Solvatochromism of Cupric Chloride and Its Conversion to Copper Oxide

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Abstract

This experiment demonstrates that copper(II) chloride dihydrate (CuCl₂·2H₂O) in

different solvents (acetone, isopropyl alcohol or water) displays divergent colors and visible-near

IR spectra. Both the reactions of these solutions with two equiv. of sodium hydroxide (NaOH)

and the direct solid-state reaction of CuCl₂·2H₂O with 2NaOH using a mortar and pestle give

copper(II) oxide (CuO). Undergraduate students learn the following: (1) d-d electronic transitions

in a transition metal complex; (2) Effects of solvent polarity changes on the electronic ground

and excited state of Cu2+ ions as well as color differences; (3) Direct solid-state reaction as a

green synthetic method; (4) Gradual formation of CuO from solution reactions of CuCl₂·2H₂O

with 2 equiv. of NaOH; (5) Characterization of chemical compounds in solutions by visible-near

IR spectroscopy and solid products by IR and powder X-ray diffraction (PXRD). This experiment

is suitable as a junior-level inorganic chemistry experiment.

Keywords: Upper-Division Undergraduate/General Chemistry Laboratory, Inorganic Chemistry,

Hands-On Learning/Manipulatives, Synthesis

1

INTRODUCTION

Solvent is often important in a chemical reaction and properties of solvents, such as polarity, acidity-basicity, and the ability to hydrogen-bond, can impact the reaction process including reaction kinetics. The choice of solvent can also impact the color and absorption spectrum of a solution. Solvatochromism refers to the phenomenon when the color of a solution changes based on the polarity of the solvent that the solute is dissolved in.¹⁻² These changes in solvent polarity lead to a difference in the electronic ground and excited state of the solute and thus, the energy gap between them changes. As a result, the absorption spectrum of the solute changes in position, intensity, and band shape, most frequently viewed as an energy shift in the local maximum of the absorbance. In the visible spectrum, solvatochromism is observed as color change. When a metal complex is dissolved in different solvents, coordination of the solvents as ligands to the metal ion may yield different complexes with various colors. Thus, the color differences among solutions of a metal complex in different solvents may not fit the definition of solvatochromism originally developed for organic compounds. 1-2 However, the colors of the solutions are a result of dissolving a compound in different solvents. In the current work, solvatochromism is used broadly referring to the case of a metal complex dissolved in different solvents.

Certain reactions may be carried out in the solid state without the use of a solvent. Such reactions may be classified as mechanochemistry.³ In some cases, the reaction products are unique, *i.e.*, different from those obtained from solution reactions.³⁻⁴ For example, Xin and coworkers have demonstrated that solid–solid reactions between 4-methylbenzenamine and $MCl_2 \cdot nH_2O$ (M = Cu^{2+} , n = 2; Co^{2+} or Ni^{2+} , n = 6) yield $M(NH_2C_6H_4Me)_2Cl_2$, while these reactions attempted in solution yield no product.⁴

The current experiment is designed to provide students an opportunity to observe the solvatochromic properties of CuCl₂·2H₂O in water, acetone, and isopropyl alcohol, by measuring the visible spectra of the solutions. In addition, students will conduct the reaction in Eq. 1 in

three different solvents as well as in the solid state, allowing them to test principles of green chemistry. Green chemistry has been a highly active research area in recent years.⁵⁻⁹ This relatively new chemistry area deals with the design of chemical products and processes that reduce or eliminate the generation of hazardous substances.⁵ "Less Hazardous Chemical Syntheses" and "Safer Solvents and Auxiliaries" are two principles of green chemistry that can be explored in this experiment.⁶ After the reactions are completed, students will use IR and PXRD spectra to characterize the products and determine if the synthesis of CuO is successful.

$$CuCl_2 \cdot 2H_2O + 2 NaOH \rightarrow CuO + 2 NaCl + 3 H_2O$$
 (Eq. 1)

LEARNING OBJECTIVES

- (1) Observe how solvents affect absorption spectra of the dissolved CuCl₂·2H₂O complex;
- (2) Study how solvents impact the reactions in solutions, including the gradual formation of CuO:
- (3) Conduct the reaction in the solid state and compare it with those in solutions.

Submitted reports by the students were used to determine if the goals of the experiment were successful.

