

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

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Erniggliite ($\text{Tl}_2\text{SnAs}_2\text{S}_6$), 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 Schwander², Reinhard Wulf³ and Andreas Edenharter³

Abstract

Erniggliite, $\text{Tl}_2\text{SnAs}_2\text{S}_6$, is a new mineral species from the famous sulfosalts 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 staldelite. 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 $\text{Tl}_2\text{SnAs}_2\text{S}_6$. 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/mm² for 10 g load (range 46–49), corresponding to a Mohs hardness of about 2–3, $D_{\text{calc}} = 5.24 \text{ g/cm}^3$. Single crystal studies yielded a trigonal cell with $a = 6.680 (3)$, $c = 7.164 (9) \text{ \AA}$, $V = 276.9 (3) \text{ \AA}^3$, 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 ($\lambda = 1.1573 \text{ \AA}$) 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 \AA is observed which is slightly shorter than the shortest Tl–S bonding of 3.268 \AA in this structure. The Sn-polyhedron is a nearly perfect trigonal antiprism with six equal Sn–S distances of 2.5614 \AA . 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-sulfosalts, 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, $\text{TlPbAs}_3\text{S}_6$ (GRAESER and SCHWANDER, 1992), stalderite, $\text{TlCu}(\text{Zn,Fe,Hg})_2\text{As}_2\text{S}_6$ (GRAE-

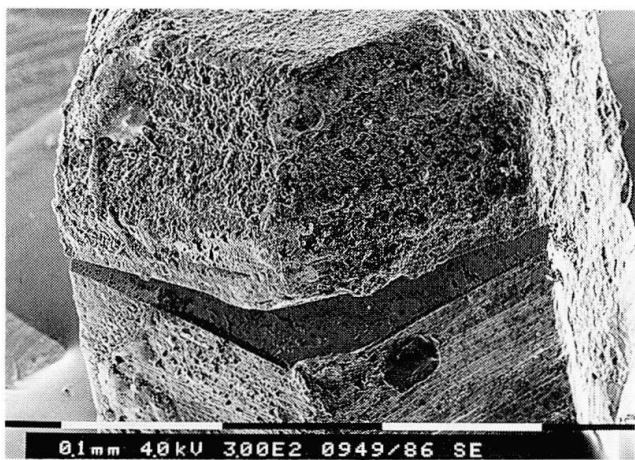


Fig. 1 Erniggliite, Lengenbach. On the SEM picture the (pseudo-) hexagonal habit of the mineral is easily recognizable. Forms are: pinacoid {0001}, hexagonal prism and rhombohedral faces. The surface is rough and uneven (picture: SEM laboratory, University of Basel).

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

Habit:	hexagonal, short prismatic	
Forms:	pinacoid {0001} hexagonal prism $\{10\bar{1}0\}$ rhombohedral faces $\{10\bar{1}1\}$ 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, birefractance:	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, $\text{TlPbAs}_3\text{S}_6$, Lengenbach (GRAESER and SCHWANDER, 1992)

SER et al., in prep.) and erniggliite, $\text{Tl}_2\text{SnAs}_2\text{S}_6$ (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

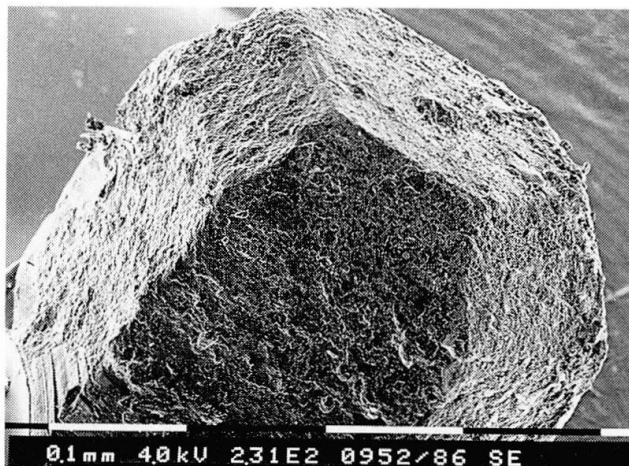


Fig. 2 Erniggliite, Sem picture under stronger magnification documenting the extremely good cleavage parallel to {0001} (SEM laboratory, University of Basel).

