

Coordination Complexes of Cobalt

Inorganic Synthesis in the General Chemistry Laboratory

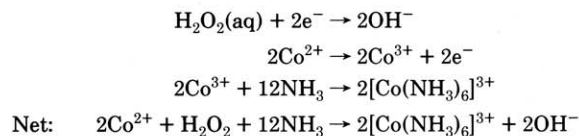
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The American Chemical Society has established guidelines for undergraduate education calling for an increased emphasis on inorganic and descriptive chemistry. One possible way of implementing these changes in our curricula is to reorganize the general chemistry sequence. By necessity, this approach will also require a revision of the introductory laboratory. Typically, laboratory experiments in general chemistry emphasize physical and analytical methods. To the student, this frequently translates into a seemingly endless series of titrations leading to extensive and tedious calculations. General chemistry laboratories suffer from the lack of visually exciting experiments that expose students to the full experience of chemistry.

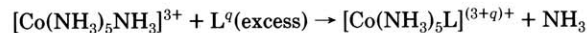
These problems can, in part, be diminished by incorporating more chemical synthesis into the introductory laboratory. Syntheses of coordination complexes are particularly attractive because they are easy to carry out in high yield, they involve relatively simple stoichiometries, and they provide a variety of highly colored compounds. Several experiments on coordination chemistry have appeared in *this Journal*; most of these have emphasized the chemistry of Co(III). Sebera (1) and Wilson (2) published two of the earliest experiments. More recently, Alexander and Dorsey (3) and Loehlin et al. (4) described freshman laboratory projects in which Co(III) complexes are prepared and studied. There have also been reports on the synthesis of optically active Co(III) complexes (5, 6), and there are brief descriptions of the syntheses of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (7), $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ (8), and $[\text{Co}(\text{en})_3]\text{Cl}_3$ (9). One paper concerns a number of metal acetylacetonate complexes (10), and experiments concerning Ni (11, 12), Fe (13, 14), and Cu (15, 16) have appeared. Most of these papers describe the synthesis of just one or two compounds, and emphasize detailed characterization. In this paper, we describe an experiment involving synthesis and spectral studies of a series of $[\text{Co}(\text{NH}_3)_5\text{L}]$ complexes (L = NH_3 , Cl^- , H_2O , NO_2^- , and ONO^-) that not only gives general chemistry students an introduction to inorganic synthesis but also allows them to conduct a systematic study on the effect of different ligands on absorption spectra.

Background

The preparation of Co(III) pentamine complexes is carried out most conveniently starting from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, which is both inexpensive and quite stable. 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 ammoniacal 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 hexaquo complex.)

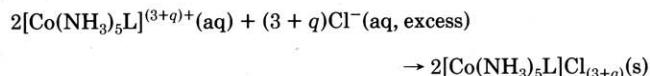


One of the six ligands in the octahedral system is substantially more labile than the other five, making it possible to carry out displacement reactions to generate the various pentamine complexes:



In this equation, q denotes the charge on the ligand L. In the preparations described here, $q = 0$ (H_2O , NH_3) or $q = -1$ (ONO^- , NO_2^- , Cl^-).

While Co(III) pentamine 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 counterions (H_3O^+ , OH^-), the resulting solid products are sufficiently pure that recrystallization or other purification methods are unnecessary.

Experimental

All procedures were adapted from either Schlessinger (17) or Jolly (18).

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

In a fume hood, add 10 g of ammonium chloride to 60 mL concentrated aqueous ammonia in a 250-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 20 g of finely divided $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in small portions. Next, add 16 mL 30% hydrogen peroxide to the brown Co slurry, using a buret that has been set up in the hood and filled by the laboratory instructor. 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 60 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 a Bunsen burner to heat the solution to 60 °C with occasional stirring. Hold the temperature between 55 °C and 65 °C for 15 min; this incubation period is necessary to allow complete displacement of all aquo ligands. Add 50 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 15 mL cold deionized water and twice with 15 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.

Caution: 30% hydrogen peroxide is a strong oxidizing agent that will cause severe burns and bleaching of skin and clothing. Burets should only be filled by qualified laboratory instructors, and students should be warned of the potential hazards of this reagent.

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

Place 5.0 g of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in a 250-mL Erlenmeyer flask, and add 75 mL of 5% aqueous ammonia. (Using aqueous ammonia as the

solvent prevents displacement of the NH_3 ligands.) Heat on a hot plate in the hood until the compound dissolves. Cool the solution to 10°C in an ice bath, then add a stirring bar, and place the flask on a magnetic stirrer. Add concentrated HCl dropwise with stirring until a red precipitate appears and a fog (ammonium chloride vapor) no longer forms above the solution. (Under these conditions ligand exchange between $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ is very rapid. The aquo trichloride complex is isolated by this procedure because it is much less soluble than is the chloro dichloride.) Cool the reaction mixture to below 10°C , then collect the product by filtration through a Buchner funnel. Wash the bright red solid twice with 25 mL 95% ethanol, and allow it to dry in the air.

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

Dissolve 5.0 g of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in 75 mL of 10% aqueous ammonia in a 250-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 conc. HCl (synthesis 2) dilutes the solution sufficiently that the aquo salt will not precipitate.) Add 5.0 g sodium nitrite followed by 5 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 25 mL cold water and 25 mL cold 95% ethanol. Transfer the solid to a piece of filter paper, and allow it to air-dry.

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

Dissolve 3.0 g of the nitrito isomer $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ in 30 mL hot water containing 6.0 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 25 mL cold 95% ethanol. Allow the product to air-dry.

