Experiment

DO Ni^{2+} AND Cu^{2+} FORM BIS- OR TRIS- COMPLEXES

A CCLI EXPERIMENT

Computers in Chemistry Laboratory Initiative

LEARNING OBJECTIVES

The objectives of this experiment are to . . .

- understand how a simple calorimeter is used to determine the maximum number of ethylenediamine molecules that will chelate to aqueous Ni^{2+} and $Cu^{2}+$.
- understand the effect of structure of a coordination compound on its reactions.

BACKGROUND

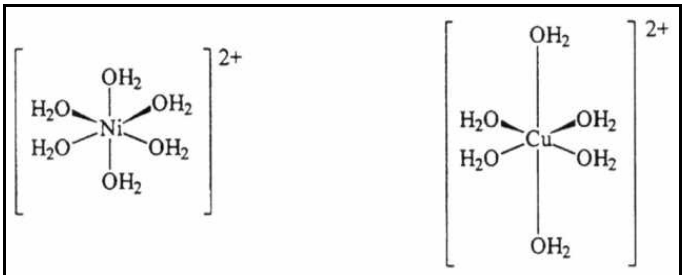

Figure 1. Diagrams showing the octahedral structure of the $[Ni(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$complexes, illustrating the longer axial distances of the copper complex.

The +2 oxidation state is very common in transition metal complexes. Transition metal ions combine easily with neutral molecules or anions (ligands) to form coordination complexes. The number of ligands that bind to a metal center (its coordination number) may vary, depending on various factors. Most complexes have the coordination number of six, and in almost all of these complexes, the ligands are arranged around the metal center in octahedral geometry. In this experiment, we will study reactions of two octahedral complexes: $[Ni(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$. The nickel complex exhibits the usual, very symmetrical, octahedral geometry. However, in the copper complex, the octahedron is distorted with two bonds longer than the remaining four, as shown in Figure 1.

Almost all Cu2+ complexes are distorted in this way for electronic reasons.

Other ligands may replace the H_2O molecules in these complexes. For example, an ammine complex of nickel is formed when NH_3 molecules react with $[Ni(H_2O)_6]^{2+}$:

NH_3 molecules displace H_2O in a stepwise fashion, and each replacement is accompanied by the evolution of heat. For example, the first two steps in the above reaction are:

$$[Ni(H_2O)_6]^{2+} + NH_3 \Leftrightarrow [Ni(H_2O)_5(NH_3)]^{2+} + H_2O \quad \Delta H = -17 \text{ kJ}$$

$$[Ni(H_2O)_5(NH_3)]^{2+} + NH3 \Leftrightarrow [Ni(H_2O)_4(NH_3)_2]^{2+} + H_2O \quad \Delta H = -17 \text{ kJ}$$

The various steps in the replacement of H_2O by NH_3 can be schematically represented in Figure 2.

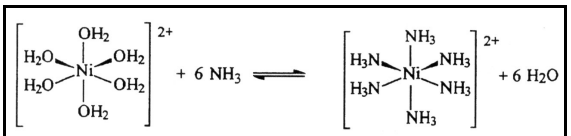

Figure 2. Diagram showing the replacement of water molecules by ammonia molecules in the nickel complex.

This reaction is generally represented as:

$$M + L \Leftrightarrow ML + \Delta H_1$$

$$ML + L \Leftrightarrow ML_2 + \Delta H_2$$

$$ML_2 + L \Leftrightarrow ML_3 + \Delta H_3$$

$$\vdots$$

$$ML_5 + L \Leftrightarrow ML_6 + \Delta H_6$$

Typically, as ligand is added to the solution of metal ion, ML is formed first. As the addition of ligand is continued, the ML_2 concentration rises, while the ML concentration drops. Then ML_3 becomes dominant with ML and ML2 becoming unimportant. This process continues until the highest complex, ML_6, is formed to the nearly complete exclusion of all others.

If the ligand in a substitution process is polydentate, it may displace as many H_2O molecules as there are points of attachment in the ligand. Ethylenediamine, $H_2NCH_2CH_2NH_2$, is a bidentate ligand, since it can attach to a metal center with its two nitrogen atoms. Such a ligand is also called a chelating ligand. Thus, ethylenediamine (*en*) displaces H_2O molecules in $[Ni(H_2O)_6]^{2+}$ two at a time, in three steps. Each replacement occurs with evolution of heat. When all six water molecules are replaced, a symmetrical, tris-chelate structure is obtained, as shown in Figure 3.

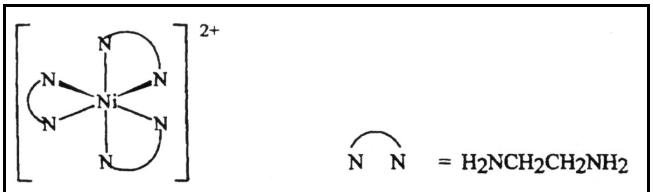

Figure 3. The replacement of 6 water molecules by 3 ethylenediamine molecules in the $[Ni(H_2O)_6]^{2+}$ complex ion, producing the $[Ni(en)_3]^{2+}$ complex ion.

The $[Cu(H_2O)_4(NH_3)_2]^{2+}$ complex poses an interesting question. As mentioned earlier, most copper(II) complexes are thermodynamically stable in a distorted geometry. Chelation by three ethylenediamine ligands would force a symmetrical structure, as in the nickel complex, since the length of the *"en"* skeleton is fixed. It remains to be seen whether the symmetry requirement will overcome the electronic factors. The purpose of this experiment is to determine which of the copper complexes will be formed: the distorted bis-chelate or the symmetrical tris-chelate.

