## 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

## 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: $\quad 6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}$
Avogadro's constant: $6.022 \times 10^{23} \mathrm{~mol}^{-1}$
Speed of light: $\quad 2.998 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}$

## 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 $\mathrm{e}_{\mathrm{g}}$ set of orbitals before they occupy the $t_{2 g}$ 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, $\boldsymbol{\Delta}_{\mathbf{O}}$ 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 $\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right] \mathrm{Cl}$ ?
A. +3
B. +2
C. +1
D. -1
3. How many $d$-electrons does nickel have in the coordination compound $\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right] \mathrm{Cl}$ ?
[2 mark]
A. 2
B. 0
C. 8
D. 6
4. The correct IUPAC name for $\left[\mathrm{FeF}_{4}\left(\mathrm{OH}_{2}\right)_{2}\right]^{-}$is:
[2 marks]
A. diaquatetrafluoroiron(III) ion
B. diaquatetrafluoroferrate(III) ion
C. diaquatetrafluoroiron(I) 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, $\boldsymbol{\Delta}_{\mathbf{O}}$ 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 $\mathrm{e}_{\mathrm{g}}$ set of orbitals before they occupy the $\mathrm{t}_{2 \mathrm{~g}}$ set of orbitals.
6. In which of the following species is the underlined carbon atom nucleophilic?
[1 mark]
A. $\mathbf{C H}_{3} \mathrm{Cl}$
B. $\mathrm{Ph} \underline{C H}_{2} \mathrm{Br}$
C. $\mathrm{CH}_{3} \underline{\mathrm{C}}_{2} \mathrm{M}_{\mathrm{g}} \mathrm{Br}$
D. $\mathbf{C C l}_{4}$
7. Based on the following abbreviated spectrochemical series $\mathrm{Cl}^{-}<\mathrm{F}^{-}<\mathrm{H}_{2} \mathrm{O}<\mathrm{NH}_{3}<\mathrm{CO}$, which of the octahedral $\mathrm{Ti}(\mathrm{III})$ complex below has its d-d electronic transitions at the shortest wavelength?
[2 marks]
A. $\left[\mathrm{TiCl}_{6}\right]^{3-}$
B. $\left[\mathrm{TiF}_{6}\right]^{3-}$
C. $\left.\mathrm{Ti}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$
D. $\left[\mathrm{Ti}(\mathrm{CO})_{6}\right]^{3+}$
8. The room temperature magnetic moment ( $\mu_{\text {eff }}$ in B.M.) for the complex $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ is found to be significantly greater than 1.73 . Which of the following expressions explains this observation?
[2 marks]
A. $\mu_{e f f}=\mu_{\text {s.o. }}(1-\alpha \lambda / \Delta)$
B. $\mu_{e f f}=g[J(J+1)]^{1 / 2}$
C. $\mu_{\text {eff }}=[n(n+2)]^{1 / 2}$
D. $\mu_{e f f}=[n(n+2)+L(L+1)]^{1 / 2}$

## 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) $\left[\mathrm{CoF}_{6}\right]^{3-}$
b) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$
c) $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
[4 marks each]

## Question 2 [20 marks]

a) For the complex $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-} \boldsymbol{\Delta}_{\mathbf{O}}$ is found to be $392 \mathrm{kJmol}^{-1}$.
i) Draw a well labeled orbital splitting diagram for this complex.
ii) Calculate the wavelength (in nanometers) at which the complex absorbs.
b) Diamagnetic $(\mu=0)$ complexes of $\mathrm{Co}(\mathrm{IIII})$ such as $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+},\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$ and $\left[\mathrm{Co}\left(\mathrm{NO}_{2}\right)_{6}\right]^{3-}$ are yellow-orange in colour. In contrast, the paramagnetic complexes $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{3} \mathrm{~F}_{3}\right]$ and $\left[\mathrm{CoF}_{6}\right]^{3-}$ 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 $\mathrm{Tb}^{3+}$ ion.
b) Calculate the effective magnetic moment, $\mu_{\text {eff }}$, for $\mathrm{Tb}^{3+}$ ion in (a) above using the expression

$$
\mathrm{g}=1+\frac{\mathrm{S}(\mathrm{~S}+1)+\mathrm{J}(\mathrm{~J}+1)-\mathrm{L}(\mathrm{~L}+1)}{2 \mathrm{~J}(\mathrm{~J}+1)}
$$

c) i) Calculate the spin-only magnetic moment one would expect for $\mathrm{Tb}^{3+}$. ii) Account for the discrepancy between $\mu_{e f f}$ and $\mu_{\text {s.o. }}$ for $\mathrm{Tb}^{3+}$.

