Chapter 22

Co-ordination Compounds

Different types of salt are formed due to addition of molecular compounds.

1. **Double salts** : Double salts are those molecular compounds which exists only in crystal lattice but lose their identity in solution.

   e.g., KCl. $MgCl_2.6H_2O \longrightarrow K^+ + Mg^{+2} + 3Cl^- + 6H_2O$.

   Double salts when dissolved in water ionise.

2. **Complex salts** : Complex salts are those molecular compounds which retain their identity in solid / crystal lattice as well as in the solution.

   e.g., Potassium ferrocyanide is a complex compound which is formed by adding KCN to a saturated solution of ferrous cyanide

   $4KCN + Fe(CN)_2 \longrightarrow K_4[Fe(CN)_6]$

   $K_4[Fe(CN)_6]$ is dissolved in water, the resulting solution does not give positive tests for ferrous or cyanide ions but we get a positive test for $[Fe(CN)_6]^{4-}$.

CO-ORDINATION COMPOUNDS

Coordination compound may be defined as a compound that results from the combination of apparently saturated molecules of different species and retain its identity in the solids as well as in dissolved state.

The formation of a coordination compound involves two components.

1. **An acceptor** : Which can accept a pair of electrons from the donor. The acceptor is usually a metal with vacant orbitals available to accept a pair of electrons from one or more neutral molecules or anions.

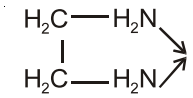
   In $[Fe(CN)_6]^{4-}$, Fe^{++} ion is an acceptor, which is also called as central metal ion, which acts as Lewis acid.

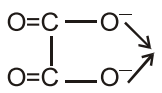
2. **A donor** : An atom or a molecule which can donate a pair of electrons is a donor. Such donor atoms or molecules are electron rich and are called **ligands**, which act as Lewis bases.

   Ligands may be neutral (NH_3, H_2O, C_6H_5N) or negatively charged species ($:CN^-, Cl^-$, Br^-) or positively charged

   Ligand is said to be unidentate if it has only one pair of electrons that it can donate *e.g.*, NH_3

   Ligand is said to be bidentate if it can bond from two positions

   e.g.,  ethylene diamine (en)

    oxalate ion ($C_2O_4^{2-}$)

   Some ligands can be coordinated to the metal or metal ion through either of two sides, they are called "Ambident" ligands. *e.g.,* nitrite ion, if attached through 'N' ($-NO_2$), it is written as nitro (or nitrito-N), if attached through O atom (–ONO–) then Nitrito (or nitrito-O).

Some Important Points

1. Number of co-ordinate bonds formed with central metal/ion is known as co-ordination number of the central species. In case of π-complexes all the atoms of a π-ligand are counted as co-ordination number as in case of Zeise's salt $[Pt\ Cl_3C_2H_4]^{\ominus}$ co-ordination number is 5.
2. The molecules or ions bonded directly to the central ion constitute what is often termed as co-ordination sphere, written within square brackets.
3. One more important point is the oxidation state of central metal ion. It is the charge carried by a complex ion and is the algebraic sum of charges carried by central ion & the ligands co-ordinated to it.

TYPES OF COMPLEX IONS

The complex ions can be grouped into three classes depending upon the nature of charge they carry :

1. **Complex cation :** A complex ion that has a net positive charge is called a complex cation, *e.g.,* tetraamminecopper (II), $[Cu(NH_3)_4]^{2+}$.
2. **Complex anion :** A complex ion that has a net negative charge is called a complex anion, *e.g.,* hexacyanoferrate (II), $[Fe(CN)_6]^{-4}$.
3. **Neutral Complex :** A complex that has no net charge is called a neutral complex, *e.g.,* hexacarbonyl chromium(0), $[Cr(CO)_6]$.

IUPAC Nomenclature of complex compounds

In order to name these compounds certain rules have been suggested by IUPAC.

1. The positive part of a coordination compound is named first and is followed by the negative part.
2. The ligands are named first followed by the central metal. The prefixes di- tri-, tetra- etc, are used to indicate the number of each kind of ligand present. The prefixes bis (two ligands) tris (three ligands) etc. used for polydentate ligands.
3. The ligands are named in alphabetical order. Names of the anionic ligands end in O, those of cationic in **ium.** Neutral ligands have their regular names except that H_2O is named *aqua*; NH_3 *ammine*; NO *nitrosyl*; and CO *carbonyl*.
4. The oxidation state of the central metal is indicated in roman numbers in a bracket.
5. When a complex species has negative charge, the name of the central metal ends in **–ate.** For some elements, the name of ion is based on the latin name of the metal (For example, argentate for silver).

EFFECTIVE ATOMIC NUMBER

Transition metals forms coordination compounds very readily because they have vacant 'd' orbitals which can accommodate electron pairs donated by ligands. Metal ion in co-ordination compound tends to attain nearest inert gas configuration by gaining electrons from ligand.

Effective atomic number (EAN) of metal in a complex is given by :

EAN = Z–(O.N.) + 2 × Number of lone pair donated

where Z = atomic number of metal atom

O.N. = oxidation number

BONDING IN CO-ORDINATION COMPOUND

Valence Bond Theory

Important Features of Valence Bond Theory (VBT).

