

**Teacher:** Sutapa Chakrabarty

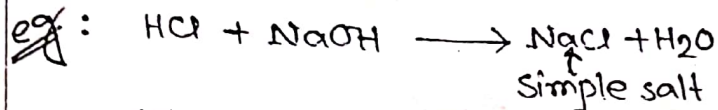
**Class :** Semester-4

**Paper:** C9T: Inorganic Chemistry

**Topic :** Coordination Chemistry

## " Simple salts :

When an acid reacts with an alkali, neutralisation takes place and a simple salt is produced.

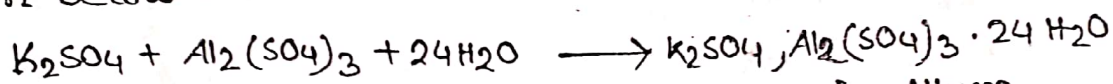


When dissolved in water these salt ionise and produce ions in sol<sup>n</sup>.

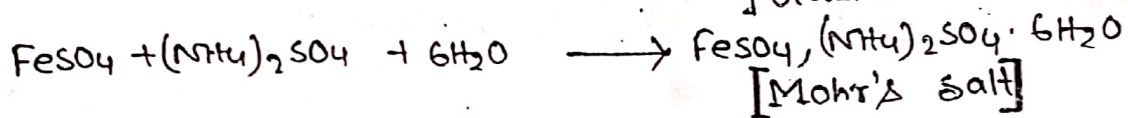
## " Molecular or Addition Compounds :

When sol<sup>n</sup> of two or more simple salts are mixed together in simple molecular proportion and the sol<sup>n</sup> thus obtained is allowed to evaporate, crystals of a new compound are obtained. These new compounds are called addition or molecular compounds.

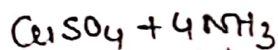
The formation of some addition compound has been shown below —



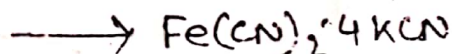
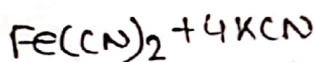
Potash Alum



[Mohr's salt]



Tetraamino copper sulphate



Potassium ferrocyanide.

## " Types of Addition Compounds :

Addition compounds are two types :

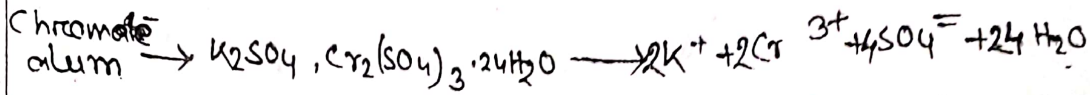
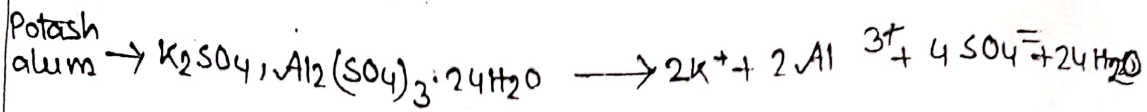
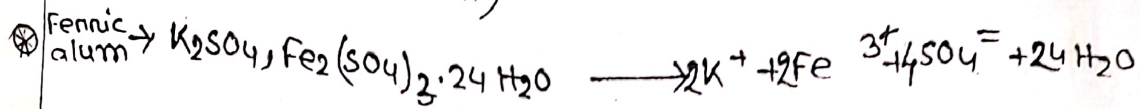
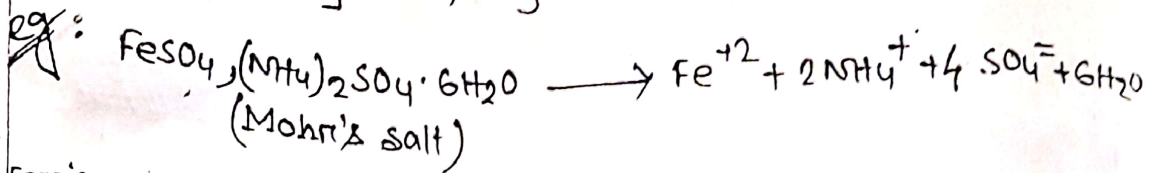
These are — i) Double salts

ii) Complex salts or co-ordination compounds.

### i) Double salt :

The molecular compound which is formed by crystallisation of a sol<sup>n</sup> containing the simple salts is called double salts. They exist only in crystalline state, when dissolved in water these dissociate into ions in the same way in which the

individual components of the double salts do.

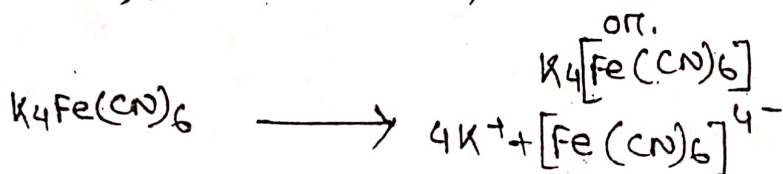
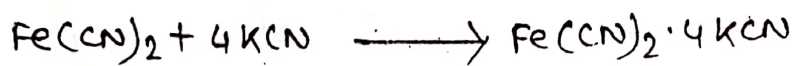


In aqueous sol<sup>n</sup> they give the test of all their constituent ions i.e. the individual components of a double salt do not lose their identity.

