Bromine Nuclear Quadrupole Resonance Studies of some Hexabromostannates: *X*-Ray Crystal Structure† of Pyridinium Hexabromostannate(IV), $[Hpy]_2[SnBr_6]$

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Bromine n.q.r. measurements have shown that the anion in $[NHMe_3]_2[SnBr_6]$ has a regular octahedral structure in the temperature range 77—300 K, and that $[SMe_3]_2[SnBr_6]$ may well have a similar structure at room temperature, whereas $[NMe_4]_2[SnBr_6]$ undergoes a phase transition to a less regular structure between 178 and 77 K. No signals were obtained from the hexabromostannates(IV) of the cations $[NEt_4]^+$, $[NPr^n_4]^+$, or $[IPh_2]^+$. A variable-temperature study of the corresponding pyridinium compound in the range 77—335 K has shown that one of the three bromine signals (^{79}Br or ^{81}Br) is at a much lower frequency than the other two, probably due to hydrogen bonding. The only evidence of a possible phase transition was a cusp at 296 ± 1 K in the temperature-dependence plot for one of the ^{81}Br resonances. The crystals of this compound are monoclinic at room temperature, with $a = 13.02(1)$, $b = 8.66(1)$, $c = 8.25(1)$ Å, $\beta = 96(1)°$, $Z = 2$, and space group $C2$. The structure has been refined to $R = 0.041$ for 926 diffractometer-measured intensities for which $F > 4\sigma(F)$. Three significantly different Sn–Br distances of 2.624(5), 2.582(1), and 2.559(6) Å were found, in agreement with the n.q.r. results where the three signals at 300 K are in a 3:2:1 intensity ratio. The relationship between Sn–Br bond lengths and bromine n.q.r. frequencies in this and other hexabromostannates is discussed.

Extensive structural studies by means of halogen n.q.r. measurements on hexahalogenometallates A_2BX_6 (X = Cl, Br, or I; A is a univalent cation) have been reported,[1–3] but few of these have involved hexabromostannates. Previous work in this area[4–8] has been described by us in a recent paper[9] on the variable-temperature ^{79}Br n.q.r. and *X*-ray crystallographic investigation of $[NH_2Me_2]_2[SnBr_6]$. This compound showed a phase transition at 253 ± 1 K, the results being attributed to stronger hydrogen bonding in the low-temperature phase. Very recently a study of the phase transitions at 157 and 144 K in $[NH_4]_2[SnBr_6]$ by means of bromine n.q.r. and neutron diffraction techniques has given information on the structures adopted in the lower temperature phases.[10] There are also few *X*-ray diffraction results for hexabromostannates. Apart from $[NH_2Me_2]_2[SnBr_6]$, which has a distorted octahedral anion at room temperature, with two bonds slightly longer (2.609 Å) than the other four (2.601 Å),[9] only K_2SnBr_6 has been investigated in recent years.[11] This compound shows a very small distortion, with three slightly different Sn–Br bond lengths. The caesium, rubidium, and ammonium salts were described in 1938 as having cubic (regular) structures,[12] while octahedral $[SnBr_6]^{2-}$ ions have been found in some salts of organic radical cations, although these are not of the A_2BX_6 type.[13,14]

