Journal of Organometallic Chemistry, 456 (1993) 25-30

JOM 23550

# $^{71}$Ga NMR studies of mixtures of gallium trichloride and trimethylgallium

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(Received September 14, 1992; in revised form December 28, 1992)

## Abstract

$^{71}$Ga NMR spectra of solutions of $GaCl_3$ and $Me_3Ga$, and of binary mixtures of $GaCl_3$–$Me_3Ga$, in n-heptane have been recorded. The resonance signals for both $Me_3Ga$ and $GaCl_3$ are unchanged on dilution over the temperature range 20–100°C. Mixtures of $GaCl_3$ and $Me_3Ga$ show only one resonance signal, whose chemical shift is determined predominantly by the nature of the coordination at gallium, indicating rapid chemical exchange of the species involved. The results of studies of methanolysis and hydrolysis, and of adduct formation, are also discussed. The $^{71}$Ga resonances of several possible external standards in the temperature range 20–100°C are also reported. The $^{71}$Ga NMR signal of a solution of $GaCl_4^-$ in 6 M aqueous hydrochloric acid, for which $\delta(^{71}Ga) = 250 \pm 0.5$ ppm downfield from the signal of a 1 M solution of $[Ga(H_2O)_6]^{3+}[ClO_4]_3^-$ in 1 M $HClO_4$, is recommended as a temperature-independent external standard for gallium NMR studies.

## 1. Introduction

There have been relatively few investigations of the $^{71}$Ga nuclear magnetic resonance (NMR) spectra of gallium compounds in non-aqueous solvents, and most of the results refer to either inorganic anionic four-coordinate gallium(III) complexes, or to octahedral species with high symmetry [1–7]. The resonances of other gallium compounds in non-aqueous media are often so broadened as to be beyond the limits of detection, owing to large quadrupole relaxation and exchange effects.

Little is known about the solution chemistry of the organometallic halides $MeGaCl_2$ and $Me_2GaCl$. These compounds can be prepared by redistribution reactions involving either $Me_4Si$–$GaCl_3$ [8–10] or $Me_3Ga$–$GaCl_3$ mixtures [11–15], and the available structural data suggests that these methylgallium(III) halides exist as halogen-bridged dimers [16–21], as does the inorganic parent $Ga_2Cl_6$ [22]. In contrast, $Me_3Ga$ is apparently monomeric in all phases [16,23]. It therefore seemed appropriate to study the solution behaviour of $GaCl_3$–$Me_3Ga$ mixtures by NMR spectroscopy in order to establish the mechanism of these redistribution processes.

## 2. Experimental details

### 2.1. General

$GaCl_3$ was prepared by the reaction of metallic Ga with gaseous chlorine, and $Me_3Ga$ by treating $GaCl_3$ with a three-fold excess of MeMgBr (analysis Ga 60.1, calcd. for $C_3H_9Ga$ 60.7%).

For NMR studies of the $GaCl_3$–$Me_3Ga$ system, samples prepared by mixing $Me_3Ga$ with an equimolar quantity of $GaCl_3$ in n-heptane were sealed under argon in 10 mm diameter tubes, together with a sealed capillary containing an aqueous solution of $[Ga(OH_2)_6](ClO_4)_3$ as internal standard, for which $\delta(^{71}Ga) = 0$ ppm. The samples were heated for 20 min at 100°C to verify their stability at this temperature prior to the detailed studies described below.

