



Experiment 1

Synthesis and Symmetry of Cobalt(III) Complexes with Tetradentate Ligands

Introduction

This is a laboratory experiment based on the following article from the *Journal of Chemical Education*: “Synthesis and Symmetry of Two Cobalt(III) Complexes with Tetradentate Ligands” *J. Chem. Educ.*, 2008, 85 (3), 420–421.

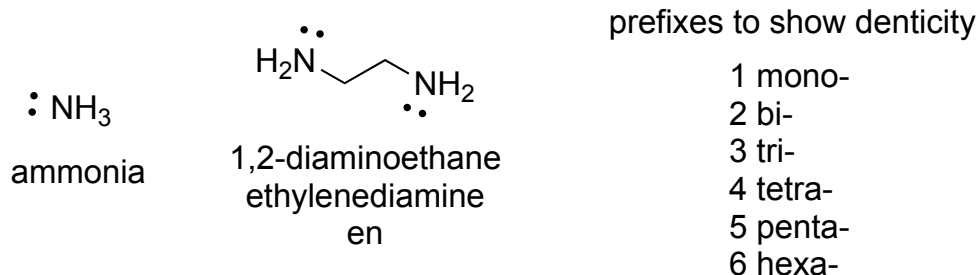
The major purposes of this laboratory as they relate to the class are:

- an introduction to simple inorganic synthesis
- an introduction to coordination compounds (studied in detail in the second half of the course)
- characterization of compounds by ^{13}C and ^{59}Co NMR spectroscopy
- the relationship of molecular symmetry to NMR spectra

Chemistry

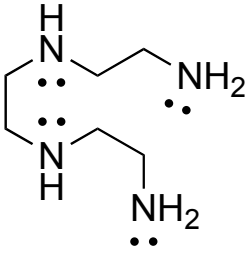
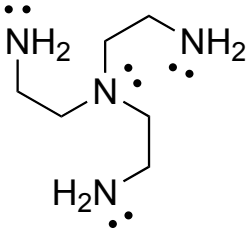
In this laboratory experiment, you'll synthesize a series of cobalt(III) coordination compounds. Here, “III” refers to the oxidation state of the cobalt atom in the molecule. The term “coordination” means that the electrons of the covalent bonds between cobalt and nitrogen both come from the nitrogen, and not from the cobalt. (Often we think of atoms bringing an electron each to their bonds.) Coordination compounds can be thought of as Lewis acid–Lewis base adducts (where the metal is the Lewis acid and the groups attached, called **ligands** are Lewis bases).

A ligand has a lone pair of electrons available for bonding (or “coordinating”) to a metal ion. When two atoms that can act as ligands are present in the same molecule, we call the whole molecule a *bidentate ligand*. The qualifying term tells how many sites on the molecule can act as ligands. A very simple example of a *monodentate ligand* is ammonia, and an analogous bidentate ligand is 1,2-diaminoethane ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$). (Note well that the non-systematic name for this compound is the less descriptive and possibly confusing *ethylenediamine*, which is abbreviated “en”.)



In this laboratory, you'll be working with monodentate, bidentate, and tetradentate ligands, with the emphasis on the behavior of the tetradentate ligand. In all cases, you'll be making compounds with cobalt in the +3 oxidation state and an **octahedral geometry**. Octahedral geometry means there are six groups around the metal atom (in this case cobalt) arranged so that all groups are 90° away from one another. A long time ago when we learned VSEPR for six groups around a central atom we learned that octahedral is the characteristic geometry when six groups are arranged around a central atom. As we continue our study of inorganic chemistry we'll find places where VSEPR doesn't work and we'll look at other theories, but happily the concepts of VSEPR can be used for all of the compounds in this lab.

We are principally investigating the different behavior of two different tetradentate ligands, abbreviated **tren** and **trien**.

Name and formula	structure	abbreviation
triethylenetetramine $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$		trien
tris(2-aminoethyl)amine $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$		tren

One of these tetradentate ligands, trien, is linear, while the other is branched. When the tetradentate ligand coordinates to the metal, it occupies four of the six available coordination sites. The other two sites will be occupied by nitrite, chloride, or the bidentate ligand en. You should consider the ways that the tetradentate ligand could bind to the cobalt that might lead to isomers.

In your synthesis, you'll be starting with cobalt in the +2 oxidation state. The reasons for this are in Chapter 12 of the textbook. A description, but not an explanation why, is that ligands are easily exchangeable on Co(+2) but are very slow to exchange places on Co(+3). So, as a synthetic strategy, we carry out our ligand exchange on Co(+2) and then oxidize the product to Co(+3) to prevent any further ligand exchange. There are many possible oxidizing agents that could be used, but we will use a cheap and plentiful one: the oxygen in the air.

