Synthesis of a Transition Metal Coordination Complex: *trans*-[Co(en)$_2$Cl$_2$]Cl

Introduction

In this experiment you will prepare a coordination compound of cobalt(III) with the bidentate ligand ethylenediamine ("en"; $NH_2CH_2CH_2NH_2$). Coordination compounds are also called complexes, and if they are ions they are called complex ions. A complex ion contains a central metal to which Lewis bases (ligands) have been attached or coordinated. The purpose of this experiment is to provide an introduction to the field of transition metal coordination chemistry and have you synthesize a coordination compound. This synthesis will allow you to experience some of the common procedures used to prepare and isolate inorganic compounds. The complex you will synthesize is *trans*-[Co(en)$_2$Cl$_2$]Cl, a green-colored cobalt transition metal complex, which will be used to study spectrophotometry and kinetics in the experiments which follow.

The principal oxidation states of cobalt are the +2 and +3 states. The aqueous $[Co(H_2O)_6]^{3+}$ ion is very unstable because it is a powerful oxidizing agent and is readily reduced by water to $[Co(H_2O)_6]^{2+}$:

$$4\,[Co(H_2O)_6]^{3+} + 2\,H_2O \rightarrow 4\,[Co(H_2O)_6]^{2+} + O_2 + 4\,H^+$$

However, the +3 oxidation state can be stabilized by replacing the coordinated water molecules with less labile ligands such as NH_3, NO, CN^-, and $NH_2CH_2CH_2NH_2$ (en). A labile complex exchanges its ligands rapidly. Lability is associated with the *d*-electron configuration of the central metal. In general, ligands coordinated to a Co^{3+} ion do not dissociate from the Co^{3+} ion rapidly, and as a consequence, they are not easily replaced by other ligands. Thus, Co^{3+} complexes can endure many laboratory manipulations, and as we shall see, some of them can be prepared in structural forms whose stable existence depends on the durability of the bonds to the cobalt atoms.

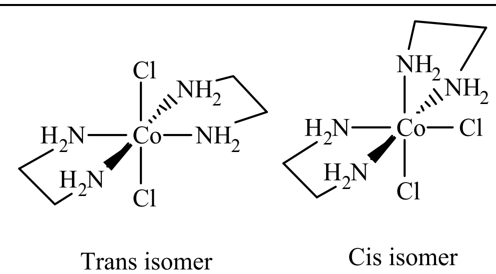

Figure 1. The *trans*- and *cis*- isomers of [Co(en)$_2$Cl$_2$]Cl.

In this assignment you will prepare a complex ion with a net +1 charge in which two molecules of ethylenediamine (en) and two chloride ions are bonded to a central Co^{3+} ion. Each of the two ethylenediamine molecules is attached to the Co^{3+} ion via the lone pairs on the basic nitrogen atoms at each end of ethylenediamine. Thus, six atoms (four nitrogen atoms and two chlorine atoms) are directly bonded to the cobalt atom and form the corners of an imaginary octahedron (eight-faced solid) with the cobalt atom at the center (see Figure 1). Notice that there are two possible structures for the complex. In one structure (the *cis*- isomer), the two chlorine atoms occupy adjacent corners of the octahedron. In the other structure (the *trans*- isomer), the two chlorine atoms occupy opposite corners of the octahedron. These structurally different complexes have different physical and chemical properties. For example, the *cis* complex is dark purple in color, while the *trans* complex looks green. In this experiment, you will prepare the chloride salt of the *trans* complex. The *trans* complex you prepare here will be used later in spectrophotometry and kinetics studies of its acid hydrolysis. Hereafter, we use the symbol "en" for the ethylenediamine molecule/ligand. It is very crucial that you measure all reagents and carry out all procedures exactly as described. Otherwise, you will synthesize an unintended complex or obtain a mixture of products.

Please **read Chapter 25 in Petrucci Textbook, 8th ed.**, as pre-laboratory preparation for this experiment.

