Solvothermal Synthesis of $[C_6H_{17}N_3]Sb_{10}S_{16}$: A New Thioantimonate(III) with an *in-situ* Formed Organic Amine Cation

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Dedicated to Prof. Dr. H. Schmidbaur on the occasion of his 70th birthday

The new thioantimonate(III) $[C_6H_{17}N_3][Sb_{10}S_{16}]$ ($C_6H_{17}N_3$ = 2-piperazine-N-ethylamine cation) was obtained under solvothermal conditions showing a unique anionic framework. The compound crystallizes in the monoclinic space group $P2_1/c$ with four formula units in the unit cell. The lattice parameters are $a = 11.530(2)$, $b = 25.042(5)$, $c = 13.709(3)$ Å, $\beta = 111.25(3)^\circ$, $V = 3689(2)$ Å^3. The thioantimonate(III) anion is formed by interconnection of nine trigonal pyramidal SbS_3 units and one SbS_4 moiety. These primary building units share common corners and edges yielding Sb_3S_3 and Sb_2S_2 hetero-rings. Further condensation leads to strong undulated two atoms thick layers extending in the [010] direction, with a modulation period of about 14 Å. Very large $Sb_{31}S_{31}$ rings within the layers show a 'double-ellipsoidal' shape with approximate dimensions of $8.9 \cdot 9.3$ Å. The cations are located at the inflexion points of the layers and act as pillars between successive layers. The layers are stacked onto each other in a way that channels parallel to [001] are formed accommodating the organic cations. A remarkable observation is that the 2-piperazine-N-ethylamine cation is formed by cyclization of tren molecules (tren = tris(2-aminoethyl)amine) under *in-situ* conditions.

Key words: Thioantimonate(III), Solvothermal Synthesis, Crystal Structure

Introduction

The structures of thioantimonate(III) compounds show some highly interesting and unique features. The most dense antimony sulfide Sb_2S_3 has a Sb : S ratio of 1 : 1.5 and the negatively charged thioantimonates(III) must have a ratio larger than 1 : 1.5. Examples are compounds with a ratio of 1 : 1.6 ($[Sb_5S_8]^-$ [1], $[Sb_{10}S_{16}]^{2-}$ [2], 1 : 1.67 ($[Sb_3S_5]^-$ [3 – 7], $[Sb_6S_{10}]^{2-}$ [8, 9], $[Sb_{12}S_{20}]^{4-}$ [10]), 1 : 1.75 ($[Sb_4S_7]^{2-}$ [11 – 21], $[Sb_{12}S_{21}]^{6-}$ [22]), 1 : 1.8 ($[Sb_5S_9]^{3-}$ [23], $[Sb_{10}S_{18}]^{6-}$ [24]), or 1:2 ($[SbS_2]^-$ [25, 26], $[Sb_2S_4]^{2-}$ [27], $[Sb_3S_6]^{3-}$ [28], $[Sb_4S_8]^{2-}$ [29], $[Sb_4S_8]^{4-}$ [30]). One remarkable feature of these compounds is that for a given Sb : S ratio different thioantimonate(III) anions are observed which then exhibit different connectivities of the primary SbS_3 and SbS_4 building units and show different dimensionalities of the anions. For the overwhelming number of thioantimonates(III) the dimensionality is mainly determined by the size of the counter cation, *i.e.* the cation exerts a structure directing effect. The most impressive example for the 'template' effect of the cations is the series of compounds containing the $[Sb_4S_7]^{2-}$ anion [11 – 21]. A three-dimensional interconnected $[Sb_4S_7]^{2-}$ anion [11] is observed in $K_2Sb_4S_7$, and with increasing size of the cation the dimensionality is reduced to two-dimensional layers [13, 15 – 18] and finally to one-dimensional chains [12, 14, 19]. Until now, several compounds with a Sb : S ratio of 1 : 1.67 were reported including the $[Sb_3S_5]^-$ [3 – 7], the $[Sb_6S_{10}]^{2-}$ [8, 9], and the $[Sb_{12}S_{20}]^{4-}$ anions [10]. One-dimensional chains are observed in $[C_6H_{15}N_2][Sb_3S_5]$ [7], $[[N(C_3H_7)_4][Sb_3S_5]$ [5], $[Ph_4P]_2[Sb_6S_{10}]$ [8] and in $[(MA)_{1.03}K_{2.97}][Sb_{12}S_{20}] \cdot 1.34\ H_2O$ [10]. Two-dimensional layered anions are found in $RbSb_3S_5 \cdot H_2O$ [4] and in $[M(C_4H_{13}N_3)_2]$-$[Sb_6S_{10}] \cdot 0.5\ H_2O$ (M = Fe, Ni) [9]. Finally, a complex three-dimensional network is formed in $TlSb_3S_5$ [6]. The description of the structures presented above base on a cut-off for the Sb-S distances of about 3 Å. But

