CO-ORDINATION CHEMISTRY

1. INTRODUCTION

When solution which contain two or more salts in simple molecular proportion are evaporated, crystals of new compounds separate out.

These compounds are called molecular or additon compounds.

Ex. $K_2SO_4 + Al_2(SO_4)_3 + 24\ H_2O \longrightarrow K_2SO_4 \quad Al_2(SO_4)_3 \quad 24H_2O$

$CuSO_4 + 4NH_3 + H_2O \longrightarrow [Cu(NH_3)_4]SO_4 \quad H_2O$

These addition compounds can be divided into two classes:

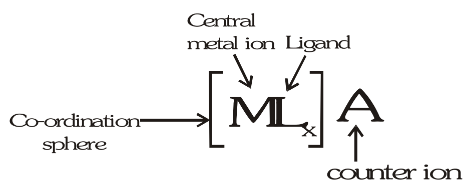
(a) Those which lose their identity in solution

In solutions these compounds break down into simpler ions. Such addition compounds which lose their identity in solutions are called double salts .

(b) Those which retain their identity in solution.

In aqueous solution, these addition compounds do not furnish all simple ions but instead give more complex ions having complicated structure .

These types of compounds are called **complex compounds or co-ordination compounds**.



2. LIGANDS

Atom/molecule/ ion, which form co-ordinate bond with central metal atom by donating its electron pair known as ligand. Ligands are electron pair donors so they are Lewis bases.

3. DENTICITY

Total number of lone pair donated by a ligand when it is bonded with metal is called denticity or number of donar sites on a ligand is called denticity.

4. THE FORMATION OF CO-ORDINATION COMPOUNDS

It can be explained by number of theories.

(A) Werner's co-ordination theory

(B) Sidwick theory or Effective Atomic Number Theory (EAN)

(C) Valence bond theory

(D) Crystal field theory

(A) Werner's co-ordination theory : Werner's co-ordination theory has the first attempt to explain the bonding in co-ordination complex. The main postulates of this theory are:

(a) In co-ordination compound metals have two types of valencies :

– Primary valency and secondary valency.

(b) Primary valencies are normally ionisable and non directional. Secondary valency is normally non ionisable and directional.

(c) Every metal has fixed secondary valencies i.e. it has a fixed co-ordination number.

(d) Primary linkages (valencies) are satisfied by negative ions while secondary valencies are satisfied by either neutral molecules or negative ions. In certain cases, a negative ion may satisfy both type of valencies.

P.V. = O.S. of central metal atom.

S.V. = Coordination number

(B) Sidwick Theory or Effective Atomic Number Concept (EAN)

Sidwick proposed effective atomic number theory to explain the stability of the complexes. EAN is defined as the total number of electrons with the metal atoms or ions after gaining electrons from the donor atoms or the ligand. The EAN generally coincides with the atomic number of next inert gas except in some cases.

EAN can be calculated by the following relation:

EAN = atomic number (Z) of the metal – oxidation state of metal ion + number of electrons gained by central atom from the donor atoms of the ligands.

(C) Valence Bond Theory

The main features of this theory are -

(a) Every metal ion when it forms a complex compound undergoes formation of coordinate covalent bond.

(b) During this bond formation, the central metal ion acts as electron pair acceptor. For this the metal ion provides vacant orbitals.

(c) The number of vacant orbitals provided is equal to the coordination number of metal ion.

Ex. In the formation of $[Fe(NH_3)_6]^{3+}$, Fe^{+3} ion provides six vacant orbitals.

In $[Cu(NH_3)_4]^{2+}$, Cu^{+2} ion provides four vacant orbitals.

(d) The metal provides vacant orbitals only after the process of hybridisation, thus vacant hybrid orbitals are provided by the metal ion.

(e) The vacant hybrid orbitals of metal ion get overlapped by orbitals of ligands containing lone pair of electrons.

(f) The number of such overlappings is equal to the coordination number of metal ion.

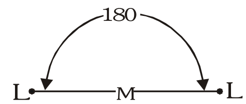
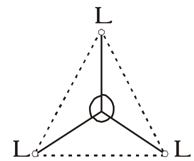
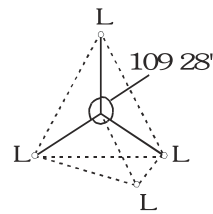
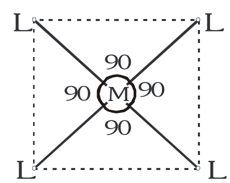
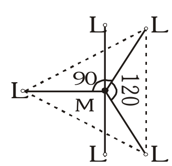
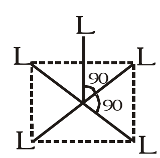
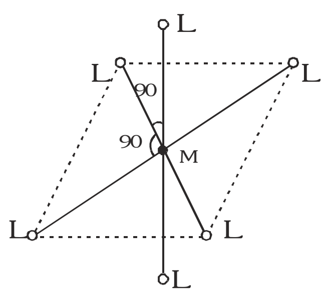
(g) The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals and these complexes are called as **Inner orbital complexes** and **Outer orbital complexes** respectively.

(h) If inner 'd' orbitals are involved in hybridisation, then it is through only the pairing of unpaired electrons in the 'd' orbitals of metal ion.

(i) Then such type of complexes will be **diamagnetic** or **less paramagnetic** and will be called as **Low spin complexes**.

(j) All outer orbital complexes have **paramagnetic** nature and they are called as **High spin complexes**.

Some Example :

Coordination Number	Hybridised orbital	Geometrical shape of the Complex	Examples of Complex
2	sp	 Linear	$[Ag(NH_3)_2]^+$ $[Ag(CN)_2]^-$
3	sp^2		$[HgI_3]^-$
4	sp^3		$[CuCl_4]^{-2}$ $[ZnCl_4]^{-2}$ $[FeCl_4]^-$ $[Ni(CO)_4]$ $[Zn(NH_3)_4]^{+2}$
4	dsp^2 The d-orbital involved is $d_{x^2-y^2}$ orbital	 Square plannar	$[PdCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$ $[Pt(NH_3)_4]^{+2}$ $[Cu(NH_3)_4]^{+2}$ $[PtCl_4]^{2-}$
5	sp^3d or dsp^3	 Trigonal bipyramidal	$Fe(CO)_5$
5	dsp^3		$[Ni(CN)_5]^{-3}$
6	d^2sp^3 / sp^3d^2 When d–orbitals are(n – 1)d–orbitals (Inner orbital complexes). or sp^3d^2 – When d–orbitals are nd orbitals (Outer orbital complexes) In both cases d–orbitals are d_{z^2} and $d_{x^2-y^2}$ orbitals	 Octahedral	$[Cr(NH_3)_6]^{+3}$ $[Ti(H_2O)_6]^{+3}$ $[Fe(CN)_6]^{-3}$ $[Co(NH_3)_6]^{+3}$ $[PtCl_6]^{-2}$, $[CoF_6]^{-3}$

Drawback of valence bond theory

(a) It describes bonding in co-ordination compounds only qualitatively but not account for the relative stabilities for different co-ordination complexes.

(b) It does not offer any explanation for optical absorption spectra (coloration) of complexes

(c) It does not describe the detailed magnetic properties of co-ordination compounds.

(D) **Crystal Field Theory :** This is a model of electronic structure of transition-metal complexes that considers how the energies of the d-orbitals of a metal ion are affected by the electric field of the ligand. According to this theory.

(a) The ligands in a transition-metal complex are treated as point charges.

(b) A ligand anion becomes simply a point of negative charge. A neutral molecule, with its electron pair that it donates to the metal atom, is replaced by a negative charge, representing the negative end of the molecular dipole.

(c) In the electric field of these negative charges, the five d orbitals of the metal atom no longer have exactly same energy. Splitting of five degenerate d-orbitals of the metal ion into sets of orbitals having different energies is called crystal field splitting.

(d) The extent of splitting of metal d-orbitals depends upon the nature and number of ligands surrounding it and the charge on the central metal ion.

(e) The extent of splitting of metal d-orbitals determines the magnetic and spectroscopic properties of the complexes.

5. STABILITY OF CO-ORDINATION COMPOUNDS IN SOLUTION

The term stability can be used in a number of different ways.

(a) **Thermodynamic stability of a complex :** It measures the extent to which this complex is formed from or is transformed into other complex, under certain conditions when the system, has attained equlibrium.

(b) **The kinetic stability:** It referes to the speed with which transformation occurs which leads to the attainment of equilibrium.

According to thermodynamic stability, the reaction between a metal ion and the ligands may be considered as a Lewis acid base reaction in solution. If the equilibrium constant is high then the complex obtained is theromodynamically stable in solution. The reaction can be written as follows : $M + nL \rightleftharpoons [ML_n]$

The stability constant K, of the complex $[ML_n]$ is given by the relation, $K = \frac{[ML_n]}{[M][L]^n}$. The greater the value of K, more stable is the complex.

The strength of a complex ion also depends upon –

(i) Higher charge of the central metal ion.

(ii) Greater base strength of the ligand.

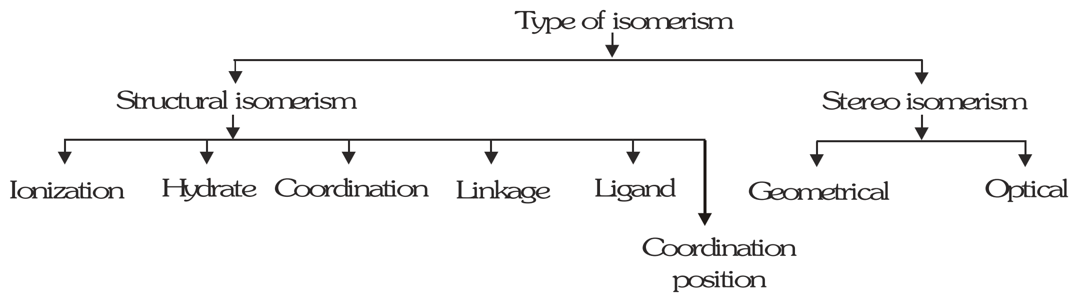
(iii) Ring formation (chelation) in structure of complexes.

6. ISOMERISM IN COMPLEXES

(a) Compounds which have the same molecular formula, but differ in their properties due to the difference in structure are called as **Isomers**.

