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UNDERGRADUATE EXPERIMENT

Determination of Electronic Spin Configuration via Evans Method

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INTRODUCTION

Paramagnetic complexes are organometallic compounds containing metal ions with unpaired d electrons. These electrons result in a magnetic dipole moment that has a small net attraction to an externally applied magnetic field. Unsurprisingly, this has a significant effect on both the observed chemical shift and lineshape in the ^1H NMR spectrum of these complexes, where the chemical shift range is much wider than observed in diamagnetic NMR spectroscopy and the resonances broaden.

Additionally, the presence of paramagnetic ions can result in a displacement of expected chemical shifts. This displacement can be used to estimate the magnetic susceptibility of transition metal complexes, and subsequently ascertain the electronic structure of transition metal ions. First demonstrated by Dennis Evans in 1959[1] and described in subsequent publications,[2-4] the change in chemical shift of an inert reference compound in the presence and absence of a paramagnetic transition metal complex is correlated to the magnetic susceptibility of the transition metal complex via equation 1:

$$X_m = \frac{6}{1000} \cdot \frac{1}{c} \cdot \frac{\Delta f}{f} \quad (1)$$

where

X_m - molar magnetic susceptibility of the transition metal complex (m^3mol^{-1})

c - concentration of the metal complex ($mol\ L^{-1}$)

Δf - change in frequency of the reference compound (Hz)

f - frequency of the spectrometer (Hz)

After determining the molar magnetic susceptibility of the transition metal complex, one can determine the number of unpaired electrons present in the system based on the effective magnetic moment by using equation 2:

$$\mu_{eff} = 798\sqrt{X_m T} = \sqrt{n(n+2)} \quad (2)$$

where

μ_{eff} - effective magnetic moment

X_m - molar magnetic susceptibility from eqn (1)

T - temperature (K)

n - number of unpaired electrons in the metal ion

In this experiment, the electronic structure of manganese(III) acetylacetonate ($Mn(acac)_3$), iron(III) acetylacetonate ($Fe(acac)_3$), and chromium(III) acetylacetonate ($Cr(acac)_3$) will be determined by performing the Evans method with the NMReady-60.

PROCEDURE

Reference Sample:
A solution of tBuOH (10% v/v) was prepared in chloroform ($CHCl_3$) and transferred into a capillary tube that was then sealed. Approximately 0.6 mL of $CDCl_3$ was added to an NMR tube along with the sealed capillary tube. A ^1H NMR spectrum was then recorded with the following parameters:

spectral width: 20 ppm	interscan delay: 1 sec
spectral center: 5 ppm	number of points: 2048
number of scans: 4	dummy scans: 0
receiver gain: auto	pulse angle: 81°

Spiked reference sample:
A solution of the paramagnetic complex, $M(acac)_3$ (M = Mn, Fe, or Cr), was prepared by accurately weighing out 5 mg of the complex and dissolving it in 0.6 mL of tBuOH (10% v/v) in $CHCl_3$. A new capillary tube was then filled with this solution and sealed. Subsequently, the capillary tube was inserted into an NMR tube and filled with approximately 0.6 mL of $CDCl_3$. The ^1H NMR spectrum was obtained with the same parameters above.

Note: a co-axial NMR insert can be used in the place of a capillary tube.

RESULTS & DISCUSSION

All three complexes studied in this experiment are hexacoordinate with octahedral geometries where the 3+ metal centre is ligated to three anionic bidentate acac ligands. Based on the number of d electrons, octahedral metal centres can have two possible electronic configurations, denoted as high spin or low spin, depending on how the d orbitals are populated, each with a unique number of unpaired electrons.[5]

A high spin state is observed when the pairing energy is greater than splitting energy. This results in electrons filling all five d orbitals first before they start pairing. A low spin state is seen when the pairing energy is less than that of the splitting energy, resulting in electrons pairing up in lower energy d orbitals before filling the higher energy orbitals. As seen in figure 1, high spin Mn(III) has 4 unpaired electrons while low spin Mn(III) has only 2 unpaired electrons. Therefore by using equation 2, the expected effective magnetic moment for Mn(III) in the high spin and low spin state is 4.90 μ_B and 2.83 μ_B, respectively. Similarly, the Fe(III) centre can occupy a high spin (5 unpaired electrons) or low spin (1 unpaired electron) configuration with an expected effective magnetic moment of 5.91 μ_B and 1.73 μ_B, respectively. On the other hand, Cr(III) only has one possible electronic configuration with three unpaired electrons, resulting in an expected effective magnetic moment of 3.87 μ_B. By comparing the expected and experimental effective magnetic moment, the electronic structure of the transition metal ions can be established.
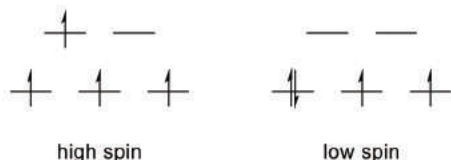