### 2.2. Spectroscopy

$^{71}$Ga NMR spectra were obtained with a Varian Unity 500 instrument operating at 152.468 MHz, using an s2pul pulse sequence. In order to prevent baseline

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0022-328X/93/$6.00

distortion in measuring the broad resonances (caused by the presence of the quadrupolar $^{71}$Ga nucleus), it was necessary to select the optimum delay between the excitation pulse and the beginning of data acquisition; in the case of $Me_3Ga$, for example, this delay did not exceed 10 μs. Other experimental precautions included relatively short acquisition times (0.02–0.1 s), and careful selection of transmitter power and receiver gain. A further precaution was to ensure that the resonance signal was centred in the recorded spectrum. Under these circumstances, the estimated reproducibility of $\delta$ was about ±5 ppm, and that of $w_{1/2}$ about ±500 Hz at 100°C for signals recorded along with the signal of a standard in one spectral window, *i.e.* for chemical shifts that do not exceed 100,000 Hz. The estimated reproducibility for signals that were measured within two spectral windows at 100°C was about ± 15 ppm for $\delta$, and about ±2000 Hz for $w_{1/2}$.

### 2.2.1. *Gallium tris(2,4-pentanedionate), Ga(acac)$_3$*

In view of the concern about external standards for $^{71}$Ga NMR spectroscopy (see below), we attempted to examine the spectrum of a solution of $Ga(acac)_3$. To prepare this compound, gallium metal (1 g, 14.3 mmol) was dissolved in concentrated $HNO_3$ (30 mL) and the resultant solution taken to dryness. The solid was dissolved in water (25 mL) and treated with Hacac (4.4 mL, 4.3 g, 42.8 mmol) and aqueous ammonia (5 mL, 4 M). The insoluble product was washed, dried, and recrystallised as colourless crystals from 95% ethanol. The compound $Ga[OC(CH_3)CHC(C_6H_5)O]_3$ was prepared by an analogous route.

## 3. Results

The $^{71}$Ga NMR results for $Ga_2Cl_6$ and $Me_3Ga$, and for their mixtures in n-heptane, are given in Table 1; each $\delta$ and $w_{1/2}$ value is the average of two measurements.

TABLE 1. $^{71}$Ga NMR spectroscopic results for $GaCl_3$–$Me_3Ga$ mixtures in n-heptane

| $GaCl_3$ : $Me_3Ga$ (mole ratio) | Concentration (w/v, %) | Temperature (°C) | $\delta$ [a] (ppm) | $w_{1/2}$ [b] (Hz) |
|---|---|---|---|---|
| 1 : 0 | 19.0 | 22 | 221 | 9950 |
| | | 100 | 221 | 5180 |
| | 4.2 | 22 | 222 | 6850 |
| | | 100 | 222 | 4200 |
| 2 : 1 | insoluble $MeGaCl_2$ | 22 | – | – |
| | | 100 | 295 | 11600 |
| 1 : 1 | 20.0 | 22 | | broad |
| | | 100 | 300 | 9100 |
| 1 : 2 | 24.0 | 22 | | broad |
| | | 100 | 354 | 18900 |
| 1 : 3 | 27.0 | 22 | | broad |
| | | 100 | 475 | 21250 |
| | 50.1 | 22 | 710 | 28000 |
| 0 : 1 | | 100 | 730 | 13500 |
| | 9.1 | 22 | 740 | 31250 |
| | | 100 | 725 | 15200 |

[a] $\delta(^{71}Ga)$ relative to external aqueous $[Ga(OH)_2]_6^{3+}$ for which $\delta(^{71}Ga) = 0$. [b] $w_{1/2}$ line width at half height.

Solutions of $GaCl_3$ and $Me_3Ga$ in n-heptane at 100°C gave signals that were unshifted from those at ambient temperature. Although $GaCl_3$ is completely soluble in n-heptane, the addition of $Me_3Ga$ at ~ 20°C ($GaCl_3$ : $Me_3Ga$ = 2 : 1) precipitates insoluble $MeGaCl_2$, while further addition of $Me_3Ga$ ($GaCl_3$ : $Me_3Ga$ ≤ 1) gives a homogeneous solution once again. The $^{71}$Ga NMR spectrum of each of these mixtures consists of a single resonance, whose characteristics were reproducible only at 60–100°C because of line broadening at ambient temperature; the temperature in question depended on $w_{1/2}$. The chemical shift varied nonlinearly with the mole fraction of $Me_3Ga$ (Fig. 1) while the line-width was at a minimum for $GaCl_3$ : $Me_3Ga$ = 1, and then increased monotonically with increasing mole fraction of $Me_3Ga$.

