CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY,
AEROSPACE RESEARCH LABORATORY, WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Solvent Effects on the Nuclear Magnetic Resonance Spectra of Aluminum β-Diketonates

BY ROBERT G. LINCK AND ROBERT E. SIEVERS

Received August 26, 1965

The effect of solvent upon the nuclear magnetic resonance signals of various aluminum β-diketonates has been investigated. The data are discussed in terms of the various contributions to the solvent-induced chemical shift; the agreement between calculated and observed values is satisfactory. When applied to aromatic solvents with large diamagnetic anisotropies, the analysis of the data leads to the postulate of solvation of the metal chelates along their C_3 axes by molecules with donor groups; for example, nitrobenzene. Aromaticity and ring currents in acetylacetonate complexes of metal ions are discussed in terms of the solvent-induced shifts and the temperature dependence of some of the signals of the aluminum complexes.

Introduction

A common feature in the numerous studies[1-5] of the nmr spectra of metal β-diketonates has been the choice of solvent; thus, almost all reported experiments have been carried out in CCl_4, $CHCl_3$, or, occasionally, benzene. Collman, *et al.*, reported that the chemical shift depended on the nature of the solvent, but did not pursue this observation further.[3] That striking solvent shifts do exist was reported briefly in a paper principally concerned with the kinetics of interchange of ligands in the aluminum acetylacetonate–aluminum hexafluoroacetylacetonate system.[6] Thus, although the chemical shift of the methyl protons in $Al(hfaa)_2(aa)$, $Al(hfaa)(aa)_2$, and $Al(aa)_3$[7] occur at successively higher fields in CCl_4, the order is reversed in benzene.

Solvent shifts of this character are not unknown in nmr studies. Hatton and Richards have observed that the two nonequivalent methyl groups in N,N-dimethylformamide shift resonance positions as the pure liquid is diluted with benzene such that the order of the pair reverses.[8]

These resonance shifts were explained on the basis of specific solute–solvent interactions, following closely the model of Reeves and Schneider[9] and Bothner-By and Glick,[10] who first studied the $CHCl_3$–benzene complex by nmr methods. Schneider has discussed the sensitivity of nmr spectroscopy as applied to investigations of weak complexes with aromatic solvents: the anisotropic nature of the aromatic magnetic susceptibility causes large shifts even when complex formation is very weak.[11] Studies on the temperature dependence of shifts due to aromatic solvents have demonstrated that the shifts are due to complex formation.[12-14]

These experimental data have not lacked quantitative explanation. The theory of such shifts has kept pace with experiment, and, in general, the shifts are well understood. Since the effect of environment must be understood before any analysis of the intramolecular shifts and subsequent arguments about aromaticity can be meaningful, and since the solvation of metal β-diketonates has been of recent interest,[15-17] it seemed appropriate to investigate in greater detail the effect of solvents on the nmr spectra of various aluminum β-diketonate derivatives.

Experimental Section

The tris complexes of aa^-,[18] $hmaa^-$,[19] and $Braa^-$[20] were prepared by standard methods. $Al(hfaa)_3$ was prepared by allowing the ligand and anhydrous $AlCl_3$ to react in CCl_4 solution. $Al(Meaa)_3$ was prepared by the method used for $Al(hmaa)_3$, after preparation of the ligand by the procedure of Sprague, *et al.*[21] $In(aa)_3$ was prepared by the method used for $Al(aa)_3$, mp 186–188.5°; lit.[22] 186–189°.

The mixed complexes of aluminum with aa^- and $hfaa^-$ were prepared by mixing stoichiometric amounts of the parent tris complexes, followed by refluxing in CCl_4 or benzene. Formation of $Al(hfaa)(aa)_2$ takes place readily (within hours); the other mixed complex requires longer periods of heating (days). The equilibrium constants for the formation of the mixed ligand complexes ($K \cong 300$)[6] are large enough to give high yields, but com-

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[1] R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).

[2] J. A. Smith and J. D. Thwaites, *Discussions Faraday Soc.*, **34**, 143 (1962).

[3] (a) J. P. Collman, R. L. Marshall, and W. L. Young, *Chem. Ind.* (London), 1380 (1962); (b) J. P. Collman, *Angew. Chem. Intern. Ed. Engl.*, **4**, 132 (1965).

[4] R. E. Hester, *Chem. Ind.* (London), 1397 (1963).

[5] R. A. Palmer, R. C. Fay, and T. S. Piper, *Inorg. Chem.*, **3**, 875 (1964), and references therein.

[6] R. G. Linck and R. E. Sievers, paper presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964.

[7] The abbreviations used in the literature to represent ligands derived from acetylacetone seem to vary with the whim of the authors. Those used in this paper do not deviate from this tradition, but are self-consistent for the ligands used here: H(aa), 2,4-pentanedione; H(hfaa), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; H(hmaa), 2,2,6,6-tetramethyl-3,5-heptanedione; H(Braa), 3-bromo-2,4-pentanedione; H(Claa), 3-chloro-2,4-pentanedione; H(Meaa), 3-methyl-2,4-pentanedione; H(tfaa), 1,1,1-trifluoro-2,4-pentanedione.

[8] J. V. Hatton and R. E. Richards, *Mol. Phys.*, **3**, 253 (1960).

[9] L. P. Reeves and M. T. G. Schneider, *Can. J. Chem.*, **35**, 251 (1957).

[10] A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

[11] W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).

[12] R. J. Abraham, *Mol. Phys.*, **4**, 369 (1961).

[13] J. V. Hatton and W. G. Schneider, *Can. J. Chem.*, **40**, 1285 (1962).

[14] H. M. Hutton and T. Schaefer, *ibid.*, **41**, 187 (1963).

[15] (a) J. F. Steinbach and J. H. Burns, *J. Am. Chem. Soc.*, **80**, 1839 (1958); (b) F. R. Clarke, J. F. Steinbach, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **26**, 1311 (1964), and references therein.

[16] P. D. Hopkins and B. E. Douglas, *Inorg. Chem.*, **3**, 357 (1964).

[17] (a) J. P. Fackler, Jr., T. S. Davis, and I. D. Chawla, *ibid.*, **4**, 130 (1965); (b) J. P. Fackler, Jr., and T. S. Davis, paper presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

[18] R. C. Young, *Inorg. Syn.*, **2**, 25 (1946).