Table 1. Technical details of data acquisition and selected refinement results for $[C_6H_{17}N_3]Sb_{10}S_{16}$.

Formula	$[C_6H_{17}N_3]Sb_{10}S_{16}$
MW [g/mol]	1861.69
Space group	$P2_1/c$
a [Å]	11.530(2)
b [Å]	25.042(5)
c [Å]	13.709(3)
β [°]	111.25(3)
Volume [Å^3]	3689.1(2)
Z	4
Temperature [K]	293
μ [mm^{-1}]	8.12
$F(000)$	3360
$d_{calcd.}$ [g·cm^{-3}]	3.352
2θ Range [°]	3 – 54
hkl Range	0/14; −32/13; −17/16
Refl. collected	13442
Reflections unique	8071
Data ($Fo > 4\sigma(Fo)$)	7082
$R_{int.}$	0.0305
$\delta\rho$ [e/Å^3]	−1.43/2.35
Parameters	334
$R1[F_o > 4\sigma(F_o)]$[a]	0.0310
wR2 for all data	0.0814
Goodness of fit	1.102

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

the assignment of the dimensionality is arbitrary in thioantimonates(III) because Sb-S distances scatter in the large range between 2.2 and 4 Å. Therefore, the description of the structures of thioantimonates(III) and the final assignment of the dimensionality is not straight forward.

Very recently we reported the solvothermal syntheses and structures of two new thioantimonates(III) with the compositions $[C_6H_{17}N_3{}^{2+}][Sb_6S_{10}]$ and $[C_7H_{13}N_2{}^{+}]_3[Sb_9S_{15}]$ ($C_6H_{17}N_3{}^{2+}$: 1-(2-aminoethyl)-piperazinium dication; $C_7H_{13}N_2{}^{+}$: 1,5-diazabicyclo[4.3.0.]non-5-en) [31]. Interestingly, in both syntheses a Sb : S ratio of 1 : 3 was used (on a mmol scale) and using tren (tris(-aminoethyl)amin) as the organic solvent and applying a Sb : S ratio of 1 : 3 another compound with a $[Sb_6S_{10}]^{2-}$ anion could be isolated. Here we report the synthesis and crystal structure of the thioantimonate(III) $[C_6H_{17}N_3][Sb_{10}S_{16}]$ exhibiting a new anionic framework.

Experimental Section

Synthesis

The solvothermal synthesis was performed using Sb, $FeCl_3$, and S (Merck, 1 : 1 : 3 mmol) as starting agents, which were mixed with 4 ml of 50% aqueous tren (Fluka) solution in a teflon lined steel autoclave with an inner volume of 30 ml. The autoclave was heated for 7 days at 200 °C yielding red single crystals of $[C_6H_{17}N_3]Sb_{10}S_{16}$ as the minor product. All attempts to synthesize the compound in higher yields and as a phase pure material were not successful. In the powder pattern of the product only elemental Sb could be identified as additional crystalline phase. The background of the pattern is modulated indicative for the presence of an amorphous material. It must be noted that syntheses without $FeCl_3$ leads to the formation of a hitherto not identified product without crystals of the title compound.

