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

INSTRUCTOR RESOURCES

A CCLI EXPERIMENT

Learning Objectives

- to understand how a simple calorimeter is used to determine the maximum number of ethylenediamine (*en*) molecules that will complex to aqueous Ni^{2+} and Cu^{2+}.

- to understand the effect of structure of a coordination compound on its reactions.

Procedure Overview

- the equimolar amounts of $[Ni(H_2O)_6]^{2+}$ or $[Cu(H_2O)_6]^{2+}$ and ethylenediamine are reacted and the heat of reaction is determined calorimetrically.

- the reaction mixture is then cooled down to the initial temperature, and a second equivalent of "en" is added. The process is repeated until the addition of the next equivalent of "en" fails to produce a significant temperature change. The small temperature increase observed when further replacement is not possible is due to the heat of dilution of ethylenediamine.

- by measuring the evolved heat, it is possible to determine the maximum number of ethylenediamine molecules that have complexed in each reaction.

Name ______________________________ Section ___________ Date __________________

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

Report Sheet

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

	Step1	Step 2	Step 3	Step 4
Initial temperature (°C)	__________	__________	__________	__________
Final temperature (°C)	__________	__________	__________	__________

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

	Step1	Step 2	Step 3	Step 4
Initial temperature (°C)	__________	__________	__________	__________
Final temperature (°C)	__________	__________	__________	__________

Concentration of ethylenediamine __________ *M*

Volume of ethylenediamine in each step __________ ml

Concentration of $[Cu(H_2O)_6]^{2+}$ or $[Ni(H_2O)_6]^{2+}$ __________ *M*

Volume of $[Cu(H_2O)_6]^{2+}$ or $[Ni(H_2O)_6]^{2+}$ __________ ml

Name ______________________________ Section __________ Date __________________

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

Report Sheet (page 2)

Calculations

1. Calculate the number of moles of ethylenediamine in each 5 ml portion.

2. Calculate the number of moles of each metal complex.

3. For each step, calculate the heat, q_n, using 3.8 J/(g °C) and 1.1 g/ml for the specific heat and density of the solution, respectively, and 30 J/ ºC for the heat capacity of the calorimeter.

$$q_n = (3.8\ J/g°C) \times (1.1\ g/ml) \times (ml\ soln) \times (t_i - t_f) + (30\ J/°C) \times (t_i - t_f)$$

Provide a sample calculation and record all of your results in the space below.

4. For each step, calculate the enthalpy change, ΔH_n, from q and the moles of "en" used in that step. Provide a sample calculation and record your results in the table below.

Complex	ΔH_1	ΔH_2	ΔH_3	ΔH_4
$[Ni(H_2O)_6]^{2+}$				
$[Cu(H_2O)_6]^{2+}$				

Name ______________________________ Section ___________ Date __________________

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

Questions/Problems

1. How many molecules of ethylenediamine react with each molecule of $[Ni(H_2O)_6]^{2+}$ and with $[Cu(H_2O)_6]^{2+}$? Explain your conclusion.

2. In your experimental trials, how did you conclude that no additional bonding of ethylenediamine to aqueous $[Ni(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ had occurred?

3. Which of the two possible complexes of copper are formed: the symmetrical tris-chelate or distorted bis-chelate? Explain the reasons for this occurrence.

4. Provide equations for all reactions that occurred in your calorimeter.

5. Provide definitions for the following terms.
   a. coordination compound

   b. ligand

   c. monodentate,

   d. bidentate

   e. chelating ligand

   f. coordination number

Name ______________________________ Section __________ Date _________________

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

Suggested Answers to Questions/Problems

1. How many molecules of ethylenediamine react with each molecule of $[Ni(H_2O)_6]^{2+}$ and with $[Cu(H_2O)_6]^{2+}$? Explain your conclusion.

   3 molecules react with **$[Ni(H_2O)_6]^{2+}$** ***since there are six available bonding sites and during each step, one molecule of the bidentate ethylenediamine ligand replaces two water molecules.***

   2 molecules react with **$[Cu(H_2O)_6]^{2+}$** ***since two of the six Cu– H_2O bonds are longer than the other four, and if these two water molecules are not replaced, the copper complex can retain the preferred distorted geometry.***

2. In your experimental trials, how did you conclude that no additional bonding of ethylenediamine to aqueous $[Ni(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ had occurred?

   When there was only a small increase in temperature that could be attributed to the heat of dilution of ethylenediamine.

3. Which of the two possible complexes of copper are formed: the symmetrical tris-chelate or distorted bis-chelate? Explain the reasons for this occurrence.

   The symmetrical tris-chelate complex is not formed since the electronic factors force the distorted, bis-chelate geometry.

