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NUCLEAR QUADRUPOLE RESONANCES OF $AlBr_3 \cdot SbBr_3$, $AlI_3 \cdot SbI_3$, AND $AlBr_3 \cdot BiBr_3$

Tsutomu OKUDA, Koji YAMADA, Hideta ISHIHARA, and Hisao NEGITA
Department of Chemistry, Hiroshima University, Hiroshima 730

The NQR spectra and their Zeeman effects in $AlX_3 \cdot SbX_3$ (X=Br, I) and $AlBr_3 \cdot BiBr_3$ were observed. The former adducts consist of AlX_4^- and SbX_2^+, although there are weak bonds between SbX_2^+ and AlX_4^- ions through the halogens of AlX_4^- ion. On the other hand, $AlBr_3 \cdot BiBr_3$ shows somewhat different feature compared with the formers.

The formation of adducts $AlBr_3 \cdot SbBr_3$, $AlI_3 \cdot SbI_3$, and $AlBr_3 \cdot BiBr_3$ has been reported in literatures.[1] According to the electron diffraction study, $AlBr_3 \cdot SbBr_3$ has an ethane-like structure ($Br_3Al\text{-}SbBr_3$) in a gaseous state.[2] However, their chemical bondings and their crystal structures have not been apparent. In the present investigation, we have observed NQR spectra of $AlBr_3 \cdot SbBr_3$, $AlI_3 \cdot SbI_3$, and $AlBr_3 \cdot BiBr_3$, and examined Zeeman effects on the spectra by using respectivr single crystals. Adducts $AlBr_3 \cdot SbBr_3$, $AlI_3 \cdot SbI_3$, and $AlBr_3 \cdot BiBr_3$ were prepared by melting the equivalent amount of the relevant halides in a sealed tube. The single crystal of these compounds were grown by the Bridgman-Stockbarger method. The NQR spectrometer used in this experiment was a super-regenerative oscillator and signals were observed on an oscilloscope. The Zeeman effects were examined by means of the zero-splitting cone method.[3]

$AlBr_3 \cdot SbBr_3$

The resonance lines of ^{79}Br, ^{81}Br, ^{121}Sb, and ^{123}Sb could be observed. Each resonance line could be assigned easily, on the basis of the quadrupole moment ratios, $Q(^{123}Sb)/Q(^{121}Sb) = 1.2745$ and $Q(^{79}Br)/Q(^{81}Br) = 1.1974$.[4] Table 1 shows the resonance frequencies of ^{81}Br and ^{121}Sb. As is obvious from this table this compound shows four ^{81}Br resonance lines near 80 MHz and two near 145 MHz. The former lines may be assigned to $AlBr_4^-$ ion and the latter may be assigned to $SbBr_2^+$ ion. The quadrupole coupling constant (e^2Qq) and the asymmetry parameter (η) of ^{121}Sb were determined from the frequency ratio, $\nu_1(1/2\text{-}3/2)/\nu_2(3/2\text{-}5/2)$, by using a table of eigenvalues for the NQR spectra of spin 5/2. These lines yield large e^2Qq and η compared with those of $SbBr_3$,[5] so that the existence of bent $SbBr_2$ units is presumed. Figure 1 shows the zero-splitting patterns of Br(5), Br(6), and Sb, where Br(5) and Br(6) are the bromine atoms which are bonded to antimony. The appearance of observed patterns indicates that this crystal belongs to a monoclinic system, and hence a crystallographic b-axis is shown in Fig. 1. Asymmetry parameters of Br(5) and Br(6) determined from these patterns are very small. Therefore, the principal z-axis of the efg tensor of the bromine atoms should coincide with the bonding direction (Br-Sb). The bond angle ($\angle$BrSbBr) in an $SbBr_2$ unit was determined to be 97.3°. This value is almost equal to that of $SbBr_3$.[6] In the case of ^{121}Sb (nuclear spin $I=5/2$) it has become apparent that the center of the zero-splitting pattern for ν_1 is directed to the y-axis of the efg tensor of anti-

Table 1. NQR parameters of $AlBr_3 \cdot SbBr_3$, $AlI_3 \cdot SbI_3$, and $AlBr_3 \cdot BiBr_3$ (296 K)

Compounds		ν_1/MHz	ν_2/MHz	ν_3/MHz	ν_4/MHz	η/%	e^2Qq/h/MHz
$AlBr_3 \cdot SbBr_3$	^{121}Sb	97.460	113.30			82.1	412.18
	$^{81}Br(1)$	76.637				53.4	160.39
	Br(2)	79.088				47.7	164.06
	Br(3)	81.930				30.7	166.40
	Br(4)	82.689				14.1	165.91
	Br(5)	143.63				2.4	287.26
	Br(6)	149.99				1.1	299.98
$AlI_3 \cdot SbI_3$	^{121}Sb	75.681	94.832			73.6	343.22
	$^{127}I(1)$	118.18	200.48			38.2	686.59
	I(2)	118.86	232.68			12.9	778.31
	I(3)	123.04	201.73			42.6	694.95
	I(4)	123.19	214.40			34.7	731.06
	I(5)	186.88	373.79			0.0	1245.9
	I(6)	207.39	414.00			3.8	1380.4
$AlBr_3 \cdot BiBr_3$	^{209}Bi	36.941	46.126	72.422	97.364	27.0	587.69
	$^{81}Br(1)$	75.691				20.4	152.41
	Br(2)	76.760				86.8	171.71
	Br(3)	81.003				52.6	169.30
	Br(4)	83.937				42.6	172.86
	Br(5)	95.316				53.9	199.63
	Br(6)	148.30				2.7	296.56

