Microscale Synthesis of Hexaamminechromium(III) Nitrate Using Liquid Ammonia Generated in the Laboratory

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The synthesis of hexaamminechromium(III) as the nitrate (*1*, *2*) or chloride (*3*) salt using liquid ammonia as the solvent has been previously described. It is an experiment suitable for an advanced inorganic chemistry course as an example of the use of a nonaqueous inorganic solvent. The experiment can also be used as a follow-up to the preparation of $CrCl_3$ using a tube furnace (*1*), since the $CrCl_3$ can be used directly as a starting material in the preparation of hexaamminechromium(III); or as a means of producing a sample that can be used for the determination of magnetic susceptibility (*1*), since the use of hexaamminechromium(III) with its three unpaired 3d electrons illustrates the effect of quenching the orbital contribution to the magnetic moment.

A drawback to the procedure as originally described is that liquid ammonia is extremely toxic and corrosive. The disposal through evaporation of the amounts involved is a hazard, especially in larger laboratory sections. The accidental spillage or leakage of the very volatile liquid ammonia can add to the hazards of this experiment. Moreover, it is relatively expensive to purchase even the smallest tank of ammonia and the necessary valves (which are subject to corrosion with use). This cost may not be justified when one must work with a limited budget or if this experiment is used only once a year with a small laboratory section. There is also the need to store the unused ammonia safely or to return it to the supplier to avoid demurrage costs, which again adds to the cost of the experiment.

These problems are eliminated or minimized by scaling down the experiment to microscale size and by directly generating the small amounts of liquid ammonia required for the microscale preparation.

Summary of Experiment

The liquid ammonia is produced by heating a concentrated aqueous ammonia solution to the boiling point and passing the vapors through a NaCl–ice-water trap to remove water before condensing the remaining ammonia vapors in a dry ice–2-propanol bath.

All operations involving ammonia are carried out in a hood. When sodium metal is added to liquid ammonia, it dissolves to produce a solution containing an ammoniated sodium cation, $Na^+(am)$, and an ammoniated electron $e^-(am)$ (eq 1), which produces a characteristic blue color (*4*, *5*). The symbol (am) is used to indicate an ammonia solution just as (aq) is used to indicate a water solution.

$$Na(s) = Na^+(am) + e^-(am) \qquad (1)$$

This unstable solution decomposes to produce sodium amide via the reduction of ammonia by the solvated electron (eq 2). In this experiment, the rate of this decomposition is increased by the use of an iron(III) salt as a catalyst.

$$2NH_3(\ell) + e^-(am) = 2NH_2^-(am) + H_2(g) \qquad (2)$$

Liquid ammonia is a polar enough solvent to dissolve the $CrCl_3$. The amide ion, NH_2^-, catalyzes the reaction of $CrCl_3$ with ammonia using a conjugate base substitution reaction mechanism (*6*) to produce hexaamminechromium(III) (eq 3).

$$CrCl_3(am) + 6NH_3(\ell) = [Cr(NH_3)_6]Cl_3(s) \qquad (3)$$

This product is dissolved in dilute hydrochloric acid and isolated as the nitrate salt by adding concentrated nitric acid to the solution (eq 4).

