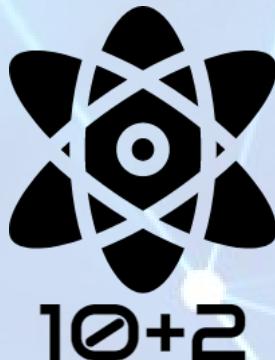


# 10+2 PCM NOTES

BY

## JOYOSHISH SAHA

(PDF version handwritten notes of Maths, Physics and Chemistry  
for 10+2 competitive exams like JEE Main, WBJEE, NEST, IISER  
Entrance Exam, CUCET, AIPMT, JIPMER, EAMCET etc.)



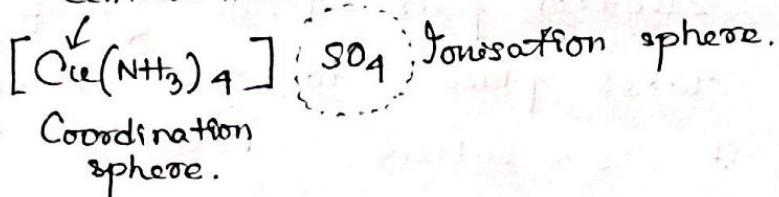
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*With best wishes from Joyoshish Saha*

# Coordination Compounds.

- \* **Coordination/Complex Compound:** The compounds in which some of the constituent ions lose their identity while some do not break up completely into individual ions, are called complex compounds. eg.  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ ,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ .
- \* For a complex compound, the species which is in coordination sphere undergoes ionisation.

central metal



- \* **Ligands:** The neutral molecules, anions or cations which are directly linked with the central atom or ion are called ligands. The ligands are attached to the central metal atom or ion through coordinate bonds or dative linkage.

- **Dentifity of Ligand:** The number of ligating atoms present in a

ligand is called dentifity of ligand.

eg.  $\text{CN}^-$  has dentifity 1,  $\text{COO}^-$  has dentifity 2,  $[\text{EDTA}]^{4-}$  has dentifity 6.

- **Classification of Ligands:**

1. **Mono or unidentate:** Ligands with one donor site eg.

$\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{H}_2\ddot{\text{O}}$ ,  $\text{CN}^-$ ,  $\text{NO}_2^-$ ,  $\text{OH}^-$ ,  $\text{CO}$  etc.

**2. Bidentate** : Ligands which have two donor atoms at two positions.

e.g. Ethylenediamine, oxalate, glycine etc.

**3. Polydentate** : The ligands having several donor atoms.

e.g. Diethylenetriamine has 3 donor atoms (tridentate), EDTA (Ethylene diamine tetra acetate) has 6 donor atoms (hexadentate).

- When coordination of more than one sigma electron pair donor group from the ligand takes place to the same central atom, it is called chelation. The resulting complex has ring structure & such ligand is called chelating ligand.

Chelating ligands form more stable complexes than similar ordinary complexes, in which the ligands act as monodentate.

\* **Effective atomic number (EAN)** : Resultant number of electrons with the metal atom or ion after gaining electrons from the donor atoms of ligands.

$$\text{EAN} = \left( \begin{array}{l} \text{atomic no.} \\ \text{of metal} \end{array} \right) + \left( \begin{array}{l} \text{electrons gained} \\ \text{from donor atoms} \\ \text{of ligands} \end{array} \right) - \left( \begin{array}{l} \text{electrons lost} \\ \text{in ion formation} \end{array} \right)$$

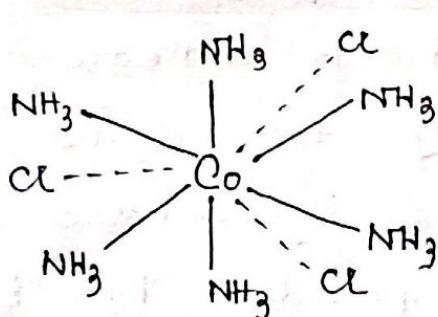
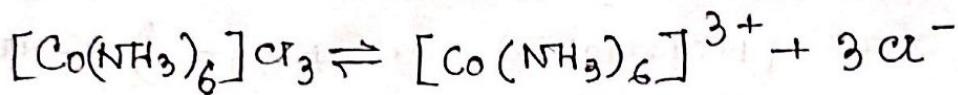
\* **Werner's Coordination Theory** : It explains the nature of bonding in complexes. Metals show two different kinds of valencies.