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 ₂ SnAs ₂ S ₆				

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

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, FeK α -radiation, intensities determined densitometrically.					
Cell parameters refined from the powder data.					

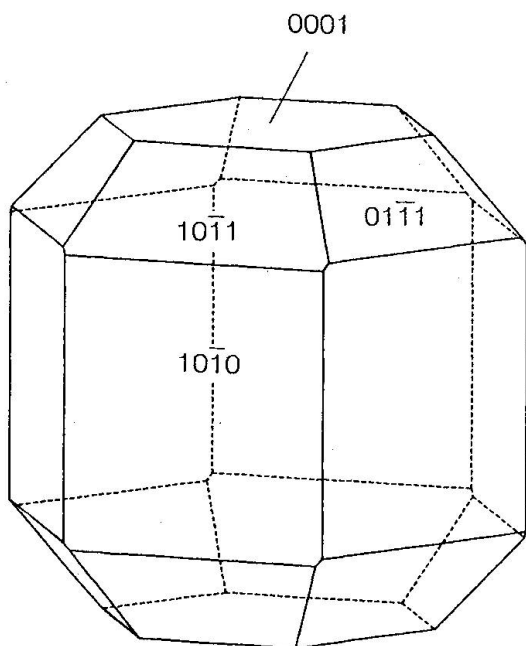


Fig. 3 Erniggliite, idealized computer drawing (SHAPE), showing the common habit of the mineral.

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).

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 sulfosalts 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, $\text{Tl}_2\text{SnAs}_2\text{S}_6$.

Data collection	
Instrumentation Radiation source Monochromator Wavelength Polarization Beam stability control Time between standards Recording technique Step width Time/step, No. of steps 2θ range Index range No. of reflections	5-circle diffractometer (Stoe Stadi 4) Synchrotron (HASYLAB at DESY) Double crystal (Ge 111), $\Delta\lambda/\lambda \approx 3 \times 10^{-4}$ 1.1573 Å $\approx 93\%$ 2 standard reflections and real time monitoring of polarization and intensity 30 minutes Omega step scan 0.010° 0.3–1.0 sec, 41 9.28–100.0° $-8 < h < 8, -8 < k < 8, 0 < l < 9$ 1589 (total), 448 (unique)
Data reduction, structure solution and refinement	
Scaling method Absorption correction min/max transmission Merging R-values R_{int}	By monitor and standard reflection intensities Semi-empirical from Psi-scans 0.12, 0.22 0.099/0.061, before/after corr. 0.0691
Solution method Refinement Scattering curves Weighting scheme Extinction correction Extinction coefficient Final R values $F^2 > 2\sigma(F^2)$, 445 refl. all data, 448 refl. No. of refined parameters	Automated Patterson Superposition (SHELXL—92) Full-matrix least-squares on F^2 f_o from International Tables f', f'' according to CROMER (1983) $w = 1/[\sigma^2 + (0.01 \cdot P)^2 + 1.28 P]$, where $P = (F_o^2 + 2F_c^2)/3$ $F_c' = kF_c [1 + 0.001 \cdot F_c^2 \lambda^3 / \sin \Theta]^{-1/4}$ $k = 0.0064$ (6) $R_w(F^2) = 0.0607, R(F) = 0.0242$ $R_w(F^2) = 0.0611, R(F) = 0.0253$ 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/mm², 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 birefractance or pleochroism phenomena; internal reflections

Tab. 5 Final fractional atomic coordinates and anisotropic thermal parameters U_{ij} of erniggliite ($\text{Tl}_2\text{SnAs}_2\text{S}_6$) from synchrotron data ($\lambda = 1.1573 \text{ \AA}$). $T_{\text{hkl}} = \exp[-2\pi^2 \cdot (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$

	x	y	z	$U_{\text{equ}} [\text{\AA}^2]$
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 deter-

mination. 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: TlAs_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 $\text{Tl}_2\text{SnAs}_2\text{S}_6$ could be calculated. Erniggliite represents the first Lengenbach sulfosalts with Sn as a major element and, moreover, it is the first and only Tl-Sn-sulfosalts 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 sulfosalts 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 _{4,5,6}	3.2681(6)			Tl	-	S _{1,2,3}	144.96 (1)	3×		
	-	S _{1,2,3}	3.3695(5)				-	S _{4,5,6}	73.305(4)	3×		
	-	S _{4,5,6}	3.7473(7)			S ₄	-	Tl	-	S _{5,6}	109.709(6)	2×
mean Tl-S			3.4616			S ₅	-	Tl	-	S ₆	109.709(6)	
						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)			S ₁	-	Sn	-	S _{2,3}	82.607(3)	2×
	-	S _{4,5,6}	2.5614(6)			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)			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

