Chem 400
Inorganic Chemistry Laboratory

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Objectives: This laboratory is intended to introduce the student to some of the more common experimental techniques and methods used by inorganic chemists. Another important goal is the review of methods and techniques which were encountered in earlier laboratory courses in chemistry. As in any laboratory course, principles and theories which are covered in lecture will be illustrated as well. A wide variety of synthetic procedures, methods of purification and characterization, and types of instrumentation will be used.

Grading: Grades are based on the following:
- Laboratory Reports (formal write up, laboratory notebook)
- Experimental Results (i.e., how much effort do you put into the lab)
- Techniques, safety practices, preparation, etc.

Glassware: Laboratory glassware is incredibly expensive. Note that a condenser costs about $50. When experiments are carried out using glassware, some things will get broken and we expect that. However, excessive breakage, or breakage resulting from carelessness are unacceptable laboratory practices—poor laboratory technique, and will be graded accordingly. When you break glassware be sure to dispose of it correctly. For broken beakers, Erlenmeyer flasks, etc., that do not have ground glass joints, just dispose of the broken glass in the broken glass container, not just in a trash can. For glassware with ground glass joints, the joints, if they themselves are not broken, should be salvaged. For flasks with star cracks, save the flask—it can be repaired by a glassblower.

Safety: Because flammable liquids and corrosive and health-damaging chemicals are frequently encountered in the chemical laboratory, unsafe laboratory practices cannot and will not be tolerated. Safety clothing: Safety glasses (or prescription glasses) are required at all times while in the laboratory. Rubber gloves are required while carrying out experimental work, handling chemicals, etc. A laboratory coat or apron is recommended but not required. Know where the fire extinguisher, safety shower, and eyewash fountain are located.

Chemical Waste Disposal: In order to avoid environmental contamination, laboratory chemicals must be disposed of properly. Non-halogenated solvents must be poured into the “non-chlorinated waste” jug; halogenated solvents are poured into the “chlorinated waste” jug. Solid chemical waste is placed in the appropriate chemical waste bucket, broken glass is placed into the broken glass container. Never put solids, organic wastes, or heavy-metal salts down the drain!
Laboratory Notebooks: The notebook serves as a source of information for you to carry out the experiment and provides a record of your experiment, observations, etc. You should record your work as you have done it (third person, past tense) in concise form but with sufficient clarity and detail so that a person of equivalent training and experience could repeat your experiment. This should constitute the basis of the Experimental Section of your formal write-up.

Laboratory Reports: Your formal write-up (typed, handwritten lab reports are not acceptable) should include the following:

Title of the Experiment
Abstract (a few sentences which summarize, in general terms, the experiment, reactions, procedure, and results).
Introduction (a few sentences which introduce the reader--the instructor--to the experiment).
Experimental Section (this should be a brief and to-the-point description of the experimental details; third person, past tense, passive voice; see an issue of the journal *Inorganic Chemistry* to see how an experimental section is written).
Results (a one or two sentence summary of the results of your experiment. Use a table whenever this will improve presentation).
Discussion It will be useful and necessary to interpret your experimental results in this Discussion Section. A Discussion Section should include chemical reactions and important reaction mechanisms. You need to indicate to the instructor that you fully understand all of the techniques and chemical concepts involved in the experiment. Often, you are asked to include study questions/exercises in your discussion and to draw some conclusions from your results. Incorporate these study questions into your discussion. Don't just have "naked" answers numerically listed. Note that a good Discussion Section will often require consulting additional literature sources (the Inorganic Chemistry textbook, the library, chemical journals, or the internet). Be sure to adequately reference sources that you use in your writeup (that is, reference facts gathered or statements made from literature sources, use numerical superscripts in your writeups and compile the references at the end of your writeup; don't just have a bibliography at the end and make me guess which of these you got your information from).
References and Notes Failure to adequately reference your sources does not do justice to those people on whom you are basing your write-up and may constitute plagiarism. Give adequate references to all literature sources. See a recent issue of the *Inorganic Chemistry* to see how references are handled, listed, and abbreviated. This section will be worth 10% of your write-up score.

