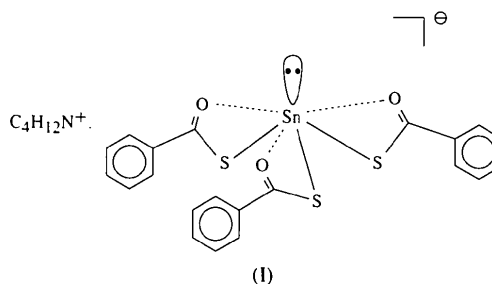


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The structure determination of (I) shows it to consist of discrete anions and cations. Both the Me₄N⁺ and [Sn(SOCPh)₃][−] ions lie on a crystallographic threefold axis; a view of the anion is shown in Fig. 1. The three SOCP[−] ligands are bonded to Sn^{II} primarily through their S atoms. The coordination sphere around the Sn atom can be described as a trigonal pyramid with the three S atoms occupying the base [S··S distance 3.658(3) Å] and the Sn atom at the apex. The geometry is consistent with the presence of a stereochemically active lone pair on Sn. The Sn—S distance of 2.592(2) Å is longer than those of 2.532(1)–2.552(1) Å found for trigonal pyramidal [Sn(SPh)₃][−] (Dean, Vittal & Payne, 1985). Weak coordination to the three carbonyl O atoms, however, also occurs in [Sn(SOCPh)₃][−]; the Sn··O distance of 2.967(2) Å is less than the sum of the relevant van der Waals radii (3.7 Å; Bondi, 1964). The Sn atom is 1.64(1) Å from the S₃ plane and 0.14(1) Å from the O₃ plane. The dihedral angle between the SnSCO planes is 101.5(2)°. In the PhCOS[−] ligands, the COS planes are twisted from the phenyl ring planes by 18.5(2)°.

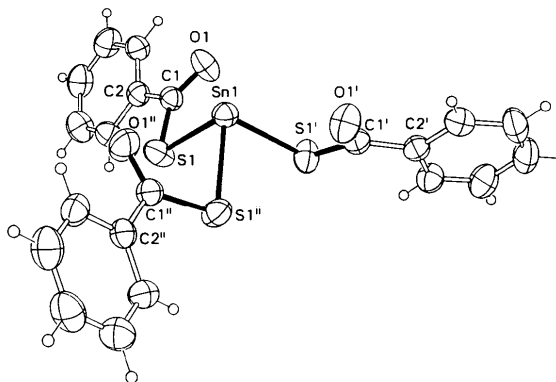


Fig. 1. A view of the [Sn(SOCPh)₃][−] anion showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

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Tetramethylammonium Tris(thiobenzoato-O,S)tin(II)

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Abstract

The synthesis, structure and ¹¹⁹Sn NMR spectrum of the title compound, (C₄H₁₂N)[Sn(C₇H₅OS)₃], are reported. Crystallographic threefold symmetry is present in both the anion and cation. In the [Sn(SOCPh)₃][−] anion, the Sn^{II} coordination geometry is trigonal pyramidal, with the S atoms forming the basal plane and the Sn atom at the apex; the Sn—S distance is 2.592(2) Å. In addition, weak intramolecular interactions occur between the Sn atom and the carbonyl O atoms [Sn··O 2.967(2) Å]. The ¹¹⁹Sn NMR chemical shift of the title compound is −227 p.p.m. (MeCN, 295 K).

Comment

The chemistry of metal thiobenzoates has not been extensively investigated (Cras & Willems, 1987; McCormick, Beremon & Baird, 1984). We have reported the structures of the thiobenzoate complexes of Cd^{II} (Vittal & Dean, 1993), Pb^{II} and Bi^{III} (Burnett, Dean & Vittal, 1993).

Reaction of SnCl₂·2H₂O, Et₃NH⁺·SOCPh[−] and Me₄NCl in the ratio 1:3:1 afforded the title compound, (I), in low yield. The ¹¹⁹Sn chemical shift is −227 p.p.m., the resonance being significantly more shielded than that of [Sn(SPh)₃][−], the chemical shift of which is 140–146 p.p.m. (Arsenault & Dean, 1983; Dean, Vittal & Payne, 1985). Thus, structural information about the [Sn(SOCPh)₃][−] anion is highly desirable.

The methyl groups of the Me₄N⁺ cation are disordered. The two disorder models (occupancies of 0.6 and 0.4) are related by an inversion at N1 along the C8—N1 axis. In the crystal lattice, each Me₄N⁺ cation

is surrounded by eight $[\text{Sn}(\text{SOCPh})_3]^-$ anions. A view of the $[\text{Sn}(\text{SOCPh})_3]^-$ anions surrounding an Me_4N^+ cation is shown in Fig. 2. The distance between the benzene rings encasing the Me_4N^+ cation is 8.80 (5) Å and the corresponding Sn...Sn spacing along the *c* axis is 14.333 (3) Å. The large void available to the cation may account for its orientational disorder.

