


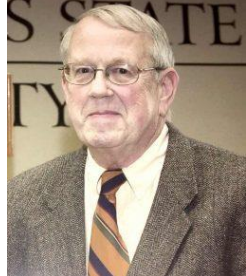



The Synthesis of Potassium Trioxalatoferrate(III):

CHEM 121 Final Lab Practical and Applied Assessment:

Part 1a: During Lab Period of the 15th Week Lab Period
Part 1b: On Canvas, End of 15th Week to Beginning of 16th Week

Part 2: Lab Theory Exam Proctored in Computer Lab in Advance of Your Post-Course Assessment Exam of the Same Evening

In Memory

				
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Student's Name: _____

Date: _____

Directions

This is an exam. You may talk to no one except Dr. Carman about this exam as you are working it up.

The exam packet is to be printed in color on 8.5"x11" white paper and one experimental page per piece of paper (one page per sheet), i.e., no front-to-back printing (you may need the back for calculations). The packet is to be stapled together with one staple in the upper left corner.

All work is to be shown on/in this packet: NO attached papers.

Legibility: if Dr. Carman is unable to read your work, it's incorrect – write neatly for credit.

You may not use any web sources except for Dr. Carman's lectures to complete this exam. If you need other sources, you are to use chemistry textbooks in the library and cite them.

The experimental portion of this exam will begin once you enter the lab. There will be no pre-lab lecture – your supplies will be on the bench in front of the lecture bench. Questions for Dr. Carman for clarification are permitted.

Once you have completed the experimental part of the exam, you are to work it up and then enter your results in Canvas. Upon entering your results and responses into Canvas, the hard copy is due to Dr. Carman for additional grading when you walk in for your lab theory exam

No partial credit will be given.

The exams will not be returned to you after completion and scoring. As with any other exam in Dr. Carman's courses, no questions regarding the exam will be entertained.

Good luck! The content you have studied and practiced this semester in CHEM 121 has well prepared you for this activity: you have the skills!

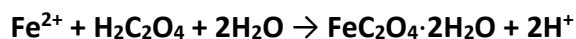
Introduction

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.

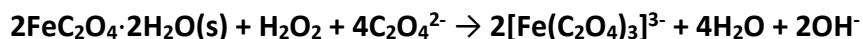
Iron, perhaps the most familiar element in the first transition series, forms a large number of complexes. The purpose of this laboratory final examination is to synthesize a complex of iron(III), potassium trioxalatoferrate(III), study its magnetic properties and some of its chemistry and evaluate/assess your chemistry lab and chemistry problem solving skills in CHEM 121.

Synthesis of Potassium Trioxalatoferrate(III)

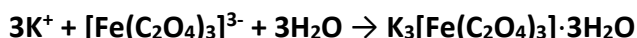
The synthetic process will begin with the light green double salt ferrous ammonium sulfate hexahydrate. Addition of oxalic acid to this salt produces insoluble yellow ferrous oxalate by the following reaction:



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

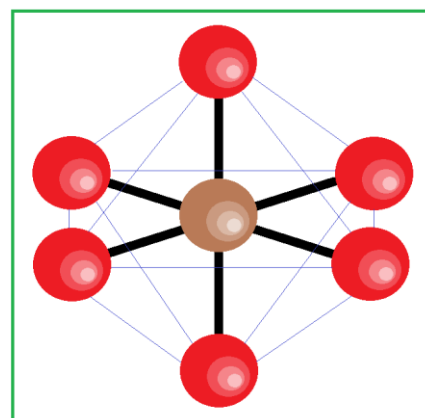
Many of the compounds and solutions of transition metals are highly colored. Let's consider why this is so. In the first-row transition elements, the five 3d orbitals are not equal in energy. For example, in the presence of atoms which donate electron pairs to form an octahedral complex, a splitting 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 (“take 6 bonds”) and are octahedral in structure. The table, below summarizes the various molecular geometry shapes with their coordination number, hybridization and an example of each:

Molecular Geometry	Examples	Orbital 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 “brown sphere”, each electron pair in the trioxalotoferrate(III) ion coming from a different oxygen atom (red spheres at corners; brown sphere represents 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. Ligand Field Strength 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, Cr³⁺ ion does not have any electrons in the two higher-energy 3d orbitals and therefore, forms inner orbital complexes. On the other hand, Ni²⁺ always has electrons in the higher 3d orbitals (Ni²⁺ 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.

