A Variable-temperature ^{79}Br Nuclear Quadrupole Resonance and *X*-Ray Crystallographic Investigation of Dimethylammonium Hexabromostannate(IV), $[NH_2Me_2]_2[SnBr_6]$ †

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A variable-temperature ^{79}Br n.q.r. study of dimethylammonium hexabromostannate, $[NH_2Me_2]_2[SnBr_6]$, in the range 77—300 K, has shown that a phase transition occurs at 253 ± 1 K. At room temperature the crystals of the compound are orthorhombic, with a = 14.88(1), b = 7.61(1), c = 7.60(1) Å, Z = 2, and space group *Pnnm*. The structure has been refined to R = 0.076 for 846 diffractometer-measured intensities for which $I > 3\sigma(I)$. Two Sn–Br bonds in the anion are slightly longer [2.609(3) Å] than the remaining four [2.601(2) Å], in agreement with the n.q.r. results for the higher temperature phase. The results are interpreted in terms of stronger H-bonding in the low temperature phase.

While many structural studies on hexahalogenometallates of the type A_2BX_6 (where A is a univalent cation), which often have antifluorite (K_2PtCl_6) structures, have been carried out by following the temperature dependence of halogen n.q.r. frequencies,[1-3] very few hexabromostannates have been investigated in this way. The ammonium compound $[NH_4]_2[SnBr_6]$ shows phase transitions at 144 and 157 K, with three ^{79}Br signals from 77 to 144 K, two between 144 and 157 K, and a single resonance only at higher temperatures.[4] K_2SnBr_6 behaves similarly, with phase transitions at 375 and 396—399 K.[4] The occurrence of the higher temperature transition has also been detected by calorimetry, which gave a value of 399.8(4) K.[5] For this compound the room temperature crystal structure shows very slight distortion in the octahedral anion, with two Sn–Br bonds longer than the other four (two at 2.597, two at 2.591, and two at 2.590 Å),[5] thus accounting for the three observed ^{79}Br n.q.r. signals. The methylammonium salt $[NH_3Me]_2[SnBr_6]$, on the other hand, gives only a single ^{79}Br frequency from 77 to 300 K, showing that all the bromines are equivalent, although an anomaly in the temperature-dependence plot at 149 K was confirmed as due to a structural phase transition of second or higher order by thermal measurements.[6]

There have also been very few *X*-ray diffraction studies of hexabromostannates. Apart from the recent results for K_2SnBr_6,[5] the caesium, rubidium, and ammonium compounds were described in 1938 as having cubic (regular) structures at room temperature.[7] In agreement with this conclusion, these compounds have all been reported to give single ^{79}Br n.q.r. signals at or just above room temperature.[8-10] Octahedral $[SnBr_6]^{2-}$ ions have also been found in some salts of organic radical cations,[11,12] but these compounds are not of the A_2BX_6 type.

As well as being interested in obtaining more information on hexabromostannate structures, we were particularly concerned to investigate possible correlations between ^{79}Br n.q.r. frequencies and Sn–Br bond lengths in these compounds. Good correlations between halogen n.q.r. frequencies and bond lengths, with longer bonds corresponding to lower frequencies, have been found for certain types of compound, including those containing ICl_4^- ions where the ^{35}Cl frequencies are very sensitive to distortions from D_{4h} symmetry,[13] and various substituted cyclic chlorophosphazenes.[14,15] A reasonable correlation between the Sn–Cl bond length and the ^{35}Cl n.q.r. frequency has also been established for octahedral complexes of the type $SnCl_4{\cdot}2L$,[16] although no such relationship was apparent for hexachlorostannates of fairly small cations such as K^+, Rb^+, and Cs^+, possibly owing to anion–anion interactions.[17] The hexachlorostannates of larger cations such as 4-chloropyridinium, where the anion is tetragonally distorted from octahedral symmetry by H-bonding,[18,19] do follow this relationship approximately, however.[16] We have therefore studied the temperature dependence (77—300 K) of the ^{79}Br n.q.r. frequencies of the title compound, in which H-bonding may reasonably be expected, possibly leading to distortion of the anion; we have also determined the crystal structure of the compound at room temperature.

