^{81}Br and ^{27}Al NQR of AlBr$_3$ · 2 C$_5$H$_5$N, AlBr$_3$ · 1.5 CH$_3$CN, and AlBr$_3$ · 2 CH$_3$CN *

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^{81}Br NQR was studied in AlBr$_3$ · 2 C$_5$H$_5$N, AlBr$_3$ · 1.5 CH$_3$CN, and AlBr$_3$ · 2 CH$_3$CN. From the NQR spectra it is apparent that the solid compounds are build up by ion pairs [AlBr$_2$(C$_5$H$_5$N)$_4^+$, AlBr$_4^-$], [Al(CH$_3$CN)$_6^{3+}$, 3 AlBr$_4^-$], and [AlBr(CH$_3$CN)$_5^{2+}$, 2 AlBr$_4^-$ · CH$_3$CN], respectively. ^{27}Al NQR detected by SEDOR technique supports these structural models. Using these NQR parameters, the metal-ligands interactions in the six-coordinated complexes is discussed on the basis of the donor strength. In the case of AlBr$_3$ · 2 CH$_3$CN two types of reorientational motion of the AlBr$_4^-$ tetrahedra were detected from the spin lattice relaxation times and from fade-out phenomena of the ^{81}Br NQR signals.

Introduction

Aluminum or gallium hallide forms many 1 : 1 compounds with donor molecules, X$_3$M-Donor, in which the central metal M has a tetrahedral configuration with three-fold symmetry. In these cases the donor strength may be evaluated from the halogen and Al or Ga nuclear quadrupole coupling constants as was reported by Tong in his ^{35}Cl and ^{69}Ga NQR study for the GaCl$_3$-Donor system [1]. That is to say, the NQR frequency of the terminal Cl decreases slightly but that of Ga decreases drastically with increasing donor strength. On the other hand, by means of ^{27}Al NMR spectroscopy many types of 4-, 5-, and 6-coordinated complexes have been reported in solutions of the AlX$_3$-organic Lewis base system [2–8]. Some of them have been isolated as crystals and studied by infrared and Raman spectroscopy [9–11] and by X-ray diffraction [12–15]. In these compounds only AlX$_4^-$ tetrahedra were found as the anionic species. There are many ^{81}Br or ^{35}Cl NQR data available for this anion [16, 17]. However, little is known about the chemistry of the 5- and 6-coordinated complexes of aluminum. Especially coordination complexes having mixed ligands such as AlX$_3$D$_2$, AlX$_3$D$_3$, AlX$_2$D$_4^-$, and AlXD$_5^{2+}$ (X = Cl, Br; D = donor molecule) are very interesting systems for NQR studies in order to get information about the cis-trans effect, the donor strength of the ligand, and the electronic distribution around the central metal. In this paper we report on ^{81}Br and ^{27}Al NQR of the title compounds and discuss their structure, dynamics, and bonding.

Experimental

AlBr$_3$ · 2 Py (Py: pyridine) has a congruent melting point at 185 °C. Single crystals were grown from the melt containing stoichiometric amounts of AlBr$_3$ and Py using the Bridgman method [18]. Found: C, 28.12; H, 2.48; N, 6.51%. Calcd. for AlBr$_3$ · 2 Py: C, 28.27; H, 2.37; N, 6.59%. On the other hand in the AlBr$_3$-MeCN (MeCN: acetonitrile) system, only the 1 : 1 compound has a congruent melting point but the 1 : 1.5 and 1 : 2 compounds decompose below their melting points. These two compounds were crystallized from acetonitrile solutions. Because of their strong hygroscopy the C, H, N-analysis was very difficult, but the ratio of the CH$_3$CN was determined to be 1.05 : 1.53 : 2.00 for 1 : 1, 1 : 1.5, 1 : 2 compounds, respectively. The 1 : 2 compound was also identified by the X-ray powder diagram reported by Dalibart et al. [10].

