

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, ⁶⁹Ga and ⁷¹Ga, both of which have a common spin of $I = 3/2$ but different quadrupole moments, $Q = 1.68 \times 10^{-29} \text{ m}^2$ and $Q = 1.06 \times 10^{-29} \text{ m}^2$, respectively. Aluminum, which is chemically similar to Ga, has the quadrupole moment of $Q = 1.49 \times 10^{-29} \text{ m}^2$ which is intermediate between those of ⁶⁹Ga and ⁷¹Ga. Well-resolved Ga magic angle spinning (MAS) NMR spectra are difficult to obtain because for a given electric field gradient (EFG) the central transitions (CTs) of ⁶⁹Ga and ⁷¹Ga are broadened by a factor of about 11 and 4.8, respectively, compared to that of ²⁷Al.¹ Of the relatively few studies on the Ga MAS NMR spectra of Ga(III) compounds, most of these compounds have had oxygen-donor ligands.¹ In this work, the solid-state structures of two *N,N*-disubstituted dithiocarbamate complexes of trivalent gallium ion, Ga(S₂CNR₂)₃ ($R = \text{CH}_3$ or C_2H_5) were characterized by ⁷¹Ga and ⁶⁹Ga 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.² The NMR parameters for the two complexes were compared with those for tris(acetylacetonato) gallium(III), Ga(acac)₃, in which the acetylacetone ions form six-membered chelate rings with the gallium.³

Figure 1 shows the ⁷¹Ga and ⁶⁹Ga MAS NMR spectra of Ga(S₂CNEt₂)₃, Ga(S₂CNMe₂)₃, and Ga(acac)₃ complexes where Et = C_2H_5 and Me = CH_3 . The CT peaks in their ⁷¹Ga 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 ⁶⁹Ga MAS NMR spectra of the complexes other than Ga(S₂CNMe₂)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 (δ_{iso}), quadrupole coupling constant (C_Q), and asymmetry parameter (η) in Table 1, both ⁷¹Ga and ⁶⁹Ga MAS NMR spectra were simulated using a STARS program (Varian Inc.). The ratio (~1.59) of C_Q values of the ⁷¹Ga and ⁶⁹Ga nuclei for each complex was almost equal to that (1.58) of their quadrupole moments. The ⁷¹Ga C_Q values obtained in this work were comparable to those of ⁷¹Ga nuclei in the octahedral sites (GaO_6) in MgGa_2O_4 ($C_Q = 7.6 \text{ MHz}$) and $\text{Y}_3\text{Ga}_5\text{O}_{12}$ ($C_Q = 4.1 \text{ MHz}$),⁴ and decreased in the following order, as listed in Table 1: Ga(S₂CNEt₂)₃ > Ga(acac)₃ > Ga(S₂CNMe₂)₃. The slightly smaller C_Q value for the Ga(S₂CNMe₂)₃ complex compared to that for the Ga(S₂CNEt₂)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. Massiot *et al.* presented a linear

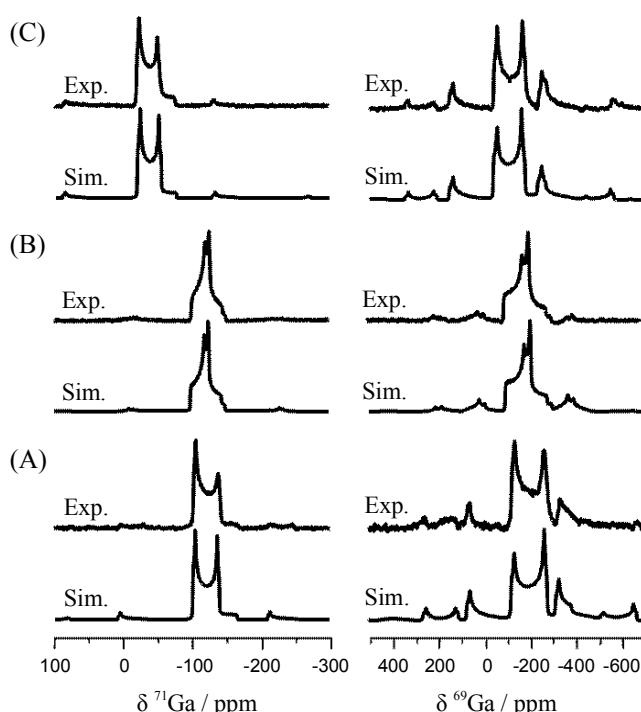


Figure 1. Experimental (top) and simulated (bottom) ⁷¹Ga and ⁶⁹Ga MAS NMR spectra of (A) Ga(S₂CNEt₂)₃, (B) Ga(S₂CNMe₂)₃, and (C) Ga(acac)₃ complexes.

