A salt is formed by the neutralization of an acid by a base. There are different types of salts. They are:

a) Simple salt

A simple salt is formed by the neutralization of an acid by a base.

\[ \text{KOH} + \text{HCl} \rightarrow \text{KCl} + \text{H}_2\text{O} \]

Normally, a simple salt ionizes in water and produces ions in solution. The solution of the simple salt exhibits the properties of its component ions.

b) Molecular (or) addition compounds

i) Double salts

These are molecular compounds which are formed by the evaporation of solution containing two (or) more salts in stoichiometric proportions. Hence the molecular compounds which dissociate in solution into its constituent ions are known as double salt. Double salts retain their properties only in solid state. They are also called as lattice compounds.

Example

\[ \text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O} - \text{Potash alum} \]

\[ \text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O} - \text{Mohr’s salt} \]

\[ \text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O} \rightarrow 2\text{K}^+ + 2\text{Al}^{3+} + 4\text{SO}_4^{2-} + 24\text{H}_2\text{O} \]

The double salts give the test of all their constituent ions in solution.

ii) Coordination (or complex) compounds

Coordination compound is ‘a compound formed from a Lewis acid and a Lewis base’. The molecular compounds, do not dissociate into its constituent ions in solution are called coordination compounds.

Example

\[ \text{Fe(CN)}_2 + 4\text{KCN} \rightarrow \text{Fe(CN)}_2 \cdot 4\text{KCN (or) K}_4[\text{Fe(CN)}_6] \]

Ferrous cyanide

\[ \text{Fe(CN)}_2 \cdot 4\text{KCN} \rightarrow 4\text{K}^+ + [\text{Fe(CN)}_6]^{4-} \]

Complex anion

In \( K_4[\text{Fe (CN)}_6] \) the individual components lose their identity. The metal of the complex ion is not free in solution unlike metal in double salt in solution.

Nature of coordination (or) complex compounds

i) An anionic complex compound contains a complex anion and simple cation.

\[ K_4[\text{Fe(CN)}_6] \rightarrow 4\text{K}^+ + [\text{Fe (CN)}_6]^{4-} \]

simple cation complex anion

ii) A cationic complex contains complex cation and simple anion

\[ [\text{Co(NH}_3)_6]\text{Cl}_3 \rightarrow [\text{Co(NH}_3)_6]^{3+} + 3\text{Cl}^- \]

Complex cation simple anion

iii) In the case of a complex compound, \([\text{Cr (NH}_3)_6][\text{Co(CN)}_6]\), it gives both complex cation and complex anion

\[ [\text{Cr(NH}_3)_6][\text{Co(CN)}_6] \rightarrow [\text{Cr(NH}_3)_6]^{3+} + [\text{Co(CN)}_6]^{3-} \]

complex cation complex anion
TERMINOLOGY USED IN COORDINATION CHEMISTRY

(a) Lewis Acid
All electron acceptors are Lewis acids.

(b) Lewis Base
All electron donors are Lewis base.

(c) Central metal ion
In the complex ion an acceptor accepts a pair of electrons from the donor atoms. The acceptor is usually a metal / metal ion to which one (or) more of neutral molecules (or) anions are attached. The acceptor metal cation is referred to as central metal cation. Hence, central metal cation in a complex serves as a lewis acid.

(d) Ligand (Latin word meaning to bind)
A ligand is an ion (or) a molecule capable of functioning as an electron donor. Therefore the neutral molecules or ions which are directly attached to the central metal ion are called as ligand (or) coordination groups. These coordination groups or ligands can donate a pair of electrons to the central metal ion (or) atom. Hence, in a complex compound ligands act as Lewis bases.

Examples:

\[
\text{[Ni(NH}_3\text{)_6]}^{2+} : \text{Ligand} = \text{NH}_3 \text{molecule and Central metal ion} = \text{Ni}^{2+}
\]

\[
\text{[Co(NH}_3\text{)_5Cl]}^{2+} : \text{Ligands} = \text{NH}_3 \text{molecule and Cl}^{-} \text{ ion}
\]

Types of ligands
Ligands can be classified on the basis of charge, number of donor site and bonding

(a) On the basis of charge

(i) Negative ligands : ligands which carry negative charge e.g. CN\(^-\), Cl\(^-\), Br\(^-\), NH\(_2\)\(^-\), NO\(_2\)\(^-\) etc

(ii) Positive ligands : ligand which carry positive charge e.g. NO\(_2^+\), NO\(^+\), NH\(_3\)\(^+\) etc

(iii) Neutral ligands: ligands which do not carry any charge e.g. H\(_2\)O, NH\(_3\), PH\(_3\), CO etc

(b) On the basis of number of donor sites

(i) Monodentate or unidentate ligands: Ligands which coordinate to central atom or ion through one donor atom and form only one coordinate bond are called monodentate/ unidentate ligands
E.g. H\(_2\)O, NH\(_3\), OH\(^-\), CN\(^-\), O\(^2-\) etc

(ii) Bidentate ligands : ligands which coordinate to central metal atom or ion through two donor atoms and form coordinate bonds are called bidentate ligands eg,
(iii) **Polydentate ligands:** Ligands which coordinate to central metal atom or ion through more than two donor atoms are called polydentate ligands and the resulting complex is called polydentate ligands e.g. EDTA is hexadentate ligand.

(c) **On the basis of bonding**

(i) **Chelating ligands:** A bidentate or polydentate ligand which forms two or more coordinate bonds with central metal atom or ion in such a way that a five or six membered ring is formed is called chelating ligand and the resulting complex is called metal chelate. This property is called chelation e.g.

(ii) **Ambidentate ligands:** Monodentate ligand containing more than one coordinating atoms are called ambidentate ligands e.g. NO\(_2^-\) can coordinate with metal atom or ion through either N or O atom.

(e) **Coordination number**

   The total number of coordinate bonds through which the central metal ion is attached with ligand is known as coordination number.

   Example: For example in \(K_4[Fe(CN)_6]\) the coordination number of Fe(II) is 6 and in \([Cu(NH_3)_4]SO_4\) the coordination number of Cu(II) is 4.

