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

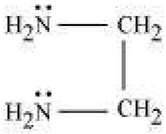
Answer

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:

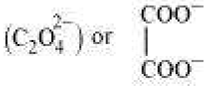
(a) Unidentate ligands: Ligands with only one donor sites are called unidentate ligands. For e.g., $\ddot{N}H_3$, Cl^- etc.

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

(a) Ethane-1,2-diamine



(b) Oxalate ion

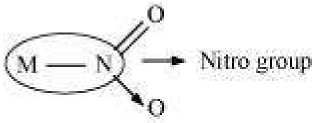


$(C_2O_4^{2-})$ or $\begin{matrix} COO^- \\ | \\ COO^- \end{matrix}$

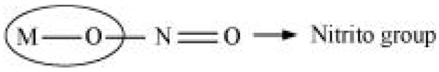
(c) Ambidentate ligands:

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

(a)

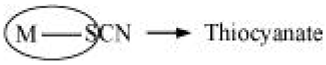


(The donor atom is N)



(The donor atom is oxygen)

(b)



(The donor atom is S)

$M-NCS \longrightarrow$ Isothiocyanate

(The donor atom is N)

Question 9.5:

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

(i) $[Co(H_2O)(CN)(en)_2]^{2+}$

(ii) $[CoBr_2(en)_2]^{+}$

(iii) $[PtCl_4]^{2-}$

(iv) $K_3[Fe(CN)_6]$

(v) $[Cr(NH_3)_3Cl_3]$

Answer

(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.

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

$$x - 1 = +2$$

$$x = +3$$

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

Let the oxidation number of Pt be *x*.

The charge on the complex is −2.

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

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

$x = +2$

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

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

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

$$\begin{array}{llll}(\mathbf{v}) & [\mathrm{Cr} & (\mathrm{NH_3})_3 & \mathrm{Cl_3}] \\ & \downarrow & \downarrow & \downarrow \\ & x & +\ 3(0) & +\ 3(-1) = 0 \\ & & x-3=0 & \\ & & x=+3 & \end{array}$$

Question 9.6:

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)

Answer

(i) $[\mathrm{Zn(OH)}]^{2-}$

(ii) $K_2[PdCl_4]$

(iii) $[Pt(NH_3)_2Cl_2]$

(iv) $K_2[Ni(CN)_4]$

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

(vi) $[Co(NH_3)_6]_2\ (SO_4)_3$

(vii) $K_3[Cr(C_2O_4)_3]$

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

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

(x) $[Co[NO_2)(NH_3)_5]^{2+}$

Question 9.7:

Using IUPAC norms write the systematic names of the following:

(i) $[Co(NH_3)6]Cl_3$

(ii) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

(iii) $[Ti(H_2O)6]^{3+}$

(iv) $[Co(NH_3)_4Cl(NO_2)]Cl$

(v) $[Mn(H_2O)6]^{2+}$

(vi) $[NiCl_4]^{2-}$

(vii) $[Ni(NH_3)_6]Cl_2$

(viii) $[Co(en)_3]^{3+}$

(ix) $[Ni(CO)_4]$

Answer

(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

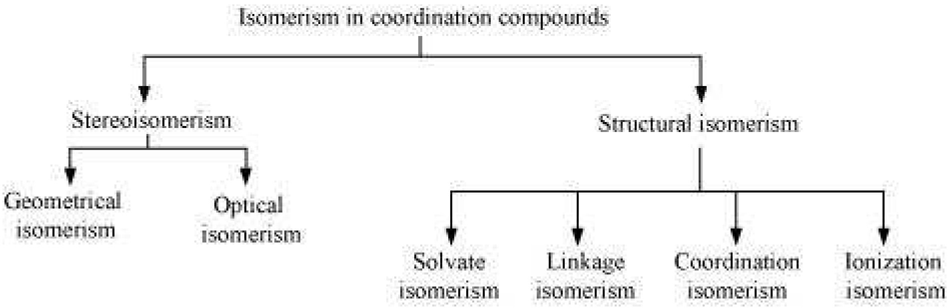
(viii) Tris(ethane-1, 2-diammine) cobalt(III) ion

(ix) Tetracarbonylnickel(0)

Question 9.8:

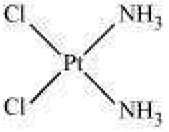
List various types of isomerism possible for coordination compounds, giving an example of each.

Answer

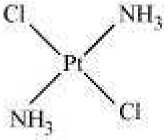


(a) Geometric isomerism:

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



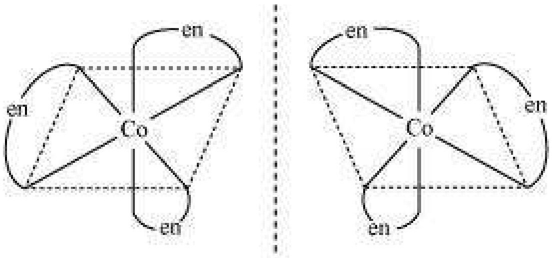
Cis–isomer



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.

$[Co(NH_3)_6] [Cr(CN)_6]$ and $[Cr(NH_3)_6] [Co(CN)_6]$

(e) Ionization isomerism:

This type of isomerism arises when a counter ion replaces a ligand within the coordination sphere. Thus, complexes that have the same composition, but furnish different ions when dissolved in water are called ionization isomers. For e.g., $Co(NH_3)_5SO_4)Br$ and $Co(NH_3)_5Br]SO_4$.

