

Chapter 09

Coordination Compounds

LECTURE-1

A coordination compound contains a central metal atom or ion surrounded by several oppositely charged ions or neutral molecules. These ions or molecules are bonded to the metal atom or ion by a coordinate bond.

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

They do not dissociate into simple ions when dissolved in water.

Double salt

When two salts in the stoichiometric ratio are crystallized together from their saturated solution they are called double salts

Example: $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (Mohr's salt)

They dissociate into simple ions when dissolved in water.

Coordination entity:

A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules.

Example: In $K_4 [Fe(CN)_6]$, $[Fe(CN)_6]^{4-}$ – represents coordination entity.

Central atom or ion:

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.

Example: In $K_4 [Fe(CN)_6]$, Fe is the central metal ion.

Ligands:

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 a ligand.

It may be neutral, positively, or negatively charged.

Examples: H_2O , CN^- , NO^+ etc.

Coordination number:

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.

Example: In the complex $K_4 [Fe(CN)_6]$, the coordination number of Fe is 6.

Coordination sphere:

The central atom/ion and the ligands attached to it are enclosed in the square bracket and are collectively termed as the coordination sphere.

Example: In the complex $K_4 [Fe(CN)_6]$, $[Fe(CN)_6]^{4-}$ is the coordination sphere.

Counter ions:

The ions present outside the coordination sphere are called counter ions.

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.

Examples: $[PtCl_4]^{2-}$ is square planar, $Ni(CO)_4$ is tetrahedral while $[Cu(NH_3)_6]^{2+}$ 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.

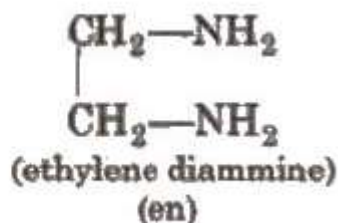
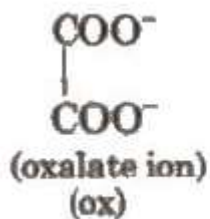
Denticity: The number of ligating (linking) atoms present in the ligand is called denticity.

Unidentate ligands:

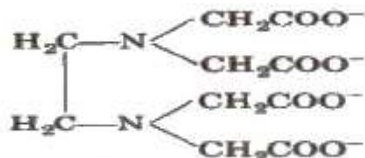
1. The ligands whose only one donor atom is bonded to the metal atom are called unidentate ligands.

Examples: H_2O , NH_3 , CO , CN^-

2. **Bidentate:** It is the ligand, which has two donor sites.



3. **Polydentate** It is the ligand, which has several donor sites. e.g., $[\text{EDTA}]^{4-}$ is a hexadentate ligand.



(iv) **Ambidentate ligands** These are the monodentate ligands that can ligate through two different sites, e.g., NO^{-2} , SCN^{-} , etc.

(v) **Chelating ligands** Di or polydentate ligands cause cyclization around the metal atom which is known as a chelate. Such ligands use two or more donor atoms to bind a single metal ion and are known as chelating ligands.

The more the number of chelate rings, the more is the stability of the complex.

The stabilization of coordination compounds due to chelation is known as the **chelate effect**.

π – acid ligands are those ligands which can form π – bond and σ -bond by accepting an appreciable amount of $1t$ electron density from the metal atom to empty π or π – orbitals.

Oxidation Number of Central Atom

The charge of the complex if all the ligands are removed along with the electron pairs that are shared with the central atom, is called the oxidation number of the central atom.

e.g., $[\text{Cu}(\text{CN})_4]^{3-}$, the oxidation number of copper is +1, and represented as Cu(I).

Types of Complexes

1. Homoleptic complexes

Complexes in which the metal atom or ion is linked to only one kind of donor atoms are called homoleptic complexes e.g., $[\text{Co}(\text{NH}_3)_6]^{3+}$

2. Heteroleptic complexes

Complexes in which the metal atom or ion is linked to more than one kind of donor atoms are called heteroleptic complexes e.g., $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

3. Labile and Inert complexes

Complexes in which the ligand substitution is fast are known as labile complexes and in which ligand substitution is slow are known as inert complexes.