Experimental

We will carry out this laboratory over four consecutive weeks. There will be some out of class time required to set up ^{13}C and ^{59}Co NMR experiments during that time. Also, during week 2 of the experiment, you'll need to come by the lab once a day to check that the solution has not evaporated, and to add fresh acid if needed.

Before each laboratory meeting, you should prepare your laboratory notebook according to the notebook preparation guidelines and the specifics of the experiment given below. Your preparation ahead of time is essential for a smooth time in the lab and getting all the work done within the scheduled time.

Week 1

This week you will prepare one cobalt complex. The procedure will not take the entire time.

Here is the published procedure, which is written in the style of a journal article, with a bit more guidance. Still, it is intentionally written for a student that has passed through organic chemistry and is able to "read between the lines" and "fill in the blanks" on things that are written with the expectation they are being read by a skilled practicing chemist.

Synthesis of $[\text{Co}(\text{tren})(\text{NO}_2)_2]\text{Cl}$

Measure out 11.9 grams of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and add to 10 mL of water in a 125-mL side-arm flask. Add 7.25 grams of solid NaNO_2 and swirl until the solid has dissolved. Make a second solution by adding 4.4 mL of concentrated hydrochloric acid (12 M) to 10 mL of water. Measure 7.5 mL of tris(2-aminoethyl)amine and cautiously add to the HCl solution. **(Caution: the amine reacts with the HCl in a neutralization reaction that is fairly exothermic. The amine must be slowly added to the acid solution.)** Add this solution to the cobalt solution and place the flask in an ice bath. Place a stopper fitted with a glass tube into the top of the flask; the glass tube should be long enough so that the end is immersed in the solution. Attach the flask to a vacuum line or water aspirator and draw a vigorous stream of air through the solution for 90 minutes. The yellow-brown solid should precipitate as it is formed. Recover the product by suction filtration. A yield of approximately 65-70% is typical for this reaction.

So, for example, you need to figure out what type of container in which to weigh the starting solid compounds. Weigh paper and weigh boats are not able to comfortably do more than about 3 grams of a substance. So, you'll need to find really large weigh boats, do multiple weighings (not efficient), or use some other piece of equipment to hold the solid during the weighting operation.

To measure volumes (this comes up a lot) you're expected to reason out when precision is needed and when it is not. Liquids needed this week are 4.4 mL hydrochloric acid, 10 mL water, and 7.5 mL tren. Which should be measured quantitatively? In our line of work, quantitative will mean a graduated cylinder or disposable plastic syringe and non-quantitative will mean a beaker; this is more or less in keeping with the thoughts you should have from organic chemistry. (The exception is when we do kinetic experiments in which case we need to break out the volumetric glassware!)

Prepare your notebook with a procedure in your own words and add the information prescribed in the **Guide to Notebook Preparation**.

Week 2

This week you'll synthesize another cobalt complex, recrystallize the one you made last week, and then do a ligand substitution on last week's compound. Think about how to get the first two processes done concurrently as much as possible. Here are the published procedures. Think about how to read into them what will be specifically required of you. Prepare your notebook for the synthesis. For the recrystallization, most of the writing in the notebook will be while you are attempting the recrystallization.

Synthesis of $[\text{Co}(\text{trien})(\text{NO}_2)_2]\text{Cl}$

The synthesis of $[\text{Co}(\text{trien})(\text{NO}_2)_2]\text{Cl}$ is analogous to that given above for $[\text{Co}(\text{tren})(\text{NO}_2)_2]\text{Cl}$ but with two exceptions. First, triethylenetetramine hydrate is a solid, so a specific mass (rather than volume) must be used. Second, the reaction should be carried out in an ice bath. The reason for this is that triethylenetetramine coordinates to form three different geometric isomers; carrying out the reaction at reduced temperature minimizes the formation of other isomers.

Prepare a cobalt chloride – sodium nitrite solution the same as for Week 1 and place in an ice bath. Measure out 7.31 grams of triethylenetetramine hydrate and dissolve in 10 mL of deionized water. Carefully add to this solution 4.4 mL of concentrated hydrochloric acid. Last, add this solution to the cobalt chloride – sodium nitrite solution and aerate for 90 minutes you did the previous week. A yield of approximately 80% is typical for this reaction.

Recrystallization of $[\text{Co}(\text{tren})(\text{NO}_2)_2]\text{Cl}$

While the first solution is aerating, recrystallize the $[\text{Co}(\text{tren})(\text{NO}_2)_2]\text{Cl}$ from the first week as follows. Dissolve the compound in the minimum amount of hot water required to achieve complete dissolution, then allow the solution to cool to room temperature. Place the solution in an ice bath and cool further before filtering. Recover the product by suction filtration.

