Crystal Structure and Phase Transition of 4-Aminopyridinium Tetrabromoantimonate(III) as Studied by Bromine and Antimony NQR, Proton NMR, and Single Crystal X-Ray Diffraction

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The crystal structure of the room temperature phase (RTP) of the title compound was determined at 297 K (monoclinic, space group C2/c, a = 1384.2(2), b = 1377.8(3), c = 755.5(2) pm, β = 121.58(1)°). A complicated disorder was found for the cation. A phase transition from the low-temperature phase (LTP) to the RTP was found at (224 ± 1) K (Tc). The 1H NMR spectra showed a sharp motional narrowing at ca. T = Tc, indicating the occurrence of a reorientational motion of the cation in the RTP in accord with the disorder. It was found that another reorientational motion is excited in the LTP. Four 81Br NQR lines (132.71, 115.38, 61.54 and 59.31 MHz at 77 K) and two Sb NQR lines (53.78 and 33.76 MHz at 77 K) were found in the LTP, while a single 81Br NQR line was observed at T > 276 K (ca. 121.80 MHz at 300 K). Crystal dynamics are discussed on the basis of the temperature dependence of the NQR, 1H NMR line width, and 1H NMR T1.

Key words: 4-NH₂PyHSbBr₄; Crystal Structure; Phase Transition; NQR; 1H NMR.

Introduction

It is well known that antimony(III) halides tend to form 1:1 or 1:2 complexes with aromatic amine halides as well as aliphatic ones. However, the physical properties of the complexes with aromatic amines have been studied only little compared to those with aliphatic ones. In this circumstances, the structure and crystal dynamics of 4-aminopyridinium tetrabromoantimonate(III) (abbreviated as 4-NH₂PyHSbBr₄) have been investigated in detail [1 - 3]. In these crystals infinite chains formed by the SbX₄⁻ anions are packed so as to make a rigid tunnel-like structure wherein the planar cations are stacked [4, 5]. The phase transitions of these compounds have been correlated to the reorientations of the cations, and the pyridine N-H···X hydrogen bonds are known to play an important role in the mechanism of the phase transitions [3].

It is interesting to replace the C₅H₅N⁺ by 4-NH₂-C₅H₅N⁺ because the size of the latter is considerably larger than that of the former and moreover the amino NH₂ group, as well as the pyridine N-H group of the 4-aminopyridinium ion, can contribute to the formation of hydrogen bonds. In the present work we investigated the structure, phase transition and crystal dynamics of 4-aminopyridinium tetrabromoantimonate(III) (abbreviated as 4-NH₂PyHSbBr₄) by means of X-ray diffraction, Br and Sb NQR, thermal analysis, and 1H NMR.

Experimental

Crystals of 4-NH₂PyHSbBr₄ were obtained from a concentrated hydrobromic acid solution containing stoichiometric amounts of Sb₂O₃ and 4-NH₂C₅H₅-NHBr. The latter was obtained by adding hydro-
The C, H, and N analyses were consistent with the chemical formula, as shown by the corresponding ratios of the measured and calculated weights(%) ; C: 11.11/11.19; H: 1.32/1.32; N: 5.20/5.22. The NQR spectra were recorded in the frequency range of 20 < ν/MHz < 140 by the method reported in [6]. The temperature range for the NQR measurements was 77 < T/K < 400.

The thermal analysis was carried out by using a home-made DTA apparatus and a commercial DSC (Rigaku 8058).
Results

Bromine and Antimony NQR and Thermal Analysis

Six NQR signals were detected at 77 K (Table 2). Four of them (ν_{1-4}(^{81}Br)) could be unambiguously assigned to {^{81}Br} by the observation of the corresponding {^{79}Br} lines. The rest of them (ν_{1}(Sb) and ν_{2}(Sb)) should be attributed to the antimony nucleus. However, the assignment of them to the proper transitions has been remained unknown. The temperature dependence of the {^{81}Br} and Sb NQR frequencies is shown in Figure 1. Two Sb NQR lines (ν_{1}(Sb) and ν_{2}(Sb)), as well as two {^{81}Br} NQR lines (ν_{3}(^{81}Br) and ν_{4}(^{81}Br)) were found to fade out in the range ca. 180 < T/K < ca. 200. The rests of the {^{81}Br} NQR lines (ν_{1}(^{81}Br) and ν_{2}(^{81}Br)) could be observed up to ca. 226 ±1 K. In the range of ca. 226 < T/K < ca. 271, no NQR signals were detected and at T > ca. 271 K a single {^{81}Br} NQR line (ν_{a}(^{81}Br)) was detected as shown in Figure 1. By the thermal analyses a thermal anomaly was found at T_{c} = (224±1) K, as shown on the DTA curve in Figure 2. An enthalpy change of ca. 2.1 kJ/mol was obtained from the DSC measurements.

