

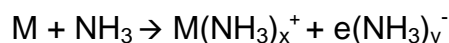
## ADVANCED INORGANIC CHEMISTRY

### EXPERIMENT 1

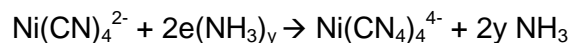
#### Synthesis and Characterization of Hexamminechromium (III) nitrate [Cr(NH<sub>3</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>3</sub>

In this experiment, not only will the synthesis of [Cr(NH<sub>3</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>3</sub> be carried out, but techniques involved in handling liquid ammonia will be acquired.

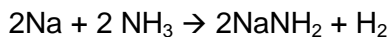
Anhydrous liquid NH<sub>3</sub> has a boiling point of -33 o C but can be used in chemical reactions, either as a reactant or as a solvent, without any special equipment. Of course, it will vaporize at a significant rate if it is used at room temperature without external cooling. This is not, however, a serious problem if the experiments are conducted in an effective hood. In certain cases, any inconvenience created by the low boiling point of the liquid and the noxious nature of the gas is greatly exceeded by the advantageous chemical properties of the solvent. The colorless liquid has the very unusual property of dissolving metals such as Li, Na, K, and Cs to give blue solutions. Numerous studies of the electrical conductivity of various concentrations of such solutions indicate that the metals are actually present as solvated (i.e., ammoniated) metal ions and electrons:



Such solutions are very strong reducing agents. For example, Ni(CN)<sub>4</sub><sup>2-</sup> can be reduced with potassium metal in liquid NH<sub>3</sub> to give Ni(CN)<sub>4</sub><sup>4-</sup>, an ion that is isoelectronic with Ni(CO)<sub>4</sub> and contains Ni in an oxidation state of zero.



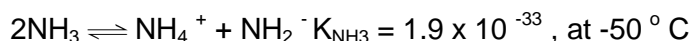
In this reaction the liquid NH<sub>3</sub> not only provides a medium for accommodating the very reactive metallic potassium but also is a sufficiently polar solvent to dissolve the reacting metal complex. The product of the reaction has been obtained as the potassium salt, K<sub>4</sub>[Ni(CN)<sub>4</sub>]. To be sure, alkali metals do react with NH<sub>3</sub> but very slowly. The reaction is analogous to that of such metals with H<sub>2</sub>O.



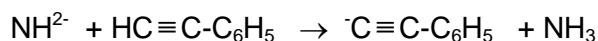
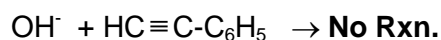
The addition of a small quantity of a ferric, Fe(III), salt catalyzes the reaction greatly by an **unknown mechanism**. The ferric salt is, under the conditions of the reaction, very rapidly reduced by the ammoniated electrons to very finely divided metallic iron, which probably is the actual catalytic agent.

Sodium amide, NaHN<sub>2</sub>, in NH<sub>3</sub> is analogous to NaOH in H<sub>2</sub>O. As OH<sup>-</sup> is called a base in H<sub>2</sub>O, NH<sub>2</sub><sup>-</sup> is called a base in NH<sub>3</sub>. Like water, which dissociates into hydronium and hydroxide ions, 2H<sub>2</sub>O ⇌ H<sub>3</sub>O<sup>+</sup> + OH<sup>-</sup> K<sub>w</sub> = 1.0 × 10<sup>-14</sup> at 25 °C.

NH<sub>3</sub> dissociates in a similar manner but to a significantly lesser extent:



Thus, basic NH<sub>3</sub> solutions are those that contain a higher concentration of NH<sub>2</sub><sup>-</sup> than of NH<sub>4</sub><sup>+</sup>. An acidic solution is one that contains a relatively high concentration of NH<sub>4</sub><sup>+</sup>. Needless to say, the NH<sub>4</sub><sup>+</sup> ion is not a very strong proton donor compared to H<sub>3</sub>O<sup>+</sup> in H<sub>2</sub>O, and for reactions requiring a strong acid or proton donor, liquid NH<sub>3</sub> is a poor choice. On the other hand, a reaction that requires a very strong base will greatly benefit from the higher basicity of NH<sub>2</sub><sup>-</sup> compared with OH<sup>-</sup>. This difference might be illustrated by comparing their reactions with acetylenes. From these reactions, it is clear that NH<sub>2</sub><sup>-</sup> is sufficiently basic to remove H<sup>+</sup> but OH<sup>-</sup> is not. The alkali metal acetylides such as K[C≡C-C<sub>6</sub>H<sub>5</sub>] are relatively stable but do react with water to form KOH and the original acetylene.

