03 Coordination Compounds

Introduction:

(a) The concept of co-ordination compounds arises from the complex formation tendency of transition elements.

(b) These compounds play a vital role in our lives, as chlorophyll of plants, vitamin B_{12} and haemoglobin of animal blood are the co-ordination compounds of Mg, Co and Fe respectively.

(c) The co-ordination compounds play important role in analytical chemistry, polymerisation reactions, metallurgy and refining of metals, photography, water purification etc.

(d) Co-ordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

Addition compounds:

When solutions containing two or more salts in simple molecular proportion are evaporated, crystals of new compound separate out.

These compounds are called molecular or addition compounds.

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

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

These addition compounds can be divided into two classes :

(A) Double Salts

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 .

Example :

Potash alum $K_2SO_4 . Al_2(SO)_4)_3 . 24H_2O$ when dissolved in water breaks down into $K^{\oplus}, SO_4^{2\ominus}, Al^{3\oplus}$ ions and therefore is an example of **double salt**.

(B) Coordination Compounds

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.

Example :

Potassium ferrocyanide $K_4[Fe(CN)_6]$ does not furnish simple $K^{\oplus}$, $Fe^{2\oplus}$ and $CN^{\ominus}$ ions but gives $K^{\oplus}$ ions and complex ferrocyanide ions, $[Fe(CN)_6]^{4\ominus}$. These types of compounds are called **complex compounds or co-ordination compounds**.

Stability of coordination compounds:

The stability of a coordination compound $[ML_n]$ is measured in terms of the stability constant (equilibrium constant) given by the expression,

$\beta_n = [ML_n]/[M(H_2O)_n][L]^n$

for the overall reaction :

$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$

By convention, the water displaced is ignored, as its concentration remains essentially constant. The above overall reaction takes place in steps, with a stability (formation) constant, K_1, K_2, K_3, ... K_n for each step as represented below :

$M(H_2O)_n + L \rightleftharpoons ML(H_2O)_{n-1} + H_2O$

$K_1 = [ML(H_2O)_{n-1}] / \{[M(H_2O)_n][L]\}$

$ML_{n-1}(H_2O) + L \rightleftharpoons ML_n + H_2O$

$K_n = [ML_n] / \{[ML_{n-1}(H_2O)][L]\}$

$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$

$\beta_n = K_1 \times K_2 \times K_3 \times ..... \times K_n$

β_n, the stability constant, is related to thermodynamic stability when the system has reached equilibrium. Most of the measurements have been made from aqueous solutions, which implies that the complex is formed by the ligand displacing, water from the aqua complex of the metal ion. Ignoring the charge and taking L as an unidentate ligand, the stepwise formation of the complex is represented as shown above. K_1, K_2, K_3 ..... K_n representing the stepwise stability (or formation) constants.

The above is thermodynamic stability criteria, there can be another kind of stability called kinetic stability, which measures the rate of ligand replacement.

On the basis of stability of complex ion, complex ions are further divided as follows:

(i) Perfect complexes : The compounds in which complex ion is fairly stable and further dissociation or feebly dissociation is not possible in solution state.

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

$\downarrow$

$Fe^{2\oplus} + 6CN^{\ominus}$ (Feebly dissociated)

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

(ii) Imperfect complexes : Those complexes in which complex ion is less stable and is reversibly dissociated to give enough simple ions and thus respond to their usual qualitative test.

Ex. $K_2[Cd(CN)_4] \longrightarrow 2K^{\oplus} + [Cd(CN)_4]^{2\ominus}$

$\Downarrow$

$Cd^{2\oplus} + 4CN^{\ominus}$ (appreciably dissociated)

Various terms involved in coordination compounds:

(a) Complex ion :

An aggregate of metal ion with anions, cation or neutral molecules is called as **complex ion.**

(b) Central metal ion :

(i) The metal ion which forms complex ion in combination with anions or neutral molecules is called as **central metal ion**.

(ii) Central metal ion acts as an electron pair acceptor and forms coordinate bond with ligands.

(c) Coordination number :

(i) The number of ligands that combine with the central metal ion to form the complex ion is called as coordination number.

(ii) From every ligand central metal ion accepts lone pair of electrons. Thus, the number of lone pair of electrons accepted by the central metal ion in the formation of a complex is called as coordination number.

(d) Coordination sphere (entity) :

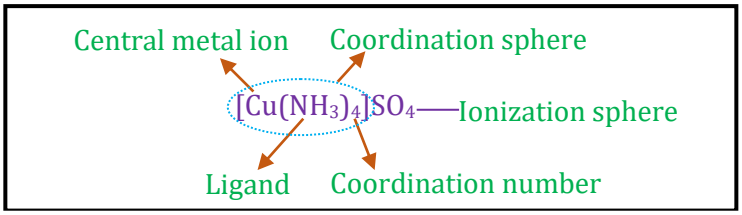
(i) The central metal atom and the ligands directly attached to it are collectively termed as the coordination sphere.

(ii) Coordination sphere is written inside square bracket, for example $[Co(NH_3)_6]^{3\oplus}$

(iii) The part outside the bracket is called **ionisation sphere**.

(iv) The species present in the coordination sphere are nonionizable.

(v) The species present in the ionization sphere are ionisable.



(e) Oxidation state :

(i) It is a number which represents the electric charge on the central metal atom of a complex ion.

(ii) **Ex.** the oxidation number of Fe, Co and Ni in $[Fe(CN)_6]^{4\ominus}$, $[Co(NH_3)_6]^{3\oplus}$ and $Ni(CO)_4$ is +2, +3 and zero respectively.

(f) Charge on the complex ion :

It is the algebraic sum of the total charge of the ligands and central metal ion.

(g) Ligands :

(i) The anions or neutral molecules which combine with central metal ion to form complex ion are called as ligands.

(ii) They act as electron pair donor Lewis bases, but strong crystal field ligands like CO, $CN^{\ominus}$ etc can accept electron pair from the metal ion, because these ligands are π - acids.

On the basis of type of ligands complex compounds are divided as follows:

(i) Homoleptic complexes :

Complex in which all the ligands are identical is called homoleptic complex.

Ex. $[Co(NH_3)_6]^{2\oplus}$

(ii) Heteroleptic complexes :

Complex in which all the ligands are not identical is known as heteroleptic complex.

Ex. $[Fe(en)_2Cl_2]^{1\oplus}$

Type of complexes:

1. Cationic complex : [ ]$^{n\oplus}$

Complex in which co-ordination sphere contain positive charge.

$[Cr(H_2O)_6]Cl_3$, $[Co(en)_2\ (NH_3)_2]^{3\oplus}$

2. Anionic complex : [ ]$^{m\ominus}$

Complex in which co-ordination sphere contain negative charge.

Eg. $K_4[Fe(CN)_6]$, $[Cr(OX)_2(H_2O)_2]^{\ominus}$

3. Neutral complex : [ ]^0

Complex in which co-ordination sphere contain no charge.

Eg. $[Fe(CO)_5]$, $[Fe(CO)_2(NO)_2]$

Classification of ligands:

1. On the basis of charge:

(i) Negative ligands : eg. $H^{\ominus}$, $OH^{\ominus}$, $O_2^{2\ominus}$, $O^{2\ominus}$, etc.

(ii) Positive ligands : eg. $NO^{\oplus}$, $N_2H_5^{\oplus}$

(iii) Neutral ligands : eg. H_2O, NH_3, NO, O_2, etc.

2. On the basis of denticity:

The number of electron pairs donated to central metal by ligands is known as DENTICITY. Depending on number of electron pairs donated, these are classified in following categories.

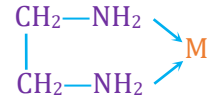
(a) Unidentate/monodentate ligands :

Ligands which donate one pair of electron to the central metal are called unidentate ligands.

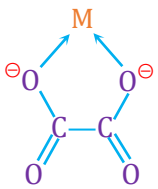
$X^{\ominus}$, $CN^{\ominus}$, $NO_2^{\ominus}$, NH_3, Pyridine, $OH^{\ominus}$, $NO_3^{\ominus}$, H_2O, $SO_3^{2\ominus}$, CO, NO, $OH^{\ominus}$, $O^{2\ominus}$, $(C_6H_5)_3P$ etc.

(b) Bidentate ligands :

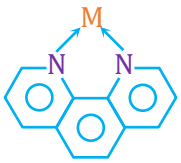
Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands.



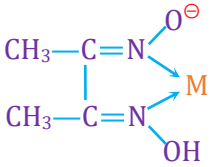
Ethylenediamine(en)



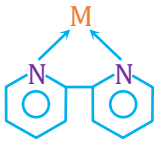
Oxalate(ox)



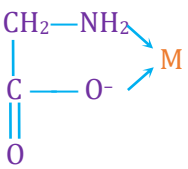
1, 10-Phenanthroline (O-phen)



Dimethyl glyoximion (DMG)



2,2'-Dipyridyl (Dipy)

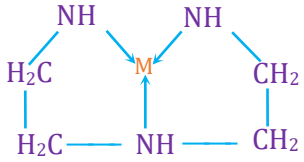


Glycinato (Gly)

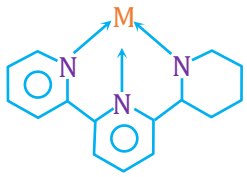
(c) Tridentate ligands :

The ligands which donate three pairs of electrons to the central metal are called tridentate ligands

Example.



Diethylene triamine (Dien)

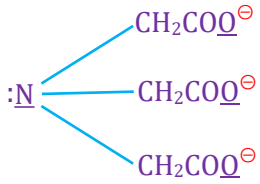


2, 2′, 2″-Terpyridine (Terpy)

(d) Tetradentate ligands :

Those ligands which donate four electron pairs to the central metal are known as tetradentate ligands,

Example : (Underline atoms are donating atom)

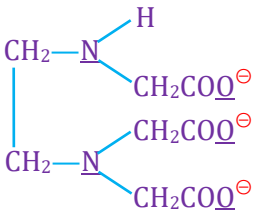


Nitrilotriacetato ($nta^{3\ominus}$)

(e) Pentadentate ligands :

Those ligands which donate five electron pairs to the central metal are known as pentadentate ligands.

Example : Ethylenediamine triacetate ion. (Underline atoms are donating atom)



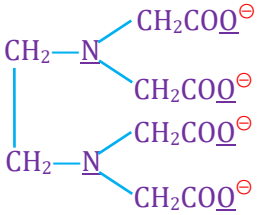
$(EDTA)^{3\ominus}$

Ethylenediaminetriacetate ion

(f) Hexadentate ligands :

Those ligands which donate six electron pairs to the central metal are known as hexadentate ligands.

Example : (Underline atoms are donating atom)

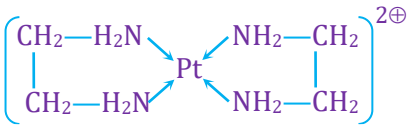


Ethylenediaminetriacetate ion $(EDTA)^{4\ominus}$

(g) Chelating ligands :

Polydentate ligands whose structures permit the attachment of two or more donor site to metal ion simultaneously, thus resulting in cyclic structure are called chelating ligands and compound formed is known as **chelate compound**.

Example :



(h) Ambidentate ligands :

Ligands which can ligate through two different atoms present in it are called ambidentate ligands. At a time only one atom can donate.

