UNIT 9

COORDINATION COMPOUNDS

1. Introduction

Complex compounds or coordination compounds are those molecular compounds which retain their identity in solid as well as in solution are known as complex compounds. In these compounds metal atoms are bound to a number of anions. **Example**,

 K_4 [Fe(CN)₆] + H₂O \rightarrow 4K⁺ + [Fe(CN)₆]⁴⁻

2. Types of Complex

(i) Anionic complex

 $K_{3}[Fe(C_{2}O_{4})_{3}] \rightarrow 3K^{+} + [Fe(C_{2}O_{4})_{3}]^{3-}$

anionic complex

(ii) Cationic complex

 $[CoCl_2(en)_2]Cl \rightarrow [CoCl_2(en)_2]^+ + Cl^$ cationic complex

(iii)Neutral complex

[Ni(CO)₄] neutral complex

3. Ligands

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands.

Types of Ligands

(i) Unidentate, a ligand which is bound to a metal ion through a single donor atom.

e.g., H₂O, NH₃, CO, Cl⁻, NH₂⁻ etc.

(ii) Didentate, a ligand which is bound to a metal ion through a two donor atoms.

e.g.,	COO⁻	$CH_2 - \ddot{N}H_2$
	I COO⁻	$H_2 - \ddot{N}H_2$
	Oxalate ion	ethylene diamine

(iii)Polydentate, a ligand which is bound to a metal ion through a several donor atoms.

e.g., ethylene diamine tetraacetate ion [EDTA]⁴⁻.

(iv) Ambidentate ligands, which can ligate through two different atoms.

 $e.g., -NO_2 - ONO, -SCN - NCS$ etc.

(v) Chelate ligands, these may be a di- or polydentate ligand which form closed ring with central metal ion. Closed ring is known as chelate ring. Number of more chelate ring in complex, complex will be more stable. The number of such ligating groups is called the denticity.

4. Homoleptic and Heteroleptic Complexes

Complexes in which a metal is bound to only one kind of donor groups *e.g.*, $Co(NH_3)_6]^{3+}$ are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups *e.g.*, $[Co(NH_3)_4Cl_2]^+$, are known as heteroleptic.

5. Nomenclature of Coordination Compounds

Cationic Complex

 $[Cr(NH_3)_3(H_2O)_3]Cl_2$

triamminetriaquachromium (III) chloride

- (i) Prefixes mono, di, tri, etc. are used to indicate the number of the individual ligands and ligands are named in an alphabetical order.
- (ii) Central metal atom and oxidation state indicated by Roman numeral in parenthesis.

(iii)Name of ionisable anion.

Anionic Complex

 $K_{3}[Fe(CN)_{6}]$

Potassium hexacyanoferrate (III)

(i) Name of ionisable metal and oxidation state

(ii) Name of ligand in an alphabetical order

(iii)Central metal atom + ate and oxidation state

Neutral Complex

 $[Pt(NH_3),Cl(NO_2)]$

Diammine chloronitrito-N-platinum (II)

- (i) Name of ligands in an alphabetical order
- (ii) Central metal atom and oxidation state

6. Isomerism in Coordination Compounds

Stereo isomerism and structural isomerism are the two principal types of isomerisms which are known among coordination compounds.

Stereo Isomerism

It occurs due to different arrangements of ligands around central metal atom. It is of two types : geometrical isomerism and optical isomerism.

Geometrical Isomerism

It arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behavior are found in square planar and octahedral complexes.

(i) Square planar complex of formula $[MX_2L_2]$ (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a *cis* isomer, or opposite to each other in a *trans* isomer.

 $e.g., [Pt(NH_3), Cl_2]$

(ii) Square planar complex of the type [MABXL] (where A, B, X, L are unidentates) shows three isomers – two cis and one trans. Such isomerism is not possible for tetrahedral geometry.

 $e.g., [Pt(NH_3)(Br)(Cl)(Py)]$

(iii) Octahedral complexes of formula $[MX_2L_4]_1$ in which the two ligands X may be oriented *cis* or *trans* to each other.

