Zeitschrift: Schweizerische mineralogische und petrographische Mitteilungen = Bulletin suisse de minéralogie et pétrographie

Band: 72 (1992)

Heft: 3

Artikel: Erniggliite (Tl2SnAs2S6), a new mineral from Lengenbach, Binntal (Switzerland) : description and crystal structure determination based on data from synchrotron radiation

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DOI: https://doi.org/10.5169/seals-54913

SCHWEIZ. MINERAL. PETROGR. MITT. 72, 293–305, 1992

Erniggliite ($Tl_2SnAs_2S_6$), a new mineral from Lengenbach, Binntal (Switzerland): description and crystal structure determination based on data from synchrotron radiation

Dedicated to Prof. Ernst Niggli on the occasion of his 75th anniversary

by *Stefan Graeser*[1,2], *Hans Schwander*[2], *Reinhard Wulf*[3] and *Andreas Edenharter*[3]

Abstract

Erniggliite, $Tl_2SnAs_2S_6$, is a new mineral species from the famous sulfosalt locality Lengenbach, Binntal (Switzerland). It occurs in small cavities in a dolomitic rock of Triassic age. Associated are a large number of various, mainly Tl-bearing As-sulfosalts such as hutchinsonite, hatchite, wallisite, lorandite, bernardite, abundant realgar and orpiment and two additional new minerals, edenharterite and stalderite. The mineral is characterized by its conspicuous hexagonal habit and an uncommon micaceous cleavage parallel to {0001}. Individual crystals are very small and do not exceed 0.5 mm. Chemical composition (electron microprobe, mean of 3 analyses) is: Tl 47.91, Sn 13.55, As 17.01, S 22.20, total 100.67 wt% leading to the mineral formula $Tl_2SnAs_2S_6$. The mineral has a steel-grey colour, in fresh cleavage fragments it occurs shiny black, the streak is reddish-black. Microhardness is 47.7 kg/mm^2 for 10 g load (range 46–49), corresponding to a Mohs hardness of about 2–3, D_{calc} = 5.24 g/cm^3. Single crystal studies yielded a trigonal cell with a = 6.680 (3), c = 7.164 (9) Å, V = 276.9 (3) $Å^3$, space group is $P\bar{3}$ and Z = 1. The strongest lines in the X-ray powder pattern are (d_{obs}, I_{obs}, hkl): 3.343 (100)(110), 3.029 (63)(111), 3.060 (50)(102), 2.679 (48)(201), 4.510 (40)(011), 1.866 (38)(212), 2.25 (37)(202), 1.930 (36)(030).

Single crystal diffraction measurements were carried out with synchrotron radiation (λ = 1.1573 Å) on the 5-circle diffractometer at HASYLAB, Hamburg. The structure was solved by an Automated Patterson Interpretation (SHELXS 92) using 448 unique reflections. The refinement of positional parameters and anisotropic temperature factors under consideration of anomalous dispersion correction terms and isotropic extinction lead to a final weighted R value of 0.0253 for all data. In this structure, As builds a trigonal pyramid with three sulfur atoms at the base and As at the top of the polyhedron which is common in As-bearing sulfosalts. However, Tl and Sn form two new coordination polyhedra with sulfur, not known so far from sulfosalts and Tl-Sn-sulfides. The Tl-polyhedron can be described as an antiprism formed by a slightly deformed hexagonal and trigonal base with the central atom Tl shifted towards the hexagonal base. Moreover, a remarkably short Tl–As distance of 3.259 Å is observed which is slightly shorter than the shortest Tl–S bonding of 3.268 Å in this structure. The Sn-polyhedron is a nearly perfect trigonal antiprism with six equal Sn–S distances of 2.5614 Å. The structure is based on layers // (0001) which are formed by a three dimensional network of Tl-polyhedra and As-pyramids. These layers are only connected by the Sn–S antiprisms, explaining the excellent cleavage of the crystals.

The name is for Ernst Niggli, Professor emeritus in mineralogy and petrography at the University of Berne, and president for many years of the "Arbeitsgemeinschaft Lengenbach".

Keywords: Erniggliite, new mineral, Tl-Sn-As-sulfosalt, microprobe analyses, synchrotron radiation, Lengenbach, Binntal, Switzerland.

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1. Introduction

The locality Lengenbach, Binntal, situated in an outcrop of Triassic dolomite of the Penninic Mte. Leone nappe, is known for its special sulfide and sulfosalt minerals since more than 200 years. After a break of almost 50 years, from the beginning of World War I until 1958 during which the extraction of the special minerals had come to a complete standstill, a syndicate of Swiss museums and university institutions ("Arbeitsgemeinschaft Lengenbach", AGL) resuscitated the exploitation works. For more than 20 years this activity had been relatively successful, but then, in the early eighties, the extraction of interesting minerals became more and more problematic. This was partly due to technical reasons, but even more to mineralogical considerations, which made further work in the classical quarry very uncertain. On the one hand, the excavation of minerals at one small site over almost 200 years had led to a deep hole with perpendicular walls up to 20 meters high that endangered any activity at its bottom. On the other hand, the number of interesting minerals gradually decreased with increasing depth. Finally, two alternatives arose for the syndicate – the question of either giving up any exploitation or starting at a new site. Exactly at this critical moment, in 1985, a huge loose block fell into the old quarry which, when split up, turned out to be full of highly interesting minerals. Within less than two years, the study of this material produced three new mineral species, all of them representing new thallium-arsenic-sulfosalts: edenharterite, $TlPbAs_3S_6$ (GRAESER and SCHWANDER, 1992), stalderite, $TlCu(Zn,Fe,Hg)_2As_2S_6$ (GRAESER et al., in prep.) and erniggliite, $Tl_2SnAs_2S_6$ (this paper). The discovery of the three new minerals clearly favoured the syndicate's decision to continue work at a higher level in an easterly direction instead of giving up any mineral extraction at

Tab. 1 Physical and optical properties of erniggliite from Lengenbach.

Habit:	hexagonal, short prismatic
Forms:	pinacoid {0001}
	hexagonal prism {10$\bar{1}$0}
	rhombohedrons {10$\bar{1}$1} and {01$\bar{1}$1}
Colour:	steel-grey to black-grey
Streak:	reddish-black
Cleavage:	{0001} extremely good (micaceous)
Hardness:	VHN_{10} = 47.7 kg/mm^2 – Mohs hardness: 2–3 cleavage fragments are flexible
Density:	5.24 g/cm^3 (calculated)

Ore microscopy (Leitz MPV compact):

Colour:	greyish white
Internal reflections:	none
Anisotropism, bireflectance:	none observed – only sections on {0001} studied

Reflectivity: (measured in air, WTiC standard)

	erniggliite[1]	edenharterite[2]
470 nm	28.6 (27.0–29.8)	28.5–30.5
543 nm	27.3 (26.8–27.7)	28.5–31.5
587 nm	26.9 (25.9–27.4)	27.0–28.5
657 nm	25.1 (23.9–25.5)	27.0–29.0

[1]) Erniggliite, Lengenbach – on {0001} sections only
[2]) Edenharterite, $TlPbAs_3S_6$, Lengenbach (GRAESER and SCHWANDER, 1992)

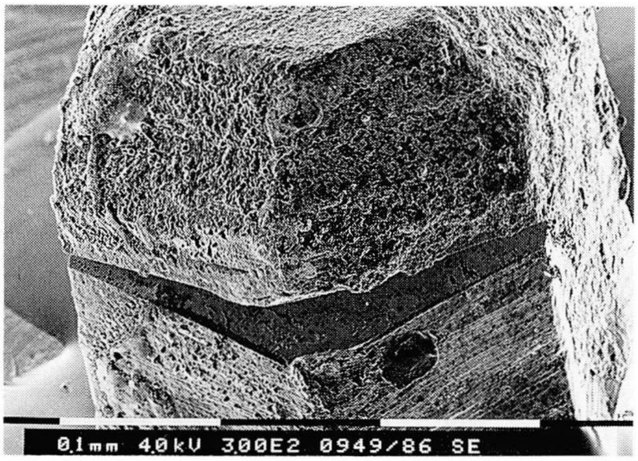

Fig. 1 Erniggliite, Lengenbach. On the SEM picture the (pseudo-) hexagonal habit of the mineral is easily recognizable. Forms are: pinacoid {0001}, hexagonal prism and rhombohedral faces. The surface is rough and uneven (picture: SEM laboratory, University of Basel).

