

# **(C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>)Sb<sub>4</sub>S<sub>7</sub> a Thioantimonate(III) with a Layered [Sb<sub>4</sub>S<sub>7</sub>]<sup>2-</sup> Anion in the Presence of a Diprotonated Amine as Structure Director**

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*Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70<sup>th</sup> birthday*

The new thioantimonate(III) (C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>)Sb<sub>4</sub>S<sub>7</sub> (C<sub>6</sub>N<sub>2</sub>H<sub>16</sub> = 1,6-diaminohexane) was synthesized under solvothermal conditions using Sb, S and 1,6-diaminohexane (1,6-DAH). The compound crystallizes as orange needles in the triclinic space group *P* $\bar{1}$  with lattice parameters *a* = 6.9834(5), *b* = 11.8748(10), *c* = 13.6588(12) Å,  $\alpha$  = 115.248(9),  $\beta$  = 100.165(9) and  $\gamma$  = 92.568(9)°. A central SbS<sub>4</sub> group shares edges with two other SbS<sub>4</sub> moieties forming Sb<sub>3</sub>S<sub>8</sub> units which are joined by SbS<sub>3</sub> pyramids sharing vertices to form a chain of alternating Sb<sub>3</sub>S<sub>8</sub> and SbS<sub>3</sub> units. One S atom of the SbS<sub>3</sub> pyramid connects neighboring chains into sheets which contain large Sb<sub>10</sub>S<sub>10</sub> heterorings. The sheets are then further connected into four atoms thick double sheets. Six edge-linked SbS<sub>4</sub> units are condensed yielding a complex Sb<sub>6</sub>S<sub>14</sub> building block. Layers of diprotonated amines and thioantimonate(III) layers are stacked along [001] in a sandwich-like fashion with an interlayer distance of 8.46 Å. The amine layer is two molecules thick with the amines being oriented parallel to the anionic layers. The title compound represents the first example for a layered [Sb<sub>4</sub>S<sub>7</sub>]<sup>2-</sup> anion with a diamine as structure director. The compound is an optical semiconductor with a band-gap of about 1.9 eV.

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

## **Introduction**

Thioantimonates(III) exhibit several chemical and structural features resembling the chemistry of silicates or zeolites. Analogous to structures of silicates with isolated anions, anionic chains, layered anions and three-dimensional networks, also thioantimonates(III) are known which contain isolated ring anions, one-dimensional chains, two-dimensional layers and three-dimensional networks. In addition, silicates show a large range for the Si:O ratio and this phenomenon is also found in thioantimonates(III). The Sb:S ratio varies from 1:1.625 to 1:2 and examples are [Sb<sub>8</sub>S<sub>13</sub>]<sup>2-</sup> [1–5] for 1:1.625, [Sb<sub>3</sub>S<sub>5</sub>]<sup>-</sup> [6–10], [Sb<sub>6</sub>S<sub>10</sub>]<sup>2-</sup> [11–13], [Sb<sub>9</sub>S<sub>15</sub>]<sup>3-</sup> [13], [Sb<sub>12</sub>S<sub>20</sub>]<sup>4-</sup> [14] for 1:1.667, [Sb<sub>4</sub>S<sub>7</sub>]<sup>2-</sup> [15–28], and [Sb<sub>12</sub>S<sub>21</sub>]<sup>6-</sup> [26] for 1:1.75, [Sb<sub>5</sub>S<sub>9</sub>]<sup>3-</sup> [29], [Sb<sub>10</sub>S<sub>18</sub>]<sup>6-</sup> [30] for 1:1.8, and [SbS<sub>2</sub>]<sup>-</sup> [31, 32], [Sb<sub>2</sub>S<sub>4</sub>]<sup>2-</sup> [33], [Sb<sub>3</sub>S<sub>6</sub>]<sup>3-</sup> [34], [Sb<sub>4</sub>S<sub>8</sub>]<sup>2-</sup> [35], [Sb<sub>4</sub>S<sub>8</sub>]<sup>4-</sup> [36] for 1:2. But there are some remarkable differences between silicates and thioantimonates(III). Under normal conditions Si is always in

a tetrahedral environment of O atoms, whereas Sb(III) can be surrounded by 3 to 6 S atoms. The Si-O bond is relatively rigid and shows only a small variation, whereas Sb-S bond lengths scatter over a large range from about 2.3 Å up to the sum of the van der Waals radii of about 3.8 Å. Finally, the Si-O-Si angle is flexible with values between 90 and 180°, but Sb-S-Sb angles are distributed in a narrow range from about 90 to 110°.

