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UTILISATION OF THE STATIC EVANS METHOD TO MEASURE MAGNETIC SUSCEPTIBILITIES OF TRANSITION METAL ACETYLACETONATE COMPLEXES AS PART OF AN UNDERGRADUATE INORGANIC LABORATORY CLASS

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Abstract. The Evans method is routinely utilised to collect paramagnetic susceptibility data via the employment of relevant Nuclear Magnetic Resonance (NMR) methods. As the sample is normally spun, the lack of such a function on benchtop NMR instrumentation required a "static" approach to be employed. We have utilised the static Evans method approach to measure the magnetic susceptibilities, and subsequently the effective magnetic moment, of a series of synthesised transition metal acetylacetonate complexes in order to appraise the *d*-electron configuration. The obtained values were compared to those obtained using a Guoy balance and theoretical calculations. The collection of T_1 relaxation data further exemplifies the effect of the paramagnetic centre in terms of aiding relaxation, and therefore links to Magnetic Resonance Imaging (MRI) contrast agents, thus providing students with real-world perspective of the experiment conducted.
Keywords: benchtop-NMR; Evans method; transition metal chemistry

Introduction

In 1959, Evans reported a method for the determination of paramagnetic susceptibility of substances using Nuclear Magnetic Resonance (NMR) spectroscopy (Evans, 1959). This method requires a solution of the substance investigated, along with an inert reference material (such as *tert*-butanol), to be introduced to an NMR tube, in to which is placed a capillary with the same concentration of reference material. The sample is spun within the NMR spectrometer during the measurement and the resulting spectrum acquired displays a frequency difference between the two resonance lines of the inert reference substance. This frequency difference is directly proportional to the magnetic susceptibility, χ_M, of the substance under investigation provided the mass of substance used is known. Thus, magnetic sus-

ceptibility values are readily obtainable, as are values for the effective magnetic moment, μ_{eff}, at a given temperature, T, using the SI unit derived equation:

$$\mu_{eff} = 798\sqrt{\chi_M T}$$
(1)

The deduction of effective magnetic moments for transition metal complexes are insightful in to the electronic population of the *d*-orbitals (Deutsch & Poling, 1969). This population has a direct effect on the magnetic properties of the metal complex produced due to electron pairing i.e. a complex can be paramagnetic or diamagnetic. This insight can be utilised to ascertain the geometry of a metal complex, or if a ligand produces a strong or weak ligand field, for example.

Whilst the Evans method has been utilised for undergraduate experiments using high-field instrumentation (Nataro & Fosbenner, 2009; Schubert, 1992), doing likewise for benchtop NMR instrumentation requires some modification of the original method. This is mainly because benchtop NMR instruments do not spin the sample during acquisition. A rotationless method is therefore required. Engel and co-workers have reported such a method (Engel et al., 1973) although their motivations were to overcome line broadening effects, contact or pseudo-contact shifts and overlapping of the reference signal by solvents present. Their approach is a variation of the diamagnetic susceptibility determination described by Reilly and co-workers (Reilly et al., 1955). The method requires the reference material to be placed in the outer cavity of the concentric tube whilst the inner cavity contains the paramagnetic substance. The reference sample experiences a magnetic inhomogeneous field, causing the reference sample to split in to a doublet. Measuring the frequency difference between the two peaks of the doublet for various concentrations of paramagnetic substance enables χ_M to be determined, provided the geometric factors of the tube (the concentricity factor) and frequency of the instrument are known. If the sample is spun, the field becomes more homogeneous, resulting in the normal (i.e. non-split) signal for the reference being observed.

The equation originally reported to derive χ_M using this static method has required correction (Orrell & Sik, 1980). The correct concentricity factors are now incorporated. The equation, utilising SI units rather than CGS units, is:

$$\chi_M = \left(\frac{\Delta v}{\Delta c}\right)\left(\frac{1+\chi_5}{1+\chi_3}\right)\left(\frac{a_3^2}{v_0\,a_1^2}\right)$$
(2)

where Δv is the frequency difference between the two peaks of the doublet, c is the concentration of the paramagnetic material, v_0 is the frequency of the instrument, a_1 is the inside radius of the inner tube, a_3 is the outside radius of the annulus and χ_3 and χ_5 are molar susceptibilies of the reference material and air respectively. The term involving χ_3 and χ_5 can be ignored, as it is effectively unity, and so the equation simplifies to

$$\chi_M = \left(\frac{\Delta v}{\Delta c}\right)\left(\frac{a_3^2}{v_0\, a_1^2}\right) \tag{3}$$