Experimental

The compound $[NH_2Me_2]_2[SnBr_6]$ was prepared by adding a solution of dimethylammonium chloride in an excess of concentrated (47%) aqueous HBr to a solution of tin(IV) bromide in the same solvent, in an overall 2 : 1 molar ratio. The precipitate which formed was filtered off and redissolved in hot concentrated aqueous HBr, and the solution allowed to cool slowly, yielding long yellow prismatic needles of the title compound, which were dried in a desiccator (Found: C, 6.95; H, 2.95; Br, 66.2; N, 4.1. $C_4H_{16}Br_6N_2Sn$ requires C, 6.95; H, 2.35; Br, 69.5; N, 4.05%).

^{79}Br N.q.r. spectra were obtained by means of a Decca spectrometer with a prototype high frequency head, using Zeeman modulation. This instrument differed from the mid-range spectrometer used for ^{35}Cl measurements and described previously,[20] in that the head was bulkier, making cooling more difficult. If liquid nitrogen was used as coolant, for example, the Dewar flask round the sample needed refilling after *ca.* 2 h. The inside of the sample can required, in addition, an atmosphere of dry helium, supplied from a cylinder, to prevent water from condensing on a variable capacitor used for frequency variation. A cryostat was used for temperatures intermediate between that of liquid nitrogen (77 K) and room temperature, in which nitrogen gas was led *via* a heating element to the spectrometer. The heating current was regulated by a thermostat; the temperature was controlled by presetting the thermostat and adjusting the flow rate of nitrogen. The sample temperature was monitored by a Comark copper–constantan thermometer attached to the outside of the brass can which contained the sample, the whole system being well lagged with cotton wool. Temperatures stable to within ±0.1 K could be obtained after 20—30 min had been allowed

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† *Supplementary data available* (No. SUP 23562, 5 pp.): observed and calculated structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1.

(i) Fractional atomic parameters ($\times 10^4$) and isotropic temperature factors ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	*U*
Sn	5 000 *	5 000 *	5 000 *	
Br(1)	3 523(2)	6 846(5)	5 000 *	
Br(2)	5 666(2)	7 002(3)	2 551(4)	
N	3 613(18)	6 879(37)	0 *	65(8)
C(1)	2 751(22)	5 961(46)	0 *	66(9)
C(2)	3 665(29)	8 871(59)	0 *	95(13)
H(1)	3 980 *	6 443 *	1 160 *	60 *
H(2)	2 684 *	4 511 *	0	60 *
H(3)	2 364 *	6 264 *	1 160	60 *
H(4)	4 357 *	9 258 *	0 *	90 *
H(5)	3 332 *	9 340 *	1 160 *	90 *

(ii) Anisotropic temperature factors ($Å^2 \times 10^3$)

	Sn	Br(1)	Br(2)
U_{11}	42(1)	59(2)	69(1)
U_{22}	50(1)	91(3)	73(1)
U_{33}	36(8)	72(8)	51(8)
U_{23}	0 *	0 *	15(1)
U_{13}	0 *	0 *	2(1)
U_{12}	−1(1)	29(2)	20(1)

* Parameter calculated, or fixed by symmetry requirements.

for thermal equilibration. Because of the spectrometer design, however, the temperature could be reduced only to *ca.* 180 K by this means. Temperatures between 180 and 77 K were obtained more crudely by allowing the sample to warm up from 77 K and scanning quickly; the temperature was measured when the centre of the resonance appeared to be reached. The study of this temperature region was necessarily less detailed than at higher temperatures, however, particularly since the compound gave two separate resonances, at different frequencies. Only one of these could be recorded at each temperature. Resonance frequencies were determined with an accuracy of ±5 kHz by interpolation between the spectrometer frequency markers, which were calibrated by means of a frequency counter (Advance Instruments T.C. 16).

The crystal used for *X*-ray data collection had dimensions of $0.12 \times 0.20 \times 0.88$ mm.

Crystal Data.—$C_4H_{16}Br_6N_2Sn$, $M = 690.3$, Orthorhombic, $a = 14.88(1)$, $b = 7.61(1)$, $c = 7.60(1)$ Å, $U = 860.60$ Å^3, space group *Pnnm*, $D_m = 2.67$ Mg m^{-3}, $Z = 2$, $D_c = 2.66$ Mg m^{-3}, $F(000) = 628.0$, $\mu = 150.28$ cm^{-1} for Mo-K_α radiation, $\lambda = 0.7107$ Å.