mony and for ν_2 it is directed to the z-axis when η is greater than 41%.[7] Thus it is apparent from Fig. 1 that the direction of the y-axis of this antimony atom coincides almost with a bisector of the two Sb-Br bonds. Furthermore, the z-axis is almost perpendicular to the plane of the $SbBr_2$ unit. The asymmetry parameters of Br(1), Br(2), Br(3), and Br(4) are all large. According to the X-ray analysis of $AlCl_3.ICl_3$[8] and $AlCl_3.TeCl_4$[9] these compounds form ionic crystals, $AlCl_4^-ICl_2^+$ and $AlCl_4^-TeCl_3^+$, respectively, although $AlCl_4^-$ and ICl_2^+ ions or $AlCl_4^-$ and $TeCl_3^+$ ions are linked by weak bonds through chlorine atoms of $AlCl_4^-$. Therefore, it is concluded that $AlBr_3.SbBr_3$ consists of $AlBr_4^-$ and $SbBr_2^+$ ions, and there are weak bonds between the component ions.

$AlI_3.SbI_3$

In the case of iodine (I=5/2) both ν_1 and ν_2 were observed. On the basis of the asymmetry parameters determined from the zero-splitting patterns, all resonance lines were paired as is shown in Table 1. The feature of the spectrum is very similar to that of $AlBr_3.SbBr_3$.

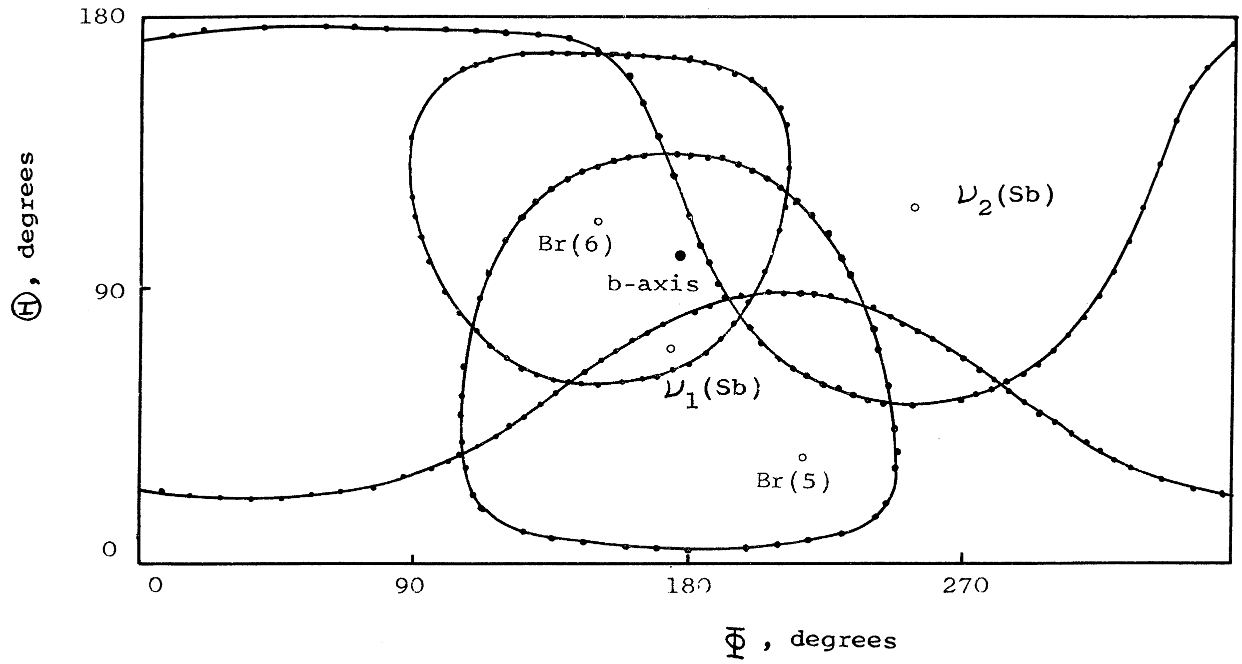

Fig. 1. Zero-splitting patterns of Br(5), Br(6), and Sb which were assigned to $SbBr_2$ unit. Because of the monoclinic system, two zero-splitting patterns were observed for each resonance line. However, half of them are shown in this figure.

$AlBr_3 \cdot BiBr_3$

The asymmetry parameters of Br(1), Br(2), Br(3), and Br(4), which may be assigned to an $AlBr_4^-$ ion, are very large as those in the former compounds. However, the following characteristic features have been found in $BiBr_2$ unit. Br(5) which may be bounded to bismuth yields small e^2Qq and large η compared with those of Br(6). Therefore, it may be considered that Br(5) forms bridging bond with neighbouring bismuth atom and Br(6) is the only terminal atom bonded to bismuth. An increase in the e^2Qq of bismuth by forming adduct is large compared with antimony in $AlBr_3 \cdot SbBr_3$ and $AlI_3 \cdot SbI_3$. The asymmetry parameter of bismuth is small compared with that of antimony in the former compounds. The z-axis of bismuth almost coincides with that of Br(6).

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