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($\text{TIPbAs}_3\text{S}_6$) and jentschite ($\text{TIPbAs}_2\text{SbS}_6$) from Lengenbach, Binntal
(Switzerland)

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Crystal structure and crystal chemistry of the homeotypes edenharterite (TlPbAs₃S₆) and jentschite (TlPbAs₂SbS₆) from Lengnabach, Binntal (Switzerland)

by Peter Berlepsch¹

Abstract

Edenharterite (orthorhombic, *Fdd2*, *a* 15.4764(8), *b* 47.602(3), *c* 5.8489(4) Å) and jentschite (monoclinic, *P2₁/n*, *a* 8.0958(5), *b* 23.917(2), *c* 5.8876(5) Å, β 108.063(8)°) belong to a series of recently discovered Tl-sulfosalts that origin from the new quarry at Lengnabach, Binntal (Switzerland). Quantitative electron microprobe analyses on eight jentschite crystals showed seven of them to be inhomogenous. For one crystal the nominal formula TlPb_{1.01(4)}As_{2.47(6)}Sb_{0.54(3)}S_{5.9(1)} was calculated. Jentschite shows much lower contents of Sb than it was expected from the ideal formula.

The structure of edenharterite was anisotropically refined using 1070 reflections with *I* > 3σ*I* to a final R-value of 0.054. The structure of jentschite was solved with direct methods and anisotropically refined using 1766 reflections with *I* > 3σ*I* to a final R-value of 0.049. Structure refinements and bond valence estimations revealed an ordered structure of Sb and As. The two minerals are homeotypes, as could be demonstrated by fitting the two structures. Using adequate atomic clusters the transformation matrix between new and old coordinates in crystal system is approximately the unit matrix, and a pseudo-symmetry operator *x*-0.25, *y*, *z*-0.34 (translation) was found.

Edenharterite shows small, jentschite large variations in the As- and Sb-contents. The minerals belong to two different solid solution series. In the literature a similar variation of As and Sb in natural and synthetic rebulites is reported, and for bernardite a comparable As, Sb solid solution behaviour can be expected. At this time it seems as if the amount of Sb incorporated in the structures is not responsible for the formation of either edenharterite or jentschite.

Keywords: edenharterite, jentschite, homeotype, crystal structure, crystal chemistry, Lengnabach (Binntal, Switzerland).

Introduction

The Lengnabach quarry in the valley of Binn, Valais, Switzerland, known for more than 200 years, is one of the the world's classic mineral localities, famous for the wealth of well crystallized lead-arsenic sulfosalts (HOFMANN et al., 1993). Within the last hundred years, this locality has provided the systematic mineralogy with a remarkable number of new sulfosalt species (GRAESER et al., 1995a). The quarry is beeing operated by the "Arbeitsgemeinschaft Lengnabach" (Lengnabach syndicate) since 1958 solely for the exploitation of mineral specimens (see e.g. NOWACKI, 1970; STALDER et al., 1978; HOFMANN et al., 1993).

Approximately fifty different sulfides and sulfosalts have been described from the Lengnabach (see e.g. HOFMANN et al., 1993). Among these minerals eleven new sulfosalts with Tl as a major element, briefly Tl-sulfosalts, have been found (cf. Tab. 5 in GRAESER et al., 1995a). The classical old site had to be abandoned in 1986 for technical reasons but also for the increasingly unattractive mineral content. Since 1986 minerals of Lengnabach origin from the new quarry adjacent to the old mining site (see e.g. GRAESER et al., 1992). In this part of the Triassic dolomite marble a greater variation in the chemical composition of Tl-sulfosalts was observed in comparison to the Tl-sulfosalts from the old quarry. Before 1986 the chemistry of the so far known Tl-sulfosalts from

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Tab. 1 Chemical composition (idealized) and cell parameters from single crystal measurements of edenharterite and jentschite.

Mineral	Edenharterite	Jentschite
Formula	TlPbAs ₃ S ₆	TlPbAs ₂ SbS ₆
X-system	orthorhombic	monoclinic
Space gr.	<i>Fdd2</i>	<i>P 2₁/n</i>
<i>a</i> (Å)	15.4764(8)	8.0958(5)
<i>b</i> (Å)	47.602(3)	23.917(2)
<i>c</i> (Å)	5.8489(4)	5.8876(5)
β (°)	90.0	108.063(8)
<i>V</i> (Å ³)	4308.9(5)	1083.8(2)
<i>Z</i>	16	4

Lengenbach was described mainly with the elements Tl, Pb, Cu, Ag, As and S (GRAESER and GUGGENHEIM, 1990). However, the recently found Tl-sulfosalts contain additional major elements such as Sn (ernigglite, GRAESER, 1988; GRAESER et al., 1992); Zn, Fe and Hg (stalderite, GRAESER, 1988, GRAESER et al., 1995a) or Sb (jentschite, GRAESER et al., 1995b). Although PAŠAVA et al. (1989) reported up to 15 wt% of Sb in bernardite (TlAs₅S₈), they did not regard it as a major element in this mineral. As reported in GRAESER et al. (1995a), bernardite from Lengenbach contain significant amounts of Sb too.

By comparing edenharterite (TlPbAs₃S₆, GRAESER and SCHWANDER, 1992; BERLEPSCH, 1995) with jentschite (TlPbAs₂SbS₆) some interesting observations could be made (GRAESER et al., 1995b): the two minerals have similar chemical compositions but different symmetries (Tab. 1). It was supposed that a close relationship exists between jentschite and edenharterite (GRAESER and EDENHARTER, oral communication). The aim of the present work is to show the kind of relationship that exists between these two minerals.

For this purpose quantitative chemical analyses were made of both edenharterite and jentschite by means of an electron microprobe (EMP). Furthermore the structure of jentschite was solved and that one of edenharterite refined, since previously obtained structural data of this compound (BERLEPSCH, 1995) were not satisfying.

Chemical investigations

EXPERIMENTAL

Chemical descriptions of edenharterite have been published previously by GRAESER and SCHWANDER (1992) as well as BERLEPSCH (1995). To the pre-existing ten analyses of edenharterite crystal L 20435 fifteen additional analyses were performed to reach a total of 25. For the EMP analy-

ses of jentschite, eight crystals and crystal aggregates were taken from sample L 24428. The single crystals were identified as jentschite by X-ray methods (Gandolfi camera). The crystal aggregates were investigated semi-quantitatively by means of energy-dispersive spectroscopy (EDS) performed on a scanning electron microscope (PHILIPS SEM 515). These foregoing analyses showed the aggregates to be an association of jentschite and wallisite (Tl(Cu,Ag)PbAs₂S₅).

