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The thallium sulfarsenites Tl_3AsS_3 and $TlAsS_2$ [thallium(I)-thioarsenates(III)]: structural characterization and syntheses

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Abstract

Crystals of Tl_3AsS_3 and $TlAsS_2$ (mineral lorandite) were synthesized from approximately equimolar mixtures of $TlNO_3$ and arsenic with excess of sulfur in aqueous ammonia solution under hydrothermal conditions. The structure of Tl_3AsS_3 [$a = 5.695(2)$ Å, $b = 12.205(3)$ Å, $c = 21.634(8)$ Å; $Z = 8$; $D_{2h}^{15}-Pbca$] represents a new type of neso-sulfarsenite, the structure of $TlAsS_2$ [$a = 12.32(6)$ Å, $b = 11.33(5)$ Å, $c = 6.12(2)$ Å; $\beta = 104.4(7)^\circ$; $Z = 8$; $C_{2h}^5-P2_1/a$] an ino-sulfarsenite. In both compounds the Tl–S distances are > 2.9 Å and within the range from 2.9 Å to 3.5 Å, the Tl atoms are one-sided, four, five or six coordinated to S atoms. An exception is the atom Tl(3) in Tl_3AsS_3 , which shows up to 3.5 Å a clear coordination (Tl–S from 2.90 Å to 3.01 Å, S–Tl–S from 71.6° to 79.2°). The As atoms are three coordinated to S atoms with As–S from 2.16 Å to 2.34 Å and S–As–S angles from 94° to 102° .

Keywords: Hydrothermal synthesis; Mineral lorandite; Neso-sulfarsenite; Ino-sulfarsenite

1. Introduction

Syntheses and crystal chemical characterizations of 'sulfosalts' [1], especially sulfarsenates with trivalent and/or pentavalent arsenic [thioarsenates(III) and (V)] represent one of the main topics of scientific work at the present institute. Synthesis instructions for these compounds under hydrothermal conditions in alkaline solutions were reported in [2,3] and, for example, worked out for alkaline-silver(I)-thioarsenates(III, V) in [4–6]. A compilation of structures with AsS_4 groups (pentavalent arsenic) in relation to bond lengths, bond angles and distortion parameters is given in [4]. Dispositions to a compilation of structures with AsS_3 groups (trivalent arsenic) were made in the description of the structure of $NH_4Ag_2(AsS_2)_3$ [7].

The first structure determination of $TlAsS_2$ (lorandite) was described in [8], and a refinement of the crystal structure in [9]. In this structure refinement a reliability index of 0.09 was obtained and no anisotropic displacement factors for the S atoms were calculated.

An excellent compilation of data (116 references) for the crystal chemistry, mineralogy and geochemistry of the element thallium by Zemmann [10] should also be mentioned in connection with the structure determinations described in this article.

2. Experiments

Single crystals of Tl_3AsS_3 and $TlAsS_2$ were synthesized from approximately equimolar mixtures of $TlNO_3$ (Merck, Nr. 8144), elementary arsenic (Johnson Matthey, Alfa Products), and a pronounced excess of sulfur (sulfur sublimatum, DAB 6, 'apoka', Austria) in concentrated ammonia water. The reaction time in 'Teflon'-lined steel autoclaves filled to $\sim 80\%$ capacity (saturation vapour pressure) was one week, the temperature $\sim 250^\circ C$.

Preliminary investigations of the synthesized crystals were made with a Weissenberg-type single-crystal X-ray camera applied with a Cu tube. Details of the experimental work on structure determination are summarized in Table 1. The atomic coordinates for the different Tl atom positions in Tl_3AsS_3 were found by direct method strategy, those of the other atoms by subsequent Fourier and difference Fourier summations. For $TlAsS_2$ the starting parameters for refinement were taken from [9]. During the final stage of refinement, anisotropic displacement factors were allowed to vary. The structure parameters are given in Table 2, and some relevant interatomic distances are compiled in Table 3. In both structure calculations complex neutral scattering functions for the different atoms [11] were

Table 1
Summary of crystal data, X-ray measurements and structure refinements

	Tl ₃ AsS ₃	TlAsS ₂
<i>a</i> (Å)	5.695(2)	12.32(6)
<i>b</i> (Å)	12.205(3)	11.33(5)
<i>c</i> (Å)	21.634(8)	6.12(2)
β (°)	–	104.4(7)
<i>Z</i>	8	8
Space group	<i>Pbca</i> (No. 61)	<i>P2₁/a</i> (No. 14)
Measured reflections	4185	4434
Internal $R(F_o^2)$	0.021	0.050
Unique data set	1837	2039
Data with $F_o > 4\sigma F_o$	721	925
Number of variables	64	73
<i>R</i> (based on $F_o > 4$)	0.050	0.049
$R_w; w = [\sigma(F_o)]^{-2}$	0.042	0.045

