Chapter 9
Coordination Compounds

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1 Marks Questions

1. What is the shape of $\left[Fe\ (CO)_5\right]$?

Ans. $\left[Fe\ (CO)_5\right]$

Geomectry = Trigonal bipyramidal/span>

2. What do you understand by stability of a complex and instability constant of coordination compounds?

Ans. The stability of a complex in solution is the degree of association between the two species involved in the state of equilibrium. The instability constant is reciprocal of the formation constant. It is also called dissociation constant.

3. How is EDTA used in estimation of hardness of water?
Ans. Hard water is titrated with Na_2-EDTA complex for estimation of its hardness. During the process, the $Ca^{2+} and\ Mg^{2+}$ ions form complex with EDTA replacing Na^+. The method is based on the difference in the stability constant of calcium and magnesium complexes.

4. Explain the role of complexes in metallurgy with an example.

Ans. Some extraction processes make use of complex formation e.g. during metallurgy of Gold, it combines with cyanide in the presence of oxygen and water to form the complex

$\left[Au\ (CN)_2\right]-$ in aqueous solution by addition of zinc.

5. How is excess of copper and iron removed from body?

Ans. Excess of copper and iron are removed by chelating Ligands D – penicillamine and desferrioxime B through the formation of coordination compounds.

6. Define – isomerism.

Ans. Isomerism is the phenomenon of existence of two or more compounds with same chemical formula but a different arrangement of atoms.

7. Indicate the types of isomerisms shown by the complex – $K\left[Fe\ (H_2O)_2(en)_2Cl_2\right]$ **?**

Ans. Both geometrical and optical isomerisms will be present.

8. Give an example of coordination isomerism?

Ans. Example of coordination isomerism is

$\left[Cr\ (NH_3)_6\right]\left[Co\ (CN)_6\right]$ and $\left[Co\ (NH_3)_6\right]\left[Cr\ (CN)_6\right]$

9. What are complex compounds?

Ans. Complex compounds or coordination compounds are those compounds in which the metal atoms are bound to a number of anions or neutral molecules.

10. Give some examples of coordination compounds.

Ans. Examples of coordination compounds are chlorophyll, haemoglobin and vitamin B_{12}.

11. What were the two valences given by Werner for coordination compounds?

Ans. Werner gave the concept of two valences-

(a) Primary or ionisable valences.

(b) Secondary or non ionisable valences.

12. Enlist the common shapes of Werner's complexes.

Ans. The common shapes given by Werner were – octahedeal, tetrahedral and square planar.

13. What do you understand by the term coordination number?

Ans. The total number of ligand donor atoms to which a metal is directly bonded is called its coordination number e.g. in complex $\left[PtCl_4\right]^{2-}$, the coordination number of Pt is 4.

14. Define oxidation state of a metal. Distinguish between homoleptic and hetroleptic ligands.

Ans. The oxidation number of a metal is the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the metal atom or ion.

15. What IUPAC names of following complexes?

(i). $\left[Co\ (NH_3)_6\right]^{3+}$

(ii). $\left[Fe\ (C_2O_4)_3\right]^{3-}$

(iii). $\left[Ni\ (CN)_4\right]^{2-}$

(iv). $\left[Pt(NH_3)_4\,Cl_2\right]^{2+}$

(v). $[NiCl_4]^{2-}$

(vi). $\left[Co(NH_3)_5\,ONO\right]^{2+}$

(vii). $\left[Co\ (NH_3)_5\,Cl\right]Cl_2$

(viii). $\left[Cr\ (CN)\ (H_2O)_5\right]^{2+}$

(ix). $\left[Co\ (NO_2)_6\right]^{3-}$

(x). $\left[Co\ (en)_3\right]Cl_3$

Ans.(i) Hexamminecobalt (III)ion

(ii). Trioxalatoferrate (III) ion

(iii). Tetracyanonickelate (II) ion

(iv). Tetraamminedichlidooroplatinum (IV) ion

(v). Tetrachloridoonickelate (II) ion

(vi). Pentamminenitrito –O-cobalt (III) ion

(vii). Pentamminechlorido cobalt (III) Chloride

(viii). Pentaquacyano chromium (III) ion

(ix). Hexanitrito –N-cobaltate (III) ion

(x). Tris (ethylenediamine) Cobalt (III) Chloride

16. Write formula for the following compounds.

i). Hexammineplatinum (VI) Chloride

ii). Potassium hexacyanoferrate (III) ion

iii). diamminedichloridoplatinum (III) ion

iv). Tetramminedichloridocobalt (III) ion

v). Amine chlorobis (elhylenediamine) cobalt (III) ion.

vi). Hexaamminechromium (III) hexacyanocobaltate (III)

vii).Pentamminenitro –N- Cobalt (III) Chloride.

viii).Pentamminebromidoocobalt (III) sulphate

ix). triamminediaquachlorocobalt (III) Chloride

x). Tetramminedichloridooplatinum (IV) Bromide

Ans.(i) $\left[Pt\ (NH_3)_6\right] Cl_6$

(ii). $K_3\left[Fe\ (CN)_6\right]$

(iii). $\left[Pt\ (Cl)_2(NH_3)_2\right]^+$

(iv). $\left[Co\ (NH_3)_4 Cl_2\right]^+$

(v). $\left[Co\ Cl\ (en)_2 (NH_3)\right]^{2+}$

(vi). $\left[Cr\ (NH_3)_6\right]\left[CO(CN)_6\right]$

(vii). $\left[Co\ (NH_3)_5 NO_2\right]\ Cl_2$

(viii). $\left[Co\ (NH_3)_5 Br\ \right]\ SO_4$

(ix). $\left[Co\ (NH_3)_3 (H_2O)_2 Cl\ \right]\ Cl_2$

(x). $\left[Pt\ Cl_2 (NH_3)_4\right]\ Br_2$

17. How many ions are produced from the complex $\mathrm{Co(NH_3)_6Cl_2}$ in solution?

(i) 6 (ii) 4 (iii) 3 (iv) 2

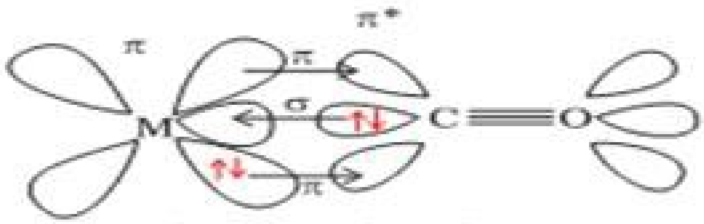
Ans. (iii) The given complex can be written as $\mathrm{Co(NH_3)_6Cl_2}$.

Thus, $\left[\mathrm{Co(NH_3)_6}\right]^+$ along with two Cl- ions are produced.

2 Marks Questions

1.Explain the synergic bonding in metal carbonyls.

Ans. The metal – carbon bond in metal carbonyls has both s & P- character. The M – C σ bond is formed by donation of lone pair of electrons of carbonyl carbon into a vacant orbital of metal. The M – C π bond is formed by the donation of a pair of electron from a filled d- orbital of metal to the vacant π orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect that strengthens the bond.



Synergic bonding

2. Give some example showing importance of complexes in biological system?

Ans. Examples of complexes in biological system.-

1. Chlorophyll is a complex of Mg.
2. Haemoglobin is a complex of iron.
3. Cyanocobalamine , Vit B_{12}, is a complex of cobalt.

3.Give examples of complexes in

a) Chemical analysis
b) Industrics

Ans. (a) Chemical analysis –

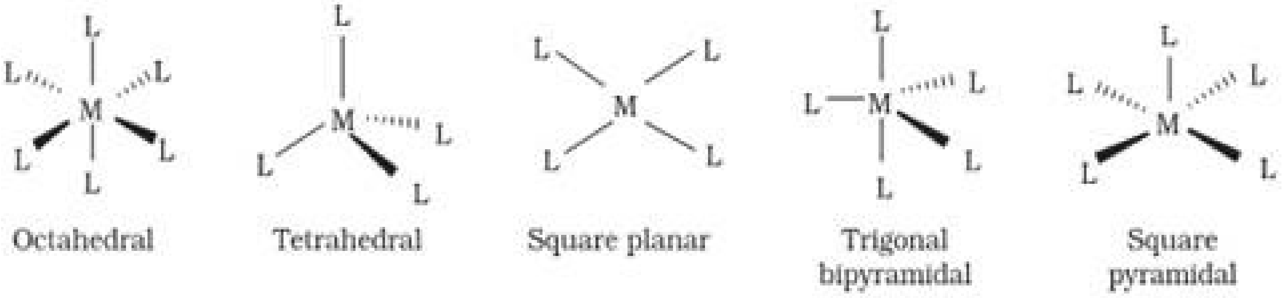
Qualitative and Quantitative analysis methods involve use of Ligands like EDTA, DMG etc.
(b) Industries.
Hydrogenation of alkenes is done by using a sodium complex called Wilkinson catalyst. In black and white photography, silver complexes are used.

4.Distinguish between homoleptic and hetroleptic ligands.

Ans. Homoleptic complexes are those in which only one type of ligand or donor group is present e.g. $\left[Pt(NH_3)_6\right]^{3+}$ has only NH_3 as ligand. Whereas hetroleptic complexes are those in which different types of ligands are present eg. $\left[Pt(NH_3)_4Cl_2\right]^{+}$ has two type of ligands- NH_3 and Cl^-.

5.What are the different shapes or coordination polyhedra in the complexes?

