The Synthesis and Reactions of a Cobalt Complex

A project for freshman laboratory

The design of suitable experiments for the general chemistry laboratory presents a challenging problem. Appropriate activities at the freshman level ought to introduce students to needed laboratory techniques and basic chemical principles. At the same time the experiments should capture students’ interest. An important factor in maintaining this interest is the opportunity for successful completion of the laboratory work. Students tend to become rather discouraged if their efforts seem to produce few results.

Added to these requirements in many institutions are other pressures resulting from the large sizes of freshman laboratory sections and the attendant logistical problems. The work must fit conveniently into three-hour modules. Chemicals must not be inordinately expensive. Required equipment must be readily available. The principles of the experiment must be grasped by the teaching assistants who staff the laboratories and have the most direct contact with students. Finally, the results should be amenable to “objective” grading preferably involving unknowns and/or product yields to be handed in. Results of this kind encourage useful discussions among students but prevent excessive cooperation in writing laboratory reports.

With so many criteria to be satisfied it is little wonder that large numbers of freshman experiments do not also offer possibilities for interesting discussions with brighter students, for extending the work involved and for conveying some of the excitement of a developing research problem (1).

Description of the Experiment and Student Results

At the University of Cincinnati we have had considerable success with a project-type experiment lasting for three laboratory periods during the first quarter of the freshman laboratory.

During the first week students prepare a sample of cis-[Co(NH₃)₆]Cl₂(NO₃)·0.5H₂O (2) (side infra). Preparation of the tetrammine carbonato complex from 10 g of Co(NO₃)₂·6H₂O resulted in an average yield of 3.5 g (40%) from 510 freshmen in the Autumn of 1978. The literature reports a yield of 70% from a similar preparative procedure (2). It is likely that our student yields could have been increased by working on a larger scale (say, 15 g) and by adding portions of NH₄HCO₃ to the mother liquor from the first crop to obtain a second crop of crystals. Although the product can be purified by recrystallization (2), it is sufficiently pure for synthetic purposes. When we asked some students to attempt recrystallization, a significant fraction could not obtain a crystalline product on dissolution in hot water, filtration, cooling, and addition of alcohol.

During the second laboratory period students were given unknowns and asked to allow these to react with 3 g portions of [Co(NH₃)₆]Cl₂(NO₃)·0.5H₂O. The unknowns all contain acid which induces hydrolysis of the carbonato ligand. The presence of anions in solution will lead to anion on heating, the net reactions being:

\[
\text{[Co(NH₃)₆]Cl₂(NO₃)·0.5H₂O} + \text{3 g} \rightarrow \text{cis-[Co(NH₃)₆]Cl₂(NO₃)·0.5H₂O} + \text{CO₂} + \text{3H₂O}
\]

\[
\text{[cis-[Co(NH₃)₆Cl₂(NO₃)·0.5H₂O]} \rightarrow \text{[cis-[Co(NH₃)₆Cl₂(NO₃)]·0.5H₂O} + \text{CO₂} + \text{3H₂O}
\]

The synthesis and spectral measurements will not require a full six hours of working time, we have found it advantageous to dovetail this experiment with others.

1 Because the second synthesis and spectral measurements will not require a full six hours of working time, we have found it advantageous to dovetail this experiment with others.

2 The cis-[Co(NH₃)₆(H₂O)Cl₂]Cl isolated from this procedure is sometimes contaminated with small quantities of trans-[Co(NH₃)₆Cl₂]Cl and [Co(NH₃)₆]Br₂Cl₂. This does not affect the identification from the spectrum. However, purification may be easily effected by converting the chloride to the sulfate. See Reference (3).


Table 1

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\delta_{max} (\text{nm}))</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Co(NO₃)₂(NO₃)₂⁺</td>
<td>510, 363</td>
<td>red-violet</td>
</tr>
<tr>
<td>cis-Co(NO₃)₂(H₂O)₃⁺</td>
<td>502, 355</td>
<td>red-violet</td>
</tr>
<tr>
<td>Co(NO₃)₂(NO₃)₂⁺</td>
<td>440</td>
<td>yellow</td>
</tr>
<tr>
<td>trans-Co(NO₃)₂Br₂⁺</td>
<td>490 (sh)</td>
<td>yellow-green</td>
</tr>
</tbody>
</table>

