Synthesis and Characterization of Coordination Compounds[1]

Authors: D. Afzal, R. G. Baughman, H. D. Ervin, A. E. Moody, H. D. Wohlers, and J. M. McCormick*
Previous update: March 15, 2013 & January 11, 2017; June 4, 2017 & Dec 31,2020 updates by V. Pultz

Introduction

Coordination compounds (also known as complex ions or simply complexes) are formed by the reaction of a Lewis acid (an electron pair acceptor, usually a transition metal) with a Lewis base (an electron pair donor), which is known as a ligand. What is unique about coordination compounds is that they are formed from chemical species that have an independent existence and that this association is often readily reversible (i. e., there is an equilibrium between the solvated metal ion and the ligand). For example, $NiCl_2$ reacts with NH_3 in aqueous solution to form the compound $Ni(NH_3)_6Cl_2$ which contains the complex ion $[Ni(NH_3)_6]^{2+}$. This process is easily reversed (by the addition of H^+) to give back the starting materials. This type of behavior was thought to be very peculiar by chemists in the 1800's. They were familiar with compounds like CO_2, which although it could be made from C and O_2, does not act like it is some loose association of C and O_2. It wasn't until the ground-breaking work of Werner (for which he won the Nobel Prize in chemistry) in the late 19th and early 20th centuries that chemists began to understand these compounds. Werner's work was greatly expanded on in the 20th century especially after it was discovered that coordination chemistry was relevant to the understanding the role of metal ions in biological systems.

You could prepare a complex of Co^{3+} with ethylenediamine, $NH_2CH_2CH_2NH_2$ (abbreviated: en). You will prepare a complex of Fe^{3+} with the oxalate ion, $C_2O_4^{2-}$ (abbreviated: ox^{2-}). Ethylenediamine and oxalate are examples of bidentate ligands, which means that they have two different atoms that can donate electron pairs to a metal ion. Ethylenediamine does this through lone pairs on its nitrogen atoms, while oxalate donates electron pairs from two of its four oxygen atoms. In these complexes the metal ion is directly bonded to six other atoms in what is called an octahedral geometry (if we connected the six atoms, the resulting solid would be an octahedron, and hence the name of this geometry). There are a number of ways in which six atoms can be arranged around a central atom in an octahedral geometry, and each of these different arrangements may give rise to compounds with the same chemical formula, but have different arrangements of their atoms (*isomers*). For example, compounds in which the actual connections between atoms (bonds) are different are called *constitutional isomers*. In this exercise you will be synthesizing and studying compounds where the bonds are the same, but the atoms are arranged differently in space (*stereoisomers*). Compounds of this type are classified as either *enantiomers* (the two compounds are mirror images of each other) or *diastereomers* (the compounds are not mirror images).

Because en is a bidentate ligand, the dichlorobis(ethylenediamine)cobalt(III) complex, $[Co(en)_2Cl_2]^+$, that you could prepare exists as three isomers; one pair of enantiomers and their diastereomer. The isomer where the chlorides are situated on either side of the Co^{3+} (180° from each other) is called the *trans* isomer (Fig. 1), while the isomer where the chlorides are next to each other in the octahedron (90° from each other) is the *cis* isomer. In addition, there are two different ways in which we can put two Cl atoms *cis* to one another, and these are enantiomers

(Fig. 2). The tris(oxalato)ferrate(III) ion, $[Fe(ox)_3]^{3-}$, exists as two enantiomers (there is no diastereomer). In one the three oxalates form a right-handed propeller, and in the other they form a left-handed propeller (both are shown in Fig. 3).

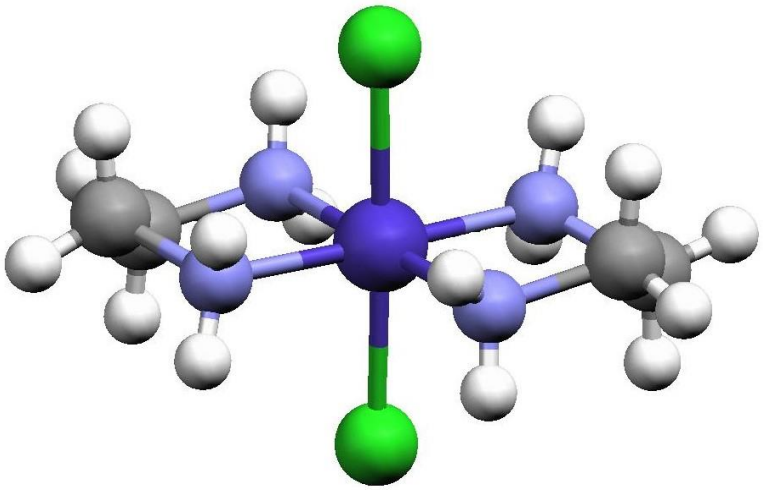

Figure 1. Structure of *trans*-$[Co(en)_2Cl_2]^+$ redrawn from the Cambridge Crystal Structure Database entry CENCOS using the Mercury molecular visualization software package.

