# Coordination Compounds

### Fastrack Revision

#### ► Coordination Compounds

A coordination compound contains a central metal atom or ion surrounded by number of oppositely charged ions or neutral molecules. These ions or molecules are re-bonded to the metal atom or ion by a coordinate bond.

Example: K<sub>4</sub>[Fe(CN)<sub>6</sub>].

They do not dissociate into simple ions when dissolved in water.

#### ▶ Double Salt

 When two salts in stoichiometric ratio are crystallised together from their saturated solution, they are called double salts.

Example: FeSO<sub>4</sub>.(NH<sub>a</sub>)<sub>2</sub>SO<sub>4</sub>, 6H<sub>2</sub>O(Mohr's salt)

 They dissociate into simple ions when dissolved in water.

#### Terms Related to Coordination Compounds

#### ► Coordination Entity

A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. Example: In K<sub>4</sub>[Fe(CN)<sub>6</sub>], [Fe(CN)<sub>6</sub>]<sup>4-</sup> represents coordination entity.

#### ► Central Atom or Ion

In a coordination entity, the atom/ion to which a fixed number of lons/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion.

**Example:** In  $K_4[Fe(CN)_6]$ ,  $Fe^{\circ}$  is the central metal ion.

#### ▶ Ligands

➤ A molecule, ion or group that is bonded to the metal atom or ion in a complex or coordination compound by a coordinate bond is called ligand.

➤ It may be neutral, positively or negatively charged. Examples: H<sub>2</sub>O, CN<sup>-</sup>, NO<sup>+</sup>, etc.

#### **▶** Donor Atom

An atom of the ligand attached directly to the metal is called the donor atom.

**Examples:** In the complex  $K_4[Fe(CN)_6]$ , CN is a donor atom.

#### ► Coordination Number

The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded.
Example: In the complex K₄[Fe(CN)₀], the coordination number of Fe is 6.

#### ► Coordination Sphere

➤ The central atom/ion and the ligands attached to it are enclosed in square brackets and are collectively termed as the coordination sphere.

**Examples:** In the complex  $K_4[Fe(CN)_6]$ ,  $[Fe(CN)_6]^{4-}$  is the coordination sphere.

#### ► Counter lons

 The ions present outside the coordination sphere are called counter ions.

**Examples:** In the complex  $K_4[Fe(CN)_6]$ ,  $K^\circ$  is the counterion.

#### ► Coordination Polyhedron

The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom.

**Examples:** [PtCl<sub>4</sub>]<sup>2-</sup> is square planar, Ni(CO)<sub>4</sub> is tetrahedral while [Cu(NH<sub>3</sub>)<sub>6</sub>]<sup>3 $\circ$ </sup> is octahedral.

- ▶ 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.
- ▶ **Denticity:** The number of ligating (linking) atoms present in ligand is called denticity.

#### Types of Ligands

#### ▶ On the Basis of Number of Donor Sites

#### 1. Unidentate Ligands

- The ligands whose only one donor atom is bonded to metal atom are called unidentate ligands.
- Examples: H<sub>2</sub>O, NH<sub>3</sub>, CO, CN

#### 2. Didentate Ligands

The ligands which contain two donor atoms or ions through which they are bonded to the metal ion.

Examples: Ethylenediamine (H2NCH2CH2NH2) has

two nitrogen atoms, oxalate ion  $\begin{pmatrix} COO^-\\I\\COO^- \end{pmatrix}$  has two

oxygen atoms which can bind with the metal atoms.

#### 3. Polydentate Ligand

When several donor atoms are present in a single ligand, the ligand is called polydentate ligand.

**Examples:** In N(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>, the ligand is said to be polydentate and ethylenediaminetetraacetate ion (EDTA<sup>4–</sup>) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

#### ▶ On the Basis of Linkage

#### 1. Chelate

- An inorganic metal complex in which there is a close ring of atoms caused by attachment of a ligand to a metal atom at two points.
- ➤ An example is the complex ion formed between ethylenediamine and cupric ion, [Cu(NH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup>.

#### 2. Ambidentate Ligand

➤ Ligands which can ligate (link) through two different atoms present in it are called ambidentate ligands.

**Examples:** NO<sup>2-</sup> and SCN<sup>-</sup>. Here, NO<sup>2-</sup> can link through N as well as O while SCN<sup>-</sup> can link through S as well as N atom.

#### Isomerism in Coordination Compounds

#### ► Structural Isomerism:

- (i) Ionisation Isomerism: When the complexes with same composition give different ions in solution. e.g.  $[Co(NH_3)_5 Br]SO_4$  and  $[Co(NH_3)_5 SO_4]Br$ .
- (ii) Solvate/Hydrate Isomerism: When complex differ in the number of water (solvent) molecules present as ligand, e.g. [Cr(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub>, [Cr(H<sub>2</sub>O)<sub>5</sub>Cl]Cl<sub>2</sub>.H<sub>2</sub>O and [Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>3</sub>]Cl·2H<sub>2</sub>O.
- (iii) Linkage Isomerism: When complexes differ only in the point of attachment of the ambidentate ligand with central metal atom. e.g. [Co(NH<sub>2</sub>)<sub>5</sub> (ONO)]<sup>2+</sup> and [Co(NH<sub>3</sub>)<sup>5</sup>(NO<sub>2</sub>)]<sup>2-</sup>.
- (iv) Coordination Isomerism: When the interchange of ligands take place between cationic and anionic entities of different metal ions present in a complex. e.g. [Co(en)<sub>3</sub>] [Cr(CN)<sub>6</sub>] and [Cr(en)<sub>1</sub>] [Co(CN)<sub>6</sub>].

#### **▶** Stereoisomerism

- (i) Geometrical Isomerism: When similar groups are present in adjacent position, it is *cls*. When they are present in opposite position it is *trans*. It occurs in square planar compound of type [MA<sub>2</sub>B<sub>2</sub>], [MA<sub>2</sub>BC], [M(AB)<sub>2</sub>] and octahedral complexes of type [MA<sub>4</sub>B<sub>2</sub>], [M(AA)<sub>2</sub>B<sub>2</sub>] or [M(AA)<sub>2</sub>BC] shows *fac* and *mer* geometrical isomers.
- (ii) Optical Isomerism: This is shown by complexes whose mirror images are non-super imposable. Such complexes are called optical isomers. It is shown by octahedral complexes and exists in two forms-laevo and dextro.

#### ► Uses of Coordination Compounds

- Coordination compounds provide critical insights into the functioning and structure of vital components of biological system.
- Coordination compounds also find extensive applications in metallurgical processes, analytical and medicinal chemistry.

#### Werner's Coordination Theory

The postulates of Werner's theory are:

 Metal shows two different kinds of valencies: primary valency and secondary valency.

- The ions/groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.
- The most common geometrical shapes in coordination compounds are octahedral, square planar and tetrahedral.

#### **Primary Valency**

- > This valency is normally ionisable.
- > It is equal to positive charge on central metal atom.
- These valencles are satisfied by negatively charged ions.

**Example:** In CrCl<sub>3</sub>, the primary valency is three. It is equal to oxidation state of central metal ion.

#### Secondary Valency

- > This valency is non-ionisable.
- The secondary valency equals the number of ligand atoms coordinated to the metal. It is also called coordination number of the metal.
- It is commonly satisfied by neutral and negatively charged, sometimes by positively charged ligands.
- ➤ Oxidation Number of Central Atom: The oxidation number of the central atom in a complex 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.
- ► Homoleptic Complexes: Those complexes in which metal or ion is coordinate bonded to only one kind of donor atoms.

**Example:**  $[CoCl_2(NH_3)_4]^*$ ,  $[Co(NH_3)_5Br]^{2*}$ 

#### Valence Bond Theory

- ➤ According to this theory, the metal atom or ion under the influence of ligands can use its (n - 1), 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.

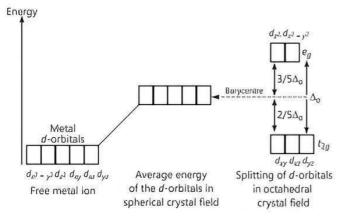
Coordination Number	Type of Hybridisation	Shape of Hybrid
4	sp³	Tetrahedral
4	dsp <sup>2</sup> sp <sup>3</sup> d	Square planar
5	sp³d	Trigonal bipyramidal
6	sp³d² (nd orbitals are involved—outer orbital complex or high spin or spin free complex)	
6	d <sup>2</sup> sp <sup>3</sup> (n – 1) d-orbitals are involved—inner orbital or low spin or spin paired complex)	

#### ▶ Magnetic Properties of Coordination Compounds

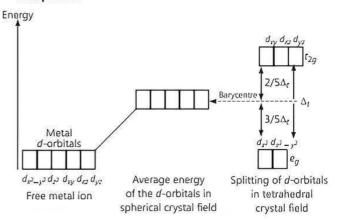
- A coordination compound is paramagnetic in nature if it has unpaired electrons and diamagnetic if all the electrons in the coordination compound are paired.
- Magnetic moment  $\mu = \sqrt{n(n+2)}$ , where n is number of unpaired electrons.

#### ► 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.
- > It is a theoretical assumption.
- ▶ Crystal Field Splitting in Octahedral Coordination Complexes:



#### ▶ Crystal Field Splitting in Tetrahedral Coordination Complexes:



- For the same metal, the same ligands and metalligand distances, the difference in energy between e and  $t_{2g}$  level is  $\Delta_t = \frac{4}{9} \Delta_0$
- $\boldsymbol{e_{q}}$  orbitals have higher energy in octahedral and lower energy in tetrahedral complexes.  $t_{2g}$  orbitals have higher energy in tetrahedral and lower energy in octahedral complexes.

#### ▶ Bonding in Metal Carbonyls

- Metal carbonyls are homoleptic complexes in which carbon monoxide (CO) acts as the ligand. Example:
- The metal-carbon bond in metal carbonyls possess both s and p character.
- The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

### **Practice** Exercise

### Multiple Choice Questions 🔰

- Q1. Heteroleptic complex is:
  - a. (Fe(CN)<sub>6</sub>)<sup>4</sup>-
- b.  $(Co(NH_9)_9SO_4)^+$
- c. [Hgl,]2-
- d.  $(Co(NH_p)_c)^{3+}$
- Q 2. The coordination number of Co in [Co(en), Cl,]Cl is:

- Q 3. What is the secondary valency of cobalt in [Co(en,)Cl,]+? (CBSE 2023)
- c. 2
- d. 8
- Q4. In which of the following does the central atom exhibit an oxidation state of +3? (CBSE 2023)
  - a. K<sub>2</sub>(Ni(CN)<sub>4</sub>)
- b. K<sub>4</sub>[Fe(CN)<sub>6</sub>]
- c.  $[Fe(C_2O_4)_3]^3$ -
- d. (Cu(NH<sub>2</sub>)<sub>0</sub>)<sup>2</sup>

  √
- Q 5. The oxidation number of Cr in  $[Cr(H_2O)_4Cl_2]^+$  ion is:

- Q 6. The oxidation state of Fe in [Fe(CO)<sub>s</sub>] is:
  - (CBSE 2023)

- a. + 2
- b. 0
- C + 3
- d. +5

- Q7. When 1 mol CrCl<sub>3</sub>· 6H<sub>2</sub>O is treated with excess of AgNOx, 3 mol of AgCl are obtained. The formula of the complex is: (NCERT EXEMPLAR)
  - a.  $(CrCl_3 (H_2O)_3) \cdot 3H_2O$  b.  $(CrCl_2 (H_2O)_4) \cdot Cl \cdot 2H_2O$
  - c. (CrCl (H<sub>2</sub>O)<sub>6</sub>) Cl<sub>2</sub>· H<sub>2</sub>O d. (Cr (H<sub>2</sub>O)<sub>6</sub>) Cl<sub>3</sub>
- Q 8. Which of the following ligands is an ambidentate Ugand? (CBSE 2023)
  - a. CO
- b. NO<sub>2</sub>
- c. NH<sub>a</sub>
- d. H<sub>2</sub>O
- Q 9. Which of the following is a polydentate ligand? (CBSE 2023)

  - b. H<sub>2</sub>N CH<sub>2</sub> CH<sub>2</sub> NH<sub>2</sub>
  - c. EDTA4-
  - d. C<sub>2</sub>O<sub>2</sub><sup>2</sup>-
- Q 10. A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent? (NCERT EXEMPLAR)
  - a. Thiosulphato
- b. Oxalato
- c. Glycinato
- d. Ethane-1.2 diamine

Q 11.	The stabilisation of co to chelation is called t the following is the mo	the c	helate effect. Wh	ich of ecies?
	a. [Fe(CO) <sub>s</sub> ]	h l	(Fe(CN) <sub>6</sub> ) <sup>3-</sup>	iii Dariy
			(Fe(H <sub>2</sub> O) <sub>6</sub> ) <sup>3+</sup>	
0.12	Indicate the complex io		The state of the s	etrical
4 11.	isomerism:	JII **I	(NCERT EXEM	
	a. (Cr(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ) <sup>+</sup>	b. I	Day to style of the second of	
			(Co(CN) <sub>5</sub> (NC)) <sup>3</sup> -	
0 13.	The compounds			and
	[Co(SO <sub>4</sub> ) (NH <sub>3</sub> ) <sub>5</sub> ] Cl rep			
			ERT EXEMPLAR, CBSE	2023)
	a. linkage isomerism			
	b. lonisation isomerism	1		
	c. coordination isomer	ism		
	d. no isomerism			
Q 14.	Which of the following	g co	ordination comp	ounds
	exhibits linkage isomer	rism	? (CBSE	2023)
	a. $(Co(NH_3)_3Cl_3)$			
	b. $(Co(NH_3)_5(CO_3))Cl$			
	c. $(Co(NH_3)_5NO_2)(NO_3)_2$			
	d. (Co(en) <sub>3</sub> )Cl <sub>3</sub>			
Q 15.	The compounds [Cr(H <sub>2</sub>	0)60	Cl <sub>3</sub> , [Cr(H <sub>2</sub> O) <sub>5</sub> Cl]C	12·H2O
	and [Cr(H2O)4Cl2]Cl·2H	20 e	xhibit: (CBSE	2023)
	a. linkage isomerism			
	b. geometrical isomeris	sm		
	c. lonisation isomerism	1		
	d. hydrate isomerism			
Q 16.	The number of stereois	some	ers of [Pt(NH3)2 Cl	<sub>2</sub> ] is:
	a. 1	b	2	
	c. 4	d. :	3	
Q 17.	Match the column I wi appropriate choice:	ith c	olumn II and ma	rk the
		14.		