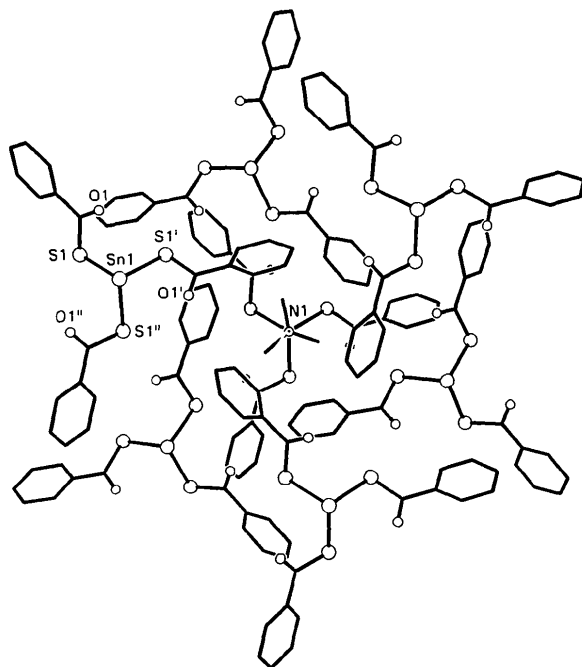


Fig. 2. A view looking down the *c* axis (threefold) showing the $[\text{Sn}(\text{SOCPh})_3]^-$ anions surrounding an Me_4N^+ cation. One anion on top of the Me_4N^+ cation has been omitted for clarity, as have the H atoms.

Experimental

All the chemicals employed were of reagent grade and used as received. The synthesis was carried out under an argon atmosphere. Thiobenzoic acid (2 ml, 14.7 mmol) was added to a solution of Et_3N (1.85 ml, 13.3 mmol) in methanol (10 ml). To the resulting yellow solution was added with stirring $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.998 g, 4.4 mmol) dissolved in methanol (10 ml), producing a yellow precipitate. A solution containing Me_4NCl (0.484 g, 4.4 mmol) in methanol (10 ml) was added with stirring to the yellow mixture, followed by CH_2Cl_2 (35 ml) and MeCN (10 ml). The mixture was warmed to 313 K for 30 min resulting in a turbid yellow solution which was filtered hot and left to crystallize at 278 K. The pale-yellow diffraction-quality crystals obtained were separated by decantation and washed with methanol and diethyl ether, and then dried in a stream of argon (yield 0.85 g; 31.7%). Analysis: $\text{C}_{25}\text{H}_{27}\text{NO}_3\text{S}_3\text{Sn}$ requires C 49.68, H 4.50, N 2.32%; found C 49.60, 49.82, H 4.50, 4.60, N 2.31, 2.36%. The C, H and N analyses were performed by Guelph Chemical Laboratories Ltd. The ^{119}Sn NMR spectrum (296 K, 74.60 MHz) was measured and referenced to neat SnMe_4

as described previously by Dean & Srivastava (1985). The sample was prepared in MeCN in 0.03 M concentration.

Crystal data

$(\text{C}_4\text{H}_{12}\text{N})[\text{Sn}(\text{C}_7\text{H}_5\text{OS})_3]$
 $M_r = 604.35$
 Rhombohedral
 (hexagonal axes)
 $R3c$
 $a = 12.709 (2) \text{ \AA}$
 $c = 28.667 (6) \text{ \AA}$
 $V = 4009.6 (14) \text{ \AA}^3$
 $Z = 6$
 $D_x = 1.502 \text{ Mg m}^{-3}$
 $D_m = 1.50 (5) \text{ Mg m}^{-3}$
 D_m measured by flotation

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 30 reflections
 $\theta = 12.4\text{--}13.5^\circ$
 $\mu = 1.216 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Cube
 $0.34 \times 0.32 \times 0.28 \text{ mm}$
 Yellow

Data collection

Siemens P4 diffractometer
 $2\theta/\omega$ scans
 Absorption correction:
 SHELXTL/PC Gaussian
 (Sheldrick, 1990b)
 $T_{\text{min}} = 0.638$, $T_{\text{max}} = 0.695$
 1881 measured reflections
 1076 independent reflections
 1022 observed reflections
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0158$
 $\theta_{\text{max}} = 27.49^\circ$
 $h = -1 \rightarrow 14$
 $k = -13 \rightarrow 14$
 $l = -1 \rightarrow 37$
 3 standard reflections monitored every 297 reflections
 intensity variation: 3.6%

Refinement

Refinement on F^2
 $R(F) = 0.0251$
 $wR(F^2) = 0.0635$
 $S = 1.056$
 1076 reflections
 118 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 2.279P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = -0.001$
 $\Delta\rho_{\text{max}} = 0.60 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$