*Measured in aqueous solution.

\[
\text{[Co(NH₃)₄]Cl}_2(\text{NO₃}) + 2\text{HClO}_4 \rightarrow 2\text{X} + \text{[Co(NH₃)₄]Cl}_2(\text{NO₃}) + \text{CO}_2 + 3\text{H}_2\text{O} (1)
\]

\[
(X = \text{NO}_3, \text{NO}_2, \text{Br})
\]

\[
\text{[Co(NH₃)₄]Cl}_2(\text{NO₃}) + 2\text{HClO}_4 + 3\text{Cl}^− \rightarrow \text{cis-[Co(NH₃)₄(\text{H}_2\text{O})Cl]Cl}_2 + \text{CO}_2 + \text{NO}_3^- + 2\text{H}_2\text{O} (2)
\]

If the reaction mixture is immediately cooled in an ice bath without the heating step, a diaquo product can be isolated.

\[
\text{[Co(NH₃)₄]Cl}_2(\text{NO₃}) + 2\text{HClO}_4 + 3\text{X} \rightarrow \text{cis-[Co(NH₃)₄(\text{H}_2\text{O})Cl]X}_2 + \text{CO}_2 + \text{NO}_3^- + 2\text{H}_2\text{O} (3)
\]

\[
(X = \text{NO}_3, \text{Cl, Br})
\]

Average student yields for the products are as follows: cis-[Co(NH₃)₄(H₂O)Cl]Cl₂ 64%; [Co(NH₃)₄(NO₃)₂]Cl₂ 59%; trans-[Co(NH₃)₆]BrCl 61% (Lit. 80% (3)).

Our students did not prepare the dinitrato complex (Lit. 33% yield (2)) because its spectrum was indistinguishable from that of [Co(NH₃)₄(H₂O)Cl]Cl₂ in the region accessible on Spectronic 20 instruments. If more sophisticated spectrophotometers were available, the compound could be included. The diaquo visible spectrum is also indistinguishable from that for the dinitrato compound. However, infrared measurements could distinguish these.

A few students who were given 48% HBr as an unknown obtained a brown product containing CoO instead of the anticipated green trans-[Co(NH₃)₄Br₂]Br. We are uncertain as to the reason for this behavior unless it could have resulted from heating to too high a temperature.

During the remainder of the laboratory time (after drying the complex in air for at least 45 min) students were asked to make up solutions of the products they prepared and to measure the visible spectrum using Spectronic 20's. The products could then be identified by comparison of the measured spectrum with posted spectra of the complexes.¹ A solution of proper concentration can be obtained by weighing precisely around 0.5 g of product and using a 250-ml volumetric flask. [Co(NH₃)₄Br₂]Br is not very soluble and only about 0.2 g will dissolve in 250 ml of water.

Spectral parameters of products measured on a Cary 14 are reproduced in the Table. The spectra reveal that cis-[Co(NH₃)₄Cl(NO₃)]⁺ and cis-[Co(NH₃)₄(H₂O)Cl]⁺ are distinguishable only in the region below 370 nm. Thus, unless either an instrument having a range in this region or an infrared spectrophotometer is available, only one of these complexes is suitable for student preparation.²

In our laboratories some 86% of freshman students correctly identified their complexes from the visible spectrum. After completing identification, students were asked to write a balanced chemical equation describing the reaction of [Co(NH₃)₄]Cl₂NO₃ with a salt containing the appropriate anion in acid solution. They were given the information that carbonate ion reacts with acid to afford carbon dioxide and water. This was a particularly challenging aspect of the experiment for many students who were accustomed to balancing...
PROTOCOLE 118

chemical equations as a formal exercise rather than using them to
describe actual reactions.

From the balanced equation students were asked to calculate the
yield. Although most were able to do this correctly, it came as a con-
siderable surprise to many that a yield of considerably less than 100%
was obtained and that this was to be expected in actual chemical
preparations.

Finally, students located the positions of peak maxima and calcu-
lated molar absorptivity. The values of this varied considerably and were
usually not particularly close to literature values owing presumably
to the fact that no recrystallization was carried out and to inadequacies
in technique in using volumetric flasks.