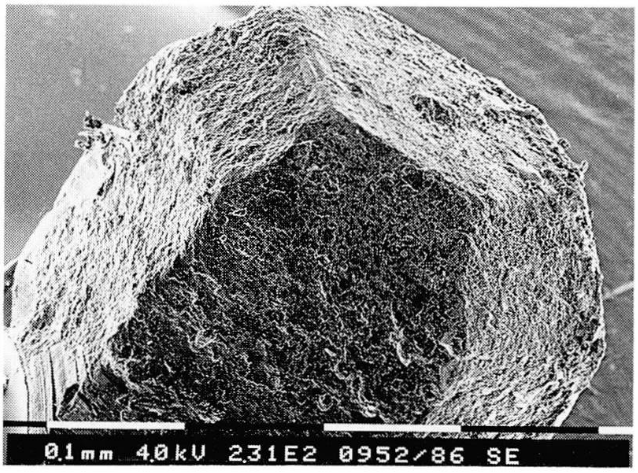

Fig. 2 Erniggliite, Sem picture under stronger magnification documenting the extremely good cleavage parallel to {0001} (SEM laboratory, University of Basel).

Tab. 2 Electron microprobe analyses of erniggliite from Lengenbach, Binntal.

	A	B	C	D	E
Tl	47.78	47.50	48.44	47.91	47.00 wt%
Sn	13.52	13.56	13.57	13.55	13.65
As	16.97	17.05	17.02	17.01	17.23
S	22.16	22.36	22.07	22.20	22.12
Total	100.43	100.47	101.10	100.67	100.00 wt%
Structural formula (based on 11 atoms):					
Tl^{1+}	2.03	2.01	2.06	2.03	2.0
Sn^{4+}	0.99	0.99	0.99	0.99	1.0
As^{3+}	1.97	1.97	1.97	1.97	2.0
S	6.01	6.03	5.98	6.01	6.0

A, B, C analyses of individual grains
D mean of 3 analyses
E theoretical composition for $Tl_2SnAs_2S_6$

Tab. 3 X-ray diffraction data for erniggliite from Lengenbach.

h	k	l	$d_{(obs)}$	$d_{(calc)}$	I/I_1
1	0	0	5.80	5.79	16
0	1	1	4.50	4.50	40
1	1	0	3.343	3.340	100
1	0	2	3.060	3.046	50
1	1	1	3.029	3.027	63
2	0	0	2.893	2.893	19
2	0	1	2.679	2.682	48
1	1	2	2.443	2.443	28
2	0	2	2.250	2.250	37
2	1	1	2.091	2.091	23
0	3	0	1.930	1.928	36
2	1	2		1.866	
			1.866		38
3	0	1		1.862	
3	0	2	1.698	1.705	21
2	2	0	1.670	1.670	30
1	3	2	1.464	1.464	18
1	2	4	1.384	1.386	16
4	1	0	1.261	1.262	12
4	1	1	1.243	1.243	12
0	0	6	1.194	1.194	12

Cell parameters: a = 6.680 (3) Å
c = 7.164 (9)
V = 276.9 (3) Å^3

Debye-Scherrer camera, 90 mm diameter, FeKa-radiation, intensities determined densitometrically.
Cell parameters refined from the powder data.

Lengenbach. Since 1988, the new Lengenbach site has been operated and the results of exploitation at this higher level are quite encouraging: at least two additional unknown Tl-sulfosalts from the new site are under investigation at the moment.

Erniggliite was detected when looking through the share of the Natural History Museum Basel from the exploitation period 1985 at Lengenbach for additional material of the previously determined new mineral stalderite. No more material of this mineral could be found yet, but another unknown mineral was found in sample number L 18,393 that turned out to be the new mineral erniggliite. It is a remarkable fact that another new mineral, edenharterite, was also found in this same sample (L 18,393).

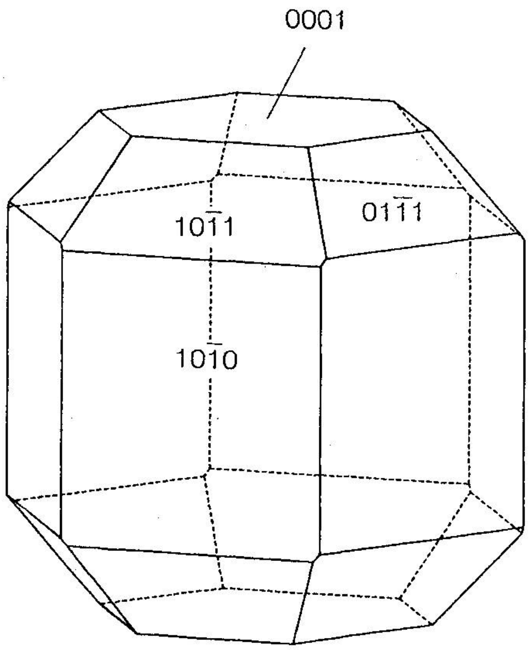

Fig. 3 Erniggliite, idealized computer drawing (SHAPE), showing the common habit of the mineral.

Name and properties of the new mineral were submitted to the "Commission on New Minerals and Mineral Names, I.M.A." for consideration. Under the number 87-025 the proposal for the new mineral was accepted unanimously by the commission.

2. Description

2.1. PHYSICAL AND OPTICAL PROPERTIES

When looking through the samples of the 1985 period, a mineral with a conspicuous hexagonal morphology attracted our attention, because, up to that moment, no sulfosalt mineral with such a morphology was known from Lengenbach. Preliminary Gandolfi-studies confirmed this assump-

Tab. 4 Summary of synchrotron data-collection parameters, structure solution and refinement of erniggliite, $Tl_2SnAs_2S_6$.

Data collection	
Instrumentation	5-circle diffractometer (Stoe Stadi 4)
Radiation source	Synchrotron (HASYLAB at DESY)
Monochromator	Double crystal (Ge 111), $\Delta\lambda/\lambda \approx 3 \times 10^{-4}$
Wavelength	1.1573 Å
Polarization	≈ 93%
Beam stability control	2 standard reflections and real time monitoring of polarization and intensity
Time between standards	30 minutes
Recording technique	Omega step scan
Step width	0.010°
Time/step, No. of steps	0.3–1.0 sec, 41
2Θ range	9.28–100.0°
Index range	$-8 < h < 8, -8 < k < 8, 0 < l < 9$
No. of reflections	1589 (total), 448 (unique)
Data reduction, structure solution and refinement	
Scaling method	By monitor and standard reflection intensities
Absorption correction	Semi-empirical from Psi-scans
min/max transmission	0.12, 0.22
Merging R-values	0.099/0.061, before/after corr.
$R_{int.}$	0.0691
Solution method	Automated Patterson Superposition (SHELXL—92)
Refinement	Full-matrix least-squares on F^2
Scattering curves	f_o from International Tables f', f'' according to CROMER (1983)
Weighting scheme	$w = 1/[\sigma^2 + (0.01 \cdot P)^2 + 1.28\,P]$, where $P = (F_o^2 + 2F_c^2)/3$
Extinction correction	$F_c' = kF_c\,[1 + 0.001 \cdot F_c^2\lambda^3/\sin\Theta]^{-1/4}$
Extinction coefficient	$k = 0.0064\ (6)$
Final R values	
$F^2 > 2\sigma(F^2)$, 445 refl.	$R_w(F^2) = 0.0607, R(F) = 0.0242$
all data, 448 refl.	$R_w(F^2) = 0.0611, R(F) = 0.0253$
No. of refined parameters	19

tion, as the Gandolfi diagram was not identifiable with that of any known mineral species.

Erniggliite occurs in druses (solution cavities) and fissures in the dolomite. The mineral forms euhedral crystals of short prismatic, clearly hexagonal habit less than 1 mm in length. The surface of the crystals is rough, especially when observed under higher magnification. It reveals a conspicuously good, micaceous cleavage perpendicular to the c-axis, very uncommon to other Lengenbach sulfosalts. The colour is grey to black on its surface but shiny black on fresh cleavage planes. The mineral is opaque, even in thin cleavage lamellae; these lamellae are flexible, comparable with thin crystals of the mineral lengenbachite. The streak colour is reddish-black, very similar to that of stalderite, but clearly distinctive from edenharterite. The hardness, measured as Vicker's hardness numbers in the polished section gave values between 46–49 kg/mm^2, according to a Mohs hardness of 2–3.

