# INORGANIC CHEMISTRY CH 431
# LABORATORY INSTRUCTIONAL MANUAL INTRODUCTION

The University of Texas at Austin
Department of Chemistry

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8. Final Project

*Experiments 6 and 7 may be performed in a different order depending on the specific section you are in.*

Point breakdown for lab assignments

| **Assignment** | **Total Points** |
|---|---|
| **1.** SciFinder Literature search homework | 50 |
| **2.** Thermochromism experimental and results (truncated lab report) | 50 |
| **3.** Symmetry lab report (full report) | 100 |
| **4.** EPR lab report (full report) | 100 |
| **5.** Crystal field theory lab report (full report) | 100 |
| **6.** Molybdenum lab report (full report) | 100 |
| **7.** Ferrocene lab report (full report) | 100 |
| **8.** Final projects (powerpoint presentation) | 100 |

## Inorganic Chemistry (CH 431) Laboratory Manual

This manual details the experiments and procedures to be followed in the laboratory section of CH 431. Details for specific experiments will be provided to you as the semester proceeds. Read through it and use this manual as a guide for safety, grading, and the conducting of experiments during the semester. Please be advised that there may be instances when this manual may not be followed exactly due to space, time, or safety considerations. Your T.A. will advise you of any possible changes as well as answer any questions you may have about the course.

### Preparing for each experiment:

You are expected to be adequately prepared before coming to each of the laboratory class periods. This includes, but is not limited to, a thorough reading of the experiment that is to be performed. You should have a good idea of what it is you are going to do before coming to the laboratory class period. Please read the introduction and safety precautions that follow before coming to your first laboratory class period. The information contained in these sections concerns your safety and the inert nitrogen gas atmosphere apparatus. These instructions and safety precautions will apply to all of the experiments and they should be referred to periodically throughout this laboratory course.

**PRE-LAB:** A detailed pre-lab must be completed in your laboratory notebook prior to the lab period to ensure that you are ready to start the experiment once you get to the laboratory. This pre-lab will count for part of your lab report grade and will be evaluated by your TA prior to starting your experiment. An example laboratory notebook pre-lab page is provided for you on the CH 431 Canvas page. This pre-lab includes:

1) The balanced reaction equation for the experiment. Please include compound structures (drawn by hand using pen or using ChemDraw software).
2) A table that lists the compounds to be used and their amounts, equivalence, molecular weights, appearance, and hazards. This should follow the general template below:

| Reagent | Amount | Equivalence | Molecular Weight (g/mol) | Appearance | Hazards |
|---|---|---|---|---|---|
| Water | 40 mL | 13 | 18 | Clear liquid | N/A |
| $Me_2Cl_2Si$ | 20 mL | 1 | 129 | Clear liquid | Corrosive |
| NaCl | 2 g | 0.2 | 58 | White solid | N/A |

3) The complete procedure written into the lab notebook. It does not need to be copied verbatim, but well enough so that it can be used to complete the lab experiment.

**LAB NOTEBOOK**: Following the pre-lab section, all specific observations of your experiment should be recorded in your lab notebook. These include masses and volumes measured, observations of what is occurring in your reaction flask (bubbling? Color changes? Precipitate formation?), any spectroscopic measurements performed and their results, etc.

## Safety Guidelines

The following safety rules will be obeyed at all times by everyone in the laboratory. Failure to properly abide by these rules will be grounds for dismissal from the laboratory period and/or dropped from the course.

- Safety goggles will be worn at all times by all personnel in the laboratory. Anyone discovered in the laboratory not wearing safety goggles will be dismissed from the laboratory section. NO EXCUSES!
- No open-toed shoes or shorts will be allowed in the laboratory.
- All flasks used in the laboratory should be labeled, whether they are solvents, compounds, or starting materials. Any flasks or vials discovered without labels will be discarded by the T.A.
- Note the location and types of fire extinguishers (e.g., CO2, dry powder, etc.) that have been strategically placed around the laboratory room.
- Do not pour any organic solvents or wastes down the sink. Deposit all waste in the properly labeled containers.
- Research the hazards associated with the starting materials and products formed in the reaction before you attend lab. This information can be found by referring to the Material Safety Data Sheets (MSDS) located in the chemistry library.

## Attendance Policy

It is absolutely required that you attend each laboratory session and arrive on time. Late arrivals (unless previously OK'ed by your TA) will be penalized via deduction from lab report grades. There will be a 5 point penalty for every 10 minutes you are late to your laboratory session, with a maximum of 30 minutes. This penalty will be applied to the lab report of the experiment which you were late. If you are more than 30 minutes late, then you will not be allowed to complete that day's laboratory experiment. This policy will apply to both days of two week experiments.

All absences must be accompanied by proof of a legitimate reason for missing lab (doctor's note, etc.). If you must miss lab, then you must communicate with your TA the reason for your absence. If approved, you must make your best effort to make-up the experiment in another laboratory section in a timely manner. Failure to do so will result in a zero for that laboratory experiment.

**General Report Guidelines**
Each report will be worth 100 points. Attendance and a complete pre-lab are mandatory. Failure in either regard will have a negative effect on your report grade.

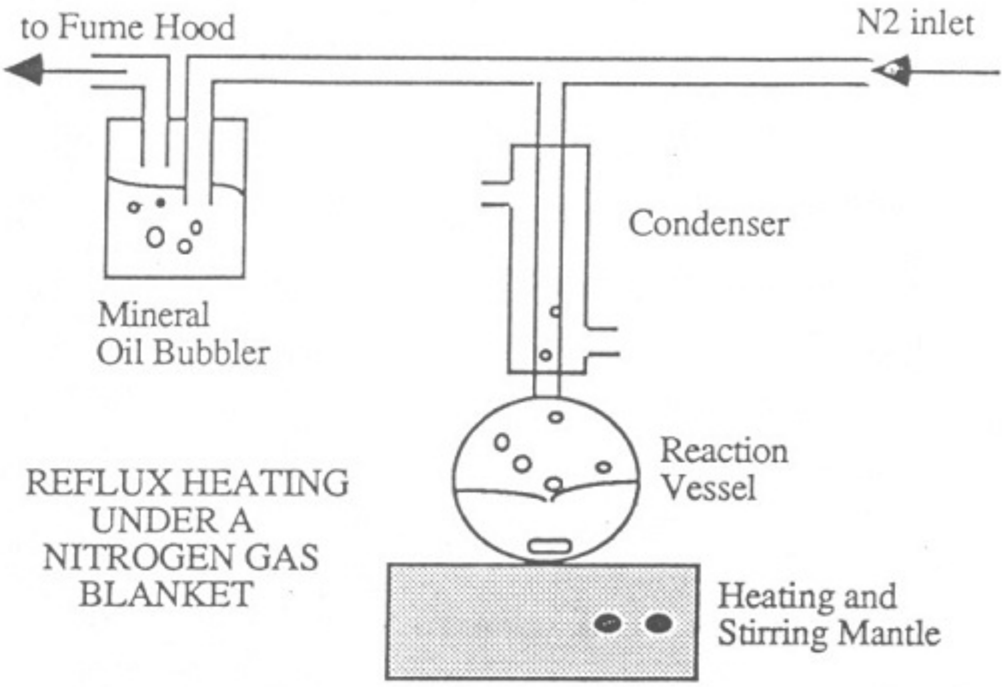
An electronic template will be provided for you to structure your report. Follow the template carefully, as a full explanation of the report requirements is contained in each section. In general, your reports should be structured in accordance with the ACS Style Guide, which can be found on reference in the chemistry library. Please use this reference as a guide for writing each report. For specific examples, please use the current peer reviewed literature as a guide (e.g. *]. Am. Chem. Soc.*, *Inorg. Chem.*, etc.).