## 4. Discussion

### 4.1. *General Comments*

The range of chemical shifts for non-aqueous solutions of gallium(III) compounds studied in this work is about 740 ppm. In addition to the general trend for an increasing range of chemical shifts with increasing atomic number for the nuclei of a given Main Group of elements [24], the largest changes in resonance fre-

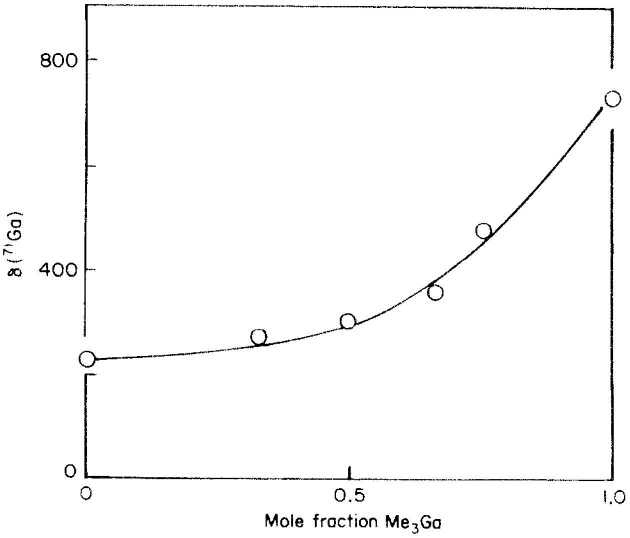


Fig. 1. $^{71}$Ga NMR chemical shifts (in ppm) at 100°C as a function of the mole fraction of $Me_3Ga$ in $GaCl_3$–$Me_3Ga$ mixtures in n-heptane.

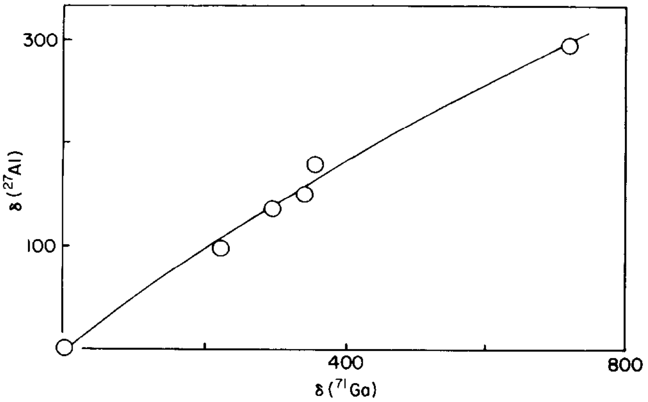


Fig. 2. The correlation between $^{27}$Al and $^{71}$Ga chemical shifts in analogous compounds.

quency in these gallium compounds arise principally from the changes in the number and type of ligands in the coordination kernel, so that the chemical shift is dominated by the paramagnetic contribution to the shielding constant. In keeping with the concept of the significance of the orbital distribution of the valence electrons [24], it is to be expected that the four-coordinate nucleus in dimeric $Ga_2Cl_6$ (*ca.* 220 ppm) or $GaCl_4^-$ (*ca.* 200 ppm [1]) would exhibit a higher shielding effect than the three-coordinate nucleus in monomeric $Me_3Ga$ (*ca.* 720 ppm), as is demonstrated by the results in Table 1. Similarly, the symmetry at the gallium nucleus determines $w_{1/2}$ in these compounds, provided that chemical exchange is not taking place, or that the exchange lifetime is long compared with the correlation time for the rotation of the molecules in solution. The values in Table 1 confirm that these conditions apply for the systems under investigation.

