IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2016, 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 II

Inorganic Chemistry

**Tuesday 14th June 2016, 14:00-16:30**

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.

2.I1 – Molecular Orbitals & Inorganic Chemistry

Answer any **TWO** of parts a), b), **OR** c) of this question.

a) Answer **ALL** parts of this question. Consider the partial MO diagram below. Do **NOT** redraw the whole MO diagram.
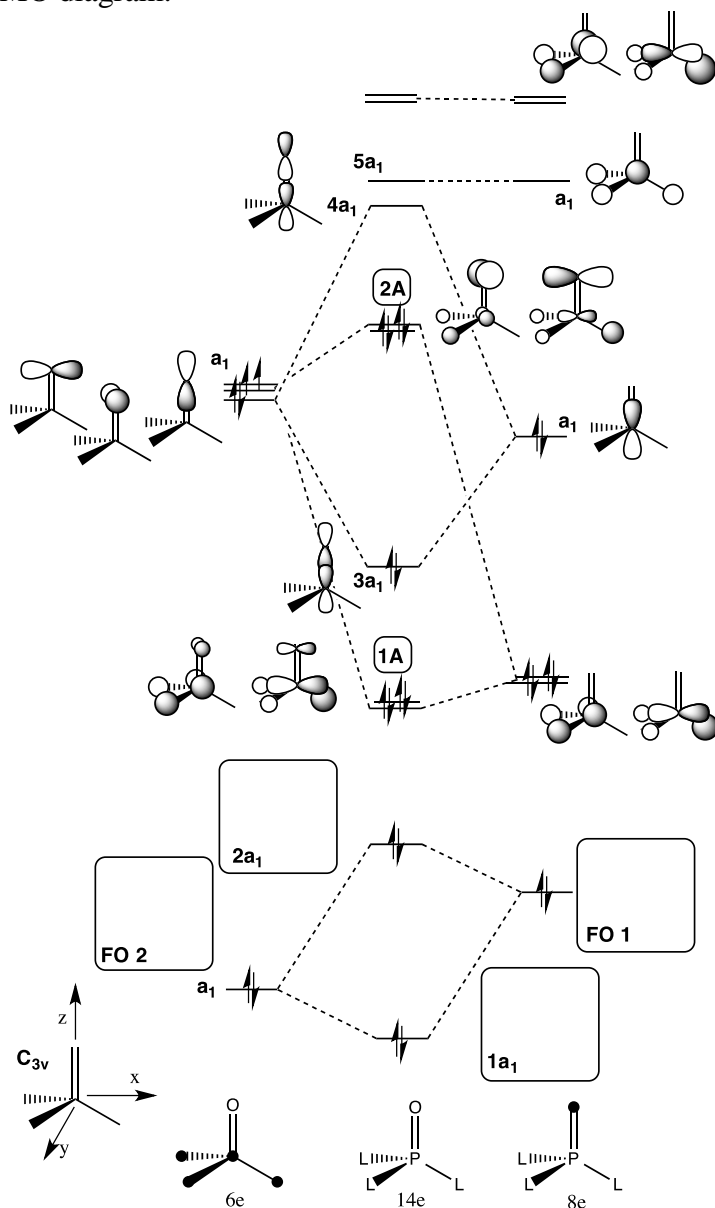
i) **Draw** the missing fragment orbitals **FO1** and **FO2** and the missing **1a₁** and **2a₁** MOs. **Identify** the missing symmetry labels **1A** and **2A**.

