

Octahedral distortion caused by hydrogen bonding in tris(diethylammonium) hexachloridoantimonate(III)

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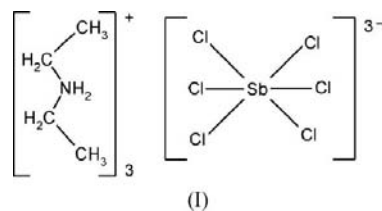
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The factors influencing the distortion of inorganic anions in the structures of chloridoantimonates(III) with organic cations, in spite of numerous structural studies on those compounds, have not been clearly described and separated. The title compound, $[(C_2H_5)_2NH_2]_3[SbCl_6]$, consisting of isolated distorted $[SbCl_6]^{3-}$ octahedra that have C_3 symmetry and $[(C_2H_5)_2NH_2]^+$ cations, unequivocally shows the role played by hydrogen bonding in the geometry variations of inorganic anions. The organic cations, which are linked to the inorganic substructure through $N-H \cdots Cl$ hydrogen bonds, are clearly responsible for the distortion of the octahedral coordination of Sb^{III} in terms of differences (Δ) in both $Sb-Cl$ bond lengths [$\Delta = 0.4667$ (6) Å] and $Cl-Sb-Cl$ angles [$\Delta = 9.651$ (17) $^\circ$].

Comment

Chloridoantimonates(III) with organic cations are considered as organic-inorganic perovskite-like hybrid materials. They consist of organic cations within anionic inorganic substructures. The interest in this group of compounds is focused on two areas: (a) the structural phase transitions, some of them to polar phases, which mainly arise from the large polarizability of the complex anions, changes in the dynamic disorder of the organic cations and consequent changes in the hydrogen-bonding scheme; (b) the complex crystal chemistry – the inorganic chloridoantimonate(III) anions may assume several structural geometries with varying degrees of distortion depending on the size, shape and hydrogen-bonding ability of the organic cations (Fischer & Norman, 1994; Sobczyk *et al.*, 1997; Mitzi, 2001; Bujak & Angel, 2005, 2006). The distortion of chloridoantimonate(III) inorganic units is associated with the presence of the lone pair of electrons on the central Sb^{III} atom (Wang & Liebau, 1996). This distortion has been correlated to a 'primary deformation' connected with the tendency of $[SbCl_6]^{3-}$ octahedra and $[SbCl_5]^{2-}$ square pyramids to share Cl atoms with each other in forming more

complicated arrangements, and a 'secondary deformation' resulting from the presence of interactions between oppositely charged organic and inorganic components of the structures (Bujak & Zaleski, 2001, 2002).



The title compound, (I), is a perfect model structure for understanding and separating the factors influencing distortion of inorganic polyhedra in chloridoantimonates(III) because the inorganic substructure consists of single isolated units (the 'primary deformation' factor is thus eliminated), the organic cations are fully ordered, the positions of the H atoms are well defined (Fig. 1) and only one crystallographically independent Cl atom is involved in relatively strong well defined hydrogen-bonding interactions (Fig. 2). Compound (I), in the rhombohedral $R3c$ space group, is isomorphous with its bismuth analogue tris(diethylammonium) hexachlorido-bismuthate(III) (Lazarini, 1987; Jarraya *et al.*, 1993). The structure of (I) consists of inorganic $[SbCl_6]^{3-}$ octahedra and organic $[(C_2H_5)_2NH_2]^+$ cations that adopt an extended relative conformation of the ethyl groups with expected dimensions (Wahlberg, 1978). The $[SbCl_6]^{3-}$ octahedra show C_3 symmetry with three short [2.4715 (4) Å] and three longer [2.9382 (4) Å] $Sb-Cl$ bonds, distributed mutually in a *trans* fashion, with a difference of 0.4667 (6) Å. The $Cl-Sb-Cl$ angles are also significantly distorted. They range from 83.450 (12) $^\circ$, the angle between the short and longer bonds, to 93.101 (12) $^\circ$, the angle between the longer $Sb-Cl$ bonds (Table 1), giving a difference of 9.651 (17) $^\circ$. Although the distortion found in (I) is relatively large and somewhat unusual, it is not the first example of such large differences in $Sb-Cl$ bond distances. A similar situation,

