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 (T_c). The ^{1}H NMR spectra showed a sharp motional narrowing at ca. $T = T_c$, 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 ^{81}Br 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 ^{81}Br 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, ^{1}H NMR line width, and ^{1}H NMR T_1.

Key words: 4-$NH_2PyHSbBr_4$; Crystal Structure; Phase Transition; NQR; ^{1}H 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 changes in $(C_5H_5NH)SbX_4$ (X = Cl and Br, abbreviated as $PyHSbX_4$) have been investigated in detail [1 - 3]. In these crystals infinite chains formed by the SbX_4^- 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 $C_5H_5NH^+$ by 4-NH_2-$C_5H_4NH^+$ because the size of the latter is considerably larger than that of the former and moreover the amino NH_2 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-$NH_2PyHSbBr_4$) by means of X-ray diffraction, Br and Sb NQR, thermal analysis, and ^{1}H NMR.

Experimental

Crystals of 4-$NH_2PyHSbBr_4$ were obtained from a concentrated hydrobromic acid solution containing stoichiometric amounts of Sb_2O_3 and 4-$NH_2C_5H_4$-NHBr. The latter was obtained by adding hydro-

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Table 1. Experimental conditions for the crystal structure determination and crystallographic data of 4-$NH_2PyHSbBr_4$.

Formula	$C_5H_7Br_4N_2Sb$
Formula weight	536.49
Crystal habit	Needle (pale yellow)
Size/(mm)^3	0.04×0.07×0.20
Temperature/K	297
Absorption coeff. (μ/m^{-1})	1526.2
Diffractometer	Rigaku AFC5R
Wavelength/pm	71.07 (MoK_α)
Monochromator	Graphite (002)
Scan	$\omega/2\theta$
$(\sin\theta/\lambda)_{\max}$/pm^{-1}	0.006496
Reflections measured	1533
Symmetry independent	1475
Considered, $F_0 > 3\sigma(F_0)$	603
Number of free parameters	37
$F(000)$	968.00
$R(F)$	0.056
$R_w(F)$	0.043
Lattice constants a/pm	1384.2(2)
b/pm	1377.8(3)
c/pm	755.5(2)
β/°	121.58(1)
$V_{\text{ucell}} \times 10^{-6}$/(pm)^3	1227.4(5)
Space group^a	$C_{2h}{}^6$ - C2/c
Formula units/Unit cell (Z)	4
ρ_{calc}/Mg·m^{-3}	2.903

[a] Point positions: x, y, z; $-x, y, \frac{1}{2}-z$; $-x, -y, -z$; $x, -y, \frac{1}{2}+z$; $\frac{1}{2}+x, \frac{1}{2}+y, z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; $\frac{1}{2}-x, \frac{1}{2}-y, -z$; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

Table 2. ^{81}Br and Sb NQR frequencies (ν_i/MHz) of 4-$NH_2PyHSbBr_4$.

Nucleous	Line number	at 77 K	at 150 K	Line number	at 300 K
^{81}Br	$\nu_1(^{81}Br)$	132.71	132.03	$\nu_a(^{81}Br)$	121.80
	$\nu_2(^{81}Br)$	115.38	114.95		
	$\nu_3(^{81}Br)$	61.54	61.32		
	$\nu_4(^{81}Br)$	59.31	59.19		
Sb	ν_1(Sb)	53.78	53.08		
	ν_2(Sb)	33.76	33.39		

bromic acid to an aqueous solution of 4-$NH_2C_5H_4N$. 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 $20 < \nu/\text{MHz} < 140$ by the method reported in [6]. The temperature range for the NQR measurements was $77 < T/\text{K} < 400$.

