

# COORDINATION COMPOUNDS

## ➤ Addition Compounds or molecular compounds: -

When two or more salts are mixed in proper proportions and evaporate then, crystals of compounds are formed. These crystals of compounds are called as addition compounds or molecular compounds.

There are two types of addition compounds: -

- ❖ Double Salts
- ❖ Coordination Compounds

### 1) Double Salt: -

When Salt dissolved in water then, individual components shows their individual property is called as double salt.

E.g., i) when carnallite  $[\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}]$  dissolved in water then it gives, the test for  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  ions.

ii) When potash alum  $[\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}]$  dissolved in water then it gives the test for  $\text{K}^+$ ,  $\text{Al}^{3+}$ ,  $\text{SO}_4^{2-}$  ions.

iii) When Mohr's salt  $[\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}]$  dissolved in water then it gives test for  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  ions.

### 2) Coordination Compounds or Complex Compounds: -

When the compound dissolved in water then individual components does not shows their individual property is called as coordination compound or complex.

i) when complex ion  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is dissolved in water then, it does not give the test for  $\text{Co}^{3+}$  ion and  $\text{NH}_3$ .

ii) When complex  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is dissolved in water then, it does not give a test for  $\text{Fe}^{2+}$ ,  $\text{CN}^-$  ions because these two ions are present in the coordination Sphere.



Complex ion [not ionised]

## ➤ Distinguish Between Double Salt and Complex Compound: -

Double Salt	Complex Compound
i) Individual Components Shows their individual properties.	i) Individual components do not shows their individual properties.
ii) It gives the test of each ion.	ii) It does not give the test of each ion in the Coordination Sphere.
iii) It loses their Identity.	iii) It does not lose their identity.
iv) They are crystalline in nature.	iv) They may or may not be e crystalline in nature.
v) Their crystals have definite geometrical shape.	

vi) Ex. Karnalite, Potash alum

v) Their shape depends upon hybridisation of metal ion.

vi) Ex: -  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $\text{K}_4[\text{Fe}(\text{CN})_6]$

➤ **Terms used in coordination compounds: -**

**1) Central Metal Ion or Central Metal Atom: -**

In the complex, the metal atom or ion attached to ligands through coordinate bonds in the coordination sphere is called central metal ion / atom.

E.g.: -  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$

In this complex ion,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$  are central metal ions.

**2) Ligands: -**

The species (atoms / ions / molecules) which donate pair of electrons and forms coordinate bond are called as ligands.

Ligand may be positive, negative or neutral molecules.

a) Positive Ligands: - They have positive charge.

E.g.,  $\text{NO}^+ \rightarrow$  Nitrosonium ion

$\text{NH}_2\text{-NH}_3^+ (\text{N}_2\text{H}_5^+) \rightarrow$  Hydrazinium ion

$\text{NO}_2^+ \rightarrow$  Nitronium ion.

b) Negative Ligands: -

They have negative charge.

E.g.,  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{CN}^-$ , etc.

c) Neutral ligands: -

They have no charge.

E.g.,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{R-OH}$ ,  $\text{R-NH}_2$ ,  $\text{NH}_2\text{-OH}$ ,  $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$

➤ **Classification of Ligands: -**

a) Positive Ligands: -

Ligand	Charge	Name of ligand in Complex
$\text{NO}^+$	+1	Nitrosonium
$\text{NO}^{2+}$	+1	Nitronium
$\text{NH}_2\text{-NH}^{3+}$	+1	Hydrazinium

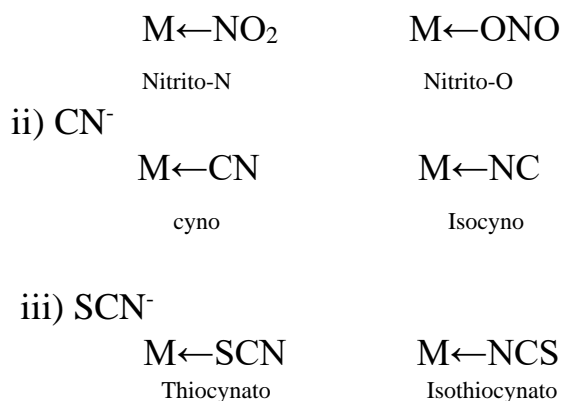
b) Neutral Ligands: -

Ligand	Charge	Name of ligand in Complex
$\text{H}_2\text{O}$	0	Aquo/ Aqua
$\text{NH}_3$	0	Ammine
$\text{CO}$	0	Carbonyl
$\text{NO}$	0	Nitrosyl
$\text{C}_5\text{H}_5\text{N}$	0	Pyridine
$\text{CH}_3\text{-NH}_2$	0	Methyl amine
$\text{PH}_3$	0	Phosphine
$\text{NH}_2\text{-C-NH}_2$	0	Urea
$\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$	0	Ethylenediamine (en)
$\text{Ph}_3\text{P}$	0	Triphenyl Phosphine
$\text{H}^-$	-1	Hydrido
$\text{O}^{2-}$	-2	Oxo
$\text{O}_2^{2-}$	-2	Peroxo
$\text{OH}^-$	-1	Hydroxo
$\text{F}^-$	-1	Fluoro [Flurido]
$\text{Cl}^-$	-1	Chloro [Chlorido]
$\text{Br}^-$	-1	Bromo [Bromido]
$\text{I}^-$	-1	Iodo [Iodido]
$\text{CH}_3\text{COO}^-$	-1	Acetato
$\text{CN}^-$	-1	Cyno
$\text{NC}^-$	-1	Isocyno
$\text{S}^{2-}$	-2	Sulphido
$\text{SO}_3^{2-}$	-2	Sulphito
$\text{SO}_4^{2-}$	-2	Sulphato
$\text{NH}_2^-$	-1	Amido
$\text{NH}^{2-}$	-2	Imido
$\text{NO}_3^-$	-1	Nitrato
$\text{NO}_2^-$	-1	Nitro [Nitrito-N]
$\text{ONO}^-$	-1	Nitrito [Nitrito-O]
$\text{N}^{3-}$	-3	Nitrido
$\text{N}_3^-$	-1	Azido
$\text{SCN}^-$	-1	Thiocynato
$\text{NCS}$	-1	Isothiocynato
$:\text{NH}_2\text{-CH}_2\text{-COO}^-$	-1	Glycinato (gly)
$\text{S}_2\text{O}_3^{2-}$	-2	Thiosulphato
$\text{C}_2\text{O}_4^{2-}$	-2	Oxalato
$\text{CO}_3^{2-}$	-2	Carbonato
$\text{CH}_3\text{-C=N-O:}$	-1	Dimethylglyoximato

c) Ambident Ligands: -

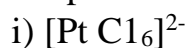
The ligands that can binds through more than one atom are called as ambident ligand.

E.g., i)  $\text{NO}_2^-$

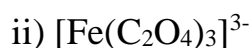


**d) Coordination Number: -**

The total number of coordinate bonds attached to central metal ion in the complex is called as coordination number.



In this, 6  $\text{Cl}^-$  unidentate ligands, attached to Pt therefore C.N. of  $\text{Pt}^{4+}$  is six.



In this, three bidentate ligands  $(\text{C}_2\text{O}_4)^{2-}$  are attached to Fe therefore C.N. of  $\text{Fe}^{3+}$  is six.



In this one hexadentate ligand is attached to  $\text{Fe}^{2+}$  therefore C.N. of  $\text{Fe}^{2+}$  is six.

**e) Coordination Sphere: -**

The space or region where ligands donate electron pair to the central metal ion and forms coordinate bond in a definite geometrical pattern is called as coordination Sphere.

It is denoted by '[ ]'.

**f) Counter Ion: -**

Counter ion may be +ve or -ve.

The +ve counter ion is always kept at LHS of complex ion.

The negative counter ion is always kept at RHS of complex ion.

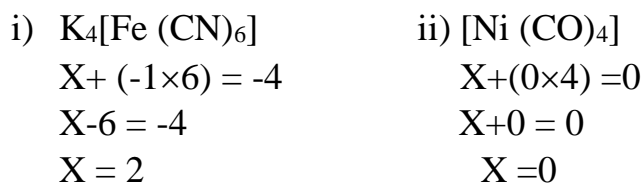


The counter ion is  $\text{K}^+$  and complex ion is  $[\text{Fe}(\text{CN})_6]^{4-}$ .

