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A Comparison of Proton and Deuteron Nuclear Magnetic Resonance of Some Paramagnetic Transition Metal Complexes. I

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Abstract: Although isotropic proton nmr shifts have been widely used for investigating paramagnetic transition metal complexes, the usefulness of the method is limited in that few paramagnetic complexes exhibit sufficiently narrow nmr line widths. The Solomon–Bloembergen theory of nuclear relaxation in paramagnetic systems indicates that if protons are replaced by deuterons, the deuteron nmr line widths should be smaller by a factor of ~40 than the corresponding proton nmr line widths. To test this experimentally, the deuteron and proton nmr line widths of a number of paramagnetic transition metal acetylacetonate complexes and their deuterated analogs have been measured for comparison. The deuteron spectra show significantly better overall resolution in most instances, and deuteron nmr line widths are much narrower than the corresponding pmr line widths. The expected 40-fold decrease in line width is found only for the Cr(III) complex, although the results for the Ti(III) and V(III) complexes are within experimental error of this value.

During the past decade, the isotropic nmr shift phenomenon has gained increasing importance as a tool for investigating molecular properties.[1] The term "isotropic shift" is meant to include nuclear resonance shifts arising from Fermi hyperfine contact interactions or from electron–nuclear dipolar (pseudocontact) interactions in paramagnetic substances.

A large portion of the work involving isotropic shifts has been carried out by chemists interested in the bonding and stereochemistry of paramagnetic transition metal complexes. In these systems the hyperfine contact interaction is the result of an imbalance of electron spin on the ligand due to spin transfer between metal and ligand. The spin imbalance may reach ligand nuclei by means of σ or π molecular orbitals, causing changes in local magnetic fields and resulting in nuclear resonance shifts. The dipolar interaction is most simply described as a through-space coupling between ligand nuclei and unpaired electrons on the metal ion. The dipolar nmr shift for a nucleus depends on its orientation with respect to the ligand-field axis of the complex and upon its distance from the metal ion. Dipolar shifts occur only for complexes having g-value anisotropy. In many transition metal complexes, both types of interaction contribute to the observed nmr shifts.

Use of isotropic shifts is by no means restricted to transition metal complexes. Nmr spectra of organic radicals have been obtained, using another radical as the solvent in some cases; also spectra of organic bi-, tri-, and tetraradicals have been examined.[1,2] Recently, organic chemists have become interested in using paramagnetic complexes of lanthanide series ions as "shift reagents" for the purpose of amplifying chemical shift differences in spectra of certain organic compounds.[3] Of interest to biochemists is the use of the isotropic shift phenomenon for elucidating structures of large molecules such as ferredoxin, hemoglobins, cytochrome *c*, and others.[4]

At present the general utility of the isotropic shift phenomenon is severely restricted because most para-

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(1) (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); (c) R. H. Holm, *Accounts Chem. Res.*, 2, 307 (1969).

(2) (a) B. M. P. Hendriks, G. W. Canters, C. Corvaja, J. W. M. DeBoer, and E. DeBoer, *Mol. Phys.*, 20, 193 (1971), and references therein; (b) R. W. Kreilick, *J. Amer. Chem. Soc.*, 90, 5991 (1968); (c) F. Yamauchi and R. W. Kreilick, *ibid.*, 91, 3429 (1969); (d) P. W. Kopf and R. W. Kreilick, *ibid.*, 91, 6569 (1969); (e) P. W. Kopf, R. Kreilick, D. G. B. Boocock, and E. F. Ullman, *ibid.*, 92, 4531 (1970).

(3) For an extensive list of references, see R. E. Rondeau and R. E. Sievers, *ibid.*, **93**, 1522 (1971).

(4) (a) M. Poe, W. D. Phillips, C. C. McDonald, and W. Lovenberg, *Proc. Nat. Acad. Sci. U. S.*, **65**, 797 (1970); (b) K. Wüthrich, R. G. Shulman, and J. Peisach, *ibid.*, **60**, 373 (1968); (c) R. J. Kurland, D. G. Davis, and C. Ho, *J. Amer. Chem. Soc.*, 90, 2700 (1968); (d) R. G. Shulman, S. Ogawa, K. Wüthrich, T. Yamane, J. Peisach, and W. E. Blumberg, *Science*, 165, 251 (1969); (e) A. Kowalsky, *Biochemistry*, 4, 2382 (1965).

magnetic substances either fail to give detectable nuclear resonances or give very broad, poorly resolved signals as a result of rapid nuclear spin relaxation induced by the paramagnetism. Those paramagnetic transition metal complexes upon which the most successful nmr studies have been carried out have very short *electron* relaxation times. Reasonably narrow nmr signals may be obtained for these complexes and, coupled with the isotropic shifts, the overall resolution may be quite good. Unfortunately, only a few transition metal ions appear to have short enough electron relaxation times to give the required resolution. A few years ago Eaton[5] made a systematic study of paramagnetic acetylacetonate complexes in order to determine which metal ions have the very short electron relaxation times necessary for observation of nmr signals of ligand protons. A short electron relaxation time precludes observation of epr signals, and thus those ions giving the best resolved nmr spectra proved to be those not especially amenable to epr studies. Eaton found reasonably narrow nmr signals only for acetylacetonates of V(III), Mn(III), and Ru(III). It is also known from other studies that complexes of Ni(II), Co(II), Cr(II), Fe(III), Eu(III), and Pr(III) sometimes exhibit well-resolved nmr spectra.[1,3,6-8]

