

Crystal and Molecular Structure of 1,2,4-Triazolium Chloride and its Salt with Antimony Trichloride - Bis(1,2,4-triazolium) pentachloroantimonate(III)-1,2,4-triazolium Chloride

Maciej Bujak and Jacek Zaleski

Institute of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland

Reprint requests to Prof. J. Zaleski. Tel./Fax: ++48 774410741. E-mail: zaleski@uni.opole.pl

Z. Naturforsch. 57 b, 157–164 (2002); received September 13, 2001

1,2,4-Triazolium Cation, Chloroantimonates(III), Hydrogen Bonds

The structures of 1,2,4-triazolium chloride ($C_2H_4N_3$)Cl and its derivative with antimony trichloride - $(C_2H_4N_3)_2[SbCl_5] \cdot (C_2H_4N_3)Cl$ containing unsubstituted 1,2,4-triazolium cations were determined. $(C_2H_4N_3)Cl$ crystallizes in the monoclinic system, space group $P2_1/n$ with the unit cell dimensions at 86 K: $a = 9.425(2)$, $b = 8.557(2)$, $c = 11.158(2)$ Å, $\beta = 95.87(3)^\circ$; $V = 895.2(3)$ Å³, $Z = 8$, $d_c = 1.566$, $d_m = 1.56(2)$ g·cm⁻³. At room temperature, crystals of $(C_2H_4N_3)_2 \cdot [SbCl_5] \cdot (C_2H_4N_3)Cl$ are orthorhombic, space group $P2_12_12_1$, $a = 8.318(2)$, $b = 11.381(2)$, $c = 19.931(4)$ Å, $V = 1886.8(7)$ Å³, $Z = 4$, $d_c = 1.917$, $d_m = 1.91(2)$ g·cm⁻³. In both crystals the 1,2,4-triazole rings are planar. The anionic sublattice of $(C_2H_4N_3)_2[SbCl_5] \cdot (C_2H_4N_3)Cl$ consists of polymeric $[SbCl_5]_n^{2-}$ zig-zag chains composed of distorted $[SbCl_6]^{3-}$ octahedra connected via their vertices and the single Cl^- anions. The cavities between the inorganic chains are filled by 1,2,4-triazolium cations. The nature of the distortion of the $[SbCl_6]^{3-}$ polyhedra has been studied by examining correlations between the Sb-Cl bond lengths and the strength of hydrogen bonds, which join the anionic sublattice and the organic cations. This study confirms that the deformation of the $[SbCl_6]^{3-}$ octahedra is caused by hydrogen bonds.

1. Introduction

The new group of ferroic crystals – halogenoantimonates(III) and halogenobismuthates(III) with organic cations – has been the subject of intense investigations for the last several years [1 - 3 and references therein]. Salts belonging to this group may be obtained by mixing amine and antimony/bismuth oxide in a solution of the appropriate HX acid (X = Cl, Br or I). The anionic sublattices of these salts are almost always built of deformed $[MX_5]^{2-}$ square pyramids or $[MX_6]^{3-}$ octahedra (M = antimony(III) / bismuth(III)). These polyhedra exist as isolated units or are linked through bridging halogen atoms forming more complicated arrangements.

Interest in halogenoantimonates(III) and halogenobismuthates(III) results from the discovery of phase transitions to polar phases in some members of this family of compounds [4]. These phase transitions are mainly connected with the changes in the dynamic properties of the cationic sublattices. The cations at ambient temperature typically possess considerable freedom of reorientations in the

solid state. On decreasing temperature these reorientations are frozen. The motions inside the cationic sublattices are often associated with changes in the hydrogen bonding scheme joining the cations to the inorganic sublattices.

The unique crystal chemistry of halogenoantimonates(III) and halogenobismuthates(III) is connected with the tendency of $[MX_5]^{2-}$ square pyramids and $[MX_6]^{3-}$ octahedra to join with each other through bridging halogen atoms. It results in a large number of types of anionic sublattices characteristic of each stoichiometry. The observed differences in M-X bond lengths and X-M-X angles from the mean values characteristic of non-deformed polyhedra were shown to be associated with the shift of the lone electron pair of the M(III) atom in the direction of the interaction. In a series of our earlier works we correlated the differences in M-X bond lengths to primary deformations resulting from the tendency of $[MX_6]^{3-}$ octahedra to share halogen atoms and secondary deformations resulting from intermolecular interactions. The intermolecular interactions such as N-H...X hydrogen bonds additionally distort $[MX_6]^{3-}$ octahedra shifting the

Table 1. Summary of the crystallographic data for $(C_2H_4N_3)Cl$ and $(C_2H_4N_3)_2[SbCl_5] \cdot (C_2H_4N_3)Cl$.

