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^{81}Br NQR and ^{119}Sn Mössbauer Spectra for $SnBr_3^-$ Anions

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The structures of the $SnBr_3^-$ anions in $MSnBr_3$ (M=$(CH_3)_2NH_2$, $(CH_3)_3NH$) and $MSnBr_3 \cdot H_2O$ (M=K, NH_4) were deduced by means of ^{81}Br NQR spectroscopy. The former compounds have three ^{81}Br NQR lines in the frequency range 73—80 MHz at 77 K, indicating the presence of pyramidal $SnBr_3^-$ anions. The anion structure of the latter hydrate, on the other hand, was presumed to be square-pyramid with one terminal and two bridging Br atoms, because two of the ^{81}Br NQR frequencies were considerably low compared with that of the terminal atom. Phase transitions were observed for the latter hydrates. Associated with these, drastic increases of the NQR frequencies were observed only for the bridging atoms, suggesting significant changes in the bridging network.

The trihalostannate(II) anion, SnX_3^- (X=Cl and Br), in the solid state still provides us with interesting structural subjects. Two quite different structures for the SnX_3^- anions have been reported for $CsSnCl_3$[1] and $CsSnBr_3$:[2] The former contains a discrete anion with bond angles ∠XSnX, close to 90°, like an isoelectronic $SbCl_3$; however the latter contains a regular octahedron with six bridging bromines. The latter is a typical example of a hypervalent state of Sn(II). In this case the available orbitals of the tin atom are mainly 5p orbitals, since both the participation of the outer 5d orbitals to the bond may be small and the 5s orbital is full. On account of the orbital deficiency of the Sn(II) state, the trans Br-Sn-Br bond is regarded as being a three-center four-electrons bond (abbreviated as a 3c-4e bond) and each Sn-Br bond is weaker than that of a normal two-center two-electron bond (2c-2e). Some interesting phenomena associated with the 3c-4e bond have been observed for anions such as $SbBr_4^-$,[3] $SbBr_6^{3-}$,[4] and I_3^-.[5] For these structural and bonding subjects, halogen NQR is a useful technique owing to the high sensitivity of the NQR frequency to the bond nature.

Halogen NQR studies for trihalostannate(II) anions were only reported for $CsSnX_3$ (X=Cl, Br, and I).[6] In this paper the structure and bonding of $SnBr_3^-$ anions are discussed on the basis of ^{81}Br NQR and ^{119}Sn Mössbauer data. Furthermore, a possible model of a structural change accompanied by a phase transition is proposed for $MSnBr_3 \cdot H_2O$ (M=K, NH_4) utilizing the 3c-4e bond.

Experimental

All compounds, except for $NH_4SnBr_3 \cdot H_2O$, were crystallized from aqueous solutions containing stoichiometric amounts of $SnBr_2$ and relevant alkali bromide or alkylammonium bromide. $NH_4SnBr_3 \cdot H_2O$ was obtained from an aqueous solution containing about twice the stoichiometric amount of NH_4Br. H_2O and Br were analyzed by means of TG and potentiometric titration with $AgNO_3$, respectively. Anal. for $(CH_3)_3NHSnBr_3$. Found: C, 8.23; H, 2.42; N, 3.051; Br, 57.31%. Calcd for $C_3H_{10}NSnBr_3$: C, 8.61; H, 2.41; N, 3.35; Br, 57.28%. Anal. for $(CH_3)_2NH_2SnBr_3$. Found: C, 5.73; H, 2.07; N, 3.27; Br, 59.34%. Calcd for $C_2H_8NSnBr_3$: C, 5.94; H, 1.99; N, 3.46; Br, 59.26%. Anal. for $KSnBr_3 \cdot H_2O$. Found: Br, 56.4; H_2O, 4.22%. Calcd for $KSnBr_3 \cdot H_2O$: Br, 57.7; H_2O, 4.34%. Anal. for $NH_4SnBr_3 \cdot H_2O$. Found: H, 1.24; N, 3.72; Br, 60.77; H_2O, 4.18%. Calcd for $NH_4SnBr_3 \cdot H_2O$; H, 1.53; N, 3.55; Br, 60.77; H_2O, 4.31%.

