# A Comparison of Proton and Deuteron Nuclear Magnetic Resonance of Some Paramagnetic Transition Metal Complexes. II[1]

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**Abstract:** Proton magnetic resonance spectra of complexes of 1,1,1-trifluoro-2,4-pentanedione and (+)-3-acetylcamphor with several paramagnetic transition metal ions are compared with deuteron magnetic resonance spectra of the analogous complexes in which the ligands are deuterated at a methyl position. Fluorine magnetic resonance spectra for complexes having $CF_3$ groups are compared with the proton and deuteron spectra. Complexes of the above ligands are capable of existing in more than one stereoisomeric form, and multiple nuclear resonance signals are possible for each ligand substituent. Although it was initially anticipated that the deuteron spectra would be better resolved than the proton spectra, as has been found for other complexes of these metal ions, the deuteron spectra reported herein generally show no significant improvement in resolution over the proton spectra. Deuteron resonance signals are broader than expected, presumably as a result of nuclear quadrupolar relaxation. Proton, deuteron, and fluorine isotropic shifts and line widths are compared, and conclusions are drawn regarding the usefulness of deuteron magnetic resonance for investigating stereoisomerism in paramagnetic metal complexes.

Proton nuclear magnetic resonance has been used on many occasions for studying stereoisomerism in paramagnetic transition metal complexes.[2] Due to the presence of unpaired electrons and attendant isotropic resonance shifts of ligand protons, signals of corresponding protons on different stereoisomers may appear well separated for a paramagnetic complex, whereas for a diamagnetic complex of similar structure these signals may seriously overlap. Use of isotropic shifts for these studies is limited to complexes of those metal ions having relatively short electron relaxation times, otherwise the resonance signals are severely broadened.

According to the relaxation theories of Solomon and Bloembergen[3] for paramagnetic systems, deuteron nmr (dmr) signals should be narrower by a factor of ~42 than proton nmr (pmr) signals, assuming the proton and deuteron occupy identical sites on the molecule.[4] Thus it would appear that dmr is capable of revealing information in some cases which cannot be obtained by pmr on account of signal broadening. In a recent experimental test of the Solomon–Bloembergen theory, we compared pmr and dmr line widths obtained for a series of protonated and deuterated paramagnetic transition metal acetylacetonate complexes.[1] In all cases deuteron resonances were found to be considerably narrower than the corresponding proton resonances; however, the factor of ~42 reduction in line width for dmr was not always found. The deviation from theory was attributed at least in part to electric quadrupole broadening for dmr which is not included in the Solomon–Bloembergen treatment and which cannot be estimated *a priori*. The most significant *decreases* in line width on going from pmr to dmr were found for the tris(acetylacetonates) of $Ti^{3+}$, $V^{3+}$, and $Cr^{3+}$. The complexes of $V^{3+}$, $Mn^{3+}$, $Ru^{3+}$, $Cu^{2+}$, and $VO^{2+}$ showed the *narrowest* dmr signals (all less than 10 Hz wide at half-maximum amplitude).

Having demonstrated the superior resolution of dmr over pmr for these molecules of high symmetry, we became interested in evaluating the utility of dmr for study of stereoisomerism in paramagnetic complexes. The present paper describes the results of our comparison of dmr and pmr for detecting and identifying geometrical and optical isomers of transition metal complexes. The unsymmetrical ligand, trifluoroacetylacetone, Htfac, is used for studies of geometrical (cis and trans) isomerism, whereas the chiral ligand (+)-3-acetylcamphor, Hatc, is chosen for its ability to generate several diastereomers in tris chelate complexes. Both ligands may be deuterated at the chelate ring methyl group. The choice of trifluoroacetylacetone was prompted by the fact that the resolutions of $^1H$, $^2H$, and $^{19}F$ nmr could be compared directly for complexes of this ligand. The metal ions used are those found previously[1] to give narrow dmr signals and significant improvement in resolution of dmr over pmr.

## Experimental Section

**Ligands.** 1,1,1-Trifluoro-2,4-pentanedione (trifluoroacetylacetone) was obtained from PCR, Inc., and used without further purification. (+)-3-Acetylcamphor was synthesized from (+)-3-bromocamphor using the procedure described by Brühl.[5]

Trifluoroacetylacetone was deuterated by the following procedure. A mixture of approximately 40 ml of diketone, 70 ml of deuterium oxide, and a small amount of $Na_2CO_3$ was allowed to reflux over a 6-day period. This was followed by extraction with

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[1] Part I: A. Johnson and G. W. Everett, Jr., *J. Amer. Chem. Soc.*, **94**, 1419 (1972).

