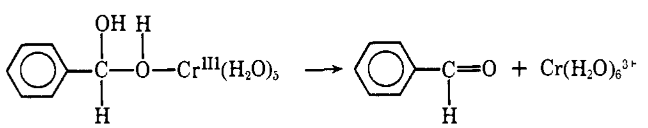
probably reacts by hydrating and then decomposing to the carbonyl for (*via* C–O bond cleavage)



At present these ideas are at best reasonable conjectures, and further work will be necessary before the system is understood. The most useful evidence for diagnosis would be the absorptivities over a range of wavelength as a function of time.

Acknowledgment. Financial support for this research by the National Institutes of Health, both for Grant No. GM 13638 and for Fellowship support for A. Z., 1967–1970, is gratefully acknowledged.

Proton and Deuteron Nuclear Magnetic Resonance Isotope Shifts in Partially Deuterated Tris(2,4-pentanedionato)vanadium(III)

Richard R. Horn[1] and G. W. Everett, Jr.*

Contribution from the Department of Chemistry, The University of Kansas, Lawrence, Kansas 66044. *Received May 17, 1971*

Abstract: The proton and deuteron nmr spectra of tris(2,4-pentanedionato)vanadium(III) show three signals in the methyl resonance region when the ligand is partially deuterium substituted. The relative areas of these signals vary with the extent of deuteration. A series of complexes has been investigated in which the extent of deuteration at the ligand methyls ranges from 0 to 93%. For each complex the relative abundances of the four possible methyl groups CH_3–, CH_2D–, CHD_2–, and CD_3– were determined from mass spectra. A good correlation is found between the relative abundances of these groups and the relative nmr signal areas for each complex. It is concluded that the three proton resonance signals may be attributed to CH_3–, CH_2D–, and CHD_2–, and that the three deuteron resonance signals arise from CD_3–, CHD_2–, and CH_2D– groups on the ligands. Possible origins of the observed isotope shifts are discussed.

The shift of a nuclear magnetic resonance signal resulting from isotopic substitution at a neighboring site was first observed by Wimett in 1953 upon comparing the proton and deuteron spectra of H_2, D_2, and HD.[2] Several years later Tiers discovered a chemical shift difference in the ^{19}F resonances of n-C_3F_7H and n-C_3F_7D and subsequently observed a much smaller chemical shift difference in the methyl proton resonances of $C_6H_5CH_3$ and $C_6H_5CH_2D$.[3] Since that time "isotope shifts" have been reported for a number of compounds, utilizing ^1H, ^{59}Co, ^{19}F, and ^{13}C nmr, and several attempts have been made to explain the origin of the effect. The literature up to 1967 has been reviewed.[4]

In a recent report from this laboratory, which compares the resolution of proton nmr (pmr) and deuteron nmr (dmr) for several paramagnetic transition metal acetylacetonate complexes and their deuterated analogs, an unexpected splitting of methyl resonance signals for the V(III) and Mo(III) complexes was mentioned.[5] The splitting has now been examined in detail for the V(III) complex. Results of this investigation are presented along with arguments supporting our conclusion that the observed splittings are isotope shifts arising from incomplete deuteration of the ligand methyls. The shifts reported here for the paramagnetic V(III) complex are an order of magnitude larger than those generally found upon deuterium substitution in diamagnetic compounds.

Experimental Section

Deuteration of Ligands. 2,4-Pentanedione (Matheson Coleman and Bell) was deuterated by the following procedure. A mixture of the diketone and deuterium oxide, in a 1:8 mole ratio, respectively, is refluxed over a period of 24 hr in the presence of a small amount of Na_2CO_3. The mixture is then extracted with diethyl ether, and the product is recovered from the ether solution by evaporating the solvent. Fresh deuterium oxide is added to this product, and the above procedure is repeated a number of times sufficient to attain the desired extent of deuteration. A rough estimate of the degree of deuteration may be made from the pmr spectrum of the crude product. Six repetitions were necessary to obtain the 93% deuterated ligand. At the end of the final deuteration cycle, the product is distilled. An accurate measure of the extent of deuteration may be obtained from the mass spectrum of the final product.

