

Chapter 5: Coordination Compounds

NCERT · Class 12 · Chemistry

In-text questions

Question 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

Ans: The formula of Tetraamminediaquacobalt (III) chloride is $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Cl}_3$.

Ans: The formula of Potassium tetracyanonickelate(II) is $\text{K}_2[\text{Ni}(\text{CN})_4]$.

Ans: The formula of Tris(ethane-1,2-diamine) chromium(III) chloride is $[\text{Cr}(\text{en})_3]\text{Cl}_3$

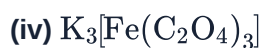
Ans: The formula of Amminebromidochloridenitrito-N-platinate(II) is $[\text{Pt}(\text{NH}_3)\text{BrCl}(\text{NO}_2)]^-$

Ans: The formula of Dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate is $[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2$

Ans: The formula of Iron(III) hexacyanoferrate(II) is $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

Question 2

Write the IUPAC names of the following coordination compounds:



Solution

Ans: The IUPAC name of the compound is Hexaamminecobalt(III) chloride.

Ans: The IUPAC name of the compound is Pentaamminechloridocobalt(III) chloride.

Ans: The IUPAC name of the compound is Potassium hexacyanoferrate (III).

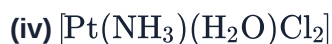
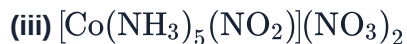
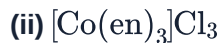
Ans: The IUPAC name of the compound is Potassium trioxalatoferrate(III).

Ans: The IUPAC name of the compound is Potassium tetrachloridopalladate(II).

Ans: The IUPAC name of the compound is Diamminechloride (methylamine) platinum(II) chloride.

Question 3

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



Solution

Ans: Both geometrical isomers (cis and trans) are possible for this compound. These are given below:

The trans-isomers of this compound is optically inactive but the cis-isomer is optically active. Therefore, it can also show optical isomerism. This is given below:

Ans: This compound can show optical isomerism. The structure is given below:

Its optical isomers are given below:

Ans: It can show three types of isomerism.

A pair of optical isomer, these are given below:

It can show linkage isomerism. These are given below:



It can also show ionization isomerism. These are given below:



Ans: Geometrical isomerism of this compound is possible. Both cis-form and trans-form are given below:

Question 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

Ans: If isomers of ionization are ionized into water, various ionization isomers are ionized. These ions react differently to various products with different reagents. The compounds given in the questions are tested with AgNO_3 solution and BaCl_2 solution. The reactions are given below:



Question 5

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

Solution

Ans: In d^8 configuration, Ni is in +2 oxidation state. This is shown below:

As we can see that in the question, there are 4 ligands in the compound which means it is a square planar complex.

Since, CN^- is a strong field ligand and it will cause the pairing of the 3d electrons. This will lead to dsp^2 hybridization. It is given below:

Since, all the electrons are paired, $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic complex.

Since, Cl^- is a weak field ligand and it will not cause the pairing of the 3d electrons. This will lead to sp^3 hybridization. It is given below:

Since, two electrons are unpaired, $[\text{NiCl}_4]^{2-}$ is paramagnetic complex.

Question 6

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

Solution

Ans: As we can see that in the question, there are 4 ligands in the compound which means it is a tetrahedral complex.

Since, Cl^- is a strong field ligand and it will not cause the pairing of the 3d electrons. This will lead to sp^3 hybridization. It is given below:

Since, two electrons are unpaired, $[\text{NiCl}_4]^{2-}$ is paramagnetic complex.

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. This leads unpaired 3d electrons to be coupled with one another. It also leads the 4s to go to the 3d orbital, which results in a hybridization of sp^3 . Since in this situation, $[\text{Ni}(\text{CO})_4]$ is diamagnetic as no unpaired electrons are present.

Question 7

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

Solution

Ans: In the given complexes, Fe is the central metal ion and in both the cases the oxidation state of Fe is +3. Therefore, it will be in d^5 configuration.

Since CN^- is a strong field ligand, it causes unpaired electrons to be paired. There is just one unpaired electron in the d-orbital thus remaining.

So, we can calculate the magnetic moment as:

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

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

$$\mu = \sqrt{3}$$
$$\mu = 1.732 \text{ BM}$$

Since H_2O is a weak field ligand, it does not cause unpaired electrons to be paired. There are five unpaired electrons in the d-orbital.

So, we can calculate the magnetic moment as:

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

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

$$\mu = \sqrt{35}$$
$$\mu = 5.91 \text{ BM}$$

Therefore, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is strongly paramagnetic while $[\text{Fe}(\text{CN})_6]^{3+}$ is weakly paramagnetic complex.

Question 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.

Solution

Ans: In $[\text{Co}(\text{NH}_3)_6]^{3+}$ the oxidation state of Co is in +3 oxidation state, which will cause the configuration of Co as d^6 .