HAZARDS

All experimental procedures should be carried out in fume hoods. Students should wear gloves and safety goggles at all times during the experiment. Copper(II) chloride dihydrate is harmful if swallowed. It causes eye, skin, and respiratory tract irritation. Target organs include respiratory system, eyes, and skin. Copper(II) chloride dihydrate is also toxic to aquatic organisms, and it may cause long-term adverse effects in the aquatic environment. Sodium hydroxide is corrosive. It can cause severe burns to the skin. Acetone and isopropyl alcohol are

flammable solvents. Students should be reminded to keep these solvents away from flames. Acetone causes irritation once in contact with skin and eyes. Isopropyl alcohol causes serious eye irritation. Breathing vapors of both organic compounds cause drowsiness or dizziness. For specific safety instructions, please refer to the students' handouts and Safety Data Sheets (SDSs) available for free from chemical companies.

EXPERIMENTAL SECTION

CuCl₂·2H₂O (Analytical reagent, Mallinckrodt), acetone (Me₂C=O, Certified ACS, Fisher Scientific), isopropanol (i-PrOH, Certified ACS, Fisher Scientific), and NaOH (Certified ACS, Fisher Scientific) were used as received. Deionized water was prepared in house and used for the experiments below.

IR spectra were obtained on a Bruker Alpha II Compact FT-IR Spectrometer in the ATR (attenuated total reflectance) mode. UV-visible-near IR spectra were recorded on an Agilent 8453 UV-visible spectroscopy system or an Agilent Cary 100 UV-visible spectrophotometer. Powder X-ray diffraction (PXRD) was conducted on a Panalytical Empyrean diffractometer with a Cu K_{α} source.

UV-visible Spectroscopic Characterization of CuCl₂·2H₂O in Acetone, Isopropanol, and Water

Three samples of CuCl₂·2H₂O (170 mg, 1.00 mmol) were each added to three vials along with 10 mL of acetone, isopropanol, and water, respectively. Spectra were taken for each solution at 380-900 nm as well as 300-1100 nm. A serial dilution using volumetric glassware was required to obtain a spectrum within the optimum absorbance range of the instruments, with concentrations of CuCl₂·2H₂O at 0.020 M, 0.002 M, and 0.0015 M in solutions of water, isopropanol, and acetone, respectively, showing the best spectra.

Formation of CuO in Acetone, Isopropanol, and Water and from the Solid-State Reaction

CuCl₂·2H₂O (170 mg, 1.0 mmol) was dissolved in three vials containing 10 mL of acetone, isopropanol, and deionized water, respectively. NaOH pellets (80 mg, 2.0 mmol) were ground in a mortar and pestle, and then added to each solution. These solutions were kept stirring for 2 days. Supernatants were removed by filtration and the products were washed with their respective solvents and then washed with 15 mL of water. Products were further dried using a heat gun at 100(10) °C, leaving dark brown or black powders of CuO. Yield was determined to be 86.4%, 90.1%, and 89.1% for the reactions done in acetone, isopropanol and water reactions respectively.

For the solid-state reaction, CuCl₂·2H₂O (340 mg, 2.0 mmol) and NaOH (160 mg, 4.0 mmol) were added to a clean and dry mortar and pestle. The solid mixture was ground together until a color change to brown or black was observed. The color change typically occurs within a few minutes. The black powder product was then dried with a heat gun. After collection, washing with water to remove NaCl, and re-drying, the yield of the isolated product 52.2%. There were solids left on both mortar and pestle that could not be removed by spatula, likely reducing the yield.

The four solid products from the reactions were characterized by IR spectra at 400-4000 cm⁻¹. In addition, the products were characterized by powder X-ray diffraction in the 2θ range of 5-70 degree (°) to confirm that they were CuO.

The use of an oven or a hot plate at about 100 °C instead of the use of a heat gun to dry the products has been shown to yield similar results.

RESULTS AND DISCUSSION

Visible Spectra of CuCl₂·2H₂O in Different Solvents

CuCl₂·2H₂O dissolved in water, isopropanol, and acetone gives solutions visibly blue,

green, and yellow-green, respectively, as shown in Figure 1. Boeré has recently published the single-crystal structure of CoCl₂·2H₂O.¹⁰

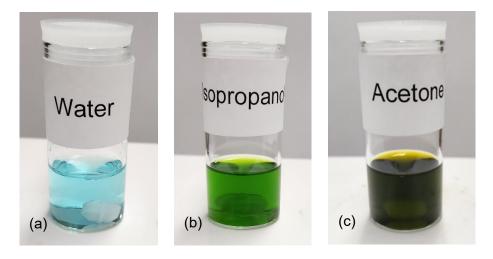


Figure 1. Solutions of CuCl₂·2H₂O in three different solvents: (a) Water; (b) Isopropanol; (c) Acetone.

