CHAPTER

9

Coordination Compounds

Syllabus

Coordination compounds- Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT.

CASE STUDY / PASSAGE BASED QUESTIONS

1

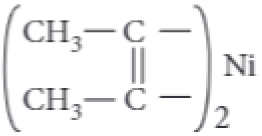
Read the passage given below and answer the following questions :

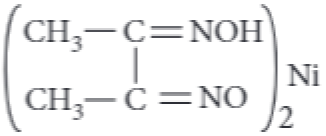
The molecular compounds which are formed from the combination of two or more simple stable compounds and retain their identity in the solid as well as in the dissolved state are called coordination compounds. Their properties are completely different from the constituents. In coordination compounds, the central metal atom or ion is linked to a number of ions or neutral molecules, called ligands, by coordinate bonds. For example, Dimethyl glyoxime (dmg) is a bidendate ligand chelating large amounts of metals.

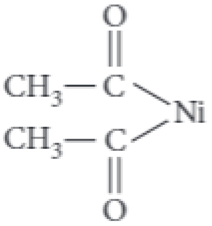
When dimethyl glyoxime is added to alcoholic solution of $NiCl_2$ and ammonium hydroxide is slowly added to it, a rosy red precipitate of a complex is formed.

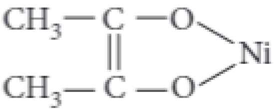
The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The structure of the complex is

(a) 

(b) 

(c) 

(d) 

(ii) Oxidation number of Ni in the given complex is

(a) +3
(b) +1
(c) +2
(d) zero.

(iii) Hybridisation and structure of the complex is

(a) sp^3, tetrahedral
(b) dsp^2, square planar
(c) sp^3, square planar
(d) sp^3d, trigonal bipyramidal.

OR

Which of the following is true about this complex?

(a) It is paramagnetic, containing 2 unpaired electrons.

(b) It is paramagnetic, containing 1 unpaired electron.

(c) It is paramagnetic, containing 4 unpaired electrons.

(d) It is diamagnetic with no unpaired electron.

(iv) Which one will give test for Fe^{3+} ions in the solution?

(a) $[Fe(CN)_6]^{3-}$

(b) $[Fe(CN)_6]^{2-}$

(c) $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$

(d) $Fe_2(SO_4)_3$

2

Read the passage given below and answer the following questions :

Coordination compounds are formulated and named according to the IUPAC system.

Few rules for naming coordination compounds are :

(I) In ionic complex, the cation is named first and then the anion.

(II) In the coordination entity, the ligands are named first and then the central metal ion.

(III) When more than one type of ligands are present, they are named in alphabetical order of preference without any consideration of charge.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The IUPAC name of the complex $[Pt(NH_3)_3Br(NO_2)Cl]Cl$ is

(a) triamminechlorobromonitroplatinum(IV) chloride

(b) triamminebromonitrochloroplatinum(IV) chloride

(c) triamminebromidochloridonitroplatinum(IV) chloride

(d) triamminenitrochlorobromoplatinum(IV) chloride.

(ii) The IUPAC name of $[Ni(CO)_4]$ is

(a) tetracarbonylnickel(II)

(b) tetracarbonylnickel(0)

(c) tetracarbonylnickelate(II)

(d) tetracarbonylnickelate(0).

(iii) As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is

(a) tetraaquadiamminecobalt(II) chloride

(b) tetraaquadiamminecobalt(III) chloride

(c) diamminetetraaquacobalt(II) chloride

(d) diamminetetraaquacobalt(III) chloride.

(iv) Which of the following represents correct formula of dichlorido*bis*(ethane-1, 2-diamine)cobalt(III) ion?

(a) $[CoCl_2(en)]^{2+}$

(b) $[CoCl_2(en)_2]^{2+}$

(c) $[CoCl_2(en)]^{+}$

(d) $[CoCl_2(en)_2]^{+}$

OR

Correct formula of pentaamminenitro-O-cobalt(III) sulphate is

(a) $[Co(NO_2)(NH_3)_5]SO_4$

(b) $[Co(ONO)(NH_3)_5]SO_4$

(c) $[Co(NO_2)(NH_3)_4](SO_4)_2$

(d) $[Co(ONO)(NH_3)_4](SO_4)_2$

3

Read the passage given below and answer the following questions :

Iron forms many complexes in its +2 and +3 oxidation states such as $[Fe(H_2O)_6]^{2+}$ (*A*); $[Fe(CN)_6]^{4-}$ (*B*); $[Fe(H_2O)_6]^{3+}$ (*C*); $[Fe(CN)_6]^{3-}$ (*D*), etc., They exhibit, different magnetic properties and undergo different hybridisation of iron.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following statements is correct?
- (a) (*B*) is paramagnetic while (*C*) is diamagnetic.
- (b) Both (*B*) and (*D*) are outer orbital complexes.
- (c) Both (*A*) and (*C*) are paramagnetic.
- (d) (*A*) is outer orbital complex and (*C*) is inner orbital complex.