The chemical analyses were carried out on each crystal of jentschite by means of EMP (JEOL JXA-8600 superprobe, ZAF correction). On all crystals the major elements Tl, Pb, As, Sb, S and the trace elements Cu, Ag, Zn, except two samples, were quantitatively analysed using the lines and spectrometer crystals of standards TlAsS₂ (S *K_α* PET, As *L_α* TAP and Tl *M_α* PET), Sb₂S₃ (Sb *L_α* PET), PbS (Pb *M_α* PET) and CuFeS₂ (Cu *K_α* LiF), Ag₂S (Ag *L_β* PET), ZnS (Zn *K_α* LiF). The conditions of measurement were acceleration voltage 15 kV, beam current 10 nA (20 nA for edenharterite samples), scanned area 15 μm². The results of the analyses are given in table 2.

CHEMICAL COMPOSITION

The results of the edenharterite analyses (BERLEPSCH, 1995) may be summarized as follows: all analysed crystals contain significant amounts of Sb (up to 2.7 wt%) but in general no Sn. This is in contradiction to the data of GRAESER and SCHWANDER (1992). The detection of Sb in edenharterite is of special interest for comparing the mineral with jentschite.

In case of jentschite the analysed crystals except one are inhomogenous with the standard deviations σ_{n-1} greater than the analytical errors. Here, 1σ refers to the count statistics on jentschite. Attempts to explain these inhomogeneities failed. So far in one case, sample G, a zonation could be observed by means of back scattered electron image (BSE image). Yet, both zones (bright: Sb rich, G₁; dark: As rich, G₂) are themselves inhomogenous. So far neither zonations nor topographical effects or operative manipulations could be used as explanation for the inhomogeneities. Therefore only minimum/maximum ranges of the EMP data are listed in table 2, except for crystal E. EMP data from crystal E showed minimal variations compared to data from the other seven samples. By accepting a 2 σ analytical error the crystal was found to be apparently homogenous. For these data the average values have been calculated, resulting in a normalized formula given in table 2.

Tab. 2 EMP data of jentschite (N = 25 if not indicated else). Except for sample E, the mean standard deviations are significantly higher than the analytical error (a.e.). Therefore only minimum-maximum ranges are given in wt%. Details are explained in the text. ¹⁾ N = 24; ²⁾ N = 12; ³⁾ N = 13.

Jentschite	A	B	C	D	E ¹⁾	F	G ₁ ²⁾	G ₂ ³⁾	H	
a.e.	range (wt%)	range (wt%)	range (wt%)	range (wt%)	wt%	σ^{-1}	range (wt%)	range (wt%)	range (wt%)	range (wt%)
Tl	0.55	22.28–24.35	23.32–25.34	22.53–24.42	22.10–24.71	23.94 0.54	22.85–24.77	22.93–24.43	23.21–24.89	23.46–25.53
Pb	0.82	22.65–26.03	22.06–26.54	25.43–28.15	22.19–26.24	24.45 0.78	23.93–26.74	22.16–24.59	23.14–25.48	23.90–27.39
As	0.25	20.37–24.47	20.16–26.03	20.30–23.24	18.21–22.25	21.69 0.20	20.23–21.98	20.79–22.82	23.72–25.59	20.67–25.33
Sb	0.11	4.06– 8.62	3.17–10.50	6.66– 7.73	8.06–10.91	7.68 0.22	8.12– 9.72	6.39– 8.55	2.67– 5.67	3.29– 7.70
S	0.29	20.43–22.26	21.80–23.23	20.73–22.41	21.03–22.84	22.29 0.37	19.98–22.06	21.08–22.18	21.41–22.52	21.74–23.43
Cu	< 0.04	–	–	< 0.04	< 0.04	–	< 0.04	< 0.04	< 0.04	< 0.04
Ag	< 0.05	–	–	< 0.05	< 0.05	–	< 0.05	< 0.05	< 0.05	< 0.05
Zn	< 0.05	–	–	< 0.05	< 0.05	–	< 0.05	< 0.05	< 0.05	< 0.05
Σ	97.2–100.3	98.7–103.5	99.1–102.8	97.7–102.7	100.1	1.0	98.4–102.5	95.3–100.2	96.7–100.1	98.7–102.8
a. e. = analytical error (1σ , wt%, from count statistics on jentschite)							c. b. = charge balance			
Crystal	Normalized jentschite formula (Tl = 1)						Σ As + Sb		c. b.	
E	Tl ₁ Pb ₁₀₍₄₎ As _{2.47(6)} Sb _{0.54(3)} S _{5.9(1)}						3.01(6)		0.02(2)	

In the preliminary description of jentschite, GRAESER et al. (1995b) presented the ideal formula $TlPbAs_2SbS_6$ which corresponds to 13.91 wt% of Sb. In our samples the highest Sb value was measured in sample D. It is 10.91 wt% (Tab. 2). This is significantly less than the expected theoretical value, but comparable to the data of GRAESER and EDENHARTER (oral communication). The minimum content of Sb were found to be 2.67 wt% (Sb-poor zone G₂) which is less than the maximum Sb content measured in edenhartherite (BERLEPSCH, 1995). In jentschite As and Sb vary in the range $As_{2.25}Sb_{0.83}$ to $As_{2.83}Sb_{0.18}$. BALIĆ-ŽUNIĆ et al. (1994) reported a similar variation in synthetic rebulites. The As, Sb solid solution in this mineral extends from $Tl_5Sb_{3.6}As_{9.4}S_{22}$ to $Tl_5Sb_{5.3}As_{7.7}S_{22}$. Recently jankovite ($Tl_5Sb_9(As, Sb)_4S_{22}$), a mineral related to rebulite was described (CVETKOVIĆ et al., 1995). The As, Sb solid solution behaviour in bernardite has not yet been investigated in detail (PAŠAVA et al., 1989).

The variations in chemical composition in both minerals, jentschite and edenhartherite, are mainly due to a simple substitution process between the elements As and Sb. The first assumption that these two Tl-sulfosalts belong to the same isomorphous solid solution series had to be rejected because isomorphism is not possible between two phases with different crystal systems (orthorhombic edenhartherite, monoclinic jentschite). Furthermore maximum contents of Sb in edenhartherite exceeds minimal contents of Sb in jentschite. From these observations it is concluded that the two minerals belong to two different solid solution series. In figure 1 the variable

compositions of edenhartherite and jentschite as well as those compositions of some pure compounds are sketched.

Structure refinements

EXPERIMENTAL

Subsequently data are given for jentschite followed by analogous edenhartherite data in parenthesis. The X-ray data were collected on a crystal fragment, measuring about $0.035 \times 0.045 \times 0.095$ mm³ ($0.025 \times 0.035 \times 0.115$ mm³), by means of a CAD4 automatic single-crystal diffractometer (ENRAF NONIUS) with Kappa geometry. The lattice parameters were determined and re-

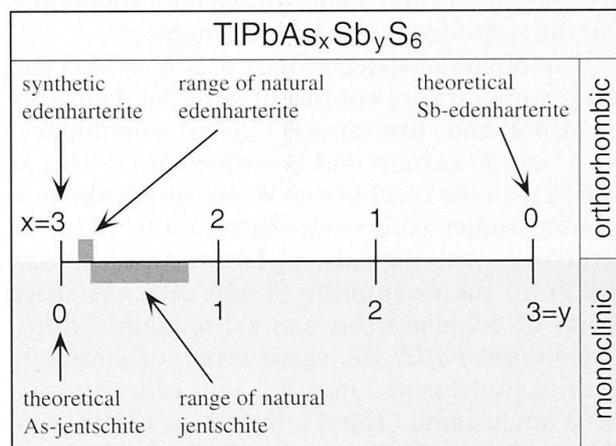


Fig. 1 Sketch with a graphical representation of the variable compositions of edenhartherite and jentschite. Details are explained in the text.

