# Bernardite, a new thallium arsenic sulphosalt from Allchar, Macedonia, with a determination of the crystal structure

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## Abstract

The new mineral bernardite has been identified on one specimen from Allchar, Macedonia, Yugoslavia, together with orpiment and realgar. It forms black crystals, the size of which may exceed 1 mm. The streak is deep red; on an arbitrarily oriented section $R(589\,\text{nm})$ ranges from 23.8 to 24.7% in air, from 10.2 to 11.6% in oil. Microprobe analyses together with an X-ray structure analysis suggest the ideal formula $TlAs_5S_8$, with a possible replacement of As by Sb up to 15 wt. %. Monoclinic; $a$ 15.647(4), $b$ 8.038(3), $c$ 10.750(3) Å, $\beta$ 91.27(3)°; space group $P2_1/c$; $Z = 4$; $R = 0.049$, $wR = 0.036$ for 2410 reflections. The atomic arrangement consists of a 3-dimensional $As_5S_8$ framework with eight-coordinated Tl in its holes. The mineral is named for Doc. Dr Jan H. Bernard, Prague, Czechoslovakia.

KEYWORDS: bernardite, new mineral, thallium sulpharsenite, Allchar, Macedonia, $TlAs_5S_8$.

## Introduction

THE As–Sb–Tl deposit of Allchar (other spellings Allshar and Alshar) in the south of Macedonia, Yugoslavia, is world-famous for its thallium minerals. It is the type locality of the well known species lorandite, $TlAsS_2$, and vrbaite, $Tl_4Hg_3As_8Sb_2S_{20}$ (formula according to Caye *et al.*, 1967, and Ohmasa and Nowacki, 1971). Within the last few decades the following new minerals were first described from this locality: raguinite, $TlFeS_2$ (Laurent *et al.*, 1969); picotpaulite, $TlFe_2S_3$ (Johan *et al.*, 1970); parapierrotite, $TlSb_5S_8$ (Johan *et al.*, 1975); rebulite, $Tl_5As_8Sb_5S_{22}$ (Balić-Žunić *et al.*, 1982); simonite, $TlHgAs_3S_6$ (Engel *et al.*, 1982); and an unnamed mineral with composition $Tl_3AsS_4$ (El Goresy and Pavićević, 1988; Pavićević and El Goresy, 1988).

This paper adds to this list the monoclinic mineral bernardite with the ideal formula $TlAs_5S_8$, and presents also its crystal structure. The species and the name were approved by the Commission on New Minerals and Mineral Names, IMA. For a preliminary note see Pašava *et al.* (1988).

## Occurrence and general description

Bernardite was found on only one of numerous specimens that were collected by a group of Czech geologists in 1975 and 1976 at the late-Tertiary hydrothermal metasomatic deposit of Allchar, Southern Macedonia, Yugoslavia. For literature on the deposit the reader is referred to Pavlović and Arsenijević (1956), Ivanov (1965, 1986), Janković (1960, 1982, 1988) and Pavićević (1988). The bernardite-bearing specimen evidently originated in the As–Tl-rich zone of the deposit which

is poor in Sb and which is characteristic for the central part of the southern zone of the ore district (Ivanov, 1965). Its position in the general mineral sequence is unclear: quartz, opal, bravoite, pyrite–arsenopyrite, gold–melnikovite, marcasite–stibnite–vrbaite, lorandite–realgar–orpiment–barite, sulphur, followed by oxidation products (cf. Ivanov, 1965). Bernardite might have formed with the other thallium minerals.

The mineral occurs with realgar and orpiment. It forms black, thick tabular crystals, usually ≤1 mm in size, but the largest crystal had dimensions of *ca.* 4 × 3 × 1.5 mm. The surface of the crystals is only in part well developed, and is commonly corroded.

The name was given in honour of Docent Dr Jan H. Bernard, a metallogenist, ore-deposit geologist, and mineralogist of the Geological Survey of Czechoslovakia, Prague, who first recognized the new mineral and drew our attention to it.

Holotype specimens have been deposited with the mineral collections of the Národni Museum in Prague and of the Naturhistorisches Museum in Vienna. The grains used for the reflectance measurements and for the X-ray work will be kept in the collection of the Institut fuer Mineralogie und Kristallographie der Universitaet Wien.