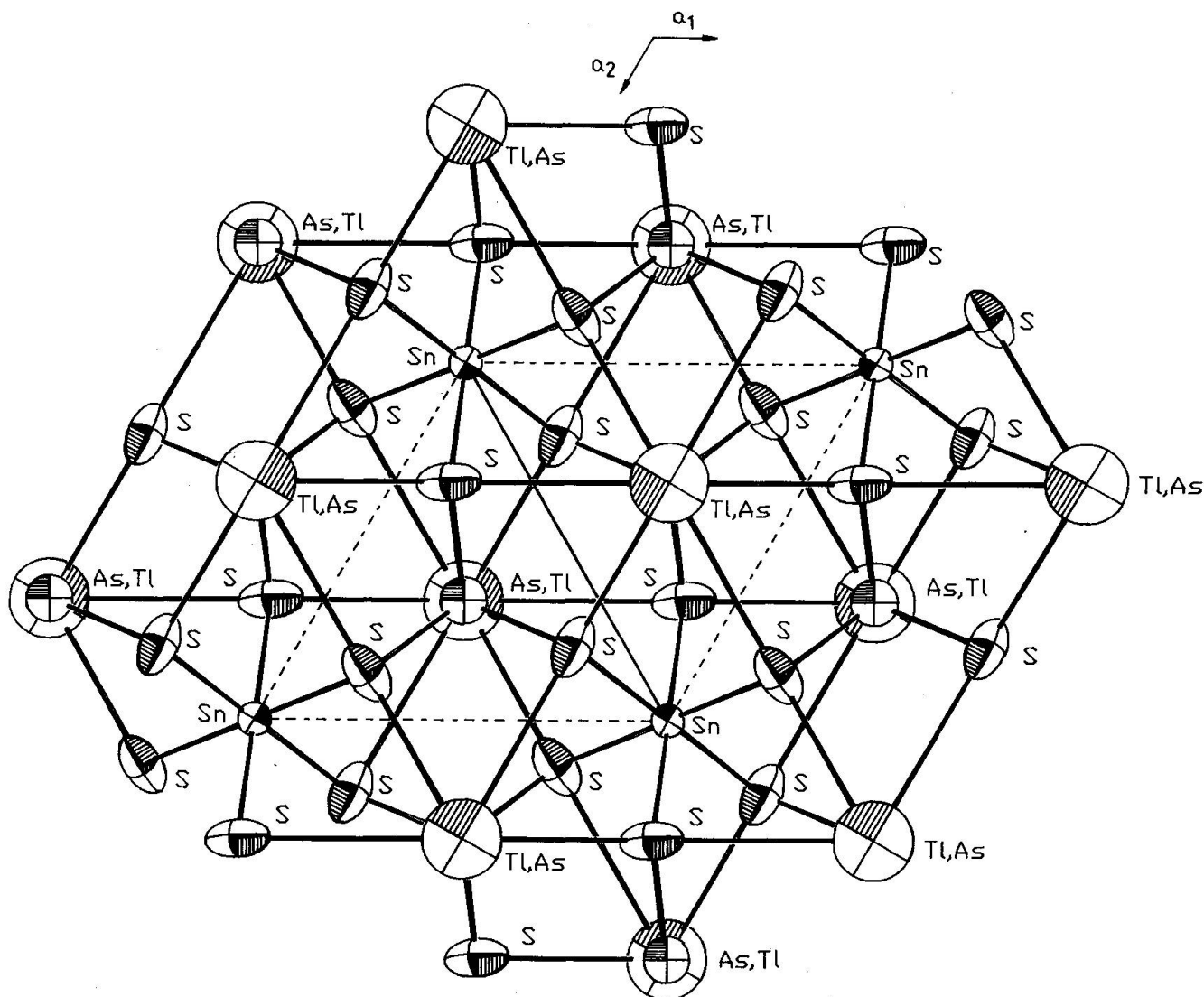


Fig. 4 Projection of the structure of erniggliite // *c*-axis (the unit cell is marked with broken lines).

