Structural Change in $(C_5H_5NH)SbBr_4$ with Temperature

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Summary ^{81}Br N.q.r. spectroscopy has revealed a drastic structural change in the $(C_5H_5NH)SbBr_4$ crystal; above 253 K the $SbBr_4^-$ anion has the trigonal bipyramid structure, whereas below 253 K the axial bonds become asymmetric and the $SbBr_4^-$ anion is more reasonably described as $SbBr_3{\cdot}Br^-$ at 77 K.

Antimony tribromide forms a variety of compounds in which the ions $SbBr_2^+$, $SbBr_4^-$, $Sb_2Br_9^{3-}$, and $SbBr_6^{3-}$ occur.[1–5] In these ions the 5s lone-pair electrons and the secondary bonding[6] play an important role in determining their structures. The title compound is interesting, because the anion changes its structure with temperature as a result of the *trans*-effect of the secondary bonding. Figure 1 shows the temperature dependence of the ^{81}Br and ^{121}Sb ($1/2 \longleftrightarrow 3/2$ and $3/2 \longleftrightarrow 5/2$) n.q.r. frequencies.

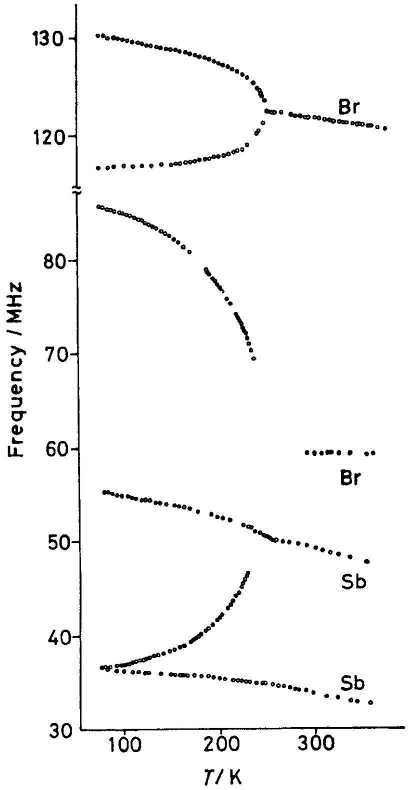
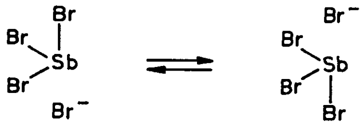


Figure 1. Temperature dependence of the ^{81}Br and ^{121}Sb n.q.r. frequencies in $(C_5H_5NH)SbBr_4$.

According to the *X*-ray analysis at room temperature,[2] the anion forms an infinite chain *via* bromine bridges and each antimony atom has a distorted octahedral environment with two terminal and four bridging Br atoms. If we ignore the longer bridging bonds for simplicity, the anion is regarded as a trigonal bipyramid with one lone pair at an equatorial position. At room temperature two ^{81}Br n.q.r. lines were detected, in accordance with the crystal structure, *i.e.* the anion has a two-fold axis. The higher one was assigned to the Br atom in the equatorial position, from its bond length, and the lower to the axial Br atom. This assignment is also supported by the ^{81}Br n.q.r. Zeeman effect. In general, it is thought that the equatorial bonds are formed with sp^2-hybrid orbitals of the Sb atom and axial bonds are formed with the remaining p-orbital, because the d-orbital contribution is assumed to be small in main group elements. In this case, the axial bonds are electron-rich and are called three-centre four-electron (3c–4e) bonds.



