Bis(n-butylammonium) pentachloroantimonate(III) \((\text{C}_4\text{H}_9\text{NH}_3)_2[\text{SbCl}_5]\) was obtained in a reaction of \(n\)-butylammonium chloride and antimony trichloride (molar ratio 2:1; cation:Sb) in acidic aqueous solution. To obtain further information about the mechanism of the earlier reported phase transitions at 229 and 315 K the structure was determined at 100, 260 and 340 K. The orthorhombic system was found in all phases, space groups \(Ibam\) at 340 K and \(Pccn\) at 260 and 100 K. In all phases the anionic sublattice consists of \([\text{SbCl}_6]^{3-}\) octahedra, connected via cis chlorine atoms, forming one-dimensional zig-zag \{\([\text{SbCl}_5]^2-\)\}_n chains extended along the \(c\) direction. The \(n\)-butylammonium cations are located between the inorganic chains, with \(-\text{NH}_3^+\) groups facing the oppositely charged polyanions. The phase transitions are of the order-disorder type. They are related to changes in molecular dynamics of the \(n\)-butylammonium cations. At high temperature the cations reorient, on decreasing temperature the reorientations are successfully frozen. This leads to the formation of N-H...Cl hydrogen bonds, which significantly deform the octahedral coordination of the Sb atoms.

**Key words:** Chloroantimonates(III), \(n\)-Butylammonium Cation, Phase Transition, Disorder