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New Thioantimonates(III) with Different Sb:S Ratios: Solvothermal Syntheses and Crystal Structures of $[(C_3H_{10}NO)(C_3H_{10}N)][Sb_8S_{13}]$, $[(C_2H_8NO)(C_2H_8N)(CH_5N)][Sb_8S_{13}]$, $[(C_6H_{16}N_2)(C_6H_{14}N_2)][Sb_6S_{10}]$, and $[C_8H_{22}N_2][Sb_4S_7]$

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Dedicated to Professor Hanskarl Müller-Buschbaum on the Occasion of His 80th Birthday

Keywords: Thioantimonates(III); Antimony; Sulfur; Solvothermal synthesis; Crystal structures

Abstract. Four new thioantimonates(III) with compositions $[(C_3H_{10}NO)(C_3H_{10}N)][Sb_8S_{13}]$ (**1**) (C_3H_9NO = 1-amino-3-propanol, C_3H_9N = propylamine), $[(C_2H_8NO)(C_2H_8N)(CH_5N)][Sb_8S_{13}]$ (**2**) (C_2H_7NO = ethanolamine, C_2H_7N = ethylamine, CH_5N = methylamine), $[(C_6H_{16}N_2)(C_6H_{14}N_2)][Sb_6S_{10}]$ (**3**) ($C_6H_{14}N_2$ = 1,2-diaminocyclohexane) and $[C_8H_{22}N_2][Sb_4S_7]$ (**4**) ($C_8H_{20}N_2$ = 1,8-diaminooctane) were synthesized under solvothermal conditions. Compound **1**: triclinic space group $P\bar{1}$, a = 6.9695(6) Å, b = 13.8095(12) Å, c = 18.0354(17) Å, α = 98.367(11), β = 96.097(11) and γ = 101.281(11)°; compound **2**: monoclinic space group $P2_1/m$, a = 7.1668(5), b = 25.8986(14), c = 16.0436(11) Å, β = 96.847(8)°; compound **3**: monoclinic space group $P2_1/n$, a = 11.6194(9), b = 10.2445(5) Å, c = 27.3590(18) Å, β = 91.909(6)°; compound **4**: triclinic space group $P\bar{1}$, a = 7.0743(6), b = 12.0846(11), c = 13.9933(14) Å, α = 114.723(10), β = 97.595(11), γ = 93.272(11)°. The main structural feature of the two atoms thick layered $[Sb_8S_{13}]^{2-}$ anion in **1** are large nearly rectangular pores with dimensions 11.2 × 11.7 Å. The layers are stacked perpendicular to [100to] to form tunnels being directed along [100 I]. In contrast to **1** the structure of **2** contains a $[Sb_8S_{13}]^{2-}$ chain anion with $Sb_{12}S_{12}$ pores measuring about 8.9 × 11.5 Å. Only if longer Sb–S distances are considered as bonding interactions a layered anion is formed. The chain anion $[Sb_6S_{10}]^{2-}$ in compound **3** is unique and is constructed by corner-sharing SbS_3 pyramids. Two symmetry-related single chains consisting of alternating SbS_3 units and Sb_3S_3 rings are bound to Sb_4S_4 rings in chair conformation. Finally, in the structure of **4** the SbS_3 and SbS_4 moieties are joined corner-linked to form a chain of alternating SbS_4 units and $(SbS_3)_3$ blocks. Neighboring chains are connected into sheets that contain relatively large $Sb_{10}S_{10}$ heterorings. The sheets are further connected by sulfur atoms generating four atoms thick double sheets.

Introduction

The fascinating structural variability of chalcogenometalates of group 15 elements was recently reviewed.[1–3] There are several possible approaches to rationalize the broad structural chemistry of thioantimonates(III) and one way is to categorize the structures according to their dimensionality, i.e., isolated anions, one-dimensional chains, two-dimensional layers and three-dimensional networks. But as mentioned in an earlier contribution the dimensionality strongly depends on the Sb–S bond lengths considered for the structure description,[4] and often only Sb–S distances up to 2.6 Å are considered as bonds. Another possibility is to sort the different thioantimonates(III) with respect to the charge compensating cations, i.e., pure inorganic compounds, thioantimonates(III) containing transition metal complexes or protonated organic amine molecules. The title compounds belong to the group of thioantimonates with organic amines or amino alcohols acting as structure directors and cations. Several thioantimonates(III) were reported in the past displaying the Sb:S ratio observed in the new compounds. Thioantimonates(III) with Sb:S = 1:1.625 solely show the $[Sb_8S_{13}]^{2-}$ anion[4–12] whereas for Sb:S = 1:1.667 several different anions were isolated like $[Sb_3S_5]^-$,[13–17] $[Sb_6S_{10}]^{2-}$,[10,18–24] $[Sb_9S_{15}]^-$,[20] and $[Sb_{12}S_{20}]^{4-}$.[25] Finally, for Sb:S = 1:1.75 two different thioantimonate(III) anions are observed, namely $[Sb_4S_7]^{2-}$[11,15,26–49] and $[Sb_{12}S_{21}]^{6-}$.[37] We briefly summarize some structural features of the compounds with the three above mentioned Sb:S ratios. The $[Sb_8S_{13}]^{2-}$ anion in $Cs_2[Sb_8S_{13}]$[5] is three-dimensional containing SbS_4 units like in the 3D network of $[(maH)_2][Sb_8S_{13}]$ (for abbreviations see Table 1)[6] and of $[(maH)_{0.5}(NH_4)_{1.5}][Sb_8S_{13}]\cdot 2.8H_2O$.[7] A 2D $[Sb_8S_{13}]^{2-}$ anion is observed in $Rb_2[Sb_8S_{13}]\cdot 3.28H_2O$,[7] in $[(pyrH)_2][Sb_8S_{13}]\cdot 0.15H_2O$,[9] $[(i\text{prH})_2][Sb_8S_{13}]$ and $[(1,2\text{-dapH})_2][Sb_8S_{13}]$.[4] The SbS_3 pyramids of $[(pyrH)_2][Sb_8S_{13}]\cdot 0.15H_2O$[9] form layered anions. Similar to this network topology is that of $[(i\text{prH})_2][Sb_8S_{13}]$ and $[(1,2\text{-dapH})_2][Sb_8S_{13}]$.[4] The two compounds

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$[dienH_2][Sb_8S_{13}]\cdot 1.5H_2O$ and $[ampH_2][Sb_8S_{13}]\cdot 2.5H_2O$ show a similar network topology of the 2D anion.[4] Whereas in the above mentioned compounds SbS_3 pyramids and SbS_4 moieties coexist, the 1D anionic structure of $[(en)_2][Sb_8S_{13}]$[8] is solely constructed by interconnection of SbS_3 pyramids.

Table 1. List of the abbreviation used in this paper.

