

# SYNTHESIS AND TITRATION OF A COPPER SALT

## Introduction

Many transition metals form octahedral complexes with  $\text{H}_2\text{O}$  when in aqueous solution. Examples include pink  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ , green  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , and pale-blue  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . Addition of ammonia to such solutions results in a series substitution reactions in which the water molecules are replaced by ammonia molecules. For example, when concentrated aqueous ammonia is added to  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , the color changes to the violet color of the  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  ion. One might easily assume that a similar reaction occurs with copper, resulting in the formation of  $[\text{Cu}(\text{NH}_3)_6]^{2+}$ . In the case of copper, however, only the first four water molecules are replaced, forming the deep blue-violet  $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$  ion. Replacement of the fifth and sixth water molecules occurs only in very concentrated solutions.

The purpose of this experiment is to determine the correct formula for the complex ion that is produced when ammonia is added to water. Is it really  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  that is produced, or is it  $[\text{Cu}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  or even  $[\text{Cu}(\text{NH}_3)_6]^{2+}$ ? The first part of the procedure will involve the preparation and isolation of the sulfate salt of this complex ion,  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{SO}_4$ . In the second part of the procedure you will titrate three samples of this solid with 1.00 M HCl to determine the mass percent of ammonia in the sample. The HCl will react with the  $\text{NH}_3$  to form  $\text{NH}_4^+$  which does not have a lone pair of electrons and cannot serve as a ligand. Therefore  $\text{H}_2\text{O}$  molecules will replace  $\text{NH}_3$  in the complex ion. The end point of the titration will be signaled by a change in color from the deep-blue of the  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  ion to the much paler blue of the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion. From the volume of HCl added and molarity of the HCl, you can determine the number of moles of HCl added. Since one HCl reacts with one  $\text{NH}_3$ , the number of moles of HCl added equals the number of moles of  $\text{NH}_3$  in the sample. From the number of moles of  $\text{NH}_3$ , you can determine the mass of  $\text{NH}_3$  in the sample.

## Precautions

*Any work with 15M  $\text{NH}_3$  should only be performed in a working hood!*

*Copper-containing solutions should not be dumped down the sink! All copper-containing solutions should go in the waste bottles at the end of the period*

## Procedure

### Part 1: Synthesis of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$

Weigh out 7.0 grams of copper sulfate pentahydrate. Transfer the solid to a 125 mL Erlenmeyer flask and add 15 mL of water. Heat the flask to dissolve the solid, and then

cool to room temperature. Add 15 M  $\text{NH}_3$  to the solution, a few mL at a time. The solution should immediately change from the pale-blue color of  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  to the intense blue of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ . An initial precipitate of  $\text{Cu}(\text{OH})_2$  may form. Continue adding  $\text{NH}_3$  until all of this precipitate has dissolved and a solution with no trace of cloudiness is obtained.

To this solution, add 15 mL of 95% ethanol. An immediate precipitate of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  should be observed. Filter the resulting solid through a Buchner funnel using suction filtration and wash with two additional portions of 95% ethanol. Allow the solid to air dry and obtain the mass of product obtained.

## **Part 2: Titration of the Sample**

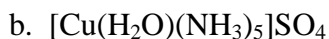
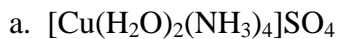
Obtain three 125 mL Erlenmeyer flasks and buret. Weigh out approximately 1.0 – 1.5 grams of solid  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  into each flask. It is a good idea to use a slightly different mass for each trial. Add 15-20 mL of water to each flask and swirl to dissolve the solid. The resulting solution may appear cloudy. Since this solution does not contain an excess of  $\text{NH}_3$ , some of the coordinated  $\text{NH}_3$  will be replaced with  $\text{H}_2\text{O}$ . This results in the formation of neutral species such as  $[\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_2](\text{OH})_2$  or  $[\text{Cu}(\text{NH}_3)_2(\text{OH})_2]$ , which are most likely responsible for the cloudiness of the solution.

The titration may be conducted like a standard acid-base titration. Slowly swirl the flask by hand as the  $\text{HCl}$  is added. The  $\text{HCl}$  may be added fairly rapidly at the beginning of the titration. However, this must be slowed to a dropwise addition near the endpoint of the titration. A fairly pronounced color change from the deep-blue color of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  to the pale-blue color  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  should occur at the endpoint of the titration. The resulting solution should be clear with no trace of cloudiness. Repeat the procedure for the second and third flasks. Based upon the volume of  $\text{HCl}$  added and the molarity of the  $\text{HCl}$ , calculate the number of moles of  $\text{NH}_3$  and mass percent of  $\text{NH}_3$  in each sample.

<b>Synthesis and Titration of a Copper Salt Pre-Laboratory</b>	<b>Name:</b>
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1. Calculate the theoretical amount of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  that could be obtained from 7.0 grams of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Show your work.

2. For each of the following formulas, calculate the mass percent of  $\text{NH}_3$ .



3. A solid sample of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  was titrated with 1.00 M HCl according to the procedure described for this laboratory. If 15.5 mL of the HCl was used to titrate 1.10 grams of solid  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ , calculate the mass percent of  $\text{NH}_3$  in the sample.

<b>Synthesis and Titration of a Copper Salt Report Page 1</b>	<b>Name:</b>
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**Part 1: Synthesis of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$**

Mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	
Mass of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ obtained	
Mass of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ expected	
Percent yield	

In the space below record your observations regarding the synthesis of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ . Show your calculations for the expected mass and percent yield.

<b>Synthesis and Titration of a Copper Salt Report Page 2</b>	<b>Name:</b>
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**Part 2: Titration of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$**

	Flask 1	Flask 2	Flask 3
Mass of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$			
Initial volume of buret			
Final volume of buret			
Volume of HCl dispensed			
Moles of HCl dispensed			
Moles of $\text{NH}_3$ in sample			
Mass of $\text{NH}_3$ in sample			
Mass percent of $\text{NH}_3$			
Average mass percent			

<b>Synthesis and Titration of a Copper Salt Post-Laboratory Questions</b>	<b>Name:</b>
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1. Refer to the formulas listed in the pre-laboratory exercise. Based upon the theoretical mass percent of  $\text{NH}_3$  calculated in this experiment, which formula to you think is correct?

2. Give a reason why your mass percent may not exactly match one of the values calculated in the pre-laboratory exercise.

3. Why is the complex ion isolated as a solid? What would be wrong with the following procedure? (1) make a known copper sulfate pentahydrate solution, (2) add an excess of  $\text{NH}_3$  to form the complex ion, (3) titrate the sample with standardized  $\text{HCl}$ .

4. Is the copper(II) ion labile or inert? Would this make a difference in our ability to perform this experiment?