

## 7. ISOMERISM IN COORDINATION COMPOUNDS

Two or more substances having the same molecular formula but different spatial arrangements are called isomers and the phenomenon is called isomerism. Coordination compounds show two main types of isomerism-

A) Structural Isomerism

B) Stereoisomerism

**STRUCTURAL ISOMERISM:-** It arises due to the difference in structures of coordination compounds. It is further subdivided into the following types-

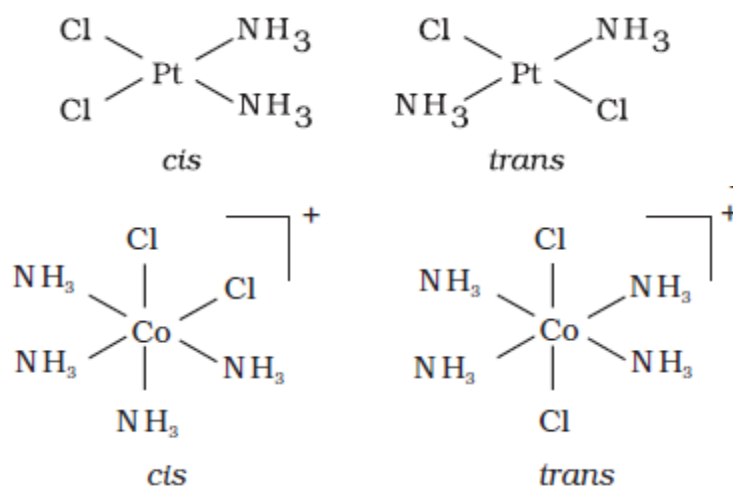
- 1) **Ionisation isomerism :** This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionization isomers  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ .
- 2) **Hydrate or solvate isomerism:** This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet) and its solvate isomer  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (grey-green).
- 3) **Linkage Isomerism:** Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand,  $\text{NCS}$ -, which may bind through the nitrogen to give  $\text{M-NCS}$  or through sulphur to give  $\text{M-SCN}$ .
- 4) **Coordination isomerism:** It arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex .  
Example  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  &  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

**STEREOISOMERISM:** Stereo isomers have the same chemical formula and chemical bonds but they have different spatial arrangement. They are of two kinds

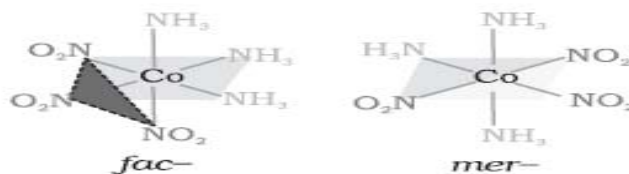
A. Geometrical isomerism

B. Optical isomerism

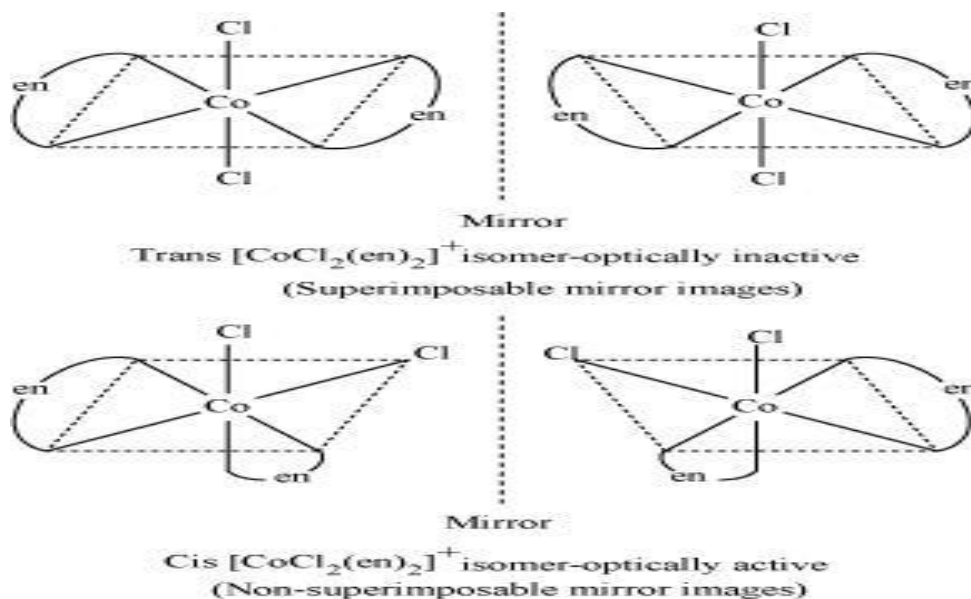
**GEOMETRICAL ISOMERISM-** This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6. In a square planar complex of formula  $[\text{MX}_2\text{L}_2]$  (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer  $[\text{MABXL}]$ -Where A,B,X,L are unidentates  
Two cis- and one trans- isomers are possible.



