## NATIONAL UNIVERSITY OF LESOTHO

## **Department of Chemistry and Chemical Technology**

B. Sc. Gen., B. Sc. Chem. Tech. & B. Sc. Ed. Supplementary Examination

#### C4710: Inorganic Year IV Chemistry

#### 20 August 2023

[100 Marks]

Time: 3 hrs

#### **Instructions:**

- 1. The question paper has **five** (5) printed pages.
- 2. Answer **ALL** questions.
- 3. For **Section 1**, answer all the Multiple Choice Questions on the same page.
- 4. For Section 2, begin each question on a new page.
- 5. Number your questions clearly.
- 6. Write neatly and legibly.
- 7. Periodic table and Tanabe-Sugano diagrams are attached.

#### **Constants:**

Planck's constant:	6.626 x 10 <sup>-34</sup> J s
Avogadro's constant:	$6.022 \text{ x } 10^{23} \text{ mol}^{-1}$
Speed of light:	2.998 x 10 <sup>8</sup> m s <sup>-1</sup>

#### **SECTION 1: Multiple Choice Questions [13 marks]**

- 1. According to Crystal Field Theory, which one of the following statements is FALSE? [1 mark]
  - A. In an octahedral crystal field, the *d* electrons on a metal ion occupy the  $e_g$  set of orbitals before they occupy the  $t_{2g}$  set of orbitals.
  - B. Diamagnetic metal ions cannot have an odd number of electrons.
  - C. Low spin complexes can be paramagnetic.
  - D. In high spin octahedral complexes,  $\Delta_0$  is less than the electron pairing energy, and is relatively very small.
- 2. What is the oxidation number of the central metal in the coordination compound [Ni(NH<sub>3</sub>)<sub>5</sub>Cl]Cl?

[1 mark]

- A. +3 B. +2 C. +1 D. -1
- 3. How many *d*-electrons does nickel have in the coordination compound [Ni(NH<sub>3</sub>)<sub>5</sub>Cl]Cl? [2 mark]
  A. 2
  B. 0
  C. 8
  D. 6

4. The correct IUPAC name for [FeF<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>-</sup> is: [2 marks]
A. diaquatetrafluoroiron(III) ion
B. diaquatetrafluoroferrate(III) ion
D. diaquatetrafluoroferrate(II) ion

- 5. According to Crystal Field Theory, which one of the following statements is FALSE? [2 mark]
  - A. Diamagnetic metal ions cannot have an odd number of electrons.
  - B. Low spin complexes can be paramagnetic.
  - C. In high spin octahedral complexes,  $\Delta_0$  is less than the electron pairing energy, and is relatively very small.
  - D. In an octahedral crystal field, the d electrons on a metal ion occupy the  $e_g$  set of orbitals before they occupy the  $t_{2g}$  set of orbitals.
- 6. In which of the following species is the underlined carbon atom nucleophilic?[1 mark]A.  $\underline{C}H_3Cl$ B.  $Ph\underline{C}H_2Br$ C.  $CH_3\underline{C}H_2M_gBr$ D.  $\underline{C}Cl_4$

7. Based on the following abbreviated spectrochemical series  $Cl^- < F^- < H_2O < NH_3 < CO$ , which of the octahedral Ti(III) complex below has its d-d electronic transitions at the shortest wavelength?

#### [2 marks]

- A.  $[TiCl_6]^{3-}$  B.  $[TiF_6]^{3-}$  C.  $Ti(NH_3)_6]^{3+}$  D.  $[Ti(CO)_6]^{3+}$
- 8. The room temperature magnetic moment ( $\mu_{eff}$  in B.M.) for the complex [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> is found to be significantly greater than 1.73. Which of the following expressions explains this observation?

[2 marks]

- A.  $\mu_{eff} = \mu_{s.o.}(1-\alpha\lambda/\Delta)$
- B.  $\mu_{eff} = g[J(J+1)]^{\frac{1}{2}}$
- C.  $\mu_{eff} = [n(n+2)]^{\frac{1}{2}}$
- D.  $\mu_{eff} = [n(n+2) + L(L+1)]^{\frac{1}{2}}$

#### **SECTION 2: Calculations and Structured Questions**

#### **Question 1 [12 Marks]**

Determine the molecular/ligand field term symbols for the metal centres in the following complexes (Include *d*-orbital splitting diagrams in your answer):

a) 
$$[CoF_6]^{3-}$$
  
b)  $[Co(NH_3)_6]^{3+}$   
c)  $[Cu(H_2O)_6]^{2+}$  [4 marks each]

#### Question 2 [20 marks]

- a) For the complex  $[Fe(CN)_6]^{3-} \Delta_0$  is found to be 392 kJmol<sup>-1</sup>.
  - i) Draw a well labeled orbital splitting diagram for this complex. [4 marks]
  - ii) Calculate the wavelength (in nanometers) at which the complex absorbs. [4 marks]
- b) Diamagnetic ( $\mu = 0$ ) complexes of Co(III) such as  $[Co(NH_3)_6]^{3+}$ ,  $[Co(en)_3]^{3+}$  and  $[Co(NO_2)_6]^{3-}$  are yellow-orange in colour. In contrast, the paramagnetic complexes  $[Co(H_2O)_3F_3]$  and  $[CoF_6]^{3-}$  are blue. Qualitatively account for these differences in colour and magnetic moment for the Co(III) complexes. [12 marks]

