Chem E-1a Friday Review Notes Chapter 20: Coordination Compounds

Formulas of Coordination Compounds:

•Coordination compounds contain a metal surrounded by various ligands with (perhaps) one or more counter ions.

•In the formulas of coordination compounds, the coordination complex is written inside square brackets, and any counter ions (if present) are written outside the square brackets.

•The formula for a coordination complex will consist of a metal and some number of ligands.

•Be sure that you differentiate between ligands (that are enclosed within the square brackets) and counter ions (that are outside of the square brackets).

•Consider these examples:



Nomenclature of Coordination Compounds:

•See the lecture notes or the textbook pages 713-714.

Determining the oxidation state of a metal in a coordination compound:

•Consider the overall charge on the compound (or complex).

•Account for the charges of any counter ions in order to determine the charge on the coordination complex.

•Account for the charges of the ligands in order to determine the oxidation state of the metal.

Determining the number of *d* electrons on the metal:

First count the total number of valence s and d electrons on the neutral metal atom.
Then subtract electrons for positive oxidation states or add electrons for negative oxidation states in order to determine the total number of d electrons on the metal.
Note that in coordination complexes, metals have no valence s electrons. The interaction of the ligands with the metal causes any s electrons (if they would have otherwise still been there) to have been promoted into the d orbitals.

•For example, if a coordination complex has iron, Fe, with an oxidation state of 0, then the iron will have 8 d electrons. (Despite the fact that the electron configuration of a neutral iron atom is [Ar]4s²3d⁶.)

Writing the electron configurations for the *d*-orbitals of a coordination complex:

•The *d* orbitals of the metal split into different energy levels when the metal forms a coordination complex.

•The way in which the orbitals split depends on the coordination number (i.e. how many ligands there are) and the geometry of the ligands around the metal.

•In this class, we will only be drawing the electron configurations for octahedral coordination complexes with six ligands.

•In octahedral complexes, the *d* orbitals split as follows:

$$\Delta \oint \begin{array}{c} e_{g} & \overline{d_{x2-y2}} & \overline{d_{z2}} \\ t_{2g} & \overline{d_{xy}} & \overline{d_{xz}} & \overline{d_{yz}} \end{array}$$

•In this diagram, Δ represents the energy difference between the three lower-energy orbitals and the two higher-energy orbitals.

•The size of Δ is dependent on the types of ligands, according to the **spectrochemical series**:

$$Cl^{-} < F^{-} < H_2O < NH_3 < en < NO_2^{-} < CN^{-}$$

Weak-field ligands Smaller Δ Strong-field ligands Larger Δ

•When placing the *d* electrons into the *d* orbitals for a coordination complex, there are 2 possible ways to fill the orbitals.

•If Δ is small, then the complex is called "high-spin" and electrons fill one electron per orbital until all five orbitals have one electron, before the electrons pair up with each other.

•If Δ is large, then the complex is called "low-spin" and electrons fill the three lower-energy orbitals completely first, before any electrons are added to the higher-energy orbitals.

•Note that the distinction between high-spin and low-spin complexes only exists when there are between 4 and 7 d electrons. (If there are fewer than 4 or more than 7 electrons, then either method of filling the orbitals with electrons will yield the same electron configuration, so there is no distinction between high-spin and low-spin.)



Weak-field ligands Small Δ High-spin complex (d⁴ to d⁷ only)



Strong-field ligands Large Δ Low-spin complex (d⁴ to d⁷ only)

Determining the color of a coordination complex:

Coordination compounds are often colored because the energy gap between the *d* orbitals typically corresponds to wavelengths of light in the visible spectrum.
When a photon of light is absorbed, an electron is promoted from a lower-energy *d* orbital to a higher-energy *d* orbital.

•The substance will appear the **opposite** color of the light that is absorbed, based on the color wheel:



•For example, if a complex absorbs orange light, then the complex will appear blue.

•The wavelength (or the energy) of the light absorbed is dependent on the size of the energy gap Δ . A small Δ will result in low energy light being absorbed, whereas a larger Δ will result in higher energy light being absorbed. Thus we can relate the size of the energy gap Δ , which we have already seen is a result of the types of ligands bound to the metal, with the color of light absorbed and consequently the color that a complex appears:



•If a complex is unable to absorb visible light, then it will be colorless.

•A complex in which electrons cannot be promoted from the lower to the higher energy level is colorless.

•One example is a metal with 10 *d* electrons. Since all *d* orbitals are completely filled, no electrons can be promoted, and the complex will be colorless.

•Another example is a high-spin complex with 5 d electrons. The electrons are not able to "flip" their spin when they are promoted, so with 5 d electrons high-spin none of the electrons can be promoted.

Drawing Isomers of coordination complexes:

•We will be drawing isomers of octahedral coordination complexes, using an octahedral template:



•The goal is to draw all possible *different* arrangements of the ligands around the central metal, without repeating any structures.

•If you have 2 of a single ligand, they can be arranged either **trans** (directly opposite each other) or **cis** (next to each other):



•If you have 3 of a single ligand, they can be arranged either **mer** (meridial, with two of the ligands trans) or **fac** (facial, or on one face, with all ligands cis to each other):



•An easy way to keep track of what structures you have drawn is to list what is trans to what. An octahedral structure will have three trans relationships, and listing these can help you determine if you have drawn a unique structure or if you have repeated a structure that has already been drawn. For example:

> $\begin{array}{c|c} Br \\ CI \\ M \\ CI \\ H \\ OH_2 \end{array}$ $\begin{array}{c|c} Has the following trans relationships: \\ Br-Br \\ CI-H_2O \\$ Cl-NH₃

- •Finally, after you have drawn a structure, you must determine if it is chiral or achiral. •A chiral structure is not superimposable on its mirror image.
 - •The mirror image of a chiral structure is called an **enantiomer**.
 - •A chiral structure will not have an internal plane of symmetry.
 - •An achiral structure is superimposable on its mirror image.
 - •The mirror image of an achiral structure is the exact same structure.
 - •An achiral structure will have an internal plane of symmetry.
- •An easy test for chirality in octahedral complexes is to look at the trans relationships. •If a ligand is trans to itself, the structure must be achiral:



Br is trans to Br, so this structure **must** be achiral regardless of what ligands are in the other 4 positions.

•If there is a pair of matching trans ligands, the structure must be achiral:



Br_M, Br is trans to Cl and another Br is trans to another Cl. This structure **must** be achiral, regardless of what ligands are in the other 2 positions.

•If neither of the above conditions are met, then the structure must be chiral. (***NOTE: The above rules only apply to monodentate ligands. Bidentate and Tridentate ligands can present scenarios that violate these rules.)

•If a structure is chiral, then you can draw its mirror image (enantiomer) as a separate isomer:

