Synthesis of Tris(2,4-pentanedionato)chromium(III)[1]

Purpose: A chromium(III) complex is synthesized and the purity is determined using mass spectrometry.

Prelab Reading: (expected prior to your lab): To learn about coordination complexes see section 19.2 in Olmstead and Williams.

Introduction

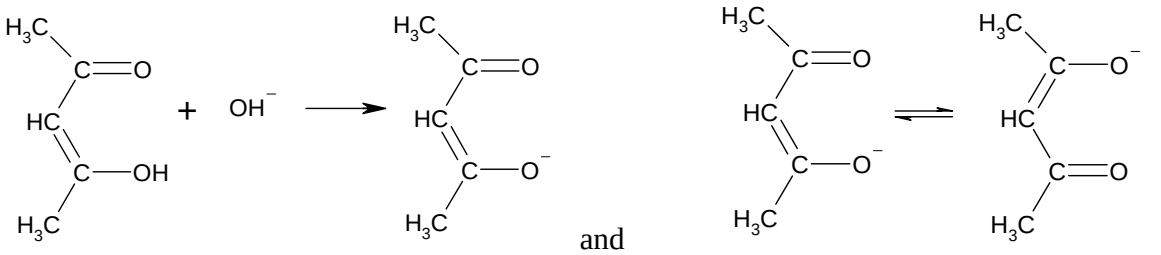
The synthesis of new compounds is one of the most central and interesting parts of chemistry. In this laboratory you will synthesize tris(2,4-pentanedionato)chromium(III), which is also written $Cr(acac)_3$ for short. The synthesis of the product and the presence of any undesired byproducts will be verified using mass spectrometry (MS).

Coordination compounds (or complexes) consist of a central atom surrounded by various other atoms, ions, or small molecules, which are called ligands. Common ligands include water, Cl^-, and carbon monoxide (CO), such as in the coordination compounds $Fe(H_2O)_6^{3+}$, $FeCl_6^{3-}$, and $Fe(CO)_6$, respectively. For another example, a majority of enzymes are coordination compounds, where the central atom is a metal ion like Fe^{3+} or Zn^{2+} and the ligands are amino acids in the protein. The bonding between the central atom or ion and the ligands is usually weaker than the strong covalent bonds found in molecular compounds like H_2O and CH_4. It is sometimes difficult to decide if a substance is a molecular compound or a coordination compound. The most common dividing line is that complexes have more ligands than the central atom oxidation number. Silicon tetrafluoride, SiF_4, is not a coordination compound, as there are four ligands on the Si(IV). But $[SiF_6]^{2-}$ is considered a coordination compound as there are six ligands on the Si(IV).

In this experiment the ligand is based on 2,4-pentanedione, which is also called acetylacetone or acacH for short. In the presence of base, 2,4-pentanedione, acacH, readily loses a proton to form the acetylacetonate anion, $acac^-$:

$$acacH + OH^- \rightarrow acac^- + H_2O \qquad (1)$$

Acetylacetonate anion is the ligand in this experiment. The structures for these compounds and this reaction are shown below:



acacH acac⁻ acac⁻ acac⁻ (2)

The two different representations of the acetylacetonate anion on the right are called resonance forms; they differ only in the location of the electrons. The real structure of $acac^-$ is an average of the two resonance forms. These resonance forms show that the two oxygen atoms are equivalent. The $acac^-$ ligand interacts with the central metal through these two negatively charged oxygens.

In this experiment, the basic solution needed to remove the proton from the acacH is provided by ammonia, NH_3. In water, ammonia acts as a base yielding hydroxide ion:

$$NH_3 + H_2O \rightarrow NH_4^+(aq) + OH^-(aq) \quad (3)$$

To keep the reaction mixture from becoming too basic, the ammonia is generated slowly by the hydrolysis of urea:[1-4]

$$(NH_2)_2C{=}O + H_2O \rightarrow 2NH_3 + CO_2 \quad (4)$$

Acetylacetonate 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 octahedral coordination about the central metal ion, giving the formula $Cr(acac)_3$. The structure of the chromium(III) complex is shown in Figure 1. Since the outer part of the complex consists of organic groups, most metal acetylacetonates are hydrophobic, and therefore insoluble in water.

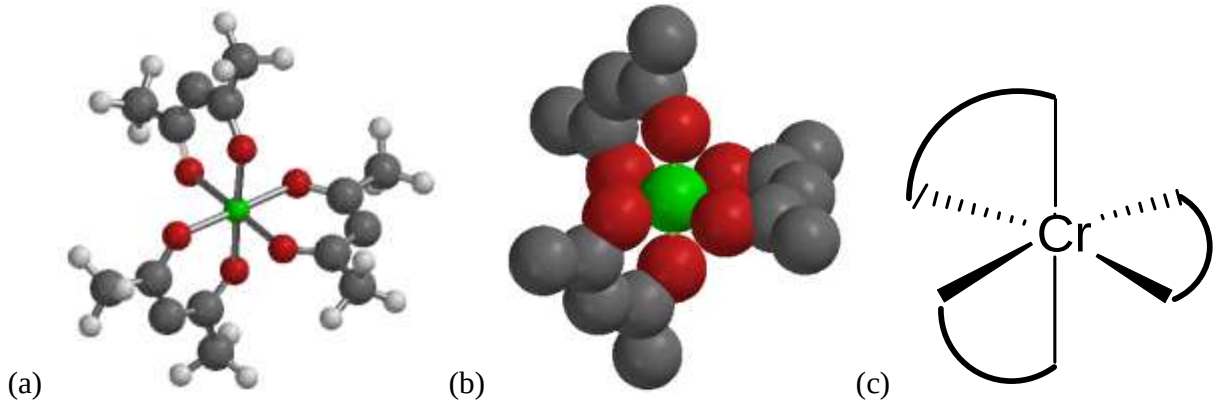


Figure 1. The structure of $Cr(acac)_3$: (a) ball-stick structure, (b) Van der Waals spheres without H atoms, and (c) diagrammatic structure with the bidentate ligand simply represented as an arc.

