

Synthesis of Metal Acetylacetonates: Preparation of Tris(2,4-pentanedionato)chromium(III)

PRE-LAB ASSIGNMENT:

Reading: expected prior to your lab

1. To learn about coordination complexes see 24.1 in Chemistry by Brown, LeMay, Bursten
2. The introduction and procedure in this hand-out.

Questions: expected to be completed and turned in on Tuesday, Feb17th, before 4PM. Please drop off in your assigned shelf of the white bookcase located in Keyes (outside Rm. 313B).

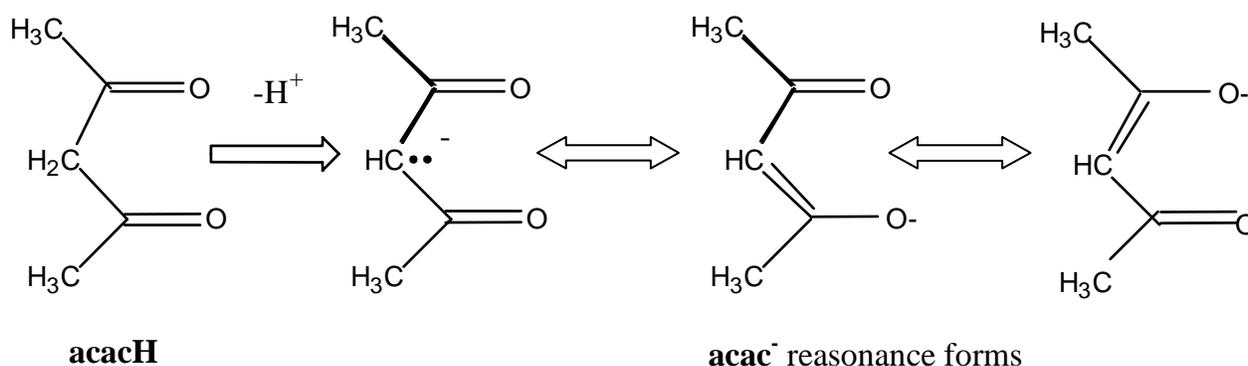
1. Write an outline of the procedural steps for this experiment. You do not need to include instrument "how-to" steps, nor data analysis.
2. Find the following literature values for $\text{Cr}(\text{acac})_3$: molar mass, boiling point, and melting point. Always cite the literature source you referenced.
3. If you begin with 0.62mmol of $\text{CrCl}_3 \cdot \text{H}_2\text{O}$ and synthesized 35mg of $\text{Cr}(\text{acac})_3$. What is your % yield for this experiment? Show all of your work.

INTRODUCTION

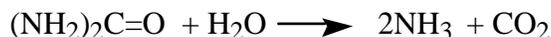
Chapters 2, 3, and 4 in your textbook present information about atoms, molecules, chemical compounds and reactions. In this laboratory exercise, you will react three different compounds, or reagents, to produce a colored product, the coordination compound, $\text{Cr}(\text{acac})_3$. The synthesis of the product and the presence of byproducts will be verified by using LCMS (electrospray mass spectrometry) and melting point determination.

Coordination compounds (or complexes) consist of a central atom surrounded by various other atoms, ions, or small molecules (called ligands). There is only a tenuous distinction at best between coordination complexes and molecular compounds. The most common dividing line is that complexes have more ligands than the central atom oxidation number. Silicon tetrafluoride, SiF_4 , would not be a coordination compound, as there are four ligands on the Si(IV). But $[\text{SiF}_6]^{2-}$ would be considered a coordination compound as there are six ligands on the Si(IV). In this experiment, the coordination compound tris(2,4-pentanedionato)chromium(III) is synthesized and characterized using LCMS and melting point determination. We can use this information to verify the synthesis of the product, $\text{Cr}(\text{acac})_3$. The ratio of product and the presence of any urea containing byproducts can also be determined.