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [Å$^2 \cdot 10^3$] for $[C_6H_{17}N_3]Sb_{10}S_{16}$.

Atom	x	y	z	U_{eq}
Sb(1)	8311(1)	10366(1)	4808(1)	20 (1)
Sb(2)	8002(1)	8853(1)	4272(1)	28(1)
Sb(3)	9844(1)	9125(1)	7204(1)	24(1)
Sb(4)	13144(1)	9692(1)	8107(1)	22(1)
Sb(5)	16434(1)	10123(1)	9230(1)	22(1)
Sb(6)	15408(1)	10161(1)	6421(1)	25(1)
Sb(7)	18722(1)	10637(1)	7423(1)	24(1)
Sb(8)	20349(1)	10795(1)	10316(1)	21(1)
Sb(9)	21942(1)	11238(1)	8458(1)	24(1)
Sb(10)	21241(1)	12687(1)	8721(1)	29(1)
S(1)	6428(1)	10717(1)	3353(1)	24(1)
S(2)	9043(1)	9904(1)	3595(1)	22(1)
S(3)	7291(2)	9525(1)	5227(1)	27(1)
S(4)	10079(1)	8708(1)	5631(1)	24(1)
S(5)	11969(2)	8883(1)	8343(1)	27(1)
S(6)	15207(1)	9324(1)	9402(1)	26(1)
S(7)	17085(1)	9692(1)	7877(1)	24(1)
S(8)	14723(1)	10609(1)	7709(1)	25(1)
S(9)	16677(2)	10944(1)	6189(1)	32(1)
S(10)	18325(1)	11014(1)	8934(1)	25(1)
S(11)	19859(2)	11428(1)	7137(1)	30(1)
S(12)	21539(2)	11566(1)	9979(1)	27(1)
S(13)	21048(1)	10212(1)	9255(1)	23(1)
S(14)	22665(2)	12141(1)	8188(2)	35(1)
S(15)	22991(2)	13126(1)	10059(2)	76(1)
S(16)	20982(2)	13294(1)	7257(2)	47(1)
N(1)	6143(8)	12338(4)	3136(8)	75(3)
N(2)	7629(10)	12917(4)	4924(7)	74(3)
N(3)	4038(9)	11614(4)	2330(10)	105(5)
C(1)	5893(9)	12895(4)	3261(8)	54(2)
C(2)	6245(10)	13030(5)	4388(8)	71(3)
C(3)	7945(14)	12363(5)	4799(14)	133(8)
C(4)	7478(11)	12243(5)	3602(12)	113(6)
C(5)	5678(11)	12171(6)	2054(11)	101(5)
C(6)	4276(10)	12038(5)	1715(10)	86(4)

U_{eq} is calculated as one third of the trace of the orthogonalised U_{ij} tensor.

Single crystal X-ray diffractometry

Intensity data were collected on a AED2 four circle diffractometer at room temperature using graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.7107 Å). The intensities were corrected for Lorentz, polarization ef-

Table 3. Selected interatomic distances [Å] and angles [°] for $[C_6H_{17}N_3]Sb_{10}S_{16}$.