You will need to retain the product for use in the Spectrophotometry and Kinetics experiments that follow.

Procedure

Safety: Place all waste solutions/precipitates into the proper waste container. Wear gloves when using ethylenediamine, 30% & 10% hydrogen peroxide, and 12 M hydrochloric acid; these three chemicals can cause severe burns. Never attempt to smell any solution as the odors can be irritating in high concentrations. Avoid standing between your product and the fumehood as a solution is heating. Wear your goggles!

You will work in pairs for this experiment. The actual data analyses and the written reports must be done entirely independently of your lab partner or other students. Make sure that you avoid unauthorized collaboration and plagiarism. All suspected violations of the Code of Academic Conduct will be referred to Student Judicial Affairs

Synthesis of *trans*-[Co(en)$_2$Cl$_2$]Cl

1. You will need the following chemicals for this synthesis:
   a) $CoCl_2 \cdot 6H_2O(s)$
   b) 3 M ethylenediamine (en)
   c) 10 % H_2O_2
   d) 12 M HCl (in the fumehood)
   e) ethanol

2. Prepare a hot water bath by placing about 125-175 mL of deionized water in a 250 mL beaker and begin heating the water with a Bunsen burner immediately upon entering the laboratory.

3. Accurately weigh 2.4 grams of $CoCl_2 \cdot 6H_2O(s)$ and place it in a 50 mL Erlenmeyer flask. Add 8 mL of deionized water to dissolve. Do the next step in the FUMEHOOD. After all of the solid has dissolved add 8 mL of the ligand ethylenediamine ($C_2N_2H_8$) to the cobalt solution. Carefully make observations regarding any color or temperature changes and record these in your notebook.

Question A: Explain why the color changes occur during this reaction.

Question B: Write a balanced chemical equation for this process. The product is $Co(en)_2Cl_2$.

4. Return to the laboratory bench with your cobalt solution and make 12 mL of a 10% H_2O_2 solution from a 30% H_2O_2 stock solution. **Slowly** add 8 mL of the 10% H_2O_2 to the cobalt solution. Let the flask sit for 5 minutes at room temperature with occasional swirling and note any color or temperature changes. Transfer the solution to your small casserole. Rinse the flask with 8 mL of deionized water and add this rinse solution to the solution in the casserole.

Question C: Explain why the color changes during this process.

Question D: An excess of H_2O_2 has been used in this step since cobalt(II) is oxidized in the presence of the decomposing hydrogen peroxide. In the reduction half reaction of H_2O_2 in a basic solution hydroxide ions are formed, $2e^- + H_2O_2(aq) \rightarrow 2OH^-(aq)$. Write a balanced ionic equation for the redox reaction occurring in step 4.

As a side note: The decomposition of hydrogen peroxide takes place as self-reaction involving both oxidation and reduction processes. Therefore, a by-product reaction occurring here is $2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + 2O_2(g)$. This reaction is catalyzed by the presence of transition metal ions.

5. Place the small casserole over the 250 mL beaker that is partially filled with the boiling water, as is shown in Figure 2. Be careful to avoid breathing the vapors that may rise out of the casserole. Next, quickly but carefully add 12 mL of concentrated HCl and note any color changes. Continue heating the casserole on top of the beaker for about **~50 minutes**. Do not heat for more than 50 minutes! During this 50 minutes the volume of the **cobalt solution** should be reduced to one quarter of the original volume (you may want to use another casserole with the targeted volume of water for comparison). As the volume of solution in the casserole is reduced, a crust of crystals (like a thin slurry) will begin to form on the surface of the liquid. Do not allow the solution to completely evaporate from the casserole. Thus, you may have to add a few mL of deionized water to avoid this, but only add a minimum. You may also need to add small amounts of water to the **beaker** in order to maintain this volume of water while boiling.