In this paper, we utilise the static method in conjunction with a benchtop NMR instrument to deduce χ_M for a series of synthesised metal acetylacetonate (acac) complexes. The values obtained are compared to those obtained using a Gouy balance. ^{1}H NMR data of the complexes are also acquired to visually inspect for paramagnetic or diamagnetic properties, as are T_1 data to demonstrate the effect of magnetic complexes with respect to relaxation. The suite of experiments represents a suitable inorganic undergraduate laboratory practical that aligns with material being taught as part of a second year undergraduate inorganic unit. It also introduces students to the difference in appearance of paramagnetic and diamagnetic ^{1}H NMR spectra.

Results and discussion

Four metal acetylacetonate complexes, $Mn(acac)_3$, $Fe(acac)_3$, $Co(acac)_3$ and $Co(acac)_2(H_2O)_2$, were synthesised as detailed in the experimental section. These syntheses yield multi-gram quantities therefore furnishing students with enough material to complete all relevant analyses. As all of these complexes are octahedral in their structure, they allow students to predict the μ_{eff} for the high- and low-spin electronic configurations based on spin-spin contributions readily using

$$\mu_{eff} = \sqrt{S(S+2)} \tag{4}$$

where S is the number of unpaired electrons in the *d*-orbitals. $Mn(acac)_3$, $Fe(acac)_3$, $Co(acac)_3$ and $Co(acac)_2(H_2O)_2$ possess 4, 5, 6 and 7 *d*-electrons respectively. Consequently, all of the complexes can either be high- or low-spin and will therefore have differing values of μ_{eff} dependent on the how the electrons are paired. Students should be encouraged to predict the values of the low- and high-spin *d*-electron configurations using crystal field splitting diagrams.

The magnetic properties of the metal complexes are readily explored using ^{1}H NMR spectroscopy. As most of the complexes studied are paramagnetic, their ^{1}H NMR spectra display signals that have been significantly shifted and broadened. In the case of $Fe(acac)_3$, the signals are so broad that they are not readily detectable, whereas the other complexes produce spectra that can be interpreted. Representative spectra are shown in Fig. 1. These spectra are obtained in a relatively short time-frame and provide the students with diagnostic information on the magnetic properties of the complexes prepared. It should be noted that the spectrum of $Co(acac)_3$ can be integrated (Fig. 1B), so that students can ascertain the chemical identity of the complex. The symmetrical nature of this complex should be highlighted to the students to aid in their understanding of the ^{1}H NMR spectrum obtained.
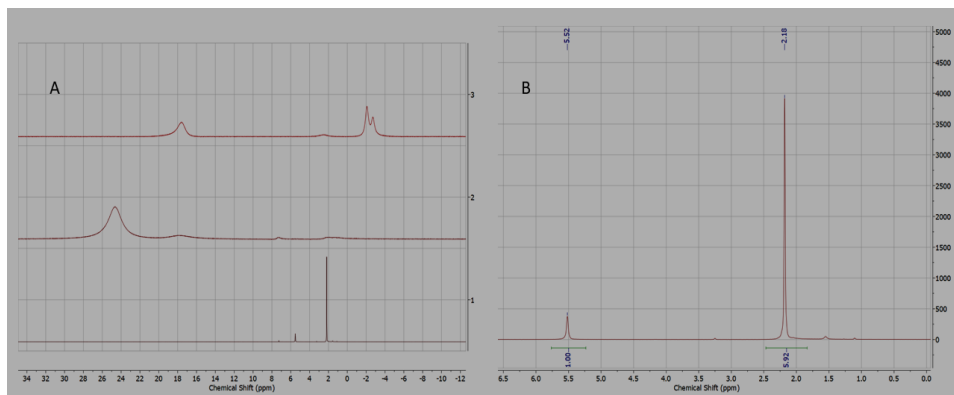
Figure 1. A: ^1H NMR spectra of $Co(acac)_3$ (spectrum 1), $Mn(acac)_3$ (spectrum 2) and $Co(acac)_2(H_2O)_2$ (spectrum 3); B: Integrated ^1H NMR spectrum of $Co(acac)_3$. All spectra collected in $CDCl_3$ with the exception of $Co(acac)_2(H_2O)_2$ which was acquired in DMSO-d_6

