9

Coordination Compounds

Multiple Choice Questions (MCQs)

Q. 1 Which of the following complexes formed by Cu^{2+} ions is most stable?

(a) $Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}, \quad \log K = 11.6$

(b) $Cu^{2+} + 4CN^- \longrightarrow [Cu(CN)_4]^{2-}, \quad \log K = 27.3$

(c) $Cu^{2+} + 2en^- \longrightarrow [Cu(en)_2]^{2+}, \quad \log K = 15.4$

(d) $Cu^{2+} + 4H_2O \longrightarrow [Cu(H_2O)_4]^{2+}, \quad \log K = 8.9$

Ans. *(b)* Greater the value of log K, greater will be stability of complex compound formed.

For reaction,

$$Cu^{2+} + 4CN^- \longrightarrow [Cu(CN)_4]^{2-}$$

$$K = \frac{[(Cu(CN)_4)^{2-}]}{[Cu^{2+}][CN^-]^4} \text{ and } \log K = 27.3$$

For this reaction, log K has highest value among the given four reactions. Hence, K will also be higher among these four. *i.e.,* stability of the complexes will be highest among these four complexes.

Q. 2 The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes, $[Co(NH_3)_6]^{3+}$,$[Co\ (CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$

(a) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

(b) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$

(c) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$

(d) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

Thinking Process

This problem is based on the concept of crystal field splitting and colour of coordination compounds. Follow the steps to answer this question

(i) Arrange the given complexes in increasing order of their crystal field splitting energy.

(ii) Now arrange them in decreasing order of the wavelength of light.

(iii) As energy and wavelength are related as $\Delta E = h\nu = \frac{hc}{\lambda}$

Ans. ***(c)*** As we know that, strong field ligand split the five degenerate energy levels with more energy separation than weak field ligand, *i.e.,* as strength of ligand increases crystal field splitting energy increases.

Hence, $$\Delta E = \frac{hc}{\lambda}$$

$$\Rightarrow \quad \Delta E \propto \frac{1}{\lambda} \Rightarrow \lambda \propto \frac{1}{\Delta E}$$

As energy separation increases, the wavelength decreases.

Thus, the correct order is

$$[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$$

Here, strength of ligand increases, ΔE increases, CFSE increases and λ absored decreases.

Hence, correct choice is (c).

Q. 3 When 0.1 mol $CoCl_3(NH_3)_5$ is treated with excess of $AgNO_3$, 0.2 mol of AgCl are obtained. The conductivity of solution will correspond to

(a) 1 : 3 electrolyte
(b) 1 : 2 electrolyte
(c) 1 : 1 electrolyte
(d) 3 : 1 electrolyte

Ans. ***(b)*** One mole of $AgNO_3$ precipitates one mole of chloride ion. In the above reaction, when 0.1 mole $CoCl_3(NH_3)_5$ is treated with excess of $AgNO_3$, 0.2 mole of AgCl are obtained thus, there must be two free chloride ions in the solution of electrolyte.

So, molecular formula of complex will be $[Co(NH_3)_5Cl]Cl_2$ and electrolytic solution must contain $[Co(NH_3)_5Cl]^{2+}$ and two Cl^- as constituent ions. Thus, it is 1 : 2 electrolyte.

$$[Co(NH_3)_5Cl]Cl_2 \longrightarrow [Co(NH_3)_5Cl]^{2\oplus}(aq) + 2Cl^-(aq)$$

Hence, option (b) is the correct.

Q. 4 When 1 mole of $CrCl_3 \cdot 6H_2O$ is treated with excess of $AgNO_3$, 3 moles of AgCl are obtained. The formula of the complex is

(a) $[CrCl_3(H_2O)_3]\cdot 3H_2O$
(b) $[CrCl_2(H_2O)_4]Cl\cdot 2H_2O$
(c) $[CrCl(H_2O)_5]Cl_2\cdot H_2O$
(d) $[Cr(H_2O)_6]Cl_3$

Ans. ***(d)*** 1 mole of $AgNO_3$ precipitates one free chloride ion (Cl^-).

Here, 3 moles of AgCl are precipitated by excess of $AgNO_3$. Hence, there must be three free Cl^- ions.

So, the formula of the complex can be $[Cr(H_2O)_6]Cl_3$ and correct choice is (d).

Q. 5 The correct IUPAC name of $[Pt(NH_3)_2Cl_2]$ is

(a) Diamminedichloridoplatinum (II)
(b) Diamminedichloridoplatinum (IV)
(c) Diamminedichloridoplatinum (0)
(d) Dichloridodiammineplatinum (IV)

Thinking Process

This problem is based on IUPAC nomenclature of coordination compound. IUPAC nomenclature of any coordination compound can be done as follows

(i) Positively charged ions are named first.

(ii) Negatively charged ions are named in alphabetical order of ligands including their numbers followed by metal ending with –ium and oxidation state in the bracket.

Ans. ***(a)*** The complex compound is $[Pt(NH_3)_2Cl_2]$.

The ligands present in the compound are

(i) NH_3 – neutral ligand represented as amine.

(ii) Cl – anion ligand (ending with-o-) represented as chlorido di prefixed to represent two ligands.

The oxidation number of platinum in the compound is 2. Hence, correct IUPAC name of $[Pt\ (NH_3)_2Cl_2]$ is

Diammine dichloridoplatinum (II)

So, (a) option is correct.

Q. 6 **The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species?**

(a) $[Fe(CO)_5]$ (b) $[Fe(CN)_6]^{3-}$ (c) $[Fe(C_2O_4)_3]^{3-}$ (d) $[Fe(H_2O)_6]^{3+}$

Ans. ***(c)*** Chelation (formation of cycle by linkage between metal ion and ligand) stabilises the coordination compound. The ligand which chelates the metal ion are known as chelating ligand.

Here, only $[Fe(C_2O_4)_3]^{3-}$ is a coordination compound which contains oxalate ion as a chelating ligand. Hence, it stabilises coordination compound by chelating Fe^{3+} ion.

Q. 7 **Indicate the complex ion which shows geometrical isomerism.**

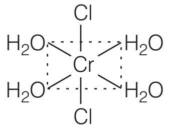
(a) $[Cr(H_2O)_4Cl_2]^+$ (b) $[Pt(NH_3)_3Cl]$ (c) $[Co(NH_3)_6]^{3+}$ (d) $[Co(CN)_5(NC)]^{3-}$

Thinking Process

This problem includes concept of isomerism in coordination compound. Complex of MA_4B_2 type show geometrical isomerism.

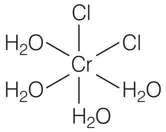
Ans. ***(a)*** $[Cr(H_2O)_4Cl_2]^+$ shows geometrical isomerism because it is a MA_4B_2 type coordination compound which contains two set of equivalent ligands, four H_2O and 2 Cl.

Hence, the possible geometrical isomers are



trans-isomer

and



cis-isomer

Hence, correct choice is (a).

