Co - ordination Compounds
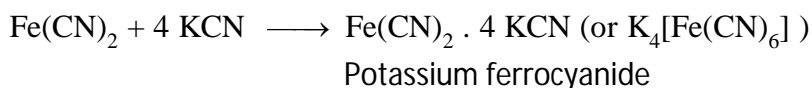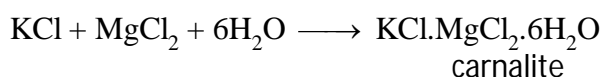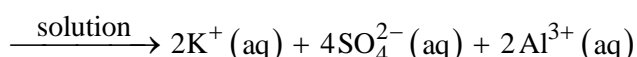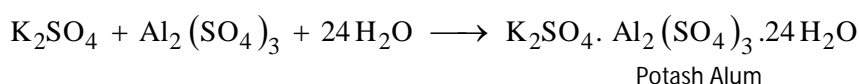
I. Molecular or Addition Compounds

When a solution made by mixing two or more simple stable compounds in simple molecular (stochiometric) proportions is allowed to evaporate, crystals of new substances may separate out. These substances are termed as molecular or addition compounds. Some common examples are :

$$KCl + MgCl_2 + 6H_2O \longrightarrow \underset{\text{carnalite}}{KCl.MgCl_2.6H_2O}$$

$$Fe(CN)_2 + 4\ KCN \longrightarrow \underset{\text{Potassium ferrocyanide}}{Fe(CN)_2 .\ 4\ KCN\ (or\ K_4[Fe(CN)_6]\ )}$$

The molecular or addition compounds are of two types :

(a) Double Salts or Lattice Compounds :

(i) The addition compounds which are stable only in crystalline state and lose their identity in solution form are called double salts.

(ii) When dissolved in water, these salts dissociate completely to give all the ions as are given by the compounds from which these were formed.

$$K_2SO_4 + Al_2\left(SO_4\right)_3 + 24\,H_2O \longrightarrow \underset{\text{Potash Alum}}{K_2SO_4.\ Al_2\left(SO_4\right)_3.24\,H_2O}$$

$$\xrightarrow{\text{solution}} 2K^+\left(aq\right) + 4SO_4^{2-}\left(aq\right) + 2\,Al^{3+}\left(aq\right)$$

(iii) The molar conductivity of such a solution would correspond to all the ions as given by the constituent compounds.

(b) Co-ordination Complexes (or Compounds) :

(i) The addition compounds which do not lose identity even in solution form (i.e., they are stable in solid as well as dissolved state) are called complex compounds.

(ii) In solution form, these compounds do not furnish all the ions which are given by the constituent compounds.

$$2\ KCN + Ni\,(CN)_2 \longrightarrow K_2[Ni(CN)_4] \xrightarrow{\text{solution}} 2K^+\,(aq) + [Ni(CN)_4]^{2-}$$
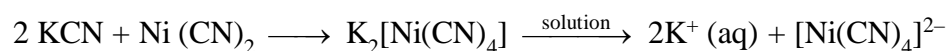
(iii) The molar conductivity of such a solution would correspond to fewer ions as given by the constituent compounds. In above example, the addition compound of KCN and $Ni(CN)_2$ does not give Ni^{2+} and CN^- ions in aqueous solution and hence the molar conductivity of such a solution is because of two K^+ ions and one $[Ni(CN)_4]^{2-}$ ion and not because of two K^+ ions, one Ni^{2+} ions and four CN^- ions.

II. Co-ordination Compounds and Complex Ions :

Co-ordination compounds are the compounds in which the central metal atom is linked to a number of ligands (ions or neutral molecules) by co-ordinate bonds i.e. by donation of lone pairs of electrons by these ligands to the central metal atom.

If a such a compound carries positive or negative charge, it is called a complex ion, e.g. $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$. Hence co-ordination compounds may also be defined as those compounds which contain complex ions, e.g., $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$, etc. In general, a complex ion is represented as $[ML_n]^{\pm x}$ where M is the metal ion, L represents ligands, n is the co-ordination number of metal ion and x is the net charge on the complex.

There are following four types of complexes :

(i) Cation as complex ion, (carrying a net positive charge) e.g., $[Co(NH_3)_6]^{3+}$ in $[Cr(NH_3)_6]Cl_3$.

(ii) Anion as complex ion, (carrying a net negative charge) e.g., $[Fe(CN)_6]^{3-}$ in $K_3[Fe(CN)_6]$.

(iii) Cation and anion both as complex ion. For e.g., $[Pt(Py)_4][PtCl_4]$.

(iv) Neutral complex (A complex carrying no net charge) e.g., $[Ni(CO)_4]$ etc.

The formation of a complex ion involve following two things :

(i) Ligands should have atleast one lone pair of electrons which can be donated to central metal atom or ion.

(ii) The central atom or ion should have vacant orbitals so as to accommodate the electrons donated by the ligands.

TERMINOLOGY OF CO-ORDINATION COMPOUNDS :   Section - 2

1. Centre of Coordination (Central atom/ion or Acceptor atom/ion) :

The cation or neutral atom to which one or more ligands neutral molecules or anions are attached or co-ordinated is the centre of co-ordination.

The central, atom/ion must have empty orbitals as it acts as an acceptor and thus has to accommodate electron pairs donated by the donor atom of the ligand. This explains why the transition metal having empty d-orbitals, form co-ordination compounds very readily.

For example in the complexes $[Ni(NH_3)_6]^{2+}$ and $[FeCN)_6]^{3-}$, Ni^{2+} and Fe^{3+} respectively are the central ions.
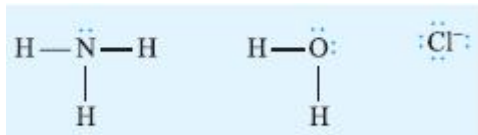
2. Ligands :

Any atom, ion or molecule which can donate alteast a pair of electrons to the central atom to form a coordinate bond (or dative linkage) is called as ligand or coordinating group. Further in a ligand, the particular atom which actually donates the electron pair is called the donor atom.

The ligands act as *Lewis* bases as they donate one or more electron pair to the central metal atoms or ions which act as *Lewis* acids by accepting electrons.

Types of Ligands :

Ligands can be of following types depending on the denticity of the ligand i.e the number of donor atoms present in a ligand. (Precisely, denticity of a ligand is the maximum number of donor atoms present in the ligand which can be utilised to coordinate (or ligate) with the central atom simultaneously).

(i) Monodentate or unidentate Ligands : They have one donor atom, i.e. they supply only one electron pair to the central atom. e.g. F^-, Cl^-, Br^-, H_2O, NH_3, CO, SCN^-, NO^-, NH_3, H_2O etc.
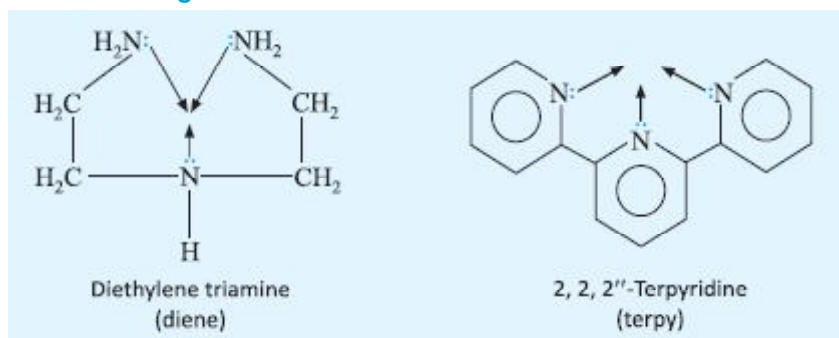

(ii) Polydentate ligands or Multidentate ligands : These ligands coordinate using two or more donor atoms. Structures of some bidentate or didentate, terdentate, tetradentate ligands have been shown below:
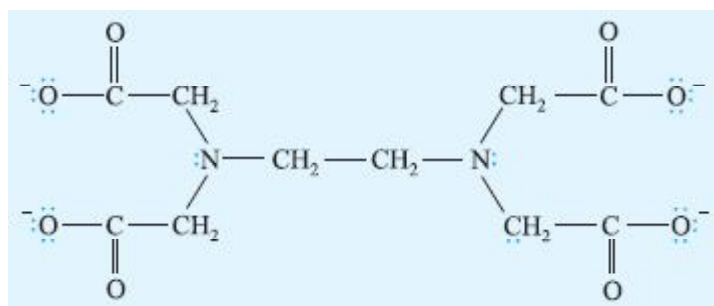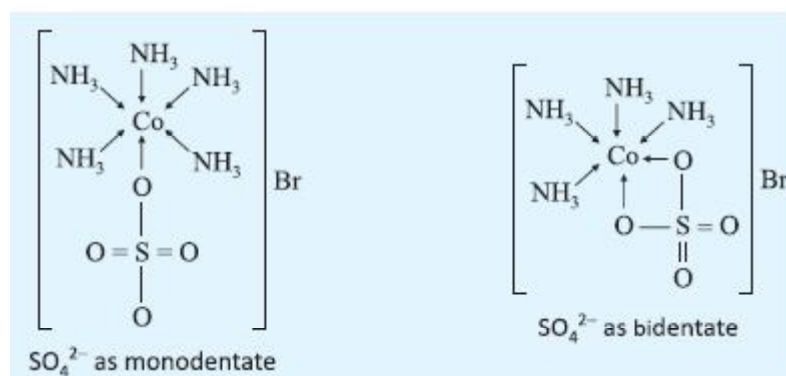
➤ **Bidentate ligands :**

➤ **Terdentate ligands :**

Diethylene triamine
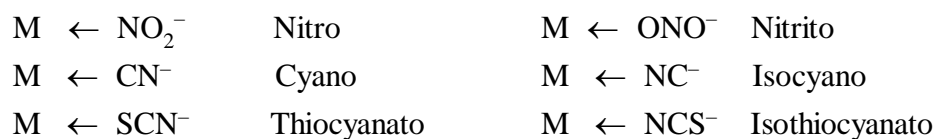(diene)

2, 2, 2″-Terpyridine
(terpy)
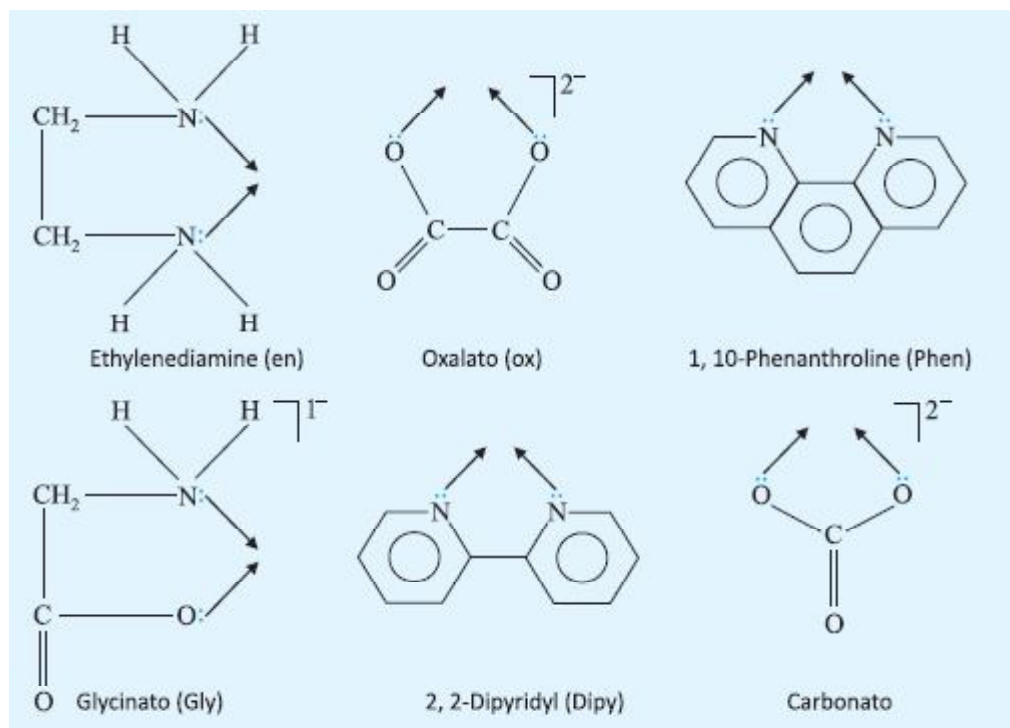
➤ **Hexadentate ligand :**

Note : Polydentate ligands have flexible character. It is not necessary that all the donor atoms present in the polydentate ligands should form co-ordinate bonds with central metal atom or ion. For example, ethylenediaminetetraacetate ion (EDTA) which is hexadentate ligand can also function as pentadentate or tetradentate ligand with certain metal ions. Sulphate ion (SO_4^{2-}), can act both as monodentate as well as bidentate as shown :

SO_4^{2-} as monodentate

SO_4^{2-} as bidentate

Ambidentate Ligands : There are certain ligands which have two or more donor atoms in forming complexes only one donor atom is attached to metal ion. Such ligands are called ambidentate ligands or in other words these are the ligands which can ligate through two different atoms present in it. Examples of such ligands are the NO_2^-, CN^-, SCN^- ions. NO_2^- ion can coordinate to a central metal atom/ion either through nitrogen or the oxygen atoms as depicted below :

$M \leftarrow NO_2^-$	Nitro		$M \leftarrow ONO^-$	Nitrito
$M \leftarrow CN^-$	Cyano		$M \leftarrow NC^-$	Isocyano
$M \leftarrow SCN^-$	Thiocyanato		$M \leftarrow NCS^-$	Isothiocyanato

Chelation : When coordination of two or more donor atoms from a polydentate ligand to a single central atom/ion takes place forming a closed or cyclic ring structure, it is called chelation and the ligand a chelating ligand. The close ring compound thus formed is called chelate (or metal chelate).

Some Important Characteristic of Chelates :

(a) **Chelating Effect :** Chelating ligands form more stable complexes than the monodentate analogs. The complex ion/compound have such ligands does not dissociate easily.

(b) **Formation of Rings :** Generally the chelate complexes with 5 or 6 membered rings are more stable. Out of these, 5 membered rings are very stable when they involve saturated ligands, e.g., ethylenediamine, which contains five membered stable ring structure. On the other hand 6-membered ring structures acquire maximum stability when they involve unsaturated ligands containing conjugate double bonds.

(c) **Steric Hindrance :** Ligands with large groups form unstable rings than the ligands with smaller groups due to steric hindrance.

(d) The complex compound having maximum number of rings formed with the ligands is most stable. For example, a complex $[M(en)_3]^{3+}$ is less stable than a complex $[M(EDTA)]^-$ because in the former there are 3 rings while in the latter has 5 rings.

(e) **Entropy effect :** The stability of the chelate complex is explained on the basis of entropy effect. To elaborate, let us take an example of ethylene diamine ligand (en). When one end of 'en' is coordinated the probability of coordination of the other end is high because this end is bound to stay close to the central atom/ion. This shows that it is easier to form a chelate ring than forming coordinate bonds with two independent molecules. Thermodynamically, the increased stability due to chelation can be attributed to an increase in the degree of freedom of the system. A large change in entropy but only small heat of reaction generally accompany the chelation process.

3. **Co-ordination Number (C.N.) :** The number of atoms (of the ligands) that are directly bound to the central metal atom/ion by coordinate bonds is known as the co-ordination number of the central atom/ion. It is actually the number of sigma bonds which the ligands form with the central metal atom/ion. Pie bonds, if formed between the ligands and the central metal/ion, are not counted for this purpose.
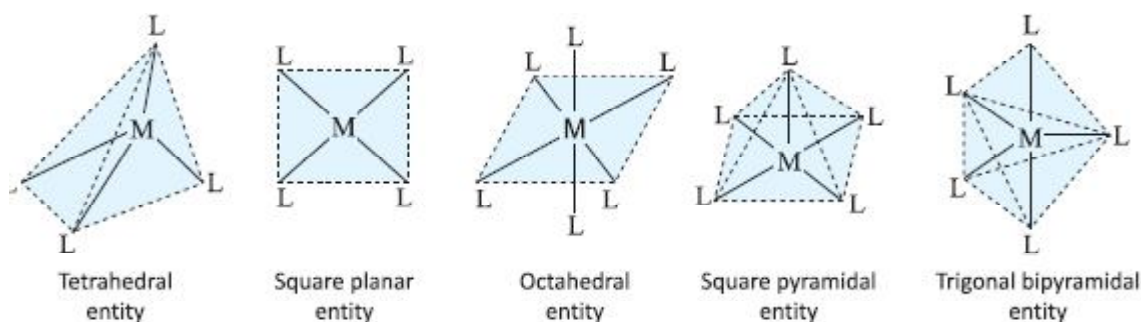
Co-ordination Number of Complexes

Complexes	Ligands	C.N.
$[Ag(NH_3)_2]^+$	NH_3	2
$[HgI_3]^-$	I^-	3
$[PtCl_4]^{2-}$, $[Ni(CO)_4]$	Cl^-, CO	4
$[Fe(CO)_5]$, $[Co(CN)_5]^{3-}$	CO, CN^-	5
$[Co(NH_3)_6]^{3+}$, $W(CO)_6$	NH_3, CO	6
$[Mo(CN)_7]^{3-}$	CN^-	7
$[W(CN)_8]^{4-}$	CN^-	8
$[Co(en)_3]^{3+}$, $[Fe(C_2O_4)_3]^{3-}$	en, $C_2O_4^{2-}$	6
$[Co(H_2O)_2(NH_3)_4]^{3+}$	H_2O and NH_3	2 + 4 = 6

4. Co-ordination entity (sphere) :

The central metal atom/ion & the ligands that are directly attached to it, enclosed in a square bracket, are collectively called as co-ordination sphere (or entity). The ionisable groups are written outside the bracket and are called *counter ions*. The co-ordination sphere behaves as a single unit because the ligands present in the co-ordination sphere are held tightly by the metal ion. Any ion present outside this sphere is separated from the complex, when compound is dissolved in the water. Eg : In the following compounds $[Cr(NH_3)_6]Cl_3$, $K_4[Fe(CN)_6]$, $K_2[PtCl_4]$, $[Ni(CO)_4]$, $K_2[Ni(CN)_6]$ the respective coordination entities are : $[Cr(NH_3)_6]^{3+}$; $[Fe(CN)_6]^{4-}$; $[PtCl_4]^{2-}$; $[Ni(CO)_4]$; $[Ni(CN)_4]^{2-}$; and the counter ions are Cl^-, K^+, K^+, (no counter ion) and K^+.

5. Co-ordination polyhedron :

The spatial arrangement of the ligand atoms which are directly attached to the central metal atom or ion, in definite direction thereby giving a definite geometry to the complex ion or compound, is called coordination polyhedron around the central atom or ion. The most common coordination polyhera are octahedral, square planar and tetrahedral.



Tetrahedral entity   Square planar entity   Octahedral entity   Square pyramidal entity   Trigonal bipyramidal entity

Different shapes of co-ordination polyhedron. M : central atom/ion,   L : a unidentate ligand

6. Oxidation number of central atom :

It is is defined as the charge that the central metal ion would carry if all the ligands are removed alongwith electron pairs. It is calculate as follows :

Example : $K_4[Fe(CN)_6]$

$$K_4[Fe(CN)_6] \longrightarrow 4\ K^+ + [Fe(CN)_6]^{4-}$$
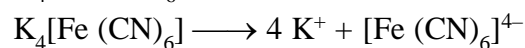
Charge on complex ion $= -4$

Let charge on Fe $= x$,

Now charge on cynide ion $(CN^-) = -1$

$\Rightarrow \qquad x + 6 \times (-1) = -4$

$\Rightarrow \qquad x = +2$

Hence oxidation no of Fe $= +2$ (or II)

Complexes	Central metal ion	Ligands	Oxidation Number
$[Co(NH_3)_6]^{3+}$	Co	6 NH_3	III
$[NiCl_4]^{2-}$	Ni	4 Cl^-	II
$[Co(CN)_5F]^{3-}$	Co	5 CN^- & 1 F^-	III
$[Ni(CN)_4]^{2-}$	Ni	4 CN^-	II
$[Ni(CO)_4]$	Ni	4 CO	0
$[Ni(H_2O)_6]^{2+}$	Ni	6 H_2O	II
$[Fe(CN)_6]^{4-}$	Fe	6 CN^-	II
$[Cu(NH_3)_4]^{2+}$	Cu	4 NH_3	II

7. Homoleptic and Hetroleptic Complexes :

Complexes in which central atom is coordinated with only one kind of ligands are called homoleptic complexes, eg. $[Co(NH_3)_6]^{3+}$. Complexes in which central atom is co-ordinated with more than one kind of ligands are called hetroleptic complexes, eg. $[Co(NH_3)_4Cl_2]^+$.

8. Effect atomic Number (EAN rule and Sidgwick Theory) :

In order to explain the stability of co-ordination complexes Sidgwick proposed effective atomic number (EAN) rule. He suggested that a metal ion will continue accepting electron pairs till the total number of electrons in the metal ion (after gaining electrons from the donor atoms of the ligands) becomes equal to that of the next higher noble gas. This total number of electrons is called the effective atomic number (EAN) of the metal. This will become clear by taking the example of heaxamminecobalt(III) ion, $[Co(NH_3)_6]^{3+}$.

Aomic number of cobalt $= 27$.

In the present complex, cobalt is present in the oxidation state of +3.