Due to the micaceous structure of the mineral, optical properties could be studied only in sections parallel to {0001}. Under the ore microscope, therefore, the mineral appeared completely isotropic. The colour of the mineral in reflected light is (greyish-) white, without bireflectance or pleochroism phenomena; internal reflections

Tab. 5 Final fractional atomic coordinates and anisotropic thermal parameters U_{ij} of erniggliite ($Tl_2SnAs_2S_6$) from synchroton data (λ = 1.1573 Å). $T_{hkl} = \exp[-2\pi^2 \cdot (U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{13}hla^*c^*+2U_{12}hka^*b^*)]$

	x	y	z	U_{equ} [Å^2]
Sn	0.0000	0.0000	0.0000	0.0103(3)
Tl	0.3333	0.6667	0.3823(1)	0.0377(3)
As	0.3333	0.6667	0.9266(1)	0.0161(4)
S	0.2051(2)	0.3346(2)	0.7684(2)	0.0196(7)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn	0.0077(3)	0.0077(3)	0.0156(3)	0.000	0.000	0.0039(2)
Tl	0.0461(3)	0.0461(3)	0.0208(3)	0.000	0.000	0.0231(2)
As	0.0163(4)	0.0163(4)	0.0157(4)	0.000	0.000	0.0081(2)
S	0.0269(7)	0.0102(6)	0.0180(5)	0.0015(4)	0.0056(5)	0.0065(5)

could not be observed. All the properties given in table 1 were obtained from such sections as no sections parallel to the c-axis were preparable.

With one of the tiny crystals (about 0.5 mm long) we tried to identify the indices of the face forms by measurement with an optical goniometer. Unfortunately the rough quality of the faces prevented the detection of clear reflexion signals. Nevertheless, an indistinct light concentration indicated a value of about 54° for the angle ρ of the rhombohedrons, and a similar value was obtained by measurement of the angle between the pinacoid {0001} and the rhombohedral faces under the microscope. The calculated angle ρ for the form {$10\bar{1}1$} of erniggliite is 51.1°, so, with some probability, the rhombohedral faces have the indices {$10\bar{1}1$} and {$01\bar{1}1$}, respectively (see Fig. 3).

2.2. CHEMICAL COMPOSITION

Preliminary investigations have been carried out by SEM techniques (Cambridge Stereoscan Mark 2A, equipped with EDS system). The SEM pictures display the hexagonal habit of the crystals and their rough surface and, moreover, the conspicuous micaceous cleavage of erniggliite is clearly documented by the pictures under stronger magnification (see Figs 1, 2). The EDS diagram unequivocally indicated the composition of the major elements Tl, Sn, As, S. Among the Tl-sulfosalts known so far, no compound between Tl, Sn, As could be found; even from the chemical composition it became obvious that the mineral must represent a new mineral species. So the next step was to obtain a quantitative chemical determination. Three chemical analyses were carried out on individual grains by means of an electron microprobe (ARL instrument, SEMQ with EDS-system TN 2000, ZAF program). The following materials were used as standards: $TlAsS_2$ (Tl, As, S), galena (Pb), and pure elements (Sn, Pb). The results of the analyses are shown in table 2. From the analytical data a mineral formula with the expression $Tl_2SnAs_2S_6$ could be calculated. Erniggliite represents the first Lengenbach sulfosalt with Sn as a major element and, moreover, it is the first and only Tl-Sn-sulfosalt known so far.

When it became obvious that the mineral under investigation represented a new mineral, we informed Prof. G.H. Moh (Heidelberg), a keen specialist in Tl-sulfosalts, about the preliminary qualitative composition (Tl–Sn–As–S) of the unknown mineral. One of his coworkers, N. Wang, started experimental studies with this information. He succeeded in synthesizing a powdery sulfosalt phase from these elements that, by an X-ray powder diffraction study, turned out to be absolutely identical with our new mineral. The results of this experimental study will be published elsewhere (Wang and Graeser, in prep.).

2.3. X-RAY DIFFRACTION STUDY

First diffraction experiments were carried out by Gandolfi techniques. They yielded a simple and characteristic pattern which was not identifiable with that of any known mineral species. In order to eliminate any (non-) orientation effects by the Gandolfi techniques, a small fragment of the crystal was sacrificed for a normal Debye-Scherrer powder pattern (Tab. 3) which turned out to be

Tab. 6 Interatomic distances and angles in erniggliite (standard deviations in brackets).

distances (Å)			angles (°)		
Tl – As	3.2594(4)		As – Tl – $S_{4,5,6}$	70.767(5)	3×
			– Tl – $S_{1,2,3}$	144.96 (1)	3×
Tl – $S_{4,5,6}$	3.2681(6)	3×	– Tl – $S'_{4,5,6}$	73.305(4)	3×
– $S_{1,2,3}$	3.3695(5)	3×			
– $S'_{4,5,6}$	3.7473(7)	3×	S_4 – Tl – $S_{5,6}$	109.709(6)	2×
			S_5 – Tl – S_6	109.709(6)	
mean Tl–S	3.4616		$S_{4,5,6}$ – Tl – $S_{1,2,3}$	101.395(3)	3×
			$S_{4,5,6}$ – Tl – $S_{2,3,1}$	80.825(3)	3×
			$S_{4,5,6}$ – Tl – $S_{3,2,1}$	140.45 (2)	3×
			$S_{4,5,6}$ – Tl – $S'_{4,5,6}$	144.07 (2)	3×
			$S_{4,5,6}$ – Tl – $S'_{5,4,6}$	56.56 (1)	3×
			$S_{4,5,6}$ – Tl – $S'_{6,5,4}$	57.14 (1)	3×
			S_1 – Tl – $S_{2,3}$	59.626(8)	2×
			S_2 – Tl – S_3	59.626(8)	
			$S_{1,2,3}$ – Tl – $S'_{4,5,6}$	107.786(5)	3×
			$S_{1,2,3}$ – Tl – $S'_{5,6,4}$	74.204(4)	3×
			$S_{1,2,3}$ – Tl – $S'_{6,4,5}$	132.25 (1)	3×
			S'_4 – Tl – $S'_{5,6}$	112.098(5)	2×
			S'_5 – Tl – S'_6	112.098(5)	
Sn – $S_{1,2,3}$	2.5614(6)	3×	S_1 – Sn – $S_{2,3}$	82.607(3)	2×
– $S_{4,5,6}$	2.5614(6)	3×	S_2 – Sn – S_3	82.607(3)	
			S_4 – Sn – $S_{5,6}$	97.393(3)	2×
			S_5 – Sn – S_6	97.393(3)	
As – $S'_{1,2,3}$	2.2421(8)	3×	S_1 – As – $S_{2,3}$	96.691(3)	2×
			S_2 – As – S_3	96.691(3)	

Symmetry code

1:	x,	y,	z	2:	–y,	x–y,	z	3:	y–x,	–x,	z
4:	–x,	–y,	–z	5:	y,	y–x,	–z	6:	x–y,	x,	–z

practically identical with the Gandolfi pattern, with minor shifts of the intensities. Consequently, the mineral was studied by a single crystal investigation with Weissenberg and Precession techniques. Due to the micaceous cleavage and the flexibility of the mineral, it was quite difficult to separate suitable single crystal fragments. From the single crystal study a cell with hexagonal symmetry was derived, primarily, yet the subsequent structure determination clearly proved the trigonal symmetry of the mineral.

