CHAPTER-5

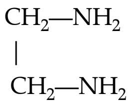
COORDINATION COMPOUNDS

Topic-1 Concept of Complexes, Ligands, IUPAC Nomenclature of Mononuclear Coordination Compounds

Concept covered: *Double salt, Coordination compound, Ligands, Denticity, Coordination number, IUPAC of coordination compounds*

Revision Notes

- **Coordination compound:** A coordination compound contains a central metal atom or ion surrounded by a number of oppositely charged ions or neutral molecules. It retains their identity in solid as well as in dissolved state. There is a coordinate bond between metal atom and these ions or molecules, e.g., $[Cu(NH_3)_4]^{2+}$.
- **Double salt:** When two salts in equimolar ratio are crystallised together from their saturated solution, they are called double salts. These are stable in solid state but dissociate into constituent ions in the solution. e.g., $FeSO_4(NH_4)_2SO_4.6H_2O$ (Mohr's salt).
- **Properties of double salts:**
  - **(i)** They give simple ions in aqueous solution because they are ionic compounds.
  - **(ii)** They do not contain coordinate bonds.
  - **(iii)** They exist only in solid state as double salt.
  - **(iv)** They are soluble in water.
- **Coordinate bonds:** A type of covalent bond in which one of the atom donates a pair electrons. It can be considered as a combination of transfer and sharing of electrons. Coordinate bonds are also called semipolar bonds.
- **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.
     - **(ii)** Anionic complex entity: It is the complex ion which carries negative charge.
  2. Central atom or ions
  3. Ligand
- **Central metal atom or ions:** The atom or ion to which a fixed number of ions or groups are bound to central atom or ion. It is also referred as Lewis acid. It is generally transition or inner transition element. e.g., in $K_4[Fe(CN)_6]$, Fe^{2+} is central metal ion.
- **Ligand:** A ligand is an ion or a small molecule having at least one lone pair of electrons and capable of forming a coordinate bond with central atom/ion in the coordination entity. e.g., Cl^-, OH^-, CN^-, CO, NH_3, H_2O, etc. A ligand may be neutral or charged species. It always acts as a Lewis base.
- **Types of Ligands:**
  - **(i) Monodentate ligand:** A ligand which forms only one bond with central atom/ion, or have only one donor atom. e.g., CO, NO, NH_3, H_2O, OH^-, etc.
  - **(ii) Bidentate or didentate ligand:** A ligand which forms two bonds with central atom/ion or two donor atoms/ion. e.g., 1, 2-ethane diamine or ethylene diamine (en).



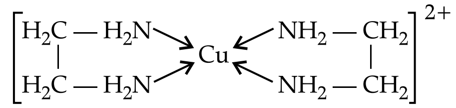
$$\begin{array}{l} CH_2—NH_2 \\ | \\ CH_2—NH_2 \end{array}$$

  - **(iii) Polydentate ligand:** A ligand which forms more than two bonds with central atom/ion or have more than two donor atoms, e.g., Ethylenediamine tetracetate (EDTA). Ligands which have three donor atoms per ligand are called as tridentate ligand, e.g., (dien) diethyl triamine. Tetradentate ligands are ligands that bind with four donor atoms to a central atom to form a coordination complex, e.g., diethylenetetramine. Pentadentate ligands bind with five donor atoms, e.g., triethylenetetramine and hexadentate ligands bind with six donor atoms, e.g., EDTA.

(iv) Chelating ligand: Di or polydentate ligands cause cyclisation around the metal atom which are known as chelate, such ligands uses two or more donor atoms to bind a single metal ion and are known as chelating ligand.

More the number of chelate rings, more is the stability of complex. The stabilisation of coordination compounds due to chelation is known as chelate effect. e.g., $[Pt(en)_2]Cl_2$.

