TI-bearing sulfosalt from the Lengenbach quarry, Binn Valley, Switzerland: Philrothite, $TIAs_3S_5$

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ABSTRACT

Philrothite, ideally TlAs₃S₅, is a new mineral from the Lengenbach quarry in the Binn Valley, Valais, Switzerland. It occurs as very rare crystals up to 200 μ m across on realgar associated with smithite, rutile and sartorite. Philrothite is opaque with a metallic lustre and shows a dark brown streak. It is brittle; the Vickers hardness (VHN₂₅) is 128 kg/mm² (range: 120–137) (Mohs hardness of 3–3½). In reflected light philrothite is moderately bireflectant and weakly pleochroic from dark grey to light grey. Under crossed polars it is anisotropic with grey to bluish rotation tints. Internal reflections are absent. Reflectance percentages for the four COM wavelengths (R_{min} and R_{max}) are: 26.5, 28.8 (471.1 nm), 25.4, 27.2 (548.3 nm), 24.6, 26.3 (586.6 nm) and 24.0, 25.1 (652.3 nm), respectively.

Philrothite is monoclinic, space group $P_{2_1/c}$, with a = 8.013(2), b = 24.829(4), c = 11.762(3) Å, $\beta = 132.84(2)^{\circ}$, V = 1715.9(7) Å³, Z = 8. It represents the N = 4 homologue of the sartorite homologous series. In the crystal structure $[R_1 = 0.098$ for 1217 reflections with $I > 2\sigma(I)$], Tl assumes tricapped prismatic sites alternating to form columns perpendicular to the *b* axis. Between the zigzag walls of Tl coordination prisms, coordination pyramids of As(Sb) form diagonally-oriented double layers separated by broader interspaces which house the lone electron pairs of these elements.

The eight strongest calculated powder-diffraction lines [*d* in Å (I/I_0) (*hkl*)] are: 12.4145 (52) (020); 3.6768 (100) ($\overline{1}61$); 3.4535 (45) (131); 3.0150 (46) ($\overline{1}53$); 2.8941 (52) ($\overline{1}81$); 2.7685 (76) (230); 2.7642 (77) ($\overline{2}34$); 2.3239 (52) (092). A mean of five electron microprobe analyses gave Tl 26.28(12), Pb 6.69(8), Ag 2.50(4), Cu 0.04(2), Hg 0.07(2), As 32.50(13), Sb 3.15(3), S 26.35(10), total 97.58 wt.%, corresponding, on the basis of a total of nine atoms, to $(TI_{0.789}Pb_{0.198})_{\Sigma=0.987}$ (As_{2.662}Sb_{0.159}Ag_{0.142}Cu_{0.004}Hg_{0.002})_{$\Sigma=2.969$ S_{5.044}. The new mineral has been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (2013-066) and named for Philippe Roth (*b*. 1963), geophysicist and well known mineral expert on the Lengenbach minerals for more than 25 years.}

KEYWORDS: philrothite, new mineral, Tl-sulfosalt, Lengenbach, Switzerland.

Introduction

THE Lengenbach quarry located in the Binn Valley, Canton Valais, Switzerland is one of the

* E-mail: luca.bindi@unifi.it DOI: 10.1180/minmag.2014.078.1.01 premium localities for TI-bearing sulfosalts. More than 15 TI-bearing minerals are reported from this quarry and for 12 of them Lengenbach is the type locality, with dalnegroite $TI_{5-x}Pb_{2x}$ (As,Sb)_{21-x}S₃₄ ($x \sim 1$) (Nestola *et al.*, 2010; Bindi *et al.*, 2010) and raberite $TI_5Ag_4As_6SbS_{15}$

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(Bindi *et al.*, 2012) being the more recently described species.

The specimen containing philrothite comes from the realgar-rich zone (the so-called zone 1; Graeser *et al.*, 2008) and was sampled in 1988. Minerals associated with philrothite are realgar, smithite, rutile and sartorite. This mineral, as well as the other Tl minerals at Lengenbach, presumably represent products of late-stage Tland As-bearing hydrothermal solutions during Alpine metamorphism (Hofmann and Knill, 1996).