^{81,79}Br NQR were searched in the frequency range from 20 to 100 MHz with a super-regenerative spectrometer or a pulsed spectrometer (Matec model 5100+525). The former was sensitive, even near the phase transition temperature (T_c) or at high temperature where the relaxation time (T_1) was short, $T_1 < 100$ μs. On the other hand, a pulse spectrometer was applied at low temperature where only the spin echo signal was detected due to its large line width. NQR lines were assigned with the aid of the quadrupole moment ratio, $(Q(^{79}\mathrm{Br})/(Q(^{81}\mathrm{Br})=1.1971)$.

^{119}Sn Mössbauer spectra were recorded by means of a constant acceleration-type spectrometer.

Results

^{81}Br NQR for $MSnBr_3$ (M=$(CH_3)_2NH_2$ and $(CH_3)_3NH$). Table 1 shows the ^{81}Br NQR frequencies for tribromostannate(II) anions. Three ^{81}Br NQR were detected in the frequency range of 73—80 MHz at 77 K for these two compounds. This frequency range is consistent with that expected from the ^{35}Cl NQR frequency for $CsSnCl_3$, where three NQR lines were observed at about 10.8 MHz for the pyramidal $SnCl_3^-$ anion.[6] Accordingly, it is thought that these compounds contain discrete $SnBr_3^-$ anions and, therefore, a frequency of about 73—80 MHz at 77 K corresponds to the normal 2c-2e bond for this anion.

^{81}Br NQR for $MSnBr_3 \cdot H_2O$ (M=K and NH_4). Although there has been no crystal structure determination for both compounds, it was suggested by means of IR spectra that the water molecule associates with the cation for the chloride analog.[7] As Table 1 shows, ^{81}Br NQR lines were detected over the wide frequency region 35—83 MHz, suggesting the existence of both terminal and bridging Br atoms. Figure 1 shows the temperature dependence of the ^{81}Br NQR frequencies. The disappearance of NQR signals was observed just below and above the phase-transition temperature (T_c). The highest NQR signal is exceptional and shows a small dip in the corresponding temperature range (Fig. 2). From this figure the phase-transition temperature was determined to be T_c=273±0.5 K.

Table 1. ^{81}Br NQR Frequencies for $MSnBr_3$ and $MSnBr_3 \cdot H_2O$

Compound	Temperature/K	Frequency/MHz	
$(CH_3)_2NH_2SnBr_3$	77	78.06, 77.76, 72.92	
	293	74.90, 74.28, 71.65	
$(CH_3)_3NHSnBr_3$	77	80.11, 79.77, 79.29	
$KSnBr_3 \cdot H_2O$	77	78.25, 78.07,	58.25, 56.33, 55.09, 52.23
	298	75.96,	40.45, 37.25
$NH_4SnBr_3 \cdot H_2O$	77	84.40, 79.79,	59.09, 58.12, 53.18, 51.62
	300	79.89,	38.56, 37.63

Estimated error ±0.01 MHz.

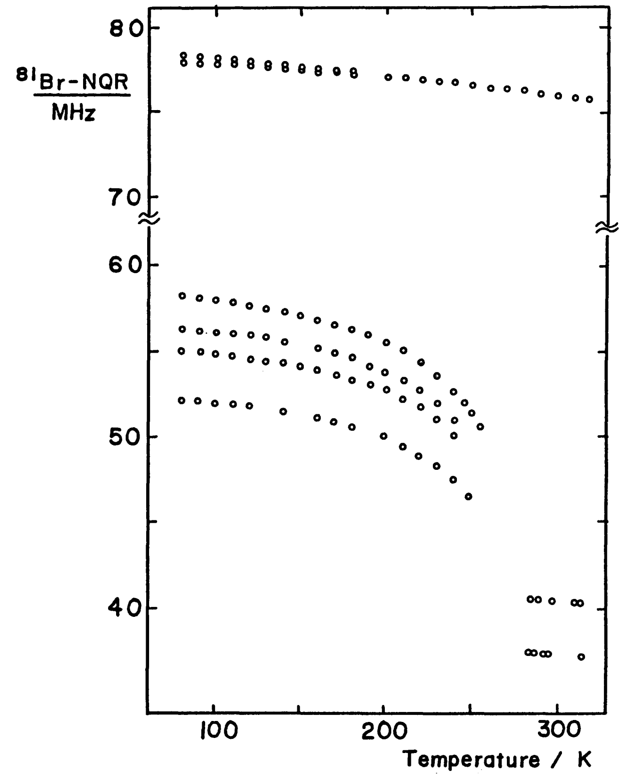

Fig. 1. Temperature dependence of the ^{81}Br NQR frequencies for $KSnBr_3 \cdot H_2O$.