$[CN^{\ominus}\ NC^{\ominus}]$ $[NO^{\ominus}\ ONO^{\ominus}]$ $[SCN^{\ominus}\ NCS^{\ominus}]$ $[CNO^{\ominus}\ NCO^{\ominus}]$ $[S_2O_3^{2\ominus}\ OSO_2S^{2\ominus}]$ $[SeCN^{\ominus}\ NCSe^{\ominus}]$

Example :

$CN^{\ominus}$ can coordinate through either the nitrogen or the carbon atom to central metal ion.

(i) Flexidentate ligands :

Ligands which sometimes do not use all the donor sites to get coordinated with central metal ion are known as flexidentate ligands.

Ex. $SO_4^{2\ominus}$, $CO_3^{2\ominus}$ etc.

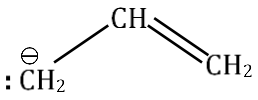
Type of ligands:

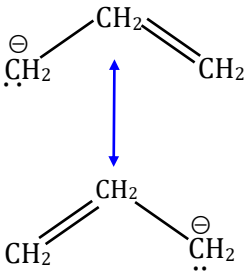
Organic ligands : No suffix will be added in the name of organic ligand.

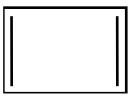
- $:\overset{\ominus}{C}H_3$ Methyl
- $:\overset{\ominus}{C}_2H_5$ ethyl

Hapticity: is the coordination of a ligand to a metal center via an uninterrupted and contiguous series of atoms. The hapticity of a ligand is described with the Greek letter η ('eta').

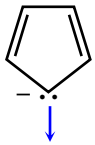
- C_2H_4 $H_2C = CH_2$ η^2-ethene $2e^{\ominus}$
- $\overset{\ominus}{C}_3H_5:$

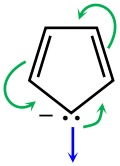
(i) σ-$\overset{\ominus}{C}_3H_5$  η^1-Allyl $2e^{\ominus}$

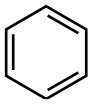
(ii) π-$\overset{\ominus}{C}_3H_5$  η^3-allyl $4e^{\ominus}$

- C_4H_4 :  η^4-cyclobutadiene $4e^{\ominus}$

- $\overset{\ominus}{C_5H_5}$

(i) σ-$\overset{\ominus}{C_5H_5}$  Cyclopentadienyl $2e^{\ominus}$

(ii) π-$C_5\overset{\ominus}{H_5}$  η^5-cyclobutadiene $6e^{\ominus}$

- C_6H_6 :  η^6-benzene $6e^{\ominus}$

3. On the basis of nature of bonding between central metal atom and ligand:

(i) Normal or classical ligands :

Ligand which only donate electron pair to central metal ion & form coordinate (σ)bond

e.g. $OH^{\ominus}$, $NH_2^{\ominus}$, $Cl^{\ominus}$, $N^{3\ominus}$, $O^{2\ominus}$ etc.

(ii) Non classical or π-acid or π-acceptor ligands :

Ligand which donate electron pair to central metal ion & form coordinate σ bond but simultaneously they accept electron pair from central metal ion through back bonding or synergic bonding.

e.g. CO, $NO^{\oplus}$, $CN^{\ominus}$, R_3P, R_3As etc.

Synergic bonding in metal carbonyls:

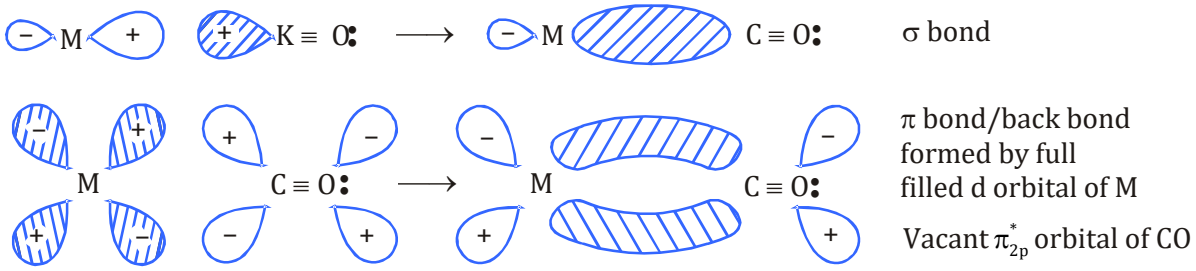
They are of 2 types

(a) σ donor and π acceptor ligands

Ligands which donate their lone pair to central metal ion through σ bond and simultaneously accept $e^{\ominus}$ pair from central metal ion through π bond.

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 d orbital on the metal atom and empty π^* molecular orbital of CO molecule. This type of bonding between M and CO is called **synergic bonding.**



[Schematic of orbital overlaps in metal carbonyls]

Conclusion of synergic bonding :

(a) M–C bond strength increases; M–C bond length decreases; because double bond character increases

(b) C–O bond strength decreases; C–O bond length increases; because bond order of C–O decreases (CO accepts $e^{\ominus}$ pair into its antibonding molecular orbital)

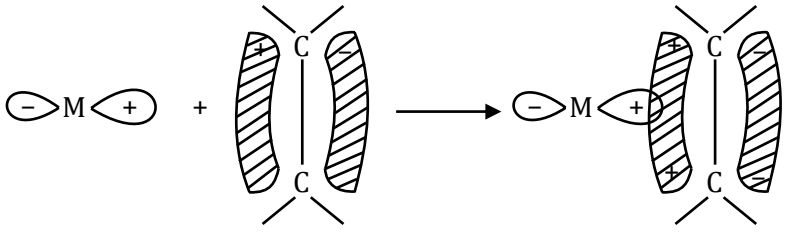
(b) π-donor and π-acceptor ligands

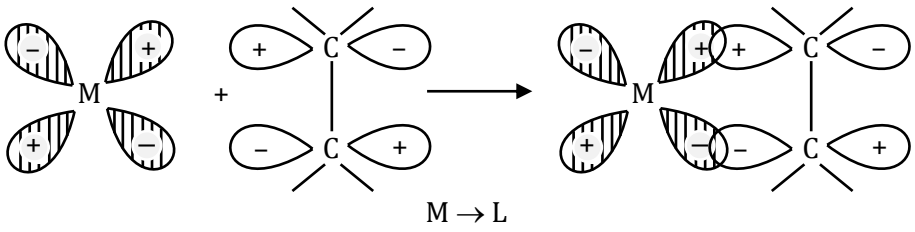
Ligands which donate π electron pair to central metal ion & also accept electron pair from central metal ion through synergic bonding.

(i) $H_2C=CH_2$ (η^2 - ethylene) : it is a 2π electron donor

(ii)  (η^6 - benzene) : it is a 6π electron donor

(iii)  / $[C_5H_5]^{\ominus}$ (η^5 -cyclopentadienyl) : it is a 6π electron donor





for example

(a) $[Cr(\eta^6-C_6H_6)_2]$ sandwich like structure

(b) $[Fe(\eta^5-C_5H_5)_2]$ ferrocene (sandwich like structure)

(c) $K[PtCl_3(\eta^2-C_2H_4)]$ (Zeise's salt)

Organometallic Compounds:

Compound in which C atom of a hydrocarbon or a ligand is directly bonded with a metal/metalloid/non metal is known as organometallic compounds.

eg. R–Zn–R dialkyl zinc (Frankland reagent)
R–Mg–X Alkyl Magnesium halide (Grignards reagent) } OMC

Sodium acetate	$CH_3-\overset{\overset{O}{\|\|}}{C}-ONa$	} Not OMC
Sodium ethoxide	C_2H_5-O-Na	
Sodium Mercaptide	H_3C-SNa	

These are not organometallic compounds because in these compounds metal is not directly attached with carbon atom.

$B(OCH_3)_3$ $\left[\begin{matrix} H_3CO \\ H_3CO \end{matrix}\!\!>\!B-OCH_3\right]$ is not OMC and $B(OCH_3)_2CH_3$ $\left[CH_3-B<\begin{matrix} COH_3 \\ OCH_3 \end{matrix}\right]$ is OMC

Note :

Carbides and carbonates are not considered OMC because in these compounds metal carbon bond has ionic nature.

Classification of Organometallic Compounds

OMC can be classified into three main categories –

(a) **σ - bonded OMC :** These compounds are formed mostly by non transition and metalloid elements.

Ex. R – Mg – X (Grignard's reagent)
$(CH_3)_2Zn$ (Dimethyl zinc or Frankland's reagent)
R_2Cd (dialkyl cadmium)
$(C_2H_5)_4Pb$ (Tetra ethyl lead) – used as antiknocking agent in petrol.
$(C_2H_5)_3Al + TiCl_4$ (Ziegler natta catalyst) – Heterogeneous catalyst, used in polymerisation of alkene.

(b) **π - bonded OMC** : These are usaully formed by transition metals.

Ex. Ferrocene $[Fe(\eta^5 - C_5H_5)_2]$
Zeise's salt $K[PtCl_3(\eta^2 - C_2H_4)]$
Chromocene $[Cr(\eta^5 - C_5H_5)_2]$

(c) **σ and π - bonded OMC** : Transition metals of gp. 6, 7, 8, 9 and 10 in their zero oxidation state form such type of OMC. The carbonyl compounds of these metals have both σ and π bonds.

Ex. $[Ni(CO)_4]$, $[Fe(CO)_5]$, $[Mn_2(CO)_{10}]$ etc.

Werner's coordination theory

Werner's coordination theory was the first attempt to explain the bonding in coordination compounds. The main postulates of this theory are :

(a) Metals possesses two types of valencies - Primary valency and secondary valency.

(b) Primary valencies are ionisable and are exhibited by a metal in the formation of its simple salts such as $CoCl_3$, $CuSO_4$ and AgCl. In these salts the primary valencies of Co, Cu and Ag are 3, 2, 1 respectively. Now-a-days primary valencies are referred to as oxidation state of their metal ion.

(c) Secondary valencies are non-ionisable and are exhibited by a metal in the formation of its complex ions such as $[Co(NH_3)_6]^{3\oplus}$, $[Cu(NH_3)_4]^{2\oplus}$ and $[Ag(NH_3)_2]^{\oplus}$. In these complex, the secondary valencies of $Co^{3\oplus}$, $Cu^{2\oplus}$, $Ag^{\oplus}$ are 6, 4 and 2 respectively. These are refered to as co-ordination number (C.N.) of the metal cation.

(d) Primary linkages (valencies) are satisfied by negative ions while secondary valencies are satisfied by neutral molecules, negative ions or in some cases positive ions also.

(e) Every metal atom or ion has a fixed number of secondary valencies. In other words, the co-ordination number of the metal atom is usually fixed.

(f) Every metal has tendency to satisfy both its primary and secondary valencies.

(g) The ligands satisfying secondary valency are always directed towards fixed positions in space about the central metal atom or ion. Thus, the co-ordination compounds have a definite geometry. Werner deduced that in $CoCl_3.5NH_3$ one chloride changed form being a primary to a secondary valency. Thus, only two of the three chlorine atoms are ionic and 5 NH_3 and one Cl form co-ordinate bonds to $Co^{3\oplus}$ ion. Formula of some cobalt complexes.