Anions with stoichiometry [Sb<sub>4</sub>S<sub>7</sub>]<sup>2-</sup> are particularly prevalent in thioantimonates(III) and examples include K<sub>2</sub>Sb<sub>4</sub>S<sub>7</sub> [15], (NH<sub>4</sub>)<sub>2</sub>Sb<sub>4</sub>S<sub>7</sub> [16], Rb<sub>2</sub>Sb<sub>4</sub>S<sub>7</sub> · H<sub>2</sub>O [17], Cs<sub>2</sub>Sb<sub>4</sub>S<sub>7</sub> [18], K<sub>2</sub>Sb<sub>4</sub>S<sub>7</sub> · H<sub>2</sub>O [19], SrSb<sub>4</sub>S<sub>7</sub> · 6H<sub>2</sub>O [20], Rb<sub>2</sub>Sb<sub>4</sub>S<sub>7</sub> [21], (C<sub>4</sub>N<sub>2</sub>H<sub>8</sub>)Sb<sub>4</sub>S<sub>7</sub> [8], [M(C<sub>2</sub>N<sub>2</sub>H<sub>8</sub>)<sub>3</sub>]Sb<sub>4</sub>S<sub>7</sub> (M = Mn, Fe, Co, Ni) [22–24], (C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub>)<sub>2</sub>Sb<sub>4</sub>S<sub>7</sub> [25], [Ni(C<sub>4</sub>H<sub>13</sub>N<sub>3</sub>)<sub>2</sub>]-Sb<sub>4</sub>S<sub>7</sub> · H<sub>2</sub>O [26], [Mn(C<sub>4</sub>H<sub>13</sub>N<sub>3</sub>)<sub>2</sub>]Sb<sub>4</sub>S<sub>7</sub> [27] and (C<sub>6</sub>H<sub>20</sub>N<sub>4</sub>)[Sb<sub>4</sub>S<sub>7</sub>] [24], (H<sub>3</sub>N(CH<sub>2</sub>)<sub>4</sub>NH<sub>3</sub>)Sb<sub>4</sub>S<sub>7</sub>, (CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>)<sub>2</sub>Sb<sub>4</sub>S<sub>7</sub>, ((CH<sub>3</sub>)<sub>2</sub>CHNH<sub>3</sub>)<sub>2</sub>Sb<sub>4</sub>S<sub>7</sub>, (CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>3</sub>)<sub>2</sub>Sb<sub>4</sub>S<sub>7</sub>, and (CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>-Sb<sub>4</sub>S<sub>7</sub> [28]. (C<sub>6</sub>H<sub>20</sub>N<sub>4</sub>)Sb<sub>4</sub>S<sub>7</sub> [24]. Of these, only K<sub>2</sub>Sb<sub>4</sub>S<sub>7</sub> [15] shows a three-dimensional [Sb<sub>4</sub>S<sub>7</sub>]<sup>2-</sup>

anionic framework, and with increasing size of the cation, the dimensionality is reduced to two-dimensional layers and finally to one-dimensional chains [23, 37]. The compounds with organic amines as structure directors may be regarded as inorganic-organic hybrid materials, with the arrangements of the organic ammonium ions being often reminiscent of what is observed in layered clays. For instance, in vermiculites with a high layer charge, the alkyl-ammonium ions adopt a paraffin-like orientation. In addition, in many organically ‘templated’ thioantimonates(III) the -NH<sub>3</sub><sup>+</sup> groups adopt a special arrangement with respect to the S atoms of the thioantimonate network [10, 38–40]. It can be assumed that this special orientation of the ammonium groups allows H···S bonding interactions. Furthermore, in the layered compounds the inter-layer spacing covers a large range from for instance 6.56 Å for (C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub>)<sub>2</sub>Sb<sub>4</sub>S<sub>7</sub> [25] to 9.90 Å for (CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>Sb<sub>4</sub>S<sub>7</sub> [28]. In our continuing work in the field of solvothermal syntheses of thioantimonates(III) we applied 1,6-diaminohexane as ‘template’ with the aim to prepare a layered thioantimonate(III) with the diamines acting like ‘pillars’. Here we present the crystal structure and optical spectroscopy data for the compound (C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>)Sb<sub>4</sub>S<sub>7</sub>.