 $e.g., [Co(NH_3)_4Cl_2]^+$

(iv) Octahedral complexes of formula $[MX_2A_2]$ where X are unidentates and A are didentate and form *cis* and *trans* isomers.

 $e.g., [CoCl_2(en)_2]$

(v) Octahedral coordination entities of the type $[Ma_3b_3]$ like $[Co(NH_3)_3(NO_2)_3]$. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meriodional (mer) isomer.

Optical Isomerism

- It arises when mirror images cannot be superimposed on one another. These mirror images are called as enantiomers. The two forms are called *dextro* (*d*) and *laevo* (*l*).
- Optical isomerism is common in octahedral complexes but at least one didentate ligand should be present.

e.g., $[Co(en)_3]^{3+}$, $[PtCl_2(en)_3]^{2+}$ etc.

Structural Isomerism

In structural isomerism, isomers have different bonding pattern. Different types of structural isomerism is as follows :

(i) Linkage isomerism, arises in a coordination compound containing ambidentate ligand.

e.g., $[Co(NH_3)_5(NO_2)]Cl_2$ $[Co(NH_3)_5(ONO)]Cl_2$

(ii) Coordination isomerism, arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

e.g., $[Co(NH_3)_6][Cr(CN)_6]$ $[Cr(NH_3)_6][Co(CN)_6]$

(iii) Ionisation isomerism, when the ionisable anion exchange with anion ligand.

e.g., $[CO(NH_3)_5SO_4]Br \text{ and } [Co(NH_3)_5Br]SO_4$

(iv) Solvate isomerism, is also known as 'hydrate isomerism'. In this case water is involved as a solvent.

e.g., $[Cr(H_2O)_{4}]Cl_{4}$, $[Cr(H_2O)_{5}Cl_{2}H_2O, [Cr(H_2O)_{4}Cl_{2}]Cl_{2}H_2O]$

7. Bonding in Coordination Compounds

Werner's Theory

(i) In complex compounds, metal atom exhibit two types of valencies – primary valency and secondary valency.

(ii) Primary valencies are satisfied by anions only while secondary valencies are satisfied by ligands. Primary valency depends upon oxidation number of central metal atom while secondary valency represents coordination number of central metal atom.

(iii)Primary valencies are ionisable and are non-directional while secondary valencies are non-ionisable and directional. Therefore, geometry of complex is decided by secondary valencies.

Valence Bond Theory

According to this theory, the metal atom or ion under the influence of ligands form inner orbital and outer orbital complex. These hybridized orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

(i) Six ligands (unidentate) (octahedral entity) Generally central atom belongs 3*d* series and ligands can be monodentate or didentate but coordination number should be six and shape of complexes will be octahedral and form two types of complexes.

(a) Inner orbital complexes, which are formed due to participation of (n-1)d orbitals in hybridisation is (d^2sp^3) and shape of complex will be octahedral.

(b) Outer orbital complexes, which are formed due to participation of nd orbitals in hybridisation is (sp^3d^2) . Generally halides (F⁻, Cl⁻, Br⁻, I⁻), SCN⁻, S²⁻ form outer orbital complexes and other ligands form inner orbital complexes.

e.g., Inner orbital complex, $[Co(NH_3)_6]^{3+}$

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All electrons are paired therefore, complex will be diamagnetic in nature.

e.g., Outer orbital complex, $[CoF_6]^{3-}$



Complex has unpaired electrons, therefore, complex will be paramagnetic in nature.

• Generally halides (F⁻, Cl⁻, Br⁻, I⁻) ligands, $[Ni(CO)_4]$, $[Co(CO)_4]$, $[Zn(NH_3)_4]^{2+}$ complexes form outer orbital complexes and other form inner orbital complexes. For example,

1. Inner orbital complex, $[Ni(CN)_{4}]^{2-1}$



All electrons are paired. Complex will be diamagnetic in nature.

