## INTRODUCTION

- (a) The concept of coordination compounds arises from the complex formation tendency of transition elements.
- (b) These compounds play a vital role in our lives, as chlorophyll of plants and haemoglobin of animal blood are also coordination compounds of Mg and Fe respectively
- (c) One of the earliest known coordination compound is prussian blue which was accidently prepared by a Berlin color maker, Diebach in 1704.
- (d) The field of such compound is expanding due to their utilization in metallurgy, analytical chemistry and polymerisation.

## MOLECULAR OR ADDITION COMPOUNDS



(b) Some common examples are as follows.  $CuSO_4 + 4NH_3 \rightarrow CuSO_4. 4NH_3$   $AgCN + KCN \rightarrow KCN. AgCN$ simple stable Addition or compounds molecular compounds  $4 KCN + Fe(CN)_2 \rightarrow Fe(CN_2) \cdot 4KCN$   $K_2SO_4 + Al_2 (SO_4)_3 + 24H_2O \rightarrow$   $K_2SO_4. Al_2(SO_4)_3. 24 H_2O$ Alum

- (c) The molecular or addition compounds are of two type Double salts lattice compound and coordination or complex compound
- 1. Double salts or lattice compounds
- (a) The addition compounds which are stable in solid state only but are broken down into individual constituents when dissolved in water are called double salts or lattice compounds.
- (b) Their solution have the same properties as the mixture of individual compounds
- (c) For example when carnallite (KCl. MgCl<sub>2</sub>. 6H<sub>2</sub>O) is dissolved in water it exhibits the properties of KCl and MgCl<sub>2</sub>

#### 2. Coordination or complex compounds

- (a) The addition compounds in which some of the constituent ions or molecules lose their identity and when dissolved in water they do not break up completely into individual ions are called coordination compounds
- (b) The properties of their solutions are different than those of their constituents.
- (c) In such compounds there is complex ion which is a central metal ion with lewis bases attached to it through coordinate covalent bonds.
- (d) On the basis of stability of complex ion, complex ions are further divided as follows.
  - Perfect complexes : Those in which complex ion is fairly stable and is either not dissociated or feebly dissociated in solution state, e.g.

$$K_{4}[Fe(CN)_{6}] \rightarrow 4K^{+} + [Fe(CN)_{6}]^{4-}$$

$$\downarrow$$

$$Fe^{2+} + 6CN^{-}$$

(feebly dissociated)

The ferrocyanide ion  $[Fe(CN)_6]^{4-}$  is so insignificantly dissociated that it can be considered as practically undissociated and does not give the test of Fe<sup>2+</sup> or CN<sup>-</sup> ions

(ii) Imperfect complexes : Those in which complex ion is less stable and is reversibly dissociated to give enough simple ions and thus imparts their tests, e.g.

$$K_2[Cd(CN)_4] \rightarrow 2K^+ + [Cd(CN)_4]^{2-}$$
↓

 $Cd^{2+} + 4CN^{-}$ 

(appreciably dissociated)

#### Note :

An imperfect complex may be too unstable to exist and may be completely dissociated in solution, it then becomes a double salts

#### Solved Examples

**Ex.1** The number of ions formed in aqueous solution by the compound  $[Co(NH_3)_4Cl_3]Cl$  is :

(A) 2	(B) 3
(C) 4	(4) 7

Sol. (A)

The dissociation of given compound is as follows  $[Co(NH_3)_4Cl_2]Cl \Leftrightarrow [Co(NH_3)_4Cl_2]^+ + Cl^-$ 

**Ex.2** Why  $NH_3$  forms co-ordinate complexes, while the isoelectronic species  $CH_4$  does not ?

Sol. NH<sub>3</sub> has lone pair of electrons on N unlike CH<sub>4</sub>

## VARIOUS TERMS USED IN COORDINATION COMPOUNDS

To understand concepts related to coordination compounds and their nature it is essential to discuss some important terms. These are as follows.

- 1. Central ion : (Centre of coordination)
- (a) The cation to which one or more neutral molecules or anions are attached is called as centre of coordination
- (b) Since the central ion acts as an acceptor and thus has to accommodate electron pairs donated by the donor atom of the ligands, it must have empty orbitals
- (c) This explains why the transition metals having empty d-orbitals form coordination compounds very readily.
- (d) In the complexes  $[Ni(NH_3)_6]^{2+}$  and  $[Fe(CN)_6]^{3-}$ ,  $Ni^{2+}$  and  $Fe^{3+}$  respectively are the central ions.
- 2. Ligand :
- (a) The neutral molecules, anions or cations which are directly linked with the central metal atom or ion in a complex ion are called ligands.
- (b) Ligand donate a pair of electrons to the central atom
- (c) Ligands are attached to the central metal ion or atom through coordinate bonds or dative linkage

- (d) Ligands are normally polar molecules like  $\ddot{N}H_3$ ;  $H_2\ddot{O}$  or anions such as  $Cl^-$ ,  $OH^-$ ,  $CN^-$  etc. which contain at least one unshared pair of valency electrons.
- (e) With few exceptions, free ligands have lone pair of electron that is not engaged in bonding for example.

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:C \equiv N:^{-}, :CI:^{-}
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- 2.1 Types of Ligands on the basis of number of donor atoms present in them :
- (A) Mono-or unidentate ligands : They have one donor atom, i.e. they supply only one electron pair to central metal atom or ion.

Examples :  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $H_2O$ ,  $NH_3$ ,  $CN^-$ ,  $NO_2^-$ ,  $ON^-$ , CO

(B) Bidentate ligands : Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands. Some examples are :



(C) **Tridentate ligands :** The ligands having three donor atoms are called tridentate ligands. Examples are:



Diethylene triamine (Dien)



2,2',2"-Terpyridine (terpy)

**(D)** Tetradentate ligands : These ligands possess four donor atoms. Examples are:



(E) **Pentadentate ligands :** They have five donor atoms. For example, ethylenediamine triacetate ion.