The ^{81}Br NQR spectra were detected by a superregenerative spectrometer and also by a Matec pulse spectrometer. The spin lattice relaxation times were measured by the 90° – 90° or 4-pulse method [19].

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A homemade attachment was used to measure T_1 with the 4-pulse method in which a recovery of an echo amplitude was monitored. This method is useful for samples with a strong echo signal but very short T_2^*.

The ^{27}Al NQR was detected by a spin echo double resonance method (SEDOR) in the frequency range from 250 kHz to 3 MHz monitoring a strong ^{81}Br NQR signal as was described elsewhere [20].

Results and Discussion

$AlBr_3 \cdot 2MeCN$

Figure 1 shows the temperature dependence of the ^{81}Br NQR frequencies for $AlBr_3 \cdot 2MeCN$. At 77 K eight ^{81}Br NQR lines were detected in the frequency range from 78 to 83 MHz, and furthermore one signal was observed at 73 MHz, about 10% lower in frequency. Only the lowest NQR signal out of nine showed a positive temperature coefficient, $d\nu/dT > 0$, suggesting that it has considerably different bonding properties. There are no single crystal structure data available for this compound. On the basis of X-ray powder diffraction [10], the bromide was reported to be isomorphous with the chloride. According to the chloride structure, the $AlCl_3 \cdot 2MeCN$ crystal consists of ion pairs, $AlCl(MeCN)_5^{2+}$ and $2AlCl_4^-$, and one solvent MeCN molecule [12]. The NQR spectra shown in Fig. 1 are consistent with the chloride structure, i.e., eight NQR signals at about 80 MHz could be assigned to the two $AlBr_4^-$ anions and the lowest one at about 73 MHz belongs to the Br atom in the cation having the octahedral coordination $AlBr(MeCN)_5^{2+}$.

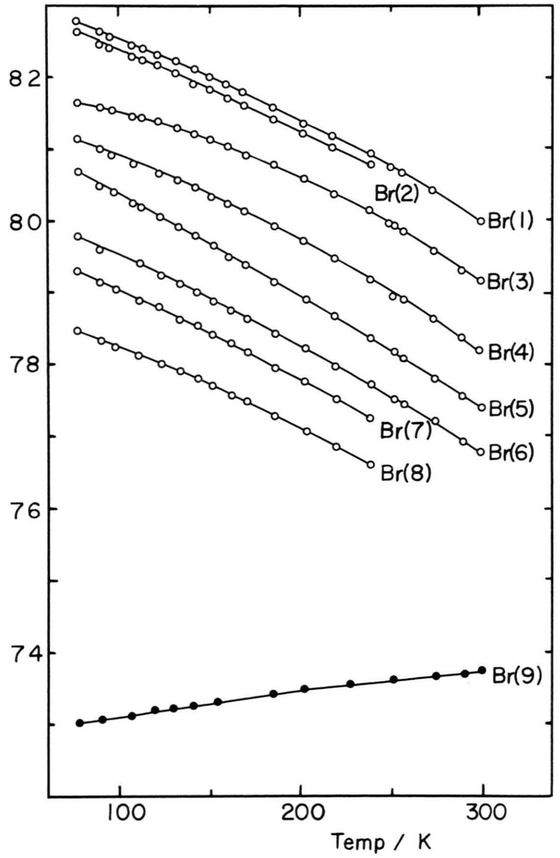

Fig. 1. Temperature dependence of the ^{81}Br NQR in $AlBr_3 \cdot 2MeCN$.

Table 1. ^{81}Br NQR frequencies of $AlBr_3 \cdot 2Py$, $AlBr_3 \cdot 2MeCN$ and $AlBr_3 \cdot 1.5MeCN$.

