

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trimethylammonium Tin Sulfide

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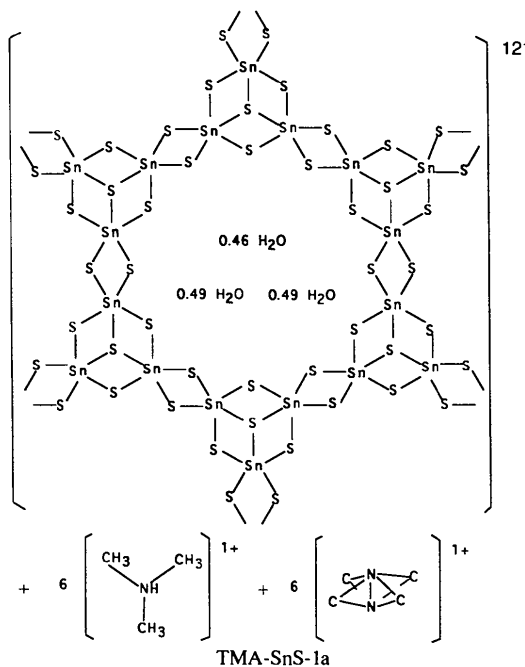
Abstract

The structure of trimethylammonium tin sulfide-water (1/0.72), [(CH₃)₃NH]₂[Sn₃S₇]·0.72H₂O, consists of sheets with 24-membered ring openings containing alternating Sn and S atoms. Organic molecules resulting from the breakdown of the starting tetramethylammonium template reside between these sheets, which are stacked parallel to (001).

Comment

Crystalline microporous metal sulfides form a novel family of open framework materials (Bedard, Wilson, Vail, Bennett & Flanigen, 1989; Bedard, Vail, Wilson & Flanigen, 1989, 1990). The structural details of some of the antimony (Dittmar & Schäfer, 1978; Eisenmann & Schäfer, 1979; Sheldrick & Häusler, 1988; Parise, 1990, 1991; Parise & Ko, 1992; Tan, Ko & Parise, 1994), tin (Sheldrick, 1988; Ko, Cahill & Parise, 1994; Parise, Ko, Rijssenbeek, Nellis, Tan & Koch, 1994) and

germanium sulfides (Bedard, Wilson, Vail, Bennett & Flanigen, 1989) have been reported. Recently, Parise, Ko, Rijssenbeek, Nellis, Tan & Koch (1994) solved the structure of tetramethylammonium tin sulfide (TMA-SnS-1) (Bedard, Vail, Wilson & Flanigen, 1989). This substance was synthesized hydrothermally from slurries of SnS₂, tetramethylammonium hydroxide (TMA-OH), elemental S and H₂O. It has a framework similar to that described by Sheldrick & Braunbeck (1990) for the alkali metal selenide analogue CS₂Sn₃Se₇. Here, we report a closely related compound obtained after prolonged heating of the same organic template (TMA-OH) but with different Sn and S reactants. The new structure is designated TMA-SnS-1a.



The primary building unit for TMA-SnS-1a is a [SnS₅]⁶⁻ trigonal bipyramid, which is common in both open and dense tin sulfide frameworks (Krebs, 1983). The secondary building unit (Fig. 1a) is an Sn₃S₄ semi-cube formed by three edge-sharing [SnS₅]⁶⁻ trigonal bipyramids. Six semi-cubes, oriented alternately up and down, define a 24-membered ring as shown in Fig. 1(b). The rings, approximately 8.3 Å in radius, bridge through semi-cubes forming Sn₃S₇ sheets similar to that found in TMA-SnS-1. The structure (Fig. 2) consists of sheets stacked parallel to (001).

Bond-valence sums (Brown & Wu, 1976) were consistent with oxidation states of +4 and -2 for Sn and S, respectively. Therefore, the Sn₃S₇ sheet is negatively charged with charge compensation being achieved by protonation of either the framework or the extra-framework organic species residing between the sheets.