\[ \Delta H_{v} = 2.1 \text{ kJ/mol from DSC} \]

Fig. 2. The DTA trace of 4-NH{\textsubscript{2}}PyHSbBr{\textsubscript{4}}.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>B_{eq}/B_{iso} \times 10^{-4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>0.5000</td>
<td>0.0820(1)</td>
<td>0.7500</td>
<td>2.86(4)</td>
</tr>
<tr>
<td>Br(1)</td>
<td>0.3555(1)</td>
<td>0.0824(1)</td>
<td>0.3141(2)</td>
<td>3.98(5)</td>
</tr>
<tr>
<td>Br(2)</td>
<td>0.6286(2)</td>
<td>0.2085(1)</td>
<td>0.7265(3)</td>
<td>5.01(5)</td>
</tr>
<tr>
<td>N</td>
<td>0.5000</td>
<td>0.533(3)</td>
<td>0.2500</td>
<td>16(1)*</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.5000</td>
<td>0.355(3)</td>
<td>0.2500</td>
<td>11(1)*</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.405(2)</td>
<td>0.382(1)</td>
<td>0.231(3)</td>
<td>6.3(5)*</td>
</tr>
<tr>
<td>C(3)</td>
<td>0.408(2)</td>
<td>0.503(2)</td>
<td>0.232(3)</td>
<td>7.5(5)*</td>
</tr>
</tbody>
</table>

Fig. 3. Temperature dependence of the line width of the {\textsuperscript{1}}H NMR spectrum. The broken lines are guides to the eye.

N atom of the NH{\textsubscript{2}} group, were refined by the usual method with isotropic thermal parameters. The final refinement gave R = 0.056 and R_{w} = 0.043.

\[ \Delta H_{v} = 2.1 \text{ kJ/mol from DSC} \]

Fig. 4. Temperature dependence of the spin-lattice relaxation time (T_{1}) of {\textsuperscript{1}}H NMR. The solid and broken curves are calculated by (1) and (2).

1\textsuperscript{H} NMR Measurements

The line width of the {\textsuperscript{1}}H NMR spectrum is shown in Fig. 3 as a function of temperature. The line width was found to decrease abruptly at ca. (222.3 ±0.5) K. The temperature is significantly lower than T_{c} obtained by the thermal analysis and the NQR measurements (obtained as the temperature at which ν_{1}(^{81}Br) and ν_{2}(^{81}Br) disappeared). This disagreement in the temperature could be attributed to one or both of the fol-
The X-ray structures of the anion and cation in the crystal of 4-NH$_2$PyHSbBr$_4$ with numbering scheme for atoms.

Table 4. Interatomic distances and bond angles in the structure of 4-NH$_2$PyHSbBr$_4$. The distances X-Y are given in pm and the angles X-Y-Z in degree.

<table>
<thead>
<tr>
<th>Distance</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb-Br(1)</td>
<td>281.9(2)</td>
</tr>
<tr>
<td>Sb-Br(2)</td>
<td>256.3(3)</td>
</tr>
<tr>
<td>Br(1)-Sb-Br(1')</td>
<td>93.47(9)</td>
</tr>
<tr>
<td>Br(1)-Sb-Br(1'')</td>
<td>86.69(9)</td>
</tr>
<tr>
<td>Br(1)-Sb-Br(2')</td>
<td>89.2(1)</td>
</tr>
<tr>
<td>Br(1')-Sb-Br(2)</td>
<td>175.46(9)</td>
</tr>
<tr>
<td>Br(1')-Sb-Br(2')</td>
<td>94.3(2)</td>
</tr>
</tbody>
</table>

Br(1'): x, -y, 1/2 + z; Br(1''): 1 - x, -y, 1 - z; Br(1''): 1 - x, -y, 1 - z.

Discussion

In RTP of 4-NH$_2$PyHSbBr$_4$ distorted SbBr$_6$ octahedra share their two edges to result in an infinite chain structure (Figure 5). Bridging and terminal bromine atoms are labelled as Br(1) and Br(2), respectively. The bond lengths and bond angles obtained for the present anion are almost identical to those reported for (C$_5$H$_5$NH)SbX$_4$ (X = Cl and Br) [5]. As can be seen in Fig. 6, the infinite chains are packed parallel to the crystallographic c axis to form a tunnel-like structure and the 4-NH$_2$PyH cations are stacked therein. Thus the crystal structure of the present complex is as a whole quite similar to those found in (C$_5$H$_5$NH)SbX$_4$ (X = Cl and Br) in spite of the considerably large size of the 4-NH$_2$PyH cation. Unfortunately it was diffi-
Fig. 6. The crystal structure of 4-NH$_2$PyHSbBr$_4$ viewed along the crystallographic c axis.

dicult to determine the precise structure of the cation owing to the disorder, and the tentative assignment for N and C(1) given in Fig. 5 could be inverted.

