

Chemistry

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(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) $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]\text{Cl}_3$
- (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) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

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



Chemistry

(www.tiwariacademy.com)

(Chapter 9)(Coordination compounds)

XII

Answer

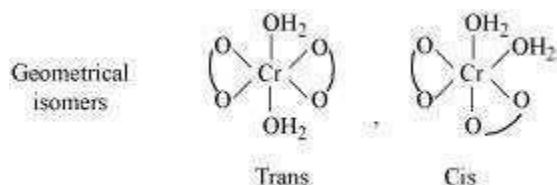
- (i) Hexaamminecobalt(III) chloride
 - (ii) Pentaamminechloridocobalt(III) chloride
 - (iii) Potassium hexacyanoferrate(III)
 - (iv) Potassium trioxalatoferrate(III)
 - (v) Potassium tetrachloridopalladate(II)
 - (vi) Diamminechlorido(methylamine)platinum(II) chloride
- Question 9.3:**

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

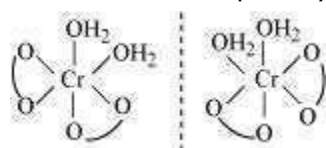
- i. $K[Cr(H_2O)_2(C_2O_4)_2]$
- ii. $[Co(en)_3]Cl_3$
- iii. $[Co(NH_3)_5(NO_2)](NO_3)_2$
- iv. $[Pt(NH_3)(H_2O)Cl_2]$

Answer

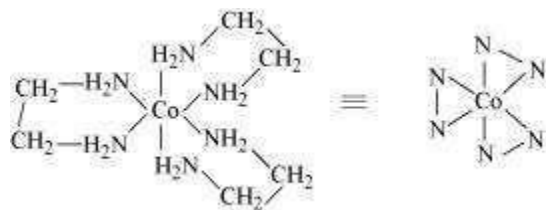
- i. Both geometrical (*cis*-, *trans*-) isomers for $K[Cr(H_2O)_2(C_2O_4)_2]$ can exist. Also, optical isomers for *cis*-isomer exist.



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.

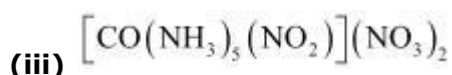
Chemistry

(www.tiwariacademy.com)

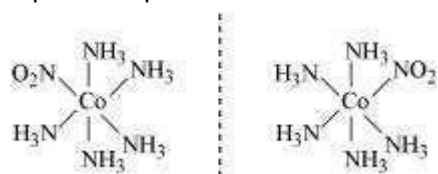
(Chapter 9)(Coordination compounds)

XII

Two optical isomers are possible for this structure.



A pair of optical isomers:



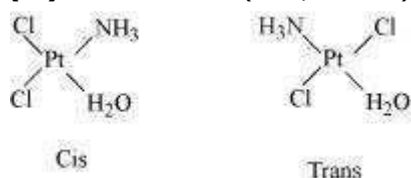
It can also show linkage isomerism.



It can also show ionization isomerism.



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



Question 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.

Answer

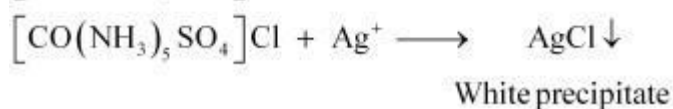
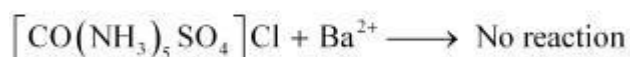
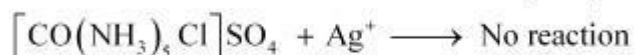
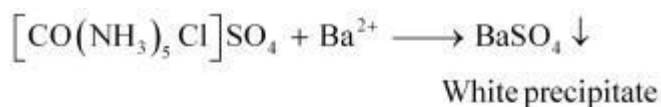
When ionization isomers are dissolved in water, they ionize to give different ions. These ions then react differently with different reagents to give different products.

Chemistry

(www.tiwariacademy.com)

(Chapter 9)(Coordination compounds)

XII

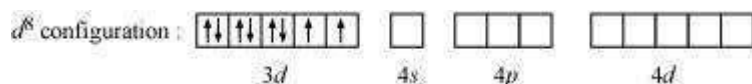


Question 9.5:

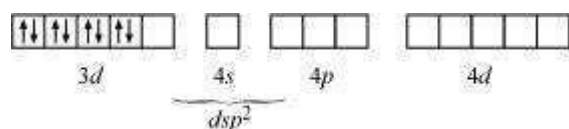
Explain on the basis of valence bond theory that $[\text{Ni}(\text{CN})_4]^{2-}$ ion with square planar structure is diamagnetic and the $[\text{NiCl}_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

Answer

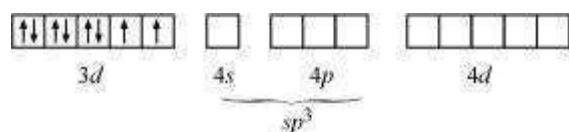
Ni is in the +2 oxidation state i.e., in d^8 configuration.