Compounds	^{81}Br NQR freq. [MHz]		Assignment
	77 K	300 K	
$AlBr_3 \cdot 2MeCN$	82.770	79.980	$AlBr_4^-$
	82.612		
	81.631	79.110	
	81.150	78.162	
	80.683	77.374	
	79.773	76.767	
	79.288		
	78.468		
	73.037	73.745	$AlBr(MeCN)_5^+$
$AlBr_3 \cdot 1.5MeCN$	81.18, 80.93		$AlBr_4^-$
	80.63, 80.23		
	79.83, 79.72		
	79.65, 78.79		
	78.32, 78.12		
	77.97, 77.32		
$AlBr_3 \cdot 2Py$ [a]	83.587	81.331	$AlBr_4^-$
	83.064	81.328	
	81.960	79.667	
	81.375	79.589	
	69.582 [b]	69.955	$AlBr_2(Py)_4^+$
		69.875	

[a] Ref. [24]. – [b] Doublet.

On the other hand, the ^{27}Al NQR frequencies detected by the SEDOR technique for this compound are listed in Table 2. In the SEDOR experiment we could determine not only the ^{27}Al NQR frequency but also their assignment, because the sensitivity of the SEDOR spectra depends upon the dipole-dipole interaction between them [21, 22]. Using the spin echo signal of the Br(1), Br(2), Br(7), or Br(8), two transitions, corresponding to ν_1 and ν_2 were detected at 256 and 363 kHz at 77 K, suggesting the presence of slightly distorted $AlBr_4^-$ tetrahedra. On the other hand, monitoring the spin echo signals other than described above showed only one ^{27}Al NQR signal at 256 kHz. The reason for this single NQR signal is still unsolved; it may be a doublet of two signals or its ν_1 transition is too low to be detect with our spectrometer.

An attempt to detect ^{27}Al NQR signals in the $AlBr(MeCN)_5^{2+}$ cation was unsuccessful, probably due to its too small coupling constant. If this is true, it means that Al-Br and Al-MeCN have almost the same bonding properties as will be described later.

As shown in Fig. 1 three NQR lines out of nine disappeared at about 210 K. These Br(2), Br(7), and Br(8) lines were assigned to the same $AlBr_4^-$ anion on the basis of the SEDOR experiment. It is interesting to note that only the Br(1) signal which could be assigned to the same $AlBr_4^-$ anion was still observed up to about room temperature, i.e., a reorientational motion about one Al-Br(1) three-fold axis begins before the onset of the isotropic motion. In order to investigate this anion dynamics we have determined the relaxation times T_1 in the temperature range from 77 to room temperature, see Figure 2. As is apparent from this figure, there are three different types of T_1 vs. temperature curves. The first group, in which Br(2), Br(7), and Br(8) are involved, shows a sudden T_1 decrease at about 180 K. The second group, in which Br(1), Br(3), Br(4), Br(5), and Br(6) are involved, shows a similar behavior with the first one but T_1 decrease at about 240 K. Br(9) belongs to the third group and takes about one order longer T_1 values without a sudden decrease of the relaxation times, suggesting that reorientation of the octahedra does not take place in this investigated temperature range. In general, the NQR relaxation times may be described as

$$1/T_1 = a\,T^n + b\,\exp(-V/RT)\,, \qquad (1)$$

where the first and second terms represent the contribution from lattice vibrations and from reorientational motion having the activation energy V, respectively [23]. Table 3 lists the best fit parameters a, n, b and V using non-linear least squares method.