2. Outer orbital complex, [CoCl₄]⁻



Complex has unpaired electrons. Complex will be paramagnetic in nature.

Crystal Field Theory

The five *d*-orbitals are split into lower and higher energy level due to approach of ligands is known as crystal field theory. The five *d*-orbitals in a gaseous metal atom/ion have same energy.

(i) Crystal field splitting in octahedral coordination entities.



• Energy separation is denoted by Δ_{α} (the subscript o is for octahedral).

• The energy of the two e_g orbitals (higher energy orbitals) will increase by $(3/5)\Delta_o$ and that of the three t_{2g} (lower energy orbitals) will decrease by $(2/5)\Delta_o$.

• If $\Delta_0 < p$, the fourth electron enters one of the e_g , orbitals giving the configuration

 $t_{2g}^3 e_g^1$. Ligands for which $\Delta_0 < p$ are known as weak field ligands and form high spin complexes.

• If $\Delta_0 > p$, it becomes more energetically favourable for the fourth electron to

occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g$. Ligands which produce this effect are known as strong field ligands and form low spin complexes, where p represents the energy required for electron pairing in a single orbital.

(ii) Crystal field splitting in tetrahedral coordination entities.



• In tetrahedral coordination entities, $\Delta_t = (4/9)\Delta_0$. Consequently the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

Due to less crystal field stabilization energy, it is not possible to pair electrons • and so all the tetrahedral complexes are high spin.

8. Colour in Coordination Compounds

• In complex compounds *d*-orbitals split in two sets t_{2a} and e_{a} . These have different energies. The difference in energies lies in visible region and electron jump from ground state $t_{2\rho}$ level to higher state e_{ρ} level. This is known as d-d transition and it is responsible for colour of coordination compounds.

d-d transition takes place in d^1 to d^9 ions, so the ions having d^1 to d^9 configuration • are coloured. On the other hand, the ions d^0 and d^{10} configuration do not show d-d transition.

9. Importance and Applications of Coordination Compounds

Hardness of water is estimated by simple titration with Na₂EDTA. The Ca²⁺ and Mg²⁺ ions form stable complexes with EDTA.

• Some important extraction processes of metals, like those of silver and gold make use of complex formation.

Similarly, purification of metals can be achieved through formation and ٠ subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_{4}]$, which is decomposed to yield pure nickel.

Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, [(PH₃P)₃RhCl], a Wilkinson catalyst, is used for the hydrogenation of alkenes.

Ligand	F-	Cl⁻	Br⁻	ľ	OH⁻	CN-	O ^{2–}	O ₂ ²⁻	0 ₂ -	CO ₃ ²⁻	PH_{3}
Name	fluoro	chloro	bromo	iodo	hy- droxo	cyano	охо	per- oxo	super-oxo	car-bon- ato	phos- phine
Ligand	SO ₄ ²⁻	NO ₂ -	ONO-	SCN-1	NCS	CH ₃ COO-	C5H5N	S ²⁻	S ₂ O ₃ ²⁻	NO ₃ -	SO ₃ ²⁻
Name	sulpha- to	nitro	nitrito	thiocy- anato	iso- thio- cyana- to	acetate	pyridine (Py)	sul- phido	thiosul- phato	nitrato	sulphi- to
Ligand	NC-	$(C_6H_5)_3P$	CS	NH_2^-	NH ²⁻	H ₂ NCSNH ₂	$C_2 O_4^{2-}$	H ₂ O	NH3	СО	NO
Name	isocy- ano	triphenyl phos- phine	thio- carbo- nyl	amido	imido	thiourea (tu)	oxalate (ox)	aqua	ammine	carbo- nyl	nitro- syl

