REACTION OF ANTIMONY TRICHLORIDE WITH THIAMINE CHLORIDE (TCI, VITAMIN B₁): SYNTHESIS AND CRYSTAL STRUCTURE OF THE NEW THIAMINIUM CHLOROANTIMONATE(III) (HT)₂[Sb₄Cl₁₆].2CH₃CN

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Abstract

The title compound was isolated from the mother liquor resulting from reaction of thiamine chloride monohydrate (TCI.H₂O) with antimony trichloride in acetonitrile. Its crystal structure was solved by X-ray diffraction (crystal data: triclinic, space group P(-)1 (No. 2), *a* = 10.6060(10) Å, *b* = 10.8010(10) Å, *c* = 13.2720(10) Å, α = 110.780(10)°, β = 92.62(2)°, γ = 101.65(2)°, *V* = 1380.7(2) Å³, and *Z* = 2). The compound is formed by thiaminium [(HT)²⁺] cations and [Sb₄Cl₁₆]⁴⁻ anions. The four Sb atoms of this chloroantimonate anion are linked in a chain by pairs of bridging Cl ligands. Further Cl ligands make the coordination number of the central [Sb(1)] and terminal [Sb(2)] atoms up two six and five respectively. Very weak Sb(2)-Cl...Sb(2) interactions [Cl...Sb(2) = 3.860 Å] interconnect the anions in a pseudopolymeric arrangement. Thiaminium adopts its S conformation and forms a strong hydrogen bond with a μ -Cl ligand, distorting the double bridges between Sb(1) and Sb(2).

Introduction

Antimony(III) halides are powerful halide acceptors¹. This property has allowed the preparation of halogenoantimonates(III) in which the anions are formally [SbX₄]⁻, [Sb₂X₉]³⁻, [SbX₅]²⁻ or [SbX₆]³⁻, where X is usually chloride or bromide. Although the formulae of these compounds might suggest the presence of discrete ions, in the solid state they usually adopt more complex structures due to association via μ -X bonds. Thus compounds with M[SbCl₄] stoichiometry (*M* = monocation), in spite of their formulae, are formed by oligomeric ([Sb₂Cl₈]²⁻ or [Sb₄Cl₁₆]⁴⁻) or polymeric ([SbCl₄]⁻) anions. Dinuclear anions usually contain six terminal and two bridging chlorine atoms, the two antimony atoms having approximately square pyramidal coordination spheres with the apices *trans*- or *cis* with respect to the common base plane:

These types of anion have been found in tetra-*n*-propyl- and tetra-*n*-butylammonium tetrachloroantimonate(III)², [Mo₂(μ -C₈Me₈)(μ -Cl)(η -C₅H₅)₂][SbCl₄].CH₂Cl₂³, N³-{dispiro[fluorene-9,2'-thietane-3',9'-fluorene]-4'-ylidene}-N',N'-dimethylbenzamidinium tetrachloroantimonate(III)⁴ and *tert*-butylammonium tetrachloroantimonate(III)⁵, although most of these compounds contain only the *trans* isomer. In triethylammonium tetrachloroantimonate(III)⁶, the same coordination number is achieved by trigonal bipyramidal antimony atoms linked in chains by axial μ -Cl bonds.

The coordination number can be increased, without increasing the X/ Sb ratio, by raising the nuclearity of the oligomer and the number of bridging atoms. Thus [Sb₄Cl₁₆]⁴⁻ in tetraethylammonium tetrachloroantimonate(III)² has a cubane-like structure with four antimony and four chlorine atoms occupying alternate corners of a distorted cube.

This cubane-like structure is also adopted by [Fe(η -C₅H₅)(CO)₂Cl]₄[SbCl₃]₄⁷ while in phenothiazine tetrachloroantimonate(III)⁸, one-, two- and three-coordinated Cl species coexist in a

rather different $[\text{Sb}_4\text{Cl}_{16}]^{4-}$ framework that also makes each Sb hexacoordinate.

If dimeric $[\text{Sb}_2\text{Cl}_8]^{2-}$ units associate by means of weak additional Cl bridges, the result is quasi-polymeric structure with six-coordinate antimony atoms in which the octachlorodiantimonate(III) anions retain their individual identity.

