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Tl_2S: Re-Determination of Crystal Structure and Stereochemical Discussion

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The crystal structure of synthetic carlinite, Tl_2S, was re-determined by single crystal and powder X-ray diffraction methods. The cell parameters obtained from Rietveld refinement are $a = 12.150(2)$ Å, $c = 18.190(4)$ Å, $V = 2325.5(7)$ Å^3. A single crystal data refinement proved Tl_2S crystallizing in the trigonal space group $R3$ with $M = 440.8\,\mathrm{g\,mol^{-1}}$, $Z = 27$, $R = 0.076$, and $wR = 0.145$. The atomic arrangement found is that of a strongly deformed *anti*-CdI_2 type, but the deformation is clearly different from that given by previous workers. In the five crystallographically different STl_6 octahedra the S–Tl distances vary between 2.82 and 3.09 Å, the Tl–Tl edges between 3.52 and 4.58 Å. The common features of these octahedra are (i) each one with a definitely smaller vs larger Tl_3 face in *trans*-position, both faces parallel or sub-parallel (00.1), and (ii) each three shorter and longer S–Tl distances to the atoms of the larger and smaller Tl_3 faces, respectively. The Tl–Tl contacts between different Tl_2S sheets are on the average definitely shorter than the ones within the sheet and they can be smaller than the Tl–Tl contacts in the small Tl_3 faces of the STl_6 octahedra. The atomic arrangement indicates that the single electron pairs of the monovalent Tl atoms are not arranged all parallel to the *z*-axis, as one would expect for Tl_2S with an ideal *anti*-CdI_2 structure. The surrounding of the S atoms resembles that of one-third of the Cl atoms in yellow InCl. The absorbance of Tl_2S is very low at wave numbers approximately $< 9000\,\mathrm{cm^{-1}}$. © 2002 Elsevier Science (USA)

Key Words: **Tl_2S; carlinite; thallium stereochemistry; crystal structure refinement.**

INTRODUCTION

Synthetic Tl_2S is known to be a black, soft and extremely platy substance. In nature it was described as the rare mineral carlinite (1). Earlier crystal structure work (2, 3) has shown that the atomic arrangement is similar to that of the *anti*-CdI_2 type, but with lattice parameters *a* and *c* tripled. In the following, several investigations dealt with the high-temperature behavior of Tl_2S up to approximately 700°C (4, 5) and its polymorphism dependency on synthesis conditions (6). As the accuracy of the papers cited does not meet today's standards, we decided to re-determine the crystal structure of Tl_2S to gain a better basis for a stereochemical discussion.

EXPERIMENTAL

In a first step, a fine powder of Tl_2S was obtained by reaction of $TlNO_3$ with $(NH_4)_2S$. A strongly diluted, alkaline solution of $(NH_4)_2S$ was slowly added to an aqueous solution of $TlNO_3$ under continuous stirring at 30°C till no further precipitation was observed. The reaction product was washed several times with acetone and dried under vacuum (<0.1 mbar) at room temperature. In the subsequent treatment the powder was heated up to 600°C in a porcelain crucible inserted in a recipient of quartz glass under improved vacuum conditions (<0.01 mbar). The melt was then slowly cooled for 6 h to 400°C, kept for 12 h at this temperature, which is 48 °C below a given melting point (7) or 50°C below a rhombohedral to hexagonal phase transition (5), and finally cooled to room temperature within 6 h. The obtained regulus showed a strong metallic lustre and was composed of crystalline domains several mm in size. The crystal fragments exhibited a perfect cleavage parallel to (00.1) and could easily be deformed, which prohibited the separation of crystals suitable for work on conventional single-crystal diffractometers.

By careful parting several thin platelets of Tl_2S were isolated and inspected by Weissenberg and Precession photographs. Finally, a fragment with the approximate dimensions $100 \times 50 \times 5\,\mu\mathrm{m}^3$ was selected for single-crystal data collection. It was performed at room temperature with a Nonius Mach3 CCD diffractometer equipped with a 0.3 mm capillary optics collimator. The measured intensities were corrected for Lorentz and polarization effects, and a numerical absorption correction was applied. A trial

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TABLE 1
Crystal Data and Structure Refinement for Tl_2S

Crystallographic and sample data		Data collection and reduction	
Chemical formula	Tl_2S	Temperature (K)	293
Mol weight ($g\,mol^{-1}$)	440.8	Radiation (Å)	0.71073
Crystal system	trigonal	θ range (°)	2.96-30.47
Space group	$R3$ (no. 146)	hkl range	$-17 < h < 17$
a (Å)	12.150(2)		$-17 < k < 17$
c (Å)	18.190(4)		$-25 < l < 23$
V ($Å^3$)	2325.5(7)	No. of measured F_o^2	20756
Z	27	$\mu(MoK\alpha)$ (mm^{-1})	93.7
Density calc. ($g\,cm^{-3}$)	8.498	Absorption correction	numerical
Crystal form	platelet	No. of independent F_o^2	3120
Crystal size (mm^3)	$0.1 \times 0.05 \times 0.005$	No. of $F_o^2 > 4\sigma(F_o^2)$	2449
Crystal appearance	metallic lustre	$R_{int}\ F_o^2$	0.21
Single-crystal refinement		**Rietveld refinement**	
F(000)	4806	2θ range (°)	9–131
No. of variables	84	I_{max} (counts)	23 400
Extinction coefficient	0.0004(1)	No. of observations	6101
R[a]	0.076	No. of background points	28
R for $F_o > 4\sigma(F_o)$	0.055	No. of variables	10
wR[a]	0.145	No. of reflections	1839
wR for $F_o^2 > 4\sigma(F_o^2)$	0.132	Rwp/Rp[b]	7.6/4.7
$\rho_{min/max}$ ($e\,Å^{-3}$)	−2.6/2.4	Rp′/RB[b]	12.5/9.4

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma\, w|F_o|^2]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (0.05 \times P)^2 + 170 \times P]$, $P = [\max \text{ of } (0 \text{ or } F_o^2)] + 2\, F_c^2/3$.

[b] R-values as defined by Hill and Fischer (32).

