

## The crystal structure of synthetic christite, $\text{HgTlAsS}_3$

By **KEVIN L. BROWN**

Chemistry Division, D.S.I.R. Private Bag, Petone, New Zealand

and **FRANK W. DICKSON**

Department of Geology, Stanford University, Stanford, California

(Received 24 June 1976)

### Auszug

Die Kristallstruktur von synthetischem Christit,  $\text{HgTlAsS}_3$ , wurde bestimmt und bis zu  $R = 0,044$  verfeinert. Die Gitterkonstanten sind  $a = 6,113 \pm 0,001$ ,  $b = 16,188 \pm 0,004$ ,  $c = 6,111 \pm 0,001 \text{ \AA}$ ,  $\beta = 96,71 \pm 0,02^\circ$ ;  $Z = 4$ ; Raumgruppe  $P2_1/n$ .

Die Struktur besteht aus  $\text{AsS}_3$ -Pyramiden, die durch  $\text{HgS}_4$ -Tetraeder zu einer zweidimensionalen Schicht parallel  $\{010\}$  verbunden werden. Die Tl-Atome liegen zwischen den Schichten; sie halten diese durch schwache Bindungen zusammen, was die beobachtete vollkommene Spaltbarkeit nach  $\{010\}$  erklärt. Die aus Pulveraufnahmen berechneten Daten stimmen gut mit denen des natürlichen Christits überein.

### Abstract

The crystal structure of synthetic christite,  $\text{HgTlAsS}_3$  has been determined. The crystal is monoclinic with the space group  $P2_1/n$ . Four formula units are contained in a unit cell of dimensions  $a = 6.113 \pm 0.001$ ,  $b = 16.188 \pm 0.004$ ,  $c = 6.111 \pm 0.001 \text{ \AA}$ ,  $\beta = 96.71 \pm 0.02^\circ$ . The structure was refined by full-matrix least-squares methods using diffractometer data to a conventional discrepancy index,  $R$ , of 0.044.

The structure consists of  $\text{AsS}_3$  pyramids connected by  $\text{HgS}_4$  tetrahedra to form a polymeric two-dimensional sheet structure parallel to  $\{010\}$ . The thallium atoms lie between the sheets, connecting them together with weak bonds, which gives the perfect  $\{010\}$  cleavage observed. The calculated powder diffraction pattern agrees well with that of natural christite.

### Introduction

This investigation was prompted by a study of the new mineral christite (RADTKE, DICKSON, SLACK and BROWN, 1976), from the Carlin gold mine, Nevada, U.S.A., where several other rare thallium

minerals occur (RADTKE and DICKSON, 1975). As the natural material proved unsuitable for a single-crystal analysis, synthetic christite was prepared for single-crystal study.

### Experimental

Crystals were prepared by recrystallizing synthetic  $\text{HgTlAsS}_3$  powder in contact with a 1%  $\text{Na}_2\text{B}_4\text{O}_7$  solution in a sealed gold tube at  $285^\circ\text{C}$  and 250 bars pressure for 4 days. Individual euhedral crystals grew on the tube wall, but most of the product was a porous holocrystalline cake. The atomic spacings of ground individual crystals were identical to spacings of the holocrystalline mass and of the new mineral, christite.

The crystals obtained were plate-like and orange in colour. After considerable difficulty with multiple and curved crystals, a crystal suitable for an x-ray diffraction analysis was found.

The synthetic crystal of christite selected for single-crystal study was tabular, flattened parallel to  $\{010\}$ , slightly elongated parallel to the  $c$  axis, and was enclosed by the  $\{010\}$ ,  $\{\bar{1}01\}$  pinacoids and the  $\{110\}$  and  $\{011\}$  prisms. Overall dimensions were  $0.07 \times 0.03 \times 0.11$  mm. The crystal is bright orange, in contrast to the deep red shown by large crystals and thick plates.  $\text{HgTlAsS}_3$  is soft and shows a perfect cleavage parallel to  $\{010\}$  along with several other less developed cleavages. The crystals deform easily in a ductile manner. Approximate unit-cell constants and space-group absences were obtained from Weissenberg and precession photographs. The systematic absences  $0k0$ ,  $k = 2n + 1$ ;  $h0l$ ,  $h + l = 2n + 1$  found are consistent with space group  $P2_1/n$ .