In the presence of base, 2,4-pentanedione, acacH , (or acetyl acetone), readily loses a proton to form the acetylacetonate anion, acac^- , as shown. **NOTE: Each "acac" molecule contains a 5 - carbon backbone. The two "invisible" carbons that are bonded to the double bonds containing oxygen are "understood" to be there in this type of chemical drawing.**



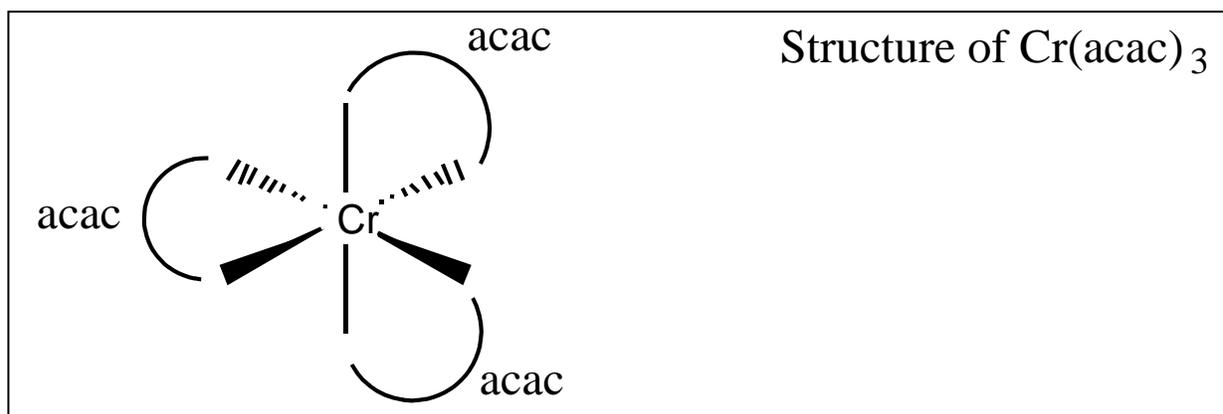
Hydrogen atoms on α -carbon atoms that are adjacent to carbonyl, C=O, groups are relatively acidic. The three different representations of the acetyl acetonate anion are called resonance forms (they differ only in the location of the electrons). In this experiment, the basic solution needed to remove the proton from the (acac) is provided by generating ammonia, NH₃, via the hydrolysis of urea:



In water, ammonia acts as a base:



Acetyl acetonate is an example of a bidentate (bi-two, dent-teeth) ligand, since it can bond to a metal via both oxygen atoms. Ligands of this type are also often called chelating (chelos-claw) ligands. Three acac ligands are therefore needed to complete the octahedral coordination about the central metal ion, giving formula [M(acac)₃]ⁿ⁺. The structure of the chromium(III) complex is shown in the Figure. Since the outer part of the complex consists of organic groups, most metal acetylacetonates are hydrophobic, and insoluble in water.



WEEK ONE PROCEDURE:

A. Preparation of Tris(2,4-pentanedionato)chromium(III)

NOTE: (1) Safety Recommendations

Chromium(III) chloride hexahydrate. Chromium compounds are considered mildly toxic. Chromium(III) compounds, in general, have little toxicity. Certain of them, however, have been listed as carcinogens by the EPA.

2,4-Pentanedione. (Also known as acetylacetone.) The compound is a mild irritant to the skin and mucous membranes. It is a flammable liquid.

Urea. Urea is not generally considered dangerous and is classified as a diuretic.

Chemical Data

Compound	FW	Amount	mmol	bp (°C)	mp(°C)	Density
CrCl ₃ ·6H ₂ O	266.4	130 mg	0.49		83	1.760
Urea	60.06	500 mg	8.3		133-135	1.335
2,4-Pentanedione	100.12	0.4 mL	3.84	140 -23		0.975
Cr(acac) ₃	(Pre-lab Assignment)					

NOTE: (2) Time Required for Experiment: 2.5 h.

1. Experimental Procedure¹: In a 10-mL Erlenmeyer flask fitted with a microwatch glass cover and containing a magnetic stirring bar, place 2.0 mL of distilled water (graduated cylinder) and 130 mg (0.49 mmol) of chromium(III) chloride hexahydrate. When the chromium complex has dissolved, add 500 mg (8.3 mmol) of urea and 0.40 mL (3.8 mmol) of acetylacetone. A large excess of acacH is used, as it helps the reaction go to completion.

NOTE: The acacH should be dispensed in the HOOD.
The reaction should be run in the HOOD.

Clamp the Erlenmeyer flask in an evaporating dish of boiling water set on a magnetic stirring hot plate. Heat the mixture, with stirring, for ~1 hour. As the urea releases ammonia and the solution becomes basic, deep maroon crystals will begin to form. These form as a crust at the surface of the reaction mixture.

