B.Sc. Semester – II
Subject: - CHE - 201: Coordination Compound
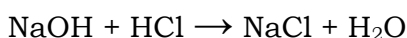## Prepared By: - Dr. Dipen Shah

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➢ Contents:

❖ Definition of some terms

➢ **Simple Salts:** When an acid reacts with an alkali it produce salt and water. This types of reactions are known as neutralization reaction for example

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

When such types of salts are dissolved in water it give ions in solution. The nature of salt (acid or basic or normal) depends on extent of neutralization. Mixed salts contain more than one acidic or basic radicals e.g. $NaKSO_4$.
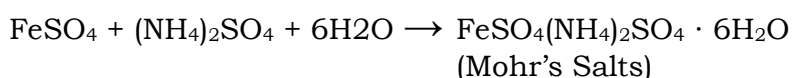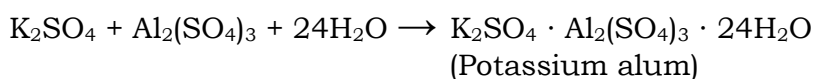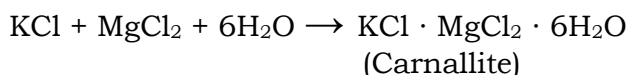
➢ **Molecular or Addition compounds:** When solution having two or more kinds of salts (simple molecule) in stoichiometric amounts and are evaporated then we will obtain crystal of new compound know as molecular or addition compounds.

There are of two types of compounds depending on their behavior in aqueous solution.

- **Double salts or Lattice compounds:** The addition compounds having the following characteristics are called double salts.

  They exist in crystalline state.

  When they dissolved in water it produced ions which are the same as the individual compounds of the double salts. For example

  $KCl + MgCl_2 + 6H_2O \longrightarrow KCl \cdot MgCl_2 \cdot 6H_2O$
  (Carnallite)

  $K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
  (Potassium alum)

  $FeSO_4 + (NH_4)_2SO_4 + 6H2O \longrightarrow FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$
  (Mohr's Salts)

  In aqueous solution double salt give the test of all their individual components (ions) and do not lose their identity.

- **Coordination (or complex) compounds:** It has been observed that when solution of $Fe(CN)_2$ and KCN are mixed together and evaporated, potassium ferrocyanide, $Fe(CN)_24KCN$ is obtained which in aqueous solution does not give test for the Fe^{+3} and CN^- ions, but gives test of K^+ ion and ferrocyanide $[Fe(CN)_6]^{-4}$ ion.

  $Fe(CN)_2 + 4KCN \longrightarrow Fe(CN)_24KCN \rightleftharpoons 4 K^+ + Fe(CN)_6^{-4}$
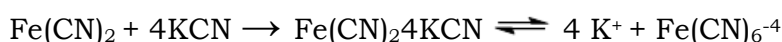
  Thus we see that in molecular compound like $Fe(CN)_24KCN$, the individual compounds lose their identity. Such molecular compounds are called coordination (or complex) compounds. The difference between a double salt and complex compound appears to be one of the degree rather than of a more fundamental unit.

A complex compound contains a simple cation and a complex anion or a complex cation and a simple anion or a complex cation and a complex anion, e.g. $K_2[Pt^{IV} Cl_6]$, $[Pt_{IV}(NH_3)Br_2]Br_2$ and $[Co^{IV} (NH_3)_6] [Cr^{III} (C_2O_4)_3]$ are all complex compounds. The term complex compound is used synonymously with the term coordination compound.

In the above complex compounds the ions $[Pt^{IV} Cl_6]^{2-}$, $[Pt^{IV} (NH_3)Br_2]^{2+}$ and $[Co^{IV} (NH_3)_6]^{3+}$ $[Cr^{III} (C_2O_4)_3]^{3-}$ are called complex ions. Thus a complex ion is an electrically charged radical which is formed by the union of a metal cation with one or more neutral molecules or anions.

➢ **Ligands:** The neutral molecules or ions (usually anions) which are attached with the central metal ion are called ligands, e.g. in the complex ion, $[Fe(CN)_6]^{3-}$ the six CN^- ions are the ligands. In most of complexes a ligand act a donor partner, i.e. it donates one (or more) electron pair (or pairs) to the central metal ion. Note that in metallic carbonyls the ligand viz CO molecule act both as donor and acceptor (M ⇌ CO).

The ligands are arranged round the metal ion inside the first sphere of attraction in preferred geometries. The common geometries are; linear, equilateral, triangular, tetrahedral square planar, trigonal bipyramidal, square pyramidal and octahedral.

➢ **Coordination Number (C.N.) or ligancy:** It is the total number of atom of the ligands that can coordinate to the central metal ion. Numerically coordination number represents the total number of the chemical bonds formed between the central metal ion and the donar atoms of the ligands. Thus in $[Fe^{III} (CN)_6]^{3-}$, C.N. of Fe^{3+} is six while in $[Ni^{II} (NH_2—CH_2—CH_2—H_2N)_3]^{2+}$ C.N. of Ni^{2+} is also six since ethylene diamine molecule $NH_2—CH_2—CH_2—H_2N$ has two donor nitrogen atoms. Note the number of ligands in $[Ni^{II} (NH_2—CH_2—CH_2—H_2N)_3]^{2+}$ is only three. Coordination number is usually considered to be a fixed number for a particular metal but now a large number of complexes is known in which the metal ion has more than one C.N.

➢ **Coordination sphere:** The central metal ion and the ligands that are directly attached to it are enclosed in a square bracket which Werner has called coordination sphere or first sphere of attraction. The anions being outside the square bracket form the second sphere of attraction.

❖ **Werner's work**

In 1893 the swiss chemist Werner proposed theory called Werner's theory of coordination compound to explain the bonding in coordination complexes. He was able to explain the nature of bonding of complexes. Important postulates of Werner' theory are:

1. Metals possess two types of valencies primary or ionizable valency and secondary or non-ionizable valency.
   (a) Primary valencies of the central metal ion are satisfied by negative ions. For examples in simple salts such as $CoCl_3$, $CuSO_4$ and $AgCl$, the primary valencies of Co, Cu and Ag are 3, 2 and 1 respectively. In complex compounds its attachment to metal ion is shown by dotted lines. In modern terminology it corresponds to oxidation state of metal atom or ion and is ionizable.
   (b) The secondary valencies are satisfied by either –ve ions or neutral molecules. Its attachment to metal is shown by thick lines and is non-ionizable. It corresponds to coordination number of metal ion or atom.
2. Every metal ion a tendency to satisfy both its primary and secondary valencies. In order to meet this requirement, a negative ion must satisfy both types of valenceis.
3. Every metal has fixed number of secondary valenceis.
4. Secondary valencies (or ligands satisfying the secondary valencies) are always detected towards fixed positions in space around the central metal ion.

The geometry of complex is determined by the number and arrangement of such ligands in space. For example, if a metal ion has secondary valency of four, the geometry of complex can be tetrahedral or square planar. On the other hand, if secondary valency is six, the complex is expected to be octahedral.

The primary valencies are non-directional and play no important role in determining the geometry of a complex compound. Thus on the basis of Werner's theory the complex $CoCl_3.6NH_3$ may be represented as shown in the figure.

Cobalt has three primary or ionizable valencies (shown by dotted lines) satisfied by chlorine. It has six secondary valencies (shown by dark lines)

$CoCl_3.6NH_3$
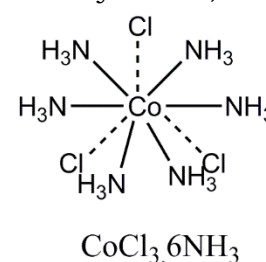
and are satisfied by ammonia molecules. In modern notation the complex ion is shown in square brackets with ionable ligands outside the coordinate sphere. The primary valencies are ionic bonds, whereas secondary velencies are coordinate bonds. Thus the complexes can be rewritten as shown in following table.