The unit-cell parameters were refined by a least-squares treatment of the setting angles of 12 reflections centred automatically on a Hilger and Watts Y290 automatic diffractometer, using zirconium-filtered molybdenum radiation ( $\lambda = 0.71069$  Å). Crystal data are given in

Table 1

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$\text{HgTlAsS}_3$ , Formula weight = 576.07
Monoclinic, $P2_1/n$
$a = 6.113(1)$ , $b = 16.188(4)$ , $c = 6.111(1)$ Å, $\beta = 96.71(2)^\circ$
$V = 600.6$ Å <sup>3</sup> , $Z = 4$
$D_c = 6.37$ g · cm <sup>-3</sup>
$\mu$ (MoK $\alpha$ ) = 596 cm <sup>-1</sup>

Table 1. In this and following tables, estimated standard deviations in the least significant figures are given in parentheses.

The intensities were measured by the  $\omega/2\theta$  scan technique with a scan step of  $0.01^\circ$  and a counting time of 1.5 sec/step. Each reflection was scanned through a range of  $0.8^\circ$  centred on the peak. The local background was measured for 25 seconds at each end of the scan using the stationary-counter/stationary-crystal technique. To monitor the crystal and electronic stability, the intensities of three reflections were measured periodically throughout the data collection, but only random fluctuations of  $\pm 3\%$  were observed. All independent reflections in the sphere with  $\theta < 25^\circ$  were measured. The integrated intensities and their standard deviations were calculated as described by CORFIELD *et al.* (1967). The 702 reflections for which  $I > 3\sigma_I$  were used in the subsequent analysis.

### Structure determination and refinement

A three-dimensional Patterson synthesis enabled the positions of the mercury, thallium and arsenic atoms to be found. Least-squares refinement followed by a difference Fourier synthesis revealed the positions of the three sulphur atoms. All atoms were then refined by full-matrix least-squares (STEWART *et al.*, 1972), the mercury, thallium and arsenic atoms having anisotropic and the sulphur atoms having isotropic thermal parameters. Scattering factors were those of CROMER and MANN (1968) with the anomalous dispersion corrections for mercury, thallium and arsenic of CROMER (1965). The function minimized in the least-squares refinement was  $\sum w_i (|F_o| - |F_c|)^2$ , where  $F_o$  and  $F_c$  are the observed and calculated structure factors and the weight  $w_i = 4F_o^2/\sigma(I)^2$ . At this stage  $R_1 = \sum (|F_o| - |F_c|)/\sum |F_o| = 0.115$  and  $R_2 = [\sum w_i (|F_o| - |F_c|)^2/\sum w_i |F_o|^2]^{1/2} = 0.150$ .

Corrections for absorption were applied (TEMPLETON and TEMPLETON, 1974) by the analytical method of DE MEULENAER and TOMPA (1965); the transmission coefficients ranging from 0.204 to 0.042. Three further cycles of full-matrix least squares with the temperature factors refined as above the discrepancy indices  $R_1 = 0.046$  and  $R_2 = 0.050$ . The mercury and thallium positions were now interchanged and the atom parameters were refined as above to convergence resulting in  $R_1 = 0.045$  and  $R_2 = 0.049$ . A test on the ratio of the weighted residuals (HAMILTON, 1965) showed that the second refinement was not significantly better at the 90% confidence level. The mercury and thallium positions were again interchanged

