

# SYNTHESIS AND ANALYSIS OF A COORDINATION COMPOUND OF COPPER

In this experiment you will synthesize a compound by adding  $\text{NH}_3$  to a concentrated aqueous solution of copper sulfate. The blue  $\text{CuSO}_4$  solution will turn a still deeper blue and a mass of small deep blue-to-violet crystals will form as ethyl alcohol is added. On the basis of the analysis of this solid for  $\text{Cu}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_3$ , you will be able to propose a formula for the compound.

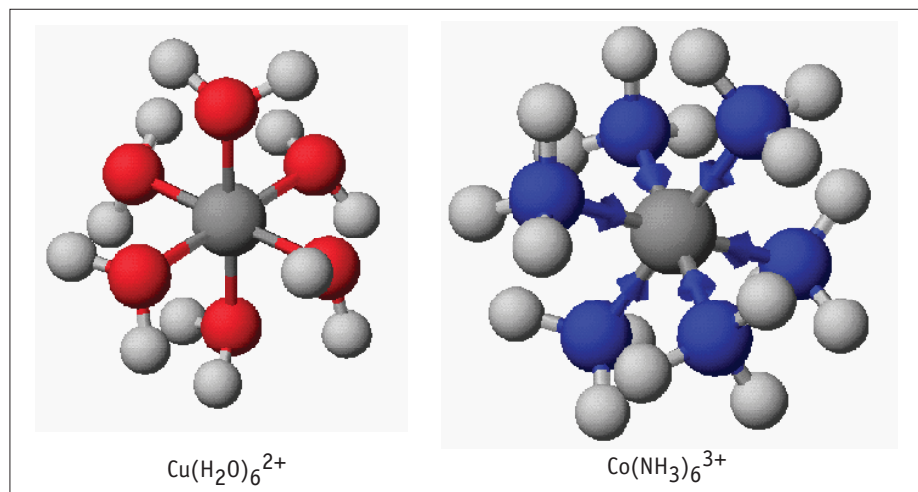
## THEORY

Four principal species are present initially in the reaction mixture: copper (II) ions [actually  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  ions], ammonia molecules ( $\text{NH}_3$ ), sulfate ions ( $\text{SO}_4^{2-}$ ), and water. The product of the synthesis is therefore presumed to be formed by the reaction of two or more of these species. Ethanol is also present, but it is an indirect participant in the reaction. In aqueous solutions ethanol, which is miscible with water but of lower dielectric constant, decreases the solubility of ionic compounds. The marked color change that occurs in the reaction is an important clue to the nature of the product. The product is analyzed for copper (II) ions, sulfate ions, and ammonia molecules. Water is determined as the mass of a sample of the compound that is not accounted for as one of these three species.

The analyses to be performed in this experiment are quantitative and are of three types: *gravimetric*, *volumetric*, and *spectrophotometric*. The gravimetric analysis is for sulfate ions; the volumetric analysis is for ammonia molecules; and the spectrophotometric analysis is for copper ions. With careful attention to detail and techniques one can obtain excellent results for each part of the analysis.

The general formula of the unknown compound is  $\text{Cu}_x(\text{NH}_3)_y(\text{SO}_4)_z \cdot a \text{H}_2\text{O}$

You performed gravimetric, volumetric, and spectrophotometric analyses in earlier experiments.



### Complex ions containing bound water and ammonia.

The structure of  $\text{Cu}^{2+}$  ion in water is on the left. Note that the water molecules are bound, through oxygen atoms, to the copper ion. In this experiment you will make a compound that has  $\text{NH}_3$  molecules bound to the copper(II) ion through N atoms, similar to the complex ion  $[\text{Co}(\text{NH}_3)_6]^{3+}$ .

## PROCEDURE

### A. Synthesis of the Compound

1. Weigh out 10.0 grams of copper sulfate pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , on a triple beam balance, and place the crystals in a 250 mL beaker.
2. Add 10-15 mL of water to the solid and then in a hood add 20 mL of 15 M  $\text{NH}_3$  (concentrated ammonia). Stir to dissolve the crystals as ascertained by holding the beaker up to the light.
3. Over a period of 1 minute, slowly add 20 mL of 95% ethanol (ethyl alcohol) to the solution, stir, and cool to room temperature.
4. Meanwhile, prepare 30 mL of a solution from 15 mL each of concentrated ammonia and 95% ethanol. Cover all your solutions containing ammonia with watch glasses (to prevent the fumes of  $\text{NH}_3$  from saturating the lab atmosphere), and return to your desk.
5. Set up an apparatus for *vacuum filtration*. Moisten the filter paper and turn on the aspirator. Carefully filter the slurry of crystals that has formed in the copper-containing solution and suck off all the solution.

In the event that a significant amount of crystalline product remains in the beaker, you should use the filtrate from the filter flask to wash the crystals onto the filter paper. To prevent backup of tap water into the filter flask, which would render the filtrate useless as a wash, pull the hose off the aspirator while the water is still running. Remove the filter funnel and pour the filtrate from the filter flask back into the beaker that contains the crystals. Reassemble the filter apparatus and collect the remaining product on the filter paper.



