per faraday, as it involves a two-electron transfer.

15.3.5 Complexation in Metallurgy

The ability of metals to form complexes is employed in extracting some metals from their ores.

Extraction of silver The MacArthur – Forrest Process

In the cyanide process of extracting silver, the formation of a complex silver cyanide is used. The metallurgical process can be denoted by the following equations:

$$\underset{\text{(Argentite)}}{2Ag_2S} + 8CN^- + O_2 + 2H_2O \longrightarrow 4[Ag(CN)_2]^- + 2S + 4OH^-$$

$$2[Ag(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2Ag$$

Extraction of gold The extraction of gold from its ore involves a process similar to the one considered for silver. The metallurgy of gold using CN^- can be denoted by the following equations:

$$4\,Au(s) + 8CN^-(aq) + O_2(g) + 2H_2O(l) \longrightarrow$$
$$4\,[Au(CN)_2]^-(aq) + 4OH^-(aq)$$

The soluble gold complex is easily separated from the insoluble materials of the ore. Then it is reduced with Zn to obtain gold.

$$2[Au(CN)_2]^-(aq) + Zn(s) \longrightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s)$$

As silver and gold usually occur only in small quantities in their ores, the cyanide process makes their extraction easy, which otherwise would have been difficult.

The dissolution of gold in aqua regia Gold is not reacted by common acids; however, it is reacted by aqua regia ($3HCl$ + HNO_3). The dissolution of a metal in an acid is determined by the ability of the acid to oxidise the metal. Gold being unreactive (a noble metal), it is not oxidised by even strong acids. Aqua regia promotes the complexation of Au(III) to $AuCl_4^-$ thereby aiding the dissolution of gold in it.

$$Au \xrightarrow{HNO_3} Au^+ \xrightarrow{HNO_3} Au^{3+} \xrightarrow{Cl^-} [AuCl_4]^-$$

COPPER METAL DISSOLVES IN AQUEOUS POTASSIUM CYANIDE

This unique process is attributed to complexation of copper to $[Cu(CN)_4]^{3-}$. This complex is extremely stable and this reduces the oxidation potential for the Cu(o)/Cu(I) couple. Consequently, in presence of CN^-, water itself oxidises copper forming Cu(II) and H_2. Then Cu(II) forms $[Cu(CN)_4]^{3-}$:

$$2\,Cu^{2+}(aq) + 4\,CN^-\,(aq) = 2\,CuCN\,(s) + (CN)_2$$

$$Cu\,CN\,(s) + 3\,CN^- = [Cu(CN)_4]^{3-}\,(aq)$$

Similarly, metallic copper dissolves in NH_3 (l);the oxidation potentials favour this process:

$$Cu\,(s) + NH_3\,(l) \xrightarrow{-0.12\ V} \left[\overset{I}{Cu}\,(NH_3)_2\right]^+$$

$$[Cu(NH_3)_2]^+ \xrightarrow[NH_3(l)]{-0.01\ V} \left[\overset{II}{Cu}\,(NH_3)_4\right]^{2+}$$

Purification of nickel by Mond's process In the metallurgy of nickel, the metal is obtained by the reduction of its oxide with carbon. The nickel thus obtained is purified by complexation. It is first converted into volatile $Ni(CO)_4$ by reacting it with CO. Then, the carbonyl product is decomposed thermally to obtain 99.9 percent pure metal.

$$\begin{aligned}
&\text{nickel ore} \longrightarrow NiO\\
&NiO \xrightarrow{C} Ni\,(\text{impure})\\
&\underset{\text{impure}}{Ni} \xrightarrow{CO,\,50°C} [Ni(CO)_4]\\
&[Ni(CO)_4] \xrightarrow{180°C} Ni\,(\text{pure})
\end{aligned}$$

15.3.6 Complexes in Water Softening

The wastage of soap by its reaction with Ca^{2+} and Mg^{2+} in water is prevented by sequestering these ions with complexing agents, such as polyphosphates and polydentate amino acids.

Martell and Calvin divided chelates into two categories: water-soluble chelates and water-insoluble chelates. The former are called sequestering agents which are used in aqueous solutions for masking interfering metals in a system.

15.4 METAL COMPLEXES IN AGRICULTURE

Metals such as iron, copper, zinc, manganese, and molybdenum are essential micronutrients for healthy plant growth. Deficiency in any of these metal nutrients leads to disease in plants. For example, iron deficiency in a plant produces yellow leaves and consequently photosynthesis in the plant is affected. This disease is called *iron chlorosis*. This disease tends to occur in alkaline soil, when Fe(III) present in the soil is converted to insoluble $Fe(OH)_3$, which cannot be transported to the plant cells. Then, the addition of soluble Fe(III)-EDTA complex to the soil eliminates this disease.

In food canning industries, chelating agents are used for food preservation. Traces of metal ions present naturally in fruits, fruit juices, etc. tend to oxidise the food ingredients leading to food spoilage. This is prevented by chelating and stabilising the metal ion oxidants. For example, the oxidant Cu^{2+} can be inactivated by citrate chelate.

Coordination compounds are used in
- Analytical chemistry
- Medical treatment
- Industrial processes
    - Catalysis
    - Metallurgy
    - Water softening
    - Spent nuclear fuel processing
- Agriculture
- Solar energy conversion

EXERCISES

*1. What is the basis of employing ferroin, $[Fe(o\text{-}phen)_3]^{2+}$ as an indicator in redox titrimetry.

*2. Among complexometric titrations, chelatometric titrations are preferred in analytical chemistry; explain.

*3. **Match the following:**

a) Rinmann's green	(i) $Fe_4[Fe(CN)_6]_3$
b) Prussian blue	(ii) $CoAl_2O_4$
c) Thenard's blue	(iii) $[Co(SCN)_4]^{2-}$
d) Vogel's blue	(iv) $CoZnO_4$

*4. **Match the following:**

metal ion	*spot test reagent*	*product colour*
a) Cu(II)	(i) quinalizarin	(A) blue
b) Sb(III)	(ii) cupron	(B) white
c) Al(III)	(iii) quinaldic acid	(C) red
d) Zn(II)	(iv) phosphomolybdic acid	(D) green

5. **Comment on the following:**
   a) The composition and structure of Turnbull's blue and those of Prussian blue are identical.
   b) When Ni(II) in presence of Fe(III) is spotted with DMG, the prior addition of tartrate is necessary.
   c) An aqueous mixture of Fe(II) and Fe(III) can be separated using the dipyridyl ligand.

*6. Write an equation for each of the following:
   a) an excess aqueous potassium cyanide is added to Ni^{2+} (aq).
   b) gold is dissolved in aqua regia.

7. **Match the following:**

a) Mo	(i) vitamin B_{12}
b) Co	(ii) carbonic anhydrase
c) Zn	(iii) nitrogenase

8. **Explain the following:**
   a) Complexes of EDTA with Fe instead of simple iron salts are used in plant foods.
   b) Copper and nickel ions which induce rancidity in canned food items are rendered ineffective with EDTA.
   c) A solid mixture of $Zn(OH)_2$ and $Mg(OH)_2$ can be separated with $NH_3(aq)$.
   d) $CoCl_3$ is unstable in water solution but $[Co(NH_3)_6]Cl_3$ is not.
   e) $ZnCO_3$ but not ZnS is soluble in $NH_3(aq)$.

9. Justify the statement : Organic ligands are preferred over inorganic ligands in gravimetry.

*10. Write the formulae of the complex species involved in each of the following:
   a) The photographic fixing process.
   b) The copperplating of an object in presence of CN^-

11. Which one of the following is not blue?
    a) $[Cu(NH_3)_4]^{2+}$
    b) $[Ni(NH_3)_6]^{2+}$
    c) $[Co(SCN)_4]^{2-}$
    d) $[Co(NO_2)_6]^{3-}$
12. Ammoniacal silver nitrate should always be prepared freshly and never stored in the laboratory; explain.

ANSWERS

1. The complex $[Fe(o\text{-phen})_3]^{2+}$ is intensely coloured. In a redox titration, the addition of excess oxidant immediately after the equivalence point, oxidizes this Fe(II) complex to faintly coloured Fe(III) complex; this change of colour, signals the end point.
2. A complexometric titration involves a reagent (titrant) which complexes the analyte. If the two form a chelate, then the method is called chelatometric titration. A single polydentate ligand (chelant) with *n* donor sites forms a more stable complex than *n* monodentate ligands. In a titration 100% completion of reaction is a necessity, which is achieved easily in one step with a chelant than with a non-chelant. With a chelant, the amount of ligand required to reach the end-point is a simple fraction — 1/1, 1/2, 1/3, etc — of the amount of metal ion present.
3. a) (iv) b) (i) c) (ii) d) (iii)
4. a) ii D
   b) iv A
   c) i C
   d) iii B
6. a) $Ni^{2+} + 2\,CN^- \rightarrow Ni(CN)_2\downarrow \xrightarrow{\text{excess } CN^-} [Ni(CN)_4]^{2-}(aq)$
   b) $Au + 4\,HCl + HNO_3 \rightarrow HAuCl_4$
10. a) $[Ag(S_2O_3)_2]^{3-}$
    b) $[Cu(CN)_4]^{3-}$

Chapter 16 Preparation of Coordination Compounds

The theories of coordination chemistry were developed after the preparation of some coordination compounds. The behaviour of these compounds, which are unique compared to that of the other compounds, stimulated new thinking on structure and bonding and thus new concepts and theories on these compounds were proposed. Therefore, the preparation of coordination compounds is an important aspect of coordination chemistry.

16.1 PURPOSES OF PREPARING COORDINATION COMPOUNDS

1. To understand the route through which these compounds are formed.
2. To obtain pure samples of these compounds and study their physical and chemical properties and structures.
3. To develop industrially useful products.

16.2 PREPARATION AND ISOLATION OF COORDINATION COMPOUNDS

There are no general methods for preparing the coordination compounds; each compound is prepared adopting a method suitable for it. Using proper reactants and adopting favourable experimental conditions to obtain the maximum yield of the product are the key factors for synthesising a coordination compound.

The isolation of the metal complex from the reaction mixture is an art, which can be perfected by practice. Three commonly used methods of isolation are indicated below:

1. The reaction mixture is evaporated to a concentrated solution and then it is cooled in an ice-salt bath. The crystallisation of the complex is promoted by adding a seed crystal of the complex and scratching the inner walls of the container inside the solution.

2. Sometimes, a highly water soluble complex is forced to precipitate by adding an organic solvent, such as alcohol, in which the complex is sparingly soluble.
3. An anionic complex is precipitated easily by the addition of a suitable cation and vice versa.

A complex isolated by any of these methods may be purified by recrystallisation, sublimation or chromatography. The recrystallisation of complexes has to be effected carefully at as low a temperature as possible, as many of them undergo thermal decomposition. The purity of the complex is checked by m.p., conductance, and spectroscopy. Elemental analysis – to find out the percentage composition of the complex – may also be carried out to check the identity of the complex.

16.2.1 Methods of Preparing Complexes

Metal complexes are prepared commonly by the following methods:

Direct reaction between the metal salt and the ligands The reaction between $ZnSO_4(s)$ and $NH_3(l)$ directly produces the complex $[Zn(NH_3)_4]SO_4$.

$$ZnSO_4(s) + 4\,NH_3(l) \longrightarrow [Zn(NH_3)_4]SO_4$$

Substitution reaction in aqueous medium This is a convenient way of preparing a complex; in this reaction, the water ligands are replaced by other ligands.

$$[Cu(H_2O)_6]^{2+} \xrightarrow{NH_3\,(aq)} [Cu(NH_3)_4]^{2+} \xrightarrow{SO_4^{2-}} [Cu(NH_3)_4]SO_4$$

Substitution reaction in non-aqueous solvent A non-aqueous solvent is used if the reactant aquacomplex is too stable to undergo substitution. For example, $[Cr(H_2O)_6]^{3+}$ is very stable; therefore, when attempts are made to convert it to its ethylenediamine complex, only the following reaction occurs:

$$\underset{\text{violet}}{[Cr(H_2O)_6]^{3+}} + 3\,en \xrightarrow{H_2O} \underset{\text{green}}{[Cr(H_2O)_3(OH)_3]}\downarrow + 3\,enH^+$$

However, when the same reaction is repeated in ether, the ethylenediamine complex is obtained;

$$\underset{\text{purple}}{CrCl_3} + 3\,en \xrightarrow{\text{ether}} \underset{\text{yellow}}{[Cr(en)_3]Cl_3}$$

If the reactant ligand is insoluble in water, then also a non-aqueous solvent is employed for the preparation of the complex. For example, the water-insoluble bipyridyl is used as an alcoholic solution in the following synthesis:

$$\underset{\text{colourless}}{[Fe(H_2O)_6]^{2+}} + \underset{\text{in alcohol}}{3\,bipy} \rightarrow \underset{\text{red}}{[Fe(bipy)_3]^{2+}} + 6\,H_2O$$

Thermal decomposition of complexes A solid complex on heating may produce another complex. For example, when pale pink $[Co(H_2O)_6]Cl_2$ is heated, it forms $[CoCl_4]^{2-}$:

$$\underset{\text{pink}}{2[Co(H_2O)_6]Cl_2} \rightarrow \underset{\text{blue}}{Co[CoCl_4]} + 12\,H_2O$$

$[Pt(NH_3)_4]Cl_2$ on heating to about 500 K, forms $[PtCl_2(NH_3)_2]$

Oxidation A complex of a metal in its higher oxidation state may be produced by oxidising a complex of the same metal in its lower oxidation state; such reactions are usually accompanied by substitution. For example, when aqueous cobaltous nitrate is reacted with aqueous ammonia, ammonium nitrate and hydrogen peroxide, a cobaltic complex is formed.

$$2[\overset{\text{(II)}}{Co}(H_2O)_6](NO_3)_2 + 8\,NH_3 + 2NH_4NO_3 + H_2O_2 \rightarrow$$
$$2[\overset{\text{(III)}}{Co}(NO_3)(NH_3)_5](NO_3)_2 + 14\,H_2O$$

In presence of activated charcoal, the same reactants yield $[Co(NH_3)_6]Cl_3$

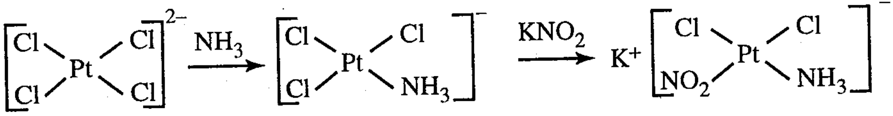
Reduction Certain metal complexes containing the metals in their low oxidation states can be prepared by reduction. Such reductions are effected in the absence of oxygen, as oxygen destabilises low oxidation states of metals. An example for such a preparation is the formation of tetracyanonickelate (o) by K / NH_3 (l) reductant:

$$K_2[\overset{\text{(II)}}{Ni}(CN)_4] \xrightarrow{K/NH_3(1)} K_4[\overset{\text{o}}{Ni}(CN)_4]$$

Another example is the formation of Cr(III) complex from Cr(VI):

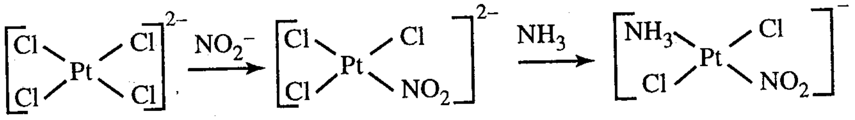
$$K_2\overset{\text{VI}}{Cr_2}O_7 + H_2C_2O_4 + K_2C_2O_4 \rightarrow K_3[\overset{\text{III}}{Cr}(C_2O_4)_3] + CO_2 + H_2O$$

Employing trans effect With the use of suitable reagents, the trans effect can form the basis for synthesising certain complexes. The following steps illustrate such a method:



Potassium cis–dichloronitroammineplatinate(II)

On reversing the order of reagent addition — KNO_2 first and then NH_3 — the trans isomer is formed.



16.3 PREPARATION OF METAL COMPLEXES

The preparations of some metal complexes are described in the following pages.

16.3.1 Tetramminecopper(II) Sulphate

$[Cu(NH_3)_4]SO_4 \cdot H_2O$

Chemicals required:

Copper sulphate
Ammonia
Alcohol

Procedure Dissolve 3g of $CuSO_4 \cdot 5H_2O$ in the least amount of water to obtain a saturated solution in a 50-ml beaker. Add liquor ammonia (7 ml) to this solution drop by drop from a dropping funnel with constant stirring of the reaction mixture. A blue precipitate formed first would then dissolve in excess ammonia to produce a deep blue solution. Now add 25 ml of alcohol to the reaction mixture and stir the mixture. Keep the beaker aside for about 30 minutes; blue crystals of the complex would be formed. Filter off the complex, wash it with about 5 ml of alcohol and dry the crystals in a desiccator overnight.

Exercises

1. What is the role of alcohol in this preparation?
2. Copper-ammonia complex is more soluble than copper pyridine complex in water; what is the reason?
3. Suggest a procedure for estimating the percentage of copper in a mole of this complex.
4. What is the geometry of the complex ion in the product?

