OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
CHM 401: TRANSITION METAL CHEMISTRY 4 UNITS
HARMATTAN 2024/2025 MID-SEMESTER EXAMINATION

Time: 45 Minutes

1. Predict the number of unpaired electrons and hence calculate the magnetic moment of the complexes $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$

2. ai. What is lanthanide contraction?
   ii. What are the consequences? 4f 5d 6s
   b. The actinide elements, Thorium, Protactinium and Uranium were the only actinides known before 1940. Then they were thought to be part of the "d" series of elements. Justify this assumption.
   c. Why do the lanthanide ions give rise to very sharp bands in their electronic spectra?

Potassium hexachlorovanadate (II)

3. a. Write the correct IUPAC name of $K_4[(VCl_6)]$. para
   b. Determine the hybridization, shape and magnetic property of $K_4[(VCl_6)]$.
   c. Draw the crystal field splitting diagram of this complex and calculate CFSE.
   d. State if will $K_4[(VCl_6)]$ be
      iv. labile or inert
      v. LaPorte allowed or forbidden electronic transition
      vi. spin allowed or forbidden electronic transition
      and give reason(s) for your answers.

K^{+4} $[VCl_6]^{-4}$

$x + 6(-1) = -4$

$x = 6 - 4$

$x = 2$

21 Sc
22 Ti
23 V
24 C
25 M
26 F
C
N
C
Z

sp - linear

sp^2 = Trigonal plan

sp^3 - Tetrahedral

d^2sp - square planar d^2sp

0.4 — e_g

-0.6 — — t_{2g}

Weak field

CFSE = $n\Delta + mp$

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Degree Examination Part IV
CHM 401: TRANSITION METAL CHEMISTRY 4 UNITS
Harmattan Semester Examination (2023/2024 Session)

Time Allowed: 2 hours **Date: 26th February 2026**

INSTRUCTION:
1. Attempt **FIVE (5)** Questions in All
2. Question **(ONE) 1** is Compulsory
3. Attempt *at least* **ONE (1)** Question from Each Section

SECTION A

Question (ONE) 1 is compulsory

Ti K OH

1(a). Draw the structure μ-amido-μ-hydroxo-bis(tetraaquoiron(III)) ion.

(b). To prepare $[Cu(NH_3)_4(H_2O)_2]Cl_2$, $CuCl_2$ was dissolved in water and then concentrated NH_3 solution and NH_4Cl were added with continuous heating and stirring. Use each of bond theories to briefly explain how Cu can bond with 6 molecules.

(c). Group the following into hard acid, soft acid, hard base, soft base and then using 2 examples each to show which pair would form predominately electrostatic character and which pair would be predominately covalent in character. OH^-, Ti^{4+}, SCN^-, Mn^{2+}, F^-, Cu^{2+}, Cr^{3+}, ox^{2-}, Fe^{3+}, Au^+, CO, I^-, Ag^+.

(d). The d^3 configuration has a relationship with one or more of these configurations - d^2, d^4, d^6, d^7, d^8 or d^9. State the one(s) that it has a (i) direct (ii) indirect relationship with and how it so.

$3 \times 4/2$, $6+1/2$

(e). From (d) above write electronic transition each would undergo in an octahedral field (include multiplicity).

2, 8, 8, 2 Manganese $Cu(OH)_2$

2(a). Name the following complexes:
- (i) $Ca[MnCl_5]^{2-}$ 12
- (ii) $Mg[FeBr_6]^{2-}$ 2, 8, 2
- (iii) $Na_2[Fe(CN)_6]^{2-}$

$7/2 + 1$

(b). The complex $Ca[MnCl_5]$, was formed by mixing $MnCl_2$, $CaCl_2$ and conc HCl. Predict the following giving full explanations:

$7(3/2)+1$

- (i) hybridization
- (ii) shape and
- (iii) magnetic property

$5-2=3$
$6-2=4$
$6-2=4$

np + Δm

3

(c). Consider these complexes $Mg[FeBr_6]^{2+}$ and $Na_2[Fe(CN)_6]^{2+}$
- (i) Draw their crystal field splitting pattern
- (ii) Calculate their CFSE.
- (iii) If the UV-Vis spectrum of each of the complexes where to be obtained, give an explanation about the nature of their electronic transition i.e. if they would be Laporte and spin allowed or forbidden. Δ + mp

d^2/d^7
d^3/d^8

$A_{1g} \leftarrow T_{1g}(F)$ $-6 = -4$

$T_{1g}(P) \leftarrow T_{1g}(F)$ $Ti^{2+} = d^2$

T_{2g} (d). $\leftarrow T_{1g}(F)$ The UV-Vis spectrum of the $K_4[TiCl_6]^{4-}$ had absorptions bands at 18,200 cm^{-}, 23,500 cm^{-} and 30,600 cm^{-}. From the Tanabe Sugano diagram, @$\frac{\Delta}{B} = 30$ the Racah parameter B was estimated to be 603.8 cm^{-}.

(i) Write the molecular orbital electronic configuration of Ti in the complex.
(ii) What is the ground state term symbol of Ti in the complex?
(iii) Assign these absorption bands to electronic transition and arrange in order of increasing energy.
(iv) Calculate Δ.
(v) Determine the value of distortion due to$T_1(P)$ and $T_1(F)$ interaction **in nm**, if transition with highest energy is equivalent to <u>$0.6\Delta_{oct} + 15B + 2x$.</u>

SECTION B

3(a). Illustrate the existence of varying oxidation states in Transition Metals using $_{25}M$ giving example where necessary.

(b). Using appropriate theory and the ligands NH_3 and CN^-, predict the magnetic behaviour of Fe^{2+} and Mn^{2+} in an octahedral environment and calculate the magnetic moment of the respective metal complexes.

4(a). Explain in detail, the various magnetic behaviour exhibited by transition metals giving relevant example in each case

(b). Why are compounds of Ti^{4+} and Zn^{2+} typically white? Account for the very paled colour displayed by Mn^{2+} compounds.

21 $Sc = 3d^1 4s^2$
22 $Ti = 3d^2 4s^2$
23 $V = 3d^3 4s^2$
24 $Cr = 3d^5 4s^1$
25 $Mn = 3d^5 4s^2$
$Fe = 3d^6 4s^2$
$Co = 3d^7 4s^2$
$Ni = 3d^8 4s^2$
$Cu = 3d^{10} 4s^1$
$Zn = 3d^{10} 4s^2$

SECTION C

5(a). Name the actinide elements in the correct order and give their chemical Symbols.

(b). Discuss the relationship between the observed <u>oxidation states</u> of the lanthanides and their <u>electronic structures</u>. +3

(c). List the different methods employed in the separation of lanthanides. Which is the most effective?

s a_{1g}
p t_{1u}
d t_{2g}
d e_g

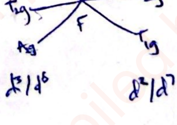
$e_g = t_{2g} < a_{1g} < t_{1u}$

6(a) Name the lanthanide elements in the correct order and give their chemical Symbols.

(b). Why were cerium and Europium the easiest lanthanides to isolate before the development of ion-exchange chromatography?

(c). Compare and contrast the formation of complexes by lanthanides and actinides.

$[Mn(NH_3)_6]^{2+}$



$[Fe(CN)_6]^{4-}$

-2 -1

CHM 401 TUTORIAL Qs

1a Why is the chemistry of the lanthanide elements homologous?

b. Why were cerium and Europium the easiest lanthanides to isolate before the development of ion-exchange chromatography?

2a Compare and contrast the formation of complexes by lanthanides and actinides.

b. The ions Am^{3+} ($5f^6$) and Eu^{3+} ($4f^6$) are both coloured pink. The absorption bands in

Am^{3+} are broader than those in Eu^{3+}. Suggest explanation(s) for this observation.