Q. 8 **The CFSE for octahedral $[CoCl_6]^{4-}$ is 18,000 cm^{-1}. The CFSE for tetrahedral $[CoCl_4]^{2-}$ will be**

(a) 18,000 cm^{-1} (b) 16,000 cm^{-1} (c) 8,000 cm^{-1} (d) 20,000 cm^{-1}

Ans. ***(c)*** CFSE for octahedral and tetrahedral complexes are closely related to each other by formula $\Delta_t = \frac{4}{9}\Delta_0$.

where, Δ_0 = CFSE for octahedral complex, Δ_t = CFSE for tetrahedral complex

According to question, $\Delta_0 = 18{,}000\ cm^{-1}$

$$\therefore \quad \Delta_t = \frac{4}{9}\Delta_0 = \frac{4}{9} \times 18{,}000\ cm^{-1}$$

$$= 4 \times 2{,}000\ cm^{-1} = 8{,}000\ cm^{-1}$$

Hence, correct choice is (c).

Q. 9 Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ are

(a) linkage isomers (b) coordination isomers

(c) ionisation isomers (d) geometrical isomers

Ans. *(a)* The ligand(s) which has two different bonding sites are known as ambident ligands *e.g.,* NCS, NO_2 etc.

Here, NCS has two binding sites at N and S.

Hence, NCS (thiocyanate) can bind to the metal ion in two ways

$$M \leftarrow \text{NCS or } M \rightarrow \text{SNC}$$

Thus, coordination compounds containing NCS as a ligand can show linkage isomerism *i.e.*, $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ are linkage isomers.

Hence, correct choice is (a).

Q. 10 The compounds $[Co(SO_4)(NH_3)_5]Br$ and $[Co(SO_4)(NH_3)_5]Cl$ represent

(a) linkage isomerism (b) ionisation isomerism

(c) coordination isomerism (d) no isomerism

Ans. *(d)* Compounds having same molecular formula but different structural formula are known as isomers. $[Co(SO_4)_2(NH_3)_5]Br$ and $[Co(SO_4)(NH_3)_5]Cl$ have not same molecular formula. Hence, they are not isomers.

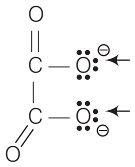
Q. 11 A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent?

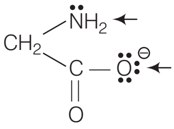
(a) Thiosulphato (b) Oxalato

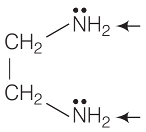
(c) Glycinato (d) Ethane-1, 2-diamine

Ans. *(a)* A chelating ligand has two or more binding donor atoms to a single metal ion

e.g.,

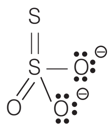

Oxalato


Glycinato


Ethane-1, 2 diamine

Here (←) denotes binding site.

thiosulphato ($S_2O_3^{2-}$) is not a chelating ligand because geometrically it is not favourable for $S_2O_3^{2-}$ to chelate a metal ion.



Q. 12 Which of the following species is not expected to be a ligand?

(a) NO (b) NH_4^+

(c) $NH_2CH_2CH_2NH_2$ (d) CO

Ans. *(b)* Ligand must donate a pair of electron or loosely held electron pair to metal and form a *M—L* bond.

e.g., $:\ddot{N}=O$, $\ddot{N}H_2CH_2CH_2\ddot{N}H_2$, $:CO$,

Among $\overset{+}{N}H_4$ does not have any pair of electron.

Hence $\overset{+}{N}H_4$ is not a ligand.

Q. 13 What kind of isomerism exists between $[Cr(H_2O)_6]Cl_3$ (violet) and $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (greyish-green)?

(a) Linkage isomerism
(b) Solvate isomerism
(c) Ionisation isomerism
(d) Coordination isomerism

Ans. *(c)* Soluate isomerism to shown when two compounds having same molecular formula differ by whether or solvent molecule is directly bonded to metal ion or is present as free solvent molecules in the crystal lattice.

When water is present as solvent and show this type of isomerism then it is known as hydrate isomerism.

Coordination compound $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]H_2O \cdot Cl_2$ are solvate isomers, because water is exchanged by chloride ion. This is why both of them show different colour on exposure to sunlight.

Q. 14 IUPAC name of $[Pt(NH_3)_2Cl(NO_2)]$ is

(a) Platinum diaminechloronitrite
(b) Chloronitrito-N-ammineplatinum (II)
(c) Diamminechloridonitrito-N-platinum (II)
(d) Diamminechloronitrito-N-platinate (II)

Ans. *(c)* Correct IUPAC name can be written as

The ligands present in the given coordination compound are

(i) (NH_3) represented as amine
(ii) Cl^{s} represented as chlorido
(iii) NO_2^{s} represented as nitrito-N

According to IUPAC rule, ligands are named in an alphabetical order before central atom. Prefex di-will be used to indicate the number of NH_3 ligands present.

Oxidation state of metal is indicated by Roman numeral in parenthesis.

So, IUPAC name will be

diamminechloronitrito-N-platinum (II)

Hence, option (c) is correct.

Multiple Choice Questions (More Than One Options)

Q. 15 Atomic number of Mn. Fe and Co are 25, 26 and 27 respectively. Which of the following inner orbital octahedral complex ions are diamagnetic?

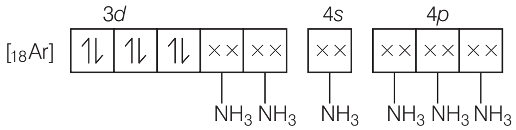
(a) $[Co(NH_3)_6]^{3+}$ (b) $[Mn(CN)_6]^{3-}$ (c) $[Fe(CN)_6]^{4-}$ (d) $[Fe(CN)_6]^{3-}$

Thinking Process

This problem is based on magnetic property of coordination compound. Coordination compound containing at least one unpaired electron(s) are paramagnetic and coordination compounds all containing all paired electrons are diamagnetic in nature.

Ans. ***(a, c)***

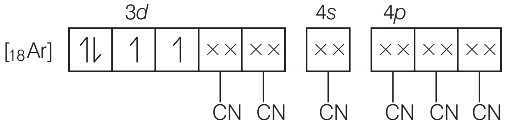
Molecular orbital electronic configuration of Co^{3+} in $[Co(NH_3)_6]^{3+}$ is



Number of unpaired electron = 0

Magnetic property = Diamagnetic

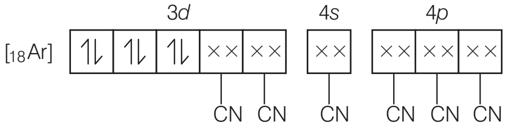
Molecular orbital electronic configuration of Mn^{3+} in $[Mn(CN)_6]^{3-}$



Number of unpaired electrons = 2

Magnetic property = Paramagnetic

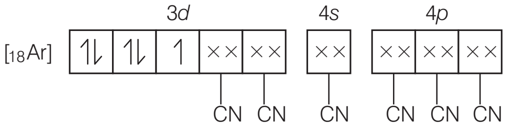
Molecular orbital electronic configuration of Fe^{2+} in $[Fe(CN)_6]^{4-}$ is



Number of unpaired electron = 0

Magnetic property = Diamagnetic

Molecular orbital electronic configuration of Fe^{3+} in $[Fe(CN)_6]^{3-}$



Number of unpaired electron = 1

Magnetic property = Paramagnetic

Thus, $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{4-}$ are diamagnetic.