16.3.2 Tris-(thiourea)copper(I) Sulphate

$[Cu(tu)_3]_2SO_4 \cdot 2H_2O$

Chemicals required:

Thiourea
Copper(II) sulphate pentahydrate.

Procedure Dissolve 2.5 g of thiourea in 15 ml of water in a beaker. In another beaker dissolve 2.5g of $CuSO_4 \cdot 5H_2O$ in 15 ml of water. Cool the two solutions in ice. Add slowly the copper(II) sulphate solution to the thiourea solution, stirring the mixture thoroughly. Keep the resultant solution aside for about 15 minutes, while crystals would be formed (sometimes, only an oil would be formed). Now to the reaction mixture add a solution of thiourea (1g in 10 ml of water). Stir the mixture and allow it to stand for about 15 minutes. White crystals of the complex would be formed. Filter the crystals through a Buchner funnel.

Recrystallisation Dissolve one half of the product in a solution of 0.10g of thiourea in 15 ml of water containing a few drops of 1 M sulphuric acid. Heat the solution to about 70°C to dissolve the product. Then, cool the solution. Filter the pure crystals on a Buchner funnel. Wash them with 5 ml of water first and then with 5 ml of alcohol. Dry the crystals in air.

Note: Thiourea acts as a reducing agent, converting Cu(II) to Cu(I) and then as a complexing agent in this preparation.

Exercises

1. Draw the structure of the complex.
2. Is it a chelate?
3. How many ions would be formed on dissolving it in a suitable ionising solvent?
4. Why is the complex white unlike the main reactant, $CuSO_4 \cdot 5H_2O$?

16.3.3 Tetrapyridinecopper(II) Persulphate

$[Cu(C_5H_5N)_4]S_2O_8$

Chemicals required:

Copper sulphate pentahydrate
Ammonium persulphate
Pyridine

Procedure Dissolve 1.3g of $CuSO_4 \cdot 5H_2O$ in 10 ml of water in a 50-ml beaker. Dissolve 2.6g of ammonium persulphate in 10 ml of water in another beaker. Add this solution to the copper sulphate solution. Then add redistilled pyridine (4 ml) drop by drop to the mixture with stirring. Violet-blue crystals would be formed. Filter these crystals by suction and wash them with about 20 ml of water containing three drops of pyridine. Dry the crystals in air.

Note: Pyridine is toxic and therefore avoid spillage and handle it with care; avoid inhaling it.

16.3.4 Potassium Tetracyanonickelate(II)

$K_2[Ni(CN)_4]$

Chemicals required:

Nickel(II) sulphate
Potassium cyanide

Procedure Dissolve 3g of nickel(II) sulphate hexahydrate in 10 ml of water. Prepare a solution of potassium cyanide by dissolving 1.3g of KCN solid in 3.5 ml of water. Add slowly, with stirring the KCN solution to the nickel(II) sulphate and stir the mixture with a glass rod. Filter off the nickel(II) cyanide formed and wash it with water. Dissolve this product in a solution of KCN (1.5g in 3 ml of water). The red solution formed is evaporated to half its volume with a small Bunsen flame in a fume-hood. Cool the solution; the orange-yellow crystals formed are filtered off and dried in a current of air.

Caution KCN is highly toxic. Avoid spilling it anywhere. Wash the apparatus and your hands thoroughly after the experiment. Perform the experiment inside a fume-hood.

16.3.5 Potassium Trioxalatochromate(III)

$K_3[Cr(C_2O_4)_3]$

Chemicals required:

Potassium oxalate
Oxalic acid
Potassium dichromate

Procedure Take 100 ml of water in a 250-ml beaker. Dissolve in it 3g of potassium oxalate monohydrate and 1g of oxalic acid dihydrate. To the clear solution add 2.5g of potassium dichromate slowly with vigorous stirring. Evaporate the water in the solution by heating the solution slowly using a small flame. When the contents of the beaker are nearly dry, remove the beaker from the burner and allow it to cool. Crystals of the complex would be formed. Transfer the crystals to the Buchner funnel. Add about 10 ml of acetone to the beaker and transfer the contents to the funnel. Wash the crystal with about 10 ml of acetone and dry them by applying suction to the funnel. Record the yield of the complex.

Exercises

1. Write the equation to represent the formation of the complex.
2. Draw the structure of the complex.
3. What is the hybridisation involved in the metal ion?
4. Can this complex exhibit optical isomerism?
5. Predict its magnetic moment.
6. Suggest a method for estimating the chromium in the complex.

16.3.6 Hexaquachromium(III) Chloride

$[Cr(H_2O)_6]Cl_3$

Chemicals required:

Potassium chromium(III) sulphate (chrome alum)
Hydrogen chloride

Procedure Take 25 ml of distilled water in a 100-ml beaker. Add to this, powdered chrome alum in small portions with vigorous stirring; stop adding when the solution becomes saturated. Cool the solution in ice for about ten minutes and then decant the solution into a 100-ml conical flask containing a few pieces of ice. Pass a steady stream of hydrogen chloride gas through the cold solution for about fifteen minutes (inside a fume cupboard). Greenish-blue crystals of the complex are formed. Filter off these crystals, wash them with about 10 ml of acetone and dry them in air.

16.3.7 Hexamminecobalt(III) Chloride

$[Co(NH_3)_6]Cl_3$

Chemicals required:

Cobalt(II) chloride hexahydrate
Charcoal
Hydrogen peroxide (6 per cent, 20 volume)
Ammonia solution
Ammonium chloride

Procedure Add 0.5g of decolourising charcoal into a 100-ml conical flask. Dissolve 4.5g of cobalt(II) chloride and 3g of ammonium chloride in 5ml of water. Heat this solution gently. Then, pour this hot solution into the conical flask containing the charcoal. To the mixture in the conical flask now add 10 ml of concentrated ammonia solution with stirring. Cooling the mixture under the cold tap water, add slowly 10 ml of 6 per cent hydrogen peroxide. Then heat the contents of the flask to 60°C and maintain the temperature at 60°C for about 30 minutes. Now the pink colour of the solution disappears indicating the completion of reaction. Cool the mixture in ice-cold water. Filter the solids on a Buchner funnel.

Transfer the solids from the funnel to a beaker containing a boiling solution of 1.5 ml of concentrated hydrochloric acid and 40 ml of water. All the solids, except the charcoal dissolve. Filter the hot suspension. Add to the filtrate 5 ml of concentrated hydrochloric acid and cool it in ice. Orange crystals of the complex are formed. Filter these crystals on a Buchner funnel and dry them between the folds of filter papers. Record the yield.

Note:

1. The role of charcoal, a heterogeneous catalyst, in this preparation is unique and also not fully understood. It is believed to catalyse an otherwise very slow intermediate reaction,

   $$[Co(NH_3)_5OH]^{2+} \xrightarrow{NH_3} [Co(NH_3)_6]^{3+} + OH^-$$

   In the absence of charcoal, chloropentamminecobalt(III) chloride $[Co(NH_3)_5Cl]Cl_2$ is formed.
2. Hydrogen peroxide oxidises Co(II) to Co(III).
3. Many other oxidising agents can oxidise Co(II) to Co(III) in the presence of suitable ligands. $KMnO_4$, $K_2Cr_2O_7$, PbO_2 and SeO_2 are such effective oxidising agents; however, H_2O_2 is the preferred one as it does not introduce foreign metal ions to the reaction mixture.
4. In this complex Co(III) is stabilised by ammonia. The H_2O ligands cannot stabilise Co(III) because of the low crystal field stabilisation energy of the aqua-complex compared to that of the ammine-complex.
5. Co(III) is an oxidant; it can oxidise I^- to I and therefore it can be estimated by iodometry. The complex is decomposed to cobalt(III) oxide on boiling it with aqueous sodium hydroxide. This oxide liberates iodine from potassium iodide in acid medium. The liberated iodine can then be titrated with a standardised solution of sodium thiosulphate.

16.3.8 Sodium Hexanitrocobaltate(III)

(Sodium cobaltinitrite) $Na_3[Co(NO_2)_6]$

Chemicals required:

Sodium nitrite
Cobalt nitrate

Procedure Dissolve 5g of sodium nitrite in 5 ml of hot water. Cool the solution to 50°C. Then, to the solution add 2g of cobalt nitrate powder with vigorous stirring. To the continuously stirred solution, add 2 ml of 50 per cent aqueous acetic acid drop by drop. A dark-brown solution is obtained. Transfer this solution to a 100-ml conical flask provided with a two-holed rubber bung fitted with an inner tube reaching the bottom of the flask and an outlet tube for drawing air through the solution. Draw a current of air through the solution for about thirty minutes using a filter pump. This destroys any excess of nitrous acid present in the solution. If the solution is not clear, it is then filtered. The clear brown filtrate is cooled in an ice-bath. Then to the ice-cold solution 10 ml of ethanol is added drop by drop with stirring. Bright orange crystals are formed. These are filtered by suction, washed thrice with ethanol and then dried in air.

$$Co(NO_3)_2 + 5\,NaNO_2 + 2\,HNO_2 \longrightarrow Na_3[Co(NO_2)_6] + 2NaNO_3 + NO + H_2O$$

16.3.9 Dicuproustetraiodomercurate(II)

Cu_2HgI_4

Chemicals required:

Copper sulphate
Sodium sulphite
Sodium chloride
Mercuric nitrate
Potassium iodide

Procedure Dissolve 3g of $Na_2SO_3 \cdot 7H_2O$ and 2.5g of NaCl in 25 ml of water in a 100-ml beaker. Boil this solution gently and to the boiling solution add an aqueous copper sulphate (1.3g in 13 ml of water). A greenish precipitate formed initially dissolves subsequently to produce a yellow solution. This solution contains copper as Cu(I).

Dissolve 0.8 g of $Hg(NO_3)_2$ in 13 ml of boiling water. To this add aqueous 10 per cent KI till the initial HgI_2 formed dissolves to give clear HgI_4^{2-}. To this solution add the hot Cu(I) solution prepared earlier. A deep purple solid Cu_2HgI_4 is precipitated. Cool the reaction mixture to room temperature (the solid turns red on cooling). Filter the red solid and dry it in a desiccator.

Note: The reversible change of colour of a substance on changing the temperature is known as *thermochromism*. Cu_2HgI_4 exhibits thermochromism; it is red at room temperature and purple at higher temperatures. The change of colour is due to change in crystal structure. This crystal structure transition temperature can be recorded by gradually heating the solid; the temperature at which the red colour changes to purple is the transition temperature (67°C).

Ag_2HgI_4 is also thermochromic; it is yellow at room temperature and changes to orange at 50°C.

16.3.10 Diaquabis(ethylenediamine)copper(II) Iodide

$[Cu(en)_2(H_2O)_2]I_2$

Chemicals required:

Copper(II) acetate monohydrate
Ethylene diamine
Potassium iodide
Ethyl alcohol

Procedure Dissolve 1.9 g of copper(II) acetate monohydrate in 5 ml of water in a beaker. Add to this solution 2 ml of ethylenediamine dropwise with stirring. To this mixture, add a solution of potassium iodide (4.2 g dissolved in minimum volume of water). The reaction mixture is then heated to 60°C on a water bath for about 15 minutes. Then it is cooled in an ice bath. To the cold solution, 10 ml of ethyl alcohol is added; the violet crystals formed are filtered. A part of the product is recrystallised with a minimum volume of hot water. The crystals are washed with 10 ml of ethyl alcohol and then dried by drawing air through the funnel. Record the yield.

Exercises

1. What is the role of alcohol in this preparation?
2. Draw the structure of the product.
3. Is the Jahn-Teller distortion expected in this complex? How can this be experimentally checked?

16.3.11 Hexamminenickel(II) Chloride

$[Ni(NH_3)_6]Cl_2$

Chemicals required:

Nickel nitrate
Ammonia
Ammonium chloride

Procedure Dissolve 6g of nickel nitrate in minimum amount of water and add to this solution a 25 per cent ammonia solution such that the initially formed precipitate dissolves completely. Then add a saturated solution of ammonium chloride (10 ml) drop by drop with stirring followed by 2N ammonia (10 ml). Filter off the product in a Buchner funnel, and wash it first with about 2 ml of ammonium chloride solution followed by 2 ml of liquor ammonia – ethanol (1:1) mixture and finally with 10 ml of ethanol. Dry the product.

16.3.12 Tetramminecarbonatocobalt(III) Nitrate

$[Co(NH_3)_4CO_3]NO_3$

Chemicals required:

Cobalt nitrate hexahydrate
Ammonia
Ammonium carbonate
Ethanol

Procedure Dissolve 2 g of ammonium carbonate in 10 ml of water and add to this solution 5 ml of 25 per cent ammonia solution. Transfer this solution to a conical flask fitted with two glass tubes through a two-holed cork. Now add a solution of cobalt nitrate (3 g in 6 ml of water) to the solution in the conical flask. Connect the flask to a water pump and draw air through the reactants (1 hour) to oxidise Co(II) to Co(III).

Filter the solution if it contains any solid and collect the filtrate in a porcelain dish. Keep the dish over a water bath, add 1 g of ammonium carbonate and evaporate the solution; when crystals start appearing in the solution, remove the dish from the water bath and keep it aside for crystallisation to be completed. Filter off the crystals on a Buchner funnel, wash them with a small amount of ice-cold water and then with ethanol. Dry the salt in air by keeping it spread-out on a watch glass.

Exercises

1. Write the equations involved in this preparation.
2. Is the complex a chelate? Draw its structure.
3. What would be the action of dilute HCl on the complex?

EXERCISES

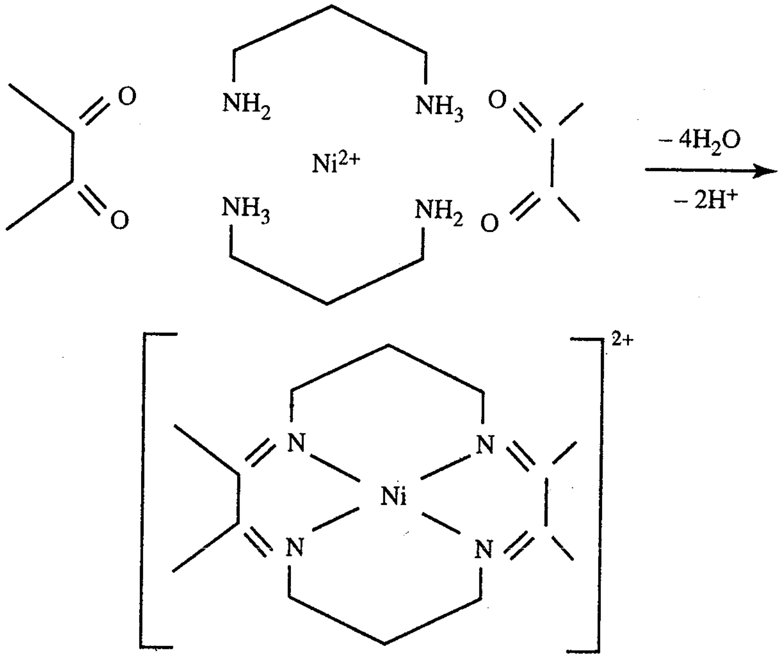
*1. Illustrate: template synthesis.

2. A moist metal complex should not be dried by applying heat to it; explain.

3. Write equations denoting the preparation of each of the following from simple reagents:
   - a) $[Pt(NH_3)_6]Cl_4$
   - b) $[Ni(C_2H_4)_3]$
   - c) $K[Pt(NH_3)(NO_2)Cl_2]$

ANSWERS

1. Template synthesis involves the formation of a complex with macrocyclic ligands. In this method, a metal ion is used to assemble a group of ligands; the product then undergoes a condensation reaction to form a macrocyclic ligand. A common template synthesis involves the Schiff's base condensation of an amine and a ketone. Initially, a Schiff's base (anil) is formed by condensation with simultaneous coordination to a metal ion. The following equation illustrates a template synthesis.



Chapter 17

Solved Spectral Problems in Coordination Chemistry

17.1 ELECTRONIC SPECTROSCOPY

Problem 17.1.1 The electronic spectrum of $[Ti(H_2O)_6]^{3+}$ has an absorption maximum at 20,300 cm^{-1}. Calculate the ligand field stability per ligand for this complex.

Solution As it is a one-electron, d^1 simple system, Δ_0 can be directly related to the maximum frequency of absorption observed.