Since NH_3 is a strong field ligand, it causes unpaired electrons to be paired. This will lead to d^2sp^3 hybridization. This is shown below:

Therefore, it is an inner orbital complex.

In $[\text{Ni}(\text{NH}_3)_6]^{2+}$ the oxidation state of Ni is in +2 oxidation state, which will cause the configuration of Ni as d^8 .

Since NH_3 is a strong field ligand, it causes unpaired electrons to be paired. There is only one d-orbital left and it cannot form the d^2sp^3 . Therefore, it will act as a weak field ligand. This will lead to sp^3d^2 hybridization. This is shown below:

Therefore, it is an outer orbital complex.

Question 9

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

Solution

Ans: The given complex is $[\text{Pt}(\text{CN})_4]^{2-}$. In this complex the central metal ion is platinum and its oxidation state is +2. It forms a square planar structure. This means that it will have the hybridization of dsp^2 . So, the electronic configuration Pt (+2) of is $5d^8$.

In the complex, CN^- is a strong field ligand which will cause the pairing of all the unpaired electrons. Therefore, there will be no unpaired electrons.

Question 10

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

Solution

Ans: In $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, the Mn is in +2 oxidation state and its electronic configuration is d^5 . The crystal field is octahedral. Water is a weak field ligand. Therefore, the arrangement of the electrons in $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ will be $t_2g^3 eg^2$.

In $[\text{Mn}(\text{CN})_6]^{2-}$, the Mn is in +2 oxidation state and its electronic configuration is d^5 . The crystal field is octahedral. Cyanide is a strong field ligand. Therefore, the arrangement of the electrons in $[\text{Mn}(\text{CN})_6]^{2-}$ will be $t_2g^5 eg^0$.

Question 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} .

Solution

Ans: We are given the overall stability constant $(\beta_4) = 2.1 \times 10^{13}$.

The overall complex dissociation equilibrium constant is the reciprocal of the overall stability constant. This is given below:

$$\text{Overall dissociation constant} = \frac{1}{\beta_4} = \frac{1}{2.1 \times 10^{13}} = 4.7 \times 10^{-14}$$

NCERT Exercise

Exercise questions

Question 1

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

Solution

Ans: Werner's theory is the first theory to explain the nature of bonding in coordination compounds.

The main postulates of this theory are:

(i) Two types of valencies, primary and secondary valencies, are present in coordinated compound metals.

(ii) Negative ions are primary valencies, which are ionizable. The dotted line is depicted

(iii) The primary valence is equivalent to the metal ion oxidation number.

Secondary valencies are non-ionizing and neutral ions are both fulfilled. It is shown by a solid line.

(vi) The secondary valence refers to the metal ion coordination number.

(v) Those valencies project in the space allocated to a given geometry of the coordination compound in a specified direction.

Question 2

FeSO₄ solution mixed with (NH₄)₂SO₄ solution in 1:1 molar ratio gives the test of Fe²⁺ ion but CuSO₄ solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of Cu²⁺ ion. Explain why?

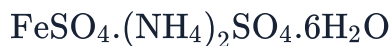
Solution

Ans: Let us see the reactions happening in both the cases.



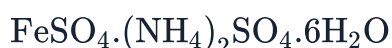


The compound

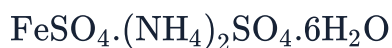


is Mohr's salt while $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ is Tetraamminocopper(II) sulphate.

Both



and $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ are classified as compounds, with one main distinction, i.e., the former is an example of a double salt, while the latter is a compound for co-ordination.



is a double salt and it contains the Fe^{2+} ions that are in ionizable form. Therefore, it will give the Fe^{2+} test.

$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ is a coordination compound and it contains the Cu^+ ion and it is not in an ionizable form. Therefore, it doesn't give the Cu^+ ion test.

Question 3

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

Solution

Ans: All of them are explained below:

(i) Coordination entity

A central metal atom or an ions connected to a set number of ions or molecules known as ligands comprises a coordination entity.

For example:

$[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Fe}(\text{CN})_6]^{4+}$ are cationic complex.

$[\text{PtCl}_4]^{2-}$, $[\text{Ag}(\text{CN})_2]^-$ are anionic complex.

$[\text{Ni}(\text{CO})_4]$, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$ are neutral complex.

(ii) Ligand

Ligands are regarded as the neutral molecules or negated ions which surround the metal atom in a coordinating entity. Ligands are generally polar and have a pair of valence electrons at least one unshared. For example, H_2O , CN^- , NH_3 , CO etc are some ligands.

(iii) Coordination number

A coordination number of central-metal atom is called the total number of ligands (whether neutral or negative ion) that are connected to the central-metal atom in the coordinating sphere. It is also known for its ligancy.

For example, $\text{K}_2[\text{PtCl}_6]$ contains platinum as the central metal ion and chloride ions as ligands. Since, there are 6 ligands, therefore the coordination number is 6.

