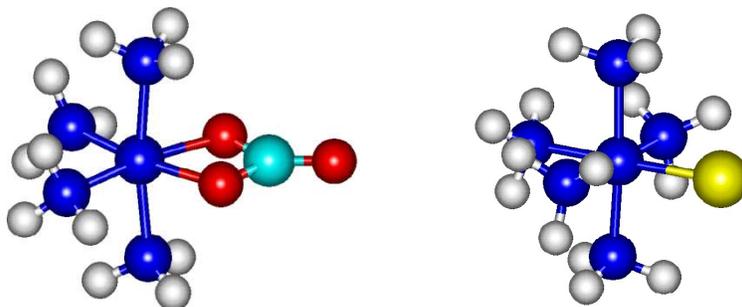


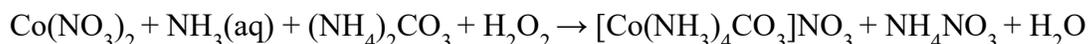
Synthesis and characterization of [Co(NH₃)₄CO₃]NO₃ and [Co(NH₃)₅Cl]Cl₂

Introduction:

Experiments involving the aqueous preparation of cobalt(III) complexes have been a familiar feature in many textbooks written for use in the inorganic chemistry laboratory.^[1-8] Coordination compounds of Co(III) have been of particular interest because their complexes, kinetically inert, undergo ligand exchange very slowly compared with various other transition metals. The metal complex Ni(NH₃)₆²⁺ reacts very rapidly with water, undergoing a ligand substitution reaction, to form Ni(H₂O)₆²⁺. The analogous reactions of Co(NH₃)₆³⁺ and Cr(NH₃)₆³⁺ occur very slowly in aqueous solution. Ligand field and molecular orbital theory may be used to qualitatively explain the differences in reactivity.^[9] The slow reactivities of octahedral complexes have led to extensive investigations of these compounds. In this experiment, you will prepare the coordination compounds [Co(NH₃)₄CO₃]NO₃ and [Co(NH₃)₅Cl]Cl₂ via ligand substitution reactions.



Part I: The synthesis of [Co(NH₃)₄CO₃]NO₃ involves the following *unbalanced* equation,



Cobalt nitrate [Co(NO₃)₂] is deliquescent (tends to absorb atmospheric water vapor). Upon exposure to atmospheric moisture, cobalt nitrate has the formula Co(NO₃)₂•6H₂O.

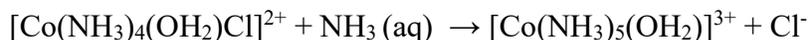
Co(II) complexes react very rapidly by ligand exchange, thus a possible first step in the reaction:



The intermediate tetraamminecarbonatocobalt(II) could then be oxidized by addition of H₂O₂ to form [Co(NH₃)₄CO₃]⁺. Compounds with a carbonate ligand are useful intermediates in the synthesis of coordination complexes. The carbonate ion is easily

removed by the additional of HCl and the carbonate forms carbon dioxide. The carbonate ion is a bidentate ligand and leaves two open coordination sites. Water molecules or chloride ions may occupy the open coordination sites. Water is not a particularly strong ligand and addition of ions such as X^- , NH_3 , or NO_2^- leads to the replacement of these coordinated water molecules.

Part II: The synthesis of $[Co(NH_3)_5Cl]Cl_2$ involves the following equations,



Characterization of the metal complexes will involve several techniques. The use of infrared spectroscopy examines the frequencies of the vibrational modes of the molecule. For example, absorption is anticipated at frequencies characteristic of the stretching and bending modes of the CO_3^{2-} , NH_3 , and NO_3^- groups in $[Co(NH_3)_4CO_3]NO_3$. The spectrum of the CO_3^{2-} in the metal complex is different than for the ion in Na_2CO_3 , whereas the absorption bands resulting from the vibrational modes of the NO_3^- counterion in the metal complex are similar to those observed in $NaNO_3$. The IR spectrum of $[Co(NH_3)_5Cl]Cl_2$ consists of absorptions primarily attributed to the NH_3 groups. Other stretching modes (e.g. Co-N, Co-Cl) are, in principle, also measurable, but may occur at a lower frequency than can be observed in a typical infrared spectrophotometer.