2.4. OCCURRENCE, GEOCHEMICAL CONSIDERATIONS

Erniggliite is not only the first Sn-bearing sulfosalt mineral of the Lengenbach occurrence, it seems to represent the first Tl-Sn-As-sulfosalt described to date. In the long history of more than 250 years of mineralogical research in Lengenbach, no mineral with Sn as a major element has been detected among the wide spectrum of its minerals. As a minor element, however, Sn could be determined in the course of a trace element study of some sulfide minerals from the dolomitic rocks in Binntal; galena and sphalerite as well may contain the element Sn in concentrations up to 400 ppm (GRAESER, 1969). In various studies on the formation of the remarkable As-sulfosalt mineralization at Lengenbach, we postulated the hydrothermal transport of several elements like As, Cu, Tl, etc. from outside (by remobilization of Cu-As-ore concentrations in the gneisses in the south) into the dolomitic rocks where they formed the sulfosalt minerals by reaction with the

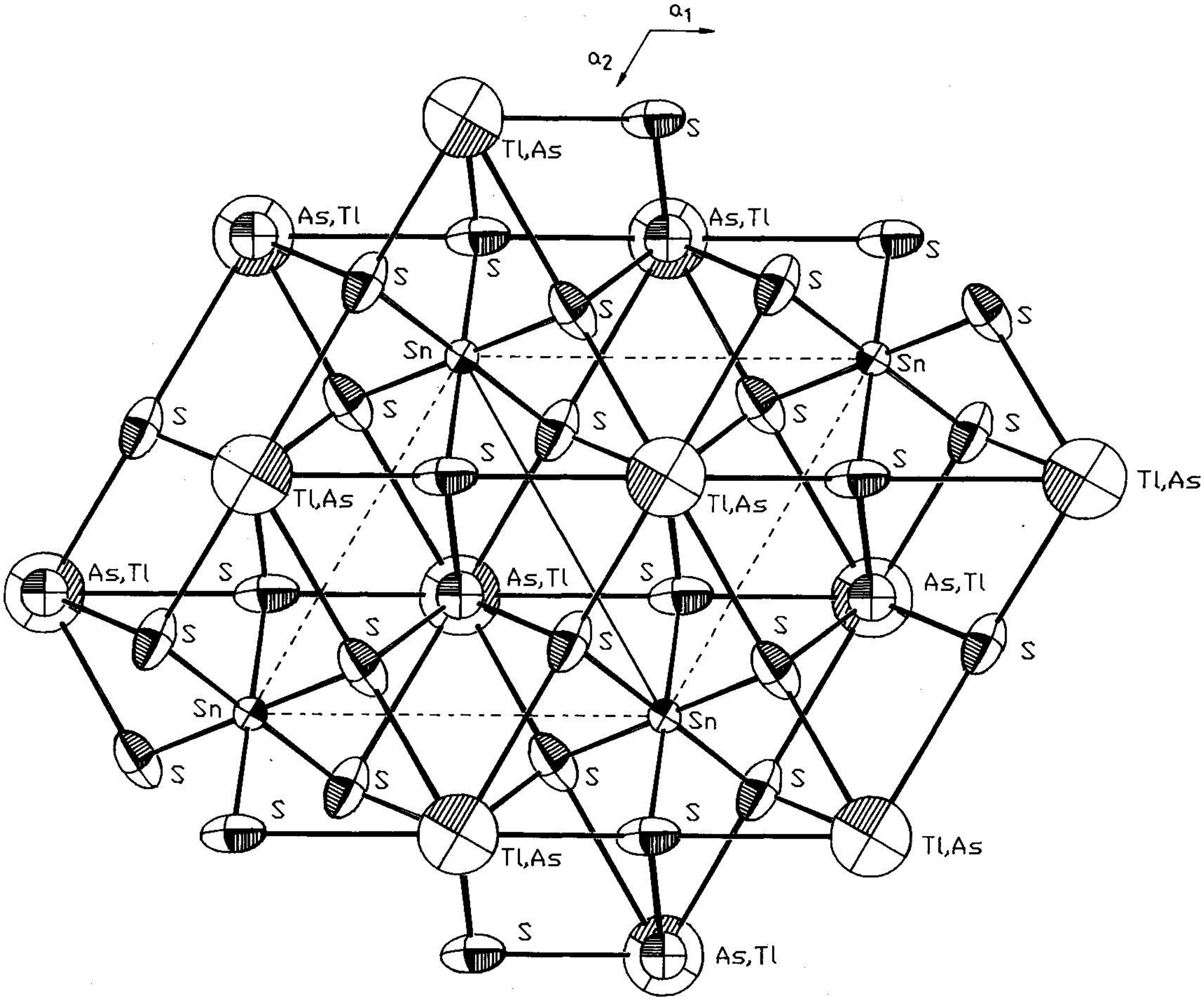

Fig. 4 Projection of the structure of erniggliite // c-axis (the unit cell is marked with broken lines).

minerals preexistent in the dolomite, like galena, pyrite, sphalerite, etc. (GRAESER 1965, 1975). On their way through the gneisses towards north, these hydrothermal solutions gradually cooled, became oversaturated, and were partly precipitated, leading to a very uncommon mineralization within the gneisses. One of these special minerals in the gneisses, asbecasite, a Be-Ca-As-oxide (described as a new mineral species by GRAESER, 1966), showed an unexpected content of 2.1 wt% SnO_2. Obviously, the element Sn too, was transported into the dolomites together with As, Cu, Tl, etc. and, under extremely special conditions, even led to the formation of sulfosalts with Sn as a major element in the dolomite.

Erniggliite, in its characteristic habit, represents the only Lengenbach sulfosalt mineral with unequivocally (pseudo-) hexagonal symmetry and together with its conspicuous excellent cleavage along {0001}, may not be mistaken for any other Lengenbach mineral. Therefore, it is highly improbable that erniggliite occurred in the old classical Lengenbach quarry – such a characteristical mineral would not have escaped the keen attention of the old mineralogists! The mineral was found together with the two other new minerals edenharterite, $TlPbAs_3S_6$ (GRAESER and SCHWANDER, 1992) and stalderite, $TlCu(Zn,Fe,Hg)_2As_2S_6$ (GRAESER et al., in prep.) in a loose block from the upmost border of the classical Lengenbach quarry. So it presumably originates from a considerably higher level than had ever been worked for the extraction of minerals. It is a strange fact that in the very restricted area of the mineralized dolomitic rock in Lengenbach, geochemical factors change rapidly within a few meters. The special zone of the dolomite containing the Tl-rich minerals obviously could not be found in the old quarry

