

The crystal structure of rebulite, $\text{Tl}_5\text{Sb}_5\text{As}_8\text{S}_{22}$

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Abstract. The crystal structure of a new sulfosalt, $\text{Tl}_5\text{Sb}_5\text{As}_8\text{S}_{22}$, has been determined. The crystal is monoclinic with space group $P2_1/c$. Four formula units are contained in a unit cell of dimensions $a_0 = 17.441(5)$, $b_0 = 7.363(2)$ and $c_0 = 32.052(7)$ Å, $\beta = 105.03(7)^\circ$. The structure was determined by direct methods and refined to a final R -value of 0.057 for 5665 observed reflections.

The Sb and As coordination polyhedra are connected to form a three-dimensional framework. The Tl coordination polyhedra also form a three-dimensional framework interpenetrating the Sb–As framework. The Sb and As coordination polyhedra share common vertices, edges and even one face with the Tl coordination polyhedra.

The mean Tl–S, Sb–S and As–S distances are 3.36, 2.55, 2.29 Å respectively.

1. Introduction

The crystals of a thallium sulphosalt, which was recognized as a new mineral, originate from the region of Allchar (Macedonia, Yugoslavia). The investigations of some physicochemical properties of the mineral, whose proposed name is rebulite, are still being done and will be published later. Here we describe the crystal structure investigations of rebulite.

The crystals for the structure determination were kindly provided by Prof. T. Ivanov (Faculty of Mining and Geology, Štip, Yugoslavia). The structure was determined by joint efforts in the Department of Mineralogy and

Petrology of the Faculty of Science in Zagreb and the Laboratory of Crystallography, University of Berne. The X-ray measurements were made separately; the initial structure investigations led to the same atomic model for the structure, which was then refined and yielded the results described in the following text.

2. Experimental

The measurements at Zagreb

The rotation and Weissenberg photographs of several rebulite crystals, together with the results from the measurements with the optical goniometer (the later carried out and kindly provided by V. Zebec from the Mineralogical Museum, Zagreb) yielded the initial lattice parameters and the space-group symmetry ($P2_1/c$).

The crystals of rebulite are of a dark-gray color with submetallic luster and a brownish red streak. For the structure determination, a crystal of isometric shape, about 2 mm in size, was chosen. The crystal forms present were: $\{100\}$, $\{001\}$ and $\{111\}$ (Fig. 1). A small fragment of the crystal was cut off and ground into a sphere of 0.225 mm diameter. The final determination of the lattice parameters and the intensity measurements were made with the Philips PW 1100 diffractometer, at the Department of General and Inorganic Chemistry, Faculty of Science, by M. Bruvo. $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). A graphite monochromator was used. The lattice parameters were determined with the aid of the peakhunt program, from 18 reflections in the range $6^\circ \leq \theta \leq 18^\circ$ and refined by a least-squares program. In the course of the crystal-orientation rechecking, results were controlled 14 times during the data collection. The mean values, calculated from those measurements, are: $a = 17.439(5)$, $b = 7.360(3)$, $c = 32.045(7) \text{ \AA}$ and $\beta = 105.07(3)^\circ$. The intensities were measured by the $\theta/2\theta$ scan technique (moving detector) and with a variable background measuring time, in the range $3^\circ < \theta < 70^\circ$. During the data collection, the crystal orientation and the intensities of the $\bar{5}08$, $\bar{3}1\bar{6}$ and 500 reflections were rechecked. The changes in the intensities of the reference reflections were later used for putting all intensities on the same scale. The intensities were corrected for Lorentz-polarisation effects and absorption, yielding 5890 independent reflections. Among them were 9 weak reflections of the type $h0l$ with l odd (not in accordance with the presence of a c glide plane). The reason for their appearance was not sought for, and they were discarded for the structure determination. 5734 reflections with $F_o > 3\sigma_{F_o}$ were used for the structure determination, where σ_{F_o} was calculated as $\frac{1}{2}\sigma_{F_o^2}$ for the weak reflections and as $\sigma_{F_o^2}/4F_o^2$ for the strong reflections. $\sigma_{F_o^2}$ was calculated from the equation:

$$\sigma_{F_o^2}^2 = \sigma_I^2 + \left(\frac{t_S}{t_B}\right)^2 (\sigma_{B_1}^2 + \sigma_{B_2}^2) + \left\{ E \left[I \frac{t_S}{t_B} (B_1 + B_2) \right] \right\}^2,$$

where: I = measured intensity in the peak, t_S = time for scan, t_B = time for background, B_1 = left background intensity, B_2 = right background intensity, E = mean error for the strong reflections.

The measurements at Berne

A crystal of rebulite 3 mm in size was used, the shape of which is shown in Figure 1. All the faces in the zone $[010]$ viz. (100) , (001) , $(\bar{1}00)$ and $(00\bar{1})$ are striated. The results of the optical goniometer investigations were kindly provided by W. Rothmayr. For X-ray investigations a small fragment was cut off. Thereby it was noticed, that within the rebulite crystal small light red crystals of $\text{TlHgAs}_3\text{S}_6$ and TlHgAsS_3 have grown (Engel, Nowacki, Balić-Žunić and Šćavničar, 1982). One half of this fragment was later used for electron microprobe analysis. With the other half a small sphere of diameter 0.145 mm was ground; it was mounted on a fiber of Lindemann glass (diameter 0.051 mm) with nail polish (Cutex).

Preliminary Weissenberg photographs with $\text{CuK}\alpha$ radiation indicated that the crystal belongs to the monoclinic system. Systematic extinctions $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ indicated the unique space group $P2_1/c$.