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

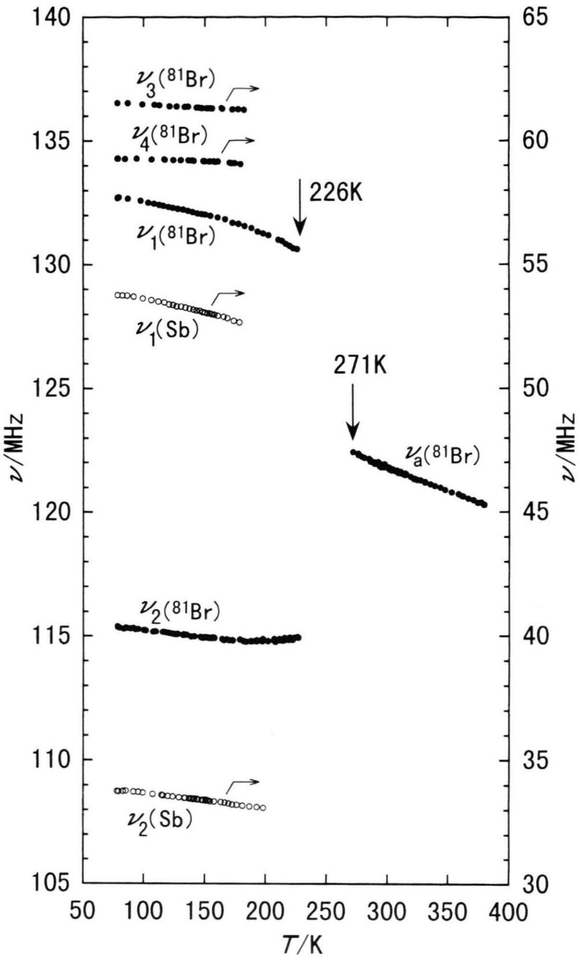

Fig. 1. Temperature dependence of ^{81}Br and Sb NQR frequencies.

The ^{1}H NMR spectra and the nuclear spin-lattice relaxation time (T_1) were measured with a phase coherent pulsed spectrometer. A 90°-t-90° pulse sequence and a single phase detection method in Fourier Transform (FT) technique were used for the measurements of T_1 and the NMR spectra, respectively.

Details of the single crystal X-ray experiment and the crystallographic data are summarized in Table 1. The structure was solved by the direct method [7] and refined by the full matrix least squares method [8]. The Sb and Br atoms were refined with anisotropic thermal parameters. A complex disorder was found for the cation, and moreover the N atom of the amino group could not be found on the Fourier map. Because it was difficult to assume an appropriate disorder model for the cation, its C and N atoms, except for the

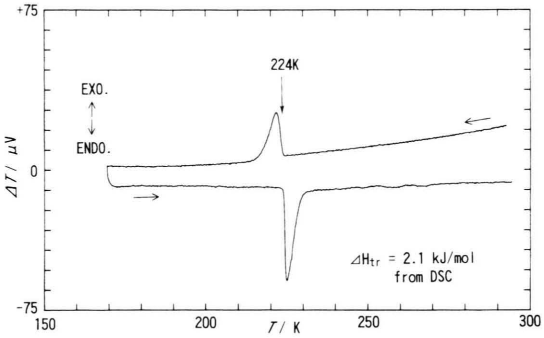

Fig. 2. The DTA trace of 4-$NH_2PyHSbBr_4$.

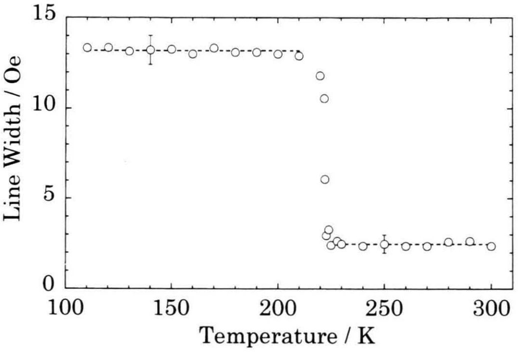

Fig. 3. Temperature dependence of the line width of the ^1H NMR spectrum. The broken lines are guides to the eye.

N atom of the NH_2 group, were refined by the usual method with isotropic thermal parameters. The final refinement gave $R = 0.056$ and $R_w = 0.043$.

