

Structure of Trimeric Diphenyltin(IV) Sulfide

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Abstract. 2,2,4,4,6,6-Hexaphenylcyclotri(stannathiane), $C_{36}H_{30}S_3Sn_3$, $M_r = 914.90$, monoclinic, $P2_1/n$, $a = 12.214$ (2), $b = 21.787$ (5), $c = 13.591$ (3) Å, $\beta = 94.70$ (1)°, $V = 3605$ (2) Å³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $T = 295$ (2) K, $D_x = 1.686$ g cm⁻³, $Z = 4$, $F(000) = 1776.0$, $\mu = 20.85$ cm⁻¹, $R = 0.050$ for 2660 unique reflections [$I \geq 2\sigma(I)$]. The trimer consists of a six-membered ring of alternating Sn and S atoms with each Sn atom tetrahedrally coordinated by two S atoms and two phenyl C atoms. The average Sn—S and Sn—C bond distances are 2.399 (5) and 2.13 (1) Å, respectively.

Introduction. Attempted recrystallization of bis(*O*-methoxyethyldithiocarbonato)diphenyltin(IV) from hot methanol yielded the unexpected trimeric compound diphenyltin sulfide. The chemistry of the trimer formation from bis(*O*-methoxyethyldithiocarbonato)diphenyltin (IV) and the structure of the parent complex are being further investigated. The structure of the trimeric diphenyltin sulfide is reported here.

No complete structure determination has so far been reported for this well known compound (Berwe & Haas, 1987), even though the unit-cell dimensions and space group have been published for what appears to be a different crystalline form (Kunchur & Borhani, 1976).

Experimental. Crystals of $[SnS(C_6H_5)_2]_3$ were obtained by heating a solution of $(CH_3O-CH_2CH_2OCS_2)_2Sn(C_6H_5)_2$ in methanol to its boiling point and allowing it to cool to room temperature. Preliminary oscillation and Weissenberg photographs showed a monoclinic crystal with systematic absences for the chosen cell consistent with the space group $P2_1/n$.

An Enraf–Nonius CAD-4F diffractometer and graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) were used. Cell dimensions were obtained by least-squares refinement of angular values obtained for 25 reflections with $17.9 \leq 2\theta \leq 36.8^\circ$. Intensity data were collected using the $\omega/2\theta$ scan technique ($2 \leq 2\theta \leq 50^\circ$: $-2 \leq h \leq 14$, $-2 \leq k \leq 25$, $-16 \leq l \leq 16$); the crystal was relatively weakly scattering and no significant data could be measured

beyond $2\theta = 50^\circ$. No significant variation in intensity was observed on the basis of three check reflections remeasured after every 1000 s of X-ray exposure. Corrections were applied for Lorentz and polarization effects and for absorption (SHELX76; Sheldrick, 1976); maximum and minimum transmission factors 0.8874 and 0.7648 respectively, no correction was made for extinction. Equivalent reflections of the 9034 measured intensities were merged ($R_{int} = 0.030$) giving 6306 unique reflections of which 2660 satisfied $I \geq 2\sigma(I)$.

Sn and S positions were obtained from the analysis of a three-dimensional Patterson map (SHELXS86; Sheldrick, 1985) and remaining non-H atoms were located in subsequent difference maps. All non-H atoms were refined with anisotropic thermal parameters using full-matrix least squares based on F (SHELX76; Sheldrick, 1976). All H atoms were included in the model at calculated positions with a common isotropic thermal parameter refined. A weighting scheme of the form $w = k/(\sigma^2 F + 0.0005|F|^2)$ was used and refinement of 380 parameters converged at $R = 0.050$, $wR = 0.044$, $k = 1.4655$, $S = 1.171$, $(\Delta/\sigma)_{max} = 0.025$ and residual electron density in the range -0.65 to 0.85 e Å⁻³. An analysis of variance showed no special features. The neutral-atom scattering factors used were those incorporated in SHELX76 (Sheldrick 1976) and all calculations were performed on the University of Melbourne VAX 11/780 and 11/8650 computers. Fractional atomic coordinates are listed in Table 1* and bond distances and angles (excluding phenyl ring geometry) are given in Table 2.