(b) Isomerism is commonly considered, to be the characteristic of only organic compounds, it is also found although less frequently among inorganic substances.

Classification of isomerism



Note :

General formula	Total No. of geometrical isomers
Mabcdef	15
Ma_2bcde	9
Ma_2b_2cd	6
$Ma_2b_2c_2$	5
Ma_3bcd	4
Ma_3b_2c	3
Ma_3b_3	2
Ma_4bc	2
Ma_4b_2	2
Ma_5b	Nil
Ma_6	Nil

Here M = central atom. a, b, c, d, e, f = Monodentate ligands

NUMBER OF POSSIBLE ISOMERS FOR SPECIFIC COMPLEXES

Formula	Number of stereoisomers	Pairs of Enantiomers
Ma_2b_2	2	0
Ma_3b_3	2	0
Ma_4bc	2	0
Ma_3bcd	5	1
Ma_2bcde	15	6
Mabcdef	30	15
$Ma_2b_2c_2$	6	1
Ma_2b_2cd	8	2
Ma_3b_2c	3	0
M(AA)(BC)de	10	5
M(AB)(AB)cd	11	5
M(AB)(CD)ef	20	10
$M(AB)_3$	4	2

Note: Uppercase letters represent chelating ligands and lowercase letters represent monodentate ligands.

SOLVED THEORETICAL ILLUSTRATION

INTRODUCTION

1. Why potash alum ($K_2SO_4.Al_2(SO_4)_3.24H_2O$) is in the category of double salt ?

Ans. When potash dissolves into water it completely ionise into their constituent ions K^+, Al^{+3}, SO_4^{2-}.

When addition compound which are completely ionises into its constituent ions then it is called double salt so potash alum is in the category of double salt.

2. What type of ions furnishes by potassium ferrocyanide $K_4[Fe(CN)_6]$ dissolve in water ? Is it a complex compound, if yes then why ?

Ans. When potassium ferrocyanide dissolves in water it give two type of ions K^+ & $[Fe(CN)_6]^{-4}$

$$K_4[Fe(CN)_6] \xrightarrow{H_2O} 4K^+_{(aq.)} + [Fe(CN)_6]^{-4}_{(aq.)}$$

Yes it is a complex compound because it is not dissociated completely into its contituent ions (K^+, Fe^{+2}, CN)

3. Why $K_4[Fe(CN)_6]$ does not gives the test of CN^- ion ?

Ans. When $K_4[Fe(CN)_6]$ potassium ferrocyanide dissolves into water it give two type of ions K^+ & $[Fe(CN)_6]^{-4}$

The complex ion $[Fe(CN)_6]^{-4}$ is fairly stable and further dissociation or feebly dissociation is not possible in solution state.

Ex. $K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$

$$[Fe(CN)_6]^{4-} \downarrow Fe^{2+} + 6CN^- \text{ (Feebly dissociated)}$$

The ferrocyanide ion $[Fe(CN)_6]^{4-}$ is so insignificantly dissociated so that it can be considered as practically undissociated and does not give the test of Fe^{2+} or CN^- ions

DO YOURSELF - I

1. Predict which among the following properties given below belong to double salt and co-ordination compounds.

(a) Compounds in which the individual properties of the constituents are usually lost (................).

(b) Alum's (................).

(c) The blue coloured solution prepared by Cu^{+2} (aq.) and NH_3(aq.) (NH_4OH) does not show the presense of Cu^{+2} (................).

(d) Compounds which are stable in the solid state but break up into its constituents in aqeous solution (................).

(e) Aqueous solution of carnallite (................).

(f) The compounds in which central metal ion form dative bonds with species surrounding it (................).

(g) Mohrs salt (................).

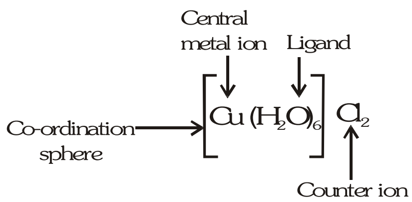
Ans. Hints are given on last page.

IMPORTANT TERMS

4. Define the given terms with respect to complex compounds and represent them by an example ?

(i) complex-ion (ii) central metal ion (iii) co-ordination number
(iv) ligand (v) co-ordination sphere

Ans.



(i) **Complex ion :** A complex ion may be defined as an electrically charged radical which is formed by the combination of a simple cation with one/more neutral molecules or one/more simple anions or in some cases positive group also.

(ii) **Central ion :** The cation to which one or more neutral molecules or anions are attached is called the centre of co-ordination or central ion. Since, the central ion acts as an acceptor and thus has to accommodate electron pairs donated by ligands, it must have empty orbitals.

(iii) **Co-ordination number :** The total number of co-ordinate covalent bond form by central metal in complex called the co-ordination number of the central metal ion .

(iv) **Ligand :** Atom/molecule/ ion, which form co-ordinate bond with central metal atom by donating its electron pair.

(v) **Co-ordination sphere :** The central atom and the ligands which are directly attached to it are enclosed in square bracket are collectively termed as the co-ordination sphere.

5 Explain different type of ligands on the basis of denticity and also give example ?

Ans. Type of ligands on the basis of denticity :

(a) **Unidentate ligands**

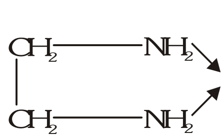
Ligands which have only one e^- donor atom.

X^-, CN^-, NO_2^-, NH_3, Pyridine, OH^-, NO_3^-, H_2O, CO, NO, OH^-, O^{-2}, $(C_6H_5)_3P$ etc.

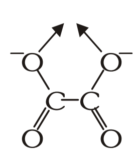
(b) **Bidentate ligands**

Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands. **Ex.**

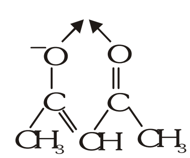
Symmetrical Unsymmetrical



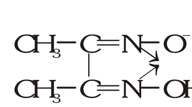
Ethylenediamine (en) or Ethan-1,2-diamine



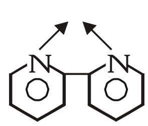
Oxalate $(ox)^{2-}$



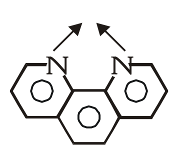
Acetyle-acetonate $(acac)^-$



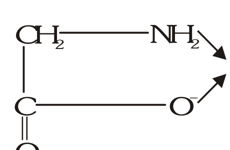
Dimethyl glyoxim ion $(DMG)^-$



2, 2'-Dipyridyl (Dipy)



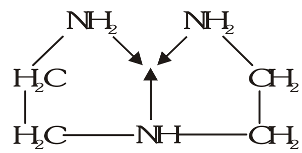
1, 10-Phenanthroline (O-phen)



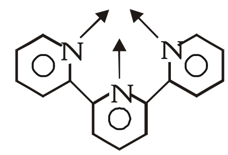
Glycinato $(Gly)^-$

(c) **Tridentate ligands**

The ligands having three donor atoms are called tridentate ligands. **Ex.**



Diethylenetriamine (Dien)

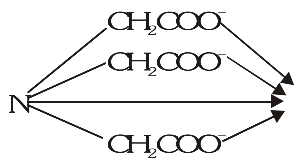


2, 2', 2''-Terpyridine (Terpy)

(d) **Tetradentate ligands**

Those ligands possess four donor atoms,

Ex. Nitriloacetato

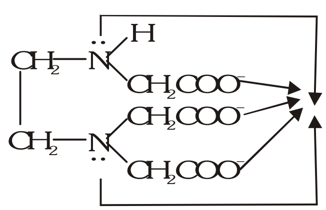


Nitriloacetato (nta)$^{3-}$

(e) **Pentadentate ligands**

They have five donor atoms.

Ex. Ethylenediaminetriacetate ion.



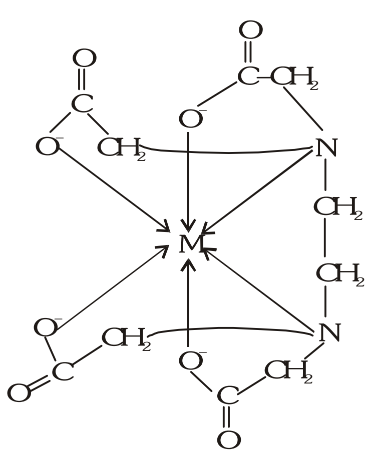
$(EDTA)^{-3}$

Ethylenediaminetriacetate ion

6. Define hexadented ligand with explanation ?

Ans. Ligand which have six donor atoms.

For **eg.**



[Metal with a Hexadented ligand]

Ethylenediaminetetraacetate ion $(EDTA)^{-4}$

7. (a) What is chelation?

(b) Which type of ligand show chelation and what are they called? give example.

Ans. (a) Polydentate ligand when attached with central metal ion forms one or more rings this is known as chelate or chelate ring and the phenomenon is called chelation.

(b) Polydentate ligand forms atleast four member rings with central metal ion show chelation. These ligands are known as **chelating ligand**.

Ex. (i) $\begin{array}{cc} CH_2 & -CH_2 \\ | & | \\ NH_2 & NH_2 \end{array}$ (ii) $C_2O_4^{2-}$ (iii) $EDTA^{4-}$

8. Why some ligands are called ambidentate ligand? write them.

Ans. Ligand which have two doner sites (atoms) but at a time only one site (atom) donates are known as ambidentate ligand. They are $\left[\begin{array}{l} CN^- \\ NC^- \end{array}\right.$ $\left[\begin{array}{l} NO_2^- \\ ONO^- \end{array}\right.$ $\left[\begin{array}{l} SCN^- \\ CNS^- \end{array}\right.$ $\left[\begin{array}{l} CNO^- \\ NCO^- \end{array}\right.$ $\left[\begin{array}{l} S_2O_3^{2-} \\ OSO_2S^{2-} \end{array}\right.$

Ex. CN^- can coordinate through either the nitrogen or the carbon atom to a central metal ion.

9. What do you mean by flexidentate ligand ?

Ans. Ligands which have two or more than two donor sites but sometimes in complex, formation they do not use all donor sites this type of ligands are called flexidentate ligand.

Ex. SO_4^{2-} , CO_3^{2-} .

DO YOURSELF - II

1. $[Pt(NH_3)_3Cl_2Br]\ Cl$ Now answer the following from above complex.

(a) Write the formula of complex sphere ?

(b) What is the charge on complex ion ?