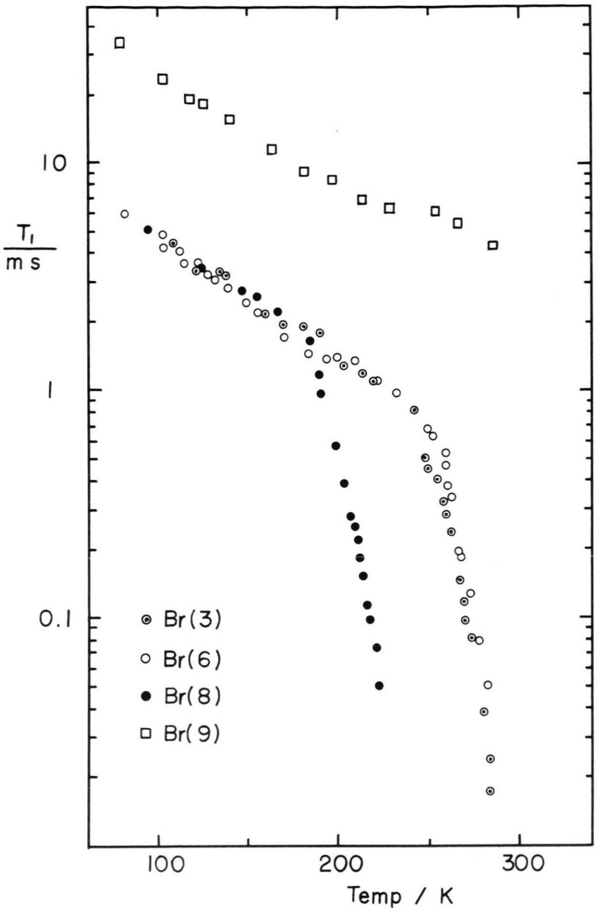

Fig. 2. Temperature dependence of the ^{81}Br spin-lattice relaxation times for $AlBr_3 \cdot 2$ MeCN.

Table 2. ^{27}Al NQR parameters for $AlBr_3 \cdot 2$ MeCN, $AlBr_3 \cdot 1.5$ MeCN and $AlBr_3 \cdot 2$ Py (estimated error in resonance frequency, ± 5 kHz).

Temp.	ν_1 [kHz]	ν_2 [kHz]	e^2Qqh^{-1} [kHz]	η	Assignment
		$AlBr_3 \cdot 2$ MeCN			
77	256	363	1284	0.596	$AlBr_4^-$
		256			$AlBr_4^-$
		$AlBr_3 \cdot 1.5$ MeCN			
77	259	400	1393	0.498	$AlBr_4^-$
	256	435	1489	0.379	$AlBr_4^-$
	311	520	1785	0.401	$AlBr_4^-$
		$AlBr_3 \cdot 2$ Py			
77	374	628	2154	0.395	$AlBr_4^-$
	684	1322	4431	0.165	$AlBr_2Py_4^+$
275	310	550	1869	0.319	$AlBr_4^-$
	602	1151	3864	0.190	$AlBr_2Py_4^+$

Table 3. Best fit parameters of the experimental $1/T_1$ data in equation (1).

Assignment	a [10^{-1} sec]	n	b [10^{15} sec]	V [kJ mol^{-1}]
Br(3)	0.499	1.81	439	70.7
Br(6)	0.468	1.83	128	69.5
Br(8)	3.34	1.41	0.113	41.9
Br(9)	0.25	1.60	–	–

From the T_1 measurement against the temperature, two types of reorientational motions could be detected below its decomposition point. At one of the $AlBr_4^-$ tetrahedral sites, in spite of its spherical shape a reorientation about the Al-Br(1) three-fold axis takes place at about 180 K with an activation energy 41.9 kJ/mol. The reorientational motion of the other tetrahedron is presumably more isotropic because four NQR signals showed the same behavior in the T_1 vs. temperature curves.

