IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2011, 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

Thursday 23rd June 2011, 14:00-16:00

PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING OF ANY PRIOR CORE COURSE.

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

2.I2 – Main Group Chemistry

Answer **BOTH** part a) **AND** part b) and **EITHER** part c) **OR** part d) of this question.

a) The compounds B_4H_{10} and S_2N_2 can both be described as arachno clusters. Show how electron counting (Wade's) rules can be used to determine the structure of each compound. Draw each compound and comment on any differences in structure (apart from the presence of H atoms in the borane) and suggest a reason for the differences.

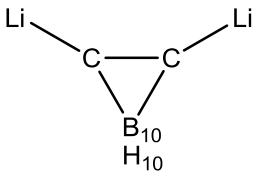
(10 marks)

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

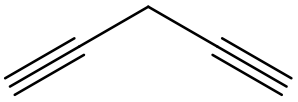
Identify the products and balance the equations for the following reactions:

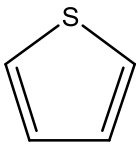
i) $2\ NaBH_4 + I_2 \longrightarrow$

ii) $Et_3Bi + SO_2Cl_2 \longrightarrow$

iii) 

$+\ 2\ CH_2O \xrightarrow{\text{aqueous work up}}$

iv)  $+\ Et_2GeH_2 \longrightarrow$

v) 

$+$ *n*-BuLi $\longrightarrow$

(10 marks)

c) Outline a method by which a siloxane (silicone) material suitable for making rubber tubing in medical applications can be made from simple chlorosilanes. Sketch a structure of such a siloxane and give a useful property that such a polymer might have for this application.

(5 marks)

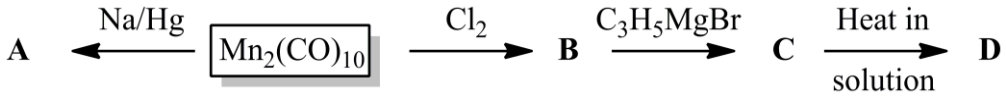
d) Order R_3E compounds (E = N, P, Bi) for their ability to act as σ-donor ligands in transition metal complexes. Give reasons for your answer. Which is the better σ-donor ligand, NH_3 or NEt_3? Give a reason for your answer.

(5 marks)

2.I3 – Transition Metal, Coordination and Organometallic Chemistry

Answer **BOTH** part a) **AND** part b) and **EITHER** part c) **OR** part d) of this question.

a) For the scheme below identify compounds **A** – **D** inclusive by drawing their structures and writing a balanced equation for each transformation (C_3H_5 = allyl).



A – An air-sensitive solid which behaves as a 1:1 electrolyte in solution.
B – A white solid with an IR spectrum displaying three bands in the range 1900 – 2100 cm^{-1}.
C – A white solid with M = 236 g/mol and an IR spectrum similar to B.
D – A white solid with a ^1H NMR spectrum in $CDCl_3$ solution that displays a doublet (integration 4) and a quintet (integration 1). The mass spectrum shows a molecular ion at m/z = 208 with further peaks at m/z = 180, 152.

(8 marks)

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

i) Using a simple crystal field approach, derive the d-orbital splitting diagram for the linear complex $[Au(PPh_3)Cl]$.

(4 marks)

ii) The reaction of $[Au(PPh_3)Cl]$ with Cl_2 results in a new complex with formula $[Au(PPh_3)Cl_3]$. Using a simple crystal field approach, give the d-orbital splitting diagram for the complex $[Au(PPh_3)Cl_3]$. Predict the spin-only magnetic moment μ_{so}.

(3 marks)

iii) The reaction of $[Au(PPh_3)Cl_3]$ with pyridine results in a substitution reaction. Draw the reaction product and explain its formation.

(4 marks)

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

i) Determine the oxidation state, d-configuration and the geometry in the following two complexes: $[Ni(CO)_4]$ and $[Co(PPh_3)_2Br_2]$.

ii) The rate law for the reaction of $[Ni(CO)_4]$ with PEt_3 shows a zero order dependence on the concentration of PEt_3, the rate law for the reaction of $[Co(PPh_3)_2Br_2]$ with PEt_3 shows a first order dependence. Explain these observations.

(6 marks)

d) Arrange the following compounds in order of decreasing C-O stretching frequency, ν(CO), and give reasons for your answer.

CO (g) $[Mn(CO)_6]^+$ $[Fe(CO)_4]^{2-}$ $[V(CO)_6]^-$ $[Cr(CO)_6]$ $H_3B(CO)$

(6 marks)

2.I4 – Crystal and Molecular Architecture

Answer part a) and **EITHER** part b) **OR** part c) of this question.

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

i) Draw a body-centred cubic structure (BCC) consisting of only one atom type as a sketch **and** in plan view.

(4 marks)

ii) Does CsCl adopt the BCC structure? Give an example of a metal which adopts a BCC structure. What is the coordination number of the atoms in this structure?

(3 marks)

iii) Show *by calculation* that the percentage of the total volume occupied by spheres in a BCC structure of one atom type is approximately 68%.

(4 marks)

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

(1 mark)

v) If *a* is the length of the side of the unit cell, what is the *shortest* distance between the atomic centres in the BCC structure?

(3 marks)

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

i) Draw a fully labelled plan view of the Cubic Close Packed structure (CCP) of nickel metal.

(2 marks)

ii) Using plan diagrams, show the position of the octahedral and tetrahedral holes in the CCP structure.

(2 marks)

iii) Nickel (58.7 amu) has a density of 8.91 g cm^{-3}. How many nickel atoms are there in the unit cell? Calculate the lattice parameter, *a*, for nickel.

(3 marks)

iv) Both NaCl and AgCl are based on the CCP structure. Using these compounds as examples, describe Schottky and Frenkel defects.

(3 marks)

QUESTION CONTINUED OVERLEAF

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

i) What is a ‘solid solution’? Describe the two types of solid solution.

(3 marks)

ii) Ruby is an example of a solid solution. Give the equation which represents the formation of ruby.

(2 marks)

iii) Explain the origin of the colour of ruby.

(2 marks)

iv) Briefly explain why metals such as Zn, Mg and Ti are less ductile than those such as Cu, Ag and Au?

(3 marks)