

NQR Study of AlBr_3 Complexes with Dimethylsulfide

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^{81}Br - ^{27}Al SEDOR as well as ^{81}Br NQR spectroscopy have been applied to the molecular complexes of AlBr_3 with $(\text{CH}_3)_2\text{S}$. The formation of two kinds of complex compounds, $[(\text{CH}_3)_2\text{S}]_2\text{AlBr}_3$ and $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$, has been recognized. The compound $[(\text{CH}_3)_2\text{S}]_2\text{AlBr}_3$ is a solid at ambient temperature, while the compound $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ is a liquid with a melting point of 287 K. The crystalline state of $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ shows a complex polymorphism consisting of Forms 1, 2 and 3 in which conformation isomers of $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ seem to exist. The structures of the complex compounds are discussed together with the results of *ab initio* MO calculations.

Key words: ^{81}Br and ^{27}Al NQR, Polymorphism,
 AlBr_3 Complexes with $(\text{CH}_3)_2\text{S}$

Introduction

In organic syntheses AlBr_3 is used as a catalyst which functions as a Lewis acid. The investigation of Lewis donor-acceptor complexes of AlBr_3 by means of the nuclear quadrupole resonance (NQR) is intriguing in that it may shed light on the understanding of the structures as well as the electronic states of intermediates in the organic reactions. In NQR studies on a series of AlBr_3 donor-acceptor complexes [1, 2], we have met a polymorphism of $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ which is dependent on the solidification method used. In addition, it was found that the ^{81}Br NQR data of $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ reported by Maksyutin *et al.* [3] correspond exactly to those of $[(\text{CH}_3)_2\text{S}]_2\text{AlBr}_3$ instead of $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$. Here we measured the temperature dependence

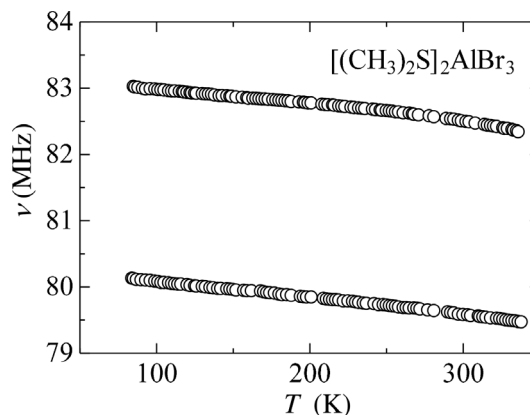


Fig. 1. The temperature dependence of ^{81}Br NQR frequencies in $[(\text{CH}_3)_2\text{S}]_2\text{AlBr}_3$.

of ^{81}Br and ^{27}Al NQR frequencies at 77 K of both compounds in order to get information on the bonding and structures in the crystalline states. The structures were also investigated with *ab initio* MO calculations. The formation and stability of modifications of $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ are reported.

Results and Discussion

Two ^{81}Br NQR lines with an intensity ratio of 1 : 2 were observed for $[(\text{CH}_3)_2\text{S}]_2\text{AlBr}_3$, using a continuous wave (CW) spectrometer. Their frequencies at 77 K are listed in Table 1. The temperature dependence of the resonance frequencies was measured in the temperature range from 77 to about 340 K. Fig. 1 shows no indication of any phase transition in this temperature range. The ^{81}Br NQR frequencies at 77 K are in good agreement with those of $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ (CAS Reg. No. 15171-28-5) reported by Maksyutin *et al.* [3] as listed in Table 1, showing that their compound was $[(\text{CH}_3)_2\text{S}]_2\text{AlBr}_3$. The two ^{81}Br NQR lines with the intensity ratio of 1 : 2 in $[(\text{CH}_3)_2\text{S}]_2\text{AlBr}_3$ indicate that the coordination of the Al atom leads to C_s symmetry, most likely in a trigonal bipyramid with three equatorial Br and two apical S atoms in its structure.