Hence, correct choices are options (a) and (c).

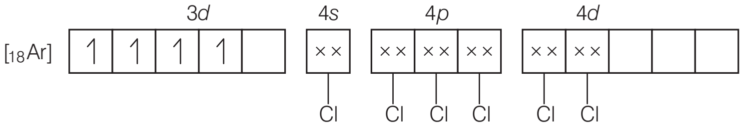
Q. 16 Atomic number of Mn, Fe, Co and Ni are 25, 26, 27 and 28 respectively. Which of the following outer orbital octahedral complexes have same number of unpaired electrons?

(a) $[MnCl_6]^{3-}$ (b) $[FeF_6]^{3-}$

(c) $[CoF_6]^{3-}$ (d) $[Ni(NH_3)_6]^{2+}$

Ans. *(a, c)*

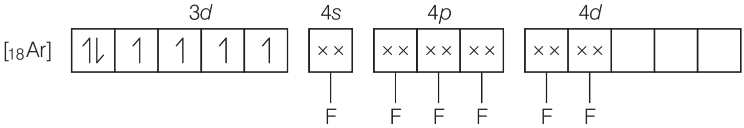
Molecular orbital electronic configuration of Mn^{3+} in $[MnCl_6]^{3-}$ is



Number of unpaired electrons = 4

Magnetic property = Paramagnetic

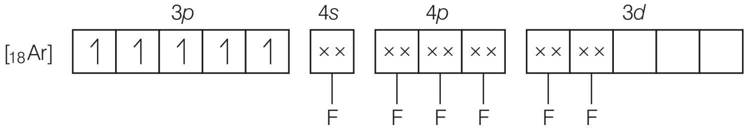
Molecular orbital electronic configuration of Co^{3+} in $[CoF_6]^{3-}$ is



Number of unpaired electrons = 4

Magnetic property = Paramagnetic

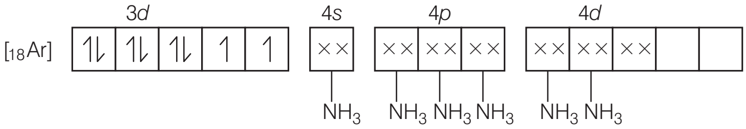
Molecular orbital electronic configuration of Fe^{3+} in $[FeF_6]^{3-}$ is



Number of unpaired electrons = 5

Magnetic property = Paramagnetic

Molecular orbital electronic configuration of Ni^{2+} in $[Ni(NH_3)_6]^{2+}$ is



Number of unpaired electrons = 2

Magnetic property = Paramagnetic

Thus, $[MnCl_6]^{3-}$ and $[CoF_6]^{3-}$ are paramagnetic having four electrons each.

Hence, correct choices are (a) and (c).

Q. 17 Which of the following options are correct for $[Fe(CN)_6]^{3-}$ complex?

(a) d^2sp^3 hybridisation

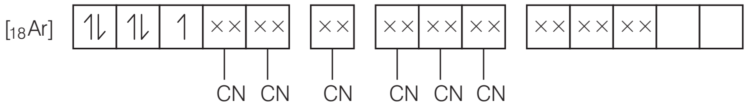
(b) sp^3d^2 hybridisation

(c) Paramagnetic

(d) Diamagnetic

Ans. *(a, c)*

According to VBT, the molecular orbital electronic configuration of Fe^{3-} in $[Fe(CN)_6]^{3-}$ is



Hybridisation = d^2sp^3

Number of unpaired electron = 1

Magnetic property = Paramagnetic

Hence, correct choices are options (a) and (c).

Q. 18 An aqueous pink solution of cobalt(II) chloride changes to deep blue on addition of excess of HCl. This is because ....

(a) $[Co(H_2O)_6]^{2+}$ is transformed into $[CoCl_6]^{4-}$

(b) $[Co(H_2O)_6]^{2+}$ is transformed into $[CoCl_4]^{2-}$

(c) tetrahedral complexes have smaller crystal field splitting than octahedral complexes

(d) tetrahedral complexes have larger crystal field splitting than octahedral complex

Ans. *(b, c)*

Aqueous pink solution of cobalt (II) chloride is due to electronic transition of electron from t_{2g} to e_g energy level of $[Co(H_2O)_6]^{2+}$ complex. When excess of HCl is added to this solution

(i) $[Co(H_2O)_6]^{2+}$ is transformed into $[CoCl_4]^{2-}$.

(ii) Tetrahedral complexes have smaller crystal field splitting than octahedral complexes because $\Delta_t = \frac{4}{9}\Delta_0$

Hence, options (b) and (c) are correct choices.

Q. 19 Which of the following complexes are homoleptic?

(a) $[Co(NH_3)_6]^{3+}$

(b) $[Co(NH_3)_4Cl_2]^+$

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

(d) $[Ni(NH_{3_4}Cl_2]$

Ans. *(a, c)*

Homoleptic complex The complex containing only one species or group as ligand is known as homoleptic ligand.

e.g., $[Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$

Here, $[Co(NH_3)_6]^{3+}$ contain only NH_3 as a ligand and $[Ni(CN)_4]^{2-}$ contain CN as a ligand. While other two complexes $[Co(NH_3)_4Cl_2]^+$ and $[Ni(NH_3)_4Cl_2]$ contain NH_3 and Cl as ligands.

Hence, options (a) and (c) are correct choices.

Q. 20 Which of the following complexes are heteroleptic?

(a) $[Cr(NH_3)_6]^{3+}$

(b) $[Fe(NH_3)_4Cl_2]^+$

(c) $[Mn(CN)_6)]^{4-}$

(d) $[Co(NH_3)_4Cl_2]$

Ans. *(b, d)*

Heteroleptic complexes Coordination complexes which contain more than one type of ligands are known as heteroleptic complexes.

e.g., $[Fe(NH_3)_4Cl_2]^+$ contain NH_3 and Cl as a ligand is as heteroleptic complex. Similarly, $[Co(NH_3)_4Cl_2]$ contain NH_3 and Cl as ligand is also a heteroleptic complex.

Hence, optons (b) and (d) are correct choices.

Q. 21 Identify the optically active compounds from the following

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

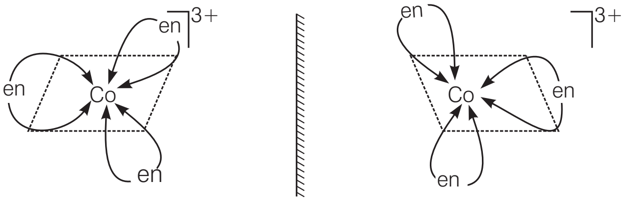
(b) *trans* $-[Co(en)_2Cl_2]^+$

(c) *cis* $-[Co(en)_2Cl_2]^+$

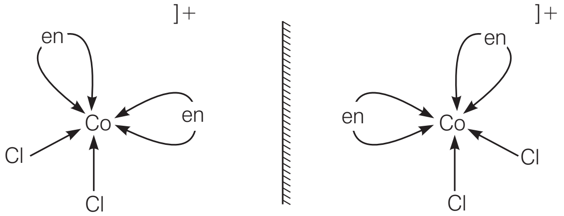
(d) $[Cr(NH_3)_5Cl]$

Ans. ***(a, c)***

$[Co(en)_3]^{3+}$ and *cis* – $[Co(en)_2Cl_2]^+$ are optically active compounds because their mirror images are non-superimposable isomer.