Ans. The various coordination polyhedra are –



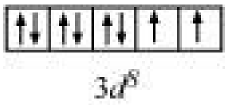
6.What is the difference between a double salt and a complex? Explain with an example.

Ans. Double salts dissociate completely into simple ions when dissolved in water e.g., Mohr salt, $FeSO_4(NH_4)_2SO_4, 6H_2O$ will dissolve in water and give ferrous, ammonium and sulphate ions. On the other hand, the complex ions do not completely dissociate into all constituent ions e.g. $K_4[Fe(CN)_6]$ will dissociate to give potassium ions and $\left[Fe(CN)_6\right]^{4-}$ ions only.

7.**Predict the number of unpaired electrons in the square planar $\left[\mathrm{Pt(CN)_4}\right]^{2-}$ ion.**

Ans. $\left[\mathrm{Pt(CN)_4}\right]^{2-}$

In this complex, Pt is in the +2 state. It forms a square planar structure. This means that it undergoes $\mathrm{dsp^2}$ hybridization. Now, the electronic configuration of Pd(+2) is .

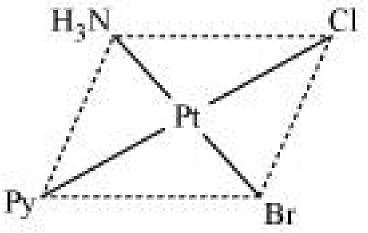


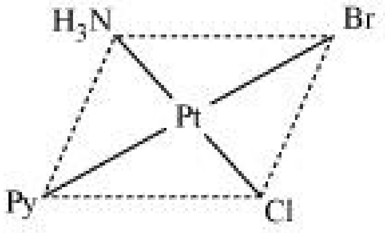
$5d^8$

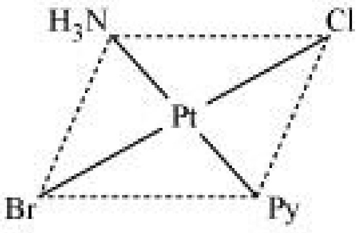
CN^- being a strong field ligand causes the pairing of unpaired electrons. Hence, there are no unpaired electrons in $[Pt(CN)_4]^{2-}$.

8.**Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?**

Ans. $[Pt(NH_3)(Br)(Cl)(py)]$







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.

9.**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. The ligands present on the R.H.S of the series are strong field ligands while that on the L.H.S are weak field ligands. Also, strong field ligands cause higher splitting in the *d* orbitals than weak field ligands.

$$I- < Br^- < S^{2-} < SCN^- < Cl^- < N_3 < F^- < OH^- < C_2O_4^{2-}$$
$$\sim H_2O < NCS^- \sim H^- < CN^- < NH_3 < en \sim SO_3^{2-} < NO_2^- < phen < CO$$

10.**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.

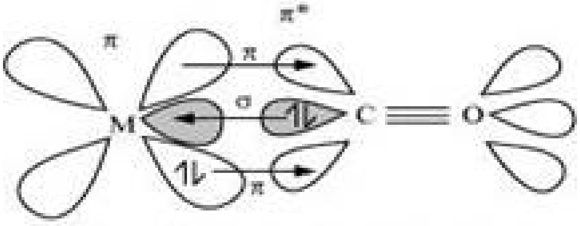
In $[Ni(CN)_4]^{2-}$, the electrons are all paired as CN^- is a strong field ligand. Therefore, *d*-*d* transition is not possible in $[Ni(CN)_4]^{2-}$. Hence, it is colourless.

11. $\left[Fe(CN)_6\right]^{4-}$ and $\left[Fe(H_2O)_6\right]^{2+}$ are of different colours in dilute solutions. Why?

Ans. The colour of a particular coordination compound depends on the magnitude of the crystal-field splitting energy, Δ. This CFSE in turn depends on the nature of the ligand. In case of $\left[Fe(CN)_6\right]^{4-}$ and $\left[Fe(H_2O)_6\right]^{2+}$, the colour differs because there is a difference in the CFSE. Now, CN^- is a strong field ligand having a higher CFSE value as compared to the CFSE value of water. This means that the absorption of energy for the intra *d-d* transition also differs. Hence, the transmitted colour also differs.

12. Discuss the nature of bonding in metal carbonyls.

Ans.The metal-carbon bonds in metal carbonyls have both σ and Π characters. σ bond is formed when the carbonyl carbon donates a lone pair of electrons to the vacant orbital of the metal. A Π bond is formed by the donation of a pair of electrons from the filled metal *d* orbital into the vacant anti-bonding Π^* orbital (also known as back bonding of the carbonyl group). The σ bond strengthens the Π bond and vice-versa. Thus, a synergic effect is created due to this metal-ligand bonding. This synergic effect strengthens the bond between CO and the metal.



Synergic bonding in metal carbonyls

13.**The oxidation number of cobalt in $K\left[Co(CO)_4\right]$ is**

(i) +1 (ii) +3

(iii) -1 (iv) -3

Ans. We know that CO is a neutral ligand and K carries a charge of +1.
Therefore, the complex can be written as $K^+\left[Co(CO)_4\right]^-$. Therefore, the oxidation number of Co in the given complex is -1. Hence, option (iii) is correct.

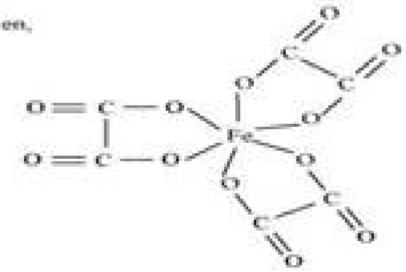
14.Amongst the following, the most stable complex is

(i) $\left[Fe(H_2O)_6\right]^{3+}$ **(ii)** $\left[Fe(NH_3)_6\right]^{3+}$

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

Ans. We know that the stability of a complex increases by chelation. Therefore, the most stable complex is $\left[Fe(C_2O_4)_3\right]^{3-}$.

Then,



3 Marks Questions

1.What is geometric isomerism? When can a compound show.

(1) Cis – Trans isomerism

(2) Fac and Mer isomerism.

Ans. The isomerism that arises in hetroleptic complexes due to different possible geometric arrangements of the ligands is called geometric isomerism.

1) Cis and Trans isomerism can occur in square planar complexes of formula $[MX_2L_2]$ (X&L are unidentate ligands), square planar complexes of formula MAB X L & octahedral complexes of formula MX_2L_4 .

2) Fac and mer isomerism can occur in octahedral complexes of formula Ma_3b_3 .

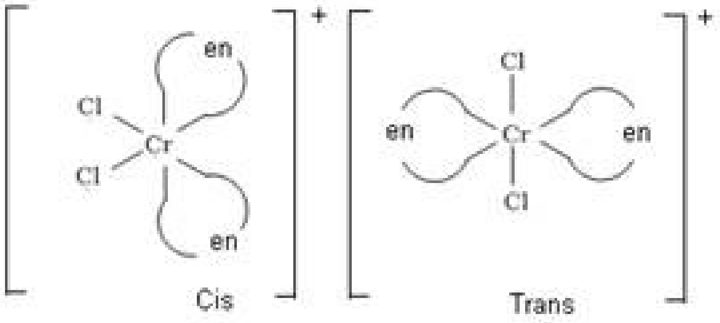
2.How do optical isomer differ from each other?

Ans. Optical isomers differ in the direction in which they rotate the plane of polarized light in a polarimeter.

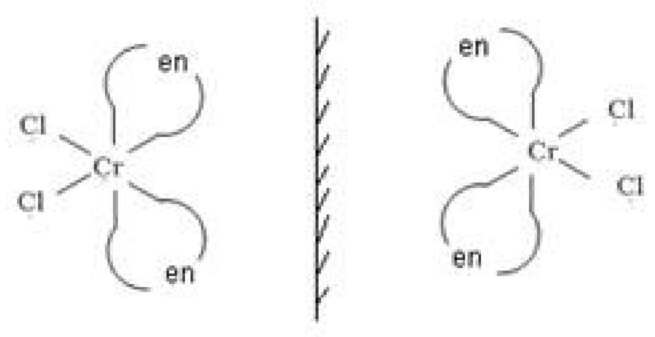
3.Make the cis and trans forms of the complex $[Cr\,Cl_2(en)_2]^+$. Which one of these will be optically active?

Ans. $[Cr\,Cl_2(en)_2]^+$

Cis and trans forms.



The cis form will be optically active.



mirror

4.Which isomerism is shown by a compound having ambidentate ligand? Give example.

Ans.A complex having ambident ligand will show linkage isomerism e.g $[Cr\ (NH_3)_5(NO_2)\ ]\ Cl_2\ has\ NO^-_2$ as ambident Ligand and its Linkage isomer will be $\left[Cr\ (NH_3)_5(ONO)\ \right]Cl_2$.

5.What is ionization isomerism? Give an example.

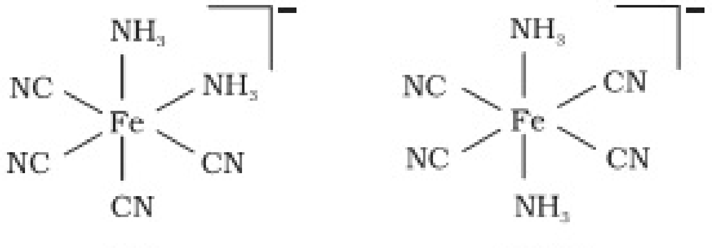
Ans. Ionisation isomerism arises when the counter ion in a complex salt is itself a potential Ligand and can displace a Ligand which can then become counter ion e.g. $\left[CO\ (NH_3)_5\,SO_4\right]Br$ and $\left[CO\ (NH_3)_5\,Br\right]SO_4$ are ionization isomer.