1. The central metal provides empty hybrid orbitals as required by the ligands *i.e.*, coordination number to form complex.

2. Each ligand should have at least one lone pair of electron.
3. The lone pair of electrons of the ligand overlap with empty hybrid orbital of metal.
4. If *d*-orbitals are involved in hybridisation that may be either inner viz $(n-1)$ *d*-orbital or the outer viz (n) *d*-orbital. The compounds formed by these two ways are known as inner orbital and outer orbital compounds respectively. Generally the inner orbital compounds are low spin and outer orbital compounds are high spin compounds.
5. If the compound has one or more unpaired electron, the compound is paramagnetic and if it does not contain unpaired electron, it is diamagnetic.
6. The magnetic moment of metal complex calculated by using spin only magnetic moment as $\mu = \sqrt{n(n+2)}$ Bm, where 'n' is the number of unpaired electrons.

ISOMERISM

1. Structural Isomerism

(a) Hydrate isomerism – Compounds which have same molecular formulae but differ in the number of water molecule as ligands and as molecules of hydration are called hydrate isomers.

e.g., $[Co(H_2O)_6]Cl_3$ & $[Co(H_2O)_4Cl_2]Cl.2H_2O$

(b) Ionisation isomerism – Compounds which give different ions in solution but have same molecular formulae are called ionization isomers.

e.g., $[Co(NH_3)_5SO_4]Br$ & $[Co(NH_3)_5Br]SO_4$

(c) Linkage isomerism – Occurs when more than one atom in a monodentate ligand functions as a donor.

e.g., $[Co(NH_3)_5NO_2]Cl$ & $[Co(NH_3)_5ONO]Cl$

(d) Co-ordination isomerism – This isomerism is possible when both positive and negative ions of a salt are complex ion.

e.g., $[Cr(NH_3)_6][Co(CN)_6]$

(e) Co-ordination position isomerism – This type of isomerism arises in the bridged complexes due to difference in the attachment of ligands with the metal atom.

e.g., $\left[(NH_3)_4Co\begin{matrix}OH\\Cl\end{matrix}Co(NH_3)_2Cl_2\right]SO_4$

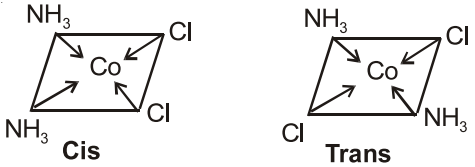
and $\left[Cl(NH_3)_3Co\begin{matrix}OH\\Cl\end{matrix}Co(NH_3)_3Cl\right]SO_4$

2. Stereoisomerism

(a) Geometrical isomerism is common in square planar and octahedral complexes.

Square planar complexes with general formula; $[MA_2X_2]^{\pm n}$, $[MA_2XY]^{\pm n}$, $[MABX_2]^{\pm n}$, $[MABXY]^{\pm n}$, $[M(AB)_2]^{\pm n}$ show isomerism.

Example :

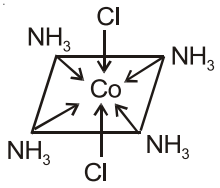


Note : *$[M_{ABCD}]$ shows 3 geometrical isomers.*

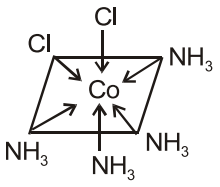
Tetrahedral complexes do not show geometrical isomerism.

(b) Octahedral complexes with general formula, $[MA_4X_2]$, $[MA_4XY]$, trans. $[M(AA)_2X_2]$ shows geometrical isomerism.

(i) *e.g.*,

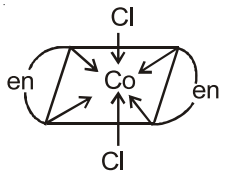


Trans-$[Co(NH_3)_4Cl_2]$

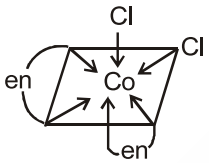


Cis-$[Co(NH_3)_4Cl_2]$

(ii)

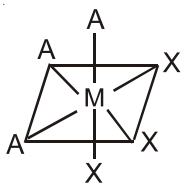


Trans-$[Co(en)_2Cl_2]$

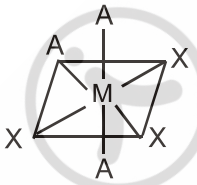


Cis-$[Co(en)_2Cl_2]$

(c) The complex with formula $[MA_3X_3]$ show facial and meridonial isomerism.



Fac-$[MA_3X_3]$



Mer-$[MA_3X_3]$

Note : *Complex with general formula $[M_{(a)(b)(c)(d)(e)(f)}]$ shows 15 geometrical isomers.*

3. Optical Isomerism

(a) Tetrahedral complexes with formula $[M_{(a)(b)(c)(d)}]$ or $M(AB)_2$ shows optical isomerism

(b) Octahedral complexes having formula $[M_{(a)_2(b)_2(c)_2}]^{\pm n}$, $[M_{(a)(b)(c)(d)(e)(f)}]$, $[M(AA)_3]$, $[M(AA)_2b_2]$, $[M(AA)_2b_2c_2]$ containing symmetrial bidentate ligand will show optical isomerism.

Note : *Square planar complexes do not show optical isomerism.*

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