# 16

Co	lumn I (Complex)	(	Column II (Isomerism)
	$(Co(NH_3)_6Cr(CN)_6)$	(1)	Geometrical isomerism
(B)	$(Co(en)_2(NO)_2CI)Br$	(ii)	Optical isomerism
(C)	(Pt(en) <sub>2</sub> Cl <sub>2</sub> )	(iii)	Coordination isomerism
(D)	$(Cr(CN)_2(NH_3)_4)^{2+}$	(iv)	Linkage isomerism

- b. (A)  $\rightarrow$  (ii). (B)  $\rightarrow$  (iii). (C)  $\rightarrow$  (i). (D)  $\rightarrow$  (iv)
- c. (A)  $\rightarrow$  (iii), (B)  $\rightarrow$  (iv), (C)  $\rightarrow$  (ii). (D)  $\rightarrow$  (i)
- d. (A)  $\rightarrow$  (I). (B)  $\rightarrow$  (III). (C)  $\rightarrow$  (IV). (D)  $\rightarrow$  (II)
- Q18. The number of unpaired electron of Fe in the complex compound  $[Fe(H_2O)_6]^{2^{+}}$  is:
  - a. 2

b. 3

c. 4

- d. None of these
- Q 19. The formula of the complex iron (III) hexacyanidoferrate (II) is: (CBSE 2023)
  - a.  $Fe_2(Fe(CN)_6)_3$
- b. Fe<sub>4</sub>(Fe(CN)<sub>6</sub>)<sub>3</sub>
- c. Fe(Fe(CN)<sub>6</sub>)
- d. Fea(Fe(CN)<sub>6</sub>)<sub>2</sub>

Q 20. The formula of the complex dichloridobis (ethane-1, 2-diamine) platinum (IV) nitrate is:

- a.  $[PtCl_2(en)_2(NO_3)_2]$  b.  $[PtCl_2(en)_2](NO_3)_2$
- c.  $[PtCl_2(en)_2(NO_3)]NO_3$  d.  $[Pt(en)_2(NO_3)_2]Cl_2$
- Q 21. The colourless complex ion among the following
  - a.  $[Cu(NH_3)_4]^{2+}$

b. [Zn(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>

c.  $[Fe(H_2O)_6]^{3+}$ 

d.  $[Fe(CN)_6]^{3-}$ 

- Q 22. Give reason for the statement,  $[Ni(CN)_{\alpha}]^{2-}$  is diamagnetic while  $[NiCl_4]^{2-}$  is paramagnetic in
  - a. In (NICL<sub>6</sub>)<sup>2-</sup>, no unpaired electrons are present while in  $(Ni(CN)_4)^2$  two unpaired electrons are
  - b. In  $(NI(CN)_6)^{2-}$ , no unpaired electrons are present while in  $[NICl_{\alpha}]^{2-}$  two unpaired electrons are present
  - c. [NICl<sub>ss</sub>]<sup>2-</sup> shows dsp<sup>2</sup> hybridisation hence it is paramagnetic.
  - d.  $(Ni(CN)_a)^{2-}$  shows  $sp^3$  hybridisation hence it is diamagnetic.
- Q 23. The CFSE of  $[CoCl_c]^{3-}$  is 18000 cm<sup>-1</sup> the CFSE for [CoCl<sub>4</sub>] will be: (CBSE SQP 2022-23)
  - a. 18000 cm<sup>-1</sup>

b. 8000 cm<sup>-1</sup>

c. 2000 cm<sup>-1</sup>

d. 16000 cm<sup>-1</sup>

Q 24. The crystal field splitting energy in tetrahedral crystal field ( $\Delta$ ,) is equal to: (CBSE 2023)

a. 
$$\frac{4}{9}\Delta_0$$
 b.  $\frac{9}{4}\Delta_0$  c.  $\frac{4}{3}\Delta_0$  d.  $2\Delta_0$ 

- Q 25. The magnitude of CFSE (crystal field splitting energy,  $\Delta_o$ ) can be related to the configuration of d-orbital in a coordination entity as:
  - a. if  $\Delta_0 < P_1$  the configuration is  $t_{20}^3 e_0^1 = \text{weak field}$ ligand and high spin complex
  - b. If  $\Delta_0 > P$ , the configuration is  $t_{2g}^3 e_g^1 = \text{strong field}$ ligand and low spin complex
  - c. If  $\Delta_0 > P$ , the configuration is  $\mathfrak{t}_{2g}^4 e_g^0 = \text{strong field}$ ligand and high spin complex
  - d. if  $\Delta_0 = P$ , the configuration is  $t_{2g}^{\Delta} e_g^0 = \text{strong field}$ ligand and high spin complex

### Assertion & Reason Type Questions >

Directions (Q. Nos. 26-35): Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:

- a. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
- b. Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
- c. Assertion (A) is true but Reason (R) is false.
- d. Assertion (A) is false but Reason (R) is true.

**Q 26.** Assertion (A): Toxic metal ions are removed by the chelating ligands.

**Reason (R):** Chelate complexes tend to be more stable. (NCERT EXEMPLAR)

**Q 27.** Assertion (A):  $[Cr(H_2O)_6]Cl_2$  and  $[Fe(H_2O)_6]Cl_2$  are reducing in nature.

**Reason (R):** Unpaired electrons are present in their *d*-orbitals. (NCERT EXEMPLAR)

**Q 28.** Assertion (A): Complexes of MX<sub>6</sub> and MX<sub>5</sub>L type (X and L are unidentate) do not show geometrical isomerism.

**Reason (R):** Geometrical isomerism is shown by complexes with coordination number 6.

Q 29. Assertion (A): Linkage isomerism arises in coordination compounds containing ambidentate ligand.

**Reason (R):** Ambidentate ligand has two different donor atoms. (NCERT EXEMPLAR)

Q 30. Assertion (A): EDTA is used to determine hardness of water.

Reason (R): EDTA is a bidentate ligand. (CBSE 2023)

**Q 31.** Assertion (A): [Fe(CN)<sub>6</sub>]<sup>3-</sup> ion shows magnetic moment corresponding to two unpaired electrons.

**Reason (R):** Because is has  $d^2 sp^3$  type hybridisation. (NCERT EXEMPLAR)

Q 32. Assertion (A):  $[Cu(NH_3)_4]^{2+}$  is coloured while  $[Cu(CN)_4]^{2+}$  ion is colourless.

**Reason (R):**  $[Cu(NH_3)_4]^3$  has  $dsp^2$  hybridisation.

**Q 33.** Assertion (A):  $[Ni(CN)_4]^{2-}$  has square planar and  $[NiCl_4]^{2-}$  has tetrahedral shape.

**Reason (R):**  $[Ni(CN)_4]^{2-}$  is diamagnetic while  $[NiCl_4]^{2-}$  is paramagnetic.

Q 34. Assertion (A): Low spin tetrahedral complexes are rarely observed.

**Reason (R):** Crystal field splitting energy is less than pairing energy for tetrahedral complexes.

(CBSE 2023)

**Q 35.** Assertion (A): In tetrahedral complexes, low spin configurations are rarely observed.

Reason (R): 
$$\Delta_t = \left(\frac{4}{9}\right) \Delta_0$$

#### **Answers**

1. (b) [Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>)<sup>+</sup>



Complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic.

2. (d) 6

In the given complex, Co is bound with two bidentate ligand (en) and two unidentate ligand (Cl)

 $\therefore$  Coordination number =  $2 \times 2 + 2 \times 1 = 4 + 2 = 6$ 

- 3. (a) The en (ethylene diamine) ligand is a bidentate ligand which means that it can form two coordinate covalent bonds with the cobalt ion. Two en forms two coordinate covalent bonds each with cobalt and two bonds are made with Cl. Hence, the secondary valency of cobalt is 6.
- 4. (c) [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3</sup>-
- 5. (a) 3

Let oxidation number of Cr be x.

Oxidation number of  $H_2O=0$ , oxidation number of Cl  $\omega=1$ 

**6.** (b) Let the oxidation number of Fe in Fe(CO)<sub>5</sub> be *x*. Carbonyl is a neutral ligand having no charge. So, the oxidation number of Fe would be

$$x - 0 \times 5 = 0$$

or,

$$x = 0$$

Hence, the oxidation number of iron in this complex is  $\Omega$ .

**7**. (d)  $(Cr (H_2O)_6) Cl_3$ 

- **8.** (b) NO<sub>2</sub> is an ambidentate ligand because it can attach to the central metal atom through atoms of two different elements.
- 9. (c) EDTA4-
- 10. (a) Thiosulphato
- 11. (c)  $Fe(C_2O_4)_3$ ]<sup>3-</sup>

C<sub>2</sub>O<sub>4</sub><sup>2-</sup> (oxalate) is bidentate ligand and forms chelate complexes which are more stable than similar complexes containing unidentate ligands.

12. (a)  $(Cr(H_2O)_4 Cl_2)^+$  $(Cr(H_2O)_4 Cl_2)^+$  is a  $(ML_4X_2)$  type complex compound which shows geometrical isomerism.

13. (d) no isomerism



Isomers are two or more compounds that have the same chemical formula but a different arrangement of atoms.

The given compounds represents no isomerism as they have different formula.

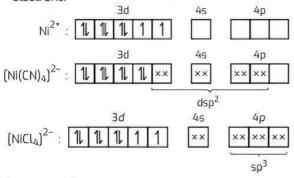
- 14. (c) The NO<sub>2</sub> group can link using oxygen atom as ONO, hence it can show linkage isomerism.
- 15. (d) In the given compounds, the number of water molecules present in the coordination sphere and in the ionisation sphere is different. Hence, they exhibit hydrate isomerism.
- 16. (b) 2
- 17. (c) (A)  $\rightarrow$  (iii), (B)  $\rightarrow$  (iv), (C)  $\rightarrow$  (ii). (D)  $\rightarrow$  (I)
- 18. (c) 4
- 19. (b) Fe<sub>4</sub>[Fe(CN)<sub>e</sub>]<sub>3</sub>
- **20**. (b) [Pt Cl<sub>2</sub>(en)<sub>2</sub>] (NO<sub>3</sub>)<sub>2</sub>

#### 21. (b) [Zn(NH<sub>3</sub>)<sub>6</sub>]<sup>2</sup>

Complex ion	Colour
$(Cu(NH_3)_4)^{2+}$	Deep/Royal blue
$(Zn(NH_{3})_{4})^{2+}$	Colourless
(Fe(H <sub>2</sub> O) <sub>6</sub> ) <sup>3+</sup>	Brown rust
(Fe(CN) <sub>6</sub> ) <sup>3</sup> -	Red

22. (b) In (Ni(CN)<sub>a</sub>)<sup>2-</sup>, no unpaired electrons are present while in [NiCl<sub>4</sub>]<sup>2-</sup> two unpaired electrons are present.

> In (Ni(CN)<sub>4</sub>)<sup>2-</sup> there is no unpaired electrons because CN is a strong field ligand thus it pair up the electrons



#### 23. (b) 8000 cm<sup>-1</sup>

((CoCl<sub>6</sub>)<sup>3-</sup> and (CoCl<sub>4</sub>)<sup>-</sup> have octahedral and tetrahedral geometries respectively.

For  $((CoCl_6)^{3-}$ , the CFSE  $\Delta_0 = 18000 \text{ cm}^{-1}$ .

The relationship between the crystal field stabilisation energies for octahedral tetrahedral field is

$$\Delta_1 = 4/9D_0$$

Substituting value in the above expression, we

 $(CoCl_{\omega})^{-} = 4/9 \times 18000 \text{ cm}^{-1} = 8000 \text{ cm}^{-1}$  $\Delta_r = (4/9) \times 18000 \text{ cm}^{-1} = 8000 \text{ cm}^{-1}$ 

## **24.** (a) $\frac{4}{9}\Delta_0$

- **25.** (b) if  $\Delta_0 > P$ , the configuration is  $t_{20}^3 e_g^1 = \text{strong field}$ ligand and low spin complex If CFSE  $(\Delta_0)$ < P (Energy required for pairing), the electrons do not pair up and fourth electron goes to  $e_a$  of higher energy. Hence, high spin complex is formed. Pairing of electrons does not take place in case of weak field ligands.
- 26. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
- 27. (b) Both are reducing in nature as the unpaired electrons get paired up by reduction thus gaining electrons. Hence, reason is not the correct explanation of assertion.
- 28. (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
- 29. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

- **30**. (c) EDTA is a hexadentate ligand and is used to remove hardness of water. Hence, assertion is true but reason is false.
- **31.** (d) [Fe(CN)<sub>c</sub>]<sup>3</sup>— ion shows magnetic moment corresponding to one unpaired electron. Hence, assertion (A) is false but  $[Fe(CN)_c]^{3-}$  has  $d^2sp^3$ hybridisation, is true.
- 32. (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
- 33. (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
- **34**. (a) Crystal field stabilisation energy for tetrahedral complexes is less than pairing energy. As Δ, < pairing energy, so electron occupies a higher energy orbital because less energy is required than occupying a lower energy orbital and pairing with another electron. Hence, electron does not pair up to form low spin complexes.
- 35. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

Case Study 1

### Case Study Based Questions >

Co-ordination compounds show structural isomerism and it is different from the nature of the isomerism which we generally come across in organic compounds. The structural isomers may be classified as ionisation, hydrate, co-ordination and linkage isomers depending upon their nature. The electrical conductivity of these isomers depends upon the number of ions which they furnish upon dissociation in aqueous solution. The isomers belonging to a particular type can also be distinguished from each other with the help of certain tests. In addition to the structural isomerism, the co-ordination compounds are also involved in geometrical and optical isomerism.

### Read the given passage carefully and give the answer of the following questions:

Whereas optical isomerism is normally shown

by octahedral complexes, both octahedral and

square planer complexes can exhibit geometrical

- Q1. An aqueous solution of CoCl<sub>2</sub> on addition of excess of concentrated HCl turns blue due to the formation of:
  - a.  $(Co(H<sub>2</sub>O)_{\Lambda}CI_{2})$
- b. (Co(H<sub>2</sub>O)<sub>4</sub>Cl<sub>4</sub>)<sup>2</sup>-
- c. (CoCl<sub>4</sub>)2-

isomerism.