(c) How many ligands are in complex ?

(d) What is the co-ordination number ?

(e) What is the oxidation number of central metal ?

(f) How many ions are formed on ionisation ?

(g) The number of halide ion will be ....

(h) Will the aqueous solution of above complex give Cl^- test ?

(i) Will the above solution give AgBr when treated with $AgNO_3$?

(j) One mole of above complex gives how many moles of AgCl and AgBr when treated with excess of $AgNO_3$?

(k) Will Pt ion present in aqueous solution or not ?

NOTE : Hints are on last page.

NOMENCLATURE

10. What are the conventions to write the IUPAC name of co-ordination compounds ?

Ans. IUPAC nomenclature of coordination compounds :

The main rules of naming of complexes are –

(a) Like simple salts, the positive part of the coordination compound is named first.

Ex. $K_4[Fe(CN)_6]$ the naming of this complex starts with potassium.

$[Cr(NH_3)_6]Cl_3$ the naming of this complex starts with name of complex ion.

(b) Coordination sphere are to be named the ligand first than metal atom or ion

(c) The ligands can be neutral, anionic or cationic.

(i) The neutral ligands are named as the molecule

Ex. C_5H_5N pyridine, $(C_6H_5)_3P$ Triphenyl phosphine, $H_2N - CH_2-CH_2-NH_2$ ethylene diamine. The neutral ligands which are not named as the molecule are CO carbonyl, NO nitrosyl, H_2O Aqua, NH_3 ammine.

(ii) Anionic ligands ending with 'ide' are named by replacing the 'ide' with suffix 'O'.

Symbol	Name as ligand	Symbol	Name as ligand
Cl^-	Chloro/Chlorido	N^{3-}	Nitrido
Br^-	Bromo/Bromido	O_2^{2-}	Peroxo
CN^-	Cyano	O_2H^-	Perhydroxo
O^{2-}	Oxo	S^{2-}	Sulphido
OH^-	Hydroxo	NH^{2-}	Imido
H^-	Hydrido	NH_2^-	Amido

Ligands whose names end in 'ite' or 'ate' become 'ito' i.e., by replacing the ending 'e' with 'o' as follows.

Symbol	Name as ligand	Symbol	Name as ligand
CO_3^{2-}	Carbonato	SO_3^{2-}	Sulphito
$C_2O_4^{2-}$	Oxolato	CH_3COO^-	Acetato
SO_4^{2-}	Sulphato	NO_2^-	(bonded through oxygen) nitrito-O
NO_3^-	Nitrato		(bonded through nitrogen) nitrito-N
$S_2O_3^{-2}$	Thiosulphato		

(iii) Positive ligands naming ends with 'ium' $NH_2-NH_3^+$ Hydrazinium, NO_2^+ nitronium, NO^+ nitrosonium

(d) If ligands are present more than once, then their repitition is indicated by prefixes like di, tri, tetra etc. However, when the name of the ligand includes a number, **Ex**. dipyridyl, ethylene diamine, then bis, tris, tetrakis are used in place of di, tri, tetra, etc.

(e) If ligand already contains prifix (eg. ethylenediamine) or if it is Polydented ligends the prifixes bis–, tris, tetrakis–, pentakis–, are used instead.

Ex. $[Pt(en)_2Cl_2]Cl_2$ dichlorobis (ethylenediamine) platinum (IV) chloride.

(f) When more than one type of ligand are present in the complex, then the ligands are named in the alphabetical order.

(g) After naming of ligands the central metal ion is to be named immediately followed by its oxidation state in Roman numbers in brackets. (as per IUPAC)

If the central metal comes in anionic complex sphere then the central metal ion is to be named as it is.

If the complex provides anionic complex ion then the name of central metal ion ends in 'ate'

Ex. $(NH_4)_2[CuCl_4]$ Ammonium tetrachlorocuprate(II)

(h) After the naming of central metal ion, anion which is in the outer sphere is to be named.

The naming of some of the complexes is done as follows – (as per IUPAC)

11. Write IUPAC name of following Complex compounds ?

(i) $K_4[Fe(CN)_6]$ (ii) $K_2[Pt\ Cl_6]$

(iii) $[Co\ (NH_3)_6]\ Cl_3$ (iv) $[Cr(H_2O)_4Cl_2]\ Cl$

(v) $[Pt(NH_3)_2Cl_4]$ (vi) $[Co(NH_3)_3\ Cl_3]$

Ans. (i) Potassium hexacyanoferrate(II) (ii) Potassium hexachloroplatinate(IV)

(iii) Hexamminecobalt(III) chloride (iv) Tetraaquadichlorochromium(III) chloride

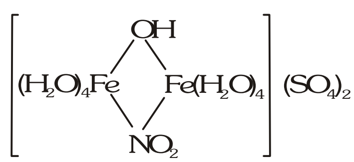
(v) Diamminetetrachloroplatinum(IV) (vi) Triamminetrichlorocobalt(III)

12. (a) What are bridging ligands ?

(b) How to show bridging ligands in naming, explain with suitable example.

Ans. (a) If a complex ion has two or more than two metal atoms then it is termed polynuclear. The ligand which connects the two metal ions is called as **Bridging ligand or Bridge group**.

(b) A prefix of Greek letter μ, is repeated before the name of each different kind of bridging group.



Tetraaquairon(III)-μ-hydroxo-μ-nitrotetraaquairon(III) sulphate

DO YOURSELF - III

1. Write IUPAC name of following complex compounds ?

(i) $K_3[Co(NO_2)_6]$

(ii) $Na_3[Fe(CN)_5\ NO]$

(iii) $[NiCl_4]^{-2}$

(iv) $[Ru(NH_3)_5Cl]^{+2}$

(v) $[Fe(en)_3]Cl_3$

(vi) $[Ni\ (Gly)_2]$

WERNER THEORY

13. Deduce the different complex and modern formula for $PtCl_4.nNH_3$ where n = 2, 3, 4, 5, 6 also show the number of ions precipitated when these compounds react with excess of $AgNO_3$ solution and also show the number of ions given into aqueous solution ?

Ans.

Complex	Modern formula	No. of Cl^- Ions precipitated	Total number of ions
$PtCl_4$ $6NH_3$	$[Pt(NH_3)_6]Cl_4$	4	5
$PtCl_4$ $5NH_3$	$[Pt(NH_3)_5Cl]Cl_3$	3	4
$PtCl_4$ $4NH_3$	$[Pt(NH_3)_4Cl_2]Cl_2$	2	3
$PtCl_4$ $3NH_3$	$[Pt(NH_3)_3Cl_3]Cl$	1	2
$PtCl_4$ $2NH_3$	$[Pt(NH_3)_2Cl_4]$	0	0(non-electrolyte)

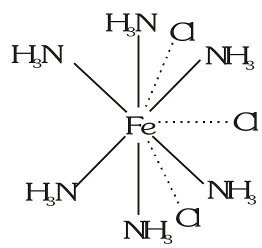
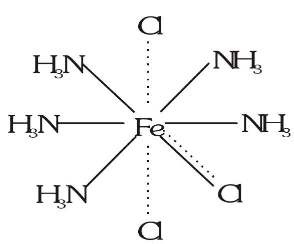
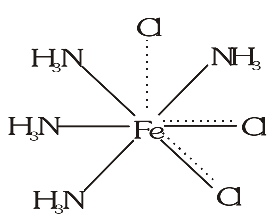
14. How to draw werner representation of complex compound and represent the following ?

(i) $Fe(NH_3)_6Cl_3$ (ii) $Fe(NH_3)_5Cl_3$ (iii) $Fe(NH_3)_4Cl_3$

Ans. Primary valency show by dotted line. P.V. = oxidation state of central metal atom

Secondary valency show by solid line (continous line). S.V. = coordination number

Ligand which satisfies both secondary and primary valency are attached by solid line with dotted line.

(i)	$Fe(NH_3)_6Cl_3$	 P.V. = 3 S.V. = 6 Both = 0	$[Fe(NH_3)_6]Cl_3$ Dotted lines indicate primary valency and continuous lines indicate secondary valency of metal ion.
(ii)	$Fe(NH_3)_5Cl_3$	 P.V. = 3 S.V. = 6 Both = 1	$[Fe(NH_3)_5Cl]Cl_2$ In this complex 'Cl' groups act as primary valencies and one of the 'Cl' acts as primay as well as secondary valency.
(iii)	$Fe(NH_3)_4Cl_3$	 P.V. = 3 S.V. = 6 Both = 2	$[Fe(NH_3)_4Cl_2]Cl$ In this complex 'Cl' groups act as primary valency and two of the 'Cl' group act as primary valencies as well as secondary valencies.

DO YOURSELF - IV

1. Draw werner representation of following complexes ?

(i) $PtCl_4.6NH_3$ (ii) $PtCl_4.4NH_3$ (iii) $PtCl_2.2NH_3$

EFFECTIVE ATOMIC NUMBER

15. Calculate EAN of following complexes ?

$[Co(NH_3)_6]Cl_3$; $K_4[Fe(CN)_6]$; $K_2[Pt\ Cl_6]$; $K_3\ [Fe(CN)_6]$; $[Ni\ (NH_3)_6]Cl_2$

Ans.