S. No.	Werner Formula	Modern Formula	Cation	Anion	Total no. of ions
1.	$CoCl_3.6NH_3$	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]^{3+}$	$3Cl^-$	4
2.	$CoCl_3.5NH_3$	$[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_5Cl]^{2+}$	$2Cl^-$	3
3.	$CoCl_3.4NH_3$	$[Co(NH_3)_4Cl_2]Cl$	$[Co(NH_3)_4Cl_2]^+$	Cl^-	2
4.	$CoCl_3.3NH_3$	$[Co(NH_3)_3Cl_3]$	Non-ionizable	---	---

➢ **Evidence of Werner's theory of coordination compounds**

The following evidence supports Werner's theory.

(i) Validity of Werner's Co(III)-Ammonia (structure 1 to 4) given in table is supported by chemical reactivity or by precipitation data i.e., by precipitating the number of chlorine as chloride ion by adding silver nitrate solution to freshly prepared solution of the complexes. The number of chloride ions precipitated are 3, 2, 1 and zero respectively providing primary or ionizable valencies of complexes as given by Werner.

(ii) Measurement of molar-conductivities of solutions of coordination compound also helps to estimate the number of ions in solution. For example a value of 500 ohm^{-1} or more indicates the presences of 4 ions, between 200-250 ohm^{-1} indicates 2 ions. It may also be noted that when the number of coordinate anions is same as the oxidation number of central cation, the coordination compound is a non-electrolyte.

The validity of formulating the Werner's compounds $CoCl_3.6NH_3$ and $CoCl_3.5NH_3$ as $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$ respectively is supported by conductance measurement. Experimentally the conductivities of $CoCl_3.6NH_3$ and $CoCl_3.5NH_3$ fall in the range expected for 4 and 3 ions respectively and hence Werner's compounds are represented as $[Co(NH_3)_6]Cl_3$ (4 ions) and $[Co(NH_3)_5Cl]Cl_2$ (3 ions).

➢ **Application of Werner's theory of Coordination compound**

(i) It is successful in explaining the formation and behaviors of coordination compounds which could not be explained on the basis of electronic theory of valency.

(ii) It could predict the geometry of different complexes with coordination number 4 (tetrahedral or square planer) and 6 (octahedral).

(iii) It could explain the existence of isomerism in coordination compounds. It could predict both geometrical and optical isomerism in coordination compound.

(iv) It could predict the other form of isomerism in coordination compounds. e.g. ionization or coordination or linkage isomerism etc. which are different from both geometrical and optical isomerism.

❖ **Type of ligand**

The following two ways have been used to classify the ligands:

1. **Classification base on donor and acceptor properties of the ligands**

I. Ligand having one (or more) lone pairs (or pairs) of electron

Such ligand are further classified as:

a. Ligands which contain vacant π-type orbitals that can receive back donated π-electrons from the metal ion in low oxidation state. Important examples of such ligands are CO, NO, CN, isocyanides, R—N=C, R₃P, R₃As, α, α-dipyridyl, o-phenanthroline and unsaturated organic molecules. All this ligands also have filled donor orbitals in addition to vacant π-type acceptor orbitals. Thus in the complexes formed by these ligands both metal and the ligand function both as donors and acceptors (M $\underset{\pi}{\overset{\sigma}{\rightleftarrows}}$ L).

b. Ligands which do not have vacant π-type orbitals. Such type of ligands have not vacant orbitals to receive back donated π-electrons from the metal e.g. H₂O, NH₃, F.

II. Ligands having no lone pairs of electrons but have π-bonding electrons, e.g. ethylene, benzene, cyclopentadenyl ion.

## 2. Classification based on the number of donor atoms present in the ligands.

The ligands of this class may be of the following types:

I. Monodentate or unidentate ligands: The ligands which have only one donor atom and hence can coordinate to the central metal ion at one site only are called monodentate or unidentate ligands.

The ligands may be neutral molecules, negatively charged ions (anions) or positively charged ions (cations), e.g.

   a. Neutral monodentate ligands: The names of neutral ligands are not systematic. Some examples are: H_2O (aquo), NH_3 (ammine), CO (carbonyl), CS (thiocarbonyl), NO (nitosyl), NS (thionitosyl).

   b. Negative monodentate ligands: If the name of anions end in –ide, -ite or –ate the endings of the names of the ligands used are –ido, -ito and –ato respectively. Some examples of negative ligands are: $CHCOO^-$ (acetato), F^- (fluoro), Cl^- (chloro), Br^- (bromo), I^- (iodo), CN^- (cyano), OCN^- (cyanato), SCN^- (thiocyanato, when S-atom of the ligand coordinates with the metal ion), NCS^- (isothiocyanato, when N-atom of the ligand coordinates with the metal ion), NO_2^- (nitro, when the ligand coordinates with the metal ion through N-atom), NO_2^- (nitrito, when the ligand coordinates with the metal ion through O-atom), OH^- (hydroxo or sometimes hydroxyl), H^- (hydrido) etc.

   c. Positive monodentate ligands: Examples of positively charged monodentate ligands are NO^+ (nitrosylium) and $NH_2NH_3^+$ (hydrazium). Quite obviously the names of these ligands have the suffix –ium.

II. Bidentate, tridentate.........polydentate ligands: The ligands having two, three, four, five or six donor atoms are called bi, tri or ter, tetra or quadri, penta, hexa or sexi dentate ligands respectively. The bidentate, tridentate etc. are called polydentate or multidentate ligands (literally dentate means toothed).

The polydentate ligands may further be subdivided according to the nature of their donor atoms. For example ethylene diamine, NH_2—$(CH_2)_2$—NH_2 is a bidentate ligand with two
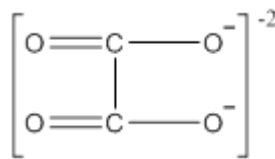
neutral donors viz. N-atoms, whereas oxalate ion is bidentate having two acidic (anionic) donors viz O^-, Glycinato ion, is $[H_2NCH_2COO^-]$ is again a bidentate with one neutral donor viz. N-atom and an acidic donor viz.O^-.

Bridging ligands: A complex with more than one central metal atom is called a polynuclear complex or bridge complex. i.e. a monodentate ligands may have more than one free electron pairs, may be simultaneously coordinate with two or more atoms. The ligand forms two σ-bonds with two metal atoms/ions and acts as a bridge between metal atoms. Such a ligand is a called a bridge ligand and a complex is known as bridge complex. e.g.
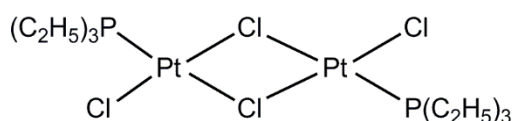

Examples of bridge ligand are: OH^-, F^-, Cl^-, NH_2, CO, O^{2-}, SO_4^{-2} etc.