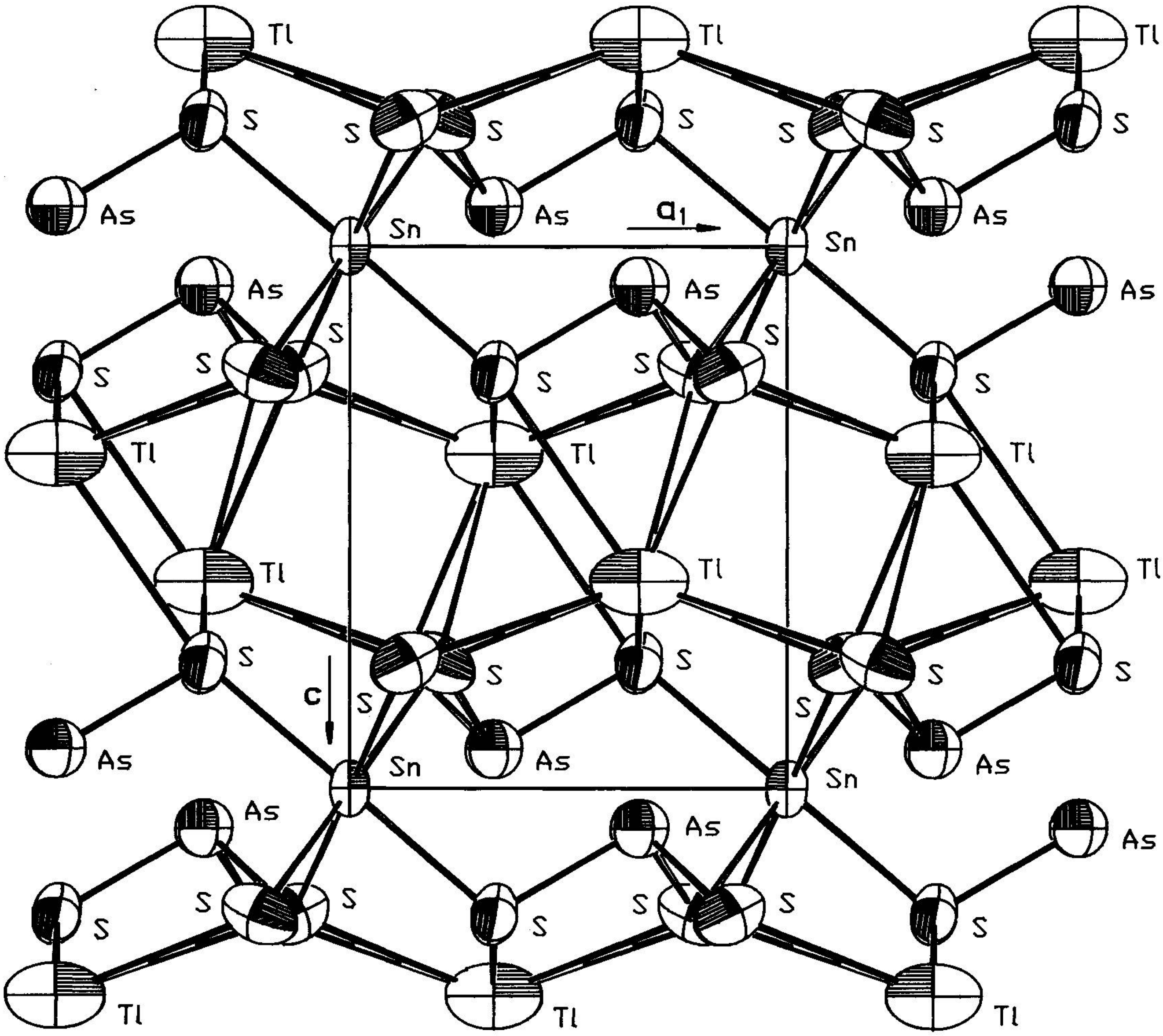

Fig. 5 Projection of the structure of erniggliite // a_2^*-axis.

because it was eroded by the Lengenbach stream long before. For details of the differences between the old and the new working sites in Lengenbach, see also the description of edenharterite (GRAESER and SCHWANDER, 1992).

Meanwhile, 5–6 years have passed since the first indications of the three new Lengenbach minerals. Edenharterite has been found in more than 100 clearly identified samples since its discovery. In the case of stalderite, about 10 samples have been collected, but for erniggliite only two samples exist, with about 6–8 minute crystals, in all. The Tl-Sn-As-sulfosalt erniggliite seems to represent by far the rarest member of the three new Tl-minerals from Lengenbach.

3. Experimental

3.1. USE OF SYNCHROTRON RADIATION

Synchrotron radiation results from the acceleration of relativistic electrons in storage rings, which were primarily used for high energy collision experiments, and was regarded for a long time only as an energy consuming undesired byproduct. Meanwhile, due to the excellent radiation properties, e.g. the high intensity at a wide spectral range up to the hard X-ray range, these storage rings have been improved and optimized especially for the generation of synchrotron radiation. Hereby the high intensity wavelength range depends in

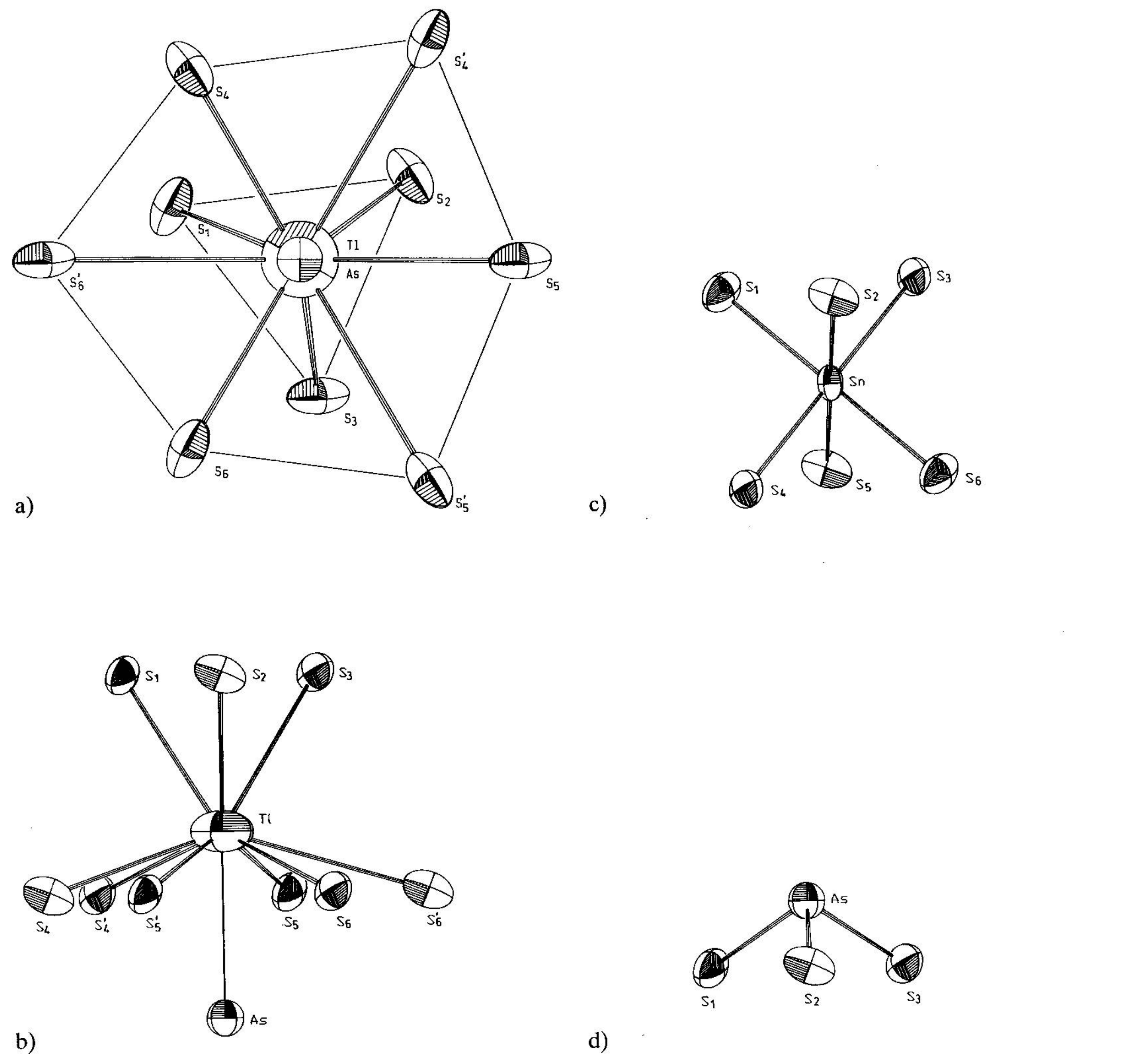

Fig. 6 Me-coordination polyhedra. a) TlS_9-polyhedron viewed along the c-axis; b) TlS_9-polyhedron rotated 50° around the a_2-axis; c) SnS_6 trigonal antiprism; d) AsS_3 trigonal pyramid.

each case on the characteristics of the storage rings. Consequently, worldwide several laboratories have been built up with specific experimental stations. For crystallographers and mineralogists the development of high precision single crystal diffractometry and powder diffraction are of special interest. The main advantages of using synchrotron radiation in single crystal work are:

1) *Variabel wavelength* → the wavelength can be adapted to the problem studied (e.g. use of anomalous dispersion effects).

2) *High intensity* → smaller crystals can be used to reduce problems arising from faulty extinction and absorption correction. Additionally, even very weak reflections are measured with a high significance level.

3) *High degree of polarization* → reflections with a high 2Θ-angle can be measured significantly.

To take advantage of these features we decided to use synchrotron radiation in case of the new mineral erniggliite. Our aim was, to obtain an excellent data set for a precise structure determination with low standard deviation of the atomic parameters in order to get exact structural data for the systematics of Tl–Sn sulfosalts. Since

Tab. 7 Observed and calculated structure factors of erniggliite.

