

**CHAPTER 13 -- The
Synthesis, Chemistry and
Magnetic Properties of
Potassium
Trioxalatoferrate(III)**

NAME:

Lab Section:

Date:

Sign-Off:

CHAPTER 13: The Synthesis, Chemistry and Magnetic Properties of Potassium Trioxalatoferrate(III)

In Memory of



Edmund C. Shearer, Ph.D., Professor of Chemistry,
Fort Hays State University, Hays, KS

Dr. Shearer was a physical chemist who taught students about inorganic chemistry, qualitative analysis and physical chemistry. He had a remarkable manner about him that brought an incurable excitement to chemistry and learning about it. Those of us who knew him will always remember his infectious giggle, his remarkable sense of humor and his ability to get us to “kick it up a notch” the closer we got to Spring Break.

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Introduction

One important property of transition metals is their ability to form a large number of coordination compounds. A coordination compound forms when a central metal atom or ion accepts pairs of electrons from Lewis bases to form a coordination sphere. The ions or molecules donating electron pairs are called ligands. The number of electron pairs accepted by the central metal atom or ion is its coordination number.

Iron, perhaps the most familiar element in the first transition series, forms a large number of complexes. The purpose of this laboratory exercise is to synthesize a complex of iron(III), potassium trioxalatoferrate(III), and study its magnetic properties and some of its chemistry.

Synthesis of Potassium Trioxalatoferrate(III)

The synthetic process will begin with the light green double salt ferrous ammonium sulfate hexahydrate. Addition of oxalic acid to this salt produces insoluble yellow ferrous oxalate by the following reaction:



This precipitate is then oxidized by hydrogen peroxide in the presence of oxalate ion to form the desired bright green complex ion in solution:



The complex is then made to precipitate as a potassium salt by destroying the excess hydroxide and decreasing the polarity of the solvent by adding ethyl alcohol. The precipitation reaction is:



Bonding in iron complexes

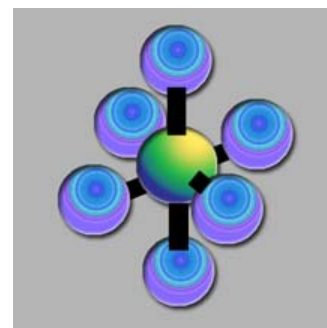
Many of the compounds and solutions of transition metals are highly colored. Let's consider why this is so. In the first-row transition elements, the five 3d orbitals are not

equal in energy. For example, in the presence of atoms which donate electron pairs to form an octahedral complex, a splitting of energy levels (called Crystal field splitting) occurs, producing 2 higher energy d orbitals and 3 lower energy d orbitals. When the d subshell is partially filled, an electron can be excited from a lower energy d orbital to a higher one on absorption of light from the visible region. This imparts the color we observe in these compounds. The size of the energy splitting depends on the atoms donating the electron pairs. Examples of colors are the light green Fe(II) in ferrous ammonium sulfate, characteristic of solutions containing $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and yellow Fe(III) solutions, containing a mixture of such ions as $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$. On the other hand, phosphate complexes of iron(III) solutions are generally colorless.

Characteristically, iron(III) complexes have a coordination number of 6 and are octahedral in structure. The table, below summarizes the various molecular geometry shapes with their coordination number, hybridization and an example of each:

Shape/Structure	Examples	Hybridization	Coordination Number
Linear	Acetylene (ethyne)	sp	2
Triangular (planar; triangular; trigonal planar)	Ethylene (ethene)	sp ²	3
Tetrahedral	Methane	sp ³	4
Square planar	Pt, Pd, Ni	dsp ²	4
Trigonal bipyramidal	p ⁵⁺	dsp ³	5
Octahedral	s ⁶⁺	d ² sp ³	6

The figure, right, illustrates the octahedral structure. Observe that each “corner” donates 2 pairs of electrons to the center “red dot”, each electron pair in the trioxalotoferrate(III) ion coming from a different oxygen atom (corners; center dot is the Fe(III)).



How does this bonding occur? There are at least two theories to help explain the bonding. For the purposes of this lab, we will use the valence bond explanation. First, let's examine the electron configurations of Fe and Fe³⁺ using the tabular format, below, where arrows represent electron location by spin:

	3d					4s	4p			4d			
Fe ⁰ [Ar ¹⁸]	↑↓	↑	↑	↑	↑	↑↓							
Fe ³⁺ [Ar ¹⁸]	↑	↑	↑	↑	↑								

Remember that d subshells have 5 orbitals (represented by the 5 boxes, above) and p subshells have 3 orbitals (represented by the 3 boxes, above).

