

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 AgNO₃ 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 $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ does not give precipitate with silver nitrate solution.
Reason : The given complex is non-ionisable.
- (ii) **Assertion :** The complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ gives precipitate corresponding to 2 mol of AgCl with AgNO₃ solution.
Reason : It ionises as $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Cl}^-$.

OR

- Assertion :** $\text{CoCl}_3 \cdot 4\text{NH}_3$ gives 1 mol of AgCl on reacting with AgNO₃, its secondary valency is 6.
Reason : Secondary valency corresponds to coordination number.
- (iii) **Assertion :** 1 mol of $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ will give 1 mol of AgCl on treating with AgNO₃.
Reason : Cl⁻ ions satisfying secondary valence will not be precipitated.
 - (iv) **Assertion :** $\text{CoCl}_3 \cdot 3\text{NH}_3$ is not conducting while $\text{CoCl}_3 \cdot 5\text{NH}_3$ is conducting.
Reason : The complex of $\text{CoCl}_3 \cdot 3\text{NH}_3$ is $[\text{CoCl}_3(\text{NH}_3)_3]$ while that of $\text{CoCl}_3 \cdot 5\text{NH}_3$ is $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$.

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.

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- (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.

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.

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- (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.

A transition metal complex consists of a central metal ion surrounded by ligands. A **ligand** is an ion or molecule with a lone pair of electrons that forms a coordinate bond with a transition metal ion.

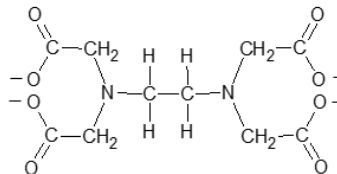
1. For each of the ligands below, **mark** on any lone pairs which are able to form coordinate bonds, and **identify** the ligand as *unidentate* (can form one coordinate bond), *bidentate* (can form two coordinate bonds) or *multidentate* (can form three or more coordinate bonds). (4 marks)

(a)



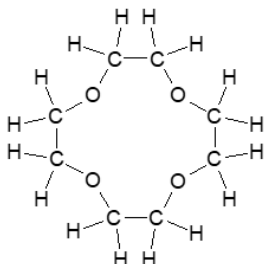
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(b)



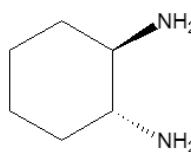
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(c)



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(d)



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For each of the complexes listed (a)-(c) below, draw a 3-dimensional representation of its structure, and identify the name given to its shape.

(a) $[\text{CoCl}_4]^{2-}$

(b) $[\text{Fe}(\text{en})_3]^{2+}$

(c) $[\text{PtCl}_2(\text{NH}_3)_2]$

(*en* = $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$)



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(6 marks)