

## CO-ORDINATION COMPOUNDS

### Double salt and Complex salt

A salt that keeps its identity only in solid state is called a double salt. In solution they dissociate into component ions. E.g.: Mohr's salt  $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ , Carnalite  $[\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}]$ , Potash alum  $[\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}]$ .

The salt that keeps its identity both in solid and solution states is called a complex salt. e.g.: potassium ferrocyanide

$\{\text{K}_4[\text{Fe}(\text{CN})_6]\}$ ,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ ,  $\text{K}_2[\text{PtCl}_4]$ ,  $[\text{Ni}(\text{CO})_4]$  etc.

### Some definitions

**1. Co-ordination entity:** The central metal atom or ion and ligands form a co-ordination entity. For example,  $[\text{CoCl}_3(\text{NH}_3)_3]$  is a co-ordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{PtCl}_2(\text{NH}_3)_2]$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ .

**2. Central atom/ion:** In a co-ordination entity, the atom/ion to which a fixed number of ions/neutral molecules are attached is called the central atom or ion. For example, the central atom/ion in the co-ordination entities:  $[\text{NiCl}_2(\text{H}_2\text{O})_4]$ ,  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  are  $\text{Ni}^{2+}$ ,  $\text{Co}^{3+}$  and  $\text{Fe}^{3+}$  respectively.

These central atoms/ions are also referred to as Lewis acids, since they accept electron pairs from ligands.

**3. Ligands:** The ions or neutral molecules bound to the central atom/ion in the coordination entity are called ligands. For a species to act as ligand, it can donate atleast one pair of electron to the central atom. The atom of the ligand which is directly bonded to the central atom or ion is called co-ordinating atom or donor atom. Examples for ligands are  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{F}^-$ ,  $\text{I}^-$ ,  $\text{OH}^-$ ,  $\text{CN}^-$ ,  $\text{NC}^-$ ,  $\text{CNO}^-$ ,  $\text{NCO}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{CNS}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CO}$  etc.

### Types of ligands

Based on the number of donor atoms of the ligand that binds to a metal ion or atom, the ligands are classified as follows:

**a) Monodentate or unidentate ligand:** A ligand that binds to the central atom/ion through a single donor atom, is said to be unidentate ligand. E.g.:  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CN}^-$ ,  $\text{NC}^-$ ,  $\text{SCN}^-$  etc.

**b) Bidentate (Didentate) ligands:** A ligand that binds to the central atom through two donor atoms is called a bidentate ligand.

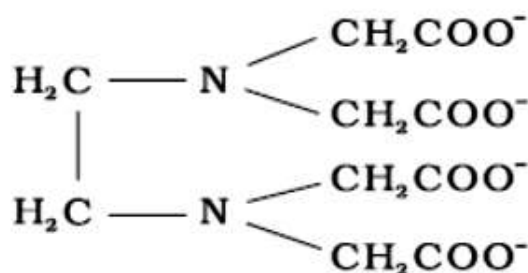
E.g.: Ethane-1,2-diamine or ethylenediamine ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ) notated as 'en' and oxalate ion ( $\text{C}_2\text{O}_4^{2-}$ ).

**c) Polydentate ligand:** A ligand that binds to the central atom through more than two donor atoms is called polydentate ligand. E.g.: Triethylamine ammonia

$[\text{N}(\text{CH}_2\text{-CH}_2\text{-NH}_2)_3]$ ,

Ethylenediamine tetraacetate ion ( $\text{EDTA}^{4-}$ ) etc.

Ethylenediamine tetraacetate ion ( $\text{EDTA}^{4-}$ ) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.



Ethylenediamine tetraacetate ion ( $\text{EDTA}^{4-}$ )

Ligands are also classified as:

**i) Ambidentate ligands:** They are unidentate ligands which contain more than one donor atoms. They can co-ordinate through two different atoms. Examples of such ligands are the  $\text{NO}_2^-$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$ ,  $\text{CNO}^-$  etc.  $\text{NO}_2^-$  ion can co-ordinate either through nitrogen or through oxygen atom to the central metal atom/ion. If the donor atom is N, it is written as  $\text{NO}_2^-$  and is called nitrito (N) and if it is O, it is written as  $\text{ONO}^-$  and is called nitrito(O). Similarly,  $\text{SCN}^-$  ion can co-ordinate either through sulphur atom ( $\leftarrow \text{SCN}$  - thiocyanato) or through nitrogen atom ( $\leftarrow \text{NCS}$  - isothiocyanato).

