

Preparation of $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$ with Liquid Ammonia

Introduction

In this experiment we will not only synthesize hexammine chromium(III) nitrate, $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$, but also gain experience in handling liquid ammonia.

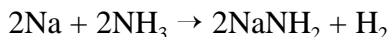
Anhydrous liquid ammonia has a boiling point of $-33.35\text{ }^\circ\text{C}$, which might suggest that it would be a difficult material to handle, particularly in light of the familiar noxious odor of the gas. However, owing to hydrogen bonding, liquid ammonia has a relatively high heat of vaporization (23.3 J/mol vs. 40.7 J/mol for H_2O). Thus, if kept in an insulated vessel (e.g., a Dewar flask), its rate of vaporization is sufficiently slow and controlled to make it a practical nonaqueous medium. If all work is done in a good fume hood, liquid ammonia poses no extraordinary hazards.

The colorless liquid has the very unusual property of dissolving alkali metals to give bronze colored solutions when concentrated ($>1.0\text{ M}$) or blue colored solutions when less concentrated. These solutions are strongly paramagnetic, with magnetic susceptibilities that decrease with increasing concentration. Various studies indicate that they are composed of solvated (i.e., ammoniated) cations and solvated electrons:



Nearly complete electron pairing occurs at concentrations $>0.1\text{ M}$, which accounts for the decreasing magnetic susceptibility with increasing concentration. The bronze color of concentrated solutions is due to an absorption at ca. 6500 \AA , and the blue color of dilute solutions results from the short wavelength tail of a broad and intense absorption band at ca. $15,000\text{ \AA}$. The latter band is ascribed to the solvated electron species.

Solutions of metals in liquid ammonia are very strong reducing agents and react very much like the free metals themselves. In all cases, the reduction process appears to involve free solvated electrons, $\text{e}(\text{NH}_3)_\text{y}^-$. The resistance of ammonia itself to reduction provides a medium in which highly reduced states are thermodynamically stable. Actually, alkali metals do react very slowly with NH_3 in a manner analogous to their behavior with water.



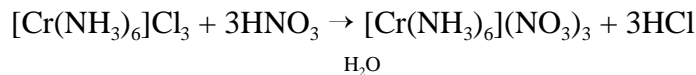
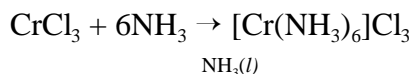
The addition of a small quantity of an iron(III) salt strongly catalyzes the reaction. The mechanism of catalysis is uncertain but appears to involve rapid reduction of Fe^{3+} to very finely divided metallic iron, which is probably the actual catalytic agent.

Like liquid H₂O, liquid NH₃ is an ionizing solvent with an autoprotolysis equilibrium:



Just as H₃O⁺ and OH⁻ are, respectively, the strongest acid and base species in water, so too are NH₄⁺ and NH₂⁻ the strongest acid and base species in liquid ammonia. Thus NH₄Cl is a strong acid, and NaNH₂ is a strong base in liquid ammonia (cf. HCl and NaOH in water). Nonetheless, NH₄⁺ is not a very strong proton donor compared to H₃O⁺ in water. Thus, liquid ammonia would be a poor choice as a solvent for reactions requiring a strong proton donor acid. On the other hand, a reaction that requires a very strong base will greatly benefit from the higher basicity of NH₂⁻ compared with OH⁻.

In this experiment we will carry out the synthesis of [Cr(NH₃)₆](NO₃)₃ by the following two-step process:



If anhydrous CrCl₃ were simply allowed to react with liquid ammonia, a major product would be [Cr(NH₃)₅Cl]Cl₂. The displacement of the last Cl⁻ proceeds very slowly unless catalytic amounts of NaNH₂ are present. While the mechanism of catalysis is not known in detail, it may be assumed that the greater nucleophilic character of NH₂⁻ as compared to NH₃ allows attack at the Cr atom with displacement of Cl⁻ to give [Cr(NH₃)₅NH₂]²⁺. This intermediate species either removes a proton from solvent NH₃ or acquires a proton when treated with nitric acid (second step above) to produce the cation [Cr(NH₃)₆]³⁺, which is precipitated as the relatively insoluble nitrate salt.