The NQR measurements of $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ were carried out using a pulsed spectrometer. Crystals of $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ show a complicated polymorphism consisting of Forms 1, 2 and 3. Form 1 was obtained by annealing the crystals at 277 K (10 K below m. p. = 287 K) for three months after crystallization. It exhibited six ^{81}Br NQR lines with equal intensities be-

Compound		Nucleus	Frequency (MHz)			
			77 K		200 K [273 K]	
[(CH ₃) ₂ S] ₂ AlBr ₃		⁸¹ Br	83.02(1) ^a		82.77	
			80.13(2)		79.84	
[(CH ₃) ₂ S]AlBr ₃ ^b	Form 1	⁸¹ Br	86.65(1)	82.38(1)	85.04	81.92
			85.46(1)	81.63(1)	84.33	81.17
			83.54(1)	81.01(1)	82.65	80.21
	Form 2	⁸¹ Br [²⁷ Al]	85.32(1)	[0.963]	84.25	
			83.77(1)	[0.962]	82.51	
			82.55(1)	[0.957]	81.12	
	Form 3	⁸¹ Br	—	—	[84.14]	
			—	—	[81.45]	
			—	—	[80.78]	

Table 1. ^{81}Br and ^{27}Al NQR frequencies at 77 and 200 K.

^a The numbers in parentheses denote intensity ratios; ^b the ^{81}Br NQR frequency values at 77 K of 83.025 and 80.08 for $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ in ref. [3] coincide with those of $[(\text{CH}_3)_2\text{S}]_2\text{AlBr}_3$ in the present study.

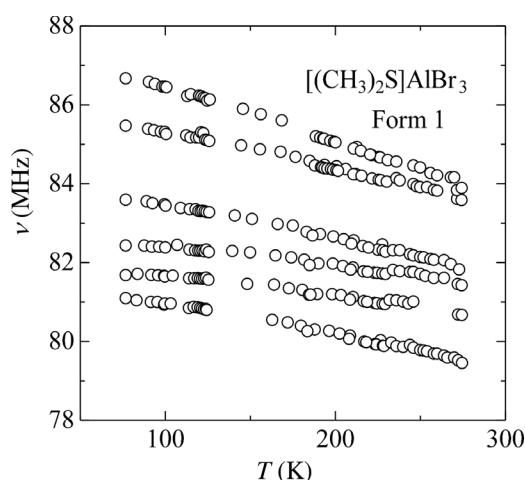


Fig. 2. The temperature dependence of ^{81}Br NQR frequencies in Form 1 of $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$.

tween 77 and 287 K (Table 1 and Fig. 2). Form 2 was obtained by an immediate cooling of the liquid sample from r. t. without the annealing process. This modification was characterized by three ^{81}Br NQR lines (Table 1). When the temperature was decreased, all the resonance lines disappeared around 248 K as shown in Fig. 3. On further cooling, three NQR lines however appeared around 235 K and below. This disappearance of the resonance lines indicates the occurrence of a phase transition between 235 and 248 K. The occurrence of a slight structural change is expected at the phase transition, as an almost continuous change is seen between both high- and low-temperature dependence curves. The resonance lines of the low-temperature phase of Form 2 faded out to become unobserved around 150 K and below. This disappearance may be due to some kind of disorder of molecules which gives rise to a weakening of the ^{81}Br NQR lines, because three weak lines could be observed at 77 K

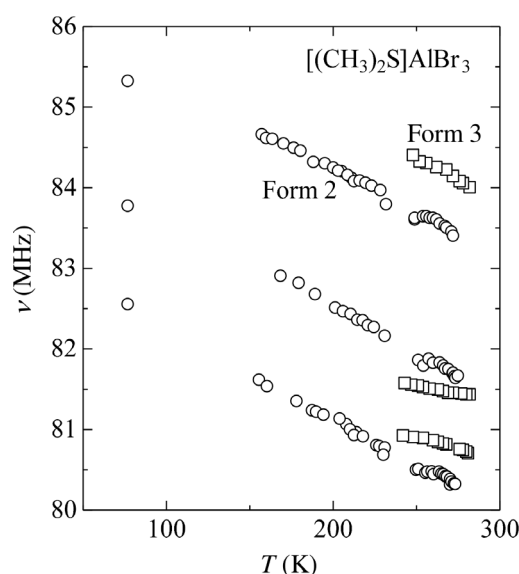


Fig. 3. The temperature dependence of ^{81}Br NQR frequencies in Forms 2 and 3 of $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$.

each of which was situated on an extension of the above curves. On heating above 77 K, the resonance lines followed exactly the frequency vs. temperature curves back up to 235 K, at which temperature the resonance lines disappeared. However, further heating above ca. 257 K up to the melting point of 287 K produced three new lines different from those of Form 2. This observation shows the existence of the third modification, Form 3. All resonance lines of Form 3 could be observed on cooling down to ca. 242 K, which was lower by 15 K compared to the appearance temperature of the lines on heating. The DTA measurements on heating runs showed no heat anomaly due to a phase transition around 235 K. These observations show the existence of at least three modifications for the crystalline states of $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$. Form 1 should be the

stable form because it is obtained by annealing, while Forms 2 and 3 are metastable forms.

