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Nuclear Quadrupole Resonance of 1,4-Dioxane Complexes with Gallium(II) and Gallium(III) Halides

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Nuclear quadrupole resonance spectra due to ^{35}Cl, ^{69}Ga, ^{81}Br, and ^{127}I nuclei have been recorded for complexes of Ga_2X_4 (X = Cl, Br, I) and GaX_3 (X = Cl, Br) with 1,4-dioxane. The electron density on the Ga atom donated by the O atom has been calculated according to the Townes–Dailey theory. The results show that the electron transfer from O to Ga is considerably smaller in the Ga_2X_4 complex than in the GaX_3 complex. The phase transition of $Ga_2Cl_4{\cdot}2C_4H_8O_2$ has been examined by measuring the temperature dependence of the NQR frequency and ^{35}Cl spin–lattice relaxation times. A second-order phase transition occurs near 181 K. The molecular motion in $GaCl_3{\cdot}C_4H_8O_2$ has also been discussed on the basis of the observed ^{35}Cl spin–lattice relaxation time.

Introduction

It has been reported that gallium dichloride and dibromide readily form coordination compounds with a variety of O- and N-donor ligands and that these compounds of empirical formula $Ga_2X_4L_2$ complexes probably have structures of the type $(GaL_4)^+(GaX_4)^-$, where L is a monodentate ligand and X is a halogen atom.[1] Recently, Beamish et al. found that $Ga_2Cl_4{\cdot}2C_4H_8O_2$ is a neutral complex of gallium(II) that has an ethane-like structure with a Ga–Ga bond.[2] They also proposed from the Raman spectra that the bromide and iodide analogues have a similar structure. Thereafter, Small and Worrall showed that $Ga_2Br_4{\cdot}2C_4H_8O_2$ and $Ga_2Cl_4{\cdot}2C_5H_5N$ have Ga–Ga bonds similar to $Ga_2Cl_4{\cdot}2C_4H_8O_2$ by means of X-ray analysis.[3,4] More recently, Beamish et al. reported that Raman spectra indicate that a number of $Ga_2X_4{\cdot}2L$ (X = Cl, Br) complexes have Ga–Ga bonds, and this was confirmed for $Ga_2Cl_4{\cdot}2C_5H_5N$ by X-ray structure analysis.[5]

With respect to the Ga–Ga bond, Evans and Taylor first proposed on the basis of Raman spectra that $((CH_3)_4N)_2Ga_2X_6$ (X = Cl, Br, I) complexes have ethane-like structures,[6] and later, Brown and Hall confirmed the existence of such a Ga–Ga bond by X-ray analysis.[7] We have previously reported the nuclear quadrupole resonances (NQR) in $R_2Ga_2X_6$ (R = $(CH_3)_4N$, $(C_2H_5)_4N$; X = Cl, Br) complexes and shown that the charge on each atom in the $Ga_2X_6^{2-}$ anion is independent of the cation but depends on the halogen atom.[8] In connection with these results, we observed the NQR of $Ga_2X_4{\cdot}2C_4H_8O_2$ in order to examine the bond nature and molecular motion. In the course of preparing the gallium(II) complexes, we found that the chloride produced mixtures of gallium(II) and gallium(III) complexes. The structure of $GaCl_3{\cdot}C_4H_8O_2$ was shown by X-ray diffraction to contain 5-coordinate gallium.[9] Therefore, we prepared also $GaX_3{\cdot}C_4H_8O_2$ (X = Cl, Br) complexes and observed their NQR in order to compare their bonding properties and molecular motion with those of $Ga_2X_4{\cdot}2C_4H_8O_2$.

Experimental Section

Ga_2Cl_4 was prepared by reducing $GaCl_3$ with Ga at about 470 K and purified by distilling off the unreacted $GaCl_3$. Ga_2Br_4 and Ga_2I_4 were prepared by heating equimolar amounts of Ga and $HgBr_2$ at about 430 K and Ga and HgI_2 at about 480 K, respectively, and purified by eliminating Hg.[10] The Ga_2X_4 complexes were prepared by reaction of Ga_2X_4 with 1,4-dioxane according to the method previously reported by Beamish et al.[2] These compounds were identified by C and H elemental analyses as listed in Table I. Furthermore, they were checked by Raman spectra, which gave characteristic bands at 112, 237, 340, 374, 394, 465, and 488 cm^{-1} for $Ga_2Cl_4{\cdot}2C_4H_8O_2$, 168, 193, 210, 240, 272, 285, 325, and 483 cm^{-1} for $Ga_2Br_4{\cdot}2C_4H_8O_2$, and 143, 229, 267, 304, and 478 cm^{-1} for $Ga_2I_4{\cdot}2C_4H_8O_2$, in agreement with the values of the literature.[2,5] The GaX_3 complexes were prepared by dissolving GaX_3 in 1,4-dioxane and by removing the solvent.