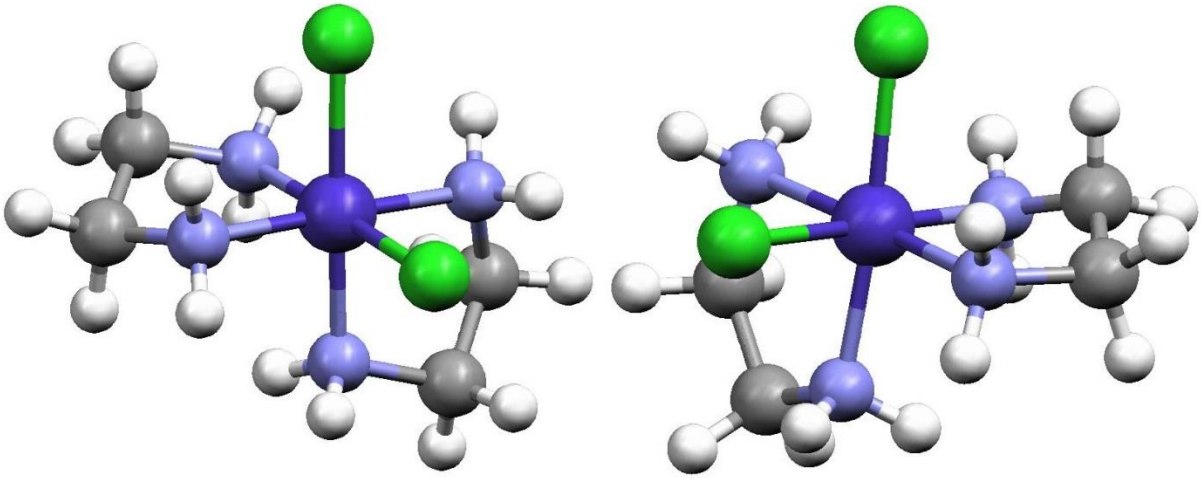

Figure 2. Structures of the two *cis*-$[Co(en)_2Cl_2]^+$ enantiomers redrawn from the Cambridge Crystal Structure Database entries CENCOC and CLECOC using the Mercury molecular visualization software package. The isomer on the left is designated as Λ (lambda) while the isomer on the right is designated as Δ (delta) and this is determined by the orientation of the two en ligands. When one en is placed horizontally at the back of the octahedron defined by the six atoms surrounding the Co, the other en cuts across the face of the octahedron either with a positive slope (Λ enantiomer) or a negative slope (Δ enantiomer).