Procedure

Liquid ammonia is very volatile, irritating, and toxic. **All operations with liquid ammonia must be conducted in an efficient fume hood.** Fortunately, the intolerably pungent odor usually forces the worker from the danger area before the gas reaches fatal concentrations. Keep in mind that the temperature of liquid ammonia is approximately -33°C . Relative to this, any room-temperature materials that may be added to the liquid are "hot" enough to cause boiling and may cause bumping. Therefore, **wear eye protection and either rubber or plastic gloves throughout the course of this preparation.** Any liquid ammonia coming in contact with skin should be flushed with copious quantities of water.

Liquid ammonia may be delivered from a cylinder of the compressed gas by carefully opening the valve while the tank is tipped so that the bottom is elevated higher than the top. Larger ammonia cylinders have a goose-neck eductor tube inside them, which facilitates delivery of the liquid in this position. With the cylinder tipped and the outlet of the main valve pointing upward, the eductor tube will be immersed in the liquid inside the tank. Smaller cylinders, which usually do not have eductor tubes, simply need to be tipped at a greater angle to deliver the liquid. With either type of cylinder, it is important to realize that the main valve is only an on-off valve, not a regulator. The flow rate can be adjusted with the needle valve. Either a rubber or plastic tube connected to the valve outlet can be used to direct the flow into a receiving vessel.

Metallic sodium will be added to liquid ammonia to produce a blue solution, as described in the Introduction. In cutting the sample piece, be sure to cut off any coatings of white NaOH that may be present and blot off any mineral oil that may adhere from sodium stored under oil. **Wear dry rubber or plastic gloves while handling sodium.** Dispose of any sodium scraps by adding them to a small amount of methanol, CH_3OH , which reacts briskly to form H_2 and NaOCH_3 . **Avoid open flames.** After the sodium has completely reacted, the solution may be washed down the drain with a flush of water. Do not discard the sodium metal in a waste basket or sink.

Obtain a 60-mL nonsilvered Dewar test-tube. Carefully introduce approximately 40 mL of liquid NH_3 into the Dewar, using the procedure described above. To the liquid NH_3 , add approximately 0.1 g of freshly cut sodium metal. (This sample is approximately the size of a very small pea.) To the resulting blue solution add a small crystal of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or some other ferric salt, thereby catalyzing the reaction that produces NaNH_2 with accompanying loss of the blue color. Stir the solution, if necessary, to discharge the blue color. The resulting dark solution contains finely divided metallic iron. Add 2.5 g of finely powdered CrCl_3 (previously ground with a mortar and pestle) *in small portions* to the ammonia solution. Only small portions of CrCl_3 should be used to avoid boiling the solution over the sides of the test tube. The relatively warm CrCl_3 will increase the rate of evaporation of the liquid ammonia. If necessary, delivery some liquid ammonia into another vessel (an ordinary beaker may be used) and from it add enough to the reaction Dewar to restore the volume level. Once all the CrCl_3 has been added,

allow the brown precipitate to settle and then pour off the supernatant liquid. Transfer the precipitate to an evaporating dish and allow it to dry. (Note: It is important that the following steps be done as quickly as possible to avoid reaction of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ with Cl^- to form $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$.) Quickly dissolve the solid in 10 mL of 0.75 M HCl, which has been previously heated to 40 °C. Suction filter the solution with a medium frit and then add 4 mL of concentrated (16 M) HNO_3 . Cool the mixture in an ice bath to precipitate yellow $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$. Suction filter the precipitate on a medium frit and wash successively with very dilute HNO_3 solution, 95% ethanol, and finally diethyl ether. Allow the product to air dry on the frit. Determine the yield. Since the compound slowly decomposes in light, it should be stored in a brown bottle or a container wrapped in aluminum foil.

Prepare a dilute solution of $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$ in water and record its uv-visible spectrum from 250 to 750 nm.

Laboratory Report

1. Submit your sample, clearly labeled with the names of all group members participating in the preparation.
2. Submit your uv-visible spectrum.
3. Your written report should include statements of yield and percent yield, and brief explanations of any departures from the procedure.
4. Why is the precipitated $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$ washed with dilute HNO_3 rather than with water? What is the purpose of the ethanol and ether washes?
5. Could $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (i.e., $[\text{trans-CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$) be used in place of anhydrous CrCl_3 in this experiment? Explain.