Preparation of Hexammine Chromium(III) Nitrate with Liquid Ammonia

Name

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Abstract

Hexammine chromium(III) nitrate, $[Cr(NH_3)_6](NO_3)_3$, was synthesized through a two-step process, first reacting anhydrous $CrCl_3$ with liquid ammonia to produce $[Cr(NH_3)_6]Cl_3$. The dried $[Cr(NH_3)_6]Cl_3$ was then reacted with dilute $HNO_3(aq)$ to form $[Cr(NH_3)_6](NO_3)_3$. The synthesis produced 0.8790 g at 75 % $[Cr(NH_3)_6](NO_3)_3$ product yield. The final $[Cr(NH_3)_6](NO_3)_3$ product was significantly pure as determined by its pale yellow color and visible absorption spectrum which offered peaks at 304, 351 and 465 nm, for which the lower energy transitions are in high agreement with literature values of 351 and 463 nm, respectively[4].

Introduction

The preparation of hexammine chromium(III) nitrate, $[Cr(NH_3)_6](NO_3)_3$, can be performed by a minimally complicated two-step process involving ammoniation of $CrCl_3$. It is a convenient synthesis for gaining practical expertise in working with liquid ammonia and for the study of metal-centered *d-d* electron transitions.

The initial synthesis step involves the addition of anhydrous chromium(III) chloride, $CrCl_3$, to a solution of liquid ammonia, which reacts as:

$$CrCl_3(s) + 6NH_3(l) \underset{NH_3(l)}{\rightleftharpoons} [Cr(NH_3)_6]Cl_3(s) \qquad \text{(Rxn.1)}$$

However, reaction 1 is preempted by reaction of the $NH_3(l)$ solvent with Na(*s*) in the presence of an Fe^{3+} catalyst through a reaction similar to alkali metal chemistry with water:

$$2Na(s) + 2NH_3(l) \overset{Fe^{3+}}{\rightleftharpoons} 2NaNH_2(l) + H_2(g) \qquad \text{(Rxn.2)}$$

where Fe^{3+}, incorporated here through the iron salt, $Fe(NO_3)_3{\cdot}9H_2O$, acts through an undefined mechanism, likely secondary to the reduction of Fe^{3+} to Fe, which sets Fe as the true catalyst.

Regardless of the mechanism of action, however, this pretreatment produces $NaNH_2$ which is a strong enough nucleophile to remove the final Cl^- ligated directly bound to the central chromium of $[Cr(NH_3)_5Cl]Cl_2$ to produce $[Cr(NH_3)_5NH_2]^{2+}$. In the absence of $NaNH_2$, the $[Cr(NH_3)_5Cl]Cl_2$ intermediate would be the major product of reaction 1, as NH_3 is not a strong enough nucleophile to displace the final Cl^-. The intermediate $[Cr(NH_3)_5NH_2]^{2+}$ then acquires an additional proton by either removal from solvent $NH_3(l)$ or when introduced to HNO_3 in a latter step. It is interesting to note that the resistance of ammonia to reduction enables the stability as well as adds to the plausibility of the proposed highly reduced Fe(0) state for the catalysis.

The impure $[Cr(NH_3)_6]Cl_3$ product precipitates as a brown insoluble and can be collected for further manipulation by decanting the $NH_3(l)$ and subsequently neutralizing any remnant aqueous NH_3, which will react with water through reaction 3, with a warm dilute $HCl(aq)$ solution illustrated by reaction 4:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad \text{(Rxn.3)}$$

$$NH_4^+ + Cl^- \rightleftharpoons NH_4Cl \qquad \text{(Rxn.4)}$$

The chromium(III) complex can then react further as:

$$[Cr(NH_3)_6]Cl_3(aq) + 3HNO_3(aq) \rightleftharpoons [Cr(NH_3)_6](HNO_3)_3(s) + 3HCl(aq) \qquad \text{(Rxn.5)}$$

where the $[Cr(NH_3)_6](HNO_3)_3$ product is soluble in water at room temperature, but crystallizes out as a pale canary yellow solid upon solution cooling. The precipitate can then be purified further by washing sequentially with very dilute $HNO_3(aq)$, 95% ethanol and lastly, diethyl ether.

The ability to synthesize $[Cr(NH_3)_6](NO_3)_3$ is desirable for spectroscopic investigation as well as for magnetic susceptibility experimentation.