Another type of geometrical isomerism occurs in octahedral coordination entities of the type  $[\text{Ma}_3\text{b}_3]$  like  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ . If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer.



b) **OPTICAL ISOMERISM:** Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral. The two forms are called dextro (d) and laevo (l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, l to the left). Optical isomerism is common in octahedral complexes involving didentate ligands. In a coordination entity of the type  $[\text{CoCl}_2(\text{en})_2]^{2+}$ , only the cis-isomer shows optical activity



### TYPES OF HYBRIDISATION

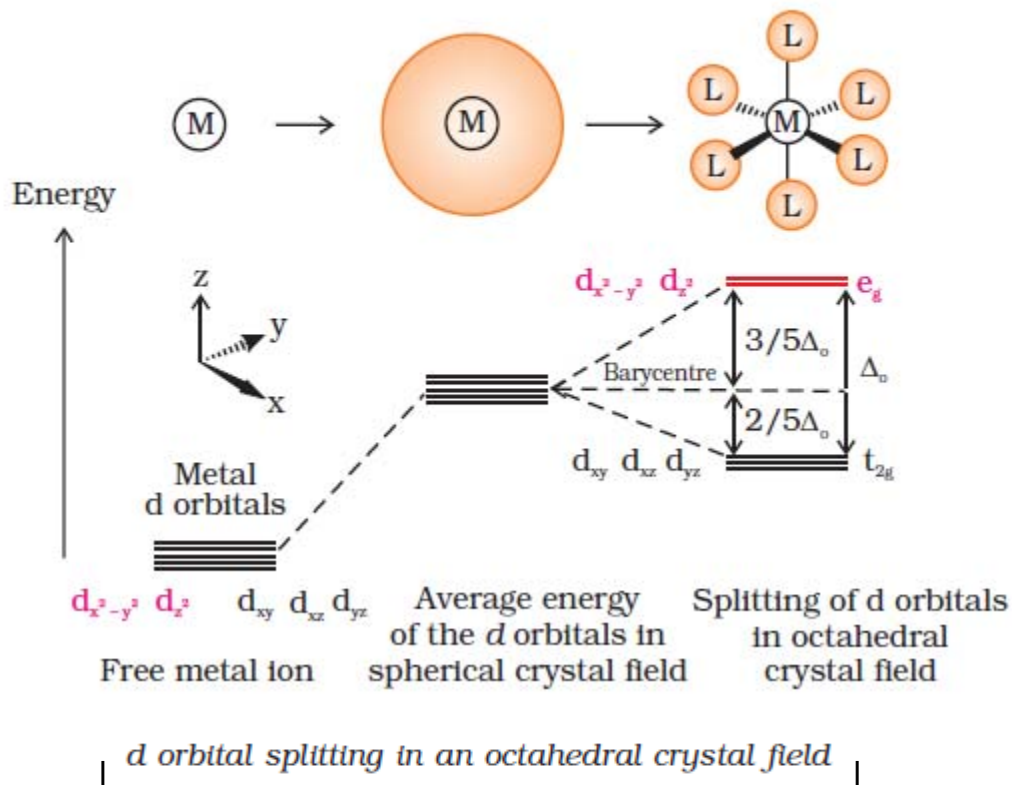
Coordination number	Type of hybridisation	Acquired geometry
4	$sp^3$	Tetrahedral
4	$dsp^2$	Square planar
5	$sp^3d$	Trigonal bipyramidal
6	$sp^3d^2$	Octahedral
6	$d^2sp^3$	Octahedral

### 8. CRYSTAL FIELD THEORY:

1. The metal-ligand bond is ionic arising purely from electrostatic interactions between the metal ion and the ligand.
2. Ligands are treated as point charges or dipoles in case of anions and neutral molecules.
3. In an isolated gaseous metal atom or ion the five d-orbitals are degenerate.
4. Degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal /ion.
5. In a complex the negative field becomes asymmetrical and results in splitting of the

d-orbitals.

### A) CRYSTAL FIELD SPLITTING IN OCTAHEDRAL COORDINATION ENTITIES



1. For  $d^4$  ions, two possible patterns of electron distribution arise:

(i) If  $\Delta_o < P$ , the fourth electron enters one of the  $e_g$  orbitals giving the

configuration  $t^3_{2g} e^1_g$ . Ligands for which  $\Delta_o < P$  are known as weak

field ligands and form high spin complexes.

(ii) If  $\Delta_o > P$ , it becomes more energetically favourable for the fourth electron to occupy a  $t_{2g}$  orbital with configuration  $t^4_{2g} e^0_g$ . Ligands which produce this effect are known as strong field ligands and form low spin complexes.