Table I. Analytical Data

compd	% C found	% C calcd	% H found	% H calcd
$Ga_2Cl_4{\cdot}2C_4H_8O_2$	18.54	21.00	3.92	3.53
$Ga_2Br_4{\cdot}2C_4H_8O_2$	15.21	15.11	2.47	2.51
$Ga_2I_4{\cdot}2C_4H_8O_2$	11.06	11.66	1.93	1.94
$GaCl_3{\cdot}C_4H_8O_2$	17.05	18.18	3.25	3.03
$GaBr_3{\cdot}C_4H_8O_2$	13.45	13.08	2.58	2.01

Table II. NQR Frequencies in $Ga_2X_4{\cdot}2C_4H_8O_2$

compd	nucleus	freq/MHz 77 K	freq/MHz 293 K
$Ga_2Cl_4{\cdot}2C_4H_8O_2$	^{35}Cl	16.13	15.51
		15.48	
	^{69}Ga	39.83	40.18
$Ga_2Br_4{\cdot}2C_4H_8O_2$	^{81}Br	109.42	107.68
		107.67	106.62
		106.76	104.94
		101.65	100.29
	^{69}Ga	30.54	30.69
		29.67	30.50
$Ga_2I_4{\cdot}2C_4H_8O_2$	^{127}I	139.83	138.01
		134.09	132.53
	^{69}Ga	28.09	28.05

NQR spectra were observed by using superregenerative spectrometers and Matec pulsed spectrometers. The NQR frequency was measured by use of a signal generator and frequency counter with an estimated accuracy of ±0.002 MHz for ^{35}Cl and ^{69}Ga and ±0.02 MHz for ^{81}Br. The spin–lattice relaxation time was measured by the 90°–90° pulse method to within an error of 10%. The temperature of the sample was measured with a thermocouple to an accuracy of ±1 K.

Results and Discussion

$Ga_2X_4{\cdot}2C_4H_8O_2$ (X = Cl, Br, I). Table II lists observed NQR frequencies in $Ga_2X_4{\cdot}2C_4H_8O_2$ (X = Cl, Br, I). The halogen NQR frequencies in these complexes are higher than those of $Ga_2X_6^{2-}$ (X = Cl, Br) ions (mean frequencies are 13.61 MHz of ^{35}Cl for the chloride and 94.73 MHz of ^{81}Br for the bromide) but in the

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same frequency region as that of Ga_2X_4 (15.8–15.9 MHz of ^{35}Cl, 102.4–107.7 MHz of ^{81}Br, and 113.6–163.7 MHz of ^{127}I).[8,11] The ^{69}Ga NQR frequencies in the present complexes are considerably higher than those of $Ga_2X_6^{2-}$ ions and Ga_2X_4 (on the average 23.04 MHz for $Ga_2X_6^{2-}$ (X = Cl, Br) and 16.9 MHz for Ga_2I_4). At room temperature one ^{35}Cl resonance line and one ^{69}Ga resonance line were observed for $Ga_2Cl_4{\cdot}2C_4H_8O_2$, four ^{81}Br and two ^{69}Ga lines for the bromide analogue, and two ^{127}I lines and one ^{69}Ga line for the iodide analogue. This spectrum of the bromide complex is consistent with that expected from the X-ray analysis,[3] but that of the chloride complex is not.[2] Since crystals of the chloride complex belong to space group $P\bar{1}$ and the molecule has no symmetry elements, four ^{35}Cl and two ^{69}Ga resonance lines should be observed. Our NQR results, however, suggest C_{2h} symmetry at room temperature and C_i at the lower temperature. The NQR lines of the iodide complex indicate that the molecule has C_i symmetry like the low-temperature phase of the chloride complex.