When iron(III) forms 6 coordinate-covalent bonds with its ligands, into which orbitals can these electrons go? Chemists have learned that iron(III) accepts these 12 electrons in two different ways. Letting arrows represent iron electrons and **colored** X's represent accepted electrons (electron pairs), the two possible electron configurations are:

	3d					4s	4p			4d			
Fe ³⁺ [Ar ¹⁸]	↑↓	↑↓	↑	XX	XX	XX	XX	XX	XX				
Fe ³⁺ [Ar ¹⁸]	↑	↑	↑	↑	↑	XX	XX	XX	XX	XX	XX		

There are similarities and differences in these two possibilities.

Let's examine the similarities first. In each case, 2 electrons enter the 4s orbital and 6 electrons enter the 4p orbital. We observe 4 electrons entering a d orbital, in one case the 3d, in the other case the 4d. We use this similarity and the process of hybridization to explain the octahedral structure of the ion. The process of hybridization uses the principles of quantum mechanics. A group of atomic orbitals are "reshuffled" into a new set of orbitals. The number of hybrid orbitals produced equals the number of atomic orbitals consumed. In this case, we take one s, three p and two d orbitals (6 in all) to make six hybridized orbitals. Quantum mechanics tells us that these six new orbitals point to the corners of an octahedron. Each of these orbitals is a d²sp³ orbital.

The difference occurs in the use of 3d orbitals to accept donated electron pairs in one case and 4d orbitals in the other. To distinguish between these two cases, we call the first type of complex an inner orbital complex and the second type an outer orbital complex. The type of complex formed depends on the field strength of the ligand. This topic is addressed by ligand field theory, which is beyond the scope of the laboratory exercise and of the course.

When 3d orbitals are used for bonding, a rearrangement of the iron's 3d electrons is required. This results in only one unpaired electron. The five unpaired electrons are retained in the second case. This difference will cause the magnetic properties of the two complexes to be different, a topic explored later. Part of this exercise will be to determine into which case the [Fe(C₂O₄)₃]³⁻ ion fits.

Chemical reactions of complexes

Unlike iron, many transition metals do not form both inner and outer orbital complexes. For example, Cr^{3+} ion does not have any electrons in the two higher-energy 3d orbitals and therefore, forms inner orbital complexes. On the other hand, Ni^{2+} always has electrons in the higher 3d orbitals (Ni^{2+} has 8 d electrons) and will always make outer orbital octahedral complexes.

Because of the location of the electrons, one would expect inner orbital complexes to be more stable than outer orbital complexes. The coordinate covalent bonds in chromium(III) complexes, for example, are quite strong so that they are relatively inert to displacement or substitution reactions. On the other hand, the bonds of outer orbital complexes of iron(III) are more polar, and therefore are more easily broken. Substitution reactions should take place much more readily. Coordinate covalent compounds of this type are said to be labile. We will explore this aspect of the $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ ion in our experimental work.

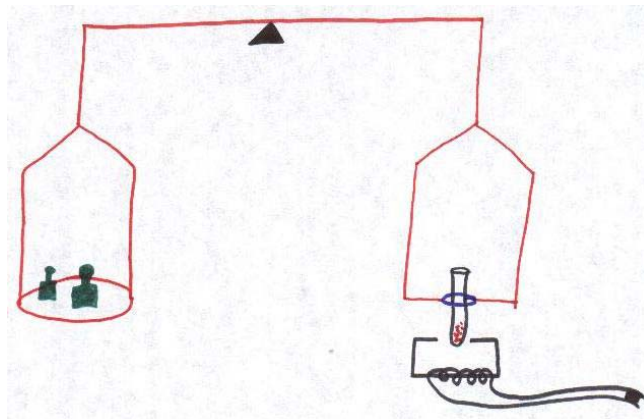
Magnetic properties of complex ions

We have seen that different complexes may have in them a different number of unpaired electrons. In the case of Fe(III) octahedral complexes, inner orbital complexes have one unpaired electron while outer orbital complexes have five unpaired electrons. Because of this difference, the magnetic properties of the two types of complexes will be different.