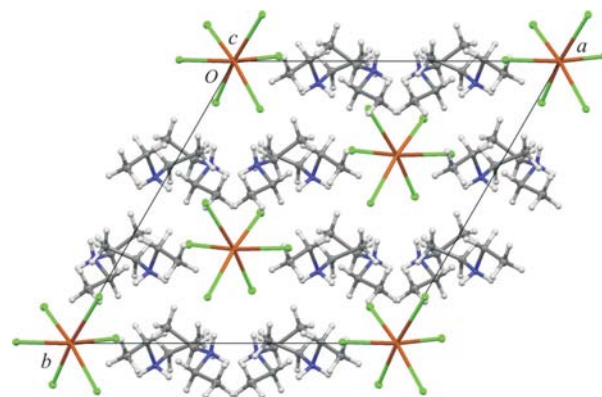
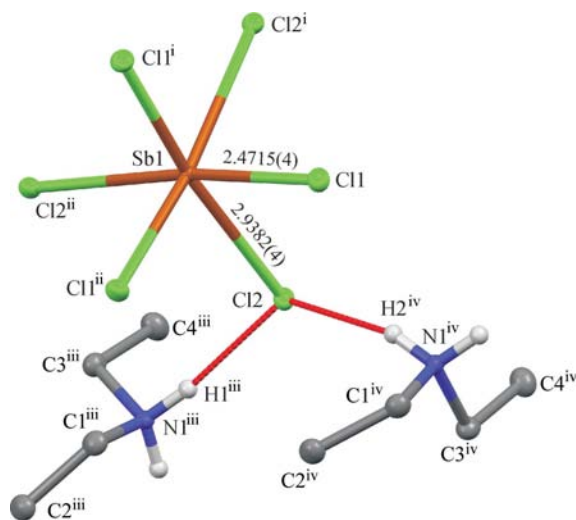


Figure 1
The packing of (I). Displacement ellipsoids are drawn at the 50% probability level.


Figure 2

The octahedral $[\text{SbCl}_6]^{3-}$ anion in (I) with $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen-bonded (red lines in the electronic version of the paper) organic cations causing its distortion. Distances are given in Å. Displacement ellipsoids are drawn at the 50% probability level. H atoms on C atoms have been omitted for clarity. [Symmetry codes: (i) $-y, x - y, z$; (ii) $-x + y, -x, z$; (iii) $x, x - y, z - \frac{1}{2}$; (iv) $-x + y + \frac{1}{3}, -x + \frac{2}{3}, z - \frac{1}{3}$]

with even larger $\text{Sb}-\text{Cl}$ deviations, was found in the structures of pentakis(benzidinediium) bis[hexachloridoantimony(III)] tetrachloride sesquihydrate (Dobrzycki & Woźniak, 2009), 2-ammonioguanidinium 2-aminoguanidinium hexachloridoantimonate(III) (Bujak *et al.*, 2001) and diethylenetriammonium hexachloridoantimonate(III) (Vezzosi *et al.*, 1984).

The observed differences in $\text{Sb}-\text{Cl}$ bond lengths and $\text{Cl}-\text{Sb}-\text{Cl}$ angles correlate well with the presence of $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds between the anionic substructure and the organic cations (Table 2 and Fig. 2). All $\text{N}-\text{H}\cdots\text{Cl}$ interactions are associated with the longer $\text{Sb1}-\text{Cl2}$ distances, causing the distortion of inorganic units from the ideal octahedral symmetry. The distortion is realized by a shift of the central Sb^{III} atoms from the centre of the octahedra, by ca 0.1 Å, along the crystallographic c axis towards the three Cl1 atoms. Taking into account the geometrical parameters of the hydrogen bonds and their influence on the geometry of the inorganic substructure, they can be considered as a relatively strong among $\text{Sb}-\text{Cl}\cdots\text{H}-\text{N}$ interactions (Bruno *et al.*, 2002; Steiner, 2002).