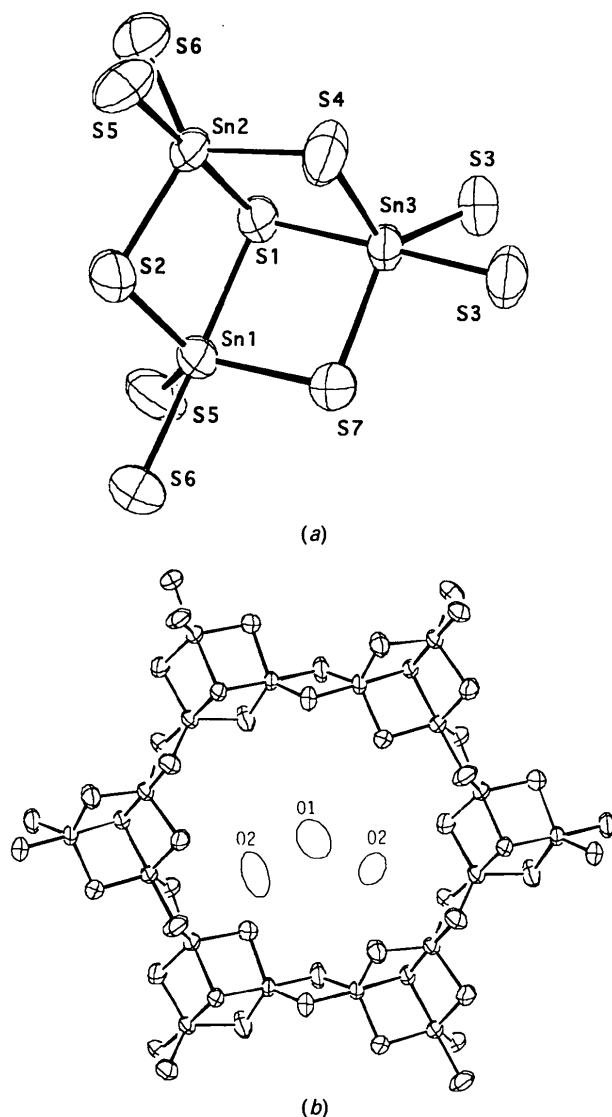


Fig. 1. ORTEP (Johnson, 1965) drawing of (a) an Sn_3S_4 semi-cube, the secondary building unit, and (b) a 24-membered ring consisting of alternating Sn and S atoms. O atoms from water molecules are shown inside the opening. Probability ellipsoids are drawn at 74%.

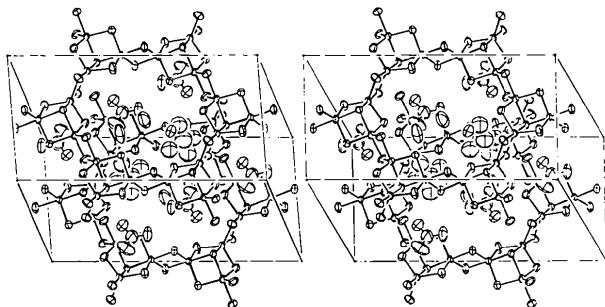


Fig. 2. Stereo ORTEP (Johnson, 1965) drawing of the structure of trimethylammonium tin sulfide. The origin of the unit cell is in the back bottom left-hand corner, with the a axis horizontal and the b axis vertical. Probability ellipsoids are drawn at 64%.

Two kinds of organic species resulting from the breakdown of the starting template TMA were found. One possesses a trigonal pyramidal geometry and is either trimethylammonium, $(\text{CH}_3)_3\text{NH}^+$, or trimethylamine, $(\text{CH}_3)_3\text{N}$. This N atom points towards the cavity of the Sn_3S_4 semi-cube with distances to the three nearest S atoms ranging from 3.87 (3) to 4.04 (3) Å. The second species is disordered with fractional site occupancies which were refined while isotropic displacement parameters (B_{iso}) were constrained. The sums of the site occupation factors of the N and C atoms are 0.9 (1) and 3.1 (1), respectively.

The pathways of the decomposition of TMA in the cavities of some molecular sieves (e.g. Y-type faujasite, offretite and SAPO-37) have been studied (Wu, Kuhl, Whyte & Venuto, 1971; Wu, Whyte & Venuto, 1971; Briend, Lamy, Peltre, Man & Barthomeuf, 1993). The major products of the decomposition of the tetraalkylammonium group at low temperatures (423–548 K) were trimethylamines and protons. The latter were assumed to form hydroxyl groups on the framework. In the synthesis of TMA-SnS-1a, the tetramethylammonium group might decompose in a similar fashion. H atoms were not located in this study. Based on previous work (Parise, 1991; Parise & Ko, 1992; Ko, Cahill & Parise, 1994; Tan, Ko & Parise, 1994; Parise, Ko, Rijssenbeek, Nellis, Tan & Koch, 1994), we assume the protons required for charge compensation are bound to trimethylamine. Therefore, the ordered molecule is assumed to be trimethylammonium. The disordered one, which has a pyramidal shape and two orientations, is assumed to be another trimethylammonium ion, oriented either upward or downward in different cells. However, we cannot exclude the possibility of hydrosulfuryl groups and other protonated species.