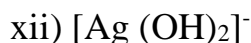
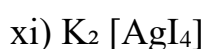
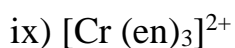
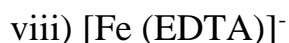
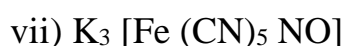
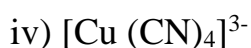
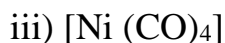


The counter ion is  $\text{Cl}^-$  and complex ion is  $[\text{Co}(\text{NH}_3)_6]^{3+}$ .

➤ **Oxidation states: -**



Calculate oxidation state of the following (HW)



➤ **Nomenclature of Coordination Compounds (Rules): -**

- positive ion is named first followed by negative ion.

E.g.,



In this complex, complex ion is +ve ion, it should be named first then -ve Chloride ion.



In this complex, potassium ion is +ve ion is named first then the complex ion  $[Fe(CN)_6]^{4-}$

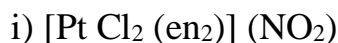
- Name of Ligands:

The ligands are named in alphabetical order (according to name of ligands not the prefix).

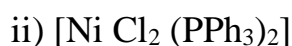
E.g.,  $[(Pt, Br, Cl, (NO_2), (NH_3)]$ , in this complex the ligands are named in the order of Amminebromochloronitrito-N.

- The negative ligands will be end with -O or -ido. The +ve ligands will be end with 'ium', neutral group have no special ending.
- The number of ligands in the complex is denoted by prefixes di, tri, tetra to show the number of ligands. But suppose if the name of ligands itself contain di, tri, tetra...., etc then in such cases following prefixes is used and such ligands are kept in bracket to avoid confusion.

2	Di	Bis
3	Tri	Tris
4	Tetra	Tetrakis
5	Penta	Pentakis
6	Hexa	Hexakis



In this Complex name of ligands is Dichlorobis(ethylenediamine).



In this Complex name of ligands is Dichlorobis(triphenylphosphine).

- Name of metal ion: -

The name of metal ion depends upon the charge on complex ion.

a) If the complex ion carries positive charge or neutral then, metal is named is normal way.

E.g., i) Co in complex cation is called as cobalt.

ii) Pt in complex cation is called as platinum.

b) If the complex ion carries -ve charge then, the name of metal ends with suffix **-ate**.

E.g., i) Co in complex anion is called as cobaltate.

ii) Pt in Complex anion is called as platinate.

c) But for some metals, the Lattin names are used in the complex anion.

Iron [Fe] = Ferrate

Silver [Ag] = Argentate

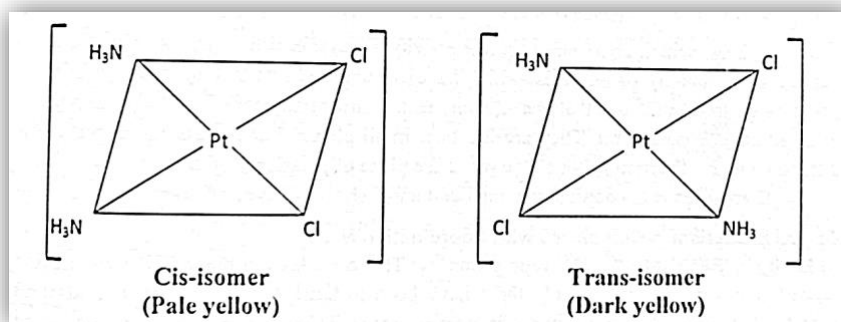
Gold [Au] = Aurate

Lead [Pb] = Plumbate

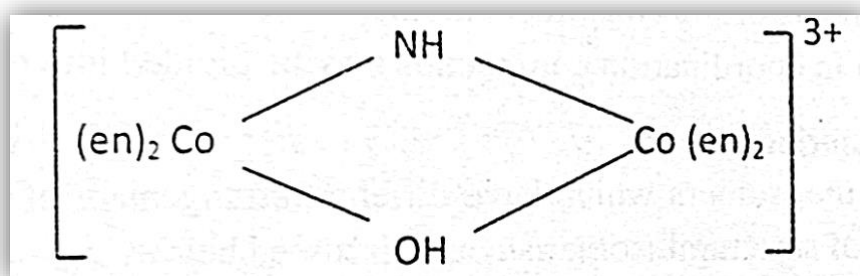
Tin [Sn] = Stannate

Copper [Cu] = cuprate

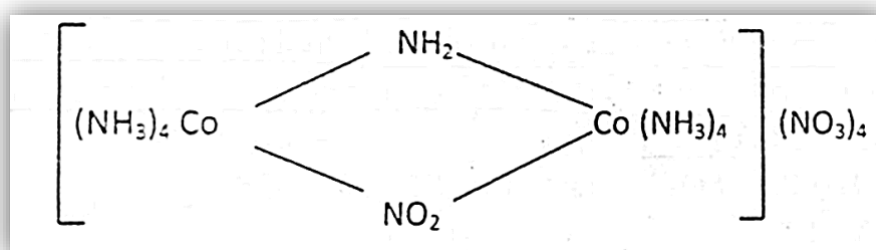
- The oxidation state of central metal atom is shown by Roman numbers in the bracket after the name of metals.
  - The prefixes Cis and Trans is used to show same side and opposite side of geometrical location.
- E.g.,  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  Cis and Trans diamminedichloroplatinum (II).

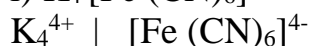


- The name of bridge complex is prefixed by  $\mu$ .
- i)  $[(\text{NH}_3)_5\text{Cr}-\text{OH}-\text{Cr}(\text{NH}_3)_5]\text{Cl}_5$   
 Pentaamine chromium-(III)-  $\mu$ -hydroxypentaamine chromium-(III) chloride
- ii) bis(ethylenediamine)cobalt (III)-  $\mu$ -imido- $\mu$ -hydroxo bis-(ethylenediamine)cobalt(III) ion



- iii) tetraamminecobalt (III)-  $\mu$ -amido- $\mu$ -nitrito-N-tetraamminecobalt (III) nitrate





No. of ligand  $\rightarrow 6 \rightarrow$  Hexa

Name of ligand  $\rightarrow CN^- \rightarrow$  Cyno

Complete name of ligand  $\rightarrow$  Hexacyno

Name of metal ion  $\rightarrow$  Ferrate

O.S. of metal ion  $\rightarrow x + (-1 \times 6) = -4$

$$x - 6 = -4$$

$$x = +2$$

Complete name of complex  $\rightarrow$  Potassiumhexacynoferrate (II)

➤ **Rules for writing the formula of coordination compounds: -**

i) The Central atom or ion is placed First.

ii) The ligands are placed in alphabetical order.

iii) The Coordination complex is enclosed in square brackets [ ].

iv) No Space is kept between representation of ionic species within the formulae.

v) The Charge is indicated outside the square bracket with my number before sign. E.g.,  $[Co (NH_3)_6]^{3+}$

vi) The charge of cation is balanced by charge on anion.

E.g., i) Tetraamine aquo Chlorocobalt (III) chloride.



➤ **Sidgwick Electronic Theory: -**

This theory is used for the formation of coordination compounds and gave the concept of EAN. According to this theory, Ligands donate electron pair(s) to the central metal ion and forms a coordinate bond.

➤ **Effective Atomic Number (EAN): -**

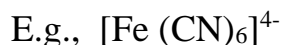
The total number of electrons associated with central metal ion and electrons donated by ligands is called as effective atomic number. It is calculated by,

$$EAN = (Z-n) + (2 \times C.N.)$$

Where, Z = Atomic number of metals

n = Oxidation state (no. of electron lost by metal)

C.N. = Coordination number



At. No. of Fe (Z) = 26

O.S. of Fe (n) = +2

$CN^-$  is unidentate ligand therefore C.N. = 6



$$\begin{aligned}
 \therefore \text{EAN} &= (\text{Z}-n) + (2 \times \text{C.N.}) \\
 &= (26 - 2) + (2 \times 6) \\
 &= 24 + 12 \\
 &= 36
 \end{aligned}$$

EAN of Fe in  $[\text{Fe}(\text{CN})_6]^{4-}$  is 36.

