Synthesis and Analysis of a Coordination Compound
AP Chemistry Laboratory #15

Introduction

Coordination compounds are interesting substances, usually highly colored and containing a complex ion in their structures. In this lab, green crystals of the coordination compound potassium trioxalatoferrate(III) trihydrate are synthesized. These crystals are then analyzed to determine their identity and the percent yield of the experiment.

Concepts

- Coordination compound
- Lewis acids and bases
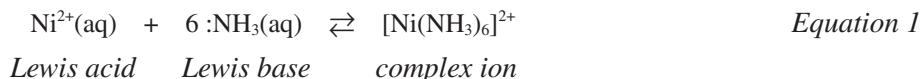- Complex ions
- Ligands
- Coordination number

Background

Coordination compounds are compounds that contain a metal atom or ion bonded to a group of molecules or ions. While these compounds may be neutral molecules, most are ionic compounds consisting of a *complex ion* (a metal ion with its attached molecules or ions) and a counter ion or ions to balance the charge. The molecules or ions attached to the central metal atom are called *ligands*.

$FeCl_2 \cdot 6H_2O$ is a typical coordination compound. The formula as written reflects the compound makeup, but not its structure. When writing the formula for coordination compounds, brackets are put around the metal and its ligands, indicating the actual structure and bonds in the compound. For $FeCl_2 \cdot 6H_2O$ the formula becomes $[Fe(H_2O)_6]Cl_2$.

The number of ligands atoms bonded to the metal ion is called the *coordination number* of the metal ion. This value is usually, but not always, 2, 4, or 6 and depends on the particular metal ion.

Ligands have lone pairs of electrons that can be used to form a bond with the metal ion. The ligand acts as a *Lewis base* and the metal ion acts as a *Lewis acid*.

$$Ni^{2+}(aq) \quad + \quad 6 :NH_3(aq) \quad \rightleftarrows \quad [Ni(NH_3)_6]^{2+} \qquad \qquad \textit{Equation 1}$$

$$\textit{Lewis acid} \qquad \textit{Lewis base} \qquad \textit{complex ion}$$

The bonding in coordination compounds involves the overlap of the metal d-orbitals and the ligand lone pair orbitals. If two atoms in a ligand donate lone pair electrons to form separate single bonds with the metal ion, the ligand is said to be a bidentate ligand. As many as six atoms in an individual ligand can be bonded with the metal ion.
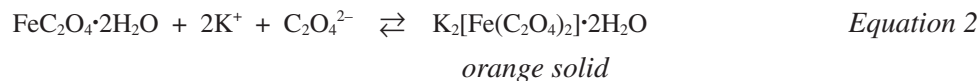
In Part 1, ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, is reacted with oxalic acid to form an intermediate compound, iron(II) oxalate dihydrate, $FeC_2O_4 \cdot 2H_2O$. This compound is isolated and

then converted in Part 2 to potassium trioxalatoferrate(III) trihydrate, $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$, by oxidation with hydrogen peroxide in the presence of potassium oxalate and oxalic acid.
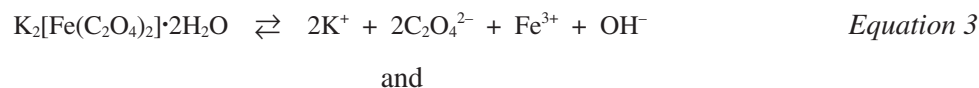
In Part 1, the reaction to form the intermediate compound is:

$$Fe^{2+} + C_2O_4^{2-} + 2H_2O \rightleftarrows FeC_2O_4 \cdot 2H_2O(s) \qquad\qquad \textit{Equation 1}$$
$$\textit{iron(II) oxalate dihydrate}$$
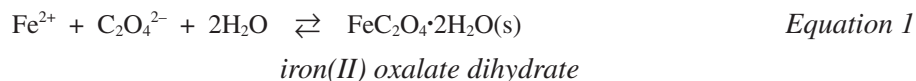
In Part 2, the iron(II) oxalate dihydrate is first reacted with potassium oxalate, forming an orange complex of iron(II) and oxalates.

$$FeC_2O_4 \cdot 2H_2O + 2K^+ + C_2O_4^{2-} \rightleftarrows K_2[Fe(C_2O_4)_2] \cdot 2H_2O \qquad\qquad \textit{Equation 2}$$
$$\textit{orange solid}$$

It is this iron(II) compound that is oxidized by the hydrogen peroxide. Initially, the $K_2[Fe(C_2O_4)_2] \cdot 2H_2O$ is oxidized to iron(III) hydroxide, $Fe(OH)_3$, a brown precipitate.