Note. Single-crystal equipment: Nonius Mach3 goniometer, CCD area detector, graphite monochromator, capillary optics collimator. Measurement: 28 mm crystal–detector distance, frames with 2° rotation width and 2 × 30 s exposure time/frame, one set of φ and five sets of ω scans (total 405 frames) to complete whole sphere.

to refine the structural parameters given by Man (3) with least-squares methods failed. Therefore, the structure was re-determined by direct methods. Information on crystal data, procedures of measurements and refinements are compiled in Table 1. Programs used are Collect (8), Denzo-SMN (9), and SHELX-97 (10). Because of the poor quality of the crystals, the extremely platy nature and the high absorption, anomalous dispersion effects could not be taken into account. This holds also for the investigation of Friedel's law violations. Refined structure parameters are listed in Table 2. This table also gives the atomic coordinates of an "ideal" Tl_2S structure of the *anti*-CdI_2 type, in which the z coordinates of the S atoms are all equal to zero and all Tl atoms have as absolute values of z the average of the arithmetic mean of the six absolute z (Tl) values. In addition, the atomic shifts in space between the experimental and the "ideal" structure are listed. According to the recommendation of Sheldrick (10) none of the z coordinates were fixed during the refinement. The displacement parameters (Table 2) do not indicate that positions are only partly occupied, or should be split in appreciable amounts.

Because of the poor quality of the material the final R value for $F_o^2 > 4\sigma(F_o^2)$ was only 0.055. We refined the structure also with a restricted data set using only reflections with $\theta < 24.5°$; R was now 0.039 for 1014 $F_o^2 > 4\sigma(F_o^2)$. Within the limits of accuracy the atomic coordinates were the same as in Table 2, and the standard deviations for the coordinates of the S atoms were even smaller, because at low diffraction angles the ratio of the scattering factors f_S/f_{Tl} is larger than at high diffraction angles. As a consequence, there is no doubt that the reported structure is correct within the limits of accuracy given.

As the quality of the selected "best" suitable crystal did not allow a reliable determination of the cell parameters, X-ray powder data using Cu$K\alpha$ radiation were collected on a Philips X'Pert MPD θ–θ diffractometer with an automatic divergence slit, sample spinner, graphite secondary monochromator, and a proportional counter. Due to the ductile properties and a rapid oxidation to Tl_2SO_4 under ambient grinding conditions the powder sample was prepared under liquid nitrogen and immediately packed into a sample holder using the back-loading technique. For the cell refinement the program Pc-Rietveld Plus (11) was applied, using the atomic coordinates and isotropic displacement parameters of the single-crystal structure refinement. As a distinct texture parallel (00.1) was still evident in the X-ray powder pattern, the region of the (00.6) reflection with a maximum

TABLE 2
Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Tl_2S (first line), in Comparison with the "ideal" Structure (second line)

Atom	Site	x	y	z^a	Ueq (Å^2)^b	Δ (Å)^c
Tl1	9*b*	0.1257(1)	0.2030(1)	−0.0781(1)	0.0457(4)	0.43(0.36)
		0.1111	0.2222	−0.0914		
Tl2	9*b*	0.4685(1)	0.9065(1)	−0.0969(1)	0.0452(4)	0.28(0.26)
		0.4444	0.8888	−0.0914		
Tl3	9*b*	0.8065(1)	0.5719(1)	−0.0992(1)	0.0449(4)	0.34(0.30)
		0.7777	0.5555	−0.0914		
Tl4	9*b*	0.2407(1)	0.1060(1)	0.1046(1)	0.0451(4)	0.35(0.26)
		0.2222	0.1111	0.0914		
Tl5	9*b*	0.5399(1)	0.7488(1)	0.0846(1)	0.0453(4)	0.33(0.30)
		0.5555	0.7777	0.0914		
Tl6	9*b*	0.8712(1)	0.4124(1)	0.0850(1)	0.0457(4)	0.36(0.34)
		0.8888	0.4444	0.0914		
S1	3*a*	0.0	0.0	0.0365(14)	0.047(4)	0.66(0.00)
		0.0	0.0	0.0		
S2	3*a*	0.3333	0.6667	−0.0255(10)	0.047(3)	0.46(0.00)
		0.3333	0.6667	0.0		
S3	3*a*	0.6667	0.3333	−0.0261(10)	0.048(4)	0.47(0.00)
		0.6667	0.3333	0.0		
S4	9*b*	0.0025(8)	0.6630(10)	0.0269(7)	0.041(2)	0.49(0.07)
		0.0	0.6667	0.0		
S5	9*b*	0.9992(9)	0.3234(10)	−0.0200(6)	0.047(3)	0.38(0.11)
		1.0	0.3333	0.0		

[a] To facilitate the comparison with the "ideal" structure, the origin of the experimental structure was chosen with an arithmetic mean of the z coordinates of the Tl atoms in the Tl_2S sheet around $z = 0$ equals to zero.

[b] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

[c] Atomic shifts between experimental and "ideal" structure (for definitions see text), in this column the values in parentheses give the 'horizontal' component of the shift.

intensity about 10 times higher than the remaining intensities was excluded from the refinement. A similar powder pattern characteristic, however, with a wrong indexing of (22.0), was reported in (1). The refined cell parameters $a = 12.150(2)$ Å and $c = 18.190(4)$ Å agree well with the range of reported values for a (12.12–12.22 Å) and c (18.17–18.21 Å) in the literature (1–3, 12). Due to the higher accuracy, the cell parameters of the Rietveld refinement were used in the final single-crystal structure refinements and in the crystallochemical calculations.

Unpolarized absorption measurements were carried out using a Bruker IFS 66v/S FTIR spectrometer with an attached Bruker IRscope II microscope. The spectra were recorded in the spectral range 15000–650 cm^{-1} using different combinations of light sources (tungsten lamp, globar), beam splitters (quartz, KBr) and detectors (Ge-diode and liquid nitrogen cooled MCT). The resolution was set to 10 cm^{-1} and the measuring diameter was 32 μm. Spectra were averaged over 128 scans. A phase correction mode of the interferogram was performed according to (13), cf. Griffiths and de Haseth (14). The Norton–Beer weak mode was chosen as the apodization function.

