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Nuclear Quadrupole Resonance of $AlBr_3$ Molecular Complexes

Tsutomu Okuda,* Hiroshi Ohta, Hideta Ishihara, Koji Yamada, and Hisao Negita
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730

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We observed the ^{81}Br NQR of several molecular complexes of $AlBr_3$ with amines such as $(CH_3)_3N$, C_5H_5N, $C_6H_5NH_2$, and $(C_6H_5)_2NH$. All the ^{81}Br resonance lines were found in the frequency range of 78—86 MHz at room temperature except for $AlBr_3 \cdot 2C_5H_5N$. From the Zeeman analysis, it was proved that $AlBr_3 \cdot 2C_5H_5N$ should be expressed with the molecular formula $2AlBr_3 \cdot 4C_5H_5N$ and contains cation species $AlBr_2(C_5H_5N)_4^+$ with two ^{81}Br resonance lines near 70 MHz and anion species $AlBr_4^-$ with four ^{81}Br resonance lines near 80 MHz. The two ^{81}Br resonance lines of $AlBr_3 \cdot (CH_3)_3N$ disappeared at about 40 °C due to hindered rotation of the whole molecule. The lower two ^{81}Br resonance lines of $AlBr_2(C_5H_5N)_4^+$ have positive temperature coefficients.

Aluminum tribromide is a Lewis acid and forms a number of molecular complexes with organic bases. The mechanism of complex formation is assumed to be mainly due to the interaction between the lone pair of the donor atom and the vacant sp^3 hybrid orbital of the Al atom.

NQR has been widely used for the study of these complexes of the $n\sigma$ type. Some NQR frequencies have been reported for molecular complexes of the type $AlBr_3 \cdot L$ (L=ethers, ketones, and pyridine).[1,2] However, no NQR result has been reported for the molecular complexes of the type $AlBr_3 \cdot 2L$.

In this investigation, we prepared several molecular complexes of $AlBr_3$ with amines and observed the ^{81}Br NQR spectra in order to examine the character of Al–Br bonds and the molecular structure.

Experimental

The complexes of $AlBr_3 \cdot (CH_3)_3N$ and $AlBr_3 \cdot 2(CH_3)_3N$ were prepared by the procedure described in the literature.[3,4] The others were obtained by melting the stoichiometric amounts of $AlBr_3$ and L ($L=C_5H_5N$, $C_6H_5NH_2$, and $(C_6H_5)_2NH$) in closed glass ampoules. The single crystals of $AlBr_3 \cdot C_6H_5NH_2$ and $AlBr_3 \cdot 2C_5H_5N$ were grown by the method described previously.[5] The spectrometer used in the present experiment was a super-regenerative oscillator, and the absorption lines were observed on an oscilloscope. The Zeeman effect was examined by means of the zero-splitting cone method in a weak magnetic field of about 250 G provided by a Helmholtz coil. The temperature dependences of NQR frequencies were measured in the temperature range from liquid nitrogen temperature to the melting point. The temperature of the sample was determined using a copper-constantan thermocouple.

Results and Discussion

Table 1 shows ^{81}Br NQR frequencies and the signal-to-noise ratios in several molecular complexes of $AlBr_3$ with amines, determined at room temperature.

$AlBr_3 \cdot (CH_3)_3N$ and $AlBr_3 \cdot 2(CH_3)_3N$. $AlBr_3 \cdot (CH_3)_3N$ shows two ^{81}Br resonance lines with the intensity ratio of about 1:2. Though the crystal structure of this complex has not been determined as yet, $AlCl_3 \cdot (CH_3)_3N$ has been shown to have an ethane-like structure containing an Al–N bond, by means of X-ray diffraction.[6] The molecular structure of the bromide seems to be similar to that of the chloride in the light of the NQR results.