^{81}Br - ^{27}Al spin echo double resonance (SEDOR) measurements were carried out for the ^{81}Br NQR lines of Form 2. The ^{27}Al NQR frequencies obtained are listed in the brackets next to the corresponding ^{81}Br NQR frequencies in Table 1. These ^{27}Al SEDOR spectra are due to the transitions of $m = \pm 1/2 \leftrightarrow m = \pm 3/2$ for $I = 5/2$. The spectra of $m = \pm 3/2 \leftrightarrow m = \pm 5/2$ could not be observed. The ^{27}Al NQR frequency values are well in accordance with each other with an average frequency of 0.961 MHz, confirming that the three Br atoms are bonded to the same Al atom. It appears that three of the six NQR lines of Form 1 and the three ^{81}Br NQR lines of Form 2 are almost identical in frequency at 77 K (Table 1), showing that there are two different $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ molecules in the crystal structure of Form 1, and that one of them may have a geometrical structure similar to that of the molecule in Form 2.

While the crystal structures of both compounds have not yet been determined, we practiced *ab initio* MO calculations to get optimized structures of the molecules by using WINGAMESS with a 6-31+G** basis set [4]. The results of the calculations predict that the optimized geometrical structure of the $[(\text{CH}_3)_2\text{S}]_2\text{-AlBr}_3$ molecule has C_s symmetry for which the S–Al–S and Al–Br(1) bonds lie on the mirror plane and two Br(2) atoms are related by the plane as shown in Fig. 4. This structure is in agreement with that derived from the NQR results. The bond lengths and angles were obtained as $d(\text{Al–Br}(1)) = 2.339 \text{ \AA}$, $d(\text{Al–Br}(2)) = 2.328 \text{ \AA}$ and $d(\text{Al–S}) = 2.633 \text{ \AA}$, and $\angle\text{Br}(1)\text{–Al–Br}(2) = 118.5^\circ$ and $\angle\text{Br}(2)\text{–Al–Br}(2) = 123.1^\circ$, respectively. The NQR results suggest the existence of one C_1 symmetric molecule in Forms 2 and 3, and two different C_1 symmetric molecules in Form 1. The optimized structure of the $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ molecule has C_1 , but almost C_s symmetry (Fig. 4). The opti-

mized parameters are: $d(\text{Al–Br}(1)) = 2.297 \text{ \AA}$, $d(\text{Al–Br}(2)) = 2.286 \text{ \AA}$, $d(\text{Al–Br}(3)) = 2.286 \text{ \AA}$ and $d(\text{Al–S}) = 2.428 \text{ \AA}$, and $\angle\text{Br}(1)\text{–Al–Br}(2) = 115.1^\circ$, $\angle\text{Br}(1)\text{–Al–Br}(3) = 115.0^\circ$ and $\angle\text{Br}(2)\text{–Al–Br}(3) = 117.2^\circ$. The calculated Al–Br bond lengths are a little longer in $[(\text{CH}_3)_2\text{S}]_2\text{AlBr}_3$ than in $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ with the average values of 2.331 and 2.290 \AA , respectively. The relation $\nu \propto f(1/d^3)$ is usually held between the NQR frequency ν and the bond length d . The above trend of the bond lengths is then also coincident with the fact that the average ^{81}Br NQR frequency in $[(\text{CH}_3)_2\text{S}]_2\text{-AlBr}_3$ is lower than that in $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$: the values are 81.09 and 83.45 MHz at 77 K, respectively. The bond lengthening or frequency lowering may be explained by considering that the coordination number of the Al atom is higher and thus the Al–Br bonds are more ionic in $[(\text{CH}_3)_2\text{S}]_2\text{AlBr}_3$ than in $[(\text{CH}_3)_2\text{S}]\text{-AlBr}_3$.