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 DART-MS, the mass spectroscopy of inorganic complexes required very expensive ion sources, operating with only solid samples[5]. DART-MS allows the rapid characterization of solids and liquids.

What is a mass spectrometer? A mass spectrometer is an instrument that accurately measures the masses and relative abundances of the ions formed from atoms or molecules. Figure 2 is a diagram of a time-of-flight mass spectrometer. A mass spectrometer consists of three general parts: the ion source, the mass analyzer, and the ion detector. The sample is introduced into the source by dipping a thin glass rod into the sample and placing the glass rod in the beam of the source. The mass analyzer is held at high vacuum so that the ions can travel through the instrument without colliding with gas molecules from the air. The detector can be as simple as a metal plate, which measures the current carried by the ions. The output of the detector is

analyzed by computer to produce the mass spectrum, which is a plot of the count of the number of ions per second as a function of the mass-to-charge ratio. The mass-to-charge ratio is called the m/z ratio.

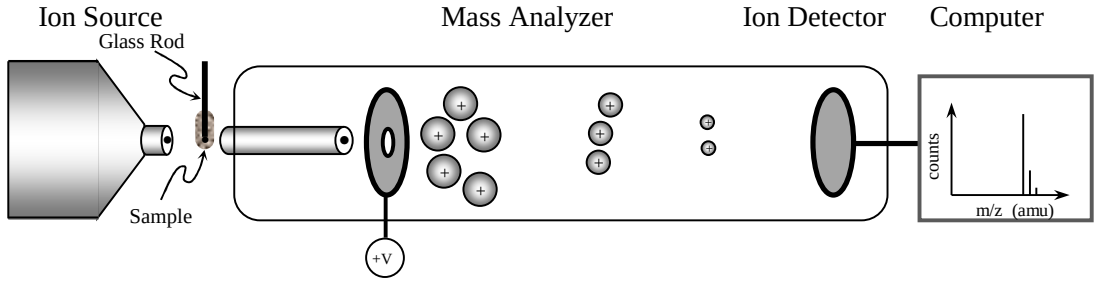


Figure 2: A time-of-flight mass spectrometer. Large mass ions travel slowly. The DART source produces protonated water clusters, e.g. $(H_2O)_4H^+$, that transfer a proton to the sample.

In a DART source, the sample is introduced into the ion source as a gas, liquid, or solid. A mass spectrum is a histogram of the abundance of the ions resulting from a molecule, plotted versus m/z. The primary ions formed in the source of our mass spectrometer are the **protonated ions** which are formed by transferring an H^+ to the molecule. For example, the ion formed from ethanol is called the MH^+ ion:

$$C_2H_6O\ (g) + H^+\ (g) \rightarrow C_2H_7O^+\ (g) \qquad (5)$$

or schematically as:

$$M\ (g) + H^+\ (g) \rightarrow MH^+\ (g) \qquad (6)$$

The ion formed from the molecule has a mass 1.007825 amu greater than the mass of the original molecule. The mass spectrum for ethanol is shown in Figure 3.

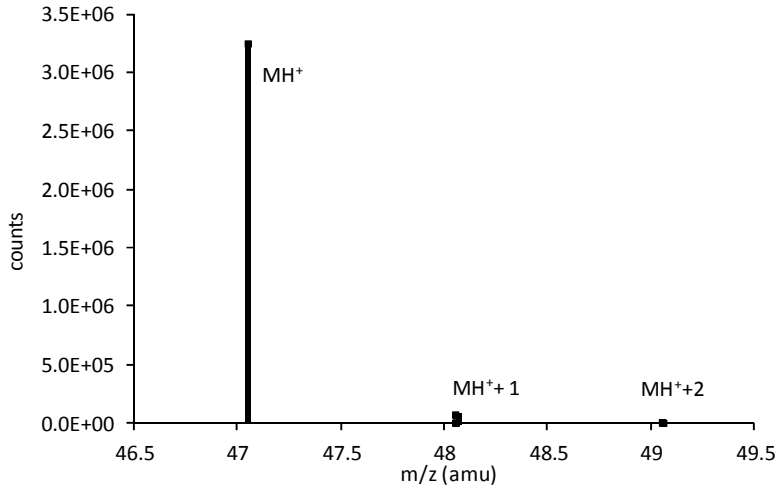


Figure 3: Mass spectrum of ethanol as the MH^+ ion.

The substitution of the naturally occurring isotopes of each of the elements gives an **isotope cluster**. Each of the three lines in the mass spectrum of ethanol results from the original

molecule; they are the MH^+, MH^++1, and MH^++2 ions. The MH^++1 ion results primarily from the substitution of one $^{13}_{6}C$ atom for a $^{12}_{6}C$. The MH^++2 ion results primarily from the substitution of one $^{18}_{8}O$ for a $^{16}_{8}O$.