Data collection: $2\theta/\omega$ scans; 50 steps/reflection, increased for α_1 – α_2 splitting; 0.03° and 0.5–2.0 s/step; standard reflections each 120 min; 2θ max = 60°.

used. The Lorentz and polarization effects were corrected in the usual ways [12]. ($|F_o| - |F_c|$) lists were deposited at the Institute for Mineralogy and Crystallography, University of Vienna, Austria.

3. Results and discussion

The compound Tl₃AsS₃ crystallizes in extremely thin black ledges, elongated parallel to [100] and one pronounced crystallographic form, {001}. TlAsS₂ forms deep

red prismatic crystals elongated parallel to [001] and with the crystallographic forms {100}, {110} and {201}.

The atomic arrangement in both compounds shows common features. The Tl atoms as well as the As atoms are one-sided coordinated to S atoms. Such coordination polyhedra are typical for the crystal chemical behaviour of elements with lone-pair electrons and the stereometric activity of these electrons. Examples for the coordination chemistry of such elements in oxidation states with lone-pair electrons in crystal structures are compiled in an article by Alcock [13]. Nevertheless, rules concerning the coordination of tetravalent Te (an oxidation state with lone-pair electrons) were worked out in an article by Zemmann [14] some years earlier.

The shortest Tl–Tl distances, 3.54 Å in TlAsS₂ and 3.61 Å in Tl₃AsS₃ are comparable with Tl–Tl distances in elementary Tl: 3.40 Å and 3.45 Å respectively [15]. The Tl–Tl distances > 3.5 Å in the two compounds are therefore an indication of only weak interactions between these atoms. Pronounced covalent interactions between Tl atoms are likely: for example, in the Tl sulfosalt christite, TlHgAsS₃, in which Tl–Tl distances of 3.39 Å have been determined [16]. Tl–As distances < 3.5 Å are very common in the atomic arrangement of Tl sulfarsenites, and an extreme example for such covalent Tl–As interactions was determined in ernigliite, Tl₂SnAs₂S₆, with 3.26 Å [17]. The shortest distance in Tl₃AsS₃ is 3.49 Å, a distance definitely greater than the sum of the atomic radii of Tl and As with ~ 3.0 Å.

Table 2
Structural parameters with estimated standard deviations in parentheses. U_{ij} are given in pm². The anisotropic displacement factors are defined as $\exp[-2\pi^2 \sum_i \sum_j U_{ij} h_i a_i^* a_j^*]$

Tl ₃ AsS ₃									
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tl(1)	0.5880(4)	0.2237(1)	0.6844(1)	436(14)	327(10)	316(12)	–13(4)	–26(12)	–7(9)
Tl(2)	0.0872(4)	0.6710(1)	0.4745(1)	408(13)	286(9)	365(11)	–2(4)	23(11)	–6(10)
Tl(3)	0.0425(5)	0.4305(1)	0.6917(1)	493(22)	390(10)	436(13)	39(4)	70(13)	–39(10)
As	0.4570(10)	0.9475(3)	0.0846(2)	252(43)	236(23)	219(24)	–7(6)	–43(23)	–7(22)
S(1)	0.3686(26)	0.1268(9)	0.0901(6)	372(88)	192(56)	438(90)	6(22)	–20(65)	39(49)
S(2)	0.1200(25)	0.3929(10)	0.1822(7)	328(82)	474(75)	418(86)	54(25)	–80(75)	–88(57)
S(3)	0.8478(22)	0.9427(11)	0.0842(6)	197(68)	381(72)	321(76)	11(23)	21(53)	28(55)