A structure of this kind is adopted by $\{\text{Fe}(\text{9}[\text{aneS}_3)_2\}[\text{Sb}_2\text{Cl}_8]^{9-}$, in which the intradimeric Sb...Cl bond lengths range from 2.382(2) Å to 2.959(3) Å while the interdimeric Sb...Cl bond length is longer (3.345 Å), though shorter than the sum of the van der Waals radii (4.00 Å¹⁰). In $[\text{Mg}(\text{MeCN})_6][\text{Sb}_2\text{Cl}_8]^{11}$, too, the interdimeric Sb...Cl bond [3.580(2) Å] is significantly longer than the intradimeric bonds. These structures can formally be included with those of pyridinium¹² and ferrocenium¹³ tetrachloroantimonates(III) structures as formed by polymeric chains of edge sharing $[\text{SbCl}_6]$ octahedra. The polymeric structures of diphenylammonium¹⁴ and anilinium¹⁵ derivatives are based on more complex arrangements of such octahedra.

Formal addition of a chloride ion to $[\text{Sb}_2\text{Cl}_8]^{2-}$ gives $[\text{Sb}_2\text{Cl}_9]^{3-}$, probably the best known antimony chloride anion. Again, this formula indicates only the simplest stoichiometry: according to a recent review¹⁶, $\text{M}_3[\text{Sb}_2\text{Cl}_9]$ compounds are very often formed by polymeric arrangements of $[\text{SbCl}_6]$ octahedra in the solid state, even though structures containing the discrete dinuclear nonachlorodiantimonate(III) anion are also known.

Few chloroantimonates(III) with a Cl/Sb ratio greater than 4.5 have been studied by X-ray diffraction. One is $\text{M}[\text{SbCl}_5]$ (M = dimethylsulfoxidum)¹⁷, in which $[\text{SbCl}_6]$ octahedra are connected by adjacent vertices in infinite $\text{SbCl}_4\text{...Cl...SbCl}_4$ chains. A similar structure is observed in tris(methylammonium)hexachloroantimonate(III), in spite of its stoichiometry (one of the six chloride ions is occluded in the lattice)¹⁸. These structures differ from that of $(\text{NH}_4)_2[\text{SbCl}_5]^{19}$, which is often included in textbooks as an example of an antimony(III) compound containing a square pyramidal anion with a stereochemically active lone pair of electrons. A dinuclear anion $[\text{Sb}_2\text{Cl}_{10}]^{4-}$, formed by two edge-sharing $[\text{SbCl}_6]$ octahedra, was recently prepared by reacting antimony trichloride with thiamine chloride hydrochloride²⁰.

It is clear from the above that considerable uncertainty remains concerning the factors determining the adoption of a specific structure by a chloroantimonate(III) of given stoichiometry. In the case of $[\text{Sb}_2\text{Cl}_9]^{3-}$, the following have been suggested²¹: the size of the cation, the possibility of specific interaction with the anion, and the residual charges carried by the halogen atoms. The relevance of the solvent in which the compounds are prepared cannot be overlooked because the species in solution are clearly influenced by this variable².

As a contribution to understanding of the dominant structural factors implied in $[\text{SbCl}_{3+n}]^{n-}$ solid state chemistry, in this paper we report a new tetrachloroantimonate(III) of thiaminium, $(\text{HT})_2[\text{Sb}_4\text{Cl}_{16}]$, that we have isolated in the course of our research on the chemical interactions of vitamin B₁ (thiamine). This new compound contains the same bulky dication as $(\text{HT})_2[\text{Sb}_2\text{Cl}_{10}]^{20}$.

Experimental

Materials and Methods. Thiamine chloride hydrochloride (TCl.HCl, Merck) and antimony trichloride (Merck) were used as supplied. Thiamine chloride monohydrate (TCl.H₂O) was prepared from TCl.HCl using the method of Pletcher et al²². Elemental analyses (C, H, N and S) were performed with a Carlo Erba 1108 microanalyser. Melting points were determined with an electrically heated Gallenkamp apparatus.

$(\text{HT})_2[\text{Sb}_4\text{Cl}_{16}] \cdot 2\text{CH}_3\text{CN}$. Solid TCl.H₂O (0.474 g, 1.5 mmol) was suspended in a stirred solution of SbCl₃ (0.360 g, 1.6 mmol) in acetonitrile (30 ml), and stirring was continued for 24 h. The white suspended solid was filtered out, and the filtrate was concentrated and left in a refrigerator for a few days, affording white crystals that were filtered out and dried *in vacuo*. M.p. 134 °C (Found: C, 20.48; H, 2.32; N, 8.20; S, 3.87%. $\text{C}_{14}\text{Cl}_8\text{H}_{21}\text{N}_5\text{OSSb}_2$ requires C, 20.13; H, 2.51; N, 8.38; S,

3.83%).