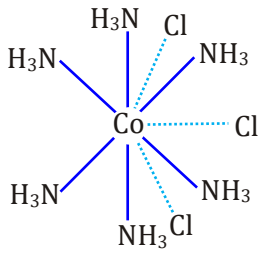
Example :

Old	New	No. of $Cl^{\ominus}$ lons	Total No. of ions precipitated
(i) $CoCl_3 . 6 NH_3$	$[Co(NH_3)_6]Cl_3$	3	4
(ii) $CoCl_5 . 5 NH_3$	$[Co(NH_3)_5Cl]Cl_2$	2	3
(iii) $CoCl_3 . 4 NH_3$	$[Co(NH_3)_4Cl_2]Cl$	1	2

Complex	Modern formula	No. of $Cl^{\ominus}$ lons	Total number of ions precipitated
$PtCl_4.6NH_3$	$[Pt(NH_3)_6]Cl_4$	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)

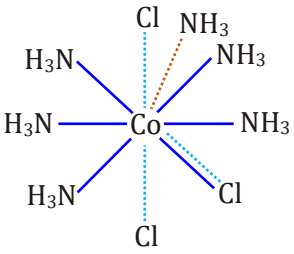
Werner's representation of complexes:

(i) $Co(NH_3)_6Cl_3$

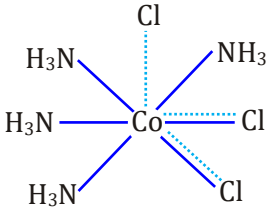


$[Co(NH_3)_6]Cl_3$

Dotted lines indicate primary valency and continuous lines indicate secondary valency of metal ion.

(ii) $Co(NH_3)_5Cl_3$  $[Co(NH_3)_5Cl]Cl_2$

In this complex two 'Cl' groups act as primary valencies and one of the 'Cl' acts as secondary valency also.

(iii) $Co(NH_3)_4Cl_3$  $[Co(NH_3)_4Cl_2]Cl$

In this complex one 'Cl' group act as primary valency and two of the 'Cl' groups act as secondary valencies also.

Experimental evidence of werner's theory:

(a) Precipitation of primary valencies on the addition of a suitable reagent.

Ex. $Fe(NH_3)_6Cl_3$ forms 3 moles of AgCl in the form of precipitate on addition of $AgNO_3$ solution. This indicates that the complex ionises as

$Fe(NH_3)_6\,Cl_3 \xrightarrow{H_2O} [Fe(NH_3)_6]^{3\oplus} + 3\,Cl^{\ominus}$

(b) Electrical conductance of complexes : More the number of ions provided greater is the electrical conductance of the complex in aqueous medium.

Electrical conductivity ∝ no. of Ions

Ex. The electrical conductance of aqueous $[Fe(NH_3)_6]\,Cl_3$ is greater than that of aqueous solution of $[Fe(NH_3)_5Cl]Cl_2$.

$[Fe(NH_3)_5Cl]Cl_2 \longrightarrow [Fe(NH_3)_5Cl]^{2\oplus} + 2Cl^{\ominus}$ **(Total 3 ions)**

Effective atomic number' (E.A.N.) rule or Sidgwick rule:

According to Sidgwick, metal atom present in coordination compound continues to accept electron pairs donated by the ligands till the total number of electrons on metal atom and those donated by ligands reaches to next noble gas configuration. This is known as **Effective atomic number' (E.A.N.) rule or Sidgwick rule**.

It is calculated by the following formula

E.A.N. = (Atomic number) – (Oxidation number) + (coordination number × 2)

Ex. Effective atomic number of cobalt in $[Co(NH_3)_6]^{3\oplus}$ can be calculated as follows :

Atomic number of cobalt = 27

Oxidation state of cobalt in complex = +3

Number of electrons in $Co^{3\oplus}$ ion are (27–3 = 24)

During coordinate covalent bonding, $Co^{3\oplus}$ ion gains 6 pairs of electrons.

Thus Effective atomic number of cobalt is $[Co(NH_3)_6]^{3\oplus}$ 24+12 = 36.

Complex (Oxidation State)	Metal Number of Metal	Atomic number	Coordination	Effective atomic number (E.A.N.)
$K_4[Fe(CN)_6]$	+2	26	6	(26 – 2) + (6 × 2) = 36 [Kr]
$[Cu(NH_3)_4]SO_4$	+2	29	4	(29 – 2) + (4 × 2) = 35
$[Co(CH_3)_6]Cl_3$	+3	27	6	(27 – 3) + (6 × 2) = 36 [Kr]
$Ni(CO)_4$	0	28	4	(28 – 0) + (4 × 2) = 36 [Kr]
$K_2[Ni(CN)_4]$	+2	28	4	(28 – 2) + (4 × 2) = 34
$K_2[PtCl_6]$	+4	78	6	(78 – 2) + (6 × 2) = 86 [Rn]
$K_3[Cr(C_2O_4)_3]$	+3	24	6	(24 – 3) + (6 × 2) = 33
$K_3[Fe(C_2O_4)_3]$	+3	26	6	(26 – 3) + (6 × 2) = 35
$K_2[HgI_4]$	+2	80	4	(80 – 2) + (4 × 2) = 86 [Rn]
$[Ag(NH_3)_2]Cl$	+1	47	2	(47 – 1) + (2 × 2) = 50
$K_2[PdCl_4]$	+2	46	4	(46 – 2) + (4 × 2) = 52

Sidgwick rule:

If calculated effective number of electrons on central atom/ion comes out to be equal to the next noble gas electronic configuration (atomic number like 36, 54, 86) then that particular carbonyl complex will be more stable.

Note:

If calculated E.A.N. comes out to be more than next noble gas electronic configuration then that particular carbonyl complex acts as reducing agent.

Example

$[Mn(CO)_6]$ $\xrightarrow{-e^{\ominus}}$ $[Mn(CO)_6]^{\oplus}$

E.A.N. = 37, less stable → E.A.N. = 36, more stable

Note:

If calculated E.A.N. comes out to be less than next noble gas electronic configuration then that particular carbonyl complex acts as oxidizing agent.

Example

$[V(CO)_6]$ $\xrightarrow{-e^{\ominus}}$ $[V(CO)_6]^{\ominus}$

E.A.N. = 35, less stable → E.A.N. = 36, more stable

IUPAC Nomenclature of coordination compounds:

The present system of nomenclature derived from the suggestions of **Alfred Werner** and recommended by the Inorganic Nomenclature Committee of the I.U.P.A.C. 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.

(b) Then after ligands of the coordination sphere are to be named.

(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
$Cl^{\ominus}$	Chloro/Chlorido	$N^{3\ominus}$	Nitrido
$Br^{\ominus}$	Bromo/Bromido	$O_2^{2\ominus}$	Peroxo
$CN^{\ominus}$	Cyano	$B^{3\ominus}$	Borido
$O^{2\ominus}$	Oxo	$S^{2\ominus}$	Sulphido
$OH^{\ominus}$	Hydroxo	$NH^{2\ominus}$	Imido
$H^{\ominus}$	Hydrido	$N_3^{\ominus}$	Azido

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

$CO_3^{2\ominus}$	Carbonato	$SO_3^{2\ominus}$	Sulphito
$C_2O_4^{2\ominus}$	Oxolato	$CH_3COO^{\ominus}$	Acetato
$SO_4^{2\ominus}$	Sulphato	$NO_2^{\ominus}$	(bonded through oxygen) nitrito
$NO_3^{\ominus}$	Nitrato		(bonded through nitrogen) nitro
$S_2O_3^{2\ominus}$	Thiosulphato		

(iii) Positive ligands naming ends in 'ium' $NH_2 — NH_3^{\oplus}$ (Hydrazinium), $NO_2^{\oplus}$ (nitronium), $NO^{\oplus}$ (nitrosonium)

(d) If ligands are present more than once, then their repetition 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) When more than one type of ligand is present in the complex, then the ligands are named in the alphabetical order.

(Prior to this naming of ligands was followed in the order - negative, neutral and positive ligands)

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

If the complex is neutral or provides a cationic complex ion, 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'

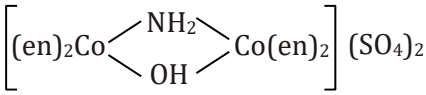
(g) After the naming of central metal ion, anion which is in the outer sphere is to be named.

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

S.No.	Complex Compounds	IUPAC Name
(i)	$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate (II)
(ii)	$K_2[Pt\ Cl_6]$	Potassium hexachloroplatinate (IV)
(iii)	$[Co\ (NH_3)_6]\ Cl_3$	Hexammine cobalt (III) chloride
(iv)	$[Cr(H_2O)_4Cl_2]\ Cl$	Tetra aqua di chloro chromium (III) chloride
(v)	$[Pt(NH_3)_2Cl_4]$	Diammine tetra chloroplatinum (IV)
(vi)	$[Co(NH_3)_3\ Cl_3]$	Triammine trichloro cobalt (III)
(vii)	$K_3[Co(NO_2)_6]$	Potassium hexanitro cobaltate (III)
(viii)	$Na_3[Fe(CN)_5\ NO]$	Sodium pentacyano nitrosyl ferrate (II)
(ix)	$[NiCl_4]^{2\ominus}$	Tetrachloro nickelate (II) ion
(x)	$[Ru(NH_3)_5Cl]^{2\oplus}$	Pentammine chlororuthenium (III) ion
(xi)	$[Fe(en)_3]Cl_3$	Tris (ethylenediamine) iron (III) chloride
(xii)	$[Ni\ (Gly)_2]$	Bis (glycinato) nickel (II)

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

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



bis(ethylenediamine)cobalt(III)μ-amido-μ-hydroxobis(ethylenediamine)cobalt(III) sulphate

IUPAC nomenclature of some specific complexes:

1. **Prussiane Blue : $Fe_4[Fe(CN)_6]_3$**
   Iron(III) hexacyanidoferrate(II)
   $Fe^{3\oplus}$ + $[Fe\ (CN)_6]^{4\ominus}$
   ferriferrocyanide

2. **Turn bull's blue : $Fe_3[Fe(CN)_6]_2$**
   $Fe^{2\oplus}$ + $[Fe(CN)_6]^{3\ominus}$
   Iron(II) hexacyanidoferrate(III)
   Ferroferricyanide

3. **$Fe_2[Fe(CN)_6]$**
   Iron(II) hexacyanidoferrate(II)
   Ferroferrocyanide

4. **Zeise's salt : $K[PtCl_3(C_2H_4)]$**
   Potassium trichloridoη^2–etheneplatinate(II)

5. **cis-platin : cis-$[Pt(NH_3)_2Cl_2]$**
   Anti Cancer
   cis-diamminedichloridoplatinum(II)

6. **Brown Ring Complex**
   $\left[\overset{1\oplus}{Fe}(H_2O)_5(\overset{1\oplus}{NO})\right]SO_4$
   Pentaaquanitrosyliumiron(I) sulphate

7. **Sodium nitroprusside**

$Na_2\left[\overset{2\oplus}{Fe}(CN)_5\left(\overset{\oplus}{NO}\right)\right]$

Sodium pentacyanidonitrosyliumferrate(II)

8. **Wilkinson's catalyst**

$[Rh(PPh_3)_3Cl]$

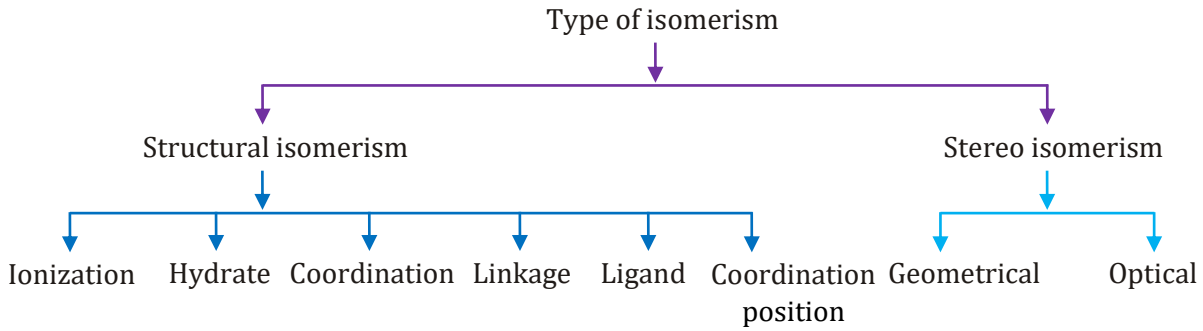
Chloridotris-(triphenylphosphine)rhodium(I).

