UNIVERSITY OF SWAZILAND

FINAL EXAMINATION May 2013

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:

(i) $Na[HFe(CO)_4]$

(ii) $[Co(C_2O_4)_3]^{3-}$

(iii) $[TaF_8]^{3-}$

[6]

b) Write formula for the following complexes:

(i) Dinitratotetraaminecobalt(III) sulphate

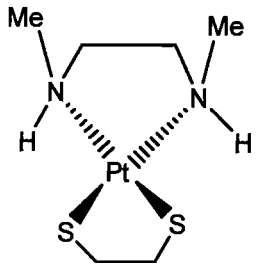
(ii) Trihydridotris(triphenylphosphine)ruthenium(III)

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

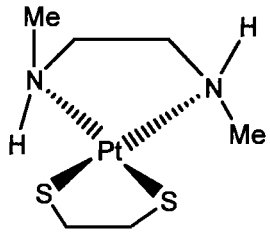
[6]

c) i) Ignoring conformations of chelate rings, sketch possible geometric isomers that may result from the complex $[Pt(H_2NCH_2CHMeNH_2)_2]Cl_2$, where chelate rings form a square planar environment. **[8]**

ii) Indicate whether any of the isomers (I and II) given below would exhibit optical activity. Give a brief explanation of how you arrive at your conclusion.



I



II

[**Note:** In each structure, both chelate rings lie in the same plane; on the other hand, methyl (Me) groups lie either below or above the plane containing the chelate rings, giving rise to cis- and trans- isomers as shown].

[5]

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_3^-, CO_3^{2-}, Cu^+, Cl^-

[6]

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) $CdI_2(s) + CaF_2(s) \rightleftharpoons CdF_2(s) + CaI_2(s)$

ii) $CaI_2(aq) + Cu_2O(s) \rightleftharpoons CaO(s) + 2CuI(s)$

iii) $HgCl_2(aq) + H_2S(aq) \rightleftharpoons HgS(s) + 2HCl(aq)$

[6]

c) Give 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

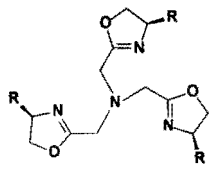
iii) Chelating ligands

iv) Macrocyclic ligands containing at least four N donor atoms

v) Crown ether ligands

[10]

d) Consider a ligand L whose structure is shown below.



R = Ph, CH_2Ph, $CH\text{-}CH(CH_3)_2$

What is the structure of the complex $[CuCl(L)]^+$? Draw the structure of the complex.

[3]

Question Three

a) Consider the type of isomerism possible in the following compounds. **Draw** the different isomers for each compound to illustrate the type of isomerism exhibited by each of these complexes.

i) $[CoI_3(SCN)]^{2-}$, tetrahedral

ii) $[Cr(en)_2Cl_2]^+$ {en = $H_2NCH_2CH_2NH_2$}

[12]

b) Calculate the CFSE for each of the two complexes, $[Mn(H_2O)_6]^{2+}$ and $[Co(CN)_6]^{3-}$. 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 liand take place.

i) R_2N^-, R=H or alkyl

ii) R_3P

[6]

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.

[10]

b) Aqueous solutions of $[V(H_2O)_6]^{3+}$ show absorptions at 17 200 and 25 600 cm^{-1} assigned to the $^3T_{2g} \leftarrow {}^3T_{1g}(F)$ and $^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$ transitions respectively. Estimate values of B and Dq for the complex. **[10]**

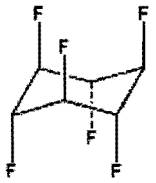
c) Complexes $[NiCl_2(PPh_3)_2]$ and $[PdCl_2(PPh_3)_2]$ are paramagnetic and diamagnetic, respectively. What does this tell you about their structures? Explain how you arrive at your answer.

[5]

Question Five

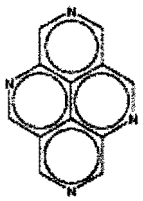
a) Use the accompanying flow-chart diagram (decision tree), to determine the correct point group symbol for each of the systems below.

i)



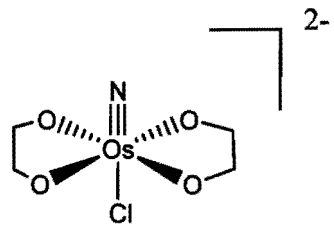
[3]

ii)