Supplementary List of Ligands



Ethylene diamine triacetate ion EDTA³⁻

H₂NCH₂CH₂NHCH₂CH₂NH₂ Diethylenetriamine (diene) CH₂COO OII

$$CH_2 - N$$

 CH_2COO^-
 $CH_2 - N$
 CH_2COO^-
 CH_2COO^-

Ethylene diamine triacetate ion
$$EDTA^{3-}$$



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Q. 14.	Give one use of Ziegler Natta catalyst.						
Ans.	Heterogeneous catalysis or in high density polymerisation.						
Q. 15.	Name the metal present in :						
	(i) Chlorophyll (ii) Haemoglobin (iii) Vit. B-12						
	(iv) cis platin						
Ans.	(i) Mg (ii) Fe (iii) Co (iv) Pt						
Q. 16.	The chemical formula of Wilkinson's catalyst is :						
	$(C_6H_5)_3P.RhCl$ Which of the two is more stable – $K_4[Fe(CN)_6]$ Or $K_3[Fe(CN)_6]$?						
	$K_4[Fe(CN)_6]$ because Fe has d^6 configuration in this case.						
	How many moles of AgCl will be precipitated when an excess of AgNO ₃ is						
	added to a molar solution of [CrCl(H ₂ O) ₅]Cl ₂ ?						
Ans.	2 moles because 2 Cl ⁻ ions are present as counter ion in the complex.						
Q. 19.	Which type of ligands form chelates ?						
Ans.	Polydentate ligand.						
Q. 20.	Arrange the following complexes in order of increasing electrical conductivity :						
	[CO(NH ₃) ₃ Cl ₃], [Co(NH ₃) ₅ Cl]Cl ₂ , [Co(NH ₃) ₄]Cl ₃						
Ans.	$[CO(NH_3)_3Cl_3] < [Co(NH_3)_4]Cl_3 < [Co(NH_3)_5Cl]Cl_2$						
	More number of ions < more electrical conductivity						
SHO	RT ANSWER-I TYPE QUESTIONS (2 Marks)						
Q. 1.	Calculate the magnetic moments of the following complexes :						
	(i) $[Fe(CN)_{c}]^{-4}$ (ii) $[FeF_{c}]^{-3}$						
Ans.	(i) $Fe^{+2} \rightarrow 3d^6$. CN ⁻ is a strong ligand so e^- pair 4p, no unpaired e^- then magnetic moment						
	$\mu_{BH} = \sqrt{n(n+2)}$						
<i>n</i> =	= 5, So $\mu = \sqrt{n(n+2)}$						

$$\mu = \sqrt{5(5+2)}$$

$$\mu = \sqrt{35} = 5.96 \text{ BM}$$

- **Q. 2.** Explain the following :
 - (i) NH_3 act as a ligand but NH_4^+ does not.
 - (ii) CN⁻ is a ambidentate ligand.
- Ans. (i) NH_3 has one lone pair while NH_4^+ does not.
 - (ii) Because it has two donor atoms in a monodentate ligand.

Q. 3. Mention the main postulates of Werner theory.

- Ans. (i) Metal ion has two types of valency.
 - (ii) Primary valency and secondary valency.
 - (iii) Secondary valency is equal to coordination number.

Q. 4. Draw the structure of :



Q. 5. How does EDTA help as a cure for lead poisoning ?

- **Ans.** Calcium in Ca-EDTA complex is replaced by lead in the body. The more soluble compled lead-EDTA is eliminated in urine.
- Q. 6. Define homoleptic and heteroleptic complexes.
- Ans. Homoleptic : When metal atom/ion is linked with one type of ligands. Example, $[Ni(CO)_4]$.

Heteroleptic : With the more than one kind of ligands. Example, $[Co(NH_3)_4Cl_2]^+$.