The energy of transition

$$\begin{aligned}
\Delta E &= hc\bar{v} \\
&= (6.62608 \times 10^{-34}\,\text{Js}) \times (2.997 \times 10^{8}\,\text{ms}^{-1}) \times (20{,}300\ \text{cm}^{-1}) \\
&= (6.62608 \times 10^{-34}\,\text{Js}) \times (2.997 \times 10^{8}\ \text{ms}^{-1}) \times (20{,}300\ \text{cm}^{-1} \times 100) \\
&= 403125 \times 10^{-24}\ \text{J / molecule} \\
&= (403125 \times 10^{-24}) \times \frac{6.022 \times 10^{23}}{1000}\quad \text{kJ / mole} \\
&= 243\ \text{kJ / mole} \\
&= 243/6 = 41\ \text{kJ / ligand}
\end{aligned}$$

Problem 17.1.2 The electronic spectrum of $[V(H_2O)_6]^{3+}$ is depicted below (Fig. 17.1). Explain.

Solution The spectrum consists of two bands, at 17,200cm^{-1} and 25,600 cm^{-1}

Three $d-d$ transitions are possible for this d^2 system.

$$\begin{aligned}
{}^3T_{2g}(F) &\leftarrow {}^3T_{1g}(F) \\
{}^3T_{1g}(P) &\leftarrow {}^3T_{1g}(F) \\
{}^3A_{2g}(F) &\leftarrow {}^3T_{1g}(F)
\end{aligned}$$

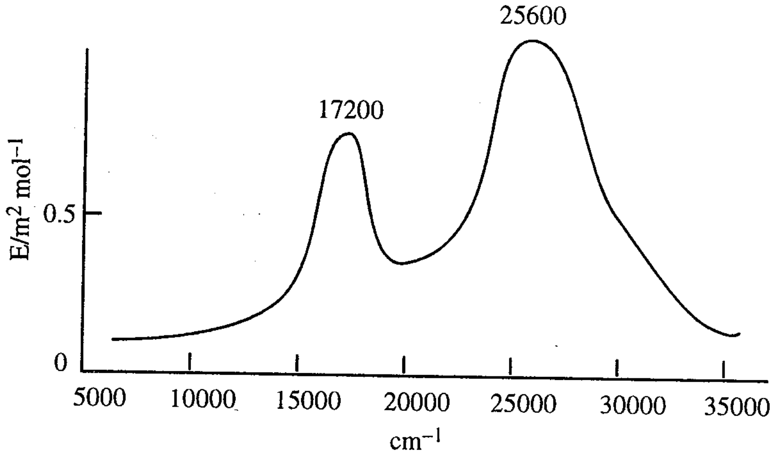


Fig. 17.1 Absorption spectrum of $[V(H_2O)_6]^{3+}$

Based on the Tanabe-Sugano diagram for a d^2 ion, these three transitions should involve increasing frequency; the first two are the spin-allowed transitions from $^3T_{1g}$ ground term and are assigned the frequencies 17,200 cm^{-1} and 25,600 cm^{-1} respectively. The absence of the third absorption in the spectrum indicates that it should be a very weak band with too small ε to be recorded. This third transition is forbidden by the g $\nleftrightarrow$ g selection rule and it corresponds to the simultaneous excitation of two electrons; both of these factors are expected to make this band weak.

In addition, charge transfer bands commence in the same region expected for this weak absorption (36000 cm^{-1}); this weak band therefore overlaps with the CT band.

When V^{3+} is held in solid state (in Al_2O_3), this weak band becomes observable; in this situation, the CT band occurs at a higher frequency, not overlapping with this weak band.

Problem 17.1.3 The electronic spectrum of $[Fe(H_2O)_6]^{2+}$ consists of a band with doublet structure. Explain.

Solution Fe^{2+} is a d^6 system. The energy level diagram for the d^6 system indicates that the observed spectral band is due to the spin-allowed transition

$$^5E_g \leftarrow {}^5T_{2g}$$

It is a weak absorption band at 10,000 cm^{-1}, which is responsible for the pale green colour of aqueous Fe(II) solution. The doublet structure of this band arises due to a low symmetry ligand field component which lifts the two-fold orbital degeneracy of the ^5E_g term.

Problem 17.1.4 The MLCT transitions are common in complexes containing aryl ligands; justify this.

Solution An aryl ligand, such as bipyridine or phenolate ion has empty π^* orbitals. Such orbitals have low energies and therefore promotion of electrons into them is easy; then, electron transfer from the metal ion, especially if the metal is in its low oxidation state, can occur easily. Thus the MLCT transitions in such complexes are common.

Problem 17.1.5 LMCT transitions in tetraoxoanions such as MnO_4^- and CrO_4^{2-} are prominent; explain.

Solution The Mn(VII) in MnO_4^- and Cr(VI) in CrO_4^{2-} are in their high oxidation states. Such oxidation states contain vacant metal *d* orbitals with ability for accepting electrons from the ligands; thus in each of these, low-energy acceptor level is available. Each oxygen has lone pairs of electrons; an oxygen lone pair can be promoted into a low-lying empty e_g metal orbital. These two factors favour M ← L transitions.

The purple colour of MnO_4^- and the yellow colour of CrO_4^{2-} arise from such LMCT transitions, which occur in the visible region.

Problem 17.1.6 Explain the following LMCT energy order:

$$CrO_4^{2-} < MoO_4^{2-} < WO_4^{2-}$$

Solution The LMCT energy should decrease as the ability of the metal for accepting electron from ligands increases (for the same ligands). A metal ion , which is most easily reduced to its lower oxidation state would readily accept the ligand electrons. The stability of lower oxidation states is in the order; Cr > Mo > W. Thus, Cr(VI) can accept electrons more easily than W(VI). This results in least LMCT for CrO_4^{2-} . Among the three M(VI) ions, Cr(VI) is the most easily reduced.

Problem 17.1.7 $[Cr(H_2O)_6]^{3+}$ is pale violet, but CrO_4^{2-} is intensely yellow; what causes this colour difference?

Solution The absorption by $[Cr(H_2O)_6]^{3+}$ is due to spin-allowed but Lapporte-forbidden ligand- field transition. The Lapporte-forbidden nature of this absorption makes the molar absorption coefficient (ε) very low; therefore, the colour of the aqua species is pale.

In , CrO_4^{2-} the Cr(VI) has a d^0 configuration; therefore no ligand field transitions are possible in this. However, LMCT is possible, i.e., electron transfer from the oxide ion to the metal ion as Cr is in its highest oxidation state. This CT transition, as CT transitions are, both spin-allowed and Lapporte-allowed; consequently, this produces intense yellow colour.

Problem 17.1.8 Explain why the pale red colour of $[Co(H_2O)_6]^{2+}$ solution changes to intense colour on adding to it excess conc. hydrochloric acid.

Solution The change of pale colour to intense colour is due to the transformation of the octahedral complex to the tetrahedral complex:

$$\underset{\text{(octahedral)}}{[Co(H_2O)_6]^{2+}} \longrightarrow \underset{\text{(tetrahedral)}}{[CoCl_4]^{2-}}$$

The regular octahedral complex has a centre of symmetry and therefore the intensities of its absorption bands are low; consequently it has pale colour. On the other hand, the tetrahedral complex lacks a centre of symmetry and therefore the intensities of its absorption bands are high; this results in intense colour for the complex.

Generally, relatively strong absorption bands are obtained for $d-d$ transition in complexes which lack centres of symmetry, such as cis complexes of the type MA_4B_2 and tetrahedral complexes.

Problem 17.1.9 The empirical ligand (H_2O) parameter $h = 1.0$ and the empirical metal parameter k for $Ni^{2+} = 0.12$. Calculate the Racah parameter B for this complex. The absorption spectrum of $[Ni(H_2O)_6]^{3+}$ indicates electronic transitions at 9000, 14000 and 25000 cm^{-1}. Using the d^8 Tanabe-Sugano diagram, comment on these absorption values.

Solution The ratio (β) of the Racah parameter for the complex (B_{complex}) and that for the free ion is given by

$$\beta = \frac{B_{\text{complex}}}{B_{\text{free ion}}} = 1 - hk$$

(This relationship denotes the reduction in B value for the complex from that of the free ion value in terms of the empirical parameters h for the ligand and k for the metal.)

$$\beta = 1 - (1.0 \times 0.12)$$
$$= 0.88$$

$$\therefore \quad \frac{B_{\text{complex}}}{B_{\text{free ion}}} = 0.88$$

$$\frac{B_{\text{complex}}}{1034} = 0.88 \quad (\text{as} \quad B_{\text{free ion}} = 1034)$$

Therefore $\quad B_{\text{complex}} = 0.88 \times 1034 = 906 \text{ cm}^{-1}$

The lowest energy 9000 cm^{-1} must correspond to Δ_0

$$\therefore \quad \Delta / B = 9000/906 = 9.9$$

Now by reading up from the point corresponding to Δ / B, (9.9) on the abscissa of the d^8 Tanabe-Sugano diagram, the E/B values of 16.5 and 29 can be obtained. These correspond to transition energies of 15000 and 26000 cm^{-1} respectively. These values agree satisfactorily with the experimental values of 14000 and 25000 cm^{-1}.

These two energies correspond to the transitions

$$3A_{2g} \rightarrow 3T_{1g} \quad (F)$$
$$3A_{2g} \rightarrow 3T_{1g} \quad (P)$$

Problem 17.1.10 From the electronic spectrum of $[Cr(H_2O)_6]^{3+}$, the Δ_0 for this complex has been evaluated to be 17600 cm^{-1}. The Racah parameter B = 918 cm^{-1}. Using the Tanabe-Sugano diagram, evaluate the wave number of the first two spin-allowed bands in its spectrum.

Solution This complex is an octahedral d^3 system ($t_{2g}^3 e_g^0$). The transition involves $t_{2g}^3 e_g^0 \rightarrow t_{2g}^2 e_g^1$. The term symbols that can arise from the quartet $t_{2g}^2 e_g^1$ excited configuration are $^4T_{2g}$ and $^4T_{1g}$.

The two spin-allowed transitions are $^4T_2 \leftarrow {}^4A$ and $^4T_1 \leftarrow {}^4A$

$$\Delta_0 / B = 17600/918 = 19.2$$

Then the point corresponding to Δ_0 / B = 19.2 is located on the x-axis of the Tanabe-Sugano diagram (simplified) (Fig. 17.2):

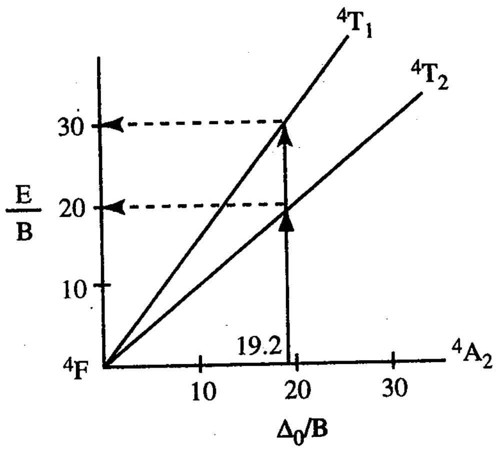


Fig. 17.2 Simplified Tanabe-Sugano diagram for d^3 system

A vertical line is drawn from this point to cut the $^4T_2$ and $^4T_1$ lines. From the points of intersection of the vertical line and the $^4T_2$ and $^4T_1$ lines, horizontal lines are drawn to the y-axis. The E / B values are noted corresponding to the points at which the horizontal lines thus drawn cut the y-axis. These are found to be 20 and 30.

Then the energy (E) of the first transition

$$^4T_2 \leftarrow {}^4A_2 = (918\ \text{cm}^{-1})(20) \quad (\text{as } E/918\ \text{cm}^{-1} = 20)$$
$$= 18400\ \text{cm}^{-1}$$

The energy of the second transition

$$^4T_1 \leftarrow {}^4A_2 = (918\ \text{cm}^{-1})(30)$$
$$= 27{,}500\ \text{cm}^{-1}$$

Problem 17.1.11 $[Cr(H_2O)_6]^{3+}$ has a maximum absorption of visible light at 17400 cm^{-1}. Calculate its Δ value.

Solution $\Delta = 1/\lambda = 1/17400\ \text{cm}^{-1} = 5.747 \times 10^{-5}$ cm
$= 5747$ Å

Δ for $[Cr(H_2O)_6]^{3+}$ corresponds to absorption of light at 5747 Å.

Problem 17.1.12 The energy difference (Δ) between the t_{2g} and e_g levels in $[Co(NH_3)_6]^{3+}$ is 22900 cm^{-1}. Predict the colour of this complex.

Solution $\lambda = 1/\bar{v} = 1/22900\ \text{cm}^{-1} = 4.37 \times 10^{-5}\text{cm} = 437\ \text{nm} = 4370$ Å

The absorption band at about 4400 Å corresponds to absorption of blue light. Then, the complex should exhibit the colour complementary to blue; it should be orange.

Problem 17.1.13 The electronic spectrum of $[Cr(NCS)_6]^{3-}$ shows absorption bands at 16000, 17700, 23800 and 32400 cm^{-1}. Interpret these data.

Solution

(i) The very low intensity band at 16000 cm^{-1} should be due to a spin-forbidden transition; it is likely from $^2E_g \leftarrow {}^4A_{2g}$ transition.

(ii) Two spin-allowed but Laporte-forbidden transitions, $^4T_{1g} \leftarrow {}^4A_{2g}$ and $^4T_{2g} \leftarrow {}^4A_{2g}$ are possible in this d^3 complex. The bands at 17700 cm^{-1} and 23800 cm^{-1} may represent those two transitions respectively.

(iii) The very high absorption at 32400 cm^{-1} is a likely charge transfer absorption, and not a (*d-d*) band.

(iv) NCS^- ligands have low-lying π^* orbitals; therefore M → L charge transfer is possible in this complex.

17.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

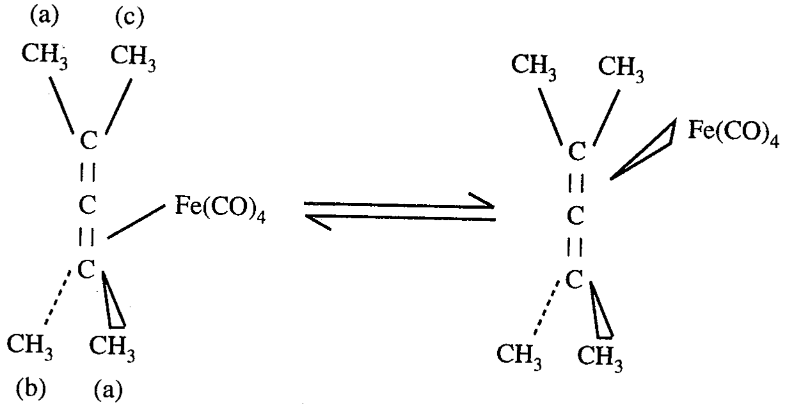
Problem 17.2.1 The proton NMR spectrum of tetramethylallenetetracarbonyliron(o) consists of a single peak at room temperature. However, at –60° C, it consists of three independent peaks in the ratio 1:1:2. Explain.

Solution $[(CH_3)_2C=C=C(CH_3)_2(CO)_4Fe]$

The change in the spectrum with temperature indicates that the complex has a fluxional structure.

At room temperature, the single NMR signal shows that the twelve protons in the structure of the complex are identical, giving rise to a single resonance, experiencing an average environment. This structure is characteristic of a fluxional structure.

As the temperature is lowered, the protons become inequivalent. The low-temperature spectrum shows the existence of three types of protons (3 : 3 : 6). A possibility is a structure containing three cis-hydrogen atoms, three trans-hydrogen atoms and the remaining six hydrogen atoms in a plane perpendicular to its carbon-iron bond.



This inter-conversion should be fast at room temperature; it should be so fast, that the proton NMR cannot distinguish the two distinct configurations, but senses only the average configuration.

At low temperatures, the inter-conversion should be slow on the NMR time-scale, rendering the protons inequal.

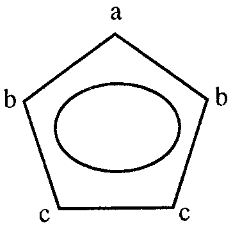
Problem 17.2.2 The ^1H NMR spectrum of $(C_5H_5)_4Ti$ consists of two broad symmetric peaks at 25°C. On increasing the temperature to 60°C, a single sharp absorption results. However, as the temperature is lowered to –27°C, two lines of equal intensity are obtained; explain these observations.

Solution The effect of temperature on the spectrum indicates fluxionality of the molecule. The two peaks at 25°C must be due to two different modes of linkage of the C_5H_5 ligands with Ti.

As the two broad peaks are symmetric, two of the C_5H_5 groups must be bonded to Ti in one mode and the other two C_5H_5 in another mode. (This fact is confirmed by crystal structure analysis; two of the C_5H_5 groups are monohapto and the other two are pentahapto). As the temperature is increased, the interconversion of the two pairs of C_5H_5 groups with respect to their modes of binding should increase; at 60°C this interconversion should be so fast in terms of the NMR time scale that the two signals average out into one.

On lowering the temperature to –27°C , the opposite should occur, that is, the interconversion should be slowed such that the two pairs of C_5H_5 groups produce independent signals. At this temperature, the monohapto groups and the pentahapto groups in the molecule have finite life times.