3a. The actinide elements, Thorium, Protactinium and Uranium were the only actinide known before 1940. Then they were thought to be part of the "d" series of elements. Justify this assumption.

b. What are the main sources of thorium and uranium?

4a. What are the factors determining the stability of the oxidation states of lanthanides?

b. Complete the following:

(i) $^{239}_{94}Pu + n, \gamma \rightarrow ?? + n, \gamma \rightarrow ?? + \beta \rightarrow {}^{241}_{95}Am$

(ii) $^{235}_{92}U + ?? \rightarrow {}^{236}_{92}U + {}^{1}_{0}n \rightarrow {}^{237}_{92}U + \beta \rightarrow {}^{237}_{93}Np$

5a. Write short notes on the Electronic spectra of lanthanides.

b. What do you understand by Lanthanide Contraction?

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CHM 401 TEST- (TRANSITION METAL CHEMISTRY) -2023/2024 SESSION Time- 50 mins

1a. What is the IUPAC name of the compound, $K_2[MnCl_4]$?

b. Predict the hybridization, shape and magnetic property of the complex.

c. Draw the crystal splitting of the complex and calculate the crystal field stabilization energy.

d. The colour of the complex is magenta; which of the following (from i – iv) would be the most likely shade of the colour of the complex. State the reason(s) for your answer.

(i) Very pale ($\varepsilon_{max} = 0.5\ dm^3mol^{-1}cm^{-1}$)
(ii) moderately pale ($\varepsilon_{max} = 3.0\ dm^3mol^{-1}cm^{-1}$)
(iii) moderately intense ($\varepsilon_{max} = 250\ dm^3mol^{-1}cm^{-1}$)
(iv) very intense ($\varepsilon_{max} = 10{,}000\ dm^3mol^{-1}cm^{-1}$)

2. Explain giving relevant example(s) the catalytic activity/complex formation properties of transition metals.

3a. Why is the chemistry of the lanthanide elements homologous?

b. List the different methods employed in the separation of lanthanides. Which is the most effective?

c. What are the factors determining the stability of the oxidation states of lanthanides?

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$

Sc. Ti V Cr Mn

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CHM 401: TRANSITION METAL CHEMISTRY 4UNITS
Harmattan Semester Examination (2023/2024 Session)

Time Allowed: 2 hours **Date: 26th February 2025**

INSTRUCTION: ATTEMPT ALL QUESTIONS IN SECTION A, AND TWO OTHER QUESTIONS FROM SECTION B

SECTION A

24 $3d^5$ $4s^1$

1(a). Illustrate the existence of varying oxidation states in transition metals using Manganese Metal ions.

(b). Predict the magnetic behavior of the following complexes using appropriate theory and hence calculate the magnetic moment of each of them:

(i) $[Co(H_2O)_6]^{+3}$ (ii) $[Mn(CN)_6]^{-3}$ (iii) $[Fe(CN)_6]^{-4}$ (iv) $[Fe(NH_3)_6]^{+3}$

2(a). Sodium nitroprusside ($Na_3[(Fe(NO_2)(CN)_5])$, an octahedral complex is used as an antihypertensive. Predict the hybridization and magnetic property of this drug.

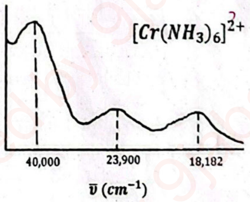
(b) When exposed to UV-Vis light, electronic transition would occur. State the nature of these transitions and the reason(s) for your answer.

(c) Explain the difference between $\pi-$donor and $\pi-$acceptor ligands. Give 2 examples of each.

(d) Consider these complexes of chromium; $[Cr(CO)_6]$ and low spin $[Cr(NH_3)_6]^{2+}$. Write the molecular orbital electronic configuration of each and underline the orbitals where ligand field splitting occurs.

(e) The image is the absorption spectra of $[Cr(NH_3)_6]^{2+}$. Assign the peaks using term symbols.

(f) The Nephelauxetic effect (β) of the NH_3 ligands at $\frac{\Delta_{oct}}{B} = 20$ is 0.676. If the Racah parameter of the free Cr^{2+} is 1050 cm^{-1}, calculate Racah parameter of Cr^{2+} in the complex and Δ_{oct} in joules ($h = 6.62 \times 10^{-34}$ J.s; $c = 3.0 \times 10^{10}$ cm/s)



3(a) What are lanthanide elements?

(b) Why is it difficult to separate the lanthanide ions?

(c) The ions Americium (III), Am^{3+} ($5f^6$) and Europium (III), Eu^{3+} ($4f^6$) are both coloured pink but the absorption bands in the electronic spectra of Americium (III) complexes are broader than those in the electronic spectra of Europium (III) complexes. Suggest explanation(s) for this observation.

(d) What are the main sources of thorium and uranium?

(e) Complete the following:

(i) $^{239}_{94}Pu + n, \gamma \rightarrow ?? + n, \gamma \rightarrow ?? + \beta \rightarrow {}^{241}_{95}Am$.

(ii) $^{235}_{92}U + ?? \rightarrow {}^{236}_{92}U + {}^{1}_{0}n \rightarrow {}^{237}_{92}U + \beta \rightarrow {}^{237}_{93}Np$

SECTION B

4(a) Explain in details, the various magnetic behavior exhibited by transition metals giving relevant example in each case

(b) (i) Why are compounds of Ti^{4+} and Zn^{2+} typically white?

(ii) Account for the very pale colour displayed by Mn^{2+} compounds.

5(a) Draw the structure of octaamminediaquo-μ-sulphato-κ^2 O-dicopper(II) ion.
Use valence bond theory to explain the bonding between ions/molecules in a coordination compound.

(b) Which of one would be more stable and why, $[CoF_6]^{3-}$ and $[CoI_6]^{3-}$?

(c) Two complexes Complex-A and Complex-B, were subjected to UV-Vis analysis and their λ_{max} were 425nm and 682 nm respectively. If their central metal is Fe^{2+}, based on crystal field theory, answer the following questions:

(i) Which complex would have a large crystal field splitting and why?

(ii) What can you say about the nature of the ligands in (i)?

(iii) Draw the crystal field splitting of both complexes.

(iv) Which complex would be high spin and paramagnetic and why?

(v) Both complexes have Laporte forbidden transition but which one has spin allowed transition and why?

(d) According to ligand field theory, there are interrelationships between certain d-configurations.

(i) Draw and complete the table below for d^1, d^4, d^6 and d^9 configurations

d^n	-2	-1	0	+1	+2	S	2S+1	L	Ground State Term Symbol

(ii) Which pair(s) have a direct relationship?

(iii) Which pair(s) have an inverse relationship?

(iv) What is the implication of these relationships?

(v) Write the electronic transition for an octahedral complex of each of these using term symbols.

6(a) What do you understand by Lanthanide Contraction?

(b) Why were cerium and Europium the easiest lanthanides to isolate before the development of ion-exchange chromatography?

(c) The actinide elements, Thorium, Protactinium and Uranium were the only actinide known before 1940. Then they were thought to be part of the "d" series of elements. Justify this assumption.

(d) Compare and contrast the formation of complexes by lanthanides and actinides

Academic intelligence — to understand that doing assignment even if it's not used in CA help you study concepts.

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CHM 401 TEST-(TRANSITION METAL CHEMISTRY) -2022/2023 SESSION

1i. In terms of bonding between a metal and its ligands, what is/ are the difference(s) between valence bond theory and crystal field theory?

ii. What is the name IUPAC of the complex $Na_3[Cr(F)_6]$ and draw the structure?

iii. Write the molecular orbital electronic configuration of the complex.

iv. Would you describe the complex as inert or labile? Give reason(s) for your choice?

v. Using full term symbol show the electron transition(s) that this complex would undergo. $[Cr = 3d^5, 4s^1]$.