- d.  $(Co(H_2O)_2Cl_2)$
- Q 2. Which one is the most likely structure of CrCl<sub>3</sub>6·H<sub>2</sub>O if 1/3 of the total chlorine in the compounds is precipitated by adding AgNO, solution?
  - a. CrCl<sub>3</sub>·6H<sub>2</sub>O
- b. (Cr(H<sub>2</sub>O)<sub>3</sub>)Cl<sub>3</sub>)(H<sub>2</sub>O)<sub>3</sub>
- c. (Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>)Cl<sub>2</sub>H<sub>2</sub>O d. (Cr(H<sub>2</sub>O)<sub>6</sub>Cl)Cl<sub>2</sub>H<sub>2</sub>O

- Q 3. One mole of the complex compound Co(NH)<sub>5</sub>Cl<sub>3</sub> gives 3 mole of ions on dissolution in water. One mole of the same complex reacts with two moles of AgNO<sub>3</sub> to yield two moles of AgCl(s). The structure of the complex is:
  - a.  $(Co(NH_3)_3Cl_3).2NH_3$  b.  $(Co(NH_3)_4Cl_2)Cl.NH_3$
  - c. (Co(NH<sub>3</sub>)<sub>4</sub>Cl)Cl<sub>2</sub>.NH<sub>3</sub> d. <math>(Co(NH<sub>3</sub>)<sub>5</sub>Cl)Cl<sub>2</sub>
- Q 4. Which of the following will not show geometrical isomerism?
  - a. (Cr(NH<sub>3</sub>)<sub>A</sub>Cl<sub>2</sub>)Cl
- b. (CoCl<sub>2</sub>(en)<sub>2</sub>Cl
- c.  $(Co(NH_3)_5NO_2)Cl_2$
- d.  $[Pt(NH_3)_2Cl_2]$ .

#### **Answers**

- 1. (c) (CoCl<sub>6</sub>)2-
- 2. (c) [Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>]Cl·2H<sub>2</sub>O
- 3. (d) (Co(NH<sub>2</sub>)<sub>5</sub>Cl)Cl<sub>2</sub>
- 4. (c) (Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>)Cl<sub>2</sub>

#### Case Study 2

Metal complexes show different colours due to d-d transitions. The complex absorbs light of specific wavelength to promote the electron from  $t_{2g}$  to  $e_g$  level. The colour of the complex is due to the transmitted light, which is complementary of the colour absorbed.

The wave number of light absorbed by different complexes of Cr ion are given below:

Complex	Wave number of light absorbed (cm <sup>-1</sup> )	Energy of light absorbed (kJ/mol)
(CrA <sub>6</sub> )³-	13640	163
(CLB <sup>6</sup> )3+	17830	213
(CrC <sub>0</sub> )3°	21680	259
(CLD <sup>e</sup> ) <sub>3</sub> -	26280	314

Read the given passage carefully and give the answer of the following questions:

(CBSE SQP 2023-24)

Q1. Out of the ligands 'A', 'B', 'C' and 'D', which ligand causes maximum crystal field splitting? Why?

OR

Which of the two, 'A', or 'D' will be a weak field ligand? Why?

- Q 2. Which of the complexes will be violet in colour? [CrA<sub>6</sub>]<sup>3-</sup> or [CrB<sub>6</sub>]<sup>3+</sup> and why? (Given: If 560-570 nm of light is absorbed, the colour of the complex observed is violet.)
- Q 3. If the ligands attached to Cr<sup>3+</sup> ion in the complexes given in the table above are water, cyanide ion, chloride ion and ammonia (not in this order)

Identify the ligand, write the formula and IUPAC name of the following:

(i) [CrA<sub>6</sub>]3+

(ii) [CrC<sub>6</sub>]3+

#### Answers

1. 'D' causes maximum crystal field splitting. Energy is directly proportional to the wave number. Maximum energy of light is required for an electron to jump from  $t_{2a}$  to  $e_a$  in case of  $(CrD_6)^{3-}$ .

OR

'A' will be a weak field ligand. The splitting caused is least in this case as the energy required for electron to jump from  $t_{2g}$  to  $e_g$  is minimum.

- 2.  $(CrB_6)^{3\circ}$  will be violet in colour because wavelength of light absorbed is 1/17830 = 560nm for the complex while 1/13640 = 733nm for  $(CrA_6)^{3-}$  complex.
- 3. (i) (CrCl<sub>6</sub>)<sup>3−</sup>, Hexachloridochromate (III) ion
  - (ii)  $(Cr(NH_3)_6)^{3\circ}$ , Hexaamminechromium (III) ion

 $A = Cl^{-}$ ,  $B = H_{2}O$ ,  $C = NH_{3}$ ,  $D = CN^{-}$ 

#### Case Study 3

In coordination compounds, metals show two types of linkages, primary and secondary. Primary valencies are ionisable and are satisfied by negatively charged ions. Secondary valencies are non-ionisable and are satisfied by neutral or negative ions having lone pair of electrons. Primary valencies are non-directional while secondary valencies decide the shape of the complexes.

Read the given passage carefully and give the answer of the following questions: (CBSE 2023)

- Q 1. If PtCl<sub>2</sub>. 2NH<sub>3</sub> does not react with AgNO<sub>3</sub>, what will be its formula?
- Q 2. What is the secondary valency of  $[Co(en)_{\tau}]^{3+}$ ?
- Q 3. (i) Write the formula of Iron (III)

  Hexacyanidoferrate (II).
  - (ii) Write the IUPAC name of [Co(NH<sub>3</sub>)<sub>5</sub>Cl] Cl<sub>2</sub>.

OR

Write the hybridisation and magnetic behaviour of  $[Ni(CN)_4]^{2-}$ .

[Atomic number: Ni = 28]

#### Answers

- 1. If PtCl<sub>2</sub>.2NH<sub>3</sub> does not react with AgNO<sub>3</sub>, then the formula of the compound would be (Pt (NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>).
- The secondary valency of (Co(en)<sub>3</sub>)<sup>3+</sup> is 6 as there are 4 NH<sub>3</sub> molecules and 2Cl<sup>-</sup> ions linked to the cobalt atom.
- 3. (i) The formula is Fe<sub>4</sub> (Fe(CN)<sub>6</sub>)<sub>3</sub>.
  (ii) The ILIPAC name of (Co(NH.), CI) Cl. is pent

(ii) The IUPAC name of  $(Co(NH_3)_5Cl)Cl_2$  is pentaammine chlorido cobalt (III) chloride.

OR

In the presence of strong field CN $^-$  ions, all the electrons are paired up. The empty 3d, 3s and two 4p orbitals undergo dsp $^2$  hybridisation to make bonds with CN $^-$  ligands in square planar geometry. Hence,  $(Ni(CN)_4)^{2-}$  is diamagnetic.

### Case Study 4

Coordination compounds are widely present in the minerals, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems and medicine. Alfred Werner's theory postulated the use of two types of linkages (primary and secondary), by a metal atom/ ion in a coordination compound. He predicted the geometrical shapes of a large number of coordination entities using the property of isomerism. The Valence Bond Theory (VBT) explains the formation, magnetic behaviour and geometrical shapes of coordination compounds. It, however, fails to describe the optical properties of these compounds. The Crystal Field Theory (CFT) explains the effect of different crystal fields (provided by the ligands taken as point charges) on the degeneracy of d-orbital energies of the central metal atom/ion.

# Read the given passage carefully and give the answer of the following questions: (CBSE 2023)

- Q1. When a coordination compound NiCl<sub>2</sub>.6H<sub>2</sub>O is mixed with AgNO<sub>3</sub> solution, 2 moles of AgCl are precipitated per mole of the compound. Write the structural formula of the complex and secondary valency for Nickel ion.
- Q 2. Write the IUPAC name of the ionisation isomer of  $[Co(NH_3)_5(SO_4)]$  Cl.
- Q 3. Using valence bond theory, predict the geometry and magnetic nature of:
  - (i) [Ni(CO)<sub>4</sub>]
  - (ii) [Fe(CN)<sub>6</sub>]<sup>3-</sup>

[Atomic number: Ni = 28, Fe = 26]

OR

#### Give reasons:

- (i) Low spin tetrahedral complexes are not formed.
- (ii)  $[Co(NH_3)_6]^{3+}$  is an inner orbital complex whereas  $[Ni(NH_3)_6]^{2+}$  is an outer orbital complex. [Atomic number: Co = 27, Ni = 28]

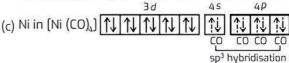
#### Answers

- 1. The structural formula of the complex is  $(Ni(H_2O)_6)Cl_2$  and the secondary valency for nickel ion is 6 in it.
- **2.** The IUPAC name of the ionisation isomer of  $(Co(NH_3)_g(SO_4))Cl$  is pentaammine sulphato cobalt (III) chloride.
- **3**. (i) In  $(Ni(CO)_4)$ , oxidation state of Ni is zero.

(b) NI atom after the rearrangement in presence of strong CO ligands.

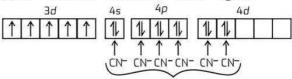


Co causes pairing of 4 electrons into 3*d*-orbitals.



It is diamagnetic as all the electrons present in it are paired.

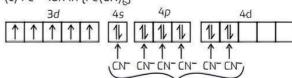
- (ii) We have  $_{26}Fe = (Ar)3d^64s^2$  $Fe^{3*} lon = (Ar)3d^5$
- (a)  $Fe^{3+}$  ion 3d 4s 4P 4d
- (b) Fe3+ ion under influence of weak F ligand



sp3d2 hybridisation

It is strongly paramagnetic in nature.

(c)  $Fe^{3}$  lon ln  $(Fe(CN)_6)^{3}$ 



Thus,  $(Fe(CN)_6)^{3-}$  is strongly paramagnetic in nature with  $sp^3d^2$  hybridisation.

OR

- (i) For tetrahedral complexes, the crystal field stabilisation energy is lower than pairing energy, so they are rarely formed in low spin state.
- (ii) As inner d-electrons are involved in the complex  $(Co(NH_3)_6)^{3+}$ , it is an inner orbital complex. But outer (4d) electrons are involved in the hybridisation of the complex  $(Ni(NH_3)_6)^{3+}$  so, it is an outer orbital complex.

## Very Short Answer Type Questions

- Q 1. Calculate the effective atomic number of iron in  $[Fe(CN)_6]^{3-}$ . [Atomic number of Fe = 26]
- Ans. Effective atomic number of Iron in  $(Fe(CN)_{\varepsilon})^{3-}$  can be calculated as:

Effective atomic number of Iron

atomic number of Fe—oxidation number of Fe
 + 2 × coordination number (or no. of ligands)
 26 − (+ 3) + 2 × 6 ≈ 26 − 3 + 12 ≈ 35.

- Q 2. When excess of AgNO<sub>3</sub> is added to the molar solution of [CrCl(H<sub>2</sub>O)<sub>5</sub>]Cl<sub>2</sub>, how many moles of AgCl get precipitated?
- Ans. Since the compound (complex) contains two CI<sup>-</sup> ions out of the coordination sphere. So these react with AgNO<sub>3</sub> solution to give 2 moles of AgCL

Q 3. Arrange the following complexes in the increasing order of conductivity of their solution:

 $[\operatorname{Co}(\operatorname{NH}_3)_3\operatorname{Cl}_3], \qquad [\operatorname{Co}(\operatorname{NH}_3)_4\operatorname{Cl}_2]\operatorname{Cl},$ 

[Co (NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub>, [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> (NCERT EXEMPLAR)

Ans. All the given complexes are octahedral complexes. The conductivity of solutions of complexes depend upon the number of ions given by the complex in the solution. Thus, the correct order of conductivity is:

 $\frac{\left(\text{Co}\left(\text{NH}_{3}\right)_{3}\text{Cl}_{3}\right)<\left(\text{Co}\left(\text{NH}_{3}\right)_{5}\text{Cl}\right)\text{Cl}_{2}}{<\left(\text{Co}\left(\text{NH}_{3}\right)_{4}\text{Cl}_{2}\right)\text{Cl}<\left(\text{Co}\left(\text{NH}_{3}\right)_{6}\right)\text{Cl}_{3}}$ 

- Q 4. A coordination compound CrCl<sub>3</sub>.4H<sub>2</sub>O precipitates silver chloride when treated with silver nitrate. The molar conductance of its solution corresponds to a total of two ions. Write structural formula of the compound and name it.

  (NCERT EXEMPLAR)
- **Ans.** Since, the molar conductivity of the solution of the complex corresponds with two ions, this means that it contains a complex ion and a counter ion. Formation of silver chloride with AgNO<sub>3</sub> shows that the counter ion is chloride ion.

Thus, the structure of the complex is as follows:  $[Cr(H_2O)_4Cl_2]^+Cl^-:$  tetraaquadichloridochromate(III) chloride.

- Q 5. Explain the structural isomerism of coordination compounds with suitable example.
- Ans. The isomerism which arises due to different structural arrangement in the coordination compounds having same molecular formula is called structural isomerism. e.g., for the molecular formula [Pt(NH<sub>3</sub>)<sub>4</sub> Cl<sub>2</sub>Br<sub>2</sub> the two possible structural isomers are [Pt(NH<sub>3</sub>)<sub>4</sub> Cl<sub>2</sub>] Br<sub>2</sub> and [Pt(NH<sub>3</sub>)<sub>4</sub> Br<sub>2</sub>] Cl<sub>2</sub>.
- Q 6. Write the IUPAC name of Ionisation isomer of [(NH<sub>3</sub>)<sub>3</sub> PtNO<sub>2</sub>]Cl.
- Ans. Ionisation isomer of  $((NH_3)_3PtNO_2)Cl$  is  $(Pt(NH_3)_3Cl)$   $NO_2$ . Its IUPAC name is <u>triamminechloridoplatinum</u> (II) nitrate.
- Q 7. Write the IUPAC name of ionisation isomer of [Pt(NO<sub>2</sub>)(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>2</sub>]Br.
- Ans. Ionisation isomer of  $(Pt(NO_2) (H_2O) (NH_3)_2)$  Br is  $(Pt(H_2O)(NH_3)_2Br)NO_2$ . Its IUPAC name is diammine-aquabromidoplatinum (II) nitrate.
- Q 8. The most stable complex among the following is:

(i) [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>

(ii) [Fe(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>

(iii)  $[Fe(C_2O_4)_3]^{3-}$  (iv)  $[FeCl_6]^{3-}$ 

- Ans. In the given complexes, Fe is in +3 oxidation state. Since  $C_2O_4^{2-}$  is a bidentate chelate ligand. It forms chelate ring. So, complex given in option (iii) is most stable.
- Q 9. Calculate the overall complex dissociation equilibrium constant for the  $Cu(NH_3)_4^{2+}$  ion, given that  $\beta_4$  for this complex is  $2.1 \times 10^{13}$ . (NCERT INTEXT)
- **Sol.** Overall dissociation constant is the inverse of overall stability constant.