Abbreviation	chemical name	chemical formula
1,4-dab	1,4-diaminobutane	$C_4H_{12}N_2$
1,2-dach	1,2-diaminocyclohexane	$C_6H_{14}N_2$
1,4-dach	1,4-diaminocyclohexane	$C_6H_{14}N_2$
1,6-dah	1,6-diaminohexane	$C_6H_{16}N_2$
1,2-dap	1,2-diaminopropane	$C_3H_{10}N_2$
1,3-dap	1,3-diaminopropane	$C_3H_{10}N_2$
1,8-dao	1,8-diaminooctane	$C_8H_{20}N_2$
aep	1-(2-aminoethyl)-piperazine	$C_6H_{15}N_3$
amp	3-aminomethylpiperazine	$C_6H_7N_2$
apro	1-amino-3-propanol	C_3H_9NO
cyclam	1,4,8,11-tetraazacyclotetradecane	$C_{10}H_{24}N_4$
DBN	1,5-diazabicyclo[4.3.0]non-5-ene	$C_7H_{12}N_2$
deen	*N*,*N*-diethylethylenediamine	$C_6H_{16}N_2$
depn	3-dimethylpropanediamine	$C_5H_{14}N_2$
dien	diethylenetriamine	$C_4H_{13}N_3$
dmen	*N*,*N*-dimethylethylenediamine	$C_4H_{12}N_2$
ea	ethylamine	C_2H_7N
en	ethylenediamine	$C_2H_8N_2$
etam	ethanolamine	C_2H_7NO
ipa	*isopropyl*amine	C_3H_9N
ipr	*isopropyl*amine	C_3H_9N
ma	methylamine	CH_5N
Me_4N^+	tetramethylammonium	$(CH_3)_4N^+$
nba	butylamine	$C_4H_{11}N$
npa	propylamine	C_3H_9N
pea	pentylamine	$C_5H_{13}N$
pip	piperazine	$C_4H_{10}N_2$
Ph_4P	tetraphenylphosphonium	$C_{24}H_{20}P$
Pr_4N^+	tetrapropylammonium	$(C_3H_7)_4N^+$
pyr	pyrrolidine	C_4H_9N
tren	tris(2-aminoethyl-)amine	$C_6H_{18}N_4$

For Sb:S = 1:1.667 different anions were reported ranging from a 3D anionic network with a two-dimensional system of channels in $[Me_4N][Sb_3S_5]$[13] to 2D in $[1,2\text{-dachH}][Sb_3S_5]$, $[1,4\text{-dachH}][Sb_3S_5]$[17] and $[deenH_2][Sb_{10}S_{16}]\cdot H_2O$,[11] and one-dimensional chains in $[Pr_4N][Sb_3S_5]$,[15] $[(Ph_4P)_2][Sb_6S_{10}]$,[18] $[aepH_2][Sb_6S_{10}]$ and in $[DBNH][Sb_9S_{15}]$.[20] The $[Sb_9S_{15}]^{3-}$ anion is structurally unique because it contains a central chain only formed by SbS_4 units and two further chains being formed by SbS_3 pyramids which enwrap the central chain.

Anions with stoichiometry $[Sb_4S_7]^{2-}$ are particularly prevalent in thioantimonates(III) and examples include $K_2[Sb_4S_7]$, $[(NH_4)_2][Sb_4S_7]$, $Rb_2[Sb_4S_7]$, $Cs_2[Sb_4S_7]$, $K_2[Sb_4S_7]\cdot H_2O$, $Sr[Sb_4S_7]\cdot 6H_2O$, $Rb_2[Sb_4S_7]$, $[Ni(en)_3][Sb_4S_7]$, $[Ni(1,2\text{-dap})_3][Sb_4S_7]$, $[pipH_2][Sb_4S_7]$, $[Mn(en)_3][Sb_4S_7]$, $[trenH_2][Sb_4S_7]$, $[Co(en)_3][Sb_4S_7]$, $[(eaH)_2][Sb_4S_7]$, $[Ni(dien)_2][Sb_4S_7]\cdot H_2O$, $[Mn(dien)_2][Sb_4S_7]\cdot 0.5H_2O$, $[(n\text{paH})_2][Sb_4S_7]$, $[(n\text{baH})_2][Sb_4S_7]$, $[(peaH)_2][Sb_4S_7]$, $[(i\text{paH})_2][Sb_4S_7]$, $[1,4\text{-dabH}_2][Sb_4S_7]$, $[Ni(1,2\text{-dap})_3][Sb_4S_7]$, $[Co(1,2\text{-dap})_3][Sb_4S_7]$, $[Cr(tren)Sb_4S_7]$.[11,15,26–39,45,47] There are only few examples for a 3D $[Sb_4S_7]^{2-}$ anionic framework, namely $K_2[Sb_4S_7]$,[26] $[Ni(cyclam)][Sb_4S_7]$, $[cyclamH_2][Sb_4S_7]$ and $[Co(cyclam)]_x[cyclamH_2]_{1-x}[Sb_4S_7]$.[49] Most compounds with the $[Sb_4S_7]^{2-}$ anion follow the trend that with increasing size of the cation, the structurally dimensionality of the anion is reduced to two-dimensional layers and finally to one-dimensional chains.[34,50]

In our continuing work in the field of solvothermal syntheses of thioantimonates(III) we applied diamines and amino alcohols as structure directing molecules. The latter were used because only very little is known about thioantimonates containing such molecules.[40] In this paper we report the solvothermal syntheses and crystal structures of the four new thioantimonates(III) $[(C_3H_{10}NO)(C_3H_{10}N)][Sb_8S_{13}]$ (**1**), $[(C_2H_8NO)(C_2H_8N)(CH_5N)][Sb_8S_{13}]$ (**2**), $[(C_6H_{16}N_2)(C_6H_{14}N_2)][Sb_6S_{10}]$ (**3**) and $[C_8H_{22}N_2][Sb_4S_7]$ (**4**).

Experimental Section

Synthesis

The title compounds were prepared under solvothermal conditions in steel autoclaves with Teflon liners of 30 mL volume. Compound **1** was obtained by heating antimony (1 mmol) and sulfur (3 mmol) in 100 % 1-amino-3-propanol (4 mL) for 7 d at 160 °C. The compound crystallized as violet needles and is stable on air. The yield of the product was about 90 % based on antimony. Compound **2** was obtained using Ph_3Sb (1 mmol), sulfur (3 mmol) and 100 % ethanolamine (6 mL). The mixture was heated for 13 d at 170 °C giving red needles with a yield of 95 % based on antimony. For compound **3** a mixture of antimony (0.67 mmol), aluminum (0.67 mmol), sulfur (2.42 mmol) and 100 % *trans*-1,2-diaminocyclohexane (5 mL) was heated at 190 °C for 10 d. Red needle-like crystals were obtained in a yield around 80 % based on antimony. The role of aluminum in the synthesis has not been fully understood, but it is necessary to prepare **3**. If no aluminum is used, needle-like crystals of stibnite (Sb_2S_3) are obtained. For **4**, Ph_3Sb (1 mmol) and sulfur (3 mmol) were used with 100 % 1,8-diaminooctane (4 mL). The slurry was heated at 180 °C for 7 d giving orange plates with a yield of 80 % on antimony. All compounds were filtered off and washed with water, ethanol, or acetone after the reaction was finished and cooled to room temperature. CHN analyses **1**: $[(C_3H_{10}NO)(C_3H_{10}N)][Sb_8S_{13}]$ (1527.10 $g\cdot mol^{-1}$); C 4.6 (calcd. 4.72); H 1.2 (1.32); N 1.9 (1.83) %; **2**: $[(C_2H_8NO)(C_2H_8N)(CH_5N)][Sb_8S_{13}]$ (1530.10 $g\cdot mol^{-1}$); C 4.0 (calcd. 3.92); H 1.2 (1.38); N 2.6 (2.75) %; **3**: $[(C_6H_{16}N_2)(C_6H_{14}N_2)][Sb_6S_{10}]$ (1281.56 $g\cdot mol^{-1}$); C 11.4 (calcd. 11.25); H 2.3 (2.36); N 4.1 (4.37) %; **4**: $[C_8H_{22}N_2][Sb_4S_7]$ (857.74 $g\cdot mol^{-1}$); C 11.5 (calcd. 11.20); H 2.8 (2.59); N 3.4 (3.27) %.

