

UNIVERSITY OF SWAZILAND

FINAL EXAMINATION May 2016

TITLE OF PAPER: INORGANIC CHEMISTRY

COURSE NUMBER: C301

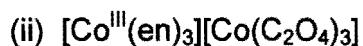
TIME ALLOWED: THREE (3) HOURS

**INSTRUCTIONS: THERE ARE SIX (6) QUESTIONS.
ANSWER ANY FOUR (4) QUESTIONS.
EACH QUESTION IS WORTH 25 MARKS.**

**A PERIODIC TABLE AND OTHER USEFUL DATA HAVE BEEN
PROVIDED WITH THIS EXAMINATION PAPER.**

Question One

a) Name the following complexes:



[6]

b) Write formula for the following complexes:

(i) Dinitratotetraaminocobalt(III) sulphate

(ii) Potassium tetrachlorocobaltate(II)

(iii) μ -hydroxobis[pentaamminechromium(III)] chloride

[6]

c) i) Define each of the following and an example:

I. Linkage isomers

II. Coordination isomers

[6]

ii) Amino acids can act as ligands towards transition metal ions. The simplest amino acid is glycine, $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$. Draw the structure of the glycinate ligand, $\text{H}_2\text{NCH}_2\text{CO}_2^-$, acting as a bidentate ligand towards a metal ion M. Draw possible geometrical isomers arising from the square planar complex $\text{Cu}(\text{H}_2\text{NCH}_2\text{CO}_2)_2$. [7]

Question Two

- a) Classify each of the following species as hard, soft, or borderline Lewis acids or bases. Which of the Lewis bases would prefer to form adducts with each of the acids? Fe^{3+} , I^- , CH_3S^- , CO_3^{2-} , Cu^+ , Hg^{2+}

[4]

- b) Predict whether the equilibrium constant for each of the following reactions is expected to favour the forward reaction or the reverse reaction. Explain.

- i) $\text{CdI}_2(\text{s}) + \text{CaF}_2(\text{s}) \rightleftharpoons \text{CdF}_2(\text{s}) + \text{CaI}_2(\text{s})$
- ii) $\text{CaI}_2(\text{aq}) + \text{Cu}_2\text{O}(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + 2\text{CuI}(\text{s})$
- iii) $\text{HgCl}_2(\text{aq}) + \text{H}_2\text{S}(\text{aq}) \rightleftharpoons \text{HgS}(\text{s}) + 2\text{HCl}(\text{aq})$

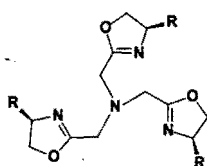
[8]

- c) Give Lewis structures of two examples of each of the following:

- i) Monodentate ligands with oxygen as the donor atom
- ii) Monodentate ligands with nitrogen as the donor atom
- iii) Chelating ligands
- iv) Macrocyclic ligands containing at least four N donor atoms
- v) Crown ether ligands

[10]

- d) Consider a neutral ligand L whose structure is shown below. Based on your



$\text{R} = \text{Ph}, \text{CH}_2\text{Ph}, \text{CH}-\text{CH}(\text{CH}_3)_2$

knowledge of coordination properties of chelating ligands, draw the structure of the complex $[\text{CuCl}(\text{L})]^+$.

[3]

Question Three

- a) Consider the formation of a complex ion $[\text{AlF}_6]^{3-}$ by reacting an aqua complex ion, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, with fluoride ions, F^- .
- i) Write all the stepwise reactions involved in the formation of the complex ion $[\text{AlF}_6]^{3-}$ [6]
- ii) Write the overall reactions for steps 2, 4 and 6, and give corresponding expressions for overall stability constants β_2 , β_4 , and β_6 [6]
- b) Calculate the CFSE for each of the two complexes, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{CN})_6]^{3-}$. Justify your assumptions of high-spin or low-spin in each case. [7]
- c) Classify each of the following ligands as pi-acceptor or pi-donor ligands. For each case use suitable orbital diagrams to illustrate how bonding between the ligand and a metal ion may take place. [6]
- i) CO ii) $(\text{CH}_3\text{CH}_2)_3\text{P}$