The use of conductivity measurements enables the determination of the number of ions in solution. Two electrodes are immersed in a solution and a potential is applied between them, resulting in a current produced in the external circuit that connects the two electrodes. The electrical communication between the two electrodes in solution involves the movement of ions in the solution. Assuming no appreciable solution electrolysis occurs, the magnitude of the current observed generally obeys Ohm's Law: $V = iR$, where V is the applied potential, i is the measured current, and R is the resistance of the solution.

The experimentally determined conductivity reflects contributions from all ions present in solution that are mobile and can carry the current. The conductivity is concentration dependent, thus measured values for different solutions are not easy to compare directly. The *molar conductivity* (sometimes termed *equivalent conductivity*) is the quantity that is used. The molar conductivity is symbolized by Λ_m , and is defined as the solution

conductivity (κ) normalized by the concentration (C): $\Lambda_m = \kappa / C$. Each singly charged ion has a molar conductivity near $60 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. A solution of the 1:1 electrolyte has a conductivity near $120 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Large and slow moving or highly charged ions tend to result in a lower conductivity value. Species involving H^+ and OH^- , i.e. acids and bases, have hydrogen-bonding chain conduction mechanisms and deviate from the typical range given above. The following table lists a range of molar conductivities for various ion conductors in aqueous solution.^[10]

Number of ions	molar conductivity, $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
2 (1:1)	96-150
3 (1:2)	225-273
4 (1:3)	380-435
5 (1:4)	540-560

The following three compounds, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, have a different number of ionizable chloride ions and thus exhibit different molar conductivities. Conductivity measurements enable one to distinguish between the compounds. Details about the basic physicochemical concepts underlying ionic conductivity are presented elsewhere.^[11]

Experimental Section: Safety

Investigate the properties and briefly list in your lab notebook any special hazards associated with each of the following reagents: cobalt nitrate hexahydrate $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, concentrated aqueous ammonia NH_3 , concentrated hydrochloric acid HCl , ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$, hydrogen peroxide H_2O_2 .

Experimental Section: Techniques

Review safety, basic glassware, weighing using a top-loading balance and analytical balance, quantitative transfer, repipet, using a pipet, vacuum filtration, volumetric flasks, conductivity measurements, infrared spectroscopy, UV-Visible spectroscopy.

Experimental Procedures

Part I: Synthesis and characterization of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$

Ammonium carbonate, used as a smelling salt, is an irritant to the mucous membranes and reactions should be kept in a fume hood as much as possible. Before weighing, open the bottle in the hood to remove ammonia vapor from the bottle. The powder tends to clump

together and it may be necessary to break apart the $(\text{NH}_4)_2\text{CO}_3$ using a rubber mallet/plastic bag and/or grind using a glass mortar and pestle prior to weighing. Cobalt nitrate hexahydrate is hygroscopic and will absorb atmospheric moisture. Use a top loading balance for the synthesis and an analytical balance for the characterization step.

Dissolve 0.208 mol of $(\text{NH}_4)_2\text{CO}_3$ in 60 mL of H_2O in a beaker under constant stirring. Add 60 mL of concentrated aqueous NH_3 (ammonium hydroxide). Pour this solution, while stirring, into a solution containing 0.0515 mol of $[\text{Co}(\text{OH}_2)_6](\text{NO}_3)_2$ in 30 mL of H_2O . *Slowly* add 8 mL of a 30% H_2O_2 solution dropwise (**Warning: H_2O_2 is a strong oxidizing agent that can cause severe burns. Use proper gloves while handling. If a spill occurs, wash the affected areas immediately with water.**). Concentrate to about 80-90 mL using a hot plate. The use of an evaporating dish may be used in place of a beaker to facilitate evaporation. Using an alcohol thermometer and ensuring the bulb doesn't contact the stirbar, maintain the temperature of the solution near 85°C . Do not allow the solution to reach 100°C and boil. Add 5 g of $(\text{NH}_4)_2\text{CO}_3$, in small portions, during the course of the evaporation. Suction filter the hot solution if there are any undissolved materials. Cool to about 5°C in an ice water bath and then isolate the red crystalline product by suction filtration into a clean side-arm Erlenmeyer flask. Transfer the filtrate to a separate 250 mL Erlenmeyer flask and retain. Wash the product with a small amount of ice-cold water and then with a small amount of 95% ethanol. Allow the product to dry, place on a watch glass, dry in a drying oven at 100°C (if available). Place the product in a weighed sample bag, weigh the product and sample bag, and determine the percent yield. If needed, further reduce the volume of the retained filtrate and perform a second evaporation using the evaporating dish and second filtration.

