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The crystal structure of a thallium sulfosalt, $Tl_8Pb_4Sb_{21}As_{19}S_{68}$ *

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Abstract. $Tl_8Pb_4Sb_{21}As_{19}S_{68}$ is triclinic, space group $P\,1$, with $a = 16.320$ Å, $b = 42.636$ Å, $c = 8.543$ Å, $\alpha = 83.98°$, $\beta = 89.06°$, and $\gamma = 83.20°$. Starting from a one : eight substructure, the one : two substructure was solved by Patterson methods and was refined by ordinary Fourier and least-squares techniques. The final R value is 11.6% for 8.160 observed reflections.

The bulk of the structure consists of two similar kinds of Tl, Pb networks, both running // to (010). All Tl atoms are coordinated by nine S atoms. The coordination polyhedra around the Tl atoms are trigonal prisms with three additional S atoms against the three side faces. The coordination polyhedra around the Pb atoms are also trigonal prisms with one, two or three additional S atoms against one, two or three side faces. The SbS_3 and AsS_3 pyramids form isolated groups, corresponding to type Va_1 ($1 < \phi < 2$) of the classification of Nowacki (1968, 1969, 1970).

The average $Tl^{IX}-S$ distances range from 3.34 to 3.41 Å; the mean $Pb^{VII}-S$, $Pb^{VIII}-S$, and $Pb^{IX}-S$ distances are 3.03, 3.16, and 3.23 Å, respectively. The mean bond distances for $Sb-S$ in SbS_3 and $As-S$ in AsS_3 pyramids are from 2.45 to 2.68 Å, and from 2.26 to 2.39 Å, respectively.

Introduction

A specimen of a black Tl sulfosalt, labeled as "chabourneite" from Jas Roux, France was used for the present investigation. The purpose was to elucidate the coordination of sulfur atoms around the thallium atoms. They show quite an interesting feature when compared with the structures of sulfosalts already solved. Chabourneite was first described and investigated by Mantienne

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(1974). He determined the lattice constants $a = 16.33$ Å, $b = 8.530$ Å, $c = 21.24$ Å, $\alpha = 93.85°$, $\beta = 95.40°$, $\gamma = 104.48°$, space group $P1$ (or $P\bar{1}$) and the cell content 2 ($Tl_{4.5}Pb_{1.5}Sb_{13}As_8S_{38}$).

Preliminary crystal data obtained from oscillation and Weissenberg photographs, as well as electron-microprobe analyses, showed that the mineral investigated is not identical with chabourneite. Based upon the differences this crystallized natural mineral may be a new thallium sulfosalt or a variety of chabourneite.

Experimental

A prismatic single crystal of dimensions $0.13 \times 0.13 \times 0.22$ mm was chosen for the determination of the cell constants and the intensity measurements as well as the determination of the chemical composition by electron-microprobe analysis.

In Table 1 are given:

I. The composition determined by x-ray structure analysis $Tl_8Pb_4Sb_{21}As_{19}S_{68}$;

II, III, IV. The minimal, maximal, and mean values of the 15 electron-microprobe analyses of the sample investigated;

V, VI. Two electron-microprobe analyses of chabourneite by Mantienne (1974).

The lattice parameters, obtained by a least-squares refinement of angular settings of ten pairs of equivalent reflections (measured at room temperature within the range $5° < \theta < 10°$ with Mo$K\alpha$ radiation) are $a' = a = 16.320(3)$ Å, $b' = b/2 = 21.318(6)$ Å, $c' = c = 8.543(2)$ Å, $\alpha' = \alpha = 83.98(1)°$, $\beta' = \beta = 89.06(1)°$, and $\gamma' = \gamma = 83.20(1)°$. The crystal data are: space group: $P1$, $Z = 1$, $Tl_8Pb_4Sb_{21}As_{19}S_{68}$, $V = 2935.0$ Å^3, $D_x = 4.88$ gcm^{-3}, λ(Mo$K\alpha$) = 0.7107 Å, μ(Mo$K\alpha$) = 282.0 cm^{-1}, $F_{000} = 3762.0$, and cell mass $M = 8624.5$.

The x-ray films showed an intensity distribution characteristic for a superstructure with a substructure halving the a, b, and c directions.

Table 1. Calculated and observed weight percentages of the constituent elements of the Tl sulfosalt and of chabourneite, as investigated by electron-microprobe analyses

			Tl	Pb	Sb	As	S	Σ
I	$Tl_8Pb_4Sb_{21}As_{19}S_{68}$ Crystal-structure analysis		18.96	9.61	29.65	16.50	25.28	100.00
II	Electron-microprobe	min.	17.54	8.97	30.90	15.81	25.29	98.51
III	analyses	max.	18.51	9.92	31.56	16.22	26.13	102.34
IV		mean	18.08	9.36	31.28	15.95	25.77	100.44
V	Chabourneite		19.6	6.8	33.5	13.2	26.2	99.3
VI	(Mantienne, 1974)		21.6	7.0	33.2	13.2	25.3	100.3

Intensities with $h = 2n$, $k = 2n$, and $l = 2n$ were generally strong, and those with $h = 2n + 1$, $l = 2n + 1$, and a small number of intensities with $k = 2n + 1$ were generally weak; so we collected data for the subcell a, c, and $b/2 = 21.318$ Å.

The intensities were measured by the ω-scan technique at room temperature on a Philips PW 1100 four-circle, automatic, computer-controlled diffractometer with graphite-monochromatized Mo$K\alpha$ radiation. The intensities and ω angles of three standard reflections, measured periodically every 2 h, showed no appreciable variation during the course of the data collection. The integration speed was $0.04° s^{-1}$ and the integration interval $1.2° \theta$. Of the 18,359 measured reflections (8,995 observed) within the range $3° < \theta < 30°$, 8,160 independent reflections with intensity greater than $2.5\sigma(I)$ were used for the structure determination.

Structure determination and refinement

Wilson statistics for the substructure data in the cell $a/2$, $b/2$, and $c/2$ (using only reflections with $h = 2n$, $l = 2n$) were calculated. The result showed the space group to be ambiguously centrosymmetric. One Tl and three Sb atom positions were determined from a three-dimensional Patterson synthesis. A further Sb atom and seven S atoms were located by subsequent series of Fourier syntheses and least-square refinements in space group $P\bar{1}$. A structure-factor calculation with atomic coordinates yielded an R value of 34% for all 3,085 reflections with $h = 2n$, $l = 2n$. This level of refinement was considered to be sufficient to start the solution of the substructure in the cell $a/2$, $b/2$, c. But attempts to refine this substructure by the least-squares method in space group $P\bar{1}$ were not successful. The space group was changed and a structure-factor calculation with 4 Tl, 16 Sb, 4 As and 28 S atoms yielded an R value of 22% for all 4,781 reflections with $h = 2n$. A three-dimensional Fourier synthesis computed with these atoms showed up another six sulfur atoms. Least-squares refinements to improve the positional and thermal parameters reduced the R value to 15%. No attempts were made to distinguish between thallium and lead at this stage.

Further block-diagonal, least-squares refinements of the structure in the cell a, $b/2$, c started with the initial R value of 42% for all 8,160 observed reflections. Fourier and difference Fourier syntheses as well as the calculated interatomic distances among heavy atoms showed up 1 Sb and 3 As atoms, and twelve positions of Sb atoms presumably positions of 4 Pb atoms and 8 As atoms. After a series of isotropic block-diagonal, least-squares refinements, the R value fell to 14.5%. The refinement was continued with anisotropic thermal parameters for all non-sulfur atoms. At this point the data were also corrected for absorption, and, as would be expected, the isotropic thermal parameters of sulfur atoms were refined much better. The atomic coordinates changed only slightly without significant influence on the bond distances. A unit weight was assumed for all observations, and the final

R value was 11.6 %. This relatively high R value presumably is due partially to the fact that we are dealing with a substructure. The number of parameters to be determinated (1,481) in the true structure lies outside of the posibility for refinement. A final difference Fourier map showed no significant peaks. The neutral-atom scattering factors were taken from Lonsdale (1962). The table containing observed and calculated structure factors may be obtained from the author.

Description of the structure

The values obtained for the atomic positions and temperature factors with e.s.d.'s are given in Table 2. The atomic coordinates listed in this Table were used to calculate bond lengths (Table 3) and bond angles (Table 4).

The arrangement of the atoms projected down the a axis (given in Fig. 1) shows the two layers present in the structure at approximately $y \sim 0.3$ and 0.7. The two layers (Figs. 2 and 3) are very similar networks of Tl and of Pb atoms. The coordination polyhedra around all the Tl atoms in both networks are trigonal prisms with three additional S atoms against the three side faces. These prisms with common bases build infinite chains // to the c axis. The coordination polyhedra around the Pb atoms are similar to the Tl polyhedra, but the number of additional S atoms against the side faces of the prisms varies from one to three. In the first layer at $y \sim 0.3$, seven-coordinated Pb(1) with Tl(1) and Tl(3), as well as eight-coordinated Pb(2) with Tl(4) and Tl(2), build infinite networks over the two common edges [S(13), S(14) and S(21), S(22)] and two common surfaces [S(25), S(26), S(27) and S(17), S(18), S(20)] of their polyhedra (Fig. 2). A second network of Tl and Pb polyhedra in the layer at $y \sim 0.7$ (Fig. 3) is built in a similar way. Here the nine-coordinated Pb(3) is connected with Tl(5) and Tl(7) over the two common surfaces [S(37), S(39), S(40) and S(51), S(52), S(63)], and the eight-coordinated Pb(4) with Tl(6) and Tl(8) over the one edge [S(43), S(44)] and one surface [S(46), S(47), S(48)] of their polyhedra.

