do not reproduce the observed trends, other than $f^{\alpha}_{rr} >$ f^{β}_{rr} for octahedral complexes.

Adjustment of the repulsive exponent was necessary to obtain agreement with experiment, so the n values determined from known force constants of SnX_4 molecules were employed in the calculation of $SnX_6{}^{2-}$ force constants. This procedure resulted in fairly good agreement between observed and calculated force constants for $SnX_6{}^{2-}$ (Table XII). Similarly, the ratio of calculated force constants for $SnX_6{}^{2-}$ to SnX_4 averages 0.47, which compares favorably with the observed ratio of 0.55 (averaged for X = Cl, Br, and I). In fact, this ratio of force constants is not very sensitive to the repulsive exponent, since a value of 12 for n leads to a calculated

average force constant ratio of 0.44. We conclude that an ionic model effectively reproduces the reduction in stretching force constant upon an increase in coordination number.

Direct Characterization of the Mixed Complexes of Gallium(III) with N,N-Dimethylformamide and 2,4-Pentanedione. Proton Magnetic Resonance Study of First Coordination Sphere Stiochiometry and Kinetics of Ligand Exchange[1a]

BY W. G. MOVIUS AND N. A. MATWIYOFF[1b]

At temperatures below 40° the proton nmr signals of N,N-dimethylformamide (DMF) in the first coordination sphere of Ga(III) can be distinguished. From relative intensities of these signals, a primary solvation number of 6 can be calculated for Ga(III). From the temperature dependence of the proton relaxation rates, the solvent (DMF) exchange parameters k_1 (sec^{-1} at 25°), $\Delta H^{\ddagger}$ (kcal/mol), and $\Delta S^{\ddagger}$ (eu) were calculated to be 1.7, 14.6, and -8.3, respectively. Proton nmr spectra of solutions of $Ga(DMF)_6{}^{3+}$ and tris(2,4-pentanedionato)gallium(III) [$Ga(acac)_3$] were used to characterize the complexes $Ga(acac)(DMF)_4{}^{2+}$ and $Ga(acac)_2(DMF)_2{}^{+}$. Thermodynamic parameters were obtained from the temperature dependence of the equilibria among these species. Gallium-71 nmr spectra of $Ga(DMF)_6{}^{3+}$ are reported. Data from this study are compared with those obtained for the analogous Al(III) and Be(II) complexes.

Introduction

Recently it has been shown that nuclear magnetic resonance (nmr) techniques can provide detailed information about the structure and lability of the coordination compounds of diamagnetic cations having d^0 and d^{10} electronic configurations.[2-15] The tech-

niques are of special interest because the properties of the cations preclude a direct study of their complexes with most of the conventional experimental techniques. Simple solvent complexes that have been characterized *directly* using nmr methods include $Al(OH_2)_6{}^{3+}$,[2a,4,11] $Ga(OH_2)_6{}^{3+}$,[2a,8,9,11] $Be(OH_2)_4{}^{2+}$,[2a,4] $Mg(OH_2)_6{}^{2+}$,[13,14] $Mg(CH_3OH)_6{}^{2+}$,[12,14] $Mg(CH_3OH)_n(H_2O)_{6-n}{}^{2+}$,[3] $Al(DMSO)_6{}^{3+}$,[6] $Al(DMF)_6{}^{3+}$,[7] and $Be(DMF)_4{}^{2+}$.[10] (DMSO represents dimethyl sulfoxide and DMF represents N,N-dimethylformamide.)

We are particularly interested in kinetic and thermodynamic ligand–ligand interactions in mixed complexes

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(11) D. Fiat and R. E. Connick, *ibid.*, **90**, 608 (1968).

(12) S. Nakamura and S. Meiboom, *ibid.*, **89**, 1765 (1967).

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(15) W. G. Movius and N. A. Matwiyoff, *ibid.*, **90**, 5452 (1968).

of these cations and have found that the mixed complexes of metal ions with DMF and the 2,4-pentanedionato ion (acac⁻) can be studied conveniently using proton nmr spectroscopy. In a recent study[10], it was shown that although ligand–ligand interactions are small or compensating as reflected in the thermodynamic parameters for the formation of Be(acac)-(DMF)₂⁺ from Be(DMF₄)²⁺ and Be(acac)₂ in DMF, such interactions must have a pronounced effect on the kinetic parameters for DMF chemical exchange from Be(DMF)₄²⁺ and Be(acac)(DMF)₂⁺. In contrast to this behavior, we have found that ligand–ligand interactions have a significant effect on both the kinetic and the thermodynamic parameters for the corresponding mixed complexes of Al(III), $Al(acac)_n(DMF)_{6-2n}^{(3-n)+}$.[15] In an extension of those studies and as part of a general investigation of Ga(III) complexes in nonaqueous solvents, we wish to report here the direct characterization of the complexes Ga(DMF)₆³⁺, Ga(acac)-(DMF)₄²⁺, and Ga(acac)₂(DMF)₂⁺.

