UNIVERSITY OF SWAZILAND

SUPPLEMENTARY FINAL EXAMINATION

ACADEMIC YEAR 2008/2009

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 A TABLE OF CONSTANTS HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER.

NON-PROGRAMMABLE ELECTRONIC CALCULATORS MAY BE USED

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Question One

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

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

[6 mks]

b) Give the formula and draw the structure of each of the following:

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

[6 mks]

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

i) $[Pt(en)_2Cl_2]Br_2$
ii) $Pd(bpy)(NCS)_2$
iii) $Rh(acac)_3$

[13 mks]

Question Two

a) A monomeric complex of cobalt gave the following result on analysis:

Species	Co	NH_3	Cl^-	SO_4^{2-}	H_2O
%, by mass	21.24	24.77	12.81	34.65	?

The compound is diamagnetic and contains no other groups or elements, except that water might be present.

i) Using the above data, calculate the formula of the compound
ii) Check if there is any water present. If water is present, what is the final formula of the compound?
iii) Sketch the structures of all possible isomers

[8 mks]

b) The value of μ_{eff} for $[CoF_6]^{3-}$ is 5.63 BM. Explain why this value does not agree with the value of magnetic moment calculated from the spin-only formula. **[6 mks]**

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 mks]**

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 mks]**

Question Three

a) A reaction of *trans*-$[Pt(PEt_3)_2(Ph)Cl]$ with thiourea, tu, in methanol follows a two-term rate law with

$$k_{obs} = k_1 + k_2[tu]$$

Give a plausible mechanism for the reaction. Suggest how the values of k_1 and k_2 may be obtained. **[8 mks]**

b) $[V(H_2O)_6]^{3+}$ has absorption bands at 17800, 25700 and 34500 cm^{-1}. Using the Tanbe-Sugano diagram for a d^2 configuration, estimate values of Δ_o and B for this complex. **[17 mks]**

Question Four

a) Complete and balance the following reactions:

i) $Cr + Cl_2 \longrightarrow$

ii) $Mo + Cl_2 \longrightarrow$

iii) $Cr + O_2 \longrightarrow$

iv) $Mo + O_2 \longrightarrow$

[4 mks]

b) Sketch the structures of chromium(II) acetate and copper(II) acetate and comment on any unusual features they have. **[6 mks]**

c) Explain each of the following:

i) TiO_2 is white but $TiCl_3$ is violet

[4 mks]

ii) Physical and chemical properties of Zr and Hf are much more similar than the properties of Zr and Ti

[4 mks]

d) Write a balanced reaction equation to depict what happens when the pH of a solution containing $[VO_4]^{3-}$ ions is gradually reduced.

[3 mks]

e) Write equations to show the reaction of Cr_2O_3 with sulfuric acid

[4 mks]

Question Five

a) Starting with $[Rh(H_2O)_6]$ and chloride ion, Cl^-, suggest a method for preparing each of the following:

i) *trans*-$[RhCl_2(H_2O)_4]^+$

ii) *mer*-$[RhCl_3(H_2O)_3]$

iii) *trans*-$[RhCl_4(H_2O)_2]^-$

[7 mks]

b) $[Fe(H_2O)_6]^{2+}$ has a peak which is slightly split around 1000 nm. By using the appropriate Tanabe-Sugano diagram, account for the likely origin of this absorption. Then account for the splitting of the absorption band

[8 mks]

c) Discuss, with examples (one for each), the difference between outer-sphere and inner-sphere mechanisms. State what is meant by a self-exchange mechanism.

[7 mks]

d) What reason can you suggest for the sequence Co>Rh>Ir in the rates of H_2O exchange of $[M(H_2O)_6]^{3+}$ ions?

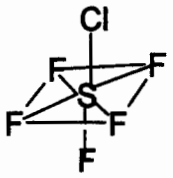
[3 mks]

Question Six

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

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

ii) SF_5Cl



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

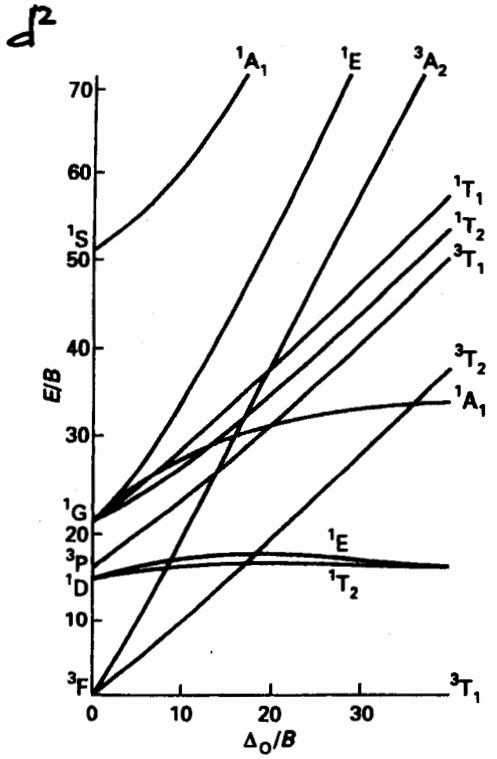
iv) d_{xy} orbital (whose shape is sketched below)