Complex	oxidation state of the metal	Atomic number of the metal	Co-ordination Number	Effective atomic number (EAN)
$[Co(NH_3)_6]Cl_3$	+ 3	27	6	(27 − 3) + (6 2) = 36 (Kr)
$K_4[Fe(CN)_6]$	+ 2	26	6	(26 − 2) + (6 2) = 36 (Kr)
$K_2[Pt\ Cl_6]$	+ 4	78	6	(78 − 4) + (6 2) = 86 (Rn)
$K_3\ [Fe(CN)_6]$	+ 3	26	6	(26 − 3) + (6 2) = 35*
$[Ni\ (NH_3)_6]Cl_2$	+ 2	28	6	(28 − 2) + (6 2) = 38*

DO YOURSELF - V

1. Calculate EAN of the following complexes ?

(i) $[Ni(CO)_4]$ (ii) $K_2[Ni(CN)_4]$ (iii) $K_2[HgI_4]$ (iv) $[Ag(NH_3)_2]Cl$

VALENCE BOND THEORY

16. Write hybridisation, geometry, magnetic nature of $K_4[Fe(CN)_6]$; $[Zn(NH_3)_4]SO_4$; $[Ni(CN)_4]^{-2}$ using VBT ?

Ans. (i) $K_4\ [Fe(CN)_6]$

Fe ⇒ [Ar] $3d^6\ 4s^2$

Fe^{+2} ⇒ [Ar] $3d^6\ 4s$

Fe^{+2} ⇒ [Ar] $\underbrace{\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}_{3d}\ \underbrace{\boxed{}}_{4s}\ \underbrace{\boxed{}\boxed{}\boxed{}}_{4p}$

In presence of ligand

Fe^{+2} ⇒ [Ar] $\overset{3d}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\underset{CN^-}{\boxed{xx}}\underset{CN^-}{\boxed{xx}}}\ \overset{4s}{\underset{CN^-}{\boxed{xx}}}\ \overset{4p}{\underset{CN^-}{\boxed{xx}}\underset{CN^-}{\boxed{xx}}\underset{CN^-}{\boxed{xx}}}$

Hybridisation = d^2sp^3

geometry - octahedral

magnetic nature - diamagnetic

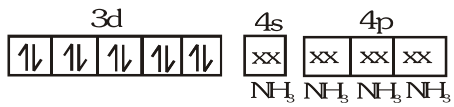
(ii) $[Zn(NH_3)_4]SO_4$

Zn ⇒ [Ar] $3d^{10}\ 4s^2$

Zn^{+2} ⇒ [Ar] $3d^{10}\ 4s$

Zn^{+2} ⇒ [Ar] $\underbrace{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}}_{3d}\ \underbrace{\boxed{}}_{4s}$

In presence of ligand

$Zn^{+2} \Rightarrow [Ar]$ 

Hybridisation = sp^3

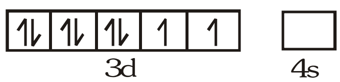
geometry - tetrahedral

magnetic nature - diamagnetic

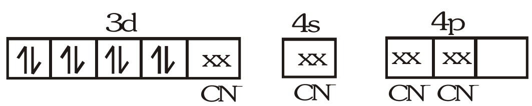
(iii) $[Ni(CN)_4]^{-2}$

$Ni \Rightarrow [Ar]\ 3d^8\ 4s^2$

$Ni^{+2} \Rightarrow [Ar]\ 3d^8\ 4s$

$Ni^{+2} \Rightarrow [Ar]$ 

In presence of ligand

$Ni^{+2} \Rightarrow [Ar]$ 

Hybridisation = dsp^2

geometry - Square planar

magnetic nature - diamagnetic

DO YOURSELF - VI

1. Write Hybridisation, geometry, magenatic moment of following complexes ?

(i) $[MnCl_4]^{-2}$ (ii) $[Mn(CN)_6]^{-4}$ (iii) $[Mn(H_2O)_6]^{+2}$

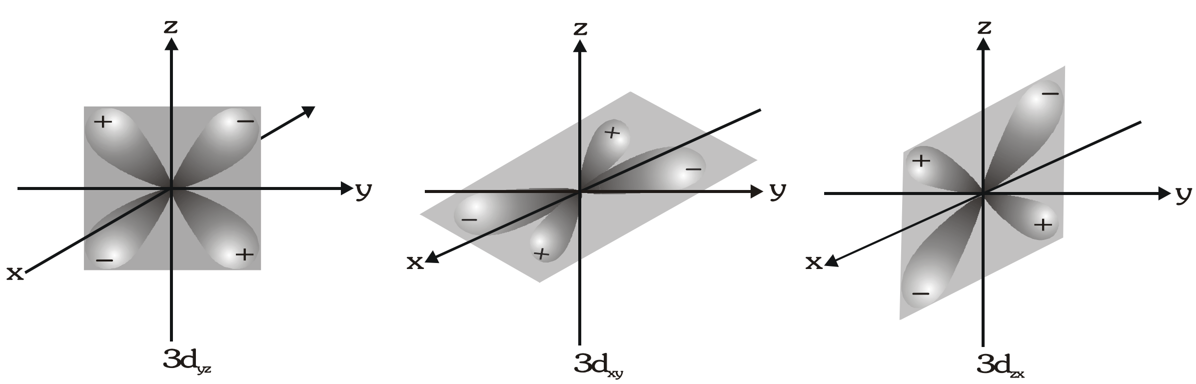
2. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory :

(i) $[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$ (iii) $[Co(C_2O_4)_3]^{3-}$ (iv) $[CoF_6]^{3-}$

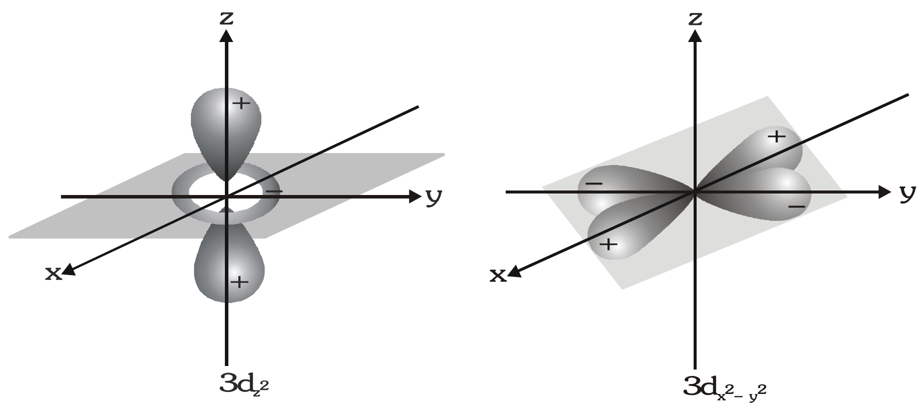
CRYSTAL FIELD THEORY

17. Draw shape of d-orbitals ?

Ans. In d subshell their are five d-orbitals d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2} their geometry are :



Electron density between the axis



Electron density along the axis

18. Explain the term Degenerate orbitals :

Ans. Orbitals which have same energy in a subshell are known as degenerate orbitals.

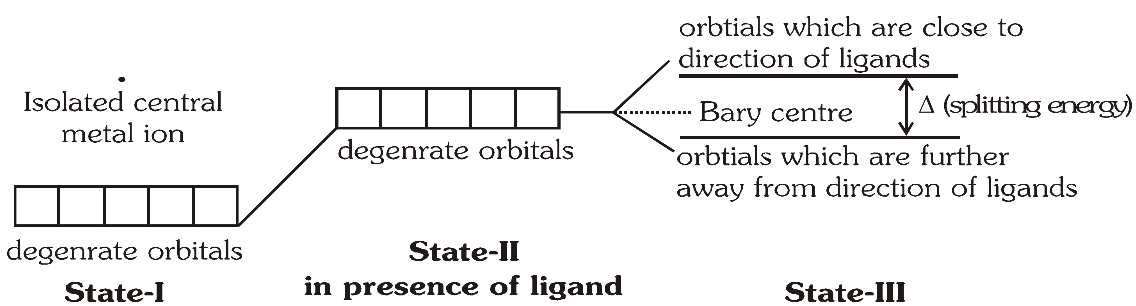
19. What is crystal field splitting ?

Ans. According to CFT the interaction between a transition metal and ligands arises from the attraction between the positively charged metal cation and negative charge of ligand.

As a ligand approaches the metal ion, the electrons of ligand will be closer to some of the d-orbitals and farther away from other causing a loss of degenercy.

The electrons in the d-orbitals and those in the ligand repel each other due to repulsion between like charges. Thus the d-electrons closer to the ligands will have a higher energy than those further away as a results in the d-orbitals splitting in energy.

This loss of degeneracy of d-orbital is known as crystal field splitting.

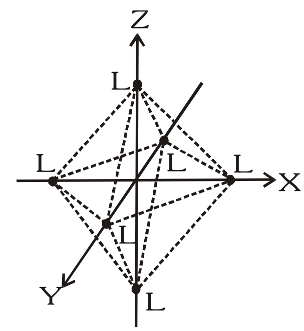


The state I represents degeneracy of all the five d-orbitals in the isolated central ion. The state II represents hypothetical degeneracy of all the orbitals at a higher energy level if the negative charge of all the ligands is assumed to be uniformly affecting the electrons in the d-orbitals of the metal ion. The state III represents crystal field splitting.

20. Explain crystal field splitting into octahedral complex ?

Ans. In a octahedral complex, the co-ordination number is 6. The metal ion is at the centre and the ligands occupy the six corners of the octahedron as shown in figure.

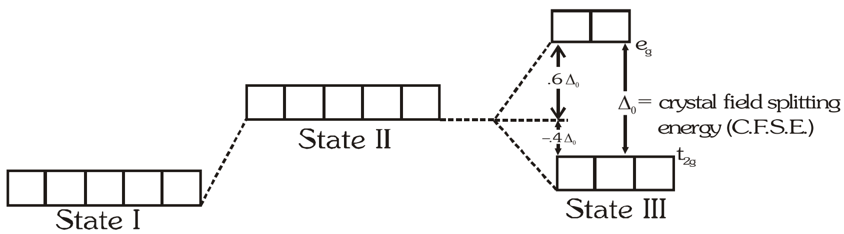
We know that two orbitals, $d_{x^2-y^2}$ and d_{z^2} are oriented along the axis while the remaining three orbitals, viz., d_{xy}, d_{yz} and d_{zx} are oriented in between the axis.



the two orbtials $d_{x^2-y^2}$ and d_{z^2} are designated as e_g orbitals while the three orbitals d_{xy}, d_{yz} and d_{zx} are designated as t_{2g} orbitals. As the six ligands approach the central ion along the axis, e_g orbitals, is repelled more by the ligand than in the t_{2g} orbitals.

In other words, the energy of the d_{z^2} and $d_{x^2-y^2}$ orbitals increases much more than the energy of the d_{xy}, d_{yz} and d_{zx} orbitals.

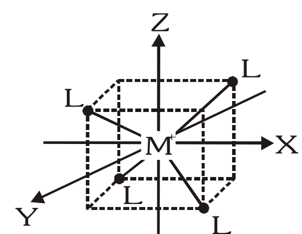
Thus, in octahedral complexes, the five d-orbitals split up into two sets : one set consisting of two orbitals ($d_{x^2-y^2}$ and d_{z^2})of higher energy (e_g orbitals) and the other set consisting of three orbitals (d_{xy}, d_{yz} and d_{zx}) of lower energy (t_{2g} orbitals).



