Investigation of Nickel and Copper Coordination Complexes

Learning Objectives

The objectives of this experiment are to

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

Background

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 coordination number, the number of ligands that bind to a metal center may vary, depending on various factors. Most complexes have a coordination number of 6, 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: \([\text{Ni(H}_2\text{O)}_6]^{2+}\) and \([\text{Cu(H}_2\text{O)}_6]^{2+}\). 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:

\[
\text{[Ni(H}_2\text{O)}_6]^{2+} \quad \text{[Cu(H}_2\text{O)}_6]^{2+}
\]

Almost all Cu$^{2+}$ complexes are distorted in this way for electronic reasons.

Other ligands may replace the H$_2$O molecules in these complexes. For example, an ammine complex of nickel is formed when NH$_3$ molecules react with \([\text{Ni(H}_2\text{O)}_6]^{2+}\):

\[
\left[\begin{array}{c}
\text{H}_2\text{O} \\
\text{H}_2\text{O} \\
\text{H}_2\text{O} \\
\text{H}_2\text{O} \\
\text{H}_2\text{O} \\
\text{H}_2\text{O}
\end{array}\right]^{2+} + 6\text{NH}_3 \rightleftharpoons \left[\begin{array}{c}
\text{H}_2\text{O} \\
\text{H}_2\text{O} \\
\text{H}_2\text{O} \\
\text{H}_2\text{O} \\
\text{NH}_3 \\
\text{NH}_3
\end{array}\right]^{2+} + 6\text{H}_2\text{O}
\]

NH$_3$ molecules displace H$_2$O in a stepwise fashion, and each replacement is accompanied by the evolution of heat. The reaction:

\[
[\text{Ni(H}_2\text{O)}_6]^{2+} + \text{NH}_3 \rightleftharpoons [\text{Ni(H}_2\text{O)}_5(\text{NH})_2]^{2+} + \text{H}_2\text{O} \quad \Delta H = -17 \text{ kJ/mol}
\]

is followed by

\[
[\text{Ni(H}_2\text{O)}_5(\text{NH})_2]^{2+} + \text{NH}_3 \rightleftharpoons [\text{Ni(H}_2\text{O)}_4(\text{NH})_3]^{2+} + \text{H}_2\text{O} \quad \Delta H = -17 \text{ kJ/mol}
\]

and so on, until all the water molecules are replaced by ammonia. It can be schematically represented in the
following way:

\[
\begin{align*}
M + L & \leftrightarrow ML & \Delta H_1 \\
ML + L & \leftrightarrow ML_2 & \Delta H_2 \\
ML_2 + L & \leftrightarrow ML_3 & \Delta H_3 \\
\vdots & \vdots & \vdots \\
ML_{n-1} + L & \leftrightarrow ML_n & \Delta H_n
\end{align*}
\]

Typically, as ligand is added to the solution of metal ion, ML is formed first. As the addition of ligand is continued, the ML₂ concentration rises, while the ML concentration drops. Then ML₃ becomes dominant with ML and ML₂ becoming unimportant. This process continues until the highest complex, MLₙ, is formed to the nearly complete exclusion of all others.

If the ligand in a substitution process is polydentate, it may displace as many H₂O molecules as there are points of attachment in the ligand. Ethylenediamine, H₂NCH₂CH₂NH₂, 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 H₂O molecules in [Ni(H₂O)₆]²⁺ two at a time, in a maximum of three steps. Again each replacement occurs with evolution of heat.

\[
\begin{align*}
\left[ \begin{array}{c}
\text{H}_2\text{O} \\
\text{H}_2\text{O} \\
\text{OH}_2 \\
\end{array} \right]^{2+} + \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 & \leftrightarrow \left[ \begin{array}{c}
\text{H}_2\text{O} \\
\text{H}_2\text{O} \\
\text{OH}_2 \\
\end{array} \right]^{2+} + 2\text{H}_2\text{O}
\end{align*}
\]

When all six water molecules are replaced, a symmetrical, tris-chelate structure is obtained:

\[
\begin{align*}
\text{N} & \text{N} \\
\text{N} & \text{N} \\
\text{N} & \text{N}
\end{align*}
\]

\[\text{N} \text{N} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2\]

The [Cu(H₂O)₆]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(H₂O)₆]²⁺ and [Cu(H₂O)₆]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 hexaaqua complex
ion 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 process will be repeated until the addition of the next equivalent of en fails to produce a significant temperature change.

The nested coffee cup 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:

\[
\text{Heat} = (\text{specific heat of solution}) \times (\text{total grams solution}) \times (\Delta T) \quad \text{or} \quad q = s \times m \times \Delta T
\]

The solutions of both complexes have a very similar specific heat equal to approximately 3.8 J/g°C and density of 1.1 g/mL. The final enthalpy of reaction calculation requires a conversion from concentration of the limiting reactant (en) to moles, as expressed in the equation:

\[
\Delta H = \frac{q}{\text{moles}}
\]

Temperature measurement in this experiment is made with a thermistor. Temperature vs. time data will be plotted 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.

**Experimental Procedure**

**Thermistor calibration**

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

**Reaction of \([\text{Ni(H}_2\text{O)}_6]^{2+}\) with ethylenediamine**

1. Pour 50 mL of 0.15 M \([\text{Ni(H}_2\text{O)}_6]^{2+}\) solution into your calorimeter, using a graduated cylinder. Note the color of the solution.
2. Record the temperature of the solution.
3. Put gloves on. 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. Lift the calorimeter lid momentarily, note the solution color, and then add 5 mL of en to the calorimeter carefully, but rapidly. Stirring thoroughly, record the temperature every 15 seconds for about 3 minutes.
5. You are now ready for the next addition. Repeat steps 3 and 4 two more times.

**Reaction of \([\text{Cu(H}_2\text{O)}_6]^{2+}\) with ethylenediamine**

1. Repeat the experiment exactly as above using 0.15 M \([\text{Cu(H}_2\text{O)}_6]^{2+}\) solution instead of \([\text{Ni(H}_2\text{O)}_6]^{2+}\).
Data Analysis & Results

1. Plot and print the graphs of your data, temperature vs. time. Include a line to connect the data points. In Excel, choose the “scatter with data points connected by smoothed lines” chart sub-type.

2. From your plot of temperature against time, determine the initial and final temperatures (T_i and T_f) for each step in both the Ni and Cu reaction sequences. For each addition (step) calculate the enthalpy of reaction per mole of ethylenediamine for both metals. Report an average enthalpy of reaction for each metal.

3. How many molecules of ethylenediamine react with each molecule of \([\text{Ni(H}_2\text{O)}_6]^{2+}\) and with \([\text{Cu(H}_2\text{O)}_6]^{2+}\)? In other words, how many ethylenediamine additions resulted in a rise in temperature. Justify your results in your conclusion section.

4. Report the colors of the solutions before each addition. Address why you think the color changed during the reaction in your conclusion.