$\Rightarrow$ Total no of electrons in $Co^{3+} = 27 - 3 = 24$.

Since each NH_3 ligand donates two electrons to the cobalt ion,

Electrons donated by 6 NH_3 ligands $= 6 \times 2 = 12$.

EAN of Co^{3+} i.e. total no of electron present in Co^{3+} in complex $= 24 + 12 = 36$

(36 is the atomic number of Krypton (Kr), the next nearest noble gas)

In general,

EAN = (atomic number – oxidation state) + (C.N. $\times$ 2)

or   EAN = atomic no of the metal – no of electrons lost in ion formation + no of electrons gained from ligands.

In the above example since the number 36 corresponds to the atomic number of krypton, according to Sidgwick, the complex will be stable. Though EAN rule (which states that those complexes are stable whose EAN is the same as the atomic number of the next noble gas) is applicable in many cases, there are several examples in which EAN rule is not obeyed.

Illustration - 1 *Apply the concept of EAN rule, on the complexes $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$. What conclusion do you draw about the validity of the EAN rule from these two complexes ?* (Atomic number of Fe = 26)

SOLUTION :

(a) $[Fe(CN)_6]^{4-}$: Let O.S. of Fe in $[Fe(CN)_6]^{4-}$ = x

So, $x + 6(-1) = -4$ $\Rightarrow$ $x = +2$

Also, C.N. of Fe in $[Fe(CN)_6]^{4-} = 6$

($\because CN^-$ is a unidentate ligand)

So, EAN of Fe = (Z – O.S.) + 2 (C.N.)

= (26 – 2) + 2 $\times$ 6 = 36

= Atomic number of Kr (next nearest inert gas).

So, in $[Fe(CN)_6]^{4-}$, EAN rule is valid.

(b) $[Fe(CN)_6]^{3-}$: Let O.S. of Fe in $[Fe(CN)_6]^{3-}$ = x

So, $x + 6(-1) = -3$

So, $x = +3$

Again, C.N. of Fe in $[Fe(CN)_6]^{3-} = 6$

($\because CN^-$ is a unidentate ligand)

So, EAN of Fe = (26 – 3) + 2 $\times$ 6 = 35 $\neq$ atomic number of Kr (36) (next nearest inert gas)

Thus EAN rule is not valid in $[Fe(CN)_6]^{3-}$.

Illustration - 2 / *Predict the formulae of the carbonyl complexes of Fe* (26) *and Cr* (24).

SOLUTION :

(a) Molecular formula of iron carbonyl $[Fe(CO)_n]$

Calculation of the value of 'n' (C.N.)

Oxidation state of metal in carbonyls $= 0$

Again, according to EAN rule, EAN of Fe $= 36$ (atomic number of Kr, next higher noble gas)

But, EAN $= (Z - O.S.) + 2 \times (C.N.)$

$\Rightarrow \quad 36 = (26 - 0) + 2 \times n$

So, n $= 5$

Thus, formula of iron carbonyl is $[Fe(CO)_5]$.

(b) Molecular formula of chromium carbonyl $[Cr(CO)_m]$

Again, O.S. of Cr in $[Cr(CO)_m] = 0$

C.N. of Cr $= m$

Again, according to EAN rule, EAN of Cr $= 36$ (atomic number of Kr, next higher noble gas)

But, EAN $= (Z - O.S.) + 2 \times (C.N.)$

$\Rightarrow \quad 36 = (24 - 0) + 2 \times m$

So, m $= 6$

So, formula of chromium carbonyl $= [Cr(CO)_6]$.

Illustration - 3 / *Calculate the EAN of the underlined atoms in the following complexes*

(A) $\left[\underline{Au}Cl_2\right]^-$ **(B)** $\left[\underline{Fe}(C_2O_4)_3\right]^{3-}$ **(C)** $\left[\underline{Ca}(EDTA)\right]^{2-}$ **(D)** $\left[\underline{Ni}(NH_3)_3(en)(Py)\right]^{+2}$

SOLUTION :

(a) $[\underline{Au}Cl_2]^-$ (Z for Au $= 79$)

Let O.S. of Au be x.

So, $x + 2(-1) = -1 \quad \Rightarrow \quad x = +1$

Again, C.N. of Au $= 2$

     ($\because$ Cl$^-$ is a unidentate ligand)

So, EAN $= (Z - O.S.) + 2 \times (C.N.)$

     $= (79 - 1) + (2 \times 2) = 82$.

(b) $\left[\underline{Fe}(C_2O_4)_3\right]^{3-}$ (Z of Fe $= 26$)

Let O.S. of Fe be x.

So, $x + 3(-2) = -3$

So, $x = +3$

Again, C.N. of Fe $= 6$

($\because$ $C_2O_4^{2-}$ is a bidentate ligand)

So, EAN $= (26 - 3) + (2 \times 6) = 35$.

(c) $\left[\underline{Ca}(EDTA)\right]^{2-}$ (Z for Ca $= 20$)

Let O.S. of Ca be x.

So, $x + 1 \times (-4) = -2$

So, $x = +2$

Again, C.N. of Ca $= 6$

($\because$ EDTA^{4-} is a hexabidentate ligand)

So, EAN $= (20 - 2) + (2 \times 6) = 30$.

(d) $\left[\underline{Ni}(Py)(en)(NH_3)_3\right]^{2+}$ (Z for Ni $= 28$)

Let O.S. of Ni be x

$x + 0 + 0 + 3 \times 0 = 2$ (all are neutral ligands) ;

So, $x = +2$

($\because$ Py and NH$_3$, both are unidentate ligand while (en) is a bidentate ligand)

So, EAN $= (28 - 2) + (2 \times 6) = 26 + 12 = 38$.

Illustration - 4 1 *mole of* $CoCl_3.4NH_3$, *on reaction with excess of* $AgNO_3$ *gives one mole of a white precipitate.*

**(a)** *What is the formula of complex ?*   **(b)** *What is the C.N. of cobalt in this complex ?*

SOLUTION :

Since the complex gives one mole of AgCl (a white precipitate) with $AgNO_3$ solution, it indicates that out of 3 Cl^- ions, only one is outside the co-ordination sphere, and the remaining Cl^- ions, are inside the co-ordination sphere.

$\Rightarrow$ Two Cl^- ions and all the four NH_3 molecules are inside the co-ordination sphere.

(a) So, the formula of the complex is

$$[CoCl_2(NH_3)_4]\, Cl \rightleftharpoons [CoCl_2(NH_3)_4]^+ + Cl^- \xrightarrow{\ AgNO_3\ } AgCl\downarrow \text{ (white ppt.)}$$
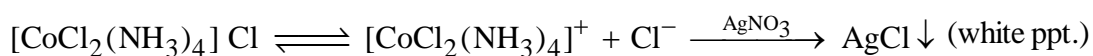
(b) Hence, the complex is $[CoCl_2(NH_3)_4]Cl$

C.N. of Co in this complex = 6.

NOMENCLATURE OF CO-ORDINATION COMPOUNDS :   Section - 3

Co-ordination compounds are formulated and named according to the system set up by Inorganic Nomenclature Committee of the International Union of Pure and Applied Chemistry (IUPAC). The following rules are observed while writing formulae and naming co-ordination compounds.

➤ **Rules for Formula writing of Mono-Nuclear Co-ordination Compounds :**

(i) Formula of the cation whether simple or complex is written first followed by that of the anion.

(ii) Sequence of symbols within the coordination formula

   ➤ The central atom is listed first.

   ➤ The ligands are then listed in alphabetical order based on the way the ligand is represented in the formula.[+++]
   The placement of the ligand in the list does not depend on the charge of the ligand.***

   ➤ If an abbreviation is used in a formula to represent a ligand the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical list.

   ➤ Wherever possible, the ligand formula should be written in such a way that the donor atom is closest to the central atom to which it is attached.

   ➤ All the ligands are formuated without any space in between, also there should be no space between the ligands the the central metal atom within the co-ordination sphere.

Note :

+++ Following things should be kept in mind :
- A single letter symbol always precedes a two-letter symbol with the same initial letter, e.g. B before Be ; O before OH, the group NH_3 is treated as a single symbol and so is listed after Na.
- Where the entities to be arranged in a formula are polyatomic,
  - ➤ The order of citation is decided by selecting the first symbol in the formula of a polyatomic group.
    For example, C_5H_5, SCN, NO_2 and OH are ordered under C, S, N and O respectively.
  - ➤ If the first symbols are the same, the symbol with the lesser right index is cited first,
    e.g. NO_2 precedes N_2O_2.
  - ➤ If this still does not discriminate, the subsequent symbols are used alphabetically and numerically to define the order, e.g. NH_2 precedes NO_2 which precedes NO_3.
- To summarise and exemplify, the order of citation of some nitrogen-containing compounds is :

$$N^{3-}, \ NH_2^-, \ NH_3^-, \ NO_2^-, \ NO_3^-, \ N_2O_2^{\ 2-}, \ N_3^-$$
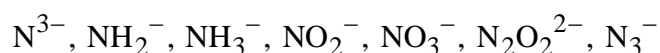
*** In order to simplify the rules and to resolve ambiguities that may arise when it is not clear whether a ligand is charged or not, the charge on a ligand is no longer considered in determining ligand order in the formulae of co-ordination compounds.

(iii) Use of enclosing marks : The formula for the entire co-ordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulae are enclosed in parentheses. Ligand abbreviations are also usually enclosed in parentheses

(iv) Ionic charges and oxidation numbers : If the formula of a charged co-ordination entity is to be written without that of the counter-ion, the charge is indicated outside the square bracket as a right superscript, with the number before the sign. The oxidation number of a central atom may be represented by a Roman numeral, which should be placed as a right superscript on the element symbol.

Examples :

1. $[PtCl_6]^{2-}$ 2. $[Cr(OH_2)_6]^{3+}$

3. $[Cr^{III}(NCS)_4(NH_3)_2]^-$ 4. $[Cr^{III}Cl_3(OH_2)_3]$

5. $[Fe^{-II}(CO)_4]^{2-}$

Other Examples :

1. $[Al(OH)(OH_2)_5]^{2+}$

2. $[PtBrCl(NH_3)(NO_2)]^-$

3. $[PtCl_2(NH_3)(py)]$

4. $[Co(en)F_2(NH_3)_2]^+$, but $[CoF_2(NH_2CH_2CH_2NH_2)(NH_3)_2]^+$

5. $[Co(NH_3)_5(N_3)]^{2-}$

➤ **Rules for Naming of Mono-Nuclear Co-ordination Compounds :**

(i) Order of naming ions : The positive ion (cation) is named first followed by the negative ion (anion) irrespective of whether cation is complex or anion is complex. The complex part is written as one word e.g., $[Co(NH_3)_6]Cl_3$, hexaamminecobalt(III) chloride.

(ii) Naming of ligands : Different types of ligands are named differently. (refer to the table)

(a) Negative ligands (organic or inorganic) : These type of ligands end in '-o', e.g., CN^- (cyano), Cl^- (chloro), NO^{2-} (nitro), O^{2-} (oxo). If the name of the anionic ligands ends in –ide, –ite or –ate, the last 'e' is replaced by 'O' giving –ido, –ito or –ato e.g. SO_4^{2-} (sulphato), NH_2^- (amido), ONO^- (nitrito) etc.

(b) Neutral ligands : These type of ligands have no special ending and are used as such except for NH_3 (ammine), H_2O (aqua), CO(carbonyl), CS (Thiocarbonyl) and NO (nitrosyl).

(c) Positive ligands : These type of ligands are used as such. These type of ligands generally end in –ium, e.g., $NH_2–NH_3^+$ (hydrazinium), NO^+ (nitrosonium), NO_2^+ (nitronium) etc.

(d) Organic ligands : Organic free radicals are given their own names, e.g., $CH_3^°$ (methyl), $C_2H_5^°$ (ethyl). For organic neutral molecules, their names are used, e.g., $P(C_6H_5)_3$-triphenylphosphine, C_2H_5N-pyridine (py) etc.

Note : Enclosing marks "( )" are required for (a) neutral and cationic ligand names. (however, common ligands such as aqua, ammine, carbonyl, nitrosyl, methyl, ethyl, *etc*., do not require enclosing marks, unless there is ambiguity) ; (b) for inorganic anionic ligands containing numerical prefixes (such as triphosphato) ; (c) for any compositional name (such as carbon disulfide) ; (d) for any substituted organic ligand (even if there is no ambiguity in its use); (e) and wherever necessary to avoid ambiguity.

Denticity	Name	Ligand	Charge	Name of ligand in the complex	Donor Atom
Positive Ligands					
Monodentate	Nitrosonium ion	NO^+	+1	Nitrosonium	N
	Nitronium ion	NO_2^+	+1	Nitronium	N
	Hydrazinium ion	$NH_2NH_3^+$	+1	Hydrazinium	N

Neutral Ligands

	Name	Ligand	Charge	Name of ligand in the complex	Donor Atom
Monodentate	Water	H_2O	0	Aqua/aquo	O
	Ammonia	NH_3	0	Ammine	N
	Carbon monoxide	CO	0	Carbonyl	C
	Nitrgen Oxide	NO	0	Nitrosyl	N
	Thiocarbonyl	CS	0	Thiocarbonyl	S
	Thionitrosyl	NS	0	Thionitrosyl	N
	Pyridine (py)	C_5H_5N	0	Pyridine (py)	N
	Methyl amine	CH_3NH_2	0	Methylamine	N
	Dinitrogen	N_2	0	Dinitrogen	N
	Dioxygen	O_2	0	Dioxygen	O
	Phosphine	PH_3	0	Phosphine	P
	Urea	$\overset{\overset{\displaystyle O}{\|\|}}{H_2N - C - NH_2}$	0	Urea	O
	Thio-urea (tu)	$\overset{\overset{\displaystyle S}{\|\|}}{H_2N - C - NH_2}$	0	Thio-urea	S
	Triphenylphosphine	Ph_3P	0	Triphenylphosphine	P
	Acetone	CH_3COCH_3	0	Acetone	O

Denticity	Name	Ligand	Charge	Name of ligand in the complex	Donor Atom
Bidentate	Ethylenediamine (en) (a bidentate ligand)	$NH_2(CH_2)_2NH_2$	0	Ethylenediamine (en)	2 N-atoms
Tridentate	Diethylene triamine	$\begin{array}{c} H_2C - \ddot{N}H - CH_2 \\ \|\qquad\qquad\| \\ H_2C - \ddot{N}\quad\ddot{N} - CH_2 \\ H_2\ \ H_2 \end{array}$	0	diethylenetriamine (dien)	3 N-atoms
Tetradentate	Triethylene tetramine	$\begin{array}{c} H_2C - \ddot{N}H(CH_2)_2\ddot{N}H_3 \\ \| \\ H_2C - \ddot{N}H(CH_2)_2\ddot{N}H_3 \end{array}$	0	triethylene-tetramine (trien)	4 N-atoms

Negative Ligands

Monodentate	Hydride ion	H^-	-1	hydrido	H
	Oxide ion	O^{2-}	-2	oxo	O
	Perioxide ion	O_2^{2-}	-2	peroxo	O
	Perhydroxide ion	O_2H^-	-1	perhydroxo	O
	Hydroxide ion	OH^-	-1	hydroxo	O
	Fluoride ion	F^-	-1	fluoro (fluorido)	F
	Chloride ion	Cl^-	-1	chloro (chlorido)	Fl
	Bromide ion	Br^-	-1	bromo (bromido)	Br
	Iodide ion	I^-	-1	iodo (iodido)	I
	Acetate ion	CH_3COO^-	-1	acetato (acetatido)	O
	Cyanide ion	$\leftarrow [:\overset{\ominus}{C} = N:]^-$	-1	cyano (cyanido)	C
	Isocyanide ion	$[:\overset{\ominus}{C} \equiv N:]\rightarrow$	-1	Isocyano	N
	Sulphite ion	SO_3^{2-}	-2	sulphito	O
	Sulphide ion	S^{2-}	-2	sulphido or thio	S
	Hydrogen-sulphide ion	HSO_3^-	-1	hydrogensulphito	O
	Amide ion	NH_2^-	-1	amido	N
	Imide ion	NH^{2-}	-2	imido	N
	Nitrate ion	NO_3^-	-1	nitrato	N
	Nitro ion	NO_2^-	-1	nitro (nitrito-N)	N
	Nitrito ion	ONO^-	-1	nitrito (nitrito-O)	O
	Nitrido ion	N^{3-}	-3	nitrido	N
	Azide ion	N_3^-	-1	azido	N

Denticity	Name	Ligand	Charge	Name of ligand in the complex	Donor Atom
	Cyanate ion	CNO^-	−1	cyanato	O
	Isocynate ion	OCN^-	−1	isocyanato	N
	Thiocyanate ion	SCN^-	−1	thiocyanato	S
	Isothiocyanate ion	NCS^-	−1	isothiocyanato	N
	Hydrogen-carbonate ion	HCO_3^-	−1	hydrogencarbonato	O
Bidentate	Acetyl acetonate ion	$CH_3-C-CH=C-CH_3$ (with $\overset{\|}{O}$ and $\overset{\|}{O^-}$)	−1	acetylacetonato (acac)	2 O-atoms
	Glycinate ion	$NH_2-CH_2-COO^-$	−1	glycinato (gly)	1 N-atom and 1 O-atom
	Sulphate ion	SO_4^{2-}	−2	sulphato	2 O-atoms
	Thiosulphate ion	$S_2O_3^{2-}$	−2	thiosulphato	2 O-atoms
	Dimethylglyoxime	$\begin{array}{l} O^- \\ \| \\ CH_3-C=N: \\ \| \\ CH_3-C=N: \\ \| \\ OH \end{array}$	−1	dimethylglyoximato	2 N-atoms
	Oxalate ion	$C_2O_4^{2-}$	−2	Oxalato	2 O-atoms
	Carbonate ion	CO_3^{2-}	−2	carbonato	2 O-atoms
Pentadentate	Ethylenediamine-triacetate ion	$CH_2-\overset{\cdot\cdot}{N}(CH_2COO^-)_2$ $\|$ $CH_2-\overset{\cdot\cdot}{N}HCH_2COO^-$	−3	$(EDTA^{3-})$	2 N-atoms and 3 O-atoms
Hexadentate	Ethylenediamine-tetra-acetate ion	$CH_2N(CH_2CO_2^-)_2$ $\|$ $CH_2N(CH_2CO_2^-)_2$	−4	$(EDTA^{4-})$	2 N-atoms and 4 O-atoms

(iii) **Prefixes :** Two kinds of numerical prefix are available for indicating the number of each type of ligand within the name of the co-ordination entity.

(a) Prefixes di, tri, *etc*. are generally used for simple ligands. Enclosing marks around the ligand are not required. e.g., if there are four NH_3 molecules as ligands, we shall write tetraammine. Here note that both 'a' i.e. last 'a' of tetra and first 'a' of ammine are to be retained.

(b) Prefixes bis, tris, tetrakis, *etc*. are used with complex expressions (generally with those ligands which include a numerical prefix in their names) and wherever required to avoid ambiguity. Enclosing marks in the nested order must be placed around the multiplicand.

Elaboration : These prefixes are used for ligands containing di,tri etc in their names eg dipyridyl or ethylenediamine, thus, their numbers are indicated by prefixed, bis-, tris-, tetrakis-, etc., for example : $[PtCl_2(NH_2CH_2CH_2NH_2)_2](NO_3)_2$ is named as dichlorobis (1, 2-ethanediamine) platinum (IV) nitrate.

(iv) Preference order : All ligands whether negative, neutral or positive, are named in an alphabetical order. The prefixes di, tri, etc. are not to be considered while determining this alphabetical order. The names of the ligands are followed by the name of the central metal atom/ion. e.g. $[PtCl(NH_3)_4(NO_2)]SO_4$ is named as tetraamminechloronitroplatinum (IV) sulphate.

(v) Naming of complex ion : Ligands are named first, followed by the metal atom. The ending of the name of the metal depends upon the nature of the complex ion.

(a) If the complex ion is cation or the compound is non-ionic, the name of the central metal ion is written as such followed by its oxidation state indicated by Roman numeral (such as II, III, IV) in the parenthesis at the end of the name of the metal without any space in between the two. (0) is used for an oxidation state of zero and a negative oxidation state is shown by a negative sign before the Roman numeral.

(b) If the complex ion is anion, the name of the central metal atom is made to end in "–ate" followed by the oxidation number in brackets without any space between them.

(c) While naming complex acid of transition metals, ending 'ic' is used, e.g. $H_4[Pt(CN)_6]$ is named as hexacyanoplatinic(II) acid.

Complex Ions

Example	Negative complex	Positive/neutral complex
Ni	nickelate	nickel
Pb	plumbate	lead
Sn	stannate	tin
Fe	ferrate	iron

(vi) Naming of the optical isomers : Dextro and Laevo rotatory optically active compounds are respectively designated either by (+) and (–) or by d– and $\ell-$ e.g. dextro rotating $K_3[Cr(C_2O_4)_3]$ is named as potassium (+)trioxalatochromate(III) or potassium d–trioxalatochromate(III).

