

Synthesis of a Cobalt Complex

Lab #6, Chem 36

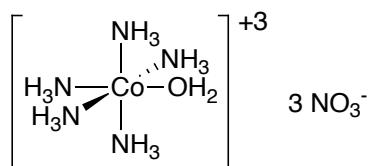
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Introduction

The most extensively studied class of octahedral transition metal compounds are cobalt(III) complexes in which ammonia (or other neutral molecules, closely related to ammonia, called amines) occupy some or all of the six coordination positions. The (III) in the name is a way of indicating the +3 oxidation state of the Co^{3+} ion. These complexes played a decisive role in early formulations of the structure of transition metal compounds and they continue to be important model systems for contemporary research into the properties of complex ions.

The first and simplest cobalt ammine complex ion, $[\text{Co}(\text{NH}_3)_6]^{3+}$, was prepared in 1798. Alfred Werner, a German chemist, studied the cobalt amines extensively in the late 19th and early 20th centuries. He correctly interpreted his observations as requiring an octahedral geometry of the ligands about the metal. Modern transition metal chemistry has evolved from his work for which he was awarded the Nobel Prize in chemistry in 1913. The intensity of ongoing research interest in cobalt ammine complexes is measured by the fact that a recent *Chemical Abstracts* cumulative index to the chemical literature has about 5000 entries referring to articles on the subject over a five year period.

This laboratory experiment involves the preparation of aquapentaammine-cobalt(III) as a nitrate salt, $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{NO}_3]_3$:

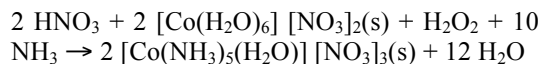


Note the spelling of the complex name. There are molecules which, as a class, are called **amines**, but the ammonia as a ligand is called **ammine** in the chemical's name. Water as a ligand is called **aqua** (formerly aquo) in the name.

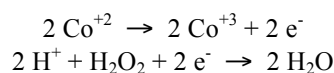
Once a successful synthesis has been carried out, a number of reactions of the complex will be explored that will establish the purity of the product and characterize some of its chemical behavior in weeks two, three, and four.

Complexes of amines with cobalt(III) are nearly always prepared from a cobalt(II) salt, the amine, and a reagent which will convert

cobalt(II) to cobalt(III). The procedure used here is typical, with hydrogen peroxide serving as the reagent (called an "oxidizing agent" for its ability to remove an electron) and ammonia as the amine. Here is the stoichiometric net reaction for this synthesis:



The oxidation-reduction half-reactions consist of the oxidation of cobalt (II) to cobalt (III) and the reduction of the hydrogen peroxide:

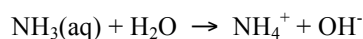


The purpose of each reagent in the mixture is described below.

About the Reagents

Cobalt Nitrate ($[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) is a typical hydrated cobalt(II) salt which consists of octahedral $\text{Co}(\text{H}_2\text{O})_6^{2+}$ cations and nitrate anions in the solid. It is extremely soluble in water and the solubility increases rapidly with increasing temperature.

Ammonia is an aqueous solution of NH_3 gas (sometimes laboratory bottles bear the old-fashioned label "ammonium hydroxide" or NH_4OH). The solution is basic due to the following equilibrium:



The 6 M solutions used here should be treated with respect. Aqueous ammonia is quite volatile, losing ammonia gas. In low concentrations, exposure to the gas causes irritation to the eyes and throat. At higher concentrations it is extremely toxic. Although the 6 M reagent does not present a serious hazard, **ammonia solutions should be covered or kept in the hood throughout the procedure**. Dilute ammonia solutions are familiar as household cleaning agents. They derive their effectiveness from the degradative action of basic solutions on natural fats. Ammonia provides the ammine ligands for your complex.

Ammonium nitrate (NH_4NO_3) is a common salt that requires no special precautions in standard laboratory applications. It is a major product of the chemical industry, largely because

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of its use as a source of nitrogen in fertilizers. When exposed to extreme heat and/or pressure it is explosive. Several major industrial disasters have occurred when fires have initiated the explosion of large stocks of ammonium nitrate. The truck bomb of the Oklahoma City bombing was filled ammonium nitrate. Ammonium nitrate is added to the reaction mixture to provide nitrate ions and to increase the concentration of NH_3 (aq) in solution. According to LeChatelier's Principle, addition of NH_4^+ ions will push the equilibrium between NH_3 and NH_4^+ to the reactant, or NH_3 , side of the above equation.

