



**Autumn Examinations 2010 / 2011**

**Exam Code(s)** 3BS9, 10A1

**Exam(s)**

**Module Code(s)** CH307 Inorganic Chemistry

**Module(s)**

**Paper No.** I

**External Examiner(s)** Professor K. Molloy

**Internal Examiner(s)** Dr. A. Erxleben, Dr. T. Higgins , Dr. L. Jones

**Instructions:** Answer **one** question from **each** section.  
All questions are worth 25 marks.

**Duration** 2 hrs

**No. of Pages** 4 Following this page

**Discipline(s)** Chemistry

**Course Coordinator** Dr. A. Erxleben

**Requirements** log tables with periodic table

## Section A

### Answer one question from this section

1. Answer each of the following:

- (a) Describe the crystal field splitting patterns for (i) octahedral, (ii) tetrahedral, and (iii) square planar geometries. **[6 marks]**
- (b) Give examples, one in each case, of a transition metal coordination compound that exhibits (i) octahedral, (ii) tetrahedral, and (iii) square planar geometries. Explain the rationale for your choices. **[6 marks]**
- (c) Explain the term 'crystal field stabilisation energy' and discuss the influence of this energy on the occurrence of tetrahedral geometry in Ni(II) coordination compounds. **[7 marks]**
- (d) Describe a simple laboratory method for distinguishing tetrahedral from octahedral coordination in Ni(II) compounds. Explain the basis of the method. **[6 marks]**

2. Answer each of the following:

- (a) Draw a fully labelled molecular orbital bonding scheme for the octahedral cation,  $[\text{Mn}(\text{NH}_3)_6]^{2+}$ . **[5 marks]**
- (b) Show how the molecular orbital bonding schemes differ for the octahedral ions  $[\text{MnCl}_6]^{4-}$  and  $[\text{Mn}(\text{CN})_6]^{4-}$ . **[10marks]**
- (c) Use Molecular Orbital Theory to account for the relative positions of cyanide, ammonia and chloride in the spectrochemical series. **[10marks]**

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## Section B

### Answer one question from this section

3. Answer each of the following:

(a) Compare the roles played by sodium and calcium in biological systems. [8 marks]

(b) Give examples of metallo-proteins, one in each case, where the metal is coordinated by (i) histidine, (ii) a carboxylate and (iii) any other amino acid residue. Sketch the structure of the active site for each of your examples. [9 marks]

(c) Give one example of a metallo-protein that functions as a switch (or trigger). Draw a structure for the active metal centre and clearly identify the ligands that coordinate the metal ions. [8 marks]

4. Answer each of the following:

(a) Write a brief note on substitution mechanisms of metal complexes. Clearly distinguish between the dissociative, associative and interchange substitution mechanism. [9 marks]

(b) The reaction of  $[\text{PtCl}(\text{dien})]$  (dien = diethylenetriamine) with  $\text{NH}_3$  in water is carried out under pseudo-first order conditions. The reaction product,  $[\text{Pt}(\text{NH}_3)(\text{dien})]$ , is formed *via* the solvolytic pathway. Plot  $k_{\text{obs}}$  vs. concentration of  $\text{NH}_3$ . Explain how you have reached your answer. [7 marks]

(c) How does each of the following modifications affect the rate of the substitution of X in *trans*- $[\text{PtXCl}(\text{NH}_3)_2]$ ? In each case, justify your answer.  
(i) Changing the trans ligand from Cl to  $\text{CH}_3$   
(ii) Adding bulky substituents to the  $\text{NH}_3$  ligands  
(iii) Carrying out the reaction at higher pressure. [9 marks]

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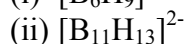
## Section C

### Answer one question from this section

5. Answer each of the following:

(a) Briefly outline Wade's Rules with respect to rationalising the structures of Boranes. [7 marks]

(b) Using Wades' rules determine the structures and give the correct nomenclature for the following boranes:



[10marks]

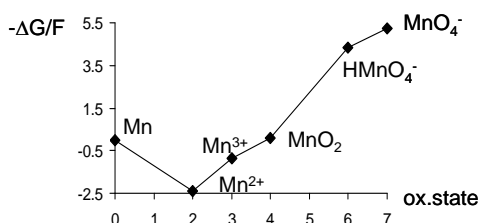
(c) Use Wade's rules to determine the structure of the carborane  $[\text{C}_2\text{B}_3\text{H}_5]$  and draw the three possible isomers associated with this molecule.

[8 marks]

6. Answer each of the following:

(a) Write a brief note on the acid-base properties of the vanadium oxides  $\text{V}_2\text{O}_5$ ,  $\text{VO}_2$ ,  $\text{V}_2\text{O}_3$ ,  $\text{VO}_2$  and  $\text{VO}$ . [9 marks]

(b) The Frost-Ebsworth diagram for manganese in aqueous solution, pH 0 is shown below. Which species do you expect to disproportionate in water, pH 0? Justify your answer.

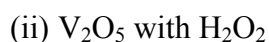
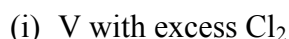


[4 marks]

(c) The reaction of  $\text{VOSO}_4$  with acetylacetonate gives a green product **A**. The IR spectrum shows a VO stretching vibration at  $990\text{ cm}^{-1}$ . When **A** is reacted with n-propylamine, product **B** is obtained. The VO stretching vibration of **B** appears at  $960\text{ cm}^{-1}$ . Draw the structures of **A** and **B** and comment on the IR data.

[7 marks]

(d) Write balanced equations for the following reactions:



[5 marks]

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## Section D

### Answer one question from this section

7. Answer **each** of the following:

(a) Define and give one example for each of the following:

- (i) an electron deficient organometallic complex
- (ii) a  $\pi$ -acceptor ligand
- (iii) an  $\eta^5$ -ligand
- (iv) a  $\pi$ -donor ligand
- (v) a ligand which can be both a  $\sigma$ -donor and  $\pi$ -acceptor
- (vi) a  $\sigma$ -donor ligand

[13marks]

(b) Give the correct  $[ML_aX_b]^{c+}$  formalism for the following organometallic complexes and determine the metal oxidation state and the valence electron count.

- (i)  $[Mn(CO)_2(PF_3)_2Br]$
- (ii)  $[Mo(\eta^3\text{-allyl})(CO)_4I]$
- (iii)  $[W(\eta^6\text{-}C_6H_6)(CO)(P(OPh)_3)_2]$
- (iv)  $[Fe(\eta^4\text{-}CH_2CHCHCH_2)(CO)_3]$

[12marks]

8. Answer **each** of the following:

(a) Draw the structure of Ferrocene along with the product(s) it forms upon reaction with a mixture of  $AlCl_3$  and the haloketone  $CH_3COCl$ . Give a brief description of the role  $AlCl_3$  plays in this reaction. [6 marks]

(b) Explain why  $[Co(\eta^5\text{-Cp})_2]$  is readily oxidised to the cationic  $[Co(\eta^5\text{-Cp})_2]^+$ . What is the general name given to these type of organometallic compounds? [6 marks]

(c) The reaction of  $Fe(CO)_5$  with the ligand Cyclopentadiene ( $\eta^5\text{-Cp}$ ) produces a mixed ligand compound of formula  $[(\eta^5\text{-Cp})_2Fe_2(CO)_4]$ .

(i) Show that this compound obeys the 18 electron rule (show your workings clearly). [6 marks]

(ii) Draw both the *cis* and *trans* isomers for this compound. [4 marks]

(iii) If you were unable to obtain a crystal structure, what method would you use to characterise the Fe-CO bonding observed in this compound? [3 marks]