**ii) Chelating Ligands:** Di- or polydentate ligands can bind to the central atom through two or more donor atoms and form ring complexes. Such complexes are called chelates and such types of ligands are said to be chelating ligands. Complexes containing chelating ligands are more

stable than those containing unidentate ligands. For e.g. the complex  $[\text{Co(en)}_3]^{3+}$  is a chelate and ethane-1,2-diamine (en) is a chelating ligand.

**4. Denticity:** The number of donor atoms of a particular ligand that are directly bonded to the central atom is called denticity. For unidentate ligands, the denticity is 1, for didentate ligands it is 2 and so on.

**5. Co-ordination number:** The co-ordination number (C.N) of a metal ion in a complex can be defined as the total number of ligand donor atoms to which the metal is directly bonded. For example, in the complex ion  $[\text{PtCl}_6]^{2-}$  the co-ordination number of Pt is 6 and in  $[\text{Ni}(\text{NH}_3)_4]^{2+}$ , the co-ordination number of Ni is 4. Similarly, in the complex ions,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  and  $[\text{Co(en)}_3]^{3+}$ , the co-ordination number of both Fe and Co, is 6 because  $\text{C}_2\text{O}_4^{2-}$  and en (ethane-1,2- diamine) are bidentate ligands. The co-ordination number of the central atom/ion is determined only by the number of sigma bonds formed by the ligand with the central atom/ion. Generally, the co-ordination number of most of the complexes is 2, 4 or 6.

**6. Co-ordination sphere:** The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the co-ordination sphere. The ionisable groups are written outside the bracket and are called simple ions or counter ions. For example, in the complex  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , the coordination sphere is  $[\text{Fe}(\text{CN})_6]^{4-}$  and the counter ion is  $\text{K}^+$ .

**7. Co-ordination polyhedron:** The spatial arrangement of the ligands around the central atom/ion defines a co-ordination polyhedron about the central atom. The most common co-ordination polyhedra are octahedral, square planar and tetrahedral. For example,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is octahedral,  $[\text{Ni}(\text{CO})_4]$  is tetrahedral and  $[\text{PtCl}_4]^{2-}$  is square planar.

**8. Oxidation number of central atom:** The oxidation number of the central atom in a complex is defined as the residual charge on it, if all the ligands are removed along with their electron pairs that are shared with the central atom. The oxidation number is represented by a Roman numeral in simple brackets. For example, oxidation number of copper in  $[\text{Cu}(\text{CN})_4]^{3-}$  is +1 and it is written as Cu(I).

## 9. Homoleptic and Heteroleptic complexes:

Complexes which contain only one type of ligand are called homoleptic complexes. E.g.:  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$  etc.

Complexes which contain more than one type of ligands are called heteroleptic complexes.

e.g.,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ ,  $[\text{Cu}(\text{NH}_3)_2\text{Cl}_2]$  etc.

## IUPAC Nomenclature of Co-ordination Compounds

The following rules are used while naming co-ordination compounds:

- The cation is named first in both positively and negatively charged co-ordination entities.
- The ligands are named in alphabetical order before the name of the central atom/ion.
- Names of the anionic ligands end in -o, those of neutral and cationic ligands are the same except 'aqua' for  $\text{H}_2\text{O}$ , 'ammine' for  $\text{NH}_3$ , 'carbonyl' for CO and 'nitrosyl' for NO.
- Prefixes mono, di, tri, etc., are used to indicate the number of individual ligands in the co-ordination entity. When the names of the ligands include a numerical prefix, then the terms bis (for 2 such ligands), tris (for 3), tetrakis (for 4) are used. Here the name of the ligand is placed in simple bracket.
- Oxidation state of the metal is indicated by Roman numeral in simple bracket.
- If the complex ion is a cation, the central atom is named same as the element. If the complex ion is an anion, the name of the metal ends with the suffix -ate. For example ferrate for iron, cobaltate for cobalt, zincate for Zn etc.
- The neutral complex molecule is named similar to that of the cationic complex.

## Isomerism in Co-ordination Compounds

Compounds that have the same molecular formula but different structural formula or spatial arrangement of atoms are called isomers and the phenomenon is called isomerism. Isomers differ in physical or chemical properties. The isomerism shown by co-ordination compounds are broadly divided into two – structural isomerism and stereo isomerism.

### 1) Structural Isomerism

These are isomers which differ in the structural arrangement of ligands around the

central atom. They are of four types:

**1. Ionisation Isomerism:** It arises due to the inter change of ions between the inside and outside of co-ordination sphere. They give different types of ions in aqueous solution. In order to show this isomerism, the ion outside the co-ordination sphere can also act as ligand.

An example is  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ .

**2. Linkage isomerism:** It arises in a co-ordination compound containing ambidentate ligand, which can bind to the central atom through more than one donor atoms. For example complexes containing thiocyanate ligand,  $\text{SCN}^-$ , may bind either through nitrogen to give  $\text{M}-\text{NCS}$  or through sulphur to give  $\text{M}-\text{SCN}$ . Another e.g. is  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ , in which the nitrite ligand is bound through oxygen ( $-\text{ONO}$ ), and  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$  in which the nitrite ligand is bound through nitrogen ( $-\text{NO}_2$ ).

**3. Co-ordination Isomerism:** If both anionic and cationic parts are complexes, the isomerism arises due to the interchange of ligands between cationic and anionic entities. This type of isomerism is called co-ordination isomerism. An example is  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ , in which the  $\text{NH}_3$  ligands are bound to  $\text{Co}^{3+}$  and the  $\text{CN}^-$  ligands to  $\text{Cr}^{3+}$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ , the  $\text{NH}_3$  ligands are bound to  $\text{Cr}^{3+}$  and the  $\text{CN}^-$  ligands to  $\text{Co}^{3+}$ .

**4. Solvate isomerism:** This form of isomerism is also known as '**hydrate isomerism**' if water is involved as the solvent. This is similar to ionisation isomerism. Solvate isomers differ in the no. of solvent molecule which are directly bonded to the metal ion as ligand.

An example is  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet) and its solvate isomer  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (grey-green).

## II) Stereoisomerism

These are isomers which differ only in the spatial arrangement of ligands around the central atom. They have same atom to atom bond. These are of two types:

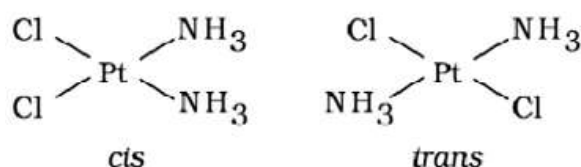
- Geometrical isomerism
- Optical isomerism

**i) Geometrical Isomerism:** This type of isomerism is shown by heteroleptic complexes. It arises due to the different possible geometric arrangements of the ligands around the central atom. It is

mainly found in co-ordination complexes with co-ordination numbers 4 (square planar complexes) and 6 (octahedral complexes). Geometrical isomer in which the same ligands are on the same side of the central metal atom is called *cis isomer* and the isomer in which the same ligands are on the opposite side is called *trans isomer*.

Square planar complexes with formula  $[\text{MX}_2\text{L}_2]$  (X and L are unidentate ligands) can show this isomerism.

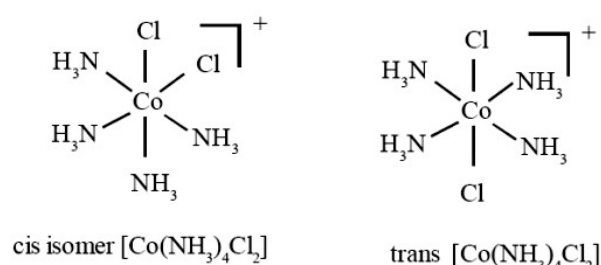
E.g.:  $[\text{Cu}(\text{NH}_3)_2\text{Cl}_2]$



Square planar complexes of the type  $\text{MABXL}$  (where A, B, X, L are unidentate ligands) show three geometrical isomers-two *cis* and one *trans*.

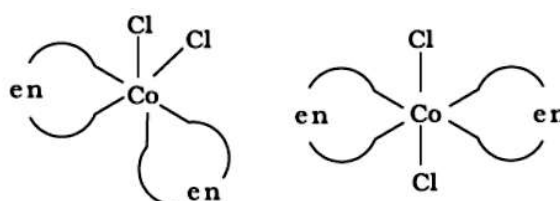
Octahedral complexes with formula  $[\text{MX}_2\text{L}_4]$  can also show this type of isomerism. Here the two ligands X may be oriented *cis* or *trans* to each other.

e.g.:  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$



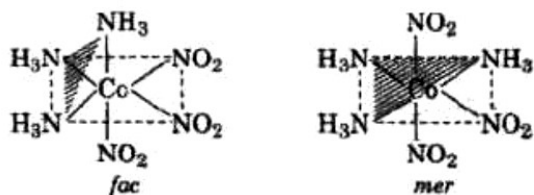
This type of isomerism also arises when bidentate ligands (L - L) are present in complexes with formula  $[\text{MX}_2(\text{L} - \text{L})_2]$

e.g.:  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$



**Fac-mer isomerism:** It is a type of geometrical isomerism occurs in octahedral co-ordination entities of the type  $[\text{Ma}_3\text{b}_3]$ . If similar ligands occupy three adjacent positions of an octahedral face, it is called **facial (fac) isomer**.

