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THE NQR AND STRUCTURE OF HEXABROMOANTIMONATE(III) AND BISMUTHATE(III) IONS

Tsutomu OKUDA,* Morio HIURA, Etsuo KOSHIMIZU, Hideta ISHIHARA
Yoshihiko KUSHI, and Hisao NEGITA
Department of Chemistry, Faculty of Science, Hiroshima University, Naka-ku, Hiroshima 730

^{79}Br NQR spectra were observed in $(R_2NH_2)_3MBr_6$ (R=C_2H_5, n-C_3H_7; M=Sb, Bi). Widely spaced resonance lines and their unusual temperature dependence were found in the diethylammonium salts. These findings are accounted for in terms of the crystal structure determined by means of X-ray diffraction.

The $M(III)Br_6^{3-}$(M=Sb, Bi) ions have seven electron pairs including one lone pair electrons in the valence shell of the central atom,[1] so that it is interesting to examine the shape of the MBr_6^{3-} ion, that is, the arrangement of seven electron pairs. The X-ray crystallographic data are available for $(NH_4)_4Sb_2Br_{12}$[2] and $[(CH_3)_2NH_2]_3BiBr_6$[3] which consist of approximately octahedral MBr_6^{3-} anions. However, if the lone pair electrons are stereochemically active or if the cation affects strongly the anion, the shape of the anion will be considerably distorted from the regular octahedron. In the present work, NQR and X-ray diffraction were observed in order to examine the shape and bond character of MBr_6^{3-} ions.

The compounds were prepared according to the literature.[4] The NQR spectrometers used were super-regenerative oscillators employing a frequency modulation or a Zeeman modulation mode.

The observed ^{79}Br NQR frequencies are listed in Table 1. ^{81}Br resonances were also observed at the frequencies expected from the quadrupole moment ratio Q(^{79}Br)/Q(^{81}Br). For the diethylammonium salts, a new ^{79}Br NQR signal was found in the lower frequency region in addition to the higher line reported previously by Brill and Long.[5] The difference between two ^{79}Br NQR frequencies is quite large. Such widely spaced resonance lines have scarcely been observed in normal compounds

where the central atom has the same coordination state, except for the mixed-valence Sb(III, V) compounds.[6] The ^{121}Sb resonance lines were observed at 13.13 MHz for $\nu_1(1/2 \leftrightarrow 3/2)$ and 26.27 MHz for $\nu_2(3/2 \leftrightarrow 5/2)$ at 77 K.

On the other hand, only one ^{79}Br resonance line was observed in the dipropylammonium salts. Its frequency is nearly equal to the mean frequency of the resonance lines in the diethylammonium salts, and comparable to the NQR frequencies of the $SbBr_6^{3-}$ ion in $R_4Sb_2Br_{12}$ (R=NH_4, Rb).[6]

Table 1. ^{79}Br NQR frequencies in the diethylammonium and dipropylammonium salts at 77 K

Compound	ν /MHz[a]
$[(C_2H_5)_2NH_2]_3SbBr_6$	39.02 [Br(2)]
	123.68 [Br(1)]
$[(n\text{-}C_3H_7)_2NH_2]_3SbBr_6$	78.26
$[(C_2H_5)_2NH_2]_3BiBr_6$	45.85
	104.87
$[(n\text{-}C_3H_7)_2NH_2]_3BiBr_6$	72.89

a) Experimental error is within $\pm$ 0.01 MHz.

Figure 1 shows the temperature dependence of ^{79}Br NQR lines in $[(C_2H_5)_2NH_2]_3SbBr_6$. The higher line shows a positive temperature coefficient whereas the lower line shows a negative one. As the temperature rose from 77 K, the higher line became gradually weaker and faded out at about 120 K. This line appeared at about 170 K and its frequency and intensity increased with increasing temperature while the frequency decreased through a peak at about 270 K. Figure 2 shows the temperature dependence of ^{121}Sb NQR line. This bears a strong resemblance to the temperature dependence of the higher line in Fig. 1. The resonance frequency of ^{79}Br NQR line in $[(n\text{-}C_3H_7)_2NH_2]_3SbBr_6$ decreased monotonously with an increase in temperature and its temperature coefficient is very small.