The nine Tl – S bonds increase progressively in the interval 3.16 – 3.74 Å (Table 3). The average values of the nine Tl – S distances in the Tl polyhedra range from 3.34 to 3.41 Å, in good agreement with the value of 3.32 Å for the sum of the ionic radii of Tl^+ and S^{2-} found in TlS (Hahn and Klingler, 1949), suggesting the bonding of Tl to be ionic in these structures. This structure is the first sulfosalt structure with a nine-fold coordinated Tl. The environment of the Tl atoms is somewhat similar to the environment of Tl in imhofite (Divjaković and Nowacki, 1976), where the Tl polyhedron is a prism with two additional S atoms against two side faces, with an average Tl – S distance of 3.36 Å.

The Tl atoms in this sulfosalt have a tendency to interact with each other as in the Tl-bearing sulfosalts vrbaite (Ohmasa and Nowacki, 1971; Tl – Tl = 3.75 Å), hatchite (Marumo and Nowacki, 1967; Tl – Tl = 3.78 Å) and lorandite (Fleet, 1973; Tl – Tl = 3.54 and 4.03 Å). In the present structure the

Table 2. Final positional and thermal parameters ($\times 10^4$, except thermal parameters of sulfur atoms). The anisotropic temperature factor is exp $[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$. Standard deviations in units of the last significant digits are given in parentheses

Atom	x	y	z	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Tl(1)	2448(4)	3152(3)	4230(7)	38(3)	15(1)	120(9)	− 9(3)	−41(8)	−19(5)
Tl(2)	2388(3)	3147(2)	9060(5)	23(2)	8(1)	56(6)	− 7(2)	−19(5)	− 5(4)
Tl(3)	7341(3)	3219(2)	4106(6)	32(2)	12(1)	87(7)	−18(3)	−45(7)	0(5)
Tl(4)	7351(3)	3183(2)	9264(6)	18(2)	13(1)	98(8)	−11(2)	− 1(6)	−18(5)
Tl(5)	2773(3)	6892(2)	685(6)	31(2)	13(1)	81(7)	−16(3)	−23(6)	−12(5)
Tl(6)	2743(3)	6849(2)	5527(5)	16(2)	9(1)	75(7)	− 3(2)	− 3(5)	−19(4)
Tl(7)	7692(3)	6856(3)	589(7)	24(2)	16(1)	122(9)	− 6(3)	−18(7)	−27(5)
Tl(8)	7753(3)	6853(2)	5817(5)	18(2)	7(1)	70(6)	− 9(2)	−15(5)	− 2(4)
Pb(1)	23(3)	2224(2)	4399(7)	24(2)	9(1)	166(10)	− 4(2)	−10(7)	19(5)
Pb(2)	5045(3)	2246(2)	9247(6)	21(2)	9(1)	87(7)	− 5(2)	−33(6)	3(4)
Pb(3)	103(3)	7810(2)	613(6)	30(2)	10(1)	103(8)	−12(2)	−51(7)	5(4)
Pb(4)	5074(4)	7798(3)	5287(7)	26(2)	13(1)	161(10)	− 8(3)	−19(8)	12(6)
Sb(1)	1594(5)	597(3)	9426(9)	15(3)	6(2)	68(11)	− 7(3)	−39(9)	− 6(6)
Sb(2)	3305(4)	1296(3)	2156(8)	9(3)	9(2)	36(9)	− 8(3)	−13(7)	2(6)
Sb(3)	6598(6)	653(4)	9365(11)	25(4)	12(2)	123(14)	−11(4)	−52(12)	−32(8)
Sb(4)	8349(6)	1184(4)	2196(9)	35(4)	10(2)	55(11)	−11(4)	−54(11)	7(7)
Sb(5)	4968(5)	2358(4)	4173(10)	27(4)	11(2)	85(12)	−12(4)	−44(11)	− 6(8)
Sb(6)	9918(6)	2298(4)	9639(10)	36(4)	6(2)	77(12)	−14(4)	−55(11)	5(7)
Sb(7)	112(5)	3918(3)	6521(8)	13(3)	8(2)	54(10)	− 6(3)	−14(8)	− 8(6)
Sb(8)	5078(4)	3942(3)	1575(8)	13(3)	7(2)	55(10)	−10(3)	−23(8)	− 5(6)
Sb(9)	1664(4)	5234(4)	1142(9)	18(3)	8(2)	69(11)	−11(4)	−36(9)	− 3(7)
Sb(10)	3445(4)	4860(3)	8690(8)	9(2)	5(1)	42(9)	− 5(3)	−23(7)	− 4(5)
Sb(11)	6681(5)	5221(3)	6155(9)	21(3)	6(2)	62(10)	−12(3)	−40(9)	− 7(6)
Sb(12)	8478(4)	4857(3)	3703(8)	10(2)	9(2)	33(9)	− 8(3)	−11(7)	−10(6)
Sb(13)	78(4)	6095(3)	8276(8)	12(3)	6(1)	39(9)	−10(3)	−18(7)	− 4(5)
Sb(14)	5036(4)	6151(3)	3291(8)	13(3)	7(2)	50(9)	−10(3)	−22(8)	3(6)
Sb(15)	180(4)	7655(3)	5751(8)	6(2)	5(1)	39(9)	1(3)	− 3(7)	− 6(5)
Sb(16)	5197(5)	7686(4)	633(10)	22(3)	6(2)	112(13)	− 8(4)	−57(11)	0(7)
Sb(17)	1801(5)	8779(4)	7636(9)	17(3)	15(2)	44(10)	−11(4)	−13(9)	− 5(7)
Sb(18)	6749(4)	8735(3)	2519(8)	12(3)	8(2)	36(9)	− 5(3)	−22(8)	−12(6)
Sb(19)	6855(5)	8821(4)	7720(9)	18(3)	11(2)	68(11)	− 5(4)	− 6(9)	− 6(7)
Sb(20)	8346(5)	9321(4)	4760(9)	31(4)	13(2)	58(11)	−26(4)	−48(10)	− 8(7)
Sb(21)	4873(5)	9805(5)	7350(9)	19(3)	25(3)	42(10)	− 5(4)	−51(9)	−22(8)
As(1)	224(8)	348(7)	2583(15)	13(5)	18(4)	55(17)	− 6(4)	−15(14)	−33(13)
As(2)	1708(7)	698(5)	5146(13)	6(4)	9(3)	28(14)	−16(5)	−12(11)	−11(9)
As(3)	3293(6)	1340(5)	7254(12)	8(4)	3(2)	37(14)	−10(5)	−16(12)	4(9)
As(4)	5281(7)	411(5)	2450(12)	7(4)	7(2)	27(14)	− 4(5)	−16(12)	− 9(9)
As(5)	6776(7)	772(5)	5077(12)	6(4)	8(3)	20(13)	−11(5)	13(11)	− 7(9)
As(6)	8342(6)	1407(5)	7391(13)	5(4)	9(3)	35(14)	−13(5)	− 3(11)	−20(10)
As(7)	156(7)	3728(5)	1632(12)	11(4)	4(2)	24(14)	− 8(5)	− 8(12)	− 6(9)
As(8)	5154(7)	3746(5)	6523(12)	10(4)	5(2)	20(13)	− 5(5)	−11(11)	− 4(9)
As(9)	1547(6)	4973(5)	6313(12)	8(4)	2(2)	24(13)	− 4(4)	−16(11)	− 3(8)
As(10)	3612(6)	5092(5)	3495(12)	8(4)	2(2)	23(13)	− 7(4)	−16(11)	5(8)
As(11)	6543(6)	4994(5)	1284(12)	5(4)	2(2)	23(13)	− 2(4)	−13(11)	− 4(8)
As(12)	8631(6)	5073(5)	8511(12)	7(4)	2(2)	20(13)	− 4(4)	−16(11)	− 3(8)

Table 2. (Continued)