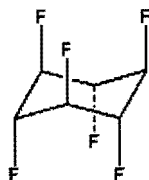
Question Four

- a) Copper(II) complexes are typically blue with one visible absorption band in their electronic spectra whereas copper(I) complexes are generally colourless. Explain. Assign spectroscopic labels to the states involved in the transition for an octahedral Cu^{2+} complex. Your answer should include electronic configurations of Cu(I) and Cu(II) ions. [Help: Remember the "Hole" formalism relationship between d^N and d^{10-N}] [10]
- b) Aqueous solutions of $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ show absorptions at 17 200 and 25 600 cm^{-1} assigned to the ${}^3\text{T}_{2g} \leftarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{T}_{1g}(\text{F})$ transitions respectively. Estimate values of B and Δ_o for the complex. Predict the position of the third absorption band (ν_3 , in cm^{-1}). [10]
- c) Complexes $[\text{NiCl}_2(\text{PPh}_3)_2]$ and $[\text{PdCl}_2(\text{PPh}_3)_2]$ are paramagnetic and diamagnetic, respectively. What does this tell you about their structures? Explain how you arrive at your answer. [5]

Question Five

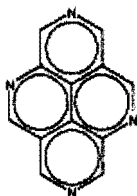
a) Use the accompanying flow-chart diagram (decision tree), to determine the correct point group symbol for each of the systems below.

i)



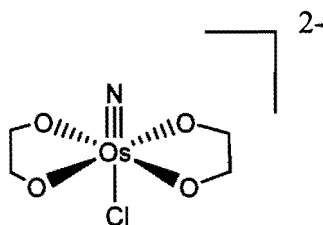
[3]

ii)



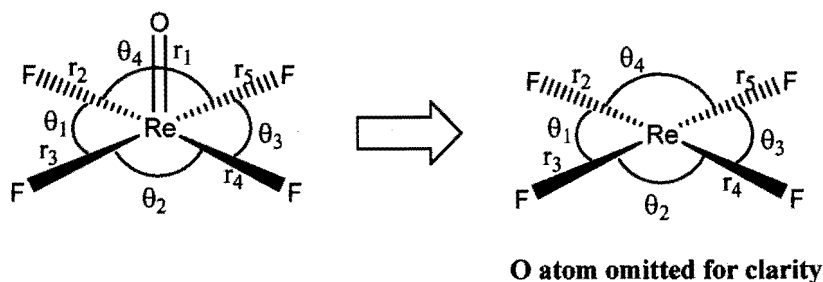
[3]

iii)



[3]

- b) The structure of tetrafluorooxorhenium(VI), ReOF_4 (C_{4v} symmetry), can be diagrammed as below. Use the accompanying C_{4v} character table to carry out the following tasks. Let the basis set for internal bond displacement coordinates be r_1, r_2, r_3, r_4, r_5 with r_1 being assigned to the $\text{Re}=\text{O}$ bond; and let F-Re-F bond angle displacement coordinates be $\theta_1, \theta_2, \theta_3,$ and θ_4 . Use this information to answer questions that follow. **[16]**



- i) Using internal coordinates, determine the total reducible representation for **Re-F stretching modes** and decompose it into irreducible representations.
[Note: Use of Cartesian coordinates (x, y, z) for each atom is not necessary]
- ii) Using internal coordinates, determine the total reducible representation for **in-plane bending modes** (involving $\angle \text{FReF}$ angles only) and decompose it into irreducible representations.
- iii) Determine symmetries and the number of allowed IR-active and Raman-active bands for the molecule due to Re-F stretching.
- iv) Use the projection operator method to determine the SALCs for Re-F **stretching vibrations** and sketch them. For any doubly degenerate (E) representation present, generation of the first SALC for such a representation will suffice.

Question Six

- a) Extraction of metals from minerals involves the use of a number of reductants (or oxidants) depending on the nature of the metal. Complete the following equations after identifying the reductant (R) or oxidant (Ox):
 - i) $\text{Fe}_2\text{O}_3 + \text{R} \longrightarrow$
 - ii) $\text{Cu}_2\text{S} + \text{Ox} \longrightarrow$
 - iii) $\text{Ti(s)} + \text{Ox} \longrightarrow$

[6]

- b) Consider the elements Sc, Ti, V, Cr, Mn and Fe
- i) Write the electron configuration for each of the elements [3]
 - ii) Give the group oxidation number for each element [3]
 - iii) Briefly, discuss the stability of group oxidation states for these elements. [6]
- c) If you were given a piece of gold and asked to dissolve it, state the type of reagent you would use. Give the reaction equation that accompanies the process. [7]