CAUTION: DO NOT PLAGIARIZE TEXTBOOKS, JOURNAL ARTICLES, OR OTHER STUDENTS. USE YOUR OWN WORDS!!
Experiment 1
Preparation of \([\text{Co(NH}_3\text{)}_4\text{CO}_3\text{]}\text{NO}_3\)

Introduction

Coordination compounds of Co(III) and Cr(III) have been of particular interest because their complexes undergo ligand exchange very slowly compared with complexes of many other transition metal ions. For example, Ni(NH$_3$)$_6^{2+}$ reacts virtually instantaneously with H$_2$O to form Ni(OH$_2$)$_6^{2+}$. Under the same conditions, the analogous reactions of Co(NH$_3$)$_6^{3+}$ and Cr(NH$_3$)$_6^{3+}$ occur very slowly. This difference in behavior of complexes of different metal ions has been accounted for by ligand field theory and molecular orbital theory.

The slow reactivity of Co(III) complexes has made them suitable for extensive investigations. The structure of the octahedral Co(III) complex which you will prepare is:

![Chemical Structure of [Co(NH$_3$)$_4$CO$_3$]NO$_3$]

Procedure

Dissolve 20 g (0.21 mol) of (NH$_4$)$_2$CO$_3$ in 60 mL of H$_2$O and add 60 mL of concentrated aqueous NH$_3$. While stirring, pour this solution into a solution containing 15 g (0.052 mol) of [Co(OH$_2$)$_6$(NO$_3$)$_2$] in 30 mL of H$_2$O. Then slowly add 8 mL of a 30% H$_2$O$_2$ solution (CAUTION: Strong oxidizing agent! Can cause severe burns! Use gloves! Wash affected areas immediately with water!). Pour the solution into a beaker and concentrate to 90-100 mL using a hot plate in the fume hood. Do not allow the solution to boil. During the evaporation time add, in small portions, 5 g (0.05 mol) of (NH$_4$)$_2$CO$_3$. Suction filter (glass frit filter with water aspirator) the hot solution. Cool the filtrate in an ice water bath, and isolate the red crystalline product by suction filtration. Wash the product with a small amount of ice-cold water and then with a small amount of ethanol. Determine the yield and obtain an IR spectrum of your product. Turn in your product in a labeled sample vial. Your laboratory report should include a discussion of your product yield and the IR spectrum. Include the following questions in your discussion:

- Balance the equation for the reaction in this experiment:
  \[\text{Co(NO}_3\text{)}_2 + \text{NH}_3(\text{aq}) + (\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}_2 \rightarrow [\text{Co(NH}_3\text{)}_4\text{CO}_3\text{]}\text{NO}_3 + \text{NH}_4\text{NO}_3 + \text{H}_2\text{O}\]

- In the final isolation of the product, why was the solid washed with ethanol after having first been washed with water?

- How do [Co(NH$_3$)$_5$CO$_3$]NO$_3$ and [Co(NH$_3$)$_5$CO$_3$]NO$_3$ differ structurally? How would you experimentally distinguish between these two compounds?

Experiment 2
Synthesis of (TPP)Ni

Introduction

Metal ions play vital roles in many biological processes and at least six transition metals (iron, copper, manganese, cobalt, nickel, and molybdenum) are essential to almost all life on earth. These metals are key components of many important proteins. In some cases, the metals coordinate to the nitrogen, sulfur, or oxygen atoms in the side chains of certain amino acids that make up the protein’s structure; among these metal binding amino acids are histidine, cysteine, methionine, tyrosine, aspartic acid, and glutamic acid. In other cases, however, the transition metals are bound to special ligand, the most important of which are the porphyrins. Metal-bearing porphyrin complexes are called metalloporphyrins.

Porphyrins have the general structure shown below; they are compounds with a central 16-membered ring consisting of four pyrrole subunits linked by one-carbon bridges. The porphyrin ring is polyunsaturated and completely conjugated; consequently, porphyrins and their complexes with transition metals are intensely colored. In metalloporphyrins, a metal atom coordinates to the four nitrogen atoms and displaces the two central hydrogen atoms. One important metalloporphyrin complexes that is found in all animals is the iron porphyrin called hemoglobin. In vertebrates, hemoglobin is responsible for the transport of dioxygen from the lung to cells throughout the body. Metalloporphyrin complexes serve a variety of other important biochemical roles; for example, they serve as electron transfer relays and as oxidation catalysts.

