



# MURANG'A UNIVERSITY OF TECHNOLOGY

## SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF APPLIED SCIENCES

UNIVERSITY ORDINARY EXAMINATION

2017/2018 ACADEMIC YEAR

EXAMINATION FOR MASTER OF SCIENCE IN CHEMISTRY

ACH 604: ADVANCED CO-ORDINATION CHEMISTRY

DURATION: 3 HOURS

DATE: 22<sup>ND</sup> AUGUST, 2018

TIME: 9.00 – 12.00 NOON

### **Instructions to Candidates:**

1. Answer **Any Four** questions.
2. Mobile phones are not allowed in the examination room.
3. You are not allowed to write on this examination question paper.

**QUESTION ONE (25 marks)**

- a) The absorptions for the complex ion  $[Co(NH_3)_6]^{3+}$  occurs at 470nm
- Predict the colour of the complex (2 marks)
  - Calculate the crystal field stabilization energy in KJ/mol (2 marks)
- b)  $[Ni(CN)_4]^{2-}$  ion has a square planer geometry and has been found to be diamagnetic whereas the  $[NiCl_4]^{2-}$  ion is tetrahedral geometry and is paramagnetic. Show the crystal field diagrams for these two complexes (6 marks)
- c) 3d transitional metals complexes are mostly high spin while 4d and 5d metal complexes are mostly low spin. Explain and give reasons for this observation (5 marks)
- d) Write a mechanism showing the following transformation

(10 marks)

**QUESTION TWO (25 marks)**

- a) Chromium (III) Chloride forms six-coordinate complexes with bipyridine including Cis –  $[Cr(bipy)_2Cl_2]^+$  which reacts slowly with water to produce two products, Cis $[Cr(bipy)_2(H_2O)Cl]^{2+}$  and Cis $[Cr(bipy)_2(H_2O)_2]^{3+}$ . Determine the complex with largest splitting energy ( $\Delta_o$ ) (4 marks)
- b) Using Ligand Field Theory and suitable splitting diagram, discuss and outline how electrons populate Ligand field diagram of  $Mn^{3+}$  complex in a low spin and high spin state in octahedral complex (8 marks)
- c) The total electron pairing energy  $\pi_{total}$  has two components,  $\pi_c$  and  $\pi_e$ . Determine the total pairing energy of the following complexes.
- $d^4$  high spin complex (2 marks)
  - $d^8$  (2 marks)
  - $d^6$  low spin complex (2 marks)

- d) Give a mechanism to show the following transformation

(7 marks)

**QUESTION THREE (25 marks)**

- a) Consider the following complex

If the complex has splitting energy ( $\Delta_o$ ) of  $9,350 \text{ cm}^{-1}$ . Unstabilising coulombic term ( $nc$ ) of  $19,600 \text{ cm}^{-1}$  and exchange stabilising term ( $ne$ ) of  $-2,000 \text{ cm}^{-1}$ . Determine if the complex is high spin or low spin (10 marks)

- b) Using Ligand Field Theory and MO suitable diagram, explain how  $\bar{x}$  – donor and acceptor ligands affects splitting energy and its relationship to spectrochemical series. Use suitable examples where necessary (10 marks)

- c) The octahedral crystal field energy  $\Delta_o$  of  $\text{Co}(\text{CN})_6^{3-}$  is found to be  $6.74 \times 10^{-19}$ . ..... Determine:

- i. The absorption wavelength of the complex (3 marks)  
ii. Predict the colour of the solution (2 marks)

**QUESTION FOUR (25 marks)**

- a) Write detailed chemical mechanism for the following ring closing metathesis (RCM)
- b) Explain any two methods commonly used to form/prepare carbenes (5 marks)
- c) Consider the following chromium complex

Determine:

- i. The oxidation number of chromium ion (2 marks)
- ii. The d- count (2 marks)
- iii. The  $d^n$  electronic configuration using crystal field theory at strong field (3 marks)
- iv. The Crystal Field Stabilization Energy (CFSE) (3 marks)

**QUESTION FIVE (25 marks)**

- a) Use the following sonogashiva coupling reaction to explain oxidative and reductive elimination reaction steps of transition metal catalysts

(7marks)

- b) Write detailed chemical mechanism for the following reaction

(8 marks)

- c) i. Consider a complex of  $Cr^{3+}$  ion. Determine the d-count and draw its  $d^n$  electronic configuration (4 marks)
- ii. If the complex is a compound  $[CrCl_6]^{3-}$  and the wavelength of most intensely absorbed light is 740nm. Predict the splitting energy and the colour of the complex (6 marks)