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 I

Thursday 23rd June 2011, 09:30-11:30

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.

1.I1 – Molecular Structure

Answer parts a) **AND** b) and **EITHER** part c) or d) of this question.

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

i) What are the ions present in the compound $[NH_4][PCl_3F_3]$?

(1 mark)

ii) Using VSEPR theory, predict the pseudo-structure and structure of each ion (include a drawing of both structures in your answer).

(4 marks)

iii) Does either of the two ions possess stereoisomers? If so, draw the structures of these isomers.

(1 mark)

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

i) Sketch and label the molecular orbital (MO) energy level diagram for NO. 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.

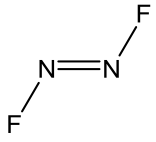
(10 marks)

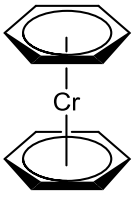
ii) Using your diagram rationalise the following data: the dissociation energy for NO is 627 kJ mol^{-1} whilst that of NO^+ is 1048 kJ mol^{-1}.

(3 marks)

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

i) Indicate the principal axis of symmetry and determine the point group for each of the following molecules:

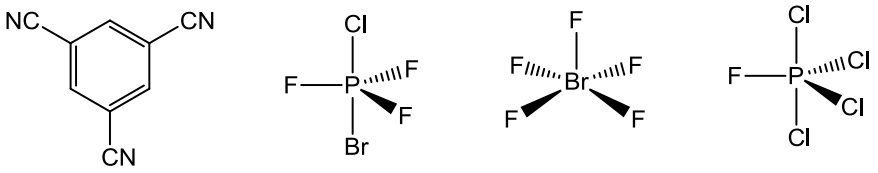




(4 marks)

QUESTION CONTINUED OVERLEAF

ii) For the following molecules, indicate if they possess a horizontal plane of symmetry (σ_h):



(2 marks)

d) Answer **ALL** parts of this question:

i) Using the VSEPR theory, predict whether HCN is linear or bent.

(2 marks)

ii) What is the hybridization of the C atom?

(1 mark)

iii) Applying Valence Bond theory, show a bonding scheme using the hybridization you have suggested (including sketches of the orbitals involved).

(3 marks)

1.I2 – Periodicity and Inorganic Reactivity

Answer **BOTH** parts a) **AND** b) of this question.

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

i) $BeCl_2$ is monomeric and linear in the vapour state. In the solid state, it forms polymeric infinite chains containing tetrahedral Beryllium atoms. Draw the structure of $BeCl_2$ in each of these states, indicating the hybridisation of the Be centres and the type of bonding present. Suggest a reason why $BeCl_2$ likes to form polymers in the solid state.

(8 marks)

ii) $BeCl_2$ dissolves in diethyl ether (Et_2O) to give a monomeric complex. Suggest a structure for this compound.

(3 marks)

b) Answer any **TWO** of the following three parts.

i) Account for the difference in boiling points of NF_3 (-129 ºC) and NH_3 (-33 ºC). Would you expect either of these molecules to act as a Lewis base? Give your reasoning.

(7 marks)

ii) Discuss the structure of white phosphorus (P_4) with particular reference to the origin of its high reactivity. What is the structure of the product from the reaction of white phosphorus with excess O_2?

(7 marks)

iii) Give reasons why the B-F bond dissociation energy in BF_3 is much larger than the C-F bond dissociation energy in CF_4.

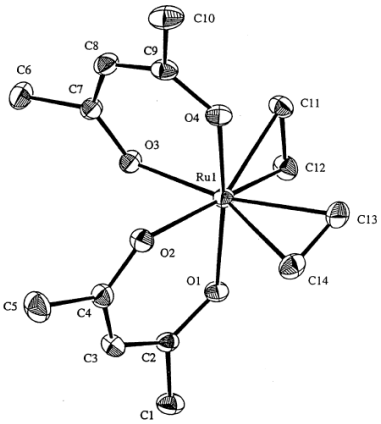
(7 marks)