In each of the monohapto rings, there are three types of ring protons:



However, separate resonances for these are not observed; this must be due to rapid migration of the metal-carbon bond from one carbon to another within each ring even at –27°C. Further decrease in temperature would produce separate signals for these *a, b, c* protons.

Problem 17.2.3 How many ^1H NMR signals are expected for the following complex? $[Fe(\eta^1-C_5H_5)(\eta^5-C_5H_5)(CO)_2]$

Solution Two ^1H NMR signals are expected , one for η^1-C_5H_5 and the other for η^5-C_5H_5 (it is assumed that the five protons in η^1-C_5H_5 are averaged; the five protons in η^5-C_5H_5 are equivalent).

Problem 17.2.4 The ^{13}C NMR of $[Fe(CO)_5]$ has only one signal; explain.

Solution The geometry of the complex is trigonal bipyramid; therefore, it is expected to produce two different signals, one corresponding to the axial CO groups and the other corresponding to the equatorial CO groups. The presence of only one signal indicates that it is fluxional, rendering all the CO groups chemically equivalent.

Problem 17.2.5 The Vaska's compound $[IrCl(CO)(PPh_3)_2]$ forms octahedral Ir(III) complexes in oxidative additive reactions with H_2, Cl_2, HX, MeI and RCOOH. Such a complex is octahedral in which the two phosphine ligands are trans to each other, the remaining ligands Cl, CO, A and B (A and B are two components of the reactant) lying in a plane.

What spectral data can prove the trans-geometry of the PPh_3 ligands?

Solution ^1H NMR can prove the trans-geometry of the PPh_3 ligands.

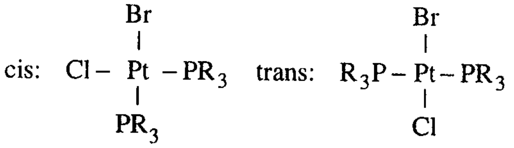
Problem 17.2.6 Explain the following proton NMR data:

Complex	^1H δ (ppm)
$H_2Fe(CO)_4$	− 11
$[HFe(CO)_4]$	− 9

Solution The chemical shifts for these two systems are negative, viz., upfield from TMS ($\delta = o$). This indicates that there is very high shielding of these protons. Such a proton shielding in a complex is due to the paramagnetic contributions from the transition metal to which the proton is directly attached.

Problem 17.2.7 Suggest an experimental method for distinguishing between the isomers of $[PtClBr(PR_3)_2]$.

Solution Corresponding to the formula, two isomers, cis-isomer and trans-isomer are possible:



$$\text{cis:}\quad \begin{array}{c}\text{Br}\\ | \\ \text{Cl}-\text{Pt}-\text{PR}_3\\ | \\ \text{PR}_3\end{array} \qquad \text{trans:}\quad \begin{array}{c}\text{Br}\\ | \\ \text{R}_3\text{P}-\text{Pt}-\text{PR}_3\\ | \\ \text{Cl}\end{array}$$

^{31}P NMR spectroscopy can be used to distinguish between these isomers. The trans isomer is a C_{2v} molecule and the two phosphine ligands are related by symmetry elements C_2 axis (Cl-Pt-Br axis) and the σ_v mirror plane that is perpendicular to the molecular plane. Therefore, the two PR_3 groups are expected to have the same chemical shift in the ^{31}P NMR spectrum.

In the cis-isomer, the two PR_3 groups are not related by the σ mirror plane of this C_2 molecule; this makes the two groups chemically nonequivalent giving rise to two independent ^{31}P absorptions.

17.3 INFRA RED SPECTROSCOPY

Problem 17.3.1 Explain the following IR spectroscopic data:

Carbonyl species	ν_{CO} / cm^{-1}
$[Mn(CO)_6]^+$	~ 2090
$[V(CO)_6]$	~ 2000
$[V(CO)_6]^-$	~ 1860

Solution These carbonyls are iso-electronic. The decrease in frequency values indicates a decrease in C-O bond strength and reduction in bond order.

The bond order and in turn the bond strength for C – O in a carbonyl depends on the extent of metal- carbon bond.

$$M - C \equiv O \qquad M \overset{\cdots}{-} C \overset{\cdots}{=} O$$

weaker stronger stronger weaker

When the extent of metal - carbon bonding increases, the C – O bond order/ strength decreases. ($C \equiv O$ to $C = O$) Therefore, the frequency will decrease.

In $[Mn(CO)_6]^+$, the shift of electrons from metal to carbon for forming a bond is inhibited and therefore, the C – O bond is close to $C \equiv O$. This produces a higher strength of CO absorption. In $V(CO)_6$, a partial additional M – C bonding is possible which decreases the bond order in CO and therefore, the CO absorption frequency decreases to ~ 2000 cm^{-1}. In $[V(CO)_6]^-$, because of the negative charge, shift of electrons from metal to carbon for bond formation is easy and therefore, the CO absorption is further decreased.

Problem 17.3.2 Rationalize the following data:

Species	CO stretching frequency (cm^{-1})
CO	2145
$Mo(CO)_6$	2000
$Mo(CO)_3(NH_3)_3$	1855

Solution The stretching frequencies provide a qualitative measure of the C – O bond strengths. The decrease in C-O frequency from 2145 in the free CO molecule to 2000 in $Mo(CO)_6$ indicates a weakening of the C – O bond in the complex. In the molybdenum complex, there is M – C bonding which, decreases the C – O bond strength. The M – C bonding increases further with NH_3 ligands in $Mo(CO)_3(NH_3)_3$ because, the electron availability in the metal is increased by the presence of NH_3 ligands. This bonding further weakens the C – O bond and therefore, the C – O stretching frequency decreases in the ammine complex.

Problem 17.3.3 A complex of the metal M having the formula $[M(CO)_4(PMe_3)_2]$ exists in two isomeric forms. One shows four IR bands at 2016, 1915, 1900 and 1890 cm^{-1}, whereas, the other shows only one strong band at 1890 cm^{-1}. Explain these data.

Solution These data indicate that the two isomers have different symmetries; there is a direct relationship between the symmetry of a carbonyl molecule and the number of IR active CO stretching modes.

The isomer which shows four CO stretching bands should be the cis-isomer. The one with only one band should be the trans-isomer.

In the cis-isomer, four distinct forms of CO stretching vibrations are possible, all of which can absorb IR radiation.

In the trans-isomer, of the four stretching modes only two can absorb IR radiation. These form a degenerate vibration and being equivalent, they have the same frequency. Therefore, for this isomer only a single strong band at 1890 cm^{-1} is observed.

Problem 17.3.4 The C-O stretching frequencies for $[Ni(CO)_4]$, $[Co(CO)_4]^-$ and $[Fe(CO)_4]^{2-}$ are 2060, 1890 and 1790 cm^{-1} respectively; account for this.

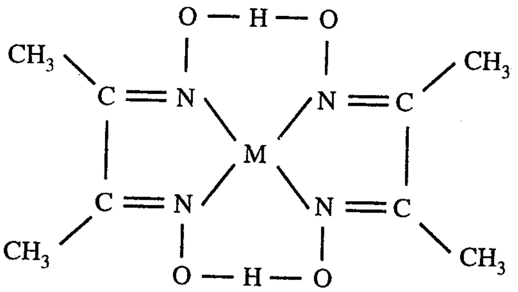
Solution The ν_{C-O} values decrease from the nickel complex to the iron complex indicating weakening of the C-O bond. This can be explained on the basis of M- C π bonding. As the extent of this π bonding increases, electrons are depleted on M and therefore the C-O bond weakens. In the carbonylate anions, the metal has a greater electron density to be released for π bonding, enhancing the M-C π bonding and consequently decreasing the C-O bond strength.

M-C-O

← electron flow –

Problem 17.3.5 In the dimethylglyoxime complexes of Cu(II), Ni(II), Co(II) and Fe(II), the frequency of the C=N vibration decreases from Cu(II) to Fe(II).

Solution The decreasing $\nu_{C=N}$ is due to increasing conjugation in the ring from the Cu(II) to Fe(II) chelate. In these complexes C=N bond constitutes a part of the chelate ring:



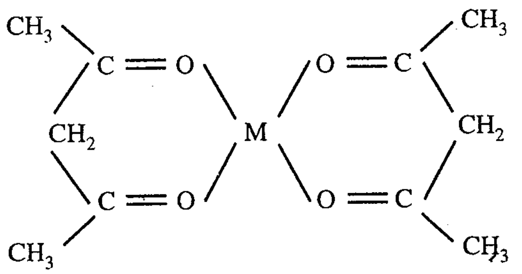
From Cu(II) to Fe(II), the ionization potential [M(II) → M(III)] decreases. This decrease helps electron transfer in the direction metal → ligand. With such an increase in back-coordination, the non-sigma-bonding *d* electrons of the central atom can participate increasingly in conjugation in the chelate ring. This causes a decrease in the frequency of the C=N stretching vibration.

Problem 17.3.6 Explain the following data obtained for acetylacetone complexes of Pd(II), Cu(II), Ni(II) and Co(II):

M(II)	ν_{CO}	ν_{CC}	log β_2
Pd(II)	1547	1570	27.1
Cu(II)	1554	1580	14.9
Ni(II)	1592	1592	10.4
Co(II)	1601	1601	9.5

Solution The ν_{CO} of acetylacetone attached in the complexes decreases with increasing stability of the complexes; the carbon-oxygen bond strength decreases, with increasing β_2. This implies that the M–OC bond strength increases from Co(II) to Pd(II).

A strong conjugation in the chelate ring of each complex is expected.



Conjugation renders the C–O and C–C bonds of equal strengths; this is evident from the almost same ν_{CO} and ν_{CC} stretching vibration frequencies for each complex. These two bonds may correspond to C=O and C=C.

Problem 17.3.7 Account for the following infrared vibrational frequencies of carbon monoxide and the metal carbonyls:

System	CO stretching vibration (cm^{-1})	M-C stretching vibration (cm^{-1})
CO	2143	–
$Ni(CO)_4$	2057	422
$[Co(CO)_4]^-$	1918	532, 439
$[Fe(CO)_4]^{2-}$	1788	550, 464

Solution In a metal carbonyl, as the M-C bond is strengthened (increasing the stability of the carbonyl) the CO stretching frequency decreases. (As the stability of the complex increases, the strength of the CO bond decreases). Applying this principle to these data, it is evident that the carbonyl stability order is

$$Ni(CO)_4 < Co(CO)_4 < Fe(CO)_4$$

This is also the order for increasing electron transfer in the direction metal → ligand; this causes a decrease in the CO bond order. The increasing back-bonding increases the M-C bond strength and hence the M-C stretching vibration.

Problem 17.3.8 The work of A. Tramer (J.Chem. Phy., 1962,232) indicates the following infrared frequencies $\nu_{C\text{-}S}$ and $\nu_{C\equiv N}$ in complexes studied by him. How can these values be explained?

Complex	$\nu_{C\text{-}S}$ (cm^{-1})	$\nu_{C\equiv N}$ (cm^{-1})
$K_2[Hg(SCN)_4]$	715	2107, 2114
$K_2[Zn(NCS)_4]$	821, 816	2043, 2080
KSCN	750	2050

Solution The variation of the two frequencies compared to those in KSCN indicates that the two complexes contain the ligands bonded differently. The decrease in the C-S stretching vibration for the thiocyanate complex $K_2[Hg(SCN)_4]$ compared to that for KSCN shows that the C-S bond in the complex is weakened on coordination to the metal. However, in the isothiocyanate complex, $K_2[Zn(NCS)_4]$ it is strengthened. These two opposite changes may be justified based on the bonding patterns,

M-S-C≡N : thiocyanate
S=C=N-M : isothiocyanate

The strength of the N≡C bond has become stronger in the thiocyanate complex; however, it remains almost unchanged in the isothiocyanate complex.

Problem 17.3.9 R.G.Inskeep (J. Inorg. Nucl. Chem, 24, 763, 1962) reported the following stretching vibrations (cm^{-1}) of the metal-nitrogen bond in 2,2'-bipyridyl and 1, 10-phenanthroline complexes of transition metals. Rationalize these data.

Central metal	Bipy	*o*-phen
Fe(II)	423	530
Co(II)	264	288
Ni(II)	286	299
Cu(II)	297	300
Zn(II)	280	288

Solution The stretching frequencies are the highest with Fe(II) complexes, the other complexes having more or less the same (low) frequency values. The differential behaviour of the Fe(II) complex originates from strongest metal-ligand back-coordination in it.

(a) The ionization potential for M(II) → M(III) is lowest for iron.
(b) The two Fe(II) complexes have low-spin electron configuration.
(c) These two factors promote back-coordination; these strengthen the M-L bond resulting in high vibrational frequencies.

Problem 17.3.10 In the infrared spectrum of the polymeric complex $Na_2[Co(CN)_5]_x$ two C≡N stretching frequencies occur: explain.

Solution Two different C≡N stretching frequencies are indicative of two modes of linkages of the CN groups in the complex; one mode may involve terminal CN groups and the other bridge CN groups. Usually, the terminal CN frequency occurs at a higher value than the bridge CN frequency. For this complex, the corresponding values are 2130 cm^{-1} and 2202 cm^{-1} respectively.

Problem 17.3.11 How can infrared spectroscopy be used to distinguish between the cis-isomer and trans-isomer of a metal complex of the type MX_4Y_2 (X and Y are monodentate) or MZ_2Y_2 where Z is bidentate ligand and Y is monodentate ligand.

Solution The trans-MX_4Y_2 has tetragonally-distorted octahedral (square-pyramidal) symmetry. In the case of cis-MX_4Y_2, the octahedral symmetry of the regular complex is expected to suffer rhombic distortion. Therefore, the trans isomer belongs to the D_{4h} point group and the cis isomer to the C_{2v} group. The lowering of the symmetry of the cis molecule produces more number of infrared active vibrations. Several normal vibrations, which are not active according to the selection rules in a molecule with D_{4h} symmetry (trans), become active in a molecule with C_{2v} symmetry (cis). Therefore, the infrared spectrum of cis-MX_4Y_2 has more bands than the spectrum of trans-MX_4Y_2.

These arguments are valid also for the isomers of MZ_2Y_2.

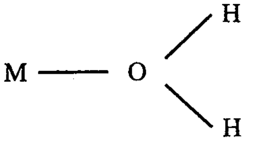
For example, for the trans-[Co(biby)$_2$Cl$_2$]Cl, the infrared spectrum consists of seven absorptions; however, for its cis-isomer, the spectrum consists of fourteen absorptions.

Problem 17.3.12 Metal complexes may contain water molecules bound in two different ways:

(1) water coordinated to the metal in the inner sphere as a ligand and
(2) water trapped in the crystal lattice of the complex, attached by weak hydrogen bonds to the anion of the complex, or to the other water molecules present in the inner sphere.

Explain how these two modes of association may be distinguished by a spectral method.

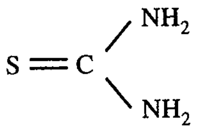
Solution Infrared spectroscopy can be used to distinguish between these two modes of association of water molecules in a complex. When a water molecule is coordinated to the metal, it has the structural unit



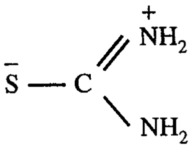
This unit results in a rocking vibration at 900 cm^{-1}, a wagging vibration at 768 cm^{-1} and the M-O stretching vibration at 673 cm^{-1}.

Water molecules accommodated in the crystal lattice of salts are bound by lattice forces and weak hydrogen bonds and produce the normal vibration of the water molecule namely, symmetric and asymmetric OH stretching vibrations (3550 – 3200 cm^{-1}) and the deformation vibration (1630 – 1600 cm^{-1}). The occurrence of hydrogen bonds linking the water molecules to the anions is indicated by the fine structure of the OH stretching band. For example, with $CaSO_4 \cdot 2H_2O$, eight narrow bands between 3500 and 3400 cm^{-1} arise due to the hydrogen bonds. OH_2 ..... SO_4 ..... H_2O.

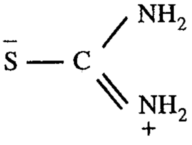
Problem 17.3.13 The ligand thiourea may coordinate in a complex in the form of any one of the following three limiting structures:



(a)



(b)



(c)

K. Swaminathan and H.M.N. Irving (J. Inorg. Nucl. Chem, 26, 1291, 1964) found that the deformation vibrations of the NH$_2$ group of thiourea, recorded at 1617 cm^{-1} and 1086 cm^{-1}, do not change appreciably on coordination to Mn(II) or Co(II). However, the CS stretching band of the free ligand at 730 cm^{-1} is shifted to lower frequencies on complexation. What do these observations indicate?

Solution These two observations indicate that thiourea is coordinated to the metal through its sulphur atom, the two NH$_2$ groups remaining "free" (unbonded to metal) in the complex. If the NH_2 groups were coordinated, then, their deformation vibrations would have been altered in the complex.