DESCRIPTION OF THE ATOMIC ARRANGEMENT

The results of our re-determination of the crystal structure of Tl_2S deviate from those published previously (2, 3) in some essential features, although the structure can still be considered to belong to a strongly deformed *anti*-CdI_2 type. As a consequence, a new description and a new discussion of the stereochemistry seem to be needed.

Important interatomic distances and some bond angles are given in Table 3, a projection of the structure parallel to the x_1-axis in Fig. 1, and a projection of a single "Tl_2S sheet" parallel to the z-axis in Fig. 2. In the description and the discussion of the structure, interatomic distances will always be given to two decimals ($\sigma < 0.01$ Å), although for the Tl–Tl distances three decimals would be adequate ($\sigma < 0.005$ Å).

The geometry of the atomic arrangement in Tl_2S is that of a strongly distorted *anti*-CdI_2 structure type, with both a and c tripled. However, while in the *anti*-CdI_2 type itself all the S–Tl distances in the STl_6 octahedra would be of equal length, they vary in the experimentally determined structure from 2.82 to 3.09 Å, i.e., by approximately 10%. The Tl–Tl edges of the STl_6 octahedra vary even more strongly, this holds especially for the ones exactly or approximately

TABLE 3
Selected Interatomic Distances (Å), Angles (°) and Areas (Å^2) for Tl$_2$S

S1–Tl4 (3 ×)	2.82^a	S2–Tl5 (3 ×)	2.97^a	S3–Tl6 (3 ×)	2.97^a	S4–Tl5	2.82^a	S5–Tl5	2.94^a
S1–Tl1 (3 ×)	3.00^b	S2–Tl2 (3 ×)	2.84^b	S3–Tl3 (3 ×)	2.85^b	S4–Tl6	2.84^a	S5–Tl6	2.99^a
						S4–Tl4	2.85^a	S5–Tl4	3.02^a
Tl4–Tl4	4.40^c	Tl5–Tl5	3.79^c	Tl6–Tl6	3.76^c	S4–Tl1	2.96^b	S5–Tl1	2.80^b
Tl1–Tl1	3.73^d	Tl2–Tl2	4.38^d	Tl3–Tl3	4.37^d	S4–Tl2	3.03^b	S5–Tl3	2.86^b
Tl1–Tl4	4.00^e	Tl2–Tl5	4.02^e	Tl3–Tl6	4.07^e	S4–Tl3	3.09^b	S5–Tl2	2.89^b
Tl1–Tl4	4.16^e	Tl2–Tl5	4.12^e	Tl3–Tl6	4.14^e				
						Tl4–Tl5	4.52^c	Tl5–Tl6	3.85^c
Tl4–S1–Tl4	102	Tl5–S2–Tl5	79	Tl6–S3–Tl6	79	Tl4–Tl6	4.27^c	Tl5–Tl4	3.91^c
Tl1–S1–Tl	177	Tl2–S2–Tl2	101	Tl3–S3–Tl3	100	Tl5–Tl6	4.61^c	Tl6–Tl4	3.54^c
Tl1–S1–Tl4	91	Tl2–S2–Tl5	87	Tl3–S3–Tl6	89	Tl1–Tl2	3.91^d	Tl1–Tl3	4.34^d
Tl1–S1–Tl4	87	Tl2–S2–Tl5	90	Tl3–S3–Tl6	91	Tl1–Tl3	3.52^d	Tl1–Tl2	4.58^d
						Tl2–Tl3	3.55^d	Tl3–Tl2	4.25^d
Tl–Tl contacts between the Tl$_2$S sheets ($<$Tl–Tl$>$ = 3.63)						Tl5–Tl1	4.05^e	Tl5–Tl1	4.05^e
						Tl5–Tl2	4.12^e	Tl5–Tl2	4.02^e
Tl1–Tl4	3.64	Tl2–Tl4	3.48	Tl3–Tl5	3.59	Tl6–Tl2	4.08^e	Tl6–Tl3	4.07^e
Tl1–Tl6	3.77	Tl2–Tl4	3.50	Tl3–Tl6	3.63	Tl6–Tl3	4.14^e	Tl6–Tl2	4.08^e
Tl1–Tl6	3.78	Tl2–Tl5	3.63	Tl3–Tl5	3.63	Tl4–Tl1	4.00^e	Tl4–Tl1	4.16^e
						Tl4–Tl3	4.22^e	Tl4–Tl3	4.22^e
Areas of Tl$_3$ triangles parallel (00.1)									
(i) faces of the STl$_6$ octahedra						Tl5–S4–Tl6	109	Tl5–S5–Tl6	81
						Tl5–S4–Tl4	106	Tl5–S5–Tl4	82
Around S1		Tl1–Tl1–Tl1	6.04	Tl4–Tl4–Tl4	8.73	Tl6–S4–Tl4	97	Tl6–S5–Tl4	72
Around S2		Tl5–Tl5–Tl5	6.22	Tl2–Tl2–Tl2	8.31	Tl1–S4–Tl2	82	Tl1–S5–Tl3	100
Around S3		Tl6–Tl6–Tl6	6.12	Tl3–Tl3–Tl3	8.27	Tl1–S4–Tl3	71	Tl1–S5–Tl2	107
Around S4		Tl1–Tl2–Tl3	5.76	Tl4–Tl5–Tl6	8.61	Tl2–S4–Tl3	71	Tl3–S5–Tl2	96
Around S5		Tl4–Tl5–Tl6	6.11	Tl1–Tl2–Tl3	8.10	Tl5–S4–Tl1	89	Tl5–S5–Tl1	90
						Tl5–S4–Tl2	90	Tl5–S5–Tl2	87
(ii) *not* faces of the STl$_6$ octahedra						Tl6–S4–Tl2	88	Tl6–S5–Tl3	88
						Tl6–S4–Tl3	88	Tl6–S5–Tl2	88
Tl1–Tl1–Tl3	6.30	Tl3–Tl3–Tl2	6.97	Tl5–Tl5–Tl6	7.02	Tl4–S4–Tl1	87	Tl4–S5–Tl1	91
Tl2–Tl2–Tl1	7.88	Tl4–Tl4–Tl5	7.83	Tl6–Tl6–Tl4	6.31	Tl4–S4–Tl3	91	Tl4–S5–Tl3	92

[a] To Tl atom "above" the S atom.