4. Provide equations for all reactions that occurred in your calorimeter.

$$[Ni(H_2O)_6]^{2+}_{(aq)} + en_{(aq)} \rightarrow [Ni(H_2O)_4(en)]^{2+}_{(aq)} + 2\ H_2O$$

$$[Ni(H_2O)_4(en)]^{2+}_{(aq)} + en_{(aq)} \rightarrow [Ni(H_2O)_2(en)_2]^{2+}_{(aq)} + 2\ H_2O$$

$$[Ni(H_2O)_2(en)_2]^{2+}_{(aq)} + en_{(aq)} \rightarrow [Ni(en)_3]^{2+}_{(aq)} + 2\ H_2O$$

$$[Cu(H_2O)_6]^{2+}_{(aq)} + en_{(aq)} \rightarrow [Cu(H_2O)_4(en)]^{2+}_{(aq)} + 2\ H_2O$$

$$[Cu(H_2O)_4(en)]^{2+}_{(aq)} + en_{(aq)} \rightarrow [Cu(H_2O)_2(en)_2]^{2+}_{(aq)} + 2\ H_2O$$

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

Suggested Answers to Questions/Problems (page 2)

5. Provide definitions for the following terms.

   a. coordination compound: *any species involving the formation of coordinate covalent bonds of ligands to a metal center.*

   b. ligand: *a species that is capable of donating one or more electron pairs to a central metal atom or ion.*

   c. monodentate: *a ligand that has only one pair of electrons that it can donate.*

   d. bidentate ligand: *a ligand that can donate two electron pairs.*

   e. chelating ligand: *a ligand capable of donating two or more electron pairs and facilitating the formation of a ring upon its bonding to a metal center.*

   f. coordination number: *the number of coordination sites that a metal center can provide for ligands to attach to.*