X-ray Structure Determination

The single-crystal X-ray intensity data were collected at room temperature on a STOE AED 4-circle diffractometer, IPDS-1 or IPDS-2 Imaging Plate Diffraction System from STOE & Cie with graphite-monochromated Mo-K_α radiation (AED for **1**, **2** and **4**, IPDS-2 for **3**). Selected crystal data and details of the structure determination are summarized in Table 2. The raw intensities were corrected for Lorenz and polarization effects. A numerical absorption correction was performed for all data. The structures were solved with direct methods using SHELXS-97[51] and the refinement was performed against F^2 using SHELXL-97.[52] All non-hydrogen atoms except disordered carbon, nitrogen, and oxygen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and refined isotropically using a riding model. The structure directing molecules in **1** and a part of them in **2** are disordered. The electron densities in **1** together with the results of chemical analysis indicate the presence of the two organic molecules 1-amino-3-propanol and propylamine. The molecules were refined isotropically yielding large isotropic displacement parameters, unreasonable bond lengths and several split positions. All attempts to find a reasonable model failed and therefore we decided to use the SQUEEZE option in the Platon program suite to remove the disordered amine molecules. In **2** in addition to ethanolamine also ethylamine and methylamine are present. But only the ethanolamine molecule could be refined with reasonable results. The oxygen and nitrogen atoms in the ethanolamine molecule were arbitrarily assigned and the hydrogen atoms were not considered. In the structure of **3** two different trans-diaminocyclohexane could be located in the difference Fourier maps. One molecule is disordered but could be refined very well isotropically while the second molecule exhibited some disorder which could not tackled using a split model. Hence, the second molecule was refined with isotropic displacement parameters and the remaining electron densities were not considered. It was not possible to identify the protonated nitrogen atoms of the amine molecules of **1**, **2** and **3** and the charge balancing hydrogen atoms where therefore randomly distributed. Therefore, the chemical formulae reported in Table 2 may differ but this does not affect the inorganic part of the structures. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC-830314 (**1**), -830295 (**2**), -830296 (**3**), and -830297 (**4**)). Copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1E2, U.K. (Fax: +44-1223-336033 or E-Mail deposit@chemcrys.cam.ac.uk.

Results and Discussion

Compound **1** crystallizes in space group $P\bar{1}$ (Table 2) with all antimony and sulfur atoms being located on general positions. All antimony atoms form SbS_3 trigonal pyramids (Table 3, Figure 1). A central structural motif of the structure is a $Sb_{10}S_{10}$ ring generated by a center of inversion of the SbS_3 units involving Sb(1–5) and the symmetry related atoms (Figure 1).

Along [010] smaller Sb_5S_5 rings are condensed on both sides of the $Sb_{10}S_{10}$ rings yielding strands with a sequence $\cdots Sb_{10}S_{10}–Sb_5S_5–Sb_4S_4–Sb_5S_5–Sb_{10}S_{10}\cdots$. The layered anion is then constructed by interconnection of the strands through a Sb_2S_4 group, which is formed by two edge-sharing SbS_3 pyramids. The connection mode generates a large central ring $Sb_{18}S_{18}$ with dimensions of 11.2 × 11.7 Å. The almost linear anionic layers are two atoms thick with an interlayer distance of about 3.5 Å. The layers are stacked along [100] generating channels along [010] (Figure 2). The protonated amino alcohol molecules could not be located but it can be assumed that they are located above/below the large cavities. The presence of monoprotonated amino alcohol molecules was proven with IR spectroscopy with absorptions located at 1600, 2400, 3400 and 1064 cm^{-1} being typical for $R–NH_3^+$ respectively R–OH species. Like in many other thioantimonates(III) the antimony atoms have sulfur atoms at longer distances, which are called secondary bonds. In **1** Sb(2) and Sb(3) have one additional

Table 2. Selected crystal data and refinement results for compounds **1**–**4**.

	1	**2**	**3**	**4**
Compound	$[(C_3H_{10}NO)(C_3H_{10}N)][Sb_8S_{13}]$	$[(C_2H_8NO)(C_2H_8N)(CH_5N)][Sb_8S_{13}]$	$[(C_6H_{16}N_2)(C_6H_{14}N_2)][Sb_6S_{10}]$	$[C_8H_{22}N_2][Sb_4S_7]$
Sum formula	$C_6H_{20}N_2OS_{13}Sb_8$	$C_5H_{21}N_3OS_{13}Sb_8$	$C_{12}H_{30}N_4S_{10}Sb_6$	$C_8H_{22}N_2S_7Sb_4$
a /Å	6.9695(6)	7.1668(5)	11.6194(9)	7.0743(6)
b /Å	13.8095(12)	25.8986(14)	10.2445(5)	12.0846(11)
c /Å	18.0354(17)	16.0436(11)	27.3590(18)	13.9933(17)
α /°	98.367(11)	90	90	114.723(10)
β /°	96.097(11)	96.847(8)	91.909(6)	97.595(11)
γ /°	101.281(11)	90	90	93.272(11)
V /Å^3	1667.9(3)	2956.6(3)	3254.9(4)	1068.68(17)
Z	2	4	4	2
Calc. density /g·cm^{-3}	3.041	3.437	2.615	2.665
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/m$	$P2_1/n$	$P\bar{1}$
Crystal color	violet needles	red needles	red needles	orange plates
Temperature /K	293	293	293	293
Scan range	$2.3 \le \theta \le 28.1$	$2.0 \le \theta \le 27.0$	$1.5° \le \theta \le 24.6°$	$3 \le \theta \le 27$
Index range	$-9 \le h \le 9$	$-8 \le h \le 7$	$-12 \le h \le 13$	$-9 \le h \le 9$
	$-18 \le h \le 18$	$-33 \le h \le 27$	$-11 \le k \le 11$	$-15 \le h \le 15$
	$-23 \le h \le 23$	$-20 \le h \le 20$	$-31 \le l \le 31$	$-18 \le h \le 18$
Reflections collected	18508	15700	14030	11757
Independent reflections	7955	6399	5398	4614
R_{int}	0.0486	0.0533	0.0622	0.0631
Number of parameters	191	210	233	191
R_1 for $F_o > 4\sigma(F_o)$	0.0312	0.0498	0.0594	0.0360
$wR2$ for all reflections	0.0798	0.1323	0.1627	0.0897
$\Delta\rho$ /e·Å^{-3}	–1.45/1.18	–1.668/2.106	–1.905/1.198	–1.470/0.985
μ /mm^{-1}	7.18	8.11	5.56	5.68

Table 3. Bond lengths /Å and angles /° for $[(C_3H_{10}NO)(C_3H_{10}N)][Sb_8S_{13}]$ (**1**).