- Q. 7. [NiCl₄]²⁻ is paramagnetic while [Ni(CO)₄] is diamagnetic though both are tetrahedral. Why ?
- **Ans.** In $[NiCl_4]^{-2}$, Ni has $3d^84s^0$ configuration, Cl⁻ can't pair up while in $[Ni(CO)_4]$, Ni has $3d^84s^2$ configuration, CO pair up electrons
- Q. 8. The oxidation number of cobalt in the complex :
 - (i) $K[Co(CO)_4]$ (ii) $[Co(C_2O_4)_3]^{-3}$

Ans. (i) -1 (ii) +3

- Q. 9. What are t_{2g} and e_{g} orbitals ?
- Ans. In a free transition metal ion, the *d*-orbitals are degenerate. When it form complex, the degeneracy is split and *d*-orbitals split into t_{2p} and e_p orbitals.
- Q. 10. What is the solution in which photographic film is washed ? What reaction takes place ?
- Ans. Hypo solution.

 $AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

Q. 11. What is spectrochemical series ?

Ans. The arrangement of ligands in order of their increasing crystal field splitting field strength.

- Q. 12. What are the assumptions of Crystal Field theory.
- Ans. (i) Ligand act as a point charge.
 - (ii) Metal ion has electrostatic attraction force with the ligand.(Or any other)
- Q. 13. $CuSO_4$ is colourless while $CuSO_4$.5H,O is coloured. Why?
- Ans. $CuSO_4$ does not has any ligand, so splitting of *d*-orbital take place while $CuSO_4.5H_2O$ has water ligand.
- Q. 14. What is the difference between inner and outer orbital complexes ?
- Ans. Inner sphere complex : When *d*-orbital of inner shell take part in hybridisation.Outer sphere complex : When *d*-orbital of outermost shell take part in hybridisation.
- Q. 15. How is stability of coordination compound determined in aqueous solution?
- Ans. By using stability constant.

More stability constant, more stability.

- Q. 16. In a complex ion [Co(NH₃)₅NO₂]Cl₂,
 - (i) Identify the ligand.
 - (ii) Oxidation number of metal ion.
- **Ans.** (i) NH_3 , NO_2 .

(ii) + 3

- Q. 17. Explain how the nature of ligand affects the stability of complex ion.
- Ans. Strong ligand : More stability

Weak ligand : Less stability

Q. 18. What is meant by denticity of a ligand ? Find out denticity of :

(i) $C_2 O_4^{-2}$ (ii) EDTA

Ans. The number of ligand group/coordinating group.

(i) 2 (ii) 6

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

- Q. 1. A coordination compound has the formula CoCl₃.4NH₃. It does not liberate NH₃ but forms a precipitate with AgNO₃. Write the structure and IUPAC name of the complex compound. Does it show geometrical isomerism ?
- **Ans.** Formula : $[Co(NH_3)_4Cl_2]Cl$

Name : Tetraaminedichloridocobalt(III) chloride Yes, it show geometrical isomerism.

- Q. 2. Why does a tetrahedral complex of the type [MA₂B₂] not show geometrical isomerism ?
- Ans. Because all position of tetrahedral is same in orientation.

- Q. 3. The molar conductivity of the complex CoCl₃.4NH₃.2H₂O is found to be same as that of 3 : 1 electrolyte. What is the structural formula. Name and number of geometrical isomer of the complex.
- Ans. As coordination number of Co is 6 and complex should be A_3B or AB_3 type, formula is $[Co(NH_3)_4(H_2O)_2]Cl_3$.

Name : Tetraaminediaqua cobalt (III) chloride

Geometrical isomer : 2 (cis and trans)

Q. 4. $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless. Why ?

- Ans. $[Ti(H_2O)_6]^{3+}$: In this core Ti⁺³ has one unpaired e^- while Sc⁺³ does not has any unpaired electron.
- Q. 5. Describe with an example of each, the role of coordination compounds in :
 - (i) Biological system
 - (ii) Analytical chemistry
 - (iii) Medicinal chemistry
- Ans. (i) Vit. B-12, it is a antipernicious anemia factor.
 - (ii) Determining and estimation of metal.
 - (iii) EDTA is used in lead poisoning.
- Q. 6. Write the type of isomerism exhibited by the following complexes :
 - (i) $[Co(NH_3)_5Cl]SO_4$
 - (ii) $[Co(en)_3]^{+3}$
 - (iii) $[Co(NH_3)_6][Cr(CN)_6]$
- Ans. (i) Ionization
 - (ii) Optical
 - (iii) Coordination isomerism

