IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 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

ADVANCED CHEMISTRY THEORY IIA

Inorganic Chemistry

Thursday 13th January 2011, 14:00-15:30

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

2I1 – Molecular Orbitals in Inorganic Chemistry

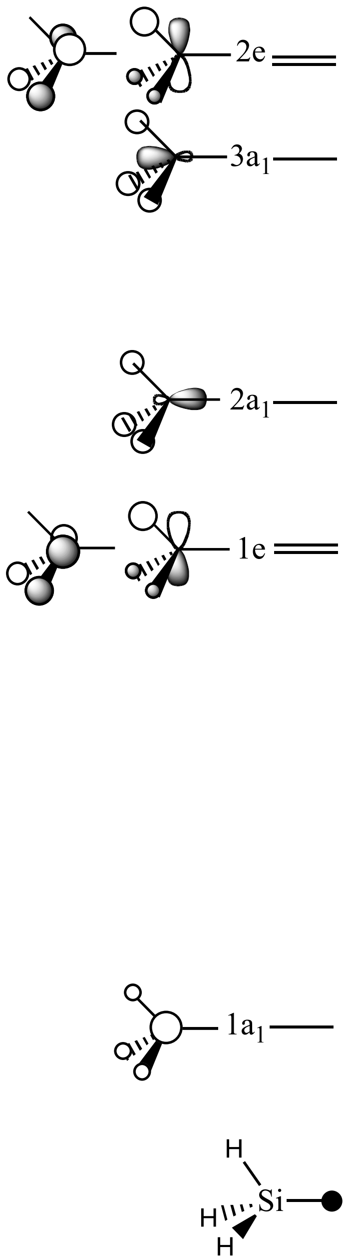
Answer part a) and **EITHER** part b) **OR** part c) of this question.

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

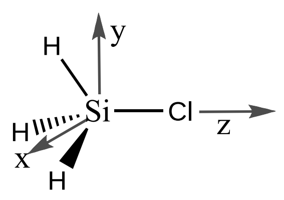
i) Construct and **annotate** a valence MO diagram for SiH_3Cl (C_{3v} point group). Use the axial system defined in **A**, and the fragment orbitals for SiH_3 shown in **B** below. Place the Cl pAOs at approximately the same energy as the $2a_1$ FO of the SiH_3 fragment, and assume the MOs of SiH_3Cl do not undergo mixing. (12 marks)

ii) With reference to your MO diagram give a reason why SiH_3Cl is a chemically reactive molecule. (3 marks)

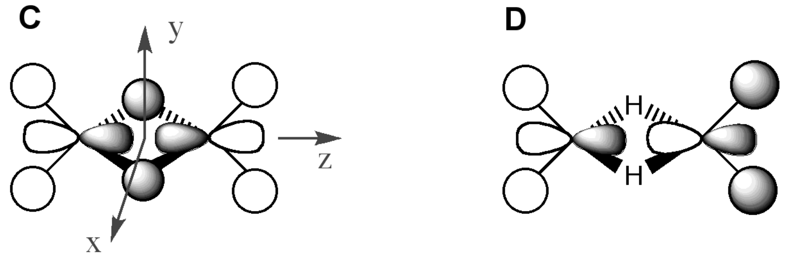
B



A



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



i) Annotate a diagram of MO **C**, identify and explain the features that are important in evaluating the overall bonding or antibonding character of this MO.

(6 marks)

ii) Determine the point group for B_2H_6 and hence the symmetry labels for MOs **C and D**. Explain any appropriate short cuts you use and show your working.

(4 marks)

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

The axial alignment of a transition metal (M) complex MX_2L_4 (where X and L are σ-bonding ligands, is shown in **E** below. The point group of MX_2L_4 is D_{4h}, and the ligand fragment orbitals are given in **F**.

i) Identify the symmetry labels of the metal orbitals, and the ligand fragment orbitals **F(1)-F(6)**

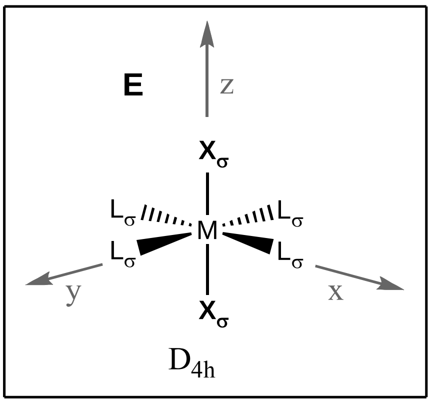
(3 marks)

