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Evan's Method: An NMR Technique to Quantify the Number of Unpaired Electrons in Metal Complexes

--Manuscript Draft--

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Overview

Magnetic Susceptibility

While most organic molecules are diamagnetic, having all electrons paired up in bonds, many transition metal complexes are paramagnetic, having ground states that have unpaired electrons. ~~You~~ One may recall Hund's rule (from general chemistry) which states that for orbitals of similar energies, electrons will fill the orbitals to maximize the number of unpaired electrons before pairing ~~up~~. Transition metals have partially populated d-orbitals whose energies are perturbed to varying extents by coordination of ligands to the metal. Thus, the d-orbitals reside in close energy to one another, but are not all degenerate. This allows for complexes to be diamagnetic, with all electrons paired ~~up~~, or paramagnetic, with unpaired electrons.

Knowing the number of unpaired electrons in a metal complex can provide clues into the oxidation-state and geometry of the metal complex, as well as into the ligand field (crystal field) strength of the ligands. These properties greatly impact the spectroscopy and reactivity of transition metal complexes, and so are important to understand.

One way to "count" the number of unpaired electrons is to measure the magnetic susceptibility, χ , of the coordination compound. Magnetic susceptibility is the measure of magnetization of a material (or compound) when placed in an applied magnetic field. Paired electrons are slightly repelled by an applied magnetic field, and this repulsion increases linearly as the strength of the magnetic field increases. On the other hand, unpaired electrons are attracted (to a larger extent) to a magnetic field, and the attraction increases linearly with magnetic field strength. Therefore, any compound with unpaired electrons will be attracted to a magnetic field.¹

When we measure the magnetic susceptibility, we obtain information on the number of unpaired electrons from the magnetic moment, μ . The magnetic susceptibility is related to the magnetic moment, μ , by **Equation 1**:²

$$\mu = \sqrt{8(\chi_M T)} \quad (1)$$

The constant $\sqrt{8} = [(3k_B)/N\beta^2]$, where β = Bohr magneton of the electron (0.93×10^{-20} erg gauss⁻¹), N = Avogadro's number, and k_B = Boltzmann constant

χ_M = molar magnetic susceptibility (cm³/mol)

T = temperature (K)

μ = magnetic moment, measured in units of Bohr magneton, $\mu_B = 9.27 \times 10^{-24}$ JT⁻¹

The magnetic moment for complexes is given by **Equation 2**:¹

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$$\mu_{S+L} = g\sqrt{[S(S+1)] + \left[\frac{1}{4}L(L+1)\right]} \quad (2)$$

g = gyromagnetic ratio = 2.00023 μ_B

S = spin quantum number = $\sum m_s$ = [number of unpaired electrons, n]/2

L = orbital quantum number = $\sum m_l$

This equation has both orbital and spin contributions. For first-row transition metal complexes, the orbital contribution is small and hence can be omitted, so the spin-only magnetic moment is given by **Equation 3**:

$$\mu_s = g\sqrt{[S(S+1)]} = 2\sqrt{[S(S+1)]} = \sqrt{[n(n+2)]} \quad (3)$$

The spin-only magnetic moment can thus directly give the number of unpaired electrons. This approximation can also be made for heavier metals, though orbital contributions may be significant for second and third row transition metals. This contribution may be so significant that it inflates the magnetic moment sufficiently enough such that the compound appears to have more unpaired electrons than it does. Therefore, additional characterization may be required for these complexes.

In this experiment, the solution magnetic moment of tris(acetylacetonato) iron(III) ($\text{Fe}(\text{acac})_3$) is determined experimentally using Evan's method in acetonitrile.

Principles

Different Methods of Measuring Magnetic Susceptibility

There are many methods to measure the magnetic susceptibility. In the late 19th century, Louis Georges Gouy developed the Gouy balance, which is a highly accurate method to measure magnetic susceptibility. In this approach, an analytic balance is used to mass a magnet, and the change in mass observed upon placing a paramagnetic sample between the poles of the magnet is related to the magnetic susceptibility. This method is not practical, as suspending the sample between the poles of the magnet is not trivial. This requires four measurements of mass between which the magnet cannot move, and for air-sensitive samples must be done within a glovebox. More modern magnetic susceptibility balances are available, but this requires the purchase of such a balance.

Another method is to use a SQUID (Superconducting QUantum Interference Device) magnetometer. This requires several mg of solid sample, and unless other magnetic measurements are to be done on the sample, is not practical or cost-effective for paramagnetic complexes that can be made into solutions.