### B) CRYSTAL FIELD SPLITTING IN TETRAHEDRAL COORDINATION ENTITIES

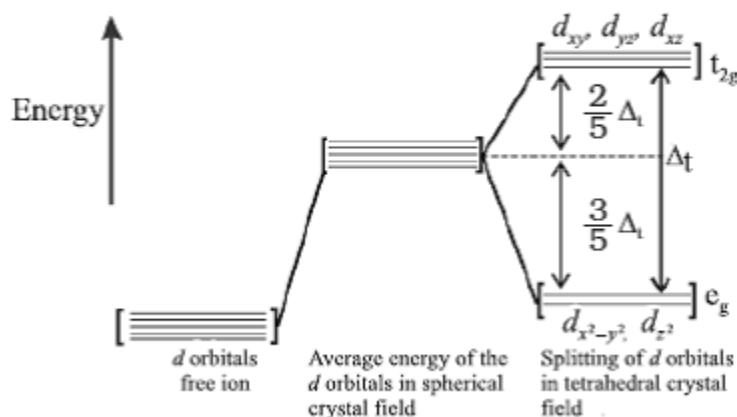
1. The four surrounding ligands approach the central metal atom/ion along the planes between the axes.

2. The  $t_{2g}$  orbitals are raised in energy ( $2/5$ )  $t$ .

3. The two  $e_g$  orbitals are lowered in energy ( $3/5$ )  $t$

4. The splitting is smaller as compared to octahedral field splitting,  $t=(4/9) \Delta_o$ .

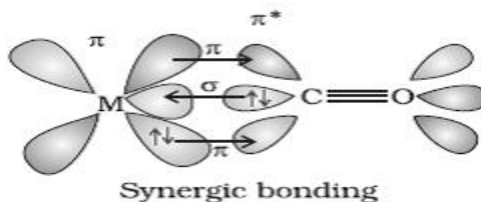
5. Pairing of electrons is rare and thus complexes have generally high spin configurations.



### BONDING IN METAL CARBONYLS

The metal-carbon bond in metal carbonyls possess both  $\sigma$  and  $\pi$  character. The M-C  $\sigma$  bond

is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M-C  $\pi$  bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding  $\pi^*$  orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal .



### SOLVED QUESTIONS

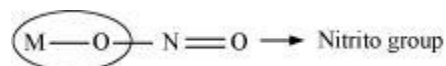
#### 1 MARK QUESTIONS

1. What are ambidentate ligands? Give two examples for each.

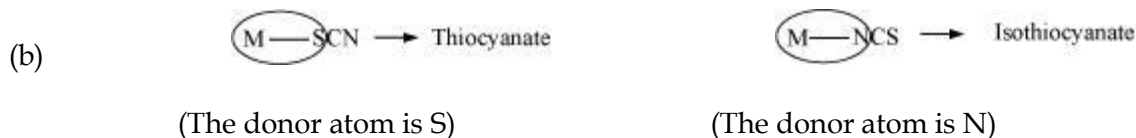
ANS. Ambidentate ligands are ligands that can attach themselves to the central metal atom through two different atoms. For example:



(The donor atom is N)



(The donor atom is oxygen)



**Q2. Using IUPAC norms write the formula for the following: Tetrahydroxozincate(II)**

**ANS.**  $[\text{Zn}(\text{OH})_4]^{2-}$

**Q3. Using IUPAC norms write the formula for the following: Hexaamminecobalt(III) sulphate**

**ANS.**  $[\text{Co}(\text{NH}_3)_6]_2 (\text{SO}_4)_3$

**Q4. Using IUPAC norms write the formula for the following: Pentaamminenitrito-O-cobalt(III)**

**ANS.**  $[\text{Co}(\text{ONO}) (\text{NH}_3)_5]^{2+}$

**Q5. Using IUPAC norms write the systematic name of the following:  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$**

**ANS.** Hexaamminecobalt(III) chloride

**Q6. Using IUPAC norms write the systematic name of the following:**

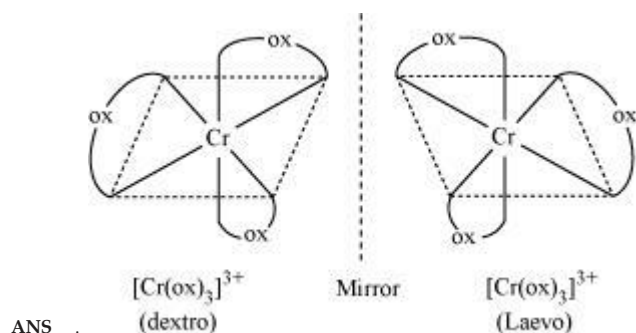
**$[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$**

**ANS.** Diamminechlorido(methylamine) platinum(II) chloride

**Q7. Using IUPAC norms write the systematic name of the following:  $[\text{Co}(\text{en})_3]^{3+}$**

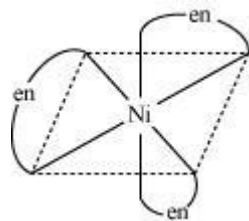
**ANS.** Tris(ethane-1, 2-diammine) cobalt(III) ion

**Q8. Draw the structures of optical isomers of:  $c[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$**



**Q9. What is meant by the chelate effect? Give an example.**

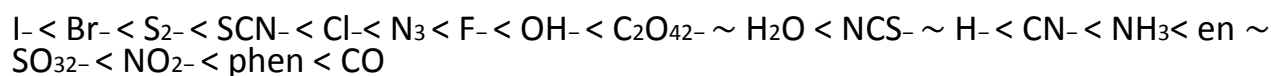
**ANS.** When a ligand attaches to the metal ion in a manner that forms a ring, then the metal-ligand association is found to be more stable.



