SECOND PUBLIC EXAMINATION

Honour School of Chemistry

CHEMISTRY PART IB

INORGANIC CHEMISTRY – PAPER I

TRINITY TERM 2018

Thursday 31 May, 2.30 p.m. – 5.30 p.m.

Time allowed: 3 hours

Candidates should answer FOUR questions

Group Theory tables are available

Please begin your answer to each question in a new booklet.

The numbers in square brackets indicate the approximate marks that the examiners intend to assign to each part of the question.

The following abbreviations are used:

\[ \text{Me} = \text{CH}_3, \quad \text{Et} = \text{CH}_2\text{CH}_3, \quad '\text{Pr} = \text{CH}(\text{CH}_3)_2, \quad '\text{Bu} = \text{C}(\text{CH}_3)_3, \]

\[ \text{Ph} = \text{C}_6\text{H}_5, \quad \text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2, \]

B.M. = Bohr magneton, \quad LMCT = ligand–metal charge transfer,

BCS = Bardeen–Cooper–Schrieffer, \quad \text{THF} = \text{tetrahydrofuran}

\[
\begin{align*}
\text{bipy} & \quad \begin{array}{c}
\text{phen}
\end{array}
\end{align*}
\]

Do not turn over until told that you may do so.
1. Answer **ALL** parts (a) – (c)

(a) Comment on the rate constants \(k_{\text{ct}}\) at 298 K for the electron transfer reactions given below.

<table>
<thead>
<tr>
<th>Reductant</th>
<th>Oxidant</th>
<th>(k_{\text{ct}} / \text{M}^{-1} \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cr(H}_2\text{O})_6\text{]}^{2+})</td>
<td>([\text{Cr(H}_2\text{O})_6\text{]}^{3+})</td>
<td>(&lt; 10^{-5})</td>
</tr>
<tr>
<td>([\text{Ru(NH}_3\text{)}_6\text{]}^{2+})</td>
<td>([\text{Ru(NH}_3\text{)}_6\text{]}^{3+})</td>
<td>(6.6 \times 10^2)</td>
</tr>
<tr>
<td>([\text{Cr(H}_2\text{O})_6\text{]}^{2+})</td>
<td>([\text{Co(NH}_3\text{)}_5\text{(OH)}\text{]}^{2+})</td>
<td>(1.5 \times 10^6)</td>
</tr>
</tbody>
</table>

(b) Answer **BOTH** parts (i) and (ii)

(i) Discuss the following data which give the product distributions for the replacement of \(\text{Cl}^-\) by \(\text{H}_2\text{O}\) in the cobalt complexes under acidic or basic conditions.

<table>
<thead>
<tr>
<th>Complex</th>
<th>% <em>cis</em> product</th>
<th>% <em>trans</em> product</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acidic conditions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>cis-</em>([\text{Co(en)}_2\text{(NH}_3\text{)}\text{Cl}])^{2+}</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td><em>trans-</em>([\text{Co(en)}_2\text{(NH}_3\text{)}\text{Cl}])^{2+}</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td><strong>Basic conditions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>cis-</em>([\text{Co(en)}_2\text{(NH}_3\text{)}\text{Cl}])^{2+}</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td><em>trans-</em>([\text{Co(en)}_2\text{(NH}_3\text{)}\text{Cl}])^{2+}</td>
<td>67</td>
<td>33</td>
</tr>
</tbody>
</table>

(ii) Predict whether you would expect the rate of hydrolysis of *cis-* and *trans-*\([\text{Co(en)}_2\text{(NH}_3\text{)}\text{Cl}]\)^{2+} to be faster or slower in acidic conditions compared to basic conditions, giving your reasoning.

*Question continues*
(c) Answer ALL parts (i) – (iii)

(i) Describe the two mechanistic pathways usually seen for ligand
substitution reactions at square planar complexes such as PtCl₂(NH₃)₂.

[4]

In a non-coordinating solvent substitution of the two Me₂SO ligands in cis-
PtPh₂(Me₂SO)₂ by a single molecule of phen has a rate law of the form
Rate = \( k_{\text{obs}} \) [complex]
with
\[
k_{\text{obs}} = a[\text{phen}] + \frac{b[\text{phen}]}{c[\text{Me₂SO}] + d[\text{phen}]}
\]
where \( a, b, c \) and \( d \) are constants.

(ii) Identify the two mechanistic pathways that are being observed under
these solution conditions.

[3]

(iii) Show how your proposed mechanisms give rise to the rate law.

