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Structure, phase transitions and molecular dynamics in ferroelastic crystal pyrrolidinium hexachloroantimonate(V), $[C_4H_8NH_2][SbCl_6]$ ☆

Ryszard Jakubas [a,*], Beata Bednarska-Bolek [a], Jacek Zaleski [b], Wojciech Medycki [c], Krystyna Hołderna-Natkaniec [d], Piotr Zieliński [e], Mirosław Gałązka [e]

[a] *Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland*
[b] *Institute of Chemistry, University of Opole, Oleska 48, 45-951 Opole, Poland*
[c] *Institute of Molecular Physics, PAS, Smoluchowskiego 17, 60-179 Poznań, Poland*
[d] *Institute of Physics, UAM, Umultowska 85, 61-614 Poznań, Poland*
[e] *H. Niewodniczański Institute of Nuclear Physics, PAN, 31-342 Kraków, Poland*

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Abstract

The crystal structure of the pyrrolidinium hexachloroantimonate(V), $[C_4H_8NH_2][SbCl_6]$, abbreviated PCA, has been determined by means of X-ray diffraction at 300 and 340 K. The space groups are monoclinic $P2_1/n$ (phase III) and orthorhombic *Pmnb* (phase II), respectively. The crystal undergoes two structural phase transitions: first-order type at 356/329 K (heating/cooling) from phase (I) to (II) and second-order type at 323 K from phase (II) to (III). Dielectric studies suggest the plastic crystals behaviour above 356 K (phase I). Proton spin-lattice relaxation time (T_1) and second moment (M_2) of polycrystalline $[C_4H_8NH_2][SbCl_6]$ have been determined at 77–370 K, at 90 and 25 MHz. Temperature dependence of the M_2 indicates that the continuous increase in the freedom of rotational motion of the pyrrolidinium cations takes place over the phase (III). The ferroelastic domain structure of $[C_4H_8NH_2][SbCl_6]$ is observed over the phase (III). Mechanisms of phase transitions in PCA are discussed.

Keywords: Chloroantimonate(V); Structure; Phase transition; Ferroelastic

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1. Introduction

Ionic complexes containing $SbCl_6^-$ anions and exotic cations, such as substituted porphyrin analogs, tris(4-bromophenyl) aminium or thietanium species [1–3] have been extensively studied in the last decade. Of special interest is their significance for the understanding of biological processes, e.g., photosynthetic and catalytic reactions.

Hexachloroantimonate(V) ionic salts with small organic cations revealed interesting dynamical properties. A complicated sequence of phase transitions, involving ferroelastic ones, has been discovered in the chloroantimonates(V) family salts depending on the organic cations: tetramethylphosphonium [4], triethylammonium [5], guanidinium [6] and piperidinium [7,8]. The compositions obtained up to now allow one to distinguish two subclasses of chloroantimonates(V): (i) $R\mathrm{SbCl}_6$, and (ii) $R_2^+(\mathrm{SbCl}_6^-)(\mathrm{Cl}^-)$, where R is organic cations. In the structure of $R\mathrm{SbCl}_6$ salts the isolated $SbCl_6$ octahedra are connected with the organic cations by weak N–H···Cl hydrogen bonds. In the case of $R_2^+(\mathrm{SbCl}_6^-)(\mathrm{Cl}^-)$ compounds apart from the isolated $SbCl_6$ units one can distinguish isolated Cl^- ions hydrogen bonded with the organic cations. The ferroelastic type phase transitions (PTs) encountered in both subclasses of

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☆ Crystallographic data for the structures reported in this paper (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 246722 and 246773. Copies of this information may be obtained free of charge from the Director, CCDC, 12 UNION Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

* Corresponding author.
E-mail address: rj@wchuwr.chem.uni.wroc.pl (R. Jakubas).

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crystals usually exhibit a continuous nature with most probably a “displacive” mechanism. It turned out that the high temperature paraelastic phase shows features of plastic phases. Numerous PTs found in both subgroups are characterized by an “order–disorder” mechanism related to the dynamics of both the organic cations and the $SbCl_6$ octahedra.

Closely related to the title compound, the recently found pyrrolidinium analogue, $(C_4H_8NH_2{}^+)_2(SbCl_6{}^-)(Cl^-)$ [9] is characterised by quite a complex phase situation exhibiting five solid-solid phase transitions: at 351/374 K (cooling/heating, respectively), 356 K (on heating), 152 K (on cooling), 135/141 K and 105/134 K. The ferroelastic phase occurs between 152 and 135 K. The order–disorder mechanism of the phase transitions at 105 and 374 K was attributed to the motion of the pyrrolidinium cations. Since we were successful in synthesizing and growing single crystals of a new pyrrolidinium analogue having simpler stoichiometry ($RSbCl_6$) it seemed interesting to compare the ferroic properties of both materials.

