

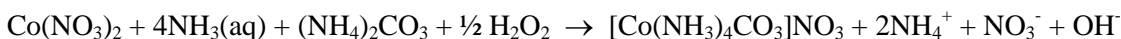
PREPARATION OF COBALT COMPLEXES

Introduction

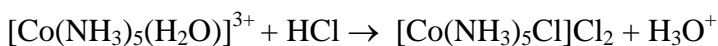
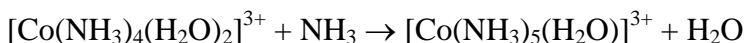
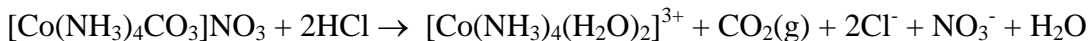
Cobalt (III) complexes have been some of the most widely studied since they are kinetically inert and undergo ligand exchange reactions very slowly. In contrast, cobalt(II) compounds are labile and undergo such reactions very rapidly. A very common synthetic procedure for the synthesis of cobalt(III) complexes involves oxidation of the corresponding cobalt(II) salt in the presence of the desired ligands. For example, the preparation of yellow-brown $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ can be obtained from the oxidation of $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ in the presence of NH_3 and activated charcoal.

Carbonato compounds sometimes make useful intermediates in the synthesis of cobalt complexes. The carbonate ion is easily removed by the additional of HCl , which expels the carbonate as carbon dioxide. Since the carbonate ion is a bidentate ligand, this leaves two open coordination sites. After expulsion of the carbonate, water molecules usually occupy the open coordination sites. Water, however, is not a particularly strong ligand, and addition of compounds such as Cl^- , NH_3 , or NO_2^- leads to the replacement of these coordinated water molecules.

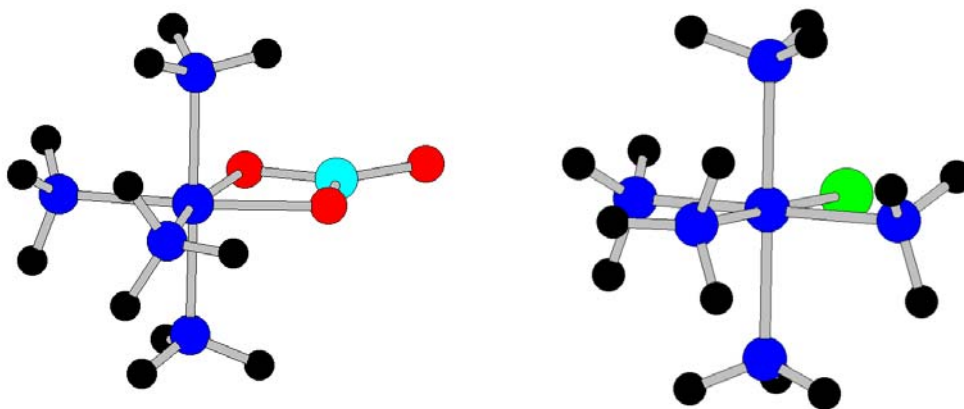
In the first part of this laboratory you will prepare the compound $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$ by the H_2O_2 oxidation of $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ in the presence of NH_3 and $(\text{NH}_4)_2\text{CO}_3$.



In the second part of the experiment you will expel the carbonate ion as carbon dioxide by the addition of excess HCl , resulting in the initial formation of $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$. The excess acid is then neutralized with NH_3 , resulting in the formation of $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$. Lastly, HCl is added to form $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.



Structural illustrations of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$ (left) and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ (right) are shown below.



Precautions:

Take special care when working with concentrated HCl and NH₃. Keep these compounds under your hood at all times. Also beware that ammonium carbonate smells strongly of ammonia. If the vapors become too strong, leave the laboratory.

30% H₂O₂ is also a hazardous material. Wear gloves when handling this reagent. If you get any on your skin wash it away immediately.

Part One: Preparation of [Co(NH₃)₄CO₃]NO₃

Prepare a solution of [Co(H₂O)₆](NO₃)₂ by dissolving 15 grams in 30 mL of deionized water. Prepare a second solution by dissolving 20 grams of solid ammonium carbonate in 60 mL of water in a 1000-mL beaker. Carefully add 60 mL of concentrated aqueous ammonia to the ammonium carbonate solution. Pour the cobalt solution into the ammonia-ammonium carbonate solution. Slowly, one mL at a time, add 8 mL of 30% H₂O₂ to the mixture. Effervescence (evolution of a gas) will most likely be observed as the H₂O₂ is added. This is due primarily to the decomposition of some of the H₂O₂, which is catalyzed by traces of certain metal ions. What gas is produced? The solution should change color as the H₂O₂ is added.

Transfer the solution to a hotplate and begin a slow concentration of the solution. Attempt to maintain a temperature of around 70°C. You must use an actual thermometer to monitor the temperature – the hotplate does not give you an accurate measure of the solution temperature. As the solution is concentrated, slowly add five additional grams of solid ammonium carbonate. Effervescence will most likely be observed as the ammonium carbonate decomposes into carbon dioxide and ammonia. Carbon dioxide is not particularly soluble in water and is released as a gas. Ammonia, however, is far more soluble in water. The purpose of adding the ammonium carbonate, therefore, is to maintain the NH₃ concentration. Once the volume of solution has dropped to 100 mL or

below, transfer the beaker in an ice bath. The product will precipitate as the solution is cooled. Suction filter the cooled solution to recover the product. Rinse the red crystals with 15-20 mL of acetone, and record the amount recovered.

Part Two: Synthesis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Dissolve 5.0 grams $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$ in approximately 50 mL of water and add 5-10 mL of concentrated HCl to expel the carbonate ion. At this time the principal species in solution is most likely $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$. Add concentrated ammonia until the *vapor* tests basic with red litmus paper, and then add 5 mL excess. Heat for 20 minutes. As before, avoiding boiling of the solution. During this time the $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ is converted into $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ as one of the coordinated water molecules is replaced. Cool the solution slightly and slowly add 75 mL of concentrated HCl. Reheat the solution for 20-30 minutes. During this time, the color should change as the second coordinated water molecule is replaced. Allow the solution to cool to room temperature, during which time purple-red crystals should precipitate from solution. Recover the product using suction filtration and wash with several mL of acetone.

Synthesis of Cobalt Complexes Part 1 Pre-Laboratory	Name:
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Look up the properties and any special hazards associated with each of the following reagents.

1. Cobalt nitrate hexahydrate $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$

2. Ammonia, NH_3

3. Ammonium Carbonate, $(\text{NH}_4)_2\text{CO}_3$

4. Hydrogen Peroxide, H_2O_2

Synthesis of Cobalt Complexes Part 1 In-Laboratory	Name:
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Record your observations regarding the synthesis of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$. Some things you should include are volumes or masses of reactants used, description of the starting materials, and any particular observations associated with the addition of specific reagents

Synthesis of Cobalt Complexes Part 2 Pre-Laboratory	Name:
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Look up the properties and any special hazards associated with each of the following reagents.

1. Concentrated HCl

2. Chloropentaamminecobalt(III) chloride, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Synthesis of Cobalt Complexes Part 2 In-Laboratory	Name:
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Record your observations regarding the synthesis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. Some things you should include are volumes or masses of reactants used, description of the starting materials, and any particular observations associated with the addition of specific reagents.