2. Predict the magnetic behaviour of the following complexes using crystal field theory and hence calculate the magnetic moment: (i) $[Fe(H_2O)_6]^{+3}$ (ii) $[Mn(CN)_6]^{-3}$ (iii) $[Fe(CN)_6]^{-4}$ (iv) $[Fe(NH_3)_6]^{+2}$, (v) $[Ni(NH_3)_6]^{+2}$.

3i. What are lanthanide elements?

ii. Why were cerium and Europium the easiest lanthanides to isolate before the development of ion-exchange chromatography?

iii. Write short notes on the electronic spectra of lanthanides.

CHM401 EXAM QUESTION 2022/2023 SESSION

i. Draw the structure of this complex μ-amido-μ-hydroxo-bis(tetraamminecobalt(III)) ion

ii. If the hybridization of a d^6 metal in a complex is d^2sp^3, what would be the implication of this in terms its
  a. spin,
  b. Lability,
  c. shape,
  d. nature of the ligand or metal
  (Short answers only)

iii. Explain how the splitting in a complex with coordination number of 6 occurs.

iv. According to ligand field theory a d^8 ion has a relationship with d^2 and the d^3 ions. Explain these relationships and what is the implication in terms of multiplicity and electronic transition in an octahedral field.

i. What is the name of the complex $[NiBr_4]^{2-}$?
ii. Predict the shape, hybridization and magnetic property of the complex'
iii. Draw its crystal field splitting and calculate the crystal field stabilization energy.
iv. Based on the electronic transition selection rules, will its transition be allowed or forbidden, explain.
v. The electronic spectra of $[NiBr_4]^{2-}$ had 3 peaks at 14705, 17860, and 23809 cm-^{1}. From Tanabe Sugano diagram it was derived that $\frac{\Delta_t}{B} = 10$ and $\frac{E_3}{B} = 28$; $\frac{E_2}{B} = 16$; $\frac{E_1}{B} = 10$. Calculate
  a. The racah parameter B of the complex
  b. Δ_t
  c. Calculate the crystal field stabilization energy from (iii) above in joules where h = 6.63×10^{-34}Js and c 3.0×10^{8} m/s.
  d. Nephelauxetic ratio б, where the B_{free} ion = 1030 cm^{-1}

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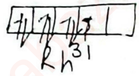
CHM 401 TEST-(TRANSITION METAL CHEMISTRY) - ~~2020/2021~~ 2021/2022 SESSION

1. $RhCl_3$ and $CoCl_2$ were dissolved in water to form their corresponding aquo complexes. X-ray studies show that the Rh^{3+} complex is square planar and the Co^{2+} complex is octahedral. wrong question on Rh^{3+}

   i. What is the hybridization of the central metal ions? ; 2
   ii. Use simple illustration to show how you deduced their hybridizations; 2
   iii. What will be their magnetic properties?; 2
   iv. Which one will be high spin and which low spin?; 2
   v. Draw the chemical structure of each of the complexes; 2
   vi. Based on ligand field theory, how many peaks would be expected in the electronic spectra of these complexes?; 2
   vii. Write the transition(s) that would occur using term symbols and where applicable in the order of increasing energy. 2

   $(Rh^0 = 4p^6 4d^8 5s^1 \quad Co^0 = 3p^6 3d^7 4s^2)$. 6

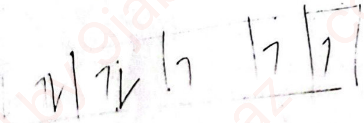
   wrong question



2. Discuss the variable oxidation states in the 3d, 4d and 5d transition metals.

3. a. What are lanthanide elements?
   b. Why is it difficult to separate the lanthanide ions?;
   c. List the different methods employed in the separation of lanthanides. Which is the most effective? methods employed

T_2



CHM401, 2021/2022
Exam

(1)

a) What does it mean when a complex is described with the following terms? (i) High spin (ii) Low spin (iii) Paramagnetic (iv) Diamagnetic

b) Generally speaking, coordination complexes are compounds which consist of a central metal atom or ions surrounded by a definite number of electron donating molecules or ions.

i. Classify the following as **Hard Acid, Hard Base, Soft Acid and Soft Base** – OH^-, Sc^{3+}, Cl^-, Au^+, Co^{2+}, Au^{3+}, Co^{3+}, NH_3, Pd^+, I^-, Cr^{3+}, CO, Fe^{2+}, Cu^{2+}, F^-, Fe^{3+}, $C_2O_4^{2-}$, Ag^+, CN^-, Cu^+

ii. With respect to coordination chemistry, what are (*) soft acids (**) hard bases?

c) In CHM316 you learnt that any metal complex that's undergoes reactions with $t_{1/2} \leq 1$ min at room temperature and about 0.1 M solution is described as being kinetically labile. Predict which of these complexes would be labile and which would be inert and give reason(s) for your answer (i) $[Co(en)_3]Cl_3$, (ii) $Na_2[CoF_4]$, (iii) $[Mo(CO)_6]$, (iv) $[Fe(H_2O)_6]Br_2$, (v) $[Cr(NH_3)_6]Cl_3$, (vi) $Na_2[HgCl_4]$

d) These are 16 microstates of d^2 metal ion.

i. Calculate the M_L and M_S of each state and group them.

ii. Determine the L, S and J values are for each group

iii. Write the term symbols

iv. Arrange them in the order of increasing energy.

	-2	-1	0	+1	+2	M_L	M_S
a.	↓	↑					
b.	↓		↑				
c.	↓			↑			
d.	↓				↑		
e.		↓	↑				
f.		↓		↑			
g.		↓			↑		
h.			↓	↑			
i.			↓		↑		
j.				↓	↑		
k.	↓↑						
l.		↓↑					
m.			↓↑				
n.				↓↑			
o.					↓↑		

Grouping M_S	Grouping M_L	L	Term symbols	S	(2S+1)	J values	Full term symbols

Use the format of the table above

(2)

The aquo complex of $RhCl_3$ was saturated with CO gas at very low temperature resulting in the formation of $[Rh(CO)_6]Cl_3$. ($Rh^0 = 4p^6 4d^8 5s^1$).

a) What is the name of this product?
b) Using Valence Bond Theory, predict its hybridization and magnetic property
c) Draw the crystal field splitting of the complex and calculate its Δ.
d) Is this complex centrosymmetric or non-centrosymmetric? And why?
e) Are its electronic transition Laporte allowed or forbidden give justification for this?
f) Is its electronic transition spin allowed or forbidden, and why?
g) Therefore, ε_{max} for this complex be with which range: < 1, 1 – 10, 10 – 1000 or 1000 – 50,000 $dm^3 mol^{-1} cm^{-1}$
h) Would its colour pale or intense?
i) Based on ligand field theory, what kind of the ligands are in the complex?
j) Write out the molecular electronic configuration of the complex.
k) Which molecular orbitals will be involved in electronic transition.
l) Ligand field theory has been able to explain why CO is a strong field ligand, why is this so?
m) Would this complex undergo back bonding if YES how and if NO why?

SECTION A

MARKING GUIDE

(1)

a.

i. A high spin complex has no forced pairing of electrons of the electrons of its central metal.
ii. A low spin complex has the electrons of the central metal forced to pair.
iii. A paramagnetic complex has unpaired electron(s).
iv. A diamagnetic complex has no unpaired electron(s).

2 marks

b.

20/10

i.