How does a Time-of-Flight Mass Analyzer work? In a time-of flight mass spectrometer, the m/z ratio of the ions from the source are analyzed by giving the ions a push from an electric field to force them to travel a long-evacuated tube to a detector, Figure 2. The push from the electric field gives each ion the same kinetic energy, per unit charge on the ion. The kinetic energy of particle is given by

$$E_k = ½ m\upsilon^2 \qquad (7)$$

where m is the mass of the ion and υ is the velocity. Since all the ions, for a given charge, have the same kinetic energy, heavy ions travel slowly and light ions travel rapidly. Determining the travel time from the source to the detector then allows the velocity to be determined and from the velocity the mass is calculated. The advantage of the time-of flight mass analyzer is excellent accuracy, precision, and resolution. The resolution is the ability to distinguish ions with similar masses. The mass accuracy of Colby's instrument is 2 ppm with careful calibration.

Isotope clusters and Average Molar Mass Determination: The elemental symbols, abundance, and atomic masses for the naturally occurring isotopes of several elements are given in the Table 1.

Table 1: Isotopic Masses (amu) [abundance]

^{1}H 1.007825 [99.9885] ^{2}H 2.014102 [0.115]							^{3}He 3.016029 [0.000137] ^{4}He 4.002603 [99.999863]
^{6}Li 6.015122 [7.59] ^{7}Li 7.016004 [92.41]	^{9}Be 9.012182 [100]	^{10}B 10.012937 [19.9] ^{11}B 11.009305 [80.1]	^{12}C 12.000000 [98.93] ^{13}C 13.003355 [1.07]	^{14}N 14.003074 [99.632] ^{15}N 15.000109 [0.368]	^{16}O 15.994915 [99.757] ^{17}O 16.999132 [0.038] ^{18}O 17.999161 [0.205]	^{19}F 18.998403 [100]	^{20}Ne 19.992440 [90.48] ^{21}Ne 20.993847 [0.27] ^{22}Ne 21.991386 [9.25]
^{23}Na 22.989770 [100]	^{24}Mg 23.985042 [78.99] ^{25}Mg 24.985837 [10.00] ^{26}Mg 25.982593 [11.01]	^{27}Al 26.981538 [100]	^{28}Si 27.976927 [92.2297] ^{29}Si 28.976495 [4.6832] ^{30}Si 29.973770 [3.0872]	^{31}P 30.973762 [100]	^{32}S 31.972071 [94.93] ^{33}S 32.971458 [0.76] ^{34}S 33.967867 [4.29] ^{36}S 35.967081 [0.02]	^{35}Cl 34.968853 [75.78] ^{37}Cl 36.965903 [24.22]	^{36}Ar 35.967546 [0.3365] ^{38}Ar 37.962732 [0.0632] ^{40}Ar 39.962383 [99.6003]

We can draw a number of conclusions from this table.

- Many elements have more than two naturally occurring isotopes.
- The $^{7}_{3}Li$ example shows that the lightest isotope is not necessarily the most abundant.
- Except for $^{12}_{6}C$, none of the isotopic masses are integers; even through the proton number and mass number are integers.
- The $^{35}_{17}Cl$ and $^{37}_{17}Cl$ example shows that naturally occurring isotopes don't necessarily occur in steps of one mass number: $^{36}_{17}Cl$ is not found in nature.

- Some elements have only one naturally occurring isotope, such as ${}^{19}_{9}F$ (some other elements with only one natural isotope are ${}^{31}_{15}P$, ${}^{59}_{27}Co$, and ${}^{127}_{100}I$).

A naturally occurring sample of an element is comprised of all the possible naturally occurring isotopes of that element. The atomic mass of an element is the abundance weighted average of the isotopes of the element. For example, the atomic mass of carbon (the mass you find on the periodic table, but not in Table 1) is 12.0107, which is equal to the abundance weighted average mass of the isotopes of carbon found in Table 1.

Molecules also have an isotopic distribution. Consider protonated ethanol ion for example, $C_2H_7O^+$. Using the lightest isotopes, the **parent mass** is given by the isotopic mass with all ${}^{12}_{6}C$, ${}^{2}_{1}H$, and ${}^{16}_{8}O$:

$$\mathcal{M}({}^{12}C_2{}^{1}H_7{}^{16}O^+) = 2(12.000000) + 7(1.007825) + 15.994915 = 47.04969 \text{ amu} \qquad (8)$$

The parent mass is usually labeled just MH^+, for short. However, one in every 100 carbon atoms is a ${}^{13}_{6}C$, Table 1. If one ${}^{13}_{6}C$ is substituted for a ${}^{12}_{6}C$ then the mass of the ethanol ion is:

$$\mathcal{M}({}^{12}C{}^{13}C{}^{1}H_7{}^{16}O^+) = 12.000000 + 13.003355 + 7(1.007825) + 15.994915 = 48.053045 \text{ amu} \qquad (9)$$

This isotopic mass is one larger than the parent mass, to four significant figures, giving MH^++1. Alternately, one in every thousand hydrogen atoms is a ${}^{2}_{1}H$, but the natural abundance of ${}^{2}_{1}H$ is so low that the contribution to the MH^++1 abundance is insignificant (see Note 1). Consider next the contributions to a mass at MH^++2. Roughly two in every thousand oxygen atoms is a ${}^{18}_{8}O$. If ${}^{18}_{8}O$ is substituted for the ${}^{16}_{8}O$ then the mass of ethanol is:

$$\mathcal{M}({}^{12}C_2{}^{1}H_6{}^{2}H{}^{18}O^+) = 2(12.000000) + 6(1.007825) + 2.014102 + 17.999161 = 49.053936 \text{ amu} \qquad (10)$$

This isotopic mass is two larger than the parent mass, to four significant figures, giving MH^++2 (see Note 2).