## Experimental Section

### Synthesis

The compound (C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>)Sb<sub>4</sub>S<sub>7</sub> was prepared under solvothermal conditions in a Teflon-lined steel autoclave. A mixture of Sb (1 mmol) and S (3 mmol) was heated for 7 d in 4 ml of 1,6-diaminohexane. The product was collected by filtration and washed with deionized water and acetone and dried in vacuum. The compound crystallizes as orange needles and is stable on air. The yield of the product was about 90% based on Sb. (C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>)Sb<sub>4</sub>S<sub>7</sub> (829.5): calcd. C 8.4, H 3.2, N 2.0; found C 8.2, H 2.9, N 1.7.

### X-ray structure determination

The X-ray intensity data were collected at 293 K using a STOE AED 4 with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The raw intensities were treated in the normal way applying a Lorentz polarization correction. The structure was solved using SHELXS-97 [41]. Crystal structure refinement was carried out against F<sup>2</sup> with SHELXL-97 [42]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters using a riding

Table 1. Selected crystallographic data and refinement results for (C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>)Sb<sub>4</sub>S<sub>7</sub>.

<i>a</i> [Å]	6.9834(5)
<i>b</i> [Å]	11.8748(10)
<i>c</i> [Å]	13.6588(12)
$\alpha$ [°]	115.248(9)
$\beta$ [°]	100.165(9)
$\gamma$ [°]	92.568(9)
<i>V</i> [Å <sup>3</sup> ]	999.18(14)
<i>d</i> <sub>calc</sub> [g cm <sup>−3</sup> ]	2.758
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
$2\theta$ [deg]	6–56
<i>hkl</i> Range	−8 ≤ <i>h</i> ≤ 8, −15 ≤ <i>k</i> ≤ 15, −18 ≤ <i>l</i> ≤ 18
No. coll. Refl.	7421
No. unique Refl.	3620
Refl. <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> )	2669
No. par.	173
<i>R</i> 1 ( <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> ))	0.0462
<i>wR</i> 2 ( <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> ))	0.1154
<i>R</i> 1 (all refl.)	0.0665
<i>wR</i> 2 (all refl.)	0.1230
GOF	0.982
δ( <i>F</i> )/e Å <sup>−3</sup>	−1.280/1.075

model. Details of data collections and refinement results are summarized in Table 1. Bond lengths and angles are listed in Tables 2–4. The crystal investigated was non-merohedrally twinned. Therefore, both individuals were indexed separately and integrated using the TWIN option in the STOE IPDS-1 software package.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-296852. 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 email: deposit@ccdc.cam.ac.uk).

### Spectroscopy

The Raman spectrum was measured from 100 to 3500 cm<sup>−1</sup> with a Bruker IFS 66 Fourier transform Raman spectrometer (wavelength: 514.5 nm, T = 20 K).

## Results and Discussion

The new compound (C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>)Sb<sub>4</sub>S<sub>7</sub> crystallizes in the triclinic space group *P* $\bar{1}$  with all atoms located in general positions (Table 1). For the discussion of the structure Sb-S distances up to about 3.1 Å are considered as bonding contacts. But one should keep in mind that Sb-S distances scatter over a large range from about 2.3 to 4 Å and therefore, the assignment