An approximate point distribution follows, however this may change depending on the experiment. Any changes will be clarified by your TA and included in documents associated with an experiment. **Late lab reports will be subject to minus 10% per day they are late.**

| | |
|---|---|
| Pre-lab | 5 |
| Proper template use/formatting | 5 |
| Abstract | 5 |
| Introduction | 20-25 |
| Experimental method | 10-15 |
| Results & Discussion | 40-50 |
| Conclusion | 3-5 |
| References | 2-5 |
| Spectra and Notebooks Pages | 5-15 |

## Inert Atmosphere Arrangement

Most of today's inorganic chemistry involves the manipulation of compounds which are sensitive to air. This laboratory will use a nitrogen gas source for the inert atmosphere as shown in the following setup:



This is one of the most simple and yet effective techniques in working with air sensitive compounds. This system involves conducting the refluxing, distilling, and other steps in the synthesis of a compound, under a blanket of nitrogen gas. The key point to remember when using an inert atmosphere is that a slight positive pressure must be maintained. This means that a slow, steady flow of nitrogen gas should be visible through the bubbler, ensuring that any leaks will flow out of the system and not in to it.

It would be wise to become familiar in the handling air-sensitive materials *before* coming to the first lab period. The library should have this information.

## Experiment 1: SciFinder Exercise

This is an exercise that you must complete outside of lab this week. Your TA will hold office hours in case you have questions.

1) Follow the steps in “CH431_SciFinderGuide.pdf” posted on Piazza. This takes you through the basics of how to sign up for a SciFinder account and perform a structure search. Further guidance on how to use SciFinder can be found on YouTube: https://youtu.be/2s-KpZ5tYBs?list=PLB5yoyDBtQbWofS6c7g1riYrc2nD1Y3BR

2) Complete the “CH431_SciFinder_homework.docx” posted on Piazza. This assignment will be due in your designated lab section during Week 4 (September 12-16)

## Experiment 2: Preparation and Luminescent Thermochromism of Unusual Tetranuclear Copper(I)-Pyridine-Iodide Clusters

### Background

In this experiment you will synthesize a copper polynuclear cluster starting from common reagents and following a very simple procedure. These copper complexes form unique, tetranuclear, cubane-like clusters which are different than most common metal coordination complexs. You will then demonstrate a peculiar photophysical property of this material: the color of its luminescent emission varies sharply when it is cooled in liquid nitrogen versus when it is at room temperature (phenomenon called luminescent thermochromism).

**Safety Note:** Copper salts are harmful and dangerous for the environment. Acetonitrile and pyridine are highly flammable. Concentrated sulfuric acid is corrosive. Pyridine and many substituted pyridines are very toxic. The preparation should be carried out under a fumehood. Gloves and goggles should be worn at all times. The waste solutions MUST be collected in the waste containers provided.

**Pre-Lab Note:** Your pre-lab should be written in three parts for this lab. The first part will be the synthesis of the copper(I) iodide. The second part will be the synthesis of the $Cu_4I_4Py_4$ clusters and the third part will be the demonstration of the luminescent thermochromism. An example pre-lab write-up for a multi-step lab is provided for you on Canvas. If you have any questions about this pre-lab, don't hesitate to contact your TA for help.

### Procedure

### Synthesis of Copper(I) Iodide (CuI)

1. Dissolve $CuSO_4•5H_2O$ (6.5mmol) in 15 mL of water in a 50 mL beaker. Using a separate beaker, cool 20 mL of acetone to 0 $^oC$.
2. In a separate 100 ml beaker equipped with a stir bar, dissolve $Na_2SO_3$ (4.0 mmol) in 30 mL of water.
3. When all of the $Na_2SO_3$ has dissolved, slowly add concentrated sulfuric acid (4.0 mmol) to the solution. **CAUTION! A small amount of toxic $SO_2$ (g) will be evolved. Make sure to perform this step in a fume hood!**
4. To the 100 mL beaker, add the $CuSO_4$ solution.
5. In a separate 50 mL beaker, dissolve KI (6.5mmol) in 10 mL of water.
6. Once the solid is fully dissolved, add the KI solution to the solution in the 100 mL beaker. Precipitation of the CuI should be instantaneous but allow the solution to stir for 5 minutes to maximize your yield of CuI.
7. Collect the precipitate using vacuum filtration, then wash the precipitate twice with 100 mL of water each time, followed by two washes with the cold acetone.
8. Pull vacuum on the precipitate for 5 minutes to allow it to fully dry, then collect the precipitate and record the mass.

### Synthesis of the $Cu_4I_4Py_4$ Cluster

**Note:** For this portion, you will need to calculate how much KI, ascorbic acid, and pyridine (Py) you will need based on your yield from the CuI synthesis above. The equivalence (eq) for each reagent is provided for you below, with the CuI being your limiting reagent. If you are unsure about how to do this, please consult your TA for help.

1. In a 100 mL beaker, dissolve all of the synthesized CuI in 15 mL of acetonitrile.
2. While the solution is stirring, add ascorbic acid (0.02 eq) and potassium iodide (0.70 eq). This should result in a yellow solution.
3. In a 10 mL vial, dissolve pyridine (1.00 eq) in 5 mL of acetonitrile. **Pyridine has a very strong smell to it. Keep the solution in the fume hood as much as possible.**
4. Add the pyridine solution to the yellow CuI solution and allow it to stir for 5 minutes.
5. Add 25 mL of water to the solution to complete the precipitation of the $Cu_4I_4Py_4$ clusters.
6. Collect the solid via vacuum filtration then wash it with 50 mL of water twice followed by a single wash with 50 mL of ethanol.
7. Pull vacuum over the solid for 5 minutes to allow it to dry.
8. Collect the solid and record your yield.

### Demonstration of Luminescent Thermochromism

1. Add a spatula-tip of the $Cu_4I_4Py_4$ cluster to a 10 mL vial then add a few drops of water to form a suspension.
2. Expose the sample to long-wave UV light and record any observations you see.
3. Using tweezers, dip the vial in the Dewar flask containing liquid nitrogen for 20 seconds. **CAUTION! Liquid nitrogen is a cryogen and will cause burns with contact to your skin.**
4. Immediately expose the sample again to the UV light. Leave the vial in front of the UV light and allow it to warm back to room temperature. Record any observations that you see, take pictures if that is helpful.

**Lab Report:** For this report, you will only need to write an experimental section and a results and discussion section. Please also attach your lab notebook pages. The pre-lab is worth 15 points, the experimental section is worth 15 points, and the results & discussion section is worth 20 points.

### Reference

Parmeggiani, F.; Sacchetti, A. *J. Chem. Educ.* **2012**, *89*, 946.

## Experiment 3 - Cobalt Symmetry Lab

### Background

Group theory (symmetry and point groups) helps us understand the bonding and properties of molecules. In fact, the symmetry of a compound can help us predict its spectroscopic properties (NMR, IR, etc.). Conversely, the spectroscopic features of a compound can help us predict its symmetry and structure. In organic chemistry, for example, we can predict how many $^1$H NMR peaks different benzene derivatives have (benzene: 1 peak, bromobenzene: 3 peaks, 1,2-dibromobenzene: 2 peaks). This is all based on the symmetry of these compounds. This same method can be used for three-dimensional metal complexes. In this laboratory you will prepare two cobalt(III) complexes derived from two different tetradentate ligands, and the symmetries of these complexes will be explored using $^{13}$C nuclear magnetic resonance spectroscopy ($^{13}$C NMR). Figure 1 below shows the general structures of the two cobalt complexes you will by synthesizing, where X can be considered any general anion. Note the subtle difference in the naming of the ligands: trien (triethylenetetramine) versus tren (tris(2-aminoehtyl)amine).

