

UNIVERSITY OF LONDON

BSc/MSci DEGREE – June 2001, for Internal Students of the
Imperial College of Science, Technology and Medicine

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

INORGANIC CHEMISTRY II

Tuesday 19th June 2001, 2.00 – 5.00pm

ATTEMPT ALL QUESTIONS

**USE A SEPARATE ANSWER BOOK FOR EACH
QUESTION**

Question 1 Main Group Chemistry

Answer part (a) **AND TWO** parts from (b) **TO** (d)

(a) Describe three general types of bonding to be found in organometallic compounds of the main group elements and illustrate your answer using suitable compounds and draw their structures. Give examples, using balanced equations, of how an organometallic compound of each of the following elements can be prepared: potassium, beryllium, gallium and tin.

(15 marks)

(b) Draw the structure of $[\text{B}_5\text{H}_8]^-$ and use electron counting rules to account for the structure.

(5 marks)

(c) How can a $[\text{Fe}_4\text{S}_4(\text{SR})_4]$ cluster with a core of the type found in the nitrogen-fixing enzyme nitrogenase be prepared in the laboratory? Draw the structure of the cluster and draw also three other modes by which S^{2-} can function as a bridging ligand.

(5 marks)

(d) Give balanced equations for the following reactions:

- (i) A synthesis of PCl_5 .
- (ii) The reaction of PCl_5 with two equivalents of water.
- (iii) The complete hydrolysis of PCl_5 .
- (iv) The reaction of PCl_5 with NH_4Cl .

(5 marks)

Question 2 Transition Metal Chemistry

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

Part (a).

EITHER

- (i) Show how the molecular orbital scheme for an octahedral complex ligated by σ -donor ligands may be modified to take account of π -interactive ligands. Illustrate your answer with reference to the complexes $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{CN})_6]^{3-}$. (10 marks)

OR

- (ii) Discuss evidence to support the proposal that ligand substitution in d^8 -square planar complexes is generally an associative process. (10 marks)

Part (b)

Explain **THREE** of the following observations

- (i) Octahedral Ni(II) complexes have magnetic moments (μ_{eff}) in the range 2.9 to 3.4 BM, tetrahedral Ni(II) complexes have magnetic moments up to 4.1 BM and square planar Ni(II) complexes are diamagnetic. (5 marks)
- (ii) Find x , y , and z in the formulae of the following compounds by determining the oxidation state of the central metal from the experimental values of the effective magnetic moment μ_{eff} .

Compound	$\mu_{\text{eff}}/\text{BM}$
$[\text{VCl}_x(\text{bipy})]$	1.77
$\text{K}_y[\text{V}(\text{ox})_3]$	2.80
$[\text{Mn}(\text{CN})_6]^{z-}$	3.94

What assumption have you made and how valid is it?

(bipy = 2,2'-bipyridine; ox = oxalato)

(5 marks)

- (iii) Ligand substitution reactions at 4-coordinate platinum(II) centres generally have ΔS^\ddagger and $\Delta V^\ddagger < 0$, whilst for 4-coordinate platinum(0), ΔS^\ddagger and $\Delta V^\ddagger > 0$. (5 marks)
- (iv) The $[\text{CoCl}_4]^{2-}$ ion is a regular tetrahedron. The complex $[\text{CuCl}_4]^{2-}$, however, has a flattened tetrahedral structure and absorptions at 11,500 and 14,500 cm^{-1} . (5 marks)

Question 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 $[\text{Rh}(\text{PPh}_3)_3]^+$ 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 seen 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, chemical shifts and relative intensities of signals.

(Assume that no coupling to carbon nuclei is observed. ^{31}P is 100% abundant $I = 1/2$, ^{103}Rh is 100% abundant $I = 1/2$.) (16 marks)

- (b) Draw the ^{27}Al and ^{19}F spectra of $[\text{AlF}_4]^-$. Label the coupling constants and give relative intensities for all the signals.

(Assume that ^{19}F is 100% abundant $I = 1/2$ and that ^{27}Al is 100% abundant $I = 5/2$.)

