



THE CATHOLIC UNIVERSITY OF EASTERN AFRICA

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MAIN EXAMINATION

MAY – JULY 2016 TRIMESTER

FACULTY OF SCIENCE

DEPARTMENT OF CHEMISTRY

REGULAR PROGRAMME

CHEM 301: COORDINATION CHEMISTRY

Date: JULY 2016

Duration: 2 Hours

INSTRUCTIONS: Answer Question ONE and ANY OTHER TWO Questions

- Q1. a) Give the systematic names of the following coordination compounds
- i $K_4 [Fe(CN)_6]$
 - ii $Fe(CO)_5$
 - iii $Pt(NH_3)_2Cl_4$
 - iv $[Pt(H_2NCH_2CH_2NH_2)_2Cl_2]Cl_2$ **(8 marks)**
- b) Draw the structures of the following coordination compounds
- i Δ - amminechloridobis (ethylenediamine) cobalt (I)
 - ii \wedge - bis(ethylenediamine) *K-S* thiocyanido) iron (III)
 - iii Mer-triaquatriamminechromium (III) chloride **(6 marks)**
- c) Define the following terms
- i Ligand
 - ii Coordination number
 - iii Ambidentate ligand **(3 marks)**
- d) State any THREE factors that determines the coordination number of a complex. **(3 marks)**
- e) i What is the Jahn – Teller effect **(2 marks)**

- ii Calculate the crystal field stabilization energy (CFSE) for octahedral d^7 high and low spin complexes. **(3 marks)**
- iii What is *trans*-effect? Show the sequence of substitution required to get cisplatin, $Cis[Pt(NH_3)_2Cl_2]$ and transplatin, $trans - [Pt(NH_3)_2Cl_2]$ **(5 marks)**

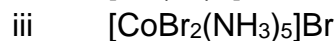
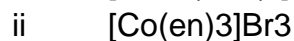
- Q2. a) A chelate effect is an entropy factor discuss consider $[Cu(en)(NH_2CH_3)]^{2+}$ with $\log B_4 = 6.6$ Vs $[Cd(en)_2]^{2+}$ $\log B_4 = 10.6$ **(5 marks)**
- b) The table below shows the stability constraints for each of the stages in the replacement of four of the aqua molecules in $[Cu(H_2O)_6]^{2+}$

Ion	K_n	Value ($mol^{-1}dm^3$)
$[Cu(NH_3)(H_2O)_5]^{2+}$	K_1	1.78×10^4
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	K_2	4.07×10^3
$[Cu(NH_3)_3(H_2O)_3]^{2+}$	K_3	9.55×10^2
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	K_4	1.74×10^2

- i Write the equation for the formation of each ion from the previous one with one ammonia less, and use this to write an expression for each stability constant. **(5 marks)**
- ii Write an expression for the overall stability constant for the formation of the complex ion $[Cu(NH_3)_4(H_2O)_2]^{2+}$ **(2 marks)**
- iii Use the values in the table for K_1 , K_2 , K_3 and K_4 to calculate the overall stability constant. **(2 marks)**
- c) The magnitude of Δ_0 for CrL_6 (Cr^{3+}) complexes is 26310 cm^{-1} ($L = CN$), 15250 cm^{-1} ($L = H_2O$) AND $9,620\text{ cm}^{-1}$ ($L = I$). Explain the relative order in terms of the ligand bonding properties. **(6 marks)**
- Q3. a) The complex $[Ni(CN)_4]^{2-}$ is diamagnetic while $[NiCl_4]^{2-}$ is paramagnetic. Explain this phenomenon and predict their possible structures. **(5 marks)**
- b) $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_4]^{2+}$ both appear blue in solution because of the presence of Cu^{2+} ions. However the two solutions are not identical. How would the appearance of the two solutions differ? If you are given an

unlabelled sample of each, how could the two solutions be distinguished without collecting any spectra? **(5 marks)**

c) Determine the number of moles of AgBr which will be formed by reaction of one mole of the following compounds with an excess of $\text{AgNO}_3(\text{aq})$



d) Discuss the various techniques currently available to characterize coordination complexes and useful information obtained from each technique. **(7 marks)**

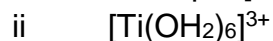
Q4. a) i State the Laporte's rule. **(2 marks)**

ii Explain why the stability of Co^{3+} complex is > than for Co^{2+} complex even if the ionic size of the central metal ion is almost same. **(2 marks)**

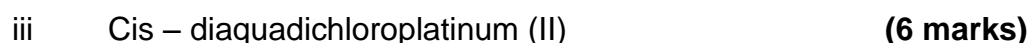
iii It is useful to note that the ligands producing the most splitting are those that can engage in metal to ligand back-bonding. State THREE factors that affect these splitting. **(3 marks)**

b) $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ has absorption bands at $\lambda_1 = 17,000 \text{ cm}^{-1}$ and $\lambda_2 = 25,000 \text{ cm}^{-1}$. Using Tanabe –Sugano for d^2 estimate the values of Δ_0 and B for this complex. **(7 marks)**

c) Write the d orbital configurations and use the Tanabe Sugano diagrams to identify the ground electronic term of



Q5. a) Draw the structures of the following complexes



- b) Briefly explain the following reaction mechanisms
- i Associative reaction
 - ii Dissociative reaction
 - iii Interchange mechanism
- (6 marks)**
- c) Use a simple molecular orbital diagram to illustrate why ligands such as CO or ethylene lead to larger Δ_0 in octahedral complexes compared to simple σ -donors like NH_3
- (8 marks)**

END