Table 2. *Positional parameters for synthetic christite*

Atom	$x$	$y$	$z$
Tl	0.1633(2)	0.45039(8)	0.3366(2)
Hg	0.0793(2)	0.25013(8)	0.9207(2)
As	0.5759(5)	0.3916(2)	0.9254(5)
S(1)	0.2046(10)	0.3917(5)	0.8587(12)
S(2)	0.1419(12)	0.2408(5)	0.3559(14)
S(3)	0.1421(11)	0.1077(4)	0.7962(12)

Table 3. *Thermal parameters* ( $\times 10^2$ ). The form of the thermal ellipsoids is given by  $\exp -2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)$ 

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Tl	2.79(6)	3.82(8)	3.50(7)	0.25(6)	0.73(5)	-0.38(7)
Hg	3.03(7)	2.94(7)	4.07(8)	-0.33(5)	0.01(6)	-0.27(6)
As	1.95(15)	2.21(17)	3.09(18)	-0.18(13)	0.59(13)	0.22(14)
S(1)	1.8(4)	3.2(5)	2.9(5)	0.2(3)	-0.5(3)	-0.3(4)
S(2)	1.9(4)	3.1(5)	2.4(5)	-0.4(3)	0.2(3)	0.4(4)
S(3)	1.9(4)	2.2(4)	3.3(5)	0.1(3)	-0.1(3)	0.2(4)

and the sulphur atoms were now refined to convergence with anisotropic thermal parameters which gave final values of  $R_1 = 0.044$  and  $R_2 = 0.048$ , which is significantly better at the 95% confidence level. An analysis of the weighting scheme showed that the average  $w_i(|F_o| - |F_c|)^2$  was approximately constant over a range of  $\sin \theta$  and  $|F_o|$  values. A final difference Fourier showed no residual density greater than 10% of that expected for a sulphur atom. The final positional parameters are given in Table 2 and their thermal parameters in Table 3. Observed and calculated structure-factor amplitudes for the observed reflections are given in Table 4.

### Results and discussion

As the x-ray scattering factors for mercury and thallium atoms are very similar, it was not possible to distinguish them by an x-ray diffraction analysis. The two "heavy" atom sites in this structure are in different coordination environments. One site (A) provides the bridge between  $\text{AsS}_3$  pyramids and is tetrahedral in coordination with shorter bond lengths (2.46–2.66 Å), the second site (B) shows no clear-cut coordination and the bonding is much weaker (3.11–3.52 Å). In the crystal structure of vrbaitite (OHMASA and NOWACKI, 1971), a mercury or thallium atom is in a similar environment to site A; strong