(ii) The complex having maximum magnetic moment is
(a) (*A*) (b) (*B*) (c) (*C*) (d) (*D*)

OR

Which of the following does not represent correct configuration of the *d*-orbitals in the given complexes?
(a) (*A*) : $t_{2g}^4 e_g^2$ (b) (*B*) : $t_{2g}^6 e_g^0$ (c) (*C*) : $t_{2g}^4 e_g^1$ (d) (*D*) : $t_{2g}^5 e_g^0$

(iii) The spin only magnetic moment of complexes (*A*), (*B*), (*C*) and (*D*) are respectively (in BM)
(a) $2\sqrt{6}, 0, \sqrt{35}, \sqrt{3}$ (b) $0, 2\sqrt{6}, \sqrt{35}, \sqrt{3}$ (c) $\sqrt{15}, 2\sqrt{6}, \sqrt{3}, 0$ (d) $\sqrt{3}, \sqrt{8}, 0, \sqrt{15}$

(iv) Which of the given complexes are outer orbital complexes?
(a) (*A*) and (*B*) only (b) (*B*) and (*C*) only (c) (*A*) and (*C*) only (d) (*B*) and (*D*) only

4

Read the passage given below and answer the following questions :

To explain bonding in coordination compounds various theories were proposed. One of the important theory was valence bond theory. According to that, the central metal ion in the complex makes available a number of empty orbitals for the formation of coordination bonds with suitable ligands. The appropriate atomic orbitals of the metal hybridise to give a set of equivalent orbitals of definite geometry.

The *d*-orbitals involved in the hybridisation may be either inner *d*-orbitals *i.e.*, $(n - 1)d$ or outer *d*-orbitals *i.e.*, *nd*. For example, Co^{3+} forms both inner orbital and outer orbital complexes, with ammonia it forms $[Co(NH_3)_6]^{3+}$ and with fluorine it forms $[CoF_6]^{3-}$ complex ion.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following is not true for $[CoF_6]^{3-}$?
- (a) It is paramagnetic.
- (b) It has coordination number of 6.
- (c) It is outer orbital complex.
- (d) It involves d^2sp^3 hybridisation.

(ii) $[Cr(H_2O)_6]Cl_3$ (at. no. of Cr = 24) has a magnetic moment of 3.83 B.M. The correct distribution of 3*d*-electrons in the central metal of the complex is
- (a) $3d^1_{xy}, 3d^1_{x^2-y^2}, 3d^1_{yz}$
- (b) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{zx}$
- (c) $3d^1_{xy}, 3d^1_{zy}, 3d^1_{z^2}$
- (d) $3d^1_{x^2-y^2}, 3d^1_{z^2}, 3d^1_{xz}$

OR

Which of the following is true for $[Co(NH_3)_6]^{3+}$?

(a) It is an octahedral, dimagnetic and outer orbital complex.
(b) It is an octahedral, paramagnetic and outer orbital complex.
(c) It is an octahedral, paramagnetic and inner orbital complex.
(d) It is an octahedral, dimagnetic and inner orbital complex.

(iii) The paramagnetism of $[CoF_6]^{3-}$ is due to

(a) 3 electrons (b) 4 electrons (c) 2 electrons (d) 1 electron.

(iv) Which of the following is an inner orbital or low spin complex?

(a) $[Ni(H_2O)_6]^{3+}$ (b) $[FeF_6]^{3-}$ (c) $[Co(CN)_6]^{3-}$ (d) $[NiCl_4]^{2-}$

5

Read the passage given below and answer the following questions :

Valence bond theory considers the bonding between the metal ion and the ligands as purely covalent. On the other hand, crystal field theory considers the metal-ligand bond to be ionic arising from electrostatic interaction between the metal ion and the ligands. In coordination compounds, the interaction between the ligand and the metal ion causes the five *d*-orbitals to split-up. This is called crystal field splitting and the energy difference between the two sets of energy level is called crystal field splitting energy. The crystal field splitting energy (Δ_o) depends upon the nature of the ligand. The actual configuration of complexes is divided by the relative values of Δ_o and *P* (pairing energy).

If $\Delta_o < P$, then complex will be high spin.
If $\Delta_o > P$, then complex will be low spin.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following ligand has lowest Δ_o value?

