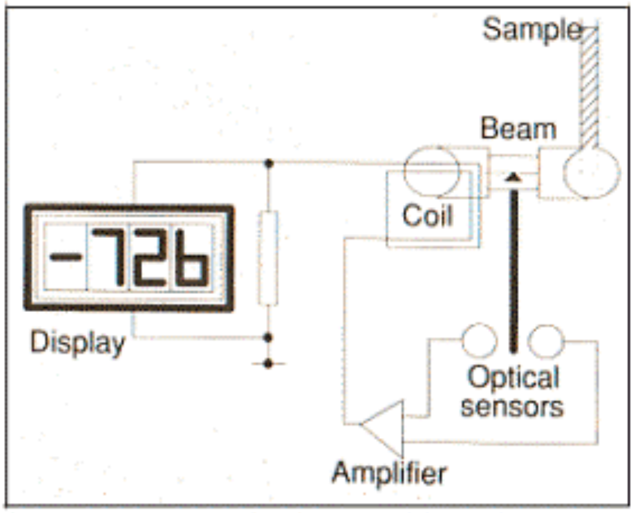
Experiment 4: Exploring paramagnetism in transition metal complexes

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

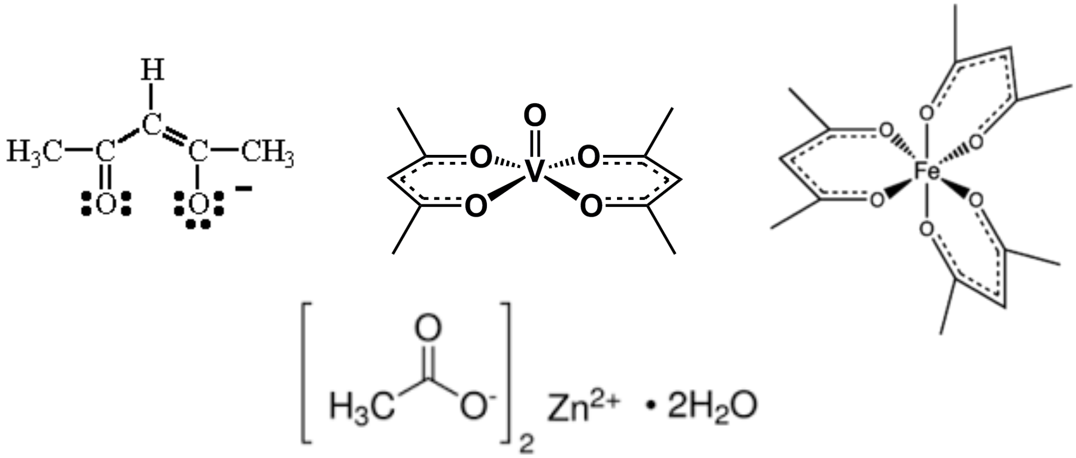


Figure 2. Compounds used in this experiment. Top left: acetylacetonate ligand. Top middle: vanadium complex. Top right: iron complex. Botton: zinc complex

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:

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

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**:

$$\chi_m = \chi_g \times M \qquad \textbf{(2)}$$

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

$$\mu_{eff} = 2.828\sqrt{\chi_m \times T} \qquad \textbf{(3)}$$

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 μ_{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).