Sb(1)–S(3)	2.390(3)	S(3)–Sb(1)–S(1)	98.33(11)
Sb(1)–S(1)	2.460(3)	S(3)–Sb(1)–S(2)	88.12(9)
Sb(1)–S(2)	2.539(3)	S(1)–Sb(1)–S(2)	87.51(10)
Sb(2)–S(4)	2.415(3)	S(4)–Sb(2)–S(7) <sup>a</sup>	110.54(10)
Sb(2)–S(7) <sup>a</sup>	2.471(3)	S(7) <sup>a</sup> –Sb(2)–S(3)	81.38(9)
Sb(2)–S(3)	2.653(3)	S(4)–Sb(2)–S(3)	87.91(9)
Sb(2)–S(5)	2.775(3)	S(4)–Sb(2)–S(5)	88.38(8)
Sb(3)–S(5)	2.412(2)	S(7) <sup>a</sup> –Sb(2)–S(5)	86.70(8)
Sb(3)–S(7)	2.491(3)	S(3)–Sb(2)–S(5)	165.37(9)
Sb(3)–S(6)	2.562(3)	S(5)–Sb(3)–S(7)	91.58(9)
Sb(4)–S(2) <sup>b</sup>	2.409(3)	S(7)–Sb(3)–S(6)	85.15(9)
Sb(4)–S(1) <sup>c</sup>	2.475(3)	S(2) <sup>b</sup> –Sb(4)–S(1) <sup>c</sup>	93.32(10)
Sb(4)–S(6)	2.435(6)	S(6)–Sb(4)–S(1) <sup>c</sup>	90.11(9)
Sb(4) <sup>b</sup> –S(2)–Sb(1)	105.49(10)	Sb(4)–S(6)–Sb(3)	93.40(10)
Sb(3)–S(5)–Sb(2)	97.97(9)	Sb(2) <sup>a</sup> –S(7)–Sb(3)	104.09(10)
Sb(1)–S(1)–Sb(4) <sup>c</sup>	104.81(10)	Sb(1)–S(3)–Sb(2)	92.03(9)

Table 2. Selected interatomic distances (Å) and angles (°) for (C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>)Sb<sub>4</sub>S<sub>7</sub>. Estimated standard deviations are given in parentheses.

Symmetry codes: <sup>a</sup>  $-x+3, -y+2, -z+1$ ; <sup>b</sup>  $-x+2, -y+1, -z+1$ ; <sup>c</sup>  $-x+3, -y+1, -z+1$ .

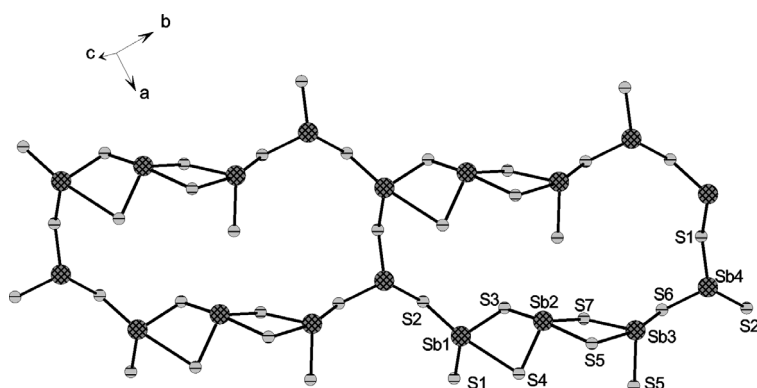


Fig. 1. The connectivity pattern of the SbS<sub>4</sub> and SbS<sub>3</sub> units in (C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>)Sb<sub>4</sub>S<sub>7</sub> with atom labeling.

Table 3. Long Sb–S distances [Å] in (C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>)Sb<sub>4</sub>S<sub>7</sub>. Estimated standard deviations are given in parentheses.

Sb(1)–S(4)	3.089(2)	Sb(3)–S(4)	3.269(2) <sup>a</sup>
Sb(4)–S(4)	3.393(2) <sup>b</sup>	Sb(2)–S(5)	3.587(2) <sup>c</sup>
Sb(4)–S(4)	3.717(2)		

Symmetry codes: <sup>a</sup>  $2-x, 1-y, 1-z$ ; <sup>b</sup>  $-1+x, y, z$ ; <sup>c</sup>  $2-x, 2-y, 1-z$ .

Table 4. N–H···S distances and angles [Å, °] for (C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>)Sb<sub>4</sub>S<sub>7</sub>.

