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A Dynamic ^{1}H-NMR Study of Tris(trifluoro-2,4-pentanedionato) Chelates of Aluminum(III) and Gallium(III)

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It has been twenty years since Fay and Piper first demonstrated that the fluxional behavior of the aluminum(III), gallium(III) and indium(III) chelates of 1,1,1-trifluoro-2,4-pentanedione(tfac-H) can be followed by ^{19}F-NMR spectroscopy [1, 2]. This classic study established the utility of nuclear magnetic resonance spectroscopy as a useful technique for the study of stereochemical nonrigid inorganic complexes. Their ^{19}F-NMR study showed that the spectra of the Al(tfac)$_3$ and Ga(tfac)$_3$ complexes to have four resonances below 89° and 50 °C, respectively. Three of the four fluorine resonances are attributed to the three nonequivalent CF$_3$ groups of the meridional (*trans*) isomer and the fourth fluorine resonance is due to the equivalent CF$_3$ group of the facial (*cis*) isomer. As the temperature is increased the four fluorine coalesce into one resonance with a coalescence temperature (T$_c$) of 103° and 61.5° for Al(tfac)$_3$ and Ga(tfac)$_3$, respectively. By approximate methods, Fay and Piper calculated various kinetic parameters. Their experimental data were interpreted in terms of an intramolecular exchange of the facial and meridional isomers which took place *via* a bond rupture or a twist mechanism. The In(tfac)$_3$ showed only one resonance down to −57 °C. Due to the historical nature of their study, it seems appropriate that the fluxional behavior of these compounds should be reexamined to obtain a more exact treatment of the kinetic parameters involved in order to ascertain the exchange phenomenum. This paper reports a ^{1}H-NMR spectral and computer simulation study of the *mer*-Al(tfac)$_3$ and mer-Ga(tfac)$_3$ species. The data obtain from the analyses of ^{1}H-NMR spectra will be compared to that obtained from ^{19}F-NMR spectra.

The nonexchanging ^{1}H-NMR spectrum of *trans*-Al(tfac)$_3$ exhibits three resonances centered at 5.98 ppm (C–H) and three resonances centered at 2.23 ppm (CH$_3$) relative to TMS. *Trans*-Ga(tfac)$_3$ exhibited these same resonances at 5.92 and 2.25 ppm, respectively. Because of the poor resolution in the spectrum of the methine protons, the methyl protons are treated by computer simulation exchange-broadened spectra to obtain exchange rate constants (k) [3]. These rate constants are used to determine activation parameters which will then be used to elucidate the mechanism of the ligand exchange for *trans*-Al(tfac)$_3$ and *trans*-Ga(tfac)$_3$.

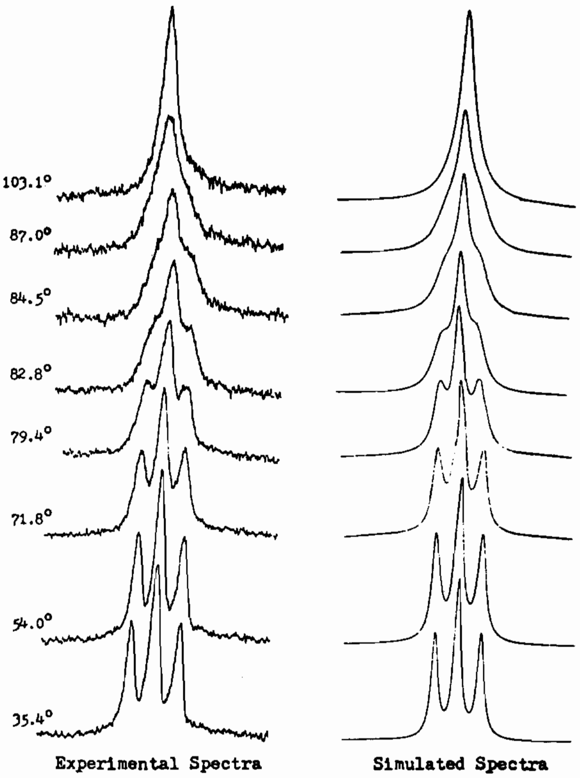

Fig. 1. *Trans*-Al(tfac)$_3$ experimental and simulated ^{1}H-NMR spectra of the CH$_3$ resonances. The middle peak is of larger intensity due to some *cis*-Al(tfac)$_3$ impurity. The coalescence temperature (T$_c$) is 84.5° and its corresponding simulated spectrum has a rate constant (k) of 0.65 sec^{-1}.