(iv) Coordination polyhedron

The coordination polyhedrons on the core atom may be described as the spatial arrangement of the ligands directly associated in the coordinating field to the central metal ion.

For example, square planar is a coordination polyhedron.

(v) Homoleptic complex

These are the complexes where the metal ion is linked to just one type of donor group. For example, $[\text{PtCl}_6]^{2-}$ is a homoleptic complex.

(vi) Heteroleptic complex.

These are the complexes where the metal ion is linked to more than one type of donor group. For example, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ is a heteroleptic complex.

Question 4

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

Solution

Ans: These are explained below:

(i) Unidentate ligand

Ligands with only one donor sites are called unidentate ligands. For example, Cl^- and NH_3 are unidentate ligand.

(ii) Didentate ligand.

Ligands that have two donor sites are called didentate ligands. For example, ethane-1,2-diamine and oxalate ion. These are given below:

(iii) Ambidentate ligand

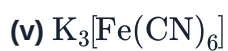
Ligands that can attach themselves to the central metal atom through two different atoms are called ambidentate ligands. For example, NO_2 group and SCN group.

NO_2 group can attack from the nitrogen atom and oxygen atom. SCN group can attack from nitrogen atom and sulfur atom.

Question 5

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





Solution

Ans: Let us assume that the coordination number of Co is x.

Therefore, we can write:

$$x + 0 + (-1) + 2(0) = +2$$

$$x - 1 = +2$$

$$x = +3$$

So, the coordination number of cobalt is +3.

Ans: Let us assume that the coordination number of Pt is x.

Therefore, we can write:

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

$$x = +2$$

So, the coordination number of platinum is +2

Ans: Let us assume that the coordination number of Cr is x.

Therefore, we can write:

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

$$x - 3 = 0$$

$$x = +3$$

So, the oxidation number of chromium is +3

Ans: Let us assume that the coordination number of Co is x.

Therefore, we can write:

$$x + 2(-1) + 0 = +1$$

$$x - 2 = +1$$

$$x = +3$$

So, the oxidation number of cobalt is +3

Ans: This can be written as $[\text{Fe}(\text{CN})_6]^{3-}$

Let us assume that the coordination number of Fe is x.

Therefore, we can write:

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

$$x - 6 = -3$$

$$x = +3$$

So, the oxidation number of iron is +3

Question 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)

Solution

Ans: The formula of Tetrahydroxozincate(II) is $[\text{Zn}(\text{OH})_4]^{2-}$

Ans: The formula of Potassium tetrachloridopalladate(II) is $\text{K}_2[\text{PdCl}_4]$

Ans: The formula of Diamminedichloridoplatinum(II) is $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

Ans: The formula of Potassium tetracyanonickelate(II) is $\text{K}_2[\text{Ni}(\text{CN})_4]$

Ans: The formula of Pentaamminenitrito-O-cobalt(III) is $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$

Ans: The formula of Hexaamminecobalt(III)sulphate is $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$

Ans: The formula of Potassium tri(oxalato)chromate(III) is $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$

Ans: The formula of Hexaammineplatinum(IV) is $[\text{Pt}(\text{NH}_3)_6]^{4+}$

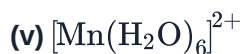
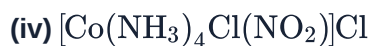
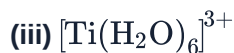
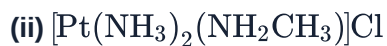
Ans: The formula of Tetrabromidocuprate(II) is $[\text{CuBr}_4]^{2-}$

Ans: The formula of Pentaamminenitrito-N-cobalt(III) is $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$

Question 7

Using IUPAC norms write the systematic names of the following:

(i) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$



Solution

Ans: The IUPAC name of the compound is Hexaamminecobalt(III) chloride.

Ans: The IUPAC name of the compound is Diamminechloride (methyl amine) platinum(II) chloride.

Ans: The IUPAC name of the compound is Hexaaquatitanium(III) ion.

Ans: The IUPAC name of the compound is Tetraamminechloridonitrito-N-cobalt(III) chloride.

Ans: The IUPAC name of the compound is Hexaaquamanganese(II) ion.

Ans: The IUPAC name of the compound is Tetrachloridenickelate(II) ion.

Ans: The IUPAC name of the compound is Hexaamminenickel(II) chloride.

Ans: The IUPAC name of the compound is Tris (ethane-1, 2-diamine) cobalt(III) ion.

Ans: The IUPAC name of the compound is Tetracarbonyl nickel(0).

Question 8

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

Solution

Ans: Let us see the types of isomerism. These are discussed below with examples.

