Identification of Unknown Metal Acetylacetonate Complexes via Evan's Method

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Abstract

Evan's method is a promising analytical technique for detection of paramagnetic metal complexes, with applications for pollutant detection in environmental chemistry. This experiment demonstrated successful synthesis of $Mn(acac)_3$ (41% yield), calculation of magnetic moments via ^1H NMR and Evan's method, and qualitative determination of unknown compounds. The unknown compounds (Unknowns 1–4) were identified as follows: low-spin $Co(acac)_3$, $Cr(acac)_3$, high-spin $Fe(acac)_3$, and $Cu(acac)_2$, with corresponding magnetic moments (in units of μ_B) 0, 2.56, 2.99, and 1.96 respectively. Future studies should improve upon this work by using more vigorous stirring and finer filters during synthesis and filtration of $Mn(acac)_3$, by accounting for diamagnetic corrections and LS-coupling, and by properly shimming and calibrating NMR instruments prior to analysis via Evan's method.

Introduction

Paramagnetism arises in inorganic complexes that possess unpaired electrons, which allow it to generate a magnetic field parallel to an external magnetic field. This property causes metal complexes to generate unique NMR spectra due to their influence on the internal magnetic field, and can be exploited to determine the identity of any paramagnetic complex. One such experimental technique is *Evan's method*, which utilizes a sealed capillary of "control" diamagnetic solution, attaining an NMR spectrum of the (paramagnetic) metal complex solution with the capillary submerged, and determining the identity of the complex via the difference in the chemical shifts Δf of $CHCl_3$ in different magnetic environments.

Upon determination of Δf (in Hz), the *magnetic susceptibility* χ_M is related by the expression[1]

$$\chi_M = \frac{3\Delta f}{4\pi F c}, \tag{1}$$

where F is the field strength (in Hz) and c is the molar concentration of the complex, in mol/mL. χ_M is in turn related to the *magnetic moment* μ by the relation

$$\mu = \sqrt{8\chi_M T}, \tag{2}$$

where T is the temperature in K.

Evan's method is thus especially useful for determination of both the presence and identity of inorganic metal complexes. This could be exploited in future studies to yield a novel method of detecting transition metal pollutants in the environment, which have become increasingly prevalent throughout the ecosystem, and have demonstrated a serious cause for concern in both our ecology and public health, even at sublethal concentrations.[2,3] While analyti-

cal techniques for pollutant detection certainly exist and have advanced considerably in the past decade,[4–6] they often demonstrate a lack of large-scale extensibility and a burdensome economic cost. Evan's method thus presents as a promising direction for pollutant detection.

$$\mathrm{MnO_4^-} + \mathrm{H^+} + 3\,\mathrm{Hacac} \xrightarrow[5\,\mathrm{min}]{100\,^\circ\mathrm{C}} \mathrm{Mn(acac)_3} + 2\,\mathrm{H_2O} + \mathrm{O_2}$$

Scheme 1: Synthesis of $Mn(acac)_3$ via reduction of $KMnO_4$ in a boiling aqueous solution of acetylacetone.

In this experiment, $Mn(acac)_3$ was synthesized via aqueous reduction of $KMnO_4$ in the presence of acetylacetone (Scheme 1), and Evan's method was used to determine the magnetic moments of $Mn(acac)_3$ and four other unknown metal acetylacetonate complexes, hereafter labelled Unknowns 1–4. The magnetic moments, determined via ^{1}H NMR, were then used to identify the unknowns and assign them to a transition metal complex. Metal acetylacetonate complexes are an important reagent in many industrial reactions,[7] and were thus chosen to demonstrate the efficacy of Evan's method in their detection and identification. Furthermore, acetylacetonate complexes have a higher likelihood of being paramagnetic, as their low ligand field strength favors formation of high-spin complexes.[8]

Results and Discussion

A percent yield of 41% was recorded for the synthesis of $Mn(acac)_3$. This yield is quite low, and could have resulted from either failure to vigorously stir the reaction mixture or from loss of product during the coarse glass frit filtration step. It is unlikely that there is a thermodynamic or kinetic effect limiting the yield, as literature studies reporting the exact same reaction times, temperatures, and molar ratios report a percent yield of 87%.[9] Future studies wishing to improve yields should use more vigorous stirring and use a more fine filtration apparatus.

The unknown samples were all observed to be strongly colored first-row transition metals. Furthermore, all unknowns were tris-chelated except Unknown 4, which was bis-chelated. All unknowns except Unknown 1 exhibited a paramagnetic shift in their respective ^{1}H NMR spectra. A summary of observations is tabulated in Table 1.

Table 1: Summary of observations for each sample.