Results

Bromine and Antimony NQR and Thermal Analysis

Six NQR signals were detected at 77 K (Table 2). Four of them ($\nu_{1-4}(^{81}Br)$) 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 ($\nu_3(^{81}Br)$ and $\nu_4(^{81}Br)$) were found to fade out in the range ca. $180 < T/K <$ ca. 200. The rests of the ^{81}Br NQR lines ($\nu_1(^{81}Br)$ and $\nu_2(^{81}Br)$) 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 ($\nu_a(^{81}Br)$) was detected as shown in Figure 1. By the thermal analyses a thermal anomaly was found at $T_c = (224 \pm 1)$ 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.

Table 3. Positional and thermal parameters $B_{eq}/B^*_{iso}/(pm)^2$ in the crystal structure of 4-$NH_2PyHSbBr_4$. Estimated standard errors in parentheses. Those for the atoms in the cation are tentative. The N atom of the amino group could not be found on the Fourier map.

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

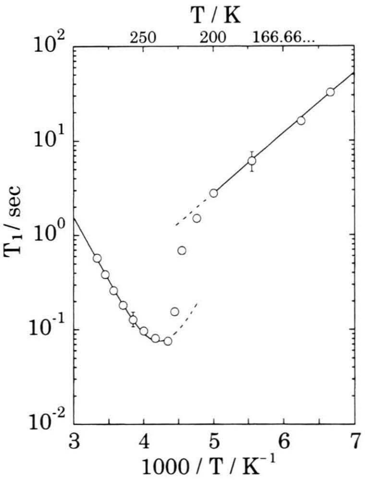

Fig. 4. Temperature dependence of the spin-lattice relaxation time (T_1) of ^1H NMR. The solid and broken curves are calculated by (1) and (2).

^1H NMR Measurements

The line width of the ^1H 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 $\nu_1(^{81}Br)$ and $\nu_2(^{81}Br)$ disappeared). This disagreement in the temperature could be attributed to one or both of the fol-