Empirical formula	$C_2H_4ClN_3$	$C_6H_{12}Cl_6N_9Sb$
Colour; habit	colourless; irregular	colourless; pillar
Crystal size (mm ³)	$0.38 \times 0.30 \times 0.28$	$0.40 \times 0.40 \times 0.25$
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
Unit cell dimensions (Å, °)	$a = 9.425(2), b = 8.557(2), c = 11.158(2)$ $\beta = 95.87(3)$	$a = 8.318(2), b = 11.381(2), c = 19.931(4)$
Volume [Å ³]	895.2(3)	1886.8(7)
Z	8	4
Formula weight	105.53	544.70
Density (calculated) (g·cm ⁻³)	1.566	1.917
Density (measured) (g·cm ⁻³)	1.56(2)	1.91(2)
Absorption coeff. (mm ⁻¹)	0.681	2.319
Temperature (K)	86(1)	297(2)
Diffractometer / Scan type		KUMA KM-4/ ω - θ
Radiation		Mo-K α ($\lambda = 0.71073$ Å)
θ Range (°)	2.7 - 25.1	2.0 - 25.1
Index ranges	$-11 \leq h \leq 11, -10 \leq k \leq 0, -13 \leq l \leq 0$	$0 \leq h \leq 9, 0 \leq k \leq 13, -23 \leq l \leq 23$
Reflections collected / unique	1674 / 1589	3736 / 3328
Observed refls [$I > 2\sigma(I)$]	1345	3072
Program		SHELX-97
Solution		Patterson method
Refinement method		Full-matrix least squares on F^2
Weight scheme	$w = 1/[\sigma^2(F_0^2) + (0.0306P)^2 + 0.3787P]$	$w = 1/[\sigma^2(F_0^2) + (0.0368P)^2 + 0.2129P]$ where $P = (F_0^2 + 2F_c^2)/3$
Refined parameters	133	199
Final R indices [$I > 2\sigma(I)$]	$R_1=0.023; wR_2=0.061$	$R_1=0.022; wR_2=0.065$
R Indices (all data)	$R_1=0.033; wR_2=0.065$	$R_1=0.027; wR_2=0.069$
Goodness of fit on F^2	1.087	1.209
Largest diff. peak/hole (e·Å ⁻³)	0.20 / -0.24	0.29 / -0.69

halogen atoms in the direction of the positive charge located on the cations [5].

Until now most investigations were related to simple alkylammonium derivatives. We decided to extend our studies [6, 7] to cations containing more than one nitrogen atom [8, 9]. 1,2,4-Triazole, which was selected, possesses a five-membered aromatic ring containing three heteroatoms [10].

So far only one salt containing 1,2,4-triazolium cations was reported for the whole group of halogenoantimonates(III) and halogenobismuthates(III) - $(C_2H_4N_3)[Sb_2F_7]$ [11]. Its structure is built of isolated binuclear $[Sb_2F_7]^-$ anions and $(C_2H_4N_3)^+$ 1,2,4-triazolium cations connected to an anionic sublattice by N-H...F and C-H...F hydrogen bonds.

Experimental Section

1,2,4-Triazole (> 98%), antimony trichloride (> 99%; both Merck-Schuchardt, Germany) and hydrochloric acid (35 - 38%, pure p.a.; POCh, Poland) were the start-

ing materials used for the synthesis of 1,2,4-triazolium chloroantimonate(III) $(C_2H_4N_3)_2[SbCl_5] \cdot (C_2H_4N_3)Cl$ and 1,2,4-triazolium chloride $(C_2H_4N_3)Cl$. The crystals were prepared by dissolving antimony trichloride (2.28 g, 10 mmol) in a minimum of aqueous (ca. 18%) hydrochloric acid (10 - 20 ml). This solution was combined with an aqueous solution (10 - 20 ml) of 1,2,4-triazole (2.07 - 6.91 g, 30 - 100 mmol). Concentrated (35 - 38%) hydrochloric acid was added until the white precipitate disappeared. The molar ratio of 1,2,4-triazole to antimony trichloride was varied from 3:1 to 10:1. Crystals of $(C_2H_4N_3)_2[SbCl_5] \cdot (C_2H_4N_3)Cl$ were obtained in the range of molar ratios from 3:1 to 7:1. The increase of the molar ratio of 1,2,4-triazole to antimony trichloride above 8:1 leads to the simultaneous crystallization of $(C_2H_4N_3)_2[SbCl_5] \cdot (C_2H_4N_3)Cl$ and $(C_2H_4N_3)Cl$. The transparent X-ray quality crystals were grown by slow evaporation of the solvent at room temperature. Density measurements were made by a flotation method using mixtures of chloroform, carbon tetrachloride and bromoform.