TlAsS ₂									
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tl(1)	0.0522(1)	0.3123(1)	0.1620(2)	208(7)	339(6)	326(6)	–10(2)	37(2)	–3(2)
Tl(2)	0.1012(1)	0.0557(1)	0.7356(2)	189(6)	336(6)	332(6)	–9(2)	35(2)	–15(2)
As(1)	0.1952(2)	0.8340(2)	0.2269(5)	162(16)	219(13)	270(15)	–2(4)	15(5)	–10(4)
As(2)	0.1366(2)	0.5863(2)	0.5343(5)	137(14)	204(14)	308(16)	2(4)	37(5)	–1(4)
S(1)	0.1251(6)	0.3134(6)	0.7172(12)	168(39)	329(34)	358(41)	36(12)	55(13)	23(12)
S(2)	0.1496(6)	0.5559(6)	0.1851(12)	224(40)	257(32)	306(38)	–26(12)	17(13)	16(12)
S(3)	0.1673(6)	0.7877(5)	0.5759(12)	157(38)	207(33)	390(43)	4(10)	49(13)	–4(10)
S(4)	0.1820(6)	0.0380(5)	0.2742(12)	248(42)	237(35)	285(38)	7(10)	28(13)	13(11)

Table 3

Selected interatomic distances (Å) and angles (°). Tl polyhedra <3.5 Å, As polyhedra <3.0 Å (e.s.d.'s in parentheses)

Tl₃AsS₃

Tl(1)–S(3) = 2.99(1)	Tl(2)–S(1) = 3.00(1)
–S(1) = 3.01(1)	–S(3) = 3.07(1)
–S(2) = 3.02(1)	–S(3') = 3.08(1)
–S(2') = 3.22(1)	–S(1') = 3.44(2)
–S(2'') = 3.35(1)	–As = 3.492(5)

Tl(3)–S(2) = 2.90(1)
–S(1) = 2.96(1)
–S(3) = 3.01(1)

As	S(3)	S(1)	S(2)
S(3)	2.23(1)	3.54(1)	3.46(1)
S(1)	104.4(6)	2.25(1)	3.48(1)
S(2)	101.0(5)	101.2(5)	2.26(2)

TlAsS₂

Tl(1)–S(2) = 2.999(6)	Tl(2)–S(1) = 2.940(7)
–S(1) = 3.071(7)	–S(2) = 2.987(6)
–S(2') = 3.209(7)	–S(4) = 3.204(7)
–S(1') = 3.292(7)	–S(4') = 3.225(7)
–S(3) = 3.440(6)	–S(3) = 3.353(6)
–S(4) = 3.484(6)	

As(1)	S(1)	S(3)	S(4)
S(1)	2.167(6)	3.48(1)	3.47(1)
S(3)	102.2(3)	2.306(8)	3.41(1)
S(4)	100.7(3)	94.6(3)	2.340(7)

As(2)	S(2)	S(4)	S(3)
S(2)	2.209(7)	3.45(1)	3.52(1)
S(4)	99.2(3)	2.316(7)	3.38(1)
S(3)	102.2(3)	93.8(2)	2.316(7)

The As atoms form together with the S atoms of the first coordination sphere typical trigonal AsS₃ pyramids. These pyramids are isolated and combined by S atoms to the Tl polyhedra, e.g. in Tl₃AsS₃, or connected to AsS₂ chains, and these chains are combined to the Tl polyhedra in TlAsS₂. The As–S distances within the chain period are markedly longer (As–S = 2.31 Å and 2.34 Å) than the As–S distance to the non-bridging S atom (As–S = 2.17 Å). Comparable relations were determined for the As–O distances between bridging and non-bridging distances in chain structures in two inoarsenates(III): Pb(AsO₂)Cl and Pb₂(AsO₂)₃Cl [18].

In Fig. 1 the structure of Tl₃AsS₃ is given in a projection onto the (100) plane. This figure shows clearly the one-sided coordination of the Tl atoms, by three or four S atom neighbours up to 3.3 Å. In Fig. 2 the structure of TlAsS₂ lorandite in a projection parallel to [001] is drawn. The AsS₂ chains and their interconnection by the one-sided coordinated Tl atoms are remarkable.