Effective Atomic Number (EAN)

This concept was proposed by Sidgwick. In a complex, the EAN of the metal atom is equal to the total number of electrons present in it.

$$\text{EAN} = Z - \text{ON of metal} + 2 * \text{CN}$$

(where Z = atomic number of the metal atom)

ON = oxidation number of metal

and CN = coordination number of the complex)

An ion with a central metal atom having EAN equal to the next inert gas will be more stable.

LECTURE-2

IUPAC Naming of Complex Compounds

Naming is based on a set of rules given by IUPAC.

1. The name of the compound is written in two parts (i) name of cation, and (ii) name of the anion.
2. The cation is named first in both positively and negatively charged coordination complexes.
3. The dissimilar ligands are named in an alphabetical order before the name of central metal atom or ion.
4. For more than one similar ligands, the prefixes di, tri, tetra, etc are added before its name. If the di, tri, etc already appear in the complex then bis, tris, tetrakis are used.
5. If the complex part is an anion, the name of the central metal ends with the suffix 'ate'.
6. Names of the anionic ligands end in 'o', names of positive ligands end with 'ium', and names of neutral ligands remain as such. But exceptions are there as we use aqua for H₂O, ammine for NH₃, carbonyl for CO, and nitrosyl for NO.
7. The oxidation state for the metal in cation, anion, or neutral coordination compounds is indicated by a Roman numeral in parentheses.
8. The name of the complex part is written as one word.
9. If the complex ion is a cation, the metal is named the same as the element.
10. The neutral complex molecule is named similar to that of the complex cation.

Some examples are

(i) $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$
triamminetrichlorochromium (III) chloride

(ii) $[\text{Co}(\text{H}_2\text{CH}_2\text{CH}_2\text{H}_2)_3]_2(\text{SO}_4)_3$
tris (ethane-1,2-diamine) cobalt (III) sulphate

(iii) $[\text{Ag}(\text{NH}_3)_2] [\text{Ag}(\text{CN})_2]$
diamminesilver (I) dicyanoargentate(I)

(iv) $K_4 [Fe(CN)_6]$
potassium hexacyanoferrate (II)

LECTURE-3

Isomerism in Coordination Compounds

Coordination compounds exhibit the following types of isomerism:

1. Structural Isomerism

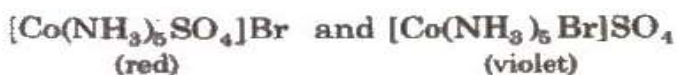
In this isomerism, isomers have different bonding patterns. Different types of structural isomers are

(i) **Linkage isomerism** This type of isomerism is shown by the coordination compounds having ambidentate ligands. e.g.,

$[Co(NH_3)_5(NO_2)]Cl$ and $[Co(NH_3)_5(ONO)]Cl$ or pentaammine nitrito- N Cobalt (III) chloride and pentaammine nitrito-O' Cobalt (III) chloride.

(ii) **Coordination isomerism** This type of isomerism arises from the interchange of ligands between cationic and anionic complexes of different metal ions present in a complex, e.g., $[Cr(NH_3)_6] [Co(CN)_6]$ and $[Co(NH_3)_6] [Cr(CN)_6]$

(iii) **Ionization isomerism** This isomerism arises due to the exchange of ionizable anion with the anionic ligand. e.g.,



(iv) **Solvate isomerism** This is also known as hydrate isomerism. In this isomerism, water is taken as a solvent. It has a different number of water molecules in the coordination sphere and outside it. e.g.,

$[Co(H_2O)_6]Cl_3$, $[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$, $[Co(H_2O)_3Cl_3] \cdot 3H_2O$

2. Stereoisomerism

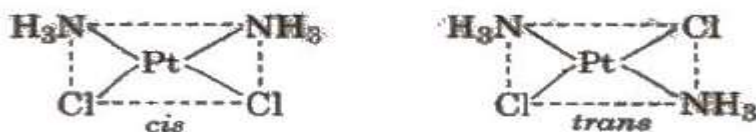
Stereoisomers have the same chemical formula and chemical bonds but they have a different spatial arrangement. These are of two types :

(i) **Geometrical isomerism** Geometrical isomers are of two types i.e., cis and trans isomers. This isomerism is common in complexes with coordination numbers 4 and 6.

Geometrical isomerism in complexes with coordination number 4

(i) Tetrahedral complexes do not show geometrical isomerism.