Where bromine (usually ^{79}Br) n.q.r. and *X*-ray data are available, a good correlation between the number of resonances observed and the number of distinct Sn–Br distances has been found. K_2SnBr_6 shows three equally intense ^{79}Br resonances at room temperature,[4] as expected from the crystal structure,[11] while the compounds Cs_2SnBr_6, Rb_2SnBr_6, and $[NH_4]_2[SnBr_6]$ give single lines close to room temperature,[8–10] in accordance with the O_h symmetry of the anion.[12] $[NH_2Me_2]_2[SnBr_6]$ yields two ^{79}Br signals at room temperature in a 2:1 intensity ratio, fully in agreement with the structure;[9] the results, moreover, are as expected in that the longer Sn–Br bond distance corresponds to the lower ^{79}Br n.q.r. frequency. Correlations between halogen n.q.r. frequencies and bond lengths have previously been established in various compounds, including some cyclic chlorophosphazenes[15,16] and tetrachloroiodates[17,18] as well as octahedral tin complexes of the type $SnCl_4 \cdot 2L$(L = MeCN, Me_2SO, or PCl_3O).[19] No such correlation was apparent in hexachlorostannates of monatomic cations such as K^+, Rb^+, and Cs^+, possibly because of anion–anion repulsions,[20] but hexachlorostannates of larger cations such as 4-chloropyridinium[21,22] did follow this relationship approximately.[19] We were interested in extending the range of hexabromostannates studied which show deviations from O_h symmetry, to check the scope and validity of bond length–frequency correlations. We have therefore determined the temperature dependence (in the range 77—335 K) of the more readily observable Br n.q.r. frequencies of $[Hpy]_2[SnBr_6]$ [Hpy = pyridinium(1+)], together with its crystal structure at room temperature. Some bromine n.q.r. frequencies are also given for $[NHMe_3]_2[SnBr_6]$, $[SMe_3]_2[SnBr_6]$, and $[NMe_4]_2[SnBr_6]$, although detailed temperature-dependence studies were not carried out for these compounds. No signals between 110 and 142 MHz could be detected from $[NEt_4]_2[SnBr_6]$, $[NPr^n_4]_2[SnBr_6]$, or $[IPh_2]_2[SnBr_6]$ at 77, *ca.* 190, or 300 K, despite repeated searches. This behaviour could possibly be due to the size of the cation, which effectively dilutes the $[SnBr_6]^{2-}$ concentration.

Experimental

Preparations.—$[NMe_4]_2[SnBr_6]$. This compound was prepared by dissolving NMe_4Br in an excess of concentrated (47%) aqueous HBr (conc. HBr), and then adding sufficient $SnBr_4$, dissolved in the same solvent, to make up a 2:1 molar ratio of the reactants (in favour of NMe_4Br). The precipitate which formed was filtered off and recrystallised from conc. HBr. The resultant yellow crystals were washed with CH_2Cl_2 and dried *in*

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† *Supplementary data available* (No. SUP 56220, 2 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

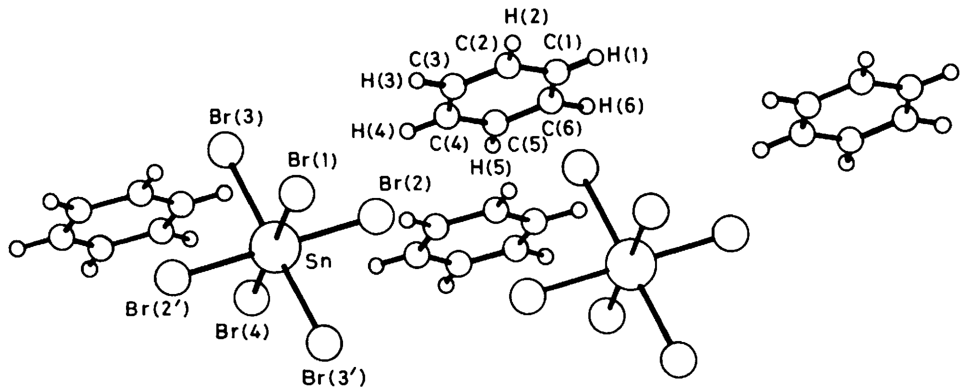

Figure 1. View of two $[SnBr_6]^{2-}$ anions with four symmetry-related pyridinium cations [(′) indicates the symmetry relation $-x, y, -z$]

Table 1. Carbon, H, and N microanalyses for some hexabromostannates(IV)

