

# **The Synthesis and Analysis of Ammine Complexes of Copper and Silver Sulfate: An Undergraduate Laboratory Project**

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## **Lab Documentation**

Written Directions for Students:

Note: Copper sulfate is considered “highly toxic” (LDLO, oral, man = 857 mg/kg; LD<sub>50</sub>, rat, oral = 300 mg/kg) and should be handled with care to avoid ingestion or inhalation of dust. We recommend that all reagents be handled in an appropriate hood. Because of the corrosive nature of concentrated aqueous ammonia and sodium hydroxide care must be exercised to avoid contact with skin. We recommend the use of gloves along with approved safety goggles.

**Preparation of  $[\text{Ag}(\text{NH}_3)_2]\text{SO}_4$**  A 2.17 g sample of silver sulfate (Fisher, CAS 10294-26-5) was weighed into a 150 mL Erlenmeyer flask. A 10 mL portion of concentrated ammonia (Fisher, CAS 1336-21-6) was added along with 2 mL of distilled water. The mixture was heated gently on a hotplate (low setting) with occasional stirring until the solid silver sulfate dissolved. A 10 mL portion of ethanol (Fisher, CAS 64-17-5) was

added, and after cooling in an ice bath for about an hour, the very light silver-gray (almost white) precipitate was suction filtered through a medium pore glass-fritted filter crucible. The product was washed with 5 mL of ethanol and allowed to dry in the filter crucible for about 10 minutes before being placed in a desiccator for a week. Although less prone to photodecomposition than many silver salts, the product should be kept away from direct sunlight. Typical yields of 1.8 g correspond to an 80 % yield.

**Preparation of  $\text{Cu}(\text{NH}_3)_4\text{SO}_4$**  A 2.00 g sample of copper sulfate pentahydrate (Fisher, CAS 7758-98-7) was weighed into a 100 mL beaker. A 10 mL portion of distilled water was added and the mixture gently swirled to dissolve the copper sulfate. A 10 mL portion of concentrated ammonia (Fisher, CAS 1336-21-6) was added and the mixture stirred until the initial pale blue precipitate dissolved to form a deep blue-purple solution. A 10 mL portion of ethanol (Fisher, CAS 64-17-5) was added, and after cooling in an ice bath for about an hour, the dark purple-blue precipitate was suction filtered using a medium porosity glass-fritted filter crucible. The product was washed with 5 mL of ethanol and allowed to dry in the filter crucible for about 10 minutes before being placed in a desiccator for a week. Typical yields of 1.7 g correspond to a 90 % yield.

**Analysis of  $[\text{Ag}(\text{NH}_3)_2]\text{SO}_4$**  Three samples of approximately 0.1 g ( $\pm 0.1$  mg) of the product were weighed by difference into separate 250 mL Erlenmeyer flasks. A 20.00 mL portion of approximately 0.2 M nitric acid (previously standardized to four significant figures against primary grade sodium carbonate, Fisher, CAS 497-18-8) was

added to each flask with a buret, and the solutions were swirled until the samples completely dissolved. The solutions were then titrated against approximately 0.2 M NaOH (previously standardized to four significant figures with potassium hydrogen phthalate, Fisher, CAS 877-24-7) using 3-4 drops of methyl red as an indicator (red to yellow transition). A few drops of the 0.2 M nitric acid were added to each flask so that the following precipitation occurred from a slightly acidic solution. A 10 mL portion of approximately 0.2 M NaCl was added to each flask, and a white precipitate of AgCl formed. The flasks were placed on a hotplate and heated to near boiling and allowed to digest for about half an hour. The flasks were allowed to cool and the solutions were filtered through pre-weighed, medium porosity, glass-fritted filter crucibles. The precipitates were washed with 5–10 mL of approximately 0.05 M nitric acid, were placed in a drying oven for two hours at 110°C, and were allowed to cool in a desiccator before weighing to  $\pm 0.1$  mg.

**Analysis of  $\text{Cu}(\text{NH}_3)_4\text{SO}_4$**  Three samples of approximately 0.1 g ( $\pm 0.1$  mg) of the product were weighed by difference into separate 250 mL Erlenmeyer flasks. A 20.00 mL portion of approximately 0.2 M nitric acid (previously standardized to four significant figures against primary grade sodium carbonate, Fisher, CAS 497-18-8) was added to each flask with a buret, and the solutions were swirled until the samples completely dissolved. The solutions were then titrated against approximately 0.2 M NaOH (previously standardized to four significant figures with potassium hydrogen phthalate, Fisher, CAS 877-24-7) using 3-4 drops of methyl red as an indicator (red to yellow transition). After the titration was completed, two pellets of sodium hydroxide

(approximately 0.2 g, Fisher, CAS 1310-73-2) were added to each flask and the solutions were heated to just below boiling for one hour. The black precipitate of copper oxide which formed was filtered through pre-weighed, medium porosity, glass-fritted filter crucibles and washed with approximately 10 mL of distilled water. The precipitates were placed in a drying oven for two hours at 110°C, and were allowed to cool in a desiccator before weighing to  $\pm 0.1$  mg.

Directions for the Instructor:

Both diamminesilver(I) sulfate and tetraamminecopper(II) sulfate were readily formed in high yield provided that the “mother liquor” was not too dilute with respect to the reactants. Consequently, students should be reminded not to use more solvent than described in the procedures. Also, accurate values for the ammonia content of the title compounds were found using the mild drying process described (a week in a desiccator). Although the drying time can be shortened, the use of a drying oven is discouraged because of the volatility of ammonia.

The analytical techniques described are more than adequate to determine the stoichiometry of the compounds to 1–5 %. Although appropriate laboratory technique should be taught and encouraged, “full analytical rigor” (i.e., all of the methodology normally associated with careful analysis) is not required to produce results useful in finding the composition of the compounds.

The experiment readily divides into two 3–4 hour sessions to form a two week project. In the first session, the student would synthesize one or both of the title compounds and standardize the nitric acid and sodium hydroxide solutions (store in a tightly closed bottle). During the intervening week the compounds are allowed to dry in a desiccator. In the second session, the student would perform the analysis. In addition, the project is easily structured for students to work in teams. For example, a team of two students would allow each to synthesize one of the title compounds, however, both could work together to create shared solutions of standardized acid and base. Moreover, each student could perform some of the analysis, and then combine the data to find the complete stoichiometry of the compound(s). If desired, additional metal ammonia complexes can be synthesized and analyzed to provide a more diverse group of products with a coordination number up to six. For example,  $\text{Co}(\text{NH}_3)_6\text{SO}_4$ ,  $\text{Ni}(\text{NH}_3)_6\text{SO}_4$ , and  $\text{Zn}(\text{NH}_3)_4\text{SO}_4$  can be synthesized and analyzed with minimal modification to the procedures herein described.

Finally, the instructor may want to provide rationalizations for the different coordination numbers observed in the products. For example, the two coordinate silver ammine complex can be rationalized in valence bond terms by  $sp$  hybridization of the  $d^{10}$  silver ion (mixing a  $5s$  and  $5p$  orbital). Each “empty”  $sp$  hybrid orbital then “overlaps” with one  $sp^3$  hybrid on the ammonia molecule which contains a lone pair of electrons. In this way an ordinary two electron bond is formed.