Geometrical isomerism:

In heteroleptic complexes this isomerism is prevalent. The various geometric arrangements of the ligands are responsible for it. For example:

Optical isomerism:

The isomerism of this sort occurs in chiral compounds. Isomers represent each other's mirror reflections and are not superimposable. For example:

Linkage isomerism:

When the coordination sphere has ambidentate ligand, this isomerism occurs. For example, $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})](\text{NO}_3)_2$

Coordination isomerism:

This form of isomerism occurs when ligands of various metal ions in the complex are exchanged among cationic and anionic entities. For example, $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

Ionization isomerism:

The counter-ion replaces the ligand in the coordinating sphere, this is the kind of isomerism. Thus, ionisation isomers are termed complexes which have the same composition but which provide distinct

ions when dissolved in water. For example,

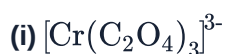


Solvate isomerism:

Solvent isomers differ in that the solvent molecule is directly connected to the metal ion or is simply in the crystal grid as a free solvent molecule. For example, $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}](\text{H}_2\text{O})\text{Cl}_2$

Question 9

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



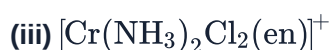
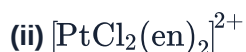
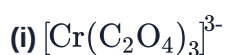
Solution

Ans: For this complex no geometrical isomerism is possible there is only one type of ligand and it is a bidentate ligand.

Ans: For this compound there are two geometrical isomers possible, i.e., Facial-form and Meridional form. These are given below:

Question 10

Draw the structures of optical isomers of:

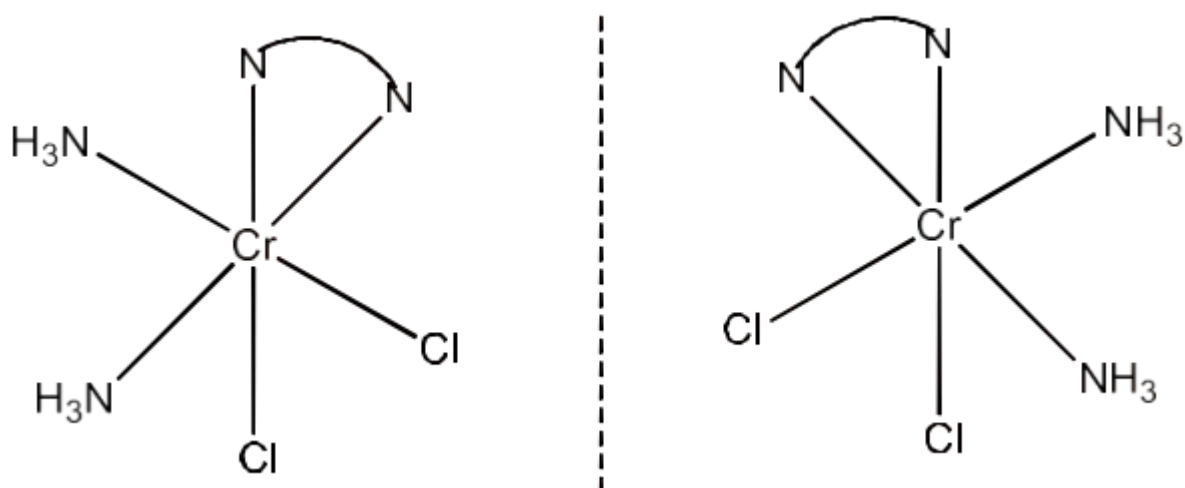


Solution

Ans: The structure is given below:

Ans: The structure is given below:

Ans: The structures are given below:

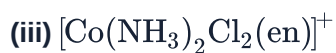
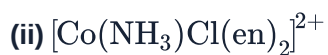
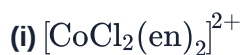


This is of the cis-form

This is of the trans-form

Question 11

Draw all the isomers (geometrical and optical) of:



Solution

Ans: The structures of optical isomers are given below:

In total, three isomers are possible.

Ans: The structures of isomers are given below:

Trans-isomer is optically inactive

Ans: The structures of all the isomers are given below:

Question 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

Ans: There are three isomers possible:

No one will display optical isomers from the given isomers. Optical isomerization of tetrahedral compounds is uncommon. You only accomplish this in the presence of unsymmetric chelating substances.

Question 13

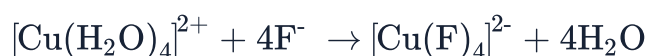
Aqueous copper sulphate solution (blue in colour) gives:

Solution

Ans: Aqueous CuSO_4 solution exists as $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4$ which has blue color due to $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ions.

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

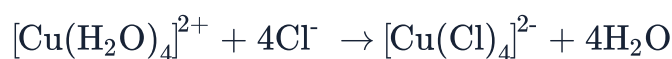
When KF is added, the weak H_2O ligand is replaced by F^- ligands forming $[\text{CuF}_4]^{2-}$ ions which is a green precipitate. The reaction is given below:



(ii) a bright green solution with aqueous potassium chloride

Explain these experimental results.