6.How do solvate isomers differ from each other?

Ans. The solvate isomers differ by wether or not a solvent molecule is directly bonded to the metal ion or is merely present on free solvent molecules in the crystal.

7.Draw the geometrical isomers of $\left[Cr\ (NH_3)_2(CN)_4\right]^-$ **?**

Ans. Geometrical isomers



cis *trans*

8.Give evidence that $\left[Co(NH_3)_5Cl\right]SO_4$ **and** $\left[Co(NH_3)_5SO_4\right]Cl$ **are ionization isomers.**

Ans. When ionization isomers are dissolved in water, they ionize to give different ions. These ions then react differently with different reagents to give different products.

$$\left[CO(NH_3)_5Cl\right]SO_4 + Ba^{2+} \rightarrow \underset{\text{White precipitate}}{BaSO_4\downarrow}$$

$$\left[CO(NH_3)_5Cl\right]SO_4 + Ag^{+} \rightarrow \text{Noreaction}$$

$$\left[CO(NH_3)_5SO_4\right]Cl + Ba^{2+} \rightarrow \text{Noreaction}$$

$$\left[CO(NH_3)_5SO_4\right]Cl + Ag^{+} \rightarrow \underset{\text{White precipitate}}{AgCl\downarrow}$$

9. The hexaquo manganese (II) ion contains five unpaired electrons, while the hexacyanoion contains only one unpaired electron. Explain using Crystal Field Theory.

Ans.

$\left[Mn(H_2O)_6\right]^{2+}$	$\left[Mn(CN)_6\right]^{4-}$
Mn is in the +2 oxidation state.	Mn is in the +2 oxidation state.
The electronic configuration is d^5.	The electronic configuration is d^5.

The crystal field is octahedral. Water is a weak field ligand. Therefore, the arrangement of the electrons in $\left[Mn(H_2O)_6\right]^{2+}$ is t2g3eg2.	The crystal field is octahedral. Cyanide is a strong field ligand. Therefore, the arrangement of the electrons in $\left[Mn(CN)_6\right]^{4-}$ isT2g5eg0.

Hence, hexaaquo manganese (II) ion has five unpaired electrons, while hexacyano ion has only one unpaired electron.

10. Calculate the overall complex dissociation equilibrium constant for the $Cu(NH_3)_4^{2+}$ ion, given that β_4 for this complex is 2.1×10^{13}

Ans. $\beta_4 = 2.1\times10^{13}$

The overall complex dissociation equilibrium constant is the reciprocal of the overall stability constant, β_4 .

$$\frac{1}{\beta_4}=\frac{1}{2.1\times10^{13}}$$

$$=4.7\times10^{-14}$$

11. Explain the bonding in coordination compounds in terms of Werner's postulates.

Ans. Werner's postulates explain the bonding in coordination compounds as follows:

(i) A metal exhibits two types of valencies namely, primary and secondary valencies. Primary valencies are satisfied by negative ions while secondary valencies are satisfied by both negative and neutral ions.

(In modern terminology, the primary valency corresponds to the oxidation number of the metal ion, whereas the secondary valency refers to the coordination number of the metal ion.

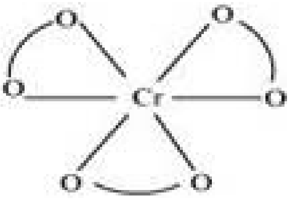
(ii) A metal ion has a definite number of secondary valencies around the central atom. Also, these valencies project in a specific direction in the space assigned to the definite geometry of the coordination compound.

(iii) Primary valencies are usually ionizable, while secondary valencies are non-ionizable.

12.How many geometrical isomers are possible in the following coordination entities?

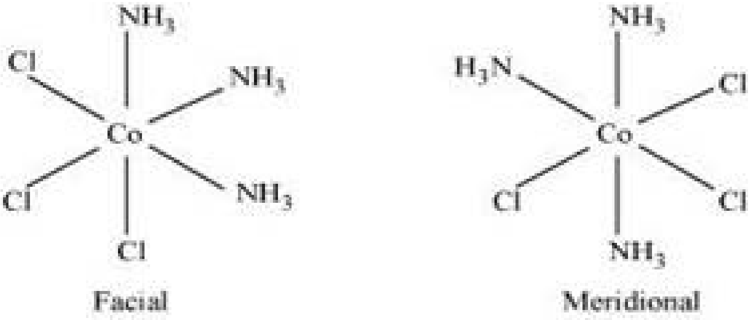
(i) $\left[Cr(C_2O_4)_3\right]^{3-}$ **(ii)** $\left[Co(NH_3)_3Cl_3\right]$

Ans.**(i)** For $\left[Cr(C_2O_4)_3\right]^{3-}$, no geometric isomer is possible as it is a bidentate ligand.



(ii) $\left[Co(NH_3)_3Cl_3\right]$

Two geometrical isomers are possible.



13.**Aqueous copper sulphate solution (blue in colour) gives:**

(i) a green precipitate with aqueous potassium fluoride, and

(ii) a bright green solution with aqueous potassium chloride

Explain these experimental results.

Ans. Aqueous $CuSO_4$ exists as $\left[Cu(H_2O)_4\right]SO_4$. It is blue in colour due to the presence of

$\left[Cu(H_2O)_4\right]^{2+}$ ions.

(i) When KF is added:

$$\left[Cu\left(H_2O\right)_4\right]^{2+} + 4F^- \rightarrow \underset{\text{(green)}}{\left[Cu\left(F\right)_4\right]^{2-}} + 4H_2O$$

(ii) When KCl is added:

$$\left[Cu\left(H_2O\right)_4\right]^{2+} + 4Cl^- \rightarrow \underset{\text{(bright green)}}{\left[CuCl_4\right]^{2-}} + 4H_2O$$

In both these cases, the weak field ligand water is replaced by the F^- and Cl^- ions.

14. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_2S_{(g)}$ is passed through this solution?

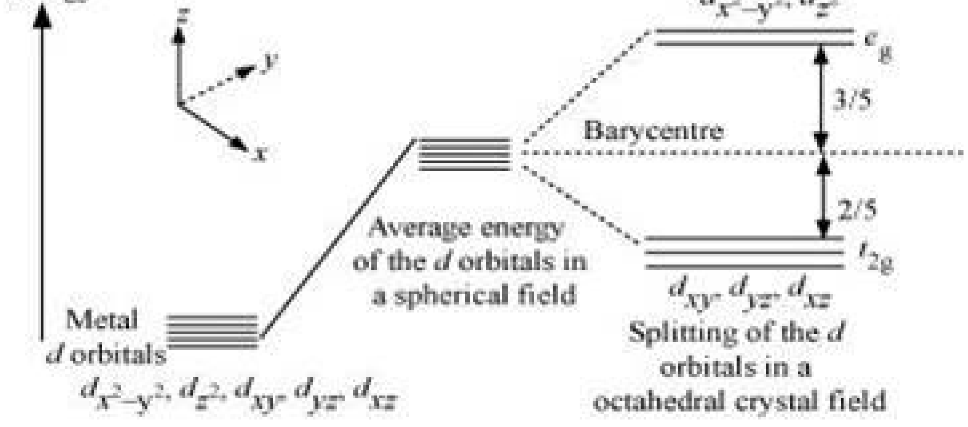
Ans. $CuSO_{4(aq)} + 4KCN_{(aq)} \rightarrow K_2\left[Cu\left(CN\right)_4\right]_{(aq)} + K_2SO_{4(aq)}$

i.e., $\left[Cu\left(H_2O\right)_4\right]^{2+} + 4CN^- \rightarrow \left[Cu\left(CN\right)_4\right]^{2-} + 4H_2O$

Thus, the coordination entity formed in the process is $K_2\left[Cu\left(CN\right)_4\right]$. $K_2\left[Cu\left(CN\right)_4\right]$ is a very stable complex, which does not ionize to give Cu^{2+} ions when added to water. Hence, Cu^{2+} ions are not precipitated when $H_2S_{(aq)}$ is passed through the solution.

15.**Draw figure to show the splitting of *d* orbitals in an octahedral crystal field.**

Ans.



The splitting of the *d* orbitals in an octahedral field takes palce in such a way that $d_{x^2-y^2}$, d_{z^2} experience a rise in energy and form the e_g level, while d_{xy}, d_{yz} and d_{zx} experience a fall in energy and form the t_{2g} level.

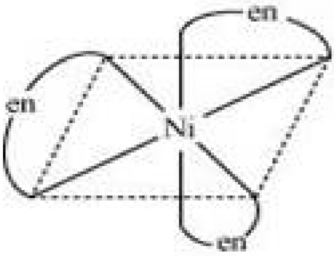
16.**What is meant by the *chelate effect*? Give an example.**

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. In other words, we can say that complexes containing chelate rings are more stable than complexes without rings. This is known as the chelate effect.