When the positions are around the meridian of the octahedron, it is called **meridional (mer) isomer**. Eg.  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ .



Tetrahedral complexes do not show geometrical isomerism because in a tetrahedron all the positions are equivalent.

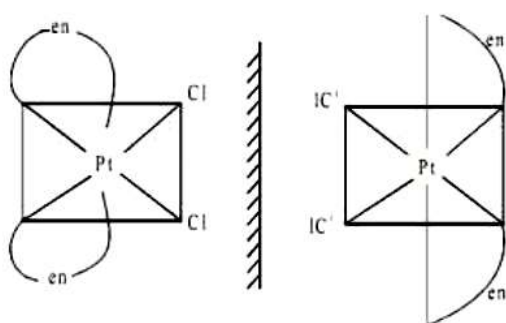
So the relative positions of the ligands attached to the central metal atom are the same with respect to each other.

## ii) Optical Isomerism

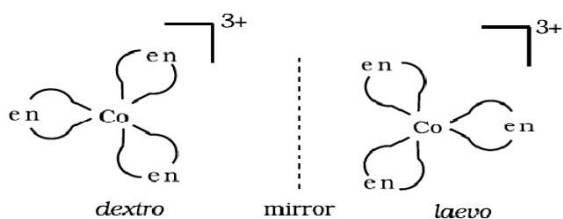
Optical isomers are mirror images that cannot be superimposed on one another. These are also called *enantiomers*. The molecules or ions that cannot be superimposed are called *chiral*.

There are two forms of optical isomers - *dextro (d)* and *laevo (l)* depending upon the direction they rotate the plane of polarised light in a polarimeter (*d* rotates to the right, *l* to the left). Optical isomerism is common in octahedral complexes involving bidentate ligands.

In a co-ordination entity of the type  $[\text{PtCl}_2(\text{en})_2]^+$ , **only the cis-isomer shows optical activity**. The trans-isomer has a plane of symmetry and is optically inactive.



Another e.g. is  $[\text{Co}(\text{en})_3]^{3+}$



## Theories of Co-ordination Compounds

### 1. Werner's Co-ordination Theory

It was Alfred Werner who first proposed a theory for co-ordination compounds. He studied the amino complexes of Co, Pt etc. and proposed the following postulates:

1. Every metal has two types of valencies – primary ( $1^0$ ) valency and secondary ( $2^0$ ) valency. Primary valency is ionisable, while secondary valency is non-ionisable.
2. Primary valency is denoted by dotted lines, while secondary valency is denoted by thick lines.
3. Primary valency gives the oxidation state of the metal, while secondary valency gives the co-ordination number of the metal.
4. Primary valency is always satisfied by –ve ions, while secondary valency may be satisfied by –ve ions or neutral molecules.
5. Every metal has a fixed number of secondary valencies. In order to satisfy this requirement, some –ve ions may perform dual character – i.e., they act as primary and secondary valencies simultaneously.
6. The primary valencies are non-directional, while the secondary valencies are directional. i.e. they are directed to some fixed positions in space.
7. Since secondary valencies are directional, co-ordination compounds have a definite geometry and they show isomerism.

**Demerits:** Werner could not explain why only certain elements form co-ordination compounds. Also he could not explain the directional nature of bonds in co-ordination compounds and their magnetic and optical properties.

In order to explain the above properties, many theories such as Valence Bond Theory (VBT), Crystal Field Theory (CFT), Ligand Field Theory (LFT) and Molecular Orbital Theory (MOT) are proposed.

### 2. The Valence Bond Theory (VBT)

This theory was put forward by Linus Pauling. The important postulates of this theory are:

1. In co-ordination compounds, the central metal atom/ion provides some vacant orbitals in order to accommodate the electrons donated by the ligands. The number of vacant orbitals formed is equal to the co-ordination number of the metal atom.
2. The vacant orbitals of the metal undergo



hybridisation to form a set of new orbitals called hybrid orbitals. The type of hybridisation gives the shape of the compound.

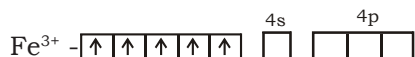
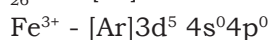
3. Tetrahedral, square planar and octahedral complexes are formed as a result of  $sp^3$ ,  $dsp^2$  and  $d^2sp^3$  ( $sp^3d^2$ ) hybridisation respectively.
4. Each ligand should contain at least one pair of electron.
5. The vacant hybrid orbitals of the metal overlap with the filled orbitals of the ligands to form ligand – metal co-ordinate bond.
6. If a complex contains unpaired electron, it is paramagnetic and if it contains only paired electron, it is diamagnetic.