During this hour you will complete a simple molecular structure calculation in Spartan. The directions for Spartan can be found below: **Simple Molecular Structure Calculations**. You will also have an opportunity try **Using Excel**: see procedure below. You will want to reference the Appendix of your Lab Syllabus for helpful Excel how-to instructions.

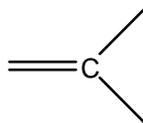
2. Isolation of Product: Cool the reaction flask to room temperature. Collect the crystalline product by suction filtration using a Gooch funnel. Wash the crystals with three 0.20 mL portions of distilled water. Air dry the product by running air through the gooch funnel. Scrape the crystals that have been collected onto a **pre-weighed** piece of filter paper. Set the piece of filter paper onto a large watch glass cover. You will use a small amount of this product for electrospray mass spectroscopy during this laboratory session. The rest of your product will be stored in your lab drawer to dry out completely. It will be used to determine the percent yield and the melting point of your product next week. When cleaning up, please rinse the gooch crucible with isopropanol before washing with water.

Simple Molecular Structure Calculations

While you are waiting to run your LC-MS sample we would like to introduce you to some molecular modeling tools. Molecular Modeling is the use of physical or computer generated models to help understand the shape, bonding, or reactivity of molecules. The Colby science departments are graced by the Paul J. Schupf Scientific Computing Center (located in Keyes 404). Within this facility are many computer resources that allow students to study chemical molecules and systems. For example, the software available includes molecular orbital, molecular mechanics and dynamics, and chemometric analysis software. One of the simplest programs to learn is known as Spartan. The new OSX computers in the General Chemistry laboratory allow every student to access the power of the Schupf lab computers from the General Chemistry lab. To start Spartan from the lab Mac simply click on the **Spartan Icon** on the right side of the desktop. We will use Spartan to calculate the 3D shape of the acetylacetonate anion, acac, ligand used in this experiment.

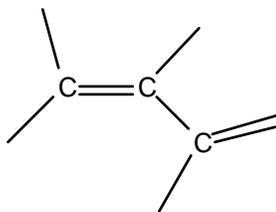
Building the Molecule:

- ⊖ Select **New Molecule** from the file menu.
- ⊖ You should now be in the builder screen. The left side of the window shows molecules under construction. The right side of the screen shows your construction tools, pieces of molecules.
- ⊖ Select the SP² hybridized carbon (the one that looks like the picture below):

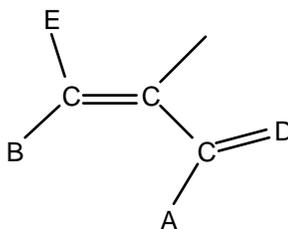


and click on the construction screen. The fragment should appear on the screen. You may use the Apple key-mouse combination to rotate the fragment.

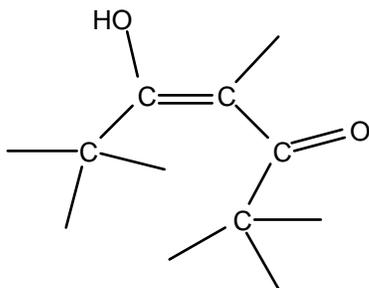
- θ Now click on a single line (bond) and on a double line (double bond) to add to the fragment. It should look something like the picture below:



- θ Finally, connect methyl fragments (carbon with four bonds) onto your fragment at positions A and B. Connect an oxygen fragment with two bonds onto position E and an oxygen fragment with a double bond onto position D.



The final molecule should look something like the picture below.



This is acetylacetonate anion, acac, ligand with a proton (hydrogen) on the oxygen.

- θ Use the delete tool to delete the hydrogen.
- θ Finally, use the Minimize option to move atoms into a low energy position.
- θ Save your molecule and exit the builder.
- θ The builder exits to the general Spartan viewing window. You may rotate and scale your molecule to view it from different positions. Use the **Mode** options to display your molecule in several display formats. Print one view of your molecule and paste it into your lab notebook. You may rotate the molecule using the Apple key-mouse combination. You may scale the molecule using the Shift-Option-mouse combination. Pressing the 3 key will display the molecule in 3D. Put on the 3D goggles to view the molecule in 3D.
- θ We have built the entire Cr(acac)₃ molecule for you. Open this molecule in Spartan and look at the molecule using several different viewing options.