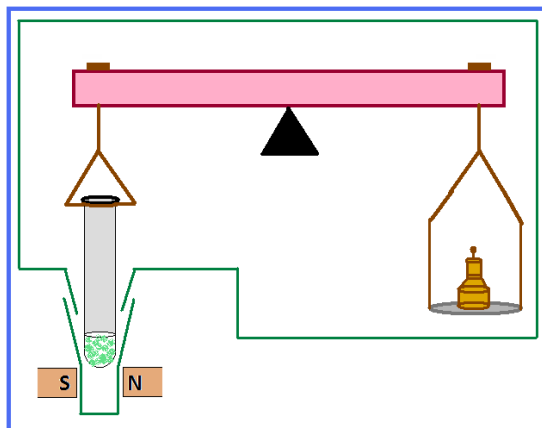
Magnetic properties of complex ions

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.

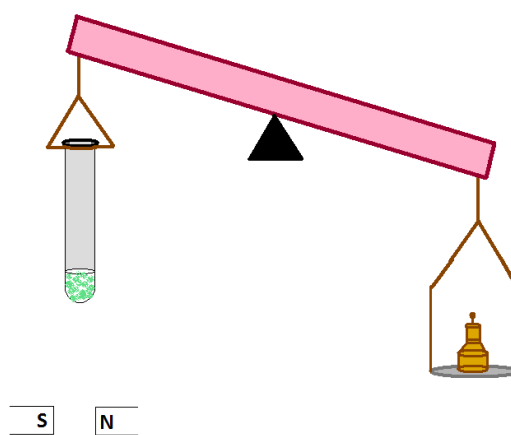
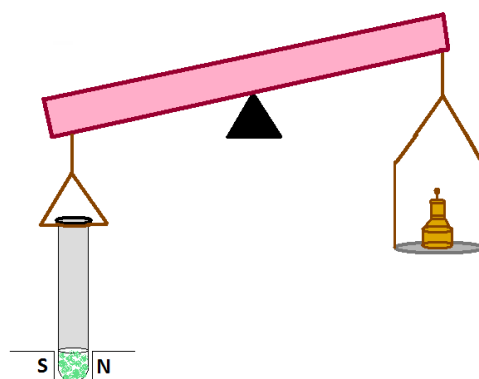
Substances that have unpaired electrons in them are said to be paramagnetic. They will be strongly attracted to a magnetic field, primarily according to the number of unpaired electrons. The measure of the attraction to a magnetic field is called magnetic susceptibility.

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, above top right, of a Guoy Balance.** A Guoy balance (Magnetic Susceptibility Balance is what we use, 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 (**figure, middle right**). 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 (**figure at lower right**). Diamagnetism is being used in high speed railways.



properties of the two types of complexes



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) 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, mathematically, 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

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 (use a disposable pipet) and heat it gently until the solid dissolves (this takes around 10 minutes on the hot plate). Add 25 mL of 1M oxalic acid and heat carefully until the mixture boils (on the hot plate for about 10 minutes).

CAUTION:

Continuously stir the mixture because it has a tendency to bump and spatter. Be sure to wear your safety goggles and lab coat 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 (on the hot plate for around 10 minutes) while stirring continuously (you'll obtain a yellow salt at this point). 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 (about 5 minutes on the hot plate) 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 (set the buret to drip at a rate of about 1 drop per second). Continuously stir the mixture (use your thermometer for stirring) 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 drop-wise with continuous stirring.

NOTE: It's not un-common during this portion of the experiment to observe your reaction product go from a light green solution with orange precipitate to a reddish-brown precipitate to a rust-colored precipitate. After the addition of the oxalic acid your reaction mixture WILL produce very nice light green crystals. Be patient with it.

If the mixture remains cloudy, rapidly filter the solution through ordinary filter paper into a 100 mL beaker; if not cloudy, don't filter: advance. After the solution has cooled somewhat, add 10 mL ethanol. If any cloudiness appears, reheat the mixture to dissolve any precipitate. Cover the beaker with a paper towel that has your name on it and set it on the lecture bench. Solid $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ will precipitate into rather large, bright green crystals over the next several hours. Chemically speaking, the reagent quantities (of the reactants) were designed such that all were in excess of the original ferrous ammonium sulfate hexahydrate.

Magnetic moment of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$.

Obtain an already prepared sample of complex and a pestle and mortar. Thoroughly grind a sample of the crystals into a very fine, uniform powder. About 1 mL of solid sample is sufficient.