(f) Solvate isomerism:

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

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

Violet Blue-green Dark green

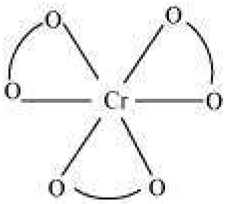
Question 9.9:

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

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

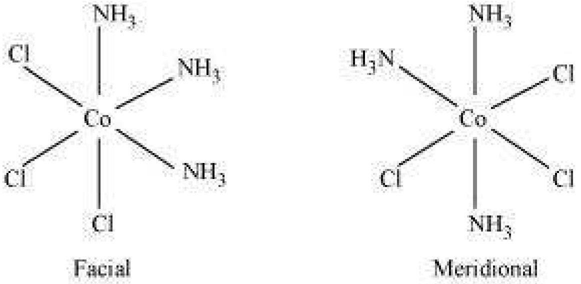
Answer

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



(ii) $[Co(NH_3)_3Cl_3]$

Two geometrical isomers are possible.



Question 9.10:

Draw the structures of optical isomers of:

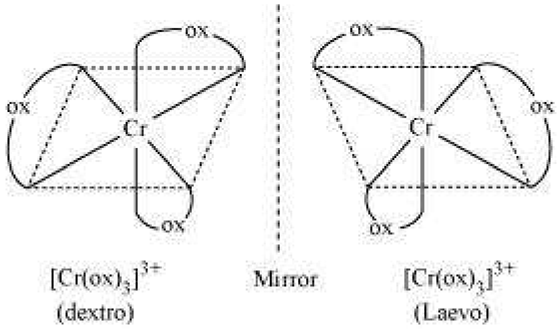
(i) $[Cr(C_2O_4)_3]^{3-}$

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

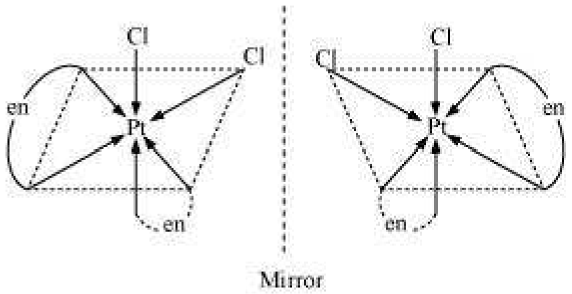
(iii) $[Cr(NH_3)_2Cl_2(en)]^{+}$

Answer

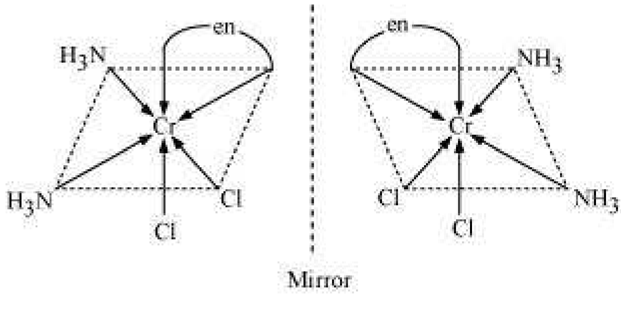
(i) $[Cr(C_2O_4)_3]^{3-}$

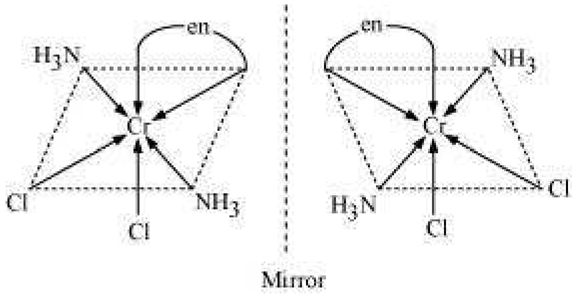


(ii) $[PtCl_2(en)_2]^{2+}$



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





Question 9.11:

Draw all the isomers (geometrical and optical) of:

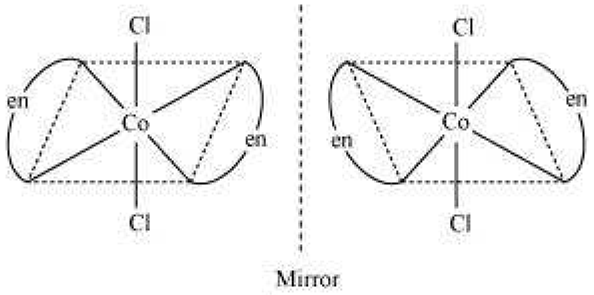
(i) $[CoCl_2(en)_2]^+$

(ii) $[Co(NH_3)Cl(en)_2]^{2+}$

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

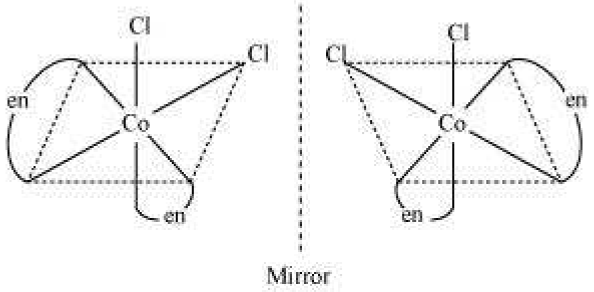
Answer

(i) $[CoCl_2(en)_2]^+$



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

(Superimposable mirror images)

