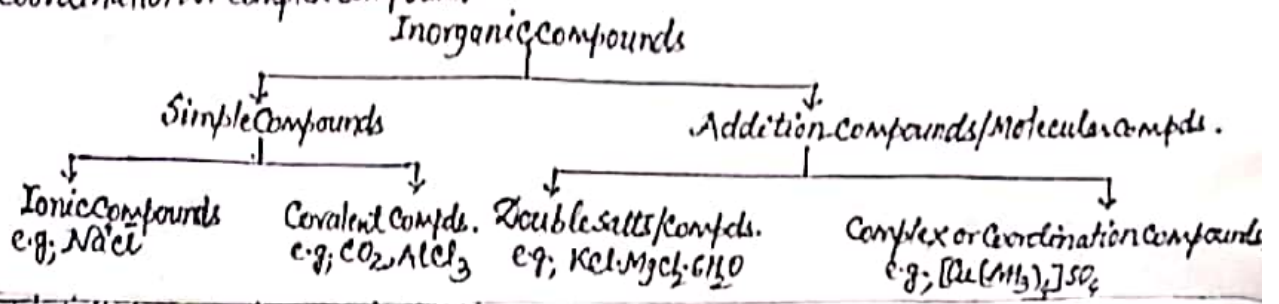


B. Sc-II (Hons), Paper-III B, Group-A
 Unit-3 Coordination Chemistry (By Dr. Birendra Kumar, Maharaja College)

Coordination chemistry is a branch of chemistry (inorganic) which deals with the study of coordination or complex compounds.



⇒ Double salts/Compounds: Those addition/molecular compounds which are stable in the solid state but dissociates into constituent ions in the water/any other polar solvent are called double salts. The properties of double salt are similar as those of its constituent ions. They are prepared by simple crystallization (physical method) of aqueous solution containing two simple stable salts in 1:1 (mole) proportion.
 e.g., $K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \xrightarrow[\Delta/cool]{\text{Crystallization}}$ $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ (Potashalum)
 $\xrightarrow{\text{Water}}$ $2K^+ + 2Al^{3+} + 4SO_4^{2-}$ (Constituent ions)
 Here potashalum is a double salt of K_2SO_4 & $Al_2(SO_4)_3$.

⇒ Complex or Coordination Compounds: Those addition/molecular compounds which do not give all their constituent ions in the solution/water/any other polar solvent are called complex or coordination compounds. Since they have at least one complex or coordination entity (M-L bond), so called complex or coordination compds. Their properties are different from its constituents. They are prepared by chemical reaction/method from simple stable compds.
 e.g., $CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}SO_4^{2-} \xrightarrow{\text{Water}} [Cu^{2+}(NH_3)_4]^{2+} + SO_4^{2-}$
 (Copper sulphate sol.) (Liq. ammonia) (Tetraamminecopper(II) sulphate) (Complex compd.) (Complex ion) (Simple ion)
 Here $[Cu(NH_3)_4]SO_4$ is a complex compound, which does not give Cu^{2+} & SO_4^{2-} ions in solution, rather it gives only SO_4^{2-} ion and Cu^{2+} as a complex ion, $[Cu(NH_3)_4]^{2+}$.

* Neutral complexes/coordination compds, e.g., $[Ni(CO)_4]$, $[Pt(NH_3)_2Cl_2]$, $[W(dmg)_2]$ etc. do not undergo ionisation, hence they do not give any ions in aqueous solution.

⇒ Distinction between double salt & Complex salt:

| Double salt | Complex salt |
|---|---|
| 1. Double salt lost its identity in the solution, i.e., dissociates into constituent ions when dissolve in water/any other polar solvent. | 1. Complex salt retain its identity in the solution, i.e., does not dissociate into all its constituent ions. Metal remains as complex ion as in solid state. |
| 2. It is usually formed by two simple salts in 1:1 (mole) proportion using physical method (e.g. crystallization.) | 2. It is formed two or more simple compounds but may or may not in 1:1 (mole) proportion using chemical reaction/method. |
| 3. It is an ionic compound and does not contain coordinate bond. | 3. It may or may not ionic compd, but the complex ion or species always contains coordinate bond (M-L). |
| 4. Its properties are similar as those of constituent ions/compounds. | 4. Its properties are different from ^{these} of constituent compounds. |
| 5. The metal ions show their normal valencies in it. | 5. The metal ion satisfies its two types of valencies: Primary (ionisable) & secondary (non-ionisable) in it. |

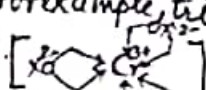
⇒ Some important terms in Coordination Compounds:

* Central metal atom/ion: A metal atom or ion present in the central part of a complex ion or coordination entity is called central atom/ion. It may be +vely charged or neutral. Central metal atom/ion has 2 or more vacant orbitals (hybrid), accepts electron pair (l.p) from ligands, so acts as Lewis acid. e.g; In $[Ni(CO)_4]$, Ni is central atom. $C\equiv O$ is ligand.