1. Primary valency: Non-directional & non-labile. It is equal to the oxidation state of the central metal ion.

2. Secondary Valency: Directional & non-labile.

It is equal to the coordination number of the metal. It is commonly satisfied by neutral & negatively charged or sometimes by positively charged ligands.

\* The ionisation of the coordination compound is written as:



Representation of  
CoCl<sub>3</sub> · 6NH<sub>3</sub> complex  
according to Werner's  
theory.

\* IUPAC Nomenclature: i) The cation is named first, then the anion.  
ii) In naming the coordination sphere, ligands are named first in alphabetical order followed by metal atom & then oxidation state of metal by roman numerical in parantheses. iii) Name of complex compound is started with a small letter & the complex part is written as one word. iv) Name of anionic ligands end in -o e.g. Cl<sup>-</sup> → chlorido.

v) Neutral ligands (with a few exceptions) retain their names, e.g.  $\text{NH}_3$  → ammonia. vi) Name of cationic ligands end in -ium, e.g.  $\text{NO}_2^+$  → Nitronium. vii) Certain ligands are represented by abbreviations in parentheses instead of their complex structural formulae, e.g. ethylenediamine (en). viii) Ambidentate ligands are named by using different names of ligands or placing the symbol of donor atom. e.g.  $-\text{SCN}^-$  (Thiosyanato-S or Thiocyanato),  $-\text{NCS}^-$  (Thiocyanato-N or Isothiocyanato),  $-\text{ONO}^-$  (Nitrito-O or Nitro),  $-\text{NO}_2^-$  (Nitrito-N or Nitro). ix) The prefixes di-, tri-, tetra-, penta- are used to indicate the number of each ligand. If the ligand name includes such a prefix, the ligand name should be placed in parentheses & preceded by bis-(2), tris-(3), tetrakis-(4), pentakis-(5). x) When the coordination sphere is anionic, name of central metal ends in -ate.

$\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$  : Potassium pentacyanonitrosyl ferrate (II).

$[\text{CoCl}_2(\text{NO}_2)(\text{NH}_3)_3]$  : Triammine dichloronitro cobalt (III).

$[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$  : Tetraammine platinum (IV) tetrachloroplatinate (IV).

### \* Isomerism:

A) Structural Isomerism: It is displayed by compounds that have different ligands within their coordination sphere.

i) Ionisation isomerism: Isomers that give different ions in solution. e.g.  $[(\text{Co}(\text{NH}_3)_5 \text{Br})\text{Cl}]$ ,  $[\text{Co}(\text{NH}_3)_5 \text{Cl}] \text{Br}$ .

ii) Hydrate isomerism: Isomers having different number of  $\text{H}_2\text{O}$  as a ligand and as water of hydration.

e.g.  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ ,  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ ,  
 $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot \text{H}_2\text{O}$ .

iii) Coordination isomerism: The ligands are interchanged in both the cationic & anionic ions.

e.g.  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ ,  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ .

iv) Linkage isomerism: When ambidentate ligand is coordinated with its different donor atoms.

e.g.  $[\text{Co}(\text{NH}_3)_5 \text{ONO}]\text{Cl}_2$ ,  $[\text{Co}(\text{NH}_3)_5 \text{NO}_2]\text{Cl}_2$ .

B) Stereoisomerism: Displayed by compounds which contain the same ligands in their coordination sphere but differ in the spatial arrangements of ligands around the central atom.

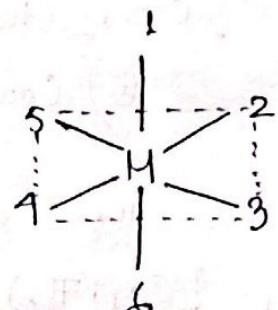
i) Geometrical Isomerism: Arises due to different possible geometric arrangement of the ligands.