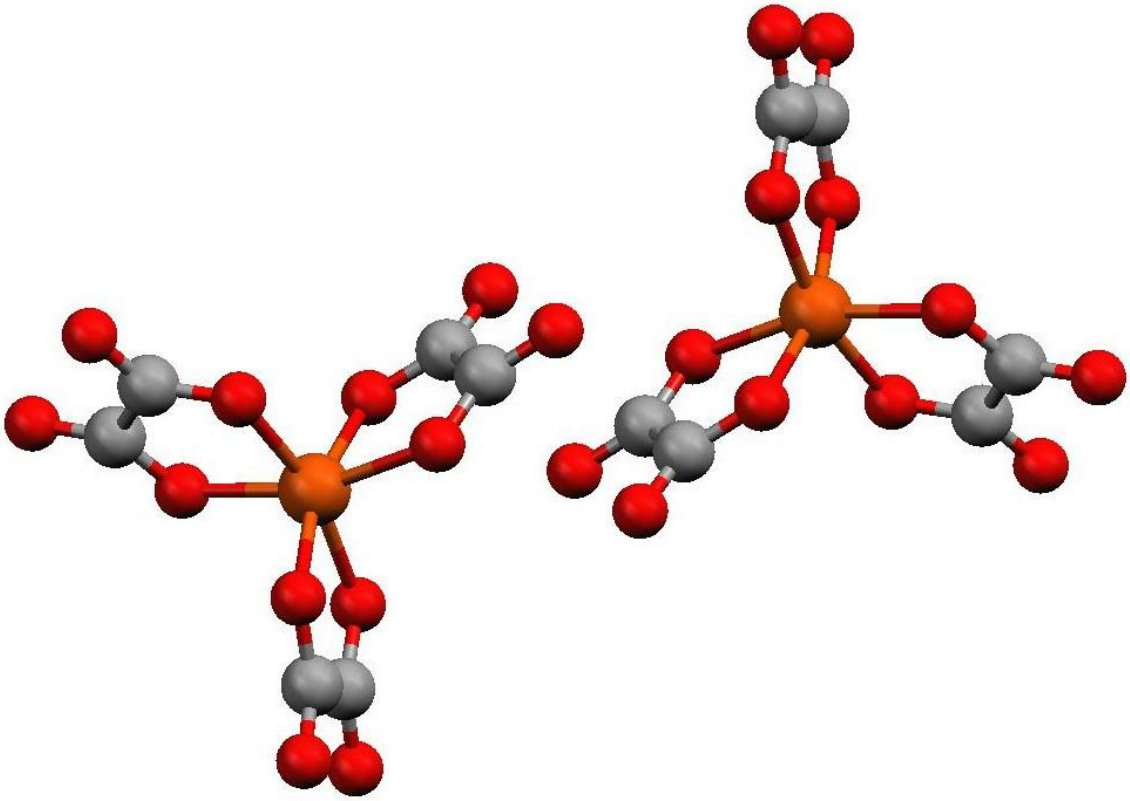

Figure 3. Structures of the $[Fe(ox)_3]^{3-}$ enantiomers redrawn using the Mercury molecular visualization software package from data collected by Professor Russell Baughman at Truman State University on crystals prepared by Truman students. The Λ enantiomer is the one on the left and the Δ enantiomer is the one on the right. Unlike the cobalt complex, where both enantiomers can be separated and isolated by crystallization, the enantiomers of the iron complex cannot be separated. This is because there is a rapid pathway available in solution to interconvert the enantiomers.

Another interesting property of the transition metals is that their reactivity depends on several factors including the metal ion's charge, the number and type of donor atoms, and the number of d electrons present on the metal ion. It is the later property which we will exploit in this exercise both in the synthesis and then in the reactions of the compounds. The Co^{2+} ion has a $3d^7$ electronic configuration and Fe^{3+} has a $3d^5$ electronic configuration. Metal ions with these electronic configurations rapidly exchange their ligands and are referred to as labile. The $3d^6$ Co^{3+} is an example of an inert ion, that is, an ion that does not rapidly exchange its ligands.

You could synthesize *trans*-$[Co(en)_2Cl_2]^+$ from $CoCl_2 \cdot 6H_2O$ according to the overall balanced chemical equation given in Scheme 1. In the mechanism by which this compound is formed Co^{2+} is initially chelated by one en and then a second en, with each step being described by an equilibrium constant. Once two, or more, en have become bound to the Co^{2+}, H_2O_2 (or, in some cases, O_2 from the air) is able to oxidize the metal center to Co^{3+}. Since further substitution of a Co^{3+} complex is slow, the reaction will essentially be over at that point. Thus by careful manipulation of the amount of en present and when the oxidant is introduced, we can force the

formation of a Co^{3+} complex with either two or three en bound to the metal. Because the Co^{3+} complexes are inert we could subsequently convert *trans*-$[Co(en)_2Cl_2]^+$ to *cis*-$[Co(en)_2Cl_2]^+$ and then separate (resolve) its enantiomers.

$CoCl_2 \cdot 6H_2O$ + 2 en + xs H_2O_2 + xs HCl $\rightarrow$ *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl$ + other products

Scheme 1. Synthetic route to *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl$ starting from $CoCl_2 \cdot 6H_2O$.

Both the *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ complex ions undergo hydrolysis in acidic aqueous solution, as shown in Scheme 2. This reaction can proceed through one of two mechanisms (both are shown in Scheme 3): a dissociative mechanism, where the Cl^- leaves the complex before the H_2O enters, or an associative mechanism, where the H_2O enters the complex before the Cl^- leaves.

$$[Co(en)_2Cl_2]^+ + H_2O \rightarrow [Co(en)_2(H_2O)Cl]^{2+} + Cl^-$$

Scheme 2. The hydrolysis reaction of either *cis*- or *trans*-$[Co(en)_2Cl_2]^+$ under acidic conditions. Note that, in general, starting with the *trans* isomer yields the corresponding *trans* isomer and starting with the *cis* isomer gives the corresponding *cis* isomer of the product.

Associative Mechanism

$[Co(en)_2Cl_2]^+ + H_2O \rightarrow [Co(en)_2(H_2O)Cl_2]^+$

$[Co(en)_2(H_2O)Cl_2]^+ \rightarrow [Co(en)_2(H_2O)Cl]^{2+} + Cl^-$

Dissociative Mechanism

$[Co(en)_2Cl_2]^+ \rightarrow [Co(en)_2Cl]^{2+} + Cl^-$

$[Co(en)_2Cl]^{2+} + H_2O \rightarrow [Co(en)_2(H_2O)Cl]^{2+}$

Scheme 3. Possible mechanisms for the acidic hydrolysis of *cis*- or *trans*-$[Co(en)_2Cl_2]^+$.