IUPAC Names (Some Examples)

Neutral Complexes :

$[Co(NH_3)_3]Cl_3$	triamminecobalt(III) chloride
$[Ni(CO)_4]$	tetracarbonylnickel(0)
$[Fe(CO)_5]$	pentacarbonyliron(0)
$[Pt(NH_3)_2]Cl_2$	diammineplatinum(II) chloride
$[Co(NH_3)_3(NO_2)_3]$	triamminetrinitrocobalt(III)
$[Cu(Gly)_2]$	diglycinatocopper(II)
$[Ni(DMG)_2]$	bis(dimethylglyoximato)nickel(II)
$[CuCl_2\{O=C(NH_2)_2\}_2]$	dichloridobis(urea)copper(II)

Complex Cations :

$[Co(OH_2)_6]^{2+}$	hexaaquacobalt(II) ion
$[Zn(NH_3)_4]^{2+}$	tetraamminezinc(II) ion
$[Pt(en)_2]^{2+}$	bis(ethylenediammine)platinum(II) ion
$[Ni(en)_3]^{3+}$	tris(ethylenediammine)nickel(III) ion
$[PtCl_2(NH_3)_2]Cl_2$	diamminedichloroplatinum(IV) chloride
$[Cu(NH_3)_4(OH_2)_2]Cl_2$	tetraamminediaquacopper(II) chloride
$[Co(NH_3)_5(ONO)]Cl_2$	pentaamminenitritocobalt(III) chloride
$[CoCl(NH_3)_4(OH_2)]Cl$	tetraammineaquachlorocobalt(II) chloride
$[Ag(NH_3)_2]Cl$	diamminesilver(I) chloride

Complex anions

$K[AgCl_2]$	potassium dichloroargentate(I)
$Ba[CuCl_4]$	barium tetrachlorocuprate(II)
$K_3[Fe(CN)_6]$	potassium hexacyanoferrate(III)
$K_4[Fe(CN)_6]$	potassium hexacyanoferrate(II)
$Cu_2[Fe(CN)_6]$	copper hexacyanoferrate(II)
$[Au(CN)_4]^{2-}$	tetracyanoaurate(II) ion
$[CoBr_4]^{2-}$	tetrabromocobaltate(II) ion
$[HgI_4]^{2-}$	tetraiodomercurate(II) ion
$[Ni(CN)_4]^{2-}$	tetracyanonickelate(II) ion
$[Fe(C_2O_4)_3]^{3-}$	tri(oxalato)ferrate(III) ion
$[CrCl_2(en)_2]Cl_2$	dichlorobis(ethylenediammine)chromium(IV) chloride
$K_3[Cr(C_2O_4)_3]$	potassium trioxalatochromate(III)

Complexes containing cationic and anioic ions

$[Cr(NH_3)_6][Co(CN)_6]$	hexaamminechromium(III) hexacyanocobaltate(III)
$[Pt(NH_3)_4][CuCl_4]$	tetraammineplatinum(II) tetrachlorocuprate(II)
$[Cr(NH_3)_6][Co(C_2O_4)_3]$	hexaamminechromium(III) trioxalatocobaltate(III)
$[Pt(py)_4][PtCl_4]$	tetrapyridineplatinum(II) tetrachloroplatinate(II)
$[PtCl_2(NH_3)_4][PtCl_4]$	tetraamminedichloroplatinum(II) tetrachloroplatinate(IV)

Note : **1.** The stable oxidation states of some of the transition metals of the three series are given below. These would be helpful to find the oxidation states of the metal ions while naming complexes having cation and anion both as complexes.

(i)   First Transition Series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2, +3,	+2, +3,	+2, +3,	+2, +3,	+2, +3,	+2, +3	+2, +3	+1, +2	+2
	+4	+4, +5	+6	+4, +7					

(ii)   Second Transition Series

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+3	+4	+3, +5	+6	+4, +6,	+3	+3	+2, +4	+1	+2
				+7					

(iii)   Third Transition Series

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
+3	+4	+5	+6	+4, +6,	+3, +4,	+1, +3	+2, +4	+1, +3	+1, +2
				+7	+6	+4			

2.   Naming of linkage isomers : Read the following eg carefully $\rightarrow$ $[Co(NH_3)_5(NO_2)]^{2+}$ has two isomeric forms having red and yellow colours.

➤   The red colour isomer $[CO(NH_3)_5(ONO)]^{2+}$ is named as :

pentaamminenitrito-O-cobalt(III) [or pentaamminenitritocobalt(III)] while ;

➤   The yellow isomer $[Co(NH_3)_5(NO_2)]^{2+}$, is named as

pentaamminenitrito-N-cobalt(III) [or pentaamminenitrocobalt(III)].

3.   For some compounds common names are more popular than there IUPAC names eg. ferrocyanide rather than hexacyanoferrate(II) for $[Fe(CN)_6]^{4-}$ and ferricyanide rather than hexacyanoferrate(III) for $[Fe(CN)_6]^{3-}$
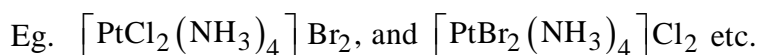
Isomerism in Co-ordination Compounds

Isomers are compounds having same chemical formula but different arrangment of atoms. Because of different arrangment of atoms, they differ in one or more physical or chemical property. This phenomenon is called as isomerism.
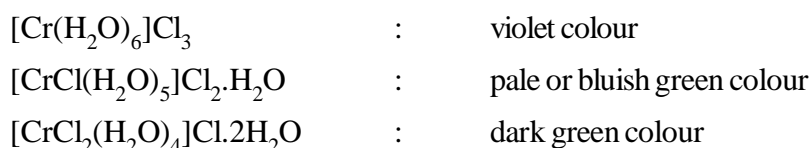
The type of isomerism found in co-ordination compound is :

1. **Structural isomerism :** It is displayed by compounds that have different ligands within their co-ordination sphere. It may be further sub-divided into different types as follows:

   (A) Ionization isomerism : The co-ordination compounds exhibiting this type of isomerism give different ions in solution. It occurs when the counter ion in a co-ordination compound is itself a potential ligand.
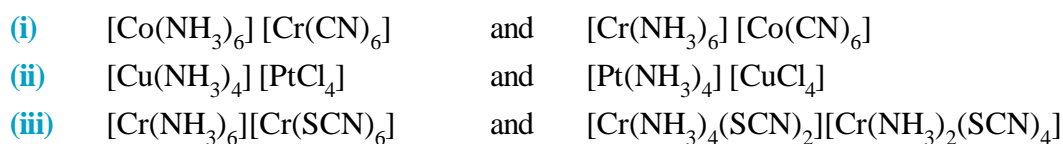
   $$\text{Eg.} \quad \left[PtCl_2 \left(NH_3 \right)_4 \right] Br_2, \text{ and } \left[PtBr_2 \left(NH_3 \right)_4 \right] Cl_2 \text{ etc.}$$

   (B) Solvent isomerism : This is a special type of ionisation isomerism which arises when solvent molecules can form co-ordination bonds with the central atom/ion. In this, compounds having same composition differ in the number of solvent molecules present as ligands (in the co-ordination sphere) and as free solvent molecules of hydration (present outside the co-ordination sphere). This form of isomerism is known as *"hydrate isomerism"* in case where water is involved as a solvent. For example, there are three isomers of hexa-hydrates of chromic chloride with empirical formula $CrCl_3.6H_2O$.

$[Cr(H_2O)_6]Cl_3$	:	violet colour
$[CrCl(H_2O)_5]Cl_2.H_2O$	:	pale or bluish green colour
$[CrCl_2(H_2O)_4]Cl.2H_2O$	:	dark green colour

   Apart from their distinctive colours, the three isomers can be identified by the addition of excess of aqueous silver nitrate to their aqueous solutions, which precipitates silver chloride in the molar ratio of 3 : 2 : 1 respectively.

   (C) Co-ordination isomerism : This type of isomerism is observed in the co-ordination compounds having both cationic and anionic complex ions. The ligands are interchanged in both the cationic and anionic ions to form isomers. For example :

(i)	$[Co(NH_3)_6] [Cr(CN)_6]$	and	$[Cr(NH_3)_6] [Co(CN)_6]$
(ii)	$[Cu(NH_3)_4] [PtCl_4]$	and	$[Pt(NH_3)_4] [CuCl_4]$
(iii)	$[Cr(NH_3)_6][Cr(SCN)_6]$	and	$[Cr(NH_3)_4(SCN)_2][Cr(NH_3)_2(SCN)_4]$

   (D) Linkage isomerism : Co-ordination compounds having ambidentate ligands like NO_2^- and SCN^-, exhibit this type of isomerism. For example: $[Co(NH_3)_5(NO_2)]^{2+}$ has two isomeric forms having red and yellow colours. The red colour isomer is $[CO(NH_3)_5(ONO)]^{2+}$, while the yellow isomer is $[Co(NH_3)_5(NO_2)]^{2+}$. In the first cation we have Co-(ONO) link, while in the second case, Co-(NO_2) link is there.

2. **Stereo-isomerism :** This isomerism in coordination compounds is due to differences in arrangement of ligands in space around a given metal atom or ion. It is of following two types :
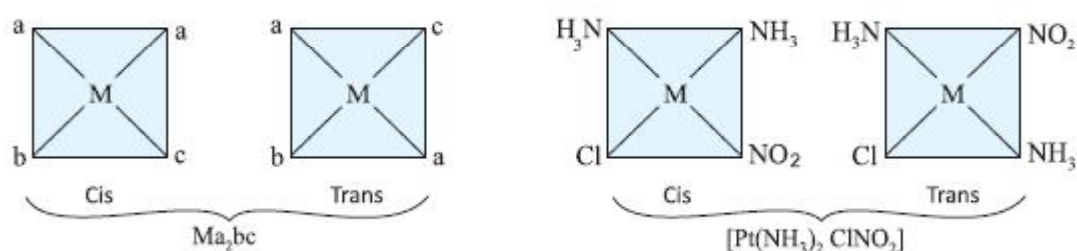
(A) Geometrical isomerism

(i) **Cis-trans isomerism :** This type of isomerism occurs in complexes having square planar and octahedral arrangement respectively. When similar groups are adjacent to each other, it is called cis isomer, whereas when similar groups are opposite to each other, it is called trans isomer.

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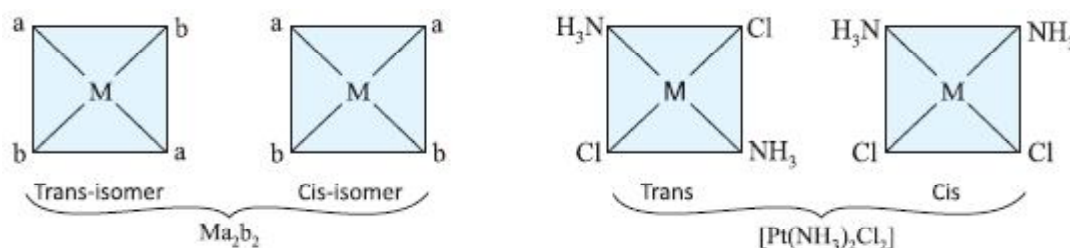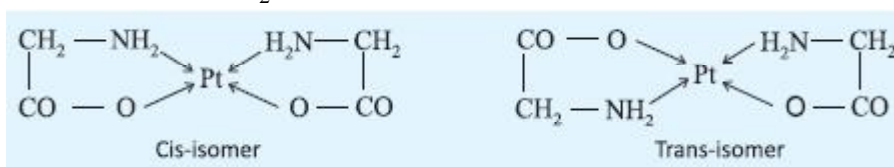

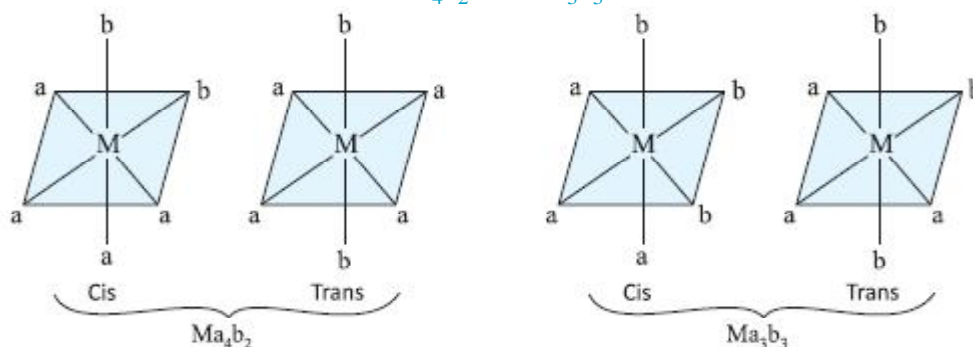(b) Complexes with general formula Ma_2bc can have cis-and trans-isomers.

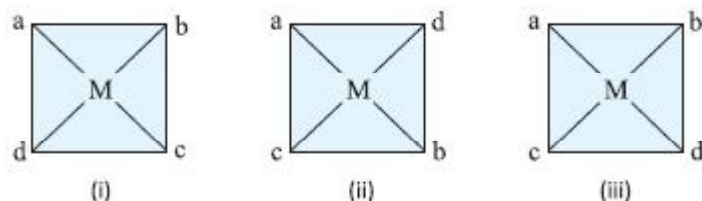(c) Square planar complexes having unsymmetrical bidantate ligands can also show geometrical isomerism.

For example $[Pt(Gly)_2]$ exhibit geometrical isomerism.

(d) Octahedral complexes : of type Ma_4b_2 and Ma_3b_3 exhibit geometrical isomerism.

Note : ➤ Complexes with general formula Mabcd can have three isomers isomers.

➤ Octahedral complexes of general formula, Mabcdef, can have fifteen isomers.

➤ The complexes of general formulae, Ma_3b or Mab_3, or Ma_4 of square planar geometry do not show isomerism.

➤ Geometrical isomerism does not occur in tetrahedral complexes, because the relative positions of the ligands attached to the central metal atom or ion is same w.r.t. each other.

(ii) Facial and Meridionial isomerism : Another type of geometrical isomerism occurs in octahedral co-ordination entities of the type $[Ma_3b_3]$ like $[Co(NH_3)_3(NO_2)_3]$. If each trio of donor atoms occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer shown in figure. Geometric isomer differ in their physical characterstics, out of which, dipole moments and visible/UV spectra are important.
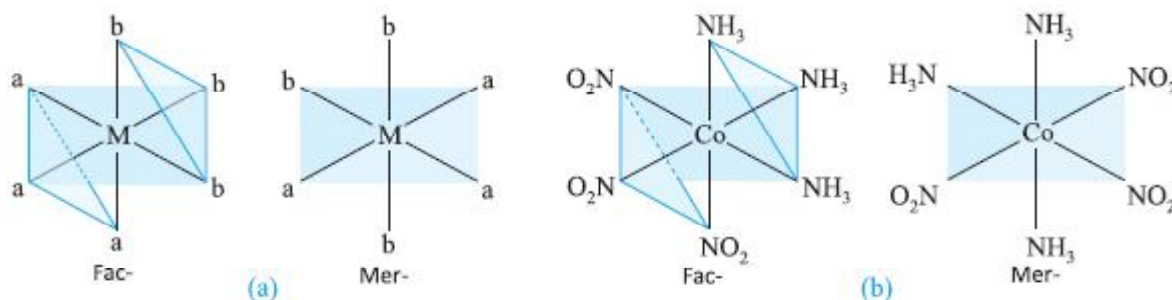
Note : $[Ma_3b_3]$ is more popularly classified using Facial & Meridional Isomerism as compared to *cis-trans* isomerism.

(B) Optical isomerism : The co-ordination compounds having same molecular formula but differing in their abilities to rotate directions of the plane of polarized light are said to exhibit optical isomerism and such molecules are called optical isomers (enantiomers or enantiomorphs).

(a) The optical isomers are pair of molecules which are non-super imposable mirror images of each other.

(b) They possess the property of chirality. The essential requirement for a substance to be optically active is that the substance should not have a plane of symmetry in its structure.

(c) Optical isomers of a compound have identical physical and chemical properties.

(d) The isomers which rotate the plane of polarized light to left direction are termed Leavo (ℓ-form). While the isomers which rotate the plane of polarized light to right direction are termed Dextro (d-form) .

➤ Optical isomers rarely occur in square planar complexes on account of the presence of axis of symmetry.

➤ Optical isomerism is expected in tetrahedral complexes of the type *Mabcd* but no optical isomer has been isolated until now.

➤ General formulae of optically active complexes :

(i) $[M(AA)_3]^{n\pm}$, $[M(AA)_2a_2]^{n\pm}$, $[M(AA)_2ab]^{n\pm}$, $[M(AA)a_2b_2]^{n\pm}$ (where AA are symmetrical bidentate ligands)

(ii) $[Ma_2b_2c_2]^{n\pm}$, $[Mabcdef]^{n\pm}$, $[M(AB)_3]^{n\pm}$ (where AB are unsymmetrical ligands)
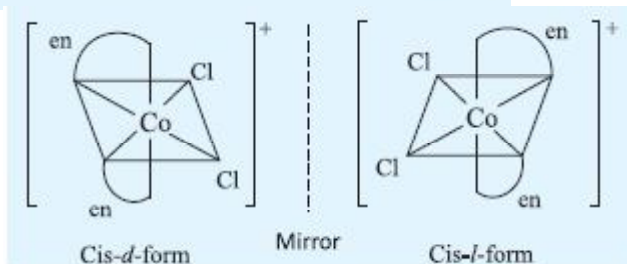
For Examples :

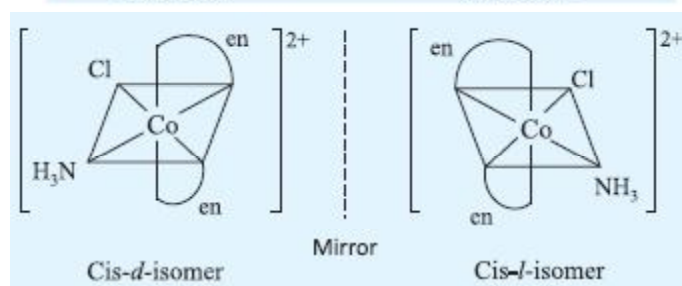**(A)** $[M(AA)_3]^{n\pm}$: eg. $[Co(en)_3]^{3+}$

d-form   Mirror   *l*-form   'Meso' or optically inactive form (if exists)
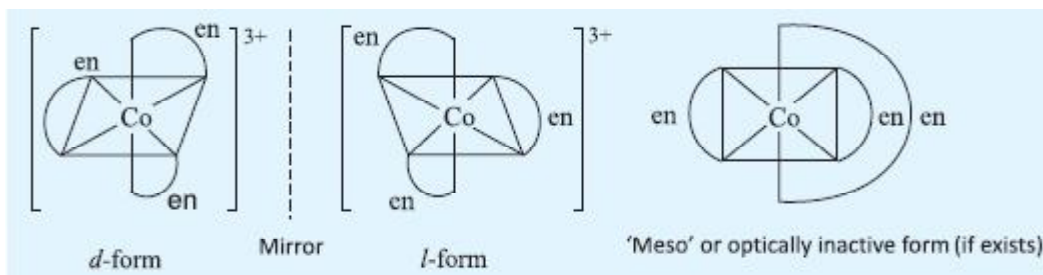
(B) $[M(AA)_2a_2]^{n\pm}$ $[Co(en)_2Cl_2]^+$

Note : The trans form of $[M(AA)_2a_2]^{n\pm}$ does not show optical isomerism.