(a) CN^- (b) CO (c) F^- (d) NH_3

(ii) The crystal field splitting energy for octahedral (Δ_o) and tetrahedral (Δ_t) complex is related as

(a) $\Delta_t = \frac{1}{2}\Delta_o$ (b) $\Delta_t = \frac{4}{9}\Delta_o$ (c) $\Delta_t = \frac{3}{5}\Delta_o$ (d) $\Delta_t = \frac{2}{5}\Delta_o$

(iii) On the basis of crystal field theory, the electronic configuration of d^4 in two situations : (i) $\Delta_o > P$ and (ii) $\Delta_o < P$ are

	(i)	(ii)
(a)	$t_{2g}^4 e_g^0$	$t_{2g}^3 e_g^1$
(b)	$t_{2g}^3 e_g^1$	$t_{2g}^4 e_g^0$
(c)	$t_{2g}^3 e_g^1$	$t_{2g}^3 e_g^1$
(d)	$t_{2g}^4 e_g^0$	$t_{2g}^4 e_g^0$

(iv) Using crystal field theory, calculate magnetic moment of central metal ion of $[FeF_6]^{4-}$.

(a) 1.79 B.M. (b) 2.83 B.M. (c) 3.85 B.M. (d) 4.9 B.M.

OR

Electronic configuration of *d*-orbitals in $[Ti(H_2O)_6]^{3+}$ ion in an octahedral crystal field is

(a) $t_{2g}^1 e_g^0$ (b) $t_{2g}^2 e_g^0$ (c) $t_{2g}^0 e_g^1$ (d) $t_{2g}^1 e_g^1$

6

Read the passage given below and answer the following questions :

Metal carbonyl is an example of coordination compounds in which carbon monoxide (CO) acts as ligand. These are also called homoleptic carbonyls. These compounds contain both σ and π character. Some carbonyls have metal-metal bonds. The reactivity of metal carbonyls is due to (i) the metal centre and (ii) the CO ligands. CO is capable of accepting an appreciable amount of electron density from the metal atom into their empty π or π^* orbitals. These types of ligands are called π-accepter or π-acid ligands. These interactions increases the Δ_o value.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) What is the oxidation state of metal in $[Mn_2(CO)_{10}]$?
(a) +1 (b) –1 (c) +2 (d) 0

(ii) Among the following metal carbonyls, the C – O bond order is lowest in
(a) $[Mn(CO)_6]^+$ (b) $[Fe(CO)_5]$ (c) $[Cr(CO)_6]$ (d) $[V(CO)_6]^-$

OR

Which of the following can be reduced easily?
(a) $V(CO)_6$ (b) $Mo(CO)_6$ (c) $[Co(CO)_4]^-$ (d) $Fe(CO)_5$

(iii) The oxidation state of cobalt in $K[Co(CO)_4]$ is
(a) +1 (b) +3 (c) –1 (d) 0

(iv) Structure of decacarbonyl manganese is
(a) trigonal bipyramidial (b) octahedral (c) tetrahedral (d) square pyramidal.

7

Read the passage given below and answer the following questions :

Werner, a Swiss chemist in 1892 prepared and characterised a large number of coordination compounds and studied their physical and chemical behaviour. He proposed that, in coordination compounds, metals possess two types of valencies, *viz.* primary valencies, which are normally ionisable and secondary valencies which are non-ionisable. In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess of $AgNO_3$ solution in cold, but some remained in solution. The number of ions furnished by a complex in a solution can be determined by precipitation reactions. The measurement of molar conductance of solutions of coordination compounds helps to estimate the number of ions furnished by the compound in solution.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) **Assertion :** The complex $[Co(NH_3)_3Cl_3]$ does not give precipitate with silver nitrate solution.
Reason : The given complex is non-ionisable.

(ii) Assertion : The complex $[Co(NH_3)_4Cl_2]Cl$ gives precipitate corresponding to 2 mol of AgCl with $AgNO_3$ solution.
Reason : It ionises as $[Co(NH_3)_4Cl_2]^+ + Cl^-$.

OR

Assertion : $CoCl_3{\cdot}4NH_3$ gives 1 mol of AgCl on reacting with $AgNO_3$, its secondary valency is 6.
Reason : Secondary valency corresponds to coordination number.

(iii) Assertion : 1 mol of $[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$ will give 1 mol of AgCl on treating with $AgNO_3$.
Reason : Cl^- ions satisfying secondary valanceis will not be precipitated.

(iv) Assertion : $CoCl_3{\cdot}3NH_3$ is not conducting while $CoCl_3{\cdot}5NH_3$ is conducting.
Reason : The complex of $CoCl_3{\cdot}3NH_3$ is $[CoCl_3(NH_3)_3]$ while that of $CoCl_3{\cdot}5NH_3$ is $[CoCl(NH_3)_5]Cl_2$.

