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Refinement of the Crystal Structure of Synthetic Tl_3AsS_4*

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The crystal structure of a synthetic sulfosalt, Tl_3AsS_4, has been refined. The crystal is orthorhombic with space group Pnma. Four formula units are contained in a unit cell of dimensions $a = 0.8893(3)$, $b = 1.0868(5)$ and $c = 0.9088(3)$ nm. The final R-value is 0.04 for 759 observed reflections.

The Tl(1) has seven nearest S atoms with a mean Tl-S bond length of 0.329 nm. Tl(2) has five nearest S atoms with a mean Tl-S bond length of 0.318 nm. The Tl coordination polyhedra form a three-dimensional framework. The As atom has a tetrahedral coordination by four S atoms at a mean distance of 0.216 nm. The AsS_4 tetrahedra are isolated.

INTRODUCTION

In our continuing investigation of sulfosalts the $Tl_2S - As_2S_5$ system has attracted special interest because of the tetrahedral coordination of the As atom by four S atoms. Only two other sulfosalts, energite[1] and luzonite[2], two polymorphs of Cu_3AsS_4, have been known until now to have a similar coordination of the As atom. In this system Tl_3AsS_4 was first obtained by Hawley[3] from an aqueous solution. Larger crystals of up to 2—3 cm in length were grown by Roland et al.[4] by heating a stoichiometric mixture in silica tubes. In our laboratory Edenharter[5] obtained small crystals of Tl_3AsS_4 by hydrothermal synthesis and recently Bohac[6] has crystallized Tl_3AsS_4 in a salt flux experiment using KSCN. The physical properties of Tl_3AsS_4 were described by Roland et al.[4] and by Fritz et al.[7]. These latter authors also determined the crystal structure of Tl_3AsS_4 but only at a low accuracy and they did not state any R-value. Therefore, the refinement of the crystal structure of Tl_3AsS_4 was undertaken in order to obtain accurate information on the Tl and As coordination polyhedra.

EXPERIMENTAL

Single crystals of synthetic Tl_3AsS_4 were obtained by Edenharter[5]. The shape of the crystal used for X-ray investigation is shown in Figure 1. The size of the crystal is $0.15 \times 0.11 \times 0.15$ mm.

Preliminary Weissenberg photographs with CuK_α radiation indicated that the crystal belongs to the orthorhombic system. Systematic extinctions are: $0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$; $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$, which permit $Pnma$ and $Pn2_1a$ as possible space groups. Because of the findings

* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

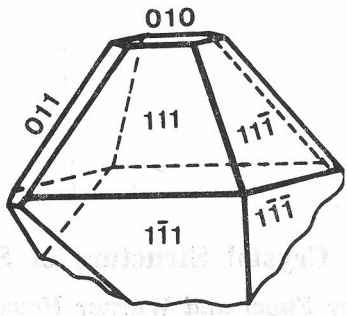

Figure 1. Shape of the crystal used for X-ray investigation.

by Roland et al.[4] that no piezoelectric effect could be observed, the centrosymmetric space group Pnma was assumed. For our investigation we used the standard setting for the space group. Therefore, our crystal axes are obtained from those stated by Roland et al. through the transformation

$$a = c_R, \quad b = b_R, \quad c = a_R.$$

For intensity measurements the crystal was ground to a small sphere of diameter 0.104(4) mm; it was fixed on a fine fiber of Lindemann glass with nail polish (Cutex). The determination of the lattice parameters and the intensity measurements were made with the NONIUS CAD4 diffractometer and MoK_α-radiation ($\lambda_{\alpha 1}=0.070926$, $\lambda_{\alpha 2} = 0.071354$ nm) and a graphite monochromator. 21 reflections determined with the NONIUS peak hunting procedure in the range $12° < 2\vartheta < 28°$ were carefully centered. Accurate cell parameters were calculated with a least-squares procedure and led to the orthorhombic cell constants $a = 0.8893(3)$ $b = 1.0868(5)$ $c = 0.9088(3)$ nm. The intensities of 4261 reflections in the range $2° \leq 2\vartheta \leq 56°$ were measured by the $\omega - 2\vartheta$ scan technique. Every 100 reflections the orientation of the crystal and every 2.8 h the intensity of the (1 3 2) reflection were checked. During the measurements no significant deviation was observed. After averaging equivalent reflections, a set of 1118 independent reflections remained, of which 359 were unobserved with $I \leq 2.58\,\sigma\,(I)$. The agreement factor between equivalent observed reflections was 0.05. 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 $1/2m$ of the time of the peak scan. The intensities were corrected for the Lorentz-polarisation effect [according to Hope[8]] and absorption [$\mu\,(MoK_\alpha) = 60.0$ mm^{-1}]. The calculated density for 4 formula units Tl_3AsS_4 is 6.17 gcm^{-3} which agrees well with the observed density of 6.20 gcm^{-3} measured by Roland et al.[4].