Thus, overall dissociation constant =  $\frac{1}{\beta_4} = \frac{1}{2.1 \times 10^{13}}$ 

 $= \underline{4.7 \times 10^{-14}}.$ 

- Q 10. What type of isomerism is shown by complex [Co(NH<sub>2</sub>)<sub>5</sub>Cl]SO<sub>4</sub>? (CBSE 2019)
- Ans. Ionisation isomerism.
- Q 11. Arrange the following in increasing order of crystal field splitting energy: (CBSE 2019)

 $[Cr(CN)_{6}]^{3-}$ ,  $[Cr(NH_{3})_{6}]^{3+}$ ,  $[CrCl_{6}]^{3-}$ 

- **Ans.**  $(CrCl_6)^{3-} < (Cr(NH_2)_6)^{3\circ} < (Cr(CN)_6)^{3-}$
- Q 12. Write the coordination number and oxidation state of Platinum in the complex [Pt(en)<sub>2</sub>Cl<sub>2</sub>]. (CBSE 2019)
- Sol. Coordination number of platinum in the complex  $[Pt(en)_2Cl_2]$  is 6 as <u>'en'</u> is a bidentate ligand.

Let the oxidation state of Pt is x.

$$\therefore \qquad x+0+2(-1)=0$$

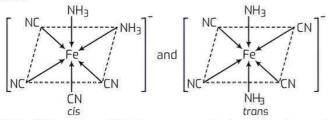
or x = +2

Hence, oxidation state of Platinum is  $\pm 2$ .

- Q 13. How many ions are formed by the complex [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> in aqueous solution?
- Ans. Four lons:  $[Co(NH_3)_6]Cl_3(oq) \rightarrow (Co(NH_3)_6]^{3+}(oq)$ +  $3Cl^-(oq)$
- Q 14. Write the formula and IUPAC name of prussian blue.
- Ans. Fe<sub>4</sub>(Fe(CN)<sub>6</sub>)<sub>3</sub>: Iron(III) hexacyanoferrate(II).
- Q 15. Write the IUPAC name of [Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>.
- Ans. Tetraamminedichloridochromium(III) ion.
- Q 16. Write the IUPAC name of  $[Pt(NH_3)_2Cl_2]Cl_2$ .
- Ans. Diamminedichloridoplatinum(IV) chloride.
- Q 17. What is the CN of central metal ion in  $[Fe(C_2O_4)_3]^{3-7}$ ?
- Ans. The CN of Fe3+ is six.
- Q 18. Give the IUPAC name of [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub>.
- Ans. Hexaamminecobalt(III) chloride.
- Q 19. [Ni(CO)<sub>4</sub>] possesses tetrahedral geometry while [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> has square planer geometry. Why?
- **Ans.** Ni atom in  $(Ni(CO)_4)$  is  $sp^3$  hybridised while the hybridisation of Pt atom in  $(Pt(NH_3)_2Cl_2)$  is  $dsp^2$ .
- Q 20. Write the IUPAC name of the complex  $Na_{q}[CrF_{4}(OH)_{2}]$ .
- Ans. Sodium tetrafluoridodihydroxochromate(III).
- Q 21. Write the IUPAC name of the complex [Cr(H<sub>2</sub>O)<sub>5</sub>Cl]Cl<sub>2</sub>.
- Ans. Pentaaquachloriodochromium (III) chloride.
- Q 22. Give a ligand which is bidentate and give an example of the complex formed by this ligand.
- Ans.  $NH_2$ — $CH_2$ — $CH_2$ — $NH_2$  or (en) :  $(Co(en)_2Cl_2)NO_3$  (bidentate Ugand) (complex)
- Q 23. Which isomerism is shown by the complex  $[Cr(H_2O)_5NCS]^{2+}$ ?
- **Ans.** The given complex shows <u>linkage isomerism</u>. The isomer has the structure:  $[Cr(H_2O)_6SCN]^{2\nu}$ .
- Q 24. Give the IUPAC name of [Pt(NH<sub>3</sub>)<sub>2</sub>Cl(CH<sub>3</sub>NH<sub>2</sub>)]Cl.
- **Ans.** Diamminechlorido (methaneamine) platinum(II) chloride.

- Q 25. Write the formulas of the compounds (I) hexaammineplatinum(IV) chloride (ii) dichloride tetraamminecobalt(III) ion.
- **Ans.** (i)  $[Pt(NH_3)_6]Cl_4$  (ii)  $[Co(NH_3)_4Cl_2]^{\circ}$
- Q 26. Write IUPAC name of K<sub>5</sub> [Fe(CN)<sub>5</sub>NO].
- Ans. Potassium pentacyanonitrosylferrate(II).
- Q 27. Give the names of the two complexes which are used in medicines.
- **Ans.** EDTA: Used for the treatment of lead poisoning. *Cis*-platin: Used as anti-tumor agent in cancer therapy.
- Q 28. Write IUPAC name of [Pt(NH<sub>x</sub>)<sub>2</sub>Cl<sub>2</sub>].
- Ans. Diamminedichloridoplatinum(II).
- Q 29. Draw structures of geometrical isomers of [Fe(NH<sub>3</sub>)<sub>2</sub>(CN)<sub>4</sub>].

Ans.



- Q 30. Write the IUPAC name and hybridisation of  $K_2[CoCl_4(en)]$ .
- Ans. IUPAC name: Potassium tetrachlorido (ethane-1. 2-diamine) cobaltate (II).

**State of hybridisation**: It is an octahedral complex. Since Cl<sup>-</sup> ion is a weak field ligand, it cannot cause electron pairing. As a result, outer d-orbitals are involved in hybridisation. It is, therefore,  $\underline{sp^3d^2}$  in nature.

- Q 31. Write the name of  $[Co(NH_3)_4(H_2O)_2]Cl_3$ .
- Ans. Tetraamminediaquacobalt(III) chloride.
- Q 32. Write the IUPAC name of Fe<sub>4</sub>[Fe(CN)<sub>6</sub>].
- Ans. Iron(III) hexacyanoferrate(II).
- Q 33. Write the IUPAC name of the complex  $[Pt(NH_3)_4 [NiCl_4].$
- Ans. Tetraammineplatinum(II) tetrachloridonickelate(II).
- Q 34. Give IUPAC name of [Cr(H2O)4Cl2]Cl.
- Ans. Tetraquadichloridochromium(III) chloride.
- Q 35. (i) Give the electronic configuration of the d-orbitals of Ti in  $[\mathrm{Ti}(\mathrm{H_2O})_6]^{3+}$  ion in the octahedral crystal field.
  - (ii) Why is this complex coloured? Explain on the basis of distribution of electrons in d-orbitals.
- Ans. (i) In the octahedral complex, Ti is in + 3 oxidation state and has  $t_{2g}^{-1}e_g^0$  configuration of Ti<sup>3+</sup>ion.
  - (II) The unpaired  $\exists d$ -electron is present in the  $t_{2g}$  level in the ground state. The next higher energy level available is  $e_g$ . Thus, there is  $\underline{d}$ - $\underline{d}$  transition from  $t_{2g}$  to  $e_g$   $\left(t_{2g}^{-1}e_g^0 \to t_{2g}^{-0}e_g^1\right)$ . This is responsible for the colour of the complex.

- Q 36. Write IUPAC name of K<sub>2</sub>[PdCl<sub>4</sub>].
- Ans. Potassiumtetrachloridopalladate(II).
- Q 37. Write the IUPAC name of complex; [Fe(en)<sub>2</sub>Cl<sub>2</sub>]Cl and mention the oxidation of iron.
- Ans. IUPAC name: Dichlorido (ethane-1 . 2-diamine) iron(III) chloride. Oxidation state of Fe: +3.
- Q 38. Why are  $\pi$ -complexes known for transition metals only?
- Ans. Since, transition metal atoms have either half-filled or vacant d-orbitals, they can accept ligands with electron density resulting in  $p\pi d\pi$  bonding. Therefore,  $\pi$ -complexes are possible.
- Q39. CO is a stronger ligand than NH<sub>3</sub> for many metals. Explain.
- Ans. CO is a stronger field ligand than NH<sub>3</sub> because of <u>lack</u> of bonding leading to synergic effect. As a result, the bond between the ligand CO and metal (M) becomes stronger as compared to bond between NH<sub>3</sub> and metal which is simply a co-ordinate bond.
- Q 40. Name the following compounds according to IUPAC system:
  - (i)  $[Co(NH_3)_4(H_2O)Cl]Cl_2$  (ii)  $[CrCl_2(en)_2]CL$
- Ans. (i) Tetraammineaquachloridocobalt(III) chloride.
  - (ii) Dichloridobls (ethane-1, 2-diammine) chromium (III) chloride.
- Q 41. Write the name, the state of hybridisation, the shape and the magnetic behaviour of the following complexes:

$$[Co(Cl_4]^-, [Ni(CN)_4]^2-, [Cr(H_2O)_2(C_2O_4)_2]^-$$

- **Ans.** (CoCl<sub>A</sub>): Tetrachloridocobaltate(III) ion. <u>sp³</u> hybridised. tetrahedral in shape, paramagnetic in nature.
  - $(Ni(CN)_4)^{2-}$ : Tetracyanonickelate(II) ion,  $\underline{dsp}^2$  hybridised, square planar in shape,  $\underline{dlamagnetic}$  in nature.
  - $(Cr(H_2O)_2(C_2O_4)_2)^-$ : Diaquadioxalatochromate(III) Ion.  $\underline{d^2sp^3}$  hybridised. octahedral in shape, paramagnetic in nature.
- Q 42. (i) Give the electronic configuration of the d-orbitals of Ti in  $[Ti(H_2O)_6]^{3+}$  ion and explain why this complex is coloured? [At. No. of Ti = 22]
  - (ii) Write IUPAC name of [Cr(NH<sub>3</sub>)<sub>3</sub> (H<sub>2</sub>O)<sub>3</sub>]Cl<sub>3</sub>
- Ans. (i) Oxidation state of Ti:  $x + 6(0) = \pm 3$ Configuration of Ti<sup>3</sup> ion (Ar) 3d \(^1 4s^0).

  Complex is coloured due to the presence of an unpaired electron leading to d-d transition.
  - (ii) Triamminetriaquachromium(III) chloride.
- Q 43. Give the names of the following complexes according to IUPAC system.
  - (i)  $[CoCl_2(en)_2]Cl$  (ii)  $K_3[Fe(CN)_6]$
- Ans. (i) Dichloridobis(ethane)-1, 2-diammine cobalt(III) chloride.
  - (II) Potassiumhexacyanoferrate(III).

- Q 44. What is the denticity of co-ordination compound used in the treatment of lead poisoning?
- Ans. The co-ordination compound is EDTA and its denticity
- Q 45. Write the IUPAC name of  $K_x[Cr(C_2O_4)_x]$ .
- Ans. Potassiumtrioxalatochromate(III).
- Q 46. (i) Write the IUPAC name of the complex  $[Co(Br_2) (en_2)]^+$ .
  - (ii) What type of isomerism is shown by the complex [Co(NH<sub>s</sub>)<sub>5</sub>SO<sub>4</sub>]Br?
- Ans. (i) IUPAC name: Dibromidobis (ethane-1, 2-diamine) cobalt(III) ion.
  - (ii) The complex exhibits ionisation isomerism.
- Q 47. Write IUPAC name of the complex [Cr(NHz),Cl2]+. What type of isomerism does it exhibit?
- Ans. The **IUPAC** name the complex: Tetraamminedichloridochromium(III) ion. It exhibits cis-trans isomerism (geometrical isomerism).
- Q 48. Which of the following is a more stable complex and why?

 $[Co(en)_z]^{3+}$  and  $[Co(NH_3)_6]^{3+}$ .

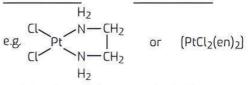
- **Ans.** The complex  $(Co(en)_3)^{3/2}$  is more stable because en is a bidentate chelating ligand.
- Q 49. What type of isomerism is exhibited by complex  $[Co(en)_{z}]^{3+}$ ?
- Ans. The complex exhibits optical isomerism.
- Q 50. Write the formula of pentamminesulphatocobalt
- Ans. Formula of the complex: (Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>6</sub>)CL
- Q 51. Write the IUPAC names of [Ag(NH<sub>3</sub>)<sub>2</sub>]Cl and  $K[Ag(CN)_{3}].$
- Ans. Diamminesilver (1) chloride and potassium dicyanoargentate.
- Q 52. Write the IUPAC name of the complex [Ag(NH<sub>3</sub>)<sub>2</sub>]  $[Ag(CN)_{2}].$
- Ans. Diammine silver(I) Dicyanoargentate.
- Q 53. (i) Write the IUPAC name of the following complex: [Cr(en),]Cl,.
  - (ii) Write the formula for the following complex: Potassium trioxalatochromate.
- Ans. (i) Tris (ethane-1, 2-diammine) chromium(III) chloride. (ii)  $K_3(Cr(C_2O_4)_3)$ .
- Q 54. (i) Write the IUPAC name of the complex: [Cr(NH<sub>e</sub>),Cl,(en)]CL
  - (ii) Write the formula of the complex: Pentaamminenitritocobalt(III). (CBSE 2015)
- Ans. (i) Diaamminedichlorido (ethane 1.2-diamine) chromium(III) chloride.
  - (ii)  $[Co(NH_3)_5(ONO)]^{2}$
- Q 55. Write the formula of the ionisation isomer of [Cr(H<sub>2</sub>O)<sub>4</sub>Br<sub>2</sub>]Cl.
- **Ans.** The formula of ionisation isomer is:  $(Cr(H_2O)_4BrCl)Br$ .