8

Read the passage given below and answer the following questions :

Arrangement of ligands in order of their ability to cause splitting (Δ) is called spectrochemical series. Ligands which cause large splitting (large Δ) are called strong field ligands while those which cause small splitting (small Δ) are called weak field ligands. When strong field ligands approach metal atom/ion, the value of Δ_o is large, so that electrons are forced to get paired up in lower energy t_{2g} orbitals. Hence, a low-spin complex is resulted from strong field ligand. When weak field ligands approach metal atom/ion, the value of Δ_o is small, so that electrons enter high energy e_g orbitals rather than pairing in low energy t_{2g} orbitals. Hence, a high-spin complex is resulted from weak field ligands. Strong field ligands have tendency to form inner orbital complexes by forcing the electrons to pair up. Whereas weak field ligands have tendency to form outer orbital complex because inner electrons generally do not pair up.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) Assertion : In tetrahedral coordination entity formation, the *d* orbital splitting is inverted and is smaller as compared to the octahedral field splitting.
Reason : Spectrochemical series is based on the absorption of light by complexes with different ligands.

(ii) Assertion : In high spin situation, configuration of d^5 ions will be $t_{2g}^3\, e_g^2$.
Reason : In high spin situation, pairing energy is less than crystal field energy.

OR

Assertion : F^- ion is a weak field ligand and forms outer orbital complex.
Reason : F^- ion cannot force the electrons of d_{z^2} and $d_{x^2-y^2}$ orbitals of the inner shell to occupy d_{xy}, d_{yz} and d_{zx} orbitals of the same shell.

(iii) Assertion : The crystal field model is successful in explaining the formation, structures, colour and magnetic properties of coordination compounds.
Reason : In spectrochemical series, ligands are arranged in a series of increasing field strength.

(iv) Assertion : NF_3 is a weaker ligand than $N(CH_3)_3$.
Reason : NF_3 ionizes to give F^- ions in aqueous solution.

9

Read the passage given below and answer the following questions :

Ligands are atoms or ions which can donate electrons to the central atoms. Ligands can be monodentate, bidentate or polydentate as well. Few ligands can coordinate with the central atom through more than one site, these are called ambidentate ligands. When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a chelating ligand.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Glycinate ion is an example of monodentate ligand.
Reason : Glycinate contains N and O as donor atoms.

OR

Assertion : EDTA forms complex with divalent metals of 3*d*-series in the ratio of 1 : 1.
Reason : EDTA has 4 —COOH groups.

(ii) **Assertion :** Oxalate ion is a bidentate ligand.
Reason : Oxalate ion has two donor atoms.

(iii) **Assertion :** A chelating ligand must possess two or more lone pairs at such a distance that it may form suitable strain free 5 and 6 membered rings with the metal ion.
Reason : $H_2N–NH_2$ is a chelating ligand.

(iv) **Assertion :** In Zeise's salt coordination number of Pt is five.
Reason : Ethene is a monodentate ligand.

10

Read the passage given below and answer the following questions :

For understanding the structure and bonding in transition metal complexes, the magnetic properties are very helpful. Low spin complexes are generally diamagnetic because of pairing of electrons, whereas high spin complexes are usually paramagnetic because of presence of unpaired electrons. Larger the number of unpaired electrons, stronger will be the paramagnetism. However magnetic behaviour of a complex can be confirmed from magnetic moment measurement. Magnetic moment $\mu = \sqrt{n(n+2)}$ B.M. where n = number of unpaired electrons. Greater the number of unpaired electrons, more will be the magnetic moment.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Both $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ have same magnetic moment.
Reason : Number of unpaired electrons in Cr^{2+} and Fe^{2+} are same.

(ii) **Assertion :** $[Fe(H_2O)_5NO]SO_4$ is paramagnetic.
Reason : The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons.

(iii) **Assertion :** $[Co(en)_3]^{3+}$ is paramagnetic.
Reason : It is an inner orbital complex.

(iv) **Assertion :** $[Ni(CO)_4]$ is diamagnetic and tetrahedral in shape.
Reason : $[Ni(CO)_4]$ contains no unpaired electrons and involves dsp^2 hybridisation.

OR

Assertion : $[Ni(CN)_4]^{2-}$ is diamagnetic complex.
Reason : It involves dsp^2 hybridisation and there is no unpaired electron.

ASSERTION & REASON

In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

11. **Assertion :** $[Fe(CN)_6]^{3-}$ has d^2sp^3 type hybridisation.
Reason : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.