**CAUTION:**  
acetone is  
flammable

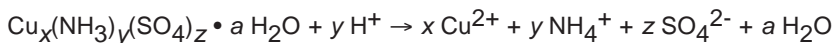
Turn off the aspirator and carefully pour 10 mL of the ammonia-ethanol solution onto the crystals. Break up all lumps of solid to permit the liquid to penetrate the mass completely and then turn on the aspirator to suck off the liquid. Repeat the washing procedure twice with additional 10 mL portions of ammonia-ethanol. Next wash twice with 10 mL portions of 95% ethanol and finally with two 10 mL portions of acetone, breaking up the mass of crystals with a spatula in each step before turning on the aspirator. (At this point your crystals should appear nearly “dry,” that is, not moistened with liquid to any great extent. If you feel they could be dried more, add additional amounts of acetone as described above.) To remove the last traces of moisture and other solvents from your solid, draw air through the crystals for at least 5 minutes, using your spatula to break up any remaining lumps.

6. Put the crystals in a large test tube or small beaker, lightly cover, and leave them in your desk to dry thoroughly until the next laboratory period.
7. When you come to the laboratory period following the one in which the crystals were prepared, inspect them to insure they are dry and then weigh the entire sample to the nearest 0.1 gram. Record the mass on the report form, and then go on to the next portion of the experiment.

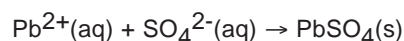
## ANALYSIS OF THE COMPOUND

A. Gravimetric Analysis for Sulfate Ion,  $\text{SO}_4^{2-}$ 

1. Weigh to the nearest milligram about 0.9-1.1 gram of your compound (after making absolutely sure it is dry).
2. Dissolve the solid compound in 10 mL of 6 M nitric acid ( $\text{HNO}_3$ ). The reaction occurring at this point is



3. Obtain 5-6 mL of 1 M lead acetate [ $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ ], and add it dropwise to the acid solution until precipitation is complete. The reaction now occurring is



Use the following procedure to check for completeness of precipitation: First allow all the white precipitate to settle to the bottom of the beaker. Using your eyedropper, allow one drop of lead acetate solution to run down the side of the beaker into the light blue solution. If precipitation of the  $\text{SO}_4^{2-}$  ion is not yet complete, you will see a white precipitate of  $\text{PbSO}_4$  form just as the drop slides down the beaker wall and into the solution. If you do not observe a white solid forming at this point, then precipitation is complete and you can proceed.

During addition of nitric acid to the unknown compound in water the originally deep violet solution will turn light blue.

4. Once you have decided that precipitation of the  $\text{PbSO}_4$  is complete, weigh a piece of filter paper to the nearest milligram. Assemble the apparatus for *gravity filtration*. After properly folding the paper into a cone, place it in the funnel, moisten it with a little water, and adjust it so that it fits the funnel snugly. Be careful not to tear the paper. Using a stirring rod to guide the flow of liquid, carefully fill the filter cone about one-half full of the lead sulfate-water slurry. When this has drained nearly empty, repeat the operation, and continue this process until the transfer of lead sulfate to the filter is complete. It is important that you do not lose any of the precipitate in the transfer to the filter paper.
5. The filtration described above may be quite slow. Since you must do a duplicate determination, you may wish to start the second one while the first one is filtering.
6. After most of the liquid has collected from the filtration, check it once again for completeness of precipitation by adding a few drops of lead acetate. If a white precipitate forms (the solution becomes cloudy), add another milliliter of lead acetate solution and refilter.
7. Rinse the beaker with small portions of water and use these rinsings to wash the precipitate on the filter paper. Finally use your wash bottle to rinse the filter paper and precipitate free from the original copper-containing solution.
8. Rinse the precipitate with a small portion (say 10 mL) of acetone.
9. When the liquid from the last washing has drained out, remove the filter paper (be careful not to tear it!) and place it in a 250 mL beaker or evaporating dish to dry until the next laboratory period. When you are certain

Recall that you did a gravity filtration when making an iron oxalate complex in the first experiment, when making alum, and then doing the gravimetric analysis of a barium salt.

Acetone,  $\text{H}_3\text{COCH}_3$ , forms hydrogen bonds with water. This assists in removing water from the precipitate and thereby hastening its drying.

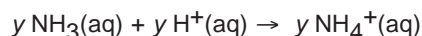
that your  $\text{PbSO}_4$  precipitate is dry, weigh the precipitate and filter paper to the nearest milligram, recording the mass on your report form. (This weighing is normally done in the lab period following the one in which the precipitate was collected.)

10. As noted above, a *duplicate determination of the amount of sulfate must be carried out.*

This portion of the experiment is usually performed during the second or third period assigned to the experiment.