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{H} & \quad \text{N} \\
\text{N} & \quad \text{H} \\
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_3 & \quad \text{R}_4 \\
\text{R}_5 & \quad \text{R}_6 \\
\text{R}_7 & \quad \text{R}_8 \\
\text{R}_9 & \quad \text{R}_{10} \\
\text{R}_{11} & \quad \text{R}_{12} \\
\end{align*}
\]

Naturally occurring porphyrins generally have a variety of different organic groups \(R_1 - R_{12}\) on the periphery (exterior) of the ring. To synthesize such polysubstituted porphyrin rings is a challenging task for chemists. For many purposes, however, the characteristic chemical properties associated with metalloporphyrins are exhibited by simpler analogues with small peripheral groups. The most important examples of such synthetic analogues are the complexes of meso-tetraphenylporphyrin (abbreviated \(\text{H}_2\text{TPP}\)), where the “meso” designation means that the phenyl groups are located on the four carbon atoms that bridge between the pyrrole rings. All the other peripheral groups in \(\text{H}_2\text{TPP}\) are hydrogen atoms. The chemical formula of \(\text{H}_2\text{TPP}\) is \(C_{44}H_{30}N_4\). In this experiment you will prepare \(\text{H}_2\text{TPP}\) and convert it to its nickel complex Ni(TPP), whose structure is shown above.

This experiment begins with the preparation of \(\text{H}_2\text{TPP}\) by the condensation of four molecules each of benzaldehyde and pyrrole. This is not a high yield reaction but the starting materials are inexpensive and the product is easily isolated. The low yields of this reaction illustrate the difficulty of assembling a large ring in a “one pot” reaction. In some cases, but not this one, the yields of such cyclization reactions can be improved by adding metal ions to the solution, which assist in the assembly of the macrocycle by binding to the reactants and orienting them in such a fashion to favor formation of the ring.

Procedure

\text{Meso-Tetraphenylporphyrin, } C_{44}H_{30}N_4 \text{ (H}_2\text{TPP)}

Place a Teflon-coated stir bar in a one-neck 100 mL round bottom flask and add 40 mL of propanoic acid (sometimes called propionic acid). Fit the flask with a reflux condenser and use small amounts of silicon grease on the joint. Heat the acid to reflux using an oil bath. When the propanoic acid begins to boil vigorously, add a mixture of 1.65 mL (15.75 mmol) of benzaldehyde and 1.0 mL (5.0 mmol) of pyrrole...
by pouring this solution down the reflux condenser. Measure out these liquids using a syringe or pipet. Rinse the pyrrole and benzaldehyde down the condenser with 10 mL of propanoic acid. Continue to reflux the solution for 30 minutes, and then remove the heat and let the flask cool for a few minutes. Filter the dark brown mixture using a medium-porosity glass-frit. Wash the crude product with 10 mL of methanol to remove the tarry impurities. Rinse the mixture with small amounts of additional methanol until the washings are clear and purple crystals are left on the frit. Allow the crystals to dry by pulling air through them for a few minutes. Collect the purple crystals and record the yield. Discard the wash solutions by pouring them into the containers provided for them.

**(Tetraphenylporphyrinato)nickel(II), Ni(TPP)**

The reaction set up is the same as in the previous part. Place 0.1 g (0.16 mmol) of H$_2$TPP in a one-neck 100 mL round bottom flask along with a stir bar. Add 20 mL of dimethylformamide and 0.5 g of NiCl$_2$. Attach a condenser and reflux for one hour. When the reaction is done (check using UV-vis spectroscopy), cool the reaction mixture to room temperature in an ice-water bath for 5-10 minutes, and then add 50 mL of distilled water to precipitate the porphyrinic material. Transfer the slurry to a separatory funnel and extract three times with 25 mL of dichloromethane. Collect the organic layer each time, also collecting the aqueous phase (which is usually pale blue). Then pour the combined organic extracts back into the separatory funnel and extract it with 50 mL of distilled water. Dry the organic layer using Na$_2$SO$_4$, filter the drying agent off, then concentrate the organic layer to dryness using a rotary evaporator. Check the purity of your product using thin-layer-chromatography (TLC), if impurities are still present, purify your product using column chromatography.