Ethylenediamine triacetato ion

(F) Hexadentate ligands : They have six donor atoms. The most important example is ethylenediamine tetraacetate ion.



Ethylenediamine tetraacetato ion (EDTA)4-

#### (G) Chelating ligands.

- (a) Polydentate ligands whose structures permit the attachment of two or more donor sites to the same metal ion simultaneously, thus closing one or more rings are called chelating ligands and the compounds formed are known as chelate compounds.
- (b) A chelate may be defined as a ring structure formed by the combination of a polydentate ligand having two or more donor atoms with a metal ion forming part of the ring.
- (c) The process of formation of chelates is called chelation.
- (d) Chelate complexes are more stable than ordinary complexes in which the ligand is a monodentate
- (e) This increased stability of the compound due to chelation is called the chelate effect
- (f) In the complex ion given below, 5 membered rings are formed. So all these are called chelate complexes



- (g) Generally the chelate complexes with 5 or 6 membered rings are more stable.
- (h) Out of these, 5 membered rings are very stable when they involve saturated ligands.
  - (i) On the other hand 6-membered ring structures acquire maximum stability when they involve unsaturated ligands containing conjugate double bond. This is due to the resonance effects involving metal d-orbitals and ligand p-orbital electrons.

- **2.2 Classification of ligands on the basis of donor** and acceptor properties of the ligands
- (A) Ligands having one (or more) lone pair (or pairs) of electrons
- (a) Ligands which contain vacant  $\pi$ -type orbitals that can receive back donated  $\pi e^-$  from M-ion in low oxidation state.

e.g.: CO, NO, CN, NC, R–N=C,  $R_3P$ ,  $R_3As$  $\alpha,\alpha$ –dipyridyl, o-phenanthroline

- (b) All these ligands also have filled donor orbital in addition to vacant π-type acceptor orbitals.
- (c) Thus in there complexes both metal and ligand function as donors and acceptors

$$(M \xrightarrow{\sigma}_{\pi} L)$$

- (d) Ligands which do not have vacant orbitals to receive back donated electron from metals eq. H<sub>2</sub>O, NH<sub>3</sub> F.
- (B) Ligands having no lone pairs of electrons but have p bonding electron eq. Ethylene, benzene, cyclopentadenyl-ion

#### Note:

- (1) Polydentate ligands have Flexidentate character it is not necessary that all the donor atoms present in the polydentate ligands should form coordinate bonds with central metal atom or ion.
- (2) There are certain ligands which have two or more donor atoms but during formation of complexes only one donor atom is attached to metal ion. Such ligands are called ambidentate ligands such as CN, CNS

#### **3** Coordination number :

- (a) The number of atoms of the ligands that are directly bond to the central metal atom or ion by coordinate bonds is known as the coordination number of the metal atom or ion.
- (b) It is actually the number of coordinate covalent which the ligands form with the central metal atom or ion

 (c) Some common coordination numbers exhibited by metal ions are 2,4,6. The light transition metals exhibit 4 and 6 coordination numbers while heavy transition metals may exhibit coordination number more than 6

(d) For example, the coordination number of Ni in the complex  $[Ni(NH_3)_4]Cl_2$  is 4 and that of Pt in the complex  $K_2[PtCl_6]$  is 6

## 4. Coordination sphere :

- (a) The central metal atom and the ligands directly attached to it are collectively termed as the coordination sphere
- (b) Coordination sphere is written inside square bracket, for example  $[Co(NH_3)_6]^{3+}$
- (c) The central metal atom and the ligands inside the square bracket behave as a single entity
- (d) The part outside the bracket is called ionisation sphere.
- (e) The species present in the coordination sphere are nonionizable
- (f) The species present in the ionization sphere are ionisable



## 5. Oxidation state

- (a) It is a number which represents the electric charge on the central metal atom of a complex ion
- (b) For example, the O.N. of Fe, Co and Ni in [Fe(CN)<sub>6</sub>]<sup>4-</sup>, [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> and Ni(CO)<sub>4</sub> is +2, +3 and zero respectively
- (c) The charge of the complex is the sum of the charges of the constituent parts.

### 6. Effective atomic number (EAN)

- (a) In order to explain the stability of the complex, Sidgwick proposed effective atomic number
- (b) It can be defined as the resultant number of electrons with the metal atom or ion after gaining electrons from the donor atoms of the ligands.
- (c) The EAN generally coincides with the atomic number of next noble gas in some case.
- (d) EAN is calculated by the following relation EAN = atomic number of the metal-number of electrons lost in ion formation + number of electrons gained from the donor atoms of the ligands
- (e) The EAN values of different metal in their respective complexes are tabulated as follows

Complex	Metal (Oxid. state)	At. No. of metal	Coordination number	Effective atomic number
$K_4[Fe(CN)_6]$	+2	26	6	$(26 - 2) + (6 \times 2) = 36$ [Kr]
$[Cu(NH_3)_4]SO_4$	+2	29	4	$(29 -2) + (4 \times 2) = 35$
$[Co(CH_3)_6]Cl_3$	+3	27	6	$(27 - 3) + (6 \times 2) = 36$ [Kr]
Ni(CO) <sub>4</sub>	0	28	4	$(28 - 0) + (4 \times 2) = 36$ [Kr]
$K_2[Ni(CN)_4]$	+2	28	4	$(28 - 2) + (4 \times 2) = 34$
$K_{2}[PtCl_{6}]$	+4	78	6	$(78 - 4) + (6 \times 2) = 86 [Rn]$
$K_{3}[Cr(C_{2}O_{4})_{3}]$	+3	24	6	$(24 - 3) + (6 \times 2) = 33$
$K_{3}[Fe(CN)_{6}]$	+3	26	6	$(26 -3) + (6 \times 2) = 35$
K <sub>2</sub> [HgI <sub>4</sub> ]	+2	80	4	$(80 - 2) + (4 \times 2) = 86$ [Rn]
$[Ag(NH_3)_2]Cl$	+1	47	2	$(47 -1) + (2 \times 2) = 50$
$K_2[PdCl_4]$	+2	46	4	$(46 -2) + (4 \times 2) = 52$