	Found (%)			Calc. (%)		
Compound	C	H	N	C	H	N
$[NMe_4]_2[SnBr_6]$	12.8	3.4	3.8	12.9	3.2	3.8
$[NHMe_3]_2[SnBr_6]$	10.1	3.1	4.0	10.0	2.8	3.9
$[SMe_3]_2[SnBr_6]$	9.4	2.6	—	9.6	2.4	—
$[Hpy]_2[SnBr_6]$	15.5	1.8	3.5	15.8	1.6	3.7
$[NEt_4]_2[SnBr_6]$	22.8	5.1	3.2	22.4	4.7	3.3
$[NPr^n_4]_2[SnBr_6]$	29.7	6.6	2.9	29.7	5.8	2.9
$[IPh_2]_2[SnBr_6]$	24.9	1.4	—	24.8	1.7	—

vacuo. Carbon, H, and N analyses for this and the other hexabromostannates prepared in this work are given in Table 1; they were obtained as described previously.[23] The compound $[NHMe_3]_2[SnBr_6]$ was similarly prepared, except that NMe_3 in ethanol (33% w/w) was used instead of NMe_4Br.

$[SMe_3]_2[SnBr_6]$. This compound was obtained by adding a 2:1 molar ratio of SMe_3I to $SnBr_4$ in excess conc. HBr, producing an instant white precipitate. This was separated, washed with acetone, recrystallised from conc. HBr, washed again with acetone and low-boiling (30—40 °C) light petroleum, and dried in a desiccator. As well as C, H, and N microanalyses, S (by oxygen flask combustion followed by titration as sulphate) and Sn (by atomic absorption) were also analysed for this compound (Found: S, 8.50; Sn, 15.8. $C_6H_{18}Br_6S_2Sn$ requires S, 8.50; Sn, 15.8%).

$[Hpy]_2[SnBr_6]$. This complex was prepared by adding together a 2:1 molar ratio of pyridine (py) and tin(IV) bromide in conc. HBr, separating the precipitate, and recrystallising it from conc. $HBr-H_2O$ (1:1). The yellow crystals were washed with CH_2Cl_2 and Et_2O.

$[NEt_4]_2[SnBr_6]$. This complex was obtained by stirring a 2:1 ratio of NEt_4Cl and $SnBr_4$ in conc. HBr for 1 h. The precipitate which formed was isolated and recrystallised from conc. $HBr-H_2O$ (1:1), yielding yellow crystals of the product, which were washed with CH_2Cl_2 and dried *in vacuo*. The compound $[NPr^n_4]_2[SnBr_6]$ was similarly prepared from NPr^n_4I and $SnBr_4$ (2:1) in an excess of conc. HBr. The solution was heated to boiling and filtered hot to remove traces of iodine. On cooling crystals of the product appeared; these were separated and washed with CH_2Cl_2 and Et_2O.

$[IPh_2]_2[SnBr_6]$. This compound was obtained by stirring a 2:1 molar ratio of IPh_2Br and $SnBr_4$ in CH_2Cl_2 for 48 h. The yellow powder which resulted was filtered off and washed with CH_2Cl_2 and low-boiling light petroleum. In addition to C and H, microanalyses for Sn, Br, and I[23] were carried out (Found: Br, 41.6; I, 22.4; Sn, 10.1. $C_{24}H_{20}Br_6I_2Sn$ requires Br, 41.3; I, 21.9; Sn, 10.2%).

Bromine n.q.r. spectra were recorded as described previously.[9]

Crystal Data.—$C_{10}H_{12}Br_6N_2Sn$, $M = 758.1$, monoclinic, $a = 13.02(1)$, $b = 8.66(1)$, $c = 8.25(1)$ Å, $\beta = 96(1)°$, $U = 925.1$ Å^3, space group $C2$, $D_m = 2.70$ Mg m^{-3}, $Z = 2$, $D_c = 2.72$, $F(000) = 692$, Mo-K_α radiation, $\mu = 139.83$ cm^{-1}, $\lambda = 0.7107$ Å.