The determination of the lattice parameters and the intensity measurements were made with the NONIUS CAD4 diffractometer and $\text{MoK}\alpha$ radiation ($\lambda\alpha_1 = 0.70926$, $\lambda\alpha_2 = 0.71354 \text{ \AA}$) and a graphite monochromator. 20 reflections determined with the NONIUS peak hunting procedure in the range $15^\circ < 2\theta < 25^\circ$ were carefully centered. Accurate cell parameters were calculated with a least-squares procedure and led to the monoclinic cell constants (2nd setting) $a = 17.444(6)$, $b = 7.367(1)$, $c = 32.06(2) \text{ \AA}$ and $\beta = 105.0(1)^\circ$.

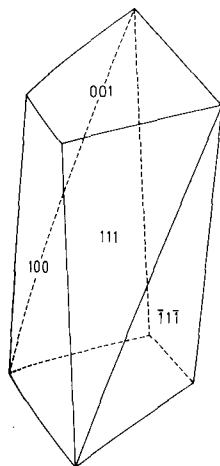


Fig. 1
The general shape of the crystals used for investigations

Table 1. Results of the chemical analyses of rebulite (AAS = atomic absorption spectrometry, EMA = electron microprobe analysis)

	AAS	EMA	$\text{Ti}_5\text{Sb}_5\text{As}_8\text{S}_{22}$
Ti	32.41	32.76	34.81
Sb	21.90	22.88	20.75
As	20.00	20.46	20.41
S	—	24.33	24.03
Σ	—	100.43	100.00

The intensities of all independent reflexions in the range $2^\circ \leq 2\theta \leq 56^\circ$ were measured by the $\omega-2\theta$ scan technique. Every 200 reflections the orientation of the crystal was controlled and every 3.5 h the intensity of the (034) reflection was rechecked. During the measurement no significant deviations could be observed. A total of 9849 reflections were measured. After averaging multiple measurements 9214 independent reflections remained, of which 3549 were unobserved with $I \leq 2.58 \sigma(I)$. The standard deviation was calculated as $\sigma^2(I) = P + m^2(B_1 + B_2)$, wherein P is the peak scan and B_1, B_2 are the background measurements for $1/2_m$ of the time of the peak scan. The intensities were corrected for Lorentz-polarisation effects according to Hope, 1971 and absorption [$\mu(\text{MoK}\alpha) = 301.8 \text{ cm}^{-1}$].

The chemical composition was determined by atomic absorption spectrometry by Z. Grobanski (Perkin-Elmer Laboratories, Überlingen) and by means of an electron microprobe analysis (Type ARL, ETH Zürich) by A. Edenharter (the mean values of the 16 measurements on different places on the fragment). The results of the chemical analyses are given in Table 1 together with the theoretical values for the idealized formula. The aspects of the chemical analyses' results will be discussed in a separate paper on rebulite together with the other physico-chemical results. The calculated density for $\text{Ti}_5\text{Sb}_5\text{As}_8\text{S}_{22}$ is 4.90 g/cm^3 for 4 formula units in the unit cell, the observed density is 4.81 g/cm^3 (picnometric determination by T. Ivanov).

3. Structure determination and refinement

The structure investigations were started separately with the data obtained at Zagreb and at Berne.

From the intensities obtained at Zagreb, the structure model was calculated with the aid of MULTAN 80 (Main et al., 1980). 16 Strongest peaks from the programs' output were assigned to 4 Ti, 5 Sb and 7 As respectively, according to the data on the chemical composition available at that time. Starting with those atom positions, from subsequent difference

Fourier syntheses [program FOURR of the X-ray 76 system (Stewart et al., 1976)], one Tl position was changed to Sb, two Sb to Tl, one As discarded and three new As positions, together with all 22 S positions, were revealed. From a still high R -value, it followed that the atomic parameters were only rough, so two cycles of the step refinement (program STEPRF of the X-ray 76) were calculated, followed by two cycles of the Fourier refinement (program FOUREF of the X-ray 76), resulting in a significant drop of the R -value from 0.39 to 0.14. Even more than this, the fact that the same structure model was obtained at Berne, was considered a proof for its correctness.

The structure model at Berne was obtained as follows: the absolute scale factor was determined from a Wilson plot. The structure factors were converted to normalized E -values; the statistical distribution shows agreement with the theoretical values, given in brackets, for the centrosymmetric space group $P2_1/c$:

$$\langle E \rangle 0.797 (0.789),$$

$$\langle E^2 \rangle 1.016 (1.000),$$

$$\langle |E^2 - 1| \rangle 0.973 (0.968).$$

Phases were directly determined with the program SIGMA of KRIPROG (Engel, 1978) according to the symbolic addition procedure. The 13 highest peaks in the E -map were assumed to be 5 Tl, 5 Sb and 3 As. A Fourier-synthesis calculated with these atom positions revealed all 18 metal positions and 18 sulfur positions. In a subsequent Fourier-synthesis the complete structure could be seen. The assignment of the Tl, Sb and As atoms to the metal positions could only be made from the calculated metal-sulfur bond lengths. After several cycles of least-squares refinements including all atoms with isotropic temperature factors the R -value was 0.11 for all observed reflections. From that point on, the refinement was made together using only the data collected at Berne. From a difference Fourier-synthesis followed that an assumed Sb position with a high negative peak had to be changed to As(1). Likewise an As position with a positive peak was changed to Sb(3), but with an occupancy of 0.8 only. Further refinements with anisotropic temperature factors and anomalous dispersion correction (Tl: $\Delta f' = -3.556$, $\Delta f'' = 9.659$; Sb: $\Delta f' = -0.816$, $\Delta f'' = 1.546$; As: $\Delta f' = -0.030$, $\Delta f'' = 2.007$; S: $\Delta f' = 0.110$, $\Delta f'' = 0.124$) reduced the R -value to 0.087. After this last refinement, the Sb(5) atom showed an extremely elongated temperature ellipsoide. This position was therefore split into two positions designated as Sb(5) and As(5') each with an occupancy of 0.5. The site occupancies were refined with the program CRYLSQ of the X-ray 76. The occupancies of As(1), As(2) and As(7) are 1.15, 1.06 and 1.07 respectively. If we assume these positions to be occupied partly by As and partly by Sb and in such a way that the occupancies of both add up to 1, the partial occupancies of Sb can be determined to be 0.27, 0.11 and 0.13