Discussion. Crystals of diphenyltin sulfide $(Ph_2SnS)_3$ are molecular, with one trimeric molecule forming the asymmetric unit. The numbering scheme used is shown in Fig. 1 and the molecular packing is

* Tables of anisotropic thermal parameters, calculated H-atom coordinates, observed and calculated structure factors, phenyl ring geometry, selected intermolecular contacts and mean planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52771 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates of the non-H atoms for diphenyltin sulfide

$$B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33}).$$

	x	y	z	B_{eq} (Å ²)
Sn(1)	0.09761 (9)	0.12073 (5)	0.32179 (7)	3.77 (6)
Sn(2)	0.32167 (9)	0.15821 (5)	0.14803 (7)	3.93 (6)
Sn(3)	0.30779 (9)	0.00082 (5)	0.26147 (7)	3.9 (6)
S(1)	0.1252 (3)	0.1498 (2)	0.1557 (3)	4.6 (2)
S(2)	0.4195 (4)	0.0912 (2)	0.2641 (3)	5.2 (2)
S(3)	0.1544 (4)	0.0177 (2)	0.3579 (3)	6.0 (2)
C(11)	0.172 (1)	0.1865 (7)	0.425 (1)	4.0 (5)
C(12)	0.207 (1)	0.2418 (7)	0.394 (1)	5.1 (5)
C(13)	0.243 (2)	0.2858 (8)	0.462 (1)	6.8 (5)
C(14)	0.244 (1)	0.2733 (9)	0.562 (1)	6.7 (6)
C(15)	0.207 (1)	0.2182 (9)	0.591 (1)	6.1 (6)
C(16)	0.170 (1)	0.1740 (9)	0.524 (1)	5.7 (5)
C(17)	-0.076 (1)	0.1194 (9)	0.337 (1)	4.8 (5)
C(18)	-0.134 (1)	0.1713 (1)	0.324 (1)	6.9 (6)
C(19)	-0.246 (2)	0.173 (1)	0.342 (1)	8.9 (6)
C(110)	-0.295 (2)	0.122 (1)	0.370 (2)	10.5 (6)
C(111)	-0.237 (2)	0.069 (1)	0.387 (2)	11.3 (6)
C(112)	-0.126 (1)	0.0671 (9)	0.367 (1)	7.2 (6)
C(21)	0.390 (1)	0.2454 (7)	0.188 (1)	4.8 (5)
C(22)	0.375 (1)	0.2941 (7)	0.121 (1)	5.6 (5)
C(23)	0.419 (1)	0.3506 (8)	0.142 (2)	6.7 (5)
C(24)	0.477 (2)	0.3606 (9)	0.228 (2)	8.4 (6)
C(25)	0.492 (2)	0.316 (1)	0.301 (1)	8.0 (6)
C(26)	0.450 (1)	0.2566 (8)	0.277 (1)	6.2 (5)
C(27)	0.342 (1)	0.1399 (6)	-0.004 (1)	4.0 (5)
C(28)	0.259 (2)	0.1080 (8)	-0.061 (1)	6.3 (6)
C(29)	0.279 (2)	0.101 (1)	-0.162 (1)	8.6 (6)
C(210)	0.370 (2)	0.123 (1)	-0.201 (1)	8.5 (6)
C(211)	0.447 (2)	0.155 (1)	-0.140 (1)	9.7 (6)
C(212)	0.431 (2)	0.1632 (9)	-0.046 (1)	7.3 (6)
C(31)	0.404 (1)	-0.0657 (7)	0.342 (1)	3.9 (5)
C(32)	0.374 (1)	-0.1273 (8)	0.339 (1)	4.9 (5)
C(33)	0.436 (2)	-0.1718 (8)	0.395 (1)	5.9 (5)
C(34)	0.527 (2)	-0.1514 (9)	0.454 (1)	6.2 (5)
C(35)	0.559 (1)	-0.0912 (9)	0.454 (1)	5.6 (6)
C(36)	0.500 (1)	-0.0488 (7)	0.400 (1)	4.7 (5)
C(37)	0.260 (1)	-0.0260 (6)	0.114 (1)	4.4 (5)
C(38)	0.342 (2)	-0.0359 (8)	0.052 (1)	5.7 (5)
C(39)	0.318 (2)	-0.0538 (9)	-0.046 (1)	9.0 (6)
C(310)	0.206 (2)	-0.0611 (9)	-0.077 (2)	9.7 (6)
C(311)	0.125 (2)	-0.0519 (8)	-0.019 (2)	8.5 (6)
C(312)	0.150 (2)	-0.0345 (9)	0.078 (1)	6.5 (5)