Tab. 3 Summarized parameters of data collection and reduction and of structure refinement.

	Edenharterite	Jentschite
Crystal data	cf. Tab. 1	cf. Tab. 1
Data collection		
Diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4
Geometry	Kappa	Kappa
Radiation Cu K_{α} (\AA)	1.54180	1.54180
Monochromator	Graphite	Graphite
Scan technique	$\omega - 2\theta$	$\omega - 2\theta$
Scan width ($^{\circ}$)	$0.78 + 0.29 \tan \theta$	$0.83 + 0.19 \tan \theta$
Scan speed range ($^{\circ}/\text{min}$)	0.9–20.1	0.8–20.1
Max. $\sin(\theta)/\lambda$ (\AA^{-1})	0.6332	0.6332
2θ range ($^{\circ}$)	4.64–155	4.26–155
Index range	$-7 < h < 0, -19 < k < 0, -59 < l < 0$	$-7 < h < 7, -10 < k < 0, -29 < l < 29$
No. of measured reflections	1249	4885
Data reduction		
Lp correction	Yes	Yes
Abs. correction method	Ψ scans	Ψ scans
Abs. coefficient μ (cm^{-1})	791.15	950.54
Correction range	3.63–10.08	5.19–16.37
Merging-R	–	5.82
Structure refinement		
No. of used reflections	1070 [$I > 3\sigma_I$]	1766 [$I > 3\sigma_I$]
No. parameters last circle	101	101
Final R/wR-values	0.054 / 0.060	0.049 / 0.058
Max. final shift/e.s.d.	0.038	0.081
Final delta rho range ($e/\text{\AA}^3$)	–4.37 to 2.54	–4.90 to 4.35

fined by the least-squares method, using 25 reflections within the angular range $24.90^{\circ} < \theta < 45.73^{\circ}$ ($8.14 < \Theta < 46.58^{\circ}$). Diffraction intensities were measured within the 2θ range $4.26\text{--}155.0^{\circ}$ ($4.64\text{--}155^{\circ}$), using graphite monochromatized CuK_{α} radiation ($\lambda = 1.54178 \text{ \AA}$) and operating in the $\omega\text{-}2\theta$ scan mode. The data reduction included background and Lorentz-polarization corrections. The data were empirically corrected for absorption by using ψ scans. Tables 1 and 3 summarize parameters and results of the data collections and the subsequent structure refinements.

The obtained space groups $P 2_1/n$ ($F2dd$) and cell parameters are consistent with the data from GRAESER and EDENHARTER (oral communication) and GRAESER and SCHWANDER (1992a) as well as with the results from Weissenberg and precession studies (this work; BERLEPSCH, 1995). In agreement with the rules of DONNAY and ONDIK (1973) for the orientation of unit cells, the space group of edenharterite was subsequently transformed into $Fdd2$. The space group of jentschite was not transformed into $P 2_1/a$ in order to keep the β angle small (Tab. 1). Based on 1766 (1070) independent reflections with $I_{\text{obs}} > 3\sigma[I_{\text{obs}}]$, the structures were solved (refined) using direct methods (SIR92, ALTOMARE et al., 1994) and the existing structural model for edenharterite

(BERLEPSCH, 1995). With anisotropic temperature factors and anomalous dispersion terms the refinements converged at R values of 0.049 (0.054).

DISCUSSION AND COMPARISON OF THE STRUCTURES

A detailed description of the structure of synthetic $\text{TlPbAs}_3\text{S}_6$ is given by BALIĆ-ŽUNIĆ and ENGEL (1983). A short comparison of the crystal structures of natural $\text{TlPbAs}_3\text{S}_6$ (edenharterite) and synthetic $\text{TlPbAs}_3\text{S}_6$ is given by BERLEPSCH (1995). It can be concluded that the two structures are very similar.

Site occupancies (occ), final fractional atomic coordinates, and isotropic as well as anisotropic displacement parameters U_{ij} of edenharterite and jentschite are listed in table 4. With one exception only Me–S (Me = Tl, Pb) distances shorter than the smallest Me–As distance were taken into account for the discussion and comparison of the structures. Selected distances and angles are listed in tables 5 and 6. A projection of the crystal structure of jentschite along the c-axis is given in figure 4.

Thallium: In edenharterite Tl is surrounded by seven close S atoms, the Tl–S distances ranging from 3.211 to 3.369 \AA (mean 3.309 \AA). In

Tab. 4 Site occupancies, final fractional atomic coordinates, isotropic ($U_{\text{iso}} \cdot 100$) and anisotropic displacement parameters ($U_{ij} \cdot 100$) of edenharterite (TlPbAs₃S₆, above) and jentschite (TlPbAs₂SbS₆, below).