Atom	x	y	z	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As(13)	11(7)	6299(5)	3273(11)	11(4)	3(2)	8(12)	−11(5)	− 6(11)	− 2(8)
As(14)	4931(7)	6339(5)	8253(12)	12(4)	5(2)	10(12)	−12(5)	−21(11)	− 4(8)
As(15)	1885(7)	8718(5)	2649(13)	9(4)	8(2)	39(15)	−15(5)	−27(12)	8(10)
As(16)	3574(7)	9431(5)	538(13)	6(4)	4(2)	48(15)	− 4(5)	11(12)	−13(9)
As(17)	3436(6)	9357(5)	4759(12)	5(4)	11(3)	30(14)	−13(5)	−28(11)	−21(10)
As(18)	8535(7)	9371(5)	667(13)	5(4)	4(2)	43(15)	1(5)	4(12)	−12(9)
As(19)	9865(7)	9686(6)	7392(12)	5(4)	17(3)	1(12)	−16(6)	−32(11)	− 4(10)
S(1)	1021(17)	1180(13)	2716(31)	1.2(4)					
S(2)	685(16)	1023(12)	6850(29)	0.9(4)					
S(3)	2407(16)	1635(12)	5049(29)	0.9(4)					
S(4)	2271(16)	1602(12)	9219(30)	1.0(4)					
S(5)	4464(16)	834(12)	277(30)	1.1(4)					
S(6)	4199(16)	723(12)	4323(30)	1.1(4)					
S(7)	6014(17)	1291(13)	2759(31)	1.3(4)					
S(8)	5787(15)	1065(11)	6919(28)	0.8(4)					
S(9)	7480(17)	1704(13)	5045(31)	1.3(4)					
S(10)	7352(16)	1596(12)	9234(30)	1.0(4)					
S(11)	9462(16)	778(12)	287(30)	1.0(4)					
S(12)	9203(17)	592(13)	4397(31)	1.3(4)					
S(13)	1012(17)	2746(13)	1885(31)	1.2(4)					
S(14)	931(16)	2864(12)	6819(29)	1.0(4)					
S(15)	2814(17)	4305(12)	1019(31)	1.2(4)					
S(16)	2802(16)	4387(12)	6585(29)	0.9(4)					
S(17)	3848(17)	2446(12)	1955(31)	1.2(4)					
S(18)	3808(16)	2271(12)	6904(29)	1.0(4)					
S(19)	4336(16)	3501(12)	4571(30)	1.0(4)					
S(20)	4384(15)	3535(12)	8666(29)	0.9(4)					
S(21)	5888(16)	2886(12)	1883(29)	0.9(4)					
S(22)	6005(17)	2817(13)	6729(31)	1.3(4)					
S(23)	7815(16)	4376(12)	1511(29)	0.9(4)					
S(24)	7811(16)	4310(12)	6040(29)	1.0(4)					
S(25)	8723(16)	2300(12)	1877(30)	1.0(4)					
S(26)	8779(16)	2398(12)	7168(30)	1.1(4)					
S(27)	9350(16)	3498(12)	3690(29)	1.0(4)					
S(28)	9406(16)	3462(12)	9575(30)	1.0(4)					
S(29)	1011(16)	4438(12)	4488(30)	1.0(4)					
S(30)	950(16)	4418(12)	8411(29)	0.9(4)					
S(31)	4276(16)	5579(12)	1429(29)	1.0(4)					
S(32)	4084(16)	5656(12)	5393(30)	1.1(4)					
S(33)	5948(15)	4457(11)	3403(30)	0.7(4)					
S(34)	5966(15)	4450(11)	9504(28)	0.8(4)					
S(35)	9043(15)	5662(11)	384(28)	0.7(4)					
S(36)	9270(15)	5586(11)	6384(29)	0.8(4)					
S(37)	794(16)	6559(12)	1068(29)	0.9(4)					
S(38)	825(16)	6552(12)	5329(29)	0.9(4)					
S(39)	1452(16)	7728(12)	2772(30)	1.0(4)					
S(40)	1277(16)	7692(12)	7736(30)	1.1(4)					
S(41)	2335(16)	5708(12)	3282(29)	0.9(4)					
S(42)	2345(17)	5739(13)	8750(31)	1.2(4)					

Table 2. (Continued)

Atom	x	y	z	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(43)	4230(16)	7168(12)	2933(30)	1.1.(4)					
S(44)	4121(17)	7222(13)	8034(31)	1.3(4)					
S(45)	5787(15)	6601(12)	206(29)	0.9(4)					
S(46)	5778(15)	6495(12)	6159(29)	0.9(4)					
S(47)	6338(16)	7610(12)	2582(29)	0.9(4)					
S(48)	6305(15)	7854(11)	7965(28)	0.7(4)					
S(49)	7310(16)	5761(12)	3813(30)	1.0(4)					
S(50)	7356(15)	5661(12)	8227(29)	0.9(4)					
S(51)	9085(16)	7139(12)	3069(30)	1.0(4)					
S(52)	9296(16)	7174(12)	7843(29)	1.0(4)					
S(53)	833(16)	9320(12)	5589(30)	1.0(4)					
S(54)	755(16)	9209(12)	9457(30)	1.1(4)					
S(55)	2835(15)	8514(12)	752(29)	0.9(4)					
S(56)	2736(16)	8467(12)	4765(30)	1.1(4)					
S(57)	2633(15)	51(12)	1951(29)	0.9(4)					
S(58)	2586(16)	21(12)	7856(29)	1.0(4)					
S(59)	4409(16)	9100(12)	2846(29)	1.0(4)					
S(60)	4179(17)	8814(13)	7072(32)	1.3(4)					
S(61)	5878(16)	9373(12)	5520(31)	1.1(4)					
S(62)	5772(14)	9334(11)	9420(27)	0.6(4)					
S(63)	7873(16)	8427(12)	576(30)	1.1(4)					
S(64)	7644(16)	8389(12)	4714(30)	1.1(4)					
S(65)	7566(17)	9887(13)	2045(31)	1.3(4)					
S(66)	7657(16)	115(12)	7842(31)	1.1(4)					
S(67)	9419(15)	9018(11)	2836(28)	0.8(4)					
S(68)	9128(17)	8748(12)	7237(31)	1.2(4)					

Table 3. Interatomic distances in the Tl sulfosalt. Standard deviations are given in parentheses

Tl(1)	−S(3)	3.25(3) Å	Tl(2)	−S(14)	3.23(3) Å
	−S(19)	3.28(3)		−S(15)	3.27(3)
	−S(17)	3.30(3)		−S(4)	3.31(3)
	−S(13)	3.36(3)		−S(16)	3.34(3)
	−S(14)	3.36(3)		−S(30)	3.37(3)
	−S(29)	3.41(3)		−S(13)	3.38(3)
	−S(18)	3.46(3)		−S(18)	3.44(3)
	−S(15)	3.58(3)		−S(20)	3.46(3)
	−S(16)	3.58(3)		−S(17)	3.55(3)
Mean (9)		(3.40)	Mean (9)		(3.37)
Tl(3)	−S(24)	3.16(3) Å	Tl(4)	−S(21)	3.32(3) Å
	−S(22)	3.22(3)		−S(26)	3.32(3)
	−S(9)	3.23(3)		−S(22)	3.32(3)
	−S(21)	3.25(3)		−S(34)	3.33(3)
	−S(33)	3.28(3)		−S(10)	3.39(3)
	−S(23)	3.29(3)		−S(25)	3.44(3)

Table 3. (Continued)

Tl(3)	–S(27)	3.41(3)	Tl(4)	–S(28)	3.49(3)
	–S(25)	3.49(3)		–S(23)	3.50(3)
	–S(26)	3.70(3)		–S(24)	3.59(3)
Mean (9)		(3.34)	Mean (9)		(3.41)
Tl(5)	–S(44)	3.21(3) Å	Tl(6)	–S(32)	3.16(3) Å
	–S(43)	3.23(3)		–S(38)	3.28(3)
	–S(42)	3.25(3)		–S(43)	3.34(3)
	–S(39)	3.26(3)		–S(44)	3.35(3)
	–S(41)	3.32(3)		–S(41)	3.38(3)
	–S(37)	3.39(3)		–S(39)	3.43(3)
	–S(55)	3.48(3)		–S(56)	3.44(3)
	–S(31)	3.51(3)		–S(40)	3.47(3)
	–S(40)	3.68(3)		–S(42)	3.54(3)
Mean (9)		(3.37)	Mean (9)		(3.38)
Tl(7)	–S(47)	3.16(3) Å	Tl(8)	–S(49)	3.19(3) Å
	–S(35)	3.18(3)		–S(50)	3.22(3)
	–S(45)	3.25(3)		–S(51)	3.23(3)
	–S(51)	3.28(3)		–S(52)	3.26(3)
	–S(63)	3.40(3)		–S(64)	3.30(3)
	–S(50)	3.51(3)		–S(46)	3.40(3)
	–S(49)	3.52(3)		–S(36)	3.44(3)
	–S(52)	3.56(3)		–S(48)	3.60(3)
	–S(48)	3.57(3)		–S(47)	3.74(3)
Mean (9)		(3.38)	Mean (9)		(3.38)
Pb(1)	–S(27)	2.81(3) Å	Pb(2)	–S(20)	2.83(3) Å
	–S(13)	2.87(3)		–S(18)	2.86(3)
	–S(25)	3.03(3)		–S(22)	2.89(3)
	–S(1)	3.07(3)		–S(17)	3.04(3)
	–S(14)	3.08(3)		–S(21)	3.17(3)
	–S(26)	3.12(3)		–S(5)	3.29(3)
	–S(2)	3.23(3)		–S(8)	3.47(3)
				–S(7)	3.71(3)
Mean (7)		(3.03)	Mean (8)		(3.16)
Pb(3)	–S(37)	2.76(3) Å	Pb(4)	–S(46)	2.90(3) Å
	–S(39)	2.87(3)		–S(43)	2.97(3)
	–S(51)	3.01(3)		–S(60)	3.00(3)
	–S(40)	3.10(3)		–S(44)	3.03(3)
	–S(52)	3.22(3)		–S(48)	3.09(3)
	–S(54)	3.33(3)		–S(47)	3.10(3)
	–S(67)	3.43(3)		–S(59)	3.37(3)
	–S(68)	3.61(3)		–S(61)	3.77(3)
	–S(63)	3.72(3)			
Mean (9)		(3.23)	Mean (8)		(3.15)