In hopes that isotropic shift studies may be extended to a wider range of paramagnetic substances, we are currently investigating deuterium nmr, dmr, of a variety of paramagnetic compounds. Deuterium substitution is feasible in many instances and should not significantly affect the properties of the compound under investigation. Furthermore, selective deuteration results in relatively simple dmr spectra, especially for large molecules. The use of dmr for diamagnetic compounds[9] is not as widespread as that of pmr, since the dmr signals are broadened by quadrupolar relaxation and the sensitivity is much smaller than for pmr. However, for paramagnetic substances dmr is expected to have superior resolution to pmr (*vide infra*). In this paper are presented the results of our comparison of pmr and dmr for a series of paramagnetic transition metal acetylacetonate complexes. Preliminary results were communicated earlier.[10]

Theory

The equations expressing the longitudinal and transverse relaxation times of nuclei in paramagnetic molecules, derived by Solomon and Bloembergen,[11] are shown below.

$$\frac{1}{T_1} = \frac{2}{15}\frac{S(S+1)\gamma_I^2g^2\beta^2}{r^6}\left[3\tau_c + \frac{7\tau_c}{1+\omega_s^2\tau_c^2}\right] + \frac{2}{3}\frac{S(S+1)A^2}{\hbar^2}\left[\frac{\tau_e}{1+\omega_s^2\tau_e^2}\right] \quad (1)$$

$$\frac{1}{T_2} = \frac{1}{15}\frac{S(S+1)\gamma_I^2g^2\beta^2}{r^6}\left[7\tau_c + \frac{13\tau_c}{1+\omega_s^2\tau_c^2}\right] + \frac{1}{3}\frac{S(S+1)A^2}{\hbar^2}\left[\tau_e + \frac{\tau_e}{1+\omega_s^2\tau_e^2}\right] \quad (2)$$

In these equations S is the electron spin quantum number, g is the Landé factor, β is the Bohr magneton, γ_I is the nuclear magnetogyric ratio, r is the electron–nuclear distance, τ_c is the electron–nuclear dipolar interaction time, ω_s is the Larmor frequency for the electron, A is the electron–nuclear hyperfine coupling constant, and τ_e is the correlation time for hyperfine coupling.

The above equations are simplified versions of the complete expressions for T_1^{-1} and T_2^{-1}. Here it is assumed that $\omega_I \ll \omega_s$ and $\omega_I^2\tau_c^2 \ll 1$, where ω_I is the nuclear Larmor frequency.[12] Also, the equations assume an isotropic electron g factor[13] and make no distinction between longitudinal and transverse electron relaxation times.[14] However, these approximations have no effect on the arguments presented in this paper, where pmr and dmr of identical molecules (except for isotopic substitution) are compared.

Equations 1 and 2 both have a term containing r^{-6}, expressing the contribution from an electron–nuclear dipolar interaction, and a second term involving A^2 which gives the contribution from the hyperfine coupling interaction. Since A^2 is proportional to γ_I^2 through eq 3, both terms of eq 1 and 2 contain γ_I^2.

$$A = (4/3)\hbar\gamma_e\gamma_I[\Psi(0)]^2 \quad (3)$$

Thus, nuclear relaxation rates and nmr line widths are directly proportional to the square of the magnetogyric ratio of the nucleus under observation.

If a proton in a paramagnetic molecule is replaced by a deuteron, the only parameter in (1) and (2) expected to change significantly is γ_I, and it follows that the dmr signal should be narrower than the corresponding pmr signal by a factor of $\gamma_H^2/\gamma_D^2 = 42.4$. Signal broadening resulting from the nuclear quadrupole moment of deuterium is expected to be small compared to paramagnetic broadening unless the line widths are only a few hertz wide.

The overall resolution of an nmr spectrum is determined not only by line widths but also by chemical shift differences and signal-to-noise ratio. Chemical shift differences are proportional to γ_I, and the chemical shift differences in hertz between deuteron resonances will be smaller than those of corresponding proton resonances by a factor of $\gamma_H/\gamma_D = 6.51$. Where pmr and dmr are run at the same magnetic field strength,

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

(6) (a) S. Y. Shaw and E. P. Dudek, *Inorg. Chem.*, **8**, 1360 (1969); (b) G. N. LaMar, *ibid.*, **8**, 581 (1969); (c) C. R. Powers and G. W. Everett, Jr., *J. Amer. Chem. Soc.*, **91**, 3468 (1969); (d) L. H. Pignolet and W. D. Horrocks, Jr., *ibid.*, **91**, 3976 (1969); (e) F. F.-L. Ho, L. E. Erickson, S. R. Watkins, and C. N. Reilley, *Inorg. Chem.*, **9**, 1139 (1970); (f) L. E. Erickson, F. F.-L. Ho, and C. N. Reilley, *ibid.*, **9**, 1148 (1970); (g) G. W. Everett, Jr., and C. R. Powers, *ibid.*, **9**, 521 (1970); (h) L. H. Pignolet, W. D. Horrocks, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 1855 (1970); (i) G. N. LaMar and E. O. Sherman, *ibid.*, **92**, 2691 (1970); (j) D. Doddrell and J. D. Roberts, *ibid.*, **92**, 4484, 6839 (1970).

(7) (a) R. J. Fitzgerald and G. R. Brubaker, *Inorg. Chem.*, **8**, 2265 (1969); (b) G. N. LaMar, *J. Amer. Chem. Soc.*, **92**, 1806 (1970).

(8) (a) G. N. LaMar and G. R. Van Hecke, *ibid.*, **91**, 3442 (1969); (b) G. N. LaMar and G. R. Van Hecke, *J. Chem. Phys.*, **52**, 5676 (1970).

(9) (a) R. C. Dougherty, G. D. Norman, and J. J. Katz, *J. Amer. Chem. Soc.*, **87**, 5801 (1965); (b) L. K. Montgomery, A. O. Clouse, A. M. Crelier, and L. E. Applegate, *ibid.*, **89**, 3453 (1967), and references in these papers.

(10) A. Johnson and G. W. Everett, Jr., *ibid.*, **92**, 6705 (1970).