## 2 / 3 MARK QUESTIONS

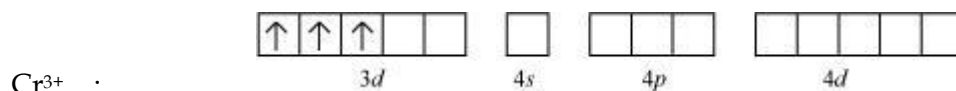
**Q1. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.**

**ANS.** A spectrochemical series is the arrangement of common ligands in the increasing order of their crystal-field splitting energy (CFSE) values.



**Q2.  $[Cr(NH_3)_6]^{3+}$  is paramagnetic while  $[Ni(CN)_4]^{2-}$  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.

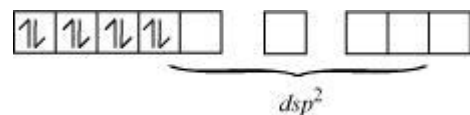


Therefore, it undergoes  $d^2sp^3$  hybridization and the electrons in the 3d orbitals remain unpaired. Hence, it is paramagnetic in nature.

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



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

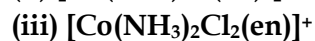
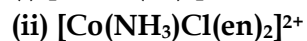
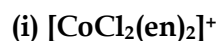


**Q3. A solution of  $[Ni(H_2O)_6]^{2+}$  is green but a solution of  $[Ni(CN)_4]^{2-}$  is colourless. Explain.**

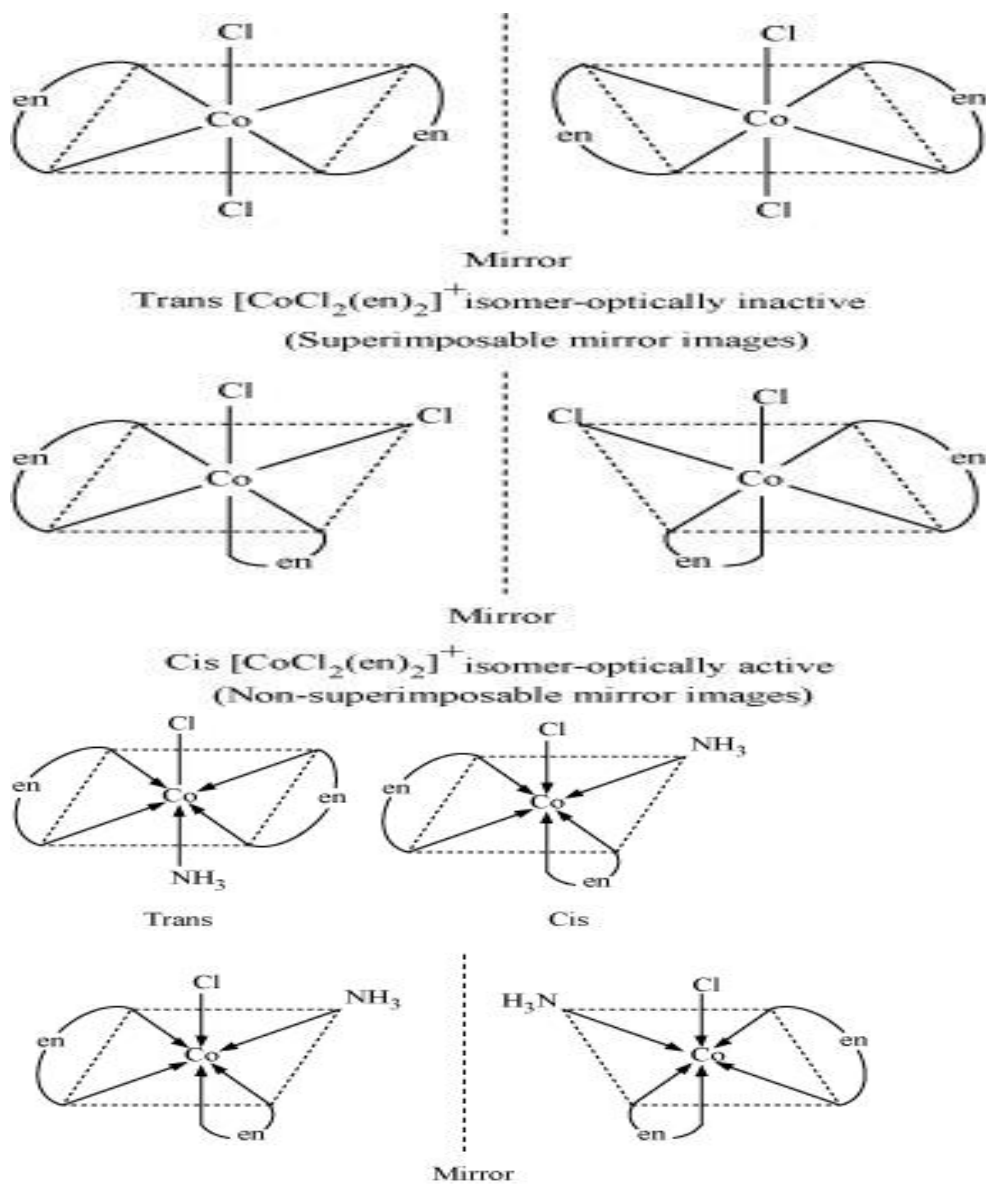
**ANS.** In  $[Ni(H_2O)_6]^{2+}$ ,  $H_2\ddot{O}$  is a weak field ligand. Therefore, there are unpaired electrons in  $Ni^{2+}$ . In this complex, the d electrons from the lower energy level can be excited to the higher energy level i.e., the possibility of d-d transition is present. Hence,  $[Ni(H_2O)_6]^{2+}$  is coloured.