Table 1. Minimum $(R_1)$ and maximum $(R_2)$ reflectance values in percent, measured on an arbitrarily oriented section in air and in oil. Standard deviations: < 0.10.

| λ(nm) | $N_{oil}$ | $R_1$ | $R_2$ | $^{im}R_1$ | $^{im}R_2$ |
|---|---|---|---|---|---|
| 400 | 1.5363 | 29.6 | 32.3 | 15.3 | 17.9 |
| 420 | 1.5320 | 28.9 | 31.8 | 14.6 | 17.6 |
| 440 | 1.5290 | 28.1 | 31.3 | 14.0 | 17.1 |
| 460 | 1.5262 | 27.4 | 30.6 | 13.3 | 16.5 |
| 480 | 1.5240 | 26.8 | 29.9 | 12.8 | 15.8 |
| 500 | 1.5224 | 26.0 | 28.9 | 12.2 | 14.9 |
| 520 | 1.5210 | 25.4 | 27.8 | 11.7 | 14.1 |
| 540 | 1.5196 | 25.0 | 26.7 | 11.3 | 13.3 |
| 560 | 1.5182 | 24.5 | 25.8 | 10.8 | 12.6 |
| 580 | 1.5168 | 24.0 | 25.1 | 10.4 | 11.9 |
| 600 | 1.5153 | 23.6 | 24.4 | 10.1 | 11.3 |
| 620 | 1.5139 | 23.3 | 23.9 | 9.8 | 10.8 |
| 640 | 1.5125 | 23.1 | 23.4 | 9.5 | 10.4 |
| 660 | 1.5112 | 22.9 | 23.0 | 9.3 | 10.0 |
| 680 | 1.5099 | 22.8 | 22.8 | 9.2 | 9.8 |
| 700 | 1.5085 | 22.8 | 22.5 | 9.1 | 9.7 |
| 470 | 1.5245 | 27.1 | 30.3 | 13.1 | 16.1 |
| 546 | 1.5192 | 24.9 | 26.5 | 11.1 | 13.2 |
| 589 | 1.5160 | 23.8 | 24.7 | 10.2 | 11.6 |
| 650 | 1.5118 | 23.0 | 23.2 | 9.4 | 10.2 |

### Physical and chemical characteristics

Our specimen of bernardite was not suitable for investigation on the optical goniometer because the crystal faces were dull, and in part corroded and/or striated. However, the indexing of the forms of a relatively large, loose crystal (dimensions ~1 mm × 3 mm × 3 mm) could be effected on a Stoe four-circle X-ray diffractometer. To this end, the cell parameters and the orientation of the grain relative to the internal coordinate system were determined by routine methods. After that, each face was brought into a position parallel to the optical axis of the goniometer by the driving device. This allowed a preliminary determination of the Miller indices. For confirmation, the crystal was automatically turned into the position with the lattice plane corresponding to the indices exactly parallel to the optical axis of the device, and the coincidence was checked by observation with the microscope. Although this procedure is definitely less accurate than optical goniometry, the indices of the forms could be determined unequivocally. Respective to the cell parameters (see below, Table 3, corresponding to $a:1:c = 1.947:1:1.337$, $\beta = 91.27°$) the prominent forms are {100}, {012} and {210}; subordinate forms are {201}, {$\overline{2}$01} and {010}.

No cleavage was observed; the fracture is subconchoidal to uneven. The Mohs' hardness is approximately 2. The density of the loose crystal mentioned above was measured using a Berman microbalance. The mean value of several determinations was $D_m = 4.5(1)\,g\,cm^{-3}$. This is ~10% higher than the theoretical density calculated from the formula $TlAs_5S_8$, i.e. $D_x = 4.11\,g\,cm^{-3}$ (Cf. Table 3), and also higher than the density calculated from the bernardite with highest Sb content found by us (cf. Table 2), corresponding approximately to the formula $TlAs_4SbS_8$, which led to $D_x = 4.34\,g\,cm^{-3}$. A possible explanation for our experimental result would be that the crystal used contained inclusions of another mineral with higher density, e.g. lorandite.

Only one grain could be used for reflectance work. Minimum and maximum values were measured with polarized light in air and in oil on a carefully polished, but arbitrarily oriented, section from 400 to 700 nm in steps of 20 nm. The results, together with those for the four recommended wavelengths of the Commission on ore Mineralogy (COM) of the IMA, are given in Table 1. The reflectance standards used were (W, Ti)C and SiC, and immersion measurements were made with a liquid conforming to DIN 58884.