Hydrogen peroxide (H_2O_2) is another ubiquitous chemical. Its commonplace applications include use as a disinfectant and as a bleaching agent. Industrially it is widely used for bleaching, particularly in the processing of paper pulp. Although concentrated solutions, such as 30% by weight, cause severe burns, the 3% solutions used here do not. The concentration of 3% H_2O_2 is 0.9 M. (% concentrations are almost always expressed as **weight percents**.) In your synthesis reaction, hydrogen peroxide is the oxidizing agent that oxidizes the cobalt (II) reactant to the cobalt (III) product.

Concentrated **nitric acid** (HNO_3 , 16 M) is the **most hazardous reagent used in this experiment**. It is a typical strong acid in **its capacity to burn skin and other tissue**. It has the added peculiarity of turning exposed skin yellow. Gloves are recommended, although they provide only temporary protection from this strong acid--be careful! Although pure nitric acid solutions are colorless, the laboratory reagent is sometimes significantly discolored due to the presence of NO_2 and N_2O_4 , which are decomposition products of nitric acid when exposed to light. Nitric acid provides the H^+ that appears in the reduction half-reaction.

Ethyl alcohol (ethanol, $\text{C}_2\text{H}_5\text{OH}$) should require no introduction. A 95% ethanol-5% water solution is the standard laboratory form. It is that mixture of water and ethanol that has a boiling point, (78.15 °C), which is lower than that of pure ethanol (78.3 °C), pure water (100 °C), or any other mixture. The residual water, therefore, cannot be removed by simple distillation. The solutions are quite volatile and easily ignited. **Exposure to open flame should be avoided**. Alcohol is included in the reaction mixture to allow the product to precipitate. The product complex is soluble in water, but insoluble in ethanol.

Waste Disposal

All reaction mixtures and cobalt-containing solutions should be placed in the labelled waste drums. Unused acid and base solutions can be rinsed down the drain with lots of water.

Procedure

Refer to the stoichiometric net reaction as you first read through this procedure. You will be asked to calculate a final percent of theoretical yield (percent yield, for short) for your product. Thus, you must know the initial numbers of moles of all the reactants involved, to at least two significant figure accuracy. **Keep this in mind** as you weigh solids or measure solutions.

Solutions of reagents will be available in the lab in repipets set to deliver the appropriate amount into separate, clean beakers. Put a watch glass over the top of the beakers and take them to your hood. At the appropriate point in the procedure, add each reagent to your synthesis beaker, in your hood, not at the repipet. Do not remeasure the volume of any solution delivered by repipet, since greater accuracy is not necessary. Rinse the ammonia beaker with water as soon as you add it to your reaction beaker. Keep your reaction beaker in the hood at all times, to minimize fumes.

Synthesis Procedure

Weigh 3.6 g (0.012 mol) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2.5 g (0.031 mol) NH_4NO_3 on an electronic top-loading balance (not on an analytical balance). Record the weights and place these solids in a 400 mL beaker (or 500 mL Erlenmeyer). Add no more than 10 mL hot water from a hot water bath (dippers made from 10-mL beakers will be provided) and swirl until the solids are dissolved. Place the beaker on a stirring plate in the hood and add 40 mL 6 M ammonia (0.24 mol).

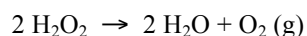
Over a period of about 30 min add with stirring 25 mL (0.022 mol) 3% H_2O_2 in small (0.8 mL/min.) amounts. Best yields will be achieved if the 3% H_2O_2 is added via an eyedropper while stirring the solution. Addition can be more rapid at first than towards the end. Add a total of 15 mL during the first 15 minute period and a total of 10 mL during the final 15 minutes. After addition is complete, allow the solution to sit with occasional stirring for 10 minutes or until bubbling stops, whichever comes first. The slow addition of H_2O_2

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minimizes the extent of a non-productive side reaction that hydrogen peroxide undergoes by not allowing large concentrations of peroxide to build up. This side reaction causes oxygen gas to bubble out of the solution especially when relatively little unreacted cobalt(II) remains. It is the common mode of peroxide self-decomposition:

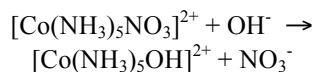


Slowly and carefully, add 30 mL (0.48 mol) 16 M HNO₃. Let the solution cool for 10 minutes. Add a volume of 95% ethyl alcohol (also called ethanol and abbreviated EtOH) approximately equal to the volume of solution already in the large beaker. The precipitate should become visible at this stage.¹ If it does not, notify your TA and review your procedure to this point. Allow the mixture to sit for 10 minutes to allow time for precipitation to proceed and then collect the solid by vacuum filtration on a Büchner funnel, as described in the Techniques section.