Non-superimposable isomers of $[Co(en)_3]^{3+}$



Non-superimposable isomers of $[Co(en)_2Cl_2]^+$

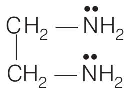
Hence, (a) and (c) are correct choices.

Q. 22 Identify the correct statements for the behaviour of ethane-1, 2-diamine as a ligand.

(a) It is a neutral ligand
(b) It is a didentate ligand
(c) It is a chelating ligand
(d) It is a unidentate ligand

Ans. ***(a, b, c)***

Molecular formula of ethane-1, 2-diamine is



$$\begin{array}{l} CH_2-\ddot{N}H_2 \\ | \\ CH_2-\ddot{N}H_2 \end{array}$$

(a) Ethane-1, 2-diamine is a neutral ligand due to absence of any charge.

(b) It is a didentate ligand due to presence of two donor sites one at each nitrogen atom of amino group.

(c) It is a chelating, ligand due to its ability to chelate with the metal.

Hence, options (a), (b) and (c) are correct choices.

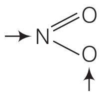
Q. 23 Which of the following complexes show linkage isomerism?

(a) $[Co(NH_3)_5(NO_2)]^{2+}$
(b) $[Co(H_2O)_5CO]^{3+}$
(c) $[Cr(NH_3)_5]SCN^{2+}$
(d) $[Fe(en)_2Cl_2]^+$

Ans. ***(a, c)***

Coordination compounds containing a ligand with more than one non-equivalent binding position (known as ambident ligand) show linkage isomerism.

e.g., $[Co(NH_3)_5(NO_2)]^+$ contains NO_2 which have two donor sites N and O can be shown by arrow (→) as



$[Cr(NH_3)_5SCN]^{2+}$ contains SCN which have two different donor sites S and N can be shown by arrow (→) as

$$\rightarrow S - C \equiv N \leftarrow$$

Hence, $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Cr(NH_3)_5SCN]^{2+}$ show linkage isomerism. While $[Co(H_2O)_5\ CO]^{3+}$ and $[Fe(en)_2Cl_2]^+$ has no ambident ligand. So, these two will not show linkage isomerism.

Hence, options (a) and (c) are correct choices.

Short Answer Type Questions

Q. 24 Arrange the following complexes in the increasing order of conductivity of their solution

$$[Co(NH_3)_3Cl_3],\ [Co(NH_3)_4Cl_2]Cl,\ [Co(NH_3)_6]Cl_3,\ [Cr(NH_3)_5Cl]Cl_2$$

Thinking Process

This problem is based on the concept of conductivity of coordination compound. Greater the number of ions, greater the conductivity of coordination compound.

Ans. Ions or molecules present outside the coordination sphere are ionisable. A complex which gives more ions on dissolution, is more conducting.

$$\underset{\text{(1 ion)}}{[Co(NH_3)_3Cl_3]} < \underset{\text{(2 ions)}}{[Co(NH_3)_4Cl_2]Cl} < \underset{\text{(3 ions)}}{[Cr(NH_3)_5Cl]Cl_2} < \underset{\text{(4 ions)}}{[Co(NH_3)_6]Cl_3}$$

Here, number of ions increases and conductivity increases.

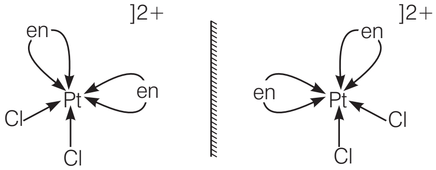
Q. 25 A coordination compound $Cr\ Cl_3 \cdot 4H_2O$ precipitates silver chloride when treated with silver nitrate. The molar conductance of its solution corresponds to a total of two ions. Write structural formula of the compound and name it.

Ans. Formation of white precipitate with $AgNO_3$ shows that atleast one Cl ion is present outside the coordination sphere. Moreover only two ions are obtained in solution, so only one Cl^- is present outside the sphere.

Thus, the formula of the complex is $[Co(H_2O)_4Cl_2]Cl$ and its IUPAC name is Tetraaquadichloridocobalt (III) chloride.

Q. 26 A complex of the type $[M(AA)_2X_2]^{n+}$ is known to be optically active. What does this indicate about the structure of the complex? Give one example of such complex.

Ans. An optically active complex of the type $[M(AA)_2X_2]^{n+}$ indicates *cis*-octahedral structure, *e.g.*, *cis*-$[Pt(en)_2Cl_2]^{2+}$ or *cis*-$[Cr(en)_2Cl_2]^+$ because its mirror image isomers are non-superimposable.



Non-superimosable isomers of $[Pt(en)_2Cl_2]^{2+}$

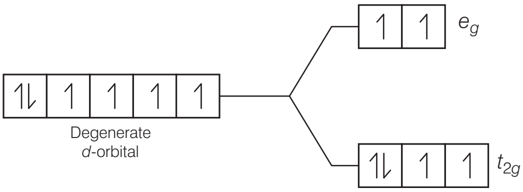
Non-superimposable isomers of $[Pt(en)_2Cl_2]^{2+}$.

Q. 27 Magnetic moment of $[MnCl_4]^{2-}$ is 5.92 BM. Explain giving reason present.

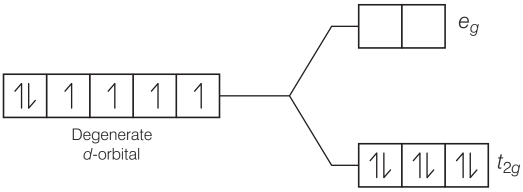
Ans. The magnetic moment 5.92 BM shows that there are five unpaired electrons present in the *d*-orbitals of Mn^{2+} ion. As a result, the hybridisation involved is sp^3 rather than dsp^2. Thus tetrahedral structure of $[MnCl_4]^{2-}$ complex will show 5.92 BM magnetic moment value.

Q. 28 On the basis of crystal field theory explain why Co(III) forms paramagnetic octahedral complex with weak field ligands whereas it forms diamagnetic octahedral complex with strong field ligands.

Ans. With weak field ligands; $\Delta_o < P$, (pairing energy) so, the electronic configuration of Co (III) will be $t_{2g}^4 e_g^2$ *i.e.,* it has 4 unpaired electrons and is paramagnetic.



With strong field ligands, $\Delta_o > P$ (pairing energy), so pairing occurs thus, the electronic configuration will be $t_{2g}^6 e_g^0$. It has no unpaired electrons and is diamagnetic.



Q. 29 Why are low spin tetrahedral complexes not formed?

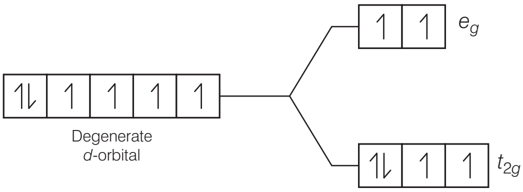
Ans. In tetrahedral complex, the *d*-orbital is splitting to small as compared to octahedral. For same metal and same ligand $\Delta_t = \frac{4}{9}\Delta_0$.

