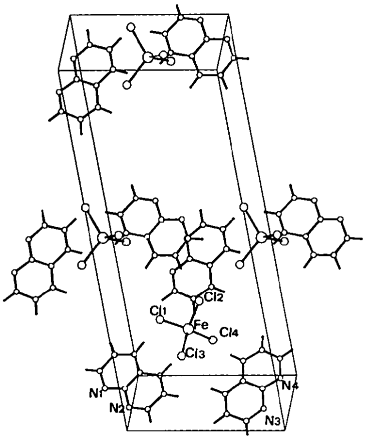

Fig. 1. A perspective view (down the *c* axis) of the contents of the unit cell.

to the C atoms were introduced at calculated positions. It has been proposed (Bacci, Dei & Morassi, 1973) that in protonated naphthyridine the proton could be symmetrically bridging between the two N atoms, but this is unlikely on account of the unfavourable energy predicted by molecular orbital calculations (Pacinotti, 1981). Thus, it is likely that only one of the two N atoms is protonated. The location of the proton is suggested from a comparison of all of the C—N—C angles in the title compound and in the structure of the free NN molecule at 163 K (Dapporto, Ghilardi, Mealli, Orlandini & Pacinotti, 1984): the average C—N—C angle is 117.0 (2)° in the latter case. The angle in question should increase if the N atom is bound to an acid (either a proton or a metal atom in a donor–acceptor relationship). This is normally observed for pyridine molecules as well. In the title compound, the angles at N(1) and N(2) of the first NN molecule are 116 (1) and 117 (1)°, respectively, while those at N(3) and N(4) of the second NN molecule are 119 (1) and 114 (1)°; N(3) is therefore the most probable host site for the proton.

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Structure of Di(*n*-butyl)bis(*N*,*N*-dipropyldithiocarbamato)tin(IV)

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Abstract. $[Sn(C_4H_9)_2(C_7H_{14}NS_2)_2]$, $M_r = 585.6$, triclinic, $P\bar{1}$, $a = 9.7836\ (7)$, $b = 12.3437\ (6)$, $c = 13.2950\ (8)$ Å, $\alpha = 101.750\ (4)$, $\beta = 103.606\ (5)$, $\gamma = 94.872\ (5)°$, $V = 1512.9\ (2)$ Å^3, $Z = 2$, $D_m = 1.28$, $D_x = 1.29$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.12$ mm^{-1}, $F(000) = 612$, room temperature, final $R = 0.044$ for 5055 unique observed reflections. The dithiocarbamate (dtc) ligands are anisobidentately chelated to tin(IV), with one longer and one shorter Sn—S bond. The overall geometry at the Sn atom is highly distorted from *trans* octahedral. Four S atoms are nearly coplanar but are greatly distorted from square-planar geometry (*cis* S—Sn—S angles range from 63.9 to 148.6°).

Introduction. Crystallographic studies of organotin dithiocarbamato complexes have revealed a variety of coordination geometries around the Sn atom.

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Thus, bis(*N*,*N*-diethyldithiocarbamato)diphenylstannane (Lindley & Carr, 1974) contains two bidentate dithiocarbamato groups giving rise to a distorted *cis*-octahedral geometry around the Sn atom, whereas in (dimethyldithiocarbamato)trimethylstannane (Sheldrick & Sheldrick, 1970; Sheldrick, Sheldrick, Dalton & Jones, 1970) and in bis(diethyldithiocarbamato)dimethylstannane (Lockhart, Manders, Schlemper & Zuckerman, 1986) coordination numbers of the Sn atoms are five and six, respectively.

In this paper we report the structure of $[(n\text{-Bu})_2Sn(S_2CNPr_2)_2]$. One aim of this work was to make a contribution to understanding the metal–ligand bonds in organotin dtc complexes.