$$K_2[Fe(C_2O_4)_2] \cdot 2H_2O \rightleftarrows 2K^+ + 2C_2O_4^{2-} + Fe^{3+} + OH^- \qquad\qquad \textit{Equation 3}$$
$$\text{and}$$
$$Fe^{3+} + 3OH^- \rightleftarrows Fe(OH)_3(s) \qquad\qquad \textit{Equation 4}$$
$$\textit{brown solid}$$

When more oxalic acid is added, the iron(III) hydroxide dissolves. The iron(III) ion in solution forms a complex ion with the oxalate ligands, yielding a clear green solution of the complex ion, $Fe(C_2O_4)_3^{3-}$.

$$3H^+ + Fe(OH)_3(s) \rightleftarrows Fe^{3+} + 3H_2O \qquad\qquad \textit{Equation 5}$$
$$Fe^{3+} + 3C_2O_4^{2-} \rightleftarrows Fe(C_2O_4)_3^{3-} \qquad\qquad \textit{Equation 6}$$

The potassium salt of this ion is soluble in water, but only slightly soluble in ethanol. The addition of ethanol forces the precipitation of the product salt.

$$3K^+ + Fe(C_2O_4)_3^{3-} + 3H_2O \rightleftarrows K_3[Fe(C_2O_4)_3] \cdot 3H_2O(s)$$

Experiment Overview

The purpose of this experiment is to synthesize the coordination compound potassium trioxalatoferrate(III) trihydrate, $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$. Once produced, the product will be identified by colorimetric methods and the percent yield of the product will be determined. Many coordination compounds absorb visible light. The absorbance of a solution of the synthesized product will be taken at three wavelengths. The ratios of these absorbances will then be used to identify the product as $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$.

Pre-Lab Questions

1. Define the terms *Lewis acid* and *Lewis base*.

2. Define the terms *ligand* and *coordination number*.

3. What are the oxidation numbers of the metal atoms in each of the following coordination compounds?

   a. $[Ni(NH_3)_6](NO_3)_2$

   b. $K_3[Co(CN)_6]$

   c. $[Pt(NH_3)_3Br]Cl$

4. For each of the following ligands, draw the Lewis structures and indicate the atom that donates an electron pair for complex ion formation.

   a. NH_3

   b. CN^-

   c. $C_2O_4^{2-}$

5. What is the coordination number of the metal in each of the following compounds?

   a. $[FeCO(CN)_5](NO_3)_3$

   b. $[Ag(CN)_2]Cl$

   c. $[Cr(H_2O)_2Cl_2]Br$

6. Suppose a student synthesizes potassium trioxalatoferrate(III) trihydrate, $K_3[FeC_2O_4)_3]\cdot3H_2O$, by starting with 11.356 g of ferrous ammonium sulfate, $Fe(NH_4)_2SO_4\cdot6H_2O$.

   a. What is the theoretical yield, in grams, for $K_3[FeC_2O_4)_3]\cdot3H_2O$?

   b. If 9.376 g of $K_3[FeC_2O_4)_3]\cdot3H_2O$ were actually synthesized, what is the percent yield?

Materials

Part 1

Ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2\cdot6H_2O$, 10 g	Heat-resistant gloves
Sulfuric acid solution, H_2SO_4, 2 M, 1 mL	Hot plate
Oxalic acid solution, $H_2C_2O_4$, 10%, 65 mL	Stirring rod
Distilled or deionized water	Thermometer, 0–100 °C
Beral-type pipet	Beaker, 150-mL
Graduated cylinder, 50-mL	Beaker, 400-mL
Ceramic fiber square	Erlenmeyer flask, 250-mL

Part 2

Oxalic acid solution, $H_2C_2O_4$, 10%, 65 mL	Graduated cylinder, 50-mL
Hydrogen peroxide solution, H_2O_2, 6%, 17 mL	Graduated cylinder, 10-mL
Potassium oxalate solution, $K_2C_2O_4$, 25%, 18 mL	Ceramic fiber square
Ethyl alcohol, CH_3CH_2OH, 95%, 20 mL	Hot plate
Ethyl alcohol, CH_3CH_2OH, 50%, 20 mL	Heat-resistant gloves
Acetone, CH_3COCH_3, 20 mL	Stirring rod
Distilled or deionized water	Thermometer, 0–100 °C
Beral-type pipets, 2	Beaker, 150-mL
Büchner funnel and adapter	Beaker, 50-mL, 2
Filter flask, 250-mL	Erlenmeyer flask, 250-mL
Wash bottle	Aspirator trap assembly
Watch glass	Filter funnel
Vacuum tubing, 2 pieces	Filter paper, quantitative
Balance, 0.001-g precision	

