

is enough to reverse the asymmetry (4). Considering the metallaboranes, the presence of the $\{(C_5Me_5)Co\}$ moiety (6) favours bonding between the bridging H atom and B(5). However, as structural and solution NMR studies (Venable & Grimes, 1982) on this species show, this effect is not strong enough to cause any deviation in the pattern of bridging H atoms usually seen in $B_{10}H_{14}$ and its metallaborane analogues. Finally, in (7) when the metal is in the 5 position, a similar preference of the 5–6 bridging H atom towards the adjacent B atom is shown. However, a secondary effect is an increase [relative to (3)] in the asymmetry of the B(6)—B(7) bridging proton. It therefore appears that the observed *endo*-H atom at B(7) in the structure of (1) is a reflection of the directing influences of both the OEt substituent and the position of the metal.

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Structure of Di(*n*-butyl)bis(*N,N*-diethyldithiocarbamato)tin(IV) at 153 K

BY V. VRÁBEL, J. LOKAJ, E. KELLÖ AND J. GARAJ

Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Czechoslovakia

AND A. C. BATSANOV AND YU. T. STRUCHKOV

A. N. Nesmeyanov Institute of Organoelement Compounds, USSR Academy of Sciences, 28 Vavilov Street, Moscow 117813, USSR

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Abstract. $[Sn(C_4H_9)_2(C_5H_{10}NS_2)_2]$, $M_r = 529.5$, monoclinic, Pc , $a = 12.434$ (2), $b = 11.913$ (3), $c = 18.822$ (4) Å, $\beta = 115.31$ (1)°, $V = 2520.4$ (9) Å³, $Z = 4$, $D_m = 1.39$, $D_x = 1.40$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 1.34$ mm⁻¹, $F(000) = 1096$, low temperature (153 K), final $R = 0.021$ for 4225 unique observed reflections. The structures of the two crystallographically independent molecules show only minor differences. The *N,N*-diethyldithiocarbamate (dtc) ligands in both molecules are chelated to tin in an unsymmetrical fashion, with one longer (2.90–3.05 Å) and one shorter (2.50–2.55 Å) Sn—S bond. The Sn atom has a distorted octahedral environment.

Introduction. Interest in dtc complexes of diorganotin species arises in part because of their varied structures (Morris & Schlemper, 1979*a,b*; Lindley & Carr,

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1974; Lockhart, Manders & Schlemper, 1985; Lockhart, Manders, Schlemper & Zuckerman, 1986) and because of their biological activity (Bruckner, Hartel & Ger, 1961; Collins & Wiese, 1955). Crystallographic studies of these complexes have revealed a variety of coordination geometries around the Sn atom, ranging from tetrahedral to distorted octahedral. The coordination geometry depends on the bonding mode of the dtc moiety. In a continuing effort to understand the coordination chemistry of such complexes we have now determined the crystal structure of di(*n*-butyl)bis(*N,N*-diethyldithiocarbamato)tin(IV).

Experimental. The title compound was prepared by dissolving equimolar quantities of sodium *N,N*-diethyldithiocarbamate and di-*n*-butyltin dichloride

Table 1. Final positional parameters for non-H atoms and equivalent isotropic thermal parameters (\AA^2) with *e.s.d.*'s in parentheses

$B_{\text{eq}} = \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$. Coordinates for Sn and S atoms $\times 10^5$, N and C atoms $\times 10^4$.

Molecule A	x	y	z	B_{eq}
Sn	0	50018 (4)	0	1.165 (8)
S(1)	22469 (12)	51776 (11)	7830 (8)	1.93 (4)
S(2)	10010 (12)	71748 (11)	-1759 (8)	2.08 (4)
S(3)	1616 (12)	30310 (12)	5494 (8)	2.10 (4)
S(4)	-22553 (12)	8206 (12)	-5530 (8)	2.13 (4)
N(1)	3319 (4)	7090 (4)	754 (2)	2.0 (1)
N(2)	-1760 (4)	1734 (4)	-9 (3)	1.9 (1)
C(1)	2277 (5)	6559 (4)	466 (3)	1.7 (2)
C(2)	3402 (5)	8260 (5)	505 (3)	2.7 (2)
C(3)	3538 (6)	8333 (6)	-251 (4)	4.1 (2)
C(4)	4435 (5)	6582 (5)	1328 (3)	2.5 (2)
C(5)	4686 (6)	6875 (6)	2178 (3)	3.9 (2)
C(6)	-1353 (5)	2759 (4)	-19 (3)	1.8 (2)
C(7)	-3010 (5)	1417 (5)	-498 (4)	2.7 (2)
C(8)	-3784 (6)	1575 (6)	-41 (5)	4.3 (3)
C(9)	-1011 (5)	802 (5)	462 (3)	2.4 (2)
C(10)	-579 (6)	90 (5)	-22 (4)	3.0 (2)
C(11)	-671 (5)	6011 (4)	665 (3)	1.8 (2)
C(12)	-1717 (5)	6745 (4)	149 (3)	1.8 (2)
C(13)	-2149 (5)	7480 (5)	635 (3)	2.7 (2)
C(14)	-3189 (5)	8230 (5)	126 (4)	3.1 (2)
C(15)	-214 (5)	4755 (5)	-1186 (3)	2.0 (2)
C(16)	-1261 (5)	5382 (5)	-1803 (3)	2.3 (2)
C(17)	-1303 (5)	5270 (5)	-2614 (3)	2.8 (2)
C(18)	-2406 (6)	5808 (7)	-3260 (4)	4.2 (2)