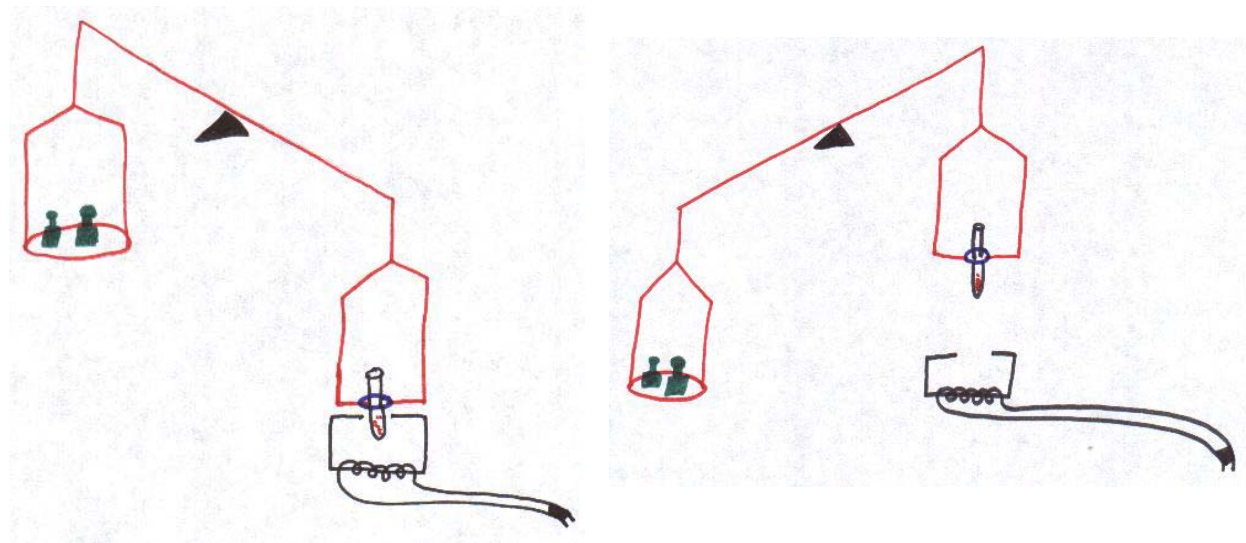
Substances that have unpaired electrons in them are said to be paramagnetic. They will be strongly attracted to a magnetic field, primarily according to the number of unpaired electrons. The measure of the attraction to a magnetic field is called magnetic susceptibility.

Substances that do not have unpaired electrons are said to be diamagnetic. These substances don't interact strongly with a magnetic field, and are in fact slightly repelled by a magnetic field.

We can determine the magnetic susceptibility of a compound using a Guoy balance. A crude figure is shown, right, of a Guoy Balance. A Guoy balance (Magnetic Susceptibility Balance is what they are using, now) is a balance on a knife-edge. It has a pan on one arm and a test tube holder on the other that has an electromagnet associated with (under) it. One places the sample in the test tube and adds



masses to the pan to balance it out. The masses are recorded and the electromagnet turned on. If the sample is paramagnetic, the sample is attracted to the electromagnet. Masses are added to re-balance it. The difference in the masses (the apparent increase in the mass when the magnetic field is on is a measure of the sample's magnetic susceptibility) is used to calculate exactly how many electrons are in the outer shell and are unpaired. If the sample is diamagnetic, the sample is repelled from the electromagnet. This has no practical use of which I am aware. The figure, below, diagrams a very simple view of a Guoy balance to illustrate the effects on both para- and diamagnetic substances:



The electromagnet is represented on the right side of each of the graphics, above. The image, below, is that of a Mark I MSB:



Mark I

From the information obtained from this experimental method, the number of unpaired electrons is determined. This is the way it works.

The magnetic moment (μ) of a substance in units of Bohr magnetons is given by:

$$\mu = 2.84 (X_m T)^{1/2}$$

where X_m is the magnetic susceptibility and T is the Kelvin temperature. Another way to measure the magnetic susceptibility is to use a different type of balance. It's called a Magnetic Susceptibility Balance (MSB; see image, above) and is the instrument we'll use in this experiment.

Just as in the case of the Guoy balance, the MSB employs a magnetic field to determine the interaction of the magnetic field with the sample. A sample is placed in a very carefully prepared tube and lowered into a magnetic field. The magnets which apply the field are suspended from a torsion wire. The stress the sample places on the magnets is reflected in the amount of twist placed on the torsion wire. The electronics of the instrument measure this and report out the result in magnetic susceptibility units.