When ligands occupy adjacent positions these are referred to as cis-positions. When ligands occupy opposite position, these are referred to as -trans-positions. (cis-trans isomerism).

The complexes having coordination number 4 adopt tetrahedral or square planar geometry. Geometrical isomerism is not possible in tetrahedral complexes.

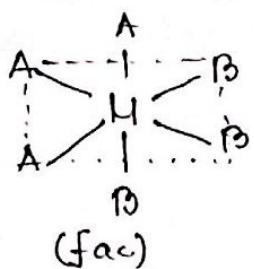
Square planar complexes of the type  $MA_2X_2$ ,  $MA_2XY$ ,  $MABXY$ . can exist as geometrical isomers.

In octahedral complexes, position 1-6, 2-4, 3-5 are trans while 1-2, 1-3, 1-4, 1-5, 2-3, 2-5, 6-4 etc are cis to each other.

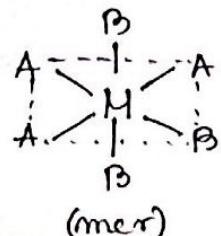


Octahedral complexes of the type  $MA_6$  or  $MA_5B$  would not show geometrical isomerism as expected.

In octahedral complexes of type  $MA_3B_3$  if 3 same ligand occupy adjacent positions at the corner of an octahedral face then it is facial (fac) isomer & when positions are around the meridian of the octahedron then it is meridional (mer) isomer.



(fac)



(mer)

ii) Optical Isomerism: Shown by the isomers which rotate the plane of polarised light equally but in opposite directions. They are called enantiomers. They possess the property of chirality.

The essential condition for a substance to show optical activity is that the substance should not have an element of symmetry in its structure.

Complex of the type  $M(AA)_3$  (where AA is symmetrical bidentate ligand) such as

$[Co(en)_3]^{3+}$  &  $[Cr(ox)_3]^{3-}$  exist as optical isomers. Complex of the type cis  $[M(AA)_2X_2]$  or  $[M(AA)_2XY]$  also exhibit optical activity. Trans form of these type does not show optical isomerism.

### \* Bonding in Coordination Compound:

• Valence Bond Theory: Central metal can use appropriate number of s-, p-, d- orbitals for hybridisation depending upon the total number of ligands.

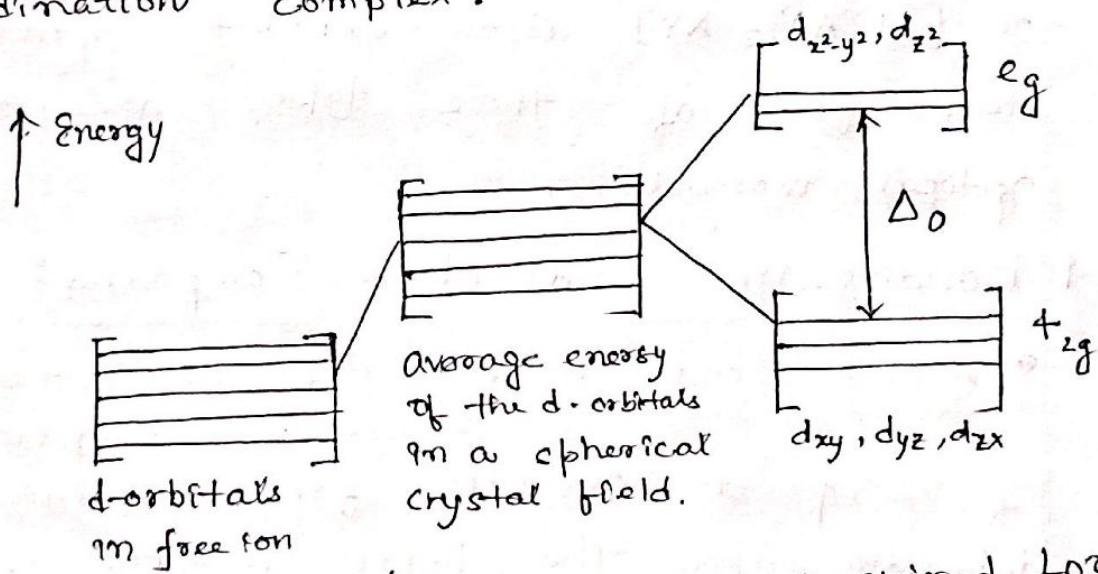
The outer orbital (high spin) or inner orbital (low spin) complexes are formed depending upon whether outer d-orbitals or inner d-orbitals are used.

