UNIVERSITY OF SWAZILAND

FINAL EXAMINATION

ACADEMIC YEAR 2009/2010

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.

ELECTRONIC CALCULATORS MAY BE USED

PLEASE DO NOT OPEN THIS PAPER UNTIL AUTHORISED TO DO SO BY THE CHIEF INVIGILATOR.

"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) cis-$[CrCl_2(NH_3)_4]^+$
- ii) $[Cr(en)_3][Cr(ox)_3]$
- iii) Trans-$K[Cr(NCS\text{-}N)_4(NH_3)_2]$
- iv) $W(Me)_6$

[6 mks]

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

- i) *Mer*-trihydridotris(triphenylphosphine)ruthenium(III)
- ii) Ethylenediaminetetracetatonickelate(II)
- iii) μ-oxobis(trioxochromate(VI))

[6 mks]

c) Show how a planar four-coordinate complex $[M(H_2NCH_2CH_2NHMe)_2]^{2+}$, results in both geometrical isomers and optical isomers. Draw all the possible isomers of the complex and identify the isomer that does not have any mirror planes but is not chiral. **[8 mks]**

d) Explain the following:

- i) Aqueous copper(II) sulphate turns blue litmus paper red
- ii) The addition of ammonia solution to aqueous copper(II) sulphate gives a pale blue precipitate at first and then a deep blue solution when more ammonia solution is added.

[5 mks]

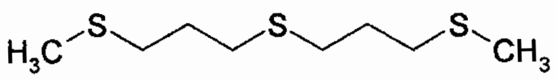
Question Two

a) The reaction of $[ZrCl_4(dppe)]$ (where dppe is a bidentate phosphine ligand, $Ph_2PCH_2CH_2PPh_2$) with $Mg(CH_2)_2$ gives $[Zr(CH_3)_4(dppe)]$. NMR spectra indicate that all methyl groups are equivalent. Draw octahedral and trigonal prism structures for the complex and identify which structure is consistent with NMR data

[10 mks]

b) Suggest how the ligand whose structure is sketched below would coordinate to Ru^{2+} in the six-coordinate complex, $[RuL_2]^{2+}$. How many chelate rings are formed in the complex?.

[3 mks]



c) For $[Pd(CN)_4]^{2-}$, a value of β_4 has been found to be 62.3 (at 298K) in aqueous solution. For $[Au(CN)_2]^-$, a value of β_2 has been found to be 10^{39} (at 298K) in aqueous solution.

i) Write the equations that describe the processes to which these constants refer. In each case, write the expressions for β and calculate ΔG^o (298K). **[9 mks]**

ii) Comment on the magnitudes of the values of ΔG^o you have obtained. Explain why the two values are so different.

[3 mks]

Question Three

a) Comment on the following observations:

i) In its complexes, Co(III) forms strong bonds to O- and N-donor ligands, moderately strong bonds to P-donor ligands, but only weak bonds to As bonds.

[4 mks]

ii) Values of logK for the reaction:

$$Zn^{2+}(aq) + X^-(aq) \rightleftarrows [ZnX]^+(aq)$$

are 0.7 for X=F⁻, -0.2 for X= Cl, -0.6 for X=Br, -1.3 for X=I

[4 mks]

b) Explain each of the following observations

i) $[Co(CN)_5]^{3-}$ is a catalyst for the conversion of $[Co(CN)_5\text{-}NCS]^{3-}$ to $[Co(CN)_5\text{-}SCN]^{3-}$.

[4 mks]

ii) A ligand-bridged intermediate has been observed in the reaction

$$[Co(H_2O)_5NCS]^{2+}(aq) + Hg^{2+}(aq) \longrightarrow [Co(H_2O)_6]^{2+}(aq) + [HgSCN]^+(aq)$$

[4 mks]

c) Arrange the following complexes in order of increasing rate of substitution by H_2O:

$[Co(NH_3)_6]^{3+}$, $[Rh(NH_3)_6]^{3+}$, $[Ir(NH_3)_6]^{3+}$

[3 mks]

d) Use the trans effect to suggest routes to *cis*- and *trans*-$[PtCl_2(NH_3)_2]$ from $[Pt(NH_3)_4]^{2+}$ or $[PtCl_4]^{2-}$

[6 mks]

Question Four

a) Draw sketches to identify the following symmetry elements:

i) A C_3 axis and a σ_v plane in NH_3

ii) A C_4 axis, a σ_h plane and a σ_d plane in the square planar complex $[PtCl_4]^{2-}$

iii) A C_2 axis and a center of inversion in *trans*-1,2-dichloroethene

[7 mks]

b) Which of the following has an S_n axis? In each case, illustrate how the the S_n^1 operation is effected.