## 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.
ii) Using the preparation of $\mathrm{Pb}\left(\mathrm{CH}_{3}\right)_{4}$ 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).
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 antiMarkovnikov addition products.
a) State Markovnikov's rule in relation to these two reactions.
b) State the two factors that cause the formation of the observed products and briefly explain how these factors cause the observed reaction outcomes.
c) Use the complete mechanism of the addition reaction between 2-methyl-2-butene and borane $\left(\mathrm{BH}_{3}\right)$ as an example to illustrate your answers to a) and b) above.
[5 marks]

## Question 6 [10 marks]

Identify compounds $\mathbf{A}-\mathbf{J}$ in the following reactions:
[10 marks]
a)
$\mathrm{SiO}_{2}+$

b)

c)


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lanthanides
actinides

| $\begin{gathered} 57 \\ \stackrel{L}{L} \text { a } \\ 138.91 \end{gathered}$ | $\begin{gathered} 58 \\ \mathrm{Ce} \\ 140.12 \end{gathered}$ | $\begin{gathered} 59 \\ \mathrm{Pr}_{140.91} \end{gathered}$ | $\begin{gathered} 60 \\ \mathrm{Nd} \\ 144.24 \end{gathered}$ | 61 Pm <br> (145) | $\begin{gathered} 62 \\ \text { Sm } \\ 150.36 \end{gathered}$ | $\begin{gathered} 63 \\ \text { Eu } \\ 151.97 \end{gathered}$ | $\begin{gathered} 64 \\ \mathrm{Gd} \\ 157.25 \end{gathered}$ | $\begin{gathered} 65 \\ \text { Tb } \\ 158.93 \end{gathered}$ | $\begin{gathered} 66 \\ \text { Dy } \\ 162.50 \end{gathered}$ | $\begin{gathered} 67 \\ \mathrm{Ho} \\ 164.93 \end{gathered}$ | $\begin{gathered} 68 \\ { }_{16 r} \\ 167.26 \end{gathered}$ | $\begin{gathered} 69 \\ \mathrm{Tm} \\ 168.93 \end{gathered}$ | $\begin{gathered} 70 \\ \mathrm{Yb} \\ 173.04 \end{gathered}$ | $\begin{gathered} 71 \\ \mathrm{Lu}_{174.97} \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 89 Ac <br> (227) | $\begin{gathered} 90 \\ \text { Th } \\ 232.04 \end{gathered}$ | $\begin{gathered} 91 \\ \mathrm{~Pa} \\ 231.04 \end{gathered}$ | $\bigcup_{238.0}^{92}$ | $\begin{gathered} 93 \\ \stackrel{N}{N p} \\ 237.05 \end{gathered}$ | $\begin{gathered} 94 \\ \mathrm{Pu} \\ (244) \end{gathered}$ | $\begin{gathered} 95 \\ \mathrm{Am} \\ (243) \end{gathered}$ | $\begin{gathered} 96 \\ \text { Cm } \\ (247) \end{gathered}$ | 97 <br> Bk <br> (247) | $\begin{gathered} 98 \\ \text { Cf } \\ (251) \end{gathered}$ | $\begin{gathered} 99 \\ \text { Es } \\ (252) \end{gathered}$ | $\begin{aligned} & 100 \\ & \text { Fm } \\ & (257) \end{aligned}$ | $\begin{gathered} 101 \\ \text { Md } \\ (258) \end{gathered}$ | $\begin{gathered} 102 \\ \text { No } \\ (260) \end{gathered}$ | $\begin{gathered} 103 \\ \mathrm{Lr} \\ (260) \end{gathered}$ |

## Tanabe -Sugano Diagrams for Octahedral d ${ }^{\mathbf{n}}$ Complexes



$d^{4}$ with $C=4.16 B$

$d^{5}$ with $C=4.477 B$

$d^{6}$ with $C=4.8 C$

$d^{7}$ with 4.633B

$d^{8}$ with $C=4.709 B$