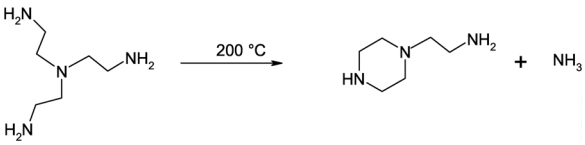
Sb(1)-S(2)	2.416(2)	Sb(1)-S(1)	2.516(2)
Sb(1)-S(3)	2.575(2)	Sb(2)-S(3)	2.450(2)
Sb(2)-S(4)	2.470(2)	Sb(2)-S(15a)	2.494(2)
Sb(3)-S(5)	2.456(2)	Sb(3)-S(4)	2.497(2)
Sb(3)-S(16a)	2.509(2)	Sb(4)-S(1b)	2.453(2)
Sb(4)-S(5)	2.523(2)	Sb(4)-S(6)	2.569(2)
Sb(4)-S(2b)	2.926(2)	Sb(5)-S(7)	2.485(2)
Sb(5)-S(6)	2.510(2)	Sb(5)-S(8)	2.595(2)
Sb(6)-S(8)	2.452(2)	Sb(6)-S(7)	2.511(2)
Sb(6)-S(9)	2.533(2)	Sb(7)-S(10)	2.465(2)
Sb(7)-S(9)	2.475(2)	Sb(7)-S(11)	2.484(2)
Sb(8)-S(13)	2.396(2)	Sb(8)-S(10)	2.477(2)
Sb(8)-S(12)	2.506(2)	Sb(9)-S(12)	2.438(2)
Sb(9)-S(11)	2.474(2)	Sb(9)-S(14)	2.485(2)
Sb(10)-S(15)	2.442(3)	Sb(10)-S(14)	2.445(2)
Sb(10)-S(16)	2.448(2)		
S(1)-Sb(1)-S(3)	97.45(5)	S(2)-Sb(1)-S(1)	92.17(5)
S(2)-Sb(1)-S(3)	93.63(5)	S(3)-Sb(2)-S(4)	96.80(5)
S(3)-Sb(2)-S(15a)	91.01(2)	S(4)-Sb(2)-S(15a)	93.67(7)
S(4)-Sb(3)-S(16a)	94.54(6)	S(5)-Sb(3)-S(4)	92.89(6)
S(5)-Sb(3)-S(16a)	90.35(7)	S(1b)-Sb(4)-S(5)	92.60(6)
S(1b)-Sb(4)-S(2b)	82.18(5)	S(1b)-Sb(4)-S(6)	90.23(5)
S(5)-Sb(4)-S(6)	91.69(5)	S(5)-Sb(4)-S(2b)	91.86(5)
S(6)-Sb(4)-S(2b)	171.76(5)	S(6)-Sb(5)-S(8)	99.12(5)
S(7)-Sb(5)-S(6)	93.26(6)	S(7)-Sb(5)-S(8)	87.23(5)
S(7)-Sb(6)-S(9)	98.53(6)	S(8)-Sb(6)-S(7)	89.87(5)
S(8)-Sb(6)-S(9)	95.08(6)	S(9)-Sb(7)-S(11)	94.06(6)
S(10)-Sb(7)-S(9)	91.93(6)	S(10)-Sb(7)-S(11)	95.54(6)
S(10)-Sb(8)-S(12)	96.62(6)	S(13)-Sb(8)-S(10)	95.83(5)
S(13)-Sb(8)-S(12)	91.76(5)	S(11)-Sb(9)-S(14)	90.26(6)
S(12)-Sb(9)-S(11)	97.24(6)	S(12)-Sb(9)-S(14)	89.94(6)
S(14)-Sb(10)-S(16)	89.85(6)	S(15)-Sb(10)-S(14)	90.86(8)
S(15)-Sb(10)-S(16)	99.13(2)		

fects. The structure was solved with direct methods using SHELXS-97 [32] and refinement was done against F^2 using SHELXL-97 [33]. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and refined using the riding model with free varying isotropic displacement parameters. The technical details of data acquisition and some selected refinement results are summarized in Table 1. The atomic coordinates and equivalent isotropic displacement parameters are presented in Table 2.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 250600. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (Fax: +44-(0)1223-336033 or E-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

The new compound $[C_6H_{17}N_3][Sb_{10}S_{16}]$ crystallizes in the monoclinic space group $P2_1/c$ with four



Scheme 1.

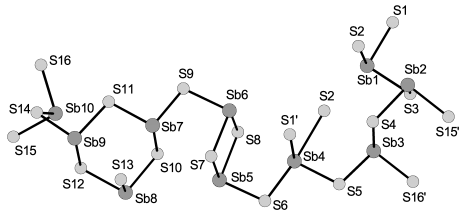


Fig. 1. Interconnection of the trigonal SbS_3 pyramids and the SbS_4 units in $[C_6H_{17}N_3][Sb_{10}S_{16}]$ together with labeling. Note that the primed atoms are generated by symmetry operations.

formula units per unit cell with 10 independent Sb and 16 unique S atoms.

