[81]Br NQR and ^{1}H NMR of Guanidinium Hexabromoantimonate(V) [C(NH$_2$)$_3$]SbBr$_6$: Phase Transition and Molecular Motion

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Guanidinium hexabromoantimonate(V) [C(NH$_2$)$_3$]SbBr$_6$ was prepared. It was black in color at room temperature and showed a tendency to turn yellow by loosing bromine in open air. Six [81]Br NQR lines were observed at 77 K. On heating, four of the six lines faded out around 200 K, while the remaining two lines could be observed up to room temperature. This temperature behavior suggests a preferential libration or reorientation around a pseudo C$_4$ axis of the octahedral [SbBr$_6$]$^-$ anion. DTA measurement revealed a small heat anomaly at $T_{c1} = 273$ K (on heating), showing a thermal hysteresis, and a sharp and large anomaly at $T_{c2} = 314$ K. The temperature dependence curve of ^{1}H NMR T_1 is characterized by a single minimum of 26 ms (32 MHz) near 280 K, which is assigned to the C$_3$ reorientation of the planar [C(NH$_2$)$_3$]$^+$ cations. Its activation energy (E_a) is 43.3 kJ/mol.

Key words: [C(NH$_2$)$_3$]SbBr$_6$; Phase Transition; Molecular Motion; [81]Br NQR; ^{1}H NMR T_1.

Introduction

The formation of hexabromoantimonate(V) compounds containing organic ammonium ions which are intensely colored (usually black) is well known [1]. These compounds are of interest in connection with the mixed-valence compounds such as R$_4$Sb^{III}Sb^{V}Br$_{12}$ (R = NH$_4$, Rb, Cs), which are jet-black in color. However, relatively few works on these compounds have been done until now. Bromine NQR is a very useful method for the investigation of the electronic states of these compounds owing to its high sensitivity [2]. In our former applications of this method to several compounds of hexabromo-antimonates(V) no or incomplete NQR signals were detected. This failure may be attributed to the complicated molecular motions of the cations and / or anions in these crystals. Recently, Jakubas *et al.* synthesized light yellow crystals of [C(NH$_2$)$_3$]SbCl$_6$ [3]. They found two structural phase transitions and determined the crystal structure at 298 K and 240 K.

In crystals the guanidinium ion [C(NH$_2$)$_3$]$^+$ is usually found to be planar or nearly planar, undergoing a simple reorientational motion around its C$_3$ symmetry axis [4]. We have prepared guanidinium hexabromo-antimonate(V) [C(NH$_2$)$_3$]SbBr$_6$, hoping to detect the bromine NQR signals of its anion, and report on [81]Br NQR, ^{1}H NMR T_1, and DTA measurements to investigate the chemical bonding, molecular motion of the [C(NH$_2$)$_3$]$^+$ ion, and phase transitions.

Experimental

The [C(NH$_2$)$_3$]SbBr$_6$ crystals were obtained by cooling a hot concentrated hydrobromic acid solution of stoichiometric amounts of Sb$_2$O$_3$ and [C(NH$_2$)$_3$]Br with a slight excess of bromine, and the [C(NH$_2$)$_3$]Br crystals by adding hydrobromic acid to an aqueous solution of [C(NH$_2$)$_3$]$_2$CO$_3$. The [C(NH$_2$)$_3$]SbBr$_6$ crystals were black at room temperature and red at liquid nitrogen temperature. The compound was sta-

Table 1. ^{81}Br NQR frequencies of [C(NH$_2$)$_3$]SbBr$_6$ at representative temperatures.

T/K	ν/MHz					
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
77	172.02	164.50	163.89	161.59	160.98	159.45
190	170.47	164.25	163.35	159.40	160.26	158.70
273		163.20			159.30	

ble in a sealed glass ampoule but turned yellow by loosing bromine in open air. The elemental analyses were consistent with the chemical formula; found / calcd.; weight %: C: 1.83 / 1.82; H: 0.92 / 0.91; N: 6.53 / 6.35, Sb: 19.30 / 18.37; Br: 72.08 / 72.50 for [C(NH$_2$)$_3$]SbBr$_6$.

