1. Thermochemistry and Complex Ions

Introduction

Complexes and complex ions have been known since very late in the eighteenth century. However, their structures were not understood until Alfred Werner explained them almost a century later. Since then we have learned that these substances not only are commonplace but also have significant commercial usefulness as well as biological importance.

Although complexes and complex ions have diverse compositions and structures, they have one feature in common. Each has a metal atom or ion that is bound to a number of ligands through covalent bonds (Ebbing/Gammon, Section 23.3).

Purpose

The object of this experiment is to determine the maximum number of ethylenediamine molecules that will bind to a Cu^{2+} ion in aqueous solution. You will find the answer after you measure the heat that is evolved or absorbed when aqueous Cu^{2+} ions react with increments of ethylenediamine.

Background

The coordination number of a metal atom or ion in a complex is the total number of bonds between the metal and the ligands. The most common coordination number is 6 (Ebbing/Gammon, Section 23.3).

Many transition-metal ions will bond to several molecules of water. A complex ion with a coordination number of 6 is the usual result. For example, Ni^{2+} ions exist as $Ni(H_2O)_6{}^{2+}$ ions in aqueous solutions. The structure of this substance is octahedral, as shown in Figure 1.1.

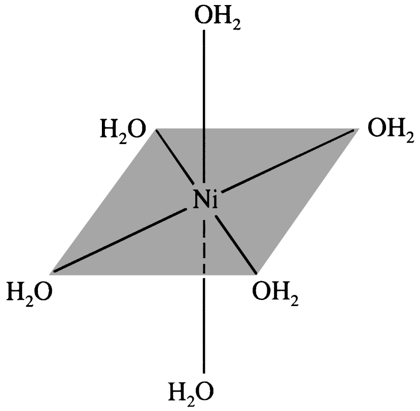

FIGURE 1.1
The octahedral structure of the $Ni(H_2O)_6{}^{2+}$ ion.

Table 1.1 Enthalpy Changes for the Reactions of NH_3 with $Ni(H_2O)_6^{2+}$

Reaction	ΔH (kJ/mol)
$Ni(H_2O)_6^{2+}(aq) + NH_3(aq) \rightarrow Ni(H_2O)_5(NH_3)^{2+}(aq) + H_2O(l)$	−17
$Ni(H_2O)_5(NH_3)^{2+}(aq) + NH_3(aq) \rightarrow Ni(H_2O)_4(NH_3)_2^{2+}(aq) + H_2O(l)$	−17
$Ni(H_2O)_4(NH_3)_2^{2+}(aq) + NH_3(aq) \rightarrow Ni(H_2O)_3(NH_3)_3^{2+}(aq) + H_2O(l)$	−17
$Ni(H_2O)_3(NH_3)_3^{2+}(aq) + NH_3(aq) \rightarrow Ni(H_2O)_2(NH_3)_4^{2+}(aq) + H_2O(l)$	−17
$Ni(H_2O)_2(NH_3)_4^{2+}(aq) + NH_3(aq) \rightarrow Ni(H_2O)(NH_3)_5^{2+}(aq) + H_2O(l)$	−18
$Ni(H_2O)(NH_3)_5^{2+}(aq) + NH_3(aq) \rightarrow Ni(NH_3)_6^{2+}(aq) + H_2O(l)$	−18

Other ligands may replace water in these complex ions. Each replacement is accompanied by the evolution or absorption of heat. For example, $Ni(H_2O)_6^{2+}$ reacts successively with six molecules of NH_3. Each of these reactions is exothermic. These reactions and their enthalpies are shown in Table 1.1. You will see that each reaction occurs with roughly the same change in enthalpy.

Both H_2O and NH_3 are monodentate ligands (Ebbing/Gammon, Section 23.3). Bidentate and polydentate ligands replace more than one molecule of water in these complex ions. For example, ethylenediamine ($H_2NCH_2CH_2NH_2$) replaces two *adjacent* molecules of water in a $Ni(H_2O)_6^{2+}$ ion, as shown in Figure 1.2. These molecules must be adjacent because the distance between the nitrogen atoms in ethylenediamine is not very large.