The chemical composition was determined by

| | 1 | 2 | 3 | 4 | 5 | 6 | $TlAs_5S_8$ |
|---|---|---|---|---|---|---|---|
| Tl | 23.3 | 23.4 | 22.0 | 22.7 | 22.5 | 22.8 | 24.46 |
| As | 43.7 | 43.4 | 35.7 | 35.2 | 35.7 | 36.4 | 44.84 |
| Sb | 0.1 | 0.4 | 9.3 | 10.4 | 10.2 | 10.0 | - |
| S | 31.5 | 32.6 | 31.1 | 29.8 | 29.9 | 31.8 | 30.70 |
| | 98.6 | 99.8 | 98.1 | 98.1 | 98.3 | 101.0 | 100.00 |

Operating conditions: 25 kV excitation voltage, 10 nA specimen current. Lines used: Tl-Lα, As-Kα and S-Kα. Standards: natural lorandite for Tl, As, and S; natural stibnite for Sb.

electron-microprobe analysis, using natural lorandite and stibnite as standards. Due to the lack of material, only six point analyses on one grain were made; the results are given in Table 2. The formulae derived from the analytical results vary approximately between $Tl(As_{1-x}Sb_x)_5S_8$ and $Tl(As_{1-x}Sb_x)_5S_9$, with $0.0 \leqslant x \leqslant 0.15$. As the structure determination clearly corresponds to the first formula, we consider this to be the correct one. According to our analyses, the ratio Sb/As is not constant throughout the investigated grain; the experimental values of $x$ cluster around 0.0 and 0.14.

### X-ray crystallography and structure determination

Preliminary photographic single-crystal X-ray work showed that bernardite is monoclinic with space group $P2_1/c$. The crystallographic constants as obtained by a least-squares refinement of the Bragg angles of 56 reflections ($18° < \theta < 23°$), carefully measured on a four-circle X-ray diffractometer, are presented in Table 3.

The structure was determined from nearly 4000 single crystal reflections by direct methods and least-squares refinement; details are given in Table 3. Complex neutral-atomic scattering factors (Cromer and Waber, 1974) were used in all calculations. Table 4 presents the atomic coordinates and the anisotropic displacement parameters (Brock, 1984; Fischer and Tillmanns, 1988); the latter do not show unusual values. The average value of the ratio (longest axis)/(shortest axis) of the r.m.s. displacement ellipsoids is 1.3(2), the largest value results for As(1) with 1.8. In a final difference Fourier synthesis, the largest residual peaks had a height of approximately one tenth of that of the S atoms. They occur mainly near to As(1), but the height never exceeded 10% of a sulphur atom.

Lists of observed and calculated structure amplitudes have been deposited at the Institut fuer Mineralogie und Kristallographie der Universitaet Wien, and with the Mineralogy Library, British Museum (Natural History).

### Discussion of the crystal structure

Important interatomic distances and bond angles are compiled in Table 5. Fig. 1 presents the projection of the structure parallel to [010], and Fig. 2 gives a detail in projection parallel to [001]. The atomic arrangement is characterized by an $[As_5S_8]$ framework with the Tl atom housed in a large hole.

The atom As(2) to As(5) form pyramidal $AsS_3$ groups with each three S atoms (As–S = 2.25–2.35 Å, S–As–S = 91.5–99.8°). A fourth S neighbour follows with As–S $\geqslant$ 3.09 Å. For As(1) the situation is somewhat less clear: the bond lengths in the $AsS_3$ pyramid vary more strongly than for the other four As atoms, namely from 2.22 to 2.51 Å, and a fourth S neighbour has only As–S = 2.99 Å. Thereby, a tendency to a one-sided four-coordination is indicated. A coordination to four S atoms would be more usual for Sb(III). As the chemical analyses of bernardite show Sb contents up to 10 wt.% (Table 2), it seems important to note that for the As(1) atom the r.m.s. anisotropic displacements as obtained from the least-squares refinement—neglecting any possible replacement of As by Sb—are not conspicuously small and, therefore, do not indicate a concentration of Sb on this position. A similar large spread of bond lengths in an $AsS_3$ pyramid as observed by us for As(1) is only rarely reported in the literature (e.g. Edenharter, 1976), and apparently only for structures in which not all minor details could be determined with high precision.