i) CO_2 (linear)

ii) BF_3 (trigonal planar)

iii) MoO_4^{2-} (tetrahedral

[8 mks]

c) Assign a point group to each to each of the following:

i) NH_2Cl (trigonal pyramidal)

ii) $[S(S)O_3]^{2-}$, thiosulphate (tetrahedral, one of the S atoms is the central atom)

iii) SO_2Cl_2 (tetrahedral, S is the central atom)

[10 mks]

Question Five

a) What d-orbital splitting pattern would you expect for trigonal bipyramidal complex (D_{3h} point group)? Explain how you arrive at your final answer.

[10 mks]

b) The magnetic moment of a certain Co(II) complex is 4.0 BM. What is its d-electron configuration? **[7 mks]**

c) The complex $[NiCl_4]^{2-}$ is paramagnetic with two unpaired electrons, while $[Ni(CN)_4]^{2-}$ is diamagnetic. Deduce the structures of these two complexes and explain the observations in terms of ligand field theory.

[8 mks]

Question Six

Consider a sulphite ion, SO_3^{2-} which has a pyramidal shape and belongs to C_{3v} point group.

a) How many vibrational modes are expected to be present in the ion?
[1 mk]

b) Use internal coordinates to determine the symmetries of all the **stretching** modes of vibration in the ion. Indicate whether they are IR and/or Raman active. **[8 mks]**

c) Use internal coordinates to determine the symmetries of all the **bending** modes of vibration in the ion. Indicate whether they are IR and/or Raman active. **[8 mks]**

d) Use the projection operator method to determine the SALC for each of the **stretching modes**. Sketch each of the modes.
[8 mks]

Periodic table

1
H
1.008

1 ← Atomic number, Z

H ← Element symbol

1.008 ← Relative atomic mass, A_r

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.008																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.01	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.54	30 **Zn** 65.41	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.91	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** 98.91	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.40	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.30
55 **Cs** 132.91	56 **Ba** 137.34	**La–Lu**	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	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** 204.37	82 **Pb** 207.19	83 **Bi** 208.98	84 **Po** 210	85 **At** 210	86 **Rn** 222
87 **Fr** 223	88 **Ra** 226.03	**Ac–Lr**	104 **Rf** [261]	105 **Db** [262]	106 **Sg** [266]	107 **Bh** [264]	108 **Hs** [277]	109 **Mt** [268]	110 **Ds** [271]	111 **Rg** [272]	112 **Uub** [285]						

Lanthanoids	57 **La** 138.91	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** 158.92	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
Actinoids	89 **Ac** 227.03	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** 244.07	97 **Bk** 249.08	98 **Cf** 252.08	99 **Es** 252.09	100 **Fm** 257.10	101 **Md** 258.10	102 **No** 259	103 **Lr** 262

4. The C_{nv} Groups

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

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)