Cis-*d*-form   Mirror   Cis-*l*-form

(C) $[M(AA)_2 ab]^{n\pm}$ $[Co(en)_2(NH_3)Cl]^{2+}$

Cis-*d*-isomer   Mirror   Cis-*l*-isomer

(D) $[M(AA)a_2b_2]^{n\pm}$ eg . $[CrCl_2(en)(NH_3)_2]^+$.
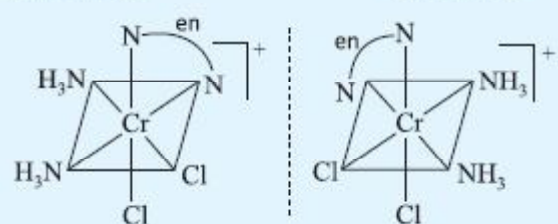
(E) $[Ma_2b_2c_2]^{n\pm}$ eg : $[Pt(py)_2 (NH_3)_2 Cl_2]^{2+}$

Cis-*d*-isomer   Mirror   Cis-*l*-isomer
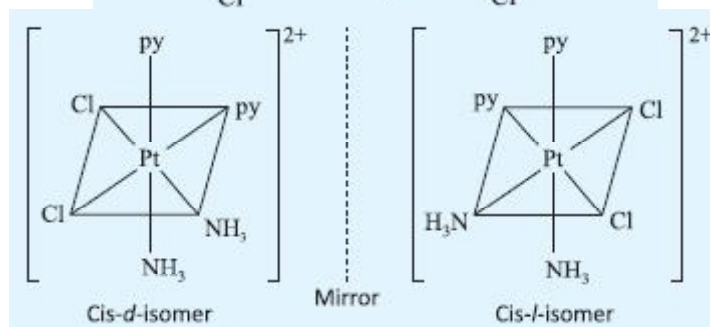
(F) [Mabcdef]   eg : [Pt(py)NH$_3$NO$_2$ClBrI]

d-isomer   Mirror   l-isomer

(G) [M(AB)$_3$]   eg : [Cr(gly)$_3$]

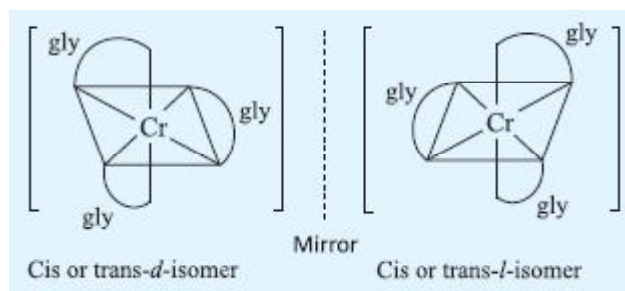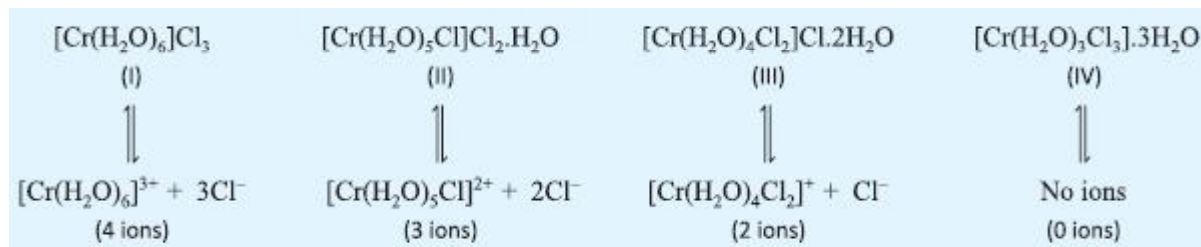Cis or trans-d-isomer   Mirror   Cis or trans-l-isomer

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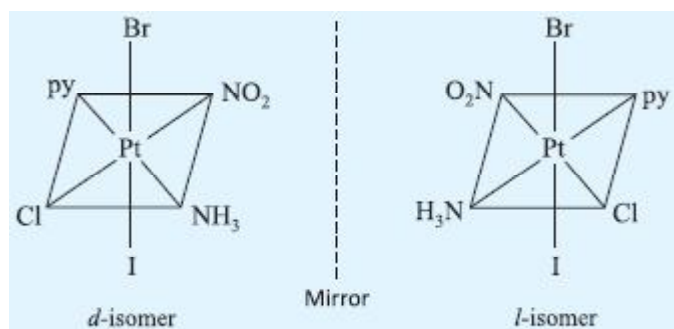
Illustration - 5   *Write hydrate isomers of the following, and also discuss the conductance of the isomers.*
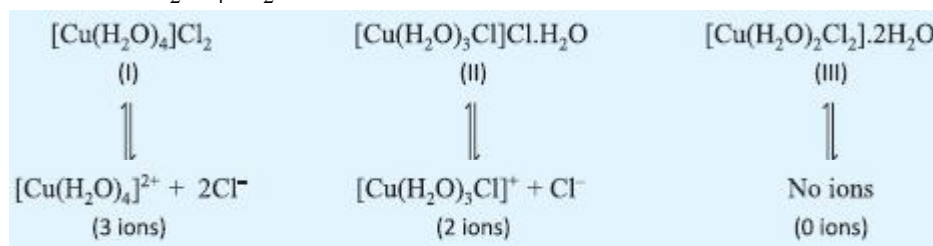
(*a*) $[Cr(H_2O)_6]Cl_3$ (*b*) $[Cu(H_2O)_4]Cl_2$

SOLUTION :

(*a*) Hydratic isomers of $[Cr(H_2O)_6]Cl_3$

$[Cr(H_2O)_6]Cl_3$	$[Cr(H_2O)_5Cl]Cl_2.H_2O$	$[Cr(H_2O)_4Cl_2]Cl.2H_2O$	$[Cr(H_2O)_3Cl_3].3H_2O$
(I)	(II)	(III)	(IV)
⇕	⇕	⇕	⇕
$[Cr(H_2O)_6]^{3+} + 3Cl^-$	$[Cr(H_2O)_5Cl]^{2+} + 2Cl^-$	$[Cr(H_2O)_4Cl_2]^+ + Cl^-$	No ions
(4 ions)	(3 ions)	(2 ions)	(0 ions)

Greater the number of ions, $[Cr(H_2O)_5Cl]^{2+} + 2Cl^-$ more is the conductance. Hence, decreasing order of conductance is I > II > III > IV.

(*b*) Hydrate isomers of $[Cu(H_2O)_4]Cl_2$

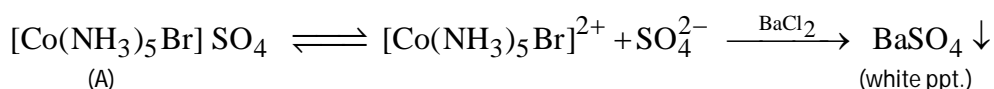| $[Cu(H_2O)_4]Cl_2$	$[Cu(H_2O)_3Cl]Cl.H_2O$	$[Cu(H_2O)_2Cl_2].2H_2O$
(I)	(II)	(III)
⇕	⇕	⇕
$[Cu(H_2O)_4]^{2+} + 2Cl^-$	$[Cu(H_2O)_3Cl]^+ + Cl^-$	No ions
(3 ions)	(2 ions)	(0 ions)

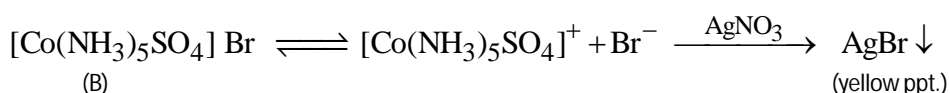Hence, decreasing order of conductance is I > II > III.

Illustration - 6 *One mole of the complex has two isomers A and B. Each has one Co^{3+}, five NH_3, one Br^- and one SO_4^{2-} stoichiometrically. A gives white precipitate with $BaCl_2$ while B gives yellow precipitate with $AgNO_3$. What are A and B ? What is the type of isomerism shown by them ?*

SOLUTION :

(*a*) Since A gives white precipitate of $BaSO_4$ with $BaCl_2$ solution, A is

$$[Co(NH_3)_5 Br] SO_4 \rightleftharpoons [Co(NH_3)_5 Br]^{2+} + SO_4^{2-} \xrightarrow{BaCl_2} BaSO_4 \downarrow$$
$$\quad (A) \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (white\ ppt.)$$

(*b*) Since B gives a yellow precipitate of AgBr with $AgNO_3$, B is :

$$[Co(NH_3)_5 SO_4] Br \rightleftharpoons [Co(NH_3)_5 SO_4]^+ + Br^- \xrightarrow{AgNO_3} AgBr \downarrow$$
$$\quad (B) \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (yellow\ ppt.)$$

Also, A and B are ionisation isomers.

Illustration - 7 (*a*) *Write structures of all geometric isomers of square planar complexes.*

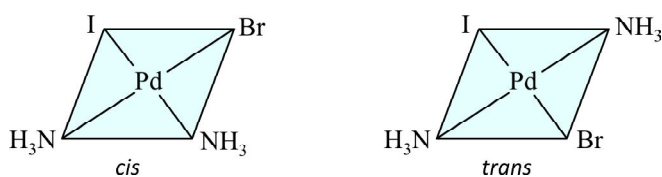   (*i*) $[Pd(NH_3)_2(Br)(I)]$ (*ii*) $[Ni(en)Cl_2]$
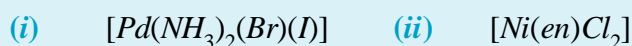
(*b*)   *For which of the following complexes are optical isomers possible ? Explain your answers and draw structures of enantiomers.*   (*i*) $[Cr(NH_3)_4(C_2O_4)]^+$ (*ii*) $[Cr(NH_3)_2(C_2O_4)_2]^-$

(*c*)   *The compounds(s) that exhibit(s) geometrical isomerism is(are) :*

   (*i*) $[Pt(en)Cl_2]$ (*ii*) $[Pt(en)_2]Cl_2$ (*iii*) $[Pt(en)_2Cl_2]Cl_2$ (*iv*) $[Pt(NH_3)_2Cl_2]$

SOLUTION :

(*a*) (*i*)   Geometrical isomers of $[Pd(NH_3)_2(Br)(I)]$

(*ii*) $[Ni(en)Cl_2]$ Only one isomer is possible as ethylene diamine (en) cannot span the trans position.
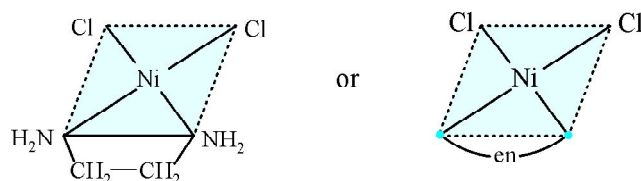
(**b**) Optical isomerism is possible in $[Cr(NH_3)_2(C_2O_4)_2]^-$ (because it is of the type $[M(AA)_2a_2]^{n\pm}$) but $[Cr(NH_3)_4(C_2O_4)]^+$ will not exhibit optical isomerism.

Note : General formulae of optically active complexes :

      (**i**) $[M(AA)_3]^{n\pm}$, $[M(AA)_2a_2]^{n\pm}$, $[M(AA)_2ab]^{n\pm}$, $[M(AA)a_2b_2]^{n\pm}$ (where AA are symmetrical -bidentate ligands)

      (**ii**) $[Ma_2b_2c_2]^n$, $[Mabcdef]$, $[M(AB)_3]^{n\pm}$ (where AB are unsymmetrical ligands)

The geometrical isomeris of $[Cr(NH_3)_2(C_2O_4)]^-$ are (one *trans* and three *cis* isomers) :
Now, only *cis*-isomers can exhibit optical isomerism because *trans*-isomers have two superimposable mirror images.
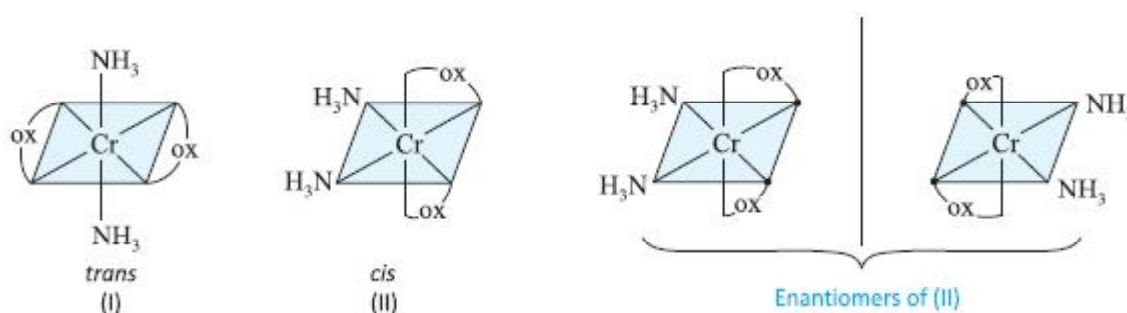
Thus, $[Cr(NH_3)_2(C_2O_4)]^-$ has two geometrical (one *trans* and one *cis*) isomers while two optical isomers.

(**c**) $[Pt(en)_2]Cl_2$ can not show geometrical isomerism as all ligands attached to the central atom (Pt) are same and $[Pt(en)Cl_2]$ does not show geometrical isomerism as discussed in Q.7(a) part (ii). Rest both $[Pt(en)Cl_2]Cl_2$ and $[Pt(NH_3)Cl_2]$ are capable of showing geometrical isomerism as shown below :
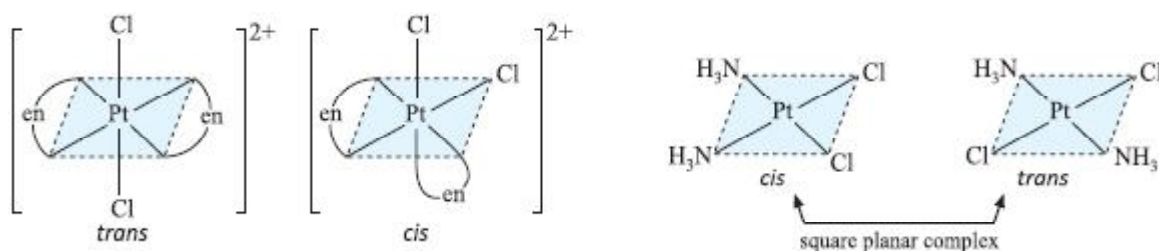
WERNER'S CO-ORDINATION THEORY   Section - 4

Werner's Co-ordination Theory

Alfred Werner was the first to formulate a theory to give a correct explaination for the characteristics of the co-ordination compounds. The fundamental postulates of Werner's theory are :

(i) Metals possess two types of valencies, namely, primary (principal) and secondary (auxillary) valency.

(ii) Primary valencies are those which a metal normally exhibits in the formation of its simple salts. Thus, in the formation of $PtCl_4$, $CuSO_4$ and $AgCl$ the primary valencies of Pt, Cu and Ag are 4, 2 and 1 respectively. Primary valencies may be ionisable. They are non-directional and are only satisfied by negative ions.

(iii) Secondary valencies are those which a metal cation exercises towards a neutral molecule or negative group in the formation of its co-ordination complexes. Secondary valencies are non-ionisable and are satisfied by negative ions, neutral molecules (or even somtimes by some positive groups), having atleast one lone pair of electrons (like H_2O, NH_3). In every case, the co-ordination number of the metal must be fulfilled. In modern terminology, the primary valency corresponds to oxidation number and secondary valency to the co-ordination number of the central metal.

(iv) The secondary valencies are always directed towards a fixed position in space about the central metal ion. The number and arrangements of ligands in space determines the sterochemistry of a complex. For example, in case of six secondary valencies the arrangement of secondary valencies is a regular octahedral while in case of four secondary valencies arrangement might be either in a square planar or a tetrahedral manner. Thus, this postulate predicates of existence of a variety of isomerisms in co-ordination compounds. Remember that primary valencies are non-directional.

(v) To distinguish between the two types of valencies, Werner introduced square brakets [ ] to enclose atoms making up the co-ordination complex and which are therefore not ionised. The portion enclosed in the brackets is known as co-ordination sphere and the portion present outside the bracket as ionising sphere.

(vi) It is the directional nature of secondary valency due to which co-ordination compounds exhibits the phenomenon of isomerism.

The important aspect of the structure of five different complexes of $PtCl_4$ with ammonia prepared by Werner are shown in table.

Co-ordination compounds of $PtCl_4$ with NH_3

Complex	Modern formula	Number of Cl^- ions	Total number of ions formed
$PtCl_4.6\,NH_3$	$[Pt(NH_3)_6]Cl_4$	4	5
$PtCl_4.6\,NH_3$	$[PtCl(NH_3)_5]Cl_3$	3	4
$PtCl_4.6\,NH_3$	$[PtCl_2(NH_3)_4]Cl_2$	2	3
$PtCl_4.6\,NH_3$	$[PtCl_3(NH_3)_3]Cl$	1	2
$PtCl_4.6\,NH_3$	$[PtCl_4(NH_3)_2]$	0	0 (non-electrolyte)

In all these compounds, platinum exhibits a primary valency (oxidation number) of four and secondary valency (co-ordination number) of six.

(vii) Primary valency in the complex, is represented by '. . . . .' and secondary valency by '_____'.

(viii) In all cases, metal or metal ion should satisfy both primary and secondary valencies. Some negative ions may satisfy primary as well as secondary valencies (dual nature). In the complexes, they are represented as '........'.
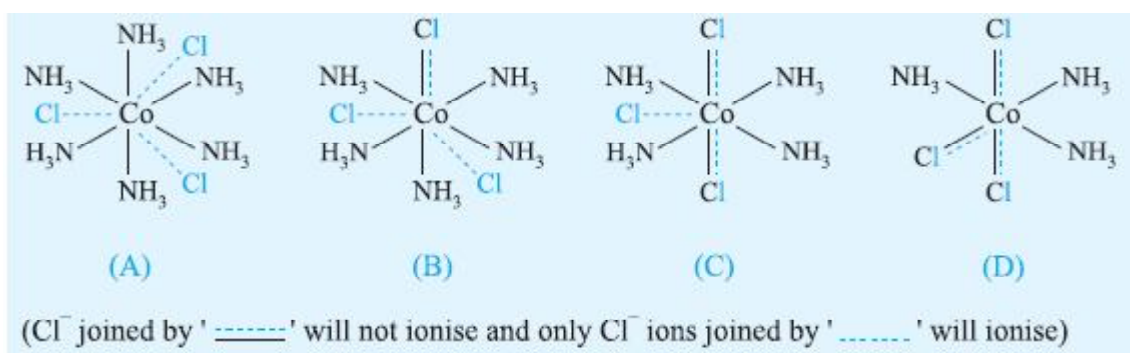
Werner's Representation of Complexes

Consider the case of $CoCl_3.xNH_3$,   where the maximum value of x = C.N. of Co(3+) (which is 6) and the minimum value of x = C.N. - O.N. = 3

Various structures are summarised in Table.

Werner's co-ordination compounds

	Werner complex	Modern notation	Ionisation	Secondary valency satisfied by	Primary valency satisfied by
(A)	$CoCl_3.6NH_3$	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]^{3+}+3Cl^-$	six (NH_3)	three (Cl^-)
(B)	$CoCl_3.5NH_3$	$[CoCl(NH_3)_5]Cl_2$	$[CoCl(NH_3)_5]^{2+}+2Cl^-$	five (NH_3) and one (Cl^-)	three (Cl^-) including one (Cl^-) with dual nature
(C)	$CoCl_3.4NH_3$	$[CoCl_2(NH_3)_4]Cl$	$[CoCl_2(NH_3)_4]^++Cl^-$	four (NH_3) and two (Cl^-)	three (Cl^-) including two (Cl^-) with dual nature
(D)	$CoCl_3.3NH_3$	$[CoCl_3(NH_3)_3]$	$[CoCl_3(NH_3)_3]$	three (NH_3) and three (Cl^-)	three (Cl^-) all with dual nature

- From table, it is clear that conductance of the complexes will be in the order $D < C < B < A$.
- They are represented as shown in the next page.

(A)   (B)   (C)   (D)

(Cl^- joined by ' ------ ' will not ionise and only Cl^- ions joined by ' .... ' will ionise)

Note : Compund A & B have colours yellow and purple respectively but compound C (with empirical formula $[CoCl_2(NH_3)_4]Cl$) is found to exist in two colours i.e green and violet showing that there must be two isomers for empirical formula $[CoCl_2(NH_3)_4]Cl$.

Werner was the first to describe the bonding features in co-ordination compounds. But his theory could not answer basic questions like :

(i)   Why only certain elements possess the remarkable property of forming co-ordination compounds ?

(ii)   Why the bonds in co-ordination compounds have direction optical properties ?

(iii)   Why co-ordination compounds have characteristic magnetic aqnd optical properties ?

Many approaches have been put forth to explain the nature of bonding in co-ordination compounds viz. Valence Bond Theory (VBT). Cristal Field Theory (CFT). Ligand Field Theory (LFT) and Molecular Orbital Theory (MOT). However we shall be restricting ourselves to VBT and CFT only.

BONDING IN CO-ORDINATION COMPOUNDS : VALENCE BOND THEORY Section - 5

The theory was developed by Pauling in 1931. The basic principles involved in this theory are :

(a)   Orbital hybridization : The model utilizes the hybridisation of s, p and d valence orbitals of central metal atom or ion (in which electron pairs donated by the ligands are accomodated) to account for observed structures and magnetic properties.

(b)   Bonding between ligand and the metal atom or ion : From the valence point of view, formation of complex involves reaction between lewis bases (ligands) and lewis acids (metal atom/ion) with the formation of co-ordinate covalent (or dative) bonds between them.

(c)   Relation between the observed magnetic behaviour and the bond type : That is, the geometry of co-ordination entity can be predicted if its magnetic behaviour is known.

The following are the main postulates of this theory :

(i)   Metal-ligand bond arises by the donation of pairs of electrons by ligands to the empty hybridised orbitals of central metal atom or ion. Remember it is basically overlap of atomic orbital of both the entities

(ii)   In order to accommodate these electrons, the metal ion must possess same number of vacant orbitals of equal energy. These orbitals of metal atom (s,p or d) undergo hybridisation to give a set of hybrid orbitals of equal energy and with definite directional properties. These vacant hybrid orbitals now overlap with the ligands to form strong coordinate bonds.

(iii)   The non-bonding electrons of the metal occupy the inner orbitals. They are grouped in accordance with Hund's rule. However, under the influence of some strong ligands, there may be some rearrangement of inner electrons in the atomic orbitals (against Hund's rule). During rearrangement generally pairing takes place and consequently some orbitals are vacated and made available for hybridisation.

(iv) (For Octahedral complexes only) The d-orbitals involved in the hybridisation may be either $(n-1)$ d-orbitals or n d-orbitals***. The complexes formed in two ways are referred to as Inner orbitals complex (or entity) or Outer orbital complex (entity). On the basis of spin they are also referred as low spin and high spin   complexes respectively.

(*** 'n' refers to the outermost principle shell of the central metal atom)

(v) If a complex contains unpaired electrons, it is paramagnetic in nature, whereas if it does not contain unpaired electrons, it is diamagnetic in nature.