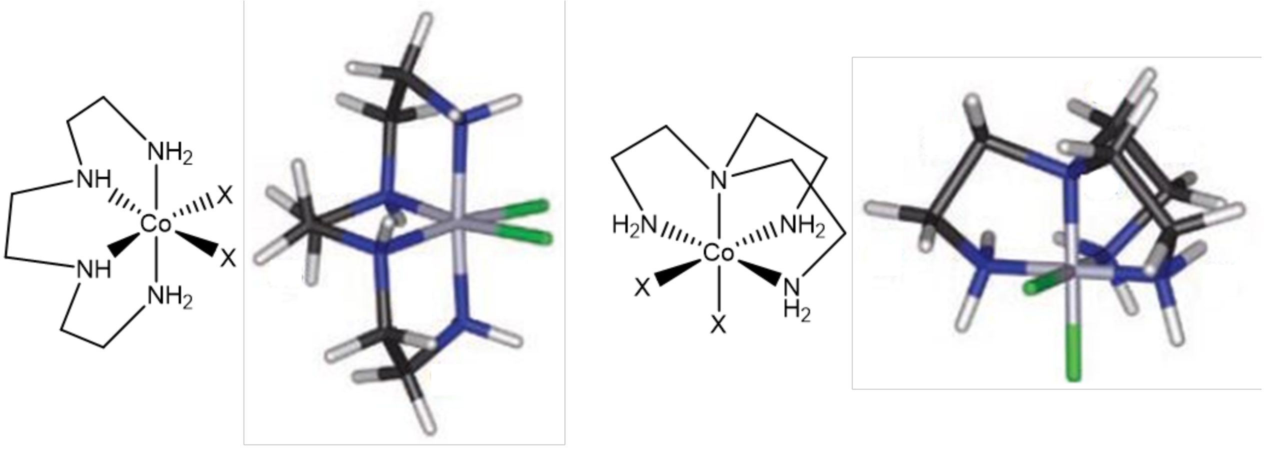


**Figure 1.** General structures of $[Co(trien)X_2]^+$ (left) and $[Co(tren)X_2]^+$ (right).

This experiment will be divided into two weeks. The first week will be devoted to the synthesis of $[Co(tren)(NO_2)_2]Cl$ and $[Co(trien)(NO_2)_2]Cl$. The second week will involve the purification of these two complexes. The experiment will be performed in groups of 4, where half of the group will make $[Co(tren)(NO_2)_2]Cl$ and the other half will make $[Co(trien)(NO_2)_2]Cl$. However, your lab report should include the procedure for both complexes.

**Safety Note:** Tris(2-aminoethyl)amine, triethylenetetramine hydrate, and 12M HCl are all corrosive. Sodium nitrite ($NaNO_2$) is a potential carcinogen. Care should be taken not to mix the $NaNO_2$ with the 12M HCl, as this releases toxic $NO_2$ gas.

## Procedure – Week 1

### Synthesis of [Co(tren)($NO_2$)$_2$]Cl

1. Dissolve $CoCl_2$•$6H_2O$ (6.98 mmol) in 2.27 mL of $H_2O$ in a 25 mL Schlenk flask.
2. To this solution, add $NaNO_2$ (24.06 mmol).
3. In a separate beaker, make 3.27 mL of 3.67 M HCl from 12.1M HCl. Submerge the beaker in a room temperature water bath while making the HCl solution. **Remember, always add acid to water!**
4. To the 3.67 M HCl solution that is still submerged in a room temperature water bath, slowly add tris(2-aminoethyl)amine (11.35 mmol) in a dropwise fashion.
5. Slowly add the tris(2-aminoethyl)amine solution to the $CoCl_2$•$6H_2O$/$NaNO_2$ solution.

*The set-up for steps 6-9 will be demonstrated by your TA. The purpose of these steps is to oxidize the Co(II) complex made in step 5 into the desired Co(III) complex.*

6. Place a septum pierced with a glass tube onto the top of the Schlenk flask, making sure the tube is submerged into the solution.
7. Attach the air aspirator to the sidearm of the Schlenk flask then clamp the flask onto a ring stand.
8. Cool the solution to 0 $^oC$ then pull air through the solution using the air aspirator for 90 minutes, keeping the solution at 0 $^oC$.
9. While the solution is aerating, cool 20 mL of water to 0 $^oC$.
10. Collect the yellow-brown precipitate by vacuum filtration.
11. Rinse the precipitate with ice-cold water three times.
12. Allow the precipitate to air dry for 1 week.

### Synthesis of [Co(trien)($NO_2$)$_2$]Cl

1. Dissolve $CoCl_2$•$6H_2O$ (6.98 mmol) in 2.27 mL of $H_2O$ in a 25 mL Schlenk flask.
2. To this solution, add $NaNO_2$ (24.06 mmol). Stir the solution until everything is fully dissolved then cool the solution to 0 $^oC$.
3. In a separate beaker, dissolve triethylenetetramine hydrate (1.66 g) in 2.27 mL of $H_2O$. Place this beaker in a room temperature water bath.
4. To the triethylenetetramine solution, CAREFULLY add 1 mL of 12.1M HCl in a dropwise fashion.
5. Slowly add the triethylenetetramine solution to the $CoCl_2$•$6H_2O$/$NaNO_2$ solution.

*The set-up for steps 6-9 will be demonstrated by your TA. The purpose of these steps is to oxidize the Co(II) complex made in step 5 into the desired Co(III) complex.*

6. Place a septum pierced with a glass tube onto the top of the Schlenk flask, making sure the tube is submerged into the solution.
7. Attach the air aspirator to the sidearm of the Schlenk flask then clamp the flask onto a ring stand. Re-submerge the Schlenk flask in a 0 $^oC$ bath.
8. Pull air through the solution using the air aspirator for 90 minutes, keeping the solution at 0 $^oC$.
9. While the solution is aerating, cool 20 mL of water to 0 $^oC$.
10. Collect the golden yellow precipitate by vacuum filtration.

11. Rinse the precipitate with ice-cold water three times.
12. Allow the precipitate to air dry for 1 week.

**Procedure – Week 2**

**Recrystallization of [Co(tren)($NO_2$)$_2$]Cl and [Co(trien)($NO_2$)$_2$]Cl**

**NOTE: The procedure to recrystallize both cobalt complexes is the same, but they must be performed in separate beakers.**

1. Heat 20 mL of $H_2O$ to ~70 $^oC$. At the same time, cool 20 mL of acetone and 10 mL of water to 0 $^oC$.
2. While the water is heating, collect the precipitate from week 1 and place in a beaker.
3. Fully dissolve the precipitate in the smallest amount of hot $H_2O$ as possible.
4. Allow the solution to cool to room temperature, then place the beaker in an ice bath for 20 minutes.
5. Collect the product by vacuum filtration.
6. Wash the precipitate with ice-cold water twice, then with ice-cold acetone three times.
7. Dry the product by pulling air through the Buchner funnel for 5 minutes.
8. Record the mass of the collected product.
9. A $^{13}C$ NMR spectrum of each complex will be provided for you.

**Discussion Questions**

1. In step three of the synthesis of [Co(trien)($NO_2$)$_2$]Cl, why was the beaker placed in a water bath?
2. In terms of $1s^2$ $2s^2$ etc., what is the electronic configuration of N? What is the electron configuration of Co? $Co^{2+}$? $Co^{3+}$?
3. List all the symmetry operations present in the [Co(trien)$X_2$]$^+$ and [Co(trien)$X_2$]$^+$ structures provided for you above. For simplicity, ignore the hydrogens in the structures.
4. What are the point groups of [Co(trien)$X_2$]$^+$ and [Co(trien)$X_2$]$^+$?
5. How do the $^{13}C$ NMR spectra of the two complexes synthesized in lab compare to each other? If they are different, explain why. If they are the same, also explain why.
6. What would the point group of the two complexes above be if one of the X ligands was different than the other (so [Co(trien)XL]$^+$ and [Co(trien)XL]$^+$)? How many peaks in the $^{13}C$ NMR would you expect to see of each complex?
7. Scifinder: Find another paper that uses [Co(tren)($NO_2$)$_2$]Cl (not the J Chem Ed paper referred to below). Give the citation and title of this paper.