The magnetic moment  $\mu = \sqrt{n(n+2)}$   
 $n \rightarrow$  no. of unpaired electrons.

- Crystal field Theory: It assumes the ligands to be point charges & there is electrostatic force of attraction between ligands & metal atom or ion. When ligands approach the central metal atom or ion, then the five degenerate orbitals do not possess equal energy any more & results in splitting, which depends upon nature of ligand field strength.

- The greater the ease with which the ligand can approach the metal ion, the greater will be the crystal field splitting caused by it.

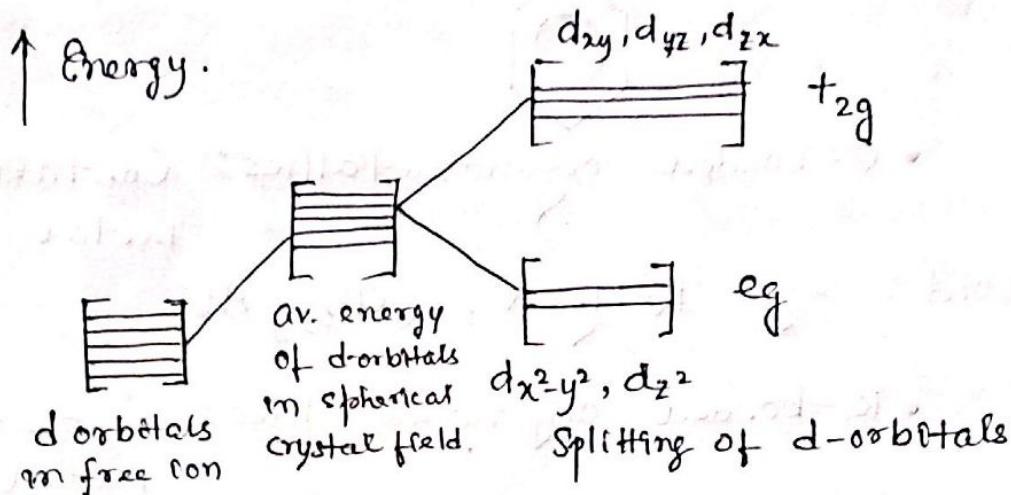
- Crystal field splitting in octahedral coordination complex:



- If  $\Delta_0 < P$  ( $P$  is energy required for forced pairing of electrons), then the electrons will remain unpaired in a high spin complex as formed.

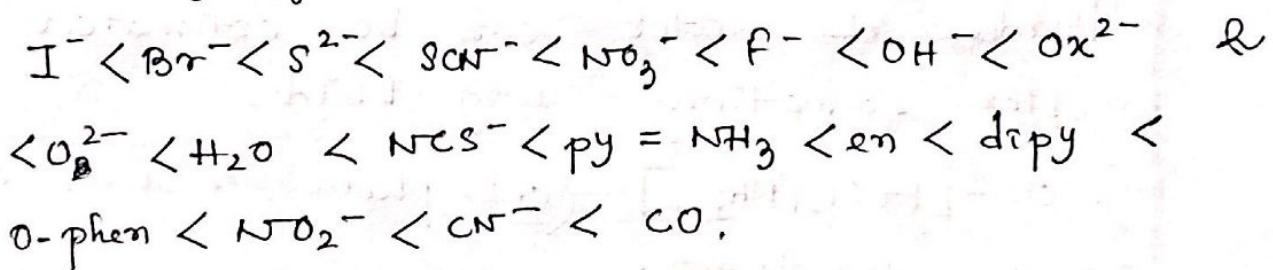
- If  $\Delta_0 > P$ , pairing of electrons takes place & low spin complex is formed.