When aqueous $[Ni(H_2O)_4(NH_3)_2]^{2+}$ and $[Cu(H_2O)_4(NH_3)_2]^{2+}$ complexes react successively with several increments of ethylenediamine, each replacement of two water molecules with the *"en"* occurs with evolution of heat. By measuring the evolved heat, it is possible to determine the maximum number of ethylenediamine molecules that have chelated in each complex ion.

A series of trials will be performed on each complex in a calorimeter. A solution of one of the hexaquo complex ions will be reacted with an equimolar amount of *"en"*. The heat of reaction will be determined from the increase in temperature of the solution. The reaction mixture will then be cooled down to the initial temperature to ensure that both reactants are at the same temperature at the onset of each reaction, and a

second equivalent of *"en"* will be added. The process will be repeated until the addition of the next equivalent of *"en"* fails to produce a significant temperature change.

The nested beakers calorimeter will be used in this experiment. The reactions will be carried out in the inner beaker and the temperature change (ΔT) will be measured. Assuming adiabatic conditions (no heat loss), the reaction heat all goes into warming the solution *and* beakers. This heat quantity can be calculated as follows:

Heat = (specific heat of solution) x (grams solution) x (ΔT) + (heat capacity of beakers) x (ΔT)

The solutions of both complexes have very similar specific heats equal to approximately 3.8 J/g °C and densities of 1.1 g/ml. The estimated beakers' heat capacity is 30 J/ °C. The final heat of reaction calculation requires a conversion from concentration of the limiting reactant (*en*) to moles, as expressed in the equation:

$$\Delta H = \frac{\text{Heat}}{\text{Moles}}$$

Temperature measurement in this experiment is made with a Temperature probe. The ***MicroLAB*** program **Temp.Time.exp** will be used to determine the temperature vs. time data for the two reactions.

From these plots, ΔT values will be determined.

SAFETY PRECAUTIONS

As usual, any skin contacted with reagents should be washed immediately. Safety goggles must be worn at all times in the lab. Ethylenediamine must be handled with extreme care: it should be dispensed in the fumehood and gloves should be worn while handling this compound. Dispose of the wastes into the special containers provided in the fumehood.

BEFORE PERFORMING THIS EXPERIMENT . . .

... you will need a ***MicroLAB*** program capable of collecting temperature readings as a function of time. Use **temp.time.exp** for this.

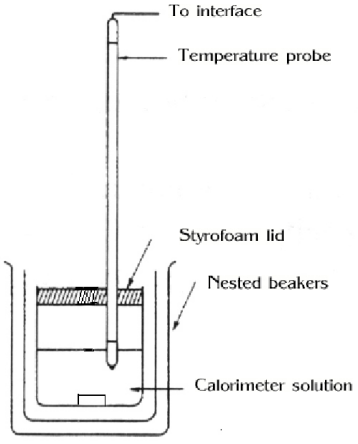

Figure 4. Schematic of calorimeter arrangement of nested beakers, Styrofoam lid and temperature probe.

EXPERIMENTAL PROCEDURE

Temperature probe calibration

Calibrate your temperature probe using an ice/water mixture for the lower temperature calibration and hot tap water for the upper two temperature calibrations.

Reaction of $[Ni(H_2O)_4(NH_3)_2]^{2+}$ with ethylenediamine

1. Pour 50 ml of 0.15 *M* $[Ni(H_2O)_4(NH_3)_2]^{2+}$ solution into a 100 ml beaker, using a graduated cylinder.
2. Prepare the calorimeter by nesting together 100, 250, 400 and 600 ml beakers. Thread the stirring rod and temperature probe through the Styrofoam lid and position the lid on the inner beaker. The temperature probe should be as deep in solution as possible, but without touching the glass. Let the apparatus stand so that the components attain the same temperature.
3. Put on gloves. **In the fumehood**, dispense exactly 5 ml of 1.5 *M* ethylenediamine into a 10 cm test tube. Stopper the test tube before removing it from the fumehood. *Keep your test tube in the test tube block.*
4. Start the ***MicroLAB*** program and collect data for about two minutes. Set the stirring to vigorous without splashing. Record this temperature in your lab notes (**t1**)
5. Lift the calorimeter lid momentarily and add the 5 ml of *"en"* to the inner beaker *carefully*, but rapidly until a well defined temperature trend (cooling or constant) is established (~3 min.).
6. Carefully remove the inner beaker and place it in a cold water bath. Continue to monitor temperature and stir the solution with the temperature probe. Remove the beaker from the bath when the temperature is about 0.1 °C lower than the initial temperature (**t1**). Dry the beaker on the outside and return it to the calorimeter. Make sure that the temperature does not differ from t1 by more than 0.1 °C. Let the apparatus stand, with continued stirring, so that the components attain the same temperature (t1 ± 0.1 °C).
7. You are now ready for the next trial. Repeat steps 2, through 5 as many times as necessary, until you are convinced that no more *"en"* molecules react with the complex. Stop the program.

Reaction of $[Cu(H_2O)_4(NH_3)_2]^{2+}$ with ethylenediamine

1. Repeat the experiment exactly as above using 0.15 *M* $[Cu(H_2O)_4(NH_3)_2]^{2+}$ solution instead of $[Ni(H_2O)_4(NH_3)_2]^{2+}$.

DATA ANALYSIS

1. Reload the data files for each of the above experiments and print the graphs of your data. **DO NOT PRINT DATA TABLES.**
2. From your plot of temperature versus time, determine the initial and final temperatures (t_i and t_f) for each step in both reactions. Calculate the heats of reaction per mole of ethylenediamine for the two reactions.