Symmetrical and unsymmetrical bidentate ligands: Bidentate ligands may be symmetrical or unsymmetrical ligands. In symmetrical bidentate ligands the two coordinating atoms are the same, while in unsymmetrical bidentate ligands the two coordinating atoms (donor atoms) are different. Thus symmetrical and unsymmetrical bidentate ligands are generally represented as (AA) and (AB) respectively, where A and B are the two donor atoms.
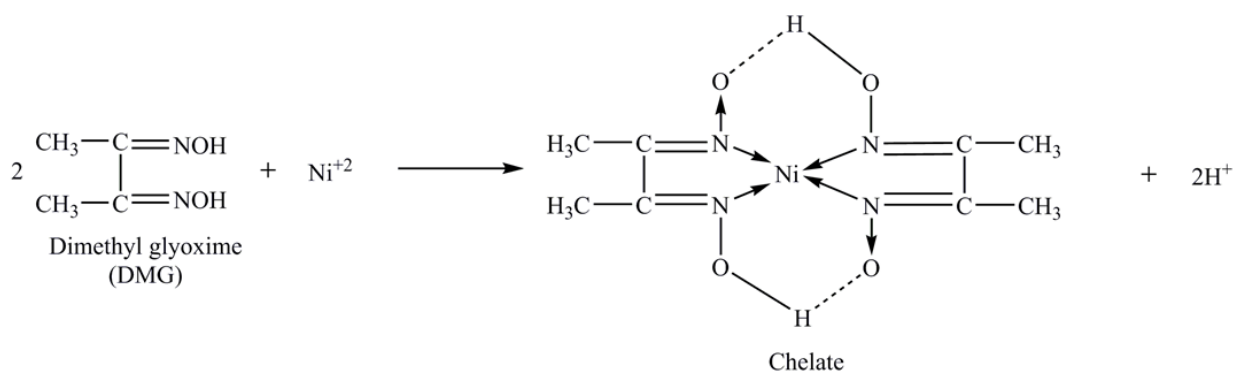
❖ Chelate Compounds

Chelates are the special types of co-ordination compounds containing one or more rings in their structure. The ring structure are formed linking metal ion with polydentate ligand. The ring structure compound one called chelates. The polydentate ligand are called chelating agents and the process of formation is called chelation.
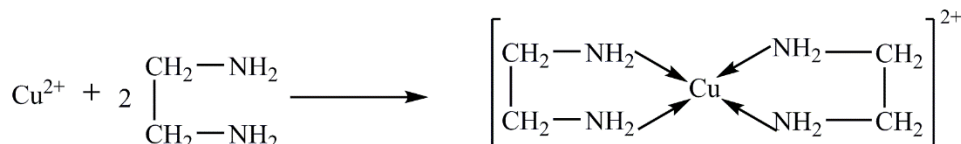
For example, Ethylenediamine a bidentate ligand forms a complex with Cu-ions.

This complex contains a pair of five membered ring and this is called a chelate.

Another familiar examples of chelation is nickel-DMG complex which is formed when nickel ion reacts with DMG in an ammoniacal medium.

Chelates have been classified as bidentate, tridentate, quardidentate and hexadentate depending upon whether the chelating agent is bidentate, tridentate, quardidentate or hexadentate respectively.

➢ **Application of chelate compounds.**

(i) In analytical chemistry: some ions quantitative identified by the formation of stable and colored chelates e.g. Al^{+3}, Ni^{+2}, Mg^{+2}, etc. Chelate agents are used for the titration of certain metal ions.

(ii) In water softening: Due to hardness of water (Ca^{+2} and Mg^{+2} ions), soap form sticky precipitation and wasted. But by complexing the metal ions, we can prevent, the precipitation of soap with Ca^{+2} and Mg^{+2} ions. So excess complexing agents such as polyphosphates and polydentate amino acids present in hard water can prevent the precipitation. Thus hard water is effectively softened.

Sequestration: The suppression of the precipitation reaction of Ca^{+2} and Mg^{+2} ions which are responsible for the hardness of water is known as sequestration.

(iii) In the elimination (to remove) of harmful radioactive metals from the body: EDTA (ethylene diamine tetraacetic acid) is the best chelating agent, therefore, it is used in the elimination of harmful radioactive metals from the body.

Vit.B_{12}, essential for human body is a cobalt complex. Hemoglobin in red blood cells contains certain porphyrin complex. Chlorophyll is green plant pigment containing a magnesium porphyrin complex.

(iv) In solvent Extraction: Some neutral chelate have low solubility in water but they have considerable solubility in organic solvents. Thus in presence of ligand that are capable to form inner complexes, many metals like Zr and Hf can be extracted into water-immiscible organic phase. e.g. Trifluoroacetyleacetone is very important organic solvent for extraction of Zr and Hf metals. Also cupferron used in refinement of number of metals.
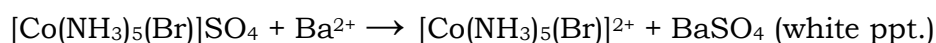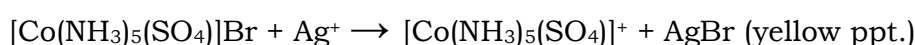
(v) In food preservation: Fruit, fruit juices, food stuffs etc. are preserved with the help of some chelating compounds.

❖ **Isomerization of coordination compounds**

Compound which have the same chemical formula but different structural arrangement are called isomers and the phenomenon is known as isomerism. Werner classified isomer into following classes.
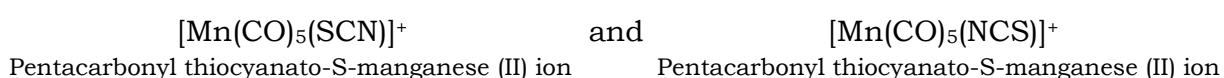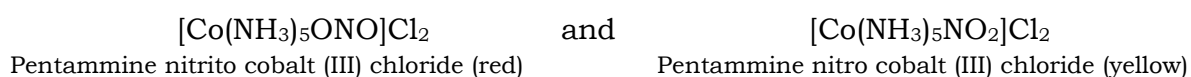
(A) Structural isomerism: This isomerism arises due to the different in the structures of complexes. It is following types.

(i) Ionization isomerism: Complexes which have the same empirical formula but give different ions in solution are called ionization isomers.
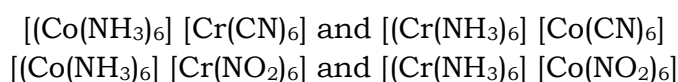
$[Co(NH_3)_5(SO_4)]Br + Ag^+ \rightarrow [Co(NH_3)_5(SO_4)]^+ + AgBr$ (yellow ppt.)

$[Co(NH_3)_5(Br)]SO_4 + Ba^{2+} \rightarrow [Co(NH_3)_5(Br)]^{2+} + BaSO_4$ (white ppt.)

Other examples are: $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

(ii) Linkage or salt isomerism: Linkage isomerism arises when the ligand may attach to the metal ion of a complex in different ways. Such ligands are called ambidentate ligands,

$[Co(NH_3)_5ONO]Cl_2$ and $[Co(NH_3)_5NO_2]Cl_2$
Pentammine nitrito cobalt (III) chloride (red)   Pentammine nitro cobalt (III) chloride (yellow)

$[Mn(CO)_5(SCN)]^+$ and $[Mn(CO)_5(NCS)]^+$
Pentacarbonyl thiocyanato-S-manganese (II) ion   Pentacarbonyl thiocyanato-S-manganese (II) ion
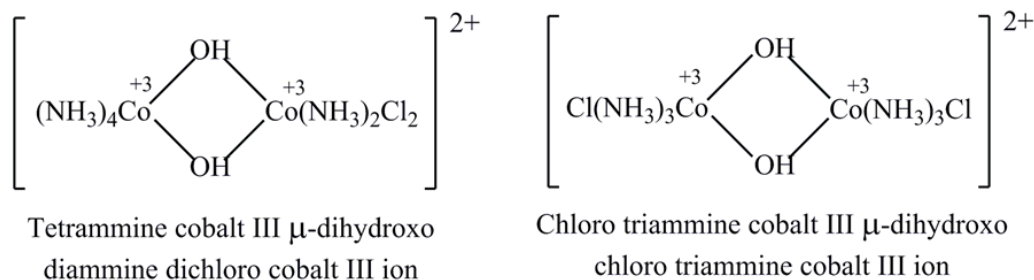
(iii) Coordination isomerism: When both positive and negative ions are complex, isomerism is possible due to interchange of ligands between the two complex ions. This type of isomerism is called coordination isomerism and is illustrated by the following examples:

$$[(Co(NH_3)_6] [Cr(CN)_6] \text{ and } [(Cr(NH_3)_6] [Co(CN)_6]$$
$$[(Co(NH_3)_6] [Cr(NO_2)_6] \text{ and } [(Cr(NH_3)_6] [Co(NO_2)_6]$$

In $[(Co(NH_3)_6] [Cr(CN)_6]$, $[(Co(NH_3)_6]^{+3}$ is a cation and $[Cr(CN)_6]^{-2}$ is an anion. Ligands interchange their positions to form $[(Cr(NH_3)_6] [Co(CN)_6]$. Cation is written first.

