

Synthesis of Metal Acetylacetonates

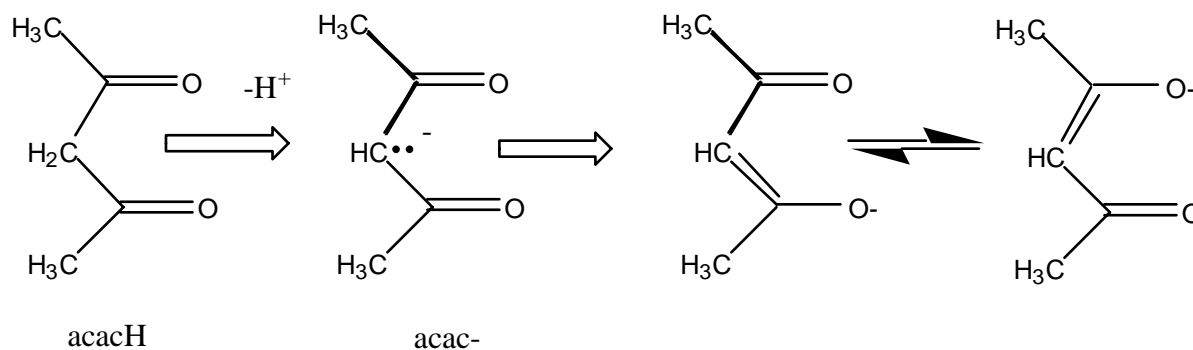
Preparation of Tris(2,4-pentanedionato)chromium(III)

Adapted from Z. Szafran; R.M. Pike; M.M. Singh; *Microscale Inorganic Chemistry*, Wiley: New York, 1991.

Introduction

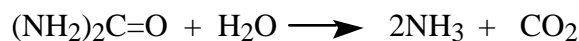
Coordination compounds (or complexes) consist of a central atom surrounded by various other atoms, ions, or small molecules (called ligands). There is only a tenuous distinction at best between coordination complexes and molecular compounds. The most common dividing line is that complexes have more ligands 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.

In the presence of base, 2,4-pentanedione, acacH , readily loses a proton to form the acetylacetonate anion, acac^- , as shown.



Hydrogen atoms on α -carbon atoms that are adjacent to carbonyl, $\text{C}=\text{O}$, groups are relatively acidic. The three different representations of the acetyl acetate anion are called resonance forms (they differ only in the location of the electrons).

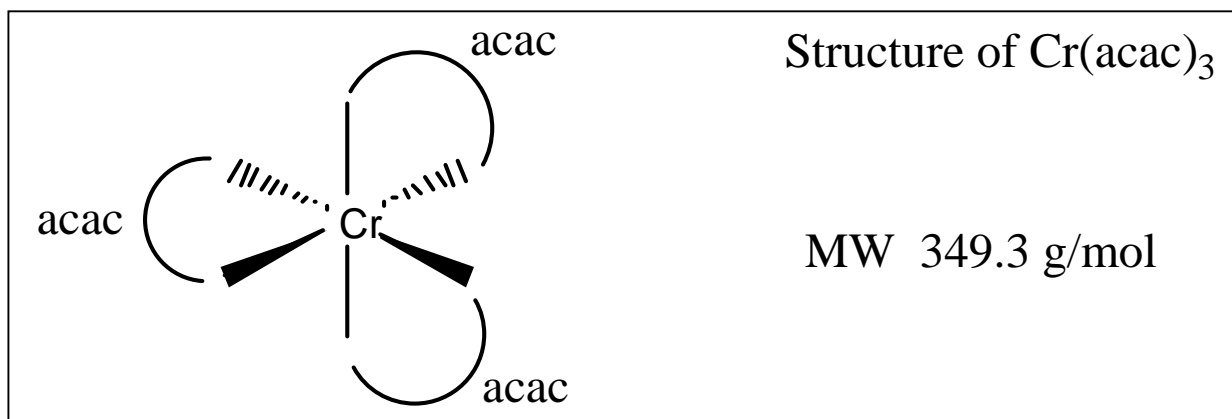
In this experiment, the basic solution needed to remove the proton from the acac is provided by generating ammonia, NH_3 , via the hydrolysis of urea:



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 $[M(\text{acac})_3]^{n+}$. 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.



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. 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

Required Equipment

Magnetic stirring hot plate, 10-mL Erlenmeyer flask, microwatch glass, magnetic stirring bar, 10-mL graduated cylinder, 2 mL syringe, evaporating dish, Gooch funnel, filter paper.

Time Required for Experiment: 2.5 h.

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.

<p>NOTE: The acacH should be dispensed in the HOOD.</p>
--

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 form as a crust at the surface of the reaction mixture.

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. Dry the product on a piece of filter paper, and determine the percentage yield (week two)

Characterization of Product

Take the melting point of the material (week two). Complete the second part of the lab, characterization by electrospray-MS (week one). You may use the metal complex finder program available on the class web page to analyze your MS data.

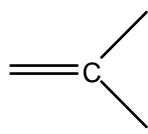
Simple Molecular Structure Calculations

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.

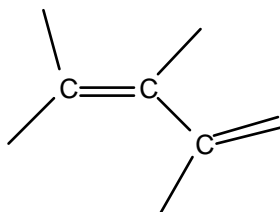
Building the Molecule:

- ⊖ 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)

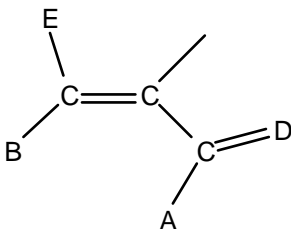


and click on the construction screen. The fragment should appear on the screen. You may use the Apple key-mouse combination to rotate the fragment.

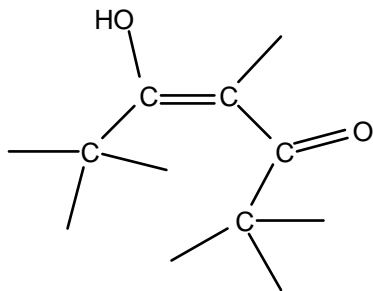
- ⊖ Now click on a single line (bond) and on a double line (double bond) to add to the fragment. It should look something like the picture below.



- ⊖ 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.

- ⊖ Use the delete tool to delete the hydrogen.
- ⊖ Finally, use the Minimize option to move atoms into a low energy position.
- ⊖ Save your molecule and exit the builder.
- ⊖ 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.
- ⊖ 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.
- ⊖ If you have time, try building a short segment of DNA using the builder. It will take about 15 nucleotides to make a clearly observable helix.

Report: Based on your LC-MS, percent yield, and melting point data were you successful at making the Cr(acac)₃ complex? Describe two reasonable changes that you could make to the experimental procedure to improve the yield of the synthesis.

References

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.