Inorganic Chemistry (CH258)   Spring 2004   Gustavus Adolphus College

PREPARATION AND SPECTRAL ANALYSIS OF COPPER(II) COMPLEXES

Introduction

A. Tetraamminecopper(II) Sulfate Monohydrate

$$CuSO_4 \cdot 5H_2O + 4NH_3 \longrightarrow Cu(NH_3)_4^{2+}SO_4^{2-} \cdot H_2O$$

This preparation is designed to illustrate a simple synthesis of a coordination complex, and to provide a second copper complex for comparison with the bis(diethylammonium) tetrachlorocuprate(II).

You have already prepared this complex several times during the qualitative analysis scheme: its intense blue color makes it a good indicator for the presence of copper. If the reaction is carried out with high concentrations of copper(II) and ammonia present, the sulfate salt of the complex can be precipitated by the addition of ethanol to an aqueous solution of copper sulfate and ammonia. Infrared analysis of the product can then be used to confirm the presence of ammonia in the solid.

B. Bis(diethylammonium) Tetrachlorocuprate(II)

$$(C_2H_5)_2NH_2^+Cl^- + CuCl_2 \longrightarrow [(C_2H_5)_2NH_2^+]_2CuCl_4^{2-}$$

Most copper(II) complexes are tetracoordinate. This means that two different geometries, tetrahedral and square-planar, are possible. The particular compound that you will prepare in this experiment undergoes a transition between square planar and tetrahedral geometries when it is heated. Even though the four ligands, all chloride, remain the same, the ligand fields experienced by the copper in the two different geometric environments are different; this difference causes the colors of the complexes to differ. Compounds that exhibit such temperature-dependent color changes are called <u>thermochromic</u>.

In this preparation, the choice of cation is critical. The diethylammonium ion is a strong hydrogen bond donor, and it turns out that in this particular case, the chloride ions which are bound to copper can also act as hydrogen bond acceptors. These interactions have a substantial impact upon the crystal structure of the compound.

As is the case with hydroxy compounds, hydrogen-bonded N-H bond stretches absorb over a broad frequency range, thus showing broad absorptions that contain little fine structure. In contrast, when either O-H or N-H occurs as an isolated functional group, the stretching absorption is sharp. In a compound that contains both bound and unbound O-H or N-H groups, a superposition of the sharp band or bands over the broad hydrogen-bonded absorption is seen. The relative intensities of these features give an indication of the relative abundances of the two types of functional group. Analysis of the infrared spectra of the two forms of diethylammonium tetrachlorocuprate(II) should thus reveal which of the two has the greater degree of hydrogen bonding.

Experimental Procedures

A. Tetraamminecopper(II) Sulfate Monohydrate

In the hood, make a solution of 2 mL of concentrated aqueous ammonia and 1.5 mL of water, then dissolve 1.25 g of copper sulfate pentahydrate in the solution by swirling.

Add, in a **slow**, **dropwise** manner, with continual swirling, 2.5 mL of ethanol. The ammine complex salt should precipitate as deep purple-blue crystals. Cool the mixture in an ice water bath for about 15 minutes, then isolate the product by suction filtration. Rinse the product on the funnel with a small amount of ethanol, then spread it out on a watch glass to dry. Store it in a desiccator over anhydrous calcium chloride until your next lab period.

Weigh the product for calculation of the percent yield, then record the infrared spectrum of the compound as a KBr pellet.

B. Bis(diethylammonium) Tetrachlorocuprate(II)

Place solid diethylammonium chloride (0.005 mol, 0.55 g) and finely powdered copper(II) chloride hydrate (0.0025 mol, 0.43 g) in a 125 mL Erlenmeyer flask. Mix thoroughly by shaking, then gently heat the mixture of solids on a steam bath or with a hot water bath. Heat, with occasional swirling, until the mixture is completely liquified. Leave to cool to room temperature, then cool in an ice bath. Break up the solidified mass of product with a glass rod, then rinse thoroughly with about 5 mL of 20% isopropyl alcohol in ethyl acetate. Rinse twice more with pure ethyl acetate, or until the product appears as free-floating small needles. Isolate the product by suction filtration.

WATCH OUT FOR FLAMES AROUND YOU BEFORE PERFORMING THE NEXT STEP.

To facilitate drying, rinse the product on the funnel with a small amount of diethyl ether. The product is hygroscopic, so it must be stored in a desiccator.

Heat a small portion of the product gently so as to observe the color change due to the thermochromic transition.

Record the infrared spectrum of the compound as a KCl pellet. KCl should be used rather than the more usual KBr so as to avoid exchange of chloride for bromide in the copper complex. Two spectra should be recorded: one at room temperature and one at about 70°C.

Visible/near-IR spectra, recorded at low and high temperatures, will be provided by the instructor.

Inorganic Chemistry Laboratory Report - Copper(II) Complexes

Name:_____________________________ Lab section (day):________ Date:__________

A. Tetraamminecopper(II) Sulfate Monohydrate

1. Calculate the percent yield of the product.

2. What sort of coordination geometry around copper would you expect for the tetraamminecopper(II) complex which you prepared? In this case, the general spectral region of the d-d transition can be inferred directly from the color of the complex; note, however that this is not always the case. Provide a rationale for your answer, based on a comparison with the color of the tetrachlorocuprate(II) complex and your knowledge of the relative magnitudes of splitting produced by different types of ligand fields.

3. How does the infrared spectrum of the product show the presence of ammonia? You should be able to identify both stretching and bending vibrations from N-H, as well as evidence of hydrogen bonding in the compound.

4. Identify the infrared bands associated with S-O stretching and bending from the sulfate counterion.

B. Diethylammonium Tetrachlorocuprate(II)

1. Calculate the percent yield of diethylammonium tetrachlorocuprate(II).

2. Decide, on the basis of the absorption maxima for the d-d transitions of the low- and high-temperature forms of the complex, which is tetrahedral and which is square-planar. Provide an explicit rationale for your choice.

3. Assign the infrared bands that are due to C-H stretching, N-H stretching, and N-H bending.

4. Decide, on the basis of the N-H stretching region of the infrared spectra of the two forms of the complex, which contains the stronger hydrogen bonding. Provide an explanation of your reasoning.

Pre-lab Questions - Copper Complex Preparations

1. Draw structures, showing all bonds and formal charges, for the chemical species given below.

   diethylammonium ion   tetrachlorocuprate(II)

2. What are the two most symmetrical geometries possible for a tetracoordinate coordination complex?