[b] To Tl atom "below" the S atom.

[c] Within the plane "above" the S atom.

[d] Within the plane "below" the S atom,

[e] Common edges between the STl$_6$ octahedra in the Tl$_2$S sheet, arithmetic mean: 4.10(7) Å.

Note. Errors for the S–Tl distances <0.01, the Tl–Tl distances <0.005 Å, and for all bond angles $<0.5°$; arithmetic means over all five STl$_6$ octahedra of the three shorter/longer S–Tl distances: 2.84(2)/2.99(4) Å; of the Tl–Tl edges in the smaller / larger Tl$_3$, triangles parallel (00.1): 3.73(16) / 4.40(15) Å.

parallel to (00.1). In the *anti*-CdI$_2$ type they would all be of equal length, in the experimental structure, however, they vary from 3.52 to 4.61 Å, i.e., by approximately 30% (!). In the cases where it is not forbidden by symmetry they vary by approximately 10% even within such individual Tl$_3$ triangles. All five crystallographically different types of STl$_6$ octahedra in Tl$_2$S have two Tl$_3$ faces exactly or approximately parallel to (00.1). Contrary to the *anti*-CdI$_2$ type, one of the two is always distinctly larger, approximately by one-fourth in area (Table 3). This deformation of the STl$_6$ octahedra has one kind of orientation around S1 and S4 and another one around S2, S3 and S5. The shorter S–Tl distances always point to atoms of the larger Tl$_3$-triangle (Table 3).

In spite of the greatly varying Tl–Tl distances the Tl$_2$S sheet is rather flat. Geometrically identical Tl$_2$S sheets in which each Tl atom forms the apex of a TlS$_3$ pyramid are stacked along the *z*-axis according to the *R* centering. Therefore, each Tl atom has, in addition to its nine Tl neighbors within the sheet, three more Tl contacts to a neighboring sheet to complete a strongly distorted 12-coordination of Tl atoms. The histograms of Fig. 3 show that the Tl–Tl contacts within the Tl$_2$S sheet split up into three classes:

(i) edges of the small Tl$_3$ faces parallel (00.1) 3.73(16) Å;
(ii) edges of the large Tl$_3$ faces parallel (00.1) 4.40(15) Å;
(iii) oblique edges in the STl$_6$ polyhedra 4.10(7) Å.

They further show that the Tl–Tl contacts between neighboring Tl$_2$S sheets are relatively short, namely 3.62(10) Å (see second paragraph of "Discussion"), and the 12-coordination of the Tl atoms is so strongly distorted

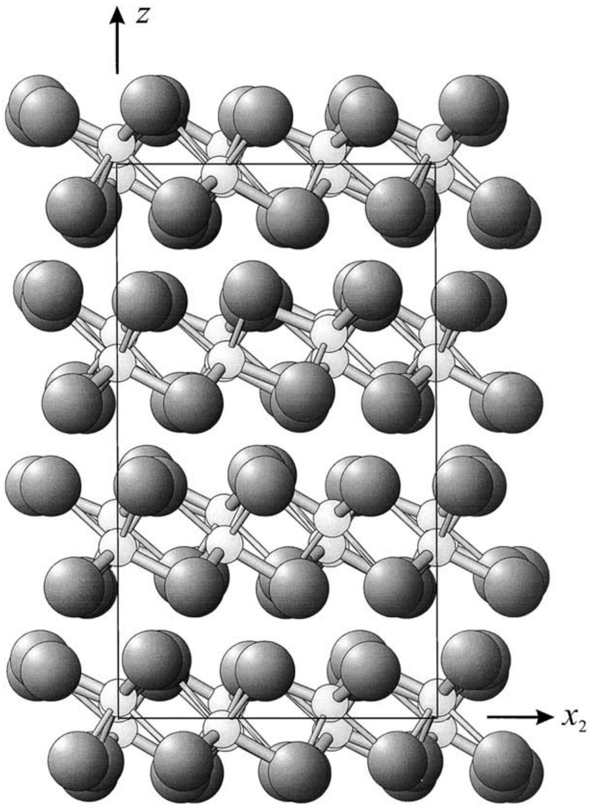

FIG. 1. Ball and stick projection of the atomic arrangement in Tl_2S along x_1 with Tl (dark gray), S (light gray balls), Tl–S <2.90 Å (thick), and 2.90 Å < Tl–S < 3.10 Å (thin sticks).

that (in addition to three close S neighbors at 2.80–3.09 Å) each Tl atom has at least one S-neighbor at a distance smaller than that to the most distant neighbor in the 12-coordination to Tl atoms.

It should be noted that for a theoretical Tl_2S structure of the "ideal" *anti*-CdI_2 type (Table 2) the histogram of the distances around Tl in Fig. 3 would give only three Tl–Tl signals: at 4.05 Å (multiplicity 6), at 4.06 and at 3.60 Å (both with multiplicity 3). The Tl–Tl contacts between different "Tl_2S sheets" in the experimental structure are relatively short (see above). From this point of view it is somewhat misleading to speak of a stacking of "Tl_2S sheets". A way to avoid this would be to consider the atomic arrangement to be a distorted hexagonal close packing of Tl atoms with S atoms occupying octahedral voids in layers parallel to (00.1). In this context it seems interesting to note that also in the 2H-modification of PbI_2, which corresponds to the simple CdI_2 type, the I–I edges of the PbI_6 octahedron (4.447, 4.573 Å, each 6×) are all longer than the interlayer I–I contacts (4.177 Å) (15).