[19] G. S. Hammond, D. C. Nonhebel, and C. S. Wu, *Inorg. Chem.*, **2**, 73 (1963).

[20] R. W. Kluiber, *J. Am. Chem. Soc.*, **82**, 4839 (1960).

[21] J. M. Sprague, L. J. Beckham, and H. Adkins, *ibid.*, **56**, 2665 (1934).

[22] T. Moeller and E. Gulyas, *J. Inorg. Nucl. Chem.*, **5**, 254 (1958).

TABLE I

ANALYTICAL DATA

Compound	% C		% H		% metal		Mp, °C	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Lit.
$Al(aa)_3$	55.35	55.55	6.39	6.48			192–195	194.6[a]
$Al(hfaa)_3$	27.79	27.78	0.48	0.46			73–75	73–74[b]
$Al(hmaa)_3$	68.27	68.71	9.78	9.96	4.71	4.68	263.5–264.5	264–265[c]
$Al(Meaa)_3$	58.76	58.61	7.02	7.34	7.19	7.47	206–209	
$Al(Braa)_3$[d]	32.38	32.10	3.32	3.21	5.02	4.82	210–212	215.5–216[e]
$Co(hfaa)(aa)_2$[f]	39.09	38.79	3.36	3.25	12.39	12.69	141–142	

[a] Reference 18. [b] M. L. Morris, R. W. Moshier, and R. E. Sievers, *Inorg. Chem.*, **2**, 411 (1963). [c] Reference 19. [d] Calcd: Br, 42.75. Found: Br, 42.50. [e] Reference 20. [f] Calcd: F, 24.93. Found: F, 24.57.

plete purification was not necessary; by assignment of the signals of the pure tris complexes and then integration of the remaining signals, all peaks in the nmr spectra could be unambiguously assigned. Confirmation of the assignment was obtained by gas chromatography of the complexes.[6] For purposes of future identification of these mixed complexes, small samples were collected from the exit port of a gas chromatography column and melting points were obtained: $Al(hfaa)_2(aa)$, mp 62–64°; $Al(hfaa)(aa)_2$, mp 83–84°.

To prepare $Co(hfaa)(aa)_2$, a mixture of $Co(aa)_3$ and H(hfaa) was refluxed in benzene for 4 days; the resulting solution was washed with water, dried over $CaCl_2$, filtered, and evaporated. An alumina column was used to separate the various mixed complexes, the $Co(hfaa)(aa)_2$ being eluted when the wash of benzene–hexane exceeded 20% benzene. The complex was recrystallized from hexane. Table I gives the analytical data.

All solvents were used as received from commercial sources. In cases of doubtful purity, high-amplitude nmr spectra and vapor phase chromatography of the pure solvents were recorded to verify purity.

The spectra were recorded on a Varian A-60 spectrometer. Solvent and solute were mixed in the spectrometer tube, and a capillary of pure tetramethylsilane (TMS) was added. The concentration of samples never exceeded 0.2 *M* (approximately 7 mole %). Even at this concentration, dilution of samples caused a shift of the resonance position. This shift usually amounted to no more than 0.5–1.0 cps. However, the values recorded in the tables are either the line position obtained by extrapolation to infinite dilution or the position of the resonance line on a sample at the limits of detectibility (approximately 0.005 *M*). The values for the chemical shifts are believed accurate to ±0.5 cps. All spectra were recorded in the temperature range 38–39°.

Results

The chemical shift of a proton in a solute is given by[11,23]

$$\delta = \delta_g + \delta_b + \delta_w + \delta_E + \delta_a + \delta_c \qquad (1)$$

where δ_g is the shift of the molecule in the gas phase—the intramolecular chemical shift—δ_b is the contribution proportional to the bulk susceptibility of the medium, δ_w is the contribution due to van der Waals forces between solute and solvent, δ_E is the shift due to the reaction field of a polar solute, δ_a is the shift due to the magnetic anisotropy of the solvent, and δ_c is the contribution due to complex formation.

In a study of solvent effects with an internal reference, the data of interest take the form

$$({}^{Y}_{X}\delta^{S} - {}_{ref}\delta^{S}) - ({}^{Y}_{X}\delta^{S'} - {}_{ref}\delta^{S'}) \qquad (2)$$

where ${}^{Y}_{X}\delta^{S}$ is the resonance position of nucleus Y in compound X dissolved in solvent S. Expanding this expression, using eq 1 and rearranging, leads to

$$({}^{Y}_{X}\delta^{S}_{w} - {}^{Y}_{X}\delta^{S'}_{w}) - ({}_{ref}\delta^{S}_{w} - {}_{ref}\delta^{S'}_{w}) + ({}^{Y}_{X}\delta^{S}_{E} - {}^{Y}_{X}\delta^{S'}_{E}) - ({}_{ref}\delta^{S}_{E} - {}_{ref}\delta^{S'}_{E}) + \ldots \qquad (3)$$

Expression 3 is useful in elucidating solvent effects on the solute, independent of reference, only if the terms involving the reference resonance shifts are small compared to the terms involving the solute. This would be true if $({}_{ref}\delta^{S} - {}_{ref}\delta_{g})$ were independent of solvent; but the arbitrary reference compound, being a solute, can show solvent effects. Even symmetrical nonpolar compounds have $({}_{ref}\delta^{S} - {}_{ref}\delta_{g})$ dependent on solvent, as has been experimentally verified by Bothner-By.[24] His data show the $({}^{Y}_{X}\delta^{S} - {}^{Y}_{X}\delta_{g})$ is dependent not only on S, but also on X, even for such standard reference compounds as tetramethylsilane, cyclopentane, and neopentane.

Thus, the use of an internal standard must be justified by cancellation of the various terms in expression 3 involving the reference or eliminated by investigation of a system where the shifts due to the solute–solvent interactions are specific for the solute and large compared to the variation in the other terms in (3) and do not occur for the reference. In investigations of reaction field effects for polar molecules some workers have used nonpolar internal references;[25,26] the study of the benzene–acetonitrile complex[11] shows shifts of the order of 50 cps (at 60 Mc/sec), a large value compared to van der Waals shifts, (0–10 cps). Another technique has been used for solutes that contain two nonequivalent protons: one of the protons can be used as a reference for the other.[8] This technique may be applied to most of the molecules discussed here; for this purpose φ is defined as the difference in chemical shift between terminal protons and those on the acetylacetonate ring.

