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Proton Magnetic Resonance Spectrum of Magnesium Acetylacetonate in Chloroform-*d*. Evidence for Conformational Equilibrium

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It has been known for some time that the proton magnetic resonance (^{1}H NMR) spectra of most bis and tris diamagnetic metal acetylacetonate (abbreviated as "acac") complexes consist of a pair of singlets.[1,2] One is due to the $-CH_3$ protons and the other to the ring proton (Figure 1). The intensity ratio of the two signals is 6:1. The chemical shifts of these protons are relatively insensitive to the solvent used and to the particular metal in the complex.[3,4] An exception to these observations has, however, been noted. Eaton[4] has reported that $Mg(acac)_2$, dissolved in $CDCl_3$, exhibits two peaks due to methyl resonances. This doubling was ascribed to nonequivalent methyl groups and it was concluded that the compound was not symmetric. Other investigators have reported the ^{1}H NMR spectrum of $Mg(acac)_2$ in dimethyl-d_6 sulfoxide and observed only one peak attributable to methyl resonances.[5]

A possible explanation for the observed solvent dependence of the ^{1}H NMR spectrum of $Mg(acac)_2$ can be based on the existence of a solvent-dependent equilibrium between two geometrical isomers of the bis-bidentate chelate system. According to this explanation, the two methyl resonances in $CDCl_3$ can be attributed to the presence of significant concentrations of both isomers, whereas the single methyl resonance observed in dimethyl-d_6 sulfoxide would indicate that one isomer is preferred in this solvent.

There are two preferred molecular symmetries for bis-acetylacetonate complexes. The four oxygens of the acac ligands may be arranged in a distorted tetrahedral configuration around the metal atom (D_{2d} symmetry) or they may be placed in one plane (D_{2h} symmetry). Detailed structural data indicating which form is more stable in the gas phase or in solution do not exist. Semiempirical molecular orbital calculations have been performed in the CNDO/2 approximation[7] on both the D_{2d} and D_{2h} structure types, and it was found that the D_{2d} isomer was more stable than the D_{2h} by ~0.45 eV (~10 kcal/mol).[8] It is possible to convert one isomer into the other by a 90° rotation of one acac ring as a whole about the metal atom.

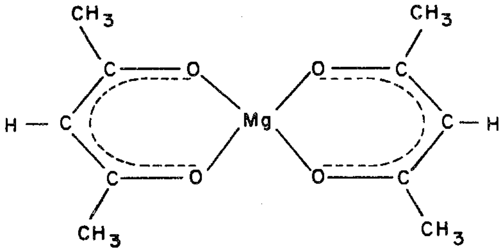

Figure 1. Structure of $Mg(acac)_2$.

To examine the possibility of whether one methyl resonance of $Mg(acac)_2$ in $CDCl_3$ is in fact due to the $-CH_3$ protons of a D_{2d} isomer and the other to a D_{2h} isomer, the ^{1}H NMR spectra of a series of bis-acetylacetonate comlexes were recorded in a variety of solvents. Since the chemical shift of the methyl groups on an acac ring appears to depend primarily on the geometry of the complex and not on the identity of the central metal ion, it seemed reasonable to compare the shifts of some D_{2d} and D_{2h} complexes with the values found for $Mg(acac)_2$.

It is known that $Be(acac)_2$ adopts a D_{2d} conformation[9] and that $Ca(acac)_2$ and $Ba(acac)_2$ probably are of D_{2h} symmetry.[1] It is also known that, in the absence of polymerization, four-coordinate zinc β-diketonates are D_{2d}.[10,11]

A final test for conformational equilibrium may be made by obtaining the chemical shifts of protons in unsymmetric β-diketone ligands.[12] If one of the $-CH_3$ groups on each chelating ring in Figure 1 is replaced by a phenyl group, one obtains the benzoylacetone complex (abbreviated as "bzac"). If this chelate were found in the D_{2h} form, two methyl resonances would be observed, while only one should be observed if the D_{2d} conformation were adopted. The ^{1}H NMR spectrum of this complex was also recorded in a variety of solvents.

Experimental Section

All β-diketonates were prepared according to the standard methods summarized by Fernelius and Bryant,[6] and their purity was checked by ir spectroscopy. All solvents were NMR quality and used without further purification. Due to the low solubility of the chelates in $CDCl_3$, only saturated solutions could be employed. Chemical shifts were measured relative to TMS using a Varian A-60A spectrometer, whose probe temperature was 36°C. The variable-temperature NMR spectra were measured on a JEOL PS100P/EC-100 pulsed Fourier transform spectrometer, having a spectral range of 1 kHz and using 4000 data points in the frequency domain. Temperature control was effected with a JEOL JNMVT3B model, and the probe temperature was measured with a Yellow Springs Instrument thermistor. The temperatures quoted are accurate to ±1°C.