(vi) On the basis of value of magnetic moment, we can predict the number of unpaired electrons present in the complex. If we know the number of unpaired electrons in the metal complex, then it is possible to predict the geometry of complex species.

$$\text{Magnetic Moment, } \mu_s = \sqrt{n\,(n+2)} \text{ B.M.}$$

B.M. = Bohr Magneton, it is the unit of magnetic moment
s = spin only value
n = no. of unpaired electrons in the central metal atom/ion

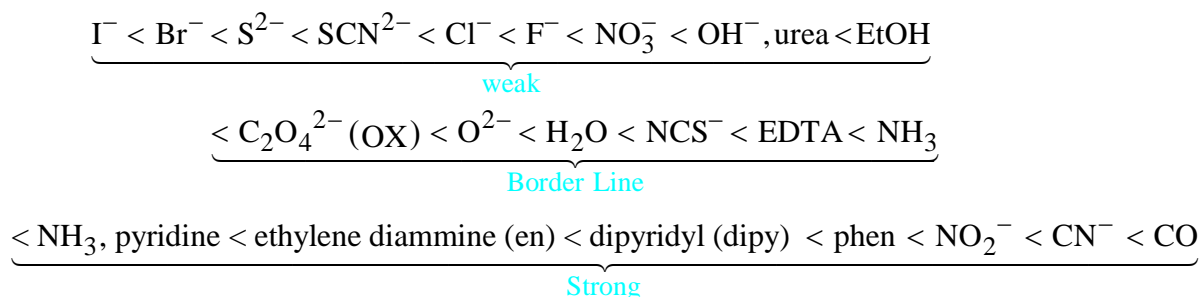| Magnetic moment (Bohr magnetons)	0	1.73	2.83	3.83	4.90	5.92
Number of unpaired electrons	0	1	2	3	4	5

(vii) Octahedral, square planar and tetrahedral complexes are formed as a result of d^2sp^3 (or sp^3d^2), dsp^2 and sp^3 hybridisation respectively.

For predicting the type of geometry (structure) of a complex species, the following guidelines would be helpful :

(i) Electronic configuration of first transition series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$3d^1\ 4s^2$	$3d^2\ 4s^2$	$3d^3\ 4s^2$	$3d^5\ 4s^1$	$3d^5\ 4s^2$	$3d^6\ 4s^2$	$3d^7\ 4s^2$	$3d^8\ 4s^2$	$3d^{10}\ 4s^1$	$3d^{10}\ 4s^2$

(ii) For co-ordination number 4, the hybridizations possible are sp^3 and dsp^2, having tetrahedral and square planar geometries respectively, while for co-ordination number 6, the hybridizations possible are d^2sp^3 and sp^3d^2, having octahedral geometry in both the cases.

(iii) There are two types of ligands namely strong field and weak field ligands. A strong field ligand is capable of forcing the electrons of the metal atom ion to pair up (if required). A weak field ligand is incapable of making the electrons of the metal atom/ion to pair up.

(iv) Some ligands have been arranged below from the weakest to the strongest. This arrangement is called as spectrochemical series. (As shown in the next page)

$$I^- < Br^- < S^{2-} < SCN^{2-} < Cl^- < F^- < NO_3^- < OH^-, urea < EtOH$$
<center>weak</center>

$$< C_2O_4^{2-}(OX) < O^{2-} < H_2O < NCS^- < EDTA < NH_3$$
<center>Border Line</center>

$$< NH_3, pyridine < ethylene\ diammine\ (en) < dipyridyl\ (dipy) < phen < NO_2^- < CN^- < CO$$
<center>Strong</center>

Note :
- This series has been determined experimentally and is not a postulate of VBT. However, we can use it to predict the structure, electronic configuration, magnetic properties etc. of a co-ordination complex.
- Ligands given in the borderline criteria act both as strong and weak field ligands. By knowing the value of magnetic moment, it may be suggested that whether they act as a strong and weak ligand in a particular case.
- Generally NH_3 behaves as a strong field ligand and H_2O (or ligands nearby it in the series) as a weak field ligand. The compound $[Co(OX)_3]^{3-}$, is one of the few rare examples where oxalate (OX^-) ligand acts as a strong field ligand.

**(vi)** The common types of hybridisations are :

| C.N.	Hybridization	Geometry	Example
2	sp	Linear	$[Ag(NH_3)_2]Cl$, $K[Ag(CN)_2]$
3	sp^2	Trigonal planar	$K[HgI_3]$
4	sp^3	Tetrahedral	$[MnX_4]^{2-}$, $[FeCl_4]^{2-}$, $[Ni(CO)_4]$, $[Ni(X_4)]^{2-}$, $[ZnCl_4]^{2-}$ Where $X = Cl^-, Br^-, I^-$
4	dsp^2	Square planar	$[Cu(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$
5	sp^3d	Square pyramidal	$[SbF_5]^{2-}$
5	dsp^3	Trigonal bipyramidal	$[Fe(CO)_5]$, $[CuCl_5]^{3-}$
6	sp^3d^2	Octahedral	$[Fe(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, $[FeF_6]^{3-}$, $[Co(H_2O)_6]^{2+}$
6	d^2sp^3	Octahedral	$[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3-}$

(A) Four coordinated complexes :
   (A. 1)   Tetrahedral Complexes

**Illustration - 8**   *Discuss the formation of* $[Ni(CO)_4]^0$

SOLUTION :   Oxidation state of Nickel in this complex is '0'. Its electronic configuration is $[Ar]\, 3d^8\, 4s^2$.
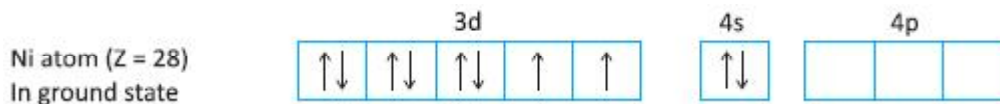
The CO ligand being a strong ligand will force the pairing of electrons in two half filled orbitals and then the pair of electrons from 4s will go to 3d orbital, and thus, the 4s orbital is vacated and can now accept an electron pair.
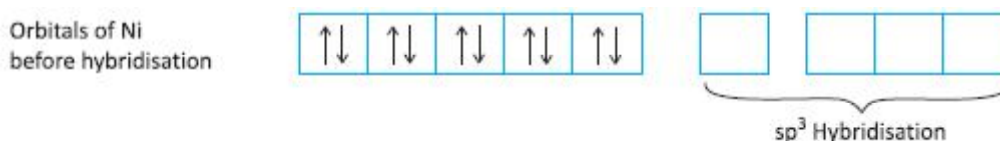
Now, the empty 4s and 4p orbitals (i.e 4s, $4p_x$, $4p_y$ and $4p_z$) hybridize (or mix) to form four equivalent sp^3 hybrid orbitals, each of which accepts an electron pair.
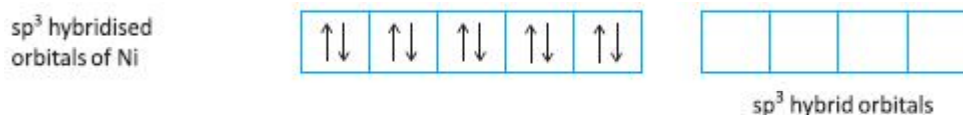
Now, each of the four sp^3 hybrid orbitals accepts an electron pair from carbon monoxide ligands forming $Ni(CO)_4$.
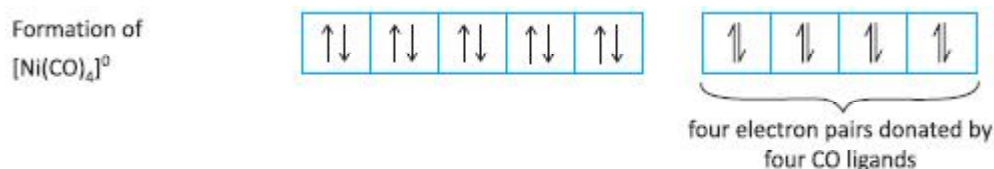
Thus, the resulting complex has tetrahedral structure and diamagnetic due to absence of unpaired electrons (magnetic moment = 0).

Illustration - 9   *Discuss the formation of* $[CoCl_4]^{2-}$

SOLUTION :

Oxidation state of Co in complex = +2 ;   Outer electronic configuration of :   Co atom = $3d^7 4s^2$

$\Rightarrow$ $Co^{2+} = 3d^7$
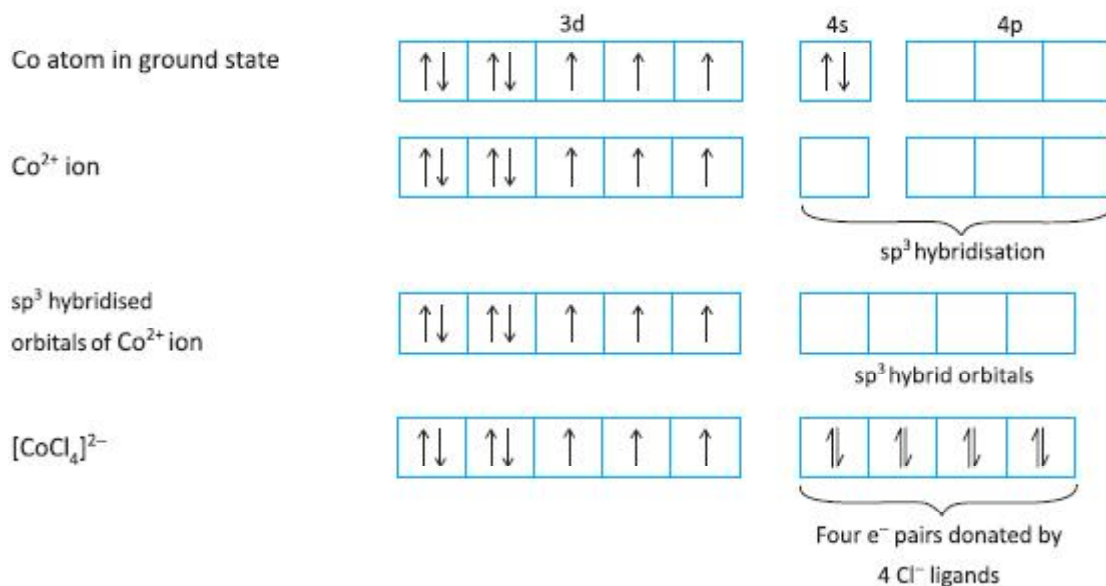
(i) Cl^- being weak ligand is unable to force the pairing of electrons.

(ii) Hybridisation : sp^3

(iii) Geometry : Tetrahedral

(iv) Magnetism :

➤ No. of unpaired electrons $= 3$

➤ Paramagnetic

➤ Magnetic moment

$$(\mu_s) = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ B.M.}$$

Illustration - 10 *Discuss the formation* $[Zn(NH_3)_4]^{2+}$.

SOLUTION :

Oxidation state of Zn in complex $= +2$; Outer electronic configuration of : Zn atom $= 3d^{10}4s^2$

$\Rightarrow$ $Zn^{2+} \equiv 3d^{10}$

(i)   Hybridisation : sp^3

(ii)   Geometry : tetrahedral

(iii)   Magnetism :

➤   No. of unpaired $e^- = 0$

➤   Diamagnetic

➤   Magnetic moment, $\mu_s = 0$ B.M.

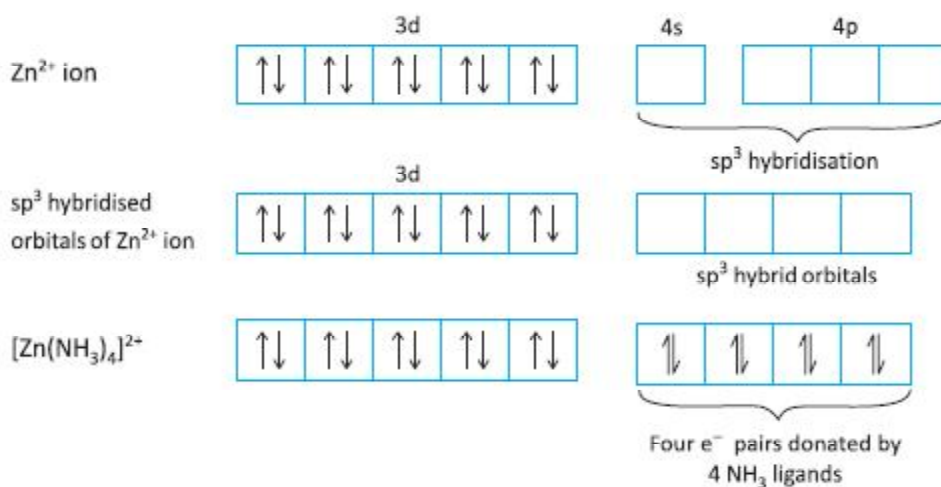**(A.2)**   **Square planar complexes :**

Illustration - 11   *Discuss the formation of $[Pt(NH_3)_2Cl_2]$.*

SOLUTION :

Oxidation state of Pt in complex = +2 ; Outer electronic configuration of :   Pt atom $\equiv 5d^8 6s^2$

$\Rightarrow$ Pt^{2+} ion $\equiv 5d^8$
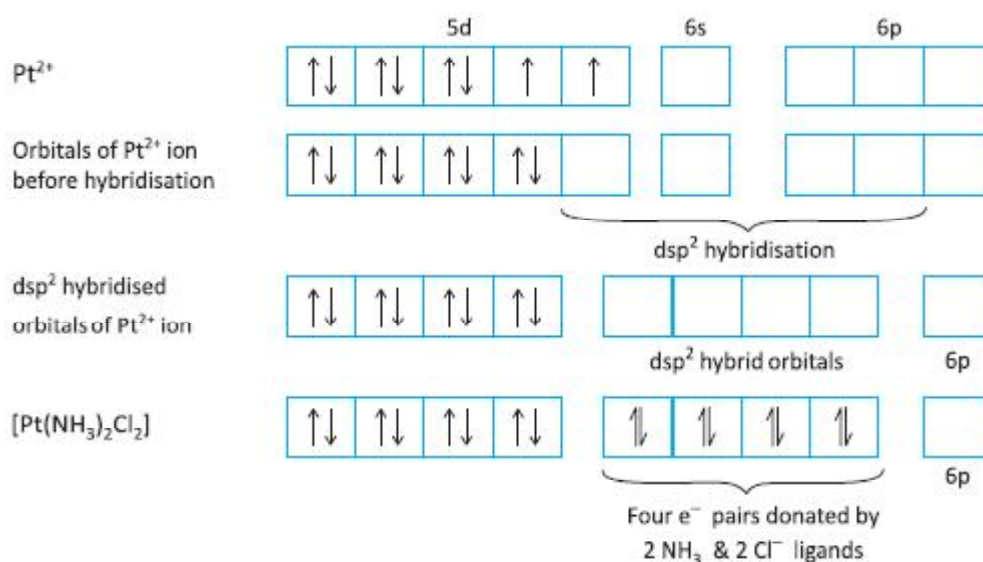
(i) NH_3 being a strong ligand forces pairing of electrons of two half filled 5d-orbitals.

(ii)   Hydrisation : dsp^2

(iii) Geometry :   Square planar

(iv)   Magnetism

➤   No. of unpaired $e^- = 0$

➤   Diamagnetic

➤   Magnetic moment, $\mu_s = 0$

Illustration - 12   *Disscuss the formation of $[Cu(NH_3)_4]^{2+}$.*

SOLUTION :

Oxidation state of Cu $\equiv$ +2   ;   Outer electronic configuration of :   Cu atom $\equiv 3d^{10}4s^1$

$\Rightarrow$ Cu^{2+} ion $\equiv 3d^9$

(i) Hybridisation : dsp^2

(ii) Geometry : Square planar

(iii) Magnetism

➤ No. of unpaired e$^-$ = 1

➤ Paramagnetic

➤ Magnetic moment,

$$\mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.732 \text{ B.M}$$

Illustration - 13 *Discuss the formation of* **(A)** $[Ni(CN)_4]^{2-}$ **(B)** $[NiCl_4]^{2-}$

SOLUTION :

(A) Formation of $[Ni(CN)_4]^{2-}$;

Oxidation state of Ni = +2 ; Outer electronic configuration of : Ni atom = 3d^{8}4s^2
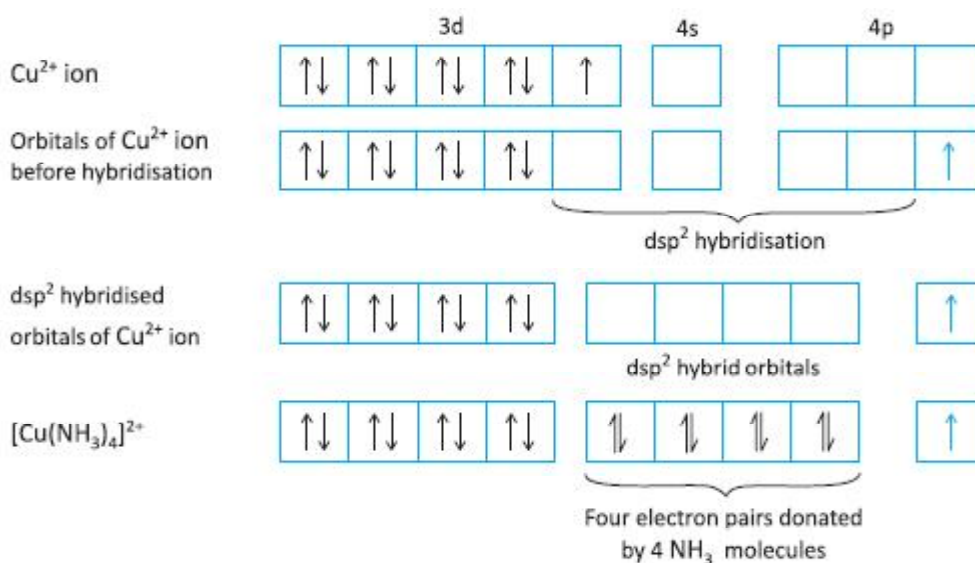
$\Rightarrow$ Ni^{2+} ion = 3d^8
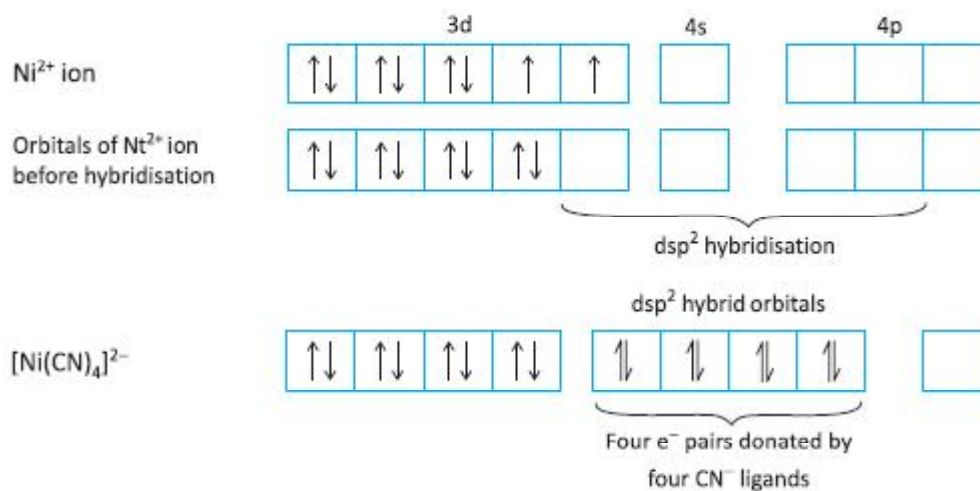
(i) CN⁻ being a strong ligand, forces pairing of electron of two half filled 3d orbitals.

(ii) Hybrisation : dsp^2

(iii) Geometry : Square planar

(iv) Magnetism

➤ No. of unpaired $e^- = 0$

➤ Diamagnetic

➤ Magnetic moment $= 0$ B.M

(B) Formation of $[NiCl_4]^{2-}$

Oxidation state of Ni = +2 ; Outer electronic configuration of : Ni atom = $3d^8 4s^2$
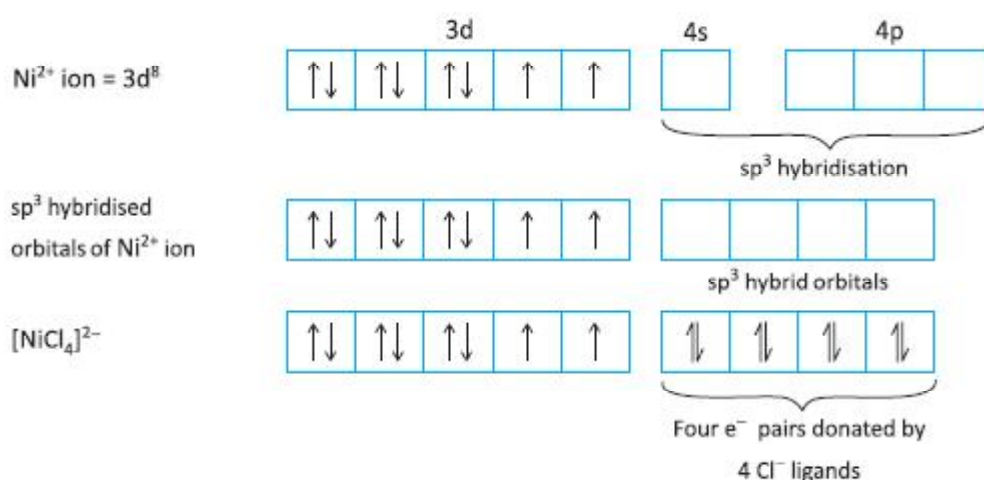
$\Rightarrow$ Ni²⁺ ion = $3d^8$

(i) Cl⁻ being weak ligand is unable to force the pairing of electrons.