9. **Switzer's Reagent**

$[Cu(NH_3)_4]SO_4$

Tetraamminecopper(II) sulphate

Classification of isomerism:



Structural isomerism:

It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere.

(a) Ionisation isomerism :

The type of isomerism which is due to the exchange of groups or ions between the coordination sphere and the ionisation sphere.

Example.

(i) $Co(NH_3)_4Br_2SO_4$ can be represented as
$[Co(NH_3)_4Br_2]SO_4$ (red violet) and $[Co(NH_3)_4SO_4]Br_2$ (red)
These complexes give sulphate ion and bromide ion respectively

(ii) $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

(iii) $[Co(NH_3)_4(NO_3)_2]SO_4$ and $[Co(NH_3)_4SO_4](NO_3)_2$

(b) Hydrate isomerism :

This type of isomerism is due to presence of different number of water molecules inside a 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.

These complexes differ from one another with respect to the number of water molecules acting as ligands. Other hydrate isomers are

$[Co(NH_3)_4(H_2O)Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl.H_2O$

(c) Linkage isomerism :

(i) This type of isomerism arises due to presence of ambidentate ligands like $NO_2^{\ominus}$, $CN^{\ominus}$ and $SCN^{\ominus}$

(ii) These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.

(iii) Such type of isomers are distinguished by infra red (I.R.) spectroscopy.

Examples.
- $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5\ ONO]Cl_2$
- In $NO_2^{\ominus}$ ligand, the coordinating sites are nitrogen (i.e., $NO_2^{\ominus}$ Nitro ligand) or through oxygen (i.e. $ONO^{\ominus}$ Nitrito ligand)
- The nitro isomer is yellow and is stable to acids whereas nitrito isomer is red and is decomposed by acids.

(d) Coordination isomerism :

(i) This type of isomerism is exhibited when the complex has two complex ions in it - 'Cationic and anionic'.

(ii) This type of isomerism is caused by the interchange of ligands between the two complex ions of the same complex.

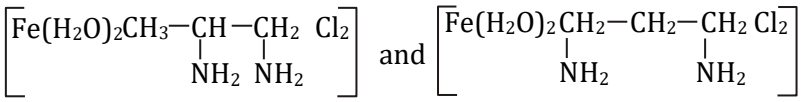
Examples. $[Co(NH_3)_6]\ [Cr(CN)_6]$ and $[Co(NH_3)_6]\ [Cr(C_2O_4)_3]$
$[Cr(NH_3)_6]\ [Co(CN)_6]$ $[Cr(NH_3)_6]\ [Co\ (C_2O_4)_3]$

(e) Ligand isomerism :

(i) Ligands with $C_3H_6(NH_2)_2$ have two different structures i.e. 1, 3-diamino propane and 1, 2-diaminopropane (propylene diamine).

(ii) Those complexes which have same molecular formula, but differ with respect to their ligands are called as **Ligand isomers**.

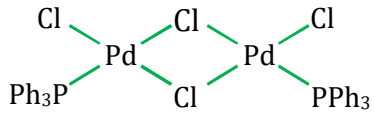
Examples $[Fe(H_2O)_2C_3H_6(NH_2)_2Cl_2]$ has two different structures

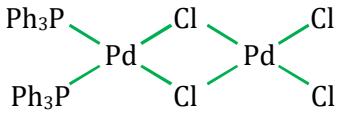


(f) Co-ordination Position Isomerisation:

It is shown by polynuclear complexes, due interchange of ligands between the different metal nuclei.

Example.





(g) Polymerization Isomerism :

This is not true isomerism because it occurs between compounds having the same empirical formula, but different molecular weights.

Example. $[Pt(NH_3)_2Cl_2]$
$[Pt(NH_3)_4]\ [PtCl_4]$

Stereo isomerism :

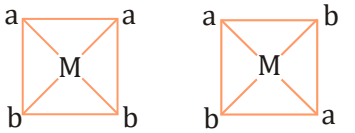
(a) They have same molecular formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion.
(b) The two stereo isomers which are possible are - Geometrical and Optical.

Geometrical or cis - trans isomers:

(a) The ligands occupy different positions around the central metal ion.
(b) When two identical ligands are coordinated to the metal ion from same side then it is **cis isomer**. (Latin, cis means same).
(c) If the two identical ligands are coordinated to the metal ion from opposite side then it is **trans isomer** (in Latin, trans means across).
(d) These geometrical isomers differ in physical as well as in chemical properties.
(e) Geometrical isomerism is most important in compounds with coordination numbers 4 and 6.
(f) 4-coordinated complexes with tetrahedral geometry do not exhibit cis-trans isomerism.
(g) It is exhibited by 4-coordinated complexes with square planar geometry.

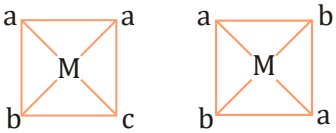
1. Geometrical isomers with coordination number = 4 (Square planar complexes):

(i) Complexes with general formula, **[Ma_2b_2]** (where both a and b are monodentate) can have cis and trans isomers.



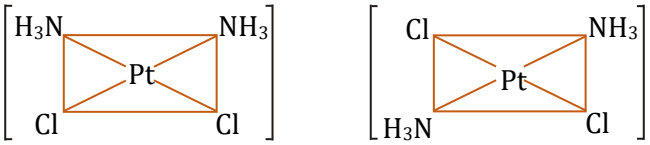
cis-isomer trans-isomer

(ii) Complexes with general formula **[Ma_2bc]** can have cis and trans isomers.



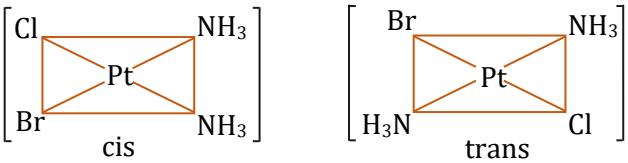
cis trans

Example: [Pt $(NH_3)_2Cl_2$]



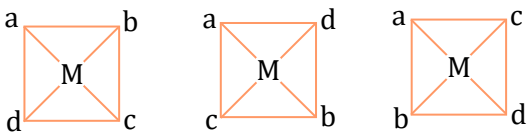
(cis-platin) anti cancer trans

Example: [$Pt(NH_3)_2ClBr$]



cis trans

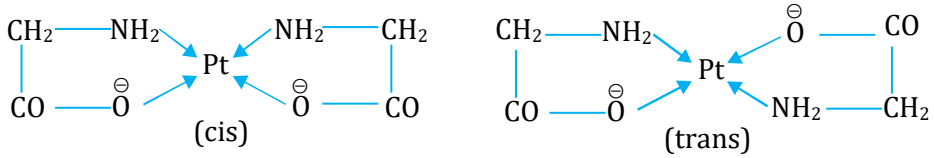
(iii) Complexes with general formula, [Mabcd] can have three isomers.



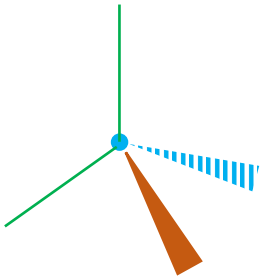
(i) (ii) (iii)

(iv) Complexes with general formula, $[M(AB)_2]$ can have two isomers.

Example: Diglycinato platium (iv) complexes



2. Geometrical and optical isomerism for tetrahedral complexes (Coordination number=4):



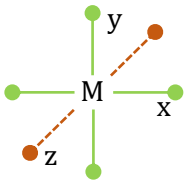
$[Ma_4]$
$[Ma_3b]$
$[Ma_2b_2]$
$[Ma_2bc]$
$[M(AA)_2]$
$[M(AA)b_2]$
$[M(AA)bc]$
$[M(AB)c_2]$

- All are optically inactive
- geometrical isomers = Not defined

$[Mabcd]$
$[M(AB)_2]$
$[M(AB)cd]$

- All are optically active
- geometrical isomers = Not defined

3. Stereo isomerism for Octahedral complexes (for monodentate ligand):



Optical isomers:

(a) Optically active complexes are those which are nonsuperimposable over the mirror image structure.

(b) An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.

(c) 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 '+'.**

(d) Thus, complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as **optical isomers**.

(e) The 'd' and 'ℓ' isomers of a compound are called as **Enantiomers or Enantiomorphs.**

(f) Only those 6-coordinated complexes in which there are chelating agents i.e. bidentate ligands, exhibit optical isomerism. This is due to the absence of elements of symmetry in the complex.

(g) Optical isomerism is not found in square planar complexes on account of the presence of axis of symmetry.

1. For monodentate ligands:

S.No.	Complexes	Geometrical Isomers	Stereo Isomers	Optically inactive	Optically active	Enantiomeric pairs
1.	$[Ma_6]$	Not defined	Not defined	1	0	0
2.	$[Ma_5b]$	Not defined	Not defined	1	0	0
3.	$[Ma_4b_2]$	2	2	2	0	0
4.	$[Ma_4bc]$	2	2	2	0	0
5.	$[Ma_3b_3]$	2	2	2	0	0
6.	$[Ma_3b_2c]$	3	3	3	0	0
7.	$[Ma_3bcd]$	4	5	3	2	1
8.	$[Ma_2b_2c_2]$	5	6	4	2	1
9.	$[Ma_2b_2cd]$	6	8	4	4	2
10.	$[Ma_2bcde]$	9	15	3	12	6
11.	[Mabcdef]	15	30	0	30	15

Illustration 1:

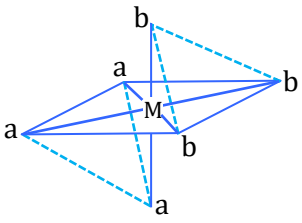
Draw all the stereoisomers of

1. $[CoCl_3(NH_3)_3]$

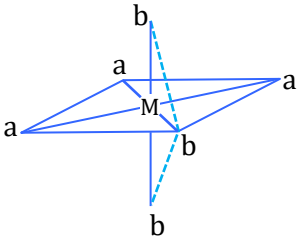
2. $[Pt(py)_2(NH_3)_2Cl_2]^{2\oplus}$

Solution:

1. $[CoCl_3(NH_3)_3]$ is $[Ma_3b_3]$ type of complex which shows Facial and Meridional isomerism.

