**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JANUARY 2013, 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

**Wednesday 09th January 2013, 09:30-11:00**

**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.**

## 2I.1 – Molecular Orbitals in Inorganic Chemistry

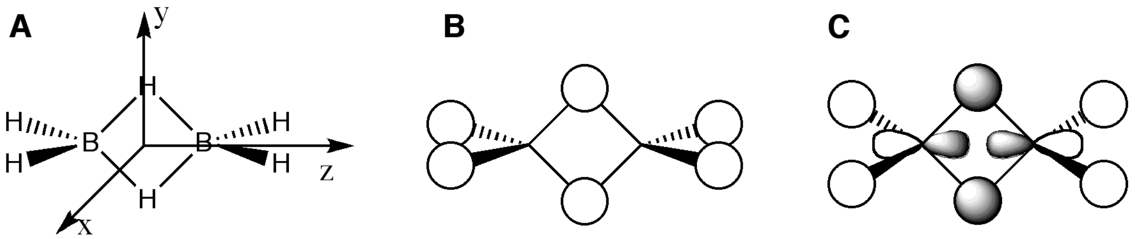
Answer part a) and **EITHER** part b) **OR** part c) of this question.

a) Construct and **annotate** a valence MO diagram for linear $[CuL_2]^-$ ($D_{\infty h}$ point group), where L is a 1e donor sigma bonding ligand such as Me. Assume that the MOs do not undergo mixing.

(14 marks)

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

Diborane shown in **A** below belongs to the $D_{2h}$ point group.




i) Determine the reducible representation $\Gamma_{6Hs}$ for the 6 H1s AO basis functions shown in **B.**

(2 marks)

ii) Determine if the $b_{1u}$ irreducible representation is a component of the reducible representation $\Gamma_{6Hs}$. **Show your working**.

(4 marks)

iii) Identify the symmetry of the MO shown in **C** and briefly explain your reasoning.

(1 mark)

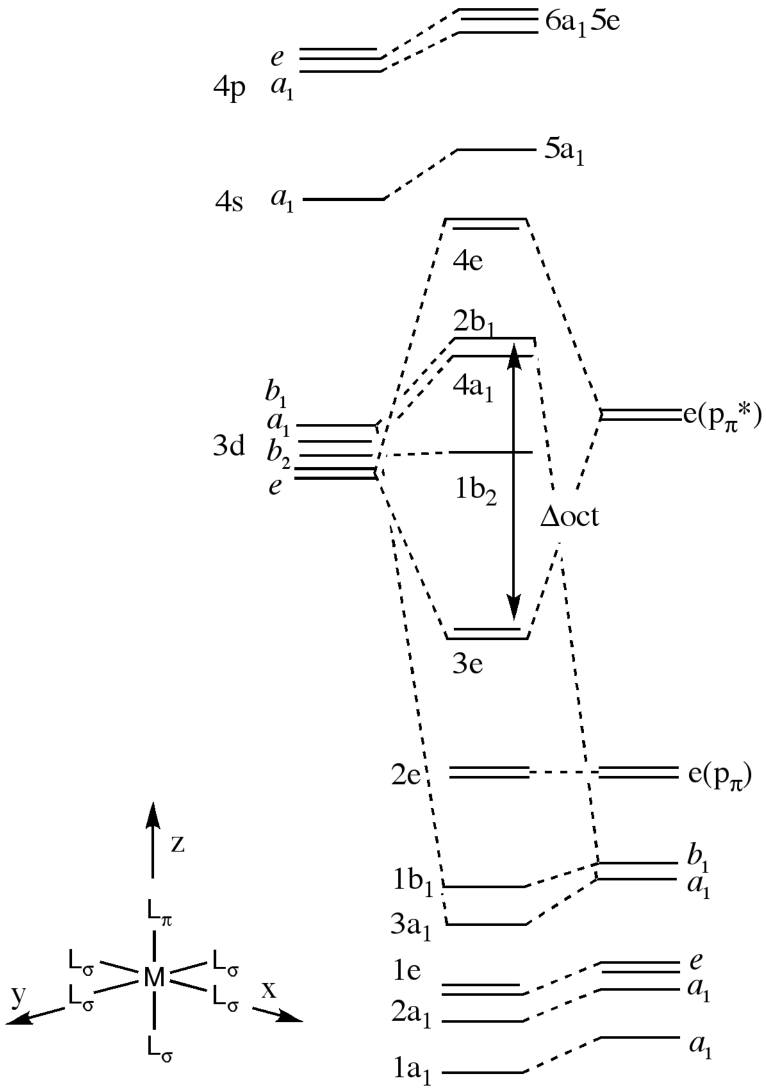
iv) Sketch the MO shown in **C**, identify and annotate features that are important for evaluating the bonding character.