In the solid state, contributions to the NQR frequency arise mainly from the intramolecular chemical bond and slightly from the crystal field. The influence of the crystal field is very difficult to evaluate because it changes from substance to substance. For simplicity, the influence of the crystal field was neglected in the present calculation. In these complexes, the Ga atom is coordinated by two Cl atoms, one Ga atom, and one O atom. If the z axis is along the direction of the Ga–Ga bond, the Ga–O bond lies in the xz plane, and the molecule has a symmetry plane perpendicular to the Y axis, four hybrid orbitals are given by

$$\begin{aligned}\Psi_1 &= a\psi_s - d\psi_{px} + g\psi_{pz}\\ \Psi_2 &= b\psi_s + e\psi_{px} + f\psi_{py} + h\psi_{pz}\\ \Psi_3 &= b\psi_s + e\psi_{px} - f\psi_{py} + h\psi_{pz}\\ \Psi_4 &= c\psi_s - i\psi_{pz}\end{aligned} \qquad (1)$$

where $a = (1 - (\sin^2\beta)/N^2 - (\cos^2\beta)/M^2)^{1/2}$, $b = (^1/_2 - (\sin^2\alpha\cos^2\gamma)/N^2 - (\cos^2\alpha)/M^2)^{1/2}$, $c = (M^2 - 1)^{1/2}/M$, $d = (\sin\beta)/N$, $e = (\sin\alpha\cos\gamma)/N$, $f = (1/2)^{1/2}$, $g = (\cos\beta)/M$, $h = (\cos\alpha)/M$, $i = 1/M$, $M^2 = 1 + 2\cos^2\alpha\cos^2\beta$, and $N^2 = 2\sin^2\alpha\cos^2\gamma + \sin^2\beta$. α, β, and γ are the angles ∠X–Ga–Ga and ∠O–Ga–Ga and the projected ∠X–Ga–X angle in the xy plane, respectively. Both Ψ_2 and Ψ_3 are used for the Ga–X bonds and the Ψ_1 and Ψ_4 orbitals are used for the Ga–O and Ga–Ga bonds, respectively. If the populations of orbitals Ψ_1, Ψ_2 and Ψ_3, and Ψ_4 are denoted by A, B, and C, respectively, the electric field gradient components for ^{69}Ga are given by

$$\begin{aligned}q_{zz}/q_0 &= P/M - T/2N - B/2\\ q_{yy}/q_0 &= B - P/2M - T/2N\\ q_{xx}/q_0 &= T/N - P/2M - B/2\\ q_{xz}/q_0 &= (1/2NM)(6A\sin\alpha\cos\alpha\cos\gamma - 3B\sin\beta\cos\beta)\\ q_{xy}/q_0 &= q_{yz}/q_0 = 0\end{aligned} \qquad (2)$$

where $P = 2B\cos^2\alpha + A\cos^2\beta + C$, $T = 2B\sin^2\alpha\cos^2\gamma + A\sin^2\beta$, and q_0 is the electric field gradient due to a single 4p electron. In order to diagonalize this tensor, we must rotate the coordinate axes about the y axis. The rotation angle θ is represented by

$$\tan 2\theta = 2q_{xz}/(q_{zz} - q_{xx}) \qquad (3)$$

Consequently, a new set of e^2Qq_{XX}, e^2Qq_{YY}, and e^2Qq_{ZZ} are obtained and its principal component is given by

$$e^2Qq_{ZZ} = (e^2Qq_{zz}/2)(1 + (1/\cos 2\theta)) + (e^2Qq_{xx}/2)(1 - (1/\cos 2\theta)) \qquad (4)$$

The asymmetry parameter η is given by

$$\eta = (e^2Qq_{XX} - e^2Qq_{YY})/e^2Qq_{ZZ} \qquad (5)$$

The population of B is derived from the average of the halogen quadrupole coupling constants by the relation