Hard Acid	Soft Acid
$Sc^{3+}, Au^{3+}, Co^{3+}, Cr^{3+}, Fe^{3+}$	$Au^{+}, Co^{2+}, Pd^{+}, Fe^{2+}, Cu^{2+}, Ag^{+}, Cu^{+}$
Hard Bases	Soft Base
$OH^{-}, Cl^{-}, NH_3, F^{-}, C_2O_4^{2-}$	I^{-}, CO, CN^{-}

2

2 marks

ii. Soft acids are the central metal of the complex that are easily polarized.
ii. Hard bases are the ligands of the complex that are not easily polarized

1 mark

c.

i.	$[Co(en)_3]Cl_3$	Inert (1)	Chelating effect of ethylenediamine (en); en is a strong field ligand would result high crystal field stabilization energy (CFSE) and therefore low spin d^6 configuration of Co^{3+}. (4 ticks)	5
ii.	$Na_2[CoF_4]$	Labile (1)	Co belongs 3d group and their M^{2+} ions are labile; F^- is a weak field ligand, would create low CFSE. (3 ticks)	4
iii.	$[Mo(CO)_6]$	Inert (1)	Mo belong to the 4d group and their metal ion are inert and CO being a strong field ligand would cause high CFSE (3 ticks)	4
iv.	$[Fe(H_2O)_6]Br_2$	Labile (1)	Fe belongs 3d group and their M^{2+} ions are labile; F^- is a weak field ligand, would create low CFSE. (3 ticks)	4
v.	$[Cr(NH_3)_6]Cl_3$	Inert (1)	The d^3 configuration of Cr^{3+}. (2 ticks)	3
vi.	$Na_2[HgCl_4]$	Labile (1)	Hg^{2+} has a completely filled d-orbital and Cl^- is a weak field ligand resulting in low CFSE. (3 ticks)	4

24/4

6 marks

14

d.

	-2	-1	0	+1	+2	M_L	M_S	
a.	↓	↑				-3	0	✓✓
b.	↓		↑			-2	0	✓✓
c.	↓			↑		-1	0	✓✓
d.	↓				↑	0	0	✓✓
e.		↓	↑			-1	0	✓✓
f.		↓		↑		0	0	✓✓
g.		↓			↑	+1	0	✓✓

1/1

4 marks

7.

h.			↓	↑		+1	0	✓ ✓
i.			↓		↑	+2	0	✓ ✓
j.				↓	↑	+3	0	✓ ✓
k.	↓↑					-4	0	✓ ✓
l.		↓↑				-2	0	✓ ✓
m.			↓↑			0	0	✓ ✓
n.				↓↑		+2	0	✓ ✓
o.					↓↑	+4	0	✓ ✓

30

30
24
54

18

$\frac{55}{11}$

55
11

5

23

5 male

Grouping M_S	Grouping M_L	L	Term symbols	S	(2S+1)	J values	Full term symbols
0 ✓	+4, +3, +2, +1, 0, -1, -2, -3, -4	4	G	0	1 singlet	4 only	${}^1G_4$
0 ✓	+2, +1, 0, -1, -2	2	D	0	1 singlet	2 only	${}^1D_2$
0	0	0	S	0	1 singlet	0 only	${}^1S_0$

24
8

J values = (L + S), [(L + S)-1], [(L + S) -2] …

$${}^1G_4,\ {}^1D_2,\ {}^1S_0 \checkmark \quad \checkmark$$

— [illegible] 9

$\xrightarrow{\hspace{3cm}}$

Increasing order in energy ✓

6 marks

57
24
$\frac{24}{4} = 6$

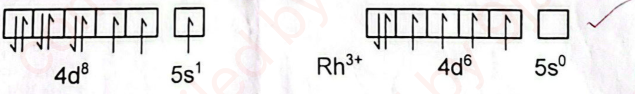
30
24
54
55

(2)

a. $[Rh(CO)_6]Cl_3$ = Hexacarbonylrhodium(III) chloride (1 mark)

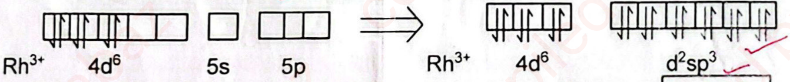
b. Rh in complex is in the +3 oxidation state $[Rh(CO)_6]^{3+}$ charge on CO is 0 because its neutral and the counter ion Cl^- has charge of -1 ✓

$$Rh + 6(0) + 3(-1) = 0$$
$$Rh + (0) + (-3) = 0$$
$$\therefore Rh = +3 \checkmark$$



10/2

Each CO is donating a lone pair of electrons. Therefore, for Rh to accommodate these 12 electrons (from 6 CO) it would need to form 6 hybrid orbitals. The 4d orbital are large, they would bond strongly and it would rather pair the electrons. So also CO is a strong field ligand and would force pairing. This would make the two of its 4d orbital vacant and then it would use this vacant 4d, 5s and all of its 5p orbitals to generate d^2sp^3 hybridization. The complex is diamagnetic – having no unpaired electrons.

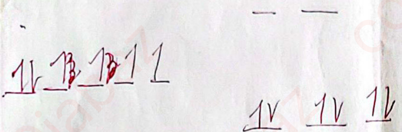


5 marks

c. It is an octahedral complex and therefore would split into t_{2g} and e_g orbitals.

$$\mathbf{CFSE = E_{LF} - E_{IF}}$$
$$E_{LF} = (n\Delta + mP)$$

$E_{IF} = (mP)$

 2 marks	$Rh^{3+} = t_{2g}^6, e_g^0$ $E_{LF} =$ $6 \times (-0.4\Delta_{oct}) + 3p = \quad -2.4\Delta_{oct} + 3P$ $E_{IF} = 1p$ $CFSE = E_{LF} - E_{IF} =$ $-2.4\Delta_{oct} + 3P - p$ $= -2.4\Delta_{oct} + 2P$ 3 marks

d. It is centrosymmetric because it an octahedral complex having the same ligands and a centre of symmetry or inversion centre. (1 mark)

e. Its electronic transitions are Laporte forbidden because they are d – d transitions, having a centre of symmetry. (1 mark)

f. Its electronic transitions are spin allowed because there will be no change in spin moving from t_{g2} to e_g. (1 mark)

g. Since its transitions are Laporte forbidden but spin allowed, it , ε_{max} would fall around $1 - 10\ dm^3mol^{-1}cm^{-1}$ (1 mark)

h. It is most likely to have a pale colour. (1 mark)

$\frac{10}{2} = 5$

i. CO is a π-acceptor ligand (1 mark)

j. $Rh^{3+} = 6e^-$
$6CO = 12\sigma e^-$
$Total = 18e^-$

$$a_{1g}^2, t_{1u}^6, e_g^4, t_{2g}^6, e_g^{*0}, t_{2g}^{*0}, a_{1g}^{*0}, t_{1u}^{*0}$$

(1 mark)

/

k. $t_{2g}^6 \rightarrow e_g^{*0}$ will be involved in the electronic transition. (1 mark)

l. LFT showed that with π-acceptor ligands they stabilize the t_{2g} i.e. lowering it energy thereby increasing the gap between the t_{2g} and the e_g^* and in effect increasing Δ_{oct} (1 mark)

m. Yes CO will undergo back bonding. This is because the 3d-orbital (π-orbital) of carbon is vacant and therefore be available for the metal to donate electrons. (1 mark)

DEPARTMENT OF CHEMISTRY

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA

CHM 401 TEST-(TRANSITION METAL CHEMISTRY) -2019/2020 SESSION

1. Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in terms of the following:

(i) Electronic Configurations (ii) Oxidation state

(Note: your answer should not be more than five lines each).