Q. 7. Explain the following :

- (i) CO is stronger ligand than NH₃.
- (ii) Low spin octahedral complexes of nickel are not known.
- (iii) Aqueous solution of $[Ti(H_2O)_6]^{+3}$ is coloured.
- Ans. (i) CO has high value of crystal field splitting energy than Cl.
 - (ii) Ni has d^8 configuration which does not affect by field strength of ligand.
 - (iii) In this case, Ti⁺³ has $t_{2g}^{1} e_{g}^{0}$ configuration. It can perform *d*-*d* transition.
- Q. 8. Write all the geometrical isomers of [Pt(NH₃)(Br)(Cl)(Py)] and how many of these will exhibit optical isomerism ? Here, Py = Pyridine.



Monodentate ligand in square planar complex do not show optical isomerism.

LONG ANSWER TYPE QUESTIONS (5 Marks)

- Q. 1. A metal ion M^{n+} having d^4 valence electronic configuration combines with three didentate ligands to form a complex compound. Assuming $\Delta_0 > p$:
 - (i) Draw the diagram showing *d*-orbital splitting during this complex formation.
 - (ii) What type of hybridisation will Mⁿ⁺ have ?
 - (iii) Name the type of isomerism exhibited by this complex.
 - (iv) Write the electronic configuration of metal Mⁿ⁺.
- **Ans.** (i) If $\Delta_0 > p$ then



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(ii) d^2sp^3
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(iii) $[M(AA)_3]$ type complex show optical isomerism.

(iv)
$$t_{2g}^{4} e_{g}^{0}$$

- Q. 2. (i) Discuss the nature of bonding in metal carbonyls.
 - (ii) Draw figure to show the splitting of *d*-orbitals in an octahedral crystal field and write electronic configuration of M^{s+} ion when :
 - (a) $p > \Delta_0$
 - (b) $\Delta_0 > p$
- Ans. (i) The metal carbon bond in metal carbonyls possess both σ and π character. The M – C σ bond if formed by the M \leftarrow C = O while M – C π bond if formed by the donation of a pair of electron from filled *d*-orbital of metal to antibonding π^* orbital of CO.



- Q. 3. (i) $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solution. Why ?
 - (ii) A complex is prepared by mixing CoCl₃ and NH₃ in the molar ratio of 1 : 4. 0.1M solution of this complex was found to be freeze at -0.372° C. What is the formula of the complex ? K_r = 1.86°C/M
- Ans. (i) In both the cases Fe is in + 2 state, it has 4 unpaired electrons but CN⁻ and H₂O has different crystal field splitting energy.
 - (ii) $\Delta T_f = i K_f m$

i = 2 means complex dissociate into two ions.

Hence the formula is [Co(NH₃)₄Cl₂]Cl

VALUE BASED QUESTIONS (4 Marks)

- **Q. 1.** A lots of children, working in a lead industry were rescued by NGO's activists. The children were sent to the hospital and found to be excess exposure to lead so called lead poisoning. Lead is very poisonous.
 - (i) Name the ligand (compound) used for treatment of lead poisoning.
 - (ii) Name the cell wherein lead is used.
 - (iii) Write the reaction involved for removal of lead from living organism.
 - (iv) During this rescue operation, which values are shown by NGO's activists?
- **Q. 2.** Cancer is not a communicable disease. It occurs due to unlimited growth of body cells leading to tumours. We should shake hands, eat together with people suffering from cancer. These activities boost up the confidence in them for living.
 - (i) Write the name of coordination compound used as a chemotherapeutic agent to curb the growth of tumours.
 - (ii) Draw the structure of this coordination compound.
 - (iii) How is copper poisoning treated by the use of Ca-EDTA complex ?
 - (iv) By showing such attitude to cancer patients, mention the values reflected by us.