### Short Answer Type-I Questions



- Q 1. What is meant by the chelate effect? (NCERT EXERCISE)
- **Ans.** If the donor atoms of a bidentate or polydentate ligand are arranged in such a way that they form five or six membered ring when coordinates with central metal ion, then the complex becomes more stable and the effect is called chelate effect.



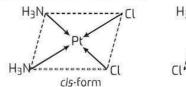
- Q 2. (i) What is a chelate complex? Give one example.
  - (ii) What are heteroleptic complexes? Give one example. (CBSE 2023)
- Ans. (i) A chelate complex is a complex formed when a metal ion is bonded to two or more molecules of a chelating agent. e.g., Complex ion formed between ethylene diammine and cupric ion -{Cu(NH<sub>2</sub>CH<sub>2</sub>  $NH_2)_2)^{2+}$ .
  - (ii) Complexes in which a metal is bound to more than one kind of donor groups are called heteroleptic complexes. e.g. (Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>)° Is a heteroleptic complex.
- Q 3. Define the following:
  - (i) Complex ion.
  - (ii) Coordination number.
- Ans. (i) Complex ion: The electrically charged species formed by the union of a central metal atom or ion with one or more ligands is called a complex e.g..  $(Ag(CN)_2)^-$  is a complex ion. In this complex, the central Ag\* Ion Is attached to two CN- Ugands.
  - (ii) Coordination number: The number of coordination bonds formed by the central metal atom or ion with the ligands in a complex, is called the coordination number of the metal.

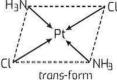
If the complex contains only monodentate ligands, then the coordination number of metal is the number of monodentate ligands.

If the complex contains polydentate Ugands, the coordination number of metal is the denticity of ligand or the number of the ligands.

e.q., In the complex (PtCl<sub>2</sub>(en)<sub>2</sub>), the coordination number of Pt  $\infty$  1 × 2 + 2 × 2  $\infty$  2 + 4  $\infty$  6.

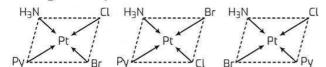
- Q 4. Write the IUPAC name and geometrical isomer of [Pt  $(NH_3)_2Cl_2$ ].
- Ans. IUPAC name of  $[Pt(NH_3),Cl_3]$ diamminedichloridoplatinum (II). It shows following two geometrical isomers:





# Q 5. Write all the geometrical isomers of [Pt(NH<sub>3</sub>)(Br) (Cl)(Py)] and how many of these will exhibit optical isomers? (NCERT EXERCISE)

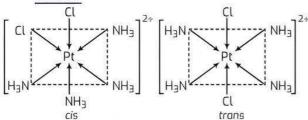
**Ans.** Following three geometrical isomers are possible for the given compounds:



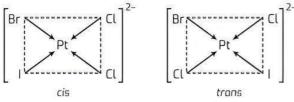
Isomers of this type do not exhibit optical isomerism. Optical isomerism is <u>rare in square planar or tetrahedral complexes</u>. In these complexes, it is possible only when they have asymmetric chelating ligand.

- Q 6. Draw all the possible isomers of the following:
  - (i)  $[Pt(NH_2)_4 Cl_2]^{2+}$
  - (ii) [PdCl<sub>2</sub>Brl]<sup>2-</sup>

Ans. (i) [Pt(NH<sub>3</sub>)<sub>4</sub> Cl<sub>2</sub>)<sup>2+</sup> has following two geometrical isomers:



(ii) For the complex [PdCl<sub>2</sub>BrI]<sup>2-</sup>, following two geometrical isomers are possible:



Q 7. The formula Co(NH<sub>3</sub>)<sub>5</sub>CO<sub>3</sub>Cl could represent a carbonate or a chloride. Write the structures and names of possible isomers. (CBSE SQP 2022-23)

Ans. The possible isomers are  $(Co(NH_3)_5CO_3)Cl$  i.e., pentaaminecarbonatocobalt(III) chloride and  $(Co(NH_3)_5Cl)CO_3$  i.e., Pentaaminechloridocobalt (iii) carbonate.

Q 8. A solution of  $[Ni(H_2O)_6]^{2+}$  is green but a solution of  $[Ni(CN)_4]^{2-}$  is colourless. Explain. (NCERT EXERCISE)

Ans. NI in (NI(H<sub>2</sub>O)<sub>6</sub>)<sup>2+</sup> has 3d<sup>8</sup> configuration and is in +2 oxidation state. In this complex, it contains two unpaired electrons which remain unpaired due to the presence of weak field ligand, H<sub>2</sub>O. Due to the presence of unpaired electrons, these show d-d transition. d-d transition absorbs red light and emits its complementary green colour.

In case of  $(Ni(CN)_4)^{2-}$  also. Ni has  $3d^8$  configuration and +2 oxidation state but due to the presence of strong field ligand CN-, the two unpaired electrons present in 3d-orbitals, pair up. Thus, in this complex Ni does not have any unpaired electron. So, no d-d transition is possible, thus, it is colourless.

# Q 9. $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2\circ}$ are of different colours in dilute solutions. Why? (NCERT EXERCISE)

Ans. In both the complexes. Fe Is In +2 oxidation state with 3d<sup>6</sup> configuration *i.e.*, it contains four unpaired electrons. In the presence of weak field ligand H<sub>2</sub>O, these remain unpaired, whereas in the presence of strong field ligand CNT, these pair up and the complex has no unpaired electron. Due to the difference in number of unpaired electrons, these two complexes give different colours in dilute solutions.

- Q 10. Give the formulae of the following compounds:
  - (i) Potassium tetrahydroxidozincate(II)
  - (ii) Hexaammineplatinum(IV) chloride. (CBSE 2020)

Ans. (i)  $K_2$  [Zn(OH) $_4$ ].

(ii) [Pt(NH<sub>2</sub>)<sub>6</sub>]Cl<sub>4</sub>.

- Q 11. Write IUPAC names of the following:
  - (i) [Co(en)<sub>2</sub>(H<sub>2</sub>O)(CN)]<sup>2+</sup>

(ii) [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> (CBSE 2023)

**Ans.** (i) Aquacyano *bis*- (ethylene diammine) cobalt (III) ion (ii) Hexaammine nickel (II) chloride.

- Q 12. Write IUPAC names of the following coordination entities:
  - (i) [Co(NH<sub>3</sub>)<sub>4</sub>Cl(NO<sub>2</sub>)]Cl

(ii)  $[PtCl_2(en)_2]^{2+}$  (CBSE 2023)

**Ans.** (i) Tetra ammine chlorido nitrito –N– cobalt (III) chloride.

(ii) Dichlorido*bis* (ethane-1, 2-diammine) platinum (IV) ion.

- Q 13. Using IUPAC names, write the formula for the following:
  - (i) Sodium dicyanidoaurate(l).
  - (ii) Tetraamminechloridonitrito-N-platinum (IV) sulphate. (CBSE 2017)
- **Ans.** (I) Sodium dicyanidoaurate(I)

Let the formula of the given compound is  $Na[Au(CN)_3]^x$ 

In this formula.

Charge of anion ∞ +1

Charge on complex ion will be, x = 1 - 2 = -1

So, anion neutralises the charge on cation.

The formula of the given compound = Na(Au(CN)<sub>2</sub>)

(ii) Tetraamminechloridonitrito-N-platinum(IV) sulphate

Let the formula of the given compound is  $(Pt(NH_3)_6(Cl)(ONO))^{\times} SO_4$ .

In this formula.

Charge of anion ∞ -2

Charge on complex ion will be, x = -1 - 1 + 4 = + 2So, anion neutralises the charge on cation.

The formula of the given compound  $= [Pt(NH_3)_4Cl(ONO)]SO_4.$ 

Q 14. (i) Write the IUPAC name of the isomer of the following complex:

[Pt(NH<sub>x</sub>)<sub>2</sub>Cl<sub>2</sub>]

(ii) Write the formula for the following: Tetraammineaquachloridocobalt(III) nitrate.

(CBSE 2017)

- Ans. (i) The IUPAC name of (Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>) is cis/transdiamminedichloridoplatinum(II).
  - (ii) The formula of Tetraammineaquachloridocobalt (III) nitrate is  $(Co(NH_3)_4(H_2O)Cl)(NO_3)_2$
- Q 15. (i) Write the IUPAC name of the Isomer of the following complex:  $[Co(NH_x)_cCl]SO_A$ 
  - (ii) Write the formula for the following: Diamminechloridonitrito-N-platinum(II)

(CBSE 2017)

Ans. (i) Pentaamminesulphatocobalt(III) chloride.

(ii) [Pt(NH<sub>2</sub>)<sub>2</sub>Cl(NO<sub>2</sub>)].

- Q 16. Give the formula of the following compounds:
  - (i) Potassium trioxalatoaluminate(III)
  - (ii) Tetraammineaquachloridocobalt(III) chloride. (CBSE 2020)

**Ans.** (i)  $K_3[Al(C_2O_4)_3]$ 

(ii)  $(Co(NH_3)_4(H_2O)Cl)Cl_2$ 

- Q 17. Give the formula of the following compounds:
  - (i) Pentamminecarbonatocobalt(III) chloride
  - (ii) Potassium tetracyanidonickelate(II) (CBSE 2020)

Ans. (i)  $(Co(NH_3)_5(CO_3))Cl$ 

(II)  $K_2(NI(CN)_4)$ .

- Q18. Using IUPAC names, write the formulae for the following:
  - (i) Tris (ethane-1, 2-diammine) chromium(III) chloride.
  - (ii) Potassium tetrahydroxozincate(II). (CBSE 2017)
- Ans. (i) Tris (ethane-1, 2-diammine) chromium(III) chloride Let the formula of the given compound is  $(Cr(en)_3)^{\times}Cl^{-}$

In this formula,

Charge on anion ∞ - 1

Charge on complex ion will be. x = 3 + 0 = 3

So, the formula of the given compound

 $= (Cr(en)_3)Cl_3$ 

(II) Potassium tetrahydroxozincate(II)

Let the formula of the given compound is  $K(Zn(OH)_{a})^{x}$ .

In this formula, x ∞ 2 – 4 ∞ <u>~ 2</u>

So, the formula of the given compound is  $K_2(Zn(OH)_4)$ .

- Q 19. Using IUPAC names, write the formulae for the following:
  - (i) Potassium trioxalatoaluminate(III).
  - (ii) Dichloridobis (ethane-1, 2-diammine) cobalt (CBSE 2017)

**Ans.** (I) Potassium trioxalatoaluminate(III)

 $K_{a}(Al(C_{2}O_{4})_{a})$ 

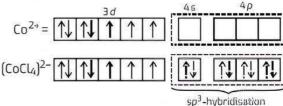
(ii) Dichloridobis (ethane-1, 2-diammine) cobalt(III) (CoCl<sub>2</sub>(en)<sub>2</sub>)<sup>4</sup>

Q 20. Determine the structure and magnetic behaviour of [CoCl<sub>4</sub>]<sup>2-</sup> using valence bond theory.

Ans. <sub>27</sub>Co: [Ar] 45<sup>2</sup> 3d<sup>7</sup>

 $Co^{2+}$ : (Ar)  $4s^{0}$   $3d^{7}$ 

Cl- is a weak field ligand, so pairing of electron does not occur.

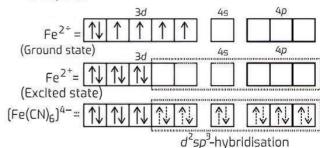


Due to  $sp^2$  -hybridisation, its structure is tetrahedral and presence of three unpaired electrons make it paramagnetic

Q 21. Determine the structure and magnetic behaviour of [Fe(CN)<sub>6</sub>]<sup>4 -</sup> ion on the basis of valence bond theory.

**Ans.**  $_{26}$ Fe= (Ar)  $4s^2$   $3d^6$ 

CN is a strong field ligand, so pairing of electrons take place.

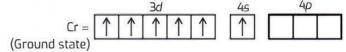


Due to  $d^2sp^3$ -hybridisation, its structure is octahedral and because of the absence of unpaired electrons, it is diamagnetic.

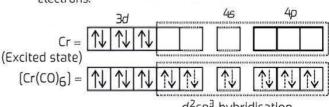
Q 22. Explain the structure and magnetic behaviour of [Cr(CO)<sub>6</sub>] using valence bond theory.

[Atomic number of Cr = 24]

Ans. 24 Cr = (Ar) 4s1 3d S



CO is a strong field ligand, so pair up the unpaired electrons.



d<sup>2</sup>sp<sup>3</sup>-hybridisation

Thus, it is  $d^2sp^3$ -hybridised and hence it has octahedral geometry. Because of the absence of unpaired electrons, it is diamagnetic.

- Q 23. [NiCl<sub>4</sub>]<sup>2-</sup> is paramagnetic while [Ni(CO)<sub>4</sub>] is diamagnetic though both are tetrahedral. Why?
- Ans. In the complex  $[NiCl_{\omega}]^2$ , Ni is in  $\pm 2$  oxidation state and has the configuration  $3d^84s^0$ . The Cl<sup>-</sup> ion being a weak ligand cannot pair up the two unpaired electrons present in 3d-orbitals. This means that 3d-orbitals are not involved in hybridisation. The complex is  $sp^3$ -hybridised (tetrahedral) and is paramagnetic in nature.

In the other complex  $(Ni(CO)_4)$ , the oxidation state of Ni is zero and electronic configuration is  $3d^84s^2$ . In the presence of the ligand CO, the 4s-electrons shift to the two half filled 3d-orbitals and make all the electrons paired. The valence 4s and 3p-orbitals are involved in hybridisation. The complex is tetrahedral but diamagnetic.

- Q 24. Predict the number of unpaired electrons in the square planar [Pt(CN)<sub>4</sub>]<sup>2-</sup>ion. (NCERT INTEXT)
- **Ans.** The element Pt(Z =78) is present in group 10 with electronic configuration  $5d^96s^1$ . The divalent cation Pt<sup>2+</sup> has  $5d^8$  configuration.

For square planar complex, Pt(II) is in  $\underline{dsp^2}$  hybridisation state. To achieve this, the two unpaired electrons present in 5d-orbitals get paired. The complex has therefore, no unpaired electrons.

- Q 25. What is the co-ordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is that no precipitate of copper sulphide is obtained when H<sub>2</sub>S(g) is passed through the solution?

