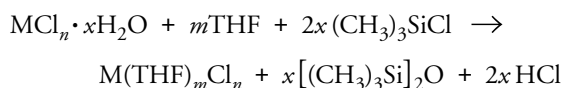


Manipulation of a Schlenk Line: Preparation of Tetrahydrofuran Complexes of Transition-Metal Chlorides

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Inorganic laboratory is a requirement for a chemistry major at this university. Before taking this course few students have experience handling air-sensitive materials using Schlenk techniques. This experiment introduces them to the techniques they will employ in later syntheses (1). This is a modification of the procedure developed by Boudjouk and So (2) to generate anhydrous tetrahydrofuran (THF) complexes of transition-metal chlorides from metal-chloride hydrates. Such THF complexes are useful synths because the weakly bound THF ligands are displaced easily by other ligands (3); in fact, this modification was developed initially within the context of our own research efforts (4). The general reaction for their synthesis is



Concurrent with the manipulations that are taught, several principles from both general chemistry and the inorganic lecture course are brought to life; these are highlighted in the section below. The most intriguing observation is the cooling of a liquid as it undergoes a vacuum distillation. Students are often surprised to feel how cold the flask becomes, and it takes several leading questions about the evaporation process until they understand what is happening. Finally, as a reward for their labors, the students observe a dramatic color change

when each reaction is complete.¹ Considering most students previously synthesized only white solids in organic laboratory, this exercise offers the instructor a chance early in the semester to show one phenomenon that makes inorganic syntheses distinctive.

Laboratory Procedure

This procedure is carried out on a standard double-bank (vacuum–inert gas) manifold (Figure 1). Approximately 0.1 mmol of a hydrate² ($CrCl_3 \cdot 6H_2O$ or $CuCl_2 \cdot 2H_2O$) and a magnetic stir bar are placed in a two-necked flask. This flask is attached to the Schlenk line, evacuated, and then filled with nitrogen gas (twice). Dry, deoxygenated THF (about 8 mL) from a solvent still³ is added via syringe.

Chlorotrimethylsilane is added to a small round-bottomed flask, which is connected to the Schlenk line. The chlorotrimethylsilane is then degassed by three freeze-pump-thaw cycles. Next, the chlorotrimethylsilane is transferred to the two-necked flask via a vacuum distillation: the two-necked flask is cooled in liquid nitrogen, and the stopcocks to the chlorotrimethylsilane and two-necked flask are opened, allowing the vapor to condense onto the THF solution.

Finally, the frozen mixture is allowed to thaw. As the mixture just begins to thaw and is able to be stirred, the color will change rather dramatically: $CrCl_3$, from deep kelly green to a bright purple–pink or $CuCl_2$, from aqua green to dark yellow. The volatile materials, including the hexamethyldisiloxane, are removed by pumping. As our focus with this exercise is teaching Schlenk techniques, we deem the color change sufficient to indicate the desired complex, $Cr(THF)_3Cl_3$ or $Cu(THF)_{0.8}Cl_2$, has formed. If further characterization is desired, the students can acquire IR spectra of the solid that remains after the volatiles are removed. (A table of IR frequencies can be found in the Supplemental Material.^W)

Hazards

Tetrahydrofuran (THF) is an extremely flammable liquid whose vapor may cause flash fire; do not distill to dryness as it may form explosive peroxides. Chlorotrimethylsilane is a corrosive liquid that reacts violently with water; avoid skin contact as it will cause severe burns. Both THF and chlorotrimethylsilane are harmful if swallowed or inhaled; they will cause irritation to skin, eyes, and respiratory tract.

Any glassware under vacuum is at some risk to breakage. All glassware should be checked for deep scratches or “starburst” fractures. To further reduce the risk of explosion do not heat any flask with a heat gun or directly on a hot plate, but rather use a warm-water bath.

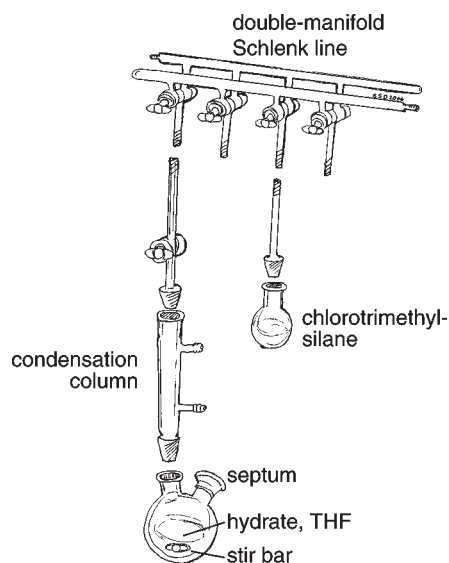


Figure 1. Experimental setup.

Questions

Students are asked the following questions to reinforce principles:

1. Why do gases bubble out of the THF solution during the first thaw of degassing cycle? [Henry's law; gases less soluble as temperature rises.]
2. Why does the chlorotrimethylsilane cool down dramatically as it distills? [During evaporation more energetic molecules leave surface; as average kinetic energy of remaining molecules decreases, so does temperature.]
3. Why does the color change as the mixture thaws? [Ligand field theory]
4. Why might it be preferred to remove the solvent and other volatile components on the Schlenk line, rather than using a rotary evaporator? [Maintain closed system; important for air-sensitive compounds.]

Acknowledgment

The authors thank Susan Schrimpf Davis for the artwork.

^wSupplemental Material

Instructions for the students and notes for the instructor are available in this issue of *JCE Online*.

Notes

1. The students perform this exercise either the week before or after they construct a short spectrochemical series for Cu^{2+} com-

plexes (5); the two exercises together reinforce the concept of ligand field theory.

2. A more extensive list is found in ref 2, but $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ are the only two transition-metal hydrates whose tetrahydrofuran complexes can be synthesized by the procedure outlined here.

3. The THF can be drawn directly from a fresh bottle if a still is not available; the excess chlorotrimethylsilane will react with the small quantity of water in commercial THF.

Literature Cited

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