In conclusion, AlBr_3 works as a dibasic acid for $(\text{CH}_3)_2\text{S}$ to form $[(\text{CH}_3)_2\text{S}]_2\text{AlBr}_3$ and as a monobasic acid in $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$. The $[(\text{CH}_3)_2\text{S}]_2\text{AlBr}_3$ molecule has a structure of C_s symmetry in which the Al atom has a trigonal-bipyramidal coordination with three Br atoms in the equatorial positions and two S atoms in the axial positions. The $[(\text{CH}_3)_2\text{S}]\text{-AlBr}_3$ molecule has a structure of C_1 symmetry with a tetrahedral coordination of the Al atom. There are two metastable crystalline forms, Forms 2 and 3, in addition to the stable Form 1. In the crystal structure of Form 1 there are two different asymmetric units of $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$. Form 2 undergoes a phase transition between 235 and 248 K. Form 3 is formed when Form 2 is heated above the phase transition temperature. Considering the proximity of their ^{81}Br NQR frequencies, the polymorphism of $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ suggests the existence of conformation isomers in each modification.

Experimental Section

$[(\text{CH}_3)_2]_2\text{AlBr}_3$ was synthesized by adding directly a slight excess of dimethylsulfide to AlBr_3 under cooling with a dry ice-acetone bath. The crystals were obtained as colorless powders.

$[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ was synthesized by mixing equimolar quantities of dimethylsulfide and AlBr_3 in carbon disulfide. Subsequent evaporation of the solvent left the sample as a liquid residue at r.t. All preparations were conducted under a dry N_2 atmosphere. Both compounds were found to be very sensitive to hydrolysis, but they could be stored in sealed tubes. The melting points were 339 and 287 K for

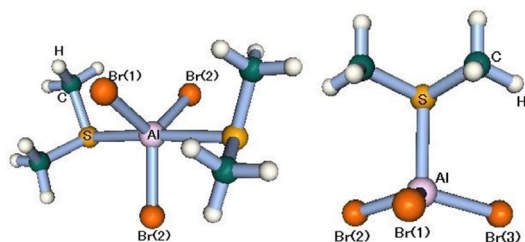


Fig. 4. The optimized geometrical structures of $[(\text{CH}_3)_2\text{S}]_2\text{-AlBr}_3$ and $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$.

$[(\text{CH}_3)_2\text{S}]_2\text{AlBr}_3$ and $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$, respectively. The latter value conforms to an observation by de Loth [5] that $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$ is a liquid at r.t. The observed / calculated Br contents were 61.13 % / 61.31 % and 71.16 % / 72.89 % for $[(\text{CH}_3)_2\text{S}]_2\text{AlBr}_3$ and $[(\text{CH}_3)_2\text{S}]\text{AlBr}_3$, respectively.

The ^{81}Br nuclear quadrupole resonance (NQR) spectra were observed at temperatures above 77 K by using a home-made super-regenerative type oscillator and a Matec pulsed NQR spectrometer for observing the spin echo signals. The ^{27}Al NQR spectra were obtained by the ^{81}Br - ^{27}Al SEDOR method [6, 7].

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- [1] H. Ishihara, S. Nakashima, K. Yamada, T. Okuda, A. Weiss, *Z. Naturforsch.* **1990**, 45a, 237–242.
- [2] T. Okuda, H. Ohta, H. Ishihara, K. Yamada, H. Negita, *Bull. Chem. Soc. Jpn.* **1980**, 53, 2721–2723.
- [3] Y. K. Maksyutin, E. V. Bryukhova, G. K. Semin, E. N. Gur'Yanova, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 11, 2658–2660.
- [4] Calculations were done with the 6-31+G** basis set for optimized structures of $(\text{CH}_3)_2\text{S}-\text{AlBr}_3-\text{S}(\text{CH}_3)_2$ by using WINGAMEES (version 11). See: M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, 14, 1347–1363; M. S. Gordon, M. W. Schmidt in *Theory and Applications of Computational Chemistry: the first forty years*, (Eds.: C. E. Dykstra, G. Frenking, K. S. Kim, G. E. Scuseria), Elsevier, Amsterdam, **2005**, pp. 1167–1189.
- [5] P. de Loth, *Compt. Rend.* **1965**, 261, 4758–4760.
- [6] N. Weiden, A. Weiss, *J. Magn. Reson.* **1975**, 20, 334–340.
- [7] K. Yamada, T. Okuda, *J. Phys. Chem.* **1985**, 89, 4269–4272.