

CHAPTER - 06

CO-ORDINATION COMPOUNDS

The transition metals form a large number of complex compounds in which the metal atoms/ions are bound to a number of anions or neutral molecules. Such compounds are called co-ordination compounds. The chemistry of co-ordination compounds is an important area of modern inorganic chemistry and provides insights into the chemical bonding, molecular structure and functioning of vital components of biological systems. Chlorophyll, haemoglobin and vitamin B₁₂ are co-ordination compounds of magnesium, iron and cobalt respectively. A variety of metallurgical processes, industrial catalysts and analytical reagents involve the use of coordination compounds. Co-ordination compounds also find applications in electroplating, textile dyeing and medicinal chemistry.

Werner's theory of co-ordination compounds

The first ideas about the structures of co-ordination compounds were formulated by Alfred Werner, a swiss chemist. He prepared and characterised a large no. of co-ordination compounds and studied their physical and chemical behaviour. Werner proposed the concept of a primary valence and a secondary valence for a metal ion. Binary compounds like CrCl₃, CoCl₂ and PdCl₂ have primary valence of 3, 2 and 2 respectively. Werner found that in a series of compounds of CoCl₃ and NH₃, only some of the chloride ions could be precipitated as AgCl on adding excess of AgNO₃ solution, but some others could not be

1 mole CoCl₃.6NH₃(yellow) gave 3 mol AgCl

1 mole CoCl₃.5NH₃(purple) gave 2 mol AgCl

1 mol CoCl₃.4NH₃ (green) gave 1 mol AgCl

1 mol CoCl₃.4NH₃ (violet) gave 1 mol AgCl

These observations together with the results of conductivity measurements in solution can be explained if (i) six groups in all, either Cl⁻ ions or NH₃ molecules or both, remain bonded to the cobalt ion during the reaction and (ii) the compounds are formulated as shown below.

Formulation of CoCl₃–NH₃ complexes

Colour	Formula	Conductivity in solution corresponds to
Yellow	[Co(NH ₃) ₆] ³⁺ 3Cl ⁻	1 : 3 electrolyte
Purple	[Co(NH ₃) ₅ Cl] ²⁺ 2Cl ⁻	1 : 2 electrolyte
Green	[Co(NH ₃) ₄ Cl ₂] ⁺ Cl ⁻	1 : 1 electrolyte
Violet	[Co(NH ₃) ₄ Cl ₂] ⁺ Cl ⁻	1 : 1 electrolyte

Although the last two compounds above have identical empirical formula CoCl₃.4NH₃, they have different properties they are therefore isomers.

These observations led Werner to propound his theory of coordination compounds. The main postulates are:

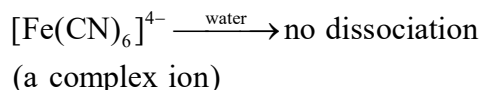
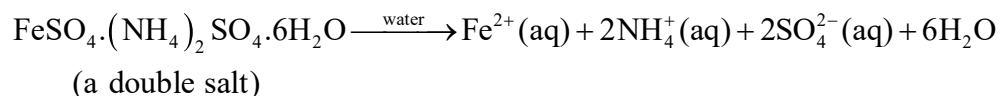
1. In coordination compounds, metals show two types of linkages (valences)-primary and secondary.
2. The primary valences are normally ionisable and are satisfied by negative ions.
3. The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions or both. The secondary valence of a metal is equal to its co-ordination number and is fixed for a metal.
4. The ions/groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

In the modern theory, such spatial arrangements are called **co-ordination polyhedra**. The species within the square bracket are called **co-ordination entities** and the ions outside the square bracket are called **counter ions**.

Werner further postulated that octahedral, tetrahedral and square planar shapes are more common in coordination compounds of transition metals. Thus $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ are octahedral entities, $[\text{Ni}(\text{CO})_4]$ is tetrahedral and $[\text{PtCl}_4]^{2-}$ is square planar.

Difference between a double salt and a complex

Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However, they differ in the fact that double salts such as carnallite $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, Mohr's salt $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, potash alum $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ etc dissociate completely into simple ions when dissolved in water. But complex ions such as $[\text{Fe}(\text{CN})_6]^{4-}$ of $\text{K}_4[\text{Fe}(\text{CN})_6]$ do not dissociate into Fe^{2+} and CN^- ions.



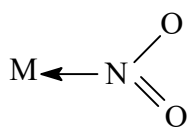
Ligands

The ions or molecules bound to the central metal atom/ion in the coordination entity are called ligands. These may be simple ions like Cl^- , small molecules like H_2O or NH_3 , larger molecules like $\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$ or even macromolecules such as proteins. Some coordination compounds may contain positively charged ligands also. Eg. of cationic ligands are hydrazinium ion $\text{NH}_2\text{—NH}_3^+$, nitrosonium ion NO^+ etc.