Three isolated peaks, one at a special position [4(e)] and the others symmetry related, were located within each 24-membered ring opening (Fig. 1b). They were assigned to water molecules since this compound was synthesized hydrothermally. The geometric relationships $\text{O}(1)\cdots\text{O}(2) = 2.69(2)$ Å and $\text{O}(2)\cdots\text{O}(1)\cdots\text{O}(2) = 120(1)^\circ$ are suggestive of an oxonium H_7O_3^+ cation, which has been characterized in other crystalline hydrates (Mootz & Fayos, 1970; Lundgren, 1972; Lundgren & Lundin, 1972). In this structure, the oxonium cation might be bound to the framework through $\text{O}\cdots\text{H}\cdots\text{S}$ bonding (Mereiter, Preisinger & Zellner, 1984), as suggested by the distances of 3.36 (2) and 3.53 (2) Å between atom O(2) and its two nearest S atoms.

Experimental

The title compound crystallized hydrothermally from amorphous SnS_2 , tetramethylammonium hydroxide (TMA-OH), elemental sulfur and H_2O , which were mixed in a molar ratio of 3:2:2:30 and stirred to form a brownish slurry. The elemental sulfur was dissolved completely in 40% TMA-OH solution

prior to mixing with the other components. The slurry was heated at 423 K for one week under autogenous hydrothermal conditions in a Pyrex-lined bomb. The yield was 85% (based on SnS₂).

Crystal data

(C₃H₁₀N)₂[Sn₃S₇]·0.72H₂O

M_r = 713.70

Monoclinic

*C*2/*c*

a = 22.965 (3) Å

b = 13.196 (3) Å

c = 15.823 (3) Å

β = 108.28 (1)°

V = 4553.1 (15) Å³

Z = 8

D_x = 2.082 Mg m⁻³

Data collection

Picker diffractometer

ω/2θ scans

Absorption correction:

analytical

T_{min} = 0.607, *T_{max}* = 0.778

5321 measured reflections

4281 independent reflections

4111 observed reflections

[*I* > 3σ(*I*)]

Refinement

Refinement on *F*²

R = 0.058

wR = 0.041

S = 1.54

4108 reflections

166 parameters

H atoms were not located

w = 1/[σ²(*I*) + 0.0009*I*²]^{1/2}

(Δ/σ)_{max} = 0.02

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 12

reflections

θ = 12–14°

μ = 3.89 mm⁻¹

T = 294 K

Pinacoids

0.14 × 0.04 × 0.04 mm

Transparent

R_{int} = 0.024

θ_{max} = 28.0°

h = -30 → 30

k = 0 → 17

l = 0 → 20

1 standard reflection

monitored every 20

reflections

intensity decay: 25%

Δρ_{max} = 0.65 e Å⁻³

Δρ_{min} = -1.06 e Å⁻³

Extinction correction:

isotropic secondary

Extinction coefficient:

0.54 (1) × 10⁻⁴

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

*B*_{iso} for O(1) to C(7); *B*_{eq} = (8π²/3)Σ_iΣ_jU_{ij}*a_i^{*}a_j^{*}* for others.

	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} / <i>B</i> _{iso}
Sn(1)	1.00	0.29415 (2)	0.69483 (4)	0.26085 (5)	3.5 (1)
Sn(2)	1.00	0.28688 (2)	0.96773 (4)	0.25925 (5)	3.5 (1)
Sn(3)	1.00	0.42598 (2)	0.84104 (4)	0.26001 (4)	3.4 (1)
S(1)	1.00	0.3135 (1)	0.8339 (1)	0.1553 (2)	3.5 (1)
S(2)	1.00	0.2472 (1)	0.8272 (2)	0.3248 (2)	4.6 (1)
S(3)	1.00	0.4650 (1)	0.8460 (2)	0.1365 (2)	4.3 (1)
S(4)	1.00	0.3971 (1)	0.9920 (2)	0.3256 (2)	5.1 (1)
S(5)	1.00	0.2385 (1)	0.5935 (2)	0.1374 (2)	4.7 (1)
S(6)	1.00	0.2248 (1)	1.0620 (2)	0.1345 (2)	4.4 (1)
S(7)	1.00	0.4047 (1)	0.6851 (2)	0.3277 (2)	4.6 (1)
N(1)	1.00	0.3888 (6)	1.1529 (10)	0.0364 (12)	12.7 (8)
C(1)	1.00	0.4553 (6)	1.1417 (12)	0.0530 (11)	9.8 (6)
C(2)	1.00	0.3558 (6)	1.0626 (11)	0.0449 (10)	8.2 (6)
C(3)	1.00	0.3626 (8)	1.2510 (12)	0.0456 (12)	12.2 (8)
O(1)	0.23 (2)	1/2	0.3510 (26)	1/4	13.6 (17)
O(2)	0.49 (2)	0.3959 (8)	0.4532 (16)	0.2357 (16)	11.9 (10)
N(2)	0.63 (4)	0.3742 (15)	0.6249 (24)	-0.0411 (21)	14.2 (9)
C(3)	0.27 (3)	0.406 (3)	0.651 (5)	0.023 (4)	12.4 (18)
C(4)	0.98 (2)	0.3400 (9)	0.6663 (15)	-0.0002 (13)	11.9 (6)