Scheme

Alternatively, the axial bonds are described by the resonance structures in the Scheme. ^{81}Br N.q.r. frequencies also support this model, *i.e.* the resonance frequency of the axial Br atom is one-half that of the equatorial one. Below the phase-transition temperature, 253 ± 1 K, the two-fold symmetry axis disappeared. The splitting of the ^{81}Br n.q.r. frequencies is quite large, especially for the axial atom, and reaches *ca.* 50 MHz at 77 K. Therefore, it is reasonable to consider that the splitting is largely due to a change in the nature of the chemical bonds. Wide-line ^1H n.m.r. spectra show that the $C_5H_5NH^+$ ion is static, on the n.m.r. time scale, below 150 K and a narrowing is observed continuously from 150 K up to *ca.* 400 K. We can conclude, then, that in the lower temperature region one of the limiting structures in the Scheme is more stabilized, with an apparently increased polarizing power of the cation. According to Alcock[6] the longer Sb–Br bond is called the secondary bond with respect to the *trans* Sb–Br bond. It is known that the presence of symmetric and asymmetric I_3^- ions depends on the cation radius[7] and the 3c–4e bond has a similar effect on the I_3^- ions. Therefore, the following points may be concluded. The axial bond in the $SbBr_4^-$ ion is regarded as a 3c–4e bond which uses only one p-electron of the Sb atom. Furthermore, the energy difference between symmetric and asymmetric 3c–4e bonds is fairly small, because it is caused only by the temperature change.

On the other hand, at this stage there is no obvious reason for the splitting of n.q.r. frequencies due to the equatorial Br atoms at low temperature. Further experimental work will be needed to clarify this point.

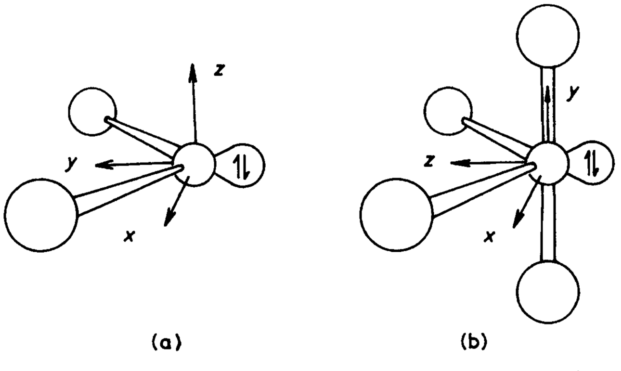


Figure 2. Orientations of the efg axes. (a) Antimony in the $SbBr_2^+$ ion and (b) antimony in the $SbBr_4^-$ ion.

We also observed a ^{121}Sb n.q.r. Zeeman effect for this compound at room temperature in order to estimate the valence-electron distribution about the Sb atom. The principal axes of the electric-field gradient (efg axes) are shown in Figure 2 and compared with those of the $SbBr_2^+$ ion which exists in $SbBr_3{\cdot}AlBr_3$.[1] It is interesting that the

z- and y-axes interchange their orientations in these two ions. If we assume that the equatorial bonds are formed by the sp^2-hybrid orbital of the Sb atom,[8] the different orientations of the efg axes can be explained by the fact that the axial p-electron density at the Sb atom of the $SbBr_4^-$ ion is considerably larger than that of the $SbBr_2^+$ ion. In both cases, however, the existence of the lone-pair electrons with some p-electron character makes an important contribution to their efg axes. The axial p-electron density estimated from the ^{121}Sb n.q.r. is in good agreement with that obtained from the axial ^{81}Br n.q.r. This finding also indicates that the axial bond is a 3c–4e bond.

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[1] E. Chemouni and A. Potier, *J. Inorg. Nucl. Chem.*, 1971, **33**, 2353.
[2] P. W. DeHaven and R. A. Jacobson, *Cryst. Struct. Commun.*, 1976, **5**, 31.
[3] S. K. Porter and R. A. Jacobson, *J. Chem. Soc. A*, 1970, 1359.
[4] S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 1966, **5**, 743.
[5] C. R. Hubbard and R. A. Jacobson, *Proc. Iowa Acad. Sci.*, 1968, **75**, 85.
[6] N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.
[7] D. Nakamura and M. Kubo, 'Advances in Nuclear Quadrupole Resonance,' Heyden & Sons, London, 1975, vol. **2**, p. 117.
[8] T. Okuda, K. Yamada, H. Ishihara, and H. Negita, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 3136.