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% SnO₂. 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 characteristic mineral would not have escaped the keen attention of the old mineralogists! The mineral was found together with the two other new minerals edenharterite, TlPbAs₃S₆ (GRAESER and SCHWANDER, 1992) and stalderite, TlCu(Zn,Fe,Hg)₂As₂S₆ (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

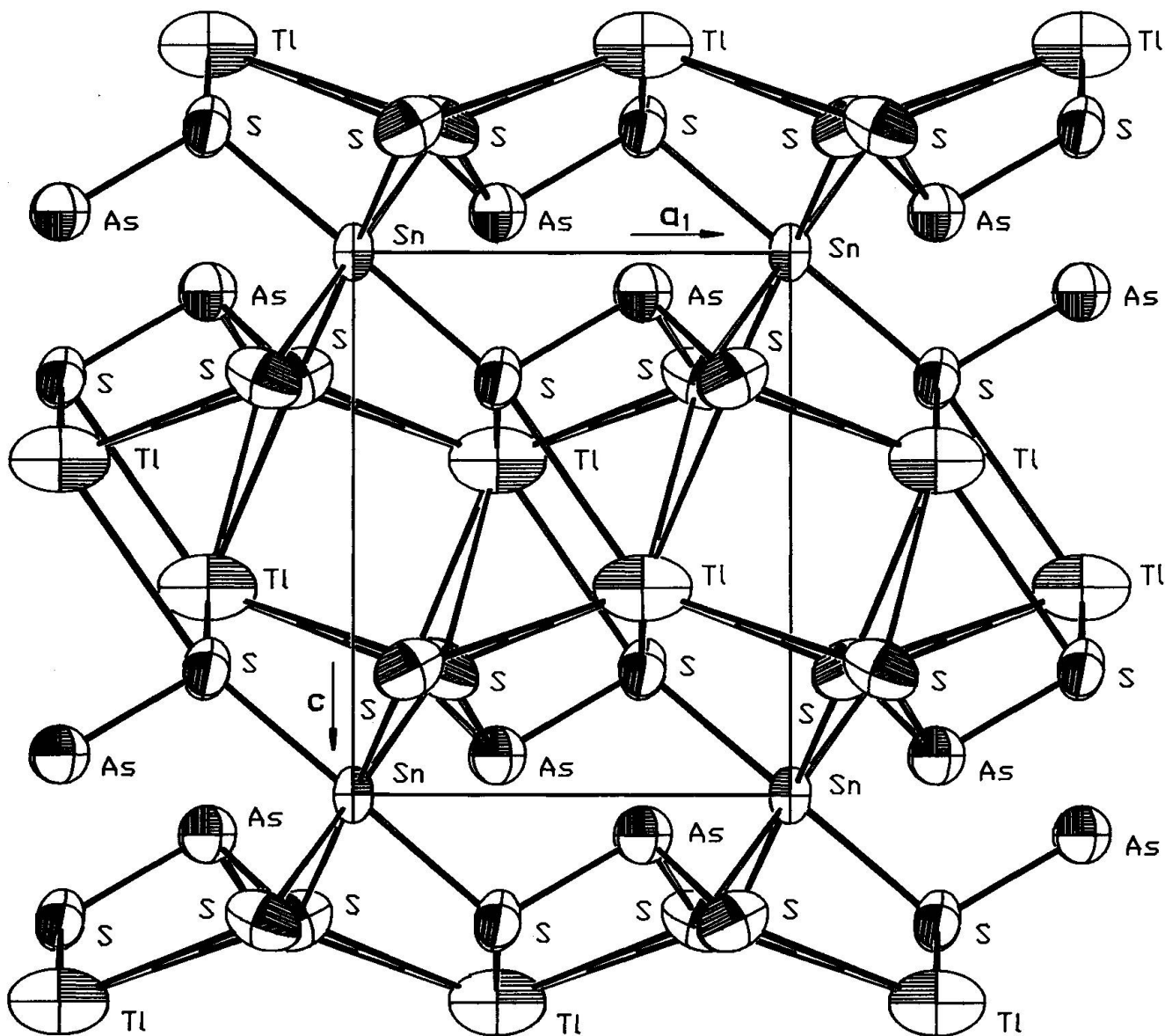


Fig. 5 Projection of the structure of erniggliite // a_2^* -axis.

