

## Co-ordination Compounds

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- **Co-ordination compounds:**

1. A coordination compound contains a central metal atom or ion surrounded by number of oppositely charged ions or neutral molecules. These ions or molecules re bonded to the metal atom or ion by a coordinate bond.
2. Example:  $K_4[Fe(CN)_6]$
3. They do not dissociate into simple ions when dissolved in water.

- **Double salt**

1. When two salts in stoichiometric ratio are crystallised together from their saturated solution they are called doublesalts
2. Example:  $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$  (Mohr's salt)
3. They dissociate into simple ions when dissolved in water.

- **Coordination entity:**

1. A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules.
2. Example: In  $K_4[Fe(CN)_6]$ ,  $[Fe(CN)_6]^{4-}$  - represents coordination entity.

- **Central atom or ion:**

1. In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion.
2. Example: In  $K_4[Fe(CN)_6]$ ,  $Fe^{+}$  is the central metal ion.

- **Ligands:**

1. A molecule, ion or group that is bonded to the metal atom or ion in a complex or coordination compound by a coordinate bond is called ligand.
2. It may be neutral, positively or negatively charged.
3. Examples:  $H_2O$ ,  $CN^-$ ,  $NO^+$  etc.

- **Donor atom:**

1. An atom of the ligand attached directly to the metal is called the donor atom.
2. Example: In the complex  $K_4[Fe(CN)_6]$ , CN is a donor atom.

- **Coordination number:**

1. The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded.
2. Example: In the complex  $K_4[Fe(CN)_6]$ , the coordination number of Fe is 6.

- **Coordination sphere:**

1. The central atom/ion and the ligands attached to it are enclosed in square bracket and are collectively termed as the coordination sphere.
2. Example: In the complex  $K_4[Fe(CN)_6]$ ,  $[Fe(CN)_6]^{4-}$  is the coordination sphere.

- **Counter ions:**

1. The ions present outside the coordination sphere are called counter ions.
2. Example: In the complex  $K_4[Fe(CN)_6]$ ,  $K^+$  is the counter ion.

- **Coordination polyhedron:**

1. The spatial arrangement of the ligand atoms which are directly attached to the central atom/ ion defines a coordination polyhedron about the central atom.
2. The most common coordination polyhedra are octahedral, square planar and tetrahedral.
3. Examples:  $[PtCl_4]^{2-}$  is square planar,  $Ni(CO)_4$  is tetrahedral while  $[Cu(NH_3)_6]^{3+}$  is octahedral.

- **Charge on the complex ion:** The charge on the complex ion is equal to the algebraic sum of the charges on all the ligands coordinated to the central metal ion.

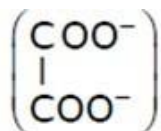
- **Denticity:** The number of ligating (linking) atoms present in ligand is called denticity.

- **Unidentate ligands:**

1. The ligands whose only one donor atom is bonded to metal atom are called unidentate ligands.
2. Examples:  $H_2O$ ,  $NH_3$ ,  $CO$ ,  $CN^-$

- **Didentate ligands:**

1. The ligands which contain two donor atoms or ions through which they are bonded to the metal ion.
2. Examples: Ethylene diamine ( $H_2NCH_2CH_2NH_2$ ) has two nitrogen atoms, oxalate ion



has two oxygen atoms which can bind with the metal atom.

- **Polydentate ligand:**

1. When several donor atoms are present in a single ligand, the ligand is called polydentate ligand.
2. Examples: In  $N(CH_2CH_2NH_2)_3$ , the ligand is said to be polydentate and Ethylenediaminetetraacetate ion ( $EDTA^{4--}$ ) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

- **Chelate:**

1. An inorganic metal complex in which there is a close ring of atoms caused by attachment of a ligand to a metal atom at two points.
2. An example is the complex ion formed between ethylene diamine and cupric ion,  $[Cu(NH_2CH_2NH_2)_2]^{2+}$ .

- **Ambidentate ligand:**

1. Ligands which can ligate (link) through two different atoms present in it are called ambidentate ligand.
2. Example:  $\text{NO}_2^-$  and  $\text{SCN}^-$ . Here,  $\text{NO}_2^-$  can link through N as well as O while  $\text{SCN}^-$  can link through S as well as N atom.

- **Werner's coordination theory:**

1. Werner was able to explain the nature of bonding in complexes.
2. The postulates of Werner's theory are:
  - a). Metal shows two different kinds of valencies: primary valence and secondary valence.
  - b). The ions/ groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.
  - c). The most common geometrical shapes in coordination compounds are octahedral, square planar and tetrahedral.