Visible spectra of each solution in the range of 380-750 nm¹¹⁻¹² were obtained (Figure 2a). For the visible spectra of all three solutions, there is a broad absorption peak >780 nm in the near-IR range, as shown in Figure 2b. These absorptions have maximums at 815 nm, 855 nm, and 927 nm for the water, isopropanol, and acetone solutions, respectively. The near-IR peaks extend into the right side of the visible spectra. For the water solution in Figure 2a the extended near-IR peak leads to the absorption in red wavelengths. According to the color circle/wheel, ¹³⁻¹⁵ absorption in one color leads to the observation of the complementary color. Thus, the absorption in red wavelengths gives the solution blue color, as seen in Figure 1a. For the isopropanol solution, there is a strong UV absorption at 346 nm extending to the left side of the visible spectrum (Figure 2a). The extension of this UV peak leads to the absorption of the violet-blue wavelengths of the solution. Using the color circle/wheel¹³⁻¹⁴ or more simply the RGB (red, green and blue) model, ¹⁶ absorptions of both red and blue colors for the isopropanol

solution leaves green color to the solution, which is observed (Figure 1b). For the acetone solution, there are absorptions of both red (from the extension of the near-IR peak at 927 nm) and purple-blue color wavelengths (from the extension of the UV peak at 347 nm) as the isopropanol solution. In addition, there is a peak at 472 nm extending to about 550 nm in the blue-green range, making the isopropanol solution much darker (Figure 1c).

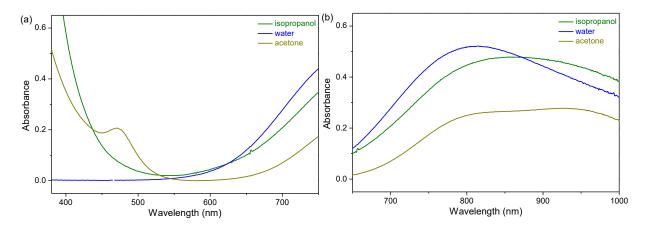


Figure 2. (a) Visible spectra of CuCl₂·2H₂O in acetone, isopropanol, and water at 380-750 nm; (b) Spectra at 650-1000 nm focusing on the low energy visible and near-IR range. Pure solvents were used as references for the spectra. Full spectra at 300-1100 nm are given in Figure S3.

The near-IR peaks of the copper chloride solutions in the three solutions (Figure 2b) show the solvatochromic effect, ^{12,17} as shown in Figure 3 and Table S4. In acetone, the least polar of the three solvents, the near-IR peak is at 927 nm, the longest wavelength (and lowest energy) of the three absorption peaks. In water, the most polar of the three solvents, the near-IR peak is at 815 nm, the shortest wavelength (and highest energy) of the three absorption peaks. In isopropanol with polarity between acetone and water, its near-IR peak is 855 nm between those of acetone and water.

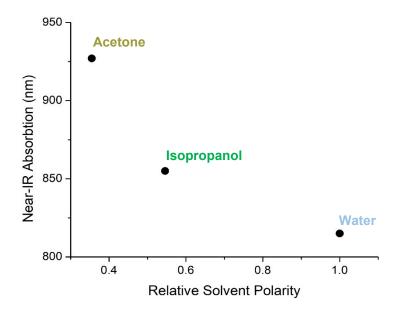


Figure 3. Plot of near-IR peaks in water, isopropanol, and acetone vs. relative solvent polarities. The relative polarities are normalized from measurements of the transition energy at 25 °C of the long-wavelength visible absorption of a standard pyridinium N-phenolate betaine dye in Ref. 17.

This solvatochromic property matches that described as negative solvatochromism,¹⁻² when the transition energy increases as the solvent polarity increases, as shown in Figure 4.¹⁸ For the solute molecule with a dipole moment, the increase in solvent polarity leads to a larger dipole moment in the ground state than that in the excited state of the solute molecule.