Determine the yield and obtain an IR spectrum of your products. Turn in your product in labeled sample vials. Your laboratory report should include a discussion of your product yields, the $^1$H NMR and the IR spectrum. Include the following questions in your discussion:

- The insertion of a metal ion into the porphyrin ring is sometimes very slow even though the reaction is very favorable thermodynamically. Suggest a reason why that is the case.
- Suggest a mechanism for the cyclization reaction between pyrrole and benzaldehyde to form the porphyrin.
**Experiment 3**  
**Preparation of Ferrocene**

**Introduction**

In this experiment ferrocene is prepared by reaction of the anion of cyclopentadiene with iron(II) chloride. Abstraction of one of the acidic allylic protons of cyclopentadiene with base gives the aromatic cyclopentadienyl anion. It is considered aromatic because it conforms to the Hückel rule in having $4n + 2$ \( \pi \) electrons. Two molecules of this anion will react with iron(II) to give ferrocene, the most common member of the class of organometallic compounds referred to as metallocenes. In this centrosymmetric sandwich-type \( \pi \) complex, all carbon atoms are equidistant from the iron atom. The extraordinary stability of ferrocene (stable to 500°C) can be attributed to the sharing of the 12 \( \pi \) electrons of the two cyclopentadienyl rings with the six outer shell electrons of iron(II) to give the iron a stable 18-electron inert gas configuration. Ferrocene is soluble in organic solvents, can be dissolved in concentrated sulfuric acid and recovered unchanged, and is resistant to other acids and bases as well (in the absence of oxygen). This behavior is consistent with that of an aromatic compound; ferrocene is found to undergo electrophilic aromatic substitution reactions with ease.

Cyclopentadiene readily dimerizes at room temperature by a Diels-Alder reaction to give dicyclopentadiene. This dimer can be "cracked" by heating (an example of the reversibility of the Diels-Alder reaction) to give low-boiling cyclopentadiene. In most syntheses of ferrocene the anion of cyclopentadiene is prepared by reaction of the diene with metallic sodium. Subsequently, this anion is allowed to react with anhydrous iron(II) chloride. In this experiment, however, the anion is generated using powdered potassium hydroxide, which functions as both a base and a dehydrating agent.

\[
\begin{align*}
\text{dicyclopentadiene} & \xrightarrow{\triangle} 2 \text{ cyclopentadiene} \\
\text{cyclopentadiene} & \xrightarrow{\text{KOH, DME}} \text{ potassium cyclopentadienide} \\
\FeCl_2 & \xrightarrow{2 \text{ KCp, DMSO}} \text{ Fe}
\end{align*}
\]

The anion of cyclopentadiene rapidly decomposes in air, and iron(II) chloride, although reasonably stable in the solid state, is readily oxidized to the iron(III) state in solution. Consequently this reaction must be carried out in the absence of oxygen, accomplished by bubbling nitrogen gas through the solutions to displace dissolved oxygen and to flush air from the apparatus.
Procedure
Measure 20 mL of technical grade dicyclopentadiene (85% pure) into a 50-mL flask, add a boiling chip, and arrange for fractional distillation into an ice-cold receiver. Heat the dimer with a heating mantle until it refluxes briskly. In about 5 min the monomeric diene will begin to distill slowly and will have a boiling point in the range of 40-42°C. If the boiling point rises above 44°C, add less heat. While the distillation is taking place, rapidly weigh 25 g of finely powdered potassium hydroxide (crush and then grind 27 g of KOH pellets in a large mortar and quickly weigh 25 g of the resulting powder) into a 250-mL Schlenk flask, add 60 mL of dimethoxyethane (DME) and immediately cool the mixture in an ice bath. Swirl the mixture in the ice bath for 1-2 min, stopper the flask with a rubber septum, then bubble nitrogen through the solution for about 2 min (see right). Shake the mixture to dislodge the cake of KOH from the bottom of the flask and to dissolve as much of the base as possible (much will remain undissolved).