(ii) Square planar complexes of formula $[MX_2L_2]$ (X and L are unidentate) show geometrical isomerism. The two X ligands may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer, e.g.,

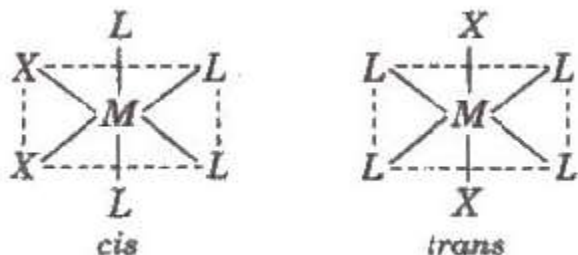


(iii) The square planar complex of the type $[MABXL]$ (where A, B, X, L, are unidentate ligands) shows three isomers, two cis, and one trans.

e.g., $[Pt(NH_3)(Br)(Cl)(Py)]$.

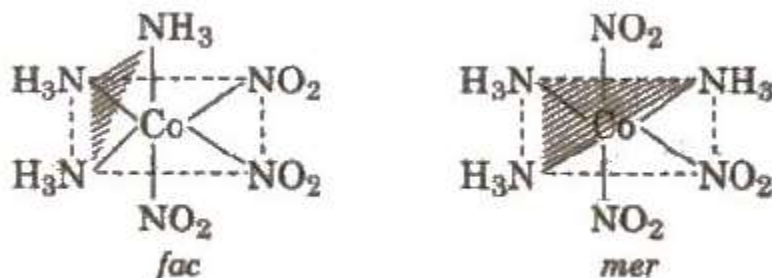
Geometrical isomerism in complexes with coordination number 6

Octahedral complexes of formula $[MX_2L_4]$, in which the two X ligands may be oriented cis or trans to each other, e.g., $[Co(NH_3)_4Cl_2]^+$.



Octahedral complexes of formula $[MX_2A_2]$, where X is unidentate ligands and A are bidentate ligands, form cis and trans isomers, e.g., $[CoCl_2(en)_2]^+$

In octahedral complexes of formula $[MA_3X_3]$, if three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, it is known as facial (fac) isomer when the positions are around the meridian of the octahedron, it is known as meridional (mer) isomer. e.g., $[Co(NH_3)_3(NO_2)_3]$



(ii) **Optical isomerism** These are the complexes that have chiral structures. It arises when mirror images cannot be superimposed on one another. These mirror images are called enantiomers. The two forms are called Dextro (d) and laevo (l) forms.

Tetrahedral complexes with the formula $[M(AB)_2]$ show optical isomers and octahedral complexes (cis form) exhibit optical isomerism.

LECTURE 04

Bonding in Coordination Compounds

Werner's Theory

Metals exhibit two types of valencies in the formation of complexes.

These are primary valencies and secondary valencies.

1. Primary valencies correspond to the oxidation number (ON) of the metal and are satisfied by anions. These are ionizable and non-directional.

2. Secondary valencies correspond to the coordination number (CN) of the metal atom and are satisfied by ligands. These are non-ionizable and directional. Hence, geometry is decided by these valencies.

Valence Bond Theory (VBT)

This theory was proposed by L. Pauling in 1930 s. According to this theory, when a complex is formed, the metal ion/atom provides empty orbitals to the surrounding ligands. The coordination number shows the number of such empty orbitals, i.e., the number of empty orbitals is equal to the coordination number. These empty orbitals hybridized before participation in bonding and the nature of hybridization depends on the nature of metal and on the nature of approaching ligand.