The problem is further complicated by the interconversion of the *cis*- and *trans*- isomers, as shown in Scheme 4. Luckily, this reaction is known to be much slower than the hydrolysis reaction to be studied, and as long as the reaction temperature is not taken much above 70°C for an extended period of time the *cis*-*trans* isomerization reaction need not be considered.

trans-$[Co(en)_2Cl_2]^+ \rightarrow$ *cis*-$[Co(en)_2Cl_2]^+$

Scheme 4. Reaction converting *trans*-$[Co(en)_2Cl_2]^+$ to *cis*-$[Co(en)_2Cl_2]^+$.

You will determine the activation energy of the first-order hydrolysis of *trans*-$[Co(en)_2Cl_2]^+$ under acidic conditions. You will be using a quenching method to study the reaction kinetics (compare to the direct measurement method that was used in the CHEM 130 *Kinetics of Crystal Violet Bleaching* experiment). With a quenching method a small portion of the reaction mixture is withdrawn at specific times and the reaction is then stopped by either adding reagent that stops the reaction (usually by rapidly reacting with one of the reactants) or by rapidly cooling or freezing the sample. For the reaction that we are studying, we will use the latter method to quench the reaction. Each lab group will be assigned different temperatures at which to study the reaction, and from the pooled data you prepare an Arrhenius plot and determine the reaction's activation energy.

The overall balanced chemical reaction for synthesis of the $[Fe(ox)_3]^{3-}$ is shown in Scheme 5. It is the sum of three steps, each corresponding to the stepwise reversible binding of ox^{2-} to Fe^{3+}. The metal remains in the labile 3+ oxidation state throughout the reaction, and so by adding a sufficient amount of ox^{2-}, we can force the reaction essentially completely to $[Fe(ox)_3]^{3-}$. Because the complex is labile, we cannot resolve the $[Fe(ox)_3]^{3-}$ enantiomers, but we can use the complex's lability to confirm the 3:1 ox:Fe^{3+} stoichiometry.

$FeCl_3 \cdot 6H_2O + 3\ K_2C_2O_4 \cdot H_2O \rightarrow K_3[Fe(ox)_3] \cdot 3H_2O$ + other products

Scheme 5. Synthesis of $K_3[Fe(ox)_3] \cdot 3H_2O$.

You will confirm the 3:1 oxalate:Fe stoichiometry in your complex in much the same way as Werner did. First you will acidify a solution of $[Fe(ox)_3]^{3-}$ which will force the sequential equilibria that formed the complex back to Fe^{3+} (aq) and $H_2C_2O_4$. The amount of Fe and oxalate present will then be determined by redox titration against a standard $KMnO_4$ solution.

Experimental

Read each week's procedure carefully and plan what you will do before coming to the laboratory. Each week of this three-week exercise presents different challenges, and unprepared students will find it difficult to finish in the allotted time.

Synthesis Week
Check out the following items from the stockroom: Büchner funnel and filter flask.

Synthesis of *trans*-Dichlorobis(ethylenediamine)cobalt(III) Chloride Hydrochloride[2,3]

You will use sample already synthesized for you. If you are curious about the synthesis, see http://vpultz.sites.truman.edu/files/2017/06/Synthesis-and-Characterization-of-Coordination-Compounds2017Jun4.pdf or https://chemlab.truman.edu/files/2017/08/CHEM-131-Laboratory-Manual.pdf

Synthesis of Potassium Tris(oxalato)ferrate(III) trihydrate[4,5]

In your clean, dry 8-inch test tube dissolve 1.6 g $FeCl_3 \cdot 6H_2O$ (measured precisely) in 4 mL of distilled water. Gently heat the solution in a hot water bath on a hot plate to speed the dissolution of larger chunks of the ferric chloride.

Precisely and accurately weigh out between 6.0 and 6.5 g $K_2C_2O_4 \cdot H_2O$ and place it in a clean, dry 50-mL beaker. Add 10 mL of distilled water and gently heat on a hot plate with stirring until all of the potassium oxalate has dissolved. It is not necessary to boil the solution.

Once the oxalate salt has dissolved, quickly and carefully pour the hot oxalate-containing solution into the test tube containing the iron solution. Swirl to mix. Allow the reaction mixture to cool slowly to room temperature. Once the test tube is cool to the touch, transfer it to an ice bath and continue cooling.

Green crystals of the product may form during the initial cooling to room temperature, but they might not form until the ice cooling step. If crystals do not form after 30 min of cooling, try gently scratching the bottom of the test tube with a stirring rod or add a seed crystal (a crystal of the product obtained from another preparation), which your instructor will provide.