[12 mks]

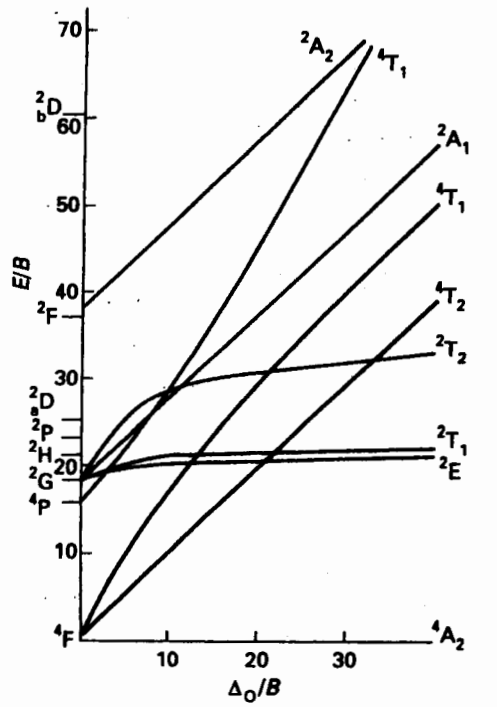
b) Determine the symmetries of CO **<u>stretching modes</u>** for the complex $[M(CO)_5X]$ (which has C_{4v} point group). Which of the modes are IR active? Which ones are Raman active?

[13 mks]