The static method requires acquiring a series of measurements whereby the concentration of metal complex being analysed is varied. We found that when making the solutions of metal complex for the static Evans method that a concentration of 0.25 M should not be exceeded. Concentrations below 0.25 M have been recommended prior to this work (Engel, et al., 1973; Orrell & Sik, 1980). We noticed that solutions became saturated above this concentration and thus the value of Δv obtained was not accurate. $CDCl_3$ was found to be mutually convenient for dissolving the metal complexes and the reference (tert-butanol), with the exception of $Co(acac)_2(H_2O)_2$; deuterated DMSO was utilised as a solvent in this instance. Figure 2 shows an example of how the methyl protons of the tert-butanol reference is split by the presence of a paramagnetic substance, which in this instance is $Fe(acac)_3$.

At least five concentrations were measured for each metal complex. Students can use a stock solution of metal complex and simply dilute down for the next, lower, concentration. A linear trend line should relate these points to one another, the gradient of which is $Δv/Δc$ in Eq. (3). Fig. 3 shows the graph produced when $Mn(acac)_3$ was analysed in this way. Provided the geometrical parameters of the concentric tubes used are known along with the frequency of the NMR instrument employed, χ_M can be calculated. The line splitting of the methyl protons of *tert*-butanol is small (~10 Hz) in the presence of $Co(acac)_3$, even at relatively high concentrations. In addition, it is difficult to ascertain which peaks should be utilised to measure $Δv$. The measurement of χ_M using the static method is therefore not encouraged for samples of $Co(acac)_3$.

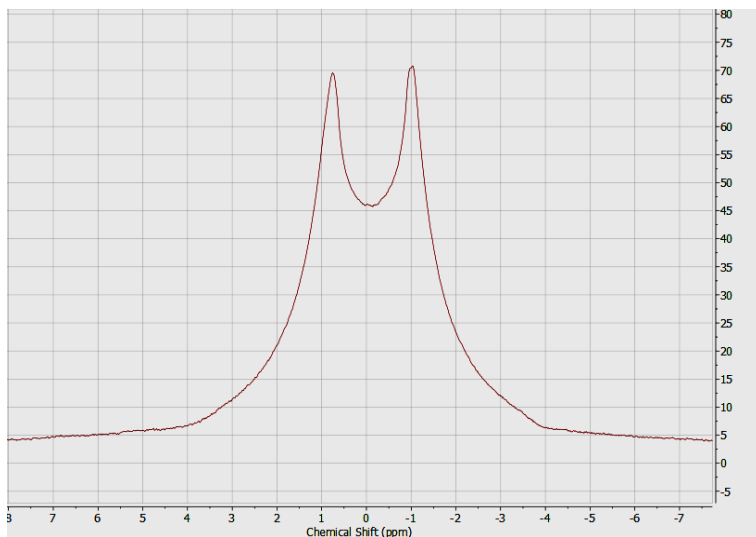**Figure 2.** ^{1}H NMR spectrum acquired using the static Evans' method in which 3% tert-butanol in $CDCl_3$ is in the outer tube and $Fe(acac)_3$ in $CDCl_3$ (0.12 M) is in the insert. Peak shown is the split peak of the methyl protons of tert-butanol. The splitting of the peak is 105.6 Hz
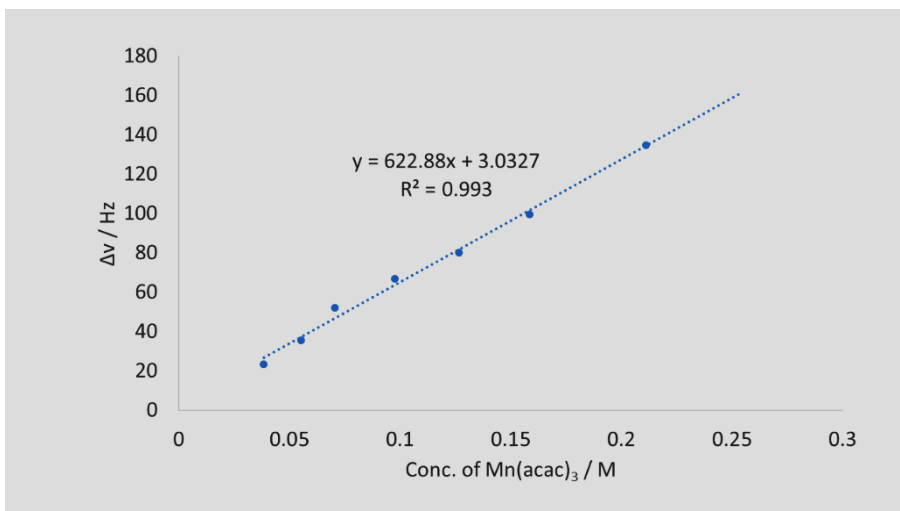