### Applications of VBT

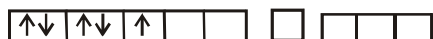
It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory.

E.g.: 1)  $[\text{Fe}(\text{CN})_6]^{3-}$

Here the central atom Fe is in +3 oxidation state.



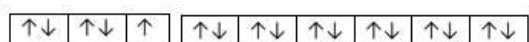
In this complex, the co-ordination number of Fe is 6 and hence the no. of vacant orbitals required = 6. In presence of the ligand  $\text{CN}^-$ , the electrons in 3d level get paired.



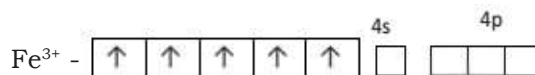
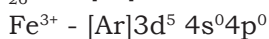
Now the two 3d orbitals, one 4s orbital and three 4p orbitals undergo  $d^2sp^3$  hybridization to form 6 new orbitals. Six pairs of electrons, one from each  $\text{CN}^-$  ions, occupy these six hybrid orbitals. Thus, the complex has *octahedral geometry* and is *paramagnetic* because of the presence of one unpaired electron.

In the formation of this complex, since the inner *d* orbitals (3d) are used for hybridization, the complex is called an **inner orbital** or **low spin** or **spin paired complex**.

2)  $[\text{FeF}_6]^{3-}$



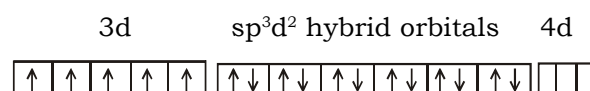
Here the central atom Fe is in +3 oxidation state.



In this complex the co-ordination number of Fe is 6 and hence the no. of vacant orbitals required = 6. In presence of the ligand  $\text{F}^-$ , the electrons in 3d level do not get paired.



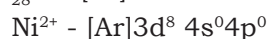
Now the one 4s orbital, three 4p orbitals and two 4d orbitals undergo  $sp^3d^2$  hybridization to form 6 new orbitals. These hybrid orbitals overlap with the filled orbitals of the ligand to form ligand– metal co-ordinate bond.



Since the hybridization is  $sp^3d^2$ , the shape of the molecule is *octahedral* and due to the presence of 5 unpaired electrons, it is *highly paramagnetic*. In the formation of this complex, since the outer orbitals (4d) are used for hybridisation ( $sp^3d^2$ ), it is called **outer orbital** or **high spin** or **spin free complex**.

3)  $[\text{Ni}(\text{CN})_4]^{2-}$

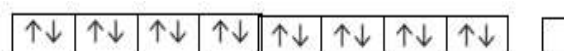
Here the central atom Ni is in +2 oxidation state.



In this complex the co-ordination number of Ni is 4 and hence the no. of vacant orbitals required = 4. Even though it contains 4 orbitals, in presence of the ligand  $\text{CN}^-$ , the electrons in 3d level get paired.

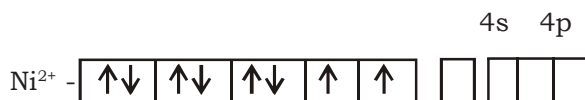


Now the one 3d orbital, one 4s orbital and two 4p orbitals undergo  $dsp^2$  hybridization to form 4 new orbitals. Four pairs of electrons, one from each  $\text{CN}^-$  ions, occupy these four hybrid orbitals. Thus, the complex has *square planar geometry* and is *diamagnetic*, because of the absence of unpaired electron.

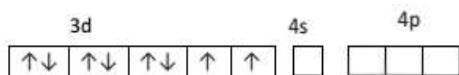


4)  $[\text{NiCl}_4]^{2-}$  : Here the central atom Ni is in +2 oxidation state.





In this complex the co-ordination number of Ni is 4 and hence the no. of vacant orbitals required = 4. In presence of the ligand  $\text{Cl}^-$ , the electrons in 3d level do not get paired.



Now the one 4s orbitals and three 4p orbitals undergo  $sp^3$  hybridization to form 4 new orbitals. These four hybrid orbitals are occupied by the four electron pairs from each  $\text{Cl}^-$  ligands. Thus, the complex has *tetrahedral* geometry and is *paramagnetic* because of the presence of unpaired electron.