(f) **Coordination sphere**

   The central metal ion and the ligands that are directly attached to it, are enclosed in a square bracket, called coordination sphere or first sphere of attraction.

(g) **Oxidation number or Oxidation state of central metal atom/ ion**

   It is the number that represent an electric charge with an atom or ion actually has or appears to have when combined with other atom e.g. \([Cu(NH_3)_4]^2+\) NH\(_4^-\) is neutral, monodentate ligand. Let oxidation state of the metal ion be \(x\) then

   \[x + 4(0) = +2 \implies x = 2\] Oxidation number of Cu is +2
Rules for writing formula of coordination compounds

(i) Formula of the cation whether simple or complex must be written first followed by anion.

(ii) The coordination sphere the sequence of symbols is:
First metal name followed by anionic ligand then neutral ligand finally cationic ligand. Ligands of same type are arranged alphabetically.

(iii) Polyatomic ligands are enclosed in parentheses.

For example, \( \text{In Na[PrBrCl(NO}_2\text{)]\text{NH}_3(NO)} \)
sequence in coordination sphere is metal atom, alphabetical sequence of anionic ligand \( \text{Br}^-\), \( \text{Cl}^-\), \( \text{NO}_2^-\), followed by neutral ligand \( \text{NH}_3\) and then cationic ligand \( \text{NO}^+\).

IUPAC nomenclature of coordination compounds

The rules are outlined below

1. In naming the entire complex, the name of the cation is given first and the anion second (just as for sodium chloride), no matter whether the cation or the anion is the complex species.

2. In the complex ion, the name of the ligand or ligands precedes that of the central metal atom (This procedure is reversed for writing formulae).

3. Ligand names generally end with ‘O’ if the ligand is negative (‘chloro’ for \( \text{Cl}^-\), ‘cyano’ for \( \text{CN}^-\), ‘hydrido’ for \( \text{H}^-\)) and unmodified if the ligand is neutral (‘methylamine’ for \( \text{MeNH}_2\)). Special ligand names are ‘aqua’ for water, ‘ammine’ for ammonia, ‘carbonyl’ for CO, nitrosyl’ for NO.

4. A Greek prefix (mono, di, tri, tetra, penta, hexa, etc.) indicates the number of each ligand (mono is usually omitted for a single ligand of a given type). If the name of the ligand itself contains the terms mono, di, tri, like triphenylphosphine, ligand name is enclosed in parentheses and its number is given with the alternate prefixes bis, tris, tetrakis instead.

For example, \( [\text{Ni(PPh}_3\text{)}_2\text{Cl}_2] \) is named dichlorobis(triphenylphosphine) nickel(II).

5. A Roman numeral or a zero in parentheses is used to indicate the oxidation state of the central metal atom.

6. If the complex ion is negative, the name of the metal ends in ‘ate’ for example, ferrate, cuprate, nickelate, cobaltate etc.

7. If more than one ligand is present in the species, then the ligands are named in alphabetical order regardless of the number of each.

For example, \( \text{NH}_3\) (ammine) would be considered as ‘a’ ligand and come before \( \text{Cl}^-\)(chloro).

Some additional notes

i) Some metals in anions have special names
B Borate ,Au Aurate, Ag Argentate, Fe Ferrate, Pb Plumbate, Sn Stannate, Cu Cuprate, Ni Nickelate

ii) Use of brackets or enclosing marks. Square brackets are used to enclose a complex ion or neutral coordination species.

Examples
\( [\text{Co(en)}_3\text{Cl}_3] \) tris(ethylenediamine)cobalt(III) chloride
CO-ORDINATION COMPOUNDS

[Co(NH₃)₃(NO₂)₃] triamminetrinitrocobalt (III)
K₂[CoCl₄] potassiumtetrachlorocobaltate(II)

Note that it is not necessary to enclose the halogens in brackets.

### Name of Negative ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Name</th>
<th>Ligand</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁻</td>
<td>Hydrido</td>
<td>HS⁻</td>
<td>Mercapto</td>
</tr>
<tr>
<td>O²⁻</td>
<td>Oxo</td>
<td>NH₂⁻</td>
<td>Amido</td>
</tr>
<tr>
<td>O₂⁻</td>
<td>Peroxo</td>
<td>NH₂⁻</td>
<td>Imido</td>
</tr>
<tr>
<td>O₂H⁺</td>
<td>Perhydroxo</td>
<td>NO₃⁻</td>
<td>Nitrato</td>
</tr>
<tr>
<td>OH⁻</td>
<td>Hydroxo</td>
<td>ONO⁻</td>
<td>Nitrite</td>
</tr>
<tr>
<td>F⁻</td>
<td>Fluoro</td>
<td>NO₂⁻</td>
<td>Nitro</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>Chloro</td>
<td>N⁻³</td>
<td>Nitrile</td>
</tr>
<tr>
<td>Br⁻</td>
<td>Bromo</td>
<td>P³⁻</td>
<td>Phosphido</td>
</tr>
<tr>
<td>I⁻</td>
<td>Iodo</td>
<td>N₃⁻</td>
<td>Azido</td>
</tr>
<tr>
<td>CO₃⁻</td>
<td>Carbonato</td>
<td>CNO⁻</td>
<td>Cyanato</td>
</tr>
<tr>
<td>C₂O₄⁻</td>
<td>Oxalate</td>
<td>NCO⁻</td>
<td>Cyanato</td>
</tr>
<tr>
<td>CH₃CO₂⁻</td>
<td>Acetate</td>
<td>SCN⁻</td>
<td>Thiocyanato</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>Sulphato</td>
<td>HCO₃⁻</td>
<td>Hydrogencarbonato</td>
</tr>
<tr>
<td>SO₂⁻</td>
<td>Sulphito</td>
<td>S₀₆⁻²</td>
<td>Tetrathionato</td>
</tr>
<tr>
<td>S⁻</td>
<td>Sulphido</td>
<td>HSO₄⁻</td>
<td>Hydrogensulphito</td>
</tr>
<tr>
<td>NH₂CH₂CO₂⁻</td>
<td>Glycinato</td>
<td>C₅H₅⁻</td>
<td>Cyclopentadienyl</td>
</tr>
<tr>
<td>(OCCH₂)₂NCH₂CH₂CH₂N (CH₂CO₂)₂</td>
<td>Ethylenediammine tetraacetato (EDTA)</td>
<td>S₂O₃²⁻</td>
<td>Thiosulphato</td>
</tr>
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</table>

