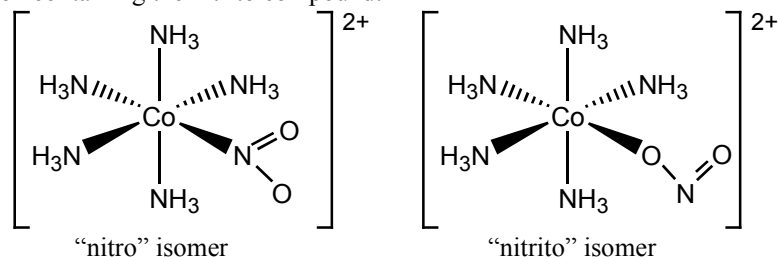


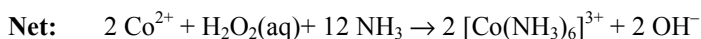
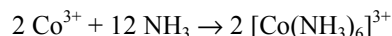
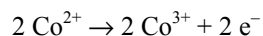
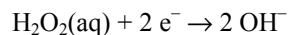
COORDINATION COMPLEXES OF COBALT

Introduction

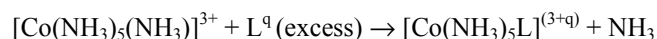
In this lab, you will synthesize two cobalt coordination complexes, $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$, and investigate linkage isomerism. Linkage isomerism involves ligands that are capable of bonding through one type of atom in one situation and another type of atom in a different situation. The nitrite ligand can link to metals through the N atom (“nitro” complexes) or the O atom (“nitrito” complexes) (see below). The nitrito isomer is less stable, and can be converted to the nitro isomer slowly by standing at room temperature, or quickly by heating or addition of HCl to a solution containing the nitrito compound.



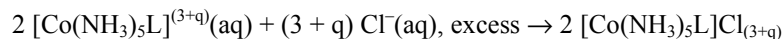
The preparation of Co(III) pentaammine complexes is carried out most conveniently starting from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. The first step in the syntheses of these complexes requires oxidation to convert the metal from the +2 to the +3 oxidation state. The oxidation reaction is best carried out using concentrated H_2O_2 in basic ammonia solution. Hydrogen peroxide as an oxidizing agent generates only OH^- as reduced product, and the presence of ammonia guarantees that the Co^{3+} will be stabilized immediately by formation of amine complex(es). (The Co^{3+} ion is not stable in aqueous media since it forms the strongly oxidizing hexaaqua complex.)



One of the six ligands in the octahedral system is substantially more labile than the other five, making it possible to carry out displacement reactions to generate the various pentaammine complexes. In this equation, q denotes the charge on the ligand L.



While Co(III) pentaammine complexes are generally rather soluble in water, their chloride salts can be precipitated from solution by excess HCl.



If these reactions are carried out in aqueous media containing only the ligands of interest and innocuous counter ions (H_3O^+ , OH^-), the resulting solid products are sufficiently pure that recrystallization or other purification methods are unnecessary.

Experimental

1. Synthesis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

- Accurately weigh out between 4.8–5.2 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and record the mass in your lab notebook.
- Under the hood, add 2.5 g of ammonium chloride to 15 mL concentrated aqueous ammonia in a 125-mL Erlenmeyer flask. [The combination of NH_4Cl and $\text{NH}_3(\text{aq})$ guarantees a large excess of the NH_3 ligand.]
- Stir the ammonium chloride solution vigorously using a magnetic stirring plate while adding 5 g of finely divided $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in small portions.
- Next, add 4 mL 30% hydrogen peroxide to the brown Co slurry. An addition rate of about 2 drops per second is usually sufficient, but care should be taken to avoid excessive effervescence in this exothermic reaction. (If the reaction shows signs of excessive effervescence, turning off the magnetic stirrer momentarily will usually prevent overflow of the solution.)
- When the effervescence has ceased, add 15 mL conc. HCl with continuous stirring, pouring about 1–2 mL at a time.
- At this point, the reaction may be removed from the hood. Use the stirring hot plate to heat the solution to 60 °C with slow stirring. Hold the temperature between 55 °C and 66 °C for 15 min; this incubation period is necessary to allow complete displacement of all water ligands.
- Add 15 mL deionized water, and allow the solution to cool to room temperature.
- Collect the purple product by filtration through a Buchner funnel; wash it three times with 5 mL cold deionized water and twice with 5 mL ice-cold 95% ethanol. (The solutions must be cold to prevent undue loss of product by redissolving.)
- Transfer the product to a crystallizing dish, loosely cover with Al foil, and allow to dry until the following laboratory period. Assuming the cobalt compound is the limiting reactant, calculate a percent yield.