HT ²⁺**Table 1.** Crystal data and structure refinement

Empirical formula	C ₁₄ H ₂₁ Cl ₈ N ₅ O S Sb ₂	
Formula weight	834.52	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P(-)1 (No. 2)	
Unit cell dimensions	<i>a</i> = 10.6060(10) Å	α = 110.780(10)°
	<i>b</i> = 10.8010(10) Å	β = 92.62(2)°
	<i>c</i> = 13.2720(10) Å	γ = 101.65(2)°
Volume	1380.7(2) Å ³	
Z	2	
Density (calculated)	2.007 Mg/m ³	
Absorption coefficient	2.825 mm ⁻¹	
F(000)	804	
Crystal size	0.21 x 0.25 x 0.31 mm ³	
Theta range for data collection	1.65 to 25.00°	
Index ranges	-12 ≤ <i>h</i> ≤ 12, -12 ≤ <i>k</i> ≤ 12, -15 ≤ <i>l</i> ≤ 0	
Reflections collected	5102	
Independent reflections	4871 [R(int) = 0.0435]	
Completeness to theta = 25.00°	100.0 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4871 / 0 / 283	
Goodness-of-fit on F ²	1.096	
Final R indices [I > 2σ(I)]	R1 = 0.0489, wR2 = 0.0754	
R indices (all data)	R1 = 0.1324, wR2 = 0.1061	
Extinction coefficient	0.00220(19)	
Largest diff. peak and hole	0.716 and -0.755 e.Å ⁻³	

Crystallography. Table 1 lists crystal and structure refinement data for the new compound. The intensities of reflections were measured in $\omega/2\theta$ scan mode on an Enraf-Nonius CAD4 diffractometer using Mo-K α radiation, and were corrected for Lorentz polarisation factors. Absorption corrections were applied at a later stage in the refinement⁴⁰ (max., min. correction factors = 1.52, 0.69).

The structure of the compound was solved by the standard heavy atom Patterson method followed by normal difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. All

hydrogen atoms except O(5 γ)-H were included as fixed contributors at positions found in the difference synthesis, all with a common isotropic temperature factor that refined to $U = 0.092 \text{ \AA}^2$ or, in the acetonitrile methyl group, $0.119 \text{ \AA}^2$. The R values are defined by $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$. Scattering factors were taken from International Tables for Crystallography²². Graphics were done using ORTEP²⁶ and SCHAKAL²⁷.

Results and discussion

Reaction of TCl·H₂O with SbCl₃ in acetonitrile gave, very surprisingly, a chloroantimonate(III) of thiaminium even though the starting thiamine was not protonated at N(1') (for thiaminium numbering, see the formula in the Introduction). A plausible explanation for this is that antimony trichloride is partially hydrolyzed by the hydration water of TCl·H₂O or by water contained in the hygroscopic starting halide:

Be that as it may, the crystalline solid isolated is composed of associated $[\text{Sb}_2\text{Cl}_8]^{2-}$ anions, thiaminium (HT)⁺ cations, and acetonitrile molecules occluded in the lattice (Fig. 1). The most relevant bond distances and bond angles are listed in Table 2.

Fig 1. ORTEP drawing of the asymmetric unit, showing the numbering scheme.

The chloroantimonate(III) anion can be considered, in the first instance, as formed by *trans* octachlorodiantimonate units in which each antimony atom is coordinated to five chlorine atoms in a square-pyramidal configuration. Similar structural units have been found previously²⁻⁵. In this case, however, the dimer is rather asymmetric, probably because a hydrogen bond pulls Cl(5) towards N(1') and away from the Sb atoms. Thus Cl(5) lies 2.907 Å from Sb(1) and 3.025 Å from Sb(2) whereas Cl(4) lies 2.667 Å from Sb(2) and 2.994 Å from Sb(1). The Sb-Cl(5)-Sb bridge is nevertheless the more symmetric of the two, the difference in length between its two sides being only about 0.1 Å as against 0.3 Å for Sb-Cl(4)-Sb.