Table 3. (Continued)

Sb(1)	−S(58)	2.39(3) Å	Sb(2)	−S(6)	2.50(3) Å
	−S(4)	2.51(3)		−S(5)	2.63(3)
	−S(2)	2.69(3)		−S(17)	2.69(3)
Mean (3)		(2.53)	Mean (3)		(2.61)
Sb(1)	−S(57)	2.83(3)	Sb(2)	−S(3)	2.96(3)
	−S(1)	3.27(3)		−S(57)	3.01(3)
	−S(54)	3.40(3)		−S(4)	3.02(3)
Sb(3)	−S(66)	2.40(3) Å	Sb(4)	−S(12)	2.50(3) Å
	−S(10)	2.47(3)		−S(25)	2.51(3)
	−S(8)	2.51(3)		−S(11)	2.56(3)
Mean (3)		(2.46)	Mean (3)		(2.52)
Sb(3)	−S(65)	3.02(3)	Sb(4)	−S(10)	3.03(3)
	−S(62)	3.26(3)		−S(9)	3.04(3)
	−S(7)	3.41(3)		−S(65)	3.20(3)
Sb(5)	−S(19)	2.58(3) Å	Sb(6)	−S(28)	2.52(3) Å
	−S(17)	2.63(3)		−S(25)	2.71(3)
	−S(21)	2.68(3)		−S(26)	2.81(3)
Mean (3)		(2.63)	Mean (3)		(2.68)
Sb(5)	−S(18)	2.99(3)	Sb(6)	−S(13)	2.95(3)
	−S(7)	3.02(3)		−S(14)	3.12(3)
	−S(22)	3.09(3)		−S(11)	3.40(3)
	−S(8)	3.57(3)		−S(1)	3.70(3)
Sb(7)	−S(14)	2.47(3) Å	Sb(8)	−S(21)	2.46(3) Å
	−S(29)	2.51(3)		−S(34)	2.51(3)
	−S(30)	2.53(3)		−S(33)	2.54(3)
Mean (3)		(2.50)	Mean (3)		(2.50)
Sb(7)	−S(28)	2.95(3)	Sb(8)	−S(19)	2.93(3)
	−S(27)	3.00(3)		−S(20)	3.00(3)
Sb(9)	−S(41)	2.51(3) Å	Sb(10)	−S(42)	2.44(3) Å
	−S(42)	2.51(3)		−S(16)	2.46(3)
	−S(15)	2.57(3)		−S(15)	2.48(3)
Mean (3)		(2.53)	Mean (3)		(2.46)
Sb(9)	−S(37)	3.00(3)	Sb(10)	−S(20)	3.05(3)
	−S(30)	3.35(3)		−S(31)	3.32(3)
				−S(32)	3.35(3)
Sb(11)	−S(50)	2.43(3) Å	Sb(12)	−S(24)	2.51(3) Å
	−S(49)	2.47(3)		−S(23)	2.54(3)
	−S(24)	2.52(3)		−S(49)	2.55(3)
Mean (3)		(2.47)	Mean (3)		(2.53)

Table 3. Continued)

Sb(11) −S(46)	2.93(3)	Sb(12) −S(27)	3.07(3)
−S(33)	3.31(3)	−S(36)	3.26(3)
−S(34)	3.41(3)	−S(35)	3.33(3)
Sb(13) −S(52)	2.49(3) Å	Sb(14) −S(43)	2.39(3) Å
−S(36)	2.51(3)	−S(31)	2.53(3)
−S(35)	2.62(3)	−S(32)	2.58(3)
Mean (3)	(2.54)	Mean (3)	(2.50)
Sb(13) −S(38)	2.91(3)	Sb(14) −S(46)	2.95(3)
−S(37)	2.98(3)	−S(45)	3.00(3)
Sb(15) −S(52)	2.49(3) Å	Sb(16) −S(45)	2.46(3) Å
−S(40)	2.50(3)	−S(47)	2.50(3)
−S(38)	2.52(3)	−S(43)	2.73(3)
Mean (3)	(2.50)	Mean (3)	(2.56)
Sb(15) −S(68)	3.10(3)	Sb(16) −S(48)	2.91(3)
−S(39)	3.26(3)	−S(44)	3.16(3)
−S(51)	3.28(3)		
−S(67)	3.73(3)		
Sb(17) −S(54)	2.45(3) Å	Sb(18) −S(64)	2.40(3) Å
−S(53)	2.47(3)	−S(63)	2.53(3)
−S(40)	2.56(3)	−S(47)	2.56(3)
Mean (3)	(2.49)	Mean (3)	(2.50)
Sb(17) −S(56)	2.96(3)	Sb(18) −S(65)	2.92(3)
−S(58)	3.10(3)	−S(62)	3.18(3)
−S(55)	3.14(3)	−S(61)	3.26(3)
Sb(19) −S(48)	2.33(3) Å	Sb(20) −S(64)	2.41(3) Å
−S(62)	2.50(3)	−S(67)	2.46(3)
−S(61)	2.58(3)	−S(68)	2.60(3)
Mean (3)	(2.47)	Mean (3)	(2.49)
Sb(19) −S(63)	2.97(3)	Sb(20) −S(65)	2.76(3)
−S(64)	3.03(3)	−S(12)	3.18(3)
−S(66)	3.20(3)	−S(66)	3.38(3)
Sb(21) −S(62)	2.38(3) Å		
−S(61)	2.42(3)		
−S(60)	2.55(3)		
Mean (3)	(2.45)		
Sb(21) −S(6)	3.20(3)		
−S(8)	3.21(3)		
−S(5)	3.50(3)		
As(1) −S(12)	2.31(3) Å	As(2) −S(2)	2.29(3) Å
−S(1)	2.33(3)	−S(3)	2.41(3)
−S(11)	2.38(3)	−S(1)	2.45(3)
Mean (3)	(2.34)	Mean (3)	(2.38)

Table 3. (Continued)

As(3)	−S(18)	2.24(3) Å	As(4)	−S(5)	2.34(3) Å
	−S(3)	2.38(3)		−S(7)	2.38(3)
	−S(4)	2.41(3)		−S(6)	2.44(3)
Mean (3)		(2.34)	Mean (3)		(2.39)
As(5)	−S(8)	2.31(3) Å	As(6)	−S(10)	2.27(3) Å
	−S(9)	2.41(3)		−S(26)	2.30(3)
	−S(7)	2.45(3)		−S(9)	2.45(3)
Mean (3)		(2.39)	Mean (3)		(2.34)
As(7)	−S(27)	2.23(3) Å	As(8)	−S(20)	2.24(3) Å
	−S(28)	2.31(3)		−S(22)	2.27(3)
	−S(13)	2.37(3)		−S(19)	2.29(3)
Mean (3)		(2.30)	Mean (3)		(2.27)
As(9)	−S(29)	2.27(3) Å	As(10)	−S(31)	2.28(3) Å
	−S(16)	2.27(3)		−S(32)	2.31(3)
	−S(30)	2.31(3)		−S(41)	2.33(3)
Mean (3)		(2.28)	Mean (3)		(2.31)
As(11)	−S(34)	2.29(3) Å	As(12)	−S(35)	2.29(3) Å
	−S(33)	2.30(3)		−S(50)	2.30(3)
	−S(23)	2.32(3)		−S(36)	2.32(3)
Mean (3)		(2.30)	Mean (3)		(2.30)
As(13)	−S(51)	2.20(3) Å	As(14)	−S(44)	2.16(3) Å
	−S(37)	2.32(3)		−S(46)	2.26(3)
	−S(38)	2.36(3)		−S(45)	2.35(3)
Mean (3)		(2.29)	Mean (3)		(2.26)
As(15)	−S(55)	2.26(3) Å	As(16)	−S(57)	2.32(3) Å
	−S(56)	2.28(3)		−S(55)	2.41(3)
	−S(39)	2.30(3)		−S(59)	2.41(3)
Mean (3)		(2.28)	Mean (3)		(2.38)
As(17)	−S(59)	2.32(3) Å	As(18)	−S(65)	2.21(3) Å
	−S(56)	2.33(3)		−S(67)	2.37(3)
	−S(60)	2.45(3)		−S(63)	2.40(3)
Mean (3)		(2.37)	Mean (3)		(2.33)
As(19)	−S(53)	2.31(3) Å			
	−S(54)	2.37(3)			
	−S(68)	2.47(3)			
Mean (3)		(2.38)			

Table 4. Bond angles in the Tl sulfosalt. Standard deviations are given in parentheses