D–H	d(H···A)	∠DHA	A
N1–H1A	2.618	159.28	S1 <sup>a</sup>
N1–H1B	2.997	155.89	S7 <sup>b</sup>
N1–H1C	2.689	160.96	S6 <sup>c</sup>
N2–H2A	2.824	120.46	S4 <sup>d</sup>
N2–H2A	2.954	121.95	S2 <sup>e</sup>
N2–H2B	2.369	167.32	S7 <sup>f</sup>
N2–H2C	2.563	160.16	S3 <sup>g</sup>

Symmetry codes: <sup>a</sup>  $-x+3, -y+1, -z+1$ ; <sup>b</sup>  $-x+2, -y+1, -z+1$ ; <sup>c</sup>  $-x+2, -y+1, -z+1$ ; <sup>d</sup>  $x-1, y-1, z$ ; <sup>e</sup>  $x, y-1, z$ ; <sup>f</sup>  $-x+2, -y+1, -z+1$ ; <sup>g</sup>  $-x, y-1, z$ .

of the dimensionality is often arbitrary. The primary building units (PBUs) of (C<sub>6</sub>N<sub>2</sub>H<sub>18</sub>)Sb<sub>4</sub>S<sub>7</sub> are one trigonal SbS<sub>3</sub> pyramid and three SbS<sub>4</sub> units (Fig. 1). The

Sb–S distances in SbS<sub>3</sub> groups scatter less (2.390(3)–2.562(3) Å) than in the SbS<sub>4</sub> moieties (2.412(2)–2.967(3) Å) (Table 2). In the SbS<sub>4</sub> groups the two long Sb–S bond lengths are in *trans* position and the angles S–Sb–S are about 165°. Sb–S bond lengths and angles are in the range observed in many other thioantimonates(III) [15–28]. All Sb atoms increase their coordination spheres with S atoms at distances up to 3.8 Å (Table 3) forming another SbS<sub>4</sub> group (Sb(1)) and three distorted SbS<sub>5</sub> rectangular pyramids.

The layered [Sb<sub>4</sub>S<sub>7</sub>]<sup>2−</sup> anion is constructed in the following way. The Sb(2)S<sub>4</sub> group shares edges with two other SbS<sub>4</sub> moieties forming an Sb<sub>3</sub>S<sub>8</sub> unit as a secondary building unit (SBU) (Fig. 1). These SBUs are then joined by SbS<sub>3</sub> pyramids sharing vertices yielding a chain of alternating Sb<sub>3</sub>S<sub>8</sub> and SbS<sub>3</sub> units (Fig. 1). The S(1) atom of the SbS<sub>3</sub> pyramid connects neighboring chains to form sheets within the *ab* plane that contain relatively large Sb<sub>10</sub>S<sub>10</sub> heterorings (Fig. 1). These sheets are then further connected through S(5) into four atoms thick double sheets (Fig. 2). The double sheets contain six edge-

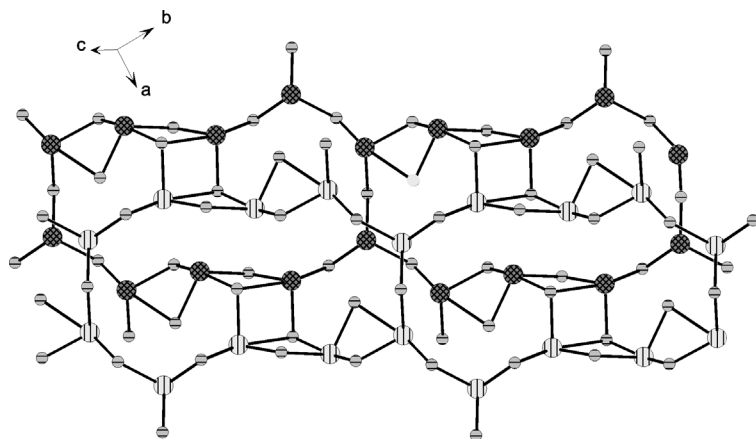


Fig. 2. The double layer in  $(\text{C}_6\text{N}_2\text{H}_{18})\text{Sb}_4\text{S}_7$ . Note that Sb atoms of the second sheet are drawn with a different shading.

