Lab 10 Prelab: Synthesis of Metal Acetylacetonates

CHEM 411 Week 7, Day 1-2

Microscale Inorganic Chemistry (MIC) pages 224-229
Groups of 2 students, 3-4 hours

Learning Objectives:

- Synthesize, isolate, recrystallize and characterize 3 metal acac complexes
- Write a clear and concise research paper describing this experiment in the style of the ACS journal *Inorganic Chemistry*
- Demonstrate proficiency in the Evans Method technique
- Calculate molar susceptibility and magnetic moment for paramagnetic species
- Analyze and compare magnetic moment values with literature references

Essential Lab Techniques:

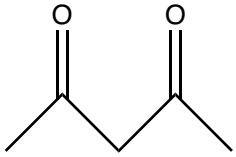
- Suction filtration
- IR
- ^{1}H NMR
- Evans Method
- Recrystallization
- ^{13}C NMR
- Use of the meltemp to determine melting point

Modifications from *MIC*:

- Please use the modified synthetic approach found in this document below.
- Recrystallization can be attempted for all products but is only required for $Cu(acac)_2$
- Any **potassium permanganate contaminated waste** must go in a separate waste container labeled **Oxidizer Waste**. Do not mix anything contaminated with $KMnO_4$ in other waste streams. This may cause oxidation of other metals.
- For all products obtain IR, NMR, and Melting Point.

I. Pertinent Information:

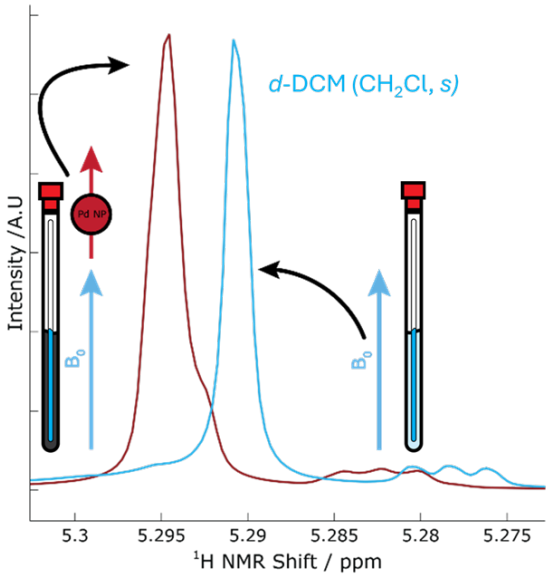
In this experiment we will be synthesizing metal complexes containing the chelating acetylacetonate ligand (abbreviated acac). The structure of the protonated form, acacH, is shown below. Think about how the deprotonated form of this molecule can bind to a metal center. To prepare for this lab, please read pages **224 - 229 in *Microscale Inorganic Chemistry (MIC).*** During your reading, take notes on the chemistry and how this complexation reaction works.



Once we synthesize the compounds, this lab allows us to explore magnetism and its determination through use of NMR with the Evans Method. This method involves measuring

the difference between two of the same reference peaks in the NMR; the magnetic compound will shift the reference peak. To prepare to use this method, please read pages **49 - 57** in ***Microscale Inorganic Chemistry (MIC).*** During your reading, take notes on the chemistry and how this method works.

To prepare your sample for the Evans Method, dissolve 5-10 mg of the desired compound (record the exact weight) in 0.5 mL of 10% *t*-butanol in $CDCl_3$. Transfer this solution to a regular NMR tube. Prepare a reference sample of solely 0.5 mL of 10% *t*-butanol in $CDCl_3$ in a regular NMR tube. If a paramagnetic species is present in the sample tube, it will cause a shift in the position of the *t*-butanol peak (0.9 to 2 ppm). There is an increased effective magnetic field when the analyte has a magnetic moment. We can calculate the molar susceptibility by measuring the difference between the peaks. The molar susceptibility is directly related to the magnetic moment of the analyte. A schematic is shown below illustrating the measurement with *d*-DCM used as the reference (this is slightly different than our technique, but the principle is still the same. You will first calculate the observed molar susceptibility (χ_{molar}^{obs} or χ_M) using the frequency difference in Hertz (Δf), the concentration of the sample *c* (in mol-dm^{-3}), and the frequency of the spectrometer (*f*) in Hz as shown in Equation 1. To obtain the effective magnetic moment of the species (μ_{eff}) you will use the simplified formula shown in Equation 2; be sure to use units of Kelvin for the temperature T. You will then compare your calculated value to the approximate (appr) magnetic moment (μ_{eff}) which is calculated using Equation 3; *n* is the number of unpaired electrons.



$$\chi_{Molar}^{obs} = \frac{6}{1000}\left(\frac{\Delta f}{c * f}\right) \qquad (1)$$

$$\mu_{eff} = 798\sqrt{\chi_M * T} \qquad (2)$$

$$\mu_{eff} = \sqrt{n(n+2)}\ (appr) \qquad (3)$$

Figure 1. (left) Schematic illustration of a paramagnetic shift of deuterated DCM due to the presence of a paramagnetic species. (right) Equations needed to calculate measured and approximate magnetic moment.

Throughout the semester we have been working on building writing skills with the goal of writing a cohesive research paper. This is the experiment you will use to draft and finalize a complete research paper. Like previous weeks, you will format it in the same way as the

ACS journal *Inorganic Chemistry*. Please read through https://publish.acs.org/publish/author_guidelines?coden=inocaj#manuscript_types to learn how to format your work. Also use the resources on Canvas to help guide your writing of this section.

