

# Coordination Compounds

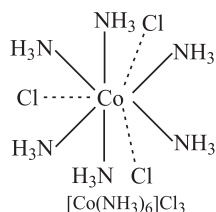
RAKESH KUMAR  
Lecturer in Chemistry



## Recap Notes

- **Werner's coordination theory :**

- It explains the nature of bonding in complexes. Metals show two different kinds of valencies:
- **Primary valency :** Non directional and ionisable. It is equal to the oxidation state of the central metal ion.
- **Secondary valency :** Directional and non-ionisable. It is equal to the coordination number of the metal. It is commonly satisfied by neutral and negatively charged or sometimes by positively charged ligands.
- The ionisation of the coordination compound is written as :  
$$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$$



Representation of  $\text{CoCl}_3 \cdot 6\text{NH}_3$  complex according to Werner's theory

- **Addition compounds :** The compounds formed by combination of two or more simple compounds are called *addition compounds*. They are of two types :
  - **Double salt :** A compound formed by combination of two or more simple compounds, which is stable in solid state only is called *double salt*. In solution it breaks into component ions. *e.g.*,

$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ ; Potash alum  
 $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ; Mohr's salt  
 $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ; Carnallite

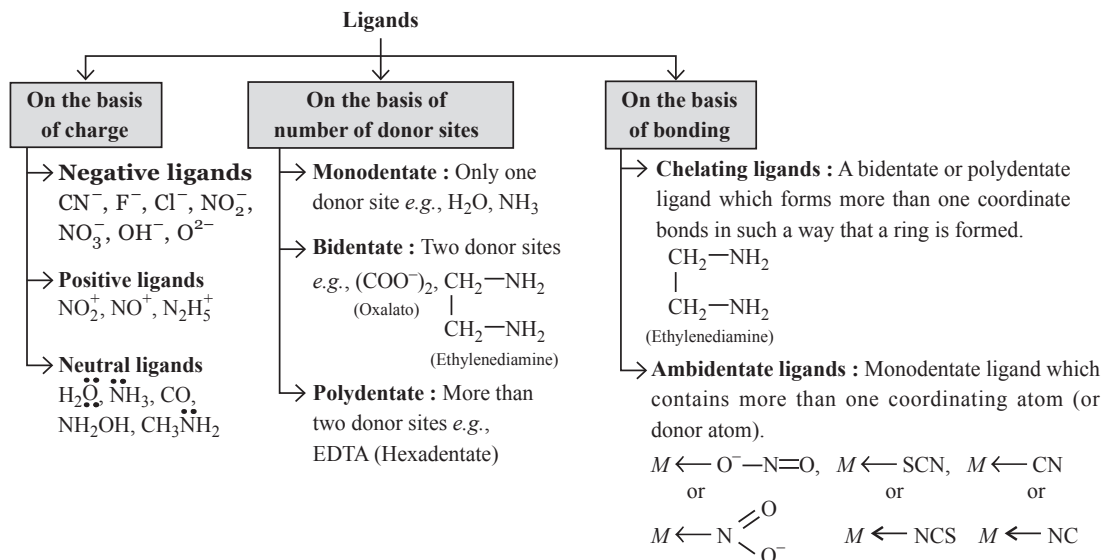
- **Complex compound :** A compound formed by combination of two or more simple compounds which retain its identity both in solid and solution states is called *complex compound*.

*e.g.*,  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , Potassium ferrocyanide  
 $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ , Cupramine sulphate

- **Some important terms pertaining coordination compound :**

- **Coordination entity :** The central metal atom or ion and ligand taken together is called *coordination entity*. It may be positive, negative or neutral.  
*e.g.*,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Ni}(\text{CO})_4]$
- **Central atom :** The atom or ion with which definite number of ligands are attached in a definite geometry is called *central atom/ion*. Any atom/ion which has high positive charge density or vacant orbitals of suitable energy may be central atom or ion, *e.g.*, transition metals, lanthanoids. It is Lewis acid (electron acceptor).
- **Ligands :** Molecules or ions which are bound to the central atom/ion in the coordination entity are called *ligands*. A molecule or ion which has high negative charge or dipole or lone pair of electrons may be ligands. It is Lewis base (electron donor).