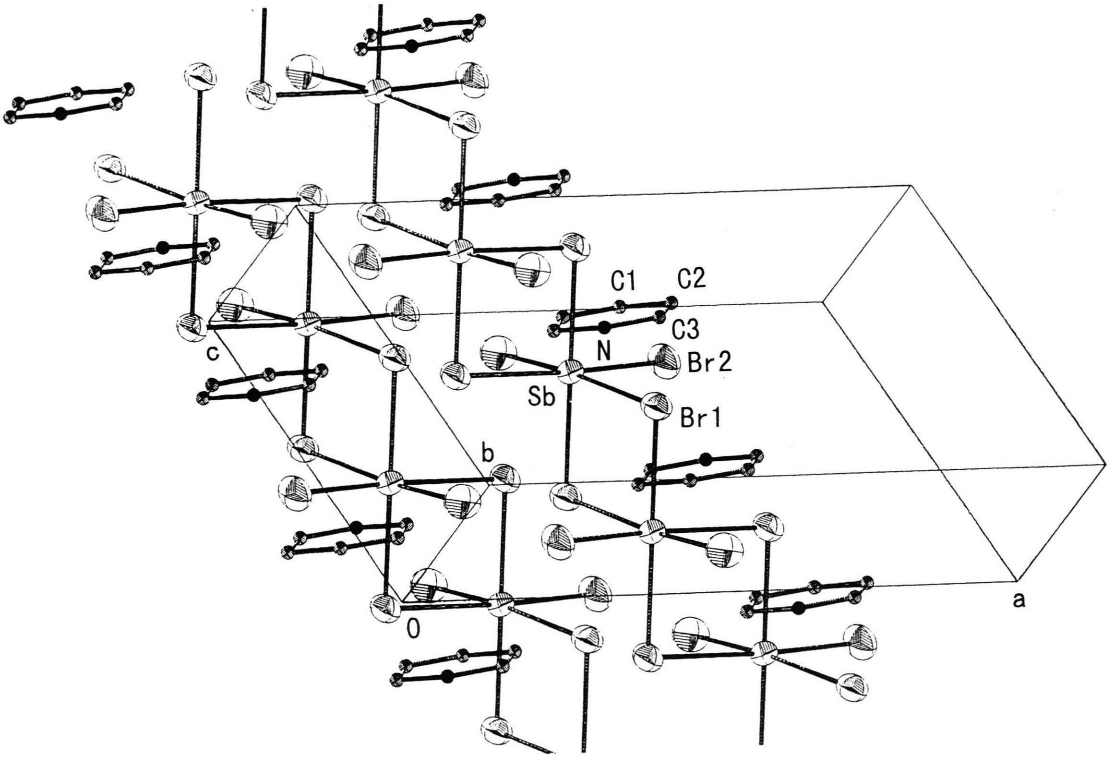

Fig. 5. The X-ray structures of the anion and cation in the crystal of 4-$NH_2PyHSbBr_4$ with numbering scheme for atoms.

Table 4. Interatomic distances and bond angles in the structure of 4-$NH_2PyHSbBr_4$. The distances X-Y are given in pm and the angles X-Y-Z in degree.

Sb-Br(1)	281.9(2)	Sb-Br(1')	322.1(3)
Sb-Br(2)	256.3(3)		
Br(1)-Sb-Br(1')	93.47(9)	Br(1)-Sb-Br(1")	86.69(9)
Br(1)-Sb-Br(1"')	179.8(2)	Br(1)-Sb-Br(2)	90.7(1)
Br(1)-Sb-Br(2')	89.2(1)	Br(1')-Sb-Br(1")	90.7(1)
Br(1')-Sb-Br(2)	175.46(9)	Br(1")-Sb-Br(2)	87.66(8)
Br(2)-Sb-Br(2')	94.3(2)	Sb(1)-Br(1)-Sb(1')	93.31(9)

Br(1'): $x, -y, \frac{1}{2} + z$; Br(1"): $1 - x, -y, 1 - z$: Br(1"'), Br(2'): $1 - x, y, \frac{3}{2} - z$.

lowing two possibilities; (1) the line width decreases to the minimum value before the temperature reaches T_c on heating, (2) a super heating occurs. Figure 4 shows the temperature dependence of the spin-lattice relaxation time (T_1) of ^1H NMR.

The Crystal Structure of the Room Temperature Phase

Figure 5 shows a chain of the anion and an approximate structure of the cation without the NH_2 group. The crystal structure viewed along the *c* axis is shown in Figure 6. The fractional atomic coordinates for the atoms are listed in Table 3, although those for the atoms in the cation are tentative. Table 4 contains bond lengths and bond angles for the anion.

Discussion

In RTP of 4-$NH_2PyHSbBr_4$ 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 $(C_5H_5NH)SbBr_4$ [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_2PyH cations are stacked therein. Thus the crystal structure of the present complex is as a whole quite similar to those found in $(C_5H_5NH)SbX_4$ (X = Cl and Br) in spite of the considerably large size of the 4-NH_2PyH cation. Unfortunately it was diffi-

