
Chapter – 9 (Coordination Compounds)

Exercise questions:

Question: 1 Explain the bonding in coordination compounds in terms of Werner's postulates.

Answer:

Following are the postulates of Werner's theory:

- i.) In coordination compound metals shows two types of linkages – primary and secondary.
- ii.) The primary valences are normally ionisable and are satisfied by negative ions.
- iii.) The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valences is equal to the coordination no. and is fixed for a metal.
- iv.) The ions/groups bound by the secondary linkages to the metal have characteristics spatial arrangements corresponding to different coordination numbers.

Question: 2 FeSO_4 solution mixed with $(\text{NH}_4)_2\text{SO}_4$ solution in 1 : 1 molar ratio gives the test of Fe^{2+} ion but CuSO_4 solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

Answer:

FeSO_4 does not form any complex with $(\text{NH}_4)_2\text{SO}_4$. Instead, they form a double salt,

$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (Mohr salt) which dissociates completely in ion in the solution. Hence, it gives the test of Fe^{2+} ions. CuSO_4 solution mixed with aqueous ammonia in 1 : 4 molar ratio forms the complex with the formula $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ in which the complex ion, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ does not dissociate to give Cu^{2+} ions. Hence, it does not give the tests of Cu^{2+} ion.

Question: 3 Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

Answer:

- 1.) Coordination entity: Coordination entity constitutes a central metal atom or ion bounded to a fixed no. of ions or molecules.
For example, $[\text{CoCl}_3(\text{NH}_3)_3]$, $[\text{Ni}(\text{CO})_4]$.

- 2.) Ligand: The ions or molecules bound to the central atom/ion in the coordination entity are called ligands.
For example, H_2O , NH_3 .
- 3.) Coordination number: The coordination number of a metal ion in complex can be defined as the no. of ligand donor atom to which the metal is directly bonded.
For example, In PtCl_6^{2-} , the coordination no. of Pt is 6. In $[\text{Ni}(\text{NH}_3)_4]^{2+}$, the coordination no. of Ni is 4.
- 4.) Coordination polyhedron: The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom.
For example, $[\text{PtCl}_4]^{2-}$ is square planar, $[\text{Ni}(\text{CO})_4]$ is tetrahedral.
- 5.) Homoleptic complexes: Complexes in which a metal is bound to only one kind of donor group are known as homoleptic complexes.
For example, $[\text{Co}(\text{NH}_3)_6]^{3+}$
- 6.) Heteroleptic complexes: Complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic complexes.
For example, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.

Question: 4 What is meant by unidentate, didentate and ambidentate ligands? Give two examples of each.

Answer:

- 1.) Unidentate ligands: When a ligand is bound to a metal ion through a single donor atom, the ligand is known as unidentate ligand.
For example, Cl^- , H_2O .
- 2.) Didentate ligand: When a ligand can be bind through two donor atoms, the ligand is said to be didentate ligand.
For example, (ethane-1,2-diamine), (oxalate).
- 3.) Ambidentate ligand: Ligand which can ligate through two different atoms is called ambidentate ligand.
For example, NO_2^- , SCN^- .

Question: 5 Specify the oxidation numbers of the metals in the following coordination entities:

- i.) $[\text{Co}(\text{H}_2\text{O})(\text{CN})(\text{en})_2]^{2+}$

- ii.) $[\text{CoBr}_2(\text{en})_2]^+$
 iii.) $[\text{PtCl}_4]^{2-}$
 iv.) $\text{K}_3[\text{Fe}(\text{CN})_6]$
 v.) $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$

Answer:

Let x be the oxidation no. of metal in the following compounds;

- i.) $X + 0 + (-1) + 2(0) = +2$
 $X - 1 = 2$
 $X = 1$
- ii.) $X + 2(-1) + 2(0) = +1$
 $X - 2 = 1$
 $X = 3$
- iii.) $X + 4(-1) = -2$
 $X - 4 = -2$
 $X = +2$
- iv.) $3(+1) + x + 6(-1) = 0$
 $3 + x + (-6) = 0$
 $X = 3$
- v.) $X + 3(0) + 3(-1) = 0$
 $X + (-3) = 0$
 $X = 3$

Question:6 Using IUPAC norms write the formula of following:

- i.) **Tetrahydroxozincate(II)**
 ii.) **Potassium tetrachloridopalladate(II)**
 iii.) **Pottasium tetracyanickelate(II)**
 iv.) **Diamminedichloridoplatinum(II)**
 v.) **PENTAamminenitrito- O- cobalt(III)**
 vi.) **Hexaamminecobalt(III) sulphate**
 vii.) **Potassium tri(oxalate)chromate(III)**
 viii.) **Hexaammineplatinum(IV)**
 ix.) **Tetrabromidocuprate(II)**
 x.) **Pentaamminenitrito-N-cobalt(III)**

Answer;

- i.) $[\text{Zn}(\text{OH})_4]^{2-}$
 ii.) $\text{K}_2[\text{PdCl}_4]$
 iii.) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

- 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:7 Using IUPAC norms write the systematic names of the following:

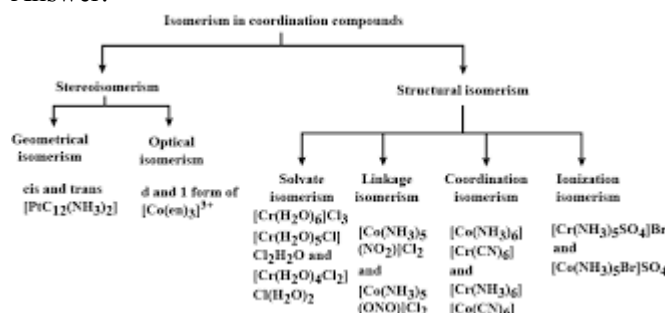
- i.) $[Co(NH_3)_6]Cl_3$
- ii.) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$
- iii.) $[Ti(H_2O)_6]^{3+}$
- iv.) $[Co(NH_3)_4Cl(NO_2)]Cl$
- v.) $[Mn(H_2O)_6]^{2+}$
- vi.) $[NiCl_4]^{2-}$
- vii.) $[Ni(NH_3)_6]Cl_2$
- viii.) $[Co(en)_3]^{3+}$
- ix.) $[Ni(CO)_4]$

Answer:

- (i) Hexaamminecobalt(III) chloride
- (ii) Diamminechlorido(methylamine) platinum(II) chloride
- (ii) Hexaqua titanium(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:8 List various types of isomerism possible for coordination compound, give an example of each.

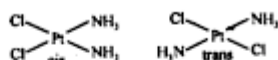
Answer:



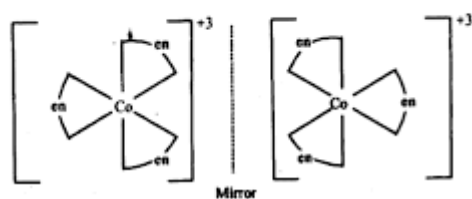
(a.) Geometrical isomerism: This type of isomerism is common in heteroleptic complex. It arises due to the different possible geometric arrangements of the ligands.

(b.) Optical isomerism: This type of isomerism arises in the chiral molecules. Isomers are mirror images of each other and are not superimposable.

(i) Geometrical isomerism



(ii) Optical isomerism.

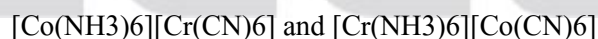


(c.) Linkage isomerism: This type of isomerism is found in complexes that contain ambidentate ligands.



Yellow to red form

(d.) Coordination isomerism: This type of isomerism arises when the ligands are interchanged between cationic and anionic entities of different metal ions present in the complex.



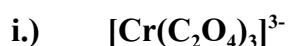
(e.) Ionisation isomerism: This type of isomerism arises when a counter ion replaces a ligand within the coordination sphere. Thus, complexes have the same composition, but furnish different ions when dissolved in water are called ionisation isomers.

For example: $[Co(NH_3)_5SO_4]Br$ 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 free solvent molecule in the crystal lattice.

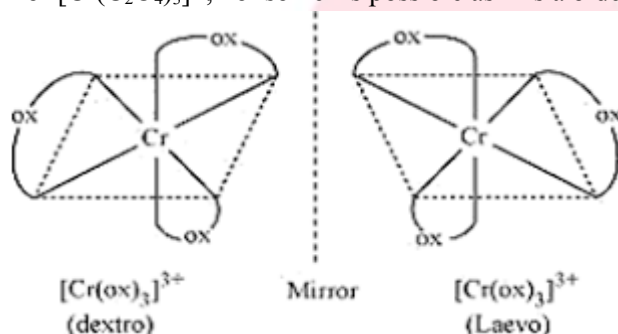
Eg. Violet blue green to dark green

Question:9 How many geometrical isomers are possible in the following coordination entities?