Hence, the orbital splitting energies are not enough to force pairing. As a result, low spin configurations are rarely observed in tetrahedral complexes.

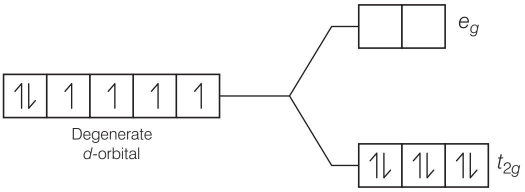
Q. 30 Give the electronic configuration of the following complexes on the basis of crystal field splitting theory. $[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and $[Cu(NH_3)_6]^{2+}$.

Ans. According to spectrochemical series, ligands can be arranged in a series in the order of increasing field strength *i.e.*, $F^- < NH_3 < CN^-$.

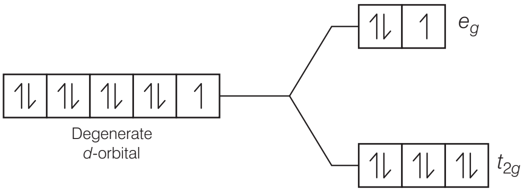
Hence, CN^- and NH_3 being strong field ligand pair up the t_{2g} electrons before filling e_g set.
$[CoF_6]^{3-}$;$Co^{3+} = (d^6)\, t_{2g}^4 e_g^2$



$[Fe(CN)_6^{4-}, Fe^{2+} = (d^6)\, t_{2g}^6\, e_g^0$



$[Cu(NH_3)_6]^{2+}, Cu^{2+} = (d^9) t_{3g}^6 e_g^3$



Q. 31 Explain why $[Fe(H_2O)_6]^{3+}$ has magnetic moment value of 5.92 BM whereas $[Fe(CN)_6]^{3-}$ has a value of only 1.74 BM?

Ans. As we know, $\mu_m = \sqrt{n(n+2}$ BM

where, μ_m = magnetic moment

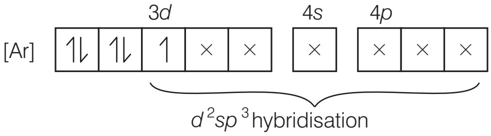
μ_n = number of unpaired electrons

It $\mu_m = 1.74$ *i.e.*, $n = 1$

and $\mu_m = 5.92$ *i.e.*, $n = 5$

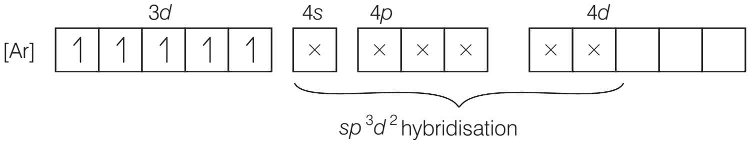
$[Fe(CN)_6]^{3-}$ involves d^2sp^3 hybridisation with one unpaired electron (as shown by its magnetic moment 1.74 BM) and $[Fe(H_2O)_6]^{3+}$ involves sp^3d^2 hybridisation with five unpaired electrons (because magnetic moment equal to 5.92 BM).

CN^- is stronger ligand than H_2O according to spectrochemical series. $\Delta_0 > P$ for CN^- hence, fourth electron will pair itself. Whereas for water pairing will not happen for $[Fe(CN)_6]^{3-}$ the electronic configuration of Fe^{3+} is



One unpaired electron

For $[Fe(H_2O)_6]^{3+}$ the electronic configuration of Fe^{3+} is



Five unpaired electron

Hence, $[Fe(CN)_6]^{3-}$ and $[Fe(H_2O)_6]^{3+}$ are inner orbital and outer orbital complex respectively.

Q. 32 Arrange following complex ions in increasing order of crystal field splitting energy (Δ_0).

$[Cr(Cl)_6]^{3-}$, $[Cr(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$.

Ans. CFSE is higher when the complex contains strong field ligand. Thus, crystal field splitting energy increases in the order

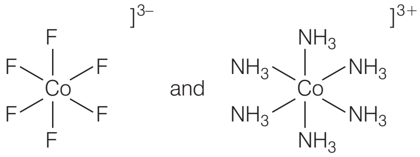
$$[Cr(Cl)_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(CN)_6]^{3-}.$$

Because according to spectrochemical series the order of field strength is

$$Cl^- < NH_3 < CN^-$$

Q. 33 Why do compounds having similar geometry have different magnetic moment?

Ans. It is due to the presence of weak and strong field ligands in complexes. If CFSE is high, the complex will show low value of magnetic moment and *vice-versa*, *e.g.* $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$, the former is paramagnetic, and the latter is diamagnetic because F^- is a weak field ligand and NH_3 is a strong field ligand while both have similar geometry.



Q. 34 $CuSO_4 \cdot 5H_2O$ is blue in colour while $CuSO_4$ is colourless. Why?

Ans. In $CuSO_4 \cdot 5H_2O$, water acts as ligand and causes crystal field splitting. Hence, *d-d* transition is possible thus $CuSO_4 \cdot 5H_2O$ is coloured. In the anhydrous $CuSO_4$ due to the absence of water (ligand), crystal field splitting is not possible and hence, it is colourless.

Q. 35 Name the type of isomerism when ambidentate ligands are attached to central metal ion. Give two examples of ambidentate ligands.

Ans. Ligand having more than one different binding position are known as ambidentate ligand. *e.g.,* SCN has two different binding positions S and N. Coordination compound containing ambidentate ligands are considered to show linkage isomerism due to presence of two different binding positions.

e.g., (i) $[Co(NH_3)_5SCN]^{3+}$ and

(ii) $[Fe(NH_3)_5(NO_2)]^{3+}$

Matching The Columns

Q. 36 Match the complex ions given in Column I with the colours given in Column II and assign the correct code.

Column I (Complex ion)		Column II (Colour)	
A.	$[Co(NH_3)_6]^{3+}$	1.	Violet
B.	$[Ti(H_2O)_6]^{3+}$	2.	Green
C.	$[Ni(H_2O)_6]^{2+}$	3.	Pale blue
D.	$[Ni(H_2O)_4(en)]^{2+}(aq)$	4.	Yellowish orange

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	4	5	(b)	4	3	2	1
(c)	3	2	4	1	(d)	4	1	2	3

Ans. **A.** → (4) **B.** → (3) **C.** → (2) **D.** → (1)

Colour of coordination compound is closely related to CFSE of coordination compound. Depending upon the CFSE of given coordination compounds. Correct matching will be as follows

Column I (Complex ion)		Column II (Colour)	
A.	$[Co(NH_3)_6]^{3+}$	4.	Yellowish orange
B.	$[Ti(H_2O)_6]^{3+}$	3.	Pale blue
C.	$[Ni(H_2O)_6]^{2+}$	2.	Green
D.	$[Ni(H_2O)_4(en)]^{2+}(aq)$	1.	Violet

Hence, correct choice is (b).