In  $[\text{Ni}(\text{CN})_4]^{2-}$ , the electrons are all paired as  $\text{CN}^-$  is a strong field ligand. Therefore, d-d transition is not possible in  $[\text{Ni}(\text{CN})_4]^{2-}$ . Hence, it is colourless. As there are no unpaired electrons, it is diamagnetic.

Q2. Draw all the isomers (geometrical and optical) of:



ANS. (i)  $[\text{CoCl}_2(\text{en})_2]^+$

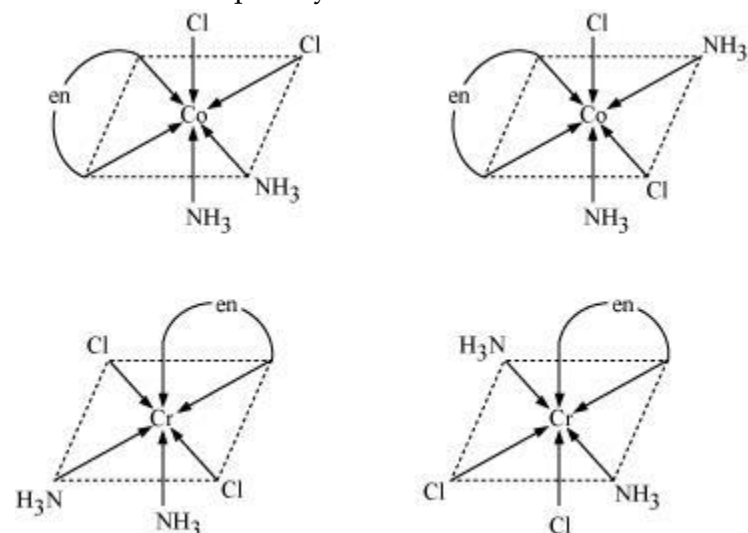


In total, three isomers are possible.



Trans-isomers are optically inactive.

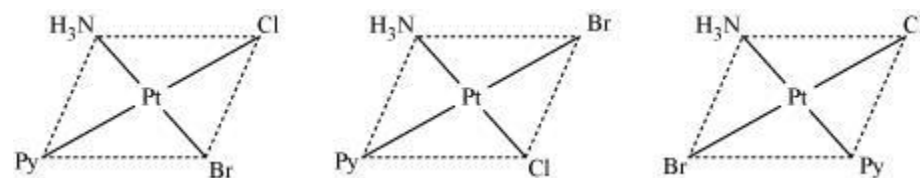
Cis-isomers are optically active.



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

**Q3. Write all the geometrical isomers of  $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{py})]$  and how many of these will exhibit optical isomers?**

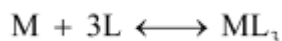
ANS.  $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{py})]$



From the above isomers, none will exhibit optical isomers. Tetrahedral complexes rarely show optical isomerization. They do so only in the presence of unsymmetrical chelating agents.

**Q4. 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.



$$\text{Stability constant, } \beta = \frac{[\text{ML}_3]}{[\text{M}][\text{L}]^3}$$

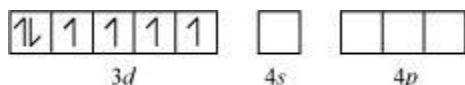
For this reaction, the greater the value of the stability constant, the greater is the proportion of  $\text{ML}_3$  in the solution.

