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The crystal structure of simonite, $TlHgAs_3S_6$

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Abstract. The crystal structure of a new sulfosalt, $TlHgAs_3S_6$, has been determined. The crystal is monoclinic with space group $P2_1/n$. Four formula units are contained in a unit cell of dimensions $a_0 = 5.948(2)$ Å, $b_0 = 11.404(6)$ Å, $c_0 = 15.979(5)$ Å, $\beta = 90.15(1)°$. The structure was determined by direct methods and refined to a final R-value of 0.05 for 2462 observed reflections.

The AsS_3 pyramids form infinite AsS_2-chains parallel [101]. The Hg atom has a deformed octahedral coordination by 3 + 3 S atoms. The octahedra form a double chain parallel to [100]. The Tl atom is coordinated by 7 + 2 S atoms. The coordination polyhedra form layers parallel to (001).

The mean Tl–S, Hg–S and As–S distances are 3.43, 2.86, 2.27 Å, respectively.

1. Introduction

Small crystals of light red colour and of irregular shape, 0.1–0.2 mm in size were found within a crystal of rebulite, $Tl_5Sb_5As_8S_{22}$ (Balić-Žunić, Šćavnićar, and Engel, 1982). The microprobe analysis gave the composition $TlHgAs_3S_6$. Preliminary lattice parameters and the space group were determined from Weissenberg photographs and indicated that this is a new sulfosalt for which we propose the name simonite. With S : As = $\varphi = 2$, the structure of this sulfosalt belongs to the group IV a_3 of the classification proposed by Nowacki (1969, 1970).

2. Experimental

A small crystal of $TlHgAs_3S_6$ of irregular shape, 0.2 mm in size was used for X-ray investigations. Preliminary Weissenberg photographs with Cu$K\alpha$ radiation indicated that the crystal belongs to the monoclinic system. Systematic extinctions $h0l$, $h+l=2n+1$, $0k0$, $k=2n+1$ indicated the unique space group $P2_1/n$.

For intensity measurements the crystal was ground to a small sphere of diameter 0.167 mm; it was mounted on a fine fiber of Lindemann glass of diameter 0.06 mm with nail polish (Cutex). The determination of the lattice parameters and the intensity measurements were made with the NONIUS CAD4 diffractometer and Mo$K\alpha$-radiation ($\lambda_{\alpha 1}=0.70926$, $\lambda_{\alpha 2}=0.71354$ Å) and a graphite monochromator. 23 Reflections determined with the NONIUS peak hunting procedure in the range $15^\circ < 2\theta < 39^\circ$ were carefully centered. Accurate cell parameters were calculated with a least-squares procedure and led to the monoclinic cell constants (2nd setting) $a_0 = 5.948(2)$, $b_0 = 11.404(6)$, $c_0 = 15.979(5)$ Å and $\beta = 90.15(1)^\circ$. The intensities of 5687 reflections in the range $2^\circ \leq 2\theta \leq 60^\circ$ were measured by the $\omega - 2\theta$ scan technique. Every 200 reflections the orientation of the crystal and every 4.2 h the intensity of the (137) reflection were checked. During the measurement no significant deviations could be observed. After averaging multiple measurements 3147 independent reflections remained, of which 685 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 $\frac{1}{2m}$ of the time of the peak scan. The intensities were corrected for Lorentz-polarization effects according to Hope (1971) and absorption [μ (Mo$K\bar{\alpha}$) = 399.93 cm^{-1}].

The chemical composition was determined by means of an electron microprobe (Typ ARL, University Berne) by R. Oberhänsli. The analysis of 5 measurements at different places on two small crystals gave the following

Table 1. Crystal data

Formula	$TlHgAs_3S_6$
Formula weight	822.12
Space group	$P2_1/n$
a_0	5.948(2) Å
b_0	11.404(6) Å
c_0	15.979(5) Å
β	90.15(1)°
Z	4 formula units/unit cell
ϱ_{calc}	5.036 g cm^{-3}
μ(Mo$K\bar{\alpha}$)	399.93 cm^{-1}
Radiation	Mo$K\alpha$ ($\lambda_1 = 0.70926$ Å, $\lambda_2 = 0.71354$ Å)

mean values: Tl = 24.00 (24.86), Hg = 23.80 (24.40), Sb = 1.68 (0.00), As = 25.55 (27.34), S = 24.97 (23.40) Σ = 100.00 (100.00) %. The theoretical values for $TlHgAs_3S_6$ are given in brackets. The calculated density for 4 formula units $TlHgAs_3S_6$ is 5.036 g cm^{-3}.