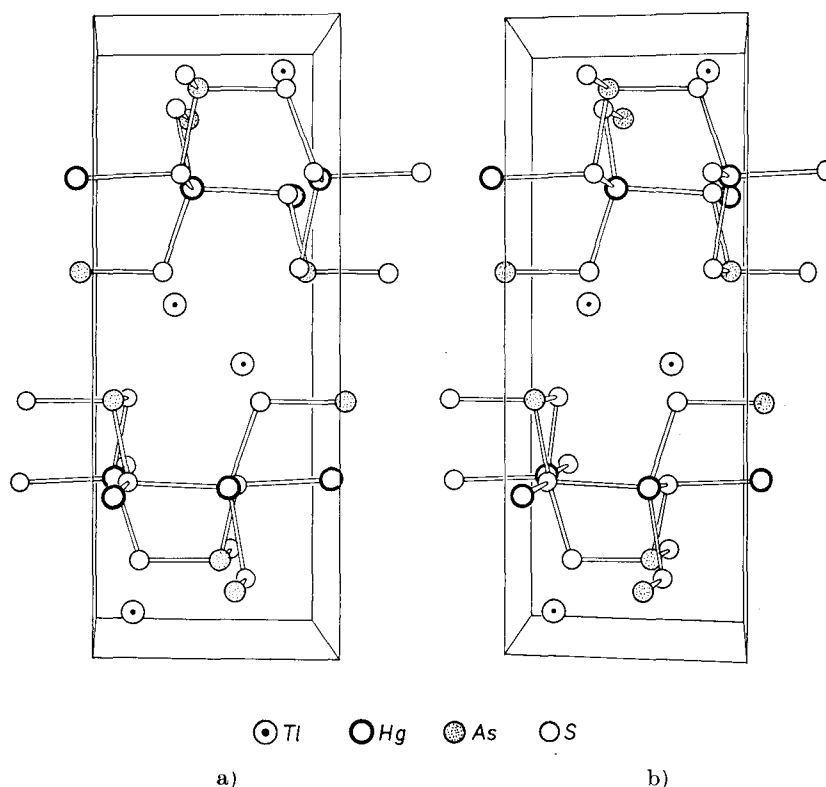


Fig. 1. A stereoscopic view of the unit cell

space-group evidence exists for vrbaitite that mercury occupies this position. Consequently, we have assigned site A as a mercury atom and site B as a thallium atom.

The crystal structure consists of trigonal pyramids of  $\text{AsS}_3$  linked together by mercury atoms to form a two-dimensional sheet-like network (see Figs. 1 and 2). The sheets are parallel to  $\{010\}$  and occur every  $b/2$  in the  $y$  direction. The thallium atoms are located between the sheets, bonded weakly to their nearest neighbours. The structure falls into the category  $\text{IIa}$ , ( $\phi = 3$ ) of sulphosalt classification suggested by NOWACKI (1969, 1970). Bond lengths and angles are given in Table 5.

The  $\text{AsS}_3$  pyramid is similar to that found in other sulphosalts [*e.g.* FLEET (1973), TAKÉUCHI, OHMASA and NOWACKI (1968)]. The As—S bond lengths of 2.258(10), 2.232(7) and 2.255(10) Å come into

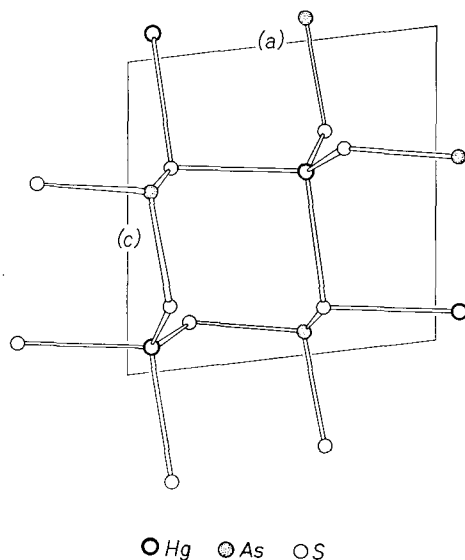


Fig. 2. A view projected down (010) of one sheet

the ‘non-bridge’ category described by TAKÉUCHI and SADANAGA (1969). The S—As—S bond angles are slightly larger (mean =  $101.3^\circ$ ) than the mean observed ( $98.66^\circ$ ) by TAKÉUCHI and SADANAGA. An As—Tl contact of  $3.50(1)$  Å occurs in the fourth tetrahedral coordination position of the arsenic atom.

The sulphur atoms S(1) and S(3) each have only two nearest neighbours: one mercury and one arsenic atom. The S(2) sulphur atom has three nearest neighbours: two mercury atoms and one arsenic atom. This difference in coordination is reflected in the Hg—S(2) bond lengths of  $2.65(1)$  and  $2.66(1)$  Å compared with Hg—S(1) and Hg—S(3) bond lengths of  $2.461(7)$  and  $2.472(7)$  Å respectively. The four sulphur atoms around the mercury atom form a distorted tetrahedron, similar to that found in other mercury compounds (GRDENIĆ, 1965). There are no other contacts less than  $3.5$  Å around the mercury atom. The expected tetrahedral covalent Hg—S bond length (PAULING, 1960) is  $2.52$  Å which is intermediate between the two different types found here.