1.I3 – Coordination Chemistry

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

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

$[Ru(acac)_2(\eta^2\text{-}C_2H_4)_2]$ (**1**) reacts with pyridine to form $[Ru(acac)_2(\eta^2\text{-}C_2H_4)(py)]$ (**2**). The molecular structures of **1** and **2** are shown below (acac = acetoacetonate; py = pyridine).[1]



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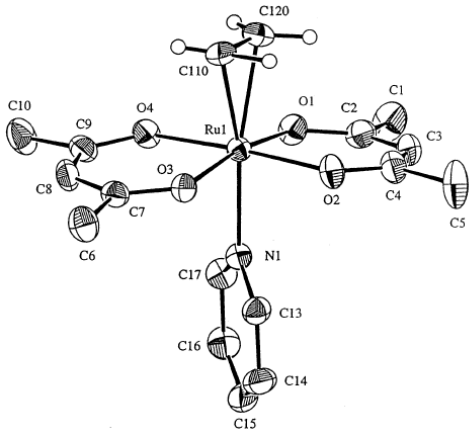


2

i) Provide the formal IUPAC chemical names of compounds **1** and **2**.

(4 marks)

ii) Draw any geometrical and optical isomers of compounds **1** and **2**.

(4 marks)

iii) Show the η^2-bonding of ethene to a d-block metal, as described by the Dewar-Chatt-Duncanson model.

(4 marks)

QUESTION CONTINUED OVERLEAF

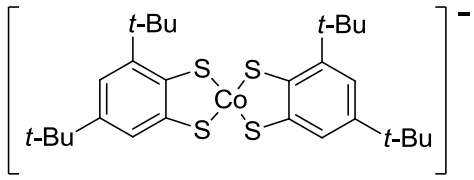
[1] M. A. Bennett, M. J. Byrnes and A. C. Willis, *Organometallics*, 2003, **22**, 1018.

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

i) The complex of formula $CoBr(NH_3)_5(SO_4)$ exists as two isomers **X** and **Y**. When aqueous barium chloride is added to **X** a white precipitate is formed, but no precipitate forms when the test is repeated with **Y**. Conversely, the reaction between **Y** and silver nitrate solution gives a cream precipitate, whilst no such precipitate forms with **X**. Identify **X** and **Y**, the type of isomerism exhibited, the number of d electrons in the metal's valence shell and explain the observations.

(7 marks)

ii) The monoanionic cobalt complex **3** has a square-planar (D_{4h}) structure and possesses an μ_{eff} of 2.83 B.M at 298 K.[2] Use the crystal field theory to explain the observed paramagnetism of this compound.



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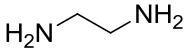
(6 marks)

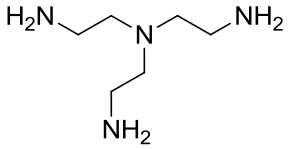
QUESTION CONTINUED OVERLEAF

[2] K. Ray, A. Begum, T. Weyhermuller, S. Piligkos, J. van Slageren, F. Neese and K. Wieghardt, *J. Am. Chem. Soc*., 2005, **127**, 4403.

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

The logarithm of the overall equilibrium constant for the reaction of $[Zn(H_2O)_6]^{2+}$ with 2 moles of ethylenediamine (en) is 10.8. The logarithm of the overall equilibrium constant for the reaction of $[Zn(H_2O)_6]^{2+}$ with 1 mole of 2, 2', 2"-triaminoethylamine (tren), $N(CH_2CH_2NH_2)_3$, is 14.6.

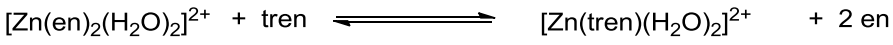
en = 

tren = 

i) Write the overall (balanced) equations for the reaction with the en ligand. Use these to illustrate stepwise and overall formation constants, and show how they are related to each other.

(4 marks)

ii) From the data given above, determine the equilibrium constant for the following reaction.



(5 marks)

iii) Calculate the standard Gibbs' free energy (at 298K) of the reaction in ii). Is this reaction thermodynamically favourable? Rationalise your answer.

(4 marks)