Intensity data for 1 172 independent reflections were collected with a Stoe Stadi-2 automatic two-circle diffractometer using graphite-monochromatised Mo-K_α radiation. Measurements were made with a variable ω scan for the layers $l = 0$—8. After processing with an initial data reduction program, the 846 reflections for which $I > 3\sigma(I)$ were corrected for absorption and used to calculate a Patterson map.[21] From this, the positions of the tin atom and one bromine [Br(2)] were found. The remaining non-hydrogen atoms were located from an (F_o-F_c) map calculated using the co-ordinates of Sn and Br(2). Atomic positions (other than those fixed by symmetry) and temperature factors (anisotropic for Sn and Br, isotropic for C and N) were refined in alternate cycles with the inter-layer scale factors. All calculations were performed with the SHELX program.[21] The *R* value obtained prior to the inclusion of hydrogen atoms was 0.080. Hydrogens were included at positions calculated by the AFIX routine in SHELX (see Discussion section) and given isotropic temperature factors similar to those of the atoms to which they are attached. The final *R* value was 0.076. Final atomic positions and temperature factors are given in Table 1. Unique bond distances and angles are shown in Figure 1.

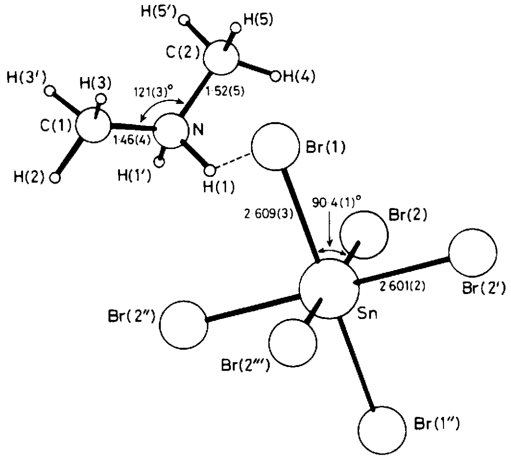

Figure 1. View of the $[SnBr_6]^{2-}$ anion with one cation. The symmetry-related dimethylammonium ion at $(-x, -y, z)$ is omitted for clarity. The dotted line indicates one of several hydrogen bonds in the structure. Symmetry relations: (′) = $x, y, -z$; (″) = $-x, -y, z$; (‴) = $-x, -y, -z$

Results and Discussion

(*a*) ^{79}Br *N.Q.R. Measurements.*—The title compound showed two ^{79}Br n.q.r. frequencies in the temperature range 300—77 K (Table 2, Figure 2). (At 77 K only, the lower frequency resonance was split into two equally intense components.) Only one frequency could be measured at each temperature between *ca.* 180 and 77 K (see Experimental section); the signals were therefore measured alternately, as shown in Table 2. The resonance at higher frequency was approximately twice as intense as the lower frequency signal at all temperatures; this agrees completely with the crystal structure at room temperature described in the following section. The temperature-dependence graph in Figure 2 reveals a dramatic phase change at 253 ± 1 K, with a clear discontinuity in the plots for both resonances at this point. On further cooling, several smaller discontinuities were apparent before the compound settled into a low temperature phase at 242 ± 1 K. The interpretation of structural phase changes in compounds of the type R_2MX_6 has been discussed extensively by Armstrong and co-workers,[2,3] who have given a theoretical treatment of certain types of transition which enables the space group in the new phase to be determined. Their theories cannot be applied in the present case, however, since they require the splitting of a single resonance into more components at a phase transition, which does not occur here.