### Magnetic Properties of Co-ordination Compounds

By knowing the magnetic moment, we can predict the geometry of complexes. For e.g.  $[\text{Mn}(\text{CN})_6]^{3-}$  has magnetic moment of two unpaired electrons while  $[\text{MnCl}_6]^{3-}$  has a paramagnetic moment of four unpaired electrons.  $[\text{Fe}(\text{CN})_6]^{3-}$  has magnetic moment of a single unpaired electron while  $[\text{FeF}_6]^{3-}$  has a paramagnetic moment of five unpaired electrons.  $[\text{CoF}_6]^{3-}$  is paramagnetic with four unpaired electrons while  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  is diamagnetic. This can be explained by valence bond theory in terms of formation of inner orbital and outer orbital co-ordination entities.  $[\text{Mn}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  are inner orbital complexes involving  $d^2sp^3$  hybridisation, the former two complexes are paramagnetic and the latter diamagnetic. On the other hand,  $[\text{MnCl}_6]^{3-}$ ,  $[\text{FeF}_6]^{3-}$  and  $[\text{CoF}_6]^{3-}$  are outer orbital complexes involving  $sp^3d^2$  hybridisation and are paramagnetic corresponding to four, five and four unpaired electrons.

### Limitations of Valence Bond Theory

Even though the VB theory explains the formation, structures and magnetic behaviour of co-ordination compounds, it has the following limitations:

- (i) It involves a number of assumptions.
- (ii) It does not give quantitative interpretation of magnetic data.

(iii) It does not explain the colour exhibited by co-ordination compounds.

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

(v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-co-ordinated complexes.

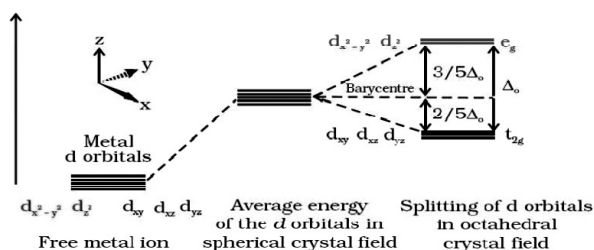
(vi) It does not distinguish between weak and strong ligands.

### 3. Crystal Field Theory

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond as purely ionic. Here the ligands are treated as point charges in case of anions or as dipoles in case of neutral molecules. The five  $d$  orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. But when this negative field is due to ligands in a complex, the degeneracy of the  $d$  orbitals is lost. It results in splitting of the  $d$  orbitals. This splitting of  $d$ -orbitals is termed as Crystal field splitting and it depends on the nature of the field.

#### (a) Crystal field splitting in octahedral co-ordination entities (octahedral field)

In an octahedral co-ordination entity there are six ligands surrounding the metal atom/ion and they are along the axis of the octahedron. So the repulsion between the electrons in metal  $d$  orbitals and the electrons (or negative charges) of the ligands is greater for the  $dx^2-y^2$  and  $dz^2$  orbitals, which are pointing towards the axes, than the  $dxy$ ,  $dyz$  and  $dxz$  orbitals, which are directed between the axes. So the energy of the  $dx^2-y^2$  and  $dz^2$  orbitals (called  $e_g$  orbitals) will be raised and that of the  $dxy$ ,  $dyz$  and  $dxz$  orbitals (called  $t_{2g}$  orbitals) will be lowered. Thus, the degeneracy of the  $d$  orbitals has been removed. 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  $e_g$  orbitals will increase by  $(3/5) \Delta_o$  and that of the three  $t_{2g}$  orbitals will decrease by  $(2/5) \Delta_o$ .



Strong field ligands produce large splitting whereas weak field ligands produce small splitting of  $d$  orbitals.

### Filling of electrons

For  $d^1$ ,  $d^2$  and  $d^3$  coordination entities, the  $d$  electrons occupy the  $t_{2g}$  orbitals singly in accordance with the Hund's rule. For  $d^4$  ions, two possible patterns of electron distribution arise:

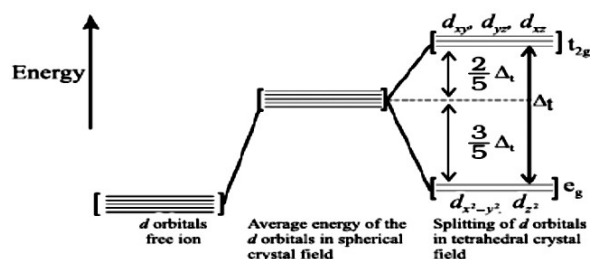
- (i) the fourth electron could either enter the  $t_{2g}$  level and pair with an existing electron, or
- (ii) it could enter into the  $e_g$  level.

