

# CBSE Class 12 physics Important Questions Chapter 9 Coordination Compounds

#### **5 Marks Questions**

#### 1. What are ligands? Explain different types of ligands.

Ans. The ions or molecules bound to central atom or ion in the coordination entity are ligands e.g  $\left\lceil Fe(CN)_5 \right\rceil^{4-}$  has six  $CN^-$  ligands.

Types:-

- (1) On the basis of charges on them ligands can be negative, positive (e.g.  $H_3O^+$ ,  $NH_4^+$  etc.) or neutral (e.g. CO,  $NH_3$ ,  $H_2O$ ).
- (2) On the basis of their donor atoms ligands can be monodentate or unidentate (one donor atom) e.g- $H_2O$ ,  $NH_3$ ,  $Cl^-$  etc, or didentate (two donor atoms)  $H_2NCH_2CH_2NH_2$  or  $C_2O_4^{2-}$  etc. or polydentate (several donor atoms) e.g  $\lceil EDTA \rceil^{4-}$  is a hexadentate ligand.
- (3) Ligands which can ligate through two different atoms are called ambidentate ligands eg.  $NO_2^-$  and  $SCN^-$  ions. Whereas when a di $^-$  or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is called chelate ligand.
- 2. Write the formulas for the following coordination compounds:
- (i) Tetraamminediaquacobalt (III) chloride
- (ii) Potassium tetracyanonickelate (II)
- (iii) Tris(ethane-1,2-diamine) chromium(III) chloride
- (iv) Amminebromidochloridonitrito-N-platinate (II)



#### (v) Dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate

#### (vi) Iron(III) hexacyanoferrate (II)

Ans. (i) 
$$\left[ CO(H_2O)_2(NH_3)_4 \right] Cl_3$$

(ii) 
$$K_2 \left[ N_i \left( CN \right)_4 \right]$$

(iii) 
$$\left[ \operatorname{Cr} \left( \operatorname{en} \right)_{3} \right] \operatorname{Cl}_{3}$$

(vi) 
$$\left[ Pt(NH)_3 BrCl(NO_2) \right]$$

(v) 
$$\left[ \text{PtCl}_2(\text{en})_2 \right] (\text{NO}_3)_2$$

(vi) 
$$\operatorname{Fe_4}[\operatorname{Fe}(\operatorname{CN})_6]_3$$

#### 3. Write the IUPAC names of the following coordination compounds:

(i) 
$$\left[ \text{Co}(\text{NH}_3)6 \right] \text{Cl}_3$$
 (ii)  $\left[ \text{Co}(\text{NH}_3)_5 \text{Cl} \right] \text{Cl}_2$ 

(iii) 
$$K_3 \Big[ Fe \big( CN \big)_6 \Big]$$
 (iv)  $K_3 \Big[ Fe \big( C_2 O_4 \big)_3 \Big]$ 

(v) 
$$K_2[PdCl_4]$$
 (vi)  $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$ 

Ans. (i) Hexaamminecobalt(III) chloride

- (ii) Pentaamminechloridocobalt(III) chloride
- (iii) Potassium hexacyanoferrate(III)
- (iv) Potassium trioxalatoferrate(III)
- (v) Potassium tetrachloridopalladate(II)
- (vi) Diamminechlorido(methylamine)platinum(II) chloride



### 4. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

(i) 
$$K \left[ Cr \left( H_2 O \right)_2 \left( C_2 O_4 \right)_2 \right]$$
 (ii)  $\left[ Co \left( en \right)_3 \right] Cl_3$ 

$$\textbf{(iii)}\left[\text{Co}\left(\text{NH}_3\right)_5 \left(\text{NO}_2\right) \left(\text{NO}_3\right)_2\right] \ \ \textbf{(iv)}\left[\text{Pt}\left(\text{NH}_3\right) \left(\text{H}_2\text{O}\right) \text{Cl}_2\right]$$

Ans. Both geometrical (*cis*-, *trans*-) isomers for  $K[Cr(H_2O)_2(C_2O_4)_2]$  can exist. Also, optical isomers for *cis*-isomer exist.

$$\begin{array}{c|c}
O & OH_2 \\
O$$

(ii) Two optical isomers for  $\left[ CO(en)_{3} \right] Cl_{3}$  exist.

Two optical isomers are possible for this structure.



(iii) 
$$[CO(NH_3)_5(NO_2)](NO_3)_2$$

A pair of optical isomers:

It can also show linkage isomerism.

$$\left[ \text{CO(NH}_3)_5 \left( \text{NO}_2 \right) \right] \left( \text{NO}_3 \right)_2 \text{ and } \left[ \text{CO(NH}_3)_5 \left( \text{ONO} \right) \right] \left( \text{NO}_3 \right)_2$$

It can also show ionization isomerism.

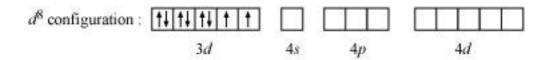
$$[Co(NH_3)_5(NO_2)](NO_3)_2$$
  $[CO(NH_3)_5(NO_3)](NO_3)(NO_2)$ 

(iv) Geometrical (cis-, trans-) isomers of  $[Pt(NH_3)(H_2O)Cl_2]$  can exist.

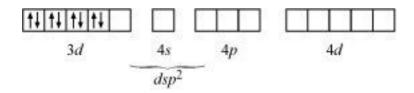
5. Explain on the basis of valence bond theory that  $\left\lceil N_i \left(CN\right)_4 \right\rceil^{2^-}$  ion with square planar structure is diamagnetic and the  $\left\lceil N_i C l_4 \right\rceil^{2-}$  ion with tetrahedral geometry is paramagnetic.