Tris(2,4-pentanedionato)vanadium(III). Since the V(III) complexes in solution are susceptible to oxidation by air, all solvents were thoroughly degassed, and solutions of the complexes were handled under a nitrogen atmosphere or *in vacuo* using apparatus

---

(1) NASA Predoctoral Trainee, 1969–present.

(2) T. F. Wimett, *Phys. Rev.*, **91**, 476 (1953).

(3) (a) G. V. D. Tiers, *J. Amer. Chem. Soc.*, **79**, 5585 (1957); (b) G. V. D. Tiers, *J. Chem. Phys.*, **29**, 963 (1958).

(4) H. Batiz-Hernandez and R. A. Bernheim, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 63 (1967).

(5) A. Johnson and G. W. Everett, Jr., *J. Amer. Chem. Soc.*, **92**, 6705 (1970).

described previously.[6] In the solid state the complexes may be exposed to air for short periods without apparent decomposition.

The fully protonated complex was prepared by adding 1.58 g (0.01 mol) of VCl_3 to 50 ml of water containing 3.00 g (0.03 mol) of 2,4-pentanedione and 1.59 g (0.015 mol) of Na_2CO_3. The solution was stirred for about 15 min, then ~50 ml of toluene was added forming a second liquid phase. The phases were mixed over an 8-hr period by vigorous stirring. The toluene phase, containing the complex, was removed and evaporated to half volume. Crystals of the complex formed upon cooling the toluene solution overnight at −20°. Recrystallization was achieved using benzene and petroleum ether (bp 30–60°).

The partially deuterated complexes were prepared in the same fashion, except that a D_2O–H_2O mixture having a mole ratio approximately equal to the fractional deuteration of the ligand was used in place of water. This procedure prevented appreciable change in the extent of ligand deuteration during synthesis of the complex. The extent of deuteration for each complex was determined from its mass spectrum. All complexes gave satisfactory carbon and hydrogen microanalyses when the experimental values for hydrogen were corrected for fractional deuteration. Melting points were all within 181–187°.

Mass Spectra. Mass spectra of ligands and V(III) complexes were routinely run on a Varian CH-5 mass spectrometer with the sample reservoir at 60° and an electron-beam energy of 70 eV. Corrections were made for background intensities measured under the same conditions, but ^{13}C corrections were found to be insignificant. The relative proportions of CH_3–, CH_2D–, CHD_2–, and CD_3– were determined from the intensities of the corresponding acetyl ion peaks at *m/e* 43, 44, 45, and 46, respectively. The acetyl ion is one of the dominant ions formed upon fragmentation of 2,4-pentanedione.[7] It was assumed that fragmentation is not significantly affected by deuterium isotope effects. The overall fractional methyl group deuteration for each sample was calculated from the acetyl ion intensities. Results are presented in Table II.

Nmr Experiments. Spectra of samples in sealed 5-mm nmr tubes were recorded on a Varian HA-100 instrument operating at 100.000 MHz for pmr and 15.351 MHz for dmr. The solvent used was a mixture of benzene and benzene-d_6, providing convenient reference signals for both pmr and dmr of the same sample. Chemical shifts relative to benzene or benzene-d_6 were measured by sidebanding. Results are tabulated in Table I. Most spectra were run at a probe temperature of 32°. Other probe temperatures were measured by means of methanol or ethylene glycol standards (pmr) or an iron–constantan thermocouple (dmr).