Results and Discussion

The ^{1}H NMR chemical shifts of $Mg(acac)_2$, $Be(acac)_2$, $Zn(acac)_2$, $Ca(acac)_2$, and $Ba(acac)_2$ in various solvents are collected in Table I. It may be seen that the shifts tend to cluster in two groups: one occurring from 102 to 110 Hz (1.70–1.83 ppm) downfield from TMS and the other from 116 to 121 Hz (1.93–2.02 ppm). All bis complexes exhibit one methyl resonance in one group or the other, but only $Mg(acac)_2$ in $CDCl_3$ shows resonances in both groups.

It is apparent from Table I that D_{2h} methyl resonances occur between 102 and 110 Hz, while D_{2d} protons are found between 116 and 121 Hz. Thus, one may assign the methyl resonance of $Mg(acac)_2$ in $CDCl_3$ at 108 Hz to a D_{2h} isomer and the peak at 121 Hz to a D_{2d} isomer. $Mg(acac)_2$ was quite soluble in dimethyl sulfoxide, acetone, dioxane, and pyridine, and the resulting chemical shifts indicate the presence of only a D_{2h} isomer. One expects these solvents to coordinate directly to

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Table I. Chemical Shifts of Bis-Acetylacetonate Complexes[a]

	$-CH_3(D_{2h})$	$-CH_3(D_{2d})$	-CH
	(a) $Mg(acac)_2$		
$CDCl_3$	108	121	331
DMSO-d_6	102		304
Acetone-d_6	110		315
Dioxane	107		311
Pyridine	106		312
	(b) $Be(acac)_2$		
CCl_4		116	328
$CDCl_3$		121	334
	(c) $Zn(acac)_2$		
CCl_4		121	322
$CDCl_3$		119	326
	(d) $Ca(acac)_2$		
$CDCl_3$	107		309
DMSO-d_6	103		306
	(e) $Ba(acac)_2$		
$CDCl_3$	106		308
DMSO-d_6	102		302

[a] The shifts are in Hz from TMS taken at a frequency of 60 MHz.

Table II. Chemical Shifts of Bis-Benzoylacetone Complexes[a]

	$-CH_3(D_{2h})$	$-CH_3$- (D_{2d})	-CH- (ring)	-CH- (C_6H_5)
	(a) $Mg(bzac)_2$			
$CDCl_3$	109, 110	123	334	455
DMSO-d_6	103, 104		308	441
Acetone-d_6	112, 113		319	443
	(b) $Be(bzac)_2$			
$CDCl_3$		118	330	458
CCl_4		124	335	460
	(c) $Ca(bzac)_2$			
DMSO-d_6	104, 105		308	445
Acetone-d_6	106, 107		310	441

[a] The shifts are in Hz from TMS taken at a frequency of 60 MHz.

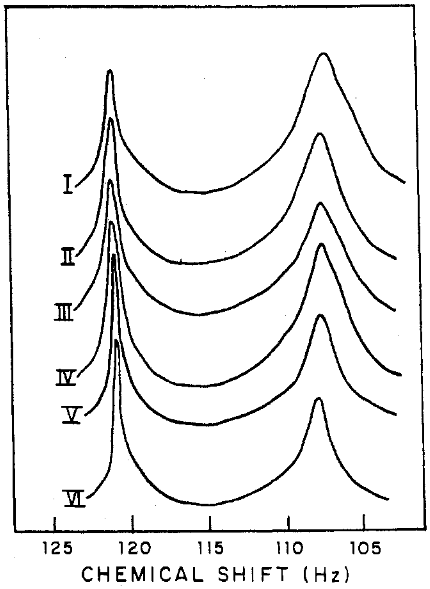

Figure 2. Variable-temperature ^1H NMR spectra of $Mg(acac)_2$ in $CDCl_3$. Numbers I, II, III, and IV were taken at 24, 35, 45, and 54°C, respectively, and were obtained in sequence. Numbers V and VI show the spectra at 29 and 24°C, respectively, and result from the subsequent cooling of the sample.

the empty fifth and sixth positions, which forces the two ligands to lie in one plane and accounts for the high solubility. In fact, pyridine is able to coordinate to some zinc(II) and copper(II) β-diketonates so strongly that the adduct is isolatable.[13] On the other hand, $CDCl_3$ is not expected to coordinate to the metal ion strongly (it is only slightly soluble in $CDCl_3$) and thus we expect to observe a mixture of D_{2d} and D_{2h} conformations. CCl_4 could not possibly coordinate to $Mg(acac)_2$ and the complex is absolutely insoluble in this solvent.