Philrothite was approved as a new mineral by the CNMNC (2013-066). The mineral name honours Dr Philippe Roth (b. 1963), a well known mineral expert on the Lengenbach minerals for more than 25 years. He is currently President of the FGL (Forschungsgemeinschaft Lengenbach; literally: research community Lengenbach) and has analysed several specimens from this deposit and published many articles about Lengenbach minerals including a book on the minerals first discovered in Switzerland and minerals named after Swiss individuals (Roth, 2007). The name reflects part of the first name (Phil for Philippe) and the last name (Roth). The holotype material is deposited in the mineralogical collection of the Museum of Mineralogy of the Department of Geosciences at the University of Padova (Italy). under catalogue number MMP M12605.

In this study we report the description of the new mineral philrothite together with the determination of its crystal structure.

Physical and optical properties

Philrothite occurs as very rare crystals on realgar (Fig. 1). The mineral exhibits an anhedral grain morphology, and shows no inclusions of, or intergrowths with, other minerals. The maximum grain size of philrothite is ~200 µm. It is black in colour and shows a dark brown streak. The mineral is opaque in transmitted light and exhibits a metallic lustre. No cleavage is observed and the fracture is uneven. The calculated density (Z = 8)for the empirical formula is 4.635 g/cm^3 . Unfortunately, the density could not be measured because of the small grain size. Micro-indentation measurements carried out with a VHN load of 25 g gave a mean value of 128 kg/mm² (range: 120-137) corresponding to a Mohs hardness of $3 - 3\frac{1}{2}$.

In plane-polarized incident light philrothite is moderately bireflectant and weakly pleochroic



FIG. 1. SEM-BSE image of irregular grains of philrothite (brighter phase) on realgar.

from dark grey to a light grey. Between crossed polars, philrothite is anisotropic with grey to bluish rotation tints. Internal reflections are absent and there is no optical evidence of growth zonation.

Reflectance measurements were performed in air by means of a MPM-200 Zeiss microphotometer equipped with a MSP-20 system processor on a Zeiss Axioplan ore microscope. The filament temperature was ~3350 K. An interference filter was adjusted, in turn, to select four wavelengths for measurement (471.1, 548.3, 586.6 and 652.3 nm). Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. Reflectance percentages for the four COM wavelengths (R_{min} and R_{max}) are 26.5, 28.8 (471.1 nm), 25.4, 27.2 (548.3 nm), 24.6, 26.3 (586.6 nm), and 24.0, 25.1 (652.3 nm), respectively.

X-ray crystallography and crystal-structure determination

A small crystal fragment (55 μ m × 60 μ m × 65 μ m) was selected for the single-crystal X-ray diffraction study that was carried out using a STOE-STADI IV CCD single-crystal diffract-ometer (Table 1). The analysis of the systematic absences led unequivocally to the choice of the space group $P2_1/c$. The positions of most of the atoms (Tl and As/Sb atoms) were determined by means of direct methods of the *SHELXS* program (Sheldrick, 2008). A least-squares refinement on F^2 using these heavy-atom positions and isotropic temperature factors produced an *R* factor of

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Crystal data	
Ideal formula	TlAs ₃ S ₅
Crystal system	monoclinic
Space group	$P2_1/c$
Unit-cell parameters (Å, °)	8.013(2) 24.829(4) 11.762(3) 132.84(2)
Unit-cell volume (Å ³)	1715.9(7)
Ζ	8
Crystal size (mm)	$0.055 \times 0.060 \times 0.065$
Data collection	
Diffractometer	STOE-STADI IV CCD
Temperature (K)	298(3)
Radiation, wavelength (Å)	$MoK_{\alpha}, 0.71073$
2θ max for data collection (°)	59.66
Crystal-detector dist. (mm)	60
h, k, l ranges	-11 - 10, -34 - 32, -16 - 15
Axis, frames, width (°), time per frame (s)	ω, 645, 1.00, 50
Total reflections collected	18958
Unique reflections (R_{int})	4788 (0.156)
Unique reflections $I > 2\sigma(I)$	1217
Data completeness to θ_{max} (%)	99.4
Absorption correction method	X-RED and X-SHAPE
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1217/0/85
$R_1 [I > 2\sigma(I)], wR_2 [I > 2\sigma(I)]$	0.0985, 0.1324
R_1 all, wR_2 all	0.1158, 0.1501
Goodness-of-fit on F^2	1.215
Largest diff. peak and hole (e^{-}/A^{3})	3.92, -3.52