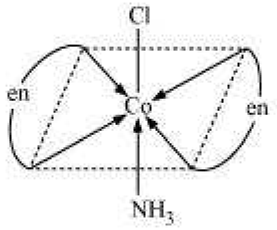


Cis $[CoCl_2(en)_2]^+$ isomer-optically active

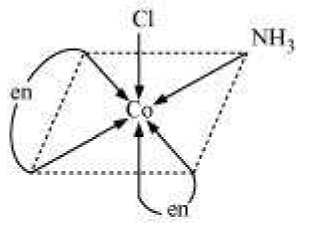
(Non-superimposable mirror images)

In total, three isomers are possible.

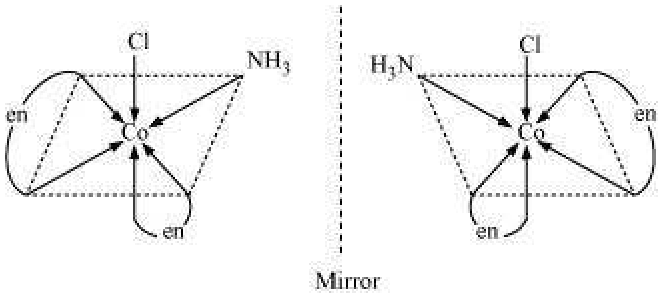
(ii) $[Co(NH_3)Cl(en)_2]^{2+}$



Trans



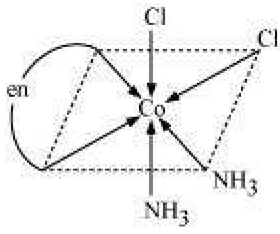
Cis

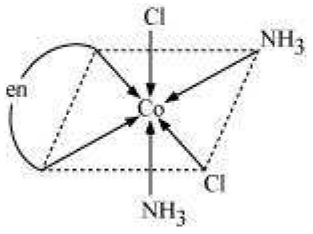


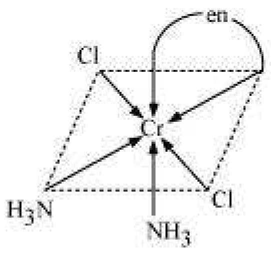
Trans-isomers are optically inactive.

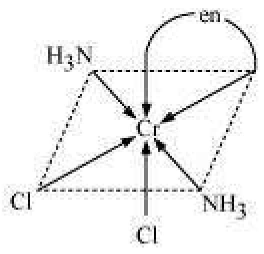
Cis-isomers are optically active.

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







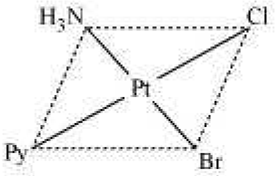


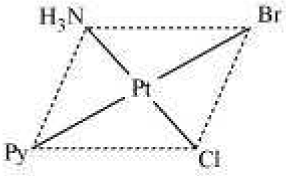
Question 9.12:

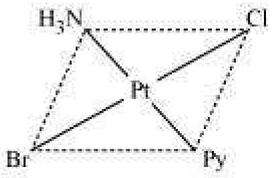
Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?

Answer

$[Pt(NH_3)(Br)(Cl)(py)$







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.

Question 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.

Answer

Aqueous $CuSO_4$ exists as $[Cu(H_2O)_4]SO_4$. It is blue in colour due to the presence of $[Cu[H_2O)_4]^{2+}$ ions.

(i) When KF is added:

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

(ii) When KCl is added:

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

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

Question 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 $H_2S(g)$ is passed through this solution?

Answer

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

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

Thus, the coordination entity formed in the process is $K_2[Cu(CN)_4]$. $K_2\left[Cu(CN)_4\right]$ 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 $H_2S_{(g)}$ is passed through the solution.

Question 9.15:

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

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

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

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

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

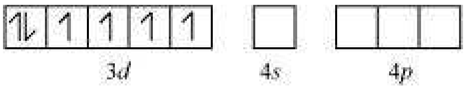
Answer

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

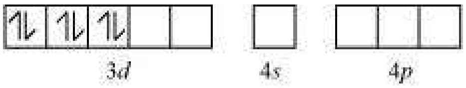
In the above coordination complex, iron exists in the +II oxidation state.

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

Orbitals of Fe^{2+} ion:

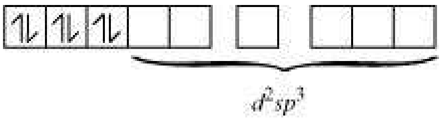


As CN^- is a strong field ligand, it causes the pairing of the unpaired 3*d* electrons.



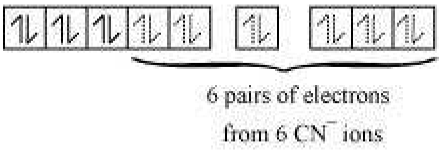
Since there are six ligands around the central metal ion, the most feasible hybridization is d^2sp^3.