### ii) Complex salt or Co-ordination Compounds:

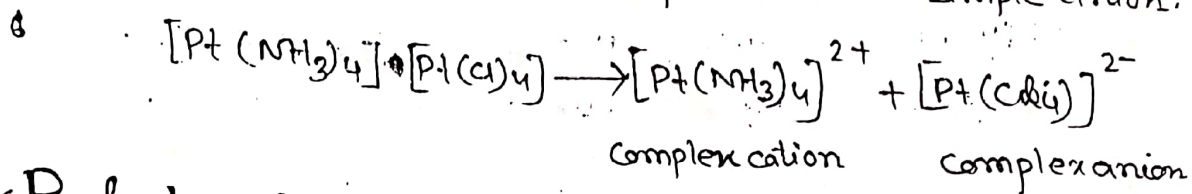
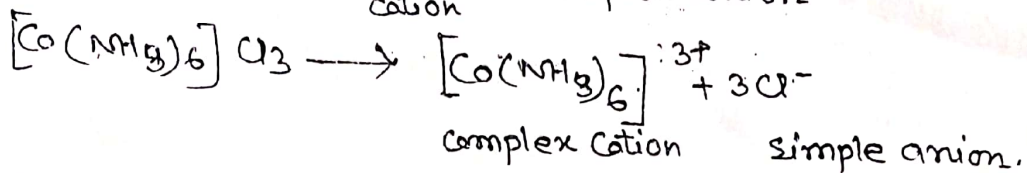
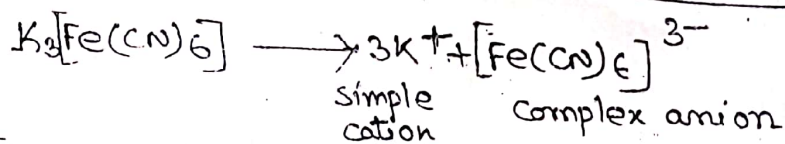
The molecular compound which is formed by a result of combination of two normal salts in definite molar ratio, dissociates in sol<sup>n</sup> not to give all the component ions but two component ions form a new ion, is called complex salt and the ion is called complex ion.

eg: When sol<sup>n</sup> of  $\text{Fe}(\text{CN})_2$  and  $\text{KCN}$  are mixed together and evaporated,  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is obtained which in aqueous sol<sup>n</sup> does not give the test for  $\text{Fe}^{+2}$  and  $\text{CN}^-$  ions but gives the test for  $\text{K}^+$  ion and  $[\text{Fe}(\text{CN})_6]^{4-}$  ions.



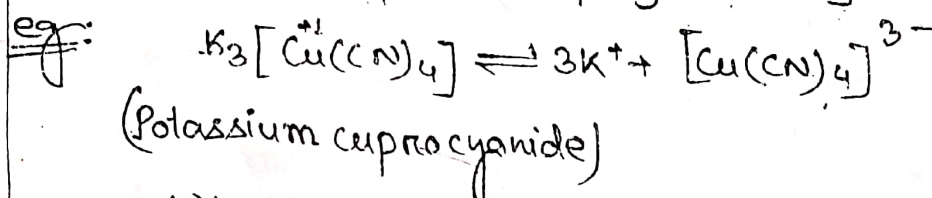
Thus we see that in  $\text{K}_4[\text{Fe}(\text{CN})_6]$  the individual components lose their identity.

A complex salt contains a simple cation and a complex anion or a simple anion and a complex cation or complex cation and complex anion as shown below —



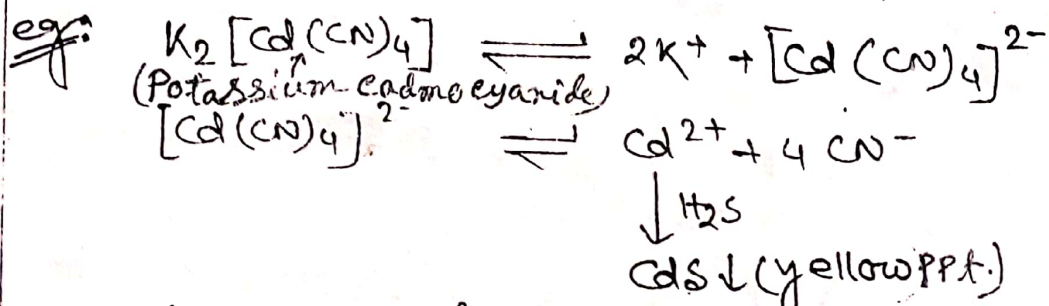
## Perfect and Imperfect Complex :

The complex compounds whose complex ions are highly stable and almost remain undissociated in sol<sup>n</sup> are called perfect complex compounds and the complex ions are called perfect complex ion.



When  $H_2S$  is passed into the sol<sup>n</sup> of  $K_3[Cu(CN)_4]$  no ppt of  ~~$Cu_2S$~~  is obtained. Hence free  $Cu^{2+}$  ions are absent in the sol<sup>n</sup> i.e.  $[Cu(CN)_4]^{3-}$  ion remains undissociated in sol<sup>n</sup>. Thus  $[Cu(CN)_4]^{3-}$  is an example of perfect complex ion.

The complex compounds whose complex ions are less stable and partially dissociated in sol<sup>n</sup> are called imperfect complex compounds and the complex ions are called imperfect complex ions.



Aqueous sol<sup>n</sup> of  $K_2[Cd(CN)_4]$  contains free  $Cd^{2+}$  ions because yellow pptn of  $CdS$  is obtained when  $H_2S$  gas is passed into these sol<sup>n</sup> but the

existence of complex ion  $[\text{Cd}(\text{CN})_4]^{2-}$  in the sol<sup>n</sup> has also been proved. Hence complex ion partially dissociated in sol<sup>n</sup>. Thus  $[\text{Cd}(\text{CN})_4]^{2-}$  ion is an example of imperfect complex ion.

### ● Difference among perfect complex salt, imperfect complex salt and double salt :-

The main diff. among perfect complex, imperfect complex and double salt depends on the extent of dissociation of the salt in sol<sup>n</sup>. In perfect complex salt, the complex ion remains completely undissociated. But, in imperfect complex salt, the complex ion partially dissociates while in double salt the constituent ions completely dissociate i.e. no existence of complex ion in sol<sup>n</sup>.

ex: In  $\text{K}_3[\text{Cu}(\text{CN})_4]$  the  $[\text{Cu}(\text{CN})_4]^{3-}$  ion is a perfect complex ion because it remains undissociated in the aqueous sol<sup>n</sup> of  $\text{K}_3[\text{Cu}(\text{CN})_4]$ .

But in  $\text{K}_2[\text{Cd}(\text{CN})_4]$ , the  $[\text{Cd}(\text{CN})_4]^{2-}$  ion is an imperfect complex ion. Because it partially dissociates in sol<sup>n</sup> i.e. an aqueous sol<sup>n</sup> of  $\text{K}_2[\text{Cd}(\text{CN})_4]$  contains free  $\text{K}^+$ ,  $\text{Cd}^{+2}$ ,  $\text{CN}^-$  and  $[\text{Cd}(\text{CN})_4]^{2-}$  ions.