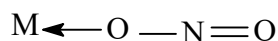
When a ligand is bound to a metal atom/ion through a single donor atom as with Cl^- , NH_3 or H_2O , the ligand is said to be **monodentate** or **unidentate**. When a ligand can bind through two donor atoms as in $\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$ (ethylene diamine or ethane-1,2-diamine) or $\text{C}_2\text{O}_4^{2-}$ (oxalate), the ligand is said to be **bidentate** or **didentate** and when several donor atoms are present in a single ligand as in edta^{4-} , the ligand is said to be **polydentate** (edta^{4-} , for example, is hexadentate)

When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a chelate ligand. The no. of ligating groups is called the **denticity** of the ligand. Such complexes, called chelate complexes are more stable than similar complexes containing unidentate ligands.

A ligand which can ligate through two different atoms is called **ambidentate ligand**. Examples of such ligands are NO_2^- and SCN^- ions. NO_2^- can coordinate either through its N or its O.



Nitrite-N-complex



Nitrito-O-complex

Similarly SCN⁻ ion can coordinate through its S or N atom.

Co-ordination number

The C.No of a metal atom/ion in a complex is the no.of ligand donor atoms to which the metal is directly bonded. For example in the complex ions [PtCl₆]²⁻ and [Ni(NH₃)₄]²⁺ the C. No of Pt and Ni are 6 & 4 respectively. In the complex ions [Co(en)₃]³⁺ and [Fe(C₂O₄)₃]³⁻, the C. No of both Co and Fe is 6 because en and C₂O₄²⁻ are bidentate ligands.

Homoleptic and heteroleptic complexes

Complexes in which a metal is bound to only one kind of ligands eg. [Co(NH₃)₆]³⁺, [Ni(CO)₄] are known as homoleptic. Complexes in which a metal is bound to more than one kind of ligands eg [Co(NH₃)₄Cl₂]⁺ are known as heteroleptic.

IUPAC nomenclature of coordination compounds

Isomerism in coordination compounds

Two principal types of isomerism are known among coordination compounds. Each of these can be further subdivided.

A) Structural isomerism

1. Linkage isomerism : This kind of isomerism arises in a coordination compound containing an ambidentate ligand. eg. The ligand NO₂⁻ (nitrite ion) can bind itself to the central metal either through its N(-NO₂) (nitrito-N-complex) or its O (-ONO) (nitrito-O-complex) giving rise to two isomers which are called linkage isomers.

Eg . [Co(NH₃)₅(NO₂)Cl₂] (yellow) and [Co(NH₃)₅(ONO)Cl₂] (red)

2. Ionisation isomerism : This form of isomerism 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.

Eg: [Co(NH₃)₅Br]SO₄ and [Co(NH₃)₅(SO₄)]Br are ionisation isomers.

3. Co-ordination isomerism : Arises when both the cation and the anion of a coordination compound are complexes and the ligands in them may interchange positions.

Eg : [Cu(NH₃)₄]²⁺ [PtCl₄]²⁻ and [Pt(NH₃)₄]²⁺ [CuCl₄]²⁻
 cation anion cation anion

Another eg. is [Cr(en)₃]³⁺ [Co(CN)₆]³⁻ and [Co(en)₃]³⁺ [Cr(CN)₆]³⁻
 cation anion cation anion

4. Solvate isomerism : This form of isomerism is known as hydrate isomerism when the solvent involved is water. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice.

Eg : [Cr(H₂O)₆]Cl₃ (violet) and [Cr(H₂O)₅Cl]Cl₂.H₂O (grey-green) are hydrate isomers.

B) Stereoisomerism

Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement.

1. Geometrical isomerism : A few typical examples of coordination entities in which geometric isomerism is possible are given below.

C.NO	Shape	Type	Example	No. of geometric isomers
4	Square planar	$[MA_2B_2]$	$[Pt(NH_3)_2Cl_2]$	2(cis and trans)
4	Square planar	$[MAB_2C]$	$[Pt(NH_3)Cl_2(Py)]$	2(cis and trans)
4	Square planar	$[MABCD]$	$[Pt(NH_3)BrCl(Py)]$	3 (2 cis and 1 trans)
4	Square planar	$[M(A-B)_2]$	$[Pt(gly)_2]$	2 (cis and trans)
6	Octahedral	$[MA_4B_2]$	$[Co(NH_3)_4Cl_2]^+$	2 (cis and trans)
6	Octahedral	$[MA_2B_4]$	$[Pt(NH_3)_2Cl_4]$	2 (cis and trans)
6	Octahedral	$[MA_3B_3]$	$[Cr(NH_3)_3Cl_3]$	2 (facial and meridional)
6	Octahedral	$[MA_2B_2C_2]$	$[Co(NH_3)_2(H_2O)_2Cl_2]^+$	5
7	Octahedral	$[MA_2(B-B)_2]$	$[CoCl_2(en)_2]^+$	2 (cis and trans)