Observed and calculated structure factors for EDEHEXE in P-3 Page 1

h	k	l	10Fo	10Fc	10s
0	1	0	392	412	5
-1	2	0	1994	1960	30
0	2	0	776	764	6
-2	3	0	411	426	6
-1	3	0	123	132	1
0	3	0	1627	1645	14
-3	4	0	385	389	4
-2	4	0	2007	1930	23
-1	4	0	77	61	2
0	4	0	374	383	2
-4	5	0	1081	1052	16
-3	5	0	248	248	3
-2	5	0	122	106	9
-1	5	0	1062	1035	27
0	5	0	158	152	1
-5	6	0	178	176	4
-4	6	0	150	147	1
-3	6	0	815	799	14
-2	6	0	253	244	5
-1	6	0	191	191	5
0	6	0	905	903	14
-6	7	0	113	114	2
-5	7	0	781	769	22
-4	7	0	127	120	2
-3	7	0	46	39	3
-2	7	0	807	785	18
-1	7	0	99	85	4
0	7	0	61	58	1
-7	8	0	375	377	7
-6	8	0	94	88	2
-5	8	0	114	106	3
-4	8	0	669	655	18
-3	8	0	209	211	5
-2	8	0	25	16	3
-1	8	0	375	377	12
0	0	1	69	46	10
-1	1	1	369	358	8
0	1	1	1106	1091	31
1	1	1	290	284	6
-3	2	1	231	212	5
-2	2	1	1601	1610	47
-1	2	1	186	156	24
0	2	1	477	450	10
1	2	1	756	744	11
2	2	1	155	142	4
-5	3	1	138	110	13
-4	3	1	765	749	12
-3	3	1	40	35	2
-2	3	1	325	326	9
-1	3	1	954	933	19
0	3	1	48	46	2
1	3	1	418	409	11
2	3	1	521	516	24
3	3	1	119	114	6
-7	4	1	122	123	6
-6	4	1	568	559	25
-5	4	1	295	295	8
-4	4	1	171	155	3
-3	4	1	436	434	2
-2	4	1	125	82	33
-1	4	1	218	206	6
0	4	1	943	915	15
1	4	1	293	288	10
2	4	1	80	60	8
3	4	1	286	279	18
4	4	1	275	270	19
-8	5	1	254	255	17
-7	5	1	238	226	16
-6	5	1	343	341	19
-5	5	1	541	525	9
-4	5	1	52	46	5
-3	5	1	199	191	2
-2	5	1	654	630	6
-1	5	1	65	60	1
0	5	1	96	83	6
1	5	1	420	409	21
2	5	1	230	224	11
3	5	1	303	304	18
-8	6	1	44	45	6
-7	6	1	144	139	10
-6	6	1	179	174	5
-5	6	1	189	185	8
-4	6	1	643	627	12
-3	6	1	391	382	7
-2	6	1	55	23	7
-1	6	1	174	167	6
0	6	1	191	194	10
1	6	1	164	156	8
2	6	1	247	242	21
-8	7	1	61	55	4

h	k	l	10Fo	10Fc	10s
-7	7	1	41	31	5
-6	7	1	290	285	10
-5	7	1	149	148	2
-4	7	1	177	170	6
-3	7	1	403	362	26
-2	7	1	155	153	6
-1	7	1	256	261	15
0	7	1	326	323	18
1	7	1	52	43	5
-7	8	1	296	296	14
-6	8	1	90	89	3
-5	8	1	53	50	2
-4	8	1	104	101	2
-3	8	1	171	164	5
-2	8	1	313	315	13
-1	8	1	274	285	19
0	0	2	117	132	1
-1	1	2	1555	1596	31
0	1	2	1389	1409	30
1	1	2	941	952	16
-3	2	2	1084	1090	33
-2	2	2	656	693	9
-1	2	2	1080	1056	25
0	2	2	1599	1611	19
1	2	2	902	924	17
2	2	2	251	256	3
-5	3	2	773	774	18
-4	3	2	1005	1010	28
-3	3	2	703	712	7
-2	3	2	1372	1380	15
-1	3	2	1163	1143	14
0	3	2	727	720	8
1	3	2	1230	1226	38
2	3	2	519	512	17
3	3	2	540	525	27
-7	4	2	454	439	29
-6	4	2	238	235	10
-5	4	2	628	638	16
-4	4	2	1013	1042	21
-3	4	2	646	670	8
-2	4	2	242	239	1
-1	4	2	758	756	9
0	4	2	427	428	6
1	4	2	626	617	21
2	4	2	684	669	35
3	4	2	222	207	15
4	4	2	241	242	20
-8	5	2	363	359	27
-7	5	2	275	281	18
-6	5	2	771	762	30
-5	5	2	379	395	8
-4	5	2	532	541	14
-3	5	2	917	931	4
-2	5	2	608	617	5
-1	5	2	560	549	27
0	5	2	719	725	21
1	5	2	599	585	30
2	5	2	305	298	22
3	5	2	533	538	52
-8	6	2	351	358	21
-7	6	2	188	183	12
-6	6	2	214	226	5
-5	6	2	375	377	11
-4	6	2	313	308	4
-3	6	2	651	646	9
-2	6	2	766	773	26
-1	6	2	305	293	19
0	6	2	247	234	14
1	6	2	337	331	25
2	6	2	74	55	7
-7	7	2	406	424	12
-6	7	2	337	339	14
-5	7	2	271	279	6
-4	7	2	589	596	11
-3	7	2	346	343	10
-2	7	2	265	268	14
-1	7	2	533	547	37
0	7	2	100	84	6
-6	8	2	461	466	15
-5	8	2	112	107	3
-4	8	2	195	196	3
-3	8	2	206	204	11
-2	8	2	150	130	11
0	0	3	954	971	29
-1	1	3	581	596	4
0	1	3	503	504	3
1	1	3	1237	1275	28
-3	2	3	356	375	8
-2	2	3	57	45	2
-1	2	3	958	963	15

h	k	l	10Fo	10Fc	10s
0	2	3	173	160	1
1	2	3	475	482	10
2	2	3	635	644	20
-5	3	3	68	63	1
-4	3	3	174	169	5
-3	3	3	853	868	13
-2	3	3	393	401	2
-1	3	3	280	273	2
0	3	3	859	860	14
1	3	3	344	343	7
2	3	3	291	280	5
3	3	3	789	768	35
-7	4	3	56	52	3
-6	4	3	80	72	5
-5	4	3	481	479	17
-4	4	3	191	174	11
-3	4	3	528	526	3
-2	4	3	689	692	3
-1	4	3	279	278	3
0	4	3	130	45	39
1	4	3	484	477	13
2	4	3	185	183	8
3	4	3	196	187	11
4	4	3	231	231	19
-8	5	3	50	48	4
-7	5	3	321	313	16
-6	5	3	132	122	5
-5	5	3	136	138	3
-4	5	3	765	760	12
-3	5	3	97	100	1
-2	5	3	161	156	1
-1	5	3	784	777	25
0	5	3	49	41	2
1	5	3	81	76	5
2	5	3	340	323	15
3	5	3	30	29	3
-8	6	3	171	176	14
-7	6	3	234	247	17
-6	6	3	381	383	9
-5	6	3	80	71	3
-4	6	3	50	35	7
-3	6	3	350	348	3
-2	6	3	180	176	7
-1	6	3	367	364	19
0	6	3	369	368	13
1	6	3	45	37	7
2	6	3	98	96	6
-7	7	3	196	200	5
-6	7	3	82	83	4
-5	7	3	387	387	13
-4	7	3	46	43	2
-3	7	3	84	81	10
-2	7	3	375	378	24
-1	7	3	44	15	16
0	7	3	49	51	3
-6	8	3	160	163	6
-5	8	3	284	297	8
-4	8	3	376	372	11
-3	8	3	57	24	11
-2	8	3	29	24	2
0	0	4	315	330	10
-1	1	4	1369	1352	5
0	1	4	508	502	3
1	1	4	750	764	16
-3	2	4	1230	1240	23
-2	2	4	86	43	3
-1	2	4	896	912	7
0	2	4	1173	1185	5
1	2	4	340	334	7
2	2	4	177	183	4
-5	3	4	865	868	38
-4	3	4	485	479	16
-3	3	4	542	561	8
-2	3	4	998	1003	4
-1	3	4	464	461	5
0	3	4	554	572	11
1	3	4	731	727	23
2	3	4	236	192	41
3	3	4	235	233	11
-7	4	4	569	590	35
-6	4	4	123	39	38
-5	4	4	443	444	14
-4	4	4	808	820	14
-3	4	4	289	279	1
-2	4	4	150	156	1
-1	4	4	1138	1139	9
0	4	4	69	39	4
1	4	4	432	425	17
2	4	4	665	654	24
3	4	4	113	102	7