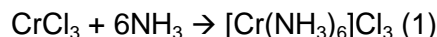


These acetylides have been used extensively not only in organic syntheses, but also in the formation of inorganic complexes. One inorganic application is based on the close similarity of the electronic state of the carbon atom in the C≡N - ligand to that in -C≡C-C<sub>6</sub>H<sub>5</sub>. Indeed, it is possible to displace the CN - ligand from the square planar Ni(CN)<sub>4</sub><sup>2-</sup> complex with the acetylide ion.



This strongly basic nature of the NH<sub>2</sub><sup>-</sup> ion thus makes possible the synthesis of an unusual inorganic compound. In this experiment you will carry out the preparation of the

octahedral coordination compound,  $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$ , according to the equations (in  $\text{NH}_3$  solvent!):



If anhydrous  $\text{CrCl}_3$  is simply allowed to react with liquid  $\text{NH}_3$  as in equation (1), a major product of the reaction is  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ . The displacement of the last Cl –proceeds very slowly; hence, the reaction is conducted in the presence of catalytic amounts of  $\text{NaNH}_2$ . While the mechanism of catalysis has not been investigated, it might be assumed that the greater nucleophilicity of  $\text{NH}_2^-$  - as compared to  $\text{NH}_3$  allows attack at the Cr atom with displacement of the Cl - to give  $[\text{Cr}(\text{NH}_3)_5\text{NH}_2]^{2+}$ . This intermediate either removes a proton from  $\text{NH}_3$  to regenerate the  $\text{NH}_2^-$  - or acquires a proton when treated with acid in step (2). The product cation,  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ , is precipitated as the relatively insoluble nitrate salt.

### Experimental Procedure

***Liquid ammonia is a very volatile, irritating, and toxic material; all operations involving it must be conducted in a hood. Fortunately, its intolerably pungent odour usually forces the researcher from the danger area before the gas reaches fatal concentrations.***

Although the boiling point of liquid  $\text{NH}_3$  is  $-33^\circ \text{C}$ , its high heat of vaporization prevents it from evaporating rapidly. Evaporation may be further minimized by cooling the reactants before dissolution in the  $\text{NH}_3$ . For many reactions, it is therefore possible to work in ordinary beakers, flasks, and other glassware. Open vessels containing liquid  $\text{NH}_3$ , of course, allow atmospheric moisture to condense into the solvent. Depending upon the sensitivity of the reactants to  $\text{H}_2\text{O}$ , protection against moisture may or may not be required. Such protection ranges from none to stoppering the flask with a drying tube to carrying out the reaction on a vacuum line. In this particular preparation the presence of small amounts of  $\text{H}_2\text{O}$  has no significant effect on the reaction. For this reason, few precautions against moisture will be taken. Liquid  $\text{NH}_3$  Solution of  $\text{NaNH}_2$  The following operations must be conducted in the hood. It is recommended that rubber or plastic gloves be worn while handling liquid  $\text{NH}_3$ . Introduce approximately 40 mL of liquid  $\text{NH}_3$  into a large test-tube which is itself in a larger test-tube. (The layer of air between the

test-tubes provides insulation to reduce the evaporation rate of the liquid  $\text{NH}_3$ .) The liquid  $\text{NH}_3$  is prepared by passing  $\text{NH}_3$  gas over a cold finger chilled with liquid  $\text{N}_2$ . See the instructor for details. To the liquid  $\text{NH}_3$  is added approximately 0.1 g (4.3 mmoles) of freshly cut sodium metal.

Weigh the Na metal. It is better to have more rather than less than 0.1 g. (Be sure to cut off any coatings of NaOH that may be present on the sodium. Dispose of any sodium scraps by adding them to a small beaker of anhydrous  $\text{CH}_3\text{OH}$ , which reacts briskly to form  $\text{H}_2$  and  $\text{NaOCH}_3$ . After the sodium has completely reacted, the solution may be washed down the drain with a flush of water. Do not discard sodium metal in a waste basket or sink.) The resulting blue solution is decolorized by catalyzing the reaction to  $\text{NaNH}_2$  with a small crystal of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  or other ferric salt (do not use a large amount). Stir the solution, if necessary, to discharge the blue color.

Hexaamminechromium(III) Nitrate,  $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$

The dark solution, which contains finely divided iron, is treated in small portions with 2.5 g (15.8 mmoles) of finely powdered  $\text{CrCl}_3$  (use mortar and pestle). Only small portions of the relatively warm  $\text{CrCl}_3$  should be added in order to avoid boiling the solution over the sides of the test tube. After the reaction is complete (wait 10-15 minutes after the addition of the last portion of the  $\text{CrCl}_3$ ), chill an evaporating dish with liquid  $\text{N}_2$  and then transfer the entire reaction product (plus excess liquid  $\text{NH}_3$ ) into it. Swirl occasionally to facilitate the evaporation of the  $\text{NH}_3$ . Make sure that the product is completely dry (free of  $\text{NH}_3$ ) by smelling it carefully. The odour of  $\text{NH}_3$  should be faint, and the product should be powdery.