Mohr's salt is a double salt because the constituent ions of the salt completely dissociate in aqueous sol<sup>n</sup> of  $\text{Fe}(\text{SO}_4)_2 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$  containing free  $\text{Fe}^{+2}$ ,  $\text{NH}_4^+$  and  $\text{SO}_4^-$  ions i.e. this sol<sup>n</sup> does not contain any complex ion.

### ● Ligands :

The neutral molecules or ions which are attached with the central metal ion of the complex compound are called ligands.

ex: In the complex ion  $[\text{Fe}(\text{CN})_6]^{3-}$  the 6-CN<sup>-</sup> ions

are the ligands. In most of complexes a ligand acts as a donor partner i.e. it donates e-pair to the central metal ion. In  $[Cu(NH_3)_4]^{2+}$  complex ion, the 4- $NH_3$  are the ligands.

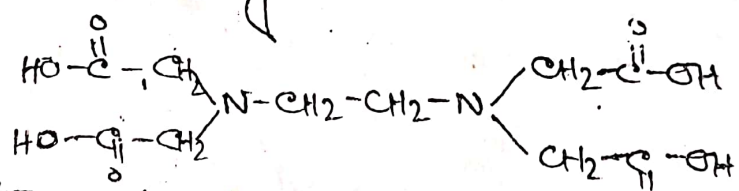
Co-ordination Number (CN):

It is the total no. of the atoms of the ligands that can co-ordinate to the central metal ions i.e. 'CN' represents the total no. of chemical bonds formed by the central metal ions and the donor atoms of the ligands. Thus in  $[Cu(NH_3)_4]^{2+}$  ion, the 'CN' of  $Cu^{2+}$  is 4 while in  $[Ni(en)_3]^{2+}$  ion the 'CN' of  $Ni^{2+}$  is 6, since each 'en' molecule has two donor atoms. Note that the no. of ligands in  $[Ni(en)_3]^{2+}$  is only 3.

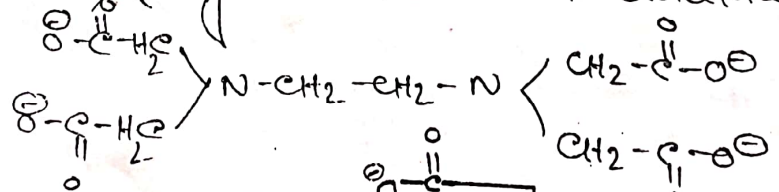
\* en  $\Rightarrow$  Ethylene diamine ( $H_2N-CH_2-CH_2-NH_2$ ).

In  $[Ca(EDTA)]^{2-}$  ion the 'CN' of  $Ca^{2+}$  is 6, since  $EDTA^{4-}$  ion has 6-donor atoms. But in this complex ion the no. of ligands is 1.

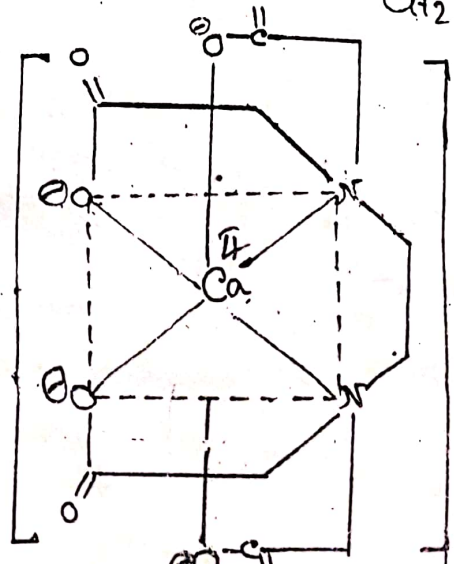
\*  $EDTAH_4 \Rightarrow$  Ethylenediamine tetraacetic acid,



$[EDTA]^{4-} \Rightarrow$  (Ethylenediamine tetraacetate anion)



$[Ca(EDTA)]^{2-}$  ion:



## Inner sphere or Co-ordination sphere and Outer sphere or Ionization sphere :-

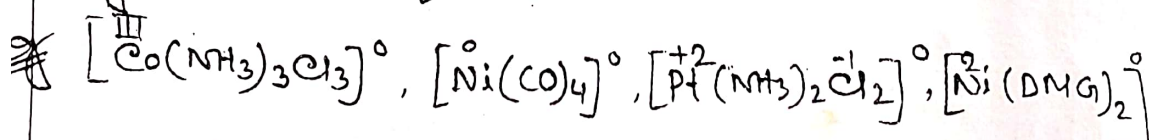
While writing the structural formula of a given complex compound the central metal atom and the ligand attached with it are always written with in square bracket  $[\ ]$ . This square bracket is called inner sphere or co-ordination sphere.

The portion outside the co-ordination sphere is called outer sphere or ionization sphere.

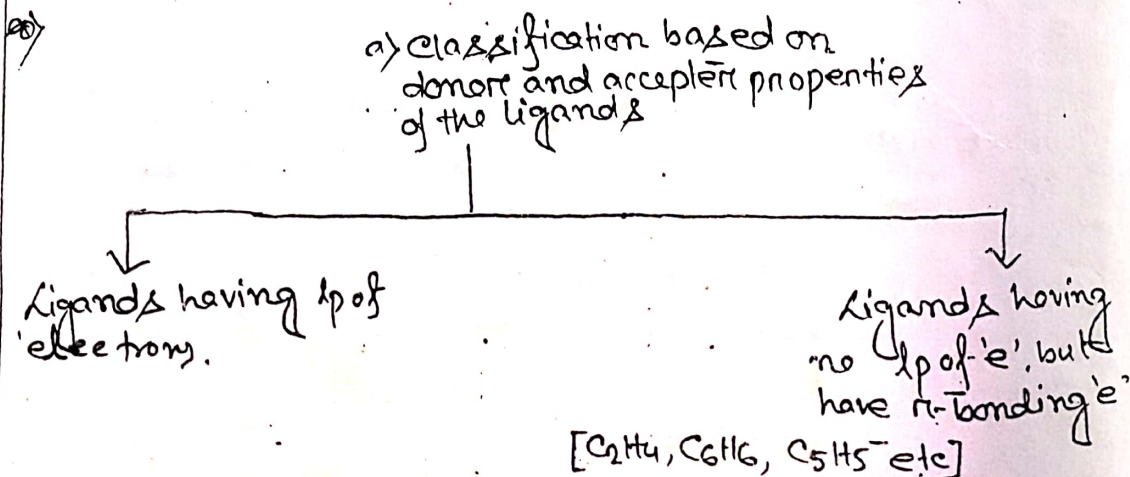
Thus in  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , the square bracket which contains the central metal ion  $\text{Co}^{+3}$  and the ligands 5- $\text{NH}_3$  molecules and one  $\text{Cl}^-$  ion is the inner sphere or co-ordination sphere and the portion that contains two  $\text{Cl}^-$  ions is called outer sphere or ionization sphere.

