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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 \leftrightarrow 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 ($m = \pm 1/2 \leftrightarrow \pm 3/2$) may be assigned to the terminal and the bridging I atoms by considering their frequencies, indicating an existence of one dimensional infinite 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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