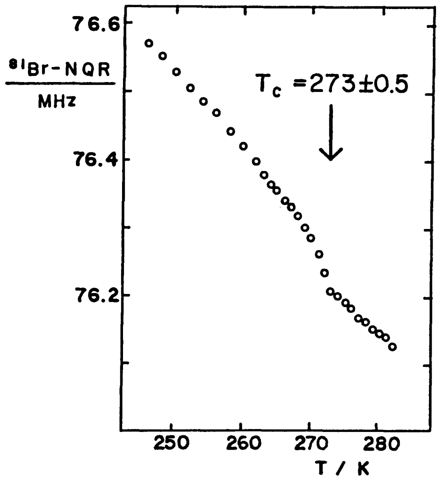

Fig. 2. Temperature dependence of the highest ^{81}Br NQR frequency in $KSnBr_3 \cdot H_2O$ near phase transition temperature.

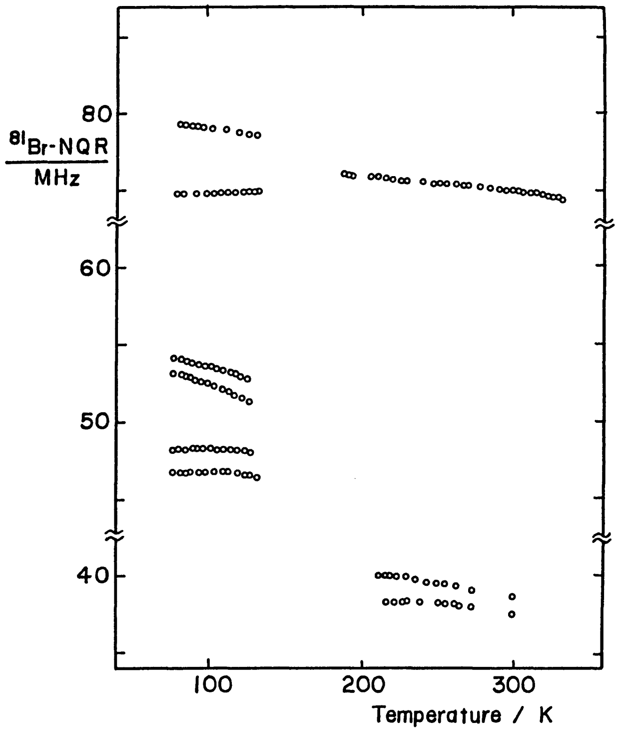

Fig. 3. Temperature dependence of the ^{81}Br NQR frequencies for $NH_4SnBr_3 \cdot H_2O$.

Because of the continuity of the highest ^{81}Br NQR frequency, this phase transition was supposed to be second-order type. Below T_c each line split into two, but the highest frequency line could not be resolved into two until about 90 degrees below T_c. This is due to its very small splitting compared with the line width. A phase transition was also observed for $M=NH_4$ (Fig. 3); unfortunately, the transition temperature was not determined owing to the disappearance of the NQR signals between 130 and 190 K. According to our preliminary T_1 measurements for both compounds, these disappearances of the NQR signals arise from their very short relaxation times (T_1) and also from the large line width ($1/T_2^*$) near T_c to detect NQR signals. Below T_c three NQR lines split into six lines for both compounds, suggesting at least two Sn sites. In connection with these phase transitions the most interesting feature is that the drastic increases of the NQR frequencies for the lower four lines with decreasing temperature. At 77 K the NQR frequencies

Table 2. ^{119}Sn Mössbauer Parameters for $MSnBr_3$ and $MSnBr_3 \cdot H_2O$ at 93 K[a)]