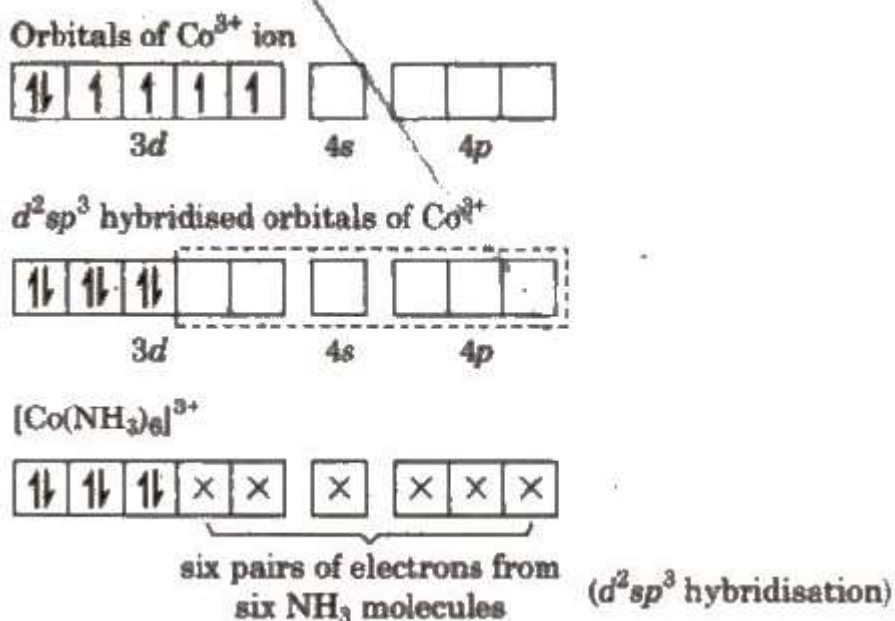
Inner orbital complexes or outer orbital complexes

When outer d-orbitals are used in bonding, the complexes are called outer orbital complexes. They are formed due to weak-field ligands or high spin ligands and hybridization is sp^3d^2 . They have an octahedral shape.

When d-orbitals of $(n - 1)$ shell are used, these are known as an inner orbital complex, they are formed due to strong-field ligands or low spin ligands and hybridization is d^2sp^3 . They are also octahedral in shape.

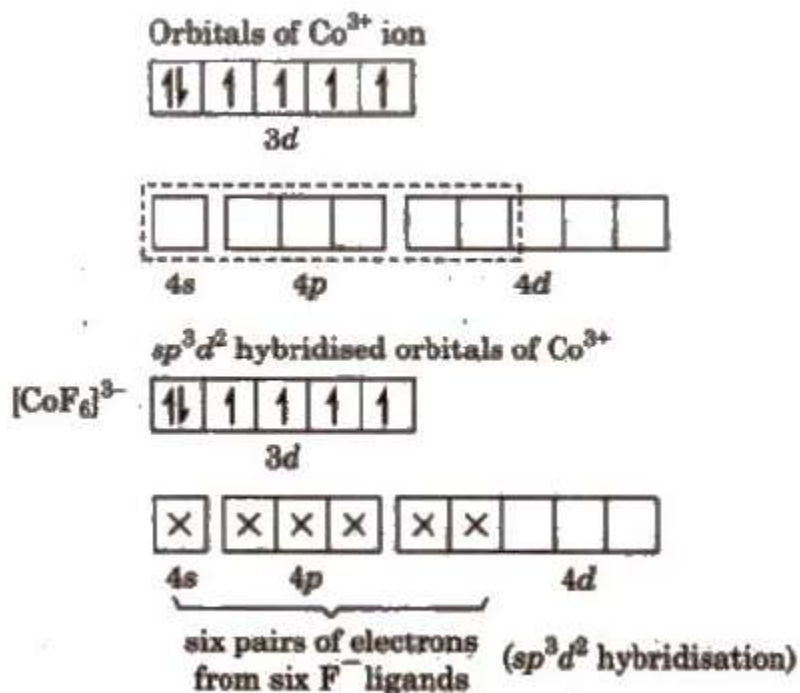
1. **6 – ligands** (unidentate), **octahedral entity.**

(i) **Inner orbital complex** $[\text{Co}(\text{NH}_3)_6]^{3+}$



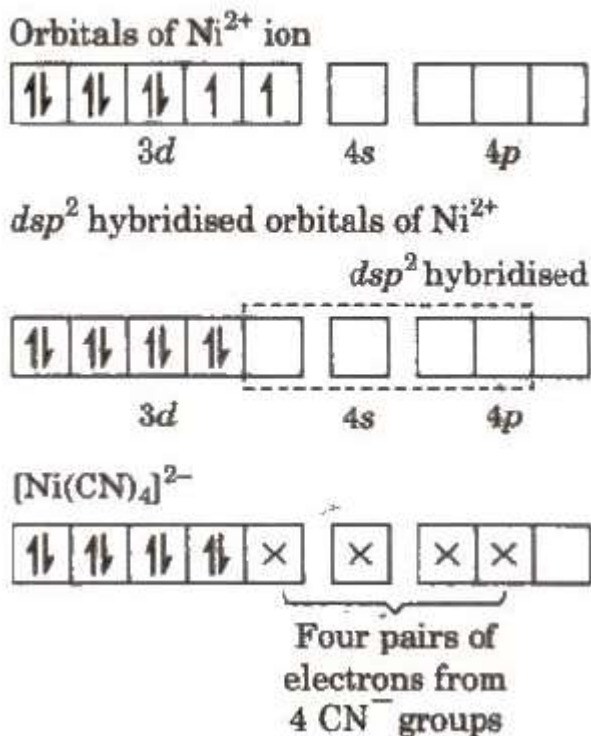
All electrons are paired, therefore complex will be diamagnetic.