C(5)	0.76 (3)	0.3827 (12)	0.7098 (22)	-0.0902 (18)	13.7 (8)
C(6)	0.79 (4)	0.4384 (12)	0.5689 (20)	-0.0058 (18)	13.8 (8)
C(7)	0.61 (3)	0.3737 (16)	0.5810 (28)	0.0609 (23)	13.7 (11)

Table 2. Selected geometric parameters (Å, °)

Sn(1)—S(1)	2.612 (2)	Sn(2)—S(6)	2.390 (3)
Sn(1)—S(2)	2.435 (2)	Sn(3)—S(1)	2.596 (2)
Sn(1)—S(5)	2.381 (3)	Sn(3)—S(3 ^{III})	2.527 (2)
Sn(1)—S(6 ^I)	2.542 (2)	Sn(3)—S(3)	2.392 (2)
Sn(1)—S(7)	2.427 (2)	Sn(3)—S(4)	2.432 (2)
Sn(2)—S(1)	2.613 (2)	Sn(3)—S(7)	2.439 (2)
Sn(2)—S(2)	2.437 (2)	N(1)—C(1)	1.474 (16)
Sn(2)—S(4)	2.438 (2)	N(1)—C(2)	1.441 (16)
Sn(2)—S(5 ^I)	2.523 (2)	N(1)—C(3)	1.452 (17)
N(1)···O(2 ^{IV})	3.87 (3)	O(1)···O(2)	2.69 (2)
N(1)···S(4 ^{IV})	3.89 (3)	O(2)···S(2 ^I)	3.53 (2)
N(1)···S(7 ^{IV})	4.04 (3)	O(2)···S(7)	3.36 (2)
S(1)—Sn(1)—S(2)	87.04 (7)	Sn(1)—S(1)—Sn(3)	87.27 (7)
S(1)—Sn(1)—S(5)	91.45 (8)	Sn(2)—S(1)—Sn(3)	87.50 (7)
S(1)—Sn(1)—S(6 ^I)	179.0 (1)	Sn(1)—S(2)—Sn(2)	95.44 (8)
S(6 ^I)—Sn(1)—S(7)	92.83 (8)	Sn(3)—S(3)—Sn(3 ^{III})	91.1 (1)
S(1)—Sn(2)—S(2)	86.95 (7)	Sn(2)—S(4)—Sn(3)	95.39 (8)
S(1)—Sn(2)—S(4)	86.75 (7)	Sn(1)—S(5)—Sn(2 ^I)	90.7 (1)
S(1)—Sn(2)—S(5 ^{II})	178.6 (2)	Sn(1 ^{II})—S(6)—Sn(2)	90.0 (1)
S(1)—Sn(2)—S(6)	91.63 (8)	Sn(1)—S(7)—Sn(3)	95.20 (8)
S(2)—Sn(2)—S(4)	113.1 (1)	C(1)—N(1)—C(2)	117 (1)
S(2)—Sn(2)—S(5 ^{II})	91.79 (9)	C(1)—N(1)—C(3)	121 (1)
S(2)—Sn(2)—S(6)	122.8 (1)	C(2)—N(1)—C(3)	119 (1)
S(4)—Sn(2)—S(5 ^{II})	93.11 (9)	C(4)—N(2)—C(5)	99 (3)
S(4)—Sn(2)—S(6)	123.9 (1)	C(4)—N(2)—C(6)	132 (3)
S(5 ^{II})—Sn(2)—S(6)	89.64 (8)	C(4)—N(2)—C(6)	132 (3)
S(1)—Sn(3)—S(3)	91.84 (8)	C(4)—N(2)—C(7)	59 (2)
S(1)—Sn(3)—S(3 ^{III})	179.1 (3)	C(5)—N(2)—C(6)	107 (3)
S(1)—Sn(3)—S(4)	87.27 (7)	C(5)—N(2)—C(7)	146 (3)
S(1)—Sn(3)—S(7)	87.31 (7)	C(6)—N(2)—C(7)	78 (2)
S(3)—Sn(3)—S(3 ^{III})	88.83 (9)	C(4)—N(3)—C(5)	75 (3)
S(3 ^{III})—Sn(3)—S(4)	92.84 (8)	C(4)—N(3)—C(6)	128 (5)
S(3)—Sn(3)—S(4)	123.2 (1)	C(4)—N(3)—C(7)	64 (3)
S(3)—Sn(3)—S(7)	124.1 (1)	C(5)—N(3)—C(6)	92 (4)
S(3 ^{III})—Sn(3)—S(7)	91.84 (8)	C(5)—N(3)—C(7)	130 (5)
S(4)—Sn(3)—S(7)	112.6 (1)	C(6)—N(3)—C(7)	92 (4)
Sn(1)—S(1)—Sn(2)	87.24 (7)		

