(b) CN^- is a stronger ligand than Cl^- 5,5,5

7. (i) Describe the polarisation theory to explain the trans effect.

(ii) The experimentally detemined lattice energy for MnO agree with the calculated value; however, for FeO and CoO, the experimentally determined lattice energy values are higher than the calculated values. Why ?

(iii) For the complex $[Cr(H_2O)_6]^{2+}$ the mean pairing energy P = 23500cm^{-1} and magnitude of Δ_0 = 13900 cm^{-1} 5,5,5

(a) Will the complex exist in a high or low Spin arrangement ?

(b) Write the electronic configuration of the complex ion.

(c) Calculate CFSE of the complex in kJ mol^{-1}.

(d) Will the complex be labile or inert ?

(e) Will it have a regular geometry or a distorted geometry ?

8. (i) A complex is prepared by mixing $CoCl_3$ and NH_3 in the molar ratio of 1:4 A0.01 molal solution of this complex was found to freeze at – 0.0372°C, What is the formula of the complex and expected range of conductivity ? Given that the molal depression constant of water Kr = 1.86 °C/m.

(ii) Taking suitable example, explain the macrocyclic effect on the thermodynamic stability of complexes.

(iii) A metal ion forms three complexes. $[M(Br)_6]^{4-}$, $[M(CN)_6]^{4-}$ and $[M(H_2O)_6]^{2+}$: The colours of the complexes are red green and blue, but not necessarily in the same order. Match the complexes with the appropriate colour and explain. 5,5,5

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[This question paper contains 4 printed pages]

Your Roll No. : .....

Sl. No. of Q. Paper : **1805**

Unique Paper Code : 2172012401

Name of the Paper : DSC 10 (Coordination Chemistry and Reaction Mechanism)

Name of the Course : **B.Sc.(Hons.) Chemistry**

Semester : IV

Time : 3 Hours ***Maximum Marks : 90***

Instructions for Candidates :

(a) Write your Roll No. on the top immediately on receipt of this question paper.

(b) Attempt any **SIX** questions in **all.**

(c) **All** questions carry equal marks.

1. (a) Write the name for the following complexes according to IUPAC rules.

(i) $(CH_3)_4$ N $[Cr(NH_3)_2(NCS)_4]$ (ii) $[Co(NH_3)_5(N_3)]SO_4$

(iii) $[Pt(py)_4]$ $[PtCl_4]$ (iv) $[Rh(en)_3]_2(SO_4)_3$

(v) $[(CO)_4\ Fe(u\text{-}CO)_2Fe(CO)_4]$

(b) Write the formula for the following complexes according to IUPAC rules :

(i) μ-amido-μ superoxobis [triammineechloridocobalt(III)] sulphate

(ii) Tetraamminedithiocyanato-N-chromium (III) tetrachlorozincate (II)

P.T.O.

(iii) Sodium bis (thiosulphato) argentate (I)

(iv) Potassium pentachloridonitridoosmate (VI)

(v) Tris(propane 1:2-diamine) cobalt (III) sulphate

(c) A compound $CoCl_3 \cdot 4NH_3$ contains only one Cl^- ion that precipitates as AgCl on the addition of Ag^+ ions. Based on Werner's coordination theory, give a brief explanation of the observation. How was it concluded that the complex is octahedral ? 5,5,5

2. (i) Draw the molecular orbital energy level diagram for σ – bonding in the case of $[Co(CN)_6]^{3-}$ octahedral complex ion. Discuss the effect of metal to ligand pi bonding on the 10 Dq value.

(ii) Use CFT to explain the following :

(a) Tetrahedral complexes are always high spin.

(b) $[Ti(H2O)_6]^{3+}$ ion has purple colour.

(iii) A complex, $Co(NH_3)_2(H_2O)_2Cl_2Br_2$ exists in two isomeric forms, A and B. Form A gives two moles of AgBr when treated with $AgNO_3$, while the other form yields one mole of AgBr. Give a proper explanation, identify the type of isomerism and write the structural formula of A and B. 5,5,5

3. (i) Which geometrical isomer of $[Cu(en)_2(H_2O)_2]^{2+}$ is thermodynamically more stable and why ? Also, compare and explain its stability with the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex.

(ii) Draw a crystal field splitting diagram for a z-out octahedral complex and explain that square planar complexes are an extreme case of Jahn-Teller distortion.

(iii) Which of the following complexes has a higher 10 Dq value and why ? 5,5,5

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

(b) $[Fe(C_2O_4)_3]^{4-}$ and $[Fe(C_2O_4)_3]^{3-}$

4. (i) The magnetic moment value of $[Mn(CN)_6]^{3-}$ ion is 2.8 B.M. Predict the type of hybridisation of the central metal ion and lability of the complex according to VBT.

(ii) Using VBT, explain $[NiCl_4]^{2-}$ is paramagnetic, but $[Ni(CH)_4]^{2-}$ is diamagnetic.

(iii) $[Co(en)_3]^{2+}$ and $[Co(NO_2)_6]^{4-}$ are easily oxidizable. Explain this observation according to VBT and CFT ? 5,5,5

5. (i) Derive the relationship between stepwise formation constants (K_n) and overall formation constant (βn).

(ii) Predict and explain the lability or inertness of the following complexes :

(a) $[V(NH_3)_6]^{3+}$ (b) $[MnCl_6]^{3-}$

(iii) Use trans effect and write the steps involved in the synthesis of cis and trans isomers of $[Pt(C_2H_4)(NH_3)Cl_2]$ from $PtCl_4^{2-}$ 5,5,5

6. (i) (a) Draw all possible geometrical isomers for $[Pt(py)_2(NH_3)_2Cl_2]^{2+}$

(b) How the Kurnakov test is used to distinguish between geometrical isomers of $[PtCl_2(NH_3)_2]$.

(ii) Describe a simple method to distinguish between the following of complexes

(a) $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$

(b) $[Cr(NH_3)_6]$ $[Cr(NO_2)_6]$ and $[Cr(NH_3)_4(NO_2)_2]$ $[Cr(NH_3)_2(NO_2)_4]$

(iii) Explain why ?

(a) 4d and 5d elements usually form low-spin complexes

P.T.O.