

**Ollscoil na hÉireann, Gaillimh**  
***National University of Ireland, Galway***

**SUMMER EXAMINATIONS, 1999**

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

**(INCLUDING DENOMINATED DEGREES)**

**CHEMISTRY CH-401**

*Second Paper*

Professor D.J. Cardin  
Professor P. McArdle  
Professor R.N. Butler  
Professor. D. Cunningham  
Professor. M. J. Hynes  
Dr. T. Higgins

Time allowed: *Three* hours

(Answer *five* questions)

1. Write short notes or explanations for each of the following:
- (a) Pulse FT NMR is a more sensitive experimental method than cw NMR. [15 Marks]
  - (b) Explain how the SPT (Selective Polarisation Transfer) technique can be applied to the C-H system to increase sensitivity for carbon. [15 Marks]
  - (c) Explain the terms Spin-Spin and Spin-Lattice relaxation. [15 Marks]
  - (d) What quantity can be derived from the width at half height of a singlet in a normal  $^1\text{H}$  NMR spectrum? Describe any precautions that need to be observed in this type of measurement. [15 Marks]
  - (e) Give some organometallic examples of molecules that exhibit time averaged NMR spectra. Outline the mechanism which is believed to be operative in the examples you quote. Molecules which show time averaged spectra in IR region are quite rare. Can you suggest a reason for this? [40 Marks]

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2. Answer (a) and (b).

- (a) What is meant by the statement that  $M(CO)_3$  and  $BH$  are isolobal ? How many electron pairs does an  $Ru(CO)_3$  unit have for skeletal bonding in metal clusters ? If it is accepted that the number of electron pairs devoted to skeletal bonding will give a *closo*, *nido* and *arachno* structures for  $n+1$ ,  $n+2$  and  $n+3$  pairs then give electron counts and predictions for the structures of  $Rh_6(CO)_{16}$ ,  $Os_5C(CO)_{15}$  and  $H_2Os_5(CO)_{15}$  [60 Marks]
- (b) The Re-Re distance in the anion  $[Re_2Cl_8]^{2-}$  is 2.24 Å. Explain both why this distance is shorter than the sum of the covalent radii for the metals and the eclipsed geometry observed. [40 Marks]

3. Contrast the roles adopted by calcium and zinc in biological systems. Describe, in some detail, the mechanism of action of any one zinc metalloenzyme. [100 Marks]

4. Describe the iron porphyrin species involved in the mechanism of insertion of an oxygen atom into a C-H bond by cytochrome P450. For each species, identify the oxidation state of the metal, the coordinated ligands, the nature of any coordinated oxygen and the possible resonance forms. Discuss any experimental evidence which supports the involvement of these species. [100 Marks]

5. Answer each of the following:

- (a) Discuss the superiority of molecular orbital theory over crystal field theory in rationalising the relative positions of ligands in the spectrochemical series. [80 marks]
- (b) Why is water higher than either the hydroxide or oxalate ions in the spectrochemical series ? [20 marks]

6. Describe the current state of the art with regard to electron transfer reactions in transition metal complexes. [100 Marks]

7. Answer each of the following:

- (a) Briefly outline the method for locating heavy atom positions using the Patterson technique. [20 Marks]
- (b) While determining the structure of an organometallic complex, heavy atoms were found to be located at the corners and on the centres of two opposite faces of an orthorhombic unit cell. Calculate a structure factor for this cell (based on the metal atoms alone) and hence determine a special absence condition for a C-centred cell. [40 Marks]
- (c) Outline the role of neutron diffraction in structure determination. [40 Marks]

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