**Ans.** Ni is in the +2 oxidation state i.e., in  $d^{g}$  configuration.



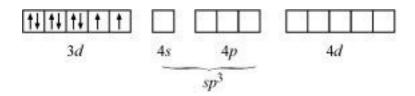


There are 4  $\rm CN^-$  ions. Thus, it can either have a tetrahedral geometry or square planar geometry. Since  $\rm CN^-$  ion is a strong field ligand, it causes the pairing of unpaired 3d electrons.



It now undergoes  $d_{Sp}^2$  hybridization. Since all electrons are paired, it is diamagnetic.

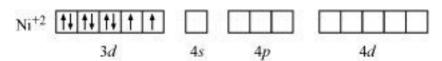
In case of  $[N_iCl_4]^{2-}$ ,  $CN^-$  ion is a weak field ligand. Therefore, it does not lead to the pairing of unpaired 3d electrons. Therefore, it undergoes  $sp^3$  hybridization.



Since there are 2 unpaired electrons in this case, it is paramagnetic in nature.

# 6. $\left[N_iCl_4\right]^2$ is paramagnetic while $\left[N_i\left(CO\right)_4\right]$ is diamagnetic though both are tetrahedral. Why?

**Ans.** Though both  $[NiCl_4]^{2-}$  and  $[Ni(CO)_4]$  are tetrahedral, their magnetic characters are different. This is due to a difference in the nature of ligands.  $CN^-$  is a weak field ligand and it does not cause the pairing of unpaired 3d electrons. Hence,  $[NiCl_4]^{2-}$  is paramagnetic.



In  $N_i$  (CO)<sub>4</sub>, Ni is in the zero oxidation state i.e., it has a configuration of  $3d^84s^2$ .

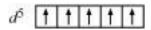




But CO is a strong field ligand. Therefore, it causes the pairing of unpaired 3d electrons. Also, it causes the 4s electrons to shift to the 3d orbital, thereby giving rise to  ${\rm sp}^3$  hybridization. Since no unpaired electrons are present in this case,  $\left[{\rm Ni}\left({\rm CO}\right)_4\right]$  is diamagnetic.

7.  $\left[ \text{Fe} \left( \text{H}_2 \text{O} \right)_6 \right]^{3+}$  is strongly paramagnetic whereas  $\left[ \text{Fe} \left( \text{CN} \right)_6 \right]^3$  is weakly paramagnetic. Explain.

**Ans.** In both  $\left[ F_e (H_2 O)_6 \right]^{3+}$  and  $\left[ F_e (CN)_6 \right]^{3-}$ , Fe exists in the +3 oxidation state i.e., in  $d^5$  configuration.



Since  $CN^-$  is a strong field ligand, it causes the pairing of unpaired electrons. Therefore, there is only one unpaired electron left in the d-orbital.



Therefore,

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

$$=\sqrt{1(1+2)}$$

$$=\sqrt{3}$$

$$=1.732 \text{ BM}$$

On the other hand,  $H_2O$  is a weak field ligand. Therefore, it cannot cause the pairing of electrons. This means that the number of unpaired electrons is 5.

Therefore,



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

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

$$=\sqrt{35}$$

= 6 BM

Thus, it is evident that  $\left[Fe(H_2O)_6\right]^{3+}$  is strongly paramagnetic, while  $\left[Fe(CN)_6\right]^3$  is weakly paramagnetic.

8. Explain  $\left[C_0\left(NH_3\right)_6\right]^{3+}$  is an inner orbital complex whereas  $\left[N_i\left(NH_3\right)_6\right]^{2+}$  is an outer orbital complex.

#### Ans.

$\left[\operatorname{Co}\left(\operatorname{NH}_{3}\right)_{6}\right]^{3+}$	$\left[Ni\left(NH_{3}\right)_{6}\right]^{2+}$
Oxidation state of cobalt = +3	Oxidation state of Ni = +2
Electronic configuration of cobalt = d <sup>6</sup>	Electronic configuration of nickel = d <sup>E</sup>
$^{3d}$ $^{4s}$ $^{4p}$ $^{4d}$ $^{4d}$ $^{4n}$ $^{4n$	If $\mathbb{NH}_3$ causes the pairing, then only one $3d$ orbital is empty. Thus, it cannot undergo $d^2 \operatorname{sp}^3$ hybridization. Therefore, it undergoes $\operatorname{sp}^3 d^2$ hybridization.



9.  $FeSO_4$  solution mixed with  $(NH_4)_2SO_4$  solution in 1:1 molar ratio gives the test of  $Fe^{2+}$  ion but  $CuSO_4$  solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of  $Cu^{2+}$  ion. Explain why?

Ans. 
$$(NH_4)_2 SO_4 + FeSO_4 + 6H_2O \rightarrow FeSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2O$$

Mohr's salt

 $CuSO_4 + 4NH_3 + 5H_2O \rightarrow \begin{bmatrix} Cu(NH_3)_4 \end{bmatrix} SO_4 \cdot 5H_2O$ 

tetraam minocopper (ii) sulphate

Both the compounds i.e.,  $FeSO_4$ .  $(NH_4)_2SO_4$ .  $6H_2O$  and  $[Cu(NH_3)_4]SO_4$ .  $5H_2O$  fall under the category of addition compounds with only one major difference i.e., the former is an example of a double salt, while the latter is a coordination compound.