## Neutral Complex :

A complex which has no charge on it, is called neutral complex. It is a non electrolyte, does not undergo ionisation and hence does not give any ions in aqueous sol<sup>n</sup>.



## Classification of Ligands :



Ligand having sp. of 'e'

Ligands which contain vacant  $\pi$ -type orbitals  
[CO, NO,  $CN^-$  etc]

Ligand which do not have vacant  $\pi$ -type orbitals  
[ $H_2O$ ,  $NH_3$  etc]

Classification based on the no. of donor atoms present in the ligands.

Monodentate

Neutral ( $H_2O, NH_3$ )  
(-)ve ( $OH^-, CN^-$ )  
(+)ve ( $NO^+, NH_2^+, NH_3^+$ )

Bidentate... polydentate.  
(Bidentate  $\rightarrow en$ )

\* Bidentate : Ethylene diamine (en), oxalate ( $ox(C_2O_4^{2-})$ )  
Carbonate ( $CO_3^{2-}$ )

Tridentate : Dien (diethylene triamine)  
 $\ddot{N}H_2-CH_2-CH_2-\ddot{N}H-CH_2-CH_2-\ddot{N}H_2$

Hexadentate : EDTA<sup>4-</sup> [Ethylene diamine tetraacetate anion]

Some special Type of Ligands :

Bridging Ligands :

A monodentate ligand may have more than one free 'e' pairs and thus may simultaneously coordinate with two or more atoms, i.e. the ligand forms two sigma bonds with two metal atoms and thus acts as a bridge b/w the metal atoms. Such a ligand is called a bridging ligand. and the resulting complex is known as bridged complex.

eg:  $Cl^-, NH_2^-, OH^-, O^-, CO, SO_4^{2-}$  etc.



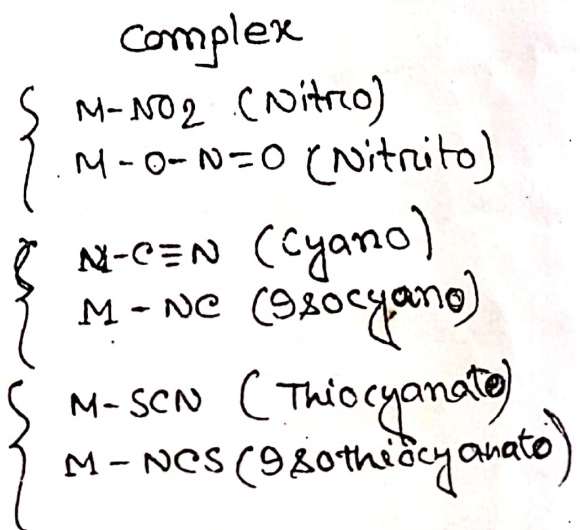
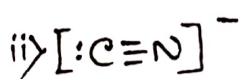
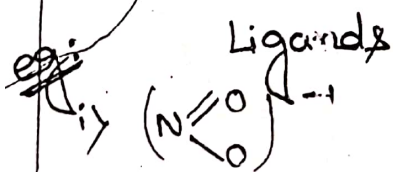
## ● Symmetrical and Unsymmetrical bidentate ligands

Bidentate ligands may be symmetrical or unsymmetrical. In symmetrical bidentate ligands the two coordinating atoms are the same, while in unsymmetrical bidentate ligands the two coordinating atoms are different. Thus symmetrical and unsymmetrical bidentate ligands are generally represented as (A-A) and (A-B) respectively, where 'A' and 'B' are <sup>the</sup> two donor atoms.

eg: Symmetrical  $\rightarrow$  en  $[NH_2-CH_2-CH_2-NH_2]$ , ox  $[C_2O_4^{2-}]$   
 Unsymmetrical  $\rightarrow$  Gly  $[CH_2 \begin{matrix} CO_2^- \\ NH_2 \end{matrix}]$

## ● Ambidentate ligands:

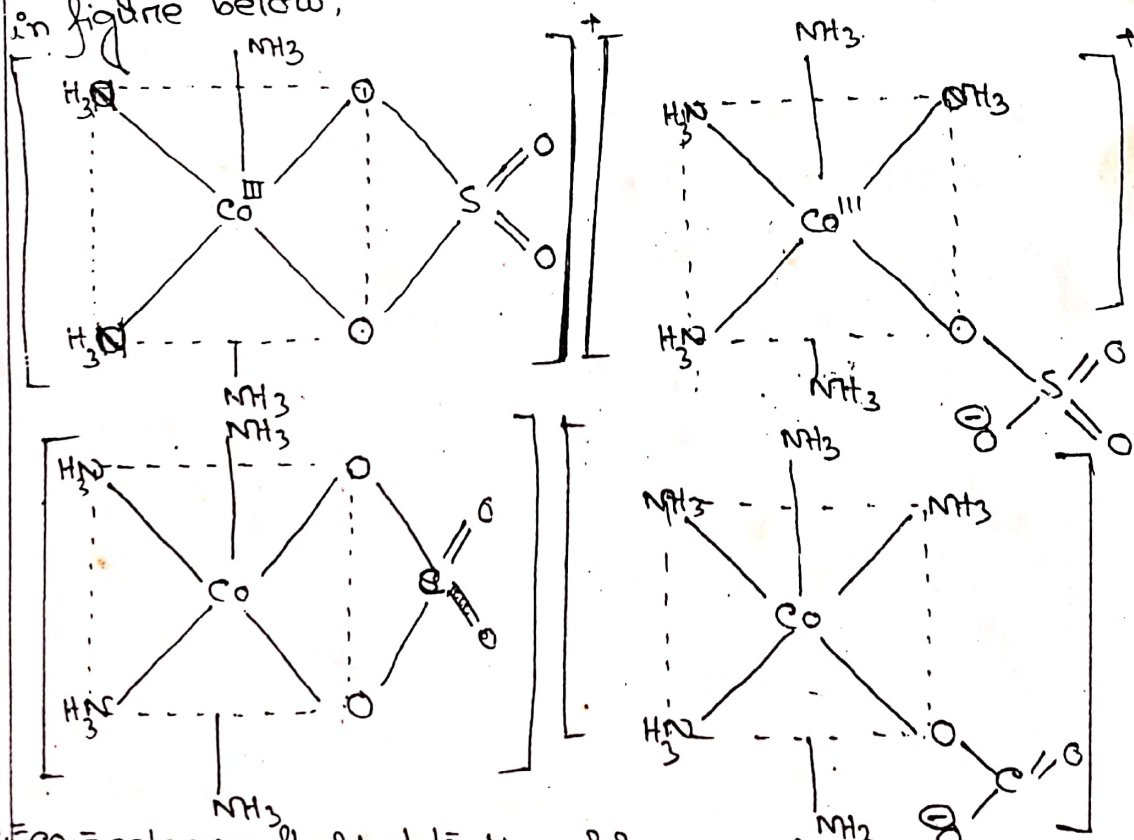
There are many ligands which have two or more different donor atoms in their structure. Such ligands can coordinate to the metal atom through any of their donor atoms and are given different names corresponding to the nature of donor atoms link to the metal atom. Such ligands are called ambidentate ligands.