Experimental Section

Reagents.—Eastman White Label N,N-dimethylformamide was purified in the manner described previously.[16] 2,4-Pentanedione was obtained from Matheson Coleman and Bell and distilled before use. Gallium perchlorate hydrate, 99.99%, was obtained from Alfa Inorganics.

Preparation of Complexes.—Tris(2,4-pentanedionato)gallium-(III), Ga(acac)₃, was prepared by the method of Morgan and Drew[17] and was recrystallized from benzene–petroleum ether (bp 30–60°); 198–200° (lit.[17] mp 194–195°).

The complex Ga(ClO₄)₃·6DMF, which has not been previously prepared, was made from the hydrated salt by the general method outlined by Drago, *et al.*[18] *Anal.* Calcd for Ga(ClO₄)₃· 6DMF: Ga, 8.65. Found: Ga, 8.57. No O–H vibrations could be detected in the ir spectra of concentrated Nujol mulls of the complex.

Measurements.—Proton nmr spectra were obtained at 60 MHz using the Varian A-60A spectrometer. The spectrometer was equipped with a variable-temperature probe and the Varian variable-temperature control system, V-6057. The systems were calibrated and the measurements were taken in the manner described previously.[6,16]

The ⁷¹Ga nmr spectra were obtained at 12 MHz using a Varian HR-40 spectrometer equipped with a 12-MHz probe and radiofrequency unit. The magnetic field was calibrated with an audio oscillator monitored by a frequency counter. Sample tubes were of 5-mm diameter. Spectra were recorded in the absorption mode under high-resolution conditions. Each of the line widths and chemical shifts reported is the average obtained from at least four spectra.

Results

Characterization of Ga(DMF)₆³⁺.—At temperatures below 40° the proton nmr spectra of DMF solutions of Ga(ClO₄)₃·6DMF are analogous to those obtained for solutions of Be(DMF)₄²⁺ [10] and Al(DMF)₆³⁺ [7,15] and consist of six signals which are tabulated in Table I and assigned in Figure 1. Three of the signals are due to

DMF in the first coordination sphere of Ga(III) (a', b', c') and three to DMF in the bulk of the solvent (a, b, c). The signals of DMF in each environment consist of a low-field formyl peak (c or c') and two high-field N-methyl peaks (a, b or a', b'). The higher field N-methyl signal in each environment is assigned to the methyl group *cis* to the oxygen atom.[16,19,20] The retention of the nonequivalence of the N-methyl groups when DMF is coordinated to Ga(III) indicates that coordination of DMF occurs *via* the oxygen atom.[16,20]

From the relative signal areas (obtained by manual integration) and the known solution composition, the number of DMF molecules coordinated in the primary solvation sphere of Ga(III) can be calculated. However, unlike the case for DMF solutions of Be(II) and Al(III), a precise primary solvation number for Ga(III) was obtained only in the narrow temperature range 0–20°. Within that range, the calculated solvation number, 5.9 ± 0.1, is independent of the temperature and the solution composition (0.05 m ≤ [Ga(III)] ≤ 0.2 m). Exchange-broadening effects above 20° and viscosity-broadening effects below 0° "smeared" the coordinated DMF signals over a large area and accurate relative areas could not be obtained because of the resulting low signal to noise ratios.[21] As a consequence, the calculated solvation number at those temperatures is not precise, 5.5 ± 0.6, but within the limits of precision does not exhibit any regular trend with temperature or the solution composition.

The temperature dependence of the line widths of the b' and c' protons of the complex Ga(DMF)₆³⁺ is summarized in Figure 2, in which log $\Delta\nu$ is plotted *vs.* $10^3/T$ for a representative set of solutions. Since the chemical shifts are independent of Ga(III) concentration and of temperature over the range +30 to −30°, the line width, $\Delta\nu$, for protons of the complex should conform to the equation[22,23]

$$\pi\Delta\nu = \frac{1}{T_2^0} + \frac{1}{\tau} = \pi\Delta\nu^0 + k_1 \qquad (1)$$

where τ represents the lifetime of DMF in the primary coordination sphere of Ga(III), k_1 represents the pseudo-first-order rate constant for the exchange of DMF between the free solvent and the complex, and $1/T_2^0$ and $\Delta\nu^0$ represent, respectively, the transverse relaxation rate and the line width of a proton of the complex in the absence of exchange. The temperature dependence of $1/\tau$ and $1/T_2^0$ can be represented by the equations

$$\frac{1}{\tau} = k_1 = \frac{kT}{h}\exp[(-\Delta H^{\ddagger}/RT) + (\Delta S^{\ddagger}/R)] \qquad (2)$$

$$\frac{1}{T_2^0} \propto \exp(-E_a/RT) \qquad (3)$$

(16) N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966).

(17) G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **119**, 1058 (1921).

