# CHEMISTRY STUDY MATERIALS FOR CLASS 12 (NCERT BASED REVISION NOTES) GANESH KUMAR DATE:- 18/01/2022

## **Coordination Compounds**

#### 1. Valence bond theory:

According to this theory, the metal atom or ion under the influence of ligands can use its (n-1)d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, and square planar.

These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

Coordination no.	Type of hybridisation	Distribution of hybrid
		orbitals in space
4	sp <sup>3</sup>	tetrahedral
4	dsp <sup>2</sup>	Square planar
5	sp <sup>3</sup> d	Trigonal bipyramidal
6	sp <sup>3</sup> d <sup>2</sup> (nd orbitals are involved – outer orbital complex or high spin or spin free complex)	Octahedral
6	d <sup>2</sup> sp <sup>3</sup> ((n-1) d orbitals are involved –inner orbital or low spin or spin paired complex)	Octahedral

2. Magnetic properties of coordination compounds: A coordination compound is paramagnetic in nature if it has unpaired electrons and diamagnetic if all the electrons in the coordination compound are paired.

Magnetic moment  $\sqrt{n(n+2)}$ 

Where n is number of unpaired electrons.

- 3. Crystal Field Theory: It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion. It is theoretical assumption.
- 4. Crystal field splitting in octahedral coordination complexes:
- 5. Crystal field splitting in tetrahedral coordination complexes:



6. For the same metal, the same ligands and metal-ligand distances, the difference in energy between  $e_g$  and  $t_{2g}$  level is

$$\Delta t = \frac{4}{9} \Delta 0$$

 Metal carbonyls. Metal carbonyls are homoleptic complexes in which carbon monoxide (CO) acts as the ligands.

For example: Ni(CO)<sub>4</sub>

The metal – carbon bond in metal carbonyls possesses both  $\sigma$ and  $\pi$  characters. The metal-carbon bond in metal carbonyls possess both *s* and *p* character. The M–C  $\sigma$  bond is formed by the donation of lone pair of electrons from the carbonyl carbon into a vacant orbital of the metal. The M–C  $\pi$  bond is formed by the donation of a pair of electrons from a filled *d* orbital of metal into the vacant antibonding  $\pi^*$  orbital of carbon monoxide. The metal to ligands bonding creates a synergic effect which strengthens the bond between CO and the metal.

#### **Coordination Compounds**

Coordination compounds are those addition molecular compounds which retain their identity in solid state as well as in dissolved state. In these compounds, the central metal atom or ion is linked by ions or molecules with coordinate bonds. e.g., Potassium ferrocyanide,  $K_4$  [Fe(CN)<sub>6</sub>].

 $K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$ Central metal atom - Ligand K<sub>4</sub>[Fe(CN)<sub>6</sub>] - Coordination number Counter ion Coordinate sphere (entity)

## **Double Salt**

<sup>4</sup>These afte the addition molecular compounds which are stable in solid state but dissociate into constituent ions in the solution. e.g., Mohr'S salt,  $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$  get dissociated into  $Fe^{2+}$ ,  $NH^+$  and  $SO^{2-}$  ions.

#### **Terms Related to Coordination Compounds**

#### 1.Complex ion or Coordination Entity

It is an electrically charged species in which central metal atom or ion is surrounded by number of ions or neutral molecules.

(i) Cationic complex entity It is the complex ion which carries positive charge.

e.g., [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>

(ii) Anionic complex entity It is the complex ion which carries negative charge.

e.g., [Fe(CN)<sub>6</sub>]<sup>4-</sup>

#### 2.Central Atom or Ion

The atom or ion to which a fixed number of ions or groups are bound is called central atom or ion. It is also referred as Lewis acid. e.g., in  $(NiCI_2(H_2O)_4]$ . Ni is central metal atom. It is generally transition element or inner-transition element.

#### 3.Ligands

Ligands are electron donating species (ions or molecules) bound to the Central atom in the coordination entity.

These may be charged or neutral. Ligands are of the following types:

(i)Unidentate It is a ligand, which has one donor site, i.e., the ligand bound to a metal ion through a single donor site. e.g., H<sub>2</sub>O, NH<sub>3</sub>, etc.

(ii)Bidentate It is the ligands, which have two donor sites.