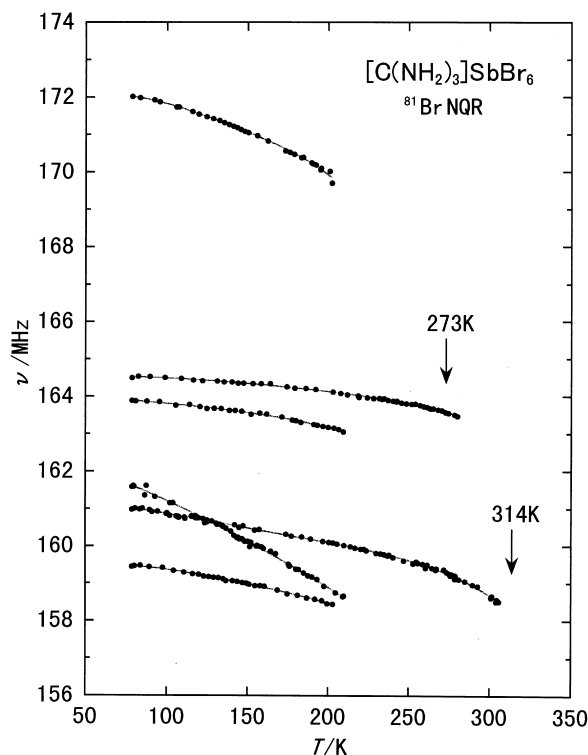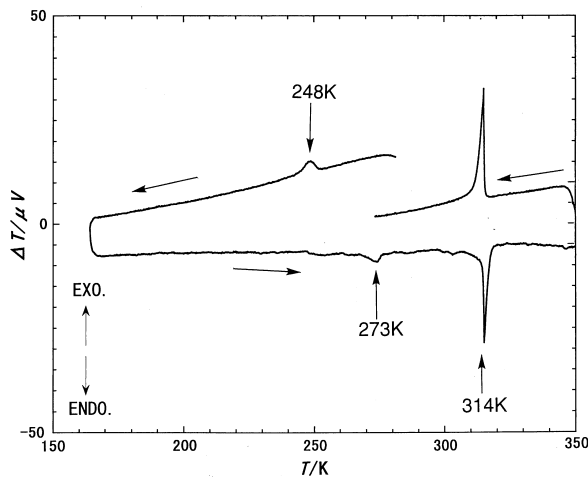The DTA measurements were done with a home-built apparatus.

The NQR spectra were obtained by using a super-regenerative spectrometer. The signals were recorded on a recorder through a lock-in amplifier with Zeeman modulation. The accuracy of frequency measurements is estimated to be within ± 0.02 MHz.

Spin-lattice relaxation times T_1 of ^{1}H NMR were measured by the inversion recovery method on a standard pulsed NMR spectrometer.

Results and Discussion

Six NQR lines, ascribed to ^{81}Br nuclei, were observed at 77 K as listed in Table 1. The assignment to ^{81}Br was confirmed by the observation of the corresponding resonance lines due to ^{79}Br. With increasing temperature from 77 K, the frequency of the resonance lines continuously decreased, as shown in Figure 1. When the temperature reached around 200 K, four of six lines faded out, while the remaining two lines could be observed up to around room temperature. It is notable that no detectable change is recognized on the frequency *vs.* temperature curves at $T_{c1} = 273$ K.

Representative curves of the DTA measurements are depicted in Figure 2. When the sample was cooled down from room temperature, a small heat anomaly appeared near 250 K (248 K at the peak position), while on heating from low temperatures this heat anomaly showed a long tail from 248 K to 273 K of its peak position. Above room temeprature, another sharp and large heat anomaly was detected without hysteresis at $T_{c2} = 314$ K. These thermal events show two phase transitions at $T_{c1} = 273$ K accompanied by a large thermal hysteresis and at $T_{c2} = 314$ K with-

Fig. 1. Temperature dependence of ^{81}Br NQR frequencies of [C(NH$_2$)$_3$]SbBr$_6$.