A double salt is an addition compound that is stable in the solid state but that which breaks up into its constituent ions in the dissolved state. These compounds exhibit individual properties of their constituents. For e.g.  $FeSO_4$ .  $(NH_4)_2SO_4$ .6 $H_2O$  breaks into  $Fe^{2+}$ ,  $NH^{4+}$  and  $SO_4^{2-}$  ions. Hence, it gives a positive test for  $Fe^{2+}$  ions.

A coordination compound is an addition compound which retains its identity in the solid as well as in the dissolved state. However, the individual properties of the constituents are lost. This happens because  $\left[ Cu \left( NH_3 \right)_4 \right] SO_4.5H_2O \ does \ not \ show \ the \ test \ for \ Cu^{2+} \ .$  The ions present in the solution of  $\left[ Cu \left( NH_3 \right)_4 \right] SO_4.5H_2O \ are \\ \left[ Cu \left( NH_3 \right)_4 \right]^{2+} \ and \ SO_4^{2-} \ .$ 

10. Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

#### Ans. (i) Coordination entity:

A coordination entity is an electrically charged radical or species carrying a positive or negative charge. In a coordination entity, the central atom or ion is surrounded by a suitable number of neutral molecules or negative ions (called ligands). For example:



$$\left[Ni\left(NH_3\right)_6\right]^{2+}$$
,  $\left[Fe\left(CN\right)_6\right]^{4+}$  = cationic complex

$$[PtCl_4]^{2-}$$
,  $[Ag(CN)_2]^-$  = anionic complex

$$[N_1(CO)_4]$$
,  $[Co(NH_3)_4Cl_2]$  = neutral complex

#### (ii) Ligands

The neutral molecules or negatively charged ions that surround the metal atom in a coordination entity or a coordinal complex are known as ligands. For example,  $\stackrel{\cdot}{N}_{H_3}H_2\stackrel{\cdot}{O}$ , Cl - , - OH. Ligands are usually polar in nature and possess at least one unshared pair of valence electrons.

#### (iii) Coordination number:

The total number of ligands (either neutral molecules or negative ions) that get attached to the central metal atom in the coordination sphere is called the coordination number of the central metal atom. It is also referred to as its ligancy.

#### For example:

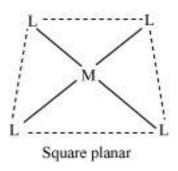
- (a) In the complex,  $K_2[PtCl_6]$ , there as six chloride ions attached to Pt in the coordinate sphere. Therefore, the coordination number of Pt is 6.
- (b) Similarly, in the complex  $[Ni(NH_3)_4]Cl_2$ , the coordination number of the central atom (Ni) is 4.

#### (vi) Coordination polyhedron:

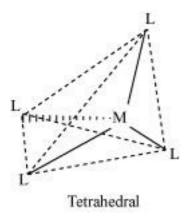
Coordination polyhedrons about the central atom can be defined as the spatial arrangement of the ligands that are directly attached to the central metal ion in the coordination sphere. For example:

(a)





#### (b) Tetrahedral



#### (v) Homoleptic complexes:

These are those complexes in which the metal ion is bound to only one kind of a donor group. For eg:  $\left[C_0(NH_3)_6\right]^{3+}$ ,  $\left[P_tCl_4\right]^{2-}$  etc.

#### (vi) Heteroleptic complexes:

Heteroleptic complexes are those complexes where the central metal ion is bound to more than one type of a donor group.

For e.g.: 
$$\left[\operatorname{Co}\left(\operatorname{NH}_{3}\right)_{4}\operatorname{Cl}_{2}\right]^{+}$$
,  $\left[\operatorname{Co}\left(\operatorname{NH}_{3}\right)_{5}\operatorname{Cl}\right]^{2+}$ 

# 11. What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.

**Ans.** A ligand may contain one or more unshared pairs of electrons which are called the donor sites of ligands. Now, depending on the number of these donor sites, ligands can be classified as follows:



- (a) Unidentate ligands: Ligands with only one donor sites are called unidentate ligands. For e.g.,  $"NH"_3$ , Cl etc.
- **(b) Didentate ligands:** Ligands that have two donor sites are called didentate ligands. For e.g.,
- (a) Ethane-1, 2-diamine

(b) Oxalate ion

#### (c)Ambidentate ligands:

Ligands that can attach themselves to the central metal atom through two different atoms are called ambidentate ligands. For example:

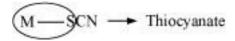
(a)

(The donor atom is N)

$$M = 0$$
 Nitrito group

(The donor atom is oxygen)

(b)





(The donor atom is S)

(The donor atom is N)

#### 12. Specify the oxidation numbers of the metals in the following coordination entities:

(i) 
$$\left[ \text{Co}(\text{H}_2\text{O})(\text{CN})(\text{en})_2 \right]^{2+}$$
 (ii)  $\left[ \text{CoBr}_2(\text{en})_2 \right]^{+}$ 

(iii) 
$$\left[\operatorname{PtCl}_{4}\right]^{2-}$$
 (iv)  $K_{3}\left[\operatorname{Fe}(\operatorname{CN})_{6}\right]$ 

(v) 
$$\left[\operatorname{Cr}\left(\operatorname{NH}_{3}\right)_{3}\operatorname{Cl}_{3}\right]$$

Ans. (i) 
$$\left[\operatorname{Co}\left(\operatorname{H}_2\operatorname{O}\right)(\operatorname{CN})(\operatorname{en})_2\right]^{2+}$$

Let the oxidation number of Co be x.

