5. COORDINATION COMPOUNDS

STUDY NOTES

5.0 In class XI, we learnt various types of chemical compounds like ionic compounds (NaCl, CaO), covalent compounds (O_2, CH_4), simple coordinate compounds (NH_4^+, H_3O^+) and Hydrogen compounds (H_2O, HCl, NH_3).

In class XII, we learn about complex **coordination compounds** (complexes) like $CoCl_3.6NH_3$, $CuSO_4.5H_2O$, $[Fe(CN)_4]^{2-}$ etc.,

In this chapter, we learn the structure, bonding, isomerism, new terminology, nomenclature of the complexes w.r.to Werner's theory, Valence bond theory (VBT) and Crystal Field Theory (CFT).

5.1 **Werner's theory** explains the structure, bonding, and isomerism of complex compounds.

It proposes that central metal atom / ion contains **two types of valences (linkages).**

i) Primary Valence ii) Secondary valence

5.1.1 **Primary valence** (ionisable) corresponds to the **oxidation number** of the central metal ion. It is satisfied by negative anions (like Cl^-) which lie outside the coordination sphere.

5.1.2 **Secondary valence** (Non-ionisable) corresponds to the **coordination number** of the central metal ion. It is satisfied by ligands (neutral molecules like NH_3 or anions) which lie inside the coordination sphere.

5.1.3 **Geometry:** Secondary valences define the shape of the complex, such as octahedral (CN 6), tetrahedral or square planar (CN 4), Linear (CN 2)

5.1.4 **Isomerism:** It explains how compounds with the same chemical formula can have different structures and properties. Two types of isomerism are a) Stereo isomerism b) Structural isomerism

a) Types of Stereoisomerism :

i) Geometrical isomerism: cis (same side), trans (opposite),

ii) Optical isomerism : Isomers with non-superimposable mirror images

b) Types of Structural isomerism: (i) Linkage isomerism (ii) Coordination isomerism (iii) Ionisation isomerism (iv) Solvate isomerism or Hydrate isomerism

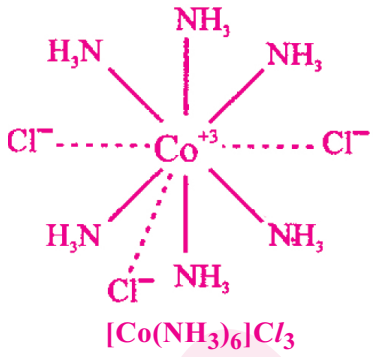
Illustrative Model Example

5.1.5 Consider the complex solution $CoCl_3.6NH_3$

It is written as $[Co(NH_3)_6]\ Cl_3$

Here the central atom is Co; Ligand is NH_3 ,

outside element in the solution is Cl.



$[Co(NH_3)_6]Cl_3$

(i) **Primary valence** of Co, that is of cation Co^{3+} is 3.

That means Co^{3+} is satisfied by $3Cl^-$ anions which are outside the coordination sphere. These $3Cl^-$ anions are ionisable in the solution.

(ii) **Secondary valence** of Co, that is the coordination number of Co =6.

That means Co^{3+} is bonded with 6 NH_3 ligand molecules.

The 6 NH_3 molecules are non-ionisable in the solution.

Also, the secondary valence 6 gives the geometry (octahedral) of the complex.

Co. 6 NH_3 written together in the brackets as $[Co(NH_3)_6]$ form the **coordination sphere.**

5.2 Basic terminology:

i) **Oxidation number (Charge on the metal):** It is the no.of electrons an atom has lost, gained or shared during bonding. In the given example oxidation number of Co^{3+} is 3.

ii) **Coordination number (CN):** It tells how many number of ligands are directly bonded to the central metal atom or ion. It defines the geometry and spatial arrangement of the complex. In the given example, **CN is 6.** That means the central atom Co is bonded with 6 NH_3 ligands.

iii) **Ligand (Electron pair donors) :** An atom, ion or molecule that donates the pair of electrons to a central metal atom/ ion to form a coordinate bond. In our example the ligand is NH_3.