(iv) Coordination Position isomerism: It is shown by those complexes which contain bridging ligands and arises when the non-bridging ligands are differently placed round the metal ion.


Tetrammine cobalt III μ-dihydroxo diammine dichloro cobalt III ion

Chloro triammine cobalt III μ-dihydroxo chloro triammine cobalt III ion

(B) Stereoisomerism or Space isomerism: When two compounds contain the same ligands coordinated to the same metal ion, but the arrangement of ligand in space is different, the two compounds are said to be stereoisomers and the phenomenon known as stereoisomerism. It is of two types.

(i) **Geometrical or Cis-trans isomerism:** Geometrical isomers have identical empirical formula but differ in properties due to different arrangement of ligands. In cis-isomer (cis-same) two identical groups are adjacent to each other, while in trans isomer (trans-across) the two groups are opposite to each other. Geometrical isomerism is not found in complexes with coordination number 2 or 3 since all the positions occupied by the ligand are adjacent to each other. It most common in complexes having coordination number 4 and 6.

- Geometrical isomerism in 4-coordinated complexes: These complexes may have either tetrahedral or square planar complexes. Note that geometrical isomerism is not shown by tetrahedral complexes, since all the four ligands have adjacent (cis) position and all the four bond angles are the same (109.5°).
- Geometrical isomerism in square planar complexes: These may be of $[Ma_2b_2]$, $[Ma_2bc]$, $[Mabcd]$ and $[M(AB)_2]$ type in which M is the central metal atom a, b, c, d are monodentate ligands and AB is an unsymmetrical bidentate ligand. Square planar complexes of $[Ma_4]$, $[Ma_3b]$, $[Mab_3]$ type do not show geometrical isomerism since the spatial arrangement of four ligands round the metal atom is same.
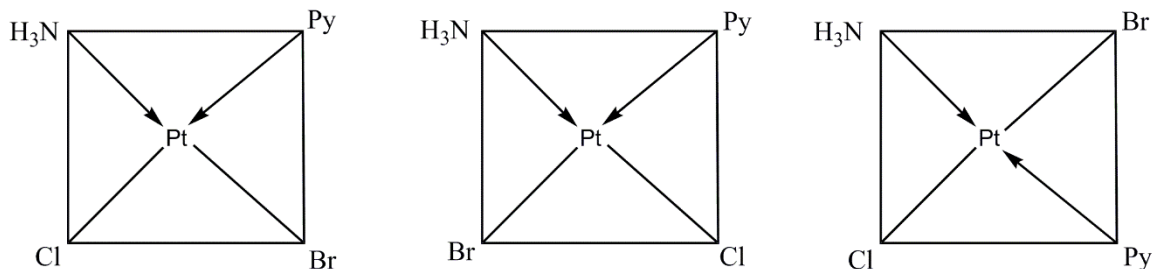
I. MA_2B_2 type example $[Pt(NH_3)_2Cl_2$

Cis
two Cl on the same side

Trans
two Cl on the opposite side
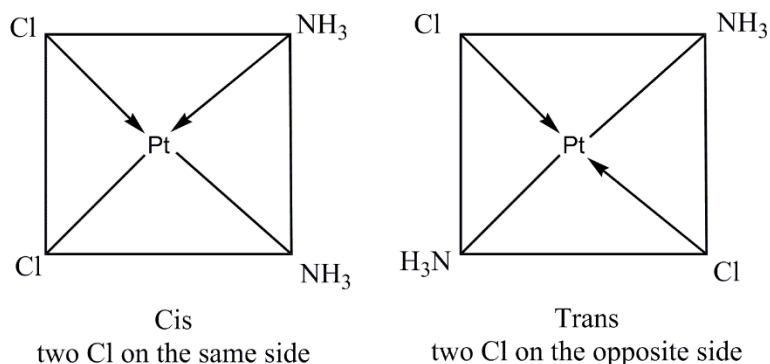
II. MA_2BC type examples $[Pt(NH_3)_2ClNO_2]$


Cis
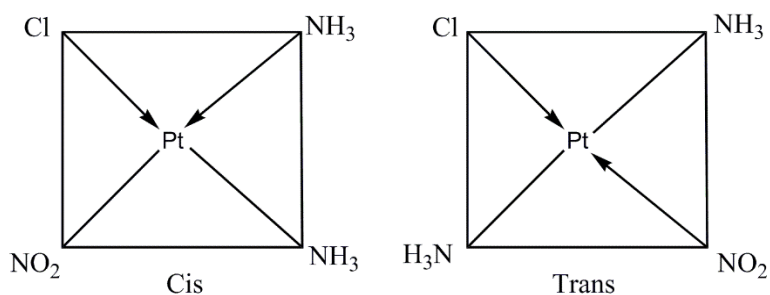
Trans

In cis from the two ammine groups are on the same side of Pt whereas in trans from the two ammine groups are on the opposite side of Pt.

III. Complexes of the type MABCD exhibits the isomers examples [Pt(py)(NH₃)BrCl]

These can be written by fixing any one ligand to one positions (say NH₃) and then placing other ligands trans to it. Three isomers of the complex [Pt(py)(NH₃)BrCl] have been actually isolated and identified.

IV. Geometrical isomers are also found in square planar complexes which have unsymmetrical bidentate ligands. Example the Pt(II)-glycinate complex in cis-and trans forms as shown below.

Cis   Trans
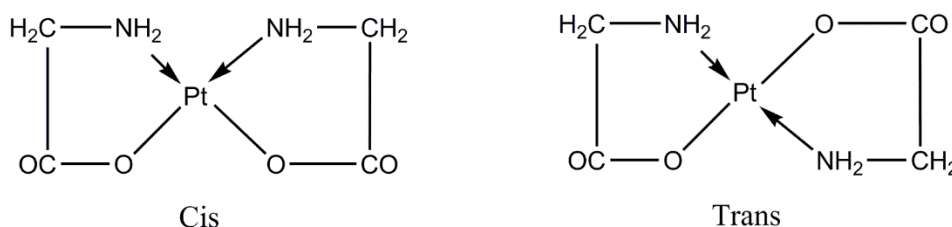
V. Geometrical isomers is also shown by bridged binuclear planar complexes of the type $M_2A_2X_4$, e.g. [PtCl₂PEt₃] where PEt₃ is triethylenephosphine.

Cis   Trans
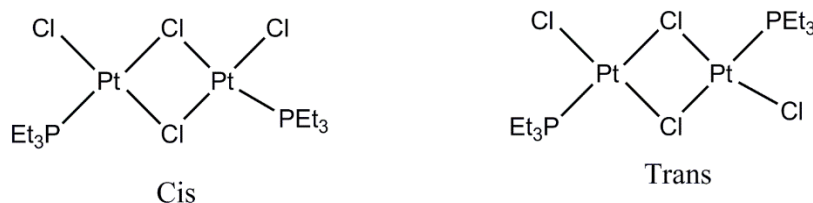
- Geometrical isomerism in Octahedral Complexes: Octahedral complexes [Ma₆], [Ma₅b], [M(AA)₃] type complexes do not show geometrical isomerism.