Intensity data for 1 093 independent reflections were collected from a crystal (0.15 × 0.12 × 0.77 mm) 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 $k = 0$—8.

The 926 reflections for which $F > 4\sigma(F)$ were corrected for absorption with routines in SHELX[24] and used to calculate a Patterson map. From this, the space group appeared to be $C2/m$, the bromine positions being located from a first difference map and the position of the pyridinium ring from a second. The position of the ring, which was very well defined, was such that in this space group the nitrogen would be symmetry-related to a carbon. The space group was accordingly changed to the lower symmetry $C2$, the tin atom and two of the bromines [Br(1) and Br(4)] being placed on two-fold special positions at $(0, y, 0)$ ($y = 0$ for Sn). Refinement was continued by the method of least squares to a final R value of 0.041 (best R for space group $C2/m$, 0.071 with a number of large peaks remaining on the difference map). The final positions of Br(1) and Br(4) show a clear move away from the symmetry-related $C2/m$ arrangement, indicating that the choice of space group $C2$ was correct. The difficulty encountered here highlights the care required in assigning a space group to compounds in which a very high proportion of the electron density is due to a small number of heavy atoms.

The nitrogen atom could not be assigned to a specific position in the ring, and for the purposes of the refinement all the ring atoms were therefore treated as carbon. Hydrogen atoms were included at calculated positions (C–H = 1.08 Å), with isotropic thermal parameters fixed at 0.05 Å^2. Anisotropic thermal parameters were refined for the tin and bromine atoms, and isotropic thermal parameters for the remaining atoms. All calculations (including a routine check for handedness, as the space group is polar) were performed with the SHELX program.[24] Final atomic co-ordinates are listed in Table 2. Unique bond distances and angles are given in Table 3. A view of the structure is shown in Figure 1.

Results and Discussion

(a) *Bromine N.Q.R. Measurements*.—Bromine n.q.r. frequencies (^{79}Br except where indicated otherwise) for the

Table 2. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for $[Hpy]_2[SnBr_6]$

Atom	*x*	*y*	*z*
Sn	0*	0*	0*
Br(1)	0*	3 035(6)	0*
Br(2)	719(1)	14(9)	3 038(1)
Br(3)	1 861(1)	16(10)	−946(2)
Br(4)	0*	7 045(7)	0*
C(1)	1 593(10)	6 063(15)	7 105(13)
C(2)	1 458(10)	6 727(15)	5 557(13)
C(3)	1 305(10)	5 789(15)	4 178(13)
C(4)	1 286(10)	4 187(15)	4 347(13)
C(5)	1 421(10)	3 522(15)	5 896(13)
C(6)	1 575(10)	4 460(15)	7 275(13)
H(1)	1 712*	6 789*	8 173*
H(2)	1 473*	7 967*	5 426*
H(3)	1 200*	6 303*	2 979*
H(4)	1 167*	3 460*	3 280*
H(5)	1 407*	2 282*	6 027*
H(6)	1 680*	3 946*	8 473*

* Parameter calculated, or fixed by symmetry requirements.

Table 3. Unique bond lengths (Å) and angles (°) for $[Hpy]_2[SnBr_6]$*

Sn–Br(1)	2.628(5)	Sn–Br(3)	2.623(1)
Sn–Br(2)	2.582(1)	Sn–Br(4)	2.559(6)
All C–C	1.395 (constrained)		
Br(1)–Sn–Br(3)	89.7(2)	Br(1)–Sn–Br(2)	89.7(2)
Br(2)–Sn–Br(3)	92.1(0)	Br(4)–Sn–Br(2)	90.3(2)
Br(4)–Sn–Br(3)	90.3(2)	All C–C–C	120.0 (constrained)

* Average Br–C (for the six non-bonding contacts less than 4.0 Å) 3.72 Å , shortest Br–C 3.43 Å, corresponding Br–H 2.75 Å. Average Br–H 2.94 Å.