TABLE 1. Crystallographic data and refinement parameters for philrothite.

$$\begin{split} R_{\text{int}} &= (n/n - 1)^{1/2} [F_o^2 - F_o \text{ (mean)}^2] / \Sigma F_o^2 \\ R_1 &= \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; \ wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}; \\ * \ w &= 1 / [\sigma^2(F_o^2) + (aP)^2 + bP], \ \text{where } P = (\max(F_o^2, 0) + 2F_c^2) / 3; \\ \text{GooF} &= \{ \Sigma [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}; \ \text{where } n \text{ is the number of reflections and } p \text{ is the number of refined parameters.} \end{split}$$

0.286. Three-dimensional difference Fourier synthesis yielded the position of the remaining sulfur atoms. The program SHELXL (Sheldrick, 2008) was used for the refinement of the structure. The occupancy of all the sites was left free to vary (Tl vs. vacancy; As vs. Sb; S vs. vacancy) and then fixed to the resulting value (Table 2). Neutral scattering curves for Tl, As, Sb and S were taken from the International Tables for X-ray Crystallography (Ibers and Hamilton, 1974). At the last stage, with anisotropic atomic displacement parameters for the two Tl atoms and no constraints, the residual value settled at R_1 = 0.0985 for 1217 observed reflections $[2\sigma(I) \text{ level}]$ and 85 parameters and at $R_1 = 0.1158$ for all 4788 independent reflections. Experimental details and R indices are given in Table 1. Fractional atomic coordinates and isotropic displacement parameters are reported in Table 2 (anisotropic ADPs for the two Tl positions can be found in the accompanying CIF). Bond distances are given in Table 3.

The authors attempted to collect a powder pattern with an automated CCD-equipped Oxford Diffraction Xcalibur PX diffractometer using $CuK\alpha$ radiation but the small size of the crystal, coupled with its poor diffraction quality (see above), failed to yield publication-quality results. The calculated X-ray powder-diffraction pattern, computed with the atom coordinates and occupancies reported in Table 2, is given in Table 4. Structure factors (Table 5) have been deposited with the Principal Editor of Mineralogical Magazine and are available at

Atom	s.o.f.	x/a	y/b	z/c	$U_{\rm iso}$
T11	Tl _{1.00}	0.636(1)	0.7863(3)	0.8763(9)	0.040(3)
T12	Tl _{1.00}	0.156(1)	0.7928(3)	0.3728(8)	0.032(2)
As1	$As_{1.00}$	-0.020(3)	0.8485(8)	0.610(2)	0.036(6)
As2	As _{1.00}	0.506(4)	0.6442(9)	0.642(2)	0.052(7)
As3	As _{1.00}	0.893(4)	0.5788(9)	0.359(3)	0.069(8)
As4	As _{0.56(2)} Sb _{0.44}	0.421(3)	0.9367(8)	0.387(2)	0.065(9)
As5	As _{1.00}	0.330(4)	0.540(1)	0.162(3)	0.085(9)
As6	As _{1.00}	0.788(3)	0.5517(8)	0.605(2)	0.039(5)
S1	S _{1.00}	0.610(8)	0.838(2)	0.421(6)	0.046(8)
S2	S _{1.00}	0.011(8)	0.667(2)	0.330(6)	0.052(8)
S3	S _{1.00}	0.528(8)	0.613(2)	0.170(6)	0.046(9)
S4	S _{1.00}	0.985(9)	0.616(3)	0.603(7)	0.079(8)
S5	S _{1.00}	0.093(8)	0.778(3)	0.600(7)	0.090(8)
S6	S _{1.00}	0.622(6)	0.726(1)	0.636(4)	0.045(8)
S7	S _{1.00}	0.770(6)	0.979(1)	0.585(4)	0.034(9)
S8	S _{1.00}	0.638(7)	0.480(2)	0.320(5)	0.028(9)
S9	S _{1.00}	0.844(7)	0.587(2)	0.828(5)	0.040(8)
S10	S1.00	0.459(9)	0.584(2)	0.433(6)	0.059(8)

TABLE 2. Atoms, site occupancy (s.o.f.), fractional atom coordinates (Å), and isotropic atomic displacement parameters (Å²) for philrothite.

http://www.minersoc.org/pages/e_journals/ dep mat mm.html).