Obtain a sample tube – they are very expensive (about \$65 apiece), so handle them carefully; keep them over the lab bench except to carry. Carry it carefully by holding it with a strip of paper towel – do not touch it with your bare hands.

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 carefully insert with light pressure only so far. Do not exert much effort to push the tube down into the compartment. When the reading settles down, **record the result as R_o** on your data sheet.

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 $R_o = -60$.

Now mass the empty tube, carrying it with your paper towel strip – 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 mass of the tube in your data sheet.

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/gently 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 ”).

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 ”.

Obtain the room temperature, record it and convert it to Kelvins.

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.

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 ¹	
Calculate the formula weight of A, above	
Calculate the formula weight of B, above	
Describe B, above	

¹ You will not be able to obtain this information as your sample will not be ready at the end of your experiment.

Assuming 3.0% hydrogen peroxide by weight has a density of 1.00 g/mL, demonstrate below (and on the following blank page if necessary, using the chemical reactions in the write up) that an excess of hydrogen peroxide was used in the oxidation step of Fe(II) to Fe(III). **Hint: think about redox balancing where you used half reactions to add up to get the final, overall, reaction as you do this. Hint: think about limiting reagents as you do this.**

Magnetic Moment of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$	
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 $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$	g/mol

Using your data from above, and the formula, below, calculate the magnetic susceptibility (X_m) of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$:

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

Your value of X_m : _____

Using your value of the magnetic susceptibility, solve for the magnetic moment (μ) using the earlier equation and using the temperature in Kelvins that you calculated earlier:

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

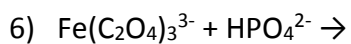
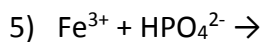
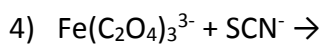
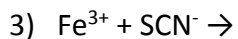
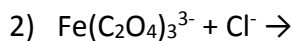
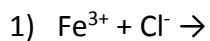
Your value of μ : _____

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

Reactions of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$		
Report of Observations		
Reagent added	Observations with $Fe(NO_3)_3$ (Fe^{3+} , in reactions below)	Observations with $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ ($Fe(C_2O_4)_3^{3-}$, in reactions below)
None – appearance before reagent added	Reddish brown solution	Light green solution
Saturated saline	Reddish brown solution	Orange solution
Thiocyanate ion	Reddish brown solution	Blood red solution
Phosphoric acid	Reddish brown solution	Black mixture

Based on the observations present in the above table, 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 (stable) or a labile complex?

Bonding of $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$

Fill in the electrons using arrows (from the Fe) and "X's" (from the oxalates) to complete the electronic configuration of the following species as illustrated in the manner of the examples in the introduction of this experiment.

	3d					4s	4p			4d				
Fe^0														
Fe^{3+}														
$\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$														

Is the $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ ion an inner or outer orbital complex?

What is the hybridization of the $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ complex?

Questions

1. Which reagent oxidizes the ferrous oxalate dehydrate?
2. What color is ferrous ammonium sulfate? What is its formula?
3. "d" subshells have how many orbitals?

4. What is the difference between inner and outer orbital complexes?

5. How many electrons are unpaired in an inner orbital complex with iron?

6. How many electrons are unpaired in an outer orbital complex with iron?

7. How many d electrons are present in Ni^{2+} ?

8. Inert or stable compounds derive from _____ orbital complexes.

9. Labile compounds derive from _____ orbital complexes.

10. Substances with unpaired orbital electrons are considered:

11. Substances with paired orbital electrons are considered:

12. Extreme paramagnetism is called:
13. Describe one method by which to remove magnetism from something.
14. Which elements are magnetic?
15. If μ = the magnetic moment in Bohr magnetons, does $2.84(X_m T)^{1/2} = [n(n+2)]^{1/2}$?
16. If you have 32 g of methane and 32 g of molecular oxygen, how much CO will you produce in the reaction?
17. What's the limiting reagent in #16? Why?
18. In a dsp^2 hybrid, roughly what does it consist of?
19. In a dsp^3 hybrid, roughly what does it consist of?

20. In an sp hybrid, roughly what does it consist of?

21. A compound is 52.17 % C, 13.04 % H and 34.78 % O. What is its empirical formula?

22. If the molecular weight for the compound in #21 is 46 g/mol, what is its molecular formula?

23. Draw a possible, and reasonably well thought out, Mass Spectrum for the compound from Questions 21 and 22.