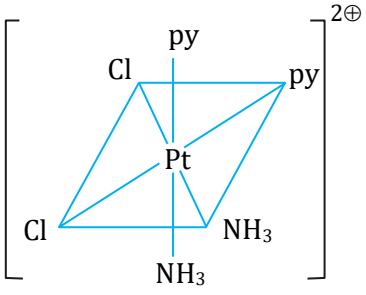


Facial (fac)
Optically inactive

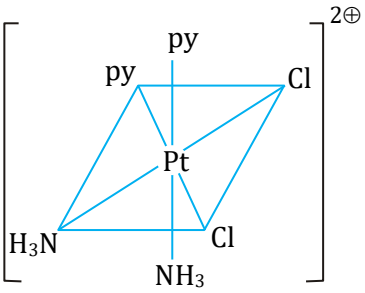


Meridional (Mer)
Optically inactive

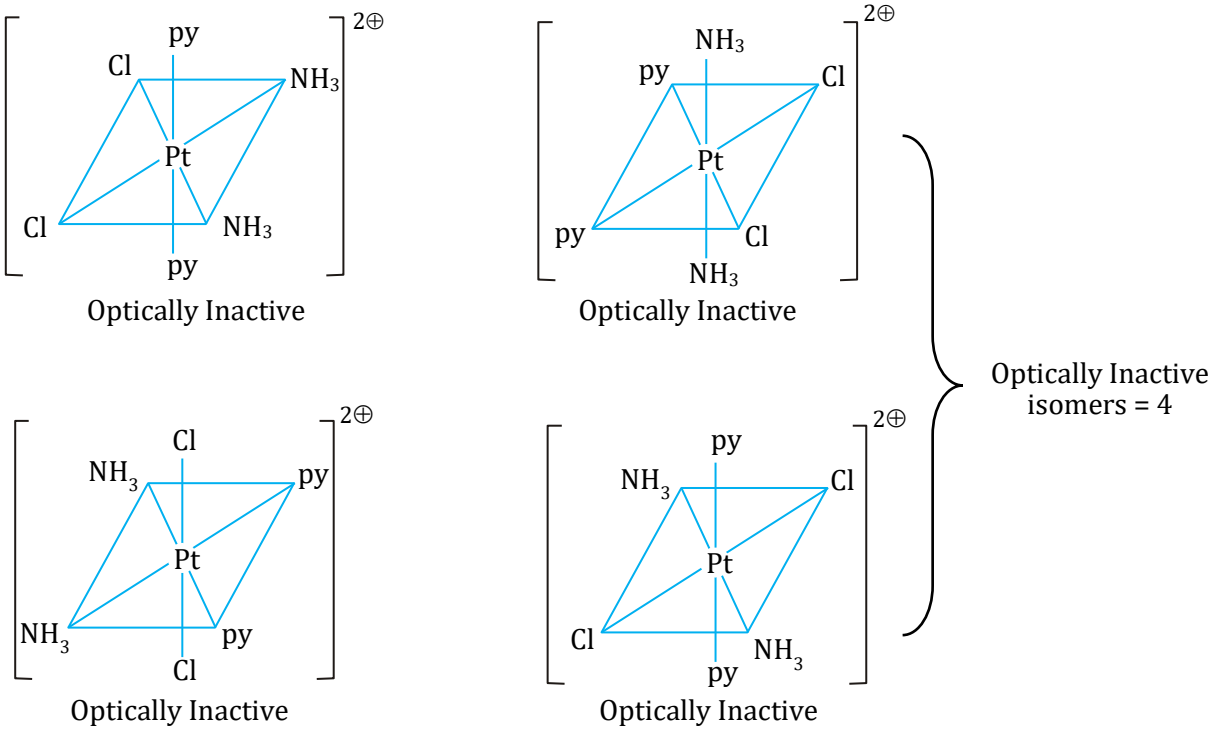
2. $[Pt(py)_2(NH_3)_2Cl_2]^{2\oplus}$ is $[Ma_2b_2c_2]$ type of complex



Mirror



Optically Active isomers = 2



2. For symmetrical bidentate ligand:

S.No.	Complexes	Geometrical Isomers	Stereo Isomers	Optically inactive	Optically active	Enantiomeric pairs
1.	$[M(AA)_3]$	Not defined	2	0	2	1
2.	$[M(AA)_2b_2]$	2	3	1	2	1
3.	$[M(AA)_2bc]$	2	3	1	2	1
4.	$[M(AA)b_4]$	Not defined	Not defined	1	0	0
5.	$[M(AA)b_3c]$	2	2	2	0	0
6.	$[M(AA)b_2c_2]$	3	4	2	2	1
7.	$[M(AA)b_2cd]$	4	6	2	4	2
8.	$[M(AA)bcde]$	6	12	0	12	6

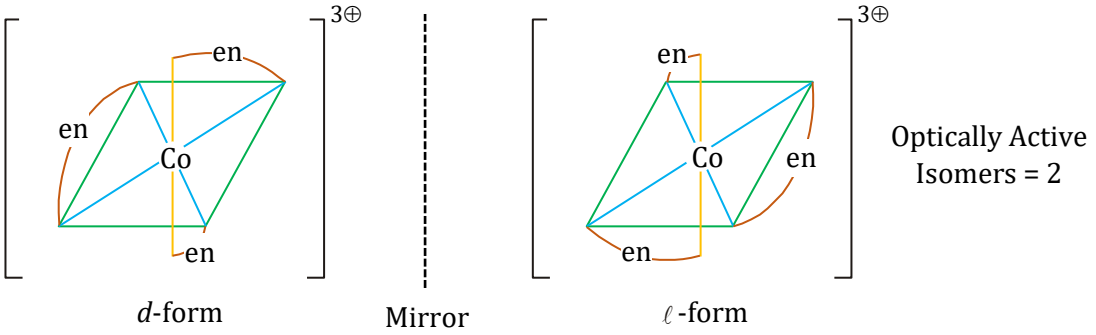
Illustration 2:

Draw all the stereoisomers of

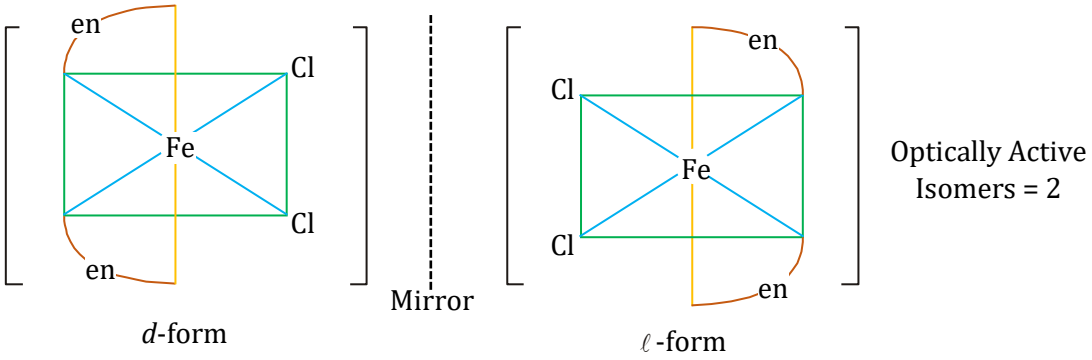
1. $[Co(en)_3]^{3\oplus}$ 2. $[Fe(en)_2Cl_2]$

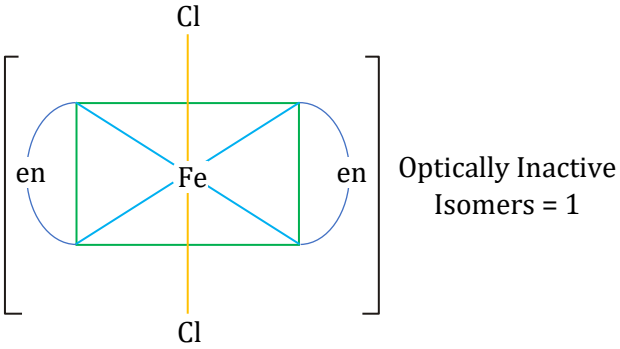
Solution:

1. $[Co(en)_3]^{3\oplus}$ is $[M(AA)_3]$ type of complex.



2. $[Fe(en)_2Cl_2]$ is a type of $[M(AA)_2b_2]$ complex.





3. For Unsymmetrical bidentate ligand:

S.No.	Complexes	Geometrical Isomers	Stereo Isomers	Optically inactive	Optically active	Enantiomeric pairs
1.	$[M(AB)_3]$	2	4	0	4	2
2.	$[M(AB)_2c_2]$	5	8	2	6	3
3.	$[M(AB)_2cd]$	6	11	1	10	5
4.	$[M(AB)c_4]$	Not defined	Not defined	1	0	0
5.	$[M(AB)c_3d]$	3	4	2	2	1
6.	$[M(AB)c_2d_2]$	4	6	2	4	2
7.	$[M(AB)c_2de]$	7	12	2	10	5
8.	$[M(AB)cdef]$	12	24	0	24	12

Advance level Illustrations on isomerism:

Illustration 3:

Which type of isomerism is shown by $[Co(NH_3)_4Br_2]Cl$?

(A) Geometrical and Ionisation (B) Optical and Ionisation

(C) Geometrical and Optical (D) Geometrical only

Ans. (A)

Solution:

$$[Co(NH_3)_4Br_2]Cl \xrightarrow{\text{Ionisation}} [Co(NH_3)_4BrCl]\,Br$$

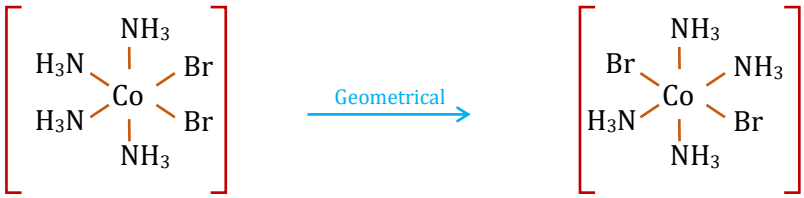


Illustration 4:

Statement-1 : The geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ are optically inactive.

Statement-2 : Both geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ possess axis of symmetry.

(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

Ans. (B)

Solution:

Geometrical isomers of $[M(NH_3)_4Cl_2]$ are optically inactive due to the presence of plane of symmetry

Illustration 5:

The ionization isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is –

(A) $[Cr(H_2O)_4(O_2N)]Cl_2$

(B) $[Cr(H_2O)_4Cl_2](NO_2)$

(C) $[Cr(H_2O)_4Cl(ONO)]Cl$

(D) $[Cr(H_2O)_4Cl_2(NO_2)].H_2O$

Ans. (B)

Solution:

$[Cr(H_2O)_4Cl(NO_2)]Cl \rightarrow Cl^{\ominus}$ ion

$[Cr(H_2O)_4Cl_2](NO_2) \rightarrow NO_2^{\ominus}$ ion

Illustration 6:

Match the complexes in column-I with their stereo properties is column-II

Column I	Column II
(A) $[CoCl_3(NH_3)_3]$	(P) Has a facial isomer
(B) $[Cr(ox)_3]^{3\ominus}$	(Q) Cis form is optically active
(C) $[CrCl_2(ox)_2]$	(R) Trans form is optically inactive
(D) $[RhCl_3(Py)_3]$	(S) Has a meridional form
	(T) Two optically active isomer

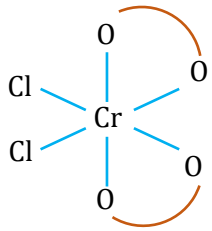
Ans. A-P,S; B-T; C-Q,R,T; D-P,S

Solution:

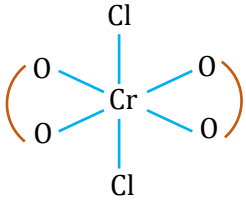
(A) $[Ma_3b_3]$ type complex shows both facial & meridional form of isomer

(B) $[M(AA)_3]$ type complex due to absence of plane of symmetry are optically inactive

(C)

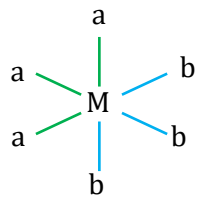


no P.O.S
so optically active
so also has enantiomer

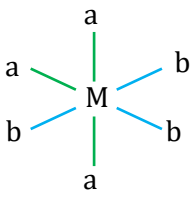


has P.O.S
so optically inactive

(D) $[Ma_3b_3]$ type complex shows facial & meridional



fac ;



mer

Illustration 7:

Statement-1: Complexes containing three bidentate groups such as $[Cr(ox)_3]^{3\ominus}$ and $[Co(en)_3]^{3\oplus}$ do not show optical activity.