Sb(1)–S(2)	2.4602(13)	S(2)–Sb(1)–S(3)	97.08(5)
Sb(1)–S(3)	2.4888(14)	S(2)–Sb(1)–S(1)	90.75(5)
Sb(1)–S(1)	2.5188(13)	S(3)–Sb(1)–S(1)	93.41(4)
Sb(2)–S(5)	2.4228(13)	S(5)–Sb(2)–S(4)	92.25(4)
Sb(2)–S(4)	2.5216(12)	S(5)–Sb(2)–S(3)	95.49(4)
Sb(2)–S(3)	2.5457(13)	S(4)–Sb(2)–S(3)	97.67(4)
Sb(3)–S(4)	2.4524(13)	S(4)–Sb(3)–S(6)	99.36(5)
Sb(3)–S(6)	2.4563(13)	S(4)–Sb(3)–S(9)	92.40(5)
Sb(3)–S(9)	2.5137(14)	S(6)–Sb(3)–S(9)	86.45(4)
Sb(4)–S(7)	2.4422(13)	S(7)–Sb(4)–S(6)	90.92(5)
Sb(4)–S(6)	2.5197(13)	S(7)–Sb(4)–S(11)	91.39(4)
Sb(4)–S(11)	2.6564(12)	S(6)–Sb(4)–S(11)	90.57(4)
Sb(5)–S(8)	2.4091(12)	S(7)–Sb(4)–S(5)	85.91(4)
Sb(5)–S(2)^a	2.5937(12)	S(6)–Sb(4)–S(5)	90.74(4)
Sb(5)–S(7)	2.5998(12)	S(11)–Sb(4)–S(5)	177.02(4)
Sb(6)–S(10)	2.4218(15)	S(8)–Sb(5)–S(2)^a	90.27(4)
Sb(6)–S(9)	2.4966(14)	S(8)–Sb(5)–S(7)	91.75(4)
Sb(6)–S(10)^b	2.5335(16)	S(7)–Sb(5)–S(2)^a	94.52(4)
Sb(7)–S(11)	2.4212(13)	S(10)–Sb(6)–S(9)	100.11(5)
Sb(7)–S(12)	2.4938(12)	S(10)–Sb(6)–S(10)^b	87.73(5)
Sb(7)–S(13)^c	2.6034(15)	S(9)–Sb(6)–S(10)^b	97.56(5)
Sb(8)–S(13)	2.4296(13)	S(11)–Sb(7)–S(12)	98.08(4)
Sb(8)–S(12)	2.4642(13)	S(11)–Sb(7)–S(13)^c	93.36(5)
Sb(8)–S(1)^a	2.5087(14)	S(12)–Sb(7)–S(13)^c	94.18(4)
		S(13)–Sb(8)–S(12)	94.44(5)
Sb(2)–S(8)^a	3.0337(12)	S(13)–Sb(8)–S(1)^a	94.22(5)
Sb(3)–S(5)	3.0737(12)	S(12)–Sb(8)–S(1)^a	92.55(5)
Sb(4)–S(5)	2.8997(12)		
Sb(4)–S(8)	3.0656(12)		
Sb(5)–S(5)^a	3.0537(12)		
Sb(5)–S(8)^a	2.9704(12)		

Symmetry transformations used to generate equivalent atoms: ^{a} $-x+1, -y, -z+1$; ^{b} $-x+1, -y, -z$; ^{c} $-x, -y+1, -z+1$

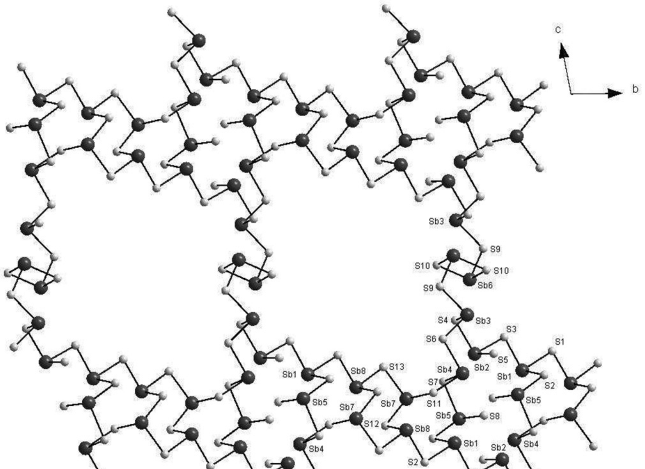

Figure 1. The layered $[Sb_8S_{13}]^{2-}$ anion in compound **1** with the large central $Sb_{18}S_{18}$ rings.

sulfur neighbor whilst Sb(4) and Sb(5) have two secondary bonds (Table 3).

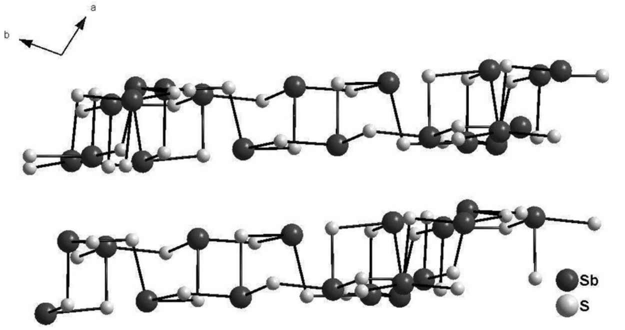

Figure 2. The stacked $[Sb_8S_{13}]^{2-}$ layers in compound **1**.

Compound **2** crystallizes in the monoclinic space group $P2_1/m$ (Table 2) with all crystallographically independent antimony atoms being located on general positions. Two of the thirteen unique sulfur atoms are located on a mirror plane. Like in **1** the antimony atoms are in a trigonal pyramidal environment of sulfur atoms to form SbS_3 units (Table 4, Figure 3).

Table 4. Bond lengths /Å and angles /° for $[(C_2H_8NO)(C_2H_8N)(CH_5N)][Sb_8S_{13}]$ (**2**).

Sb(1)–S(2)	2.463(3)	S(2)–Sb(1)–S(3)	94.97(11)
Sb(1)–S(3)	2.464(3)	S(2)–Sb(1)–S(1)	94.44(11)
Sb(1)–S(1)	2.493(3)	S(3)–Sb(1)–S(1)	89.60(11)
Sb(2)–S(5)	2.431(3)	S(5)–Sb(2)–S(4)	95.54(13)
Sb(2)–S(4)	2.4853(19)	S(5)–Sb(2)–S(3)	97.01(11)
Sb(2)–S(3)	2.491(3)	S(4)–Sb(2)–S(3)	95.48(14)
Sb(3)–S(6)	2.421(3)	S(6)–Sb(3)–S(5)	93.80(10)
Sb(3)–S(5)	2.514(3)	S(6)–Sb(3)–S(2)	92.83(10)
Sb(3)–S(2)	2.528(3)	S(5)–Sb(3)–S(2)	95.92(11)
Sb(4)–S(7)	2.418(3)	S(7)–Sb(4)–S(8)	93.60(10)
Sb(4)–S(8)	2.539(3)	S(7)–Sb(4)–S(11)	87.55(10)
Sb(4)–S(11)	2.685(3)	S(8)–Sb(4)–S(11)	94.80(10)
Sb(5)–S(8)	2.457(3)	S(7)–Sb(4)–S(6)	87.15(9)
Sb(5)–S(10)	2.490(3)	S(8)–Sb(4)–S(6)	93.85(9)
Sb(5)–S(9)	2.497(3)	S(11)–Sb(4)–S(6)	170.12(9)
Sb(6)–S(11)	2.427(3)	S(8)–Sb(5)–S(10)	95.40(10)
Sb(6)–S(10)	2.523(3)	S(8)–Sb(5)–S(9)	90.66(13)
Sb(6)–S(12)	2.687(3)	S(10)–Sb(5)–S(9)	90.41(14)
Sb(7)–S(14)	2.468(3)	S(11)–Sb(6)–S(10)	92.72(11)
Sb(7)–S(13)	2.599(3)	S(11)–Sb(6)–S(12)	90.12(10)
Sb(8)–S(13)^b	2.431(3)	S(10)–Sb(6)–S(12)	94.57(11)
Sb(8)–S(1)^a	2.464(3)	S(11)–Sb(6)–S(7)	83.91(9)
Sb(8)–S(14)	2.468(3)	S(10)–Sb(6)–S(7)	92.58(10)
		S(12)–Sb(6)–S(7)	170.90(10)
Sb(3)–S(7)	3.099(3)		
Sb(4)–S(6)	2.870(3)		
Sb(6)–S(7)	2.842(3)		
Sb(7)–S(2)^a	3.086(3)		

Symmetry transformations used to generate equivalent atoms: ^{a} $-x+1, -y+1, -z$; ^{b} $-x+2, -y+1, -z-1$

The Sb(1–3)S_3 and Sb(4–6)S_3 pyramids form six-membered Sb_3S_3 rings in chair conformation by corner-sharing. Neighboring rings are joined by common vertices to form Sb_6S_{11} building blocks (Figure 3). A Sb_4S_4 ring constructed by vertex-sharing of Sb(7)S_3 and Sb(8)S_3 pyramids and their symmetry related units links the Sb_6S_{11} moieties to form the two atoms thick zigzag $[Sb_8S_{13}]^{2-}$ chain anion running along [010]. The connection Scheme generates a large $Sb_{12}S_{12}$ ring with pore dimensions of 11.6 × 8.9 Å. Along [100] the channels are