Types & Names of Ligands :

a) **Neutral ligands:** NH_3 - ammine, H_2O- aqua , CO- Carbonyl, NO- Nitrosyl

b) **Anionic ligands:** Cl^- - chloro, Br^- - bromo, CN^-- cyano, OH^-- hydroxo

c) **Prefixes for number of ligands:** 1- mono, 2- di, 3- tri, 4- tetra, 5- penta, 6- Hexa,

Ex: $6NH_3$ - hexaamine . $\begin{matrix} CH_2-NH_2 \\ | \\ CH_2-NH_2 \end{matrix}$ - Ethylene dimine (En)

iv) **Coordination sphere:** Central metal ion along with its ligands, put in square brackets.

Common Lingand Complexes

1) Ammine Complexes (NH_3 as ligand) : i) $[Cu(NH_3)_4]^{2+}$ ii) $[Co(NH_3)_6]^{3+}$

2) Halo Complexes (Halide ligands: Cl^-, Br^-) : i) $[Pt(Cl_4)]^{2-}$ ii) $[Cu(Br_4)]^{2-}$

3) Aqua Complexes (H_2O as ligand) : i) $[Fe(H_2O)_6]^{3+}$ ii) $[Co(H_2O)_6]^{2+}$

4) Carbonyl Complexes (CO as ligand): i) $[Ni(CO)_4]$ ii) $[Fe(CO)_5]$

5) Chelate Complex (Polydentate ligand): i) $[Cu(en)_2]^{2+}$ ii)$[Fe(EDTA)]^-$

5.3 Nomenclature of Coordination Compounds:

(CN with Ligand + Metal with Oxidation Number + Counter ion)

Ex: $[Co(NH_3)_6]\ Cl_3$: **Hexaammine cobalt (III) chloride**

Step 1: Ligand with CN prefix : Start with the name of ligand with its prefix as mentioned in 3.1

6 NH_3 ligands = Hexaammine

Step 2: Metal name (Central ion):

a) For cationic or neutral complexes, metal name is unchanged. **(cobalt)**

b) For anionic complexes, metal name ends with **ate**: Ni- Nickelate, Zn-Zincate, Pd-Palladate

Step 3: Oxidation Number : Roman numerals in brackets. **Ex:** Co^{3+} →cobalt (III)

Step 4: Counter ion, if any: Write the counter ion if any in the last.

Examples:

$[NiCl_4]^{2-}$: Tetrachloronickelate (II) ion

$[Zn(OH)_4]^{-2}$: Tetrahydroxozincate (II) ion

$K_2[PdCl_4]$: Potassium tetrachloropalladate(II)

5.4. Valence Bond Theory (VBT): It explains bonding, geometry and the magnetic properties of complexes using hybridisation and electron pair donations.

VBT explains overlapping of hybrid orbitals of central atom with ligand orbitals.

The total number of electrons in the central metal in complex possesses after co-ordination is called **Effective Atomic Number [EAN]** of the metal.

5.4.1 Hybridisation & Geometrical shapes :

d^2sp^3 / sp^3d^2 → Octahedral

sp^3→ Tetrahedral

dsp^2→ Square planar

5.4.2 Magnetic behavour :

Diamagnetic (paired electrons)

Paramagnetic (unpaired electrons)

Strong ligand causes forced pairing of electrons in d-orbital (Diamagnetic)

Weak ligand do not cause pairing of electrons (Paramagnetic)

5.5 Importance & Applications of Coordination Compounds:

Biological Importance: Haemoglobin (Fe complex), Chlorophyll (Mg complex)

Industrial Uses: Catalysts (**Ex:** hydrogenation), Extraction of metals

Medical Uses: Chelation therapy, Anticancer drugs (**Ex:** cis-platin)

Analytical Uses: Detection of metal ions, Water hardness estimation