Figure 3. Plot of Δv for the split peak of the methyl protons of tert-butanol vs $\Delta[Mn(acac)_3]$ which shows a linear relationship between the data points. $\Delta v/\Delta c$ was found to be 622.88 Hz mol^{-1} dm^3. Data collected at 35.4°C

It is noteworthy that the temperature of the NMR probe needs to be determined prior to data collection. This is required when deducing μ_{eff} as it is proportional to the square-root of temperature. Furthermore, magnetic susceptibility changes with temperature. This has ramifications when acquiring the ^{1}H NMR spectrum required in order to obtain Δv for a given concentration of metal complex. We found that a cooled ethylene glycol sample took around 10 minutes to equilibrate to a stable temperature within the magnet. Thus, when acquiring data for the metal complexes, ample time needs to be given to enable the sample to equilibrate, or the samples placed in a water bath matching the temperature of the probe prior to analysis. We found that by running a series of ^{1}H NMR data acquisitions (n = 4, number of scans per spectrum = 16, recycle time = 5 s) on a sample that was at room temperature prior to insertion in to the NMR spectrometer, that the value of Δv could change by as much as ~60% prior to stabilisation. Evidently, this would have a large effect on the trend line produced upon graphically inspecting the data.

The predicted and experimentally determined μ_{eff} values obtained for the four metal complexes synthesised are shown in Table 1. There is good agreement between the Guoy balance data and that of the NMR method utilised herein. Both sets of data compare well with the theoretical values, thus enabling the students to deduce the high- or low-spin electronic configuration of the *d*-orbitals. The only sample that does show variation is the $Co(acac)_2(H_2O)_2$ complex. This is not due to experimental error, but more that the equations utilised consider spin-only paramagnetism. The difference between the experimental and theoretical μ_{eff} values (~0.5 BM) is due to contribution from orbital angular momentum. Departure from spin-only values are regularly observed for high-spin 3d[7] complexes (Burns et al., 2016; Chandra et al., 2006; Edwards et al., 2006; Singh et al., 2006; Tsitovich et al., 2018) and is observed for the $Co(acac)_2(H_2O)_2$ complex utilised here. The inclusion of the $Co(acac)_2(H_2O)_2$ complex therefore encourages students to consider carefully the electronic occupation of the *d*-orbitals in order to reason why there is a difference between experimental and theoretical values. The use of crystal field splitting diagrams is again encouraged here.

Table 1. Predicted and experimentally determined μ_{eff} values for the four metal complexes investigated

Complex	High-spin predicted μ_{eff} / BM	Low-spin predicted μ_{eff} / BM	μ_{eff} determined from Guoy balance / BM	μ_{eff} determined from NMR method / BM
$Mn(acac)_3$	4.90	2.83	4.7 – 4.9	4.75
$Fe(acac)_3$	5.92	1.73	5.6 – 6.1	6.15
$Co(acac)_3$	4.90	0	0	Not measureable
$Co(acac)_2(H_2O)_2$	3.87	1.73	4.3 – 5.2	4.40

The effect of the metal complexes prepared was further studied by measuring the spin-lattice relaxation (T_1) of the methyl protons of *tert*-butanol. Again, the magnetic properties of the complexes prepared is the focus of the study; paramagnetic metal complexes shorten T_1 values considerably whereas diamagnetic complexes have little effect. The significant shortening of T_1 values, as exemplified in figure 4 for $Mn(acac)_3$, is one of the main reasons why gadolinium(III), iron(III) and manganese(II) complexes have been developed and utilised as MRI (Magnetic Resonance Imaging) contrast agents (Felton et al., 2014; Revia & Zhang, 2016; Tsitovich et al., 2014; Yadollahpour et al., 2016). This link should be impressed upon students so that they can contextualise the experiment in to a real-world setting. Table 2 reports the values obtained by conducting a series of inversion recovery experiments.

