Reading guide and suggested problems for Chapter 6, 9, 10

For the few lectures, we will be taking small pieces of Chapters 6 and 9 in our discussion of Coordination Compounds, however the focus will be mainly on Chapter 10, which extends our MO treatments to metal complexes, which subsequently help explain some of the interesting properties of metal complexes.

## Learning goals:

1) Understand the nature of metal-ligand bonds in a coordination complex.

2) Know some of the basic terminology associated with coordination complexes.

3) Understand and derive the bonding that occurs in metal complexes.

4) Know the affects of sigma only ligands, pi donor ligands, and pi acceptor ligands on the bonding, the spectrochemical series.

5) Connect the properties of metal complexes, including thermodynamic stability, magnetic moment, and electronic spectra, to their bonding interactions.

## Suggested reading

## Chapter 6: Acid-Base and Donor-Acceptor Chemistry.

**6.4:** (~1 page) This details how Lewis acid-base interactions are essentially interactions between the LUMO of one species with the HOMO of another. This is the kind of interaction we observe between metal and ligand in coordination complexes.

**6.6:** In this section, you only need to read the definition of hard and soft acids and bases (HSABs) and how hard-hard and soft-soft interactions are more favorable.

**Section 6.6.1:** This section describes how HSAB is applied to metals and ligands. Tables 6.14 and 6.15 list different HSABs. It is important for you to understand the trends of what species are described as soft and hard as opposed to memorizing both tables. For example,  $S^{2-}$  is softer than  $O^{2-}$ ,  $Fe^{3+}$  is harder than  $Fe^{2+}$ .

**Chapter 9: Coordination Chemistry I: Structures and Isomers.** This chapter has a lot of information about nomenclature and such. I do not expect you to understand any nomenclature except for the following:

Coordination Compound, Ligand (Intro, section 9.1) Chelating ligand. Mono-, bi-, and multi-dentate ligand (9.2 first two paragraphs) Trans- and Cis isomers (9.3.1 and 9.3.2) Fac- and Mer- isomers (9.3.4 first paragraph, Figure 9.9)

**9.4** of this chapter talks about Coordination Numbers and Structures. A lot of factors can influence the coordination number and geometry of a complex, and we will delve into this in future lectures. The first two paragraphs including factors **1-4** will shape our discussions of why metal complexes have certain coordination numbers and geometries. You do not need to read sections 9.4.1-9.4.4 for now, however I may ask you to look at these sections in the future.

## Chapter 10:

**Section 10.1: Evidence for Electronic structures:** The following four sections describe how properties of metal complexes can be derived from their electronic structures.

**10.1.1. Thermodynamic Data.** This section describes the concept of stability constants, which indicate the strength of bonding in coordination complexes. Of greatest importance is the HSAB concept and the *chelate effect*.

**10.1.2 Magnetic Susceptibility.** This section describes what magnetic susceptibility is and how to calculate the magnetic moment,  $\mu$ , of a compound. We will be using the spinonly magnetic moment,  $\mu_s = 2^*(S(S+1))^{1/2} = (n(n+2))^{1/2}$  in this course. This also describes how you can measure magnetic susceptibility in the lab, which we will apply in the lab part of the course.

**10.1.3 Electronic Spectra.** Not much content in this section, but depending on the structure of a metal complex, it can have a different electronic spectrum (UV-vis).

**10.1.4 Coordination numbers and shapes.** We can sometimes predict the geometric structure of a compound based on the electronic structure of a complex.

**Section 10.2: Bonding Theories.** This section gives a general overview of different theories that have been used to describe the electronic structure of metal complexes. We will mainly be using a combination of crystal field theory and ligand field theory to think about this.

**10.2.1 Crystal Field Theory**. CFT uses the idea that repulsion between the metal d orbitals and the electrons in the ligands results in d orbitals being different energies. This is a simplified method that doesn't take into account bonding and antibonding interactions.

**Section 10.3 Ligand Field Theory.** Crystal field theory and molecular orbital theory are combined to make Ligand Field Theory. This provides a much more thorough picture of the bonding that occurs in metal complexes, though the treatment is more complex than in crystal field theory.

10.3.1 Molecular orbitals for Octahedral Complexes. VERY IMPORTANT SECTION!
10.3.2 Orbital Splitting and Electron Spin. Larger d orbital splittings lead to formation of *low spin* complexes, smaller d orbital splittings lead to formation of *high spin* complexes.
10.3.3 Ligand Field Stabilization Energy. LFSE helps determine whether complexes will be low or high spin.

**10.3.4, 10.3.5.** Ligand field treatment of square planar and tetrahedral complexes. Note that LFSE is smaller for tetrahedral complexes compared to octahedral.

**Section 10.4 Angular Overlap.** This theory provides yet another way of looking at metal complexes, describing how sigma donor, pi donor, and pi acceptor ligands affect orbital energies. Think of this treatment as a way to simplify the MO diagrams.

**10.4.1, 10.4.2, 10.4.3.** These sections describe sigma, pi donor, and pi acceptor interactions with metal d orbitals in an octahedral complex.

**10.4.4. Spectrochemical Series.** VERY IMPORTANT SECTION! The types of ligands you have on a metal center will affect the magnitude of its d orbital splitting and will give a complex a different characteristic color (related to the absorbance wavelength in its UV-vis

spectrum). You should know **the spectrochemical series** listed at the end of this section, understanding that it goes from pi acceptors, to sigma only donors, to pi donors.

**10.4.5 Magnitudes of**  $\Delta$ **.** The only parameter I care about in this section is the  $\Delta$ , or the magnitude of the d orbital splitting. The magnitude of d orbital splitting is dependent on both the identity of the ligands (spectrochemical series) as well as the nature of the metal center. You are NOT responsible for the angular overlap parameters described in Tables 10.12 and 10.13.

**Section 10.5 The Jahn-Teller Effect.** Unequal occupancy of degenerate orbitals leads to distortion of a complex's geometry so that the orbitals are no longer degenerate. This is especially prevalent in complexes with 9 d electrons.

**Section 10.7 Other shapes.** Using crystal field, ligand field, and angular overlap, you should be able to derive the d orbital splitting in complexes of other geometries. We will go over examples in class.

*Relevant homework problems:* 10.1, 10.2, 10.3, 10.5, 10.6, 10.8

10.11: just do calculation for  $\Gamma_{\sigma}$ 

10.12, 10.13, 10.14, 10.16, 10.17, 10.21

10.23, 10.25, 10.31, 10.32

Challenge problems: 10.30, 10.33