(18) R. S. Drago, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963).

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

(20) B. B. Wayland, R. S. Drago, and H. F. Henneike, *J. Am. Chem. Soc.*, **88**, 2455 (1966).

(21) Despite the low intensity of the coordinated DMF signals, precise line widths were obtained without difficulty in this temperature range.

(22) L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959).

(23) H. M. McConnell, *ibid.*, **28**, 430 (1958).

TABLE I

PROTON CHEMICAL SHIFTS OF Ga(III) COMPLEXES IN DMF AT 60 MHz AND 30°[a]

Solute in DMF	DMF protons						acac protons					
	a	b	c	a'	b'	c'	1	1'	1''	2	2'	2''
Ga(ClO₄)₃ (0.2 m)	...	−11	−315	−20	−31	−340	...	...	...	...	...	...
Ga(acac)₃ (0.2 m)	...	−11	−315	...	...	...	+49	...	...		...	...
Ga(ClO₄)₃ + Ga(acac)₃	...	−11	−315	−20	−31	−340	+49	+43	+39	−169	−178	−184

[a] Shifts are in hertz downfield relative to signal a; assignments are based on the proton sites defined in Figure 1.

where $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ represent the entropy and enthalpy of activation for the solvent exchange reaction, and E_a can be viewed as an apparent Arrhenius activation energy associated with the transverse relaxation rate of a proton in $Ga(DMF)_6{}^{3+}$.[24]

The data in Figure 2 for each proton and concentration can be fit with two straight lines: the ones at lower temperatures, because of their small positive slopes, are associated with the transverse relaxation of protons in the first coordination sphere of Ga(III);[25] the one at higher temperatures, which *independently* fits the data for *both* protons and *all* solution compositions studied, is associated with line broadening due to exchange of DMF. Chemical-exchange parameters calculated from the data in Figure 2 are k_1(at 25°) = 1.7 sec⁻¹, $\Delta H^{\ddagger}$ = 14.6 ± 2 kcal/mol, and $\Delta S^{\ddagger}$(at 25°) = −8.3 ± 2 eu.

Characterization of Ga(acac)(DMF)₄²⁺ and Ga(acac)₂(DMF)₂⁺.—In the proton nmr spectra of solutions containing Ga(ClO₄)₃·6DMF and Ga(acac)₃, signals due to DMF in the first coordination sphere of Ga(III), to DMF in the bulk of the solvent, and to the acac⁻ ligand are distinguished (see Table I and Figures 1 and 3). Those upfield from the DMF methyl signals are assigned to methyl groups of acac⁻ (1, 1', 1''), those downfield are assigned to the vinyl protons of acac⁻ (2, 2', 2''). Employing considerations discussed at length previously for the analogous Be(II) and Al(III) systems,[10, 15] the following assignments are readily made: 1 and 2 to acac in the complex Ga(acac)₃, 1' and 2' to acac⁻ in both the *cis* and *trans* complexes of Ga(acac)₂(DMF)₂⁺, 1'' and 2'' to acac⁻ in the complex Ga(acac)(DMF)₄²⁺.

(24) N. Bloembergen, "Nuclear Magnetic Relaxation," W. A. Benjamin, Inc., New York, N. Y., 1961; C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(25) From Figure 2 it is evident that the apparent E_a values associated with the relaxation of the c' and b' protons are different and it is further evident that the relaxation rates of the b' protons are dependent upon the solution composition whereas those of the c' protons are not. The larger apparent relaxation rates of the c' compared to the b' protons, which were also noted for the complexes of Al(III) and Be(II),[7,10,15] are associated with the coupling of the formyl proton (c') with the CH₃ group *trans* to it (a'). We can offer no explanation for the composition dependence of the relaxation rates of the b' protons. It should be noted that for the Be(II) and Al(III) complexes, no composition dependence of the relaxation rates of any coordinated proton resonance was detected."[7,10,15] However, as discussed in the text, the Ga(III)–DMF solutions are unusual in that they exhibit a pronounced dependence of viscosity upon the solute ratio, Ga(acac)₃ : Ga(DMF)₆³⁺. In this context it may be significant that the DMF complexes of all three cations above are quite hindered sterically and that, in the preferred conformation of DMF's within the complexes, the c' protons are oriented toward the cation and are "insulated" from interactions with the "bulk" solvent, whereas the b' protons are oriented outward from the metal ion and toward the "bulk" solvent.
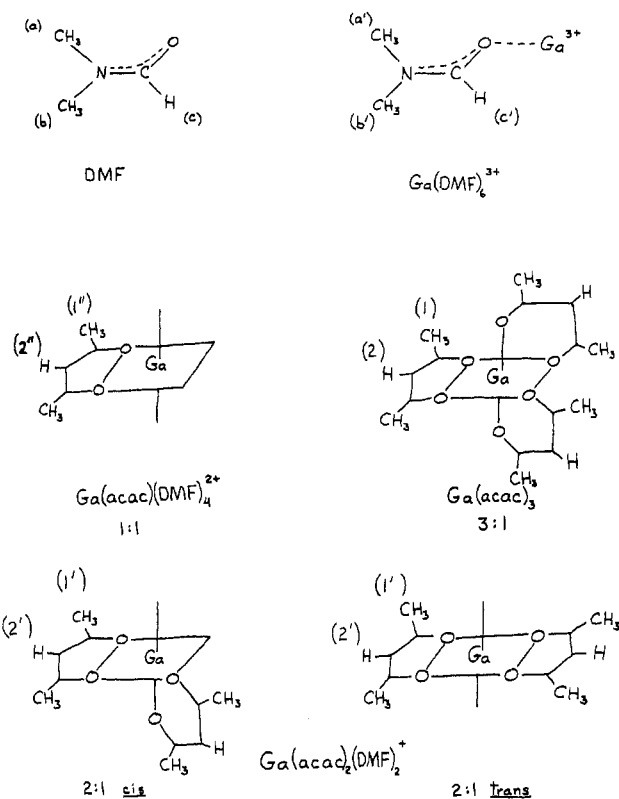