I. [MA₄B₂] type the cis and trans isomers in tetramminedinitro cobalt(III) ion [Co(NH₃)₄(NO₂)₂]⁺ are given below.

Cis   Trans
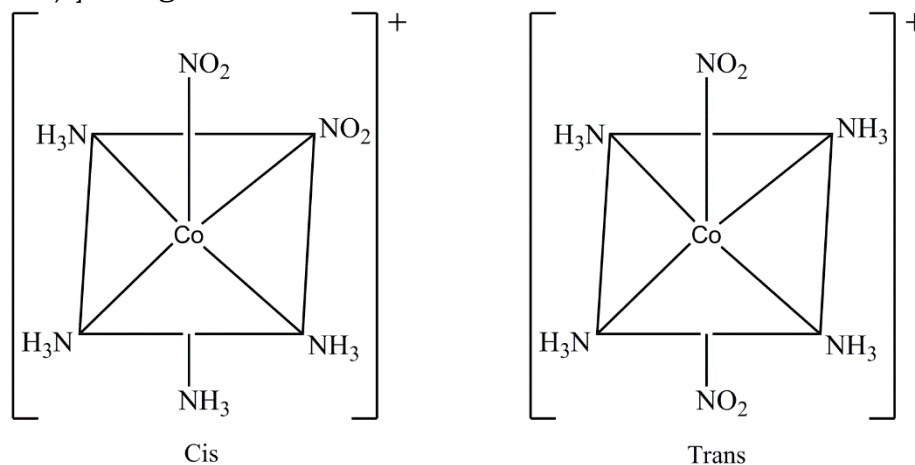
II. [MA₃B₃] type the cis and trans isomers in triamminetrichloro cobalt(III) ion [Co(NH₃)₃(Cl)₃]⁺ are given below.

Cis   Trans
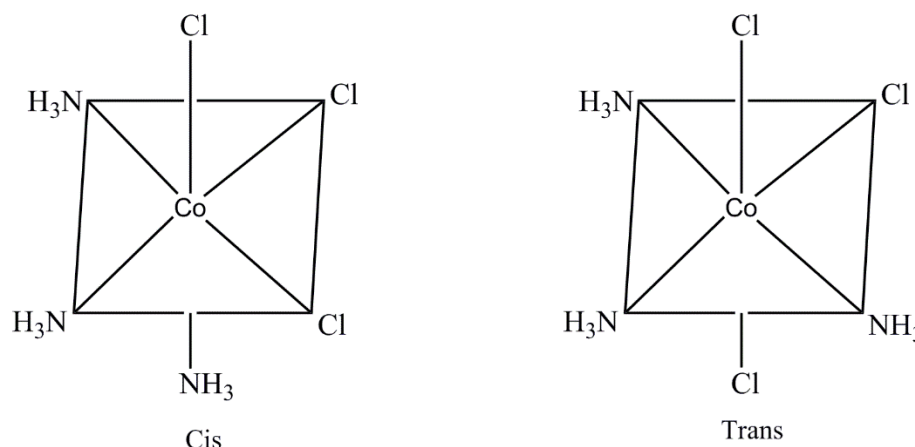
III. Complexes of the type [M(ABCDEF)] also exhibit geometrical isomerism. Theoretically fifteen different isomers are possible but in actual practice for a complex, [Pt(py)(NH$_3$)(NO$_2$)Cl Br I] only three isomers have been isolated.

IV. Unsymmetrical bidentate ligands in octahedral also exhibit geometrical isomerism (similar to square planar complexes). For example the chromium-triglycinato complex is found to exist in cis- and trans- forms.
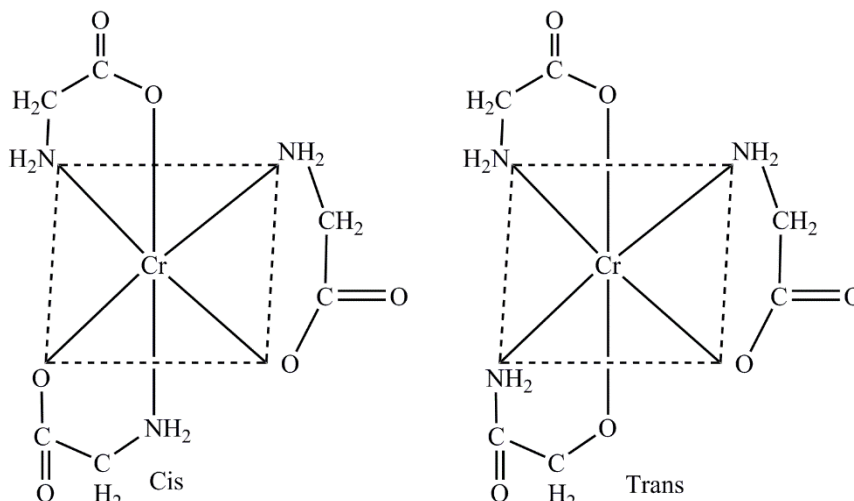
(ii) Optical or *d –l* or Mirror-image Isomerism: Here the compounds have the same properties but differ in their behavior toward polarized light. The two optically active forms are dextro or laevo (*d or l*). *d* rotates polarized light to the right and *l* to the left. To show optical activity, the molecule should be asymmetric (no plane of symmetry) and should not be superimposable on its mirror image. Optical isomers are also called optical antipods or enantiomorphs or enantiomers. Optically inactive isomer is known as meso, racemic, *dl* or (±) form. Optical inactive produced in *dl*-mixture is said to be due to external compensation.

Optical isomerism is common in octahedral complexes involving bidentate groups, e.g. [Co(en)$_2$Cl$_2$]$_+$.
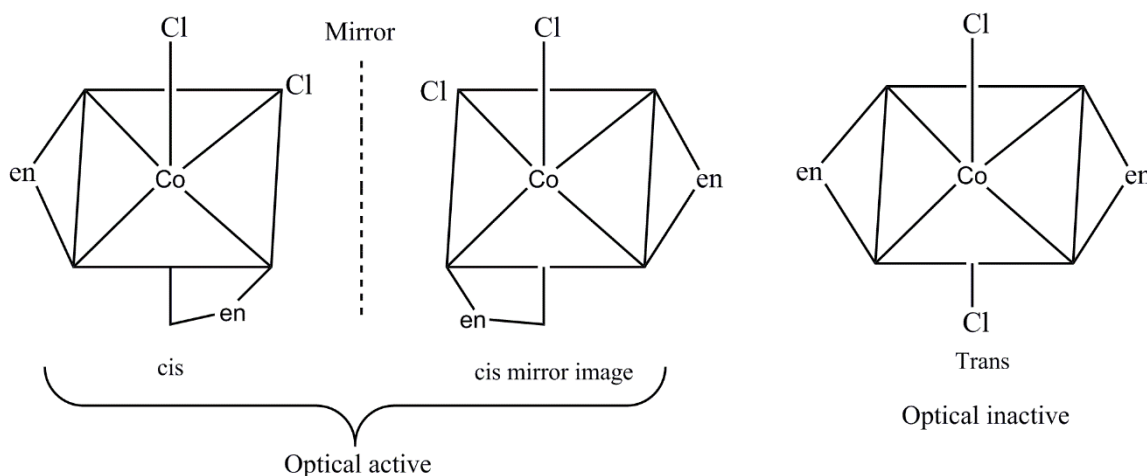
> **Stability of coordination compounds**

Definition of Stability

The term stability can be used in a number of different ways. The statement that complex is stable is rather loose, since several interpretations can be placed upon it. When the term stability is used without qualification, it means that the complex exists and under suitable condition it may be stored for long time. This term cannot be generalized for complexes, since complex may be quite stable to one reagent and may decompose readily in presence of another reagent. This term may also refer to the action of heat or light on compound.