Table 1. NMR parameters obtained by simulating ⁷¹Ga and ⁶⁹Ga MAS NMR spectra of Ga(S₂CNEt₂)₃, Ga(S₂CNMe₂)₃, and Ga(acac)₃ complexes

Complex	δ_{iso} (ppm)	$C_Q(\text{MHz})$		η
		⁷¹ Ga	⁶⁹ Ga	
Ga(S ₂ CNEt ₂) ₃	-90.0 \pm 2.0	6.3	10.0	0.09
Ga(S ₂ CNMe ₂) ₃	-98.0 \pm 0.1	5.0	8.0	0.75
Ga(acac) ₃	-10.5 \pm 0.5	5.9	9.3	0.12

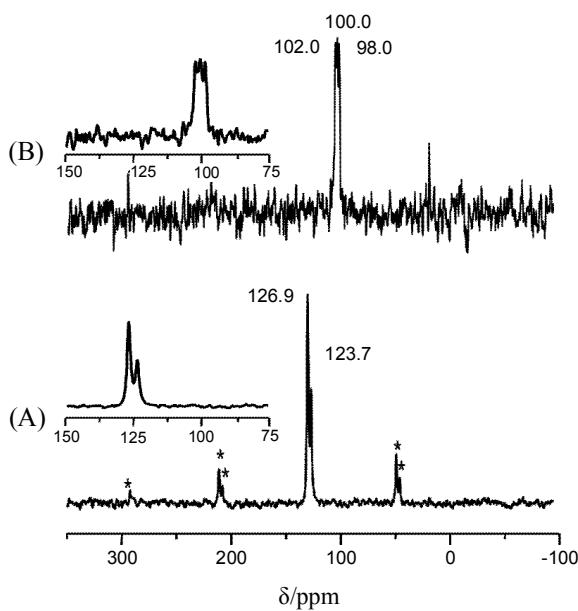


Figure 2. Experimental ^{15}N CP MAS NMR spectra of (A) $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$ at a spinning rate of 5 kHz and a contact time of 5 ms and (B) $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$ at a spinning rate of 7 kHz and a contact time of 3 ms. The spinning side bands are marked by asterisks.

correlation, with a scale factor of 3.1 for $^{71}\text{Ga}/^{27}\text{Al}$, between the EFG values of ^{71}Ga and ^{27}Al for structurally analogous Ga and Al compounds in which only oxygen atoms occupy the first coordination sphere.⁴ Considering that the reported ^{27}Al C_Q value in tris(acetylacetonato)aluminum(III), $\text{Al}(\text{acac})_3$, is 3.03 MHz⁵ and that C_Q is proportional to the product of EFG and quadrupole moment, the estimated ratio of EFG values of $\text{Ga}(\text{acac})_3$ to $\text{Al}(\text{acac})_3$ was 2.7, which was close to the Massiot's scale factor.

The η value reflects the deviation from electronic cylindrical symmetry around the nucleus. The η value for the $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$ complex in a triclinic crystal system² was much larger than that for the $\text{Ga}(\text{S}_2\text{CNEt}_2)_3$ and $\text{Ga}(\text{acac})_3$ complexes in monoclinic crystal systems.^{3,6} This difference in the η 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_Q and η are more strongly influenced by electric fields in closer distances, the η values are mainly determined by the local symmetry of a complex unit. The difference in the symmetry between $\text{Ga}(\text{S}_2\text{CNEt}_2)_3$ and $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$ 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 the $\text{Ga}(\text{S}_2\text{CNEt}_2)_3$ complex with a 2-fold axis showed two peaks at δ 126.9 and 123.7, the area ratio of which was *ca.* 2:1, while that of the $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$ complex, which has no 2-fold axis, showed three peaks at δ 102.0, 100.0, and 98.0. The η value (0.12) for the $\text{Ga}(\text{acac})_3$ complex was very similar to that (0.15)⁵ for the $\text{Al}(\text{acac})_3$ complex. The lower signal-to-noise ratio for the spectrum of $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$ in Figure 2(B) than that of $\text{Ga}(\text{S}_2\text{CNEt}_2)_3$ in Figure 2(A) is due to the lower efficiency of CP for $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$. The higher mobility of terminal methyl group in $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$ induces weaker ^{15}N signal by CP from the