- Coordinating of chelating ligand with a metal results in the formation of a closed cyclic ring and the compound is known as chelate. e.g., ethylenediamine complexed with Cu (II) ion forms a chelate:

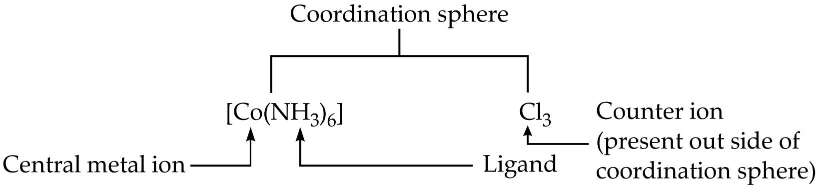


- **Applications of Chelates:**
  - **(i)** In the softening of hard water.
  - **(ii)** In the separation of lanthanoids and actionids.
  - **(iii)** In the detection as well as estimation of some metal ions such as nickel (II) ion.

(v) Ambidentate ligand: A ligand which can form bond with two different atoms. e.g., NO_2^- or ONO^-, SCN^- or NCS^-.

(vi) Flexidentate ligand: A ligand which forms different number of bonds with central atom/ion in different complexes. e.g., EDTA.

- **Coordination number:** It is defined as the number of coordinate bonds formed by central atom, with the ligands. It may also be defined as total number of chemical bonds formed between central metal ion and donor atom of ligand e.g., in $[Ni(NH_3)_6]^{2+}$, the coordination number of Ni^{2+} is 6.
- The central metal ion and the ligands directly attached to it are written inside a square bracket [ ]. It is called **coordination sphere. Werner** called it first sphere of attraction.



- **Coordination polyhedron:** The spatial arrangement of the ligand atoms which are directly attached to the central atoms or ions define a coordination polyhedron about the central atom e.g., $[PtCl_4]^{2-}$ is square planar.
- **Charge on the complex ion:** The charge on the complex ion is equal to the algebraic sum of the charges on all the ligands coordinated to the central metal ion.
- **Donor atom:** An atom in the Lewis base that forms the bond with the central atom/ion is called donor atom because it donates the pair of electrons.
- **Denticity:** The number of ligating groups in a ligand is called as denticity, e.g., unidentate, didentate, etc.
- **Oxidation number of central atom:** It is defined as the charge it would carry, if all the ligands are removed along with the electron pairs that are shared with the central atom. It can be calculated by taking the sum of oxidation state of metal and total ligands equal to charge present on its coordination sphere.
- **Types of Complexes:**
  1. Homoleptic
  2. Heteroleptic

1. **Homoleptic and Heteroleptic complexes:** Complexes in which the metal atom or ion is linked to only one type of ligands are called homoleptic complexes., e.g., $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{4-}$, etc. The complexes in which the metal atom or ion is linked to more than one kind of ligands are called heteroleptic complexes, e.g., $[Co(NH_3)Cl_2]^+$ and $[Cr(en)_2Cl_2]^+$, etc.
2. **Homonuclear and Polynuclear complexes:** Complexes in which only one metal atom is present are known as homonuclear complexes. e.g., $[Co(NH_3)_6]Cl_3$ and $[Cu(NH_3)]_4SO_4$. Complexes in which more than one metal atom is present are known as polynuclear complexes.

- **Counter ions:** The ions which are not included in the primary coordination sphere are known as counter ions. e.g., in $K_4[Fe(CN)_6]$, K^+ ions are counter ions.
- **IUPAC rules for naming complex compounds are:**
  - **(i)** Name of compound is written in two parts **(a)** name of cation **(b)** name of anion.
  - **(ii)** The cation whether simple or complex is named first followed by anion.
  - **(iii)** Ligands are named in alphabetical order.
  - **(iv)** For indicating the number of each kind of ligand within the coordination entity, two kinds of numerical prefixes are used (di, tri, tetra, etc.) For ligands containing any of these prefixes in their names, their

numbers are indicated by prefixes bis, tris, tetrakis, etc. Anionic ligands end with *-o*. Neutral ligands retain their names while cationic end with *-ium*.

(v) The coordination sphere is written in square bracket.