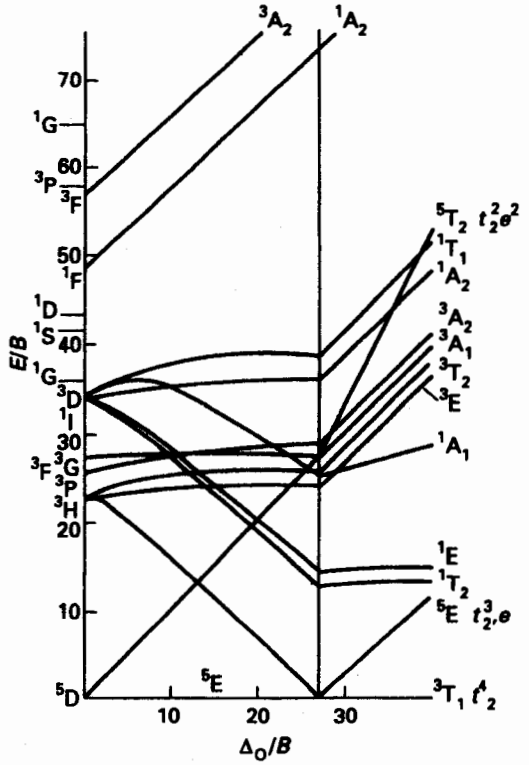
1. d^2 with $C = 4.42B$



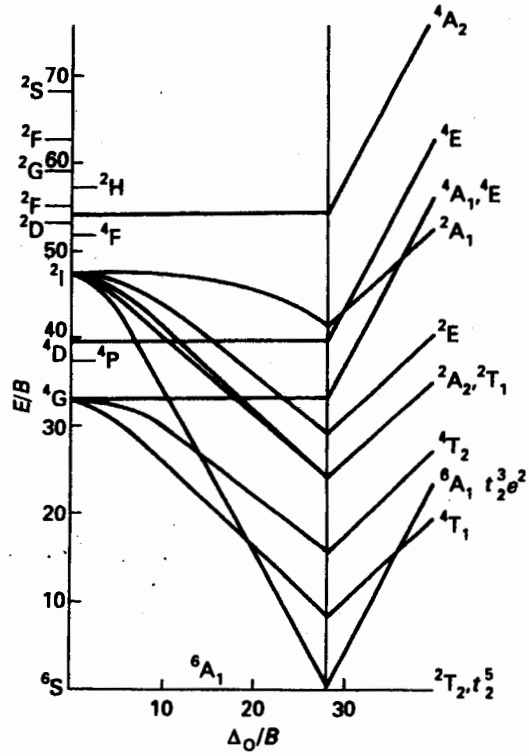
2. d^3 with $C = 4.5B$



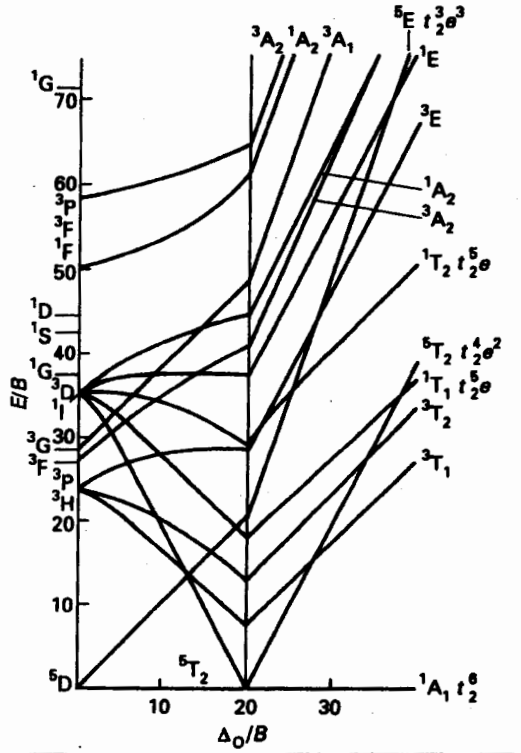
3. d^4 with $C = 4.61B$



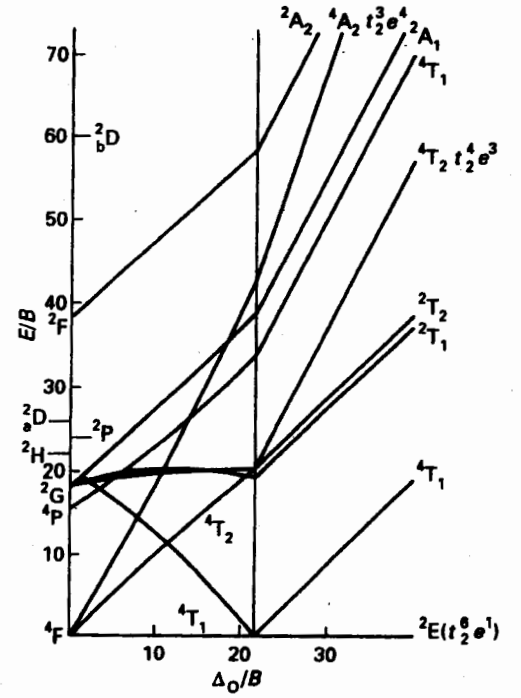
4. d^5 with $C = 4.477B$



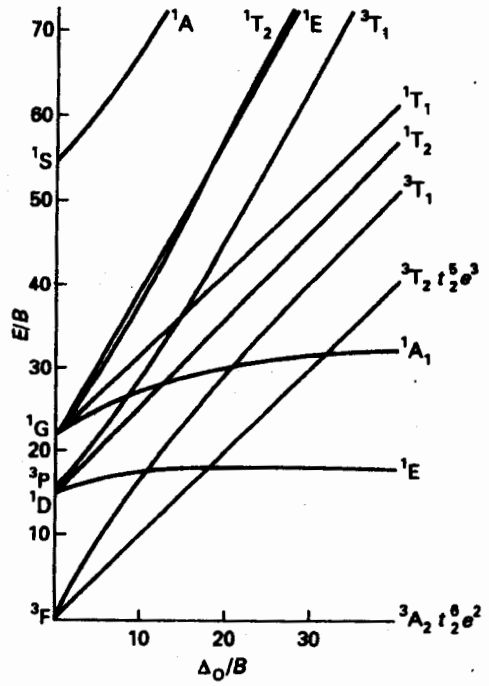
5. d^6 with $C = 4.8B$



6. d^7 with $C = 4.633B$



7. d^8 with $C = 4.709B$



C_{4v} (4mm)	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	$h = 8$	
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)	(zx, yz)

Periodic Table of the Elements

GROUP 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc 98.906*	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La ★ 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po 209.98*	85 At 209.99*	86 Rn 222.02*
87 Fr 223.02	88 Ra 226.03*	89 Ac ▲ 227.03	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (269)	109 Mt (266)	110 (273)	111 (272)	112 (294)						

★Lanthanide series	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 146.92*	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
▲Actinide series	90 Th 232.04*	91 Pa 231.04*	92 U 238.03	93 Np 237.05*	94 Pu 239.05*	95 Am 241.06*	96 Cm 244.06*	97 Bk 249.08*	98 Cf 252.08*	99 Es 252.08*	100 Fm 257.10*	101 Md 258.10*	102 No 259.10*	103 Lr 262.11*

Note: Atomic masses shown here are the 1993 IUPAC values with a maxium of five significant figures (T. B. Coplen *et al.*, *Inorg. Chim. Acta* 1994, *217*, 217).
An asterisk indicates the mass of a commonly known radioisotope. Numbers in parentheses are the mass numbers of the corresponding longer-lived isotope.