CH2-NH2 200CH2-NH2 (oxalate ion) (ethylene diammine) (ox) (en)

(iii)Polydentate It is the ligand, which have several donor sites.

e.g., [EDTA]<sup>4-</sup> is hexadentate ligand.



- (iv) Ambidentate ligands These are the monodentate ligands which can ligate through two different sites, e.g., NO<sub>2</sub><sup>-1</sup>, SCN<sup>2-</sup>, etc.
- (v) Chelating ligands Di or polydentate ligands cause cyclisation around the metal atom which are known as chelate ligands, such ligands uses' two or more donor atoms to bind a single metal ion and are known as chelating ligands.

More the number of chelate rings more are the stability of complex.

The stabilization of coordination compounds due to chelation is known as **chelate effect**.

#### 4. Coordination Number

It is defined as the number of coordinate bonds formed by central metal atom, with the ligands.

e.g., in [PtCl<sub>6</sub>]<sup>2-</sup>, Pt has coordination number 6. In case of monodentate ligands,

Coordination number = number of ligands in polydentate ligands.

Coordination number = number of ligands x denticity

#### **5.Coordination Sphere**

The central ion and the ligands attached to it are enclosed in square bracket which is known as coordination sphere. The ionisable group written outside the bracket is known as counter ions. The spatial arrangement of the ligands which are directly attached to the central atom or ion is called coordination polyhedron around the central atom or ion.

## 7.Oxidation Number of Central Atom

The charge of the complex if all the ligands are removed along with the electron pairs that are shared with the central atom is called oxidation number of central atom. e.g.,  $[CU(CN_4)_{3-}, oxidation number of copper is +1, and represented as Cu(I).$ 

## **Types of Complexes**

## 1. Homoleptic complexes

Complexes in which the metal atom or ion is linked to only one kind of donor atoms, are called homoleptic complexes e.g.,  $[Co(NH_3)_6]^{3+}$ 

## 2. Heteroleptic complexes

Complexes in which the metal atom or ion is linked to more than one kind of donor atoms are called heteroleptic complexes e.g.,  $[Co(NH_3)_4Cl_2]^+$ 

## 3. Labile and Inert complexes

Complexes in which the ligand substitution is fast are known as labile complexes and in which ligand substitution is slow, are known as inert complexes.

## Effective Atomic Number (EAN)

This concept was proposed by Sidgwick. In a complex, the EAN of metal atom is equal to the total number of electrons present in it.

EAN = Z - ON of metal + 2 x CN

(Where, Z = atomic number of metal atom ON = oxidation number of metal

and CN = coordination number of complex)

An ion with central metal atom having EAN equal to next inert gas will be more stable.

### **IUPAC Naming of Complex Compounds**

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Naming is based on set of rules given by IUPAC.

- 1. Name of the compound is written in two parts;
  - (i) name of cation and (ii) name of anion.
- 2. The cation is named first in both positively and negatively charged coordination complexes.
- 3. The dissimilar ligands are named in an alphabetical order before the name of central metal atom or ion.
- 4. For more than one similar ligand, the prefixes di, tri, tetra, etc are added before its name. If the di, tri, etc already appear in the complex then bis, tris, tetrakis are used.
- 5. If the complex part is anion, the name of the central metal ends with suffix 'ate'.
- 6. Names of the anionic ligands end in '0', names of positive ligands end with 'ium' and names of neutral ligands remain as such. But exceptions are there as we use aqua for H<sub>2</sub>O, ammine for NH<sub>3</sub>, carbonyl for CO and nitrosyl for NO.
- 7. Oxidation state for the metal in cation, anion or neutral coordination compounds is indicated by Roman numeral in parentheses.
- 8. The name of the complex part is written as one word.
- 9. If the complex ion is a cation, the metal is named same as the element.
- 10. The neutral complex molecule is named similar to that of the complex cation.

#### Some examples are

Co-ordination Compound	IUPAC Name	
(i) [Cr(NH <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>3</sub>	triamminetrichlorochromium (III) chloride	
(ii) [Co(H <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> H <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	tris (ethane-I,2-diamine) cobalt (III) sulphate	
(iii) [Ag(NH <sub>3</sub> ) <sub>2</sub> ] [Ag(CN) <sub>2</sub> ]	diamminesilver (I) dicyanoargentate(I)	
(iv) K4 [Fe(CN)6]	potassium hexacyanoferrate (II)	