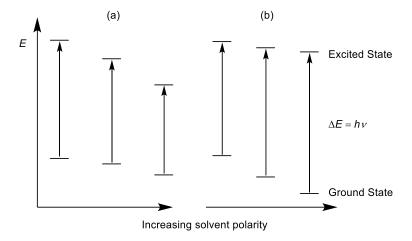


Figure 4. Representation of solvent effects of polar solutes in polar solvents.^{2,18} (a) Positive solvatochromism (bathochromic or red shift): Absorption energy decreases, or moves to longer wavelengths, as the solvent polarity increases. (b) Negative solvatochromism (hypsochromic or blue shift): Absorption energy increases, or moves to shorter wavelengths, as the solvent polarity increases. This figure is adapted with permission from Ref. 18. Copyright 1988 John Wiley and Sons.

It should be pointed out that $CuCl_2 \cdot 2H_2O$ dissolved in isopropanol and acetone may lead to the coordination of the organic molecules as ligands to Cu^{2+} ions, affording in essence different complexes than $Cu(H_2O)_n^{2+}$ (n = 4, 5, 6), the Cu^{2+} complex in water. ¹⁹⁻²⁸ In fact, the spectrum in acetone (Figure 2) show a peak at 472 nm. The nature of this transition is not clear but it is likely from the interaction of acetone with, or its binding to, the Cu^{2+} ion. ²⁸⁻³¹ Thus, strictly speaking, the color differences among solutions of $CuCl_2 \cdot 2H_2O$ in water, isopropanol, and acetone discussed here may not fit the definition of solvatochromism originally developed for organic compounds dissolved in solvents with different polarities. ¹⁻² However, broadly speaking, the colors of the three solutions in Figure 1 and spectra in Figure 2 are a result of dissolving the compound $CuCl_2 \cdot 2H_2O$ in different solvents. Another note is that, even for the Cu^{2+} -water complex, $Cu(H_2O)_n^{2+}$, its aqueous structure, including the number of water ligands, n, is the

subject of earlier^{28,32} and recent experimental and theoretical studies.^{19-27,32} Thus, there are research opportunities to study the Cu²⁺ complexes in different solvents, including water, isopropanol, and acetone. For the current work, the discussions are limited to those at the undergraduate level, including solvatochromism that may include the same metal complex dissolved in different solvents.

In an octahedral transition metal complex with six ligands, five d orbitals of the metal ions are split into t_{2g} and e_g levels (Figure 5). For d^9 complexes such as $Cu(H_2O)_6^{2+}$, the nine electrons leave one hole in the d orbitals. For $d_{x^2-y^2}$ and d_{z^2} orbitals in the e_g level, one orbital contains two electrons and the other has just one electron. In order to lower the energy, $Cu(H_2O)_6^{2+}$ undergoes the so-called Jahn-Teller distortion. The two H_2O ligands along the z axis are elongated, making the Cu-O bond lengths in the z direction longer than those in the z plane, as observed in the crystal structures of $[Cu(H_2O)_6]SiF_6$ and $[Cu(H_2O)_6](BrO_3)_2.^{19,22}$ One orbital in the e_g level, d_{z^2} with two electrons in the case of $Cu(H_2O)_6^{2+}$, is lower in energy than $d_{x^2-y^2}$ with one electron. Electrons in the filled orbitals d_{z^2} , d_{xz} , d_{yz} or d_{xy} in Figure 5 may be excited to the partially filled $d_{x^2-y^2}$, giving spectra in the UV, visible or near-IR range.³¹

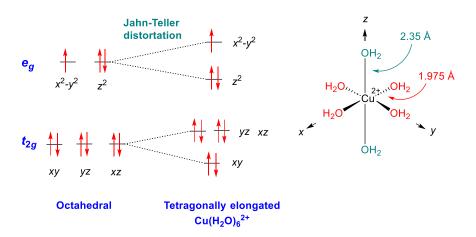


Figure 5. Splitting of the five d orbitals in a d^9 octahedral complex into t_{2g} and e_g levels and Jahn-Teller distortion in Cu(H₂O)₆²⁺, giving a tetragonal-elongated structure.

