# Chapter\_09

# **Coordination Compounds**

- Double salts are the addition compounds that lose their identity in solution. They exist only in solid state and have properties same as those of constituent compounds, e.g. Mohr's salt FeSO<sub>4</sub> · (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> · 6H<sub>2</sub>O, Potash alum K<sub>2</sub>SO<sub>4</sub> · Al<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub>.24H<sub>2</sub>O
- **2. Coordination compounds** or **complexes** do not completely lose their identity in solution. They exist in solid state as well as in solution. Their properties are different from their constituents.
- **3.** According to **Werner's theory**, primary valency is ionisable (i.e. species present outside the coordination sphere is ionisable) whereas secondary valencies are not.
- 4. Some Important Terms Pertaining to Coordination Compounds
  - Molecules or ions which donate a lone pair of electrons to the central atom or ion are called ligands. The number of donor sites present in a ligand is called its denticity. e.g. en (ethylene diamine) is a bidentate (didentate) ligand and EDTA is a hexadentate ligand.
  - When a ligand can ligate through any of its two different atoms, it is called **ambidentate ligand**. e.g. NO<sub>2</sub><sup>-</sup>, SCN<sup>-</sup>, ONO.
  - The total number of ligands to which the metal is directly attached is called coordination number (C.N).
    e.g. [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, C.N. = 6

 $[Co(en)_3]^{3+}$ , C.N. = 3 × 2 = 6

(: en is bidentate ligand)

### 5. Formulae of Mononuclear Coordination Entities

- Following rules are applied while writing the formulae :
- The central atom is listed first.
- The ligands are then listed in alphabetical order. The placement of a ligand, in the list does not depend on its charge.
- Polydentate ligands are also listed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.
- The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulae are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.
- There should be no space between the ligands and the metal within a coordination sphere.
- When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign.
- The charge of the cation(s) is balanced by the charge of the anion (s).
- 6. Naming of Mononuclear Coordination Compounds The following rules are used while naming coordination compounds :

- The cation is named first in both positively and negatively charged coordination entities. (if present outside the coordination sphere)
- The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing formula).
- Names of the anionic ligands end in -'o', those of neutral and cationic ligands are the same except aqua for H<sub>2</sub>O, ammine for NH<sub>3</sub>, carbonyl for CO and nitrosyl for NO. These are placed within small brackets ().
- Prefixes mono, di, tri, etc. are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, *bis, tris, tetrakis* are used, for the ligand to which they refer being placed in parenthesis.
- Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.
- If the complex ion is a cation, the metal is named the same as the element, e.g. Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix—'ate', e.g. Co in a complex anion, [Co(SCN)<sub>4</sub>]<sup>2-</sup> is called cobaltate. For some metals, the Latin names are used in the complex anions, e.g. ferrate for Fe.
- The neutral complex molecule is named similar to that of the complex cation.
- 7. Compounds having the same molecular formula but different arrangement of atoms are called **isomers** and the phenomenon is called **isomerism**. *Isomerism are of two types :* 
  - Structural isomerism
    - (i) Complexes exhibit **linkage isomerism** when ambidentate ligands, like NO<sub>2</sub>, SCN, etc are present.
    - (ii) Complexes exhibit coordination isomerism when cationic and anionic entities are interchangable between two complexes of two different metals.
    - (iii) Hydration isomerism arises due to difference in the number of water molecules inside and outside the coordination sphere.
    - (iv) **Ionisation isomerism** arises due to interchange between ligand and counter ion.
      - e.g.  $[Co(NH_3)_5 \cdot SO_4]Br$  and  $[Co(NH_3)_5Br]SO_4$ .
  - Stereoisomerism,
    - (i) **Geometrical isomerism** is shown by complexes of the type  $[MA_2B_2]$ , [MABXL],  $[MA_3B_3]$ ,  $[MA_2XY]$ ,  $[MA_4X_2]$ ,  $[M(AA)_2X_2]$  where M = metal, A, B, X, L, Yare unidentate ligands and AA = bidentate ligand. Here, if same group occupies adjacent positions, the isomer is called *cis* and if the same group occupies opposite positions, the isomer is called *trans*.