**Reference**

McClure, M. *J. Chem. Ed.* **2008**, *85*, 420.

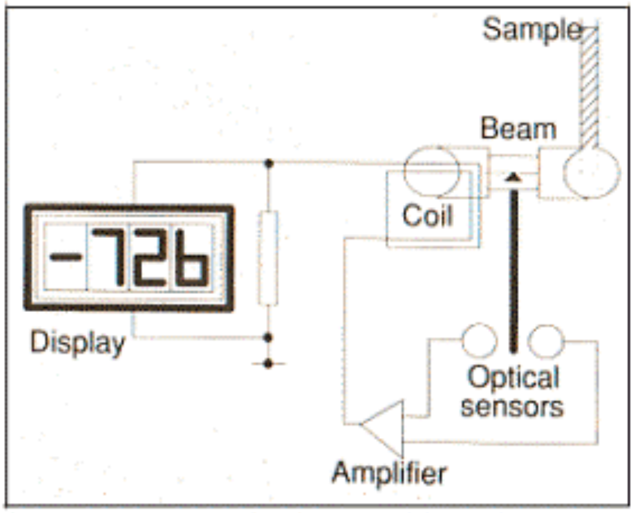
**Lab report**

You should write a full lab report for this experiments including an introduction (2-3 paragraphs approximately), experimental, results, discussion (including discussion questions), and conclusion.

## Experiment 4: Exploring paramagnetism in transition metal complexes

The relative energies of the d-orbitals in transition metal complexes impart this class of compounds with many of the interesting properties they exhibit including their vibrant colors and magnetic properties. More specifically, the electron occupancy of the d-orbitals is often responsible for these properties. A paramagnetic compound refers to a compound that contains unpaired electrons. Contrastingly, a diamagnetic compound refers to a compound in which all of the electrons are paired. The presence of unpaired electrons often dictates the spectroscopic studies allowed in the analysis of transition metal complexes. For example, the presence of unpaired electrons in a paramagnetic compound dramatically reduces relaxation times in NMR spectroscopy, resulting in broad signals that provide little information. Instead, these type of compounds may be studied by other techniques such as electron paramagnetic resonance (EPR) spectroscopy, super-quantum interference device (SQUID), or magnetic circular dichroism (MCD). These spectroscopic techniques in concert with each other can provide useful information about the electronic environment surrounding the metal center including the number of unpaired electrons, ligand interactions, and temperature-dependent paramagnetism.

Many of these same properties of paramagnetic compounds can also be studied by a simple benchtop analysis using an Evan's balance, a more modern version of the Guoy balance. Miessler, Fischer, and Tarr, section 10.1.2, has a nice discussion of paramagnetism and use of the Guoy method to measure magnetic susceptibility. The Evan's balance (see figure below) uses two magnets that will be affected by the presence of a paramagnetic species, causing a beam deflection that can then be detected by optical sensors. The number output from the instrument can then be converted to a magnetic susceptibility and effective magnetic moment using a series of equations that will be detailed below. For more information on how this instrument works, refer to this website:
http://www.sherwood-scientific.com/msb/msbindex.html



**Moving Magnetic Field and Null Point Detection**

**Figure 1.** Schematic of Evan's balance.

In this study, you will use an Evan’s balance to calculate a magnetic moment for three compounds (**Figure 2**), which can then be used to calculate the number of unpaired electrons that each compound has. This can further provide information on the coordination environment around the metal center. In this experiment, transition metal complexes containing vanadium, iron, and zinc centers will be synthesized and studied in order to compare experimental magnetic moments with predicted values and also determine the number of unpaired electrons in the compounds of interest.

Additionally, an EPR spectrum of the vanadium compound will be obtained to further show how paramagnetic compounds can be spectroscopically characterized. EPR (electron paramagnetic resonance spectroscopy), is a technique that probes systems with unpaired electrons. EPR is a technique similar to NMR spectroscopy, but utilizes the spin flip of electron $m_s$ values in contrast to the nuclear spin, or I, of atoms. These electron transitions are very low in energy, necessitating EPR measurements to be performed at liquid nitrogen or liquid helium temperatures (4 K). As a result of the small energy transitions, the signals associated with EPR transitions tend to be broad, and are instead reported as a derivative of the intensity. Similar to NMR, signals from unpaired electrons can be split by coupling of the electron spin with the nuclear spin of neighboring nuclei according to the equation 2NI+1. For example, the EPR signal of a single unpaired electron with 4 equivalent neighboring phosphorus atoms (I=1/2) will result in the singlet electron signal being split into a quintet because 2(4)(1/2)+1=5. In this experiment, the bis(acetylacetonato)oxovanadium(IV) compound provides a nice, easily interpretable EPR spectrum in which the 2NI+1 rule is evident. For more information, see this website: [http://epr.cm.utexas.edu/what-epr](http://epr.cm.utexas.edu/what-epr)

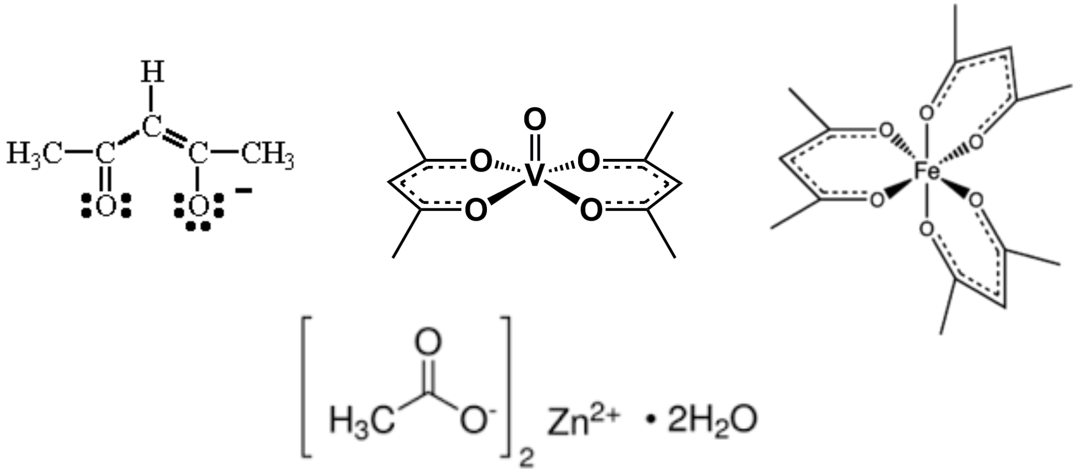


**Figure 2.** Compounds used in this experiment. Top left: acetylacetonate ligand. Top middle: vanadium complex. Top right: iron complex. Botton: zinc complex

**Procedure**

*Note: For greater time efficiency, these syntheses should be carried out simultaneously, with each partner preparing one complex.*

**Synthesis of bis(acetylacetonato)oxovanadium (IV)**

1. In a small beaker or flask (50 mL) with a magnetic stir bar, dissolve vanadyl sulfate (6.14 mmol) in 10 mL deionized water.
2. Add acetylacetone (14.60 mmol) and stir for 15 minutes.
3. Slowly add very small portions (roughly the size of a spatula tip) of solid sodium bicarbonate to the reaction mixture with vigorous stirring. Continue adding until the evolution of $CO_2$ ceases. The sodium bicarbonate will be used in excess, so it is not important to know exactly how much is added.
4. Stir the reaction for an additional 15 minutes.
5. Collect the solid by vacuum filtration. Wash the solid with 5 mL portions of cold DI water until all of the excess sodium bicarbonate has been removed. Then perform two washes with 5 mL portions of cold acetone, each.
6. Pull vacuum over the solid for 5 minutes to allow it to fully dry.
7. Collect an IR spectrum of the complex and prepare a sample for magnetic susceptibility measurements as outlined below. Your TA will provide you with the EPR spectrum of the complex.