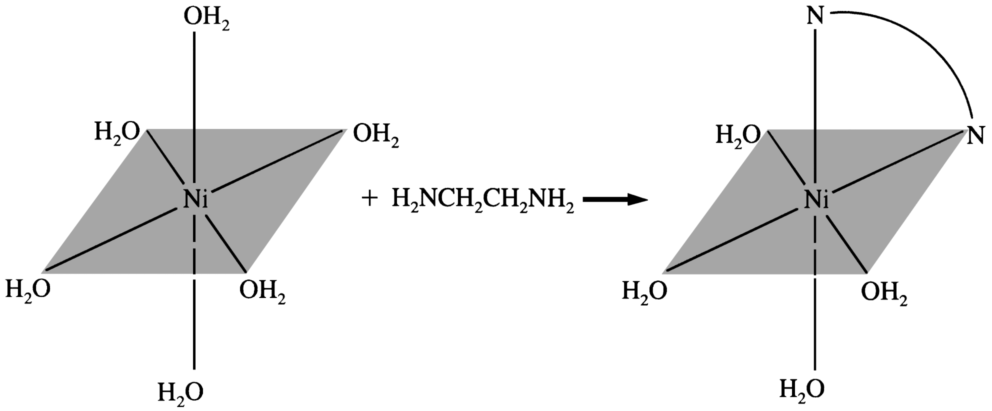

FIGURE 1.2 The reaction of ethylenediamine with the $Ni(H_2O)_6^{2+}$ ion. Note that $N^\frown N$ represents ethylenediamine.

There are six available sites in an octahedron, so three bidentate molecules of ethylenediamine replace six unidentate molecules of water. The three reactions leading to $Ni(en)_3^{2+}$ and the accompanying enthalpy changes are given in Table 1.2. (The universal abbreviation for ethylenediamine, en, is used throughout the table.) You will draw the structure of a $Ni(en)_3^{2+}$ ion in the Prelaboratory Assignment.

Table 1.2 Enthalpy Changes for the Reactions of Ethylenediamine with $Ni(H_2O)_6^{2+}$

Reaction	ΔH (kJ/mol)
$Ni(H_2O)_6^{2+}(aq) + en(aq) \rightarrow Ni(H_2O)_4(en)^{2+}(aq) + 2H_2O(l)$	−38
$Ni(H_2O)_4(en)^{2+}(aq) + en(aq) \rightarrow Ni(H_2O)_2(en)_2^{2+}(aq) + 2H_2O(l)$	−38
$Ni(H_2O)_2(en)_2^{2+}(aq) + en(aq) \rightarrow Ni(en)_3^{2+}(aq) + 2H_2O(l)$	−41

Idiosyncrasy of Cu^{2+} ions

The octahedral structure of $Ni(H_2O)_6^{2+}$ is perfectly regular, with six equidistant $Ni{-}OH_2$ bonds. However, the structure of $Cu(H_2O)_6^{2+}$ is decidedly different. This octahedron is distorted because four coplanar $Cu{-}OH_2$ bonds are shorter than the other two. The result is the elongated octahedron shown in Figure 1.3.

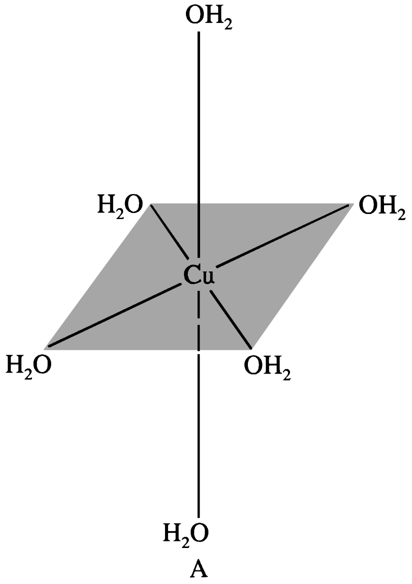

FIGURE 1.3
(A) The distorted octahedral structure of the $Cu(H_2O)_6^{2+}$ ion, compared to (B) the perfectly regular structure of $Ni(H_2O)_6^{2+}$.

This distortion is due to the electronic structure of the complex ion, but the explanation is too involved to pursue here. All that you need to know at this point is that the distortion persists when other ligands replace water. A bidentate ligand such as ethylenediamine presents a special problem. The distance between the nitrogen atoms in this ligand is fixed because the $-CH_2CH_2-$ backbone cannot expand or contract. As a result, it remains to be seen whether this ligand is capable of spanning each of the twelve edges of the elongated octahedron of Cu^{2+} with equal ease. If it is not, the maximum number of these ligands that can bind to Cu^{2+} is not three, as with $Ni(en)_3^{2+}$, but fewer than three.