In order to discuss the unusual results of the resonance frequency and temperature dependence, we have determined the crystal structure of these compounds by means of X-ray diffraction. Crystals suitable for the X-ray analysis were grown from acetone. The space group of $[(C_2H_5)_2NH_2]_3SbBr_6$ is R3c, and the unit cell parameters are a=15.155(6), c=20.085(4) Å, and Z=6 on the basis of a hexagonal cell. For $[(n\text{-}C_3H_7)_2NH_2]_3SbBr_6$, the space group is $R\bar{3}c$, a=13.649(6), c=31.548(8) Å, and Z=6 on a hexagonal cell. Intensity measurements were made with a Rigaku four-circle diffractometer AFC-5 using Mo-K_α radiation (λ_1=0.70926 Å). 511 and 577 independent reflections which are larger than three times their standard deviations,

were solved by using Patterson and Fourier method, R=0.077 and R=0.088 for $[(C_2H_5)_2NH_2]_3SbBr_6$ and $[(n\text{-}C_3H_7)_2NH_2]_3SbBr_6$, respectively.

The structures of the $SbBr_6^{3-}$ ions in the two compounds are given in Fig. 3. In the dipropylammonium salt, an $SbBr_6^{3-}$ ion on a $\bar{3}$ axis forms a nearly regular octahedron. In the case of the diethylammonium salt, an $SbBr_6^{3-}$ ion is on a three-fold axis, but the Sb atom is displaced from the center of the octahedron along the three-fold axis. The trans Br(1)-Sb-Br(2) bonds are nearly linear, 175.6(3)°, but fairly asymmetric, 2.622(8) vs. 3.061 Å.

Each Br atom in the dipropylammonium salt has one short Br···N contact, 3.36(4) Å. On the other hand, in the diethylammonium salt, Br(2) forms two short Br···N contacts, 3.29(5) and 3.31(5) Å, while Br(1) has no significant Br···N contact. Therefore, there are three kinds of Br atoms in these complexes, namely, Br atom with (1) a weak Br···N contact; (2) a short Br···N contact; (3) two short Br···N contacts. If the short contact is formed by a hydrogen bond Br···H-N and lone pair electrons of the Br atom take part in its bond formation,

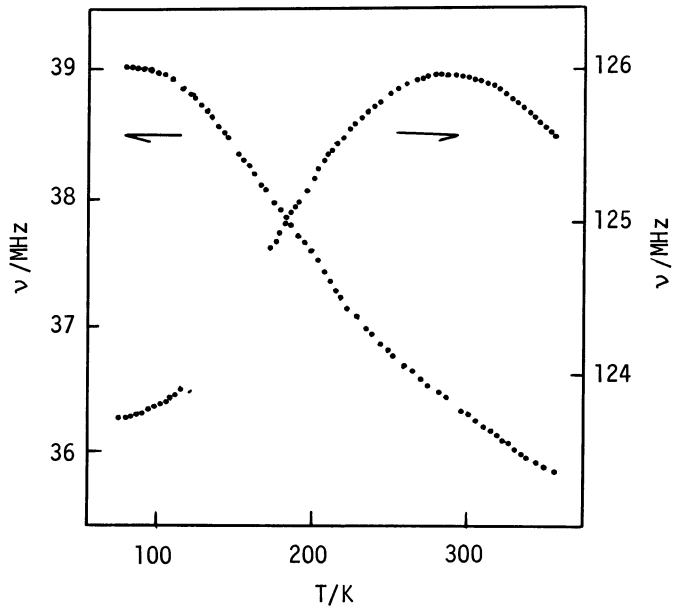

Fig. 1. Temperature dependence of ^{79}Br NQR frequencies of $[(C_2H_5)_2NH_2]_3SbBr_6$.