Table I. Chemical Shift Values for Partially Deuterated Tris(2,4-pentanedionato)vanadium(III)

Group	Proton resonance[a] δ, Hz[c]	Proton resonance[a] δ, ppm	Deuteron resonance[b] δ, Hz[c]	Deuteron resonance[b] δ, ppm
CH_3	−3835 ± 5	−38.35		
CH_2D	−3885 ± 8	−38.85	−560.8 ± 0.8	−36.53
CHD_2	−3941 ± 12	−39.41	−570.7 ± 1.0	−37.18
CD_3			−579.8 ± 0.7	−37.77
3-CH	−3152 ± 6	−31.52		
3-CD			−475.4 ± 0.2	−30.97

[a] At 100 MHz; chemical shifts relative to benzene. [b] At 15.35 MHz; chemical shifts relative to benzene-d_6. [c] Average values; errors are standard deviations.

Relative areas of the methyl signal components were determined by two independent methods. (1) The envelope of signals was resolved into its components by simple inspection. Areas were then measured with a planimeter. (2) A Du Pont 310 curve resolver, with breakpoints set to match the well-isolated methylene (3-CH) resonance, was used to resolve the signals and measure their areas. Agreement between the two methods was generally good, and the results of several independent determinations on each spectrum were averaged. Results are shown in Table II.

Results

The pmr spectrum of tris(2,4-pentanedionato)vanadium(III), hereafter abbreviated $V(acac)_3$, was first reported by Forman, *et al.*[8] The spectrum consists of a strong methyl resonance and a weaker resonance assigned to 3-CH. At 32° in benzene solution the signals occur at 38.35 and 31.52 ppm downfield, respectively, of the benzene resonance. Both signals are appreciably downfield of their diamagnetic resonance positions as a result of the isotropic shift effect.[9] In a pmr study of several paramagnetic acetylacetonate complexes, Eaton found $V(acac)_3$ to show the least paramagnetic signal broadening.[10] Thus $V(acac)_3$ was one of the

Table II. Comparison of Nmr and Mass Spectral Data

Complex	Group	Rel abundance[a]	Dmr area Calcd[b]	Dmr area Exptl[c]	Pmr area Calcd[b]	Pmr area Exptl[c]
I	CD_3–	0.00	0.00	0.06		
(12%)[d]	CHD_2–	0.03	0.17	0.31	0.01	0.05
	CH_2D–	0.29	0.83	0.63	0.22	0.30
	CH_3–	0.68			0.77	0.65
II	CD_3–	0.06	0.18	0.14		
(33%)[d]	CHD_2–	0.24	0.47	0.42	0.12	0.16
	CH_2D–	0.35	0.35	0.44	0.35	0.34
	CH_3–	0.35			0.53	0.50
III	CD_3–	0.24	0.41	0.35		
(59%)[d]	CHD_2–	0.40	0.45	0.49	0.32	0.45
	CH_2D–	0.24	0.14	0.16	0.39	0.39
	CH_3–	0.12			0.29	0.16
IV	CD_3–	0.49	0.62	0.56		
(78%)[d]	CHD_2–	0.41	0.35	0.37	0.63	0.66
	CH_2D–	0.06	0.03	0.07	0.19	0.26
	CH_3–	0.04			0.18	0.08
V	CD_3–	0.90	0.96	0.97		
(93%)[d]	CHD_2–	0.05	0.04	0.03	0.25	0.14
	CH_2D–	0.00	0.00	0.00	0.00	0.00
	CH_3–	0.05			0.75	0.86

[a] Determined from the corresponding acetyl ion intensities in mass spectra of the complexes. [b] Areas expected for nmr signals based on mass spectral abundances. [c] Average values of several determinations for each complex. Standard deviations are around ±0.02 for dmr and ±0.06 for pmr. [d] Overall percentage methyl deuteration.

---

[6] R. H. Holm, F. Röhrscheid, and G. W. Everett, Jr., *Inorg. Syn.*, **11**, 72 (1968).

[7] J. H. Bowie, D. H. Williams, S.-O. Lawesson, and G. Schroll, *J. Org. Chem.*, **31**, 1384 (1966).

[8] A. Forman, G. N. Murrell, and L. E. Orgel, *J. Chem. Phys.*, **31**, 1129 (1959).