Q. 37 Match the coordination compounds given in Column I with the central metal atoms given in Column II and assign the correct code.

Column I (Coordination compound)		Column II (Central metal atom)	
A.	Chlorophyll	1.	Rhodium
B.	Blood pigment	2.	Cobalt
C.	Wilkinson catalyst	3.	Magnesium
D.	Vitamin B_{12}	4.	Iron

Codes

	A	B	C	D		A	B	C	D
(a)	3	4	1	2	(b)	3	4	5	1
(c)	4	3	2	1	(d)	3	4	1	2

Ans. A. → (3) **B.** → (4) **C.** → (1) **D.** → (2)

Central metal ions present on coordination compounds determine the properties of coordination compound and their biological role.

	Column I (Coordination compound)		**Column II** (Central metal atom)
A.	Chlorophyll	3.	Magnesium
B.	Blood pigment	4.	Iron
C.	Wilkinson catalyst	1.	Rhodium
D.	Vitamin B_{12}	2.	Cobalt

Hence, correct choice is (a).

Q. 38 Match the complex ions given in Column I with the hybridisation and number of unpaired electrons given in Column II and assign the correct code.

	Column I (Complex ion)		**Column II** (Hybridisation, number of unpaired electrons)
A.	$[Cr(H_2O)_6]^{3+}$	1.	dsp^2, 1
B.	$[Co(CN)_4]^{2-}$	2.	sp^3d^2, 5
C.	$[Ni(NH_3)_6]^{2+}$	3.	d^2sp^3, 3
D.	$[MnF_6]^{4-}$	4.	sp^3d^2, 2

Codes

	A	B	C	D		A	B	C	D
(a)	3	1	4	2	(b)	4	3	2	1
(c)	3	2	4	1	(d)	4	1	2	3

Ans. **A.** → (3) **B.** → (1) **C.** → (4) **D.** → (2)

Formation of inner orbital complex and outer orbital complex determines hybridisation of molecule which *inturn* depends upon field strength of ligand and number of vacant *d* orbitals.

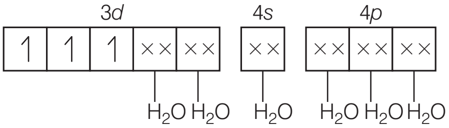
(i) Strong field ligand forms inner orbital complex with hybridisation d^2sp^3.

(ii) Weak field ligand forms outer orbital complex with hybridisation sp^3d^2.

According to VBT, hybridisation and number of unpaired electrons of coordination compounds can be calculated as

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

MOEC (Molecular orbital electronic configuration) of Cr^{3+} in $[Cr(H_2O)_6]^{3+}$ is

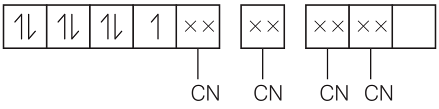


Hybridisation = d^2sp^3

n (number of unrpaired electrons) = 3

B. $[Co(CN)_4]^{2-}$

MOEC of Co^{2+} in $[Co(CN)_4]^{2-}$ is

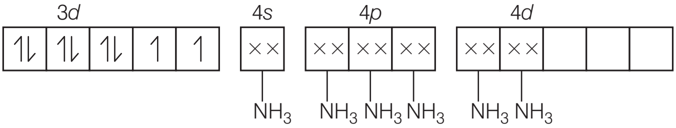


Hybridisation = dsp^2

$n = 1$

C. $[Ni(NH_3)_6]^{2+}$

MOEC of Ni^{2+} in $[Ni(NH_3)_6]^{2+}$ is

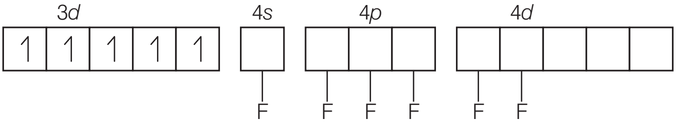


Hybridisation = sp^3d^2

$n = 2$

D. $[MnF_6]^{4-}$

MOEC of Mn^{2+} in $[MnF_6]^{4-}$ is



Hybridisation = sp^3d^2

$n = 5$

Hence, correct choice can be represented by (a).

Q. 39 Match the complex species given in Column I with the possible isomerism given in Column II and assign the correct code.

	Column I (Complex species)		**Column II** (Isomerism)
A.	$[Co(NH_3)_4Cl_2]^+$	1.	Optical
B.	*cis* – $[Co(en)_2Cl_2]^+$	2.	Ionisation
C.	$[Co(NH_3)_5(NO_2)]Cl_2$	3.	Coordination
D.	$[Co(NH_3)_6][Cr(CN)_6]$	4.	Geometrical

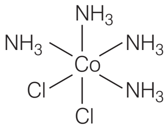
Codes

	A	B	C	D		A	B	C	D
(a)	1	2	4	3	(b)	4	3	2	1
(c)	4	2	1	3	(d)	4	1	2	3

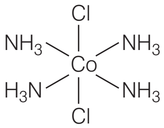
Ans. **A.** → (4) **B.** → (1) **C.** → (2) **D.** → (3)

Isomerism in coordination compound is decided by type of ligands and geometry of coordination and arrangement of ligands.

A. $[Co(NH_3)_4Cl_2]^+$ shows geometrical isomerism due to presence of two types of ligand whose $[Co(NH_3)_4Cl_2]^+$ arrangement around central metal ion.

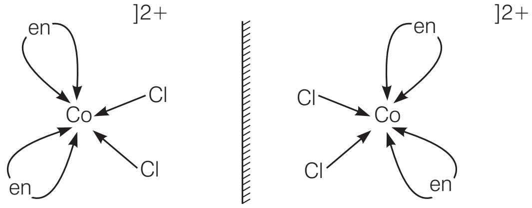


cis-isomer



trans-isomer

B. *cis* – $[Co(en)_2Cl_2]^+$ shows optical isomer due to its non-superimposable mirror image relationship.



C. $[Co(NH_3)_5(NO_2)]Cl_2$ shows ionisation isomer due to its interchanging ligand from outside the ionisation sphere.

D. $[Co(NH_3)_6][Cr(CN)_6]$ shows coordination isomer due to interchanging of ligand in between two metal ions from one coordination sphere to another coordination sphere.

Hence, correct choice is (d).

Q. 40 **Match the compounds given in Column I with the oxidation state of cobalt present in it (given in column II) and assign the correct code.**

Column I (Compound)	**Column II** (Oxidation state of Co)
A. $[Co(NCS)(NH_3)_5](SO_3)$	1. +4
B. $[Co(NH_3)_4Cl_2]SO_4$	2. 0
C. $Na_4[Co(S_2O_3)_3]$	3. +2
D. $[Co_2(CO)_8]$	4. +3

Code

	A	B	C	D		A	B	C	D
(a)	1	2	4	3	(b)	4	3	2	1
(c)	3	1	4	2	(d)	4	1	3	2

Ans. **A.** → (4) **B.** → (1) **C.** → (3) **D.** → (2)

Oxidation state of CMI (central metal ion) can be calculated by considering the oxidation state of whole molecule is equal to charge present on coordination sphere.

