IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2010, 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 IIB

Tuesday 15th June 2010, 14:00-16:00

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

2.I2 – Main Group Chemistry

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

a) Answer **ALL** parts.

Describe the likely solid-state structure of the following organometallic compounds. In each case, explain your reasoning:

i) EtLi
ii) MeRb
iii) *i*-Pr_2AlBr
iv) Ph_2SiCl_2
v) Ph_2SnCl_2

(10 marks)

b) Given the reagents below, describe a multi-step synthetic route to achieve the transformation shown in the scheme below. With balanced equations and reference to the pKa values provided, explain your reasoning. (Assume that the pKa for D_2O is the same as that for H_2O.)

Reagents	pKa values	
Li metal	HO-H	16
D_2O	Benzene	43
PhC≡C-H	PhC≡C-H	22
PhBr		

(8 marks)

c) Use electron counting (Wade's) rules to determine the structure of the following species. (The non-methyl carbon atoms in (ii) are bonded to each other.)

i) $[Sb_2Pb_2]^{2-}$
ii) $(MeIn)C_2B_4H_6$

(7 marks)

d) Propose a synthetic route to both the following inorganic polymers. Comment briefly on their properties and stabilities.

i) $[NP(NEt_2)_2]_n$
ii) $[SN]_n$

(7 marks)

2.I3 – Transition Metal, Coordination and Organometallic Chemistry

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

a) Give a synthetic pathway to the following organometallic complexes:

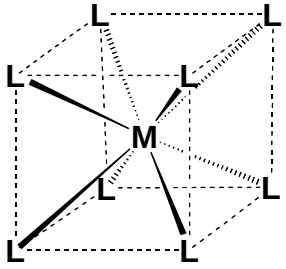
i) $FeCp_2$

ii) $Fe(CO)_5$

iii) $Cr(CO)_6$

(4 marks)

b) Answer **ALL** parts.



i) Using a simple crystal field approach, derive the d-orbital splitting diagram for a hypothetical transition metal complex ML_8 (shown above) with a cubic coordination geometry.

(4 marks)

ii) Discuss the similarities and the differences of the ML_8 splitting diagram with the splitting diagram for a ML_4 complex with tetrahedral coordination geometry. Comment on the magnitude of the splitting parameter Δ_c for cubic compared to Δ_t for tetrahedral geometry. Discuss the implications with respect to the magnetic behaviour of ML_8 complexes.

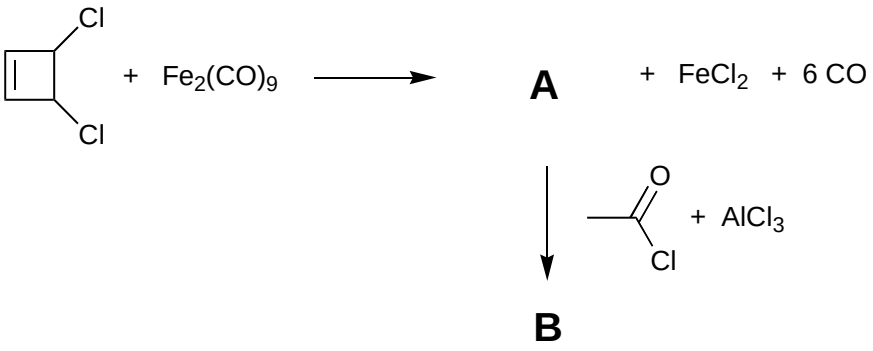
(5 marks)

iii) Determine the expected spin-only magnetic moment μ_{so} for the hypothetical cubic complex $[Mo(CN)_8]^{3-}$. What bands could be expected in the UV-vis spectrum?

(4 marks)

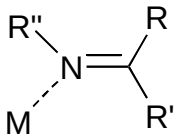
QUESTION CONTINUED OVERLEAF

c) The classic reaction between dichloro-cyclobutene and $Fe_2(CO)_9$ resulted in the first synthesis of a cyclobutadiene complex **A**. What is the structure and the electron count for complex **A**? The cyclobutadiene ligand exhibits aromatic character in this complex. Complex **A** reacts with a mixture of $AlCl_3$ and acetylchloride to produce complex **B**. Give the structure of complex **B** and explain its formation.



(8 marks)

d) Discuss the nature of the metal nitrogen bond in metal imine complexes of the type shown below. Illustrate your answer with a picture. Discuss how coordination of the imine ligand to a metal centre will affect the ν(C=N) stretching frequency in the IR spectrum.



(8 marks)

2.I4 – Crystal and Molecular Architecture

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

a) Answer **ALL** parts.

i) Draw a sketch of the unit cell of a cubic close-packed structure (CCP), consisting of only one atom type. What is the stacking sequence of the close packed layers?

(4 marks)

ii) Use the sketch you have drawn for part i) to show the location of ONE of the octahedral holes and ONE of the tetrahedral holes.

(2 marks)

iii) Show *by calculation* that the percentage of the total volume occupied by spheres in a CCP structure is approximately 74%.

(4 marks)

iv) Place cubic close-packed (CCP), primitive cubic (PC), hexagonal close-packed (HCP), body-centred cubic (BCC), in order of efficiency of packing.

(2 marks)

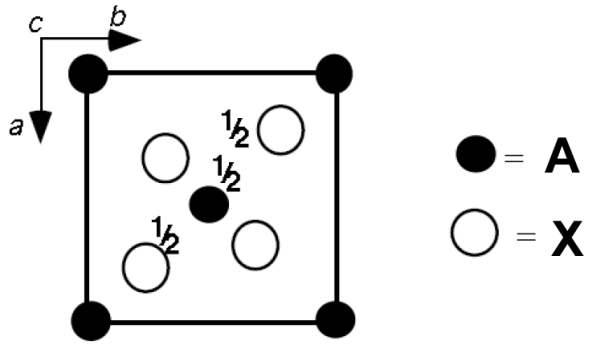
v) Give the coordination number and geometry of Na and Cl ions in the *Halite* (NaCl) structure. Explain how this structure relates to the one drawn in part (i).

(3 marks)

QUESTION CONTINUED OVERLEAF

b) Answer **ALL** parts

For solid A_mX_n, shown in plan view below (tetragonal viewed along the *c*-axis, heights above the $z = 0$ plane are expressed as fractions of *c*):



i) Identify the stoichiometry of the structure, stating how many A_mX_n formula units there are in the unit cell.

(2 marks)

ii) State the coordination number and coordination geometry of both A and X.

(2 marks)

iii) Using $a=b=4.594$ Å and $c=2.958$ Å, $\alpha=\beta=\gamma=90^o$ calculate the density of this compound in g cm^{-3}. (Mass: A=47.9 amu, X=16.0 amu)

(6 marks)

c) Answer **ALL** parts

ZnS in its Blende (also known as *Sphalerite*) form has a face-centred cubic lattice with motif S at (0,0,0) and Zn at (¼,¼,¼).

i) Draw a plan of the structure projected along [001].

(5 marks)

ii) Identify the coordination number and geometry around each ion.

(2 marks)

iii) Calculate how many ZnS units are in this unit cell.

(1 mark)

iv) Name the other common form of ZnS and the structure type adopted.

(2 marks)