

Chapter 9: Coordination Compounds

Exercise

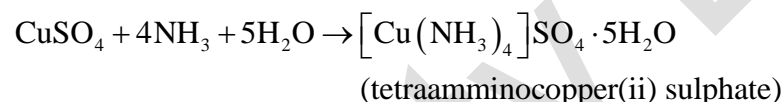
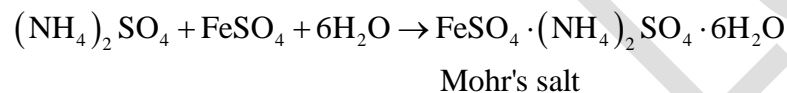
9.1. Explain the bonding in coordination compounds in terms of Werner's postulates.

Solution: Werner's postulates explain coordination compound bonding as follows:

- A metal has two types of valencies: primary valencies and secondary valencies. Negative ions satisfy primary valencies, while both negative and neutral ions satisfy secondary valencies. (In modern terminology, the primary valency corresponds to the metal ion's oxidation number, whereas the secondary valency refers to the metal ion's coordination number.)
- A metal ion has a fixed number of secondary valencies surrounding its central atom. Furthermore, these valencies project in a specific direction in the space assigned to the coordination compound's definite geometry.
- Primary valencies are typically ionizable, whereas secondary valencies are not.

9.2. FeSO_4 solution mixed with $(\text{NH}_4)_2\text{SO}_4$ 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?

Solution:

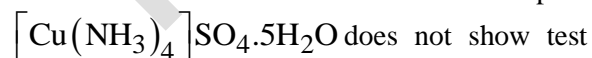


Both the compounds i.e., $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and $[\text{Co}(\text{NH}_3)_4]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ are addition compounds with the exception of one major difference: the former is an example of a double salt, whereas the latter is a coordination compound.

A double salt is an addition compound that is stable in solid form but disintegrates into its constituent ions when dissolved. These compounds exhibit the constituents' individual properties. For example, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ dissociates into Fe^{2+} , NH_4^+ , and SO_4^{2-} ions. Hence, it produces a positive test for Fe^{2+} ions.

A coordination compound is an addition compound that retains its identity in both the solid and dissolved states. However, the constituents' individual properties are lost.

This occurs because the complex



does not show test for copper ions.

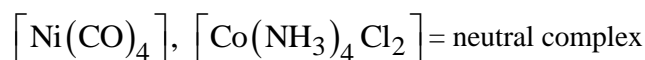
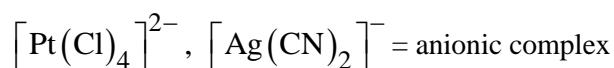
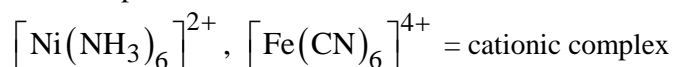
9.3. Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

Solution:

Coordination entity:

A coordination entity is a positively or negatively charged electrically charged radical or species. The central atom or ion of the coordination unit is surrounded by an appropriate number of neutral or negative ions (so-called ligands).

For example:



Ligands

Ligands are the neutral molecules or negatively charged ions that surround the metal atom in a coordination entity or a coordinational complex. For example, $\ddot{\text{N}}\text{H}_3$, $\ddot{\text{H}}_2\ddot{\text{O}}$, Cl , OH . Ligands are typically polar and contain at least one unshared pair of valence electrons.

Coordination number:

The coordination number of the central metal atom is the total number of ligands (neutral molecules or negative ions) that attach to the central metal atom in the coordination sphere. It is also known as its liganacy.

As an example:

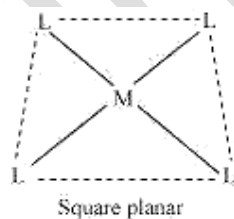
(a) There are six chloride ions attached to Pt in the coordinate sphere in the complex, $\text{K}_2[\text{PtCl}_6]$. As a result, Pt's coordination number is 6.

(b) Similarly, the coordination number of the central atom (Ni) in the complex $[\text{Ni}(\text{NH}_3)_4]\text{Cl}_2$ is 4.

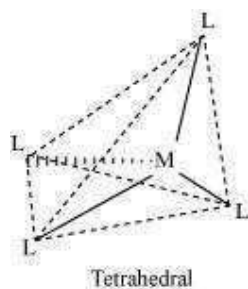
Coordination polyhedron:

Coordination polyhedrons around the central atom are the spatial arrangements of the ligands in the coordination sphere that are directly attached to the central metal ion.

(a)

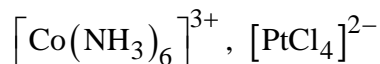


(b) Tetrahedral



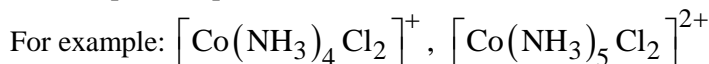
Homoleptic complexes:

These are complexes in which the metal ion is only bound to one type of donor group. For example:



Heteroleptic complexes:

Heteroleptic complexes have the central metal ion bound to multiple types of donor groups.



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

Solution:

A ligand may contain one or more unshared pairs of electrons, which are referred to as ligand donor sites. Now, ligands are classified as follows based on the number of these donor sites:

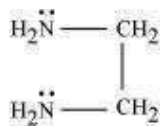
(a) **Unidentate ligands:** Ligands that have only one donor site are referred to as unidentate ligands.

For e.g., $\ddot{\text{N}}\text{H}_3$, Cl^- etc.

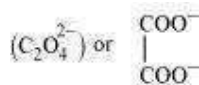
(b) **Didentate ligands:** Ligands that have two donor sites are referred to as didentate ligands.

For e.g.,

(a) Ethane-1,2-diamine



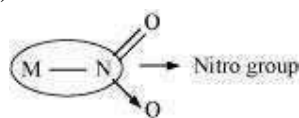
(b) Oxalate ion



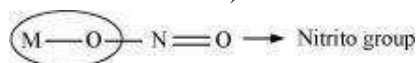
(c) **Ambidentate ligands:**

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

(a)



(The donor atom is N)

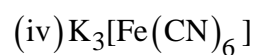
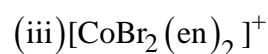
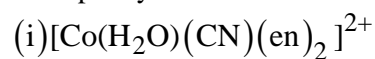


(The donor atom is oxygen) (b)

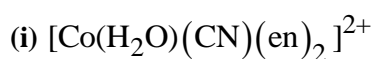
$\text{M} \rightarrow \text{SCN} \rightarrow \text{Thiocyanate}$
 (The donor atom is S)

$\text{M} \rightarrow \text{NCS} \rightarrow \text{Isothiocyanate}$
 (The donor atom is N)

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



Solution:



Let the oxidation number of Co be x . The charge on the complex is +2.

$$\begin{array}{cccc}
 [\text{Co} & (\text{H}_2\text{O}) & (\text{CN}) & (\text{en})_2]^{2+} \\
 \downarrow & \downarrow & \downarrow & \downarrow \\
 x & + & 0 & + (-1) + 2(0) = +2 \\
 & & x - 1 & = +2 \\
 & & x & = +3
 \end{array}$$