TABLE 1. ^{81}Br NQR FREQUENCIES IN $AlBr_3$ MOLECULAR COMPLEXES AT ROOM TEMPERATURE

Compounds		ν (MHz)	S/N
$AlBr_3 \cdot (CH_3)_3N$		79.108	4
		80.471	9
$AlBr_3 \cdot 2(CH_3)_3N$		83.168	4.5
		84.290	2.5
$AlBr_3 \cdot C_5H_5N$		79.575	7
		80.565	5
		81.424	7
$AlBr_3 \cdot 2C_5H_5N$	A	69.875	5.5
	B	69.955	5
	C	79.589	5
	D	79.667	5
	E	81.328	4.5
	F	81.331	4.5
$AlBr_3 \cdot C_6H_5NH_2$	A	79.194	3
	B	79.899	3.5
	C	84.853	4
$AlBr_3 \cdot (C_6H_5)_2NH$		78.497	4
		85.380	4.5
		85.511	4.5
Al_2Br_6[a]		79.84	(bridge)
		92.45	(terminal)
		93.61	(terminal)

a) T. Okuda *et al.*, *J. Chem. Phys.*, **52**, 5489 (1970).

The temperature dependences of ^{81}Br NQR frequencies were observed. Each resonance line began to broaden at about 30 °C and was no longer observable at about 40 °C, which is much below its melting point 156.9 °C. This disappearance is probably due to the hindered rotation of the whole molecule in the same manner as $BCl_3 \cdot (CH_3)_3N$ and $BBr_3 \cdot (CH_3)_3N$.[7,8] In the slope of the resonance frequency *versus* temperature curve we could not observe any abnormality which would be due to the reorientation of a methyl group or the rotation of a trimethylammonio group.[7]

Two ^{81}Br resonance lines were observed for $AlBr_3 \cdot 2(CH_3)_3N$. Their resonance frequencies are considerably higher than those of $AlBr_3 \cdot (CH_3)_3N$. Beattie *et al.* suggested from the study of the Raman spectra that the central Al atom in $AlBr_3 \cdot 2(CH_3)_3N$ is coordinated trigonal-bipyramidally, having two N atoms at axial sites and three Br atoms at equatorial sites.[4] This configuration about the Al atom is supported from the

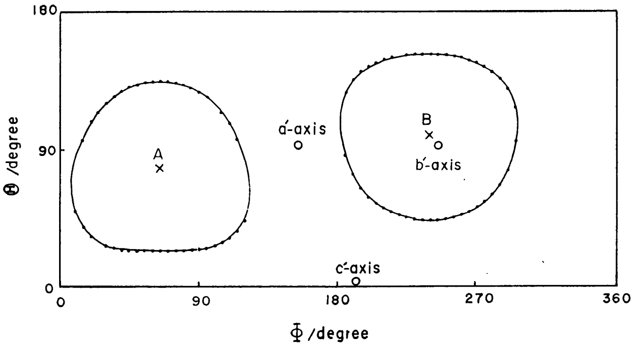


Fig. 1a. Zero-splitting patterns of ^{81}Br Zeeman lines of $AlBr_2(C_5H_5N)_4^+$ ion in $AlBr_3 \cdot 2C_5H_5N$.

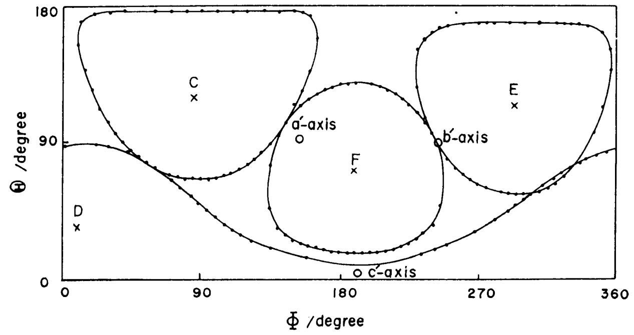


Fig. 1b. Zero-splitting patterns of ^{81}Br Zeeman lines of $AlBr_4^-$ ion in $AlBr_3 \cdot 2C_5H_5N$.

present results, because the difference in resonance frequencies is small.