When KCl is added, Cl^- ligand replace the weak H_2O ligands forming $[\text{CuCl}_4]^{2-}$ ion which has bright green color. The reaction is given below:



Question 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

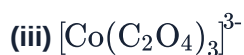
Ans: The reactions are given below:



Thus, the process-formed coordination entity is $\text{K}_2[\text{Cu}(\text{CN})_4]$, which is highly stable, which does not ionise to add Cu^{2+} ions to water. Therefore when the H_2S (g) passes through the solution, Cu^{2+} ions are not precipitated.

Question 15

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



Solution

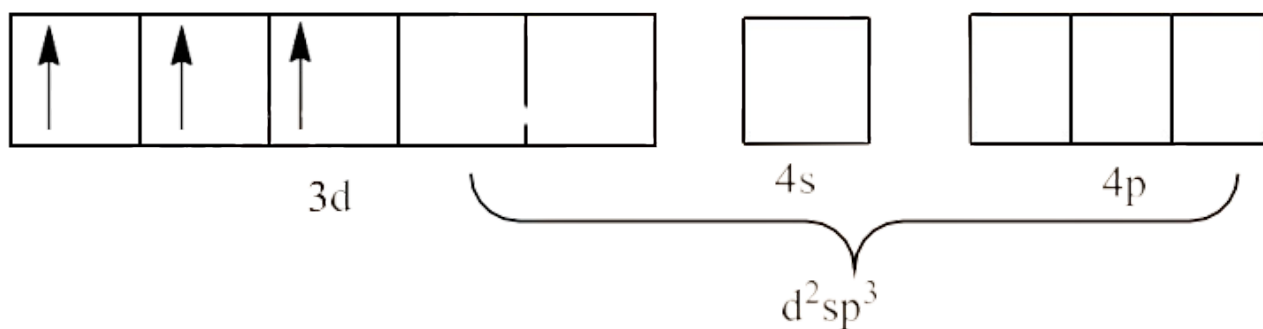
Ans: In $[\text{Fe}(\text{CN})_6]^{4-}$ the oxidation state of Fe is in +2 oxidation state, which will cause the configuration of Fe as d^6 .

Since CN^- is a strong field ligand, it causes unpaired electrons to be paired. This will lead to d^2sp^3 hybridization. This is shown below:

Therefore, the geometry of the complex is octahedral and it is a diamagnetic complex.

Ans: In $[\text{Fe}(\text{F})_6]^{3-}$ the oxidation state of Fe is in +3 oxidation state, which will cause the configuration of Fe as d^5 .

Since F^- is a weak field ligand, it does not cause pairing of electrons. This will lead to sp^3d^2 hybridization. This is shown below:



The geometry of the complex is octahedral and it is paramagnetic.

Ans: In $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ the oxidation state of Co is in +3 oxidation state, which will cause the configuration of Co as d^6 .

Since oxalate is a strong field ligand, it causes unpaired electrons to be paired. This will lead to d^2sp^3 hybridization. This is shown below:

Therefore, the geometry of the complex is octahedral and it is a diamagnetic complex.

Ans: In $[\text{CoF}_6]^{3-}$ the oxidation state of Co is in +3 oxidation state, which will cause the configuration of Co as d^6 .

Since F^- is a weak field ligand, it does not cause pairing of electrons. This will lead to sp^3d^2 hybridization.

The geometry of the complex is octahedral and it is paramagnetic.

Question 16

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

Solution

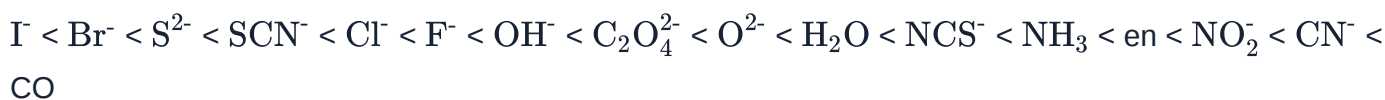
Ans: We know that there are five subshells of d-orbital, i.e., d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$ and d_{z^2} . When the energy is provided, the splitting occurs in such a way that $d_{x^2-y^2}$ and d_{z^2} experience the rise in energy so, they form e_g level, while d_{xy} , d_{yz} and d_{zx} experience the low energy level so, they form t_{2g} level. This is shown below:

Question 17

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

Solution

Ans: A spectrochemical set of ligands is the organisation of their crystal field splitting energy (CFSE) values in the ascending order. The ligands on the R.H.S are strong ligands of fields whereas L.H.S is weak ligands of field. In d-orbitals, strong field ligands are more divided than weak field ligands. The series is given below:



Question 18

What is crystal field splitting energy? How does the magnitude of Δ_0 decide the actual configuration of d orbitals in a coordination entity?

Solution

Ans: D-orbitals degenerate into two levels (e_g and t_{2g}) in the presence of ligands in the spherical field surroundings. The separation of degenerated levels by the presence of ligands is called the splitting of the crystal field, and the energy difference between two levels (e_g and t_{2g}) is called the splitting energy of the crystal field. The name is Δ_0 .

The electrons are filled once the orbitals have divided. The filling of the fourth electron is done in two different methods after 1 electron (each) has been filled in 3 t_{2g} orbitals.