➤ **Effective Atomic Number Rule or EAN Rule: -**

The total number of electrons associated with central metal ion and electrons donated by ligands is equal to the atomic number of nearest zero group element is called as EAN rule.

Metal Atom	Atomic No.	Complex / Complex ion	O.S.	C.N.	EAN = (Z-n) + (2 × C.N.)
<b>Fe</b>	26	$[\text{Fe}(\text{CN})_6]^{4-}$	+2	6	$(26-2) + 12 = 36$ (Kr)
<b>Co</b>	27	$[\text{Co}(\text{NO}_2)_6]^{3+}$	+3	6	$(27-3) + 12 = 36$ (Kr)
<b>Cu</b>	29	$[\text{Cu}(\text{H}_2\text{O})_4]^+$	+1	4	$(29-1) + 8 = 36$ (Kr)
<b>Pd</b>	46	$[\text{Pd}(\text{Cl})_6]^{2-}$	+4	6	$(46-4) + 12 = 54$ (Xe)
<b>Pt</b>	78	$[\text{Pt}(\text{NH}_3)_6]^{4+}$	+4	6	$(78-4) + 12 = 86$ (Rn)
<b>Fe</b>	26	$[\text{Fe}(\text{CN})_6]^{3-}$	+3	6	$(26-3) + 12 = 35$
<b>Cu</b>	29	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	+2	4	$(29-2) + 8 = 35$
<b>Ni</b>	28	$[\text{Ni}(\text{NH}_3)_4]^{2+}$	+2	6	$(28-2) + 12 = 38$
<b>Pt</b>	78	$[\text{Pt}(\text{NH}_3)_4]^{2+}$	+2	4	$(78-2) + 8 = 84$
<b>Ni</b>	28	$[\text{Ni}(\text{CO})_4]$	0	4	$28 + 8 = 36$
<b>Zn</b>	30	$[\text{Zn}(\text{NH}_3)_4]^{2+}$	+2	4	$(30-2) + 8 = 36$
<b>Co</b>	27	$[\text{Co}(\text{NH}_3)_6]^{3+}$	+3	6	$(27-3) + 12 = 36$

➤ **Drawbacks of Sidgwick's Theory: -**

- i) This theory does not explain the stability of complexes which does not obey EAN rule.
- ii) This theory does not explain the directional nature of coordinate bond.

## ➤ Werner's Theory of Coordination: -

This theory is used to explain the nature of bonding in Complex Compounds. According to this theory,

i) Each metal ion has two types of valencies:

a) Primary valency b) secondary valency

ii) Primary valency represent oxidation state of metal ion and it is ionisable and it is denoted by dotted line.....

iii) Secondary valency represents coordination number of metal ion. It is non ionisable and it is denoted by solid line ———

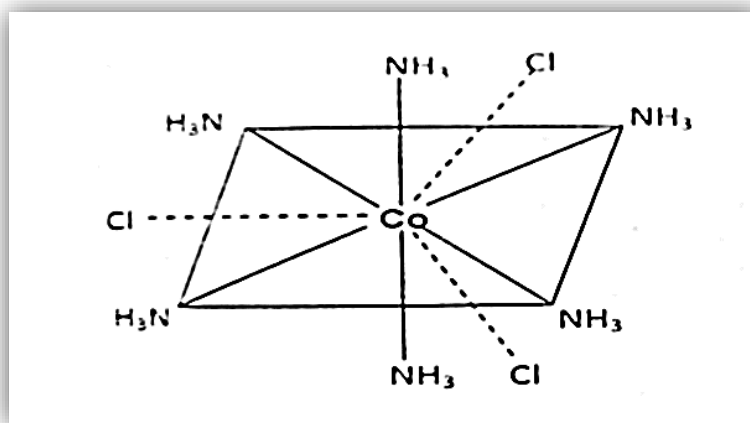
iv) Metal ion satisfy both the valancies.

v) Secondary valency of metal ion is fixed. It is directional in nature, therefore, it represents geometry of complex.

To distinguish two types of valancies, Werner introduced square bracket '[ ]' The species present in square bracket are non-ionisable while outside the square bracket are ionisable.

### 1. $\text{CoCl}_3 \cdot 6\text{NH}_3$ : -

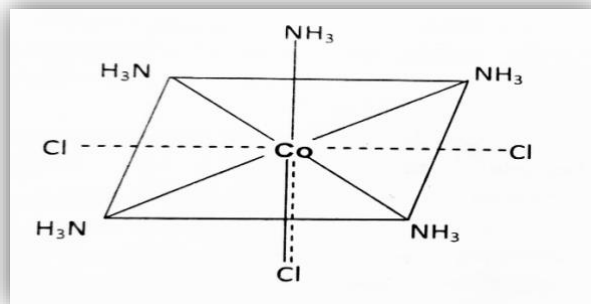
This complex contains six  $\text{NH}_3$  groups which satisfy six secondary valencies and these  $\text{Cl}^-$  ions which satisfy primary valencies. Therefore, complex may be formulated as  $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$ .



### 2. $\text{CoCl}_3 \cdot 5\text{NH}_3$ : -

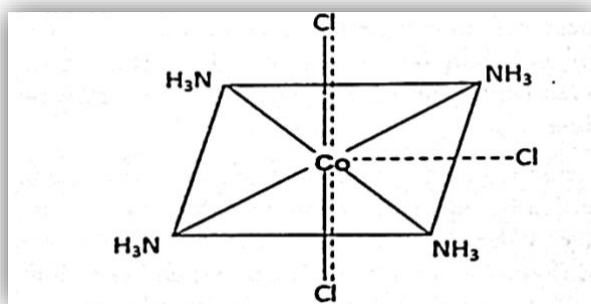
This complex contains 5  $\text{NH}_3$  groups which satisfy five secondary valencies. But secondary valency of cobalt is six. Therefore, one of the secondary valencies is satisfied by one  $\text{Cl}^-$  ion.

The primary valency of cobalt is three, which satisfies three  $\text{Cl}^-$  ions. This shows that one of the  $\text{Cl}^-$  ions satisfies both primary and secondary valencies. Therefore, this complex may be formulated as  $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Cl}_2$ .



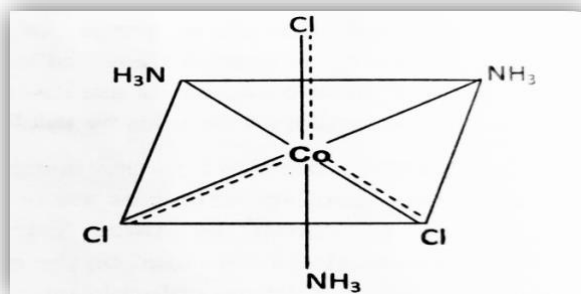
### 3. $\text{CoCl}_3 \cdot 4\text{NH}_3$ :-

This complex contains four  $\text{NH}_3$  groups which satisfy four secondary valencies. But secondary valency of cobalt is six. Therefore, two secondary valencies are satisfied by two  $\text{Cl}^-$  ions. The primary valency is three which is satisfied by three  $\text{Cl}^-$  ions. This shows that two  $\text{Cl}^-$  ions satisfy both primary and secondary valencies. Therefore, the complex may be formulated as;  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ .



### 4. $\text{CoCl}_3 \cdot 3\text{NH}_3$ :-

This complex contains three  $\text{NH}_3$  groups which satisfy three secondary valencies. But secondary valency of cobalt is six. Therefore, three secondary valencies are satisfied by three  $\text{Cl}^-$  ions. The primary valency is three which is satisfied by three  $\text{Cl}^-$  ions. This shows that three  $\text{Cl}^-$  ions satisfy both primary and secondary valencies. Therefore, the complex may be formulated as  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ .



### ➤ Experimental Verification of Werner's Theory: -

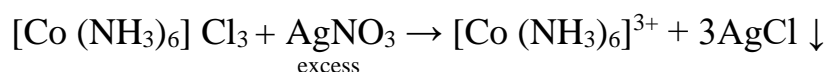
According to Werner's theory, primary valency is ionisable while secondary valency is non-ionisable. This can be verified experimentally by two methods:

- i) Precipitation method
- ii) Conductivity method

• **Precipitation Method: -**

**a) For [Co (NH<sub>3</sub>)<sub>6</sub>] Cl<sub>3</sub>: -**

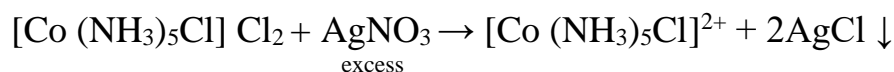
When excess of AgNO<sub>3</sub> reacts with [Co (NH<sub>3</sub>)<sub>6</sub>] Cl<sub>3</sub> gives precipitation of three molecules of AgCl, which corresponds to three Cl<sup>-</sup> ions in ionisation sphere.



When HCl reacts with [Co (NH<sub>3</sub>)<sub>6</sub>] Cl<sub>3</sub>, no reaction takes place. This indicates that NH<sub>3</sub> molecules are not removed by HCl. All NH<sub>3</sub> molecules are present in coordination sphere and satisfy secondary valency.

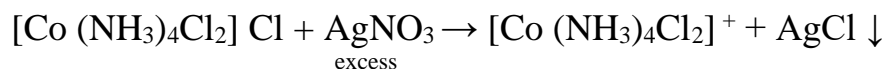
**b) For [Co (NH<sub>3</sub>)<sub>5</sub> Cl] Cl<sub>2</sub>: -**

When excess of AgNO<sub>3</sub> reacts with [Co (NH<sub>3</sub>)<sub>5</sub>Cl] gives precipitation of two molecules of AgCl which corresponds to two Cl<sup>-</sup> ions in ionisation sphere.



when HCl reacts with [Co (NH<sub>3</sub>)<sub>5</sub>Cl] Cl<sub>2</sub>, no reaction takes place.

**c) For [Co (NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>] Cl: -**



**d) For [Co (NH<sub>3</sub>)<sub>3</sub> Cl<sub>3</sub>]: -**



➤ **Conductivity Method: -**

The conductivity of solution depends upon number of ions.  
The number of ions and molar conductivity is

Complex	Complex Ions	No. of Ions	Molar Conductivity
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	$[\text{Co}(\text{NH}_3)_6]^{3+}$ , $3\text{Cl}^-$	4	$390 \text{ Mho}^{-1}\text{Mol}^{-1}$
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ , $2\text{Cl}^-$	3	$260 \text{ Mho}^{-1}\text{Mol}^{-1}$
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ , $\text{Cl}^-$	2	$102 \text{ Mho}^{-1}\text{Mol}^{-1}$
$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	0	0

➤ **Valence Bond Theory [VBT] of Transition Metal Complexes: -**

This theory was developed by Pauling in 1931.

• **Postulates / Assumptions / salient features of VBT: -**

- i) The metal atom or ion present in the complex provide definite number of vacant orbitals like s, p, d for the formation of coordinate bonds with ligands.
- ii) The number of vacant orbitals provided by central metal ion is equal to coordination number.
- iii) These vacant orbitals undergo hybridisation and forms same number of hybrid orbitals.
- iv) Each ligand donates pair of electrons to the vacant orbitals.
- v) The vacant orbitals of metal ion overlap with filled orbitals of ligands and forms coordinate bond between metal and ligand.
- vi) The geometry of metal ion depends upon hybridisation of metal orbitals.

Types of Hybridisations	Shape of Complex
sp	Linear
sp <sup>2</sup>	Trigonal Planer
sp <sup>3</sup>	Tetrahedral
dsp <sup>2</sup>	Square Planer
sp <sup>3</sup> d	Trigonal Bipyramidal
dsp <sup>3</sup>	Square Pyramidal / TBP
sp <sup>3</sup> d <sup>2</sup>	Octahedral
d <sup>2</sup> sp <sup>3</sup>	Octahedral
sp <sup>3</sup> d <sup>3</sup>	Pentagonal Bipyramidal

vii) larger is the overlapping stronger is the bond.

viii) If inner d-orbitals [(n-1) d] are used for hybridisation then, complex is called as inner orbital complex.

ix) If outer d-orbitals [nd] are used for hybridisation then complex is called as outer orbital complex.

- x) The non-bonding electrons are arranged according to Hund's rule.
- xi) But in presence of Strong ligands like CO, CN, NO<sub>2</sub>, en, NH<sub>3</sub>, the electrons can be pair up against Hund's Rule.
- xii) The order of strength of ligands is according to spectrochemical Series.  
CO > CN<sup>-</sup> > NO<sub>2</sub><sup>-</sup> > en > NH<sub>3</sub> > Pyridine > EDTA<sup>4-</sup> > NCS<sup>-</sup> > H<sub>2</sub>O > C<sub>2</sub>O<sub>4</sub><sup>2-</sup> > OH<sup>-</sup> > F<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > Cl<sup>-</sup> > SCN<sup>-</sup> > I<sup>-</sup>.
- xiii) If central metal ion of complex contain unpaired electrons shows paramagnetic property while paired electrons shows diamagnetic property.

- **Magnetic Properties of Complexes: -**

The complex which contains unpaired electrons is called paramagnetic complex or substance or high spin complex or outer orbital complex. While the complex which contain paired electrons (↑↓) are Called as diamagnetic complex / compound or low spin complex or inner orbital complex.

The magnetic properties of complexes are calculated by using magnetic moment (μ) by formula;

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

where, μ = magnetic moment

n = No. of unpaired electrons

B.M. = Bohr Magneton (unit of magnetic moment)

This formula is also called as 'spin only formula'.

No. of Unpaired Electrons	Magnetic Moment (BM)
1	1.73
2	2.83
3	3.87
4	4.90
5	5.92

- **Geometry of Coordination Compounds: -**

- **Complexes with d<sup>1</sup>d<sup>2</sup>d<sup>3</sup> configuration: -**

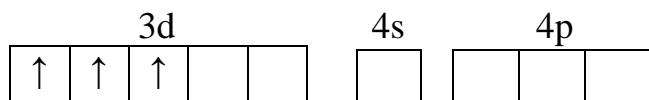
When central atom contains 1,2, or 3 electrons and occupy first three d-orbitals and remaining two orbitals remain vacant. The two vacant 3d-orbitals hybridised with one (4S) and three (4P) orbitals gives d<sup>2</sup>sp<sup>3</sup> hybrid orbitals and forms octahedral complex.

**Formation of [Cr (NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> ion**

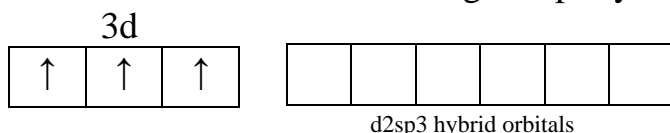
Atomic No. of Cr = 24

Oxidation State of Cr is +3.

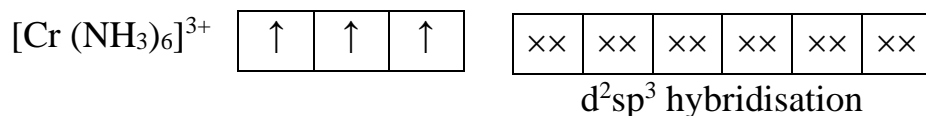
Electronic configuration of  $\text{Cr}^{3+}$  is  $3d^3$ .



These six vacant orbitals undergo  $d^2sp^3$  hybridisation.



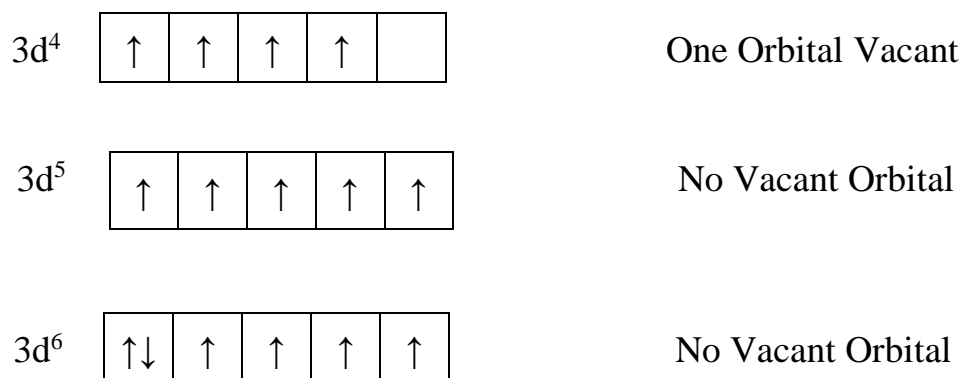
In the formation of  $[\text{Cr}(\text{NH}_3)_6]$



The complex is formed by  $d^2sp^3$  hybridisation with octahedral geometry. It contains three unpaired electrons therefore it is paramagnetic and high Spin complex.