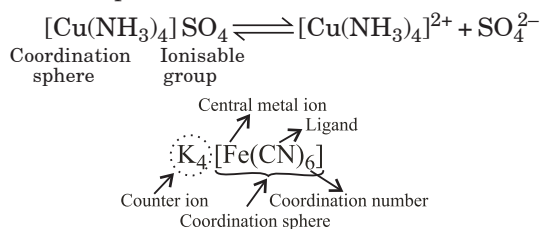
## ► Classification of ligands :



- **Coordination number (C.N.)** : The total number of coordinate bonds through which the central metal atom or ion is attached with ligands is known as coordination number. Examples :  $[\text{Ag}(\text{CN})_2]^-$  : C.N. = 2,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  : C.N. = 4,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  : C.N. = 6

- **Coordination sphere** : The central atom and the ligands which are directly attached are collectively known as coordination sphere. It is non-ionisable and written enclosed in square brackets. The ionisable groups are written outside the brackets.

Example :



- **Coordination polyhedron** : The spatial arrangement of the ligand atoms which are directly attached to the central atom defines a coordination polyhedron about the central atom, *e.g.*,  $[(\text{Co}(\text{NH}_3)_6)]^{2+}$  is octahedral  $[\text{Ni}(\text{CO})_4]$  is tetrahedral. Octahedral is most common coordination polyhedron.

## • Homoleptic and heteroleptic complexes:

- **Homoleptic complexes** : Complexes in which a metal is bound to only one kind of ligands are called *homoleptic complexes*.

*e.g.*,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Cu}(\text{CN})_4]^{3-}$

- **Heteroleptic complexes** : Complexes in which the central atom is bound to different type of ligands are called *heteroleptic complexes*.

*e.g.*,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$ ,  $\text{K}_2[\text{Fe}(\text{CN})_5\text{NO}]$ ,  
 $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$

## • Nomenclature of coordination compounds :

- **Rules for writing the formula of coordination compounds :**

- Formula of the cation whether simple or complex must be written first, followed by anion.
- The coordination sphere is written in square brackets.
- Within the coordination sphere the sequence of symbols is, first the metal atom followed by anionic ligand then neutral ligand finally cationic ligand. Ligands of same type are arranged alphabetically.
- Polyatomic ligands are enclosed in parentheses.
- The number of cations or anions to be written in the formula is calculated on the basis that total positive charge must be equal to the total negative charge, as the complex as a whole is electrically neutral.

► **Rules for naming coordination compounds :**

- The cation is named first then the anion.
- In naming coordination sphere, ligands are named first in alphabetical order followed by metal atom and then oxidation state of metal by a roman numeral in parentheses.
- The complex part is written as one word.
- When the coordination sphere is anionic, name of central metal ends in *-ate*.

► **Naming of ligands :**

- Name of anionic ligands end in *-o*.  
*e.g.*,  $\text{Cl}^-$  : Chlorido
- Neutral ligands (with a few exceptions) retain their names *e.g.*,  $\text{NH}_3$  : Ammine  
Name of cationic ligands end in *-ium*.  
*e.g.*,  $\text{NO}_2^+$  : Nitronium
- Certain ligands are represented by abbreviations in parentheses instead of their complex structural formulae.  
*e.g.*, ethylenediamine(*en*).
- Ambidentate ligands are named by using different names of ligands or by placing the symbol of donor atom.

*e.g.*,  $\text{SCN}^-$  (Thiocyanato-S or Thiocyanato),  $\text{—NCS}^-$  (Thiocyanato-N or Isothiocyanato),  $\text{—ONO}^-$  (Nitrito-O or Nitrito),  $\text{—NO}_2$  (Nitrito-N or Nitro)

- The prefixes *di-*, *tri-*, *tetra-*, *penta-* and *hexa-* are used to indicate the number of each ligand. If the ligand name includes such a prefix, the ligand name should be placed in parentheses and preceded by *bis-*(2), *tris-*(3), *tetrakis-*(4), *pentakis-*(5) and *hexakis-*(6).

● **Bonding in coordination compounds :**

► **Valence bond theory :** It was developed by Pauling.

- A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of coordinate bonds with the ligands.
- Central metal ion can use appropriate number of *s*, *p* or *d*-orbitals for hybridisation depending upon the total number of ligands.
- The outer orbital (high spin) or inner orbital (low spin) complexes are formed depending upon whether outer *d*-orbitals or inner *d*-orbitals are used.