Table 4. Bromine n.q.r. frequencies for some hexabromostannates A_2SnBr_6

A^+	Bromine n.q.r. frequencies[a] 77 K	Intermediate temp.	300 K
$[NH_3Me]^+$	131.726	Not recorded	130.820
$[NHMe_3]^+$	138.871	137.991 (186 K)	137.170
$[NMe_4]^+$	140.30[b](1) 140.60[b](1) 141.37[b](2)	138.670 (178 K)	137.736
$[SMe_3]^+$	—	—	138.10[b]
$[Hpy]^+$	119.034[c](2) 120.910[c](1) 122.595	118.764[c](2) (190.6 K) 119.583[c](1) 122.822	116.565[c](1) 118.000[c](2) 123.660

[a] ±0.005 MHz unless stated otherwise; relative intensities are given in parentheses. [b] ±0.05 MHz. [c] ^{81}Br frequencies (all others are ^{79}Br frequencies).

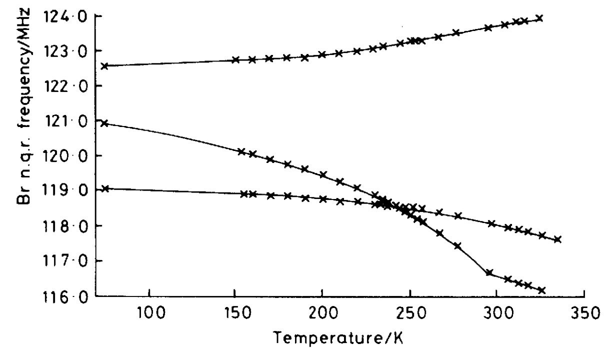

Figure 2. Temperature-dependence plot (77—335 K) for some Br n.q.r. frequencies of $[Hpy]_2[SnBr_6]$

hexabromostannates at 77, 300, and an intermediate temperature (where signals were observable) are shown in Table 4. In addition the resonance from $[NH_3Me]_2[SnBr_6]$ at 77 K, previously reported at 131.75 ± 0.05 MHz,[5] was recorded as a check on the apparatus, and appeared at 131.726 MHz. No signals were detected for $[NEt_4]_2[SnBr_6]$, $[NPr^n{}_4]_2[SnBr_6]$, or $[IPh_2]_2[SnBr_6]$ at any temperature.

$[NHMe_3]_2[SnBr_6]$ showed a single ^{79}Br resonance throughout, indicating a regular octahedral structure for the anion in this compound. A single signal was also detected for $[SMe_3]_2[SnBr_6]$ at 300 K, suggesting the presence of a symmetrical anion. The resonance was very weak, however, and if other, weaker signals had been present they would probably not have been detected. $[SMe_3]_2[SnCl_6]$ has similarly been reported as giving only one ^{35}Cl resonance at room temperature.[25,26] No signals were found from $[SMe_3]_2[SnBr_6]$ at lower temperatures. $[NMe_4]_2[SnBr_6]$ also exhibited a single resonance at 178 and 300 K, but gave three signals in an approximate 1:1:2 intensity ratio at 77 K. The results imply the occurrence of a structural phase transition between 77 and 178 K, with distortion of the anion from a regular octahedral configuration at high temperatures to a lower symmetry structure. The exact nature of the low-temperature phase could not be readily predicted from the three signals observed, since the sum of their relative intensities was not a factor of six. This could be due to the presence of at least two molecules in the unit cell (the sum of the intensities is a factor of twelve), but a failure to observe other, weaker signals cannot be entirely discounted, since the resonances seen were quite weak. Unfortunately experimental difficulties in attaining steady temperatures between 77 and 178 K precluded a more detailed study of the phase change.