(11) (a) I. Solomon, *Phys. Rev.*, **99**, 559 (1955); (b) N. Bloembergen, *J. Chem. Phys.*, **27**, 572 (1957); (c) R. S. Codrington and N. Bloembergen, *ibid.*, **29**, 600 (1958); (d) R. A. Bernheim, T. H. Brown, H. S. Gutowsky, and D. E. Woessner, *ibid.*, **30**, 950 (1959).

(12) In a magnetic field of ~23,500 G, $\omega_s \approx 10^{11}$ rads sec^{-1} and $\omega_I \approx 10^9$ rads sec^{-1} (proton) or $\approx 10^8$ rads sec^{-1} (deuteron). For molecules which are nonlabile on the nmr time scale, τ_c is dominated by the molecular tumbling time, $\tau_r \approx 10^{-11}$ sec, or by the electron relaxation time τ_s (whichever is shorter) through the relation $1/\tau_c = (1/\tau_r) + (1/\tau_s)$.

(13) H. Sternlicht, *J. Chem. Phys.*, **42**, 2250 (1965).

(14) (a) A. M. Chmelnick and D. Fiat, *ibid.*, **49**, 2101 (1968); (b) J. Reuben, G. H. Reed, and M. Cohn, *ibid.*, **52**, 1617 (1970).

the relative sensitivities of proton and deuteron signals are about 100 to 1, assuming an equal number of nuclei.[15] If the latter is not a handicap, the overall resolution of the dmr spectrum should be better by a factor of 6.5.

The above relationships have been pointed out previously,[16–18] but dmr investigations of paramagnetic systems in solution have thus far dealt only with certain transition metal ions in D_2O[16,17] and with deuterated biphenyl and naphthalene radical anions in 1,2-dimethoxyethane.[2a,19]

Experimental Section

Deuteration of Ligand. 2,4-Pentanedione was deuterated by refluxing a mixture of approximately 30 ml of the diketone, 50 ml of deuterium oxide, and a small amount of Na_2CO_3 over a 48-hr period. The mixture was then extracted with diethyl ether and the diketone was recovered from the ether solution by evaporating the solvent. This partially deuterated product was added to fresh D_2O, and the above procedure was repeated until the desired extent of deuteration ($\geq 80\%$) was attained. Pmr of the partially deuterated product was used to assess the extent of deuteration. The final product was distilled prior to preparation of the complexes.

Preparation of Complexes. Most of the 2,4-pentanedionatometal ($n+$) complexes, hereafter abbreviated $M(acac)_n$, were prepared by well-established literature methods.[20] Complexes of deuterated ligand were prepared in the same manner except that D_2O was used, where required, in place of H_2O.

$Fe(acac)_3$ was prepared by a modification of the procedure given by Hantzsch and Desch.[21] To an aqueous solution containing 0.01 mol of $FeCl_3$ were added 0.03 mol of sodium acetate and 0.06 mol (twofold excess) of ligand. The mixture was heated for 10–20 min, then allowed to cool slowly to room temperature. The red precipitate was collected, washed with water, and dried in air. Recrystallization was achieved using a 1:5 (by volume) benzene–petroleum ether solution.

$V(acac)_3$ was prepared by adding VCl_3 to an aqueous solution containing ligand and Na_2CO_3 using the procedure described in detail by Horn and Everett.[22] Solutions of V(III) were protected from aerial oxidation by carrying out all procedures *in vacuo* or under purified nitrogen using apparatus designed for this purpose.[23]

A modification of the procedure outlined in Gmelin[24] was used in preparation of $Ru(acac)_3$. A mixture of 2.0 g of commercially available $RuCl_3 \cdot 1\text{–}3H_2O$ (Alfa Inorganics), 20 ml of 0.3 *M* HCl, 20 ml of toluene, and 10 g of ligand was refluxed under nitrogen until a red color developed (~1 hr). An additional 80 ml of toluene was introduced, and a solution of 10 g of Na_2CO_3 in 100 ml of water was slowly added to neutralize the acid. The mixture was then stirred under nitrogen for an additional 12 hr. The toluene layer containing the complex was removed and reduced in volume to ~20 ml. Approximately 50 ml of petroleum ether was added, and the red complex precipitated upon cooling at $-10°$ for several hours. The crude product was recrystallized three times using a solution of toluene in petroleum ether (1:5 by volume). It is not necessary to work in a nitrogen atmosphere once the complex is formed.

Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium(III), $Eu(thd)_3$, was prepared according to Eisentraut and Sievers.[25]

With the exception of $Ti(acac)_3$, which is extremely air sensitive, all the complexes gave satisfactory elemental microanalyses. Hydrogen analyses for the deuterated complexes were scaled up by a factor representing the fractional deuteration of the ligand and the relative percentages of D and H in D_2O and H_2O, respectively.

Nmr Spectra. A Varian HA-100 spectrometer operating at 100.000 MHz (proton) and 15.351 MHz (deuteron) was used to record nmr spectra of the complexes. Chloroform-*d* was used as the solvent in all cases. Solutions were generally ~0.2 *M* in complex. Samples of $Ti(acac)_3$, $Mo(acac)_3$, and $V(acac)_3$ were sealed in nmr tubes under rigorously oxygen-free conditions. The chloroform-*d* signal was used as a reference for dmr; tetramethylsilane was the reference used for pmr. Chemical shifts and line widths at half-height were measured by side banding. Data are presented in Table I.

Results and Discussion

Acetylacetonate complexes were chosen for initial dmr studies of paramagnetic compounds for several reasons. As a ligand, acetylacetone is extremely versatile, forming complexes with all the transition metals.[26] Both the ligand and many of its complexes have high symmetry, resulting in simple nmr spectra. Complexes of acetylacetone are generally easy to prepare, and the ligand is readily deuterated. Although pmr chemical shifts and line widths for a number of paramagnetic acetylacetonate complexes were reported earlier,[5] we chose to repeat some of the work in order to be able to compare pmr and dmr under identical experimental conditions.