methyl protons than from the methylene in $\text{Ga}(\text{S}_2\text{CNEt}_2)_3$.

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.^{4,7} The metal shielding in d^{10} metal complexes with chalcogen-donor atoms tends to increase in the following order : O < S < Se.⁸ Therefore, the Ga nuclei in $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$ and $\text{Ga}(\text{S}_2\text{CNEt}_2)_3$ complexes were more shielded than those in the six-coordinate gallium compounds with oxygen-donor ligands and also than those in the four-coordinate gallium compounds with sulfur-donor ligands such as $\gamma\text{-Ga}_2\text{S}_3$.⁹ As listed in Table 1, the resonance of the $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$ complex was more shielded than that of the $\text{Ga}(\text{S}_2\text{CNEt}_2)_3$ 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 $\text{Ga}(\text{S}_2\text{CNR}_2)_3$.¹⁰ Massiot *et al.* found a linear correlation, $\delta(^{71}\text{Ga}) \text{ (ppm)} = 2.84 \times \delta(^{27}\text{Al}) \text{ (ppm)} - 1$, between ^{27}Al and ^{71}Ga chemical shifts for structurally analogous Al and Ga compounds in which only oxygen atoms occupy the first coordination sphere. The new chemical shift point, (0, -10.5), for $\text{Al}(\text{acac})_3$ ⁵ and $\text{Ga}(\text{acac})_3$ was slightly deviated from the correlation line.

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_Q values for pseudo-octahedral $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$ and $\text{Ga}(\text{S}_2\text{CNEt}_2)_3$ complexes were comparable to those for the octahedral site (GaO_6) in various gallium oxides. The difference in the η values between $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$ and $\text{Ga}(\text{S}_2\text{CNEt}_2)_3$ complexes was explained in terms of the symmetry of complexes and was also reflected in their ^{15}N CP MAS spectra.

Experimental Section

The method for synthesizing $\text{Ga}(\text{S}_2\text{CNEt}_2)_3$ and $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$ complexes has been described in a previous paper.⁹ The $\text{Ga}(\text{acac})_3$ powder (99.99% purity) was purchased from Aldrich and used without any further purification. ^1H , ^{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: ^1H NMR: for $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$, δ 3.41 (s, -CH₃); for $\text{Ga}(\text{S}_2\text{CNEt}_2)_3$, δ 1.30 (t, $J = 7.2$ Hz, -CH₃), δ 3.79 (q, $J = 7.2$ Hz, -CH₂-); for $\text{Ga}(\text{acac})_3$, δ 2.01 (s, -CH₃), δ 5.43 (s, -CH=), ^{13}C NMR: for $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$, δ 45.1 (-CH₃), δ 202.5 (> C-N); for $\text{Ga}(\text{S}_2\text{CNEt}_2)_3$, δ 12.1 (-CH₃), δ 49.5 (-CH₂-), δ 201.1 (> C-N); for $\text{Ga}(\text{acac})_3$, δ 27.3 (-CH₃), δ 100.3 (-CH=), δ 192.9 (C=O), ^{71}Ga NMR: for $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$, δ -96.8; for $\text{Ga}(\text{S}_2\text{CNEt}_2)_3$, δ -86.2; for $\text{Ga}(\text{acac})_3$, δ -10.1.

Solid-state ^{71}Ga and ^{69}Ga 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 μs for ^{71}Ga and 2 μs for ^{69}Ga with a pulse repetition delay time of 2 s. Transients between 1024 and 3000 were accumulated for acquiring the spectra. The chemical shifts of ^{71}Ga and ^{69}Ga 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 $\pi/2$

pulse for CP was 7 μ s. 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}N were referenced to external NH_4Cl powder.

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