Decant the solution above the crystals and discard. Recrystallize the crude product by adding approximately 5 to 8 mL of hot distilled water to the crystals in the test tube, heat gently, and shake gently to affect total dissolution. Decant the green solution containing the product into a clean, dry beaker and discard any residue that remains in the test tube.

Cover the beaker with a watch glass and set it aside to cool slowly. When the beaker is cool to the touch, transfer it to an ice bath and continue to cool. Green crystals should form within about 20 min. If they do not, consult your instructor for assistance.

While waiting, set up the vacuum filtration apparatus. Place a piece of filter paper in the Büchner funnel to collect your crystals. Wet the filter paper with a couple drops of distilled water. With the aspirator on, transfer the contents of your beaker into the Büchner funnel. Use a spatula or glass stirring rod as necessary. Add about 2 mL of ice-cold distilled water to your beaker, swirl and pour this into the Büchner funnel. Repeat with another 2 mL of ice-cold distilled water. This will help remove all of your contents from the beaker. Wash the crystals twice with two 3-mL portions of acetone. **CAUTION!** Acetone is flammable, so do all these manipulations in the hood. Dry the product on the filter and then transfer it to a watch glass or weigh boat. Cover with a paper towel and place it in your drawer to dry.

Titration Week

Use the method of half-reactions to balance the redox reaction that you will use in this analysis **before** coming to the lab.

$MnO_4^- + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$ (acid aqueous solution)

The optimal amount of titrant is around 20 mL, allowing two trials when the buret is filled. In this experiment the titrant has an approximate molarity of 0.01 M MnO_4^- and you use very pure $K_2C_2O_4 \bullet H_2O$ to determine the molarity more precisely. Based on the optimal amount of titrant and its approximate molarity, how much pure $K_2C_2O_4 \bullet H_2O$ should be your target mass? Show all work.

Prepare titration tables using
http://vpultz.sites.truman.edu/files/2014/06/Hydrolysis-of-Oil-of-Wintergreen_titration-tables.pdf
as a model, but make appropriate changes.

Before beginning any work this week obtain the mass of the dry potassium tris(oxalato)ferrate(III) trihydrate.

Standardization of 0.01 M Potassium Permanganate Solution

Obtain approximately 75 mL of un-standardized 0.01 M $KMnO_4$ solution. **CAUTION!** Potassium permanganate is a strong oxidizing agent! Immediately wash any spilled on your skin with copious amounts of water.

Wash your buret several times, as your instructor will demonstrate, with no more than 2 mL of the permanganate solution. Each time allow the solution to drain through the buret's tip into a waste beaker. After the final wash fill the buret to near the 0.00-mL mark such that the upper part of the meniscus is at or below the 0.00-mL mark. Make sure that there are no bubbles in the buret tip. Run some of the solution through to clear any bubbles (gentle taping might help dislodge any recalcitrant bubbles). Refill the buret, if necessary. Record the initial volume of solution in the buret. Because the MnO_4^- ion is so strongly colored, make all your volume readings from the top of the meniscus, and your instructor may allow you to record to the nearest 0.1 mL.

Accurately weigh out the approximate mass of $K_2C_2O_4 \cdot H_2O$ that you calculated you will need to standardize the MnO_4^- solution (helpful hint: it should be around 0.1 g) and record the actual mass. Place the oxalate in an Erlenmeyer flask and add about 30 mL of distilled water and 5 mL of 6 M H_2SO_4. Swirl the flask gently to dissolve the solid.

Place the flask on a stirring hotplate in the hood and carefully heat the solution to approximately 60 °C. Do **not** boil! Remove the flask from the hotplate (a folded paper towel makes an excellent hot pad). This titration must be performed fairly quickly so that the solution does not cool too much. Be sure that you swirl the flask as you add the permanganate solution and wash down any solution that splashes on the side of the flask with a small stream of distilled water. If the solution cools too much, reheat. Titrate the sample with the permanganate solution until the slightest purple color persists for at least 30 sec. Record the final buret reading. Calculate the volume of permanganate used and from it determine the $[MnO_4^-]$. Repeat until three determinations agree with each other within 2%.

Determination of Oxalate in Potassium Tris(oxalato)ferrate(III) Trihydrate
Accurately weigh out about 0.1 g of your $K_3[Fe(ox)_3]\cdot 3H_2O$ and record the mass to the nearest 0.001 g. Put in an Erlenmeyer flask. Add 30 mL distilled water and 5 mL of 6 M H_2SO_4. Swirl to dissolve the solid and then heat to 60 °C, again taking care not to boil the solution. Titrate as described above to the first permanent purple color. Record the buret readings, calculate the volume of titrant dispensed, and determine the % $C_2O_4^{2-}$ by mass in the sample.

Determination of Iron in Potassium Tris(oxalato)ferrate(III) Trihydrate
Before social distancing guidelines were necessary, we took each trial from the oxalate analysis and analyzed for iron. But you will not do the titration to determine the amount of iron. If you are curious, see the previous version of this experiment which also had you synthesize the cobalt compound. Part of the procedure involved addition of Zn and heating in a hood until the yellow color (from Fe^{3+}) disappears (Fe^{2+} is colorless in solution). The filtration had to be done quickly to minimize the amount of Fe^{2+} that is re-oxidized to Fe^{3+} by O_2 in the air.

Kinetics Week
Determination of the Activation Energy for Hydrolysis of *trans*-Dichlorobis(ethylenediamine)cobalt(III) Chloride[6,7]

You will work in pairs at a table, but maintain social distancing as much as possible. You will use a Vernier spectrometer connected to the USB port of your laptop computer which is running LoggerPro to monitor the progress of the reaction. Operation is similar to what is described at http://chemlab.truman.edu/instrumentation/oos/ooinstructions/ and you should quickly see the colorful display shown in Figure 2. You will make simple absorbance measurements.

At some point before beginning your kinetics runs you must calibrate the spectrometer using a cuvette filled with distilled water. **Important!** Use the same cuvette for both the blank and for the actual measurements. Before inserting the cuvette into the spectrometer thoroughly wipe the cuvette's windows with a KimWipe. Any bubbles adhering to the cuvette's windows may be dislodged by **gently** tapping the cuvette with your finger. Do **NOT** tap the cuvette on the table! Be sure that the cuvette's clear windows are aligned perpendicular to the spectrometer's long side when you insert it into the spectrometer. (The spectrometers may have a triangle by one side of the square hole where you insert the cuvette, and a triangle on the cuvette should be on that side.) Insert the cuvette into the spectrometer as reproducibly as possible each time. Light in the spectrometer must go through the clear sides of the cuvette.

Be sure that your large test tube and all of your small test tubes are clean. You will run the reaction in the large test tube and use nine small test tubes to store the aliquots removed from the reaction mixture. Place 3 mL of distilled water in each of the small test tubes and mark the water level; discard the water and dry the test tubes.

Each bench will be assigned two temperatures at which to run the reaction; the pairings are usually 40/65 °C, 45/60 °C and 50/55 °C with two benches in each lab section running the same temperature pairing. Water baths set for each of these temperatures will be on your benches. Do **NOT** change the settings on any bath! Use the thermometer to find the actual

bath temperature to the nearest 0.1 °C; record the value. **Note:** it is not critical that you are exactly at your assigned temperature; the temperature reading should be stable and you must record the actual temperature at which the data were collected. Heat water in your own beaker to make the 70 °C water bath.

Place 30 mL of 0.01 M HNO_3 in your large test tube and place it in the water bath. Place 1 mL of cold distilled water in a small plastic centrifuge tube (volumes are marked on the side). Keep the centrifuge tube cold in an ice bath until ready for use.

For each of your assigned temperatures, estimate how often to take samples. The timing between samples will vary with temperature. At 40 °C you must follow the reaction for at least 40 minutes, but at 65 °C you will only need to follow the reaction for 5 minutes. The first removal of reaction mixture is at $t = 0$, but your ninth removal is at 40 min for 40 °C and at 5 min for 65 °C. In both cases **about 3 mL of solution must remain after the ninth removal so that the last amount of solution can be put in the 70-°C water bath and the absorbance at "time = infinity" can be measured**. To estimate how long you should follow the reaction at 45 °C you might take the following approach. When you increase the temperature from 40 to 65 °C (a temperature difference of 25 °C), you decrease the total observation time from 40 min to 5 min (a time difference of 35 min). If you assume a linear relationship, for every 25 °C increase in temperature, you can decrease the total observation time by 35 min, or for every 5 °C increase in temperature, you can decrease the total observation time by 7 min. So a 5 °C increase in temperature from 40 °C might lead to a 7 min decrease from 40 min. You would follow the reaction for 33 minutes, and withdraw 8 samples after time = 0, so the average time between sample withdrawals would be 33/8 min, but this spacing of time between withdrawals is just a guideline. It would be perfectly acceptable to withdraw samples at the following times measured in minutes: 0, 4, 8, 12, 16.5, 20.6, 24.75, 29, 33 where accuracy of the time measurement is crucial, but the time spacing between withdrawals is much less important. If it takes your group 15 seconds to withdraw the first sample, then record the time as 0.25 min instead of 0 min.

To perform a kinetics run, precisely weigh out approximately 0.2 g of *trans*-$[Co(en)_2Cl_2]Cl{\cdot}HCl$. Place this in the small centrifuge tube containing the cold water, close the tube and shake vigorously to dissolve the solid. Pour the entire contents of the centrifuge tube into your large test tube and mix thoroughly. Do this as quickly as possible; it is best if this can be accomplished without removing the large test tube from the water bath. Start timing from when the solution is completely mixed. Recording to the nearest second is especially critical at higher temperatures where the reaction proceeds faster and you follow it for a shorter time.