Table 2. Bond lengths [Å] and angles [°] in (HT)₂[Sb₄Cl₁₆].2CH₃CN

Sb(1)-Cl(6)	2.376(3)	C(4)-N(3)	1.387(12)
Sb(1)-Cl(7)	2.413(3)	C(4)-C(4α)	1.477(13)
Sb(1)-Cl(8)	2.457(3)	N(4'α)-C(4')	1.300(11)
Sb(1)-Cl(5)	2.907(3)	N(1')-C(2')	1.333(11)
Sb(1)-Cl(4)	2.994(3)	N(1')-C(6')	1.342(11)
Sb(1)-Cl(8) ⁱ	3.360(3)	N(3)-C(2)	1.324(12)
Sb(2)-Cl(3)	2.365(3)	N(3)-C(3,5')	1.465(11)
Sb(2)-Cl(2)	2.402(3)	C(5')-C(6')	1.333(12)
Sb(2)-Cl(1)	2.556(3)	C(5')-C(4')	1.415(12)
Sb(2)-Cl(4)	2.667(3)	C(5')-C(3,5')	1.526(12)
Sb(2)-Cl(5)	3.025(3)	C(2')-C(2'α)	1.500(12)
Sb(2)-Cl(1) ⁱⁱ	3.859(4)	C(5)-C(5α)	1.485(14)
S(1)-C(2)	1.664(9)	C(5β)-O(5γ)	1.350(15)
S(1)-C(5)	1.710(10)	C(5β)-C(5α)	1.492(16)
N(3')-C(2')	1.317(11)	N'-C'	1.127(12)
N(3')-C(4')	1.371(10)	C'-C''	1.437(14)
C(4)-C(5)	1.341(12)		
Cl(6)-Sb(1)-Cl(7)	88.87(11)	C(2')-N(3')-C(4')	118.0(8)
Cl(6)-Sb(1)-Cl(8)	90.18(12)	C(5)-C(4)-N(3)	110.7(9)
Cl(7)-Sb(1)-Cl(8)	93.71(11)	C(5)-C(4)-C(4α)	128.9(9)
Cl(6)-Sb(1)-Cl(5)	86.45(11)	N(3)-C(4)-C(4α)	120.4(8)
Cl(7)-Sb(1)-Cl(5)	90.08(10)	C(2')-N(1')-C(6')	119.8(8)
Cl(8)-Sb(1)-Cl(5)	174.88(11)	C(2)-N(3)-C(4)	114.9(8)
Cl(6)-Sb(1)-Cl(4)	83.50(10)	C(2)-N(3)-C(3,5')	120.4(9)
Cl(7)-Sb(1)-Cl(4)	169.49(11)	C(4)-N(3)-C(3,5')	124.6(9)
Cl(8)-Sb(1)-Cl(4)	93.53(10)	C(6')-C(5')-C(4')	118.5(8)
Cl(5)-Sb(1)-Cl(4)	82.26(10)	C(6')-C(5')-C(3,5')	124.3(8)
Cl(6)-Sb(1)-Cl(8) ⁱ	163.45(10)	C(4')-C(5')-C(3,5')	117.2(8)
Cl(7)-Sb(1)-Cl(8) ⁱ	82.81(10)	N(3')-C(2')-N(1')	123.4(8)
Cl(8)-Sb(1)-Cl(8) ⁱ	76.18(10)	N(3')-C(2')-C(2'α)	118.6(8)
Cl(5)-Sb(1)-Cl(8) ⁱ	107.76(9)	N(1')-C(2')-C(2'α)	117.9(8)
Cl(4)-Sb(1)-Cl(8) ⁱ	106.34(9)	N(4'α)-C(4')-N(3')	115.2(8)
Cl(3)-Sb(2)-Cl(2)	91.12(12)	N(4'α)-C(4')-C(5')	125.3(8)
Cl(3)-Sb(2)-Cl(1)	88.52(11)	N(3')-C(4')-C(5')	119.4(8)
Cl(2)-Sb(2)-Cl(1)	88.45(12)	C(5')-C(6')-N(1')	120.8(8)
Cl(3)-Sb(2)-Cl(4)	87.96(12)	N(3)-C(3,5')-C(5')	111.3(7)
Cl(2)-Sb(2)-Cl(4)	89.65(12)	N(3)-C(2)-S(1)	111.3(8)
Cl(1)-Sb(2)-Cl(4)	175.97(11)	C(4)-C(5)-C(5α)	126.2(10)
Cl(3)-Sb(2)-Cl(5)	78.90(10)	C(4)-C(5)-S(1)	111.5(7)
Cl(2)-Sb(2)-Cl(5)	169.13(12)	C(5α)-C(5)-S(1)	122.3(8)
Cl(1)-Sb(2)-Cl(5)	95.51(11)	O(5γ)-C(5β)-C(5α)	112.3(10)
Cl(4)-Sb(2)-Cl(5)	85.75(10)	C(5)-C(5α)-C(5β)	114.8(10)
Cl(3)-Sb(2)-Cl(1) ⁱⁱ	155.00(9)	C(2)-S(1)-C(5)	91.6(5)
Cl(2)-Sb(2)-Cl(1) ⁱⁱ	65.80(10)	N'-C'-C''	179.1(13)
Cl(1)-Sb(2)-Cl(1) ⁱⁱ	99.79(9)		
Cl(4)-Sb(2)-Cl(1) ⁱⁱ	82.65(10)		
Cl(5)-Sb(2)-Cl(1) ⁱⁱ	123.14(8)		
Sb(2)-Cl(4)-Sb(1)	97.11(10)		
Sb(1)-Cl(5)-Sb(2)	91.47(9)		