Proton and deuteron chemical shifts and line widths at half-height are compared in Table I for ten paramagnetic acetylacetonate complexes and their deuterated analogs in $CDCl_3$ solution. Data are given for the methyl resonance only, since the 3-CH or 3-CD resonance is often not apparent. In addition, data for the α, β, and γ nmr signals of pyridine and pyridine-d_5 coordinated to $Ni(acac)_2$, $Co(acac)_2$, and $Eu(thd)_3$ are presented.

Comparison of Pmr and Dmr Chemical Shifts. The large chemical shifts observed for most of the complexes are comprised primarily of isotropic shifts arising from the hyperfine contact interaction (eq 4) and/or

$$\frac{\Delta f_i}{f_0} = -A_i \frac{\gamma_e}{\gamma_I} \frac{g_e \beta_e S(S+1)}{3kT} \qquad (4)$$

the dipolar interaction as outlined in the introduction. Proton chemical shifts given in Table I for $M(acac)_n$ complexes are in reasonable agreement with those reported earlier.[5] Slight deviations from the previous values are probably due to slight differences in probe temperatures, since isotropic shifts are proportional[27] to $1/T$ according to eq 4, and to experimental error where signals are very broad. The methyl chemical shift for $VO(acac)_2$ is in good agreement with that reported recently by Dichmann, *et al.*[28]

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(15) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 480. This ratio refers to signal heights of absorption mode signals under optimum conditions, *i.e.*, for rf fields (H_1) just below saturation where $H_1{}^2\gamma^2T_1T_2 = 1$.

(16) G. Laukien and F. Noack, *Z. Phys.*, **159**, 311 (1960).

(17) P. Diehl and T. Leipert, *Helv. Chim. Acta*, **47**, 545 (1964).

(18) J. Reuben and D. Fiat, *J. Amer. Chem. Soc.*, **91**, 1242 (1969).

(19) G. W. Canters, B. M. P. Hendriks, and E. DeBoer, *J. Chem. Phys.*, **53**, 445 (1970).

(20) $Ti(acac)_3$, D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961); $VO(acac)_2$, B. E. Bryant and W. C. Fernelius, *Inorg. Syn.*, **5**, 115 (1957); $Cr(acac)_3$, W. C. Fernelius and J. E. Blanch, *ibid.*, **5**, 130 (1957); $Mo(acac)_3$, M. L. Larson and F. W. Moore, *ibid.*, 8, 153 (1964); $Mn(acac)_3$, R. G. Charles, *ibid.*, 7, 183 (1963); $Co(acac)_2$, J. B. Ellern and R. O. Ragsdale, *ibid.*, 11, 82 (1968); $Co(acac)_3$, B. E. Bryant and W. C. Fernelius, *ibid.*, **5**, 188 (1957); $Ni(acac)_2$, $Cu(acac)_2$, R. G. Charles and M. A. Paulikowski, *J. Phys. Chem.*, 62, 440 (1958).

(21) A. Hantzsch and C. H. Desch, *Justus Liebigs Ann. Chem.*, **323**, 1 (1902).

(22) R. R. Horn and G. W. Everett, Jr., *J. Amer. Chem. Soc.*, **93**, 7173 (1971).

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

(24) "Gmelins Handbuch der anorganischen Chemie," 8th ed, Ruthenium Erganzungsband, Verlag Chemie, Weinheim, 1970, p 468.

(25) K. J. Eisentraut and R. E. Sievers, *J. Amer. Chem. Soc.*, **87**, 5254 (1965).

(26) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, 7, 361 (1966).

(27) This is only approximately true in many cases, since eq 4 as shown is oversimplified. For a discussion of the approximations implicit in (4), see (a) R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, 2, 286 (1970); (b) W. D. Perry and R. S. Drago, *J. Amer. Chem. Soc.*, **93**, 2183 (1971).

(28) K. Dichmann, G. Hamer, S. C. Nyberg, and W. F. Reynolds, *Chem. Commun.*, 1295 (1970).

Table I. Pmr and Dmr Data for Metal Complexes[a]

Complex	Chemical shifts[b]		Line widths[c]		Ratio[d]
	Pmr	Dmr	Pmr	Dmr	pmr/dmr
Ti(acac)$_3$	~−55	−55.5	4300	140	31 ± 10
V(acac)$_3$	−45.04	−44.2	45	1.4	32 ± 8
Cr(acac)$_3$	−40.20	−38.4	1400	33	42 ± 8
Mn(acac)$_3$	−25.20	−23.8	95	7.7	12 ± 2
Fe(acac)$_3$	−21.80	−21.3	920	34	27 ± 6
Mo(acac)$_3$	−124.9	−136.5	310	14	22 ± 7
Ru(acac)$_3$	+5.35	+5.34	34	1.9	18 ± 4
Ni(acac)$_2$	−5.14	−4.45	150	16	9 ± 3
Cu(acac)$_2$	−1.00	−0.50	120	5.0	24 ± 9
VO(acac)$_2$	−2.30	−1.95	90	3.2	28 ± 9
Ni(acac)$_2$·2py[e] (α)	−38.70	−30.9	1150	59[g]	20 ± 4
(β)	−16.90	−14.0	165	6.0[g]	28 ± 9
(γ)	−9.93	−9.12	36	5.4[g]	7 ± 3
Co(acac)$_2$·2py[e] (α)	−25.80	−23.9	143	3.7	39 ± 12
(β)	−7.58	−5.64	21	2.2	10 ± 5
(γ)	+1.75	+3.65	21	3.6	6 ± 4
Eu(thd)$_3$·py[f] (α)	−19.05	−17.4	39	5.0	8 ± 3
(β)	−10.95	−10.1	33	6.5	5 ± 3

[a] In chloroform-*d* solution at 32°. Data refer to the methyl resonance for M(acac)$_n$ complexes and to α, β, and γ pyridine resonances for M(acac)$_n$·$x$py complexes. [b] In parts per million from tetramethylsilane. [c] In hertz. Values shown are observed line widths less diamagnetic line widths [values found for Co(acac)$_3$ (Hz), 1.0 (pmr) and 2.0 (dmr); for pyridine, 1.0 (pmr) and 1.4 (dmr)]. These are averages of several determinations with deviations from the mean of 5–20%. [d] Approximate ratio of pmr and dmr line widths. Error limits reflect uncertainty in line widths. [e] Solution contains ~2 mol of pyridine per mole of M(acac)$_2$ complex. [f] Solution contains ~1 mol of pyridine per mole of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium(III). γ resonance obscured by *tert*-butyl signal. [g] Line widths have been scaled up by 1.35 (see text).