12. **Assertion :** The ligands nitro and nitrito are called ambidentate ligands.
Reason : An ambidentate ligand can attach to metal through two different atoms.

13. **Assertion :** Thiocarbonyl is a neutral ligand.
Reason : Thiocarbonyl has three donor atoms but behaves as a bidentate ligand.

14. **Assertion :** The ligand N_3^- is named as nitride.
Reason : N_3^- is derived from HN_3.

15. **Assertion :** $[CrCl_2(H_2O)_4]NO_3$ is dichlorotetraaquachromium(III) nitrate.
Reason : In writing the name of the complex cation is written first followed by the anion.

16. **Assertion :** $[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic.
Reason : $[Fe(CN)_6]^{3-}$ has +3 oxidation state while $[Fe(CN)_6]^{4-}$ has +2 oxidation state.

17. **Assertion :** $[Cu(NH_3)_4]^{2+}$ is coloured while $[Cu(CN)_4]^{3-}$ ion is colourless.
Reason : $[Cu(NH_3)_4]^{2+}$ has dsp^2 hybridisation.

18. **Assertion :** $[Al(NH_3)_6]^{3+}$ does not exist in aqueous solution.
Reason : NH_3 is a neutral ligand.

19. **Assertion :** $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.
Reason : $d-d$ transition is not possible in $[Sc(H_2O)_6]^{3+}$.

20. **Assertion :** Low spin complexes have less number of unpaired electrons.
Reason : $[FeF_6]^{3-}$ is a low spin complex.

21. **Assertion :** $[Cr(NH_3)_6]^{3+}$ is paramagnetic.
Reason : $[Cr(NH_3)_6]^{3+}$ shows d^2sp^3 hybridisation.

22. **Assertion :** $[Ni(CN)_4]^{2-}$ has square planar and $[NiCl_4]^{2-}$ has tetrahedral shape.
Reason : $[Ni(CN)_4]^{2-}$ is diamagnetic while $[NiCl_4]^{2-}$ is paramagnetic.

23. **Assertion :** All the octahedral complexes of Ni^{2+} must be outer orbital complexes.
Reason : Outer orbital octahedral complexes are given by weak ligands.

24. **Assertion :** Ethylenediaminetetraacetate ion forms an octahedral complex with the metal ion.
Reason : It has six donor atoms which coordinate simultaneously to the metal ion.

25. **Assertion :** Aqueous solution of potassium ferrocyanide does not give the test of iron (II).
Reason : Potassium ferrocyanide is not poisonous like potassium cyanide.

26. **Assertion :** $[Pt(NH_3)_2Cl_2]$ is square planar.
Reason : The oxidation state of platinum is + 2.

27. **Assertion :** The $[Ni(en)_3]Cl_2$ (*en* = ethylenediamine) has lower stability than $[Ni(NH_3)_6]Cl_2$.
Reason : In $[Ni(en)_3]Cl_2$ the geometry of Ni is octahedral.

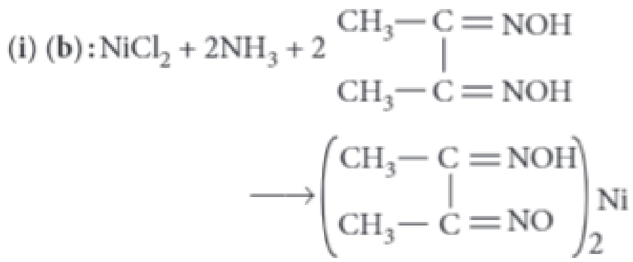
28. **Assertion :** $Cu(OH)_2$ is soluble in NH_4OH but not in NaOH.
Reason : $Cu(OH)_2$ forms a soluble complex with NH_3.

29. **Assertion :** The second and third transition series elements have lesser tendency to form low spin complex as compared to the first transition series.
Reason : The CFSE (Δ_o) is more for 5*d* and 4*d*.

30. **Assertion :** Zeise's salt is a π-bonded organometallic compound.
Reason : The oxidation number of platinum in Zeise's salt is +2.

HINTS & EXPLANATIONS

1. (i) **(b) :**



$$NiCl_2 + 2NH_3 + 2\begin{matrix}CH_3-C=NOH\\ |\\ CH_3-C=NOH\end{matrix} \longrightarrow \left(\begin{matrix}CH_3-C=NOH\\ |\\ CH_3-C=NO\end{matrix}\right)_2 Ni$$

(ii) **(c)**

(iii) **(b)**

OR

(d) : It has no unpaired electrons hence, it is diamagnetic.