Figure 3 shows the ^{27}Al NMR spectra recorded at 327 K using a powder sample. Because of the first order quadrupole effect we could detect only the central transition ($1/2 \leftrightarrow -1/2$). As is apparent from this figure, the derivative curve is unsymmetrical not due to the second order quadrupole effect but to the overlapping of the two peaks with different chemical shifts. According to the high resolution NMR spectra in the $AlBr_3$-MeCN system, the ^{27}Al chemical shifts assigned to the $AlBr_4^-$ and $AlBr(MeCN)_5^{2+}$ ionic species were determined to be 80 and − 31 ppm from the external standard $Al(H_2O)_6^{3+}$ [6]. The observed chemical shifts in Fig. 3 are of the order expected from solution NMR data. The lower field line which could be assigned to the $AlBr_4^-$ tetrahedron shows motional narrowing at this temperature due to the $AlBr_4^-$ reorientation as was described above. On the other hand, the high field spectrum, which was assigned to the $AlBr(MeCN)_5^{2+}$ cation, has a peak to peak line-width of about 3.2 Gauss (3.55 kHz) and no second order quadrupole effect. Therefore, the reason for no ^{27}Al NQR signal with the SEDOR technique is due its too small quadrupole coupling constant. From the NMR and the SEDOR experiments an estimated value for the e^2Qq/h is below 1 MHz.

$AlBr_3 \cdot 1.5\,MeCN$

This compound shows very complicated spectra at 77 K as shown in Figure 4. This spectrum was taken point by point changing the frequency at intervals of 50 kHz, and the echo intensity was plotted. Each NQR line has a very short T_2^* of about 20 µsec and therefore a very large line width. At least 12 lines were detected, suggesting three non-equivalent $AlBr_4^-$ anions from their NQR frequencies. Three pairs of ^{27}Al NQR lines were also detected by the SEDOR technique; their small e^2Qq/h suggest the presence of $AlBr_4^-$ anions. According to the literature about the ^{27}Al NMR for the acetonitrile solution of $AlBr_3$, the following cations and anion have been characterized: $Al(MeCN)_6^{3+}$, $AlBr(MeCN)_5^{2+}$, $AlBr_2(MeCN)_4^+$, and $AlBr_4^-$ [6]. Therefore, the structure of the $AlBr_3 \cdot 1.5\,MeCN$

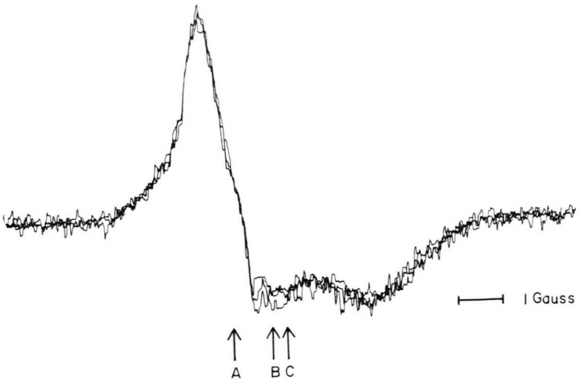

Fig. 3. ^{27}Al NMR spectra of the $AlBr_3 \cdot 2\,MeCN$ powder sample recorded at 327 K and 16 MHz. Modulation width: 1.25 Gauss. The arrows A, B, and C indicate the chemical shift due to $AlBr_4^-$, $Al(H_2O)_6^{3+}$, and $AlBr(MeCN)_5^{2+}$ from [6].

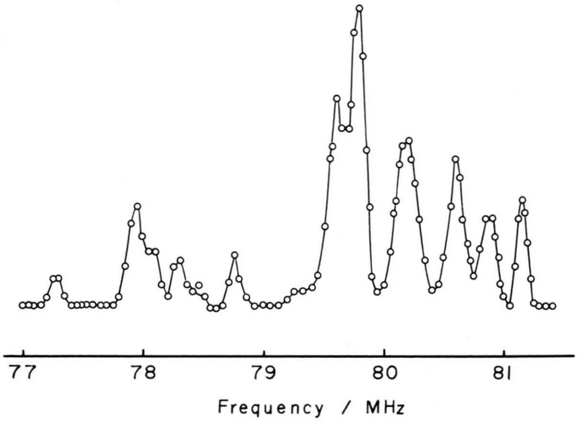

Fig. 4. ^{81}Br NQR spectra for $AlBr_3 \cdot 1.5\,MeCN$ at 77 K. The echo amplitude is plotted against the frequency at intervals of 50 kHz.

compound may be described as $[Al(MeCN)_6^{3+}, 3AlBr_4^-]$. This structure was also confirmed by IR and Raman spectroscopy [11].