Finally, and what will be demonstrated here, is the use of an NMR spectrometer to measure the magnetic susceptibility. This approach was developed by Dennis Evans in 1959. It is simple and relies on the effect a paramagnet in solution has on the chemical shift of a reference compound, usually the solvent. Data collection can be done on any NMR spectrometer, the data is easy to interpret, and sample preparation is straightforward and

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requires little material. It has become the standard method to obtain magnetic susceptibility data for inorganic complexes.

The measurement of magnetic susceptibility by the Evan's method relies on the fact that the unpaired electrons from the paramagnet in solution will result in a change of the chemical shift of all species in solution (**Figure 1**). Thus, by noting the chemical shift difference of a solvent molecule in the presence and absence of a paramagnetic species, the magnetic susceptibility can be obtained via **Equation 4** (for a high-field NMR spectrometer):³

$$\chi_M = \frac{3\Delta f}{4\pi Fc} \quad (4)$$

Δf = frequency difference in Hz between the shifted resonance and the pure solvent resonance

F = spectrometer radiofrequency in Hz

c = concentration of paramagnetic species (mol/mL)

Data is readily obtained by collecting a ¹H NMR spectrum of a sample that contains a capillary of pure solvent, with a solution of the paramagnet surrounding the capillary within the NMR tube (**Figure 2**).

Procedure

1. Preparation of Capillary Insert

- 1.1. Using a lighter or other gas flame, melt the tip of a long Pasteur pipette. Gently rotate the pipette tip in the flame until a small bulb forms. Allow the glass to cool.
- 1.2. In a scintillation vial, prepare a 50:1 (volume) solution of deuterated:proteo acetonitrile. Pipette 2 mL of deuterated solvent, and to this add 40 μ L of proteo solvent. Cap the vial.
- 1.3. Carefully add a few drops of the solvent mixture to the sealed glass pipette. Gently flick the tip of the sealed pipette so that the liquid enters the capillary. Repeat until the solution has a depth of ~ 2 inches from the bottom of the capillary. Make sure that there are no bubbles of air.
- 1.4. Cap the pipette with a 14/20 rubber septum. Using a 3-mL syringe capped with a needle, insert the needle into the pipette, and pull out 3 mL of air. This creates a partial vacuum, facilitating the next step.
- 1.5. Seal the top of the capillary. Horizontally clamp the pipette to a ring stand. Use a lighter to soften the glass above the solution in the bottom of the pipette. Once the glass softens, begin to rotate the tip of the pipette and pull the tip of the pipette away from the clamped base. Let the sealed capillary cool.

2. Preparation of Paramagnetic Solution

2.1. Using an analytical balance, mass a scintillation vial and lid. Note the mass.

2.2. Mass out 5--10 mg of the $\text{Fe}(\text{acac})_3$ in the scintillation vial, and note the mass. ($\text{Fe}(\text{acac})_3$ has a very high solution magnetic moment. Therefore 5--10 mg will generate a large change of the chemical shift. Typically 10--15 mg is a more appropriate mass to use for Evan's method samples.)

2.3. Pipette ~600 μL of the prepared solvent mixture into the vial containing the paramagnetic species. Cap, and note the mass. Make sure that the solid completely dissolves.

3. Preparation of NMR Sample

3.1. In a standard NMR tube, carefully drop the capillary insert at an angle, as to not break it.

3.2. Pipette in the solution containing the paramagnetic species.

3.3. Cap the NMR tube. For air-sensitive samples, wrap Parafilm around the cap.

4. Data Collection

4.1. Acquire and save a standard ^1H NMR spectrum.

4.2. Note the temperature of the probe.

4.3. Note the radiofrequency.

5. Data Analysis and Results

5.1. Using the mass and density of the solvent, calculate the volume of the solvent used to prepare the paramagnetic solution.

5.2. Calculate the concentration (M) of the paramagnetic solution.

5.3. Calculate the peak separation of the solvent resonance between that of pure solvent (in the capillary) and that shifted by the paramagnet (outside of capillary) (Δ_{ppm}). If this is done in ppm, convert it to Hz by **Equation 5:**

$$\Delta f(\text{Hz}) = \frac{\Delta_{\text{ppm}} F}{10^6} \quad (5)$$

F = spectrometer radiofrequency in Hz

5.4. Calculate the magnetic susceptibility using **Equation 4.**

5.5. Calculate the magnetic moment using **Equation 1.**

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5.6. Compare the magnetic moment obtained with that predicted for n -unpaired electrons from **Equation 3**. The magnetic susceptibility will be slightly greater than the anticipated spin-only value given in the table but should be less than that which corresponds to $n+1$ unpaired electrons.