(4.5 marks)
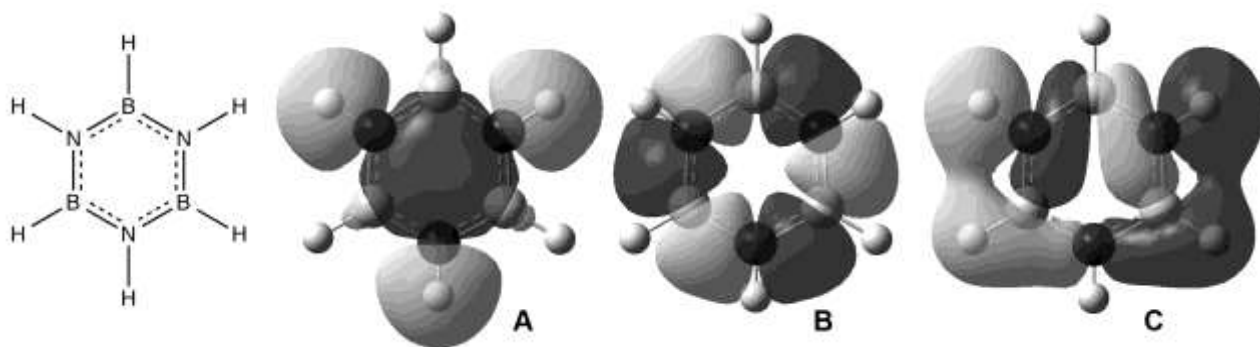
ii) **Provide two** annotations relevant to this diagram

(2 marks)

iii) **Describe two** conditions for *strong* mixing. **Identify** the MOs that can mix, **draw a diagram** showing the process of MO mixing and **identify** the lower energy mixed MO.
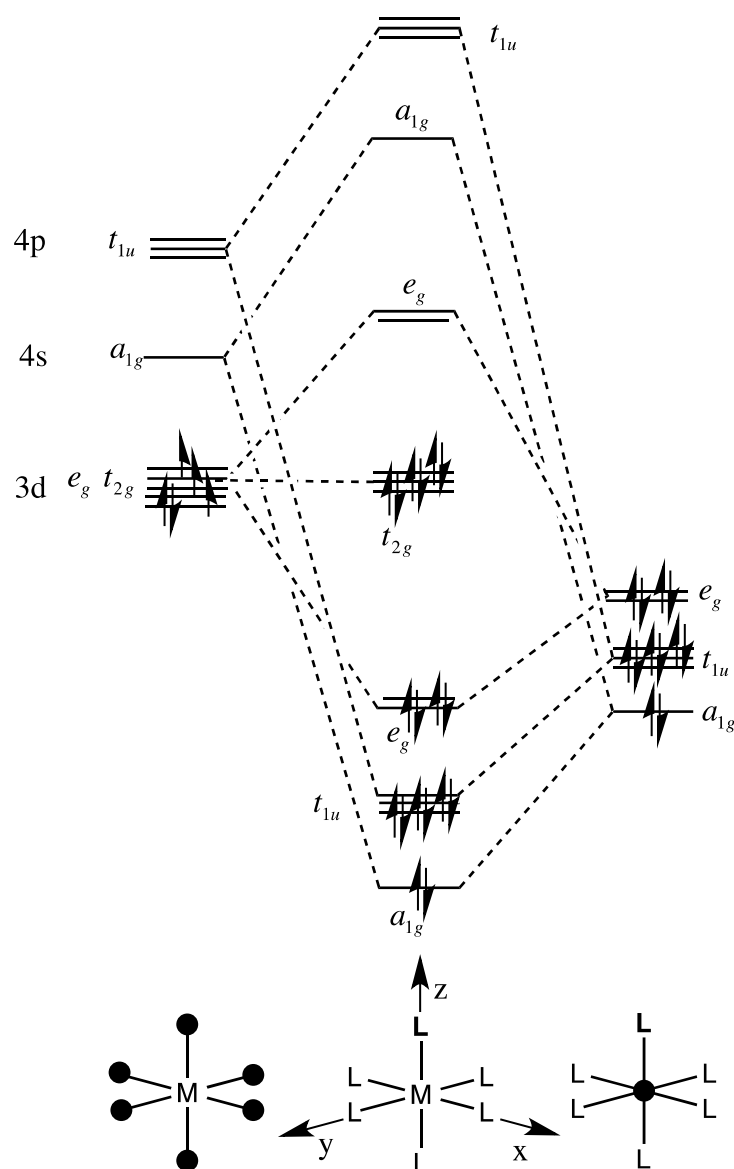
(6 marks)

b) Answer **ALL** parts of this question. Consider the computed MOs below.

i) **Draw** a linear combination of atomic orbitals (LCAO) diagram for each MO.