The charge on the complex is +2.

[Co (H<sub>2</sub>O) (CN) (en)<sub>2</sub>]<sup>2+</sup>  

$$\downarrow \qquad \downarrow \qquad \downarrow \qquad \downarrow$$
  
 $x + 0 + (-1) + 2(0) = +2$   
 $x - 1 = +2$   
 $x = +3$ 

(ii) 
$$\left[ Pt \left( Cl \right)_4 \right]^{2-}$$

Let the oxidation number of Pt be *x*.

The charge on the complex is -2.



$$\begin{bmatrix} Pt & (C1)_4 \end{bmatrix}^{2-}$$

$$x + 4(-1) = -2$$

$$x = +2$$

(iii) 
$$\left[ \text{Co} \left( \text{Br} \right)_2 \right]^{2+}$$
 $\downarrow \qquad \downarrow \qquad \downarrow$ 
 $x + 2(-1) + 2(0) = +1$ 
 $x - 2 = +1$ 
 $x = +3$ 

(iv) 
$$K_3$$
 [Fe(CN)<sub>6</sub>]

i.e., 
$$\left[ \text{Fe} \quad (\text{CN})_6 \right]^{3-}$$

$$\downarrow \qquad \downarrow$$

$$x + 6(-1) = -3$$

$$x = +3$$

(v) 
$$\begin{bmatrix} \operatorname{Cr} & (\operatorname{NH}_3)_3 & \operatorname{Cl}_3 \end{bmatrix}$$

$$\downarrow \qquad \downarrow \qquad \downarrow$$

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

$$x - 3 = 0$$

$$x = +3$$

- 13. Using IUPAC norms write the formulas for the following:
- (i) Tetrahydroxozincate(II)
- (ii) Potassium tetrachloridopalladate(II)
- (iii) Diamminedichloridoplatinum(II)



- (iv) Potassium tetracyanonickelate(II)
- (v) Pentaamminenitrito-O-cobalt(III)
- (vi) Hexaamminecobalt(III) sulphate
- (vii) Potassium tri(oxalato)chromate(III)
- (viii) Hexaammineplatinum(IV)
- (ix) Tetrabromidocuprate(II)
- (x) Pentaamminenitrito-N-cobalt(III)

Ans. (i) 
$$[Z_n(OH)_4]^{2-}$$

(iii) 
$$\left[ \text{Pt} \left( \text{NH}_3 \right)_2 \text{Cl}_2 \right]$$

(iv) 
$$K_2 \left[ Ni \left( CN \right)_4 \right]$$

(v) 
$$\left[ \text{Co} \left( \text{ONO} \right) \left( \text{NH}_3 \right)_5 \right]^{2+}$$

(vi) 
$$\left[ \text{Co} \left( \text{NH}_3 \right)_6 \right]_2 \left( \text{SO}_4 \right)_3$$

(vii) 
$$K_3 \left[ Cr \left( C_2 O_4 \right)_3 \right]$$

(viii) 
$$\left[ Pt(NH_3)_6 \right]^{4+}$$

(ix) 
$$\left[ Cu \left( Br \right)_4 \right]^{2-}$$

(x) 
$$\left[ \text{Ci}(\text{NO}_2)(\text{NH}_3)_5 \right]^{2+}$$



#### 14. Using IUPAC norms write the systematic names of the following:

(i) 
$$\left[ \text{Co} \left( \text{NH}_3 \right)_6 \right] \text{Cl}_3$$
 (ii)  $\left[ \text{Pt} \left( \text{NH}_3 \right)_2 \text{Cl} \left( \text{NH}_2 \text{CH}_3 \right) \right] \text{Cl}$ 

(iii) 
$$\left[ \text{Ti} \left( \text{H}_2 \text{O} \right)_6 \right]^{3+}$$
 (iv)  $\left[ \text{Co} \left( \text{NH}_3 \right)_4 \text{CI} \left( \text{NO}_2 \right) \right] \text{CI}$ 

(v) 
$$\left[\mathrm{Mn}\left(\mathrm{H_2O}\right)_6\right]^{2+}$$
 (vi)  $\left[\mathrm{NiCl_4}\right]^{2-}$ 

(vii) 
$$\left[\mathrm{Ni}\left(\mathrm{NH_3}\right)_6\right]\mathrm{Cl_2}$$
 (viii)  $\left[\mathrm{Co}\left(\mathrm{en}\right)_3\right]^{3+}$ 

(ix) 
$$\left[ Ni(CO)_4 \right]$$

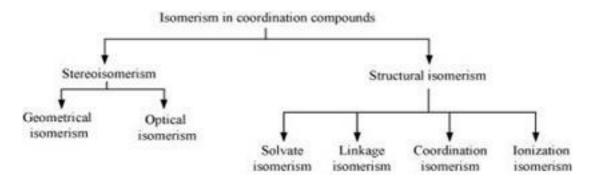
Ans. (i) Hexaamminecobalt(III) chloride

- (ii) Diamminechlorido(methylamine) platinum(II) chloride
- (iii) Hexaquatitanium(III) ion
- (iv) Tetraamminichloridonitrito-N-Cobalt(III) chloride
- (v) Hexaquamanganese(II) ion
- (vi) Tetrachloridonickelate(II) ion
- (vii) Hexaamminenickel(II) chloride
- (viii) Tris (ethane-1, 2-diammine) cobalt(III) ion
- (ix) Tetracarbonylnickel (0)

# 15. List various types of isomerism possible for coordination compounds, giving an example of each.

Ans.