[2] (a) D. L. Johnston, I. Bertini, and W. DeW. Horrocks, Jr., *Inorg. Chem.*, **10**, 865 (1971); (b) R. F. Evilia, D. C. Young, and C. N. Reilley, *ibid.*, **10**, 433 (1971); (c) L. E. Erickson, D. C. Young, F. F.-L. Ho, S. R. Watkins, J. B. Terrill, and C. N. Reilley, *ibid.*, **10**, 441 (1971); (d) L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, **93**, 360 (1971); (e) L. H. Pignolet, W. DeW. Horrocks, Jr., and R. H. Holm, *ibid.*, **92**, 1855 (1970); (f) L. H. Pignolet and R. H. Holm, *ibid.*, **92**, 1791 (1970); (g) G. N. LaMar, *ibid.*, **92**, 1806 (1970); (h) G. N. LaMar and E. O. Sherman, *ibid.*, **92**, 2691 (1970); (i) G. N. LaMar and G. R. Van Hecke, *ibid.*, **92**, 3021 (1970); (j) *Inorg. Chem.*, **9**, 1546 (1970); (k) I. Bertini, D. L. Johnston, and W. DeW. Horrocks, Jr., *ibid.*, **9**, 693, 698 (1970); (l) G. W. Everett, Jr., and C. R. Powers, *ibid.*, **9**, 521 (1970); (m) G. W. Everett, Jr., and Y. T. Chen, *J. Amer. Chem. Soc.*, **92**, 508 (1970); (n) R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969), and references cited in this paper.

[3] (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).

[4] These relationships are treated in detail in ref 1.

[5] J. W. Brühl, *Ber.*, 37, 746 (1904).

**Table I.** Nmr Data for Metal Complexes[a]

| Complex | Isotropic shifts[b] | | | Line widths[c] | | | Line width ratios | |
|---|---|---|---|---|---|---|---|---|
| | $^1H$ | $^2H$ | $^{19}F$ | $^1H$ | $^2H$ | $^{19}F$ | $^1H/^2H$ | $^1H/^{19}F$[d] |
| $Mn(tfac)_3$[c] | −40.5 | −40.3 | −29.5[f] | 210 | 40 | 127[f] | 5.3 | |
| | −38.4 | −38.5 | −18.2 | 275 | 40 | 179 | 6.9 | 1.3(trans) |
| | −31.2 | −31.3 | −12.9 | 205 | 35 | 185 | 5.9 | |
| | | | −5.4 | | | 182 | | |
| $Ru(tfac)_3$[e] | +2.6 | +2.5 | +2.5 | 58 | 8.4 | 35 | 6.9 | |
| | +7.8[f] | +7.4[f] | +6.3[f] | 50[f] | 8.6[f] | 28[f] | 5.8 | 1.8(cis) |
| | +11.2 | +10.7 | +9.6 | 55 | 9.2 | 42 | 6.0 | 1.5(trans) |
| | +18.8 | +17.9 | +15.2 | 73 | 6.9 | 46 | 11 | |
| $V(tfac)_3$[e] | −69.8 | −68.6 | −50.5[g] | 129 | 29 | 64 | 4.4[h] | |
| | −61.3 | −60.2 | −41.8[f,g] | 115 | 30 | | 3.8[h] | |
| | −56.4[f] | −55.7[f] | −40.9[g] | 124[f] | 26[f] | 64 | 4.8[h] | 1.7(trans) |
| | −52.8 | −52.0 | −35.1[g] | 76 | 26 | 61 | 2.9[h] | |
| $Cu(tfac)_2$[e] | +3.3 | +3.3 | | 157 | 11 | ∼1200[i] | 14 | |
| $Mn(atc)_3$[j] | −15.5 | −15.7 | | | | | | |
| | −14.9 | −14.2 | | | | | | |
| | −13.0 | −13.2 | | | | | | |
| | | ∼−12 | | | | | | |
| | +6.3 | +6.5 | | 92 | 14 | | 6.6 | |
| | +9.1 | +9.6 | | 117 | 16 | | 7.3 | |
| | +11.6 | +11.7 | | 109 | 15 | | 7.3 | |
| | +14.3 | +14.2 | | 104 | 16 | | 6.5 | |
| $V(atc)_3$[e] | −48.3[k] | −46.2 | | | | | | |
| | −45.7[k] | −43.7[l] | | 59 | 14 | | 4.2 | |
| | −38.4[k,l] | −36.7[l] | | 79 | 20 | | 4.0 | |
| | −33.6[k] | −31.9 | | | | | | |
| | −31.7[k] | −30.4 | | | | | | |
| | −31.0[k] | −29.6 | | 49 | 16 | | 3.1 | |

[a] Data refer to the methyl and trifluoromethyl resonances for $M(tfac)_n$ complexes and to the acetyl methyl resonances for $M(atc)_3$ complexes. [b] In parts per million relative to free ligand resonances. [c] In hertz at half maximum amplitude. Data shown are averages of several determinations with deviations from the mean of 4–22% ($^1H$), 1–31% ($^2H$), and 1–23% ($^{19}F$). [d] Figures given for trans isomers are (average $^1H$ values)/(average $^{19}F$ values), since individual $^{19}F$ and $^1H$ signals cannot be related. [e] Data obtained from $CHCl_3$ solutions at 32°. [f] Signal assigned to the cis isomer. [g] Data from ref 16. [h] Low values attributed in part to isotope effects (see text). [i] From acetone solution at 32°. [j] Data obtained from $CCl_4$ solutions at 32°. [k] Data from ref 9a. [l] Signal envelope contains more than one resonance.

ethyl ether. The partially deuterated ligand was recovered from the ether solution by solvent evaporation and added to a fresh solution of $D_2O$ and $Na_2CO_3$. After allowing this mixture to reflux for approximately 10 days, the ligand was recovered by distillation. Pmr of the product was used to assess the extent of deuteration which was generally ≥80%.