(ii) Hybridisation : sp^3

(iii) Geometry : Tetrahedral

(iv) Magnetism

➤ No. of unpaired $e^- = 2$

➤ Paramagnetic

➤ Magnetic moment

$$= \sqrt{2(2+2)} = 2.83 \, \text{B.M}$$

Thus the c-oordination entities $[Ni(CN)_4]^{2-}$ & $[NiCl_4]^{2-}$ illustrate the useful rule originally called" the magnetic criteria of bond type", That is, the geometry of a co-ordinated entity can be predicted if its magnetic properties are known. In above case this theory allows prediction of geometry of a four co-ordinated d^8 complex : If the complex is diamagnetic then its shape will be "Square Planar" and if it is paramagnetic then its shape will be "Tetrahedral".

Note : The above generalisation of VB theory is not accurate and is one of its draw backs.

(B) Six Co-ordinated Complexes

In an octahedral complex, two types of complexes occur i.e., inner orbital complex and outer orbital complex. This distinction between inner and outer orbital complex is based purely on magnetic measurements. In inner, orbital complex, $(n-1)d$ orbitals are used for hybridization whereas in outer orbital complex, nd orbitals are used.

d²sp³ hybridization
(inner orbital complex)

sp³d² hybridization
(outer orbital complex)
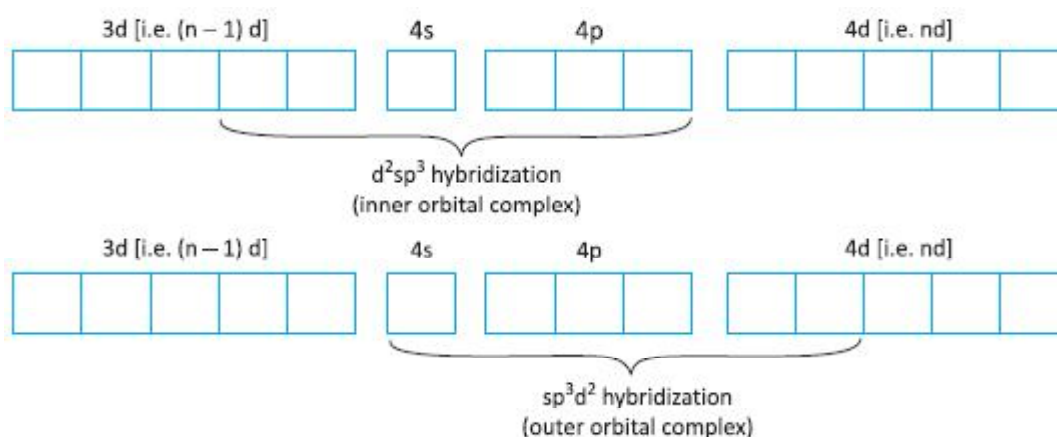
Illustration - 14   *Discuss the formation of* $[Cr(NH_3)_6]^{3+}$.

SOLUTION :

Oxidation state of $Cr = +3$;   Outer electronic configuration of :   Cr atom $= 3d^5\, 4s^1$

$\Rightarrow$ Cr^{3+} ion $= 3d^3$
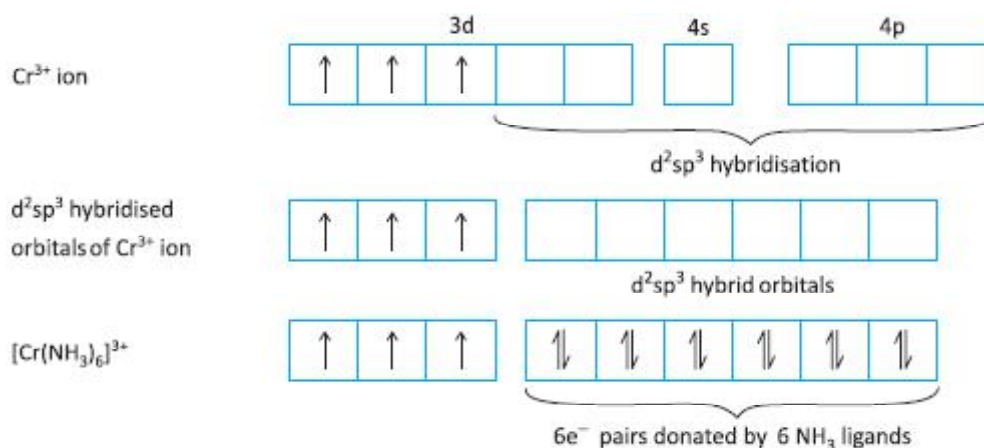
(i)   Hybridisation : d^2sp^3

(ii)   Geometry = Octahedral

(iii)   Inner orbital complex

(iv)   Spin paired (low spin complex)

(v)   Magnetism :

➤   No. of unpaired e $= 3$

➤   Paramagnetic

➤   Magnetic moment,

$$\mu_s = \sqrt{3(3+2)} = 3.287 \text{ B.M}$$

Illustration - 15 / *Discuss the formation of Ferricyanide ion,* $[Fe(CN)_6]^{3-}$.

SOLUTION :

Oxidation state of Fe = +3 ;   Outer electronic of figuration of :   Fe atom = $3d^6 \ 4s^2$

$\Rightarrow$ Fe^{3+} ion = $3d^5$
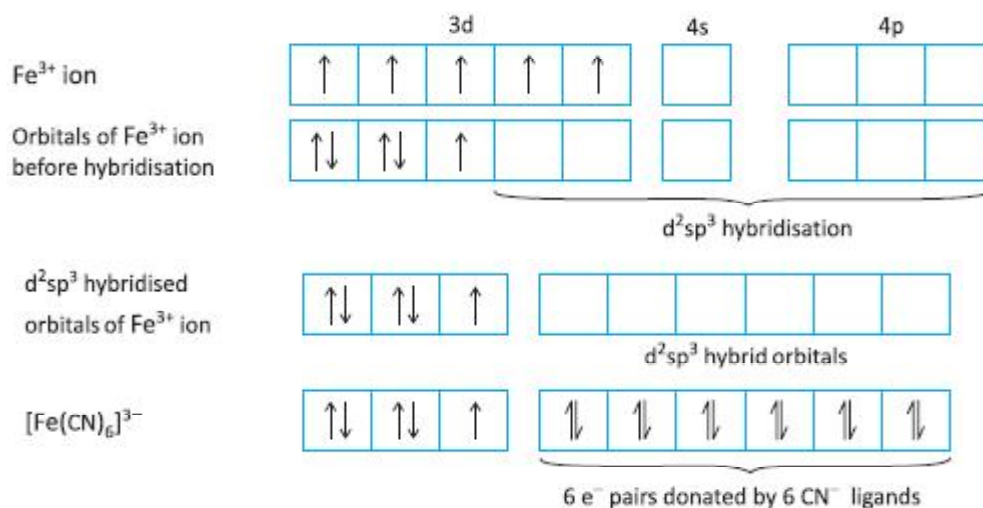
(i)   CN$^-$ being strong ligand forces pairing of electrons of half field 3d-orbitals

(ii)   Hybridisation : d^2sp^3,

      Geometry : Octahedral

(iii)   Inner orbital complex,

      Spin paired (low spin complex)

(vi)   Magnetism :   No. of unpaired e = 1

➤   Paramagnetic

➤   Magnetic moment,

      μ_s =1.732 B.M

Illustration - 16 / *Formation of* $[CoF_6]^{3-}$:

SOLUTION :

Oxidation state of Co = +3 ;   Outer electronic configuration of :   Co atom $\equiv 3d^7 4s^2$

$\Rightarrow$ Co^{3+} ion = $3d^6$
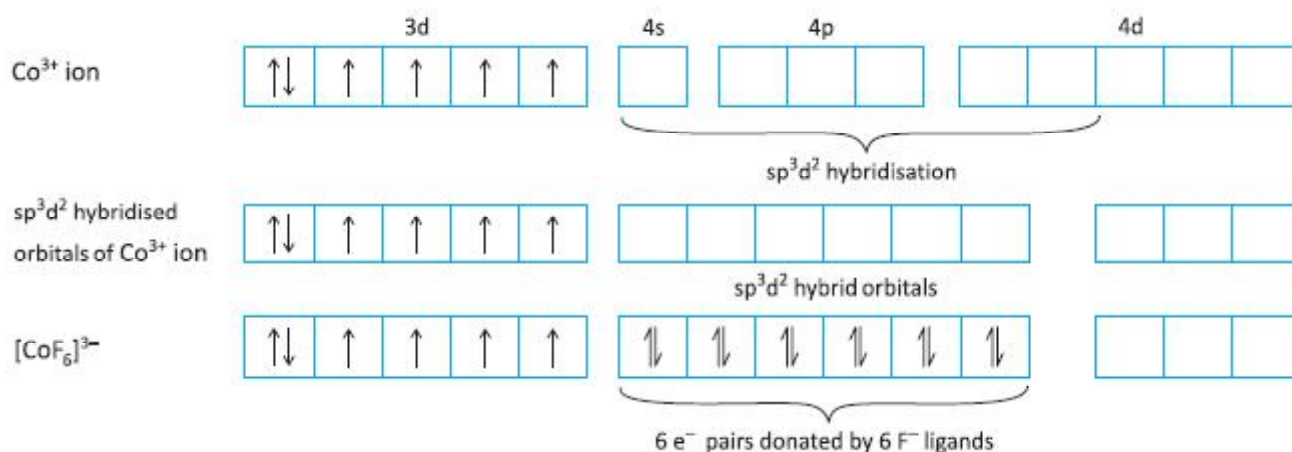
(i) F⁻ being weak ligand is not able to force pairing of electrons.

(vi) Magnetism :
- ➤ No. of unpaired e = 4
- ➤ Paramagnetic
- ➤ Magnetic moment,

$$\mu_s = \sqrt{4(4+2)} = 4.90 \text{ B.M}$$

(ii) Hybridisation : sp^3d^2

(iii) Geometry = Octahedral

(iv) Outer orbital complex

(v) Spin free (high spin complex)

Illustration - 17 *Formation of $[Ni(NH_3)_6]^{2+}$*

SOLUTION :

Oxidation state of Ni = +2 ;   Outer electronic configuration of :   Ni atom $\equiv 3d^84s^2$

$\Rightarrow$ Ni^{2+} ion = $3d^8$
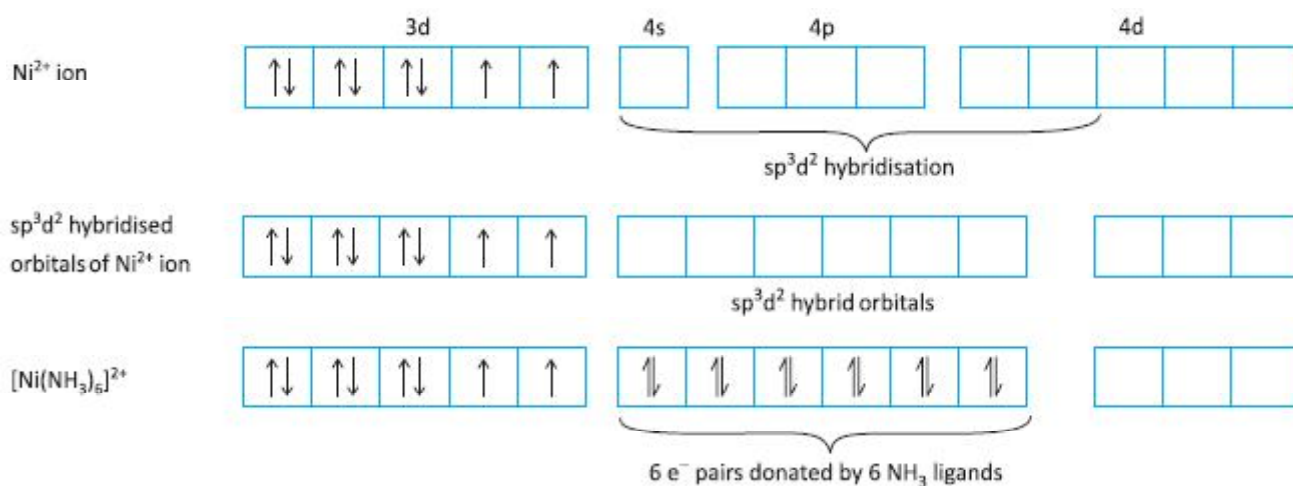
(i) NH_3 being weak ligand is not able to force pairing of electrons.

(vi) Magnetism :
- ➤ No. of unpaired e = 2
- ➤ Paramagnetic
- ➤ Magnetic moment,

$$\mu_s = \sqrt{2(2+2)} = 2.83 \text{ B.M}$$

(ii) Hybridisation : sp^3d^2

(iii) Geometry : Octahedral

(iv) Outer orbital complex

(v) Spin free (high spin complex)

Geometry and magnetic nature of some complexes (Application of valence bond theory)

S.No.	Atom/Ion Complex	Configuration	Oxidation state of metal	Type of hybridization	Geometry (Shape)	No. of unpaired electrons	Magnetic nature
1.	$Ni^{2+}(d^8)$	(3d: ↑↓ ↑↓ ↑↓ ↑ ↑) (4s) (4p)	+2			2	Paramagnetic
	$[NiCl_4]^{2-}$	(3d: ↑↓ ↑↓ ↑↓ ↑ ↑) (sp³)	+2	sp^3	Tetrahedral	2	Paramagnetic
	$[Ni(CN)_4]^{2-}$	(↑↓ ↑↓ ↑↓ ↑↓ :) (dsp²) Rearrangement	+2	dsp^2	Square planar	0	Diamagnetic
	$[Ni(H_2O)_6]^{2+}$	(3d: ↑↓ ↑↓ ↑↓ ↑ ↑) (sp³d²) (4d)	+2	sp^3d^2(Outer)	Octahedral	2	Paramagnetic
2.	$Ni\ (d^8s^2)$	(↑↓ ↑↓ ↑↓ ↑ ↑) (↑↓)	0			2	Paramagnetic
	$[Ni(CO)_4]$	(↑↓ ↑↓ ↑↓ ↑↓ ↑↓) (sp³) Rearrangement	0	sp^3	Tetrahedral	0	Diamagnetic
	$[Ni(PPh_3)_4]$	(↑↓ ↑↓ ↑↓ ↑↓ ↑↓) (sp³) Rearrangement	0	sp^3	Tetrahedral	0	Diamagnetic
3.	$Cu^{2+}(d^9)$	(3d: ↑↓ ↑↓ ↑↓ ↑↓ ↑) (4s) (4p)	+2			1	Paramagnetic
	$[CuCl_4]^{2-}$	(↑↓ ↑↓ ↑↓ ↑↓ ↑) (sp³)	+2	sp^3	Tetrahedral	1	Paramagnetic
	$[Cu(NH_3)_4]^{2+}$	(↑↓ ↑↓ ↑↓ ↑↓ :) (dsp²) ... ↑	+2	dsp^2	Square planar	1	Paramagnetic

Note : One electron is shifted from 3d to 4p-orbital

No.	Species	Orbital diagram (3d, 4s, 4p)	Charge	Hybridization	Geometry	Unpaired e⁻	Magnetic property
3.	$[Mn^{2+}(d^5)]$	↑ ↑ ↑ ↑ ↑ (3d); 4s; 4p	+2			5	Paramagnetic
	$[Mn(CN)_6]^{4-}$	↑↓ ↑↓ ↑ :: :: / :: / :: :: :: — Rearrangement d^2sp^3	+2	d^2sp^3(inner)	Octahedral	1	Paramagnetic
	$[MnCl_4]^{4-}$	↑ ↑ ↑ ↑ ↑ :: / :: :: :: — sp^3	+2	sp^3	Tetrahedral	5	Paramagnetic
3.	$Cr^{3+}(d^3)$	↑ ↑ ↑ (3d); 4s; 4p	+3			3	Paramagnetic
	$[Cr(NH_3)_6]^{3+}$	↑ ↑ ↑ :: :: / :: / :: :: :: — d^2sp^3	+3	d^2sp^3(inner)	Octahedral	3	Paramagnetic
6.	$Co^{3+}(d^6)$	↑↓ ↑ ↑ ↑ ↑ (3d); 4s; 4p	+3			4	Paramagnetic
	$[Co(NH_3)_6]^{3+}$	↑↓ ↑↓ ↑↓ :: :: / :: / :: :: :: — Rearrangement d^2sp^3	+3	d^2sp^3(inner)	Octahedral	0	Diamagnetic
	$[CoF_6]^{3-}$	↑↓ ↑ ↑ ↑ ↑ :: / :: :: :: / :: :: — sp^3d^2	+3	sp^3d^2(Outer)	Octahedral	4	Paramagnetic
7.	$Co^{2+}(d^7)$	↑↓ ↑↓ ↑ ↑ ↑	+2			3	Paramagnetic
	$[Co(H_2O)_6]^{2+}$	↑↓ ↑↓ ↑ ↑ ↑ :: / :: :: :: / :: :: — sp^3d^2	+2	sp^3d^2(Outer)	Octahedral	3	Paramagnetic
8.	$Fe^{2+}(d^6)$	↑↓ ↑ ↑ ↑ ↑ (3d); 4s; 4p	+2			4	Paramagnetic
	$[Fe(CN)_6]^{4-}$	↑↓ ↑↓ ↑↓ :: :: / :: / :: :: — Rearrangement d^2sp^3	+2	d^2sp^3(inner)	Octahedral	0	Diamagnetic
	$[Fe(H_2O)_6]^{2+}$	↑↓ ↑ ↑ ↑ ↑ :: / :: :: :: / :: :: — sp^3d^2	+2	sp^3d^2(Outer)	Octahedral	4	Paramagnetic
	$[Fe(NH_3)_6]^{2+}$	↑↓ ↑ ↑ ↑ ↑ :: / :: :: :: / :: :: — sp^3d^2	+2	sp^3d^2(Outer)	Octahedral	4	Paramagnetic
9.	$Fe^{3+}(d^5)$	↑ ↑ ↑ ↑ ↑	+3			5	Paramagnetic
	$[Fe(CN)_6]^{3-}$	↑↓ ↑↓ ↑ :: :: / :: / :: :: :: — Rearrangement d^2sp^3	+3	d^2sp^3(inner)	Octahedral	1	Paramagnetic
10.	$Fe(d^6s^2)$	↑↓ ↑ ↑ ↑ ↑ / ↑↓	0		Trigonal Bipyramidal	4	Paramagnetic
	$[Fe(CO)_5]$	↑↓ ↑↓ ↑↓ ↑↓ :: / :: / :: :: :: — Rearrangement dsp^3	0	dsp^3(inner)	Bipyramidal	0	Diamagnetic

Drawbacks of Valence Bond Theory :

(i)   It can't explain why some complexes of metal ion use inner orbitals (d^2sp^3, low spin complexes) whereas some other make high spin complexes (sp^3d^2).

(ii)   It can't predict effectively whether a four co-ordinated complex is tetragonal or square planar e.g., $[Cu(NH_3)_4]^{2+}$ is suggested to have sp^3 configuration by V.B. Theory but X-rays study shows its geometry as square planar, i.e. dsp^2.

(iii) It doesn't explain the variation of magnetic properties of complex with temperature.

(iv)   It doesn't explain or predict any distortion in symmetrical complexes.

(v)   There is no quantitative interpretation of magnetic data.

(vi)   It has nothing to say about the spectral properties of co-ordination compounds.

(vii) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of co-ordination compounds.

(viii) It does not distinguish between strong and weak ligands.

CRYSTAL FIELD THEORY :   Section - 6

Crystal field theory is now much more widely accepted than the valence bond theory. It assumes that the attraction between the central metal and ligands in a complex is purely electrostatic. The transition metal which forms the central atom in the complex is regarded as a positive ion of charge equal to the oxidation state. This is surrounded by negative ligands or neutral molecules which have a lone pair of electrons. If the ligand is a neutral molecule such as NH_3, the negative end of the dipole in the molecule is directed towards the metal ion. The electrons of the central metal are under repulsive force from those of the ligands. Thus, the outer most electrons (which are generally present in the d orbitals) of central transition metal atom/ion occupy those d orbitals which farthest away from the direction of approach of ligands.

In the crystal field theory, the following assumptions are made.

(i)   Ligands are treated as point charges.

(ii) There is no interaction between metals orbitals and ligand orbitals.

(iii) The arrangement of the ligands around the central metal ion is such that the repulsion between these negative points is minimum.

(v)   Splitting of d-orbital energies : The five d-orbitals in an isolated gaseous metal atom/ion are degenerate i.e. they have equal energy. If a spherically symmetric field of negative charges is placed around the metal, the orbitals will remain degenerate, but all of them will be raised in energy as a result of repulsion between the negative field and the electrons in the orbitals. If the field results from the influence of real ligands (either anions or the negative ends of dipolar ligands such as NH_3 or H_2O), the symmetry of the field will be less than spherical and the degeneracy of the d-orbitals will be removed. It is this splitting of d orbital energies and its effects that form the basis of crystal field theory.