**Synthesis of $Fe^{III}(acac)_3$**

1. In a small beaker (50 mL), dissolve iron (III) chloride hexahydrate (3.7 mmol) in approximately 20 mL deionized water with a magnetic stir bar.
2. Add 20% aqueous KOH solution until the pH of the solution is 8
3. Let the precipitate settle, and decant the colorless supernatant. Note: it may be necessary to add additional deionized water in order to decant the solution
4. Vacuum filter the precipitate and wash two times with 10 mL cold water
5. Transfer the precipitate to a new beaker (50 mL) and add acetylacetone (12.2 mmol) mixing thoroughly with a glass rod to create a slurry
6. Let the reaction stand for 30 minutes at room temperature with occasional stirring, then cool in a ice bath for 15 minutes
7. Vacuum filter the product and sufficiently dry by pulling air over the product
8. Collect an IR spectrum of the complex and prepare a sample for magnetic susceptibility measurements as outlined below.

**Benchtop Magnetic Susceptibility Analysis**

*You should perform this analysis with the vanadium and iron compounds you synthesized, as well as with zinc acetate dihydrate ($Zn(CH_3COO)_2\bullet 2H_2O$) (three compounds total). Make sure to record all values for all three complexes!*

1. Place an empty tube into the balance and obtain the reading, which should be recorded as $R_0$ in your notebook.
2. Measure approximately 0.1000 g of the metal complex of interest and record the exact mass in your lab notebook as “m”
3. Transfer the metal complex into one of the magnetic susceptibility tubes and record the length of the sample (in cm) in the tube in your lab notebook as “L”
4. Place the tube in the balance and obtain the reading, which should be recorded as “R” in your lab notebook
5. Obtain the calibration constant from your TA, this should be recorded as “C” in your lab notebook.

**Calculation Guide:**

The reading from the magnetic susceptibility balance enables you to directly calculate the gram susceptibility of a compound using **equation 1** below:

$$\chi_g = \frac{CL(R - R_0)}{10^9 m} \tag{1}$$

Where,

C = calibration constant of the balance

L= length of sample in cm (1>1.5cm.)

m = mass of sample in gm

R = balance reading for sample in tube

Ro = balance reading for empty tube

Note: The calibration constant (C) and the balance reading for the empty tube will be provided for you $R_0$.

The gram susceptibility can be converted to a molar susceptibility by multiplying by the molar mass of the metal complex as shown in **equation 2**:

$$\chi_m = \chi_g \times M \tag{2}$$

Finally, the experimental magnetic moment, or $\mu_{eff}$, can be calculated by **equation 3**:

$$\mu_{eff} = 2.828\sqrt{\chi_m \times T} \tag{3}$$

**Discussion Questions:**

1. Give the point group and predict the number of unpaired electrons for the V(IV), Fe(III), and Zn(II) compounds.

2. What are the theoretical spin-only $\mu_{eff}$ for each compound? What are the experimental values you obtained for each compound? Why might these values be different?

3. Predict the EPR spectrum of the vanadium complex. How many lines do you observe in the experimental spectrum?

4. What is the role of sodium bicarbonate in the synthesis of bis(acetylacetonato)oxovanadium(IV)? How does potassium hydroxide function differently than sodium bicarbonate in the synthesis of $Fe(acac)_3$?

5. SciFinder: What is the most recent journal article (not patent) to use bis(acetylacetonato)oxovanadium(IV) as a reactant or reagent? Provide the title of the article, the authors, and the journal in which the article can be found. Make sure to provide the proper citation for this article in your references section.

**Lab report requirements:** A full lab report will be required for this experiment. Please show your work for the calculations described in the "Calculations Guide" (above) as an appendix at the end of your report. These can be written out by hand or typed.

**References:**

1. Ebsworth, E. V. A.; Rankin, D. W. H.; Cradock, S., Chapter 3: Electron Spin and Nuclear Quadrupole Resonance Spectroscopy. In *Structural Methods in Inorganic Chemistry*, Second ed.; CRC Press: Boca Raton, 1991; pp 115-141.

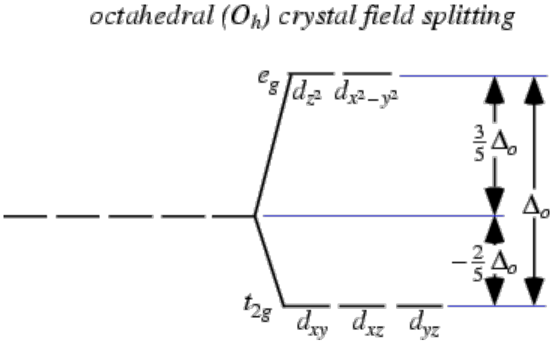
2. Choudhary, B. M.; et. al. Process for the preparation of metal acetylacetonates. U.S. Patent 2,004,056,737, July 8, 2004.

3. Sherwood Scientific. Magnetic Susceptibility Balance. http://www.sherwood-scientific.com/msb/msbindex.html. (accessed on Oct. 3, 2016).

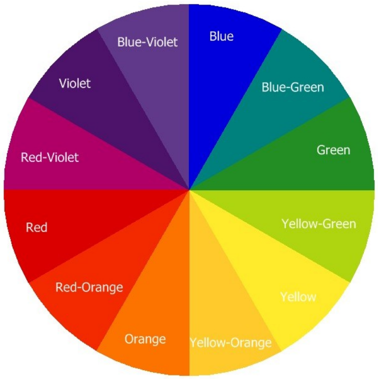
## Experiment 5 – Coordination Complexes of Cobalt and the Spectrochemical Series

### Background

As discussed in class, crystal field theory predicts that the degeneracy of the valence d-orbitals of a transition metal will be broken by the electrostatic field created by coordinated ligands. The symmetry of the complex and the ligand field splitting energy (a measure of field strength) determines the energy differences between the valence d-orbitals in a transition metal complex. In an octahedral field, these are the $t_{2g}$ and $e_g$ symmetry sets of orbitals, as shown below.



In transition metal complexes, these energy differences fall within the ultra-violet and visible ranges, giving the often intense colors associated with transition metal chemistry. Thus, UV/Vis spectroscopy (a form of electronic spectroscopy) can be used to directly measure the energy differences between these electronic states. The observed color of an object is due to perception of the light reflected (i.e. not absorbed) by it. Thus, the color of a substance is the compliment of the color absorbed by it, which can be deduced using the color wheel below. For example, if a compound appears red, it is absorbing primarily green light.



In this experiment, you will be empirically determining a spectrochemical series for several ligands discussed in lecture ($Cl^-$, $H_2O$, $ONO^-$, $NO_2^-$, $NH_3$) based upon the UV/Vis spectra of a series of analogous high-spin pseudo-octahedral Co(III) complexes. Each group will synthesize a different complex and share their spectrum with the rest of the class. A comparison of these collected spectra will allow for determination of the relative field strengths of the ligands.

**Topics to include in your Introduction:** Background information on coordination compounds, ligand field strengths, and spectrochemical series; definition and theory behind UV-Vis spectroscopy.