Molecule B	x	y	z	B_{eq}
Sn	49650 (4)	19732 (3)	24480 (3)	1.247 (8)
S(1)	72056 (12)	18229 (11)	30637 (8)	2.00 (4)
S(2)	60003 (13)	-18 (12)	19175 (9)	2.36 (4)
S(3)	53978 (11)	37305 (12)	32579 (8)	2.03 (4)
S(4)	28495 (12)	30689 (11)	24079 (8)	2.04 (4)
N(1)	8355 (4)	227 (4)	2699 (8)	2.0 (1)
N(2)	3639 (4)	4730 (4)	3444 (2)	1.6 (1)
C(1)	7274 (4)	626 (4)	2566 (3)	1.7 (2)
C(2)	9474 (5)	801 (5)	3200 (3)	2.2 (2)
C(3)	9925 (6)	1496 (6)	2716 (4)	3.4 (2)
C(4)	8488 (5)	-854 (5)	2350 (4)	3.0 (2)
C(5)	8419 (7)	-1846 (5)	2820 (4)	4.4 (3)
C(6)	3899 (4)	3926 (4)	3062 (3)	1.5 (1)
C(7)	4544 (5)	5494 (4)	4011 (3)	2.0 (2)
C(8)	4978 (7)	5079 (6)	4847 (3)	3.1 (2)
C(9)	2414 (5)	4931 (5)	3344 (3)	2.0 (2)
C(10)	1817 (5)	5847 (6)	2736 (4)	3.3 (2)
C(11)	4374 (5)	644 (4)	2965 (3)	2.2 (2)
C(12)	3238 (5)	89 (5)	2337 (3)	2.5 (2)
C(13)	2679 (5)	757 (5)	2675 (3)	2.9 (2)
C(14)	1565 (6)	-1271 (5)	2048 (4)	3.3 (2)
C(15)	4413 (5)	2515 (5)	1252 (3)	2.0 (2)
C(16)	3337 (5)	1883 (5)	675 (3)	2.0 (2)
C(17)	2910 (5)	2308 (5)	-165 (3)	2.5 (2)
C(18)	1799 (6)	1718 (6)	-734 (4)	3.5 (2)