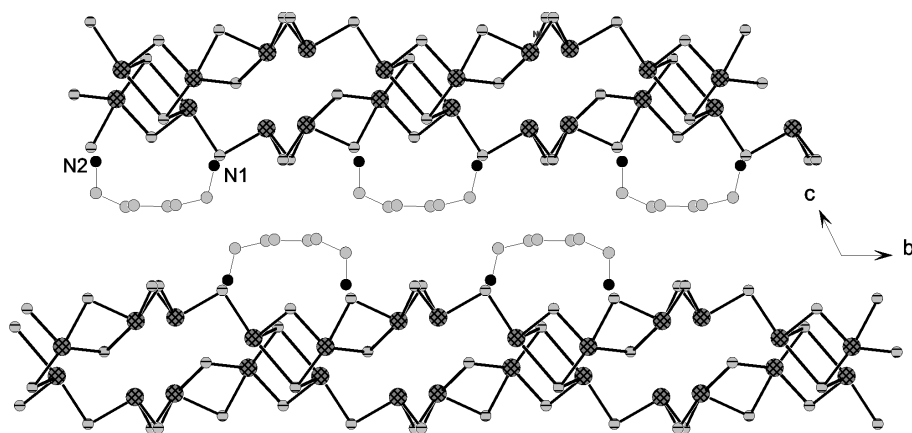


Fig. 3. The arrangement of the cations and anions in  $(\text{C}_6\text{N}_2\text{H}_{18})\text{Sb}_4\text{S}_7$ .

linked  $\text{SbS}_4$  units yielding a complex  $\text{Sb}_6\text{S}_{14}$  building block (Fig. 2). The individual layers are stacked along [001] with the diprotonated amine molecules lying in between (Fig. 3). The two N atoms of an amine molecule are directed towards S atoms of one thioantimonate(III) anion, *i.e.* the amines are oriented parallel to the anionic layers. Along [010] the orientation of the amines is ...up-down-up-down... to form a two molecules thick organic layer (Fig. 3) and the shortest interlayer distance amounts to 8.46 Å. All H atoms bound to the two N atoms are involved in  $\text{H}\cdots\text{S}$  bonding interactions with distances ranging from 2.369 to 2.997 Å with corresponding N-H...S angles between 120.46 and 167.32° (Table 4).

A short comparison with the hitherto known organically 'templated' compounds containing  $[\text{Sb}_4\text{S}_7]^{2-}$  anions is given here. The topology of the anionic network of the title compound is very similar with that of  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{Sb}_4\text{S}_7$  [25],  $(\text{CH}_3(\text{CH}_2)_2\text{NH}_3)_2\text{Sb}_4\text{S}_7$ ,  $(\text{CH}_3)_2\text{CHNH}_3)_2\text{Sb}_4\text{S}_7$ ,  $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2\text{Sb}_4\text{S}_7$ , and  $(\text{CH}_3(\text{CH}_2)_4\text{NH}_3)_2\text{Sb}_4\text{S}_7$  [28], and only small differences are observed for Sb-S bond lengths and S-Sb-S angles. But in all these compounds the structure directors are mono-amines. The structures of the two compounds with diamines,  $(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)_2\text{Sb}_4\text{S}_7$  and  $(\text{pipH}_2)_2\text{Sb}_4\text{S}_7$  as well as that of  $(\text{C}_6\text{H}_{20}\text{N}_4)_2\text{Sb}_4\text{S}_7$  with a tetramine contain a thioantimonate(III) chain anion. Therefore, the title compound is the first example with a layered  $[\text{Sb}_4\text{S}_7]^{2-}$  anion containing a diamine as structure director.

*Optical spectroscopy*

Charge compensation requires that the amine molecules are diprotonated in  $(\text{C}_6\text{N}_2\text{H}_{18})\text{Sb}_4\text{S}_7$ . In the IR spectrum the absorptions located at 1068, 1473, 1552, 1635, 2858, 3108 and 3400  $\text{cm}^{-1}$  are typical for  $\text{R-NH}_3^+$  groups. In the Raman spectrum (Fig. 4)