S(14) – Tl(1) –	S(16)	85.2(7)°	S(13) – Tl(2) –	S(15)	89.6(7)°
S(14) –	S(18)	87.5(7)	S(13) –	S(17)	83.0(7)
S(16) –	S(18)	81.5(7)	S(15) –	S(17)	74.2(7)
S(13) –	S(15)	85.0(7)	S(14) –	S(16)	91.5(7)
S(13) –	S(17)	87.3(7)	S(14) –	S(18)	90.0(7)
S(15) –	S(17)	73.5(7)	S(16) –	S(18)	85.5(7)
S(14) –	S(13)	78.5(7)	S(13) –	S(14)	81.4(7)
S(16) –	S(15)	83.7(7)	S(15) –	S(16)	69.7(7)
S(18) –	S(17)	76.9(7)	S(17) –	S(18)	77.5(7)
S(29) –	S(14)	66.9(7)	S(30) –	S(13)	81.0(7)
S(29) –	S(13)	81.8(7)	S(30) –	S(14)	68.5(7)
S(29) –	S(15)	72.8(7)	S(30) –	S(16)	60.4(7)
S(29) –	S(16)	58.9(6)	S(30) –	S(15)	69.2(7)
S(19) –	S(16)	61.1(6)	S(20) –	S(15)	64.3(7)
S(19) –	S(15)	72.5(7)	S(20) –	S(16)	59.8(7)
S(19) –	S(17)	64.2(7)	S(20) –	S(18)	60.1(6)
S(19) –	S(18)	58.9(7)	S(20) –	S(17)	62.1(6)
S(3) –	S(18)	58.8(9)	S(4) –	S(17)	75.1(7)
S(3) –	S(17)	73.4(6)	S(4) –	S(18)	62.7(6)
S(3) –	S(13)	73.7(6)	S(4) –	S(14)	69.3(7)
S(3) –	S(14)	69.5(8)	S(4) –	S(13)	71.2(8)
S(29) –	S(19)	112.2(7)	S(30) –	S(20)	113.0(7)
S(29) –	S(3)	133.2(8)	S(30) –	S(4)	132.0(8)
S(19) –	S(3)	109.8(7)	S(20) –	S(4)	113.4(7)
S(22) – Tl(3) –	S(24)	91.6(7)	S(21) – Tl(4) –	S(23)	87.4(7)°
S(22) –	S(26)	81.3(7)	S(21) –	S(25)	86.9(7)
S(24) –	S(26)	75.3(7)	S(23) –	S(25)	80.4(7)
S(21) –	S(23)	92.1(7)	S(22) –	S(24)	82.8(7)
S(21) –	S(25)	87.2(7)	S(22) –	S(26)	85.9(7)
S(23) –	S(25)	82.6(7)	S(24) –	S(26)	75.0(7)
S(22) –	S(21)	79.4(7)	S(21) –	S(22)	83.5(7)
S(24) –	S(23)	73.4(7)	S(23) –	S(24)	82.8(7)
S(26) –	S(25)	78.5(6)	S(25) –	S(26)	72.7(7)
S(33) –	S(22)	81.8(7)°	S(34) –	S(21)	68.3(7)°
S(33) –	S(21)	69.6(7)	S(34) –	S(22)	82.9(7)
S(33) –	S(23)	62.7(8)	S(34) –	S(24)	74.5(7)
S(33) –	S(24)	71.7(7)	S(34) –	S(23)	61.1(6)
S(27) –	S(24)	66.1(7)	S(28) –	S(23)	61.0(6)
S(27) –	S(23)	60.9(7)	S(28) –	S(24)	71.6(6)
S(27) –	S(25)	58.8(7)	S(28) –	S(26)	61.1(7)
S(27) –	S(26)	63.8(6)	S(28) –	S(25)	56.6(7)
S(9) –	S(26)	57.9(9)	S(10) –	S(25)	66.6(8)
S(9) –	S(25)	64.2(6)	S(10) –	S(26)	61.2(7)
S(9) –	S(21)	80.9(7)	S(10) –	S(22)	67.3(7)
S(9) –	S(22)	67.2(8)	S(10) –	S(21)	78.5(7)
S(33) –	S(27)	116.3(7)	S(34) –	S(28)	115.0(7)
S(33) –	S(9)	140.6(10)	S(34) –	S(10)	137.5(7)
S(27) –	S(9)	103.1(7)	S(28) –	S(10)	107.0(7)

Table 4. (Continued)

S(41)	Tl(5)	S(39)	82.9(7)°	S(42)	Tl(6)	S(40)	76.1(7)°
S(41)		S(43)	90.0(7)	S(42)		S(44)	82.1(7)
S(39)		S(43)	89.1(7)	S(40)		S(44)	85.6(7)
S(42)		S(40)	77.0(7)	S(41)		S(39)	79.4(7)
S(42)		S(44)	88.9(8)	S(41)		S(43)	86.9(7)
S(40)		S(44)	84.3(7)	S(39)		S(43)	84.4(7)
S(41)		S(42)	72.1(7)	S(42)		S(41)	85.0(7)
S(39)		S(40)	76.8(7)	S(40)		S(39)	75.7(6)
S(43)		S(44)	81.0(7)	S(44)		S(43)	81.6(7)
S(37)		S(41)	60.9(7)	S(38)		S(42)	71.4(7)
S(37)		S(42)	65.5(7)	S(38)		S(41)	62.2(6)
S(37)		S(40)	62.4(6)	S(38)		S(39)	60.6(6)
S(37)		S(39)	59.5(7)	S(38)		S(40)	62.2(7)
S(55)		S(39)	59.0(7)	S(56)		S(40)	67.4(6)
S(55)		S(40)	73.6(7)	S(56)		S(39)	58.4(7)
S(55)		S(44)	76.5(7)	S(56)		S(43)	70.3(7)
S(55)		S(43)	68.7(7)	S(56)		S(44)	75.2(7)
S(31)		S(43)	67.4(7)	S(32)		S(44)	80.9(8)
S(31)		S(44)	79.3(7)	S(32)		S(43)	69.0(7)
S(31)		S(42)	70.1(7)	S(32)		S(41)	62.2(6)
S(31)		S(41)	61.8(7)	S(32)		S(42)	73.1(8)
S(37)		S(55)	109.7(6)	S(38)		S(56)	107.0(7)
S(37)		S(31)	115.0(7)	S(38)		S(32)	115.1(7)
S(55)		S(31)	132.3(8)	S(56)		S(32)	135.2(8)

S(49)	Tl(7)	S(47)	75.8(7)°	S(50)	Tl(8)	S(48)	88.5(7)°
S(49)		S(51)	79.7(7)	S(50)		S(52)	94.7(7)
S(47)		S(51)	88.4(7)	S(48)		S(52)	91.7(6)
S(50)		S(48)	84.8(6)	S(49)		S(47)	72.3(7)
S(50)		S(52)	84.7(6)	S(49)		S(51)	85.5(7)
S(48)		S(52)	87.4(6)	S(47)		S(51)	79.9(7)
S(49)		S(50)	86.2(7)	S(50)		S(49)	71.8(7)
S(47)		S(48)	71.1(6)	S(48)		S(47)	79.2(6)
S(51)		S(52)	81.3(6)	S(52)		S(51)	78.6(7)
S(45)		S(49)	74.8(7)	S(46)		S(50)	61.0(7)
S(45)		S(50)	63.8(6)	S(46)		S(49)	64.2(7)
S(45)		S(48)	57.8(6)	S(46)		S(47)	64.8(6)
S(45)		S(47)	62.3(7)	S(46)		S(48)	62.1(7)
S(63)		S(47)	65.2(7)	S(64)		S(48)	64.2(5)
S(63)		S(48)	66.3(8)	S(64)		S(47)	59.2(9)
S(63)		S(52)	74.2(7)	S(64)		S(51)	69.4(7)
S(63)		S(51)	67.1(7)	S(64)		S(52)	81.4(7)
S(35)		S(51)	78.6(7)	S(36)		S(52)	67.7(7)
S(35)		S(52)	67.4(6)	S(36)		S(51)	76.0(7)
S(35)		S(50)	59.6(6)	S(36)		S(49)	71.3(7)
S(35)		S(49)	74.1(7)	S(36)		S(50)	62.7(7)
S(45)		S(63)	111.8(7)	S(46)		S(64)	106.6(7)
S(45)		S(35)	116.0(7)	S(46)		S(36)	115.9(6)
S(63)		S(35)	131.4(7)	S(64)		S(36)	137.3(9)

Table 4. (Continued)