The electron can be either in the e_g orbital (giving birth to t_{2g}^3, e_g^1 similar electrical configuration) or in the t_{2g} orbital (giving rise to t_{2g}^4, e_g^0 like electronic configuration). The electrons enter the e_g orbital when the Δ_0 value of the ligand is lower than pairing energy (p).

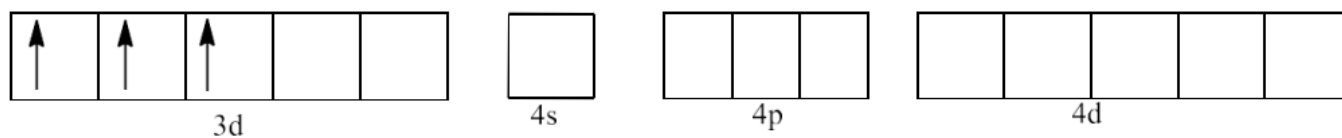
On the other hand, if a ligand's Δ_0 value exceeds the pairing energy (P), the electrons then enter t_{2g} orbital.

Question 19

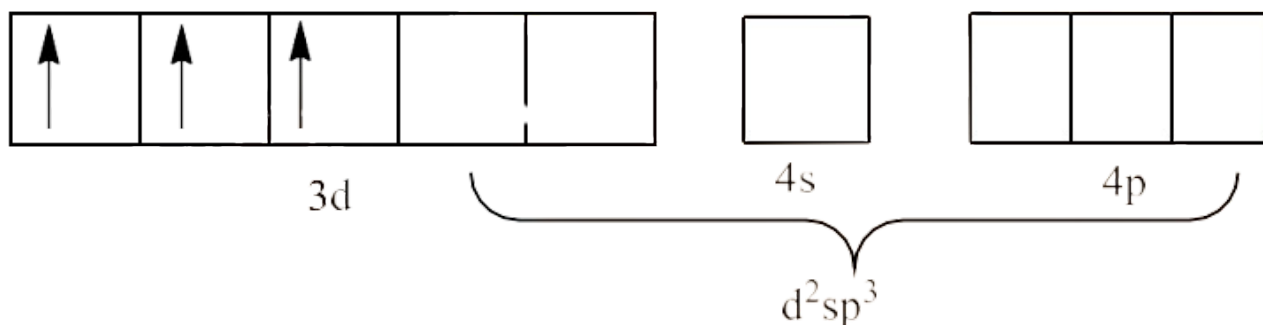
$[\text{Cr}(\text{NH}_3)_6]^{3+}$ is paramagnetic while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic. Explain why?

Solution

Ans: In $[\text{Cr}(\text{NH}_3)_6]^{3+}$ the oxidation state of Cr is in +3 oxidation state, which will cause the configuration of Cr as d^3 .

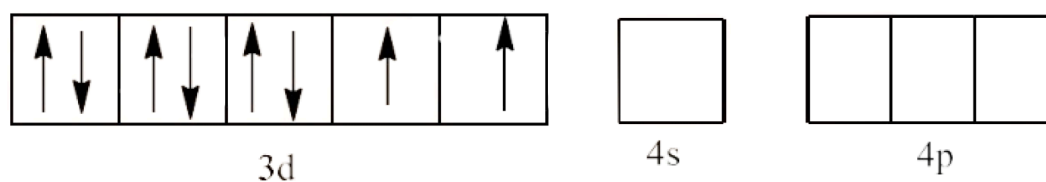


Since NH_3 is a weak field ligand, it does not cause pairing of electrons. This will lead to d^2sp^3 hybridization.



The geometry of the complex is octahedral and it is paramagnetic.

In $[\text{Ni}(\text{CN})_4]^{2-}$ the oxidation state of Ni is in +2 oxidation state, which will cause the configuration of Ni as d^8 .



Since CN^- is a strong field ligand, it causes unpaired electrons to be paired. This will lead to dsp^2 hybridization. This is shown below:

Therefore, the geometry of the structure is square planar and it is diamagnetic.

Question 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 colorless. Explain.

Solution

Ans: $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, the field ligand H_2O is weak. Unpaired electrons are therefore available in Ni^{2+} . In this complex d electrons can be stimulated to the higher energy level from the lower energy level, i.e. there is a potential to change d to d-orbital. Therefore, it has color. The $[\text{Ni}(\text{CN})_4]^{2-}$ have a strong ligand in the form of CN^- . As a result, the transition to d-d in $[\text{Ni}(\text{CN})_4]^{2-}$ is not feasible. It's colorless, therefore.

Question 21

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

Solution

Ans: The color of a certain coordinating chemical relies on the amount of the energy dividing the crystal field, Δ_0 . In turn, this CFSE depends on the ligand nature. The colors of $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ vary because the CFSE is different. Now, CN^- is a powerful field ligand with greater CFSE than the CFSE water value. This means that intra-d-d transition absorption of energy also differs. The color also differs, however.