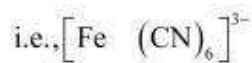
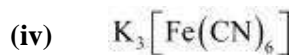


Let the oxidation number of Pt be x . The charge on the complex is -2.

$$\begin{array}{cc}
 [\text{Pt} & (\text{Cl})_4]^{2-} \\
 \downarrow & \downarrow \\
 x & + 4(-1) = -2x \\
 & = +2
 \end{array}$$

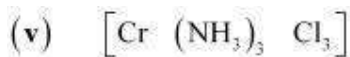


$$\begin{array}{ccc}
 [\text{Co} & (\text{Br})_2 & (\text{en})_2]^{2+} \\
 \downarrow & \downarrow & \downarrow \\
 x & + 2(-1) & + 2(0) = +1 \\
 x - 2 & = +1 \\
 x & = +3
 \end{array}$$



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

$$x = +3$$



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

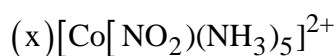
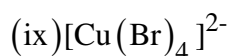
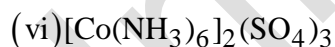
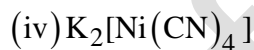
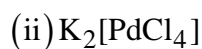
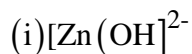
$$x - 3 = 0$$

$$x = +3$$

9.6. Using IUPAC norms write the formulas for the following:

- (i) Tetrahydroxozincate(II)
- (ii) Potassium tetrachloropalladate(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)

Solution:



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

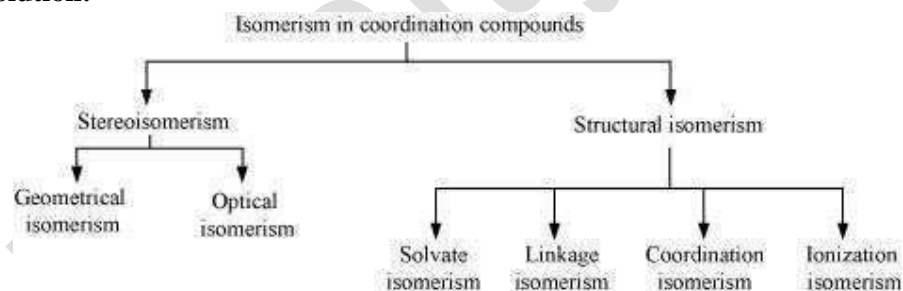
- (i) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
- (ii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$
- (iii) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
- (iv) $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{Cl}$
- (v) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
- (vi) $[\text{NiCl}_4]^{2-}$
- (vii) $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$
- (viii) $[\text{Co}(\text{en})_3]^{3+}$
- (ix) $[\text{Ni}(\text{CO})_4]$

Solution:

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

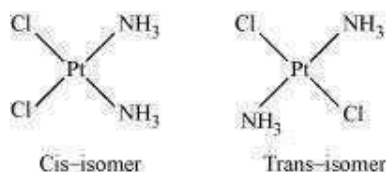
9.8. List various types of isomerism possible for coordination compounds, giving an example of each.

Solution:



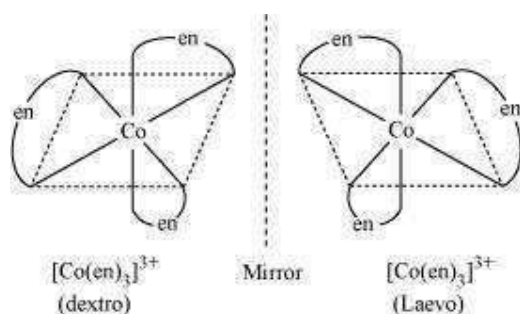
(a) Geometric isomerism:

Isomerism of this type is common in heteroleptic complexes. It results from the various geometric arrangements of the ligands. For example:

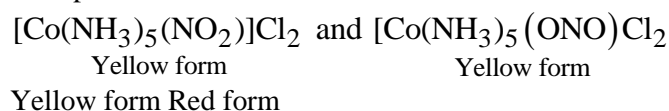


(b) Optical isomerism:

This isomerism occurs in chiral molecules. Isomers are mirror images of one another and cannot be superimposed.

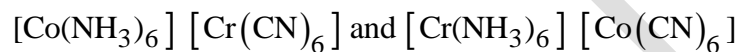


(c) Linkage isomerism: This isomerism is found in complexes containing ambidentate ligands. For example:



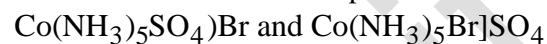
(d) Coordination isomerism:

This type of isomerism occurs when the ligands in the complex are exchanged between cationic and anionic entities of different metal ions.



(e) Ionization isomerism:

When a counter ion replaces a ligand within the coordination sphere, this type of isomerism occurs. Ionization isomers are complexes that have the same composition but produce different ions when dissolved in water. For example:



(f) Solvate isomerism:

The difference between sulfate isomers is whether the solvent molecule is directly bonded to the metal ion or is simply present as a free solvent molecule in the crystal lattice.

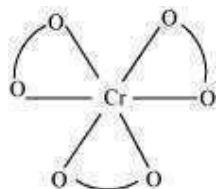


9.9. How many geometrical isomers are possible in the following coordination entities?



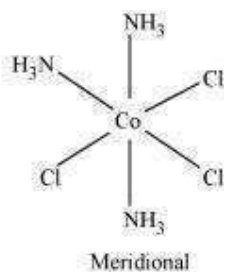
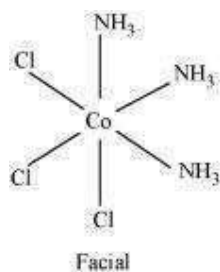
Solution:

(i) For $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$, there is no geometric isomer is possible because bidentate ligand is present.

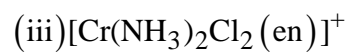
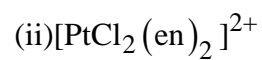
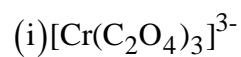




Two geometrical isomers are possible.

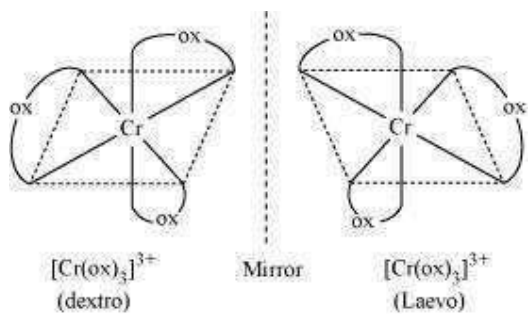


9.10. Draw the structures of optical isomers of:

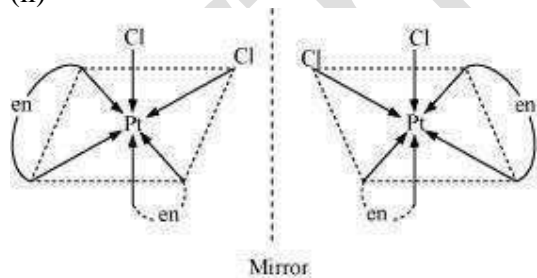


Solution:

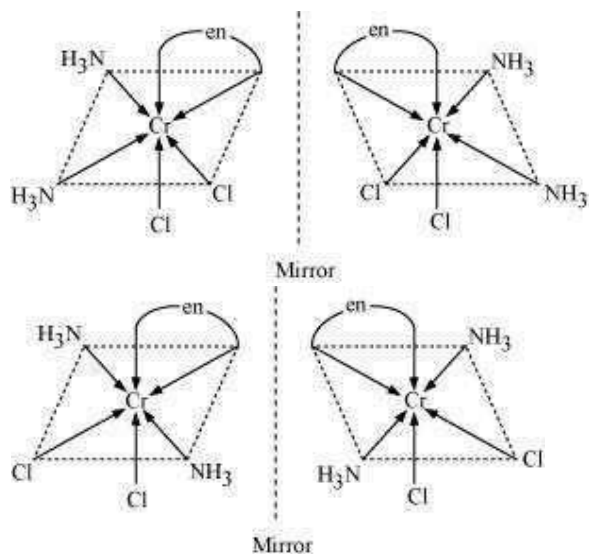
(i) ⁻



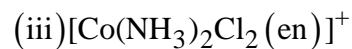
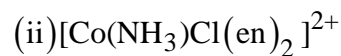
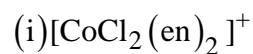
(ii)



(iii)

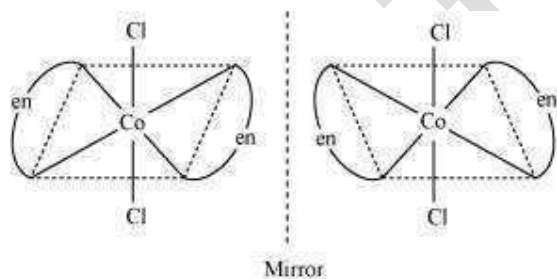


9.11. Draw all the isomers (geometrical and optical) of:



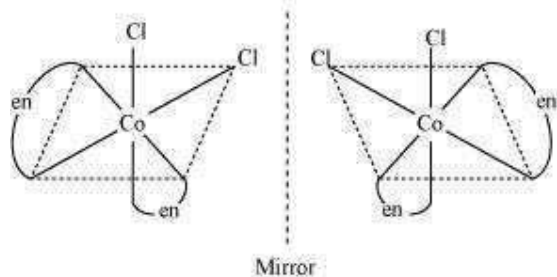
Solution:

(i)



Trans $[\text{CoCl}_2(\text{en})_2]^+$ isomer-optically inactive

(Superimposable mirror images)

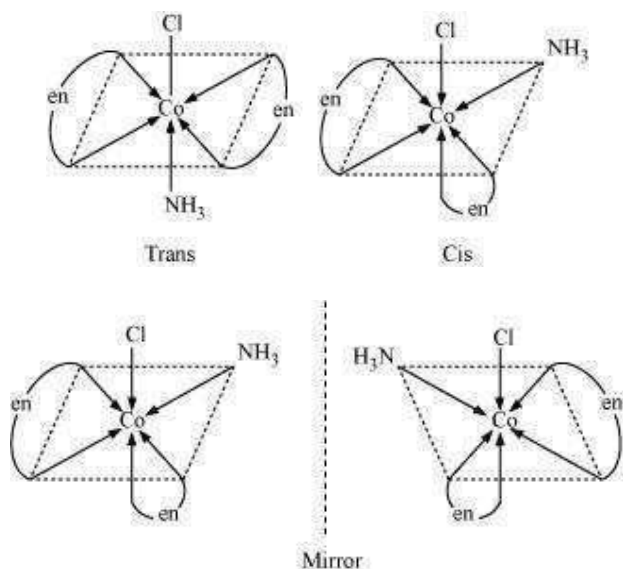


Cis $[\text{CoCl}_2(\text{en})_2]^+$ isomer-optically active

(Non-superimposable mirror images)

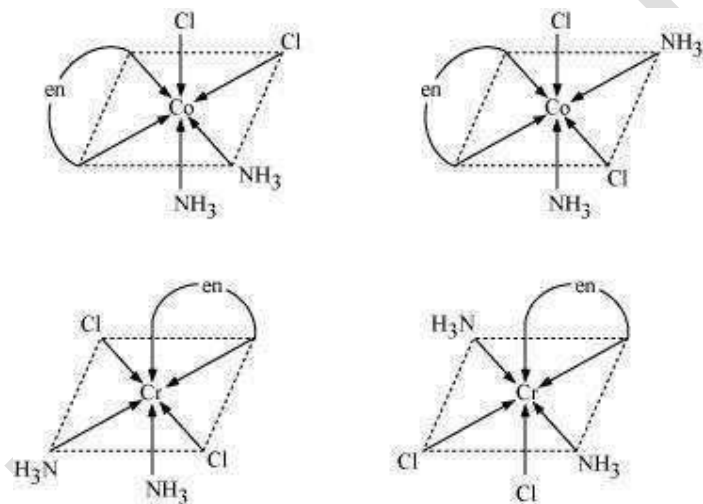
Therefore, there are total three isomers possible.

(ii)



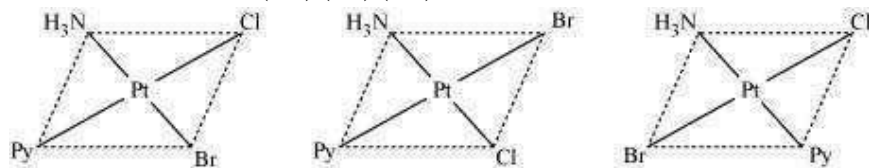
Trans-isomers are optically inactive. Cis-isomers are optically active.

(iii)



9.12. 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?

Solution: $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{py})]$



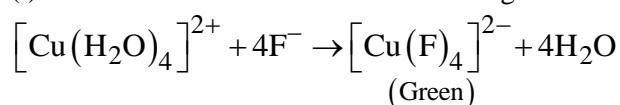
None of the isomers listed above will have optical isomers. Optical isomerization in tetrahedral complexes is uncommon. They only do so when unsymmetrical chelating agents are present.

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

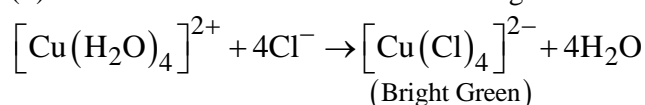
- (i) a green precipitate with aqueous potassium fluoride, and
- (ii) a bright green solution with aqueous potassium chloride Explain these experimental results.

Solution: $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4$ is the chemical formula for aqueous CuSO_4 . It is blue because of the presence of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ions.

(i) On the addition of KF. The reaction is given below.



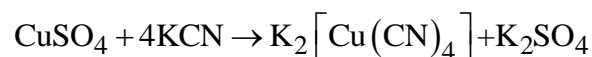
(ii) On the addition of KF. The reaction is given below.



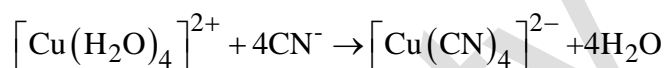
In both of these cases, the fluoride and chloride ions replace the weak field ligand water.

9.14. 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 $\text{H}_2\text{S}(\text{g})$ is passed through this solution?