$$T_{\text{hkl}} = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)].$$

Eden.	occ	x/a	y/b	z/c	U_{iso}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tl(1)	1.00	0.2952(1)	0.03053(3)	0.1850(3)	3.46	5.51(9)	3.25(6)	2.43(7)	0.35(6)	-0.53(7)	-0.54(6)
Pb(1)	1.00	0.02544(8)	0.12228(2)	-0.0008(3)	2.01	4.02(6)	1.69(4)	1.20(5)	-0.01(4)	-0.02(5)	-0.01(4)
As(1)	0.93(3) 0.07(3)	0.0120(2)	0.03411(6)	0.1156(6)	2.40	4.0(2)	1.7(1)	2.2(2)	-0.4(1)	-0.4(1)	-0.1(1)
Sb(1)											
As(2)	1.00	0.0962(2)	0.07577(6)	0.5656(6)	1.97	3.6(2)	1.5(1)	1.4(2)	-0.1(1)	0.2(1)	0.1(1)
As(3)	1.00	0.3029(2)	0.08303(6)	0.7757(5)	1.99	3.5(2)	2.0(1)	1.1(1)	0.1(1)	-0.3(1)	0.0(1)
S(1)	1.00	0.3927(4)	0.0045(1)	0.621(1)	2.32	2.8(3)	1.6(3)	2.9(4)	-0.1(3)	-0.6(3)	-0.2(2)
S(2)	1.00	0.4975(5)	0.0405(2)	0.001(1)	2.58	4.2(4)	2.8(3)	2.1(3)	-1.0(3)	0.9(4)	-1.1(3)
S(3)	1.00	0.1425(5)	0.0809(1)	0.204(1)	1.80	3.8(4)	1.9(3)	0.8(3)	0.1(2)	0.1(3)	0.2(3)
S(4)	1.00	0.2068(5)	0.0470(1)	0.682(1)	2.05	3.9(4)	1.3(3)	2.1(3)	0.2(3)	-1.1(3)	-0.5(2)
S(5)	1.00	-0.1157(5)	0.0815(1)	-0.041(1)	2.10	3.5(4)	1.7(3)	1.8(3)	-0.5(3)	0.6(3)	0.1(2)
S(6)	1.00	0.2209(5)	0.1213(1)	0.708(1)	2.08	4.1(4)	1.6(3)	1.4(4)	-0.2(2)	0.2(3)	-0.2(3)
Jen.	occ	x/a	y/b	z/c	U_{iso}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tl(1)	1.00	0.0964(1)	0.06125(5)	0.8597(2)	3.44	3.92(6)	3.04(5)	3.98(6)	0.31(4)	1.64(5)	-0.57(5)
Pb(1)	1.00	0.0586(1)	0.25436(3)	0.9145(2)	1.95	2.79(4)	1.30(4)	2.66(4)	0.00(3)	1.49(3)	-0.10(3)
Sb(1)	0.55(2) 0.45(2)	-0.4625(2)	0.07058(7)	0.4896(3)	1.95	2.2(1)	1.39(9)	3.0(1)	-0.62(7)	0.86(8)	0.40(6)
As(1)											
As(2)	1.00	-0.3126(3)	0.15277(9)	0.0354(4)	1.50	1.9(1)	1.0(1)	2.4(1)	-2.9(8)	1.16(9)	0.05(8)
As(3)	1.00	0.0966(3)	0.16492(9)	1.4450(4)	1.88	2.4(1)	1.5(1)	2.2(1)	0.09(9)	1.2(1)	0.01(9)
S(1)	1.00	0.2784(7)	0.0122(2)	1.392(1)	2.21	2.2(3)	1.3(2)	3.8(3)	-0.0(2)	0.8(2)	-0.2(2)
S(2)	1.00	0.4908(8)	0.0839(2)	0.869(1)	2.44	3.1(3)	2.7(3)	3.2(3)	-0.8(2)	2.0(3)	-1.3(2)
S(3)	1.00	-0.2097(7)	0.1637(2)	0.7283(9)	1.82	2.3(3)	1.4(2)	2.6(3)	0.0(2)	1.4(2)	-0.2(2)
S(4)	1.00	-0.0976(7)	0.0944(2)	1.257(1)	1.84	2.4(3)	1.1(2)	2.9(3)	0.5(2)	1.2(2)	0.1(2)
S(5)	1.00	0.2732(7)	0.1634(2)	1.220(1)	1.91	2.1(2)	1.3(2)	3.5(3)	-0.2(2)	1.5(2)	-0.1(2)
S(6)	1.00	-0.0612(7)	0.2426(2)	1.308(1)	1.63	2.5(3)	0.9(2)	3.2(3)	-0.2(2)	1.9(2)	-0.1(2)

jentschite Tl is surrounded by six close S, the Tl-S distances ranging from 3.222 to 3.419 Å (mean 3.306 Å). A seventh S occurs at a distance a little longer than the shortest Tl-As distance (Tab. 5). However, this S can not be neglected in order to have reasonable Tl-S polyhedra. The S atoms form a distorted trigonal prism defined by six atoms, with one additional atom beyond one prism face (Fig. 2). In both edenharterite and jentschite Tl and S form $\frac{1}{2}[\text{TlS}_6]$ double chains along [001]. In jentschite this double chain is compressed. This leads to a shorter Tl-Tl distance of 3.918 Å compared to 4.354 Å in edenharterite.

Lead: In both minerals Pb is surrounded by seven close S atoms. Six S form a much more regular trigonal prism (compared to S around Tl), with the additional atom beyond one prism face (Fig. 2). The Pb-S distances vary between 2.830 and 3.471 Å (mean 3.075 Å) in edenharterite compared to 2.791-3.408 Å (mean 3.068 Å) in jentschite. Pb and S form $\frac{2}{3}[\text{PbS}_3]$ planes parallel (010). The Pb-Pb distances are similar in edenharterite (4.144 Å) and jentschite (4.208 Å).

Arsenic and Antimony: In both structures, the site occupancy of As versus Sb on the three As

positions were refined keeping the sums of As + Sb = 1. The result for edenharterite might be doubtful because of the small Sb amount (Tab. 4). In jentschite, however, the refinement shows unequivocally one site dominantly being occupied by Sb and two sites being occupied by As. Sb and As, therefore, build up an ordered structure. Both As and Sb form trigonal MeS_3 (Me = As, Sb) pyramids with Me at the apex (Fig. 3). In edenharterite the As(1)S₃ pyramid shows larger As-S distances (mean 2.322 Å) compared to the other two AsS₃ pyramids (mean 2.281 Å and 2.277 Å). This can be regarded as another hint for the location of Sb at the As(1) site. In jentschite SbS₃ exhibits, as expected, distinctly longer Sb-S distances compared to the As-S distances (mean values: 2.428 Å versus 2.271 Å and 2.275 Å). Although the Sb(1) position contains large amounts of As the Sb-S distances are in good agreement with the values given by EDENHARTER (1976).

In edenharterite six AsS₃ form finite [As₆S₁₂] groups whereas in jentschite four AsS₃ and two SbS₃ form [As₄Sb₂S₁₂] groups (Fig. 3). In edenharterite these groups can be described as four-edged As₂S₂ rings with two As₂S₅ molecules in cis posi-

Tab. 5 Selected interatomic distances (Å) in edenharterite (left) and jentschite (right). Me–S distances are listed for values less than analogous Me–As distances (Me = Tl, Pb). The arrangement was selected for easy comparison of the data. ¹⁾ Longer than the Tl–As distance. ²⁾ Mean of six (mean of seven: 3.333 Å). ³⁾ Primitive lattice translations are not indicated.