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



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

Then,

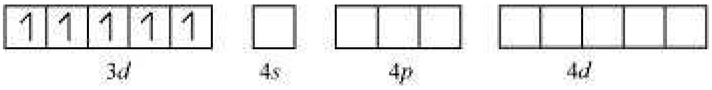


Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons).

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

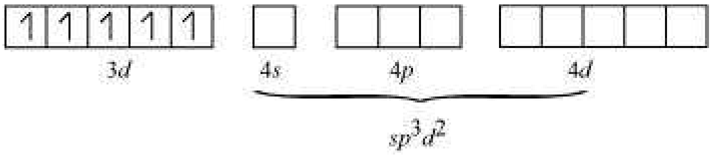
In this complex, the oxidation state of Fe is +3.

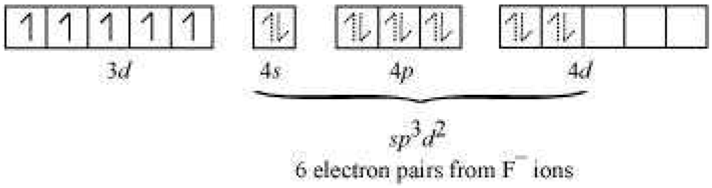
Orbitals of Fe^{+3} ion:



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:



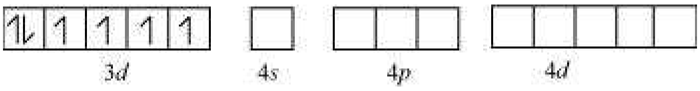


Hence, the geometry of the complex is found to be octahedral.

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

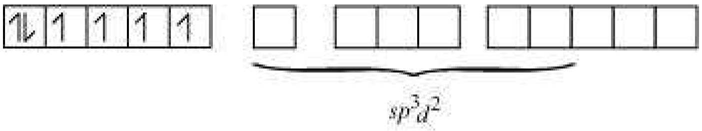
Cobalt exists in the +3 oxidation state in the given complex.

Orbitals of Co^{3+} ion:

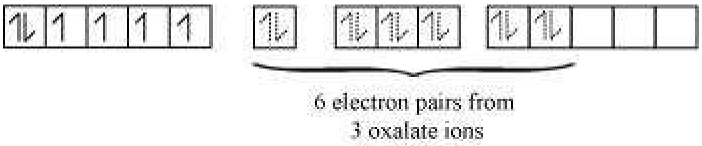


Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the 3*d* orbital electrons. As there are 6 ligands, hybridization has to be either sp^3d^2 or d^2sp^3 hybridization.

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.

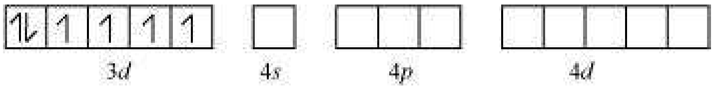


Hence, the geometry of the complex is found to be octahedral.

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

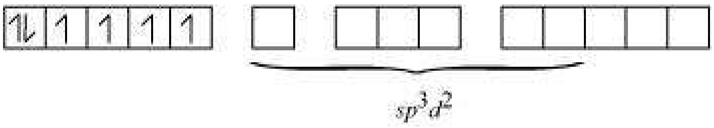
Cobalt exists in the +3 oxidation state.

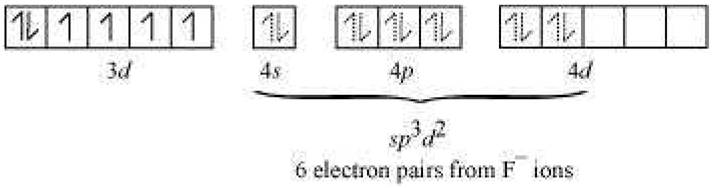
Orbitals of Co^{3+} ion:



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:



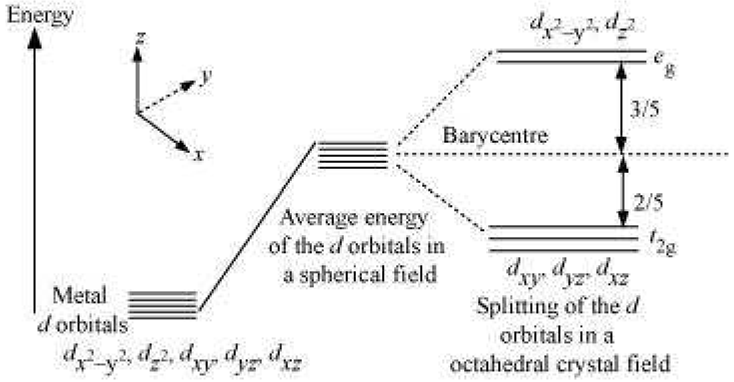


Hence, the geometry of the complex is octahedral and paramagnetic.

Question 9.16:

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

Answer



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.

Question 9.17:

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

Answer

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.

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

Question 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?

Answer

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_o.

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_o 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_o value of a ligand is more than the pairing energy (P), then the electrons enter the t_{2g} orbital.

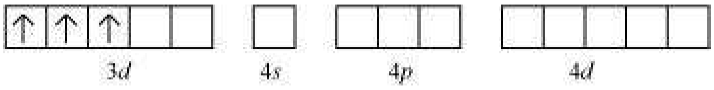
Question 9.19:

$[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?