DISCUSSION

Of the earlier structural work on Tl_2S a more detailed comparison is possible only with the electron-diffraction study by Man (3). The atomic arrangement determined by us deviates from that given by Man not merely by minor

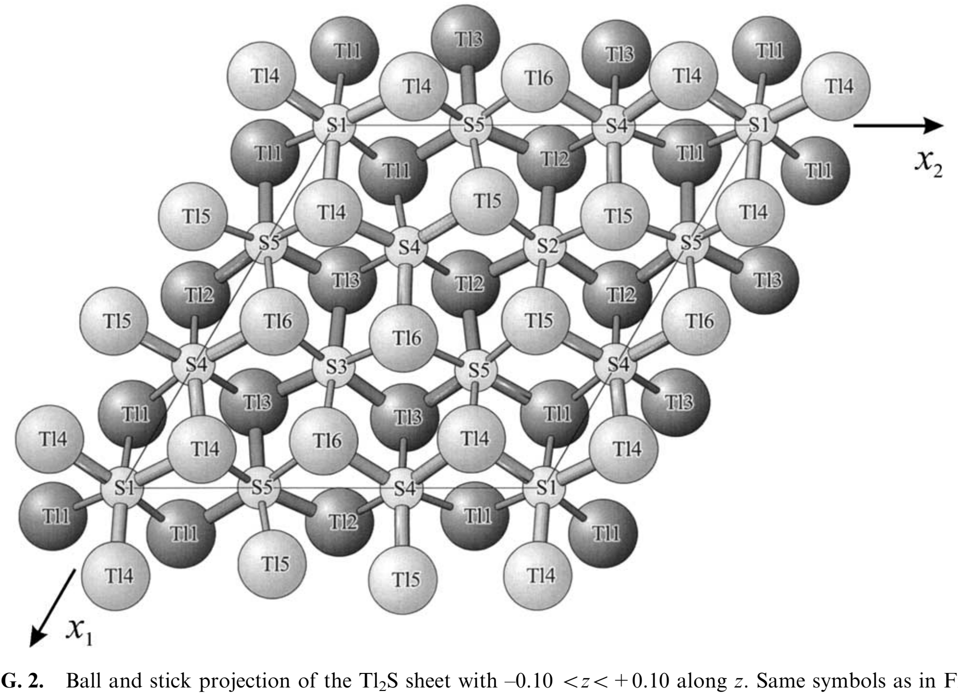

FIG. 2. Ball and stick projection of the Tl_2S sheet with $-0.10 < z < +0.10$ along z. Same symbols as in Fig. 1.

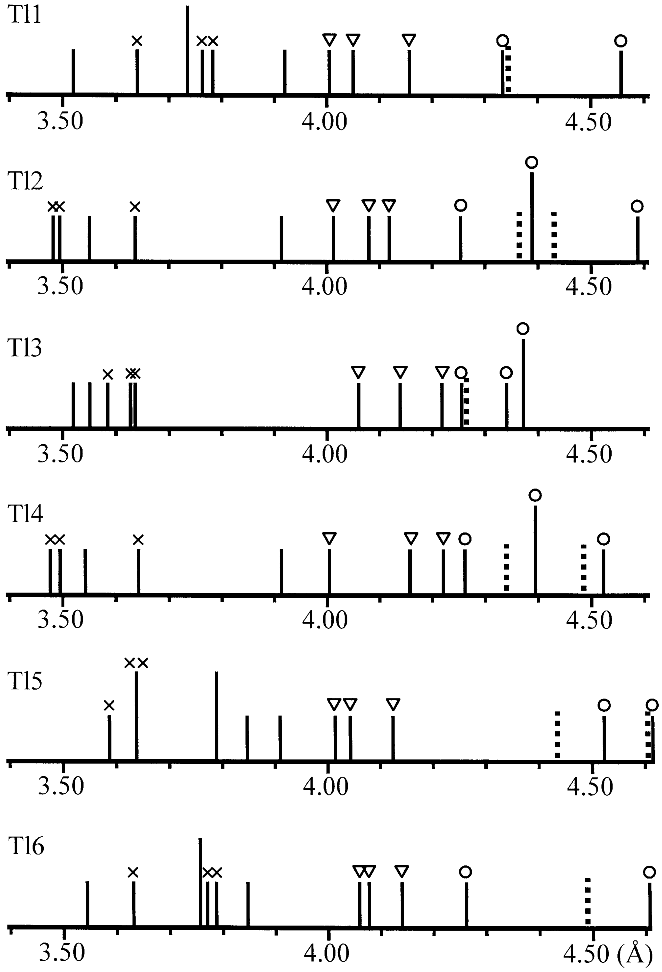

FIG. 3. Histograms of the contacts of the six kinds of Tl atoms to their neighbors. The contacts to the three nearest S neighbors, i.e., to those with Tl–S $\leq$2. 89 Å, are always omitted. Full lines: Tl neighbors. No signature: small Tl_3 triangles of the STl_6 octahedra; circles: large Tl_3 triangles in the STl_6 octahedra; triangles: common Tl–Tl edges in the Tl_2S sheet (labelled ^{e} in Table 3); crosses: Tl–Tl contacts between neighboring Tl_2S layers. Note that Tl1, Tl5 and Tl6 belong each to one large and two small Tl_3 triangles parallel to the sheet, while Tl2 and Tl3 belong to one small and two large Tl_3 triangles. Dotted lines: Tl–S contacts to S atoms of neighboring STl_6 octahedra.

atomic shifts. This is most clearly seen in the sequence of the main distortions of the three crystallographically different STl_6 octahedra with point symmetry 3 along the *z*-axis (Fig. 4). According to Man (3) all three have the same direction, but we found that only two of them have the same direction, while the third has the opposite one. It is to be noted that our structure is considerably better proven than that by Man (3) as she obtained $R(h,0,l) = 0.294$ and did not publish standard deviations of the atomic coordinates.

The interatomic distances in Tl_2S (Table 3) agree with the experience from other inorganic compounds. The shortest Tl–Tl contact (= 3.48 Å) compares well with analog values from the literature. Shorter Tl–Tl contacts have been reported for monovalent and for metallic thallium only rarely: hexagonal Tl (3.40, 3.45 Å: 16), cubic Tl (3.36 Å: 16), tetragonal $Tl(TlS_4)$ (3.40 Å: 17), Tl_4SnS_4 (3.44, 3.46 Å: 18), Tl_7Sb_2 (3.21, 3.43 Å: 19). The lengths of the contacts of the Tl atoms to their neighbors vary greatly (Fig. 3) as is common for monovalent thallium (see, e.g., 20, 21). All five kinds of S atoms have a clear-cut, although considerably distorted, octahedral coordination of Tl atoms with S–Tl = 2.80–3.09 Å. Up to now this kind of Tl coordination around S seems not to have been found in any other compound. The gap to further Tl neighbors is $\geq$1.16 Å.The shortest S–Tl contact (2.80 Å) belongs to the smallest ones reported in the literature, i.e., in $Tl_2Sn_2S_3$ (2.81(2) Å: 20), but slightly larger ones are quite common, e.g., in Tl_4SnS_3 (2.87(3), 2.88(7) Å: 22), in jankovicite, $Tl_5Sb_9(As_1Sb)_4S_{22}$ 2.890(4) Å: 23), and in lorandite, $TlAsS_2$ (2.91(2) Å: 24). It seems worth noting that the average S–Tl distance in the STl_6 octahedra in Tl_2S (2.92 Å) is smaller than the S–Pb distance in the SPb_6 octahedron of galena, PbS (2.97 Å).