Experimental. Colourless crystals of the title compound were prepared by dissolution of the sodium salt of dipropyldithiocarbamic acid in ethanol and adding ethanol solution of the chloride of tin dibutylene. The product was recrystallized from chloroform–ethanol. Elemental analysis found: N, 4.81; C, 45.19; S, 21.98; H, 7.96%. Calculated for $C_{22}H_{46}N_2S_4Sn$: N, 4.78; C, 45.12; S, 21.90; H, 7.96%. To obtain the intensity data a crystal 0.2 × 0.1 × 0.3 mm was chosen. Density measured by flotation in $ZnSO_4$ solution. 24 reflections ($14 < 2\theta < 26°$) were used for measuring lattice parameters; maximum $\sin\theta/\lambda = 0.765$ Å^{-1}; intensities ($h = 0$ to 13, $k = -18$ to 18, $l = -20$ to 20) measured on a Hilger & Watts Y/290 diffractometer with Mo $K\alpha$ radiation; graphite monochromator, $\omega/2\theta$ scan. Three standards measured every 100 reflections showed ±2% intensity variation; corrections for Lorentz and polarization effects, but not for absorption. 6089 reflections measured, 5055 unique, and 5055 reflections with $I \geq 2.0\sigma(I)$ considered observed and used for structure determination. Structure solved by the heavy-atom method; full-matrix least-squares refinement on F; H atoms located in difference electron density map [except H atoms of the butyl group C(19)–C(22)]; refinement continued on all positional parameters, anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms; weighting scheme $w = 1/[\sigma^2|F_o| + (0.01|F_o|)^2]$. In final cycle $R = 0.044$, $wR = 0.052$; 492 variables; maximum shift/e.s.d. = 0.16; final electron density fluctuations 0.48 and -0.42 e Å^{-3}. All calculations performed with an Eclipse S/200 computer using the *INEXTL* programs (Gerr, Yanovsky & Struchkov, 1983). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Table 1. *Final positional parameters for non-*H *atoms* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Sn	356.8 (3)	2130.3 (2)	2435.3 (2)	5.14 (1)
S(1)	1136 (1)	3404 (1)	4273 (1)	5.85 (3)
S(2)	1476 (2)	4523 (1)	2554 (1)	7.23 (4)
S(3)	−431 (1)	765 (1)	3439 (1)	5.95 (4)
S(4)	−883 (1)	−109 (1)	1122 (1)	8.16 (5)
N(1)	2348 (4)	5489 (2)	4626 (2)	5.1 (1)
N(2)	−1703 (5)	−1266 (3)	2411 (3)	7.0 (1)
C(1)	1721 (4)	4580 (3)	3870 (3)	5.2 (1)
C(2)	2576 (5)	5517 (3)	5755 (3)	5.7 (1)
C(3)	4002 (5)	5149 (4)	6227 (4)	6.7 (2)
C(4)	4201 (7)	5125 (5)	7376 (4)	9.4 (2)
C(5)	2845 (5)	6529 (3)	4354 (4)	6.0 (1)
C(6)	1716 (6)	7289 (4)	4228 (4)	7.6 (2)
C(7)	2206 (7)	8345 (4)	3979 (5)	9.4 (2)
C(8)	−1071 (5)	−311 (3)	2299 (3)	6.1 (1)
C(9)	−1900 (6)	−1446 (4)	3433 (4)	6.6 (2)
C(10)	−3308 (6)	−1127 (5)	3591 (4)	8.1 (2)
C(11)	−3556 (7)	−1383 (5)	4609 (5)	9.5 (3)
C(12)	−2401 (8)	−2190 (4)	1469 (4)	9.4 (2)
C(13)	−1400 (10)	−2992 (5)	1278 (6)	12.7 (3)
C(14)	−2176 (13)	−3928 (5)	274 (6)	17.4 (5)
C(15)	−1569 (5)	2603 (4)	1621 (3)	6.2 (1)
C(16)	−1603 (6)	2647 (4)	464 (4)	7.3 (2)
C(17)	−3010 (6)	2899 (5)	−127 (5)	9.0 (2)
C(18)	−3058 (8)	2961 (6)	−1242 (5)	11.2 (3)
C(19)	2279 (6)	1772 (6)	1975 (5)	9.8 (2)
C(20)	3479 (13)	1806 (14)	2708 (10)	12.9 (6)
C(21)	4921 (11)	1365 (8)	2448 (10)	9.3 (4)
C(22)	4714 (10)	664 (10)	1421 (8)	16.6 (5)

Discussion. Final atomic coordinates of non-H atoms and equivalent isotropic thermal parameters are listed in Table 1,* bond distances and angles in Table 2. A perspective drawing of the molecule and numbering of the atoms is shown in Fig. 1.