The state I represents degeneracy of all the five d-orbitals in the isolated central ion. The state II represents hypothetical degeneracy of all the orbitals at a higher energy level if the negative charge of all the ligands is assumed to be uniformly affecting the electrons in the d-orbitals of the metal ion. The state III represents crystal field splitting discussed above.

21. **Explain crystal field splitting into tetrahedral complex ?**

Ans. The co-ordination number for tetrahedral complexes is 4. The tetrahedral arrangement of four ligands surrounding a metal ion may be visualized by placing ligands at the alternate corners of a cube, as shown in figure.

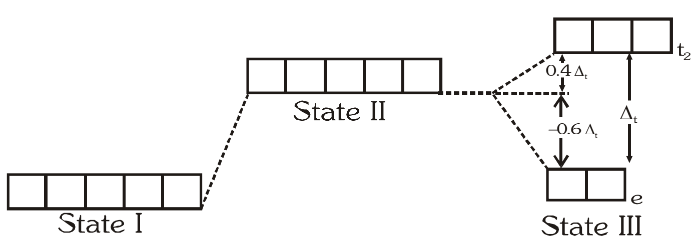


Tetrahedral arrangement of four lignads

It can be shown that in a tetrahedral structure, none of the d-orbitals points exactly towards the ligands.

When ligand approaches it is more close d_{xy}, d_{yz}, d_{xz} in comparision of $d_{x^2-y^2}$ and d_{z^2} because d_{xy}, d_{yz}, d_{zx} are between the axis and d_{z^2} and $d_{x^2-y^2}$ are along the. So d_{xy}, d_{yz}, d_{zx} feels more repulsion as compare to d_{z^2} and $d_{x^2-y^2}$.

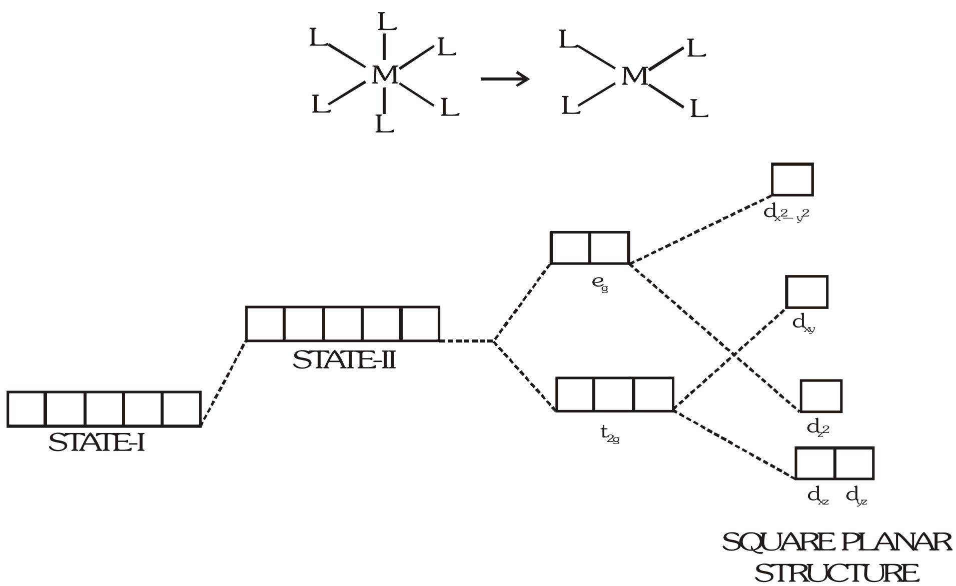
Thus, the d orbitals are also split into two groups but in a reverse order. The three orbitals, d_{xy}, d_{yz} and d_{xz}, designated as t_2 orbitals, now have higher energy than the two orbitals $d_{x^2-y^2}$ and d_{z^2} designated as e-orbitals.



22. **Compare the energy of d-orbitals in square planar complex with respect to crystal field splitting ?**

Ans. The splitting of d-orbitals in square planar complexes can be understood by gradually withdrawing two ligands lying along the Z axis from an octahedral complex. As the ligands lying on the Z axis are moved away, the ligands in the XY plane come more closely to metal. As a result of this, the electrons in d-orbitals in the XY plane experience greater repulsion from the electrons of ligands in a square planar complex than in an octahedral complex. This causes an increase in the energy of d-orbitals in XY plane. i.e., an increase in the energy of $d_{x^2-y^2}$ and d_{xy} orbitals in square planar complexes compared to their energies in octahderal complexes, as illustrated in figure.

Further, since the ligands lying on the Z axis have been moved away, the electrons in the d orbitals along the Z axis as well as in the XZ and YZ planes experience relatively smaller repulsions from the electrons of the ligands. This results in appreciable fall in the energy of d_{z^2} orbital as well as d_{xz} and d_{yz} orbitals. These changes are shown in figure.



Crystal field splitting in spuare planar complexes

23. **Define (a) crystal field stablisation energy (b) Pairing energy ?**

Ans. **(a) Crystal field stablisation energy** : The lowering in the energy of a transition metal ion in a given ligand environment due to crystal field effects.

(b) Pairing energy : The energy required to pair the electrons.

24. **Explain the term**

(a) Inner orbital complex and outer orbital complexes ?

(b) Low spin and high spin complexes ?

Ans. (a) The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals and these complexes are called as **Inner orbital complexes** and **outer orbital complexes** respectively.

For example in d^2sp^3 hybridisation (n–1)d, ns and np orbitals are mixed it forms inner orbital complex and in sp^3d^2 ns, np and nd orbitals are mixed so it forms outer orbitals complex.

(b) When the strong field ligand approaches to metal ion value to splitting energy (Δ) is greater than, pairing energy, so it is unfavourable to put electron into high energy orbitals. Therefore, the lower energy orbitals are completely filled before population of the upper sets starts according to the Aufbau principle. Such type of complexes are called low spin complex.

For low spin complexes

splitting energy (Δ) > pairing energy (P.E.)

Weak field ligand causes a small splitting of the d-orbitals where splitting energy is less than pairing energy. It is easier to put electrons into the higher energy set of orbitals than to pair up in the same low energy orbitals because two electrons in the same orbitals repel each other. So one electron is put into each of the five d-orbitals before any pairing occur in accordance with hund rule.

Such complexes are known as high spin complex.

For high spin complexes splitting energy (Δ) < pairing energy (P.E.)

25. In octahedral complex if central metal have configuration d^1, d^2,d^3 always make inner orbtial complex, Why ?

Ans. Central metal ion which have d^1, d^2,d^3 configuration have at least two vacant orbitals in any ligand environment or with any central metal ion with any oxidation state. So always make inner orbital complex.

26. How to calculate the crystal field stablising **energy (C.F.S.E.) for octahedral and tetrahedral complex?**

Ans. (i) For octahedral CFSE $=\left[-0.4\left(n_{t_{2g}}\right)+0.6\left(n_{eg}\right)\right]\Delta_0$ + Paring energy **(P.E.)**

where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals

n_{eg} = number of electron in eg orbitals

Δ_0 = crystal field **splitting** energy

(ii) For tetrahedral CFSE = $\left[-0.6\left(n_e\right)+0.4\left(n_{t_2}\right)\right]\Delta_t$ +Paring energy **(P.E.)**

where n_{t_2} = number of electron in t_2 orbitals

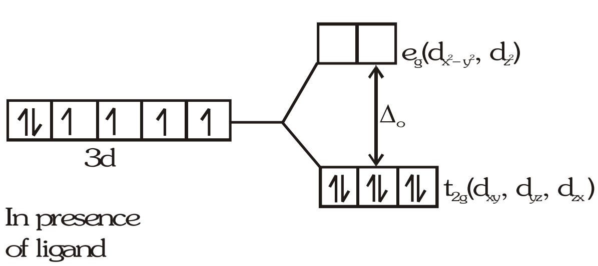
n_e = number of electron in e orbitals

Δ_t = crystal field **splitting** energy

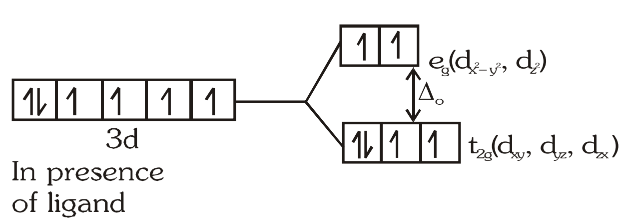
27. Explain the formation of $Na_4[Fe(CN)_6]$ and $Na_4[FeF_6]$? Show which is low spin and which is high spin complex and also calculate the Crystal field stablisation energy (CFSE) ?

Ans. In given compounds CN^- is strong field ligands and F^- is weak field ligand and in both compounds ions is in +2 oxidation state d^6 configuration.

So in $Na_4[Fe(CN)_6]$



$Na_4[FeF_6]$



For octahedral CFSE $= \left[-0.4\left(n_{t_{2g}}\right)+0.6\left(n_{eg}\right)\right]\Delta_0 +$ P.E.

where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals

n_{eg} = number of electron in e_g orbitals

$Na_4[Fe(CN)_6]$ CFSE $= -2.4\ \Delta_o + 3P$. [$n_{t_{2g}} = 6,\ n_{eg} = 0$]

$Na_4[Fe(F)_6]$ CFSE $= -0.4\ \Delta_o + P$ [$n_{t_{2g}} = 4,\ n_{eg} = 2$]

where P = pairing energy to pair up electron.

28. What are the factors which affect the splitting in C.F.T ?

Ans. factor affecting splitting

(i) Strength of ligand [C.F.S.E. is more in case of S.F.L. as compare to W.F.L.]