TABLE I

Crystal Data of Tl_3AsS_4

Formula	Tl_3AsS_4
Formula weight	816.34
space group	*Pnma*
a	0.8893(3) nm
b	1.0868(5) nm
c	0.9088(3) nm
Z	4 formula units / unit cell
ϱ_{calc}	6.17 gcm^{-3}
ϱ_{obs}	6.20 gcm^{-3}
$\mu\,(MoK_\alpha)$	60.0 mm^{-1}
Radiation	MoK_α ($\lambda_1 = 0.070926$, $\lambda_2 = 0.071354$ nm)

TABLE II

The Final Atomic Coordinates and Anisotropic Temperature Factors with Standard Deviations for Tl_3AsS_4. [$T = exp - (h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2hk \beta_{12} + 2hl \beta_{13} + 2kl \beta_{23})$]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Tl(1)	0.0612(1)	0.0493(1)	0.1958(1)	0.0079(1)	0.0043(7)	0.0083(1)	0.0009(2)	—0.0003(2)	—0.0007(2)
Tl(2)	0.3838(2)	0.25	—0.1094(2)	0.0059(2)	0.0124(2)	0.0068(2)	0	0.0007(3)	0
As(1)	0.2797(3)	0.25	0.4738(3)	0.0032(4)	0.0037(3)	0.0040(3)	0	—0.0001(6)	0
S(1)	0.3061(9)	0.25	0.2352(9)	0.0057(9)	0.0056(7)	0.0028(8)	0	0.000(1)	0
S(2)	0.0036(9)	0.25	0.9314(9)	0.0036(9)	0.0063(8)	0.0049(9)	0	0.001(2)	0
S(3)	0.1568(7)	0.0872(6)	0.5352(7)	0.0075(8)	0.0048(5)	0.0072(7)	—0.003(1)	0.001(1)	0.004(1)

STRUCTURE DETERMINATION AND REFINEMENT

The absolute scale factor was determined from a Wilson plot. The structure factors were converted to normalized *E*-values; however, the statistical distribution shows poor agreement with the theoretical values, given in brackets, for the centrosymmetric space group *Pnma*, probably due to the different kinds of atoms and their special arrangement.

$$\langle E \rangle \quad 0.843 \quad (0.798)$$
$$\langle E^2 \rangle \quad 1.000 \quad (1.000)$$
$$\langle |E^2 - 1| \rangle \quad 0.877 \quad (0.968)$$

Phases were directly determined with the program SIGMA of KRIPROG[9] according to the symbolic addition procedure. The resulting *E*-map clearly revealed the two Tl positions and the As position. The three S positions were found in a subsequent Fourier synthesis. The main features of the structure found agreed with the proposed structure of Fritz et al.[7]. Further refinement with anisotropic temperature factors and anomalous dispersion correction taken from the International Tables, Vol. IV[10] reduced the R-value to 0.04 for 759 observed reflections. The final atomic coordinates and thermal parameters are given in Table II. All calculations and drawings were done using the program system KRIPROG.