Table 2. Fractional coordinates and anisotropic temperature factors with standard deviation for the atoms of rebulite. $T = \exp -(h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2hk \beta_{12} + 2hl \beta_{13} + 2kl \beta_{23})$

Atom	x	y	z	Occu-pancy	B_{isotr}	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Tl(1)	0.30905(8)	0.2987(2)	0.45738(5)	1.01	2.9	0.00275(5)	0.0115(2)	0.00081(1)	-0.0002(2)	0.00063(4)	-0.0003(1)
Tl(2)	0.69251(9)	0.1470(2)	0.28730(5)	1.00	3.4	0.00287(5)	0.0155(3)	0.00083(2)	-0.0008(2)	0.00036(5)	-0.0009(1)
Tl(3)	0.12171(8)	0.4011(2)	0.06272(4)	1.01	2.9	0.00274(5)	0.0143(2)	0.00064(1)	0.0008(2)	0.00049(4)	0.0002(1)
Tl(4)	0.89889(7)	0.3259(2)	0.18642(4)	1.01	2.3	0.00219(4)	0.0074(2)	0.00064(1)	-0.0003(1)	0.00020(3)	0.0001(1)
Tl(5)	0.47617(8)	0.3655(2)	0.11055(5)	1.01	2.7	0.00271(5)	0.0106(2)	0.00083(1)	-0.0006(2)	0.00136(4)	0.0000(1)
Sb(1)	0.6896(1)	0.3257(3)	0.43188(6)	0.98	1.7	0.00126(6)	0.0087(3)	0.00050(2)	0.0013(2)	0.00069(5)	0.0009(1)
Sb(2)	0.3068(1)	0.0979(2)	0.31611(6)	0.99	1.4	0.00117(5)	0.0062(3)	0.00038(2)	-0.0001(2)	0.00035(5)	0.0004(1)
Sb(3)	0.0852(1)	0.1893(3)	0.42811(8)	0.79	1.9	0.00133(7)	0.0095(4)	0.00051(2)	0.0016(3)	0.00024(7)	0.0002(2)
Sb(4)	0.9206(1)	0.1884(3)	0.32652(7)	0.95	1.8	0.00163(6)	0.0071(3)	0.00050(2)	-0.0002(2)	0.00041(6)	-0.0007(1)
Sb(5)	0.8993(2)	0.4529(6)	0.4251(1)	0.45	1.9	0.0007(1)	0.0086(7)	0.00074(5)	0.0011(4)	0.0002(1)	0.0004(3)
As(5')	0.9138(3)	0.4467(7)	0.4212(2)	0.55	1.6	0.0005(1)	0.0081(9)	0.00059(6)	0.0012(5)	0.0001(1)	0.0008(3)
As(1)	0.2960(2)	0.0691(3)	0.1679(1)	1.15	1.5	0.0011(1)	0.0081(4)	0.00034(2)	-0.0002(3)	0.0002(1)	-0.0006(2)
As(2)	0.7020(2)	0.3425(3)	0.0860(1)	1.06	1.3	0.0012(1)	0.0054(4)	0.00034(2)	-0.0005(3)	0.0001(1)	-0.0003(2)
As(3)	0.8799(2)	0.1950(4)	0.0469(1)	1.01	1.5	0.0012(1)	0.0079(5)	0.00034(3)	0.0004(3)	0.0000(1)	-0.0003(2)
As(4)	0.1234(2)	0.1976(4)	0.2118(1)	1.02	1.5	0.0011(1)	0.0075(5)	0.00039(3)	0.0006(3)	0.0004(1)	-0.0002(2)
As(5)	0.5362(2)	0.2525(4)	0.4893(1)	1.00	1.5	0.0010(1)	0.0087(5)	0.00033(3)	-0.0009(3)	0.0002(1)	0.0003(2)
As(6)	0.4727(2)	0.1767(4)	0.2609(1)	0.98	1.2	0.0008(1)	0.0071(5)	0.00029(2)	-0.0004(3)	0.0003(1)	0.0001(2)
As(7)	0.4826(2)	0.4159(4)	0.3614(1)	1.07	1.6	0.0013(1)	0.0070(4)	0.00040(3)	-0.0006(3)	0.0000(1)	-0.0001(2)
As(8)	0.1162(2)	0.3688(4)	0.3161(1)	1.00	1.4	0.0012(1)	0.0049(4)	0.00044(3)	0.0009(3)	0.0003(1)	-0.0001(2)

Table 2 (Continued)