Answer

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.

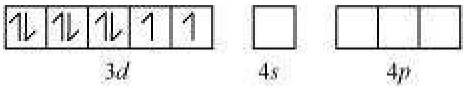
Cr^{3+}



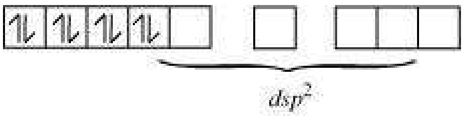
Therefore, it undergoes d^2sp^3 hybridization and the electrons in the 3*d* orbitals remain unpaired. Hence, it is paramagnetic in nature.

In $[Ni(CN)_4]^{2-}$, 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.

Question 9.20:

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

Answer

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.

Question 9.21:

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

Answer

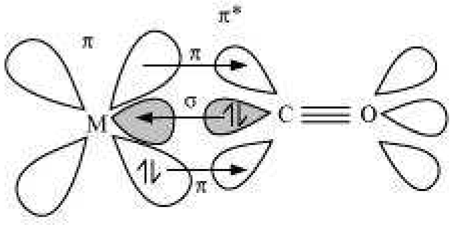
The colour of a particular coordination compound depends on the magnitude of the crystal-field splitting energy, Δ. This CFSE in turn depends on the nature of the ligand. In case of $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$, the colour differs because there is a difference in the CFSE. Now, CN^- is a 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.

Question 9.22:

Discuss the nature of bonding in metal carbonyls.

Answer

The metal-carbon bonds in metal carbonyls have both σ and π characters. A 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

Question 9.23:

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

(i) $K_3[Co(C_2O_4)_3]$

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

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

(iv) $[Mn(H_2O)_6]SO_4$

Answer

(i) $K_3[Co(C_2O_4)_3]$

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-$[Cr(en)_2Cl_2]Cl$

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 $t_{2g}^3\ e_g^2$.

Question 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:

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

Answer

(i) Potassium diaquadioxalatochromate (III) trihydrate.

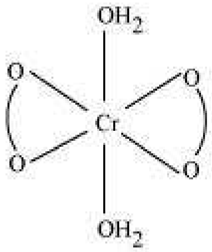
Oxidation state of chromium = 3

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

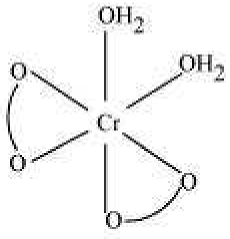
Coordination number = 6

Shape: octahedral

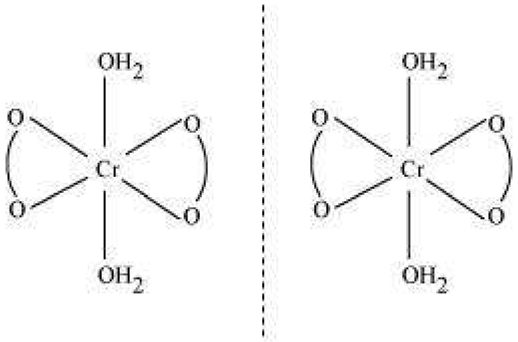
Stereochemistry:



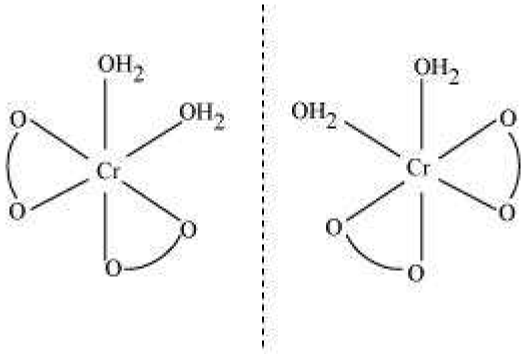
Trans



Cis



Trans is optically inactive



Cis is optically active

Magnetic moment, μ $= \sqrt{n(n+2)}$

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

$= \sqrt{15}$

~ 4BM

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

IUPAC name: Pentaamminechloridocobalt(III) chloride

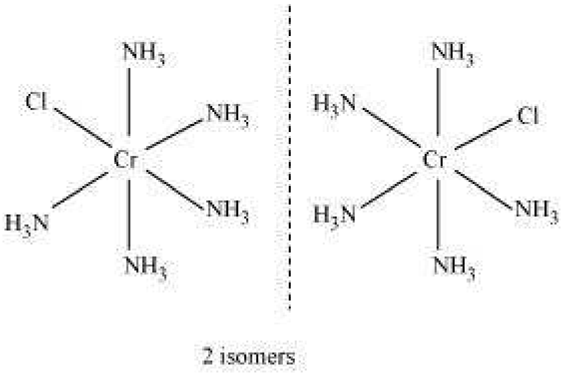
Oxidation state of Co = +3

Coordination number = 6

Shape: octahedral.