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 $3d$ electrons.



It now undergoes dsp^2 hybridization. Since all electrons are paired, it is diamagnetic. In case of $[\text{NiCl}_4]^{2-}$, Cl^- ion is a weak field ligand. Therefore, it does not lead to the pairing of unpaired $3d$ electrons. Therefore, it undergoes sp^3 hybridization.



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



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(Chapter 9)(Coordination compounds)

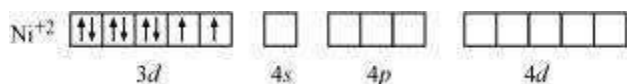
XII

Question 9.6:

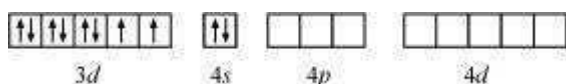
$[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ is diamagnetic though both are tetrahedral. Why?

Answer

Though both $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]$ 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 $3d$ electrons. Hence, $[\text{NiCl}_4]^{2-}$ is paramagnetic.



In $[\text{Ni}(\text{CO})_4]$, 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 $3d$ 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, $[\text{Ni}(\text{CO})_4]$ is diamagnetic.

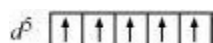
Question 9.7:

$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is strongly paramagnetic whereas $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic.

Explain.

Answer

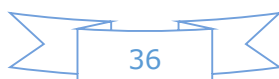
In both $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$, Fe exists in the +3 oxidation state i.e., in d^5 configuration.



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,



Chemistry

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(Chapter 9)(Coordination compounds)

XII

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

On the other hand, H₂O is a weak field ligand. Therefore, it cannot cause the pairing of electrons. This means that the number of unpaired electrons is 5.

Therefore,

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

Thus, it is evident that $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is strongly paramagnetic, while $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic.

Question 9.8:

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

Answer

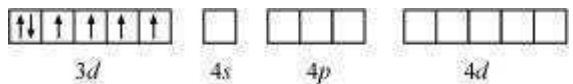
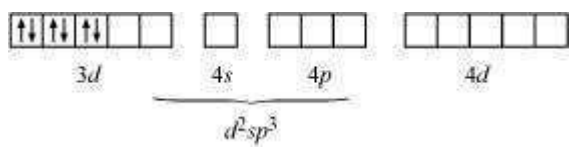
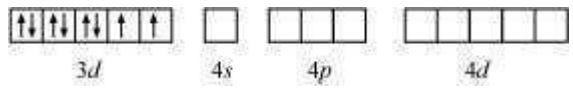
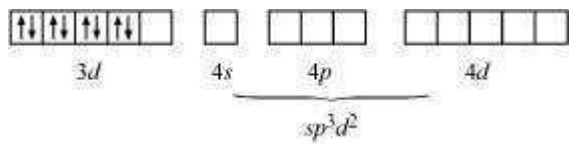
| | |
|--|--|
| $[\text{Co}(\text{NH}_3)_6]^{3+}$ | $[\text{Ni}(\text{NH}_3)_6]^{2+}$ |
| Oxidation state of cobalt = +3 | Oxidation state of Ni = +2 |
| Electronic configuration of cobalt = d^6 | Electronic configuration of nickel = d^8 |

Chemistry

(www.tiwariacademy.com)

(Chapter 9)(Coordination compounds)

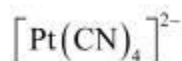
XII

| | |
|---|--|
|  <p>NH₃ being a strong field ligand causes the pairing. Therefore, Ni can undergo d^2sp^3 hybridization.</p>  <p>Hence, it is an inner orbital complex.</p> |  <p>If NH₃ 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.</p>  <p>Hence, it forms an outer orbital complex.</p> |
|---|--|

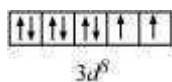
Question 9.9:

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

Answer



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

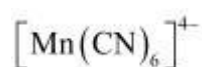
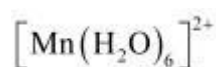


CN^- being a strong field ligand causes the pairing of unpaired electrons. Hence, there are

no unpaired electrons in $[\text{Pt}(\text{CN})_4]^{2-}$.

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



Chemistry

(www.tiwariacademy.com)

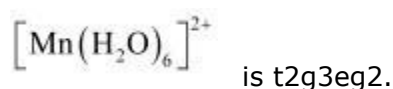
(Chapter 9)(Coordination compounds)

XII

Mn is in the +2 oxidation state.

The electronic configuration is d^5 .

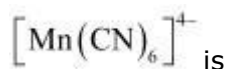
The crystal field is octahedral. Water is a weak field ligand. Therefore, the arrangement of the electrons in



Mn is in the +2 oxidation state.

The electronic configuration is d^5 .

The crystal field is octahedral. Cyanide is



$t_{2g}^5 e_g^0$.

Hence, hexaquo 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 $\text{Cu}(\text{NH}_3)_4^{2+}$ 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 .

$$\begin{aligned} \frac{1}{\beta_4} &= \frac{1}{2.1 \times 10^{13}} \\ \therefore &= 4.7 \times 10^{-14} \end{aligned}$$