- **Primary valence**

1. This valence is normally ionisable.
2. It is equal to positive charge on central metal atom.
3. These valencies are satisfied by negatively charged ions.
4. Example: In  $\text{CrCl}_3$ , the primary valency is three. It is equal to oxidation state of central metal ion.

- **Secondary valence**

1. This valence is non –ionisable.
2. The secondary valency equals the number of ligand atoms coordinated to the metal. It is also called coordination number of the metal.
3. It is commonly satisfied by neutral and negatively charged, sometimes by positively charged ligands.

- **Oxidation number of central atom:** The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom.
- **Homoleptic complexes:** Those complexes in which metal or ion is coordinate bonded to only one kind of donor atoms. For example:  $[Co(NH_3)_6]^{3+}$
- **Heteroleptic complexes:** Those complexes in which metal or ion is coordinate bonded to more than one kind of donor atoms. For example:  
 $[CoCl_2(NH_3)_4]^+$ ,  $[Co(NH_3)_5Br]^{2+}$

● **Isomers:** Two or more compounds which have same chemical formula but different arrangement of atoms are called isomers.

- **Types of isomerism:**

- a). Linkage isomerism
- b). Solvate isomerism or hydrate isomerism
- c). Ionisation isomerism
- d). Coordination isomerism
  - 1. Structural isomerism
  - 2. Stereoisomerism
    - a). Geometrical isomerism
    - b). Optical isomerism

- **Structural isomerism:**

1. It arises due to the difference in structures of coordination compounds.
2. Structural isomerism, or constitutional isomerism, is a form of isomerism in which molecules with the same molecular formula have atoms bonded together in different orders.

- **Ionisation isomerism:**

1. It arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion.
2. Example:  $[Co(NH_3)_5Br] SO_4$  and  $[Co(NH_3)_5SO_4] Br$

- **Solvate isomerism:**

1. It is isomerism in which solvent is involved as ligand.
2. If solvent is water it is called hydrate isomerism, e.g.,  $[Cr(H_2O)_6] Cl_3$  and  $[CrCl_2(H_2O)_4] Cl_2 \cdot 2H_2O$ .

- **Linkage isomerism:**

1. It arises in a coordination compound containing ambidentate ligand.
2. In the isomerism, a ligand can form linkage with metal through different atoms.
3. Example:  $[Co(NH_3)_5ONO] Cl_2$  and  $[Co(NH_3)_5NO_2] Cl_2$ .

- **Coordination isomerism:**

1. This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.
2. Example:  $[Co(NH_3)_6] [Cr(C_2O_4)_3]$  and  $[Cr(NH_3)_6] [Co(C_2O_4)_3]$ .

- **Stereoisomerism:** This type of isomerism arises because of different spatial arrangement.

- **Geometrical isomerism:** It arises in heteroleptic complexes due to different possible geometrical arrangements of ligands.

- **Optical isomerism:** Optical isomers are those isomers which are non-superimposable mirror images.

- **Valence bond theory:**

1. According to this theory, the metal atom or ion under the influence of ligands can use its  $(n-1)d$ ,  $ns$ ,  $np$  or  $ns$ ,  $np$ ,  $nd$  orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, and square planar.
2. These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

Coordination Number	Type of hybridisation	Shape of hybrid
4	$sp^3$	Tetrahedral
4	$dsp^2$	Square planar
5	$sp^3d$	Trigonalbipyramidal
6	$sp^3d^2$ (nd orbitals are involved – outer orbital complex or high spin or spin free complex)	Octahedral
6	$d^2sp^3$ ( $n - 1$ ) d orbitals are involved –inner orbital or low spin or spin paired complex)	Octahedral