Compound	Line width	Isomer shift	Quadrupole splitting
		mms^{-1}	
$(CH_3)_3NHSnBr_3$	0.83	3.89	0.88
$(CH_3)_2NH_2SnBr_3$	0.86	3.55	0.82
$KSnBr_3 \cdot H_2O$	0.89	3.73	0.74
	0.89	3.60	1.02
$NH_4SnBr_3 \cdot H_2O$	0.93	3.67	0.98
$CsSnBr_3$[b)]	0.84	3.96	0

a) Estimated error ±0.05 mms^{-1}. b) Ref. 2.

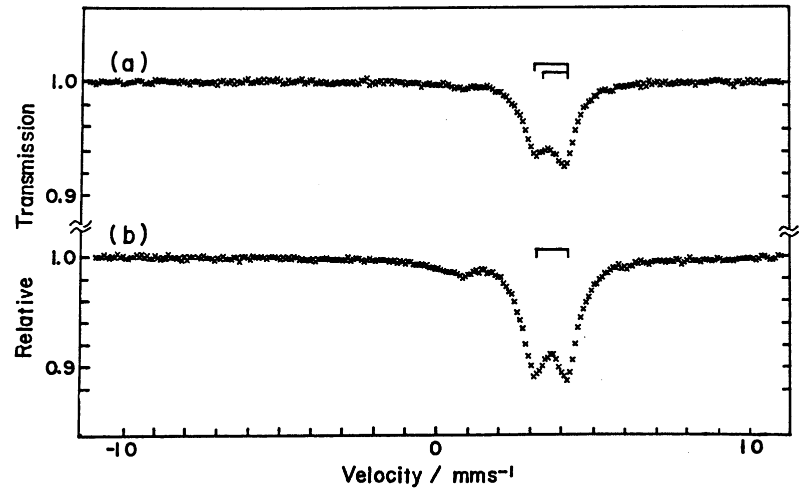

Fig. 4. ^{119}Sn Mössbauer spectra for $KSnBr_3 \cdot H_2O$ (a) and (NH_4)-$SnBr_3 \cdot H_2O$ (b) at 93 K.

increased about 40% more than those of the high-temperature phase. These finding were not understandable only from the change of the crystal fields. No anomalous peak associated with these phase transitions was detected for $MSnBr_3 \cdot H_2O$ from the DTA measurements in the corresponding temperature.

^{119}Sn Mössbauer Effect. Table 2 shows the Mössbauer parameters of $MSnBr_3(M=(CH_3)_2NH_2, (CH_3)_3NH)$ and $MSnBr_3 \cdot H_2O$ ($M=K, NH_4$). All these compounds showed quadrupole doublets. In the latter hydrates, however, the doublets are slightly asymmetric, even for powdered samples (Fig. 4). This is consistent with the NQR result; that is, there are at least two crystallographically different Sn sites at 93 K. In the potassium salt the spectrum was analyzed as two quadrupole doublets (Table 2).

Discussion

Structures of $SnBr_3^-$ Anions Based on the 3c-4e Bond Model. Figure 5 shows three structural models for the SnX_3^- anions based on the 3c-4e bonds. Model **A** exists in the perovskite $CsSnBr_3$, in which the Sn forms regular octahedron with six bridging Br atoms. In this case typical 3c-4e bonds are formed in the three orthogonal directions. While model **C** exists in $CsSnCl_3$,[1)] in which the Sn forms distorted octahedron with three short Sn-Cl bonds and three interanionic interactions Sn ··· Cl (not shown in this figure). In this structure it is also possible to consider that the Sn atom in $CsSnCl_3$ forms extremely unsymmetrical 3c-4e bonds along the three orthogonal directions. If one of the three 3c-4e bonds in the model **A** structure becomes asymmetric, it changes to model **B**. Several structural changes associated with the symmetric-asymmetric 3c-4e bond have been observed for Sb(III) compounds when the temperature or the counter cation was changed.[3,4)]

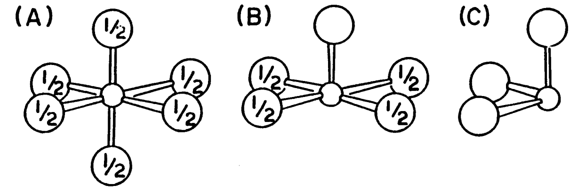

Fig. 5. Structural models for SnX_3^- anion, where 1/2 denotes bridging halogen.