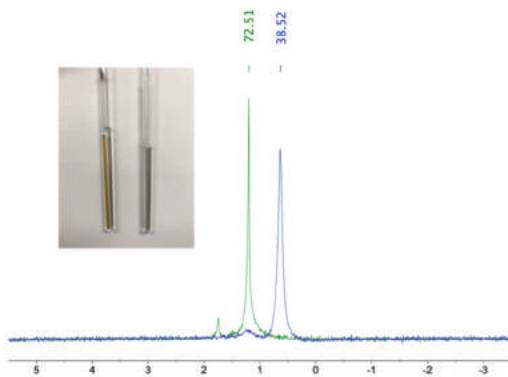**Figure 1. High and low spin electronic configuration of Mn(acac)$_3$.**

high spin   low spin

Figure 2. ^{1}H NMR spectrum of the reference sample (green) overlaid with the reference sample spiked with Mn(acac)$_3$ (blue). Peaks are labelled in Hz. Inset: NMR tubes with the capillary tubes used for the Evans method.

As shown in figure 2, the presence of Mn(acac)$_3$ in the reference solution resulted in a significant change in the chemical shift of tBuOH. The difference in chemical shift of tBuOH observed with Mn(acac)$_3$ is 33.99 Hz. This value can then be used with equation 1 to calculate the molar magnetic susceptibility.

$$X_m = \frac{6}{1000} \cdot \frac{1}{c} \cdot \frac{\Delta f}{f} \quad (1)$$

$$X_m = \frac{6}{1000} \cdot \frac{1}{0.026\,M} \cdot \frac{33.99\,Hz}{60000000\,Hz}$$

$$X_m = 1.31 \times 10^{-7}\,m^3 mol^{-1}$$

Once X_m is determined, this value can be inserted into equation 2 to determine the effective magnetic moment, μ_{eff}.

$$\mu_{eff} = 798\sqrt{X_m T} \quad (2)$$

$$\mu_{eff} = 798\sqrt{(1.31 \times 10^{-7}\,m^3 mol^{-1})(305.15\,K)}$$

$$\mu_{eff} = 5.04\,\mu_B$$

As the experimental value of μ_{eff} (5.04 μ_B) is much closer to the value calculated for the high spin configuration (4.90 μ_B) compared to the low spin configuration (2.83 μ_B), the Mn(III) ion in this complex was determined to be high spin. Subsequently, following the same analysis, Fe(acac)$_3$ was found to be high spin while the electronic configuration of Cr(acac)$_3$ was corroborated with calculated μ_{eff} values of 5.32 μ_B and 4.33 μ_B, respectively. The values used in the calculations and the results are summarized in table 1.

Table 1. Experimental parameters and μ_{eff}

Cmpd	Conc (M)	Temp (K)	Δf (Hz)	μ_{eff} (exp)
Mn(acac)$_3$	0.0260	305.15	34.05	5.04 μ_B
Fe(acac)$_3$	0.0241	305.15	34.99	5.32 μ_B
Cr(acac)$_3$	0.0248	305.15	23.92	4.33 μ_B

CONCLUSIONS

In this experiment, the effective magnetic moment and spin state of 3 paramagnetic complexes were determined by performing the Evans method with the NMReady-60. This was accomplished by measuring the difference in chemical shift of tBuOH in the presence and absence of a metal complex. The experiment is quick and accessible to undergraduate students allowing for an excellent introduction to paramagnetic transition metal complexes.

REFERENCES

[1]Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
[2]Schubert, E. M. *J. Chem. Educ.* **1992**, 69, 62.
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[4]Nataro, C.; Fosbenner, S. M. *J. Chem. Educ.* **2009**, 86, 1412.
[5]Oberoi, A.; Nuckles, J. High Spin and Low Spin Complexes https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_(Inorganic_Chemistry)/Crystal_Field_Theory/High_Spin_and_Low_Spin_Complexes *(accessed Apr 22, 2019).*

DATA ACCESSIBILITY

The data can be processed directly on the NMReady-60 and printed and/or exported directly to a USB or networked file where it can be worked up using third party NMR processing software.

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