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5.7. Give the number of unpaired electrons for the paramagnetic species.

6. Troubleshooting

6.1. If two well-resolved solvent peaks are not observed, try the following:

6.1.1. Use a spectrometer with a greater field strength to increase the chemical shift difference (in ppm) of the two peaks.

6.1.2. Make the sample more concentrated, so that the shift is larger.

6.2. Sometimes the value does not make sense. If a value that is too low is obtained try the following:

6.2.1. Repeat, taking greater care in massing out the solvent and paramagnetic species.

6.2.2. Make sure that the paramagnetic species being used is pure. Even solvent impurities in crystals will affect the mass and hence concentration.

6.2.3. For large molecules, the diamagnetism may be so significant that a diamagnetic correction must be made. This is readily calculated following instructions found here. [\[Bain, 2008 #2853\]](#) This term is subtracted to **Equation 4**:

$$X_M = \frac{3\Delta f}{4\pi Fc} - \text{diamagnetic correction}$$

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6.3. Sometimes the value does not make sense. If a value that is too high is obtained try the following:

6.3.1. Same as 6.2.1 - 6.2.3.

6.3.2. For heavier metals, inclusion of orbital contributions may be necessary.

7. Air-Sensitive Samples

7.1. Air-sensitive samples can readily be analyzed using this technique. Steps 1.2-1.4, 2, and 3 are simply done inside of a glove-box.

Representative Results

Experimental Results

	Fe(acac) ₃	Acetonitrile
<i>m</i> (g)	0.0055	0.4076
MW (g/mol)	353.17	n/a
<i>n</i> (mol)	1.56* <u>x</u> 10 ⁻⁵	n/a
Density (g/mL)	n/a	0.83*
Volume (mL)	n/a	0.49

$$\mathbf{c \text{ (mol/mL) } 3.18*x 10^{-5}}$$

NMR shifts	Peak 1	Peak 2
δ (ppm)	1.94	-0.1

$$\Delta_{ppm} \quad 2.04$$

NMR Instrument

Temperature (K)	298
Field, <i>F</i> (Hz)	300* <u>x</u> 10 ⁶

* the density of the solvent can be approximated to the density of the solvent used

Calculations

$$\Delta f(Hz) = \frac{\Delta_{ppm} F}{10^6} = \frac{(2.04)(300*x 10^6)}{10^6} = 612 \text{ Hz}$$

$$X_M = \frac{3\Delta f}{4\pi F c} = \frac{3(612)}{4\pi(300*x 10^6)(3.18*x 10^{-5})} = 0.0153 \text{ cm}^3/\text{mol}$$

$$\mu = \sqrt{8(\chi_M T)} = \sqrt{8(0.0153)(298)} = \mathbf{6.04 \mu_B}$$

Theoretical Results for given *S* and *n* values:

<i>S</i>	<i>n</i>	μ_S
1/2	1	1.73
1	2	2.83
3/2	3	3.87
2	4	4.90
5/2	5	5.92

For 5.5 mg of Fe(acac)₃ dissolved in 0.492 mL solvent, with a 300 MHz instrument a peak separation of 2.04 ppm is observed, which gives $X_M = 1.53 \times 10^{-2}$ and $\mu_{\text{eff}} = 6.04$. This μ_{eff} value is consistent with an *S* = 5/2 complex, which has 5 unpaired electrons.

Summary

Evan's method is a simple and practical method for obtaining the magnetic susceptibility of soluble metal complexes. This provides the number of unpaired electrons in a metal complex, which is pertinent to the spectroscopy, magnetic properties, and reactivity of the complex.

Applications

Measuring the magnetic susceptibility of paramagnetic species gives the number of unpaired electrons, which is a key property of metal complexes. As the reactivity of metal complexes is influenced by its electronic structure—that is, how the d-orbitals are populated—it is important to establish the number of unpaired electrons. The magnetic susceptibility can be used to determine the geometry of the metal complex in solution, give insight into the ligand field strength, and can provide evidence for the correct formal oxidation-state assignment of the metal complex. In the [modules-videos](#) on Group Theory and MO Theory of Transition Metal Complexes, we will introduce how to predict d-orbital splitting diagrams as well as how to use data from Evan's Method to help determine the geometry of a metal complex and provide evidence for the oxidation state of the metal center.