Concept of the experiment

The bonding of one or more ligands to a metal ion can be detected by thermochemical methods. Moreover, these methods are sensitive enough to determine the number of ligands that have been bonded. Consider the following example. Suppose that we do not know the final outcome of the reaction of ethylenediamine with aqueous Ni^{2+} ions and that we want to know how many molecules of the ligand will bind to a Ni^{2+} ion in aqueous solution. By adding increments of ethylenediamine to a solution of the metal ions, we would find that the ratio, moles of en : moles of aqueous Ni^{2+} ions, controlled the amount of heat that was evolved.

When we increased the ratio from 1:1 through 2:1 to 3:1, a steady increase in the quantity of evolved heat would occur. However, when we increased the ration to 4:1, we would find that the evolved heat was roughly the same as the heat that evolved when the ratio was 3:1. The lack of additional heat would be our signal that no additional bonding had occurred. We would then infer that the final complex ion in the solution is $Ni(en)_3^{2+}$ and that three molecules of ethylenediamine can bind to a Ni^{2+} ion.

Why does this method work? Let us take the reactions and enthalpies in Table 1.2 and use Hess's law to derive Table 1.3. For example, the third equation in Table 1.3 and its accompanying enthalpy can be obtained by adding the first, second, and third entries in Table 1.2.

Table 1.3 Another Way to Look at Enthalpy Changes for the Reactions of Ethylenediamine with $Ni(H_2O)_6^{2+}$

Reaction	**ΔH (kJ/mol)**
$Ni(H_2O)_6^{2+}(aq) + en(aq) \rightarrow Ni(H_2O)_4(en)^{2+}(aq) + 2H_2O(l)$	−38
$Ni(H_2O)_6^{2+}(aq) + 2en(aq) \rightarrow Ni(H_2O)_2(en)_2^{2+}(aq) + 4H_2O(l)$	−76
$Ni(H_2O)_6^{2+}(aq) + 3en(aq) \rightarrow Ni(en)_3^{2+}(aq) + 6H_2O(l)$	−117

The new table is organized so that you can readily see the effects of the ratio, moles of en : moles of aqueous Ni^{2+} ions. The table shows that the evolved heat increases steadily as this ratio increases from 1:1 to 3:1. When the ratio is 4:1, however, the heat would be roughly the same as the heat that evolves when the ratio is 3:1, because no additional bonding can occur.

You will apply an identical technique to determine the maximum number of ethylenediamine molecules that will bond to a Cu^{2+} ion in aqueous solution. The required measurements are the heats evolved or absorbed when the ratio, moles of en : moles of aqueous Cu^{2+} ions, is increased successively.

The heat evolved or absorbed during each of these studies will be measured by means of a coffee-cup calorimeter, described in Appendix: Using a Coffee-Cup Calorimeter. Definitions of the system and its surroundings (Ebbing/Gammon, Section 6.2) in terms of this calorimeter can be found there. If you did the experiment on "Thermochemistry and Hess's Law," "A Student's View of Liquids and Solids," or "Spontaneity," you will be familiar with the calorimeter, the technique, and the calculations.

Procedure

Getting started

1. Work with a partner.
2. Obtain a coffee-cup calorimeter.
3. You will be using a 5.0 *M* solution of ethylenediamine in this experiment.

> **CAUTION: Handle this solution carefully. If you spill it on you, wash the contaminated area thoroughly and report the incident to your laboratory instructor. You may need further treatment.**