3. Structure determination and refinement

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 $P2_1/n$

$\langle E \rangle$	0.817	(0.789)
$\langle E^2 \rangle$	1.008	(1.000)
$\langle \lvert E^2-1 \rvert \rangle$	0.936	(0.968).

Phases were directly determined with the program SIGMA of KRIPROG (Engel, 1978) according to the symbolic addition procedure. The two high peaks in the E-map clearly indicated the two heavy atoms and were first both assigned to Tl atoms. Three weaker peaks were provisionally assigned to As atoms, an assumption which later proved to be correct, whereas the S atoms could not be identified. A Fourier synthesis calculated with these metal atom positions revealed all S atoms. After several cycles of least-squares refinement including all atoms with isotropic temperature factors, the R-value was 0.11 for all observed reflections. The correct assignement of the Tl and Hg atom to the heavy metal positions could at this stage be done from the calculated metal-sulphur bond lengths. The Hg atom shows three shorter bond lengths of 2.40 to 2.72 Å as also found in the Hg bearing sulfosalts such as vrbaite (Ohmasa and Nowacki, 1971), galchaite (Divjaković and Nowacki, 1975), livingstonite (Srikrishnan and Nowacki, 1975) and christite (Brown and Dickson, 1976). The Tl atom shows bond lengths of 3.2 to 3.8 Å as is typical for Tl (Edenharter, 1976). Further refinements with anisotropic temperature factors and anomalous dispersion correction taken from the International Tables Vol. IV (Ibers and Hamilton, 1973) reduced the R-value to 0.05 for 2462 observed reflections and 0.07 for all reflections respectively. The final atomic coordinates and thermal parameters are given in Table 2. All calculations and drawings were done with the program system KRIPROG (Engel, 1978).

4. Description of the structure

Tables 3 and 4 present the interatomic distances and bond angles. The Tl atom forms a 7 + 2 irregular coordination polyhedron. Seven S atoms are

Table 2. The final atomic coordinates and anisotropic temperature factors with standard deviation for $TlHgAs_3S_6$.
$[T = \exp -(h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2\, hk\, \beta_{12} + 2\, hl\, \beta_{13} + 2\, kl\, \beta_{23})]$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Tl	0.3855(1)	0.38393(6)	0.31816(5)	0.0196(2)	0.00493(5)	0.00321(3)	−0.0024(1)	0.0025(1)	0.00059(6)
Hg	0.9365(1)	0.39814(6)	0.09751(4)	0.0191(2)	0.00510(5)	0.00131(2)	0.0017(1)	−0.0008(1)	−0.00079(5)
As(1)	1.0192(2)	0.1308(1)	0.4320(1)	0.0100(3)	0.0027(1)	0.00123(5)	−0.0006(3)	−0.0011(2)	−0.0002(1)
As(2)	0.3989(2)	0.1584(1)	0.0825(1)	0.0084(3)	0.0032(1)	0.00130(5)	−0.0013(3)	0.0002(2)	0.0005(1)
As(3)	0.7025(2)	0.1301(1)	0.2515(1)	0.0096(3)	0.0030(1)	0.00116(5)	0.0020(3)	0.0001(2)	0.0001(1)
S(1)	0.3778(6)	0.3419(3)	0.1202(2)	0.0111(8)	0.0040(2)	0.0018(1)	0.0029(7)	−0.0007(5)	−0.0006(3)
S(2)	0.7801(6)	0.1313(3)	0.1131(2)	0.0124(8)	0.0035(2)	0.0015(1)	0.0019(7)	0.0003(5)	0.0006(3)
S(3)	0.3931(6)	0.1419(3)	0.4502(2)	0.0108(8)	0.0041(2)	0.0013(1)	0.0005(7)	−0.0008(5)	0.0004(3)
S(4)	0.9279(6)	0.3272(3)	0.4420(2)	0.0132(9)	0.0034(2)	0.0015(1)	0.0018(7)	−0.0008(5)	0.0004(3)
S(5)	0.0716(6)	0.1394(3)	0.2882(2)	0.0108(8)	0.0035(2)	0.0013(1)	−0.0016(7)	−0.0006(5)	−0.0005(3)
S(6)	0.8772(6)	0.4393(3)	0.2430(2)	0.0112(8)	0.0029(2)	0.0014(1)	0.0023(7)	0.0004(5)	0.0000(3)