Edenharterite				Jentschite			
Tl(1)	–	As(3) ₁	3.463(3)	Tl(1)	–	As(3) ₁	3.480(3)
Tl(1)	–	S(1) ₁	3.211(7)	Tl(1)	–	S(1) ₁	3.240(6)
	–	S(1) ₄	3.373(7)		–	S(1) ₁	3.419(5)
	–	S(2) ₁	3.344(8)		–	S(2) ₁	3.222(6)
	–	S(3) ₁	3.369(7)		–	S(3) ₁	3.399(5)
	–	S(4) ₁	3.309(9)		–	S(4) ₁	3.294(5)
	–	S(4) ₁	3.337(8)		–	S(4) ₁	3.495(6) ¹⁾
	–	S(5) ₁	3.218(7)		–	S(5) ₁	3.260(5)
		mean	3.309			mean	3.306 ²⁾
Pb(1)	–	As(3) ₃	3.518(3)	Pb(1)	–	As(2) ₂	3.528(2)
Pb(1)	–	S(3) ₁	2.931(7)	Pb(1)	–	S(3) ₂	2.937(5)
	–	S(3) ₃	3.044(7)		–	S(3) ₁	3.024(5)
	–	S(5) ₁	2.931(7)		–	S(5) ₂	2.980(5)
	–	S(5) ₃	3.029(7)		–	S(5) ₁	3.009(5)
	–	S(6) ₁	3.471(8)		–	S(6) ₂	3.327(5)
	–	S(6) ₃	2.830(7)		–	S(6) ₁	2.791(5)
	–	S(6) ₃	3.290(7)		–	S(6) ₁	3.408(6)
		mean	3.075			mean	3.068
As(1)	–	S(1) ₁	2.323(7)	Sb(1)	–	S(1) ₁	2.436(6)
	–	S(1) ₄	2.358(7)		–	S(1) _{–1}	2.446(6)
	–	S(2) ₁	2.284(9)		–	S(2) ₁	2.401(6)
		mean	2.322			mean	2.428
As(2)	–	S(2) ₁	2.302(8)	As(2)	–	S(2) ₁	2.289(6)
	–	S(3) ₁	2.247(8)		–	S(3) ₁	2.228(5)
	–	S(4) ₁	2.295(8)		–	S(4) ₁	2.297(6)
		mean	2.281			mean	2.271
As(3)	–	S(4) ₁	2.334(7)	As(3)	–	S(4) ₁	2.337(6)
	–	S(5) ₁	2.244(8)		–	S(5) ₁	2.230(6)
	–	S(6) ₁	2.254(8)		–	S(6) ₁	2.257(6)
		mean	2.277			mean	2.275
Symmetry codes ³⁾				Symmetry codes ³⁾			
1	X, Y, Z	3	1/4+X, 1/4–Y, 1/4+Z	1	X, Y, Z		
2	1/4–X, 1/4+Y, 1/4+Z	4	1/2–X, –Y, 1/2+Z	2	1/2–X, 1/2+Y, 1/2–Z		

tion. In contradiction to that in jentschite the four-edged ring consists of Sb₂S₂ with two As₂S₅ molecules in trans position (Fig. 3). This explains the different symmetries in edenharterite and jentschite.

Bond valences were estimated (ALTERMATT and BROWN, 1985) and the obtained results are given in table 7. For the estimations the same conditions have been chosen as for the discussion of the structures (see above). The estimated values are in good agreement with the results from the structure refinements. It should be noted that the estimations are influenced (and the results might be even better) by accepting a larger range of Me–S distances. However, this leads to fivefold

coordination in case of As and Sb, which is in contradiction to the described trigonal MeS₃ pyramids.

Two minerals are homeotypes if 1) the form and arrangement of the coordination polyhedra is the same, or similar, and 2) they differ in space group symmetry and crystal chemistry. Edenharterite and jentschite have different space groups and different chemical formulae (Tab. 1) but they exhibit, as described above, very similar Me–S coordination polyhedra (Me = Tl, Pb, As, Sb). This similarity can be quantified by regularization.

Regularizing is a tool, implemented in the program CRYSTALS (WATKIN et al., 1985), that calculates by a least squares fit the similarity between

Tab. 6 Selected interatomic angles ($^{\circ}$) in edenharterite (left) and jentschite (right). Details are explained in the text. Cf. table 5 for symmetry codes.

Edenharterite				Jentschite			
S(1) ₁ –	Tl(1) –	S(1) ₄	107.6(2)	S(1) ₁ –	Tl(1) –	S(1) ₋₁	108.0(1)
S(1) ₁ –	–	S(2) ₁	82.6(2)	S(1) ₁ –	–	S(2) ₁	83.8(2)
S(1) ₁ –	–	S(3) ₁	125.3(2)	S(1) ₁ –	–	S(3) ₁	124.2(1)
S(1) ₁ –	–	S(4) ₁	65.7(2)	S(1) ₁ –	–	S(4) ₁	64.8(1)
S(1) ₁ –	–	S(4) ₁	169.5(2)	S(1) ₁ –	–	S(4) ₁	171.7(1)
S(1) ₁ –	–	S(5) ₁	72.2(2)	S(1) ₁ –	–	S(5) ₁	70.5(1)
S(1) ₄ –	–	S(2) ₁	147.3(2)	S(1) ₋₁ –	–	S(2) ₁	146.6(1)
S(1) ₄ –	–	S(3) ₁	75.6(2)	S(1) ₋₁ –	–	S(3) ₁	77.6(1)
S(1) ₄ –	–	S(4) ₁	70.4(2)	S(1) ₋₁ –	–	S(4) ₁	67.6(1)
S(1) ₄ –	–	S(4) ₁	81.9(2)	S(1) ₋₁ –	–	S(4) ₁	82.9(1)
S(1) ₄ –	–	S(5) ₁	142.9(2)	S(1) ₋₁ –	–	S(5) ₁	144.9(1)
S(2) ₁ –	–	S(3) ₁	124.5(2)	S(2) ₁ –	–	S(3) ₁	122.1(1)
S(2) ₁ –	–	S(4) ₁	93.8(2)	S(2) ₁ –	–	S(4) ₁	96.4(1)
S(2) ₁ –	–	S(4) ₁	129.6(2)	S(2) ₁ –	–	S(4) ₁	129.5(1)
S(2) ₁ –	–	S(5) ₁	69.7(2)	S(2) ₁ –	–	S(5) ₁	68.3(1)
S(3) ₁ –	–	S(4) ₁	60.8(2)	S(3) ₁ –	–	S(4) ₁	60.9(1)
S(3) ₁ –	–	S(4) ₁	64.8(2)	S(3) ₁ –	–	S(4) ₁	62.6(1)
S(3) ₁ –	–	S(5) ₁	75.3(2)	S(3) ₁ –	–	S(5) ₁	75.5(1)
S(4) ₁ –	–	S(4) ₁	123.3(2)	S(4) ₁ –	–	S(4) ₁	120.2(2)
S(4) ₁ –	–	S(5) ₁	64.0(2)	S(4) ₁ –	–	S(5) ₁	64.4(1)
S(4) ₁ –	–	S(5) ₁	115.9(2)	S(4) ₁ –	–	S(5) ₁	117.3(1)
S(3) ₁ –	Pb(1) –	S(3) ₃	160.9(3)	S(3) ₋₂ –	Pb(1) –	S(3) ₁	162.5(2)
S(3) ₁ –	–	S(5) ₁	92.8(2)	S(3) ₋₂ –	–	S(5) ₋₂	94.0(1)
S(3) ₁ –	–	S(5) ₃	88.8(2)	S(3) ₋₂ –	–	S(5) ₁	88.2(1)
S(3) ₁ –	–	S(6) ₁	69.7(2)	S(3) ₋₂ –	–	S(6) ₋₂	69.9(1)
S(3) ₁ –	–	S(6) ₃	82.5(2)	S(3) ₋₂ –	–	S(6) ₁	82.2(1)
S(3) ₁ –	–	S(6) ₃	127.9(2)	S(3) ₋₂ –	–	S(6) ₁	129.3(1)
S(3) ₃ –	–	S(5) ₁	88.5(2)	S(3) ₁ –	–	S(5) ₋₂	87.1(1)
S(3) ₃ –	–	S(5) ₃	83.1(2)	S(3) ₁ –	–	S(5) ₁	85.1(1)
S(3) ₃ –	–	S(6) ₁	123.8(2)	S(3) ₁ –	–	S(6) ₋₂	123.4(1)
S(3) ₃ –	–	S(6) ₃	78.5(2)	S(3) ₁ –	–	S(6) ₁	80.4(1)
S(3) ₃ –	–	S(6) ₃	71.0(2)	S(3) ₁ –	–	S(6) ₁	67.8(1)
S(5) ₁ –	–	S(5) ₃	158.1(3)	S(5) ₋₂ –	–	S(5) ₁	160.5(2)
S(5) ₁ –	–	S(6) ₁	126.9(2)	S(5) ₋₂ –	–	S(6) ₋₂	124.4(1)
S(5) ₁ –	–	S(6) ₃	85.8(2)	S(5) ₋₂ –	–	S(6) ₁	87.6(2)
S(5) ₁ –	–	S(6) ₃	78.0(2)	S(5) ₋₂ –	–	S(6) ₁	73.6(1)
S(5) ₃ –	–	S(6) ₁	74.0(2)	S(5) ₁ –	–	S(6) ₋₂	74.4(1)
S(5) ₃ –	–	S(6) ₃	72.8(2)	S(5) ₁ –	–	S(6) ₁	73.5(1)
S(5) ₃ –	–	S(6) ₃	117.6(2)	S(5) ₁ –	–	S(6) ₁	119.4(1)
S(6) ₁ –	–	S(6) ₃	75.7(2)	S(6) ₋₂ –	–	S(6) ₁	77.5(1)
S(6) ₁ –	–	S(6) ₃	136.6(3)	S(6) ₋₂ –	–	S(6) ₁	137.6(2)
S(6) ₃ –	–	S(6) ₃	145.6(3)	S(6) ₁ –	–	S(6) ₁	143.4(2)
S(1) ₁ –	As(1) –	S(1) ₄	91.4(3)	S(1) ₁ –	Sb(1) –	S(1) ₋₁	90.4(2)
S(1) ₁ –	–	S(2) ₁	89.4(3)	S(1) ₁ –	–	S(2) ₁	85.6(2)
S(1) ₄ –	–	S(2) ₁	98.7(3)	S(1) ₋₁ –	–	S(2) ₁	95.7(2)
S(2) ₁ –	As(2) –	S(3) ₁	97.9(3)	S(2) ₁ –	As(2) –	S(3) ₁	97.1(2)
S(2) ₁ –	–	S(4) ₁	96.3(3)	S(2) ₁ –	–	S(4) ₁	96.3(2)
S(3) ₁ –	–	S(4) ₁	96.2(3)	S(3) ₁ –	–	S(4) ₁	97.2(2)
S(4) ₁ –	As(3) –	S(5) ₁	98.1(3)	S(4) ₁ –	As(3) –	S(5) ₁	99.7(2)
S(4) ₁ –	–	S(6) ₁	101.1(3)	S(4) ₁ –	–	S(6) ₁	101.6(2)
S(5) ₁ –	–	S(6) ₁	101.4(3)	S(5) ₁ –	–	S(6) ₁	101.4(2)