Note : There are five d-orbitals namely, $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}$ which have been shown below :
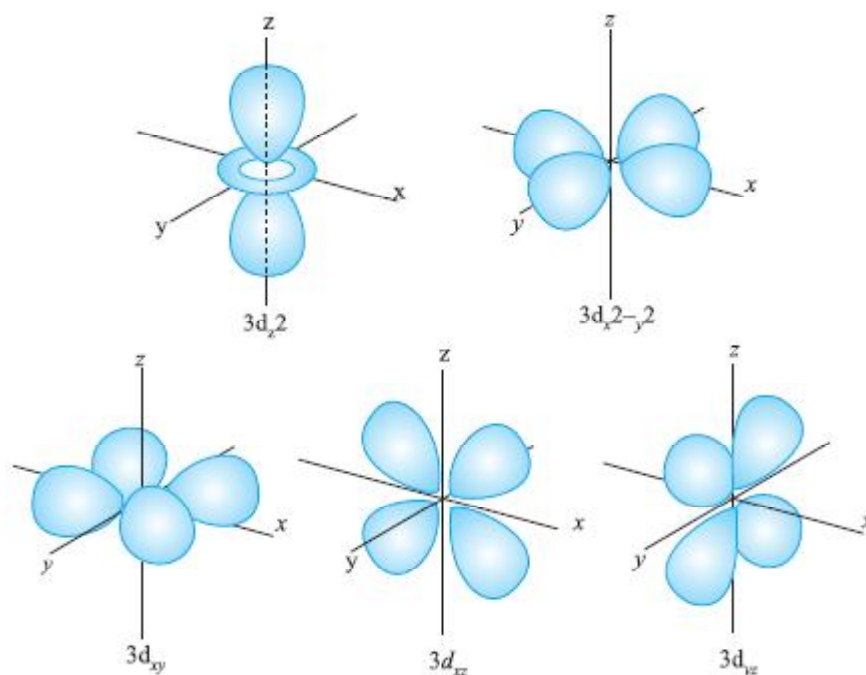
Fig : Spatial arrangement of five *d*-orbitals.

It is better to divide the set of d orbitals in two groups :

(i) The orbitals in which lobes lie on the axes $(d_{x^2-y^2}, d_{z^2})$ **:** referred to as "e_g" orbitals in Octahedral symmetry and "e" orbitals in Tetrahedral symmetry. (Also called as doubly degenerate orbitals.)

(ii) The orbitals in which lobes lie in between the axes (d_{xy}, d_{yz}, d_{zy}) : referred to as "t_{2g}" orbitals in Octahedral symmetry and "t_2" orbitals in Tetrahedral symmetry. (Also called triply degenerate orbitals.)

A. Crystal field splitting of d-orbitals in octahedral complexes :

In an octahedral complex, the metal is at the centre of the octahedron and the ligands approach it along the six corners of the octahedral. The directions x, y, and z point to three adjacent corners of the octahedron.

The lobes of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) point along the axes x, y and z. The lobes of the t_{2g} orbitals (d_{xy}, d_{xz} and d_{yz}) point in between the axes. It follows that the approach of six ligands along the x, y, z, $-x, -y$ and $-z$ direction will increase the energy of the orbitals $d_{x^2-y^2}$ and d_{z^2} (which point along the axes) more than it increase the energy of the d_{xy}, d_{xz} and d_{yz} orbitals (which point between the axes).

Fig : Complete set of d-orbitals in an octahedral field produced by six ligands. The e_g orbitals are shaded and the t_{2g} orbitals are unshaded. The torus of the d_{z^2} orbital has been omitted for clarity

Thus, under the influence of an octahedral ligand field the d orbitals split into two groups of different energies with "e_g" orbitals having higher energy than the "e_{eg}" orbitals. To understand this splitting more clearly we can assume it to be a two step process as shown in fig.
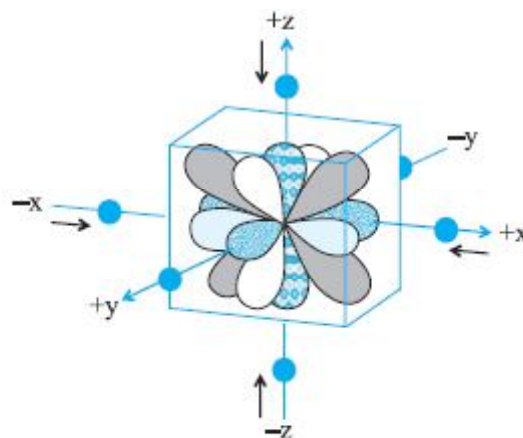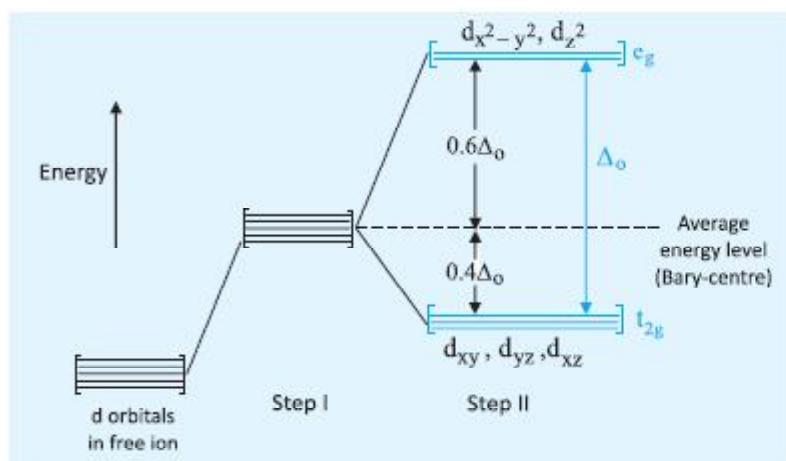

Fig: d-orbitals splitting in an octahedral crystal field.

Step I : Average energy of the d-orbitals of metal atom/ion in a hypothetical spherical crystal field.

Step II : Splitting of d-orbitals of metal atom/ion in octahedral crystal field.

In the first step, the ligands approach the central metal, producing a hypothetical spherical field which repels all of the d-orbitals to the same extent. In the second, the ligands exert an octahedral field, which splits the orbital degeneracy. In going from the first to the second step, average energy (the barycenter, or "centre of gravity") of the orbitals must remains constant and thus, the two e_g orbitals to be the further

repelled by 0.6 Δ_0 while the three t_{2g} orbitals are stabilized to an extent of 0.4 $_0$ as shown in figure. This constancy of the barycenter of the d-orbitals holds for all complexes, regardless of geometry.

Significance of Δ_o : Consider a d^1 co-ordination entity e.g., $[Ti(H_2O)_6]^{3+}$ formed in aqueous solutions of $Ti^{3+}(d^1)$ ion, now the single d-electron occupies one of the lower energy t_{2g} orbitals. Similarly in the d^2 and d^3 co-ordination entities, the d-electrons will occupy the lower energy t_{2g} orbitals in accordance with the Hund's rule. For d^4 ions, two possible patterns of electron distribution arise depending upon the relative values of Δ_o and P where P represents the energy required for electron pairing in a single orbital called the pairing energy.

(i) If $\Delta_o < P$ (weak field, high spin situation), the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$ (see fig). If now a fifth electron is added to a weak field co-ordination entity, the configuration becomes $t_{2g}^3 e_g^2$.

(ii) If $\Delta_o > P$ (strong field, low spin situation), pairing will occur in the t_{2g} level with e_g level remaining unoccupied giving configuration $t_{2g}^4 e_g^0$. [Note : the pairing will occur (and consequently the e_g level will remain unoccupied) till the entities of d^6 ions.]
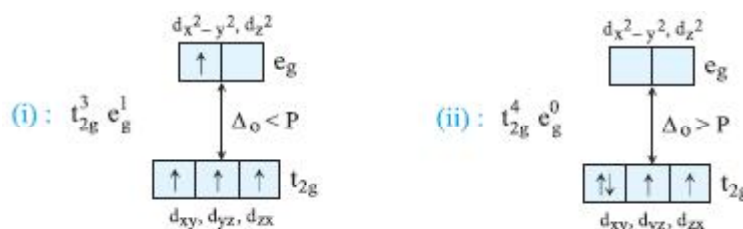
Note : Calculations show that co-ordination entities with four to seven d-electrons are more stable for strong field as compared to weak field cases.

Crystal field effects for weak and strong octahedral fields

d^n	Weak field			Strong field		
	Configuration	Unpaired electrons	CFSE	Configuration	Unpaired electrons	CFSE
d^1	t_{2g}^1	1	$0.4\Delta_o$	t_{2g}^1	1	$0.4\Delta_o$
d^2	t_{2g}^2	2	$0.8\Delta_o$	t_{2g}^2	2	$0.8\Delta_o$
d^3	t_{2g}^3	3	$1.2\Delta_o$	t_{2g}^3	3	$1.2\Delta_o$
d^4	$t_{2g}^3 e_g^1$	4	$0.6\Delta_o$	t_{2g}^4	2	$1.6\Delta_o$
d^5	$t_{2g}^3 e_g^2$	5	$0.0\Delta_o$	t_{2g}^5	1	$2.0\Delta_o$
d^6	$t_{2g}^4 e_g^2$	4	$0.4\Delta_o$	t_{2g}^6	0	$2.4\Delta_o$
d^7	$t_{2g}^5 e_g^2$	3	$0.8\Delta_o$	$t_{2g}^6 e_g^1$	1	$1.8\Delta_o$
d^8	$t_{2g}^6 e_g^2$	2	$1.2\Delta_o$	$t_{2g}^6 e_g^2$	2	$1.2\Delta_o$
d^9	$t_{2g}^6 e_g^3$	1	$0.6\Delta_o$	$t_{2g}^6 e_g^3$	1	$0.6\Delta_o$
d^{10}	$t_{2g}^6 e_g^4$	0	$0.0\Delta_o$	$t_{2g}^6 e_g^4$	0	$0.0\Delta_o$

B. Crystal field splitting of d-orbitals in Tetrahedral Complexes :

Consider eight ligands aligned on the corners of a cube approaching a metal atom located in the center as shown in figure.

In this (cubic) arrangement, however, the ligands do not directly approach any of the metal d-orbitals, but they come closer to the orbitals directed to the edges of the cube (the d_{xy}, d_{xz} and d_{yz}) than to those directed to the centers of the cube faces

(the $d_{x^2-y^2}$ and the d_{z^2}). Hence the t_2 orbitals are raised in energy while the e orbitals are stabilized relative to the bary centre. Furthemore, since the centre-of- gravity rule holds, the upper levels are raised by

$0.4\Delta_o$ and the lower ones stabilized by $0.6\Delta_o$ from the bary center, giving an energy level scheme that is exactly the inverse of that for octahedral symmetry.
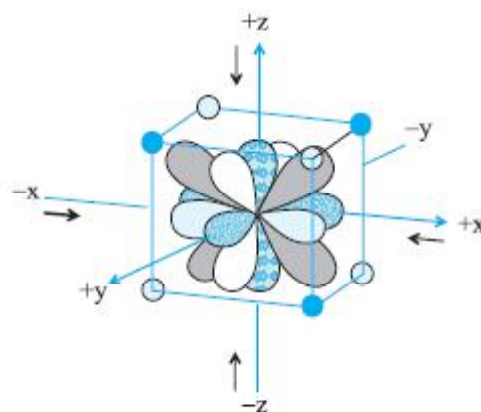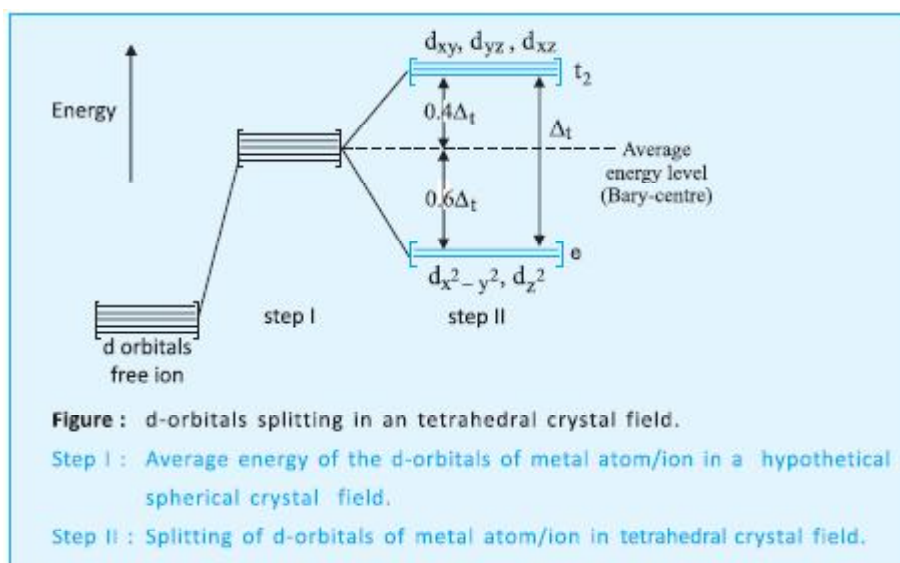

Figure : Complete set of d-orbitals in a cubic field. Either set of tetrahedral ligands (● or ○) produces a field one-half as strong as the cubic field

If four ligands are removed from alternate corners of the cube in figure, the remaining ligands form a tetrahedron about the metal.

The energy level scheme for tetrahedral symmetry shown in figure is qualitatively the same as that for cubic, but the splitting (Δ_t) is only half as large because there are half as many ligands. The two sets of degenerate in this arrangement are labelled as t_2 (d_{xy}, d_{xz}, d_{yz}) and e $(d_{x^2-y^2}, d_{z^2})$. The g subscripts which were used for the octahedral and cubic field are no longer appropriate because the tetrahedron lacks a centre of inversion.
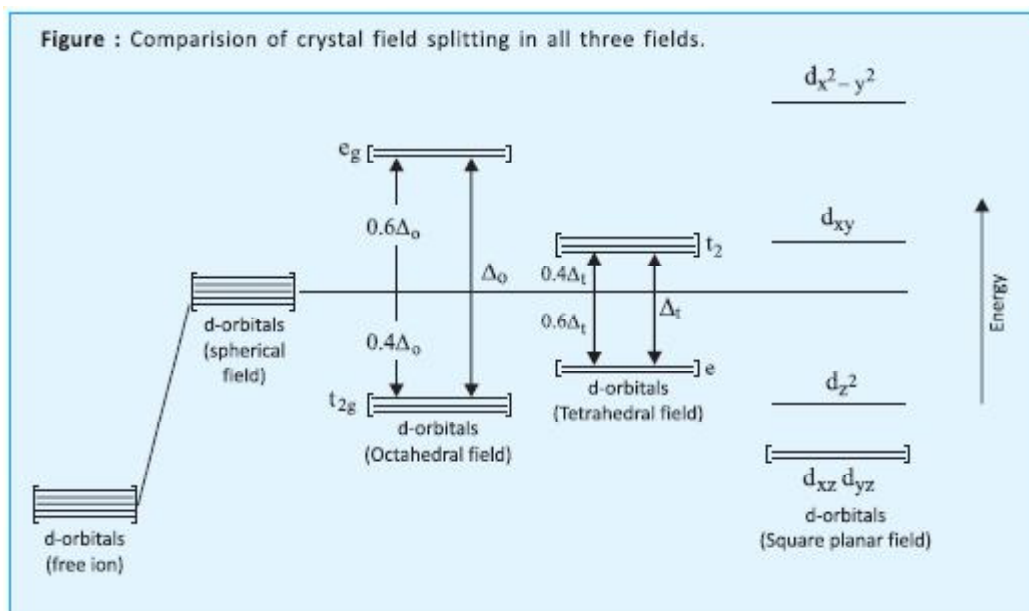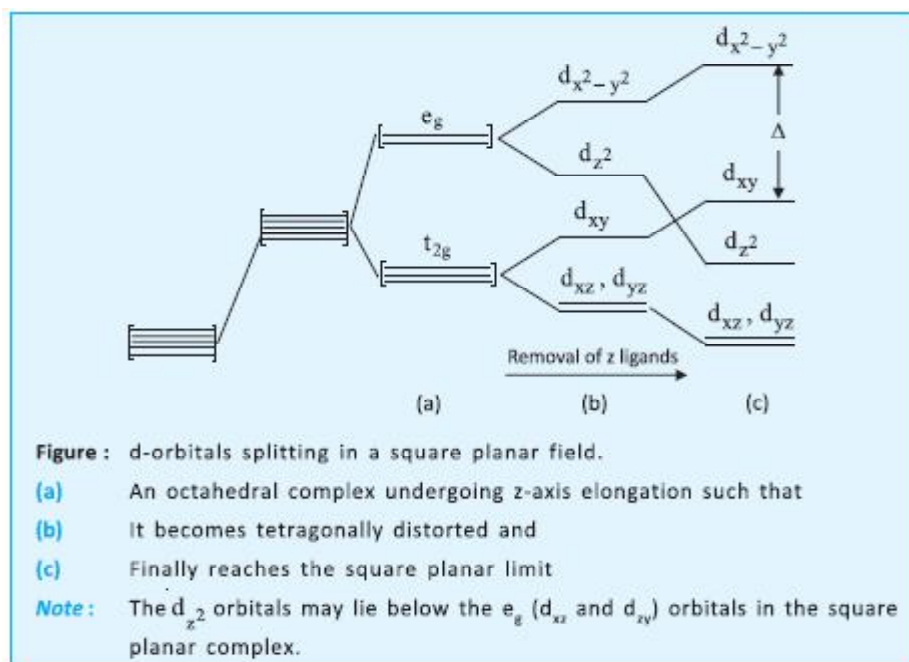

Figure : d-orbitals splitting in an tetrahedral crystal field.

Step I : Average energy of the d-orbitals of metal atom/ion in a hypothetical spherical crystal field.

Step II : Splitting of d-orbitals of metal atom/ion in tetrahedral crystal field.

***Note* :** In tetrahedral complexes, mostly $\Delta_t < P\,(\Delta_t \cong \dfrac{4}{9}\Delta_o)$ and hence they generally form high complexes

C.　Crystal field splitting of d-orbitals is square planar complexes :

The square planar geometry may be considered to be derived from octahedral by removing the two ligands which were approaching the central atom along the Z-axis (called tetragonal distortion). The splitting may also be explained as : As the lobes of $d_{x^2-y^2}$ point towards the ligands, this orbital has highest energy.

Though lobes d_{xy} orbitals lie between the ligands but they are coplanar with them, hence this orbital is next higher in energy. The lobes of d_{z^2} orbital point out of the plane of the complex but the torous around its centre lies in the plane, therefore d_{z^2} orbital is next higher in energy. The lobes of d_{xz} and d_{yz} orbitals point out of the plane of the complex, hence they are least affected by the electrostatic field of the ligands, and thus have lowest but equal energy. It must be kept in mind that the average energy of the orbitals remains constant in this redistribution of energy as in previous cases. (the stronger the surrounding field, the higher the $d_{x^2-y^2}$ orbital will be raised, however the lower, occupied orbitals will drop in energy by a corresponding amount)

The square planar geometry is favoured by metal ions having a d^8 configuration in the presence of a strong field. This combination gives low spin complexes with the eight d-electron occupying the low-energy d_{xy}, d_{yz}, d_{z^2} and d_{xy} orbitals, while the high-energy orbital remains unoccupied.

Figure : d-orbitals splitting in a square planar field.

(a)   An octahedral complex undergoing z-axis elongation such that

(b)   It becomes tetragonally distorted and

(c)   Finally reaches the square planar limit

Note :   The d_{z^2} orbitals may lie below the e_g (d_{xz} and d_{zy}) orbitals in the square planar complex.

Figure : Comparision of crystal field splitting in all three fields.

Number of unpaired electrons in octahedral and tetrahedral complex.

[(W.F.) is the configuration for high spin and weak field complexes) (S.F) is the configuration for low spin and strong field complexes)
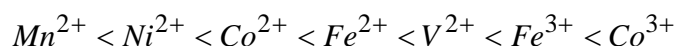
Electronic configuration	Octahedral Complex		Number of unpaired electrons	Tetrahedral complex		Number of unpaired electrons
d^1		$(e_g$ set) $(t_{2g}$ set)	1		$(t_2$ set) $(e$ set)	1
d^2		$(e_g$ set) $(t_{2g}$ set)	2		$(t_2$ set) $(e$ set)	2
d^3		$(e_g$ set) $(t_{2g}$ set)	3		$(t_2$ set) $(e$ set)	3
d^4	(W.F.)	$(e_g$ set) $(t_{2g}$ set)	4		$(t_2$ set) $(e$ set)	4
	(S.F.)	$(e_g$ set) $(t_{2g}$ set)	2			
d^5	(W.F.)	$(e_g$ set) $(t_{2g}$ set)	5		$(t_2$ set) $(e$ set)	5
	(S.F.)	$(e_g$ set) $(t_{2g}$ set)	1			
d^6	(W.F.)	$(e_g$ set) $(t_{2g}$ set)	4		$(t_2$ set) $(e$ set)	4
	(S.F.)	$(e_g$ set) $(t_{2g}$ set)	0			

d^7	(W.F.) (e_g set) ① ① / (t_{2g} set) ⇅ ⇅ ①	3	(t_2 set) ① ① ① / (e set) ⇅ ⇅	3
	(S.F.) (e_g set) ① ○ / (t_{2g} set) ⇅ ⇅ ⇅	1		
d^8	(e_g set) ① ① / (t_{2g} set) ⇅ ⇅ ⇅	2	(t_2 set) ⇅ ① ① / (e set) ⇅ ⇅	2
d^9	(e_g set) ⇅ ① / (t_{2g} set) ⇅ ⇅ ⇅	1	(t_2 set) ⇅ ⇅ ① / (e set) ⇅ ⇅	1
d^{10}	(e_g set) ⇅ ⇅ / (t_{2g} set) ⇅ ⇅ ⇅	0	(t_2 set) ⇅ ⇅ ⇅ / (e set) ⇅ ⇅	0

D. Factors affecting the magnitude of orbital splitting energy (Δ) :

The important factors are as follows :

(i) Oxidation state of the metal ion : The magnitude of Δ_o increases as the charge on the metal ion increases. For example, for first row of transition metal ions, the values of Δ_o for M^{3+} complexes are roughly 50% larger than the values for M^{2+} complexes.