## 5 MARKS QUESTIONS

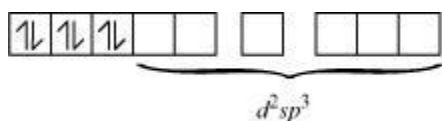
Q1. (a) Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(i)  $[\text{Fe}(\text{CN})_6]^{4-}$  (ii)  $[\text{FeF}_6]^{3-}$  (iii)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  (iv)  $[\text{CoF}_6]^{3-}$

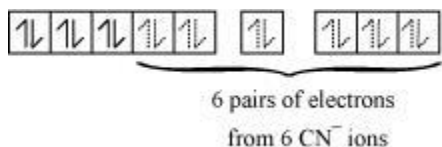
ANS. (i)  $[\text{Fe}(\text{CN})_6]^{4-}$  In the above coordination complex, iron exists in the +II oxidation state.  $\text{Fe}^{2+}$ : Electronic configuration is  $3d^6$  Orbitals of  $\text{Fe}^{2+}$  ion:



As  $\text{CN}^-$  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  $d^2sp^3$ .  $d^2sp^3$  hybridized orbitals of  $\text{Fe}^{2+}$  are:



6 electron pairs from  $\text{CN}^-$  ions occupy the six hybrid  $d^2sp^3$  orbitals. Then,

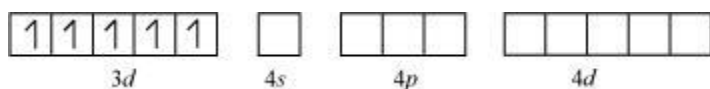


Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons).

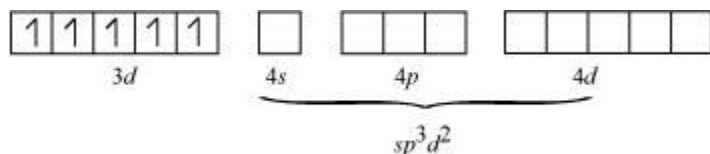
(ii)  $[\text{FeF}_6]^{3-}$

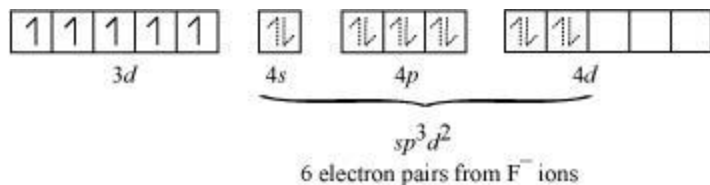
In this complex, the oxidation state of Fe is +3.

Orbitals of  $\text{Fe}^{3+}$  ion:



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

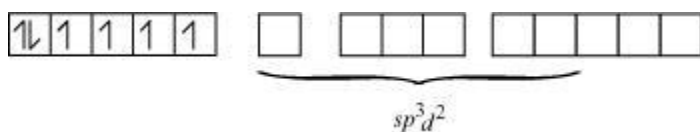




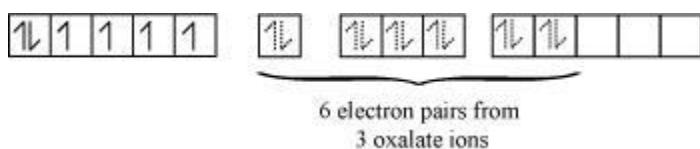
Hence, the geometry of the complex is found to be octahedral.

**(iii)  $[Co(C_2O_4)_3]^{3-}$**

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  $sp^3d^2$  or  $d^2sp^3$  hybridization.  $sp^3d^2$  hybridization of  $Co^{3+}$ :



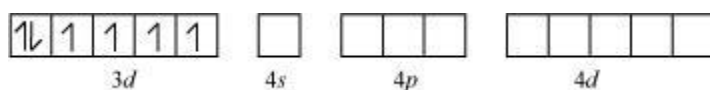
The 6 electron pairs from the 3 oxalate ions (oxalate anion is a bidentate ligand) occupy these  $sp^3d^2$  orbitals.



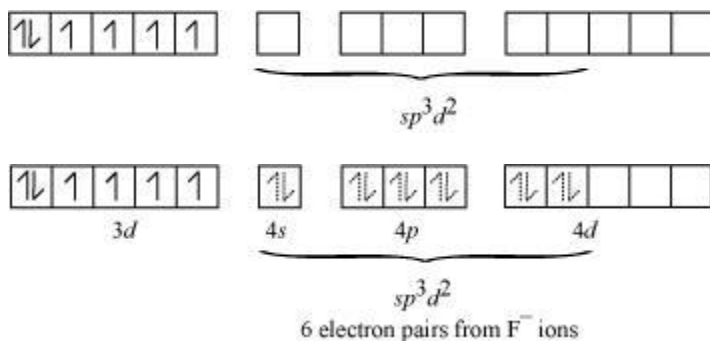
Hence, the geometry of the complex is found to be octahedral.

**(iv)  $[CoF_6]^{3-}$** -Cobalt exists in the +3 oxidation state.

Orbitals of  $Co^{3+}$  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:



Hence, the geometry of the complex is octahedral and paramagnetic.