Investigation of $[Hpy]_2[SnBr_6]$ revealed one of the deficiencies of the prototype high-frequency spectrometer used in this work,[9] which in the range 100—150 MHz only functioned consistently between 100 and 142 MHz. There were some blank spots between 110 and 110 MHz, and the region from 142 to 149 MHz could only be scanned on intermittent occasions. Three signals were readily detected at 77 K, at 119.034, 120.910, and 122.595 MHz. The first two were assigned to ^{81}Br nuclei, since on one occasion when the spectrometer was functioning between 142 and 149 MHz two strong signals were detected at *ca.* 143 and 145 MHz (77 K). The observed ^{81}Br frequencies when multiplied by the theoretical ratio 1.19707[27] give predicted ^{79}Br frequencies of 142.5 and 144.7 MHz. No signal was found at 146.8 MHz, however, as would be expected for an ^{81}Br resonance frequency of 122.595 MHz. The latter signal was confirmed as arising from ^{79}Br nuclei by observation of ^{81}Br resonances at 102.423 MHz (77 K) and 103.385 MHz (300 K), after a careful search. At 300 K the overall intensity ratio for the three ^{81}Br signals was 3(103.385):2(118.000):1(116.565 MHz). The theoretical frequencies for ^{81}Br calculated from the observed ^{79}Br signals at 122.595 (77 K) and 123.660 (300 K) MHz are 102.41 and 103.30 MHz respectively. These low-frequency signals were of higher intensity (*ca.* 3:1 at 300 K) than the corresponding ^{79}Br resonances, probably indicating a difference in relaxation behaviour for the two nuclei.

The full temperature-dependence plot for the three signals seen between 119 and 123 MHz (at 77 K) is shown in Figure 2. The only evidence of a phase change in this compound comes

Table 5. Correlation of cation size with ^{79}Br n.q.r. frequency for some hexabromostannates (A_2SnBr_6) at 300 K

A^+	Volume of A_2SnBr_6 unit (Å^3)	Structure ref.	Average ^{79}Br n.q.r. frequency (MHz)	N.q.r. ref.
K^+	293.5	11	127.95	8
$[NH_4]^+$	296.9	12	126.53	8
Rb^+	301.1	12	128.34	7
Cs^+	315.8	12	131.69*	6
$[NH_3Me]^+$	315.1	5	130.820	This work
$[NH_2Me_2]^+$	430.3	9	133.835	9
$[Hpy]^+$	462.5	This work	132.202*	This work

* Calculated from the ^{81}Br n.q.r. frequencies.[27]

from a cusp at 296 ± 1 K in the lower frequency ^{81}Br signal. Two of the three signals faded out at *ca.* 325 K, but the middle resonance could still be detected at 335 K, as shown. Similar behaviour has been observed for $[Hpy]_2[SnCl_6]$, suggesting a common relaxation mechanism for the halogen nuclei.[25] The hexachlorostannate showed splitting of the ^{35}Cl n.q.r. signals at 140 ± 5 K,[25] but no such occurrence was found for the hexabromostannate. The two ^{81}Br curves cross at *ca.* 242 K, as shown in Figure 2. The positive (anomalous) temperature coefficient for the ^{79}Br resonance strongly suggests that these bromines may be involved in hydrogen bonding.[28] This is supported by the very much lower ^{81}Br frequency found (by calculation or observation) for this signal. The lowest frequency ^{35}Cl resonance from $NaAuCl_4{\cdot}2H_2O$ or $NaAuCl_4{\cdot}2D_2O$, which also showed an anomalous temperature-dependence, has similarly been ascribed to H- (or D-) bonded chlorines.[29]