• **Complexes with  $d^4$ ,  $d^5$ ,  $d^6$  configuration: -**

The electronic configuration in ground state is: -



They can form two types of complexes;

- i) Inner orbital complexes involving  $d^2sp^3$  hybridisation.
- ii) Outer orbital complexes involving  $sp^3d^2$  hybridisation.

**i) Inner orbital complexes involving  $d^2sp^3$  hybridisation.**

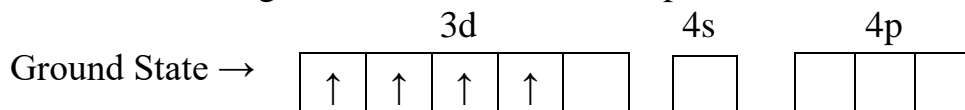
This type of complexes is formed with strong field ligands which pair up electrons and makes two d-orbitals vacant for  $d^2sp^3$  hybridisation.

### Formation of $[\text{Mn}(\text{CN})_6]^{3-}$ ion ( $d^4$ -system)

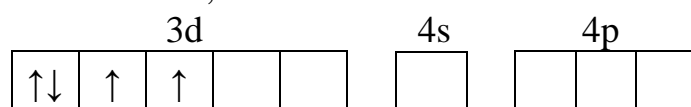
Atomic number of Mn = 25

Oxidation State of Mn = +3

Electronic Configuration of  $\text{Mn}^{3+} = 3d^4 4s^0 4p^0$

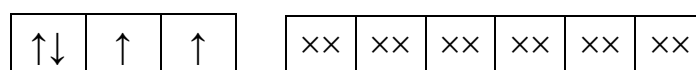


As  $\text{CN}^-$  ion is strong ligand it pairs up 3d electrons. Therefore, electronic configuration in excited state is;



These six vacant orbitals undergo  $d^2sp^3$  hybridisation.

In the formation of  $[\text{Mn}(\text{CN})_6]^{3-}$



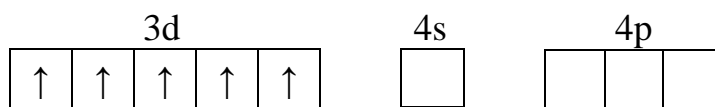
The complex is formed by  $d^2sp^3$  hybridisation with octahedral geometry. It contains two unpaired electrons therefore it is paramagnetic and high spin complex.

### Formation of $[\text{Fe}(\text{CN})_6]^{3-}$ ion ( $d^5$ -system)

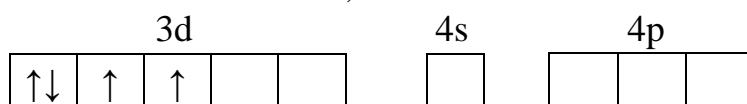
Atomic number of Fe = 26

Oxidation State of Fe = +3

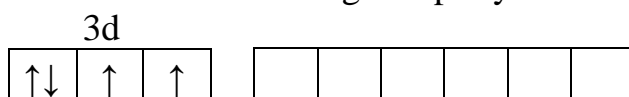
Electronic Configuration of  $\text{Fe}^{3+} = 3d^5 4s^0 4p^0$



As  $\text{CN}^-$  ion is strong ligand so it pairs up 3d electrons. Therefore, electronic configuration in excited state is;

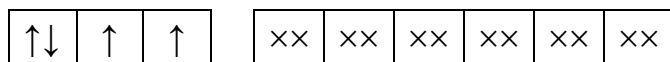


These six vacant orbitals undergo  $d^2sp^3$  hybridisation.





In the formation of  $[\text{Fe}(\text{CN})_6]^{3-}$



The complex is formed by  $d^2sp^3$  hybridisation with octahedral geometry. It contains one unpaired electron therefore it is paramagnetic and high spin complex.

**ii) Outer orbital complexes involving  $sp^3d^2$  hybridisation.**

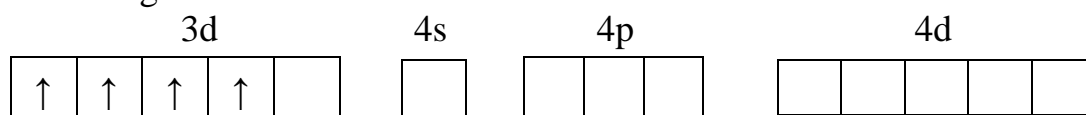
It involves one 4s, three 4p and two 4d orbitals. This type of complexes is formed with weak field ligands.

**Formation of  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  ion ( $d^4$ -system)**

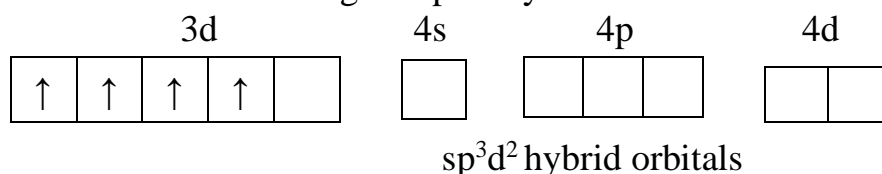
Atomic number of Cr = 24

Oxidation State of Cr = +2

Electronic Configuration of  $\text{Cr}^{3+} = 3d^4$



As  $\text{H}_2\text{O}$  is weak ligand so it does not pair up 3d electrons. Therefore, ligands use outer six orbitals and undergoes  $sp^3d^2$  hybridisation.



In the formation of  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  is;



The complex is formed by  $sp^3d^2$  hybridisation with octahedral geometry. It contains four unpaired electrons therefore it is paramagnetic and high spin complex.

**H.W.**

- 1) Formation of  $[\text{FeF}_6]^{3-}$
- 2) Formation of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
- 3) Formation of  $[\text{Ni}(\text{NH}_3)_6]^{2+}$

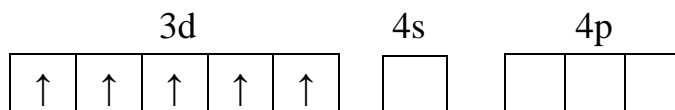
### iii) Tetrahedral Complexes with $sp^3$ Hybridisation: -

#### Formation of $[\text{Mn}(\text{Br})_4]^{2-}$ ion

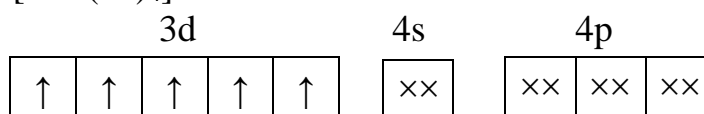
Atomic number of Mn = 25

Oxidation State of Mn = +2

Electronic Configuration of  $\text{Mn}^{2+} = 3d^5$



In the formation of  $[\text{Mn}(\text{Br})_4]^{2-}$



The complex is formed by  $sp^3$  hybridisation with Tetrahedral geometry. It contains five unpaired electrons therefore it is paramagnetic and high spin complex.

### iv) Square Planar Complexes with $dsp^2$ hybridisation: -

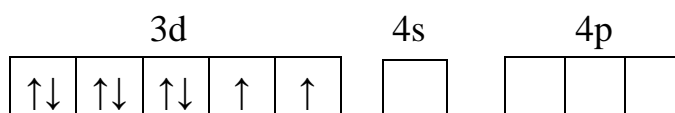
This type of complexes involves one d-orbital, one s-orbital and two p-orbitals.