### Name of neutral ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Name</th>
<th>Ligand</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅H₅N (py)</td>
<td>Pyridine</td>
<td>NH₂(CH₂)₂NH₂ (en)</td>
<td>Ethylenediammine</td>
</tr>
<tr>
<td>NH₃</td>
<td>Ammine</td>
<td>CH₃NH₂</td>
<td>Methylamine</td>
</tr>
<tr>
<td>H₂O</td>
<td>Aqua/aquo</td>
<td>CO</td>
<td>Carbonyl</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>Benzene</td>
<td>NO</td>
<td>Nitrosyl</td>
</tr>
<tr>
<td>N₂</td>
<td>Dinitrogen</td>
<td>CS</td>
<td>Thiocarbonyl</td>
</tr>
<tr>
<td>O₂</td>
<td>Dioxygen</td>
<td>NS</td>
<td>Thionitrosyl</td>
</tr>
<tr>
<td>Ph₃P</td>
<td>Triphenylphosphine</td>
<td>CH₃COCH₃</td>
<td>Acetone</td>
</tr>
</tbody>
</table>

### Name of Positive ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO⁺</td>
<td>Nitosonium</td>
</tr>
<tr>
<td>NO₂⁺</td>
<td>Nitronium</td>
</tr>
<tr>
<td>NH₂NH₃⁺</td>
<td>Hydrazinium</td>
</tr>
</tbody>
</table>
## CO-ORDINATION COMPOUNDS

### Bidentate ligands

<table>
<thead>
<tr>
<th>Name of the species</th>
<th>Formula</th>
<th>Charge</th>
<th>Abbr.</th>
<th>Donor site</th>
<th>IUPAC name of ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycinate ion</td>
<td><img src="image" alt="Glycinate structure" /></td>
<td>-1</td>
<td>gly</td>
<td>2, One N and one O atom</td>
<td>Glycinato</td>
</tr>
<tr>
<td>Dimethyl glyoxime ion</td>
<td><img src="image" alt="Dimethyl glyoxime structure" /></td>
<td>-1</td>
<td>dmg</td>
<td>2,one N and one O</td>
<td>Dimethyl glyoximato</td>
</tr>
<tr>
<td>Acetyl acetonate</td>
<td><img src="image" alt="Acetyl acetonate structure" /></td>
<td>-1</td>
<td>Acac</td>
<td>Two O atom</td>
<td>Acetylacetonato</td>
</tr>
<tr>
<td>Oxalate ion</td>
<td><img src="image" alt="Oxalate structure" /></td>
<td>-2</td>
<td>Ox</td>
<td>Two O atoms</td>
<td>Oxalato</td>
</tr>
<tr>
<td>Ethylene diamine(en)</td>
<td><img src="image" alt="Ethylene diamine structure" /></td>
<td>Zero</td>
<td>En</td>
<td>Two N atoms</td>
<td>Ethylenediamine</td>
</tr>
</tbody>
</table>

### Multidentate ligands

<table>
<thead>
<tr>
<th>Name of the species</th>
<th>Charge</th>
<th>Abbri</th>
<th>Donor site</th>
<th>IUPAC name of ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylene triamine</td>
<td>Zero</td>
<td>Dien</td>
<td>3, three N atoms (tridentate)</td>
<td>Diethylene triamine</td>
</tr>
<tr>
<td>Triethylene tetramine</td>
<td>Zero</td>
<td>Trien</td>
<td>4, Four N atoms (Tetradentate)</td>
<td>Triethylene amine</td>
</tr>
<tr>
<td>Ethylenediamine triacetate ion</td>
<td>-3</td>
<td>EDTA³⁻</td>
<td>5, Three O atoms and two N atoms (pentadenate)</td>
<td>Ethylenediamine triacetate</td>
</tr>
<tr>
<td>Ethylenediamine tetraacetate ion</td>
<td>-4</td>
<td>EDTA⁴⁻</td>
<td>6, two N and four O atoms (Hexadentate)</td>
<td>Ethylenediamine tetraacetato</td>
</tr>
</tbody>
</table>

### Few examples to elaborate above rules

- \([\text{PtCl}_2(\text{C}_2\text{H}_3\text{N})(\text{NH}_3)]\) \hspace{1cm} Amminedichloro (pyridine)platinum(II)
- \([\text{Fe(CO)}_5]\) \hspace{1cm} Pentacarbonyliron(0)
- \([\text{PtCl}_2(\text{NH}_3)_4][\text{PtCl}_4]\) \hspace{1cm} Tetraamminedichloroplatinum (IV) tetrachloroplatinate(II)
- \([\text{Cr(NH}_3)_4][\text{CuCl}_4]\) \hspace{1cm} Tetraammine chromium(0) tetrachlorocuperate(IV)
- \(\text{Na}[\text{PtBrCl(NO}_2](\text{NH}_3)]\) \hspace{1cm} Sodium amminebromochloronitro
- \([\text{Pt(py)}_4][\text{PtCl}_4]\) \hspace{1cm} Tetrapyridineplatinum(II) Tertrachloroplatinate(II)
- \([\text{CoCl}(\text{ONO})(\text{en})_2]^+\) \hspace{1cm} Chlorobis(ethylenediamine)nitritocobalt (III) ion
- \(\text{[(C}_2\text{H}_3\text{P})\text{Rh}][\text{Cl}\) \hspace{1cm} Tris(triphenylphosphine)rodium(I)chloride
- \([\text{Fe(H}_2\text{O})_4(\text{C}_2\text{O}_4)]_2\text{SO}_4\) \hspace{1cm} Tetraaquooxalatoiron(III)sulphate
### CO-ORDINATION COMPOUNDS