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 and ammonia can form complexes. If the synthesis is done carefully, no urea or ammonia complexes will form. How successful were you? We expect to find a peak for $Cr(acac)_3H^+$. DART ionization can also produce multiply charged species. For example:

$$M + 2\,H^+ \rightarrow MH_2^{2+} \qquad\qquad M + 3\,H^+ \rightarrow MH_3^{3+} \qquad (11)$$

The m/z ratios for these multiply charged ions are (M+2)/2, and (M+3)/3. For example, a protein with an M of 10,000, shows MH^+ at 10001, MH_2^{2+} at 5001, and MH_3^{3+} at 3334 m/z.

Metal complexes can already be charged in solution, so reaction with H^+ is not necessary to form an ion. The metal in inorganic complexes can also provide multiple charges. For example, $Cr(acac)^{2+}$ results in a peak at m/z of M/2. Metal complexes can show large peaks for ions that are formed in the source by the loss of one or more ligands.

$$Cr(acac)_3 \xrightarrow{-\,acac^-} Cr(acac)_2^+ \xrightarrow{-\,acac^-} Cr(acac)^{2+} \qquad (12)$$

In solution, metal complexes can also undergo ligand exchange reactions with water and other solvents:

$$Cr(acac)_3 + 2\,H_2O \rightarrow Cr(acac)_2(H_2O)_2^+ + acac^- \qquad (13)$$

So for example, $Cr(acac)_3$, is neutral, so protonation is necessary to give $Cr(acac)_3H^+$ ions. On the other hand $Cr(acac)_2^+$, $Cr(acac)_2(H_2O)^+$, and $Cr(acac)_2(urea)^+$ are already positively charged, so an additional H^+ is not necessary.

IIsotope peaks can also be very useful for transition metal complexes. The isotopes of Cr are listed in Table 2. 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 4.

Table 2. Isotopes of Cr.[6]

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 ( )

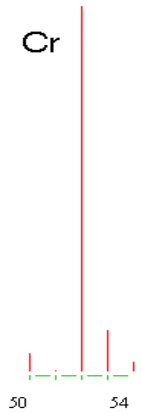


Figure 4. Cr isotope peaks

Procedure

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

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. 2,4-Pentanedione is a flammable liquid.

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

2-Propanol. (Also known as isopropyl alcohol) 2-Propanol is flammable.

Table 3: Reactant Data

Compound	FW	Amount	bp (°C)	mp(°C)	Density
$CrCl_3{\cdot}6H_2O$	266.4	130 mg		83	1.760
Urea	60.06	500 mg		133-135	1.335
2,4-Pentanedione	100.12	0.4 mL	140	-23	0.975

Required Equipment

Magnetic stirring hot plate, 10-mL Erlenmeyer flask, microwatch glass, magnetic stirring bar, 10-mL graduated cylinder, 10x75-mm test tube, evaporating dish, Gooch funnel.

1. Synthesis[1-4]

In a 10-mL Erlenmeyer flask fitted with a micro-watch 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 to shift the equilibrium towards product.

NOTE: The acacH should be dispensed and the reaction 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 h. As the urea releases ammonia and the solution becomes basic, deep maroon crystals will begin to form. These crystals form as a crust at the surface of the reaction mixture.

2. Isolation of Product

Cool the reaction flask to room temperature. Gooch crucibles are cylindrical glass filters with a porous, sintered glass bed. Record the mass of a Gooch crucible to two significant figures past the decimal point. Collect the crystalline product by suction filtration using the Gooch crucible, Figure 5. When pouring from the sample beaker, pour down the stirring rod to avoid spilling, as shown in Figure 6.

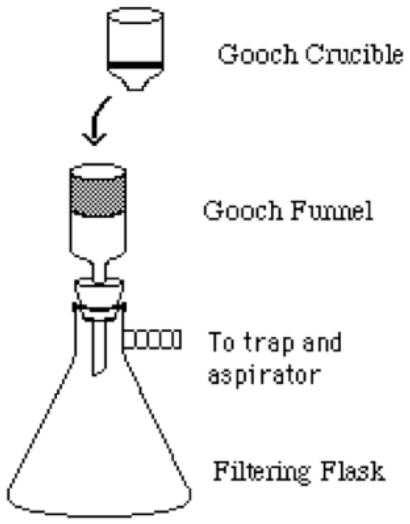


Figure 5. Filtration apparatus

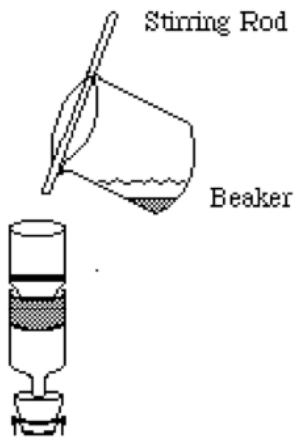


Figure 6. Pouring down a stirring rod.

Wash the crystals with three 0.20 mL portions of distilled water. Air-dry the product by pulling air through the Gooch crucible. Prepare your MS sample by transferring a few crystals on the tip of a small spatula into a 10x75 mm test tube that is ¾-filled with 2-propanol. Please see the instructions below for the MS procedure. Place the Gooch crucible on a glass Petri dish that is marked with your initials, then transfer into the pre-heated lab oven to dry for 20 mins. After about 20 mins cool the Gooch crucible to room temperature and determine the mass of product. The mass of the product is the experimental yield. The percent yield is determined as:

% yield = [experimental yield/ theoretical yield] 100%

The theoretical yield is the mass of product that is produced stoichiometrically from the limiting reagent. What is the limiting reagent in this synthesis?