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

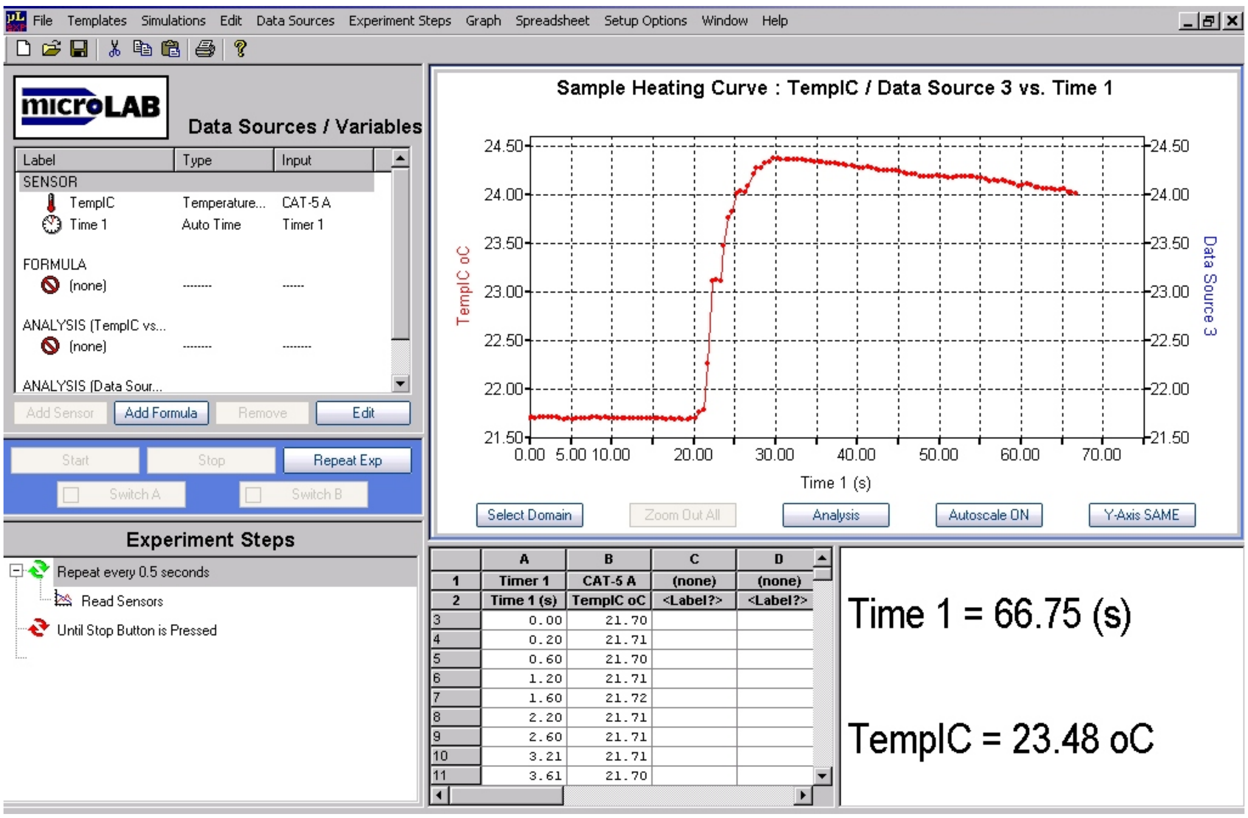
Tips and Traps

1. It is helpful to equip the inner beaker with a handle to help the student to remove the beaker for cooling.

2. Students have to make sure that the initial temperatures for each step are within 0.1°C. All the solutions used in this experiment should be kept at the same temperature in a constant temperature bath.

3. An automatic dispenser should be used for ethylenediamine to minimize the possibility of spills.

Sample ***MicroLAB*** Main Screen showing the program and a data set for an exothermic process.



	A	B	C	D
1	Timer 1	CAT-5 A	(none)	(none)
2	Time 1 (s)	TempIC oC	<Label?>	<Label?>
3	0.00	21.70		
4	0.20	21.71		
5	0.60	21.70		
6	1.20	21.71		
7	1.60	21.72		
8	2.20	21.71		
9	2.60	21.71		
10	3.21	21.71		
11	3.61	21.70		

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

Sample Data

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

	Step1	Step 2	Step 3	Step 4
Initial temperature (°C)	22.78	22.84	22.73	22.77
Final temperature (°C)	23.88	23.91	23.65	22.92

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

	Step1	Step 2	Step 3	Step 4
Initial temperature (°C)	22.84	22.84	22.82	__________
Final temperature (°C)	24.29	24.23	23.05	__________

Concentration of ethylenediamine 1.5 *M*

Volume of ethylenediamine in each step 5.0 ml

Concentration of $[Cu(H_2O)_6]^{2+}$ or $[Ni(H_2O)_6]^{2+}$ 0.15 *M*

Volume of $[Cu(H_2O)_6]^{2+}$ or $[Ni(H_2O)_6]^{2+}$ 50.0 ml

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

Sample Data (page 2)

Calculations

1. Calculate the number of moles of ethylenediamine in each 5 ml portion.

   1.5 M x 0.0050 L = 0.0075 mole per step

2. Calculate the number of moles of each metal complex.

   0.15 M x 0.050 L = 0.0075 mole

3. For each step, calculate the heat, q_n, using 3.8 J/(g °C) and 1.1 g/ml for the specific heat and density of the solution, respectively, and 30 J/ ºC for the heat capacity of the calorimeter.

   $$q_n = (3.8\ J/g^\circ C)\ x\ (1.1\ g/ml)\ x\ (ml\ soln)\ x\ (t_i - t_f) + (30\ J/^\circ C)\ x\ (t_i - t_f)$$

   Provide a sample calculation and record all of your results in the space below.

   $$q_1 = (3.8\ J/g^\circ C)\ x\ (1.1\ g/ml)\ x\ (55\ ml)\ x\ (1.10^\circ C) + (30\ J/^\circ C)\ x\ (1.10^\circ C)$$

   $$= -2.9x10^2\ J$$

4. **For each step, calculate the enthalpy change, ΔH_n, from q and the moles of "en" used in that step. Provide a sample calculation and record your results in the table below.**

   For the nickel complex: $\Delta H_1 = q_1/n = -2.9x10^2\ J/0.0075\ mol = -38\ kJ/mol$

Complex	ΔH_1	ΔH_2	ΔH_3	ΔH_4
$[Ni(H_2O)_6]^{2+}$	- 38	- 40	- 37	- 6
$[Cu(H_2O)_6]^{2+}$	- 50	- 52	- 9	

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

Laboratory Preparation (per student station)

Equipment

- two 600 ml beaker
- 400 ml beaker
- 250 ml beaker
- 100 ml beaker
- 50 ml graduated cylinder
- glass stirring rod
- insulated cover (for 100 ml beaker)
- 10 cm test tube, stopper and test tube block
- temperature probe
- homemade wire handle to withdraw 100 ml beaker

Supplies

- towel

Chemicals

Exact quantities needed are listed below. A minimum 50% excess is recommended.

- 1.5 *M* ethylenediamine (35 ml)
- 0.15 *M* $NiCl_2 \cdot 6H_2O$ (50 ml)
- 0.15 *M* $CuSO_4 \cdot 6H_2O$ (50 ml)

Safety and Disposal

- dispose of the wastes into specially marked containers in the fumehood.
- ethylenediamine has to be handled with extreme care.