At 86 K the intensity data were collected on the diffractometer equipped with the Oxford Cryosystems cooler.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ and $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
<i>(C₂H₄N₃)Cl:</i>				
C11	5298(1)	2360(1)	2243(1)	14(1)
Cl2	9689(1)	2218(1)	3225(1)	14(1)
N1	8333(2)	4201(2)	-1055(1)	13(1)
N2	8882(2)	3569(2)	21(1)	14(1)
C3	8129(2)	4221(2)	797(2)	15(1)
N4	7151(2)	5226(2)	258(1)	14(1)
C5	7295(2)	5184(2)	-918(2)	13(1)
N6	8126(2)	5549(2)	5526(1)	14(1)
N7	7327(2)	4853(2)	6331(1)	15(1)
C8	6442(2)	3976(2)	5655(2)	15(1)
N9	6660(2)	4100(2)	4475(1)	14(1)
C10	7729(2)	5107(2)	4422(2)	15(1)
H1	8680(2)	3930(2)	-1706(18)	15
H3	8230(2)	4000(2)	1602(18)	18
H4	6530(2)	5790(2)	599(17)	16
H5	6750(2)	5740(2)	-1520(17)	16
H6	8780(2)	6220(2)	5729(17)	17
H8	5730(2)	3350(2)	5935(17)	18
H9	6230(2)	3600(2)	3897(18)	17
H10	8120(2)	5480(2)	3773(18)	18
<i>(C₂H₄N₃)₂[SbCl₅] · (C₂H₄N₃)Cl:</i>				
Sb1	5552(1)	1950(1)	4070(1)	28(1)
C11	7615(2)	1430(1)	3248(1)	51(1)
Cl2	8182(2)	2502(1)	4906(1)	55(1)
Cl3	3343(2)	1429(1)	3296(1)	49(1)
Cl4	5552(2)	4055(1)	3706(1)	45(1)
Cl5	5566(2)	-374(1)	4573(1)	40(1)
Cl6	9441(2)	3531(1)	1986(1)	45(1)
N1	3157(5)	3286(4)	1903(2)	39(1)
N2	3552(5)	2246(4)	1613(2)	47(1)
C3	5105(6)	2232(5)	1652(3)	48(1)
N4	5674(5)	3200(4)	1940(2)	43(1)
C5	4420(6)	3857(4)	2097(2)	41(1)
N6	9593(6)	889(4)	1678(2)	54(1)
N7	8224(6)	333(5)	1528(4)	82(2)
C8	8696(7)	-664(6)	1291(4)	63(2)
N9	10267(5)	-746(4)	1289(3)	55(1)
C10	10802(7)	256(5)	1538(4)	60(2)
N11	5663(6)	512(4)	-350(2)	49(1)
N12	5389(6)	1592(4)	-113(3)	61(1)
C13	3844(6)	1680(5)	-118(3)	57(2)
N14	3166(5)	680(4)	-338(2)	47(1)
C15	4344(7)	-19(4)	-486(3)	52(1)

The lattice parameters were refined from setting angles of 40 reflections in the $5^\circ < \theta < 15^\circ$ range for $(\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ and 50 reflections in the $7^\circ < \theta < 14^\circ$ range for $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$. All data were subjected to Lorentz,

polarisation and semiempirical absorption correction [12] (only for the $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ crystal, $T_{\text{min}} = 0.457$, $T_{\text{max}} = 0.595$).

The hydrogen atoms in the structure of $(\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ were located from the difference Fourier maps. In the case of $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ all hydrogen atoms were included using standard geometric criteria. In both structures the isotropic U-values of hydrogen atoms were taken with coefficients being 1.2 times larger than the respective parameters of atoms to which they are bonded. The positions of hydrogen atoms in the structure of $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ were refined using a riding model.

KUMA software was used in the cell refinement, data collection [13] and data reduction processes [14]. The SHELXS-97 [15], SHELXL-97 [16] and SHELXTL [12] programs were used for the structure solutions, refinements and structure drawings.

Crystallographic data (excluding structure factors) for 1,2,4-triazolium chloride and bis(1,2,4-triazolium) pentachloroantimonate(III) - 1,2,4-triazolium chloride have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 162783 and CCDC 162784 respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.ac.uk).

The TGA measurements were performed with a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ in the temperature range 300 - 475 K on a Universal TA Instruments apparatus. The studies show that the $(\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ and $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ crystals begin to decompose above *ca.* 380 K.

The DSC studies were carried out on a Universal TA Instruments calorimeter with a cooling / heating rate of $10 \text{ K} \cdot \text{min}^{-1}$. The measurements were performed in the temperature range 160 - 360 K finding no heat anomalies.

3. Results and Discussion

The crystal data and the structure determination summary for $(\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ and $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ crystals are listed in Table 1. The final atomic coordinates and equivalent isotropic displacement parameters for atoms of both crystals are shown in Table 2.

Structure of 1,2,4-triazolium chloride, $(\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$

The structure of 1,2,4-triazolium chloride was determined at 86 and 297 K. At both temperatures crystals are monoclinic, space group $P2_1/n$. Only the

Table 3. Bond lengths (Å) and angles (°) for (C₂H₄N₃)Cl.