The alternative procedure, calculation of the various terms in eq 1, becomes necessary when such cancellations of the terms in expression 3 do not seem justifiable. To evaluate δ_w, δ_E, δ_a, and δ_c, the most useful values are the positions of the resonance lines relative to external TMS, corrected for differences in bulk susceptibility of the solvent and the TMS reference.[27]

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(23) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

(24) A. A. Bothner-By, *J. Mol. Spectry.*, **5**, 52 (1960).

(25) F. Hruska, E. Bock, and T. Schaefer, *Can. J. Chem.*, **41**, 3034 (1963).

(26) V. S. Watts and J. H. Goldstein, *J. Chem. Phys.*, **42**, 228 (1965).

(27) Note that all resonance positions are given in cps at 60 Mc/sec from external TMS; a negative sign implies a resonance at lower field.

TABLE II

OBSERVED CHEMICAL SHIFTS FOR SOME TRIS COMPLEXES RELATIVE TO EXTERNAL TMS CORRECTED FOR BULK SUSCEPTIBILITY DIFFERENCES

	$Al(aa)_3$		$Al(Meaa)_3$		$Al(hmaa)_3$	
Solvent	CH_3	CH	CH_3	3-CH_3	$(CH_3)_3$	CH
Hexane	−108.6	−316.6			−65.6	−341.6
CCl_4	−126.8	−331.4	−131.0	−120.6	−75.3	−347.8
$CHCl_3$	−124	−334	−132.5	−119.2		
CH_2Cl_2	−118	−328	−129.4	−118.1		
$CHBr_3$	−143.3	−347.0	−149.0	−132.8	−82.9	−354.2
CH_2Br_2	−130.1	−340.5	−133.6	−121.2		
C_2H_5Br	−120.6	−334.9				
1,2-$Br_2C_2H_4$	−128.2	−337.1	−130.6	−119.3	−74.4	−348.4
1,1,2,2-$Cl_4C_2H_2$	−128.9	−338.4				
Acetone	−113	−330	−117.9	−109.9	−66.4	−347.3
Benzene	−84.2	−295.8	−91.8	−70.9	−50.7	−330.3
Toluene	−85.6	−296.2				
o-Xylene	−95.7	−305.2	−102.6	−87.1	−62.2	−340.9
m-Xylene	−86.2	−296.5				
Nitrobenzene	−89.1	−307.3	−94.6	−89.6	−44.4	−327.8
Benzonitrile	−87.3	−307.0			−46.0	−327.0
Fluorobenzene	−88.2	−302.1	−95.8	−78.7	−51.9	−332.9
Chlorobenzene	−91.0	−303.3				
Bromobenzene	−86.3	−300.1			−49.6	−328.3
α,α,α-Trichlorotoluene	−94.6	−310.5			−55.0	−333.0
α,α,α-Trifluorotoluene	−88.0	−307.2			−53.7	−335.8
2-Chloropyridine	−96.2	−313.3	−100.9	−84.3	−51.2	−332.6
2,6-Dimethylpyridine	−94.3	−307.1			−54.5	−335.0

TABLE III

OBSERVED CHEMICAL SHIFTS RELATIVE TO EXTERNAL TMS CORRECTED FOR BULK SUSCEPTIBILITY DIFFERENCES FOR MIXED COMPLEXES OF hfaa $^-$ AND aa$^-$

	$Al(hfaa)(aa)_2$			$Al(hfaa)_2(aa)$			$Al(hfaa)_3$
Solvent	CH_3	CH(aa)	CH(hfaa)	CH_3	CH(aa)	CH(hfaa)	CH
Hexane	−113	−327	−369	−117	−336	−378	−387
CCl_4	−126	−336	−378	−128	−342	−386	−400
$CHCl_3$	−124	−337	−377	−126	−343	−385	−396
CH_2Cl_2	−120	−337	−376	−124	−344	−386	−398
$CHBr_3$	−131	−342	−380	−142	−356	−398	
C_2H_5Br	−123	−340	−378	−125	−349	−390	−402
1,2-$Br_2C_2H_4$	−122	−335	−376	−132	−350	−394	
1,1,2,2-$Cl_4C_2H_2$	−124	−337	−376	−124	−342	−384	
Acetone	−119	−342	−384		−354	−400	−416
Benzene	−83	−298	−358	−75	−290	−356	−346
Toluene	−84	−299	−359	−81	−297	−361	−352
Nitrobenzene	−94	−316	−362	−98	−325	−373	−385
Benzonitrile	−92	−316	−359	−96	−322	−374	−384
Chlorobenzene	−89	−305	−361	−86	−306	−365	−366
Bromobenzene	−86	−303	−357	−84	−303	−360	

Crude data were treated by use of the equation given by Pople, Schneider, and Bernstein.[28] This equation corrects for the bulk susceptibility of the medium. Values for δ_{sph}, the corrected chemical shift, are given in Tables II–IV.

In the case of $Al(aa)_3$, a nonpolar molecule (multipole effects are expected to be small), consideration of δ_E is unnecessary. If only nonaromatic solvents are discussed at first, and complex formation is assumed to be small, the only remaining term in eq 1 is the contribution due to van der Waals forces. Bothner-By's work[24] dealt with molecules that fit these assumptions; his conclusion was that ${}_{\mathrm{X}}^{\mathrm{Y}}\delta_{\mathrm{w}}^{\mathrm{S}}$ can be represented as a product of a term due to the particular solute proton (Y) and one due to the solvent (S). Thus

$$ {}_{\mathrm{X}}^{\mathrm{Y}}\delta_{\mathrm{w}}^{\mathrm{S}} = f(\mathrm{Y})g(\mathrm{S}) \tag{4} $$

$$ {}_{\mathrm{X}}^{\mathrm{Y}}\delta_{\mathrm{w}}^{\mathrm{S}} - {}_{\mathrm{X}}^{\mathrm{Y}}\delta_{\mathrm{w}}^{\mathrm{S'}} = f(\mathrm{Y})[g(\mathrm{S}) - g(\mathrm{S'})] \tag{5} $$