Synthesis of $[\text{Co}(\text{tren})\text{Cl}_2]\text{Cl}$

Retain approximately one gram of recrystallized $[\text{Co}(\text{tren})(\text{NO}_2)_2]\text{Cl}$ for the NMR study. Add the rest to a 600-mL or 800-mL beaker, followed by 50 mL of concentrated hydrochloric acid. Add a magnetic stir bar and place the beaker on a stirring hotplate. The solution should be *somewhat vigorously stirred for a period of several days*; the reaction is complete when a blue-violet solid remains in the beaker. Should the solution dry out before the reaction is complete, add additional HCl and continue stirring the solution. Preferably, this should be done in a hood. A yield of approximately 80% is typical for this reaction.

As you did for last week's lab, consider what specific lab equipment will be needed to execute these procedures and make a list in your notebook to refer to when you get to lab.

Week 3

This week you'll do a ligand substitution (substituting the bidentate ligand en for two chlorides) and recrystallize the compound you made last week. Here are the published procedures.

Synthesis of [Co(tren)(en)]Cl₃

Scrape the solid [Co(tren)Cl₂]Cl from the beaker with a spatula. Mix with ethanol and grind with a mortar and pestle. Recover the solid by suction filtration and rinse several times with additional ethanol. Set up a reflux apparatus consisting of a 50-mL round-bottom flask and reflux condenser. Measure out approximately 1 gram of this compound and add to the flask with approximately 30-40 mL of methanol. Add a stoichiometric amount of ethylenediamine. Heat the solution to reflux for a period of approximately 30 minutes or until the reaction appears complete. When complete, there should be an orange solid suspended in the solution, with no trace of the original blue-violet solid. A yield of approximately 65% is typical for this reaction.

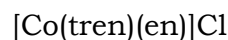
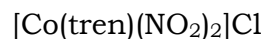
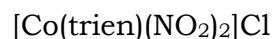
Recrystallization of [Co(trien)(NO₂)₂]Cl

Recrystallize the [Co(trien)(NO₂)₂]Cl by the same procedure used for [Co(tren)(NO₂)₂]Cl.

Note that you need to come to lab prepared with the calculation of how much ethylenediamine is the stoichiometric amount to add to 1 g of [Co(tren)Cl₂]Cl. If you weigh out a slightly different amount of the cobalt compound in lab, the correction to the amount of ethylenediamine is done as a simple proportionality.

Week 4

This is the week to get ¹³C and ⁵⁹Co NMR spectra. Make 1.0 mL of a 0.50 M solution of each of the following complexes in D₂O (deuterium oxide) with a small amount of DSS as an internal standard.



The Laboratory Report

Your report on this multi-week experiment should bring together the efforts of the various weeks into a cohesive whole. In other words, whatever form it takes, don't take the linear approach of "this week we did such-and-such, then the next week we..." Instead, you should write in the style and form of the attached research article from a recent issue of the American Chemical Society journal *Inorganic Chemistry*.

The important, required sections of the report are: Introduction, Results and Discussion, and Experimental. These will be weighted the heaviest in evaluating your report. Other sections that should be present are Abstract and Conclusion. These two sections will be given less emphasis in grading and comments on these sections will be mostly formative in nature. ("Formative" means constructive suggestions for improvement that don't bring down your grade. As a practical matter, they should be taken to heart for subsequent similar assignments.)

What should go in your report? What is important about the work you have done, and the compounds that you have made? The original lab handout gives some guidance in the form of questions. Do not answer these questions in list format in your report, but do incorporate the answers as natural components of your report.

The best reports may not be especially long, but will exhibit high quality throughout. Also, each person's report will likely have greater or lesser emphasis on different aspects of the discussion. There are countless different routes to an exemplary report.

Please hold yourself to the highest standards of professional presentation. This has two obvious aspects:

the written word.

Strive to be precise and economical in what you have to say. Edit your work yourself through two to four drafts (some people need more than this). After a couple drafts, have a scientifically literate friend read your work and offer suggestions.

visual aids.

Use care in constructing your Tables, Figures, Charts and Schemes. Let the published literature be your guide to the acceptable standard of quality in this area.

Allow yourself an appropriate amount of time, budgeted in segments over the course of days, to complete this assignment so that it reflects your best work. I will be happy to meet to discuss your report and to offer substantial, constructive suggestions at the draft stage, but **only up until 72 hours before the start of the due date**. Our most productive conversations would surely commence earlier than that.

LAB REPORT IS DUE ON WEDNESDAY OCTOBER 2.

lab report will be returned on Wednesday October 9.

Revised LAB REPORT IS DUE ON WEDNESDAY OCTOBER 23.

All work on the Laboratory Report is to be strictly your own.