Part 3

Distilled or deionized water	Spectrophotometer and cuvet
Wash bottle	Tissues or lens paper, lint-free
Graduated cylinder, 100-mL	Balance, 0.001-g precision
Beaker, 250-mL	

Safety Precautions

The sulfuric acid solution is corrosive to eyes, skin, and other tissue. Always add acid to water, never the reverse. The oxalic acid solution is a skin and eye irritant and moderately toxic by ingestion. The 6% hydrogen peroxide solution is an oxidizer and a skin and eye irritant. The 95% ethyl alcohol solution and the acetone are both flammable and dangerous fire risks. Keep both away from open flames and other sources of ignition. The addition of denaturates makes the 95% ethyl alcohol solution and the 50% ethyl alcohol solution poisonous; they cannot be made non-poisonous. The acetone is slightly toxic by ingestion and inhalation. Wear chemical splash goggles, chemical-resistant gloves and a chemical-resistant apron. Wash hands thoroughly with soap and water before leaving the laboratory.

Procedure

Part 1. Preparation of Iron(II) Oxalate Intermediate

1. On an analytical balance, accurately mass between 10.0 and 10.5 g of ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. Record the exact mass in the Data Table.

2. Obtain 30 mL of deionized water in a clean 50-mL graduated cylinder and transfer the deionized water to a clean 150-mL beaker.

3. Add the 10 g of ferrous ammonium sulfate to the 150-mL beaker and stir to dissolve.

4. Using a Beral-type pipet, transfer 6 drops (1 mL) of 2 M H_2SO_4 to the solution of ferrous ammonium sulfate. Stir to mix.

5. Obtain 50 mL of the 10% oxalic acid solution in a clean 50-mL graduated cylinder. Add this solution slowly, while stirring, to the 150-mL beaker. Yellow iron(II) oxalate now precipitates.

6. Place the 150-mL beaker on a hot plate and carefully heat the mixture to boiling. Be sure to continuously stir the contents to prevent bumping.

7. Turn off the hot plate. Carefully remove the 150-mL beaker using heat-resistant gloves and place the beaker on a ceramic fiber square to cool.

8. Continue stirring the beaker contents as they cool to prevent "bumping."

9. Obtain a 400-mL beaker and decant the supernatant liquid in the 150-mL beaker into the 400-mL beaker. The supernatant liquid is the liquid above the precipitate.

10. Add approximately 100 mL of deionized water to a clean 250-mL Erlenmeyer flask. Place the Erlenmeyer flask on the hot plate and heat water to approximately 40 °C.

11. Wash the yellow precipitate remaining in the 150-mL beaker with 3 successive portions of approximately 30 mL of hot deionized water. Decant the liquid into the 400-mL beaker between each washing.

Part 2. Synthesis of K₃[Fe(C₂O₄)₃]·3H₂0

1. Obtain 18 mL of the 25% potassium oxalate solution in a clean 50-mL graduated cylinder.

2. Add the 18 mL of 25% potassium oxalate solution to the 150-mL beaker containing the yellow iron(II) oxalate solid.

3. Heat the iron(II) oxalate/potassium oxalate mixture to 40 °C on a hot plate.

4. Add 17 mL of 6% hydrogen peroxide solution to a clean 50-mL beaker. Use a clean graduated cylinder to transfer.

5. Obtain 15 mL of the 10% oxalic acid solution in a clean 50-mL beaker. Transfer 8 mL of this solution to a clean 10-mL graduated cylinder.

6. Monitor the temperature of the iron(II) oxalate/potassium oxalate solution. When the mixture is around 40 °C, *slowly and carefully,* while stirring, add the 17 mL of 6% hydrogen peroxide solution drop-wise using a Beral-type pipet. Continuously stir the solution while adding the 6% hydrogen peroxide. A reddish brown precipitate forms.

7. Once all the 6% hydrogen peroxide solution has been added to the oxalate solution, heat the solution in the beaker to its boiling point. Be sure to continuously stir the solution as it heats.

8. When the solution is boiling, quickly add the 8 mL of 10% oxalic acid solution. Add the remaining 7 mL of 10% oxalic acid in the 50-mL beaker drop-wise to the solution using a Beral-type pipet. The composition and color of the mixture will change from brick red precipitate to an olive or brown solution with suspended brown solid.

9. Turn off the hot plate. Remove the 150-mL beaker using heat-resistant gloves and place the beaker on a ceramic fiber square to cool.