- Crystal field splitting in tetrahedral complexes can be shown:

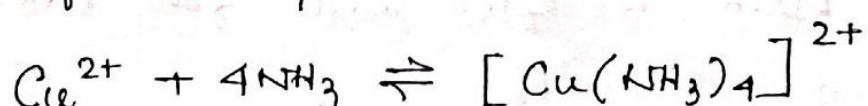


Difference in energy between eg &  $+_{2g}$  level is less.  $\Delta t = \frac{1}{9} \Delta_0$ .

\* Spectrochemical Series: Arrangement of ligands in the order of increasing field strength.



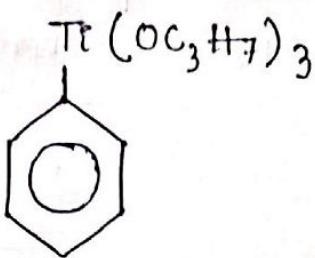
\* Stability of Complexes:



$$K = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4}, K \rightarrow \text{stability cons.}$$

- Higher the value of  $K$  higher will be stability of complex. Higher the polarising power of metal ion & basicity of ligand, higher the stability of complex.

\* Organometallic Compounds: Compounds which contain one or more metal-carbon bonds.



- $\sigma$ -bonded organometallics: Contain carbon-metal sigma bond. e.g.  $\text{R}-\text{Mg}-\text{X}$ ,  $(\text{CH}_3)_3\text{Al}$ .

- $\pi$ -bonded organometallics: Contain carbon-metal double bonds. e.g.  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$

#### \* Applications of Coordination Compounds:

i) Haemoglobin, chlorophyll, Vitamin  $\text{B}_{12}$  are complex compounds of Fe, Mg, Co.

ii) Hardness of water can be estimated by complex formation using EDTA.

iii)  $\text{cis}-[\text{PtCl}_2(\text{NH}_3)_2]$  (cis-platin) is used in cancer treatment.

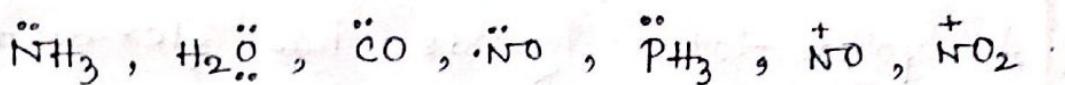
iv) EDTA is often used for treatment of lead poisoning.

v) Used in electroplating, dyes.

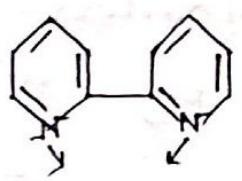
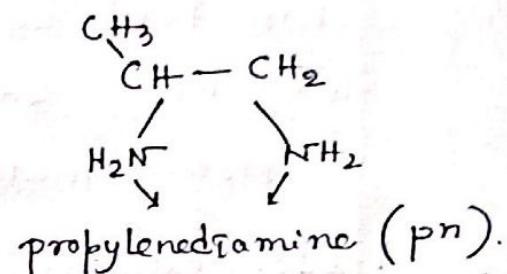
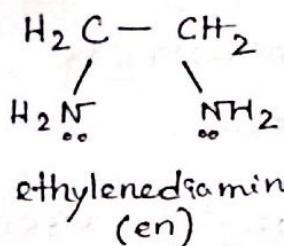
vi) Used as catalysts, e.g. Wilkinson's catalyst,  $(\text{Ph}_3\text{P})_3\text{RhCl}$  is used for dehydrogenation of alkenes, Ziegler-Natta Catalyst  $[\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}]$  is used for polymerisation of ethene.

\* Ligands:

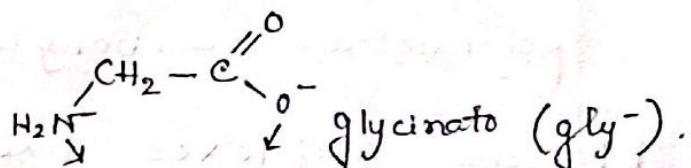
1. Monodentate:  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $O^{2-}$ ,  $S^{2-}$ ,  $OH^-$ ,  $SCN^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $CH_3COO^-$ ,  $S_2O_3^{2-}$ .