## 2. Volumetric Analysis for Ammonia, $\text{NH}_3$ .

The amount of ammonia in your compound will be determined by a conventional acid-base titration. That is, using the reaction



where  $\text{H}^+$  is from a standardized solution of strong acid, that is, from HCl.

1. Weigh out to the nearest milligram two 1 gram samples of your compound, and dissolve each in about 30 mL of water. (Do not allow the solutions to stand very long before titrating them.)
2. Add 10 drops of methyl orange indicator to each solution, and titrate each with thorough stirring with standard HCl. (The acid concentration is approximately 0.5 M; the exact concentration will be given to you.)

Recall that the general formula of the unknown compound is  $\text{Cu}_x(\text{NH}_3)_y(\text{SO}_4)_z \cdot a \text{H}_2\text{O}$

Numerous color changes occur as acid is added. The solution starts out deep blue. However, as acid is added the color changes to a blue-green and then to a pea-green when about 70% of the acid has been added. After about 85% of the ammonia has been titrated, the color is distinctly yellow. The end point is a change from yellow-orange to red-orange. However, the end point detection is made even easier by the fact that the precipitate that was present through the titration vanishes just before the end point.

3. Record your results for each titration on your report form. Check the precision of your results by dividing the volume of acid used by the sample weight; if the two runs do not agree within 1%, do another determination.

**TABLE Preparing Calibration Standards and Samples of Unknown for Spectrophotometric Analysis**

Test Tube Number	Contents
1	Add about 10 mL of 1 M HNO <sub>3</sub> from the dispenser
2	Add 4.0 mL of standard Cu <sup>2+</sup> solution and 6.0 mL of 1 M HNO <sub>3</sub> from the dispensing buret. Mix well.
3	Add 7.0 mL of standard Cu <sup>2+</sup> solution and 3.0 mL of 1 M HNO <sub>3</sub> from the dispensing buret. Mix well.
4	Add about 10 mL of standard Cu <sup>2+</sup> solution.
5	Weigh to the nearest milligram 0.2 g of unknown and add exactly 10.0 mL of 1 M HNO <sub>3</sub> . Mix well.
6	Weigh to the nearest milligram 0.3 g of unknown and add exactly 10.0 mL of 1 M HNO <sub>3</sub> . Mix well.

Be sure to record the concentration of the standard Cu<sup>2+</sup> solution on your report form.

Be sure to mix the samples well.

### 3. Spectrophotometric Analysis for Copper, Cu<sup>2+</sup>

1. Clean and dry six 18 x 150 mm test tubes (the smaller size in your drawer), and label them 1 through 6. The first four of these tubes will be used to make up the reference solutions that are then used to calibrate the Spectronic 20 spectrophotometer.
2. Prepare calibration standards and samples of the unknown compound according to the directions in the Table above.
3. After thoroughly mixing the contents of tubes 2, 3, 5 and 6, place a portion of each of the six solutions in six correspondingly numbered tubes that fit the spectrophotometer. (Fill the spectrophotometer tubes about 80-90% full.) *Measure the absorbance of each of these solutions at 645 nm* as demonstrated by your instructor and as outlined in the "Spectrophotometry" material in Section G of this manual. The infinite absorbance setting (left end of the scale) is made with nothing in the sample chamber of the spectronic 20, and the 0 absorbance setting (right end of the scale) is made using the solvent in which you dissolved your compound, that is pure 1 M HNO<sub>3</sub> (sample tube no.1).



**DATA SUMMARY SHEET**  
**SYNTHESIS OF A COPPER COORDINATION COMPLEX**

Name \_\_\_\_\_

Mass of copper sulfate used = \_\_\_\_\_

Mass of complex isolated = \_\_\_\_\_

**Analysis for Sulfate**

Mass of sample 1 = \_\_\_\_\_

Mass of sample 2 = \_\_\_\_\_

Mass of  $\text{PbSO}_4$  isolated for sample 1 = \_\_\_\_\_Mass of  $\text{PbSO}_4$  isolated for sample 2 = \_\_\_\_\_**Analysis for Ammonia**

Concentration of HCl = \_\_\_\_\_

Mass of sample 1 = \_\_\_\_\_

Mass of sample 2 = \_\_\_\_\_

mL of HCl used for sample 1 = \_\_\_\_\_

mL of HCl used for sample 2 = \_\_\_\_\_

**Analysis for Copper**

Mass of sample 1 = \_\_\_\_\_

Mass of sample 2 = \_\_\_\_\_

Average absorbance data

Sample 1 = \_\_\_\_\_

Sample 2 = \_\_\_\_\_

Sample 3 = \_\_\_\_\_

Sample 4 = \_\_\_\_\_

Sample 5 = \_\_\_\_\_

Sample 6 = \_\_\_\_\_

**◆ NOTE**

A copy of this summary data sheet should be handed in to your instructor at the end of *each* lab period. He or she will give it back to you to fill out as needed. Its purpose is to ensure that you do not lose data from a lab that counts for about one quarter of the lab grade.