C. No.	Type of hybridisation	Geometry	Examples
2	$sp$	Linear	$[\text{Ag}(\text{NH}_3)_2]^+$ , $[\text{Ag}(\text{CN})_2]^-$
3	$sp^2$	Trigonal planar	$[\text{HgI}_3]^-$
4	$sp^3$	Tetrahedral	$\text{Ni}(\text{CO})_4$ , $[\text{NiX}_4]^{2-}$ , $[\text{ZnCl}_4]^{2-}$ , $[\text{CuX}_4]^{2-}$ , where, $X = \text{Cl}^-, \text{Br}^-, \text{I}^-$
	$dsp^2$	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , $[\text{Ni}(\text{NH}_3)_4]^{2+}$
5	$dsp^3$	Trigonal bipyramidal	$[\text{Fe}(\text{CO})_5]$ , $[\text{CuCl}_5]^{3-}$
	$sp^3d$	Square pyramidal	$[\text{SbF}_5]^{2-}$
6	$d^2sp^3$	Octahedral (Inner orbital)	$[\text{Cr}(\text{NH}_3)_6]^{3+}$ , $[\text{Fe}(\text{CN})_6]^{3-}$
	$sp^3d^2$	Octahedral (Outer orbital)	$[\text{FeF}_6]^{3-}$ , $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , $[\text{Ni}(\text{NH}_3)_6]^{2+}$

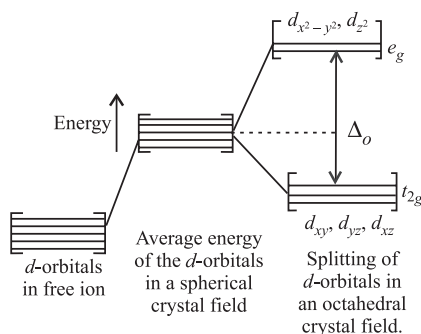
Inner orbital complexes	Outer orbital complexes
Involves inner <i>d</i> -orbitals <i>i.e.</i> , $(n - 1)d$ -orbitals.	Involves outer <i>d</i> -orbitals <i>i.e.</i> , $nd$ -orbitals.
Low spin complexes	High spin complexes
Have less or no unpaired electrons. <i>e.g.</i> , $[\text{Co}(\text{NH}_3)_6]^{3+}$ , $[\text{Co}(\text{CN})_6]^{4-}$	Have large number of unpaired electrons. <i>e.g.</i> , $[\text{MnF}_6]^{3-}$ , $[\text{CoF}_6]^{3-}$

Low spin complexes are generally diamagnetic and high spin complexes are paramagnetic.

- Paramagnetism  $\propto$  No. of unpaired electrons.
- Magnetic moment  $= \sqrt{n(n+2)}$  B.M. where  $n$  = number of unpaired electrons.

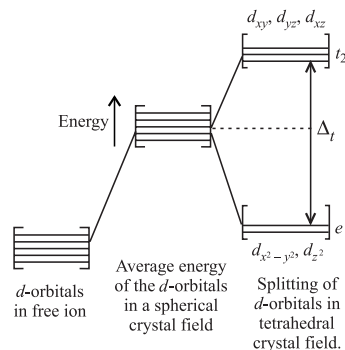
► **Crystal field theory** : It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion. When ligands approach the central metal ion, then the five degenerate orbitals do not possess equal energy any more and results in splitting, which depends upon nature of ligand field strength.

- Greater the ease with which the ligand can approach the metal ion, the greater will be the crystal field splitting caused by it.
- Crystal field splitting in octahedral coordination complexes is shown as :



- If  $\Delta_o < P$  (where ' $P$ ' is energy required for forced pairing of electrons) then the electrons will remain unpaired and a high spin complex is formed.

- If  $\Delta_o > P$ , then pairing of electrons takes place and a low spin complex is formed.
- Crystal field splitting in tetrahedral complexes is shown as :



- Difference in energy between  $e$  and  $t_2$  level is less in tetrahedral complexes.

$$\Delta_t = \frac{4}{9} \Delta_o$$

- **Spectrochemical series** : Arrangement of ligands in the order of increasing field strength.

Weak field ligands  $\xrightarrow{\text{Increasing order of CFSE } (\Delta_o)}$  Strong field ligands

$\text{I}^- < \text{Br}^- < \text{SCN}^- < \text{Cl}^- < \text{S}^{2-} < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{edta}^{4-} < \text{NH}_3 < \text{en} < \text{NO}_2^- < \text{CN}^- < \text{CO}$

- **Colour of coordination compounds** : The magnitude of CFSE ( $\Delta_o$ ) for most of the complexes is of the same order as the energy of a photon of visible light. Hence, whenever  $d-d$  transition takes place, it imparts colour to the complex. The colour of the complex is the colour complementary to the wavelength absorbed.