$$B = e^2Qq_{zz}/(1 - s)e^2Qq_0 \qquad (6)$$

where s is the s-electron character, 0.15, and e^2Qq_0 is the quadrupole coupling constant due to one p electron of a halogen atom.[12] The bond angles in the iodide complex are assumed to be equal to those of the bromide analogue because the crystal structure of the former has not been reported as yet. From the observed e^2Qq_{zz} and η, one can obtain the values of A and C. In the present study, however, either A or C must be assumed since η cannot be determined without observing of the Zeeman effect on the resonance for the nucleus with $I = {}^3/_2$. The value of C is assumed to be 1.0 because the Ga–Ga bond is covalent.[8] Then the values of A and η can be obtained from eq 4 and 5. The results are listed in Table IV. We could not obtain a reasonable value of A for the chloride complex. The ^{69}Ga NQR frequencies of the chloride complex in Table II are abnormally higher than those of the rest although these complexes have a similar molecular structure. In general, the ^{69}Ga NQR frequency of the four-coordinated Ga atom depends on the distortion of the coordination from the regular tetrahedral coordination. Our assumption that the molecule has a symmetry plane implies that its distortion is somewhat modified and becomes small. However, this is not a significant reason because the difference between two ∠Cl–Ga–Cl angles is less than 2°. Even if the two ∠Cl–Ga–Cl angles are equal, the two Ga–Cl bonds are not always equal. The different Ga–Cl bonds increase the ^{69}Ga NQR frequency. The difference in the bond nature between two Ga–Cl bonds is reflected by the difference in the ^{35}Cl NQR frequency (0.65 MHz at 77 K). This leads to the difference of 0.014 in the B value obtained from eq 6, and its contribution to the ^{69}Ga frequency should be very small. Therefore, the difference in the bond nature is not the reason for the negative A value.

The crystal field effect was neglected in the present case as mentioned above. Its contribution to the ^{69}Ga frequency is considered to be small, i.e. about 3% of the total electric field gradient because the NQR-active Ga atom is not exposed to the crystal lattice.[13] Taking into account this magnitude of the crystal field effect, the values of A in these complexes increase by about 0.03.

A possible reason of the small negative A value is the contribution of inner 3d electrons to the bonding. This possibility is present not only in the chloride complex but also in the bromide and iodide ones. When some d character is added to the 4p orbitals, a large increase in ^{69}Ga NQR frequency occurs because e^2Qq_0 due to a 3d electron is several times larger than that due to a 4p one.[14] However, it is difficult to evaluate the degree of contribution of the 3d electron. In any event, the value of A is considered to be small and a tendency for A to decrease from the chloride to the iodide seems to be correct although the absolute values in Table IV are in doubt.

Figure 1 shows the temperature dependence of the ^{35}Cl and ^{69}Ga NQR frequencies in the chloride complex. Both ^{35}Cl and ^{69}Ga resonance lines show unusual temperature dependence, indicating the presence of a phase transition. The transition point was determined to be 181 ± 1 K by extrapolation from lower temperature. This is comparable to the value (184 ± 1 K) derived from the measurement of spin–lattice relaxation times, which will be described later. Above the transition point, one ^{35}Cl resonance line is observed up to 293 K. Below the transition point, the resonance line splits into a pair of lines with equal intensity and the magnitude of splitting becomes progressively large with increasing temperature.

Figure 2 shows the temperature dependence of the ^{81}Br and ^{69}Ga NQR frequencies in the bromide. With respect to ^{81}Br

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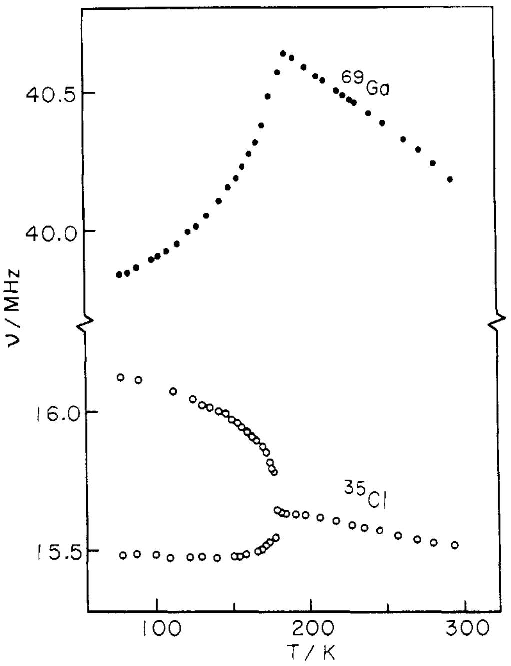

Figure 1. Temperature dependence of ^{35}Cl and ^{69}Ga NQR frequencies in $Ga_2Cl_4{\cdot}2C_4H_8O_2$.