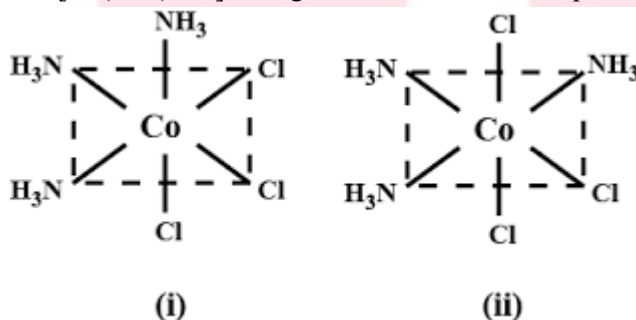


Answer:

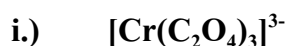
i.) For $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$, no isomer is possible as it is a bidentate ligand.



ii.) For $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$, two geometrical isomers are possible.

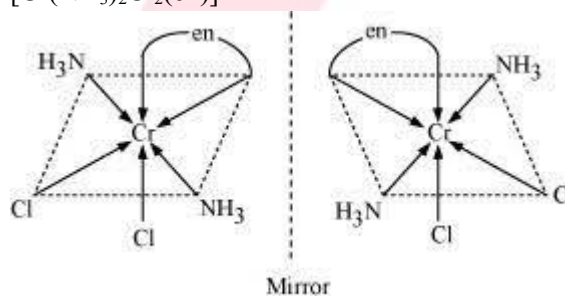
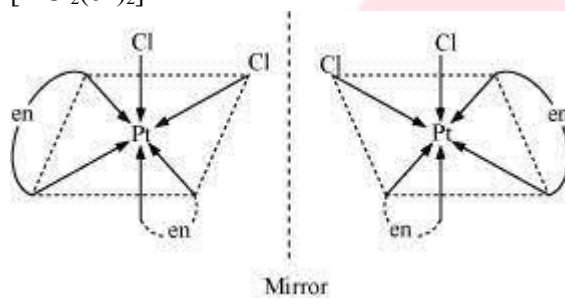
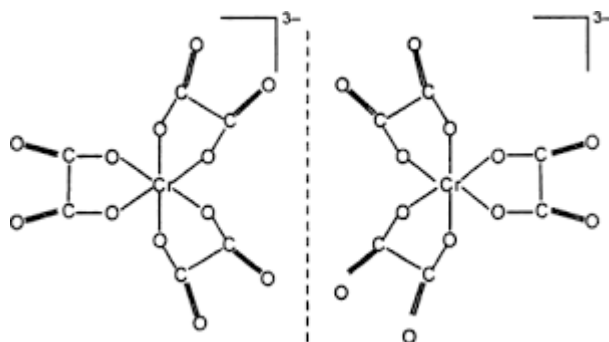


Question:10 Draw the structures of optical isomers of :



Answer:



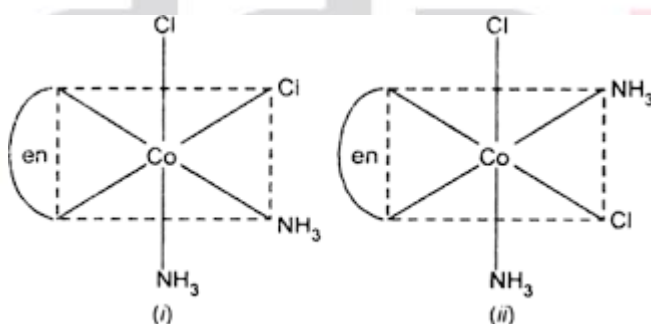
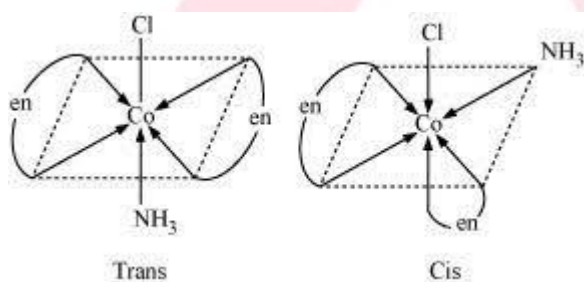
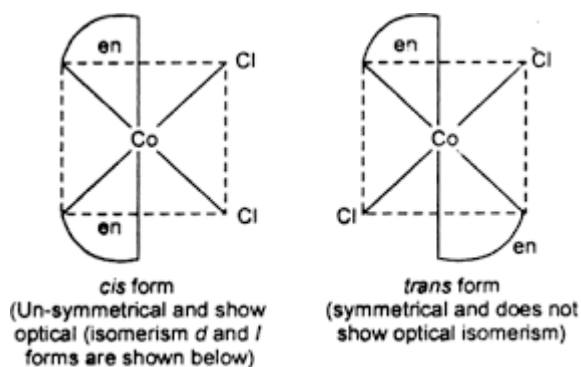