Fig. 2. DTA curves for [C(NH$_2$)$_3$]SbBr$_6$.

out detectable thermal hysteresis. In what follows, we tentatively denote three phases as LTP (low temperature phase $T < T_{c1}$), RTP (room temperature phase $T_{c1} < T < T_{c2}$), and HTP (high temperature phase $T_{c2} < T$).
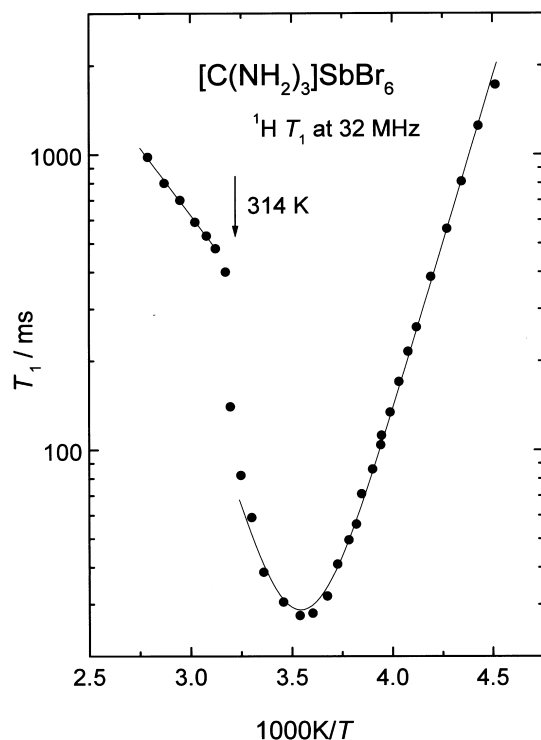
Fig. 3. Temperature dependence of [1]H T_1 at 32 MHz in [C(NH$_2$)$_3$]SbBr$_6$. A solid line shows a best-fitted curve to Eqs. (1) and (2).

Table 2. Motional parameters of the C$_3$ reorientation of the guanidinium ions of [C(NH$_2$)$_3$]SbBr$_6$ obtained by ^{1}H NMR T_1.

Phase	C / s^{-2}	τ_0 / s	E_a / kJ mol^{-1}
LTP, RTP	4.9×10^9	3.0×10^{-17}	43.3
HTP	–	–	17.5

The crystal structure of this complex is not known, but the crystal may consist of discrete cations and anions as seen in the crystal structures of (C$_2$H$_5$)$_4$NSbBr$_6$ [5] and [C(NH$_2$)$_3$]SbCl$_6$ [3]. For the latter compound, Jakubas *et al.* have carried out DSC measurements as well as the low-temperature X-ray structure analysis [3]. The DSC curves for [C(NH$_2$)$_3$]SbCl$_6$, which showed a small and large heat anomalies near 265 and 350 K, respectively, are very similar to those for the bromide analog in Figure 2. Through the structural analysis of the chloride analog it was found that one of the two crystallographically nonequivalent [SbCl$_6$]$^-$ anions in the LTP became disordered in the RTP. As described above, four of the six [81]Br resonance lines faded out near 200 K in the LTP. This may suggest the existance of only one crystallographically nonequivalent [SbBr$_6$]$^-$ anion in the present crystal and preferential libration or jumping between disordered sites of the Br atoms about a pseudo C$_4$ axis of the octahedral [SbBr$_6$]$^-$ anion. Such a motion may produce large fluctuations of the main EFG components of equatorial Br atoms with- out affecting those of the axial Br atoms. It is interesting that similar phase transitions associated with the motions of anions as well as cations occur in [C(NH$_2$)$_3$]SbCl$_6$ and [C(NH$_2$)$_3$]SbBr$_6$ in spite of the expected structure difference between them.