Problem 17.3.14 Justify the following ν_{CO} values:

Complex	ν_{CO} cm^{-1}
$[V(CO)_6]^-$	1860
$[Cr(CO)_6]$	2000
$[Mn(CO)_6]^+$	2090

Solution The increasing ν_{CO} indicates increasing C-O bond order (strength). These species are isoelectronic (each with 36 electrons). However, from the V to Mn species, the "positive" charge on the metal increases. Back-donation to π^* orbitals of CO is weaker, the more positive the charge number of the metal. Thus the back-donation order is

$$[V(CO)_6]^- > [Cr(CO)_6] > [Mn(CO)_6]^+$$

Lesser is the back-donation, lesser the electron flow away from the C-O bond and stronger is this bond.

Problem 17.3.15 Explain the following IR data:

Molecule	ν_{CO} cm^{-1}
CO	2145
$Mo(CO)_6$	2000
$Mo(CO)_3(NH_3)_3$	1855
$Mo(CO)_3(PPh_3)_3$	1949

Solution When the CO ligand bonds with a metal, the *d* orbitals of the metal form bonding molecular orbitals with the vacant antibonding π orbitals of CO molecule. The resulting back-donation weakens the C-O bond in the carbonyl relative to the bond in carbon monoxide. This causes a reduction in ν_{CO} from 2145 to 2000 cm^{-1}.

NH_3 is an electron-donor; it supplies electrons to Mo for back-donation to π^* orbitals of CO. This causes further weakening of the C-O bond; thus ν_{CO} decreases to 1855 cm^{-1}.

PH_3 is a weak electron-donor unlike NH_3; therefore, the back-bonding is not appreciable with this ligand.

17.4 MOSSBAUER SPECTROSCOPY

Problem 17.4.1 The Mossbauer spectra of some ^{57}Fe complexes show six lines each (Fig. 17.3); explain.

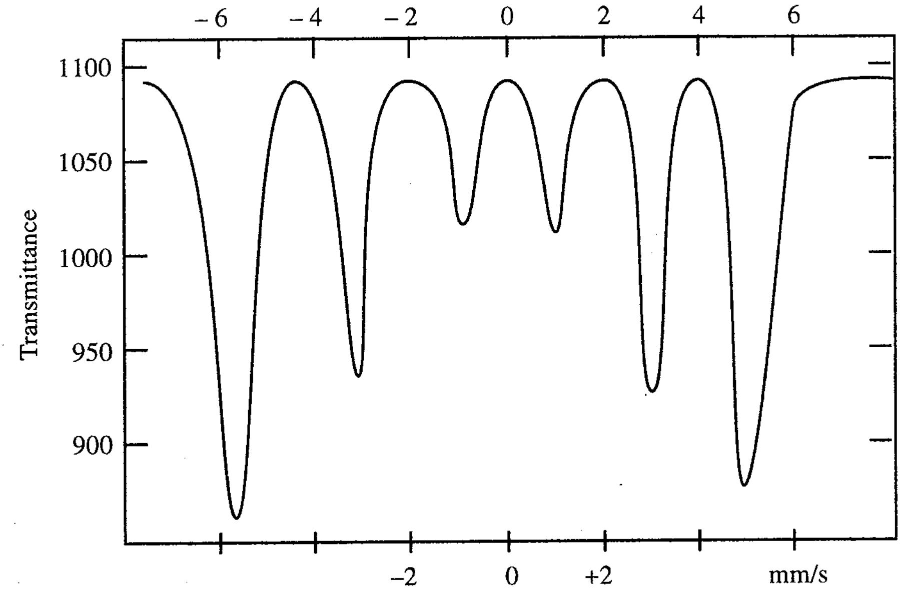


Fig. 17.3 Zeeman splitting of Mossbauer absorption

Solution In addition to the quadrupole splitting, the nuclear energy levels can also be split by the magnetic field produced by the electrons present around the nucleus. In ^{57}Fe, both the ground and the excited states will be split. A total of six lines are expected. Such splittings of spectral lines are called the nuclear Zeeman splittings. In the case of ^{57}Fe, there is an internal magnetic field experienced by the Fe nucleus. In the metallic ^{57}Fe, the magnetic field has been calculated to be 3.3×10^5 Gauss.

In a compound, when no such internal field exists, a field can be applied externally which would then cause nuclear Zeeman splittings in its spectrum.

Problem 17.4.2 Low and high spin complexes can be distinguished by Mossbauer spectroscopy; explain this statement.

Solution The nature of the occupancy of the *d* electrons in a metal influences the extent of electric field gradient at the Mossbauer nucleus. For example, the Fe^{2+} ion has six *d* electrons in the outer shell. In a strong octahedral field, its configuration is t_{2g}^6; but in a weak field the configuration is $t_{2g}^4 e_g^2$. Thus, in octahedral iron complexes, the charge distribution around the iron nucleus is of lower symmetry in the case of a weak field. Therefore, the quadrupole splittings of weak field complexes are much greater than those of strong field complexes. Therefore, the values of Mossbauer spectra can distinguish between these two types of complex of a metal.

Problem 17.4.3 Explain the following Mossbauer spectra represented in Fig. 17.4

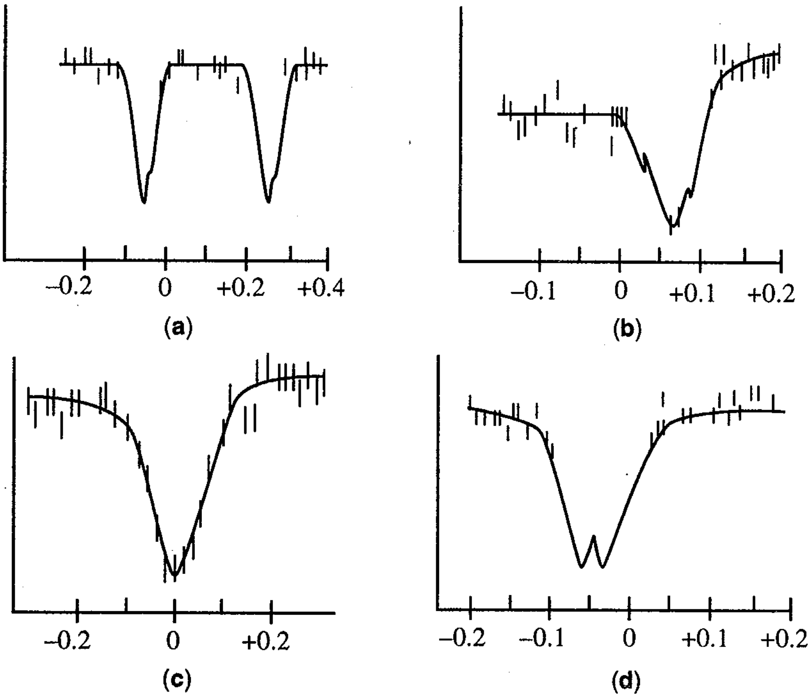


Fig. 17.4 *Mossbauer spectra of a)* $FeSO_4.7H_2O$ *b)* $FeCl_3$ *c)* $K_4Fe(CN)_6.3H_2O$ *d)* $K_3Fe(CN)_6$

Solution

a) $FeSO_4 \cdot 7H_2O$

In this salt, iron(II) has a spin-free electron configuration (d^6). The electric field around the iron nucleus is not spherical; therefore, there is a field gradient at the nucleus. This field gradient produces quadrupole splitting and consequently the Mossbauer spectrum is split into two peaks.

b) $FeCl_3$

The iron in $FeCl_3$ has d^5 electron configuration; each of its five d orbitals has one electron. Such an arrangement provides the iron nucleus with a spherical electric field. In this system, no electric field gradient at the nucleus exists and therefore the spectrum is not split.

c) $K_4[Fe(CN)_6]$

The CN^- is a strong-field ligand and therefore the electron configuration for Fe in this complex is $t_{2g}^6 e_g^0$; it is a spin-paired complex. The electric field at the iron nucleus has spherical symmetry and consequently there is no quadrupole splitting. The Mossbauer spectrum of each of the iron(II) strong field ligands (six equivalent ligands) consists of a single sharp resonance line.

d) $K_3[Fe(CN)_6]$

The electron arrangement in Fe in this complex is $t_{2g}^5 e_g^0$, which produces an electric field gradient at the iron nucleus. Therefore, quadrupole splitting is possible. The spectrum of each of the iron (III) strong field ligands (6 equivalent ligands) consists of a pair of peaks due to quadrupole splitting.

Problem 17.4.4 Explain why the Mossbauer spectrum of $[Fe(CN)_6]^{4-}$ shows a single resonance absorption but that of $[Fe(CN)_5NH_3]^{3-}$ shows a pair of resonances.

Solution In $[Fe(CN)_6]^{4-}$, the six ligands are equivalent and therefore, there is no electric field gradient at the iron nucleus. However, in $[Fe(CN)_5NH_3]^{3-}$, the six ligands are not identical; this produces an electric field gradient at the nucleus and hence a quadrupole splitting of the spectrum.

Problem 17.4.5 Explain the Mossbauer spectra represented by Fig. 17.5.

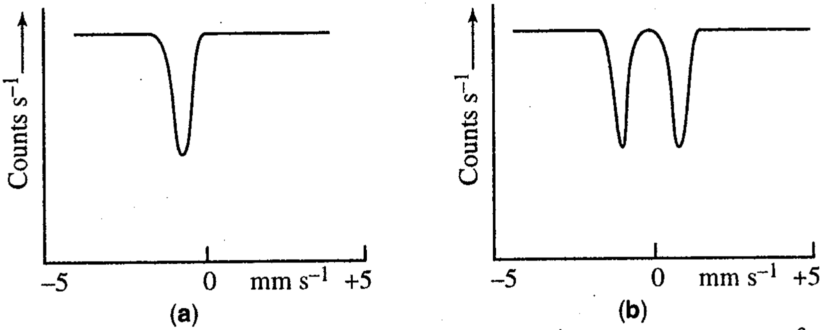
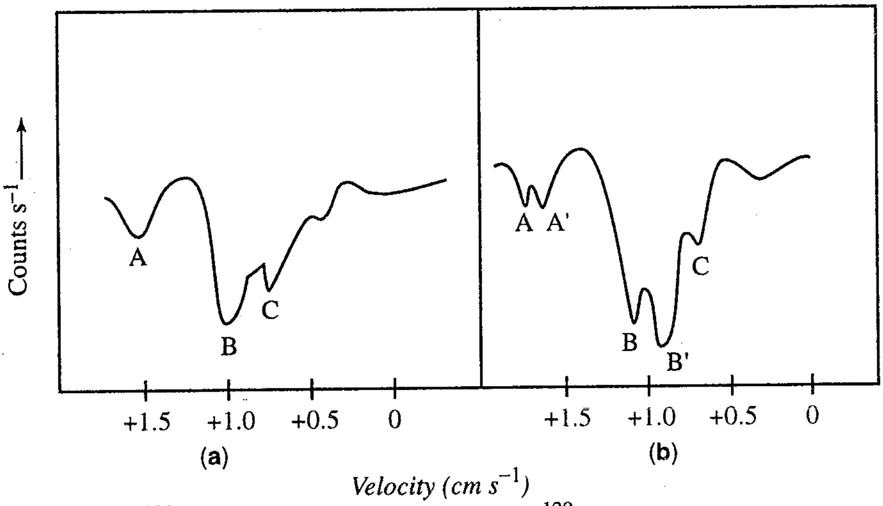


Fig. 17.5 The Mossbauer spectra of a) $[Fe(CN)_6]^{4-}$ *b)* $[Fe(CN)_5NH_3]^{3-}$

Solution The electric field around the Fe nucleus in $[Fe(CN)_6]^{4-}$ is symmetrical; therefore, there is no net field gradient at the iron nucleus. Thus its Mossbauer spectrum has a single absorption without any splitting.

When one of the CN^- ligands is replaced by the NO group, the symmetrical electric field is lost; the NO produces an internal field. (NO group is electronically different from the CN^- group). Then electric field splits the spectrum. In this example, the electric field gradient existing in the system itself produces splitting of the spectrum.

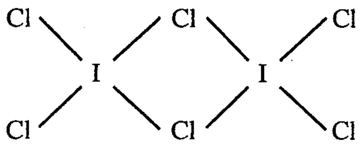
Problem 17.4.6 Explain the following Mossbauer spectra (Fig. 17.6):



a) Partial ^{129}I spectrum of I_2Cl_6 b) Partial ^{129}I spectrum of $I_2Br_2Cl_4$

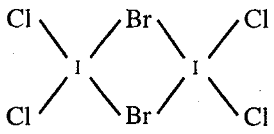
Fig. 17.6

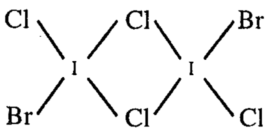
Solution The spectrum of $I_2Br_2Cl_4$ on comparison with that of I_2Cl_6 indicates that the two iodine atoms in $I_2Br_2Cl_4$ are in different environments (unlike the iodine atoms in I_2Cl_6). The structure of I_2Cl_6 can be written as

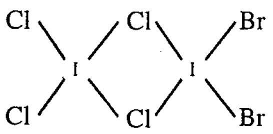


In this structure, the two iodine nuclei have identical environments.

Based on the bridged structure of I_2Cl_6, three possible structures for $I_2Br_2Cl_4$ may be considered:


(a)


(b)


(c)

Structure (a) and (b) are symmetrical and the two iodines in them are in identical environments. Then, there can be no splitting of the absorption peaks. On the other hand, in structure (c), the iodine atoms are structurally inequivalent and hence the spectrum, as observed, consists of two separate signals,one for each iodine nucleus.

Note: Separate signals are quite different from 'split' signals.

Problem 17.4.7 Which of the two, cis- $Fe(CO)_4Cl_2$ or trans- $Fe(CO)_4Cl_2$ would have the larger quadrupole splitting for iron?

Solution Both the cis- and trans- geometries involve asymmetric electron arrangement (non-spherical) at the iron nucleus. The electronegative character of the Cl ligands is expected to make the Fe–Cl bonds polar and consequently introduce asymmetry in the electron cloud around the iron nucleus; both the isomers should show quadrupole splitting in the spectrum. Such an electron cloud asymmetry is more in the cis-isomer than in the trans-isomer and therefore the quadrupole splitting should be more in the cis-isomer than in the trans-isomer.

For similar reason, the quadrupole splitting in the cis- $[Fe(NH_3)_4Cl_2]$ should be larger than that in trans - $[Fe(NH_3)_4Cl_2]$.

The Mossbauer spectra of the cis-isomer and trans-isomer of octahedral MA_2B_4 are characteristically different. The geometry of the isomer influences the electric field gradient at the central metal atom M. Generally, this gradient values in the cis-isomer and trans-isomers are in the ratio 1 : 2 and of opposite sign. For example, for ^{57}Fe resonance in cis-isomer and trans-isomer $FeCl_2$ $(p\text{-}MeO \cdot C_6H_4 \cdot NC)_4$, the chemical shift $\delta = -0.83$ and $+1.59$ mm s^{-1} respectively.

Problem 17.4.8 Interpret the following Mossbauer spectrum (Fig. 17.7) obtained for $Fe_3(CO)_{12}$.

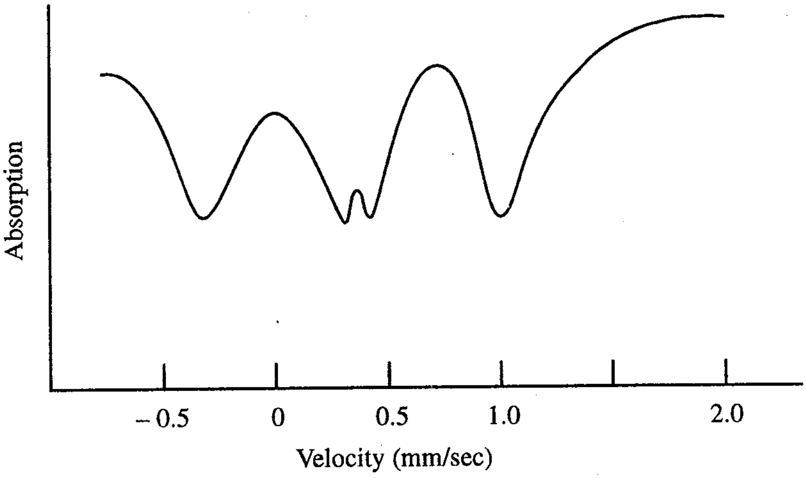


Fig. 17.7 The Mossbauer spectrum of $Fe_3(CO)_{12}$

Solution This spectrum indicates the presence of more than one type of iron in the structure of the carbonyl (The multiple asymmetric absorption peaks are not of the type expected only because of quadrupole splitting).

The outer two peaks can be assigned to one type of iron (an absorption, split into two due to a large quadrupole effect).

The inner two peaks can be assigned to a second type of iron (an absorption, split into two due to a small quadrupole effect).This Fe nucleus is in a more symmetrical environment compared to the other two Fe nuclei.

The structure of this carbonyl consistent with its Mossbauer spectrum (and also supported by its X-ray spectrum) is represented in Fig. 17.8.