2a. Draw the structure of these complexes
   i. Sodium hexanitritocobaltate(III) ✓
   ii. Tris(propylenediamine)cobalt(III) chloride ✓ ✓
   iii. Diamminediaquodiisothiocyanatocobalt(III) chloride ✓

b. The orbitals of cobalt in Complex 2a (iii) above is d^2sp^3 hybridized
   i. What would be its magnetic property? ✓ ✓
   ii. Would it be high spin or low spin? ✓ ✓
   iii. Would it be inert or labile and why? ✓ ✓

3a. Why is the chemistry of the lanthanide elements homologous?

b. What are the factors determining the stability of the oxidation states of lanthanides?

c. What are the main sources of thorium and uranium?

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Chemistry Degree
Harmattan Semester Examination for 2019/2020 Session
Part IV

CHM401 – TRANSITION METAL CHEMISTRY

Date: 1st June, 2021 TIME ALLOWED: 2½ hours

INSTRUCTION: ANSWER ANY FIVE QUESTIONS

SECTION A

1a. In the spectrochemical series, the field strength of the cyanide ion, (CN^-) ligand is greater than that of the oxalate ion, ($C_2O_4^{2-}$). That is, the CN^- ligand results in a larger crystal field splitting (Δ_o), than $C_2O_4^{2-}$. Consider these two Iron (III) complexes: $[Fe(C_2O_4)_3]^{3-}$ and $[Fe(CN)_6]^{3-}$.

- i. What is the oxidation state of the metal ions in the two compounds.
- ii. Using an appropriate representation diagram, show the electron distribution of the compounds in the crystal field environment (t_{2g} e_g.).
- iii. Calculate the theoretical magnetic moment in Bohr Magneton (BM), for each complex using appropriate equation.
- iv. Briefly comment on the Magnetic properties of these two Iron (III) complexes.

1b. Iron (Fe), Ruthenium, (Ru), and Osmium, (Os) are members of a triad (i.e. going down the group) in group VIII.

- i. Identify the metal/metals that is/are stable in +8 oxidation state among this group.
- ii. Predict the stoichiometry of the oxides formed at this oxidation state.

2. Given the half-cell reactions:

$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ -0.76 V

$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$ 0.00V

and the equation, $Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2\,(g)}$

[$F = 96485\ C\ mol^{-1}$; $R = 8.314 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1}$)

- i. Find the E^ocell for the reaction.
- ii. Calculate the ΔG^o (298 K) for the reaction.
- iii. Find the equilibrium constant K. for the reaction
- iv. Comment on the feasibility of the reaction based on the result of E^ocell, ΔG^o and K.

SECTION B

3a. What are coordination complexes?

b. Discuss <u>**briefly**</u> the theories used to explain the bonding in transition metal complexes.

4a. Using valence bond theory, predict the shape, hybridization and magnetic property of

(i) Sodium tetrabromocobaltate(II);

(ii) Sodium hexanitrocobaltate(III)

b. Based on Crystal Field Theory, draw the Crystal Field Splitting of the two complexes above.

c. Which one would have the higher molar absorptivity and why?

d. If each of these complexes were dissolved in water and then concentrated solution of HCl is added, which one would be chemically inert, give reason(s) for your answer(s).

e. Write the molecular orbital electronic configuration of sodium hexanitrocobaltate(III).

f. Which of the two complexes is likely to have just one peak in its electronic spectra?

g. Using term symbols write out the transition(s) responsible for the peak

SECTION C

5a. What do you understand by Lanthanide Contraction?

b. Why were cerium and Europium the easiest lanthanides to isolate before the development of ion-exchange chromatography?

c. Why is it difficult to separate the lanthanide ions?

List the different methods employed in the separation of lanthanides. Which is the most effective?

. d. Account for the variable oxidation states of the Actinides

6a. What are lanthanide elements?

b. The ions Americium (III), Am^{3+} ($5f^6$) and Europium (III) , Eu^{3+} ($4f^6$) are both coloured pink but the absorption bands in the electronic spectra of Americium (III) complexes are broader than those in the electronic spectra of Europium (III) complexes.

Suggest explanation(s) for this observation.

c. The actinide elements, Thorium, Protactinium and Uranium were the only actinide known before 1940. Then they were thought to be part of the "d" series of elements. Justify this assumption.

d. Compare and contrast the formation of complexes by lanthanides and actinides.

CHM401 MID-SEMESTER TEST 2018/2019

a) What is the IUPAC name of the compounds below?

i. $Ca[Ni(Br)_4]$

ii. $[Ni(en)_2(Br)_2]Br_2$

iii. $[Ni(CO)_4]Br_2$

b) Predict the hybridization, shape and magnetic property of the complexes (i) and (iii)

c) Calculate the crystal field stabilization energy of (i)

d) Briefly explain why the molar absorptivity of (i) is greater than (ii)

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Degree (Chemistry) Examination
CHM 401: TRANSITION METAL CHEMISTRY
2018/2019 Harmattan Semester Examination

Time Allowed: 2 Hours , **Date: 29th July, 2019**

Instructions: Answer Four (4) Questions in ALL with at least ONE from Each Section.

SECTION A

1.

a. Give reason(s) why the 4d and 5d transition elements have similar properties which are very different from those of the 3d elements
b. Discuss the differences between the 3d and 4d/5d elements using the following as guide: (i) oxidation state (ii) spin state (iii) abundance and (iv) coordination number.
c. What are the similarities and differences between NMR and ESR as techniques for structural elucidation
d. Write brief notes on (i) antiferromagnetism and (ii) magnetic dilution.

2.

Write comprehensive notes on the following:

a. Ionic radii of M^{2+} ions in an octahedral field
b. Formation constant
c. Hydration energies of M^{2+} ions
d. Ligand field stabilization energies

SECTION B

3.

a. What are actinide elements?
b. Why is the chemistry of the lanthanide elements homologous?
c. What are the factors determining the stability of the oxidation states of lanthanides?
d. The actinide elements, Thorium, Protactinium and Uranium were the only actinide known before 1940. Then they were thought to be part of the "d" series of elements. Justify this assumption.

4.

a. What do you understand by Lanthanide Contraction?
b. What are the main sources of thorium and uranium?
c. Write short notes on the Electronic spectra of lanthanides.
d. Why were Cerium and Europium the easiest lanthanides to isolate before the development of ion-exchange chromatography?

SECTION C

5.

a. The stability constants (logK) for the reactions of Fe^{3+} and Hg^{2+} with the halides is given below, Give a brief explanation of the trend(s) you observe.

NW 12
AI 7
NW 13
C 14
U 8
I 5
SC 17
PH 16
D 18
NC 18
A 19
L 6

	F^-	Cl^-	Br^-	I^-
Fe^{3+}	6.0	1.4	0.7	0.1
Hg^{2+}	1.0	6.7	8.9	12.9

b. Ni^{2+} and Pt^{2+} are both d^8 ions but $[NiCl_4]^{2-}$ is tetrahedral in shape and $[PtCl_4]^{2-}$ is square planar. Nickel forms square planar complexes with cyano ligands ($[Ni(CN)_4]^{2-}$). Give a brief explanation for these differences. (No diagrams/illustrations required

c. Give a brief explanation on why $[Mn(H_2O)_6]^{2+}$ is pale in colour while $[MnO_4]^-$ has a very intense colour. (No diagrams required)

d. Only state the type of bonding that exists in transition metal complexes according to (i) ligand field theory (ii) crystal field theory (iii) valence bond theory.

e. In the table below is the magnetic spin quantum number of a d^7 metal (M_s) and the corresponding orbital quantum number (M_l).

(i) Complete the table below

(ii) Combining all the J values obtained arrange in order of increasing energy.