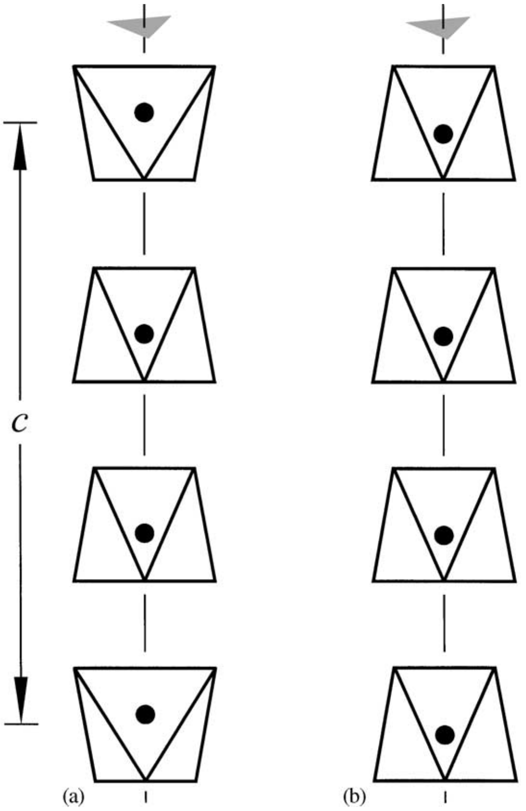

FIG. 4. Sequence of the main "up–down" distortions of the three kinds of STl_6 octahedra with symmetry 3 along the three-fold axis (a) according to the present investigation and (b) according to Man (1970). Schematically.

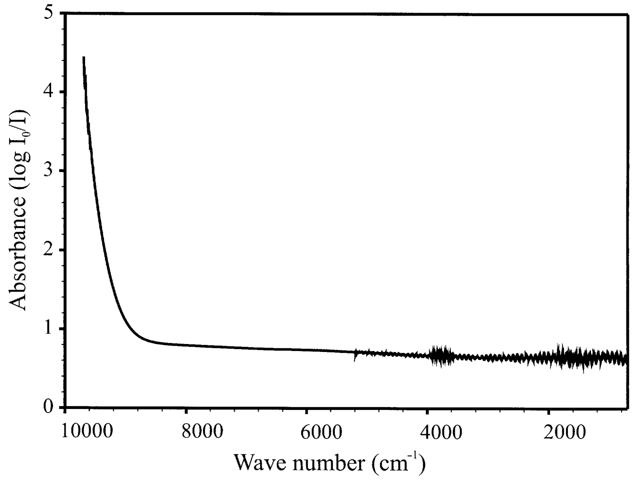

FIG. 5. IR-absorption spectrum of Tl_2S for the ordinary wave.

Although the chemical formula of Tl_2S is very simple, its atomic arrangement is rather complex. There occur six crystallographically different kinds of Tl atoms (all of point symmetry 1) and five different kinds of S atoms (three of point symmetry 3, and two of point symmetry 1). In spite of their crystallographic diversity, the surroundings of the different kinds of Tl atoms, as well as those of the S atoms, are geometrically not essentially different.

This raises the question of the possibility to build *anti*-CdI_2 sheets from equal STl_6-octahedra of local symmetry 3, each with one "large" and one "small" equilateral Tl_3-triangle parallel to (00.1). Geometric analysis shows that this is not possible (see Appendix A). In agreement with this theoretical result the edge lengths within the non-symmetry-restricted Tl_3 faces parallel to (00.1) vary by approximately 10%.

Since in all five kinds of STl_6 octahedra the S atom is shifted towards the larger one of the basal Tl_3 faces, it is further interesting to learn which kinds of trigonal "up–down" patterns are possible. This holds especially for an "up–down" ratio of exactly or approximately 1:1, because for such "up–down" ratios the tension between the "upper" and "lower" Tl plane is expected to be relatively small. Results of the geometric analysis for not too large identity periods are presented in Appendix B. Curiously enough, the "up–down" pattern of the experimental structure does not correspond to a 1:1 pattern, and, therefore, also not to the 1:1 pattern with the smallest possible cell, but to the smallest possible 4:5 pattern. This is possibly connected with the peculiarity that in the 1:1 pattern the Tl atoms of one-sixth of the STl_3 pyramids have no short bonds to neighboring STl_3 pyramids, while this is always the case for the 4:5 pattern.

Trials to derive the experimental structure from the one of the undistorted *anti*-CdI_2 type by distance least-squares computations (25) failed when using in the STl_6 octahedra one weight each for the smaller and larger S–Tl distances, the oblique Tl–Tl distances, the Tl–Tl distances of the small and of the large Tl_3 triangles parallel to (00.1) and one weight for all "inter-layer" Tl–Tl distances. In the ideal anti-CdI_2-type the lone electron pairs of Tl(I) would all be oriented exactly parallel to the *z*-axis. From the experimentally determined structure this is, however, not indicated, e.g. because in none of the five TlS_3 pyramids the three S-Tl bonds are of equal length. The observation that Tl_2S becomes transparent for electromagnetic radiation at wave numbers $<9000\,\mathrm{cm}^{-1}$ (Fig. 5) indicates that it is a semiconductor with an energy gap of approximately 1 eV (26).

