

**EXPERIMENTAL PROCEDURES FOR THE
PREPARATION AND SPECTRAL ANALYSIS OF COBALT(III) COMPLEXES¹**

Carry out preparations (1) and (2) and record the visible spectra of the products during the first week. The product from preparation (1) will be required as a starting material during the second week of the experiment.

1. Preparation of Pentaamminechlorocobalt(III) Chloride

In the hood, in a 125 mL Erlenmeyer flask, prepare a solution of 2.5 g of ammonium chloride in 15 mL of concentrated aqueous ammonia.

Weigh out 5 g of cobalt(II) chloride hexahydrate, powder it finely (if necessary), then add it in small portions, with constant swirling, to the ammonia solution. This procedure should yield a brown slurry.

BE SURE TO WEAR GLOVES WHEN YOU PERFORM THE NEXT STEP.

In the hood, add, from a buret that your instructor will fill, - at about 2 drops per second, no faster - 4 mL of 30% hydrogen peroxide, with swirling. The hydrogen peroxide solution is extremely corrosive - be careful. The reaction is exothermic, and oxygen gas is vigorously evolved. If the reaction becomes too vigorous (e.g. foaming out of the flask), stop swirling and addition of the hydrogen peroxide solution until the foaming subsides. After complete addition of the H₂O₂ solution and complete cessation of gas evolution, add 15 mL of concentrated HCl, about 2 mL at a time, with continuous swirling.

Remove the reaction mixture from the hood and heat it to about 60° C for about 15 minutes, with occasional swirling. Add 12 mL of deionized water, then allow the solution to cool to room temperature. You should now have a purple slurry of the product.

Suction filter the slurry on a Büchner funnel; wash it three times with 8 mL of cold deionized water, then twice with 4 mL of ice-cold ethanol. Spread the product out on a watch glass, cover loosely with a piece of filter paper, and leave it to dry until your next lab period.

1. Preparations based on: Williams, G. M.; Olmsted, J. III; Breksa, A. III *J. Chem Ed.* **1989**, *66*, 1043-1045.

2. Preparation of Hexaamminecobalt(III) Chloride

Dissolve 2.5 g of cobaltous chloride hexahydrate and 1.7 g of ammonium chloride in 15 mL of deionized water. Add 0.5 g of activated charcoal. Take the solution to the hood and add 23 mL of concentrated aqueous ammonia. A brown slurry should form. Cool the reaction mixture to 0°C in an ice bath. Leave the thermometer in the reaction mixture so that the temperature can be maintained below 10°C for the next step.

BE SURE TO WEAR GLOVES WHEN YOU PERFORM THE NEXT STEP.

In the hood, from a buret that your instructor will fill, slowly add - maintain the temperature below 10°C - 2.0 mL of 30% hydrogen peroxide, with swirling. The hydrogen peroxide solution is extremely corrosive - be careful.

After the hydrogen peroxide has been added, heat the reaction mixture to 60°C for about 30 minutes.

Cool the reaction mixture to 0°C to cause precipitation of the product. Suction filter the mixture of charcoal and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$.

The charcoal can be removed as follows. Place the mixture of solids in a 250 mL Erlenmeyer flask, then add 20 mL of hot water and 0.5 mL of concentrated (12 M) hydrochloric acid. Heat the mixture to 70°C, then gravity filter through a fluted filter paper while it is still hot. Let the filtrate cool to room temperature, then place the filtrate in an ice bath and add 0.5 mL of cold concentrated hydrochloric acid. Leave the mixture to cool. The product should precipitate, and can be isolated by suction filtration. Wash the cold wet solid on the filter funnel with 13 mL of ice-cold 95% ethanol. Spread the product out on a watch glass to air dry.

Spectrophotometric analysis of cobalt(III) complexes

Dissolve 20-30 mg (record the exact mass) of pentaamminechlorocobalt(III) chloride in a few mL of deionized water in a small beaker. Add this to a 10 mL volumetric flask, then use more deionized water to rinse the residual solution into the volumetric flask. Dilute to the mark with deionized water, and mix well. Record the visible spectrum on the Ocean Optics spectrophotometer.

Repeat the procedure for hexaamminecobalt(III) chloride.

The preparations that follow (3, 4, 5) are to be done during the second week of the experiment.

NOTE: You might have to scale down the quantities in the following two preparations. The degree to which this has to be done will depend on the amount of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ that you have.

3. Preparation of Pentaammineaquocobalt(III) Chloride

Place 1.0 g of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in a 125 mL Erlenmeyer flask, then add 15 mL of 5% aqueous ammonia. Heat the mixture on a hot plate until the solid dissolves. Cool the solution to 10°C in an ice bath, then add dropwise, with constant swirling, concentrated hydrochloric acid. Continue the addition of HCl until a fog of ammonium chloride no longer forms above the liquid.

Cool the reaction mixture to 10°C to precipitate the product, then collect the product by suction filtration. Wash the solid on the filter funnel with two consecutive 5 mL portions of cold 95% ethanol, then spread the product out on a watch glass to air dry.

Prepare an aqueous solution of the complex and record its visible spectrum as described on the second page of the handout.

Preparation of Isomeric Pentaamminenitritocobalt(III) Complexes

4. Complex A

Place 2.5 g of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in a 250 mL Erlenmeyer flask and suspend it in 38 mL of 10% aqueous ammonia. Dissolve as much of the solid as possible by swirling, then dissolve the remainder by gentle heating. Stir with a metal spatula if necessary.

Cool the solution to about 10°C in an ice bath, then add 2.0 M HCl² until the solution is neutral to litmus.

Add 2.5 g of sodium nitrite, swirl to dissolve, then add 2.5 mL of 6 M HCl. Swirl to mix well, then leave the reaction mixture to stand in an ice bath for about 15 minutes to precipitate the product. Suction filter the mixture on a Buchner or Hirsch funnel, then wash the solid on the funnel with successive 12 mL portions of cold water and 95% ethanol. Spread the solid out on a piece of filter paper to dry.

Take note of the color of the solid soon after it is dry, before significant isomerization to complex B occurs. An infrared spectrum of the material should also be recorded at this time.

Prepare an aqueous solution of the complex and record its visible spectrum as described on the second page of the handout.

5. Complex B

Dissolve 1.5 g of complex A in a solution made by mixing 3.0 mL of concentrated aqueous ammonia and 15 mL of hot water. Cool the solution in an ice bath, then add 15 mL of concentrated (12 M) hydrochloric acid. Leave the reaction mixture to stand in the ice bath until precipitation is complete.

Suction filter the product on a Buchner or Hirsch funnel, then rinse the solid on the funnel with 12 mL of cold 95% ethanol. Spread the product out to air-dry.

Take note of the color of the product, and obtain its infrared spectrum.

Prepare an aqueous solution of the complex and record its visible spectrum as described on the second page of the handout.

²The use of more concentrated HCl may result in formation of solid $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$.