DESCRIPTION OF THE STRUCTURE

Tables III and IV present the interatomic distances and bond angles. The coordination of the metal atoms is shown in Figure 2. The Tl(1) has seven nearest S atoms at distances from 0.31 to 0.35 nm, mean 0.329 nm, as shown

TABLE III

Interatomic Distances in Tl_3AsS_4

Tl(1) — $S(1)_1$	0.3103(6) nm	Tl(2) — $S(3)_7$	0.3079(7) nm
— $S(1)_2$	0.3209(6)	— $S(3)_8$	0.3079(7)
— $S(3)_1$	0.3226(6)	— $S(2)_8$	0.3114(8)
— $S(3)_3$	0.3259(6)	— $S(1)_1$	0.3206(8)
— $S(2)_4$	0.3286(6)	— $S(2)_4$	0.3402(8)
— $S(3)_5$	0.3455(6)		
— $S(2)_6$	0.3500(6)	mean:	0.3176 nm
mean:	0.3291 nm	Tl(2) — As	0.3730(3) nm
Tl(1) — As	0.3661(3) nm		
Tl(1) — Tl(2)	0.3736(1)		
As — $S(3)_1$	0.2153(7) nm		
— $S(3)_9$	0.2153(7)		
— $S(2)_{10}$	0.2169(9)		
— $S(1)_1$	0.2181(8)		
mean:	0.2164 nm		

Symmetry operations:

1 x, y, z	2 $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$
4 $x, y, 1 - z$	5 $-x, -y, 1 - z$
7 $\frac{1}{2} + x, y, \frac{1}{2} - z$	8 $\frac{1}{2} + x, \frac{1}{2} - y, -z$
10 $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$	3 $\frac{1}{2} - x, -y, z - \frac{1}{2}$
	6 $-x, y - {}^1/_2, 1 - z$
	9 $x, {}^1/_2 - y, z$

TABLE IV

Bond Angles in Tl_3AsS_4

$S(1)_1$ — Tl(1) — $S(1)_2$	89.7(2)°		$S(3)_7$ — Tl(2) — $S(3)_8$	70.1(2)°	
— $S(3)_1$	67.3(2)		— $S(2)_8$	86.3(2)	
— $S(3)_3$	80.3(2)		— $S(1)_1$	87.5(2)	
— $S(2)_4$	74.2(2)		— $S(2)_4$	139.5(2)	
— $S(3)_5$	127.9(2)				
— $S(2)_6$	143.8(2)		$S(3)_8$ — Tl(2) — $S(2)_8$	86.3(2)	
			— $S(1)_1$	87.5(2)	
$S(1)_2$ — Tl(1) — $S(3)_1$	85.0(2)		— $S(2)_4$	139.5(2)	
— $S(3)_3$	160.2(2)				
— $S(2)_4$	65.2(2)		$S(2)_8$ — Tl(2) — $S(1)_1$	172.4(11)	
— $S(3)_5$	75.9(2)		— $S(2)_4$	116.2(2)	
— $S(2)_6$	125.4(2)				
			$S(1)_1$ — Tl(2) — $S(2)_4$	71.3(2)	
$S(3)_1$ — Tl(1) — $S(3)_3$	106.5(2)				
— $S(2)_4$	131.0(2)		$S(3)_9$ — As — $S(3)_1$	110.5(3)°	
— $S(3)_5$	61.7(2)		— $S(2)_{10}$	111.3(2)	
— $S(2)_6$	118.5(2)		— $S(1)_1$	108.2(2)	
$S(3)_3$ — Tl(1) — $S(2)_4$	95.4(2)		$S(3)_1$ — As — $S(2)_{10}$	111.3(2)	
— $S(3)_5$	123.6(2)		— $S(1)_1$	108.2(3)	
— $S(2)_6$	63.6(2)				
			$S(2)_{10}$ — As — $S(1)_1$	107.2(4)	
$S(2)_4$ — Tl(1) — $S(3)_5$	135.6(3)		mean:	109.5°	
— $S(2)_6$	110.5(2)				
$S(3)_5$ — Tl(1) — $S(2)_6$	75.1(2)				

in Figure 2a. The coordination polyhedron is a deformed octahedron with one vertex split. A similar coordination polyhedron of the Tl atom was also found in simonite[11]. The Tl(2) has five nearest S atoms at distances from 0.307 to 0.340 nm, mean 0.318 nm, as shown in Figure 2b. The coordination polyhedron is a distorted trigonal bipyramid. Remarkably, the Tl(2) atom shows an extremely anisotropic temperature ellipsoid with a high motion perpendicular to the mirror plane. The Tl coordination polyhedra form a three-dimensional framework.