Figure 1.—DMF and acac protons corresponding to the assignments in Table I and Figure 3.

From known solution compositions, relative signal areas, and their temperature dependence over the temperature range 20–100°, thermodynamic parameters for reactions 4 and 5 were calculated and are given below. A comparison between the relative signal areas observed and those calculated from K_1 and K_2 at 80° is provided in Table II for a representative solution containing Ga(acac)₃ and Ga(DMF)₆³⁺. It should be noted that the equilibrium constants given above are merely the ratios of the first and second or second and third equilibrium quotients for the formation of $Ga(acac)_n(DMF)_{6-2n}{}^{(3-n)+}$ from $Ga(DMF)_6{}^{3+}$ and acac⁻.

For

$$Ga(DMF)_6{}^{3+} + Ga(acac)_2(DMF)_2{}^+ \rightleftarrows 2Ga(acac)(DMF)_4{}^{2+} \quad (4)$$

$K_1 = 5 \pm 1$ (25°), $\Delta H_1 = 1.0 \pm 0.5$ kcal/mol, and $\Delta S_1 = 7 \pm 2$ eu. For
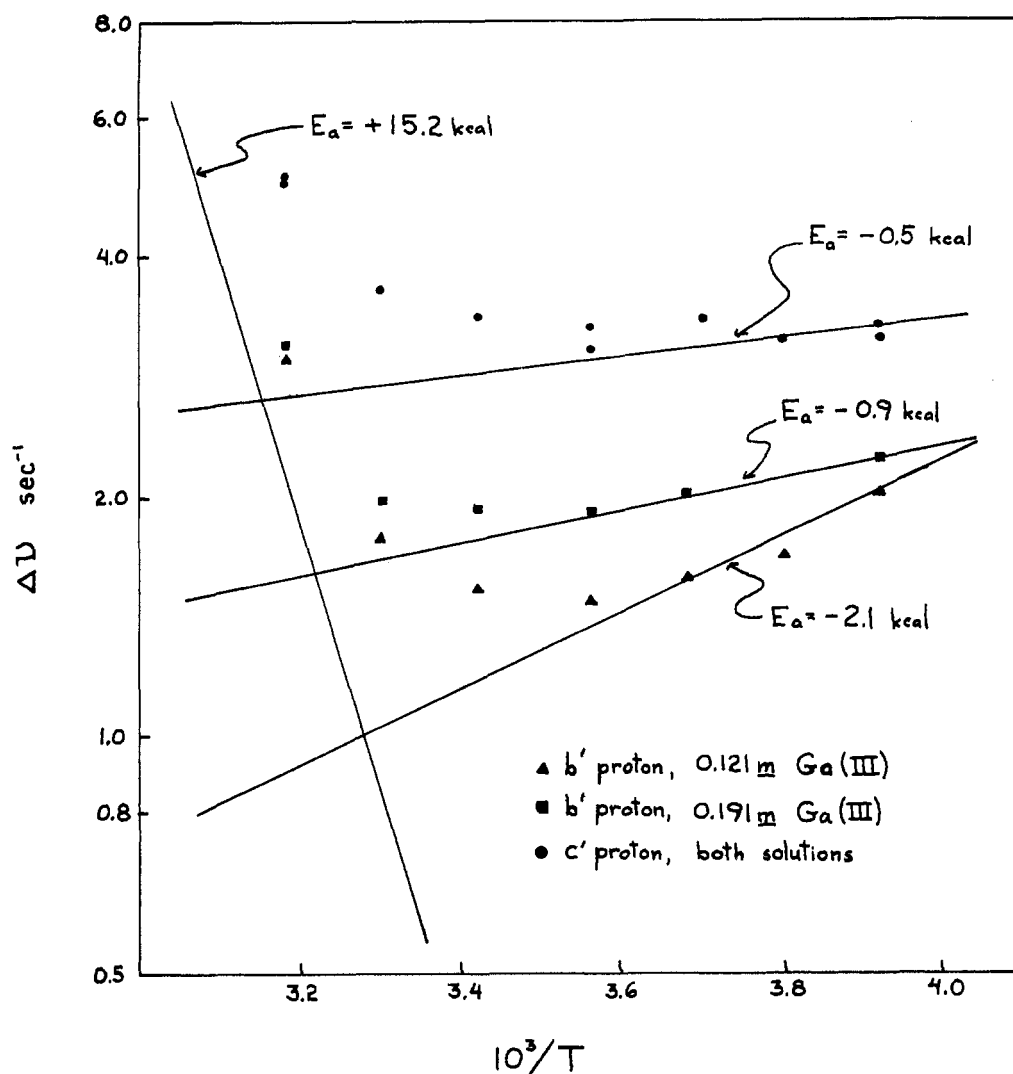
Figure 2.—Arrhenius plot of the line widths of the proton nmr signals of DMF in $Ga(DMF)_6{}^{3+}$.

