Solid-state NMR Characterization of Six-coordinated Ga(III) Complexes with Sulfur-donor Ligands

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Gallium has two isotopic nuclear magnetic resonance (NMR)-active nuclei, $^{69}$Ga and $^{71}$Ga, both of which have a common spin of $I = 3/2$ but different quadrupole moments. $Q = 1.68 \times 10^{-26} \text{ m}^2$ and $Q = 1.06 \times 10^{-27} \text{ m}^2$, respectively. Aluminum, which is chemically similar to Ga, has the quadrupole moment of $Q = 1.49 \times 10^{-26} \text{ m}^2$ which is intermediate between those of $^{69}$Ga and $^{71}$Ga. Well-resolved Ga magic angle spinning (MAS) NMR spectra are difficult to obtain because of a given electric field gradient (EFG) of the central transitions (CTs) of $^{69}$Ga and $^{71}$Ga are broadened by a factor of about 11 and 4.8, respectively, compared to that of $^{27}$Al. Of the relatively few studies on the Ga MAS NMR spectra of Ga(III) compounds, most of these compounds have had oxygen-donor ligands. In this work, the solid-state structures of two N-dsustituted dithiocarbamate complexes of trivalent gallium ion: Ga(S$_2$CNR$_2$)$_3$ (R = CH$_3$ or C$_2$H$_5$) were characterized by $^{71}$Ga and $^{69}$Ga MAS NMR spectroscopy. The dithiocarbamate ions, which are sulfur-donor ligands, form four-membered chelate rings with the gallium, thereby affording the pseudo-octahedral Ga(III) complexes. The NMR parameters for the two complexes were compared with those for tris(acetylacetonato) gallium(III) complex. The NMR parameters for the two complexes were compared with those for tris(acetylacetonato) gallium(III) complex.

Figure 1 shows the $^{69}$Ga and $^{71}$Ga MAS NMR spectra of Ga(S$_2$CNEt$_2$)$_3$, Ga(S$_2$CNMe$_2$)$_3$, and Ga(acac)$_3$ complexes where Et = CH$_3$ and Me = C$_2$H$_5$. The CT peaks in their $^{69}$Ga MAS NMR spectra, which were measured at a spinning rate of 20 kHz, displayed well-defined powder patterns for half-integer spin nuclei. On the other hand, the CT peaks in the $^{71}$Ga MAS NMR spectra of the complexes other than Ga(S$_2$CNMe$_2$)$_3$, did not exhibit the whole lineshape, although they were measured at a spinning rate of 28 kHz. To obtain NMR parameters such as the isotropic chemical shift ($\delta$$_{iso}$), quadrupole coupling constant (C$_Q$), and asymmetry parameter ($\eta$) in Table 1, both $^{69}$Ga and $^{71}$Ga MAS NMR spectra were simulated using a STARS program (Varian Inc.). The ratio (~1.59) of C$_Q$ values of the $^{69}$Ga and $^{71}$Ga nuclei for each complex was almost equal to that of $^{27}$Al quadrupole moments. The $^{69}$Ga C$_Q$ values obtained in this work were comparable to those of $^{71}$Ga nuclei in the octahedral sites (GaO$_6$) in MgGa$_2$O$_4$ (C$_Q$ = 7.6 MHz) and Y$_2$Ga$_2$O$_7$:C$_Q$ = 4.1 MHz), and decreased in the following order, as listed in Table 1: Ga(S$_2$CNEt$_2$)$_3$ > Ga(acac)$_3$ > Ga(S$_2$CNMe$_2$)$_3$. The slightly smaller C$_Q$ value for the Ga(S$_2$CNMe$_2$)$_3$ complex compared to that for the Ga(S$_2$CNEt$_2$)$_3$ complex indicated that the electronic structure around the Ga nucleus in the former complex was less deviated from spherical symmetry than that in the latter complex. Masiotti et al. presented a linear