Table 2. Bond lengths (Å), bond angles (°) and torsion angles (°) for diphenyltin sulfide (excluding phenyl rings)

Sn(1)—S(1)	2.395 (4)	Sn(1)—C(11)	2.15 (1)
Sn(1)—S(3)	2.389 (5)	Sn(1)—C(17)	2.15 (1)
Sn(2)—S(1)	2.417 (4)	Sn(2)—C(21)	2.13 (2)
Sn(2)—S(2)	2.396 (4)	Sn(2)—C(27)	2.14 (1)
Sn(3)—S(2)	2.394 (5)	Sn(3)—C(31)	2.11 (1)
Sn(3)—S(3)	2.401 (5)	Sn(3)—C(37)	2.12 (1)
S(1)—Sn(1)—S(3)	112.4 (2)	S(3)—Sn(3)—C(37)	113.0 (5)
S(1)—Sn(2)—S(2)	111.6 (2)	C(11)—Sn(1)—C(17)	108.3 (7)
S(2)—Sn(3)—S(3)	109.6 (2)	C(21)—Sn(2)—C(27)	109.8 (6)
Sn(1)—S(1)—Sn(2)	106.1 (2)	C(31)—Sn(3)—C(37)	113.5 (6)
Sn(2)—S(2)—Sn(3)	103.8 (2)	Sn(1)—C(11)—C(12)	121 (1)
Sn(1)—S(3)—Sn(3)	105.0 (2)	Sn(1)—C(11)—C(16)	118 (1)
Sn(1)—Sn(1)—C(11)	110.7 (5)	Sn(1)—C(17)—C(18)	119 (1)
S(1)—Sn(1)—C(17)	108.1 (6)	Sn(1)—C(17)—C(112)	121 (1)
S(3)—Sn(1)—C(11)	113.1 (5)	Sn(2)—C(21)—C(22)	119 (1)
S(3)—Sn(1)—C(17)	103.9 (6)	Sn(2)—C(21)—C(26)	123 (1)
S(1)—Sn(2)—C(21)	115.3 (5)	Sn(2)—C(27)—C(28)	119 (1)
S(1)—Sn(2)—C(27)	102.8 (5)	Sn(2)—C(27)—C(212)	120 (1)
S(2)—Sn(2)—C(21)	102.2 (5)	Sn(3)—C(31)—C(32)	121 (1)
S(2)—Sn(2)—C(27)	115.6 (5)	Sn(3)—C(31)—C(36)	121 (1)
S(2)—Sn(3)—C(31)	105.3 (5)	Sn(3)—C(37)—C(38)	118 (1)
S(2)—Sn(3)—C(37)	110.7 (5)	Sn(3)—C(37)—C(312)	123 (1)
S(3)—Sn(3)—C(31)	104.4 (5)		
Sn(1)—S(1)—Sn(2)—S(2)	28.7 (2)	S(1)—Sn(2)—S(2)—Sn(3)	37.5 (2)
Sn(2)—S(2)—Sn(3)—S(3)	-78.4 (2)	S(2)—Sn(3)—S(3)—Sn(1)	39.6 (2)
Sn(3)—S(3)—Sn(1)—S(1)	33.0 (2)	S(3)—Sn(1)—S(1)—Sn(2)	-70.4 (2)

