Semi-Microscale Preparation of Copper(I) Chloride

Introduction

In most of its ionic compounds copper assumes a +2 oxidation state, having the valence configuration $3d^9$. In aqueous solution the Cu^{2+} ion typically shows a light blue color, although the presence of coordinating ligand species can result in complex ions with somewhat different colors. The color in all cases is a result of the incompletely filled 3*d* subshell. If, by contrast, copper assumes a +1 oxidation state, it has the completely filled subshell configuration $3d^{10}$. This pseudo-noble gas configuration excludes the kinds of electronic transitions that give rise to the characteristic colors of most transition metal ions, such as Cu^{2+}, Cr^{3+}, Ni^{2+}, etc. Thus, Cu^+ is colorless in solution, as is Zn^{2+} and copper's second-row transition element analogue Ag^+.

Like Ag^+, Cu^+ forms an insoluble chloride, for which $K_{sp} = 1.72 \times 10^{-7}$. Unlike Ag^+, however, Cu^+ is unstable with respect to Cu^{2+} in aqueous solution. The relevant standard reduction potentials are

$$Cu^+ + e^- \rightleftharpoons Cu^0 \qquad E^o = 0.521 \text{ V}$$
$$Cu^{2+} + e^- \rightleftharpoons Cu^+ \qquad E^o = 0.153 \text{ V}$$

Taken together, these show that in aqueous solution Cu^+ ions will spontaneously disproportionate to give Cu^{2+} ions and metallic copper:

$$2Cu^+ \rightleftharpoons Cu^0 + Cu^{2+} \qquad E^o_{cell} = 0.368 \text{ V}$$

Under nonstandard conditions, the reaction potential, E_{cell}, will be given by the Nernst equation

$$E_{cell} = E^o_{cell} - (RT/n\mathcal{F})\ln\{[Cu^{2+}]/[Cu^+]^2\}$$

This suggests that any process that removes Cu^+ from solution will diminish the overall E_{cell}, thereby mitigating the disproportionation reaction. One way of achieving this is to produce the Cu^+ in the presence of excess chloride ion, resulting in production of a chloride complex of copper(I), followed by precipitation of CuCl. Both complex formation and precipitation result in removal of the Cu^+ from solution. The precipitate sequesters the Cu^+ ions in a form that is less susceptible to disproportionation. In the solid state, the lattice energy stabilizes the +1 state, and disproportionation becomes nonspontaneous:

$$2CuCl \rightleftharpoons Cu^0 + Cu^{2+} + 2Cl^- \qquad E^o_{cell} = -0.442 \text{ V}$$

This is the synthetic strategy we will use in this experiment to obtain copper in the +1 state.

Although CuCl stabilizes Cu^+ relative to disproportionation, this does not mean that the species is impervious to decomposition to the more stable Cu^{2+} ion. In contact with the preparative medium, where Cu^{2+} is being reduced to Cu^+, CuCl will resist reconversion back to Cu^{2+} and Cl^- ions so long as the reducing agent (metallic copper) is present in excess. However, during collection of the product by filtration, CuCl becomes vulnerable to oxidation from O_2, either from contact with the air or from significant amounts dissolved in wash liquids. Evidence of oxidation is the development of a pale green color due to formation of basic copper(II) chloride, $CuCl_2 \cdot 3Cu(OH)_2$. *To prevent this, it is critically important to avoid allowing any of the several wash liquids to run through the filter completely, thereby sucking air through the moist product.* As one wash liquid is nearly gone, add the next. The final washings with ether are meant to dry the product. Several ether washes (always avoiding air contact) are likely to be more effective than a single treatment. Any residual moisture should be driven off by immediate oven drying.

Procedure

1. In a 125-mL flask, bring about 100 mL of distilled water to a vigorous boil, turn off the heat, and allow the water to cool with the mouth of the flask *loosely stoppered*. This will remove much of the dissolved air from the water.
2. Add 60 mL of this water to another clean 125-mL flask, add 2 mL of ether, stopper tightly, and shake. This will help remove residual air. Keep the flask of deaerated water *tightly stoppered* until it is needed in the following procedure.
3. Dissolve 2 g of $CuCl_2 \cdot 2H_2O$ in 5 mL of water in a 50-mL Erlenmeyer flask, and then add 5 mL of concentrated hydrochloric acid and 1.5 g of fine copper turnings. Heat on a hot plate, keeping air out of the mixture by inverting a small beaker over the mouth of the flask. Avoid vigorous boiling.
4. When no further color change occurs, carefully decant the warm solution into the 125-mL flask containing the 60 mL of deaerated water. Take care to prevent unreacted copper metal from being transferred with the solution. CuCl will precipitate in the 125-mL flask as a fine white powder.
5. Collect the solid by suction filtration on a sintered glass Gooch crucible (medium frit) or small Buchner funnel and filter paper, taking care to keep the cake of precipitated CuCl covered with liquid at all times. As the level of liquid approaches the precipitate add more solution. After adding the last portion of solution and before all the liquid has been sucked through the filter, successively wash with two 4-mL portions of alcohol, and then four 4-mL portions of anhydrous ether. With each wash liquid, *gently* stir up the precipitate, let the level fall to just above the cake, and then add the next wash liquid. After the final ether wash, allow the precipitate to be sucked to dryness, about one minute beyond the point at which most liquid has passed through the filter. Immediately transfer the product (still in the filter funnel) to a warm oven (110°C) or vacuum oven (70 - 80°C), and allow to dry approximately one hour.
6. Transfer the dried product to a preweighed sample bottle and seal it tightly to prevent contact with moist air. Weigh the bottle and sample to determine the yield.

Reactions of CuCl

Prepare an aqueous solution of potassium chloride by adding approximately 0.1 g of KCl to 10 - 20 mL of water. To this solution, add a small amount of CuCl (about the amount that covers the tip of a micro-spatula). Note what happens and interpret your results.Now add a few drops of ethylenediamine, identify the precipitate so formed, and comment. [You may want to consult an inorganic chemistry text to interpret these results.]

Laboratory Report

1. Submit your sample, clearly labeled with your name on it.
2. Your written report should include balanced equations for the reactions by which CuCl is produced, a statement of grams of product and percent yield, and a brief explanation of any unexpected results or departures from the procedure.
3. Describe your observations and interpretations, including balanced chemical equations, for the reactions you carried out with CuCl and both aqueous KCl and ethylenediamine.
4. In this synthetic procedure CuCl does not precipitate until the reaction mixture is diluted with water. Explain why this occurs.
5. In this experiment copper metal functions as a reducing agent. Suggest an alternative procedure for preparing CuCl using a different reducing agent. Keep in mind that the reducing agent must be capable of being cleanly separated from the product without exposing CuCl to air oxidation. Give full citations for the source(s) of your procedure or pertinent data used in developing it.