Ollscoil na hÉireann, Gaillimh

National University of Ireland, Galway

SUMMER EXAMINATIONS, 2002

FINAL EXAMINATION FOR THE DEGREE OF B.Sc.(Honours)

(INCLUDING DENOMINATED DEGREES)

CHEMISTRY CH-401

Second Paper

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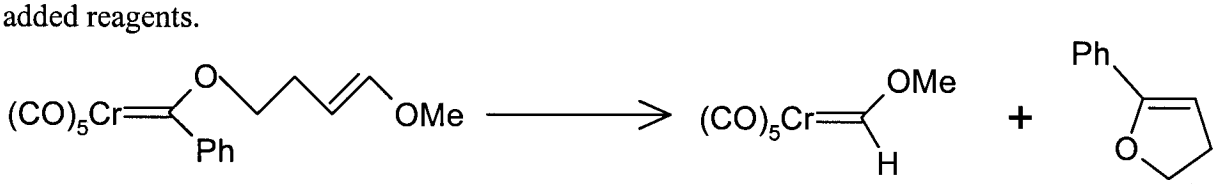
Time allowed: *Three* hours

(Answer *five* questions)

1. Answer **(a)** and **(b)**.

(a) Outline the chemistry of the two principal types of transition metal carbene complexes. Include in your answer a description of the sites of attack that these complexes provide for electrophiles and nucleophiles. **[50 marks]**

(b) Suggest a mechanism for the following reaction which takes place on warming without any added reagents.



[50 marks]

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2. Give brief explanations (approximately a half-page each) for **four** of the following statements:

(a) $[Re_2Cl_8]^{2-}$ is diamagnetic and has an eclipsed structure **[25 marks]**

(b) $[Fe_4C(CO)_{12}]^{2-}$ does not have a *closo* structure **[25 marks]**

(c) The C=C bond lengths in ethene, $[(\eta^2\text{-ethene})PtCl_3]^-$ and $(\eta^2\text{-ethene})Ni(PPh_3)_2$ are 1.34, 1.37 and 1.46 Å respectively. **[25 marks]**

(d) The ^1H NMR spectrum of $RhH(P(OEt)_3)_4$ (ignoring the Et resonances) shows just one H environment at its high temperature limit but becomes more complex at lower temperature. **[25 marks]**

(e) The ring-metal dynamic process in $(\eta^4\text{-cyclooctatetraene})Fe(CO)_3$ has an energy barrier of less than 40 kJ/mol whereas the ring-metal dynamic process in $(\eta^4\text{-cyclohepta-1,3,5-triene})Fe(CO)_3$ has an energy barrier of greater than 80 kJ/mol. **[25 marks]**

3. Answer **(a)** and **three more** of the following:

(a) Identify the ground term from the following: ^1G, ^3F, ^3P, ^1P **[10 marks]**.

(b) Explain why $[FeF_6]^{3-}$ is virtually colourless whereas $[CoF_6]^{3-}$ is coloured but exhibits only a single absorption band in the visible region of the spectrum **[30 marks]**.

(c) One of the isomers of $[CoCl_2(en)_2]^+$ has a band in the visible region of the spectrum with an extinction coefficient of ca. 38 $dm^3\ mol^{-1}\ cm^{-1}$ while the other isomer has an extinction coefficient of ca. 88 $dm^3\ mol^{-1}\ cm^{-1}$. Suggest which band is associated with the *cis* isomer and which is associated with the *trans*. Briefly explain your reasoning **[30 marks]**.

(d) Explain why for ligands having oxygen donor atoms, the following is their sequence in the Spectrochemical Series, $H_2O > OH^- > C_2O_4^{2-}$ **[30 marks]**:

(e) The Racah parameter B is 827 cm^{-1} for $[CrF_6]^{3-}$ and 640 cm^{-1} for $[Co(en)_3]^{3+}$. How does this reflect the difference in bonding in the two complexes? **[30 marks]**.

4. "Much of the current understanding of the unique properties of the current platinum drugs has come from studies with *cisplatin*."

In the light of this statement outline and discuss the chemical requirements for anti-tumour activity and the mode(s) of action (or mechanisms) of platinum(II) complexes. **[100 marks]**

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5. Answer each of the following;

(a) Describe the construction of the reciprocal lattice and show how an orthorhombic reciprocal lattice is indexed. **[25 marks]**

(b) With the aid of a diagram give an interpretation of the Bragg equation in terms of the reciprocal lattice. **[25 marks]**

(c) With the aid of a diagram, show how the reciprocal lattice concept accounts for the appearance of a rotation photograph obtained by rotating an orthorhombic crystal about its c-axis which is mounted perpendicular to a monochromatic x-ray beam. **[25 marks]**

(d) Briefly outline how the original simple rotation photograph method of collecting diffraction data has been developed to give an ultra fast data collection system. **[25 marks]**

6. Outline, without providing full mathematical details, how the spin-only formula is derived and show how the approach to the derivation of this formula is altered, and complicated, if an expression is to be obtained for the magnetic moment of a Ti^{3+} complex with perfect octahedral geometry. Indicate the form of both magnetic moment vs. temperature and magnetic moment vs. temperature/(coupling constant) plots as predicted by the latter expression. Describe the important implications that can be drawn from the plot of magnetic moment v.s. temperature/ (coupling constant) regarding magnetic moments of second and third row transition metal complexes with d^1 configurations. **[60 marks]**

With the aid of appropriate molecular orbital diagrams, describe how a bridging atom between two paramagnetic metal ions can lead to either ferromagnetic or antiferromagnetic coupling. **[20 marks]**

Account for the fact that the neutron diffraction pattern of MnO at room temperature leads to a cubic unit cell with a unit cell parameter of 4.43 Å whereas the neutron diffraction recorded at 80 K leads to a cubic unit cell parameter of 8.85 Å. **[20 marks]**

7. Discuss investigations of the ***mechanism of action of the zinc proteinases*** under the following headings.

(a) Cobalt complexes as model systems **[20marks]**
(b) Crystallographic studies of Lipscomb **[40marks]**
(c) Kinetic investigations of Mock **[40marks]**

8. Discuss the ***bioinorganic chemistry of oxygen*** under the following headings.

(a) The molecular and chemical properties of dioxygen. **[20marks]**
(b) Dioxygen transport and storage. **[40marks]**
(c) Oxygen atom transfer reactions. **[40marks]**