University of Canterbury

End-of-year Examinations 2009

Prescription Number(s):	CHEM 361
Paper Title:	Inorganic and Structural Chemistry

Time Allowed:	Three hours
Number of pages:	Eight plus periodic table and one separate answer sheet

Answer **FIVE** questions out of SIX.

All questions are of equal value.

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

TURN OVER

1. (a) The Shroud of Turin, a religious artefact thought by some to be the burial shroud of Christ, was subjected to radio-carbon dating and showed a ^{14}C decay rate of 14.2 disintegrations min^{-1} g^{-1} carbon.

What age is implied by this result if currently living organisms decay at a rate of 15.3 disintegrations min^{-1} g^{-1} carbon? ($t_{1/2}$ ^{14}C = 5730 yr).

(b) Consider the following information:

(i) The layer of dead skin on our bodies is sufficient to protect us from most alpha-particle radiation.

(ii) Plutonium is an alpha-particle producer.

(iii) The chemistry of Pu^{4+} is similar to that of Fe^{3+}.

(iv) Plutonium is readily oxidized to Pu^{4+} *in vivo*.

Using this information, explain why plutonium is one of the most toxic substances known.

(c) You have suffered an overdose of Fe(III) through accidental ingestion of an excess of vitamin supplements. From first principles, and based upon the chemical behaviour of Fe(III), design and illustrate a suitable ligand for the treatment of this condition using chelation therapy.

Your answer should include discussion of the concepts behind the use of chelation therapy and explain any potential problems associated with this treatment.

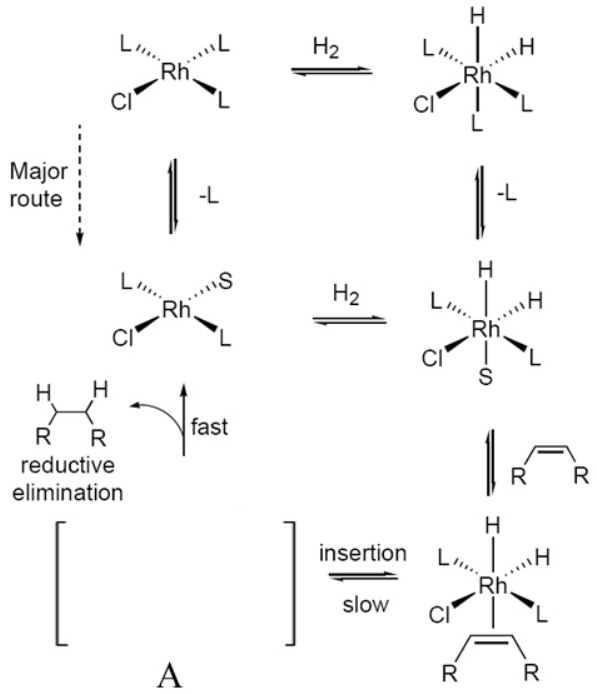
2. Answer **either** (a) **or** (b):

Either

(a) (i) Define the term asymmetric catalysis. Why are homogeneous catalysts particularly well suited for this "niche" type of catalysis (*cf.* heterogeneous catalysts)?

(ii) Name three major steps in the mechanism of olefin polymerization using Zirconocene-based Ziegler-Natta olefin polymerization catalysts.

(iii) Draw missing intermediate (A) in the scheme of catalytic hydrogenation of alkenes provided below. Assuming S (solvent) and L (phosphine) as being neutral 2-e donor ligands and Rh(0) as having 9e, perform an electron count for this intermediate.



(iv) Explain why Zirconocene-based Ziegler-Natta olefin polymerization catalysts produce long linear products whereas late transition metal-based catalysts produce branched polymers or oligomers.

Question 2 continued on following page

Question 2 continued

Or

(b) (i) Give a definition of a catalyst AND provide an appropriate graphical illustration of the role of a catalyst in enabling the reaction to proceed.

(ii) Name three major *advantages* of homogeneous catalysts. Name one major *disadvantage* of homogeneous catalysts.

(iii) Explain *in detail* how stereo-control is enforced in Zirconocene-based Ziegler-Natta polymerization catalysts. Why do syndiotactic and isotactic polypropylenes have higher melting points compared to atactic polypropylene?

(iv) Nuclear magnetic resonance has particular value in studying the fluxionality of organometallic complexes. Explain why *variable temperature* NMR is widely used in such studies?

3. (a) Using diagrams as appropriate, delineate as fully as possible how dissociative and associative reaction mechanisms may be differentiated experimentally.

(b) Put in order of increasing rate of substitution by H_2O the complexes: $[Co(NH_3)_6]^{3+}$; $[Rh(NH_3)_6]^{3+}$; $[Ir(NH_3)_6]^{3+}$; $[Mn(H_2O)_6]^{2+}$; $[Ni(H_2O)_6]^{2+}$.

Outline what factors are responsible for the order you propose.

(c) Discuss, using diagrams and examples as appropriate, the differences between *inner-sphere* and *outer-sphere* electron transfer mechanisms, and state what is meant by a self-exchange reaction.