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_4[Fe(CN)_6]$</td>
<td>Potassium hexacyanoferrate(II)</td>
</tr>
<tr>
<td>$K_3[Fe(CN)_6]$</td>
<td>Potassium pentacyanonitrosylferrate(II)</td>
</tr>
<tr>
<td>$Na[Ag(CN)_2]$</td>
<td>Sodium dicyanoargentate(I)</td>
</tr>
<tr>
<td>$[Fe(CO)_5]$</td>
<td>Pentacarbonyliron(0)</td>
</tr>
<tr>
<td>$Fe_4[Fe(CN)_6]$</td>
<td>Ferric hexacyanoferrate(II)</td>
</tr>
<tr>
<td>$[Fe(C_3H_2)]$</td>
<td>Bis(cyclopentadienyl)iron(II)</td>
</tr>
<tr>
<td>$Na_2[NC(NO)]$</td>
<td>Sodium tetraisocyanonitrosylferrate(II)</td>
</tr>
<tr>
<td>$K_3[Fe(CN)_5]$</td>
<td>Potassium pentacyanoisocyanide(II)</td>
</tr>
<tr>
<td>$Na[Ag(CN)_2]$</td>
<td>Sodium dicyanoargentate(I)</td>
</tr>
<tr>
<td>$[Fe(CO)_5]$</td>
<td>Pentacarbonyliron(0)</td>
</tr>
<tr>
<td>$Fe_4[Fe(CN)_6]$</td>
<td>Ferric hexacyanoferrate(II)</td>
</tr>
<tr>
<td>$[Fe(C_3H_2)]$</td>
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<tr>
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<td>Sodium tetraisocyanonitrosylferate(II)</td>
</tr>
<tr>
<td>$K_3[Fe(CN)_6]$</td>
<td>Potassium hexacyanoferrate(II)</td>
</tr>
<tr>
<td>$K_3[Fe(CN)_6]$</td>
<td>Potassium pentacyanonitrosylferrate(II)</td>
</tr>
<tr>
<td>$Na[Ag(CN)_2]$</td>
<td>Sodium dicyanoargentate(I)</td>
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<td>$[Fe(CO)_5]$</td>
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</tr>
<tr>
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<td>Potassium hexacyanoferrate(II)</td>
</tr>
<tr>
<td>$K_3[Fe(CN)_6]$</td>
<td>Potassium pentacyanonitrosylferrate(II)</td>
</tr>
<tr>
<td>$Na[Ag(CN)_2]$</td>
<td>Sodium dicyanoargentate(I)</td>
</tr>
<tr>
<td>$[Fe(CO)_5]$</td>
<td>Pentacarbonyliron(0)</td>
</tr>
<tr>
<td>$Fe_4[Fe(CN)_6]$</td>
<td>Ferric hexacyanoferrate(II)</td>
</tr>
<tr>
<td>$[Fe(C_3H_2)]$</td>
<td>Bis(cyclopentadienyl)iron(II)</td>
</tr>
<tr>
<td>$Na_2[NC(NO)]$</td>
<td>Sodium tetraisocyanonitrosylferate(II)</td>
</tr>
</tbody>
</table>

8) Naming of the bridging ligands of the bridged polynuclear complexes
Complexes having two or more atoms are called polynuclear complexes. In these complexes, the bridge group is indicated by separating it from the rest of the complex by hyphen and adding the prefix $\mu$- before the name of each different bridging group. Two or more bridging groups of the same type are indicated by di-$\mu$, tri-$\mu$ etc. When a bridging ligand is attached to more than two metal atoms or ion, this is indicated by subscript to $\mu$

\[
\begin{align*}
\text{NH}_2 & \quad \text{Co} \\
\text{OH} & \quad \text{Co} \\
\text{(en)}_2 & \quad \text{Co} \\
\text{(en)}_2 & \quad \text{(SO}_4)^2
\end{align*}
\]

Is named as Bis(ethylenediammine)cobalt(III)-$\mu$-amido-$\mu$-hydroxo-bis(ethylenediammine)cobalt(III)sulphate
Or $\mu$-amido-tertakis (ethylenediammine)-$\mu$-hydroxo-dicobalt(III)sulphate

Werner’s coordination theory

**Postulates of Werner’s theory**

1) Every metal atom has two types of valencies
   i) Primary valency or ionisable valency
   ii) Secondary valency or non ionisable valency
2) The primary valency corresponds to the oxidation state of the metal ion. The primary valency of the metal ion is always satisfied by negative ions.

3) Secondary valency corresponds to the coordination number of the metal ion or atom. The secondary valencies may be satisfied by either negative ions or neutral molecules.

4) The molecules or ion that satisfy secondary valencies are called ligands.

5) The ligands which satisfy secondary valencies must project in definite directions in space. So the secondary valencies are directional in nature where as the primary valencies are non-directional in nature.

6) The ligands have unshared pair of electrons. These unshared pair of electrons are donated to central metal ion or atom in a compound. Such compounds are called coordination compounds.

**Werner’s representation**

Werner represented the first member of the series \([\text{Co(NH}_3\text{)}_6]\text{Cl}_3\) as follows. In this representation, the primary valency (dotted lines) are satisfied by the three chloride ions. The six secondary valencies (solid lines) are satisfied by the six ammonia molecules.

![Werner's representation of [Co(NH\textsubscript{3})\textsubscript{6}]Cl\textsubscript{3}](image)

**Defects of Werner’s theory**

Werner’s theory describes the structures of many coordination compounds successfully. However, it does not explain the magnetic and spectral properties.

**Valence bond theory (VB Theory)**

Valence bond theory, primarily the work of Linus Pauling regarded bonding as characterized by the overlap of atomic or hybrid orbitals of individual atoms. The postulates of valence bond theory:

1) The central metal atom/ion makes available a number of vacant orbitals equal to its coordination number. These vacant orbitals form covalent bonds with the ligand orbitals.

2) A covalent bond is formed by the overlap of a vacant metal orbital and filled ligand orbitals. This complete overlap leads to the formation of a metal ligand, \(\sigma\) (sigma) bond.
CO-ORDINATION COMPOUNDS

4) A strong covalent bond is formed only when the orbitals overlap to the maximum extent. This maximum overlapping is possible only when the metal vacant orbitals undergo a process called ‘hybridisation’. A hybridised orbital has a better directional characteristics than an unhybridised one.

The following table gives the coordination number, orbital hybridisation and spatial geometry of the more important geometrics.

