UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION

ACADEMIC YEAR 2013/2014

TITLE OF PAPER: **INORGANIC CHEMISTRY I**

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.**

THE FOLLOWING HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER, AND ARE ATTACHED:

1. **Periodic Table**
2. **d^7 Tanabe-Sugano Diagram**
3. **Character Table for C_{2h} point group**
4. **Table of some hard, soft and intermediate acids and bases**
5. **Decision Tree**
6. **Table of Constants**

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"Marks will be awarded for method, clearly labelled diagrams, organization and presentation of thoughts in clear and concise language"

Question One

a) Give the IUPAC name for each of the following:

i) $K_3[Co(NO_2)_6]$
ii) $[Co(en)_3][Cr(Ox)_3]$
iii) $[Cl_3W(\mu\text{-}Cl)_3WCl_3](ClO_4)_3$
iv) $W(CH_2CH_3)_6$

[8]

b) Give the formula of each of the following:

i) Sodium pentacyanonitrosylferrate(II) dihydrate
ii) Potassium pentachloronitroosmate(IV)
iii) Tetraammineaquacobalt(III)-μ-cyanobromotetracyanocobaltate(III)

[6]

c) State the type of isomerism that may be exhibited by the following complexes, and draw structures of the isomers:

i) $[Pt(en)_2Cl_2]^{2+}$
ii) $Pd(bpy)(NCS)_2$

[11]

Question Two

a) Using hard-soft concepts, which of the following reactions are predicted to have an equilibrium constant greater than 1? Briefly explain each of your answers.

i) $ZnO + 2BuLi \rightleftarrows Zn(Bu)_2 + Li_2O$

ii) $R_3PBBr_3 + R_3NBF_3 \rightleftarrows R_3PBF_3 + R_3NBBr_3$

iii) $CH_3HgI + HCl \rightleftarrows CH_3HgCl + HI$

iv) $[AgCl_2]^- + 2CN^-(aq) \rightleftarrows [Ag(CN)_2]^- + 2Cl^-$

[8]

b) The value of μ_{eff} for $[CoF_6]^{3-}$ is found to be 5.63 BM. Given that the complex contains a d^6 Co(III) metal center, determine whether this value agrees with the value of magnetic moment calculated from the spin-only formula. If the two values are not in agreement, give a possible reason.

[6]

c) Explain why under the influence of an octahedral field, the energies of the d orbitals are raised or lowered. With respect to what are orbital energies raised or lowered? **[7]**

d) What is the expected ordering of Δ_o for $[Fe(OH_2)_6]^{2+}$, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$? Rationalize your answer. **[4]**

Question Three

a) Using only ethylenediamine (en = $H_2NCH_2CH_2NH_2$) and bromide ions as ligands, construct a cationic octahedral complex of cobalt(III). Your complex cation should have +1 charge and it should be chiral. Draw a three-dimensional structure for this complex together with its mirror image. Then draw the structure of the diastereoisomer (i.e., achiral analogue) of the enantiomers you have drawn. **[9]**

b) Consider the salt $[Co(bpy)_2(CN)_2]^+[Fe(bpy)(CN)_4]^-$.

i) Give formulas of compounds that are coordination isomers of the salt

ii) Draw two geometrical isomers arising from **only one** of the ions in the formula above

iii) Draw two enantiomers arising from **only one** of the ions in the formula above

[16]

Question Four

a) Show the mechanisms that explain why the following reactions occur far more rapidly than would be true for simple substitution or ligand replacement:

i) $[Co(NH_3)_5(H_2O)]^{3+} + NO_2^-$
ii) $[Co(NH_3)_5(CO_3)]^+ + H_3O^+$

[8]

b) For a substitution reaction shown below, the rate of reaction is found to be first order in each of the two starting materials. Suggest a mechanism for the reaction.

$Co(NO)(CO)_3 + As(C_6H_5)_3 \rightleftharpoons Co(NO)(CO)_2(As(C_6H_5)_3) + CO$

[5]

c) Complete and balance the following reactions:

i) $TiO_2 + H_2SO_4$ (concd) $\longrightarrow$

ii) $Cr_2O_3 + H_2SO_4$ (concd) $\longrightarrow$

iii) $[Cr_2O_7]^{2-} + H_2SO_4$ (concd) $\longrightarrow$

iv) $Fe_2O_3 + HCl(aq) \longrightarrow$

[12]

Question Five

a) Consider adding an aqueous solution of ammonia to an aqueous solution of copper(II) sulphate. Initially, a pale blue precipitate is formed. Upon adding excess ammonia solution, the precipitate dissolves resulting in the formation of a deep blue solution. Use suitable equations to explain the above observations.