Atom	x	y	z	Occu- pancy	B_{isotr}	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
S(1)	-0.0065(4)	0.4698(9)	0.1170(2)	1.00	1.8	0.0016(2)	0.005(1)	0.00058(7)	-0.0012(7)	-0.0001(2)	0.0006(6)
S(2)	0.1824(4)	-0.0182(9)	0.0079(2)	1.00	1.9	0.0013(2)	0.010(1)	0.00057(8)	0.0003(8)	0.0004(2)	-0.0008(5)
S(3)	0.8165(5)	0.240(1)	0.3842(3)	1.00	2.3	0.0018(2)	0.010(1)	0.00062(8)	0.0008(9)	0.0003(2)	-0.0010(2)
S(4)	0.8314(4)	0.473(1)	0.0234(2)	1.00	2.2	0.0016(2)	0.011(1)	0.00055(8)	-0.0014(9)	0.0001(2)	0.0015(5)
S(5)	0.1949(4)	0.285(1)	0.1647(2)	1.00	2.1	0.0020(2)	0.012(1)	0.00045(7)	0.0021(9)	0.0009(2)	0.0013(5)
S(6)	0.8166(4)	0.4430(9)	0.2611(2)	1.00	1.9	0.0016(2)	0.006(1)	0.00063(8)	-0.0010(8)	0.0004(2)	-0.0008(4)
S(7)	0.8047(4)	0.134(1)	0.0942(2)	1.00	1.9	0.0018(2)	0.008(1)	0.00053(7)	0.0002(7)	0.0004(2)	0.0007(4)
S(8)	0.1829(4)	0.4101(9)	0.2634(2)	1.00	1.7	0.0018(2)	0.010(1)	0.00034(6)	-0.0003(8)	0.0012(2)	0.0004(4)
S(9)	0.1935(4)	0.1641(9)	0.3596(2)	1.00	2.0	0.0014(2)	0.008(1)	0.00063(8)	0.0008(8)	0.0002(2)	0.0004(5)
S(10)	0.9937(4)	0.248(1)	0.4715(2)	1.00	1.9	0.0012(2)	0.011(1)	0.00055(7)	0.0001(8)	0.0005(2)	-0.0006(5)
S(11)	0.9832(4)	0.4522(9)	0.3666(2)	1.00	1.7	0.0018(2)	0.006(1)	0.00044(7)	-0.0006(8)	0.0002(2)	-0.0001(4)
S(12)	0.4131(4)	-0.0090(9)	0.0424(2)	1.00	1.5	0.0013(2)	0.008(1)	0.00038(6)	-0.0003(8)	0.0007(2)	-0.0008(4)
S(13)	0.5884(4)	0.2443(9)	0.3559(2)	1.00	1.6	0.0013(2)	0.008(1)	0.00041(7)	0.0000(8)	0.0005(2)	-0.0004(4)
S(14)	0.3863(5)	0.535(1)	0.0213(3)	1.00	2.7	0.0036(2)	0.007(1)	0.00068(9)	-0.0034(8)	0.0009(2)	-0.0007(5)
S(15)	0.4056(4)	0.257(1)	0.1922(2)	1.00	2.2	0.0014(2)	0.011(1)	0.00055(7)	-0.0043(8)	-0.0002(2)	0.0012(5)
S(16)	0.5910(4)	0.4379(9)	0.2219(2)	1.00	1.8	0.0017(2)	0.005(1)	0.00058(7)	-0.0004(8)	0.0003(2)	0.0001(4)
S(17)	0.5932(4)	0.1617(9)	0.0608(2)	1.00	1.9	0.0012(2)	0.008(1)	0.00059(7)	-0.0016(8)	0.0002(2)	-0.0001(5)
S(18)	0.4134(4)	0.4084(9)	0.2891(2)	1.00	1.8	0.0017(2)	0.008(1)	0.00050(7)	0.0007(8)	0.0003(2)	0.0009(4)
S(19)	0.4083(4)	0.199(1)	0.3854(2)	1.00	1.9	0.0010(2)	0.011(1)	0.00049(7)	-0.0009(8)	0.0000(2)	-0.0010(5)
S(20)	0.0154(4)	0.1931(9)	0.2784(2)	1.00	1.7	0.0015(2)	0.008(1)	0.00042(7)	-0.0001(8)	0.0003(2)	-0.0002(4)
S(21)	0.2931(4)	0.1401(9)	0.0974(2)	1.00	1.8	0.0015(2)	0.007(1)	0.00050(7)	0.0006(8)	0.0004(2)	0.0005(4)
S(22)	0.6935(4)	0.2836(9)	0.1550(2)	1.00	1.9	0.0018(2)	0.007(1)	0.00056(7)	-0.0012(8)	0.0006(2)	0.0001(4)

Table 3. Interatomic distances in rebulite

Tl(1)–S(12) ₄	3.250(7) Å	Tl(2)–S(18) ₉	3.189(7) Å
–S(14) ₄	3.260(8)	–S(16) ₁	3.195(7)
–S(17) ₈	3.303(7)	–S(13) ₁	3.274(6)
–S(19) ₁	3.305(6)	–S(6) ₁	3.330(6)
–S(7) ₈	3.331(7)	–S(3) ₁	3.366(8)
–S(9) ₁	3.408(7)	–S(5) ₉	3.429(7)
–S(2) ₄	3.461(6)	–S(15) ₉	3.494(7)
–S(4) ₉	3.592(7)	–S(8) ₉	3.498(6)
mean	3.364 Å	mean	3.347 Å
		Tl(2)–As(1) ₈	3.409(3) Å
Tl(3)–S(3) ₈	3.057(8) Å	Tl(4)–S(9) ₈	3.123(7) Å
–S(1) ₁	3.210(6)	–S(20) ₈	3.155(7)
–S(4) ₇	3.214(7)	–S(6) ₁	3.212(7)
–S(10) ₈	3.265(7)	–S(20) ₂	3.269(7)
–S(5) ₁	3.300(7)	–S(1) ₂	3.271(7)
–S(10) ₅	3.373(7)	–S(7) ₁	3.304(7)
–S(21) ₁	3.486(6)	–S(22) ₁	3.476(6)
–S(2) ₁	3.835(7)	–S(8) ₉	3.898(7)
mean	3.342 Å	mean	3.338 Å
Tl(3)–Sb(5) ₉	3.356(4) Å	Tl(4)–As(8) ₉	3.377(3) Å
Tl(5)–S(14) ₁	3.145(8) Å	Sb(1)–S(12) ₈	2.478(6) Å
–S(19) ₈	3.162(7)	–S(21) ₈	2.546(7)
–S(17) ₁	3.265(6)	–S(13) ₁	2.680(7)
–S(15) ₁	3.267(7)	–S(2) ₈	2.793(7)
–S(13) ₈	3.292(7)	mean	2.624 Å
–S(12) ₁	3.516(7)	Sb(2)–S(22) ₉	2.494(7) Å
–S(21) ₁	3.527(6)	–S(19) ₁	2.570(7)
–S(16) ₁	3.654(7)	–S(16) ₉	2.680(6)
–S(22) ₁	3.738(6)	–S(9) ₁	2.741(6)
mean	3.396 Å	mean	2.621 Å
Tl(5)–As(7) ₉	3.459(3) Å		
Sb(3)–S(1) ₁₀	2.360(7) Å	Sb(4)–S(11) ₁	2.428(7) Å
–S(10) ₃	2.413(6)	–S(20) ₂	2.537(6)
–S(4) ₉	2.428(8)	–S(1) ₉	2.591(7)
mean	2.400 Å	mean	2.519 Å
Sb(5)–S(3) ₁	2.298(9) Å	As(5')–S(10) ₁	2.349(9) Å
–S(10) ₁	2.435(8)	–S(3) ₁	2.358(9)
–S(11) ₁	2.660(7)	–S(11) ₁	2.373(8)
–S(2) ₈	2.876(8)	mean	2.360 Å
mean	2.567 Å		