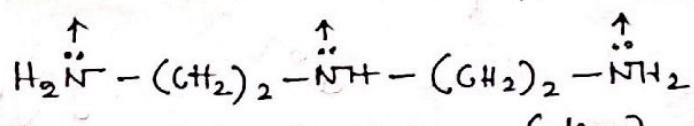
2. Bidentate:



bipyridine  
(bipy)

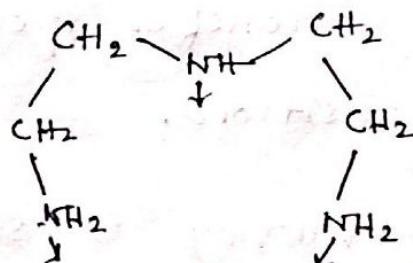


3. Tridentate:



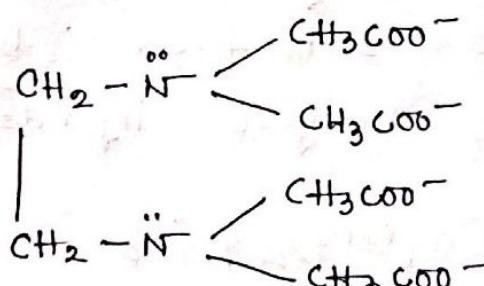
diethylenetriamine (dien).

or



4. Hexadentate:

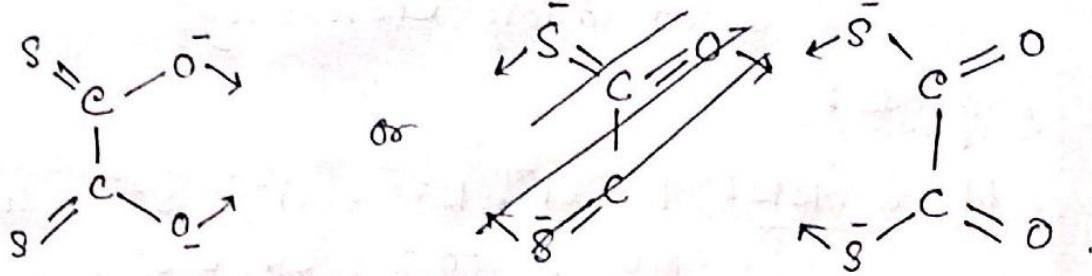
EDTA



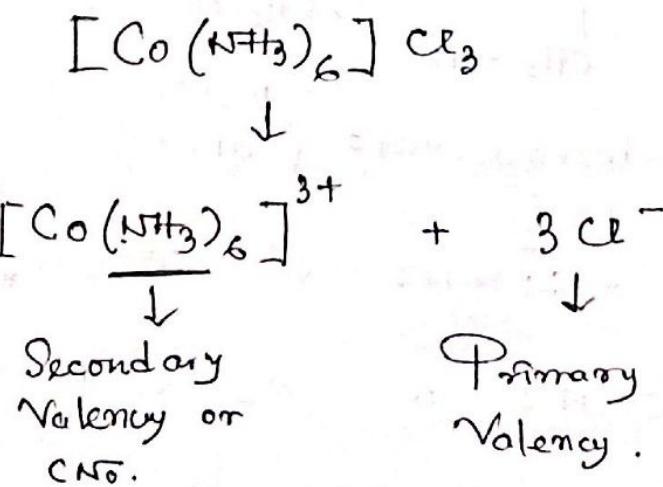
Ethylenediaminetetraacetato (edta<sup>4-</sup>).