(ii) Oxidation state of central metal ion [C.F.S.E. $\propto$ oxidation state]

(iii) Transition series (d-series) [C.F.S.E. , 5d > 4d > 3d]

(iv) Geometry (number of ligands). [$\Delta_{sq} > \Delta_0 > \Delta_t$]

$\Delta_{sq} = \dfrac{4}{3}\Delta_0$ $\qquad \Delta_t = \dfrac{4}{9}\Delta_0$

29. Which factors affect strength of ligands?

Ans. Strength of ligand depends upon :

(i) good σ donor (ii) good π acceptor (iii) high negative charge (iv) Small in size

30. What is spectro-chemical series for ligands ?

Ans. Series which shows the relative strength of ligands

I^-(weakest) < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < $C_2O_4^{2-}$ < H_2O < NCS^- < $edta^{4-}$ < NH_3 < en < CN^- < CO(strongest)

31. What is the relation between splitting energy of octahedral (Δ_0) and tetrahedral (Δ_t) ?

Ans. $\Delta_t \approx \dfrac{4}{9}\Delta_0$

32. Compare the splitting energy (Δ_0) into the following compound and give appropritate reason ?

$[Co(NH_3)_6]^{3+}$, $[Rh(NH_3)_6]^{3+}$, $[Ir(NH_3)_6]^{3+}$

Ans. In given compounds number of ligands, types of ligands and oxidation state is same for central atom belongs to same group but different transition series 3d, 4d and 5d respectively. We know that as move top to bottom size of d-orbital(3d$\rightarrow$ 4d $\rightarrow$ 5d) is increases so ligand approches to d-orbitals more closely so the repulsion between d-orbital of metal and ligand is high and splitting energy increases.

order of splitting energy $[Co(NH_3)_6]^{3+} < [Rh(NH_3)_6]^{3+} < [Ir(NH_3)_6]^{3+}$

33. Compare the splitting energy (Δ_0) in the following compound and give appropritate reason ?

$[CrCl_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, $[Cr(CN)_6]^{3-}$

Ans. In above compound oxidation state, central metal ion and number of ligand is same so compound on the basis of nature of ligand.

According to spectro chemical series strength of given lignads

$Cl^- < H_2O < NH_3 < CN^-$

We know that as strength of ligand increases splitting energy increases. So the order is

$[CrCl_6]^{3-} < [Cr(H_2O)_6]^{3+} < [Cr(NH_3)_6]^{3+} < [Cr(CN)_6]^{3-}$

34. Compare the splitting energy (Δ_0) in the following compound and give appropritate reason ?

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

Ans. As the oxidation state of central metal ion increases ligand approches more closely to the central metal ion where the d-orbital exprience the greater repulsion.

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

DO YOUR SELF-VII

1. Calculate the crystal field stablization energy (CFSE) for

(i) d^5 low spin octahedral

(ii) d^5 high spin octahedral

(iii) d^4 high spin octahedral

(iv) d^6 low spin octahedral

2. Why the spliting energy on tetrahedral complexes Δ_t is less than splitting energy of octahedral (Δ_0). Give suitable reason ?

3. Discuss the structure of the following compounds on the basis of the crystal field theory $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{3-}$

APPLICATION OF CRYSTAL FIELD THEORY

35. What are the applications of crystal field theory (C.F.T) ?

Ans. Applications of C.F.T

(i) To predict the geometry that the compound is either inner orbital or outer orbital complex.

(ii) To calculate the magnitude of paramagnetism.

(iii) To show the colour property.

(I) <u>PARAMAGNETISM</u> :

36. How to calculate the magnitude of paramagnetism of compound ?

Ans. Paramagnetism $\mu = \sqrt{n(n+2)}$ B.M.

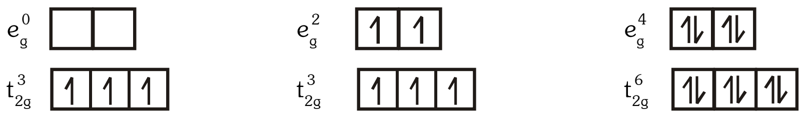
Where n is the number of unpaired electrons present in the metal ion.

37. Calculate the paramagnetism into following compound ?

$[Cr(H_2O)_6]^{3+}$ $[Fe(H_2O)_6]^{3+}$ $[Zn(H_2O)_6]^{2+}$

Ans. In all compound H_2O is a weak field ligand so pairing of electron will not occur in

(I) $[Cr(H_2O)_6]^{3+}$ (II) $[Fe(H_2O)_6]^{3+}$ (III) $[Zn(H_2O)_6]^{3+}$



(I)	(II)	(III)
n = 3	n = 5	n = 0
$\mu = \sqrt{15}$	$\mu = \sqrt{35}$	$\mu = 0$

38. Why the d^8 configuration always shows paramagnetism 2.83 B.M in octahedral complex ?

Ans. In given d^8 configuration for octahedral complex for both strong field lignad and weak field ligand is always have two unpaired electron.

Strong field ligand Weak field lignad

n = 2 n = 2

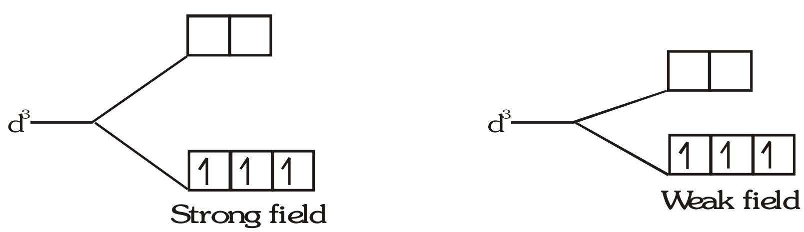
$\mu = \sqrt{n(n+2)}\,\text{B.M.} = \sqrt{2(2+2)} = 2.83$ B.M.

39. Why metal ion with $d^1, d^2, d^3, d^8, d^9, d^{10}$ configuration show fix paramagnetism in octahedral complex. Give suitable reason ? also give the value of paramagnetism for given configurations?

Ans. For $d^1, d^2, d^3, d^8, d^9, d^{10}$ configuration they have always fix number of unpaired electrons in octahedral geometry in any lignad enviroment either their is strong field lignad or weak field field lignad.

In the given configuration their is no effect of crystal field splitting :

Eg :



$d^1 \rightarrow n = 1 \Rightarrow \mu = \sqrt{1(1+2)} = 1.73$ B.M.

$d^2 \rightarrow n = 2 \Rightarrow \mu = \sqrt{2(2+2)} = 2.83$ B.M.

$d^3 \rightarrow n = 3 \Rightarrow \mu = \sqrt{3(3+2)} = 3.87$ B.M.

$d^8 \rightarrow n = 2 \Rightarrow \mu = \sqrt{2(2+2)} = 2.83$ B.M.

$d^9 \rightarrow n = 1 \Rightarrow \mu = \sqrt{1(1+2)} = 1.73$ B.M.

$d^{10} \rightarrow n = 0 \Rightarrow \mu = 0$

DO YOUR SELF-VIII

1. Calculate the paramagnetism of following configuration ?

(i) d^4 high spin octahedral	(ii) d^4 low spin octahedral
(iii) d^5 high spin octahderal	(iv) d^5 tetrahedral
(v) d^6 tetrahedral	(vi) d^8 low spin octahedral
(vii) d^7 tetrahderal	(viii) d^7 high spin octahedral.

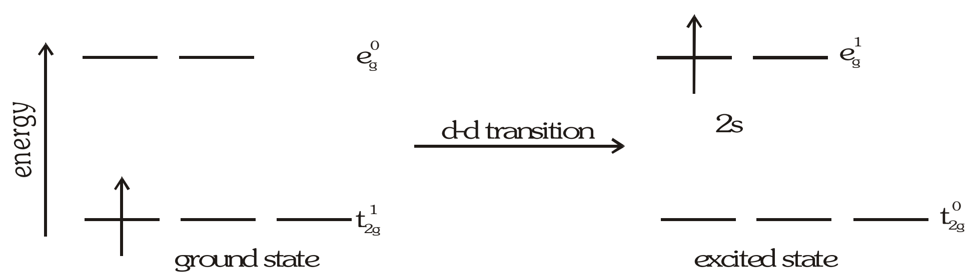
(II) <u>COLOUR PROPERTY</u> :

40. Why the complex compound show colour?

Ans. Due to d-d transition of electrons.

41. $[Ti(H_2O)_6]^{+3}$ is violet in colour explain using CFT.

Ans. In $[Ti(H_2O)_6]^{3+}$ d-robitals of Ti^{3+} lost their degeneracy in the presence of octahedral ligand field and produce t_{2g^1} & eg^0. orbital of different energy complex absorbed visible light for excitation of electron from t_{2g^0} to eg^1 (d-d transition) and show complimentary violet colour.



42. How the complex compounds show the colour?

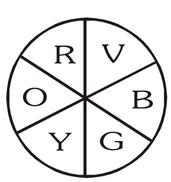
Ans. When d-electrons absrobs energy from visible region they will get excited. Absorbed energy is related to a particular wavelength.

$$\underset{\text{absorbed}}{E(\Delta)} = \frac{hc}{\lambda_{\text{absorbed}}}$$

when electrons fall into lower energy level it will show colour whose wavelength (λ) is the complimentary of absorbed wavelength ($\lambda_{\text{absorbed}}$).

43. Write down the complementry colour relationship between colour spectrum ?

Ans.



For example complementry colour of red is green.

44. Why violet coloured $[Ti(H_2O)_6]Cl_3$ becomes colourless when heated ?

Ans. When $[Ti(H_2O)_6]Cl_3$ is heated water molecules are removed and in the absence of ligand crystal field splitting does not occur and hence the substance is colourless.

DO YOUR SELF-IX

1. $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why ?

2. What will be the correct order for the wavelengths of absorption in the visible region for the following :
$[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?

ISOMERISM

45. What is isomerism ?

Ans. The compounds having same molecular formula but different physical and chemical properties on account of different structures are called isomer and the phenomenon is known as isomerism.

46. What do you mean by structural isomerism ?

Ans. It arises due to the difference in the type of chemical linkage and distribution of ligands within and outside the co-ordination sphere.

47. What is Ionisation isomerism ? Give example.

Ans. This type of isomerism which is due to the exchange of groups or ion between the coordinating sphere and the ionisation sphere. **Ex.**

(i) $Co(NH_3)_4\ Br_2SO_4$ can represent

$[Co(NH_3)_4\ Br_2]\ SO_4$ (red violet) and $[Co\ (NH_3)_4\ SO_4]Br_2$ (red)

(ii) $[Pt(NH_3)_4\ Cl_2]\ Br_2$ and $[Pt\ (NH_3)_4\ Br_2]Cl_2$

(iii) $[Co(NH_3)_4\ (NO_3)_2]SO_4$ and $[Co(NH_3)_4.SO_4]\ (NO_3)_2$

48. How can you differentiate ?

(i) $[Co(NH_3)_4SO_4]Br$ (ii) $[Co(NH_3)_5Br]SO_4$

Ans. $[Co(NH_3)_4SO_4]Br$ give does not white ppt. of $BaSO_4$ with $BaCl_2$ solution whereas isomer $[Co(NH_3)_5Br]SO_4$ does form a precipitate.