two crystal structure fragments (clusters). One cluster of 11 atoms with the composition $\text{TlPbAs}_2\text{SbS}_6$ and the geometry of jentschite has

been fitted to an adequate cluster of 11 atoms with the composition $\text{TlPbAs}_3\text{S}_6$ and the geometry of edenharterite (Fig. 5). Table 8 summarizes the de-

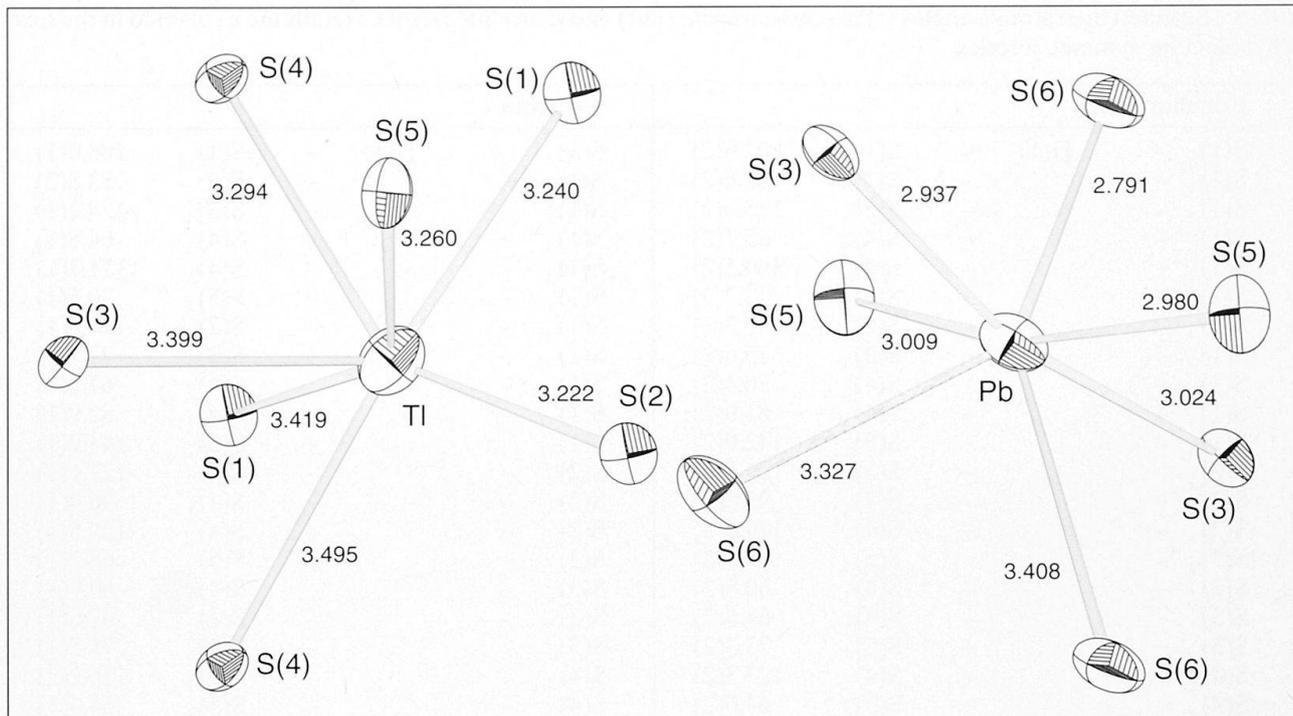


Fig. 2 TI_7 (left) and PbS_7 (right) polyhedra in jentschite. The Me atoms are surrounded by six S atoms forming more or less distorted trigonal prisms, with one additional atom beyond one of the prism faces. See text for details.

viations in best plane system after fitting. The transformation matrix between new and old coordinates in crystal system is approximately the unit

matrix. This result may be expected since adequate clusters were used. A pseudo-symmetry operator $x-0.25, y, z-0.34$ (translation) was found.