<table>
<thead>
<tr>
<th>Coordination number</th>
<th>Types of hybridization</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>sp</td>
<td>linear</td>
</tr>
<tr>
<td>4</td>
<td>sp³</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>4</td>
<td>dsp²</td>
<td>square planar</td>
</tr>
<tr>
<td>6</td>
<td>d²sp³</td>
<td>octahedral</td>
</tr>
<tr>
<td>6</td>
<td>sp³d²</td>
<td>octahedral</td>
</tr>
</tbody>
</table>

**Magnetic moment**

A species having at least one unpaired electron, is said to be paramagnetic. It is attracted by an external field. The paramagnetic moment is given by the following spin-only formula.

\[ \mu_s = \sqrt{n(n+2)} \text{ BM} \]

\( \mu_s \) = spin-only magnetic moment

n = number of unpaired electrons

BM = Bohr magneton, the unit which expresses the magnetic moment.

When the species does not contain any unpaired electron, it is diamagnetic.

**Applications of valence bond theory**

(i) If the ligand is very weak like F⁻, H₂, Cl⁻ etc. It does not force the pairing of 3d electrons and hence outer orbital octahedral complexes are formed by sp³d² hybridization.

(ii) But if the ligand is strong like CN⁻, (COO)₂⁻, ethylenediammine (en) etc, it forces the paring of 3d electrons and hence inner orbital octahedral complexes are formed by d²sp³ hybridization.

(1) Atom or ion of d-block element contain 1, 2 or 3 electrons in d-orbit (d¹,d²,d³ system)

\[
\begin{array}{c}
3d \\
\uparrow \uparrow \uparrow \uparrow
\end{array}
\quad
\begin{array}{c}
4s \\
\square
\end{array}
\quad
\begin{array}{c}
4p \\
\mid \mid \mid
\end{array}
\]

\[ d²sp³ \text{ hybridization} \]

Ti³⁺, V³⁺, Cr³⁺

Since two 3d orbitals are available for d²sp³ hybridization. Hence, these systems may accept six lone pairs from six ligands and they form octahedral complexes [Ti(H₂O)₆]³⁺, [V(H₂O)₆]³⁺, [Cr(H₂O)₆]³⁺
CO-ORDINATION COMPOUNDS

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Since due to complexation the unpaired electrons in \((n-1)\) d-orbitals are not disturbed, the magnetic moment of free metal ions remains intact in octahedral complexes.

**More possibility**

In addition to \(d^2sp^3\) hybridisation metal ions may undergo \(sp^3\) or \(dsp^2\) hybridization forming tetrahedral or square planar complexes respectively.

Since in \(sp^3\) or \(dsp^2\), the d-electrons are not disturbed, the magnetic moment of free metal ion remains intact in tetrahedral or square planar complex.

(2) Atom or ion of d-block element contain 4, 5 or 6 electrons in d-orbit (\(d^4, d^5, d^6\) system)

\(\text{Mn(III), Fe(III), Co(III), Fe(II)}\)

In above type ions, in ground state two 3-d orbitals are not vacant to participate thus 3d electrons are not disturbed and hence magnetic moment of free metal ions remains intact in outer orbital octahedral complex. Energy gap between 4s and 4d is large, the \(sp^3d^2\) hybridisation is not perfect hybridization and hence outer orbital complexes are comparatively less stable. Moreover, 4d orbitals are more extended in space than 3d orbitals and hence \(sp^3d^2\) hybrid orbitals are also more extended in space than \(d^2sp^3\) hybrids. So bond length in outer orbital octahedral complexes is comparatively longer and so they are less stable. Such complex is possible if ligand is weak.

**Another possibility**

For strong ligand like \(\text{CN}^-\) maximizes pairing of 3d electrons, two 3d orbitals may be made vacant for \(d^2sp^3\) hybridisation forming octahedral complex. As two d-orbitals of inner shell are involved in hybridisation, complex are said to be inner orbital octahedral complex. The energy of the orbitals involved in hybridisation is in continuation. The \(d^2sp^3\) hybridisation is perfect and at the same time due to less extension of 3d orbitals in space, bond length is also short. So, inner orbital octahedral complexes are more stable than outer orbital octahedral complex. As the paring of 3d electrons is forced in \(d^2sp^3\) hybridisation in these systems, hence the magnetic moment of the free metal ion undergoes change on complexation.

**One more possibility**

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In addition to inner orbital octahedral and outer octahedral complexes ions may also form tetrahedral and square planner complex by sp<sup>3</sup> and dsp<sup>2</sup> hybridization.

(3) Atom or ion of d-block element contain 7, 8 or 9 electrons in d-orbit (d<sup>7</sup>, d<sup>8</sup>, d<sup>9</sup> system)

Co(II), Ni(II), Cu(II)

<table>
<thead>
<tr>
<th>3d</th>
<th>4s</th>
<th>4p</th>
<th>4d</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑</td>
<td></td>
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</tbody>
</table>

Two vacant 3d orbitals cannot be made available for d<sup>2</sup>sp<sup>3</sup> hybridization even after maximum pairing. So, there is no chance of the formation of inner orbital octahedral complex.

Co<sup>2+</sup> under the influence of HN<sub>3</sub> as ligand

<table>
<thead>
<tr>
<th>3d</th>
<th>4s</th>
<th>4p</th>
<th>5s</th>
<th>4d</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑</td>
<td></td>
<td></td>
<td>↑</td>
<td></td>
</tr>
</tbody>
</table>

In d<sup>7</sup>, with promotion of one electron to 5s or 4d, it becomes loosely bonded to the nucleus and hence, it may easily be removed and so, Co(II) will easily be oxidized to Co(III).

In d<sup>8</sup>, after maximum pairing of 3d electrons, one 3d orbital may be vacated for dsp<sup>2</sup> hybridization and hence d<sup>7</sup>, d<sup>8</sup> systems favour the formation of square planar complexes with changed magnetic nature.

In d<sup>9</sup>, one d-orbital is not made available for dsp<sup>2</sup> hybridization. So there is no question of the formation of square planar complex by d<sup>9</sup>

More possibility (weak ligand)

However they may undergo sp<sup>3</sup>d<sup>2</sup> hybridization forming outer orbital octahedral complex with same magnetic properties as in free metal.