(iv) **(d):** (a) and (b) are coordination compounds hence cannot give free Fe^{2+} or Fe^{3+} ions in solution. (c) and (d) represent simple compounds hence are free to give ions in solution, but only $Fe_2(SO_4)_3$ contains Fe^{3+} ions. $(NH_4)_2SO_4\cdot FeSO_4\cdot 6H_2O$ contains Fe^{2+} ions not Fe^{3+} ions.

2. (i) **(c) :** Ligands are named in alphabetical order irrespective of their charge.

(ii) **(b)**

(iii) **(d)**

(iv) **(d)**

OR

(b) : Ligand NO_2^- is ambidentate ligand as it can donate electrons through either nitrogen (NO_2) or oxygen (ONO).

3. (i) **(c) :** (*A*) : sp^3d^2 hybridisation (outer orbital)
No. of unpaired electrons = 4
(*B*) : d^2sp^3 hybridisation (inner orbital)
No. of unpaired electrons = 0
(*C*) : sp^3d^2 hybridisation (outer orbital)
No. of unpaired electrons = 5
(*D*) : d^2sp^3 hybridisation (inner orbital)
No. of unpaired electron = 1

(ii) **(c) :** It has 5 unpaired electrons.

OR

(c) : As H_2O is a weak ligand so, it should be $t_{2g}^3 e_g^2$

(iii) **(a) :** Magnetic moments of (*A*), (*B*), (*C*) and (*D*) are respectively

$$\sqrt{4(4+2)}, 0, \sqrt{5(5+2)}, \sqrt{1(1+2)}$$

(iv) **(c)**

4. (i) **(d):** It involves sp^3d^2 hybridisation and not d^2sp^3.

(ii) (b) : Magnetic moment of 3.83 B.M. suggests that it has 3 unpaired electrons,

$\therefore \quad n = 3$ *i.e.*, $Cr^{3+} : 3d^3$

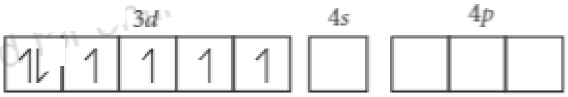
It involves d^2sp^3 hybridisation so correct distribution of electrons is $3d^1_{xy}, 3d^1_{yz}, 3d^1_{zx}$.

OR

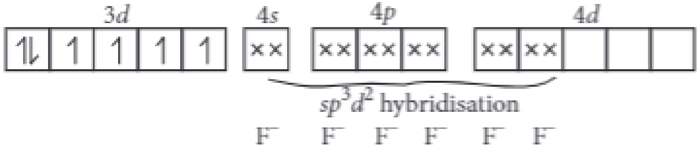
(d) : $[Co(NH_3)_6]^{3+}$ is d^2sp^3 hybridised with all electrons paired hence, it is diamagnetic and inner orbital complex.

(iii) (b):

Co^{3+}:



$[CoF_6]^{3-}$:



(iv) (c) : Inner orbital complexes are formed with strong ligands as they force electrons to pair up and hence the complex will be either diamagnetic or will have less number of unpaired electrons.

5. (i) (c) : Spectrochemical series :

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < NO_2^- < CN^- < CO$

(ii) (b)

(iii) (a) : When $\Delta_o > P$, the electrons paired up in the t_{2g} level rather than going to the e_g level, so

when $\Delta_o > P : t_{2g}^4 e_g^0$

and $\Delta_o < P : t_{2g}^3 e_g^1$

(iv) (d): $Fe^{2+} : 3d^6 \Rightarrow t_{2g}^4 e_g^2$

(Since, F^- is a weak field ligand)

Hence four unpaired electrons are present.

Magnetic moment (μ)

$$= \sqrt{n(n+2)} = \sqrt{4(4+2)} = 4.9 \text{ B.M.}$$

OR

(a) : In $[Ti(H_2O)_6]^{3+}$, Ti is in +3 oxidation state and there is only one electron in *d*-orbital.

6. (i) (d): Oxidation state of Mn in $[Mn_2(CO)_{10}]$ is zero.

(ii) (d): In $[V(CO)_6]^-$, the anionic carbonyl complex can delocalise more electron density to antibonding π-orbital ($d\pi$-$p\pi$ back bonding) of CO and thus lowers the bond order.

OR

(a) : $V(CO)_6$ can be easily reduced to $[V(CO)_6]^-$. $V(CO)_6$ has a total of 17 bonding electrons, hence it is very reactive and unstable. $[V(CO)_6]^-$ on the other hand has complete set of 18 bonding electrons as an electron is added into the bonding orbital when $V(CO)_6$ gets reduced to $[V(CO)_6]^-$. All others have 18 bonding electrons.