#### Formation of $[\text{Ni}(\text{CN})_4]^{2-}$

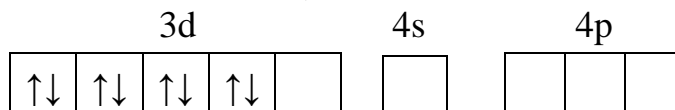
Atomic number of Ni = 28

Oxidation State of Ni = +2

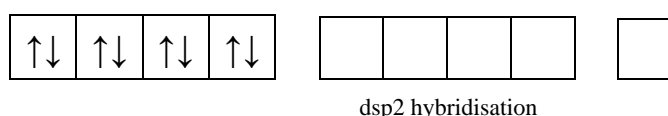
Electronic Configuration of  $\text{Ni}^{2+} = 3d^8$



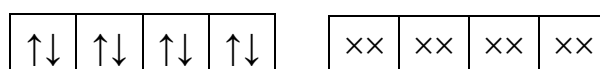
As  $\text{CN}^-$  ion is strong ligand so it pairs up d-electrons. Therefore, electronic configuration of  $\text{Ni}^{2+}$  in excited state is;



These four vacant orbitals undergo  $dsp^2$  hybridisation.



In the formation of  $[\text{Ni}(\text{CN})_4]^{2-}$



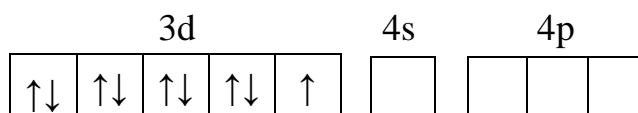
The complex is formed by  $dsp^2$  hybridisation with Square Planar geometry. It contains no unpaired electrons therefore it is diamagnetic and low spin complex.

**ii) Formation of  $[Cu (NH_3)_4]^{2+}$  Complex: -**

Atomic number of Cu = 29

Oxidation State of Cu = +2

Electronic Configuration of  $Cu^{2+} = 3d^9$



Now one electron from 3d orbital is promoted to 4p orbital and undergoes  $dsp^2$  hybridisation.

In the formation of  $[Cu (NH_3)_4]^{2+}$



$dsp^2$  hybridisation

The complex is formed by  $dsp^2$  hybridisation with Square Planar geometry. It contains one unpaired electron therefore it is paramagnetic and high spin complex.

➤ **Isomerism in Coordination Compounds: -**

The compound having Same molecular formula but different structural formula is called as isomer and this phenomenon is called as isomerism.

There are two main types of isomerism in coordination compounds;

i) Structural Isomerism

ii) Stereo Isomerism → a) Geometrical Isomerism

b) Optical Isomerism

• **Structural Isomerism: -**

The Compound having some molecular formula but different structural formula (different arrangement of ligands) is called as structural isomerism.

It is divided into four types:

a) Linkage isomerism

b) Ionisation isomerism

c) Coordination isomerism

d) Solvated or Hydrated isomerism

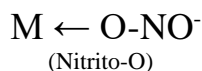
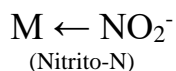
**i) Linkage Isomerism: -**

In this type of isomerism, same ligand is bonded to central metal atom through different atoms.

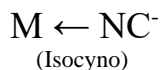
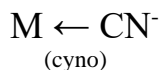
The ligand that can bind / link through more than one atom is called as ambident ligand.

E.g., CO, CN<sup>-</sup>, SCN<sup>-</sup>, NO<sub>2</sub><sup>-</sup>

a. NO<sub>2</sub><sup>-</sup> is bonded through N-atom or O-atom



b. CN<sup>-</sup> is bonded through C-atom or N-atom



### ii) Ionisation Isomerism: -

In this type of isomerism there is an exchange of ions inside and outside of the coordination sphere.

E.g., a)  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$   
Red violet Red

E.g., b)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$  and  $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{SO}_4$

c)  $[\text{Co}(\text{en})_2\text{NO}_2\text{Cl}]\text{SCN}$   
 $[\text{Co}(\text{en})_2\text{NO}_2\text{SCN}]\text{Cl}$   
 $[\text{Co}(\text{en})_2\text{SCNCl}]\text{NO}_2$

### iii) Coordination Isomerism: -

In this type of isomerism there is interchange of ligands between positive and negative ions.

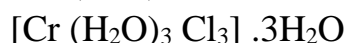
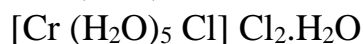
E.g., a)  $[\text{Co}(\text{NH}_3)_6]^{3+} [\text{Cr}(\text{CN})_6]^{3-}$  and  $[\text{Cr}(\text{NH}_3)_6]^{3+} [\text{Co}(\text{CN})_6]^{3-}$

b)  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$  and  $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$

### iv) Solvated or Hydrated Isomers: -

In this type of isomerism there is an exchange of water molecule inside and outside of the coordination sphere.

E.g.,  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$



### • Stereo Isomerism: -

The compound having same molecular formula but different arrangement around central metal atom / ion is called as stereo isomerism.

There are two types of stereo isomerism: -

i) Geometrical Isomerism

ii) Optical Isomerism

❖ **Geometrical Isomerism: -**

The isomerism having same molecular formula but different arrangement of ligands around the central metal atom / ion is called as geometrical isomerism.

When same ligands are at same position then it is called as cis-isomer.

When same ligands are at opposite position then it is called as trans-isomer.

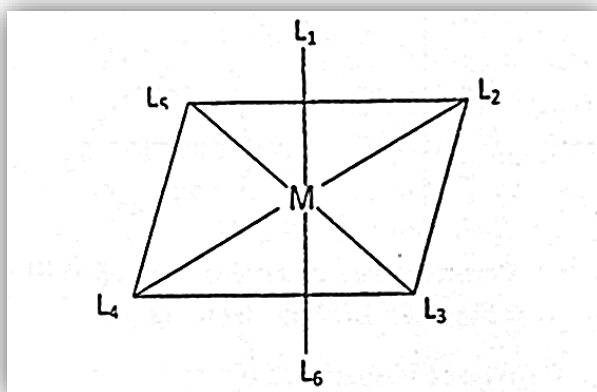
The geometrical isomerism is possible only in the complexes with coordination number 4 or greater than 4.

**1) Geometrical Isomerism in Octahedral Complexes: -**

Coordination Number = 6

Cis position = 1-2, 1-3, 2-3, 3-6, 6-4, 3-4, 4-5, 5-2, 1-4 and 5-1

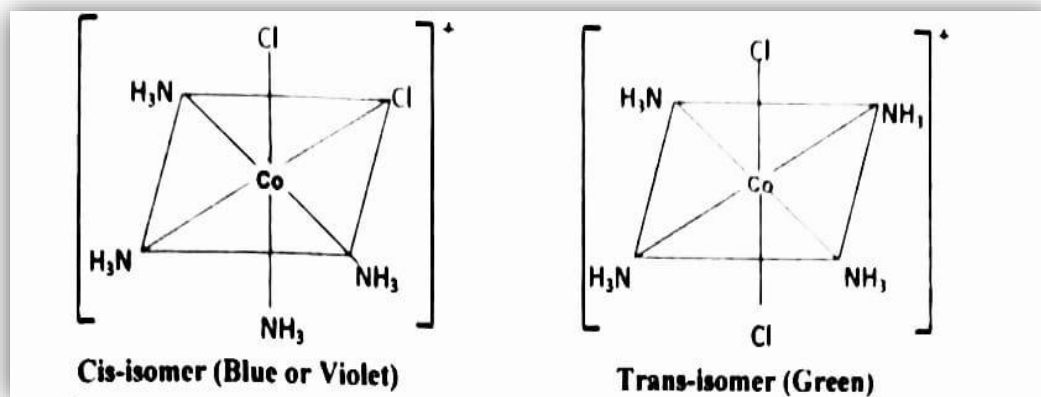
Trans position = 1-6, 2-4, and 3-5



The octahedral complexes of the type  $Ma_4b_2$ ,  $Ma_4bc$ ,  $Ma_3b_3$ ,  $M(AA)_2b_2$  shows cis and trans isomers.

**a)  $Ma_4b_2$ ,  $[Co (NH_3)_4Cl_2]^+$  and  $Ma_4bc$ ,  $[Co (NH_3)_4Cl NO_2]^+$  type complex: -**

This type of complexes exists in cis and trans isomerism.