Statement-2: Octahedral complex, $[Co(NH_3)_4Cl_2]$ shows geometrical isomerism.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

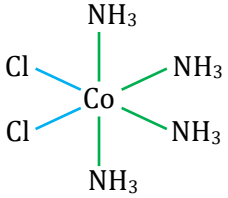
(D) Statement-1 is false, statement-2 is true.

Ans. (D)

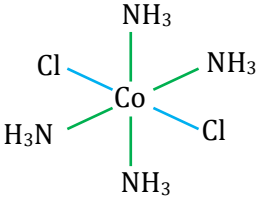
Solution:

Statement-1: $[M(AA)_3]$ type complex shows optical activity.

Statement-2 :



cis ;



trans

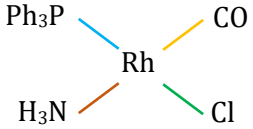
Illustration 8:

Total number of geometrical isomers for the complex $[RhCl(CO)(PPh_3)(NH_3)]$ is.

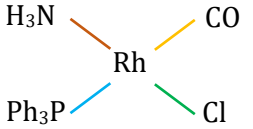
Ans. (3)

Solution:

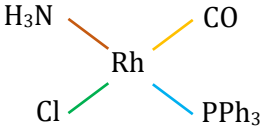
[Mabcd] square planar have 3 G.I.



;



;



Formation of co-ordination compounds:

It can be explained by number of theories.

(A) Werner's co-ordination theory

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

(C) Valence bond theory

(D) Crystal field theory

Valence Bond Theory:

This theory was mainly developed by **Linus Pauling**. The main features of this theory are -

(a) Metal ion when it forms a complex compound undergoes formation of coordinate bond.

(b) During this bond formation, the metal ion acts as electron pair acceptor. For this the metal ion provides vacant orbitals according to its coordination number.

(c) **Ex.** In the formation of $[Fe(NH_3)_6]^{3\oplus}$, $Fe^{3\oplus}$ ion provides six vacant orbitals.
In $[Cu(NH_3)_4]^{2\oplus}$, $Cu^{2\oplus}$ ion provides four vacant orbitals.

(d) These vacant orbitals undergo hybridisation before bond formation with ligands.

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

(f) If in a complex strong ligand is present then it will cause pairing of unpaired $e^{\ominus}$ in (n–1)d orbitals of central metal ion and if (n–1)d orbitals are involved in hybridisation then inner orbital complex is formed.

(g) If in the complex weak ligand is present then there will be no pairing of unapaired $e^{\ominus}$ in (n–1)d orbitals and if nd orbitals are involved in hybridisation, outer orbital complex is formed.

(h) If unpaired $e^{\ominus}$ is present in the complex then it will be paramagnetic otherwise it will be diamagnetic.

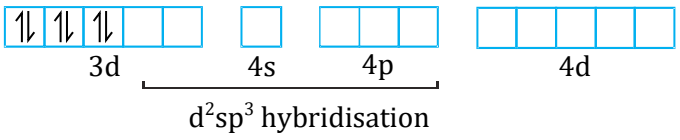
Applications of valence bond Theory:

(a) 6-coordinated complexes :

- **$[Co(NH_3)_6]^{3\oplus}$**

electronic configuration of $_{27}Co$ = [Ar] $3d^7\ 4s^2$ So, $Co^{3\oplus}$ = [Ar] $3d^6\ 4s^\circ\ 4p^\circ\ 4d^\circ$

$Co^{3\oplus}$ Due to presence of strong ligand unpaired electrons get paired up so metal ion provides vacant '3d' orbitals for hybridisation.



♦ This is a **diamagnetic complex.**

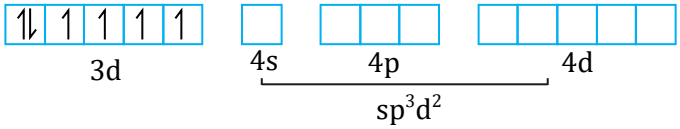
♦ As inner 'd' orbitals are involved in hybridisation, hence it is an **inner orbital complex**.

- **$[CoF_6]^{3\ominus}$**

  electronic configuration of $_{27}Co$ = [Ar] $3d^7 4s^2$, $\therefore$ $Co^{3\oplus}$ = [Ar] $3d^6\ 4s^0\ 4p^0\ 4d^0$

  $Co^{3\oplus}$ ion 

  $\because$ $F^{\ominus}$ is a weak ligand, so unpaired $e^{\ominus}$ do not get paired up and vacant 4d orbitals involved in hybridisation.



  ♦ This is a **paramagnetic** complex.

  ♦ The outer 'd' orbitals are involved in hybridisation, hence it is an **outer orbital** complex.

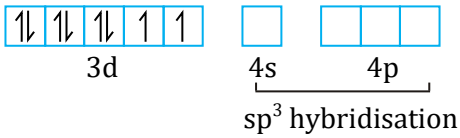
(b) 4-coordinated complexes :

- **$[NiCl_4]^{2\ominus}$**

  electronic configuration of $_{28}Ni$ = [Ar] $3d^8\ 4s^2$

  $\therefore$ $Ni^{2\oplus}$ = [Ar] $3d^8\ 4s^0\ 4p^0$

  There will be no pairing of unpaired e^- in 3d orbitals.



  ♦ $[NiCl_4]^{2\ominus}$ has **tetrahedral geometry**.

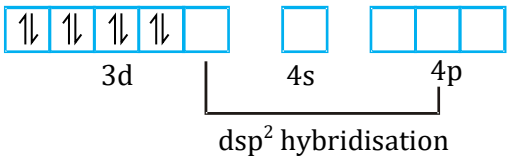
  ♦ It is a paramagnetic complex.

- **$[Ni\ (CN)_4]^{2\ominus}$**

  electronic configuration $_{28}Ni$ = [Ar] $3d^8 4s^2$

  $Ni^{2\oplus}$ = [Ar] $3d^8 4s^0 4s^0$

  $CN^{\ominus}$ is a strong ligand so unpaired $e^{\ominus}$ in 3d orbitals get paired up



  ♦ $[Ni(CN)_4]^{2\ominus}$ has square planer geometry and diamganetic in nature.

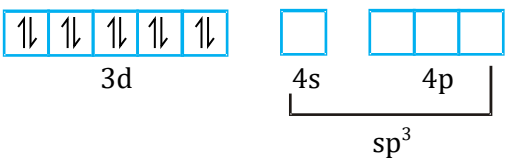
  ♦ This complex is an **inner orbital complex**

- **$[Zn(NH_3)_4]^{2\oplus}$**

  Zn = [Ar] $4s^2\ 3d^{10}$

  $\therefore$ $Zn^{2\oplus}$ = [Ar] $3d^{10} 4s^0 4p^0$

  $\because$ $Zn^{2\oplus}$ has d^{10} configuration



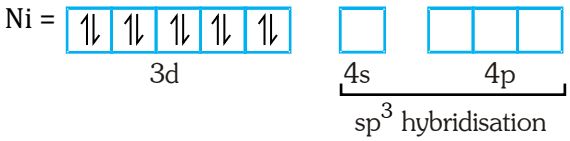
  So there is no possibility of pairing

  ♦ Because the complex is formed by sp^3 hybridisation, hence it has **tetrahedral geometry**.

  ♦ Since all electrons are paired, hence it is **diamagnetic**

- **$[Ni(CO)_4]$** Ni = [Ar] $3d^8\ 4s^2\ 4p^\circ$

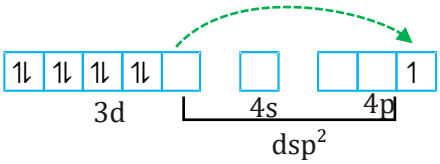
  ∵ CO is a strong ligand so unpaired $e^\ominus$ in (n–1)d orbitals get paired up.



  - Complex has sp^3 hybridisation
  - It has tetrahedral geometry.
  - It is diamagnetic complex as unpaired $e^\ominus$ is absent.

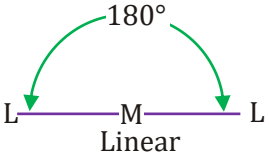
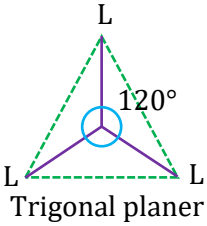
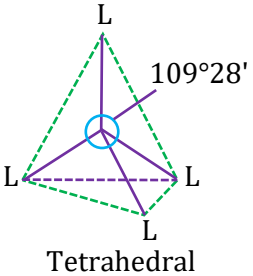
- **$[Cu(NH_3)_4]^{2\oplus}$**

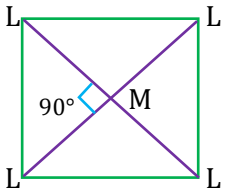
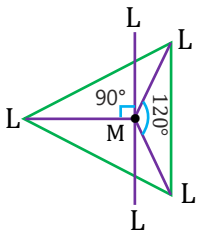
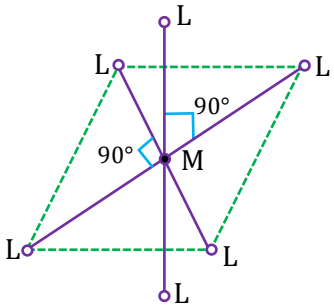
  $_{29}Cu$ = [Ar] $4s^1\ 3d^{10}$ ∴ $Cu^{2\oplus}$ = [Ar] $3d^9\ 4s^0\ 4p^0$



  ∵ NH_3 is a strong ligand so after rearrangement

  - Complex has dsp^2 hybridsation
  - It is inner orbital complex
  - It has square planer geometry
  - It is paramagnetic

Coordination Number	Hybridised orbital	Geometrical shape of the Complex	Examples of Complex
2	sp		$[Ag(NH_3)_2]^\oplus$ $[Ag(CN)_2]^\ominus$
3	sp^2		$[HgI_3]^\ominus$
4	sp^3		$[CuCl_4]^{2\ominus}$ $[ZnCl_4]^{2\ominus}$ $[Ni(CO)_4]$ $[Zn(NH_3)_4]^{2\oplus}$

4	dsp^2 $(d_{x^2-y^2}\text{orbital})$	 Square planar	$[PdCl_4]^{2\ominus}$ $[Ni(CN)_4]^{2\ominus}$ $[Pt(NH_3)_4]^{2\oplus}$ $[Cu(NH_3)_4]^{2\oplus}$ $[PtCl_4]^{2\ominus}$
5	dsp^3/sp^3d	 Trigonal bipyramidal	$[Fe(CO)_5]$
6	d^2sp^3/sp^3d^2	 Octahedral	$[Cr(NH_3)_6]^{3\oplus}$ $[Ti(H_2O)_6]^{3\oplus}$ $[Fe(CN)_6]^{3\ominus}$ $[Co(NH_3)_6]^{3\oplus}$ $[PtCl_6]^{2\ominus}$,$[CoF_6]^{3\ominus}$

Note :

In d^2sp^3, d-orbitals are (n-1)d-orbitals and forms Inner orbital complexes.