Question E: Write a balanced chemical equation for this process. The product is $[Co(en)_2Cl_2]Cl$.

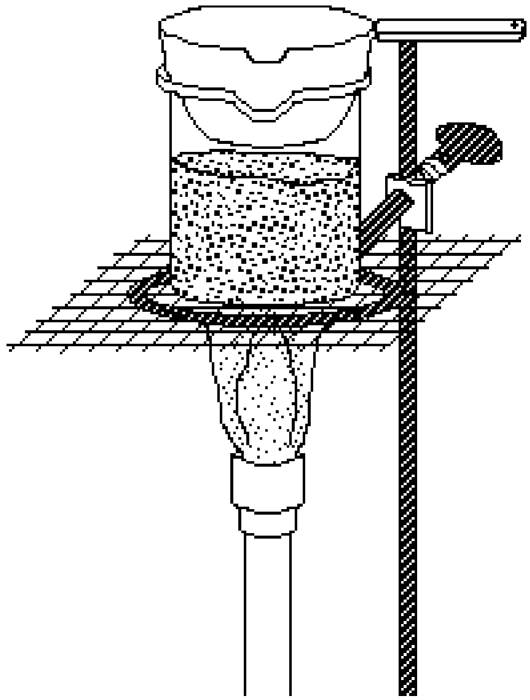

Figure 2: Heating the Casserole

6. Carefully remove the casserole and place it in an ice bath. Let the casserole **cool** for 5 minutes and then add 4 mL of 95% ethanol to force more of the water soluble product to crystallize. It is important here that you allow the casserole to cool before rinsing your product with the 95% ethanol. Allow 5 more minutes for the product to fully crystallize.

7. While the crystals are forming in step 6, set up the vacuum filtration apparatus as shown in Figure 3. This apparatus consists of a 125 mL filter flask, a black #3 neoprene adapter, and a plastic filtering funnel with a white fritted glass filter inside. Clamp the filter flask securely to the support rods. Wet the tip of the thick rubber tubing and connect it to the flask from the safety bottle that should already be attached to the aspirator on the faucet. Obtain a small circle of filter paper from the front of the room. Always use filter paper when filtering through a funnel. The filter paper is thin. Be sure you only have one sheet of filter paper. Place the filter paper against the fritted glass inside the funnel. Begin the aspirating by turning on the faucet and letting the water run into the sink. Seat the filter paper to the fritted glass by squirting a little deionized water on the filter paper. If everything is working properly, the paper should be pulled down against the fritted glass and the small spray of deionized water should be pulled through into the flask.

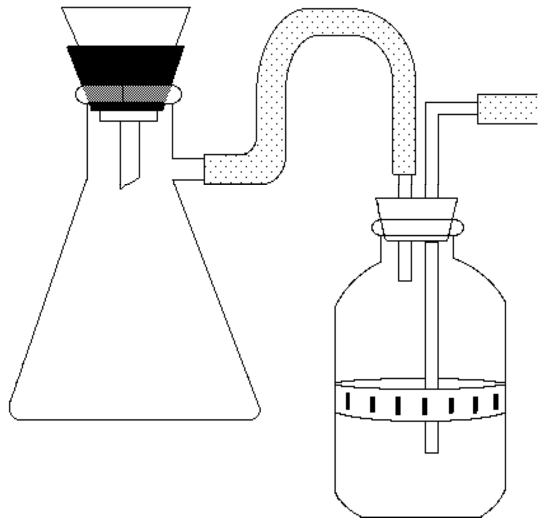

Figure 3: Filtering Apparatus

8. Once the product has crystallized, remove the casserole from the ice bath and, using a rubber policeman, carefully transfer both the solid and the solution to the funnel. After the aqueous solution has been pulled through the filter, carefully disconnect the filtration apparatus and turn off the water. Dispose the aqueous solution into the metal ion waste container. Assemble the filtration apparatus again and rinse the crystals twice with 4 mL portions of <u>95% ethanol</u>. You may use the ethanol to help transfer any product that remains in the casserole. <u>Do not use water since the product is water soluble</u>. Continue to pull air through the crystals to dry the crystalline product. The solution remaining in the Erlenmeyer flask may be washed down the drain with copious amounts of water.