If three donor ligands occupy adjacent position, the isomer is called *facial* and if they are present around meridian then the isomer is called *meridional* isomer.

#### Tetrahedral complex does not show

**geometrical isomerism** because the relative positions of unidentate ligands attached with central metal atom are same with respect to each other.

- (ii) Optical isomerism is shown by the compounds lack a plane of symmetry. Complexes of the type [M(AA)<sub>3</sub>], [M(AA)<sub>2</sub>X<sub>2</sub>], [M(AA)X<sub>2</sub>Y<sub>2</sub>] exhibit optical isomerism.
  - where, M = metal,
    - X,Y = unidentate ligand
  - and AA = bidentate ligand.
- 8. Valence bond theory From VBT, the hybridisation, magnetic behaviour and geometry of complexes are derived follows :
  - Find the oxidation state of central atom and write the electronic configuration of the metal ion.
  - Pair up the *d*-electrons, if ligands are CO, CN<sup>-</sup>, NH<sub>3</sub>, etc. (strong field ligand); (if required).
  - Now find whether unpaired electrons are present or not. If present, the complex is **paramagnetic** and if not, it is **diamagnetic**.
  - Find hybridisation and shape from the orbitals occupied by ligand, e.g. If there are 4 ligands (unidentate), hybridisation may be  $sp^3$  (tetrahedral geometry) or  $dsp^2$  (square planar geometry). If there are 6 ligands, hybridisation may be  $d^2sp^3$  or  $sp^3d^2$  (octahedral geometry).
  - If weak field ligands are present then electrons will not pair-up and the complex is coloured due to *d*-*d* transition,
- Note: Colour of KMnO<sub>4</sub> is due to charge transfer.

### 9. Crystal Field Theory

According to **CFT**, degenerate *d*-orbitals in the presence of ligands, split up into two sets of energy *viz*  $t_{2g}$  and  $e_g$  set. The splitting of degenerate levels due to the presence of ligand in a definite geometry is termed as crystal field splitting.

- The difference of energy between the two sets of degenerate orbitals (as a result of crystal field splitting) is known as **Crystal Field Stabilisation Energy** (CFSE). It is denoted by  $\Delta_o$  (for octahedral complex).
- Ligands are arranged in a series in order of increasing field strength. This series is known as spectrochemical series as shown below : I<sup>-</sup> < Br<sup>-</sup> < SCN<sup>-</sup> < CI<sup>-</sup> < S<sup>2-</sup> < F<sup>-</sup> < OH<sup>-</sup> < C<sub>2</sub>O<sub>4</sub><sup>2-</sup>
   H<sub>2</sub>O < NCS<sup>-</sup> < EDTA<sup>4-</sup> < NH<sub>3</sub> < en < CN<sup>-</sup> < CO</li>
- Depending on the relative magnitude of the CFSE (Δ<sub>o</sub>) and pairing energy (*P*), the two possibilities are:
  - (i) If Δ<sub>o</sub> < P, the fourth electron enters in one of the e<sub>g</sub> orbitals giving the configuration t<sup>3</sup><sub>2g</sub>e<sup>1</sup><sub>g</sub>. Ligands for which Δ<sub>o</sub> < P are known as weak field ligands</li>
    - and form high spin complexes.
  - (ii) If  $\Delta_o > P$ , it becomes more energetically favourable for the fourth electron to occupy a  $t_{2g}$  orbital with configuration  $t_{2g}^4 e_g^0$ . Ligands which produce this effect are known as **strong field ligands** and form **low spin complexes**.

- **10.** *cis*-platin [PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] is used for the treatment of cancer. EDTA complex of Ca is used for treating lead poisoning.
- **11. Metal carbonyls** are the compounds in which CO (carbon monoxide) is present as a ligand. The M—C  $\sigma$  bond is formed by the donation of lone pair of electrons of carbonyl carbon to vacant orbital of metal, whereas the M—C

 $\pi$  bond is formed by the donation of a *d*-electron pair of metal to the vacant antibonding  $\pi^*$  orbital of CO.