The atoms S(2) and S(4) to S(8) are clearly bonded to two As atoms. When considering As(1) as three-coordinated (As–S = 2.22–2.51 Å) also S(3) is bonded to two As atoms, but S(1) only to one. If one considers for As(1) only the two neighbours with As–S = 2.22 and 2.35 Å, both S(1) and S(3) are bonded to only one As atom. And if one takes the extreme position to include also As(1)–S(1') = 2.99 Å into the system of chemical bonds—and thereby considering As(1) to be four-coordinated—both S(1) and S(3) are bonded to two As atoms.

The Tl atom is coordinated to eight S atoms with Tl–S = 3.05–3.54 Å, then follows one As atom with Tl–As = 3.66 Å and further S atoms with Tl–S $\geqslant$ 3.75 Å. The coordination is some-

Table 3. Crystal data and experimental conditions for bernardite.

| | |
|---|---|
| $a = 15.647(4)$ Å | Stoe four-circle diffractometer |
| $b = 8.038(3)$ Å | program system STRUCSY on an ECLIPSE S 140 |
| $c = 10.750(3)$ Å | crystal size: $0.04 \times 0.08 \times 0.08$ mm$^3$ |
| $\beta = 91.27(3)°$ | graphite-monochromatized MoK$\alpha$ radiation |
| $V = 1351.7$ Å$^3$ | $2\theta/\omega$-scan mode with a step width of $0.035°$ |
| room temperature | steps/reflection: $50 + (\alpha_1, \alpha_2)$ splitting |
| space group P2$_1$/c-C$^5_{2h}$ | time/step: 0.5 to 1.5 sec |
| $Z = 4$ {TlAs$_5$S$_8$} | range of data: $2° < 2\theta < 60°$ |
| $F(000) = 1496.0$ | range of $h$ $k$ $l$: $h$, $\pm k$, $\pm l$ |
| $M_r = 835.49$ | 3 standard reflections |
| $D_x = 4.105$ g.cm$^{-3}$ | measuring interval: 2 h |
| $\mu$(MoK$\alpha$) $\sim 245$ cm$^{-1}$ | intensity variation: 2 % |
| $\lambda$(MoK$\alpha$) = 0.71073 Å | measured reflections: 7984 |
| no of variables: 128 | unique reflections: 3946 |
| R/wR = 0.049/0.036 | $R_{int}$ ($\sum(I-|I|)/\sum I$) : 0.063 |
| $w = (\sigma(Fo))^{-2}$ | reflections with Fo > 3$\sigma$(Fo): 2410 |
| max $\Delta/\sigma < 10^{-3}$ | secondary extinction g: $7(1) \times 10^{-7}$ * |

* Zachariasen (1967)

Table 4. Atomic parameters for bernardite with e.s.d.'s in parentheses. ATF = exp $(-2 \pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} h_i h_j a^*_i a^*_j)$

| Atom | x | y | z | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Tl | 0.27798(4) | 0.15448(7) | 0.82965(5) | 0.0433(3) | 0.0308(3) | 0.0353(3) | -0.0001(3) | -0.0012(2) | -0.0038(2) |
| As(1) | 0.5531(1) | 0.6694(2) | 0.9003(1) | 0.0329(7) | 0.0336(7) | 0.0279(6) | 0.0165(6) | 0.0050(5) | 0.0049(6) |
| As(2) | 0.0654(1) | 0.4545(1) | 0.8825(1) | 0.0187(6) | 0.0215(6) | 0.0245(5) | -0.0004(5) | 0.0016(5) | -0.0009(5) |
| As(3) | 0.2626(1) | 0.6342(1) | 0.9401(1) | 0.0238(6) | 0.0176(6) | 0.0236(5) | -0.0026(5) | -0.0015(5) | 0.0006(4) |
| As(4) | 0.5783(1) | 0.1216(1) | 0.8859(1) | 0.0227(6) | 0.0191(6) | 0.0231(5) | -0.0025(5) | -0.0001(5) | 0.0006(5) |
| As(5) | 0.8894(1) | 0.2148(1) | 0.8626(1) | 0.0255(6) | 0.0234(6) | 0.0225(6) | -0.0010(5) | 0.0007(5) | -0.0005(5) |
| S(1) | 0.4276(2) | 0.1105(4) | 0.3997(3) | 0.0338(18) | 0.0249(15) | 0.0255(14) | -0.0017(13) | -0.0004(13) | -0.0053(12) |
| S(2) | 0.5628(2) | 0.1451(3) | 0.0955(3) | 0.0225(14) | 0.0205(13) | 0.0253(13) | 0.0015(13) | 0.0009(11) | -0.0014(12) |
| S(3) | 0.3364(2) | 0.1051(4) | 0.0998(3) | 0.0263(16) | 0.0193(13) | 0.0310(15) | 0.0013(12) | 0.0016(13) | -0.0010(12) |
| S(4) | 0.0328(2) | 0.1809(4) | 0.8886(3) | 0.0208(15) | 0.0215(14) | 0.0455(18) | -0.0018(12) | 0.0026(14) | 0.0005(13) |
| S(5) | 0.1816(2) | 0.4148(3) | 0.0118(3) | 0.0323(17) | 0.0199(13) | 0.0257(14) | -0.0058(13) | -0.0050(13) | 0.0032(12) |
| S(6) | 0.1320(2) | 0.4494(4) | 0.6979(3) | 0.0453(20) | 0.0305(16) | 0.0279(16) | 0.0152(16) | 0.0122(15) | 0.0066(13) |
| S(7) | 0.8475(2) | 0.3294(4) | 0.5614(2) | 0.0309(16) | 0.0246(14) | 0.0215(13) | -0.0030(13) | 0.0010(12) | -0.0015(12) |
| S(8) | 0.6860(2) | 0.1778(4) | 0.3639(2) | 0.0272(16) | 0.0239(15) | 0.0214(13) | 0.0066(13) | -0.0017(12) | -0.0028(12) |