The anion structures in $MSnBr_3(M=(CH_3)_2NH_2, (CH_3)_3NH)$ can be expressed as model **C**, since three ^{81}Br NQR lines were detected in a narrow frequency region of 73—80 MHz. On the other hand, $MSnBr_3 \cdot H_2O$ ($M=K, NH_4$) yielded only one NQR signal assigned to a terminal atom at room temperature. Two more signals were detected at about one half of the terminal NQR frequency. Therefore, model **B** is most plausible for the anion structure in these hydrates from their NQR spectra. Then, the NQR frequency for the bridging Br was estimated as confirming this model on the basis of the Townes-Dailey method under following conditions: (1) The net charge on the Br atom does not change as the result of a structural change from model **A** to **C** and (2) the bridging bond angle is close to 90°; hence, the bond is formed using only p orbitals. The population of the p_z orbital, N_z, for the terminal atom could be estimated assuming $\eta=0$ using following equation:

$$(e^2Qq_{obs}/h)/(e^2Qq_p/h)=2\,\nu_{obs}/(e^2Qq_p/h)=(2-N_z), \quad (1)$$

where $(e^2Qq_p/h)=643$ MHz. Since ν_{obs} for the terminal atom is on average 78 MHz at 77 K, the populations were determined to be $N_z=1.76$ and $N_y=N_x=2$ for p_z, p_y and p_x orbitals, respectively. On the other hand, in the case of symmetrical bridge using the p_z and p_x orbitals, the p electron populations change to $N_z=N_x=1.88$ and $N_y=2$, since the net charge on the Br atom is assumed to be constant. Between these two extremes the populations can be expressed using parameter b as

$$N_z=1.76+b,$$
$$N_y=2, \quad (2)$$

and

$$N_x=2-b.$$

Then, the NQR frequency for the bridging atom is calculated as a function of b using following equations:

$$(e^2Qq_{obs}/h)/(e^2Qq_p/h)=|N_z-(N_x+N_y)/2| \quad (3)$$

$$\eta\ =3(N_y-N_x)/(2N_z-N_y-N_x), \quad \text{for } 0<b<0.08 \quad (4)$$

$$\eta\ =3(N_z-N_x)/(2N_y-N_z-N_x), \quad \text{for } 0.08<b<0.12 \quad (5)$$

$$\nu_{obs}\ =(1/4)(e^2Qq_{obs}/h)(1+\eta^2/3)^{-2/1} \quad (6)$$

Figure 6 shows the calculated NQR frequency as a function of b. This figure shows that the NQR frequency decreases drastically in forming a bridging bond and that the principal z- and y-axes of the efg tensor change their orientations with each other in the range $0.08<b<0.12$. The observed NQR frequencies, ν_{obs}, for two hydrates are about 38.5 MHz, which are in good agreement with that obtained with this model in the range $b=0.07$—0.12. One NQR line was observed for the perovskite $CsSnBr_3$ near 63 MHz,[6)] which is about 50% higher than that expected from this model. This is probably due to the fact that the bridging bond Sn-Br-Sn in the perovskite structure is linear in contrast to this model.

According to the recent crystal structure analysis for $CsSnI_3$, the SnI_3^- anion was proved to exist in the form of model **B**.[8)] The SnI_3^- anion forms a distorted octahedron in which one pair of short and long Sn-I bonds at the trans position and four Sn-I bonds with intermediate lengths exist.