The shift range from $GaCl_3$ to $Me_3Ga$ is of the order of 500 ppm, which can be compared with the values for analogous $MCl_3$–$Me_3M$ series involving the lighter elements of the same group. For monomeric compounds with M = B, the range is *ca* 50 ppm [25], and for dimeric compounds with M = Al approximately 80 ppm [26–28]. The shifts for some corresponding compounds of aluminum [27–30] and gallium are presented in Table 2.

TABLE 2. The correlation of chemical shifts of the nuclei $^{71}$Ga and $^{27}$Al in analogous compounds

| Compound | $\delta(^{71}Ga)$ | $\delta(^{27}Al)$ | Ref. |
|---|---|---|---|
| 1 $Me_3M$ | 720 | 297 | 30 |
| 2 $Me_2MCl$ | 355 | 180 | 28 |
| 3 $MeOMMe_2$ | 340 | 151 | 27,28 |
| 4 $MeMCl_2$ | 295 | 139 | 28 |
| 5 $MCl_3$ | 221 | 99 | 26 |
| 6 $[M(OH_2)_6]^{3+}$ | 0 | 0 | |

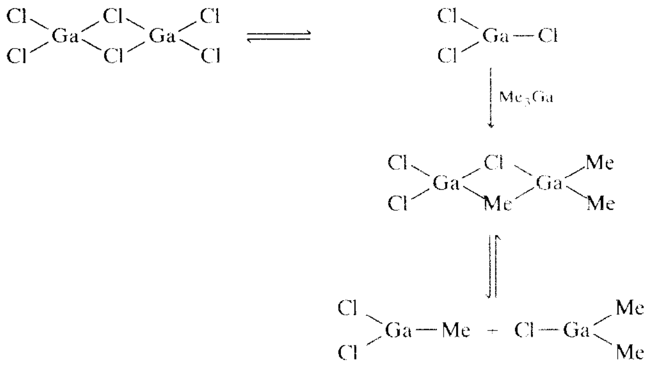
The "shielding sensitivity", as determined by the ratio of the chemical shift ranges of Ga and Al nuclei in the relevant compounds, is rather different from that found in series of $MX_4^-$ compound (X = Cl, Br, I; M = Al, Ga, In). For gallium compounds in non-aqueous solvents, the shielding sensitivity for the gallium nucleus is about 2.3 times greater that for aluminum (Fig. 2 shows a positive correlation, $r = 0.93$, statistically significant at 0.05 level). In the case of $MX_4^-$ series, the shielding sensitivity for gallium is approx. 5.3 times greater than that for aluminum, while results for $InX_4^-$ [29] show that the ratio for In : Ga is 1.4 : 1. Results are also available for octahedral $ML_6$ species of aluminum and gallium [25], and here the shielding sensitivity of the heavier element is 2.7 times greater.

The results arising from present work, and from the octahedral series, are close to the value of *ca.* 2.7 predicted from the ratio of $\langle r^{-3} \rangle_{np}$, where $r$ is the average value of radial part of the $p$-electron wave function for free gallium ($n = 4$) and aluminum ($n = 3$) atoms [24]. The difference between the scale factor 2.7 for the octahedral species and that of 5.7 for $MX_4^-$ anions may reflect the steric crowding of the ligands on the smaller $Al^{3+}$ ion in the case of octahedral species relative to the more open tetrahedral complexes [25], but an alternative explanation may be found in an increased involvement of d-orbital electrons in shielding the Ga nucleus in $GaX_4^-$ species. For the three-coordinate species listed in Table 2, steric crowding should not be a factor, and changes in the extent of d-orbital participation may therefore be significant.

### 4.2. *Spectra of $GaCl_3$–$Me_3Ga$ mixtures*

The observations that the $^{71}$Ga NMR resonances of both $GaCl_3$ and $Me_3Ga$ are essentially unchanged within experimental error on dilution in n-heptane solution, and are independent of increasing temperature, supports the predominant existence of monomeric units of $Me_3Ga$ [16,23], and undissociated dimers of $Ga_2Cl_6$ [22], in this solvent.