S(2)	Pb(1)	S(26)	79.1(8)°	S(7)	Pb(2)	S(17)	73.8(8)°
S(2)		S(14)	78.4(7)	S(7)		S(21)	58.4(7)
S(26)		S(14)	74.7(7)	S(17)		S(21)	70.1(8)
S(1)		S(25)	87.9(8)	S(8)		S(18)	75.1(8)
S(1)		S(13)	68.3(9)	S(8)		S(22)	72.4(9)
S(25)		S(13)	84.3(8)	S(18)		S(22)	85.3(8)
S(2)		S(1)	68.7(8)	S(7)		S(8)	90.2(7)
S(26)		S(25)	95.6(8)	S(17)		S(18)	95.7(8)
S(14)		S(13)	90.9(8)	S(21)		S(22)	93.7(8)
S(27)		S(26)	78.6(7)	S(5)		S(7)	61.8(9)
S(27)		S(25)	70.8(9)	S(5)		S(8)	64.1(5)
S(27)		S(13)	73.8(9)	S(5)		S(18)	81.8(7)
S(27)		S(14)	79.6(7)	S(5)		S(17)	75.5(8)
				S(20)		S(17)	76.1(7)
				S(20)		S(18)	74.7(9)
				S(20)		S(22)	72.8(9)
				S(20)		S(21)	77.4(7)
				S(5)		S(20)	140.8(11)
S(67)		S(39)	79.6(7)	S(60)		S(48)	78.6(7)°
S(67)		S(51)	78.7(8)	S(60)		S(44)	69.1(8)
S(39)		S(51)	91.1(8)	S(48)		S(44)	80.5(8)
S(68)		S(40)	71.4(8)	S(59)		S(47)	81.3(7)
S(68)		S(52)	57.8(7)	S(59)		S(43)	81.6(8)
S(40)		S(52)	67.9(8)	S(47)		S(43)	74.4(8)
S(67)		S(68)	88.5(7)	S(60)		S(59)	68.9(8)
S(39)		S(40)	92.7(8)	S(48)		S(47)	98.3(7)
S(51)		S(52)	91.6(8)	S(44)		S(43)	93.5(8)
S(54)		S(67)	64.5(6)	S(61)		S(60)	57.9(7)
S(54)		S(68)	61.9(9)	S(61)		S(59)	57.9(6)
S(54)		S(60)	70.0(7)	S(61)		S(47)	86.1(7)
S(54)		S(39)	81.9(7)	S(61)		S(48)	63.6(7)
S(37)		S(39)	71.8(9)	S(46)		S(48)	74.2(8)
S(37)		S(40)	77.3(7)	S(46)		S(47)	79.4(7)
S(37)		S(52)	77.0(7)	S(46)		S(43)	81.0(7)
S(37)		S(51)	72.7(9)	S(46)		S(44)	70.3(9)
S(63)		S(51)	65.6(7)	S(61)		S(46)	132.7(7)
S(63)		S(52)	74.1(6)				
S(63)		S(68)	57.7(6)				
S(63)		S(67)	60.7(6)				
S(54)		S(37)	136.7(10)				
S(54)		S(63)	95.2(6)				
S(37)		S(63)	127.6(8)				
S(58)	Sb(1)	S(4)	96.3(9)°	S(6)	Sb(2)	S(5)	84.9(9)°
S(58)		S(2)	90.4(9)	S(6)		S(17)	100.3(9)
S(4)		S(2)	90.9(9)	S(5)		S(17)	93.6(9)
Mean (3)			(92.5)	Mean (3)			(92.9)
S(66)	Sb(3)	S(10)	90.8(10)°	S(12)	Sb(4)	S(25)	107.1(10)°
S(66)		S(8)	91.1(10)	S(12)		S(11)	88.1(9)
S(10)		S(8)	92.9(9)	S(25)		S(11)	94.2(9)
Mean (3)			(91.6)	Mean (3)			(96.5)

Table 4. Continued)

S(19) – Sb(5) – S(17)	84.1(9)°	S(28) – Sb(6) – S(25)	77.9(8)°
S(19) – – S(21)	86.7(9)	S(28) – – S(26)	81.0(9)
S(17) – – S(21)	84.2(9)	S(25) – – S(26)	93.1(9)
Mean (3)	(85.0)	Mean (3)	(84.0)
S(14) – Sb(7) – S(29)	97.2(10)°	S(21) – Sb(8) – S(34)	97.3(9)°
S(14) – – S(30)	96.1(9)	S(21) – – S(33)	96.3(9)
S(29) – – S(30)	83.3(9)	S(34) – – S(33)	82.6(8)
Mean (3)	(92.2)	Mean (3)	(92.1)
S(41) – Sb(9) – S(42)	100.7(10)°	S(42) – Sb(10) – S(16)	94.1(9)°
S(41) – – S(15)	94.5(9)	S(42) – – S(15)	89.2(10)
S(42) – – S(15)	85.6(10)	S(16) – – S(15)	99.7(10)
Mean (3)	(93.6)	Mean (3)	(94.3)
S(50) – Sb(11) – S(49)	100.1(10)°	S(24) – Sb(12) – S(23)	99.7(10)°
S(50) – – S(24)	93.1(9)	S(24) – – S(49)	86.8(9)
S(49) – – S(24)	88.1(9)	S(23) – – S(49)	93.8(9)
Mean (3)	(93.8)	Mean (3)	(93.4)
S(52) – Sb(13) – S(36)	96.6(9)°	S(43) – Sb(14) – S(31)	98.8(9)°
S(52) – – S(35)	94.5(9)	S(43) – – S(32)	95.7(10)
S(36) – – S(35)	84.5(8)	S(31) – – S(32)	83.9(9)
Mean (3)	(91.9)	Mean (3)	(92.8)
S(52) – Sb(15) – S(40)	90.2(9)°	S(45) – Sb(16) – S(47)	83.9(9)°
S(52) – – S(38)	88.6(9)	S(45) – – S(43)	88.0(9)
S(40) – – S(38)	88.2(9)	S(47) – – S(43)	89.3(9)
Mean (3)	(89.0)	Mean (3)	(87.1)
S(54) – Sb(17) – S(53)	83.8(9)°	S(64) – Sb(18) – S(63)	92.0(9)°
S(54) – – S(40)	95.0(10)	S(64) – – S(47)	89.6(9)
S(53) – – S(40)	96.3(9)	S(63) – – S(47)	88.1(9)
Mean (3)	(91.7)	Mean (3)	(89.9)
S(48) – Sb(19) – S(62)	93.6(9)°	S(64) – Sb(20) – S(67)	95.9(10)°
S(48) – – S(61)	96.4(10)	S(64) – – S(68)	87.5(10)
S(62) – – S(61)	81.9(9)	S(67) – – S(68)	96.4(9)
Mean (3)	(90.6)	Mean (3)	(93.3)
S(62) – Sb(21) – S(61)	87.9(9)°		
S(62) – – S(60)	95.7(10)		
S(61) – – S(60)	84.8(10)		
Mean (3)	(89.5)		
S(12) – As(1) – S(1)	100.8(12)°	S(2) – As(2) – S(3)	96.4(10)°
S(12) – – S(11)	97.1(11)	S(2) – – S(1)	97.1(11)
S(1) – – S(11)	97.6(11)	S(3) – – S(1)	86.7(10)
Mean (3)	(98.5)	Mean (3)	(93.4)

Table 4. (Continued)

S(18) – As(3)	– S(3)	91.2(10)°	S(5) – As(4)	– S(7)	99.7(11)°
S(18) –	– S(4)	98.2(11)	S(5) –	– S(6)	92.7(10)
S(3) –	– S(4)	96.1(10)	S(7) –	– S(6)	93.7(11)
Mean (3)		(95.2)	Mean (3)		(95.4)
S(8) – As(5)	– S(9)	96.2(10)°	S(10) – As(6)	– S(26)	96.6(11)°
S(8) –	– S(7)	96.6(10)	S(10) –	– S(9)	98.1(11)
S(9) –	– S(7)	87.7(11)	S(26) –	– S(9)	90.6(11)
Mean (3)		(93.5)	Mean (3)		(95.1)
S(27) – As(7)	– S(28)	101.8(11)°	S(20) – As(8)	– S(22)	97.5(11)°
S(27) –	– S(13)	95.9(11)	S(20) –	– S(19)	101.4(11)
S(28) –	– S(13)	93.8(11)	S(22) –	– S(19)	96.5(11)
Mean (3)		(97.2)	Mean (3)		(98.5)
S(29) – As(9)	– S(16)	98.4(11)°	S(31) – As(10)	– S(32)	96.3(11)°
S(29) –	– S(30)	94.0(11)	S(31) –	– S(41)	99.4(10)
S(16) –	– S(30)	95.0(10)	S(32) –	– S(41)	93.8(10)
Mean (3)		(95.8)	Mean (3)		(96.5)
S(34) – As(11)	– S(33)	93.2(10)°	S(35) – As(12)	– S(50)	93.3(10)°
S(34) –	– S(23)	97.9(10)	S(35) –	– S(36)	96.9(10)
S(33) –	– S(23)	95.4(10)	S(50) –	– S(36)	97.3(10)
Mean (3)		(95.5)	Mean (3)		(95.8)
S(51) – As(13)	– S(37)	98.6(10)°	S(44) – As(14)	– S(46)	101.0(11)°
S(51) –	– S(38)	99.9(11)	S(44) –	– S(45)	96.8(12)
S(37) –	– S(38)	102.1(11)	S(46) –	– S(45)	98.3(11)
Mean (3)		(100.2)	Mean (3)		98.7)
S(55) – As(15)	– S(56)	97.8(11)°	S(57) – As(16)	– S(55)	96.1(10)°
S(55) –	– S(39)	93.6(11)	S(57) –	– S(59)	91.5(10)
S(56) –	– S(39)	94.3(11)	S(55) –	– S(59)	95.7(10)
Mean (3)		95.2)	Mean (3)		(94.4)
S(59) – As(17)	– S(56)	97.5(11)°	S(65) – As(18)	– S(67)	95.5(11)°
S(59) –	– S(60)	98.7(11)	S(65) –	– S(63)	96.9(11)
S(56) –	– S(60)	87.2(11)	S(67) –	– S(63)	98.7(10)
Mean (3)		(94.5)	Mean (3)		(97.0)
S(53) – As(19)	– S(54)	89.2(10)°			
S(53) –	– S(68)	90.4(10)			
S(54) –	– S(68)	95.3(11)			
Mean (3)		91.6)			

