CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

THIRD YEAR EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE AND BACHELOR OF EDUCATION (SCIENCE)

CHEM 313: COORDINATION CHEMISTRY

STREAMS: **TIME:2 HOURS**

DAY/DATE: THURSDAY 20/04/2023 **11.30 A.M. –1.30 P.M.**

INSTRUCTIONS

ANSWER QUESTION *ONE* AND ANY OTHER T*WO* QUESTION

QUESTION ONE [30marks]

a) One of the most important properties of the ***transition metals*** is their ability to act as **Lewis acids** that form ***homoleptic*** and ***heteroleptic complexes*** with a variety of **Lewis bases.** Such complexes in which the **coordination number** is six and four **ligands** are very common.

(i) Define the underlined terms **[3.5marks]**

(ii) Explain why NH_3 is a Lewis base and BH_3 a Lewis acid? **[1.5marks]**

(iii) Give three reasons why transition metals show tendency to form complexes **[1.5marks]**

(iv) List **ANY THREE** characteristic properties of transition elements **[3 marks]**

(v) Distinguish between a complex ion and a simple ion **[2marks]**

b). (i). Define the term exchange energy. **[1 mark]**

(ii). The magnitude of exchange energy can be calculated using the following equation

$$E^x = \sum \frac{N(N-1)}{2} K^x \cdot$$

Define all the terms in the equation and calculate the relative exchange energy for (I) Mn^{2+} ion and (II) Cu^{2+} ions **[3 marks]**

c) (i). Discuss Werner's postulates of the formation of coordination compounds **[4marks]**

(ii). Explain how Werner's postulates of the formation of coordination compounds may be quantitatively confirmed experimentally? **[3marks]**

e).A chemistry student at Chuka University isolated a set of four cobalt complexes. The student treated them with $AgNO_3$ and was able to precipitate different amounts of $AgCl$. The student also measured the molar conductance of the complexes and established that different numbers of ions are present in each complex. The student tabulated the experimental data as shown below

Complex	No of Cl- ions precipitated	No of ions
$CoCl_3.6NH_3$	3	4
$CoCl_3.5NH_3$	2	3
$CoCl_3.4NH_3$	1	2
$CoCl_3.3NH_3$	0	0

(i) Giving sufficient reasons for your answer, write the formulae and the correct IUPAC names of the above complexes. **[4 marks]**

(ii) Show the ions present in each complex **[2 marks]**

(iii) What is the coordination number of cobalt in the above complexes? **[1.5 mark]**

QUESTION TWO [20marks]

a).(i). Give the main ideas developed by Sidgwick in the interpretation of Werner's coordination theory **[3 marks]**

(ii). List the shortcomings of Sidgwick's theory of the formation of coordination compounds. **[3 marks]**

b).(i). State and the explain the electroneutrality principle **[2.5 marks]**

(ii) Arrange the following ligands in order off increasing field strength Br^-, F−, CN^-, NH_3, $[OH]^-$, H_2O **[1.5 marks]**

c). (i).What do you understand by the term ''effective atomic number''? **[1 mark]**

(ii). State the effective atomic number rule. How is it related to eighteen electron rule and what is its usefulness in coordination Chemistry? **[3marks]**

(iii). Calculate the effective atomic number(EAN) of **ANY TWO** of the following complexes and predict the number of unpaired electrons in the complexes **[3marks]**

(I) $[Cr(NH_3)_6]\ Cl_3$ (II) $[Cu(NH_3)_4)](NO_3)_2$ (III) $K_3[MnCl_6]$ [Atomic Number: Cr = 24 Mn, = 25 Cu = 29]

e). Give the names and sketch the structures of **ANY THREE** of the following ligands . Show by an arrow the donor atom(s) that is the source of electrons and state the denticity of the ligand **[3marks]**

(i). en (ii) trien (iii) acac (iv) bipy (v) dien

QUESTION THREE [20marks]

a) (i). Define the term isomerism **[1.5 marks]**

(ii). Draw all possible geometrical isomers of each of the following Complexes (I). $Ni(NH_3)_4Cl_2$ (II). $[Pt(en)_3]^{4+}$ (III). $[Pt(en)_2ClBr]^{2+}$. Which of these isomers if any can exist as enantiomers **[4 marks]**

b) (i). Draw all possible constitutional isomers of $[Ru(NH_3)_5(NO_2)]Cl$. Label the isomers as linkage isomers or ionization isomers **[3 marks]**