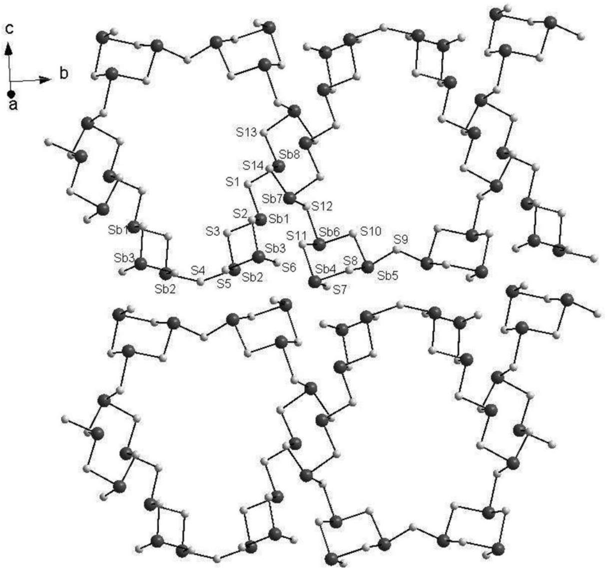

Figure 3. The $[Sb_8S_{13}]^{2-}$ chain anion in compound **2** with the $Sb_{12}S_{12}$ pores.

stacked onto each other forming tunnels which host the cations. The structure directing amino alcohol molecules are not located within the plane of the channel but rather in the interchain resp. inter-layer galleries (Figure 4). According to the CHNS analysis compound **2** contains one amino alcohol molecule but also more organic molecules with the approximate formula $C_3H_{13}N_2$, which can be explained with the presence of additional ethylamine and methylamine molecules. The IR spectrum shows a specific absorption for *R*–OH species at 1634 cm^{-1} and with TG-MS measurements the specific masses for ethanolamine at m/z = 30, 31 and 61 could be detected. These measurements verify that ethanolamine is incorporated in the structure. But spectroscopic analysis could not clearly evidence what kind of amine molecules are incorporated in **2**. The shortest interchain distance is only 2.87 Å (Sb(4)–S(6)) and considering this separation as a weak bonding interaction a layered anion is obtained. The antimony atoms Sb(3,4,6,7) each have one additional sulfur neighbor at distances between 2.842 and 3.099 Å (Table 4).

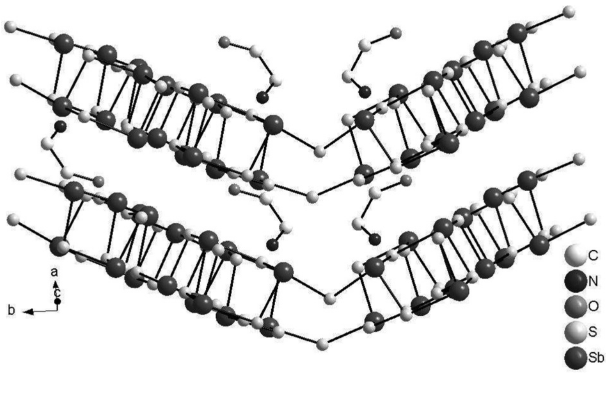

Figure 4. The undulated chain anions in compound **2** with the structure directing molecules in the interchain galleries.

A short comparison with the hitherto known compounds containing the $[Sb_8S_{13}]^{2-}$ anion is given here. The topology of the anionic network of **1** is comparable with that of the two compounds $[(i\text{prH})_2][Sb_8S_{13}]$ and $[(1,2\text{-dapH})_2][Sb_8S_{13}]$ (Table 5).[4] Whereas Sb–S bond lengths and S–Sb–S angles scatter in a similar range in all three compounds the most prominent difference is the shortest inter-chain separation which is at ≥ 2.9 Å in the latter two compounds. Compound **2** has an identical network topology like $[(\text{maH})_{0.5}(NH_4)_{1.5}][Sb_8S_{13}]$, $[\text{dienH}_2][Sb_8S_{13}]\cdot 1.5H_2O$ and $[\text{ampH}_2][Sb_8S_{13}]\cdot 2.5H_2O$ (Table 5).[4,7] Most of the other thioantimonates with the $[Sb_8S_{13}]^{2-}$ anion are layered and only two form a three dimensional (3D) network (Table 5). Such a 3D network is observed in $Cs_2[Sb_8S_{13}]$, which is a remarkable compound because one antimony atom has two short and two relatively long Sb–S bonds at 2.725 and 2.781 Å, i.e., it forms a SbS_4 unit. In the second compound with a 3D network $[(\text{maH})_2][Sb_8S_{13}]\cdot 2.8H_2O$ only SbS_3 pyramids occur with Sb–S bonds between 2.38 and 2.65 Å. The layered anion in $[1,3\text{-dapH}_2][Sb_8S_{13}]$ exhibits different types of large rings: $Sb_{19}S_{19}$ (ø: 9.9 × 7.8 Å), $Sb_{13}S_{13}$ (ø: 10.2 × 3.5 Å), Sb_8S_8 (ø: 13.2 × 4.2 Å), and $Sb_{14}S_{14}$ (ø: 6.8 × 7 Å). The largest heteroring $Sb_{30}S_{30}$ is observed for $[Co(en)_3][Sb_8S_{13}]$ with the largest dimensions of about 11 × 22 Å. The anion in the structure of $[(\text{enH})_2][Sb_8S_{13}]$ features a double-chain with shortest interchain Sb–S separation of ca. 3.16 Å. If only Sb–S bonds below 2.8 Å are considered in $[\text{depnH}_2][Sb_8S_{13}]\cdot H_2O$ the SbS_3 pyramids are corner-linked to form a chain whereas $[\text{dmenH}_2][Sb_8S_{13}]\cdot H_2O$ contains a layered anion with a SbS_4 moiety with two short and two long Sb–S bonds.

Compound **3** crystallizes in the monoclinic space group $P2_1/n$ (Table 2) and in the structure six unique antimony atoms and ten independent sulfur atoms form SbS_3 trigonal pyramids (Table 6, Figure 5).

The $Sb(4–6)S_3$ units are vertex-linked to form a Sb_3S_3 ring which is joined by $Sb(3)S_3$ yielding a chain with the sequence $\cdots SbS_3–Sb_3S_3–SbS_3\cdots$ being directed along [010]. A central Sb_4S_4 ring in chair conformation is formed by the $Sb(1,2)S_3$ pyramids and two symmetry related moieties. The Sb_4S_4 rings are corner-linked to two chains yielding the final one-dimensional $[Sb_6S_{10}]^{2-}$ anion (Figure 5). The connection scheme generates a $Sb_{14}S_{14}$ ring. Neighboring chains are stacked along [001] with an inter-layer separation of about 7.7 Å.

The relatively large inter-chain distance is caused by the arrangement of the structure directing cyclohexadiammonium ions. The amino groups are directed towards S atoms of the anion and the cyclohexyl rings are directed into the empty space in a head-to-head fashion (Figure 6, top). Due to the *n* glide plane the layers are stacked in a way that the Sb_3S_3 rings are located above/below the pockets of the $Sb_{14}S_{14}$ ring (Figure 6, bottom).

Because the hydrogen atoms of the protonated diaminocyclohexane molecules could not be located during structure refinement a detailed description of N–H···S bonding interactions is not possible.

The $[Sb_6S_{10}]^{2-}$ anion in compound **3** is unique and features a new topology. For the others thioantimonates with the $[Sb_6S_{10}]^{2-}$ anion different dimensionalities are observed (Table 7). Three compounds contain $[Sb_6S_{10}]^{2-}$ chain anions but

Table 5. Selected structural parameters in thioantimonates containing $[Sb_8S_{13}]^{2-}$ anions (SG = space group, Dim. = dimensionality).