In studying the formation of complexes in solution, two kinds of stability of complexes come in this are:

1. Thermodynamic stability: This is a measure of the extent to which the complex will form or will be transformed into another species (under certain condition), when the system has reached equilibrium. When we are concerned with this type of stability, we deal with metal-ligand bond energies, stability constants etc.

2. Kinetic stability: This refers to the speed with which transformations leading to the attainment of equilibrium will occur. When we are interested in kinetic stability, and this primarily for complex ions in solutions, we deal with rates and mechanisms of chemical reaction such as substitution, isomerization, racemization and electron or group transfer

reactions, as well as with the with the thermodynamic variables involved in the formation of intermediate species or activated complex. In the kinetic sense it is more proper to call the complexes inert or labile complexes rather than stable or unstable complexes. The complexes in which the ligands are rapidly replaced by others are called labile or non-inert complexes while those in which substitution occurs slowly are termed inert complexes.

-step wise and overall formation constants

According to J Bjerrum (1941) the formation of a complex in solution proceeds by the stepwise addition of the ligands to the metal ion. Thus the form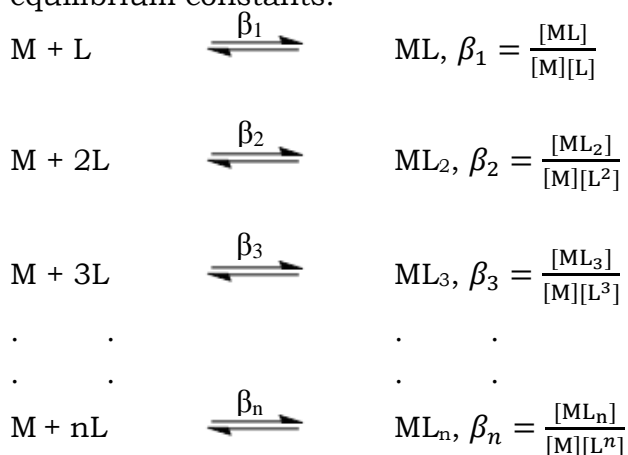ation of the complex ML_n (M = central metal cation, L = monodentate ligand and n = maximum coordination number of the metal ion M for the ligand L. n varies from one ligand to another for the same metal ion) may be supposed to take place by the following n consecutive steps and equilibrium constants.
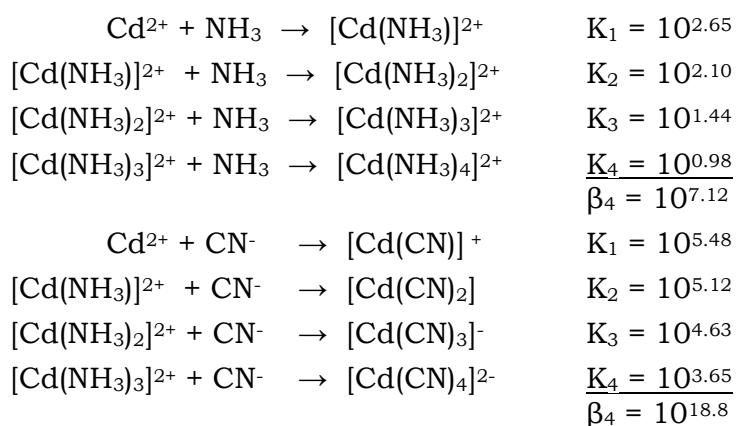
$$M + L \xrightarrow{K_1} ML, \quad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \xrightarrow{K_2} ML_2, \quad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \xrightarrow{K_3} ML_3, \quad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

. . . . .
. . . . .

$$ML_{n-1} + L \xrightarrow{K_n} ML_n, \quad K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$
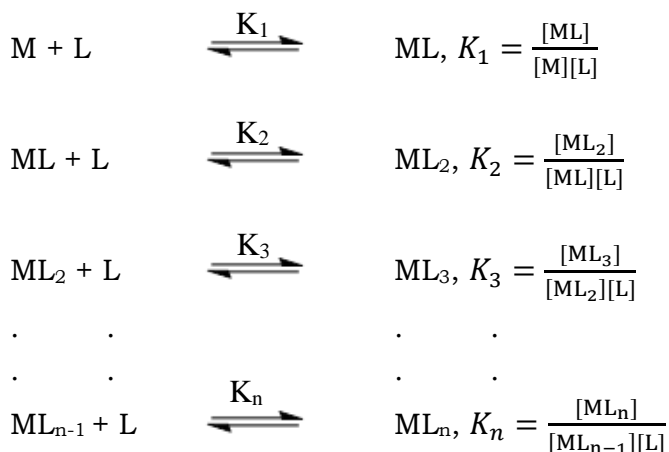
The equilibrium constant K_1, K_2, K_3.....K_n are called stepwise formation constants or stepwise stability constants.

The formation of complex ML_n may also be expressed by the following step and equilibrium constants:

$$M + L \xrightarrow{\beta_1} ML, \quad \beta_1 = \frac{[ML]}{[M][L]}$$

$$M + 2L \xrightarrow{\beta_2} ML_2, \quad \beta_2 = \frac{[ML_2]}{[M][L^2]}$$

$$M + 3L \xrightarrow{\beta_3} ML_3, \quad \beta_3 = \frac{[ML_3]}{[M][L^3]}$$

. . . . .
. . . . .

$$M + nL \xrightarrow{\beta_n} ML_n, \quad \beta_n = \frac{[ML_n]}{[M][L^n]}$$

The equilibrium constants β_1, β_2, β_3..... β_n are called overall (or cumulative) formation constants or overall (or cumulative) stability constants. β_n is termed as nth overall (or cumulative) formation constant or overall (or cumulative) stability constant.

With a few exceptions the values of successive constant decrease regularity from K_1 to K_n. i.e. $K_1 > K_2 > K_3 ...... > K_{n-1} > K_n$. This is illustrated by the data for the Cd^{II} –NH_3 system where the ligands are natural molecules and by Cd^{II} –CN^- system where the ligands are charged.

$Cd^{2+} + NH_3 \rightarrow [Cd(NH_3)]^{2+}$	$K_1 = 10^{2.65}$	
$[Cd(NH_3)]^{2+} + NH_3 \rightarrow [Cd(NH_3)_2]^{2+}$	$K_2 = 10^{2.10}$	
$[Cd(NH_3)_2]^{2+} + NH_3 \rightarrow [Cd(NH_3)_3]^{2+}$	$K_3 = 10^{1.44}$	
$[Cd(NH_3)_3]^{2+} + NH_3 \rightarrow [Cd(NH_3)_4]^{2+}$	$\underline{K_4 = 10^{0.98}}$	
	$\beta_4 = 10^{7.12}$	
$Cd^{2+} + CN^- \rightarrow [Cd(CN)]^+$	$K_1 = 10^{5.48}$	
$[Cd(NH_3)]^{2+} + CN^- \rightarrow [Cd(CN)_2]$	$K_2 = 10^{5.12}$	
$[Cd(NH_3)_2]^{2+} + CN^- \rightarrow [Cd(CN)_3]^-$	$K_3 = 10^{4.63}$	
$[Cd(NH_3)_3]^{2+} + CN^- \rightarrow [Cd(CN)_4]^{2-}$	$\underline{K_4 = 10^{3.65}}$	
	$\beta_4 = 10^{18.8}$	

The steady decrease in the values of K_1, K_2, K_3.....K_n with increasing number of ligands is due to the fact that as more and more ligands move into the coordination zone, less and less aqua molecules are available to fresh ligands for replacement. With progressive intake of ligands the metal ion becomes less electron greedy. In case of the complexes of the charged ligands are

more important factors responsible for the steady decrease are statistical, steric hindrance and coulombic factors.