Sample	Color	Δf (Hz)
$Mn(acac)_3$	Purple	1320
Unk. 1	Green	0
Unk. 2	Violet	635
Unk. 3	Crimson	1700
Unk. 4	Blue-Gray	345

A thorough determination of the unknown complexes is non-trivial, as the molar concentration of the paramagnetic solution is unknown as the molar mass is unknown, and thus Equations 1 and 2 cannot be applied directly. μ must be computed for each element of interest, and then compared with the expected μ of the corresponding complex. For instance, one would first assume an unknown to be $M(acac)_3$, and compute μ using Equations 1 and 2, compare the calculated result with the expected value for both the corresponding low and high-spin complexes, and repeat this for all possible complexes. The complex which minimizes the absolute difference $|\Delta\mu| = |\mu - \mu_{\mathrm{exp}}|$ is the identity of the unknown as evidenced by Evan's method. The summary of these results and their assignments are tabulated below.

Unknown 1 was assigned on the basis of its diamagnetism and color. The only other diamagnetic tris-chelate is Sc^{3+}, which is colorless in solution due to its lack of d-electrons.[8] Thus, the only possible identity of Unknown 1 is the low-spin complex $Co(acac)_3$. This result is interesting as the acac ligand is expected to generate high-spin complexes due to its low ligand field strength as mentioned earlier. This shows that in the extreme case of exactly 6 d-electrons, $Co(acac)_3$ preferentially forms a low-spin complex, which implies that the ligand

Table 2: Tabulated magnetic moments μ and their absolute difference $|\Delta\mu|$ with respect to their corresponding assignment. All magnetic moments are in units of μ_B. μ was calculated using the molar mass of the assigned complex.

Sample	μ	$\lvert\Delta\mu\rvert$	Assignment
$Mn(acac)_3$	4.77	0.12	–
Unk. 1	0	0	Low-spin $Co(acac)_3$
Unk. 2	2.56	0.85	$Cr(acac)_3$
Unk. 3	2.99	2.92	High-spin $Fe(acac)_3$
Unk. 4	1.96	0.23	$Cu(acac)_2$

field stabilization energy (LFSE) is just slightly lower than that of the exchange energy stabilizing the corresponding high-spin complex. This observation of low-spin $Co(acac)_3$ in the ground state is in agreement with existing literature on its magnetic properties.[10]

Unknown 4 was easily assigned to $Cu(acac)_2$ on the basis of its similar magnetic moment and its blue color being that of a Cu(II) solution.[8]

Unknowns 2 and 3 demonstrated a high $|\Delta\mu|$ as shown in Table 2, exhibiting the limitations of reliance purely on Evan's method for qualitative determination. Unknown 2 was assigned to $Cr(acac)_3$ despite its calculated magnetic moment being more similar to that of $Mn(acac)_3$ because of its similarity in color to the $Cr(acac)_3$ complex.[11,12] Similarly, Unknown 3 exhibited the famous crimson-red color of a Fe(III) solution, whose corresponding acetylacetonate complex is known to be high-spin.[12]

Unknowns 2 and 3 demonstrate different magnetic moments with respect to their assignments mainly due to poor ^{1}H NMR spectra (presented in the Supporting Information). Repetition of the same data analysis on literature values of the paramagnetic shifts[1] and another classmate's data (not included) demonstrate very similar magnetic moments to those of $Cr(acac)_3$ and high-spin $Fe(acac)_3$ respectively. Thus, future studies should attempt to properly calibrate and shim the ^{1}H NMR instrument prior to analysis via Evan's method.

Another, less pertinent source of error arises in simplication. Equation 1 fails to account for the diamagnetic correction necessary for larger complexes,[1] and Equation 2 also fails to account for the magnetic moment arising from LS-coupling observed in the heavier transition metal elements.[1,8,13] These two effects, in conjunction, could have led to the anomalously low or high calculated magnetic moments determined via ^{1}H NMR and Evan's method.

Conclusion

In conclusion, this experiment successively demonstrated synthesis of $Mn(acac)_3$, calculation of magnetic moments via ^{1}H NMR and Evan's method, and qualitative determination of unknown compounds. The yield of $Mn(acac)_3$ was determined to be lower than those of literature under the same reaction conditions, and thus future studies should ensure vigorous stirring and usage of a more fine filtration apparatus. Direct application of Evan's method was complicated by both failure to account for diamagnetic corrections and LS-coupling, and by the poor ^{1}H NMR data due to improper shimming and calibration prior to analysis. Future studies should improve on this by using more accurate formulas for the magnetic moment (c.f. Girolami et al.) and ensuring proper calibration by visualizing correct peak shapes in ^{1}H NMR spectra prior to analysis via Evan's method.

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