MACHAKOS UNIVERSITY

University Examinations 2020/2021

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PYSICAL SCIENCES

FIRST YEAR FIRST SEMESTER EXAMINATION FOR

MASTER OF SCIENCE (CHEMISTRY)

SCH 802: ADVANCED CO-ORDINATION CHEMISTRY

DATE: 14/05/2021 **TIME: 2:00 - 5:00PM**

INSTRUCTIONS:

- The paper consists of **two** sections.
- Section **A** is **compulsory** (30 marks).
- Answer any **two** questions from section **B** (each 15 marks).

SECTION A: (COMPULSORY)

QUESTION ONE (30 MARKS)

a) i) First generation Ziegler–Natta catalysts were made by reacting $TiCl_4$ with Et_3Al. Determine the compound precipitated through this reaction. (1 mark)

ii) Distinguish between a double salt and a complex (2 marks)

b) Define a Kinetically inert and labile complex (2 marks)

c) In a ligand the reaction below, identify the product of the reaction (2 marks)

$$[Co(OH_2)_6]^{2+}(aq) + Cl^-(aq) \rightarrow$$

d) Distinguish between Thermodynamic and Kinetic Stability (2 marks)

e) Platinum-containing compounds such as cisplatin and carboplatin are antitumor drugs. Draw their structural formula. (2 marks)

f) Illustrate the ground state molecular orbital (MO) electronic configuration of homonuclear diatomic molecule N_2. (2 marks)

g) Write the equation for the reduction of Cr hexacarbonyl by sodium metal (2 marks)

h) Illustrate the formation of $M \xrightarrow{\pi} CO$ bond by back donation in metal carbonyls (2 marks)

i) Platinum (II) forms square planar complexes and platinum (IV) gives Octahedral complexes. Determine how many geometrical isomers are possible for each of the following complexes and describe their structures. (3 marks)

i. $[Pt(NH_3)_3Cl]^+$

ii. $[Pt(NH_3)Cl_5]^-$

iii. $[Pt(NH_3)_2ClNO_2]$

j) Provide the systematic names of the complexes (i) $[Co(NH_3)_5Cl]Cl_2$ and (ii) $K_3[Fe(C_2O_4)_3]$ and assign secondary valences to metals in these compounds (4 marks)

k) Results of a pH study using a glass electrode in 2M NH_4NO_3 (aq) solution give values of the stepwise stability constants (at 403K) of $[Ni(OH_2)_{6-x}(NH_3)_x]^{2+}$ (x = 1–6) as $\log K_1$= 2.79; $\log K_2$ =2.26; $\log K_3$ = 1.69; $\log K_4$ =1.25; $\log K_5$= 0.74; $\log K_6$ = 0.03. Calculate

i. Overall stability constants (β_6) for $[Ni(NH_3)_6]^{2+}$ and

ii. The stepwise stability formation of $[Ni(OH_2)_5(NH_3)]^{2+}$ (ΔG^0) 403 K.

iii. If the value of $\Delta H^o_1(403K)$ = -16.8 kJ mol^{-1}, calculate $\Delta S_1(403\ K)$. (R = 8.314 JK^{-1} mol^{-1}). (6 marks)

SECTION B: ANSWER ANY TWO QUESTIONS

QUESTION TWO (15 MARKS)

a) Explain why is hydrochloric acid not used to acidify a potassium permanganate solution in volumetric estimation reaction of Fe^{2+} and $C_2O_4^{2-}$. (2 marks)

b) Addition of excess concentrated HCl to an aqueous solution of $CoCl_2$ turns blue. Write the equation for the reaction explaining the observation and a possible application. (3 marks)

c) A compound has an empirical formula $CoCl_35NH_3$. When an aqueous solution of this compound is mixed with excess of silver nitrate, 2 moles of silver chloride precipitates per mole of the compound. On reaction with excess of HCl, NH_4 is not detected. Write the formula for these reactions and explain the observation. (4 marks)

d) The mechanism of a nucleophilic substitution reaction is a sequence of elementary steps by which the reaction takes place. Classify and distinguish the types of nucleophilic substitution reactions. (6 marks)

QUESTION THREE (15 MARKS)

a) Define macrocyclic effect? (1 mark)

b) The complex $Cr_2[CoCl_4]$ has tetrahedral structure with three unpaired electrons. Write the equation for CrO_3 when it dissolves in aqueous NaOH (2 marks)

c) Though copper, silver and gold have completely filled sets of a d-orbitals they are considered as transition metals. Explain. (2 marks)

d) Magnetic measurements indicate that $[Co(OH_2)_6]^{2+}$ has 3 unpaired electrons. Determine the hybridization of the Cobalt orbitals in $[Co(OH_2)_6]^{2+}$ (2 marks)

e) Using molecular orbital theory (MO), write the ground state electron configuration for Iodine Chloride (ICl) (2 marks)

f) Metal complexes can promote nucleophilic catalysis by water ionization. Typical example of this reaction is metal complex structure with Zn^{2+} ion as coordination center. Write the mechanism of how water molecule binds to the ligand position of Zn^{2+} ion, resulting in water ionization, then Zn^{2+} bound OH^- becomes a potent nucleophile, which can attack the CO^2, converting it into HCO^{3-} (6 marks)

QUESTION FOUR (15 MARKS)

a) Determine how many unpaired electrons are there when iron (II) octahedral complex is placed in a strong field. (1 mark)

b) Provide the Lewis acid and base in the coordination complex, $Na_2[Pt(CN)_4]$. (2 marks)

c) Using any ligand of your choice, show how a five membered polydentate ring is formed

(2 marks)

d) Discuss four types of structural isomers and give an example of each. (4 marks)

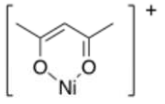
e) Identify the Ziegler Natta Catalyst in the formation of an isotactic polymer formed using Titaniumtetrachloride and Triethyl Aluminium and write the mechanism for the reaction (6 marks)

QUESTION FIVE (15 MARKS)

a) Explain how antibonding molecular orbitals are formed. (1 mark)

b) Using the complexes below, identify the bidentate ligands, before binds to $Ni^{(2+)}$

(2 marks)



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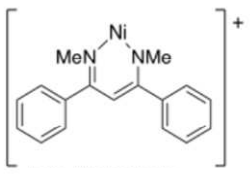

c) Explain why geometrical isomerism is not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion. (2 marks)

d) Explain why a molecule that cannot be superimposed on its mirror image is said to exhibit. (2 marks)

e) Identify all the statements below that are true or false about complex ion $[Mn(OH_2)_6]^{2+}$ with 5 unpaired electrons. (3 marks)

i. It is diamagnetic.

ii. It is a low spin complex.

iii. The metal ion is a d^5 ion.

iv. The ligands are weak field ligands.

v. It is octahedral.

f) Determine the ratio of uncomplexed to complexed Zn^{2+} ion in a solution that is 10M in NH_3, if the stability constant of $[Zn((NH_3)_4]^{2+}$ is $3x10^9$ (5 marks)