In sp^3d^2, d-orbitals are nd-orbitals and forms Outer orbital complexes.

In both cases d-orbitals are d_{z^2} and $d_{x^2-y^2}$ orbitals.

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.

Crystal Field Theory:

The drawbacks of VBT of coordination compounds are, to a considerable extent, removed by the Crystal Field Theory.

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interaction between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules. The five d-orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of polar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lost. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field.

Crystal field splitting in octahedral coordination entities :

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in d orbitals of metal and the electrons (or negative charges) of the ligands. Such a repulsion is more when the d orbitals of metal are directed towards the ligand than when it is away from the ligand. Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals (axial orbitals) which point towards the axis along the direction of the ligand will experience more repulsion and will be raised in energy; and the d_{xy}, d_{yz} and d_{zx} orbitals (non-axial) orbitals which are directed between the axis will be lowered in energy relative to the average energy in the spherical crystal field. Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the degenerate levels is due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_o (the subscript o is for octahedral). Thus, the energy of the two e_g orbitals will increase by $(3/5)\Delta_o$ and that of the three t_{2g} will decrease by $(2/5)\ \Delta_o$.

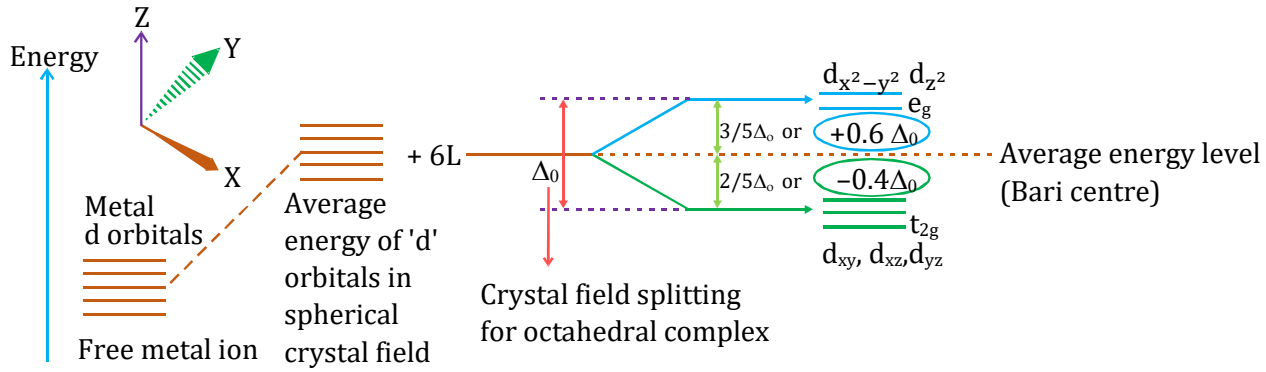


Figure showing crystal field splitting in octahedral complex.

- The crystal field splitting, Δ_o, depends upon the fields produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below :

  $I^{\ominus} < Br^{\ominus} < SCN^{\ominus} < Cl^{\ominus} < S^{2\ominus} < F^{\ominus} < OH^{\ominus} < C_2O_4^{2\ominus} < H_2O < NCS^{\ominus} < edta^{4\ominus} < NH_3 < en < NO_2^{\ominus} < CN^{\ominus} < CO$

Note:

In $SCN^{\ominus}$, S is donating atom and in $NCS^{\ominus}$, N is donating atom.

Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands. For d^4 configuration, the fourth electron will singly occupy e_g orbital (according to Hund's rule) or will undergo pairing in t_{2g} orbital, which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δ_o and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two possibilities are :

(i) If $\Delta_o < P$, the fourth electron enters in one of the e_g orbitals giving the configuration $t^3_{2g}e_g^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.

(ii) If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t^4_{2g}e^0_g$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.

Transference of electron in octahedral complexes:

"Conditions for transference of electrons "

- Central atom must be surrounded by all strong field ligands.
- Only one electron can be transferred.
- Inner orbital complex must be formed.

Note:

Atomic number 24, 25, 26 and 27 with 6 NH_3 in (+2) oxidation state are exception.

Complexes	Expected hybridisation	Real hybridisation	Reason
$[Cr(NH_3)_6]^{2\oplus}$	d^2sp^3	sp^3d^2	$\Delta_o < P$
$[Mn(NH_3)_6]^{2\oplus}$	d^2sp^3	sp^3d^2	$\Delta_o < P$
$[Fe(NH_3)_6]^{2\oplus}$	d^2sp^3	sp^3d^2	$\Delta_o < P$
$[Co(NH_3)_6]^{2\oplus}$	d^2sp^3	sp^3d^2	$\Delta_o < P$

Note:

All $Co^{3\oplus}$ complexes are d^2sp^3 hybridized except $[CoF_6]^{3\ominus}$ and $[Co(H_2O)_3F_3]$.

Complexes	Hybridisation	Reason
$[Co(H_2O)_6]^{3\oplus}$	d^2sp^3	$\Delta_o > P$
$[Co(ox)_3]^{3\ominus}$	d^2sp^3	$\Delta_o > P$
$[Co(NH_3)_6]^{3\oplus}$	d^2sp^3	$\Delta_o > P$
$[Co(EDTA)]^{\ominus}$	d^2sp^3	$\Delta_o > P$
$[Co(en)_3]^{3\oplus}$	d^2sp^3	$\Delta_o > P$
$[Co(NO_2)_6]^{3\ominus}$	d^2sp^3	$\Delta_o > P$
$[Co(CN)_6]^{3\ominus}$	d^2sp^3	$\Delta_o > P$

Crystal field splitting in tetrahedral coordination entities:

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\Delta_o$. This may attributes to the following two reasons.

(i) There are only four ligands instead of six, so the ligand field is only two thirds the size ; as the ligand field spliting is also the two thirds the size.

(ii) The direction of the orbitals does not concide with the direction of the ligands. This reduces the crystal field spliting by roughly further two third.

$$\text{So } \Delta_t = \frac{2}{3} \times \frac{2}{3} = \frac{4}{9} \Delta_o.$$

Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

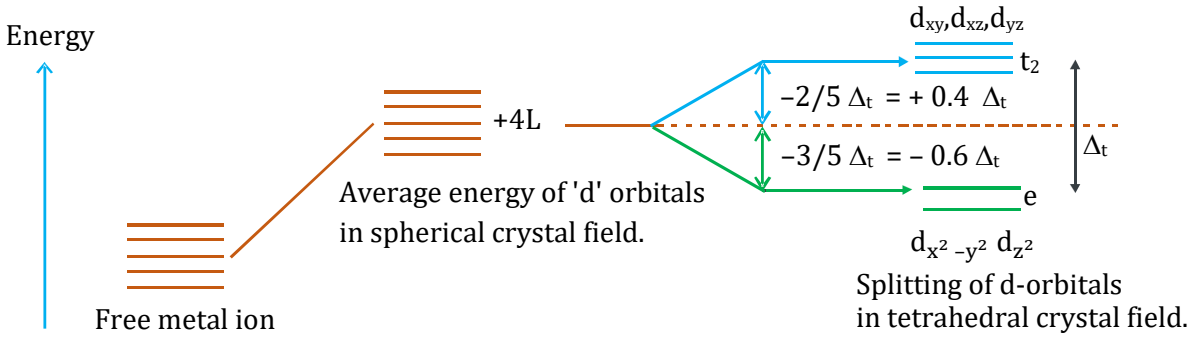


Figure showing crystal field splitting in tetrahedral complex.

Since $\Delta_t < \Delta_o$ crystal field splitting favours the formation of octahedral complexes.

Crystal Field stabilising energy in Tetrahedral field:

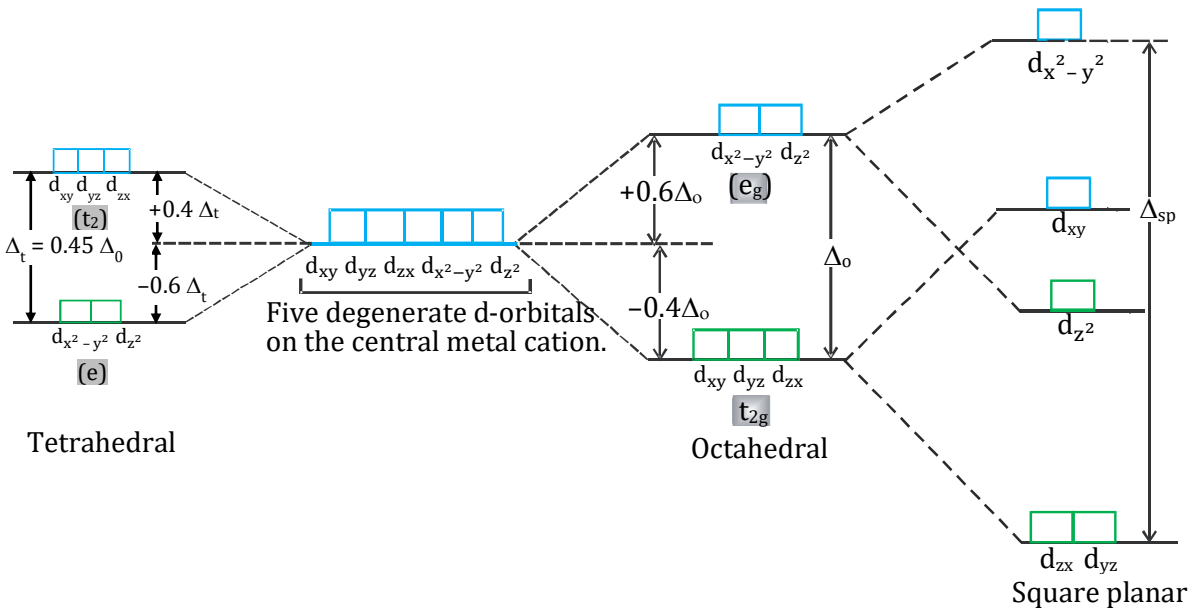
Formula: CFSE = $[-0.6\ nt_2 + 0.4\ ne]\ \Delta_t + xP$

where nt_2 & ne are number of electron(s) in t_2 & e orbitals respectively and Δ_t crystal field splitting energy for tetrahedral complex. "x" represents the number of electron pairs and P is mean pairing energy.

Crystal field splitting in square planar coordination entities:

The square planar arrangement of ligands may be considered to be one derived from the octahedral field by removing two trans-ligands located along the Z-axis. In the process, the e_g and t_{2g} sets of orbitals is lifted i.e., these orbitals will no longer be degenerate.