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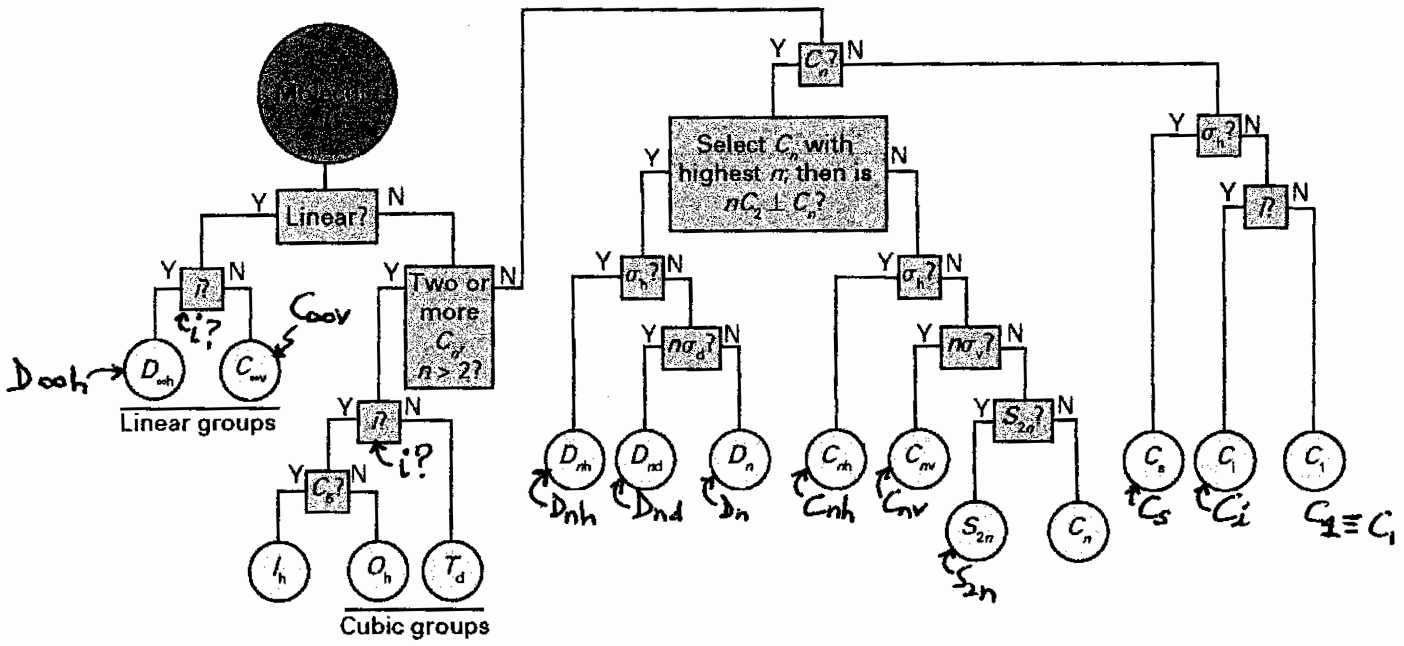
6. The D_{nh} Groups

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	−1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		$x^2 - y^2$
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	



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

Physical constants

Physical constant	Symbol	Value and SI units
Avogadro constant	L	$6.022\,136\,7 \times 10^{23}\,\mathrm{mol^{-1}}$
Boltzmann constant	k	$1.380\,658 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
Faraday constant	F	$9.648\,530\,9 \times 10^{4}\,\mathrm{C\,mol^{-1}}$
Molar gas constant	R	$8.314\,510\,\mathrm{J\,K^{-1}\,mol^{-1}}$
Planck constant	h	$6.626\,075\,5 \times 10^{-34}\,\mathrm{J\,s}$
Rydberg constant	R	$1.097\,373\,153 \times 10^{7}\,\mathrm{m^{-1}}$
Molar volume of an ideal gas at 10^5 Pa (1 bar) and 273 K	V_m	$0.022\,711\,08\,\mathrm{m^3\,mol^{-1}} = 22.711\,08\,\mathrm{dm^3\,mol^{-1}}$
Speed of light in a vacuum	c	$2.997\,924\,58 \times 10^{8}\,\mathrm{m\,s^{-1}}$
Electron rest mass	m_e	$9.109\,389\,7 \times 10^{-31}\,\mathrm{kg}$
Charge on an electron (elementary charge)	e	$1.602\,177\,33 \times 10^{-19}\,\mathrm{C}$
Proton rest mass	m_p	$1.672\,623\,1 \times 10^{-27}\,\mathrm{kg}$
Neutron rest mass	m_n	$1.674\,928\,6 \times 10^{-27}\,\mathrm{kg}$
Atomic mass unit	$m_\mathrm{u} = 1\,\mathrm{u}$	$1.660\,540\,2 \times 10^{-27}\,\mathrm{kg}$
Bohr radius	a_0	$5.291\,772\,49 \times 10^{-11}\,\mathrm{m}$
Permittivity of a vacuum	ε_0	$8.854\,187\,816 \times 10^{-12}\,\mathrm{F\,m^{-1}}$
Bohr magneton	μ_B	$9.274\,015\,4 \times 10^{-24}\,\mathrm{J\,T^{-1}}$
Ratio of circumference to diameter of a circle	π	$3.141\,592\,653\,59$

Conversions

Standard state pressure	$10^5\,\mathrm{Pa} = 10^2\,\mathrm{kPa} = 1\,\mathrm{bar}$
1 atmosphere pressure (non-SI)	$1\,\mathrm{atm} = 101\,325\,\mathrm{Pa}$
Energy[†]	$1\,\mathrm{eV} = 96.4853\,\mathrm{kJ\,mol^{-1}}$

[†] An electron volt is a non-SI unit with a value of $\approx 1.602\,18 \times 10^{-19}$ J; to compare eV and $\mathrm{kJ\,mol^{-1}}$ units, it is necessary to multiply by the Avogadro number.