**Safety Note:** Concentrated hydrochloric acid, aqueous ammonia, and hydrogen peroxide are extremely caustic, causing serious burns on contact. In addition, concentrated hydrochloric acid and ammonia produce significant amounts of caustic vapors. They must be handled with due care in the fume hood.

**Prelab:** There is no prelab for this experiment. However, your observations from the experiment should still be recorded in your laboratory notebook.

**Lab Report:** You will only need to write an experimental for the complex that you make. However, you are still required to discuss all of the complexes in the rest of the lab report.

## Procedure

### Synthesis of $[Co(NH_3)_5Cl]Cl_2$

1. In a fume hood, add 5.0 g ammonium chloride to 30 mL concentrated aqueous ammonia in a 250 mL beaker. (The combination of $NH_4Cl$ and $NH_3$ (aq.) guarantees a large excess of the $NH_3$ ligand.)

2. Stir the ammonium chloride solution vigorously while adding 10.0 g $CoCl_2 \cdot 6 H_2O$. Next, add dropwise 8 mL 30% hydrogen peroxide to the brown slurry. Note: Care should be taken to avoid excessive effervescence in this exothermic reaction. (If the reaction shows signs of excessive effervescence, turning off the magnetic stirrer momentarily will usually prevent overflow of the solution.)

3. When the effervescence has ceased, add 30 mL concentrated HCl with continuous stirring, pouring about 1 - 2 mL at a time. Cover the beaker with a watch glass and heat the solution to 60 °C while stirring. Hold this temperature and continue stirring for 15 min (this incubation period is necessary to allow complete displacement of all aquo ligands).

4. Add 25 mL deionized water and allow the solution to cool to room temperature. Collect the purple product by vacuum filtration. Wash once with 15 mL ice cold deionized water and twice with 15 mL ice cold ethanol (the solutions must be cold to prevent undue loss of product by redissolving).

5. Pull vacuum over the product for 5 minutes to allow it to dry. Transfer the product to a large watch glass then get the TA to help you place the product on the watch glass in the oven for several minutes to help speed up the drying of the product. Record the mass of the final product.

## Synthesis of $[Co(NH_3)_5(H_2O)]Cl_3$

1. Add 2.0 g $[Co(NH_3)_5Cl]Cl_2$ to a 250 mL beaker, followed by 25 mL $H_2O$ and 5 mL concentrated aqueous ammonia. (Using aqueous ammonia as the solvent prevents displacement of the $NH_3$ ligands.)

2. Cover the beaker with a watch glass and heat to 100 $^oC$ while stirring on a hot plate in the hood until the compound fully dissolves to form a dark merlot colored solution.

3. Cool the solution in an ice bath. Add concentrated HCl dropwise (~20 mL) with stirring until a red precipitate appears and a fog (ammonium chloride vapor) no longer forms above the solution. (Under these conditions, ligand exchange between $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_3)_5(H_2O)]^{3+}$ is very rapid. The aquo trichloride complex is isolated by this procedure, because it is much less soluble than the chloro dichloride.)

4. Cool the reaction mixture in an ice bath, then collect the product by vacuum filtration. Wash the bright red solid twice with 15 mL ethanol and then pull vacuum over the product for 5 minutes to allow it to dry. Record the mass of your final product.

## Synthesis of $[Co(NH_3)_5ONO]Cl_2$

1. Add 1.5 g $[Co(NH_3)_5Cl]Cl_2$, 20 mL $H_2O$, and 10 mL concentrated aqueous ammonia to a 250 mL beaker. Cover with a watch glass and heat to 100 $^oC$ in the fume hood while stirring until a merlot colored solution is formed.

2. Cool the solution in an ice bath and add 6 M HCl slowly while stirring until the solution is neutral to litmus. (Approximately 15-20 mL. The use of 6 M HCl rather than concentrated HCl dilutes the solution sufficiently so that the aquo salt will not precipitate).

3. Add 1.5 g sodium nitrite followed by 2 mL 6 M HCl. Allow the reaction mixture to stand in an ice bath for at least an hour to precipitate the product.

4. Collect the salmon colored product by vacuum filtration. Wash the product with 15 mL ice-cold water then 15 mL ice-cold ethanol. Pull vacuum over the product for 5 minutes to allow it to dry. Record the mass of your final product.

## Synthesis of $[Co(NH_3)_5NO_2]Cl_2$

1. Add 1.5 g $[Co(NH_3)_5Cl]Cl_2$, 20 mL $H_2O$, and 10 mL concentrated aqueous ammonia to a 250 mL beaker. Cover with a watch glass and heat to 100 $^{o}$C in the fume hood while stirring until a merlot colored solution is formed.

2. Cool the solution to room temperature in a room temperature water bath and add 6 M HCl slowly while stirring until the solution is slightly acidic to litmus. (Approximately 15-20 mL. The use of 6 M HCl rather than concentrated HCl dilutes the solution sufficiently so that the aquo salt will not precipitate).

3. Add 2.0 g sodium nitrite and heat covered until all of the initial red precipitate dissolves. Cool the solution in an ice bath and slowly add 20 mL concentrated HCl while stirring. Allow the reaction mixture to stand in the ice bath until precipitation of the product is complete.

4. Collect the burnt orange product by vacuum filtration. Wash the product with 15 mL ice-cold water then 15 mL ice-cold ethanol. Pull vacuum over the product for 5 minutes to allow it to dry then record the mass.

## Synthesis of $[Co(NH_3)_6]Cl_3$

1. Add 5.0 g $CoCl_2 \cdot 6H_2O$ and 3.3 g $NH_4Cl$ to 30 mL water in a 250-mL beaker. In the hood, add 1.0 g activated charcoal and 45 mL concentrated aqueous ammonia.

2. Cool the brown slurry in an ice bath and add 4 mL 30% $H_2O_2$ drop wise over several minutes. Do not allow the temperature to rise above 10 °C.

3. When effervescence has ceased, heat the resulting red-brown solution to 60 °C and maintain this temperature for 30 min. (The incubation is needed to ensure complete displacement of all aquo ligands.)

4. Cool the mixture in an ice bath; the product will precipitate from the solution. Collect the product and the charcoal by filtration. (Recrystallization will be necessary to separate the product from the activated charcoal.)

5. Place the solid in a 250 mL beaker and add 40 mL water along with 1 mL concentrated HCl. Heat the mixture to 70 °C then remove the activated charcoal by vacuum filtration by filtering the solution while it is still hot. Transfer the collected filtrate to a new beaker.

6. Place the filtrate in an ice bath in the hood and add 1 mL concentrated HCl. Collect the orange solid by vacuum filtration. Wash the product with 15 mL ice-

cold ethanol. Pull vacuum over the solid for 5 minutes to allow it to dry then record the mass.

## Preparation of UV-Vis Samples

1. In a beaker, dissolve 0.1 g of your product in 40 mL of $H_2O$.

2. Fill a cuvette ¾ of the way full with the aqueous solution of your product.

*Your TA will help you collect the absorption spectrum for your product.*

3. Collect the absorption spectrum of your product over the 400 nm – 650 nm range. Your TA will show you how to use the ultraviolet-visible spectrophotometer. Once the spectrum of each product has been recorded, your TA will provide you with the final overlayed spectrum of the products.

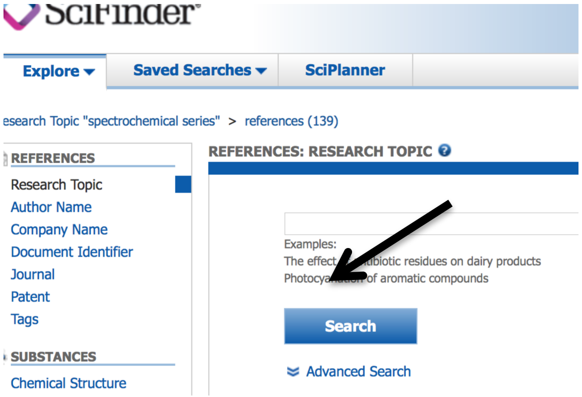
## Discussion Questions

1. Discuss the colors of the products with reference to their wavelength of maximum absorbance. It would be helpful to reference the color wheel shown at the beginning of the procedure for this question.