Solution:



That is,



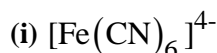
As a result of the process, the coordination entity formed is $\text{K}_2[\text{Cu}(\text{CN})_4]$. When added to water, it forms a very stable complex that does not ionize to form Cu^{2+} ions.

As a result, when $\text{H}_2\text{S}(\text{g})$ is passed through the solution, Cu^{2+} ions do not precipitate.

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



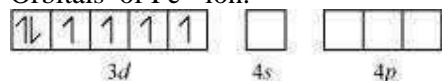
Solution:



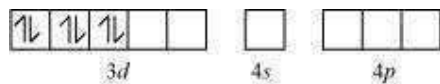
In the above coordination complex, iron exists in the +2 oxidation state.

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

Orbitals of Fe^{2+} ion:

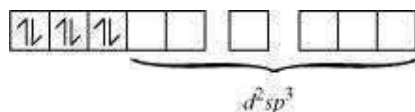


As CN^- is a strong field ligand, it causes the pairing of the unpaired $3d$ electrons.

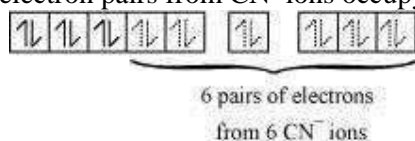


Since there are six ligands around the central metal ion, the most feasible hybridization is d^2sp^3 .

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



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

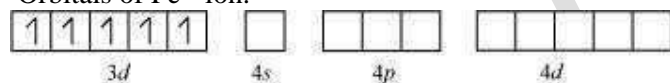


Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons).

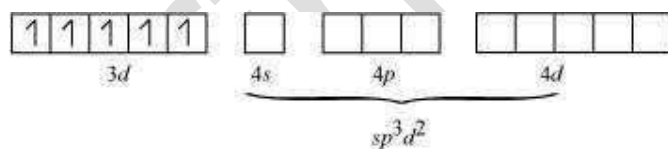
(ii) $[\text{FeF}_6]^{3-}$

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

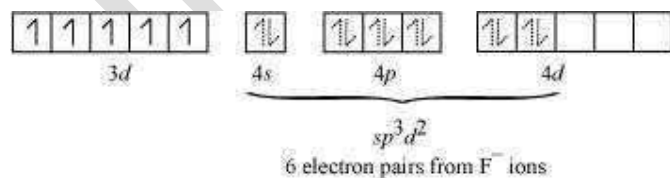
Orbitals of Fe^{+3} ion:



There are 6 fluoride ions. Thus, it will undergo sp^3d^2 or d^2sp^3 hybridization. Since fluoride ion 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:

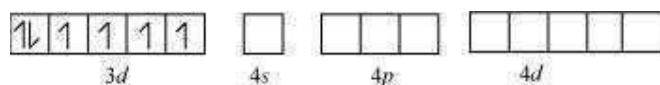


Hence, the geometry of the complex is found to be octahedral.

(iii) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$

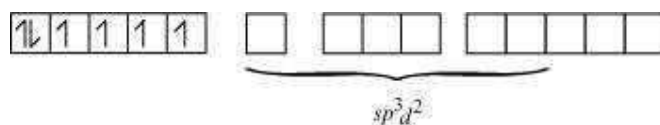
The oxidation state of cobalt is +3 in the given complex.

Orbitals of Co^{3+} ion:

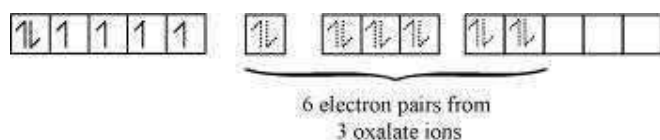


The ligand oxalate is a weak field ligand. As a result, it cannot cause the pairing of 3d orbital electrons. Since there are 6 ligands, hybridization has to be either sp^3d^2 or d^2sp^3 hybridization.

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



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

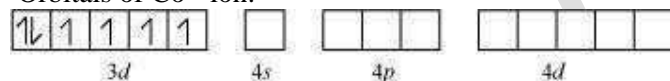


Hence, the geometry of the complex is found to be octahedral.

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

The oxidation state of cobalt is +3.

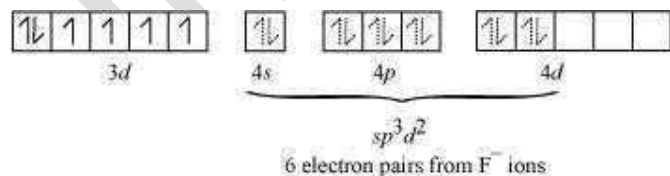
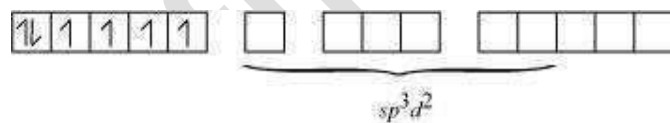
Orbitals of Co^{3+} ion:



Fluoride ion, once again, is a weak field ligand. It cannot result in the pairing of 3d electrons.

As a result, the Co^{3+} ion will undergo sp^3d^2 hybridization.

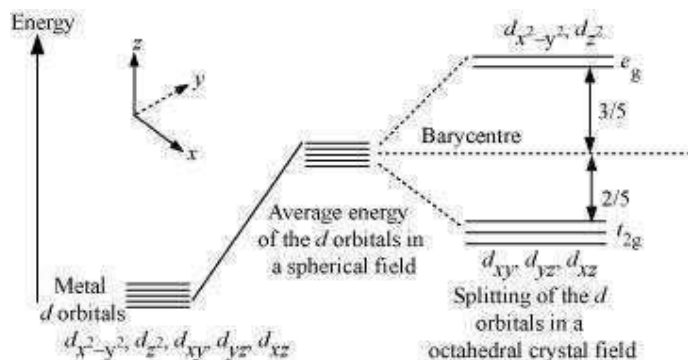
sp^3d^2 hybridized orbitals of Co^{3+} ion are:



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

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

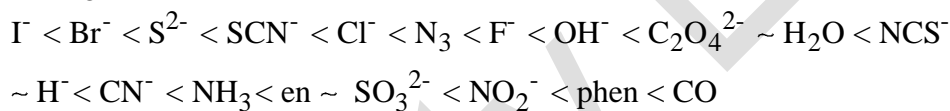
Solution:



In an octahedral field, the splitting of the d orbitals occurs 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.

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

Solution: A spectrochemical series is an arrangement of common ligands in increasing order of crystal-field splitting energy (CFSE). The ligands on the series' R.H.S are strong field ligands, while those on the L.H.S are weak field ligands. Furthermore, strong field ligands split the d orbitals more than weak field ligands.



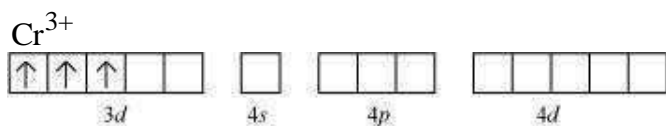
9.18. What is crystal field splitting energy? How does the magnitude of Δ_o decide the actual configuration of d-orbitals in a coordination entity?

Solution: In the presence of ligands, the degenerate d-orbitals (in a spherical field environment) split into two levels, e_g and t_{2g} . The splitting of degenerate levels caused by ligands is known as crystal-field splitting, and the energy difference between the two levels (e_g and t_{2g}) is known as crystal-field splitting energy. It is represented by the letter Δ_o .