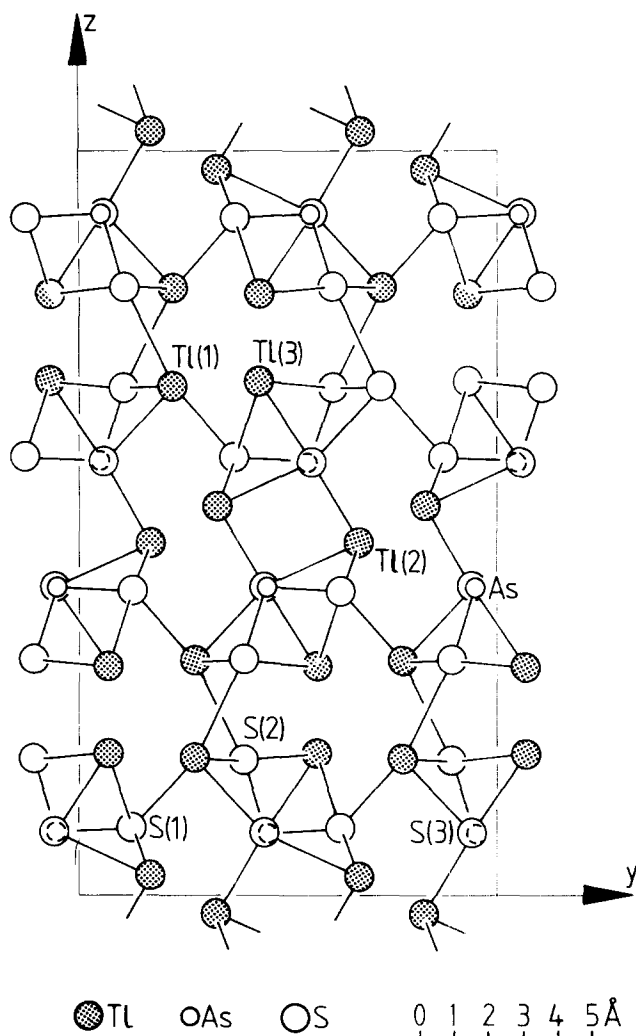


Fig. 1. Atomic arrangement in Tl₃AsS₃ given in a projection onto (100).

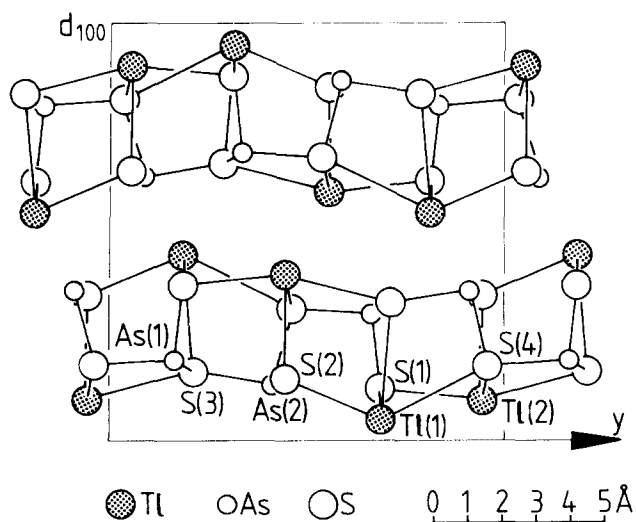


Fig. 2. The structure of TlAsS₂ (mineral lorandite) showing the AsS₂ chains and the interconnection by Tl atoms. The direction of the projection is [001].

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References

- [1] W. Nowacki, *Schweiz. Mineral. Petrogr. Mitt.*, **49** (1969) 109.
- [2] M.A. Peacock, *Univ. Toronto Studies, Geol. Ser.*, **51** (1947) 85.
- [3] R. Béland, *Econ. Geol.*, **43** (1948) 119.
- [4] F. Pertlik, *J. Solid State Chem.* (in press).
- [5] M. Auernhammer, H. Effenberger, E. Irran, F. Pertlik and J. Rosenstingl, *J. Solid State Chem.*, **106** (1993) 421.
- [6] J. Rosenstingl and F. Pertlik, *Ber. Deutsch. Min. Ges. (Beihefte z. Eur. J. Mineral.)*, **5** (1993) 96.
- [7] F. Pertlik, *Mh. Chemie* (in press).
- [8] A. Zemann and J. Zemann, *Acta Crystallogr.*, **12** (1959) 1002.
- [9] M.E. Fleet, *Z. Kristallogr.*, **138** (1973) 147.
- [10] J. Zemann, *Mitt. Österr. Mineral. Ges.*, **138** (1993) 75.
- [11] *International Tables for X-ray Crystallography*, Vol. IV, The Kynoch Press, Birmingham.
- [12] G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, 1976.
- [13] N.W. Alcock, *Adv. Inorg. Radiochem.*, **15** (1973) 1.
- [14] J. Zemann, *Mh. Chemie*, **102** (1971) 1209.
- [15] H. Lipson and A.R. Stokes, *Nature*, **148** (1941) 437.
- [16] K.L. Brown and F.W. Dickson, *Z. Kristallogr.*, **144** (1976) 367.
- [17] S. Graeser, H. Schwander, R. Wulf and A. Edenharter, *Schweiz. Mineral. Petrogr. Mitt.*, **72** (1992) 293.
- [18] F. Pertlik, *Z. Kristallogr.*, **184** (1988) 191.