Using EXCEL

A general chemistry student wants to know her grade in the course she just completed before she goes abroad for Jan Plan. Looking at the professor's syllabus she learns that her course grade is comprised of the following: 45% from 3 exams, 5% for homework, 25% for lab work, and 25% for the final exam. Her three exam grades were 64, 76, and 88. Her 11 lab grades were 100, 73, 82, 95, 83, 85, 92, 85, 64, 89, and 91. She earned 4% for her homework. Her final exam grade was an 83. Using **only** Excel (no calculators!) help this student to calculate her numerical grade. After you label the columns and rows of your spreadsheet, note any formulas. Print a copy of the spreadsheet you created and attach it to your lab notebook.

Note: Anytime you are asked to use Excel in the chemistry lab you must write out any formulas used to create the spreadsheet but that do not appear evident upon the print-out.

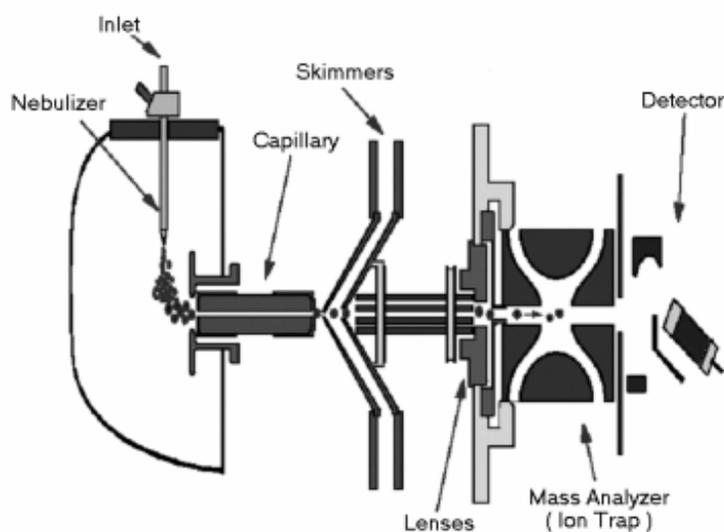
WEEK TWO PROCEDURE

4. **Characterization of product:** The product will be characterized by electrospray mass spectrometry during week one of this laboratory exercise. After drying the product for one week in your lab drawer, the product will be used to determine the percent yield and melting point (You will need to find the melting point of Cr(acac)₃. Several sources will be provided in the lab.). The procedure for taking a melting point will be demonstrated next week in lab. The procedure for electrospray mass spectroscopy follows. You may use the "metal complex finder" program that is available on the class web page to analyze the MS data (<http://www.colby.edu/chemistry/NMR/scripts/complexfind.html>).

Electrospray Mass Spectrometry of *Tris*-acetylacetonatochromium(III)

Theory

Mass spectrometry, MS, is the ideal tool for characterization of the results of synthesis experiments. However, mass spectrometers operate under high vacuum. A special source is needed to convert solid or solution samples into an ion beam under this high vacuum. Until the advent of electrospray MS, the mass spectroscopy of inorganic complexes has required very expensive ion sources, operating with only solid samples¹. Electrospray MS allows the rapid characterization of components in solution.



An electrospray source produces a fine mist of a solution by spraying the solution from a small tip in an electric field. A nebulizer, which uses a rapid flow of nitrogen gas over the tip can also be used to aid the formation of the mist. The source uses a stream of hot, dry nitrogen to dry the mist droplets. As the droplet size decreases, the ions begin to repel each other until a "Coulomb" explosion fragments the droplets and produces gas phase ions. The electric field of the source then pulls the ions into a small capillary.

The capillary and two skimmers restrict the flow of air into the low vacuum region of the MS. Ion optics carry the ions to the mass analyzer where the m/z ratio is determined. Our MS uses an ion trap for the mass analyzer.

Electrospray ion sources are soft ionization sources, that is they produce mostly protonated molecular ions, MH^+ . The proton transfer can occur in your solution or in the droplets produced by the electrospray source.



The mass of the MH^+ ion is one greater than the molecular weight, $M+1$, because of the extra hydrogen ion that gives the ion its charge. Little fragmentation of the MH^+ ion occurs, giving very simple mass spectra. This “soft” ionization should be contrasted with electron impact ionization that is most often used with GC/MS, as you did a few weeks ago. Electron impact ionization is violent and produces many fragment ions for each compound. Therefore electron impact mass spectra contain many peaks from many fragment ions. The simplicity of electrospray ionization mass spectra is very useful when analyzing complex mixtures, without separation.