M is the central metal. A, B, C and D are monodentate ligands. B–B represents a symmetrical bidentate ligand like en. A–B represents an unsymmetrical bidentate ligand like gly (glycinate ion $NH_2-CH_2-COO^-$)

2. Optical isomerism in coordination compounds arises out of chirality in the coordination entity. Optical isomers are mirror images that cannot be superimposed on one another. These are called enantiomers or enantiomorphs. The two forms are called dextro (d) and laevo (l) depending upon the direction in which they rotate the plane of polarised light in a polarimeter. Optical isomerism is common in octahedral complexes (C.No = 6) having bidentate ligands.

C.NO	Shape	Type	Example	No. of optical isomers
6	Octahedral	$[M(A-A)_3]$	$[Co(en)_3]^{3+}$, $[Cr(ox)_3]^{3-}$	2 (d and l)
6	Octahedral	$[MA_2(B-B)_2]$	Cis $[CoCl_2(en)_2]^+$ trans $[CoCl_2(en)_2]^+$	2 (d and l) Nil

Bonding in coordination compounds

Many approaches have been put forward to explain the nature of bonding in coordination compounds. eg. The Valence Bond Theory (VBT) and The Crystal Field Theory (CFT)

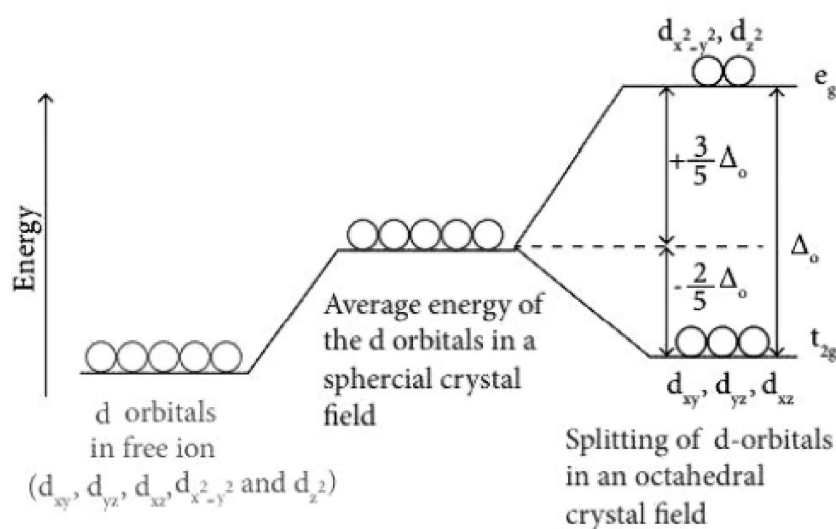
Valence bond theory: According to this theory, the metal atom or ion under the influence of the ligands uses its $(n-1)d$, ns , np or ns , np , nd orbitals for hybridisation to yield a set of equivalent hybrid orbitals of definite geometry such as octahedral, tetrahedral, square planar etc. These hybridised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

C.NO	Type of hybridisation	Orientation of hybrid orbitals in space	Example
4	sp^3	Tetrahedral	$[\text{Ni}(\text{CO})_4]$
4	dsp^2	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$
6	sp^3d^2	Octahedral	$[\text{FeF}_6]^{3-}$
6	d^2sp^3	Octahedral	$[\text{Fe}(\text{CN})_6]^{3-}$
5	dsp^3	Trigonal bipyramidal	$[\text{Fe}(\text{CO})_5]$

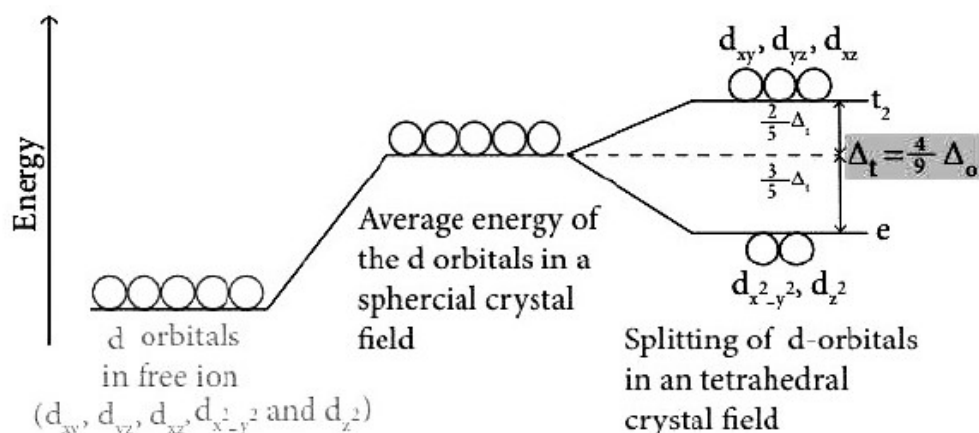
Crystal field theory:

This theory is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in the case of anions or dipoles in the case of neutral molecules. The five d-orbitals in an isolated metal atom/ion have the same energy i.e. they are degenerate. But when negative field due to ligands (either anions or the negative ends of polar molecules like NH_3 and H_2O) in a complex surround the metal atom/ion, the degeneracy of the d orbitals is lifted. It results in the splitting of d orbitals. (crystal field splitting). The pattern of splitting depends upon the nature of the crystal field.

1) SPLITTING IN OCTAHEDRAL FIELD



Crystal field splitting in tetrahedral complex



Explanation of properties by CFT

Colour of complex ions :

The colour of metal complex is due to the transition of e^- s from t_{2g} level to e_g level (octahedral complex) by the absorption of certain parts of light from visible region. As a result of this, the complex will have complementary colour of the absorbed light. This phenomenon is called d-d transition.

For eg : $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ has 1 e^- in the d orbitals. For the excitation of this electrons to e_g level, green and yellow lights are needed. The complementary colour of this is purple and the complex appears as purple.

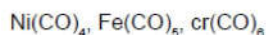
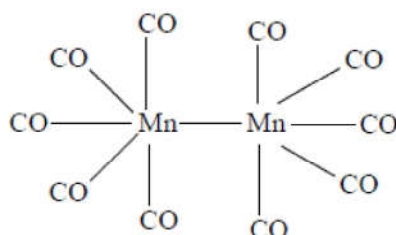
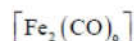
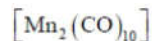
Transition metal complex ion whose central atom contains empty or completely filled d-orbitals are colourless.

Magnetic properties

- Complexes which have unpaired d e^- s show paramagnetic properties.
 - The paramagnetic property of a complex depends on the number of unpaired e^- s present in the d orbitals but the number of unpaired e^- s in the complex depends on the nature of ligand.
 - A weak field ligand forms high spin complexes.
 - A strong field ligand forms a low spin complex.
- Thus, a weak field ligand forms a paramagnetic complex while a strong field ligand forms a diamagnetic or less paramagnetic complex.

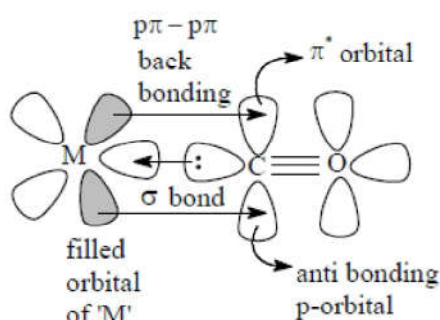
Limitations of CFT

- CFT tells nothing about the partial covalent character of metal-ligand bond.
 - CFT failed to explain the relative strength of ligands.
- eg : It gives no explanation as to why H_2O is a stronger ligand than OH^- in the spectrochemical series.
- It considers only the metal ion d orbitals without giving any consideration to the other metal orbitals (s and p) and ligand orbitals.
 - CFT cannot account for " π " bonding in complexes.

Metal carbonyls**i) Monomeric carbonyls (one - metal atom)****ii) Polymeric carbonyls (more than one 'M' atom)****Bonding in metal carbonyls**

Metal carbon bonding in metal carbonyl has σ as well as π character. The metal-carbon σ bond is formed by the donation from the carbonyl carbon to a vacant d-orbital of the metal. The $\text{M}-\text{C}$ π bond is formed by the donation of pair of e^- s from filled orbital of metal into the vacant anti-bonding orbital of CO.

\therefore CO act as a σ donor and a π acceptor [π -acid ligand. eg : Co , CN^- , PH_3 etc] with the two interaction creating a synergic effect which strengthen the bond between CO & the metal atom.

**Applications of co-ordination complexes**

- Co-ordination complex are used in the qualitative & quantitative estimation of metal ions.
eg : estimation of Ni^{2+} as its red dimethyl glyoxime complex.
- Complex formation is utilised in the extraction of metals like Ag and Au.
- Metal complexes are of great importance in biological process.
eg : chlorophyll is a complex of Mg, hemoglobin is a complex of Fe, vit B_{12} is a complex of cobalt.
- A platinum complex cis-platin $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is used in cancer treatment.
- The hexadentate ligand edta is used in the estimation of hardness of water.
- In homogenous catalysis
eg : hydrogenation of alkenes using wilkinson's catalyst (Rhodium complex)
- Tetraethyl lead is used as an antiknock agent