Question:11 Draw all the isomers (geometrical and optical) of:



Answer:

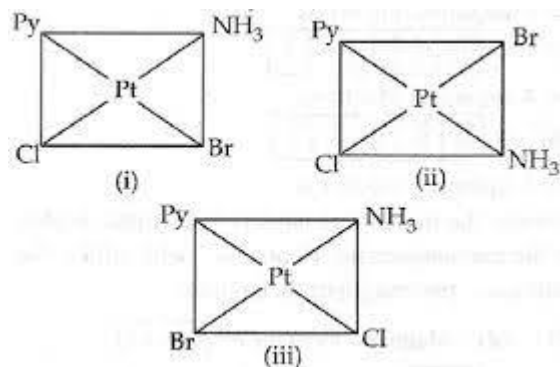




Question:12 Write all the geometrical isomers of $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{py})]$ and how many of these will exhibit optical isomers?

Answer:

All the geometrical isomers of $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{py})]$ are:



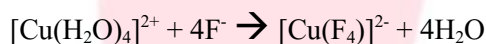
Question:13 Aqueous copper sulphate solution (blue in colour) gives:

- i.) A green precipitate with aqueous potassium fluoride
- ii.) A bright green solution with aqueous potassium chloride. Explain these experimental results.

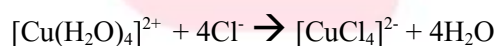
Answer:

Aqueous CuSO_4 exist as $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4$. It is blue in colour due to the presence of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ions.

- i.) When KF is added



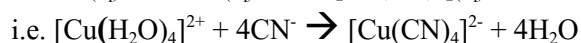
- ii.) When KCl is added



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

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?

Answer:



Thus the coordination entity formed in the process is $\text{K}_2[\text{Cu}(\text{CN})_4]$. $[\text{Cu}(\text{CN})_4]^{2-}$ is a very stable complex which does not ionise to give Cu^{2+} ions when added to water. Hence, Cu^{2+} ions are not precipitated when $\text{H}_2\text{S}(\text{g})$ is passed through the solution.

Question:15 Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory;

- i.) $[\text{Fe}(\text{CN})_6]^{4-}$
- ii.) $[\text{FeF}_6]^{3-}$
- iii.) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$
- iv.) $[\text{CoF}_6]^{3-}$

Answer:

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

Co(III) with $3d^6$ outer electronic configuration is d^2sp^3 hybridised. A diamagnetic octahedral complex is formed. It is inner orbital, low spin or spin paired complex.

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

Fe(III) with $3d^5$ outer electronic configuration is sp^3d^2 hybridised. A paramagnetic octahedral complex is formed. It is outer orbital, high spin or spin free complex.

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

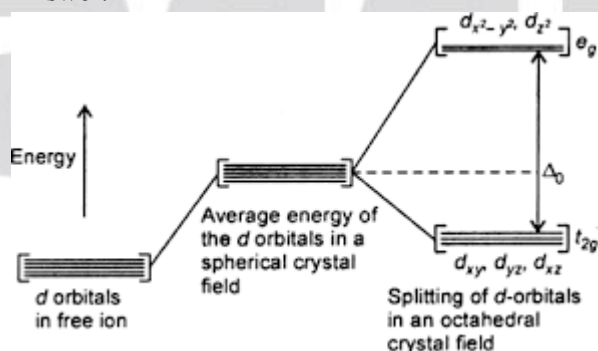
Co(III) with $3d^6$ outer electronic configuration is d^2sp^3 hybridised. A diamagnetic octahedral complex is formed. It is inner orbital, low spin or spin paired complex.

- iv.) $[\text{CoF}_6]^{3-}$

Co(III) with $3d^6$ outer electronic configuration is sp^3d^2 hybridised. A paramagnetic octahedral complex is formed. It is outer orbital, high spin or spin free complex.