**b)  $Ma_3b_3$ ,  $[Co(NH_3)_3Cl_3]$  type complex: -**

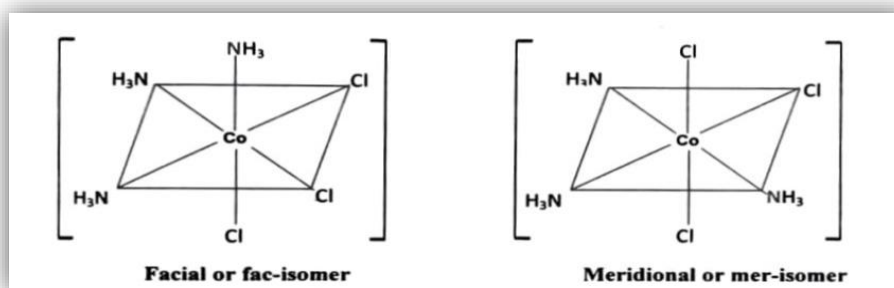
In this type of complex, when three same ligands are at same position of octahedron then it is called as facial or fac isomer.

When three same ligands are at three corners of square planar then it is called as meridional or Mer isomers.

Fac isomer = same ligands at 1, 2, 3 position and another three same ligands at 4, 5, 6 position.

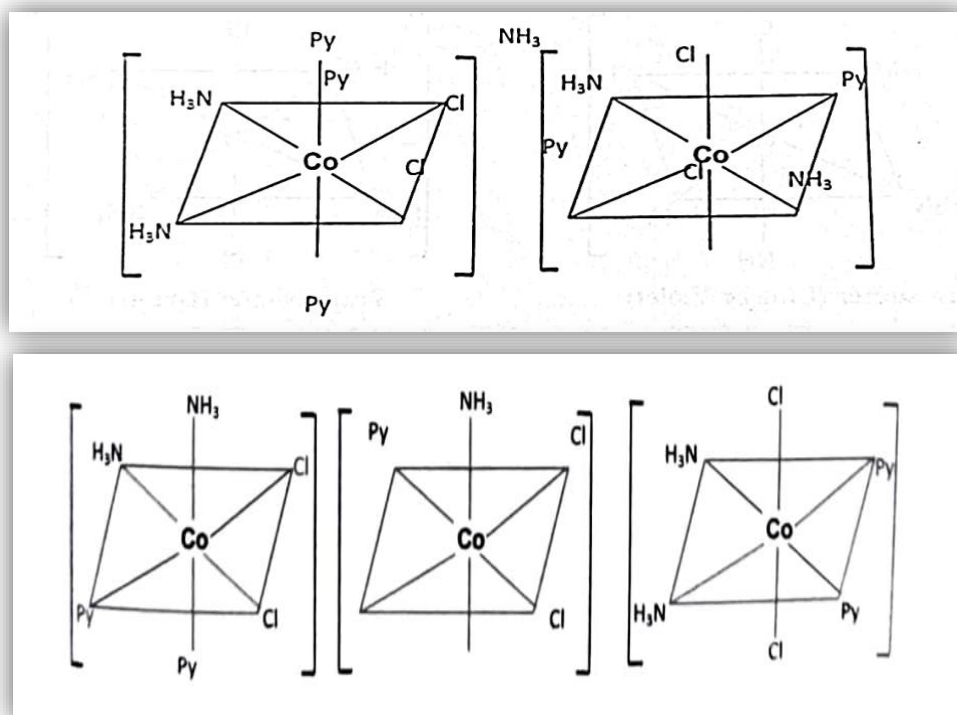
Mer isomer = same ligands at 1, 2, 4 position and another three same ligands at 3, 5, 6 position.

Other examples,  $[Co(NO_2)_3(NH_3)_3]$ ,  $[Rh-Cl_3(Py)_3]$ ,  $[Cr(NH_3)_3Cl_3]$



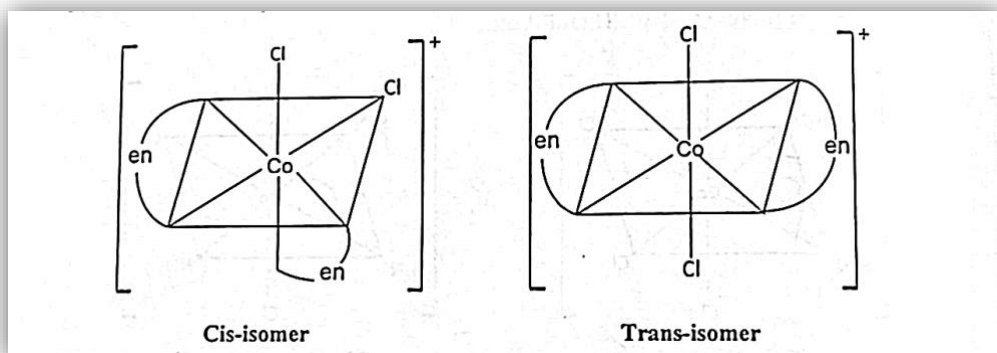
**c)  $Ma_2b_2c_2$ ,  $[Pt(NH_3)_2(Py)_2Cl_2]$  Type: -**

This type of complexes exists in five geometrical isomerism's out of which only three can be isolated.



d)  $[M(AA)_2b_2]$ ,  $[Co(en)_2Cl_2]^+$  Type: -

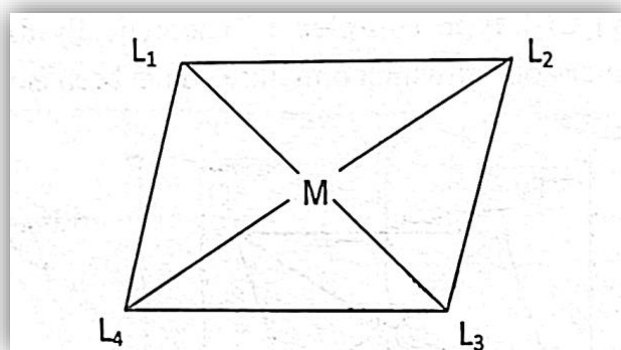
It shows two types of isomerism i.e., cis and trans.



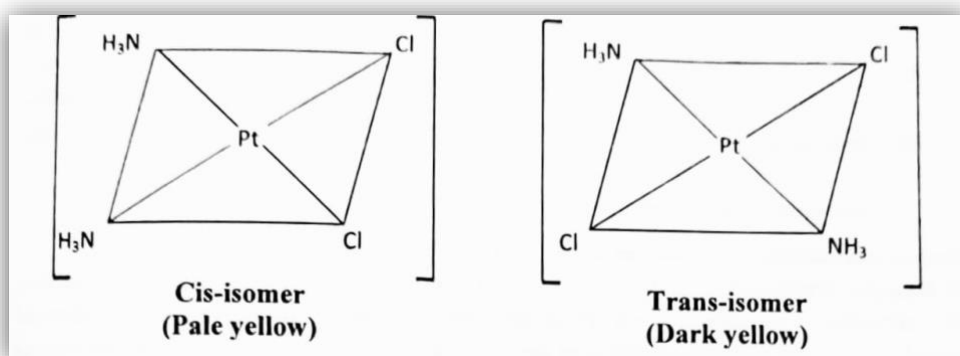
2) Geometrical Isomerism in Square Planar Complexes: -