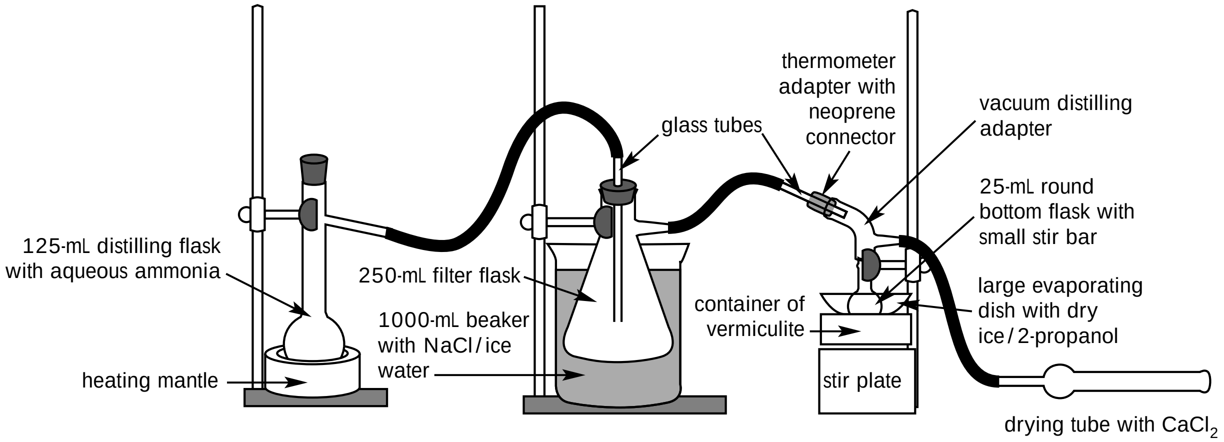

Figure 1. Apparatus for the preparation of liquid ammonia and hexaamminechromium(III).

$$[Cr(NH_3)_6]Cl_3(aq) + 3HNO_3(aq) = [Cr(NH_3)_6](NO_3)_3(s) + 3HCl(aq) \quad (4)$$

The time required for the experiment is 3 h.

Experimental Procedure

The experimental apparatus illustrated in Figure 1 is assembled. To a 125-mL side-arm distilling flask is added 50 mL of concentrated aqueous ammonia. A 250-mL filter flask is placed in a 1-L beaker containing a sodium chloride–ice-water bath that traps water and prevents it from entering the reaction vessel. A 25-mL round-bottom flask containing a small magnetic stirring bar is placed in a large evaporating dish containing a dry ice–2-propanol bath. To help insulate it, the evaporating dish is supported in a box filled with vermiculite. The 25-mL flask, evaporating dish, and box of vermiculite are placed over a stir plate.

The distilling flask containing the concentrated aqueous ammonia is heated until ca. 5 to 10 mL of liquid ammonia has been collected in the 25- mL round-bottom flask. The 25-mL round bottom flask is now disconnected from the rest of the apparatus, but still cooled in the dry ice–2-propanol bath for the remaining steps, which should be performed relatively quickly.

To the liquid ammonia in the 25-mL round-bottom flask is added ca. 0.015 g (0.65 mmol) of freshly cut sodium metal. (NOTE: Any coating of NaOH that may be present on the sodium is first cut off. Waste sodium is disposed of by placing it in a small beaker containing anhydrous methanol. After the waste sodium has completely reacted, the solution is washed down the drain using water.) Stirring is continued until the sodium has completely reacted. At this point, the liquid ammonia solution has become blue. The blue solution is decolorized by the catalytic formation of $NaNH_2$ after the addition of a very small amount of $Fe(NO_3)_3 \cdot 9H_2O$ or other ferric salt. The solution is stirred until the blue color disappears.

The dark solution, which contains finely divided iron, is now treated with 0.320 g (2.03 mmol) of finely powdered $CrCl_3$. The $CrCl_3$ that can be purchased as a sublimed 99% pure powder (Aldrich) or prepared using a tube furnace (*1*) can generally be used without further grinding. The flask is corked, and stirring is continued for ca. 20 min until the suspension has become brown.

In the hood, the mixture of liquid and solid is transferred from the 25-mL flask to the small evaporating dish. The liquid ammonia is allowed to completely evaporate to produce a dry solid. In a 10-mL beaker, this solid is then quickly dissolved, with stirring, in 3 mL of a 0.75 M HCl solution that has previously been heated to ca. 40 °C. Using a Hirsch funnel, the solution is filtered and transferred to 10-mL beaker. To this solution, 1 mL of concentrated HNO_3 is immediately added. After stirring, the mixture is cooled in an ice bath.

Using a Hirsch funnel, the yellow $[Cr(NH_3)_6](NO_3)_3$ solid that forms in the solution is suction-filtered off and washed first with a 3.5 M HNO_3 solution, then with 95% ethanol, and finally with diethyl ether. The solid yellow product is allowed to air-dry. Typically, students obtain 0.350 to 0.425 g of product (a yield of 51 to 62%). Since the compound slowly decomposes in light, it should be stored in a brown bottle or in a container wrapped in aluminum foil.