Table 3 (Continued)

As(1)–S(21) ₁	2.308(7) Å	As(2)–S(17) ₁	2.288(6) Å
–S(15) ₁	2.324(7)	–S(22) ₁	2.296(8)
–S(5) ₁	2.359(7)	–S(7) ₁	2.320(7)
mean	2.330 Å	mean	2.301 Å
As(3)–S(2) ₆	2.233(8) Å	As(4)–S(6) ₉	2.214(7) Å
–S(4) ₁	2.272(8)	–S(5) ₁	2.287(7)
–S(7) ₁	2.292(7)	–S(8) ₁	2.320(7)
mean	2.266 Å	mean	2.274 Å
As(5)–S(14) ₉	2.180(8) Å	As(6)–S(16) ₉	2.226(7) Å
–S(12) ₈	2.317(7)	–S(15) ₁	2.287(8)
–S(17) ₄	2.337(8)	–S(18) ₁	2.301(7)
mean	2.278 Å	mean	2.271 Å
As(7)–S(13) ₁	2.282(6) Å	As(8)–S(9) ₁	2.249(7) Å
–S(19) ₁	2.310(7)	–S(20) ₁	2.266(7)
–S(18) ₁	2.320(8)	–S(8) ₁	2.307(7)
mean	2.304 Å	mean	2.274 Å

Symmetry operations

1: x, y, z	2: $1 + x, y, z$	3: $x - 1, y, z$
4: $x, \frac{1}{2} - y, \frac{1}{2} + z$	5: $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$	6: $1 - x, -y, -z$
7: $1 - x, 1 - y, -z$	8: $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	9: $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$
10: $-x, y - \frac{1}{2}, \frac{1}{2} - z$		

respectively. Assuming that the position Sb(3) is occupied only by Sb the formula of rebulite would be $\text{Ti}_5\text{Sb}_{4.7}\text{As}_8\text{S}_{22}$ compared to the ideal formula $\text{Ti}_5\text{Sb}_5\text{As}_8\text{S}_{22}$ obtained from $2.5 \text{Ti}_2\text{S} + 2.5 \text{Sb}_2\text{S}_3 + 4 \text{As}_2\text{S}_3$. Further refinement led to the final R -value $R = 0.057$ and $R_w = 0.078$ for observed reflections and $R = 0.129$ for all reflections respectively. The scattering factors for the neutral atoms were used in all the calculations. The final atomic coordinates and thermal parameters are given in Table 2. In Table 3 the interatomic distances are listed.

4. Description of the structure

The structure of rebulite is represented in Figure 2. The Ti and Sb atoms show several different coordinations in the structure whereas the coordination of the As atoms was found to be equal in all positions. A partial occupancy of the Sb(3), Sb(5), As(1) and As(2) was calculated and will be described in the following text.

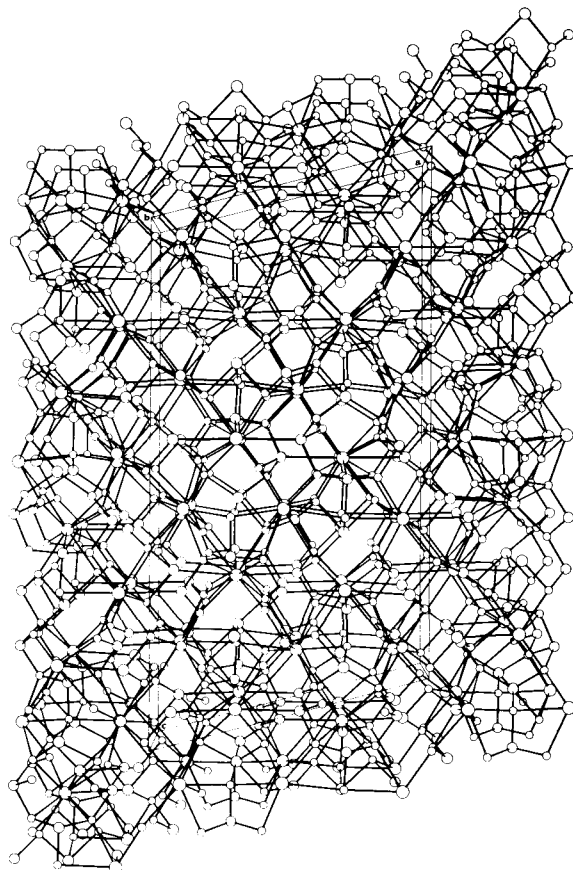


Fig. 2. The central projection of the structure of rebulite viewed along the b axis

The coordination of Tl

Three types of Tl coordination occur in the structure which are represented in Figures 3a–c. Tl(3) and Tl(4) are representative of the first type with coordination number VIII. It can be described as a deformed trigonal prism defined by six S atoms and with two additional S atoms beyond two prism faces. Of the eight neighbouring S atoms, six are closer to Tl at distances from 3.1 to 3.3 Å and two further at distances of 3.5 and 3.8 (3.9) Å, respectively. This type of coordination is similar to the Tl coordination found in some other sulphosalts i.e.: imhofite (Divjaković and Nowacki, 1976), parapirotite (Engel, 1980), TlSb_3S_5 (Gostojić, Nowacki and Engel, 1981).