Grind 7 g of iron(II) chloride tetrahydrate to a fine powder and then add 6.5 g of the green salt to 25 mL of dimethylsulfoxide (DMSO) in a 50-mL Erlenmeyer flask. Pass nitrogen through the DMSO mixture for about 2 min, stopper the flask, and shake it vigorously to dissolve all the iron(II) chloride. Transfer the solution rapidly to a 125-mL addition funnel equipped with stopcock adapter, and flush with nitrogen. Transfer 5.5 mL of the freshly distilled cyclopentadiene to the slurry of potassium hydroxide in DME using a syringe. Shake the flask vigorously and note the color change as the potassium cyclopentadienide is formed. After waiting for about 5 min for the anion to form, replace the septum on the Schlenk flask with the addition funnel (quickly to avoid admission of air to the flask). Connect the stopcock adapter using a short piece of tygon or latex tubing (see right). Add the iron(II) chloride solution to the base dropwise over a period of 20 min with vigorous swirling and shaking. Dislodge the KOH should it cake on the bottom of the flask. Continue to shake and swirl the solution for 10 min after all the iron(II) chloride is added, then pour the dark slurry into a mixture of 90 mL of 6 M HCl and 100 g of ice in a 500-mL beaker. Stir the contents of the beaker thoroughly to dissolve and neutralize all the KOH. Collect the crystalline orange ferrocene on Büchner funnel (save the filtrate), wash the crystals with water, press out excess water, and allow the product to dry overnight. Add a solution of 1 g of tin(II) chloride (stannous chloride) in 10 mL of water to the filtrate. How do you account for the color changes?

Purify your crude ferrocene by sublimation. In a hood, place your crude ferrocene in a Petri dish. Place the Petri dish on a hot plate and place a beaker of ice on top of the Petri dish. Ferrocene will sublime leaving nonvolatile impurities behind. Pure ferrocene melts at 172-174°C. Be sure to obtain a melting point and an IR spectrum of your sublimed ferrocene.

Turn in your product in a labeled sample vial. Your lab report should include the yield and discussion, all reactions, 1H-NMR and IR spectra and interpretation. Include the following questions in your discussion:
- If ferrocene is stable to air and all of the reagents are stable to air before the reaction begins, why must air be so carefully excluded from this reaction?
- What special properties do the solvents DME and DMSO have compared to diethyl ether, for example, that make them particularly suited for this reaction?
- What is there about ferrocene that allows it to sublime easily where many other compounds do not?

Experiment 4
Preparation of (Mesitylene)Mo(CO)₃

Introduction

Although it had been known for years that the π-bond in olefins was essential for their coordination to transition metals, it was not until approximately 1955 that benzene was also found to form stable complexes. As illustrated in this experiment, benzene and its derivatives do often react to displace three donor ligands. The three ligands that will be displaced in this synthesis are CO groups. Because mesitylene forms more stable complexes than benzene, it will be used as the aromatic ligand:

The reaction may be carried out simply by refluxing Mo(CO)₆ in mesitylene. The product (mesitylene)Mo(CO)₃, has a sandwich structure in which the benzene ring lies parallel to the plane of the three carbon atoms of the CO groups. A molecular orbital bonding scheme involving molecular orbitals of the aromatic benzene and s, π, and d orbitals on the metal accounts for the structure and spectral properties of these compounds.

Procedure

CAUTION: Metal carbonyls, in general, are toxic compounds and should be handled with care. They are particularly dangerous because of their relatively high volatilities. For this reason, Ni(CO)₄ (bp = 43°C) is exceedingly hazardous. On the other hand, solid carbonyl complexes such as Mo(CO)₆ do not present as serious a danger, but they should be handled in a hood. In this experiment, carbon monoxide gas is evolved. The volume of CO given off is relatively small, however, and if the reaction is carried out in a hood, the CO will not be present in sufficiently high concentrations to be dangerous.

The reaction will be conducted in the apparatus shown (right). First put 2.0 g (7.6 mmol) of Mo(CO)₆, and 10 mL (72 mmol) of mesitylene (bp = 165°C) in the 50-mL Schlenk flask. Assemble the apparatus in the hood, using a straight reflux condenser topped with stopcock adapter and mineral oil bubbler. The Mo(CO)₆ is volatile and will sublume into the condenser during the reaction. For this reason, it is desirable for the mesitylene vapors to rise high into the condenser to return any sublimed Mo(CO)₆ to the reaction flask. To allow the mesitylene to wash the Mo(CO)₆ into the flask, do not cool the condenser with water. The temperature of the room will provide adequate cooling.

