Experiment

Determining the Coordination Number of Ni^{2+} and Cu^{2+} by Enthalpy

The CCLI Initiative

Computers in Chemistry Laboratory Instruction

LEARNING OBJECTIVES

The objectives of this experiment are to . . .

- investigate the formula of the complexes formed between Ni^{2+} and ethylenediamine (en) and between Cu^{2+} and "en".
- determine the maximum number of "en" molecules that will bind to Ni^{2+} and Cu^{2+} by making heat of reaction measurements with the ***MicroLAB*** interface.
- calculate heats of reaction for the various Ni^{2+}/"en" and Cu^{2+}/"en" complexes to determine their coordination numbers.

BACKGROUND

When a metal ion such as Ni^{2+} is present in aqueous solution, it interacts with solvent water molecules and forms what is called a complex ion. For Ni^{2+} the complex ion has the formula $[Ni(OH_2)_6]^{2+}$. The complex has an octahedral geometry as shown in Figure 1.

There is some terminology that is used when describing complex ions. The metal ion is called the **central metal ion** and the molecules bonded to the central metal ion are called **ligands**. In this example the central metal ion is Ni^{2+} and the ligand is H_2O. There is a limit to the number of bonds that a central metal ion can form with ligands. In the above example this number is six. This maximum bond number is called the **coordination number** of the central metal ion. Hence the coordination number of Ni^{2+} is six. Six is a very common coordination number but certainly not the only possibility. For other central metal ions, coordination numbers of two, three, four, five, seven and eight are known as well.

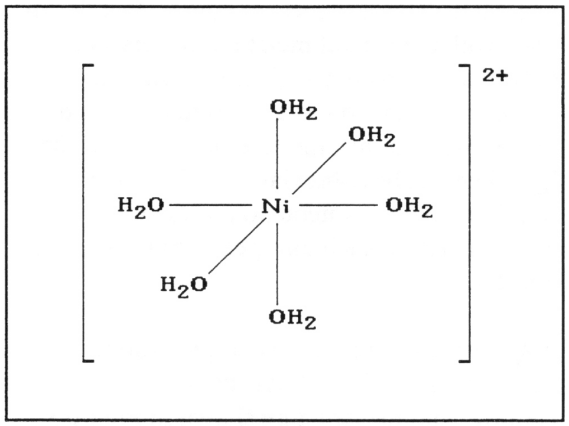

Figure 1. Structure of $Ni(OH_2)_6^{2+}$

As shown in Figure 1, bonding occurs between the Ni^{2+} ion and the *oxygen atom* in the water molecule. Recall that the oxygen atom in H_2O contains two lone electron pairs. *Ligands must always have at least one lone electron pair to bond to the central metal ion.*

If ligands other than water molecules are available in

solution, they can selectively bond to the central metal ion and displace the original water ligands. An example is ammonia, NH_3. If NH_3 is added to a solution containing $[Ni(OH_2)_6]^{2+}$, the complex $[Ni(NH_3)_6]^{2+}$ is formed. Its structure is shown in Figure 2. You probably have observed this reaction in the laboratory. If ammonia is added to an aqueous solution of $Ni(NO_3)_2$, the solution color changes from light green to a sky blue. The green color is due to the presence of $[Ni(OH_2)_6]^{2+}$ and the blue color denotes the presence of $[Ni(NH_3)_6]^{2+}$. Note that even though the ligand has changed, the coordination number of Ni^{2+} remains the same. Note as well that the bonding occurs between the Ni^{2+} ion and the *nitrogen atom* in the ammonia molecule because the nitrogen atom contains the lone electron pair.

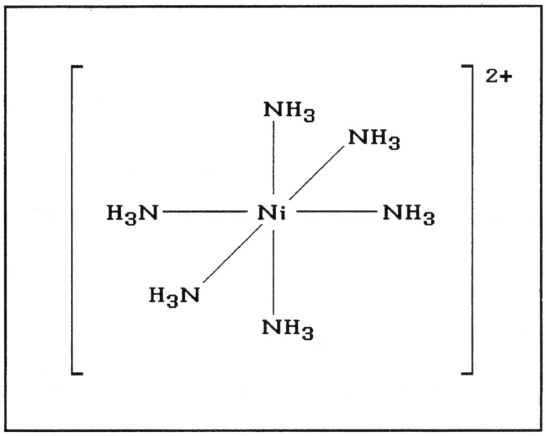

Figure 2. Structure of $Ni(NH_3)_6^{2+}$

Some ligands have a structure which allows them to form more than one bond with the central metal ion. An example is the molecule ethylenediamine (abbreviated "en"). The formula for "en" is $H_2NCH_2CH_2NH_2$. Each nitrogen atom in **"en"** has a lone electron pair and can bond to the central metal ion. This assumes, of course, that the "en" molecule is long enough to allow each nitrogen to bond with the central metal ion at adjacent coordination positions. Since the carbon atoms in **"en"** function as a chain to connect the two nitrogen atoms, the relevant nature of the ligand "en" can be abbreviated as: **N----N**. Bonding involves interaction of the free electron pair on each nitrogen with the central metal ion.