One more possibility

Also sp<sup>3</sup> hybridizations can easily occur favouring the formation of tetrahedral complexes with unchanged magnetic character.

(4) In d<sup>10</sup> Zn(II), Cu(I)

In d<sup>10</sup>, 3d orbitals are completely filled up, so, it may form tetrahedral complex by sp<sup>3</sup> hybridization or outer orbital octahedral complexes by sp<sup>3</sup>d<sup>2</sup> hybridization.

Magnetic properties of the free metal ion remains unchanged in tetrahedral or outer orbital octahedral complexes.

Defects of Valence bond theory
While the VB theory, to a larger extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following shortcomings:

(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 coordination compounds.
(iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
(v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
(vi) It does not distinguish between weak and strong ligands.

**Crystal field theory (CFT)**

Main postulates of crystal field theory are

(i) In a coordination compound there are electrostatic interaction between metal atom/ion and ligands. Ligand assumed to be a point charge
(ii) In an isolated metal atom or ion all five d-orbitals have equal energy i.e. they are degenerate
(iii) When metal atom/ion gets surrounded by ligands, there occur interaction between d-electron cloud of metal atom/ion and ligands
(iv) If the field due to ligan around metal atom is spherically symmetrical, d-orbitals of metal remains degenerated
(v) If field due to ligand surrounding metal is unsymmetrical (as in octahedral and tetra hedral complexes) the degacity of d-orbitals is splitted into two sets of orbitals
(vi) Orbitals lying in the direction of ligands (point charges) are raised to higher energy state than those orbitals lying between theligands (point charges)
(vii) The energy difference between two sets of orbitals is denoted by $\Delta_o$ for octahedral and $\Delta_t$ for tetrahedral
(viii) The magnitude of $\Delta_o$ and $\Delta_t$ depends upon the field strength of ligand around the metal
(ix) Ligands which cause larger splitting (large $\Delta$) are called strong field ligands while those which causes small splitting (small $\Delta$) are called weak filed ligands

**Spectrochemical series**

Arrangement of ligands in order of their ability to cause splitting ($\Delta$) is called spectrochemical series

$I^- < Br^- < S^2- < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < O^2- < H_2O < NCS^- < NH_3 < en < NO_2^- < CN^- < CO$

The spectrochemical series is an experimentally determined series. It is difficult to explain the order as it incorporates both the effect of $\sigma$ and $\pi$ bonding.

A pattern of increasing $\sigma$ donation is as follows

Halides donors < O donors < N donors < C donors
Crystal field splitting in octahedral complexes

The octahedral arrangement of six ligands surrounding the central metal ion can be shown as follows:

It is obvious from the figure, that ligands approaching the x, y, and z axis. The two d orbitals namely \(d(x^2 - y^2)\) and \(d(z^2)\) will suffer more electrostatic repulsion and hence their energy will be greater than other three orbitals \(d(xy), d(yx)\) and \(d(xz)\) which will have their lobes lying between the axis. Thus degenerate set of d-orbitals split into two sets:

- \(e_g\) orbitals of higher energy including \(d(x^2 - y^2)\) and \(d(z^2)\)
- \(t_{2g}\) orbitals of lower energy including \(d(xy), d(yx)\) and \(d(xz)\)

The crystal field splitting is measured in terms of energy difference between \(t_{2g}\) and \(e_g\) orbital and is denoted by a symbol \(\Delta_0\). It is generally measured in terms of \(D_q\). It is called as crystal field splitting energy or crystal field stabilization energy.

\(E_g\) orbitals are 6\(D_q\) above the average energy level and \(t_{2g}\) orbitals are 4\(D_q\) below the average energy level.

Significance of \(\Delta_0\)

A strong field ligand approaches the central metal atom/ion strongly and thus the magnitude of \(\Delta_0\) is high. Hence in the case of strong field ligand, the magnitude of \(\Delta_0\) is greater than the pairing energy (the energy required to pair up two negatively charged electrons having opposite spin in an orbital). However, under the influence of weak field ligand, \(\Delta_0\) is smaller than pairing energy (P).

Now, let us consider the \(d^4\) configuration of the central atom/ion. The first three electrons will go into \(t_{2g}\) orbitals using Hund’d rule of maximum multiplicity. The fourth electron will go in the \(e_g\) orbital when the ligands are weak as, \(\Delta_0 < P\) giving the configuration \(t_{2g}^3e_g^1\). But if the ligands are strong, then the fourth electron will pair up when any of the singly occupied \(t_{2g}\) orbitals (as \(\Delta_0 > P\)) to give the configuration \(t_{2g}^4e_g^0\)

Crystal field splitting in tetrahedral complexes
The tetrahedral arrangement of four ligands surrounding the metal ions can be shown as shown in figure.

It is obvious from the figure that none of the d-orbital point exactly towards the ligands. However, three d-orbitals $d(xy)$, $d(yz)$ and $d(xz)$ are pointing close towards ligands.

As a result of this, the energy of these three orbitals increases much more than the other two d-orbitals $d(x^2-y^2)$ and $d(z^2)$. The d-orbitals thus split in two sets of orbitals: $t_{2g}$ orbitals of higher energy including $d(xy)$, $d(yz)$, $d(xz)$ and $e_g$ orbitals of lower energy including $d(x^2-y^2)$ and $d(z^2)$.

Energy difference between two sets of orbitals is represented by $\Delta_t$. However splitting is much smaller than that in octahedral complexes:

$$\Delta_t \approx -\frac{4}{9} \Delta_o$$

Negative sign denotes that order of splitting in tetrahedral complexes is reverse of that in octahedral complexes.

Because of the small value of $\Delta_t$, electrons generally do not pair and results in formation of high-spin complex.

**Limitation of Crystal field theory**

The crystal field model is successful in explaining the formation, structures, colour and magnetic properties of coordination compounds to a large extent.

However, from the assumptions that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. The anionic ligands actually are found at the low end of the spectrochemical series.

Further, it does not take into account the covalent character of bonding between the ligand and the central atom.