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

Stereochemistry:



Magnetic Moment = 0

(iii) $CrCl_3(py)_3$

IUPAC name: Trichloridotripyridinechromium (III)

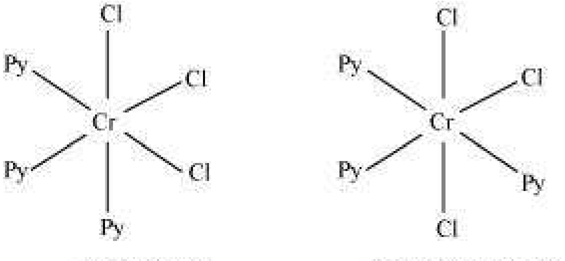
Oxidation state of chromium = +3

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, μ $= \sqrt{n(n+2)}$

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

$= \sqrt{15}$

~ 4BM

(iv) $Cs[FeCl_4]$

IUPAC name: Caesium tetrachloroferrate (III)

Oxidation state of Fe = +3

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

Coordination number = 4

Shape: tetrahedral

Stereochemistry: optically inactive

Magnetic moment:

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

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

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

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

Potassium hexacyanomanganate(II)

Oxidation state of manganese = +2

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

Coordination number = 6

Shape: octahedral.

Streochemistry: optically inactive

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

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

$$= \sqrt{3}$$

$$= 1.732 \text{ BM}$$

Question 9.25:

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

Answer

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.

$$M + 3L \longleftrightarrow ML_3$$

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

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.

2. **Basic nature of the ligand:** A more basic ligand will form a more stable complex.
2. **Presence of chelate rings:** Chelation increases the stability of complexes.

Question 9.26:

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

Answer

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:

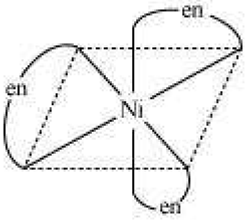
$$Ni^{2+}{}_{(aq)} + 6NH_{3(aq)} \longleftrightarrow \left[Ni\left(NH_3\right)_6\right]^{2+}{}_{(aq)}$$

$$\log\beta = 7.99$$

$$Ni^{2+}{}_{(aq)} + 3en_{(aq)} \longleftrightarrow \left[Ni\left(en\right)_3\right]^{2+}{}_{(aq)}$$

$$\log\beta = 18.1$$

(more stable)



Question 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

Answer

(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 $[Au(CN)_2]$. From this solution, gold is later extracted by the addition of zinc metal.

Question 9.28:

How many ions are produced from the complex $Co(NH_3)_6Cl_2$ in solution?

(i) 6

(ii) 4

(iii) 3

(iv) 2

Answer

(iii) The given complex can be written as $[Co(NH_3)_6]Cl_2$.

Thus, $[Co(NH_3)_6]^+$ along with two Cl^- ions are produced.

Question 9.29:

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

(i) $[Cr(H_2O)_6]^{3+}$

(ii) $[Fe(H_2O)_6]^{2+}$

(iii) $[Zn(H_2O)_6]^{2+}$

Answer

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

Then, μ $= \sqrt{n(n+2)}$

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

$= \sqrt{15}$

$\sim 4 \text{ BM}$

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

Then, μ $= \sqrt{4(4+2)}$

$= \sqrt{24}$

$\sim 5 \text{ BM}$

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

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

Question 9.30:

The oxidation number of cobalt in $K[Co(CO)_4]$ is

(i) +1

(ii) +3

(iii) −1

(iv) −3

Answer

We know that CO is a neutral ligand and K carries a charge of +1.

Therefore, the complex can be written as $K^+[Co(CO)_4]^-$. Therefore, the oxidation number of Co in the given complex is −1. Hence, option (iii) is correct.

Question 9.31:

Amongst the following, the most stable complex is

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

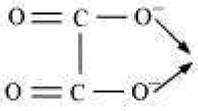
(ii) $[Fe(NH_3)_6]^{3+}$

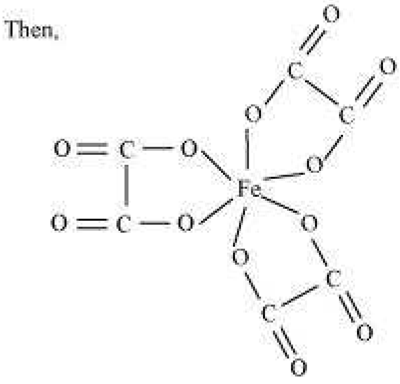
(iii) $[Fe(C_2O_4)_3]^{3-}$

(iv) $[FeCl_6]^{3-}$

Answer

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





Question 9.32:

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

$[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$

Answer

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:

$$\Delta_{\circ\,(H_2O)} < \Delta_{\circ\,(NH_3)} < \Delta_{\circ\,(NO_2^-)}$$

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

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

Question 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)

Answer

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

Question 9.2:

Write the IUPAC names of the following coordination compounds:

(i) $[Co(NH_3)_6]Cl_3$

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

(iii) $K_3[Fe(CN)_6]$

(iv) $K_3[Fe(C_2O_4)_3]$

(v) $K_2[PdCl_4]$

(vi) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

Answer

(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

Question 9.3:

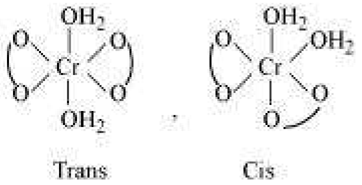
Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

i. $K[Cr(H_2O)_2(C_2O_4)_2]$
ii. $[Co(en)_3]Cl_3$
iii. $[Co(NH_3)_5(NO_2)](NO_3)_2$
iv. $[Pt(NH_3)(H_2O)Cl_2]$

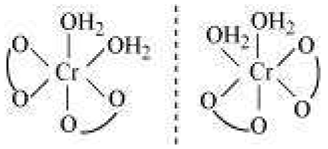
Answer

i. 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.