The inversion recovery experiments for the paramagnetic complexes demonstrate a significant reduction in the T_1 value. The paramagnetic complexes shorten the T_1 of the methyl protons of *tert*-butanol in the order $Fe(acac)_3 > Mn(acac)_3 > Co(acac)_2(H_2O)_2$. This trend reflects the experimentally determined μ_{eff} values as well as the number of unpaired electrons that the central metal ion possesses. These experimental data were obtained relatively quickly due to short time delays being required between the 180° and 90° flip angles of the pulse programme and quick recovery times between each scan. Conversely, the relaxation times for *tert*-butanol in either $CDCl_3$ or DMSO-d_6, or in the presence of $Co(acac)_3$, are relatively long. There exists only a ~5% difference in the T_1 value of the *tert*-butanol methyl protons in the presence or absence of 0.1 M $Co(acac)_3$. The diamagnetic nature of $Co(acac)_3$ can be exemplified to students through the consideration of these values.
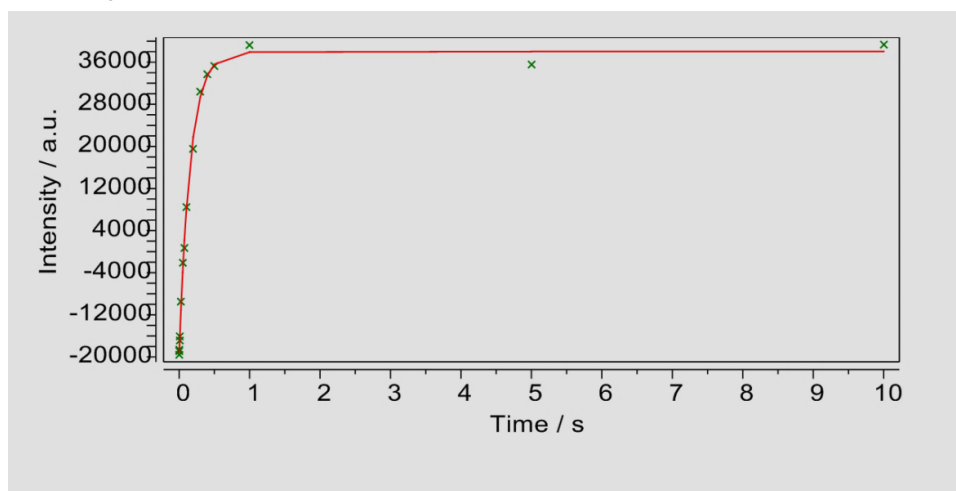

Figure 4. Inversion recovery (T_1) data for 0.1 M $Mn(acac)_3$ in $CDCl_3$

Table 2. T_1 values for the *tert*-butanol methyl protons in different solvents and in the presence of different metal acetylacetonate complexes. Solutions consisted of 3% *tert*-butanol and 0.1 M metal acetylacetonate complex (if present). All experiments conducted in air.

Entry	T_1 of *tert*-butanol /s
$CDCl_3$	3.60
$CDCl_3$ and $Co(acac)_3$	3.39
$CDCl_3$ and $Fe(acac)_3$	0.03
$CDCl_3$ and $Mn(acac)_3$	0.16
DMSO-d_6	3.60
DMSO-d_6 and $Co(acac)_2(H_2O)_2$	0.88

Experimental

All data was acquired on an Oxford Instruments Pulsar operating at 60 MHz for [1]H. The internal temperature of the probe was ascertained using a sample of neat ethylene glycol and measuring the separation (in Hz, $\Delta\delta$) between the CH_2 and OH signals. The temperature was calculated to be 35.4°C from the equation T [K] = 466.5 - 102.00 $\Delta\delta$ (Ammann et al., 1982).