The procedure used for deuteration of (+)-3-acetylcamphor is a modification of the procedure described by Girgis and Fay for deuteration of benzoylacetone.[6a] A mixture of approximately 30 ml of (+)-3-acetylcamphor, 100 ml of a 1:1 (by volume) $D_2O$–ethanol solution, and a small amount of $Na_2CO_3$ was allowed to reflux over a 2-day period. A solution of partially deuterated (at the acetyl methyl) ligand in ethanol was recovered after extracting the mixture with ethyl ether. This solution was added to fresh $D_2O$ and $Na_2CO_3$, and the above procedure was repeated until the desired degree of deuteration was attained (≥80%, by pmr, after eight cycles). The final product was distilled *in vacuo* prior to preparation of the complexes.

**Trifluoroacetylacetonate Complexes.** $Fe(tfac)_3$, $Cr(tfac)_3$, and $Mn(tfac)_3$ were prepared by the methods of Fay and Piper.[6b] $Cu(tfac)_2$ and $V(tfac)_3$ were prepared by methods closely analogous to those used in preparation of the acetylacetonate complexes.[1] All complexes gave satisfactory elemental analyses.

Synthesis of $Ru(tfac)_3$ was accomplished by the following modification of the procedure used in preparing the acetylacetonate complex.[1] A mixture of 2.0 g of commercially available $RuCl_3 \cdot 1\text{–}3H_2O$(Alfa-Ventron), 20 ml of 0.3 *M* HCl, 20 ml of toluene, and 6.2 g of ligand was allowed to reflux under a nitrogen atmosphere until a deep red color developed (1–3 hr). Then an additional 40 ml of toluene was introduced, and a solution of 7.0 g of $Na_2CO_3$ in 50 ml of water was slowly added to neutralize the acid and deprotonate the ligand. The mixture was stirred under nitrogen for an additional 12 hr, after which the toluene layer was removed and evaporated to yield a crude product. During recrystallization of this product from *n*-pentane it was found that the trans isomer, as identified by nmr, crystallizes more readily than the cis isomer. The trans isomer may be obtained in high isomeric purity by this method if so desired.[7] Once the tris complex is formed, exclusion of atmospheric oxygen is not necessary. *Anal.* Calcd for $Ru(tfac)_3$: C, 32.16; H, 2.16. Found: C, 32.44; H, 2.30.

Complexes containing deuterated ligand were prepared by the same methods except that $H_2O$ was replaced by $D_2O$ in order to prevent loss of ligand deuterium by exchange. Analyses for partially deuterated complexes were satisfactory after values for hydrogen were scaled up by a factor representing the fractional ligand deuteration and the relative weight fractions of H and D in $H_2O$ and $D_2O$, respectively.

**Acetylcamphorate Complexes.** $V(atc)_3$ was prepared according to the procedure given by Chen and Everett.[9] $Mn(atc)_3$ and $Ru(atc)_3$ were prepared using methods[9b,10] analogous to those used in preparing the corresponding acetylacetonate complexes. *Anal.* Calcd for $Mn(atc)_3$: C, 68.12; H, 8.10. Found: C, 68.03; H, 8.15. Calcd for $Ru(atc)_3$: C, 63.51; H, 7.55. Found: C, 63.38, H, 7.78. Analyses for partially deuterated complexes were satisfactory when treated as described above.

**Nmr Spectra.** A Varian HA-100 nmr spectrometer operating at 100.0 MHz (proton), 15.35 MHz (deuteron), or 94.08 MHz (fluorine) was used to record spectra of the complexes. Chloroform, chloroform-*d*, and carbon tetrachloride were generally employed as solvents. Reference compounds were benzene, tetramethylsilane, and cyclohexane (pmr); benzene-$d_6$, cyclohexane-$d_{12}$, and chloroform-*d* (dmr); and free ligand ($^{19}F$ nmr). In order to obtain maximum signal intensities (particularly for dmr), solutions approaching saturation were generally used. Samples of $V(atc)_3$ and $V(tfac)_3$ were sealed in nmr tubes under rigorously oxygen-free conditions. Chemical shifts and line widths at half-maximum amplitude were measured by side-banding. Data are presented in Table I.

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(6) (a) A. Y. Girgis and R. C. Fay, *J. Amer. Chem. Soc.*, **92**, 7061 (1970); (b) R. C. Fay and T. S. Piper, *ibid.*, **85**, 500 (1963).

(7) Recently Gordon, *et al.*,[8] prepared $Ru(tfac)_3$ by another method and achieved isomer separation by fractional crystallization and also by column chromatography.

(8) J. G. Gordon, II, M. J. O'Connor, and R. H. Holm, *Inorg. Chim. Acta*, **5**, 381 (1971).