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $1 - x, y, \frac{1}{2} - z$; (iv) $x, 2 - y, z - \frac{1}{2}$.

A linear isotropic decay correction was applied with *I_f* = *I_o*(1 - 0.000805*r*^h)

Data collection, cell refinement, absorption corrections and data reduction: local implementation of software written by L. W. Finger, Geophysical Laboratory, Carnegie Institute of Washington, Washington, DC. Program used for structure resolution and refinement, molecular graphics and preparation of materials for publication: a package of programs written and maintained by J. C. Calabrese, E. I. DuPont. Other program used for molecular graphics: *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: AB1180). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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8-(Ph₂PCH₂CH₂PPh₂)-8,7-*nido*-RhSB₉H₁₀·2CH₂Cl₂

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Abstract

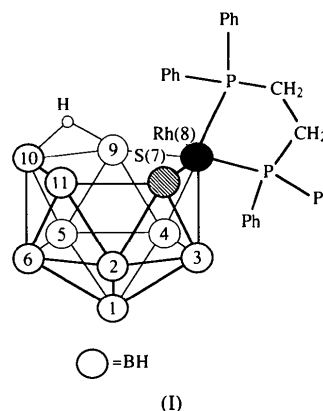
The synthesis and the solid-state structure determination by a low-temperature single-crystal X-ray diffraction study of 8-[1,2-bis(diphenylphosphinoethane)]-9,10- μ -hydrido-8-rhoda-7-thia-*nido*-undecaborane(10), [Rh(B₉-H₁₀S)(C₂₆H₂₄P₂)]·2CH₂Cl₂, as the bis(dichloromethane)

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solvate are reported. In terms of conventional electron-counting rules, this species has an anomalous polyhedral geometry; two one-electron agostic type Rh—H—C interactions are proposed as the source of an additional skeletal electron pair which satisfies cluster-bonding requirements.

Comment

We are, at present, investigating examples of unusual structural behaviour in metallaheteroboranes. As part of this programme we have become interested in the anomalous geometries observed in 11-vertex rhodathiaboranes (Ferguson *et al.*, 1990; Murphy, Spalding, Ferguson & Gallagher, 1992) which display a *nido* cage architecture while apparently possessing a cluster electron count more appropriate to a *closo* geometry (Wade, 1976; Mingos, 1984). Herein we present the synthesis and structural characterization of a further example of such species, namely 8-(Ph₂P—CH₂CH₂—PPh₂)-9,10- μ -H-8,7-*nido*-RhSB₉H₉, (I), and discuss a possible solution to this problem.



The title rhodathiaborane crystallizes with no crystallographically imposed symmetry and no close intermolecular contacts. Two molecules of dichloromethane co-crystallize with this species. This high proportion of solvate causes the crystal lattice to be very unstable with respect to solvent loss: crystal growth by solvent diffusion has to be arrested to avoid diffusion of dichloromethane out of the lattice; crystal transfer was therefore performed at 195 K (dry-ice bath) and data were collected at 210 K.

A perspective view of a single molecule, with the atomic numbering scheme adopted, is shown in Fig. 1.

As with previous examples of species of this type, the 11-vertex RhSB₉ polyhedron shows gross *nido*-icosahedral geometry. The Rh(8)—S(7) distance in the present compound is 2.366 (2) Å, shorter than in the 8,8-(PPh₃)₂- (Ferguson *et al.*, 1990) (A) and 8,8-(PPh₃)₂-9-(OEt)- (Murphy, Spalding, Ferguson & Gallagher, 1992) (B) analogues, where the correspond-