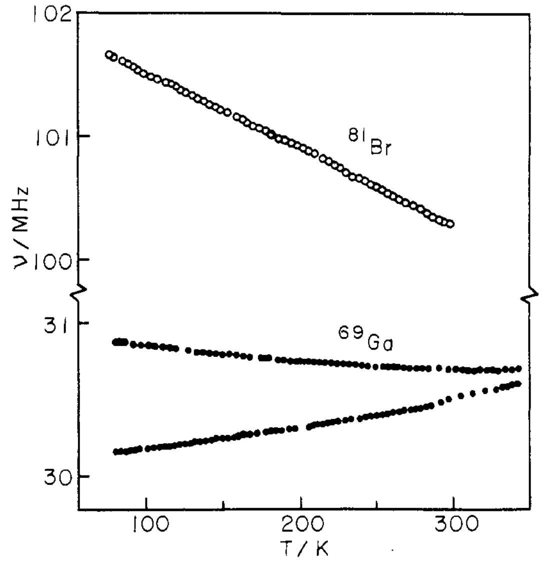

Figure 2. Temperature dependence of ^{69}Ga and ^{81}Br NQR frequencies in $Ga_2Br_4{\cdot}2C_4H_8O_2$.

resonance lines, the temperature dependence of the lowest line alone was examined because our preliminary observation of the other lines at 77, 196, and 293 K indicated that their frequencies decrease in a manner similar to that of the lowest line. The lowest ^{81}Br resonance line decreases monotonically in frequency with increasing temperature. With respect to the ^{69}Ga resonance lines, one of two lines decreases slightly but another increases with increasing temperature.

Figure 3 shows the temperature dependence of the ^{127}I and ^{69}Ga NQR frequencies in the iodide complex. As the temperature rises, two ^{127}I resonance lines decrease monotonically in frequency and the ^{69}Ga resonance line decreases only slightly.

Figure 4 shows the temperature dependence of the second moment of the ^{1}H NMR spectrum of the chloride complex. The second moment changes slightly from 18.5 ± 1.5 G^2 at 113 K to 16.6 ± 0.8 G^2 at 284 K and then shows a sharp decrease to 12.5 ± 0.7 G^2 at 303 K. No influence of the phase transition near 190 K was observed in the second moment. In this complex, 180° flip of CH_2 may occur, but this motion is hardly observed by CW ^{1}H NMR spectroscopy. In $Cl_2{\cdot}C_4H_8O_2$ the value of the second

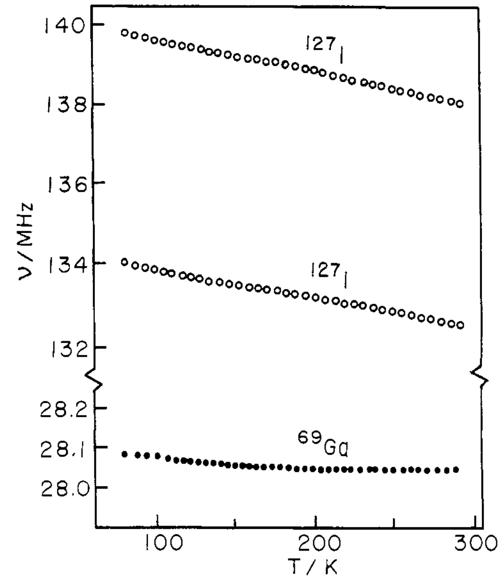

Figure 3. Temperature dependence of ^{69}Ga and ^{127}I NQR frequencies in $Ga_2I_4{\cdot}2C_4H_8O_2$.

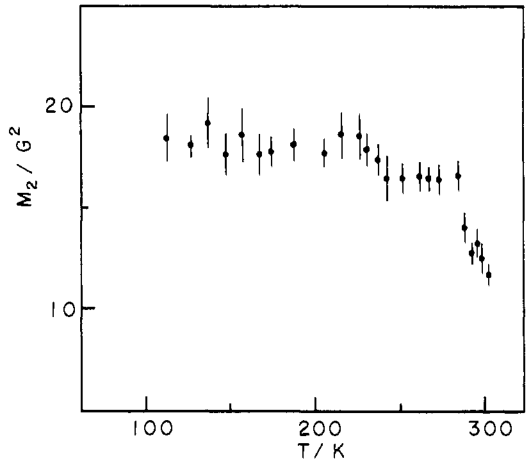

Figure 4. Temperature dependence of the second moment M_2 of the ^{1}H NMR spectrum of $Ga_2Cl_4{\cdot}2C_4H_8O_2$.