(9) (a) Y. T. Chen and G. W. Everett, Jr., *J. Amer. Chem. Soc.*, **90**, 6660 (1968); (b) Y. T. Chen, Ph.D. Thesis, University of Kansas, 1970.

(10) G. W. Everett, Jr., and R. M. King, *Inorg. Chem.*, **11**, 2041 (1972).

## Results and Discussion

**Trifluoroacetylacetonate Complexes.** When three unsymmetrical, bidentate ligands such as trifluoroacetylacetonate are coordinated to a metal ion, two geometrical isomers are possible. These are designated as cis (facial) or trans (meridional), according to the spacial arrangement of identical ligand substituents. The cis isomer has a threefold axis of symmetry relating corresponding substituents on all three ligands, whereas the trans isomer has no symmetry. Thus if the rate of isomerization is slow on the nmr time scale, the cis isomer should exhibit a single nmr signal for each ligand substituent, but up to three such resonances could be observed for the trans isomer. Cis and trans isomers are possible also when two unsymmetrical bidentate ligands are coordinated to a metal ion in a square-planar fashion. However, for both isomers in this arrangement, corresponding substituents on different ligands are related by symmetry, and one nmr signal per substituent is expected for each isomer.

The pmr spectrum of Mn(tfac)$_3$ in chloroform-*d* solution includes three intense signals in the range of 33–43 ppm downfield of TMS which are assigned to methyl resonances. Resonances of methine protons appear at higher field. Isotropic shifts of the methyl resonances and line widths at half-maximum amplitude are given in Table I. Figure 1 shows the methyl region of the spectrum. The spectrum presents little evidence for existence of the cis isomer other than the fact that the area of the upfield resonance is noticeably larger than those of the other two and could mask a small signal arising from the cis isomer.[11] However, the fluorine nmr (fmr) spectrum of this complex (*vide infra*) clearly reveals the presence of the cis isomer. Dmr of deuterated Mn(tfac)$_3$ shows a pattern of methyl resonances (Figure 1) similar in appearance to that found in the pmr spectrum.[12a] However, the overall resolution is decidedly poorer than for pmr. Table I compares pmr and dmr isotropic shifts and line widths. The fmr spectrum of Mn(tfac)$_3$, shown also in Figure 1, contains four signals in the range of 5–30 ppm downfield of the free ligand resonance.[13] Three of these have equal areas within experimental error and are assigned to the trans isomer. The remaining signal has an area approximately half that of one arising from the trans isomer and is assigned to the cis isomer.

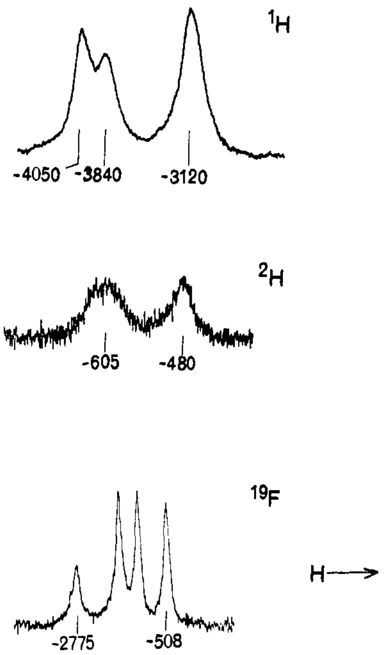

Figure 1. Nmr spectra of Mn(tfac)$_3$ in chloroform solution at 32°. Only the methyl and CF$_3$ signals are shown. Frequencies given are chemical shifts relative to free ligand.

Qualitatively the fluorine spectrum of Mn(tfac)$_3$ shows better resolution than the proton spectrum, which in turn is superior to the deuteron spectrum. Deuteron line widths are considerably smaller than proton line widths as expected, but the average ratio of $^1$H/$^2$H line widths is only 6.0 compared to the expected value of $\sim$42. Since deuteron chemical shift differences in hertz are smaller by a factor of 6.5 than those of protons, the $^1$H/$^2$H line width ratio must be greater than 6.5 if the overall resolution of dmr is to be greater than that of pmr (neglecting differences in signal-to-noise ratio). This is not the case for Mn(tfac)$_3$ as may be seen from Figure 1 and Table I. Deviations from the expected line width ratio have been observed previously[1,14] and have been attributed largely to electric quadrupolar broadening of the deuteron signals.[1] The latter relaxation mechanism is not accounted for in the Solomon–Bloembergen equations. For Mn(tfac)$_3$ the average contribution to the methyl dmr line width from electric quadrupolar relaxation is $\sim$33 Hz, assuming that this mechanism is solely responsible for the deviation from theory. Another mechanism contributing to the low $^1$H/$^2$H line width ratio is exchange broadening. It has been shown that the pmr signals of Mn(tfac)$_3$ broaden around 50° and coalesce $\sim$70° due to rapid cis $\rightleftarrows$ trans isomerism.[8] The dmr signals deuterated Mn(tfac)$_3$ coalesce at $\sim$50° and are broadened by exchange at 32°. The lower dmr coalescence temperature is a result of the smaller signal separations in hertz. However this is not primarily responsible for the low $^1$H/$^2$H line width ratio, since the ratio increases by 10% when pmr and dmr are compared under conditions of similar exchange broadening.