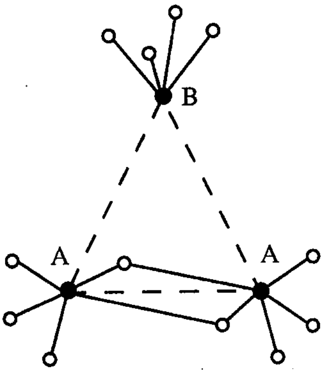


Fig. 17.8 Structure of $Fe_3(CO)_{12}$

The following are the actual data obtained from its spectrum at 80 K:

Outer doublet	Inner doublet
$\Delta E_Q = 1.13 \quad \delta = +0.11$	$\Delta E_Q \approx 0 \quad \delta = +0.05$

Problem 17.4.9 Justify the following Mossbauer data:

System	Quadrupole splitting ΔE_Q (mm s^{-1})
a) $Na_3[Fe(CN)_5NH_3]$	0.60
b) $Na_2[Fe(CN)_5NO]$	1.76
c) $FeCl_2 \cdot 4H_2O$	3.00

Solution In all the three systems, the electric field at the nucleus is not spherical and therefore quadrupole splittings occur in their spectra. These quadrupole splittings are roughly related to the differences in the *d*-orbital populations.

In (b), there is an extensive π bonding between the odd electron in the t_{2g} set of orbitals of iron and the odd electron on nitrogen (NO). More of the π electron density is localised on nitrogen because of this π bonding. In this situation, the electric field gradient at the iron nucleus is very large and therefore the quadrupole splitting in the metal complex is large. Essentially, the large quadrupole splitting is the result of very extensive π bonding in the Fe – N – O link.

The Fe in $FeCl_2 \cdot 4H_2O$ has a d^6 electron configuration. The *d* orbitals are degenerate and have asymmetric electron distribution; this is expected to produce a large electric field gradient at the iron nucleus and hence it results in a very large quadrupole splitting.

Problem 17.4.10 The Mossbauer spectrum of $Fe(CO)_5$ is depicted in Fig. 17.9. Interpret it.

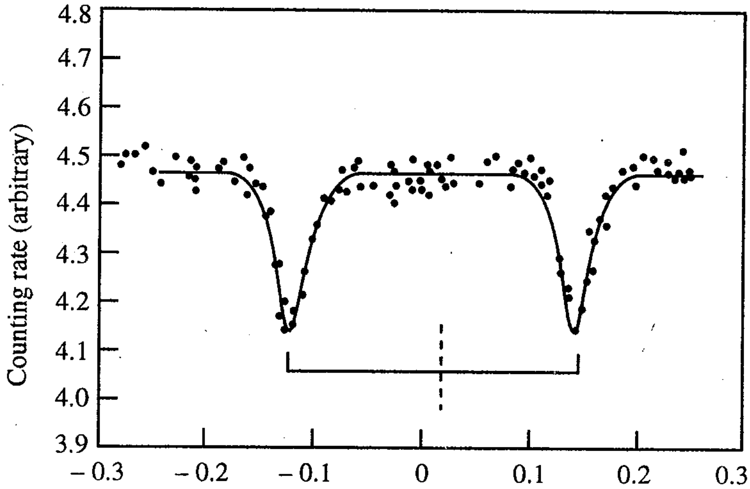


Fig. 17.9 Mossbauer spectrum of $Fe(CO)_5$

Solution This spectrum consists of a doublet; this indicates the existence of a field gradient at the nucleus. The excited energy state of Fe nucleus must obviously be split by the field gradient. This is expected of an asymmetric trigonal bipyramidal geometry, as in iron pentacarbonyl.

Problem 17.4.11 For $[Fe(CN)_5L]^{n-}$, the Mossbauer isomer shifts have been found to decrease in the series L = NH_3 > PPh_3 > SO_3^{2-} > CN > CO. Explain.

Solution The decreasing isomer shift in the series must be due to decreasing *s* electron-density experienced by the Fe nucleus. The back-donation of *d* electrons to the ligand reduces the shielding of the *s* electron from the Fe nucleus. The back - donation increases from the NH_3 complex to CO complex and hence the shielding decreases; this leads to decreasing isomer shift.

Problem 17.4.12 Rationalize the following Mossbauer spectra data:

Complex	Isomer shift, mm s^{-1}
$(Et_4N)_2SnBr_4F_2$	0.53
$(Et_4N)_2SnBr_4Cl_2$	0.77
$(Et_4N)_2SnBr_6$	0.84
$(Et_4N)_2SnBr_4I_2$	0.96

Solution Isomer shifts are caused by changes in *s* electron-density at the nucleus and are independent of the population of other atomic orbitals. Therefore, the isomer shifts can be interpreted in terms of changes in atomic charge, only for compounds with similar structures and orbital hybridisations.

The isomer shift increases from the fluoro complex to the iodo complex. This trend can be correlated with the decreasing electron-withdrawing abilities of the coordinated halide ions from F^- to I^-.

With the least electron-withdrawing iodide, the *s* electron density at the Sn nucleus should be the maximum and hence the isomer shift is the maximum.

17.5 ELECTRON SPIN RESONANCE SPECTROSCOPY

Problem 17.5.1 The electron spin resonance spectrum of $[IrCl_6]^{2-}$ in solid solution in a single crystal of $Na_2[PtCl_6]\cdot 6H_2O$ has a complex pattern. Explain.

Solution The complex pattern of the ESR spectrum indicates the occurrence of hyperfine splitting. It occurs when a paramagnetic species is near a nucleus with a spin *I*; then interaction between the nuclear spin and the electron spin causes the absorption to be split into $(2I + 1)$ components.

I for iridium nucleus = 3/2

∴ a quartet by the Ir nucleus is expected.

The isotopic chlorine nuclei, ^{35}Cl and ^{37}Cl would then split the quartet further, each Cl having *I* value of 3/2, leading to a complex spectral pattern.

The ESR spectrum of this complex indicates electron-transfer between iridium and chlorine atoms; the unpaired electron of Ir is delocalized. Such delocalization of electrons implies covalency in metal-ligand bonds.

Problem 17.5.2 Explain the following EPR spectral data:

Complex	Coupling constant of Cu	Coupling constant of N
copper salicylaldoxime	91.2	14.3
copper 5-chlorosalicylaldoxime	90.4	14.3

Solution The coupling constant in an EPR spectrum is proportional to the residence probability of the electron concerned in the immediate vicinity of the atomic nucleus.

The decrease in the copper coupling constant in the chloro-substituted complex indicates that the electron residence probability on copper is less than that in the unsubstituted complex. This can be explained based on the electron withdrawing nature of the chloro group; this nature is likely to enhance electron displacement in the direction metal → ligand; the back-donation is increased; thus the electron residence probability on copper is reduced. The nitrogen coupling constants remain the same indicating that the chloro group has no effect on the electron residence on nitrogen.

Problem 17.5.3 The EPR spectrum of a single crystal of the copper(II) complex of 5-chlorosalicylaldoxime is given below (Fig. 17.10). Interpret it.

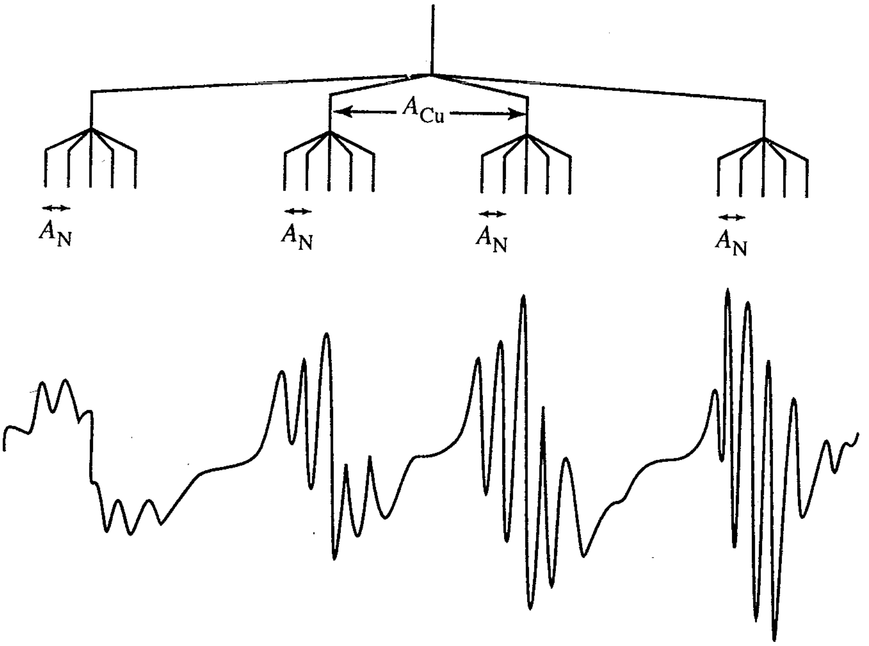


Fig. 17.10 EPR spectrum of Cu(II) 5-chlorosalicylaldoxime

Solution The EPR spectrum of the complex consists of four groups of absorptions; each group consists of five lines.

The integral spectrum shows identical intensities of the groups. Within each group, the spacings between the lines are equal, while their intensity ratio is 1 : 2 : 3 : 2 : 1. This fact indicates that these five lines are due to equivalent atomic nuclei.

Nuclei of identical type and equal coupling constants contributing to the EPR spectrum are called *equivalent atomic nuclei.* When a molecule has *n* equivalent nuclei, then $(2nI + 1)$ lines of equal spacing result in the EPR spectrum. As in this spectrum, there are five such lines in each absorption group, *n* should be equal to 2. These two nuclei should be the two nitrogen nuclei located in the immediate vicinity of the copper ion. (the spin of the nitrogen nucleus I = 1; hence, the number of lines $= 2 \times 2 \times 1 + 1 = 5$).

The residence probability of the electron at these atomic nuclei is proportional to the coupling constant A_N.

The spacing between the corresponding lines in the four groups of absorption lines is equal. As the intensities of the four groups are identical, they must arise due to one single atomic nucleus.

The signal due to the two nitrogens (5 lines) is split by this single atomic nucleus into $(2I + 1)$ signals; as $(2I + 1) = 4$, the spin *I* should be 3/2. The only atomic nucleus in the complex meeting this spin requirement is copper.

The spacing between the groups of lines, (the coupling constant, A_N) is proportional to the residence probability of the electron in the immediate vicinity of the copper nucleus.

Problem 17.5.4 The electron paramagnetic resonance spectroscopy is well-suited for distinguishing between Cu(I) and Cu(II) in complexes. Explain.

Solution The Cu(II) with d^9 configuration has an odd electron and therefore it would produce an EPR signal. On the other hand the Cu(I) species with d^{10} configuration and complete electron pairing will not produce any EPR signal.

In a Cu(I) complex, ligands with nuclei having non-zero spins (such as nitrogen or chlorine) will cause hyperfine splittings; such splittings will be proportional to the number of non-zero-spin-nuclei bonded to Cu(II).

17.6 MASS SPECTROMETRY

Problem 17.6.1 A carbonyl halide produces a mass spectrum with *m/z* values 195 (parent), 167, 139, 111, 83, 55, 67 and 16. The peak at *m/z* = 67 corresponds to the metal carbide in which the atom ratio (metal : carbon) is 1 : 1. Find out the formula of the carbonyl halide. What would be the intensity of the (M+2) peak assuming that the metal involved is isotopically pure?

Solution Let the formula of the carbonyl halide be $M(CO)_nX_y$

Where M = metal
n = number of CO ligands
X = halogen
y = number of halide ligands.

The peak with *m/z* = 195 differs from the parent peak by a mass unit of 35. Therefore X must be chlorine. If there are more than one chloride ligand in the complex, successive peaks differing by *m/z* = 35 would be obtained. The absence of such data indicates that there is only one chloride ligand in the complex. Therefore, *m/z* = 195 represents the ion $[M(CO)_n]^+$. The peaks at *m/z* = 167, 139, 111, 83 & 55, differing by successive $m = 28$ units indicate the loss of 5 CO ligands. This indicates that $n = 5$. The $m/z = 55$ should correspond to the metal ion Mn^+. The formula of the carbonyl halide is $Mn(CO)_5Cl$. The peak at $m/z = 67$ is likely to be that of $MnCl^+$ and that at $m/z = 16$ that of $^{16}O^+$. The relative intensity of M : M+2 peak would then be 100: 32 due to Cl-37.

Problem 17.6.2 For the mass spectrum of $Fe_2(CO)_9$, an ion $m/z = 224$ occurs. Identify this ion.

Solution

Mass of Fe = 55.8

Mass of CO = 28

The high m/z value of the ion indicates that it is a big fragment consisting of several CO groups and one or both of the Fe atoms.

If it contains one Fe then the number of CO in it should be $(224 - 56) / 28 = 6$.

Then, the ion could be $[Fe(CO)_6]^+$.

If it contains two Fe atoms, then the number of CO in it should be $(224 - 112) / 28 = 4$.

Then, the ion could be $[Fe_2(CO)_4]^+$.

The choice between these two can be made from the isotope peaks corresponding to the three isotopes of iron atom. The relative intensities of the isotope peaks for the $[Fe_2(CO)_4]^+$ would be twice those of the $[Fe(CO)_6]^{+\cdot}$ peaks.

Problem 17.6.3 Edgell and Risen (J. Am. Chem. Soc., 88, 5451, 1966) obtained the following mass spectral data for $HMn(CO)_5$. Guess the fragmentation pattern for this carbonyl hydride.

Solution

m/z :	196	195	168	140	112	84	56	55
			167	139	111	83		

4 sets of m/z values, each set differing by 1 unit indicates that the 4 CO groups are fragmented stepwise through two routes, one a H-containing species and the other without H.

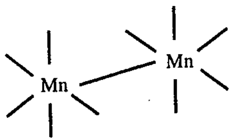
The data may be accounted based on the following schemes of fragmentation:

a) $\underset{196}{[HMn(CO)_5]^+} \rightarrow \underset{168}{[HMn(CO)_4]^+} \rightarrow \underset{140}{[HMn(CO)_3]^+} \rightarrow \underset{112}{[HMn(CO)_2]^+} \rightarrow$
$\underset{84}{[HMn(CO)]^+} \rightarrow \underset{56}{[MnH]^+} \rightarrow \underset{55}{Mn^+}$

b) $\underset{196}{[HMn(CO)_5]^+} \rightarrow \underset{195}{[Mn(CO)_5]^+} \rightarrow \underset{167}{[Mn(CO)_4]^+} \rightarrow$
$\underset{139}{[Mn(CO)_3]^+} \rightarrow \underset{111}{[Mn(CO)_2]^+} \rightarrow$
$\underset{83}{[Mn(CO)]^+} \rightarrow \underset{55}{Mn^+}$

Problem 17.6.4 Predict the m/z values of fragments expected in the mass spectrum of $Mn_2(CO)_{10}$.

Solution The structure of this binuclear carbonyl is given below:



It has an Mn-Mn bond and therefore it is expected to fragment into both binuclear and mononuclear ions. Progressive losses of CO from both the types of ions are possible:

$$\begin{tikzcd}
\underset{390}{Mn_2(CO)_{10}} \arrow[r, "-CO"] \arrow[dd] & \underset{362}{[Mn_2(CO)_9]^+} \arrow[r, "-CO"] \arrow[dr] & \underset{334}{[Mn_2(CO)_8]^+ \text{ etc.}} \arrow[r] & \underset{110}{Mn_2^+} \\
 & & {[Mn(CO)_5]^+ + [Mn(CO)_4] \text{ etc.} \rightarrow} & \\
\begin{array}{c} [Mn(CO)_5]^+ \\ 195 \\ + \\ Mn(CO)_5 \end{array} \arrow[r, "-CO"] & \underset{167}{[Mn(CO)_4]^+ \text{ etc.}} \arrow[r] & \underset{55}{Mn^+} &
\end{tikzcd}$$

(From : *Accounts Chem. Res.*, 245, 1968).

A binuclear carbonyl can decompose, to give ultimately the ions M^+ and M_2^+. The cleavage of the M-M bond depends upon the metal; heavier the metal, more easy is this cleavage.

Glossary

Acido is a term which refers to anionic ligands. Examples: Cl^- and $C_2O_4^{2-}$

Agostic is a term which denotes covalent interactions between carbon-hydrogen groups and transition metal centres in organometallic compounds; in such a structure, a hydrogen atom is bonded simultaneously to both a carbon atom and to a transition metal ion.

Ambidentate ligands are the ligands having two points of attachment but attached to the central metal ion through only one of the two donor atoms at a time. For example, NO_2^- ligand can attach itself either through nitrogen atom as $-NO_2$ or through oxygen atom as –ONO. The other examples include SCN^-, CN^-, $SeCN^-$ etc.

Ammine ligand is NH_3 (different from amine which refers to the $-NH_2$ group in organic compounds).