(6 marks)

ii) Use your diagram(s) to **identify** and **explain** key features that are important in evaluating the overall bonding or anti-bonding character of an MO.

(4 marks)

iii) **Briefly describe** how MOs like these relate to the concept of 2-centre-2-electron bonds.

(2.5 marks)

c) Answer **ALL** parts of this question. Consider the energy diagram for an octahedral complex, containing only σ-donor ligands, below.


i) **Draw energy** diagrams showing the effect of replacing one ligand with (a) a π-donor ligand and (b) a π-acceptor ligand.

(6 marks)

ii) **Discuss** your diagrams in relation to the spectrochemical series and Δ_{oct}. **Suggest two** π-donor and **two** π-acceptor ligands that could give rise to the effects in part i).

(6.5 marks)

2.I2 – Main Group Chemistry

Answer part a) and any **TWO** of parts b), c) and d) of this question.

a) Identify compounds **A** – **H** and **J** in the scheme below, giving full structures of **A** and **C**. All reactions are balanced.


A: ^{1}H NMR: 7.0-7.5 (m, 5H), 6.04 (s, 2H), 2.0 (s, 6H) ppm
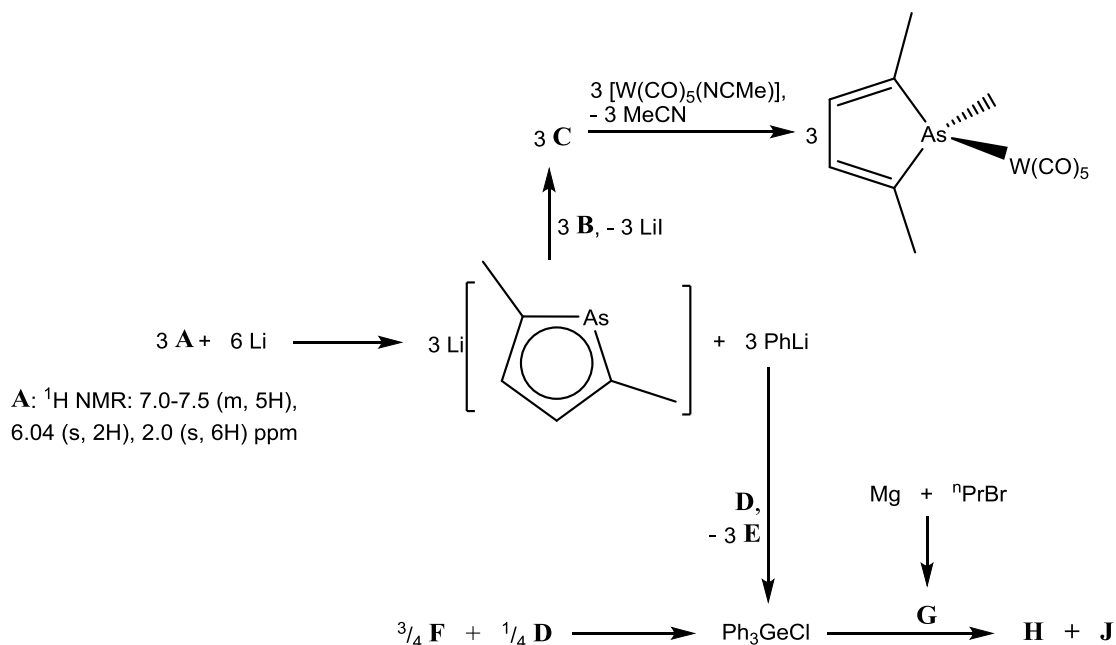
(13 marks)

b) Cryoscopic analysis was carried out on equimolar solutions of ^{n}Pr$_3$Al in both triethylamine and pentane. A higher concentration of solute particles was observed for the triethylamine solution in comparison with pentane. Explain this observation.