The filling of the electrons occurs after the orbitals have split. After one electron (each) has been filled in the three t_{2g} orbitals, the fourth electron is filled in two ways. It can enter the e_g orbital (resulting in a $t_{2g}^3 e_g^1$ electronic configuration) or the electrons can pair in the t_{2g} orbitals (giving rise to $t_{2g}^4 e_g^0$ like electronic configuration). If a ligand's Δ_o value is less than the pairing energy (P), electrons enter the e_g . If the value of Δ_o ligand is greater than the pairing energy (P), the electrons enter the t_{2g} orbital.

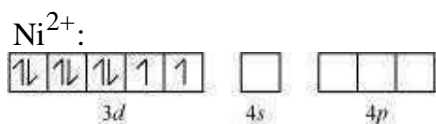
9.19. $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is paramagnetic while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic. Explain why?

Solution: Cr is in the +3 oxidation state, also known as the d^3 configuration. Furthermore, NH_3 is a weak field ligand that does not cause electron pairing in the 3d orbital.

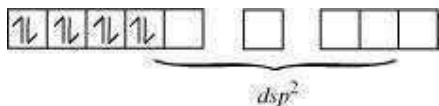


As a result, it goes through d^2sp^3 hybridization, and the electrons in the 3d orbitals remain unpaired. As a result, it is paramagnetic in nature.

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



CN^- is a powerful field ligand. It causes the electrons in the third orbital to pair. The Ni^{2+} is then hybridized with dsp^2 .



It is diamagnetic because there are no unpaired electrons.

9.20. A solution of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green but a solution of $[\text{Ni}(\text{CN})_4]^{2-}$ is colourless. Explain.

Solution: $\text{H}_2\ddot{\text{O}}$ is a weak field ligand in $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. As a result, Ni^{2+} contains unpaired electrons.

In this complex, d electrons from the lower energy level can be excited to the higher energy level, implying that a $d-d$ transition is possible. As a result, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is colored. Because CN^- is a strong field ligand, the electrons in $[\text{Ni}(\text{CN})_4]^{2-}$ are all paired. As a result, the $d-d$ transition is not possible in $[\text{Ni}(\text{CN})_4]^{2-}$. As a result, it is colorless.

9.21. $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ are of different colours in dilute solutions. Why?

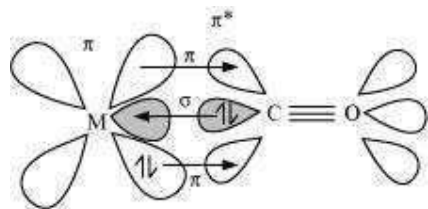
Solution: The color of a specific coordination compound is determined by the magnitude of the crystal-field splitting energy. This CFSE, in turn, is determined by the nature of the ligand. The color differs between $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ due to a difference in the CFSE. Now, CN is a powerful field ligand with a higher CFSE value than water. This means that the energy absorption for the intra $d-d$ transition varies. As a result, the transmitted color varies.

9.22. Discuss the nature of bonding in metal carbonyls.

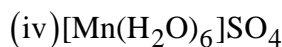
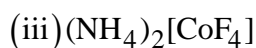
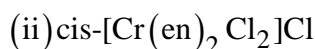
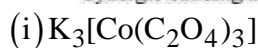
Solution: Metal-carbon bonds in metal carbonyls have both σ and π properties. When the carbonyl carbon donates a single pair of electrons to the metal's vacant orbital, a σ bond is formed. The donation of a pair of electrons from the filled metal d orbital into the vacant anti-bonding π^* orbital results in the formation of a π bond (also known as back bonding of the carbonyl group). The σ bond reinforces

the π bond, and vice versa. As a result of this metal-ligand bonding, a synergic effect is created. This synergistic effect reinforces the bond between CO and the metal.

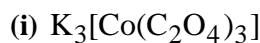
9.23. Give the oxidation state, d -orbital occupation and coordination number of the central metal ion in the following complexes:



Synergic bonding in metal carbonyls.



Solution:



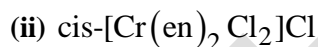
The central metal ion is Co.

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 $t_{2g}^6 e_g^0$.



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 .



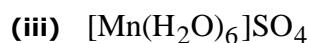
The central metal ion is Co. The coordination number is 4.

The oxidation state can be given as:

$$x - 4 = -2$$

$$= +2$$

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



The central metal ion is Mn.

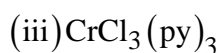
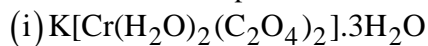
The coordination number is 6. The oxidation state can be given as:

$$x + 0 = +2$$

$$x = +2$$

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

9.24. 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:



Solution:

(i)

Potassium diaquadioxalatochromate (III) trihydrate.

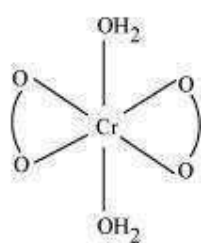
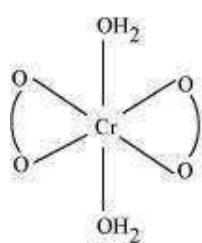
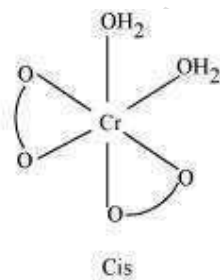
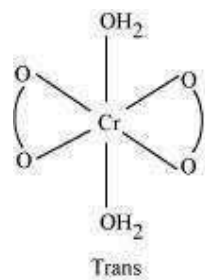
Oxidation state of chromium = 3

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

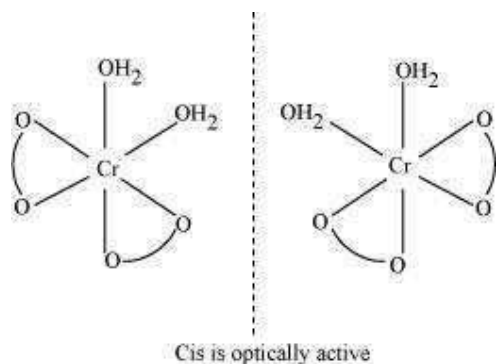
Coordination number = 6

Shape: octahedral

Stereochemistry:



Trans is optically inactive



The magnetic moment can be written as

$$\begin{aligned}\mu &= \sqrt{n(n+2)} \\ &= \sqrt{3(3+2)} \\ &= \sqrt{15} \\ &\sim 4 \text{ BM}\end{aligned}$$

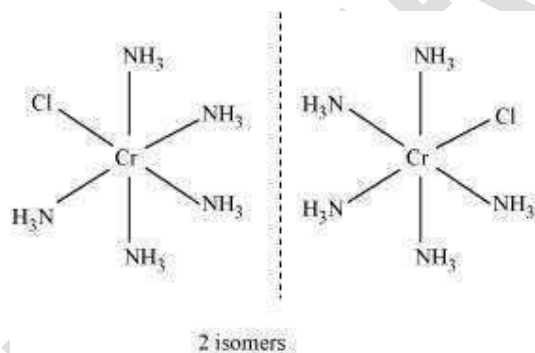
(ii) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

IUPAC name: Pentaamminechloridocobalt(III) chloride Oxidation state of Co = +3

Coordination number = 6 Shape: octahedral.

