



# MACHAKOS UNIVERSITY

University Examinations 2022/2023

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

THIRD YEAR SECOND SEMESTER EXAMINATION

BACHELOR OF SCIENCE IN ANALYTICAL CHEMISTRY

BACHELOR OF EDUCATION (SCIENCE)

BACHELOR OF EDUCATION (SPECIAL NEEDS)

SCH 301: COORDINATION AND ORGANOMETALLIC CHEMISTRY

DATE:

TIME:

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## INSTRUCTIONS

- The paper consists of **two** sections.
- Section **A** is **compulsory** (30 marks)
- Answer any **two** questions from section **B** (each 20 marks)
- Check for useful Tables behind the Question paper

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### Useful constants

$$c = 3.0 \times 10^8 \text{ m/s}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

## SECTION A

### QUESTION ONE (30 MARKS)

(a) Name the following complex ions/coordination complexes:



- (iii)  $(\text{NH}_4)_2[\text{Ni}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$  (2 marks)
- (b) The complex  $[\text{Ni}(\text{CN})_4]^{2+}$  is diamagnetic while  $[\text{NiCl}_4]^{2-}$  is paramagnetic. Explain this phenomenon using Ligand Field Theory and predict their possible structures. (3 marks)
- (c) (i) Define *trans*-effect? (2 marks)
- (ii) Given that the relative order of the *trans*-directing ability of the ligands is  $\text{NO}_2^- > \text{Cl}^- > \text{NH}_3$ . Design a selective two step synthesis for *cis* and *trans*  $[\text{Pt}(\text{NH}_3)(\text{NO}_2)\text{Cl}_2]^-$  starting with  $\text{PtCl}_4^{2-}$  (4 marks)
- (d) A chelate effect is an entropy factor. Discuss in relation to  $[\text{Cd}(\text{NH}_2\text{CH}_3)]^{2+}$   $\log\beta_4 = 6.6$  versus  $[\text{Cd}(\text{en})_2]^{2+}$   $\log\beta_4 = 10.6$  (4 marks)
- (e) Draw the structures of the following compounds:
- (i) *Mer*-triaquatramminechromium(III)chloride (2 marks)
- (ii)  $\Lambda$ -bis(ethylenediamine) $\kappa$ -s-thiocyanido)iron(III) (2 marks)
- (f) (i) Explain why  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is an inner orbital complex whereas  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is an outer orbital complex (3 marks)
- (ii) State four factors that influence the Crystal Field Splitting energy (CFSE) of coordination complexes (4 marks)

## QUESTION TWO (20 MARKS)

- (a) State three properties of organometallic compounds (3 marks)
- (b) Explain why  $\text{NH}_3$  act as a ligand but  $\text{NH}_4^+$  does not (2 marks)
- (c) Using appropriate illustrations, briefly explain the following reaction mechanisms
- (i) Associative (2 marks)
- (ii) Dissociative (2 marks)
- (d) The table below shows the stability constants for each of the stages in the replacement of four of the aqua ligands in  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ .

Ion	$K_n$	Value ( $\text{mol}^{-1}\text{dm}^3$ )
$[\text{Cu}(\text{NH}_3)(\text{H}_2\text{O})_5]^{2+}$	$K_1$	$1.78 \times 10^4$
$[\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{2+}$	$K_2$	$4.07 \times 10$
$[\text{Cu}(\text{NH}_3)_3(\text{H}_2\text{O})_3]^{2+}$	$K_3$	$9.55 \times 10^2$
$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$	$K_4$	$1.74 \times 10^2$

- (i) Write the equations for the formation of each ion from the previous one with one ammonia less, and use it to write an expression for each stability constant (4 marks)
- (ii) Write an expression for the overall stability constant for the formation of the complex ion  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  (2 marks)
- (iii) Use the values in the table to calculate the overall stability constant. (1 mark)
- (e) Briefly discuss how  $\pi$ -bonding theory influences substitution reaction on square planar complexes (4 marks)

### QUESTION THREE (20 MARKS)

- (a) With relevant equations where possible briefly explain the following terms:
  - (i) Ambidentate ligand (2 marks)
  - (ii) Acid hydrolysis (2 marks)
  - (iii) Anation (2 marks)
- (b) Write the formulae for the following complexes:
  - (i) Tetraammineaquachloridocobalt(III)chloride (2 marks)
  - (ii) Potassiumtetrahydroxidozincate(II) (2 marks)
- (c) Draw the structures the following complexes:
  - (i)  $\mu$ -amido- $\mu$ -nitrooctaamminedicobalt(III)ion (2 marks)
  - (ii)  $\mu$ -hydroxy-bis{pentaamminechromium(III)}chloride (2 marks)
  - (iii)  $\Lambda$ -Tris(ethylenediamine)cobalt(I)chloride (2 marks)
- (d) Calculate the octahedral crystal field splitting energy in kJ/mol for  $[\text{Fe}(\text{CN})_6]^{4-}$ , if the wavelength of the most intensely absorbed light is 305 nm. (4 marks)

### QUESTION FOUR (20 MARKS)

- (a) State the Effective Atomic Number (EAN)
- (b) Briefly discuss how  $\pi$ -bonding theory influences substitution reaction on square planar complexes (4 marks)
- (c) Calculate the magnetic moments of the following complexes: (4 marks)
  - (i)  $[\text{Fe}(\text{CN})_6]^{4-}$
  - (ii)  $[\text{FeF}_6]^{3-}$

**QUESTION FIVE (20 MARKS)**

- (a) Define a spectrochemical series (2 marks)
- (b) (i) State the difference(s) between inner and outer orbital complexes (2 marks)
- (ii) Explain why  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is coloured while  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  is colourless (3 marks)
- (iii) With illustrations, differentiate between ionization isomerism and solvate isomerism (4 marks)
- (c) Explain the Jahn- Teller distortion in  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  (3 marks)
- (d) For each of the following complexes  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $\text{Ni}(\text{CO})_4$  and  $[\text{FeCl}_4]^{2-}$  determine:
- (i) the configuration in the form  $t_{2g}^m e_g^n$  or  $e^m t_2^n$  as appropriate (2 marks)
- (ii) the number of unpaired electrons (2 marks)
- (iii) The LFSE as a multiple of  $\Delta_o$  or  $\Delta_t$  (2 marks)

# Periodic Table of the Elements 2006

1 H 1.01																	2 He 4.00							
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 15.99	9 F 19.00	10 Ne 20.18							
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95							
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80							
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29							
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)							
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (270)	109 Mt (268)	110 Ds (281)	111 Rg (272)														
											58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
											90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)