Formation and Characterization of CuO from Solution and Solid-State Reactions

The synthesis of CuO from the reaction of CuCl₂·2H₂O with 2 equiv of NaOH in water, isopropanol, and acetone was completed within 72 hours. The reaction in the acetone solution finished the most guickly, with no further changes in color after 4 hours. The reaction in the isopropanol solution finished in around 8 hours with no further changes in color or increase in the amount of the product. Photos of the solutions before adding NaOH and at different times after NaOH addition are given in Table S1 in Supporting Information (SI). Throughout the reaction, the isopropanol solution yielded green flecks inside the solution. They are most likely those of CuO nanoparticles, which tend to have green, green/brown, or brown/black coloring, though it could be Cu₂(OH)₃Cl which has a similar color.³³⁻³⁴ Nanoparticles of the same material such as GaAs³⁵ and gold³⁶ have been known to show different colors. After drying/heating the product solids in the current reactions, the green color disappeared, and all products were a dark brown/black color. Determination of nanoparticle synthesis, size, distribution, or other properties is outside of the scope of this experiment. The water solution took the longest to finish, with a lot of sol-gel-like materials in solution after 12 hours. This is most likely due to the large solubilities of both CuCl₂·2H₂O and NaOH in water, requiring longer time to complete the reaction.

The formation of CuO from the reaction in water *may* proceed through the so-called solgel process.³⁷⁻⁴² In such a reaction, molecules are first converted into colloids (or *sol*) which act as precursors to form integrated networks (or *gel*) of either discrete particles or a network of coordinated ions, leading to the eventual formation of solids. Sol-gel processes typically refer to the hydrolysis of metal alkoxides or silicon alkoxides such as Ti(O-*n*-Bu)₄ or Si(OEt)₄, forming TiO₂ or SiO₂.³⁷⁻³⁸ Such reactions have been used to make unique porous materials with different applications.^{37-38,40-46} Our speculation of the sol-gel process in the formation of CuO in the reaction of CuCl₂·2H₂O with NaOH is based in part on our observation of the reaction shown in Table S1. Henry and coworkers have synthesized Cu(II) hydroxide gels from the reaction of

Cu(acetate)₂ with NH₃ in the presence of a small amount of K₂SO₄.³⁹ The gels are a mixture of Cu₄(OH)₆(SO₄)·H₂O and acetate-based organic/inorganic polymers. Powder X-ray diffraction (PXRD) of powdered xerogels, which are formed from drying after water refluxing, show also the presence of CuO.³⁹ Similar processes have been used to make CuO or mixed metal oxides containing CuO.⁴⁰⁻⁴² If indeed the sol-gel process occurs in the current reaction of CuCl₂·2H₂O with NaOH, it may go through the steps in Figure 6.

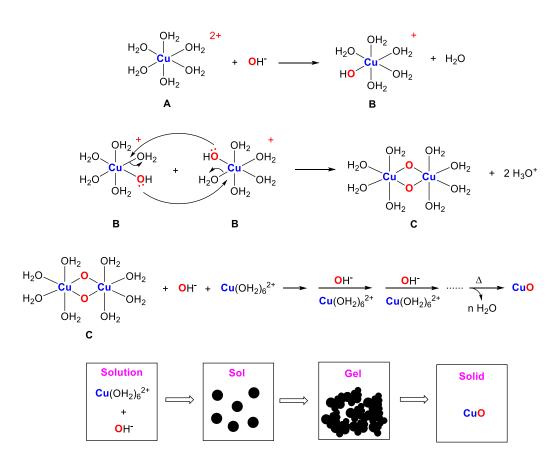


Figure 6. Schematic depiction of the sol-gel process in the formation of CuO in water.

CuO has also been formed directly by the reaction of CuCl₂·2H₂O solid with 2 equiv of NaOH solid in a mortar and pestle.^{4,47} The two solids were first each ground into powders using different mortars and pestles. The first powder was then added to the second and grinding the mixture of powders quickly led to the formation of black CuO powder. No addition of a solvent is

needed for the solid-state reaction.

Since NaCl is also a product of the reaction between CuCl₂ and 2 equiv. of NaOH, the solids from the reaction were washed by water to remove NaCl. Afterwards, the solids were each dried at about 100 °C before IR and PXRD analyses.

The products were analyzed via IR spectroscopy (Figure 7), indicating that four products are the same, showing the peaks at 475, 508, 588, 847, 895, and 987 cm⁻¹, although with different intensities. Two noticeable broad O-H stretching absorptions at about 3,300-3,500 cm⁻¹ were also observed, indicating that the solids may still retain some water from the reactions. From the data published by Ghosh and Naskar,⁴⁸ the bands around 480, 530, and 596 cm⁻¹ are Cu-O stretching vibrations in CuO.