$$Ga(acac)_3 + Ga(acac)(DMF)_4{}^{2+} \rightleftarrows 2Ga(acac)_2(DMF)_2{}^+ \quad (5)$$

$K_2 = 74 \pm 7$ (25°), $\Delta H_2 = 0.3 \pm 0.5$ kcal/mol, and $\Delta S_2 = 9 \pm 1$ eu.

Separate resonances for the *cis* and *trans* isomers of $Ga(acac)_2(DMF)_2{}^+$ cannot be distinguished in the acac regions of the pmr spectra above −20°. However, below −20° the methyl signal due to $acac^-$ in this complex (1′) broadens and splits into two peaks of nearly equal intensity. However, because viscosity broadening is very pronounced in this temperature range, accurate signal widths and relative areas could not be obtained. Consequently, we cannot assign these low-temperature components unequivocally to separate signals for *cis* and *trans* isomers of $Ga(acac)_2$-$(DMF)_2{}^+$ or to the two signals expected for the stereo-chemically distinct acac methyl groups of the *cis* isomer alone.[26] However, it is likely that the former assign-

ment is the correct one. In the analogous Al(III) system, it was found[15] that the *cis* and *trans* isomers of $Al(acac)_2(DMF)_2{}^+$ are formed in nearly equal amounts and that only one acac methyl signal could be distinguished for the *cis* isomer. As in the Al(III) system, the vinyl proton resonance (2′) is a singlet at all temperatures and has an area which is one-third that for the 1′ resonance.

Also in complete analogy to the Al(III) system, the only coordinated DMF signals discernible at high temperatures can be assigned to $Ga(DMF)_6{}^{3+}$. However, below 0°, the N-methyl resonances of DMF coordinated in $Ga(acac)(DMF)_4{}^{2+}$, a'' and b'', can be distinguished within 2 Hz of signals a' and b'.

Although viscosity broadening precluded the determination of reliable kinetic parameters, accurate areas of the a'' and b'' signals relative to those for $Ga(DMF)_6{}^{3+}$ were obtained in the ratio expected on the basis of the thermodynamic parameters obtained for reactions 4 and 5. It may be noted that DMF solutions of $Ga(ClO_4)_3$ and $Ga(acac)_3$ exhibit more viscosity broadening of the pmr signals than DMF solutions containing comparable concentrations of the cor-