Chemicals

aqueous ammonia (concentrated)
anhydrous chromium chloride ($CrCl_3$)
calcium chloride (for drying tube)
diethyl ether
dry ice
ethanol (95%)
ferric nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$
hydrochloric acid (0.75 M)
nitric acid (concentrated and 3.5 M)
2-propanol (for dry-ice bath)
sodium chloride (for sodium chloride/ice bath)

Equipment

10-mL and 1000-mL beakers
125-mL side-arm distilling flask
drying tube
small (75 mm o.d.) and large (115 mm o.d.)
  evaporating dishes
50- and 250-mL filter flasks
filter paper
5- and 15-cm glass tubes (6 mm o.d.)
heating mantle
Hirsch funnel
magnetic stirring bar
magnetic stirrer
25-mL round-bottom flask
rubber tubing
thermometer adapter with neoprene connector
vacuum distilling adapter
vermiculite

^{W}Supplemental Material

Supplemental material for this article is available in this issue of *JCE Online*.

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Synthesis of Hexaamminechromium(III) Nitrate Using Liquid Ammonia

Introduction

In this experiment we will synthesize the octahedral inorganic coordination compound hexaamminechromium(III) nitrate using the inorganic nonaqueous solvent liquid ammonia (NH_3).

Liquid NH_3 is a very volatile (b.p. = -33 ºC) and toxic material; all operations involving it must be carried out in a hood. In this preparation, liquid NH_3 acts both as a sufficiently polar solvent to dissolve the $CrCl_3$, as a medium for accommodating the very reactive metallic sodium, and as a reactant.

The first step involves dissolving sodium metal in the liquid NH_3. The reaction of sodium with NH_3 (eq 1) is slow and produces a characteristic blue color due to the formation of solvated electrons (*1, 2*). The symbol (*am*) is used in the equation to indicate an ammonia solution just as (*aq*) is used to indicate a water solution.

$$\mathrm{Na}(s) \quad = \quad \mathrm{Na}^+(am) \; + \; e^-(am) \qquad (1)$$

This solution slowly decomposes to produce the amide ion (eq 2).

$$2\mathrm{NH_3}(l) \; + e^-(am) \quad = \quad 2\mathrm{NH_2}^-(am) \; + \; \mathrm{H_2}(g) \qquad (2)$$

The rate of this reaction can be increased, however, by the addition of a small amount of a Fe(III) salt that catalyzes the reaction and causes the blue color to disappear. The Fe(III) salt is rapidly reduced by the ammoniated electrons to very finely divided metallic iron, which is probably the actual catalyst.

Sodium amide, $NaNH_2$, that is produced in the NH_3 is analogous to NaOH in H_2O. Just as OH^- is a base in H_2O, NH_2^- is a base in NH_3. The NH_2^- group, however, is a stronger base than the OH^- group, and reactions requiring a very strong base will greatly benefit from the higher basicity of NH_2^- as compared to OH^-.

The $CrCl_3$ is now dissolved in the NH_3. In the absence of the NH_2^-, the main product of the reaction is $[Cr(NH_3)_5Cl]^{2+}$ (*3, 4*). The NH_2^- , however, catalyzes the reaction of $CrCl_3$ and NH_3 to replace the Cl^- ligand and produce $[Cr(NH_3)_6]^{3+}$ (eq 3).

$$\mathrm{CrCl_3}(am) \; + \; 6\mathrm{NH_3}(l) \quad = \quad [\mathrm{Cr(NH_3)_6}]\mathrm{Cl_3}(am) \qquad (3)$$

The activity of the NH_2^- may be due to it being part of a conjugate base substitution reaction (*4*) illustrated by eqs 4 - 6.