Table 3. Interatomic distances in $TlHgAs_3S_6$

$Tl-S(1)_1$	3.199(4) Å	$Hg-S(6)_1$	2.400(3) Å
$-S(6)_1$	3.226(3)	$-S(3)_6$	2.411(4)
$-S(6)_3$	3.311(3)	$-S(1)_2$	2.725(4)
$-S(5)_8$	3.383(4)	$-S(3)_9$	3.056(4)
$-S(5)_1$	3.389(4)	$-S(2)_1$	3.192(4)
$-S(4)_3$	3.432(4)	$-S(1)_1$	3.405(4)
$-S(3)_1$	3.474(4)	mean:	2.865 Å
$-S(2)_9$	3.621(4)		
$-S(4)_1$	3.835(4)	$Hg-As(1)_7$	3.637(2) Å
mean:	3.430 Å	$-As(3)_9$	3.676(2)
$Tl-As(3)_1$	3.617(2) Å		
$As(1)-S(3)_2$	2.246(4) Å	$As(2)-S(1)_1$	2.182(4) Å
$-S(4)_1$	2.311(4)	$-S(4)_7$	2.258(4)
$-S(5)_2$	2.322(4)	$-S(2)_1$	2.338(4)
mean:	2.293 Å	mean:	2.259 Å
$As(3)-S(6)_{11}$	2.228(4) Å		
$-S(2)_1$	2.261(4)		
$-S(5)_2$	2.273(4)		
mean:	2.254 Å		

Symmetry operations:

1 x, y, z	2 $1+x, y, z$	3 $-1+x, y, z$
4 $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$	5 $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$	6 $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
7 $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$	8 $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	9 $1\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
10 $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$	11 $1\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$	12 $2-x, 1-y, 1-z$
13 $1-x, -y, -z$		

Table 4. Bond angles for Hg and As atoms in $Tl\ HgAs_3S_6$

$S(6)_1-Hg-S(3)_6$	165.4(1)°	$S(3)_2-As(1)-S(4)_1$	99.8(1)°
$-S(1)_2$	93.5(1)	$-S(5)_2$	89.4(1)
$-S(3)_9$	96.5(1)	$S(4)_1-As(1)-S(5)_2$	93.4(1)
$-S(2)_1$	93.9(1)		
$-S(1)_1$	77.7(1)	$S(1)_1-As(2)-S(4)_7$	102.1(1)
		$-S(2)_1$	97.2(1)
$S(3)_6-Hg-S(1)_2$	100.7(1)	$S(4)_7-As(2)-S(2)_1$	98.1(1)
$-S(3)_9$	87.9(1)		
$-S(2)_1$	82.3(1)	$S(6)_{11}-As(3)-S(2)_1$	95.1(1)
$-S(1)_1$	88.1(1)	$-S(5)_2$	104.0(1)
$S(1)_2-Hg-S(3)_9$	85.8(1)	$S(1)_1-As(3)-S(5)_2$	93.0(1)
$-S(2)_1$	92.6(1)		
$-S(1)_1$	151.8(1)		
$S(3)_9-Hg-S(2)_1$	169.6(4)		
$-S(1)_1$	121.5(1)		
$S(2)_1-Hg-S(1)_1$	61.8(1)		

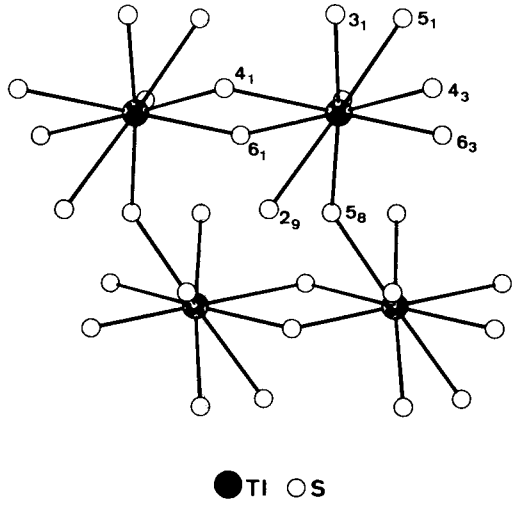

Fig. 1. Cut out of the $^2_\infty[TlS_6]$-layer. Parallel projection along the *c* axis

