

[This question paper contains 4 printed pages.]

Sr. No. of Question Paper : 8466

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Roll No.....

Unique Paper Code : 217501

Name of the Paper : CHHT-511 : Inorganic Chemistry – IV

Name of the Course : B.Sc. (H) CHEMISTRY, Part III
(Admission of 2010 and onwards)

Semester : V

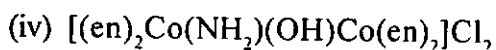
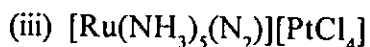
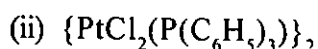
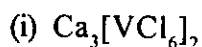
Duration : 3 Hours

Maximum Marks : 75

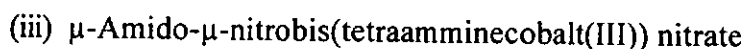
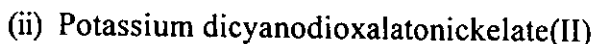
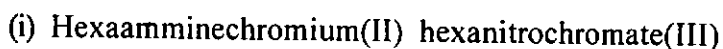
Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Do any **five** questions.
3. **All** questions carry equal marks.

1. (a) Name the following complexes according to the IUPAC system of nomenclature (**any three**) :



- (b) Write the formulae of the following complexes (**any two**).



- (c) A solution containing 2.665g of $\text{CrCl}_3 \cdot 6\text{NH}_3$ was passed through a cation exchanger. The chloride ion solution thus obtained gave 2.87g AgCl precipitate with AgNO_3 solution. Determine the structural formula of the complex and draw its structure in accordance with Werner's theory.

(Mol. wt. of $\text{CrCl}_3 \cdot 6\text{NH}_3 = 260.35$, $\text{Ag} = 108$ and $\text{Cl} = 35.45$)

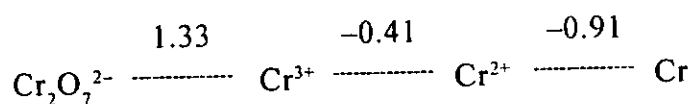
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- (d) Two compounds have the empirical formula $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$. In aqueous solution, one of these does not conduct electricity while the other does. Write their probable formulae. (6,4,3,2)
2. (a) What is the difference between an ambidentate and a bidentate ligand? Give one example of each.
- (b) Name the type of isomerism in the following pairs of isomers :
- (i) $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_6]$ and $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$
- (ii) $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ and $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$
- (c) The complex $[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2]$ exists in two isomeric forms α and β . The α -form reacts with oxalic acid to form $[\text{Pt}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$ whereas β -form gives $[\text{Pt}(\text{NH}_3)_2(\text{C}_2\text{O}_4\text{H})_2]$. Give the structures of α and β forms. Explain what physical method can be used to differentiate between the two forms.
- (d) Draw the structures of all possible stereoisomers of $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$. (4,4,4,3)
3. (a) Using the valence bond method, a) assign the electronic configuration to the central metal atom, b) predict the type of hybridization involved, c) geometry, and d) the magnetic moment (in Bohr magnetons) for: $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{FeCl}_4]^-$.
- (b) Which of the following complexes are expected to be labile and which one inert? Give reasons.
 $[\text{V}(\text{NH}_3)_6]^{3+}$, $[\text{Cr}(\text{CN})_6]^{3-}$ and $[\text{CrCl}_6]^{4-}$.
- (c) What is crystal field splitting? The CFS in tetrahedral complexes is always less than the CFS in octahedral complexes. Explain. (6,6,3)
4. (a) For the Mn^{3+} ion, the mean pairing energy, P , is found to be $28,000 \text{ cm}^{-1}$. The Δ_0 values for the complex ions $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Mn}(\text{CN})_6]^{3-}$ are $21,000 \text{ cm}^{-1}$ and $38,500 \text{ cm}^{-1}$ respectively. Calculate the CFSE for the complexes in configurations corresponding to high-spin and low-spin states and predict the possible stable configurations. Give the electron compositions of the t_{2g} and e_g levels of each.

- (b) Arrange the following complex ions in the order of increasing Δ_0 giving reasons :
- $[M(NH_3)_6]^{2+}$, $[M(CN)_6]^{4-}$, $[MCl_6]^{4-}$ and $[M(en)_3]^{2+}$.
- (c) Solutions of the complexes $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$ are coloured, one is pink and the other is blue. Assign the colour to each one giving explanation.
- (d) Why do d-orbitals of the metal cation split when ligands approach towards it ?
(6,3,3,3)
5. (a) Define Jahn-Teller theorem. Chromium(II) fluoride and manganese(II) fluoride both have a central metal ion surrounded by six fluoride ligands. Whereas the Mn-F bond lengths are all equal, two of the Cr-F bonds are longer than the remaining four. Explain giving energy level diagram ?
- (b) Which complex ion is more stable $[Co(en)_3]^{3+}$ or $[Co(dien)_2]^{3+}$ and why ?
(en = ethylenediamine; dien = diethylenetriamine)
- (c) On the basis of crystal field theory, explain the variation in the lattice energy of divalent metal halides of first transition series in an octahedral environment.
- (d) On the basis of the molecular orbital theory, explain the order of Δ_0 for octahedral complexes having the following ligands: F^- , H_2O and CO .
(6,3,3,3)
6. Explain giving reasons any five of the following observations :
- (a) Transition metals usually show variable oxidation states.
- (b) Zr and Hf have almost similar properties.
- (c) Lanthanides and actinides show sharp line-like bands in the absorption spectra in contrast to transition elements.
- (d) Actinides exhibit other than +3 oxidation states.
- (e) Among the lanthanide ions the magnetic moment of only Gd^{3+} is in agreement with the moment calculated from spin only formula.
- (f) Fe_3O_4 is inverse spinel while Mn_3O_4 is a normal spinel. (3×5)

7. (a) A blackish brown coloured solid (A) when fused with alkali metal hydroxides in presence of air produces a dark green compound (B), which on electrolytic oxidation in alkaline medium gives a dark purple coloured solution of compound (C). Compound (C) on treatment with concentrated H_2SO_4 gives another green solution (D). Identify (A), (B), (C) and (D) and give the sequence of reactions involved.

- (b) Given below are the Latimer diagram for Cr in acidic medium :



Answer the following questions (Any three) :

- (i) Write half reaction for the conversion of $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$
 - (ii) Is there any tendency of Cr^{2+} to reduce to Cr? Give reasons.
 - (iii) Calculate skip step emf for $\text{Cr}^{3+} \rightarrow \text{Cr}$ change.
 - (iv) How a state which undergoes disproportionation is shown in Ebsworth diagram?
- (c) Giving chemical equations, explain the following (Any two) :
- (i) Sodium ferrocyanide is treated with 30% nitric acid solution.
 - (ii) Amphoteric behaviour of vanadium (V) oxide.
 - (iii) TiCl_4 is treated with alcohols in the presence of NH_3 . (6,6,3)