The structure consists of isolated double-protonated 2-piperazine-N-ethylamine cations and a two dimensional $[Sb_{10}S_{16}]^{2-}$ anionic network. The 2-piperazine-N-ethylamine cation is formed under *in-situ* conditions by cyclization of tren molecules as proposed in the reaction Scheme 1.

The interatomic distances and angles are in the typical range (Table 3). We note that Parise *et al.* reported the synthesis of $[C_4H_8N_2][Sb_4S_7]$ with a piperazinium cation formed under *in-situ* conditions applying TETN (triethylenetetramine) as solvent [5].

Nine trigonal pyramidal SbS_3 units and one SbS_4 moiety are the primary building units (PBU) of the $[Sb_{10}S_{16}]^{2-}$ anion (Fig. 1).

The Sb-S bond lengths range from 2.3965(2) to 2.9261(2) Å and the S-Sb-S angles are between 82.18(5) and 171.76(5)° (Table 3). These values are in the range reported for many thioantimonates(III). The PBUs share common corners and edges yielding Sb_3S_3 and Sb_2S_2 hetero-rings as secondary building units (SBU) (Fig. 1). Further condensation leads to strong undulated two atoms thick layers extending in the [010] direction (Fig. 2). The modulation period of the layers is about 14 Å.

Very large $Sb_{31}S_{31}$ rings (Fig. 3) are observed within the layers which show a 'double-ellipsoidal' shape. The two ellipsoidal parts of the ring are separated by a bottleneck. The pores have approximate dimensions of $8.9 \cdot 9.3$ Å. The interlayer distance is be-

$D-H$	$d(H\cdots A)$	$\langle DHA$	$d(D\ldots A)$	A
N2-H2A	2.418	150.56	3.232 S10	$[x-1,-y+5/2,z-1/2]$
N2-H2B	2.621	133.09	3.302 S5	$[-x+2,y+1/2,-z+3/2]$
N3-H3A	2.684	151.97	3.495 S16	$[x-2,-y+5/2,z-1/2]$
N3-H3A	2.871	125.15	3.461 S12	$[x-2,y,z-1]$
N3-H3C	2.715	138.96	3.436 S1	
N3-H3C	2.933	140.35	3.663 S6	$[-x+2,-y+2,-z+1]$

Table 4. Geometry parameters [Å, °] for S···H bonding in $[C_6H_{17}N_3]Sb_{10}S_{16}$.

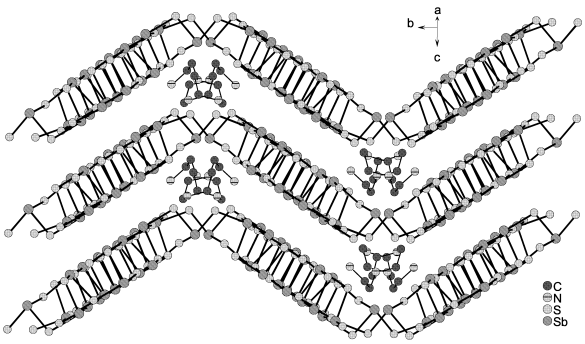


Fig. 2. The crystal structure of $[C_6H_{17}N_3][Sb_{10}S_{16}]$ viewed along [201].

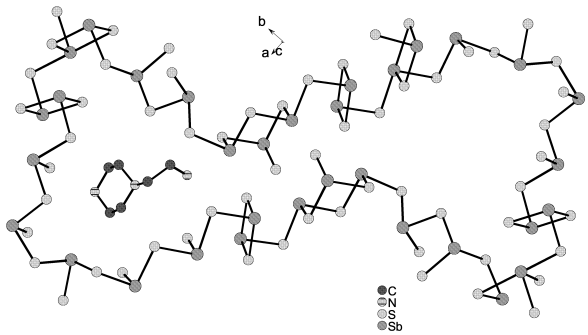


Fig. 3. The layer in $[C_6H_{17}N_3][Sb_{10}S_{16}]$ with the large double ellipsoidal $Sb_{31}S_{31}$ rings.

tween 3.6 and 4 Å. The cations are located at the inflexion points of the layers (Fig. 2) and act as pillars between successive layers. Relatively short S···H separations are observed which indicate H bonding interactions between the cation and the thioantimonate(III) anion (Table 4).