### Question 3 [15 marks]

- a) Determine the term symbol for the ground state of  $Tb^{3+}$  ion. [7 marks]
- b) Calculate the effective magnetic moment,  $\mu_{eff}$ , for Tb<sup>3+</sup> ion in (a) above using the expression

$$g = 1 + \underline{S(S+1) + J(J+1) - L(L+1)}$$
2 J(J+1) [4 marks]

c) i) Calculate the spin-only magnetic moment one would expect for  $Tb^{3+}$ . [2 marks] ii) Account for the discrepancy between  $\mu_{eff}$  and  $\mu_{s.o.}$  for  $Tb^{3+}$ . [2 marks]

#### Question 4 [19 marks]

- a) Define an organometallic compound.
- b) Synthesis of organometallic compounds of the heavy main group metals such as bismuth, lead and mercury by direct synthesis does not work.
  - i) Using words, not symbols, explain why this is the case. [1 mark]
  - ii) Using the preparation of Pb(CH<sub>3</sub>)<sub>4</sub> as an example, explain how this synthetic method is modified to overcome this problem and why this modification works. (Your answer should include balanced equations). [5 marks]
- c) Describe, with suitable diagrams, the structure and bonding of trimethylaluminium. [10 marks]

#### Question 5 [11 marks]

Hydroboration and hydroalumination of unsymmetrically substituted alkenes normally produce anti-Markovnikov addition products.

a)	State Markovnikov's rule in relation to these two reactions.									[2 marks]					
			_			_		-						 	

- b) State the two factors that cause the formation of the observed products and briefly explain how these factors cause the observed reaction outcomes. [4 marks]
- c) Use the complete mechanism of the addition reaction between 2-methyl-2-butene and borane (BH<sub>3</sub>) as an example to illustrate your answers to a) and b) above. [5 marks]

[3 marks]

## Question 6 [10 marks]

Identify compounds  $\mathbf{A} - \mathbf{J}$  in the following reactions:

[10 marks]



END ALL THE BEST!



# Department of Chemistry and Chemical Technology

																	VIII 18
1	 2		1 H 1.0079									III 13	IV 14	V 15	VI 16	VII 17	2 He 4.0026
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.011	7 N 14.007	8 O 16.000	9 F 18.998	10 <b>Ne</b> 20.180
11 <b>Na</b> 22.99	12 Mg 24.305	3	4	5	6	7	8	9	10	IB 11	IIB 12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 <b>Ar</b> 39.95
19 <b>K</b> 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	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 65.39	31 Ga 69.72	32 <b>Ge</b> 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 <b>Rb</b> 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 <b>Nb</b> 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 <b>Rh</b> 102.91	46 <b>Pd</b> 106.42	47 <b>Ag</b> 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 <b>Sb</b> 121.75	52 <b>Te</b> 127.60	53   126.90	54 <b>Xe</b> 131.29
55 <b>Cs</b> 132.9	56 Ba 137.33	La - Lu	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 <b>Re</b> 186.2	76 <b>Os</b> 190.2	77 <b>Ir</b> 192.2	78 Pt 195.1	79 <b>Au</b> 197.0	80 <b>Hg</b> 200.6	81 TI 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 <b>Ra</b> 226.0	Ac - Lr	104 Unq (261)	105 Unp (262)	106 Unh	107 Uns	<sup>108</sup> Uno	109 <b>Une</b>	110 Uun	111 Uuu	112 Uub	<sup>113</sup> Uut					

lanthanides	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	La	<b>Ce</b>	<b>Pr</b>	<b>Nd</b>	Pm	Sm	Eu	Gd	<b>Tb</b>	Dy	<b>Ho</b>	Er	Tm	Yb	Lu
	138.91	140.12	140.91	144.24	(145)	150.36	151.97	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97
actinides	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	<b>Ac</b>	Th	<b>Pa</b>	U	<b>Np</b>	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	<b>No</b>	Lr
	(227)	232.04	231.04	238.0	237.05	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(260)	(260)



## **Tanabe - Sugano Diagrams for Octahedral d<sup>n</sup> Complexes**



 ${}^{4}A_{2g} {}^{4}T_{1g}$ 80 <sup>4</sup>A<sub>1g</sub> 70  ${}^{2}A_{1g}$ 60 4F  ${}^{2}E_{g}_{2A_{2g}}, {}^{2}T_{1g}$ 50 <sup>2</sup>I E/B <sup>6</sup>A<sub>1g</sub> 40 4D  ${}^{4}T_{2g}$ 4G 30  ${}^{4}T_{1g}$ 20 10  ${}^{2}T_{2g}$ <sup>6</sup>A<sub>1g</sub> •<u>\$</u>  ${}^{2}T_{2g}$ 0 10 20 30 40 50  $\Delta_0/B$ 