$$[\mathrm{Cr(NH_3)_5Cl}]^{2+} \; + \; \mathrm{NH_2}^- \quad = \quad [\mathrm{Cr(NH_3)_4(NH_2)Cl}]^+ \; + \; \mathrm{NH_3} \qquad \text{(fast)} \qquad (4)$$

$$[\mathrm{Cr(NH_3)_4(NH_2)Cl}]^+ \quad \text{-->} \quad [\mathrm{Cr(NH_3)_4(NH_2)}]^{2+} \; + \; \mathrm{Cl}^- \qquad \text{(slow)} \qquad (5)$$

$$[\mathrm{Cr(NH_3)_4(NH_2)}]^{2+} \; + \; 2\mathrm{NH_3} \quad \text{-->} \quad [\mathrm{Cr(NH_3)_6}]^{3+} \; + \; \mathrm{NH_2}^- \qquad \text{(fast)} \qquad (6)$$

Therefore, the abstraction of the proton from one of the bound NH_3 ligands by the basic NH_2^- ion in eq 4 makes it easier for the Cl^- ligand to leave in eq 5 and to be replaced by a NH_3 ligand.

Addition of nitric acid to an aqueous solution of the hexaamminechromium(III) then gives a precipitate of the nitrate salt (eq 7).

$$[\mathrm{Cr(NH_3)_6}]\mathrm{Cl_3}(aq) \; + \; 3\mathrm{HNO_3}(aq) \quad = \quad [\mathrm{Cr(NH_3)_6}](\mathrm{NO_3})_3(s) \; + \; 3\mathrm{HCl}(aq) \qquad (7)$$

Safety Recommendations

Ammonia (CAS No. 7664-41-7). This compound is a pungent, toxic gas. It is harmful if swallowed, inhaled, or absorbed through the skin. It will irritate the eyes and nasal passages and burn the skin. Ammonia will form explosive compounds with many heavy metals and with the halogens.

Ammonium hydroxide (CAS No. 1336-21-6). Concentrated ammonium hydroxide is a 28 to 30% solution that is approximately 15 M. It is corrosive and toxic and has a pungent odor due to the release of ammonia vapors. It can therefore cause many of the same problems as ammonia.

Calcium chloride, $CaCl_2$ (CAS No. 10043-52-4). This anhydrous material is to be used in a drying tube. It is not normally not considered harmful.

Chromium chloride, $CrCl_3$ (CAS No. 10025-73-7). This anhydrous compound is highly toxic and corrosive and should not be touched or inhaled.

Diethyl ether (CAS No. 60-29-7). Diethyl ether is an extremely flammable solvent. Exposure to moisture tends to form peroxides, which may be explosive. It is also a potent narcotic.

Dry ice, CO_2 (CAS No. 124-38-9). Dry ice is solid carbon dioxide and will cause severe burns if it comes in contact with the skin.

Ethanol (95%) (CAS No. 64-17-5). Ethanol may be fatal if inhaled, swallowed, or absorbed through the skin in large amounts. It has been shown to have effects on fertility and on embryo development. The vapor may travel considerable distances to a source of ignition and flash back.

Ferric nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$ (CAS No. 7782-61-8). This compound is an oxidizer and an irritant. It is harmful if swallowed or inhaled.

Hydrochloric acid, HCl (CAS No. 7647-01-0). Concentrated hydrochloric acid is available as a 37% solution with a concentration of 12.0 M. It is extremely corrosive and toxic. A 0.75 M solution is prepared by diluting 3.13 mL of concentrated hydrochloric acid to a total volume of 50 mL with distilled water.

Nitric acid, HNO_3 (CAS No. 7697-37-2). Nitric acid is available as a 69 to 71% solution and is about 15.6 M. This acid is extremely corrosive and toxic. Toxic fumes of NO_2 may be given off. It is also a strong oxidizing agent. A 3.5 M solution is prepared by diluting 11.2 mL of concentrated nitric acid to a total volume of 50 mL with distilled water.

2-Propanol (CAS No. 67-63-0). This compound is to be used for the dry ice/acetone bath. It is not normally considered dangerous, but normal precautions should be employed.

Sodium (CAS No. 7440-23-5). This element is harmful if swallowed, inhaled, or absorbed through the skin. Contact of sodium with water can result in an explosion. Sodium is extremely destructive to the skin and tissues, and gloves should be worn when handling it. Exposure to air forms sodium oxide. Sodium should be stored under mineral oil or kerosene.