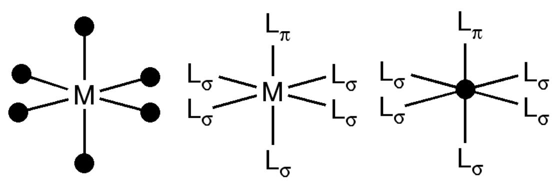
(4 marks)

QUESTION CONTINUED OVERLEAF

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

A partial energy level diagram for a TM complex of the type $[M(L_\sigma)_5(L_\pi)]$ where $L_\sigma$ is a $\sigma$-donor ligand and $L_\pi$ is a $\pi$-acceptor ligand is shown below.



i) Draw the MOs with symmetry labels $4a_1$ and 4e.

(3 marks)

ii) Which MOs are most likely to undergo mixing and why? What metal d electron configuration would be needed for mixing to occur?

(4 marks)

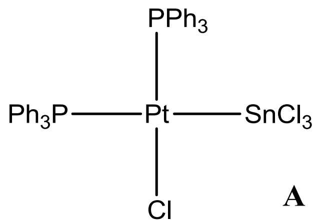
iii) Use MO theory to explain possible ways of increasing $\Delta_{oct}$ for this type of complex.

(4 marks)

## 2IS.1 – NMR and EPR Spectroscopy

Answer part a) **AND TWO** parts from b), c) **OR** d) of this question.

a) Using the data given below for NMR active nuclei, sketch and label the proton-decoupled $^{31}P$ NMR spectrum of the square planar platinum complex, **A**, below. Label the couplings present using the $^{n}J_{X\text{-}Y}$ notation and comment on the relative magnitudes of the various couplings.




**A**

Assume that:
$^{31}P$ is 100% abundant, I = 1/2;
$^{117}Sn$ and $^{119}$ Sn are both 8% abundant, I = 1/2,
$\gamma$ for $^{117}Sn$ is -9.5 for $^{119}Sn$ is -10.0 ($10^{7}$ rad $T^{-1}$ $s^{-1}$) $^{195}Pt$ is 33% abundant, I = 1/2
No other nuclei present show significant NMR activity

(15 marks)

b) At high temperature the $^{19}F$ NMR spectrum of the octahedral anion $NbF_6^-$ is a well-resolved multiplet, sketch the multiplet and label any couplings present using the $^{n}J_{X\text{-}Y}$ notation. What effect on the spectrum would be observed on lowering the temperature? Why does the change occur?

Assume that:
$^{19}F$ is 100% abundant I = 1/2
$^{93}Nb$ is 100% abundant I = 9/2

(5 marks)

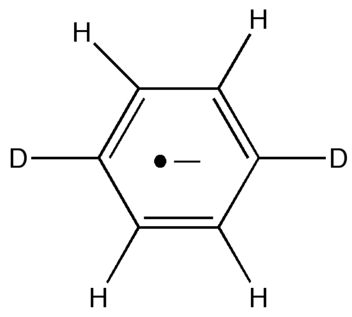
c) Sketch the $^{13}C$ NMR spectrum of deuterated acetone, $(CD_3)_2C=O$, and label any coupling present using the $^{n}J_{X\text{-}Y}$ notation. Assume that only $^{1}J$ coupling is observed.

Assume that:
$^{13}C$ is 1% abundant I = 1/2 and $^{2}D$ is 100% abundant I = 1
No other nuclei present show significant NMR activity

(5 marks)

QUESTION CONTINUED OVERLEAF

d) Sketch the EPR spectrum of the 1,4-dideuteriobenzene radical anion, **B**. Label the couplings present on the sketch and comment on the relative magnitude of the couplings.



**B**

Assume that:
$^{1}H$ is 100% abundant I = 1/2 and $^{2}D$ is 100% abundant I = 1;
$\gamma$ for $^{1}H$ is 26.7, for $^{2}D$ it is 4.1 ($10^{7}$ rad $T^{-1}$ $s^{-1}$)
No other nuclei present show significant EPR activity

(5 marks)