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

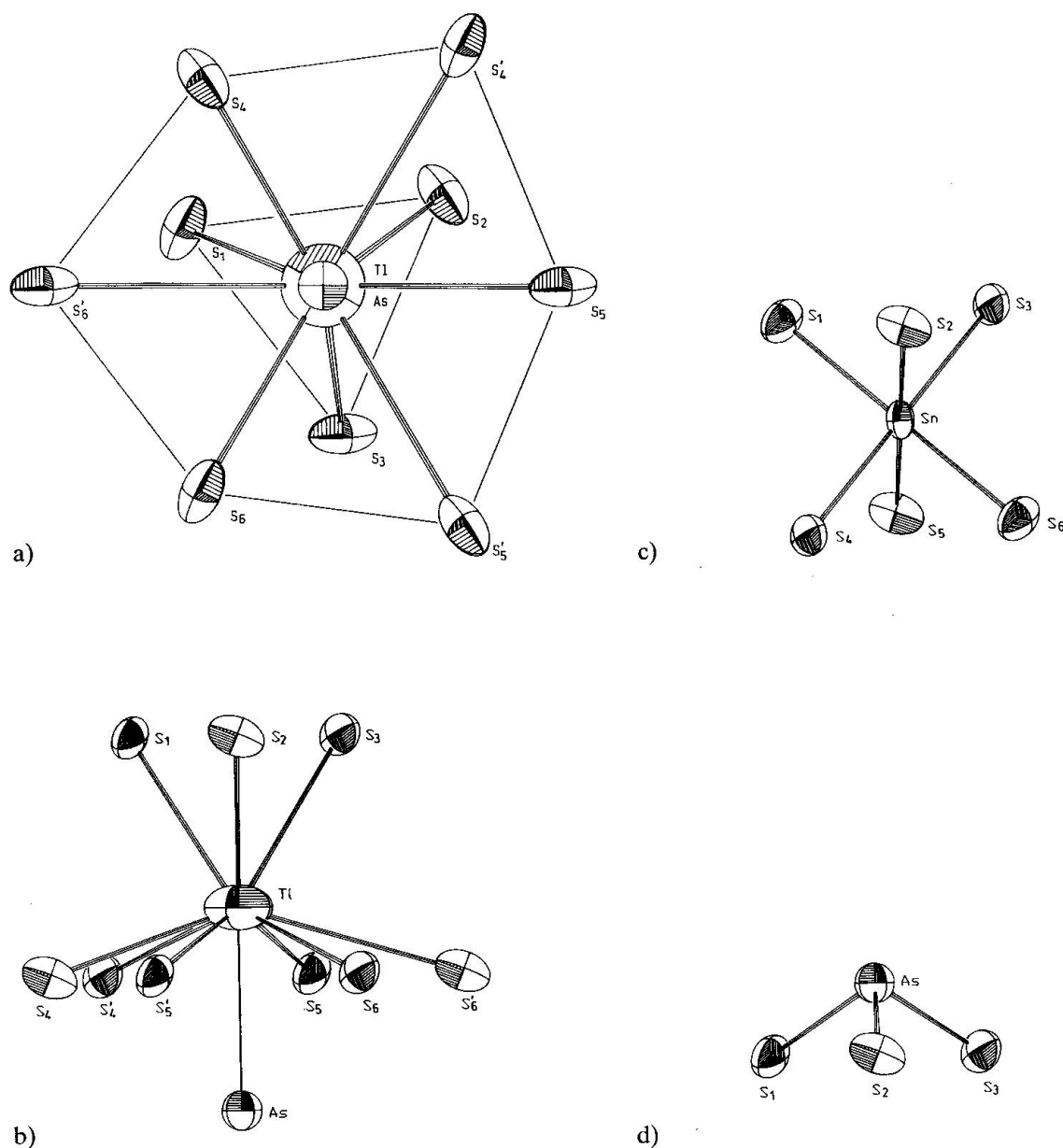


Fig. 6 Me-coordination polyhedra. a) TlS_6 -polyhedron viewed along the c -axis; b) TlS_6 -polyhedron rotated 50° around the a_2 -axis; c) SnS_6 trigonal antiprism; d) AsS_3 trigonal pyramid.