The ^1H NMR spectra of $Mg(bzac)_2$ in various solvents provide further evidence for D_{2d}–D_{2h} conformational isomerization. The data summarized in Table II show that methyl protons which were assigned as belonging to D_{2h} isomers in Table I now display two resonances, while those which were thought to be D_{2d} show only one resonance. The data for $Mg(bzac)_2$ in $CDCl_3$ again show methyl resonances characteristic of D_{2d} and D_{2h} forms.

To investigate these effects further, the NMR spectrum of $Mg(acac)_2$ in $CDCl_3$ was measured at several temperatures. The spectra obtained are shown in Figure 2. The temperature of the sample was first raised and then lowered in an attempt to see whether the observed effects were reversible. No effects attributable to different relaxation times were observed, as shown by varying the pulse repetition rate from every 2.1 sec to every 6.3 sec.

Remembering that the downfield peak is attributed to the more stable D_{2d} isomer, the first spectrum at 24.5°C shows more D_{2h} isomer than D_{2d}. The lines are not exceptionally wide, so it seems reasonable to assume that the isomers are *not* interconverting rapidly compared to the NMR time scale. However, on warming the solution up to 35°C, we find that the situation has reversed, and now the D_{2d} peak has risen higher than the D_{2h}. This observation suggests that the concentration of the D_{2d} isomer is growing at the expense of the D_{2h}.

Further warming to 45° shows a greater increase in D_{2d} peak intensity, but very little change is observed on heating from 45 to 54°. Subsequent cooling of the sample did *not* alter this pattern and it was not possible to return to the original height ratios by cooling the sample back to 24°C.

Since the original pattern could not be reestablished, it is concluded that a substantial potential energy barrier separates the two conformers. The original ratio of D_{2d}:D_{2h} must then represent the ratio present when the compound was formed. At 54°C, interconversion is possible and a new ratio (dependent on the solvation of the chelate by $CDCl_3$) is achieved. Subsequent cooling merely has the effect of preserving this ratio.

It was not possible to record reproducible numerical integrations of the data due to the low concentration of solute in the solution, but it was possible to employ graphical techniques in the estimation of peak areas. Since the spectra were not normalized to a common reference, only the peak ratios are of significance and these are displayed in Table III. The data indicate that at all temperatures, the concentration of D_{2h} isomer exceeded that of the D_{2d} isomer. This points out the danger of drawing conclusions based solely on intensity values; even though the height of the D_{2d} peak exceeded that of the D_{2h}, the latter possessed a much broader line width than the former. The data also indicate that once the limiting ratio at 54°C was reached, cooling the sample did not alter the ratio appreciably.

A rough correlation of metal ionic radius and $M(acac)_2$ configuration is possible. It has been noted[1] that a discontinuity in melting points of the series Be–Mg–Ca–Ba is seen between $Mg(acac)_2$ and $Ca(acac)_2$, and this has been ascribed to a change in conformation. The ^1H NMR data appear to indicate that the size of the Mg(II) ion is such that it allows its β-diketonate complexes to adopt either D_{2d} or D_{2h} conformation, although the D_{2d} is preferred slightly.

Table III. Ratio of the D_{2d}:D_{2h} Peak Areas

Temp, °C	D_{2d}:D_{2h}	Temp, °C	D_{2d}:D_{2h}
24	0.252	54	0.456
35	0.384	29	0.443
45	0.433	24	0.427

While two methyl resonances were observed for $Mg(acac)_2$ in $CDCl_3$, only one resonance due to ring protons was observed. If the chelate rings were not symmetric, more than one peak might be expected. However, since these protons are not affected by isomer interconversion (lying on a symmetry axis common to both conformers), only one resonance is predicted, as observed.

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Registry No. $Mg(acac)_2$, 14024-56-7; $Be(acac)_2$, 10210-64-7; $Zn(acac)_2$, 14024-63-6; $Ca(acac)_2$, 19372-44-2; $Ba(acac)_2$, 12084-29-6; $Mg(bzac)_2$, 15292-04-3; $Be(bzac)_2$, 14128-75-7; $Ca(bzac)_2$, 56513-90-7.

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Hydroxide Effects on the Electron Paramagnetic Resonance Spectrum of Aqueous Vanadyl(IV) Ion[1]

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Recently, the electron paramagnetic resonance (EPR) spectrum of the vanadyl ion (VO^{2+}) has been successfully employed as a probe of micelles,[2] anionic surfaces of acidic lipid bilayers,[3] metal-binding sites of a number of proteins,[4-9] and ATP hydrolysis.[10] In probe experiments where coordinating buffers are absent, it is often necessary to know the nature of vanadyl hydroxide species present in solution and their EPR characteristics.[6,8] We report here a quantitative EPR study of the major vanadyl hydroxide species below pH 7.