[5]

b) The electronic spectrum $[Co(H_2O)_6]^{2+}$, a d^7 complex, exhibits bands at 8100, 16000 and 19400 cm^{-1}.

i) Using the Tanabe-Sugano diagram provided, and assuming the complex has a high-spin electronic ground state, assign the electronic transitions to these bands (listed above)

ii) Consider a cobalt(II) complex $[Co(CN)_6]^{4-}$. Comment on the nature of the ground state and the spin-allowed transitions expected

[14]

c) Complete and balance the following reactions:

i) $Cu + Cl_2 \longrightarrow$

ii) $Mn + O_2 \longrightarrow$

iii) $Ti + Cl_2 \longrightarrow$

iv) $Fe + I_2 \longrightarrow$

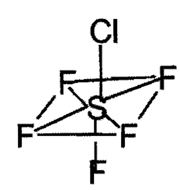
[6]

Question Six

a) With the help of the flow-chart (decision tree) which is provided, determine the point group for each of the following:

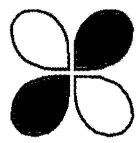
i) Cis-$[PtCl_2BrI]^{2-}$

ii) SF_5Cl



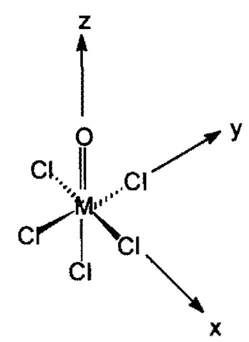
iii) *trans*-$Co(Br)(Cl)(NH_3)_4$

iv) d_{xy} orbital (whose shape is sketched below)



[12]

b) Determine the symmetries of M-Cl **stretching modes** for the six-coordinate complex $[MCl_5(O)]$ (which has C_{4v} point group and whose is sketch is given below). Which of the modes are IR active? Which ones are Raman active?



[13]

PERIODIC TABLE OF THE ELEMENTS

GROUPS

PERIODS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	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	96.907 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.