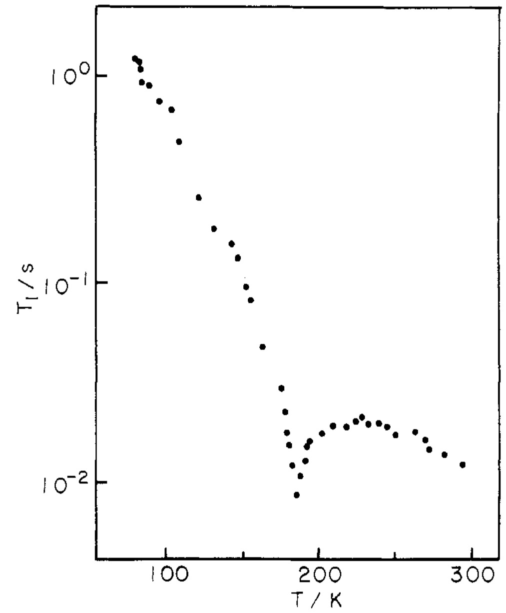

Figure 5. Temperature dependence of ^{35}Cl spin-lattice relaxation time in $Ga_2Cl_4{\cdot}2C_4H_8O_2$.

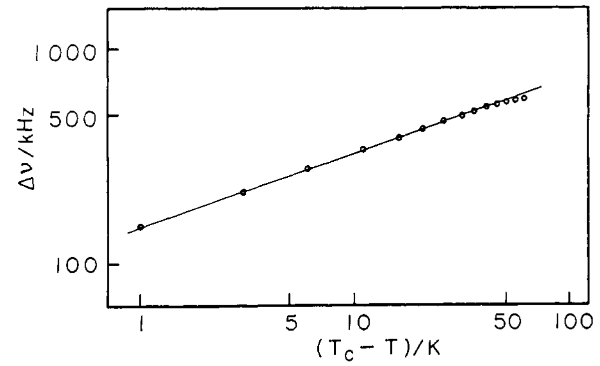

Figure 6. Separation of ^{35}Cl resonance lines below T_c vs $T_c - T$.

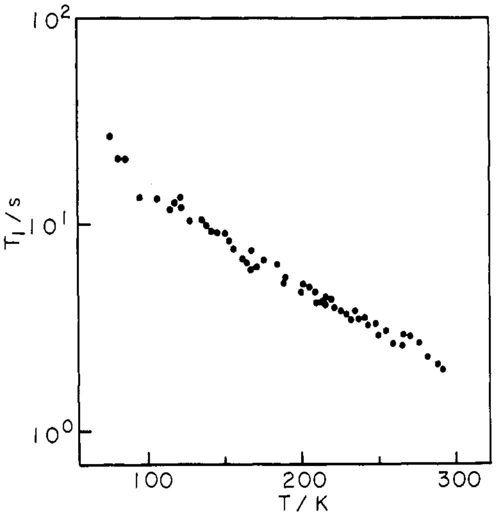

Figure 7. Temperature dependence of ^{81}Br spin–lattice relaxation time in $Ga_2Br_4 \cdot 2C_4H_8O_2$.

moment is 7.3 G^2 for the reorientation of the dioxane molecules about the O–O axis.[15] In view of this, it seems that the dioxane molecules in the chloride complex are reorientated about the O–O axis above 297 K.

Figure 5 reproduces the ^{35}Cl spin–lattice relaxation time T_1 of the chloride complex. As the temperature rises, T_1 of the higher ^{35}Cl line decreases rapidly up to ca. 184 K and makes a sharp dip. Above 230 K, $1/T_1$ decreases as predicted by the T^2 law.[16] The deviation from the T^2 law in the low-temperature region is due to the phase transition because the ^1H second moments indicate no molecular motion of the organic ligand and the ^{35}Cl resonance line splits into two lines. The phase transition is second order because no discontinuous jumps in the resonance frequencies were observed as shown in Figure 1.[17] In second-order transition, a sharp dip in T_1 is usually observed near the transition point, indicating the presence of critical fluctuations associated with the transition. The phase transition is a displacive one and not a reconstructive one because the transition was rapid and describable in terms of a structure change between the trans and lower symmetry structures caused by the rotation of the $GaCl_2O$ group around the Ga–Ga axis.