what one-sided, and this tendency becomes especially clear when considering only the four nearest S neighbours with Tl–S = 3.05–3.28 Å (Fig. 3). The smallest Tl–S bond length, i.e. Tl–S(3) = 3.05 Å, is somewhat short in comparison with the majority of such contacts reported in the literature. But it is not an isolated result: comparable values were found, e.g. in Tl$_3$VS$_4$ (Vlasse and Fournes, 1978), rebulite, Tl$_5$As$_8$Sb$_5$S$_{22}$ (Balić-Žunić *et al.*, 1982), and lorandite, TlAsS$_2$ (Fleet, 1973); in lorandite, the shortest Tl–S contact measures only 2.96(3) Å. The TlS$_8$ polyhedra have

no edges or faces in common, but from a purely geometrical point of view they are connected via S(3) atoms to chains parallel [001]. Three of the S–S edges belong also to AsS$_3$ pyramids. The stereochemical behaviour of Tl, evidently in the monovalent oxidation state, corresponds to general experience, e.g. Nowacki *et al.* (1982).

The general features of the atomic arrangement in bernardite agree with what one might expect on the basis of known arsenic sulphosalt structures, and in a closer comparison of thallium arsenic sulphosalt structures (Nowacki, 1969;
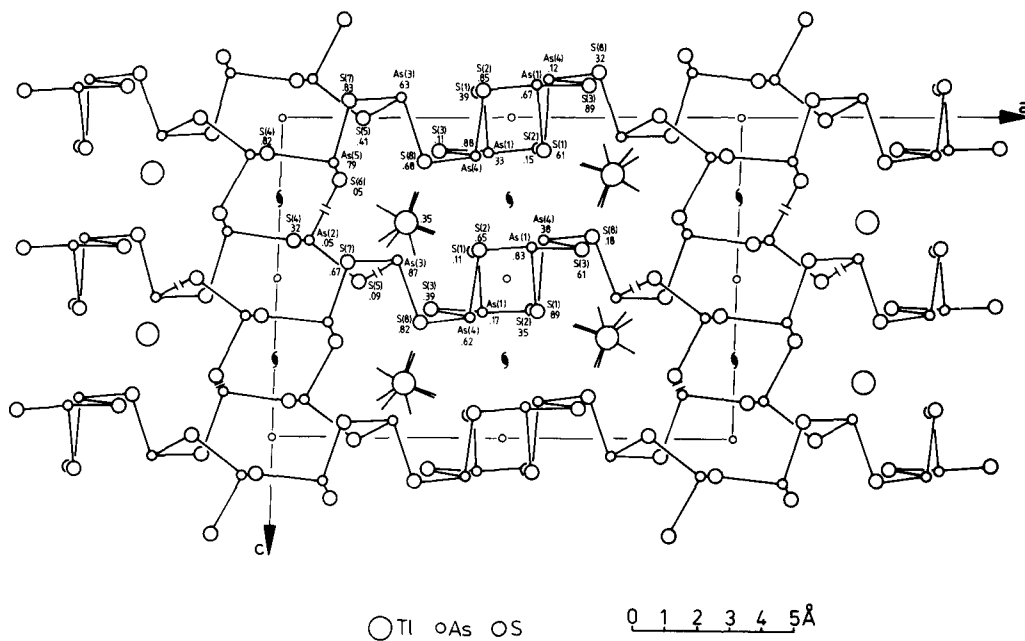
$\bigcirc$ Tl  o As  o S

FIG. 1. Projection of the crystal structure of bernardite parallel to [010].