[9] (a) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965); (b) E. deBoer and H. van Willigen, *Progr. Nucl. Magn. Resonance Spectrosc.*, **2**, 111 (1967).

first complexes to be investigated in a recent comparison of pmr and dmr line widths in paramagnetic acetylacetonate complexes.[5]

To a first approximation, the dmr spectrum of fully deuterated V(acac)$_3$ should closely resemble the pmr spectrum of the fully protonated complex. Isotropic shifts on a parts per million scale should be identical for pmr and dmr spectra of the same complex if measured under the same conditions of temperature and solvent.[5] However, it is found that where the extent of methyl group deuteration is in the range of 30-80%, three dmr signals occur in the region where the CD$_3$ resonance is expected. A single signal is found for 3-CD. Pmr spectra of the same complexes also reveal three resonance signals in the methyl region with signal separations (in hertz) larger by a factor of ~5-6 than those in the dmr spectra. Again a single signal is found for 3-CH. The relative intensities of the three methyl signals in both the pmr and the dmr spectra are found to vary with the extent of methyl deuteration.

In order to determine the origin of the multiplicity of methyl resonances, a series of five V(III) acetylacetonate complexes (I-V in Table II), varying from 12 to 93% overall methyl deuteration, was prepared. Pmr, dmr, and mass spectra of the complexes were obtained as described in the Experimental Section.

Mass Spectra. Mass spectra of partially deuterated ligands and vanadium(III) complexes in the acetyl region (m/e 43-46) reveal the relative proportions of CH$_3$-, CH$_2$D-, CHD$_2$-, and CD$_3$-, and the overall fractional deuteration of the methyls.[11] Statistical relative abundances of the four methyl groups, calculated from the overall methyl deuteration of a given complex, differ somewhat from the actual abundances. This is probably due to deuterium isotope effects operating during deuteration of 2,4-pentanedione with deuterium oxide. Also, slight changes in the abundances are found on comparing mass spectra of the ligands with those of the corresponding complexes, indicating additional isotopic exchange during preparation of the complexes. Therefore, the relative methyl group abundances given in Table II are those derived from mass spectra taken directly on the V(III) complexes.

Proton Resonance Spectra. Examination of the pmr spectra of the partially deuterated complexes (Figure 1) reveals a decrease in relative intensity of the signal at −38.35 ppm (downfield of the benzene reference) with increasing methyl deuteration. This signal occurs in the pmr spectrum of fully protonated V(acac)$_3$ and is assigned to the CH$_3$- group. Intensities of the two additional signals at −38.85 and −39.41 ppm increase with increasing methyl deuteration until deuteration is ~60% complete. Upon further deuteration, the signal at −38.85 ppm decreases in relative intensity, whereas that at −39.41 ppm continues to grow. The most plausible explanation for these observations is that the groups CH$_3$-, CH$_2$D-, and CHD$_2$ have observably different proton resonance frequencies, *i.e.*, isotope shifts. Signal assignments consistent with the above observations are as follows (in parts per million downfield of benzene): CH$_3$-, −38.35; CH$_2$D-, −38.85; and CHD$_2$-, −39.41. Chemical shift values for these groups in both hertz and parts per million are presented in Table I.

Support for these assignments is found upon comparing the experimentally determined relative areas of the pmr signals with areas predicted from mass spectral abundances of CH$_3$-, CH$_2$D-, and CHD$_2$-, assuming the above signal assignments are correct. The mass spectral abundances are weighted by the number of protons present, and both calculated and observed areas are scaled so as to sum to unity. The data are compared in Table II.

Deuteron Resonance Spectra. The dmr signal at −37.77 ppm from benzene-d_6 is the dominant signal found in the complex having an overall 93% methyl deuteration. As the percentage of deuteration decreases, this signal loses intensity relative to two new signals at −37.18 and −36.53 ppm. At 12% methyl deuteration, the signal at −36.53 ppm predominates (see Figure 1). The occurrence of these three signals is attributed to isotope shifts, and the following assignments are made (in parts per million downfield of benzene-d_6): CD$_3$-, −37.77; CHD$_2$-, −37.18; CH$_2$D-, −36.53. Chemical shifts in hertz are given in Table I.