For example:

$$Ni^{2+}_{(aq)} + 6NH_{3(aq)} \longleftrightarrow \underset{\log\beta = 7.99}{\left[Ni(NH_3)_6\right]^{2+}}_{(aq)}$$

$$Ni^{2+}_{(aq)} + 3en_{(aq)} \longleftrightarrow \underset{\substack{\log\beta = 18.1 \\ (\text{more stable})}}{\left[Ni(en)_3\right]^{2+}}_{(aq)}$$



17.**Amongst the following ions which one has the highest magnetic moment value?**

(i) $\left[Cr(H_2O)_6\right]^{3+}$ **(ii)** $\left[Fe(H_2O)_6\right]^{2+}$ **(iii)** $\left[Zn(H_2O)_6\right]^{2+}$

Ans.**(i)** No. of unpaired electrons in $\left[Cr(H_2O)_6\right]^{3+}$ = 3

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

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

$= \sqrt{15}$

$= \sim 4BM$

(ii) No. of unpaired electrons in $\left[Fe(H_2O)_6\right]^{2+}$ = 4

Then, $\mu = \sqrt{4(4+2)}$

$= \sqrt{24}$

$=\sim 5BM$

(iii) No. of unpaired electrons in $\left[Zn(H_2O)_6\right]^{2+} = 0$

Hence, $\left[Zn(H_2O)_6\right]^{2+}$ has the highest magnetic moment value.

18.**What will be the correct order for the wavelengths of absorption in the visible region for the following: $\left[Ni(NO_2)_6\right]^{4-}, \left[Ni(NH_3)_6\right]^{2+}, \left[Ni(H_2O)_6\right]^{2+}$**

Ans.The central metal ion in all the three complexes is the same. Therefore, absorption in the visible region depends on the ligands. The order in which the CFSE values of the ligands increases in the spectrochemical series is as follows:

$$H_2O < NH_3 < NO^{2-}$$

Thus, the amount of crystal-field splitting observed will be in the following order:

$$\Delta o_{(H_2O)} < \Delta o_{(NH_3)} < \Delta o_{(NO_2^-)}$$

Hence, the wavelengths of absorption in the visible region will be in the order:

$$\left[Ni(H_2O)_6\right]^{2+} > \left[Ni(NH_3)_6\right]^{2+} > \left[Ni(NO_2)_6\right]^{4-}$$

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 $\left[Fe(CN)_6\right]^{4-}$ 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 $[EDTA]^{4-}$ 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) $K_2\left[Ni(CN)_4\right]$

(iii) $\left[Cr(en)_3\right]Cl_3$

(vi) $\left[Pt(NH)_3BrCl(NO_2)\right]^-$

(v) $\left[PtCl_2(en)_2\right](NO_3)_2$

(vi) $Fe_4\left[Fe(CN)_6\right]_3$

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

(i) $\left[Co(NH_3)6\right]Cl_3$ **(ii)** $\left[Co(NH_3)_5Cl\right]Cl_2$

(iii) $K_3\left[Fe(CN)_6\right]$ **(iv)** $K_3\left[Fe(C_2O_4)_3\right]$

(v) $K_2\left[PdCl_4\right]$ **(vi)** $\left[Pt(NH_3)_2Cl(NH_2CH_3)\right]Cl$

Ans. **(i)** Hexaamminecobalt(III) chloride

(ii) Pentaamminechloridocobalt(III) chloride

(iii) Potassium hexacyanoferrate(III)

(iv) Potassium trioxalatoferrate(III)

(v) Potassium tetrachloridopalladate(II)

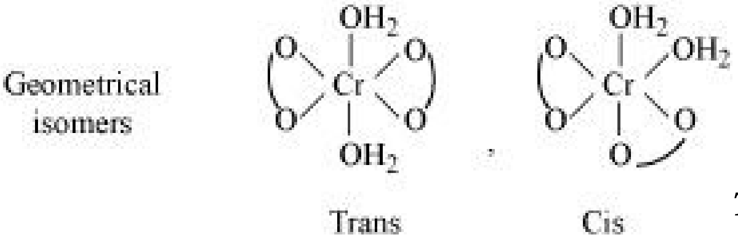
(vi) Diamminechlorido(methylamine)platinum(II) chloride

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

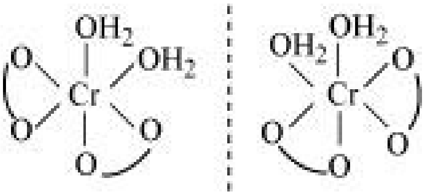
(i) $K\left[Cr(H_2O)_2(C_2O_4)_2\right]$ **(ii)** $\left[Co(en)_3\right]Cl_3$

(iii) $\left[Co(NH_3)_5(NO_2)(NO_3)_2\right]$ (iv) $\left[Pt(NH_3)(H_2O)Cl_2\right]$

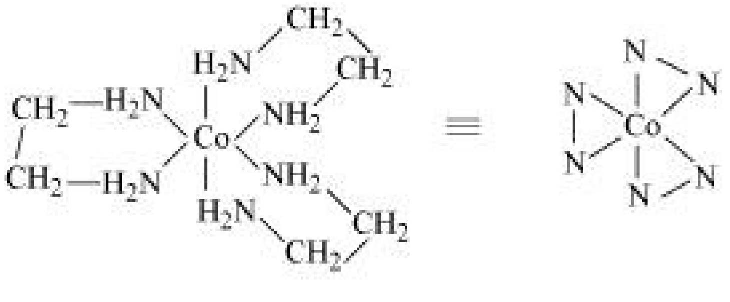
Ans. Both geometrical (*cis*-, *trans*-) isomers for $K\left[Cr(H_2O)_2(C_2O_4)_2\right]$ can exist. Also, optical isomers for *cis*-isomer exist.



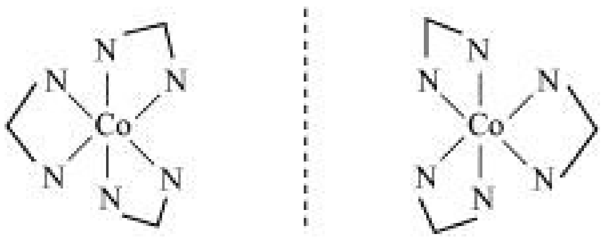
Trans-isomer is optically inactive. On the other hand, *cis*-isomer is optically active.



(ii) Two optical isomers for $\left[CO(en)_3\right]Cl_3$ exist.

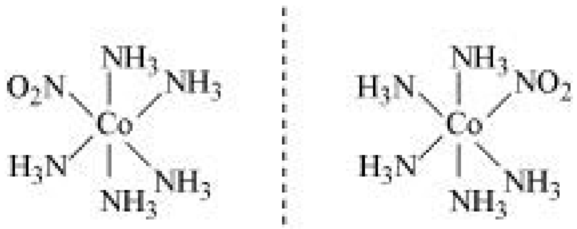


Two optical isomers are possible for this structure.



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

A pair of optical isomers:



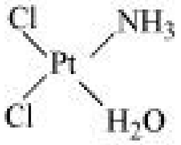
It can also show linkage isomerism.

$\left[CO(NH_3)_5(NO_2)\right](NO_3)_2$ and $\left[CO(NH_3)_5(ONO)\right](NO_3)_2$

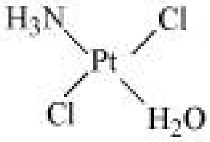
It can also show ionization isomerism.

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

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



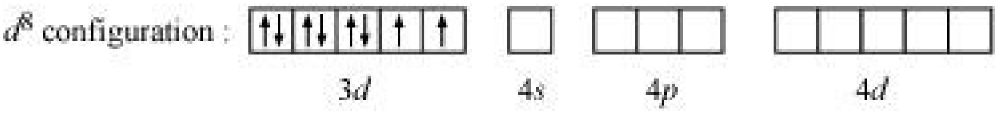
Cis



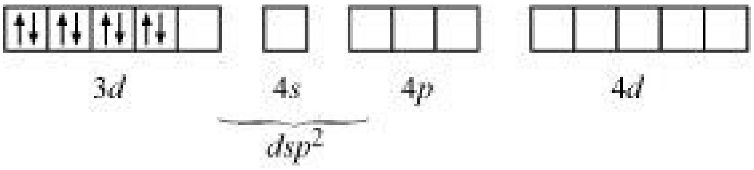
Trans

5. Explain on the basis of valence bond theory that $\left[Ni(CN)_4\right]^{2-}$ ion with square planar structure is diamagnetic and the $\left[NiCl_4\right]^{2-}$ ion with tetrahedral geometry is paramagnetic.

Ans. Ni is in the +2 oxidation state i.e., in d^8 configuration.

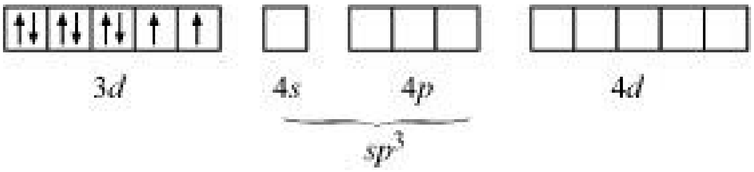


There are 4 CN^- ions. Thus, it can either have a tetrahedral geometry or square planar geometry. Since CN^- ion is a strong field ligand, it causes the pairing of unpaired 3*d* electrons.



It now undergoes dsp^2 hybridization. Since all electrons are paired, it is diamagnetic.

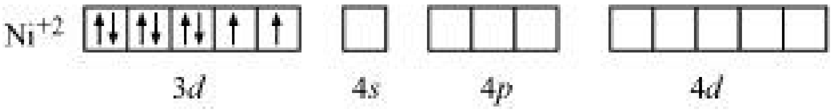
In case of $[NiCl_4]^{2-}$, CN^- ion is a weak field ligand. Therefore, it does not lead to the pairing of unpaired 3*d* electrons. Therefore, it undergoes sp^3 hybridization.



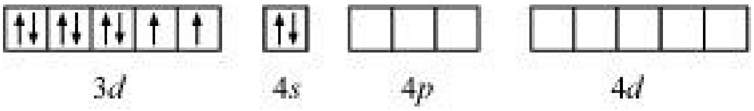
Since there are 2 unpaired electrons in this case, it is paramagnetic in nature.

6. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ 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 3*d* electrons. Hence, $[NiCl_4]^{2-}$ is paramagnetic.



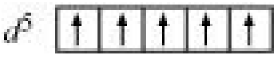
In $Ni(CO)_4$, Ni is in the zero oxidation state i.e., it has a configuration of $3d^8 4s^2$.



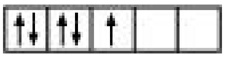
But CO is a strong field ligand. Therefore, it causes the pairing of unpaired 3*d* electrons. Also, it causes the 4s electrons to shift to the 3d orbital, thereby giving rise to sp^3 hybridization. Since no unpaired electrons are present in this case, $\left[Ni\left(CO\right)_4\right]$ is diamagnetic.

7. $\left[Fe\left(H_2O\right)_6\right]^{3+}$ is strongly paramagnetic whereas $\left[Fe(CN)_6\right]^{3}$ is weakly paramagnetic. Explain.

Ans. In both $\left[Fe\left(H_2O\right)_6\right]^{3+}$ and $\left[Fe\left(CN\right)_6\right]^{3-}$, 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 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,

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

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

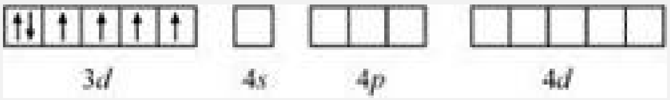
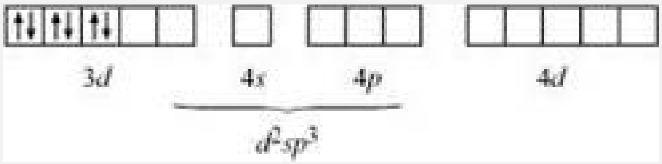
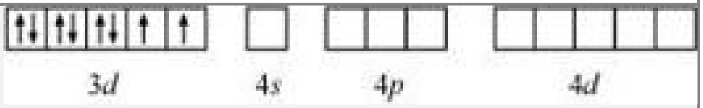
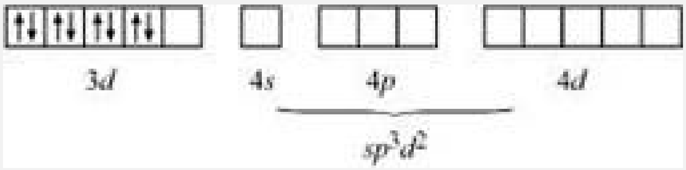
$= \sqrt{35}$

= 6 BM

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

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

Ans.

$\left[Co\left(NH_3\right)_6\right]^{3+}$	$\left[Ni\left(NH_3\right)_6\right]^{2+}$
Oxidation state of cobalt = +3	Oxidation state of Ni = +2
Electronic configuration of cobalt = d^6	Electronic configuration of nickel = d^8
 NH_3 being a strong field ligand causes the pairing. Therefore, Cobalt can undergo d^2sp^3 hybridization.  Hence, it is an inner orbital complex.	 If NH_3 causes the pairing, then only one 3*d* orbital is empty. Thus, it cannot undergo d^2sp^3 hybridization. Therefore, it undergoes sp^3d^2 hybridization.  Hence, it forms an outer orbital complex.

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. $$(NH_4)_2SO_4 + FeSO_4 + 6H_2O \rightarrow \underset{\text{Mohr's salt}}{FeSO_4.(NH_4)_2SO_4.6H_2O}$$

$$CuSO_4 + 4NH_3 + 5H_2O \rightarrow \underset{\text{tetraamminocopper (ii) sulphate}}{[Cu(NH_3)_4]SO_4.5H_2O}$$

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. $FeSO_4.(NH_4)_2SO_4.6H_2O$ 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 $[Cu(NH_3)_4]SO_4.5H_2O$ does not show the test for Cu^{2+}. The ions present in the solution of $[Cu(NH_3)_4]SO_4.5H_2O$ are $[Cu(NH_3)_4]^{2+}$ 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:

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

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

$[Ni(CO)_4]$, $[Co(NH_3)_4Cl_2]$ = 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, $\ddot{N}H_3, H_2\ddot{O}$, 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:

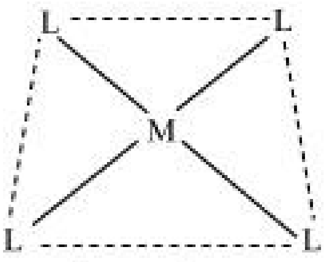
(a) In the complex, $K_2[PtCl_6]$, there as six chloride ions attached to Pt in the coordinate sphere. Therefore, the coordination number of Pt is 6.

(b) Similarly, in the complex $[Ni(NH_3)_4]Cl_2$, the coordination number of the central atom (Ni) is 4.

(vi) Coordination polyhedron:

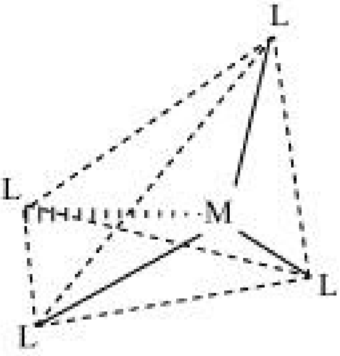
Coordination polyhedrons about the central atom can be defined as the spatial arrangement of the ligands that are directly attached to the central metal ion in the coordination sphere. For example:

(a)



Square planar

(b) Tetrahedral



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: $\left[Co\left(NH_3\right)_6\right]^{3+}$, $\left[PtCl_4\right]^{2-}$ 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.: $\left[Co\left(NH_3\right)_4 Cl_2\right]^{+}$, $\left[Co\left(NH_3\right)_5 Cl\right]^{2+}$

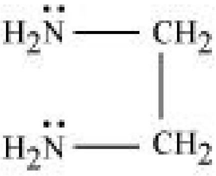
11. What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.

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:

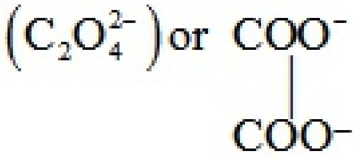
(a) Unidentate ligands: Ligands with only one donor sites are called unidentate ligands. For e.g., $\ddot{N}H_3$, Cl - etc.

(b) Didentate ligands: Ligands that have two donor sites are called didentate ligands. For e.g.,

(a) Ethane-1, 2-diamine



(b) Oxalate ion

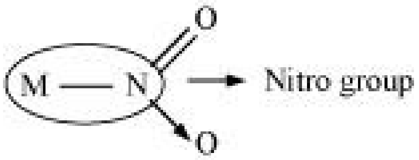


$(C_2O_4^{2-})$ or $\begin{array}{c} COO^- \\ | \\ COO^- \end{array}$

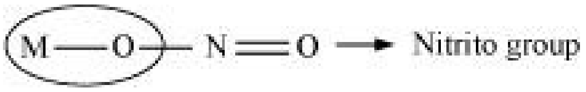
(c)Ambidentate ligands:

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

(a)

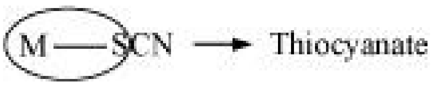


(The donor atom is N)

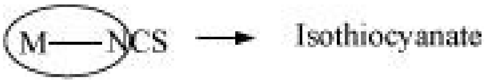


(The donor atom is oxygen)

(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) $\left[Co(H_2O)(CN)(en)_2\right]^{2+}$ **(ii)** $\left[CoBr_2(en)_2\right]^{+}$

(iii) $\left[PtCl_4\right]^{2-}$ **(iv)** $K_3\left[Fe(CN)_6\right]$

(v) $\left[Cr(NH_3)_3Cl_3\right]$

Ans. (i) $\left[Co(H_2O)(CN)(en)_2\right]^{2+}$

Let the oxidation number of Co be *x*.

The charge on the complex is +2.

$$\begin{array}{cccc} \left[Co \right. & (H_2O) & (CN) & \left.(en)_2\right]^{2+} \\ \downarrow & \downarrow & \downarrow & \downarrow \\ x + & 0 + & (-1) + & 2(0) = +2 \end{array}$$

$$x - 1 = +2$$

$$x = +3$$

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

Let the oxidation number of Pt be *x*.