Takéuchi and Sadanaga, 1969; Edenharter, 1976; Nowacki *et al.*, 1982; see also Balić-Žunić and Šćavničar, 1985, 1988). In the classification of Nowacki (1969) bernardite belongs to class V.*a*$_3$ (1 < S/As < 2; AsS$_3$ pyramids condensed to infinite nets).

Bernardite, TlAs$_5$S$_8$, is neither isotypic nor homeotypic with pierrotite, TlAs$_2$Sb$_3$S$_8$ (Engel *et al.*, 1983), or parapierrotite TlSb$_5$S$_8$ (Engel, 1980), in spite of the similarity in chemical formulae. This is evidently a consequence of the different sizes of As(III) and Sb(III), as well as of the stronger tendency of As(III) to form clear-cut AsS$_3$ pyramids as compared with the stereochemical behaviour of Sb(III).

The relationship between the structures of bernardite and hutchinsonite, TlPbAs$_5$S$_9$ (Takéuchi *et al.*, 1965) is of considerable interest, although their chemical formulae differ significantly. To derive the structure of hutchinsonite from that of bernardite, one has to proceed as follows: (1) cut the structure of bernardite along (*a*/2,*y*,*z*) into slices of thickness $d_{100}$ (~ *a*), thereby breaking the As(1)–S(2) bonds; (2) pull these slices slightly apart and arrange them mutually not as in bernardite, but rather by glide planes parallel (100) with translation direction *b*—thereby the lattice constant *a* will be doubled, and the space group becomes *Pbca*; (3) complete the coordination of

As(1) to an AsS$_3$ pyramid by a ninth S atom in the formula, with *y* coordinate near to 0.25 of the new cell; and (4) add the Pb atom appropriately, again with *y* ~ 0.25 of the new cell. The relationship is clearly seen by comparing our Fig. 1 with Fig. 10 of the paper by Takéuchi *et al.* (1965).

## Concluding remarks

As a consequence of the extremely small amount of bernardite available for our investigation and, as it was decided not to damage the two 'large' crystals, it has not been possible to devote satisfactory attention to certain aspects of its mineralogy, such as optical properties and variation in Sb content. In addition, a structure determination on a grain of exactly known chemical composition has not proved possible. These supplementary investigations have to wait until more bernardite material becomes available. Another consequence of the scarcity of the material is that we cannot give empirical X-ray powder data. Instead, Table 6 presents the theoretical powder data as derived from our single-crystal structure determination.

TlAs$_5$S$_8$ has, so far, not been synthesized in the laboratory (Klaes, 1984, 1987; Sobott, 1984;

Table 5. Tl–S distances (Å) in the coordination of the Tl atoms and As–S distances (Å), bond angles (°) and S–S distances (Å) in the coordination of the As atoms.

