UNIVERSITY OF LONDON

BSc and MSci DEGREES – August 2003, for Internal Students of Imperial College London

This paper is also taken for the relevant examination for the Associateship

INORGANIC CHEMISTRY 2

RESIT

Monday 18th August 2003, 2.00 – 5.00pm

USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

Q 1 Main Group Chemistry

Answer part (a) and **THREE** parts from (b) to (e).

(a) Discuss each of the following terms and phrases.

(i) Hydroboration

(3 marks)

(ii) 'Rieke' magnesium

(3 marks)

(iii) Methylaluminoxane (MAO) as a co-catalyst in alkene polymerisation

(4 marks)

(b) Describe the solid state structures of methyl lithium and methyl potassium and account for the differences between them.

(5 marks)

(c) Use electron counting rules to account for the structure of the carborane $C_2B_4H_6$. Draw two possible isomers of the structure.

(5 marks)

(d) Illustrate the equilibria occurring in diethyl ether solution containing a Grignard reagent. How can a diorganomagnesium compound, R_2Mg, be isolated from such a solution?

(5 marks)

(e) Poly(sulfurnitride), $(SN)_x$, may be synthesised by polymerisation of S_4N_4 and conducts electricity along the polymer chain direction. Explain why the polymerisation of S_4N_4 must be undertaken with care and how the conductivity of the polymer arises.

(5 marks)

Q2 Transition Metal Chemistry

Answer **BOTH** part (a) **AND** part (b)

(a) Answer **EITHER** (i) **OR** (ii)

(i) Give the formula for the calculation of the spin-only magnetic moment of a transition metal complex. Explain why the measured magnetic moment can sometimes deviate from the calculated spin-only value.

(10 marks)

(ii) Discuss the origins of colour in transition metal complexes.

(10 marks)

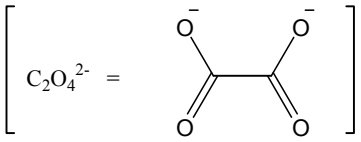
(b) Answer **THREE** of the following four questions

(i) Predict and explain the relative positions of the absorption maximum in the spectra of $[Ti(CN)_6]^{3-}$, $[TiCl_6]^{3-}$, $[Ti(H_2O)_6]^{3+}$.

(5 marks)

(ii) Find x, y and z in the following complexes by determining the oxidation state of the central metal from the experimental values of the effective magnetic moment μ_{eff}.

$K_x[Mn(CN)_5(OH)]$	$\mu_{eff} = 2.9$ BM
$[Fe(H_2O)_6]^{y+}$	$\mu_{eff} = 5.9$ BM
$K_z[Mn(C_2O_4)_3]$	$\mu_{eff} = 4.8$ BM



Explain any assumptions you have made.

(5 marks)

(iii) Explain why ligand substitution reactions at 4-coordinate palladium(II) centres generally have $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger} < 0$, whilst for 4-coordinate palladium(0), $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger} > 0$.

(5 marks)

(iv) Within each of the pairs of following complexes, which complex has the larger ligand field stabilisation energy. Explain your reasoning.

$[Cr(H_2O)_6]^{2+}$ or $[Mn(H_2O)_6]^{2+}$
$[Mn(H_2O)_6]^{2+}$ or $[Fe(H_2O)_6]^{3+}$
$[Fe(H_2O)_6]^{3+}$ or $[Fe(CN)_6]^{3-}$

(5 marks)

Q 3 NMR Methods in Inorganic Chemistry

Answer part (a) **AND EITHER** part (b) **OR** part (c)

(a) The proton decoupled ^{31}P NMR spectrum of $[Rh(PPh_3)_3]^+$ in CH_2Cl_2 solution shows two distinct sets of multiplets at low temperature, one a doublet of triplets and one a doublet of doublets. At high temperature only one doublet is observed in the spectrum. Interpret these spectra with reference to the cation geometry and the changes observed on varying the temperature. Sketch the spectra and label the coupling constants (using $^nJ_{X-Y}$ notation), chemical shifts and relative intensities of the signals. What will the ^{31}P NMR spectrum look like at temperatures approximately midway between the upper and lower limiting temperatures? Why will the spectrum have this appearance?

(Assume that ^{31}P is 100% abundant, I = ½; ^{103}Rh is 100% abundant, I = ½.)