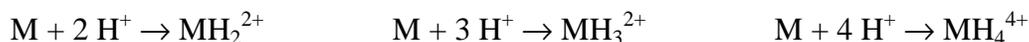
Electrospray ionization is particularly well suited to biological samples for analysis of proteins and nucleic acids. One of the newest areas of biology, proteomics, is based in large part on electrospray MS. MS has become a routine tool in all the molecular life sciences. In this experiment, however, we focus on the mass spectrometry of simple inorganic complexes. For the biologists, however, it should be noted that the majority of enzymes are also metal complexes. For examples, hemoglobin is an iron complex and many enzymes have “zinc finger” domains.

Mass Spectrometry of Inorganic Complexes

In this experiment, we will use MS to verify the synthesis of the desired product, Cr(acac)₃. We will also be able to use MS to judge the purity of the product. Urea can also form complexes. If the synthesis is done carefully, no urea complexes will form. How successful were you? We expect to find a peak for Cr(acac)₃H⁺. Transition metal complexes also show a large peak for an ion that is formed in the source by the loss of one ligand¹, which is Cr(acac)₂⁺ in our case.

For many compounds, ions are formed by acid-base reaction with the H⁺ ion, as shown in Eq. 1. However, metal complexes can already be charged, so reaction with H⁺ is not necessary to form an ion. So for example, Cr(acac)₃, is neutral, so to form an ion you would need to protonate to give Cr(acac)₃H⁺. On the other hand Cr(acac)₂⁺, and Cr(acac)₂(urea)⁺ are already positively charged, so an additional H⁺ is not necessary.

All mass spectrometers determine the m/z ratio. Electrospray ionization often produces multiply charged species (especially with proteins and nucleic acids). For example:



The m/z ratio for these multiply charged ions would be at $(M+2)/2$, $(M+3)/3$, and $(M+4)/4$. For example, a protein with a M of 10,000, would show MH^+ at 10001, MH_2^{2+} at 5001, and MH_3^{3+} at 3334 m/z . The metal in inorganic complexes can also provide multiple charges. For example, Cr(acac)₂⁺.

In your earlier mass spectrometry experiment on methylchloride and methylbromide, you used the isotope peaks to calculate the average molar mass of Cl and Br. Isotope peaks can also be very useful for transition metal complexes. The isotopes of Cr are listed in Table 1. Many metals have characteristic isotope ratios, so observing the isotope peaks in MS confirms the presence of the metal in the complex. In other words, metal complexes with one Cr should have an isotope pattern similar to Figure 1.

Table 1. Isotopes of Cr.

Isotope	Atomic mass (m _a /u)	Natural abundance (atom %)
⁵⁰ Cr	49.9460464 (17)	4.345 (13)
⁵² Cr	51.9405098 (17)	83.789 (18)
⁵³ Cr	52.9406513 (17)	9.501 (17)
⁵⁴ Cr	53.9388825 (17)	2.365 (7)

*uncertainties are given in the ()

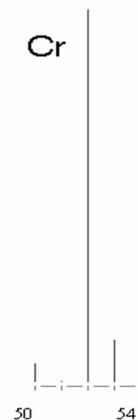


Figure 1. Cr isotope peaks

Mass Spectrometry Procedure

- Mass spectrometry is very sensitive, so we must be careful to keep the solution concentration of your sample very small (concentrations in the 1×10^{-7} M range are a good starting point). If your solution concentration is too large it will take a long time to clean your sample out of the system before the next sample can be run. Using a small spatula, place a tiny amount of your sample in a plastic centrifuge tube. Use a sample size of around the size of this dot: [•]. Add about 1.5 mL of isopropanol. Sonicate your sample tube, using an ultrasonic bath, to make sure the sample has dissolved; about 30 sec. should be sufficient. Look at your tube carefully to ensure that the entire sample has dissolved. If your sample solution looks purple at all you have too much sample and should start over again.
- Fill a 1-mL plastic syringe with sample. Hold the syringe vertically and expel the bubble.
- The “CH141Cr.m” method should already be started when you get to the MS. Select the “Tune” tab, Figure 2, and the “Expert” mode. Verify that the capillary voltage is 2200V. Switch to the “Smart” mode and verify the source settings as in Figure 3. Check the MS scan range and Rolling Averaging as shown in Figure 4. The 10 rolling averages will give good signal-to-noise plots without averaging for too long a time.