**Q3. 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)  $K[Cr(H_2O)_2(C_2O_4)_2] \cdot 3H_2O$  (ii)  $[Co(NH_3)_5Cl]Cl_2$  ANS. (i) Potassium diaquadioxalatochromate (III) trihydrate.**

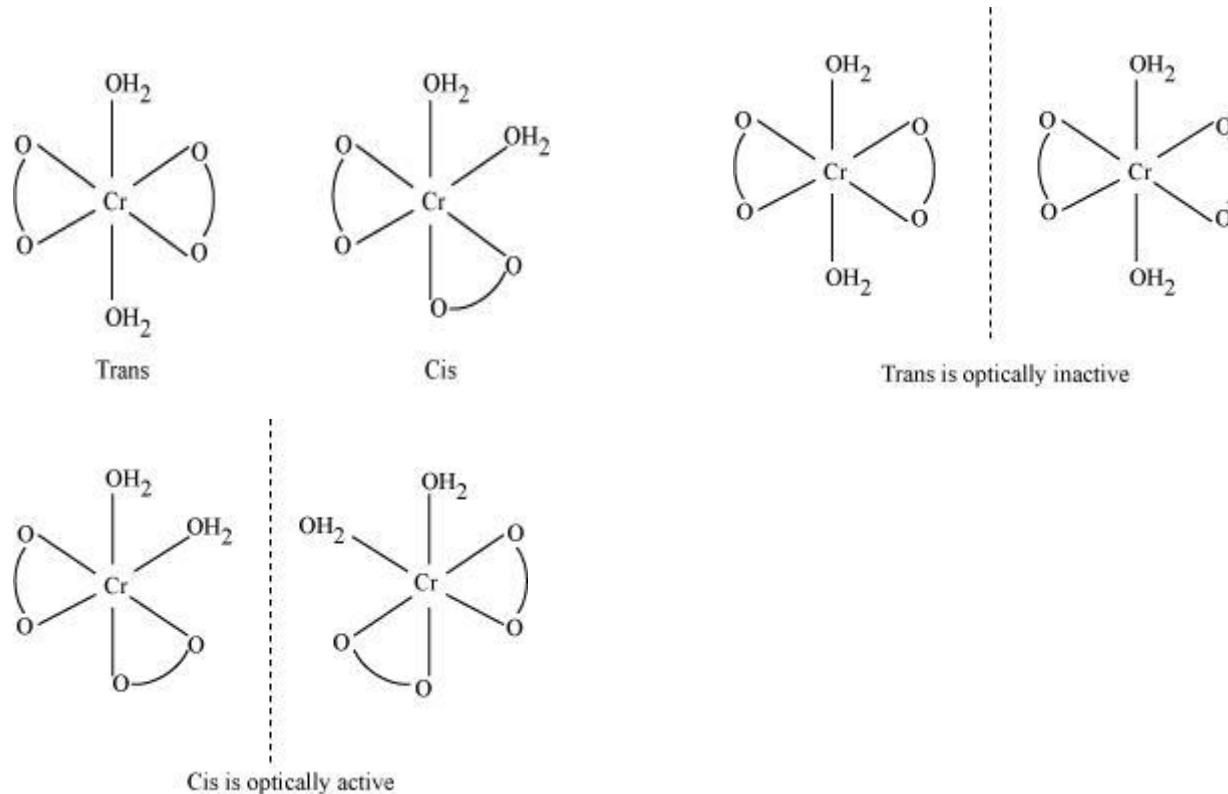
Oxidation state of chromium = 3

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

Coordination number = 6

Shape: octahedral

**Stereochemistry:**



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

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

$$= \sqrt{15}$$

~ 4BM

**(ii)  $[Co(NH_3)_5Cl]Cl_2$**

IUPAC name: Pentaamminechloridocobalt(III) chloride

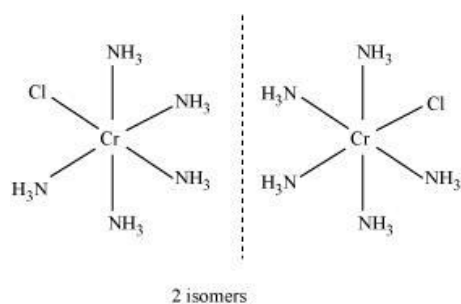
Oxidation state of Co = +3

Coordination number = 6

Shape: octahedral.

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

**Stereochemistry:**



Magnetic Moment = 0

### LEVEL 1

1. Why do tetrahedral complex not show geometrical isomerism?
2. Why does the colour changes on heating  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  .
3.  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is strongly paramagnetic whereas  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic. Explain.
4. What happens when potassium ferrocyanide solution is added to a ferric salt solution?

### LEVEL 2

5. A coordination compound has a formula  $(\text{CoCl}_3 \cdot 4\text{NH}_3)$ . It does not liberate  $\text{NH}_3$  but precipitates chloride ion as  $\text{AgCl}$ . Give the IUPAC name of the complex and write its structural formula.
6. Write the correct formula for the following co-ordination compounds.
 

	$\text{CrCl}_3 \cdot$
$6\text{H}_2\text{O}$ (Violet, with 3 Chloride ions/ Unit formula)	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$
(Light green colour with 2 Chloride ions/ unit formula)	
7. Give the electronic configuration of the d-orbitals of Ti in  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion in an octahedral crystal field.
8.  $\text{Co}(\text{II})$  is stable in aqueous solution but in the presence of strong ligands and air, it can get oxidized to  $\text{Co}(\text{III})$ . (Atomic Number of cobalt is 27). Explain.
9. Give a chemical test to distinguish between  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4\text{Br}$ . Name the type of isomerism exhibited by these compounds.
10. What is the coordination entity formed when excess of aqueous  $\text{KCN}$  is added to an aqueous solution of copper sulphate? Why is that no precipitate of copper sulphate is obtained when  $\text{H}_2\text{S}$  (g) is passed through this solution?