Question:16 Draw figure to show the splitting of d orbitals in an octahedral crystal field.

Answer:

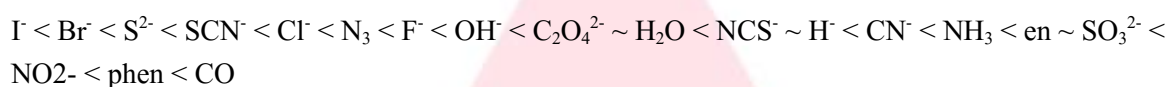


The splitting of d – orbitals in an octahedral field takes place in such a way that $d_{x^2-y^2}$, d_{z^2} experience a rise in energy and form the e_g level, while d_{xy} , d_{yz} and d_{zx} experience a fall in energy and form the t_{2g} level.

Question:17 What is spectrochemical series? Explain the difference b/w 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.



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?

Answer:

The crystal field stabilization energy is the gain in the energy achieved by preferential filling up of orbitals by electrons. It is usually less than or equal to zero. When it is equal to zero, the complex is unstable. The magnitude of CFSE depends on the no. and nature of ligands and the geometry of the complex.

Consider octahedral d^4 system. Three electrons are in lower t_{2g} level. 4th electron will enter into higher e_g level if $\Delta_0 < P$. 4th electron will enter into lower t_{2g} level if $\Delta_0 > P$. Here P is the pairing energy. It is the energy required to pair two electrons against electron repulsion in the same orbital.

Question:19 $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is paramagnetic why $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic. Explain why?

Answer:

Also, NH_3 is a weak field ligand that does not cause the pairing of the electrons in the 3d orbital. Therefore, it undergoes d^2sp^3 hybridization and the electrons in the 3d orbitals remain unpaired. Hence, it is paramagnetic in nature. As there are no unpaired electrons, 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 colourless. Explain.

In $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, Ni is in +2 state with the configuration $3d^8$, i.e., it has two unpaired electrons which do not pair up in the presence of the weak H_2O ligand. Thus, there is no unpaired electron present. Hence, it is colourless.

Question:21 $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ are of different colours in dilute solutions. Why?

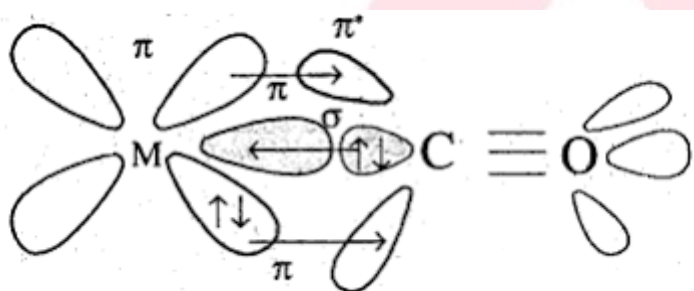
Answer:

In presence of the weak H_2O ligand, they don't pair up. In presence of strong ligand, they pair up leaving no unpaired electron. Because of the difference in the number of unpaired electrons, they have different colours.

Question: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. Thus, a synergic effect is created due to this metal-ligand bonding.



Question:23 Give the oxidation state, d orbital occupation and coordination no. 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.) $[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$

Answer:

- i.) $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$

The central metal ion is Co

Its coordination no. is 6

The oxidation state of Co is

$$X - 6 = -3 \times 3 = +3$$

The d orbital occupation for Co^{3+} is $t_{2g}^6 e_g^0$

- ii.) $(\text{NH}_4)_2[\text{CoF}_4]$
 The central metal ion is Co
 The coordination no. is 4
 The oxidation state of Co is
 $X - 4 = -2$
 $X = +2$
 The d orbital occupation for Co^{2+} is $e_g^4 t_{2g}^3$
- iii.) $\text{cis}[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$
 the central metal ion is Cr
 its coordination no. is 6
 The oxidation state of Cr
 $X + 2(0) + 2(-1) = 1$
 $X = +3$
 The d orbital occupation for Cr^{3+} is t_{2g}^3
- iv.) $[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$
 The central metal ion is Mn
 Its coordination no is 6
 The oxidation state of Mn
 $X + 2 = 0$
 $X = 2$
 The d orbital occupation for Mn^{2+} is $t_{2g}^3 e_g^2$

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:

- i.) $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$
 ii.) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 iii.) $\text{CrCl}_3(\text{py})_3$
 iv.) $\text{Cs}[\text{FeCl}_4]$
 v.) $\text{K}_4[\text{Mn}(\text{CN})_6]$