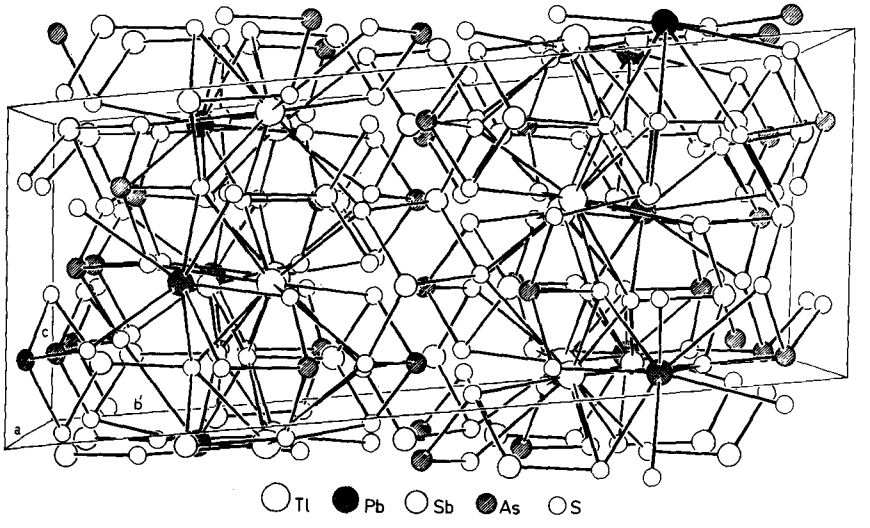

Fig. 1. Perspective view of the structure of $Tl_8Pb_4Sb_{21}As_{19}S_{68}$ as seen looking along the *a* direction in the center of the cell

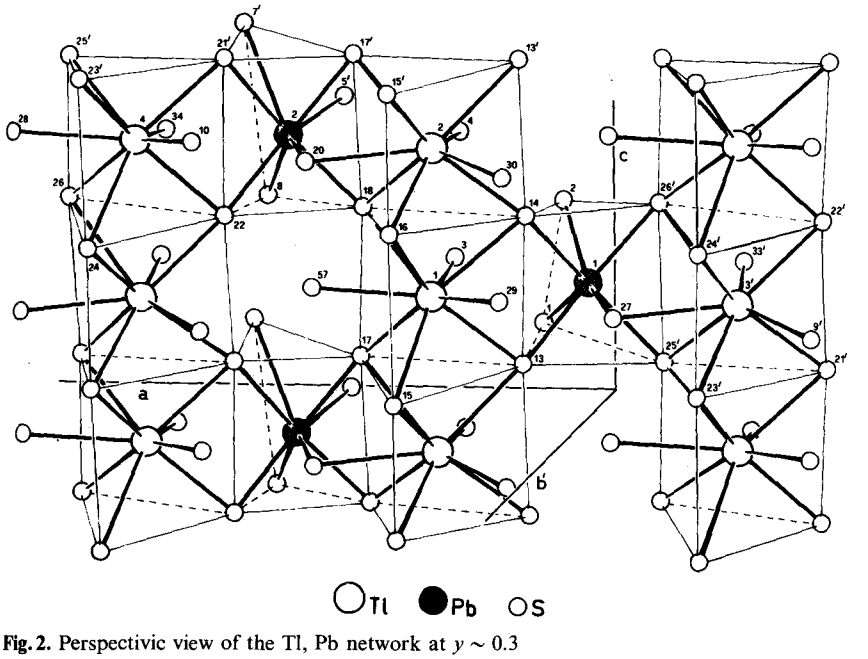

Fig. 2. Perspectivic view of the Tl, Pb network at $y \sim 0.3$

Tl atoms are connected via their common prismatic bases alternately by one shorter (4.13, 4.15, 4.13, and 4.08 Å) and one longer (4.42, 4.40, 4.42, and 4.47 Å) Tl–Tl distance.

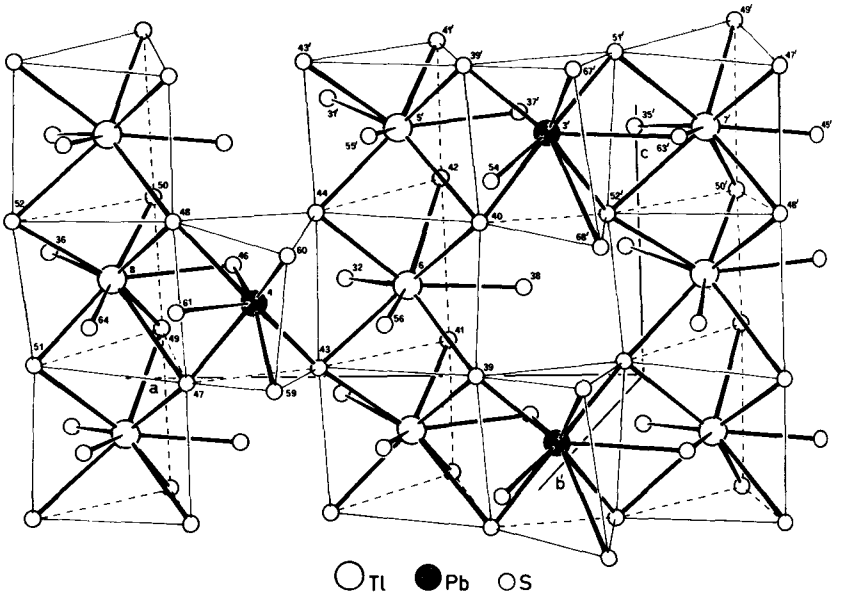

Fig. 3. Perspectivic view of the Tl, Pb network at $y \sim 0.7$

The Pb atoms are seven-coordinated in Pb(1), eight-coordinated in Pb(2) and Pb(4), and nine-coordinated in Pb(3), depending on the number of additional S atoms outside the prism in the direction perpendicular to the faces of the prism (Figs. 2 and 3). All Pb–S distances range between 2.76 and 3.77 Å. The average Pb–S distance for the Pb atom in seven-fold coordination (3.03 Å) is in agreement with the mean value of 3.04 Å for seven-coordinated Pb in many other sulfosalts (Edenharter, 1976). The average Pb–S distances for Pb in similar eight-fold coordination are: 3.18 Å in seligmannite (Edenharter and Nowacki, 1970), 3.11 and 3.15 Å in cosalite (Srikrishnan and Nowacki, 1974) and 3.14 Å in zinckenite (Portheine and Nowacki, 1975). The average Pb(2)–S and Pb(4)–S distances in this Tl sulfosalt, 3.16 Å, lie in the range of these values. The mean value for Pb–S distances (3.23 Å) of nine-fold coordinated Pb(3) is comparable with the mean values for this bond length with the same coordinated Pb ions in rathite I (Marumo and Nowacki, 1965; Pb–S = 3.19 Å), baumhauerite (Engel and Nowacki, 1969; Pb–S = 3.18 Å), dufrenoysite (Ribár, Nicca, and Nowacki, 1969; Pb–S = 3.18 Å), liveingite ≡ rathite II (Engel and Nowacki, 1970; Pb–S = 3.18 Å), and zinckenite (Portheine and Nowacki, 1975; Pb–S = 3.24 Å).

The Sb and As atoms in the structure are located in three layers (at $y \sim 0.1$, $y \sim 0.5$, and $y \sim 0.9$) as is shown in Figures 4, 5, and 6. Twenty-one Sb ions have five, six or seven S neighbors (Table 3) at distances smaller than

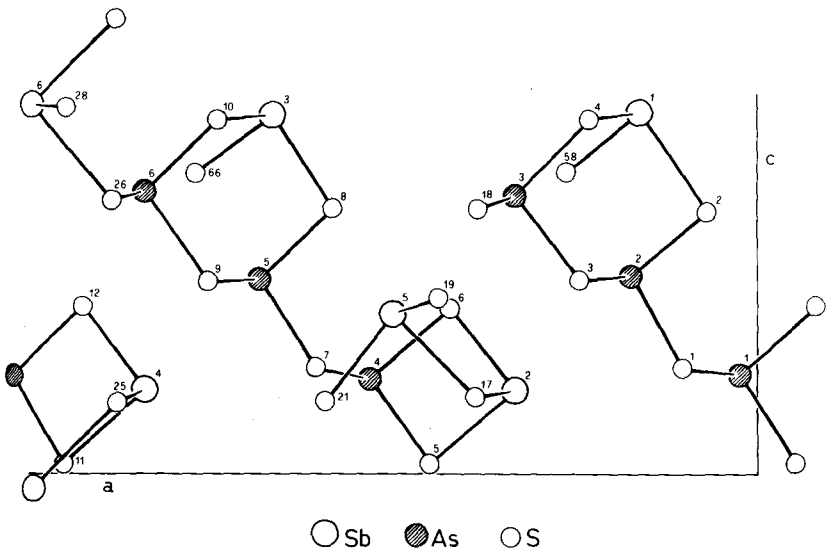

Fig. 4. (010) projection of the Sb, As layer at $y \sim 0.1$

the sum of the van der Waals' radii of Sb and S (2.2 + 1.85 = 4.05 Å). If the only nearest neighbors are taken, each Sb atom has a pyramidal coordination of three sulfurs, as do the 19 As atoms. The SbS_3 and AsS_3 pyramids in the sulfosalt build up two isolated groups. The factor ϕ, expressing the ratio of the number of sulfur to the metal atoms (Sb and As), is 1.7 and hence it falls under type V. a_1 with $1 < \phi < 2$ in the classification of the sulfosalts by Nowacki (1968, 1969, 1970).