Describe this experiment in your paper as though you were reporting doing this experiment for the first time. Include an abstract, an introduction, your synthetic approach, and a results and discussion section. You will first submit a draft of your research paper and receive feedback on how to improve for the final submission. This paper is worth ~18% of your grade so please plan accordingly. Use your past writing assignments, prelab questions, and lab results to aid in telling the story. Science can be challenging to write about but remember that you are telling a story and focus on the narrative!

II. Chemical Data Table:

In your lab notebook, construct a Chemical Data Table for this experiment. An example can be found below. Red X's mean that you don't need to fill in that part of the chart. You can print this page or scan it and attach it to your lab notebook.

Name	Structure	MW	MP/BP	Density	Quantity	mmol	Hazards	Comments
Chromium(III) Chloride Hexahydrate (10060-12-5)								
2,4-Pentanedione (acacH) (123-54-6)								
Urea (57-13-6)								
Manganese(II) Chloride Tetrahydrate (13446-34-9)								
Potassium Permanganate (7722-64-7)								

Name	Structure	MW	MP/BP	Density	Quantity	mmol	Hazards	Comments
Sodium Acetate Trihydrate (6131-90-4)								
Copper (II) Chloride Dihydrate (10125-13-0)								
Methanol (67-56-1)								
Tris(acac)chromium(III) (21679-31-2)								
Tris(acac)manganese(III) (14284-89-0)								
Bis(acac)copper (II) (13395-16-9)								

III. Synthetic Approach:

You will be synthesizing three complexes to compare: $Cr(acac)_3$, $Mn(acac)_3$, and $Cu(acac)_2$. The first two complexes are made according to the procedures in *MIC*. The third complex is made according to the synthetic approach described below.

Part A of the experiment in *MIC* is the synthesis of $Cr(acac)_3$. You should start the synthesis of Part A during the first lab period to allow sufficient time to isolate your product. During isolation of the solid you may notice a color change, but you may not see any deep maroon crystals precipitating out of solution. If this is the case, cool your sample in an ice bath. If solid still fails to precipitate, try to concentrate the sample or place it in the refrigerator until the next lab period.

While heating the solution in Part A (Cr), do Part B (Mn) or Part C (Cu) of the experiment.

In Part B of the *MIC* procedure, there is a typo in the CHEMICAL DATA chart for the quantity of sodium acetate trihydrate. The listed amount of 5.20 mg is incorrect. Instead, use **520 mg** of sodium acetate, in **two 260 mg portions**. The EXPERIMENTAL PROCEDURE instructions for the synthesis of $Mn(acac)_3$ do indicate the correct amount.

We are adding a Part C to this experiment, so you will also be synthesizing $Cu(acac)_2$. Please use the synthetic approach detailed below:

1. Dissolve 170 mg (1 mmol) of copper (II) chloride dihydrate in 1 mL of distilled water in a 10 mL Erlenmeyer flask. Stir the solution until completely dissolved.
2. In a separate 10 mL Erlenmeyer flask prepare an acetylacetonate solution (800 µL, 7.68 mmol) in 3.1 mL of methanol. Add this solution dropwise to the copper solution over a period of 20 minutes with stirring.
3. Prepare a sodium acetate solution (290 mg, 2.13 mmol) in 1.2 mL of DI water in a separate flask. Add this solution dropwise to the copper solution over a period of 5 minutes with rapid stirring.
4. Heat the reaction vessel to 80°C for 15 minutes maintaining rapid stirring. Monitor the temperature with a thermometer.
5. Cool the reaction vessel to room temperature then place in an ice bath.
6. Collect the blue-grey precipitate via suction filtration, wash with cold distilled water, and air dry for 15 minutes. Weigh and record the percentage yield.
7. Recrystallize the product in methanol.

In your lab notebook, write the procedure before performing the lab. This procedure should be concise but thorough enough so that you can set up and run the experiment without your lab manual. Drawing schematics is encouraged, especially for techniques you are not familiar with. This should be written in passive, past tense.

For more information on how to correctly set up a lab notebook read pages 31 - 34 in *MIC*.

IV. Prelab Questions:

1. Please draw the reaction for each synthesis. In doing so, identify the balanced redox half reactions. Note that the reactions may have multiple steps as acac-H needs to be deprotonated before bonding to the metal can occur.

2. Draw the *d*-orbital splitting diagrams for each product and include the appropriate number of electrons. If there more than one spin state exists, draw both. Speculate which is more likely. Are these spin states paramagnetic or diamagnetic?

3. Calculate the approximate magnetic moment for each complex using Equation 3. Use your diagrams from Question 2 to find *n*.

4. While $Cr(acac)_3$ and $Mn(acac)_3$ have similar formulas, their structures are very different. Please explain why. (Hint: Are any susceptible to distortion?)

5. Read pages 3-5 in the pdf provided on Canvas. How can we measure magnetism other than the Evans Method (EM)? Are these methods more or less sensitive than EM?

6. Draw the tautomerization of acac-H. How does this play a role in the ligand bonding mechanism?

V. Calculations:

1. Calculate the theoretical yield of $Cr(acac)_3$. Please write the molecular formula and show all work with units.

2. Calculate the theoretical yield of $Mn(acac)_3$. Please write the molecular formula and show all work with units.

3. Calculate the theoretical yield of $Cu(acac)_2$. Please write the molecular formula and show all work with units.

VI. Characterization:

For this experiment, characterization will include ^{1}H NMR and IR.

1. Make a table and predict the relevant NMR peaks and shifts for acac-H.

2. Make a table and predict the relevant IR vibrations for AcacH. Which vibrations may be impacted by metal bonding? What should happen to these vibrations (i.e will they shift)?