ORFLS (Busing, Martin & Levy, 1962). All calculations were performed on an IBM 3090 computer. *ORTEP*II (Johnson, 1976) running on a Macintosh IIcx was used for the structural diagrams.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: OH1066). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(N,N-diethyldithiocarbamato-S,S')phenyltin

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Abstract

The title structure, [Sn(C₅H₁₀NS₂)₃(C₆H₅)], consists of monomeric molecular chelate complexes in which the Sn atom has distorted pentagonal bipyramidal

coordination with five S atoms in equatorial sites. One of the dithiocarbamate ligands has a short [2.570 (2) Å] and a long [2.766 (2) Å] Sn—S distance, a second dithiocarbamate ligand has almost equal Sn—S distances [2.676 (2) and 2.602 (2) Å] and the axial–equatorial dithiocarbamate ligand has a long equatorial Sn—S distance [2.757 (2) Å] and a short axial Sn—S distance [2.458 (2) Å]. The axial Sn—C distance is 2.113 (3) Å. Distortion from the idealized pentagonal bipyramid has been attributed to the steric requirements of the four-membered MS_2C ring and to the limited bite angle of the dithiocarbamate ligand.

Comment

Organotin dithiocarbamate complexes have been the subject of numerous spectroscopic and structural studies because of their industrial importance (Evans & Karpel, 1985) and their antifungal and insecticidal properties (Kumar Das, Chen & Sinn, 1985). Although extensive biological and structural studies have been conducted on the five-coordinate Sn^{IV}–dtc (dtc = dithiocarbamate) complexes, there is less information available with regard to crystal structure determinations of seven-coordinate Sn^{IV} complexes. Morris & Schlemper (1978, 1979) investigated the crystal structures of MeSn(Et₂dtc)₃ and "BuSn(Et₂dtc)₃ which each exhibit distorted pentagonal bipyramidal geometry around the Sn atom with an S atom and methyl/ethyl group in axial positions. The metal environment in the title compound differs from that of MeSn(Et₂dtc)₃ and "BuSn(Et₂dtc)₃ in that the alkyl group is replaced by the bulkier phenyl group. This change was the reason for determining the structure of the title compound, (I).

(I)
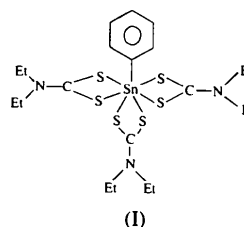
The molecular structure and atom-numbering scheme are shown in Fig. 1. The structure of the title compound consists of monomeric chelate molecules. The Sn atom is pentagonal-bipyramidally coordinated with the phenyl C atom and the S atom of one of the three dtc ligands in apical positions. One equatorial bidentate dtc ligand shows two nearly equal Sn—S bond distances [Sn—S(5) 2.676 (2) and Sn—S(6) 2.602 (2) Å]; for the anisobidentate dtc ligand there is a significant difference in the Sn—S bond distances with Sn—S(3) and Sn—S(4) having
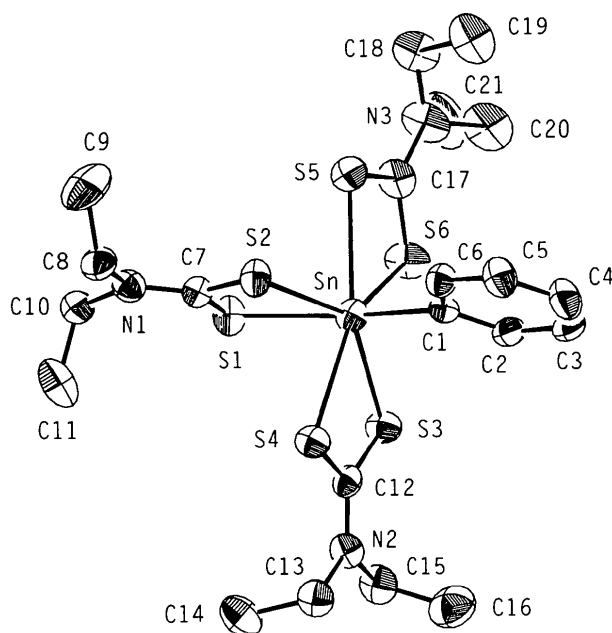
Fig. 1. Perspective drawing of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

lengths of 2.570 (2) and 2.766 (2) Å, respectively. The axial Sn—S(1) bond of 2.458 (2) Å is the shortest. All equatorial bond lengths are longer than the sum of the covalent radii (2.44 Å) and longer than the Sn—S bond distances found in less sterically hindered six-coordinate Sn—S compounds such as Sn(dtc)₄ (Harreld & Schlemper, 1971).