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

Stereochemistry:



Magnetic Moment = 0

(iii) $\text{CrCl}_3(\text{py})_3$

IUPAC name: Trichloridotripyridinechromium (III)

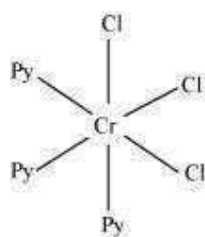
Oxidation state of chromium = +3

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

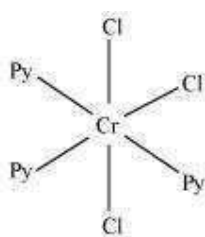
Coordination number = 6

Shape: octahedral.

Stereochemistry:



Facial isomer



Meridional isomer

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

The magnetic moment can be calculated as

$$\begin{aligned}\mu &= \sqrt{n(n+2)} \\ &= \sqrt{3(3+2)} \\ &= \sqrt{15} \\ &\sim 4 \text{ BM}\end{aligned}$$

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

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

The magnetic moment can be calculated as,

$$\begin{aligned}\mu &= \sqrt{n(n+2)} \\ &= \sqrt{5(5+2)} \\ &= \sqrt{35} \\ &\sim 6 \text{ BM}\end{aligned}$$

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

Potassium hexacyanomanganate(II)

Oxidation state of manganese = +2

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

Coordination number = 6

Shape: octahedral.

Stereochemistry: optically inactive

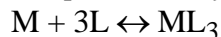
Magnetic moment can be calculated as,

$$\begin{aligned}\mu &= \sqrt{n(n+2)} \\ &= \sqrt{1(1+2)} \\ &= \sqrt{3} \\ &\sim 1.732 \text{ BM}\end{aligned}$$

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

stability of complexes.

Solution: The degree of association between the two species involved in an equilibrium state is referred to as the stability of a complex in a solution. The stability constant or formation constant can be used to express stability quantitatively.



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

The greater the value of the stability constant for this reaction, the greater the proportion of ML_3 in the solution.

There are two kinds of stability:

(a) Thermodynamic stability: At the point of equilibrium, thermodynamic stability determines the extent to which the complex will be formed or transformed into another species.

(b) Kinetic stability: This aids in determining the rate at which the transformation will occur in order to achieve equilibrium.

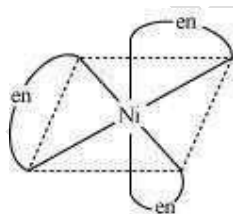
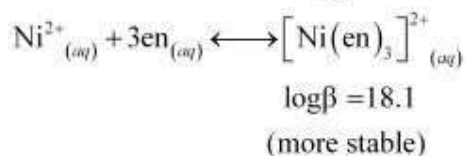
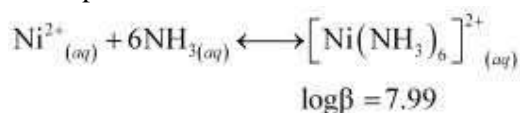
The following factors influence a complex's stability:

1. Charge on the central metal ion: The greater the charge on the central metal ion, the greater the stability of the complex.
2. The ligand's basicity: A more basic ligand will form a more stable complex.
3. The presence of chelate rings: Chelation improves complex stability.

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

Solution: The metal-ligand association is found to be more stable when a ligand attaches to the metal ion in the form of a ring. In other words, complexes with chelate rings are more stable than complexes without rings. This is referred to as the chelate effect.

For example:



9.27. 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

Solution:

(i) Role of coordination compounds in biological systems:

We know that the presence of the chlorophyll pigment allows photosynthesis to occur. This pigment is a magnesium coordination compound. Several coordination compounds play important roles in the

human biological system. For example, haemoglobin, the oxygen-carrier in blood, is an iron coordination compound.

(ii) Coordination compounds' role in medicinal chemistry:

Certain platinum coordination compounds (for example, cis-platin) are used to inhibit tumor growth.

(iii) Coordination compounds' role in analytical chemistry:

Several basic radicals are detected during salt analysis using the color changes they exhibit with different reagents. These color changes are caused by the coordination compounds or complexes formed by the basic radicals with various ligands.

(iv) Role of coordination compounds in metal extraction or metallurgy:

The extraction of certain metals from their ores involves the formation of complexes. In aqueous solution, for example, gold combines with cyanide ions to form $[\text{Au}(\text{CN})_2]$. Gold is extracted from this solution later by adding zinc metal.

9.28. How many ions are produced from the complex $\text{Co}(\text{NH}_3)_6\text{Cl}_2$ in solution?

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

Solution: (iii)

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ is the formula for the given complex. As a result, $[\text{Co}(\text{NH}_3)_6]^{2+}$ and two chloride ions are formed.

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

- (i) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- (ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
- (iii) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$

Solution:

(i) In $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, the number of unpaired electrons is 3.

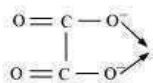
Then,

$$\begin{aligned}
 \mu &= \sqrt{n(n+2)} \\
 &= \sqrt{3(3+2)} \\
 &= \sqrt{15} \\
 &\sim 4 \text{ BM}
 \end{aligned}$$

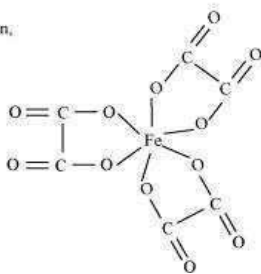
(ii) In $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, the number of unpaired electrons is 4.

Then,

$$\begin{aligned}
 \mu &= \sqrt{n(n+2)} \\
 &= \sqrt{4(4+2)} \\
 &= \sqrt{24} \\
 &\sim 5 \text{ BM}
 \end{aligned}$$



Then,



(iii) In $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$, the number of unpaired electrons is 0.

Hence, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ has the highest magnetic moment value.

9.30. The oxidation number of cobalt in $\text{K}[\text{Co}(\text{CO})_4]$ is

- (i) +1
- (ii) +3
- (iii) -1
- (iv) -3

Solution: We know that CO is a neutral ligand and that K has a +1 charge.

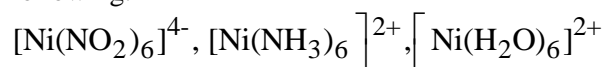
As a result, the complex is denoted as $\text{K}^+[\text{Co}(\text{CO})_4]^-$. As a result, the oxidation number of CO in the given complex is 1. As a result, option (iii) is correct.

9.31. Amongst the following, the most stable complex is

- (i) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
- (ii) $[\text{Fe}(\text{NH}_3)_6]^{3+}$
- (iii) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
- (iv) $[\text{FeCl}_6]^{3-}$

Solution: We know that chelation increases the stability of a complex. Therefore, the most stable complex is $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$.