The layers are stacked onto each other in a way that channels parallel to [001] are formed accommodating the organic cations (Fig. 4). We note that smaller channels (diameter: $6.5 \cdot 5.7$ Å) run along the *a* axis.

When long Sb-S bonds above 3.0 Å are considered (Table 5), the structure may be viewed as a 3-dimensional network. Taking these Sb-S distances into account the Sb(1,2,4,5,6,7,8) atoms are sixfold coordinated forming strong distorted octahedra, Sb(3,10) form SbS_5 units and Sb(9) is surrounded by 4 S atoms.

Table 5. The long Sb-S bonds [Å] in $[C_6H_{17}N_3]Sb_{10}S_{16}$.

Sb(1)-S(4)	3.163(2)	Sb(1)-S(6)	3.117(6)
Sb(1)-S(9)	3.437(3)	Sb(2)-S(2)	3.168(1)
Sb(2)-S(8)	3.589(7)	Sb(3)-S(2)	3.128(2)
Sb(3)-S(3)	3.352(7)	Sb(4)-S(8)	3.098(9)
Sb(4)-S(13)	3.573(3)	Sb(5)-(6)	3.405(3)
Sb(5)-S(10)	3.245(8)	Sb(5)-S(13)	3.013(6)
Sb(6)-S(1)	3.145(6)	Sb(6)-S(3)	3.211(6)
Sb(6)-S(3)	3.537(6)	Sb(7)-S(2)	3.609(3)
Sb(7)-S(7)	3.224(1)	Sb(7)-S(13)	3.122(6)
Sb(8)-S(7)	3.326(6)	Sb(8)-S(13)	3.160(9)
Sb(8)-S(16)	3.379(2)	Sb(9)-S(13)	3.109(1)
Sb(10)-S(4)	3.257(2)	Sb(10)-S(12)	3.248(5)

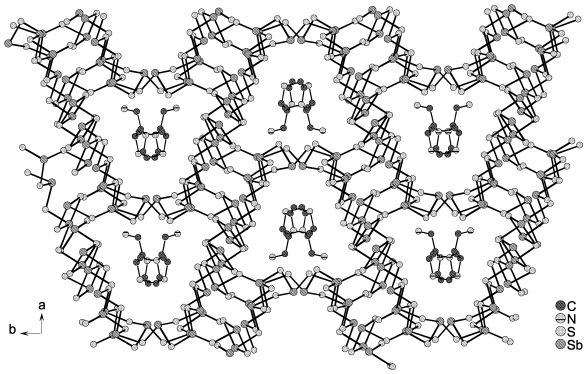


Fig. 4. The channels in $[C_6H_{17}N_3][Sb_{10}S_{16}]$ running along [001].

We note that the Sb-S bond lengths within the layers are significantly shorter than those between the layers.

The arrangement of the thioantimonate anion together with the formation of the large rings reflect the structure directing effect of the *in-situ* formed cations.

Several thioantimonates(III) with a Sb:S ratio of 1 : 1.67 were reported in the past, but all show a different connection mode compared to that in the title compound. In $[C_6H_{15}N_2][Sb_3S_5]$ one SbS_3 and two SbS_4 groups are joined to form the layered anion which comprises Sb_2S_2, Sb_4S_4 and Sb_5S_5 rings as secondary building units [7]. One-dimensional chain anions are observed in $[N(C_3H_7)_4][Sb_3S_5]$ [5] and in $[Ph_4P]_2[Sb_6S_{10}]$ [8]. In the two compounds only trigonal SbS_3 pyramids appear which are joined into Sb_5S_5 rings that are condensed yielding the chain anions.

