(Chapter 9)(Coordination compounds)

XII

Intext Questions

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) $[CO(H_2O)_2(NH_3)_4]Cl_3$

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

(iii) $[Cr(en)_3]Cl_3$

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

(v) $[PtCl_2(en)_2](NO_3)_2$

(vi) $Fe_4[Fe(CN)_6]_3$

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. $K[Cr(H_2O)_2(C_2O_4)_2$

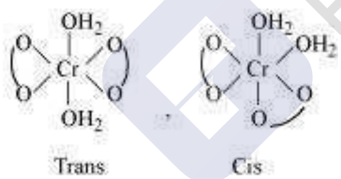
ii. $[Co(en)_3]Cl_3$

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

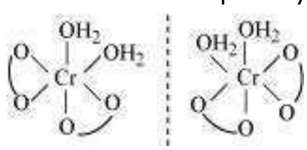
Answer

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

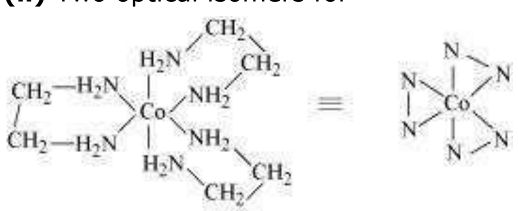
Geometrical isomers



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

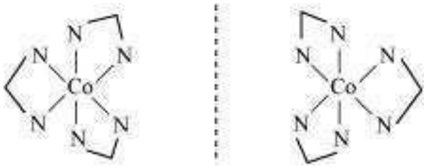


(ii) Two optical isomers for $[CO(en)_3]Cl_3$



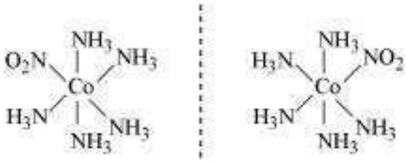
exist.

Two optical isomers are possible for this structure.



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

A pair of optical isomers:



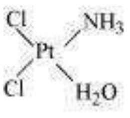
It can also show linkage isomerism.

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

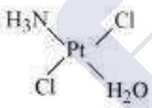
It can also show ionization isomerism.

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

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



Cis



Trans

Question 9.4:

Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ 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.

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

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

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

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

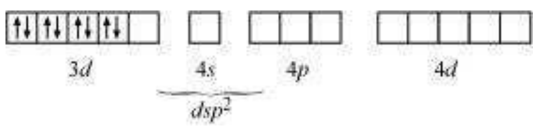
Question 9.5:

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.

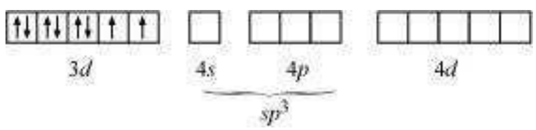
Answer

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.



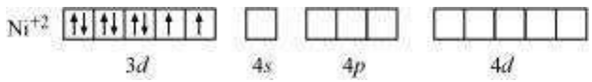
Since there are 2 unpaired electrons in this case, it is paramagnetic in nature.

Question 9.6:

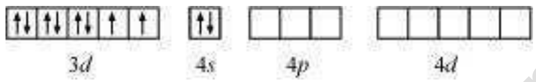
$[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

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 $3d^8\ 4s^2$.



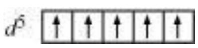
But CO is a strong field ligand. Therefore, it causes the pairing of unpaired 3*d* electrons. Also, it causes the 4s electrons to shift to the 3d orbital, thereby giving rise to sp^3 hybridization. Since no unpaired electrons are present in this case, $[Ni(CO)_4]$ is diamagnetic.

Question 9.7:

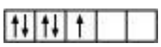
$[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

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,

$$\mu = \sqrt{n(n+2)}$$
$$= \sqrt{1(1+2)}$$
$$= \sqrt{3}$$
$$= 1.732\,\text{BM}$$

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

Therefore,

$$\mu = \sqrt{n(n+2)}$$
$$= \sqrt{5(5+2)}$$
$$= \sqrt{35}$$
$$\simeq 6\,\text{BM}$$

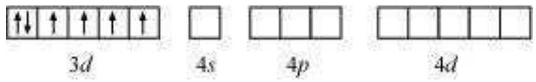
Thus, it is evident that $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic, while $[Fe(CN)_6]^{3-}$ is weakly paramagnetic.

Question 9.8:

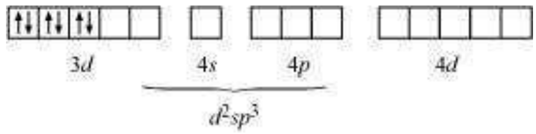
Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

Answer

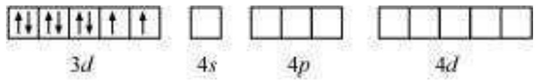
$[Co(NH_3)_6]^{3+}$	$[Ni(NH_3)_6]^{2+}$
Oxidation state of cobalt = +3	Oxidation state of Ni = +2
Electronic configuration of cobalt = d^6	Electronic configuration of nickel = d^8



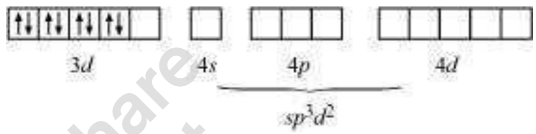
NH_3 being a strong field ligand causes the pairing. Therefore, Ni can undergo d^2sp^3 hybridization.



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.

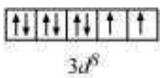
Question 9.9:

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

Answer

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

In this complex, Pt is in the +2 state. It forms a square planar structure. This means that it undergoes 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.

The electronic configuration is d^{5}.

The crystal field is octahedral. Water is a a strong field ligand. Therefore, the arrangement of the electrons in $[Mn(H_2O)_6]^{2+}$ is t2g3eg2.

Mn is in the +2 oxidation state.

The electronic configuration is d^5.

The crystal field is octahedral. Cyanide is weak field ligand. Therefore, the arrangement of the electrons in $[Mn(CN)_6]^{4-}$ 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.

$$\frac{1}{\beta_4} = \frac{1}{2.1 \times 10^{13}}$$

$$\therefore \quad = 4.7 \times 10^{-14}$$