* Ligands or Coordinating groups: Species (molecules or ions) which have one or more donatable lone pairs of electrons, and attached to the central metal atom/ion by coordinate bond(s) are called ligands or coordinating groups. Ligands are Lewis bases. Ligands have commonly N, O, S, X (halogens) as donor atom. Ligands may be neutral, positively charged or negatively charged. They may contain one or more donor atom(s), called denticity. So, ligands have been classified as follows:

(i) Monodentate ligands: Ligands which attached to central metal atom/ion by one donor atom only, are called monodentate ligands (denticity = 1). They may be neutral, anionic (-ve) or cationic (+ve).
e.g; CO , NO , CS , H_2O , NH_3 , PH_3 , $(C_6H_5)_3P$, C_5H_5N , Py , $C_6H_5NH_2$ etc (Neutral monodentate ligands).
 $:CN$, $:OH$, $:NO_2$, $ON:O:$, $:NH_2$, $:X$ ($X = F, Cl, Br, I$), SO_3^{2-} , CO_3^{2-} , NO_3^- , $C_6H_5CO^-$ etc (Anionic "
 $[NH_4]^+$, NH_3^+ , NO^+ , NO_2^+ , $C_5H_5N^+$, $(C_6H_5)_3P^+$, NH_4^+ etc (Cationic "

(ii) Bidentate ligands: Ligands which have two donor atoms/sites and form two coordinate bond at a time with central metal atom/ion are called bidentate ligands (denticity = 2).
e.g; Ethylenediamine ($H_2N-CH_2-CH_2-NH_2$), Bipyridyl ($C_5H_5N-Ni-C_5H_5$), 1,10-phenanthroline (o-phen) etc (Neutral); Oxalato ($COO-COO^-$, ox^{2-}), Glycinato ($H_2N-CH_2-COO^-$, gly^-), Dimethylglyoximate (dmg), Carbonato ($O=C=O$), Sulphato (SO_4^{2-}), Nitrate (NO_3^-) etc (Anionic).

* Chelate/Chelating ligand: When a multidentate ligand (denticity ≥ 2) simultaneously coordinates to central metal atom/ion giving a cyclic/ring structure, the ligand is called chelating ligand, and the complex thus formed is called chelate or metal chelate or chelated complex. Chelated complex is more stable than non-chelated/normal complex. For example, trioxalato chromium (III) ion is a chelate and oxalato (CO_2^{2-} or ox^{2-}) is chelating ligand. 

Chelates having 5-membered rings are more stable. Chelates with ligands having more than 6 donor groups/atoms are unstable due to steric hindrance produced by larger group.

* Complex ion or Coordination entity: Species (molecule or ion) in which a central metal atom/ion attached with a suitable number of ligands by coordinate (σ) bonds is called complex or coordination entity. This may be +vely charged (i.e. cationic), -vely charged (i.e. anionic) or neutral/molecular. It is represented by square bracket, [] which is known as coordination sphere. For example, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$, $[Ni(CO)_4]$ etc are complex ion/coordination entity/coordination spheres. Here Fe^{2+} , Co^{3+} , Ni are central metal ion/atom, and CN , NH_3 , CO are ligands. All complex/coordination compounds have at least one complex/coordination entity.

* Oxidation No./state of central metal: The charge present on central metal in a complex ion/coordination entity is called oxidation no. or state of that metal. Oxidation No. of central metal is calculated by equating the sum of oxidation no. on central metal & the ligands to the charge on the coordination sphere/complexion. O. No. of central metal may be 0 or +ve value. It is represented by roman numerals (I, II, III etc) while naming the complex. For example, in $[Fe(CN)_6]^{3-}$, O. No. of Fe is calculated as: Let O. No. of Fe = x, O. No./charge on CN (ligand) = -1 so,
 $x + 6(-1) = -3$ or $x - 6 = -3$ or $x = -3 + 6 = +3$ ∴ O. No. of Fe = +3.

O. No. of central metals in complex compounds range from 0 to +8.

(3)

* Coordination Number (C.N.): The number of coordinate (σ) bonds through which central metal atom/ion attached directly with donor atoms of the ligands in coordination sphere/entity is called coordination number of the central metal. π bond, if any present, does not count in C.N. Coordination No. of metal in complex compounds vary 2 to 9. Contribution in C.N. by monodentate, bidentate, tridentate, tetradentate etc are 1, 2, 3, 4 -- respectively, i.e. $C.N. = \text{Denticity} \times \text{No. of Ligands}$.

