69/71Ga and 115In NMR Spectroscopy of Lithium Tetra(tert-butyl)gallate and -indate: Spin-Spin Coupling Constants \( J(69/71\text{Ga},13\text{C}) \) and \( J(115\text{In},13\text{C}) \)

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Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

The \( ^{13}\text{C} \), 69/71Ga and 115In NMR spectra of lithium tetra(tert-butyl)gallate and -indate were measured under various conditions. It proved possible to determine for the first time the coupling constants \( J(69/71\text{Ga},13\text{C}) = 182 \text{ Hz}/232 \text{ Hz} \) and \( J(115\text{In},13\text{C}) = 310 \pm 10 \text{ Hz} \) for these metallates under conditions for solvent-separated ions. DFT calculations \([\text{B3LYP}/6-311+G(d,p)]\) were carried out for organogallium compounds such as tri(tert-butyl)gallium, trimethylgallium and tetramethylgallate in order to predict and confirm coupling constants \( J(\text{Ga},13\text{C}) \).

Key words: Tetra(tert-butyl)gallate, Tetra(tert-butyl)indate, \( ^{13}\text{C} \), 69Ga, 71Ga, 115In NMR, Coupling Constants, DFT Calculations

Introduction

Both NMR active isotopes of gallium, 69Ga and 71Ga, possess fairly large quadrupole moments \((I = 3/2; Q = 0.17 \text{ and } 0.11 \text{ [10}^{-24} \text{ m}^2\text{]}, \) and that of 115In is even greater \((I = 9/2; Q = 0.86 \text{ [10}^{-24} \text{ m}^2\text{]}\); 113In is of low natural abundance and has similar unfavorable nuclear properties). Therefore, with few exceptions for 69/71Ga, indirect nuclear Ga–X or 115In–X spin-spin coupling is generally not resolved [1, 2]. So far particularly important data, like \( J(69/71\text{Ga},13\text{C}) \) or \( J(115\text{In},13\text{C}) \), for comparison with the wealth of other \( ^{13}\text{C}–\text{X} \) couplings [3], are missing. Recently we have found that the 27Al NMR signal of lithium tetra(tert-butyl)alinate (1Al), dissolved in benzene in the presence of an excess of THF, is extremely narrow. Well resolved splitting due to 27Al–13C spin-spin coupling has been observed in \( ^{13}\text{C}\{^1\text{H}\} \) as well as in 27Al\{^1\text{H}\} NMR spectra of 1Al [4]. This prompted us to prepare the corresponding lithium tetra(tert-butyl)gallate (1Ga) and -indate (1In), and to study their NMR spectra under various conditions.

Results and Discussion

Tri(tert-butyl)gallium (2Ga) and tri(tert-butyl)indium (2In)

Tri(tert-butyl)gallium (2Ga) and -indium (2In) were prepared following literature procedures [5, 6]. They were characterized by \( ^{1}\text{H} \) and \( ^{13}\text{C} \) NMR spectra. Unlike the \( ^{13}\text{C}(\text{Al–C}) \) NMR signals of the aluminum analog 2Al [4], the broadening of the \( ^{13}\text{C}(\text{Ga–C}) \) NMR signal of 2Ga owing to partially relaxed 69/71Ga–13C spin-spin coupling is fairly small, indicating extremely efficient quadrupole-induced 69/71Ga nuclear spin relaxation. This was confirmed by the measurement of the 71Ga NMR spectrum of 2Ga, which shows a very broad signal (full width at half height of about 50 ± 5 kHz). It was not possible with our equipment to record the 69Ga NMR signal of 2Ga. Expectedly, there is no appreciable broadening of the 115In–13C spin-spin coupling owing to fast relaxation of 115In. Since the observed slight broadening of the 13C(Ga–C) NMR signal in the case of 2Ga results from both 69Ga and 71Ga in the neighborhood of this 13C nucleus, the respective contributions are difficult to evaluate. Therefore, the use of Eq. 1 [7, 8], where \( \Delta \nu_b \) is the broadening of the 13C(Ga–C) NMR signal caused by scalar relaxation of the second kind, cannot give accurate results [\( S_X = 3/2 \) for 71Ga; \( T_Q(71\text{Ga}) = 6.4\times10^{-6} \text{ s} \)].

\[
\Delta \nu_b = 4/3 \pi S_X (S_X + 1) [J(A,X)]^2 ] [T_Q(X)] \quad (1)
\]