Anation reaction is a reaction in which an anion replaces a coordinated solvent molecule from a solvated metal ion, in a solution. For example,

$$[Co(H_2O)_6]^{3+} + Br^- \longrightarrow [Co(H_2O)_5Br]^{2+} + H_2O$$

Antibonding molecular orbital results from subtraction of the parts of the atomic orbitals that overlap, and it does not include the region in space between the nuclei. It has a greater energy than the original atomic orbitals..

Aquation reaction with a metal complex involves the replacement of one or more ligands in it by H_2O molecules; e.g.

$$[Co(NH_3)_5L]^{3+} \xrightarrow[-L]{+H_2O} [Co(NH_3)H_2O]^{3+}$$

where L is a neutral ligand. L may be anionic also.

Bidentate ligand is a ligand that attaches itself to the same central metal through two donor atoms simultaneously. e.g., ethlenediamine, $H_2N-CH_2-CH_2-NH_2$.

A ***biphilic ligand*** is one which has the ability to donate electrons to the metal and also the ability to accept electrons from the metal, e.g., NO_2^- and PR_3.

Blue copper proteins are copper(II) complexes which function as electron transfer redox systems.

Bonding molecular orbital results from the addition of the parts of the atomic orbitals that overlap includes the region of space between the two nuclei. It is of lower energy than either of the two atomic orbitals.

A ***bridging ligand*** is a ligand attached to two metals simultaneously; such a complex is called a polynuclear complex or bridged complex.

Catalase is an enzyme which contains four Fe(III)-heme groups per molecule; it catalyses the decomposition of H_2O_2 in living cells.

Charge transfer spectrum is the spectrum arising in a complex due to transfer of charge, $L \rightarrow M$ or $M \rightarrow L$

A ***chelate*** is a complex with a closed structure formed between a metal ion and a polydendate ligand.

The ***chelate effect*** is the enhancement of the stability of a metal complex when the ligand forms a ring structure with the metal. (The stability of the chelate is more than that of an analogous non-chelated complex of the same metal. For example $[Ni(en)_3]^{2+}$ is more stable than $[Ni(NH_3)_6]^{2+}$)

Chlorophyll is a magnesium complex with tetrapyrrole belonging to the porphyrin family but with some significant modifications to the porphyrin ring.

Cis-effect is the effect of certain ligands such as the thiocyanate and hydroxide ions in greatly accelerating the hydrolysis of a complex when they are cis to the leaving group as compared to the analogous reaction in which the leaving group is in the trans-position.

Cis-trans **isomerism** is a type of isomerism in which the metal complexes (and also in other types of molecules) involving the ligands occupy different types of positions around the central atom. When the ligands are next to one another, the isomer is called the *cis*-isomer and when they are opposite to each other, the isomer is called the *trans*-isomer.

Complementary reactions are a type of redox reactions where the oxidant and the reductant change their oxidation states by an equal number of units. Only one molecule of each reactant is involved in the stochiometric equation; for example,

$$Co^{3+} + Cr^{2+} \longrightarrow Co^{2+} + Cr^{3+}$$

Complexometric titration is a titration employing a complexing agent as the titrant.

The ***coordinate bond*** is the bond formed between a ligand and a metal ion, where both the electrons required for bonding are contributed by the ligand.

Coordination chemistry deals with the chemistry (preparation, properties, structures and uses) of coordination compounds.

Coordination compound is a substance containing complex metal ions.

Coordination isomerism is exhibited by certain coordination compounds having both a complex cation and complex anion; an interchange of ligands between the two complex ions produces isomers with the same composition.

Coordination number is the number of positions available for the attachment of ligands to the central metal ion.

The ***coordination sphere*** is the region around a metal ion where linkage to ligands can occur to form a complex ion.

Crystal field effects refer to the stabilization of the transition metal complexes due to CFSE; these effects are responsible for the natural order of stability of complexes of the first-row transition metals.

Crystal field splitting is the conversion of five degenerate *d*-orbitals of the free metal ion into groups of *d*-orbitals having different energies.

Crystal field stabilization energy is the amount of energy by which the complex is stabilized over a complex that is predicted by the simple electrostatic model.

The ***crystal field theory*** was first recognized and used by the physicists Van Vleck and Bethe in 1930 to explain the colours and magnetic properties of crystalline solids, and later applied to coordination compounds.

Cytochromes contain heme-like prosthetic groups and they assist electron transfer reactions.

d-d transition is transition of electrons between lower energy and higher energy *d*-orbitals in presence of ligand field in a complex; such transitions are responsible for the UV and visible spectra of the complex.

Degenerate orbitals have the same energy.

Demasking is the process in which the masked substance regains its ability to enter into a particular reaction.

The ***Dewar–Chatt–Duncanson*** concept explains the bonding in metal-alkene complexes by including the π bonding, between filled metal orbitals and empty π^* orbitals of the alkene; in this model the *p* electrons of the metal are donated to the ligand orbitals for additional bonding.

Diamagnetic complex is not attracted to a magnet. It has no unpaired electrons.

A ***double salt*** is a compound which is an aggregate of two distinct salts; such a salt exists only in the solid state; it breaks completely into the constituent molecules or their ions in solutions;
eg; $K_2SO_4.Al_2(SO_4)_3.24\ H_2O$

Effective atomic number (EAN) is the sum of the electrons around the central metal in a complex; the total number of electrons of the metal and the number of electrons contributed by the ligands.

Electroneutrality principle of Pauling predicts that a complex would be most stable when the electronegativity of the ligand is such that the metal achieves essentially zero net electrical charge.

Electronic transitions, *d-d*, are transitions between terms that represent rearrangements of the *d* electrons. Most peaks appear in the near infra-red and visible ranges of the spectrum; sometimes these peaks even out into the ultra violet region. They are normally found between about 6000 cm^{-1} and 40,000 cm^{-1} depending on the identity of the metal, its oxidation state and the nature of the ligands. In wavelength terms, this corresponds to 250-1600 nm, a convenient range for available instrumentation.

Electron transfer reactions in complexes involve the transfer of one or two electrons from one complex (reducing agent) to the another (oxidising agent). The mechanism of such a reaction follows either an *outer-sphere activated complex* mechanism *or atom transfer, bridged activated* (inner-sphere) mechanism.

Entropy of a system is a measure of the amount of disorder in that system.

Enzymes are physiological catalysts.

Ferredoxins are electron transfer agents. These proteins are found only in lower organisms. They are important in the nitrogen fixation mechanism of plants.

A ***fluxional complex*** can exist in two isomeric forms, the interconversion between the two isomers involving very little energy. This phenomenon is called *fluxional isomerism.*

Geometric isomerism is a type of isomerism by which two identical groups in a complex may be adjacent or opposite to each other producing two different isomeric complexes.

Haemoglobin transports oxygen from its source such as lungs, gills or skin to the site of use inside the muscle cells. There the oxygen is transferred to myoglobin for use in respiration.

A ***half-sandwich complex*** consists one cyclic ligand (such as a cycloalkene) coordinated to a metal along with other non-ring ligands.

Hapticity is the number of ligand atoms that are simultaneously bonded to a metal centre in a complex. It is represented as η^x, where x denotes ligand hapticity.

Hapto from the Greek word *haptein* which means "*to fasten*". Hapticity of a ligand denotes the number of ligand atoms formally bound to the metal. For example in ferrocene, the cyclopentadienyl ligand is attached to the central iron(II) through all the five carbon atoms. Hence cyclopentadienyl ligand is a *pentahapto ligand.*

A ***high spin complex*** has electron distribution of the central metal ion similar to that found in the isolated metal ion.

Hydration isomerism is a type of isomerism exhibited by metal complexes; isomers are formed by the replacement of a coordinated group by water of hydration. For example $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2H_2O$ are hydration isomers.

The ***inner orbital complex*** is one in which the metal uses its "*inner*" (n-1)*d* orbitals for bonding with the ligands. Some organic ligands possess both salt forming groups and neutral donor groups and can, therefore, through chelate ring formation satisfy the primary valencies and coordination number of the central metal in a complex. Such a complex is an *inner complex.*

Inert complex is a complex in which the ligands cannot be easily substituted by some other ligands.

Inner sphere mechanism of electron transfer involves ,making and breaking of bonds, a ligand acting as bridge for electron transfer.

(The ligands directly bonded to the metal are said to be in the ***inner coordination sphere*** and the counter ions that balance the charge remaining on the complex after the coordination number of the central metal has been satisfied are said to be in the *outer coordination sphere*. For example, in $[Co(NH_3)_4Cl_2]NO_3$, four NH_3 and two Cl^- are said to be in the inner coordination sphere and NO_3^- is said to be in the outer coordination sphere.)

Insertion reaction is a reaction in which a ligand is inserted into a metal-ligand bond that is already present. For example

$$[CH_3 - Mn(CO)_5] + PPh_3 \longrightarrow [CH_3CO - Mn(CO)_4(PPh_3)]$$

A carbonyl ligand is inserted into Mn-CH_3 bond that is already present.

The ***instability constant*** of a complex is the reciprocal of its stability constant (1/K).

Ionization isomerism is a type of isomerism shown by certain complexes by which two or more complexes have the same molecular formula but different structures obtained through exchange of groups between the complex ion and the ions outside it; for example,

$$[Co(NH_3)_5Br]SO_4 \text{ and } [Co(NH_3)_5SO_4]Br$$

Isomers are compounds having the same molecular formula but different properties due to difference in their structures. This phenomenon is called *isomerism*.

Jahn-Teller distortions are distortions of symmetrical structures of metal complexes resulting from partially filled electronic energy levels (*d* sublevels).

Labile complex is a complex whose ligands can undergo rapid exchange with other ligands.

A ***ligand*** is a group that is coordinated (bonded) to the central metal in a complex compound.

Ligand field theory is a modified crystal field theory that includes the possibility of covalent bonding in metal complexes.

Linkage isomerism is a type of isomerism exhibited by certain metal complexes when one or more ligands are bonded differently to the metal.

A ***low-spin complex*** is a complex in which some of the unpaired electrons of the metal ion have been forced to pair.

Masking is the process in which a substance, without physical separation of it from a system is so transformed that it does not enter into a particular reaction; by this the interference by the substance in the detection or separation or estimation of another substance is achieved. This process is called also as *sequesteration*.

Masking agent is a substance which effects masking or sequesteration.

Metal ammines are coordination compounds formed between metal ions and NH_3 ligands e.g., $[Cu(NH_3)_4]SO_4$

Metal carbonyls are complexes formed by metals with CO molecules.

Metal complexes are coordination compounds.

Metallocenes are organometallic compounds such as $Fe(\eta^5 - C_5H_5)_2$ which participate in reactions similar to those of aromatic compounds.

Mixed ligand complex is a complex in which a metal is bonded to two different kinds of ligands, they are also called ternary complexes;
e.g., $[Cr(NH_3)_5H_2O]Cl_3$

Mixed valence complex contains a metal in two of its oxidation states; e.g., Prussian blue, $Fe_4[Fe(CN)_6]_3$

Multidentate ligand is a ligand which has the capacity to attach to the central metal ion through more than one point of attachment. For example, ethylenediamine, $H_2N-CH_2-CH_2-NH_2$, can attach itself to the central metal ion through its two nitrogen donors.

Nephelauxetic effect is an indirect evidence for sharing of electrons between ligands and the central metal-ion.

Nonbonding molecular orbitals are the orbitals that are not used for mixing of atomic orbitals to form bonding and anti-bonding molecular orbitals.

Non-complementary reactions are the redox reactions where the oxidant and the reductant change their oxidation states by different number of units. Different number of molecules of oxidant and reductant must be involved in the stochiometric equation. For example,

$$2\,Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$

Optical isomers are the complexes whose aqueous solutions rotate the plane of plane polarised light either to the right or to the left. The optical isomer that rotates the plane of light to the right is called the dextro isomer and the one that rotates to the left is called the ***laevo isomer***. This phenomenon is termed as *optical-isomerism.*

Organometallic compounds are compounds formed between metals and organic groups; $LiCH_3$, CH_3MgBr and $(C_5H_5)_2Fe$ are examples for this type. In such a compound, the metal is bonded through carbon to an organic molecule, radical or ion.

An ***outer orbital complex*** involves the use of the 'outer' *d*-orbitals by the central metal for bonding with the ligands.

Outer sphere mechanism involves electron transfer from a reductant complex to an oxidant complex, the reaction involving neither bond breaking nor bond formation.

The ***overall stability constant*** of a complex is the product of the step-wise stability constants.

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \times \ldots K_n$$

Oxidative addition involves an increase in the formal oxidation state and coordination number of the central metal in the complex.

Oxo-process is employed to make oxygen-containing compounds from hydrocarbons catalysed by some organometallics.

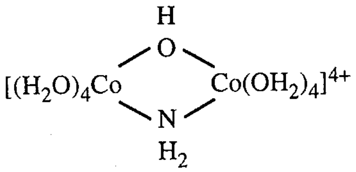
Paramagnetic complex is attracted to a magnet. It has one or more unpaired electrons.

A ***polydendate ligand*** or a multidendate ligand can attach itself to a metal ion, through more than one position of it.

Polymerization isomerism is a type of isomerism exhibited by certain complexes by which two or more complexes have the same empirical formula but different molecular formulae; for example, $[Pt(NH_3)_2Cl_2]$, and $[Pt(NH_3)_4][PtCl_4]$.

A ***polynuclear complex*** is one containing more than one metallic coordination centre joined by bridging groups.

eg.,



Primary valency is the number of charges on the complex ion. For example in $[Co(NH_3)_6]Cl_3$, the primary valence of cobalt is three because the complex ion $[Co(NH_3)_6]^{3+}$ has three positive charges. The primary valencies are ionic and nondirectional unlike the secondary valencies.

Prosthetic group is a species required by an enzyme to facilitate a particular reaction. Such species are also called coenzymes.

Prussian blue is obtained by the reaction of ferrocyanide with ferric solution.

Racah parameter-B denotes interelectron repulsion used in the interpretation of spectra. The parameter makes some allowance for covalency arising from the delocalization of *d*-electrons from the metal into the ligand. If B is reduced below the value for a free metal ion, the *d*-electrons are delocalized into the ligand orbitals. Lower the value of B, greater is this delocalization and greater the covalency.

Redox reactions are the reactions involving both reduction and oxidation. For example,

$$2\,Fe^{3+} + Sn^{2+} \longrightarrow 2\,Fe^{2+} + Sn^{4+}$$

Fe^{3+} is reduced to Fe^{2+} by Sn^{2+} which gets oxidised to Sn^{4+}

Reductive elimination involves a decrease in the formal oxidation state and coordination number of the central metal in the complex.

Reppe's catalyst is a nickel(II) complex, used for the cyclo-oligomerization of alkynes.

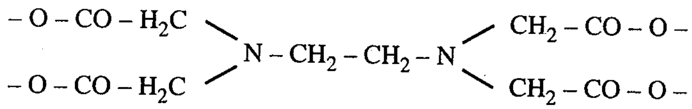
Rubredoxins are non-heme iron-sulphur proteins which participate in several biological redox reactions in anaerobic bacteria.

A ***sandwich compound*** is a metal complex in which a metal atom is bonded (sandwiched) between two flat organic molecules; e.g. ferrocene.

Secondary valency in a complex, is the number of ligands coordinated to the metal. It is called the coordination number. Thus in $[Co(NH_3)_6]Cl_3$, the secondary valencies of cobalt are 6.

A **sequesterant** is a reagent which functions as a masking agent.

Sexadentate ligand is a ligand having six points of attachment. For example, EDTA has six points of attachment to the same central metal ion.



The spectrochemical series is an order of ligand abilities to produce splitting of the *d*-energy level of a central metal in a complex ion.

The stability constant of a complex denotes the extent of stability of a complex and denoted by β.

A *stable complex* has high formation constant.

The step-wise stability constant of a complex denotes the extent of stability of a complex formed in particular step of the complex formation reaction and is denoted by K_1, K_2, K_3 etc.

Strong field ligands are ligands which cause a large crystal field splitting (e.g., NO_2^-, CN^-).

Trans-effect is the labilization of the group trans to certain ligands; such ligands (NO_2^-, Cl^-, etc). have strong trans-directing influence in substitution reactions.

Trans effect order is the arrangement of ligands in their decreasing order of labilization of trans-ligands; this order is:

$$NO_2^- > I^- > Br^- > Cl^- > NH_3 \sim CH_3NH_2 > OH^- > H_2O$$

Turnbull's blue is obtained by the reaction of ferricyanide with ferrous solution.

Two-electron transfer reactions are redox-reactions in which both oxidant and reductant change their oxidation states by two units.

A *unidentate ligand* is one that has only one pair of electrons available for donation to the central metal-ion in a complex. It can attach itself at only one position in the coordination sphere.

An *unstable complex* is one whose equilibrium constant describing its formation is very low.

Vaska's complex is trans-$Ir(CO)(PPh_3)_2$. It is obtained from sodium hexachloroiridate(III) and triphenylphosphine in ethylene glycol under an atmosphere of carbon monoxide.