The solid is then quickly dissolved in 10 mL of 0.75 M HCl that has been previously heated to 40 °C. Suction filter the solution, and if a considerable amount of solid still remains on the filter frit, wash it with an additional 10 mL of warm 0.75 M HCl. After suction-filtering, 4 mL of concentrated (16M)  $\text{HNO}_3$  is immediately added to the solution and the mixture is cooled in an ice bath. In order to speed up the precipitation of the product, the  $\text{HNO}_3$  may be added to the filter flask after the first filtration. This will precipitate much of the product immediately and will also cause the filtrate from the washing to precipitate as soon as it comes through the filter frit. It is important that these latter steps be done as quickly as possible to avoid reaction of  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  with Cl<sup>-</sup> to form  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ . The yellow  $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$  is suction-filtered off; it is washed with very dilute  $\text{HNO}_3$ , then with 95 per cent ethanol, and finally with diethyl ether. It is allowed to air-dry on the filter frit.

Determine the yield. Since the compound slowly decomposes in light, it should be stored in a brown bottle or in a container wrapped in aluminum foil. Save the product; you will need approximately 0.25 g for the determination of its magnetic susceptibility.

### **Hexamminechromium (III) nitrate $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$**

*(Caution: Use a well-ventilated hood. The product is light-sensitive)*

About 8 ml of liquid ammonia is introduced into a 125mL round-bottom flask, which is cooled in a acetone/liquid nitrogen bath. About 5 mg of clean sodium metal(not necessary to weight. about a piece of rice) and about 2 mg of iron(II) ammonium sulfate are added. After the blue color of the sodium has disappeared, 500 mg of anhydrous chromium (III) chloride is added in 20-mg portions, while the solution is constantly stirred (chromium (III) chloride must be added VERY Slowly to avoid the solution from boiling over the side of flask) After the addition has been completed, the brown precipitate is allowed to settle, and the clear, slightly colored supernatant liquid is decanted from the beaker.

The residue is transferred to a large crystallizing or evaporating disk and is allowed to stand with occasional stirring until the odor of ammonia is gone and a bright yellow, freely flowing powder remains. The yellow solid is dissolved in 5 ml of 0.75 M HCl at 40 C. After filtering the solution, 4 ml of concentrated (16 M) Nitric Acid immediately added to the solution and the mixture is cooled in an ice bath. It is important that these latter steps be done as quickly as possible to avoid reaction of  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  with  $\text{Cl}^-$  to form  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ . The yellow product is filtered and washed with very dilute nitric acid, then with 95% ethanol and finally with diethyl ether. It is allowed to air-dry on the filtration. Determine the yield. Since the compound slowly decomposes in light, it should be stored in a container protected from light.

### **Characterization required: Magnetic susceptibility and IR**

#### **Measurement of magnetic susceptibilities**

Instructions for cleaning and packing the sample tube

Operation of the balance

Determining the mass susceptibility and the Bohr magneton and interpreting this to give the number of unpaired electrons

### **Packing the sample tube**

Ensure that the tube is clean and dry (inside and out): wipe it with a tissue or clean with a "pipe cleaner" if it is not.

Take considerable care in packing the powder into the susceptibility tube since the major error in this method normally arises from inhomogeneous packing. The sample should be in the form of a reasonably fine and uniform powder. (Large crystals cannot be packed homogeneously and errors may also arise from magnetic anisotropy. Very fine powders, on the other hand, may pack unevenly unless compacted.) Lightly crush any crystalline aggregates with a plastic spatula. Introduce a small amount of the solid into the weighted sample tube, and tap the bottom of the tube gently on the bench a number of times to shake the solid down. Repeat this procedure until a sufficient length of sample (2.5-3.5cm) is obtained. Measure the sample length  $l$ , making sure that the top of the sample is horizontal.

Check the evenness of the packing by tapping the sample tube until the balance reading is constant.

After the first measurement empty out the sample, repack the tube and repeat the procedure at least once more.

Ferromagnetic materials should not be placed inside or near the balance.

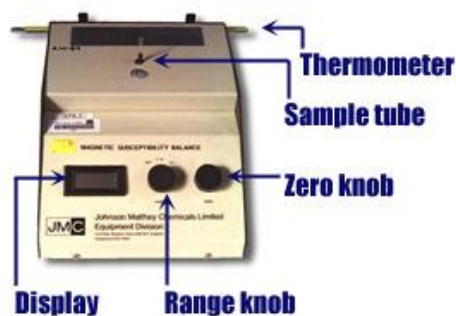
Ferromagnetic impurities introduced in sample preparation can lead to major errors.