(ii) **Outer orbital complex**, $[\text{CoF}_6]^{3-}$



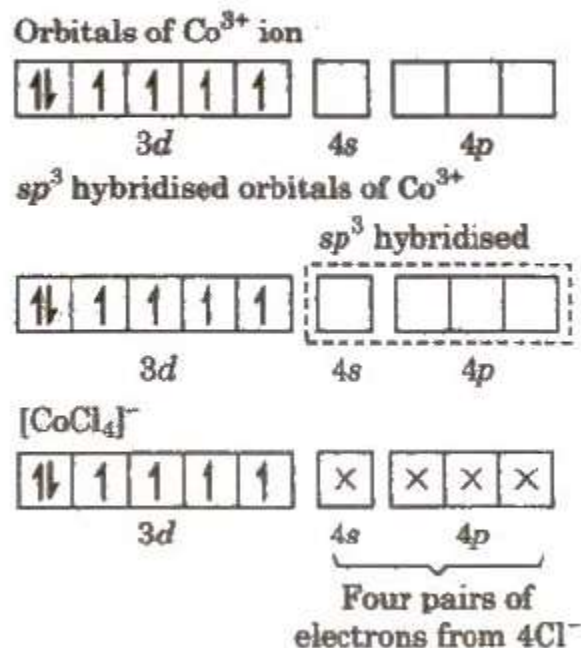
The complex has unpaired electrons, therefore, it will be paramagnetic.

(i) Inner orbital complex, $[\text{Ni}(\text{CN})_4]^{2-}$



All electrons are paired so complex will be diamagnetic.

(ii) Outer orbital complex, $[\text{CoCl}_4]^-$



Since complex has unpaired electrons. so it will be paramagnetic.

Limitations of VBT

This theory could not explain the quantization of the magnetic data, the existence of inner orbital and outer orbital complex, change of magnetic moment with temperature, and color of complexes.

LECTURE 05

Crystal Field Theory (CFT)

This theory was proposed by H. Bethe and van Vleck. Orgel. in 1952, applied this theory to coordination compounds. In this theory, ligands are treated as point charges in the case of anions and dipoles in the case of neutral molecules.

The five d-orbitals are classified as

(i) Three d-orbitals i.e., d_{xy} , d_{yz} , and d_{zx} are oriented in between the coordinate axes and are called t_{2g} - orbitals.

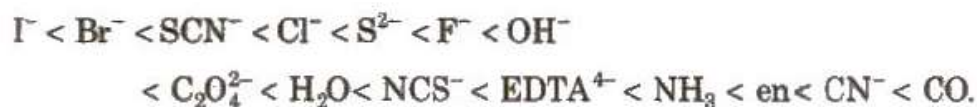
(ii) The other two d-orbitals, i.e., $d_{x^2 - y^2}$ and d_{z^2} oriented along the $x - y$ axes are called e_g - orbitals.

Due to the approach of ligands, the five degenerated orbitals split. The splitting of d-orbitals depends on the nature of the crystal field.

[The energy difference between t_{2g} and e_g level is designated by Δ and is called **crystal field splitting energy.**]

By using spectroscopic data for several coordination compounds, having the same metal ions but different ligand, the crystal field splitting for each ligand has been calculated. A series in which ligand is arranged in order of increasing magnitude of crystal field splitting is called **spectrochemical series.**

Spectrochemical series



Crystal field splitting in octahedral complexes

In the case of octahedral complexes, energy separation is denoted by Δ_o (where subscript 0 is for octahedral).