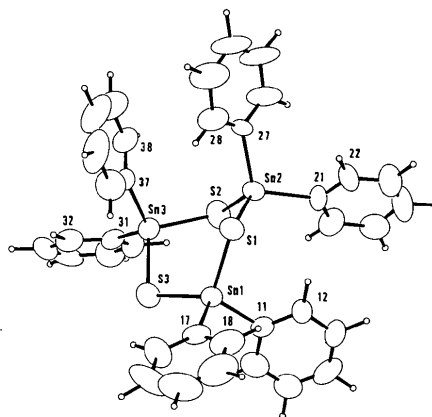


Fig. 1. A diphenyltin sulfide trimeric molecule, atom type is C unless otherwise indicated, phenyl rings number in sequence as shown (ORTEP; Johnson, 1971).

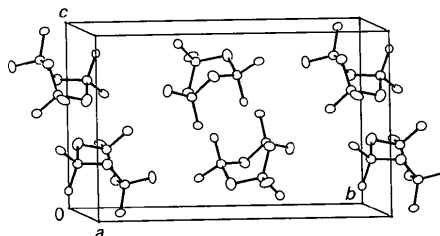


Fig. 2. The molecular packing observed in crystals of the diphenyltin sulfide trimer, only the C atoms bonded to Sn atoms are shown, the remainder of the phenyl rings are omitted for clarity (ORTEP; Johnson, 1971).

depicted in Fig. 2. The molecule consists of a six-membered ring of alternating Sn and S atoms with each Sn atom also bonded to two phenyl groups. The six Sn—S bond lengths all lie within 3σ of the average value [2.399 (5) Å], the bond angles S—Sn—S range from 109.6 (2) to 112.4 (2)° and Sn—S—Sn from 103.8 (2) to 106.1 (2)°. The conformation of the (SnS)₃ ring is such that the group of three Sn atoms and the group of three S atoms each form an almost equilateral triangle; Sn...Sn distances 3.80 ± 0.05 Å, S...S distances 3.96 ± 0.04 Å, Sn—Sn—Sn and S—S—S angles $60 \pm 1^\circ$. The dihedral angle between the plane of the three S atoms and the plane of the three Sn atoms is 41.7° and the position of the triangles is such that there are two short Sn...S non-bonded distances [Sn(2)...S(2) 4.122 (5) Å, Sn(3)...S(1) 4.129 (4) Å] with a third much longer [Sn(2)...S(3) 4.758 (5) Å]; the atoms Sn(2) and S(3) lie within 0.1 Å of the plane of the sulfur and tin triangles respectively. The torsion angles within the ring lie close to the values observed for the 'crossed' (*forme croisée*) conformation of

cyclohexane (Bucourt & Hainaut, 1965). The Sn—C lengths range from 2.11 (1) to 2.14 (1) Å and S—Sn—C angles from 102.2 (5) to 115.6 (5)°. The dihedral angles between the two phenyl rings attached to each Sn atom range from 85 (1) to 123 (1)°.