Sodium chloride, NaCl (CAS No. 7647-14-5). To be used in the sodium chloride/ice water bath. It is not generally considered toxic.

Required Equipment

10-mL and 1-L beaker, 125-mL side-arm distilling flask, drying tube, small and (75 mm OD) and large (115 mm OD) evaporating dish, 50-mL and 250-mL filter flask, filter paper, 5 and 15 cm glass tubes (6 mm OD), heating mantle, Hirsch funnel, magnetic stirring bar, magnetic stirrer, 25-mL round bottom flask, rubber tubing, thermometer adapter with neoprene connector, vacuum distilling adapter, vermiculite.

Time Required for Experiment: 3 h.

Experimental Procedure

The experimental apparatus illustrated in the Figure is assembled.

Figure: Apparatus for preparation of liquid ammonia and hexaamminechromium(III)

To a 125-mL side-arm distilling flask is added 50 mL of concentrated ammonium hydroxide.

A 250-mL filter flask is placed in a 1-L beaker containing a mixture of ice water and sodium chloride. The sodium chloride/ice water bath produces a temperature of between -5 and -10 ^{o}C. This temperature is maintained by stirring the mixture and occasionally siphoning off some of the solution and replacing it with more ice and salt. Although the sodium chloride/ice water bath is not cool enough to stop the flow of the NH_3 vapors, it is able to trap the water vapors and prevent them from entering the reaction vessel.

A 25-mL round bottom flask, containing a small magnetic stirring bar, is placed in the large evaporating dish. To the evaporating dish is added 2-propanol and then, carefully and slowly, small chunks (approximately one inch in diameter) of dry ice. Initially, the addition of the dry ice will produce vigorous bubbling due to the evolution of CO_2. This will subside, however, as the 2-propanol is cooled. The resulting dry ice/2-propanol bath produces a temperature of -78 ^{o}C. Make sure that at all times there are some small chunks of dry ice remaining in the 2-propanol to insure that the most efficient cooling is occurring.

To help insulate it, the evaporating dish containing a dry ice/2-propanol bath is supported in a box filled with vermiculite. The 25-mL flask, evaporating dish, and box of vermiculite are placed over a stir plate

The distilling flask containing the concentrated ammonium hydroxide is heated. Heating is continued until *ca.* 5 to 10 mL of liquid ammonia has collected in the 25-mL round bottom flask.

The 25-mL round bottom flask is now disconnected from the rest of the apparatus, but still cooled in the dry ice/2-propanol bath for the remaining steps, which should be performed relatively quickly.

To the liquid ammonia in the 25-mL round bottom flask is added *ca.* 0.015 g (0.65 mmoles) of freshly cut sodium metal. Stirring is continued until the sodium has completely reacted. At this point, the liquid ammonia solution has become blue in color.

Any coating of NaOH which may be present on the sodium is first cut off. Waste sodium is disposed of by adding it to a small beaker of anhydrous methanol. After the waste sodium has completely reacted, the solution is washed down the drain using water.

The resulting blue solution is decolorized by the catalytic formation of $NaNH_2$ after the addition of a very small amount of $Fe(NO_3)_3 \cdot 9H_2O$ or other ferric salt. The solution is stirred until the blue color disappears.

The dark solution, which contains finely divided iron, is treated with 0.320 g (2.03 mmoles) of finely powdered $CrCl_3$. The $CrCl_3$ that can be purchased as a sublimed 99% pure powder (Aldrich) or prepared using a tube-furnace (*1*) can generally be used without the need for further grinding. The flask is corked and stirring is continued for *ca.* 20 min until the color of the suspension has become brown.

In the hood, the mixture of liquid and solid is transferred from the 25-mL flask to the small evaporating dish. The liquid ammonia is allowed to completely evaporate to produce a dry solid.

