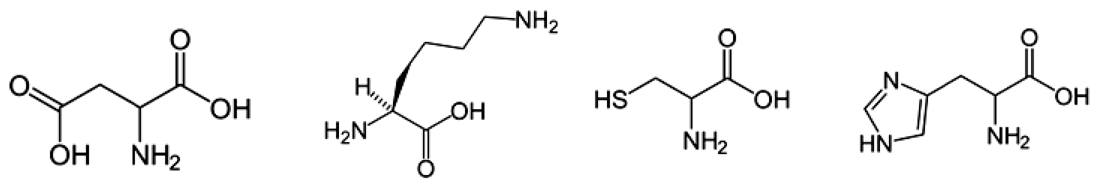
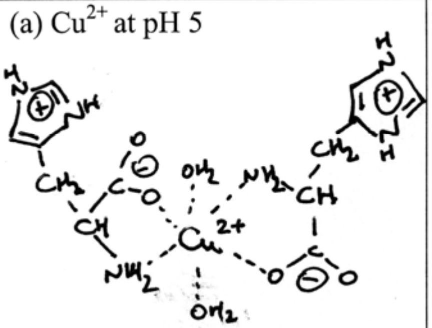
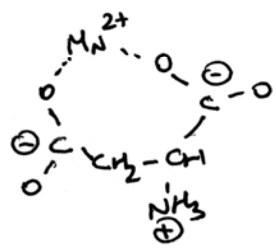
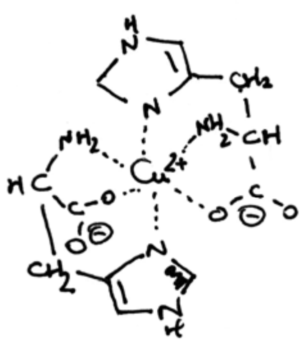
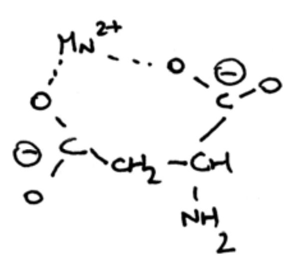
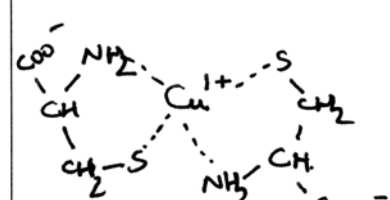
Bioinorganic Chemistry **Exam I** **Feb. 18, 2009**

Name ________________________________

(24) 1. A solution of amino acids is prepared with the following present in equimolar amounts:



For each of the following metal ions draw a structure of the complex with **one** of the above ligands that is **most likely** to form at the pH indicated.

(a) Cu^{2+} at pH 5	(b) Mn^{2+} at pH 5	(c) Cu^{1+} at pH 5
		NO complex
(d) Cu^{2+} at pH 10	(e) Mn^{2+} at pH 10	(f) Cu^{1+} at pH 10
		

(12) 2. Describe three structural features of siderophores that allow them to bind iron with extremely high affinities.

Siderophores have multiple potential donor atoms that can bind to iron

Siderophore structures are highly flexible, thus allowing the maximum number of bonds to form

Siderophores can fully satisfy the octahedral geometry requirements of iron without significant distortion

(18) 3. For each of the following questions describe two factors that determine:

(a) Why metal ions are required in biological systems?
Very few biological molecules are capable of supporting oxidation-reduction reactions, a feature for which many metal ions are well suited.

Metal ions are quite versatile and can function to stabilize protein and DNA structures, bind and transport molecules, and act as catalysts.

(b) Why particular metal ions have been selected?
Rule of abundance – an organism will select the most readily available metal ion that is capable of carrying out a particular function.

Rule of efficiency – if some choices are available an organism will chose the most efficient metal ion for a particular function

(c) What role a metal ion plays?
metal ions that have more than one stable oxidation state in aqueous solution are frequently selected for a redox role.

metal ions that can bind to macromolecules and still have open coordination sites frequently play a role in binding and transporting small molecules.

(10) 4. The redox potential of a metal-ligand complex can sometimes be quite different from that of the free metal ion. What features of biological ligands can cause these differences?

The redox potential is a measure of the equilibrium between two different oxidation states of a metal ion. Any interaction that stabilizes one oxidation state preferentially over the other will shift the equilibrium and therefore the redox potential. The features of biological ligands that can cause these shifts include:

1. nature of the donor atoms – if one oxidation state prefers a different type of donor atom than the other then the identity of the donor atoms can have a preference.

2. coordination geometry – if one oxidation state prefers a different coordination geometry than the other then the geometric constraints of a multidentate ligand can favor one oxidation state.

(18) 5. What role does the peptide bond play in metal ion binding to peptides? How does pH and the properties of different metal ions affect binding at the peptide bond? Give specific examples to support your discussion.

The atoms in a peptide bond are planar due to the partial double bond character. The peptide amide group is a very weak acid and the peptide carbonyl group is a very weak base. When the amide nitrogen is protonated weak metal ions binding can take place at the carbonyl oxygen. An example of this interaction is the coordination of Zn(II) to (gly)3, with the preference for coordination of hard metals at this position.

When the amide nitrogen is ionized then metal ion binding can occur at nitrogen. Among the metal ions that bind at the peptide amide nitrogen Cu(II) and Ni(II) are the most successful at competing with protons for binding at this site. There are numerous examples of this interaction in complexes between these metal ions and peptides.

(18) 6. For **each** of the following describe **two** factors that will determine:

(a) if a complex will form between a metal ion and a ligand.

1. How successfully does the functional group of the ligand compete against other available functional groups?

2. How successfully does the metal ion complete against protons for the potential donor atoms in the ligand?

(b) how strong a metal-ligand complex will form.

1. The lower the pK value of a functional group the greater its availability as a potential donor atom.

2. The greater the number of bonds between a metal and ligand the stronger the complex

3. The better the match between metal type and donor atom type the stronger the complex

(c) which functional groups in a multidentate ligand will bind a particular metal ion.

1. The relative pK values of the functional groups – lower pK values will have a greater tendency to bind.

2. The best match between metal type and donor atom type (hard with hard and soft with soft).

3. The geometric and steric constraints of the ligand.