- **Magnetic properties of coordination compounds:**

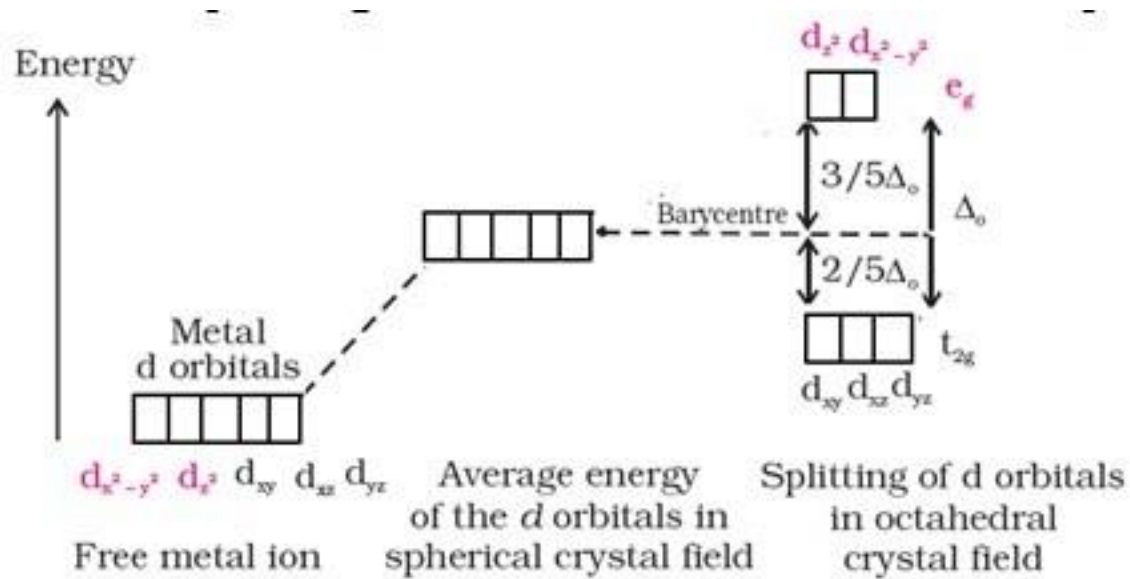
A coordination compound is paramagnetic in nature if it has unpaired electrons and diamagnetic if all the electrons in the coordination compound are paired.

Magnetic moment  $\mu = \sqrt{n(n+2)}$  where n is number of unpaired electrons.

- **Crystal Field Theory:**

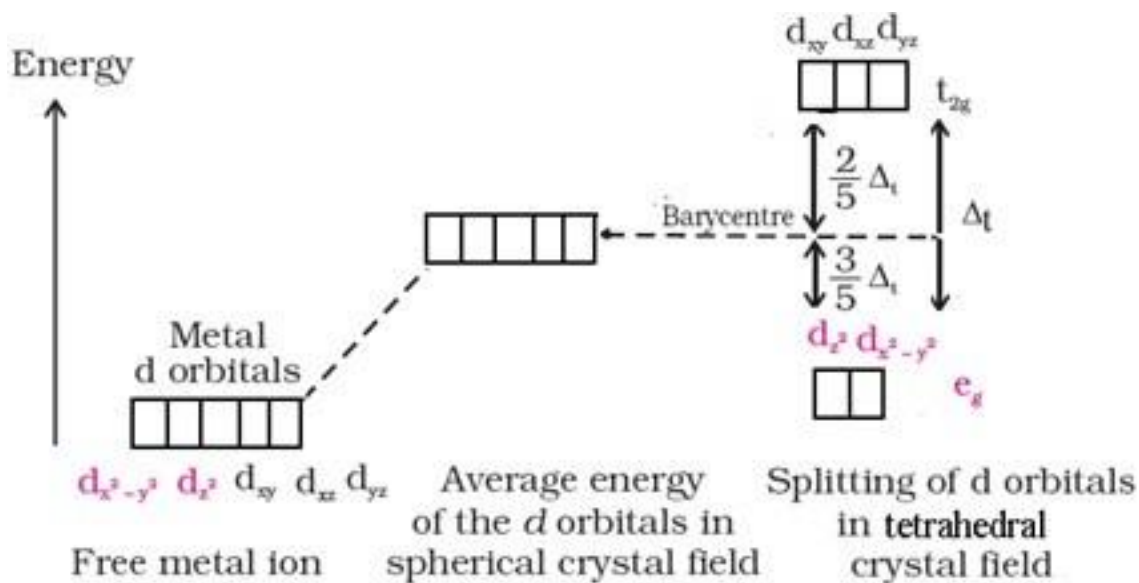
1. It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion.
2. It is theoretical assumption.

• **Crystal field splitting in octahedral coordination complexes:**





- **Crystal field splitting in tetrahedral coordination complexes:**



- For the same metal, the same ligands and metal-ligand distances, the difference in

energy between  $e_g$  and  $t_{2g}$  level is 
$$\Delta_t = -\frac{4}{9} \Delta_0$$

- **Metal carbonyls:**

1. Metal carbonyls are homoleptic complexes in which carbon monoxide (CO) acts as the ligand.
2. Example:  $Ni(CO)_4$
3. The metal-carbon bond in metal carbonyls possess both  $s$  and  $p$  character.
4. The  $M-C\sigma$  bond is formed by the donation of lone pair of electrons from the carbonyl carbon into a vacant orbital of the metal.
5. The  $M-C\pi$  bond is formed by the donation of a pair of electrons from a filled  $d$  orbital of metal into the vacant antibonding  $\pi^*$  orbital of carbon monoxide.
6. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.