(d) Explain the differences in the rate constants for the following electron transfer reactions:

$[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} \rightarrow [Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$ $\quad k = 4\ M^{-1}\ s^{-1}$

$[Fe(bpy)_3]^{2+} + [Fe(bpy)_3]^{3+} \rightarrow [Fe(bpy)_3]^{3+} + [Fe(bpy)_3]^{2+}$ $\quad k > 10^6\ M^{-1}\ s^{-1}$

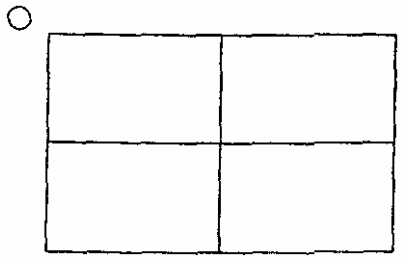
$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \rightarrow [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$ $\quad k = 10^{-6}\ M^{-1}\ s^{-1}$

(bpy = 2,2'-bipyridine).

4. (a) (10 marks)

Consider plane group *p2mg* shown below.

Rectangular *2mm* *No. 7 p2mg*

(I) 

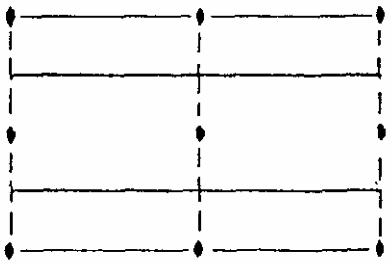
(II) 

Diagram (I) has been cleared of all information except a starting position.
Diagram (II) shows the symmetry elements of this plane group.

(i) Using the attached copy of (I), show all the equivalent positions generated by the symmetry elements in (II).

(ii) Explain each of the symmetry elements in (II) and describe how each position you have drawn was generated by one of these.

(iii) Take one of the positions you have generated and show how you could have generated it, using the appropriate symmetry element, from one other position rather than the one at the origin.

(b) (10 marks)

(i) What is the **lattice** of a structure and how does a **unit cell** relate to the lattice?

(ii) Describe the difference between the **asymmetric unit** and the **unit cell** in crystallographic terms.

(iii) Crystalline compounds can have symmetry elements not possible in isolated finite molecules. Describe these elements, using diagrams if necessary.

(iv) P$2_1/c$ is a space group symbol. Explain what each character of the symbol means.

5. (a) For each of the following compounds, suggest a one-step preparation from an appropriate **neutral metal carbonyl** complex (i.e. from a complex containing only a metal and carbonyl ligands):

(i) $[Fe(CO)_4]^{2-}$

(ii) $[CpFe(CO)_2]^-$

(b) Give one example of each of the following:

(i) A bent 16-electron sandwich complex

(ii) A stable 17-electron complex

(iii) A phosphine that can act as a strong π-acceptor ligand

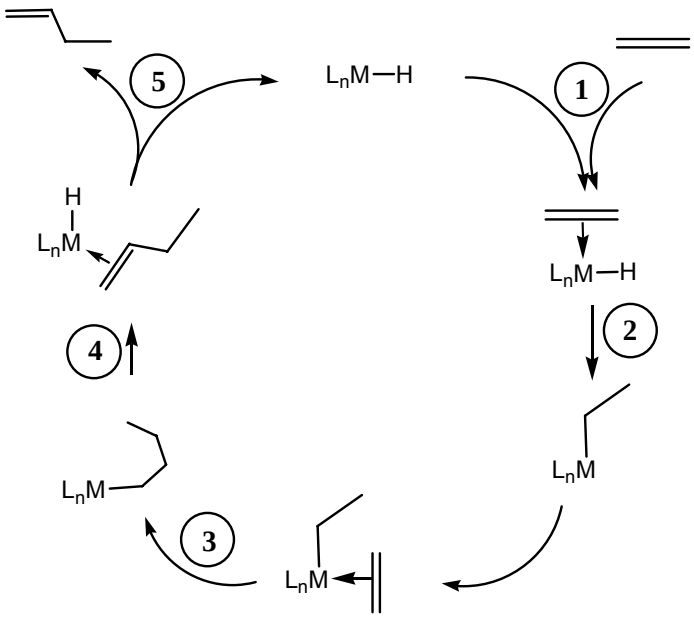
(c) Explain how NO and indenyl can promote associative substitution reactions.

(d) Describe the factors which lead to the decomposition of alkyl and aryl transition metal complexes by β-elimination and give three examples of ligands that are not expected to undergo β-elimination.

(e) Shown below is a catalytic cycle for the dimerisation of ethylene.

(i) Describe briefly what is happening in each of steps 2–4.

(ii) Ignoring *cis*/*trans* isomers, draw the possible products for a dimerisation of styrene ($PhCH{=}CH_2$).



6. (a) Explain which spectroscopic techniques you would use, and how you would employ them, in order to determine the following parameters:

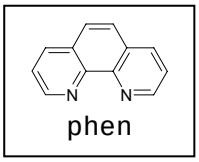
   (i) Extinction coefficient

   (ii) Excited state lifetimes

   (iii) Fluorescence quantum yields

   (b) Discuss, using diagrams and giving examples as appropriate, the changes commonly observed in the absorption and emission spectra of d-metal complexes possessing MLCT transitions following the absorption of a photon of light.

   (c) Draw and discuss a Jablonsky diagram for 1,10-phenanthroline (phen) and then modify the diagram to account for the use of this chromophore as a ligand in $[Ru(phen)_3]^{2+}$ complexes.



phen

END OF PAPER

Periodic Table on following page

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)

Answer sheet for Question 4(a) Name: .....

Student #: .....

Please answer Question 4 (a) using the following diagram and the information given in the question. Make sure you fully explain how you generated each equivalent position.

Diagram (I)