Chemical composition

A preliminary chemical analysis using energy dispersive spectrometry was performed using a SEM JEOL-5610 LV at the Museum of Natural History of Milan. The chemical composition was then determined using wavelength dispersive analysis (WDS) by means of a CAMECA-CAMEBAX electron microprobe. Major and minor elements were determined at 20 kV accelerating voltage and 20 nA beam current, 1 μ m beam size, and with 15 s as the counting time. For the WDS analyses the following lines

TABLE 3. Selected bond distances (Å) for philrothite.

T11-S1	3.14(2)	T12-S1	3.50(3)		
S2	3.53(3)	S2	3.25(4)		
S3	3.13(3)	S3	3.59(3)		
S4	3.28(3)	S4	3.34(2)		
S5	3.23(2)	S5	3.08(4)		
S5	3.13(2)	S5	3.38(4)		
S6	3.15(3)	S6	3.26(3)		
S6	3.13(3)	S6	3.15(2)		
As1-S1	2.26(1)	As2–S1	2.68(1)	As3–S2	2.50(2)
S2	2.46(1)	S6	2.27(1)	S3	2.27(1)
S5	1.95(1)	S9	2.52(1)	S4	2.64(1)
		S10	2.72(1)		
As4–S1	2.79(2)	As5–S3	2.40(2)	As6-S4	2.21(2)
S7	2.37(1)	S 8	2.32(1)	S9	2.50(2)
S7	2.77(1)	S10	2.78(2)	S10	2.16(1)
S 8	2.37(1)				

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Ι	d_{calc} (Å)	h	k	l	Ι	d_{calc} (Å)	h	k	l
52	12.4145	0	2	0	11	2.3717	ī	10	1
6	7.6257	1	1	1	7	2.3523	3	5	3
18	6.7324	1	2	1	52	2.3239	0	9	2
5	5.8756	1	0	0	17	2.2441	3	6	3
5	5.7569	1	3	1	19	2.2325	1	9	1
13	4.9071	1	4	1	16	2.2314	ī	9	3
39	4.2487	0	1	2	45	2.1561	0	0	4
21	4.0065	2	0	2	5	2.0691	0	12	0
12	3.9553	2	1	2	5	2.0664	3	5	1
27	3.8243	0	3	2	6	2.0637	3	5	5
43	3.8129	2	2	2	6	2.0245	3	8	3
100	3.6768	ī	6	1	13	1.9190	3	9	3
21	3.6337	1	2	1	15	1.9135	3	7	1
25	3.6288	1	2	3	15	1.9113	3	7	5
13	3.6062	2	3	2	7	1.9064	4	4	4
45	3.4535	1	3	1	5	1.8782	2	2	2
38	3.4492	1	3	3	8	1.8755	2	2	6
21	3.3662	2	4	2	14	1.8606	1	6	3
12	3.2560	0	5	2	14	1.8593	1	6	5
29	3.1181	2	5	2	14	1.8384	2	12	2
12	3.1036	0	8	0	7	1.8180	4	0	2
43	3.0179	1	5	1	7	1.8172	1	12	1
46	3.0150	1	5	3	6	1.8166	1	12	3
25	2.9174	2	1	0	5	1.8155	4	0	6
24	2.9123	2	1	4	13	1.8132	4	1	2
52	2.8941	1	8	1	12	1.8107	4	1	6
17	2.8784	2	6	2	5	1.8031	4	6	4
8	2.7990	1	6	1	10	1.7899	2	11	0
10	2.7967	1	6	3	11	1.7887	2	11	4
76	2.7685	2	3	0	7	1.7735	0	14	0
77	2.7642	2	3	4	5	1.7540	3	9	1
5	2.7432	1	8	2	7	1.7316	1	14	1
6	2.6885	1	1	4	8	1.7296	1	8	3
6	2.6558	2	1	2	8	1.7285	1	8	5
20	2.6554	2	4	0	6	1.5560	5	6	I
23	2.6515	2	4	4	9	1.5517	2	4	2
6	2.6425	1	2	4	5	1.3995	2	12	2
12	2.6112	5 1	2	5	6	1.369/	0	14	4
8	2.5930	$\frac{1}{1}$	/	1	6	1.3033	1	17	1
6	2.5912	1	2	3	6	1.3630	1	1/	5
2	2.5419	3 5	3	3	5	1.3184	0	3	0
9	2.4555	3	4	3					

TABLE 4. Calculated X-ray powder diffraction pattern for philrothite.