The assumptions made earlier[1] in applying the Solomon–Bloembergen relationships to a simple comparison of proton and deuteron line widths in paramagnetic molecules cannot be extended to include a comparison of proton and fluorine line widths unless it can be shown that the contribution of the hyperfine interaction to the line width is negligible. In that case the pmr/fmr line width ratio would be given by $(\gamma_H^2/\gamma_F^2)(r_F^6/r_H^6)$, where $\gamma$'s are nuclear magnetogyric ratios and $r$'s are metal-to-nuclear distances. For tris(trifluoroacetylacetonate) complexes this ratio is estimated to be $\sim$1.2–1.4. When

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(11) Proton nmr spectra of Mn(tfac)$_3$ and Ru(tfac)$_3$ were recently reported by Gordon, O'Connor, and Holm.[8] Their results are in close agreement with ours. In addition they showed that at lower temperatures the most upfield methyl resonance of Mn(tfac)$_3$ splits into two signals, one of which is of relatively low intensity and is assigned to the cis isomer.

(12) (a) Proton and deuteron isotropic shifts are expected to be identical, to the first approximation, when expressed in parts per million. The slight deviations found are attributed to experimental error and to isotope effects as discussed previously.[1,12b] (b) R. R. Horn and G. W. Everett, Jr., *J. Amer. Chem. Soc.*, **93**, 7173 (1971).

(13) The free ligand resonance may be seen in the presence of the complex, indicating that ligand exchange is slow on the nmr time scale.

(14) (a) G. Laukien and F. Noack, *Z. Phys.*, **159**, 311 (1960); (b) P. Diehl and T. Leipert, *Helv. Chim. Acta*, 47, 545 (1964).

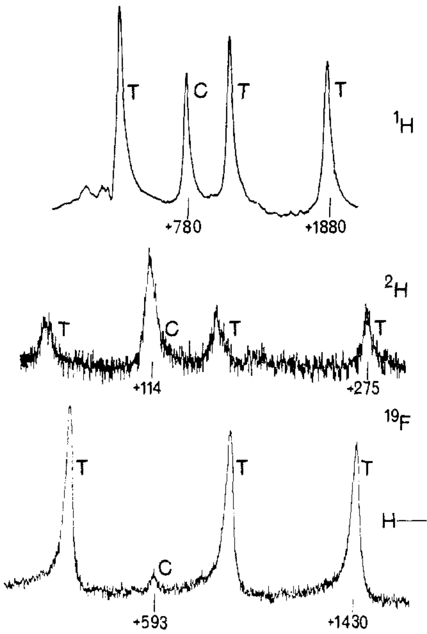

Figure 2. Nmr spectra of Ru(tfac)$_3$ in chloroform solution at 32°. Only the methyl and CF$_3$ signals are shown. Signals assigned to cis and trans isomers are labeled C and T, respectively. Frequencies given are chemical shifts relative to free ligand.

the hyperfine interaction contributes to the line width, however, one cannot assume that the contribution to the pmr line width relative to that of the fmr line width from this interaction is equal to the ratio of the squares of the nuclear magnetogyric ratios as is the case when pmr and dmr line widths are compared.[15] For Mn(tfac)$_3$ the observed isotropic shifts are likely to be primarily contact shifts, and line widths are determined by both dipolar and hyperfine interactions. Accordingly, no attempt is made here to explain the relative pmr and fmr line widths.

Four well-resolved methyl signals spread over ~16 ppm are found in the pmr spectrum of a mixture of cis and trans isomers of Ru(tfac)$_3$.[11] These are shown in Figure 2. Isotropic shifts are positive, *i.e.*, resonance signals of the complex are at high field relative to the free ligand resonance (see Table I). Four signals of low intensity at even higher field are assigned to the methine proton. The methyl signal occurring at next-to-lowest field may be assigned to the cis isomer since its relative intensity varies from spectrum to spectrum depending upon the method used to recrystallize the complex (see Experimental Section). These signals are also seen in the deuteron spectrum of deuterated Ru(tfac)$_3$ (Figure 2). Dmr chemical shifts are in reasonable agreement with those obtained by pmr, and, disregarding the decrease in signal-to-noise ratio, the dmr spectrum displays an overall resolution roughly comparable to that of the pmr spectrum. Here the average pmr/dmr line width ratio is about 7.4.