10. Continue stirring the beaker contents as they cool to prevent "bumping."

11. Once the beaker contents have cooled, filter the brown solid by gravity using a filter flask. The filtrate should be a bright green solution due to the presence of dissolved $K_3[Fe(C_2O_4)_3]$.

12. Obtain 20 mL of 95% ethyl alcohol in a clean 50-mL graduated cylinder.

13. Add the 95% ethyl alcohol to the bright green solution of $K_3[Fe(C_2O_4)_3]$. Swirl to mix—this will produce a green precipitate of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$.

14. Cover the beaker with a watch glass and store the mixture as directed by the instructor.
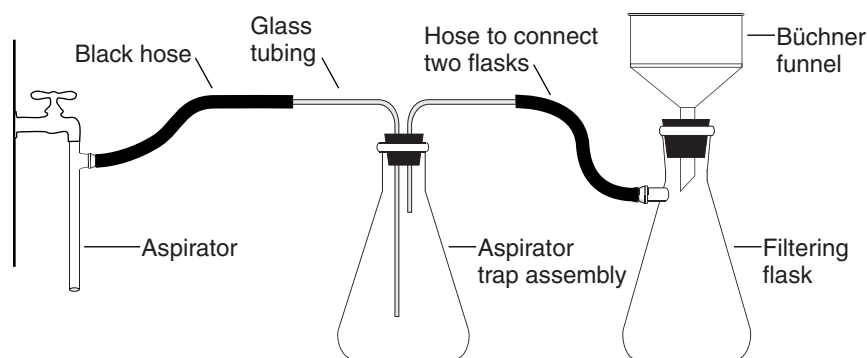
15. Set up the filtration assembly as shown in Figure 1.

Figure 1. Filtration Assembly

16. Turn on the water to start the suction in the Büchner funnel. Add the quantitative filter paper to the Büchner funnel and wet the paper with deionized water from a wash bottle.

17. Transfer the contents of the 150-mL beaker to the Büchner funnel. Wash the beaker and green precipitate with 20 mL of 50% ethyl alcohol, then 20 mL of acetone. Transfer each washing to the Büchner funnel.

18. Allow the precipitate to air dry under suction for 5–10 minutes.

19. Disconnect the hosing from the aspirator, then turn off the faucet.

20. Carefully remove the filter paper and precipitate. On an analytical balance, tare a piece of weighing paper or a weigh boat.

21. Transfer the precipitate to the weighing paper or weight boat. Record the mass of the precipitate in the Data Table as mass of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$.

Part 3. Colorimetric Identification of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$

1. On a tared piece of weighing paper or weighing boat, mass approximately 0.050 g of the green precipitate on an analytical balance.

2. Transfer the massed precipitate to a clean 250-mL beaker.

3. Obtain 100 mL of distilled water in a clean 100-mL graduated cylinder and add the distilled water to the 250-mL beaker. Stir to dissolve the green precipitate.

4. Follow the procedure for taking colorimetric measurements of the solution as directed by the instructor. Generally, spectrophotometers are used as follows: Turn the instrument on and allow it to warm up for 15 minutes. Set the wavelength at 360 nm. With no light passing through the instrument to the photo tube, set the percent transmittance to zero with the "zero" control. Handle cuvets at the top so no fingerprints are in the light path. Polish cuvets with a tissue. Place a cuvet that is about 2/3 full of distilled water into the sample holder and set the percent transmittance to 100% with the appropriate control (not the zero control). Fill a cuvet about 2/3 full of a test solution, place it in the spectrophotometer and read the absorbance. Consult the instrument manual for the details on its use.

5. Repeat step 4 for the wavelengths of 370 nm and 380 nm. Record all absorbances in the Data Table.

Disposal

Dispose of the contents of the cuvets and of the remaining test solutions as directed by your instructor. Follow your instructor's directions for rinsing and drying the cuvets. Dispose of the Part 2 filtrate solution, the product, and the product solution as directed by the instructor.

Data Table

1. Mass of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, g _____ g

2. Mass of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$, g _____ g

Wavelength, nm	Absorbance
360	
370	
380	

Post-Lab Calculations and Questions

Results Table

Theoretical yield of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$, g _____ g

Percent yield of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$, g _____ %

Absorbance Ratios	Standard	Product
360/370 nm	1.43	
370/380 nm	1.64	
360/380 nm	2.35	

1. Calculate the theoretical yield of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$, based on the sample weight of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. Enter this value in the Results Table.

2. Calculate the percent yield for the $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ product. Enter this value in the Results Table.

3. Calculate the absorbance ratios of the product solution. Calculate the 360 nm/370 nm, the 370 nm/380 nm, and the 360 nm/380 nm absorbance ratios and enter these values in the Results Table. Was the product $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$?