Solved Examples **Ex.3** The EAN of nickel in  $Ni(CO)_4$  is (A) 36 (B) 38 (C) 28 (D) 54 **Sol.** (A) Effective atomic no. (EAN) = at. no. of central atom – oxidation state +2 x (no. of ligands)  $= 28 - 0 + 2 \times 4 = 36$ **Ex.4** The charge on cobalt in  $[Co(CN)_6]^{3-}$  is (A) -6 (B) +3 (C) –3 (D) +6 Sol. (B) The algebraic sum of oxidation no. of all atoms in a complex ion is equal to charge on that ion. i.e.,  $a + 6 \times (-1) = -3$ ,  $\therefore a = +3$ **Ex.5** Co-ordination number of Co in  $[Co (NH_3)_6]^{2+}$ is (A) 4 (B) 5 (D) 8 (C) 6 Sol. (C) Co-ordination number is equal to total number of ligands in a complex. **Ex.6** The neutral ligand is (A) Chloro (B) Hydroxo (C) Ammine (D) Oxalato Sol. (C) :NH<sub>3</sub> has no charge but acts as ligand.

**Ex.7** NH<sub>2</sub>.NH<sub>2</sub> serves as :

(A) Monodentate ligand (B) Chelating ligand

- (C) Bridging ligand (D) (a) and (c) both
- **Sol. (D)** NH<sub>2</sub>.NH<sub>2</sub> serves as monodenate as well as bridging ligand because a 3-membered ring will be too strained to be stable.

## I.U.P.A.C. NAMING OF COORDINATION COMPOUNDS

Due to wide variety of coordination compounds it is essential to use a unified system of nomenclature. Though a lot of compounds are known by their trivial names only, but I.U.P.A.C. has introduced rules for the naming of coordination compounds as follows

- 1. The order of listing the ions
- (a) In common salts cation is named first and then the anion.
- (b) In the complex ion (Cation or anion) ligands are named first followed by the name of central atom
- (c) The oxidation state of the central metal is indicated by Roman numeral in brack ets immediately after its name ; (0) in dicates zero o.s.
- (d) In case the complex is non ionic, it is amed as one word e.g. [Ni(CO)<sub>4</sub>] is called tetracarbonyl nickel (0)
- (e) The suffix ate is added to the name of central metal forming anionic complex ion. In cationic complex ion, the name of metal (usual name) is fallowed by the oxidation number in bracket. However in some metals Latin names are preferred in place of English names e.g. ion as ferrate, lead as plumbate and silver as argentate.

## 2. Name of the ligand :

- (a) If there are two or more different kinds of ligands, they are named in alphabatical order without separation by hyphen.
- (b) When there are several ligands of same kind, they are listed alphabetically
- (c) Anionic ligands ending with 'ide' are named by replacing 'ide' by suffix 'O'.

e.g. Symbol	Name as	$N^{3-}$	Nitrido
	ligand		
Cl-	Chloro	$O_2^{2-}$	Peroxo
Br⁻	Bromo	$O_2H^-$	Perhydroxo
CN <sup>-</sup>	Cyano	${\bf S}^{2-}$	Sulphido
$O^{2-}$	Oxo	$NH^{2-}$	Amido
OH⁻	Hydroxo		

(d) Ligands whose names end in 'ite' or 'ate' become 'ito' or 'ato' i.e., by replacing the ending 'e' with 'o' as follows

Symbol	Name as ligand
CO <sub>3</sub> <sup>2–</sup>	Carbonato
$C_{2}O_{4}^{2-}$	Oxalato

$SO_4^{2-}$	Sulphato
$NO_3^{-}$	Niitrato
SO <sub>3</sub> <sup>2-</sup>	Sulphito
CH <sub>3</sub> COO	- Acetato
$NO_2^{-}$	(bonded through oxygen) nitrite

(bonded through nitrogen) nitro

(e) Neutral ligands are given the same names at the neutral molecules. For example. Ethylene diamine as a ligand is named ethylene diamine in the complex. However some ex ceptions to this rule are

$H_2O$		Aquo	)	
NH <sub>3</sub>		Amm	ine	
CO		Carbo	onyl	
NO		Nitro	syl	
CS		Thio	carboi	ıyl

(f) Names of positive ligands ends in 'ium' e.g.
 NH<sub>4</sub><sup>+</sup>Ammonium

NO<sup>+</sup> Nitrosylium

NH<sub>2</sub>NH<sub>3</sub><sup>+</sup> Hydrazinium

(g) If the number of a particular ligand is more than one in the complex ion, the number is indicated by using Greek numbers such as di,tri, tetra, penta, hexa, etc.

However, when the name of the ligand includes a number, e.g. dipyridyl, ethylene diamine, then bis, tris, tetrakis are used in place of di, tri, tetra, etc

- (h) In case of chelating ligands or ligands having di, tri, tetra, etc, in their name the prefixes bis, tris, tetrakis are used before ligands placed in paranthesis
  - (i) In poly nuclear complexes the bridging group is indicated in the formula of the complex by separating it from the rest of complex by hyphens and adding before its name or in poly nuclear complex (a complex with two or more metal atoms) bridging ligands (which links two metal atoms) is denoted by the prefix  $\mu$  before its name.