49. What is the Hydrate isomerism ? Give example.

Ans. The isomerism in which different number of water molecules are present inside the coordination sphere.

Example $Cr(H_2O)_6Cl_3$ has three possible structures.

(i) $[Cr(H_2O)_6]\ Cl_3$ violet

(ii) $[Cr(H_2O)_5Cl]Cl_2.H_2O$ green

(iii) $[Cr(H_2O)_4Cl_2]Cl.\ 2H_2O$ dark green

50. One mole of which hydrated isomer of $CrCl_3.6H_2O$ gives maximum moles of AgCl when treated with excess of $AgNO_3$?

Ans. $[Cr(H_2O)_6]Cl_3$

51. **What is coordination isomerism ? Give Examples.**

Ans. This type of isomerism is observed in the coordination compounds having both cationic and anionic complex ions. The ligands are interchanged in both the cationic and anionic ions to form isomers.

Ex. $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $[Co(NH_3)_6]$ $[Cr(C_2O_4)_3]$

$[Cr(NH_3)_6]$ $[Co(CN)_6]$ and $[Cr(NH_3)_6]$ $[Co(C_2O_4)_3]$

52. **What do you mean by linkage isomerim ? Give examples.**

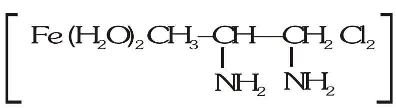
Ans. This type of isomerism occurs in complex compounds which contain ambidanate ligands like NO_2^-, SCN^-, CN^-, $S_2O_3^{2-}$. These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex. These type of isomer are distinguished by infra-red (I.R./UV/ Visible) spectroscopy.

Ex. $[Co(NH_3)_5NO_2]$ Cl_2 and $[Co(NH_3)_5$ $ONO]Cl_2$

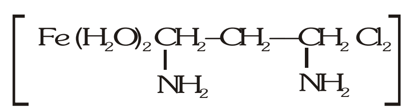
53. **What do you mean by ligand isomerism ? Give example.**

Ans. This type of isomerism occurs in complexes which have same molecular formula, but differ with respect to their ligands are called ligand isomers.

Ex. $[Fe(H_2O)_2$ $C_3H_6(NH_2)_2Cl_2]$ has two different structures.



and



54. **What do you mean by stereo isomerism ?**

Ans. Compounds which contains the same ligands in their co-ordination sphere but differ in the way that these ligands are arranged in space are known as stereo isomers and this phenomenon is known as stereo isomerism. Stereo-isomerism is of two types, viz. geometrical isomerism and optical isomerism.

55. **What do you mean by geometrical isomerism. How can you divide in two parts.**

Ans. This isomerism is due to ligands occupying different positions around the central metal atom or ion. The ligand occupy positions either adjacent or opposite to one another. This type of isomerism is also known as cis-trans isomerism

- When two identical ligands are coordinated to the metal ion from same side, the it is cis isomer. (latin, cis means same).
- If the two identical ligands are coordinated to the metal ion from opposite side then it is trans isomer. (in latin, trans means across).

56. **Why geometrical isomerism cannot arise in a tetrahedral complex ?**

Ans. Because this geometry contains all the ligands in cis (i.e. adjacent) position with respect to each other i.e. each ligand is equidistant from the other three ligands and all bond angles are the same (= 109.5). This isomerism is, however found in many square planar (C.N. =4) and octahedral (C.N. =6) complex.

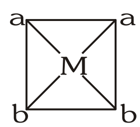
57. **Why $[Ma_4]^{n\pm}$, $[Ma_3b]^{n\pm}$, $[Mab_3]^{n\pm}$ type square planar complex do not show geometrical isomerism ?**

Ans. Because every conceivable spatial arrangement of ligands around the metal ion is exactly same.

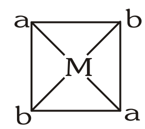
58. **Write the example of geometrical isomers with co-ordination number 4 (square planar complex) ?**

Ans. Geometrical isomers with Coordination number = 4

(i) Complexes with general formula, $\mathbf{Ma_2b_2}$ (where both a and b are monodentate) can have Cis-and trans isomers.

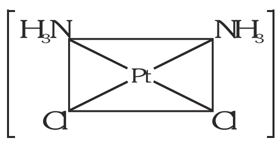


Cis-isomer

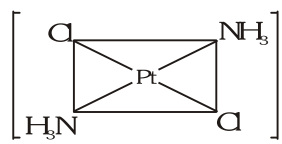


Trans-isomer

$[Pt\ (NH_3)_2Cl_2]$

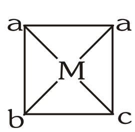


Cis(Cis-platin)
(use as anti cancer)

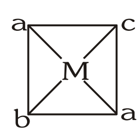


Trans

(ii) Complexes with general formula $\mathbf{Ma_2bc}$ can have Cis - and trans-isomers.

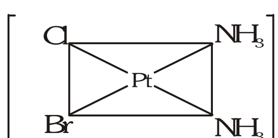


Cis

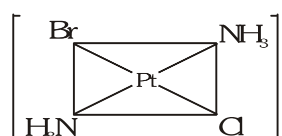


trans

$[Pt(NH_3)_2ClBr]$

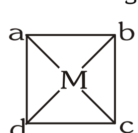


Cis

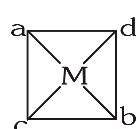


Trans

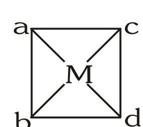
(iii) Complexes with general formula, **Mabcd** can have three isomers.



(i)



(ii)

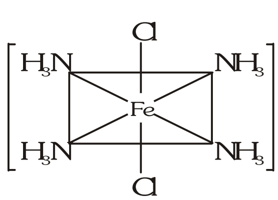


(iii)

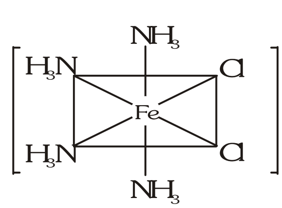
59. **Write the example of geometrical isomer with coordination number 6 ?**

Ans. Geometrical isomers with Coordination number = 6

(i) $[Fe(NH_3)_4Cl_2]$

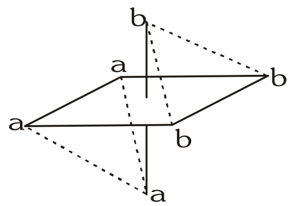


Trans

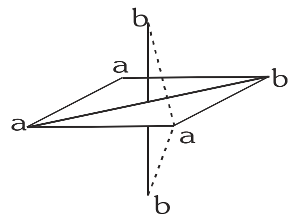


Cis

(iii) Facial and Meridional isomerism (Ma_3b_3)



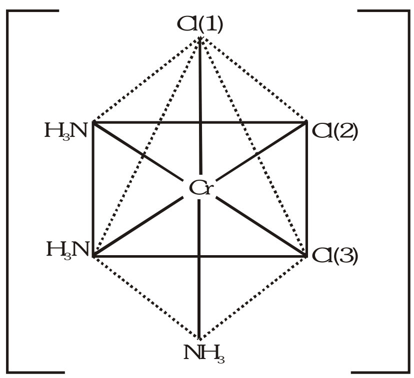
Facial (fac)



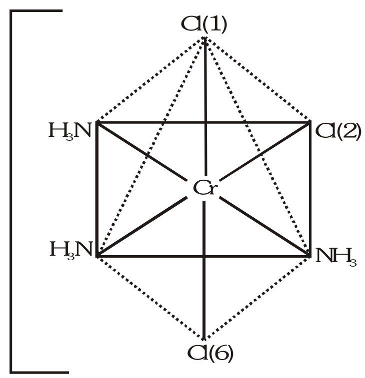
Meridional (Mer)

60. Give the isomeric form of $[Cr^{III}(NH_3)\ Cl_3]$?

Ans. $[Cr^{III}\ (NH_3)_3Cl_3]$ which exist in two isomeric forms in one isomer, the three Cl^- ions are on one triangular face and the three NH_3 molecules are on the opposite triangular face of the regular octahedron. This isomer is called 1, 2, 3 or facial isomer. In the other isomer the Cl^- ions are around an edge of the octahedron and the NH_3 molecules are around the opposite edge.



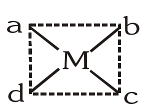
1,2,3- Isomer

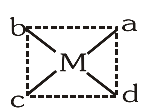


1,2,6- Isomer

61. Why following pairs are not geometrical isomers ?

(i)

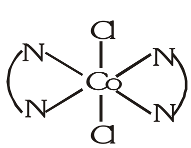


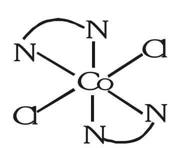


(a,c) are at trans (a,c) are at trans

(b,d) are at trans (b,d) are at trans

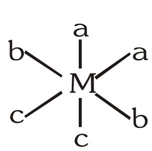
(ii)

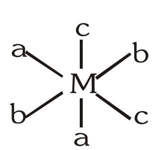




(Cl, Cl) are at trans (Cl, Cl) are at trans

(iii)





Ans. In pair (i), (ii) and (iii) all the ligands have identical space orientation but represented different side so that the pairs have two Identical complex.

62. What is optical isomerism ?

Ans. A coordination compound which can rotate the plane of polarised light is said to be optically active. When the coordination compounds have same formula but differ in their abilities to rotate directions of the plane of polarised light are said to exhibit optical isomerism and the molecules are optical isomers.

- optically active complexes are those which are non superimposable over the mirror image structure.
- If molecule does not have palen of symmetry then it is optically active.

63. What do you mean by d and ℓ -form ?

Ans. The complex which rotates plane polarised light to left hand side is laevo rotatory i.e. 'ℓ' or '–' and if the complex rotates the plane polarised light to right hand side then it is dextro rotatory 'd' or '+'.

64. Define the optically active & optically inactive forms ?

Ans. When d and ℓ forms are capable of rotating the plane of polarised light, these are said to be optically active forms or optical isomer and this phenomena is called optical activity or optical isomerism.

One which is not capable of rotating the plane of polarised light is called optically inactive.