(16 marks)

(b) Sketch the ^1H NMR spectrum of the CH_3 group in the Lewis acid-base adduct $CH_3NH_2BCl_3$. Label the spectrum using the $^nJ_{X-Y}$ notation to show the coupling constants and give the relative signal intensities. Assume that the only resolvable couplings are between the CH_3 group and the NH_2 protons ($^3J_{H-H}$ = 15 Hz) and between the CH_3 group and the ^{11}B ($^3J_{B-H}$ = 5 Hz). Why is this spectrum likely to show a large linewidth?
(Assume that ^1H is 100% abundant, I = ½; ^{11}B is 80% abundant, I = 3/2; and that no coupling to other nuclei present is observed.)

(9 marks)

(c) Give three of the problems that make the recording of good quality solid-state NMR spectra difficult. How may two of these problems be overcome?

(9 marks)

Q 4 Bioinorganic Chemistry

Answer part (a) and **EITHER** part (b) **OR** part (c)

(a) Give one example of an iron-containing enzyme. Describe the type of reactions that it catalyses and discuss its mode of action, paying particular attention to the role of the metal.

(13 marks)

(b) Explain in detail the mechanisms that bacteria have developed for the uptake of iron into the living cell.

(12 marks)

(c) Describe the role of Gd(III) ions as contrast agents in medical imaging. Explain the properties of this ion that make it suitable for this application and give one example of a gadolinium complex that is currently used in imaging. Describe the parameters that need to be optimised when designing novel gadolinium contrast agents.

(12 marks)

Q 5 Organometallic Chemistry

Answer parts (a) and (b), and **EITHER** part (c) **OR** part (d)

(a) Draw the structure of each of the following metal carbonyl compounds.

(i) $[Co_2(CO)_8]$
(ii) $[Mn_2(CO)_{10}]$
(iii) $[Mn(CO)_5Br]$
(iv) $[Tc_2(CO)_8Br_2]$

(8 marks)

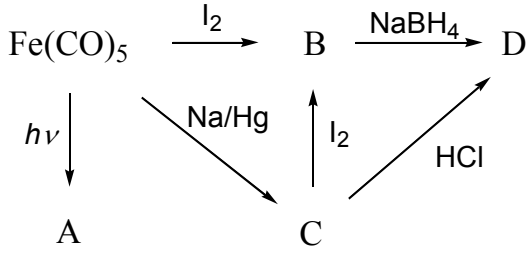
(b) Describe and illustrate the bonding between a transition metal and the following ligands: (i) CO; (ii) C_2H_4; (iii) NO.

(8 marks)

(c) Answer **BOTH** parts of this question

(i) Outline an experiment that would allow $Fe(CO)_n$ species, where n = 1-5, to be 'isolated' and studied spectroscopically.

(ii) Identify A-D in the reaction scheme below:



(9 marks)

(d) Give plausible catalytic cycles for each of the following alkene conversion processes:

i) hydroformylation
ii) isomerisation
iii) hydrogenation

(9 marks)

Q 6 Crystal and Molecular Architecture

Answer part (a) and **EITHER** part (b) **OR** part (c).

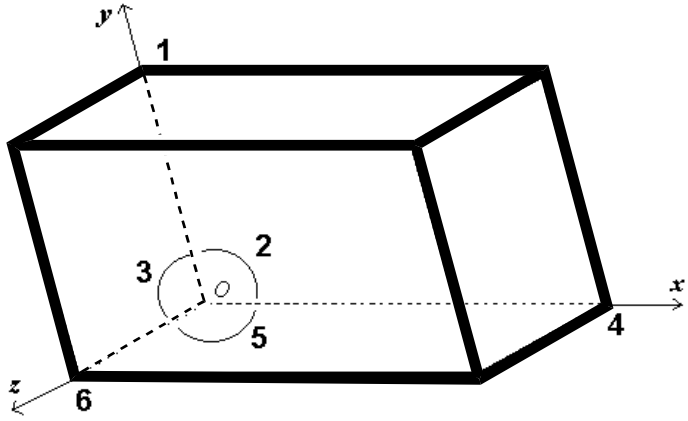
(a) Answer **ALL** parts of this question

(i) Describe the nature and location of the symmetry elements that characterise the trigonal crystal system. What is its lattice symmetry, and what effect does this symmetry have on the unit cell parameters?