The fluorine spectrum of Ru(tfac)$_3$ reveals a pattern of CF$_3$ signals remarkably similar to the methyl resonances found in the pmr and dmr spectra. The resemblance includes the relative position of the cis isomer resonance, the signal separations in parts per million, and the overall sign and magnitudes of isotropic shifts. Chemical shift differences between CF$_3$ resonances in diamagnetic M(tfac)$_3$ complexes are only of the order of a few hertz,[6b] whereas the overall spread in the fmr spectrum of Ru(tfac)$_3$ is ~1200 Hz. Clearly, chemical shift differences in the latter represent differences in isotropic shifts. If the isotropic shifts were primarily contact shifts or if they were combined contact and dipolar shifts, the striking similarity in fmr and pmr spectra observed for Ru(tfac)$_3$ would not be expected. On the other hand, if the shifts are dipolar in origin, similar pmr and fmr spectra would be expected since geometrical factors alone govern the relative directions and magnitudes of shifts for nuclei on the same molecule. These geometrical factors would differ only slightly for CH$_3$ and CF$_3$ in M(tfac)$_3$ complexes. It is concluded that the observed isotropic shifts for Ru(tfac)$_3$ are primarily dipolar shifts. This implies that the hyperfine coupling constants are small, in which case nmr line widths may be governed largely by dipolar relaxation. However, the average pmr/fmr line width ratio, 1.6, is outside the range of values (1.2–1.4) estimated for dipolar relaxation.

Proton and fluorine nmr spectra of V(tfac)$_3$ have been reported previously by Röhrscheid, *et al.*;[16] however, line widths were not given. These spectra, in addition to the dmr spectrum of deuterated V(tfac)$_3$, were recorded during the present investigation in order to make a direct comparison of line widths. Data are shown in Table I. Proton and fluorine nmr results are in good agreement with earlier values. Signals arising from cis and trans isomers are found in the methyl region of the pmr and dmr spectra and also in the fmr spectrum. Except for a smaller dmr signal-to-noise ratio, the dmr and pmr spectra are roughly comparable in resolution. Methyl deuteron signals of V(tfac)$_3$ are complicated by isotope effects as found previously for the acetylacetonate complex when the ligand is incompletely deuterated.[12b] Related signal splittings are found also in the *pmr* spectrum of partially deuterated V(tfac)$_3$. Dmr line widths given in Table I are full widths of the multiplets; thus the $^1$H/$^2$H ratios shown are smaller than those of the individual resonances. The signal of the cis isomer in the fmr spectrum is not as well resolved as in the pmr and dmr spectra.

The methyl resonance of Cu(tfac)$_2$ appears as a single signal in both pmr and dmr spectra. No splitting of the signal, indicative of nmr distinguishable isomers, could be detected in either case. The pmr/dmr line width ratio is ~14. Proton chemical shifts are in satisfactory agreement with the values reported by Zelonka and Baird.[17] No well-defined fmr signal could be detected for Cu(tfac)$_2$ in chloroform solution, in agreement with earlier findings;[17] however, a broad (~1200 Hz) fmr resonance was observed in acetone solution.

A very broad methyl resonance is observed in the pmr spectra of Fe(tfac)$_3$ and Cr(tfac)$_3$. Since a relatively high pmr/dmr line width ratio was found earlier

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(15) The variable in the term expressing the hyperfine contribution to the line width is the square of the hyperfine coupling constant, $A$, which may be expressed: $A = {}^4/_3\hbar\gamma_e\gamma_I[\Psi(0)]^2$. For protons and deuterons at a given site in a molecule, $A$ values differ only in $\gamma_I$, since $\Psi(0)$ is expected to change very little. However, on comparing protons with fluorine, both $\gamma_I$ and $\Psi(0)$ are expected to differ.

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

(17) R. A. Zelonka and M. C. Baird, *J. Amer. Chem. Soc.*, **93**, 6066 (1971).

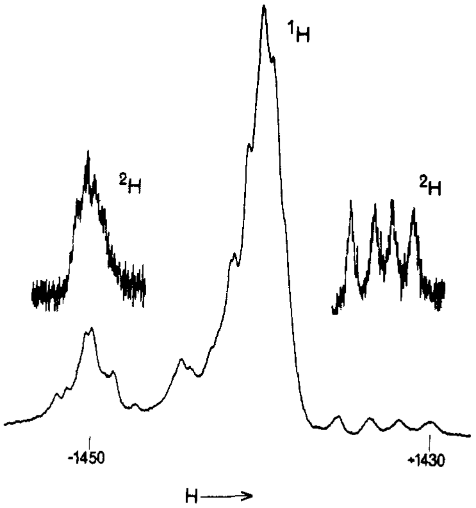

Figure 3. Proton and deuteron (inserts) nmr spectra of Mn(atc)$_3$ in carbon tetrachloride solution at 32°. Frequencies shown are chemical shifts relative to free ligand.

for the acetylacetonate complexes of these metal ions, dmr spectra of deuterated Fe(tfac)$_3$ and Cr(tfac)$_3$ were recorded in hopes of detecting signal splitting. Although dmr line widths are considerably narrower than pmr line widths, only a single signal is found for CD$_3$ in each case.