The use of plastic or non-magnetic stainless steel spatulas is therefore essential.

### **Operation of the balance**

1. Turn the RANGE knob to the x1 scale and allow 10 minutes for the apparatus to warm up.
2. Adjust the zero knob until the display reads 000. The zero should be adjusted on each scale used, and before each measurement.

- Place an empty sample tube of known weight into the tube guide and take the reading,  $R_0$ . Since glass is diamagnetic,  $R_0$  will be negative.
- Pack the sample as indicated in the first section of this page and measure the sample weight,  $m$ .
- If the display goes off the scale turn the RANGE knob to the x10 setting, re-zero and multiply the reading by 10.
- The temperature should be read from a thermometer situated close to the balance.



### Determining the mass susceptibility

The mass susceptibility  $\chi_g$  and the molar susceptibility  $\chi_{mol}$  should be calculated by means of

$$\chi_g = \frac{C_{bal}l(R - R_0)}{10^9 m}$$

where  $l$  is the sample length (in **cm**),  $m$  is the sample mass (**gm**),  $R$  is the reading for tube plus sample,  $R_0$  is the reading for the empty tube,  $C$  is the calibration constant (1.0 for our instrument).

The molar susceptibility,  $\chi_m$ , is then calculated by multiplying  $\chi_g$  by the molecular mass of the substance. The molar susceptibility is positive if the substance is paramagnetic and negative if the substance is diamagnetic. The molar susceptibility measured is a sum of the paramagnetic contribution from the unpaired electrons in the metal ion and the diamagnetic contributions from the ligands and the counter ions. This can be

expressed by:

$$\chi_{\text{total}} = \chi_{\text{para}} + \chi_{\text{dia.}} (\text{L+ ions})$$

Therefore

$$\chi_{\text{para}} = \chi_{\text{corr.}} = \chi_{\text{total}} - \chi_{\text{dia.}}$$

Note:  $\chi_{\text{dia.}}$  is negative

The diamagnetism factors for common ligands are given in the table below.

Diamagnetic Corrections for Ligands and Ions*			
Formula	$-10^6\chi_{\text{M}}, \text{cgs}$	Formula	$-10^6\chi_{\text{M}}, \text{cgs}$
Ag <sup>+</sup>	28	ClO <sub>4</sub> <sup>-</sup>	32
BF <sub>4</sub> <sup>-</sup>	37	F <sup>-</sup>	9
Ba <sup>2+</sup>	24	H <sub>2</sub> O	13
Br <sup>-</sup>	35	I <sup>-</sup>	51
Ca <sup>2+</sup>	10	K <sup>+</sup>	15
CN <sup>-</sup>	13	Mg <sup>2+</sup>	5
NCS <sup>-</sup>	31	NH <sub>3</sub>	18
CO	10	NO <sub>3</sub> <sup>-</sup>	19
CO <sub>3</sub> <sup>2-</sup>	28	Na <sup>+</sup>	7
C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	30	OH <sup>-</sup>	12
C <sub>5</sub> H <sub>5</sub> N	49	Pb <sup>2+</sup>	32
C <sub>6</sub> H <sub>6</sub>	55	SO <sub>4</sub> <sup>2-</sup>	40
Cl <sup>-</sup>	23	Zn <sup>2+</sup>	15

Once the  $\chi_{\text{corr.}}$  is determined  $\mu_{\text{eff}}$  can be calculated using:

$$\mu_{\text{eff}} = \sqrt{8\chi_{\text{corr}}T}$$

And it follows that in the absence of spin-orbit coupling the number of unpaired electrons can be determined by:

$$\mu_{\text{eff}} = \sqrt{n(n+2)}$$

### References:

- Angelici, R.J. Synthesis and Technique in Inorganic Chemistry 2nd Ed. University Science Books, 1986, pp 39
- Inorganic Synthesis, 1946, Vol. 2. pg. 153
- Journal of Physical Chemistry, 1965, 69, pp 2201

### Questions:

1. Why is it recommended that gloves be worn when handling liquid ammonia? What would you do immediately if you spilled liquid ammonia on your skin?
2. If the ammonia solution of Na were not completely converted to NaNH<sub>2</sub>, how would this affect the subsequent preparation of [Cr(NH<sub>3</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>3</sub>?

3. If a large excess of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were added to the  $\text{NH}_3$  solution of Na, how would this affect the yield of  $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$  and why?
4. Could  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (i.e.,  $[\text{trans-CrCl}_2(\text{OH}_2)_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ) be used in place of anhydrous  $\text{CrCl}_3$  in this experiment? Why?
5. Why is the precipitated  $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$  washed with dilute  $\text{HNO}_3$  rather than with water? What is the purpose of the ethanol and ether washes?