Both resonances show less negative temperature coefficients below the phase transition than above it. Since the room temperature structure indicates that hydrogen bonding is occurring between the $^-$NH protons of the cations and the bromines of $[SnBr_6]^{2-}$, this observation strongly suggests that hydrogen bonding may be stronger in the low temperature phase. Hydrogen bonding has been found to lead to anomalous (either positive or less negative than expected) temperature coefficients for the n.q.r. frequencies of halogens affected by such interactions, as in the lowest ^{35}Cl n.q.r. frequency for $NaICl_4{\cdot}2H_2O$ and $NaICl_4{\cdot}2D_2O$.[22] It may therefore be concluded reasonably that the phase transition occurs

Table 2. Temperature variation of ^{79}Br n.q.r. of $[NH_2Me_2]_2[SnBr_6]$

T/K (±0.1 K)	^{79}Br N.q.r. frequencies (MHz) (±0.005)	
301.4	135.150	131.205
287.6	135.240	131.415
281.5	135.300	131.500
276.9	135.322	131.560
271.9	135.348	131.628
266.7	135.382	131.682
261.5	135.408	131.742
259.6	135.414	131.766
257.0	135.430	131.798
255.8	135.428	131.802
254.9	135.432	131.810
253.7	135.434	131.816
252.7	135.200	131.620
251.6	135.126	131.608
249.6	135.014	131.600
246.9	135.020	131.460
242.1	134.944	131.450
236.9	134.910	131.508
231.6	134.886	131.575
226.8	134.864	131.588
221.5	134.856	131.608
217.6	134.848	
216.5		131.632
209.5	134.844	131.666
199.5	134.842	131.708
189.5	134.846	131.756
179.7		131.784
177.1	134.866	
175.0		131.804
172.0	134.874	
170.0		131.822
167.3	134.882	
165.1		131.842
161.9	134.892	
158.5		131.860
154.0	134.914	
149.0		131.886
145.2	134.932	
142.2		131.898
135.9	134.950	
134.7		131.906
99.5	134.986	
77.0	135.020	130.730, 130.575

in order to accommodate the formation of stronger H-bonds in the low temperature phase.

Another noteworthy feature of the temperature-dependence plot is the split signal for the lower frequency resonance at 77 K, both components of which are at much lower positions than the single resonance at higher temperatures. This result was clearly reproducible, and no splitting was apparent at 135 K. Unfortunately, because of the limitations of the experimental technique which had to be used between 180 and 77 K, it proved impossible to obtain measurements at a temperature intermediate between 135 and 77 K for this resonance, possibly because of splitting (which would make the signal harder to detect). The existence of a second phase transition between 135 and 77 K therefore cannot be discounted. If such a transition does occur, however, it does not appear to affect greatly the higher frequency resonance, which is not split at 77 K and shows no marked change in frequency between 135 and 77 K.

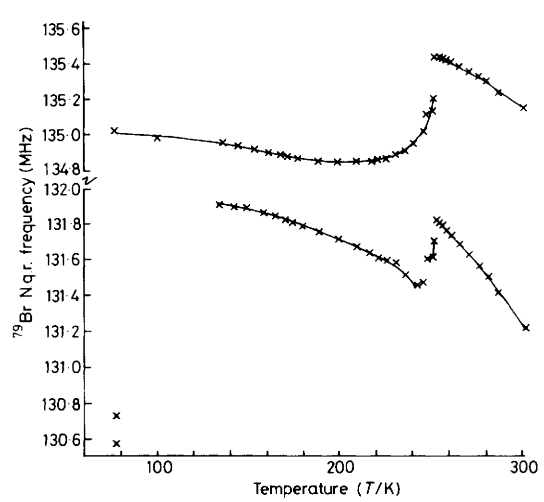

Figure 2. Temperature-dependence plot (77—300 K) for the ^{79}Br n.q.r. frequencies from $[NH_2Me_2]_2[SnBr_6]$

(*b*) *Crystal Structure Determination.*—The structure consists of almost octahedral $[SnBr_6]^{2-}$ ions hydrogen bonded to neighbouring $[NH_2(CH_3)_2]^+$ ions. As a result of symmetry considerations, there are only six unique non-hydrogen atoms in the molecule (see Figure 1). The tin atom lies on a four-fold special position at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The two dimethylammonium ions lie in the mirror plane at $z = 0$ and are symmetry-related (for clarity, only one of these is shown in Figure 1). The tin-bromine distances obtained agree well with the n.q.r. prediction that there should be two different Sn–Br distances in the anion, in an overall 2 : 1 ratio.