Question 22

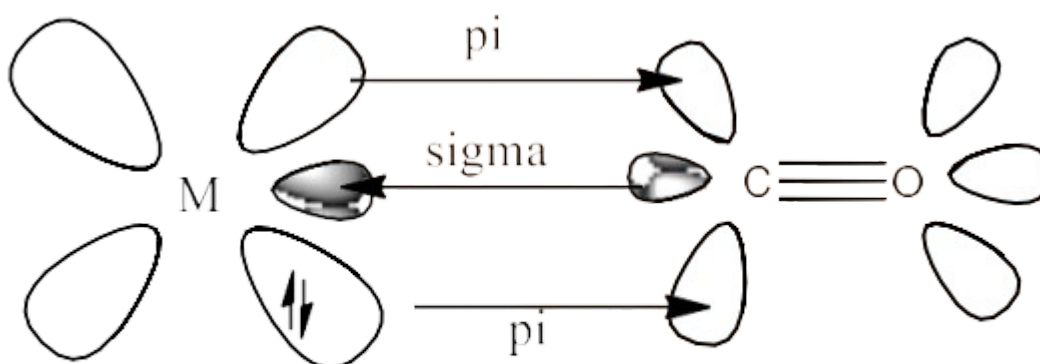
Discuss the nature of bonding in metal carbonyls.

Solution

Ans: The carbon metal linkages in metal carbonyls are characterized by both s and p. $\text{M}-\text{C}\sigma$ bond consists of a donation into an empty metal orbital of a lone pair of electrons on the carbonyl carbon.

$\text{M}-\text{C}\pi$ bond is the donation to the empty carbon dioxide vacant anti-bonding π^* orbital of a pair of electrons from the d-filled metal orbital. The reverse bonding of the carbonyl group is also known. The

ligand-metal interaction provides a synergistic effect that enhances the relationship between CO and metal. The synergistic action reinforces the connection between CO and metal. The diagram is given below:



synergic bonding in metal carbonyls

Question 23

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

- (i) $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$
- (ii) $(\text{NH}_4)_2[\text{CoF}_4]$
- (iii) $\text{cis-}[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$
- (iv) $[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$

Solution

Ans: The complex will be $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$.

Oxidation state of cobalt will be $= x - 6 = -3$

The oxidation state is $= +3$

Coordination number $= 6$

In $+3$ oxidation state of Co the configuration is $3d^6$.

So, the configuration will be $t_{2g}^6 e_g^0$

Ans: The complex will be $[\text{CoF}_4]^{2-}$.

Oxidation state of cobalt will be $= x - 4 = -2$

The oxidation state is $= +2$

Coordination number $= 4$

In $+2$ oxidation state of Co the configuration is $3d^7$.

So, the configuration will be

Ans: The complex will be $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$.

Oxidation state of chromium will be $= x + 0 - 2 = +1$

The oxidation state is $= +3$

Coordination number $= 6$

In $+3$ oxidation state of Cr the configuration is $3d^3$.

So, the configuration will be t_{2g}^3

Ans: The complex will be $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$.

Oxidation state of manganese will be $= x + 0 = +2$

The oxidation state is $= +2$

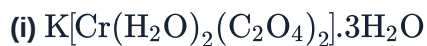
Coordination number $= 6$

In $+2$ oxidation state of Mn the configuration is $3d^5$.

So, the configuration will be $t_{2g}^3 e_g^2$

Question 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**

Ans: Its IUPAC name is Potassium diaquadioxalatochromate(III) hydrate.

Oxidation state of chromium = +3

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

Coordination number = 6

Shape = octahedral

Stereochemistry:

Number of unpaired electrons = 3

Magnetic moment =

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

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

$$\mu = \sqrt{15}$$

$$\mu=3.87 \text{ BM}$$

Ans: Its IUPAC name is Trichloridotripyridinechromium(III).

Oxidation state of chromium = +3

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

Coordination number = 6

Shape = octahedral

Stereochemistry:

Number of unpaired electrons = 3

Magnetic moment =

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

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

$$\mu = \sqrt{15}$$

$$\mu=3.87 \text{ BM}$$

Ans: Its IUPAC name is Potassium hexacyanomanganate(II).

Oxidation state of manganese = +2

Electronic configuration = $3d^5 = t_{2g}^5$

Coordination number = 6

Shape = octahedral

Stereochemistry: optically inactive

Number of unpaired electrons = 1

Magnetic moment =

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

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

$$\mu = \sqrt{3}$$

$$\mu = 1.73 \text{ BM}$$

Ans: Its IUPAC name is Pentaamminechloridecobalt(III) chloride.

Oxidation state of manganese = +3

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

Coordination number = 6

Shape = octahedral

Stereochemistry:

Number of unpaired electrons = 0

Magnetic moment = 0

Ans: Its IUPAC name is Caesium tetrachloridoferrate(II).