## Solved Examples

**Ex.8** The correct IUPAC name of  $[CoF_2(en)_2] ClO_4$  is

- (A) Difluorobis (ethylene diamine) Cobalt (III) per chlorate
- (B) Bis (ethylene diamine) difluoro cobalt (III) per chlorate
- (C) Bis (ethylene diamine) difluoro cobalt (II) per chlorate
- (D) None of these

**Sol.** (B) Follow IUPAC rules.

Ex.9 The formula of dichlorobis (urea) copper (II) is

- (A)  $[CuO = C(NH_2)_2]Cl_2$
- (B)  $[CuCl_2 \{O=C(NH_2)_2\}]$
- (C)  $[Cu{O=C(NH_2)_2}Cl]Cl$
- (D)  $[CuCl_2][O=C(NH_2)_2]H_2$
- Sol. (B) Follow IUPAC rules.
- **Ex.10** Write the formulae of the following coordination compounds
  - (I) Potassium hexanitritoferrate (III) (ii) Dichloroplatinum (IV) tetrachloropl-atinate (II)
  - (II) Bis (acetylacetonato) oxovanadium (IV) (iv) Potassium tetrahydroxozincate (II)
  - (v) Sodium pentacyanonitrosylsulphidofe rrate (III)

**Sol.** (i)  $K_3[Fe(ONO)_6]$  (ii)  $[PtCl_2][PtCl_4]$ 

(iv)  $K_2[Zn(OH)_4]$ 

(v)  $Na_{4}[Fe(CN)_{5}NOS]$ 

(iii)  $[VO(acac)_2]$ 

- **Ex.11** Which of the following names are not correct? Point out the mistakes.
  - (i)  $[Cu(H_2O) (NH_3)]Br_2$ ; Amminoaquodibromocopper (I)
  - (ii)  $Na_3[Al(C_2O_4)_3]$  Trisodium trioxalatoaluminate (III)
  - (iii) Na<sub>2</sub> [Ni(EDTA)] ; Sodium ethylenediaminetetracetato nickel (III)
  - (iv) [Co(NH<sub>3</sub>)<sub>5</sub>ONO]SO<sub>4</sub> ; Pentaamminenitrocobalt (III) sulphate
- Sol. (i) Ammine aqua copper (II) bromide
  - (ii) Sodium trioxalato aluminate (III)
  - (iii) It is correct
  - (iv) Pentammine nitrito cobalt (III) sulphate

## BONDING IN COORDINATION COMPOUNDS

#### 1. Werner's coordination theory

Alfred Werner (considered as the father of coordination chemistry) studied the structure of coordination complexes such as  $CoCl_3$ .  $6NH_3$  and  $CuSO_4$ .  $4NH_3$  in 1893. According to him-

- (a) Each metal in coordination compound possesses two types of valencies :
  - (i) primary valency or principal valencies or ionisable valencies.
  - (ii) Secondary valency or nonionisable valencies
- (b) Primary valencies are satisfied by anions only. The number of primary valencies depends upon the oxidation state of the central metal. It may change from one compound to other. These are represented by dotted lines between central metal atom and anion.
- (c) Secondary valencies are satisfied only by electron pair donor, the ions or the neutral species. These are represented by thick lines.
- (d) Each metal has a fixed number of secondary valencies also referred as coordination number. The coordination number depends mainly on the size and the charge on the central atom. The maximum number of ions or molecules that the central atom can hold by secondary valencies is known as coordination number.
- (e) The ions attached to primary valencies possess ionising nature whereas the ions attached to secondary valencies do not ionise when the complex is dissolved in a solvent.
- (f) Every central ion tends to satisfy its primary as well as secondary valencies.
- (g) The secondary valencies are directional and are directed in space about the central metal ion. The primary valencies are non-directional. The presence of secondary valencies gives rise to stereoisomerism in complexes.
- (h) Initially, Werner had pointed out coordination number of a metal atom to be four or six.

- (i) The six valencies were regarded to be directed to the corners of a regular octahedron circumscribed about the metal ion. For metals having four coordination number, the four valencies are either arranged in a planar or tetrahedral nature.
- (j) Thus on the basis of werner theory, the  $CoCl_3$ . 6 NH<sub>3</sub> is called hexamminecobalt (III) chloride because there are six ammonia ligands and the cobalt is in the +3 oxidation state, i.e. cobalt has three primary valencies and six secondary valencies. The complex can therefore be represented as shown.



**Note:** Now, it has been proposed that coordination number of a metal may be any whole number between 2 and 9

## 2. Sidgwick Theory and EAN rule

Sidgwick suggested that the metal ion will continue accepting electron pairs till the total number of electrons in the metal ion and those donated by ligands is equal to that of the next noble gas. This total number of electrons is called EAN of the metal which we have already discussed.

3. Valence Bond Theory

The salient features of the theory are summarised below.

(a) The central metal ion has a number of empty orbitals for accommodating electrons donated by the ligands. The number of empty orbitals is equal to the coordination number of the metal ion for the particular complex.

- (b) The atomic orbitals (s, p or d) of the metal ion hybridize to form hybrid orbitals with definite directional properties. These hybrid orbitals now overlap with the ligand orbitals to form strong chemical bonds.
- (c) The d-orbitals involved in the hybridization may be either inner (n - 1) d orbitals or outer n dorbitals. The complexes formed in these two ways are referred to as low spin and high spin complexes, respectively.
- (d) Each ligand contains a lone pair of electrons.
- (e) A covalent bond is formed by the overlap of a vacant hybridized metal orbital and a filled orbital of the ligand. The bond is also sometimes called as a coordinate bond.
- (f) If the complex contains unpaired electrons, it is paramagnetic in nature, while if it does not contain unpaired electrons, it is diamagnetic in nature.
- (g) The number of unpaired electrons in the complex, points out the geometry of the complex as well as hybridisation of central metal ion and vice versa. In practice, the number of unpaired electrons in a complex is found from magnetic moment measurements as illustrated below.
  - $\mu = \sqrt{n (n+2)}$  where n = no of lone pair Thus the knowledge of the magnetic moment can be of great help in ascertaining the type of complex
- (h) Under the influence of a strong ligand, the electrons can be forced to pair up against the Hund's rule of maximum multiplicity.

