University of Canterbury

End of Year Examination 2006

Prescription Number(s):	CHEM 221
Paper Title:	Inorganic & Structural Chemistry

Time Allowed:	THREE HOURS
Number of pages:	EIGHT

Answer **FIVE** of the SEVEN questions.

All questions are of equal value.

A periodic table is located on page EIGHT.

TURN OVER

1. (a) Determine the oxidation state and number of d electrons for the metal in each of the following complexes:

(i) $[TiOCl_4]^{2-}$

(ii) $[Fe(CN)(CO)_4]^{-}$

(iii) *mer*-$[VCl_3(THF)_3]$ (THF = tetrahydrofuran, C_4H_8O)

(iv) $[NiBr_3(PEt_3)_2]$

(b) (i) Sketch the cation in *trans*-$[Cr(SCN)_2(H_2O)_4]Br.2H_2O$.

(ii) Sketch a geometrical isomer of the cation in part (i).

(iii) Sketch a linkage isomer of the cation in part (i).

(iv) Sketch an ionization isomer of the *compound* in part (i).

(v) Sketch a hydrate isomer of the *compound* in part (i).

(c) Explain each of the following observations, with reference to the underlying principles:

(i) For $[Co(H_2O)_6]^{2+}$, Δ_o = 9,200 cm^{-1} whereas for $[Co(H_2O)_6]^{3+}$, Δ_o = 20,760 cm^{-1}.

(ii) $[Mn(CN)_6]^{4-}$ has one unpaired electron whereas $[MnI_4]^{2-}$ has five unpaired electrons.

(iii) Absorption bands of transition metal complexes in the visible region are usually broad.

2. (a) Name each of the following compounds:

(i) $[NiCl(NH_3)_3]Br$

(ii) $Na_3[CoF_6]$

(iii) *trans*-$[Fe(OH)_2(NMe_3)_4]$

(iv) $[Co(CN)(NH_3)_5][NiBr_4]$

(b) Draw a structure for each of the following compounds or ions:

(i) *trans*-tetraammineaquachloridocobalt(III)

(ii) *mer*- bis(acetonitrile)trichloridooxidoniobium(V)

(iii) di-μ-hydroxobis[bis(ethylenediamine)chromium(III)]

(c) Explain **TWO** of the following observations, with reference to the underlying principles:

(i) For $[Cu(NO_2)_6]^{4-}$, four Cu–NO_2 distances are 205 pm and two are 231 pm.

(ii) Complexes of 4d and 5d transition metals are almost always low spin, whereas high spin is common for complexes of 3d transition metals.

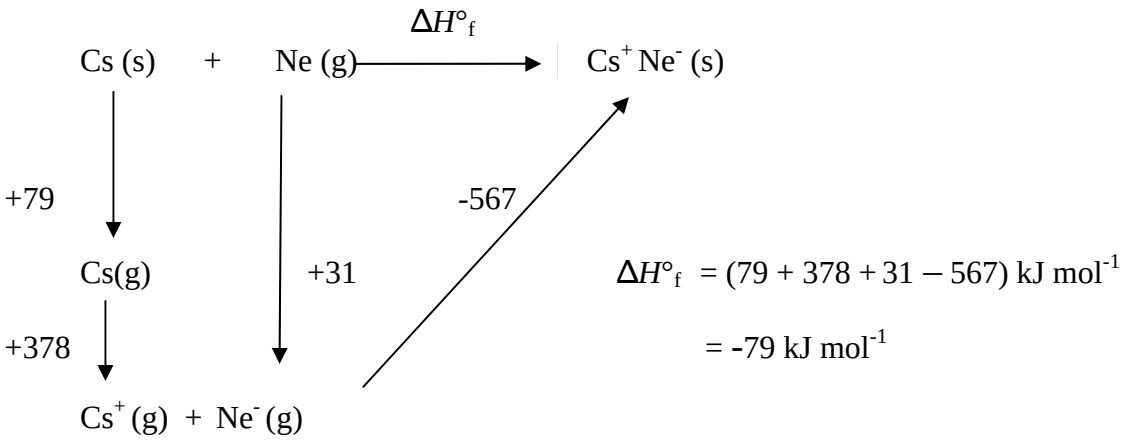
(iii) For $[Ru(H_2O)_6]^{2+}$, Δ_o = 19,800 cm^{-1} whereas for $[Ru(CN)_6]^{4-}$, Δ_o = 33,800 cm^{-1}.

3. (a) Discuss the reasons for the low reactivity of the noble gases.

(b) In the context of your answer to (a) explain why the following reaction does occur.

$$Xe + F_2 \xrightarrow[400^\circ C]{Light\ or} XeF_2$$

(c) Explain the following diagram and use it to predict whether the compound Cs^+Ne^- could be prepared.



4. (a) Outline the periodic trends in homonuclear single-bond enthalpies and provide an explanation for these trends.

(b) Why are the single-bond enthalpies for N_2, O_2, and F_2 exceptions to the trends in (a)?

(c) σ and π bonds involving C have similar and large energies. What consequences does this have?

5. (a) (i) Which transition metals are used in electron-transfer proteins and why?

(ii) Comment on the ligands available to these metal ions in biological systems.

(iii) How is the chemistry of the transition-metal ions affected by variation of these ligands?

(b) What are the main differences between intrinsic and extrinsic semiconductors? Use band energy diagrams to illustrate your answer.

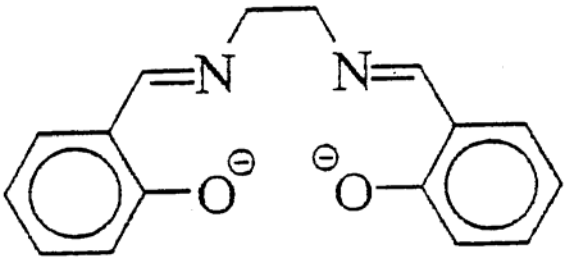
6. (a) Discuss the strategy behind the design of the "picket-fence" porphyrin, with particular reference to aspects that model the binding pocket of haemoglobin. In what way is the "picket-fence" porphyrin a successful model for haemoglobin? What are the major differences and how have they been accounted for?

(b) Cobalt (II) complexes of the salen ligand (shown below) will bind dioxygen only if:

(i) there is a pyridine derivative, or similar ligand, coordinated in an axial site, and

(ii) the solvent is non-coordinating.

Explain why this is so and discuss the wider implications of this result.



7. (a) Zinc is a special case in the first transition series.

(i) What makes zinc chemistry and hence zinc complexes different?

(ii) Where is zinc used in biology?

(b) Name one metalloprotein which contains zinc. Briefly discuss the role of that protein in a biological system. Comment on the significance of zinc in the function of the protein.

Periodic Table

1 H 1.008																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.8	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71 see below	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 see below	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110	111	112						

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0

89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.1	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (245)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)

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