Here the electron distribution depends on the relative magnitude of the crystal field splitting ( $\Delta_o$ ) and the pairing energy ( $P$ ). If  $\Delta_o < P$ , the fourth electron enters one of the  $e_g$  orbitals giving the configuration  $t_{2g}^3 e_g^1$ . Ligands for which  $\Delta_o < P$  are known as *weak field ligands* and form high spin complexes.

If  $\Delta_o > P$ , the fourth electron occupies a  $t_{2g}$  orbital with configuration  $t_{2g}^4 e_g^0$ . Ligands for which  $\Delta_o > P$  are known as *strong field ligands* and form low spin complexes.

### a) Crystal field splitting in Tetrahedral coordination entities (tetrahedral field)

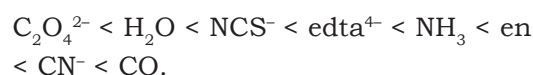
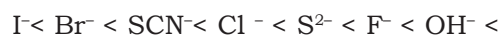
A tetrahedron can be considered as a cube in which only alternate corners are occupied by ligands and the metal ion is at the centre of the cube. The  $dx^2-y^2$  and  $dz^2$  orbitals (called  $e$  orbitals) point towards the centre of each face of the cube and the  $dxy$ ,  $dyz$  and  $dxz$  orbitals (called  $t_2$  orbitals) point towards the edge centre of the cube. Since the ligands are approaching through the corners, there is no direct interaction between the ligands and the  $d$ -orbitals. However, the ' $t_2$ ' orbitals lie closer to the ligands than the ' $e$ ' orbitals. As a result the energy of the ' $t_2$ ' orbitals increases and that of ' $e$ ' orbitals decreases. So the  $d$  orbitals split into two – triply degenerate ' $t_2$ ' orbitals with higher energy and doubly degenerate ' $e$ ' orbitals with lower energy.



The splitting in tetrahedral field is less than that in octahedral field. It is found that  $\Delta_t = 4/9 \Delta_o$ . This is because in tetrahedral field, there are only four ligands (but in octahedral field, the number of ligands is six) and there is no direct interaction between the ligands and the  $d$ -orbitals.

### Spectrochemical series

It is a series in which the ligands are arranged in the increasing order of their field strength. The series is:



It is an experimentally determined series based on the absorption of light by complexes with different ligands.

### Colour in Coordination Compounds

Most of the complexes of transition metals are coloured. This can be explained in terms of the crystal field theory. In presence of the ligands, the crystal field splitting occurs. So the electrons from lower  $d$  level ( $t_{2g}$  level) can excite to higher  $d$  level ( $e_g$  level). For this some energy is required, which is absorbed from the white light. The colour of the complex is complementary to that which is absorbed. Thus **according to crystal field theory the colour of the coordination compounds is due to  $d-d$  transition of the electron.**

For example, the complex  $[Ti(H_2O)_6]^{3+}$  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. Consequently, the complex appears violet in colour.

In the absence of ligand, crystal field splitting does not occur and hence the substance is colourless. For example, when  $[Ti(H_2O)_6]^{3+}$  is heated it becomes colourless. Similarly, anhydrous  $CuSO_4$  is white, but

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is blue in colour.

The colour of a complex depends on the *strength of ligand and the nature of the field*.

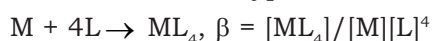
### Limitations of Crystal Field Theory

1. From the assumptions, that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. But the anionic ligands actually are found at the low end of the spectrochemical series.
2. It does not take into account the covalent character of bonding between the ligand and the central atom.

### Stability of Coordination Compounds

The stability of a complex in solution refers to the degree of association between the metal ion and ligands in the state of equilibrium. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability.

For a reaction of the type:



As the value of the stability constant increases, the stability of the complex also increases. The above reaction can be considered to take place in 4 steps:



Where  $K_1$ ,  $K_2$ ,  $K_3$  and  $K_4$  are referred to as **stepwise stability constants**.

The **overall stability constant**,

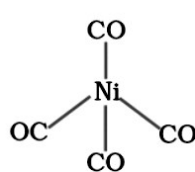
$$\beta = K_1 \times K_2 \times K_3 \times K_4$$

The stability of a complex depends on the following factors:

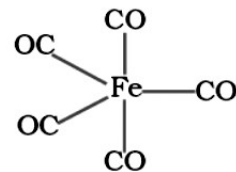
1. **The nature of the metal ion:** Greater the charge to radius of the metal ion, greater will be the stability of the complex.
2. **Nature of the ligand:** The greater the basic strength of the ligand, the greater will be the stability of the complex.
3. **Presence of chelating ligands:** increases the stability of the complex.