Table 2. Bond distances (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

	Molecule A	Molecule B
Sn—S(1)	2.550 (2)	2.525 (2)
Sn—S(2)	2.952 (1)	3.048 (2)
Sn—S(3)	2.539 (1)	2.509 (1)
Sn—S(4)	2.904 (2)	2.908 (2)
Sn—C(11)	2.145 (6)	2.146 (6)
Sn—C(15)	2.153 (5)	2.153 (5)
S(1)—C(1)	1.756 (5)	1.728 (5)
S(2)—C(1)	1.696 (6)	1.704 (6)
S(3)—C(6)	1.753 (6)	1.754 (6)
S(4)—C(6)	1.704 (6)	1.699 (5)
N(1)—C(1)	1.331 (7)	1.345 (8)
N(1)—C(2)	1.488 (7)	1.474 (7)
N(1)—C(4)	1.476 (8)	1.487 (8)
N(2)—C(6)	1.325 (7)	1.318 (7)
N(2)—C(7)	1.477 (8)	1.485 (7)
N(2)—C(9)	1.476 (7)	1.472 (8)
C(2)—C(3)	1.507 (9)	1.506 (9)
C(4)—C(5)	1.534 (8)	1.502 (9)
C(7)—C(8)	1.550 (9)	1.512 (8)
C(9)—C(10)	1.502 (9)	1.525 (8)
C(11)—C(12)	1.523 (8)	1.549 (8)
C(12)—C(13)	1.520 (8)	1.510 (9)
C(13)—C(14)	1.526 (9)	1.513 (9)
C(15)—C(16)	1.519 (8)	1.515 (8)
C(16)—C(17)	1.510 (8)	1.523 (8)
C(17)—C(18)	1.532 (9)	1.511 (9)
S(1)—Sn—S(2)	65.3 (1)	63.8 (1)
S(1)—Sn—S(3)	87.9 (1)	82.7 (1)
S(1)—Sn—S(4)	154.0 (1)	148.4 (1)
S(2)—Sn—S(3)	153.3 (1)	146.3 (1)
S(2)—Sn—S(4)	140.7 (1)	147.3 (1)
S(3)—Sn—S(4)	66.0 (1)	66.3 (1)
S(1)—Sn—C(11)	102.7 (2)	105.3 (2)
S(2)—Sn—C(11)	82.0 (2)	81.6 (2)
S(3)—Sn—C(11)	105.3 (2)	111.5 (2)
S(4)—Sn—C(11)	85.6 (2)	82.1 (2)
S(1)—Sn—C(15)	103.3 (2)	107.3 (2)
S(2)—Sn—C(15)	82.8 (2)	83.1 (2)
S(3)—Sn—C(15)	104.4 (2)	106.0 (2)
S(4)—Sn—C(15)	83.7 (2)	87.6 (2)
C(11)—Sn—C(15)	140.8 (2)	132.6 (2)
Sn—S(1)—C(1)	93.3 (2)	96.3 (2)
Sn—S(2)—C(1)	81.5 (2)	79.6 (2)
Sn—S(3)—C(6)	92.6 (2)	92.9 (2)
Sn—S(4)—C(6)	81.8 (2)	81.1 (2)
Sn—C(11)—C(1)	112.9 (4)	110.3 (4)
Sn—C(15)—C(1)	114.3 (4)	112.9 (4)
S(1)—C(1)—S(2)	119.9 (3)	120.3 (3)
S(1)—C(1)—N(1)	117.8 (4)	117.9 (4)
S(2)—C(1)—N(1)	122.4 (4)	121.8 (4)
S(3)—C(6)—S(4)	119.2 (3)	119.3 (3)
S(3)—C(6)—N(2)	118.6 (4)	117.9 (4)
S(4)—C(6)—N(2)	122.2 (4)	122.8 (4)
C(1)—N(1)—C(2)	120.3 (5)	123.4 (4)
C(1)—N(1)—C(4)	123.3 (5)	121.0 (5)
C(2)—N(1)—C(4)	116.4 (4)	115.6 (4)
C(6)—N(2)—C(7)	122.2 (5)	123.4 (4)
C(6)—N(2)—C(9)	123.7 (5)	122.0 (4)
C(7)—N(2)—C(9)	114.0 (4)	114.6 (4)
C(11)—C(12)—C(13)	111.8 (5)	113.5 (5)
C(12)—C(13)—C(14)	112.5 (5)	112.0 (5)
C(15)—C(16)—C(17)	112.2 (5)	112.9 (5)
C(16)—C(17)—C(18)	113.5 (5)	112.8 (5)
N(1)—C(2)—C(3)	113.7 (5)	111.2 (5)
N(1)—C(4)—C(5)	112.3 (5)	112.1 (5)
N(2)—C(7)—C(8)	111.1 (5)	111.8 (5)
N(2)—C(9)—C(10)	111.0 (5)	110.9 (5)

in 200 ml of ethanol. Sodium chloride precipitated from the reaction mixture immediately. When reaction was complete the mixture was filtered. The ethanol was removed by distillation under vacuum. Recrystallization from ethanol-chloroform solution gave colourless plate-like crystals. Elemental analysis found: N, 5.33; C, 40.87; S, 24.31; H, 7.24%. Calculated: N, 5.29; C, 40.83; S, 24.22; H, 7.23%.

