Chemistry 213

INVESTIGATION OF NICKEL AND COPPER COORDINATION COMPLEXES

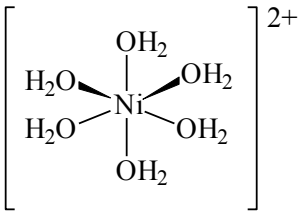
LEARNING OBJECTIVES

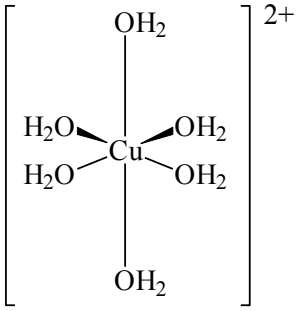
The objectives of this experiment are to

- 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

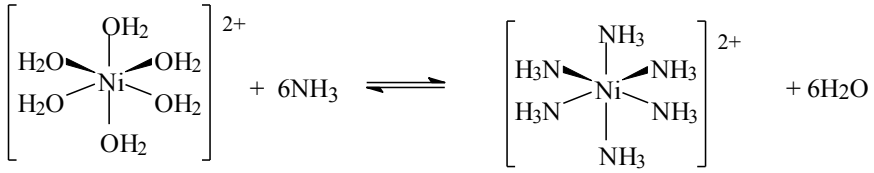
The +2 oxidation state is very common in transition metal complexes. Transition metal ions combine easily with neutral molecules or anions (ligands) to form coordination complexes. The number of ligands that bind to a metal center (its coordination number) may vary, depending on various factors. Most complexes have the coordination number of 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: $Ni(H_2O)_6^{2+}$ 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:





$[Ni(H_2O)_6]^{2+}$ $[Cu(H_2O)_6]^{2+}$

Almost all Cu^{2+} complexes are distorted in this way for electronic reasons.
Other ligands may replace the H_2O molecules in these complexes. For example, an amine 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. The reaction:

$$Ni(H_2O)_6^{2+} + NH_3 \rightleftarrows Ni(H_2O)_5(NH_3)^{2+} + H_2O \qquad \Delta H = -17 kJ/mol$$

is followed by

$$Ni(H_2O)_5(NH_3)^{2+} + NH_3 \rightleftarrows Ni(H_2O)_4(NH_3)_2^{2+} + H_2O \qquad \Delta H = -17 kJ/mol$$

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

$$M + L = ML \qquad \Delta H_1$$

$$ML + L = ML_2 \qquad \Delta H_2$$

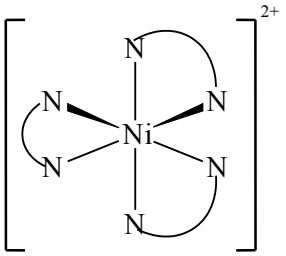
$$ML_2 + L = ML_3 \qquad \Delta H_3$$

$$ML_{n-1} + L = ML_n \qquad \Delta H_n$$

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 ML_2 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:



The $Cu(H_2O)_6^{2+}$ 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 $Ni(H_2O)_6^{2+}$ and $Cu(H_2O)_6^{2+}$ 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:

$$\text{Heat} = (\text{specific heat of solution}) \times (\text{grams solution}) \times (\Delta T)$$

The solutions of both complexes have a very similar specific heat equal to app. 3.8 J/g^{o} C and density of 1.1 g/mL. 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 thermistor. The LabWorks **Spreadsheet** program will be used to graph 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.

EXPERIMENTAL PROCEDURE

Reaction of $Ni(H_2O)_6^{2+}$ with ethylenediamine

1. Pour 50 mL of 0.15 *M* $Ni(H_2O)_6^{2+}$ solution into your calorimeter, using a graduated cylinder.

2. Put your gloves on. **In the fumehood**, dispense 5.00 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.*

Note: ethylenediamine should be dispensed in the fume hood.
Wear the gloves while handling this compound.

3. Record the temperature of the solution in the calorimeter then lift the calorimeter lid momentarily and add the 5 mL of *en* to the inner beaker *carefully*, but rapidly. Stirring thoroughly, record temperature and time for about three minutes.

4. You are now ready for the next trial. Repeat steps 2 and 3 as many times as necessary, until you are convinced that no more *en* molecules react with the complex.

Reaction of $Cu(H_2O)_6^{2+}$ with ethylenediamine

1. Repeat the experiment exactly as above using 0.15 *M* $Cu(H_2O)_6^{2+}$ solution instead of $Ni(H_2O)_6^{2+}$.

DATA ANALYSIS

1. Data analysis is to be done individually. Open a blank Excel workbook and **do all graphing and calculations in the workbook**. Submit the Rxcel file to the D2L Assignment folder.

2. Make sure all work is properly labeled and easy to follow. Graphs and tables should be done in a neat and orderly fashion.

3. Make a graph for each experiment where you overlay the time and temperature plot (Save in a separate tab). Use the graphs to determine the initial and final temperatures (t_i and t_f) for each step in both reactions.

4. Make a table where you calculate the heats of reaction per mole of ethylenediamine for each step. Calculate the average ΔH for each of the two reactions (Highlight in yellow).

5. Write a sentence stating how many molecules of ethylenediamine react with each molecule of $Ni(H_2O)_6^{2+}$ and with $Cu(H_2O)_6^{2+}$ with a brief explanation.