$AlBr_3 \cdot 2Py$

About this compound we have already reported the ^{81}Br NQR signal and its Zeeman effect and showed that the compound consists of the $AlBr_4^-$ and trans-$AlBr_2(Py)_4^+$ ion pair [24]. Furthermore, a positive temperature coefficient of the ^{81}Br NQR, $d\nu/dT$, has been observed for the trans-$AlBr_2(Py)_4^+$ cation similar to that of the $AlBr(MeCN)_5^{2+}$ cation. In this study we have now detected the ^{27}Al NQR at both the tetrahedral and the octahedral sites as shown in Table 2.

Interactions between aluminum and ligands in the tetrahedral and octahedral complexes

There are not enough data to find a general trend about the six coordinated aluminum. However, it is worthwhile to consider the metal-ligand interaction on the basis of the ^{27}Al and ^{81}Br NQR data. The quadrupole coupling constant at the Al site due to its valence electrons may be described as

$$e^2Qq/h = C\,|n_{Br} - n_D|\,, \tag{2}$$

where n_{Br} and n_D are donating electrons to the central metal from the Br^- and the organic donor molecule, respectively. This equation holds not only for the tetrahedral AlX_3D complexes but for octahedral $AlBr_2D_4^+$ or $AlBrD_5^{2+}$ complexes, too, although the proportional constant C changes with the model of the bonding orbitals adopted. In a series of tetrahedral complexes Br_3Al-Donor, the e^2Qq/h (^{27}Al) decreases drastically with increasing donor strength according to (2). Table 4 shows the ^{81}Br and ^{27}Al NQR parameters for $AlBr_3 \cdot MeCN$ and $AlBr_3 \cdot Py$. The extremely small e^2Qq/h (^{27}Al) for the $AlBr_3 \cdot Py$ compound is referred to the strong donor property of pyridine. Therefore, in a series of tetrahedral complexes, the relation $n_{Br} > n_D$ holds generally. On the other hand, the e^2Qq/h (^{27}Al) for the $AlBr(MeCN)_5^{2+}$ complex is very small suggesting $n_{Br} \risingdotseq n_D$ for this complex. As is expected from Table 4, the donor property of pyridine is stronger than that of acetonitrile, so that the opposite relation $n_{Br} < n_D$ is presumed for the $AlBr_2Py_4^+$ complex. In this connection further experimental data about central metals and ligands should be accumulated. Especially ^{14}N NQR data using the double resonance method are useful for this problem [25, 26]. In our previous ^{115}In NQR study on the $InBr_5 \cdot H_2O^{2-}$ complex, an anomalous large and positive temperature dependence of e^2Qq/h was observed and could be explained by a slight change in the bonding between the central metal and the H_2O molecule [27, 28]. Therefore, the positive temperature coefficient of the ^{81}Br NQR in these octahedral complexes of main group elements should be discussed together with the NQR data of central metal and ligands.

Table 4. ^{81}Br and ^{27}Al NQR parameters for $AlBr_3 \cdot MeCN$ and $AlBr_3 \cdot Py$ at room temperature.

Compounds	Nuclei	Frequency [MHz]		η	e^2Qqh^{-1}
		ν_1	ν_2		[MHz]
$AlBr_3 \cdot MeCN$	^{81}Br	80.514 80.725			
	^{27}Al	0.781	1.554	0.063	5.184
$AlBr_3 \cdot Py$ [a]	^{81}Br	79.575 80.565 81.424			
	^{27}Al [b]	0.064	0.128	0	0.43

[a] Ref. [24].
[b] Estimated from the quadrupole effect on the ^{27}Al NMR assuming $\eta = 0$ using a powdered sample.

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