(5 marks)

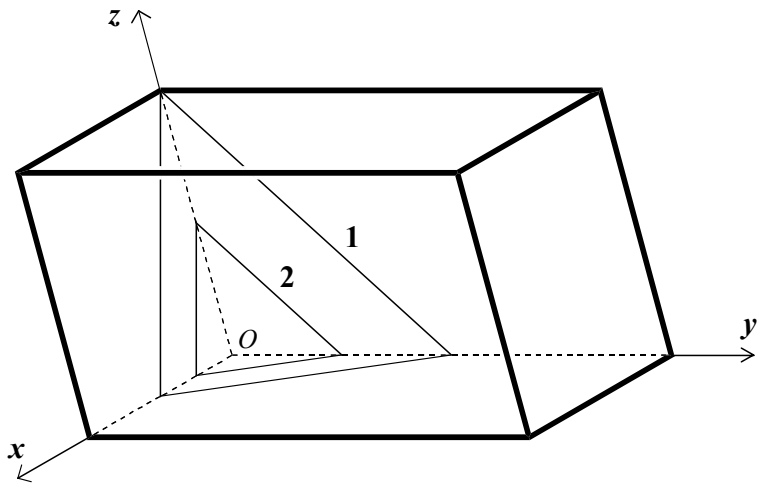
(ii) With reference to the picture of a unit cell shown below, identify the six symbols that should replace **1**, **2**, **3**, **4**, **5** and **6**.

(3 marks)



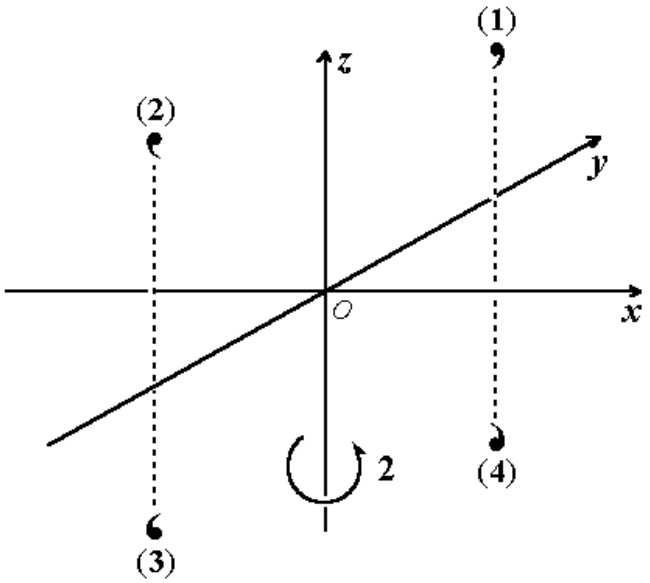
(iii) With reference to the picture of a unit cell shown below, give the indices for the two planes **1** and **2**.

(3 marks)



(iv) The figure shows a 2-fold rotation axis along z with a perpendicular xy mirror plane at $z = 0$. What are the general coordinates associated with the four positions (**1**), (**2**), (**3**) and (**4**). What additional symmetry element is generated by the combination of the 2-fold rotation and the perpendicular mirror plane, and where is it?

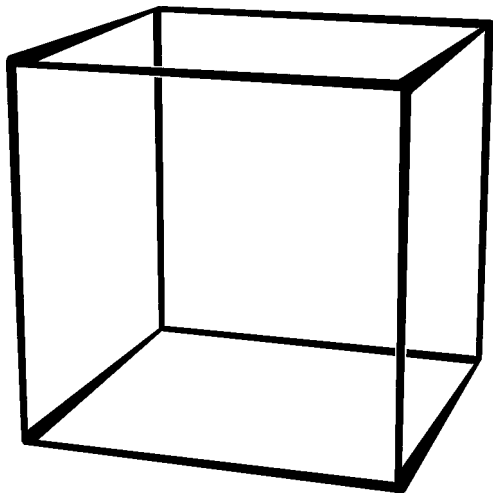
(5 marks)



(b) Answer **ALL** parts of this question

(i) Using a picture of a cube (such as that reproduced below) show the sites occupied by the hard spheres in the cubic close-packing of identical spheres, and the locations of the octahedral holes. If there are N atoms in the close-packed structure, how many octahedral holes will there be?

(3 marks)



(ii) For a close-packed structure comprised of spheres of radius r, calculate the size of an octahedral hole.

(6 marks)

(c) Answer **ALL** parts of this question

(i) Without drawing diagrams, compare and contrast the structures of sphalerite and wurtzite, two polymorphic sulfur minerals of zinc. In each case give the stoichiometries and the coordination numbers of each type of ion. What does the term polymorph mean?

(7 marks)

(ii) What are the space filling efficiencies of body-centred cubic packing and primitive cubic packing of identical hard spheres?

(2 marks)