A. $[Co(NCS)(NH_3)_5]SO_3$.

Let oxidation state of Co is x.

$$x - 1 + 5 \times 0 = +2$$

$$x = +2 + 1 = +3$$

B. $[Co(NH_3)_4Cl_2]SO_4$

Let oxidation state of Co $= x$

$\Rightarrow \quad x + 4 \times 0 + 2 \times (-1) = +2$

$\Rightarrow \quad x - 2 = +2$

$x = 4$

C. $Na_4[Co(S_2O_3)_3]$

Let oxidation state of Co $= x$

$x + 3 \times (-2) = -4$

$x - 6 = -4$

$x = -4 + 6 = +2$

D. $[Co(CO)_8]$

Let oxidation state of Co $= x$

$x - 8 \times 0 = 0$

$x = 0$

Hence, correct choice is (d).

Assertion and Reason

In the following questions a statement of assertion (A) *followed by a statement of reason* (R) *is given. choose the correct answer out of the following choices.*

(a) Assertion and reason both are true, reason is correct explanation of assertion.

(b) Assertion and reason both are true but reason is not the correct explanation of assertion.

(c) Assertion is true, reason is false.

(d) Assertion is false, reason is true.

Q. 41 Assertion (A) Toxic metal ions are removed by the chelating ligands.

Reason (R) Chelate complexes tend to be more stable.

Ans. ***(a)*** Assertion and reason both are correct and reason is the correct explanation of assertion.

Toxic metal ions are removed by chelating ligands. When a solution of chelating ligand is added to solution containing toxic metals ligands chelates the metal ions by formation of stable complex.

Q. 42 Assertion (A) $[Cr(H_2O_6)]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ are reducing in nature.

Reason (R) Unpaired electrons are present in their d-orbitals.

Ans. ***(b)*** Assertion and reason both are true but reason is not correct explanation of assertion.

Correct reason is

$[Cr(H_2O_6)]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ are reducing in nature due to formation of more stable complex ion after gaining of electron.

Q. 43 Assertion (A) Linkage isomerism arises in coordination compounds containing ambidentate ligand.

Reason (R) Ambidentate ligand has two different donor atoms.

Ans. *(a)* Assertion and reason both are correct and reason is correct explanation of assertion. Linkage isomerism arises in coordination compounds containing ambidentate ligands because ambidentate ligand has two different donor atoms.

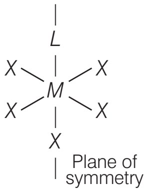
e.g., SCN, NO_2 etc.

Q. 44 Assertion (A) Complexes of MX_6 and MX_5L type (X and L are unidentate) do not show geometrical isomerism.

Reason (R) Geometrical isomerism is not shown by complexes of coordination number 6.

Ans. *(b)* Assertion and reason both are correct and reason is not correct explanation of assertion.

Complexes of MX_6 and MX_5L type (X and L are unidentate) do not show geometrical isomerism due to presence of plane of symmetry and necessary condition for showing geometrical isomerism is that complex is must of MA_4B_2 type or $[M(AB)_2X_2]$ type

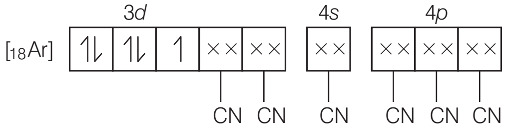


Q. 45 Assertion (A) $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.

Reason (R) Because it has d^2sp^3 type hybridisation.

Ans. *(d)* Assertion is false but reason is true.

According to VBT, MOEC of Fe^{3+} in $[Fe(CN)_6]^{3-}$ is



Hybridisation $= d^2sp^3$

$n = 1$

Hence, correct assertion is

$[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to one unpaired electron.

i.e.,

$$\begin{aligned}\mu &= \sqrt{n(n+2)} \\ &= \sqrt{1(1+2)} \\ &= \sqrt{3} = 1.73\ \text{BM}\end{aligned}$$

Long Answer Type Questions

Q. 46 Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value in the following

(a) $[CoF_6]^{3-}$, $[Co(H_2O)_6]^{2+}$, $[Co(CN)_6]^{3-}$

(b) $FeF_6^{\ 3-}$, $[Fe(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{4-}$

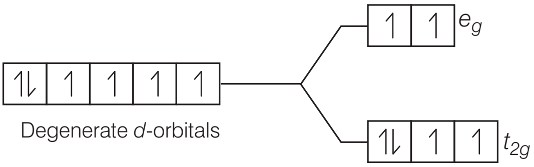
Thinking Process

This problem includes conceptual mixing of crystal field theory and magnetic moment (μ) *determination.*

$\mu = \sqrt{n(n+2)}$ *BM where,* n = *number of unpaired electrons*

Ans. **(a)** $[CoF_6]^{3-}$.

F^- is a weak field ligand.



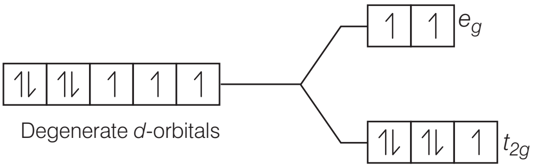
Configuration of $Co^{3+} = 3d^6$ (or $t_{2g}^4\, e_g^2$)

Number of unpaired electrons $(n) = 4$

Magnetic moment $(\mu) = \sqrt{n\,(n+2)} = \sqrt{4\,(4+2)} = \sqrt{24} = 4.9$ BM

$[Co(H_2O)_6]^{2+}$,

H_2O is a weak field ligand.



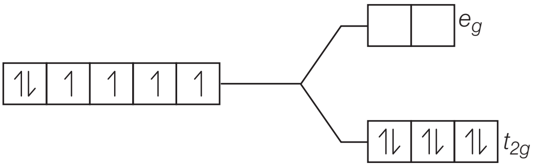
Configuration of $Co^{2+} = 3d^7$(or $t_{2g}^5\, e_g^2$)

Number of unpaired electrons $(n) = 3$

$$\mu = \sqrt{3\,(3+2)} = \sqrt{15} = 3.87 \text{ BM}$$

$[Co(CN)_6]^{3-}$ *i.e.*, Co^{3+}

$\because$ CN is strong field ligand.

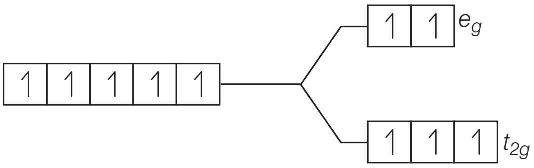


$Co^{3+} = 3d^6$(or $t_{2g}^6 e_g^0$)

There is no unpaired electron, so it is diamagnetic.

$$\mu = 0$$

(b) $[FeF_6]^{3-}$,

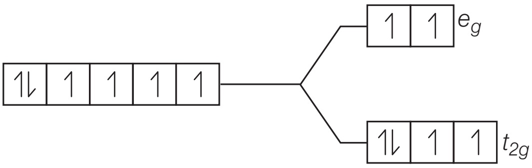


$$Fe^{3+} = 3d^5 \ (\text{or } t_{2g}^3 e_g^2)$$

Number of unpaired electrons, $n = 5$

$$\mu = \sqrt{5\,(5+2)}$$
$$= \sqrt{35} = 5.92 \text{ BM}$$

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

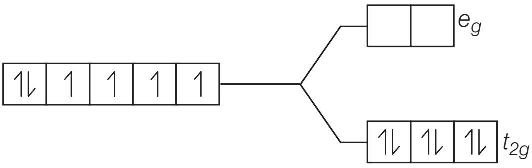


$$Fe^{2+} = 3d^6 \ (\text{or } t_{2g}^4 e_g^2)$$

Number of unpaired electrons, $n = 4$

$$\mu = \sqrt{4\,(4+2)}$$
$$Z = \sqrt{24}$$
$$= 4.98 \text{ BM}$$

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



Since, CN^- is a strong field ligand, all the electrons get paired.