The powder pattern was calculated and indexed on the basis of a = 8.013(2), b = 24.829(4), c = 11.762(3) Å, $\beta = 132.84(2)^{\circ}$, and with the atomic coordinates and occupancies reported in Table 2. The strongest intensities are given in bold.

were used: $TlM\alpha$, $PbM\alpha$, $AgL\alpha$, $CuK\alpha$, $HgL\alpha$, $AsL\alpha$, $SbL\alpha$ and $SK\alpha$. The standards employed were: synthetic Tl_2Se (Tl), galena (Pb), Ag-pure element (Ag), Cu-pure element (Cu), cinnabar (Hg), synthetic As_2S_3 (As), synthetic Sb_2S_3 (Sb)

and pyrite (S). The crystal fragment was found to be homogeneous within analytical error. The average chemical compositions (five analyses on different spots) together with wt.% ranges of elements are reported in Table 6. On the basis of

	Wt.%	Range	σ	Atom	Atomic ratios
Tl	26.28	24.33-26.98	0.12	Tl	0.789
Pb	6.69	6.25-6.92	0.08	Pb	0.198
Ag	2.50	2.30 - 2.53	0.04	Ag	0.142
Cu	0.04	0.02 - 0.09	0.02	Cu	0.004
Hg	0.07	0.00 - 0.12	0.02	Hg	0.002
As	32.50	31.97-33.09	0.13	As	2.662
Sb	3.15	3.10-3.37	0.03	Sb	0.159
S	26.35	26.12-26.91	0.10	S	5.044
Total	97.58	96.60-97.90		Σ_{atoms}	9.000

TABLE 6. Electron microprobe analyses (means, ranges and standard deviations) and atomic ratios (on the basis of nine atoms) for philrothite.

nine atoms, the empirical formula of philrothite is $(Tl_{0.789}Pb_{0.198})_{\Sigma=0.987}(As_{2.662}Sb_{0.159}Ag_{0.142}Cu_{0.004}Hg_{0.002})_{\Sigma=2.969}S_{5.044}$. The simplified ideal formula is TlAs₃S₅, which requires Tl 34.67, As 38.13, S 27.20, total 100.00 wt.%.

Results and discussion

Philrothite can be considered the N = 4 homologue of the sartorite homologous series (Makovicky, 1985, Moëlo *et al.*, 2008). In the structure (Fig. 2), Tl assumes tricapped prismatic sites alternating to form columns perpendicular to

the *b* axis, organized into zigzag layers parallel to (010). Both Tl1 and Tl2 show irregular coordinations with mean bond distances of 3.22 and 3.32 Å. Such values are in agreement with the sum of the ionic radii of Tl⁺ and S²⁻ (3.34 Å; Shannon, 1976) and suggest that the bonding of Tl should be ionic in this structure although the eccentric position of Tl2 suggests a degree of lone electron pair activity. The Tl–S distances in philrothite are also in keeping with those observed for the Tl positions (Tl1 and Tl3) in the structure of gabrielite, Tl₂AsCu₂As₃S₇ (3.38–3.49 Å; Balić-Žunić *et al.*, 2006), the Tl positions



FIG. 2. The crystal structure of philrothite projected upon (001). Grey spheres are Tl, small black ones As, and large white ones are S. Zigzag (010) walls of Tl-polyhedra and two types of lone electron pair micelles (large and small) are evident. The horizontal direction corresponds to the *b* axis. Further details are given in the text.

(T11–T15) in the structure of raberite, Tl₅Ag₄As₆SbS₁₅ (3.33–3.41 Å; Bindi *et al.*, 2012), and that found for the Tl position in sicherite, TlAg₂(As,Sb)₃S₆ (3.34 Å; Graeser *et al.*, 2001).

Between the zigzag walls of Tl coordination prisms, coordination pyramids of As(Sb) form diagonally oriented double layers [approximately $(1\overline{3}1)$] separated by broader interspaces which house the lone electron pairs of these elements (Fig. 3). Arsenic atoms in a wall of the double layer have pairs of short As-S bonds oriented either sideways (As1 and As3 outwards in respect to the layer thickness, As2 and As4 inwards, with As6 in the centre of the layer) or upwards (As5). They are interconnected via these short As-S bonds into crankshaft chains S9-M6-S10-M5-S8–M4–S7, running diagonally across the $\sim(1\overline{3}1)$ surfaces of double layers. They all have strongly trapezoidal bases of coordination pyramids. The As2 and As4 sites have a more complex scheme of bonds in the base of the pyramid (Table 3). The refinement of the site occupancies concentrated the Sb content into the mixed As4 site (Table 2).