The deformation of the coordination polyhedron is affected by numerous factors which may include steric as well as electronic effects. A comparison of structural data of some seven-coordinate dtc complexes indicates that the distortion is usual. For instance, the axial S(1)—Sn—C(1) angle in the title compound is 164.8 (1)°, in MeSn(dtc)₃ it is 163.3 (3)°, in "BuSn(Et₂dtc)₃ 166.3 (5)° and in the diorgano–dtc chelate [MeO₂C(CH₂)₂Sn(Me₂dtc)₂]₂ 154.3 (3)° (Ng, Chen, Kumar Das, Jameson & Butcher, 1989). The equatorial S—Sn—S angles deviate significantly from the ideal value of 72° because of steric requirements and the limited bite angle of the dtc ligand. The Sn—C distance [2.113 (3) Å] is comparable to the Sn—C distances in Ph₃SnS₂CN(CH₂)₅ [2.151 (4) Å average; Chandra, James, Magee, Patalinghung, Skelton & White, 1988], Ph₂Sn{S₂CN(cyclo-C₆H₁₁)₂}Cl [2.103 (5) Å average; Basu-Baul & Tiekink, 1993] and other phenyl–Sn–dtc complexes. The least-squares data reveal that the plane composed of the atoms S(2), S(3), S(4), S(5) and S(6) is not planar, with atoms S(2) and S(5) deviating from the pentagonal girdle by −0.231 (2) and 0.203 (2) Å, respectively. The Sn

atom is 0.197 (2) Å out of this plane. The structural features of PhSn(Et₂dtc)₃ are remarkably similar to those of MeSn(Et₂dtc)₃ and "BuSn(Et₂dtc)₃. It is observed that the geometry of the SnS₆C core is similar in all cases, suggesting a neglible influence of the electronic effects of the R groups bound to the Sn atom.

Experimental

Crystals were prepared by the reaction of stoichiometric amounts of phenyltin(IV) trichloride and sodium diethylthiocarbamate in methanol. After filtration to remove the precipitated NaCl, the mixture was evaporated in vacuo. A yellow solid was recrystallized from acetone. The density D_m was measured by flotation in ZnSO₄ solution.

Crystal data

[Sn(C₅H₁₀NS₂)₃(C₆H₅)]	Mo $K\alpha$ radiation
$M_r = 640.578$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 15
$P2_1/c$	reflections
$a = 11.400$ (7) Å	$\theta = 3-6.5°$
$b = 13.680$ (9) Å	$\mu = 1.33$ mm⁻¹
$c = 18.543$ (12) Å	$T = 293$ K
$\beta = 99.10$ (5)°	Prismatic
$V = 2855$ (3) Å³	0.30 × 0.15 × 0.15 mm
$Z = 4$	Yellow
$D_x = 1.49$ Mg m⁻³	
$D_m = 1.43$ (2) Mg m⁻³	

Data collection

XP2₁ diffractometer	$\theta_{max} = 27.5°$
$\theta/2\theta$ scans	$h = 0 \rightarrow 12$
Absorption correction:	$k = 0 \rightarrow 14$
none	$l = -19 \rightarrow 19$
5797 measured reflections	2 standard reflections
5627 independent reflections	monitored every 98
2681 observed reflections	reflections
[$I > 1.96\sigma(I)$]	intensity decay: <5%
$R_{int} = 0.040$	

Refinement

Refinement on F	$w = 1/[\sigma^2(F_o) + (0.015F_o)^2]$
$R = 0.046$	$(\Delta/\sigma)_{max} = 0.15$
$wR = 0.044$	$\Delta\rho_{max} = 0.50$ e Å⁻³
$S = 1.231$	$\Delta\rho_{min} = -0.79$ e Å⁻³
2555 reflections	Atomic scattering factors
280 parameters	from International Tables
H-atom parameters not	for X-ray Crystallography
refined	(1974, Vol. IV)

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Sn	0.2251 (1)	0.2332 (1)	0.0799 (1)	4.44 (1)
S(1)	0.4328 (1)	0.2557 (1)	0.1374 (1)	5.15 (3)
S(2)	0.2980 (1)	0.4246 (1)	0.0727 (1)	5.07 (3)
S(3)	0.2720 (1)	0.0680 (1)	0.0250 (1)	4.95 (3)
S(4)	0.3171 (1)	0.2470 (1)	−0.0491 (1)	4.86 (3)