(b) *Crystal-structure Determination of* $[Hpy]_2[SnBr_6]$.—The structure consists of a regular network of one $[SnBr_6]^{2-}$ ion alternating with two symmetry-related pyridinium ions roughly parallel to *c* (Figure 1). Each pair of pyridinium ions is surrounded by four $[SnBr_6]^{2-}$ ions in the *bc* plane. Since the position of the nitrogen atom could not be determined, it is not possible to state categorically whether or not the ions are linked together by specific hydrogen bonds. All of the atoms in each pyridinium ring (all treated as carbons) are close enough to bromine for a hydrogen bond to occur (Table 3). In each case there are distances between the calculated hydrogen position and that of one or more bromines that are less than the sum of the van der Waals radii (H = 1.2, Br = 1.95 Å).[30] It is possible that the positive charge may be delocalised around the pyridinium ring to some extent, enabling several weak secondary bonds to be formed between hydrogens and neighbouring bromines. However, in the related compound $[NH_2Me_2]_2[SnBr_6]$[9] there are some close approaches of bromine to methyl hydrogens where it appears that no bonding can occur and that the effect is merely steric; this may also be the case in the present compound.

In contrast with the structure of $[NH_2Me_2]_2[SnBr_6]$,[9] where four short [2.601(2) Å] and two long [2.609(3) Å] Sn–Br bond distances were found, the $[SnBr_6]^{2-}$ ion of the present compound contains three distinct distances: Sn–Br(1) 2.628(5), Sn–Br(3) 2.623(1) (equal in length within experimental error), Sn–Br(2) 2.582(1), and Sn–Br(4) 2.559(6) Å. Allowing for symmetry-related atoms, there are three long, two intermediate, and one short bond(s) between tin and bromine in this compound.

(c) *Relationship between Cation Size and* ^{79}Br *N.Q.R. Frequency for Hexabromostannates.*—Compounds of the general formula A_2SnBr_6, where A is a univalent cation, are known to crystallise in most cases with the cubic antifluorite structure, or slight distortions thereof. If the size of the $[SnBr_6]^{2-}$ ion is assumed to be approximately constant, as justified by the close similarity in Sn–Br bond lengths within all known structures which range from 2.559 to 2.628 Å, the controlling factor for the overall size of the lattice should be the size of the cation. Hence if the volume of a single A_2SnBr_6 unit is calculated from the unit-cell dimensions (*i.e.*, total unit-cell volume divided by *Z*, the number of formula units per unit cell), the value obtained should give an estimate of the relative cation sizes. The data thus calculated are shown in Table 5, together with the corresponding ^{79}Br n.q.r. frequencies; these are weighted averages, evaluated from the relative signal intensities where more than one line is observed.

Table 5 reveals a general increase in average ^{79}Br frequency with increasing cation size, which can be rationalised if the electrostatic repulsion between the anions is considered. (Although the dimensions of the rubidium, caesium, and ammonium compounds were obtained in 1938[12] and their accuracy may be less good than for structures determined more recently by improved instrumental techniques, minor errors in the measurements would not significantly affect this pattern.) Increasing repulsive forces between $[SnBr_6]^{2-}$ ions would diminish the core electron polarisations around the bromine nuclei, hence reducing the electric-field gradients at these nuclei and decreasing their n.q.r. frequencies. There appears to be a lower limit where the frequency changes very rapidly for only small changes in A_2SnBr_6 volume. This almost certainly represents the point at which the $[SnBr_6]^{2-}$ ions are in the closest possible contact, with the cations fitting into the spaces between them, and occurs at *ca.* 295 Å^3. The other limit (*i.e.*, where the average n.q.r. frequency becomes independent of cation size), corresponding to $[SnBr_6]^{2-}$ ions free from the effects of interanionic repulsions, is not easy to determine because of lack of data, but from the n.q.r. results for the $[NHMe_3]^+$, $[NMe_4]^+$, and $[SMe_3]^+$ compounds (Table 4), where no structural information is available, it may well lie between 137.5 and 138.5 MHz. Similar behaviour has been observed for ^{35}Cl nuclei in hexachlorostannates, with an analogous lower-volume limit and an upper-frequency limit.[25] The results therefore provide a way of predicting the average ^{79}Br n.q.r. frequencies at room temperature for hexabromostannates from the unit-cell dimensions, despite the limitations of the model and the approximations involved therein.