A specific example is the complex formed between Ni^{2+} and "en". It has the formula $[Ni(en)_3]^{2+}$ and the structure shown in Figure 3. Since Ni^{2+} has coordination number six and each "en" can occupy two coordination positions, three molecules of "en" react with each Ni^{2+} ion.

The reaction between $[Ni(OH_2)_6]^{2+}$ and "en" is rapid and quite exothermic. See Table 1 below.

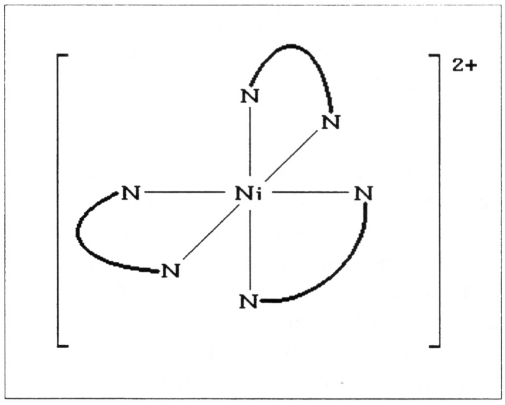

Figure 3. Structure of $Ni(en)_3^{2+}$

Table 1: Heats of Reaction of $Ni(OH_2)_6^{2+}$ with Ethylenediamine

Reaction							Δ H (kJ/mol Ni)
$[Ni(OH_2)_6]^{2+}$	+	"en"	⇔	$[Ni(OH_2)_4(en)]^{2+}$	+	$2\ H_2O$	−38
$[Ni(OH_2)_6]^{2+}$	+	2 "en"	⇔	$[Ni(OH_2)_2\ (en)_2]^{2+}$	+	$4\ H_2O$	−76
$[Ni(OH_2)_6]^{2+}$	+	3 "en"	⇔	$[Ni(en)_3]^{2+}$	+	$6\ H_2O$	−117

The maximum number of "en" molecules which will bind to Ni^{2+} can be verified by the following series of experiments in combination with the data in Table 1.

Experiment 1 Reaction of $[Ni(OH_2)_6]^{2+}$ with **"en"** in aqueous solution in a **1:1** molar ratio. Since the reaction is exothermic, the temperature of the reaction mixture will increase. If the temperature increase is measured with the ***MicroLAB*** interface, the heat of reaction in kJ/mol Ni can be calculated.

Experiment 2 Reaction of $[Ni(OH_2)_6]^{2+}$ with "en" in a **1:2** molar ratio. Again ΔT for the reaction mixture is measured and the heat of reaction is calculated. According to Table 1, the temperature change for Experiment 2 should be considerably larger than that for Experiment 1 and the heat of reaction should double.

Experiment 3 Reaction of $[Ni(OH_2)_6]^{2+}$ with "en" in a **1:3** molar ratio. ΔT is again measured and the heat of reaction calculated. Relative to Experiments 1 and 2, Table 1 predicts an even greater temperature change and heat of reaction.

Experiment 4 Reaction of $[Ni(OH_2)_6]^{2+}$ with "en" in a **1:4** molar ratio. Since all six coordination positions of Ni^{2+} are occupied by "en" with a ratio of 1 mol Ni to 3 mol "en", the results of Experiment 4 should be very similar to Experiment 3 indicating a maximum Ni to "en" mole ratio of 1:3.

If the results of Experiments 1 through 4 follow our predictions, the formula of the complex formed will have been verified as $[Ni(en)_3]^{2+}$, i.e., a maximum of 3 molecules of "en" for each Ni^{2+} ion. ***A major goal of this exercise is to carry out the above experiments and determine the maximum number of "en" molecules that will bind to*** Ni^{2+}.

Cu^{2+} ion, like Ni^{2+} ion, has a coordination number of six. In $[Ni(OH_2)_6]^{2+}$, however, all six Ni–O bonds have the same length. Such is not the case for $[Cu(OH_2)_6]^{2+}$. The $[Cu(OH_2)_6]^{2+}$ octahedron is distorted with four Cu–O bonds much shorter than the other two Cu–O bonds as shown in Figure 4.