(ii).Draw the two linkage isomers of the following complex: $[Pd(NH_3)_2(ONO)_2]$

c). Distinguish between the following pairs **[2 marks]**

(i). an enantiomer and a racemic mixture,

(ii) a levorotatory and dextrorotatory isomer

(d).(i) What do you understand by the term a chiral centre **[1.5 marks]**

(ii). Which of the following complexes are chiral: **[2 marks]**

(I).$Pt(en)Cl_2$ (II). $cisCo(NH_3)_4Br_2]^+$ (III) $cis[Cr(en)_2(H_2O)_2)]^{3+}$ (IV).$[Cr(C_2O_4)_3]^3$

e). (i)State the types of isomerism that may be exhibited by the following pair of complexes **[3 marks]**

(I) $[Co(NH_3)_5Br]SO_4$ and $Co(NH_3)_5(SO_4)]Br$

(II) $[CrCl_2(H_2O)_4]Cl.2H_2O$ and $[CrCl(H_2O)_5]Cl_2.H_2O$.

(ii) What chemical tests you would use to distinguish the pair of the compounds described in (I) and (II) pairs of the compounds? **[3 marks]**

QUESTION FOUR [20marks]

a).Give the correct IUPAC names of the following coordination compounds **[3 marks]**

(i). $Ca_3[VCl_6]$ (ii). $[TiCl_4(Et_2O)_2]$ (iii). $[Pt(NH_3)_2Cl_4]$

b). Draw correct structures of the following compounds **[3 marks]**

(i).Aquatriaminedichlorocobalt(III)chloride

(ii) Potassium hexafluoronickelate (IV)

(iii) Tris (ethylenediamine)cobalt(III)

c) (i) Discuss the factors that affect the magnitude of crystal field splitting parameter $\triangle o$ **[5 marks]**

(ii). For which member of the following pairs of complexes would $\triangle_o$ be larger

and why **[5 marks]**

I. $[Cr(H_2O)_6]^{2-}$ and $[Cr(H_2O)_6]^{3+}$

II. $[CrF_6]^{3-}$ and $[Cr(NH_3)_6]^{3+}$

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

d)(i). Weak field ligands tend to give high spin complexes, but strong field ligands tend to give low spin complexes. Explain **[2.5 marks]**

(ii). Explain why nearly all tetrahedral complexes are high spin? **[1.5 marks]**

QUESTION Five [20marks]

(a) (i).State Jahn- Teller theorem **[2 marks].**

(ii). Which of the following high-spin complexes would you expect to exhibit Jahn-Teller distortion? **[1.5 marks]**

(I). $[Cr(NH_3)_6]^{2+}$ (II) $[MnCl_6]^{3-}$ (III) $[Fe(H_2O)_6]^{3+}$ (IV) $[Cu(NH_3)_6]^{2+}$,

b). For each of the following complexes, ,

(1). $[CrF_6]^{3-}$ 2. $[V(H_2O)_6]^{3+}$ 3. $Fe(CN)_6]^{3-}$

(i) Determine the electronic configuration of the central metal ion in each of the above complexes. **[1.5marks]**

(ii) Draw the crystal field energy -level diagrams for each complex and show the placement of the d electrons. **[2 marks]**

(iii) Calculate in multiples of Δ_o or Δ_{tet} CFSE of the central metal in the above complexes. **[3 marks]**

(iv) How many unpaired electrons are there in each of the above complexes. **[1.5 marks]**

c). Indicate the coordination number, the oxidation number and the electronic configuration of the central metal in ANY **THREE** of the following complexes. **[4.5 marks]**

(i) $K_3[Co(CN)_6]$ (ii) $Mn(H_2O)_5Br]^+$ (iii).[$Mo(en)_2F_2]NO_3$ (iv)$[Ti(H_2O))_6]^{3+}$

d) (i). State the quantum mechanical selection rules necessary for light absorption by coordination compounds. **[1.5 marks]**

(ii).Which of the following complexes of Ti^{3+} exhibit the shortest wavelength absorption in the visible spectrum: $[Ti(H_2O)_6]^{3+,}$ $Ti(en)_3]^{3+}$ or $[TiCl_6]^{3-}$? Explain **[2.5 marks]**