The line width of the 13C(Ga–C) NMR signal of 2Ga is close to 3 Hz, as measured from a refocused
Table 1. $^{71}$Ga, $^{69}$Ga and $^{13}$C NMR spectroscopic data$^a$ of Bu$_3$Ga (2Ga) and [Bu$_4$Ga]Li (1Ga).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{71}$Ga $\delta$($h_{1/2}$ (Hz))</th>
<th>$^{69}$Ga $\delta$($h_{1/2}$ (Hz))</th>
<th>$\delta$(Ga–C)</th>
<th>$\delta$(CH$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu$_3$Ga</td>
<td>900 (50000 ± 5000)</td>
<td>–</td>
<td>31.3$^b$</td>
<td>30.8</td>
</tr>
<tr>
<td>[Bu$_4$Ga]Li</td>
<td>272 (8250 ± 250)</td>
<td>–</td>
<td>22.7 (br$^c$)</td>
<td>33.8</td>
</tr>
<tr>
<td>[Bu$_4$Ga]Li (n py; n = 20)</td>
<td>271 (18 ± 0.5)</td>
<td>270 (42 ± 1)</td>
<td>24.2</td>
<td>36.0</td>
</tr>
<tr>
<td>[Bu$_4$Ga]Li (n THF; n = 9)</td>
<td>271 (22 ± 0.5)</td>
<td>270 (96 ± 1)</td>
<td>23.8</td>
<td>35.4</td>
</tr>
<tr>
<td>[Bu$_4$Ga]Li (n 12-crown-4; n = 20)</td>
<td>272 (58 ± 1)</td>
<td>270 (140 ± 2)</td>
<td>24.0</td>
<td>35.8</td>
</tr>
<tr>
<td>[Bu$_4$Ga]Li (n TMEDA; n = 18)</td>
<td>271 (85 ± 1)</td>
<td>270 (185 ± 2)</td>
<td>n. o.$^d$</td>
<td>35.6</td>
</tr>
</tbody>
</table>

$^a$ In C$_6$D$_6$, at 298 K; $^b$ $h_{1/2}$ = 3.0 Hz; $^c$ exchange-broadened: $h_{1/2}$ = 12 Hz; $^d$ n. o. = not observed.

Fig. 1. $^{13}$C, $^{71}$Ga and $^{69}$Ga NMR spectra of [GaBu$_4$]Li (1Ga) in C$_6$D$_6$ under various conditions as stated. The $^{13}$C satellites in the $^{71}$Ga($^1$H) and $^{69}$Ga($^1$H) NMR spectra do not show any appreciable isotope-induced chemical shift $^{1}$J($^{13}$C,$^{1}$H) ($<$ 0.5 ppb). INEPT experiment [9] with $^1$H decoupling. This leaves a contribution between 3.5 and 5 Hz from $^{71}$Ga (natural abundance 39.6 %) and gives a predicted coupling constant $^{1}$J($^{71}$Ga,$^{13}$C) = 205 ± 30 Hz for 2Ga.

The yellow color of crystalline 2In has been traced to $\sigma \rightarrow \pi$ transitions involving the In–C $\sigma$ bonds and the In-$p_z$ orbital. Although such transitions are also present in the case of the colorless homologs 2B, 2Al and 2Ga, they are shifted to shorter wave lengths when compared with 2In. Since these transitions are magnetic-dipole allowed, they cause an increase of the paramagnetic term of $^{13}$C nuclear shielding of the $^{13}$C nuclei directly linked to B, Al, Ga and In. Indeed, the $^{13}$C(In–C) nuclei in
Ga and $^{115}$In NMR Spectroscopy

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{115}$In $\delta$(h/2(Hz))</th>
<th>$^{13}$C $\delta$(In–C)</th>
<th>$\delta$(CH$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu$_3$In</td>
<td>-</td>
<td>40.4</td>
<td>32.6</td>
</tr>
<tr>
<td>[Bu$_3$In]Li</td>
<td>(n py; n = 15)</td>
<td>516 (530 ± 5)</td>
<td>n. o.</td>
</tr>
<tr>
<td>[Bu$_3$In]Li</td>
<td>(n py; n = 100)</td>
<td>515 (130 ± 1)</td>
<td>n. o.</td>
</tr>
<tr>
<td>[Bu$_3$In]Li (n THF; n = 100)</td>
<td>517 (192 ± 3)</td>
<td>n. o.</td>
<td>35.9</td>
</tr>
</tbody>
</table>

Table 2. $^{115}$In and $^{13}$C NMR spectroscopic data$^a$ of Bu$_3$In (2In) and [Bu$_3$In]Li (1In).

$^a$ In C$_6$D$_6$, at 298 K; $^b$ exchange-broadened; $h_{1/2}$ = 30 Hz; $^c$ n. o. = not observed; extremely broad, ill-defined, weak and unresolved signal, partially overlapping with $^{13}$C(CH$_3$) NMR signals from small amounts of impurities containing Bu$^t$ groups.

