SYNTHESIS AND ANALYSIS OF A COORDINATION COMPOUND OF COPPER[1]

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In this experiment you will synthesize a compound by adding NH_3 to a concentrated aqueous solution of copper sulfate. The blue $CuSO_4$ 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 Cu^{2+}, SO_4^{2-}, and NH_3, you will be able to propose a formula for the compound.

The general formula of the unknown compound is $Cu_x(NH_3)_y(SO_4)_z \bullet aH_2O$

THEORY

Four principal species are present initially in the reaction mixture: copper (II) ions [actually $Cu(H_2O)_6^{2+}$ ions], ammonia molecules (NH_3), sulfate ions (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

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[1] Adapted from http://www.labarchive.net/labdb/get?experiment_id=113 from an experiment originally published by SUNY Oneota

results for each part of the analysis.

Synthesis of the Compound

1. Weigh 10.0 grams of copper sulfate pentahydrate, $CuSO_4 \bullet 5H_2O$ and place the crystals in a 250 mL beaker.

2. Do this step in the hood. Add 10-15 mL of water to the solid and then in a hood add 20 mL of 15 M NH_3 (concentrated ammonia). Stir to dissolve the crystals .

3. Over a period of 1 minute, add 20 mL of 95% ethanol (ethyl alcohol) to the solution, stir, and cool to room temperature.

4. 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 NH3 from saturating the lab atmosphere), and return to your desk.

5. Set up an apparatus for vacuum filtration. Carefully filter the slurry of crystals that has formed in the copper-containing solution and filter the solid

Release the vacuum 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 remove the liquid. Repeat the washing 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. 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 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

Gravimetric Analysis for Sulfate

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 in10 mL of 6 M HNO_3. The reaction occurring at this point is

$$Cu_x(NH_3)_y(SO_4)_z \bullet aH_2O + yH^+ = xCu^{2+} + yNH_4^{1+} + zSO_4^{2-} + aH_2O$$

3. Add 5-6 mL of 1 M lead acetate dropwise to the acid solution until precipitation is complete. The reaction now is

$$Pb^{2+} + SO_4^{2-} = PbSO_4(s)$$

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 disposable pipette, allow one drop of lead acetate solution to run down the side of the beaker into the light blue solution. If precipitation of the SO_4^{2-} ion is not yet complete, you will see a white precipitate of $PbSO_4$ 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.

4. Once you have decided that precipitation of the $PbSO_4$ 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 (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 that your $PbSO_4$ 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.

Volumetric Analysis for NH_3

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

$$yNH_3 + yH^{1+} = yNH_4^{1+}$$

where H^{1+} is from a standardized solution of HCl.

1. Weigh into 250 mL flasks 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.) 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.

Spectrophotometric Analysis for Cu^{2+}

1. Clean and dry six 18 x 150 mm test tubes 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 below.

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.

Table: Calibration Standards and Samples of Unknown for Spectrophotometric Analysis

Tube #	Contents
1	Add about 10 mL of 1 M HNO_3 from the dispenser
2	Add 4.0 mL of standard Cu€$^{+}$ solution and 6.0 mL of 1 M HNO_3
3	Add 7.0 mL of standard Cu€$^{+}$ solution and 3.0 mL of 1 M HNO_3
4	Add about 10 mL of standard Cu€$^{+}$ solution
5	Weigh to the nearest milligram 0.2 g of unknown and add exactly 10.0 mL of 1 M HNO_3.
6	Weigh to the nearest milligram 0.3 g of unknown and add exactly 10.0 mL of 1 M HNO_3.

Be sure to mix the samples well.

Be sure to record the concentration of the standard Cu^{2+} solution on your report form.

mass $CuSO_4 \bullet 5H_2O$		grams
yield of $Cu_x(NH_3)_y(SO_4)_z \bullet aH_2O$		grams
% yield		
Determination of Ammonia		
	Sample 1	Sample 2
mass complex (grams)		
volume titrant (mL)		
[titrant] $\underline{M}$		
moles H^{1+}		
moles NH_3		
moles NH_3/g complex		
Determination of Sulfate		
	Sample 1	Sample 2
mass complex (grams)		
mass filter paper (grams)		
mass paper + $PbSO_4$ (grams)		
mass $PbSO_4$ (grams)		
mass SO_4^{2-} (grams)		
moles SO_4^{2-}/g complex		
Determination of Copper		
	$[Cu^{2+}]$	A_{645}
Standard 1		
2		
3		
4		
mass complex(grams) 1		
mass complex (grams) 2		
moles Cu^{2+}/g complex 1		
moles Cu^{2+}/g complex 2		
Formula of Complex		
g NH_3/g complex		
g SO_4^{2-}/g complex		
g Cu^{2+}/g complex		
g H_2O/g complex		
formula of complex		