Chemical shifts, including contributions from isotropic shifts, should be independent of γ_I when given in parts per million. The contact shift, expressed by eq 4, is independent of γ_I since A is proportional to γ_I through eq 3. The expression for the dipolar shift does not contain γ_I. Thus chemical shifts of a deuteron and proton at the same site in a given complex are expected to be identical. This is seen to be true to a rough approximation for most of the complexes in Table I. However, chemical shifts are found to be somewhat smaller generally for deuterium, and the pmr–dmr differences are outside the limits of error in calibration in most instances. There are several factors that could contribute to this. (a) Any difference in the deuteron and proton probe temperatures would produce different pmr and dmr isotropic shifts as shown by eq 4. However, in the present case this may be ruled out since it was determined that the normal operating temperature of both probes is 32°. (b) Isotopic substitution is known to affect the resonance frequencies of neighboring atoms in a number of diamagnetic molecules[29] (secondary isotope effects), but little is known of primary deuterium isotope effects in nmr.[17] Isotope effects are apparently magnified in some paramagnetic complexes; for example, three methyl resonances with separations ~0.5 ppm are observed in the pmr and in the dmr spectra of V(acac)$_3$ when the ligand is partially deuterated.[22] These signals are assigned to the inequivalent methyl groups CH_3–, CH_2D–, CHD_2–, and CD_3–. A primary isotope effect is observed in that the chemical shifts of CH_3– and CD_3– differ by 0.58 ppm in benzene solution. Similar splitting of the methyl resonance is found for partially deuterated Mo(acac)$_3$ and Cu(acac)$_2$. Thus, the occurrence of isotope effects cannot be ruled out as a factor contributing to chemical shift differences in pmr and dmr of a given complex. (c) An undetermined shift in the dmr reference signal could cause gross errors in the dmr chemical shifts. Pmr signals were referenced directly to tetramethylsilane (TMS), whereas the dmr signals were measured relative to the $CDCl_3$ resonance and "corrected" to the TMS value using the diamagnetic TMS–$CHCl_3$ separation of 7.27 ppm. This assumes not only that there is no significant isotope shift for $CDCl_3$ but also that the TMS–$CHCl_3$ separation is unaffected by the presence of a paramagnetic solute. A very real possibility is that by means of hydrogen bonding[30] or other associative interaction with the complex, chloroform receives an isotropic shift. Chemical shift values for dmr determined in the above manner would be in error by the magnitude of this shift. The chloroform shift could be upfield or downfield and would depend on the concentration of the solution. We feel that factors b and c both contribute to the pmr–dmr chemical shift differences in most cases.[31] The relative importance of the two undoubtedly varies from one complex to another. However, it should be emphasized that errors in the dmr chemical shifts have no effect on the dmr line-width measurements and the pmr/dmr line-width ratios which are the topics of primary consideration in this paper.

Ni(acac)$_2$ and Co(acac)$_2$ tend to assume a coordination number of six through molecular association or by coordination to Lewis bases such as pyridine.[26] Considerable isotropic shift differences are found among α, β, and γ proton resonances of pyridine coordinated to these complexes.[32] The magnitude of

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

(30) It has been demonstrated that chloroform forms hydrogen bonds to metal complexes including β-diketonates; *cf.* (a) J. P. Fackler, Jr., T. S. Davis, and I. D. Chawla, *Inorg. Chem.*, 4, 130 (1965); (b) T. S. Davis and J. P. Fackler, Jr., *ibid.*, 5, 242 (1966); (c) M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, 88, 2966 (1966).

(31) The occurrence of isotope shifts has recently been demonstrated for several of the complexes which are soluble in a benzene–benzene-d_6 solvent mixture. Using the benzene signal as a reference in both pmr and dmr, differences in pmr–dmr chemical shifts were found which are similar in magnitude and direction to those reported in Table I and which must be attributed to isotope effects: R. R. Horn and G. W. Everett, Jr., unpublished observations.

the shifts depends on the pyridine/complex ratio, since the shifts represent a weighted average of those of free and coordinated pyridine. However, the ratio of $\alpha:\beta:\gamma$ isotropic shifts is independent of concentration. Dmr and pmr spectra were recorded for $CDCl_3$ solutions of $Ni(acac)_2$ and $Co(acac)_2$ containing approximately 2 mol of pyridine or pyridine-d_5 per mole of complex. Ratios of proton isotropic shifts ($\alpha:\beta:\gamma$) for pyridine in $Ni(acac)_2$ solution are in reasonable agreement with those reported by Happe and Ward.[32,33a] Deuteron chemical shifts for pyridine-d_5 in $Ni(acac)_2$ solution are considerably smaller than the corresponding proton shifts, and the ratios of proton and deuteron isotropic shifts are not constant.[33b] The pmr–dmr shift differences are attributed to a difference in the pyridine concentration of the two samples and to the effects discussed above.