(vi) In naming, ligands are named first in alphabetical order followed by metal atom and then the oxidation state of metal by a Roman numeral in parenthesis.

(vii) Name of coordination compounds starts with a small letter and the complex part is written as one word.

(viii) Oxidation number of central atom is indicated in Roman numerals. No space is left between the number and the rest of the name.

Examples:

(a) $[Cr(NH_3)_3(H_2O)_3]Cl_3$ triamminetriquachromium (III) chloride

(b) $K_4[Fe(CN)_6]$ potassium hexacyanoferrate (II)

Type	Charge	Ligand	Formula	Name in Complexes
Monodentate	**Neutral**	ammonia	NH_3	amine
		water	H_2O	aqua
		carbon monoxide	CO	carbonyl
		pyridine	pyr	pyridine
	Minus one	azide	N_3^-	azido
		bromide	Br^-	bromido
		chloride	Cl^-	chlorido
		cyanide	CN^-	cyanido
		fluoride	F^-	fluorido
		hydroxide	OH^-	hydroxido
		nitrite	NO_2^-	nitrito
		thiocyanate	SCN^- or NCS^-	thiocyanato
Bidentate	**Neutral**	bipyridine	bipy	bipyridine
		ethylenediamine	en	ethylenediamine
	Minus two	carbonate	CO_3^{2-}	carbonato
		oxide	O_2^-	oxo
		oxalate	$C_2O_4^{2-}$	oxolato
			SO_4^{2-}	sulfato

Key Terms

- **Coordination chemistry:** The study of the coordination compounds is known as coordination chemistry.
- **Labile complex:** A complex in which ligand substitution is fast.
- **Inert complex:** A complex in which ligand substitution is slow.
- **Synergic bonding:** A ligand donates a pair of electrons to the metal atom or ion and then accepts a pair of electrons back in its vacant orbital also from *d*-orbitals of the metal or ion. This is called synergic bonding and the ligands involved are known as π–acid ligands.
- **Effective Atomic Number (EAN):** It can be calculated for the metal atom or in the coordination complex by using following reaction:

  EAN = Atomic no. (Z) of metal atom – Oxidation number+2 C.N. where, C.N. is coordination number.

Topic-2

Isomerism, Werner's Theory, VBT, CFT, Stability and Importance of Coordination Compounds

Concept covered: *Structural and stereoisomerism in coordination compounds, Werner's Theory, Valence band theory, Crystal field theory, Application of coordination compounds*

Revision Notes

- Compounds having same molecular formula but different properties and structures are known as isomers and this phenomenon is known as **isomerism.**
- **Isomerism in coordination compounds is of two types:**

  (a) Structural isomerism: Complexes having same molecular formula but different structural formula are called as structural isomers and the phenomenon is called as structural isomerism. It is of following types:

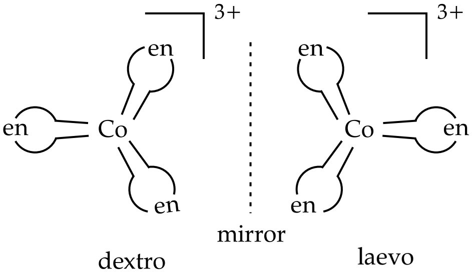
- **(i) Ionisation isomerism:** In this type of isomerism, there is an interchange of groups between the coordination sphere of the metal ion and ions outside the coordination sphere, e.g., $[Co(NH_3)_5Cl]^{2+}$ SO_4^{2-} and $[Co(NH_3)_5(SO_4)]^+$ Cl^-.
- **(ii) Coordination isomerism:** This type of isomerism arises from the interchange of ligands between cationic and anionic complexes of different metal ions present in a complex. e.g., $[Co(NH_3)_6]$ $[Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6][Co(C_2O_4)_3]$.
- **(iii) Linkage isomerism:** In this type of isomerism, the ligand can form linkage with metal through different atoms. It is shown by ambidentate ligands. e.g., nitro ($-NO_2$) group can link to metal through nitrogen ($-NO_2$) or through oxygen (—O—N = O) atom i.e.,

$[Co(NH_3)_5ONO]Cl_2$	and	$[Co(NH_3)_5NO_2]Cl_2$
Pentaamminenitro–O– cobalt (III) chloride		Pentaamminenitro–N– cobalt (III) chloride

- **(iv) Solvate isomerism:** This is also known as hydrate isomerism. In this isomerism, water is taken as solvent. It has different number of water molecules in the coordination sphere and outside. e.g., $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$(grey-green).