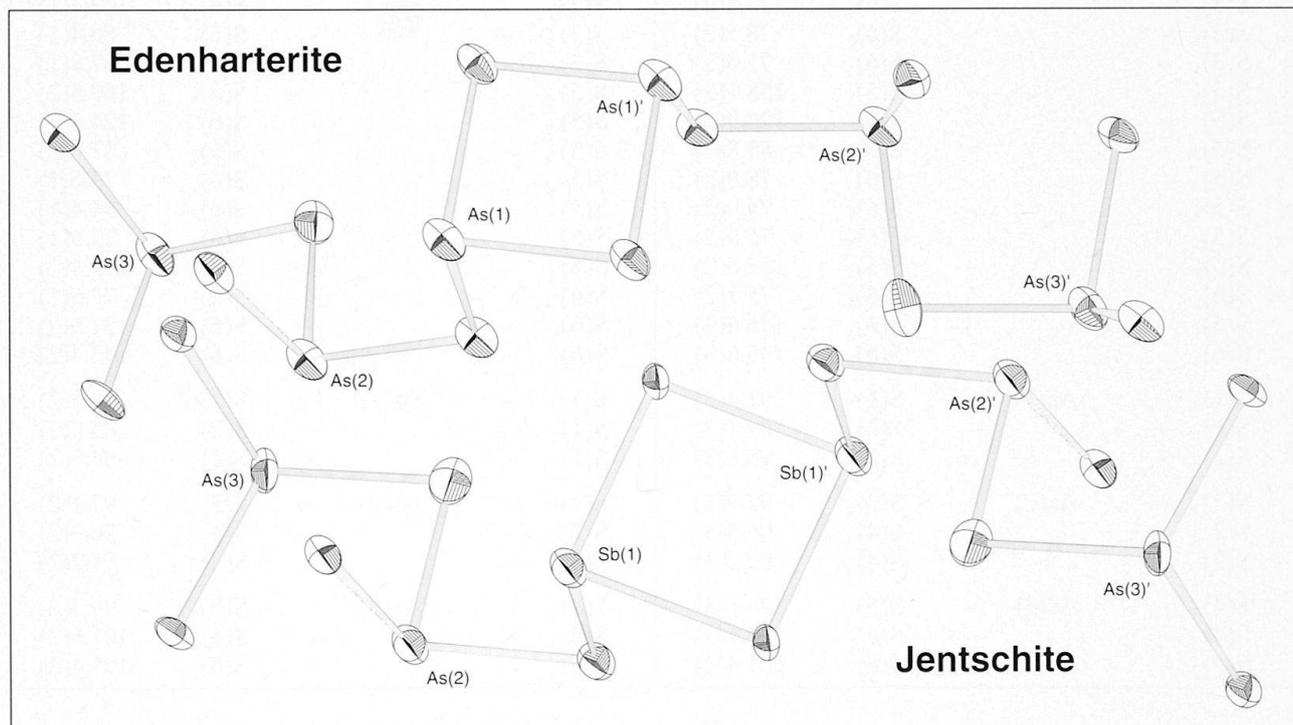


Fig. 3 $[\text{As}_6\text{S}_{12}]$ group in edenharterite: a four-membered As_2S_2 ring and two As_2S_5 molecules in cis position. In jentschite the four-membered ring consists of Sb_2S_2 with two As_2S_5 molecules in trans position. This explains the reduced symmetry in jentschite compared to edenharterite.

Tab. 7 Estimated bond valences for edenharterite (left) and jentschite (right). They are in good agreement with the results from structure refinements. See text for details.

Eden.	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	Σ	Jen.	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	Σ
Tl ₁	0.17	0.12	0.11	0.13	0.16		0.92	Tl ₁	0.15	0.16	0.10	0.13	0.14		0.85
	0.11			0.12					0.09			0.08			
Pb ₁			0.35		0.35	0.46	1.90	Pb ₁			0.34		0.31	0.51	1.93
			0.26		0.27	0.13					0.27		0.28	0.12	
						0.08								0.10	
As ₁	0.91	1.02					2.76	Sb ₁	0.87	0.96					2.67
	0.83								0.84						
As ₂		0.93	1.08	0.94			2.95	As ₂		0.96	1.13	0.94			3.03
As ₃				0.84	1.06	1.04	2.94	As ₃				0.84	1.12	1.04	3.00
Σ	2.01	2.07	1.80	2.08	1.84	1.71		Σ	1.95	2.08	1.84	1.99	1.86	1.77	

Significantly higher deviations in distances and angles were only found for As(1) and S(1). This is explained by the fact that the As(1) position in edenharterite is mainly occupied by the larger Sb(1) in jentschite (see above).

Conclusions

Edenharterite incorporates a certain amount of Sb (BERLEPSCH, 1995) without being influenced in its formation. However, Sb is not needed for

the formation of edenharterite (BALIĆ-ŽUNIĆ and ENGEL, 1983). Edenharterite shows small, jentschite large variations in their amounts of As and Sb. The minerals belong to two different solid solution series. BALIĆ-ŽUNIĆ et al. (1994) reported a similar variation of As and Sb in synthetic reulites. In bernardite a comparable As, Sb solid solution behaviour can be expected. More investigations are needed to understand the role of Sb.

The crystal structures of edenharterite and jentschite were discussed. It was shown that eden-