A comparison would be interesting with $A^{[6B]}B_2^{[3A]}$ compounds of atoms with the same electron configuration in the outermost atomic shell as in S and Tl, respectively, especially with Tl_2O, Tl_2Se, and In_2S. Unfortunately, this is hardly possible. For Tl_2O only the main features of the atomic arrangement are known with certainty (27, 28). Although the Tl atoms are arranged essentially in the hexagonal close packing as in Tl_2S, the two compounds are definitely not isostructural in detail. It seems worthwhile to note that for the pseudo-cell corresponding to the hexagonal close packing, $c/a = 1.80$ for Tl_2O, but 1.50 for Tl_2S. The structure of stoichiometric Tl_2Se does not seem to be reliably determined, and In_2S apparently is not even a stable solid phase.

It seems worth noting that in the yellow (= room-temperature) modification of InCl (29, 30) several stereochemical features are similar to those in Tl_2S. In spite of the simple formula InCl has a complex crystal structure, i.e., a strongly distorted NaCl type with the lattice parameter doubled, space group $P2_13$, $Z = 32$ (29, 30). An extensive discussion of the atomic arrangement, stressing the role of stereochemically active $(5s)^2$ lone pairs of the In atoms, was given by van der Vorst and Maaskant (31). Of special interest here are the four kinds of distorted $ClIn_6$ octahedra. Five-eighths of them have the exact or approximate symmetry 3, while the remaining three-eighths have the approximate symmetry 2 (29, 30); in Tl_2S, however, all STl_6 octahedra have the exact or approximate symmetry 3. A common feature of all known $ClIn_6$ and STl_6 octahedra with symmetry or pseudo-symmetry 3 is that three shorter bonds go to a clearly larger face of the octahedron than the three longer bonds.

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APPENDIX A

Proof that one cannot build a distorted *anti*-CdI_2 type from identical octahedra with local symmetry 3 or $3m$:

The octahedral sheet should have properties as follows: (i) It is built from isometric octahedra with local symmetry 3 or $3m$. The two faces perpendicular to the three-fold axis can have different sizes (Fig. A1), (ii) each corner belongs to three octahedra, and (iii) at each corner six edges meet parallel to the sheet.

Every such possible sheet has two nets of equilateral triangles: a "lower" and an "upper" one. The triangles of the sheets have no edges in common, but each three sides meet in one point; every ring of three triangles is necessarily rigid. There exist two principally different cases: (i) all triangles of a net have equal size, and (ii) the net has triangles of two different sizes.

Case (i) is simple. Let us suppose that the three larger triangles of the configuration are at the one side of the sheet. The corresponding configuration with the three smaller triangles is then necessarily on the other side. As both configurations are rigid and of different size, they do not fit on each other.

Case (ii) requires more detailed considerations. Figure A2(a) shows a ring of three octahedra. The isometric octahedra B and B' have symmetry 3 and share the edge P–P'. The octahedron A shares the edges P–Q and P–R with the octahedra B and B'. As P–Q and P–R have the same length, the octahedron A cannot have symmetry 3, but has to have symmetry $3m$. As it was further presumed that all octahedra have the same symmetry, the octahedra B and B' also have to have symmetry $3m$.

Figure A2(b) is not greatly different from Fig. A2(a). But now all three octahedra A, B and B' have symmetry $3m$. Because $\beta = 240°\text{-}\alpha$, and the three octahedra have necessarily the same outline, we have at point P: $\gamma = 360° - 2\alpha = 240° - \alpha$. As a consequence $\alpha = 120°$ and the (empty) octahedra A, B, and B' are identical and have symmetry $\bar{3}2/m$.

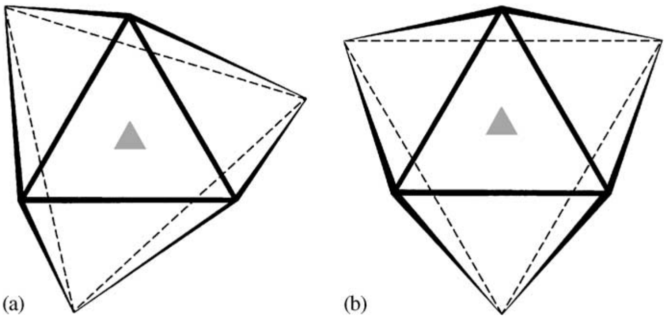

FIG. A1. AB_6 octahedra projected parallel to the 3-fold axis. (a) With symmetry 3; (b) with symmetry $3m$.

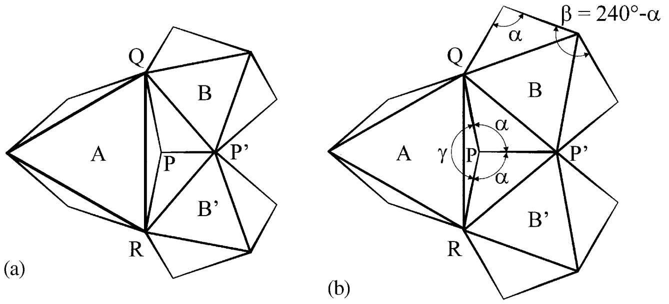

FIG. A2. Rings of three AB_6 octahedra of which two have the same kind of up-down orientation. (a) The octahedra B and B′ have symmetry 3. (b) The octahedra have symmetry $3m$, the angles α, β, and γ are in the plane of drawing. For further explanation see text.

APPENDIX B. "UP-DOWN" ORDERINGS IN Tl_2S SHEETS

In the STl_6 octahedra of the Tl_2S sheets the S atoms are shifted from the centers up or down in approximately equal amounts. Such arrangements can be symbolized by black and white octahedra in a CdI_2-type sheet. The smallest possible such pattern with trigonal symmetry and equal amounts of black and white octahedra is presented in Fig. B1(a). The cell contains each six black and six white

