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127I NQR and 1H NMR Studies of 4-Aminopyridinium Tetraiodoantimonate(III); Molecular Motion and Phase Transition

The DTA measurements of the title compound 4-NH2PyHSbI4 (Py = C5H4N) have revealed that the compound can exist in two modifications of β- and α-phases at room temperatures as shown in Fig. 1. The stable β-phase transformed to the meta-stable α-phase by heating above ca. 362 K and successive cooling. The α-phase further underwent a first-order phase transition of α(I)-phase ↔ α(II)-phase at ca. 272 K (on heating). Corresponding discontinuities were observed on the 1H NMR T1 curves at these temperatures.
Though the crystal structures have not yet been clarified for these phases, the observed resonance lines due to 127I NQR (m = ±1/2↔±3/2) may be assigned to the terminal and the bridging I atoms by considering their frequencies, indicating an existence of one dimensional infinitive anion chain structures formed of SbI6 octahedra. The β-phase was characterized by two higher-frequency lines of the terminal I atoms around ca. 136 MHz and two lower-frequency ones of the bridging I atoms around ca. 114 MHz throughout the measured temperatures (Fig. 2). Meanwhile no NQR signals were observed in the α(I)-phase, but two signals, assignable to the terminal and the bridging I atoms respectively, were observed in the α(II)-phase between 77 K and ca. 240 K, above which the disappearance of the signals occurred (Fig. 2).
The second moment M2 values of 1H NMR spectra at 290 K showed that the 4-NH2PyH+ cations resided in the rigid lattice with 8 G2 in the β-phase but in the α(I)-phase the M2 value largely reduced to 2 G2, suggesting that the cations rotate about an axis more symmetric than pseudo 3-fold axis. On the other hand, the cations in the α(II)-phase may reside in the rigid lattice as judged from the T2* values. The activation energy of 21 kJ mol-1 was estimated for the reorientational motion in the α(I)-phase from the 1H NMR T1 measurements (Fig. 3).
The results of 127I NQR as well as of 1H NMR indicate a similarity on the structures of the β-phase and the α(II)-phase to those of the low-temperature phase and the room temperature phase of 4-NH2PyHSbBr4 [1,2], respectively.

References

[1] M. Hashimoto et al., Z. Naturforsch. A 55, 167 (2000).
[2] M. Hashimoto et al., Bull. Chem. Soc. Jpn. 76,749 (2003).

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