In octahedral complexes, the six-ligands approach the central metal ion along the axis of $d_{x^2-y^2}$ and d_{z^2} orbitals.

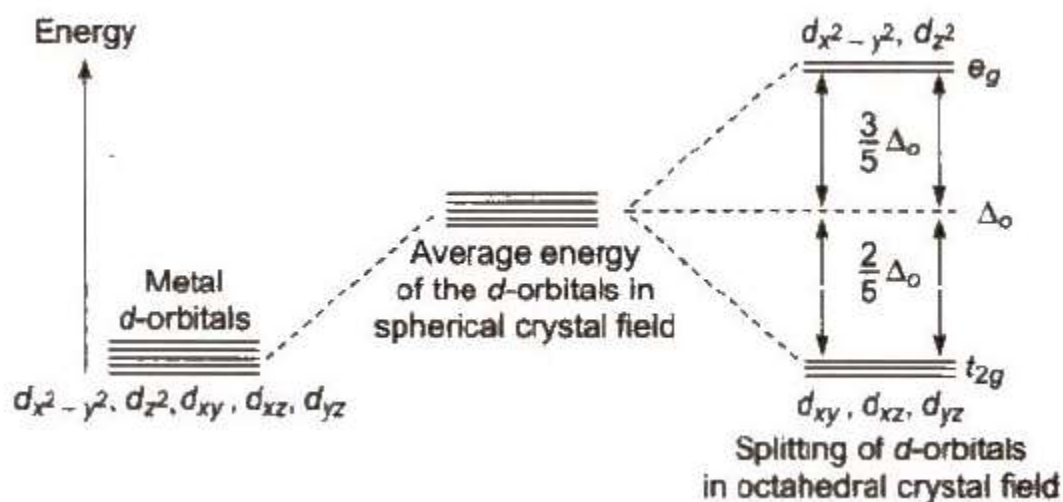
The energy of e_g set of orbitals $>$ energy of t_{2g} set of orbitals.

The energy of e_g orbitals will increase by $(3/5)\Delta_o$ and t_{2g} will decrease by $(2/5)\Delta_o$.

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 $\Delta_o < P$ is known as weak field ligands and form high spin complexes.

If $\Delta_o > P$, it becomes more energetically favorable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. (where P = energy required for e^- pairing in an orbital). Ligands which produce this effect are known as strong field ligands and form low spin complexes.



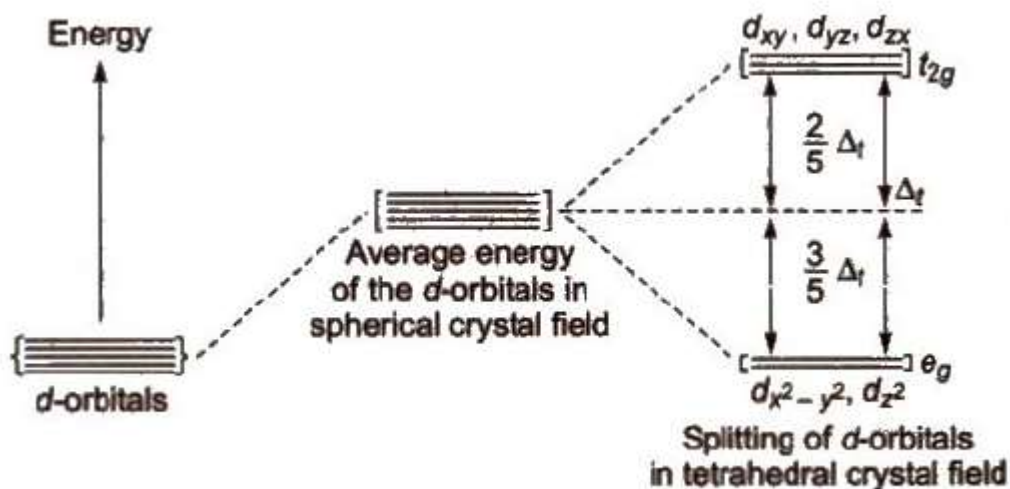
Crystal field splitting in tetrahedral complexes

In tetrahedral complexes, four ligands may be imagined to occupy the alternate corners of the cube and the metal ion at the center of the cube.

The energy of the t_{2g} set of orbitals $>$ Energy of e_g set of orbitals.