(26) It should be noted that the thermodynamic parameters for reactions 4 and 5 were calculated by assuming an equal distribution of $Ga(acac)_2(DMF)_2{}^+$ into *cis* and *trans* isomers. No curvature was detected in the linear plots log K_1 (K_2) vs. $1/T$. Such an observation is consistent either with the formation of *cis*-$Ga(acac)_2(DMF)_2{}^+$ alone or with a negligible enthalpy change for *cis–trans* isomerization. For the $Al(acac)_2(DMF)_2{}^+$ complex, the latter was found to be true.[15]
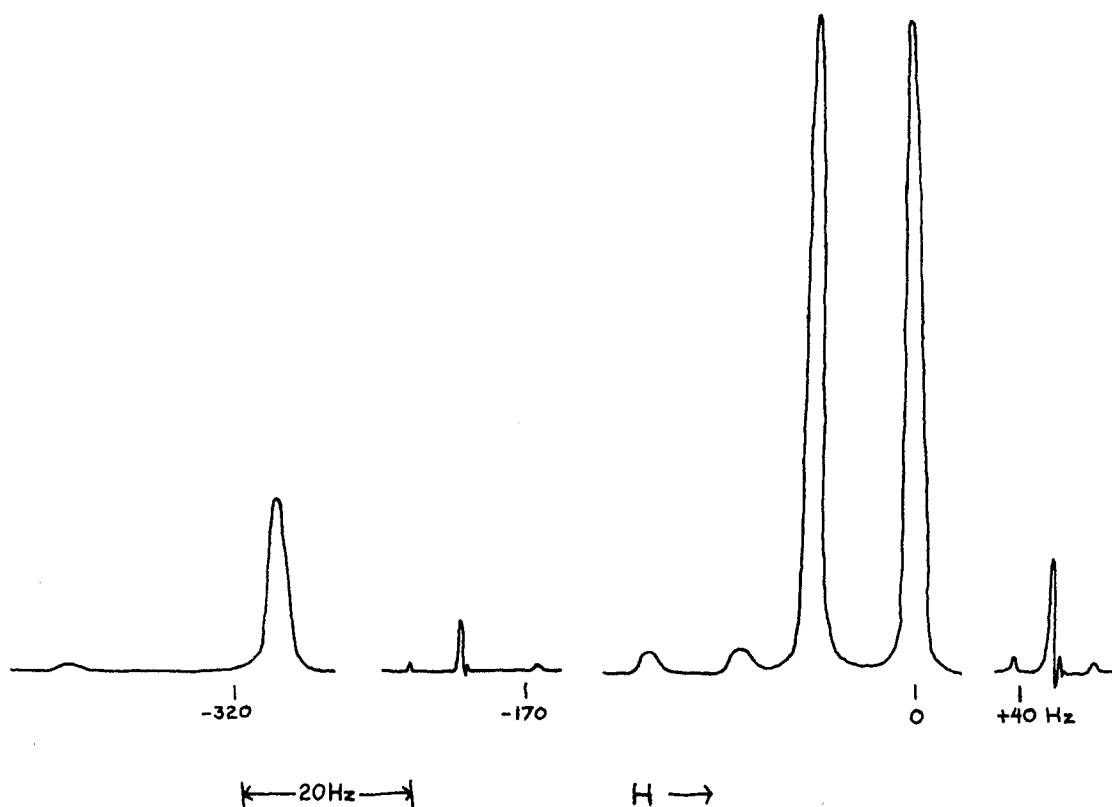
Figure 3.—The 60-MHz pmr spectrum of Ga(III)–acac–DMF complexes in DMF at 37°.

TABLE II

COMPARISON OF CALCULATED AND EXPERIMENTAL SIGNAL
AREAS FOR Ga(III)–acac COMPLEXES IN DMF[a]

Signal[b]	Exptl area	Calcd area
1	0.27 ± 0.01	0.29 ± 0.02
1'	0.71 ± 0.01	0.68 ± 0.03
1''	0.027 ± 0.005	0.03 ± 0.01

[a] At 80°, $K_1 = 7.4 \pm 3$, $K_2 = 60 \pm 10$, $[\text{Ga(DMF)}_6(\text{ClO}_4)_3] = 0.074\ m$, and $[\text{Ga(acac)}_3] = 0.180\ m$. [b] For assignments see Figure 1.

responding Be(II) and Al(III) compounds. Indeed, unlike the Be(II) and Al(III) systems, DMF solutions of $\text{Ga(ClO}_4)_3$ containing a moderate concentration ($\sim 0.2\ m$) of Ga(acac)_3 become so viscous that they do not flow freely below $-20°$. Because of this pronounced viscosity broadening, the DMF resonances of $\text{Ga(acac)}_2(\text{DMF})_2^+$ could not be detected at low temperatures (the pmr signals of the corresponding Al(III) complex are distinguished only at temperatures $\leq -15°$). The formyl proton resonances of Ga(III) complexes containing acac⁻ were not observed and, as with the corresponding Al(III) complexes, are probably due to the low signal to noise ratios for these broad, low-intensity resonances.

Gallium-71 Nmr Spectra.—There are two naturally occurring magnetically active gallium nuclei, ^{69}Ga (natural abundance, 60.1%) and ^{71}Ga (39.9%), both having nuclear spin $^3/_2$. Despite its lower natural abundance, the larger nuclear magnetic and smaller

quadrupole moments of ^{71}Ga render its nuclear resonance more intense than that of ^{69}Ga. Accordingly, in our high-resolution studies, we have found it convenient to obtain the nmr spectra of the gallium compounds at the ^{71}Ga resonance frequency.

To our knowledge, there is only one previous report of the ^{71}Ga resonance of gallium compounds in solution.[27] In Table III, some of those data are compared to the results obtained in this work. No signal from Ga(acac)_3 in DMF or benzene solutions could be observed. Presumably, the large electric field gradient at the Ga nucleus in this D_{3d} complex broadens the ^{71}Ga resonance beyond the limits of detection for the high-resolution system we employed. The aluminum-27 nmr line width for the complex Al(acac)_3 has been found to be over twice that for $\text{Al(OH}_2)_6^{3+}$.[7]

TABLE III

GALLIUM-71 CHEMICAL SHIFTS OF SELECTED
Ga(III) COMPLEXES[a]

	This work		Ref 27	
	σ	Δν	σ	Δν
Ga(DMF)$_6^{3+}$ in DMF	264	120	...	...
Ga(H$_2$O)$_6^{3+}$(aq)	239	200	257	~300
GaBr$_4^-$(aq)	175	80	188	~100
GaCl$_4^-$(aq)	0	90	0	~100

[a] σ is the chemical shift (± 10 ppm) upfield with respect to the external standard GaCl$_4^-$(aq); Δν is the full width of the line at half-maximum intensity (± 5 Hz).