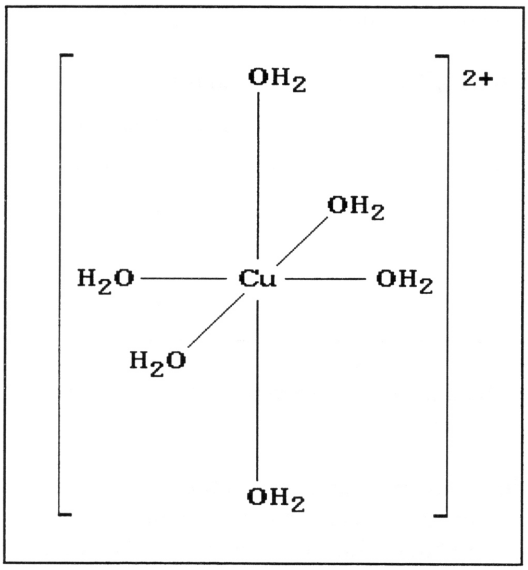

Figure 4. Structure of $Cu(OH_2)_6$

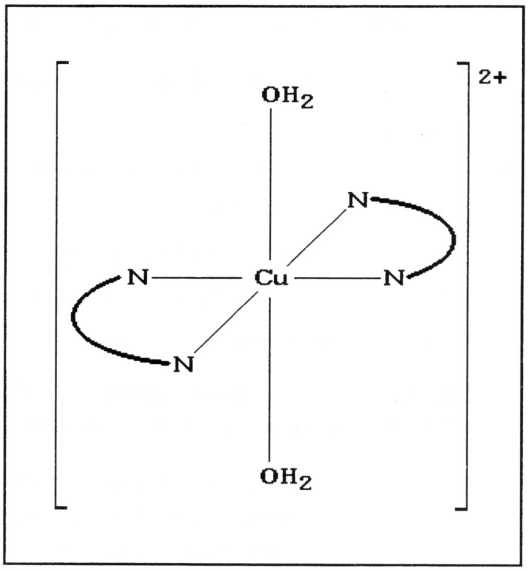

Figure 5. Possible Cu-en Structure

The four shorter Cu–O bonds form a square planar arrangement with the two longer bonds above and below the plane in two axial positions. Because of these bond length differences, it remains to be seen whether or not three "en" molecules can coordinate to Cu^{2+}. Because the carbon chain in "en" is fixed in length, it may be that an "en" molecule is not long enough to bond from a planar position up or down to an axial position. If this is the case, one would expect to be able to coordinate only two "en" molecules to Cu^{2+}. See Figure 5. If so, the predicted formula for the complex formed between $[Cu(OH_2)_6]^{2+}$ and "en" would be $[Cu(en)_2(OH_2)_2]^{2+}$, or a maximum of 2 "en" molecules for each Cu^{2+} ion. On the other hand, if the difference between planar and axial distances is not too great, 3 "en" molecules could coordinate to Cu^{2+} yielding a structure similar to the $[Ni(en)_3]^{2+}$ complex shown in Figure 3.

Analogous to $[Ni(OH_2)_6]^{2+}$ and "en", the reaction between $[Cu(OH_2)_6]^{2+}$ and "en" is rapid and quite exothermic. Hence an experimental scheme similar to that described on the preceding page can be used to determine the maximum number of "en" molecules that will bind to Cu^{2+}. ***A second major goal of this laboratory exercise is to carry out this experimental scheme and determine the maximum number of "en" molecules that will bind to Cu^{2+}.***

SAFETY PRECAUTIONS

Ethylenediamine is a basic, caustic substance. Any contacted skin should be washed immediately with soap and cool water. Any solutions containing Ni, Cu, or "en" should be placed in their respective waste bottles. Safety goggles must be worn at all times in the lab. As usual, wash hands with soap and water before leaving the lab.

BEFORE PERFORMING THIS EXPERIMENT . . .

... you will need a ***MicroLAB*** program capable of measuring and displaying temperature and time. Temperature readings should be taken every three seconds. Choose the **heat of solution** experiment under the **Time and Temperature** tab for this experiment.

EXPERIMENTAL PROCEDURE

Temperature probe calibration

Calibrate your temperature probe at three or more temperatures using an ice/water mixture for the lower temperature calibration and mixtures of cold and hot tap water (about 60°C) for the upper temperature calibrations.

Running the experiment

The calorimeter will consist of nested 100, 250, 400 and 600 ml beakers with a Styrofoam lid through which will intrude the temperature probe, which should penetrate as deep into the solution as possible without interfering with the stirring, and is then held in place with a rubber band. Insert a medium stirring bar into the inner beaker and place the assembly on top the stirrer. **Check** the stirring to insure that it works OK. Let the apparatus stand to attain thermal equilibrium while you prepare the solutions.