It turns out that the magnetic moment depends on both the orbital and spin angular momentum of the atom and the interactions between them. For first row transition elements, however, the orbital momentum makes a negligible contribution. That means we can express the magnetic moment in units of Bohr magnetons by

$$\mu = [n(n+2)]^{1/2}$$

where n is the number of unpaired electrons. Therefore, we can create a chart of expected values for a given number of unpaired electrons:

# of Unpaired Electrons	μ in Bohr magnetons
0	0
1	1.73
2	2.83
3	3.87
4	4.90
5	5.92
6	6.93
7	7.94

Experimental Procedure

A. **Preparation of the Complex.** Mass out approximately 5.00 g of ferrous ammonium sulfate hexahydrate and put it in a 250 mL beaker. Be sure to record the exact mass on the data sheet. Add about 15 mL of deionized (or distilled) water. Acidify the mixture with 6 drops of 3M sulfuric acid and heat it gently until the solid dissolves. Add 25 mL of 1M oxalic acid and heat carefully until the mixture boils.

CAUTION:

Continuously stir the mixture because it has a tendency to bump and spatter. Be sure to wear your safety goggles at all times!!!

Remove the beaker from the heat and allow the yellow precipitate to settle. After the mixture has cooled, pour off (decant) as much liquid as possible without losing any solid. Add 20 mL of distilled water to the solid and heat to near boiling while stirring continuously. Let the mixture cool and then pour off the liquid.

While the cooling stages above are taking place, prepare a nearly saturated solution of potassium oxalate by dissolving 4 g of solute in 10 mL of water. Heating may be required to get the potassium oxalate to dissolve. When the liquid from the previous paragraph has been poured off, add the potassium oxalate to the solid and heat the mixture to about 40°C. Add **very slowly** from a buret 20 mL of 3% hydrogen peroxide. Continuously stir the mixture and keep the mixture near 40°C. Adding the hydrogen peroxide too quickly often results in the formation of reddish-brown ferric hydroxide. When all the hydrogen peroxide has been added, heat the mixture to boiling and **slowly**, over a 3 to 5 minute period, add 8 mL of 1M oxalic acid dropwise with continuous stirring.

If the mixture remains cloudy, rapidly filter the solution through ordinary filter paper into a 100 mL beaker. After the solution has cooled somewhat, add 10 mL ethanol. If any cloudiness appears, reheat the mixture to dissolve any precipitate. Cover the beaker and store it as instructed until the next laboratory meeting. Solid $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ will precipitate into rather large, bright green crystals over the next several hours.

At the next laboratory period, collect the crystals by pouring off the liquid. Wash and place them on a piece of filter paper. Dry them by pressing them between two or three pieces of filter paper. Weigh accurately the dried crystals, recording their mass on your data sheet. The percent yield can now be calculated. The reagent quantities were designed such that all were in excess of the original ferrous ammonium sulfate hexahydrate.

Put a few crystals aside for use in the MSB later in the lab period.

B. Reactions of the $[Fe(C_2O_4)_3]^{3-}$ ion. Prepare a solution of your product (from the crystals) by dissolving a few milligrams of your crystals in 5 mL distilled water. Perform the following three tests on your solution, and run the same three tests using a 0.1 N iron(III) nitrate solution side-by-side with your experimentally obtained solution of crystals and water.

1. Add 2 mL of saturated saline to 1 mL of your solution (crystal and iron(III) nitrate).
2. Add 2 drops of dilute nitric acid and 1 mL of each solution to 2 mL of potassium thiocyanate solution.
3. Add 1 mL of each solution to 1 mL of 1 M phosphoric acid.

Record the results of each of the six tests. Observation is of the utmost importance to determine whether or not a reaction took place. Be especially careful to note color changes. Do NOT report “No Reaction”. That’s a conclusion, not an observation.

C. **Magnetic moment of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$.** This part of the laboratory exercise is to be performed in groups of two (2) students.