For X = CH_4 eq 5 can be solved for $[g(\mathrm{S}) - g(\mathrm{S'})]$ and the result can be combined with eq 5 for arbitrary X to yield

$$ {}_{\mathrm{X}}^{\mathrm{Y}}\delta_{\mathrm{w}}^{\mathrm{S}} - {}_{\mathrm{X}}^{\mathrm{Y}}\delta_{\mathrm{w}}^{\mathrm{S'}} = \frac{f(\mathrm{Y})}{f(\mathrm{CH_4})}[{}_{\mathrm{CH_4}}\delta_{\mathrm{w}}^{\mathrm{S}} - {}_{\mathrm{CH_4}}\delta_{\mathrm{w}}^{\mathrm{S'}}] \tag{6} $$

The data of Buckingham, *et al.*[23]—hereafter BSS—can be used to obtain $[{}_{\mathrm{CH_4}}\delta_{\mathrm{w}}^{\mathrm{S}} - {}_{\mathrm{CH_4}}\delta_{\mathrm{w}}^{\mathrm{S'}}]$, taking S′ to be hexane; $f(\mathrm{Y})/f(\mathrm{CH_4})$ is established through the use of

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(28) (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 81. (b) Volume diamagnetic susceptibility data were taken from the "Handbook of Chemistry and Physics" except for values not listed there; these were estimated from Pascal's constants (1,1,2,2-tetrachloroethane, 0.827 × 10^{-6}; benzonitrile, 0.658 × 10^{-6}; α,α,α-trifluorotoluene, 0.608 × 10^{-6}; 2-chloropyridine 0.672 × 10^{-6}; and 2,6-dimethylpyridine, 0.642 × 10^{-6}). A value of 0.432 × 10^{-6} for TMS was taken from the data of K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **37**, 1891 (1962).

TABLE IV

OBSERVED CHEMICAL SHIFTS RELATIVE TO EXTERNAL TMS CORRECTED FOR BULK SUSCEPTIBILITY DIFFERENCES FOR VARIOUS COMPLEXES

		In(aa)₃		Co(hfaa)(aa)₂		
Solvent	Al(Braa)₃	CH_3	CH	CH_3	CH(aa)	CH(hfaa)
CCl_4	−153.1	−128.1	−325.3	−134.3 −141.7	−335.8	−377.3
Benzene	−109.0	−85.6	−290.6	−84.0 −92.8	−291.2	−359.9
Nitrobenzene	−112.0	−92.9	−304.6	−100.0 −110.3	−317.8	−362.2

an arbitrary solvent, for example CCl_4,[29] and predicted values of $[{}^{Y}_{X}\delta^{S}_{w} - {}^{Y}_{X}\delta^{S'}_{w}]$ for the complexes of aluminum are obtained for the remaining S. The results of this calculation are compared with the experimental results in Table V. Bothner-By has found that different protons on the same molecule have different values of $f(Y)$; therefore, a similar but independent treatment must be made on the ring proton of Al(aa)₃. These data are also shown in Table V.

TABLE V

EXPERIMENTAL VALUES OF $[{}^{Y}_{X}\delta^{S} - {}^{X}_{Y}\delta^{\text{hexane}}]$ COMPARED TO THE CALCULATED VALUES OF $[{}^{Y}_{X}\delta^{S}_{w} - {}^{Y}_{X}\delta^{\text{hexane}}_{w}]$ FOR Al(aa)₃

	CH₃ proton		CH proton	
Solvents	Exptl	Calcd by (6)	Exptl	Calcd by (6)
CCl_4	−18.2	(−18.2)[a]	−14.8	(−14.8)[b]
$CHCl_3$	−15.4	−15.8	−17.4	−12.8
CH_2Cl_2	−9.4	−12.2	−11.4	−9.9
$CHBr_3$	−34.7	−38.1	−30.4	−31.0
CH_3Br_2	−21.5	−21.4	−23.9	−17.3
Acetone	−4.8	1.6	−13.8	1.3
C_2H_5Br	−12.0	−12.2[c]	−18.3	−9.9[c]
1,2-$Br_2C_2H_4$	−19.6	−23.4[c]	−20.5	−19.0[c]
1,1,2,2-$Cl_4B_2H_4$	−20.3	−25.0[c]	−20.3	−20.3[c]

[a] $f(Y)/f(CH_4) = 1.36$. [b] $f(Y)/f(CH_4) = 1.10$. [c] See text.

It is important at this point to extend this correlation even further. The correction for van der Waal's shift must be applied to the aromatic solvents before the aromatic and complex contributions, δ_a and δ_c, can be determined. BSS have shown that for CH_4 a linear function describes δ_w

$$[{}_{CH_4}\delta^{S} - {}_{CH_4}\delta_{g}] = {}_{CH_4}\delta_{w} = m(\Delta H) + b \qquad (7)$$

where ΔH is the heat of vaporization of the solvent at its boiling point (evaluated from the empirical equation of Hilderbrand and Scott[30]). From the data of BSS, the constants m and b may be determined; with these constants δ_w for solvents other than those used by them, as well as δ_w for aromatic solvents, may be calculated. This treatment has been applied to three other nonaromatic solvents used in this work, and the results are listed at the bottom of Table V.[31]

The contribution of δ_a and δ_c to δ can be calculated for the aromatic solvents by subtracting from the observed shifts the δ_w values, calculated by use of eq 7. The results of these calculations for some of the aromatic solvents studied are shown in Table VI; included in the table are the calculated aromatic and complex contributions for two other tris complexes—Al(hmaa)₃ and Al(Meaa)₃.