  (NCERT EXERCISE)
- Ans. On mixing the aqueous solutions of KCN and CuSO<sub>4</sub>, the complex formed is potassium tetracyanocuprate(II). Since CN+ ions are strong ligands, the complex is quite stable. It is evident from the stability constant value ( $K = 2.0 \times 10^{27}$ ). It is not cleaved by H<sub>2</sub>S gas when passed through the aqueous solution and no precipitate of CuS is formed.

$$CuSO_4(oq) + 4KCN(oq) \longrightarrow K_2[Cu(CN)_4] + K_2SO_4(oq)$$
(Soluble)

- Q 26. Aqueous copper sulphate solution (blue in colour) gives (a) green precipitate with aqueous potassium fluoride and (b) a bright green solution with aqueous potassium chloride solutions. Explain these experimental results.
- Ans. Aqueous solution of copper sulphate which is blue in colour exists as  $[Cu(H_2O)_4]SO_4$  and gives  $[Cu(H_2O)_4]^{2+}$  in solution. It is a labile complex entity in which the ligands  $H_2O$  get easily replaced by F<sup>-</sup> ions of KF and by Cl<sup>-</sup> ions of KCl.

- Q 27. Give the oxidation state, d-orbital occupation and coordination number of the central metal ion in the following complexes:
  - (i)  $K_3[Co(C_2O_4)_3]$
  - (ii)  $(NH_4)_2[CoF_4]$
  - (iii) cis-[CrCl2(en)2]Cl
  - (iv)  $[Mn(H_2O)_6]SO_4$ .

(NCERT EXERCISE)

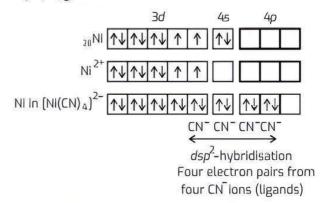
**Ans.** (i) 
$$OS = \pm 3$$
,  $CN = 6$ ,  $d$ -orbital occupation is  $3d^6 t_{2g}^6 e_g^0$ .

(ii) OS = 
$$\pm 2$$
. CN =  $\pm 4$ .  $3d^7 (t_{2g}^5 e_g^2)$ .

(iii) OS = 
$$\pm 3$$
. CN =  $6$ .  $3d^3(t_{2g}^3)$ .

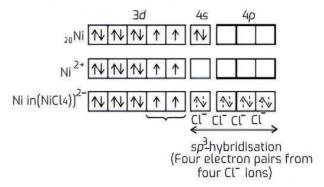
(iv) OS = 
$$\pm 2$$
. CN =  $6 \cdot 3d^6 \tilde{Q}_{2g}^5 e_g^2$ 

- Q 28. Explain on the basis of valence bond theory that  $[Ni(CN)_4]^{2-}$  ion with square planar structure is diamagnetic and the  $[NiCl_4]^{2-}$  ion with tetrahedral geometry is paramagnetic. (NCERT INTEXT)
- Ans. Magnetic behaviour of (Ni(CN<sub>4</sub>))<sup>2</sup>7: Atomic number of Ni is 28. Electronic configuration of Ni, Ni<sup>2+</sup> and (Ni(CN)<sub>4</sub>)<sup>2-</sup> are as follows:



Here, CN<sup>+</sup> being a strong field ligand, causes pairing of unpaired electrons of Ni<sup>2+</sup>. Now, it contains only paired electrons, so the complex  $(Ni(CN)_4)^{2-}$  is diamagnetic.

Magnetic behaviour of (NiCl<sub>4</sub>)<sup>2</sup>: It contains a weak field ligand Cl<sup>-</sup>, which is not capable to cause pairing of unpaired electrons.



Because of the presence of unpaired electrons in the d- subshell of (NiCl<sub>4</sub>)<sup>2-</sup>, it is a paramagnetic complex



### Short Answer Type-II Questions >

- QL (i) Why chelate complexes are more stable than complexes with unidentate ligands?
  - (ii) What is "spectrochemical series"? What is the difference between a weak field ligand and a strong field ligand?
- Ans. (i) Chelating Ugands can form a ring with central metal and have the ability to regulate electron within ring. This results in more force of attraction between central metal ion and chelating ligand, therefore, they are more stable.
  - (ii) A spectrochemical series is the arrangement of common ligands in the increasing order of their crystal-field splitting energy (CFSE) values.

#### Difference:

Weak field ligands have less values of crystal field splitting energy ( $\Delta_o < P$ ) and form high spin complexes whereas strong field ligands have high value of CFSE  $(\Delta_{\sigma} > P)$  and form low spin complexes.

- Q 2. Specify the oxidation numbers of the metals in the following coordination entities: (NCERT EXERCISE)
  - (i) [Co(H<sub>2</sub>O)(CN)(en)<sub>2</sub>]<sup>2+</sup>
  - (ii) [CoBr<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup>
  - (iii) [PtCl<sub>4</sub>]<sup>2-</sup>
  - (iv) [K<sub>1</sub>[Fe(CN)<sub>6</sub>]
  - (v)  $[Cr(NH_x)_xCl_x]$ .

**Ans.** (I)  $[Co(H_2O)(CN)(en)_2]^{2+}$ 

$$x + 0 + (-1) + 0 = +2$$
  
 $x = +3$ 

(ii) (CoBr<sub>2</sub>(en)<sub>2</sub>)<sup>3</sup>

or

or (iii) [PtCl<sub>4</sub>]2-

$$x-4=-2$$

or

$$x = +2$$

(Iv)  $K_3(Fe(CN)_6)$  or  $(Fe(CN)_6)^{3-}$ 

OF

(v) (Cr(NH<sub>2</sub>)<sub>3</sub>Cl<sub>3</sub>)

$$x + 0 + 3(-1) = 0$$

- Q 3. (i) Using IUPAC names, write the formulas for the following:
  - (a) Pentaamminenitrito-N-cobalt(III)
  - (b) Tetrahydroxidozincate(II)
  - (ii) What is crystal field splitting energy?

(COSE 2022 Term-2)

**Ans.** (i) (a)  $(Co(NO_2)(NH_3)_5)^{2+}$ 

- (b) [Zn(OH)]2-
- (ii) It is the magnitude of difference in energy between two sets of d-orbitals. i.e.,  $t_{2g}$  and  $e_{gr}$

- Q 4. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:
  - (i)  $K[Cr(H_2O)_2(C_2O_4)_2]3H_2O$
  - (ii) [CrCl<sub>3</sub>(py)<sub>3</sub>]
  - (iii) K<sub>4</sub>[Mn(CN)<sub>6</sub>]
  - (iv) [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>

(v) Cs[FeCl<sub>4</sub>]

(NCERT EXERCISE)

Ans. (i) IUPACname: Potassium diaquadioxalatochromate (III) hydrate.

0.5. of 
$$Cr = +3$$
;  $3d^3(t_{2g}^3 e_g^0)$ .  $CN = 6$ 

Shape = octahedral. three unpaired electrons.

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

$$=\sqrt{3\times5}=\sqrt{15}$$
 BM

(ii) IUPAC name: Trichloridotripyridinechromium(III)

0.5. of 
$$Cr = +3$$
:  $3d^3 (t^3_g e_g^0)$ ,  $CN = 6$ 

Shape octahedral; three unpaired electrons.

Magnetic moment ( $\mu$ )  $= \sqrt{n \partial n} +$ 

(iii) IUPAC name: Potassiumhexacyanomanganate(II)

0.5. of Mn = 
$$+2$$
:  $3d^5 (t_{2g}^5 e_g^0)$ ,  $CN = 6$ .

Shape = octahedral; one unpaired electron.

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

$$=\sqrt{1\times3}=\sqrt{3}$$
 BM

$$= 1.73 BM$$

(iv) IUPAC name: Pentaamminechloridocobalt(III) chloride

O.S. of Co 
$$= +3$$
:  $3d^6$  ( $t_{2g}^6 e_g^0$ ), CN  $= 6$ 

Shape w tetrahedral: zero unpaired electron. Magnetic moment (µ) ∞ 0

(v) IUPAC name: Caesium tetrachloridoferrate(III)

0.5. of Fe = + 3: 
$$3d^5 (e_q^2 t_{2q}^3)$$
,  $CN = 4$ 

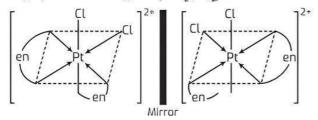
Shape ... tetrahedral: five unpaired electrons.

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

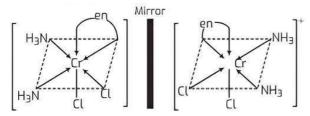
- Q 5. Draw the structures of optical isomers of:
  - (i) [PtCl<sub>2</sub>(en)<sub>2</sub>]<sup>2+</sup>
  - (ii) [Cr(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>(en)]\*

(CDSE 2015)

(i) (cis-isomer only) cis-  $[PtCl_2(en)_2]^{2\nu}$ 



(ii) (cis-isomer only) cis-(Cr(NH<sub>3</sub>)<sub>2</sub>(en))+



- Q 6. (i) Write the IUPAC name of the following complex: [Pt(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>4</sub>
  - (ii) On the basis of crystal field theory, write the electronic configuration of  $d^4$  ion, if  $(\triangle_0 < P)$ .
  - (iii) What are heteroleptic complexes?

(CBSE 2022 Term-2)

**Ans.** (I) Hexaammineplatinum(IV) chloride.

- (ii) When  $\Delta_0$  < P, fourth electron enters one of the  $e_{\sigma}$ orbitals giving the electronic configuration  $t_{2g}^{3}$   $e_{g}^{1}$
- (iii) Complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic complexes.
- Q 7. (i) Write the IUPAC name of the following complex: K,[PdCl,].
  - (ii) Using crystal field theory, write the electronic configuration of  $d^5$  ion, if  $\Delta_0 > P$ .
  - (iii) What are Homoleptic complexes?

(CBSE 2022 Term-2)

Ans. (i) Potassium tetrachloridopalladate(II)

(ii) Electronic configuration  $\omega t_{2q}^5 e_q^o$ 

- (iii) Complexes in which a metal is bound to only one kind of donor groups are known as homoleptic complexes.
- Q 8. (i) Write the IUPAC name of the following complex: [Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Cl]Cl<sub>2</sub>.
  - (ii) What is the difference between an Ambidentate ligand and a Bidentate ligand?
  - (iii) Out of  $[Fe(NH_3)_6]^{3}$  and  $[Fe(C_2O_4)_3]^{3-}$ , which complex is more stable and why?

(CBSE 2022 Term-2)

Ans. (i) Tetraammineaquachlorocobalt(III) chloride.

- (ii) A ligand which has two different donor atoms but only one of them forms a coordinate bond at a time with central metal/ion is called ambidentate ligand. On the other hand, ligand which can bind through two donor atoms is said to be bidentate ligand.
- (iii)  $[Fe(C_2O_4)_3]^{3-}$  is a chelate complex and  $[Fe(NH_3)_6]^{3+}$ is a complex containing unidentate ligand.

We know that chelate complexes are more stable than similar complexes containing unidentate Ugands. Thus.  $(Fe(C_2O_4)_3)^{3-}$  is more stable.

Q 9. (i) Write the formula for the following coordination compound:

> Bis(ethane-1, 2-diamine) dihydroxidochromium (III) chloride.

- (ii) Does ionization isomer for the following compound exist? Justify your answer. Hg[Co(SCN)<sub>4</sub>]
- (iii) Is the central metal atom in coordination complexes a Lewis acid or a Lewis base? Explain.

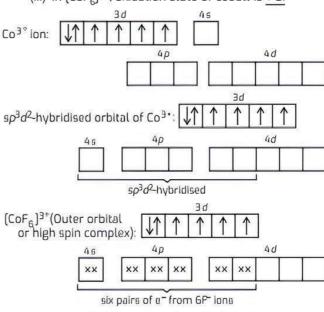
(CBSE SQP 2023-24)

(i) (Cr(en)<sub>2</sub>(OH)<sub>2</sub>)Cl or (Cr(H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>(OH)<sub>3</sub>)Cl Ans.

- (II) No, ionization isomers are possible by exchange of ligand with counter ion only and not by exchange of central metal ion.
- (III) The central atom is electron pair acceptor so it is a Lewis acid.
- Q 10. (i) Write the formula of the following coordination compound:

Iron(III) hexacyanoferrate(II).

- (ii) What type of isomerism is exhibited by the complex [Co(NH<sub>z</sub>)<sub>z</sub>Cl]SO<sub>4</sub>?
- (iii) Write the hybridisation and number of unpaired electrons in the complex  $[CoF_6]^{3-}$ . (Atomic No. of Co = 27) (CBSE 2018)
- Ans. (I) The formula of the coordination compound Iron(III) hexacyanoferrate(II) is  $Fe_4(Fe(CN)_6)_3$ .
  - (II) (Co(NH<sub>2</sub>)<sub>5</sub>Cl)SO<sub>4</sub> exhibit ionisation isomerism. Its ionisation isomer is (Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>)CL
  - (III) In  $(CoF_6)^{3-}$ , oxidation state of cobalt is + 3.



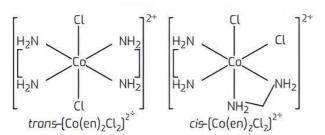
Six pairs of electrons one from each F-lon occupy the six hybrid orbitals.

Thus, the complex has octahedral geometry  $(sp^3d^2)$ . Number of unpaired electron is 4.

- Q 11. (i) Draw the geometrical isomers of  $[Co(en)_2Cl_2]^{2^{\circ}}$ . Which geometrical isomer of  $[Co(en)_2Cl_2]^{2^{+}}$  is not optically active and why?
  - (ii) Write the hybridisation and magnetic behaviour of [CoF<sub>6</sub>]<sup>3—</sup>.

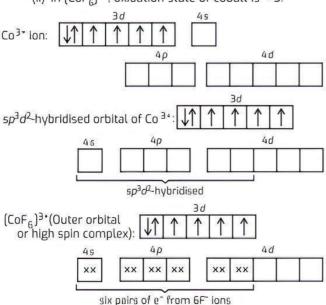
[Given: Atomic number of Co = 27] (CBSE 2023)

**Ans.** (I) The geometrical isomers of (Co(en)<sub>2</sub>Cl<sub>2</sub>)<sup>2+</sup> are:



Among the two, *cis* isomer of  $(Co(en)_2Cl_2)^{2^+}$  is optically active while the *trans* isomer is optically not active as the mirror image of the complex is superimposable.

(ii)  $\ln (CoF_6)^{3-}$ , oxidation state of cobalt is + 3.