2In are least shielded in this series with $\delta^{13}$C(In–C) = 40.4.

Lithium tetra(tert-butyl)gallate (1Ga) and lithium tetra(tert-butyl)indate (1In)

Treatment of 2Ga or 2In with tert-butyllithium (Bu$^t$Li) afforded mainly the desired gallate 1Ga or indate 1In, respectively, both soluble in benzene and also in mixtures of benzene with various donors such as an excess of pyridine, tmeda, THF, or 12-crown-4. Relevant NMR data are given in the Tables 1 and 2.

Very few examples of Ga–X spin-spin coupling have been reported, viz. for [GaH$_4$]$^-$ (X = $^1$H [10]), [Ga(NCS)$_4$]$^-$ (X = $^{14}$N [11]), and {Ga[OP(OMe)$_3$]$_6$}$^{3+}$ (X = $^{31}$P [12]), whereas $^{115}$In–X spin-spin couplings have not been detected so far. In the case of [InH$_4$]$^-$ a broad featureless $^{115}$In NMR signal was measured which was described as the result of unresolved $^{115}$In–$^1$H spin-spin coupling with $^1J(115$In,$^1$H) $\approx$ 1000 Hz [13]. From the present study of 1Ga in benzene, in the presence of a large excess of pyridine (Fig. 1), we report the first examples of coupling constants $^1J(69,71$Ga,$^{13}$C) determined from the appropriate splitting in $^{69,71}$Ga and $^{13}$C NMR spectra. Moreover, in the case of 1In, we have observed the most narrow $^{115}$In NMR signal reported so far which allowed to determine $^1J(115$In,$^{13}$C) from the $^{13}$C satellites (Fig. 2).

The small line widths of the $^{69,71}$Ga NMR signals of solutions containing 1Ga with a large excess of pyridine suggest the presence of solvent-separated ion pairs and almost ideally tetrahedral surroundings of the gallium atom. The observed ratio of the line widths $[h_{1/2}(69$Ga)/$h_{1/2}(71$Ga) = 2.4] is close to the theoretical value predicted from the square of the ratio of the quadrupole moments (2.5). It has been noted, in agreement with our own experience, that this is not always the case for unknown reasons [14]. In the case of 1In, the line width of the $^{115}$In NMR signal (Fig. 2, lower trace) corresponds to the lowest limit which can be achieved by dilution of the sample with pyridine. Nevertheless, the $^1$H(Bu$^t$) NMR signal is broad (about 90 Hz in the top) and reminds of dynamic effects caused by exchange broadening. This signal becomes less broad in the presence of a small amount of pyridine or without pyridine, which indicates fast and random interaction of the lithium cation with the hydrocarbon framework around the indium atom. Thus, it is suggested that slow (on the NMR time scale) dynamic equilibria have to be considered for solutions containing 1In and a large excess of pyridine, pointing towards ion pair interactions. More suitable donors or different cations (e. g. tetraalkylammonium) are required in order to enforce complete ion pair separation and to observe even sharper $^{115}$In NMR signals. Heating of the sample containing 1In and a large excess of pyridine induces decomposition as shown by several new fast growing $^1$H NMR signals.

Fig. 2. $^{115}$In NMR spectra of [InBu$_4$]Li (1In) in C$_6$D$_6$ under various conditions as stated.
Table 3. Reduced coupling constants $^1J$(M,13C) and $^3K$(M,13C) for Me₂M (M = 29Si, 73Ge, 119Sn) and [Bu₄M]⁺ (M = 27Al, 71Ga, 115In).

<table>
<thead>
<tr>
<th>M</th>
<th>Me₂M</th>
<th>[Bu₄M]⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1J$(M,13C) (Hz)</td>
<td>$^1J$(M,13C) (Hz)</td>
<td>$^1J$(M,13C) (nm⁻¹)</td>
</tr>
<tr>
<td>$^3K$(M,13C) (nm⁻¹)</td>
<td>$^3K$(M,13C) (nm⁻¹)</td>
<td></td>
</tr>
<tr>
<td>52.0 / +8.65 (M = 29Si)</td>
<td>+76.0 / +9.63 (M = 27Al [4])</td>
<td>-18.7 / +17.67 (M = 73Ge)</td>
</tr>
<tr>
<td>-352.0 / +31.04 (M = 115In)</td>
<td>+310 / +46.5 (M = 115In)</td>
<td></td>
</tr>
</tbody>
</table>

* $^1K$(M,13C) = 4π$^2$ $^1J$(M,13C) (h γ(M) γ(13C))$^{-1}$; b R. K. Harris, B. E. Mann (Eds.), NMR and the Periodic Table, Academic Press, London, 1978; c this work.