Oxidation state of manganese = +3

Electronic configuration = $3d^5 = e^2 t_2^3$

Coordination number = 4

Shape = tetrahedral

Stereochemistry: optically inactive

Number of unpaired electrons = 5

Magnetic moment =

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

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

$$\mu = \sqrt{35}$$

$$\mu = 5.92 \text{ BM}$$

Question 25

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

Solution

Ans: The stability of the complex in a solution relates to the extent to which the two species are in balance. In terms of stability or formation constant, stability may be expressed numerically.



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

The higher the stability constant value, the more the percentage of ML_3 in the solution is for this reaction.

Stability can be of two types:

Thermodynamic stability:

Thermodynamic stability determines to what extent the compound at the point of balance is produced or converted into another species.

Kinetic stability:

This helps to determine how quickly the change is to achieve the condition of balance.

Factors that affect the stability of a complex are:

Charge on the central metal ion: The greater the charge on the central metal ion, the greater is the stability of the complex.

Basic nature of the ligand: A more basic ligand will form a more stable complex.

Presence of chelate rings: Chelation increases the stability of complexes.

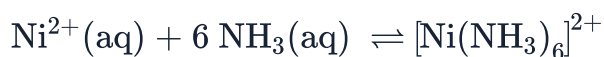
Question 26

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

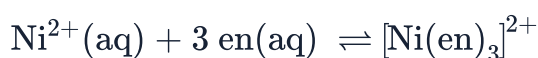
Solution

Ans: When a ligand binds to the metal ion in a way that creates a ring, the interaction of a metal ligand is more stable. In other terms, we may argue that chelate ring complexes are more stable than ring-free complexes. This is known as the Chelate effect.

For example,



For this reaction, $\log \beta = 8.61$



For this reaction, $\log \beta = 18.28$

Question 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

Ans: The presence of the chlorophyll pigment enables photosynthesis. The pigment is a magnesium co-ordinating molecule. Multiple coordinated chemicals perform essential functions in the human biological system. An iron coordination complex is, for example, the oxygen transporter of blood i.e. haemoglobin.

The cobalt coordination compound is vitamin B12, cyanocobalamin. The anaemia anti-pernicious factor. Enzymes such as carboxypeptidase A and carbon dioxide are among other biologically important molecules containing co-ordinated metal ions.

Ans: Certain platinum coordinating chemicals (e.g., cis-platinum) suppress tumour development.

Chelating ligands D-penicillamine, and desferrioxime B by forming coordination compounds, eliminate the excess of metal ions existing in a hazardous proportion in plant and animal systems such as copper or iron. EDTA is used in lead poisoning therapy.

Ans: A number of basic radicals are identified in the salt analysis using the colour changes with different reagents. These colour shift is due to the coordination of molecules or complexes formed with various ligands by the basic radicals.

For example: EDTA, DMG, etc.

Ans: The extraction process includes the production of complexes of many metals from their ores. In an aqueous solution, for instance, gold mixes to create $\text{Au}(\text{CN})_2$ with cyanide ions. Gold is then

recovered from this solution by adding zinc.

Question 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

Ans: (iii) 3

The coordination number of cobalt is 6, therefore, the complex will be $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$. When this ionizes, three ions are formed. The reaction is given below:



Question 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

Ans: The number of unpaired electrons in this compound is 3.

Magnetic moment =

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

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

$$\mu = \sqrt{15}$$

$$\mu = 3.87 \text{ BM}$$

Ans: The number of unpaired electrons in this compound is 4.

Magnetic moment =

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

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

$$\mu = \sqrt{24}$$

$$\mu = 4.89 \text{ BM}$$

Ans: The number of unpaired electrons in this compound is 0

Magnetic moment = 0

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

Question 30

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

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

Solution

Ans: The complex will be $[\text{Co}(\text{CO})_4]^-$

The oxidation state of Cobalt will be $= x + 0 = -1$

The oxidation number of Co = -1

Therefore, the answer is an option (iii) -1.

Question 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

Ans: In the compounds, Fe is the central metal ion and its oxidation state +3. As $\text{C}_2\text{O}_4^{2-}$ is a didentate chelating ligand, it can form chelating ring and hence is the most stable complex.

Therefore, the answer is an option (iii).

Question 32

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



Solution

Ans: In all three complexes, the core metal ion is identical. The absorption depends thus on the ligands in the visible area. In the spectrochemical series, the sequence in which the CFSE values of the ligands are increasing is: $\text{H}_2\text{O} < \text{NH}_3 < \text{NO}_2$.

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

$$\Delta_0(\text{H}_2\text{O}) < \Delta_0(\text{NH}_3) < \Delta_0(\text{NO}_2^-)$$

So, the wavelength of absorption in the visible region will be in the order: $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} > [\text{Ni}(\text{NH}_3)_6]^{2+} > [\text{Ni}(\text{NO}_2)_6]^{2+}$.