(6 marks)

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

   i) Use Wade's rules to account for the structure of the fluorocarborane $[CB_9HF_9]^-$ shown below. What is the structural type?
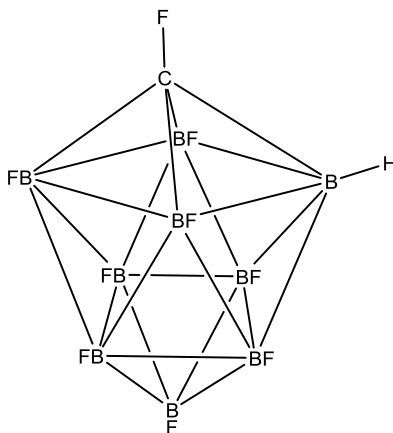
(5 marks)

   ii) An isomer of $[CB_9HF_9]^-$ with the same arrangement of skeletal atoms shows a signal in its IR spectrum at 3290 cm^{-1}. Describe how this isomer differs from the structure shown above, and assign the IR signal.

(1 mark)

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

   i) Draw the full structure of the repeating unit of linear polyphosphazene $\{R_2PN\}_n$ [R = $(Me_3Si)_2CH$].

(1 mark)

   ii) Heating to high temperatures can result in depolymerisation of linear polyphosphazenes to form small cyclic species. Explain why depolymerisation would be expected to occur much more readily when R = $(Me_3Si)_2CH$ than for R = Me.

(3 marks)

   iii) What experimental evidence might indicate the presence of delocalised P-N multiple bonding in a generic cyclic trimer $\{R_2PN\}_3$?

(2 marks)

2.I3 – Transition Metal Coordination and Organometallic Chemistry

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

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

    i) Using suitable diagrams, describe the η^1 and η^2 interactions of dinitrogen with a transition metal centre.

        (4 marks)

    ii) Explain, using suitable diagrams, the difference in the IR stretching frequencies of the nitrosyl complexes below:

        • $trans$-$[Co(en)_2(NO)Cl]^+$ $\nu(N\text{-}O) = 1615 \text{ cm}^{-1}$

        • $[Fe(CN)_5(NO)]^{2-}$ $\nu(N\text{-}O) = 1935 \text{ cm}^{-1}$

    en = ethylenediamine

        (4 marks)

b) Answer **ALL** parts of this question.
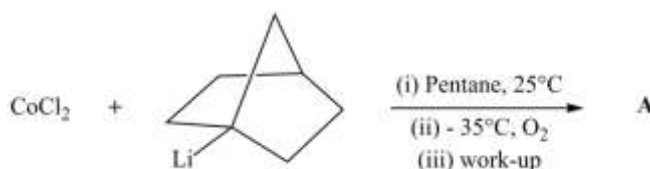
Reaction of $CoCl_2$ with 1-norbornyllithium ($C_7H_{11}Li$), followed by controlled oxidation, yields compound **A** as a brown microcrystalline solid, after removal of Li salts. Monometallic **A** is highly soluble in hydrocarbon solvents and its elemental analysis provides 13.42 % Co, 76.50 % C and 10.08 % H composition. **A** is paramagnetic, and magnetic susceptibility measurements give an effective magnetic moment of 1.89 μ_B. Conversely, and even at low temperatures, reaction of $CoCl_2$ with excess ^{t}BuLi [$(CH_3)_3C$–Li] produces Co metal, $H_{2(g)}$ and isobutylene [$(CH_3)_2C=CH_2$]; no organometallic compound could be isolated.

    i) Calculate a molecular formula for **A**, and hence give the oxidation state and number of d-electrons for the Co centre.