9. Clean and dry an evaporating dish. Carefully transfer the damp product onto the dish. Place the evaporating dish over the boiling water bath for 5 minutes to finish the drying.

10. Weigh a clean, dry plastic snap-cap vial. Transfer the dry product to the vial and weigh. Calculate the mass of the product and the percent yield. Fill out a label for the vial indicating molecular formula, the mass, the date, and the names of both you and your partner. Hand in your labeled vial to your TA before you leave. Your TA will retain your product for use in the Spectrophotometry and Kinetics experiments that follow. The post-laboratory exercises will guide you through the above calculations and questions.

Clean Up: Remove the used circle of filter paper from your funnel and dispose of it in a crock pot. Rinse the filter flask, filter, and neoprene adapter thoroughly with deionized water and return these to the front of the room. Do not place this community equipment in your locker.

Post-Laboratory Exercise Questions

The following series of questions involve the chemistry in the synthesis of trans-$[Co(en)_2Cl_2]Cl$
Which of the following reasons correctly explains the color changes that take place when ethylenediamine ($C_2N_2H_8$) is added to the solution of cobalt(II) chloride? 3 choices will be given

Which of the following balanced chemical equations correctly represents the chemical reaction that takes place when ethylenediamine ($C_2N_2H_8$) is added to the solution of cobalt(II) chloride to form dichlorobis(ethylenediamine)cobalt(II)? 3 choices will be given.

Which of the following reasons correctly explains the color changes that take place when 8 mL of the 10% H_2O_2 is added to the solution of dichlorobis(ethylenediamine)cobalt(II)? 4 choices will be given.

An excess of H_2O_2 has been used in this step since cobalt(II) is oxidized in the presence of the decomposing hydrogen peroxide. In the reduction half reaction of H_2O_2 in a basic solution hydroxide ions are formed, $2e^- + H_2O_2(aq) \rightarrow 2OH^-(aq)$. Which of the following is the correct balanced ionic equation for the redox reaction occurring when the hydrogen peroxide is added to dichlorobis(ethylenediamine)cobalt(II) solution? 3 choices will be given.

Which of the following is the correct balanced equation for the reaction that takes place when concentrated hydrochloric acid is added to dichlorobis(ethylenediamine)cobalt(III) hydroxide solution? 3 choices will be given.

The following few questions will lead you through the calculation of the percent yield of product. You were instructed to use approximately 2.4 grams of cobalt(II) chloride hexahydrate to begin the synthesis. What is the precise mass in **grams** of starting material, cobalt(II) chloride hexahydrate, that you used? Your mass precision should be reported to a thousandth of a gram.

What is the molar mass of $Co[H_2O]_6Cl_2$ 5 choices will be given.

How many moles of $Co[H_2O]_6Cl_2$ were available of the starting material?

The theoretical yield (in grams) of product is obtained by assuming that every mole of $Co[H_2O]_6Cl_2$ available as the starting material is converted to product trans-$[Co(en)_2Cl_2]Cl_2$. What value **in grams** is your theoretical yield of product?

What is the mass **in grams** of product, trans-$[Co(en)_2Cl_2]Cl$, that you collected? Your mass precision should be to a thousandth of a gram.

Based on your calculated theoretical yield and your reported mass of product, calculate the percent yield of product, trans-$[Co(en)_2Cl_2]Cl$? Report your percent yield to a tenth of a percent, i.e. 45.3%.

Concluding Remarks: Briefly discuss interpretations of your observations and results. Include in your discussion, any conclusions drawn from the results and any sources of error in the experiment.