The temperature dependence of ^{1}H NMR T_1 (32 MHz) is shown in Figure 3. It is characterized by a single minimum of 26 ms near 280 K. No change or anomaly is observed near T_{c1} on the [1]H T_1 *vs.* $1/T$ curve. Just below T_{c2}, T_1 is sharply lengthened. The planar [C(NH$_2$)$_3$]$^+$ ions usually undergo C$_3$ reorientation in crystalline solids [4]. In accord with this, the observed T_1 minimum can be assigned to the temperature dependence of T_1 on the C$_3$ reorientation of the cation. Therefore we analyze the T_1-T curve by assuming the BPP-type equation for T_1 and an Arrhenius equation for the correlation time τ of the C$_3$ reorientation:

$$T_1^{-1} = C[\tau/(1 + \omega^2\tau^2) + 4\tau/(1 + 4\omega^2\tau^2)], \quad (1)$$

$$\tau = \tau_0 \exp(E_a/RT), \quad (2)$$

where ω is an angular resonance frequency. By least-squares calculations of (1) and (2) for T_1 in the RTP and LTP, the motional constant C, the correlation time at infinite temperature τ_0, and the activation energy E_a were determined. Table 2 shows the obtained motional parameters. Just below and above T_{c2}, T_2^* of the free-induction-decay signal is not changed (*ca.* 30 μs), indicating that the motion occurring in the HTP is the same as in the LTP and RTP. Only the E_a value is obtained from the slope on the $\ln T_1$ *vs.* $1/T$ curve in case of the HTP. It is noted that the E_a of 17.5 kJ/mol in the HTP is much smaller than $E_a = 43.3$ kJ/mol in the LTP and RTP. Such an ease of cationic and anionic motions may be connected with the occurrence of the T_{c2} transition and the absence of NQR signals in the HTP phase.

A comparison of [81]Br NQR spectra at 77 K of [SbBr$_6$]$^-$ moieties is made between the present compound and the mixed valence compounds
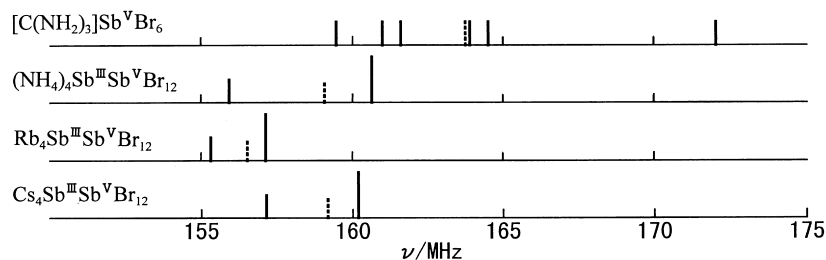
Fig. 4. Comparison of the ^{81}Br NQR spectra of $[Sb^VBr_6]^-$ ions. The dotted lines show the mean frequency positions.

$R_4Sb^{III}Sb^VBr_{12}$ (R = NH$_4$, Rb, Cs) [6] in Figure 4. The latter compounds belong to class II mixed-valence systems according to the classification by Robin and Day [7] in which valencies are distinguishable but with slight electronic delocalization. Because the ^{81}Br NQR frequencies for $[Sb^{III}Br_6]^{3-}$ ions were observed near 60 MHz [6], one can expect that the Br frequencies of the Sb^V-Br bonds become lower if the electronic delocalization occurs from $[Sb^{III}Br_6]^{3-}$ to $[Sb^VBr_6]^-$ ions in the mixed valence compounds. Therefore the average frequency of the Sb^V-Br bonds in the present non-mixed valence compound is expected to be higher than those in the mixed-valence compounds. Figure 4 shows that the average ^{81}Br NQR frequency of the present compound is by *ca.* 6 MHz higher than those of the mixed-valence compounds. This coincides with the above expectation, but the slight difference of only 6 MHz suggests that the delocalization is very small if present in $R_4Sb^{III}Sb^VBr_{12}$. It is needed to collect more NQR data for the $[Sb^VBr_6]^-$ and $[Sb^{III}Br_6]^{3-}$ moieties in order to discuss more quantitatively the mixed valence nature in $R_4Sb^{III}Sb^VBr_{12}$.

Acknowledgements

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