The charge on the complex is –2.

$$\begin{array}{cc}[\mathrm{Pt} & (\mathrm{Cl})_4]^{2-}\\ \downarrow & \downarrow\end{array}$$

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

$$x = +2$$

(iii) $$\begin{array}{ccc}\left[\mathrm{Co}\right. & (\mathrm{Br})_2 & \left.(\mathrm{en})_2\right]^{2+}\\ \downarrow & \downarrow & \downarrow\\ x & +\ 2(-1) & +\ 2(0) = +1\end{array}$$

$$x - 2 = +1$$

$$x = +3$$

(iv) $K_3[\mathrm{Fe(CN)}_6]$

$$\text{i.e.,}\begin{array}{cc}\left[\mathrm{Fe}\right. & \left.(\mathrm{CN})_6\right]^{3-}\\ \downarrow & \downarrow\\ x & +\ 6(-1) = -3\end{array}$$

$$x = +3$$

(v) $$\begin{array}{ccc}\left[\mathrm{Cr}\right. & (\mathrm{NH_3})_3 & \left.\mathrm{Cl}_3\right]\\ \downarrow & \downarrow & \downarrow\\ x & +\ 3(0) & +\ 3(-1) = 0\end{array}$$

$$x - 3 = 0$$

$$x = +3$$

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) $\left[\mathrm{Zn(OH)_4}\right]^{2-}$

(ii) $\mathrm{K_2\left[PdCl_4\right]}$

(iii) $\left[\mathrm{Pt(NH_3)_2Cl_2}\right]$

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

(v) $\left[\mathrm{Co(ONO)(NH_3)_5}\right]^{2+}$

(vi) $\left[\mathrm{Co(NH_3)_6}\right]_2\mathrm{(SO_4)_3}$

(vii) $\mathrm{K_3\left[Cr(C_2O_4)_3\right]}$

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

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

(x) $\left[\mathrm{Ci(NO_2)(NH_3)_5}\right]^{2+}$

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

(i) $\left[Co(NH_3)_6\right]Cl_3$ **(ii)** $\left[Pt(NH_3)_2Cl(NH_2CH_3)\right]Cl$

(iii) $\left[Ti(H_2O)_6\right]^{3+}$ **(iv)** $\left[Co(NH_3)_4Cl(NO_2)\right]Cl$

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

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

(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

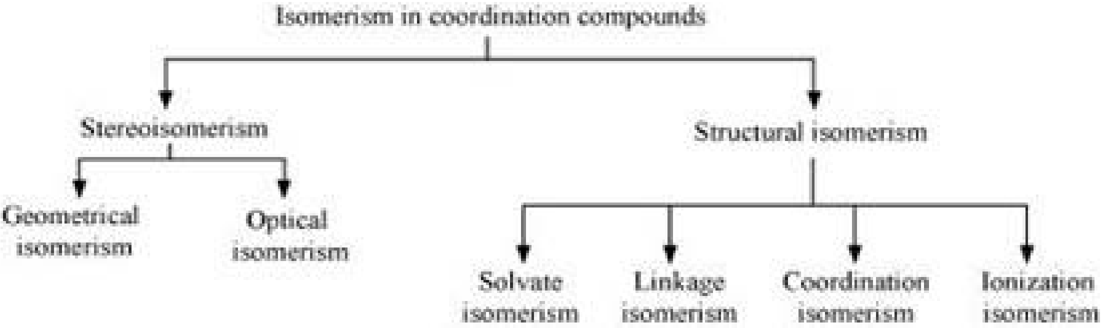
(vii) Hexaamminenickel(II) chloride

(viii) Tris (ethane-1, 2-diammine) cobalt(III) ion

(ix) Tetracarbonylnickel (0)

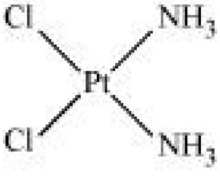
15. List various types of isomerism possible for coordination compounds, giving an example of each.

Ans.

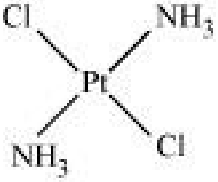


(a) Geometric isomerism:

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



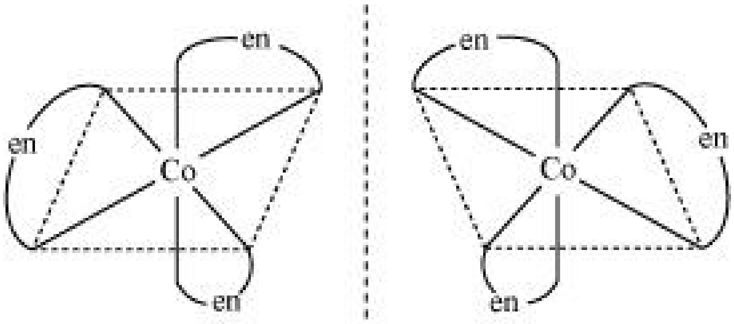
Cis–isomer



Trans–isomer

(b) Optical isomerism:

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



$[Co(en)_3]^{3+}$ (dextro) Mirror $[Co(en)_3]^{3+}$ (Laevo)

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

$[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)Cl_2]$

Yellow form Red form

(d) Coordination isomerism:

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

$\left[Co\left(NH_3\right)_6\right]\left[Cr\left(CN\right)_6\right]$ and $\left[Cr\left(NH_3\right)_6\right]\left[Co\left(CN\right)_6\right]$

(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., $Co\left(NH_3\right)_5 SO_4Br$ and $Co\left(NH_3\right)_5 BrSO_4$.

(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.

$\left[Cr\left(H_2O\right)_6\right]Cl_3\left[Cr\left(H_2O\right)_5 Cl\right]Cl_2.H_2O\left[Cr\left(H_2O\right)_5 Cl_2\right]Cl.2H_2O$

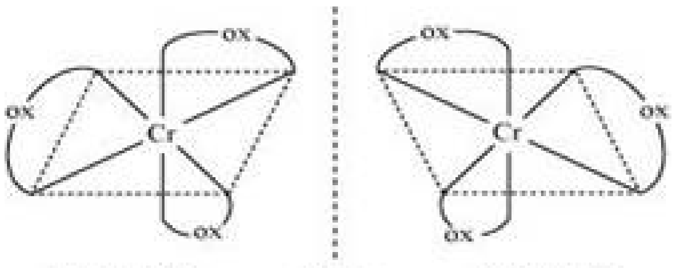
Violet Blue-green Dark green

16. Draw the structures of optical isomers of:

(i) $\left[Cr\left(C_2O_4\right)_3\right]^{3-}$ **(ii)** $\left[PtCl_2\left(en\right)_2\right]^{2+}$

(iii) $\left[Cr\left(NH_3\right)_2 Cl_2\left(en\right)\right]^{+}$

Ans. (i) $\left[Cr\left(C_2O_4\right)_3\right]^{3-}$

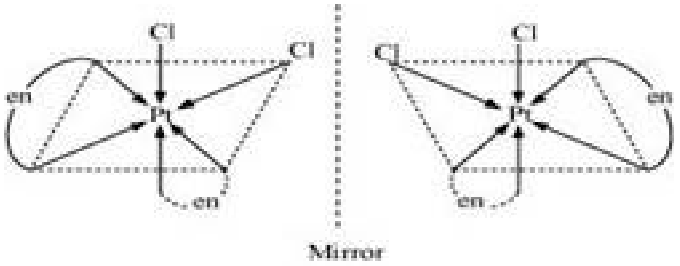


$[Cr(ox)_3]^{3+}$
(dextro)

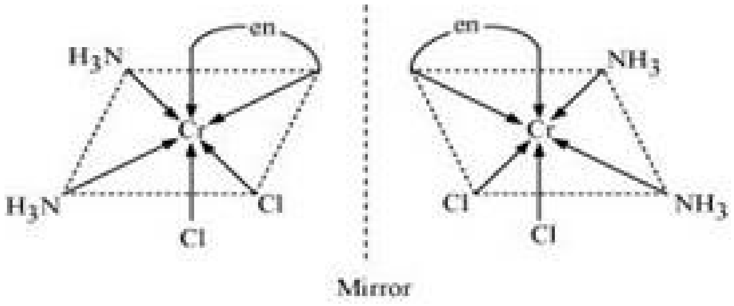
Mirror

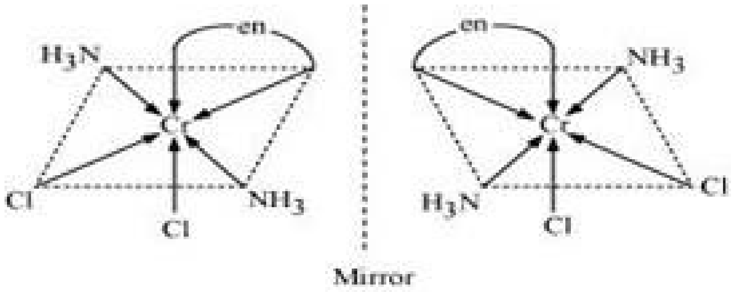
$[Cr(ox)_3]^{3+}$
(Laevo)

(ii) $\left[PtCl_2(en)_2\right]^{2+}$



(iii) $\left[Cr(NH_3)_2Cl_2(en)\right]^{+}$





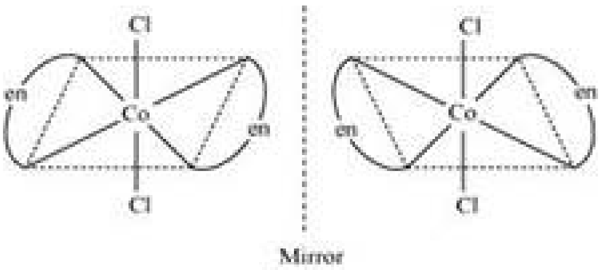
17. Draw all the isomers (geometrical and optical) of:

(i) $\left[CoCl_2(en)_2\right]^{+}$

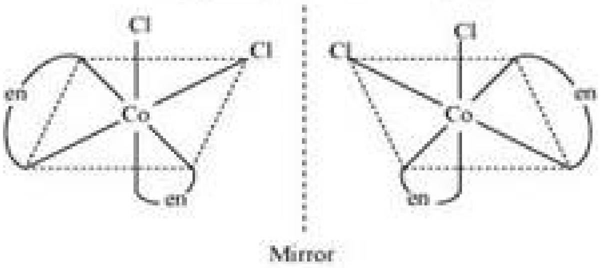
(ii) $\left[Co(NH_3)Cl(en)^2\right]^{2+}$