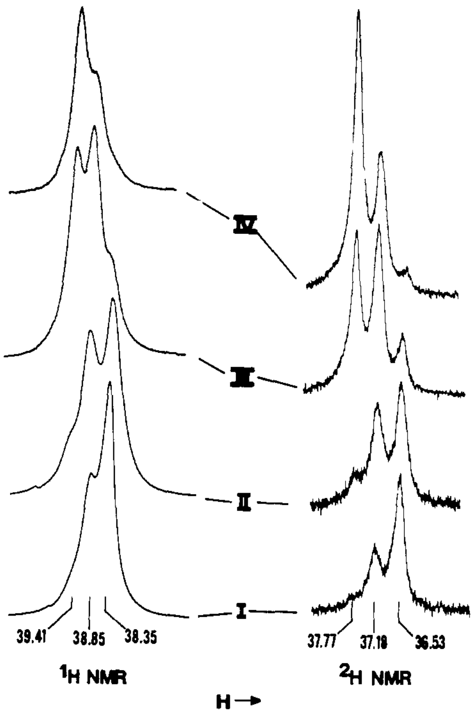


Figure 1. Pmr and dmr spectra of partially deuterated V(acac)$_3$ complexes in the methyl region. Complexes I, II, III, and IV have 12, 33, 59, and 78% overall deuteration, respectively, at the methyl group.

A comparison of the relative dmr signal areas with areas predicted from appropriately weighed mass spectral abundances of CD$_3$-, CHD$_2$-, and CH$_2$D-, assuming the above signal assignments, serves to substantiate the assignments. Results are set out in Table II.

---

(10) D. R. Eaton, *J. Amer. Chem. Soc.*, 87, 3097 (1965).

(11) We are primarily concerned with the extent of *methyl* deuteration rather than overall ligand deuteration, since the multiple nmr signals occur in the region of methyl resonance.

Discussion

The agreement between calculated and observed nmr signal areas shown in Table II varies with the extent of deuteration. Where the per cent deuteration is low (complexes I and II), better agreement is found for pmr data. This reflects uncertainties in the experimental dmr signal areas, since the signals are weak and the signal-to-noise ratio is lower than in the other complexes. Also, the mass spectral lines from deuterated acetyl ions are relatively weak, especially for CD_3–, and this introduces appreciable error in the calculated dmr signal areas. For complexes III and IV, the fit is somewhat better for dmr than for pmr. Here the narrower line widths and better resolution for the dmr spectra (Figure 1) enable more accurate measurements of signal areas. Agreement is again better for dmr in complex V, since the pmr signals are quite weak, and mass spectral intensities of protonated acetyl ions are not much above background.

The primary source of error undoubtedly resides in methods used to resolve the nmr spectra into component signals (see Experimental Section). However, the overall agreement for both pmr and dmr between measured signal areas and areas predicted from known abundances of the four methyl groups is satisfactory and supports the proposed signal assignments. It is concluded that nmr isotope shifts are indeed responsible for the multiplicity of methyl signals in the pmr and dmr spectra of partially deuterated V(acac)$_3$.

Several other possible origins of the multiple nmr signals have been considered. These are discussed in turn.

(1) Lowering of Symmetry. In fully protonated or fully deuterated V(acac)$_3$, C_2 and C_3 symmetry axes relate all six methyls, thus a single methyl resonance is expected and observed. Partial deuteration is capable of destroying one or more of these axes, leading to methyl group inequivalences which may be observable in an nmr spectrum.[12] Assuming random distribution of CH_3–, CH_2D–, CHD_2–, and CD_3– among the six sites of V(acac)$_3$, a large number of complexes exist, and most of these have several geometric isomers of low symmetry.[13] Thus a large number of pmr and dmr signals would be expected if the methyl group inequivalences are distinguishable by nmr. In contrast, no more than three nmr signals are found in any of the partially deuterated V(acac)$_3$ complexes. Furthermore, the 3-CD and 3-CH signals are not observably split in any of the spectra.