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) *Variable 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 ernigglite. 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	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s						
0	1	0	392	412	5	-7	7	1	41	31	5	0	2	3	173	160	1	4	4	4	34	23	2	-3	3	6	127	126	3
-1	0	2	1994	1960	30	-6	7	1	290	285	10	1	2	3	475	482	10	-7	5	4	67	65	4	-2	3	6	133	110	3
0	2	0	776	764	6	-5	7	1	149	148	2	2	2	3	635	644	20	-6	5	4	428	426	18	-1	3	6	689	687	3
-2	3	0	411	426	6	-4	7	1	177	170	6	-5	3	3	68	63	1	-5	5	4	147	137	2	0	3	6	115	114	4
-1	3	0	123	132	1	-3	7	1	403	362	26	-4	3	3	174	169	5	-4	5	4	293	298	5	5	3	6	237	230	7
0	3	0	1627	1645	14	-2	7	1	155	153	6	-3	3	3	853	868	13	-3	5	4	712	723	3	2	3	6	560	564	20
-3	4	0	385	389	4	-1	7	1	256	261	15	-2	3	3	393	401	2	-2	5	4	251	252	2	2	3	6	93	97	3
-2	4	0	2007	1930	23	0	7	1	326	323	18	-1	3	3	280	273	2	-1	5	4	293	297	6	-6	4	6	547	564	19
-1	4	0	77	61	2	1	7	1	52	43	5	0	3	3	859	860	7	0	5	4	700	693	25	-5	4	6	52	50	5
0	4	0	374	383	2	-7	8	1	296	296	14	1	3	3	344	343	5	1	5	4	363	354	17	-4	4	6	74	48	1
-4	5	0	1081	1052	16	-6	8	1	90	89	3	2	3	3	291	280	5	2	5	4	85	79	5	-3	4	6	588	593	5
-3	5	0	248	248	3	-5	8	1	53	50	2	3	3	3	789	768	35	-7	6	4	140	139	12	-2	4	6	333	343	2
-2	5	0	122	106	9	-4	8	1	104	101	2	-7	4	3	56	52	3	-6	6	4	18	9	4	-1	4	6	93	84	5
-1	5	0	1062	1035	27	-3	8	1	171	164	5	-5	4	3	80	72	5	-5	6	4	755	772	25	0	4	6	792	794	17
0	5	0	158	152	1	-2	8	1	313	315	13	-5	4	3	481	479	17	-4	6	4	82	74	3	1	4	6	34	36	2
-5	6	0	178	176	4	-1	8	1	274	285	19	-4	4	3	191	174	11	-3	6	4	429	436	2	2	4	6	70	61	5
-4	6	0	150	147	1	0	0	2	117	132	1	-3	4	3	528	526	3	-2	6	4	548	563	7	-6	5	6	246	253	9
-3	6	0	815	799	14	-1	1	2	1555	1596	31	-1	4	3	679	692	3	-1	6	4	172	167	7	-5	5	6	516	525	7
-2	6	0	253	244	5	0	1	2	1389	1409	30	-1	4	3	279	278	3	0	6	4	81	21	23	-4	5	6	126	110	19
-1	6	0	191	191	5	1	1	2	941	952	16	0	4	3	130	45	39	1	6	4	553	555	34	-2	5	6	131	126	3
0	6	0	905	903	14	-3	2	2	1084	1090	33	1	4	3	484	477	13	-6	7	4	235	238	7	-2	5	6	530	542	1
-6	7	0	113	114	2	-2	2	2	656	693	9	2	4	3	185	183	8	-5	7	4	52	46	4	0	5	6	118	117	1
-5	7	0	781	769	22	-1	2	2	1080	1056	25	3	4	3	196	187	11	-4	7	4	449	456	3	-1	5	6	77	68	4
-4	7	0	127	120	2	0	2	2	1599	1611	19	4	4	3	231	231	19	-3	7	4	198	199	2	1	5	6	287	285	10
-3	7	0	46	39	3	1	2	2	902	924	17	-8	5	3	50	48	4	-2	7	4	56	43	8	-5	6	6	34	15	4
-2	7	0	807	785	18	2	2	2	251	256	3	-7	5	3	321	313	16	-1	7	4	347	353	15	-4	6	6	543	552	4
-1	7	0	99	85	4	-5	3	2	773	774	18	-6	5	3	132	122	5	-4	8	4	54	55	1	-3	6	6	125	133	1
0	7	0	61	58	1	-4	3	2	1005	1010	28	-5	5	3	136	138	3	0	0	5	1074	1030	27	-2	6	6	134	129	4