END OF EXAMINATION

PERIODIC TABLE OF THE ELEMENTS

<http://www.chem.qmw.ac.uk/iupac/atwt/table.html>

1 H 1.00794																18 He 4.00260	
2 Li 6.941	3 Be 9.01218											13 B 10.81	14 C 12.011	15 N 14.0067	16 O 15.9994	17 F 18.9984	18 Ne 20.179
11 Na 22.9898	12 Mg 24.305	3 Sc	4 Ti	5 V	6 Cr	7 Mn	8 Fe	9 Co	10 Ni	11 Cu	12 Zn	13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.08	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.8
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.22	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.6	53 I 126.9	54 Xe 131.29
55 Cs 132.905	56 Ba 137.33	71 Lu 174.967	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.908	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	103 Lr (260)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (264)	108 Hs (265)	109 Mt (268)	110 Uun (269)	111 Uuu (272)	112 Uub (269)		114 Uuq		116 Uuh		118 Uuo

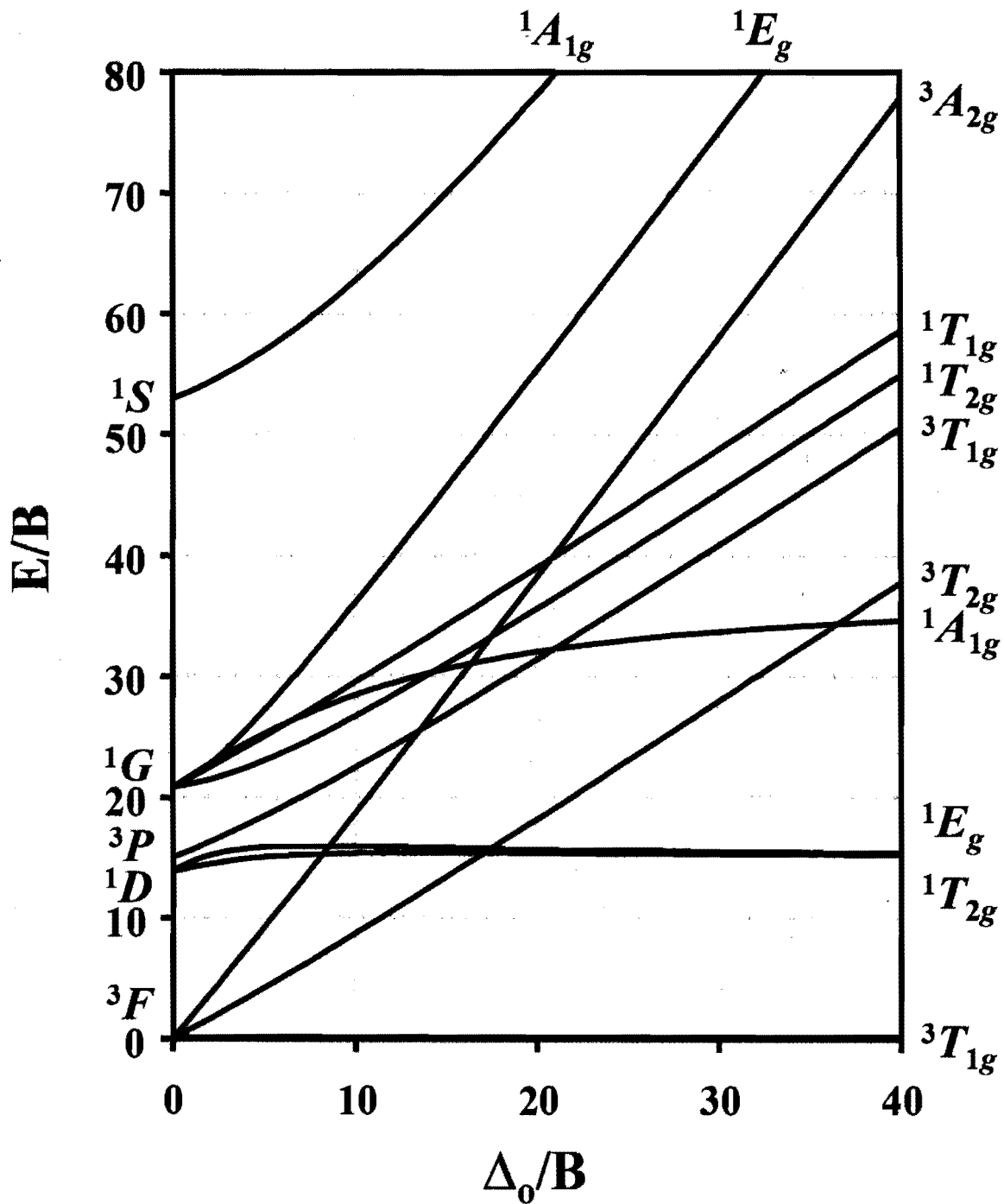
Lanthanides:

57 La 138.906	58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 161.930	68 Er 167.26	69 Tm 166.934	70 Yb 173.04
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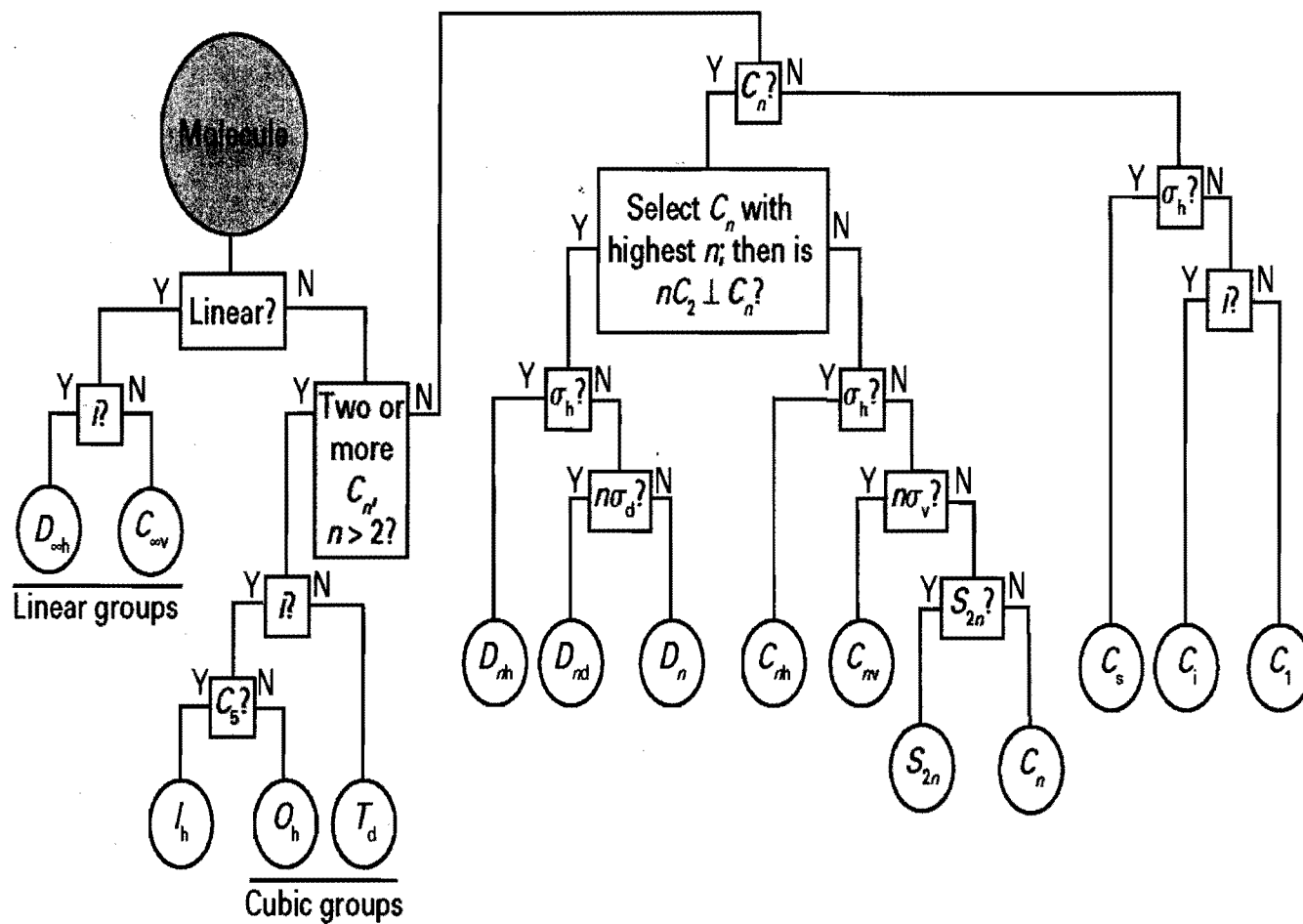
Actinides:

89 Ac 227.028	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	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)
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d^2 Tanabe-Sugano Diagram



C301 : DECISION TREE



The flow-chart (Decision tree) used for assigning point groups