[5]

End of Question

Turn over
2. Answer **BOTH** parts (a) and (b)

(a) Answer **ALL** parts (i) – (iv)

Consider the following manganese-containing solids:

\[
\begin{align*}
\text{Mn(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O} \\
K_2\text{Mn(CN)}_6 \\
\text{KMnO}_4 \\
\text{Mn}_2\text{(CO)}_{10} \\
\text{Ba}_3\text{(MnO}_4\text{)}_2\text{Cl}
\end{align*}
\]

(i) For each solid, give the Mn \(d\)-electron configuration and hence determine the number of unpaired electrons per Mn atom. \[3\]

The room-temperature effective magnetic moments per Mn atom for the same five solids are as follows (given in no particular order):

\[
\begin{align*}
\text{Solid 1} & \quad \text{diamagnetic} \\
\text{Solid 2} & \quad 5.90 \text{ B.M.} \\
\text{Solid 3} & \quad 2.69 \text{ B.M.} \\
\text{Solid 4} & \quad 0.44 \text{ B.M.} \\
\text{Solid 5} & \quad 2.18 \text{ B.M.}
\end{align*}
\]

(ii) Identify the chemical formula for each solid, giving your reasons. \[5\]

(iii) Rationalise which of the five solids would be expected to exhibit a strong temperature dependence in its effective magnetic moment. \[2\]

(iv) Rank the following molecules in order of the intensity of their main \(d-d\) transition in the visible region, giving your reasoning:

\[
\text{Mn(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O} \quad K_2\text{Mn(CN)}_6 \quad \text{Ba}_3\text{(MnO}_4\text{)}_2\text{Cl}
\]

\[3\]

*Question continues*
(b) Answer ALL parts (i) – (iv)

Consider the following two schematic energy-level diagrams which concern the filled ligand and partially filled transition-metal orbitals for tetrahedral ML₄ and octahedral ML₆ complexes with a $d^{1}$ valence electron configuration.

(i) Give the irreducible representation associated with the electric dipole operator for the $T_{d}$ and $O_{h}$ point groups.

(ii) Making use of direct products, explain which orbitals are involved in the lowest-energy ligand–metal charge transfer (LMCT) transition for $d^{1}$ ML₄ and ML₆ complexes.

(iii) Rationalise the observed trends in frequencies ($\nu/10^{3}$ cm⁻¹) for the lowest energy LMCT transition in the following octahedral ML₆ complexes:

<table>
<thead>
<tr>
<th>Complex</th>
<th>Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuCl₆]²⁻</td>
<td>19.4</td>
</tr>
<tr>
<td>[RhCl₆]²⁻</td>
<td>12.0</td>
</tr>
<tr>
<td>[PdCl₆]²⁻</td>
<td>29.4</td>
</tr>
<tr>
<td>[OsCl₆]³⁻</td>
<td>26.0</td>
</tr>
<tr>
<td>[IrCl₆]²⁻</td>
<td>19.7</td>
</tr>
<tr>
<td>[PtCl₆]²⁻</td>
<td>37.0</td>
</tr>
</tbody>
</table>

(iv) Whereas the first intense electronic absorption occurs at lower energy for the rhodium-containing complex [RhCl₆]²⁻ than for the ruthenium analogue [RuCl₆]²⁻, the opposite ordering is true for the pair [Rh(CN)₆]³⁻ / [Ru(CN)₆]⁴⁻. Identify the type of charge-transfer process occurring in the cyano complexes and hence rationalise this observation.

End of Question

Turn over
3. Answer **BOTH** parts (a) and (b).

(a) Answer **BOTH** parts (i) and (ii)

(i) Using LiMnO₂ as an example, explain the differences between thermodynamic and kinetic control in solid-state synthesis. In your answer, identify and illustrate the structures of LiMnO₂ formed under each set of conditions. [5]

(ii) Describe, using suitable illustrations, the structural and electronic consequences of **ALL** of the following intercalation processes (1) – (3)

(1) Na into TiS₂
(2) K into C₆₀
(3) Na into WO₃

[3 × 3]

*Question continues*
(b) Answer ALL parts (i) – (iv)

A representation of the crystal structure of the lanthanide hexaborides LnB$_6$ is shown below.

![Crystal structure diagram]

This structure is related to that of CsI with the lanthanide ion occupying the Cs$^+$ site and [B$_6$]$^{3-}$ units occupying the I$^-$ site.

(i) Drawing on analogies to LaO and EuO rationalise the observation that LaB$_6$ is metallic at room temperature but EuB$_6$ is a semiconductor. [3]

(ii) Identify, giving reasons, the orbitals involved at the Fermi level in LaB$_6$. [2]

At temperatures below $T_c = 0.45$ K, LaB$_6$ is a superconductor whose behaviour is well described by BCS (Bardeen–Cooper–Schrieffer) theory. The layered boride MgB$_2$ is also a BCS superconductor, but with $T_c = 39$ K. Isotopic substitution of B has a much greater relative effect on the value of $T_c$ for MgB$_2$ than for LaB$_6$. The difference in $T_c$ cannot be accounted for in terms of the density of states.