In such complexes d – orbital splitting is inverted and is smaller as compared to the octahedral field splitting.

Orbital splitting energies are so low that pairing of electrons is not possible so these are high spin complexes.

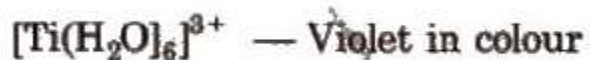


LECTURE 06

Colour in Coordination Compounds

The crystal field theory attributes the color of the coordination compounds to the transition of the electron, i.e., electron jump from t_{2g} level to higher e_g level.

In the absence of ligands, crystal field splitting does not occur and hence the substance is colorless.



Limitations of CFT

1. It does not consider the formation of π bonding in complexes.
2. It is also unable to account satisfactorily for the relative strengths of ligands e.g., it does not explain why H_2O is stronger ligand than OH^- .
3. It gives no account of the partly covalent nature of metal-metal bonds.

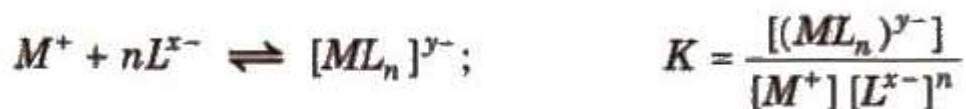
Ligand Field or Molecular Orbital Theory

This theory was put forward by Hund and Mulliken. According to this theory, all the atomic orbitals of the atom participating in molecule formation get mixed to give rise to an equivalent

number of new orbitals, called the molecular orbitals. The electrons are now under the influence of all the nuclei.

Stability of Coordination Compounds

The stability of the complex in a solution refers to the degree of association between the two species involved in the state of equilibrium. It is expressed as a stability constant (K).



The factors on which stability of the complex depends :

(i) **Charge on the central metal atom** As the magnitude of the charge on the metal atom increases, the stability of the complex increases.

(ii) **Nature of metal ion** The stability order is 3d < 4d < 5d series.

(iii) **The basic nature of ligands** Strong field ligands forms a stable complex.

The instability constant or the dissociation constant of compounds is defined as the reciprocal of the formation or stability Constant.

Importance and Applications of Coordination Compounds

1. They are used in many qualitative and quantitative analysis.
2. The hardness of water is estimated by simple titration with Na₂ EDTA.
3. Purification of metals can be achieved through the formation and subsequent decomposition of their coordination compounds.
4. They have great importance in biological systems.
5. They are used as a catalyst for many industrial processes.
6. In medicinal chemistry, there is a growing interest in chelating therapy.

LECTURE 07

Organometallic Compounds

They contain one or more metal-carbon bonds in their molecules. They are of the following types:

1. Sigma (σ) bonded compounds

Metal-carbon bond is a sigma bond, e.g., (C₂H₅)₄ Pb, Zn(C₂H₅)₂ R – Mg – X, etc.

2. Pi (π) bonded compounds

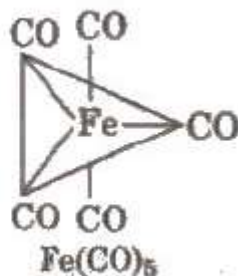
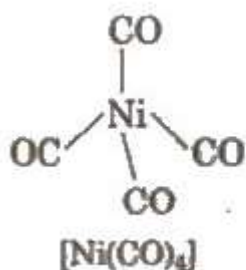
In which molecules/ions containing π bonds act as a ligand. e.g., Ferrocene, Dibenzene chromium, and Zeise's salt.

Zeise's salts are K[PtCl₃(η^2 – C₂H₄)] In which ethylene acts as a ligand that does not have a lone pair of electron.

In ferrocene, $\text{Fe}(\eta^5 - \text{C}_5\text{H}_5)_2$ represents the number of carbon atoms with which metal ion is directly attached.

3. σ and π bonded compounds

Metal carbonyls are their examples. The metal-carbon bond of metal carbonyls has both σ and π – bond character. They have CO molecule as a ligand, e.g.,



Wilkinson's catalyst ($\text{Rh}(\text{PPh}_3)_3\text{Cl}$) is used as a homogeneous catalyst in the hydrogenation of alkenes. Zeigler-Natta catalyst

$[\text{Ti Cl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}]$ acts as a heterogeneous catalyst in the polymerization of ethylene

Changing your Tomorrow