Further evidence against lowering of symmetry as the origin of the multiple resonances is derived from the following experiment. A sample of fully protonated V(acac)$_3$ was mixed in a 1:1 mole ratio with 93% methyl-deuterated 2,4-pentanedione ligand in degassed benzene, and the mixture was sealed *in vacuo* in an nmr tube. A large isotropic shift for the methyl resonance was observed in the *dmr* spectrum of this sample, proving that ligand exchange occurred. Such exchange generates "mixed ligand" complexes which have no C_3 symmetry axes and which could show nmr distinguishable methyl resonances. However, a single methyl resonance was found in both the pmr and dmr spectra of this sample.

(2) Spin–Spin Splitting. Geminal D–H spin coupling as the origin of the methyl resonance splitting can be ruled out by comparing the dmr spectra at 15.35 MHz with the pmr spectra at 100.0 MHz. The frequency separations of the pmr signals are five to six times those of the dmr signals. Since coupling constants are field and frequency independent, it must be concluded that the observed methyl resonances arise from magnetically inequivalent nuclei. Furthermore, spin–spin coupling would generate a pattern of signals having symmetry about the center signal.

(3) Diastereotopism. The existence of observable magnetic inequivalences among diastereotopically related[14] protons in metal complexes has been recognized and has recently been used for investigating intramolecular rearrangements.[15] The two protons of a CH_2D– group and the two deuterons of a CHD_2– group are diastereotopic when bound to a chiral center such as V(acac)$_3$.[16] The magnetic inequivalences would be expected to be very small, but they may be magnified by the fact V(acac)$_3$ is paramagnetic. If diastereotopism is observable in partially deuterated V(acac)$_3$, in the *absence* of isotope shifts one would expect three methyl signals in the pmr and in the dmr spectra. In each case the center signal due to CH_3– and CHD_2– (for pmr) or CD_3– and CDH_2– (for dmr) would be flanked by two satellites of equal area arising from the inequivalent nuclei on CH_2D– (for pmr) or CD_2H– (for dmr). Clearly, the observed spectra are not consistent with this (see Figure 1), and it must be concluded that diastereotopism is not responsible for the observed methyl resonance splitting.

Origin of the Isotope Shifts. Isotope shifts of the order of a few hundredths of a part per million occur in the pmr spectrum of partially deuterated 2,4-pentanedione. These are in the range (0.01–0.05 ppm) of shifts generally found in the pmr spectra of diamagnetic molecules.[4] Efforts to explain the origin of isotope shifts in polyatomic molecules have taken into consideration changes in shielding resulting from changes in bond distances and angles,[18] electrostatic interactions,[19] and vibrational energy[20] upon deuteration

---

[12] Nmr inequivalences are commonly observed in both paramagnetic and diamagnetic complexes of unsymmetrically substituted β-diketones; *cf.* (a) R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969); (b) A. Y. Girgis and R. C. Fay, *J. Amer. Chem. Soc.*, **92**, 7061 (1970); (c) J. G. Gordon, II, and R. H. Holm, *ibid.*, **92**, 5319 (1970); (d) G. W. Everett, Jr., and Y. T. Chen, *ibid.*, **92**, 508 (1970), and references cited in these papers.

[13] For example, it can be shown statistically for 59% overall methyl deuteration that the most abundant complex is ($CD_3COCHCOCHD_2$)($CHD_2COCHCOCHD_2$)($CHD_2COCHCOCH_2D$)V. This molecule in principle has five kinds of methyl protons and six kinds of methyl deuterons for each of four possible geometric isomers.

[14] K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).