Tl(5) is representative of the second type with coordination number IX. It can be described as a deformed trigonal prism with six S atoms at the vertices

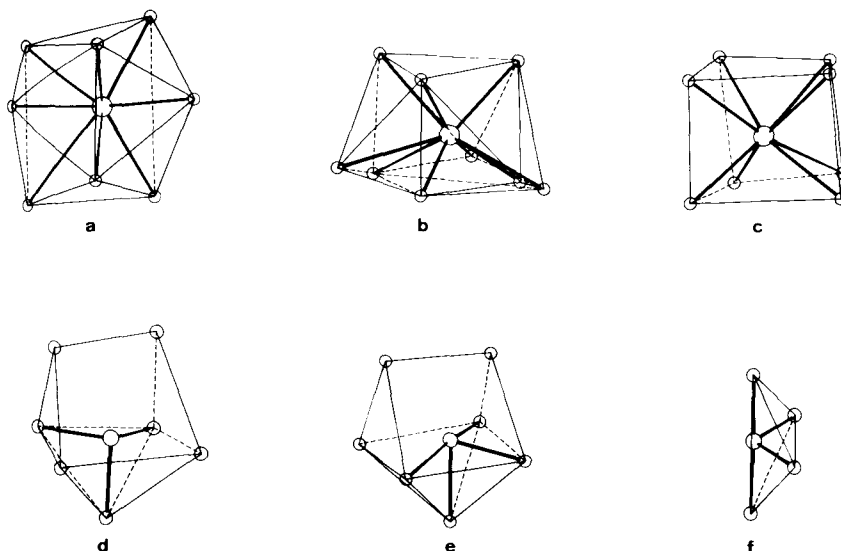


Fig.3. Coordination polyhedra of Tl and Sb

and three additional S atoms beyond the prism faces and on one side of the equatorial plane. This type of coordination has five nearest neighbours to the Tl atom at distances from 3.1 to 3.3 Å and four other atoms at distances from 3.5 to 3.7 Å. A similar coordination of Tl was previously described in chabourneite (Nagl, 1979) and parapierrhotite.

Tl(1) and Tl(2) are representative of the third type of coordination with coordination number VIII. It is a slightly deformed cubic coordination with eight S atoms at distances from 3.3 to 3.6 Å. A similar type of Tl coordination was also found in vrbaite (Ohmasa and Nowacki, 1971).

It is interesting to note that in all cases the Tl atom is neighboured by one As (or Sb in the case of partial occupancy) at distances from 3.3 to 3.6 Å. Similar Tl–As distances were observed in other Tl sulfosalts; hatchite (Marumo and Nowacki, 1967), wallisite (Takéuchi, Ohmasa and Nowacki, 1968), lorandite (Fleet, 1973), synthetic christite (Brown and Dickson, 1976), imhofite, synthetic ellisite (Gostojić, 1980), synthetic $\text{Tl}_2\text{MnAs}_2\text{S}_5$ (Gostojić, Edenharter, Nowacki and Engel, 1981).

The coordination of Sb

Three slightly different types of Sb coordination can be observed in the structure as represented in Figures 3d–f. In the first type [Sb(3) and Sb(4)],

the Sb atom is surrounded by 3 + 4 S atoms lying at the vertices of a deformed octahedron with one split vertex. Three S atoms are bonded to the Sb atom at distances from 2.4 to 2.6 Å. Two S atoms lie at greater distances of 2.9 to 3.2 Å and the two S atoms representing the split vertex lie at even greater distances of 3.6 and 3.9 Å, respectively.

In the second type of coordination the atoms Sb(1) and Sb(2) are bonded each to four S atoms at distances from 2.5 to 2.8 Å. These four atoms also occupy the vertices of a splitted octahedron and together with the three additional S atoms at larger distances from 3.0 to 3.9 Å the same type of surrounding as described above is formed.

The Sb(5) atom shows a third type of coordination. Four S atoms at distances from 2.4 to 2.9 Å form part of an octahedron but the additional S atoms are beyond 3.6 Å.

The coordination of As

In all positions the As atoms are bonded to three nearest S atoms forming an almost regular trigonal pyramid with the As atom at the apex. The mean S–As–S angle is $98.0(5.0)^\circ$. The As–S bond distances range from 2.2 to 2.4 Å.

The partial occupancy of As or Sb occurs at the positions designated Sb(3), Sb(5), As(1) and As(2) with Sb dominating in Sb(3) and As dominating in As(1) and As(2). In the position Sb(5) the occupancy of both species is almost the same. The As atoms in all these positions have the same type of coordination as the other As atoms with three nearest S atoms whereas the Sb atoms replacing As in As(1) and As(2) have a similar coordination as Sb(1) and Sb(2).

The described coordination of Sb and As are quite common and have been found in a number of sulfosalts structures.

The coordination of S

Most of the S atoms are coordinated to two As or Sb atoms respectively and two Tl atoms forming a deformed tetrahedron. Exceptions are:

- when a Sb atom occupies position Sb(5), S(2) has fivefold coordination because of the additional bond (As(5')) at the nearby position is bonded to only three atoms.
- S(3), S(6) and S(14) have one bond to an As or a Sb atom and two bonds to Tl atoms.
- S(18) has two bonds to As atoms and one bond to a Tl atom. These three bonds lie nearly in the common plane.
- S(11) is bonded to only two Sb atoms with bonds enclosing an angle of 97° , the other Sb or As atoms being at distances greater than 3.0 Å.