Symmetry transformations: i = -x+2, -y+2, -z+2; ii = -x+1, -y+1, -z+1.

These differences are reflected in the bonds of the non-bridging chloride ions, specially those placed *trans* to the bridge: the lengths of the terminal Sb-Cl bonds increase in reverse order to the lengths of the *trans*-related bridging bonds (as predicted by the three-centre four-electron approach)²¹; and the shortest Sb-Cl bonds are those involving the apical chlorides, Cl(3) and Cl(6), which have vacant (or almost vacant) *trans* positions. In fact Sb(1)-Cl(6) is slightly longer than Sb(2)-Cl(3) because the weak interaction between Sb(1) and a neighbouring [Sb₂Cl₆]²⁻ unit (*vide infra*) places Cl(8)ⁱ far away but *trans* to Cl(6).

The $[\text{SbCl}_6]$ pyramid also has distorted bond angles. Although the Cl-Sb-Cl angles in the basal plane are reasonably close to 90° (the narrowest, as expected, are those associated with the bridging chlorides), the $\text{Cl}_a\text{-Sb-Cl}_b$ angles (a = apical, b = basal) are in general rather narrower than 90° [the exceptions are $\text{Cl}(3)\text{-Sb}(2)\text{-Cl}(2)$ (91.1°) and $\text{Cl}(6)\text{-Sb}(1)\text{-Cl}(8)$ (90.2°)]. This displacement of most of the basal atoms towards the apex is the expected effect of an active lone pair in the vacant sixth position of an octahedral coordination sphere. However, the facts that this distortion does not affect all the basal chlorides and is rather small, are compatible with its being induced by weak bonding forces; the presence of additional Cl⁻ ligands close to the sixth coordination position (albeit at distances greater than 3 Å from the Sb atoms; *vide infra*) makes the existence of an active lone pair questionable on stereochemical grounds.

Fig.2. SCHAKAL drawing of $(\text{HT})_2[\text{Sb}_4\text{Cl}_{16}]$, showing the hydrogen bond between N(1') and Cl(5) and the coordination of Sb(1) and Sb(2). Strong Sb-Cl bonds are represented by bold lines, weak Sb-Cl bonds by thin lines and hydrogen bonds by dashed lines.

