University of Canterbury

End-of-year Examinations 2009

Prescription Number(s):	CHEM 241
Paper Title:	Inorganic Chemistry

Time Allowed:	Three hours
Number of pages:	Seven plus Periodic Table

Answer **FIVE** questions out of SEVEN, including AT LEAST ONE question from Section A.

All questions are of equal value.

There is a Periodic Table at the end of this paper.

TURN OVER

SECTION A

(Answer **AT LEAST ONE** question from this section.)

1. (a) Using Skeletal Electron Pair Theory (SEPT), describe or draw a structure for each of the following molecules (show your working):

   (i) B_5H_9

   (ii) $[Sn_5]^{2-}$

   (iii) $C_2B_4H_6$

   (b) Sketch the possible cage isomers for the compound in part (iii) above.

   (c) Order the following atoms/ions in terms of their size, and rationalise your chosen order: S, Cl, Br, Cl^-, Na^+

   (d) (i) Account for the following relative N/P bond energies (in kJ/mol):

N–N 167	N=N 450	N≡N 946
P–P 200	P=P 310	P≡P 490

   (ii) Do you expect an As–As single bond to be stronger or weaker than a P–P single bond? Explain your answer.

2. (a) Give brief explanations for each of the following:

(i) The N=N bond is much weaker than the C=C bond, but the N≡N bond is similar in energy to a C≡C bond.

(ii) CO_2 is a monomer, but SiO_2 is a 3D network.

(iii) "BH_3" is a dimer, B_2H_6, but NH_3 is a monomer.

(iv) CH_4 is a stable gas, but PbH_4 does not exist.

(v) $ZrH_{1.75}$ has a much higher electrical conductivity than CaH_2.

(vi) IE(N) > IE(O).

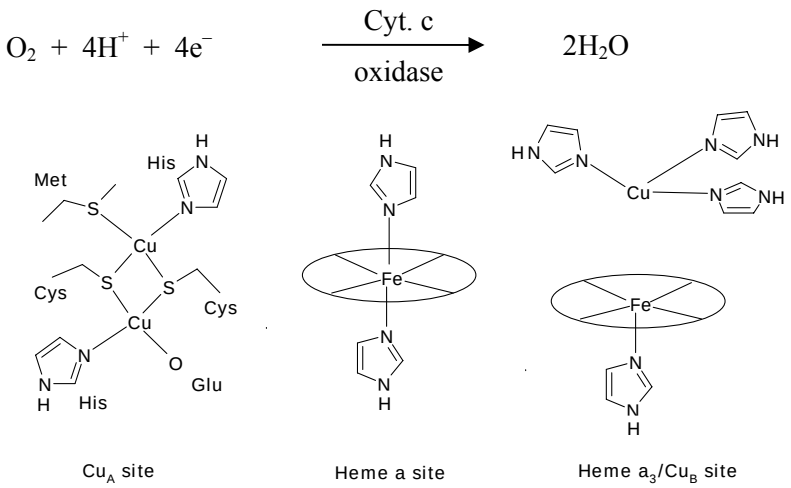
(vii) The Cl–Cl bond is stronger than the F–F and I–I bonds.

(b) List the following elements in the historical order of their isolation, and discuss reasons for the order in which they were isolated:

N, Hf, Rb, S, Si, Tc

SECTION B

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



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

(a) (i) Describe the function of each site and explain how the structural features contribute to the function.

(ii) With respect to the "Heme a_3/Cu_B" site, discuss how this is similar to, or differs from, the active sites of hemoglobin and superoxide dismutase.

(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?

4. Write an essay on the role of transition metals in biological systems. You should discuss the properties of transition metals that make them more or less suited to each specific role. You must include examples of a metalloprotein specific to each role. You may use diagrams to help illustrate your answer. You may also wish to consider the redox properties of the metals and Hard-Soft Acid-Base theory in your answer and the way that the ligands influence the activities of the metals in your examples.

5. (a) "In the presence of dioxygen, iron(II) species are readily oxidised to iron(III) species. In the presence of water, iron(III) species frequently associate into μ-oxodiiron dimers. For iron(II)-porphyrin complexes this may take only milliseconds at room temperature." (G.B. Jameson and J.A. Ibers)

Expand on the above statement by discussing:

(i) the routes by which μ-oxodiiron dimers are formed;

(ii) how these routes can be blocked in synthetic model complexes;

(iii) how these routes are blocked in myoglobin **or** haemoglobin.

(b) Explain fully each of the following terms.

(i) amino acid **residue;**

(ii) highly conserved;

(iii) apoprotein;

(iv) isomorphous replacement.

6. (a) Discuss the function of carbonic anhydrase in biological systems, particularly with respect to:

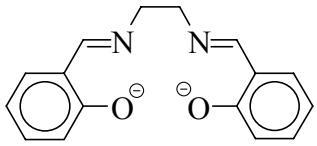
(i) the solubility of carbon dioxide in water;

(ii) the blood-buffer system.

(b) Why is zinc so suited to the role it plays in carbonic anhydrase?

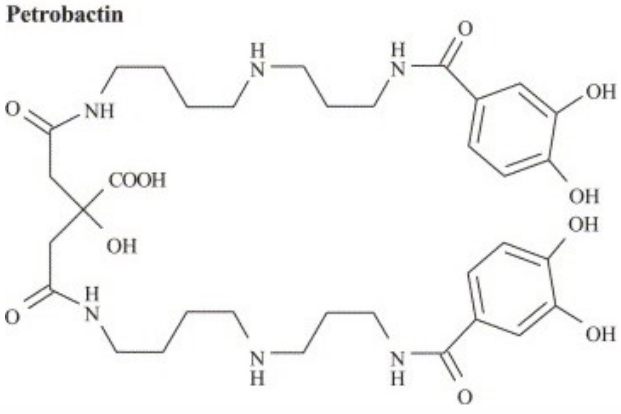
(c) You have learned of some other zinc containing enzymes. Briefly describe these, and discuss the role of zinc in one or more of them.

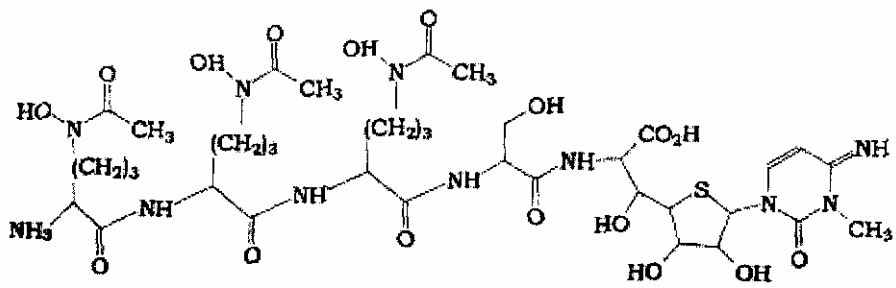
7. (a) Cobalt(II) complexes of salen ligands (shown below) will bind dioxygen only if there is a pyridine derivative, or similar ligand, coordinated in an axial site, and the solvent is non-coordinating. Explain why this is so, and discuss the implications of this result.



(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 functional groups in the following siderophores.





Albomycin

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)