N1-N2	1.369(2)	C5-N4-C3	106.6(2)
N1-C5	1.311(2)	N1-C5-H5	127(1)
N2-C3	1.300(2)	N2-N1-H1	119(1)
C3-N4	1.355(2)	N2-C3-H3	124(1)
N4-C5	1.333(2)	N4-C3-H3	124(1)
N1-H1	0.86(2)	N4-C5-H5	126(1)
C3-H3	0.91(2)	C3-N4-H4	128(1)
N4-H4	0.87(2)	C5-N1-H1	129(1)
C5-H5	0.93(2)	C5-N4-H4	126(1)
N6-N7	1.366(2)	N6-C10-N9	106.9(2)
N6-C10	1.307(2)	N7-C8-N9	111.4(2)
N7-C8	1.303(2)	C8-N7-N6	103.5(1)
C8-N9	1.358(2)	C10-N6-N7	111.7(2)
N9-C10	1.331(2)	C10-N9-C8	106.5(2)
N6-H6	0.86(2)	N6-C10-H10	124(1)
C8-H8	0.94(2)	N7-N6-H6	123(1)
N9-H9	0.84(2)	N7-C8-H8	125(1)
C10-H10	0.90(2)	C8-N9-H9	127(1)
N1-C5-N4	106.5(2)	N9-C8-H8	123(1)
N2-C3-N4	111.7(2)	N9-C10-H10	130(1)
C3-N2-N1	103.4(1)	C10-N6-H6	125(1)
C5-N1-N2	111.8(1)	C10-N9-H9	127(1)

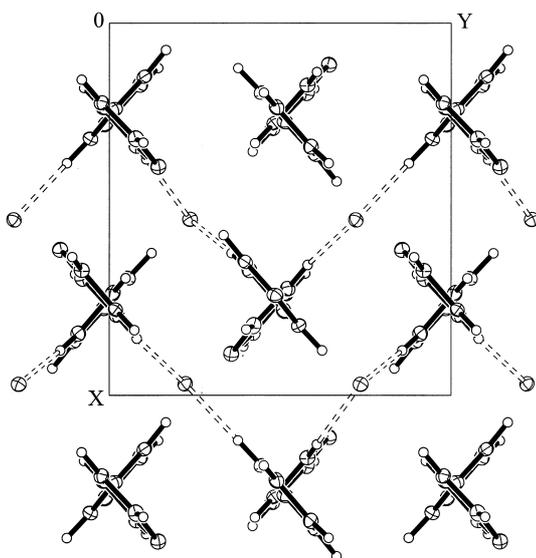


Fig. 1. Projection of the structure of 1,2,4-triazolium chloride down the *c* axis at 86 K. Broken lines represent the hydrogen bonding network (only the strongest hydrogen bonds are shown for clarity). Displacement ellipsoids are at the 50% probability level.

results based on the more accurate low temperature data set will be reported.

The structure consists of almost planar (C₂H₄N₃)⁺ 1,2,4-triazolium cations and single Cl⁻ chloride anions. The 1,2,4-triazole rings are stacked

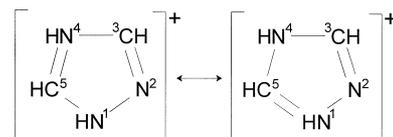


Fig. 2. Two of the most stable canonical forms of the 1,2,4-triazolium cation.

one on top of the other forming characteristic columns parallel to the [010] direction. The angle between 1,2,4-triazole rings belonging to neighbouring columns is 82.62(6)°. The chloride ions located between organic columns are joined to 1,2,4-triazolium cations through hydrogen bonds (Fig. 1). The independent part of the unit cell contains two (C₂H₄N₃)⁺ cations and two Cl⁻ anions. The bond lengths and angles for (C₂H₄N₃)Cl are presented in Table 3.

Two of the most stable canonical forms of the 1,2,4-triazolium cation are depicted in Fig. 2 [17]. In both forms the N¹-N² and C³-N⁴ bonds have a single bond character, N²-C³ has a double bond character, while the remaining N¹-C⁵ and N⁴-C⁵ bonds are intermediate between the single and double. The C-N and N-N distances which have been found in the structure of (C₂H₄N₃)Cl correspond well to the situation described above. The longest bonds in the two independent 1,2,4-triazolium cations are N¹-N² (av. 1.368(4) Å) and C³-N⁴ (av. 1.357(4) Å). The N²-C³ bond lengths are the shortest (av. 1.302(4) Å). The intermediate lengths are characteristic of N¹-C⁵ (av. 1.309(4) Å) and N⁴-C⁵ (av. 1.332(4) Å). The ring angles of the 1,2,4-triazolium cations range from 103.4(1) to 111.8(1)°. That two independent 1,2,4-triazole rings are planar, with the carbon and nitrogen atoms at an average deviation from the least square plane of 0.002(1) Å.

There are four different types of hydrogen bonds present in the structure of (C₂H₄N₃)Cl: N-H...Cl, N-H...N, C-H...Cl, and C-H...N. Comparing their geometrical parameters to the sum of the van der Waals radii of donor and acceptor atoms, and hydrogen and acceptor atoms [18, 19] they can be divided into two groups. Stronger bonds include N-H...Cl hydrogen (with N...Cl distances between 3.041(2) and 3.089(2) Å), while much weaker bonds are N-H...N, C-H...Cl, and C-H...N (Table 5). Comparable hydrogen bond geometries were found in other organic crystals containing isolated Cl⁻ anions or 1,2,4-triazole rings [20, 21].