In the temperature dependence of the $^1$H NMR line width (Fig. 3), the reduction from 13 to 2.5 Oe for $T > T_c$ clearly reveals the occurrence of a certain thermal motion of the NH$_2$PyH cations. The finite value of the line width above $T_c$ and up at least to 300 K indicates that the motion is not isotropic in this temperature range. The predominant mechanism for $T_1$ of $^1$H NMR is expected to originate from the fluctuating magnetic field caused by the magnetic dipole-dipole interaction between protons due to thermal motions. Therefore, the thermal motions are responsible for the temperature change of $T_1$. The observed $T_1$ curves in Fig. 4 are analyzed by the equations [9]

$$\frac{1}{T_1} = C \left( \frac{\tau}{1 + \omega^2 \tau^2} + \frac{4\tau}{1 + 4\omega^2 \tau^2} \right), \quad (1)$$

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

where $C$, $\omega$, $\tau$, $E_a$ represent the motional constant, the angular Larmor frequency of the proton, the correlation time, and activation energy, respectively. It is assumed that $\tau$ obeys the Arrhenius relation (2).

The solid and broken line in the LTP are obtained for the condition of $\omega \tau \gg 1$. The temperature dependence of $T_1$ in the LTP indicates the excitation of another reorientation with an activation energy of ca. 12.2 kJ/mol. The reorientation in the LTP seems to be rapidly switched into the reorientation in the RTP in the vicinity of $T_c$. The solid and broken curves in the RTP are calculated by (1) and (2) with $E_a = 25.9$ kJ/mol, $\tau_0 = 5.88 \times 10^{-15}$ s, $C = 1.92 \times 10^8$ s$^{-2}$. The solid curve is in good agreement with the experimental results. The broken curve deviates from the experimental results by the influence of the phase transition. $T_1$ reaches the minimum at 236.3 K when
ωτ is equal to 0.6158. As a mode of motion one may assume reorientation of the NH$_2$PyH group around its pseudo 6-fold axis similar to that of PyH found for (C$_5$H$_4$NH)SbX$_4$ (X = Cl and Br), although the size of the former cation is considerably larger than that of the latter.

Two groups of the $^{81}$Br NQR lines ($\nu_1$($^{81}$Br) and $\nu_2$($^{81}$Br)) and ($\nu_3$($^{81}$Br) and $\nu_4$($^{81}$Br)) observed for the LTP are assigned to the terminal and bridging Br atoms, respectively. As usual, the mean value of $\nu_1$($^{81}$Br) and $\nu_2$($^{81}$Br) is approximately equal to $\nu_3$($^{81}$Br). The separation of the two $^{81}$NQR lines of terminal Br atoms of 4-NH$_2$PyHSbBr$_4$ (ca. 17 MHz) is almost identical to that of PyHSbBr$_4$ (ca. 13 MHz). On the other hand, the separation of the two $^{81}$Br NQR lines of the bridging Br atoms of PyHSbBr$_4$ is very large (ca. 50 MHz), and the corresponding value observed for 4-NH$_2$PyHSbBr$_4$ is merely ca. 2 MHz. These findings indicate that the nature of the bond between the Sb and the bridging Br in the LTP of 4-NH$_2$PyHSbBr$_4$ differs considerably from that in PyHSbBr$_4$.

The temperature dependence of the $^{81}$Br and Sb NQR frequencies reveals considerably complicated crystal dynamics of 4-NH$_2$PyHSbBr$_4$. Namely, in the LTP, two $^{81}$Br NQR lines ($\nu_3$($^{81}$Br) and $\nu_4$($^{81}$Br)) and the Sb NQR lines faded-out at temperatures lower than $T_c$ by ca. 20 K. Above $T_c$, no NQR signals could be detected in the temperature range of $T_c < 7/1K < ca. 271$. Furthermore, the $^{81}$Br NQR of the bridging Br and the Sb NQR line could not be detected at room temperature in spite of the fact that the $^{81}$Br NQR corresponding to the terminal Br could be observed. In addition, the temperature dependence of $\nu_3$($^{81}$Br) exhibits a subtle anomaly at ca. 290 K, suggesting the possibility of another phase transition. To clarify these peculiar crystal dynamics, further investigations including the crystal structure analyses at various temperatures are in progress.

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