

University of Canterbury

## End of Year Examinations 2005

Prescription Number(s): CHEM 221

Paper Title: Inorganic & Structural Chemistry

Time Allowed: THREE HOURS

Number of pages: SIX

Answer **FIVE** questions

All questions are of equal value

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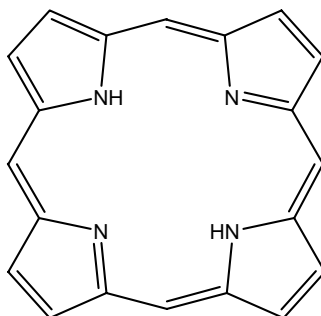
1. "Living in an oxygen environment is injurious to your health." Discuss this statement with particular reference to the oxygen species involved and the role of superoxide dismutase. Using diagrams where necessary, describe the essential features of the active site structure of  $\text{Cu}_2\text{Zn}_2$  superoxide dismutase and the so-called "ping-pong" mechanism of this enzyme. Include discussion of the experimental evidence that supports this mechanism.
  
2. (a) Catenation is the name given to the situation where atoms of an element form single bonds to each other.
  - (i) Use the following bond energy data to explain why elemental nitrogen and oxygen are usually found as diatomic molecules while the other elements are usually made up of larger arrays of atoms. Explain the trends in the bond energy data.

**Table** Approximate bond increments ( $\text{kJ mol}^{-1}$ ) for  $\sigma/\pi$  bonds for various element–element pairs

C–C 335/295	N–N 160/395	O–O 145/350	C–O 335/380	N–O 190/370
Si–Si 195/120	P–P 200/145	S–S 270/155	Si–O 420/170	P–O 335/150
Ge–Ge 165/110	As–As 175/120	Se–Se 210/125	C–S 280/265	S–O 275/250

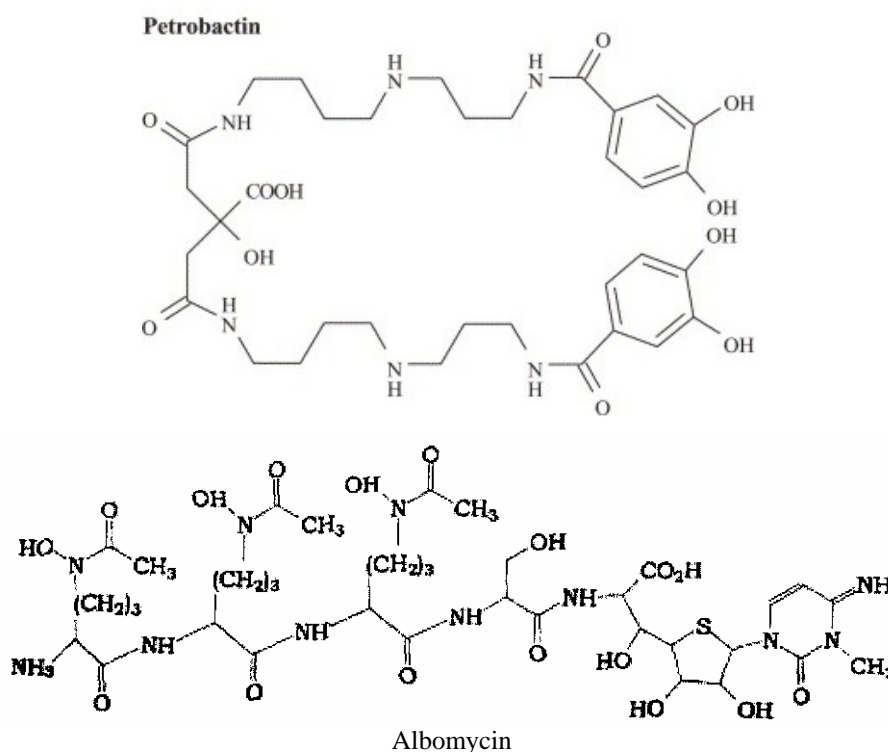
- (ii) Explain fully why heteronuclear compounds are generally more stable than homonuclear species.
  
- (b) The oxides, halides and hydrides of the s and p block elements can be classified as ionic, polymeric, or molecular covalent species. What periodic trends are seen in these classifications, and what reasons have been put forward to explain these trends?

3. The porphyrin shown below and its substituted derivatives are excellent ligands that are used in a wide range of biological systems.



- (a) Explain, in detail, why they are such good ligands.
- (b) Would you expect octahedral complexes containing this ligand to be high spin or low spin? Explain your answer using a molecular orbital approach (ligand field theory).
4. (a) Describe (or draw) and account for the general periodic trend in the first ionisation energy for the elements Li to Ne and Na to Ar.
- (b) Explain why the first ionisation energy of Be is greater than that of B and account for any other deviations from the overall trend in the remaining first row elements.
- (c) How would the trends in the second and third ionisation energies for these elements differ from those of the first ionisation energy?
- (d) Define the term “inert pair effect” and explain why it is observed.
- (e) Discuss the reasons that underlie the low reactivity of the noble gases.

5. (a) (i) Briefly indicate the role of siderophores in biological systems.
- (ii) Describe the three main modes of iron binding in siderophores.
- (iii) Name and identify (by sketching the relevant fragment) the binding sites in the following siderophores.



- (b) Write a paragraph on each of the following:

- (i) Chemistry of the lanthanides in the +3 oxidation state.

This should include an explanation of the uniformity of the chemistry across the row, and a description and explanation of the types of ligands, coordination numbers and geometries found in Ln(III) complexes.

- (ii) The function of contrast agents in magnetic resonance imaging, and the properties of  $[\text{Gd}(\text{DTPA})(\text{H}_2\text{O})]^{2-}$  that account for its use as a contrast agent.

DTPA is diethylenetriaminepentaacetic acid.

6. (a) Describe how molecular orbital theory can be extended from small molecules to infinite solids in order to develop band theory.
- (b) How does band theory allow the existence of insulators, conductors and semiconductors to be rationalised?
- (c) Explain, in detail, how the introduction of impurities can affect the electrical properties of a solid. Include reference to properties of diodes in your answer.
7. (a) Explain the terms **singlet** (S) and **triplet** (T) state.
- (b) Briefly describe the principles of photodynamic therapy (PDT) for the treatment of cancer.
- (c) Describe, in detail, the photophysical and photochemical reactions that occur during PDT. Include in your answer an explanation of why a photosensitising drug must:
- form the triplet (T) state (of the drug) with high quantum yield;
  - form a T state with energy  $\geq 94.7 \text{ kJ mol}^{-1}$ ;
  - form a T state with sufficient lifetime to undergo bimolecular reactions.

Note: sketching and referring to a Jablonski diagram showing relevant ground-state and excited-states may assist your answer.

**END OF PAPER**

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