Magnetic moment	0	1.73	2.83	3.87	4.90	5.92
(Bohr magnetons)						
Number of	0	1	2	3	4	5
unpaired						
electrons						

#### Draw back of V.B. Theory

- (i) It describes bonding in coordination compounds only qualitatively
- (ii) It does not offer any explanation for the optical absorption spectia of complex
- (iii) It does not describe the detailed magnetic properties of coordination compounds.

## 4. Crystal field Theory

This is the more advanced theory and satisfactorily explains the optical absorption spectra and magnetic properties of complexes which were not explained by V.B.T. But its details are beyond the scope of this text.

## (A) Crystal field splitting in octahedral coordination entities

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal d orbitals and the electrons (or negative charges) of the ligands.

Such a repulsion is more when the metal d orbital is directed towards the ligand than when it is away

from the ligand. Thus, the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy; and the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$ orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field.

Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy,  $t_{2g}$  set and two orbitals of higher energy,  $e_g$  set.

This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by  $\Delta_o$  (the subscript o is for octahedral). Thus, the energy of the two eg orbitals will increase by (3/5)  $\Delta_o$  and that of the three  $t_{2g}$  will decrease by (2/5)  $\Delta_o$ .



## Fig.: d orbital splitting in an octahedral crystal field

The crystal field splitting,  $\Delta_0$ , depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below:

$$\begin{split} I^- < Br^- < SCN^- < Cl^- < S2^- < F^- < OH^- \\ < C_2O_4^{\ 2^-} < H_2O < NCS^- < edta^{4-} \\ < NH_3 < en < CN^- < CO \end{split}$$

Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands.

Let us assign electrons in the d orbitals of metal ion in octahedral coordination entities. Obviously, the single d electron occupies one of the lower energy  $t_{2g}$  orbitals. In  $d_2$  and  $d_3$  coordination entities, the d electrons occupy the  $t_{2g}$  orbitals singly in accordance with the Hund's rule.

For d<sup>4</sup> ions, two possible patterns of electron distribution arise: (i) the fourth electron could either enter the  $t_{2g}$  level and pair with an existing electron, or (ii) it could avoid paying the price of the pairing energy by occupying the  $e_{a}$  level.

Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting,  $\Delta_{o}$  and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two options are:

- (i) If  $\Delta_0 < P$ , the fourth electron enters one of the  $e_g$  orbitals giving the configuration  $t_{2g}^3 e_g^1$ . Ligands for which  $\Delta_0 < P$  are known as weak field ligands and form high spin complexes.
- (ii) If  $\Delta_0 > P$ , it becomes more energetically favourable for the fourth electron to occupy a  $t_{2g}$  orbital with configuration  $t_{2g}{}^4e_g{}^0$ . Ligands which produce this effect are known as strong field ligands and form low spin complexes.

Calculations show that d<sup>4</sup> to d<sup>7</sup> coordination entities are more stable for strong field as compared to weak field cases.

## (B) Crystal field splitting in tetrahedral coordination entities

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting.

For the same metal, the same ligands and metalligand distances, it can be shown that  $\Delta_t = (4/9)$  $\Delta_o$ . Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.



Fig. : d orbital splitting in a tetrahedral crystal field.

## Solved Examples

**Ex.12** When the configuration is d<sup>7</sup> in a transition metal, the paramagnetic susceptibility will be equal to

(A) 3.87 B.M.	(B) 2.68 B.M.
(C) 5.92 B.M.	(D) 6.92 B.M.

- Sol. The magnetic moment values in Bohr magneton for 1 lone electron is 1.73, for 2 is 2.83, for 3 is 3.87, for 4 is 4.90, for 5 is 5.92, for 6 is 6.92 and so on.  $d^7$  configuration has three lone electrons, hence,  $\mu = 3.87$  BM.
- **Ex.13** The shape of the complex  $Ag(NH_3)_2^+$  is :

(A) Octahedral	(B) Square planar
(C) Tetrahedral	(D) Linear

- **Sol.** (D)  $Ag(NH_3)_2^+$  has sp- hybridisation and linear complex.
- **Ex.14** Hexafluoroferrate (III) Ion is an outer orbital complex. The number of unpaired electrons present in it is.
  - (A) 1
    (B) 5
    (C) 4
    (D) Unpredicatable
- **Sol.** (B) Electronic configuration of  $[FeF_6]^{3-}$  is :



- **Ex.15** Find out the hybridization, geometry and magnetic moment of the complexes :
  - (i)  $[Co(NH_3)_{6}]^{3+}$  (ii)  $[Cr(CN)_{6}]^{3-}$
- Sol. (i) The oxidation state of cobalt in the complex  $[Co(NH_3)_6]^{3+}$  is +3

The electronic configuration of Co<sup>3+</sup> ion is :



Rearrangement

Octahedral, zero magnetic moment

(ii) The oxidation state of chromium in the complex is +3. The electronic configuration of  $Cr^{3+}$  ion is



Octahedral, mag. moment =  $\sqrt{3x (3+2)}$ =  $\sqrt{15}$  = 3.87 BM

- **Ex.16** Complex with CN<sup>-</sup> ligands are usually
  - (A) High spin complexes(B) Low spin complexes(C) Both(D) None
- Sol. (B) A strong field ligand produces low spin complexes.
- **Ex.17** Which of the following has least conductivity in aqueous solution

(A)  $Co(NH_3)_4 Cl_3$  (B)  $Co(NH_3)_3 Cl_3$ (C)  $Co(NH_3)_5 Cl_3$  (D)  $Co(NH_3)_6 Cl_3$ 

**Sol.** (**B**) Werner's theory

 $[Co(NH_3)_3Cl_3]$  is non electrolyte

#### SHAPE OF COMPLEXES

The shape of complexes depends upon hybridization state of central atom, it is described as follows:

#### 1. Octahedral complexes :

On the basis of hybridized orbitals it can be of two type as  $d^2sp^3$  (inner orbital) or  $sp^3d^2$  (outer orbital) hybridized.