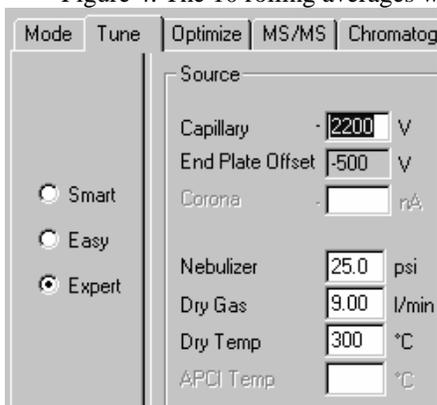


Figure 2. The capillary voltage.

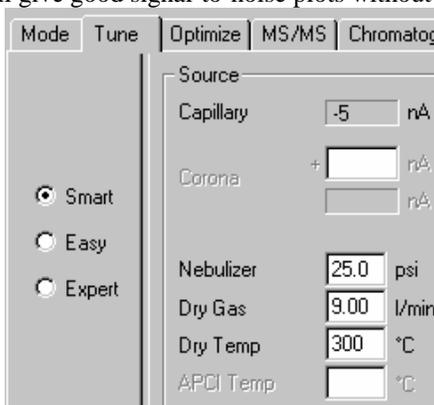


Figure 3. Source settings

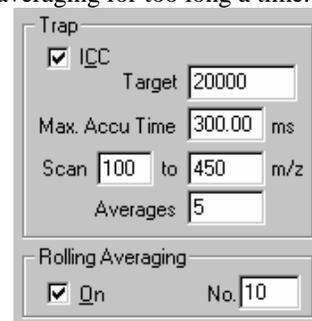


Figure 4. Rolling Averages

- The sensitivity of the instrument can be optimized for different mass ranges and different types of samples. The settings in Figure 5 have been chosen for good sensitivity for the 350 m/z peak.

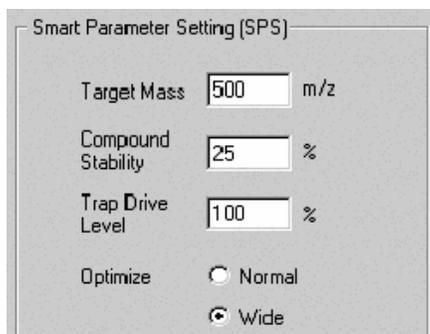


Figure 5. Ion optics settings with good response around 350 m/z for this complex.



Figure 6. Normal screen arrangement with the “stick” or “histogram” style spectrum in the upper left.

- Click on “Operate” if the system is in “Standby” mode. Click on the window arrangement icon shown in Figure 6, if not already chosen. The spectrum on the left is a “histogram” style spectrum, similar to the display on the GC/MS. The spectrum on the right is a “profile” spectrum that shows the full resolution of the mass spectrometer.
- Attach your syringe to the plastic connector on the blunt-tipped syringe needle. Insert the needle in the stainless steel injection port. Place the syringe in the v-groove of the syringe pump. Lift the syringe hold-fast over the syringe. Depress the brass button on the pusher plate with your thumb and move the pusher plate against the syringe barrel. Inject sample by pushing on the pusher plate until you can see the spray in the spray chamber window.
- Press the Run button on the syringe pump. The arrow on the LCD screen should be blinking.
- You should see continuous mass spectra being plotted. Pull down the File menu and choose Print.
- Expand the profile spectrum to show the isotope peaks around 250 m/z. To expand the plot move the mouse cursor until the cursor changes to a “↔”, see Figure 6. Then use the right mouse button to control the scale expansion and the left mouse button to control the scale offset. When you have expanded the scale sufficiently, you will see the isotope peaks clearly as shown diagrammatically in Figure 1.



Figure 6. Mouse based scaling: use the right mouse button.

- Print the expanded spectrum.
- If you wish you can increase the “histogram” spectrum plot size by clicking on the window arrangement icon shown in Figure 7. Then print the new windows.
- Please return the window arrangement to the default as shown in Figure 6.
- Remove the syringe from the injection port.
- Place the wash syringe containing isopropanol into the injection port. By hand inject about 5 mL of pure isopropanol to wash out the source for the next sample (in other words, you will need to refill the syringe at least 5 times). As you inject isopropanol by hand observe the spectrum. Note the intensity of the peak at 250 m/z. Repeatedly inject isopropanol until this 250 m/z peak is much smaller than the other noise peaks in the spectrum.
- If the next student isn't waiting, place the MS in standby mode.