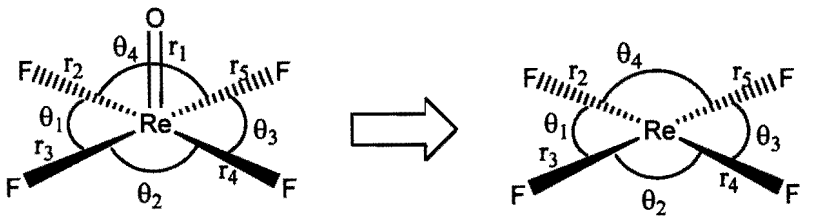
[3]

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 Re=O bond; and let F-Re-F bond angle displacement coordinates be θ_1, θ_2, θ_3, and θ_4. Use this information to answer questions that follow. **[16]**



O atom omitted for clarity

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) is not necessary]

ii) Using internal coordinates, determine the total reducible representation for **in-plane bending modes** (involving <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) $Fe_2O_3 + R \longrightarrow$

ii) $Cu_2S + Ox \longrightarrow$

iii) $WO_3 + R \longrightarrow$

[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.

[4]

iv) Titanium(IV) halides, TiX_4 (X=F, Cl, Br, I) have all been prepared. On the other hand, for manganese (IV), only MnF_4 has been prepared; preparation of the rest (X = Cl ,Br, I) has been unsuccessful. Explain.

[2]

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

CHARACTER TABLE

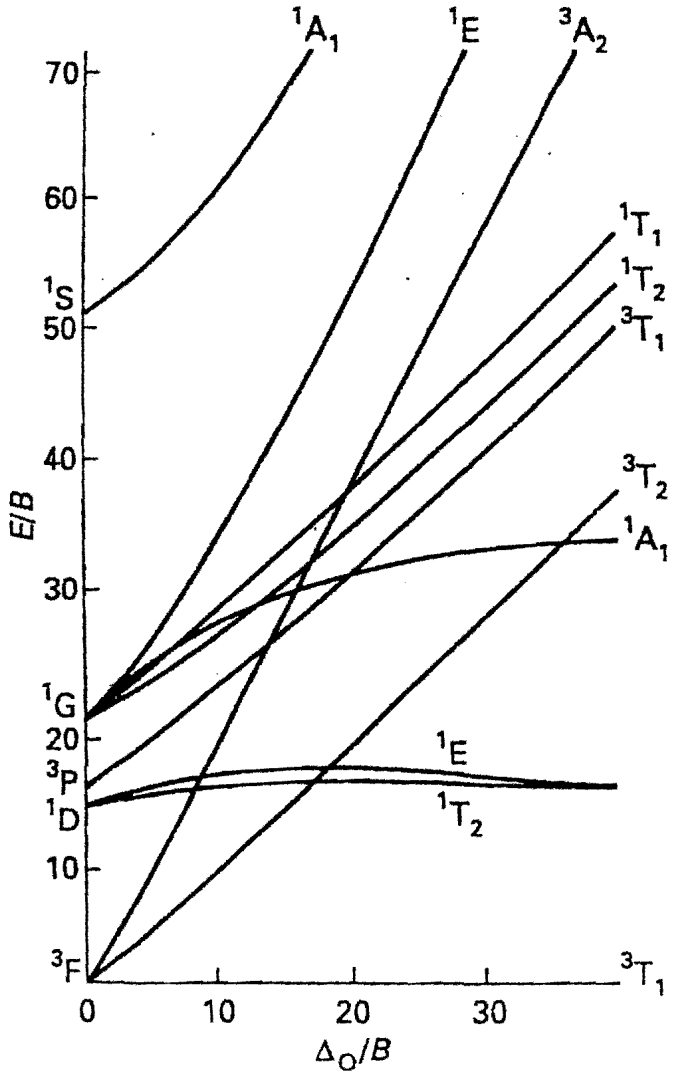
C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

NOTE:

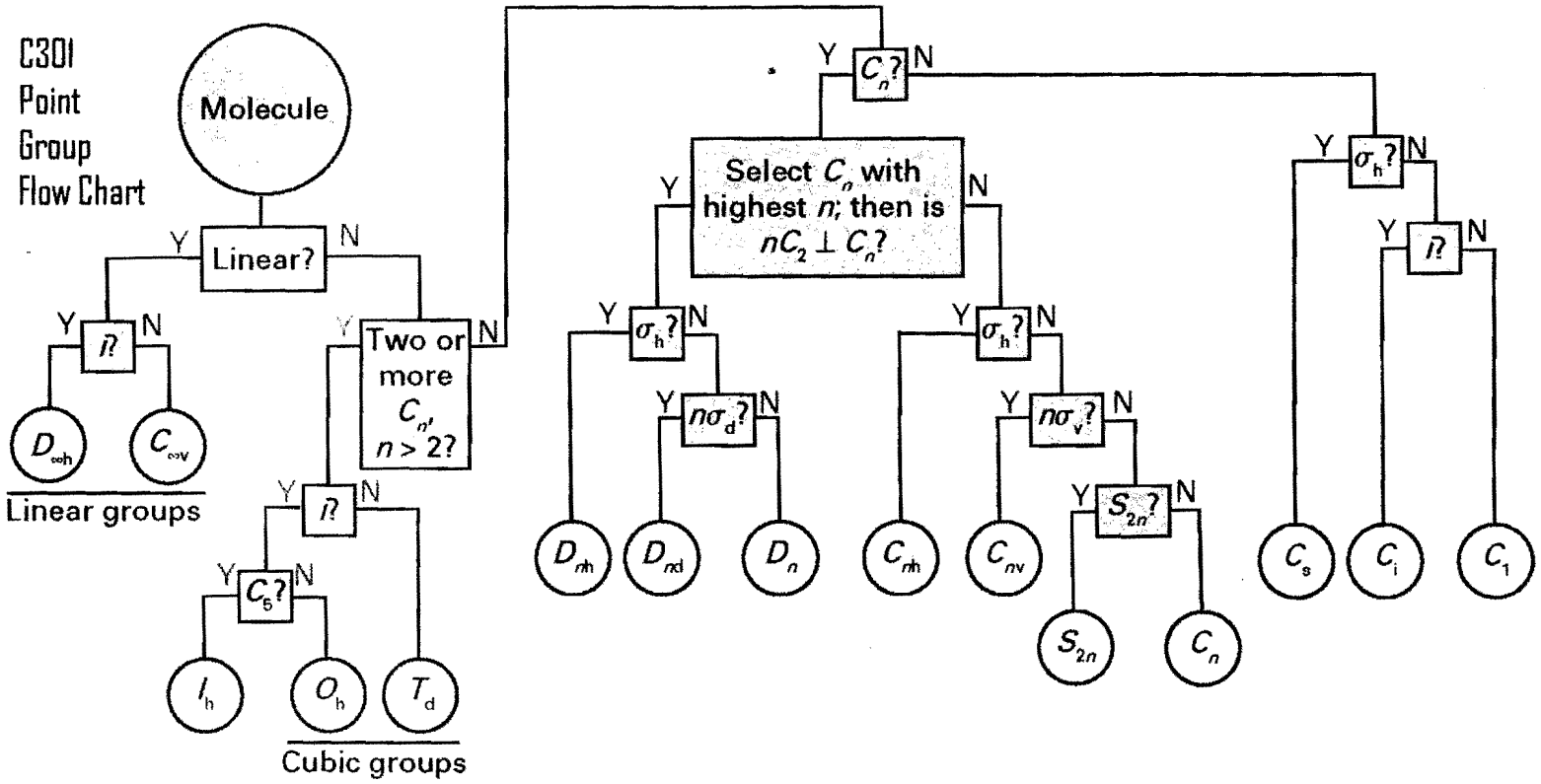
* $2C_4 \Rightarrow C_4^1$ and C_4^3

TANABE–SUGANO DIAGRAM

d^2



DECISION TREE



PERIODIC TABLE OF THE ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4											10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12											26.982 Al 13	28.0855 Si 14	30.9738 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.0983 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.9415 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.9064 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.906 Rh 45	106.42 Pd 46	107.868 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.904 I 53	131.29 Xe 54
6	132.905 Cs 55	137.33 Ba 56	138.906 *La 57	178.49 Hf 72	180.948 Ta 73	183.85 W 74	186.207 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.967 Au 79	200.59 Hg 80	204.383 Tl 81	207.2 Pb 82	208.980 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	(223) Fr 87	226.025 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109									

TRANSITION ELEMENTS

* Lanthanide series	140.115 Ce 58	140.908 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.925 Tb 65	162.50 Dy 66	164.930 Ho 67	167.26 Er 68	168.934 Tm 69	173.04 Yb 70	174.967 Lu 71
** Actinide series	232.038 Th 90	231.036 Pa 91	238.029 U 92	237.048 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

Numbers below the symbol of the element indicates the atomic numbers. Atomic masses, above the symbol of the element, are based on the assigned relative atomic mass of ^{12}C = exactly 12; ( ) indicates the mass number of the isotope with the longest half-life.

SOURCE: International Union of Pure and Applied Chemistry, I. Mills, ed., *Quantities, Units, and Symbols in Physical Chemistry*, Blackwell Scientific Publications, Boston, 1988, pp 86-98.