Compound	Dim./SG	a /Å	b /Å	c /Å	α /°	β /°	γ /°	Vol /Å^3
$[(maH)_2][Sb_8S_{13}]$[6]	3/$P\bar{1}$	15.866	11.581	8.295	71.46	75.71	82.25	1398
$[(pyrH)_2][Sb_8S_{13}]\cdot 0.15H_2O$[9]	2/$P\bar{1}$	6.929	16.747	17.976	94.84	95.41	125.28	1670
$[Co(en)_3][Sb_8S_{13}]$[10]	2/$P\bar{1}$	9.041	12.376	16.549	100.372	94.579	110.34	1687
$[(i\text{prH})_2][Sb_8S_{13}]$[4]	2/$P\bar{1}$	7.012	13.794	17.216	94.45	96.49	101.21	1614
$[(1,2\text{-dapH})_2][Sb_8S_{13}]$[4]	2/$P\bar{1}$	6.992	13.705	18.105	100.15	96.22	101.09	1658
$[maH]_{0.5}(NH_4)_{1.5}][Sb_8S_{13}]$[7]	2/$P2_1/m$	7.193	25.770	15.999		96.856		2945
$[dienH_2][Sb_8S_{13}]\cdot 1.5H_2O$[4]	2/$P2_1/m$	7.190	25.900	15.979		97.39		2951
$[ampH_2][Sb_8S_{13}]\cdot 2.5H_2O$[4]	2/$P2_1/m$	7.208	25.741	15.937		96.96		2935
$[dmenH_2][Sb_8S_{13}]\cdot H_2O$[11]	2/$P2_1/c$	9.143	23.515	13.871		105.0		2881
$[depnH_2][Sb_8S_{13}]\cdot H_2O$[12]	2/$P2_1/c$	9.237	24.05	13.912		106.06		2970
$[(enH)_2][Sb_8S_{13}]$[8]	1/$Cmc2_1$	22.874	10.058	11.338				2609
$[1,3\text{-dapH}_2][Sb_8S_{13}]$[4]	2/$I4_1md$	22.590	22.590	22.461				11461
$Cs_2[Sb_8S_{13}]$[5]	3/$P\bar{1}$	15.437	11.488	8.299	71.89	102.45	95.16	1366
$Rb_2[Sb_8S_{13}]\cdot 3.28H_2O$[7]	2/$P2_1/m$	7.190	25.760	15.973		96.541		2939

Table 6. Bond lengths /Å and angles /° for $[(C_6H_{16}N_2)(C_6H_{14}N_2)][Sb_6S_{10}]$ (**3**).

Sb(1)–S(1)	2.360(4)	S(1)–Sb(1)–S(2)	98.61(11)
Sb(1)–S(2)	2.493(3)	S(1)–Sb(1)–S(3)^a	104.90(12)
Sb(1)–S(3)^a	2.517(3)	S(2)–Sb(1)–S(3)^a	91.45(10)
Sb(2)–S(2)	2.466(3)	S(2)–Sb(2)–S(3)	93.30(11)
Sb(2)–S(3)	2.481(3)	S(2)–Sb(2)–S(4)	92.57(11)
Sb(2)–S(4)	2.499(3)	S(3)–Sb(2)–S(4)	87.17(11)
Sb(3)–S(4)	2.427(3)	S(4)–Sb(3)–S(6)	95.97(11)
Sb(3)–S(6)	2.435(3)	S(4)–Sb(3)–S(5)	93.75(11)
Sb(3)–S(5)	2.444(3)	S(6)–Sb(3)–S(5)	96.12(11)
Sb(4)–S(7)	2.439(3)	S(7)–Sb(4)–S(9)	97.88(11)
Sb(4)–S(9)	2.463(3)	S(7)–Sb(4)–S(6)	90.70(10)
Sb(4)–S(6)	2.509(3)	S(9)–Sb(4)–S(6)	86.00(11)
Sb(5)–S(7)	2.451(3)	S(7)–Sb(5)–S(8)	99.11(11)
Sb(5)–S(8)	2.458(3)	S(7)–Sb(5)–S(5)^b	85.79(10)
Sb(5)–S(5)^b	2.502(3)	S(8)–Sb(5)–S(5)^b	88.03(11)
Sb(6)–S(10)	2.371(4)	S(10)–Sb(6)–S(9)	95.72(11)
Sb(6)–S(9)	2.436(3)	S(10)–Sb(6)–S(8)	95.39(11)
Sb(6)–S(8)	2.453(3)	S(9)–Sb(6)–S(8)	95.71(12)
Sb(4)–S(10)	3.010(6)		
Sb(5)–S(10)	3.072(3)		

Symmetry transformations used to generate equivalent atoms: ^{a} $-x-1, -y+2, -z$; ^{b} $x, y-1, z$

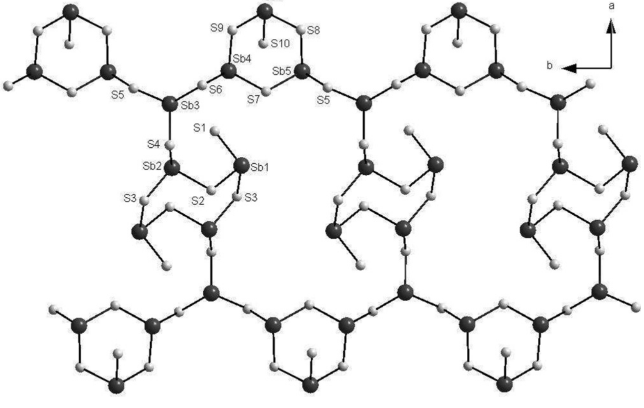

Figure 5. The $[Sb_6S_{10}]^{2-}$ chain anion in compound **3**.

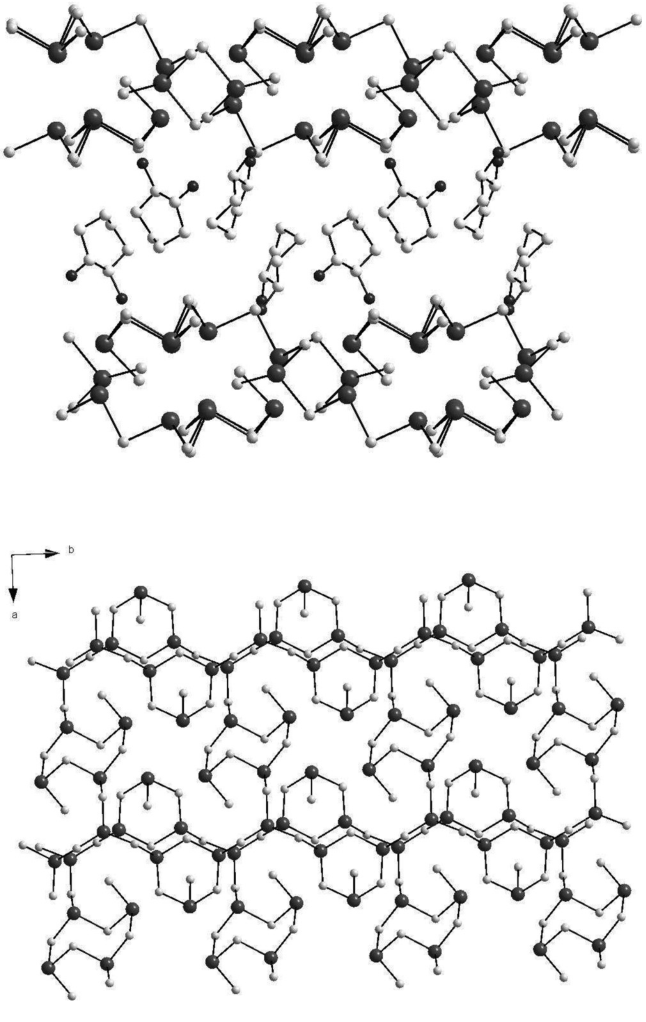

Figure 6. top: Orientation of the structure directing molecules located between the chains in the structure of **3**; bottom: arrangement of neighbored chains in the structure of **3**.

the connectivity of the SbS_3 units and the resulting topology is different compared to that in the structure of **3**. The SbS_3 moieties in the structure of $[aepH_2][Sb_6S_{10}]$[20] are corner-

Table 7. Selected structural parameters of thioantimonates containing $[Sb_6S_{10}]^{2-}$ anions (SG = space group, Dim. = dimensionality).