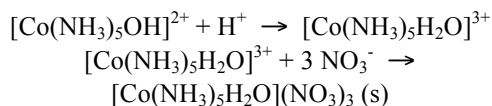
Rinse out solid remaining in the beaker with ethanol and twice rinse the solid on the filter. Pass air through the solid by suction for a few minutes to remove most of the ethanol. After filtration, the solid should be first weighed and then recrystallized, following the procedure described below.

Procedure for the Recrystallization of Aquapentaammine Cobalt(III) Nitrate

The main impurity in the initial preparation is the nitrate, [Co(NH₃)₅NO₃](NO₃)₂, rather than the desired aqua complex, [Co(NH₃)₅H₂O](NO₃)₃. To remove this impurity, the sample is first dissolved in a warm basic solution. The nitrate complex is rapidly converted to the hydroxo complex:



Then the solution is made acidic. [Co(NH₃)₅OH]²⁺, which is the conjugate base of the weak acid [Co(NH₃)₅H₂O]³⁺, adds a proton to give the aqua complex which is then precipitated as the nitrate salt:



Prepare first a 1 M ammonia solution by diluting the 6 M solution available in the lab. You will need at least 20 mL of this solution per gram of crude product. (If you are uncertain how to make this dilution, check with your TA.) Weigh the sample of crude [Co(NH₃)₅(H₂O)][NO₃]₃ (molecular mass = 348.1 g/mol) on an electronic top-loading balance, transfer it to a small (30 mL or 50 mL, if crude weight is >1g) beaker, and dissolve it in 1 M ammonia, using a maximum of 20 mL of ammonia per gram of crude product. Place the solution in a hot water bath and stir with a clean glass rod until all the solid is dissolved. Keep the solution in the hot bath for a full five minutes. (The baths will be adjusted to be close to 80 °C. Note the actual temperature, but do **not** allow the temperature to rise above 85 °C.)

Next cool the solution in an ice bath (take care that your beaker does not tip over as the ice melts!) until the temperature is **below** 5 °C as measured by your thermometer (with the bulb **fully immersed in the solution**). When the solution reaches 5 °C, add 16 M nitric acid dropwise while the solution remains in the ice bath, in the hood. A precipitate should form when sufficient HNO₃ has been added to neutralize the amount of ammonia used to dissolve the crude product. Add a ~25% excess of nitric acid with an eye dropper, stir, and allow a few minutes for precipitation to proceed in the ice bath. Test a drop of the mixture with pH paper, to confirm a strongly acidic pH. The required amount of nitric acid is easily calculated. Suppose that 3 g of crude product have been dissolved in 60 mL of 1 M NH₃. The required volume of 16 M HNO₃ is given by the following calculation:

$$V_{\text{HNO}_3} = (\text{mmoles NH}_3 \text{ present}) / (\text{conc. HNO}_3) = (60 \text{ mL}) (1 \text{ M}) / 16 \text{ M} = 3.8 \text{ mL}$$

For a 25% excess, (1.25)(3.8 mL) = 4.8 mL. Thus about 5 mL would be required.

Precipitation may be aided by scratching the inside of the beaker with a stirring rod or by adding a "seed" crystal of impure material. Collect the solid using vacuum filtration. With the wet solid still on the filter paper in the funnel, rinse twice with 95% ethanol. The ethanol rinses remove residual solution that contains ammonium nitrate from the solid. Ammonium nitrate is reasonably soluble in

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ethanol and the complex ion salt is **not** soluble in ethanol. Ethanol is miscible with water and therefore serves to remove residual aqueous solution.

Allow air to pass through the solid on the filter for a few minutes, then carefully transfer the filter and solid, to a watchglass to dry. After you have cleaned up your glassware, return to your product and scrape the solid off the filter paper and onto a piece of folded weighing paper. Transfer the solid from the paper into a clean, tared glass vial and obtain the mass of the product.

After Lab

The **Data and Results** section should include a calculation of the theoretical yield of the preparation according to the net reaction stoichiometry and the molar quantities of the different reagents used. The calculation should clearly show how the reagent that limits the overall yield was identified. The yield of product should be calculated as a percentage of the theoretical yield. Relative yields are very low in this experiment, largely because of the substantial solubility of the product. The preparation should be considered a success if 0.5 g or more of good quality recrystallized product is obtained. In this week's data sheet, you will report the crude yield of product, before recrystallization and drying, and the yield of recrystallized product. Include a description of each reagent used in the procedure in the synthesis reaction (acid-base, redox, common ion effect, precipitation, etc.). Relate this chemistry to your observations for the reaction. Include a description of each reagent used in the procedure and its purpose in the reaction.