In $RbSb_3S_5{\cdot}H_2O$ the SbS_3 groups are joined to form small Sb_2S_2 and large $Sb_{12}S_{12}$ heterorings which are connected into a two atoms thick layered anion [4]. In $TlSb_3S_5$ also only trigonal SbS_3 pyramids are observed and the thioantimonate(III) anion is a complex three-dimensional network composed of Sb_2S_2, Sb_5S_5, and Sb_8S_8 heterorings [6]. In the two thioantimonates(III) $[M(C_4H_{13}N_3)_2][Sb_6S_{10}]{\cdot}0.5H_2O$ (M = Fe, Ni) [9] five SbS_3 pyramids and one SbS_4 unit are the PBUs. The topology of the network is complex and a short description base on chains built up by the interconnection of -Sb_4S_4-SbS_3-SbS_4-Sb_4S_4- units. These chains are joined into the final layered anion *via* common corners and edges. Besides small heterorings (Sb_2S_2, Sb_4S_4, Sb_5S_5) a ring containing 32 atoms ($Sb_{16}S_{16}$) represents the largest SBU in these compounds [9]. A two atoms thick one-dimensional $[Sb_{12}S_{20}]^{4-}$ chain anion is observed in $[(NH_3CH_3)_{1.03}K_{2.97}][Sb_{12}S_{20}]{\cdot}1.34H_2O$ [10] which is composed of 10 SbS_3 pyramids and two SbS_4 moieties. A central Sb_4S_4 ring is bound to 6 Sb_3S_3 units forming the next hierarchical building block. These blocks are joined *via* S atoms and larger Sb_8S_8 heterorings are formed [10]. In the two thioantimonates(III) $[C_6N_3H_{17}{}^{2+}][Sb_6S_{10}]$ and $[C_7N_2H_{13}{}^{+}]_3[Sb_9S_{15}]$ primary building units are trigonal SbS_3 pyramids and SbS_4 moieties [31]. In the former compound five SbS_3 groups and one SbS_4 unit form Sb_3S_3 rings and Sb_3S_4 semi-cubes as the SBUs, which are joined *via* common S atoms to form the one-dimensional $\frac{1}{\infty}[Sb_6S_{10}]^{2-}$ anion [31]. In $[C_7N_2H_{13}{}^{+}]_3[Sb_9S_{15}]$ the six SbS_3 pyramids and the three SbS_4 units each form individual chains by vertex linking. Interestingly, one chain is exclusively formed by SbS_4 units whereas the other two chains are composed of SbS_3 pyramids. The chains are joined *via* common corners yielding the one-dimensional $\frac{1}{\infty}[Sb_9S_{15}]^{3-}$ multiple chain anion. Within these chains Sb_4S_4 rings as SBUs are observed [31].

Analyzing the structures of all compounds with the Sb : S ratio of 1 : 1.67 there are no obvious relationships between the number and kind of PBUs and SBUs in the different compounds, the final topology and the dimensionality of the anionic networks. Even when Sb-S distances up to about 3.9 Å are treated as weak Sb-S interactions the situation is still complex. Obviously, in several of the above mentioned compounds the organic cations are large and a higher dimensionality of the anionic framework cannot be achieved. This may be the case for the one-dimensional chains in $[[N(C_3H_7)_4][Sb_3S_5]$ [5] and $[Ph_4P]_2[Sb_6S_{10}]$ [8], where the largest extensions of the cations are about 7 Å and 9.5 Å. On the other hand, a layered thioantimonate(III) is oberved in $[M(C_4H_{13}N_3)_2][Sb_6S_{10}]{\cdot}0.5H_2O$ [9] with cations having dimensions of about 7.7 Å. As a general tendency, the dimensionality of the anionic framework is reduced with increasing size of the cation. But other factors like for instance the charge distribution on the cations or S···H interactions seem to be also important for the formation of the actual thioantimonate(III) anion.

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