This correlation is similar to that proposed by Brill *et al.*[20] for hexachlorostannates, which related interionic Cl $\cdots$ Cl distances with the n.q.r. data, and ascribed changes in ^{35}Cl n.q.r. frequencies to anion–anion repulsions. The interionic distances can only be found after a full crystal-structure determination, however, whereas unit-cell dimensions tend to be easier to obtain. Furthermore they only considered cubic systems,[20] while the present approach can be applied equally well to other types of structure at room temperature.

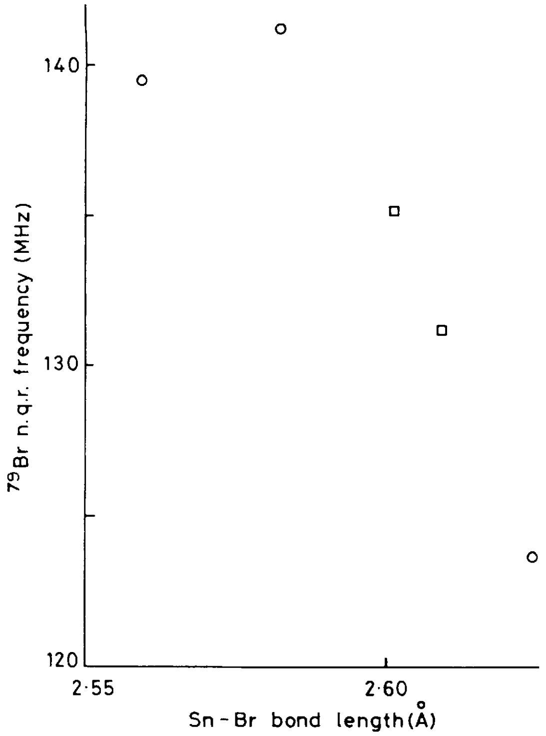

Figure 3. Relationship between ^{79}Br n.q.r. frequency and Sn–Br bond length at 300 K for $[Hpy]_2[SnBr_6]$ (○) and $[NH_2Me_2]_2[SnBr_6]$ (□)

(d) *Relationship between* ^{79}Br *N.Q.R. Frequency and Bond Length in Hexabromostannates.*—The crystal structure and n.q.r. results for $[Hpy]_2[SnBr_6]$ at room temperature as described above are consistent in that three different ^{81}Br n.q.r. signals were observed in a 3:2:1 intensity ratio, as expected for three different Sn–Br bond lengths, and the longest Sn–Br distance clearly corresponds to the lowest resonance frequency. The other two Sn–Br distances (2.559 and 2.582 Å) have the reverse relationship with the ^{81}Br n.q.r. frequencies, from their relative intensities, but the values are quite close in both cases. The plot of ^{79}Br n.q.r. frequency (calculated where necessary from the ^{81}Br values[27]) against bond length for $[NH_2Me_2]_2[SnBr_6]$ and $[Hpy]_2[SnBr_6]$ is shown in Figure 3, and there appears to be a rough correlation, although more results are clearly required before the validity of this relationship can be established.

The only other compound in which the $[SnBr_6]^{2-}$ ion is distorted from O_h symmetry and where both n.q.r. and *X*-ray data are available is K_2SnBr_6,[4,11] but the three n.q.r. signals observed are of equal intensity, so cannot be assigned to specific Sn–Br distances without assuming a relationship between n.q.r. frequency and bond length. The frequencies appear to be lower than expected from Figure 3 for the bond lengths involved, but this is not surprising in view of the small size of the cation. Hence anion–anion repulsions may affect the halogen n.q.r. frequency, as discussed in the previous section.

Acknowledgements

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