**Table 1.** NMR parameters obtained by simulating $^{69}$Ga and $^{71}$Ga MAS NMR spectra of Ga(S$_2$CNEt$_2$)$_3$, Ga(S$_2$CNMe$_2$)$_3$, and Ga(acac)$_3$ complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta$$_{iso}$ (ppm)</th>
<th>C$_Q$(MHz)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga(S$_2$CNEt$_2$)$_3$</td>
<td>-90.0 ± 2.0</td>
<td>6.3</td>
<td>10.0</td>
</tr>
<tr>
<td>Ga(S$_2$CNMe$_2$)$_3$</td>
<td>-98.0 ± 0.1</td>
<td>5.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Ga(acac)$_3$</td>
<td>-105.5 ± 0.5</td>
<td>5.9</td>
<td>9.3</td>
</tr>
</tbody>
</table>
correlation, with a scale factor of 3.1 for $^{119}$Ga$^+$ and $^{117}$Al between the EFG values of $^{119}$Ga$^+$ and $^{117}$Al for structurally analogous Ga and Al compounds in which only oxygen atoms occupy the first coordination sphere. Considering that the reported $^{117}$Al $C_{4v}$ value in tris(acetylactonato)aluminum(III), Al(acac)$_3$, is 3.03 MHz and that $C_{4v}$ is proportional to the product of EFG and quadrupole moment, the estimated ratio of EFG values of Ga(acac)$_3$ to Al(acac)$_3$ was 2.7, which was close to the Massiot's scale factor.

The $\eta$ value reflects the deviation from electronic cylindrical symmetry around the nucleus. The $\eta$ value for the Ga(S-CNMe)$_2$ complex in a triclinic crystal system was much larger (that for the Ga(S-CNEt)$_2$) and Ga(acac)$_3$ complexes in monoclinic crystal systems. This difference in the $\eta$ values can be explained theoretically in terms of the crystal system and the local symmetry of a complex unit. However, since the quadrupolar parameters such as $C_{4v}$ and $\eta$ are more strongly influenced by electric fields in closer distances, the $\eta$ values are mainly determined by the local symmetry of a complex unit. The difference in the symmetry between Ga(S-CNEt)$_2$ and Ga(S-CNMe)$_2$ complexes was also reflected in their $^{15}$N cross polarization (CP) MAS spectra. As shown in Figure 2, the $^{15}$N CP MAS spectrum of Ga(S-CNEt)$_2$ complex with a 2-fold axis showed two peaks at $\delta$ 126.9 and 123.7, the area ratio of which was ca. 2:1, while that of the Ga(S-CNMe)$_2$ complex, which has no 2-fold axis, showed three peaks at $\delta$ 102.0, 100.0, and 98.0. The $\eta$ value (0.12) for the Ga(S-CNEt)$_2$ complex was very similar to that (0.15) for the Al(acac)$_3$ complex. The lower signal-to-noise ratio for the spectrum of Ga(S-CNMe)$_2$ in Figure 2(B) than that of Ga(S-CNEt)$_2$ in Figure 2(A) is due to the lower efficiency of CP for Ga(S-CNMe)$_2$. The higher mobility of terminal methyl group in Ga(S-CNMe)$_2$ induces weaker $^{15}$N signal by CP from the methyl protons than from the methylene in Ga(S-CNEt)$_2$.

The Ga chemical shifts of the six-coordinate gallium compounds with only oxygen atoms in the first coordination sphere range from -80 to 74 ppm. The metal shielding in $^{119}$Ga by metal complexes with chalcogen-donor atoms tends to increase in the following order: O $<$ S $<$ Se. Therefore, the Ga nuclei in Ga(S-CNMe)$_2$ and Ga(S-CNEt)$_2$ complexes were more shielded than those in the six-coordinate gallium compounds with sulfur-donor ligands and also those in the four-coordinate gallium compounds with sulfur-donor ligands such as $\gamma$-Ga$_2$S$_2$. As listed in Table 1, the resonances of the Ga(S-CNMe)$_2$ complex was more shielded than that of the Ga(S-CNEt)$_2$ complex. Consistent with our results, in their liquid-state $^{71}$Ga NMR study of dithiocarbamate complexes of Ga(III) ion Dutta et al. showed that the resonance was deshielded with increasing steric hindrance of the R group in Ga(S-CNR$_2$). Massiot et al. found a linear correlation, $\delta$ ($^{119}$Ga) (ppm) = -2.76 + $\delta$ ($^{27}$Al) (ppm) - 1.2, between $^{27}$Al and $^{119}$Ga chemical shifts for structurally analogous Al and Ga compounds in which only oxygen atoms occupy the first coordination sphere.