(iii) (c) : $K[Co(CO)_4]$

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

(iv) (d): $Mn_2(CO)_{10}$ is made up of two square pyramidal $Mn(CO)_5$ units joined by Mn – Mn bond.

7. (i) (a)

(ii) (d): $[Co(NH_3)_4Cl_2]Cl + AgNO_3 \longrightarrow [Co(NH_3)_4Cl_2]^+ + AgCl\downarrow$

Thus it gives precipitate of 1 mol of AgCl.

OR

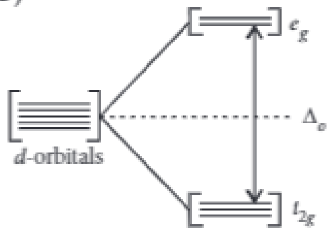
(b) : $CoCl_3 \cdot 4NH_3$ gives 1 mol AgCl on reaction with $AgNO_3$, hence the complex can be represented as $[CoCl_2(NH_3)_4]Cl$.

(iii) (a): The Cl^- ions outside the coordination sphere can only be precipitated.

(iv) (a)

8. (i) (b)

(ii) (c) :



d-orbital splitting in an octahedral crystal field

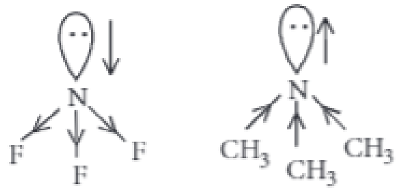
$\therefore$ In high spin situation, $\Delta_o < P$, in d^5 configuration, 4th and 5th electron are added to e_g rather than t_{2g}. So, configuration of d^5 ion will be $t_{2g}^3 e_g^2$.

OR

(a)

(iii) (b)

(iv) (c) : Due to high electronegativity of F-atoms, the lone pair of N-atom in NF_3 molecule cannot be ligated easily. Whereas in $N(CH_3)_3$, CH_3 group is a electron releasing group, thus lone pair of N-atom in $N(CH_3)_3$ molecule can be ligated easily.



Except, nitrogen fluoride, all other halides hydrolyse in water.

9. **(i) (d):** Glycinate ion is an example of bidentate ligand. It contains N and O as donor atoms.

OR

(b) : EDTA is a hexadentate ligand. It forms complex with central metal in the ratio 1 : 1 in which it binds through two nitrogen atoms and four oxygen atoms.

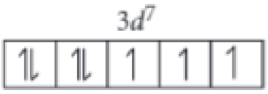
(ii) (a)

(iii) (c) : $H_2N - NH_2$ does not act as chelating ligand. The coordination by hydrazine leads to a three member highly unstable strained ring and thus it does not act as chelating agent.

(iv) (d): In Zeise's salt, coordination no. of Pt is 4. Ethylene is a monodentate ligand.

10. **(i) (a):** Spin only magnetic moment, $\mu = \sqrt{n(n+2)}$ where n = number of unpaired electrons.
As the number of unpaired electrons in Cr^{2+} ([Ar]$3d^4$) and Fe^{2+} ([Ar]$3d^6$) are same, hence $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ will have same magnetic moment.
(ii) (a): Fe^+ : [Ar] $3d^6\ 4s^1$

When the weak field ligand H_2O and strong field ligand NO^+ attack, the configuration changes as follows : Fe^+ : [Ar] $3d^7\ 4s^0$

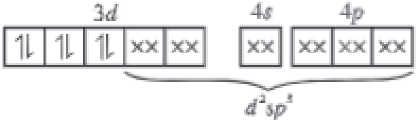


$\therefore$ Fe^+ has 3 unpaired electrons.

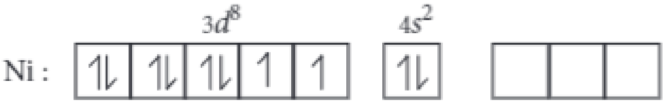
(iii) (d) : Co^{3+}

In presence of strong ethylenediamine ligand the electrons get paired.

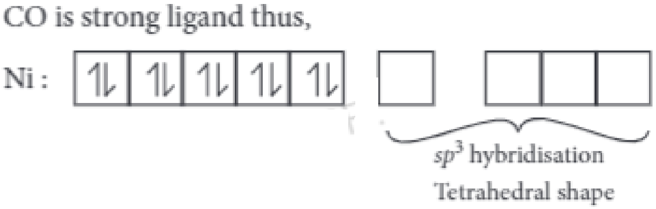
$[Co(en)_3]^{3+}$



Thus inner orbital complex with no unpaired electrons.
(iv) (c) : $[Ni(CO)_4]$ contains Ni(0).