(ii) Nature of the metal ion : In the d-block (transition) elements, within the same group, as we move from 3d to 4d to 5d elements, the Δ_o increases and hence the tendency to form low spin complexes increases. Thus the elements of the second and third transition series have greater tendency to form low spin complexes than the first transition series. It is possible to arrange the metals according to a spectrochemical series as well. The approximate order is

$$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Co^{3+}$$

$$< Mn^{3+} < Mo^{3+} < Rh^{3+} < Ru^{3+} < Pd^{4+} < Ir^{3+} < Pt^{4+}$$

(iii) Geometry of the co-ordination entity : As already stated, $\Delta_t \cong \dfrac{4}{9}\Delta_o$ i.e. Δ value for tetrahedral complexes is nearly 50% of the Δ value for octahedral complexes.

(iv) Nature of the ligand : For the same metal ion, different ligands result in different amounts, pertaining to their position in the spectro-chemical series. Strong field ligands cause higher splitting compare to the weak field ligands. (Refer to the spectrochemical series)

## MISCELLANEOUS CONCEPTS   Section - 7

A. Colour in Co-ordination Compounds :

Co-ordination compounds show a wide range of colour. When white light passes through a complex, some part of it is absorbed and thus, the light which emerges is no longer white. The colour of the compound hence observed, is complimentary to that of the wavelength which has been absorbed by the complex. Thus, colour of a complex is not because of the light absorbed but is due to the light reflected (complementary colour). The complementary colour is the colour generated from the wavelength left over; for example is green light is absorbed by the complex, it appears red.

Table given the relationship of the different wavelength absorbed and the colour observed.
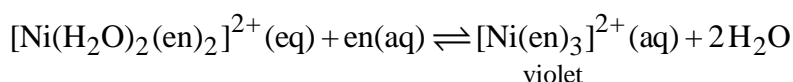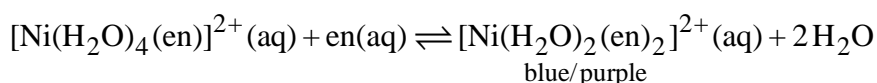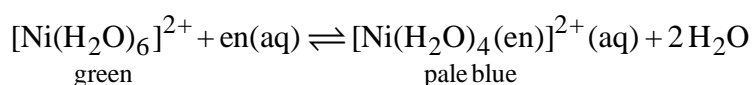
Co-ordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of co-ordination entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow Orange
$[Co(CN)_6]^{3-}$	310	Ultraviolet	Pale Yellow
$[Co(H_2O)_4]^{2+}$	600	Red	Blue

In co-ordination complexes energy difference (Δ) between two sets of d-orbitals is small. Radiations of appropriate frequency absorbed from visible region can cause excitation of d-electrons from lower energy orbital to higher energy orbitals. Remeining light is transmitted and the compound appears coloured. Consider for example, the complex $[Ti(H_2O)_6]^{3+}$, which is violet in colour. This is an octahedral complex where the single electron (Ti^{3+} is a $3d^1$ system) in the metal d orbital is in the t_{2g} level in the ground state of the complex. The next higher state available for the electron is the empty e_g level. If light corresponding to the energy of yellow-green region is absorbed by the complex, it would excite the electron from t_{2g} level to the e_g level ($t_{2g}^{\ 1}e_g^{\ 0} \longrightarrow t_{2g}^{\ 1}e_g^{\ 0}$). Consequently, the complex appears violet in colour (Figure). The crystal field theory thus, attributes the colour of the co-ordination compounds of d-d transition of the electron.

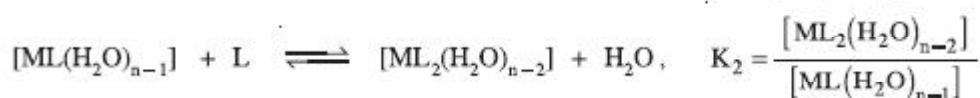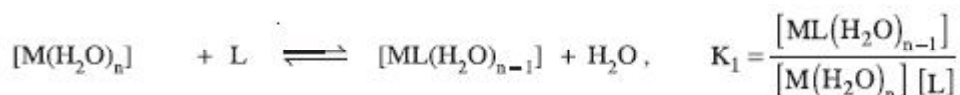Transition of an electron in $[Ti(H_2O)_6]^{3+}$
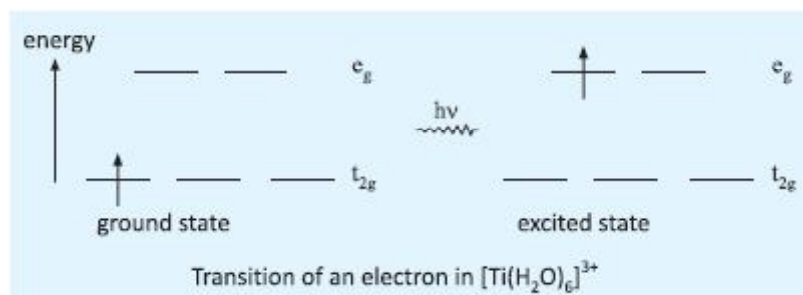
If there are no d-electrons present or completely filled d-orbitals are present then there is no d-d transition possible and complex appears colourless. For example, removal of water from $[Ti(H_2O)_6]Cl_3$ on heating renders it colourless. Similarly, anhydrous $CuSO_4$ is white, but $CuSO_4 \cdot 5H_2O$ is blue in colour.

The influence of the ligand on the colour of a complex may illustrated by considering the $[Ni(H_2O)_6]^{2+}$ complex, which forms when nickel(II) chloride is dissolved in water. If the didentate ligand, enthane-1, 2-diamine(en) is progressively added in the molar ratios en : Ni, 1 : 1, 2 : 1, 3 : 1, the following series of reactions and their associated colour changes occur :
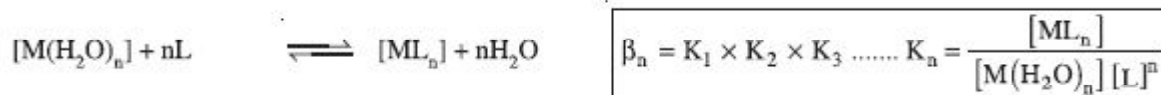
$$\underset{\text{green}}{[Ni(H_2O)_6]^{2+}} + en(aq) \rightleftharpoons \underset{\text{pale blue}}{[Ni(H_2O)_4(en)]^{2+}(aq)} + 2H_2O$$

$$[Ni(H_2O)_4(en)]^{2+}(aq) + en(aq) \rightleftharpoons \underset{\text{blue/purple}}{[Ni(H_2O)_2(en)_2]^{2+}(aq)} + 2H_2O$$

$$[Ni(H_2O)_2(en)_2]^{2+}(eq) + en(aq) \rightleftharpoons \underset{\text{violet}}{[Ni(en)_3]^{2+}(aq)} + 2H_2O$$

B.   Stability of Co-ordination Compounds in Solutions :

A co-ordination compound is formed in solution by the stepwise addition of ligands to a metal ion. Thus, formation of the complex, ML_n may be supposed to take place by the consecutive n steps.

$$[M(H_2O)_n] + L \rightleftharpoons [ML(H_2O)_{n-1}] + H_2O, \qquad K_1 = \frac{[ML(H_2O)_{n-1}]}{[M(H_2O)_n][L]}$$

$$[ML(H_2O)_{n-1}] + L \rightleftharpoons [ML_2(H_2O)_{n-2}] + H_2O, \qquad K_2 = \frac{[ML_2(H_2O)_{n-2}]}{[ML(H_2O)_{n-1}]}$$

$$\vdots$$

$$[ML_{n-1}(H_2O)] + L \rightleftharpoons [ML_n] + H_2O, \qquad K_n = \frac{[ML_n]}{[ML_{n-1}(H_2O)][L]}$$

$$[M(H_2O)_n] + nL \rightleftharpoons [ML_n] + nH_2O \qquad \boxed{\beta_n = K_1 \times K_2 \times K_3 \dots\dots K_n = \frac{[ML_n]}{[M(H_2O)_n][L]^n}}$$

$K_1, K_2 .... K_n$ are called stepwise stability constants. In general, the values of successive stability constants decrease regularly from K_1 to K_n. β_n is called the overall stability constant (and $\dfrac{1}{\beta_n}$ is called as instability constant). The higher the overall stability constant value of the complex, the more stable it is. Alternatively, values called instability constant explain the dissociation of the complex into metal ion and ligands in the solution. e.g., β_n for $[Co(NH_3)_6]^{3+}$ is 5×10^{33}.

C.   Factors affecting the stability of a complex ion :

The stability of a complex ion depends upon the following factors.

(i)   Higher the charge density on the central ion, the greater is the stability of its complexes, i.e., the higher value of $\dfrac{\text{Charge}}{\text{Radius of ion}}$, the greater is the stability of its complexes. Electronegativity of the central ion influences the stability, the higher the electronegativity of the central ion, the greater is the stability of its complex.

(ii)   The stability of the divalent metal ions of the first transition series is in the following order :

$$\text{Mn(II)} < \text{Fe(II)} < \text{Co(II)} < \text{Ni(II)} < \text{Cu(II)} > \text{Zn(II)}$$

This order is called Irving Williams order.

(iii)   The cyano and ammine complexes are far more stable than those formed by halide ions. This is due to the fact that $NH_3 \,\&\, CN^-$ are strong Lewis bases.

(iv)   Greater the basic strength of the ligand, greater is the stability of the complex.

(v)   Chelating ligands form more stable complexes as compared to monodentate ligands.

(vi)   If the ligand happens to be multidentate and cyclic without any steric effects, the stability of the complex is further increased. The effect is called macrocyclic effect.

D.   Metal Carbonyls & Bonding in Metal Carbonyls

The homoleptic carbonyls (compounds containing carbonyl ligands only) are formed by most of the transition metals. These carbonyls have simple, well defined structures. Tetracarbonylnickel (0) is tetrahedral, pentacarbonyliron (0) is trigonal bipyramidal while hexacarbonyl chromium (0) is octahedral.
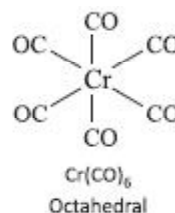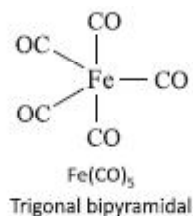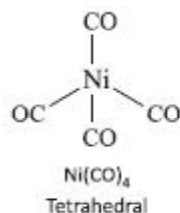
The metal-carbon bond in metal carbonyls prossess both s and p character. The M – C σ bond is formed by the donation of lone pair of electron on the carbonyl carbon into a vacant orbital of the metal. The M – C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π^* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal (and hence decreases, the bond order between C and O of CO and thereby the bond length of C – O bond increases). The C – O bond order will be in the order shown below :
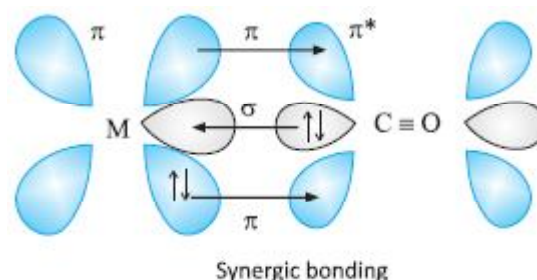
Free CO > Metal carbonyl cation > Neutral metal carbonyl > Metal carbonyl anion.

Synergic bonding

Illustration - 18 *Identify the complexes which are expected to be coloured. Explain* :

(A) $[Ti(NO_3)_4]$

(B) $\left[Cu(NCCH_3)_4\right]^+ BF_4^-$

(C) $[Cr(NH_3)_6]^{3+} 3Cl^-$

(D) $K_3[VF_6]$

SOLUTION :

(i) $[Ti(NO_3)_4]$; $\qquad Ti^{4+} : [Ar]3d^0 4s^0$, No. of unpaired electrons $= 0$, $\Rightarrow$ Colourless

(ii) $[Cu(NCCH_3)_4]^+ BF_4^-$; $\quad Cu^+ : [Ar]3d^{10}4s^0$, No. of unpaired electrons $= 0$, $\Rightarrow$ Colourless

(iii) $[Cr(NH_3)_6]^{3+} 3Cl^-$; $\qquad Cr^{3+} : [Ar]3d^3 4s^0$, No. of unpaired electrons $= 3$, $\Rightarrow$ Colourless

(iv) $K_3[VF_6]$; $\qquad V^{3+} : [Ar]3d^2 4s^0$, No. of unpaired electrons $= 2$, $\Rightarrow$ Colourless

Due to the presence of unpaired electrons in d-orbitals, two complexes i.e.,

$[Cr(NH_3)_6]^{3+} 3Cl^-$ and $K_3[VF_6]$ are coloured, others having all paired electrons arecolourless

Illustration - 19 *Write down the IUPAC names of the following compounds* :

(i) $[Co(NH_3)_5 ONO]Cl_2$ **(ii)** $K_3[Cr(CN)_6]$ **(iii)** $[Cr(NH_3)_5 CO_3]Cl$

SOLUTION :

(i) Pentaamminenitritocobalt(III) chloride (ii) Potassium hexacyanochromate(III)

(iii) Pentaamminecarbonatochromium(III) chloride

Illustration - 20 *Write the IUPAC name of the compound* $[Cr(NH_3)_5(NCS)][ZnCl_4]$. *Is this compound coloured?*

SOLUTION :

IUPAC name : Pentaammine isothiocyanatochromium (III) tetrachlorozincate (II). This compound is coloured because Cr^{3+} has unpaired electrons in d-orbitals ($3d^3$ configuration) which show colour through d-d transition.

Illustration - 21 *A, B, and C are three complexes of chromium (III) with the empirical formula $H_{12}O_6Cl_3Cr$. All the three complexes have water and chloride ion as ligands. Complex A does not react with concentrated H_2SO_4, whereas complexes B and C lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentrated H_2SO_4. Identify A, B and C.*

SOLUTION :

The compound A does not react with concentrated H_2SO_4 implying that all water molecules are co-ordinated with Cr^{3+} ion. Hence, its structure would be $[Cr(H_2O)_6]Cl_3$.

The compound B loses 6.75% of its original mass when treated with concentrated H_2SO_4. This loss is due to the removal of water molecules which is/are not directly co-ordinated to Cr^{3+} ion.

The mass of water removed per mole of the complex $= \dfrac{6.75}{100} \times$ molar mass of the complex

$$= \dfrac{6.75}{100} \times 266.5\, g = 17.98\, g$$

This corresponds to one mole of water. Hence, the structure of the compound B will be $[CrCl(OH_2)_5]Cl_2 . H_2O$
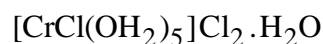
The compound C loses 13.5 % of its mass when treated with concentrated H_2SO_4 which is twice of the mass lost by the compound B. Hence, the structure of the compound C will be $[CrCl_2(OH_2)_4 Cl . 2H_2O$.
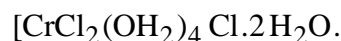
Illustration - 22 *A metal complex having composition* $Cr(NH_3)_4 Cl_2 Br$ *has been isolated in two forms* (A) *and* (B). *The form* (A) *reacts with* $AgNO_3$ *to give a white precipitate readily soluble in dilute aqueous ammonia, whereas* (B) *gives a pale yellow precipitate solution in concentrated ammonia. Write the formula of* (A) *and* (B) *and state the hybridization of chromium in each. Calculate their magnetic moments* (*spin only value*).

SOLUTION :

Compound (A) on treatment with $AgNO_3$ gives white precipitate of AgCl, which is readily solution in

dil. aq. NH_3. Therefore it has at least one Cl^- ion in the ionization sphere furthermore chromium has co-ordination number equal to 6. So its formula is $[Cr(NH_3)_4 BrCl]Cl$.

Compound (B) on treatment with $AgNO_3$ gives pale yellow precipitate of AgBr soluble in conc NH_3.

Therefore it has Br^- in the ionization sphere. So its formula is $[Cr(NH_3)_4 Cl_2]Br$.
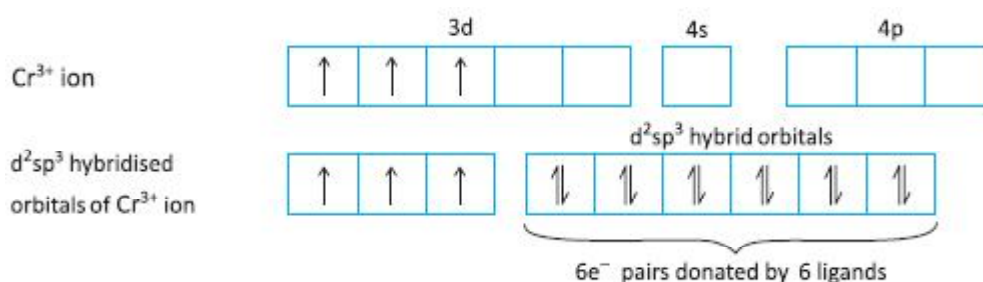
State of hybridization of chromium in both (A) and (B) is d^2sp^3.

Spin magnetic moment of (A) or (B), $\mu_{spin} = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = 3.87$ BM

Illustration - 23 *Write the IUPAC nomenclature of the given complex along with its hybridization and structure.*

$$K_2[Cr(NO)(NH_3)(CN)_4], \mu = 1.73 \ BM$$

SOLUTION :

The spin magnetic moment, μ of the complex is 1.73 BM. $\mu = \sqrt{n(n+2)} = 1.73 \Rightarrow n = 1$

It means that nucleus of the complex, chromium ion has one unpaired electron. Now, if NO is neutral then

Chromium under the influence of strong field ligand CN^- would not have any unpaired electron, so the ligand NO is unit positively charged and the IUPAC name of the compound is Potassium amminetetracyanonitrosonium chromate(I)

(a) Electronic configuration of Cr^+ : Cr^+ ion

(b) Electronic configuration of Cr^+ under the influence of strong field ligand CN^-
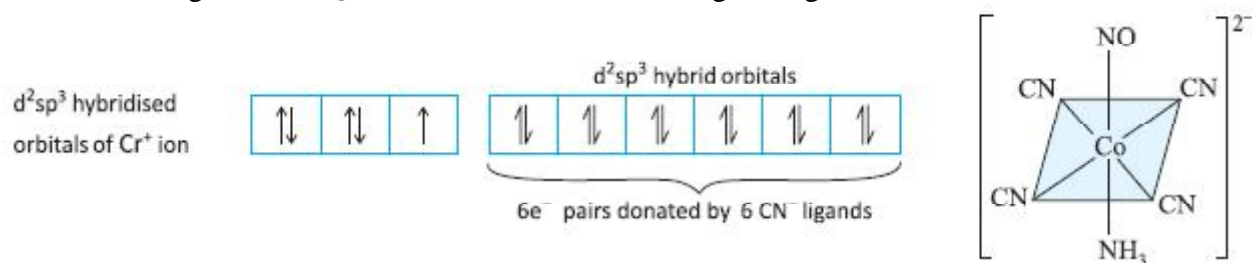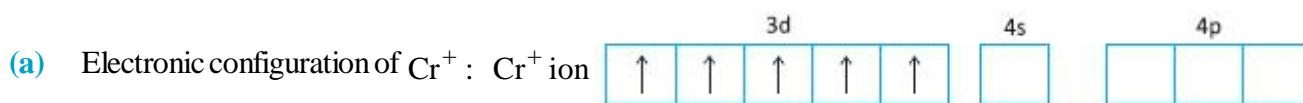
So, Hybridization of the complex is d^2sp^3 and its shape is Octahedral (as shown).

Illustration - 24 *The* 0.0001 *molal solution of a complex* AB_{10} *has the freezing point of* $-0.0015°C$ *in water. Assuming* 100% *dissociation of the complex, find the proper representation of the complex.*

$[K_f H_2O = 1.86 \ Km^{-1}]$

(A) $[AB_8]B_2$ **(B)** $[AB_3]B_7$ **(C)** $[AB_7]B_3$ **(D)** $[AB_5]B_5$

SOLUTION :

At 100% dissociation, van't hoff factor, 'i' = n (no. of ions from the complex).

Now $\left| \Delta T_f \right| = i\, K_f m$

$\Rightarrow \quad i = n = \dfrac{\left| \Delta T_f \right|}{K_f m} = \dfrac{0.0015}{1.86 \times 0.0001} = 8$

Thus there should be 8 ions in solution

$\Rightarrow$ The compound should be $[AB_3]B_7$.

NOW ATTEMPT IN-CHAPTER EXERCISE-A BEFORE PROCEEDING AHEAD IN THIS EBOOK

NOW ATTEMPT OBJECTIVE WORKSHEET BEFORE PROCEEDING AHEAD IN THIS EBOOK

My Chapter Notes