**Acetylcamphorate Complexes.** Four diastereomeric complexes are possible when three chiral, unsymmetrical, bidentate ligands such as (+)-3-acetylcamphor bind a single metal ion.[18] The two trans isomers, Δ-trans and Λ-trans, have no symmetry, and each could give up to three resonance signals for each kind of ligand hydrogen. The cis isomers, Δ-cis and Λ-cis, have a threefold symmetry axis; thus one resonance signal per kind of hydrogen is expected. Up to eight nmr signals for each kind of hydrogen may be found in a mixture of diastereomers.[2m,9,18b] In order to test the efficacy of dmr for studies of diastereoisomerism in paramagnetic complexes, pmr and dmr spectra of several tris(+)-3-acetylcamphorate complexes were recorded. The 3-acetyl methyl nmr signals are of primary interest since this position is readily deuterated.

Mn(atc)$_3$ was first prepared by Chen[9b] who found $\mu_{\text{eff}}$ = 4.98 BM (22°) for the diastereomeric mixture and examined the visible and ORD spectra. The complete pmr spectrum of Mn(atc)$_3$ in CCl$_4$ solution is shown in Figure 3. The overall appearance of the spectrum depends somewhat on the solvent used.[9b] The signals of interest are those at highest and at lowest field; these arise primarily from the acetyl methyl protons as evidenced from their diminution when this group is deuterium substituted.[19] The dmr spectrum of the deuterium substituted complex, shown in the inserts of Figure 3, reveals a well-resolved set of four signals at high field and a poorly resolved low-field set. It is apparent that at least three and probably all four diastereomers are present; however, no attempt is made here to assign signals to specific isomers. Chemical shifts and line widths are listed in Table I. For Mn(atc)$_3$ the resolutions of pmr and dmr are about the same; the average pmr/dmr line width ratio is 6.9. The primary advantage of dmr in this case lies in confirmation of the acetyl methyl signal assignments. The occurrence of both positive and negative isotropic shifts for the acetyl methyl hydrogens is surprising, since large negative shifts are found for the analogous methyls of Mn(tfac)$_3$ and the Mn(III) acetylacetonate complex. This implies that a different mechanism of spin delocalization[20] or significant dipolar shifts occur for the acetylcamphorate complex.

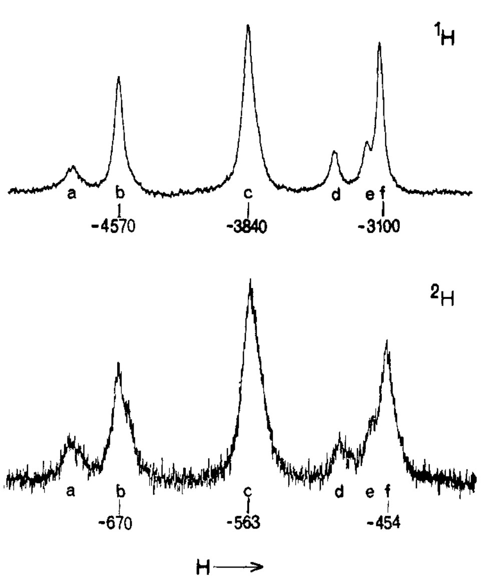

Figure 4. Proton and deuteron nmr spectra of the acetyl methyl of V(atc)$_3$ in chloroform solution at 32°. Frequencies are chemical shifts relative to free ligand.

The pmr spectrum of V(atc)$_3$ has been discussed in detail previously.[9a] Acetyl methyl signals are found in a group centered around 40 ppm downfield of tetramethylsilane. Due to overlap, only six of the eight possible pmr signals are resolved when chloroform is used as the solvent, and the presence of all four diastereomers cannot be proved.[9a] Pmr and dmr spectra of V(atc)$_3$ in the methyl region are compared in Figure 4. The deuteron spectrum shows slightly poorer resolution in general (pmr/dmr line widths are ~4), although an upfield shoulder on resonance b is apparent in the dmr spectra but not in the pmr spectra. Recent work in this laboratory has shown that signal c splits into three signals, but b remains unchanged upon addition of carbon tetrachloride to the chloroform solution.[21] Thus the shoulder on signal b cannot be assigned to the underlying resonance of another diastereomer; rather it is likely a manifestation of isotope effects such as found for other V(III) complexes of partially deuterated ligands.[12b] Line widths and isotropic shifts are listed in Table I. The differences in proton and deuteron isotropic shifts for V(atc)$_3$ are somewhat larger than for the other complexes. Here an additional[12a] source of error arises from the fact that proton signals were referenced to chloroform and converted to isotropic shifts using the diamagnetic ligand–chloro-

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(18) (a) R. M. King and G. W. Everett, Jr., *Inorg. Chem.*, **10**, 1237 (1971); (b) C. S. Springer, Jr., R. E. Sievers, and B. Feibush, *ibid.*, **10**, 1242 (1971).

(19) The signals at low field do not completely disappear upon deuteration, indicating that resonances from other protons, presumably camphor methylenes, are also present.

(20) For a discussion of spin delocalization mechanisms in tris(acetylacetonate) complexes, see D. R. Eaton, *J. Amer. Chem. Soc.*, 87, 3097 (1965).