These are some of the weaknesses of CFT, which are explained by ligand field theory (LFT) and molecular orbital theory.
Factors affecting the stability of complexes

1) A coordinate compound is formed in solution by the stepwise addition of ligands to metal ion. The overall stability constant is given by

\[ M + nL \rightleftharpoons MLn \]

\[ \beta_i = \frac{[MLn]}{[M][L]^n} \]

Higher the value of \( \beta_i \), more stable is the complex or more the quantity of ML\(_n\) be exists in solution.

Free metal ions rarely exist in the solution so that M will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them.

For simplicity, we generally ignore these solvent molecules and write stability constants as follows in the formation of ML\(_n\) are

\[ M + L \rightleftharpoons ML \quad K_1 = \frac{[ML]}{[M][L]} \]
\[ ML + L \rightleftharpoons ML_2 \quad K_2 = \frac{[ML_2]}{[ML][L]} \]
\[ ML_2 + L \rightleftharpoons ML_3 \quad K_3 = \frac{[ML_3]}{[ML_2][L]} \]

____________________

\[ ML_{n-1} + L \rightleftharpoons [ML_n] / [ML_{n-1}][L] \]

where \( K_1, K_2, \text{ etc.}, \) are referred to as stepwise stability constants.

Alternatively, we can write the overall stability constant thus:

\[ M + nL \rightleftharpoons ML4 \]

\[ \beta = \frac{[ML_n]}{[M][L]^n} \]

The stepwise and overall stability constant are therefore related as follows:

\[ \beta 4 = K_1 \times K_2 \times \ldots \times K_n \]

2) Higher is the charge density on the central metal ion, greater is the stability of the complexes. For example \([\text{Fe(CN)}_6]^{3-}\) is more stable than \([\text{Fe(CN)}]^+\).

3) More is the basic character of ligand, more stable is the complex

4) Chelating ligands form more stable complexes than the monodentated ligands
ISOMERISM
Compounds having the same chemical formula but different physical and chemical
properties due to the different structural arrangements are called isomers.
This phenomenon is known as isomerism.
Coordination compounds exhibit two major types of isomerism, namely
(A) structural isomerism and (B) stereoisomerism (space isomerism).
Each of these is further classified as shown below.

A) Structural isomerism
a) Coordination isomerism b) Ionisation isomerism
c) Hydrate or Solvate isomerism d) Linkage isomerism
e) Ligand Isomerism

B) Stereoisomerism
a) Geometrical isomerism b) Optical isomerism

A) Structural isomerism
a) Coordination isomerism
In a bimetallic complex, both complex cation and complex anion may be present. In such a
case the distribution of ligands between the two coordination spheres can vary, giving rise
to isomers called the coordination isomers. This phenomenon is called coordination
isomerism. This isomerism is illustrated by the following pairs of complexes where the
complex cation and anion contain different metal centres.
1. \([\text{Co(NH}_3\text{)}_6][\text{Cr(CN)}_6]\) and \([\text{Cr(NH}_3\text{)}_6][\text{Co(CN)}_6]\)
   Hexammine hexacyano Hexamine hexacyano
cobalt(III) chromate(III) chromium (III) cobaltate (III)

2. \([\text{PtII(NH}_3\text{)}_4][\text{CuCl}_4]\) and \([\text{Cu(NH}_3\text{)}_4][\text{PtCl}_4]\)
   Tetraammine Tetrachloro Tetraammine Tetrachloro
   platinum (II) cuprate (II) copper (II) platinate (II)

b) Ionisation isomerism
Coordination compounds having the same molecular formula but forming different ions in
solution are called ionisation isomers. This property is known as ionisation isomerism.
An example of this type of isomerism is furnished by the red-violet,
\([\text{Co(NH}_3\text{)}_5\text{Br}]\text{SO}_4\) \([\text{Co(NH}_3\text{)}_5\text{SO}_4\text{]}\text{Br}\)
pentaamminebromocobalt(III) sulphate pentaamminesulphatocobalt (III) bromide

The red-violet isomer yields sulphate ion and the red isomer furnishes bromide
ion in solution.
\([\text{Co(NH}_3\text{)}_4\text{Cl}_2]\text{NO}_2\) and \([\text{Co(NH}_3\text{)}_4\text{NO}_2\text{Cl}]\text{Cl}\)
Tetraamminedichlorocobalt(III) nitrite Tetraamminechloronitrocobalt(III) chloride
\([\text{Co(NH}_3\text{)}_5\text{NO}_3\text{]}\text{SO}_4\) and \([\text{Co(NH}_3\text{)}_5\text{SO}_4\text{]}\text{NO}_3\)
CO-ORDINATION COMPOUNDS

pentaamminenitratocobalt(III) sulphate         pentaamminesulphatocobalt(III) nitrate

c) Hydrate isomerism or Solvate isomerism
The best known examples of this type of isomerism occurs for chromium chloride "CrCl₃.₆H₂O" which may contain 4, 5, (or) 6 coordinated water molecules.
1. [Cr(H₂O)₄Cl₂]Cl₂.2H₂O - Bright green
   Tetraaquadichlorochromium(III) chloride dihydrate
2. [Cr(H₂O)₅Cl]Cl₂H₂O - grey-green
   Pentaaquachlorochromium(III) chloride monohydrate
3. [Cr(H₂O)₆]Cl₃ - Violet
   Hexaaquachromium(III) chloride
These isomers have very different chemical properties and on reaction with AgNO₃ to test for Cl⁻ ions, would find 1,2, and 3 Cl⁻ ions in solution respectively.

d) Linkage isomerism
Linkage isomerism occurs with ambidentate ligands. These ligands are capable of coordinating in more than one way. The best known cases involve the monodentate ligands SCN⁻/NCS⁻ and NO₂⁻/ONO⁻
Forexample
[Co(NH₃)₅ONO]Cl₂ the nitrito isomer - red colour
pentaamminenitritocobalt(III) chloride - O attached

[Co(NH₃)₅NO₂]Cl₂ the nitro isomer - yellow colour
pentaamminenitrocobalt(III) chloride - N attached

e) Ligand isomerism
Ligand isomerism arises from the presence of ligands which can adopt different isomeric forms. An example is provided by diaminopropane, which may have the amine groups in the terminal (1,3-) positions or in the 1,2-positions.