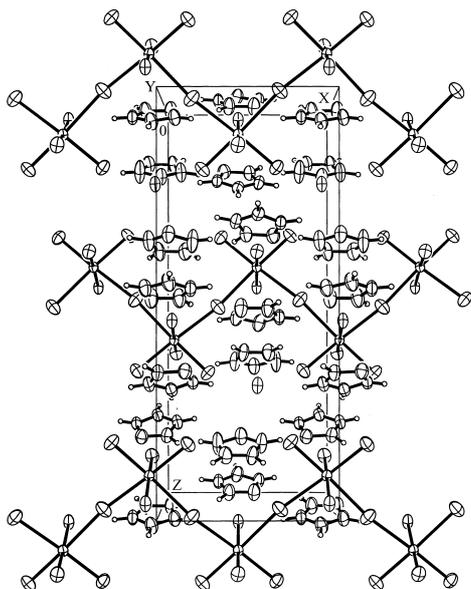


Fig. 3. The packing diagram of $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ showing $[\text{SbCl}_5]_n^{2-}$ zig-zag chains. Displacement ellipsoids are at the 50% probability level.

Structure of bis(1,2,4-triazolium) pentachloroantimonate(III) - 1,2,4-triazolium chloride, $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$

The structure of $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ consists of polymeric, one dimensional $[\text{SbCl}_5]_n^{2-}$ zig-zag chains built of $[\text{SbCl}_6]^{3-}$ octahedra sharing corners, isolated Cl^- anions and $(\text{C}_2\text{H}_4\text{N}_3)^+$ 1,2,4-triazolium cations (Fig. 3). The organic and inorganic moieties are linked to each other by N-H...Cl and C-H...Cl hydrogen bonds.

The presence of isolated chloride anions as a part of an anionic sublattice in the family of chloroantimonates(III) was also found in the structure of $(\text{CH}_3\text{NH}_3)_2[\text{SbCl}_5] \cdot (\text{CH}_3\text{NH}_3)\text{Cl}$ [22] and $[\text{C}(\text{NH}_2)_3]_2[\text{SbCl}_5] \cdot [\text{C}(\text{NH}_2)_3]\text{Cl}$ [23]. In these crystals like in the title chloroantimonate(III) the $[\text{SbCl}_6]^{3-}$ octahedra share corners forming infinite $[\text{SbCl}_5]_n^{2-}$ chains. Isolated Cl^- anions are located between the polyanionic $[\text{SbCl}_5]_n^{2-}$ chains. In the structure of $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ the $[\text{SbCl}_6]^{3-}$ units possess a configuration of distorted octahedra. The central antimony(III) atom is surrounded by six chlorine atoms, two of them are bridging and four are terminal. The bridging Sb-Cl distances (2.821(2) and 2.905(2) Å) are elongated while the terminal Sb-Cl bonds located *trans* are shortened (2.471(1) and 2.445(1) Å) as compared

Table 4. Selected bond lengths (Å) and angles (°) for $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$.

Sb1-Cl1	2.445(1)	Cl2-Sb1-Cl2 ¹	93.64(2)
Sb1-Cl2	2.821(2)	Cl2-Sb1-Cl3	177.16(5)
Sb1-Cl2 ¹	2.905(2)	Cl2-Sb1-Cl4	87.59(4)
Sb1-Cl3	2.471(1)	Cl2-Sb1-Cl5	89.75(4)
Sb1-Cl4	2.503(1)	Cl2 ¹ -Sb1-Cl3	89.18(5)
Sb1-Cl5	2.829(1)	Cl2 ¹ -Sb1-Cl4	89.90(4)
N1-N2	1.357(6)	Cl2 ¹ -Sb1-Cl5	87.41(4)
N1-C5	1.294(6)	Cl3-Sb1-Cl4	92.80(4)
N2-C3	1.295(6)	Cl3-Sb1-Cl5	90.00(4)
C3-N4	1.330(7)	Cl4-Sb1-Cl5	176.09(4)
N4-C5	1.321(6)	N1-C5-N4	106.6(4)
N6-N7	1.337(7)	N2-C3-N4	111.7(5)
N6-C10	1.268(7)	C3-N2-N1	103.1(5)
N7-C8	1.290(8)	C5-N1-N2	111.6(4)
C8-N9	1.310(7)	C5-N4-C3	106.8(4)
N9-C10	1.322(7)	N6-C10-N9	107.8(5)
N11-N12	1.336(6)	N7-C8-N9	111.6(6)
N11-C15	1.281(7)	C8-N7-N6	103.8(5)
N12-C13	1.289(7)	C8-N9-C10	105.8(5)
C13-N14	1.345(7)	C10-N6-N7	111.0(4)
N14-C15	1.296(7)	N11-C15-N14	108.1(4)
Cl1-Sb1-Cl2	84.56(5)	N12-C13-N14	110.7(5)
Cl1-Sb1-Cl2 ¹	177.21(5)	C13-N12-N11	103.8(5)
Cl1-Sb1-Cl3	92.62(5)	C15-N11-N12	111.3(5)
Cl1-Sb1-Cl4	92.15(5)	C15-N14-C13	106.1(4)
Cl1-Sb1-Cl5	90.45(4)		