        (2 marks)

    ii) Predict the geometry of compound **A**. Explain your reasoning.

        (2 marks)

    iii) Calculate the number of unpaired electrons in this complex. Comment on anything unusual about your answer, and provide an explanation for this result.

        (3 marks)

    iv) Explain the contrasting results obtained when ^{t}BuLi is used instead of 1-norbornyllithium.

        (2 marks)

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

i) Draw the molecular structure of $Cr_2(O_2CCH_3)_4(H_2O)_2$ and state the formal oxidation state and d-electron count of Cr.

(2 marks)

ii) With the aid of an approximate molecular orbital energy diagram, state the Cr_2 bond order and explain why $Cr_2(O_2CCH_3)_4(H_2O)_2$ has a $\mu_{eff} = 0$ $\mu_B.$

(4 marks)

iii) Account for the fact that $K_4Cr(CN)_6$ has a $\mu_{eff} = 3.2$ $\mu_B.$

(2 marks)

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

i) Explain why two carbonyl stretching bands are observed in the infrared spectrum of *fac-*$MoL_3(CO)_3$, and comment on the trend in the frequencies below.

L in $MoL_3(CO)_3$	$\nu(CO)$, cm^{-1}
PF_3	2055, 2090
PCl_3	1991, 2040
PPh_3	1835, 1934

(6 marks)

ii) A pure sample of the $P(OCH_3)_3$ compound, $Mo[P(OCH_3)_3]_3(CO)_3$, shows *three* bands in its infrared spectrum at $\nu(CO) = 1993$, 1919, and 1890 cm^{-1}. Explain this observation.

(2 marks)

2.I4 – Crystal and Molecular Architecture

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

a) Molybdenum disulphide (MoS_2) has a hexagonal P lattice, $\mathbf{a} = 3.14$ Å and $\mathbf{c} = 12.53$ Å, with a motif:

Mo: (1/3, 2/3, 1/4); (2/3, 1/3, 3/4);
S: (1/3, 2/3, 5/8); (1/3, 2/3, 7/8); (2/3, 1/3, 1/8); (2/3, 1/3, 3/8).

Use this information to answer **ALL** the parts of this question:

  i) Draw at least 2x2 unit cells of this structure projected along [001].

(5 marks)

  ii) Describe the coordination environment around each atom in this structure, and how the relevant polyhedra are linked.

(4 marks)

  iii) Explain why this structure is considered to be a layered compound, and state the layer spacing. Suggest why MoS_2 is commonly used as a lubricant.

(3 marks)

  iv) By identifying one of the shortest Mo-S distance(s), calculate the bond length.

(3 marks)

b) There is a series of transition metal dichalcogenide compounds with similar structures to that described for MoS_2 in part (a). Answer **BOTH** the following questions:

  i) Calculate the density of the MoS_2 structure described in part (a).

(6 marks)

  ii) Explain, stating any assumptions, how you might expect the density of the analogous structures WS_2, WSe_2 and $MoSe_2$ to compare to MoS_2 and to each other.

(4 marks)

c) Given that NiAs has a hexagonal P structure ($\mathbf{a} = 3.618$ Å, $\mathbf{c} = 5.034$ Å), with motif   Ni: (0, 0, 0); (0, 0, 1/2); As: (2/3, 1/3, 1/4); (1/3, 2/3, 3/4), answer **BOTH** the following questions:

  i) Draw at least 2x2 unit cells of this structure projected along [001]. Describe the coordination environment around each atom in this structure, and how the relevant polyhedra are linked.

(6 marks)

  ii) State, with justification, the closest Ni-Ni distance in this structure. Compare the value to the layer spacing for the structure of MoS_2 in part (a)(iii), and discuss the implications for the type of bonding present in NiAs.

(4 marks)