A suitable crystal $0.3 \times 0.2 \times 0.1$ mm was mounted in the nitrogen cold stream (153 K) of a Syntex P₂ diffractometer. Density measured by flotation (in ZnSO₄ solution). 21 reflections ($17 < 2\theta < 28^\circ$) were used for measuring lattice parameters; maximum $(\sin\theta)/\lambda = 0.6 \text{ \AA}^{-1}$, intensity data ($h = 0$ to 14, $k = 0$

to 14, $l = -21$ to 21) collected with graphite-monochromated Mo K α radiation, $\theta/2\theta$ scans; three standard reflections (030, 302, 400) measured after every 100 reflections showed no systematic variation in intensity; 4304 unique reflections; Lorentz and polarization corrections but no absorption or extinction correction; no anomalous dispersion and absolute structure determination; solution by Patterson

and Fourier techniques; refined by full-matrix least squares on F with anisotropic thermal parameters for non-H atoms, using 4225 reflections with $I \geq 2.0\sigma(I)$ and $w = 1/[\sigma^2 + (0.01|F_o|)^2]$. H atoms located in difference syntheses; refinement continued on all positional parameters, anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms; in final cycle $R = 0.021$, $wR = 0.022$; because of limitations on matrix size about half of the 755 parameters were adjusted in each refinement cycle; final $\Delta\rho$ values 0.43 and $-0.36 \text{ e } \text{Å}^{-3}$, $\Delta/\sigma \leq 0.15$. All calculations performed with an Eclipse S/200 computer using the *INEXTL* programs (Gerr, Yanovsky & Struchkov, 1983). Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final positional parameters of the two crystallographically independent molecules for non-H atoms are given in Table 1* and selected distances and angles in Table 2. Fig. 1 shows a view of one of the two crystallographically independent molecules and also gives the atom-numbering scheme.

The crystal structure consists of relatively isolated complex molecules, the closest intermolecular approach (3.538 Å, including those involving H atoms) being between the methyl C atoms of the ethyl-dtc ligands of neighbouring molecules. The Sn atoms show extremely irregular octahedral coordination. The four S atoms lie in the equatorial plane, with the Sn atom located 0.0118 (2) Å (molecule *A*) and 0.0562 (4) Å (molecule *B*) from this plane. The C(11) and C(15) atoms of the butyl groups define C—Sn—C angles of 140.8 (2)° (molecule *A*) and 132.6 (2)° (molecule *B*). Adjacent S atoms subtend S—Sn—S bond angles which deviate markedly from

90°, ranging from 63.8° in the chelate ring to 147.3° for the S(2)—Sn—S(4) angle between ligands.

The Sn—S bond distances fall into two groups, with mean values of 2.545 and 2.928 Å (molecule *A*) and 2.517 and 2.978 Å (molecule *B*), indicating that the dithiocarbamate ligands are bonded to the central atom anisobidentately. The long Sn—S distances are significantly less than the sum of the van der Waals radii (4.0 Å; Bondi, 1964) and the coordination number of Sn is unambiguously assigned as six. The geometry and bond lengths of the SnC₂S₄ core are comparable with those observed for most other octahedral complexes: Me₂Sn(S₂CNEt₂)₂ (Lockhart, Manders, Schlemper & Zuckerman, 1986; Morris & Schlemper, 1979*b*), Me₂Sn[S₂CN(CH₂)₄]₂ (Lockhart, Manders & Schlemper, 1985), (*n*-Bu)₂Sn[S₂CN(CH₂)₅]₂ (Lokaj, Kellö, Kettmann, Vrabel & Rattay, 1986) and Me₂Sn(S₂CNMe₂)₂ (Kimura, Yasuoka, Kasai & Kakudo, 1972). Only in the di(*tert*-butyl)tin ethylenebis-dtc (Jung, Sohn & Ibers, 1986) and Ph₂Sn(S₂CNEt₂)₂ (Lindley & Carr, 1974) complexes is the geometry of the SnC₂S₄ core considerably different from that found here. The former compound contains one bidentate and one monodentate ethylenebis-dtc ligand which complete a distorted trigonal bipyramid about the Sn atom. In the latter both dtc ligands are bidentate so that the Sn atom is hexacoordinate but with *cis* phenyl ligands.

Corresponding bond distances and angles of the two crystallographically independent molecules are slightly different. With the exception of the terminal ethyl C atoms both dtc groups are planar within experimental error. The bond angles and distances within the N(CH₂CH₃)₂ fragments and butyl ligands are unexceptional.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54639 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0247]

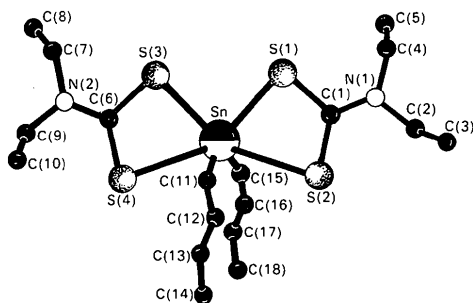


Fig. 1. The molecular structure and the atom-numbering scheme of (*n*-Bu)₂Sn(S₂CNEt₂)₂.

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