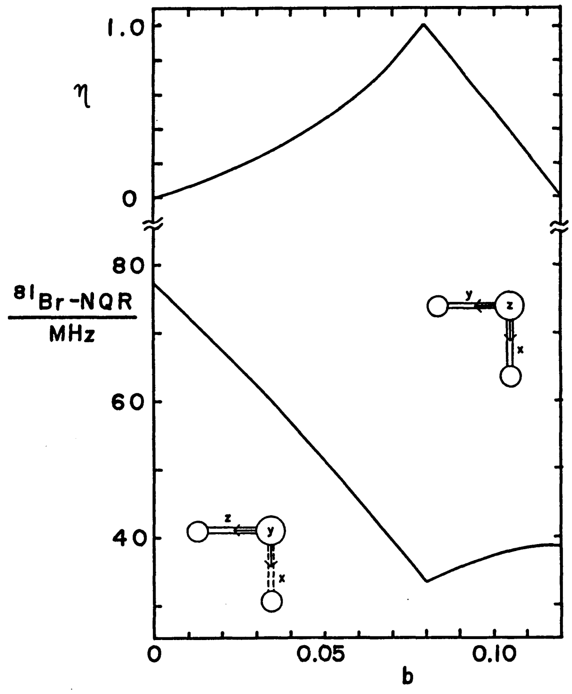

Fig. 6. Calculated ^{81}Br NQR frequencies for the bridging Br atom are plotted as a function of parameter b, where $b=0$ and $b=0.12$ correspond to terminal and symmetric bridge Br, respectively. At $b=0.08$ the efg z and y axes change their orientations each other.

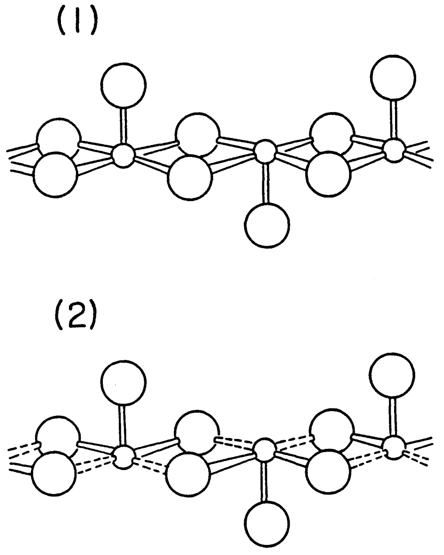

Fig. 7. Proposed structural models for high (1) and low (2) temperature phases.

Proposed Structural Changes for $MSnBr_3 \cdot H_2O$ (M=K, NH_4) below Phase Transition Temperatures. The temperature dependence of the ^{81}Br NQR for these compounds differs from each other, especially near T_c. However, the spectra at 77 K and room temperature resemble each other, suggesting similar changes take place around the Sn environments associated with the phase transitions. The drastic increases of NQR frequencies can be easily explained in terms of the slight change in the bridging Sn-Br-Sn bond, as shown in Fig. 6. That is, at high temperature the bridging Sn-Br-Sn bond is formed almost symmetrically, whereas at lower temperature one side of the bridging bond becomes weaker than the other. This change is more understandable by applying a 3c-4e bond model for the trans Br-Sn-Br as shown in Fig. 7. At temperatures above T_c the trans Br-Sn-Br bond is regarded as being a symmetrical 3c-4e bond. Below T_c, however, it becomes asymmetric Br-Sn$\cdots$Br and increases its NQR frequency (Fig. 6) owing to a decrease in parameter b. This type of structural change was also observed for $(C_5H_5NH)SbBr_4$, where the axial Br-Sb-Br bond is symmetric or asymmetric above and below T_c and, finally, the anion structure is more reasonably expressed as $SbBr_3 \cdot Br^-$ at 77 K.[3)]

Correlation between ^{119}Sn Mössbauer Parameters and Structure. As Table 2 shows, the change of the isomer shifts is considerably large compared with that of $Sn^{IV}Cl_6^{2-}$ anions.[9)] This is probably due to the fact that the SnX_3^- anion changes drastically its structure with a change in the counter cation as well as with temperature (as described above). In spite of their quit different ^{81}Br NQR spectra, the ^{119}Sn quadrupole coupling constant changes only slightly. However, the observed feature was consistent with structural models of the anion which were proposed by the ^{81}Br NQR. That is, the magnitude of the quadrupole coupling constant is expected from the point charge model as **B**>**C**>**A**. For a more satisfactory interpretation of these Mössbauer parameters, an X-ray structural determination may be required for each compound.

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