University of Canterbury

End-of-year Examinations 2009

Prescription Number(s):	CHEM 271
Paper Title:	Inorganic Chemistry

Time Allowed:	Three hours
Number of pages:	Six plus periodic table and separate sheet

Answer Question 1 and **FOUR** out of the remaining FIVE questions.

All questions are of equal value.

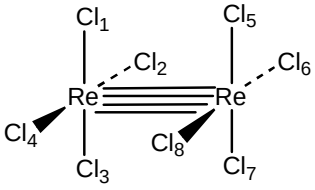
There is a periodic table at the end of this paper.

TURN OVER

Answer Question 1

1. A flow chart to determine the point group of an object is given on the separate sheet.

(a) Shown below is the $[Re_2Cl_8]^{2-}$ anion which contains a quadruple bond and exists in an eclipsed conformation.



(i) Determine its point group (show your working)

(ii) How many operations does this point group have?

(iii) Sketch the result of an S_4 operation.

(iv) Sketch the result of an i operation.

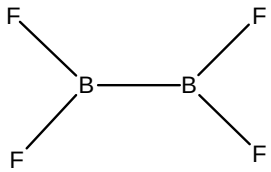
(v) Sketch the result of a C_2 rotation about the principal rotation axis.

(b) $[XeF_5]^-$ is a planar molecule.

(i) Determine its point group (show your working).

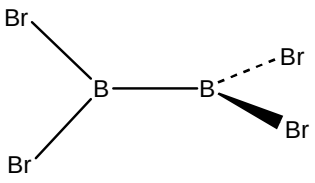
(ii) How many operations does this point group have?

(c) (i) Determine the point group (show your working) of B_2F_4 which has the planar structure shown below.



(ii) List all of its symmetry operations.

(d) (i) Determine the point group (show your working) of B_2Br_4 which has the staggered structure shown below.



(ii) List all of its symmetry operations.

Answer FOUR of the remaining FIVE questions.

2. (a) How does the strength of homonuclear bonds compare to that of heteronuclear bonds?

(b) Which **TWO factors** are important to take into account when analyzing trends in heteronuclear bond strengths?

(c) Analyze trends of the bond strengths (kJ/mol) in the series below:

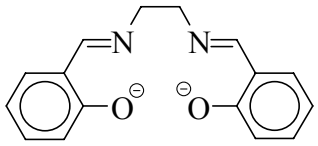
C-F	485	Si-F	565	Ge-F	452	Sn-F	414
C-F	485	C-Cl	327	C-Br	310	C-I	213
Si-F	565	Si-Cl	381	Si-Br	310	Si-I	234

3. (a) Define the terms valence state and oxidation state;

(b) A balance of which factors dictates the availability of oxidation states for s- and p- block elements?

(c) Explain why the highest oxidation state for a given p-block element is often observed in compounds formed by this element with the hardest elements (O, F).

4. (a) Cobalt(II) complexes of salen ligands (shown below) will bind dioxygen only if there is a pyridine derivative, or similar ligand, coordinated in an axial site, and the solvent is non-cordinating. Explain why this is so and discuss the implications of this result.



(b) Explain why dioxygen binds less strongly to hemoglobin than to the "picket fence" model complex.

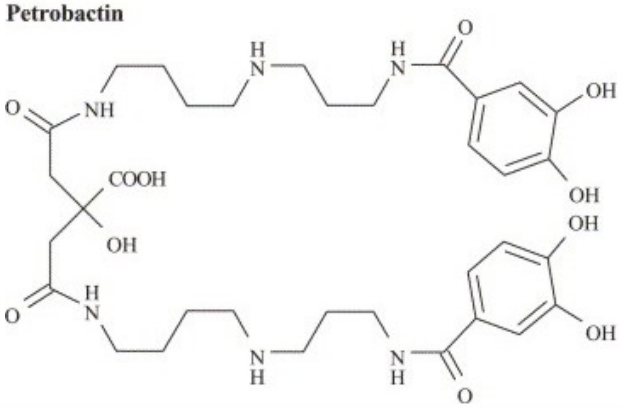
(c) Studies on a particular mutant hemoglobin revealed that, in the β-subunits only, the distal histidine had been replaced by aspartic acid. The α-subunits functioned normally, but the mutated β-subunits were permanently in the met form. Explain this observation as fully as possible. (The distal histidine is not bonded to the iron.)

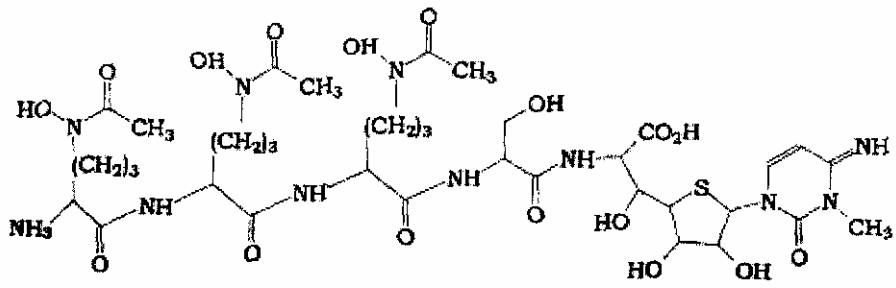
5. (a) How did Allen define the electronegativity of an element? Explain the advantages of this approach *vs.* the approach by Pauling.

(b) (i) Discuss the role of siderophores in biological systems.

(ii) There are three main modes of iron binding in siderophores. Describe these and identify and name the binding sites in the following siderphores.

Petrobactin

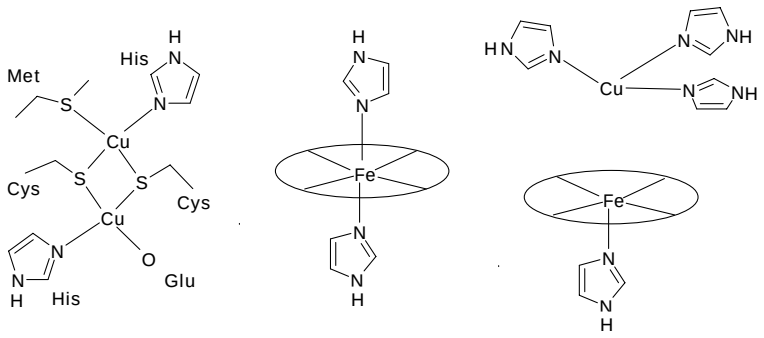




Albomycin

6. Cytochrome c oxidase is the terminal member of the respiratory electron transfer chain and one of its functions is to catalyse the four-electron reduction of dioxygen to water:

$$O_2 + 4H^+ + 4e^- \xrightarrow[\text{oxidase}]{\text{Cyt. c}} 2H_2O$$



Cu_A site

The principal metal binding sites of cytochrome c oxidase are illustrated in the diagram above.

(a) (i) Describe the function of each site and relate this to the structure shown.

(ii) How do these active sites relate to the active sites of other, simpler metalloproteins with related functions.

(b) What effects on the properties of the sites would you expect to observe if the following mutations were made:

(i) One of the Cys residues in the "Cu_A site" was replaced by Ser (i.e. the S donor replaced by O)?

(ii) One of the His residues in the "Heme a" site was replaced with Cys?

(iii) The copper ion in the "Cu_B" site was replaced by zinc?

END OF PAPER

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)

Flow Chart for Question 1