## Flexidentale Ligands :

Some bidentate or polydentate ligands have flexidentale character i.e. a bidentate or polydentate ligand may not necessarily use all its donor atoms to get coordinated to the metal ion. Such type of ligands are called flexidentale ligands.

$SO_4^{2-}$ ,  $CO_3^{2-}$ ,  $N_2$ ,  $NH_2-NH_2$  etc have two donor atoms when these ligands get coordinated to the metal atom or ion they give rise to the formation of two types of complex compounds. In one type, they get link to the metal atom through one donor atom only while in the formation of another type of the complex compound they get coordinated to the metal atom through both of its donor atoms. These are shown in figure below,



$SO_4^{2-}$ ,  $CO_3^{2-}$  acts as a flexidentale ligand in above figure.

Ethylene diamine tetraacetate anion ( $EDTA^{4-}$ ) which usually acts as a hexadentate ligand functions as a pentadentate ligand in  $[Cr(OH)(HEDTA)]^-$  and as a tetradentate ligand in  $[Pd(H_2EDTA)]^0$ . Hence this polydentate ligand behaves as a flexidentale ligand.

## Werner's Co-ordination Theory :

To explain the observed properties of complex compounds, Werner proposed a theory known as Werner's Co-ordination theory. Different postulates of Werner's coordination theory are given below :

i) In complex compound the central metal atom exhibits two types of valency - a) Primary Valency  
b) Secondary Valency. The metal atom always tends to satisfy both of its valency.

### Primary Valency :

The primary valency of the metal atom in a complex compound is equal to the oxidation state of the metal. It is always satisfied by anions. The anion satisfying the primary valency are written outside the coordination sphere, while the anion which satisfy both the valencies are written inside the coordination sphere. The primary valency is ionizable. The attachment of the species satisfying the primary valency to the metal is shown by broken line. (-----)

### Secondary Valency :

The secondary valency of the metal atom in a complex compound is equal to coordination no. of that metal. It may be satisfied by anions, cations as well as neutral molecules. The species satisfying the secondary valency are called ligands. While writing the structure of a complex compound the species satisfying secondary valency and the metal are written inside the coordination sphere. It is also called non ionizable valency. Because the species satisfying the secondary valency are not ionizable. The attachment of the species satisfying the secondary valency with the metal ion is shown by solid line.

ii) Generally the central metal ion exhibits a constant coordination no.

eg:

Metal ions	CN
a) $\text{Co}^{+3}, \text{Cr}^{+3}, \text{Fe}^{+3}$ $\text{Pt}^{+4}, \text{Fe}^{+2}$	6
b) $\text{Pt}^{+2}, \text{Pd}^{+2}, \text{Cu}^{+2}$	4
c) $\text{Ag}^+, \text{Hg}^{2+}$	2

But some metal ions may exhibit different CN in some cases.

eg: The CN of  $\text{Ni}^{+2}$  is 6 in  $[\text{Ni}(\text{NH}_3)_6]^{+2}$  and 4 in  $[\text{Ni}(\text{Cl})_4]^{2-}$

iii) The ligands around the central metal ion have definite arrangement in space

Octahedral for CN = 6

Tetrahedral or square planar for CN = 4

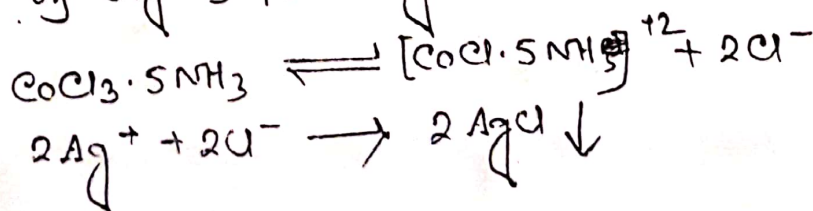
Linear for CN = 2

iv) The attachment b/w the metal and the species which satisfy both the valencies is shown by a combined solid-broken line. (— — — —)