5. Ambident:  $\leftarrow : \bar{C} \equiv N : \rightleftharpoons \text{ or } : \bar{C} \equiv N : \rightleftharpoons \rightarrow$





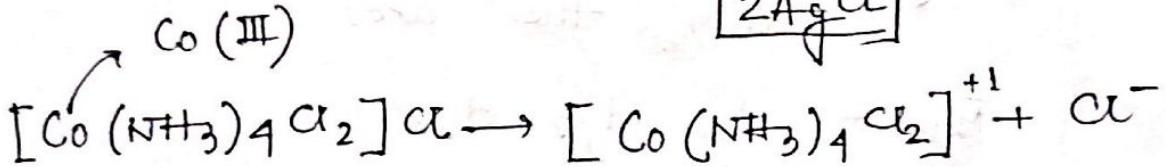
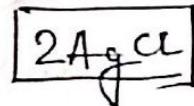
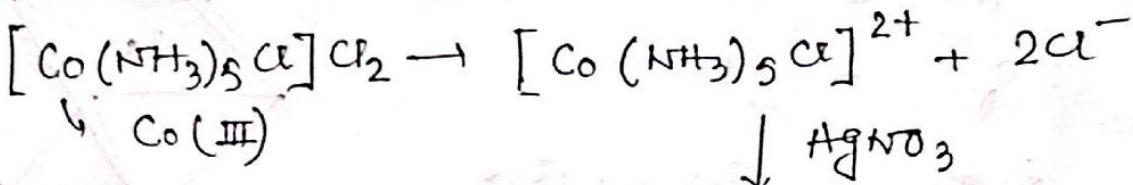
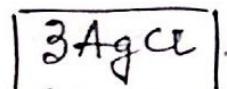
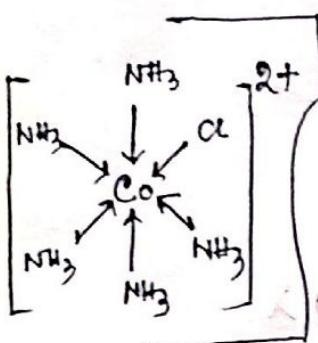
- \* A polydentate ligand has hexadentate character i.e. its all donor atoms may or may not form coordinate bonds with central metal atom.
- \* Mononuclear carbonyls are colourless & polynuclear carbonyls are deeply coloured.
- \*\* Some complexes like  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{MnO}_4^-$  etc. have  $d^0$  configuration of metal ion but have intense colour due to charge transfer spectra & not due to d-d transition.
- \* Primary valency is satisfied by ions of positive or negative charge. Secondary valency is satisfied by positive, negative, or neutral charged ligands.



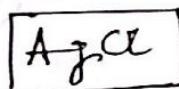
\* Werner's Experiment: With  $\text{CoCl}_3 \cdot 6\text{NH}_3$ ,  $\text{CoCl}_3 \cdot 5\text{NH}_3$ ,  $\text{CoCl}_3 \cdot 4\text{NH}_3$

$$[\text{Co}(\text{NH}_3)_6]^{+3} \text{Cl}_3 \rightarrow [\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$$

$\downarrow \text{Co(III)}$                                      $\downarrow \text{AgNO}_3$

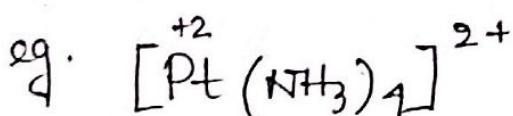


To satisfy Cobalt's secondary valency  $\text{Cl}$  enters the coordination sphere one by one.



\* EAN Rule:

EAN = (Atomic no. of metal) -  
(electrons lost in ion formation) +  
electrons gained from ligands.



$$\text{EAN}_{\text{Pt}} = 78 - 2 + 8 = 84.$$

## \* Crystal Field Scattering:

Breaking degeneracy of d orbitals:

Octahedral complex structure -

Metal atom at O.

the d-orbitals are  
of 2 types -

e<sub>g</sub> & t<sub>2g</sub> -  $d_{x^2-y^2}$ ,  $d_{z^2}$   
along the axes.

t<sub>2g</sub> -  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$

As the ligands approach electrons of metal ion 2 of ligands repel each other. This repulsion is more for  $d_{x^2-y^2}$  &  $d_{z^2}$  as they are along the axes. This breaks the degeneracy.