Given the structural similarities in the $Ga_2Cl_6$–$Me_3Ga$ and $Al_2Cl_6$–$(AlEt_3)_{1\text{-}2}$ systems [26], one might have expected $^{71}$Ga NMR resonances arising from different nearest-neighbour coordination because of non-random exchange reactions between $GaCl_3$ and $Me_3Ga$, but in fact only one $^{71}$Ga signal is found in each case, implying rapid ligand exchange between the species involved. Furthermore, the resonances recorded at 100°C for each of the 2 : 1, 1 : 1, and 1 : 2 $GaCl_3$–$GaMe_3$ mixtures are in the 300–350 ppm region, which is typical of four-coordinate complexes, rather than the value of *ca.* 730 ppm that characterises three-coordinate $Me_3Ga$. A reasonable mechanism for the exchange involving $GaCl_3 : Me_3Ga = 2 : 1$ is shown in



Scheme 1.

Scheme 1, and is based on (i) a small but kinetically significant dissociation of $Ga_2Cl_6$, (ii) the Lewis acid character of all three-coordinate gallium species, (iii) the presumed tendency for the $CH_3$ groups of $Me_3Ga$ to form weak intermolecular electron-deficient bonds, as in $Me_6Al_2$ and solid $Me_3In$ [18], and (iv) a similar mechanism proposed for $GaX_4^-/GaY_4^-$ ligand exchange, involving $X_3GaYGaY_3$ species [3]. A series of obvious extensions of this Scheme can account for mixtures with differing mole ratios of the two reactants. These results are in keeping with the findings of recent measurements of the enthalpies of mixing of $Me_3Al$–$GaCl_3$ and $Me_3Ga$–$GaCl_3$ [14,15], from which it was concluded that the affinity of chloride for aluminum is much greater than it is for gallium. An explanation of the rapid exchange in $GaCl_3$–$Me_3Ga$ mixtures is therefore to be found in the low thermodynamic stability of the intermediate species in Scheme 1.

### *4.2.1. Methanolysis and hydrolysis*

In order to avoid the possibility of any errors in the interpretation of the $^{71}$Ga NMR data because of the moisture sensitivity of $Me_3Ga$, experiments were carried out in which the methanolysis or hydrolysis products of $Me_3Ga$ were deliberately generated in the following way:

$$Me_3Ga + MeOH = Me_2GaOMe + CH_4 \qquad (1)$$

$$\textbf{(I)}$$

$$Me_3Ga + HOH = Me_2GaOH + CH_4 \qquad (2)$$

$$\textbf{(II)}$$

The results of these experiments indicate that reactions (1) and (2) cause new signals to arise at about 350 ppm, $w_{1/2}$ = 21 500 Hz for **I**, and 360 ppm, $w$ = 24 000 Hz for **II** at 100°C. These resonances are in the region associated with four-coordinate gallium(III) species. Further addition of either MeOH or $H_2O$ to the solution containing **I** or **II** did not release more gas, and the spectra of these mixtures were essentially unchanged by such additions. The dimeric structures of compounds **I** and **II** are of the type $Me_2Ga(\mu\text{-}OMe)_2GaMe_2$ [18,31–34], and the absence of further reactivity with either acids or bases at the terminal Ga–Me bonds is well established. It is clear that the signal reported in Table 1 for $Me_3Ga$ is that of an unhydrolysed sample.

### *4.2.2. $^{71}$Ga NMR studies of adduct formation*

We have briefly investigated the changes in the $^{71}$Ga resonance of $Me_3Ga$ following the addition of varying quantities of three typical donor ligands, $Et_2O$, $Me_2S$ and $Me_3N$. The results in Table 3 are for solutions in n-heptane. Analogous experiments with solutions of $Ga_2Cl_6$ in this solvent were nullified by the formation of either insoluble solids or two-phase mixtures.