(iii) $\left[Co(NH_3)_2Cl_2(en)\right]^+$

Ans. **(i)** $\left[CoCl_2(en)_2\right]^+$



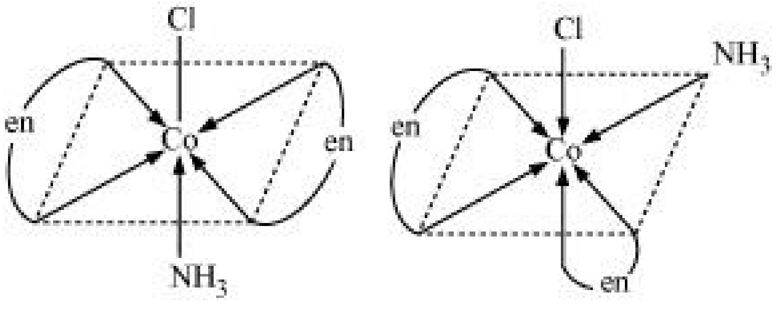
Trans $[CoCl_2(en)_2]^+$ isomer-optically inactive
(Superimposable mirror images)



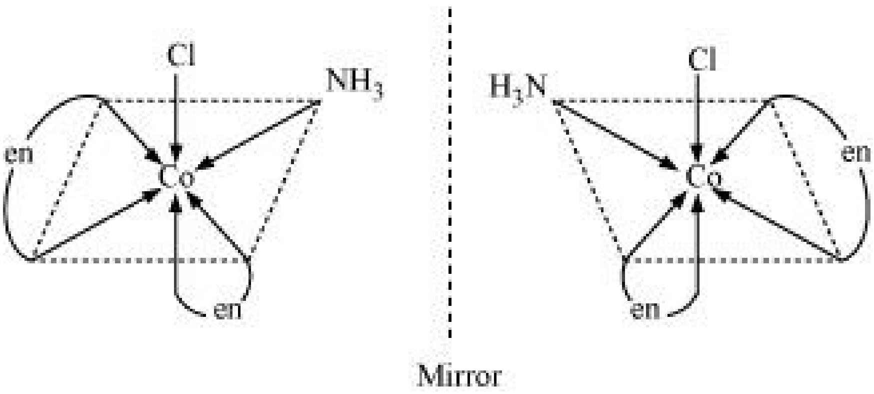
Cis $[CoCl_2(en)_2]^+$ isomer-optically active
(Non-superimposable mirror images)

In total, three isomers are possible.

(ii) $\left[Co(NH_3)Cl(en)^2\right]^{2+}$



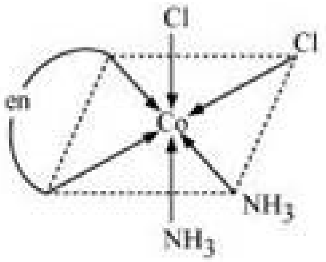
Trans Cis

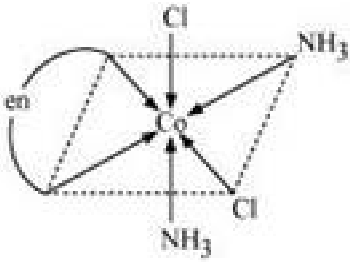


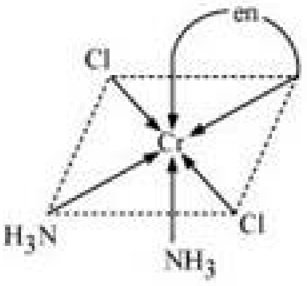
Trans-isomers are optically inactive.

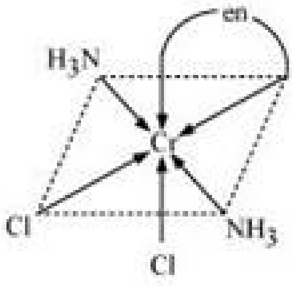
Cis-isomers are optically active.

(iii) $\left[Co(NH_3)_2Cl_2(en)\right]^+$









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

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

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

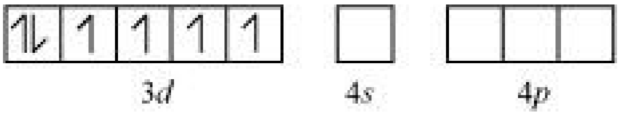
(iii) $\left[Co(C_2O_4)_3\right]^{3-}$

(iv) $\left[CoF_6\right]^{3-}$

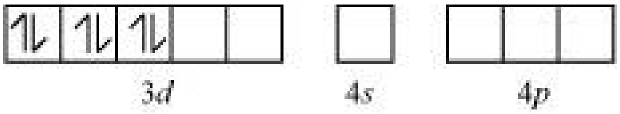
Ans. **(i)** $\left[Fe(CN)_6\right]^{4-}$ In the above coordination complex, iron exists in the +II oxidation state.

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

Orbitals of Fe^{2+} ion:

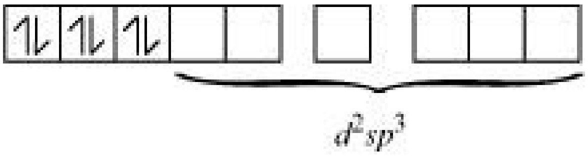


As CN^- is a strong field ligand, it causes the pairing of the unpaired 3*d* electrons.



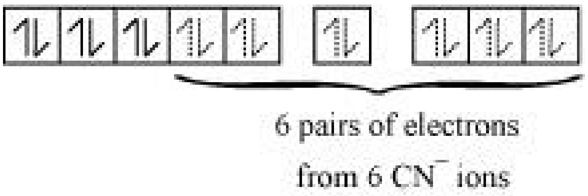
Since there are six ligands around the central metal ion, the most feasible hybridization is d^2sp^3.

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



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

Then,

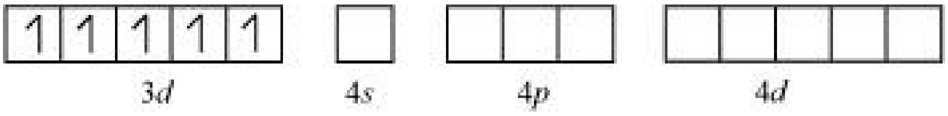


Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons).

(ii) $[FeF_6]^{3-}$

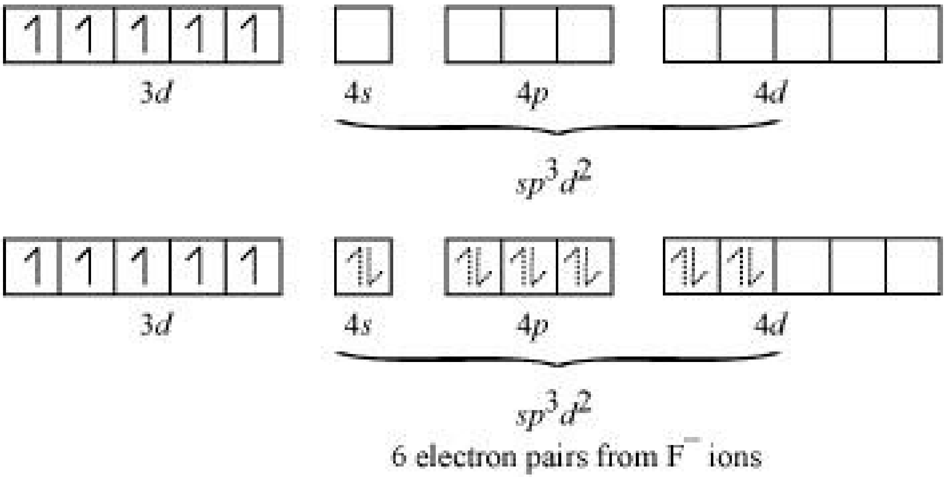
In this complex, the oxidation state of Fe is +3.

Orbitals of Fe^{3+} 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 3*d* orbital. Hence, the most feasible hybridization is sp^3d^2.

sp^3d^2 hybridized orbitals of Fe are:

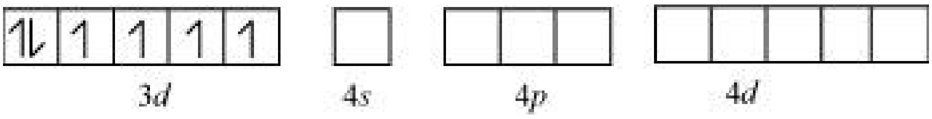


Hence, the geometry of the complex is found to be octahedral.

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

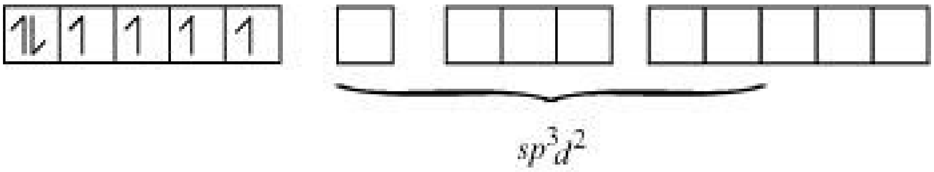
Cobalt exists in the +3 oxidation state in the given complex.

Orbitals of Co^{3+} ion:

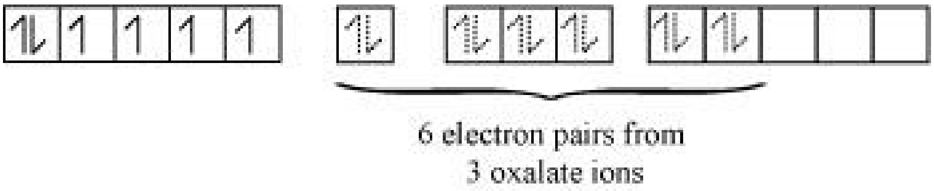


Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the 3*d* orbital electrons. As there are 6 ligands, hybridization has to be either sp^3d^2 or d^2sp^3 hybridization.