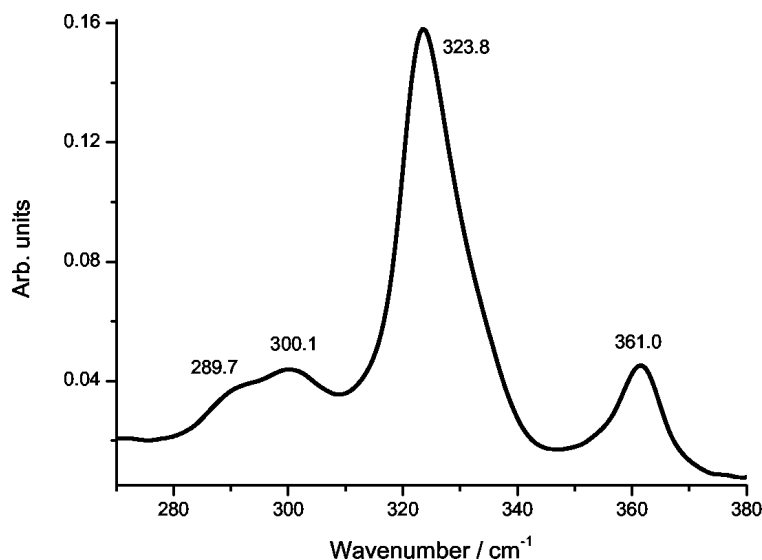


Fig. 4. Raman spectrum of  $(\text{C}_6\text{N}_2\text{H}_{18})\text{-Sb}_4\text{S}_7$ .

the most intense resonances are located at 323.8 and 361.0  $\text{cm}^{-1}$ . Weak bands are observed at 289.7 and 300.1  $\text{cm}^{-1}$ . The bands between 362 and 339  $\text{cm}^{-1}$  are typical for  $\text{SbS}_3$  units, while bands located at lower wave numbers are due to bonding interactions between  $\text{Sb(III)}$  and the next nearest S atoms [43, 44]. Pfitzner *et al.* explained resonances at 321  $\text{cm}^{-1}$  and about 290  $\text{cm}^{-1}$  with  $\text{SbS}_5$  units [43, 44]. In  $\text{MnSb}_2\text{S}_4$  the resonances are at even lower wave numbers of 300 and 283  $\text{cm}^{-1}$  which is due to the high coordination number of the Sb atoms [44]. The optical band gap of the compound was determined from the transformed UV/vis diffuse reflectance spectrum in the usual way (Kubelka-Munk relation). The optical band gap of about 1.9 eV indicates that the compound is an optical semiconductor.

### Summary

The new compound  $(\text{C}_6\text{N}_2\text{H}_{18})\text{Sb}_4\text{S}_7$  with diprotonated 1,6-diaminohexane molecules is a further example for the flexibility of thioantimonate(III) structures to adapt the size and charge requirements of the structure director. In the present compound the diamine molecules are parallel to the anionic layers with the  $\text{NH}_3^+$  groups oriented towards S atoms to ensure optimal  $\text{S} \cdots \text{H}$  bonding interactions. An interesting question is whether it is possible to synthesize a layered thioantimonate(III) with diamines which act as 'pillars' between neighboring layers. Syntheses with diamines with less conformational flexibility are under way to prove whether such thioantimonates(III) can be prepared.

- [1] K. Volk, H. Schäfer, Z. Naturforsch. **34b**, 1637 (1979).
- [2] X. Wang, F. Liebau, J. Solid State Chem. **111**, 385 (1994).
- [3] X. Wang, L. Liu, A. J. Jacobson, J. Solid State Chem. **155**, 409 (2000).
- [4] K. Tan, Y. Ko, J. B. Parise, Acta Crystallogr. **C50**, 1439 (1994).
- [5] Y. Ko, K. Tan, J. B. Parise, A. Darowsky, Chem. Mater. **8**, 493 (1996).
- [6] J. B. Parise, Science **251**, 293 (1991).
- [7] K. Volk, H. Schäfer, Z. Naturforsch. **34b**, 172 (1979).
- [8] J. B. Parise, Y. Ko, Chem. Mater. **4**, 1446 (1992).
- [9] M. Gostojic, W. Nowacki, P. Engel, Z. Kristallogr. **159**, 217 (1982).
- [10] L. Engelke, C. Näther, W. Bensch, Eur. J. Inorg. Chem. 2936 (2002).
- [11] J. Rijnberk, C. Näther, W. Bensch, Monatsh. Chem. **131**, 721 (2000).
- [12] R. Stähler, C. Näther, W. Bensch, Eur. J. Chem. 1835 (2001).
- [13] V. Spetzler, R. Kiebach, C. Näther, W. Bensch, Z. Anorg. Allg. Chem. **630**, 2398 (2004).
- [14] X. Wang, A. J. Jacobson, F. Liebau, J. Solid State Chem. **140**, 387 (1998).
- [15] H. A. Graf, H. Schäfer, Z. Naturforsch. **27b**, 735 (1972).
- [16] G. Dittmar, H. Schäfer, Z. Anorg. Allg. Chem. **437**, 183 (1977).