$AlBr_3 \cdot C_5H_5N$ and $AlBr_3 \cdot 2C_5H_5N$. As listed in Table 1, three and six ^{81}Br resonance lines were observed in $AlBr_3 \cdot C_5H_5N$ and $AlBr_3 \cdot 2C_5H_5N$, respectively. Let us label the six resonance lines A, B, ···, F, from the lower to the higher, and label the Br atoms contributing to A, B, ···, F, Br(A), Br(B), ···, Br(F). It is found that two resonance lines, A and B, are remarkably lower than the rest. The Zeeman effect on ^{81}Br resonance lines in $AlBr_3 \cdot 2C_5H_5N$ was measured using a single crystal. Zero-splitting patterns are shown in Figs. 1a and 1b. Although four zero-splitting patterns were obtained for each resonance line, these figures show only one set of them which corresponds to a molecule in order to avoid unnecessary complexity. As all the asymmetry parameters are within ten percent, as listed in Table 2, no bridging Br atom is commonly assumed to exist in this complex, and the center of the zero-splitting pattern, *i.e.*, the direction of the z-principal axis of the electric field gradient, is regarded as the direction of Al–Br bond. Angles between Al–Br bonds were thus obtained from these patterns. The crystallographic axes were not determined from the Zeeman effect alone because of the higher class of crystal symmetry, though the axes corresponding to them were obtained from the symmetry of the zero-splitting pattern. For convenience, the axes obtained from NQR are arbitrarily termed the a'-, b'-, and c'-axis; these are perpendicular to each other. Angles between these axes and Al–Br bonds are tabulated in Table 3. The Al–Br(A) bond is perpendicular to the a'-axis and exists in the b'c' plane. Bond angles, ∠Br–Al–Br, are liested in Table 4. On the basis of the results obtained, the directions of Al–Br bonds in $AlBr_3 \cdot 2C_5H_5N$ are shown in Fig. 2. Br(A) and Br(B), whose ^{81}Br NQR

Table 2. ^{81}Br NQR parameters in $AlBr_3$ molecular complexes at room temperature

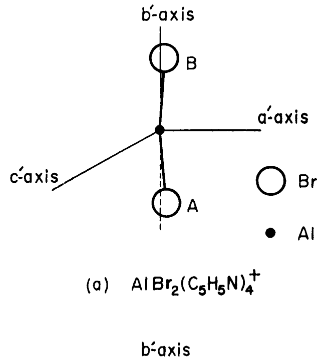
Compounds	η (%)		e^2Qq/h(MHz)
$AlBr_3 \cdot 2C_5H_5N$	A	4.0	139.71
	B	9.8	139.69
	C	3.7	159.14
	D	7.8	159.17
	E	9.7	162.40
	F	5.9	162.57
$AlBr_3 \cdot C_6H_5NH_2$	A	10.3	158.11
	B	9.0	159.58
	C	3.2	169.68

Table 3. Angles between the X-axes (X=a', b', c') and the z-axes in $AlBr_3 \cdot 2C_5H_5N$

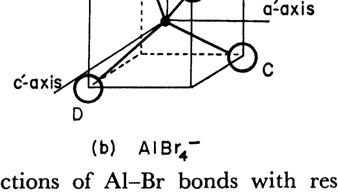
z-Axes	X=a'	X=b'	X=c'
Al–Br(A)	89.6°	170.7°	99.3°
Al–Br(B)	84.0	9.0	96.7
Al–Br(C)	69.0	137.4	125.0
Al–Br(D)	122.5	113.2	41.8
Al–Br(E)	129.7	52.7	118.2
Al–Br(F)	39.3	56.5	71.8

Table 4. Bond angles in $AlBr_3 \cdot 2C_5H_5N$

∠Br(A)–Al–Br(B)	173.5°
∠Br(C)–Al–Br(D)	109.4
∠Br(C)–Al–Br(E)	113.8
∠Br(C)–Al–Br(F)	107.9
∠Br(D)–Al–Br(E)	104.3
∠Br(D)–Al–Br(F)	113.6
∠Br(E)–Al–Br(F)	108.0



(a) $AlBr_2(C_5H_5N)_4^+$



(b) $AlBr_4^-$

Fig. 2. Directions of Al–Br bonds with respect to the a'-, b'-, and c'-axis in $AlBr_3 \cdot 2C_5H_5N$.

frequencies are much lower than the rest, are at the axial sites and four pyridines are at the equatorial sites, near the a'c' plane, because of the well-known stableness of a six-coordinated Al atom. Br(C), Br(D), Br(E), and Br(F) are considered to belong to $AlBr_4^-$. Therefore, $AlBr_3 \cdot 2C_5H_5N$ is expressed with the molecular formula $2AlBr_3 \cdot 4C_5H_5N$ and contains cation species $AlBr_2(C_5H_5N)_4^+$ and anion species $AlBr_4^-$.