#### 1.1 Inner orbital complexes :

We have already discussed that in these type of complexes the d-orbitals used are of lower quantum number i.e. (n - 1) various examples are as follow

- (a) Complexes formed by the use of inner orbitals are diamagnetic or have reduced paramagnetism.
- (b) These are called as low spin or spin paired complexes

## 1.1.1 [Fe(CN)<sub>6</sub>]<sup>4-</sup>

- (a)  $e^-$  configuration of  $Fe^{26} = [Ar] 3d^64s^2$
- (b)  $e^{-}$  configuration of  $Fe^{+2} = [Ar] 3d^{6}$



(c)  $e^-$  configuration of  $Fe^{+2}$  after rearrangement



(d) The above rearrangement is due to presence of cyanide ligand

- (e) In this state Fe<sup>2+</sup> undergoes d<sup>2</sup>sp<sup>3</sup> hybridisation to from six d<sup>2</sup>sp<sup>3</sup> hybrid orbitals, each of which accepts electron pair donated by CN<sup>-</sup> ions.
- (f) The resultant complex is inner octahedral as shown in figure and it should be diamagnetic as it has no unpaired electron. Formation of  $[Co(NH_3)_6]^{3+}$ takes place in the same manner



Octahedral shape of  $[Co(NH_3)_6]^{3+}$ 



- (d) The resulting complex is octahedral due to  $d^2sp^3$  hybridization
- (e) due to presence of unpaired  $e^-$  it is paramagnetic

1.1.3 [Cr (NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>



- (d) This  $d^2sp^3$  hybridisation leads to octahedral geometry, the complex  $[Cr(NH_3)_6]^{3+}$  will be octachedral in shape
- (e) Since the complex ion has 3 unpaired electrons it must be paramagnetic which is founded to be so
- (f) Other complexes of chromium with similar inner structure are  $[Cr(CN)_6]^{3-}$  and  $[Cr(H_2O)_6]^{3+}$

### 1.2 Outer orbital complexes.

- (a) In these complexes s, p as well as d orbitals involved in hybridization, belong to the highest quantum number (n)
- (b) complexes formed by the use of outer n, d orbitals will be paramagnetic.
- (c) These complexes are called high- spin or spin free complexes
- (d) The outer orbital complexes have greater number of unpaired electrons.

1.2.1 [CoF<sub>6</sub>]<sup>3-</sup>



- (d) Due to octahedral orientation of six  $sp^3d^2$  hybridised orbitals shape  $[CoF_6]^{3-}$  complex ion is octahedral
- (e) Due to presence of four unpaired electrons is  $3d \text{ orbital } [CoF_6]^{3-}$  ion has paramagnetic character
- (f) Other examples are  $[FeF_6]^{3-}$ ,  $[Fe(NH_3)_6]^{2+}$ ,  $[Ni(NH_3)_6]^{2+}$ ,  $[Cu(NH_3)_6]^{2+}$ ,  $[Cr(H_2O)_6]^{3+}$

## 2. Tetrahedral Complexes :

These are formed by sp<sup>3</sup> hybridisation. Complexes of Zn<sup>2+</sup> are invariable tetrahedral because they involve sp<sup>3</sup> hybrid orbitals

## 2.1 $[Zn(NH_3)_4]^{2+}$

(a) configuration of  $Zn^{30}$ 



(c)  $Zn^{2+}$  in sp<sup>3</sup> hybridised state





- (e) Since the complex is formed by sp<sup>3</sup> hybridisation, it is tetrahedral
- (f) Since all electrons are paired it is diamagnetic
- 2.2 [Ni(CO)<sub>4</sub>]
- (a) Ni<sup>28</sup>



(b) Ni after rearrangement



- (c) The empty one 4s and three 4p orbitals mix to form four sp<sup>3</sup> hybridised orbitals
- (d) each orbital accepts one electron pair from carbon monoxide molecule forming [Ni(CO)<sub>4</sub>]
- (e) The shape of nickel tetra carbonyl is tetrahedral as shown below
- (f) It is diamagnetic in nature



## 3. Square planar complex.

These are formed due to dsp<sup>2</sup> hybridisation.

These complexes tend to be formed when the central ion has only one d orbital available in the inner shell



#### Co-ordination numbers, Hybridised orbitals and geometry of some co-ordination compounds

Coordination Number	Hybridised orbital	Geometrical shape of the complex	Examples of complex
2	sp	$L \stackrel{180^{\circ}}{\checkmark} L$ Linear	$[Ag(NH_3)_2]^+$ $[Ag(CN)_2]^-$
3	sp <sup>2</sup>		[HgI <sub>3</sub> ] <sup>-</sup>
4.	sp <sup>3</sup>	L L Tetrahedral	$[FeCl_{4}]^{-1}$ $[Ni(CO)_{4}]^{0}$ $Zn(NH_{3})_{4}^{+2}$ $[ZnCl_{4}]^{-2}, [CuX_{4}]^{-2}$ where X = CN <sup>-1</sup> Cl <sup>-1</sup> , Br <sup>-1</sup> , 1 <sup>-1</sup> , CNS
4.	$dsp^2$ The d-orbital involved is $d_{x^2-y^2}$ orbital of the inner shell, i.e. it is $(n - 1)d_{x^2-y^2}$ orbital	Square planar	$[Ni(CN)_4]^{-2}$ $[Pt(NH_3)_4]^{+2}$
5.	dsp <sup>3</sup> The d-orbital is (n - 1)d <sub>z</sub> <sup>2</sup> orbital	Lottingonal bipyramidal	$[CuCl_{5}]^{-3}$ $[MoCl_{5}]^{0}$ $[Fe(CO)_{5}]^{0}$



## Solved Examples

- Ex.18 The structure of iron pentacarbonyl is
  - (A) Square planar
  - (C) Triangular
- (B) Trigonal bipyramid(D) None





xx Electron pair donated by CO.