As expected, the distortion from ideal octahedral symmetry in (I) is more pronounced than that found in its bismuth(III) analogue, where the differences in $\text{Bi}-\text{Cl}$ bond lengths and $\text{Cl}-\text{Bi}-\text{Cl}$ angles are 0.288 (2) Å and 8.89 (6)°, respectively (Jarraya *et al.*, 1993). This behaviour can be best rationalized on the basis of the valence shell electron pair repulsion (VSEPR) model (Gillespie & Nyholm, 1957; Gillespie & Robinson, 2005), together with the electronic-distortion approach (Brown, 2002), in terms of a stereochemical activity (localization) of the lone pair of electrons along with the difference in polarizability of the central Sb^{III} and Bi^{III} atoms. Intermediate $\text{Sb}-\text{Cl}$ bond lengths of 2.652 (6) and 2.6552 (3) Å are observed in the slightly distorted isolated $[\text{SbCl}_6]^{3-}$ octahedra in which all six Cl atoms are involved in

hydrogen bonding rather than just three (Schroeder & Jacobson, 1973; Podesta & Orpen, 2005). Thus in (I), the asymmetric hydrogen-bond pattern is clearly responsible for the much longer $\text{Sb1}-\text{Cl2}$ distances and the pronounced angular distortion.

Experimental

$(\text{C}_2\text{H}_5)_2\text{NH}$ (5.2 ml, 5 mmol) was added slowly, dropwise, with stirring, to 6 M HCl (10 ml), and this mixture was used to treat SbCl_3 (2.28 g, 1 mmol) dissolved in 6 M HCl (6 ml). Slow evaporation of the acid solution at room temperature yielded transparent colourless crystals of (I).

Crystal data

$(\text{C}_4\text{H}_{12}\text{N}_3)[\text{SbCl}_6]$
 $M_r = 556.90$
 Trigonal, $R3c$
 $a = 14.71917$ (18) Å
 $c = 18.9694$ (3) Å
 $V = 3559.19$ (8) Å³

$Z = 6$
 Mo $K\alpha$ radiation
 $\mu = 1.84$ mm⁻¹
 $T = 85$ K
 $0.19 \times 0.19 \times 0.15$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer
 Absorption correction: analytical [*CrysAlis RED* (Oxford Diffraction, 2009); analytical numeric absorption correction using a multifaceted crystal model based

on expressions derived by Clark & Reid (1995)]
 $T_{\text{min}} = 0.713$, $T_{\text{max}} = 0.760$
 9101 measured reflections
 2056 independent reflections
 2018 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.008$
 $wR(F^2) = 0.030$
 $S = 1.48$
 2056 reflections
 78 parameters
 1 restraint

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.53$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.54$ e Å⁻³
 Absolute structure: Flack (1983), 973 Friedel pairs
 Flack parameter: 0.001 (16)

All H atoms were located in difference Fourier maps and then refined with $\text{C}-\text{H}$ distances constrained to 0.98 or 0.99 Å (methyl groups allowed rotational freedom) and U_{eq} values for CH_3 and CH_2 hydrogens equal to 1.5 and 1.2 times, respectively, the U_{eq} value of the carrier atoms. The NH_2^+ group H-atom parameters were refined freely. The absolute structure was determined reliably.

Table 1

Selected bond angles (°).

$\text{Cl1}-\text{Sb1}-\text{Cl1}^{\text{ii}}$	91.200 (16)	$\text{Cl1}^{\text{ii}}-\text{Sb1}-\text{Cl2}$	92.570 (13)
$\text{Cl1}-\text{Sb1}-\text{Cl2}$	83.450 (12)	$\text{Cl2}^{\text{ii}}-\text{Sb1}-\text{Cl2}$	93.101 (12)
$\text{Cl1}-\text{Sb1}-\text{Cl2}^{\text{ii}}$	173.514 (13)		

Symmetry code: (ii) $-x + y, -x, z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{Cl2}^{\text{v}}$	0.87 (2)	2.28 (2)	3.135 (2)	170 (2)
$\text{N1}-\text{H2}\cdots\text{Cl2}^{\text{vi}}$	0.85 (3)	2.39 (3)	3.186 (2)	154 (2)

Symmetry codes: (v) $x, x - y, z + \frac{1}{2}$; (vi) $-y + \frac{2}{3}, x - y + \frac{1}{3}, z + \frac{1}{3}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis Pro* (Oxford Diffraction, 2009); data reduction: *CrysAlis Pro*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM3030). Services for accessing these data are described at the back of the journal.

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