Experimental Methods

Part I: Synthesis of $[Cr(NH_3)_6](NO_3)_3$

A small piece (~0.1 g) of freshly cut sodium metal, stripped of any visible NaOH formation, and cleaned of storage oil was introduced to ~40 mL of liquid NH_3 in a 60-mL nonsilvered Dewar test-tube. When the solution was uniformly dark blue, a few granules of crystal Fe(III) nitrate, $Fe(NO_3)_3 \cdot 9H_2O$, were added to the solution and the solution was allowed to sit until it the blue color disappeared, replaced by a dark brown solution with some visible suspended precipitate.

0.5 g $CrCl_3$ crushed into a fine powder was then added slowly to the $NH_3(l)$ solution so that the solution did not boil over the top of the Dewar test-tube. Additional $NH_3(l)$ was added to the solution throughout $CrCl_3$ addition to maintain a constant reaction volume. The resulting solution was transferred to a small ceramic dish with a pouring lip, the newly formed precipitate allowed to settle, and the supernatant decanted. The precipitate was then left to dry in the chemical fume hood. The completely dry precipitate was then dissolved in 10 mL of ~40 °C 0.75 M HCl. The solution was promptly filtered using a sintered glass funnel and then ~4 mL of concentrated nitric acid, HNO_3 (16 M), was added to the filtrate. The filtrate solution was then cooled in an ice bath for ~15 minutes at which point the resulting precipitate was filtered on the sintered glass funnel and washed with 5-mL portions of dilute $HNO_3(aq)$, 95% ethanol and diethyl ether. Washes were performed in the order presented and each wash was added after the previous wash was complete. The product was then allowed to air dry on the frit and the yield determined. For prolonged storage, the photo-sensitive product was placed in an amber sample vial to protect it from excess light.

Part II: Visible Spectrum of $[Cr(NH_3)_6](NO_3)_3$

A small amount of the product was dissolved in water and the UV-visible electronic absorption spectrum from 250 nm to 750 nm was recorded.

Results

The preparation of $[Cr(NH_3)_6](NO_3)_3$ produced 0.8790 g of product which was determined at 75% yield based on mass analysis. The masses and moles of materials involved in the synthesis are provided in Table 1. Percent yield was then determined based on a ratio of 1:1 for each molecule of $CrCl_3$ producing one molecule of $[Cr(NH_3)_6](NO_3)_3$ in the presence of excess ammonia and HNO_3. The total $CrCl_3$ was evaluated to be 3.45 x 10^{-3} moles, setting the maximum obtainable $[Cr(NH_3)_6](NO_3)_3$ yield at 100 percent also at 3.45 x 10^{-3} moles. Therefore, a total product yield of 0.8790 g and 2.58 x 10^{-3} moles provides a 75% yield based on simple mass analysis. Additionally, the product achieved was the characteristic canary yellow color of $[Cr(NH_3)_6](NO_3)_3$.

The electronic UV-visible absorption spectrum of the final $[Cr(NH_3)_6](NO_3)_3$ product was obtained offering three distinct maxima at 304, 351 and 465 nm.

Materials for the Synthesis of Hexammine Chromium(III) Nitrate, $[Cr(NH_3)_6](NO_3)_3$

Mass (g)	MW[3]	Moles	Component
0.5465	158.3558	3.45E-03	$CrCl_3$
27.840	1.6347	17.03	NH_3
-	-	6.40E-02	HNO_3
0.8790	340.1933	2.58E-03	$[Cr(NH_3)_6](NO_3)_3$

Table 1. Materials involved in the synthesis of hexammine chromium(III) nitrate.

Discussion

The synthesis of $[Cr(NH_3)_6](NO_3)_3$ was determined successful based on the percent yield of the product, its pale yellow color, and the UV-visible spectrum observed for the product. The percent yield at 75% is exceptionally high as it closely approaches total efficiency, which would have been complete consumption of $CrCl_3$ However, such a high percent yield is especially unlikely considering the procedure is a two-step process which includes multiple washes. Thus, while the percent yield is hesitantly large, it was considerably pure based on further qualitative analysis.

