University of Canterbury

End of Year Examinations 2007

Prescription Number(s):	CHEM 261
Paper Title:	Inorganic & Structural Chemistry

Time Allowed:	THREE HOURS
Number of pages:	SEVEN

Answer **FIVE** questions out of SEVEN.

All questions are of equal value

TURN OVER

1. Heteronuclear bonds are often stronger than homonuclear ones.

   (a) Define or explain each of the following concepts:

      (i) Electronegativity;

      (ii) Polarizing power and polarisability;

      (iii) Soft and hard atoms.

   (b) Compare and contrast these concepts and explain how they can be used to describe the bonding in heteronuclear compounds.

   (c) Explain how “hardness” and “softness” can be used to estimate the stability of heteronuclear compounds in different oxidation states, particularly in the highest oxidation state for the group.

2. Structures and bonding in boron hydrides can be rationalised using several approaches.

   (a) Using B_2H_6 as an example, discuss in detail, the nature of a 3-centre-2-electron bond.

   (b) Explain polyhedral skeletal electron pair theory and then show how Wade’s rules can be used to infer the structures of boron hydrides.

   (c) Compare the ease of use of Wade’s rules and STYX rules for higher boranes, such as B_5H_9.

3. Properties of the second-row elements (Li-Ne) are markedly different from those of the third-row (Na-Ar) elements and heavier elements. Comment on:

   (a) The variation of $Z_{eff.}$, screening percentage, atom sizes and ionization energies on going from the 2nd row to the 3rd row;

   (b) The stability of 2nd row elements O and N in diatomic compounds with multiple bonds, such as O_2 and N_2, in contrast to the catenation ability of P (P_4 etc.) and S (S_8 etc.);

   (c) The anomalously low homonuclear single-bond energies for N-N, O-O, and F-F in comparison to P-P, S-S and Cl-Cl, respectively;

   (d) Factors affecting bond energies as given in the Table below.

Bond	Bond Energy (kJ/mol)
F-F	158
Cl-F	297
Cl-Cl	242
Br-Br	193

4. (a) Compare the terms “stepwise formation constant” and “overall stability constant” and explain how they are used.

   (b) Give a detailed explanation of the origin of the chelate effect.

   (c) How is the explanation in (b) modified to account for the macrocyclic effect?

   (d) Would you expect the size of the macrocyclic effect to depend on the size of the ring and/or the number of donor atoms in the ring. Give reasons.

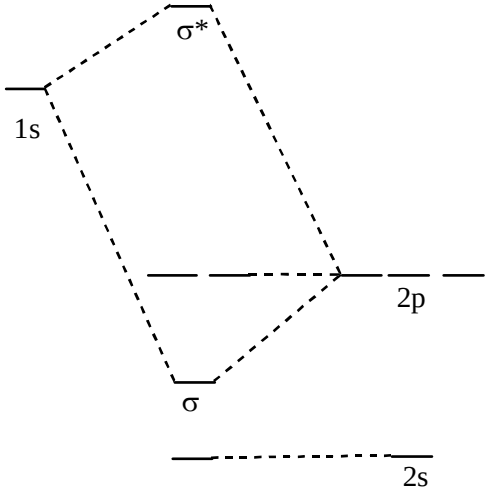
5. (a) Metal ions can be classified as labile or inert.

(i) Define what these terms mean.

(ii) Explain what factors influence the lability of a metal ion.

(iii) Discuss whether metal ion lability might be a significant factor in selection of metal ions for (1) target molecules in synthetic chemistry and (2) use in enzyme active sites.

(b) Shown below is the MO diagram for HF (without the electrons).



(i) Sketch the Lewis diagram for HF and comment on differences between the VB description of HF and the MO description.

(ii) Sketch the MOs for σ and σ^*.

(iii) Which is the HOMO?

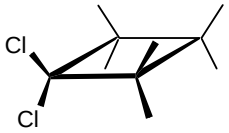
(iv) Which is the SLUMO?

(v) What does the MO diagram tell you about the polarity of the H–F bond? (Explain how you arrive at your conclusion).

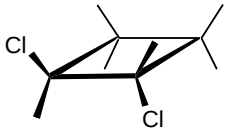
(vi) Why are the p_x and p_y orbitals not involved in the bonding with the H atom?

6. (a) Shown below are FIVE isomers of dichlorocyclobutane. For each isomer, determine its point group (note your workings through the chart below) and list all of the symmetry operations for that point group.

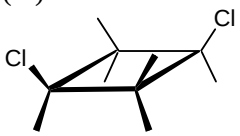
(i)



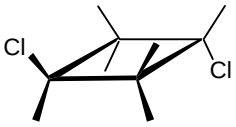
(ii)



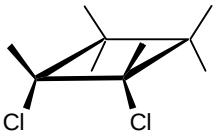
(iii)



(iv)



(v)

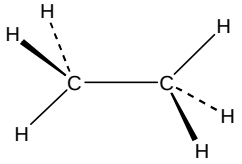


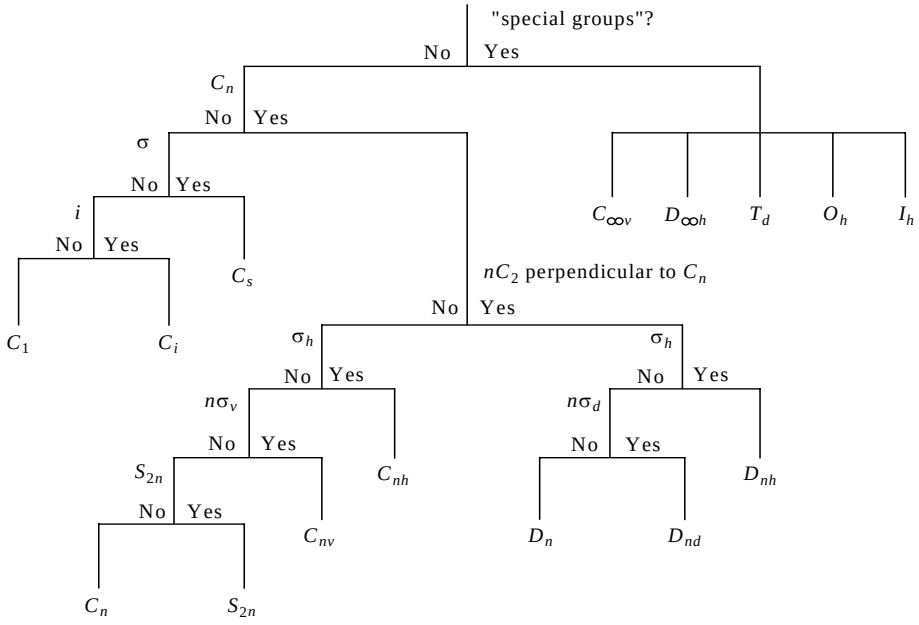
(b) Which of the molecules in part (a) is/are polar?

(c) Which of the molecules in part (a) is/are dissymmetric?

(d) Which of the molecules in part (a) is/are centrosymmetric?

(e) List all of the symmetry operations for staggered ethane, shown below.





7. (a) Explain what is meant by the expression **low molecular weight model complex** in the context of bio-inorganic chemistry.

(b) The "picket-fence porphyrin" was developed as a model for the active site in hemoglobin. Discuss:

(i) the principles that guided the design of the picket-fence complex; and

(ii) the conclusions to be drawn from the characterisation of the dioxygen adduct of the model complex.

END OF PAPER