Any detailed discussion of the results is difficult because of the necessity of recording the results at 80°C, which is well above the boiling point of each donor, in order to obtain reasonably sharp resonances. For $Et_2O$, at high $Me_3Ga:L$ mole ratios, the $^{71}$Ga resonance is essentially that of free $Me_3Ga$, with a slight increase in $w_{1/2}$. Larger quantities of $Et_2O$ produce a significant shift in the resonance frequency, with a smaller line-width, showing that complexing is occurring. Similar results are found with $Me_2S$, except that the relatively sharp resonance and chemical shift of 365 ppm indicate the formation of a stable four-coordinate complex. Solutions of $Me_3Ga$ and $Me_3N$ showed two resonances when $Me_3Ga$ is present in excess; one of these is obviously uncomplexed $Me_3Ga$, while the other, which is the only signal observed when the $Me_3N$ concentration is increased, is presumably that of the $Me_3Ga \cdot NMe_3$ 1 : 1 adduct, being in the region which is characteristic of four-coordinate tetra-

TABLE 3. $^{71}$Ga NMR resonances of mixtures of $Me_3Ga$ with some donors

| L | $Me_3Ga:L$ (mole ratio) | $\delta$ [a] (ppm) | $w_{(1/2)}$ [a] (Hz) |
|---|---|---|---|
| $Et_2O$ | 1.1 | 560 | 22 500 |
| | 0.50 | 660 | 24 500 |
| | 0.26 | 740 | 17 200 |
| $Me_2S$ | 1.25 | 365 | 13 700 |
| | 0.48 | 580 | 31 200 |
| | 0.28 | 640 | 12 200 |
| $Me_3N$ | 1.2 | 430 | 9 300 |
| | 0.50 | 430 | 15 000 |
| | 0.28 | 420 [c] | 11 000 |
| | | 730 [c] | 16 500 |

[a] As in Table 1. [b] 15% solutions in n-heptane at 80°C. [c] Relative intensities 1 : 2.

hedral gallium complexes. Earlier studies of the relative strength of organic donors towards $Me_3Ga$ [35] and $Et_3Ga$ [36] suggested that the order of donor strengths (in part) is N > O > S. The results in Table 3 are insufficient to allow any analysis of this sort, and further experiments are planned.

### 4.2.3. *Line widths*

The broad resonances observed for $GaCl_3$–$Me_3Ga$ mixtures at ambient temperatures narrow significantly at 100°C (Table 1), and these changes are typical of systems in which the rate of ligand exchange is in the intermediate region. Assuming that this exchange proceeds between three- and four-coordinate species (see Scheme 1) the lifetime for these exchanges are in the range $\tau_{ex}$ ($\sim 1/\Delta w_i$, where $\Delta w_i = w_{4coord} - w_{3coord}$) $\sim 10^5$s. The kinetic mechanism involves a series of dissociative and associative processes whose dominant terms depend, *inter alia*, on the relative concentrations of the species in question. The dimeric species (*e.g* $Cl_2GaCl(Me)GaMe_2$) can then be viewed as long-lived transition states. Because the line width is a function of the mole fractions of the species involved, the spin relaxation times, and $\tau_{ex}$, there seems to be no simple basis for meaningful discussion of the equilibrium constants in these mixtures in terms of $w_{1/2}$.