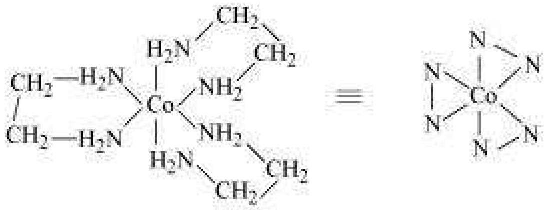
Geometrical isomers



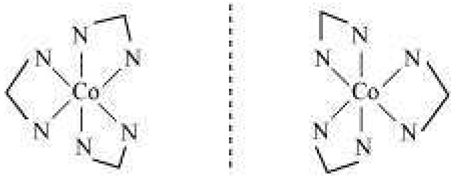
Trans-isomer is optically inactive. On the other hand, *cis*-isomer is optically active.



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

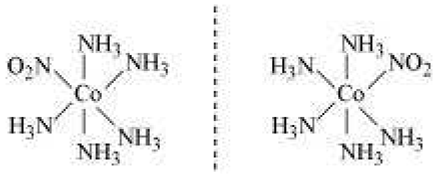


Two optical isomers are possible for this structure.



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

A pair of optical isomers:



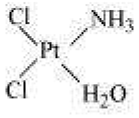
It can also show linkage isomerism.

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

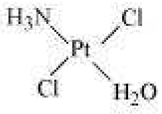
It can also show ionization isomerism.

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

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



Cis



Trans

Question 9.4:

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

Answer

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.

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

$$\left[CO\left(NH_3\right)_5Cl\right]SO_4 + Ag^{+} \longrightarrow \text{No reaction}$$

$$\left[CO\left(NH_3\right)_5SO_4\right]Cl + Ba^{2+} \longrightarrow \text{No reaction}$$

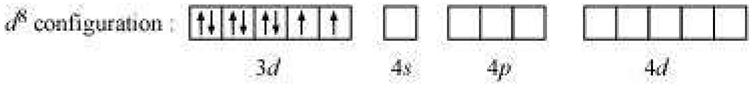
$$\left[CO\left(NH_3\right)_5SO_4\right]Cl + Ag^{+} \longrightarrow \underset{\text{White precipitate}}{AgCl\downarrow}$$

Question 9.5:

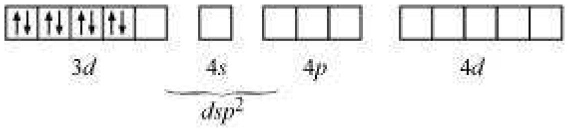
Explain on the basis of valence bond theory that [Ni(CN)$_4$]$^{2-}$ ion with square planar structure is diamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

Answer

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

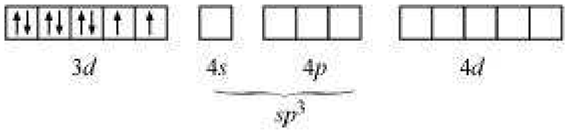


There are 4 CN^- ions. Thus, it can either have a tetrahedral geometry or square planar geometry. Since CN^- ion is a strong field ligand, it causes the pairing of unpaired 3*d* electrons.



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

In case of $[NiCl_4]^{2-}$, Cl^- 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.



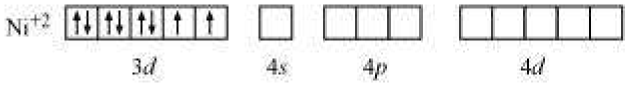
Since there are 2 unpaired electrons in this case, it is paramagnetic in nature.

Question 9.6:

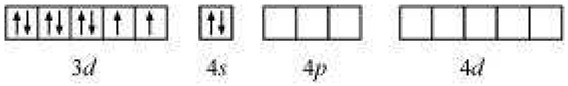
$[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

Answer

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. Cl^- 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 $3d^8\ 4s^{2.}$



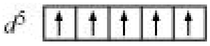
But CO is a strong field ligand. Therefore, it causes the pairing of unpaired 3*d* electrons. Also, it causes the 4s electrons to shift to the 3d orbital, thereby giving rise to *sp*^{3} hybridization. Since no unpaired electrons are present in this case, $[Ni(CO)_4]$ is diamagnetic.

Question 9.7:

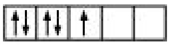
$[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

Answer

In both $\left[Fe(H_2O)_6\right]^{3+}$ and $\left[Fe(CN)_6\right]^{3-}$, Fe exists in the +3 oxidation state i.e., in *d*^{5} configuration.