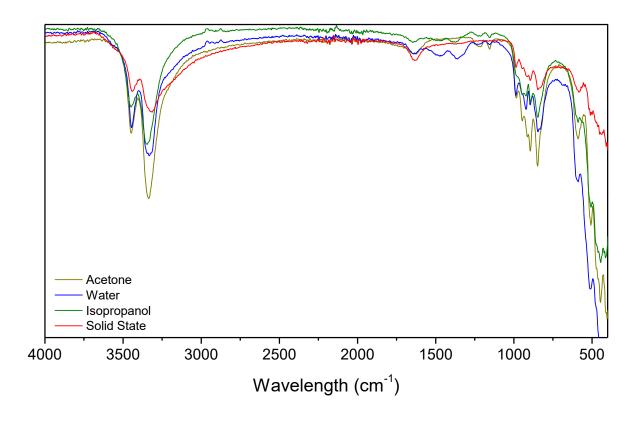


Figure 7. IR spectra of CuO products after drying. Individual spectrum is given in SI.

Powder X-ray diffraction (PXRD) is a non-destructive technique to determine crystal phase of a solid.⁴⁹ The CuO products from the reaction in the three solutions and sold state were analyzed, giving the diffraction patterns in Figure 8 showing similar crystalline phases. The most prominent peaks are at 2θ = 16.3°, 27.4°, 31.8°, 35.4°, 38.9°, 45.5°, 56.5°, 66.3°, and 68.1°. The CuO solid formed in water also shows peaks at 2θ = 53°, and 58°. From JCPDS-05-0661, the diffraction lines for the CuO monoclinic structure are 2θ = 32.47, 35.49, 38.68, 48.65, 53.36, 58.25 and 61.45. For CuO nanoparticles, Das et al. reported peaks at 2θ = 33.3°, 35.7°, 38.9°, 48.9°, 53.4°, and 58.2°.50 The PXRD patterns of the three solid products from the reactions here match those of the standard and published work. The broadness of the PXRD peaks in Figure 8 may indicate the CuO particles are not as crystalline as the standard. PXRD patterns of the products *without* washing by water are given in Figure S4, which show the presence of NaCl in the solids.

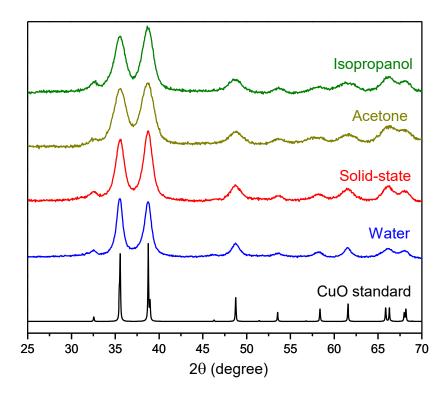


Figure 8. PXRD of CuO products from different processes. Products were dried in a furnace at 200 °C for 1 hour.

Comparison of the products from the reaction in three solutions and the solid-state shows that they all give CuO, as PXRD patterns show. The solid-state reaction is completed in a few minutes after grinding the mixture of the solids, while those in solutions take hours to show the formation of the products. One other advantage of the solid-state process is that no solvent is needed for the reaction, showing that it is greener than those conducted in solutions, especially those involving organic solvents of acetone and isopropanol. However, the isolated yield of CuO at 52.2% from the solid-state reaction is significantly lower than 86.4%-90.1% from the reactions in solution. As indicated earlier, solids on the mortar and pestle lead to at least some of the lost product.