The phase transition of this type is expressed by the order parameter R in the form[18]

$$R \propto (T_c - T)^{\gamma} \qquad (7)$$

where γ is the critical exponent and T_c is the transition point. The separation $\Delta\nu$ between the resonance lines measures the temperature dependence of the order parameter.[19,20] Figure 6 shows the plot of $\Delta\nu$ against $T_c - T$ on logarithmic scales near T_c. In the temperature region 1 K < $(T_c - T)$ < 45 K, this plot gives a straight line with $\gamma = 0.336 \pm 0.004$, which is near $^1/_3$ reported for the ferroelectric and ferromagnetic transitions.[18]

Figure 7 reproduces the ^{81}Br spin–lattice relaxation time T_1 data for $Ga_2Br_4 \cdot 2C_4H_8O_2$ from 77 to 290 K. These experimental data are expressed by the equation

$$1/T_1 = 1.37 \pm 0.05 \times 10^{-5} T^{1.82 \pm 0.03}$$

Thus, the $1/T_1$ values obey the T^2 law. Therefore, the relaxation is governed by lattice vibration.[17]

$GaX_3 \cdot C_4H_8O_2$ (X = Cl, Br). Table III lists the observed NQR frequencies in $GaX_3 \cdot C_4H_8O_2$. The ^{35}Cl and ^{81}Br resonance frequencies are considerably lower than those of terminal halogens in GaX_3 (the mean frequency is 19.66 MHz of ^{35}Cl in the chloride at 306.2 K[21] and 140.75 MHz of ^{81}Br in the bromide at 77 K[22]). This lowering is due to the electron transfer from O to Ga. Such transfer increases the ionic character of the Ga–X bond, and therefore, the halogen NQR frequencies decrease.[12]

Table III. NQR Frequencies in $GaX_3 \cdot C_4H_8O_2$

compd	nucleus	freq/MHz 77 K	freq/MHz 293 K
$GaCl_3 \cdot C_4H_8O_2$	^{35}Cl	17.75	17.66
	^{35}Cl	17.69	17.46
	^{69}Ga	24.92	26.28
$GaBr_3 \cdot C_4H_8O_2$	^{81}Br	123.76	123.00[a]
	^{81}Br	122.89	122.10[a]
	^{69}Ga	25.98	26.81

[a] At 273 K.

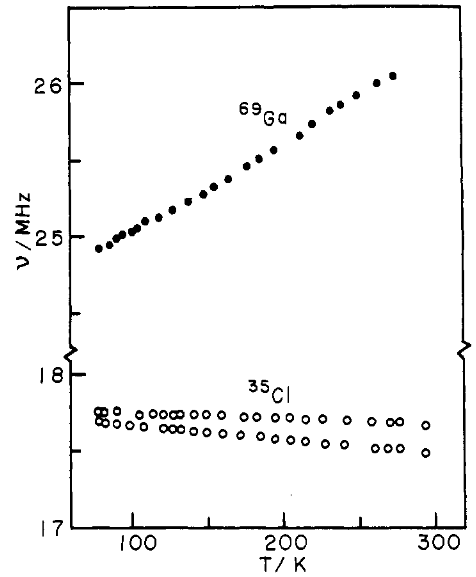

Figure 8. Temperature dependence of ^{35}Cl and ^{69}Ga NQR frequencies in $GaCl_3 \cdot C_4H_8O_2$.

Figure 8 shows temperature dependence of ^{35}Cl and ^{69}Ga NQR frequencies in the chloride complex. The two ^{35}Cl resonance lines decrease slightly in their frequencies with increasing temperature, but the separation between them increases, contrary to a general feature observed for terminal halogen atoms.[23] The ^{69}Ga reso-

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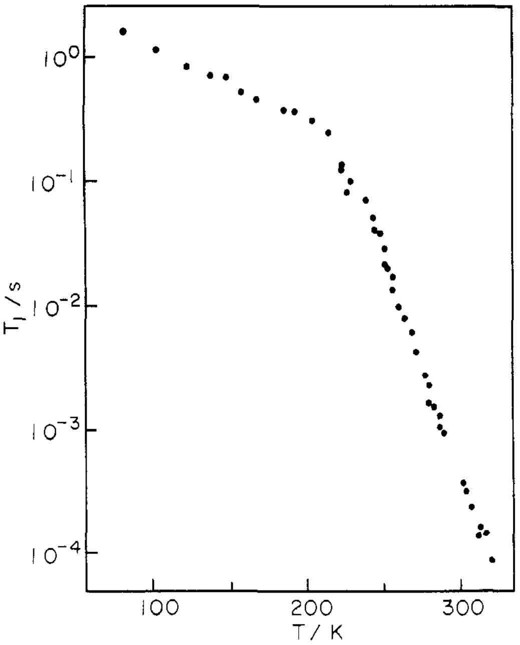

Figure 9. Temperature dependence of ^{35}Cl spin–lattice relaxation time in $GaCl_3{\cdot}C_4H_8O_2$.

nance frequency increases linearly as the temperature rises.