| | | | | | |
|---|---|---|---|---|---|
| Tl–S(1) = 3.088(3) | | | | Tl–S(5) = 3.259(2) | |
| Tl–S(2) = 3.544(2) | | | | Tl–S(6) = 3.563(3) | |
| Tl–S(3) = 3.051(2) | | | | Tl–S(7) = 3.487(3) | |
| Tl–S(3') = 3.282(2) | | | | Tl–S(8) = 3.439(2) | |
| | | | | | |
| As(1)–S(1) = 2.216(3) | [S(1)–As(1)–S(1') | = | 85.2(2) | 3.567(6)] | |
| As(1)–S(1') = 2.986(3) | S(1)–As(1)–S(2) | = | 101.9(1) | 3.546(4) | |
| As(1)–S(2) = 2.349(3) | S(1)–As(1)–S(3) | = | 94.4(1) | 3.468(4) | * |
| As(1)–S(3) = 2.505(3) | [S(1')–As(1)–S(2) | = | 88.3(1) | 3.744(4)] | |
| | [S(1')–As(1)–S(3) | = | 177.5(2.0) | 5.490(4)] | |
| | S(2)–As(1)–S(3) | = | 94.3(1) | 3.559(4) | |
| | | | | | |
| As(2)–S(4) = 2.259(3) | S(4)–As(2)–S(5) | = | 91.4(1) | 3.251(4) | |
| As(2)–S(5) = 2.286(3) | S(4)–As(2)–S(6) | = | 96.7(1) | 3.377(4) | |
| As(2)–S(6) = 2.262(3) | S(5)–As(2)–S(6) | = | 98.9(1) | 3.456(4) | * |
| | | | | | |
| As(3)–S(5) = 2.314(3) | S(5)–As(3)–S(7) | = | 96.0(1) | 3.452(4) | |
| As(3)–S(7) = 2.331(3) | S(5)–As(3)–S(8) | = | 89.7(1) | 3.229(4) | |
| As(3)–S(8) = 2.267(2) | S(7)–As(3)–S(8) | = | 98.6(1) | 3.485(4) | |
| | | | | | |
| As(4)–S(2) = 2.279(2) | [S(2)–As(4)–S(2') | = | 84.4(1) | 3.654(6)] | |
| As(4)–S(2') = 3.088(3) | S(2)–As(4)–S(3) | = | 94.3(1) | 3.330(4) | * |
| As(4)–S(3) = 2.262(3) | S(2)–As(4)–S(8) | = | 97.8(1) | 3.486(4) | |
| As(4)–S(8) = 2.347(3) | [S(2')–As(4)–S(3) | = | 81.8(1) | 3.559(4)] | |
| | [S(2')–As(4)–S(8) | = | 177.9(2.4) | 5.434(4)] | |
| | S(3)–As(4)–S(8) | = | 97.9(1) | 3.476(4) | |
| | | | | | |
| As(5)–S(4) = 2.271(3) | S(4)–As(5)–S(6) | = | 93.6(1) | 3.297(5) | |
| As(5)–S(6) = 2.253(3) | S(4)–As(5)–S(7) | = | 99.8(1) | 3.478(4) | |
| As(5)–S(7) = 2.276(2) | S(6)–As(5)–S(7) | = | 94.6(1) | 3.428(4) | |

* Common S–S edges of the TlS$_8$ polyhedron and AsS$_3$ pyramids

Note: E.s.d.'s in parentheses. Limits: Tl–S < 3.66 Å (= shortest Tl–As contact), As–S < 3.10 Å. The limit for As–S is rather arbitrary as the next larger bond length is As–S = 3.20 Å. Values in the As configuration with As–S = 2.99 and 3.09 Å in square brackets.

Table 6. X-ray powder data of bernardite. Calculated from the crystal structure. Debye-Scherrer geometry; CuKα – radiation. Reflections with normalized $I_{calc}$ < 3 omitted; $d_{hkl}$ > 1.70 Å.

| $I_{calc}$ | $d_{calc}$(Å) | h k l | $I_{calc}$ | $d_{calc}$(Å) | h k l |
|---|---|---|---|---|---|
| 37 | 15.73 | 1 0 0 | 8 | 2.99 | 2 2 -2 |
| 27 | 7.86 | 2 0 0 | 8 | 2.76 | 3 2 -2 |
| 11 | 7.18 | 1 1 0 | 17 | 2.74 | 3 2 2 |
| 13 | 5.98 | 1 1 -1 | 59 | 2.68 | 0 0 4 / 0 2 3 |
| 19 | 5.63 | 2 1 0 | | | |
| 24 | 5.10 | 1 0 -2 | 11 | 2.65 | 1 3 0 / 1 0 -4 |
| 10 | 5.05 | 1 0 2 | 19 | 2.64 | 1 2 -3 |
| 6 | 5.01 | 2 1 -1 | 6 | 2.63 | 1 2 3 |
| 24 | 4.96 | 2 1 1 | 7 | 2.61 | 0 3 1 |
| 65 | 4.46 | 0 1 2 | 30 | 2.57 | 1 3 1 |
| 32 | 4.40 | 2 0 2 / 3 1 0 | 25 | 2.55 | 2 0 -4 / 2 3 0 |
| 74 | 4.28 | 1 1 2 | 27 | 2.54 | 0 1 4 |
| 61 | 4.09 | 3 1 -1 | 25 | 2.43 | 2 1 -4 |
| 23 | 4.05 | 3 1 1 | 7 | 2.41 | 2 1 4 |
| 9 | 4.03 | 0 2 0 | 22 | 2.40 | 3 0 -4 / 3 2 -3 |
| 10 | 3.86 | 2 1 2 | | | |
| 63 | 3.78 | 0 2 1 / 3 0 -2 | 30 | 2.37 | 3 2 3 |
| 55 | 3.72 | 3 0 2 | 5 | 2.34 | 3 3 -1 |
| 21 | 3.67 | 1 2 1 | 4 | 2.28 | 3 1 4 |
| 5 | 3.59 | 2 2 0 | 13 | 2.15 | 0 3 3 |
| 54 | 3.42 | 3 1 -2 | 8 | 2.07 | 0 1 5 / 2 3 3 |
| 19 | 3.41 | 2 2 -1 | 14 | 2.02 | 0 4 0 |
| 6 | 3.40 | 2 2 1 | 14 | 2.00 | 1 4 0 |
| 20 | 3.27 | 0 1 3 | 9 | 1.99 | 3 3 -3 |
| 8 | 3.21 | 1 1 -3 | 11 | 1.98 | 0 4 1 |
| 3 | 3.19 | 1 1 3 | 5 | 1.94 | 3 1 -5 |
| 65 | 3.07 | 3 2 -1 | 6 | 1.92 | 3 1 5 |
| 100 | 3.06 | 3 2 1 | 8 | 1.77 | 3 4 2 |
| 10 | 3.03 | 2 1 -3 | 7 | 1.74 | 2 0 6 |
| 27 | 3.00 | 2 1 3 | 10 | 1.73 | 1 1 6 |