The higher the value of stability constant for a complex ion, the grater will be its stability. Alternatively $1/K$ values sometimes called instability constant, give a measure of the extent to which the equilibrium representing the formation of a complex lies to the right. A high value of $1/\beta_n$ (or $1/\beta$) means a complex ion.

Stepwise and cumulative stability constant are also expressed as $\log_{10}K_1......\log_{10}K_n$ and $\log_{10}\beta_n$ respectively.

In all the above equilibria we have not specified the charge of metal ion and degree of solvation. The former omission is of no importance, since the equilibria may be expressed as above whatever the charges. Omission of water molecules is a matter of convention, since it is usually convenient and harmless. This omission should not be allowed whenever necessary. Square brackets indicate the concentrations of the enclosed species.

Relation between β_n and $K_1, K_2, K_3.....K_n$

K's and β's are related to one another. Consider, for examples, the expression for β_3 viz.

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

On multiplying both numerator and denominator by $[ML]$ $[ML_2]$ and on rearranging, we get

$$\beta_3 = \frac{[ML_3]}{[M][L^3]} \frac{[ML][ML_2]}{[ML][ML_2]}$$

$$= \frac{[ML]}{[M][L]} \frac{[ML_2]}{[ML][L]} \frac{[ML_3]}{[ML_2][L]}$$

$$= K_1 \times K_2 \times K_3$$

$$\beta_n = \frac{[ML]}{[M][L]} \frac{[ML_2]}{[ML][L]} ... ... \frac{[ML_n]}{[ML_{n-1}][L]}$$

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

$$\log\beta_n = \log K_1 + \log K_2 + \log K_3 ... ... \log K_n$$

$$\beta_n = \sum_{n=1}^{n=n} K_n$$

From above relation it is evident that the overall stability constant, β_n (or simply β), is equal to the product of the successive (stepwise) stability constant $K_1, K_2, K_3......K_{n-1}, K_n$. This in other words means that the value of stability constant for given complex is actually made up of a number of stepwise stability constants.
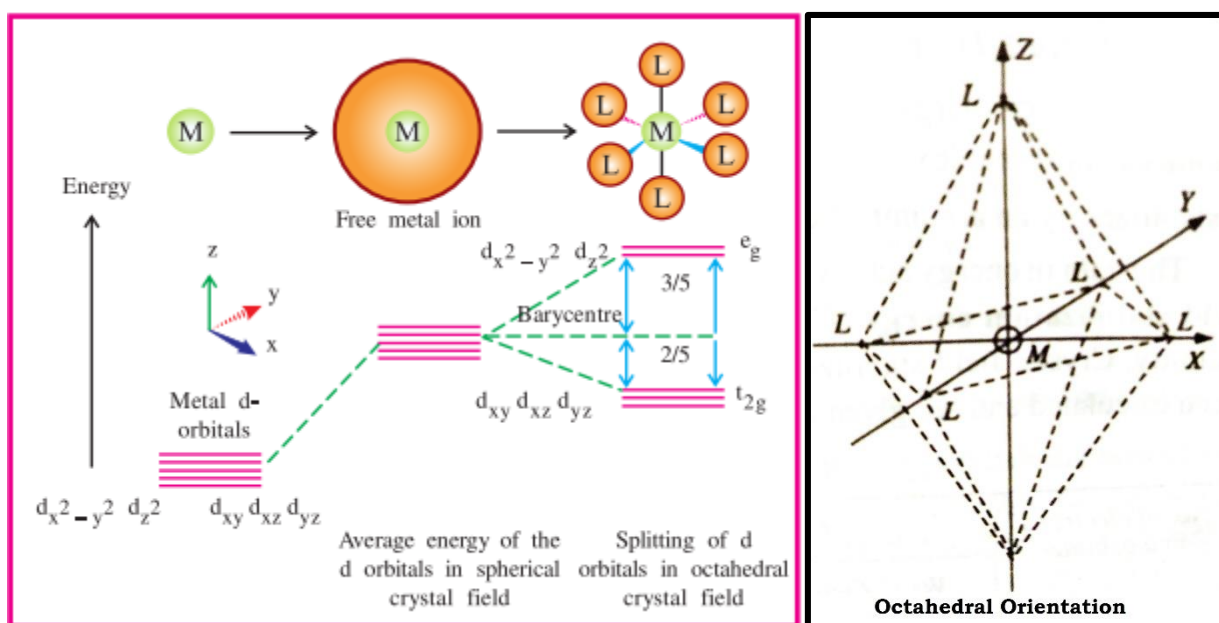
➢ Crystal Field Theory

Crystal Field Theory (CFT) is known as electrostatic model in which it is believed that there is ionic between metal and ligand. According to this theory, negatively charged ligand or polar neutral molecule forms ionic bond with metal ion. All the five types of d-orbitals are degenerate (same energy) in free gaseous from of metal or ion. In addition to this, if there is spherical negative charged field having spherical symmetry around the metal atom or ion. Even then d-orbitals remain degenerate but when ligands are arranged around the metal atom or ion then the d-orbital do not remain degenerate but gets split. The splitting of orbitals depends on the nature or crystal field. In the crystal field theory the following assumption are made.

1. The ligands are point charges which are either ions or neutral molecules with negative poles oriented towards metal cation.
2. The transition metal cation is surrounded by the ligand with lone pairs electrons.
3. The attraction between metal cation and ligand is purely ionic.
4. The valence electrons of metal will be repelled by negative field of ligands so these electrons occupy those d-orbitals which have their lobe away from direction of the ligands.
5. The effect of ligands is particularly marked on the d-electrons and it depends upon their (i) number (ii) arrangement around the cation (iii) nature of ligands. These three factors determine the crystal field.
6. It can also explain why certain geometric are more favored than others by certain metals in terms of crystal field stabilization energy.
7. The color of transition metal complexes can be explained in terms of electronic transition between the various d-orbitals of different energy.
8. The magnetic properties can be explained in terms of splitting of d-orbitals in different crystal field.

9. Different crystal fields will have different effect on the relative energies of the five d-orbitals.

(A) **Crystal field splitting in octahedral complexes:** In octahedral complex, there are six ligands around the metal atom or ion. Here there is repulsion between electrons of d-orbitals and electrons of ligand (or between negative ions), $d_{x^2-y^2}$ and d_{z^2} orbitals arranged on this axis experience more repulsion with ligand and will be raised in energy, while there is less repulsion between d_{xy}, d_{yz}, d_{xz} orbitals arranged between the axes, with ligand. Hence, their average energy of spherical crystal field decreases. As the degeneracy of these orbits is removed, it results into three orbitals having lower energy t_{2g} and higher energy possessing e_g orbitals. This type of phenomenon is called crystal field splitting. The splitting of energy of orbitals observed in octahedral complex is shown by Δ_0.thus, in e_g orbitals there will be increase by $\frac{3}{5}\Delta_0$ and there will be $\frac{2}{5}\Delta_0$ decrease in energy of three t_{2g} orbitals.