Procedure

Preparation of \([\text{Co(NH}_3\text{)}_4\text{CO}_3]\text{NO}_3\cdot0.5\text{H}_2\text{O}\)

About 10 g of \(\text{Co(NO}_3)_2\cdot6\text{H}_2\text{O}\) is weighed by difference into a 50-ml
beaker and dissolved in 10 ml distilled water. This solution is poured
into a 250-ml Erlenmeyer flask containing 15 g \((\text{NH}_3)_2\text{CO}_3\) dissolved
in 20 ml of distilled water to which has been added 25 ml conc. \(\text{NH}_3\).
After all the \(\text{Co(NO}_3)_2\cdot6\text{H}_2\text{O}\) solution is rinsed into the Erlenmeyer
the flask is swirled gently to mix the reactants.

The solution is then cooled to 5°C in an ice bath while the student
obtains 10 ml 30% \(\text{H}_2\text{O}_2\) (CAUTION: Keep \(\text{H}_2\text{O}_2\) off skin and eyes;
it is a powerful oxidizing agent and can cause painful burns.) The
hydrogen peroxide is added dropwise to the Erlenmeyer flask with
swirling. The addition should be carried out sufficiently slowly that
the solution temperature does not rise above 10°C. (Alternatively, air
could be bubbled through the solution for two hours.) Oxygen has
also been employed in similar reactions (1, 4).

After all the \(\text{H}_2\text{O}_2\) has been added, the flask is heated to 50–60°C for
twenty minutes with occasional swirling. Alternatively the steam bath
may be employed.

The flask is then cooled in ice to complete precipitation of the
product. Only occasionally is it necessary to resort to scratching or
addition of methanol to obtain crystallization. The product is collected
on a Büchner funnel by suction filtration and washed with a little cold
water and methanol.

We have found it best to isolate the product during the first working
period since a week’s standing of the reaction mixture sometimes
yields red \([\text{Co(NH}_3\text{)}_4\text{CO}_3] \text{NO}_3\). Many students obtain a second crop of
crystals of the tetraamine after a week, however.

3 Dr. Glen Direen of the University of Wisconsin, Madison, has
suggested the use of 10% \(\text{H}_2\text{O}_2\) to decrease the likelihood of peroxide
burns.

Reaction of \([\text{Co(NH}_3\text{)}_4\text{CO}_3]\text{NO}_3\) with Unknown

Students are provided with sufficient unknown to react with 3 g
of the carbonato complex. Suitable unknowns are: 10 ml conc. \(\text{HCl}:
15 ml 4 \% \text{HBr} ; 10 ml 1:1 conc. \text{HNO}_3 : \text{H}_2\text{O} ; 10 ml 1:1 conc. \text{HNO}_3 : \text{H}_2\text{O}
and 7 g \(\text{NaNO}_3\) in separate vials. The 3-g sample of the carbonato
complex is suspended in 15 ml distilled water and the liquid unknown
added a little at a time followed by the solid, if any. The solution is
maintained at 55–65°C for half an hour using a burner. At the end of
this time, the mixture is cooled in an ice bath and the product collected
on a Büchner funnel and washed with cold water and methanol.

Student Discussion and Extension of Work

Several features can serve to stimulate discussion and suggestions
for further work with bright students. For example, some possibilities
include the purpose of using ammonium carbonate in the synthesis
as opposed to other carbonates (4), the mechanism of \(\text{CO}_3\) loss on
hydrolysis (4) and the mechanism of anation (5, 6). Extension of the
work could involve elemental analyses (7), synthesis of related
products (9, 10, 11), or infrared spectra of products (12, 13).

We are currently pursuing some of these problems in the freshman
laboratory at the University of Cincinnati and will report our results
in future publications in this Journal.

Literature Cited

(1) One experiment dealing with a similar system which incorporates some of these features
is described in Olsen, G. R., J. CHEM. EDUC., 46, 569 (1969).
(2) The preparation is a slight modification of that described by Schlossinger, G., Inorg.
Synth., 6, 173 (1960).
(3) Schlossinger, G., "Inorganic Laboratory Preparations," Chemical Publishing Co., New
York, 1962.
also Ref. (3).
(7) (a) Hughes, B. G., Roddick, J. F. Hoffman, M. Z. and Hone, D. R., J. CHEM.
(12) Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds", Wiley
(13) See, for example, Alexander, J. J. and Stoffel, M. J., "Chemistry in the Laboratory,"