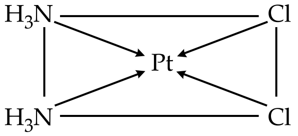
(b) Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. These are of two types:

- **(i) Optical isomerism:** Optical isomers are mirror images that cannot be superimposed on one another. These are called as *enantiomers*. The molecules or ions that cannot be superimposed are called *chiral*. The two forms are called *dextro* (*d*) and *laevo* (*l*) depending upon the direction in which they rotate the plane of polarized light in a polarimeter (*d* rotates to the right, *l* to the left). Optical isomerism is common in octadehral complexes involving bidentate ligands.

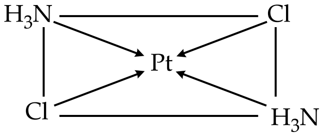


Optical isomers (*d* and *l*) of $[Co(en)_3]^{3+}$

- **(ii) Geometrical isomerism or *cis-trans* isomerism:** In tetra-coordinated square planar complexes, the cis isomer has the same groups on the same side whereas *trans*-isomer has same group on opposite side, e.g.,



cis-diamminedichloroplatinum(II) (*cis*-platinum)



trans-diamminedichloroplatinum(II)

- **Racemic mixture:** An equimolar mixture of *dextro* and *laevo* form is called racemic mixture. It has zero rotation.
- **Werner's theory:**
  - Werner was able to explain the nature of bonding in complexes. The brief outlines of Werner's theory are as: Metal shows two different kinds of valencies:
    - **(i)** Primary valency
    - **(ii)** Secondary valency
  - Primary valencies are satisfied by anions while secondary are satisfied either by oppositely charged ions or neutral molecules and sometimes by cationic groups.
  - Secondary valencies are equivalent of coordination number and they are directed in space in specific number around each central metal atom within the lattice while primary valencies correspond to oxidation number of the metal and are satisfied by anions.
- **Limitations of Werner's theory:** This theory does not explain the following queries:
  - **(i)** Why is the complex forming tendency limited to a few elements only?
  - **(ii)** Why do bonds in the coordination complexes are of directional in nature?
  - **(iii)** Why are certain complexes of magnetic nature and show geometrical and optical isomerism?
- **Valence Bond theory:** It was developed by Pauling. The brief points are:
  - **(i)** A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of coordinate bond with the ligands.
  - **(ii)** Central metal ion can use appropriate number of *s*, *p* or *d*-orbitals for hybridisation depending upon total number of ligands.
  - **(iii)** The hybridised orbitals are allowed to overlap with those ligands orbitals that can donate an electron pair for bonding.

(iv) The outer orbitals (high spin) or inner orbitals (low spin) complexes are formed depending upon whether outer *d*-orbitals or inner *d*-orbitals are used.

- **Limitations of Valence bond theory:**
  (i) It cannot explain the detailed magnetic properties of complex compounds.
  (ii) It cannot explain the optical absorption spectra of coordination compounds.
  (iii) It cannot predict property whether a particular 4-coordinate complex is square planar or tetrahedral in nature.
  (iv) It fails to make distinction between strong and weak ligands.
- **Crystal field theory (CFT):**
  (i) According to crystal field theory, ligands are point charges.
  (ii) On approaching ligands, *d*-orbitals of metal ion gets split.
  (iii) Three *d*-orbitals, i.e., d_{xy}, d_{yz}, d_{zx} are oriented in between the coordinate axes and are called t_{2g} orbitals.
  (iv) The other two d orbitals, i.e., $d_{x^2-y^2}$ and d_{z^2} oriented along *xy* axis are called e_g orbitals.
  The energy difference between t_{2g} and e_g level is designated by triangle and is called crystal field splitting energy.
  (v) e_g orbitals have higher energy in octahedral and lower energy in tetrahedral complexes.
  (vi) t_{2g} orbitals have high energy in tetrahedral complexes.
  Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak field and consequently result in small splitting of *d*-orbitals. In general, ligands can be arranged in series in the order of increasing field strength as given below and called as spectrochemical series:
  $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < O_2^- < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO < NO$