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Structure of [PhCH₂NMe₃]₂[(B₁₀H₁₂)₂Pt]

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Abstract. [PhCH₂NMe₃]₂⁺.[Pt(B₁₀H₁₂)₂]²⁻, $M_r = 735.97$, triclinic, $P\bar{1}$, $a = 9.023$ (3), $b = 10.440$ (4), $c = 11.172$ (3) Å, $\alpha = 111.55$ (3), $\beta = 108.794$ (24), $\gamma = 101.29$ (3)°, $V = 865.7$ Å³, $Z = 1$, $D_x = 1.411$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 4.111$ mm⁻¹, $F(000) = 368$, $T = 185$ (1) K, $R = 0.0166$ for 3039 independent observed reflections. The anion resides on a crystallographic inversion centre, and is slightly, but significantly, distorted from C_{2h} point symmetry as a result of crystal packing. Molecular-geometry calculations suggest that the {B₁₀H₁₂} ligand does not fit particularly well with either a *nido*-{B₁₀H₁₂}²⁻ or an *arachno*-{B₁₀H₁₂}⁴⁻ formalism.

Introduction. The precise structures of metallaboranes of the general family $MB_{10}H_{12}$ are of current interest because the {B₁₀H₁₂} ligand could formally be present in such species as either the *nido* fragment {B₁₀H₁₂}²⁻ or the *arachno* fragment {B₁₀H₁₂}⁴⁻. The structural differences between these are subtle (the pattern of connectivities is exactly the same), and only recently have they really been successfully delineated *via* application of the 'root-mean-square misfit' technique (Wynd, 1988; Wynd, Welch & Parish, 1990; Macgregor, Yellowlees & Welch, 1990).

It is important to attempt to distinguish between the formalisms of {B₁₀H₁₂}²⁻ and {B₁₀H₁₂}⁴⁻ ligands in $MB_{10}H_{12}$ metallaboranes for two reasons. Firstly, it allows access to the formal oxidation state of the metal in the complex, something that is very rarely probed. Cases where independent measure-

References

- BERWE, H. & HAAS, A. (1987). *Chem. Ber.* **120**, 1175–1182.
 BUCOURT, R. & HAINAUT, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.
 JOHNSON, C. K. (1971). *ORTEPII*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 KUNCHUR, N. R. & BORHANI, S. (1976). *J. Appl. Cryst.* **9**, 508.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1985). *SHELX86*. In *Crystallographic Computing 3*, edited by G. M. SHELDRIK, C. KRUGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.

ment of the metal oxidation state is possible are welcome, since these afford a check on the validity of the approach to distinction of the two formalisms. Secondly, it allows assessment of the 'verticity' of the metal atom, *i.e.* (the rough measure of) the extent to which it is truly involved in cluster skeletal bonding, as opposed to acting as a simple bridge between several B atoms.

The dianion [(B₁₀H₁₂)₂Pt]²⁻ has been known for many years (Klanberg, Wegner, Parshall & Muetteries, 1968). Although it is well accepted that its gross structure is the same as that of the crystallographically characterized anions [(B₁₀H₁₂)₂Ni]²⁻ (Guggenberger, 1972) and [(B₁₀H₁₂)₂Au]⁻ (Wynd & Welch, 1987), molecular parameters are not known, and so the precise form of the {B₁₀H₁₂} ligand in this species cannot be assessed. To remedy this we have resynthesized [(B₁₀H₁₂)₂Pt]²⁻ for the purposes of the accurate structural study described herein. Suitable crystals were afforded as the [PhCH₂NMe₃]⁺ salt.

Experimental. The salt [PhCH₂NMe₃]₂[(B₁₀H₁₂)₂Pt] was prepared in an analogous manner to that which previously afforded the [NMe₄]⁺ salt (Klanberg, Wegner, Parshall & Muetteries, 1968), and its purity confirmed by microanalysis (found: C, 32.3; H, 7.49; N, 3.83%. C₂₀H₅₆B₂₀N₂Pt requires: C, 32.7; H, 7.62; N, 3.81%); golden-yellow blocks grown by slow diffusion of diethyl ether into an acetonitrile solution at 243 K; slightly irregular crystal, *ca* 0.3 × 0.25 × 0.15 mm, mounted in glass capillary and slowly cooled to 185 (1) K on an Enraf–Nonius CAD-4