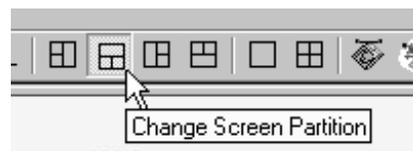


Figure 7. Bigger “stick” spectrum.

Mass Spectrometry Discussion

A Web applet is available to help you identify the peaks in your mass spectrum. The “metal complex finder” can be found on the course home page (<http://www.colby.edu/chemistry/NMR/scripts/complexfind.html>).

Use this applet to determine the identity of any ions you find between 120 and 370 m/z. A good set-up for this experiment is shown in Figure 8.

	Metal	charge	coordination
Metal 1:	Cr	3	6
Metal 2:		0	0

	Ligand	charge	protonation	coordination
Ligand 1:	acac	-1	1	2
Ligand 2:		0	0	0
Accessory Ligand 1:	urea	0 *	0 *	1
Accessory Ligand 2:		0 *	0 *	0

Figure 8. Metal Complex Ion Finder

The ions that you may find above 370 m/z are most likely plasticizers that have contaminated your reagents or from the syringe rubber tip. Since the lightest isotope of Cr is not the most abundant, start your search with the options:

Charge State: Using: and maximum metal atoms:

For a few peaks you may need to try a charge state of 2. You should identify at least 4 peaks, but try to find 5-6.

1. View your expanded plot around 250 m/z. **QUESTION:** Does the isotope cluster match the expected isotope pattern? You can check elemental isotope patterns at <http://www.webelements.com/>.
2. **QUESTION:** On the basis of your peak assignments what was the purity of your sample? Discuss your answer. Include a copy of your mass spectrum in your lab notebook.
3. **OPTIONAL:** Make an Excel spreadsheet to calculate the masses of ions made from different combinations of acac⁻, H⁺, and urea with Cr³⁺. Remember that the total charge must always be +1. So for example, Cr(acac)₃ is neutral, so to form an ion you would need to protonate to give Cr(acac)₃H⁺. On the other hand Cr(acac)₂⁺, and Cr(acac)₂(urea)⁺ are already positively charged, so an additional H⁺ is not necessary. Use the spreadsheet to determine the identity of any ions you find between 120 and 370 m/z.

WEEK TWO

5. **Characterization of product:** After drying the product for one week in your lab drawer, slowly & carefully remove the sample from your lab drawer. Place a piece of weigh paper upon the balance and touch the TARE bar (or button). Obtain the mass of the dried product sitting on the filter paper. Subtract the known mass of the pre-weighed filter paper to determine the mass of product. The mass of product will be used to determine the percent yield. **% yield = [actual yield/ theoretical yield] * 100%**
You will also want to determine the melting point of the product using the available melting point apparatus. The procedure for taking a melting point will be demonstrated for you.

References for Cr(acac)₃ synthesis

1. Fernelius, W.C.; Blanch, J.E. *Inorg. Syn.* **1957**, *5*, 130.
2. Charles, R.G. *Inorg. Syn.* **1963**, *7*, 183.
3. Fackler, J.P., Jr., "Metal β -Ketoenolate Complexes" in **Progress in Inorganic Chemistry**, F.A. Cotton, Ed., Interscience: New York, 1966, Vol. 7, p.471.

References for electrospray mass spectrometry

1. J. L. Pierce, K. L. Busch, R. G. Cooks, and R. A. Walton, "Desorption Ionization Mass Spectrometry: Secondary Ion and Laser Desorption Mass Spectra of Transition-Metal Complexes of β -Diketones," *Inorg. Chem.*, **1982**, 2597-2602.
2. <http://www.webelements.com/webelements/elements/text/Cr/isot.html>
3. <http://www.colby.edu/chemistry/NMR/scripts/complexfind.html>

Laboratory Notebook:

Week 1: Tape your clearly labeled LC-MS print-outs into your lab notebook. Be sure to answer the QUESTIONS given in the above text of Mass Spectrometry Discussion

Week 2: Clearly present your final results (address your objective). Was your objective met? What does your result indicate? Based on your LC-MS, percent yield and melting point data, were you successful at making the Cr(acac)₃ complex? Give two possible sources of random experimental error. Carefully explain how each one of these possible errors may have caused you to get the final result you reported.