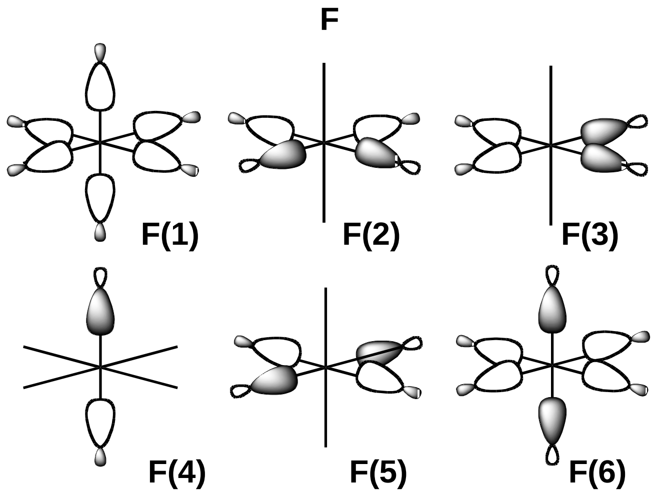
ii) Draw an **energy level** diagram for MX_2L_4 (pictures of orbitals are not required).

(6 marks)

iii) Identify Δ_{oct} on your diagram.

(1 mark)

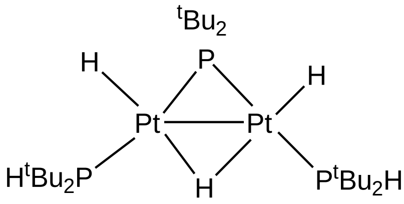




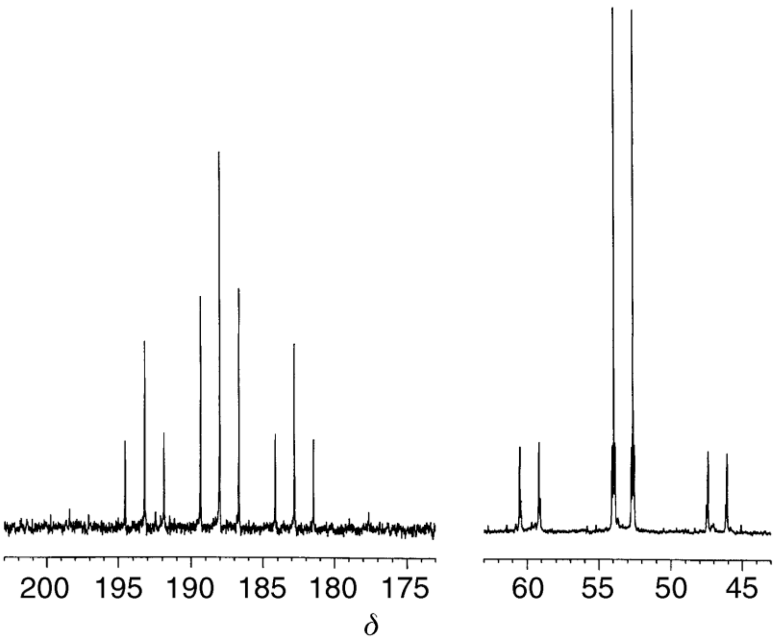
2.IS.2 – NMR and EPR Spectroscopy

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

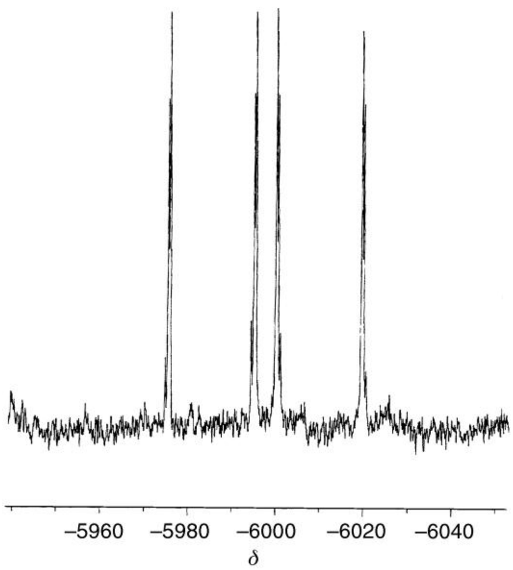
a) A dinuclear platinum complex, **1**, has two proton decoupled NMR spectra (scales are in ppm) shown below:



1



Both regions of the 202 MHz $^{31}P\{^1H\}$ NMR spectrum of **1**



107 MHz $^{195}Pt\{^1H\}$ NMR spectrum of **1**

Reproduce the spectra, label any coupling present using the $^nJ_{X\text{-}Y}$ notation, and estimate values for the coupling constants. Comment on the relative intensities of signals within each multiplet. Assume that only one-bond couplings are seen in the ^{195}Pt spectrum but that up to two-bond couplings may be seen in the ^{31}P spectrum.

(^1H and ^{31}P are both 100% abundant I = ½; ^{195}Pt is 33% abundant I = ½; assume that there are no other spin active nuclei present.)