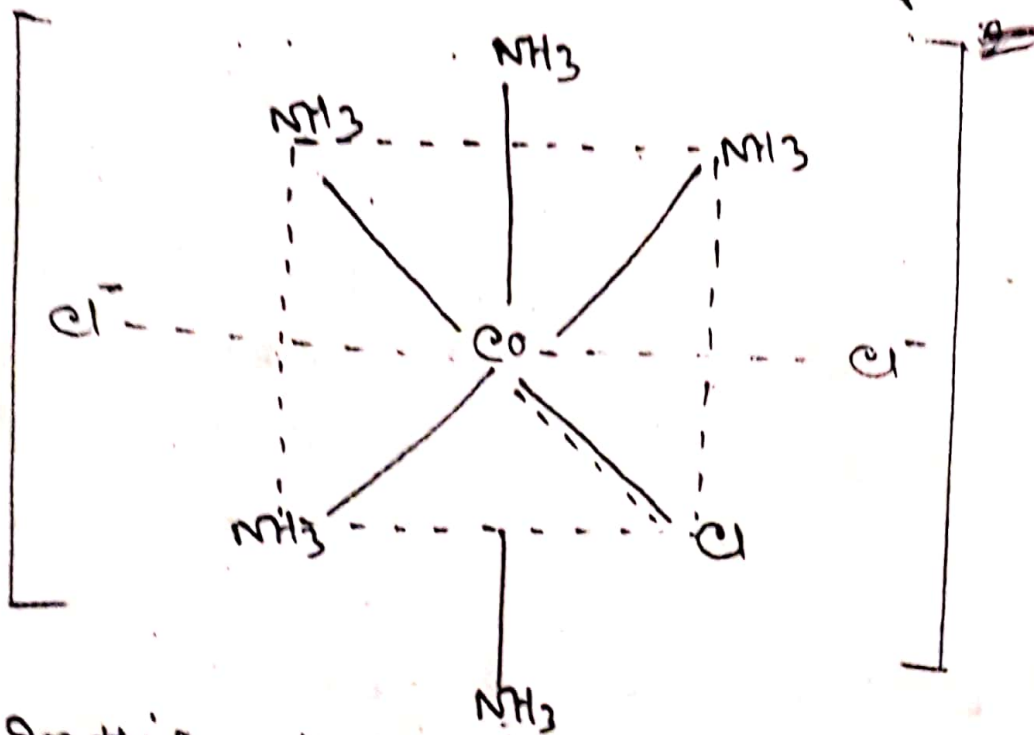
Explanation :

In the complex compound  $\text{CoCl}_3 \cdot 5\text{NH}_3$ , the primary valency of Co-atom in this compound is 3 and is satisfied by 3  $\text{Cl}^-$  ions. The attachment of these ions with  $\text{Co}^{+3}$  ion is shown by broken lines.

The treatment of this amine with the aqueous sol<sup>n</sup> of  $\text{AgNO}_3$  ppt<sup>ly</sup> only two  $\text{Cl}^-$  ions as  $\text{AgCl}$ .



The precipitation of two  $\text{Cl}^-$  indicates that two  $\text{Cl}^-$  ions are outside of the co-ordination sphere and the remaining one  $\text{Cl}^-$  and 5  $\text{NH}_3$  are present inside the coordination sphere. Thus the structure of  $\text{CoCl}_2 \cdot 5\text{NH}_3$  can be written as  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ . This structure shows that the secondary valency of Co atom ( $\text{CN} = 6$ ) is satisfied by one  $\text{Cl}^-$  ion and 5  $\text{NH}_3$  molecules placed inside the coordination sphere. The attachment of one  $\text{Cl}^-$  ion and <sup>five</sup>  $\text{NH}_3$  with Co atom is shown by solid lines. The structure of the above compound is shown in figure below.



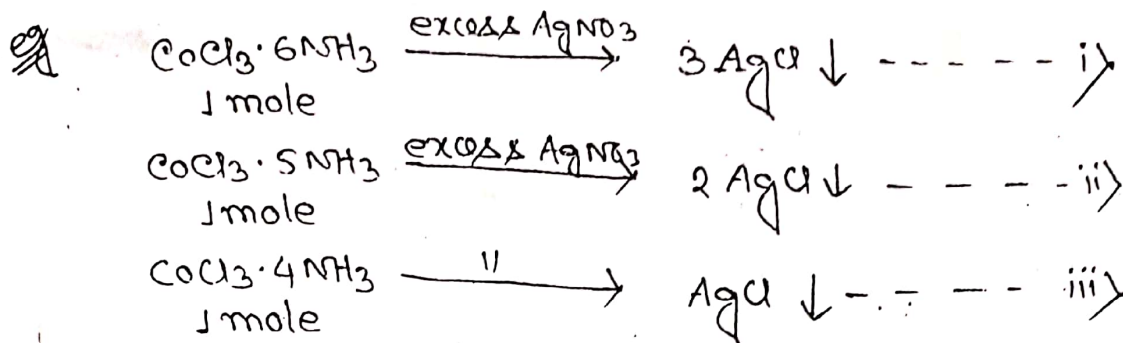
In this structure 1  $\text{Cl}^-$  ion is attached with Co atom by a combined solid-broken line, since this ion satisfied both primary as well as secondary valency of  $\text{Co}^{+3}$  ion.

## ● Experimental evidences in favour of Werner's Theory

4- Amine complexes of  $\text{Co(III)}$  chloride has been discovered by Werner and named according to their colour:

<u>Complex</u>	<u>Colour</u>	<u>Early name</u>
$\text{CoCl}_3 \cdot 6\text{NH}_3$	yellow	Lutescobaltic chloride.
$\text{CoCl}_3 \cdot 5\text{NH}_3$	Purple	Purpureo " "
$\text{CoCl}_3 \cdot 4\text{NH}_3$	Green	Praseo " "
$\text{CoCl}_3 \cdot 4\text{NH}_3$	violet	violeo " "

The reactivities of the  $\text{Cl}^-$  ions in these above compounds differ considerably. Addition of excess  $\text{AgNO}_3$  sol<sup>n</sup> to one mole of each complex produced diff. amount of precipitated of  $\text{AgCl}$ .



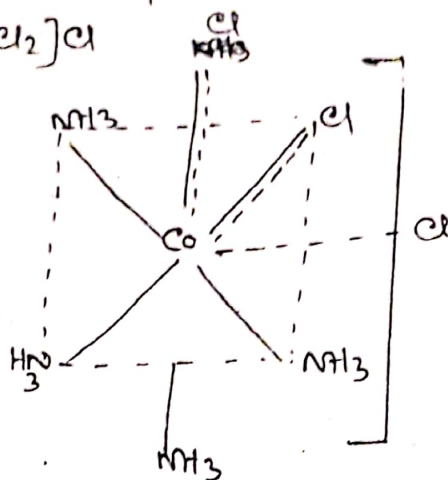
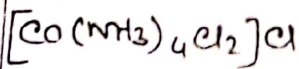
The react<sup>n</sup> iii) occurs for both the praseo and violeo complexes.