TABLE VI

CALCULATED VALUES FOR THE CONTRIBUTION TO THE CHEMICAL SHIFT DUE TO ANISOTROPIC SHIELDING AND COMPLEX FORMATION, $\delta_a + \delta_c$

	Al(aa)₃		Al(hmaa)₃		Al(Meaa)₃	
Solvent	CH_3	CH	$(CH_3)_3$	CH	1-CH_3	3-CH_3
Benzene	25.3	21.6	15.4	11.6	26.5	39.7
Toluene	26.9	23.6				
o-Xylene	20.0	17.1	7.2	3.1	20.2	27.0
Fluorobenzene	21.9	15.7	14.5	9.2	22.9	32.1
Bromobenzene	30.6	23.2				
2-Chloropyridine	22.1	11.1	19.5	12.3	23.8	31.3
Nitrobenzene	33.4	20.5	28.6	18.5	33.2	39.5

The shifts in the mixed complexes, $Al(hfaa)_x(aa)_{3-x}$, can be treated by a similar procedure; however, in this case, the presence of a dipole in the solute molecules makes the term due to δ_E no longer negligible. The dipole establishes a polar solvent cage which in turn polarizes the solute—the reaction field. In such a case δ_E is given by a function that involves the dielectric constant of the solvent,[32] and a calculation is still possible: with two solvents having nearly equal dielectric constants, ϵ, the correction due to δ_w can be applied as already outlined; the remaining shift is then due to the reaction field and should be approximately given by [32,33]

$$\delta_E = k\left(\frac{\epsilon - 1}{2\epsilon + n^2}\right) + k'\left(\frac{\epsilon - 1}{2\epsilon + n^2}\right)^2 \qquad (8)$$

where k and k' are defined below. Owing to the necessity of applying the δ_w correction first, such a procedure will not lead to good values for δ_E. From an inspection of the Al(aa)₃ data in terms of δ_w (Table V), it can be seen that an error of 5 cps can be made through this correction procedure. Depending on the magnitude of the shift due to the δ_E term, this error could obliterate the δ_E contribution.

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(29) Hexane is chosen as S′ because its δ_w contribution is smallest. Hence $[{}^{Y}_{X}\delta^{S}_{w} - {}^{X}_{Y}\delta^{\text{hexane}}_{w}]$ is the closest approximation to the absolute value of ${}^{X}_{Y}\delta^{S}_{w}$ that can be obtained without knowledge of ${}^{X}_{Y}\delta_{g}$. The arbitrary choice of CCl_4 to establish $f(Y)/f(CH_4)$ is intended to test the theory rather than to create the best fit to the data; no attempt is made here to force the data to that best fit.

(30) J. H. Hilderbrand and R. L. Scott, "Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, N. Y., 1950, p 427.

(31) BSS noted that the shifts in halogenated solvents fit eq 7 with a b value that differed from that of nonhalogenated solvents, although both series have the same slope. Accordingly, the value of b from their data for halogenated solvents has been used in the calculation.

(32) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

(33) n in eq 8 is the index of refraction of pure solute. This and α in eq 9 have been estimated from the refractions given by C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 409, using a density of 1.3 g/cc (R. B. Roof, Jr., *Acta Cryst.*, **9**, 781 (1956)). The calculations do not depend critically on these estimations.

If the values of k and k' can be calculated, the order of magnitude of the expected shift due to δ_E can be determined. Buckingham[32] has given the formulas for these parameters as

$$k = (-2 \times 10^{-12}) \frac{\mu \cos \theta}{\alpha} \qquad k' = -10^{-18} \frac{\mu^2}{\alpha} \quad (9)$$

where μ is the dipole moment of the solute, θ is its angle with the X–H bond, and α is the polarizability of the solute. Various authors have used these formulas to calculate approximate values for shifts due to reaction fields.[12,23,32,34] To estimate the values of k and k', dipole moments for $Al(hfaa)_2(aa)$ and $Al(hfaa)(aa)_2$ were calculated: $Fe(aa)_3$ was used as a model for the bond distances and angles,[35] and the bond dipole moments for $C-CH_3$ and $C-CF_3$ listed by Smyth[36] were employed.[37] The calculated dipole moment of 4.9 D. for $Al(hfaa)_2(aa)$ was used in eq 9 to compute a shift of 2 cps (to low field) for the CH proton upon a change of solvent from CCl_4 to CH_2Cl_2. The reaction-field shift calculated above is the largest that would be observed for the aliphatic solvents studied.[38] The low value of the shift is due to the r^3 factor in α which more than compensates for the increased value of μ relative to other molecules previously studied—CH_3CN,[23] *cis*-dichloroethylene,[25] CH_3I,[12] CHI_3.[12]

Discussion

The van der Waals contribution to the chemical shift–solvent effect presented in Table V is in the direction expected: increasing the atomic number of the atoms in the solvent molecule should enhance the downfield shift, as electrons of the solute are attracted by the nuclei of the solvent, and this attraction is larger the greater the charge on the nuclei of the solvent. (It must be kept in mind that the numbers in Table V refer to the van der Waals shift, relative to the shift in hexane.) The only exception to the general agreement between experimental and calculated values worthy of further mention is that of acetone.[39] The ring proton in $Al(aa)_3$ is strongly affected by acetone; the difference between the experimental value for ${}^{CH}\delta_w$ and the theoretical one is 15 cps, and the value of φ (217 cps) is high for aliphatic solvents. The most likely explanation of this phenomenon is that δ_c is not negligible. One model for this complex places the oxygen of the acetone and the ring proton in a hydrogen-bonded configuration; the shift of the ring proton would be toward lower fields, the direction found. The magnitude of the shift is similar to that found by Schaefer and Schneider for their proposed acetone–ring hydrogen bond in *para*-substituted toluenes.[40]

Although the magnitude of the shift agrees with that of Schaefer and Schneider, the position of the bonding in the complex is not established, since the shift results from a time average over all the environments of the proton. In particular, for the metal–complex systems being discussed here, there is another position of bonding that must be considered—the complexing of the acetone molecule directly to the metal center. Whether or not this is a reasonable postulate can be indicated by a crude calculation of the magnitude of the electric field at the proton due to an acetone molecule located in the octahedral face. Such a calculation, using 2.4 D. for the dipole moment of acetone, an aluminum–acetone bond distance of 2.5 A, and the equation $\delta_E = K\mu r^{-3} \cos \theta$,[32] leads to shifts of −6.1 and −0.6 cps for the ring proton and the methyl protons, respectively, if Buckingham's value[32] of the proportionality constant, K, is used (−9.5 and −1.0 cps for the constant of Musher[41]). (The data of Roof[35] were used for ligand bond distances and angles.) The reliability of these calculations is only within an order of magnitude and does not allow a choice of model; however, it is interesting that $Al(hmaa)_3$ shows a smaller shift than does $Al(aa)_3$, as expected for the metal-coordinated model, but not for the ring-proton-coordinated model on the basis of steric arguments. In the following discussion, use is made of the anisotropic nature of aromatic solvents to determine the position of solvation. The arguments to be developed will show octahedral-face coordination, a conclusion with which the acetone data are not in conflict.