On the same day, time permitting, collect an IR spectrum of the product using the Perkin Elmer Spectrum 1 Infrared Spectrometer (FT-IR). Ensure the peaks are labeled. Prepare a solution, using a 25 mL volumetric flask, with a concentration near 0.005 M. Collect the UV-Vis spectra in a cuvette from 285 nm to 700 nm. The absorbance should be between 0.5 and 1.0. Record the wavelength of maximum absorption and absorbance. Adjust the concentration and prepare a second solution if the absorbance is outside that range. Measure, using a Hanna Instruments HI9093 conductivity meter, the conductance of tap water, deionized water, the solution of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$, and solutions of KCl,

MgCl₂, and FeCl₃ (data for the latter 3 may be shared) near the same concentration as the cobalt compound. Calculate the molar conductivity for each compound.

The IR, UV-Vis spectra, and conductivity data may be collected before, during, or after the synthesis of [Co(NH₃)₅Cl]Cl₂. Utilize your time wisely. One person in the class needs to collect the IR and UV-visible data for [Co(OH₂)₆](NO₃)₂ and NaNO₃. Retain, for the next experiment, the product in a weighed and labeled (initial and last name, complete formula compound, and date) sample bag. Discard the filtrate wash solution in the appropriate “metal waste” containers in the fume hood. Do not tightly cap the waste bottle, for safety reasons, because of the decomposition of carbonates and pressure increase inside a closed container. Retain the product for the next part of the experiment.

Part II: Synthesis and characterization of [Co(NH₃)₅Cl]Cl₂

Dissolve 5.0 g of [Co(NH₃)₄CO₃]NO₃ in 50 mL of H₂O and slowly add concentrated HCl (5-10 mL) until all of the CO₂ gas is evolved. Neutralize the solution with concentrated ammonium hydroxide until the vapor above the solution tests basic with red litmus paper. Add an excess of about 5 mL of the concentrated NH₃. Heat for 20 minutes, avoiding boiling, to form [Co(NH₃)₅H₂O]³⁺. Note any color change as one of the coordinated water molecules is replaced. Cool the solution slightly and slowly add 75 mL concentrated HCl. Reheat for 20-25 minutes and note any change in color. Cool to room temperature and watch for the formation of a precipitate. Wash the compound several times by decantation with small amounts of ice-cold DI H₂O. Isolate the crystalline product by suction filtration. Wash with cold 95% ethanol and dry completely by pulling air through the crystals. The solutions used for washing should be cold to prevent the loss of product by redissolving. Removal of remaining solvent can be accomplished by drying in an oven (if available) at 100-120°C to yield [Co(NH₃)₅Cl]Cl₂. Transfer the product in a weighed sample bag, weigh the product and sample bag, and determine the percent yield.

Collect an IR spectrum of your product. Ensure the peaks are labeled. Prepare a solution for conductance and UV-Vis measurements using a 25 mL volumetric flask. Collect the UV-Vis spectrum in a plastic cuvette from 300 nm to 650 nm. Measure the conductance of deionized water and [Co(NH₃)₅Cl]Cl₂. Calculate the molar conductivity and compare to 1:1, 1:2, and 1:3 salts. Retain the product in a labeled (initial and last name, complete formula of the compound, and date) sample bag. Discard the filtrate wash solution in the appropriate “metal waste” containers in the fume hood. Do not tightly cap the waste bottle,

for safety reasons, because of carbonate decomposition and pressure increase in a closed container.

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