Remove 3 mL of the reaction mixture immediately upon mixing. Place it in one of your small test tubes and place the tube in the ice bath. Obtain the absorbance spectrum of this sample after it has cooled back to about room temperature and you have time. Record the absorbance at 505 nm and at 800 nm (this is your data point at $t = 0$). Don't forget to thoroughly wipe the cuvette's windows with a KimWipe before you place it in the spectrometer. Any bubbles adhering to the cuvette's windows may be dislodged by **gently** tapping the cuvette with your finger. Do **NOT** tap the cuvette on the table! If an absorbance measurement at 800 nm is not approximately zero, about 0.020 or smaller, re-wipe the cuvette's windows and try the measurement again.

Repeat this process until you have removed a total of nine samples, but make sure ~3 mL remains for the 70-°C water bath. **You must know precisely how long each sample was in the water bath after complete mixing until it was placed in a small test tube which was immediately put in an ice bath.** You will use times and absorbances for a kinetics graph.

Once you have removed nine samples, place the test tube containing the remaining 3 mL of the reaction mixture in the 70-°C water bath for no more than five minutes. Remove the test tube from the bath and place it in the ice bath. Once it has cooled to near room temperature, obtain the reaction mixture's absorbance spectrum, and record the absorbance at 505 nm and 800 nm; this is your $t = \infty$ data point.

Save all ten absorbance spectra for at least one run at each temperature and copy into Excel to make beautiful graphs.

Prepare a fresh sample and obtain data at the other assigned temperature. Repeat the measurements at the two temperatures as time permits.

All cobalt-containing waste is to be placed in the proper container. Any unused cobalt complex will be saved for later use. Please put it in the container provided, as directed by your instructor.

Results and Analysis

Synthesis Week

Show your calculations for the theoretical yield of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$. Assume that $FeCl_3\cdot 6H_2O$ is the limiting reagent. After you have determined the mass of your dry $K_3[Fe(ox)_3]\cdot 3H_2O$, calculate a percent yield. Show all work.

Titration Week

Show all raw data and calculated values in titration tables. Include sample calculations for trial 1 in each of the tables. Start with standardization of permanganate. Calculate the average percent oxalate by mass in your $K_3[Fe(ox)_3]\cdot 3H_2O$ and share this with the class. From the class data calculate the average percent oxalate by mass in $K_3[Fe(ox)_3]\cdot 3H_2O$, the standard deviation and the confidence interval at the 95% confidence limit. Be sure to perform a Q-test on the class data first to exclude any suspect point. Calculate the true percent oxalate by mass and determine a percent error for both your data and the class data.

Kinetics Week

Prepare a graph in Excel showing absorbance (on the *y*-axis) as a function of wavelength in which you overlaid all of the spectra for one run at each temperature. If the data were obtained correctly, the spectra should all have an absorbance of about 0 at 800 nm and there should be two *isosbestic* points (points where the absorbance does not change as a function of time, indicating that only two species were contributing to the absorbance throughout the reaction).

Your Excel workbook for each group (one lab table in most cases) must contain sheets with the wavelengths in column A and the 10 sets of absorbance values in the next 10 columns. You must have at least one sheet for each of your two temperatures. You must also have at least one graph of absorbance

versus wavelength (*Scatter with only markers* in Excel) for each of your two assigned temperatures where you plot all 10 spectra. (The greatest change in absorbance should be close to 515 nm.) Make the chart a new sheet by clicking *Move chart location* to *New Sheet*. Change the legend from Series1, etc. to give the actual time in seconds or minutes when the sample was removed from the large test tube (right-click on the chart, left-click Select Data, click on the series to be renamed, click Edit, and proceed). Fix the maximum absorbance value to around 1.1 or higher if needed to show the maximum absorbance at 505 nm for the infinite time absorbance spectrum; this absorbance depends on the concentration of the cobalt compound. The minimum absorbance must be zero. The *x*-axis scale should go from 400 to 800 nm. In the title for each graph give the temperature for the kinetics run. Label axes, and the wavelength axis must also include units. Remove the horizontal grid lines.

From the absorbance at 505 nm at each time subtract the absorbance at 800 nm at the same time; this corrects for any baseline drift or other variations that occurred between samples. With the corrected absorbance readings at 505 nm (A_t) and your corrected absorbance at infinite time (A_∞), prepare a first-order integrated rate law graph (i. e., $\ln(A_\infty - A_t)$ as a function of time) for each run. We use $A_\infty - A_t$ instead of concentration in these graphs because 1) we are following the formation of the product over time and 2) the reactant has a relatively large absorbance at this wavelength. A suggestion on how to implement these instructions is in the next paragraph.