The arrangement of atoms around the thallium atom shows no systematic coordination geometry, with seven Tl—S contacts ranging from  $3.11$ – $3.52$  Å. This is typical of thallium atoms (OHMASA and NOWACKI, 1971) which are loosely bound in ‘holes’ formed in a poly-

Table 5. *Bond lengths and angles*  
 Primed symbols refer to atoms in different asymmetric units

Bond	Length	Bond	Length
Hg—S(1)	2.460(9) Å	Tl—S(1)	3.310(9) Å
Hg—S(3)	2.471(8)	Tl—S(1')	3.110(9)
Hg—S(2)	2.646(11)	Tl—S(1'')	3.520(9)
Hg—S(2')	2.661(11)	Tl—S(2)	3.397(7)
As—S(1)	2.258(10)	Tl—S(3)	3.111(8)
As—S(2)	2.232(8)	Tl—S(3')	3.303(8)
As—S(3)	2.255(11)	Tl—S(3'')	3.509(8)
As—Tl	3.499(12)		

Bond	Angle	Bond	Angle
S(1)—Hg—S(3)	139.4(3)°	Hg—S(2)—Hg'	99.9(3)°
S(1)—Hg—S(2)	101.3(2)	Hg—S(3)—As	106.8(3)
S(1)—Hg—S(2')	104.6(2)		
S(2)—Hg—S(2')	100.2(2)		
S(2)—Hg—S(3)	104.3(2)		
S(2')—Hg—S(3)	101.2(2)		
S(1)—As—S(2)	99.6(3)		
S(1)—As—S(3)	103.9(3)		
S(1)—As—Tl	114.8(2)		
S(2)—As—S(3)	100.4(3)		
S(2)—As—Tl	120.8(2)		
S(2)—As—Tl	114.7(2)		
Hg—S(1)—As	107.2(3)		
Hg—S(2)—As	103.8(8)		
Hg'—S(2)—As	103.0(3)		

meric network of  $\text{AsS}_3$  pyramids. As in lorandite (FLEET, 1973), the thallium atom is more closely associated with one sheet than the other. All five Tl—S contacts of less than 3.45 Å are to one sheet, the remaining two Tl—S contacts to the other sheet are 3.51 and 3.52 Å. There is however a Tl—Tl bond of 3.39 Å between sheets and a Tl—As contact of 3.50 Å. The former distance is similar to the Tl—Tl distance in elemental thallium (3.40 Å; WELLS, 1962), and the thallium atoms probably provide the principal cohesive force between sheets.

Two properties of monoclinic  $\text{HgTlAsS}_3$  follow from the proposed sheet structure. The first is the perfect {010} cleavage observed in synthetic crystals and in the mineral. The polymeric  $\text{HgAsS}_3$  sheets are linked to one another mainly by long Tl—Tl contacts which would



be considerably weaker than the bonds within the sheets resulting in the micaceous cleavage. Secondly, it is possible to deform {010} cleavage fragments ductily to smooth curved surfaces. This is a consequence of the ease with which the sheets slip past one another, *i.e.* the intersheet bonds break and then reform.

The structure is pseudo-tetragonal as evidenced both by the equality of the *a* and *c* axial lengths and also by the relationship of the *x* and *z* atom coordinates. However the cell-constants do not show any relationship to routhierite (JOHAN, MANTIENNE and PICOT, 1974) which is reported as a tetragonal form of HgTlAsS<sub>3</sub>, but which contains noteworthy amounts of copper, silver, zinc and antimony.

The calculated x-ray powder diffraction data agree well with the observed data for natural christite (RADTKE *et al.*, 1976).

### Acknowledgements

The authors wish to thank Dr. F. C. MARCH of the University of Canterbury for assistance in the production of the stereoscopic diagrams.

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