DECISION TREE

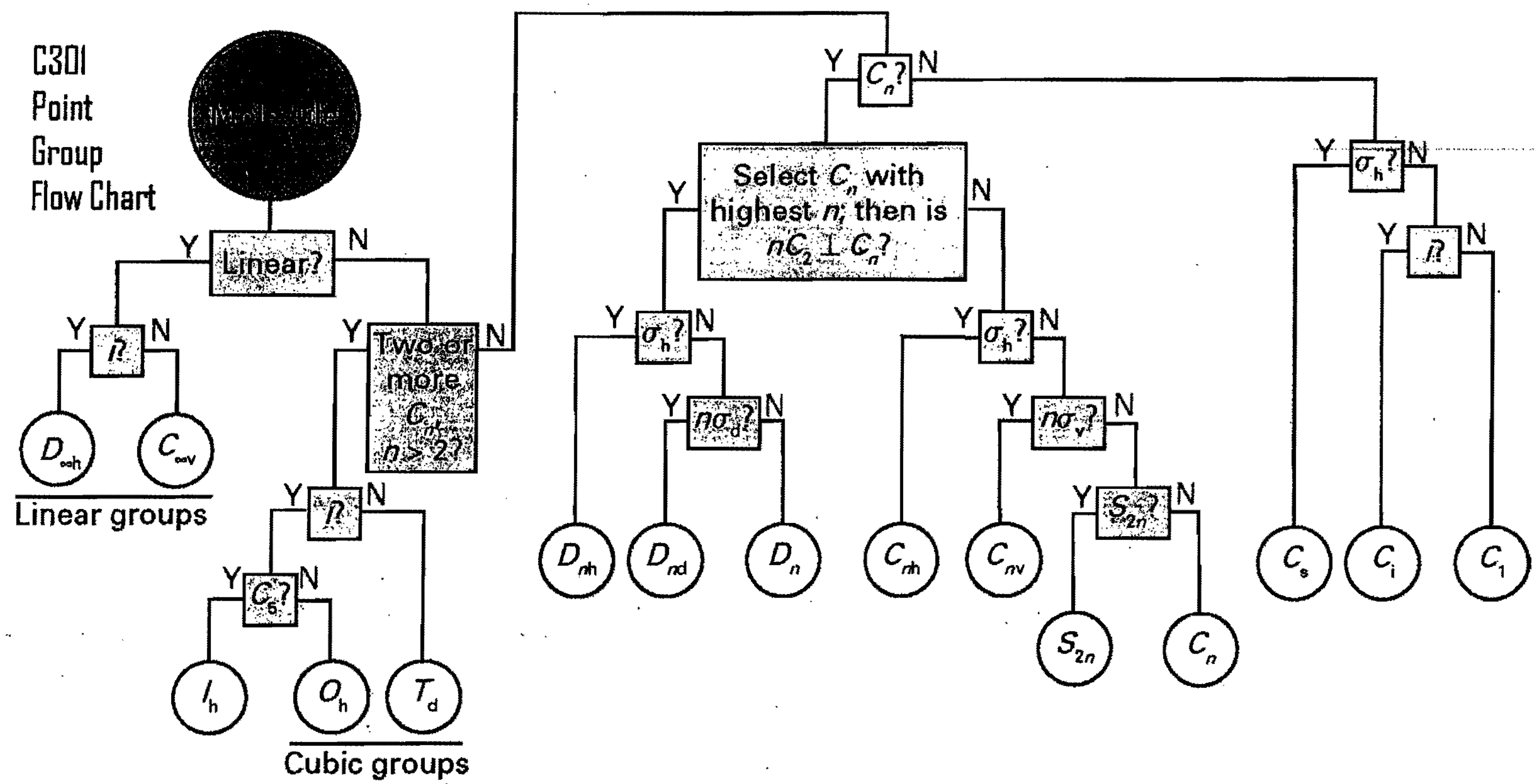


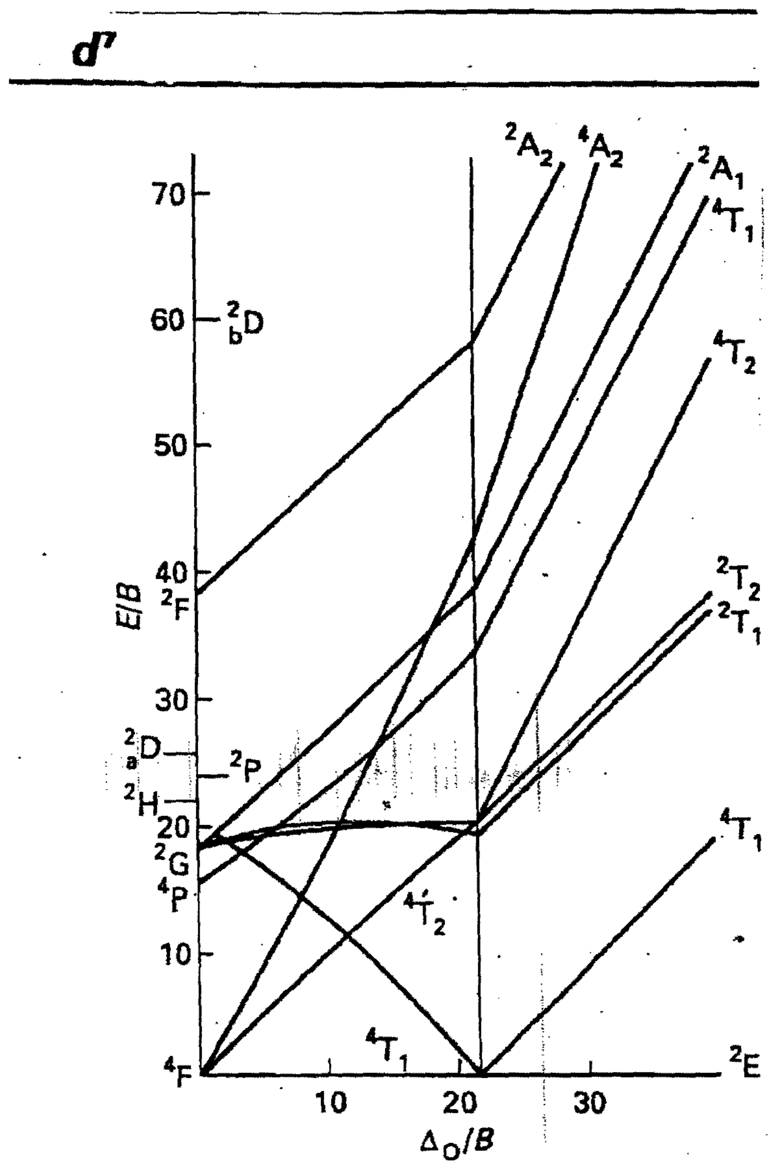
Table of hard, intermediate and soft Acids and Bases