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



Therefore,

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

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,

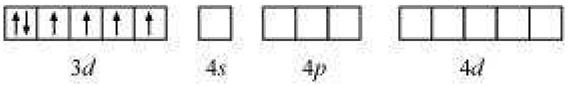
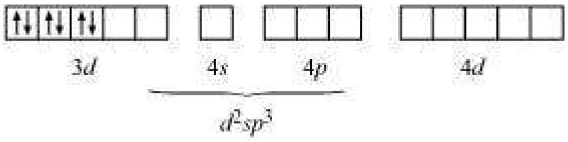
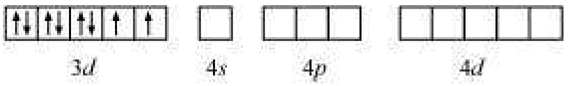
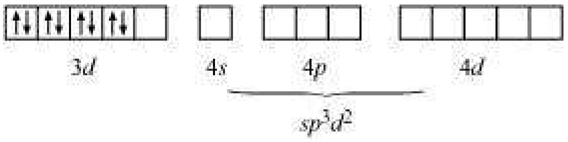
$$\begin{aligned}\mu &= \sqrt{n(n+2)}\\ &= \sqrt{5(5+2)}\\ &= \sqrt{35}\\ &\simeq 6\,\mathrm{BM}\end{aligned}$$

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

Question 9.8:

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

Answer

$[Co(NH_3)_6]^{3+}$	$[Ni(NH_3)_6]^{2+}$
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, Ni 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.

Question 9.9:

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

Answer

$[Pt(CN)_4]^{2-}$

In this complex, Pt is in the +2 state. It forms a square planar structure. This means that it undergoes 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 $\left[Pt(CN)_4\right]^{2-}$.

Question 9.10:

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

Answer

$\left[Mn(H_2O)_6\right]^{2+}$	$\left[Mn(CN)_6\right]^{4-}$
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 $\left[Mn(CN)_6\right]^{4-}$ is T2g5eg0.

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

Question 9.11:

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}.

Answer

$\beta_4 = 2.1 \times 10^{13}$

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

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

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

Question 10.1:

Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:

(i) $(CH_3)_2CHCH(Cl)CH_3$

(ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$

(iii) $CH_3CH_2C(CH_3)_2CH_2I$

(iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$

(v) $CH_3CH(CH_3)CH(Br)CH_3$

(vi) $CH_3C(C_2H_5)_2CH_2Br$

(vii) $CH_3C(Cl)(C_2H_5)CH_2CH_3$

(viii) $CH_3CH=C(Cl)CH_2CH(CH_3)_2$

(ix) $CH_3CH=CHC(Br)(CH_3)_2$

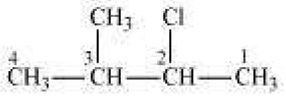
(x) *p*-$ClC_6H_4CH_2CH(CH_3)_2$

(xi) *m*-$ClCH_2C_6H_4CH_2C(CH_3)_3$

(xii) *o*-Br-$C_6H_4CH(CH_3)CH_2CH_3$

Answer

(i)

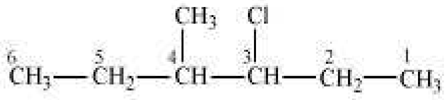


$\overset{4}{C}H_3-\overset{3}{C}H(CH_3)-\overset{2}{C}H(Cl)-\overset{1}{C}H_3$

2−Chloro−3−methylbutane

(Secondary alkyl halide)

(ii)

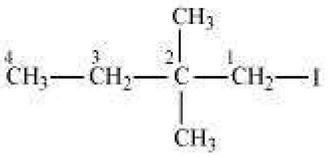


$\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{4}{C}H(CH_3)-\overset{3}{C}H(Cl)-\overset{2}{C}H_2-\overset{1}{C}H_3$

3−Chloro−4−methyhexane

(Secondary alkyl halide)

(iii)

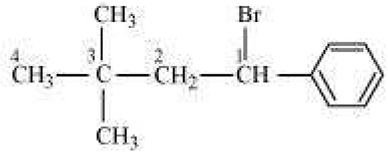


$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}(CH_3)_2-\overset{1}{C}H_2-I$

1−Iodo−2, 2 −dimethylbutane

(Primary alkyl halide)

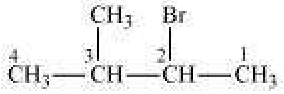
(iv)



1−Bromo−3, 3−dimethyl−1−phenylbutane

(Secondary benzyl halide)

(v)

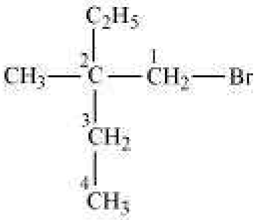


$$\overset{4}{C}H_3-\overset{\overset{CH_3}{|}}{\overset{3}{C}H}-\overset{\overset{Br}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$$

2−Bromo−3−methylbutane

(Secondary alkyl halide)

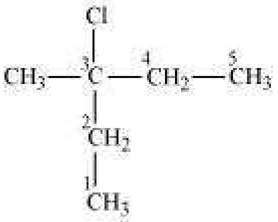
(vi)



1−Bromo−2−ethyl−2−methylbutane

(Primary alkyl halide)

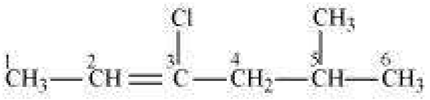
(vii)



3−Chloro−3−methylpentane

(Tertiary alkyl halide)

(viii)



$$\overset{1}{C}H_3-\overset{2}{C}H=\overset{\overset{Cl}{|}}{\overset{3}{C}}-\overset{4}{C}H_2-\overset{\overset{CH_3}{|}}{\overset{5}{C}H}-\overset{6}{C}H_3$$