The $[\text{Sb}_2\text{Cl}_8]$ units are associated in pairs by weak $\text{Sb}(1)\cdots\text{Cl}(8)'$ interactions that give Sb(1) a formal coordination number of six and a pseudo-octahedral coordination sphere (see Table 2 and Fig. 2). The $\text{Sb}(1)\cdots\text{Cl}(8)'$ distance (3.360 Å) is well within the range of antimony-chloride bond distances in compounds containing oligomeric or polymeric $[\text{SbCl}_4]$ units (2.34-3.58 Å)^{2,9,11-15}, and is significantly less than the sum of the van der Waals radii (4.0 Å¹⁰). The lattice may therefore strictly be considered as containing $[\text{Sb}_4\text{Cl}_{16}]^{4-}$ ions. These anions make weak contact with each other *via* Sb(2) and Cl(1). $[\text{Sb}(2)\cdots\text{Cl}(1)]^{\text{ii}} = 3.860$ Å; see Table 2]. If these contacts too are considered as bonds, the coordination numbers of both Sb(1) and Sb(2) are six and the anion can be described as a polymeric arrangement of edge-sharing $[\text{SbCl}_6]$ octahedra. However this description makes $(\text{HT})_2[\text{Sb}_4\text{Cl}_{16}]\cdot 2\text{CH}_3\text{CN}$ appear more similar to the polymeric chloroantimonates(III) discussed in the Introduction than is perhaps warranted, given the proximity of the $[\text{Sb}(2)\cdots\text{Cl}(1)]^{\text{ii}}$ distance to the sum of the van der Waals radii¹⁰.

The structural distortion of the $[\text{Sb}_4\text{Cl}_{16}]^{4-}$ anions, probably originates mainly in the differences between the Cl(4) and Cl(5) bridges, which derive from the fact that Cl(5), but not Cl(4), forms a strong hydrogen bond with the protonated N(1') atom of the thiaminium cation (see Fig. 2 and Table 3). This bond weakens the Sb-Cl(5) bond and so makes the Cl(5) bridge longer than the Cl(4) bridge. As was noted above, these differences in turn affect the Sb-Cl bonds *trans* to the bridging bonds. By contrast, in $(\text{HT})_2[\text{Sb}_2\text{Cl}_{10}]^{20}$, in which the $[\text{Sb}_2\text{Cl}_{10}]^{4-}$ anions are centrosymmetric, both bridging chlorides are involved in N(1')-H $\cdots$ Cl bonds. Non-ionic cation-anion

interactions, particularly hydrogen bonding, have previously been pointed to as factors that may influence the type of structure adopted by the $[\text{Sb}_2\text{Cl}_9]^{3-}$ anion²¹; the above results suggest that they may also be important for other chloroantimonate anions. Another factor, the importance of which is illustrated by the two known compounds of thiaminium $(\text{HT})_2[\text{Sb}_2\text{Cl}_{10}]^{20}$ and $(\text{HT})_2[\text{Sb}_4\text{Cl}_{16}]\cdot 2\text{CH}_3\text{CN}$, is the (chloride anion)/(antimony trichloride) mole ratio used in the reactions by which they are synthesized (2:1 for $(\text{HT})_2[\text{Sb}_2\text{Cl}_{10}]^{20}$, for which the source of thiamine was $\text{TCI}\cdot\text{HCl}$; 1:1 in our reaction, in which $\text{TCI}\cdot\text{H}_2\text{O}$ was used).

The chief structural parameters of $(\text{HT})^{2+}$ in $(\text{HT})_2[\text{Sb}_4\text{Cl}_{16}]\cdot 2\text{CH}_3\text{CN}$ are listed in Table 3 together with those reported for $(\text{HT})_2[\text{Sb}_2\text{Cl}_{10}]^{20}$, thiamine chloride monohydrate²² and thiamine chloride hydrochloride monohydrate²⁸. As usual, the pyrimidine and thiazolium rings are planar ($\chi^2 = 8.6$ and 5.7 , respectively), and, as in $(\text{HT})_2[\text{Sb}_2\text{Cl}_{10}]^{20}$, the thiaminium ion adopts the less usual S conformation²⁹, with $\phi_T [= \text{C}(5')\text{-C}(3,5')\text{-N}(3)\text{-C}(2)] = 103.8^\circ$ and $\phi_P [= \text{N}(3)\text{-C}(3,5')\text{-C}(5')\text{-C}(4')] = 167.4^\circ$ whereas in $\text{TCI}\cdot\text{HCl}$ it adopts the F conformation²⁸. The torsion angles $\phi_{5\alpha} [= \text{S}(1)\text{-C}(5)\text{-C}(5\alpha)\text{-C}(5\beta)]$ and $\phi_{5\beta} [= \text{C}(5)\text{-C}(5\alpha)\text{-C}(5\beta)\text{-O}(\gamma)]$ can be used to describe the conformation of the hydroxyethyl side chain³⁰; the values in Table 3 suggest³⁰ that the chain folds back towards the thiazolium ring to facilitate electrostatic interaction between $\text{O}(5\gamma)$ and the electron-deficient S atom, the strength of which is suggested by the distance between these two atoms (2.826 Å).

