University of Canterbury

End of Year Examinations 2007

Prescription Number(s):	CHEM 221
Paper Title:	Inorganic & Structural Chemistry

Time Allowed:	THREE HOURS
Number of pages:	FIVE

Answer **FIVE** questions out of SIX.

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.

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.

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

   (a) the variation of $Z_{\text{eff.}}$, 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 energy for N-N, O-O, and F-F in comparison to P-P, S-S and Cl-Cl, respectively.

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?

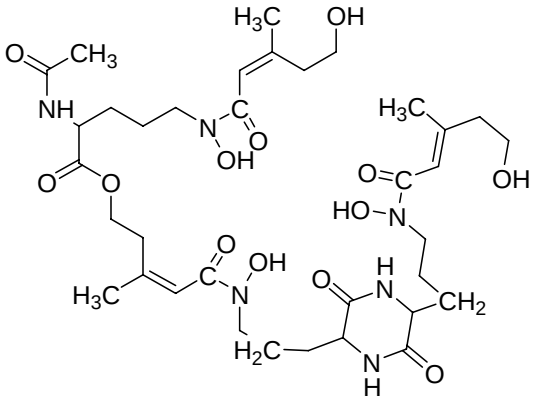
5. (a) Metal ions can be classified as labile or inert.

(i) Define what these terms mean and contrast them with the terms stable and unstable.

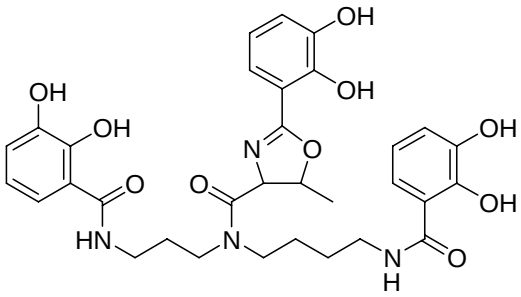
(ii) Explain what factors influence the lability of a metal ion.

(b) (i) Briefly indicate the role of the siderophores in biological systems.

(ii) There are three main modes of iron binding in siderophores. Describe these and identify and name the binding sites in the following siderophores.

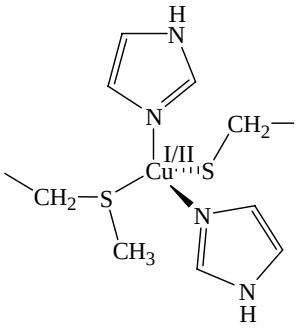


coprogen complex

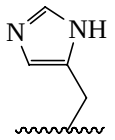


agrobactin

6. The diagrams below may be useful in answering the following questions.

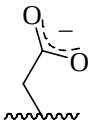


Cu(I)/Cu(II) active site at biological pH of the type-1 copper protein plastocyanin

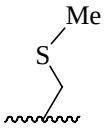


His

Cys



Asp



Met

(a) (i) Using Cu(I) and Cu(II) as examples, discuss what is meant by "hard" and "soft" acids.

(ii) Would you expect to find nitrogen or sulfur ligands associated with Cu(I) and Cu(II) ions? Explain your reasoning.

(iii) Suggest what changes you might expect to observe if the following modifications were made at the active site of the type-1 (blue) copper protein plastocyanin. Give a brief explanation of your answer.

(A) One of the histidines (His) was replaced by cysteine (Cys).

(B) The methionine (Met) was replaced by aspartate (Asp)

(b) "The reduced form of the protein is colourless but the oxidised form is intensely blue ($\varepsilon = 3000\ M^{-1}\ cm^{-1}$)". Use your knowledge of coordination chemistry to account for the following:

(i) the colour change;

(ii) the intensity of the colour of the oxidised form.

END OF PAPER