Compound	Dim./SG	a /Å	b /Å	c /Å	α /°	β /°	γ /°	Vol /Å^3
$[(Ph_4P)_2][Sb_6S_{10}]$[18]	1/$P\bar{1}$	10.390	16.002	18.245	93.65	105.06	103.67	2822
$[Fe(dien)_2][Sb_6S_{10}] \cdot 0.5H_2O$[19]	2/$C2/c$	33.789	8.570	24.620		118.411		6270
$[Ni(dien)_2][Sb_6S_{10}] \cdot 0.5H_2O$[19]	2/$C2/c$	33.595	8.536	24.651		118.411		6218
$[1,2\text{-}dapH_2][Sb_6S_{10}]$[21]	1/$P2_1/n$	17.480	10.922	18.030		111.415		3205
$[aepH_2][Sb_6S_{10}]$[20]	1/$P2_1$	6.120	17.759	11.478		90.70		1247
$[Fe(1,2\text{-}dach)_2][Sb_6S_{10}]$[22]	3/$P\bar{1}$	6.7214	9.679	12.772	72.08	88.15	89.51	789
$[Ni(dien)_2][Sb_6S_{10}]\cdot 0.43H_2O$[10]	2/$C2/c$	33.512	8.4645	24.6574		118.246		6162
$[Co(dien)_2][Sb_6S_{10}]\cdot 0.43H_2O$[10]	2/$C2/c$	33.521	8.461	24.628		118.316		6149
$[cyclamH_2][Sb_6S_{10}]$[23]	2/$P2_1/c$	9.487	15.448	10.757		105.878		1516
$[(pipH_2)_{0.5}][CuSb_6S_{10}]$[24]	2/$P2_1/n$	11.258	12.526	13.939		102.445		1919

linked to form Sb_3S_3 rings. The rings are then vertex-linked yielding the one-dimensional anion (Figure 7, top). In the structure of $[(Ph_4P)_2][Sb_6S_{10}]$[18] the SbS_3 groups share common corners generating Sb_5S_5 rings, which are condensed to form the one-dimensional anion (Figure 7, middle). In the last thioantimonate $[1,2\text{-}dapH_2][Sb_6S_{10}]$[21] featuring a one-dimensional $[Sb_6S_{10}]$ anion SbS_3 units are joined into Sb_3S_3 rings which are interconnected into a one-dimensional chain by SbS_3 moieties, i.e., a structural motif identical with that in **3**. Two further SbS_3 groups share a common edge generating a Sb_2S_4 unit (Figure 7, bottom). Two symmetry related chains are joined by the Sb_2S_4 groups into the final anion. The main structural difference of the topologies of this anion and that in **3** is the central group connecting the chains made by SbS_3 and Sb_3S_3 moieties.

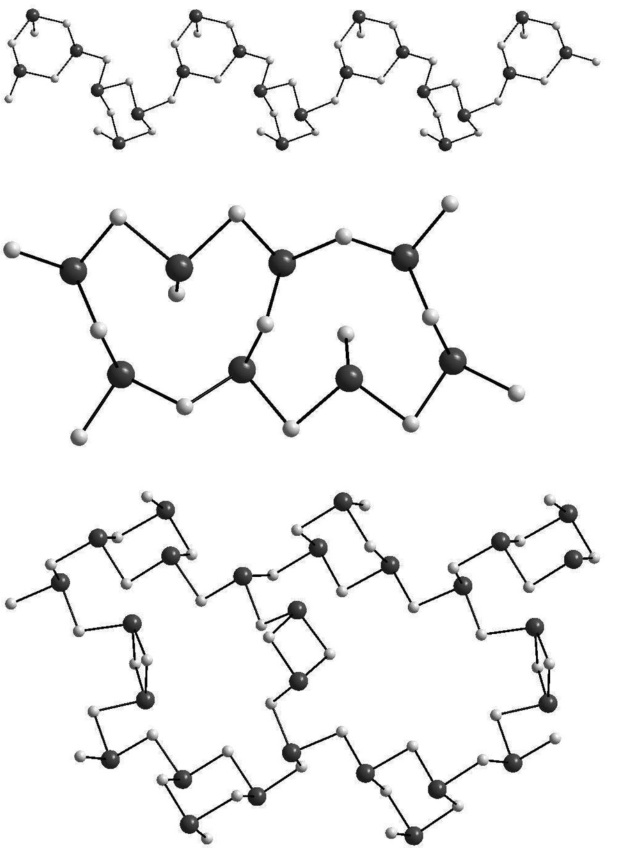

Figure 7. top: the $[Sb_6S_{10}]^{2-}$ chain anion in the structure of $[aepH_2][Sb_6S_{10}]$; middle: the thioantimonate(III) anion in the structure of $[(Ph_4P)_2][Sb_6S_{10}]$; bottom: the $[Sb_6S_{10}]^{2-}$ chain in the structure of $[1,2\text{-}dapH_2][Sb_6S_{10}]$ being structurally related to the anion in compound **3**.

Compound **4** crystallizes in space group $P\bar{1}$ (Table 2) and contains three unique SbS_3 trigonal pyramids and one unique SbS_4 unit with Sb–S bond lengths as well as the S–Sb–S angles being in the typical range observed previously in extended thioantimonates(III) (Table 8).[4–49] The SbS_3 and SbS_4 groups are corner-linked to form a chain of alternating SbS_4 units and $(SbS_3)_3$ blocks (Figure 8). Neighboring chains are connected via S(3) yielding sheets within the *ac*-plane that contain relatively large $Sb_{10}S_{10}$ heterorings (Figure 8).

The sheets are further connected through S(6) generating four atoms thick double sheets (Figure 9). All sulfur atoms have bonds to two antimony atoms except S(7) which is terminal. The individual sheets are stacked along [001] and the shortest interlayer spacing (measured from coordinate to coordinate) is about 7.6 Å, which is comparable to that for $[(npaH)_2][Sb_4S_7]$, 7.52 Å.[39]

Larger interlayer separations were found for $[(ipaH)_2][Sb_4S_7]$ (7.81 Å), $[(nbaH)_2][Sb_4S_7]$ (8.34 Å) and for $[(peaH)_2][Sb_4S_7]$ (9.90 Å),[39] whereas the interlayer distances for $[(eaH)_2][Sb_4S_7]$[36] and $[1,6\text{-}dahH_2][Sb_4S_7]$[43] are shorter at 6.56 Å and 7.05 Å, respectively. The structure directing molecule 1,8-diaminooctane contains the longest alkyl chain but a short inter-layer separation is observed which is caused by the special arrangement of the structure directing molecules. The two nitrogen atoms of the molecule are directed towards sulfur atoms of the anion and the lipophilic alkyl chains of adjacent molecules protrude into the inter-layer space (Figure 10). A similar arrangement of the organic cations was reported for the diammonium containing compound $[1,6\text{-}dahH_2][Sb_4S_7]$[43] explaining the shorter inter-layer separation compared to monoammonium containing thioantimonates(III) with the $[Sb_4S_7]^{2-}$ anion. The NH_3^+ groups of the 1,8-diaminooctane cation are oriented towards the thioantimonate anion to optimize N–H···S bonding interactions (distances: ≈ 2.4–2.6 Å; angles: ≈ 149–166°) (Table 9). The bonds are relatively strong which may be an important contribution to the fully ordered alkyl chain of the amine molecule. Such hydrogen bonding interactions are often observed in thioantimonates(III) and are also observed in e.g. Cu^+ containing thioantimonates(III).[53,54]

Table 8. Bond lengths /Å and angles /° for $[C_8H_{22}N_2][Sb_4S_7]$ (**4**).