The data for the aromatic solvents shown in Tables II–IV can be treated in several ways. The different methods yield similar results, a finding that offers more assurance that the hypothesis of octahedral-face coordination by donor solvents is correct. The most elementary argument can be made by noting that the φ values show a striking trend for $Al(aa)_3$ and $Al(hmaa)_3$: those aromatic solvents that have donor groups (including the "weak" donor atoms, such as the halogens[9]) have φ values larger than the nondonor aromatics for $Al(aa)_3$, but all aromatic solvents have φ values of about 280 cps for $Al(hmaa)_3$. This implies that the aromatic solvents with donor groups are not solvating in the same way with these two solutes.

A second method of approaching the problem of specific solvation follows from consideration of $Al(aa)_3$ as a sphere of radius 6 A. In the absence of specific complex formation, the shift of the CH proton relative to that of the CH_3 protons will be given by the relative areas occupied by each on the surface of the sphere. From the values of the anisotropic shifts for nondonor solvents listed in Table VI, the shape factor can be found to be $CH/CH_3 = 0.85$, a value in accord with a crude calculation of relative areas, weighed to account

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[34] (a) P. Diehl and R. Freeman, *Mol. Phys.*, **4**, 39 (1961); (b) for a critical assessment of this model, see P. Laszlo and J. I. Musher, *J. Chem. Phys.*, **41**, 3906 (1964).

[35] R. B. Roof, Jr., *Acta Cryst.*, **9**, 781 (1956).

[36] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 314.

[37] See ref 5 for the reliability of this procedure.

[38] For reasons to be discussed below, it is felt that acetone is a "special" solvent. Acetone is "special" in another sense—solutions of the aluminum complexes in acetone decompose when allowed to stand.

[39] It may be argued that ethyl bromide deviates as much as acetone from the correlation; this does not influence the argument, as ethyl bromide has a high dipole moment, and the effect shown by acetone may indeed be reflected here. Of the other solvents, those with dipole moments of next higher magnitude, CH_2Cl_2 and CH_2Br_2, have their dipoles oriented such that the forces responsible for the acetone shift are minimized.

[40] T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, **32**, 1218 (1960).

[41] J. I. Musher, *ibid.*, **37**, 34 (1962).

for the number of protons on each group.[42] This shape factor should be independent of the aromatic solvent, but owing to differences in the volume occupied by the aromatic solvents, the absolute values of the anisotropic shifts should vary. Table VII gives the predicted and observed values for the three tris chelates, $Al(aa)_3$, $Al(hmaa)_3$, and $Al(Meaa)_3$; the data for benzene were used to obtain the shape factor, and the ring-proton shifts were predicted from the experimental shifts of the terminal protons. Especially pertinent are the differences between the predicted and observed values. If specific complex formation is not important, these differences should be small. These data reflect the same trend seen in the values of φ; for $Al(aa)_3$ and $Al(Meaa)_3$ there is a difference between the donor and nondonor aromatic solvents of up to 10 cps, but for $Al(hmaa)_3$ all the data seem to fit the shape factor equation (± 3 cps). Examination of molecular models shows an obvious difference: for hmaa as the ligand, but not for the other two, octahedral-face coordination is not possible because the metal atom is shielded by the ligand. It is to be noted that models show only slight hindrance to solvation of the CH proton in $Al(hmaa)_3$; further, the fit of $Al(Meaa)_3$ to this correlation demonstrates that specific complexation of the aromatic donor–methylene proton type is not the cause of the difference between the donor and the nondonor aromatics.

TABLE VII

CALCULATION OF ANISOTROPIC SHIFTS FROM SOLVENT SHAPE FACTOR

	$Al(aa)_3$		$Al(Meaa)_3$		$Al(hmaa)_3$	
Solvent	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
Benzene[a]	(21.6)	21.6	(39.7)	39.7	(11.6)	11.6
Toluene	22.8	23.6				
o-Xylene	17.0	17.1	30.3	27.0	5.4	3.1
m-Xylene	24.7	25.5				
Nitrobenzene	28.4	20.5	49.8	39.5	21.5	18.5
Fluorobenzene	18.6	15.7	34.4	32.1	10.9	9.2
Chlorobenzene	20.0	18.1				
Bromobenzene	26.0	23.2				
2-Chloropyridine	18.8	11.1	35.7	31.3	14.7	12.3

[a] Shape factor calculated from data for benzene.

Yet another method for determining specific complex formation with resulting anisotropic shielding of a proton can be applied to the data presented here. Schneider has verified that the δ_a contribution to the resonance position of a proton signal is independent of the shape of the solute if no specific complexation takes place.[11] Therefore, in the absence of large contributions due to other terms in eq 1, the shift of an "inert" internal reference material (TMS, for example) and the solute should be the same. The δ_w term is the one that must be shown to be small, because for nonpolar compounds δ_E is small. Since $f(Y)/f(CH_4)$, where Y is a proton on one of the complexes, is approximately unity, it is expected that $f(Y)/f(TMS)$ will also be approximately 1. This implies that a change in solvents causes an equal van der Waals shift for all species. A comparison of the observed shifts then gives a measure of the differential anisotropic shielding and specific complexation with solvent change. These differences for the change in solvent, benzene to nitrobenzene, for various complexes studied in this work are, for the methyl and 3-position proton(s), respectively: $Al(aa)_3$, -5, -11; $Al(hmaa)_3$, $+7$, $+2$; $Al(Meaa)_3$, -3, -9; $In(aa)_3$, -7, -14; and $Al(Braa)_3$, -3; TMS, $+2$. It is especially interesting to compare the values for TMS and $Al(hmaa)_3$ with those for the other compounds: the former two shift to high field upon a change of solvent from benzene to nitrobenzene, but all the latter shift in the reverse direction. The shift to high field upon this change in solvent is expected for a system where specific solute–solvent interaction is absent, for the planar $-NO_2$ group adds to the diamagnetic anisotropy of the benzene ring and increases the high-field shift.[23] The other complexes also illustrate a consistent picture. If the cause of the observed shifts in $Al(aa)_3$ is assumed to be specific solvation, the relative magnitudes of the shifts for the remaining complexes are reasonable. The shifts are largest for $In(aa)_3$, as expected for the metal atom with the largest radius. The effect of blocking the approach of a solvent molecule to the octahedral face by the group in the 3 position is shown in the trend $Al(aa)_3 < Al(Meaa)_3 \cong Al(Braa)_3$.