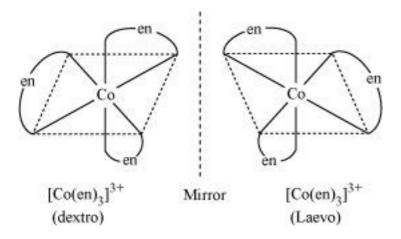


#### (a) Geometric isomerism:

This type of isomerism is common in heteroleptic complexes. It arises due to the different possible geometric arrangements of the ligands. For example:

#### (b) Optical isomerism:

This type of isomerism arises in chiral molecules. Isomers are mirror images of each other and are non-superimposable.



**(c) Linkage isomerism:** This type of isomerism is found in complexes that contain ambidentate ligands. For example:

$$\left[\text{Co}(\text{NH}_3)_5(\text{NO}_2)\right]\text{Cl}_2$$
 and  $\left[\text{Co}(\text{NH}_3)_5(\text{ONO})\text{Cl}_2\right]$ 

Yellow form Red form



#### (d) Coordination isomerism:

This type of isomerism arises when the ligands are interchanged between cationic and anionic entities of different metal ions present in the complex.

$$\left[\text{Co}\left(\text{NH}_{3}\right)_{6}\right]\!\!\left[\text{Cr}\left(\text{CN}\right)_{6}\right]\!\text{and}\left[\text{Cr}\left(\text{NH}_{3}\right)_{6}\right]\!\!\left[\text{Co}\left(\text{CN}\right)_{6}\right]$$

#### (e) Ionization isomerism:

This type of isomerism arises when a counter ion replaces a ligand within the coordination sphere. Thus, complexes that have the same composition, but furnish different ions when dissolved in water are called ionization isomers. For e.g.,  $Co(NH_3)_5 SO_4Br$  and  $Co(NH_3)_5 BrSO_4$ .

#### (f) Solvate isomerism:

Solvate isomers differ by whether or not the solvent molecule is directly bonded to the metal ion or merely present as a free solvent molecule in the crystal lattice.

$$[Cr(H_2O)_6]Cl_3[Cr(H_2O)_5Cl]Cl_2.H_2O[Cr(H_2O)_5Cl_2]Cl.2H_2O$$

Violet Blue-green Dark green

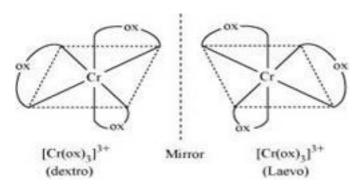
#### 16. Draw the structures of optical isomers of:

(i) 
$$\left[ \operatorname{Cr} \left( \operatorname{C}_2 \operatorname{O}_4 \right)_3 \right]^{3-}$$
 (ii)  $\left[ \operatorname{PtCl}_2 \left( \operatorname{en} \right)_2 \right]^{2+}$ 

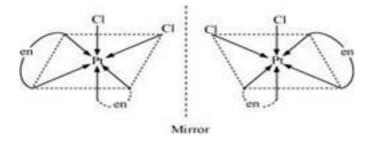
(iii) 
$$\left[\operatorname{Cr}\left(\operatorname{NH}_{3}\right)_{2}\operatorname{Cl}_{2}\left(\operatorname{en}\right)\right]^{+}$$

Ans. (i) 
$$\left[ \operatorname{Cr} \left( \operatorname{C}_2 \operatorname{O}_4 \right)_3 \right]^{3-}$$

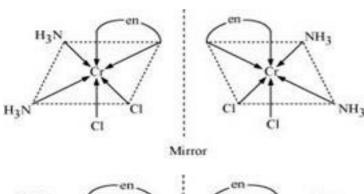


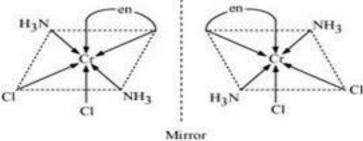


(ii) 
$$\left[\operatorname{PtCl}_{2}\left(\operatorname{en}\right)_{2}\right]^{2+}$$



(iii) 
$$\left[\operatorname{Cr}\left(\operatorname{NH}_{3}\right)_{2}\operatorname{Cl}_{2}\left(\operatorname{en}\right)\right]^{+}$$





#### 17. Draw all the isomers (geometrical and optical) of:

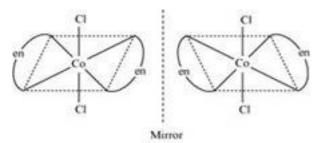
(i) 
$$\left[\operatorname{CoCl}_{2}\left(\operatorname{en}\right)_{2}\right]^{+}$$



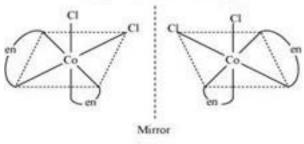
(ii) 
$$\left[ \text{Co} \left( \text{NH}_{3} \right) \text{Cl} \left( \text{en} \right)^{2} \right]^{2+}$$

(iii) 
$$\left[ \text{Co} \left( \text{NH}_3 \right)_2 \text{Cl}_2 \left( \text{en} \right) \right]^{+}$$

Ans. (i) 
$$\left[\operatorname{CoCl}_{2}\left(\operatorname{en}\right)_{2}\right]^{+}$$



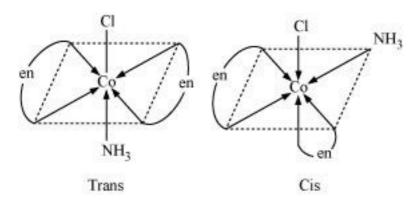
Trans [CoCl<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup>isomer-optically inactive (Superimposable mirror images)



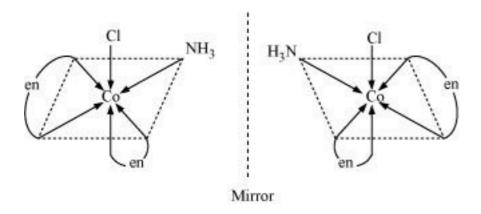
Cis [CoCl<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup>isomer-optically active (Non-superimposable mirror images)

In total, three isomers are possible.