2. From this information, compare the relative field strengths of the ligands (chloride, aquo, nitrito, nitro, and ammine) and construct a spectrochemical series. What ligand induces the largest $\Delta_o$? What ligand induces the smallest $\Delta_o$?

3. Give the electronic configuration for the cobalt ions in these complexes, along with the metal oxidation state and electron count. Calculate the ligand field stabilization energy (LFSE) for both the low spin and high spin electronic configurations. Calculate the $\mu_s$ (spin only magnetic moment) for both the low spin and high spin configurations.

**4.** In Scifinder, do a “Research Topic” search for “spectrochemical series” (see below). Only look at references that contain “spectrochemical series” as entered. What is the oldest reference you find for this topic? Make sure to use the proper citation format for this reference.



## References

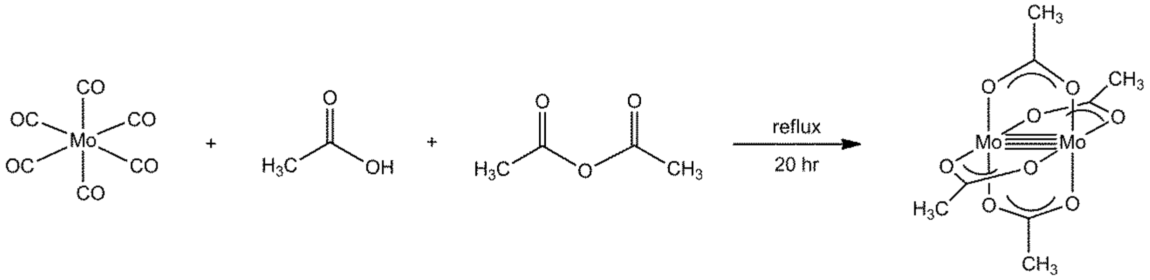
1. Williams, G. M.; Olmstead, J.; Breska, A. P. *J. Chem. Ed.,* **1989,** *66,* 1043.

2. Walton, H. F.; *Inorganic Preparations;* Latimer, W. M., Ed.; Prentice Hall: Englewood Cliffs, NJ, 1948; pp 92-93.

## Experiment 6 - Dimolybdenum Tetraacetate $Mo_2(OAc)_4$

### Background

Dimolybdenum tetracetate was originally synthesized by Wilkinson and coworkers in 1964 with a proposed structure[1] which was determined by crystal x-ray diffraction in 1965 by Lawton and Mason.[2] The product was determined to be moisture sensitive thus the reagents needed to be treated under anhydrous conditions (dry solvent, nitrogen atmosphere) to obtain an optimum yield. The decomposition occurs slowly over several days to weeks at room temperature.[3]



Molybdenum hexacarbonyl is refluxed in a solution of neat acetic acid and a small amount of acetic anhydride under nitrogen. After approximately 20 hours the solution is allowed to cool and yellow needle-like crystals are filtered, washed and dried. This Mo dimer can be used as a starting material for many Mo-Mo compounds.[4]

Metal-metal bonding has been intensely studied by Cotton and Wilkinson for several decades. Molybdenum is known for having multiply-bonded $M_2$ units than any other metal. The total number of $Mo_2$ compounds is over 1100.[5] In this experiment a quadruple Mo-Mo bond is formed. The overlap of *d*-orbitals is fundamental in understanding the geometry of the product. You will need to demonstrate an understanding of *d*-orbitals and their overlap.[6]

**$Mo(CO)_6$ has six carbonyls coordinated to it and has a simple and characteristic infrared (IR) spectrum. A copy of this spectrum will be provided for you and you will use a sample of your product to take an IR of $Mo_2(OAc)_4$. These two IRs can be compared, especially the intensity and energies of the C-O stretching frequencies. *Hint:* Are there other organic bonds that will be displayed in the IR for $Mo_2(OAc)_4$?**

**Topics to include in your Introduction:** Background information on molybdenum; background information on multiple metal-metal bonds; definition and theory behind IR spectroscopy.

**Safety Note:** The metal carbonyl, $Mo(CO)_6$, is extremely toxic. Avoid contact with your skin. It will be handed to you in 1.0 gram aliquots by your TA. This experiment should be carried out in a fume hood, under an inert nitrogen atmosphere.

## Procedure – Day 1

1. Place acetic acid (1.75 mol) and acetic anhydride (0.11 mol) in a 250 mL round bottom flask equipped with a stir bar.

2. Degas the mixture for 5 minutes with a gentle flow of nitrogen and stopper the flask with a rubber septum.

3. In one step, the TA will quickly add the molybdenum hexacarbonyl (3.79 mmol). The student will then attach a reflux condenser equipped with a nitrogen gas inlet (make sure there is a good seal between the reflux condenser and the round bottom flask). Maintain a steady flow of nitrogen to the reflux condenser in order to keep the reaction under an inert atmosphere.

4. Heat the reaction mixture until the temperature reads 180 °C on the thermometer (the TA will provide you with a high temperature thermometer). In the beginning stages of the reflux and reaction, some of the metal carbonyl will sublime into the condenser. Minimize this amount by carefully controlling the reaction temperature. You may leave once the thermometer reads 180 ± 5 °C consistently for 10 minutes.

5. Reflux the mixture for 20 hours. Your TA will return to turn off the oil baths and reflux condensers.

## Procedure – Day 2

1. A crystalline material having the appearance of yellow needles should have fallen out of the reaction mixture.

2. Vacuum filter the brownish slurry to collect the yellow needle crystals on the filter paper. If the crystalline material seems to be clinging to the sides of the round bottom flask, rinse the flask out with a small portion of ethanol. It may take several of these ethanol rinses to completely remove all of the yellow needle crystals.

3. Wash the crystals with two 40 mL portions of ethanol followed by two 40 mL portions of diethyl ether. Dry the crystals by drawing air over the filter paper using the vacuum filtration apparatus for 5 minutes.

4. Record the mass of the collected product then obtain an IR spectrum of your product. Please refer to Canvas for the IR spectrum of the starting material, $Mo(CO)_6$.

## Discussion Questions

1. Give the point groups and draw the structures of the starting material and product.

2. How many d-electrons do $Mo(CO)_6$ and $Mo_2(OAc)_4$ each have? What are the metal oxidation states for $Mo(CO)_6$ and $Mo_2(OAc)_4$?

3. Discuss the metal-metal bonding of the compound you have made in terms of the specific ($d_{xz,}$ $d_{yz}$, etc.) d-orbital overlaps. Which orbital(s) are used to bond the acetate ligands? Which orbital(s) are involved in the Mo-Mo bond? Include a diagram of all of the molecular orbitals involved.

4. What is a delta bond and how does it compare to sigma and pi bonds (geometry, energy, etc.)?

5. What was the role of acetic anhydride in this reaction?

6. SciFinder: Draw the structure of the final product into SciFinder but replace Mo with M (M stands for any metal), draw only a single bond between M and M, and use the locking tool to lock all of the atoms in the acetate ligands. Search for only conventional structures. List the three most common metals found in these structures, in order of most common to least common.