The four ligands in square planar arrangement around the central metal ion are shown in Fig. As the ligands approach through the x and y axis, they would have greatest influence on $d_{x^2-y^2}$ orbital, so the energy of this orbital, will be raised most. The d_{xy} orbital, lying in the same plane, but between the ligands will also have a greater energy though the effect will be less than that on the $d_{x^2-y^2}$ orbitals. On the other hand, due to absence of ligands along Z – axis, the d_{z^2} orbital becomes stable and has energy lower than that of d_{xy} orbital. Similarly, d_{yz} and d_{xz} become more stable. The energy level diagram may be represented as shown in figure along with tetrahedral and octahedral fields.



The value of Δ_{sp} has been found larger than Δ_o because of the reason that d_{xz} and d_{yz} orbitals interact with only two ligands in the square planar complexes, while in octahedral complexes the interaction takes place only with four ligands. Δ_{sp} has been found equal to $1.3\Delta_o$. Thus,

$\Delta_{sp} > \Delta_o$ and $\Delta_{sp} = 1.3\ \Delta_o$.

Factors influencing the magnitude of C.F.S.E.:

1. **Different charges on the cation of the same metal :**
   The cation with a higher oxidation state has a larger value of CFSE than that with lower oxidation state e.g., $[Fe(H_2O)_6]^{3\oplus} > [Fe(H_2O)_6]^{2\oplus}$

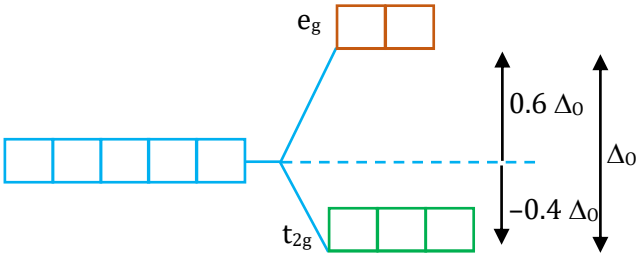
2. **Same charges on the cation but the number of d-electrons is different :**
   The metal cation the magnitude of CFSE with the increase of the number of d-electrons, e.g.,
   $[Co(H_2O)_6]^{2\oplus} > [Ni(H_2O)_6]^{2\oplus}$

3. **Quantum number (n) of the d-orbitals of the central metal ion :**
   As 'n' increase CFSE increases.
   $[Co(NH_3)_6]^{3\oplus} < [Rh(NH_3)_6]^{3\oplus} < [Ir(NH_3)_6]^{3\oplus}$

4. **Types of Hybridisation :**
   $\Delta_t = \frac{4}{9}\Delta_0$

5. **Presence of cheleting ligand increases CFSE :**
   $[Fe(Ox)_3]^{3\ominus} > [Fe(SCN)_6]^{3\ominus}$

Crystal Field stabilising energy in Octahedral field:

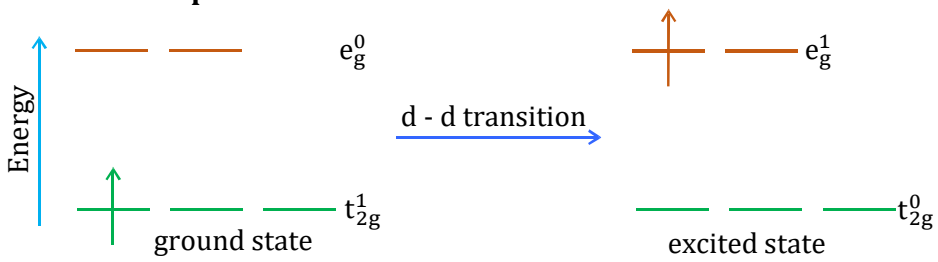


Formula : CFSE = $[-0.4\ nt_{2g} + 0.6\ ne_g]\ \Delta_0 + x.\ P$

Where nt_{2g} & ne_g are number of electron(s) in t_{2g} & e_g orbitals respectively and Δ_0 crystal field splitting energy for octahedral complex. "x" represents the number of electron pairs and P is mean pairing energy.

Colour property of complex compounds:

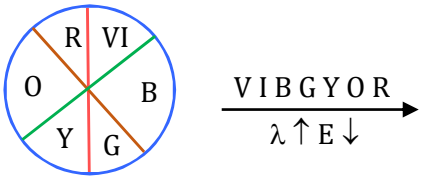
(A) Reason for colour in complexes is due to d-d-transition



Note :

In general, d^0 and d^{10} electronic configurations are colourless and d^1 to d^9 are coloured.

(B) Complentary colour wheel



For example

complementary colour of red is blue green.

Limitation of CFT:

Crystal field Theory is not very clear about the following

- The spectrochemical series : CFT assumes the interaction between central atom/ion and ligands in the complex. to be electrostatic and therefore the anionic ligands should give maximum crystal field splitting. The reverse has been found to be true, i.e. halides ($X^{\ominus}$) are at the bottom of Spectrochemical Series (Weak field ligands), $^{\ominus}OH$, a strong base gives a field which is weaker than H_2O (neutral ligand and have a larger size)
- The radial wave function of the d – orbitals and of the Ligands should have some overlap at the observed internuclear distances in the metal complexes. The ligands therefore are not point charges, but have their own electron orbitals.
- The CFT cannot account for the π - bonding in the complexes.
- CFT cannot explain the charge transfer spectra and the intensities of the absorption bonds. These are some of the limitation of CFT.

Advanced Level Illustration on VBT, CFT:

Illustration 9:

The complex ion which has no 'd' electrons in the central metal atom is :

[At No. Cr = 24, Mn = 25, Fe= 26, Co = 27]

(A) $[MnO_4]^{\ominus}$ (B) $[Co(NH_3)_6]^{3\oplus}$ (C) $[Fe(CN)_6]^{3\ominus}$ (D) $[Cr(H_2O)_6]^{3\oplus}$

Ans. (A)

Solution:

$[MnO_4]^{\ominus} \rightarrow Mn^{x\oplus}, O^{2\ominus}$

$x + 4(-2) = -1 \Longrightarrow x = +7 \Longrightarrow Mn^{7\oplus}$

$Mn = [Ar]4s^2 3d^5$

$Mn^{7\oplus} = [Ar] \Longrightarrow$ no 'd' electrons.

Illustration 10:

The coordination number of $Ni^{2\oplus}$ is 4.

$NiCl_2$ + KCN (excess) → A (cyano complex)

$NiCl_2$ + KCl (excess) → B (chloro complex)

The hybridization of A and B are

(A) dsp^2, sp^3 (B) sp^3, sp^3 (C) dsp^2, dsp^2 (D) sp^3d^2, d^2sp^3

Ans. (A)

Solution:

$CN^{\ominus}$ → Strong field ligand.

$NiCl_2$ + KCN (excess) → $[Ni(CN)_4]^{2\ominus}$

Dsp^2

$Cl^{\ominus}$ Weak field ligand.

$NiCl_2$ + KCl (excess) → $[NiCl_4]^{2\ominus}$

sp^3

Illustration 11:

Both $[Ni(CO)_4]$and $[Ni(CN)_4]^{2\ominus}$ are diamagnetic. The hybridisations of nickel in these complexes, respectively, are

(A) sp^3, sp^3 (B)sp^3, dsp^2 (C)dsp^2, sp^3 (D)dsp^2, dsp^2

Ans. (B)

Solution:

$[Ni(CO)_4]$ → Ni^0 = $[Ar]4s^2 3d^8$

Ni = [Ar] 

electrons of 4s are paired in 3d subshell

sp^3

$[Ni(CN)_4]^{2\ominus}$ → Ni^2 = $[Ar]3d^8$

$Ni^{2\oplus}$ = [Ar] 

dsp^2

Illustration 12:

The spin only magnetic moment value (in Bohr magneton units) of $Cr(CO)_6$ is

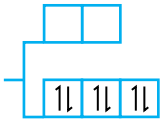
(A) 0 (B) 2.84 (C) 4.90 (D) 5.92

Ans. (A)

Solution:

$[Cr(CO)_6]$ = Cr^0 = $[Ar]4s^1 3d^5$

CO = strong field ligand.

Cr^0 

Number of unpaired electrons = zero

$\mu = 0$

Illustration 13:

Among the following complexes (**K–P**)

$K_3[Fe(CN)_6]$ (**K**), $[Co(NH_3)_6]Cl_3$ (**L**), $Na_3[Co(oxalate)_3]$ (**M**), $[Ni(H_2O)_6]Cl_2$ (**N**), $K_2[Pt(CN)_4]$ (**O**) and $[Zn(H_2O)_6](NO_3)_2$ (**P**)

The diamagnetic complex are -

(A) K, L, M, N (B) K, M, O, P (C) L, M, O, P (D) L, M, N, O

Ans. (C)

Solution:

(L) $\Longrightarrow$ $Co^{3\oplus}$ = $[Ar]3d^6$ $\Longrightarrow$ NH_3 act as strong field ligand here

(M) $\Longrightarrow$ $Co^{3\oplus}$ = $[Ar]3d^6$ $\Longrightarrow$ oxalate act as strong field ligand here

(O) $\Longrightarrow$ $Pt^{2\oplus}$ = square planar $\Longrightarrow$ all electrons are paired here

(P) $\Longrightarrow$ $Zn^{2\oplus}$ = $[Ar]3d^{10}$ $\Longrightarrow$ no unpaired electrons

Illustration 14:

The **CORRECT** order of hybridisation of the central atom in the following species.

NH_3, $[PtCl_4]^{2\oplus}$, PCl_5 and BCl_3 is [At No. Pt = 78]

(A) dsp^2, sp^3d, sp^2 and sp^3 (B) sp^3, dsp^2, sp^3d, sp^2

(C) dsp^2, sp^2, sp^3 and sp^3d (D) dsp^2, sp^3, sp^2 and sp^3d

Ans. (B)

Solution:

NH_3 : $\Longrightarrow$ sp^3

$Pt^{2\oplus}$ $\Longrightarrow$ Always shows square planar (with coordination number = 4)$\Longrightarrow$ dsp^2

PCl_5 $\Longrightarrow$ sp^3d

BCl_3 $\Longrightarrow$ sp^2

Illustration 15:

Predict the magnetic nature of A and B.

$A = K_2[Ni(CN)_4], B = K_2[NiCl_4]$

(A) Both are diamagnetic.

(B) A is diamagnetic and B is paramagnetic with one unpaired electron.

(C) A is diamagnetic and B is paramagnetic with two unpaired electrons.

(D) Both are paramagnetic.

Ans. (C)

Solution:

A = presence of strong field ligand so it is diamagnetic

B = presence of weak field ligand so it is paramagnetic with two unpaired $e^{\ominus}$

Illustration 16:

Statement-1 : $[Fe(H_2O)_5NO]SO_4$ is paramagnetic

Statement-2 : The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons.

(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

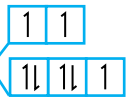
(D) Statement-1 is False, Statement-2 is True

Ans. (A)

Solution:

$\left[Fe(H_2O)_5\overset{\oplus}{N}O\right]SO_4$

$[Fe^{1\oplus} = [Ar]3d^6\ 4s^1$

$3d^7$ 

unpaired $e^{\ominus}$ s = 3, paramagnetic

Illustration 17:

The volume (in mL) of 0.1M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01M solution of $[Cr(H_2O)_5Cl]Cl_2$, as silver chloride is close to.

Ans. (6)

Solution:

Moles of $Cl^{\ominus}$ reacted $= 2 \times 0.03 \times 0.01 = 6 \times 10^{-4}$ mole.

moles of $Ag^{\oplus}$ reacted = V(lt) × 0.1 mole

$V_{AgNO_3} = 6$ ml