[15] (a) B. Jurado and C. S. Springer, Jr., *Chem. Commun.*, 85 (1971); (b) L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, **93**, 360 (1971).

[16] This assumes the rate of inversion of the chiral center ($\Delta \rightleftarrows \Lambda$ for a tris chelate complex) is slow relative to the nmr frequency separation of the diastereotopic nuclei. For certain other β-diketone complexes of V(III), the rate of $\Delta \rightleftarrows \Lambda$ inversion is found to be sufficiently slow that separate resonances may be observed for corresponding nuclei in diastereomeric complexes differing only in configuration (Δ or Λ) about the metal ion.[12d,17]

[17] Y. T. Chen and G. W. Everett, Jr., *J. Amer. Chem. Soc.*, **90**, 6660 (1968).

[18] R. A. Bernheim and H. Batiz-Hernandez, *J. Chem. Phys.*, **45**, 2261 (1966).

[19] H. S. Gutowsky, *ibid.*, **31**, 1683 (1959).

[20] L. Petrakis and C. H. Sederholm, *ibid.*, **35**, 1174 (1961).

at neighboring sites. In most cases, deuterium substitution shifts the resonance signal of a neighboring proton toward higher field. The magnitude of the shift is proportional to the extent of deuteration.

Pmr and dmr isotope shifts found for partially deuterated V(acac)$_3$ are an order of magnitude larger than those reported for diamagnetic compounds. Clearly this is a result of the paramagnetism of the complex, and in order to explain the origin of the isotope shifts one has to consider the Fermi contact and/or the electron–nuclear dipolar interactions responsible for the *isotropic* nmr shifts. It is now generally accepted that isotropic shifts of ligand nuclei in tris(β-diketonato)vanadium(III) complexes result primarily from the contact interaction.[10,12d,17,21] The electronic ground state of V(acac)$_3$ in D_3 symmetry is believed[22] to be $^3A_2$, in which case the dipolar contribution to the isotropic shift is zero.

Comparison of experimental isotropic shifts of tris(β-diketonato)vanadium(III) complexes with spin densities calculated by the McLachlan method indicates that the predominant mechanism of spin delocalization involves partial transfer of α spin from the metal ion to the lowest energy unfilled π molecular orbital of the ligand.[12d,21] This places α spin in the pπ orbitals of carbons 2 and 4 (adjacent to the methyls) of the ligand. The large downfield shift of the methyl resonance results from a direct hyperconjugative interaction[23] between the spin-containing pπ orbital of carbon and the 1s orbitals of the methyl protons. The contact shift, ΔH_i, is given by eq 1, where the symbols have their usual meanings.[9] Replacement of a methyl proton by a deuteron could affect the resonance frequency of the remaining protons only by altering A, the isotropic hyperfine coupling constant, where

$$\frac{\Delta H_i}{H_0} = -A_i \frac{\gamma_e}{\gamma_N} \frac{g_e \beta_e S(S+1)}{3kT} \qquad (1)$$

$$A = (8\pi/3h) g_e g_N \beta_e \beta_N [\Psi(0)]^2 \qquad (2)$$

Changes in A, in turn, must reflect changes in $\Psi(0)$, the value of the spin-containing wave function at the resonating nucleus.

It is known that average C–D bond distances are shorter than C–H distances by 0.001–0.005 Å (primary isotope effect).[24] There is also evidence that deuterium substitution shortens neighboring bonds (secondary isotope effect)[24c,25] and that proton substitution in CD$_4$ lengthens C–D bonds.[26] Although secondary isotope effects are expected to be extremely small, such slight changes in bond distances or angles with isotopic substitution might be expected to result in slight changes in $\Psi(0)$, since the overlap between hydrogen 1s orbitals and the spin-containing π orbitals would depend on these quantities. Higher values of $\Psi(0)$ would be expected for shorter bonds and *vice versa.*