3. Cleaning up (all chemical waste should be collected in appropriately labeled containers) Scrape the crystals that have been collected into the labeled container in the hood. To clean up, please rinse the Gooch crucible with 2-propanol before washing with water. Do the washes using the filter flask under suction. Empty the remaining 2-propanol solution of your complex in the test tube into the labeled waste container in the hood. Wash all the glassware you used with lab soap and water. Leaving everything where you found it at the beginning of the lab.

Mass Spectrometry Procedure

1. While you are waiting to use the MS: make an Excel spread sheet to calculate the masses of ions made from different combinations of $acac^-$, H^+, urea, NH_3, and H_2O with Cr^{3+}. 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. An example spreadsheet is shown below. The upper portion determines the monoisotopic masses of the most abundant, parent peak of the ligands. The lower section determines the monoisotopic masses of possible complexes. Only two possible complexes are shown, you should add additional possibilities.

A1	B	C	D	E	F	G	H	I	J	K
2										
3			Isotope	12C	1H	14N	16O		Total	
4			Isotope Mass	12	1.007825	14.00307	15.99492		g/mol	
5		acac-	Stoichiometric #	5	7	0	2		99.04462	g/mol
6		urea		1	4	2	1		60.03236	
7		NH3			3	1			17.02655	
8		H2O			2		1		18.01057	
9										
10										
11		Component	Cr3+	acac-	urea	NH3	H2O	H+	Total	
12		Mass	51.9405098	99.04462	60.03236	17.02655	18.01057	1.007825	g/mol	
13		Complex A	1	3				1	350.0822	g/mol
14		Complex B	1	2	1		1		328.0727	g/mol
15										

For example, cell J5 contains the formula:

=$E$4*E5+$F$4*F5+$G$4*G5+$H$4*H5

The $ signs prevent the cell reference from being incremented as the formula is filled-down to successive rows. For example, cell J6 was filled-down to give:

=$E$4*E6+$F$4*F6+$G$4*G6+$H$4*H6

Cell E12 simply references the monoisotopic mass of the ligand from the top section: =J5, so you don't need to type in the value by hand. The cell J13 contains the formula:

=$D$12*D13+$E$12*E13+$F$12*F13+$G$12*G13+$H$12*H13+$I$12*I13

which can be filled-down for as many possible complexes as you need.

2. Use the instructions at the end of this write-up to acquire the spectra of the 2-propanol solution of the product from your synthesis. Use the spreadsheet to determine the identity of any ions you find between 120 and 420 m/z. Identify at least 4 peaks, but try to identify 5-6.

3. Print the MS spectrum with all the identified peaks showing and label the peaks with the corresponding complex identity (e.g. $Cr(acac)_3$, $Cr(acac)_2^+$, $Cr(acac)_2(urea)^+$, etc.)

4. Determine the experimental masses of the peaks in the M^+ isotope cluster for $Cr(acac)_3$. Record the masses of the peaks in your isotope cluster in your lab notebook, including the third and fourth peaks if observed with good intensity. Does the isotope cluster match the expected isotope pattern? You can check elemental isotope patterns at http://www.webelements.com/

5. Print out your mass spectrum in a narrow m/z range spanning the peaks in your M^+ isotope cluster. Tape a copy of each MS spectrum in each lab notebook for each student in a pair.

6. A Web applet is available to help you identify the peaks in your mass spectrum: "Metal Complex Finder," the link for which is listed on the course home-page[7]. Use this applet to determine the identity of the ions you find between 120 and 420 m/z. A good set-up for this experiment is shown in Figure 7. Identify at least 4 peaks, but try to identify 5-6.

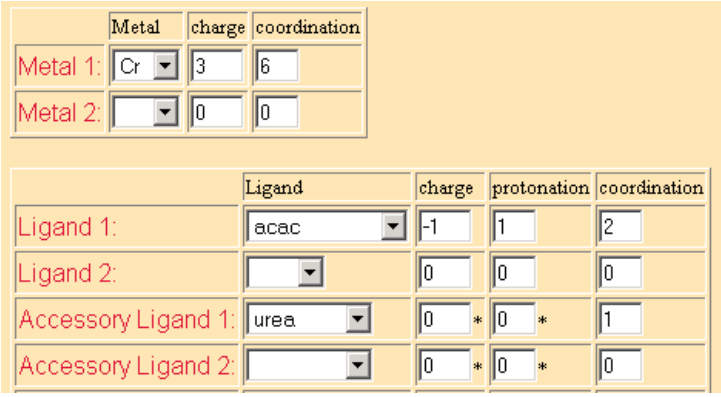
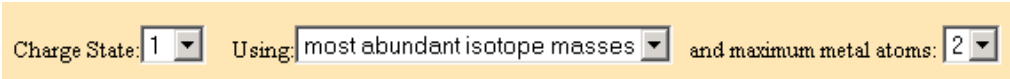


Figure 7. Metal Complex Ion Finder

Since the lightest isotope of Cr is not the most abundant, start your search with the options:



Report

You should use the **report form** to submit your laboratory report. The report should contain:

1. *Introduction*: Give a brief introduction. In the introduction state the purpose of the experiment and the principle means that you are going to use to achieve that purpose. The introduction should be just two sentences. You should not discuss the experimental procedure, nor the calculations that will be necessary in the Introduction.

2. *Theory*: In a few sentences, report that the m/z values for the expected masses of the most abundant peak in the isotope cluster for your substance and for impurities were calculated using literature values of the masses of the isotopes of the elements and reference Table 1 in the lab write-up. Report what periodic table you used to determine average molar mass of the compound as a reference in the Literature Cited section.