Sb(1)–S(1)	2.4060(17)	S(1)–Sb(1)–S(3)^a	99.52(7)
Sb(1)–S(3)^a	2.4555(18)	S(1)–Sb(1)–S(2)	89.53(6)
Sb(1)–S(2)	2.5622(19)	S(3)^a–Sb(1)–S(2)	87.08(6)
Sb(2)–S(2)	2.4240(18)	S(2)–Sb(2)–S(4)	94.55(6)
Sb(2)–S(4)	2.4447(16)	S(2)–Sb(2)–S(3)	95.73(7)
Sb(2)–S(3)	2.4854(19)	S(4)–Sb(2)–S(3)	89.34(6)
Sb(3)–S(6)	2.4227(17)	S(6)–Sb(3)–S(5)	91.27(6)
Sb(3)–S(5)	2.4940(16)	S(6)–Sb(3)–S(4)	96.64(6)
Sb(3)–S(4)	2.5566(19)	S(5)–Sb(3)–S(4)	85.70(6)
Sb(4)–S(7)	2.4260(18)	S(7)–Sb(4)–S(5)^b	111.27(7)
Sb(4)–S(5)^b	2.4667(18)	S(7)–Sb(4)–S(1)^c	87.01(6)
Sb(4)–S(1)^c	2.6653(19)	S(5)^a–Sb(4)–S(1)^c	81.67(5)
Sb(4)–S(6)	2.7798(18)	S(7)–Sb(4)–S(6)	87.48(6)
		S(5)b–Sb(4)–S(6)	87.14(5)
Sb(1)–S(7)^c	3.0848(5)	S(1)^c–Sb(4)–S(6)	164.78(6)
Sb(3)–S(6)	3.0022(3)		

Symmetry transformations used to generate equivalent atoms: ^{a} $x + 1, y, z$; ^{b} $-x + 1, -y+1, -z+1$; ^{c} $-x + 2, -y+2, -z+1$

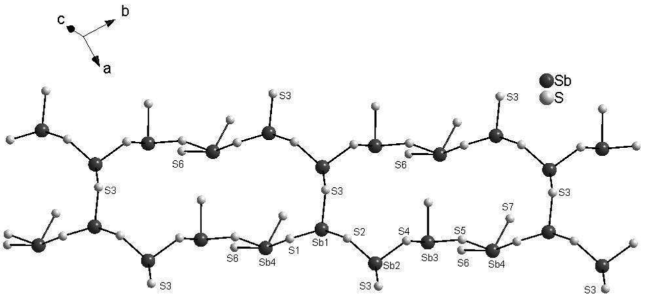

Figure 8. The chain of alternating SbS_4 units and $(SbS_3)_3$ blocks in the structure of compound **4**.

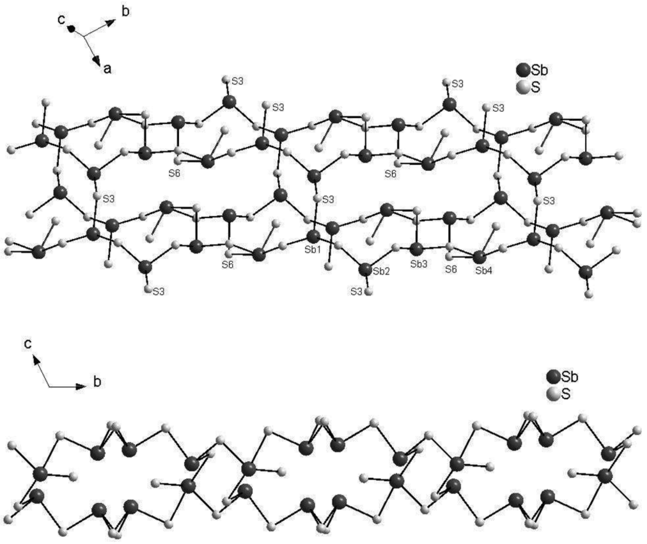

Figure 9. Interconnection of the chain of alternating SbS_4 units and $(SbS_3)_3$ blocks via S(6) atoms (top) to form the four atoms thick layered anion in compound **4**.

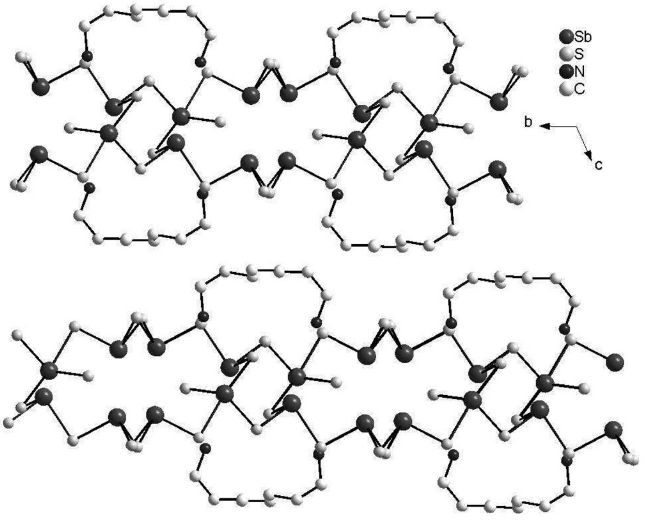

Figure 10. Arrangement of the structure directing 1,8-diaminooctane molecules in the inter-layer galleries in the structure of **4**.

Table 9. Hydrogen bonds of $[C_8H_{22}N_2][Sb_4S_7]$.

D–H	d(H···A) /Å	<DHA /°
S1 H3N2	2.4379(2)	163.877(19)
S3 H1N1	2.6028(3)	148.766(13)
S4 H3N1	2.6293(2)	165.327(18)
S5 H2N2	2.4911(3)	158.735(12)
S7 H1N2	2.5645(3)	148.717(8)

Summary

During explorative solvothermal syntheses four new thioantimonates(III) were obtained and structurally characterized. For all compounds different reaction conditions are necessary to prepare the samples in good yield. Compounds **1** and **4** were obtained using Ph_3Sb as antimony source whereas elemental antimony was supplied in the reaction slurries of **2** and **3**. In addition, the successful preparation of compound **3** required the presence of elemental aluminum but the role is not understood. It is well documented in literature that in some cases such additions are required for the preparation of a distinct compound under solvothermal conditions and a prominent example is $RbTe_6$ which could only be obtained in the presence of elemental germanium.[55] Several amino alcohols are chiral and hence they are attractive structure directing molecules. But in the present work with the simple and non chiral amino alcohols 1-amino-3-propanol and ethanolamine we observed that the reaction conditions are too drastic destroying at least partially these molecules. Whereas compounds **1**, **2**, and **4** display thioantimonate(III) network topologies reported earlier with different structure directing amines, compound **3** exhibits a new and unique one-dimensional thioantimonate(III) anion. The topology of this anions may be regarded as an extension of the previously reported $[Sb_6S_{10}]^{2-}$ anion of $[1,2\text{-}dapH_2][Sb_6S_{10}]$ (see Figure 7, bottom) by insertion of two additional SbS_3 pyramids (see Figure 5) in the central part of the anion. We are sure that further new thioantimonates will be obtained by systematical variation of the synthesis conditions.

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