## References

1. Stephenson, T. A.; Bannister, E.; Wilkinson, G. *J. Chem. Soc.,* **1964**, 2538.

2. Lawton, D.; Mason, R. *J. Am. Chem. Soc.*, **1965**, *87*, 921.

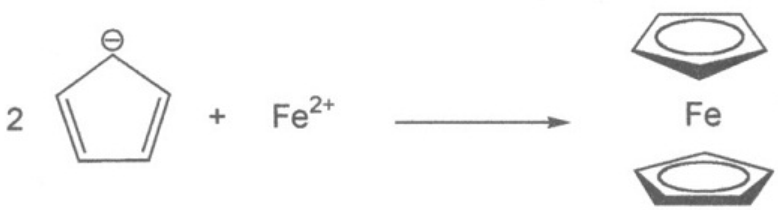
3. *Inorganic Syntheses* **1972**, *13*, 88.

4. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry,* 5th Ed.; Wiley: New York, 1988; pp 840-843.

5. Cotton, F. A. *Multiple Bonds Between Metal Atoms*; Springer: New York, 2006; Ch 4.

6. Shriver, D. F.; Atkins, P.; Langford, C. H. *Inorganic Chemistry,* 2nd Ed.; Freeman: New York, 1994; Ch 1, 24.

## Experiment 7 - Preparation and Purification of Ferrocene

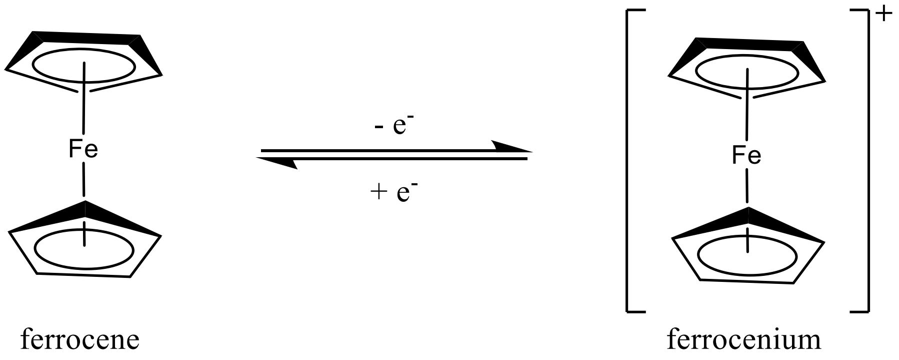


### Background

Ferrocene was synthesized originally by Paulson in an attempt to prepare the aromatic molecule fulvalene. Its precise nature was described later by Wilkinson and Woodward. Ferrocene is an organometallic compound, comprising direct bonds between a metal, in this case iron, and an organic group. The compound is remarkably stable for an organometallic compound due to its electron configuration. Any organometallic compound containing a transition metal that has 18 electrons in its outer shell has an electron configuration equivalent to a noble gas and so is reluctant to participate in reactions. Ferrocene is an 18-electron compound and so is relatively stable.

Ferrocene is a member of the family of metallocenes, compounds with the general formula $M(C_5H_5)_2$, of which there are many examples. These compounds have a number of features in common, the most interesting of which are their "sandwich" structure and their fluxional behavior. The cyclopentadienyl rings rotate rapidly about the axis defined by the center of the metal and the centroid of the ring, giving rise to an $^{I}H$ NMR spectrum that shows equivalence for all ten protons at ambient temperatures. Ferrocene has been applied in many areas of contemporary technology, including biological chemistry, and is commonly used as a reference for electrochemistry due to its characteristic, highly reversible Fe(II/III) couple.

In this experiment, we will prepare ferrocene, purify it, and examine its electrochemical properties. The electrochemical properties that you will specifically explore are the voltages (versus a $Ag/AgNO_3$ reference electrode) at which the oxidation of ferrocene occurs, the reduction of ferrocenium (the oxidized version of ferrocene) occurs, and the $E_{1/2}$ of the ferrocene/ferrocenium electrochemical signal. The $E_{1/2}$ is simply the voltage at which 50% of the product is in the reduced state and 50% of the product is in the oxidized state.



***Topics to include in your Introduction:*** Background information on ferrocene and its characterization; definition of sublimation; definition and basic theory behind electrochemistry.

***Safety Note:*** Cyclopentadiene has a strong, unpleasant odor! Use it in the fume hood.

**Procedure – Day 1**

1. Prepare a solution of $FeCl_2 \cdot 4\ H_2O$ (13.83 mmol) in dimethylsulfoxide (25 mL). Vigorous stirring on a stir plate for an extended period may be required to fully dissolve the solute. While the mixture is stirring, continue on with the rest of the experiment.

2. Degas 60 mL 1,2-dimethoxyethane (DME) with nitrogen gas in a 250 mL Schlenk flask equipped with a stir bar. Place a septum on the Schlenk flask once done degassing to minimize exposure to the air.

3. Against a strong stream of nitrogen add KOH (160.41 mmol), followed by freshly cracked cyclopentadiene (23.78 mmol). Re-seal the top of the Schlenk flask with a rubber septum then stir the reaction mixture vigorously under a nitrogen atmosphere until the solution turns a deep red color, approximately 30 minutes.

4. Attach an addition funnel to the flask and add the ferrous chloride solution to the reaction mixture slowly over a period of 25 minutes. Continue stirring for a further 30 minutes. Note: Do NOT add ANY solid to the dropping funnel, as it will clog.

5. Disassemble the apparatus and pour the contents into a 400 mL beaker containing ice and 6 M hydrochloric acid (90 mL). Rinse the Schlenk flask with a small aliquot of ice to transfer as much of the reaction mixture as possible. Stir the resulting slurry with a glass rod for 15 minutes and collect the solid by filtration (Buchner funnel). Wash the solid in the Buchner funnel with distilled water (4 x 15 mL) and air dry in your drawer until the next laboratory period.

**Procedure – Day 2**

1. Measure the yield of the dried crude product powder from the previous session. Then place the crude ferrocene onto a Petri dish in a thin layer that does not touch the sides. Make sure to break up any large clumps.

2. Cover the Petri dish with a ***pre-weighed*** watch glass and place the apparatus on a hot plate. Warm the assembly gently to 80 °C for approximately 1 hour, during which time the ferrocene will sublime onto the glass cover.

3. Remove the cover with the purified ferrocene and record the mass.

4. At this point the TA will take a small amount of one group's purified ferrocene and perform cyclic voltammetry on the sample to demonstrate ferrocene's electrochemical properties.

## Discussion Questions

1. What is the point group of both staggered and eclipsed ferrocene? Which conformation is most common in its solid state form?

2. Is ferrocene air sensitive? Why did you use Schlenk techniques in the synthesis?

3. Why did you collect the product with ice and HCl?

4. Compare the purification method of sublimation used and its yield in terms of the crude product to other common purification techniques (column chromatography, recrystallization, etc.).

5. Discuss the metal oxidation state and electron count for ferrocene in terms of its stability. Please refer to Miessler, Fischer, and Tarr chapter 13, section 3 for an explanation on electron counting.

6. At what voltage did the oxidation of ferrocene occur; at what voltage did the reduction of ferrocinium (the oxidized version of ferrocene) occur? What was the voltage for the $E_{1/2}$ of ferrocene?

7. SciFinder: Another interesting metallocene is the complex commonly known at uranocene. Provide the title of the first paper to report the preparation of uranocene and the authors on that paper.

## References

1. P. L. Paulson; T. J. Kealy, *Nature,* **1951,** *168,* 1039.

2. S. A. Miller; T. A. Tebboth; J. F. Tremaine, *J Chem. Soc.,* **1952,** 632.

3. G. Wilkinson, *J. Organometal. Chem.,* **1975,** *100,* 275.

4. D. R. van Staveren; N. Metzler·Nolte, *Chem. Rev.,* **2004,** *104,* 5931.

5. J.D. Dunitz; L. E. Orgel; A. Rich, *Acta Cryst.* **1956,** *9,* 373.