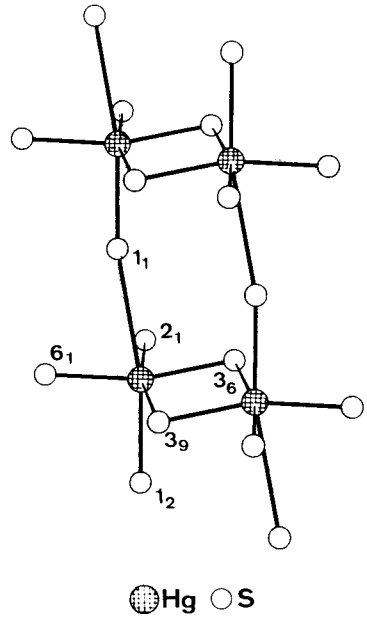

Fig. 2. Cut out of the $^1_\infty[HgS_4]$-chain

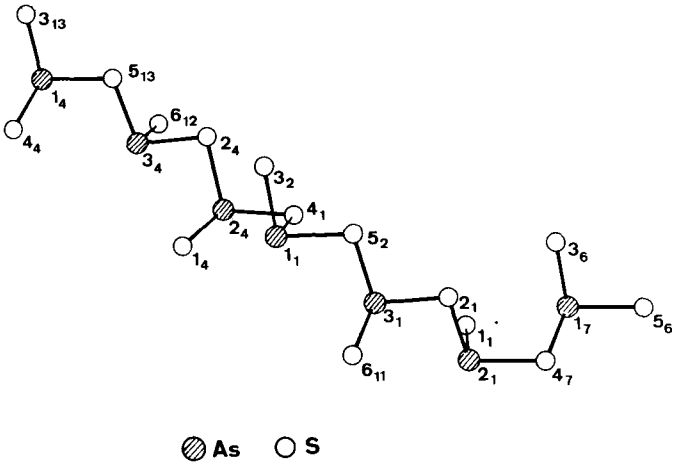

Fig. 3. Cut out of the $^1_\infty[AsS_2]$-chain

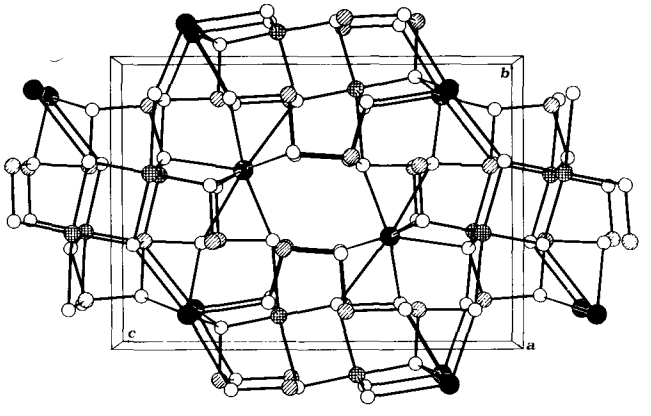

Fig. 4. The central projection of the structure of $TlHgAs_3S_6$ viewed along the *a*-axis

closer to Tl at distances from 3.20 to 3.47 Å and two further away at distances of 3.62 and 3.83 Å. The Tl coordination polyhedra share two edges and two vertices with neighbours and build up a corrugated $^2_\infty[TlS_6]$-layer parallel to the (001) plane as shown in Figure 1. The Hg atom has 3 nearest S atoms at distances from 2.40 to 2.72 Å and 3 S atoms further at 3.06 to 3.40 Å completing a deformed coordination octahedron. A similar coordination polyhedron is also found in livingstonite (Srikrishnan and Nowacki, 1975). The octahedra form a double $^1_\infty[HgS_4]$-chain parallel to [100] sharing one edge and two vertices with the neighbours as shown in Figure 2. The As atoms

are bonded to three nearest S atoms forming a trigonal pyramid with the As atom at the apex. The As–S distances range from 2.18 to 2.34 Å with mean value 2.27 Å. The S–As–S angles range from 89.4° to 104.0° with mean value 96.9°. These are very close to the mean values for AsS_3-pyramids stated by Edenharter (1976). The AsS_3-pyramids are linked together to form an infinite $^1_\infty[AsS_2]$-chain along [101] as shown in Figure 3. The S atoms are coordinated by four metal atoms forming a deformed tetrahedron. In Figure 4 the linkage of these building units is shown. The $^1_\infty[HgS_4]$-double chains lie between the $^2_\infty[TlS_6]$-layers in an askew arrangement leaving open small channels along the [100] direction. The $^1_\infty[AsS_2]$-chains cross the layers near the Tl and Hg atoms resulting in Tl–As and Hg–As distances of 3.62 and 3.64 Å respectively.

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