(21) R. M. King and G. W. Everett, Jr., unpublished results.

form separation,[9a] whereas deuteron signals were referenced directly to the free ligand signal. The possibility of chemical shift errors resulting from this procedure has been discussed previously.[1]

Proton and deuteron spectra of $\mathrm{Ru(atc)_3}$ will be discussed in detail in another publication[10] and therefore will be treated briefly here. Pmr signals of the acetyl methyl are severely overlapped by resonances of other protons, making signal assignments and line width measurements difficult. This problem is completely avoided by examining the dmr spectrum of deuterated $\mathrm{Ru(atc)_3}$. The dmr spectrum of the diastereomeric mixture reveals seven signals; one of these has a considerably larger area than the others and is presumed to contain two resonances. The four diastereomers can be separated chromatographically, and the dmr signals may be assigned to the individual diastereomers.[10] A rough estimate of relative isomer abundances can be obtained from the dmr signal areas in a spectrum of the diastereomeric mixture. Dmr resolution for this complex is somewhat better than pmr resolution; the average pmr/dmr line width ratio is ~13. One signal which appears as a singlet in the pmr spectrum is clearly split into two signals in dmr. Isotropic shifts of the acetyl methyl are all positive, as is the case for the methyls of $\mathrm{Ru(tfac)_3}$ and tris(acetylacetonato)ruthenium(III).

Previously it was shown that the pmr/dmr line width ratio was ~42 for tris(acetylacetonato)chromium(III).[1] Accordingly, the dmr spectrum of deuterated $\mathrm{Cr(atc)_3}$ was examined in hopes that resonances arising from isomers of low symmetry or from different isomers would be observably different. However, only a broad, featureless dmr signal is found for this complex.

## Conclusions

Dmr line widths were found to be considerably smaller than corresponding pmr line widths for all complexes reported in this paper. However, the dmr spectra are at best only roughly comparable in resolution to the pmr spectra, disregarding the lower signal-to-noise ratio for dmr. Since the chemical shift scale in hertz for dmr is smaller than that of pmr by a factor of $\gamma_H/\gamma_D = 6.5$, improved resolution of dmr over pmr is possible only if the pmr/dmr line width ratios *exceed* this value. This was indeed the case for the paramagnetic acetylacetonate complexes investigated earlier,[1] but in the present study the line width ratios are generally of the order of 6.5 or less. Deuteron resonance signals are considerably broader than expected, presumably as a result of deuteron nuclear quadrupolar relaxation. This relaxation mechanism appears to be more efficient in the trifluoroacetylacetonate and (+)-3-acetylcamphorate complexes than in the acetylacetonate complexes.[22] Contributions to the dmr line widths in some cases could arise from unresolved isotope effects[12b] when the ligand is incompletely deuterated.

A problem encountered in the present investigation but not for the highly symmetrical acetylacetonate complexes is the inherent low sensitivity of dmr relative to pmr.[23] Whereas all methyl deuteron resonances combine to produce a single, strong signal in the acetylacetonate complexes, these resonances often appear individually in complexes of low symmetry, thereby diluting the signal strength. This problem was overcome to a satisfactory extent by going to more concentrated solutions. Use of larger sample tubes (>5 mm diameter) or time-averaging techniques may be necessary is some instances.

Although for the complexes reported here no significant gain in overall resolution is generally realized by using dmr rather than pmr for studies of stereoisomerism, some advantages of employing dmr for such studies appear to be as follows. (1) *Pmr* signals of groups which can be deuterated may be unambiguously identified by comparing pmr and dmr spectra, since proton and deuteron chemical shifts on a parts per million scale are nearly identical. This was especially helpful in interpreting the pmr spectrum of $\mathrm{Mn(atc)_3}$. (2) When the molecule of interest contains many types of chemically different hydrogens, it may be impossible to determine the number of isomers present and their relative abundances by pmr as a result of signal overlap. However if selective deuteration is feasible, the desired information may be forthcoming in the dmr spectrum where interference by resonances of other hydrogens is avoided. This was found to be the case for $\mathrm{Ru(atc)_3}$.

It is anticipated that (1) and (2) and also any fortuitous gain in resolution for dmr will have some application in nmr studies of paramagnetic macromolecules of biological origin. The advantages of dmr in investigating organic radical ions are currently being explored.[24]

Finally it should be pointed out that for $\mathrm{Ru(atc)_3}$ dmr revealed observable signal separations where pmr failed to do so. Fluorine nmr spectra were found to be generally comparable to and often better in resolution than pmr spectra.

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(22) This is true of the paramagnetic complexes investigated; however, for diamagnetic $\mathrm{Co(tfac)_3}$ the relative methyl pmr and dmr line widths are not significantly different from those of tris(acetylacetonato)cobalt(III).[1]

(23) Where pmr and dmr are run at the same magnetic field strength, the relative amplitudes of dmr and pmr absorption mode signals under optimum conditions are about 1 : 100. *Cf.* J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 480.

(24) (a) G. W. Canters, B. M. P. Hendriks, and E. DeBoer, *J. Chem. Phys.*, 53, 445 (1970); (b) B. M. P. Hendriks, G. W. Canters, C. Corvaja, J. W. M. DeBoer, and E. DeBoer, *Mol. Phys.*, 20, 193 (1971).