	Ligands (Lewis bases)	Metal centres (Lewis acids)
Hard; class (a)	F^-, Cl^-, H_2O, ROH, R_2O, $[OH]^-$, $[RO]^-$, $[RCO_2]^-$, $[CO_3]^{2-}$, $[NO_3]^-$, $[PO_4]^{3-}$, $[SO_4]^{2-}$, $[ClO_4]^-$, $[ox]^{2-}$, NH_3, RNH_2	Li^+, Na^+, K^+, Rb^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+}, Mn^{2+}, Zn^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Y^{3+}, Th^{4+}, Pu^{4+}, Ti^{4+}, Zr^{4+}, $[VO]^{2+}$, $[VO_2]^+$
Soft; class (b)	I^-, H^-, R^-, $[CN]^-$ (*C*-bound), CO (*C*-bound), RNC, RSH, R_2S, $[RS]^-$, $[SCN]^-$ (*S*-bound), R_3P, R_3As, R_3Sb, alkenes, arenes	Zero oxidation state metal centres, Tl^+, Cu^+, Ag^+, Au^+, $[Hg_2]^{2+}$, Hg^{2+}, Cd^{2+}, Pd^{2+}, Pt^{2+}, Tl^{3+}
Intermediate	Br^-, $[N_3]^-$, py, $[SCN]^-$ (*N*-bound), $ArNH_2$, $[NO_2]^-$, $[SO_3]^{2-}$	Pb^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Os^{2+}, Ru^{3+}, Rh^{3+}, Ir^{3+}

Character Table for C_{4v} Point Group

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)

d7 Tanabe-Sugano Diagram



PHYSICAL CONSTANTS

Speed of light in a vacuum	c_0	2.99792458×10^{8} m s^{-1}
Permittivity of a vacuum	ϵ_0	$8.854187816 \times 10^{-12}$ F m^{-1}
	$4\pi\epsilon_0$	1.11264×10^{-10} c^2 N^{-1} m^{-2}
Planck constant	h	$6.6260755(40) \times 10^{-34}$ J s
Elementary charge	e	$1.60217733(49) \times 10^{-19}$ C
Avogadro constant	N_A	$6.0221367(36) \times 10^{23}$ mol^{-1}
Boltzmann constant	k	$1.380658(12) \times 10^{-23}$ J K^{-1}
Gas constant	R	$8.314510(70)$ J K^{-1} mol^{-1}
Bohr radius	a_0	$5.29177249(24) \times 10^{-11}$ m
Rydberg constant	R_∞	$1.0973731534(13) \times 10^{7}$ m^{-1} (infinite nuclear mass)
	✓ R_H	$1.09677759(50) \times 10^{7}$ m^{-1} (proton nuclear mass)
Bohr magneton	μ_B	$9.2740154(31) \times 10^{-24}$ J T^{-1}
	π	3.14159265359
Faraday constant	F	$9.6485309(29) \times 10^{4}$ C mol^{-1}
Atomic mass unit	m_u	$1.6605402(10) \times 10^{-27}$ kg
Mass of the electron	m_e	$9.1093897(54) \times 10^{-31}$ kg or $5.48579903(13) \times 10^{-4}$ m_u
Mass of the proton	m_p	$1.007276470(12)$ m_u
Mass of the neutron	m_n	$1.008664904(14)$ m_u
Mass of the deuteron	m_d	$2.013553214(24)$ m_u
Mass of the triton	m_t	$3.01550071(4)$ m_u
Mass of the α-particle	m_α	$4.001506170(50)$ m_u