Dmr signals of pyridine-d_5 in $Co(acac)_2$ are all ~1.9 ppm toward higher field than the corresponding pmr signals. This indicates a downfield shift of the chloroform reference signal by ~1.9 ppm. Ratios of α, β, and γ isotropic shifts for pyridine in $Co(acac)_2$ solution were found to be $-10.0:-0.19:+5.50$. These values differ appreciably from those reported[32] by Happe and Ward ($-10.0:-1.31:+2.30$).

Comparison of Pmr and Dmr Line Widths. Equations 1 and 2 describe the effect of unpaired electrons on T_1 and T_2 of the nuclei but do not include contributions to line widths from other sources such as electric quadrupole relaxation and magnetic field inhomogeneity. In order to compare pmr/dmr line-width ratios with the value of 42.4 predicted by theory, these latter contributions must be subtracted from the observed line widths. The signal broadening resulting from deuterium electric quadrupole relaxation is given[2a,34] by

$$\frac{1}{T_2} = \frac{3}{2}\pi^2\left[\frac{e^2qQ}{h}\right]^2\tau_r \qquad (5)$$

where e^2qQ/h is the quadrupole coupling constant. Quadrupole coupling constants for deuterium bonded to carbon vary only slightly over a range of compounds and are around 170 kHz for sp^3 bonds.[35] Thus an estimate of the quadrupolar contribution to the dmr line widths could be made from eq 5 if accurate values of τ_r were known. Since these are not known, a reasonable alternative is to assume that the field inhomogeneity and electric quadrupole effects are similar for all deuterated complexes of the same type. These contributions are assumed to be represented approximately by the observed methyl dmr line width of diamagnetic, deuterated $Co(acac)_3$ in chloroform solution for the $M(acac)_n$ complexes and by the line width observed for pyridine-d_5 in chloroform solution for the pyridine adduct complexes. Similarly, contributions from field inhomogeneity in the pmr spectra are taken as the line widths of $Co(acac)_3$ and pyridine in chloroform solution.[36] Thus the line widths shown in Table I are "corrected" values. The correction becomes important when the line widths are of the order of a few hertz.

In every case the dmr signal is considerably narrower than the pmr signal, indicating less efficient deuteron relaxation. The gain in resolution is quite evident in the spectra of $Cr(acac)_3$, $Fe(acac)_3$, and especially $Ti(acac)_3$, where resonances of the vinyl hydrogens are clearly seen in the dmr spectra but are not readily apparent in the pmr spectra. For $Ti(acac)_3$ the vinyl deuteron resonance appears as a well-resolved signal at -32.2 ppm.

The $M(acac)_3$ complexes have similar structures, and this series provides the best comparison of pmr:dmr line-width ratios as a function of the metal ion. Superior resolution of dmr over pmr is found for all these complexes, since the line-width ratios are all greater than 6.5, the factor representing the decrease in chemical shift differences in hertz for dmr relative to pmr. However, only for $Ti(acac)_3$, $Cr(acac)_3$, and $V(acac)_3$[37] do the line-width ratios approach the theoretical value of 42.4. Deviations from the theoretical ratio have been observed previously for solutions of paramagnetic metal ions in H_2O and D_2O.[16,17] Laukien and Noack[16] measured proton and deuteron T_1 and T_2 values for these solutions and found that the metal ions could be separated into two distinct groups: (1) "normal" ions, such as Fe^{3+} and Co^{2+}, for which $T_1 \approx T_2$ and the ratios T_1 (deuteron)/T_1(proton) and T_2(deuteron)/T_2(proton) are close to 42.4; (2) "anomalous" ions such as VO^{2+}, Mn^{2+}, and to some extent Cr^{3+} for which $T_1 > T_2$ and the ratios of deuteron/proton T_1's and T_2's differ significantly from the theoretical value. These authors suggested that deviations from theory could be explained by assuming that the coupling constant A is not proportional to γ_I as expressed by eq 3. The behavior of the "normal" ions was accounted for by assuming that the hyperfine term of the Solomon–Bloembergen equations is negligible in these instances.

An estimate of the relative magnitude of the two terms in the Solomon–Bloembergen equations is possible for $V(acac)_3$, $Cr(acac)_3$ and $Ti(acac)_3$. For $V(acac)_3$ it is generally agreed that the ground state is $^3A_2$ and the observed isotropic shifts are essentially contact shifts.[5,38] In this case, eq 4 may be used to obtain a meaningful value of A for the ligand methyl; the value so obtained is 0.226 G. The electron–nuclear distance is estimated[39] to be 4.5 Å, and g_{av} was calculated from the reported moment of 2.80 BM.[38c] Substitution of these quantities in eq 2 yields

$$\frac{1}{T_2} = 3.83 \times 10^{12}\left[7\tau_c + \frac{13\tau_c}{1+\omega_s^2\tau_c^2}\right] + 10.2 \times 10^{12}\left[\tau_e + \frac{\tau_e}{1+\omega_s^2\tau_e^2}\right] \qquad (6)$$

It may be seen that the relative contributions of the two terms in (6) depend on the relative magnitudes[12] of the correlation times τ_r and τ_s ($\tau_e = \tau_s$ for a mole-

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[32] J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

[33] (a) Values used for diamagnetic pyridine resonances are -8.66 (α), -7.25 (β), and -7.67 (γ) ppm; (b) ratios of $\Delta f_H/\Delta f_D$ are 1.35 (α), 1.42 (β), and 1.56 (γ).

[34] A. Abragam, "The Principles of Nuclear Magnetism," Clarendon Press, Oxford, 1961, Chapter 8.

[35] (a) J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar, *J. Chem. Phys.*, **43**, 3442 (1965); (b) D. M. Ellis and J. L. Bjorkstam, *ibid.*, **46**, 4460 (1967).

[36] (a) Values found for $Co(acac)_3$ (Hz), 1.0 (pmr) and 2.0 (dmr); (b) for pyridine, 1.0 (pmr) and 1.4 (dmr).