In addition to the crankshaft scheme, the wall also contains separate AsS_3 polyhedra (As1 and As3). The remaining As2 site has a different coordination showing four similar distances

longer than in other As polyhedra and, presumably, might concentrate some of the other minor cations (Ag). The walls are interconnected with the opposite wall of the double layer by short As-S bonds (these are the vertices of AsS₅ pyramids). The only As site which interconnects with the wall of the next double layer, by infrequent short As-S bonds, is As3. In this way, large lone electron pair micelles are formed by As1 and As2, as well as As5 and As6, with the bridging long As-S distances of the order of 3.4-3.5 Å, and small lone electron pair micelles, formed by As3 and As4, with As-S distances of the order of 2.8 Å. Interconnection of surface crankshafts and groups, as short bonds across the double layer, occurs between S9-Tl2, As6-S4, As5-S3, and As1-S5, As2-S6.

Adjacent As-based slabs are related by the 2_1 and *c* glide operations of the space group. The quality of diffraction data, revealing how poorly crystallized the only known crystals are, allowed recognition and description of principles of the structure but the details of occupancy and especially the interatomic distances are insufficiently constrained (Table 3).

The philrothite structure is related to that of pierrotite (Engel *et al.*, 1983), which is the N = 3 homologue of sartorite (Berlepsch *et al.*, 2003). In



FIG. 3. Distribution of short As–S bonds in a (131) double layer from the As-rich (010) slabs in the structure of philrothite. A crankshaft chain (diagonal, centre) and individual As1, As2 and As3 groups are illustrated, with their interconnections across the double layer. For colouring see Fig. 2.

this structure, however, stoichiometry requires alternation of Tl and Sb in each prismatic column, which is not observed in philrothite. The philrothite structure shares the principal features, which are typical of sartorite homologues, with sartorite and rathite (Berlepsch *et al.*, 2002, 2003).

According to the calculation rules of Makovicky (1985), the chemical composition of philrothite gives the homologue order *N* value of 3.76, in fair agreement with the crystallographic value of N = 4; the difference expresses analytical errors. It is only ~20% away from the ideal formula TlAs₃S₅ which is the maximum possible substitution by Tl and (As,Sb). The traces of 2Pb \leftrightarrow Ag + (Sb,As) substitution do not reach even 25% of the possible substitution range.

The Tl + (Sb,As) substitution in the sartorite homologous series is known for the compositions close to the Pb-(As,Sb) and Tl-(As,Sb) endmembers; data for the central portions of the range are absent. Thallium can substitute only in the capped prismatic sites, usually substituting for lead. The charge compensating M³⁺, connected with this substitution, can either replace Pb in the intermediate slabs or it can replace half of the Pb in the prismatic sites. The latter substitution takes place in the substituted N = 3 homologues because they do not contain Pb in the intermediate slabs. Approaching the highest substitution percentage. seen in philrothite (N = 4), the potential M^{2+} sites in the slabs are progressively replaced by M³⁺, which, according to our a priori reasoning, can move there from the prismatic sites and enable Tl to fill the prismatic sites completely.

To our knowledge, philrothite has neither synthetic analogues nor natural ones. However, although with a different structure, it is noteworthy that the chemical Sb-analogue of philrothite, the synthetic sulfosalt TISb₃S₅ (Gostojic et al., 1982), has the crystal structure which is an N = 3 homologue of lillianite (Makovicky and Balić-Žunić, 1993). It exhibits a monoclinic symmetry with unit-cell dimensions a =7.225(2), b = 15.547(3), c = 8.946(3) Å, $\beta =$ $113.55(3)^{\circ}$ and space group $P2_1/c$. The structure consists of Sb-pyramids forming infinite [Sb₃S₅] slabs parallel to (010). They are glide-reflection twinned on (010) Tl-S layers of bicapped coordination prisms. The former slabs approximate a slightly distorted PbS archetype and contain large lone electron pair micelles, arranged diagonally and en echelon.

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