Vitamin B_{12} – an anti-pernicious anemia factor – has been isolated and crystallised in 1948. It is also known as *cyanocobalamin.* Its molecule is built around a corrin ring, a modified porphyrin ring containing a cobalt(III) ion. The fifth and sixth coordination sites on the cobalt are occupied by a nitrogen atom from an imidazole ring and a cyanide ion.

Wacker's process is the industrial method of converting an olefin into an aldehyde by oxygenating the olefin in presence of $PdCl_2 - CuCl_2$ catalyst system. The reaction involves the intermediate formation of the complex $[Pd(C_2H_4)(OH)Cl_2]^-$

$$CH_2 = CH_2 + 1/2\ O_2 \xrightarrow[CuCl_2]{PdCl_2} CH_3CHO$$

Water gas shift reaction is used for manufacturing hydrogen fuel from non-petroleum sources such as coal catalysed by alkaline solutions of metal carbonyls.

Weak field ligands are ligands which cause only a small degree of crystal field splitting (e.g., Br^- , F^-).

Werner complexes are all complexes that do not contain a metal-carbon bond and all cyanide complexes.

Wilkinson's catalyst is $[Rh\,Cl(PPh_3)_3]$. It is used as a catalyst for the hydrogenation of olefins.

Ziegler-Natta catalyst is a mixture of an alkyl or halide or hydride of an element belonging to the periodic group I or II or III with a compound of a transition element belonging to the periodic group IV or V or VI or VII or VIII. An example is a mixture of $Al(C_2H_5)_3$ and $TiCl_4$.

Zeise's salt is $K[PtCl_3(C_2H_4)]H_2O$. It is obtained as stable yellow crystals when ethylene is bubbled through an aqueous solution of potassium tetrachloroplatinate(II).

$$\underset{\begin{pmatrix}\text{aqueous}\\\text{solution}\end{pmatrix}}{K_2[PtCl_4]} + C_2H_4 \longrightarrow \underset{\begin{pmatrix}\text{yellow}\\\text{crystal}\end{pmatrix}}{K[PtCl_3(C_2H_4)]} + HCl$$

Appendix-A Periodic classification of Elements

1 H 1.0079	IIA																2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.998403	10 Ne 20.179
11 Na 22.98977	12 Mg 24.305											13 Al 26.98154	14 Si 28.0855	15 P 30.97376	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.08	21 Sc 44.9559	22 Ti 47.90	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.70	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.22	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.4	47 Ag 107.868	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.9045	54 Xe 131.30
55 Cs 132.9054	56 Ba 137.33	57 La 138.9055	* 72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.09	79 Au 196.9665	80 Hg 200.59	81 Ti 204.37	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0254	89 Ac 227.0278	† 104 Rf (261)	105 Dp (262)	106 Sg (263)												

*	58 Ce 140.12	59 Pr 140.9077	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.50	67 Ho 164.9304	68 Er 167.26	69 Tm 168.9342	70 Yb 173.04	71 Lu 174.967
†	90 Th 232.0381	91 Pa 231.0359	92 U 238.029	93 Np 237.0482	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Appendix-B Electronic configurations of atoms

Element	Configuration	Term	Element	Configuration	Term
H	$1s^1$	^2S	**I**	$[Kr]4d^{10}5s^25p^5$	^2P
He	$1s^2$	^1S	**Xe**	$[Kr]4d^{10}5s^25p^6$	^1S
Li	$[He]2s^1$	^2S	**Cs**	$[Xe]6s^1$	^2S
Be	$[He]2s^2$	^1S	**Ba**	$[Xe]6s^2$	^1S
B	$[He]2s^22p^1$	^2P	**La**	$[Xe]5d^16s^2$	^2D
C	$[He]2s^22p^2$	^3P	**Ce**	$[Xe]4f^15d^16s^2$	^3H
N	$[He]2s^22p^3$	^4S	**Pr**	$[Xe]4f^36s^2$	^4I
O	$[He]2s^22p^4$	^3P	**Nd**	$[Xe]4f^46s^2$	^5I
F	$[He]2s^22p^5$	^2P	**Pm**	$[Xe]4f^56s^2$	^6H
Ne	$[He]2s^22p^6$	^1S	**Sm**	$[Xe]4f^66s^2$	^7F
Na	$[Ne]3s^1$	^2S	**Eu**	$[Xe]4f^76s^2$	^8S
Mg	$[Ne]3s^2$	^1S	**Gd**	$[Xe]4f^75d^16s^2$	^9D
Al	$[Ne]3s^23p^1$	^2P	**Tb**	$[Xe]4f^96s^2$	^6H
Si	$[Ne]3s^23p^2$	^3P	**Dy**	$[Xe]4f^{10}6s^2$	^5I
P	$[Ne]3s^23p^3$	^4S	**Ho**	$[Xe]4f^{11}6s^2$	^4I
S	$[Ne]3s^23p^4$	^3P	**Er**	$[Xe]4f^{12}6s^2$	^3H
Cl	$[Ne]3s^23p^5$	^2P	**Tm**	$[Xe]4f^{13}6s^2$	^2F
Ar	$[Ne]3s^23p^6$	^1S	**Yb**	$[Xe]4f^{14}6s^2$	^1S
K	$[Ar]4s^1$	^2S	**Lu**	$[Xe]4f^{14}5d^16s^2$	^2D
Ca	$[Ar]4s^2$	^1S	**Hf**	$[Xe]4f^{14}5d^26s^2$	^3F
Sc	$[Ar]3d^14s^2$	^2D	**Ta**	$[Xe]4f^{14}5d^36s^2$	^4F
Ti	$[Ar]3d^24s^2$	^3F	**W**	$[Xe]4f^{14}5d^46s^2$	^5D
V	$[Ar]3d^34s^2$	^4F	**Re**	$[Xe]4f^{14}5d^56s^2$	^6S
Cr	$[Ar]3d^54s^1$	^7S	**Os**	$[Xe]4f^{14}5d^66s^2$	^5D
Mn	$[Ar]3d^54s^2$	^6S	**Ir**	$[Xe]4f^{14}5d^76s^2$	^4F
Fe	$[Ar]3d^64s^2$	^5D	**Pt**	$[Xe]4f^{14}5d^96s^1$	^3D
Co	$[Ar]3d^74s^2$	^4F	**Au**	$[Xe]4f^{14}5d^{10}6s^1$	^2S
Ni	$[Ar]3d^84s^2$	^3F	**Hg**	$[Xe]4f^{14}5d^{10}6s^2$	^1S
Cu	$[Ar]3d^{10}4s^1$	^2S	**Tl**	$[Xe]4f^{14}5d^{10}6s^26p^1$	^2P
Zn	$[Ar]3d^{10}4s^2$	^1S	**Pb**	$[Xe]4f^{14}5d^{10}6s^26p^2$	^3P
Ga	$[Ar]3d^{10}4s^24p^1$	^2P	**Bi**	$[Xe]4f^{14}5d^{10}6s^26p^3$	^4S
Ge	$[Ar]3d^{10}4s^24p^2$	^3P	**Po**	$[Xe]4f^{14}5d^{10}6s^26p^4$	^3P

(contd...)

Element	Configuration	Term	Element	Configuration	Term
As	$[Ar]3d^{10}4s^2 4p^3$	^4S	**At**	$[Xe]4f^{14}5d^{10}6s^2 6p^5$	^2P
Se	$[Ar]3d^{10}4s^2 4p^4$	^3P	**Rn**	$[Xe]4f^{14}5d^{10}6s^2 6p^6$	^1S
Br	$[Ar]3d^{10}4s^2 4p^5$	^2P	**Fr**	$[Rn]7s^1$	^2S
Kr	$[Ar]3d^{10}4s^2 4p^6$	^1S	**Ra**	$[Rn]7s^2$	^1S
Rb	$[Kr]5s^1$	^2S	**Ac**	$[Rn]6d^1 7s^2$	^2D
Sr	$[Kr]5s^2$	^1S	**Th**	$[Rn]6d^2 7s^2$	^3F
Y	$[kr]4d^1 5s^2$	^2D	**Pa**	$[Rn]5f^2 6d^1 7s^2$	^4K
Zr	$[kr]4d^2 5s^2$	^3F	**U**	$[Rn]5f^3 6d^1 7s^2$	^5L
Nb	$[kr]4d^4 5s^1$	^6D	**Np**	$[Rn]5f^4 6d^1 7s^2$	^6L
Mo	$[kr]4d^5 5s^1$	^7S	**Pu**	$[Rn]5f^6 7s^2$	^7F
Tc	$[kr]4d^5 5s^2$	^6S	**Am**	$[Rn]5f^7 7s^2$	^8S
Ru	$[kr]4d^7 5s^1$	^5F	**Cm**	$[Rn]5f^7 6d^1 7s^2$	^9D
Rh	$[kr]4d^8 5s^1$	^4F	**Bk**	$[Rn]5f^9 7s^2$	^6H
Pd	$[kr]4d^{10}$	^1S	**Cf**	$[Rn]5f^{10}7s^2$	^5I
Ag	$[kr]4d^{10}5s^1$	^2S	**Es**	$[Rn]5f^{11}7s^2$	^4I
Cd	$[kr]4d^{10}5s^2$	^1S	**Fm**	$[Rn]5f^{12}7s^2$	^3H
In	$[kr]4d^{10}5s^2 5p^1$	^2P	**Md**	$[Rn]5f^{13}7s^2$	^2F
Sn	$[kr]4d^{10}5s^2 5p^2$	^3P	**No**	$[Rn]5f^{14}7s^2$	^1S
Sb	$[kr]4d^{10}5s^2 5p^3$	^4S	**Lr**	$[Rn]5f^{14}6d^1 7s^2$	^2D
Te	$[kr]4d^{10}5s^2 5p^4$	^3P			

Appendix-C Some Important Complexes

Element	Complex formula	IUPAC name	Magnetic moment in BM	Stability constant
Aluminimum	$[AlF_6]^{3-}$	hexafluoroaluminate(III) ion	0	6.9×10^{19}
	$[Al(OH)_4]^-$	tetrahydroxoaluminate(III) ion	0	1.1×10^{33}
	$[AlH_4]^-$	tetrahydridoaluminate(III) ion	0	–
Cadmium	$[Cd(NH_3)_4]^{2+}$	tetramminecadmium(II) ion	0	5.8×10^6
	$[CdBr_4]^{2-}$	tetraleromocadmiate(II) ion	0	3.4×10^2
	$[CdCl_4]^{2-}$	tetrachlorocadmiate(II) ion	0	6.3×10^2
	$[Cd(CN)_4]^{2-}$	tetracyanocadmiate(II) ion	0	6.0×10^{18}
	$[CdI_4]^{2-}$	tetraiodocadmiate(II) ion	0	2.6×10^5
	$[Cd-(EDTA)]^{2-}$	ethylenediaminetetraacetatocadmiate(II) ion	0	4.0×10^{16}
	$[Cd(en)_2]^{2+}$	bis(ethylenediamine)cadmium (II) ion	0	2.0×10^{10}
Calcium	$[Ca-(EDTA)]^{2-}$	ethylenediaminetetraacetatocalciumate(II) ion		5.0×10^{10}
Chromium	$[Cr(OH)_4]^-$	tetrahydroxochromate(III) ion		8.0×10^{29}
	$[Cr(NH_3)_6]^{3+}$	hexamminechromium(III) ion	3.87	
	$[Cr(CN)_6]^{4-}$	hexacyanochromate(II) ion	2.83	
	$[Cr(CO)_6]$	hexacarbenylchromium (0)	0	

Element	Complex formula	IUPAC name	Magnetic moment in BM	Stability constant
Cobalt	$[Co(NH_3)_6]^{2+}$	hexamminecobalt(II) ion	4.96	1.3×10^5
	$[Co(NH_3)_6]^{3+}$	hexamminecobalt(II) ion	0	2.0×10^{35}
	$[Co(SCN)_4]^{2-}$	tetrathioxyanatocobaltate(II) ion		1.0×10^3
	$[Co-EDTA]^{2-}$	ethylenediaminetetraacetatocobaltate (II) ion		1.6×10^{16}
	$[CoF_6]^{3-}$	hexafluorocobaltate(II) ion	5.3	
	$[Co(CN)_6]^{3-}$	hexacyanocobaltate(IV) ion	0	
	$[Co(NO_2)_6]^{4-}$	hexanitrocobaltate(II) ion	1.9	
Copper	$[Cu(OH)_4]^{2-}$	tetrahydroxocuprate(II) ion		3.0×10^{18}
	$[Cu(NH_3)_4]^{2+}$	tetramminecopper(II) ion	1.81	2.1×10^{13}
	$[Cu(CN)_4]^{3-}$	tetracyanocuprate(I) ion	0	2.0×10^{27}
	$[Cu(en)_2]^{2+}$	cis(ethylenediamine)copper(II) ion		2.0×10^{19}
	$[Cu-EDTA]^{2-}$	ethylenediaminetetraacetatocuprate(II) ion		6.3×10^{18}
Gold	$[Au(Cl)_4]^-$	tetrachloroaurate(III) ion		2.0×10^{21}
Iron	$[Fe(CN)_6]^{4-}$	hexacyanoferrate(II) ion	0	1.0×10^{35}
	$[Fe(CN)_6]^{3-}$	hexacyanoferrate(III) ion	2.33	1.0×10^{42}
	$[Fe(CO)_5]$	pentacarbonyliron (o)	0	
	$[Fe(NH_3)_6]^{2+}$	hexammineiron(II) ion	5.25	
	$[FeF_6]^{3-}$	hexafluoroferrate(III) ion	5.9	

(*Contd...*)

Element	Complex formula	IUPAC name	Magnetic moment in BM	Stability constant
	$[Fe-EDTA]^{2-}$	ethylenediaminetetraacetatoferrate(II) ion		2.0×10^{14}
	$[Fe(NH_3)_4]^{2+}$	tetrammineiron(II) ion		5.0×10^{3}
Magnesium	$[Mg-EDTA]^{2-}$	ethylenediaminetetraacetatomagnesium(II) ion		4.9×10^{8}
Manganese	$[Mn(CN)_6]^{3-}$	hexacyanomanganate(III) ion	3.0	
	$[Mn(CN)_6]^{4-}$	hexacyanomanganate(II) ion	2.0	
Mercury	$[HgCl_4]^{2-}$	tetrachloromercurate(II) ion		1.2×10^{15}
	$[Hg(CN)_4]^{2-}$	tetracyanomercurate(II) ion		3.2×10^{41}
	$[HgI_4]^{2-}$	tetraiodomercurate(II) ion		6.6×10^{29}
Nickel	$[Ni(CN)_4]^{2-}$	tetracyanonickelate(II) ion	0	2.0×10^{31}
	$[Ni(NH_3)_6]^{2+}$	hexamminenickel(II) ion	2.9	5.5×10^{8}
	$[Ni(CO)_4]$	tetracarbonylnickel (o)	0	
	$[Ni(DMG)_2]$	bis(dimethylglyoximato)nickel(II)	0	
	$[Ni-EDTA]^{2-}$	ethylenediaminetetraacetatonickelate(II) ion		3.6×10^{18}
	$[Ni(NH_3)_4]^{2+}$	tetramminenickel(II) ion	2.63	6.2×10^{7}
	$[Ni(en)_2]^{2+}$	bis(ethylenediamine)nickel(II) ion		3.2×10^{14}
Palladium	$[Pd(NH_3)_4]^{2+}$	tetraminepalladium(II) ion	0	
	$[PdCl_6]^{2-}$	hexachloropalladate(IV) ion	0	
Platinum	$[PtCl_4]^{2-}$	tetrachloroplatinate(II) ion	0	1.0×10^{16}
	$[PtCl_6]^{2-}$	hexachloroplatinate(IV) ion	0	

	Complex formula	IUPAC name	Magnetic moment in BM	Stability constant
Silver	$[Ag(NH_3)_2]^+$	diamminesilver (I) ion		1.7×10^7
	$[Ag(CN)_2]^-$	dicyanoargentate(I) ion		1.1×10^{21}
	$[Ag(py)_2]^+$	dipyridinesilver(I) ion		1.3×10^4
	$[Ag(S_2O_3)_2]^{3-}$	dithiosulphatoargentate(I) ion		5.2×10^{12}
Vanadium	$[V(CO)_6]$	hexacarbonylvanadium (o)	1.73	
Zinc	$[Zn(NH_3)_4]^{2+}$	tetramminezinc(II) ion	0	8.0×10^8
	$[Zn(CN)_4]^{2-}$	tetracyanozincate(II) ion	0	8.0×10^{16}
	$[Zn(C_2O_4)_3]^{4-}$	trioxalatozincate(II) ion	0	1.0×10^9
	$[Zn-EDTA]^{2-}$	ethylenediaminetetraacetatozinc(II) ion	0	3.9×10^{16}
	$[Zn(en)_2]^{2+}$	bis(ethylenediamine)zinc(II) ion	0	1.6×10^{11}

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