[37] Note that as a result of the small dmr line width for $V(acac)_3$, very small line-width errors significantly change the line-width ratio for this complex.

[38] (a) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1315 (1967); (b) G. W. Everett, Jr., and Y. T. Chen, *J. Amer. Chem. Soc.*, **92**, 508 (1970); (c) B. N. Figgis, J. Lewis, and F. Mabbs, *J. Chem. Soc.*, 2480 (1960); (d) T. S. Piper and R. L. Carlin, *Inorg. Chem.*, 2, 260 (1963); (e) G. N. LaMar and G. R. Van Hecke, *J. Amer. Chem. Soc.*, **92**, 3021 (1970).

[39] E. C. Lingafelter and R. L. Braun, *ibid.*, **88**, 2951 (1966).

cule nonlabile on the nmr time scale). The narrow line widths observed for V(acac)$_3$ indicate a short electron relaxation time τ_s, and if it is assumed that $\tau_s \ll \tau_r$, the contribution of the hyperfine term to $1/T_2$ is about one-fourth that of the dipolar term. A value for τ_s of $\sim 10^{-12}$ sec is obtained from eq 6 assuming that the methyl pmr signal is Lorentzian and that the corrected pmr line width multiplied by π represents $1/T_2$. If $\tau_s \approx \tau_r$, the contribution from the hyperfine term is about one-third that of the dipolar term, and for longer τ_s the hyperfine term dominates eq 6. In the case of Cr(acac)$_3$, for which the dipolar *shift* is zero,[5] A may be obtained from eq 4, and the equation analogous to (6) has coefficients of 7.18×10^{12} and 4.22×10^{12} for the dipolar and hyperfine terms, respectively. Since the nmr signals are very broad for Cr(acac)$_3$, it is assumed that $\tau_s \gg \tau_r$, and a value of $\tau_s \approx 10^{-9}$ sec is calculated using $\tau_r \approx 10^{-11}$ sec. Here the hyperfine term is about four times as large as the dipolar term. Dipolar shifts are estimated to be negligible[5] for Ti(acac)$_3$, and it can be shown that nmr line widths are controlled by the hyperfine interaction. Thus, for the V(III), Cr(III), and Ti(III) complexes, which seem to follow the Solomon–Bloembergen equations, the hyperfine term makes a significant if not predominant contribution to nuclear relaxation, and it would appear that eq 3 holds true.

The low pmr/dmr line-width ratios could be explained if quadrupolar broadening were generally greater than in Co(acac)$_3$ and varied from one complex to another. In the absence of any quadrupolar broadening corrections, for example, the dmr line widths of Mn(acac)$_3$, Fe(acac)$_3$, Mo(acac)$_3$, and Ru(acac)$_3$ are too large by 6.5, 13, 7.7, and 2.1 Hz, respectively. Assuming that these numbers represent contributions from quadrupolar relaxation, they can be multiplied by π and substituted for T_2^{-1} in eq 5. Using a value of 170 kHz for the quadrupole coupling constant, values of τ_r ranging from 10^{-10} to 10^{-11} sec are obtained. These values of τ_r are in the range expected[40] for molecules having a radius $\sim$5 Å in a solution having a viscosity approximately that of chloroform at 30°. Thus, the above contributions to the dmr line widths may indeed arise from quadrupole effects, although a smaller *range* of values would have been anticipated from molecules having such similar structures.

LaMar has shown that methyl group rotation is capable of modulating hyperfine interactions in paramagnetic complexes.[8b] For nonlabile complexes, the methyl rotation time τ_m is related to τ_e by eq 7. If

$$1/\tau_e = (1/\tau_s) + (1/\tau_m) \qquad (7)$$

τ_m contributes appreciably to τ_e, the effect would be a broadening of the methyl deuteron signal relative to the corresponding methyl proton signal, since $\tau_m(CD_3)$ is greater than $\tau_m(CH_3)$ by a factor of $\sqrt{2}$. This would result in low methyl pmr/dmr line-width ratios, as is found experimentally in most cases. However, for complexes where the 3-CH and 3-CD line widths could be determined, the ratio of these line widths is sometimes considerably smaller than that of the methyl groups. Thus, the effect of different τ_m values of CH$_3$ and CD$_3$ remains uncertain at present.

Other possible sources of the deviation from theory include errors in line-width measurements not included in the error limits shown in Table I. These could arise from (a) signal saturation and (b) unresolved isotope shifts for partially deuterated ligands. Changes in r and τ_r as a result of deuteration would be far too small to account for the observed deviations from theory. Efforts were made to avoid saturation during line-width measurements, although it was found that line widths of representative M(acac)$_3$ complexes do not change significantly over a range of radiofrequency power levels and sample concentrations.[10] Line widths reported in Table I are averages of several determinations with deviations from the mean of 5–20%.

Concerning source b, it has been shown that incomplete ligand deuteration can lead to observable nmr inequivalences in the four possible methyl resonances of V(acac)$_3$, Mo(acac)$_3$, and Cu(acac)$_2$ (*vide supra*). The dmr signal components are sufficiently well separated for these three complexes that the line width of a single component may be measured. Surprisingly, the methyl signal splitting is not observed for Ru(acac)$_3$, which has a line width comparable to that of V(acac)$_3$. Incompletely resolved methyl inequivalences arising from isotope effects could significantly contribute to the dmr line widths[41] if signals are narrow, and would lower the pmr/dmr line-width ratio. This was suspected as a cause of the low line-width ratio found for Mn(acac)$_3$, so a sample of the complex was prepared using $\sim$99% deuterated ligand. However, the dmr line width of this complex was essentially the same as that found for the less highly deuterated sample.