Table 3. Main Structural Parameters^{a,b} of Thiaminium/Thiamine Cations

	$(\text{HT})_2[\text{Sb}_4\text{Cl}_{16}]\cdot 2\text{CH}_3\text{CN}$	$(\text{HT})_2[\text{Sb}_2\text{Cl}_{10}]$	$\text{TCI}\cdot\text{H}_2\text{O}$	$\text{TCI}\cdot\text{HCl}\cdot\text{H}_2\text{O}$
ϕ_T	103.8	104.2	-2.6	-9.0
ϕ_P	167.4	166.8	-76.8	-76.1
$\phi_{5\alpha}$	-29.2	-	64.6	103.4
$\phi_{5\beta}$	-60.1	-	64.6	-68.2
$\text{C}(2')\text{-N}(1')\text{-C}(6')$	119.8	121.7	115.3	121.6
$\text{C}(4')\text{-N}(4'\alpha)$	1.300	1.332	1.334	1.316
$\text{C}(5\beta)\text{-O}(5\gamma)$	1.350	1.414	1.416	1.417
$\text{C}(5\alpha)\text{-C}(5\beta)\text{-O}(5\gamma)$	112.3	106.6	111.7	113.0
Ref	C	20	22	28

^a For identification of parameters, see text and Fig. 1; ^b Angles in degrees and bond lengths in Å; ^c This work

The $\text{C}(2')\text{-N}(1')\text{-C}(6')$ angle is sensitive to protonation of $\text{N}(1')$ because the proton causes contraction of the electron cloud of the nitrogen lone pair, which makes the angle wider than when $\text{N}(1')$ is unprotonated. This effect is clearly observable in the fact that this angle is wider in all the thiaminium salts than in $\text{TCI}\cdot\text{H}_2\text{O}$ (Table 3).

The $\text{C}(4')\text{-N}(4'\alpha)$ bond is even shorter in $(\text{HT})_2[\text{Sb}_4\text{Cl}_{16}]\cdot 2\text{CH}_3\text{CN}$ than in $\text{TCI}\cdot\text{HCl}\cdot\text{H}_2\text{O}$ suggesting an increase in the bond order. The same is true of $\text{C}(5\beta)\text{-O}(5\gamma)$, which is very short. This shortening may be related to the close proximity of the hydroxyl groups of neighbouring molecules [$\text{O}(5\gamma)\cdots\text{O}(5\gamma)^v = 2.80(2)$ Å, see Table 4]. Nevertheless, the $\text{C}(5\alpha)\text{-C}(5\beta)\text{-O}(5\gamma)$ angle is similar to that of thiamine chloride hydrochloride (see Table 3).

Hydrogen bonds including those connecting $\text{N}(4'\alpha)\text{H}_2$ with $\text{N}(3')$ and the acetonitrile molecule and miscellaneous close contacts are listed in Table 4.

Table 4. Hydrogen bonds and miscellaneous close contacts in $(\text{HT})_2[\text{Sb}_4\text{Cl}_{16}]\cdot 2\text{CH}_3\text{CN}$ [Å, °]

Hydrogen Bonds				
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
$\text{N}(1')\text{-HN}(1')\cdots\text{Cl}(5)$	1.100(7)	2.054(3)	3.136(8)	166.9(4)
$\text{N}(4'\alpha)\text{-HN}(4'\alpha)\cdots\text{N}'(\text{MeCN})^{\text{iii}}$	0.854(7)	2.126(9)	3.005(12)	169.2(6)
$\text{N}(4'\alpha)\text{-HN}(4'\alpha)\cdots\text{N}(3')^{\text{iv}}$	1.003(8)	2.154(7)	2.973(10)	137.6(5)

Symmetry transformations used to generate equivalent atoms: iii = $-x+1, -y+1, -z+2$; iv = $-x, -y+1, -z+2$

Close Contacts	
$\text{S}\cdots\text{O}(5\gamma)$	2.826(9)
$\text{O}(5\gamma)\cdots\text{O}(5\gamma)^v$	2.80(2)

$v = -x+2, -y+2, -z+3$

Supplementary material: Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (12 Union Road, Cambridge, CB2 1EZ, UK) with the deposition number. CCDC-124680.

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