For the Evans method experiments, the outer tube consisted of 3% *tert*-butanol in $CDCl_3$, whereas the inner tube consisted of the metal complex dissolved in $CDCl_3$. Due to poor solubility in $CDCl_3$, samples of $Co(acac)_2(H_2O)_2$ were dissolved in DMSO (likewise for the *tert*-butanol reference in this instance). The concentration of solute was 0.25 M or lower. Concentric cavity sample tubes were obtained from Wilmad. The geometric shape factors for such an arrangement were as follows: a_1 (inside radius of inner tube) = 0.0635 ± 0.0005 cm; a_2 (outside radius of inner tube) = 0.1016 ± 0.0005 cm; and a_3 (outside radius of the annulus) = 0.2104 ± 0.0005 cm. The geometric term (a_3^2/a_1^2) for these tubes was thus determined to be 11.07.

Synthesis of Mn(acac)$_3$

Manganese chloride(II) tetrahydrate (2.60 g, 0.013 mol) and sodium acetate (6.80 g, 0.083 mol) were dissolved in distilled water (100 ml) to which was added acetylacetone (10 ml, 0.097 mol). To this solution was added a solution of potassium permanganate (0.52 g, 3.30 mmol) in distilled water (25 ml) over a period of 10 minutes. Then a solution of sodium acetate (6.30 g, 0.077 mol) in distilled water (25 ml) was added, with stirring, over a period of 10 minutes. Stirring was continued and the solution heated to 60-70°C for 15 minutes, followed by cooling to room temperature and finally placed in an ice bath. The dark precipitate was collected by filtration, washed with distilled water (2 x 10 ml), and then dried in a vacuum desiccator.

Synthesis of Fe(acac)$_3$

Iron(II) chloride tetrahydrate (3.30 g, 0.017 mol) was dissolved in distilled water (25 ml). Over a period of 15 minutes, with stirring, a solution of acetylacetone (4 ml, 0.039 mol) in methanol (10 ml) was added. To the resulting red mixture, sodium acetate (5.1 g, 0.062 mol) in distilled water (15 ml) was added, resulting in the formation of a red precipitate. The solution was then heated to 80°C for 15 minutes, before allowing to cool to room temperature, prior to being placed in an ice bath. The product was collected by filtration, washed with cold distilled water (2 x 10 ml) and then transferred to a vacuum desiccator to dry.

Synthesis of Co(acac)$_2$(H$_2$O)$_2$

To a solution of acetylacetone (3.3 ml, 0.032 mol) in distilled water (15 ml) was added NaOH (1g, 0.025 mol) with stirring. This solution was added dropwise to a solution of CoCl$_2$.6H$_2$O (3 g, 0.013 mol) dissolved in distilled water (40 ml) with stirring. Stirring was continued for 15 minutes after which the orange precipitate was collected by filtration and washed with distilled water (2 x 10 ml). The product was then transferred to a vacuum desiccator to dry further.

Synthesis of Co(acac)$_3$

A solution of cobalt(II) carbonate (2.5 g, 0.021 mol) and acetylacetone (20 ml, 0.194 mol) were heated to 90°C with stirring. While heating, 10% hydrogen peroxide solution (30 ml) was added dropwise over 30 minutes. After addition was complete, heating was maintained for a further 15 minutes. The solution was then allowed to cool to room temperature before cooling further in an ice bath. The dark green precipitate was collected by filtration before being placed in an oven (100°C) to dry.

Conclusion

The employment of the static Evans method to measure χ_M for a series of synthesised first-row transition metal acetylacetonate complexes has been described. Comparison against values obtained from the Guoy balance method shows very good agreement. The ease of the static method, which simply requires students to measure the frequency difference between the split peak of the methyl resonance of *tert*-butanol for different concentrations of metal complex, means that it is comparable to the Guoy balance in terms of its accessibility by students. The static Evans method therefore offers laboratory coordinators a complimentary approach to measuring χ_M without the need for high-field instrumentation. Furthermore, the collection of ^{1}H NMR spectra of the complexes can aid students to rationalise the use of paramagnetic complexes in medicine, especially when coupled with the collection of T$_1$ relaxation data.

NOTES

1. Anton Dobzhenetskiy, Callum A. Gater, Alexander T. M. Wilcock and Ryan E. Mewis contributed equally to the production of this manuscript.

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