As(15), As(16), As(17), Sb(19), and Sb(21) (Fig. 6) form one group of composition $Sb_2As_3S_9$, which is located at $y \sim 0.9$. All other SbS_3 and AsS_3 pyramids make up a second group of composition $Sb_{19}As_{16}S_{59}$, which is in the form of chains located in all three layers. SbS_3 and AsS_3 pyramids in the layers at $y \sim 0.1$ and $y \sim 0.5$ are connected through S(21) (Figs. 4 and 5). The layers at $y \sim 0.5$ and at $y \sim 0.9$ are bridged through two sulfur atoms S(43) and S(52) (Figs. 5 and 6). The four AsS_3 pyramids of As(7), As(8), As(13), and As(14), represented in Figure 5 (layer at $y \sim 0.5$), are not connected with other Sb, As pyramids of the same layer. However, they are included in a larger group as follows: As(7) and As(8) are connected with part of the group at $y \sim 0.1$ and the other two, As(13) and As(14), with part at $y \sim 0.9$ through the bridged sulfur atoms S(28) and S(19), as well as S(38) and S(45), respectively.

All Sb and As pyramids are connected with Tl and Pb polyhedra through the one, two or three common sulfur atoms. Of the total number of 68 sulfurs, only 9 are not connected to Tl or Pb. As is shown in Figure 7, the link between neighboring cells in the direction of the b axis is made by longer additional

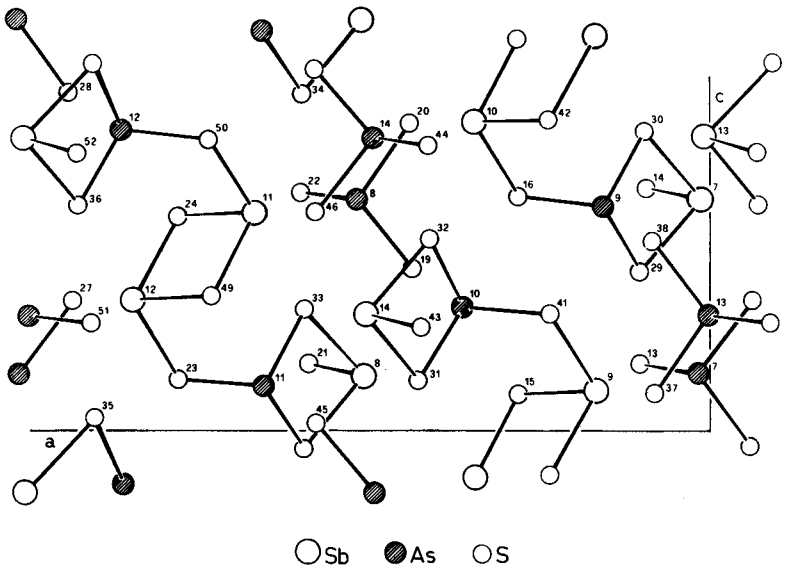

Fig. 5. (010) projection of the Sb, As layer at $y \sim 0.5$

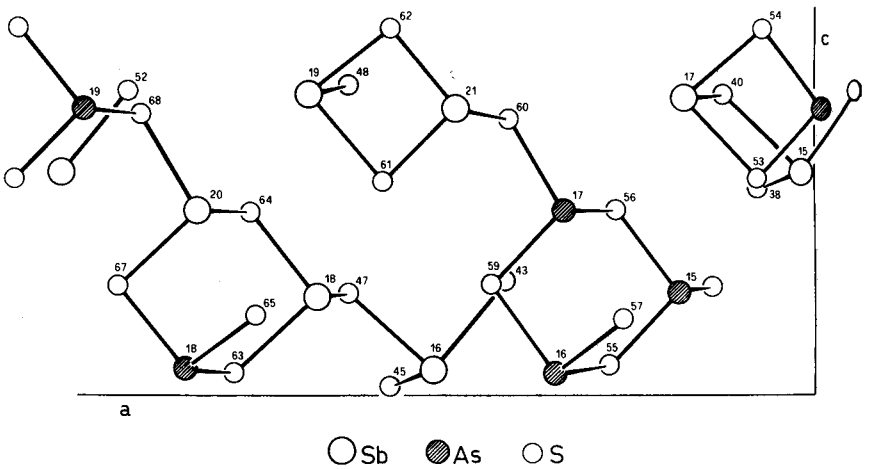

Fig. 6. (010) projection of the Sb, As layer at $y \sim 0.9$

Sb–S bonds in the range of 2.76 to 3.50 Å. The mean value of the standard deviations for all bond lengths given in Figure 7 is 0.03 Å.

The Sb atoms Sb(5), Sb(6), Sb(15), and Sb(16) alternate with Pb atoms in the c-axis direction. Three of them Sb(5), Sb(6), and Sb(15), are [3 + 4]-coordinated in a way similar to that in the structure of stibnite (Bayliss and Nowacki, 1972). The mean value of the three shortest Sb–S distances

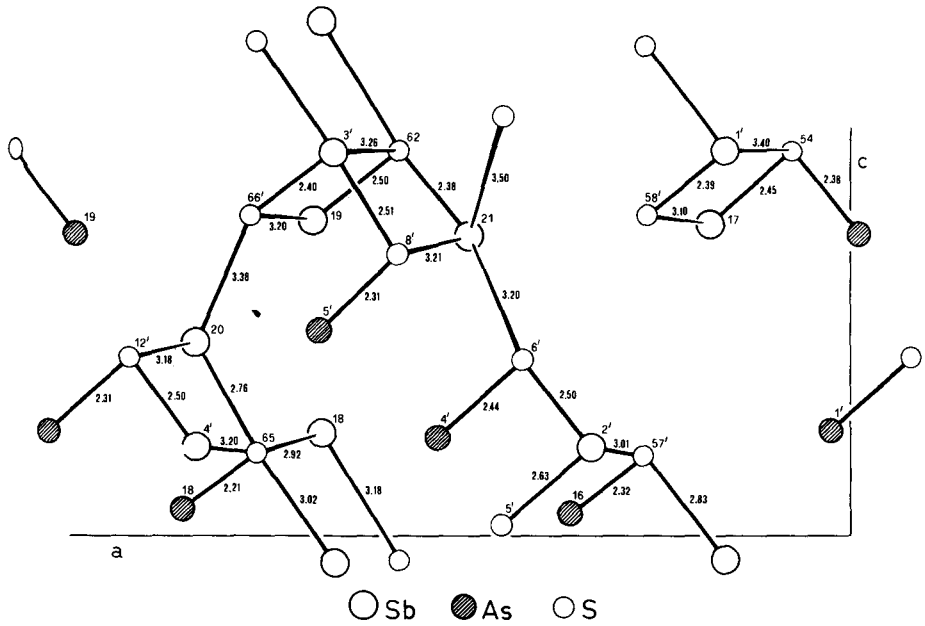

Fig. 7. Bonding between the Sb, As layer at $y \sim 0.9$ (unprimed atoms) and the layer at $y \sim 0.1$ (primed atoms with coordinates x, $y + 1$, z)

(2.67 Å) in the $Sb(6)S_3$ pyramid is much longer than the sum, 2.45 Å, of the covalent radii (Pauling, 1960), but comparable with the values found in aramayoite (Mullen and Nowacki, 1974; Sb–S = 2.67 Å) and livingstonite (Srikrishnan and Nowacki, 1975; Sb–S = 2.65 Å). All other Sb atoms build with their neighboring S atoms deformed square pyramids with [3 + 2]-coordination, or octahedra with [3 + 3]-coordination. The mean values for all Sb–S distances (2.52 Å) and S–Sb–S angles (91.3°) in SbS_3 pyramids, are in good agreement with the corresponding values derived from many sulfosalts (Edenharter, 1976; Sb–S = 2.52 Å, ∢ S–Sb–S = 93°).

The bond lengths and angles in all AsS_3 pyramids range from 2.16 to 2.47 Å, and from 86.7 to 102.1°, respectively.

We found, particularly in the layer at $y \sim 0.5$, that a mean As–S distance (2.29 Å) of AsS_3 pyramids with As(7), As(8), As(9), As(10), As(11), As(12), As(13), As(14), and As(15), is nearly equal to the value given by Camerman and Trotter (1964) for the As^{III}–S single-bond length (2.28 Å).

The average values for all distances and angles in the AsS_3 pyramids, 2.33 Å and 95.9°, are also in agreement with the mean values found for many other sulfosalts (Edenharter, 1976; As–S = 2.29 Å and ∢ S–As–S = 98.0°).

The computations were made on the IBM 370 computer of BEDAG (Bern) using the programs written by PD Dr. P. Engel (unpublished).

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