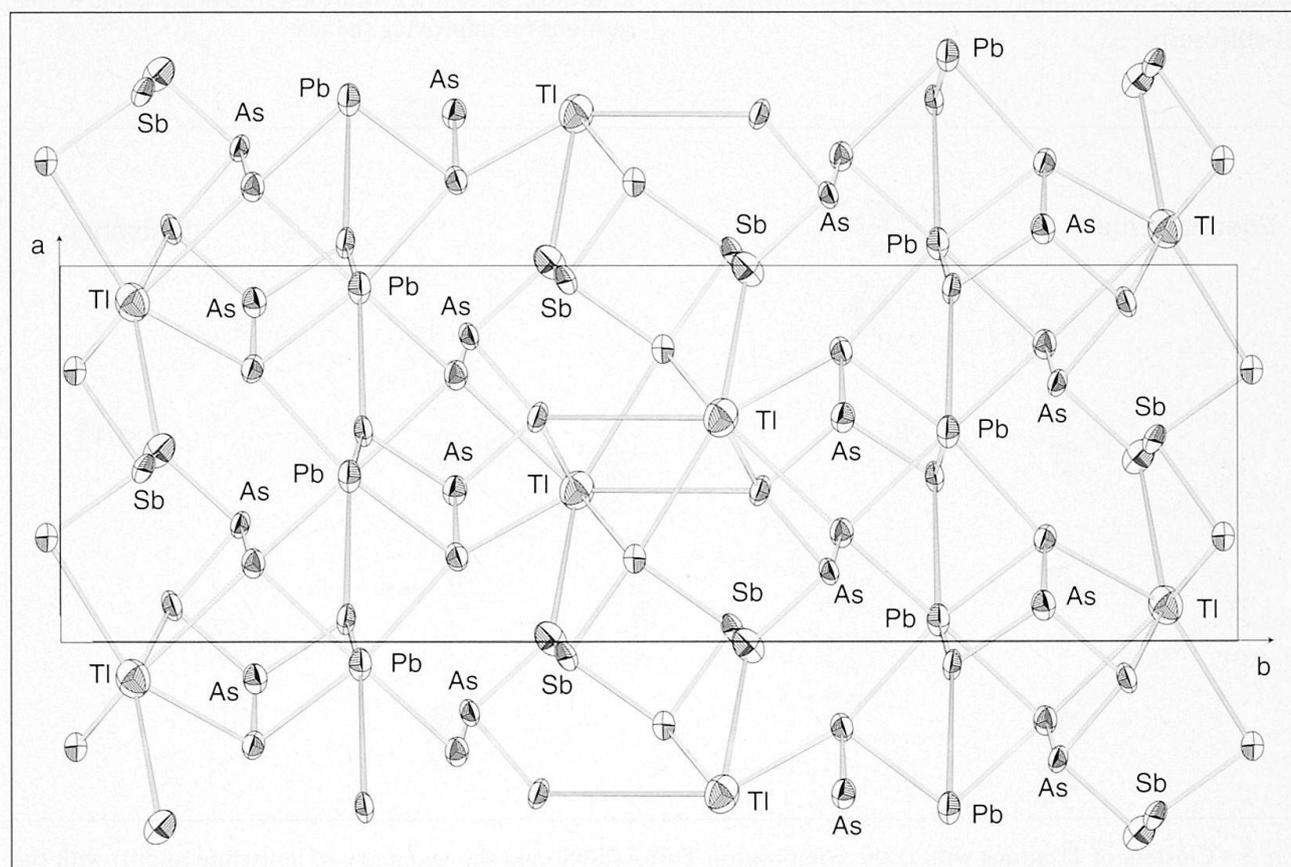


Fig. 4 Projection of the crystal structure of jentschite along the c-axis with the unit cell indicated.

Tab. 8 Regularization of the crystal structures of edenharterite and jentschite. Deviations in best plane system after fitting (RMS = root mean square). See also figure 5. Details are explained in the text.

Type	Serial	d(x)	d(y)	d(z)	Distance/Å	Angle/°
Tl ↔ Tl	1	-0.008	-0.023	0.009	0.026	0.452
Pb ↔ Pb	1	-0.010	-0.047	0.044	0.066	0.974
As ↔ Sb	1	-0.027	0.073	-0.104	0.130	1.833
As ↔ As	2	0.008	-0.004	-0.009	0.012	0.269
As ↔ As	3	0.006	0.020	-0.002	0.021	0.360
S ↔ S	1	-0.080	0.052	0.076	0.122	1.599
S ↔ S	2	0.020	-0.004	-0.027	0.034	0.513
S ↔ S	3	-0.002	-0.048	-0.005	0.048	1.095
S ↔ S	4	0.005	-0.008	0.004	0.011	0.257
S ↔ S	5	0.042	-0.007	-0.011	0.044	0.712
S ↔ S	6	0.047	-0.003	0.024	0.053	0.804
Total squared deviations		0.012	0.014	0.020	→ Total	0.046
RMS deviations		0.033	0.035	0.043	→ Mean	0.064

harterite and jentschite are homeotypes. At this time it seems as if the amount of Sb incorporated in the structures is not responsible for the formation of either edenharterite or jentschite. It can be imagined that pure Sb-edenharterite and/or pure As-jentschite exist (Fig. 1) as well as any other mixed compound. It would be of interest to verify this by doing hydrothermal synthesis. Probably other reasons than the Sb contents may be responsible to explain the formation of the different Tl-sulfosalts.

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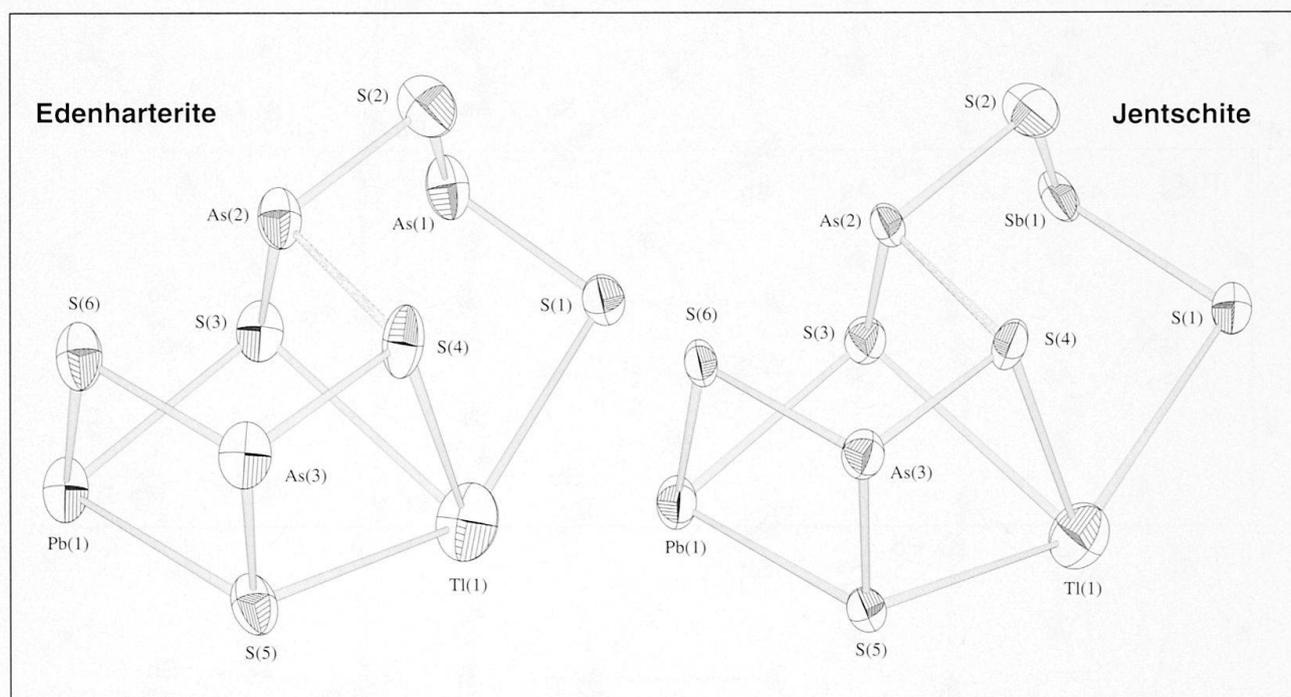


Fig. 5 Clusters of 11 atoms with i) the composition $\text{TlPbAs}_2\text{SbS}_6$ and the geometry of jentschite and ii) with the composition $\text{TlPbAs}_3\text{S}_6$ and the geometry of edenharterite that have been used for a fit to show the similarity of the two structures (see text for details). Note that the fractional coordinates in table 4 do not represent these clusters.

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