In this paper we report X-ray, differential scanning calorimetry (DSC), dilatometry and dielectric studies of a new ferroic crystal, pyrrolidinium chloroantimonate(V), $[C_4H_8NH_2][SbCl_6]$. The Proton Magnetic Resonance (^1H NMR) method is used to study the molecular motions in this crystal. Optical observations of the ferroelastic domain structure are also reported. The properties of all the ferroelastic crystals from chloroantimonates(V) family studied till now are compared and the mechanism of the paraelastic-ferroelastic phase transition in $[C_4H_8NH_2][SbCl_6]$ is proposed.

2. Experimental

$[C_4H_8NH_2][SbCl_6]$ was prepared by the reaction of $SbCl_5$ (Aldrich–99.99%), and pyrrolidine ($C_4H_8NH_2$, Aldrich–99.5%) at molar ratio 1 : 1 in concentrated 36% HCl. The resulting white solid was recrystallized twice from a methanol solution. Single crystals of the title compound were grown from the methanol solution at constant room temperature. The crystals grow in a pseudo-hexagonal manner and have a well-developed (010) faces.

A Perkin–Elmer Differential Scanning Calorimeter (DSC) Model 7 was used to measure the thermal properties of the sample, at the scanning rate of 10.0 K/min. A polycrystalline sample of 16.1 mg was placed in nonhermetic aluminum cell in the nitrogen atmosphere.

Linear thermal expansion was measured using a thermomechanical analyzer Perkin–Elmer TMA-7. The samples used in the measurements were prepared in the form of plates ($4 \times 4 \times 2\ mm^3$). The accuracy of thermal expansion determination was about 3%.

The measurements of the complex electric permittivity, ε^*, were performed with an impedance analyzer HP 4285A in the frequency range from 75 kHz to 30 MHz. The golden electrodes were deposited by evaporation on the surfaces perpendicular to the b-direction of the single crystals. The temperature of the sample was varied continuously at the rate of $0.1\ K{\cdot}min^{-1}$ in the vicinity of the phase transition points and $0.5\ K{\cdot}min^{-1}$ elsewhere. The accuracy of the measured electric permittivity value was about 5%.

The sample for NMR study was powdered, degassed for several hours and sealed in a glass tube under vacuum. The second moment M_2 and slope widths of the resonance lines were determined from the ^1H NMR spectra recorded by the continuous wave method on a spectrometer working at 25 MHz in the range 110–370 K. The T_1 measurements were done by the saturation method using the pulse sequence $n^*\pi/2 - \tau - \pi/2$ ($n = 15$) for the resonance frequency of 25 and 90 MHz, on a pulse spectrometer Bruker SXP 4/100. Single-exponential magnetisation recovery was observed in the whole temperature range.

The unit cell parameters were obtained from a least squares refinement of 25 reflections in the 2θ range of 14–25°. Data collections were carried out at 300(2) and 340.0(1) K on a Kuma KM-4-diffractometer equipped with an Oxford Cryosystem cooler. Two standard reflections were monitored every 50 measurements showing that the intensity variations were negligible. Lorentz, polarizations and semi-empirical absorption corrections were applied ($T_{min} = 0.44$, $T_{max} = 0.55$). Hydrogen atoms were included using standard geometric criteria and constrained to a distance of 0.9 Å for N–H and 0.96 Å for C–H.

KUMA software was used in the data collection, cell refinement and data reduction process [10]. The SHELXS-97 [11] and SHELXL-97 [12] programs were used for the structure solution and refinement. The structure drawings were prepared using the XP program from the SHELXTL [13]. The details of the data collection and processing are listed in Table 1. Final atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are shown in Table 2. Bond lengths and angles for anionic sublattice are given in Table 3, whereas details of hydrogen bonds are given in Table 4.

3. Results and discussion

3.1. X-ray structure determination

The independent part of the unit cell contains one $[SbCl_6]^-$ octahedron and one pyrrolidinium cation for both studied phases. Fig. 1 shows a projection of the $P2_1/n$ structure onto the bc plane at 300 K. The Sb–Cl bond lengths are in the range 2.348(2)–2.365(2) Å, whereas Cl–Sb–Cl angles between 89.2(1)° and 91.9(1)° at 300 K. At 340.0 K they do not change much indicating that the $SbCl_6{}^-$ octahedron stays fairly undeformed in the phases II and III. The pyrrolidinium cation is attached to the anionic sublattice by weak N–H···Cl hydrogen bond in both phases (see Table 4). These hydrogen bonds are significantly longer (by