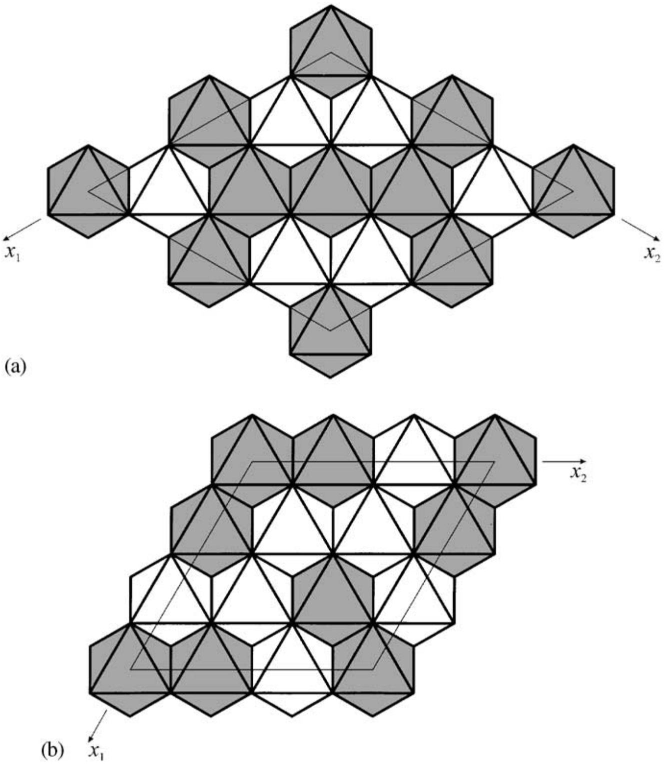

FIG. B1. Two black–white ordering patterns of AB_2 sheets as in Tl_2S. (a) Pattern with black:white = 1:1 and the smallest possible unit cell. (b) Pattern with black:white = 1:1 and the smallest possible unit cell. (b) Pattern with black:white = 4:5, corresponding to the up-down ordering of the distortions of the STl_6 octahedra in Tl_2S.

octahedra. The pattern corresponding to the structure of Tl_2S is given in Fig. B1(b). It has a somewhat smaller unit cell containing four black and five white octahedra.

REFERENCES

1. A. S. Radtke, F.W. Dickson, *Am. Mineral*. **60,** 559 (1975).
2. J. A. A. Ketelaar and E. W. Gorter, *Z. Kristallogr*. **101,** 367 (1939).
3. L. I. Man, *Sov. Phys. Crystallogr*. **15,** 399 (1970).
4. I. S. Chaus, L. E. Demchenko, N. M. Kompanichenko, Y. I. Gornikov, I. A. Sheka, and B. S. Khomenko, *Zhur. Neorg. Khim*. **22,** 2336 (1977).
5. I. S. Chaus, Y. I. Gornikov, L. E. Demchenko, N. M. Kompanichenko, and A. G. Grischuk, *Zhur. Neorg. Khim*. **24,** 622 (1979).
6. I. S. Chaus, Y. P. Krasan, N. M. Kompanichenko, and V. G. Andreichenko, *Ukrain. Khim. Zhur*. **49,** 96 (1983).
7. D. R. Lide (Ed.), "Handbook of Chemistry and Physics," 78th ed., pp. 4–37. CRC Press, Boca Raton, FL, 1997.
8. Nonius "Collect, Data Collection Software." Nonius B. V., Delft, 1999.
9. Z. Otwinowski and W. Minor, *in* "Methods in Enzymology Series, Vol. 276: Macromolecular Crystallography Part A" (C. W. Carter Jr. and R. M. Sweet Eds.), p. 307. Academic Press, San Diego, 1997.
10. G. M. Sheldrick, "SHELX-97, Program for the Solution and Refinement of Crystal Structures." Universität Göttingen, 1997.
11. R. X. Fischer, C. L. Lengauer, E. Tillmanns, R. J. Ensink, C. A. Reiss, and E. J. Fanter, *Mater. Sci. Forum* **133–136,** 287 (1993).
12. B. Reuter and A. Goebel, *Z. Anorg. Allg. Chem*. **271,** 321 (1953).
13. L. Mertz, "Transformations in Optics." John Wiley and Sons, New York, 1965.
14. P. R. Griffiths and J. A. de Haseth, "Fourier Transform Infrared Spectroscopy." John Wiley and Sons, New York, 1986.
15. T. Minagawa, *Acta Crystallogr. A* **31,** 823 (1975).
16. H. Lipson and A. R. Stokes, *Nature* **148,** 437 (1941).
17. S. Kashida and K. Nakamura, *J. Solid State Chem*. **110,** 264 (1994).
18. Y. Piffard, M. Tournoux, A.-L. Ajavon, and R. Éholié, *Rev. Chim. Minéral*. **21,** 21 (1984).
19. R. Stockhuyzen, C. Chieh, and W. B. Pearson, *Can. J. Chem*. **55,** 1120 (1977).
20. S. Del Bucchia, J. C. Jumas, E. Phillipot, and M. Maurin, *Z. Anorg. Allg. Chem*. **487,** 199 (1982).
21. W. Nowacki, A. Edenharter, P. Engel, M. Gostoijic, and A. Nagl, *in* "Ore Genesis. The State of the Art" (G. C. Amstutz *et al*., Eds.), p. 689. Springer-Verlag, Berlin, 1982.
22. S. Del Bucchia, J.-C. Jumas, E. Phillipot, and M. Maurin, *Rev. Chim. minéral*. **18,** 224 (1981).
23. E. Libowitzky, G. Giester, and E. Tillmanns, *Eur. J. Mineral*. **7,** 479 (1995).
24. T. Balic-Zunic, E. Mackovicky, and Y. Moëlo, *N. Jahrb. Mineral. Abh*. **168,** 213 (1995).
25. Chr. Baerlocher, A. Hepp, and W. H. Meier, "DLS-76, A Program for the Simulation of Crystal Structures by Geometric Refinement." ETH Zürich, 1977.
26. V. Estrella, M. Rogelio, M. T. Nair, and P. K. Nair, *Mod. Phys. Lett. B* **15,** 737 (2001).
27. M. Tournoux, R. Marchand, and M. Bouchama, *C. R. Acad. Sci. Paris* **270Sév.C,** 1007 (1970).
28. H. Sabrowski, *Z. Allg. Anorg. Chem*. **381,** 266 (1971).
29. J. M. van den Berg, *Acta Crystallogr*. **20,** 905 (1966).
30. C. P. J. M. van der Vorst, G. C. Verschoor, and W. J. A. Maaskant, *Acta Crystallogr. B* **34,** 3333 (1978).
31. C. P. J. M. van der Vorst, and W. J. A. Maaskant, *J. Solid State Chem*. **34,** 301 (1980).
32. R. J. Hill and R. X. Fischer, *J. Appl. Crystallogr*. **23,** 462 (1990).