The tendency of Mo(CO)₆ and the product to react with oxygen at high temperatures requires that the reaction be conducted in an inert atmosphere. Connect the Schlenk flask to a nitrogen cylinder using a
length of rubber tubing. Flush the apparatus with a moderate stream of nitrogen for approximately 5 min. Turn off the nitrogen and then close the stopcock. Heat the solution at a moderate boil for about 30 min with a heating mantle. Then remove the heating mantle and immediately turn on the nitrogen flow to prevent the mineral oil from being drawn back into the reaction mixture. The nitrogen flow also serves to sublime out of solution any remaining Mo(CO)\textsubscript{6}.

When the solution has cooled to room temperature, turn off the nitrogen flow and dismantle the apparatus. Add 15 mL of hexane to complete the precipitation. Suction filter the solution on a medium frit and rinse, with 5 mL of hexane, the yellow product that is contaminated with black metallic molybdenum. Purify the crude product by dissolving it in a minimum of CH\textsubscript{2}Cl\textsubscript{2} (~ 10 mL). After filtering the solution, add 25 mL of hexane to precipitate the product. Suction filter off the yellow (mesitylene)Mo(CO)\textsubscript{3}, wash twice with 4 mL of hexane, and allow the product to dry on the frit while under aspiration. A second batch of product can be obtained by reducing the volume of the mother liquor under water aspirator vacuum at room temperature. Calculate the percentage yield and obtain an IR spectrum. Since (mesitylene)Mo(CO)\textsubscript{3} will decompose over a period of weeks in the presence of light and air, it should be stored in a Schlenk tube, under nitrogen atmosphere, wrapped in aluminum foil.

Turn in your purified product, under nitrogen atmosphere, in a labeled Schlenk tube. Your lab report should include the yield of your product, a discussion, interpretation of the IR spectrum (C-O stretch, C-H stretch, aromatic vibrations). Include the following questions in your discussion:

- If the reaction of Mo(CO)\textsubscript{6} with mesitylene were conducted in the presence of air, what would probably be the decomposition products?
- How would you expect the C-O stretching frequencies in the compounds (C\textsubscript{6}H\textsubscript{6})Mo(CO)\textsubscript{3}, [1,3,5-C\textsubscript{6}H\textsubscript{3}(CH\textsubscript{3})\textsubscript{3}]Mo(CO)\textsubscript{3}, and [C\textsubscript{6}(CH\textsubscript{3})\textsubscript{6}]Mo(CO)\textsubscript{3} to vary and why?
- How would you determine in an afternoon’s experiment whether or not your isolated (mesitylene)Mo(CO)\textsubscript{3} was pure?
- If you wished to carry out the reverse reaction:
  \[
  \text{(mesitylene)Mo(CO)\textsubscript{3} + 3 CO} \rightarrow \text{Mo(CO)\textsubscript{6} + mesitylene}
  \]
  what reaction conditions (solvent, temperature, amounts of reactants, etc.) would you use? Would you expect the equilibrium constant for the reaction to be greater or less than 1?

Experiment 5
Optical Isomers of Co(en)$_3^{3+}$

Introduction
For decades it has been known that certain octahedral complexes of transition metals could be resolved into two enantiomers. Some of the earliest work in this area was done in 1912 by Alfred Werner on Co(en)$_3^{3+}$ (where en = H$_2$NCH$_2$CH$_2$NH$_2$). The enantiomers of Co(en)$_3^{3+}$ that he resolved are:

$$\begin{align*}
\text{D(+)Co(en)$_3^{3+}$} & & \text{L(-)Co(en)$_3^{3+}$} \\
\end{align*}$$

One of the enantiomers rotates plane polarized light toward the right (dextrorotatory) while the other isomer rotates the light by the same amount in the opposite (levorotatory) direction. These directions are designated (+) and (-) (or sometimes d and l), respectively.

As in any form of spectroscopy, the size of rotation depends not only on the nature of the optically active material, but also on the length, $l$, of the light path through the sample and the concentration, $c$, of the sample in a solvent. To standardize the units for expressing rotations, the specific rotation $[\alpha]$ has been defined as the rotation produced by a solution containing 1 g of solute per mL of solution and having a light path length of 1 dm.

$$[\alpha] = \frac{\alpha}{lc}$$

The wavelength, $\lambda$, of light is also specified. Using the sodium D line, the specific rotation is designated $[\alpha]_D$. In the equation above, $\alpha$ is given in degrees, $l$ in decimeters, and $c$ in grams per mL of solution.