(iii) Using a suitable equation, explain the relationship between superconducting transition temperature $T_c$ and vibrational frequencies predicted by BCS theory. [2]

(iv) Suggest possible reasons why $T_c$ is almost two orders of magnitude lower for LaB$_6$ than for MgB$_2$. [4]

*End of Question*

*Turn over*
4. Discuss **THREE** of the following experimental observations (a) – (d), identifying the significance for the biological role of the protein system concerned.

(a) Comparisons between the crystal structures of deoxy- and oxy-hemoglobin have identified differences in the position of the iron ion. In particular, the iron ion is held 0.55 Å outside the porphyrin plane in deoxy-hemoglobin while in the oxygen bound form the iron is positioned approximately in the porphyrin plane.

(b) Vibrational spectroscopy studies of the mechanism of cytochrome c oxidase have identified a band at 803 cm$^{-1}$ assigned to the stretching frequency of a Fe(IV)=O group in one of the intermediates.

(c) Studies of the pH dependence of the catalytic activity of carbonic anhydrase have identified that a single ionisable group in the protein with a pK$_a$ of 6.8 has a strong influence on the rate of catalysis. This group is believed to be a water molecule bound to zinc. For comparison, the pK$_a$ of [Zn(H$_2$O)$_6$]$^{2+}$ in aqueous solution is approximately 9.6.

(d) EPR spectroscopy studies of isomerisation reactions catalysed by coenzyme B$_{12}$-dependent enzymes have provided evidence for a low spin Co(II) intermediate.

*End of Question*
5. Answer ALL parts (a) – (d)

(a) Describe how you would characterise the molecular structure of W(CO)\textsubscript{5}(PMe\textsubscript{3})\textsubscript{2}H\textsubscript{2} and W(CO)\textsubscript{3}(PPr\textsubscript{3})\textsubscript{2}H\textsubscript{2} in both solution and solid state. How might the W–H bonding vary between these two complexes and how would you investigate it in both solution and solid state?  

(b) What are the organometallic products and their relative proportions from the following thermolysis reaction? Propose a mechanism that accounts for your proposed product distribution.

(c) What are the organometallic products obtained by the room temperature photolysis of (η-C\textsubscript{5}Me\textsubscript{3})Ir(PMe\textsubscript{3})H\textsubscript{2} in 100% n-pentane. Explain how the product distribution changes on heating to 110 °C?

(d) Explain the distribution of organic products obtained in the catalytic hydroformylation of 1-hexene using HRh(CO)\textsubscript{4}. Explain how the catalytic turnover rate and organic product distribution would change if HRh(CO)\textsubscript{4} were replaced by HRh(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}?

End of Question

Turn over
6. Answer ALL parts (a) – (c)

(a) Explain why the divalent compounds $\text{ER}_2$ ($\text{E} = \text{Si, Ge and Sn}, \text{R} = \text{alkyl}$) are typically easier to access than the equivalent $\text{CR}_2$ analogues. Discuss the factors that may influence which electronic configuration is the ground state.

(b) Answer BOTH sections (i) and (ii).

(i) By making use of a second order Jahn-Teller approach, explain the differences between the geometries adopted by the group 14 ditetrelenes $\text{R}_2\text{E} = \text{ER}_2$ ($\text{E} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}; \text{R} = \text{alkyl group}$).

(ii) Identify any significant changes to the $\text{E} = \text{E}$, $\text{E} = \text{R}$ bond lengths and $\text{R} = \text{E} = \text{E}$ bond angles in these compounds on descending the group.

(c) Suggest structures for each of the compounds (A–F).

\[\begin{align*}
\text{Ar} & \quad \text{Ar} \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br} \\
\text{N} & \quad \text{N}
\end{align*}\]

\[\begin{align*}
\text{2 equiv. NaC}_{10}\text{H}_{8} & \quad \text{THF} \\
\text{A} & \quad \text{B}
\end{align*}\]

\[\begin{align*}
\text{Ar} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{N} & \quad \text{N}
\end{align*}\]

\[\begin{align*}
\text{KC}_8, \text{hexane} & \quad \text{THF} \\
\text{C} & \quad \text{D}
\end{align*}\]

\[\begin{align*}
\text{Ar} & \quad \text{Mg} \\
\text{I} & \quad \text{OEt}
\end{align*}\]

\[\begin{align*}
\text{K, toluene} & \quad \text{THF} \\
\text{E} & \quad \text{N}_2\text{O}
\end{align*}\]

\[\text{Ar = 2,6-diisopropyl phenyl} \]

\textit{End of paper}