The correlation b/w the no. of  $\text{NH}_3$  molecules present and the no. of equivalent of  $\text{AgCl}$  pptd. led-Werner to the conclusion that in the series of complexes of  $\text{Co(III)}$  exhibits a constant coordination no. of 6. As  $\text{NH}_3$  molecules are removed they are replaced by  $\text{Cl}^-$  ions. These  $\text{Cl}^-$  ions are not free. They are covalently bound to the  $\text{Co}^{+3}$  ion. Werner thus formulated these 4 salts as  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ ,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  (Praseo and violeo).

Werner's studied the conductivities of these compound in sol<sup>n</sup>. Conductivities of the above complexes corresponds to those of 1:3, 1:2 and 1:1 electrolytes respectively, supporting above formulation of these complexes.

Werner characterized two isomers the praseo and violeo complexes corresponding to the formula  $\text{CoCl}_2 \cdot 4\text{NH}_3$ , in which CN of  $\text{Co}^{+3}$  is 6. Hence 3 possible struc<sup>r</sup> of these complexes are planar hexagon, Trigonal prism, and octahedral. These isomers expected from the former two arrangements while only two from the latter.

Only two isomers were isolated by Werner for the complex  $\text{CoCl}_3 \cdot 4\text{NH}_3$ . These facts led Werner to suggest octahedral arrangements of ligands around the metal ion in these complexes and also other complex of  $\text{CN}=\text{C}$



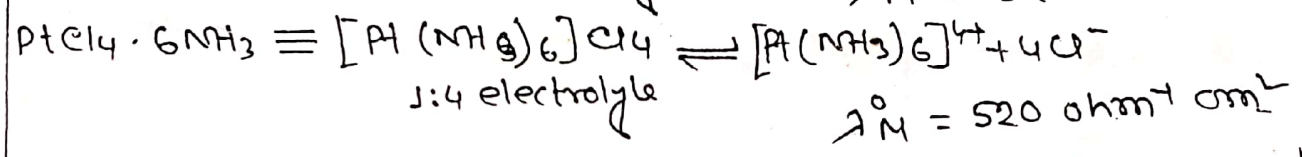
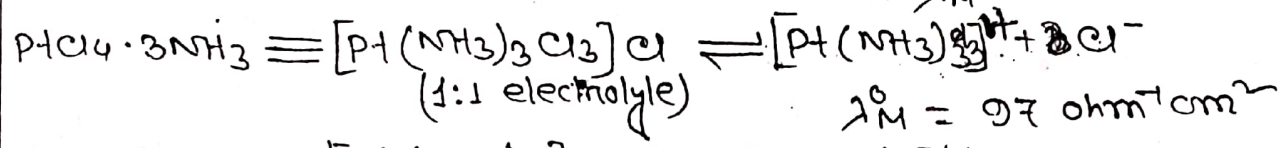
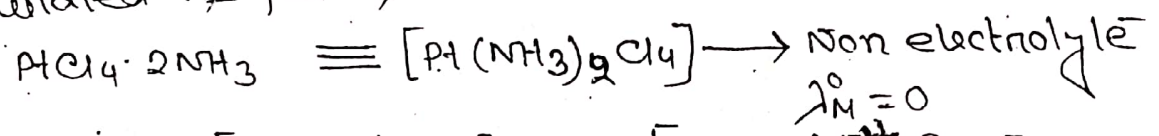
Q Molar conductance values of the complexes  
 $\text{PtCl}_4 \cdot 2\text{NH}_3$ ,  $\text{PtCl}_4 \cdot 3\text{NH}_3$  and  $\text{PtCl}_4 \cdot 6\text{NH}_3$  are  
0, 97 and 520  $\text{ohm}^{-1} \text{cm}^2$  respectively. Rationalize  
these data in the light of Werner's coordination  
theory.

Molar conductance data indicate that the 1st, 2nd and 3rd complexes behave as non-electrolyte uni-univalent (1:1) and uni-tetra valent (1:4) respectively.

According to Werner's theory the  $\text{Cl}^-$  ion may satisfy either separately or simultaneously both the primary and secondary valencies of the central metal ion. But the neutral  $\text{NH}_3$  can satisfy only the secondary valency. The CN of  $\text{Pt}^{+4}$  is 6 in all the three complexes. Hence in the 1st complex 4- $\text{Cl}^-$  ions and 2  $\text{NH}_3$  ligands will satisfy the CN of  $\text{Pt}^{+4}$ . The 4  $\text{Cl}^-$  ions will satisfy the primary valency. In the second complex 3- $\text{NH}_3$  mol and 3  $\text{Cl}^-$  ions will satisfy the secondary valency of  $\text{Pt}^{+4}$  ion while 4- $\text{Cl}^-$  ions satisfy the primary valency of  $\text{Pt}^{+4}$  ion. In the 3rd complex, 6- $\text{NH}_3$  mol satisfy the CN of  $\text{Pt}^{+4}$  ion and 4- $\text{Cl}^-$  ions satisfy the primary valency of  $\text{Pt}^{+4}$  ion.



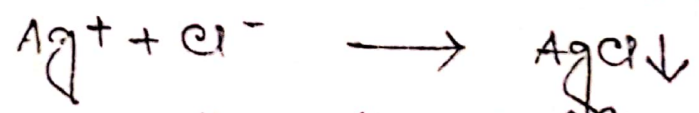
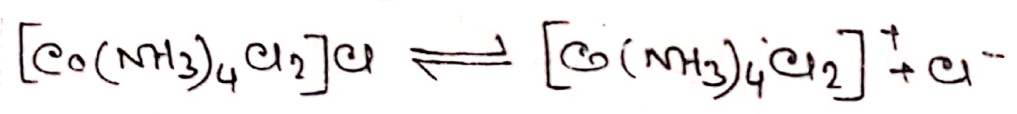
According to Werner's theory primary valency are ionisable and secondary valency are non-ionisable. The 2nd sphere of coordination (outer sphere) consists of only ions which are held by electrostatic force of attraction. Hence these are completely ionisable. Ligands with the inner sphere are held to the central metal cation by coordinate bond, hence are non ionisable. In the light of Werner's theory the complexes may be formulated as follows



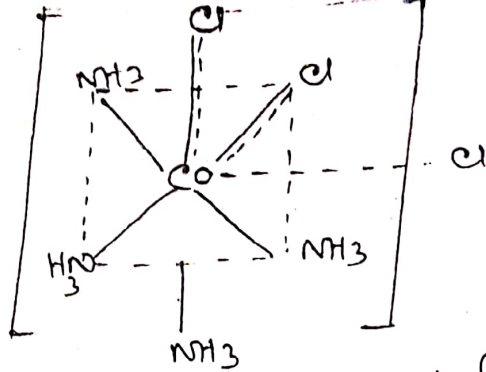
The molar conductance data are in good agreement with such formulation of the complexes in the light of Werner's coordination theory.