Symmetry code: ¹ $x - 1/2, 1/2 - y, 1 - z$.

to the average of the remaining two Sb-Cl bond lengths (2.666(2) Å). The Cl-Sb-Cl angles involving Cl atoms mutually *cis* range from 84.56(5)° to 93.64(2)°, while those located *trans* are between 176.09(4)° and 177.21(5)° (Table 4).

There are three $(\text{C}_2\text{H}_4\text{N}_3)^+$ cations in the independent part of the unit cell. The ring angles range from 103.1(5) to 111.7(5)°. The N-N (1.336(6) - 1.357(6) Å) and N-C (1.268(7) - 1.345(7) Å) distances (Table 4) are close to those found in the structure of $(\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$. The 1,2,4-triazole rings are planar with an average deviation of the C and N atoms from the least square plane of 0.004(5) Å.

In both crystals the geometry of the $(\text{C}_2\text{H}_4\text{N}_3)^+$ cations is comparable to that reported earlier [24] as well as in the structure of 1,2,4-triazole [25 - 27].

Deformation of the octahedral coordination of Sb(III) in $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$

The characteristic feature of trivalent antimony is that it possesses a lone electron pair, which occupies the 5s orbital and is almost always stereochemically

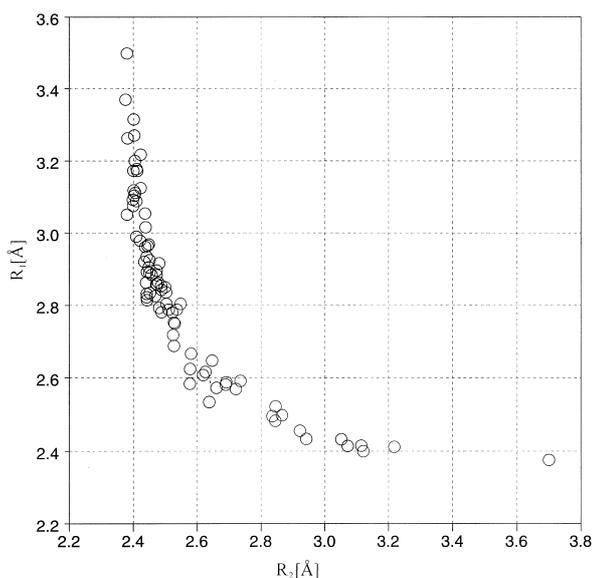


Fig. 4. The “trans” influence observed in structures of chloroantimonates(III). R_1 and R_2 represent opposite Sb-Cl distances.

active. The presence of the lone electron pair leads to the elongation of Sb(III)-Cl bonds (of ca. 0.27(1) Å) in comparison to the corresponding Sb(V)-Cl distances [28]. The considerable difference in the distortion of the environment of the central antimony atom in chloroantimonates(III) and -(V) is another feature which differs for these salts. The Sb(V) compounds show almost undistorted octahedral coordination, whereas Sb(III) octahedra show large deviations in Sb-Cl distances (up to ca. 1 Å) and Cl-Sb-Cl angles (up to ca. 15–20°) from each other.

In structures of chloroantimonates(III), in connection with the presence of the lone electron pair, the “trans” influence is observed [29]. “Short” (strong) Sb-Cl bonds are located opposite to “long” (weak) Sb-Cl bonds within the same polyhedron. The Sb-Cl distances vary from ca. 2.4 to ca. 3.7 Å. Fig. 4 presents the “trans” influence in chloroantimonates(III) [30].

In our structural investigations of chloroantimonates(III) with organic cations we are trying to explain the differences in Sb-Cl bond lengths and Cl-Sb-Cl angles within the $[\text{SbCl}_5]^{2-}$ and $[\text{SbCl}_6]^{3-}$ units taking into account the tendency of the polyhedra to join one another (primary deformation) and the intermolecular interactions between the organic and inorganic sublattices (secondary deformation).

Table 5. The H-bonds geometry (Å, °) for $(\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ and $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$.