The $Me_3Ga$–L systems (L = $Et_2O$, $Me_2S$), however, can be treated in more detail. The $\Delta w_i$ values (see Table 3) are in the order of 300 ppm, again implying intermediate rates for the forward reaction ($k_f$) in the process

$$Me_3Ga \cdot L \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Me_3Ga + L \qquad (3)$$

and $\lambda_{ex} \sim 10^{-5}$ s leads to $k_f$ $(1/\tau_{ex}) \sim 10^5$ $s^{-1}$. If the association rate constant $k_r$ is assumed to be at the diffusion limit ($10^8$ $mol^{-1}$ $s^{-1}$ L), then the dissociation constant, $K_3 = k_f/k_r$, is *ca.* $10^{-2}$–$10^{-3}$ mol $L^{-1}$ at 80°C. A limit of $K_3 < 10^{-3}$ mol $L^{-1}$ emerges for L = $Me_3N$. These values, and the conclusion that the $Me_3N$ adduct is thermodynamically more stable than those of either $Et_2O$ or $Me_2S$, are in keeping with the known properties of these molecules [18].

### 4.2.4. *External standards for $^{71}$Ga NMR spectroscopy*

In the course of this work, we have evaluated a number of solutions that might serve as temperature-independent standards in $^{71}$Ga NMR studies, and these are listed here for convenience. They include:

(1) A solution prepared by dissolving metallic Ga in 1 M $HClO_4$, to give a solution 1 M in Ga, exhibited only one $^{71}$Ga NMR signal, which was shifted to a lower field with increasing temperature, by about 4–5 ppm at 100°C relative to the signal at ambient temperature. The observed changes probably indicate a decrease in the coordination number at the Ga nucleus.

(2) Solution of either $Ga(acac)_3$ or $Ga[OC(CH_3)CHC(C_6H_5)O]_3$ in toluene showed no detectable resonance; the lowering of the symmetry from $O_h$ in $[Ga(OH_2)_6]^{3+}$ obviously causes extreme broadening of the resonance signal.

(3) An external standard prepared by dissolving gallium metal in hydrochloric acid (1 M in $GaCl_3$, in 3.6 M HCl) showed only one $^{71}$Ga resonance over the temperature range 20–100°C. At ambient temperature, the resonance was at about $0 \pm 0.5$ ppm, $w_{1/2} = 250$ Hz, (relative to $[Ga(OH_2)_6]^{3+}(ClO_4^-)_3$), but when the solution was heated, the resonance moved to a lower field and rapidly broadened, to about 170 ppm, $w_{1/2} =$ 9400 Hz, at 60°C. At 100°C, the resonance narrowed again, at about 200 ppm, $w_{1/2} = 1500$ Hz. The same effect has been described for solutions of $GaCl_3$ in various concentrations of aqueous hydrochloric acid [1] at ambient temperature, and we therefore conclude that the aqueous gallium(III)–chloride solution system can be characterized by eqn. (4):

$$Ga(H_2O)_6^{3+} \rightleftharpoons [GaCl_n(H_2O)_{m-n}]^{(3-n)+} \rightleftharpoons GaCl_4^- + H_2O \qquad (4)$$

where $m$ = 6–4; $n$ = 0–4. It is obvious that this equilibrium is shifted in favour of the anionic four-coordinate complexes both by increasing concentration of hydrochloric acid and by increasing temperature.

(4) The spectra of solutions of $GaCl_3$ dissolved in 6 M HCl (stoichiometrically 0.8–0.3 M in $GaCl_3$) exhibited only one sharp $^{71}$Ga NMR signal in the temperature range 20–100°C, and the chemical shift (250.0 ± 0.5 ppm, $w_{1/2} = 250$–$350$ Hz at ambient temperature, and $w_{1/2} = 30$–$45$ Hz at 100°C, all relative to $[Ga(OH_2)_6]^{3+}(ClO_4^-)_3$ at 20°C) was essentially independent of changes of gallium concentration and of temperature.

In view of these results, we recommend that a solution of $GaCl_3$ in 6 M hydrochloric acid serve as the external standard in $^{71}$Ga NMR studies, especially in those cases where temperature dependence is important.

## Acknowledgment

We thank A.A. El-Hadad (University of Windsor) for the preparation of samples of $Ga(acac)_3$ and $Ga[OC(CH_3)CHC(C_6H_5)O]_3$.

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