9. The compound  $CoCl_3 \cdot 4NH_3$  contains only 1- $Cl^-$  which is pptd immediately on the addition of  $Ag^+$ . Draw the str<sup>u</sup>r of the compound on the basis of W.C.T.

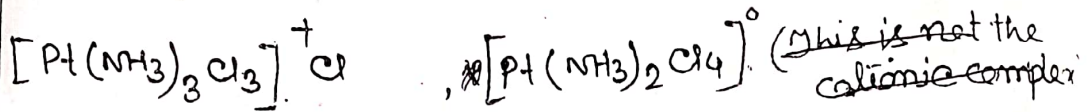
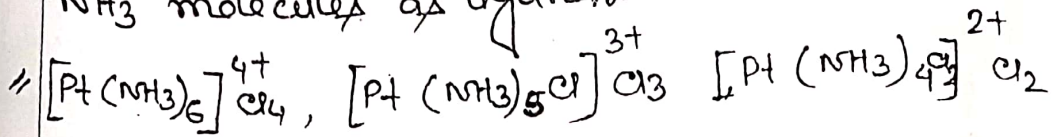
In  $CoCl_3 \cdot 4NH_3$ , the oxidation state of Co is +3. According to W.C.T the CN of  $Co^{+3}$  ion is 6. Only 1- $Cl^-$  ion is pptd on the addition of  $Ag^+$  ion indicates only 1- $Cl^-$  ion is in the outside of coordination spher<sup>e</sup> (outer). Hence the given compound can be formulated as  $[Co(NH_3)_4Cl_2]Cl$ .



Hence the str<sup>u</sup>r of given compound can be drawn as follows

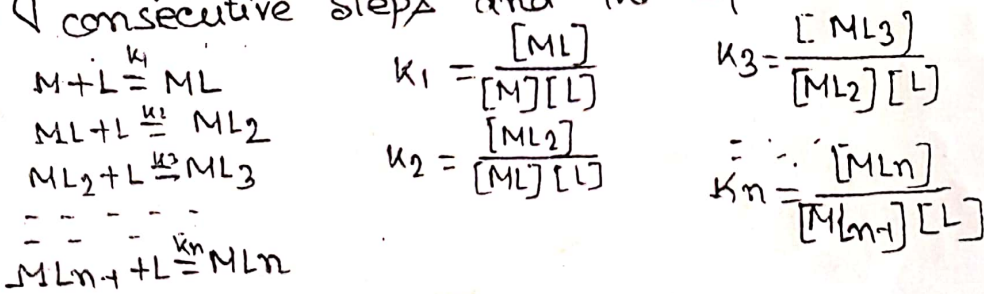


Write the structural formula of all the possible cationic complex of  $Pt^{+4}$  containing  $Cl^-$  ions and  $NH_3$  molecules as ligands.



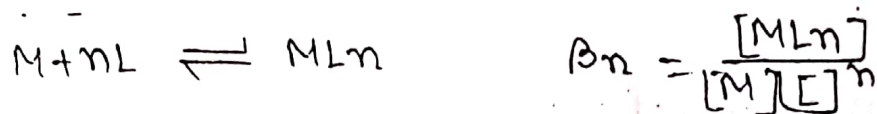
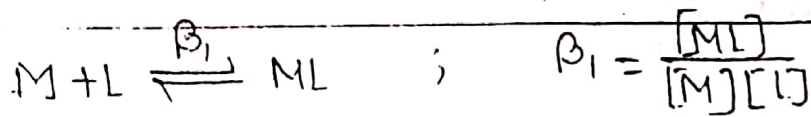
Stepwise formation constant and overall formation constant.

The formation of a complex in sol<sup>n</sup> proceeds by the stepwise addition of the ligands to the metal ion. Thus the formation of the complex  $ML_n$  ( $M$  = central metal ion,  $L$  = monodentate ligand,  $n$  = maximum coordination number for the ligand  $L$ ) may be supposed to take place by the following consecutive steps and the equm constants



The equm constants  $k_1, k_2, k_3, \dots, k_n$  are called stepwise formation constant or stepwise stability constant.

The formation of the complex  $ML_n$  may also be expressed by the following steps and equm constant.



The equm. constants  $\beta_1, \beta_2, \beta_3, \dots, \beta_n$  are called overall formation const. or overall stability const.

● Relation b/w  $\beta_n$  and  $k_1, k_2, \dots, k_n$

Stepwise formation constants ( $k_1, k_2, k_3, \dots, k_n$ ) and overall formation const. ( $\beta_1, \beta_2, \dots, \beta_n$ ) are related to one another.

eg: consider expression for  $\beta_3$

$$\beta_3 = \frac{[ML_3]}{[M][L]^3}$$

We know  $k_1 = \frac{[ML]}{[M][L]} \quad k_2 = \frac{[ML_2]}{[ML][L]} \quad k_3 = \frac{[ML_3]}{[ML_2][L]}$

$$\begin{aligned} \text{Now } k_1 \cdot k_2 \cdot k_3 &= \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]} \\ &= \frac{[ML_3]}{[M][L]^3} = \beta_3 \end{aligned}$$

Hence  $\beta_3 = k_1 \cdot k_2 \cdot k_3$

Therefore we can write,  $\beta_n = k_1 \cdot k_2 \cdot k_3 \dots k_n$   
Hence it is evident that the overall stability const ( $\beta_n$ ) is equal to the product of the stepwise stability const. ( $k_1 \cdot k_2 \dots k_n$ )

● A bivalent metal ion forms octahedral complex with a neutral bidentate ligand. Write down the complex formation equilibria in aqueous sol<sup>n</sup>. Give expression for stepwise and overall stability const. and show the relation b/w them.