- [17] G. Dittmar, H. Schäfer, Z. Anorg. Allg. Chem. **441**, 93 (1978).
- [18] G. Dittmar, H. Schäfer, Z. Anorg. Allg. Chem. **441**, 98 (1978).
- [19] B. Eisenmann, H. Schäfer, Z. Naturforsch. **34b**, 383 (1979).
- [20] G. Cordier, H. Schäfer, C. Schwidetzky, Z. Naturforsch. **39b**, 131 (1984).
- [21] W.S. Sheldrick, H.-J. Häusler, Z. Anorg. Allg. Chem. **557**, 105 (1988).
- [22] H.-O. Stephan, M.G. Kanatzidis, Inorg. Chem. **36**, 6050 (1997).
- [23] W. Bensch, M. Schur, Z. Naturforsch. **52b**, 405 (1997).
- [24] P. Vaqueiro, D.P. Darlow, A.M. Chippindale, A.V. Powell, Solid State Ionics **172**, 601 (2004).
- [25] M. Schur, W. Bensch, Eur. J. Solid State Inorg. Chem. **34**, 457 (1997).
- [26] R. Stähler, C. Näther, W. Bensch, J. Solid State Chem. **174**, 264 (2003).
- [27] M. Schaefer, D. Kurowski, A. Pfitzner, C. Näther, W. Bensch, Acta Crystallogr. **E60**, m183 (2004).
- [28] A. Puls, M. Schaefer, C. Näther, W. Bensch, A.V. Powell, S. Boissière, A.M. Chippindale, J. Solid State Chem. **178**, 1171 (2005).
- [29] W.S. Sheldrick, H.-J. Häusler, Z. Anorg. Allg. Chem. **561**, 149 (1988).
- [30] J.B. Parise, J. Chem. Soc., Chem. Commun. 1553 (1990).
- [31] K. Volk, P. Bickert, R. Kolmer, H. Schäfer, Z. Naturforsch. **34b**, 380 (1979).
- [32] H. A. Graf, H. Schäfer, Z. Anorg. Allg. Chem. **414**, 211 (1975).
- [33] G. Cordier, C. Schwidetzky, H. Schäfer, J. Solid State Chem. **54**, 84 (1984).
- [34] R. Kiebach, F. Studt, C. Näther, W. Bensch, Eur. J. Inorg. Chem. 2553 (2004).
- [35] T.J. McCarthy, M.G. Kanatzidis, Inorg. Chem. **33**, 1205 (1994).
- [36] W. Bensch, C. Näther, R. Stähler, Chem. Commun. 477 (2001).
- [37] W.S. Sheldrick, J. Chem. Soc. Dalton Trans. 3041 (2000).
- [38] M. Schur, W. Bensch, Z. Naturforsch. **57b**, 1 (2002).
- [39] V. Spetzler, H. Rijnberk, C. Näther, W. Bensch, Z. Anorg. Allg. Chem. **630**, 142 (2004).
- [40] M. Schur, A. Gruhl, C. Näther, I. Jess, W. Bensch, Z. Naturforsch. **54b**, 1524 (1999).
- [41] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Determination, University of Göttingen, Germany (1997).
- [42] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany (1997).
- [43] A. Pfitzner, Chem. Eur. J. **3**, 2032 (1997).
- [44] A. Pfitzner, D. Kurowski, Z. Kristallogr. **215**, 373 (2000).