-7	8	0	375	377	7	-3	3	2	703	712	7	-4	5	3	765	760	12	-1	1	5	773	765	2	-1	6	6	364	373	13
-6	8	0	94	88	2	-2	3	2	1372	1380	15	-3	5	3	97	100	1	0	1	5	622	636	2	0	0	7	556	544	8
-5	8	0	114	106	3	-1	3	2	1163	1143	14	-2	5	3	161	156	7	1	1	5	536	527	7	-1	1	7	820	789	7
-4	8	0	669	655	18	0	3	2	727	720	8	-1	5	3	784	777	25	-3	2	5	677	679	14	0	1	7	62	38	4
-3	8	0	209	211	5	1	3	2	1230	1226	38	0	5	3	49	41	2	-2	2	5	321	322	2	1	1	7	146	145	4
-2	8	0	25	16	3	2	3	2	519	512	17	1	5	3	81	76	5	-1	2	5	736	724	3	-3	2	7	639	629	15
-1	8	0	375	377	12	3	3	2	540	525	27	2	5	3	340	323	15	0	2	5	221	223	3	-2	2	7	73	44	1
0	0	1	69	46	10	-7	4	2	454	439	29	3	5	3	30	29	3	1	2	5	567	573	16	-1	2	7	252	256	6
-1	0	1	369	358	8	-6	4	2	238	235	10	-8	6	3	171	176	14	-2	2	5	674	667	31	0	2	7	1060	1068	26
0	1	1	1106	1091	31	-5	4	2	628	638	16	-7	6	3	234	247	17	-5	3	5	454	450	22	1	2	7	152	138	6
-2	1	1	290	284	6	-4	4	2	1013	1042	21	-6	6	3	381	383	9	-4	3	5	225	217	10	2	2	7	343	339	11
-3	2	1	231	212	5	-3	4	2	646	670	8	-5	6	3	80	71	3	-3	3	5	563	552	9	-5	3	7	516	514	13
-2	2	1	1601	1610	47	-2	4	2	242	239	1	-4	6	3	50	35	7	-2	3	5	641	645	8	-4	3	7	58	49	3
-1	0	2	186	156	24	-1	4	2	758	756	9	-3	6	3	350	348	3	-1	3	5	366	377	4	-3	3	7	205	202	2
0	1	2	477	450	10	0	4	2	427	428	6	-2	6	3	180	176	7	0	3	5	554	555	13	-2	3	7	693	693	4
-1	1	2	756	744	11	1	4	2	626	617	21	-1	6	3	367	364	19	1	3	5	606	603	19	-1	3	7	64	21	10
-2	1	2	155	142	4	2	4	2	684	669	35	0	6	3	369	368	13	2	3	5	324	320	17	0	3	7	196	200	2
-3	1	2	138	110	13	3	4	2	222	207	15	1	6	3	45	37	7	3	3	5	112	113	4	1	3	7	583	584	12
-4	1	2	765	749	12	4	4	2	241	242	20	2	6	3	98	96	6	-7	4	5	337	348	17	2	3	7	142	142	2
-5	1	2	40	35	2	-8	5	2	363	359	27	-7	7	3	196	200	5	-6	4	5	123	105	3	-5	4	7	148	150	3
-6	1	2	325	326	9	-7	5	2	275	281	18	-6	7	3	82	83	4	-5	4	5	445	450	20	-4	4	7	750	752	6
-7	1	2	954	933	19	-6	5	2	771	762	30	-5	7	3	387	387	13	-4	4	5	235	232	4	-3	4	7	219	223	2
0	1	3	48	46	2	-5	5	2	379	395	8	-4	7	3	46	43	2	-3	4	5	549	554	3	-2	4	7	324	323	2
-1	1	3	418	409	11	-4	5	2	532	541	14	-3	7	3	84	81	10	-2	4	5	636	636	3	-1	4	7	478	481	5
-2	1	3	521	516	24	-3	5	2	917	931	4	-2	7	3	375	378	24	-1	4	5	646	646	8	0	4	7	71	18	10
-3	1	3	119	114	6	-2	5	2	608	617	5	-1	7	3	44	15	16	0	4	5	169	166	6	1	4	7	166	162	3
-4	1	3	122	123	6	-1	5	2	560	549	27	0	7	3	49	51	3	1	4	5	470	459	19	-5	5	7	112	97	12
-5	1	3	568	559	25	0	5	2	719	725	21	-6	8	3	160	163	6	2	4	5	249	242	10	-4	5	7	39	35	2
-6	1	3	295	295	8	1	5	2	599	585	30	-5	8	3	284	297	8	3	4	5	152	151	11	-3	5	7	539	541	2
-7	1	3	171	155	3	2	5	2	305	298	22	-4	8	3	376	372	11	-7	5	5	300	312	18	-2	5	7	61	51	2
-8	1	3	436																										