CO is strong ligand thus,



OR

(a)

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

12. **(a) :** When a monodentate ligand has two possible donor atoms and attached in two ways to the central metal atom then that ligand is called ambidentate ligand. This leads to linkage isomerism.

13. **(c) :** Thiocarbonyl (CS) has one donor atoms.

14. **(d):** N_3^- is named as azido. It is derived from HN_3.

15. **(d):** Correct IUPAC name is tetraaquadichloridochromium(III) nitrate.

16. **(b):** $[Fe(CN)_6]^{3-}$ has one unpaired electron, hence it shows paramagnetic nature while $[Fe(CN)_6]^{4-}$ possesses no unpaired electron and thus shows diamagnetic nature.

17. **(b):** $[Cu(NH_3)_4]^{2+}$ is coloured due to the presence of unpaired electron whereas $[Cu(CN)_4]^{3-}$ has no unpaired electron.

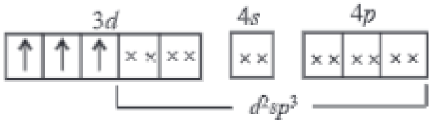
18. **(b):** The complex ion $[Al(NH_3)_6]^{3+}$ undergoes the change into new complex ion $[Al(H_2O)_6]^{3+}$ in aqueous medium due to higher heat of hydration of aluminium ion on account of its small size.

$$[Al(NH_3)_6]^{3+} + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 6NH_3$$

19. **(a) :** $[Sc(H_2O)_6]^{3+}$ has no unpaired electron in its d subshell and thus $d - d$ transition is not possible whereas $[Ti(H_2O)_6]^{3+}$ has one unpaired electron in its d-subshell which gives rise to $d - d$ transition to impart colour.

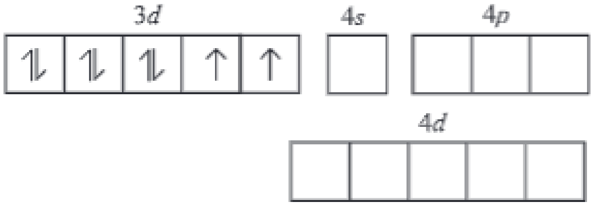
20. **(c) :** $[FeF_6]^{3-}$ is a high spin complex since F^- is a weak field ligand.

21. **(b):** The Cr^{3+} ion has three unpaired electrons. It has d^2sp^3 hybridisation and it is paramagnetic.
Cr^{3+} : $3d^3$



22. (b): In $[NiCl_4]^{2-}$, the Cl^- ligands present in the complex ion are less basic than CN^-, as such no pairing of electrons in the $3d$-subshell takes place. This results in sp^3 hybridisation and the complex so formed is tetrahedral. On the other hand, in case of $[Ni(CN)_4]^{2-}$, the CN^- ligands present in the complex ion are more basic than Cl^-, as such pairing of electrons can take place in the $3d$-subshell. Due to pairing of electrons in $3d$-subshell, one of the d-orbital becomes vacant. This results in dsp^2 hybridisation and the complex so formed is square planar and diamagnetic.

23. (b): Ni^{2+} configuration



During rearrangement only one $3d$-orbital may be made available by pairing the electrons. Thus, inner d^2sp^3 hybridisation is not possible. So, only sp^3d^2 (outer) hybridisation can occur.

24. (a)

25. (b): Being a complex salt, potassium ferrocyanide ionises to $4K^+$ and $[Fe(CN)_6]^{4-}$ ions. Absence of Fe(II) does not give the test of iron.

26. (b): The outer electronic configuration of platinum in ground state is $5d^9 6s^1$. The Pt^{2+} ion formed by the loss of two electrons has outer electronic configuration of $5d^8$. In the presence of strong ligands (NH_3 molecules) two unpaired electrons in the $5d$-subshell pair up. This is followed by dsp^2 hybridisation resulting in the formation of four hybridised vacant orbitals which accommodate four pairs of electrons from four ligands (two from ammonia and two from Cl^-). As such the resulting complex is square planar.

27. (d): $[Ni(en)_3]Cl_2$ is a chelating compound and chelated complexes are more stable than similar complexes with unidentate ligands as dissociation of the complex involves breaking of two bonds rather than one.

In $[Ni(en)_3]Cl_2$, Ni with d^8 configuration shows octahedral geometry.

28. (a)

29. (d) : $4d$ and $5d$ elements have greater tendency to form low spin complex (allows better pairing of electrons) in comparison to $3d$ because the difference in energy of t_{2g} and e_g (CFSE, Δ_o) increases in $4d$ and $5d$.

30. (b): In these complexes, the metal and ligand form a bond that involves the π-electrons of the ligand and so it is a π-bonded organometallic compound.