- **Ex.19** How would you account for the following : Ni(CO)<sub>4</sub> possesses tetrahedral geometry while  $[Ni(CN_4]^{2-}$  is square planar.
- **Sol.** In the formation of Ni(CO)<sub>4</sub>, nickel undergoes sp<sup>3</sup> hybridization, hence it is tetrahedral in shape.



In the formation of  $[Ni(CN)_4]^{2-}$ ,  $Ni^{2+}$  ion undergoes  $dsp^2$  hybridization, hence it is square planar in shape



ISOMERISM IN COMPLEXES

- (a) Compounds which have the same molecular formula, but differ in their properties due to the difference in structure ar called as **Isomers.**
- (b) Isomerism is commonly considered, to be the characteristic of only organic compounds, it is also found although less frequency among inorganic substances.

## (c) Classification of isomerism :

## STRUCTURAL ISOMERISUM

It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere.

## 1. Ionisation isomers :

The type of isomerism is due to the exchange of groups of or ion between the coordinating sphere and the ionisation sphere **Ex.** 

- (a)  $Co(NH_3)_4 Br_2SO_4$  can represent
  - (i) [Co(NH<sub>3</sub>)<sub>4</sub>Br<sub>2</sub>] SO<sub>4</sub> (red violet)
  - (ii)  $[Co(NH_3)_4]$  SO<sub>4</sub>] Br<sub>2</sub>(red).

These complexes give sulphate ion and bromide ion respectively

- (b)  $[Pt(NH_3)_4Cl_2] Br_2$  and  $[Pt(NH_3)_4Br_2]Cl_2$
- (c)  $[Co(NH_3)_4(NO_3)_2] SO_4$  and

$$[Co(NH_3)_4SO_4](NO_3)_2$$

## 2. Hydrate isomers :

This type of isomerism is due to presence of different number of water molecules inside a coordination sphere. **Ex.** 

- (a) Cr(H<sub>2</sub>O)<sub>6</sub>Cl<sub>3</sub> has three possible structure
  (i) [Cr(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub> violet
  - (ii) [Cr(H<sub>2</sub>O)<sub>5</sub>Cl] Cl<sub>2</sub>.H<sub>2</sub>O green
  - (iii) [Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>] Cl. 2H<sub>2</sub>O dark green.

These complexes differ from one another with respect to the number of water molecules acting as ligands.

Other hydrate isomers are -

- (i)  $[Co(NH_3)_4]H_2O$  Cl] Cl<sub>2</sub>
- (ii) [Co(NH<sub>3</sub>)<sub>4</sub> Cl<sub>2</sub>] Cl. H<sub>2</sub>O
- 3. Linkage or salt isomers :
- (a) This type of isomerism arises due to pres ence of ambidentate ligands like  $NO_2^-CN^-$  and  $SCN^-$
- (b) These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.

- (c) Such type of isomers are distinguished by infra red (I.R.) spectroscopy. **Ex.** 
  - (i)  $[Co(NH_3)_5NO_2] Cl_2$  and  $[Co(NH_3)_5ONO] Cl_2$
  - (ii) In NO<sub>2</sub><sup>-</sup> ligand, The coordinating sites are nitrogen (i.e., NO<sub>2</sub><sup>-</sup>Nitrogen ligand) or through oxygen (i.e. ONO Nitrogen ligand)
  - (iii) The nitro isomer is yellow and is stable to acids whereas nitrito ismoer is red and is decomposed by acids.

## 4. Coordination isomers :

- (a) This type of isomerism is exhibited when the complex has two complex ions in it -\*Cationic and anionic^.
- (b) This type of isomerism is caused by the interchange of ligands and metal ions between the two complex ions of the same complex. **Ex.** 
  - (i)  $[Co(NH_3)_6] [Cr(CN)_6]'$  $[Cr(NH_3)_6] [Co(CN)_6]$
  - (ii)  $[Co(NH_3)_6] [Cr(C_2O_4)_3]'$  $[Cr(NH_3)_6] [Co(C_2O_4)_3]$

## STEREO ISOMERISM

- (a) They have same molecule formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion.
- (b) The two stereo isomers which are possible are-Geometrical and optical.
- 1. Geometrical or cis Trans isomers :
- (a) The ligands occupy different positions around the central metal ion.
- (b) When two identical ligands are coor dinated to the metal ion from the ion same side then it is cis isomer. (Latin, cis means same).
- (c) If the two identical ligands are coordinated to the metal ion from opposite side then it is **Trans isomer** (in Latin, Trans means across)
- (d) These geometrical isomers differ in physical as well as in chemical properites.
- (e) Geometrical isomerism is most important in compounds with coordination numbers 4 and 6.
- (f) 4-coordinated complexes with tetrahedral geometry do not exhibit cis-Trans isomerism.
- (g) It is exhibited by 4-coordinated complexes with square planar geometry.

- 2. Geometrical isomers with coordination number (vi) Diglycinato platium (iv) complexes = 4 (Square planar complexes)
- (i) Complexes with general formula, **Ma**, **b**, (where both a and b are monodentate) can have Cis-and trans isomers.





С

Cis-isomer

Trans-isomer

(ii) Complexes with general formula Ma, bc can have Cis-and trans-isomers.





## (iii) [Pt (NH<sub>2</sub>),Cl<sub>2</sub>]





Cis(Cis-platin) anti cancer

## (iv) [Pt(NH<sub>3</sub>)<sub>2</sub>ClBr]



(v) Complexes with general formula, Mabcd can have three isomers.