S/N	M_s	M_l	S	L	Multiplicity	J	Term symbols
1	$+\frac{3}{2}$	$-3\ to\ +3$					
2	$+\frac{1}{2}$	$-2\ to\ +2$					
3	$+\frac{1}{2}$	$-5\ to\ +5$					
4	$-\frac{1}{2}$	$-1\ to\ +1$					
5	$+\frac{1}{2}$	$-3\ to\ +3$					
6	$+\frac{1}{2}$	$-4\ to\ +4$					

6.

Ik 21

Anhydrous $CrCl_3$ was dissolved in water to form $[Cr(H_2O)_6]Cl_3$ and dissolved in concentrated solution of NaOH to yield $Na_3[Cr(OH)_6]$.

[illegible] 23
B 20
NE 2 22m
Abuja 24
Aba 25
NEI 10
SW 9
Dalla 11
[illegible] 26

a. What is the correct IUPAC name of these complexes?

b. What is the primary and secondary valence of $Na_3[Cr(OH)_6]$?

c. Is $[Cr(H_2O)_6]Cl_3$ an inert or labile complex, give reason(s) for your answer?

d. $Na_3[Cr(OH)_6]$ is an octahedral complex, predict its hybridization and its magnetic properties.

e. Write the molecular orbital electronic for $[Cr(H_2O)_6]Cl_3$ and underline the molecular orbitals that would determine the ligand field splitting

f. Calculate the crystal field stabilization energy of $[Cr(H_2O)_6]Cl_3$

g. The ground state term symbol for $[Cr(H_2O)_6]Cl_3$ is ^4F, describe in details the significance of this term symbol.

h. According to ligand field theory, how many bands would the UV-Vis spectra of $Na_3[CrOH)_6]$ have and write the full notation electronic transition(s) responsible for these bands in order of increasing wavelength.

i. Which of these two complexes would undergo Jahn-Teller distortion? Give reasons(s) for your answer.

Huston 27
Emy 28

CHM401 TEST 2017/2018

Consider these two complexes (i) $[Fe(H_2O)_6]Cl_2$ (ii) $[Fe(en)_3]Cl_2$

a. Write their IUPAC names

b. Predict the hybridization of iron in each of the complexes?

c. Of the two complexes which would be inert towards ammonia and give one reason why?

d. From their absorption spectra $[Fe(H_2O)_6]Cl_2$ has its λ_{max} is around 675 nm and for $[Fe(en)_3]Cl_2$ its around 610 nm. Explain the reason for this difference in wavelength and what colours do you think these complexes would have?

e. Write the molecular electronic configuration of each complex.

f. Calculate S, L and J of the ground state term ^3F and ^5D and list the all allowed terms they have.

CHM401 TEST 2017/2018

Consider these two complexes (i) $[Fe(H_2O)_6]Cl_2$ (ii) $[Fe(en)_3]Cl_2$

a. Write their IUPAC names

b. Of the two complexes which would be inert and why?

c. Predict the hybridization of iron in each of the complexes?

d. From their absorption spectra $[Fe(H_2O)_6]Cl_2$ has its λ_{max} is around 675 nm and for $[Fe(en)_3]Cl_2$ its around 610 nm. Explain the reason for this difference in wavelength and what colours do you think these complexes would have?

e. Write the molecular electronic configuration of each complex.

f. Calculate S, L and J of the ground state term ^3F and ^5D and list the all possible terms they have.

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Degree (Chemistry) Examination Part IV
CHM 401: Transition Metal Chemistry
Harmattan Semester Examination (2017/2018)

Time Allowed: 2 Hours **Date: September 01, 2018**

Instructions: Answer **Four** (4) Questions in all with **at Least One** from **Each Section.**

SECTION A

1.

a. What are lanthanide elements?

b. Why is it difficult to separate the lanthanide ions?

c. List the different methods employed in the separation of lanthanides. Which is the most effective?

d. The ions, americium(III), Am^{3+} ($5f^6$) and europium(III), Eu^{3+} ($4f^6$) are both pink but the absorption bands in the electronic spectra of americium(III) complexes are broader than those in the electronic spectra of europium(III) complexes. Suggest explanations(s) for this observation.

2.

a. What are the factors that determine the stability of the oxidation states of lanthanides?

b. Compare and contrast the formation of complexes by lanthanides and actinides

c. Complete the following:

i. $^{239}_{94}Pu + n,\gamma \rightarrow ?? + n,\gamma \rightarrow ?? + \beta \rightarrow {}^{241}_{95}Am$

ii. $^{235}_{92}U + ?? \rightarrow {}^{236}_{92}U + {}^{1}_{0}n \rightarrow {}^{237}_{92}U + \beta \rightarrow {}^{237}_{93}Np$

SECTION B

3.

a. A careless group in CHM 316 were preparing 3 different chromium complexes: $[Cr(OH_2)_6]^{3+}$, $[Cr(CO)_6]^{3+}$, and $[CrF_6]^{3-}$ and forgot to label the samples. One sample was a green powder, another a yellow powder and the last was a purple powder. Identify which is which, giving excellent reasons for your identification.

b. i. What are hard acids and soft bases?

ii. Classify the following species as either hard or soft acid/base:

CO, Au^+, Ti^+, Ti^{3+}, Cl^-, I^-, Fe^{2+}, Co^{2+}, Y^{3+}, NH_3, CN^-, ox^{2-}

c. It is a fact that the higher the value of the stability constant of a complex, the more stable it is. From the table below, compare the complexes in column A and B in each row and state which would have the higher stability constant and why.

S/N	A	B
i	$K_3[Co(I)_6]$	$K_3[Co(C_2O_4)_3]$
ii	$[Fe(NH_2CH_2CH_2NH_2)_3]Cl_2$	$[Fe(NH_2CH_2CH_2CH_2NH_2)_3]Cl_2$
iii	$Na_2[(Mn(Cl)_4]$	$Na[(Mn(Cl)_4]$

1. Draw the structure of these complexes
    a. Sodium hexanitritocobaltate(III)
    b. tris(**propylenediamine**)cobalt(III) chloride
    c. Diamminediaquodiisothiocyanatocobalt(III) chloride

2. The orbitals of cobalt in Complex C above is d^2sp^3 hybridized
    a. What would be its magnetic property?
    b. Would it be high spin or low spin?
    c. Would it be inert or labile and why?

3. Which one from each pair is more stable and state why?
    a. Hexaaminecobalt(III) ion and tris(ethylenediamine)cobalt(III) ion
    b. Tris(acetylacetonato)cobalt(III) ion and tris(propylenediamine)cobalt(III) ion
    c. tris(propylenediamine)lead(II) ion and tris(ethylenediamine)lead(II) iom

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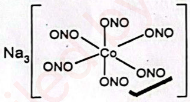
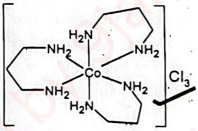
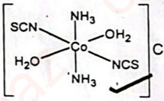
Solution to CHM401 TEST 2019/2020

(1)


a


b


c

(2)

a. For the hybridization of Co in complex C to be d^2sp^3 it means that it must be using 2 of its inner 3d orbitals, and Co^{3+} is a d^6 this means that there must be forced pairing, hence it would be diamagnetic.

b. Since there is forced pairing it would be low spin

c. Since is it is low spin d^6 then it would be inert

(3)

a	Tris(ethylenediamine)cobalt(III) ion is more stable than hexaaminecobalt(III) ion.	Ethylenediamine is a bidendate ligand and ammine is monodendate. The chelating effect of the bidendate ligand increase stability of the complex.
b	Tris(acetylacetonato)cobalt(III) ion is more stable than tris(propylenediamine)cobalt(III) ion	Although both ligands would form 6-member ring chelate, the presence of the delocalized electron in acetylacetonate ligand increases its stability.
c	tris(ethylenediamine)lead(II) iom is more stable than tris(propylenediamine)lead(II)	They both have saturated N-donor ligands however because Pb2+ is a large metal ion it would form more stable complex with ethylenediammine which would give a 5-member chelate ring.