Changes in the magnitude of the coupling constants $^1J$(M,13C) are expected to be similar in comparable compounds for Group 13 and Group 14 nuclei, if the individual nuclear magnetic properties of M are eliminated. This is shown by a comparison of the reduced coupling constants $^3K$(M,13C) = 4π$^2$ $^1J$(M,13C) (h γ(M) γ(13C))$^{-1}$, where M = 29Si, 73Ge, 119Sn (in Me₂M), and M = 27Al, 71Ga and 115In (in [MBu₄]⁺) (Table 3).

DFT calculations

The DFT calculations of the NMR data were based on the optimized gas phase geometries for 2Ga, [GaMe₄]⁻ (3Ga), and GaMe₃ (4Ga) (Scheme 1).

The X-ray structural analysis has revealed negligible intermolecular interactions for 2Ga [17], and also for 2In [17], although the quality of the structure determination of the gallane suffered from disorder. Gas phase electron diffraction studies (GED) of 2Al and 2Ga have proven the strictly monomeric nature of these compounds and indicated closely related structural features [18]. As shown in Fig. 3, the atoms C1, C2, and C3 are coplanar with the central gallium atom and the carbon atoms linked directly to it. The difference in the respective calculated Ga–C–C bond angles indicates that in addition to steric effects hyperconjugation plays an important role [4, 17, 18]. The calculated bond length Ga–C in 4Ga (199.2 pm) is shorter than in 2Ga (206.4 pm), most likely be-cause of the bulkiness of the tert-butyl groups. For [GaMe₄]⁻ (3Ga), the bond length Ga–C is calculated as 208.1 pm.

On the simple basis of the changes in the bond lengths Ga–C in 4Ga and 3Ga as well as of the concept of hybridization of the gallium atom (sp² and sp³), one expects an increase in the magnitude of the coupling constant $^1J$(71Ga,13C) in 4Ga relative to 3Ga. However, the calculated values are almost the same at 186.8 Hz (4Ga) and 185.5 Hz (3Ga). In 4Ga, the gallium atom is three-coordinate and therefore, negative contributions to the Fermi contact term have to be taken into account owing to magnetic-field induced mixing of σ and π or σ and σ* levels with small energy differences. The σ-π transitions are absent in 3Ga, and the energy difference between the σ-σ* transitions may be greater. The different electronic structure of 4Ga and 3Ga is also indicated by the calculated negative contributions from the paramagnetic spin-orbital term [19] (−11.6 Hz for 4Ga; −2.8 Hz for 3Ga). Usually, the calculations of coupling constants $^1J$(M,13C) (M = 29Si [20], 73Ge [21]) at the level of theory used here give values which are too small by about 20%. Otherwise, calculated coupling constants appear to be fairly reliable [22–25]. In the case of 2Ga, the calculated value $^1J$(71Ga,13C) is 166.7 Hz which compares well with the estimated experimental value (205 ± 30 Hz), considering the systematic error in the calculations. The experimental value $^1J$(71Ga,13C) for 1Ga (232 Hz) is thus consistent, since negative contributions to the Fermi contact term and negative contributions arising from the paramagnetic spin-orbital term are not present or much smaller in the case of the gallate 1Ga.
Experimental Section

The preparation and the handling of samples were carried out observing the necessary precautions to exclude air and traces of moisture. The solvents used were carefully dried by established methods. Starting materials such as LiBu’ (1.7 m in pentane) (Aldrich), gallium trichloride (anhydrous, beads, –10 mesh, 99.99 %) (Aldrich) and indium trichloride (anhydrous, powder, 99.999 + % metals basis) (Aldrich) were commercial products. Trit(tert-butyl)gallium (2Ga) [Sc] [1H NMR (500.1 MHz, C6D6, 298 K): δ (1J(C,1H) = 128.0), external GaCl3 in D2O] and tri(tert-butyl)indium (2In) [6b] [1H NMR (500.1 MHz, C6D6, 298 K): δ (1J(C,1H)) = 122.7] were prepared by literature procedures. Volatile materials were removed in vacuo.

NMR spectra were recorded at 23 °C on Bruker DRX 500 or Varian Inova 400 spectrometers (1H, 13C, 69Ga, 71Ga) and external InCl3 in D2O (115In) = 21.914458 MHz]. All calculations were performed using the GAUSSIAN03 program package [26]. Optimization of the gas phase geometries was carried out with DFT methods (B3LYP) [15] and the 6-311+G(d,p) basis set [16]. Frequencies were calculated analytically to characterize the stationary points of the optimized geometries as minima by the absence of imaginary frequencies.

Acknowledgement

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