Six pairs of electrons one from each F<sup>-</sup> ion occupy the six hybrid orbitals.

Thus, the complex has octahedral geometry  $(sp^3d^2)$ . Number of unpaired electrons is 4.

- Q 12. (i) What type of isomerism is shown by the complex [Co(NH<sub>3</sub>)<sub>5</sub>(SCN)]<sup>2+</sup>?
  - (ii) Why is  $[NiCl_4]^2$  paramagnetic while  $[Ni(CN)_4]^2$  is diamagnetic? (Atomic number of Ni = 28)
  - (iii) Why are low spin tetrahedral complexes rarely observed? (CBSE 2017)
- Ans. (i) Complex  $[Co(NH_3)_g(SCN)]^{2\nu}$  ion exhibit <u>linkage</u> isomerism due to presence of SCN which is an ambidentate ligand and can be linked with metal elther through N or S.  $[Cr(NH_3)_g(SCN)]^{2\nu}$  and  $[Co(NH_3)_g(NCS)]^{2\nu}$

(ii) The complex in which one or more unpaired electrons are present is paramagnetic while, those which does not contain any unpaired electron is diamagnetic.

Oxidation state of Ni is + 2 in both the complexes i.e.,  $(NiCl_a)^{2-}$  and  $(Ni(CN)_4)^{2-}$ .

Ni <sup>2+</sup> 25 4P

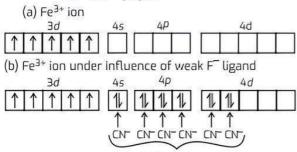
In case of  $(NiCl_b)^{2-}$ ,  $Cl^-$  is a weak field ligand so pairing of electrons in 3d-orbital does not occur, hence compound is paramagnetic with two unpaired electrons. In  $(Ni(CN)_b)^{2-}$ ,  $CN^-$  is a strong field ligand, hence pairing occurs and  $(Ni(CN)_b)^{2-}$  is diamagnetic.

- (III) For tetrahedral complexes, the <u>crystal field</u> stabilisation energy is lower than pairing energy, so they are rarely formed in low spin state.
- Q 13. (i) What type of isomerism is shown by the complex  $[Co(NH_3)_6][Cr(CN)_6]$ ?
  - (ii) Why a solution of  $[Ni(H_2O)_6]^{2+}$  is green while a solution of  $[Ni(CN)_4]^{2-}$  is colourless? (At. no. of Ni = 28)
  - (iii) Write the IUPAC name of the following complex:  $[Co(NH_3)_5(CO_3)]CL$  (CBSE 2017)
- Ans. (i) The type of isomerism exhibited by the compound  $[Co(NH_3)_6](Cr(CN)_6]$  is <u>coordination isomerism</u>. Here, both the positive and negative ions are complex ions. Isomerism may be caused by the interchange of ligands between the anion and cation. The two isomers are  $\underline{(Co(NH_3)_6)(Cr(CN)_6)}$  and  $\underline{(Cr(NH_3)_6)(Co(CN)_6)}$ .
  - (ii) Ni in [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2</sup>° has 3d<sup>8</sup> configuration and is in +2 oxidation state. In this complex, it contains two unpaired electrons which remain unpaired due to the presence of weak field ligand, H<sub>2</sub>O. Due to the presence of unpaired electrons, these show d-d transition. d-d transition absorbs red light and emits its complementary green colour.
    - In case of  $(Ni(CN)_4)^2$  also, Ni has  $3d^8$  configuration and +2 oxidation state but due to the presence of strong field ligand CN-, the two unpaired electrons present in 3d-orbitals, pair up. Thus, in this complex Ni does not have any unpaired electron. So, no d-d transition is possible, thus, it is colourless.
  - (iii) The IUPAC name is pentammine carbonato cobalt (III) chloride.
- Q 14. Answer any three of the following questions:
  - (i) Explain the type of hybridisation in [Fe(CN)<sub>6</sub>]<sup>3</sup>— on the basis of valence bond theory. (Given: Atomic number of Fe = 26)
  - (ii) Draw the geometrical isomers of [PtCl<sub>2</sub>(en)<sub>2</sub>]<sup>2+</sup> ion.

- (iii)  $[NiCl_4]^{2-}$  is paramagnetic while  $[Ni(CO)_4]$  is diamagnetic though both are tetrahedral. Why?
- (iv) Name the type of isomerism when ambidentate ligands are attached to central metal ion. Give one example of ambidentate ligand. (CBSE 2023)

**Ans.** (I) We have  $_{26}$ Fe = (Ar) $3d^{6}4s^{2}$ 

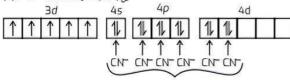
$$Fe^{3+}$$
 Ion = (Ar)3 $d^5$ 



sp<sup>3</sup>d<sup>2</sup> hybridisation

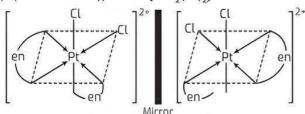
It is strongly paramagnetic in nature.

(c) Fe<sup>3</sup>\* lon In (Fe(CN)<sub>E</sub>)<sup>3</sup>-



Thus,  $[Fe(CN)_6]^{3-}$  is strongly paramagnetic in nature with  $sp^3d^2$  hybridisation.

(ii) (c/s-lsomer only) Le. c/s- [PtCl<sub>2</sub>(en)<sub>2</sub>]<sup>2</sup>°



(iii) In the complex  $\{\text{NiCl}_a\}^{2-}$ . Ni is in + 2 oxidation state and has the <u>configuration</u>  $3d^84s^0$ . The Cl<sup>-</sup> ion being a weak ligand cannot pair up the two unpaired electrons present in 3d-orbitals. This means that 3d orbitals are not involved in hybridisation. The complex is  $sp^3$ -hybridised (tetrahedral) and is paramagnetic in nature.

In the other complex (Ni(CO)<sub>4</sub>), the oxidation state of Ni is <u>zero</u> and electronic configuration is  $3d^84s^2$ . In the presence of the ligand CO, the 4s-electrons shift to the two half filled 3d-orbitals and make all the electrons paired. The valence 4s and 3p-orbitals are involved in hybridisation. The complex is tetrahedral but diamagnetic.

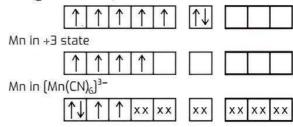
- (iv) When ambidentate ligands are attached to central metal ion, linkage isomerism is shown. e.g., NO<sup>2-</sup> can link through N as well as O.
- Q 15. Using Valence bond theory, explain the following in relation to the paramagnetic complex [Mn(CN)<sub>6</sub>]<sup>3-</sup>:
  - (i) type of hybridisation
  - (ii) magnetic moment value
  - (iii) type of complex-inner, outer orbital complex.

(CBSE SQP 2022-23)

Ans. Given paramagnetic complex is  $(Mn(CN)_6)^3$ . The electronic configuration of  $Mn = (Ar)3d^54s^2$ For  $Mn^{3+}$ , the configuration is  $(Ar)3d^4$ .

#### Distribution of electrons:

Mn (ground state)



d<sup>2</sup>sp<sup>3</sup> hybridisation

xx are electrons donated by ligand CNT.

- (i) Type of hybridisation =  $d^2sp^3$
- (ii) Magnetic moment value

$$\sqrt{n(n+2)} = \sqrt{2(2+2)} = 2.87 \text{ BM}$$

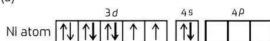
(where n = No. of unpaired electrons)

- (iii) Type of complex inner orbital complex.
- Q 16. (i) Using valence bond theory, predict the hybridisation and magnetic character of the complex: [Ni(CO)<sub>4</sub>] (Atomic number: Ni = 28)
  - (ii) Write IUPAC name of [Pt(NH<sub>5</sub>)<sub>2</sub>Cl(NO<sub>2</sub>)].
  - (iii) Why  $[Co(en)_3]^{3+}$  is a more stable complex than  $[Co(NH_3)_6]^{3+}$ ? (CBSE 2022 Tarm-2)

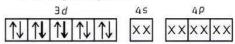
Ans. (i) In (NI(CO)<sub>4</sub>), oxidation state of Ni is zero.

$$_{28}NI = (Ar) 3d^{8} 4s^{2}$$

(a)



(b) NI atom after the rearrangement in presence of strong CO ligands.

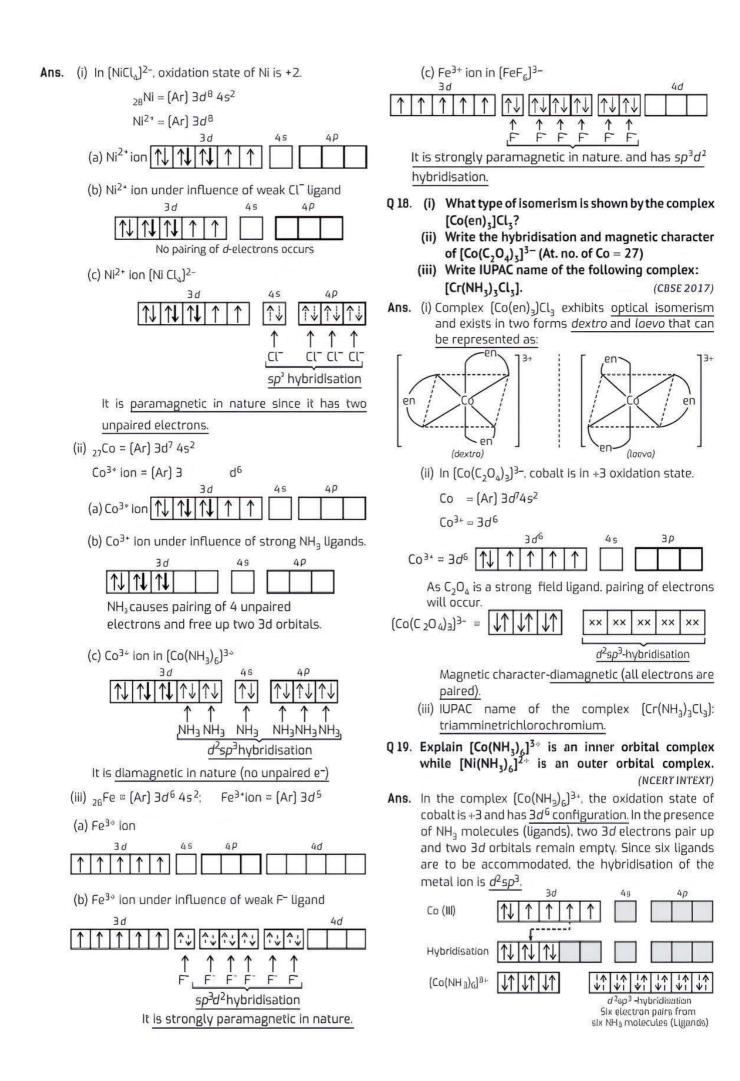


CO causes pairing of 4 electrons into 3d-orbitals.

It is <u>diamagnetic</u> as all the electrons present in it are paired.

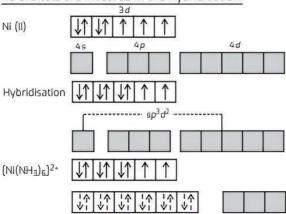
- (ii) Diamminechloridonitrito-N-platinum(II).
- (iii) (Co(en)<sub>3</sub>)<sup>3+</sup> is more stable than (Co(NH<sub>3</sub>)<sub>6</sub>)<sup>3+</sup> because it is a chelate complex due to the presence of bidentate ligand i.e. ethane-1, 2- diammine (en).
- Q 17. Write the hybridisation and magnetic character of the following complexes:
  - (i)  $[NiCl_4]^{2-}$  (ii)  $[Co(NH_3)_6]^{3+}$  (iii)  $[FeF_6]^{3-}$  [Atomic number : NI = 28, Co = 27, Fe = 26]

(CBSE 2022 Term 2)



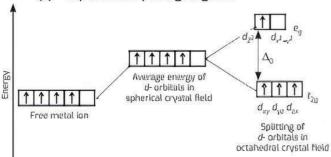
As inner *d*-electrons are involved, the complex is inner orbital complex and is diamagnetic in nature.

In the complex  $(Ni(NH_3)_6)^{3+}$ , the oxidation state of Ni is +2 and has  $3d^8$  configuration. Since six  $NH_3$  molecules (ligands) are to be accommodated, the hybridisation of metal ion is  $\underline{sp^3d^2}$ . This shows that 4d orbitals are involved in the hybridisation.



The complex is paramagnetic as well as outer orbital complex since outer (4d) electrons are involved in the hybridisation.

- Q 20. In a coordination entity, the electronic configuration of the central metal ion is  $t_{2g}^3e_g^1$ 
  - (i) Is the coordination compound a high spin or low spin complex?
  - (ii) Draw the crystal field splitting diagram for the above complex. (CBSE SQP 2022 Tarm-2)
- Ans. (i)  $t_{2g}^3 e_g^1$  configuration indicates that  $\Delta_0 < P$ . We know that <u>Ugands for which  $\Delta_0 < P$  form high spin complexes</u>.
  - (ii) Crystal field splitting diagram:



- Q 21. Answer the following questions:
  - (i) [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> (aq) is green in colour whereas [Ni(H<sub>2</sub>O)<sub>4</sub>(en)]<sup>2+</sup> (aq) is blue in colour, give reason in support of your answer.
  - (ii) Write the formula and hybridisation of the following compound:

tris(ethane-1,2-diammine) cobalt(III) sulphate
(CBSE SQP 2022 Term-2)

Ans. (i) The colour of coordination compound depends upon the type of ligand and d-d transition taking place.