3. Geometrical isomers with coordination number = 6



(ii) Facial and Meridional isomerism (Ma,b,)



## **Optically isomers :**

- (a) Optically active complexes are those which are nonsuperimposable over the mirror image structrue.
- (b) An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.
- (c) The complex which rotates plane polarised light to left hand side is laevo rotatory i.e., 'l' or '-' and if the complex rotates the plane polarised light to right hand side then it is **dextro rotatory 'd' or '+'**.

2+

- (d) Thus complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as optical isomers.
- (e) The 'd' and '*l*' isomers of a compound are called as **Enantiomers or Enantio morphs.**
- (f) Only those 6-coordinated complexes in which there are chelating agents i.e. bidentate ligands, exhibit optical isom erism. This is due to the absence of elements of symmetry in the complex.
- (g) Optical isomerism is not found in square planar complexes on account of the presence of axis of symmetry.

## **Optical isomer with Coordination number = 6**





Mirror

Mirror

Mirror

(ii) [Mabcedf]  $\rightarrow$  [Pt(py)NH<sub>3</sub>NO<sub>2</sub>ClBrI]



(iii) [M (AA)<sub>3</sub>]<sup>n+</sup>  $\rightarrow$  [Co(en)<sub>3</sub>]<sup>3+</sup>







NH<sub>3</sub>









### Solved Examples

- **Ex.20** Which of the following sets is/are example(s) of co-ordination isomerism in complexes ?
  - (A)  $[Co(NH_3)_6]$   $[Cr(CN)_6]$  and  $[Co(CN_6]$  $[Cr(NH_3)_6]$
  - (B)  $[Cr(H_2O)_5Cl]Cl_2H_2O$  and  $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ (C)  $[Co(NH_3)_5Br]SO_3$  and  $[Cr(NH_3)_5SO_4]Br$ (D)  $[Pt(NH_3)_2Cl_2]$  and  $[Pt(NH_3)_4]$   $[PtCl_4]$
- **Sol.** (A) When both positive and negative ions are complex, co-ordination isomerism may occur due to the interchange of ligands within the co-ordination sphere itself. e.g.  $[Co(NH_3)_6]$   $[Cr(CN)_6]$  and  $[Co(CN)_6]$   $[Cr(NH_3)_6]$  are two co-ordination isomers, where ammonia and cyanide ligands have been changed within the co-ordination sphere.

Choices (b), (c) and (d) are examples of hydrate isomers, ionisation isomers and polymerisation isomers, respectively.

- **Ex.21** Which of the following does/do not exhibit optical isomerism
  - (A) tetrahedral complexes
  - (B) square planar complexes
  - (C) octahedral complexes
  - (D) polynuclear complexes
- **Sol.** A square planar complex does not exhibit optical activity because it has a horizontal plane of symmetry

#### STABILITY OF COMPLEX

- (a) A complex is formed in solution by the stepwise addition of ligands to a metal ion
- (b) This can be expressed as follows  $M + L \Leftrightarrow ML$ where M = metal and L is ligand
- (c) The stability constant K for this reaction is as shown K =  $\frac{ML}{[M][L]}$
- (d) This metal can again get a ligand  $ML + L \Leftrightarrow ML_2$
- (e) The forthcoming stability constant K' is  $K_{1} = \frac{[ML_{2}]}{[ML][L]}$ its value is less than K

- (f) The higher the value of stability constant stabler is the complex.
- (g) The value of stability constants for some of the complexes are given below :

Complex	Stability constant
$[Cu(NH_3)_4]^{2+}$	4.5 x 10 <sup>11</sup>
$[Ag(NH_{3})_{2}]^{+}$	1.6 x 10 <sup>7</sup>
$[Co(NH_3)_6]^{2+}$	1.12 x 10 <sup>6</sup>
[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	5.0 x $10^{33}$
[AgCl <sub>2</sub> ] <sup>-</sup>	1.11 x 10 <sup>5</sup>
$[AgBr_2]^-$	1.28 x 10 <sup>7</sup>
$[Ag(CN)_2]^-$	$1.0 \times 10^{22}$
$[Cu(CN)_{4}]^{2-}$	$2.0 \times 10^{27}$
$[Fe(CN)_{6}]^{3-}$	7.69 x 10 <sup>43</sup>

1. Factors influencing the stability of complex

#### 1.1 Nature of central ion -

- (a) The complex will be more stable for higher values of charge density  $\left(\frac{Ch \operatorname{arge}}{\operatorname{radius}}\right)$
- (b) The higher the electronegativity of the central ion, the greater is the stability of its complexes
- (c) The higher the oxidation state of the metal the more stable is the compound
- 1.2 Nature of ligand
- (a) A basic ligand is likely to easily donate its electrons. Thus a more basic ligand will form more stable complex.
- (b) Chelating ligands form more stable complexes as compared to monodentate ligands.

#### Solved Examples

- **Ex.22**  $[Cu(CN)_4]^{2-}$  is more stable complex than  $[Cu(NH_3)_4]^{2+}$ . Explain
- **Sol.** The higher stability constant (K = 2 x 10<sup>27</sup>) for  $Cu^{2+} + 4CN^{-} \Leftrightarrow [Cu(CN)_4]^{2-}$  than for  $[Cu(NH_3)_4]^{2+}$ which is 4.5 x 10<sup>11</sup> explains stability.
- **Ex.23**  $[Ti(H_2O)_6]^{3+}$  is coloured while  $[Sc(H_2O)_6]^{3+}$  is colourless. explain
- **Sol.**  $Sc(H_2O)_6^{3+}$  has no unpaired electron in its d subshell and thus d-d transition is not possible whereas  $Ti(H_2O)_6^{3+}$  has one unpaired electron in its d subshell which gives rise to d-d- transition, to impart colour.