ICH 401

~~ICH401~~ HARMATTAN SEMESTER TEST (2016/2017)

Consider this complex $[Pt(en)_2Cl_2](NO_3)_2$, its electronic spectra has absorption maximum at 410 nm. $[c = 3.0 \times 10^8 m/s\,;\ h = 6.63 \times 10^{-34} Js]$

1. Describe the bonding between the ligands and the metal according to valence bond theory and crystal field theory.
2. Using valence bond theory, predict its hybridization, shape and magnetic property
3. What is the IUPAC name of this compound?
4. What colour would this complex have and if **en** is a strong field ligand, would this colour be intense or weak? Give reason(s) for each of your answers.
5. In that case calculate the crystal field stabilization energy of this complex if **en** is a strong field ligand.

CIS

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY

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CHM401: TRANSITION METAL CHEMISTRY
HARMATTAN SEMESTER EXAMINATION (2016/2017)

Answer four (4) questions and at least one from each section **Time allowed: 2 hours**

SECTION A

1) The oxidation state of nickel in the following complexes $[Ni(H_2O)_6]Cl_2$, $Na_2[NiCl_4]$ and $Na_2[Ni(CN)_4]$ is +2.

a) Write the IUPAC name of each of the complexes.

b) Predict the hybridization and shape of each complex using valence bond theory.

c) Draw the crystal field splitting pattern of each complex.

d) State for each complex which is centrosymmetric or non-centrosymmetric; and which would undergo symmetry allowed or forbidden; spin allowed or forbidden electronic transitions.

e) The electronic spectrum of $[Ni(H_2O)_6]Cl_2$ and $Na_2[NiCl_4]$ both exhibited broad absorption bands as listed in the table below. Using ligand field theory suggest assignments of the electronic transitions.

$Na_2[NiCl_4]$	403 nm	520 nm	865 nm
$[Ni(H_2O)_6]Cl_2$	392 nm	495 nm	800 nm

2a) Based on ligand field theory write the molecular electronic configuration of the following complexes: (i) $Cr(CO)_6$ (ii) $[CoF_6]^{3-}$ (iii) $[Co(en)_3]^{3+}$ (iv) $[CrCl_6]^{3-}$]. (Do not draw the molecular orbital energy diagrams)

b) Use simple illustrations to show the energy separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for each complex in (a) above.

c) Below are some of the possible arrangements of 2 electrons in the d-orbitals. Derive the term symbols and then arrange them in order of increasing energy.

-2	-1	0	+1	+2
↓	↑			
↓		↑		
↓			↑	
↓				↑
	↓	↑		
	↓		↑	
	↓			↑
		↓	↑	
		↓		↑
			↓	↑
↓↑				
	↓↑			
		↓↑		
			↓↑	
				↓↑

d) The electronic spectra of a Cu^{2+} complex in an octahedral field was observed to consist of one broad band with a shoulder. Explain the reason for this shoulder.

SECTION B

3a) Give reason(s) why the 4d and 5d transition metals have similar properties which are different from those of 3d metals.

b) Discuss the differences between 3d and 4d/5d elements using the following as your guide.
(i) oxidation state (ii) spin state (iii) abundance (iv) coordination number.

c) (i) What are the similarities and/or differences between NMR and ESR?
(ii) Write brief notes on (a) antiferromagnetism and (b) magnetic dilution.

4) Write comprehensive notes on the following:
(a) Ionic radii of M^{2+} ions in O_h
(b) Formation constants
(c) Hydration energies of M^{2+} ions
(d) Ligand field stabilization energy

SECTION C

5a) What are lanthanide elements?

b) Why were cerium and Europium elements the easiest lanthanides to be isolated before the development of ion-exchange chromatography?

c) Discuss the oxidation states of Actinides.

6a) Why is the chemistry of lanthanide elements homologous?

b) The actinides elements: thorium, protactinium and uranium were the only actinides known before 1940. Then they were thought to be part of the "d" series of elements. Justify this assumption.

c) Discuss the chemistry of cerium and its compounds .

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE
DEPARTMENT OF CHEMISTRY
MID-SEMESTER TEST 2014/2015 SESSION,
401: Transition Metal Chemistry; TIME ALLOWED: 1 hr

INSTRUCTIONS

- ATTEMPT ALL QUESTIONS
- Write your name and registration number on your answer script

1a. Why is it difficult to separate the lanthanide ions?

b. List the different methods employed in the separation of lanthanides.

c. What are the factors determining the stability of the oxidation states of the lanthanides?

2.

A. State the reason(s) why for transition element the <u>ns</u> orbital is filled before the <u>(n-1)d</u> orbital.

B. Classify the following as hard acid, hard base, soft acid, soft base:
$Hg^{+}, Mn^{2+}, ox^{2-}, F^{-}, Mn^{7+}, Co^{+}, CO, Co^{3+}, NH_3$

C. Consider the following nickel complexes:
$K_2[Ni(Cl)_4]$ – green, $Na_2[Ni(CN)_4]$ – orange, $Na_3[Ni(CN)_5]$ – yellow, $[Ni(NH_3)_6]Cl_2$ – blue. Nickel is in the +2 oxidation state for the complexes.

i) State the following about these complexes

a) Hybridization of the orbitals of Ni in each complex

b) The overall shape of each complex

c) The spin and magnetic property of each

ii) Calculate Δ_{oct} and Δ_{tet} for the corresponding complexes (P = Pairing energy).

iii) Briefly explain why these nickel complexes above have the following colours even though they have the same oxidation number.

3a. The second and third row element in the periodic table resemble each other, give and explain two reasons why this is so.

b. Suggest, with the aid of VBT, the probable geometry and magnetic moment (spin only value) for the following complexes:
(i) $[MnCl_6]^{3-}$ (ii) $[Fe(CN)_6]^{4-}$ and (iii) $[Co(NH_3)_6]Cl_3$.

c. Give the two methods generally used for measuring magnetic susceptibility.

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OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
BSc (CHEMISTRY) DEGREE EXAMINATION
2014/2015 Harmattan Semester
CHM 401: TRANSITION METAL CHEMISTRY-

Time allowed: 2 hours & 30 minutes **Date: Oct. 2015**

INSTRUCTIONS:

(i). ANSWER ANY FIVE QUESTIONS.

(ii) ANSWER QUESTION(S) FROM EACH SECTION IN SEPARATE BOOKLET.

SECTION A

1a. What are lanthanide elements?

b. Why is it difficult to separate the lanthanide ions?

c. Why were Cerium and Europium the easiest lanthanides to isolate before the development of ion-exchange chromatography?

2a. The actinide elements, Thorium, Protactinium and Uranium were the only actinide known before 1940. Then they were thought to be part of the "d" series of elements. Justify this assumption.

b. Compare and contrast the chemistry of the lanthanides and actinides under the following headings:-

(i) Oxidation states.
(ii) Magnetic properties.
(iii) Electronic Spectral properties.