1. Obtain a pestle and mortar. Thoroughly grind a sample of your crystals into a very fine, uniform powder. About 1 mL of solid sample is sufficient.
2. Obtain a sample tube – they are very expensive (about \$20 apiece), so handle them carefully. Carry it carefully by holding it between a piece of paper towel – do not touch it with your bare hands.
3. Take the empty tube to the MSB. The instrument should be on. Place the middle knob on the 10X setting. This means that the readout obtained must be multiplied by 10. Adjust the instrument with the zero knob until the readout says “000”. Place the empty tube into the instrument (located on top of the instrument just behind the bubble balance). Notice that the tube has a black band that allows the tube to drop in only so far. Do not exert any effort to push the tube down into the compartment. When the reading settles down, **record the result as R_o** . Expect the meter to say something like “-0006”. There is no decimal in the number. Record the results after multiplying by 10. Thus, you would record **$R_o = -60$** .
4. Now mass the empty tube, carrying it with paper towels – no oils from your hands must get on the tube. You can perform this by simply laying it on the pan or by placing it in a tared beaker. Record the empty weight of the tube in your data sheet.
5. Now introduce your sample into the tube using a semi-micro spatula and a small watch glass. Periodically tamp the sample down by tapping the bottom of the sample tube carefully on the lab bench top. Repeat additions and tappings until the length of the sample in the tube is greater than 1.5 cm. When you have sufficient sample in the tube, and when you are convinced that it is uniformly packed down, remass the tube. Measure the length of the sample and record it on the data form (this is “ l ”).
6. Now go back to the MSB, readjust the zero if necessary, and place the tube with the sample in the sample holder. After the instrument settles down, record the reading, remembering to multiply the reading by 10. This value is called “**R**”.
7. Obtain the room temperature, record it and convert it to Kelvins.

8. Clean the tube out as carefully as you can by inverting and tapping on the lab bench top. Return the tube to your lab instructor without further cleaning.

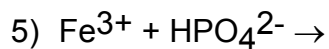
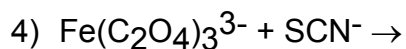
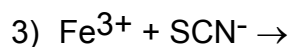
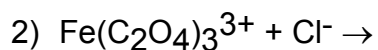
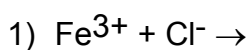
9. Work up your data per the following pages.

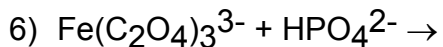
Preparation of $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$		
DATA SHEET		
A)	Mass of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ taken	g
B)	Mass of $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ obtained	g
	Calculate the formula weight of A, above	
	Calculate the formula weight of B, above	
	Calculate the theoretical yield of B, above	
	Calculate the percent yield of B, above	
	Describe B, above	

Assuming 3.0% hydrogen peroxide by weight has a density of 1.00 g/mL, demonstrate on a separate piece of paper (and staple to your experiment for turn-in), that an excess of hydrogen peroxide was used in the oxidation step of Fe(II) to Fe(III).

Reactions of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$		
Report of Observations		
Reagent added	Observations with $Fe(NO_3)_3$	Observations with $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$
None – appearance before reagent added		
Saturated saline		
Thiocyanate ion		
Phosphoric acid		

Based on the observations in the above table and those made during the synthesis, complete and balance the following as net ionic equations. If there was no reaction, so indicate.





Based on the conclusions drawn from the observations in the above table, is $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ an inert or a labile complex?

Magnetic Moment of $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ – PART 1	
Mass of MSB tube with Sample	g
Mass of MSB tube empty	g
Mass of sample (m)	g
Length of sample (l)	cm
MSB reading empty tube, R_o	
MSB reading, tube with sample, R	
Room Temperature (convert to K)	K
Formula weight of $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	g/mol

PART 2

Using your data from above, and the formula, below, calculate the magnetic susceptibility (X_m) of $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$:

$$X_m = \frac{0.998(l)(R - R_o)(\text{Formula Weight})}{10^9 (m)}$$

Your value of χ_m : _____

Using your value of the magnetic susceptibility, solve for the magnetic moment (μ) using the earlier equation:

$$\mu = 2.84 (\chi_m T)^{1/2}$$

using the temperature in Kelvins that you calculated earlier.

Your value of μ : _____

Using the table in the introductory part of this experiment, how many unpaired electrons are in your sample of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$?

_____ unpaired electrons

Bonding of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$

Fill in the electrons using arrows and "X's" to complete the electronic configuration of the following species as in the introduction of this experiment.

	3d					4s	4p			4d				
Fe^0														
Fe^{3+}														
$Fe(C_2O_4)_3^{3-}$														

Is the $Fe(C_2O_4)_3^{3-}$ ion an inner orbital or an outer orbital complex?

What is the hybridization of the $[Fe(C_2O_4)_3^{3-}]$ complex?