H<sub>2</sub>O is weak field ligand, which causes small splitting, leading to the *d-d* transition corresponding to green colour, however due to

- the presence of (en) which is strong field ligand. the splitting is increased. Due to the change in  $t_{2a}-e_{a}$  splitting, the colouration of the compound changes from green to blue.
- (ii) Formula of the compound is  $(Co(H_2NCH_2CH_2NH_2)_3)_2(SO_4)_3$ The hybridisation of the compound is:  $d^2sp^3$ .
- Q 22. (i) Calculate the spin only magnetic moment of the complex  $[FeF_6]^{3-}$ . (Atomic number of Fe = 26)
  - (ii) [Ni(CN)<sub>4</sub>]<sup>2-</sup> with square-planar structure is diamagnetic and [NiCl<sub>4</sub>]<sup>2-</sup> with tetrahedral geometry is paramagnetic. Give reason to support the statement. [Atomic number: Ni = 28]
  - (iii) Write the number of ions produced in the solution from the following complex:

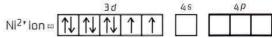
[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> (CBSE 2022 Term-2)

**Sol.** (I) No. of unpaired electrons in  $(FeF_e)^{3-l.e.}$ ,  $\underline{n=5}$ Spin only magnetic moment.  $\mu = \sqrt{n(n+2)}$ 

$$=\sqrt{5(5+2)}=\sqrt{35}=5.92\,\text{BM}$$

(ii) Oxidation state of Ni in  $(Ni(CN)_4)^{2-}$  and  $(NiCI_4)^{2-}$  is +2.

Electronic configuration of Ni<sup>2+</sup> = (Ar)  $3d^8 4s^0$ 



The presence of CN<sup>-</sup> ligand (which is a strong ligand) in  $[Ni(CN)_{\delta}]^{2-}$  causes pairing of all electrons and thus it is diamagnetic in nature but Cl<sup>-</sup> is a weak ligand which is unable to pair up the unpaired electrons and thus  $[NiCl_{\delta}]^{2-}$  is paramagnetic in nature.

- (iii) Three ions are produced in the solution from the given complex.
- Q 23. Explain with example the importance of coordination compounds in biological systems.
- Ans. Importance of coordination compounds in biological systems: Many compounds taking part in biological systems are coordination compounds. Description of some such compounds are as follows:
  - (i) Haemoglobin: Haem is a part of haemoglobin and present as red pigment of blood. It is a porphyrin complex of ion, which forms coordinate bonds with four N atoms and water molecules. Water molecule can be reversibly replaced by oxygen, resulting in the formation of oxyhaemoglobin.

Haemoglobin  $+ O_2 \Longrightarrow Oxyhaemoglobin + H_2O$  The above equilibrium can be displaced by the pressure of oxygen. In human lungs, the blood becomes saturated with oxygen and forms oxyhaemoglobin. As the blood flows in the vessels of tissues, the pressure reduces due to which bonded oxygen becomes free. Thus, it supplies oxygen to the cells of organisms.

- (ii) Chlorophyll: It is the <u>green colour pigment</u> present in the <u>green plants</u>. It is a complex of Mg<sup>2+</sup>. It helps in <u>photosynthesis</u> process occurring in plants.
- (iii) Vitamin B<sub>12</sub> (Cyanocobalamine): It is a <u>complex of</u> Co<sup>2</sup>° and used to cure anaemia.
- Q 24. Explain the importance of complex compounds in qualitative analysis by giving example.
- Ans. Importance of complex compounds in qualitative analysis: In the qualitative analysis of basic radicals, formation of different complex compounds play a key role. This is because basic radicals are identified by the colour of these complex compounds. Some such examples are as follows:
  - (i) Cu<sup>2+</sup> radical is identified by reacting it with ammonia. After the reaction, solution of blue coloured tetramminecopper(II) ion (complex ion) is formed.

$$Cu^{2*} + 4NH_3 \longrightarrow (Cu(NH_3)_4)^{2*}$$
  
Blue colour

(II) In III group, Fe<sup>3+</sup> ions are identified by adding solution of potassium ferrocyanide into the solution of Fe<sup>3+</sup> salt. After the reaction, <u>blue</u> colour complex ferriferrocyanide is formed.

$$4\operatorname{FeCl}_{3} + 3\operatorname{K}_{4}(\operatorname{Fe}(\operatorname{CN})_{6} \longrightarrow \operatorname{Fe}_{4}(\operatorname{Fe}(\operatorname{CN})_{6})_{3} + 12\operatorname{KCl}$$
Blue colour

(iii) In fourth group, on adding dimethylglyoxime to the solution of Ni<sup>2,4</sup> salt, pink or red precipitate of nickel dimethylglyoximate (complex compound) is formed.

(iv) In fourth group, on adding potassium ferrocyanide to the acidified solution of Zn<sup>2</sup> ion, <u>blue colour precipitate</u> of zinc hexacyanoferrate complex compound is formed.

$$ZnCl_2 + K_4 [Fe(CN)_6] \longrightarrow Zn_2 [Fe(CN)_6] + 4KCl$$
Blue ppt.



### Long Answer Type Questions \( \)

- Q 1. (i) Explain the bonding in coordination compounds in terms of Werner's postulates. [CO(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>.
  - (ii) Write the IUPAC name of the following complex:  $[Co(NH_x)_4Cl(NO_2)]Cl$ .
  - (iii) Write the formula for the following:
    Dichloridobis (ethane-1, 2-diamine) cobalt (III)
    chloride. (CBSE 2017, NCERT EXERCISE)

- Ans. (i) Werner's theory of coordination compounds:
  In order to explain the structure of compounds,
  Werner proposed the theory in 1893. The main
  postulates of this theory are as follows:
  - (a) Metals exhibit two types of valencies:
    - 1. **Primary or ionic valency:** It is the <u>valency</u> or oxidation state of metal in simple salts which is satisfied by only negative ions. It is ionisable and non-directional, which is represented by dotted line (.........).
    - 2. Secondary or non-ionic or extra valency: It is the coordination number of metal in the complex compound, which is mainly satisfied by neutral molecules or negative ions and sometimes by positive ions. It is non-ionisable and is represented by continuous line (—). It is directional and shows the geometry of complex.
  - (b) Each complex compound contains one or more central metal atom from which neutral molecule or negative ions are coordinately bonded. The total number of coordinate covalent bonds formed by the neutral molecules or negatively charged ligands with the metal atom or ion is called the coordination number of the metal. The sphere in which central metal atom and ligands are placed is called coordination sphere. It is represented by square brackets.
  - (c) Each metal satisfies its primary and secondary valencies. Primary valencies are satisfied by negative ions and secondary valencies are satisfied by negative ion as well as neutral molecules. Sometimes a negative ion satisfies both the primary and the secondary valencies. Thus, some anions (negative ions) can show dual nature, so they are non-ionisable in the solution.
  - (d) When a complex is dissolved in water, the anions attached by primary valencies, get ionised whereas that attached by secondary valencies remain non-ionisable.
  - (e) Primary valencies are <u>non-directional</u> whereas secondary valencies are <u>directional</u>. Geometry of coordination compounds is determined by the arrangement of secondary valencies.
  - (f) Ligands satisfying secondary valencies, can be arranged in space differently, thus they have different configuration. Hence, these compounds exhibit stereo isomerism and get hydrolysed to give three ions in the following manner:

- (ii) Tetraamminechloridonitrito-N-cobalt(III) chloride.
- (III) (CoCl<sub>2</sub>(en)<sub>2</sub>)Cl



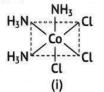
### **Chapter** Test

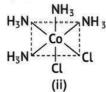
#### **Multiple Choice Questions**

Q1. Match the column I with column II and mark the appropriate choice:

	Column I		Column II
(A)	$[Ag(NH_3)_2]^+$	(i)	d²sp³, octahedral
(B)	$(Ni(CN)_4)^{2-}$	(ii)	dsp <sup>2</sup> , square planar
(C)	$(NI(CO)_4)$	(iii)	sp. linear
(D)	(Fe(CN) <sub>6</sub> ) <sup>3-</sup>	(iv)	$sp^3$ , tetrahedral

- a. (A)  $\rightarrow$  (i), (B)  $\rightarrow$  (ii), (C)  $\rightarrow$  (iii), (D)  $\rightarrow$  (iv)
- b. (A)  $\rightarrow$  (ii), (B)  $\rightarrow$  (ii), (C)  $\rightarrow$  (iv), (D)  $\rightarrow$  (i)
- c. (A)  $\rightarrow$  (iv). (B)  $\rightarrow$  (iii). (C)  $\rightarrow$  (ii). (D)  $\rightarrow$  (i)
- d. (A)  $\rightarrow$  (ii). (B)  $\rightarrow$  (i). (C)  $\rightarrow$  (iii). (D)  $\rightarrow$  (iv)
- Q 2. Which of the following statement is correct about  $[CO(H_2O)_6]^{2+}$  complex?
  - a. Electronic configuration =  $3d^7 \to t_{2g}^5 e_g^2$  no. of unpaired electrons = 3.  $\mu$  = 3.87 B.M.
  - b. Electronic configuration  $=3d^6\to t_{2g}^4e_g^2$  . no. of unpaired electrons =2,  $\mu=2.87$  B.M.
  - c. Electronic configuration  $= 3d^7 \to t^t_{2g} \ e^1_g$  , no. of the unpaired electron = 1,  $\mu = 2.87$  B.M.
  - d. Electronic configuration  $= 3d^7 \rightarrow t_{2g}^3, e_g^4$ , no. of unpaired electrons = 3,  $\mu = 3.87$  B.M.
- Q 3. The colour of the coordination compounds depend on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes  $[Co(NH_3)_5]^{3+}$ ,  $[Co(CN)_6]^{3-}$ ,  $[Co(H_2O)_6]^{3+}$ ?
  - a.  $(Co(CN)_6)^{3-} > (Co(NH_3)_6)^{3+} > (Co(H_2O)_6)^{3+}$
  - b.  $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$
  - c.  $[Co(H_2O)_6]^{3}$  >  $[Co(NH_2)_6]^{3+}$  >  $[Co(CN)_6]^{3-}$
  - d.  $(Co(NH_3)_6)^{3+} > (Co(CN_6))^{3-} > (Co(H_2O)_6)^{3+}$
- Q 4. Two isomers of a compound Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>(MA<sub>3</sub>B<sub>3</sub> type) are shown in the figure.





The isomers can be classified as:

- a. (I) fac-Isomer, (II) mer-Isomer
- b. (I) optical-isomer, (II) trans-isomer
- c. (I) mer-Isomer, (II) fac-Isomer
- d. (1) trans-isomer, (11) cis-isomer.

### Assertion and Reason Type Questions

**Directions (Q. Nos. 5-6):** Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:

- a. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
- b. Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of Assertion (A).
- c. Assertion (A) is true, but Reason (R) is false.
- d. Assertion (A) is false, but Reason (R) is true.
- **Q 5.** Assertion (A):  $[Cr(NH_3)_6]^{3\circ}$  is paramagnetic. Reason:  $[Cr(NH_3)_6]^{3+}$  shows  $d^2sp^3$  hybridisation.
- **Q 6.** Assertion (A): N(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub> and EDTA are examples of polydentate ligands.

**Reason (R):** Ligands when can ligate through two different atoms is called polydentate ligand.

#### **Case Study Based Question**

Q7. Valence bond theory describe the bonding in complexes in terms of coordinate covalent bonds resulting from overlap of field ligand orbitals with vacant metal hybrid orbitals. This theory explains magnetic behaviour and geometrical shape of coordination compounds.

Magnetic moment of a complex compound can be determined experimentally and theoretically by using spin only formula.

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

(where, n = no. of unpaired electrons)

Read the given passage carefully and give the answer of the following questions:

- (i) Write the state of hybridisation, shape and the magnetic behaviour of the  $[Cr(H_2O)_2(C_2O_4)_2]^{-1}$ .
- (ii) Why s-orbitals does not show preference to any direction?
- (iii) Why is  $[CoF_6]^{3-}$  is paramagnetic but  $[Co(NH_3)_6]^{3\circ}$  is diamagnetic in nature?

Describe the type of hybridisation, shape and magnetic properties of [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>] Cl. [Given: Atomic number of Co = 27]

#### **Very Short Answer Type Questions**

- Q 8. Explain the following:
  - $[Fe(CN)_6]^{4-}$  and  $[Fe(H_2O)_6]^{2+}$  are of different colours in dilute solutions.
- Q 9. What is the difference between a complex and a double salt?

#### **Short Answer Type-I Questions**

- Q 10. Give the name, the stereochemistry and magnetic behaviour of the following complexes.
  - (i) [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>
  - (ii) K<sub>2</sub>[Ni(CN)<sub>4</sub>]
- Q 11. (i) Write down the IUPAC name of the following complex: [Cr(en)<sub>3</sub>]Cl<sub>3</sub>
  - (ii) Write the formula for the following complex: Potassiumtrioxalato chromate (III)
- Q 12. Indicate the types of isomerisms exhibited by the complex  $[Co(NH_3)_5(NO_2)](NO_3)_2$ . [At. No. of Co = 27]

### **Short Answer Type-II Questions**

- Q 13. (i) Write the IUPAC name of the following complex:  $K_3[Cr(C_2O_4)_3]$ 
  - (ii) On the basis of crystal field theory, write the electronic configuration of  $d^5$  ion if  $\Delta_0 < P$ .
  - (iii) What are ambidentate ligands?
- Q 14. (i) Using valence bond theory, predict the hybridisation and magnetic character of following:

 $[CoF_6]^{3-}$  (Atomic number of Co = 27)

- (ii) Write IUPAC name of the following complex: [CoBr<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup>
- (iii) How many ions are produced from the complex [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> in solution?

Q 15. Write the IUPAC name and draw the structure of each of the following complex entities:

(i) 
$$\left[ co \begin{pmatrix} coo \\ coo \\ 1 \end{pmatrix}^{3} \right]_{3^{-}}$$

- (ii) [Cr(CO)<sub>6</sub>]
- (iii) [Pt Cl<sub>3</sub> (C<sub>2</sub>H<sub>4</sub>)] (Atomic no. of Cr = 25, Co = 27, Pt = 78)

### **Long Answer Type Questions**

Q 16. (i) For the complex ion [Fe(en)<sub>2</sub> Cl<sub>2</sub>]<sup>+</sup>, write the hybridisation type and magnetic behaviour. Draw one of the geometrical isomer of the complex ion which is optically active.

(Atomic No. : Fe = 26)

- (ii) State reason for the following: The molecular shape of  $Ni(CO)_4$  is not the same as that of  $[Ni(CN)_4]^{2-}$ .
- Q 17. (i) Using valence bond theory, explain the geometry and magnetic behaviour of [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>.
  - (ii) Write the IUPAC name of ionisation isomer of [Ni(NH<sub>3</sub>)<sub>3</sub> NO<sub>3</sub>] CL.
  - (iii) Write the electronic configuration of  $d^6$  on the basis of crystal field theory when:

(a) 
$$\Delta_0 < P$$
 and (b)  $\Delta_0 > P$ .