**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 I**

**Tuesday 15th June 2010, 09:30-11:30**

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

**Year 1/0610 Turn Over**

**1I.1 – Molecular Structure**

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

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

i) The photoelectron spectrum of carbon monoxide (CO) is shown below.



(Figure taken from: J. Keeler and P. Wothers, “Chemical Structure and Reactivity” OUP, Oxford, 2008)

With the aid of the above spectrum, sketch and label the molecular orbital energy level diagram for CO. On your diagram, include drawings of the MOs and electron occupancies. Indicate if significant MO mixing is expected, highlighting which molecular orbitals are likely to be involved in mixing.

(10 marks)

ii) Use your diagram to briefly explain why CO is a good π-acceptor in organometallic chemistry. Why is the C-O bond weakened when this molecule is coordinated to a metal?

(3 marks)

b) Using VSEPR theory, state the pseudostructures and structures of the following compounds. Include drawings of both structures in your answer and highlight any deviations from ideal structures.

XeF2 SF4

(6marks)

QUESTION CONTINUED OVERLEAF

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

1. Which of the following three molecules possess a centre of symmetry?

HCN C2H2 BF3

Illustrate your answer by showing the centre of symmetry on a drawing of the molecule(s) that possess one.

(2 marks)

1. Al2Cl6 has the structure shown below (each Al atom is tetrahedral). Mark all the rotational axes of symmetry and determine the point group.

(2 marks)



1. With the aid of appropriate diagrams, show that BF3 possesses an *S3* axis but NF3 does not.

(2 marks)

d) Draw the structure of *trans*-N2F2. Use an appropriate hybridisation scheme to account for the geometry around the nitrogen atoms and use valence bond theory to describe the bonding in this molecule.

(6 marks)

**1.I2 – Periodicity and Inorganic Reactivity**

Answer **BOTH** parts (a) **AND** (b).

1. Answer **ALL** parts of this question.

i) Account for the variation in bond strengths of the Group 17 diatomic molecules (shown below in kJ mol-1)

F2 Cl2 Br2 I2

158 242 192 151

(5 marks)

ii) What is the oxidation state and hybridisation of the Cl centres in ClF3 and ClF5? Give two reasons why ClF7 cannot be prepared, whereas IF7 is a known compound.

(6 marks)

1. Answer any **TWO** of the three parts i), ii) and iii).

i) Structures of Ga2H6 and Ga2Cl6 are shown below. Describe the bonding in each of these compounds and account for any differences.



(7 marks)

ii) Sulfur trioxide, SO3, is a very reactive compound easily reduced to SO2. However, on dissolving SO3 in KOH solution it forms K2SO4, in which the SO42- ion is quite inert. Why does the reactivity change although the oxidation state of the sulfur is unchanged?

(7 marks)

iii) Draw Lewis structures (including all resonance forms where appropriate) for N2O, NO2, and NO2+. On the basis of your answers, explain which of these oxides of nitrogen would be expected to form dimers at low temperatures.

(7 marks)

**1.I3 – Coordination Chemistry**

Answer **BOTH** parts (a) **AND** (b).

a) Discuss any **TWO** of the following three parts i), ii) or iii).

i) Dinitrogen (N2) is *isoelectronic* with CO. With this in mind, show how N2 can bind to a d-block metal. Draw **both** geometrical isomers of the square-planar complex [RhCl(PPh3)2(N2)], and label them clearly.

(5 marks)

ii) Solid-state structures of two tungsten complexes of the chemical formulae [WBr3(C5Me5)(CO)2] and [W2Br4(CO)8] are shown below (Figure 1). Provide the formal IUPAC chemical names of these compounds. Explain the terms: “” and “” in their nomenclature (C5Me5 = pentamethylcyclopentadienyl).



**Figure 1.**

[from: H. Blackburn, H-B Kraatz, R. Poli and R. C. Torralba, *Polyhedron*, **1995**, *14*, 2225; and F. A. Cotton, L. R. Falvello, and J. H. Meadows, *Inorg. Chem*., **1985**, *24*, 514.]

(5 marks)

QUESTION CONTINUED OVERLEAF

iii) Crystal field splitting parameters (o) for [Mn(CN)6]4- and [Fe(CN)6]3- are 30,000 and 35,000 cm-1, respectively. The Mn complex is high-spin, whereas the Fe complex is low-spin. Use the Crystal Field theory to explain these differences in o and spin state.

(5 marks)

b) Answer **ALL** parts of this question, with reference to the following:

Ethylenediamine tetraacetic acid (H4-EDTA) and glycine (gly) form stable complexes with M3+ ions of d-block elements (equations 1 and 2, respectively). Some formation constants are given in Table 1.



**Table 1.** Selected formation constants.

|  |  |
| --- | --- |
| Complex | log ** |
| [Fe(EDTA)]- | 25.7 |
| [Fe(gly)3] | 10.0 |
| [Co(EDTA)]- | 41.3 |

i) Draw the structures of **BOTH** EDTA and glycine complexes of Fe, showing clearly how the ligand coordinates.

(2 marks)

ii) Identify any isomers that may exist in the complexes you have drawn in part i).

(2 marks)

QUESTION CONTINUED OVERLEAF

iii) Compare EDTA and glycine as ligands in these complexes. Explain the term ‘denticity’ in your answer.

(3 marks)

iv) Write an equation showing an equilibrium process, from which 2 for [M(gly)2]+ is derived.

(2 marks)

v) Using log  values provided in Table 1, compare relative stabilities of the three metal complexes. Explain these observations.

(6 marks)