B) Stereoisomerism (space isomerism)
Consider two compounds containing the same ligands attached to the same central metal ion, but the arrangement of ligands in space about the central metal ion are different, then these two compounds are said to be stereoisomers and this phenomenon is known as stereoisomerism. There are two different types of stereoisomerism.
a) Geometrical isomerism or b) Optical isomerism.

a) Geometrical (or) cis-trans isomerism
Geometrical isomerism is due to ligands occupying different position around the central ion. The ligands occupy position either adjacent to one another or opposite

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CO-ORDINATION COMPOUNDS

Geometrical isomerism in 4-coordinate complex

(1) $[\text{M}_2\text{b}_2]$ type complexes Square planar

In a cis-isomer two identical (or) similar groups are adjacent to each other whereas in a trans-isomer they are diametrically opposite to each other. Square planar complexes of the type $[\text{M}_2\text{b}_2]^{n+}$ where a and b are monodentate ligands, exist as cis and trans-isomers as shown.

Example of this type of complexes are $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2]$.

The cis trans isomers of these compounds are represented as Cis-diamine dichloroplatnum(II) and trans- diammine dichloroplatinum(II)

(2) $[\text{Mabcd}]$ type complexes

Square planar complex of this type exist in three isomeric forms for example $[\text{Pt}(\text{NH}_3)(\text{Py})(\text{Cl})(\text{Br})]$ exist in the following structures.

(3) $[\text{Ma}_2\text{bc}]$ type complexes

Square planar complexes of this type also shows cis-trans isomerism. For example $[\text{Pd} (\text{Cl})_2\text{Br I}]^2−$ exists in the following cis-trans

(4) $[\text{M(AB)}_2]^{n±}$ type complex
Here m is the central metal ion and (AB) represents an unsymmetrical bidentate ligand (A) and (B) are the two ends (i.e., coordinating atoms) of the bidentate ligands. Such complexes also show trans and cis isomerism.

For example, [Pt(gly)₂]⁺; here gly represents the glycinate ligands, NH₂CH₂COO⁻ which has N (A) and O (B) atoms as its donor.

**Geometrical isomerism in 6-coordinate complex, octahedral complex**

A complex compound having the central metal ion with coordination number equal to 6 has octahedral shape. The system used for numbering different positions of ligands in an octahedron is generally assumed that the 1,2 positions are cis-positions. Normally, it is taken that 1,6 positions are trans-positions.

1. An octahedral complex of the type [Mₐ₂b₃]
   where a and b are monodentate ligands, exists as two geometrical isomers:

2. [Mₐ₃b₃] type complexes
   When each trio of donor atoms (viz ligands (a, a, and a) occupy adjacent positions at the corners of an octahedral face, we have facial isomers.

   When the positions are around the meridian of the octahedron, we get Meridional (mer) isomer.

b) Optical Isomerism
This is a phenomenon in which certain organic or inorganic compounds have the property of rotating plane polarized light. The compounds which exhibit this property are called optical isomers. The optical isomers of a compound have identical physical and chemical properties. The only distinguishing property is that the isomers rotate the plane of polarized light either to the left or right. If the rotation is on the left side, then that isomer is levo and if on right side, then isomer is dextro. The equal proportion of levo and dextro mixture is called racemic mixture.

It is generally found octahedral chelate ions. The two isomers of this type of complex are mirror image of each other and cannot super impose on each other, hence they possess chirality character.

The optical isomers of \([\text{CoCl}_2(\text{en})(\text{NH}_3)_2]^+\) are as follows.

Optical isomeric structure of \([\text{Cr(ox)}_3]^3-\) or \([\text{Cr(C}_2\text{O}_4)_3]^3-\) as follows.

Bonding in Metal Carbonyls
The homoleptic carbonyls (compounds containing carbonyl ligands only) are formed by most of the transition metals. These carbonyls have simple, well defined structures. Tetracarbonylnickel(0) is tetrahedral,

\[
\text{Ni(CO)}_4
\]

Tetrahedral

Pentacarbonyliron(0) is trigonalbipyramidal

\[
\text{Fe(CO)}_5
\]

Trigonal bipyramidal

Hexacarbonyl chromium(0) is octahedral.

\[
\text{Cr(CO)}_6
\]

Octahedral

Decacarbonyldimanganese(0) is made up of two square pyramidal Mn(CO)₅ units joined by a Mn – Mn bond.

Octacarbonyldicobalt(0) has a Co – Co bond bridged by two CO groups

Colour of coordination complexes
CO-ORDINATION COMPOUNDS

(i) Colour of a complex is not because of the light absorbed but is due to the light reflected (complementary colour) e.g. If radiation corresponding to red light are absorbed from visible region, the compound appears to have blue colour

(ii) In coordination complexes energy difference (Δ) between two d-sets of d-orbitals is small. Radiations of appropriate frequency absorbed from visible region can cause excitation of d-electron from lower energy orbital to higher energy orbital. Remaining light is transmitted and compound appears coloured

(iii) IF there are no d-electrons present or completely filled d-orbitals are present then there is no d-d transition possible and complex appears colourless

Importance and applications of Coordination Compounds
Coordination compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine. These are described below:

• Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α–nitroso–β–naphthol, cupron, etc.

• Hardness of water is estimated by simple titration with Na₂EDTA. The Ca²⁺ and Mg²⁺ ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.

• Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity [Au(CN)₂⁻] in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc

• Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to [Ni(CO)₄], which is decomposed to yield pure nickel.

• Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin B₁₂, cyanocobalamine, the anti–pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).

• Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, [(Ph₃P)₃RhCl], a Wilkinson catalyst, is used for the hydrogenation of alkenes.

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• Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, \([Ag(CN)\textsubscript{2}]^-\) and \([Au(CN)\textsubscript{2}]^-\) than from a solution of simple metal ions.

• In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, \([Ag(S\textsubscript{2}O\textsubscript{3})\textsubscript{2}]^-\).

• There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess of copper and iron are removed by the chelating ligands D–penicillamine and desferrioxime B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: cis–platin and related compounds.