(ii) 
$$\left[ \text{Co}(\text{NH}_3) \text{Cl}(\text{en})^2 \right]^{2+}$$



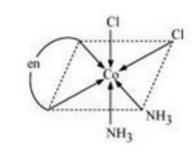


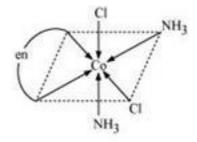


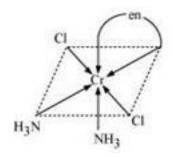
Trans-isomers are optically inactive.

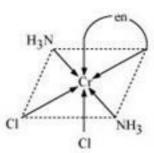
Cis-isomers are optically active.

(iii) 
$$\left[ \text{Co} \left( \text{NH}_3 \right)_2 \text{Cl}_2 \left( \text{en} \right) \right]^+$$









18. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(i) 
$$\left[ \text{Fe} \left( \text{CN} \right)_6 \right]^{4-}$$

(ii) 
$$\left[\mathrm{FeF_6}\right]^{3-}$$



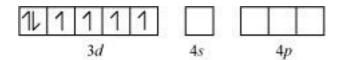
(iii) 
$$\left[ C_0 \left( C_2 O_4 \right)_3 \right]^{3-}$$

(iv) 
$$\left[\operatorname{CoF}_{6}\right]^{3-}$$

Ans. (i)  $\left[ \text{Fe} \left( \text{CN} \right)_6 \right]^{4-}$  In the above coordination complex, iron exists in the +II oxidation state.

 $Fe^{2+}$ : Electronic configuration is  $3d^6$ 

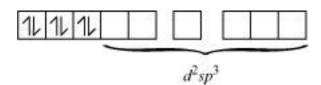
Orbitals of  $Fe^{2+}$  ion:



As  $CN^-$  is a strong field ligand, it causes the pairing of the unpaired 3d electrons.

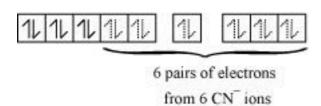
Since there are six ligands around the central metal ion, the most feasible hybridization is  $d^2sp^3\cdot$ 

 $d^2sp^3$  hybridized orbitals of  $Fe^{2+}$  are:



6 electron pairs from  $cN^-$  ions occupy the six hybrid  $d^2sp^3$  orbitals.

Then,



Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there

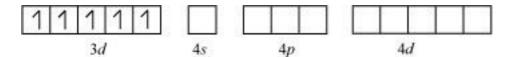


are no unpaired electrons).

(ii) 
$$\left[\mathrm{FeF_6}\right]^{3-}$$

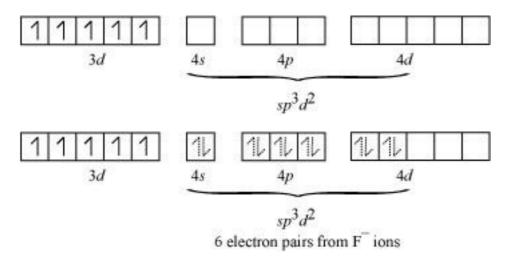
In this complex, the oxidation state of Fe is +3.

Orbitals of Fe<sup>3+</sup> ion:



There are 6 F- ions. Thus, it will undergo  $d^2sp^3$  or  $sp^3d^2$  hybridization. As  $F^-$  is a weak field ligand, it does not cause the pairing of the electrons in the 3d orbital. Hence, the most feasible hybridization is  $sp^3d^2$ .

sp<sup>3</sup>d<sup>2</sup>hybridized orbitals of Fe are:

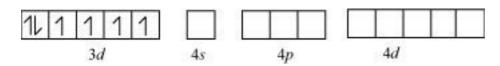


Hence, the geometry of the complex is found to be octahedral.

(iii) 
$$\left[ C_0 \left( C_2 O_4 \right)_3 \right]^{3-}$$

Cobalt exists in the +3 oxidation state in the given complex.

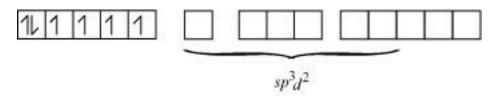
Orbitals of  $Co^{3+}$  ion:



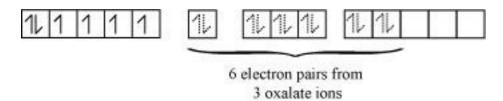


Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the 3d orbital electrons. As there are 6 ligands, hybridization has to be either  ${\sf sp}^3{\sf d}^2{\sf or}\ {\sf d}^2{\sf sp}^3$  hybridization.





The 6 electron pairs from the 3 oxalate ions (oxalate anion is a bidentate ligand) occupy these  $sp^3d^2$  orbitals.