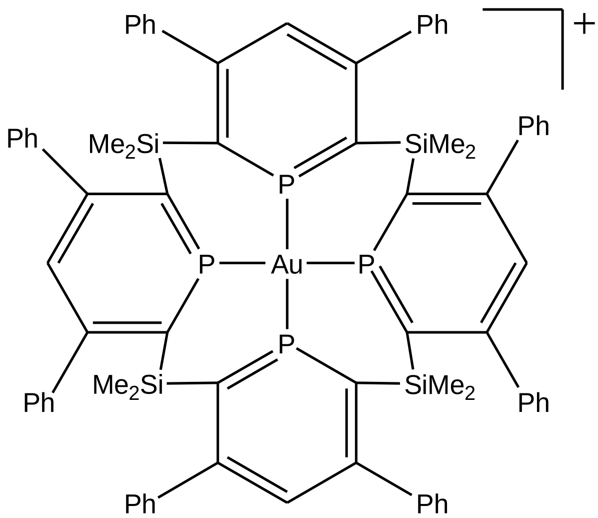
(13 marks)

QUESTION CONTINUED OVERLEAF

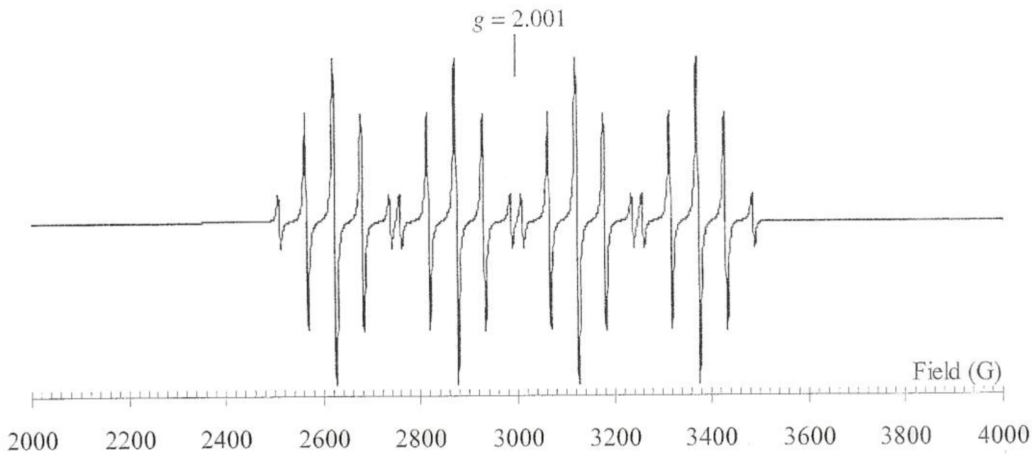
b) A single electron reduction of the Au(I) cation, **2**, gives rise to a paramagnetic species with the EPR spectrum shown below. Explain the structure of the spectrum, assign the couplings and make an estimete of their values. Comment on the evidence supporting either a ligand- or metal-based reduction.

(Assume that both ^{1}H and ^{31}P are 100% abundant I = ½; ^{197}Au is 100% abundant I = 3/2, and that there are no other spin-active nuclei present.)

(7 marks)



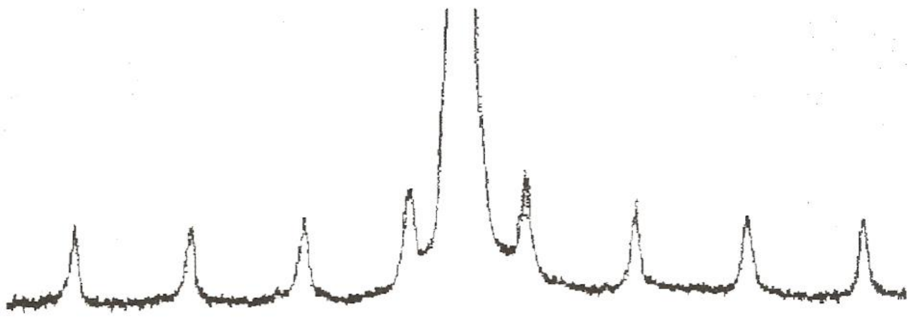
2



QUESTION CONTINUED OVERLEAF

c) The ^{1}H NMR spectrum of a compound MH_4 is shown below (the large central peak has been truncated). M has two isotopes, of 80 and 20% abundance. Sketch the spectrum and assign the peaks, indicating any coupling present. Determine the nuclear spin, I, of both isotopes present and calculate the relative intensity of the smaller peaks in the spectrum.

(5 marks)



d) Give two useful properties for a NMR standard for a spin ½ nucleus. What extra property is needed for a quadrupolar nucleus and why is this required? Why is the tetrahedral anion $[CoCl_4]^{2-}$ unsuitable as a standard for ^{59}Co NMR spectroscopy?

(5 marks)