(27) J. W. Akitt, N. N. Greenwood, and A. Storr, *J. Chem. Soc.*, 4410 (1965).

Discussion

The pmr data presented here demonstrate that the complex, $Ga(DMF)_6^{3+}$, is a kinetically well-defined species in DMF. In Table IV the kinetic parameters[7,10,11,15,28-30] for solvent exchange from the aquo and DMF complexes of Ga(III) are compared to those for the complexes of Be(II) and Al(III). It is interesting and somewhat surprising, that the trend of complex ion labilities is $Be(DMF)_4^{2+} \gg Ga(DMF)_6^{3+} > Al(DMF)_6^{3+}$. In terms of a simple electrostatic and steric model for the solvent exchange *via* an S_N1 mechanism, the lability of the Be(II) complex is "anomalously" large, especially with respect to the lability of $Al(DMF)_6^{3+}$. The charge to radius ratios of these ions are similar, 6.5 for Be(II) and 6.0 for Al(III), and by using scaled molecular models, it can be shown that the Be(II) complex is somewhat less sterically hindered than that of Al(III). In this regard it is of interest to consider whether all of the complexes exchange DMF *via* the same mechanism.

Although water exchange from most aquo complexes probably proceeds *via* an S_N1 mechanism,[31] Fiat and Connick[11] have argued that the large negative value of $\Delta S^{\ddagger}$ for $Ga(OH_2)_6^{3+}$ implies an S_N2 mechanism for its water-exchange reaction. The results obtained for $Ga(DMF)_6^{3+}$ certainly are *not* inconsistent with an S_N2 mechanism for solvent exchange, and, in particular, we note that the sterically hindered $Ga(DMF)_6^{3+}$ ion is much less labile than $Ga(OH_2)_6^{3+}$. In contrast, the Al(III) complexes presumably exchange ligands *via* an S_N1 path[31] and the sterically hindered DMF system is more labile than the aquo system. Unfortunately, since the Al(III) and Ga(III) complexes are only slightly soluble in "inert" solvents, it was not possible to study the dependence of the solvent-exchange rate on the DMF or H_2O concentration. The salt $Be(DMF)_4(ClO_4)_2$ is quite soluble in methylene chloride and it should be possible to evaluate the DMF dependence of DMF exchange from $Be(DMF)_4^{2+}$ which is a well-defined complex in this solvent. The results will be the subject of a future report.

It is evident from the thermodynamic parameters listed in Table IV that the mixed complexes of Ga(III) with $acac^-$ and DMF, $Ga(acac)_n(DMF)_{6-2n}^{3-n+}$, are neither highly favored nor disfavored with respect to the symmetrical ones, $Ga(DMF)_6^{3+}$ and $Ga(acac)_3$. The ΔS_{cor} values in Table IV were obtained by subtracting from ΔS_1 and ΔS_2 the conformational entropy contribution which was calculated in the manner discussed previously.[10, 15] A comparison of the values of ΔH and ΔS_{cor} reveals that the distribution of the mixed Ga(III) complexes is largely statistical. In this regard the Ga(III) system is similar to the analogous Be(II) system but unlike the Al(III) system for which large values of ΔH and ΔS_{cor} are associated with the formation of $Al(acac)_n(DMF)_{6-2n}^{(3-n)+}$.

The distribution of species in these systems may be influenced both by ligand–ligand interactions in the first coordination sphere of the metal ion and by solvation in the second coordination sphere. In the case of the Be(II)–DMF system, secondary solvation has little effect on the distribution of the complexes. The thermodynamic parameters for the formation of $Be(acac)(DMF)_2^+$ from $Be(acac)_2$ and $Be(DMF)_4^{2+}$ in the solvent methylene chloride are the same, within experimental error, as those obtained in the solvent DMF.[32] The low solubility of the Ga(III) and Al(III) complexes in methylene chloride and other solvents of low polarity precludes such an assessment of secondary solvation effects. Should secondary solvation be unimportant for these complexes, the thermodynamic data suggest that the Al(III) complexes containing the largest number of $acac^-$ groups are formed preferentially,[33] a result not anticipated on simple electrostatic grounds.[33]