A similar treatment of the mixed complexes is more difficult; in this case, the dipole nature of the solutes can be important if there are large differences between the dielectric constants of the solvents. Such a large difference is found upon examination of the shift of the resonance signal as the solvent is changed from benzene to nitrobenzene, the dielectric constants being 2.28 and 34.8, respectively. This difference will give a δ_E contribution to the shift of the CH proton of the aa ligand in $Al(hfaa)(aa)_2$ of 3 cps.

For benzene, the shift due to δ_a and δ_c can be estimated by using hexane as a reference; this procedure approximately cancels the van der Waals and reaction field shifts, as the heats of vaporization (see eq 7) and the dielectric constants of these two solvents are, respectively, approximately equal. The data in Table III show that the anisotropic shifts of the methyl protons and the methylene proton on the aa ligand are larger than the corresponding shifts of the methylene proton on the hfaa ligand. This is to be expected on the basis of the direction of the dipole in these mixed complexes: benzene, with its high π-electron donor ability will tend to solvate preferentially the positive end of the solute dipole. The same explanation suffices to account for the differences of the anisotropic shifts between $Al(hfaa)(aa)_2$ and $Al(hfaa)_2(aa)$. (Note that both of these molecules have a calculated dipole of the same magnitude.) In the former case, the dipole has its negative end pointing directly at the hfaa proton, but in the latter, it is between the two hfaa protons, leading to the greater anisotropic shift observed for the hfaa proton in the latter compound. Likewise, the

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(42) A referee has commented that the relative magnitude of the shape factors, $Al(Meaa)_3 > Al(aa)_3 > Al(hmaa)_3$, suggests deviations from spherical shape, causing greater shielding of the protruding protons.

direction of the positive end causes a shift of the aa protons, $Al(hfaa)_2(aa) > Al(hfaa)(aa)_2$.

An analysis of nitrobenzene is not so easily accomplished; the problem is the choice of reference. CH_2Cl_2 would seem to be the best choice, for from BSS and eq 7

$$({}_{CH_4}\delta_w^{\text{hexane}} - {}_{CH_4}\delta_w^{CH_2Cl_2}) + ({}_{CH_4}\delta_w^{\text{hexane}} - {}_{CH_4}\delta_w^{\varphi NO_2}) = ({}_{CH_4}\delta_w^{CH_2Cl_2} - {}_{CH_4}\delta_w^{\varphi NO_2})$$

or $-9 + 10 \cong 0$; further, its dielectric constant, although not equal to that of nitrobenzene, is sufficiently similar to cause only a slight deviation in the value of the function necessary (eq 8). With CH_2Cl_2 as the reference, the differences between the resonance line in CH_2Cl_2 and nitrobenzene show (a) that there is little discrimination between any of the four complexes, $Al(hfaa)_x(aa)_{3-x}$, $x = 0\text{–}3$, as might be expected since the dipole of the solute does not point directly into the octahedral face of the molecule, and (b) that the anisotropic shift is greater for benzene than for nitrobenzene with the exception of the ring proton on the hfaa ligand of $Al(hfaa)(aa)_2$ and the methyl protons on $Al(aa)_3$. The explanations of these two exceptions probably are, for the former, the direction of the dipole in this solute, as has already been discussed, and, for the latter, the lack of fluorine–π-electron density repulsions upon donor coordination of nitrobenzene in $Al(aa)_3$.

All of these data point toward solvation of the metal complexes in the octahedral faces by donor groups. Using distribution constants between water and various organic solvents, Hopkins and Douglas[16] came to the same conclusion. They found differences in the enthalpy of the reaction $(\text{complex})_{\text{org}} \rightarrow (\text{complex})_{H_2O}$ between acetylacetonate complexes of various metal ions. On the basis of the electron configuration of the metal, the directional properties of the occupied orbitals, and the variation in distribution constant between the pairs—$Cr(Meaa)_3$ and $Cr(aa)_3$; Co(propionylacetonate)$_3$ and $Co(aa)_3$—the postulate of octahedral-face coordination of water molecules was made. Further, Mason and Norman[43] have shown that the ion pair formed between $(+)Co(en)_3^{3+}$ and phosphate ion has the latter located along the C_3 axis of the Co(III) octahedron, although they argued that this configuration appears to be determined by hydrogen bonds and not by directional characteristics of the dipole–metal interaction.

To distinguish between solvation determined by hydrogen bonding to the acetylacetone complexes and that determined by dipolar interactions is not an easy problem. Fackler and co-workers[17] have argued on the basis of infrared spectra of mixtures of acetylacetonate derivatives of metal ions and $CHCl_3$ that hydrogen bonding to the chelate ring or the carbonyl oxygens takes place. There is no evidence for hydrogen bonding in the work reported here, although the experiments described heretofore were not designed to investigate such an interaction. With $CHCl_3$, or any other hydrogen-bond donor as solvent, any effects of hydrogen bonding will be small perturbations on the protons of the solute, whereas the solvent is present in such excess that the average value of its resonance position will be only slightly shifted. In view of Fackler's claim, one experiment performed under suitable conditions to discover any hydrogen-bonding interaction has been undertaken. It has been postulated that a hydrogen bond is formed when $CHCl_3$ is dissolved in ether;[11] a shift of approximately 30 cps to lower fields occurs, presumably because of the change in electric field at the chloroform proton. It may be asked whether any shift in the position of the chloroform proton takes place when $CHCl_3$ is added to a solution of $Al(aa)_3$, dissolved in some inert (nonhydrogen-bonding) solvent. When a solution of $CHCl_3$ and $Al(aa)_3$, each at 0.12 *M* in CCl_4, is examined, the positions of the lines due to the protons on both the solutes shift from their positions in the absence of the other solute. Thus, $CHCl_3$ in CCl_4 has a resonance at -464.5 cps (relative to external TMS), $Al(aa)_3$ at -144.5 (CH_3) and -349.1 (CH) cps; in the mixture, the resonances occur at -468, -143.5, and -348.4 cps, respectively. This shift of the $CHCl_3$ proton upon addition of $Al(aa)_3$ to a solution of $CHCl_3$ in CCl_4 might be ascribed to hydrogen bonding with the complex, but the magnitude of the shift is very small compared to the value expected from large hydrogen-bond interactions.[44] The concentrations used are low, favoring dissociation of any complex that might form; but higher concentration would necessitate correction for a bulk susceptibility change in the solvent and other solute–solute interactions besides $CHCl_3$–$Al(aa)_3$ hydrogen-bonding interaction (for instance, the self-association of $CHCl_3$, the difference in the various δ_w terms). There is one further argument that could be put forth concerning the low value of the shift. If hydrogen bonding did take place, the proton of the chloroform molecule would presumably be situated over a chelate ring, either bound to the oxygen or to the ring itself; further, if it is argued that the chelate ring is aromatic in the sense that a ring current exists, this will tend to shift the resonance position back to high fields. The cancellation of the hydrogen-bonded shift and the anisotropic shift could account for the low value of the observed shift. But, from the data presented here, there seems to be little evidence for large hydrogen-bonding effects.