Sobott *et al.*, 1987). Further work in the Sb- and Tl-poor part of the Tl–As–Sb–S system is urgently required to learn whether or not a low Sb content is essential for the stabilization of the bernardite structure.

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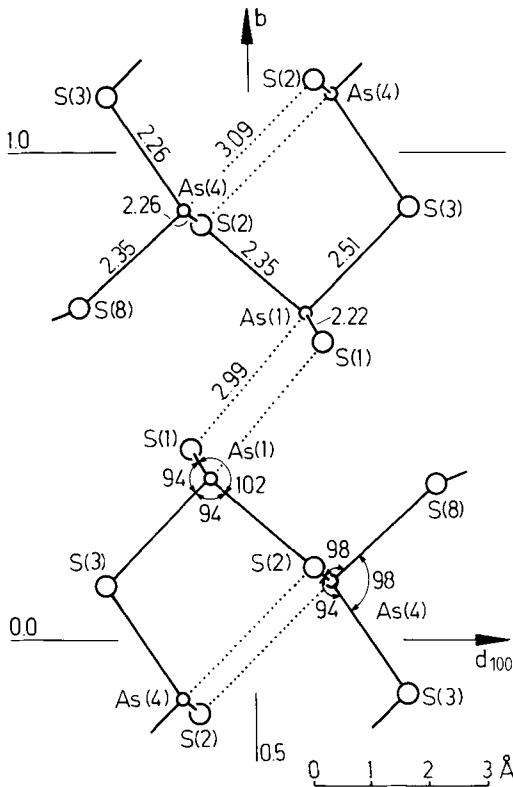Cromer, D. T. and Waber, J. T. (1974) In *International*

FIG. 2. Detail of the crystal structure of bernardite near ($\frac{1}{2}$, $y$, $\frac{1}{2}$) projected parallel to [001]. Forth-shortest As(1)–S and As(4)–S contacts dotted.



FIG. 3. $TlS_8$ polyhedron in projection parallel [100]. The numbers at the atoms give their height in Å relative to that of the Tl atom. Common edges with $AsS_3$ pyramids are indicated by broken lines. The four nearest S atoms are dotted.

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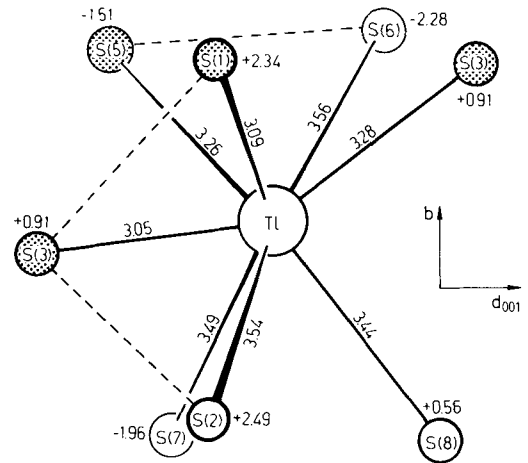
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