3. *Procedure*: State that "Tris(2,4-pentanedionato)chromium(III) was synthesized by the reaction of $CrCl_3 \cdot 6H_2O$ with 2,4-pentanedione in basic, aqueous solution." Reference the instructions in this write-up. State the manufacturer and model of the source and mass spectrometer that were used. Report the nature of your MS sample: "a dilute 2-propanol solution of the product of the reaction." In a <u>single</u> sentence, describe how the sample was introduced into the source of the mass spectrometer (they are called glass capillary tubes). Give the DART source temperature and the gas used in the source (helium or nitrogen).

4. *Results*: Provide a copy of your mass spectrum with mass spectral peaks labeled with the formula of the ion (e.g. $Cr(acac)_2^+$). Identify at least 4 peaks, but try to identify 5-6.
Present the results of the calculations from the preceding section: the experimentally determined monoisotopic masses, the theoretical masses, the errors in ppm of the most abundant peaks in the isotope clusters, and the periodic table based molar masses. Identify the limiting reagent in the synthesis. Give the experimental, theoretical, and percent yield. Make sure that each table and figure have captions and that each table or figure is referenced in the body of the text.

5. *Discussion*: In a sentence or two each: (1). For the purpose accomplished, restate the purpose of the experiment, but as completed goal. (2). Discuss the accuracy of the determination of the monoisotopic molar masses of the most abundant peak of the isotope cluster from your substance. (3). Was the factor that dominated the accuracy of your MS results a random or systematic error? Describe how you decided. (4). Describe why the monoisotopic molar mass of a substance and the periodic table based molar mass are different. (5). Identify the major impurities in your sample. (6). Give two possible sources of <u>systematic</u> error in your percent yield. (7). Based on your MS, and percent yield, were you successful at making the $Cr(acac)_3$ complex?

<u>Notes:</u>

1. The mass of the peak with one ${}^{2}_{1}H$ is slightly different than the mass of the peak with one ${}^{13}_{6}C$ substitution:

$$\mathcal{M}\ ({}^{12}C_2{}^{1}H_5{}^{2}H{}^{16}O) = 2(12.000000) + 5(1.007825) + 2.014102 + 15.994915 = 47.048142 \text{ amu}$$

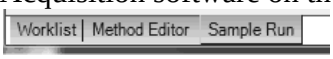
as opposed to 46.04522 with one ${}^{13}_{6}C$. These mass differences can be resolved on our instrument and can be observed on mass spectra with good signal to noise. The effect on the calculated average molar mass is negligible.

2. Other contributions to the M+2 abundance are ethanol molecules with two ${}^{13}_{6}C$ atoms or one ${}^{13}_{6}C$ and one ${}^{2}_{1}H$. However, the probability of a double substitution, such as these, is very low. For example, the probability of substituting one ${}^{13}_{6}C$ for one of the two possible C atoms in ethanol is 2(0.0107), while the probability of two ${}^{13}_{6}C$ substitutions is $(0.0107)^2$. The only major contribution to the M+2 peak is then from ${}^{18}_{8}O$ substitutions (in CHNO only molecules).

Literature Cited

1. Z. Szafran; R.M. Pike; M.M. Singh; *Microscale Inorganic Chemistry*, Wiley: New York, 1991.
2. Fernelius, W.C.; Blanch, J.E. *Inorg. Syn.* **1957**, *5*, 130.
3. Charles, R.G. *Inorg. Syn.* **1963**, *7*, 183.
4. 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.
5. 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.
6. http://www.webelements.com/webelements/elements/text/Cr/isot.html
7. http://www.colby.edu/chemistry/NMR/scripts/complexfind.html

DART-MS Instructions: Running a Sample

1. In the Data Acquisition software on the left display, click on the **Sample Run** tab on the lower-left: 

2. Type in a sample **Name**. Type in a **Comment** if you like. The **Position** and **Injection Volume** entries are not used with the DART source. Auto Increment allows you to do several runs without typing in a new file name each time. With the **Auto Increment** box checked, the operating system increments the number after the file name, each time a sample is run. Enter a file **Name**. If Auto Increment is checked, the file name must end with four integers. For example, "myspectrum0000.d". The data **Path** determines the directory the data is saved to. The data path is chosen using the browse button: [...]. For the General Chemistry lab, the data directory will be set using the path shown below.

When ready to start data collection, click on the Start button: ▶
The instrument status bar will first change to yellow: Instrument Not Ready:

Then the status bar changes to purple: Prerun. When the status bar changes to green, data collection begins and the system places a vertical red line on the **Chromatogram Plot** on the right display screen. [You can prepare the "Dip it" sampler, as described in the next step, while the instrument status is in Pre-run, but don't insert the sample until the status bar turns green.]

3. Dip a "Dip-it" sampler to a depth of ~ 1 cm in the sample solution. See Figure 1. For paste samples, cover the bottom of the glass capillary tube with a very thin film of the sample, up to 1 cm from the bottom.

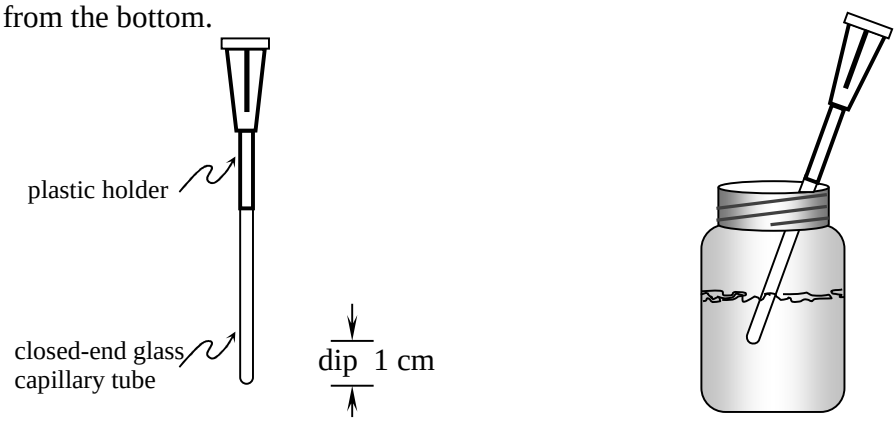


Figure 1: The "Dip-it" sampler is dipped into the sample to a depth of roughly 1 cm.