Concerning aromatic character and ring currents, there are two pertinent points to be made. Hester[4] has investigated the nmr spectrum of $Si(aa)_3^+$ in $CHCl_3$ solution and found that the resonance position of the ring proton was shifted to lower fields than is usually the case for acetylacetonate complexes. Before his conclusion about the presence of aromatic character and ring currents in the chelate rings can be accepted, it would be interesting to ask what effect the anion has on the system. Accordingly, a measurement of the position of the $Al(aa)_3$ resonance in $CHCl_3$ solution with added tetra-*n*-butylammonium iodide was made. This medium causes a shift from the resonance position in pure $CHCl_3$ of -6 and -8 cps for the methyl and ring

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(43) S. F. Mason and B. J. Norman, *Proc. Chem. Soc.*, 339 (1964).

(44) See Chapter 15 in ref 28.

proton, respectively, when the mole ratio of salt to complex is 3.0 (at approximately 0.2 *M* complex concentration). Thus even when the complex is uncharged, the presence of added salt appears to cause a downfield shift; whether the large downfield shift observed for $Si(aa)_3^+$ (−6 and −54 cps relative to the positions found in $Co(aa)_3$, for instance) might be explained by an anionic solvation mechanism could conceivably be tested by choosing a bulky anion with its charge either distributed or shielded.[45]

Secondly, the data on the two complexes, $Al(hfaa)(aa)_2$ and $Co(hfaa)(aa)_2$, are worthy of further comment. Collman and co-workers have reported that unsymmetrically substituted acetylacetonate complexes of Co(III) and Rh(III), such as $Rh(Claa)(aa)_2$, show three resonance signals in the methyl region of the nmr spectrum.[3] Complexes of this symmetry have three nonequivalent methyl groups and thus the results are expected—symmetry alone demands the nonequivalence, whether caused by a *trans* effect, by aromatic character of the chelate ring,[3] or by another mechanism. Similarly, the spectra of the mixed complexes of Al and Co(III) with $hfaa^-$ and aa^- should have two resonances in the methyl region; this occurs in the Co(III) complex (Table IV), but the aluminum complex shows only a single resonance in the methyl region (Table III). There are two possible causes for this behavior: the intramolecular exchange of the ligands could be rapid or the chemical shift of the two environments may not be sufficient to lead to an observable splitting of the two peaks. Fay and Piper[46] have shown that the intramolecular *cis* to *trans* isomerization of $Al(tfaa)_3$ is slow (with respect to nmr observation) at room temperature. But intramolecular exchange[47] of ligand positions is the cause of the failure to observe a splitting in $Al(hfaa)(aa)_2$ at 40°, as such a splitting does occur when the temperature of a solution of this complex in CH_2Cl_2 is lowered to −27°. Since the coalescence temperature is about 7°, a rate constant for the intramolecular exchange can be estimated from the splitting of 2.8 cps at −27° as the value for the resonance positions in the absence of exchange.[46] This lower-limit value of 1 sec^{-1} is about 1000 times larger than that obtained by extrapolation of the rate constant of $Al(tfaa)_3$[46] to 7°.

The observation of splitting of the methyl resonance signals in both the Al and Co(III) complexes is not proof of aromatic character and ring currents. Although there is no doubt that electrons from the metal are delocalized into the acetylacetonate ring,[48] the question of the magnitude of ring currents is not answered. Especially pertinent are the calculations of Hall, Hardisson, and Jackman, who found that a variation in the electronegativity of a substituent atom in nitrogen-substituted rings caused a decrease in the ring current.[49] In a ring composed of as many heteroatoms as the acetylacetonate ring, it is to be expected that ring currents would be small; furthermore, variation in metal atom should have a drastic effect on the magnitude of such anisotropic susceptibilities. There is at present no indication that variation in metal atom causes any striking changes in chemical shifts of protons in acetylacetonate complexes (except the experiment with $Si(aa)_3^+$ discussed above).

Acknowledgment.—This research was supported by the ARL In-House Independent Laboratory Research Funds. We are grateful to Mrs. Peggy Wifall for technical assistance.

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(45) See, for instance, J. F. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, **87**, 2529 (1965).

(46) R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).

(47) That the exchange must be intramolecular can be demonstrated by observing that reactions of the type $Al(hfaa)_2(aa) + Al(aa)_3 = 2Al(hfaa)(aa)_2$ are slow[6] and that a solution of $Al(hfaa)(aa)_2$ and either H(aa) or H(hfaa) exhibits independent resonance signals—the substitution of complexed ligand with free ligand is not rapid compared to the rate of nuclear relaxation.

(48) (a) A. Forman, J. N. Murrell, and L. E. Orgel, *J. Chem. Phys.*, **31**, 1129 (1959); (b) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

(49) G. G. Hall, A. Hardisson, and L. M. Jackman, *Discussions Faraday Soc.*, **34**, 15 (1962); *Tetrahedron*, **19**, Supplement 2, 101 (1963).