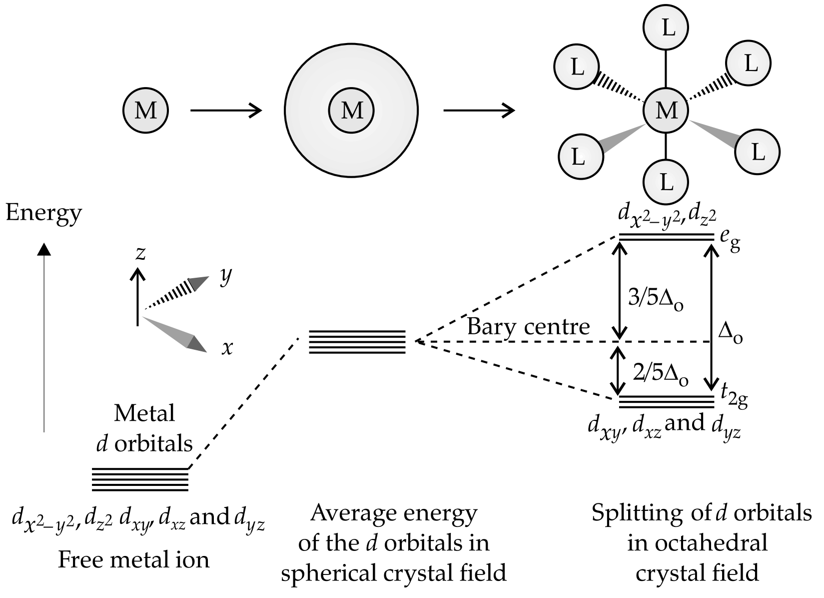
Mnemonics

Concept: Spectrochemical series : $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA < NH_3 < CN^- < CO$

Mnemonics: I Bought **S**ome **C**opies to **S**tudy **F**undamental **O**f **C**hemistry **H**e **N**urtured **E**xcellence in **N**ecessary **C**oordination **C**ompounds

Interpretation :

I^- = I
Br^- = Brought
SCN^- = Some
Cl^- = Copies to
S_2- = Study
F = Fundamental
OH^- = Of
$C_2O_4^{2-}$ = Chemistry
NCS^- = Nurtured
EDTA = Excellence in
NH_3 = Necessary
CN^- = Coordination
CO = Compounds



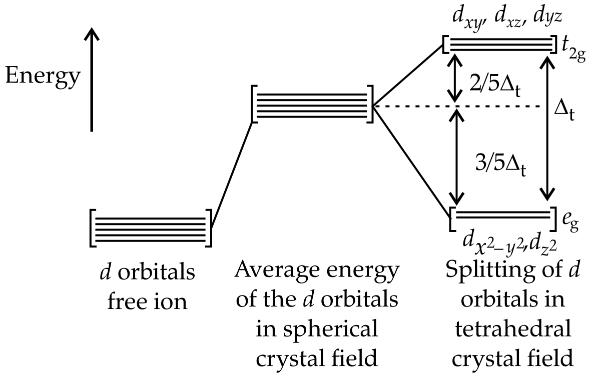


Fig.2 : *d* orbital splitting in a tetrahedral crystal field

(vii) Explanation of colour and magnetic behaviour in complexes is possible by crystal field theory.