4. When the mass spectrometer status bar is green, carefully place the "Dip-it" sampler into the groove in the sample holder and then lower the sampler until it is seated in the holder, Figure 2.

No Force is Required to Insert the Sampler into the groove

Align the capillary tube vertically until the tube slips into the groove. No force will be required. Do not push on the glass capillary, the tube is quite fragile. With proper alignment, the tube will easily slip into the groove in the sample holder. Please don't touch the tip of the "Dip-it" to the white ceramic tubes that extend into the sampling region from the left and right.

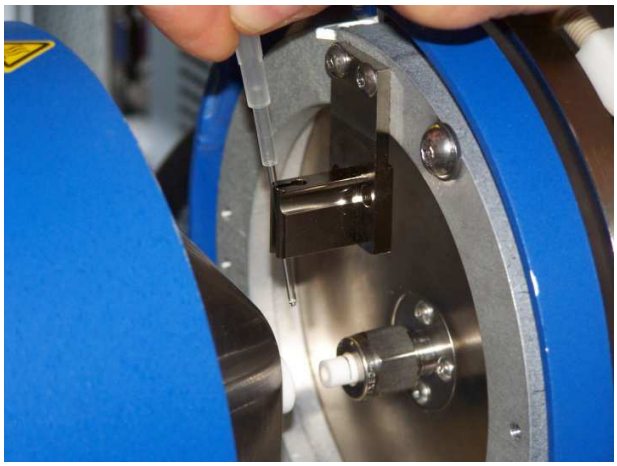


Figure 2: The "Dip-it" sampler easily slides into place. When properly seated, the tip of the sampler will be in the beam of the DART ionization source.

The DART source provides a jet of electronically excited He atoms into the source region. No voltages are present. The excited He atoms interact with water molecules in the air to produce protonated water clusters that subsequently transfer a proton to your sample.

5. Observe the mass spectral display on the right display screen. During data collection, one mass spectrum is recorded each second. The current mass spectrum is displayed in Profile and Centroid forms. The Profile form is a plot of the raw data with many points between each peak. The centroid form converts the raw data to a single histogram bar for each peak. You can observe either type of plot, they give the same information. The mass spectral plots are always scaled so that the tallest peak is full scale. Before your sample is introduced, background and noise peaks (and reference peaks if you are using a reference compound) will be displayed. Note the vertical scale on each plot. Before your sample is introduced, the full scale counts will be something like $1x10^4$. After sample introduction, a few seconds are required for the hot beam of gas in the source to evaporate your sample. Then the mass spectrum of your sample will appear on the Profile and Centroid displays. The mass spectrum of your sample will have just a few intense peaks, as opposed to the forest of peaks in the background. Your sample mass spectrum will probably be displayed using a full scale count rate of $1x10^5$ or higher.

The mass spectrum will last for just a few seconds.

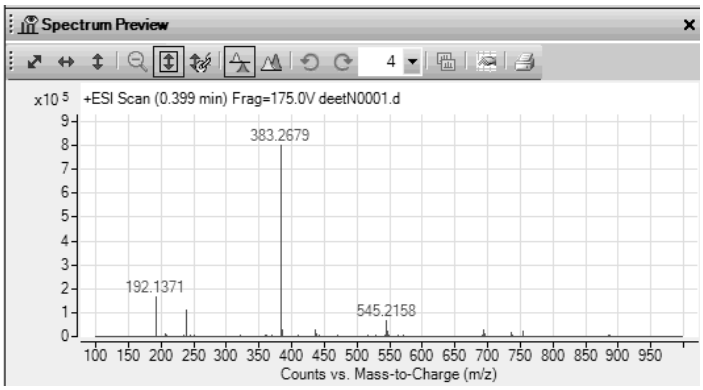
If you don't see the mass spectrum of your compound, you can redip your "Dip-it" and reinsert the sample, without stopping the sample run. The **Chromatogram Plot** window displays the

total integrated intensity under all the mass spectral peaks. This plot is usually not useful when using the DART source.

6. To analyze your spectrum, click on the **View Data** button on the Sample Run tab of the left display screen. The Qualitative Data Analysis application will start up and your data will be displayed. The **Chromatogram Results** in the top panel is a record of the total ion counts as a function of time. We need to determine from this plot when your sample mass spectrum is most intense. Click on the "Walking tool" in the icon bar that runs across the Chromatogram results window.

↑ "Walking tool"

Drag the mouse using the left mouse button across the Chromatogram Results window. The corresponding mass spectrum that corresponds to the position of the cursor is displayed in the Spectrum Preview panel at the bottom of the display window:

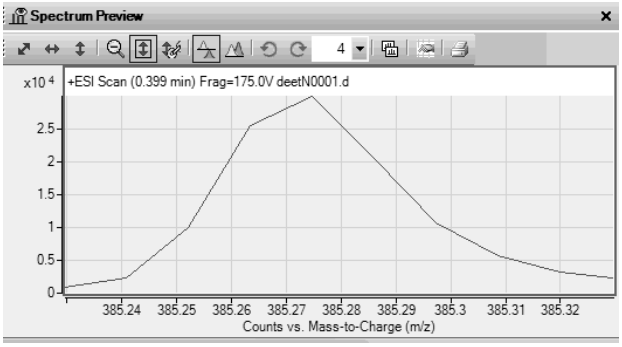


Drag the mouse over the full time range for your data until you find the spectrum of your compound that has the best signal to noise (example shown above: this example spectrum is of a commercial product that contains four major components. Only one of the major peaks will correspond to your desired product).