^{1}H-NMR spectra were obtained for *trans*-Al(tfac)$_3$ and *trans*-Ga(tfac)$_3$ in the temperature range −25 °C to 110 °C. The ^{1}H-NMR experiments were executed using Al(tfac)$_3$ and Ga(tfac)$_3$ which contain a 10–15% *cis* impurity. The rapid isomerization–racemization process of these labile complexes is probably the reason for the inability to separate the *cis*/*trans* isomers by successive recrystallizations. Decomposition of the *trans* isomer on an alumina support using liquid column chromatography has also been reported [4]. The presence of the *cis* impurity was treated as a constant concentration and its chemical shift was also assumed to be constant in this

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TABLE I. Kinetic Data for *Trans*-Al(tfac)$_3$ and *Trans*-Ga(tfac)$_3$.

Compound	T_c (℃)	k_{T_c} (sec^{-1})	$\Delta G^{\ddagger}_{T_c}$ (kcal/mol)	E_a (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)	lnA
t-Al(tfac)$_3$	84.5 ± 2	0.650 ± 5%	21.4 ± 0.1 (19.6 ± 1.7)^a	28.2 ± 2.5 (23.5 ± 1.8)^a	27.3 ± 2.5	16.2 ± 7.0	39.1 ± 3.5
t-Ga(tfac)$_3$	44.7 ± 2	0.980 ± 5%	18.7 ± 0.1 (17.2 ± 1.5)^a	22.2 ± 0.1 (20.8 ± 1.6)^a	21.8 ± 0.1	9.90 ± 0.22	35.1 ± 0.2

^{a}Ref. 2.

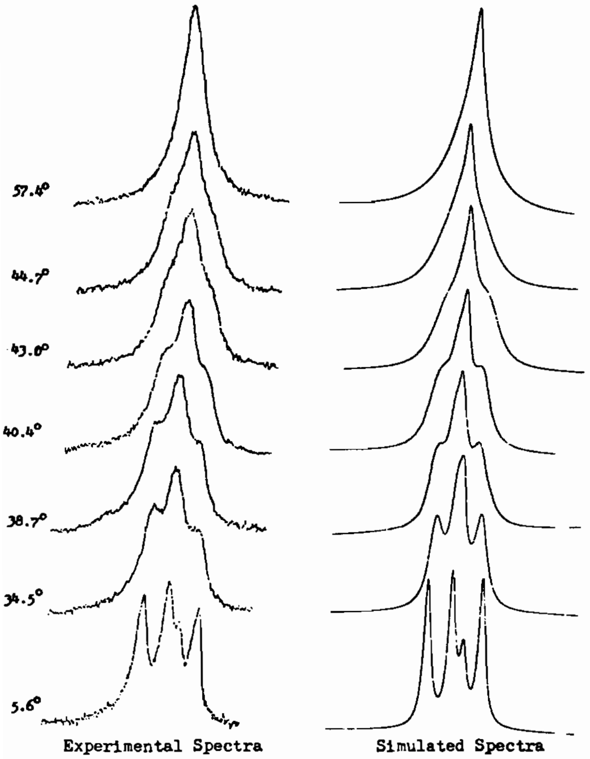

Fig. 2. *Trans*-Ga(tfac)$_3$ experimental and simulated ^{1}H-NMR spectra of the CH_3 resonances. The small peak shown in spectra taken at 5.6 ℃ is due to some *cis*-Al(tfac)$_3$ impurity. The coalescence temperature (T_c) is 44.7 ℃ and its corresponding simulated spectrum has a rate constant (k) of 0.98 sec^{-1}.

study. The *cis* isomer's transverse relaxation time (T_2) was assumed to be the same as for the *trans* isomer. This parameter for each *cis* isomer was kept constant throughout the computer simulation study. The incorporation of the *cis* isomer was necessary to enable the direct comparison of computer simulated and experimental line shapes.

Figures 1 and 2 show the temperature dependence of the methyl resonances of Al(tfac)$_3$ and Ga(tfac)$_3$. Coalescence occurs at 84.5 ± 2 ℃ for Al(tfac)$_3$ and 44.7 ± 2 ℃ for the Ga(tfac)$_3$. The unequal intensities of the *trans*-Al(tfac)$_3$ methyl resonances are due to presence of the *cis*-isomer which overlaps the central *trans* methyl resonance. The small signal to the right of the central resonance of *trans*-Ga(tfac)$_3$ is due to the *cis* impurity.