Chloroform solutions of Ni(acac)$_2$ are likely to contain monomer and trimer in equilibrium,[26] and nmr line widths may be affected by solute concentration. Also for Cu(acac)$_2$ and VO(acac)$_2$ the open coordination sites could invite intermolecular interactions which could cause τ_s to be concentration dependent. For example, it was found that the methyl resonance of VO(acac)$_2$ becomes extremely broad at high solute concentration ($\sim$0.7 *M*). In order to avoid these problems, pmr and dmr spectra were run on solutions having nearly identical concentrations. It may be seen from Table I that the line-width ratios are low for the bis complexes of Ni^{2+}, Cu^{2+}, and VO^{2+}. This may be the result of an inadequate correction for quadrupole broadening, since Co(acac)$_3$ is not closely related in structure to these complexes.

Pyridine isotropic shifts for the M(acac)$_2\cdot$2py complexes depend on the pyridine/M(acac)$_2$ ratio as discussed earlier. Line widths also depend on the mole fraction of coordinated pyridine. Thus, for the Ni(II) complex, where the difference in proton and deuteron isotropic shifts indicates a difference in the pyridine/Ni(acac)$_2$ ratio, the observed dmr line widths were multiplied by a factor of 1.35. This factor, representing the ratio of α pmr to α dmr isotropic shifts,[33b] was chosen rather than the ratio of β or γ isotropic shifts in order to minimize errors due to the CDCl$_3$ reference shift.

The line widths generally decrease with decreasing isotropic shift for Ni(acac)$_2\cdot$2py and Co(acac)$_2\cdot$2py. Isotropic shifts are essentially contact shifts for the

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(40) Estimated from the Debye–Einstein relation, $\tau_r = 4\pi\eta a^3/3kT$; *cf.* A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, p 189.

(41) This effect would contribute only to the dmr line widths, since pmr spectra were obtained for fully protonated complexes.

nickel complex, and the hyperfine term of eq 1 and 2 could contribute to signal broadening. If this were the predominant broadening mechanism, the line widths would be proportional to the square of the contact shift, since Δf^2 is proportional to A^2. This is true to a rough approximation for the α and β protons, but fails for the γ proton where the line width is much too large. Dipolar broadening must be even less significant at the γ position than at the α or β positions due to the $1/r^6$ dependence (eq 1 and 2). Thus the line width observed for the γ deuteron must result largely from quadrupolar effects. For $Co(acac)_2\cdot 2py$, the observed shifts are combined contact and dipolar shifts. Thus Δf's are not simply related to A's, and a comparison of Δf^2 with line width has no meaning. A trend apparent for $Co(acac)_2\cdot 2py$ and to some extent for $Ni(acac)_2\cdot 2py$ is that the most favorable line-width ratios are found for nuclei showing the broadest resonances, *i.e.*, the superior resolution of dmr shows up where most needed.

Signal assignments for $Eu(thd)_3\cdot py$ are made on the basis of signal areas and the magnitudes of isotropic shifts. The most downfield signal is assigned to the α-hydrogen, in analogy to the nickel and cobalt adducts discussed above where signal assignments are based on ring substitution.[32] The γ-hydrogen signal appears in solutions containing excess pyridine, but it apparently coincides with the *tert*-butyl resonance of thd at a 1:1 pyridine/$Eu(thd)_3$ ratio.

Conclusion

Dmr of most of the paramagnetic compounds investigated shows significantly improved resolution over the corresponding pmr spectra. In several instances for the $M(acac)_3$ complexes the vinyl hydrogen resonance is not apparent in the pmr spectra but shows up clearly in the dmr spectra. Reasonably well-resolved dmr spectra are found for complexes of Ti(III), Cr(III), and Fe(III), whereas pmr studies of complexes of these ions are not practical owing to extreme breadth of the resonances. The lower sensitivity of dmr over pmr proved not to be a handicap for these complexes. Although dmr line widths are narrower for all the complexes studied, in only a few cases does the pmr/dmr line-width ratio approach the value predicted by the Solomon–Bloembergen equations. It is likely that the deviations from theory result at least in part from insufficient corrections for electric quadrupole relaxation in dmr. However, accurate estimates of these corrections are not presently available.

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Nuclear Magnetic Resonance Contact Shifts and Electron Spin Distribution. Proton and Carbon-13 Contact-Shift Studies of Azanaphthalenes

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Abstract: The proton and ^{13}C contact shifts in quinoline and isoquinoline coordinated with paramagnetic nickel acetylacetonate ($Ni(AA)_2$) were studied by the ^1H (at 220 MHz) and ^{13}C (at 15.1 MHz) nmr spectroscopy. The alternating sign and attenuating magnitude of ^1H and ^{13}C contact shifts were plausibly substantiated by molecular orbital calculations (unrestricted Hartree–Fock INDO–SCF method) of electron spin densities on the proton 1s and carbon 2s atomic orbitals for model molecules, *i.e.*, 1- and 2-naphthyl radicals. The MO calculations showed that electron spin distributions on the proton and carbon s AO's in quinoline and isoquinoline are dominated by σ-electron effects. The identity of the mode of electron spin distribution between azanaphthalene–$Ni(AA)_2$ complexes and the corresponding hydrocarbon σ radicals was also discussed in terms of the potential utility of nmr contact shifts for N-containing molecules in the prediction of electronic structures of σ-hydrocarbon radicals.

The paramagnetic shifts induced by the interaction between an unpaired electron on a transition metal and the nucleus of the ligand coordinated to these ions have been the subject of recent nuclear magnetic resonance (nmr) studies.[1] A great deal of information has been deduced thereby concerning the manner of metal–ligand bonding, the geometrical structure of the transition metal complex, and the electronic structure of the ligand molecule. The six-coordinate nickel(II) and cobalt(II) complexes have been popular and relevant to the paramagnetic shift studies.[2] Most of these studies have dealt with proton paramagnetic shifts for π-conjugated ligand molecules.[2b,c]

We have previously reported the conformational or geometrical dependence of proton[3] and carbon-13

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