In another sheet in your Excel workbook record the temperature for a kinetics run and make column headings of Time (s), Absorbance at 505 nm, Absorbance at 800 nm, Corrected Absorbance at 505 nm, A_∞-A_t, and $\ln(A_\infty$-$A_t)$. (If your times are in minutes, record them starting in cell A4 and in cell B4 insert a formula to convert to seconds. It is essential that all data in the class be manipulated with the same time units.) If the temperature is in cell A1 and the column headings are in cells B3 through G3, with times in cells B4 through B12 and absorbance readings in cells C4 through D13, then cell E4 would contain the formula **=C4-D4**, cell F4 would contain the formula **=E$13-E4**, and cell G4 would contain the formula **=LN(F4)**. Copy these formulas down their columns. Cell B13 could contain the symbol ∞ or indicate 70ºC. Select cells B4 through B12, press and hold the Ctrl key, and then use your mouse to select cells G4 through G12. Insert a chart with time on the x-axis and $\ln(A_\infty$-$A_t)$ on the y-axis, and make it a new sheet. Label axes, including units of time which are in seconds, and include a title such as "Determination of Rate Constant at 55.5 ºC." Remove horizontal grid lines and legend. Insert a Trendline and as options check "Display Equation on chart" and "Display R-squared value on chart." The magnitude of the slope is your value of the rate constant at that temperature. Move down on the sheet with your time and absorbances and manipulations and repeat, perhaps recording the new temperature in cell A16. Manipulate all kinetic runs on this sheet.

It would be easiest if you rename the default sheet tabs in Excel to something like "50_degree_data" and "50_Abs-vs-Wavelength" and "50_ln-vs-time" and "Kinetics_data." Use your actual temperature instead of "50." If you did two kinetics runs, then your Excel workbook should have 7 sheets, and if you did three kinetics runs, then your Excel workbook should have 10 sheets.

From each graph determine the value of the rate constant at that temperature. Report each rate constant (along with its uncertainty at 95% confidence) and the temperature at which it was obtained to the instructor and the rest of the class. Use the class data of rate constants and associated temperatures to prepare an Arrhenius plot, similar to what is shown in Figure 14-12 of Petrucci et al., 10th ed. The equation you are using is the one after (14.21) on page 626. Determine the value of the activation energy, including units. Do the data manipulations in Excel and print this sheet. Use labels to identify data and how it is manipulated. Put your name in cell A1 or enter

your name as a header. Show all work. Print a full-page graph, label axes, print a title with your name, and add a trendline with the equation and R^2 displayed on the chart.

Does the fact that the hydrolysis reaction is first-order in the cobalt complex and your value of the activation energy allow you to conclusively rule out one of the possible mechanisms? You will need to derive the rate law predicted by each mechanism for each of the possible cases: 1) the first step is irreversible and rate determining, 2) the first step rapidly goes to equilibrium and the second step is slow, 3) the first step is reversible, but does not come to equilibrium and the second step is slow. What additional experiments could you do to help distinguish between the possible mechanisms?

Conclusions

This exercise contains elements of both a synthesis exercise and a measurement exercise

Summary of Results

In your *Summary of Results* you should have tables that summarize the results for each week:
Synthesis Week, the percent yield of $K_3[Fe(ox)_3]\cdot 3H_2O$;
Titration Week, the statistical (average, standard deviation and confidence interval) results for the $K_3[Fe(ox)_3]\cdot 3H_2O$ analyses; and
Kinetics Week, the average rate constants at each temperature that you determined and the activation energy that was determined from the class data (along with a 95% confidence interval for each, if possible).

References

1. http://chemlab.truman.edu/chemical-principles/

2. Szafran, Z.; Pike, R. M. and Singh, M. M. *Microscale Inorganic Chemistry: a Comprehensive Laboratory Experience*; John Wiley and Sons: New York, 1991.

3. Bailar, J. C., Jr. *Inorg. Synth.* **1946**, *2*, 222-225.

4. Beran, J. A. *Laboratory Manual for Principles of General Chemistry, 5th Ed.*; John Wiley and Sons: New York, 1994.

5. Marcus, S.; Sienko, M. J. and Plane, R. A. *Experimental General Chemistry*; McGraw-Hill: New York, 1988.

6. Jolly, W. L. *Encounters in Experimental Chemistry, 2nd Ed.*; Harcourt, Brace, Jovanovich: New York, 1985, 77-79.

7. Herrick, R. S.; Mills, K. V. and Nestor, L. P. *J. Chem. Educ.* **2008**, *85*, 1120-1122. Click here to view a PDF version of this article (Truman addresses and *J. Chem. Educ.* subscribers only).