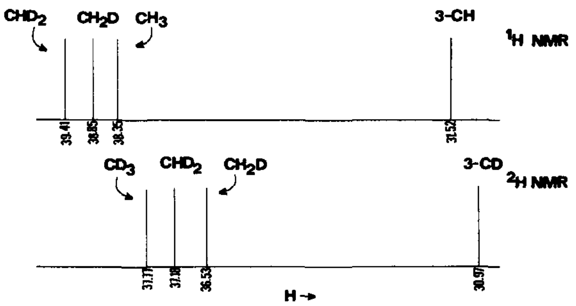


Figure 2. Schematic representation of pmr and dmr spectra of partially deuterated V(acac)$_3$ on a parts per million scale.

The relative resonance positions of the three methyl groups in the pmr spectrum of partially deuterated V(acac)$_3$, schematically presented in Figure 2, are in line with this simple hypothesis. It is seen that increasing methyl deuteration increases the observed pmr contact shift. This is consistent with decreasing C–H bond lengths and concomitant increase in $\Psi(0)$ and A. Similarly in the dmr spectrum, increasing protonation of CD$_3$– decreases the contact shift. This is consistent with increasing C–D bond lengths and decreasing $\Psi(0)$ and A. Thus it would appear that the occurrence of secondary isotope effects can account for the relative isotope shifts *within* a given spectrum. However, it is not clear why the dmr signals (in parts per million) are all upfield of the pmr signals, as shown in Figure 2. From consideration of primary isotope effects on bond lengths, one would expect greater $\Psi(0)$ for deuterium in all cases, resulting in larger contact shifts for dmr.[27] Possibly the greater electropositivity of deuterium over that of hydrogen bonded to carbon[28] is sufficient to offset the effect of a shorter C–D bond. Also, delocalization of spin through σ bonds, although not primarily responsible for the large contact shifts, may play a role in producing the much smaller isotope shifts.

Temperature Dependence of Isotope Shifts. Pmr and dmr spectra of complex III were recorded over the temperature range 30–120°. Resolution of the pmr spectra at high temperatures is poor, and the three methyl signals appear as a single broad envelope.

---

(21) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1315 (1967).

(22) (a) B. N. Figgis, J. Lewis, and F. Mabbs, *J. Chem. Soc.*, 2480 (1960); (b) T. S. Piper and R. L. Carlin, *Inorg. Chem.*, **2**, 260 (1963); (c) G. N. LaMar and G. R. Van Hecke, *J. Amer. Chem. Soc.*, **92**, 3021 (1970).

(23) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, pp 83–85.

(24) (a) L. S. Bartell, K. Kuchitsu, and R. J. DeNeui, *J. Chem. Phys.*, **35**, 1211 (1961); (b) V. W Laurie and D. R. Herschbach, *ibid.*, **37**, 1687 (1962); (c) L. S. Bartell and H. K. Higginbotham *ibid.*, **42**, 851 (1965); (d) J. E. Wollrab, "Rotational Spectra and Molecular Structure," Academic Press, New York, N. Y., 1967, p 110.

(25) R. H. Shwendeman and J. D. Kelly, *J. Chem. Phys.*, **42**, 1132 (1965).

(26) E. H. Richardson, S. Brodersen, L. Krause, and H. L. Welsh, *J. Mol. Spectrosc.*, **8**, 406 (1962).

(27) Epr of the C$_6$H$_5$D anion, for example, shows the ratio of deuteron to proton coupling constants to be larger than expected from consideration of the difference in γ_N alone [R. G. Lawler, J. R. Bolton, G. K. Fraenkel, and T. H. Brown, *J. Amer. Chem. Soc.*, **86**, 520 (1964)].

(28) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

Dmr spectra, however, clearly show three distinct signals at 120° with no apparent change in relative areas. Plots of contact shifts, measured from the free ligand resonance position, *vs.* $1/T$ are linear for all three signals, as required by eq 1.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are indebted to Professor R. L. Middaugh for several helpful discussions.