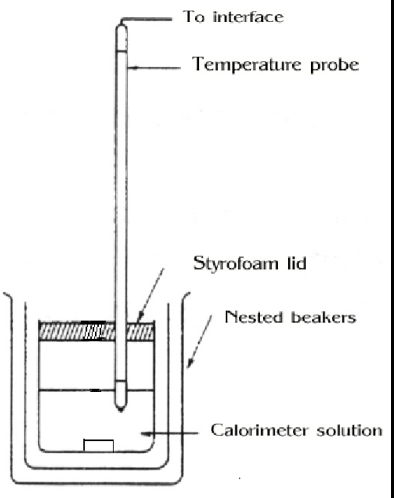

Figure 1. Schematic of calorimeter arrangement of nested beakers, Styrofoam lid and temperature probe.

The $Ni(OH_2)_6^{2+}$/ethylenediamine reaction series

1. Measure exactly 50ml of 0.15 *M* $NiSO_4$ solution into a clean, dry 50 or 100 ml graduated cylinder and dispense into the 100 ml inner beaker of the calorimeter. **Wearing gloves** and in the fume hood measure exactly 5.0 ml of 1.5 *M* ethylenediamine solution into a clean, dry 25 ml graduated cylinder and pour this into an appropriately sized test tube, **stopper before removing from the hood**, and immerse the 100 ml beaker and the test tube in a well stirred constant temperature bath at 25 °C, swirling the test tube frequently to hasten equilibration.
2. After several minutes, measure the temperature of each solution with the temperature probe. Rinse and dry the temperature probe after each measurement. ***The two solutions must not differ in temperature before the reaction is initiated***. If the two solutions differ in temperature, adjust such that both will be as close as possible to room temperature. Either cool the warmer solution in a tap water bath or warm the cooler solution in a warm water bath to approach room temperature.
3. When in thermal equilibrium, dry and transfer the $NiSO_4$ solution to the calorimeter and replace the Styrofoam lid and place the calorimeter on the magnetic. Adjust the stirring rate to vigorous but without splashing. Finally, insert the temperature probe, start the experiment program by clicking on **Start**, and collect a baseline temperature for60 about seconds.
4. **(Remember** that you will be performing several experiments and thus creating several data files. Be sure to give them different, distinguishable file names.) As the experiment starts, you should see successive, constant temperature readings of near room temperature. Allow these readings to continue for at least 60 seconds to establish an accurate initial temperature baseline value.
5. **Wearing gloves**, quickly but carefully transfer the ethylenediamine solution to the calorimeter. Reposition the temperature probe and lid assembly. As the reaction occurs, you should observe an increase in temperature. Continue taking data until a final, constant temperature plateau is well established or has a constant downward slope. The experiment can be stopped at that point.
6. Carefully remove the inner 100 ml beaker with the solution and place it in a cold water bath. Continue to stir and monitor the solution until the solution is 0.1 °C lower than the initial temperature **(t_1)**
7. Repeat steps two through six using exactly 5.0 ml of 1.5 *M* ethylenediamine.
8. Based on the results of these trials, decide whether further experimentation is warranted. If so, repeat Step seven, again using 5 ml of 1.5 *M* en followed, if necessary, by an additional 5.0 ml of 1.5 *M* "en".

The $Cu(OH_2)_6^{2+}$/ethylenediamine reaction series

This set of experiments is conducted in a manner identical to that described above except that 0.15 *M* $CuSO_4$ solution is used instead of 0.15 *M* $NiSO_4$.

Disposal: Dispose of all reacted solutions in the appropriate waste containers in the locations indicated by your instructor.

DATA ANALYSIS

In all experiments it can reasonably be assumed that the specific heat of the reaction solution is similar to water. Hence use a specific heat value of 4.18 J/(g°C) and a density of 1.00 g/ml for the reaction solution. The estimated calorimeter heat capacity is 1.0×10^1 J/°C.

Complete the following steps for the first trial and for each succeeding trial where a considerable increase

in the amount of heat evolved was observed compared to the preceding trial. ***Do this for both the $Ni(OH_2)_6^{2+}$ / "en" reaction trials and the $Cu(OH_2)_6^{2+}$ / "en" trials***.

1. Reopen each file in ***MicroLAB***. Obtain a printout of each graph if requested by your instructor.

2. Determine the final and initial temperatures for the reaction and calculate ΔT.

3. Calculate the heat of reaction, ΔH, for each trial. Write an equation for the reaction, indicating the number of moles of ethylenediamine reacting with one mole of metal ion. (See sample format in Table 1.)

4. Based on your results, indicate the maximum number of moles of ethylenediamine which can bind to one mole of metal ion. Write the correct formula for the complex ion.