Extinction correction:
 SHELXL93 (Sheldrick, 1993)
 Extinction coefficient:
 0.00025 (8)
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 Absolute configuration:
 Flack (1983) parameter = 0.05 (9)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Sn1	1	1	2/3	0.04034 (15)
S1	0.86963 (10)	0.81290 (10)	0.61426 (8)	0.0523 (3)
O1	0.7313 (4)	0.8502 (3)	0.6715 (2)	0.0599 (9)
C1	0.7343 (3)	0.7811 (3)	0.64252 (15)	0.0385 (7)
C2	0.6215 (4)	0.6628 (4)	0.6314 (2)	0.0399 (8)
C3	0.5234 (4)	0.6210 (4)	0.6620 (2)	0.0470 (9)
C4	0.4185 (4)	0.5089 (5)	0.6542 (2)	0.0598 (12)
C5	0.4102 (5)	0.4409 (4)	0.6155 (2)	0.0620 (12)
C6	0.5074 (4)	0.4822 (4)	0.5846 (2)	0.0613 (13)
C7	0.6123 (4)	0.5927 (4)	0.5923 (2)	0.0478 (9)
N1	1/3	2/3	0.5157 (3)	0.053 (2)
C8	1/3	2/3	0.5669 (5)	0.078 (5)
C9	0.2064 (10)	0.6065 (9)	0.4956 (5)	0.080 (3)
C8'	1/3	2/3	0.4641 (6)	0.086 (9)
C9'	0.2832 (16)	0.7422 (15)	0.5355 (7)	0.089 (5)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Sn1—S1	2.592 (2)	C2—C7	1.401 (5)
S1—C1	1.755 (4)	C3—C4	1.400 (7)
O1—C1	1.224 (5)	C4—C5	1.377 (8)
C1—C2	1.504 (5)	C5—C6	1.393 (8)
C2—C3	1.394 (6)	C6—C7	1.387 (6)
S1—Sn1—S1'	89.76 (6)	C7—C2—C1	122.7 (4)
C1—S1—Sn1	92.70 (13)	C2—C3—C4	120.2 (4)
O1—C1—C2	120.3 (4)	C5—C4—C3	120.1 (4)
O1—C1—S1	121.8 (3)	C4—C5—C6	120.1 (5)
C2—C1—S1	117.8 (3)	C7—C6—C5	120.2 (5)
C3—C2—C7	119.1 (4)	C6—C7—C2	120.2 (4)
C3—C2—C1	118.2 (3)		

Symmetry code: (i) $1 - x + y, 2 - x, z$.

All H atoms were placed in ideal calculated positions for the purpose of structure-factor calculations only. A common isotropic displacement parameter was refined.

Data collection: XSCANS (Siemens, 1990). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990a). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC (Sheldrick, 1990b). Software used to prepare material for publication: SHELXL93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Benzyllithium *tert*-Butyl Methyl Etherate†

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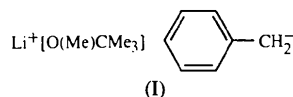
(Received 17 November 1995; accepted 19 January 1996)

Abstract

The title compound $[\text{Li}(\text{MeO}^i\text{Bu})\text{benzyl}]$, $[\text{Li}(\text{C}_7\text{H}_7)(\text{C}_5\text{H}_{12}\text{O})]$, forms infinite chains consisting of alternating lithium cations and benzyl anions, each of the latter being η^2 -coordinated through their C_α and C_{ipso} atoms to two lithium counterions.

Comment

The structure of $[\text{Li}(\text{MeO}^i\text{Bu})\text{benzyl}]$, (I) (Fig. 1), closely resembles that of $[\text{Li}(\text{OEt}_2)\text{benzyl}]$, determined previously (Beno, Hope, Olmstead & Power, 1985). Slight differences exist, mainly between the Li—C and Li—O bonds, clearly induced by the different ether coordinated to lithium. In contrast to the structure determination of $[\text{Li}(\text{OEt}_2)\text{benzyl}]$, in $[\text{Li}(\text{MeO}^i\text{Bu})\text{benzyl}]$ all H atoms could be located and refined. This enables the complete 'coordination' geometry of the benzyl-ic C_α atoms to be determined unambiguously. As a



result of the unsymmetrical η^2 -complexation of the C_α ($C7$) and C_{ipso} ($C1$) atoms of each benzyl anion by two Li atoms, the terminal C_α atoms adopt distorted trigonal bipyramidal 'pentacoordination' consisting of two H atoms and C_{ipso} in the equatorial plane (sum of the angles at C_α excluding the Li atoms: 360°) and two Li atoms in axial positions [$\text{Li}-C_\alpha-\text{Li}' = 151.6(1)^\circ$; see Fig. 1 and Table 2]. This coordination geometry of carbon was first suggested by calculations for $[\text{M}-\text{CH}_3-\text{M}]^+$ cations ($M = \text{Li}, \text{Na}$ and other metals) and could be verified in a small number of organometallic compounds (Schade, Ragué Schleyer, Dietrich & Mahdi, 1986, and references therein; Hoffmann *et al.*, 1994). The preferred coordination of benzyl anions to lithium *via* their C_α and C_{ipso} atoms was also demonstrated both by theory (Zarges, Marsch, Harms & Boche, 1989; Sygula & Rabideau, 1992, and references therein) and by structure determinations of the (pseudo)monomeric benzyllithium donor adducts $\{\text{Li}[\text{N}(\text{C}_2\text{H}_4)_3\text{N}]\text{benzyl}\}$ (Patterman, Karle & Stucky, 1970) and benzyllithium.thf.tmeda (thf = tetrahydro-

† (*tert*-Butyl methyl ether-*O*)lithium phenylmethanide.