

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: BSC & BED (SC) Y3S2****TIME: 2 HOURS****DAY/DATE: WEDNESDAY 10/04/2019****8.30 A.M 10.30 A.M.****INSTRUCTIONS**

- Answer **Questions ONE and any other TWO Questions**
- Do not write on the question paper

QUESTION ONE: [30 MARKS]

(a) (i) Define the term transition element and explain why scandium and zinc may strictly not be treated as transition elements. [2 Marks]

(ii) List any three characteristic properties of transition elements. [3 Marks]

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

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

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

Define all the terms in the equation and calculate the relative exchange energies for
 $2+d$ ions.
 $2+d \wedge Cu^d$
 Mn^d [3 Marks]

(c) (i) A metal **complex ion** is found in which the **coordination number** is six, with four H₂O and two NH₃ **ligands**. Define the underlined **terms** in this sentence. [3 Marks]

(ii) Illustrating with an example in each case differentiate between a soft and a hard base. Which of the ligands stabilize high and low oxidation states of the metal ions and why? [3 Marks]

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- (d) (i) Discuss briefly the main ideas of Werner's theory of coordination compounds. [4 Marks]
(ii) A Chemistry student at Chuka University laboratory isolated a set of three nickel complexes. To identify the complexes, the student titrated them with a solution of silver nitrate and discovered that different amounts of silver chloride were precipitated. 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 in the table below.

Complex	Moles of AgCl Precipitated by AgNO ₃	Number of ions present	Remarks
NiCl ₂ ·6NH ₃	2	3	
NiCl ₂ ·4NH ₃	0	0	
NiCl ₂ ·2NH ₃ ·2KCl	0	3	

Using the data in the table,

- (i) Write the formulae and show the ions present in each complex.
(ii) Determine the coordination number of nickel in these complexes. [6 Marks]
- (e) (i) list the drawback of Sidgwick's theory for the interpretation of Werner's theory of coordination compounds. [3 Marks]
(ii) Which of the following complexes of Ti³⁺ exhibits the shortest wavelength absorption in the visible spectrum? [Ti(H₂O)₆]³⁺, [Ti(en)₃]³⁺ or [TiCl₆]³⁺ [2 Marks]

QUESTION TWO: [20 MARKS]

- (a) Give the names and sketch the structures of the following ligands. Show by an arrow the donor atom(s) that is the source of electron pair in each ligand and state the denticity of the ligand.
(i) en (ii) acac, (iii) dien [6 Marks]
- (b) (i) Illustrating with an example, explain the meaning of the term chelate effect and show how this effect can be rationalized on the basis of thermodynamics. [3 Marks]
(ii) Define the term Macrocyclic effect and give reasons why complexes formed by macrocycles have enhanced stabilities that those formed by chelating ligands. [3 Marks]
- (c) Write the formulae for the following coordination compounds [3 Marks]
(i) Hexaamminechromium (III) nitrate.
(ii) Dichlorobis (ethylenediamine) platinum (IV) bromide
(iii) Ammoniumtetrachlorocuprate

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(d) Write names of the following coordination compounds

(i) $K_2[TiCl_6]$ (ii) $[Co(NH_3)_6]Cl_2$ (iii) $[Mn(en)_3](NO_3)$ [3 Marks]

(f) By writing formulae or by drawing structures related to any one of the following complexes, $[Pd(NH_3)_2(ONO)_2]$, $cis-[V(en)_2Cl_2]$

Illustrate the complexes which will exhibit the following types of isomerism.

(i) Geometrical isomerism (ii) linkage isomerism (iii) Optical isomerism [2 Marks]

QUESTION THREE: [20 MARKS]

(a) Consider the following complexes and answer the questions that follow. [Hint: use the spectrochemical series to decide where relevant, which are likely to be high spin and low spin complexes] [12.5 Marks]

(i) $[VCl_6]^{3-}$ (ii) $[FeF_6]^{3-}$ (iii) $[Ru(bipy)_3]^{3+}$ (iv) $NiCl_4^{2-}$ (v) $Co(NO_2)_6^{3+}$

(i) Determine the electronic configuration of the central metal ion in each of the above complexes.

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

(iii) Calculate in multiples of Δ_o or Δ_t , CFSE of the central metal in the above complexes

(iv) How many unpaired electrons are there in each of the above complexes.

(b) The complex ion $[Fe(CN)_6]^{3-}$ has one unpaired electron, whereas $[Fe(NCS)_6]^{3-}$ has five unpaired electrons. From these results, what can you conclude about whether each complex is high spin or low spin. Explain your answer. [3½ Marks]

(c) Discuss the factors that affect the magnitude of crystal field splitting parameter Δ_o . [4 Marks]

QUESTION FOUR: [20 MARKS]

(a) (i) State the Jahn-Teller theorem. [2 Marks]

(ii) Give explanation for the experimental observation that in the complex $[Cu(NH_3)_6]^{2+}$, two Cu-NH₃ bonds are longer than others. [2 Marks]

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(b) Find the number of unpaired electrons, spin only magnetic moments and the ground state term symbols (indicating how they are influenced by the ligand field.)for each of the following complexes

- (i) $[\text{CoCl}_4]^{2-}$ (ii) $[\text{Cr}(\text{CN})_6]^{4+}$ (iii) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (iv) $\text{Co}(\text{NH}_3)_6]^{3+}$
(v) $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})]^{2+}$

[10 Marks]

(c) (i) What do you understand by the term nephelauxetic effect?

[2 Marks]

(ii) State the quantum mechanical selection rules necessary for light absorption by coordination compounds.

[2 Marks]

(iii) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ both appear blue in solution because both of the complexes contain Cu^{2+} ions which absorb of light in the visible region of the spectroelectromagnetic spectrum. However the two solutions are not identical: One is darker blue while the other is pale blue. Discuss how you would differentiate the two complexes in terms of their colours without even interpreting their spectra. [2 Marks]

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