There are multiple instruments that can be used to measure the magnetic susceptibility of a paramagnetic species including a Gouy balance, SQUID, or NMR [instrumentspectrometer](#). Evan's method is a simple and practical technique that uses NMR to determine the solution magnetic moment of a paramagnet. While Evan's method is a powerful tool in the field of magnetism, there are several drawbacks to the technique. First, the molecule must be soluble in the solvent used in the experiment. If the paramagnet sample is not fully dissolved, the concentration of the solution will be incorrect, which will lead to errors in the experimentally determined solution magnetic moment. Other errors in concentration can arise if the paramagnetic sample has diamagnetic (solvent) or paramagnetic impurities.

Legend

Figure 1. Example ^1H NMR spectrum of the experiment

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Figure 2. Image of a capillary in NMR tube setup

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Materials List

Name	Comments
Materials	
Lighter or Bunsen burner	
Long-stem Pasteur pipette	
Pipette bulb	
14/20 ribbed rubber septum	
3-mL disposable syringe with needle	
Scintillation vial and cap	
NMR tube and cap (Parafilm if air-sensitive)	
Analytical balance	
1-mL and 100- μ L pipetman, with tips	
Glovebox	
Fumehood	
NMR Spectrometer	
Reagents	
d ₃ -MeCN	
MeCN	
Tris(acetylacetonato)iron(III)	

1. Miessler, G. L.; Fischer, P. J.; Tarr, D. A., *Inorganic Chemistry*. 5 ed.; Pearson: 2014.
2. Drago, R. S., *Physical Methods for Chemists*. 2 ed.; Saunders College Publishing: 1992.
3. Girolami, G. S.; Rauchfuss, T. B.; Angelici, R. J., *Synthesis and Technique in Inorganic Chemistry: A Laboratory Manual*. 3 ed.; University Science Books: Sausalito, CA, 1999.

