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, \( \beta = 121.58(1)^\circ \)). A complicated disorder was found for the cation. A phase transition from the low-temperature phase (LTP) to the RTP was found at \( (224 \pm 1) \) K \( (T_c) \). The \(^1\text{H} \) 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 \(^81\text{Br} \) 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 \(^81\text{Br} \) 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, \(^1\text{H} \) NMR line width, and \(^1\text{H} \) NMR \( T_1 \).

Key words: 4-NH\textsubscript{2}PyHSbBr\textsubscript{4}; Crystal Structure; Phase Transition; NQR; \(^1\text{H} \) NMR.