The preparation, resolution, and characterization of the optical isomers of Co(en)$_3^{3+}$ are the objects of this experiment. A solution of Co(II) is oxidized by air in the presence of ethylenediamine, en, and activated charcoal. The activated charcoal catalyzes, by an unknown mechanism, the oxidation of the rapidly formed Co(II) complex, Co(en)$_3^{2+}$, to Co(en)$_3^{3+}$.

$$\text{CoSO}_4 + 3 \text{en} \rightarrow [\text{Co(en)}_3\text{SO}_4]$$

$$4 [\text{Co(en)}_3\text{SO}_4 + \text{O}_2 + 4 \text{HCl} \rightarrow 4[\text{Co(en)}_3\text{SO}_4\text{Cl} + 2 \text{H}_2\text{O}$$

The resulting $[\text{Co(en)}_3\text{SO}_4\text{Cl}$ is not isolated from solution but is immediately resolved by diastereomer formation with optically active d-tartrate, (+)-tart,

$$\begin{align*}
\text{CO}_2^- \\
\text{HO-} & \text{C-} \text{OH} \\
\end{align*}$$

With diastereomers having differing solubility properties, and with a proper choice of resolving agent it is possible to fractionally crystallize one diastereomer, leaving the other in solution. In this case, $[(+)[\text{Co(en)}_3][(+)-\text{tart}]\text{Cl}$ is the least soluble diastereomer and preferentially crystallizes from solution as the pentahydrate. The $[(+)[\text{Co(en)}_3][(+)-\text{tart}]\text{Cl}$ is converted to $[(+)[\text{Co(en)}_3]_3\text{H}_2\text{O}$ by reaction with I$^-$. The $[\alpha]_D$ of the product is +89$^\circ$. 
The other optical isomer, \([\text{(-)}\text{Co(en)}_3]_3\), is obtained by adding I\(^-\) to the solution from which \([\text{(+)}\text{Co(en)}_3]_3[\text{(+)}\text{-tart}]\text{Cl}_5\text{H}_2\text{O}\) was previously precipitated. The solid that precipitates with I\(^-\) is a mixture of crystals of the racemate, (+) and (-) \([\text{Co(en)}_3]_3\text{H}_2\text{O}\), and of crystals of pure \([\text{(-)}\text{Co(en)}_3]_3\text{H}_2\text{O}\). The \([\text{(-)}\text{Co(en)}_3]_3\text{H}_2\text{O}\) is much more soluble in warm water than the racemate and may be extracted into solution, which on cooling reprecipitates the desired enantiomer, \([\text{(-)}\text{Co(en)}_3]_3\text{H}_2\text{O}\), whose \([\alpha]_D\) = \(-89\)^o. The optical purities of the isolated (+) and (-) enantiomers are to be evaluated by measuring their specific rotations.

**Procedure**

**Preparation of the Resolving Agent, Barium d-Tartrate.** Prepare solutions of \(\text{BaCl}_2\) and of d-tartaric acid by dissolving 12.2 g (50 mmol) of \(\text{BaCl}_2\cdot 2\text{H}_2\text{O}\) in a minimum amount of water and 7.5 g (50 mmol) of d-tartaric acid in water. After heating these solutions to 90°C, mix them and add the base ethylenediamine until the solution is neutral. Allow the solution to cool to room temperature. Filter the precipitate and wash with warm water.

**Preparation and Resolution of \text{Co(en)}_3^3+.** Prepare in an Erlenmeyer flask, a solution containing 10.3 g (170 mmol, 11.5 mL) of ethylenediamine (en) in 25 mL of water. After cooling the solution in an ice bath, add 5 mL of concentrated (12 M) \(\text{HCl}\), 14 g (50 mmol) of \(\text{CoSO}_4\cdot 7\text{H}_2\text{O}\) dissolved in 25 mL of cold water, and 2 g of activated charcoal. Bubble a rapid stream of air through this solution for 4 hours. Then add dilute \(\text{HCl}\) or ethylenediamine, as required, to the solution until its pH is 7.0-7.5. Heat the mixture in a beaker on a hot plate for 15 min. Cool the solution to room temperature, filter off the charcoal, and wash with 10 mL of water.