Recently, an X-ray study by Howard *et al.* revealed that the crystal of $AlCl_3 \cdot 2CH_3CN$ contains discrete $AlCl(CH_3CN)_5^{2+}$ and $AlCl_4^-$ ions together with one uncoordinated CH_3CN molecule per asymmetry unit.[9] Schmulbach reported from the phase study of $AlCl_3$–CH_3CN system that $AlCl_3 \cdot CH_3CN$ melts at 183.4 °C but $AlCl_3 \cdot 2CH_3CN$ melts incongruently at 74.2 °C.[10] The extraordinarily low melting point of the latter may be due to the solvation. On the other hand, the phase study of $AlBr_3$–C_5H_5N system showed that $AlBr_3 \cdot C_5H_5N$ and $AlBr_3 \cdot 2C_5H_5N$ melt congruently at 116.0 °C and 183.4—185.1 °C, respectively.[11] The tendency to melt in the 1: 1 and 1: 2 complexes is different between $AlCl_3$–CH_3CN and $AlBr_3$–C_5H_5N systems. This seems to arise from the difference in ionic structure of the 1: 2 complex between the two systems.

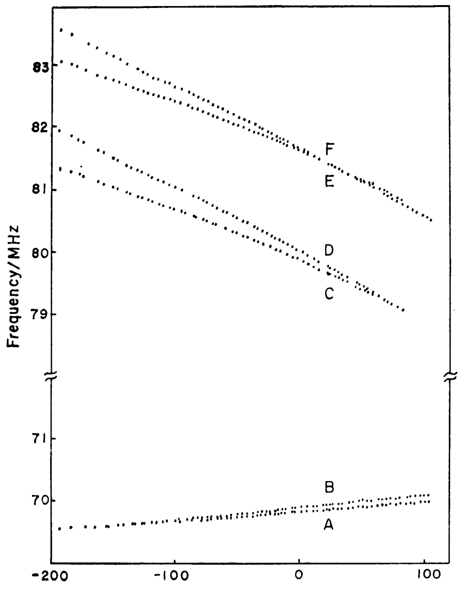


Fig. 3. Temperature dependences of ^{81}Br NQR frequencies in $AlBr_3 \cdot 2C_5H_5N$.

The temperature dependence of ^{81}Br NQR frequencies in $AlBr_3 \cdot 2C_5H_5N$ is shown in Fig. 3. In general, NQR frequencies decrease with increasing temperature as the electric field gradient of the resonant nuclei is averaged by the exciting of molecular motions. In this case, resonance frequencies corresponding to Br(A) and Br(B) increase with increasing temperature, while those of the rest decrease. Various compounds showing a positive temperature dependence have been found and the abnormality has been explained in terms of π-bonding or hydrogen bonding.[12,13] In the present case, a hydrogen bond does not occur because pyridine is not a proton donor but a proton acceptor.[14] We attributed the present positive temperature coefficient to a weak pπ–dπ bond between aluminum and bromine atoms. This is probably due to π-back donation from the $4p_x$ and $4p_y$ orbitals of the bromine atom to the vacant 3d orbital of six-coordinated aluminum atom; the resonance frequency of the bromine atom thus decreases. However, this effect is cancelled with increasing temperature because the thermal vibration breakes the π-bond. Accordingly, the frequency increases with temperature will result from the stronger effect of the latter.

$AlBr_3 \cdot C_6H_5NH_2$ and $AlBr_3 \cdot (C_6H_5)_2NH$. Three resonance lines (designated as A, B, and C) were observed in $AlBr_3 \cdot C_6H_5NH_2$. There is a large difference in the frequency between the higher and the lower resonance lines. Since resonance lines were weak, we observed only a few zero-splitting patterns whose z-principal axes formed large angles to the rf coil axis. Asymmetry parameters and quadrupole coupling constants obtained are listed in Table 2. The asymmetry parameters of Br(A) and Br(B) are rather large, whereas that of Br(C) is small. This seems to be due to the difference in intermolecular interaction.

In contrast to $AlBr_3 \cdot C_6H_5NH_2$, two ^{81}Br resonance lines were observed in the high region and one line in the low region for $AlBr_3 \cdot (C_6H_5)_2NH$. This discrepancy between the two complexes may arise from a difference in intermolecular interaction or from a dimer formation like $2AlBr_3 \cdot C_6H_6$ because of a large steric effect of the ligand. The crystal structure determination is very desirable in order to discuss this problem in more detail.

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