7. Zoom in around your peak of interest using the right mouse button.

Zooming in the data analysis application uses the RIGHT mouse button

Make sure that you can clearly see the MH^+, MH^++1, MH^++2, etc. peaks. Record the m/z values for each of these peaks. Print the spectrum by clicking on the printer icon on the icon bar at the top of the **Spectrum Preview** window. A print preview screen will open on the left display. If the plot is OK, click on the printer icon to make the print. Please see the notes below on determining data quality. If the m/z value is not labeled for your MH^++2 peak, you can expand around just that peak and read the m/z value from the horizontal scale:



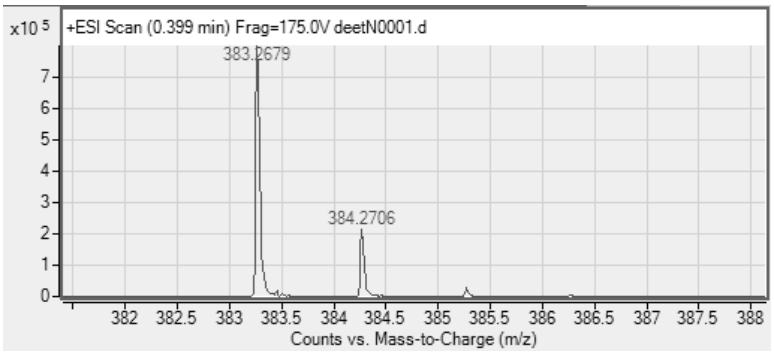
Estimate the center of the peak. You won't be able to read the mass to seven significant figures however.

8. After recording the m/z values for your peaks in your lab notebook, click the "go-away" ☒ box in the Data Analysis Application window. Answer "No" to the next two boxes that open. You don't want to save the changes that you have made to the original data file.

9. Remove your "Dip-it" sampler.

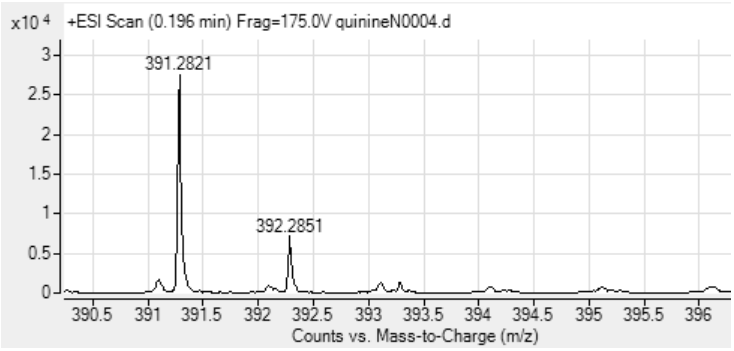
Data Quality: How do you tell the forest from the trees?

The output from every analytical instrument must be validated for usefulness. Noise has important effects for all instrumental measurements. At times it is difficult to decide if a particular signal is a real peak or part of the noise. The generally accepted rule is that to be valid, a peak must be ~3 times as high as the background noise. In other words the signal-to-noise ratio should be ~3 for a valid signal. The Profile spectrum below has sufficient signal-to-noise that even the MH^++3 is significant.



Excellent signal-to-noise

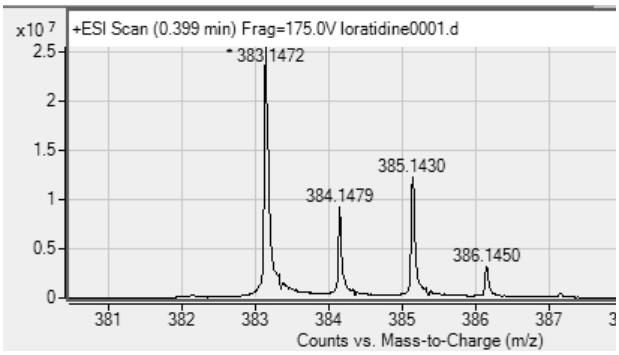
However, the following spectrum has insufficient signal-to-noise to accept even the MH^++2 peak.



Can't tell the forest from the trees for MH^++2

The purity of samples is always an issue. Samples are often mixtures of many components. For mixtures, the isotope cluster peaks for one component may overlap with the isotope cluster peaks for another component. How can you tell when overlap occurs?

Consider a molecule with only C, H, N, and O for example. The isotope cluster should have the MH^++2 peak much smaller than the MH^++1 peak, and the MH^++1 peak smaller than the MH^+ peak. If this expected order is not found, you should suspect the overlap of the isotope clusters from two different compounds. An example of this behavior is shown in the mass spectrum of loratidine (MH^+ at 383.1472 amu), below. The dihydro-form of loratidine (MH^+ at 385.1430) overlaps the MH^++2 peak of loratidine. If the ion contains Cr^{3+} the isotope pattern should resemble Figure 5. The MH^++3 peak should be smaller than the MH^++2 peak and the MH^++4 peak should be smaller than the MH^++3 peak. If the isotope cluster does not follow the expected pattern, overlap is present and you won't be able to record the mass of the MH^++3 and MH^++4 peaks. Just comment in your lab notebook that these peaks were obscured by another component in the sample.



Commercial sample of loratidine, the active ingredient in Claritin