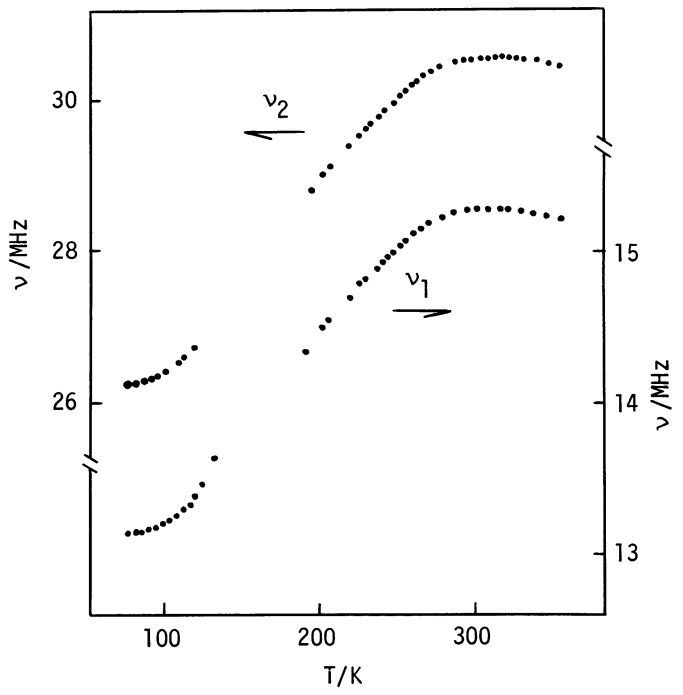

Fig. 2. Temperature dependence of ^{121}Sb NQR frequencies of $[(C_2H_5)_2NH_2]_3SbBr_6$.

the unusual results of NQR can be interpreted in terms of hydrogen bond. The NQR frequency of the Br atom depends on the strength and the number of hydrogen bond. When the hydrogen bond increases in number and/or in strength, the frequency decreases. Accordingly, the order of the frequencies is the higher line of the diethylammonium salt > the resonance line of the dipropylammonium salt > the lower line of the diethylammonium salt.

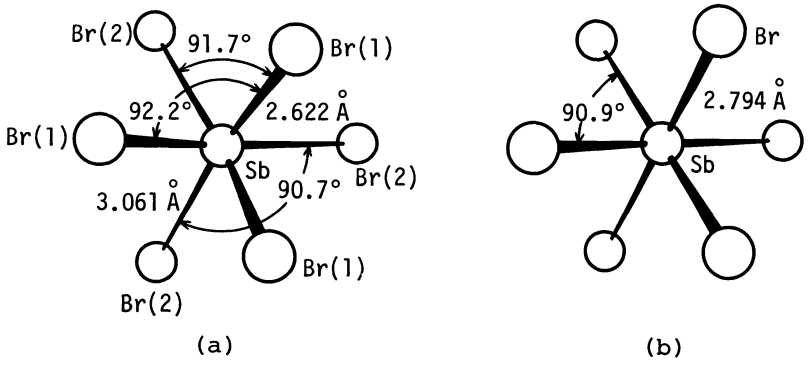

Fig. 3. Structures of the $SbBr_6^{3-}$ ions in (a) $[(C_2H_5)_2NH_2]_3SbBr_6$ and (b) $[(n\text{-}C_3H_7)_2NH_2]_3SbBr_6$.

The temperature dependence of NQR frequencies in $[(C_2H_5)_2NH_2]_3SbBr_6$ is unusual as shown in Fig. 1. As the temperature rises, the enhanced thermal motions will partially break the Sb-Br(2) bond, so that Br(2) will approximate more closely to the Br atom in diethylammonium bromide, and therefore, Br(1) will approach to the Br atom in $SbBr_3$. Thus, the resonance frequency of the former decreases and that of the latter increases with increasing temperature. Since these effects are accompanied by usual Bayer effect, the temperature curves become more complicated. In the X-ray analysis the terminal carbon atoms of the ethyl group in the diethylammonium ion have shown large thermal parameters, B=13-15 $Å^2$. These findings suggest that a kind of disorder exists in the diethylammonium ion and such disorder-character will affect the temperature dependence of NQR frequencies.

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