The canary yellow color of the product is significant as it is characteristic of the correct $[Cr(NH_3)_6](NO_3)_3$ product. Additionally, and more informatively, the UV-visible spectrum obtained for the diluted product offered peak maxima at 304, 351 and 465 nm. The lower two energy observed values matched literature values well of 351 and 463 nm, respectively[4]. The observed absorptions arise from *d-d* transitions from $^4A_{2g}$ to $^4T_{2g}$ (ν_1) and $^4A_{2g}$ to $^4T_{1g}$(F) (ν_2)[4]. Additionally, it should be noted that as solutions of HNO_3(*aq*) are colorless, the $(NO_3)^-$ ion which dissociates in aqueous solution from the $[Cr(NH_3)_6](NO_3)_3$ parent salt, is not expected to give a visible absorption spectrum and in measurements taken from 250 nm in the UV region, a high-UV absorption for $(NO_3)^-$ is not observed. The third observed peak at 304 nm can be attributed to the $^4A_{2g}$ to $^4T_{1g}$(P) (ν_3) transition and is seldom reported in literature as it is often appears as a shoulder to the intense peak at 351 nm[4].

A significant departure was made from the established procedure in terms of starting $CrCl_3$ material used. The original protocol requires the use of 2.5 g of powdered $CrCl_3$, however, only 0.5 g was incorporated in the actual experiment. All other amounts were kept constant and suggest, as is the case that $CrCl_3$ is the limiting component, and that the amount used does not affect the efficiency or reaction.

With regard to experimental procedure, it is important to note that the very dilute HNO_3(*aq*) wash of the final crude product cannot be exchanged with a wash by pure water. This is because the presence of $(NO_3)^-$ ions in the dilute solution promote the retention of the inclusive salt product through effects of Le Chatlier's principle (common ion effect). Additionally, the inclusion of $(NO_3)^-$ ions in the wash solution favors $(NO_3)^-$ salt combination over the recombination with Cl^- ions being washed out. If the $[Cr(H_2O)_6](NO_3)_3$ were to be mistakenly washed with pure water, some Cl^- ions might be reincorporated. It is clear, however, due to latter steps, during which $[Cr(H_2O)_6](NO_3)_3$ is solubilized in water in order to obtain its absorption spectrum, that displacement of NH_3 by water is not at issue for the final product. Additionally, washes with 95% ethanol and ether must be performed as the ethanol solution will solvate and remove excess HNO_3 ions and the diethyl ether solution, commonly employed for liquid-liquid extractions, will remove any residual moisture including both remnant water and ethanol. In addition, this series of washes must be performed with haste to avoid appreciable reaction of Cl^- with $[Cr(NH_3)_6]^{3+}$ as:

$$[Cr(NH_3)_6]^{3+} + Cl^- \longrightarrow [Cr(NH_3)_5Cl]^{2+} \qquad \text{(Rxn.6)}$$

where the central chromium ion would once more be directly ligated to a chlorine atom.

Furthermore, in the absence of anhydrous $CrCl_3$, hydrated $CrCl_3{\cdot}6H_2O$, more specifically *trans*-$CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$, can be substituted as the starting material. However, the reaction order may require initial replacement of Cl^- ligands and subsequent reaction with $NH_3(l)$ as:

$$[Cr(H_2O)_6]Cl_3 + 3(NO_3)^- \rightleftharpoons [Cr(H_2O)_6](NO_3)_3 + 3Cl^- \qquad \text{(Rxn.7)}$$

$$[Cr(H_2O)_6](NO_3)_3 + 6NH_3 \rightleftharpoons [Cr(NH_3)_6](NO_3)_3 + 6H_2O \qquad \text{(Rxn.8)}$$

where reaction 7 is very similar to reaction 5 in the experiment carried out here and reaction 8 is predicted based upon spectroscopic trends of similar complex coordinate systems[6]. It is possible though that this method might yield greater impurity. On a statistical basis, reaction 8 requires replacement of six coordinated ligands, whereas in the preparation performed, chromium seeks complexation with the six ammonia ligands and the final Cl^- removal is the only barrier.

A few concerns should be addressed regarding the experiment reported here. The initial $CrCl_3$ starting material was synthesized in a previous experiment, yet, as the desired product of that synthesis limited analysis was performed to ensure its purity. In fact, only a like synthesized product was tested for solubility rather than the actual $CrCl_3$ product carried over into this preparation. This may contribute to a higher percent yield than was reported achieved based upon simple mass analysis. Additionally, although the $NH_3(l)$ solvent was in significant excess, it is not known absolutely whether the $NaNH_2$ which is removes the last Cl^- in a timely manner was in excess.