In a 10-mL beaker, this solid is then quickly dissolved, with stirring, in 3 mL of a 0.75 M HCl solution which has previously been heated to *ca.* 40 °C. Using a Hirsch funnel, the solution is filtered and transfered to a 10-mL beaker. To this solution, 1 mL of concentrated HNO_3 is immediately added. After stirring, the mixture is cooled in an ice bath.

These latter steps should be done as quickly as possible to avoid reaction of $[Cr(NH_3)_6]^{3+}$ with Cl^- to form $[Cr(NH_3)_5Cl]^{2+}$.

Using a Hirsch funnel, the yellow $[Cr(NH_3)_6](NO_3)_3$ solid that forms in the solution is suction-filtered off, washed first with a 3.5 M HNO_3 solution, then with 95% ethanol, and finally with diethyl ether. The solid yellow product is allowed to air-dry. Typically, 0.350 to 0.425 g of product is obtained (a yield of 51 to 62%).

Acquire the infrared spectrum of $[Cr(NH_3)_6]NO_3$ as a Nujol mull and make assignments for the absorptions due to the vibrations of the NH_3 and NO_3^- groups (*5*).

Since the compound slowly decomposes in light, it should be stored in a brown bottle or in a container wrapped in aluminum foil. The sample should be saved since its magnetic susceptibility will be determined in a later experiment.

Literature Cited

1. Rodgers, G. E. *Introduction to Coordination, Solid State, and Descriptive Inorganic Chemistry*; McGraw Hill: New York, 1994; pp 316-7.
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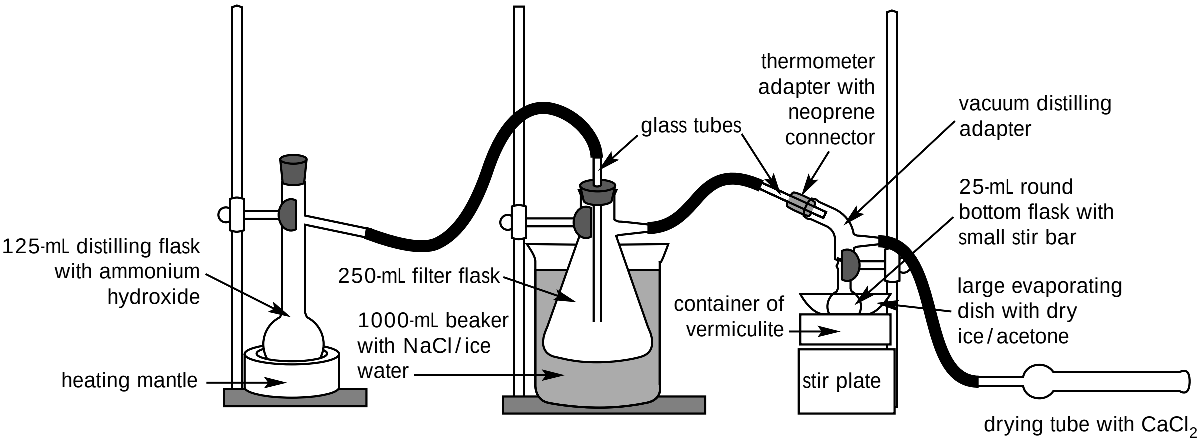
Instructors Notes

1. The ground glassware used is that with 19/22 joints.
2. Emphasize that the experiment must be performed in a hood and that the ammonia is toxic and can cause severe burns to the skin.
3. The dry ice can also cause severe burns if it comes in contact with the skin.
4. Care must be taken with the initial addition of the dry ice to the 2-propanol, especially if it is warm, since severe bubbling can take place.
5. The students should be reminded that any excess sodium must not be disposed of in the sink.
6. Approximately 1 g of sample is needed to determine magnetic susceptibility. The product from three different groups can be combined to give enough sample.


thermometer adapter with neoprene connector
vacuum distilling adapter
glass tubes
25-mL round bottom flask with small stir bar
125-mL distilling flask with ammonium hydroxide
250-mL filter flask
large evaporating dish with dry ice / acetone
container of vermiculite
1000-mL beaker with NaCl / ice water
heating mantle
stir plate
drying tube with CaCl₂