D-H...A	D-H	H...A	D...A	D-H...A
<i>(C₂H₄N₃)Cl</i> :				
N1-H1...Cl1 ^I	0.86(2)	2.30(2)	3.089(2)	153(2)
N4-H4...Cl2 ^{II}	0.87(2)	2.20(2)	3.063(2)	168(2)
N6-H6...Cl2 ^{III}	0.86(2)	2.21(2)	3.041(2)	164(2)
N9-H9...Cl1	0.84(2)	2.23(2)	3.068(2)	173(2)
N1-H1...N7 ^{IV}	0.86(2)	2.55(2)	3.025(2)	116(2)
C3-H3...Cl2	0.91(2)	2.64(2)	3.409(2)	142(2)
C5-H5...Cl1 ^V	0.93(2)	2.59(2)	3.441(2)	152(2)
C10-H10...Cl1 ^{II}	0.90(2)	2.54(2)	3.366(2)	153(2)
C5-H5...N7 ^{IV}	0.93(2)	2.62(2)	3.086(2)	111(1)
C8-H8...N2 ^{VI}	0.94(2)	2.53(2)	3.273(2)	136(2)

Symmetry codes: ^I $1/2 + x, 1/2 - y, z - 1/2$; ^{II} $3/2 - x, 1/2 + y, 1/2 - z$; ^{III} $2 - x, 1 - y, 1 - z$; ^{IV} $x, y, z - 1$; ^V $1 - x, 1 - y, -z$; ^{VI} $x - 1/2, 1/2 - y, 1/2 + z$.

D-H...A	D-H	H...A	D...A	D-H...A
<i>(C₂H₄N₃)₂[SbCl₅] · (C₂H₄N₃)Cl</i> :				
N1-H1...Cl6 ^I	0.90	2.25	3.108(4)	160
N4-H4...Cl6	0.90	2.28	3.157(4)	166
N6-H6...Cl6	0.90	2.21	3.072(4)	162
N9-H9...Cl2 ^{II}	0.90	2.59	3.363(5)	145
N11-H11...Cl5 ^{III}	0.90	2.33	3.144(5)	151
N14-H14...Cl5 ^{IV}	0.90	2.23	3.129(5)	173
C10-H10...Cl4 ^{II}	0.96	2.73	3.362(6)	124
C13-H13...Cl5 ^V	0.96	2.87	3.558(6)	130

Symmetry codes: ^I $x - 1, y, z$; ^{II} $2 - x, y - 1/2, 1/2 - z$; ^{III} $3/2 - x, -y, z - 1/2$; ^{IV} $1/2 - x, -y, z - 1/2$; ^V $1 - x, 1/2 + y, 1/2 - z$.

Most structures of chloroantimonates(III) show that the primary deformations are significantly stronger in their influence on the deformation of the octahedra than the intermolecular interactions.

In the structure of $(\text{C}_2\text{H}_4\text{N}_3)_2[\text{SbCl}_5] \cdot (\text{C}_2\text{H}_4\text{N}_3)\text{Cl}$ the cations are linked to anions by N-H...Cl and much weaker C-H...Cl hydrogen bonds. The strongest hydrogen bonds involve the isolated Cl6 atom. We have found that only two (Cl2 and Cl5) of the five independent Cl atoms in the coordination sphere of antimony(III) take part in the N-H...Cl hydrogen bonds. The N...Cl distances are between 3.072(4) and 3.363(5) Å (Table 5), corresponding well to those found in other chloroantimonates(III) [31]. The scheme of hydrogen bonds involving the Cl5 atom is presented in Fig. 5. Contrary to the situation in other chloroantimonates(III) studied so far, there is one relatively long terminal

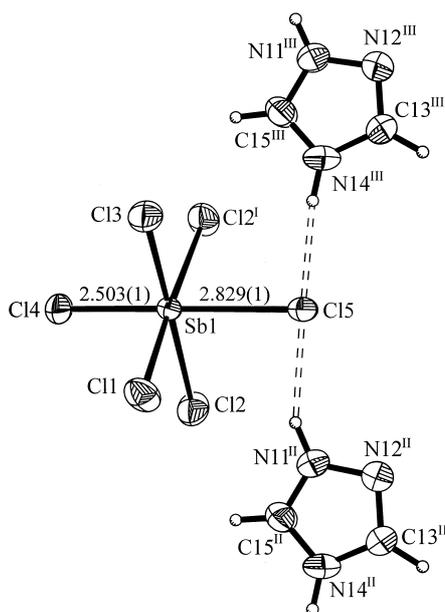


Fig. 5. The hydrogen bonding scheme involving Cl5 atom in the structure of $(C_2H_4N_3)_2[SbCl_5] \cdot (C_2H_4N_3)Cl$ (only the N-H...Cl hydrogen bonds are shown for clarity). Displacement ellipsoids are at the 50% probability level. Symmetry codes: ^I $x - 1/2, 1/2 - y, 1 - z$; ^{II} $3/2 - x, -y, z + 1/2$; ^{III} $1/2 - x, -y, z + 1/2$.

Sb-Cl distance (Sb1-Cl5, 2.829(1) Å). The length of this bond is typical of bridging chlorine atoms. The elongation results from the presence of relatively strong N-H...Cl hydrogen bonds to the Cl5 atom. $(C_2H_4N_3)_2[SbCl_5] \cdot (C_2H_4N_3)Cl$ is one of few examples where hydrogen bonds cause elongation of an Sb-Cl bond to the extent comparable to that characteristic of the primary deformation. The elongation up to 0.182(2) Å [28] results from strong N11-H11...Cl5^{III} and N14-H14...Cl5^{IV} intramolecular interactions. Although this situation is unusual it is not a first example of such a large Sb-Cl elongation caused by hydrogen bonds. A similar situation was also found in the structures of $[(CH_3)_2S(O)NH_2][SbCl_5]$ and $(C_5H_5NH_3)[SbCl_5]$ (elongations of 0.298(2) and 0.198(2) Å, respectively) [32, 33].