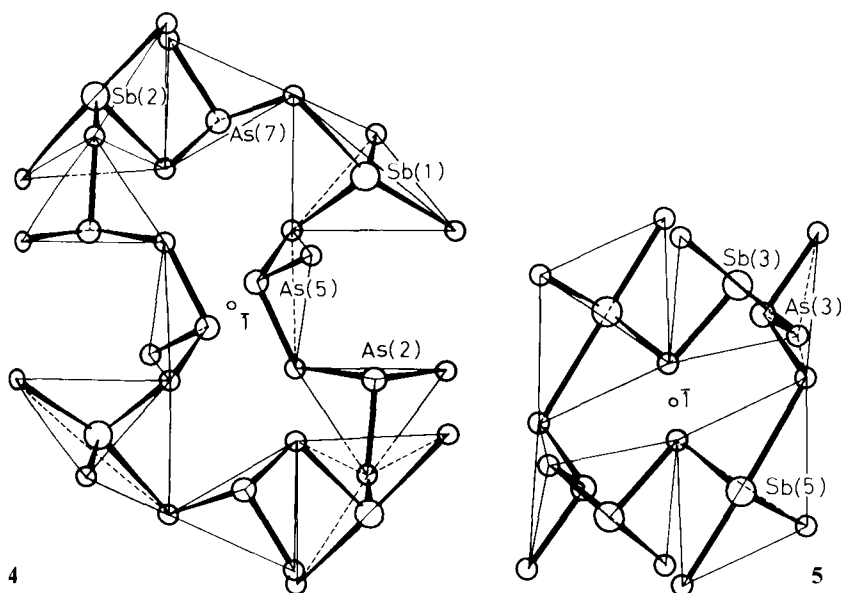


Fig. 4. The ring of Sb–As polyhedra around the center of symmetry at $\frac{1}{2}, 0, \frac{1}{2}$. Parallel projection along the b axis

Fig. 5. The ring of Sb–As polyhedra around the center of symmetry at $0, 0, \frac{1}{2}$. Parallel projection along the b axis

The linkage of the Sb and As coordination polyhedra

Considering only the nearest neighbour atoms at distances up to 2.4 Å for As atoms and 2.8 Å for Sb atoms respectively the Sb and As coordination polyhedra are connected in a three-dimensional framework which can be described as follows:

Two types of flattened spirals are formed around the screw axis. A left handed at $0, y, \frac{1}{4}$ (Fig. 6) and a right handed at $\frac{1}{2}, y, \frac{1}{4}$ (Fig. 7) respectively. These spirals are connected over the As(1) and Sb(1) polyhedra and form thus a zig-zag sheet along (001) plane. Three types of small rings occur: the first at the center $\frac{1}{2}, 0, \frac{1}{2}$ (Fig. 4) the second at the center $0, 0, \frac{1}{2}$ (Fig. 5) and the third between these two centers; they act as connectors of the zig-zag sheets. In the case of an As atom replacing the Sb(5) atom both the ring (Fig. 5) and the spiral (Fig. 6) break since As is bonded only to three S atoms and thus a rupture of the connection between Sb(1) and As(3) coordination polyhedra ensues.

As can be seen from Figures 4 to 7 the Sb and As coordination polyhedra share only common vertices and never common edges or faces.

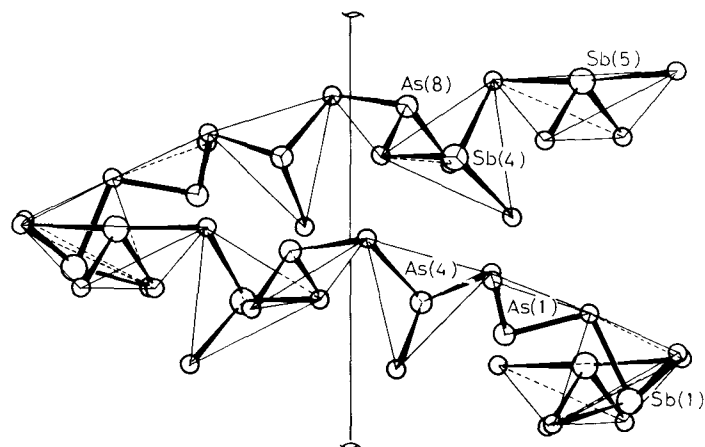


Fig. 6. One winding of the Sb–As spiral along the screw axis at $0, y, \frac{1}{4}$. Parallel projection along the a^* axis

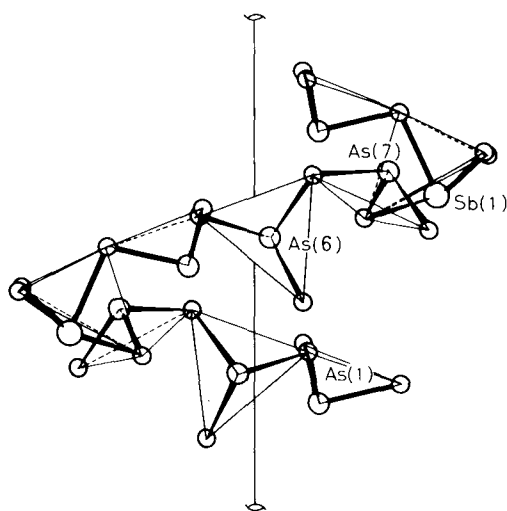


Fig. 7. One winding of the Sb–As spiral along the screw axis at $\frac{1}{2}, y, \frac{1}{4}$. Parallel projection along the a^* axis

The linkage of the Tl coordination polyhedra

The Tl coordination polyhedra form a three-dimensional framework interpenetrating the Sb–As framework. The Sb or As coordination polyhedra share with the Tl polyhedra common vertices, edges and even one face i.e. the Sb(2)/Tl(5) polyhedra contact.