h	k	l	10Fo	10Fc	10s
4	4	4	34	23	2
-7	5	4	67	65	4
-6	5	4	428	426	18
-5	5	4	147	137	2
-4	5	4	293	298	5
-3	5	4	712	723	3
-2	5	4	251	252	2
-1	5	4	293	297	6
0	5	4	700	693	25
1	5	4	363	354	17
2	5	4	85	79	5
-7	6	4	140	139	12
-6	6	4	18	9	4
-5	6	4	755	772	25
-4	6	4	82	74	3
-3	6	4	429	436	2
-2	6	4	548	563	7
-1	6	4	172	167	7
0	6	4	81	21	23
1	6	4	553	555	34
-6	7	4	235	238	7
-5	7	4	52	46	4
-4	7	4	449	456	3
-3	7	4	198	199	2
-2	7	4	56	43	8
-1	7	4	347	353	15
-4	8	4	54	55	1
0	0	5	1074	1030	27
-1	1	5	773	765	2
0	1	5	622	636	2
1	1	5	536	527	7
-3	2	5	677	679	14
-2	2	5	321	322	2
-1	2	5	736	724	3
0	2	5	221	223	3
1	2	5	567	573	16
2	2	5	674	667	31
-5	3	5	454	450	22
-4	3	5	225	217	10
-3	3	5	563	552	9
-2	3	5	641	645	8
-1	3	5	366	377	4
0	3	5	554	555	13
1	3	5	606	603	19
2	3	5	324	320	17
3	3	5	112	113	4
-7	4	5	337	348	17
-6	4	5	123	105	3
-5	4	5	445	450	20
-4	4	5	235	232	4
-3	4	5	549	554	3
-2	4	5	636	636	3
-1	4	5	646	646	8
0	4	5	169	166	6
1	4	5	470	459	19
2	4	5	249	242	10
3	4	5	152	151	11
-7	5	5	300	312	18
-6	5	5	445	448	17
-5	5	5	170	169	3
-4	5	5	258	254	4
-3	5	5	446	448	4
-2	5	5	205	205	1
-1	5	5	243	240	6
0	5	5	358	358	11
1	5	5	40	25	4
2	5	5	293	299	17
-6	6	5	302	299	11
-5	6	5	482	482	10
-4	6	5	48	26	10
-3	6	5	399	411	2
-2	6	5	221	224	2
-1	6	5	316	312	9
0	6	5	302	307	10
-5	7	5	247	253	8
-4	7	5	325	328	2
-3	7	5	56	37	7
-2	7	5	261	262	7
0	0	6	534	524	6
-1	1	6	54	23	1
0	1	6	845	852	3
1	1	6	205	189	8
-3	2	6	73	64	3
-2	2	6	1204	1169	14
-1	2	6	35	33	2
0	2	6	91	58	1
1	2	6	742	741	22
2	2	6	316	314	9
-5	3	6	48	10	8
-4	3	6	517	513	16

h	k	l	10Fo	10Fc	10s
-3	3	6	127	126	3
-2	3	6	133	110	9
-1	3	6	689	687	3
0	3	6	115	114	4
1	3	6	237	230	7
2	3	6	560	564	20
3	3	6	93	97	3
-6	4	6	547	564	19
-5	4	6	52	50	5
-4	4	6	74	48	1
-3	4	6	588	593	5
-2	4	6	333	343	2
-1	4	6	93	84	5
0	4	6	792	794	17
1	4	6	34	36	2
2	4	6	70	61	5
-6	5	6	246	253	9
-5	5	6	516	525	7
-4	5	6	126	110	19
-3	5	6	131	126	1
-2	5	6	530	542	3
-1	5	6	118	117	1
0	5	6	77	68	4
1	5	6	287	285	10
-5	6	6	34	15	4
-4	6	6	543	552	4
-3	6	6	125	133	1
-2	6	6	134	129	4
-1	6	6	364	373	13
0	0	7	556	544	8
-1	1	7	820	789	7
0	1	7	62	38	4
1	1	7	146	145	4
-3	2	7	639	629	15
-2	2	7	73	44	1
-1	2	7	252	256	1
0	2	7	1060	1068	26
1	2	7	152	138	6
2	2	7	343	339	11
-5	3	7	516	514	13
-4	3	7	58	49	3
-3	3	7	205	202	2
-2	3	7	693	693	4
-1	3	7	64	21	10
0	3	7	196	200	2
1	3	7	583	584	12
2	3	7	142	142	2
-5	4	7	148	150	3
-4	4	7	750	752	6
-3	4	7	219	223	2
-2	4	7	324	323	2
-1	4	7	478	481	5
0	4	7	71	18	10
1	4	7	166	162	3
-5	5	7	112	97	12
-4	5	7	39	35	2
-3	5	7	539	541	2
-2	5	7	61	51	2
-1	5	7	39	26	7
0	5	7	472	482	11
0	0	8	637	620	6
-1	1	8	244	243	1
0	1	8	352	342	2
1	1	8	434	434	3
-3	2	8	122	120	1
-2	2	8	36	26	1
-1	2	8	306	298	6
0	2	8	96	98	2
1	2	8	302	302	5
2	2	8	409	418	2
-4	3	8	315	314	5
-3	3	8	328	327	2
-2	3	8	225	230	2
-1	3	8	306	306	5
0	3	8	314	317	2
1	3	8	239	246	2
-4	4	8	59	47	8
-3	4	8	314	316	2
-2	4	8	432	444	3
-1	4	8	60	41	9
0	4	8	83	81	2
0	0	9	138	131	3
-1	1	9	187	180	1
0	1	9	585	592	5
1	1	9	370	370	2
-2	2	9	567	560	4
-1	2	9	328	324	4
0	2	9	59	52	3

$Tl_2SnAs_2S_6$ shows an excellent cleavage parallel (0001), it was necessary, to use a crystal as small as possible, to avoid micro-twinning and splitting of the reflection profiles.

Our single crystal X-ray diffraction measurement was carried out at the five circle diffractometer at HASYLAB (Hamburger Synchrotron Labor) at DESY (Deutsches Elektronen-Synchrotron). The main components of this experimental station for single crystal investigations, which was designed and mounted by the synchrotron working group of Prof. Dr. Kupčik from the Institute of mineralogy and crystallography, Göttingen (KUPČIK et al., 1983, 1986) are:

a) commercial four circle diffractometer (Stoe Stadi4) which is modified and adapted for synchrotron radiation use and mounted on a fifth circle for special applications,

b) fixed exit monochromator with two independent germanium [111] single crystals,

c) polarization/intensity monitor for data reduction and beam stability control,

d) beam position monitor.

The main specifications of crystallographic interest are:

a) angular resolution: 0.001°

b) wavelength range: 0.3–2.2 Å

c) wavelength resolution at 1 Å:
$\Delta\lambda/\lambda \approx 3 \times 10^{-4}$

d) degree of polarization ≈ 85–95%

For the actual diffraction measurements a tiny crystal of good quality with dimensions of 0.173 × 0.154 × 0.116 mm^3 was used.

From 23 reflections in the 2Θ-range of 21.8–81.8° the lattice constants were determined by least-squares refinement to be a = 6.678(2), c = 7.160(2), $\alpha = 90°$, $\beta = 90°$ and $\gamma = 120°$. With Z = 1 a calculated density of ρ = 5.233 g/cm^3 results. These values are in good agreement with those evaluated from the powder measurements mentioned above.

The data collection was carried out at 1.1573 Å using a modified measuring procedure (WENDSCHUH-JOSTIES and WULF, 1989) which takes into account the special properties of synchrotron radiation.

In the range of $(\sin\Theta)/\lambda \leq 0.66$ $Å^{-1}$ 1589 reflections were measured in the ω step scan mode with a step width of 0.01°. The intensity data were scaled by monitor and standard intensities and corrected for Lorentz and polarization factors using the synchrotron data reduction program Synred (WENDSCHUH-JOSTIES and WULF, 1984). Additionally, an empirical absorption correction based on ψ-scans was carried out (XEMP, SHELDRICK, 1976). The linear absorption coefficient at λ = 1.1573 Å is calculated to μ = 394.61 cm^{-1} resulting to a mean μR-value of 2.91. Table 4 summarizes the parameters and results of the data collection and the subsequent structure solution and refinement. Analysing the intensity data for systematic absences and internal consistency of equivalent reflections the spacegroups $P\bar{3}$ and P3 remained possible. Finally, from structure refinement the spacegroup $P\bar{3}$ turned out to be the correct one.