(9 marks)

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

(9 marks)

Question 4 Bioinorganic Chemistry

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

- Part (a) i) Describe the non-enzymatic role of the metallo-protein hemocyanin.
ii) Show the coordination environment around its metal centres.
iii) With the help of drawings show the changes undergone by this enzyme (paying particular attention to the metal centres) when involved in this non-enzymatic process.

(10 marks)

- Part (b) For the enzyme carbonic anhydrase:
i) Write down the reaction it catalyses
ii) Sketch its active site
iii) Explain in detail its mode of action
iv) Describe one metal complex which has been used as a bio-mimetic model for this enzymatic reaction. Explain the rationale behind this choice.

(15 marks)

- Part (c) For Cytochrome P-450:
(i) Show the type of reaction it catalyses.
(ii) Draw a schematic representation of its active site.
(iii) Discuss its proposed catalytic mechanism indicating the oxidation state of the metal centre in each step.
(iv) Which are the most important properties of the metal present in this enzyme which make it the element of choice for this catalysis?

(15 marks)

Question 5 Organometallic Chemistry

Answer part (a) **AND** part (b), **AND EITHER** part (c) **OR** part (d) :-

(a) Outline the MLXZ formalism for classifying metal complexes? Suggest reasonable structures for the following complexes and give the formal oxidation state and d electron count of the metal in each case.

- (i) $[\text{Co}(\text{H})(\text{N}_2)(\text{PPh}_3)_3]$
- (ii) $[\text{Cr}(\text{NO})_4]$
- (iii) $[\text{W}(\text{O})\text{Cl}_2(\text{C}_2\text{H}_4)(\text{PMe}_2\text{Ph})_2]$

(8 marks)

(b) What is understood by the term *synergic bonding*? Illustrate your answer with reference to *CO* and *alkene* ligands.

(8 marks)

(c) Account for the exceptional stability of 16-electron, d^8 square-planar complexes, and outline the key steps in the catalytic hydrogenation of alkenes using $[\text{RhCl}(\text{PPh}_3)_3]$.

(9 marks)

(d) A mixture of $[\text{Fe}(\text{CO})_5]$ and $[\text{Mn}_2(\text{CO})_{10}]$ dissolved in hexane was irradiated for 45 minutes with ultraviolet light from a mercury lamp. After removal of the volatile liquids, the solid residue, **A**, was sublimed onto a cold finger as red crystals. **A** was found to have moderate solubility in organic solvents, and to absorb in the infrared at 2067, 2019 and 1987 cm^{-1} . The mass spectrum of **A** showed a series of ions from m/e 166 to m/e 558; adjacent peaks in the series were separated by 28 mass units. Significant amounts of three other series of ions, beginning at m/e 55, 56 and 111 respectively, were observed: there was no series beginning at m/e 110. Deduce a structure for **A**, show that it conforms to the 18-electron rule, and relate it to the experimental observations.

[The most abundant isotopes of manganese and iron are ^{55}Mn and ^{56}Fe , respectively]

(9 marks)

Question 6 Crystal and Molecular Architecture

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

(a)

For a close-packed structure comprised of identical hard spheres of radius r , calculate

- (i) the space-filling efficiency of the array of spheres. (6 marks)
- (ii) the sizes of the tetrahedral holes. (6 marks)

In each case show your workings and clearly state any initial assumptions or facts on which your calculations are based.

(b)

- (i) The Hermann-Mauguin symbols for the Bravais lattices associated with the triclinic and monoclinic crystal systems are as follows;- triclinic, $P\bar{1}$; monoclinic, $P2/m$ and $C2/m$. What are the names of the other 5 crystal systems, and what are the Hermann-Mauguin symbols for their associated Bravais lattices? (10 marks)
- (ii) The monoclinic crystal system is defined by the lattice symmetry $2/m$. What unique symmetry elements does this lattice symmetry require, and what relationships between the unit cell parameters does this symmetry generate? (3 marks)

(c)

- (i) Without drawing diagrams, compare and contrast the structures of sphalerite and wurtzite, two polymorphic sulphur 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 crystal system is defined by the lattice symmetry $6/mmm$? What unique symmetry elements does this lattice symmetry require, and what relationships between the unit cell parameters does this symmetry generate? (6 marks)