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.

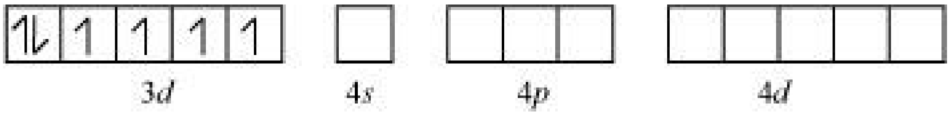


Hence, the geometry of the complex is found to be octahedral.

(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 3*d* 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 Δ_0 decide the actual configuration of *d*-orbitals in a coordination entity?

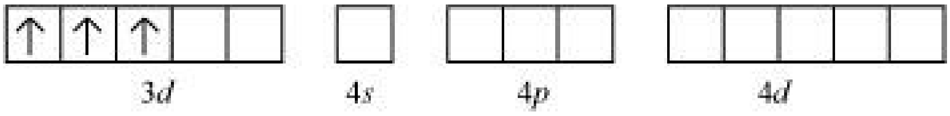
Ans. The degenerate *d*-orbitals (in a spherical field environment) split into two levels i.e., e_g and t_{2g} in the presence of ligands. The splitting of the degenerate levels due to the presence of ligands is called the crystal-field splitting while the energy difference between the two levels (e_g and t_{2g}) is called the crystal-field splitting energy. It is denoted by Δ_0.

After the orbitals have split, the filling of the electrons takes place. After 1 electron (each) has been filled in the three t_{2g} orbitals, the filling of the fourth electron takes place in two ways. It can enter the e_g orbital (giving rise to $t_{2g}^3 \; e_g^1$ like electronic configuration) or the pairing of the electrons can take place in the t_{2g} orbitals (giving rise to $t_{2g}^4 \; e_g^0$ like electronic configuration). If the Δ_0 value of a ligand is less than the pairing energy (P), then the electrons enter the e_g orbital. On the other hand, if the Δ_0 value of a ligand is more than the pairing energy (P), then the electrons enter the t_{2g} orbital.

20. $\left[Cr(NH_3)_6\right]^{3+}$ is paramagnetic while $\left[Ni(CN)_4\right]^{2-}$ 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 3*d* orbital.

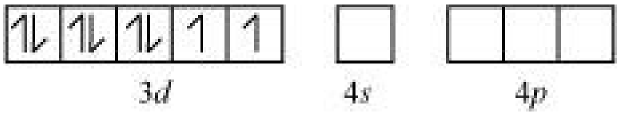
Cr^{3+}



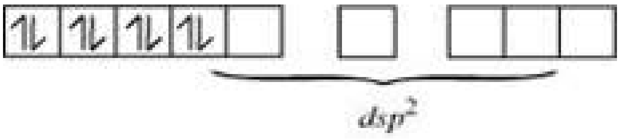
Therefore, it undergoes d^2sp^3 hybridization and the electrons in the 3*d* orbitals remain unpaired. Hence, it is paramagnetic in nature.

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

Ni^{2+} :



CN^- is a strong field ligand. It causes the pairing of the 3*d* orbital electrons. Then, Ni^{2+} undergoes 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) $K_3\left[Co\left(C_2O_4\right)_3\right]$ **(ii) cis-**$\left[Cr\left(en\right)_2Cl_2\right]Cl$

(iii) $\left(NH_4\right)_2\left[CoF_4\right]$ **(iv)** $\left[Mn\left(H_2O\right)_6\right]SO_4$

Ans. **(i)** $K_3\left[Co\left(C_2O_4\right)_3\right]$

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 Co^{3+} is $t_{2g}^{6}e_{g}^{0}$.

(ii) cis-$\left[Cr\left(en\right)_2Cl_2\right]Cl$

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) $[Mn(H_2O)_6]SO_4$

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) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$ **(ii)** $[Co(NH_3)_5Cl]Cl_2$

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

(v) $K_4[Mn(CN)_6]$

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

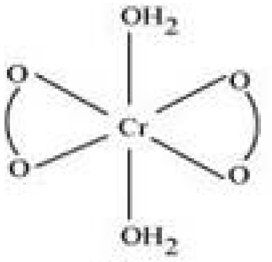
Oxidation state of chromium = 3

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

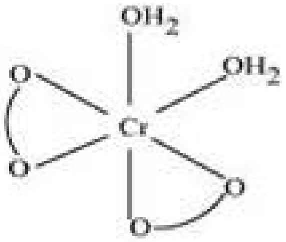
Coordination number = 6

Shape: octahedral

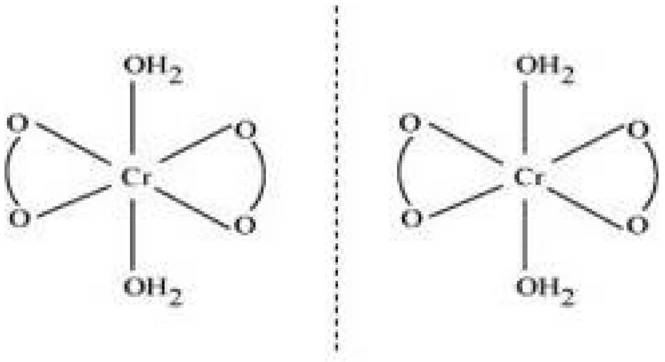
Stereochemistry:



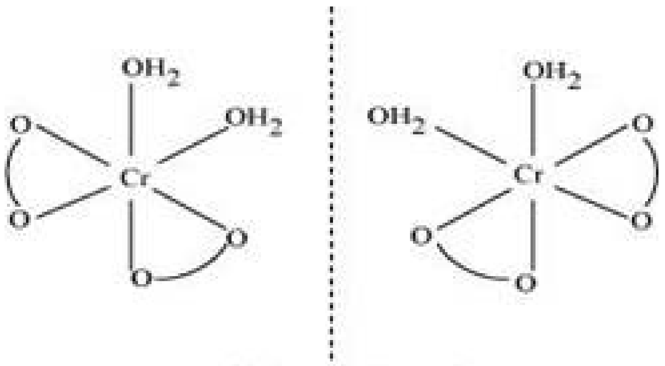
Trans



Cis



Trans is optically inactive



Cis is optically active

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

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

$= \sqrt{15}$

-4BM

(ii) $[Co(NH_3)_5 Cl]Cl_2$

IUPAC name: Pentaamminechloridocobalt(III) chloride

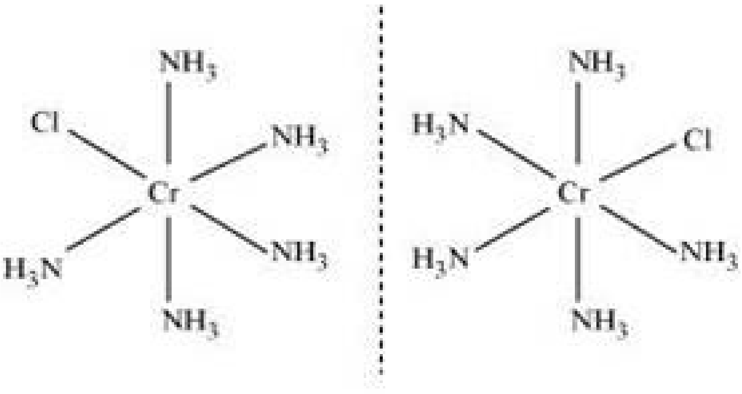
Oxidation state of Co = +3

Coordination number = 6

Shape: octahedral.

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

Stereochemistry:



2 isomers

Magnetic Moment = 0

(iii) $CrCl_3(py)_3$

IUPAC name: Trichloridotripyridinechromium (III)

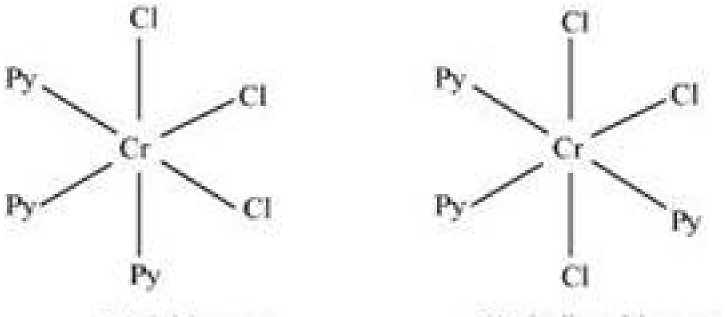
Oxidation state of chromium = +3

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

Coordination number = 6

Shape: octahedral.

Stereochemistry:



Facial isomer Meriodional isomer

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

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

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

$= \sqrt{15}$

$- 4\text{BM}$

(iv) $\text{Cs}\left[\text{FeCl}_4\right]$

IUPAC name: Caesium tetrachloroferrate (III)

Oxidation state of Fe = +3

Electronic configuration of $\text{d}^6 = \text{e}_\text{g}{}^2\text{t}_{2\text{g}}{}^3$

Coordination number = 4

Shape: tetrahedral

Stereochemistry: optically inactive

Magnetic moment:

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

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

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

(v) $\text{K}_4\left[\text{Mn}\left(\text{CN}\right)_6\right]$

Potassium hexacyanomanganate(II)

Oxidation state of manganese = +2

Electronic configuration: $\text{d}^{5+} : \text{t}_{2\text{g}}{}^5$

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 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:** Thegreater 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 $[\mathrm{Au(CN)_2}]$. From this solution, gold is later extracted by the addition of zinc metal.