In Table V are summarized the chemical shifts of the DMF protons of $Al(DMF)_6^{3+}$, $Ga(DMF)_6^{3+}$, and $Be(DMF)_4^{2+}$ relative to those of free DMF and, in addition, the shifts of the $acac^-$ protons of mixed $acac^-$–DMF complexes relative to those for $Al(acac)_3$, $Ga(acac)_3$, and $Be(acac)_2$. It has been suggested[34-36] that the magnitude of the coordinated DMF proton shifts is a linear function of the metal ion [charge]: [radius]^2 ratio and, therefore, is a measure of the relative metal ion–DMF bond strengths. It is obvious that these three metal ions do not conform to such a correlation. The correlation may have little meaning because it was derived from chemical shift studies of DMF solutions of metal halides. Although the ClO_4^- ion which was used as the counterion in these studies exerts a negligible effect on both the free and coordinated DMF chemical shifts, it has been shown[37] that halide ions in the *second coordination sphere* of a metal ion have a pronounced effect on the chemical shifts of DMF in the first coordination sphere. In any event, we feel that the trend in the shifts in these systems should be influenced not only by the electric field effect of the metal ion[38] but also by the effect of the metal ion on the magnetic anisotropy of the O–C–N π system of DMF.[39] These effects are difficult to separate and are not necessarily related to the strength of the metal ion–DMF bond.

(28) G. Czerlinski, H. Diebler, and M. Eigen, *Z. Physik. Chem.*, 246 (1959).

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TABLE IV

KINETIC AND THERMODYNAMIC PARAMETERS FOR Ga(III), Al(III), AND Be(II) COMPLEXES[a]

	Ga(III)		Al(III)		Be(II)	
	DMF[b]	H_2O[c]	DMF[d]	H_2O[c]	DMF[e]	H_2O[f]
Kinetic Parameters[g]						
k, sec^{-1}	1.7	1800	0.15	0.16	310	100
$\Delta H^{\ddagger}$, kcal/mol	14.6 (±2)	6.3	17.7 (±1)	27	14.6 (±1)	...
$\Delta S^{\ddagger}$, eu	−8.3 (±2)	−22	4.7 (±2)	28	2.6 (±2)	...
Thermodynamic Parameters[h]						
K_1	5.4	10 (30°)	0.65	5 (30°)	10	13 (20°)
K_2	74	300 (30°)	3.6	130 (30°)		
ΔH_1 (±0.5), kcal/mol	1	...	7.7	...	0	−4.9
ΔH_2 (±0.5), kcal/mol	0	...	4.9	...		
ΔS_1 (±2), eu	7	...	25	...	5	21
ΔS_2 (±2), eu	9	...	19	...		
$\Delta S_{1\ cor}$ eu	−1	...	17	...	0	16
$\Delta S_{2\ cor}$ eu	8	...	18	...		

[a] The temperature is 25° unless stated otherwise. [b] This work. [c] References 11 and 29. [d] References 7 and 15; there is an error in Table III of ref 15; k_1(25°) is 0.15 not 4 sec^{-1}. [e] Reference 10. [f] References 28 and 30. [g] Parameters for solvent exchange from Ga(DMF)$_6^{3+}$, Al(DMF)$_6^{3+}$, Be(DMF)$_4^{2+}$, and the analogous water complexes. [h] Parameters for reactions of the type of reactions 4 and 5.

TABLE V

CHEMICAL SHIFTS OF METAL COMPLEXES IN DMF SOLUTIONS AT 60 MHz

Metal	a′	b′	c′	1′	1″	2′	2″
Al(III)	20	20	17	6	10	8	13
Ga(III)	20	20	25	6	10	9	15
Be(II)	18	18	19	3	...	3	...

[a] Chemical shifts are downfield in hertz. For signals a′, b′, and c′ reference is to the a, b, and c signals, respectively, of free DMF. For signals 1′, 1″, 2′, and 2″, reference is to the appropriate signal of the complex Al(acac)$_3$, Ga(acac)$_3$, or Be(acac)$_2$. See Figure 1 for assignments.

The relatively narrow ^{71}Ga resonance of Ga(DMF)$_6^{3+}$ is consistent with the assumed octahedral coordination of Ga(III). The anomalously large line widths obtained for the aquo complex have been attributed[27] to hydrogen bonding between the complex and solvent, thus lowering the rotational correlation time, an effect that would be much reduced in DMF.

The signal due to Ga(DMF)$_6^{3+}$ is upfield from that of the aquo complex, just as the ^{27}Al nmr signal of Al(DMF)$_6^{3+}$ is upfield with respect to Al(OH$_2$)$_6^{3+}$.[7] If these shifts are dominated by the diamagnetic Lamb term, then the order of the shifts suggests that, unlike the case for transition metal ions,[40] DMF is a stronger donor toward Al(III) and Ga(III) than is water. Undoubtedly, "paramagnetic deshielding" effects[41,42] arising from the mixing of excited electronic states with the ground state do influence these shifts but a detailed discussion of them is not warranted in view of the paucity of nmr and electronic spectral data.

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