The value of the rate constant in the nonexchanging region was used in the Eyring equation to calculate $\Delta G^{\ddagger}$. The free energy of activation at the coalescence temperature was then used to calculate an approximate value of the exchange rate constant, k,

$$\Delta G^{\ddagger} = (10.32 + \log T_c/k_c)(4.576)(T_c) \qquad (1)$$

for the temperatures of interest. Values of the chemical shift (δ) of the CH_3 protons were determined by trial and error where the resonances were not well resolved in order to stimulate the exchange-broadened spectra while holding k and T_2 constant. Having found good 'fit' for δ, k was varied until a good 'fit' was also obtained. T_2 was held constant at the experimentally determined value. The Arrhenius activation energy, E_a, and frequency factor, A, were obtained from weighed least-square line plots of lnk *versus* 1/K. A plot of lnk/T *versus* 1/T was used to determine $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The activation parameters are listed in Table I. It should be noted that although the literature values for $\Delta G^{\ddagger}$ and E_a were obtained by approximation methods there is good agreement between our data and the original data. Furthermore, the original data while based on spectra from ^{19}F-NMR is in agreement with our data based on ^{1}H-NMR spectral results. The $\Delta G^{\ddagger}$ is rather insensitive to errors. An order of magnitude error link leads to an error of only 2 kcal/mol in $\Delta G^{\ddagger}$.

The dissociation and trigonal twist mechanism have already been rejected by Fay and Piper [2]. The latter mechanism can interconvert the Λ-fac and Δ-fac (also Λ-mer and Δ-mer) isomers but it fails to interconvert the fac(*cis*) to mer(*trans*) isomers. The two mechanisms which can not be eliminated are the rhombic twist and the bond rupture. Both of the mechanisms can interconvert both the optical enantiomers and the *cis*/*trans* isomers [2]. Our data gives support to a one-bond rupture mechanism by the positive value of $\Delta S^{\ddagger}$ [5, 6] whereas a negative or small $\Delta S^{\ddagger}$ value is indicative of a twist mechanism [2, 7–12]. Furthermore, the high frequency factors exp(39.1 ± 3.5) and exp(35.1 ± 0.2) for $Al(tfac)_3$ and $Ga(tfac)_3$, respectively, are not consistent with a rhombic twist mechanism. A low frequency factor has been interpreted as a relatively long time interval need to get the activation energy into the appropriate vibrational modes for the twisting motion [13].

In the work of Fay and Piper, a bond rupture mechanism for $Al(tfac)_3$ and $Ga(tfac)_3$ is suggested [2]. They have also shown that the free energy of activation at the coalescence temperature decreased with increasing dielectric constant of the solvent which was interpreted in terms of decrease of E_a as a result of the greater change separation and solution of the transition state. The bond rupture mechanism predicts greater solution in the transition state due to the presence of the partially charged dangling carbonyl group of the ligand [2].

Finally, further support for a bond rupture mechanism is presented in a topological analysis on the mechanism of stereoisomerism of aluminum substituted β-diketonates [14]. For alkyl and aryl substituents, a rhombic twist mechanism is proposed. On the other hand fluorocarbon substituents on the β-diketonate rings stereoisomerize by bond rupture which proceeds *via* a square base intermediate with bond rupture taking place at the CF_3 end of the trifluoroacetylacetonate ligand. Such an intermediate can account for the single resonance at the coalescence temperature as it allows for both racemization and isomerization rearrangement.

Experimental

The tris-(1,1,1-trifluoro-2,4-pentanedionato)aluminum(III) and gallium(III) chelate were prepared as previously reported and their corresponding *trans* isomers was isolated by the method of Fay and Piper [1, 2]. ^1H-NMR spectra were taken $CDCl_3$ from –24° to 110 °C on a Varian Model A60-A Spectrometer equipped with a Varian Model V6040 variable temperature controller. The probe temperature was calibrated at high temperatures using a ethylene glycol thermometer and a low temperature using a methanol thermometer. The low temperatures were corrected using the equations developed by Van Geet [15]. A subroutine was added to the DNMR3 program which allows the addition of two spectra, the calculated resonance for the *cis* isomer and the *trans* simulation, to be added together.

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