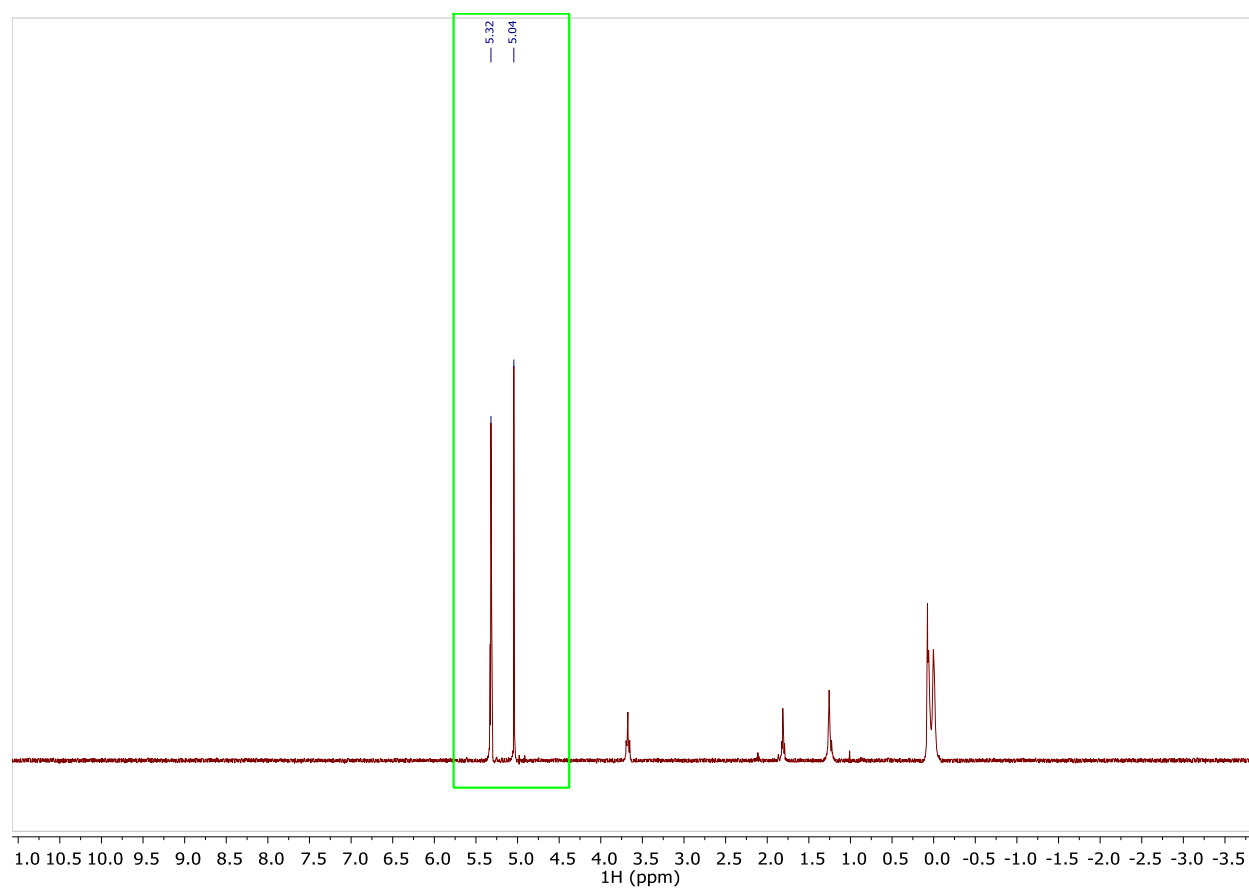


Figure 1

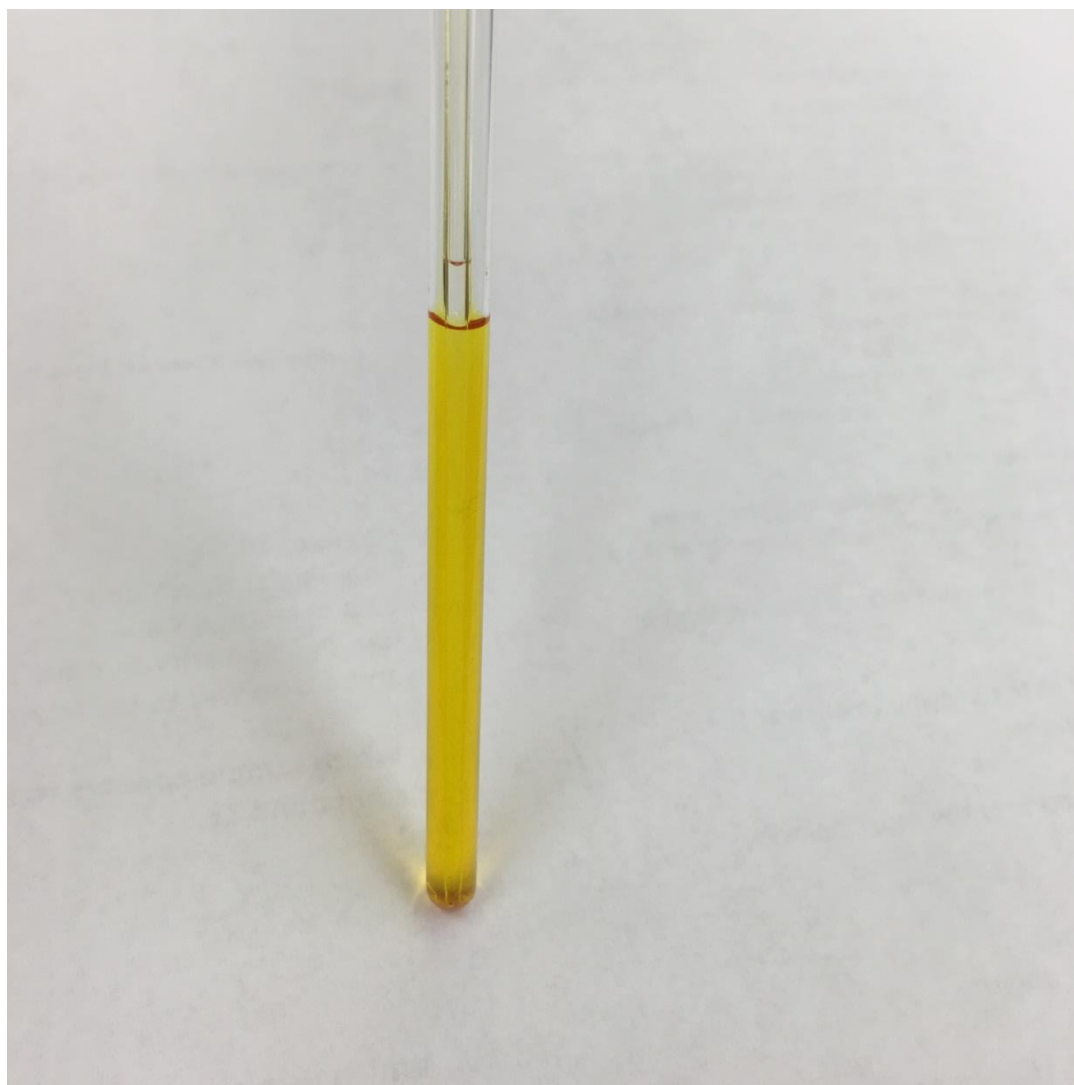


Figure 2