To the \([\text{Co(en)}_3]_3^3+\) solution just prepared, add all of the barium d-tartrate prepared previously. After heating the mixture on a hot plate for 30 min with vigorous stirring, filter off the precipitated \(\text{BaSO}_4\) and wash with a small amount of hot water. Evaporate the solution on a hot plate to 50 mL, and allow the crystals of \([\text{(+)}\text{Co(en)}_3]_3[\text{(+)}\text{-tart}]\text{Cl}_5\text{H}_2\text{O}\) to precipitate overnight. Filter off the crystals and save the filtrate for later isolation of the (-) enantiomer. Wash the crystals with 40%/v/v ethanol-water solution, and recrystallize the product by dissolving it in 15 mL of hot water followed by cooling in ice. Wash the crystals with 40% ethanol-water and then with absolute ethanol. Air-dry and determine the yield of \([\text{(+)}\text{Co(en)}_3]_3[\text{(+)}\text{-tart}]\text{Cl}_5\text{H}_2\text{O}\).

To determine the specific rotation of this compound, dilute approximately 0.5 g of the sample to a solution volume of 10 mL. Introduce this solution into a 1 dm polarimeter tube, measure the sign and magnitude of the rotation, calculate \([\alpha]_D\) for \([\text{(+)}\text{Co(en)}_3]_3[\text{(+)}\text{-tart}]\text{Cl}_5\text{H}_2\text{O}\).

To convert the diastereomer to \([\text{(+)}\text{Co(en)}_3]_3^3+\) by dissolving the \([\text{(+)}\text{Co(en)}_3]_3[\text{(+)}\text{-tart}]\text{Cl}_5\text{H}_2\text{O}\) in 15 mL of hot water and add 0.25 mL of concentrated ammonia (15 M) solution. With stirring, add a solution of 17 g (113 mmol) of \(\text{NaI}\) dissolved in 7 mL of hot water. After cooling in an ice bath, suction filter and wash the crystals with an ice cold solution of 3 g of \(\text{NaI}\) in 10 mL of water to remove the tartrate. After washing with ethanol and finally with ethyl acetate, allow the \([\text{(+)}\text{Co(en)}_3]_3^3+\) to air dry and determine the yield. Measure its \([\alpha]_D\) using a solution of approximately 0.5 g of sample in 10 mL of water.

To isolate \([\text{(-)}\text{Co(en)}_3]_3\text{H}_2\text{O}\), add 0.25 mL of concentrated \(\text{NH}_3\) solution to the filtrate from which \([\text{(+)}\text{Co(en)}_3]_3[\text{(+)}\text{-tart}]\text{Cl}_5\text{H}_2\text{O}\) was precipitated (see above). Heat the solution to 80°C and add with stirring 17 g (113 mmol) of \(\text{NaI}\). Upon cooling in an ice bath, impure \([\text{(-)}\text{Co(en)}_3]_3\text{H}_2\text{O}\) precipitates and is filtered and washed with a solution of 3 g of \(\text{NaI}\) dissolved in water at 50°C. Filter off the undissolved racemate and add 5 g of \(\text{NaI}\) to the filtrate. Crystallization of \([\text{-Co(en)}_3]_3\text{H}_2\text{O}\) occurs on cooling. Filter the precipitate, wash with ethanol and then with ethyl acetate, and finally air dry. Determine the yield and evaluate \([\alpha]_D\). Turn in your samples of \([\text{(+)}\text{Co(en)}_3]_3\text{H}_2\text{O}\) and \([\text{(-)}\text{Co(en)}_3]_3\text{H}_2\text{O}\) in labeled sample vials. This experiment is worth 40 points; 20 points for the lab report and 10 points for each product. Include the following questions in your discussion:

- Why is it not possible to resolve \text{Co(en)}_3^2+?
- In the preparation of barium d-tartrate, what was the purpose of adding ethylenediamine?
- In the purification of both (+) and (-) \([\text{Co(en)}_3]_3\text{H}_2\text{O}\), the compounds were washed with water containing \(\text{NaI}\). What was the purpose of the \(\text{NaI}\)?