Improvements to the experiment would include taking the spectrum in ammonia or other solvent and comparing its result with the spectrum taken in water. As both water and ammonia, at least, are colorless, neither will interfere spectroscopically with the spectrum. Additionally, the method may benefit from spectral comparison with like coordinated compounds such as $[Co(NH_3)_6]^{3+}$ or $[Cr(H_2O)_6]^{3+}$.

Conclusions

The preparation of $[Cr(NH_3)_6](NO_3)_3$ through the initial ammoniation of $CrCl_3$ and further metathesis replacement of Cl^- with $(NO_3)^-$ was highly successful as reflected in the 75% product yield based upon simple mass analysis. Moreover, the overall synthesis was exceedingly successful in terms of purity based upon its formation as a pale yellow solid and the observation of its UV-visible electronic absorption spectrum offering characteristic peak maxima at 351 and 465 nm. However, further experimentation is suggested for comparison with similarly coordinated systems in order to expand knowledge base of metal-centered *d-d* transitions and the effect of the ligated species on promotion.

Supporting Information Available

I. $NH_3(l)$ as a solvent

II. Solvation of alkali metals in $NH_3(l)$

III. Precipitation with dilute $HNO_3(aq)$ vs. water and discussion of ethanol and ether washes

IV. $CrCl_3 \cdot 6H_2O$ as starting material (compared to anhydrous $CrCl_3$)

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Supporting Information for

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I. Although in many organic and inorganic syntheses water is used as the solvent, it is sometimes preferable or necessary to use $NH_3(l)$ or other appropriate non-aqueous liquid. $NH_3(l)$ is a polar solvent able to dissolve $CrCl_3$ and like water, which to the contrary cannot readily dissolve $CrCl_3$, it is considerably hydrogen bonded. However, as $NH_3(l)$ boils at -33.35 °C, its handling can be problematic as most experimental items, including glassware and any reacting chemicals can induce boiling as they are generally at room temperature, far above the b.p. of $NH_3(l)$. Also like water, $NH_3(l)$ has an autodissociation equilibrium which establishes the strongest acid and base within its solvent system:

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^- \qquad \text{(Rxn.9)}$$

where $K = 1.9 \times 10^{-33}$ (50 °C) and NH_4^+ and NH_2^- are the strongest acid and base, respectively.

II. Solutions resulting from the solvation of an alkali metal in $NH_3(l)$ will vary in color depending upon the concentration of the metal. While $NH_3(l)$ itself is colorless, solvation of concentrated amounts of an alkali metal (>1 M) give rise to bronze colored solutions. On the other hand, dilute alkali metal(*am*) solutions (where (*am*) is used to denote ammonia based solutions much like (*aq*) for water) will yield blue solutions. Furthermore, such solutions of alkali metals are exceedingly paramagnetic, becoming more so with decreasing metal concentration. For solutions in excess of 0.1 M, virtually complete electron pairing is attained and magnetic susceptibility decreases swiftly.

In the reaction here between Na(*s*) and ammonia,the solvation proceeds as[7]:

$$Na(s) + NH_3(l) \rightleftharpoons Na^+[NH_3(l)] + e^-[NH_3(l)] \qquad \text{(Rxn.10)}$$

III. "With regard to experimental procedure, it is important to note that the very dilute $HNO_3(aq)$ wash of the final crude product cannot be exchanged with a wash by pure water. This is because the presence of $(NO_3)^-$ ions in the dilute solution promote the retention of the inclusive product through effects of Le Chatlier's principle. Additionally, the inclusion of

$(NO_3)^-$ ions in the wash solution favors $(NO_3)^-$ salt combination over the recombination with Cl^- ions being washed out. If the $[Cr(H_2O)_6](NO_3)_3$ were to be mistakenly washed with pure water, some Cl^- ions might be reincorporated, exchanging with $(NO_3)^-$ ligands. It is clear, however, due to latter steps, during which $[Cr(H_2O)_6](NO_3)_3$ is solubilized in water in order to obtain its absorption spectrum, that displacement of NH_3 by water is not at issue for the final product. Additionally, washes with 95% ethanol and ether must be performed as the ethanol solution will solvate and remove excess $(NO_3)^-$ ions and the diethyl ether solution, commonly employed for liquid-liquid extractions, will remove any residual moisture including both remnant water and ethanol. In addition, this series of washes must be performed with haste to avoid appreciable reaction of Cl^- with $[Cr(NH_3)_6]^{3+}$ as:

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