Acknowledgement

Maciej Bujak is a holder of the scholarship (The Annual Stipend for Young Scientists) of The Foundation for Polish Science in 2001.

- [1] J. Zaleski, Structure, phase transitions and molecular motions in chloroantimonates(III) and bismuthates(III), Opole University Press, Opole, Poland (1995).
- [2] L. Sobczyk, R. Jakubas, J. Zaleski, *Pol. J. Chem.* **71**, 265 (1997).
- [3] G. Bator, Dielectric relaxation and IR studies on phase transitions in alkylammonium halogenoantimonates(III) and bismuthates(III), TINTA, Wrocław, Poland (1999).
- [4] R. Jakubas, Structure and phase transitions in alkylammonium halogenoantimonates(III) and bismuthates(III), Wrocław University Press, Wrocław, Poland (1990).
- [5] M. Bujak, P. Osadczuk, J. Zaleski, *Acta Crystallogr.* **C55**, 1443 (1999).
- [6] J. Zaleski, A. Pietraszko, *Acta Crystallogr.* **B52**, 287 (1996).
- [7] M. Bujak, J. Zaleski, *Pol. J. Chem.* **73**, 773 (1999).
- [8] M. Bujak, L. Sikorska, J. Zaleski, *Z. Anorg. Allg. Chem.* **626**, 2535 (1999).
- [9] M. Bujak, P. Osadczuk, J. Zaleski, *Acta Crystallogr.* **C57**, 388 (2001).
- [10] L. A. Oro, M. T. Pinillos, C. Tejel, C. Foces-Foces, *Chem. Commun.* 1687 (1984).
- [11] A. A. Udovenko, Yu. E. Gorbunova, L. A. Zemnukova, Yu. N. Mikhailov, R. L. Davidovich, *Koord. Khim.* **24**, 655 (1998).
- [12] G. M. Sheldrick, SHELXTL Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA (1990).
- [13] KUMA, KUMA Diffraction Software, version 10.1.11, KUMA Diffraction, Wrocław, Poland (1999).
- [14] KUMA, KUMA Diffraction Software, version 10.0.4, KUMA Diffraction, Wrocław, Poland (1998).
- [15] G. M. Sheldrick, SHELXS-97. Program for the Solution of Crystal Structure, University of Göttingen, Germany (1997).
- [16] G. M. Sheldrick, SHELXL-97. Program for the Refinement of Crystal Structure, University of Göttingen, Germany (1997).
- [17] K. T. Potts, *Chem. Rev.* **61**, 87 (1961).
- [18] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell University Press, New York, USA (1960).

- [19] A. Bondi, *J. Phys. Chem.* **68**, 441 (1964).
- [20] W. Errington, U. Somasunderman, G. R. Willey, *Acta Crystallogr. C* **57**, 190 (2001).
- [21] E. Garcia, K-Y Lee, C. B. Storm, *Acta Crystallogr. C* **48**, 1683 (1992).
- [22] U. Ensinger, W. Schwarz, A. Schmidt, *Z. Naturforsch.* **38b**, 149 (1983).
- [23] J. Zaleski, A. Pietraszko, *J. Mol. Struct.* **327**, 287 (1994).
- [24] O. Moers, K. Wijaya, P.G. Jones, A. Blaschette, *Acta Crystallogr. C* **55**, 754 (1999).
- [25] H. Deuschl, *Ber. Bunsenges. Phys. Chem.* **69**, 550 (1965).
- [26] P. Goldstein, J. Ladell, G. Abowitz, *Acta Crystallogr. B* **25**, 135 (1969).
- [27] G. A. Jeffrey, J. R. Ruble, J. H. Yates, *Acta Crystallogr. B* **39**, 388 (1983).
- [28] K. Prassides, P. Day, A. Cheetham, *Inorg. Chem.* **24**, 545 (1985).
- [29] F. W. B. Einstein, A. C. MacGregor, *J. Chem. Soc., Dalton Trans.* 778 (1974).
- [30] F. H. Allen, O. Kennard, (3D Search and Research Using the Cambridge Structural Database), *Chemical Design Automation News* **8** (1), 1 and 31 - 37 (1993).
- [31] M. Bujak, J. Zaleski, *Acta Crystallogr. C* **55**, 1775 (1999).
- [32] B. Ragelmann, K. Klinkhammer, A. Schmidt, *Z. Anorg. Allg. Chem.* **623**, 1168 (1997).
- [33] A. Lipka, *Z. Anorg. Allg. Chem.* **469**, 218 (1980).