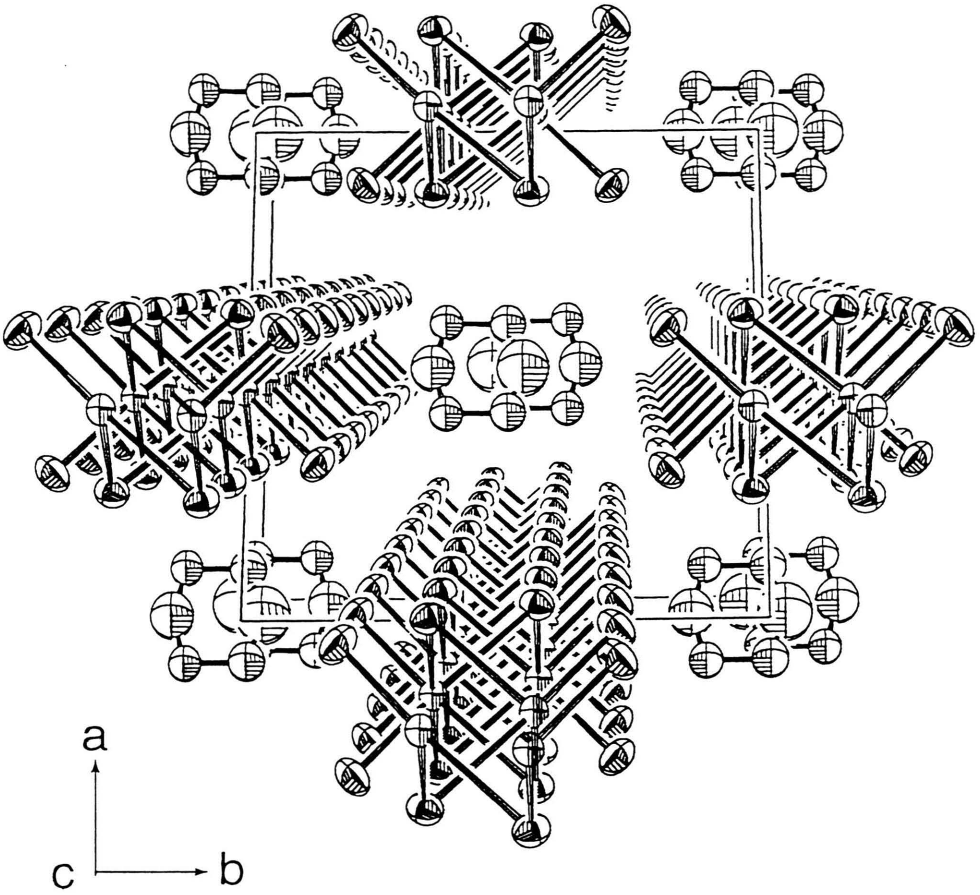

Fig. 6. The crystal structure of 4-$NH_2PyHSbBr_4$ viewed along the crystallographic *c* axis.

cult 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 ^1H 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_2PyH 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 ^1H 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]

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

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

where C, ω, τ, E_a represent the motional constant, the angular Larmor frequency of the proton, the correlation time, and activation energy, respectively. It is assumed that τ 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, $\tau_0 = 5.88\times10^{-15}$ s, $C = 1.92\times10^9$ 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

$\omega\tau$ is equal to 0.6158. As a mode of motion one may assume reorientation of the NH_2PyH group around its pseudo 6-fold axis similar to that of PyH found for $(C_5H_5NH)SbX_4$ (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 $\nu_a(^{81}Br)$. The separation of the two ^{81}NQR lines of terminal Br atoms of 4-$NH_2PyHSbBr_4$ (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-$NH_2PyHSbBr_4$ 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-$NH_2PyHSbBr_4$ 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-$NH_2PyHSbBr_4$. 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 $T_c < T/K <$ 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 $\nu_a(^{81}Br)$ 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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[1] T. Okuda, K. Yamada, H. Ishihara, M. Hiura, S. Gima, and H. Negita, J. Chem. Soc. Chem. Commun. 979 (1981).

[2] T. Okuda, Y. Aihara, N. Tanaka, K. Yamada, and S. Ichiba, J. Chem. Soc. Dalton Trans. 631 (1989).

[3] K. Yamada, T. Ohtani, S. Shirakawa, H. Ohki, T. Kamiyama, and K. Oikawa, Z. Naturforsch. **51a**, 739 (1995).

[4] S. K. Porter and R. A. Jacobson, J. Chem. Soc. **A**, 1356 (1970).

[5] P. W. DeHaven and R. A. Jacobson, Cryst. Struct. Commun. **5**, 31 (1976).

[6] H. Terao, M. Hashimoto, T. Okuda, and Al. Weiss, Z. Naturforsch. **53a**, 559 (1998).

[7] MSC, 3200 Research Forest Drive. The Woodslands. TX77381, USA (1992). Molecular Structure Corporation. TEXAN.TEXRAY Structure Analysis Package.

[8] M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spanga, and D. Viterbo, J. Appl. Crystallogr. **22**, 389 (1989).

[9] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).