ASSESSMENT OUTCOME

This experiment was performed in Chem 449 (*Advanced Synthesis Laboratory*, 2 credits) at the University of Tennessee-Knoxville. This senior lab course seeks to teach modern techniques of synthesis and characterization of organic and inorganic compounds and materials, as well as handling air-sensitive materials, chromatographic purification, spectroscopic characterization, and X-ray structure determination. Students conduct two 3 hrlabs per week and work with a partner(s). In Fall 2022, 15 students in Chem 449 conducted the experiment, including collecting visible-near IR spectra of the CuCl₂·2H₂O solutions as well as IR spectra and powder X-ray diffraction (PXRD) of the CuO products. The students had completed a junior-level inorganic chemistry course, in which metal complexes and d orbital splittings were discussed. A short prelab presentation (about 10 minutes) was given by the lecturer, introducing solvatochromism and X-ray diffraction. Students were then asked to submit a prelab report, providing their understanding of the chemistry, procedures, and hazards in the experiment. They easily completed the experiment in two lab periods. Each student was required to submit a laboratory report with the following sections: Introduction, Experimental Section, Results and Discussion, Conclusions, and References. While most understood well the

chemistry in the experiment and characterization of the products, several students did not fully explain the results of the experiment. There was some confusion over how to correctly interpret the UV-visible spectra. Some students made correlations between the width of the peaks and solvatochromic effects, as the width of the absorption band in acetone at about 350 nm in Figure S3 was larger than those in water or isopropanol. That is, they did not focus on the shift of the local maxima, but the overall width of a whole absorption peak. Other students focused on the beginnings of peaks in the visible region rather than the absorption maxima and used the shifts in the beginnings in discussing the solvatochromic shift. To remedy these shortcomings, we suggest that, in the prelab, a more detailed discussion be made by the lecturer about how to interpret and compare absorption spectra. Although this experiment was used in a senior synthetic laboratory course, we think it is suitable for junior or sophomore course, as some students also noted.

CONCLUSION

This experiment provides students an opportunity to investigate the effects of solvents on synthetic reactions as well as examining solvatochromic effects. Negative solvatochromism was observed with solutions of CuCl₂·2H₂O in water, isopropanol, and acetone, in which the Cu²⁺ complex(es) absorbs the light of lower energy as solvent polarity decreases.

Solvatochromism here is demonstrated qualitatively and quantitatively in the colors of the three solutions and their visible spectra. In the reaction of CuCl₂·2H₂O with 2 equiv. of NaOH in the solid state or in the three solutions, the final products were CuO, as identified by IR spectra and powder X-ray diffraction (PXRD). This experiment offers students opportunities to observe how solvents affect absorption spectra of a metal complex and study the formation CuO in different solutions and from a solid-state reaction. In addition, students will learn about the research opportunities in the area. Possible research topics may consist of the following: Structure of CuCl₂·2H₂O and other complexes in aqueous solution; Roles of organic solvents in the mixed

aqueous-organic solutions of CuCl₂·2H₂O; Effects of other solvents such as methanol, ethanol, and butanol on the UV-visible absorption of CuCl₂·2H₂O; Kinetics and the mechanistic pathway in the process forming CuO, including confirming that the reaction indeed proceeds through the sol-gel procedure; Use of scanning electron microscopy (SEM) to characterize the transient flecks in the reaction in isopropanol.

ASSOCIETED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.XXXXXXX.

Images of the reactions at different stages in the formation of CuO in three solutions.

Full range of electronic absorption spectra at 300-1100 nm.

PXRD patterns of the CuO products without washing showing NaCl.

PXRD patterns of the CuO products dried with a heat gun.

IR spectra of the CuO products separated for clarity.

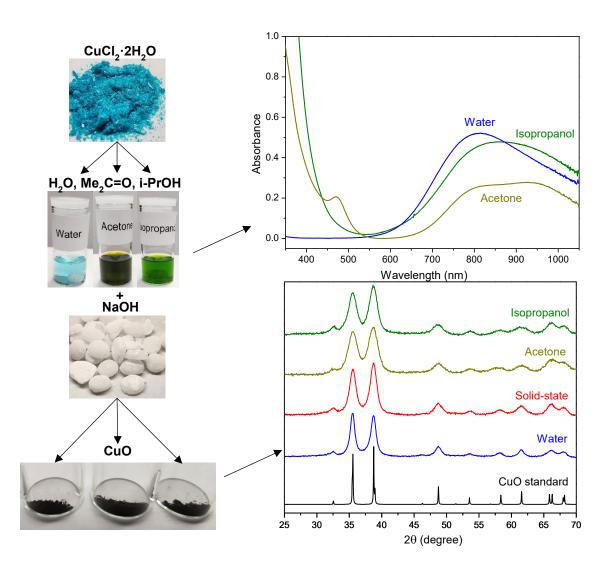
Notes

The authors declare no competing financial interest.

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Graphical Abstract



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