Experimental Section

Aqueous $VOSO_4$ (Alfa Inorganics) stock solution (0.0442 *M*) was prepared and standardized spectrophotometrically (molar extinction coefficient of 17.6 M^{-1} cm^{-1} at 750 mm).[5] A 200-ml amount of 4.42×10^{-4} *M* $VOSO_4$ (initial pH 2.5 (adjusted with HCl)) was titrated under nitrogen in a three-neck flask fitted with a combination calomel-glass pH electrode and rubber serum stoppers. Aliquots of standard 1.0 *N* NaOH solution were added with a microliter syringe. Samples were withdrawn periodically with a syringe and transferred to a serum stoppered nitrogen flushed quartz flat cell. The small amount of suspended vanadyl hydroxide precipitate was not removed prior to measuring the spectrum. The titration was performed twice to verify reproducibility. The sample was acidified with HCl at the end of the titration and EPR signal intensity measured to check for possible oxidation of the vanadyl ion. The EPR intensity was unchanged from before. Spectra were recorded on a Varian E-4 spectrometer operating at X-band and tuned according to procedures given in reference 9. The temperature was 25 ± 2°C.

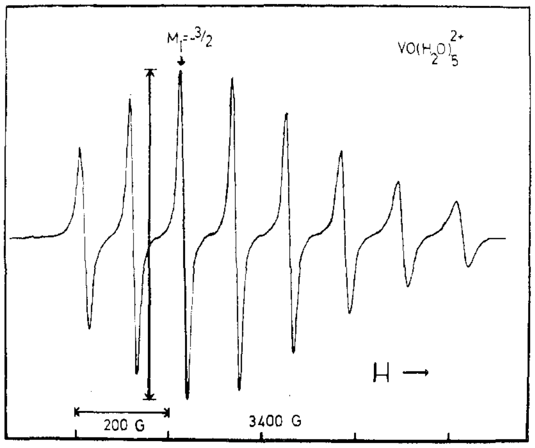

Figure 1. First-derivative isotropic EPR spectrum of $VO(H_2O)_5^{2+}$. The signal height of the $M_I = -{}^3/_2$ line used in determination of $[VO^{2+}]_{EPR}$ is indicated.

Results and Discussion

The EPR spectrum of $VO(H_2O)_5^{2+}$ is shown in Figure 1. The eight lines arise from the vanadium nuclear spin $I = {}^7/_2$. The first-derivative peak-to-peak intensity of the $M_I = -{}^3/_2$ line (notation assumes a negative nuclear hyperfine coupling constant) was used to determine the concentration of EPR-detectable vanadyl species, hereafter referred to as $[VO^{2+}]_{EPR}$. Such a procedure is valid if the unknown and standard samples are the same chemical species in the same matrix.[9] A double integration of the first-derivative line is not required in this instance. Figure 2 shows the standard curve.

In Figure 3 the marked decrease in the vanadyl EPR intensity with increasing pH is presented. Three linear regions are observed which correspond to the formation of different hydroxide species. The equilibria which can be used to explain the data in Figure 3 are

$$VO^{2+} + H_2O \underset{}{\overset{K_{1,1}}{\rightleftharpoons}} VOOH^+ + H^+ \qquad (1)$$

$$2VO^{2+} + 2H_2O \overset{K_{2,2}}{\rightleftharpoons} (VOOH)_2{}^{2+} + 2H^+ \qquad (2)$$

$$VO^{2+} + 2OH^- \overset{K_{sp}}{\rightleftharpoons} VO(OH)_2\downarrow \qquad (3)$$

For simplicity coordinated water has been omitted from the equations.

Jones and Ray[11] measured the pH of pure vanadyl sulfate in the concentration range 1×10^{-4} to 0.5 *M*. Their data have been subsequently treated by Meites[12] to obtain $K_{1,1} = 4.4 \times 10^{-6}$ for the formation of $VOOH^+$ via eq 1.

Both free VO^{2+}, i.e., $VO(H_2O)_5^{2+}$, and $VOOH^+$ are paramagnetic; however, over most of the pH range studied the $VOOH^+$ species represents only a small fraction of the total contribution to the observed EPR signal. We were never able to observe resolved spectra due to free VO^{2+} and $VOOH^+$ with room-temperature or frozen-solution (pH 4.5) samples.