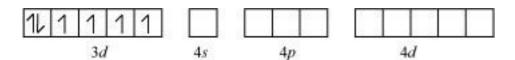


Hence, the geometry of the complex is found to be octahedral.

(iv) 
$$\left[ \text{CoF}_{6} \right]^{3-}$$

Cobalt exists in the +3 oxidation state.

Orbitals of  $C_0^{3+}$  ion:



Again, fluoride ion is a weak field ligand. It cannot cause the pairing of the 3d electrons. As a result, the  $Co^{3+}$  ion will undergo  $sp^3d^2$  hybridization.

 $sp^3d^2$  hybridized orbitals of  $Co^{3+}$  ion are:

19. What is crystal field splitting energy? How does the magnitude of  $\Delta_0$  decide the actual configuration of d-orbitals in a coordination entity?



Ans. The degenerate d-orbitals (in a spherical field environment) split into two levels i.e.,  $\mathbf{e}_{\underline{\mathbf{g}}}$  and  $\mathbf{t}_{2\underline{\mathbf{g}}}$  in the presence of ligands. The splitting of the degenerate levels due to the presence of ligands is called the crystal-field splitting while the energy difference between the two levels ( $\mathbf{e}_{\underline{\mathbf{g}}}$  and  $\mathbf{t}_{2\underline{\mathbf{g}}}$ ) is called the crystal-field splitting energy. It is denoted by  $\Delta_0$ .

After the orbitals have split, the filling of the electrons takes place. After 1 electron (each) has been filled in the three  $\mathbf{t}_{2\mathbf{g}}$  orbitals, the filling of the fourth electron takes place in two ways. It can enter the  $\mathbf{e}_{\mathbf{g}}$  orbital (giving rise to  $\mathbf{t}_{2\mathbf{g}}^{\mathbf{g}}$   $\mathbf{e}_{\mathbf{g}}^{\mathbf{l}}$  like electronic configuration) or the pairing of the electrons can take place in the  $\mathbf{t}_{2\mathbf{g}}$  orbitals (giving rise to  $\mathbf{t}_{2\mathbf{g}}^{\mathbf{g}}$   $\mathbf{e}_{\mathbf{g}}^{\mathbf{l}}$  like electronic configuration). If the  $\Delta_0$  value of a ligand is less than the pairing energy (P), then the electrons enter the  $\mathbf{e}_{\mathbf{g}}$  orbital. On the other hand, if the  $\Delta_0$  value of a ligand is more than the pairing energy (P), then the electrons enter the  $\mathbf{t}_{2\mathbf{g}}$  orbital.

20. 
$$\left[C_{r}\left(NH_{3}\right)_{6}\right]^{3+}$$
 is paramagnetic while  $\left[N_{i}\left(CN\right)_{4}\right]^{2-}$  is diamagnetic. Explain why?

**Ans.** Cr is in the +3 oxidation state i.e.,  $d^3$  configuration. Also,  $NH_3$  is a weak field ligand that does not cause the pairing of the electrons in the 3d orbital.



Therefore, it undergoes  $d^2sp^3$  hybridization and the electrons in the 3d orbitals remain unpaired. Hence, it is paramagnetic in nature.

In  $\left[N_i\left(CN\right)_4\right]^{2^-}$ , Ni exists in the +2 oxidation state i.e.,  $d^8$  configuration.



 $m CN^-$  is a strong field ligand. It causes the pairing of the 3d orbital electrons. Then,  $m Ni^{2+}$  undergoes  $m dsp^2$  hybridization.



As there are no unpaired electrons, it is diamagnetic.

# 21. Give the oxidation state, d-orbital occupation and coordination number of the central metal ion in the following complexes:

(i) 
$$K_3 \Big[ Co \left( C_2 O_4 \right)_3 \Big]$$
 (ii) cis-  $\Big[ Cr \left( en \right)_2 Cl_2 \Big] Cl$ 

(iii) 
$$(NH_4)_2[CoF_4]$$
 (iv)  $[Mn(H_2O)_6]SO_4$ 

Ans. (i) 
$$K_3 \left[ Co \left( C_2 O_4 \right)_3 \right]$$

The central metal ion is Co.

Its coordination number is 6.

The oxidation state can be given as:

$$x - 6 = -3$$

$$x = +3$$

The *d* orbital occupation for  $C_0^{3+}$  is  $t_{2g}^{6}e_{g}^{0}$ .

(ii) cis-
$$\left[\operatorname{Cr}\left(\operatorname{en}\right)_{2}\operatorname{Cl}_{2}\right]\operatorname{Cl}$$

The central metal ion is Cr.

The coordination number is 6.

The oxidation state can be given as:



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

$$x - 2 = +1$$

$$x = +3$$

The *d* orbital occupation for  $Cr^{3+}$  is  $t_{2g}^{3-}$ .

(iii) 
$$(NH_4)_2[CoF_4]$$

The central metal ion is Co.

The coordination number is 4.

The oxidation state can be given as:

$$x - 4 = -2$$

$$x = +2$$

The *d* orbital occupation for  $Co^{2+}$  is  $e_g^4 t_{2g}^3$ .

(iv) 
$$\left[\operatorname{Mn}\left(\operatorname{H}_{2}\operatorname{O}\right)_{6}\right]\operatorname{SO}_{4}$$

The central metal ion is Mn.

The coordination number is 6.

The oxidation state can be given as:

$$x + 0 = +2$$

$$x = +2$$

The *d* orbital occupation for Mn is  $t_{2g}^{3} e_{g}^{2}$ .