65. What do you mean by Enantiomorphs?

Ans. The 'd' and 'ℓ' isomers of a compound are called as enantiomers or enantiomorphs of each other.

66. Which of the molecule show optical isomerism ?

Ans. Asymmetric molecule show optical isomerism.

67. Write the properties of asymmetric molecule.

Ans. (i) Asymmetric molecule never has a plane of symmetry.

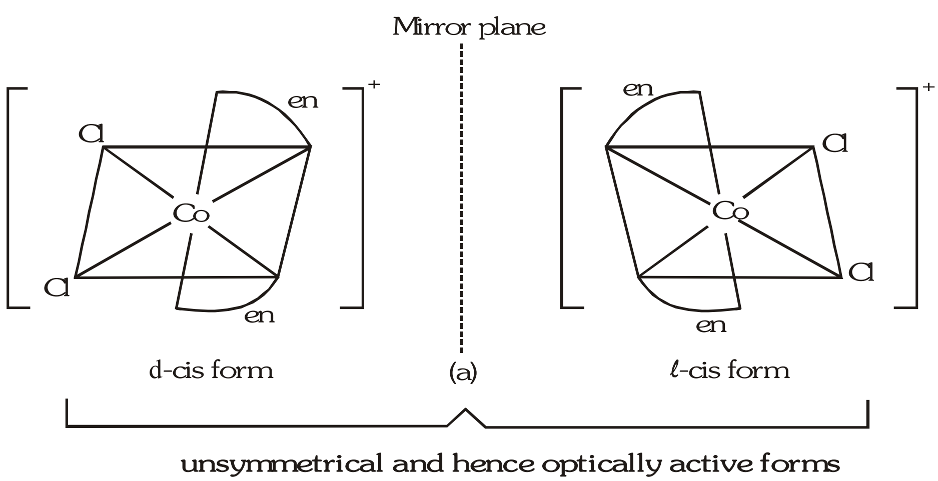
(ii) An asymmetric molecule cannot be superimposed on its mirror image.

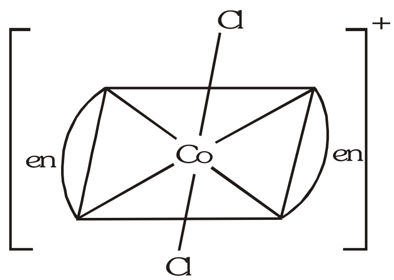
68. Why $[Ma_4]$, $[Ma_3b]$ and $[Ma_2b_2]$ type complexes do not show optical isomerism ?

Ans. Because these complexes have plane of symmetry.

69. Why Cis form of $[Co(en)_2Cl_2]^+$ ion, shows optical isomerism but trans form of this ions not shows optical isomerism.

Ans.





(b)

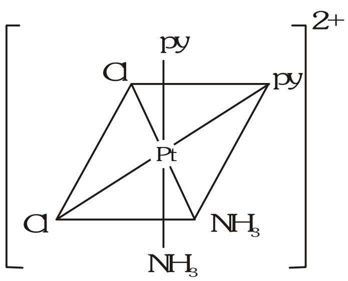
trans-meso form (symmetrical and hence optically inactive)

The cis-isomer of $[Co(en)_2Cl_2]^+$ ion shown in fig. (a) can be resolved into two optically active isomers, since it has no plane of symmetry. Its trans isomer shown at (b) cannot be resolved into two forms, since no mirror-image of this ion is possible i.e. it has a plane of symmetry. Thus trans isomer is an optically inactive forms (meso-forms)

70. **Write the example of optical isomers with coordination number 6 ?**

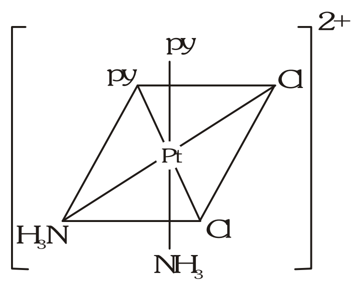
Ans. **Optical isomers with Coordination number = 6**

(i) $[Ma_2b_2c_2]^{n+} \rightarrow [Pt(py)_2(NH_3)_2Cl_2]^{2+}$



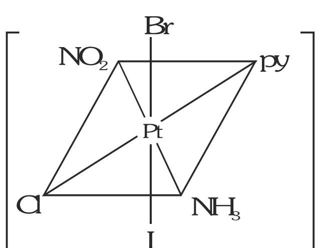
Cis-d-isomer

Mirror



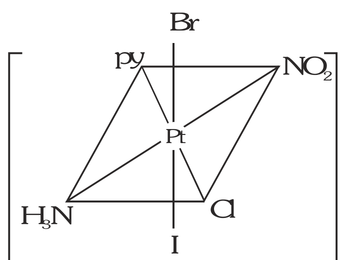
Cis-ℓ-isomer

(ii) $[Mabcdef] \rightarrow [Pt(py)\ (NH_3)\ (NO_2)\ ClBrI]$



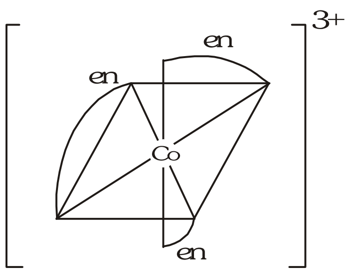
d-isomer

Mirror



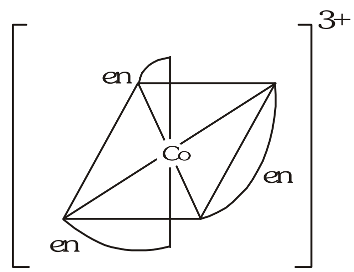
ℓ-isomer

(iii) $[M(AA)_3]^{n+} \rightarrow [Co(en)_3]^{3+}$



d-form

Mirror



ℓ-form

DO YOURSELF-X

1. Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionisation isomers ?

2. How many geometrical isomers possible in the following coordination entities ?
   (i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[Co(NH_3)_3Cl_3]$

3. Draw the structures of optical isomers of :
   (i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[PtCl_2(en)_2]^{2+}$ (iii) $[Cr(NH_3)_2Cl_2(en)]^+$

4. Draw all the isomers (geometrical and optical) of :
   (i) $[CoCl_2(en)_2]^+$ (ii) $[Co(NH_3)Cl(en)_2]^{2+}$ (iii) $[Co(NH_3)_2Cl_2(en)]^+$

5. Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers ?

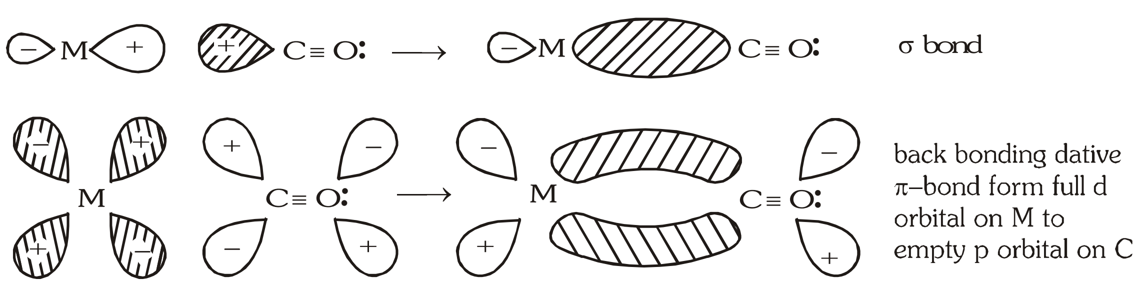
6. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers :
   (i) $K[Cr(H_2O)_2(C_2O_4)_2]$ (ii) $[Co(en)_3]Cl_3$
   (iii) $[Co(NH_3)_5(NO_2)](NO_3)_2$ (iv) $[Pt(NH_3)(H_2O)Cl_2]$

BONDING IN METAL CARBONYL

71. What is synergic bonding ?

Ans. The electronic configuration of CO molecule shows that it has lone pair of electrons on carbon and oxygen atom each. Carbon atom can donate its electron pair of a transition metal atom (M), forming OC$\rightarrow$M coordinate bond.

Since the metal atom in metal carbonyl is in zero oxidation state, the formation of M $\leftarrow$ CO σ bond accumulates a negative charge on the metal atom. The accumulation of negative charge on the metal atom can be counter balanced by transferring some negative charge from the metal atom to CO molecule (ligand). This transfer can be done by making a M $\rightarrow$ CO π bond by the overlap between an appropriate filled orbital on the metal atom and empty π_y^* or π_z^* molecular orbital on CO molecule. This type of bonding between M and CO is called synergic bonding.



Schematic of orbital overlaps in metal carbonyls.

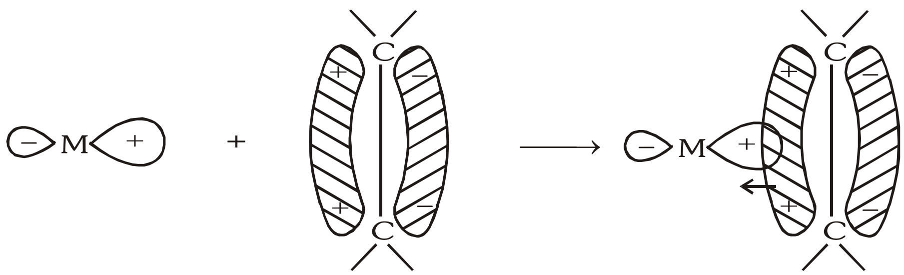
72. **What is the effect of synergic bonding ?**

Ans. The fillling or partial filling of the antibonding orbital on C reduce the bond order of C–O bond from the triple bond in CO towards a double bond. This shown by the increase in C–O bond length from 1.128 Å in CO to about 1.15 Å in many carbonyls. As decrease in (C–O) bond order their will be increase in (M–C) bond order and (M–C) bond order increases from one to towards two.

73. **Which bond is formed in Zeises salt ?**

Ans. Zeises salt K [Pt $Cl_3(\pi\text{-}C_2H_4)$]

The bonding of alkenes to a transition metal to form complexes has two components. First, the π-electron density of the alkene overlaps with a σ-type vacant orbital or the metal atom. Second is the back bonding formed by the flow of electron density from a filled d-orbital on the metal into the vacant π^*-antibonding molecular orbital on the carbon atom as shown below:



σ-overlap