The splitting of crystal field (Δ_0) depends on electric charge of metal ion and ligand. Some ligands produce strong field, so that the splitting of orbitals is more in proportion. While certain ligands produce weak field so that the splitting of orbitals is less in proportion. Generally, the series of ligands on the basis of increase in strength of fields by ligands, can be shown as below:

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA < NH_3 < en < NO_2^- < CN- < CO$

The above series is called spectral series. If in the metal ion, there are 1, 2 or 3 electrons in d-orbitals, then their arrangement will be in t_{2g} orbitals having low energy, according to Hund's rule. But if there are 4 electron (d^4) in the d-orbitals then there are two possibilities as follows:
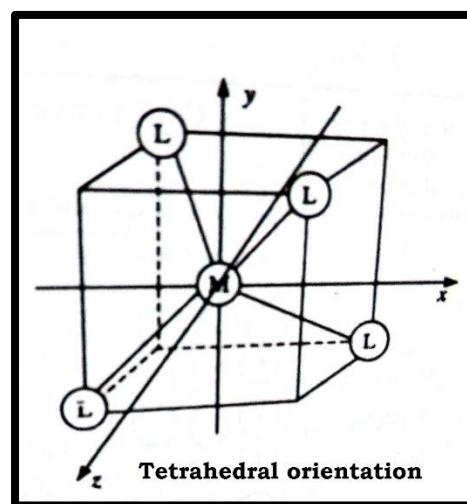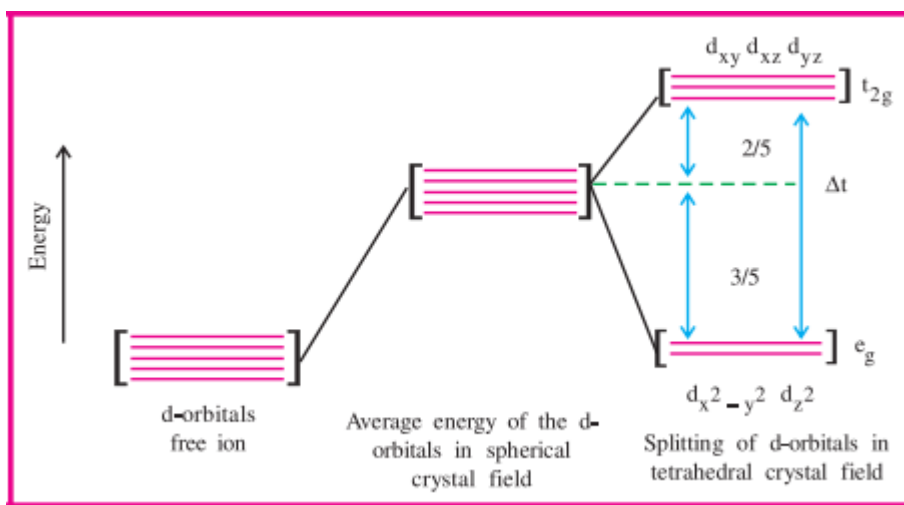
(i) The fourth electron will be arranged by pairing with any one electron in t_{2g} orbitals.
(ii) The fourth electron will be arranged in e_g orbitals neglecting giving energy for pairing.

Which of the have two possibilities can be possible depends on the splitting of crystal field (Δ_0) and on reactive magnitude energy of pairing; p.

(a) If $\Delta_0 < p$ then the fourth electron will be arranged in e_g orbitals so that electronic structure will be $t_{2g}^3 e_g^1$. For the ligands producing weak field $\Delta_0 < p$ and form complexes having higher spins.
(b) If $\Delta_0 > p$ then the fourth electron will be arranged in t2g orbital so that the electronic structure will be $t_{2g}^4 e_g^0$ for ligands producing strong field $\Delta_0 > p$ and for the having low spins.

Experimental findings that for complexes having d^4 to d^7 electronic configuration the ligands having stronger field give more stability than complexes having field.
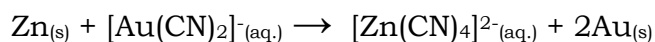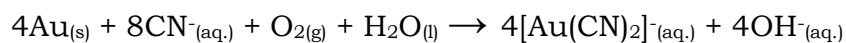
(B) **Crystal Field Splitting Tetrahedral Complexes:** In the formation of tetrahedral structure, the splitting of d-orbitals is in opposite nature to octahedral complexes. Like octahedral, if tetrahedral complex possesses equal distance between, metal, ligand, metal-ligand, then $\Delta_t = \frac{4}{9}\Delta_0$. Hence if the value of Δ_t is not sufficiently high, pairing of electrons does not occur. Hence low spin is observed in less proportions. The splitting of d-orbitals in tetrahedral structure is shown in following figure.

d-orbitals free ion | Average energy of the d-orbitals in spherical crystal field | Splitting of d-orbitals in tetrahedral crystal field

Tetrahedral orientation

> ## Application of coordination compounds:

The number and variety of applications of coordination chemistry are impressive ranging from analytical chemistry to biochemistry. The examples given here give us an idea of this diversity. Some important applications of coordination compounds are bellow.

1. In mineral world: Many minerals are coordination compounds.
2. In plant world: The process of conversion of carbon dioxide and water to starch and sugars (photosynthesis) in plants is carried out with the help of a magnesium complex (chlorophyll). The driving force that is needed to carry out this process of photosynthesis is provided by the solar energy.
3. In arts and sciences: Metal phthalocyanins (pigments) are the most useful coordination compounds used in various type of arts. The dyeing industry uses various types of dyes to get beautiful colors and patterns. All these dyes are metal lakes, the coordination complexes of certain metals. Alfred Werner demonstrated the relation of coordination with dyeing and he showed that several compounds which were capable of forming metal chelates compounds were able to dye cloth pretreated with ferric hydroxide. Many a cyano-complexes are used in metallurgical processes and electrodeposition process.
4. Extraction of metals: cyanide ions are used for the extraction of gold and silver. The crushed ore is heated with an aq. cyanide solution in the presence of air to dissolve the gold by forming the soluble complex ion $[Au(CN)_2]^-$.

   $4Au_{(s)} + 8CN^-_{(aq.)} + O_{2(g)} + H_2O_{(l)} \longrightarrow 4[Au(CN)_2]^-_{(aq.)} + 4OH^-_{(aq.)}$

   $Zn_{(s)} + [Au(CN)_2]^-_{(aq.)} \longrightarrow [Zn(CN)_4]^{2-}_{(aq.)} + 2Au_{(s)}$

   Complex formation is also useful for the purification of metals. Nickel is purified by converting the metal to the gaseous compound $Ni(CO)_4$ and then decomposing the latter to pure nickel.
5. Medicines: EDTA is a chelating agent which is used in the treatment of lead poisoning. Cis platin cis $[Pt(NH_3)_2Cl_2]$ is used in the treatment of cancer. Sodium nitroprusside, $Na_2[Fe(CN)_5NO]$ is used to lower blood pressure during surgery.
6. Qualitative Analyses: complex formation is useful for qualitative analyses.
   a. Separation of Ag^+, from Pb^{2+} and Hg^{2+} and

      $Ag^+ + 2NH_{3(aq.)} \longrightarrow [Ag(NH_3)_2]^+$ (Soluble)
   b. Separation of IIA and IIB groups: The cations of IIB group form soluble complex with yellow ammonium sulphide.
   c. Cu^{2+} ion forms complex on addition of ammonia $[Cu(NH_3)_4]^{2+}$.
   d. Cobalt (II) gives color with HCl due to the formation of complex $[CoCl_4]^{2-}$.
   e. Nickel forms a red complex $[Ni(DMG)_2]$ with dimethylglyoxime (H_2DMG).
   f. Detection of Fe^{3+} and Fe^{2+} by KCNS or $K_4[Fe(CN)_6]$ involves the formation of red colored complexion $[Fe(NCS)]^{2+}$ and K Fe$[Fe(CN)_6]$ blue precipitation respectively.
7. In artificial silk: Schweitzer's reagent i.e. tetrammine copper (II) hydroxide, $[Cu(NH_3)_4](OH)_2$ is used as a solvent for cellulose during the manufacture of artificial silk.
8. Biological applications: A number of metal complexes are of biological importance in particular:
   a. Hemoglobin in red blood cells contains an iron-porphyrin complex.
   b. Chlorophyll in green plants contains magnesium-porphyrin complex and
   c. Vitamin B_{12} is a cobalt complex.