Cis position = 1-2, 2-3, 3-4, 4-1

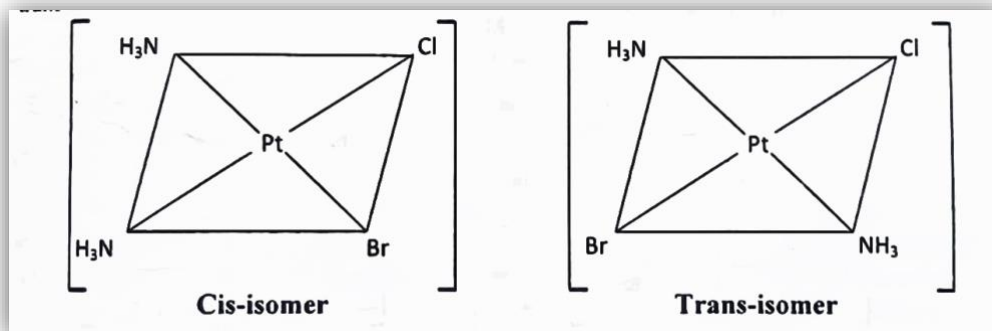
Trans position = 1-3, 2-4



a)  $Ma_2b_2$ ,  $[Pt(NH_3)_2Cl_2]$  type complex: -



**b)  $Ma_2bc$ ,  $[Pt (NH_3)_2Cl Br]$  type complex: -**



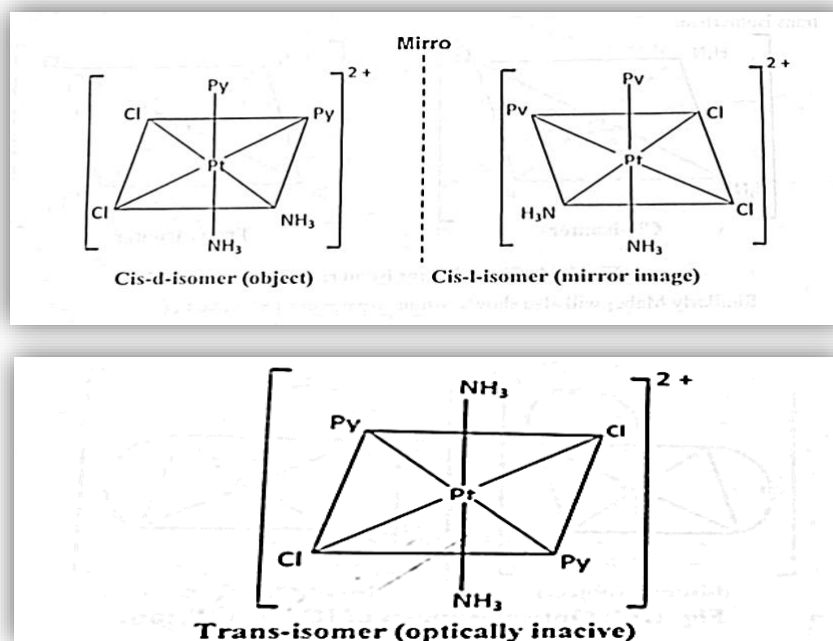
**❖ Optical Isomerism: -**

- ✓ The substance which rotates plane polarised light is called optically active compound.
- ✓ The compound having same molecular and structural formula but non-superimposable mirror image of each other is called as optical isomer, and this phenomenon is called as optical isomerism.
- ✓ This type of isomerism is shown by those complexes which do not have any element of symmetry (i.e., plane of symmetry, line of symmetry and point of symmetry).
- ✓ The optical isomers are d, l, and dl type.
- ✓ The substance which rotates plane polarised light in clockwise direction (right side) is called as dextro-rotatory or d-isomer.
- ✓ The substance which rotates plane polarised light in anticlockwise direction (left side) is called as leavo-rotatory or l-isomer.
- ✓ The d and l isomer are mirror images of each other and non-superimposable therefore they are called as enantiomers.
- ✓ The d and l isomers are optically active.
- ✓ The equimolar mixture of d-isomer and l-isomer is called as racemic mixture or dl-isomers, which is optically inactive due to external compensation.
- ✓ Optical activity is mostly observed in complex compound having coordination number 4 and 6.

**1) Optical Isomerism in Complexes with C.N. = 6**

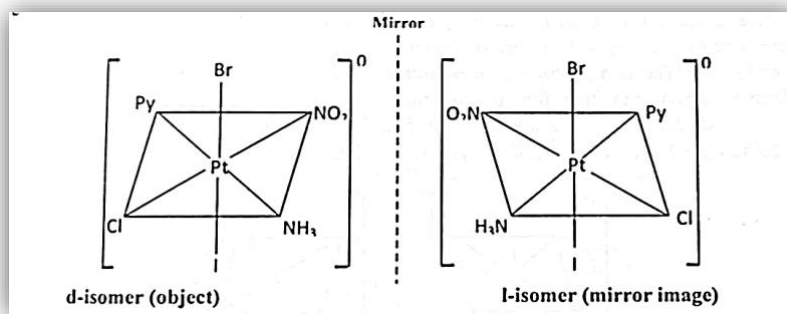
**a)  $Ma_2b_2c_2$ ,  $[Pt (NH_3)_2(Py)_2Cl_2]^{2+}$  type complex :-**





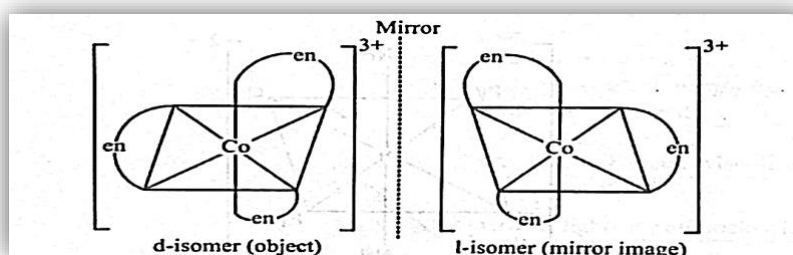
**b) Mabcdef, [Pt (Py)(NH<sub>3</sub>)(NO<sub>2</sub>)Cl.Br. I]<sup>0</sup> type complex: -**

This type of complex exists in 15 geometrical isomeric forms. Each of these 15 geometrical isomers exist in d and l isomers and gives total 30 optically active isomers. One of the 15 geometrical isomers is given in figure,

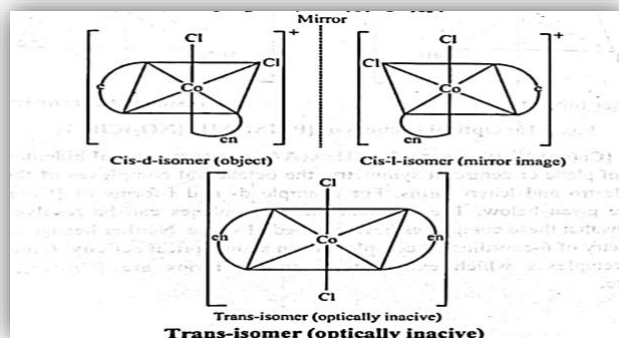


**c) [M(AA)<sub>3</sub>], [Co(en)<sub>3</sub>]<sup>3+</sup> type complex: -**

Where AA is bidentate ligand.

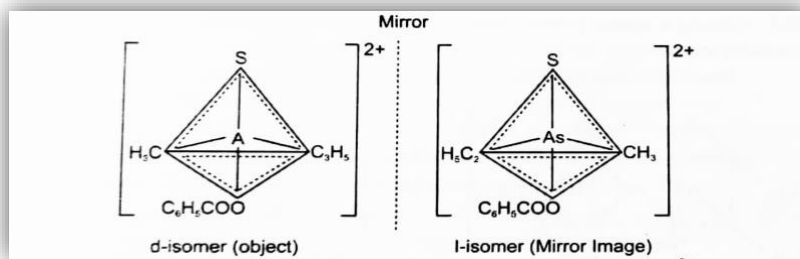


d)  $[M(AA)_2b_2]$ ,  $[Co(en)_2Cl_2]^+$  type complex: -

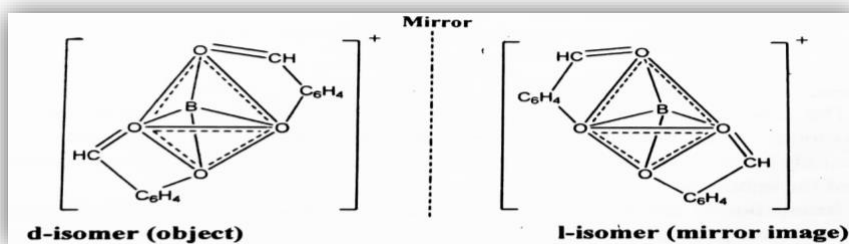


2) Optical Isomerism in Complexes with C.N. = 4 (Tetrahedral Complexes)

a)  $[Mabcd]$ ,  $[As(CH_3)(C_2H_5)(S)(C_6H_5COO)]^{2+}$  type complex: -



b)  $M(AA)_2$ ,  $[B(C_6H_4OCHO)_2]^+$  type complex: -



3) Optical Isomerism in Complexes with C.N.=4 (Square planar complexes)

E.g.,  $[Pt(NH_2-CH(C_6H_5)-CH(C_6H_5)-NH_2)(NH_2-CH_2-C(CH_3)_2-NH_2)]^{2+}$  ion