### Bonding in Metal Carbonyls

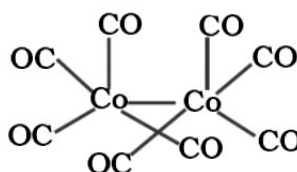
Transition metals form a large number of homoleptic carbonyls. Eg.  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Fe}(\text{CO})_5]$ ,  $[\text{Cr}(\text{CO})_6]$ ,  $[\text{Co}_2(\text{CO})_8]$ ,  $[\text{Mn}_2(\text{CO})_{10}]$  etc. These carbonyls have simple, well defined structures.



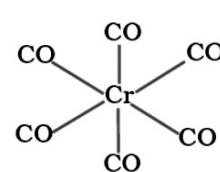
$\text{Ni}(\text{CO})_4$   
Tetrahedral



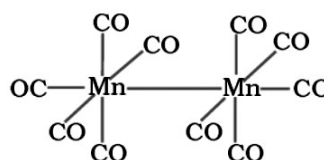
$\text{Fe}(\text{CO})_5$   
Trigonal bipyramidal



$[\text{Co}_2(\text{CO})_8]$

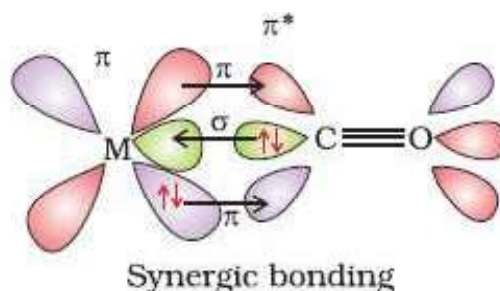


$\text{Cr}(\text{CO})_6$  Octahedral



$[\text{Mn}_2(\text{CO})_{10}]$

The metal-carbon bond in metal carbonyls possess both *s* and *p* character. The M–C *s* bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M–C *p* bond is formed by the donation of a pair of electrons from a filled *d* orbital of metal into the vacant anti-bonding  $\pi^*$  orbital of carbon monoxide. Thus the metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.



### Application of Co-ordination Complexes

#### 1. In Qualitative & Quantitative Analysis:

Co-ordination compounds find use in many qualitative and quantitative chemical analyses. For e.g.  $\text{Ni}^{2+}$  is detected and estimated by the formation of a complex with Dimethyl Glyoxime (DMG).



The brown ring test for the detection of nitrate ion is due to the formation of the brown complex  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ . The  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions are estimated by the formation of stable complexes with EDTA.

- 2. In water treatment:** The Hardness of water is estimated by simple titration with  $\text{Na}_2\text{EDTA}$  (sodium salt of EDTA). The  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions form stable complexes with EDTA. The hardness of water can be removed by the formation of a complex with calgon (Sodium polymetaphosphate)
- 3. In Metallurgy:** Metals like silver and gold are extracted by the formation of complexes with  $\text{CN}^-$  ligands. Gold forms the complex  $[\text{Au}(\text{CN})_2]^-$  and silver forms  $[\text{Ag}(\text{CN})_2]^-$  which are separated with Zn. Similarly, coordination compounds also find application in the refining of some metals. For example, impure nickel is converted to  $[\text{Ni}(\text{CO})_4]$ , which is decomposed to yield pure nickel
- 4. Biological Applications:** Coordination compounds are of great importance in biological systems. *Chlorophyll* is a co-ordination compound of **magnesium**, *Haemoglobin*, is a co-ordination compound of **iron** and *Vitamin B<sub>12</sub>* (cyanocobalamine) is a co-ordination compound of **cobalt**.
- 5. In Catalysis:** Co-ordination compounds are used as catalysts for many industrial processes. For e.g. Tris(triphenylphosphine)rhodiumchloride,  $[(\text{Ph}_3\text{P})_3\text{RhCl}]$  (Wilkinson catalyst), is used for the hydrogenation of alkenes.
- 6. In electroplating:** Articles can be electroplated with silver and gold by using the solutions of the complexes,  $[\text{Ag}(\text{CN})_2]^-$  and  $[\text{Au}(\text{CN})_2]^-$  respectively as electrolytes.
- 7. In Photography:** In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed  $\text{AgBr}$  to form a complex ion,  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ .
- 8. In medicine:** Cis-platin is used for the treatment of cancer. Excess of copper and iron in animal or plant body are removed by the chelating ligands D-penicillamine and desferrioxime B through the formation of co-ordination compounds. EDTA is used in the treatment of lead poisoning.