9.32. What will be the correct order for the wavelengths of absorption in the visible region for the following:

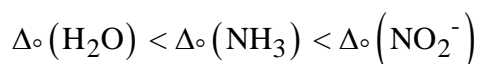


Solution:

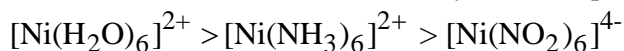
The central metal ion is the same in all three complexes. As a result, absorption in the visible region is influenced by the ligands. In the spectrochemical series, the CFSE values of the ligands increase in the following order:



As a result, the observed amount of crystal-field splitting will be in the following order:



As a result, the observed amount of crystal-field splitting will be in the following order:



Intext Questions

9.1. 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)

Solution:

- (i) $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]\text{Cl}_3$
- (ii) $\text{K}_2[\text{Ni}(\text{CN})_4]$
- (iii) $[\text{Cr}(\text{en})_3]\text{Cl}_3$
- (iv) $[\text{Pt}(\text{NH}_3)_3\text{BrCl}(\text{NO}_2)]$
- (v) $[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2$
- (vi) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

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

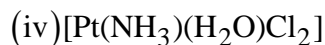
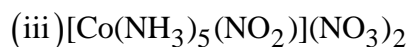
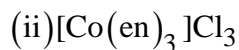
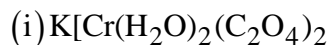
- (i) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
- (ii) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
- (iii) $\text{K}_3[\text{Fe}(\text{CN})_6]$
- (iv) $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$
- (v) $\text{K}_2[\text{PdCl}_4]$
- (vi) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$

Solution:

- (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

9.3. Indicate the types of isomerism exhibited by the following complexes and draw the structures for

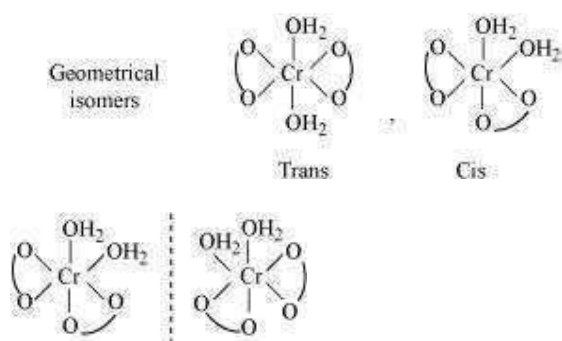
these isomers:



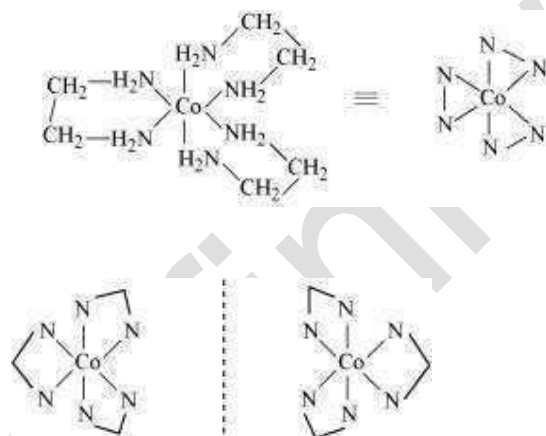
Solution:

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

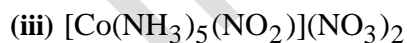
Trans-isomer is optically inactive. On the other hand, *cis*-isomer is optically active.



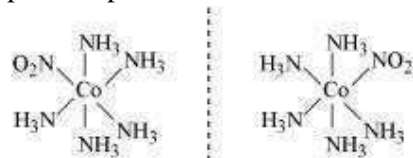
(ii) For $[Co(en)_3]Cl_3$, two optical isomers exist.



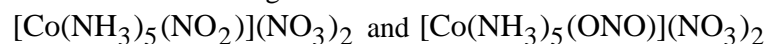
Two optical isomers are possible for this structure.



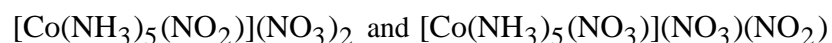
A pair of optical isomers:



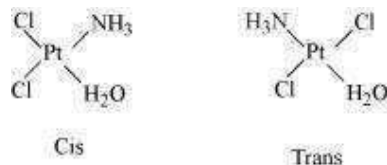
It can also show linkage isomerism.



It can also show ionization isomerism.

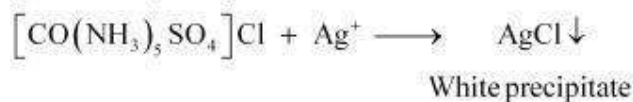
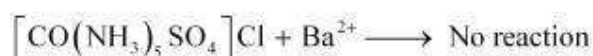
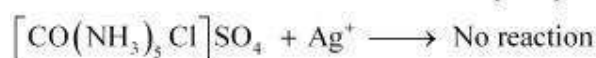
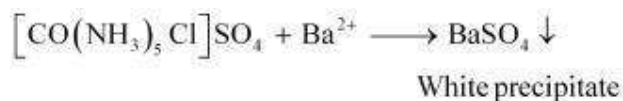


(iv) For $[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})\text{Cl}_2]$, geometrical (*cis*-, *trans*-) isomers can exist.



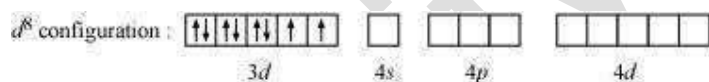
9.4. Give evidence that $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ are ionization isomers.

Solution: Ionization isomers ionize when dissolved in water, producing different ions. These ions then react with different reagents to produce different products.

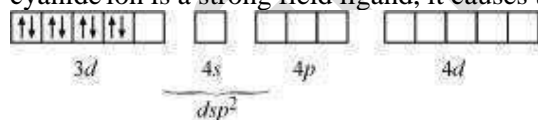


9.5. Explain on the basis of valence bond theory that $[\text{Ni}(\text{CN})_4]^{2-}$ ion with square planar structure is diamagnetic and the $[\text{NiCl}_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

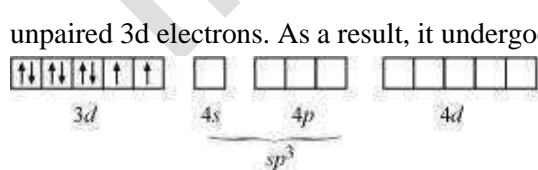
Solution: In $[\text{Ni}(\text{CN})_4]^{2-}$, Ni is in the +2 oxidation state i.e., in d^8 configuration.



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



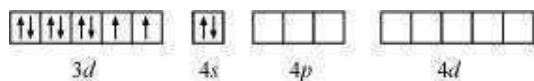
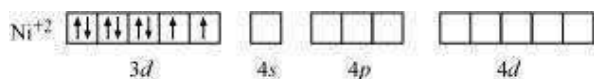
It is now being hybridized with dsp^2 . It is diamagnetic because all of its electrons are paired. Chloride ion is a weak field ligand in the case of $[\text{Ni}(\text{Cl})_4]^{2-}$. As a result, it does not result in the pairing of unpaired $3d$ electrons. As a result, it undergoes sp^3 hybridization



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

9.6. $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ is diamagnetic though both are tetrahedral. Why?

Solution: Since both complexes, $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]$ are tetrahedral, their magnetic characters are different. This is due to the different nature of the ligands. Chloride is a weak field ligand, and it does not pair unpaired $3d$ electrons. As a result, $[\text{NiCl}_4]^{2-}$ is paramagnetic.