5. Synthesis of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

Add 5.0 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 3.3 g of NH_4Cl to 30 mL water in a 250-mL Erlenmeyer flask. In the hood add 1.0 g activated charcoal and 45 mL conc. aqueous ammonia. Cool the brown slurry in an ice bath to 0°C , then add 4.0 mL 30% H_2O_2 from a buret as described for the synthesis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. Do not allow the temperature to rise above 10°C . Heat the resulting red-brown solution to 60°C , and maintain this temperature for 30 min. (The incubation is needed to ensure complete displacement of all aquo ligands.) Cool the mixture to 0°C ; the product will precipitate from the solution. Collect the product and the charcoal by filtration. Recrystallization is necessary to separate the product from the activated charcoal. Place the solid in a 250-mL Erlenmeyer flask, and add 40 mL hot water and 1.0 mL conc. HCl . Heat the mixture to 70°C , and filter while still hot. Place the filtrate in an ice bath, and add 1.0 mL cold conc. HCl . Collect the orange solid by filtration, wash with 25 mL ice-cold 95% ethanol, and allow to air-dry.

Discussion

These syntheses can be completed in four 3-h laboratory sessions. During the first period $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ is prepared, and it is used in the next laboratory session for the synthesis of the aquo and nitrito derivatives. The final two periods leave sufficient time to conduct the nitrito-nitro isomerization and to prepare the hexamine Co^{3+} salt. Visible spectra for all of the components, recorded as dilute aqueous solutions on a Beckman DU-7 or other recording spectrophotometer, 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 since this compound isomerizes to the nitro derivative rather quickly at room temperature. The other four compounds are quite stable; their spectra may be recorded as time permits.

The visible spectra of all five of the cobalt complexes are displayed in Figures 1 and 2. In each case, λ_{max} is clearly determined, allowing the students to verify the spectrochemical series (see table). In most general chemistry textbooks the nitrito ligand is omitted from the spectrochemical series. Thus, in addition to illustrating the concept of linkage isomers, $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ can act as an "unknown" in this exercise. The experiment also reinforces the concept of absorbed vs. transmitted light. Clearly, the colors of these

coordination compounds are not the "colors" of the absorbed light.

There is a great deal of chemistry involved in these syntheses. Instructors may wish to elaborate on the chemical principles involved, particularly if the experiment is carried out after these principles have been introduced in the lecture. If redox chemistry has already been covered, the oxidation step and the relative instability of $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ can be treated as practical examples of redox chemistry; otherwise, it can merely be pointed out that the cobalt is being converted from a lower to a higher oxidation state. If equilibrium concepts have already been introduced, the displacement, precipitation, and isomerization reactions can be described using these concepts, particularly Le Chatelier's principle. If the experiment is done before equilibrium ideas have been developed, these same reactions can be treated as though they proceed to completion. For more sophisticated students, it may be appropriate to note the differences between kinetic and thermodynamic control of reaction products as

Physical Properties of the Cobalt Complexes

Complex	Color	λ_{max}	Transition Energy
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	Purple	530 nm	225 kJ/mol
$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$	Red	495 nm	240 kJ/mol
$[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$	Yellow-Orange	485 nm	245 kJ/mol
$[\text{Co}(\text{NH}_3)_5\text{NH}_3]\text{Cl}_3$	Orange	475 nm	250 kJ/mol
$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$	Orange	460 nm	260 kJ/mol

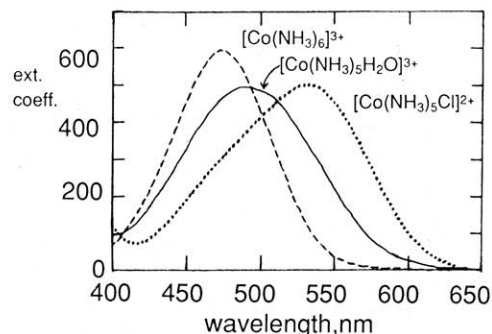


Figure 1. Visible spectra of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ (—), $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ (· · · · ·), and $[\text{Co}(\text{NH}_3)_5\text{NH}_3]^{3+}$ (-----).

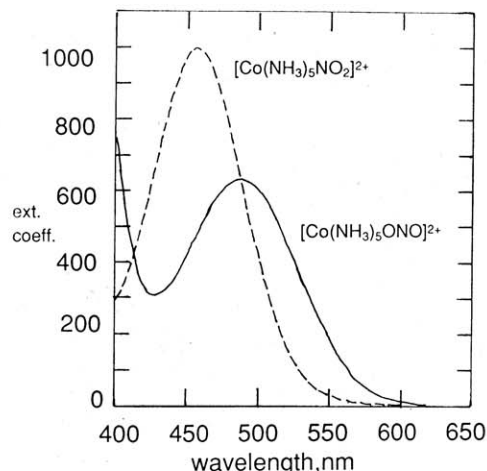


Figure 2. Visible spectra of $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$ (—) and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$ (-----).

manifested by the synthesis of the nitrito complex and its eventual conversion to the nitro form.

Principles of stoichiometry can also be reinforced by having the students weigh their products from each synthesis, compute the yield in each case (it should be clear to them that the limiting reagent is always the cobalt starting material), and draw inferences about reaction efficiencies and causes of less than quantitative yields. With sufficiently careful technique, each of these syntheses has a yield in excess of 90%, but there are ample opportunities for less skilled experimentalists to lose significant amounts of their products.

This was the first opportunity for many of the students actually to isolate compounds, and in this experiment the inherent rewards of chemical synthesis are multiplied by the visual appeal of the chemistry. Most of the students in the class enjoyed this experiment very much; several felt that it was the best laboratory exercise of the year.

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