22. 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) 
$$K\left[Cr\left(H_2O\right)_2\left(C_2O_4\right)_2\right].3H_2O$$
 (ii)  $\left[Co\left(NH_3\right)_5Cl\right]Cl_2$ 

(iii) 
$$CrCl_3(py)_3$$
 (iv)  $Cs[FeCl_4]$ 

(v) 
$$K_4 \left[ Mn \left( CN \right)_6 \right]$$

Ans. (i) Potassium diaquadioxalatochromate (III) trihydrate.

Oxidation state of chromium = 3

Electronic configuration:  $3d^3$ :  $t_{2g}^3$ 

Coordination number = 6

Shape: octahedral

#### Stereochemistry:

$$\begin{array}{c|c}
OH_2 & OH_2 \\
OH_2 & OH_2
\end{array}$$

$$Cis$$

$$OH_2 & OH_2 \\
OH_2 & OH_2$$

$$OH_2 & OH_2 \\
OH_2 & OH_2$$

Trans is optically inactive



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

$$=\sqrt{3(3+2)}$$

$$=\sqrt{15}$$

$$-4BM$$

(ii) 
$$\left[ \text{Co} \left( \text{NH}_3 \right)_5 \text{Cl} \right] \text{Cl}_2$$

IUPAC name: Pentaamminechloridocobalt(III) chloride

Oxidation state of Co = +3

Coordination number = 6

Shape: octahedral.

Electronic configuration:  $d^6$ :  $t_{2g}^{6}$ .

**Stereochemistry:** 



$$CI$$
 $NH_3$ 
 $NH_3$ 

Magnetic Moment = 0

IUPAC name: Trichloridotripyridinechromium (III)

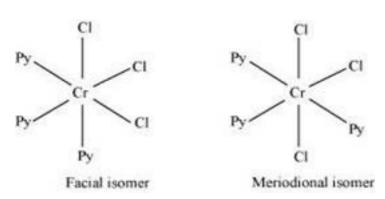
Oxidation state of chromium = +3

Electronic configuration for  $d^3 = t_{2g}^3$ 

Coordination number = 6

Shape: octahedral.

#### Stereochemistry:



Both isomers are optically active. Therefore, a total of 4 isomers exist.

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

$$=\sqrt{3(3+2)}$$



$$=\sqrt{15}$$

$$-4BM$$

(iv) 
$$Cs[FeCl_4]$$

IUPAC name: Caesium tetrachloroferrate (III)

Oxidation state of Fe = +3

Electronic configuration of  $d^6 = e_g^2 t_{2g}^3$ 

Coordination number = 4

Shape: tetrahedral

Stereochemistry: optically inactive

Magnetic moment:

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

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

$$=\sqrt{35}\sim 6BM$$

(v) 
$$K_{_{4}} \Big[ Mn \left( CN \right)_{_{6}} \Big]$$

Potassium hexacyanomanganate(II)

Oxidation state of manganese = +2

Electronic configuration:  $d^{5+}$ :  $t_{2g}^{-5}$ 

Coordination number = 6

Shape: octahedral.

Streochemistry: optically inactive



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

$$=\sqrt{1(1+2)}$$

$$=\sqrt{3}$$

$$= 1.732$$

# 23. What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

**Ans.** The stability of a complex in a solution refers to the degree of association between the two species involved in a state of equilibrium. Stability can be expressed quantitatively in terms of stability constant or formation constant.

$$M + 3L \leftrightarrow ML_3$$

Stability constant, 
$$\beta = \frac{[ML_3]}{[M][L]^3}$$

For this reaction, the greater the value of the stability constant, the greater is the proportion of  $\mathbf{ML}^3$  in the solution.

Stability can be of two types:

#### (a)Thermodynamic stability:

The extent to which the complex will be formed or will be transformed into another species at the point of equilibrium is determined by thermodynamic stability.

#### (b)Kinetic stability:

This helps in determining the speed with which the transformation will occur to attain the state of equilibrium.

#### Factors that affect the stability of a complex are:



- (a) **Charge on the central metal ion:** The greater the charge on the central metal ion, the greater is the stability of the complex.
- **(b) Basic nature of the ligand:** A more basic ligand will form a more stable complex.
- (c) **Presence of chelate rings:** Chelation increases the stability of complexes.
- 24: Discuss briefly giving an example in each case the role of coordination compounds in:
- (i) biological system
- (ii) medicinal chemistry
- (iii) analytical chemistry
- (iv) extraction/metallurgy of metals

#### Ans. (i) Role of coordination compounds in biological systems:

We know that photosynthesis is made possible by the presence of the chlorophyll pigment. This pigment is a coordination compound of magnesium. In the human biological system, several coordination compounds play important roles. For example, the oxygen-carrier of blood, i.e., haemoglobin, is a coordination compound of iron.

#### (ii) Role of coordination compounds in medicinal chemistry:

Certain coordination compounds of platinum (for example, *cis*-platin) are used for inhibiting the growth of tumours.

#### (iii) Role of coordination compounds in analytical chemistry:

During salt analysis, a number of basic radicals are detected with the help of the colour changes they exhibit with different reagents. These colour changes are a result of the coordination compounds or complexes that the basic radicals form with different ligands.

#### (iii) Role of coordination compounds in extraction or metallurgy of metals:



The process of extraction of some of the metals from their ores involves the formation of complexes. For example, in aqueous solution, gold combines with cyanide ions to form  $\left[Au(CN)_2\right].$  From this solution, gold is later extracted by the addition of zinc metal.