$\text{Tl}_2\text{SnAs}_2\text{S}_6$ 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: $0.3\text{--}2.2 \text{ \AA}$
- c) wavelength resolution at 1 \AA :
 $\Delta\lambda/\lambda \approx 3 \times 10^{-4}$
- d) degree of polarization $\approx 85\text{--}95\%$

For the actual diffraction measurements a tiny crystal of good quality with dimensions of $0.173 \times 0.154 \times 0.116 \text{ mm}^3$ was used.

From 23 reflections in the 2Θ -range of $21.8\text{--}81.8^\circ$ the lattice constants were determined by least-squares refinement to be $a = 6.678(2)$, $c = 7.160(2)$, $\alpha = 90^\circ$, $\beta = 90^\circ$ and $\gamma = 120^\circ$. With $Z = 1$ a calculated density of $\rho = 5.233 \text{ g/cm}^3$ 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 \AA using a modified measuring procedure (WENDSCHUH-JOSTIES and WULF, 1989) which takes into account the special properties of synchrotron radiation.

In the range of $(\sin\Theta)/\lambda \leq 0.66 \text{ \AA}^{-1}$ 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, SHELDRIK, 1976). The linear absorption coefficient at $\lambda =$

1.1573 \AA is calculated to $\mu = 394.61 \text{ cm}^{-1}$ resulting to a mean μ_R -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 super-sharp Patterson superposition method, implemented in the new structure solution package SHELXS-92 (SHELDRIK, 1992) which was available at that time as a pre-version. For the structure refinement we used the program SHELXL-92 (SHELDRIK, 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 unweighted $R(F)$ -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 $\text{Tl}_2\text{SnAs}_2\text{S}_6$.

According to the classification of sulfosalts as proposed by NOWACKI (1969), erniggliite with $\text{S:As} = \varphi = 3$ 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 $\text{Tl}_3\text{Pb}_4\text{Sb}_{21}\text{As}_{19}\text{S}_{68}$ (the mean value of eight (Tl-S)-polyhedra; NAGL, 1979), 3.389 Å in synthetic parapiertotite (ENGEL, 1980), 3.369 Å in rebulite (BALIĆ-ZUNIĆ 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 $r_{\text{Tl}^+} = 1.44$ Å and $r_{\text{S}^{2-}} = 1.84$ 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 ex-

plain 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 $82.607^\circ (3 \times)$ and $97.393^\circ (3 \times)$ (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 ($3 \times$) and S-As-S angles of $96.691^\circ (3 \times)$. 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 thickness 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

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