3.2. STRUCTURE SOLUTION AND REFINEMENT

Whereas direct methods failed, the structure solution succeeded by use of an automated supersharp Patterson superposition method, implemented in the new structure solution package SHELXS-92 (SHELDRICK, 1992) which was available at that time as a pre-version. For the structure refinement we used the programm SHELXL-92 (SHELDRICK, 1992), where the least-squares refinement is based on F^2. Taking into account anomalous dispersion correction terms, the refinement of atomic parameters, anisotropic temperature factors and isotropic extinction led to an unweigthed *R(F)*-value of 0.0242 for observed (445) and 0.0253 for all reflections (448). It is important to notice, that as a result of the high intensity and collimation of synchrotron radiation from a total of 448 unique reflections 445 were measured with $F^2 > 2\sigma(F^2)$. Additionally the standard deviations of atomic and thermal parameters are remarkable small. A refinement of the occupancy factors confirm the ideal formula of $Tl_2SnAs_2S_6$.

According to the classification of sulfosalts as proposed by NOWACKI (1969), erniggliite with S:As = φ = 3 belongs to the group II α_1 with isolated BS_3-pyramids, which is a common group in As-sulfosalts.

The final atomic coordinates and thermal parameters including e.s.d.'s are summarized in table 5, while the interatomic distances and angles are listed in table 6. For completeness an abbreviated F_o/F_c list is given in table 7.

3.3. DESCRIPTION OF THE STRUCTURE

The arrangements of the atoms projected //c- and // a_2^*-axis are shown in figures 4 and 5 respectively. In figures 6 a–d the Me-polyhedra are presented.

Analysing the structure of erniggliite we found two new (Me-S)-polyhedra, a TlS_9- and a SnS_6-polyhedron not known so far from sulfosalts and (Tl–Sn)-sulfides. The coordination polyhedron of Tl may be described in two different ways. If we assume, that Tl–S distances up to 3.75 Å are regarded as bonds (mean value 3.4616 Å), the resulting polyhedron is an antiprism with different bases. However, if we only consider the six shortest Tl–S distances as bonds (mean value 3.3188 Å) a distorted trigonal antiprism with additionally three longer distances is formed. Since these longer bonds are within the plane of one trigonal base, we prefer the first description and propose for this new kind of environment the name "hex-tri" antiprism. In this surrounding the Tl atom is coordinated by nine sulfur atoms with distances in the range of 3.2681 to 3.7473 Å (Tab. 6) in form of a slightly distorted antiprism with a hexagonal and a trigonal base (Figs 6 a, b). The Tl atom is shifted from the center of the polyhedron along the 3-fold rotation axis towards the hexagonal base. This base is built by those three sulfur atoms with the shortest (3 × 3.2681 Å) and those three sulfur atoms with the longest Tl–S bonds (3 × 3.7473 Å). The angles between these six bonds are 60°. According to the differences of the bondlength a distorted hexagon results. The trigonal base is formed as a perfect equilateral triangle by three sulfur atoms with equal Tl–S distances of 3.3695 Å. In the case of an ideal "hex-tri" antiprism the rotation-angle between the two bases is 30°. However, in erniggliite this angle was found to be 22°, indicating a twisting of the trigonal base for 8° towards the longer Tl–S bonds (Fig. 6a).

The mean value of all Tl-S distances for the "hex-tri" antiprism is 3.4616 Å, which is somewhat longer than mean values known from other Tl-sulfosalts with 9-fold coordinated thallium e.g. 3.38 Å in $Tl_8Pb_4Sb_{21}As_{19}S_{68}$ (the mean value of eight (Tl–S)-polyhedra; NAGL, 1979), 3.389 Å in synthetic parapierrotite (ENGEL, 1980), 3.369 Å in rebulite (BALIĆ-ŽUNIĆ et al., 1982), 3.43 Å in simonite (ENGEL et al., 1982). Except of simonite and rebulite all referenced (Tl–S)-polyhedra are distorted trigonal prisms with three additional sulfur atoms opposite to the three side faces.

The agreement of the mean value of the six shorter Tl–S bonds of 3.3188 Å with the sum of the ionic radii, 3.32 Å of Tl^+ and S^{2-} as found in TlS (HAHN and KLINGLER, 1949) and published to be $r_{Tl^+} = 1.44$ Å and $r_{S^{2-}} = 1.84$ Å (PAULING, 1968) suggest that the Tl–S bonding is mainly ionic. The three longer Tl–S bonds may indicate a stereochemical activity of the lonely electron pair of the thallium ion. In this structure a remarkable short Tl–As distance of 3.2594 Å is observed which is slightly shorter than the shortest Tl–S bonding of 3.2681 Å, whereas Tl–As interactions in other (Tl–As)-sulfosalts are usually in the range of 3.3 to 3.6 Å. The stereochemical activity mentioned above and a possible Tl–As interaction may explain the shift of the Tl atom towards the hexagonal base. Since in the structure of erniggliite the shortest Tl–Tl distance is 4.205 Å we think there is no tendency of Tl–Tl interactions as proposed for other Tl-sulfosalts e.g. lorandite with Tl–Tl distances of 3.54 and 4.03 Å (FLEET, 1973).

The Sn-polyhedron is a nearly perfect trigonal antiprism with six equal Sn–S bonds of 2.5614 Å and angles of 82.607°(3 ×) and 97.393° (3 ×) (Figs 4, 6c). Inspecting the ICSD-file (BERGERHOF et al., 1983) we did not find any (Tl–Sn)-sulfosalt referenced up to now. So we searched for (Tl–Sn)-sulfides containing Sn with a formal valence of 4+, because we assume that in the structure of erniggliite this Sn-valence is present. We found four entries, two of them refer to structures with a more or less distorted tetrahedral surrounding (KLEPP, 1984 and PIFFARD, 1984), in the third structure cited the Tl atom is coordinated by five sulfur in form of a distorted trigonal bipyramid (EULENBERGER, 1981), whereas in the fourth (Tl–Sn)-sulfide additionally a deformed octahedron occurs (PIFFARD et al., 1984).

The As atom forms with three sulfur atoms a perfect trigonal pyramid with the As atom at the apex and with As–S distances of 2.2421 Å (3×) and S–As–S angles of 96.691° (3×). This coordination polyhedron is quite common in As-sulfosalts, but was not observed before in this perfect way with the exception of ellisite, Tl_3AsS_3 (GOSTOJIĆ, 1980). The distances and angles in erniggliite are very close to the mean values for AsS_3-pyramids in sulfosalts (2.29 Å, 98.0°, EDENHARTER, 1976).

The structure of erniggliite is based on layers // (0001) (Fig. 5). The layer consists of the TlS_9-"hex-tri"-antiprisms and isolated AsS_3-pyramids, sharing common edges and corners. The thicknes of the layer corresponds exactly to the c-lattice parameter. The layers are connected only by the Sn antiprisms sharing common edges and corners with the polyhedra of the layers such that one half of the antiprism belongs to each layer respectively. This characteristic feature of the structure explains the very good cleavage of the crystals // (0001). The Tl–As interaction as mentioned above may additionally stabilize the connection of the layers.

Acknowledgement

The "Arbeitsgemeinschaft Lengenbach", the syndicate exploiting the Lengenbach minerals, kindly put the mineral at our disposal for investigation. We are greatly obliged to R. Guggenheim and M. Düggelin (SEM laboratory, University of Basel) who provided SEM pictures and the preliminary qualitative analyses. J. Saunders, Natural History Museum Basel, helped with the English text.

Special gratitude ows to Prof. Dr. V. Kupčik († 13.06.1990) for his interesting and helpful discussions concerning the use of synchrotron radiation in crystallography and mineralogy, especially problems dealing with sulfosalts. We would like to thank Prof. Dr. G. Sheldrick for the introduction to the preversion of his structure solution package SHELXL-92 and the possibility to use the computer facilities of the Anorganic Chemical Institute of Göttingen. Thanks are also due to Dr. M. Wendschuh-Josties for experimental support at the HASYLAB, Dr. M. Steins for several hints in the use of ORTEP and K. Häpe for the graphical layout of the crystal structure plots. Parts of the computations were carried out at the facilities of the Gesellschaft für wissenschaftliche Datenverarbeitung in Göttingen (GWDG). The present investigation was supported by a grant of the Bundesministerium für Forschung und Technologie (BMFT) under contract no. 05 320 IAB 8.

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Manuscript received September 5, 1992; accepted September 20, 1992.