- **Colour in coordination compounds:** Transition metal atom/ion has five degenerate *d*-orbitals in free state. On formation of coordination compounds, *d*-orbitals split into two or more parts as per geometry of complex. When light falls on the complex, it absorbs a portion of light from visible region to promote electrons from lower to higher level and transmits the rest of the light. The colour transmitted is complementary to the absorbed light. This electronic transition is known as *d-d* transition. e.g., $[Ti(H_2O)_6]^{3+}$ appears purple as it absorbs light of blue green colour for the promotion of the only electron from t_{2g} to e_g level and emits purple colour.
  - Colour of compound with similar metal and ligand in different geometry is dissimilar.
  - Colour of same metal with different ligand is different.
  - Colour of complex of same metal in different oxidation states with similar ligand in similar geometry is different.
- **Magnetic property in coordination compounds:** Coordination compounds with unpaired electrons are paramagnetic.
- Coordination compounds containing all the paired electrons are diamagnetic. Paramagnetic compounds are attracted to applied magnetic field whereas diamagnetic compounds are weakly repelled by magnetic field.
- **Shapes of Coordination compounds:**

Coordination number	**Type of hybridisation**	**Geometry of complex**
2	sp	Linear
3	sp^2	Trigonal planar
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	dsp^3, sp^3d	Trigonal bipyramidal
6	sp^3d^2, d^2sp^3	Octahedral

- **Stability of Coordination compounds:** It depends on the charge present on central atom, nature of metal ion, basic nature of ligand, presence of chelate ring and effect of multidentate cyclic ligand. It is measured as stability constant denoted as K.

  In the reaction, $M^{a+} + nL^{x-} \rightleftharpoons [ML_n]^{b+}$

$$K = \frac{[ML_n]^{b+}}{[M^{a+}][L^{x-}]^n}$$

  Higher the value of stability constant K, greater will be the stability of the complex.
- **Limitations of CFT**
  1. It does not consider the formation of π bonding in complexes.
  2. It does not explain why H_2O is stronger ligand than OH^-.
  3. It gives no account of the partly covalent nature of metal-metal bonds.
- **Importance of Coordination compounds:**

  (i) They are used in photography, i.e., AgBr forms coloured complex with sodium thiosulphate in photography.

  (ii) $K[Ag(CN)_2]$ is used as catalyst for electroplating of silver, $K[Au(CN)_2]$ is used for gold plating.

  (iii) Some of ligands oxidize Co^{2+} to Co^{3+} ion.

  (iv) EDTA is used for estimation of Ca^{2+} and Mg^{2+} in hard water.

(v) Silver and gold are extracted by treating Zn with their cyanide complexes.

(vi) Ni^{2+} is tested and estimated by DMG (dimethylglyoxime).

(vii) *Cis*-platin $[Pt(NH_3)_2Cl_2]$ is used as anti-tumor agent in treatment of cancer.

(viii) EDTA is used to remove Pb by forming Pb-EDTA complex which is eliminated in urine.

(ix) Haemoglobin contains Fe, chlorophyll contains Mg and vitamin B_{12} contains Co.

(x) Bauxite is purified by forming complex with NaOH.

Key Terms

- **Facial or fac isomer:** When three ligands with donor atoms are on the same triangular face of the octahedron, the geometrical isomer is known as facial or *fac* isomer.
- **Meridional or mer isomer:** When three ligands with donor atoms are on the same equatorial plane of the octahedron or around the meridian of the octahedron, the isomer is called meridional or *mer* isomer.
- **Macrocylic effect:** Multidentate ligands happen to be cyclic in nature without causing any steric hindrance, the stability of the complexes is further increased. This is known as macrocyclic effect.
- **Stability constants (K):** The relative stabilities of coordination complexes can be compared in terms of stability constant (K) also denoted by β (Beta).
- **Polymerisation isomerism:** This is not a true isomerism. It occurs between compounds having the same empirical formula but different molecular masses. e.g., $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_3Cl]_2[PtCl_4]$.

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