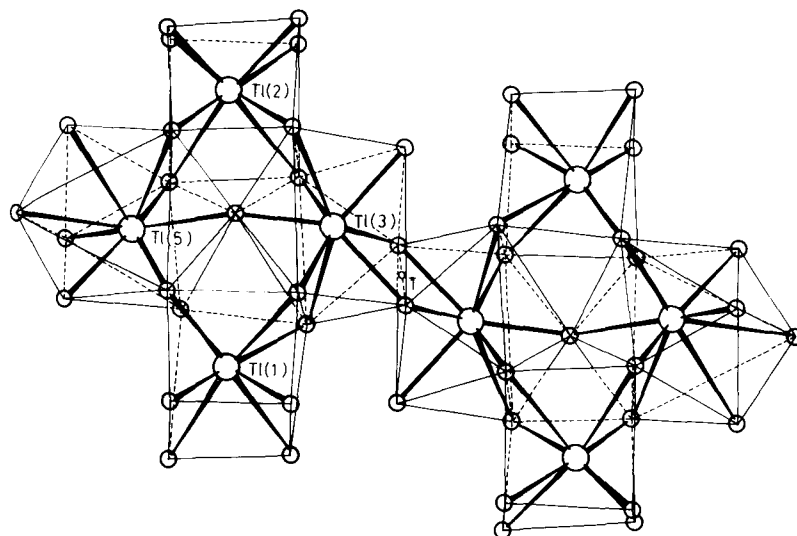


Fig. 8. The Ti structure around the center of symmetry at $0, 0, \frac{1}{2}$. Parallel projection along the b axis

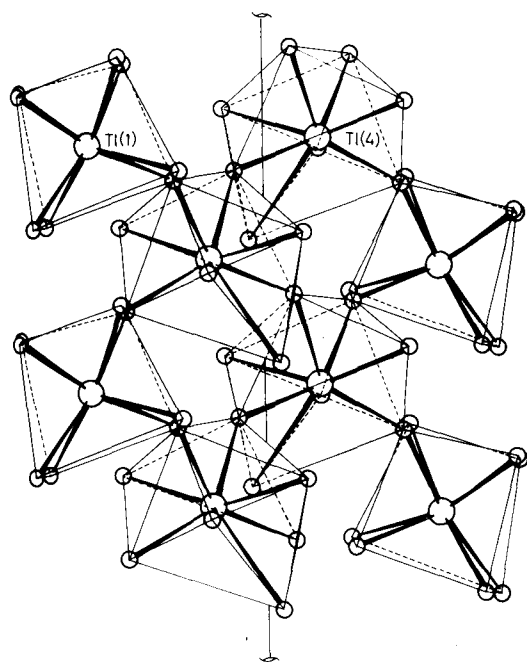


Fig. 9. Two windings of the Ti(4) spiral along the screw axis at $0, y, \frac{1}{4}$ with Ti(1) polyhedra connecting adjacent windings

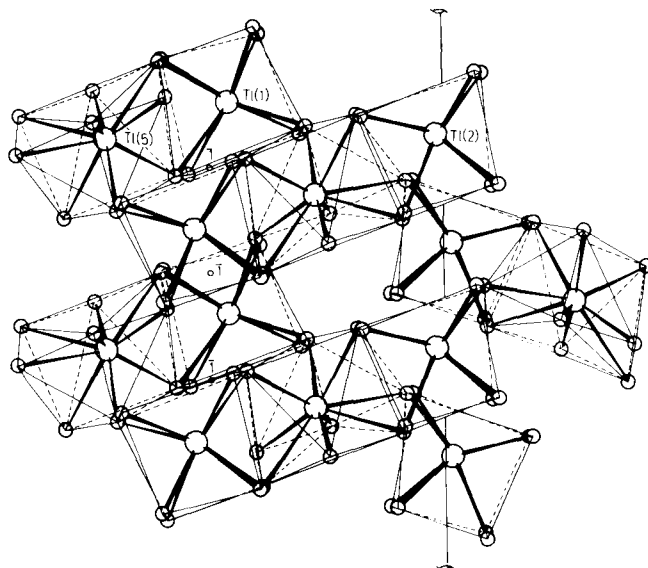


Fig. 10. Two windings of the Tl(2)–Tl(5) spiral along the screw axis at $\frac{1}{2}, y, \frac{1}{4}$ showing the interconnection through Tl(1). Parallel projection along the a^* axis

The framework of the Tl polyhedra can be described as consisting of the following structures:

1. The structure in which Tl(1) and Tl(2) polyhedra share common edges with Tl(3) and Tl(5) polyhedra; the latter two share also a common vertex. The centre of symmetry at $0, 0, \frac{1}{2}$ allows an equivalent structure to be adjoined at an edge of the Tl(3) polyhedra (Fig. 8).

2. Infinite spirals of Tl(4) polyhedra extend along the screw axes at $0, y, \frac{1}{4}$. Tl(4) polyhedra in adjacent windings are connected through Tl(1) polyhedra as shown in Figure 9.

3. Tl(2) and Tl(5) polyhedra form infinite spirals around the screw axes $\frac{1}{2}, y, \frac{1}{4}$ which are connected through the Tl(1) polyhedra (Fig. 10).

4. Tl(1) and Tl(5) polyhedra form a unit around the center of symmetry at $\frac{1}{2}, 0, \frac{1}{2}$ (Fig. 10).

It is interesting to note that the cubic coordination polyhedra show no common connecting elements. The same holds for the polyhedra of coordination IX.

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