### LEVEL 3

11. Aqueous copper sulphate solution (blue in colour) gives a green precipitate with aqueous potassium fluoride, a bright green solution with aqueous potassium chloride. Explain these experimental results.

12. A metal complex having the composition  $\text{Cr}(\text{NH}_4)_4\text{Cl}_2\text{Br}$  has been isolated in two forms, A and B. The form A reacts with  $\text{AgNO}_3$  solution to give a white precipitate readily soluble in dilute aqueous ammonia whereas B give a pale yellow precipitate soluble in concentrated ammonia solution. Write the formulae of A and B and write their IUPAC names.

13. Explain the following

i. All octahedral complexes of  $\text{Ni}^{2+}$  must be outer orbital complexes. ii.

$\text{NH}_4^+$  ion does not form any complex.

iii.  $(\text{SCN})^{-1}$  ion is involved in linkage isomerism in co-ordination compounds.

14. A metal ion  $\text{Mn}^{+}$  having  $d^4$  valence electronic configuration combines with three didentate ligands to form complexes. Assuming  $\Delta_o > P$  Draw the diagram showing d orbital splitting during this complex formation. Write the electronic configuration of the valence electrons of the metal  $\text{Mn}^{+}$  ion in terms of  $t_{2g}$  and  $e_g$ . What type of the hybridization will  $\text{Mn}^{+}$  ion have? Name the type of isomerism exhibited by this complex.

15. The coordination no. of  $\text{Ni}^{2+}$  is 4.

$\text{NiCl}_2 + \text{KCN}(\text{excess}) \rightarrow \text{A}$  ( a cyano complex )

$\text{A} + \text{Conc HCl}(\text{excess}) \rightarrow \text{B}$  ( a chloro complex )

i) Write IUPAC name of A and B

ii) Predict the magnetic nature of A and B

iii) Write hybridization of Ni in A and B

16. Explain the following

i.  $\text{Cu}(\text{OH})_2$  is soluble in ammonium hydroxide but not in sodium hydroxide solution. ii.

EDTA is used to cure lead poisoning

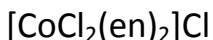
iii. Blue coloured solution of  $[\text{CoCl}_4]^{2-}$  changes to pink on reaction with  $\text{HgCl}_2$ .

## 1 MARK QUESTIONS

Q1. Write the formula for the following coordination compound:

Tetraamineaquachloridocobalt(III) chloride

Q2. Write the IUPAC name of the following coordination compound:



- Q3. Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?
- Q4. Out of the following two coordination entities which is chiral (optically active)?  
(a) *cis*- $[\text{CrCl}_2(\text{ox})_2]^{3-}$  (b) *trans*- $[\text{CrCl}_2(\text{ox})_2]^{3-}$
- Q5. The spin only magnetic moment of  $[\text{MnBr}_4]^{2-}$  is 5.9 BM. Predict the geometry of the complex ion?
- Q6.  $[\text{NiCl}_4]^{2-}$  is paramagnetic while  $[\text{Ni}(\text{CO})_4]$  is diamagnetic though both are tetrahedral. Why?

## 2 MARKS QUESTIONS

- Q1. Draw structures of geometrical isomers of  $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$
- Q2. Indicate the type of isomerism exhibited by the following complex and draw the structures for these isomers:  
 $[\text{Co}(\text{en})_3]\text{Cl}_3$
- Q3. Give evidence that  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$  are ionization isomers.
- Q4. Calculate the overall complex dissociation equilibrium constant for the  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion, given that  $\beta_4$  for this complex is  $2.1 \times 10^{13}$ .
- Q5. What is meant by unidentate ligand? Give two examples.
- Q6. What is meant by didentate ligand? Give two examples.
- Q7. What is meant by ambidentate ligands? Give two examples.
- Q8. Draw the structures of optical isomers of:  
 $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$
- Q9. Discuss the nature of bonding in metal carbonyls.
- Q10. What is meant by the *chelate effect*? Give an example.
- Q11. Draw the structures of:  
(i)  $\text{Ni}(\text{CO})_4$  (ii)  $\text{Fe}(\text{CO})_5$

## 3 MARKS QUESTIONS

- Q1. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:  
(i)  $[\text{Fe}(\text{CN})_6]^{4-}$  (ii)  $[\text{FeF}_6]^{3-}$  (iii)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$   
Also predict their magnetic behaviour.
- Q2. What is crystal field splitting energy? Draw figure to show the splitting of *d* orbitals in an octahedral crystal field. How does the magnitude of  $\Delta_o$  decide the actual configuration of *d* orbitals in a coordination entity?
- Q3. Discuss briefly giving an example in each case the role of coordination compounds in:  
(i) biological systems (iii) analytical chemistry