SECTION B

3 a. State which theory would give the simplest explanation to the following phenomena that occur with transition metal complexes

i. Carbon monoxide is a stronger field ligand than water.
ii. $[FeBr_4]^{2-}$ is tetrahedral while $Ni(CN)_4]^{2-}$ is square planar
iii. $[Co(Cl_4)]^{2-}$ is high spin while $[Co(CN_4)]^{2-}$ is low spin
iv. $[Mn(H_2O)_6]^{2+}$ is pale pink while $[Co(Cl_4)]^{2-}$ is deep red.
v. The electronic spectrum of $[Fe(H_2O)_6]^{2+}$ has only one absorption band while that of $[Co(H_2O)_6]^{2+}$ has three absorption bands.

b. $[Fe(H_2O)_6]^{3+}$ and $Fe(CN)_6]^{3-}$ are both paramagnetic and octahedral complexes. What kind of hybridization and spin will Fe possess in each complex? (Show all workings).

c. Write the correct molecular orbital electronic configuration for these complexes: $[Ni(H_2O)_6]^{2+}$, $[Cu(F)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$.

d. The d-d transition can be spin/symmetry allowed and/or forbidden. For each complex in the table below, state which is allowed and/or forbidden.

Complex	Symmetry	Spin
$Ti(H_2O)_6]^{2+}$		
$[NiCl_4]^{2-}$		

$Mn(H_2O)_6]^{2+}$		
MnO_4^-		
$Fe(H_2O)_6]^{3+}$		
$V(H_2O)_6]^{2+}$		

e. The d^9 configuration has 10 microstates, with the values L= 2 and S = ½, write it full term symbols and the notation of its electronic transitions in both an octahedral and tetrahedral complex.

4. a. Predict (show all workings) the shape, hybridization, spin and magnetic properties of $[Pt(NH_3)_4]^{2+}$and $Pt(Cl)_6]^{2-}$

   b. The diamagnetic complex, $[Co(NH_3)_6]^{3+}$, is orange while the paramagnetic complex, $Co(F)_6]^{3-}$, is blue. Based on the information provided, which of the ligands produces the stronger ligand field? Explain the reason(s) for your choice.

   c. $Cr(Cl)_4]^{2-}$and$Ni(Cl)_4]^{2-}$ are both tetrahedral complexes. How many 'd-d' bands would you expect to find in the absorption spectrum of each of the complexes? State the specific electronic transitions responsible for these bands.

   d. Draw the energy level diagram to show the splitting of the d-orbitals in a
      I. Tetrahedral field
      II. Octahedral field
      III. Jahn Teller distortion
      IV. Square planar geometry

   e. The d^3 configuration has 120 microstates and its term symbols are: $^2P,\ ^4F,\ ^2G,\ ^4P,\ ^2H,\ ^2D,\ ^2F$. Arrange these terms in increasing order.

SECTION C

5a. The second and third row transition elements have greater tendency to form polymers than the first row transition series. Give reasons for this observation.

b. The magnetic measurement for $CuSO_4.5H_2O$ at 293 K using a Guoy balance gave volume susceptibility of 1.70×10^{-4}. This compound has a density of 2.29 g cm^{-3}. Calculate the molar susceptibility for this compound.

[Cu=63.5, S=32.0, O=16.0, H=1.0]

c. Explain why $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

d. Why is Doppler effect important to Mossbauer spectroscopy?

e. Define the term "lanthanide contraction"

6a. The second and third row transition elements give large crystal field splitting energies. Give reasons for this observed phenomenon.

b. Discuss with the aid of a diagram the Instrumentation for the use of a Guoy balance

c. The hexaaquamanganese(II) ion contains five unpaired electrons while the hexacyano ion contains only one unpaired electron. Give reasons why this is so.

d. Discuss two applications each of nmr and infra-red spectroscopic techniques in the study of coordination compounds.

e. Why are Mn^{2+} compounds more stable to oxidation than Fe^{2+} to their +3 states?

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DEPARTMENT OF CHEMISTRY

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CHM401: TRANSITION METAL CHEMISTRY
MID-HARMATTAN SEMESTER EXAMINATION (2012/2013)
(PART TIME PROGRAMME)

ATTEMPT ALL QUESTIONS **TIME ALLOWED: 1 HR**

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1. Write the electronic configuration of Cr and Cr^{2+}.
2. Which section in the periodic table of d-block elements would metal with very high oxidation state be found?
3. What are coordination complexes?

[illegible]

4. For each of the complex ions below write its primary valence, secondary valence as well as the its molecular shape.
   a. $[Cu(CN)_3]^{2-}$
   b. $[Zn(CH_3)_6]^{2-}$
   c. $[Ag(NH_3)_2]^{2+}$
   d. $[Mn(Cl)_4]^{2-}$
5. List the theories used to explain bonding in transition metal complexes and only state the type of bonding used in each theory.
6. a. Classify the following either as hard acid or soft acid, hard base or soft base.
   $Co^{3+}, Ti^{+}, Sc^{3+}, Cr^{3+}, La^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Nd^{3+}, SCN^{-}, F^{-}, CN^{-}, I^{-}, NH_3, CO$

   b. From the metal ions above, list which ones can form stable complexes with CN^{-} and OH^{-}.
7. Predict the type of hybridization, geometry and magnetic properties of the following complexes.
   a. $[Pt(NH_3)_4]^{2+}$ b. $[Fe(CN)_6]^{4-}$ c. $Ni(Cl)_4]^{2-}$
8. Write the electronic configuration of Fe *(in terms of* t_{2g} *and* e_g*)* in $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$. Calculate their crystal field stabilization energy and state which is high spin, low spin, paramagnetic and diamagnetic.
9. Write the formula of the compound dischlorobis(ethylenediammine)platinum(IV) nitrate. Write the IUPAC name of this complex- $K_3[Fe(CN)_6]$.
10. $[Ni(H_2O)_4]^{2+}$ is deep green in colour while $[Mn(H_2O)_6]^{2+}$ is pale pink, explain why?
11. Compare the electronic spectra of d-block metals to those of f-block metals.

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OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
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CHM401: TRANSITION METAL CHEMISTRY
HARMATTAN SEMESTER EXAMINATION (2012/2013)
(PART TIME PROGRAMME)

Bp.61

ATTEMPT ALL QUESTIONS **TIME ALLOWED: 90 MINS**

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1. Cisplatin $[Pt(NH_3)_2Cl_2]$ is used in the treatment of cancer
   a. Write its IUPAC name.
   b. What type of hybridization does the molecular orbitals of platinum in this complex have and what is the overall shape of the molecule?
   c. What spin and magnetic properties would be exhibited by this drug and briefly state the reason(s) for your answer?

2. a. Aqueous solution of copper(II) sulphate is blue in colour but when concentrate HCl was added to the solution, the colour changed to green. However on addition of excess KCN the colour changed from blue to purple. Explain what is responsible for the colour changes.

   b. The d-d transition can be spin/symmetry allowed and/or forbidden. For each complex in the table below state which is allowed and/or forbidden.

Complex	Symmetry	Spin
a. $Ti(H_2O)_6]^{2+}$		
b. $[NiCl_4]^{2-}$		
c. $Mn(H_2O)_6]^{2+}$		
d. $[CuCl_4]^{2-}$		
e. $Co(H_2O)_6]^{2+}$		
f. $V(H_2O)_6]^{2+}$		

3. a. Draw the energy level diagram to show the splitting of the d-orbitals in a
      I. Tetrahedral field
      II. Octahedral field
      III. Jahn Teller distortion
      IV. Square planar geometry
   b. Discuss briefly the Jahn Teller distortion

In the Lab

$NaCN \cdot Fe(CN)_5 \cdot 6H_2O$ [illegible]

4. a. How would you differentiate between the double salt $NaCl{\cdot}MgCl{\cdot}6H_2O$ and the coordination complex $PtCl_4{\cdot}2NaCl$?

   $Fe(CN)_2 \cdot 4NaCN$ and tell[illegible]

   b. Write all the possible shapes that can be adopted by complexes with coordination numbers as listed below and give one example of each.
      (i) 3 (ii) 4 (iii) 5
   c. Briefly state why lathanoids have smaller atomic radius than expected.

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