$Fe^{2+} = 3d^6$ (or $t_{2g}^6 e_g^0$)

Because there is no unpaired electron, so it is diamagnetic in nature.

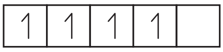
Q. 47 Using valence bond theory, explain the following in relation to the complexes given below

$$[Mn(CN)_6]^{3-}, [Co(NH_3)_6]^{3+}, [Cr(H_2O)_6]^{3+}, [FeCl_6]^{4-}$$

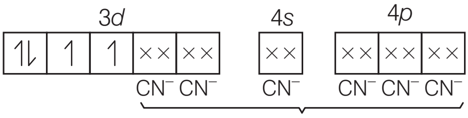
(a) Type of hybridisation
(b) Inner or outer orbital complex
(c) Magnetic behaviour
(d) Spin only magnetic moment value.

Ans. **(a)** $[Mn(CN)_6]^{3-}$

$[Mn^{3+} = 3d^4$



$[Mn(CN)_6]^{3-} =$



(i) d^2sp^3 hybridisation

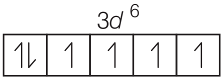
(ii) Inner orbital complex because $(n-1)d$-orbitals are used.

(iii) Paramagnetic, as two unpaired electrons are present.

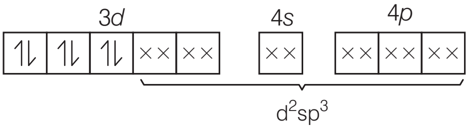
(iv) Spin only magnetic moment $(\mu) = \sqrt{2\,(2+2)} = \sqrt{8} = 2.82$ BM

(b) $[Co(NH_3)_6]^{3+}$

$Co^{3+} = 3d^6\ 4s^0$



$[Co(NH_3)_6]^{3+} =$



(NH_3 pair up the unpaired 3*d* electrons.)

(i) d^2sp^3 hybridisation

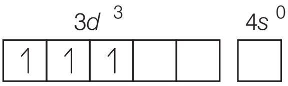
(ii) Inner orbital complex because of the involvement of $(n-1)$ d-orbital in bonding.

(iii) Diamagnetic, as no unpaired electron is present.

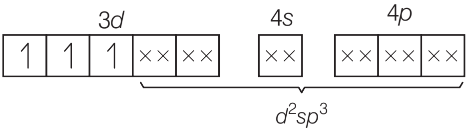
(iv) $\mu = \sqrt{n\,(n+2)} = \sqrt{0\,(0+2)} = 0$ (Zero)

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

$[Cr^{3+} = 3d^3\ 4s^0 =$



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



(i) d^2sp^3 hybridisation

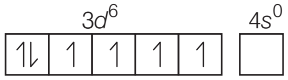
(ii) Inner orbital complex (as $(n-1)d$-orbital take part.)

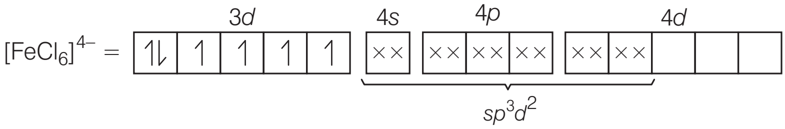
(iii) Paramagnetic (as three unpaired electrons are present.)

(iv) $\mu = \sqrt{n\,(n+2)} = \sqrt{3\,(3+2)} = \sqrt{15} = 3.87$ BM

(d) $[Fe(Cl)_6]^{4-}$

$Fe^{2+} = 3d^6$





(i) sp^3d^2 hybridisation

(ii) Outer orbital complex because *nd*-orbitals are involved in hybridisation.

(iii) Paramagnetic (because of the presence of four unpaired electrons).

(iv) $\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} = 4.9$ BM

Q. 48 $CoSO_4Cl \cdot 5NH_3$ exists in two isomeric forms 'A' and 'B'. Isomer 'A' reacts with $AgNO_3$ to give white precipitate, but does not react with $BaCl_2$. Isomer 'B' gives white precipitate with $BaCl_2$ but does not react with $AgNO_3$. Answer the following questions.

(a) Identify 'A' and 'B' and write their structural formulae.

(b) Name the type of isomerism involved.

(c) Give the IUPAC name of 'A' and 'B'.

Thinking Process

This problem is based on chemical properties of coordination compounds, ionisation isomerism, and nomenclature of coordination compounds.

Ans. '*A*' gives precipitate with $AgNO_3$, so in it Cl is present outside the coordination sphere.

'*B*' gives precipitate with $BaCl_2$, so in it SO_4^{2-} is present outside the coordination sphere.

(a) So, *A* - $[Co(NH_3)_5 SO_4]$ Cl

B-$[Co(NH_3)_5 Cl] SO_4$

(b) Ionisation isomerism (as give different ions when subjected to ionisation.)

(c) [*A*], Pentaamminesulphatocobalt (III) chloride.

[*B*], Pentaamminechloridocobalt (III) sulphate.

Q. 49 What is the relationship between observed colour of the complex and the wavelength of light absorbed by the complex?

Ans. When white light falls on the complex, some part of it is absorbed. Higher the crystal field splitting energy, lower will be the wavelength absorbed by the complex. The observed colour of complex is the colour generated from the wavelength left over.

e.g., if green light is absorbed, the complex appears red.

In terms of crystal field theory, suppose there is an octahedral complex with empty e_g level and unpaired electrons in the t_{2g} level in ground level. If the unpaired electron absorbs light corresponding is blue-green region, it will excite to e_g level and the complex will appear violet in colour.

In absence of ligand, crystal field splitting does not occur and the substance is colourless. *e.g.*, anhydrous $CuSO_4$ is while, but $CuSO_4 \cdot 5H_2O$ is blue in colour.

Q. 50 Why are different colours observed in octahedral and tetrahedral complexes for the same metal and same ligands?

Ans. Extent of splitting of *d*-orbitals is different in octahedral and tetrahedral field. CFSE in octahedral and tetra federal field are closely related as.

$$\Delta_t = \left(\frac{4}{9}\right)\Delta_o$$

where, Δ_t = crystal field splitting energy in tetrahedral field

Δ_0 = crystal field splitting energy in octahedral field

Wavelength of light and CFSE are related to each other by formula

$$\Delta_0 = E = \frac{hc}{\lambda}$$

$$E \propto \frac{1}{\lambda}$$

So, higher wavelength of light is absorbed in octahedral complexes than tetrahedral complexes for same metal and ligands. Thus, different colours are observed.