- (i) C.N. of Ag^+ in $[Ag(en)_2]^+$ is $2 \times 1 = 2$ (Since en ligand has denticity = 1)
- (ii) C.N. of Co^{3+} in $[Co(en)_3]^{3+}$ is $3 \times 3 = 6$ (Since en is a bidentate ligand, i.e. denticity = 2)
- (iii) C.N. of Cr^{3+} in $[Cr(C_2O_4)_2Cl(H_2O)]^{2-}$ is $2 \times 2 + 1 \times 1 + 1 \times 1 = 6$ (Since denticity of $C_2O_4^{2-}$ is 2 & Cl^- is 1)

* Effective Atomic No (EAN): The total number of electrons acquired by a central metal in the formation of a complex ion/coordination entity/sphere is called effective atomic number (EAN). EAN of the central metal atom/ion of a given complex species is given as:

$$EAN \text{ of the central metal atom/ion} = \text{Atomic No. of metal} - O.N. + 2 \times C.N. \text{ (i.e. No. of } \sigma \text{ bonds donated by ligands)}$$

A stable complex species is formed if the effective atomic number (EAN) of the central metal atom present in the complex species is equal to the atomic number of nearest noble gas (EAN rule). For example, $[Fe(CN)_6]^{3-}$, $EAN \text{ of } Fe^{3+} = \text{At. No. of Fe} - O.N. \text{ of Fe} + 6 \times C.N. \text{ or No. of lone pairs donated by } CN^- \text{ (ligand)} = 26 - 3 + 2 \times 6 = 23 + 12 = 35 (= \text{At. No. of } Kr)$. [Here O.N. of Fe = +3, C.N. of Fe = 6]

(ii) $[Pt(NH_3)_4Cl_2]$, $EAN \text{ of } Pt^{2+} = \text{At. No. of Pt} - O.N. \text{ of Pt} + C.N. \text{ of Pt} \times 2 = 78 - 2 + 2 \times 4 = 76 + 8 = 84$

⇒ IUPAC nomenclature of Complex/Coordination Compounds or ions:

Coordination compounds/complex ions are named systematically according to following IUPAC rules:

1. Positive part (cation) is named first followed by negative part (anion).
2. When writing name of the complex ion/coordination entity, ligands are written in alphabetical order, regardless of their charge, followed by name of central metal.
3. Naming of ligands done as follows:
 - (i) Anionic (i.e. negatively charged) ligands named as ending 'o'.
e.g. F^- (fluoro), OH^- (hydroxo), CN^- (cyano), Br^- (bromo), Cl^- (chloro), NO_2^- (nitro), NO^- (nitrito), I^- (iodo), O_2^{2-} (peroxo), S^{2-} (sulfido), O^{2-} (oxo).
 - (ii) Neutral ligands have no special ending, generally in usual form.
e.g. NH_3 (ammine), H_2O (aqua), CO (carbonyl), NO (nitrosyl), $H_2N-CH_2-CH_2-NH_2$ (ethylenediamine), C_5H_5N (pyridyl), $C_2O_4^{2-}$ (oxalato), $C_6H_5O_2^-$ (glycinato).
 - (iii) Cationic ligands are named by using ending 'ium'.
e.g. $N_2H_5^+$ or $NH_2-NH_3^+$ (hydrazinium), NO^+ (nitrosonium), NO_2^+ (nitonium).
4. The oxidation state of central metal is shown by roman numeral (I, II, III) in small bracket, immediately following its name.
5. Neutral or molecular and cationic complex ions have no special ending, i.e. central metal name in usual form.
6. In anionic complex ions, metal named by using ending 'ate' (with original name of metal).
e.g. Fe (Iron; Ferrate), Co (Cobalt; Cobaltate), Ni (Nickel; Nickelate), Cu (Copper; Cuprate), Ag (Silver; Argentate), Cr (Chromium; Chromate).

- Now, we take some examples to understand above rules for nomenclature of complex compounds/ions:
- (i) $[Ni(CO)_4]$: Tetracarbonylnickel(0)
 - (ii) $[Cu(NH_3)_4]SO_4$: Tetraamminecopper(II)sulphate
 - (iii) $[Cr(en)_3]Cl_3$: Tris(ethylenediamine)cobalt(III)chloride
 - (iv) $[Co(NH_3)_4(NH_2)_2]Cl$: Tetraamminedinitrocobalt(III)chloride
 - (v) $K_2[Cr(CN)_2O_2(NH_3)_2]$: Potassiumdiamminedioxochromate(IV)
 - (vi) $K_4[Fe(CN)_6]$: Potassium hexacyanoferrate(II)
 - (vii) $Na_3[Cr(C_2O_4)_3]$: Sodium trisoxalatochromate(III)
 - (viii) $[Ag(CN)_2]^-$: Dicyanoargentate(I)
 - (ix) $(NH_4)_2[Co(H_2O)_2Cl_4]$: Ammonium diaquatetrachloridocobaltate(II)