S(5)	0.1555 (1)	0.3215 (1)	0.1948 (1)	5.56 (3)
S(6)	0.1707 (1)	0.1115 (1)	0.1772 (1)	6.25 (4)
N(1)	0.5217 (2)	0.4304 (2)	0.1328 (1)	4.88 (9)
N(2)	0.3637 (2)	0.0719 (2)	−0.0960 (1)	4.54 (10)
N(3)	0.0667 (3)	0.1952 (2)	0.2781 (2)	6.92 (13)
C(1)	0.0508 (3)	0.2532 (2)	0.0233 (2)	3.71 (9)
C(2)	−0.0219 (3)	0.1736 (3)	0.0044 (2)	4.98 (12)
C(3)	−0.1359 (3)	0.1884 (3)	−0.0318 (2)	6.26 (14)
C(4)	−0.1781 (3)	0.2780 (3)	−0.0478 (2)	6.61 (14)
C(5)	−0.1046 (3)	0.3566 (3)	−0.0289 (2)	5.83 (13)
C(6)	0.0065 (3)	0.3442 (3)	0.0080 (2)	4.70 (11)
C(7)	0.4270 (3)	0.3770 (3)	0.1161 (2)	4.69 (11)
C(8)	0.5215 (3)	0.5333 (3)	0.1192 (2)	6.54 (14)
C(9)	0.4989 (5)	0.5900 (3)	0.1826 (3)	10.30 (21)
C(10)	0.6373 (3)	0.3885 (3)	0.1609 (2)	5.85 (13)
C(11)	0.7017 (4)	0.3614 (4)	0.1002 (3)	8.02 (15)
C(12)	0.3222 (3)	0.1242 (2)	−0.0471 (2)	4.30 (11)
C(13)	0.4081 (3)	0.1177 (3)	−0.1569 (2)	5.78 (13)
C(14)	0.5391 (4)	0.1309 (3)	−0.1414 (2)	7.33 (16)
C(15)	0.3649 (4)	−0.0342 (3)	−0.0944 (2)	6.01 (13)
C(16)	0.2573 (4)	−0.0745 (3)	−0.1396 (3)	9.05 (20)
C(17)	0.1252 (3)	0.2081 (2)	0.2238 (2)	5.11 (12)
C(18)	0.0282 (4)	0.2792 (3)	0.3179 (2)	6.82 (15)
C(19)	−0.0911 (4)	0.3149 (3)	0.2822 (2)	8.00 (16)
C(20)	0.0070 (4)	0.0893 (4)	0.2954 (2)	8.42 (17)
C(21)	0.0995 (5)	0.0586 (5)	0.3446 (3)	12.29 (25)

Table 2. *Selected geometric parameters* (Å, °)

Sn—S(1)	2.458 (2)	Sn—S(4)	2.766 (2)
Sn—S(2)	2.757 (2)	Sn—S(5)	2.676 (2)
Sn—S(3)	2.570 (2)	Sn—S(6)	2.602 (2)
Sn—C(1)	2.113 (3)		
C(1)—Sn—S(1)	164.8 (1)	S(1)—Sn—S(4)	84.0 (1)
C(1)—Sn—S(2)	96.9 (1)	S(1)—Sn—S(5)	89.1 (1)
C(1)—Sn—S(3)	98.9 (1)	S(1)—Sn—S(6)	95.6 (1)
C(1)—Sn—S(4)	91.0 (1)	S(2)—Sn—S(4)	74.6 (1)
C(1)—Sn—S(5)	87.9 (1)	S(2)—Sn—S(5)	74.9 (1)
C(1)—Sn—S(6)	96.8 (1)	S(3)—Sn—S(6)	78.4 (1)
S(1)—Sn—S(2)	67.9 (1)	S(3)—Sn—S(4)	65.5 (1)
S(1)—Sn—S(3)	92.0 (1)	S(5)—Sn—S(6)	66.6 (1)
S(4)—Sn—S(5)	149.2 (1)	S(4)—Sn—S(6)	143.9 (1)
S(3)—Sn—S(5)	145.0 (1)	S(2)—Sn—S(3)	137.1 (1)
S(2)—Sn—S(6)	138.5 (1)		

Data reduction was performed with the program *XP2*₁ (Pavelčík, 1987). The structure was solved by the Patterson method and refinement was on *F* by block-diagonal least squares. H atoms were placed at calculated positions and their coordinates and displacement parameters were fixed. Calculations were performed with a local version of the *NRC* system (Ahmed, Hall, Pippy & Huber, 1973) and *PARST* (Nardelli, 1983).

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