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

CO, on the other hand, is a powerful field ligand. As a result, it leads to the pairing of unpaired 3d electrons. It also causes the 4s electrons to shift to the 3d orbital, resulting in sp^3 hybridization. Because there are no unpaired electrons in this case, $[Ni(CO)_4]$ is diamagnetic.

9.7. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

Solution: In both $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$, Fe exists in the +3 oxidation state, that is, in d^5 .



Since cyanide ion is a strong field ligand, it causes unpaired electrons to pair. As a result, the d-orbital has only one unpaired electron.



Therefore,

$$\begin{aligned}\mu &= \sqrt{n(n+2)} \\ &= \sqrt{1(1+2)} \\ &= \sqrt{3} \\ &= 1.732 \text{ BM}\end{aligned}$$

H_2O , on the other hand, is a weak field ligand. As a result, it cannot cause electron pairing. This means that there are 5 unpaired electrons.

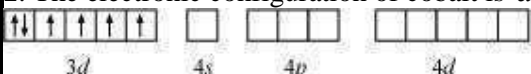
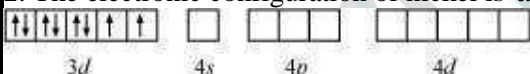
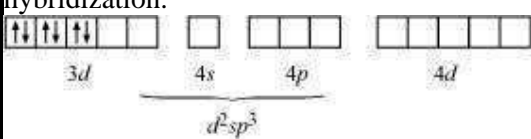
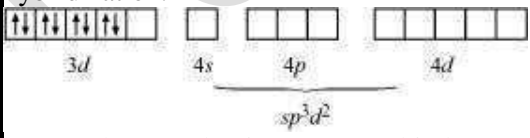
Therefore,

$$\begin{aligned}\mu &= \sqrt{n(n+2)} \\ &= \sqrt{5(5+2)} \\ &= \sqrt{35} \\ &\sim 6 \text{ BM}\end{aligned}$$

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

9.8. $[\text{Co}(\text{NH}_3)_6]^{3+}$ is an inner orbital complex whereas $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is an outer orbital complex.

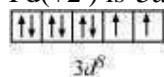
Solution:

$[\text{Co}(\text{NH}_3)_6]^{3+}$	$[\text{Ni}(\text{NH}_3)_6]^{2+}$
1. In $[\text{Co}(\text{NH}_3)_6]^{3+}$, the oxidation state of cobalt is +3.	1. In $[\text{Ni}(\text{NH}_3)_6]^{2+}$, the oxidation state of Ni is +2.
2. The electronic configuration of cobalt is d^6 . 	2. The electronic configuration of nickel is d^8 . 
3. NH_3 being a strong field ligand causes the pairing. Therefore, Ni can undergo d^2sp^3 hybridization.  Hence, the given complex is an inner orbital.	3. If NH_3 causes the pairing, then only one $3d$ orbital is empty. Thus, it cannot undergo d^2sp^3 hybridization. Therefore, it undergoes sp^3d^2 hybridization.  Hence, the complex is an outer orbital.

9.9. Predict the number of unpaired electrons in the square planar $[\text{Pt}(\text{CN})_4]^{2-}$ ion.

Solution: Pt is in the +2 state in the complex $[\text{Pt}(\text{CN})_4]^{2-}$. It takes the shape of a square planar structure. This indicates that it is undergoing dsp^2 hybridization. The electronic configuration of

$\text{Pd}(+2)$ is $5d^8$.



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

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

Solution: The oxidation state of Mn is +2, so its configuration will be $3d^5$. The distribution of these five electrons in the presence of H_2O as a ligand is $t^3_2g e^2_g$, indicating that all electrons remain unpaired. In the presence of CN^- as a ligand, the distribution is $t^5_2g e^0_g$, which means that two t_{2g} orbitals contain paired electrons and the three t_{2g} orbital contains one unpaired electron. Hence, hexaquo manganese (II) ion has five unpaired electrons, while hexacyano ion has only one unpaired electron.

Solved Examples:

1. On the basis of the following observations made with aqueous solutions, assign secondary valences to metals in the following compounds.

Formula	Moles of AgCl precipitated per mole of the compounds with excess AgNO ₃
(i) PdCl ₂ .4NH ₃	2
(ii) NiCl ₂ .6H ₂ O	2
(iii) PtCl ₂ .2HCl	0
(iv) CoCl ₂ .4NH ₃	1
(v) PtCl ₂ .2NH ₃	0

Solution:

- (i) Secondary 4
- (ii) Secondary 6
- (iii) Secondary 6
- (iv) Secondary 6
- (v) Secondary 4

2. Write the formulas for the following coordination compounds:

- Tetraammineaquachloridocobalt(III) chloride
- Potassium tetrahydroxidozincate(II)
- Potassium trioxalatoaluminate(III)
- Dichloridobis(ethane-1,2-diamine)cobalt(III)
- Tetracarbonylnickel(0)

Solution:

- $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$
- $\text{K}_2[\text{Zn}(\text{OH})_4]$
- $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$
- $[\text{CoCl}_2(\text{en})_2]^+$
- $[\text{Ni}(\text{CO})_4]$

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

- $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$
- $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$
- $[\text{CoCl}_2(\text{en})_2]\text{Cl}$
- $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$
- $\text{Hg}[\text{Co}(\text{SCN})_4]$

Solution:

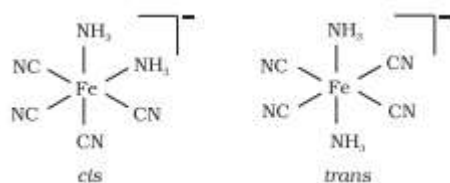
- Diamminechloridonitrito-N-platinum(II)
- Potassium trioxalatochromate(III)
- Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
- Pentaamminecarbonatocobalt(III) chloride
- Mercury (I) tetrathiocyanato-S-cobaltate(III)

4. Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion?

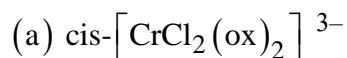
Solution: Since the relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other, tetrahedral complexes do not exhibit geometrical isomerism.

5. Draw structures of geometrical isomers of $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$.

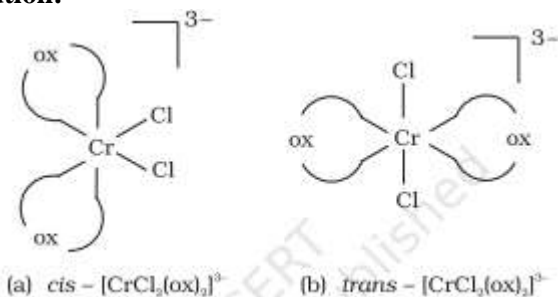
Solution:



6. Out of the following two coordination entities which is chiral (optically active)?



Solution:



Among the two entities, (a) $\text{cis-}[\text{CrCl}_2(\text{ox})_2]^{3-}$ is chiral or optically active.

7. The spin only magnetic moment of $[\text{MnBr}_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion ?

Solution: Since the coordination number of the Mn^{2+} ion in the complex ion is 4, it will be tetrahedral (sp^3 hybridisation) or square planar (dsp^2 hybridisation). However, because the complex ion has a magnetic moment of 5.9 BM, it should be tetrahedral in shape rather than square planar due to the presence of five unpaired electrons in the d orbitals.