Caution: 30% hydrogen peroxide is a strong oxidizing agent that will cause severe burns and bleaching of skin and clothing.

2. Synthesis of $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$

- Weigh out about 1 g of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and dissolve it in 15 mL of 10% aqueous ammonia in a 125-mL Erlenmeyer flask on a hot plate in the hood. Stir with a metal spatula.
- Cool the solution to about 10 °C in an ice bath, then add 2.0 M HCl until the solution is neutral to litmus. (The use of 2 M HCl rather than the conc. HCl used in the nitro synthesis dilutes the solution sufficiently that the aqua salt will not precipitate).
- Add 1.0 g sodium nitrite followed by 1 mL of 6 M HCl.
- Allow the reaction mixture to stand in an ice bath for at least an hour.
- Filter through a Buchner funnel, then wash the yellow-orange solid with 5 mL cold water and 5 mL cold 95% ethanol.
- Transfer the solid to a piece of filter paper, and allow it to air-dry.

3. Synthesis of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$

- Weigh out about 1 g of the nitrito isomer, $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$, and dissolve it in 10 mL hot water containing 2.0 mL conc. aqueous ammonia.
- Cool the solution in an ice bath, and add 30 mL conc. HCl.
- Allow the mixture to stand in the ice bath until precipitation is complete.
- Collect the product by filtration through a Buchner funnel, and wash the pale solid with 10 mL cold 95% ethanol.
- Allow the product to air-dry.

Analysis:

Visible spectra (recorded using the UV-Vis Spectrometer) for all three compounds, recorded as dilute aqueous solutions, can be collected over the course of the experiment. It is important to obtain the spectrum of $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ immediately after isolation because this compound isomerizes to the nitro derivative rather quickly at room temperature. The other compounds are quite stable: their spectra may be recorded as time permits.

Measure the infrared spectra of the two linkage isomers. Use a freshly prepared sample in the case of the nitrito isomer. Comment on any differences between the two spectra.

Molecular Modeling:

The method of bonding in the cobalt- NO_2 complexes can be determined using infrared spectroscopy. The two linkage isomers have rather different IR spectra, and the spectra can be modeled using the CAChe molecular modeling system. (See handout for more detailed instructions.)

- Build models of the two isomers. Because we are primarily interested in the NO_2 group, a simple Lewis acid (such as AlCl_3) can replace the $[(\text{NH}_3)_5\text{Co}]$ group.
- In order to calculate an IR (vibrational) spectrum, a MOPAC FORCE calculation must be performed.
- After the calculation is complete, view the two vibrational spectra. Identify the areas of the spectra related to the NO_2^- ligand. Are there differences between the two isomers? How do the calculated IR spectra compare with the experimental spectra?

Laboratory Report:

Your laboratory report should include a description of your experiment and the calculated percent yield for the first synthesis. Also, include your visible and IR spectra as well as the results of your molecular modeling calculations.

All questions or comments requested in the Experimental, Analysis, and Molecular Modeling sections must be provided in your lab report. You can submit the report using either the carbon copies of your lab notebook or in a computer text file.