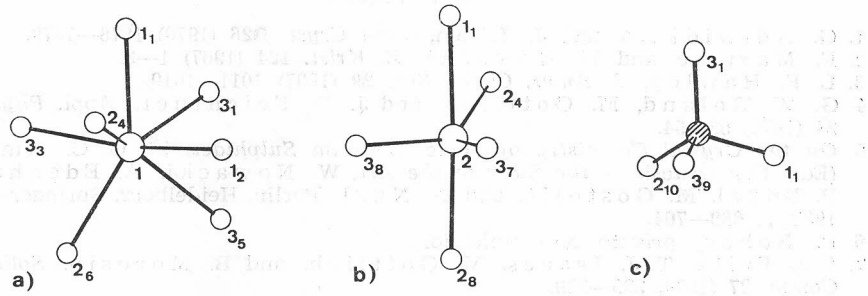

Figure 2. The coordination of the metal atoms by sulphur atoms in Tl_3AsS_4. a) the coordination of Tl(1), b) the coordination of Tl(2), c) the coordination of As.

The As atom is coordinated by four nearest S atoms at distances from 0.215 to 0.218 nm, mean 0.216 nm, as shown in Figure 2c. The coordination polyhedron is a tetrahedron. A similar coordination of the As atom was also

found in enargite[1] with As—S distances ranging from 0.216 to 0.219 nm, mean 0.218 nm, and luzonite[2] with an As—S distance of 0.226 nm which is considerably longer than in Tl_3AsS_4 and enargite due to the high Sb content in the investigated luzonite crystal. The AsS_4 tetrahedra are isolated. The S atoms are each coordinated by one As atom and four to six Tl atoms. In Figure 3. a projection of the structure of Tl_3AsS_4 along the *b*-axis is shown. According to the classification of sulfosalts proposed by Nowacki[12,13] synthetic Tl_3AsS_4 with S : As = 4 belongs to the group $I \cdot b_2$.

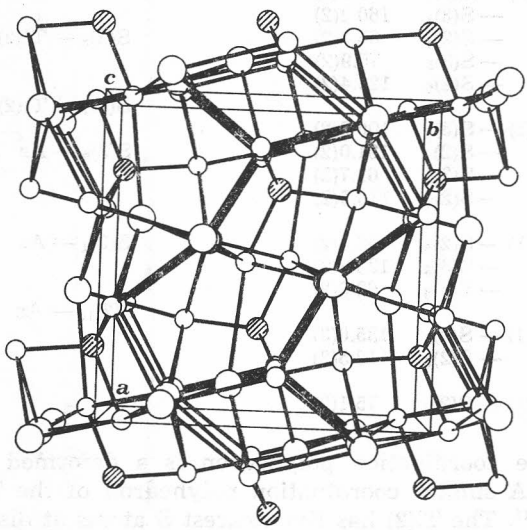

Figure 3. Central projection of the structure of Tl_3AsS_4 viewed along the b-axis.

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SAŽETAK

Utočnjavanje kristalne strukture sintetskog Tl_3AsS_4

P. Engel and W. Nowacki

Utočnjena je kristalna struktura sintetske sulfosoli Tl_3AsS_4. Kristali su rompski, prostorna grupa *Pnma*. Jedinična ćelija dimenzija $a = 0{,}8893(3)$, $b = 1{,}0868(5)$ i $c = 0{,}9088(3)$ nm sadržava četiri formulske jedinice. Konačna R vrijednost jest 0,04 za 759 opaženih refleksa.

Struktura je izgrađena od dva tipa talijevih poliedara koji čine trodimenzijsku mrežu. Tl(1) je okružen sa sedam atoma sumpora sa srednjom duljinom veze Tl — S od 0,329 nm, a Tl(2) s pet atoma sumpora i srednjom duljinom veze Tl — S od 0,318 nm. Tetraedri AsS_4 jesu izolirani, a srednja duljina veze As — S u njima iznosi 0,216 nm.