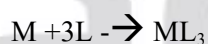
Answer:

Compound	IUPAC name	Oxidation state	Electronic configuration	Coordination number	Stereochemistry	Magnetic moment
$K[Cr(H_2O)_2(C_2O_4)_2] \cdot 3H_2O$	Potassium diaquabisoxalatochromate (III) trihydrate	+3	$[Ar]3d^3$	6	Cis and trans	3.87
$[Co(NH_3)_5Cl]Cl_2$	Pentamminechlorocobaltate(II) chloride	+3	$[Ar]3d^6$	6	No stereoisomerism	4.90
$CrCl_3(py)_3$	Trichlorotripyridine chromate(III)	+3	$[Ar]3d^3$	6	Fac. And mar. isomers	3.87
$Cs[FeCl_4]$	Cesium tetrachloroferrate(III)	+3	$[Ar]3d^5$	4	No	5.92
$K_4[Mn(CN)_6]$	Potassium hexacyanomanganate(II)	+2	$[Ar]3d^5$	6	no	5.92

Question: 25 What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

Answer:

The stability of coordination compounds in solution means the degree of association between the metal ion and the ligands involved in the state of equilibrium. Quantitatively, the stability is expressed by the equilibrium constant for the association.



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

For this reaction., the greater the value of the stability constant, the greater is the proportion of ML_3 in the solution.

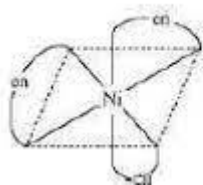
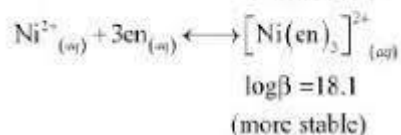
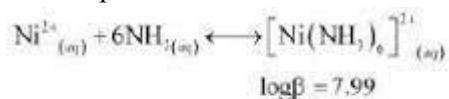
Question: 26 What is meant by the chelate effect? Give an example.

Answer:

The stability of coordination compound due to chelation is called the chelate effect. Or

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:



Question: 27 Discuss briefly giving an example in each case the role of coordination compounds in:

- i.) biological systems
- ii.) medicinal chemistry
- iii.) analytical chemistry
- iv.) extraction / metallurgy of metals.

Answer:

(i) Biological systems

Several naturally occurring biologically important compounds are coordination compounds.

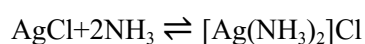
Thus, chlorophyll is a coordination compound containing Mg(II) ions. It is green pigment present in plants and is used in photosynthesis.

(ii) Medicinal chemistry

To remove metal poisoning, complexing agents are used, cis platin $[\text{PtCl}_2(\text{NH}_3)_2]$ is used in cancer chemotherapy.

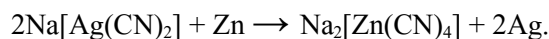
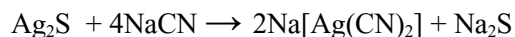
(iii) Analytical chemistry

Complex formation is used in qualitative scheme of analysis. In group I analysis, silver ion is separated from the precipitate of AgCl , Hg_2Cl_2 and PbCl_2 . Aqueous ammonia is added to the ppt. AgCl dissolves due to formation of soluble complex.



(iv) Extraction/metallurgy of metals

Metals such as gold and silver are extracted by complex formation technique. Cyanide process is used for extraction of silver and gold from its ore.



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

Answer:

- iii.) 3

The given complex can be written as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$

Thus, $\text{Co}(\text{NH}_3)_6^{2+}$ along with two Cl^- ions is produced.

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.) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$

Answer:

- i.) The no. of unpaired electrons = 3

Magnetic moment = 4BM

- ii.) The no. of unpaired electrons = 4

Magnetic moment = 5BM

- iii.) No unpaired electrons.

Hence $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, 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

Answer:

The oxidation no. of cobalt is,

$$+1 + x + 4(0) = 0$$

$$X = -1$$

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.) $[\text{FeCl}_6]^{3+}$

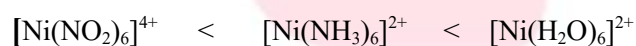
Answer:

We know that the stability of complex is increased by chelation. Hence, the most stable complex is $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3+}$

Question: 32 What will be the correct order for the wavelengths of absorption in the visible region for the following:



Answer:



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