For the bromide complex, the two ^{81}Br resonance lines decrease monotonically in frequency from 77 to 273 K but the ^{69}Ga resonance line increases in its frequency. These curves are similar to those of the chloride.

In these compounds the coordination of the Ga atom is expressed by the three equatorial orbitals of Ga–X bonds constructed by the sp^2 hybridization and two axial orbitals of Ga–O bonds using only the p$_z$ orbital. The latter O–Ga–O bonds involve three-center–four-electron (3c-4e) bonds. Their orbitals are given by

$$\Psi_1 = \psi_{pz}$$

$$\Psi_2 = (1/U)((U^2 - 1)^{1/2}\psi_s + \psi_{px})$$

$$\Psi_3 = (1/2U^2)^{1/2}(\psi_s - (U^2 - 1)^{1/2}\psi_{px}) + (1/2)^{1/2}\psi_{py}$$

$$\Psi_4 = (1/2U^2)^{1/2}(\psi_s - (U^2 - 1)^{1/2}\psi_{px}) - (1/2)^{1/2}\psi_{py} \qquad (8)$$

where $U^2 = 1 + 2\cos^2\delta$ and 2δ is ∠X–Ga–X. The Ψ_1 orbital is used for the formation of the axial bonds by 3c-4e bonds. Ψ_2, Ψ_3, and Ψ_4 are used for the Ga–X equatorial bonds. If the populations are $2A$, B, and C for Ψ_1, Ψ_2, and Ψ_3, and Ψ_4, respectively, quadrupole coupling constants are given by

$$e^2Qq_{zz} = (2A - C/2 - (B + 2C\cos^2\delta)/2U^2)e^2Qq_0$$

$$e^2Qq_{yy} = (C - A - (B + 2C\cos^2\delta)/2U^2)e^2Qq_0$$

$$e^2Qq_{xx} = ((B + 2C\cos^2\delta)/U^2 - C/2 - A)e^2Qq_0 \qquad (9)$$

where e^2Qq_0 is 125 MHz.[12] Since the values of B and C are derived from the halogen resonance frequency by using eq 6, the observed ^{69}Ga frequency yields A as listed in Table IV. The asymmetry parameter η is close to 0 because two resonance frequencies due to the halogen nucleus in each complex are similar to each other; i.e., $B \simeq C$. As Table IV shows, the value of A in the chloride complex is smaller than that in the bromide, in analogy with $Ga_2X_4{\cdot}2C_4H_8O_2$ described above. It is worth noting that the values of A in $GaX_3{\cdot}C_4H_8O_2$ are considerably larger than those found in $Ga_2X_4{\cdot}2C_4H_8O_2$.

Table IV. Calculated Orbital Populations and Asymmetry Parameters in Gallium Complexes

compd	A	B	η
$Ga_2Cl_4{\cdot}2C_4H_8O_2$	−0.011	0.339	0.80
$Ga_2Br_4{\cdot}2C_4H_8O_2$	0.221	0.389	0.43
$Ga_2I_4{\cdot}2C_4H_8O_2$	0.267	0.469	0.56
$GaCl_3{\cdot}C_4H_8O_2$	0.389	0.380	0
$GaBr_3{\cdot}C_4H_8O_2$	0.433	0.451	0

Figure 9 shows the temperature dependence of ^{35}Cl spin–lattice relaxation times in $GaCl_3{\cdot}C_4H_8O_2$. From 77 to 215 K $1/T_1$ decreases as T^2 and then decreases exponentially. Therefore, the relaxation is governed by lattice vibration at lower temperature and by reorientation of the planar $GaCl_3$ group about the O–Ga–O axis at higher temperature. Its behavior is expressed by the well-known equation[23]

$$1/T_1 = aT^n + be^{-E/RT} \qquad (10)$$

By fitting eq 10 to the experimental T_1 values, we obtain

$$1/T_1 = 2.04 \pm 0.06 \times 10^{-4}T^{1.81\pm0.03} + 4.33 \pm 0.05 \times 10^{12}e^{-5.37\pm0.02\times10/RT}$$

The activation of the reorientation is 53.7 ± 0.2 kJ/mol, and this value is comparable with those for CCl_3 groups in several organic compounds.[17]

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