In conclusion, Ga MAS NMR spectra of six-coordinate gallium complexes with sulfur-donor ligands were acquired and their NMR parameters were determined. The $C_{4v}$ values for pseudo-octahedral Ga(S-CNMe)$_2$ and Ga(S-CNEt)$_2$ complexes were comparable to those for the octahedral site (GaO$_6$) in various gallium oxides. The difference in the $\eta$ values between Ga(S-CNMe)$_2$ and Ga(S-CNEt)$_2$ complexes was explained in terms of the symmetry of complexes and was also reflected in their $^{15}$N CP MAS NMR spectra.

**Experimental Section**

The method for synthesizing Ga(S-CNEt)$_2$ and Ga(S-CNMe)$_2$ complexes has been described in a previous paper. The Ga(acac)$_3$ powder (99.99% purity) was purchased from Aldrich and used without any further purification. $^{11}$C, $^{13}$C, and $^{71}$Ga NMR spectra of the three complexes dissolved in CDCl$_3$ were obtained on a Varian Unity INOVA 500 spectrometer with the following results: $^{11}$C NMR: for Ga(S-CNEt)$_2$, $\delta$ 3.41 (s, -CH$_3$); for Ga(S-CNMe)$_2$, $\delta$ 3.70 (s, -CH$_3$). $\delta$ 3.79 (q, $J$ = 7.2 Hz, -CH$_2$). $\delta$ 5.43 (s, -CH=). $^{13}$C NMR: for Ga(S-CNMe)$_2$, $\delta$ 45.4 (CH$_2$). $\delta$ 203.5 (> C-N), for Ga(S-CNEt)$_2$, $\delta$ 121.1 (> C=CH$_2$). $\delta$ 49.5 (> C=CH$_2$). $\delta$ 201.1 (> C=O). Ga(acac)$_3$, $\delta$ 27.3 (> C=CH$_2$). $\delta$ 103.0 (> C=CH$_2$). $\delta$ 192.9 (C-O). $^{71}$Ga NMR: for Ga(S-CNMe)$_2$, $\delta$ -96.8; for Ga(S-CNEt)$_2$, $\delta$ -86.2; for Ga(acac)$_3$, $\delta$ -10.1.

Solid-state $^{1}$H and $^{13}$C NMR spectra were acquired at 14.1 T on a Unity INOVA 600 spectrometer using 2.5 mm zirconia rotors. The pulse widths for excitation were 1 $\mu$s for $^{1}$H and 2 $\mu$s for $^{13}$C with a pulse repetition delay time of 2 s. Transients between 1024 and 2000 were accumulated for acquiring the spectra. The chemical shifts of $^{1}$H and $^{13}$C were referenced to external 1 M aqueous gallium(III) nitrate solution. Nitrogen-15 CP MAS NMR spectra were also measured on a Unity INOVA 600 spectrometer with an H/X CP MAS probe equipped with 5 mm zirconia rotors. The proton n/2
pulse for CP was 7 μs. A variable amplitude CP method that is insensitive CP efficiency to spinning rates was used for improved CP efficiency at high spinning rates. The pulse repetition delay time was 5 s. Transients between 5000 and 30000 were accumulated for acquiring the spectra. Chemical shifts of $^{15}\text{N}$ were referenced to external NH$_4$Cl powder.

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References


