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

SEMESTER 1 EXAMINATIONS 2001/2002

THIRD UNIVERSITY B.Sc. EXAMINATION IN SCIENCE (INCLUDING DENOMINATED DEGREES)

Inorganic Chemistry (CH307)

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

Time Allowed: Two Hours

Answer Question 1 and Three Other questions

All questions carry 25 marks distributed as shown. Leave the first page of the Answer Book blank and list on it clearly the numbers of the questions attempted.

1. See accompanying sheet for multiple choice question.

2. Describe and contrast the mechanisms by which square-planar and octahedral transition metal complexes undergo ligand substitution reactions in solution. Describe some of the tests that might be used to differentiate the possible mechanisms. How does the complex formation reaction, in which a solvated metal ion reacts with a ligand other than water, fit into the above classification of ligand substitution reactions? **[25 marks]**

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

(a) Explain the use of the L X formalism and describe how it can be applied to electron counting in transition metal complexes. **[10 marks]**

(b) Give metal valence electron counts for the following systems and indicate those which are likely to be stable and those which are not; $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, $(\eta^5\text{-}C_5H_5)Co(CO)(PPh_3)_2$, $Mo(CO)_3(PPh_3)_2I$, $(\eta^2\text{-buta-1,3-diene})Co(CO)_4Br$ and $(\eta^3\text{-allyl})Mo(CO)_4I$. **[15 marks]**

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

(a) Explain the terms oxidative addition and reductive elimination. Discuss the mechanism of the oxidative addition reaction. **[12 marks]**

(b) Outline the difference between hetero atom stabilized and unstabilized carbene complexes. Give some examples of important processes that are catalysed by the latter type of complex. **[13 marks]**

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

(a) Describe the steps involved in the application of the TASO method to the construction of a molecular orbital correlation diagram for a molecule. Illustrate your answer using any suitable example.

(b) Use the C_{2v} point group character table to assign symmetry labels to the O-H stretching modes of the water molecule and then predict their IR and Raman allowed ness.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_x	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_z	yz

6. Give examples of metallo-proteins in which the metals exhibit the following roles (a to e). One example will suffice in each case. Illustrate your answer with descriptions of the active metal environments and of the mode of action of the metallo-protein.

(a) Catalysis.
(b) Electron transfer
(c) Structure
(d) Trigger or switch
(e) Transport.

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7. Write notes on <u>each</u> of the following.

(i) The d-orbital splitting pattern predicted by crystal field theory for coordination compounds that exhibit <u>tetragonal distorted octahedral</u> stereochemistry.
(ii) The d-orbital splitting pattern predicted by crystal field theory for coordination compounds that exhibit <u>square planar</u> geometry.
(iii) The Jahn-Teller effect.
(iv) "Cu(II) complexes usually exhibit tetragonally distorted octahedral geometry."
(v) "Pd(II) coordination compounds are usually square-planar."
(vi) "Many Ni(II) coordination compounds are diamagnetic."
(vii) "The uv-visible spectrum obtained from an aqueous solution of $[Cu(NH_3)_4(H_2O)_2]SO_4$ has one unsymmetrical peak."

8. Answer **(a)**, **(b)**, **(c)** and **(d)**.

(a) Describe the essential features of the molecular orbital diagram for the bonding in the octahedral cation $[Cr(NH_3)_6]^{3+}$.

(b) Compare this diagram with that obtained from crystal field theory.

(c) Show how the molecular orbital diagram for $[Co(NH_3)_6]^{3+}$ differs from that of the octahedral cation $[Cr(en)_3]^{3+}$. [en = ethylenediamine, a stronger sigma donor ligand than NH_3)

(d) Show how the molecular orbital diagram differs when the π-bonding anions cyanide and chloride are used as ligands.