4. Obtain directions for discarding the solutions that you will use in this experiment.

Making the measurements

1. Obtain exactly 50 mL of a 0.50 *M* solution of $CuSO_4$ in a clean, dry 50-mL or 100-mL graduated cylinder. Obtain exactly 5 mL of the 5.0 *M* solution of ethylenediamine in a clean, dry 25-mL graduated cylinder.
2. Measure the temperature of each of these solutions. Rinse the thermometer and dry it after each measurement. If the temperatures of these solutions differ by more than ±0.2°C, cool the warmer solution with tap water or warm the cooler solution with your hands until the temperatures agree. Record the mean temperature. It is the initial temperature, t_i.
3. Add the solution of $CuSO_4$ to the calorimeter.
4. Add the solution of ethylenediamine to the calorimeter.
5. Immediately place the top on the calorimeter and begin stirring.
6. Record the temperature to the nearest 0.1°C after 30 s and every 30 s thereafter for 4 min.
7. Wash, rinse, and dry the calorimeter.
8. Repeat Steps 1 through 7 using exactly 10 mL of 5.0 *M* ethylenediamine rather than 5 mL.
9. Is another trial necessary? If so, go on to Step 10.
10. Repeat Steps 1 through 7 using exactly 15 mL of 5.0 *M* ethylenediamine rather than 5 mL.
11. Is another trial necessary? If so, go on to Step 12.
12. Repeat Steps 1 through 7 using exactly 20 mL of 5.0 *M* ethylenediamine rather than 5 mL.

Making the calculations

1. Complete the following steps for each trial in which a considerable amount of heat was absorbed or evolved.
2. Plot the temperature against the time, using the graph paper provided. Use a straight line to extrapolate your results to the time of mixing. Record the extrapolated temperature. It is the final temperature, t_f.
3. Calculate q(system), using 4.184 J/(g • °C) and 1.0 g/mL for the specific heat and density of the solution, respectively, and 1.0×10^1 J/°C for the heat capacity of the calorimeter.

4. Calculate the number of moles of aqueous Cu^{2+} ions and ethylenediamine.
5. Calculate the enthalpy change, ΔH, from q(system) and the number of moles of aqueous Cu^{2+} ions.

Thermochemistry and Complex Ions

Date:	....	Student name:	....
Course:	....	Team members:	....
Section:	....		....
Instructor:	....		....

Prelaboratory assignment

1. Provide definitions for the following terms:
   a. Complex ion
   b. Complex
   c. Ligand
   d. Monodentate ligand
   e. Bidentate ligand
   f. Coordination number
   g. Calorimeter
   h. System (in this experiment)
   i. Surroundings (in this experiment)

2. a. Draw an octahedron, showing clearly that it has 6 apexes and 12 edges.

   b. Draw the structure of $Ni(en)_3^{2+}$. How many apexes are occupied by nitrogen atoms, and how many edges are spanned by the bidentate ligand?

3. What signal reveals that no additional bonding of ethylenediamine to aqueous Cu^{2+} ions will occur?

4. What special safety precautions are cited in this experiment?

Thermochemistry and Complex Ions

Date: ....

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Instructor: ....

Student name: ....

Team members: ....

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Results

Trial	**1**	**2**	**3**	**4**
Volume of 0.50 *M* $CuSO_4$ (mL)	50	50	50	50
Volume of 5.0 *M* en (mL)	5	10	15	20
t_i (°C)				
Temperature (°C) after				
30 s				
60 s				
90 s				
120 s				
150 s				
180 s				
210 s				
240 s				
t_f(°C)				
q(system) (J)				
Moles of $CuSO_4$				
Moles of en				
Mol en/mol $CuSO_4$				
ΔH (kJ/mol)				

Calculations:

Student name: .... Course/Section: .... Date: ....

Questions

1. Consider the following reactions:

$$Cu(H_2O)_6^{2+}(aq) + en(aq) \rightarrow Cu(H_2O)_4(en)^{2+}(aq) + 2H_2O(l)$$

$$Cu(H_2O)_4(en)^{2+}(aq) + en(aq) \rightarrow Cu(H_2O)_2(en)_2^{2+}(aq) + 2H_2O(l)$$

$$Cu(H_2O)_2(en)_2^{2+}(aq) + en(aq) \rightarrow Cu(en)_3^{2+}(aq) + 2H_2O(l)$$

   a. Did all of these reactions occur in your calorimeter? If not, which ones did occur? Explain your reasoning.

   b. What is the maximum number of ethylenediamine molecules that will bond to a Cu^{2+} ion?

   c. Draw the structure of the complex ion that contains the Cu^{2+} ion and the maximum number of ethylenediamine molecules.

d. Use Hess's law to calculate an enthalpy change for each of the reactions that did occur.

e. Using your final trial, calculate the heat of dilution for ethylenediamine.

Student name: .... Course/Section: .... Date: ....