In general, compounds with the formula M_2SnBr_6 (M = K, Rb, Cs, or NH_4) are found to have isolated $[SnBr_6]^{2-}$ ions with a very slightly distorted octahedral arrangement.[23] The structure of potassium hexabromostannate(IV)[5] has two Sn–Br bonds longer than the remaining four, but the bond lengths found for this compound [2 × 2.597(3), 2 × 2.590(3), 2 × 2.591(3) Å] are all shorter than those obtained in the present work. The hexachlorostannates, for which more structural information is available, have a similar geometry;[23] however, in some cases all the Sn–Cl bonds are the same length [*e.g.* tetramethylammonium hexachlorostannate(IV)[24]], in others there may be two Sn–Cl bonds shorter than the remaining four [as in the almost isostructural dimethylammonium hexachlorostannate(IV)[25]], or there may be three different Sn–Cl bond lengths [*e.g.* bis(triethylammonium) hexachlorostannate(IV)[26]]. Because of the wide variation of bond lengths obtained for these compounds (within limits), it is difficult to draw conclusions about the hexabromostannates by comparison with the known structures of the hexachlorostannates.

Throughout the structure of dimethylammonium hexabromostannate(IV), ions of opposite charge are joined by hydrogen bonds. Br(1) and Br(1″) * occur almost directly above the dimethylammonium nitrogens in the c direction, the N–Br distance being 3.80 Å. The distance from the calculated position of H(1) to Br(1) is 3.01 Å, which is less than the sum of the van der Waals radii (H 1.2, Br 1.95 Å).[27] Ions are also linked by bonds between H(1) and Br(2) [N–Br(2) 3.60, H(1)–Br(2) 2.76 Å]. These contacts also occur between neighbouring ions in different unit cells. In addition, there are some fairly short contacts between bromines and methyl hydrogens. These are more likely to be due to steric effects than to bonding interactions; the hydrogen positions are con-

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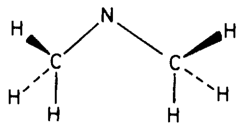
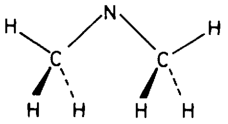
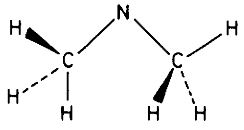
* A double prime (″) indicates the symmetry relation ($-x$, $-y$, z).



(I)



(II)



(III)

strained by both geometry and symmetry considerations. Since the hydrogen positions were calculated, there is some uncertainty about the exact orientation of the methyl groups. An electron diffraction study of dimethylamine[28] gives a best fit with experimental data when the methyl hydrogens are staggered relative to one another, while the crystal structure of dimethylnitramine[29] shows the methyl hydrogens to be in the eclipsed configuration (I). The calculated hydrogen positions for dimethylammonium hexachlorostannate(IV)[25] indicate that the hydrogens are also eclipsed in this molecule.

The three possible configurations (I)—(III) were investigated in some detail for the present compound (no partially staggered configurations are possible because of symmetry considerations). The best *R* value was obtained with configuration (II) (*R* for other configurations being worse than the value with no hydrogens present) and this was confirmed by AFIX calculations. This configuration involves closer contacts between methyl hydrogens and the bromines than configuration (I); configuration (III) would have half the number of close contacts.

As indicated above, the crystal structure and n.q.r. results at room temperature are entirely compatible. The structure shows four shorter and two longer Sn–Br bonds in a slightly distorted octahedral arrangement, while the n.q.r. spectrum shows two resonances in a 2 : 1 intensity ratio, with the higher frequency line corresponding to the shorter bond distance, as expected.[13-16] Insufficient data are available for other hexabromostannates to enable more general conclusions to be drawn about possible bond length–frequency relationships. The only other compound for which both types of results are available with sufficient accuracy is K_2SnBr_6, which shows three slightly different Sn–Br bond lengths[5] and three ^{79}Br n.q.r. signals at room temperature.[4] Since the signals are of equal intensity, however, they cannot be assigned to individual Sn–Br bond distances without assuming a relationship between bond length and frequency. The frequencies in this instance are also likely to be strongly affected by interanionic repulsions, which have been correlated with the ^{35}Cl n.q.r. frequencies in hexachlorostannates of fairly small cations, including K^+, Rb^+, and Cs^+.[17] Further work on related compounds is continuing.

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