As in the other known diorganotin(IV) bis(dithiocarbamate) structures, the octahedral coordination in $(n\text{-Bu})_2Sn(S_2CNPr_2)_2$ is greatly distorted. The Bu—Sn—Bu angle, 132.6°, is intermediate between *cis* and *trans*. The deviations from the regular ocathedral geometry, which imply sp^3d^2 hybridization of the Sn atom, may be a result of the difference in the steric effect and the electronegativity of the ligand groups attached to the Sn atom (Kimura, Yasuoka, Kasai & Kakudo, 1972). The dtc ligands are anisobidentately chelated to Sn, with one longer and one shorter Sn—S bond. The Sn—S—C—S′ bonding system is easy to discern. The longer C—S bond is associated with the shorter Sn—S bond, and likewise, the shorter C—S′ bond is associated with the longer Sn—S′ bond (the average C—S, C—S′ and Sn—S, Sn—S′ distances are 1.744, 1.688 and 2.527, 2.979 Å, respectively). The long Sn—S distances are significantly shorter than the sum of the van der Waals radii (4.0 Å; Bondi, 1964). The Sn and four S atoms of the dtc ligands are nearly coplanar but are distorted from regular

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* 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 54694 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Sn—S(1)	2.526 (1)	N(2)—C(12)	1.490 (7)
Sn—S(2)	3.021 (2)	C(2)—C(3)	1.536 (7)
Sn—S(3)	2.528 (1)	C(3)—C(4)	1.501 (7)
Sn—S(4)	2.937 (1)	C(5)—C(6)	1.510 (7)
Sn—C(15)	2.132 (5)	C(6)—C(7)	1.478 (8)
Sn—C(19)	2.163 (6)	C(9)—C(10)	1.514 (8)
S(1)—C(1)	1.743 (4)	C(10)—C(11)	1.518 (9)
S(2)—C(1)	1.694 (4)	C(12)—C(13)	1.477 (11)
S(3)—C(8)	1.745 (4)	C(13)—C(14)	1.561 (11)
S(4)—C(8)	1.682 (4)	C(15)—C(16)	1.542 (6)
N(1)—C(1)	1.334 (5)	C(16)—C(17)	1.507 (8)
N(1)—C(2)	1.457 (5)	C(17)—C(18)	1.489 (9)
N(1)—C(5)	1.478 (5)	C(19)—C(20)	1.329 (14)
N(2)—C(8)	1.337 (6)	C(20)—C(21)	1.640 (18)
N(2)—C(9)	1.473 (6)	C(21)—C(22)	1.419 (16)
S(1)—Sn—S(2)	63.9 (1)	S(1)—C(1)—N(1)	117.6 (3)
S(1)—Sn—S(3)	82.4 (1)	S(2)—C(1)—N(1)	123.1 (3)
S(1)—Sn—S(4)	147.4 (1)	S(3)—C(8)—N(2)	117.4 (3)
S(2)—Sn—S(3)	145.9 (1)	S(4)—C(8)—N(2)	123.0 (3)
S(2)—Sn—S(4)	148.6 (1)	C(1)—N(1)—C(2)	122.4 (3)
S(3)—Sn—S(4)	65.1 (1)	C(1)—N(1)—C(5)	121.1 (3)
C(15)—Sn—C(19)	132.6 (2)	C(8)—N(2)—C(9)	123.6 (4)
C(15)—Sn—S(1)	107.5 (1)	C(8)—N(2)—C(12)	121.1 (4)
C(15)—Sn—S(2)	82.1 (1)	N(1)—C(2)—C(3)	112.4 (4)
C(15)—Sn—S(3)	104.4 (1)	N(1)—C(5)—C(6)	112.3 (4)
C(15)—Sn—S(4)	83.6 (1)	N(2)—C(9)—C(10)	110.9 (4)
C(19)—Sn—S(1)	106.3 (2)	N(2)—C(12)—C(13)	110.0 (5)
C(19)—Sn—S(2)	83.9 (2)	C(2)—N(1)—C(5)	116.4 (3)
C(19)—Sn—S(3)	112.3 (2)	C(9)—N(2)—C(12)	115.0 (4)
C(19)—Sn—S(4)	85.5 (2)	C(2)—C(3)—C(4)	112.2 (4)
Sn—S(1)—C(1)	95.9 (1)	C(5)—C(6)—C(7)	113.0 (5)
Sn—S(2)—C(1)	80.6 (2)	C(9)—C(10)—C(11)	110.9 (5)
Sn—S(3)—C(8)	93.7 (2)	C(12)—C(13)—C(14)	107.8 (6)
Sn—S(4)—C(8)	81.6 (2)	C(15)—C(16)—C(17)	112.3 (4)
Sn—C(15)—C(16)	112.8 (3)	C(16)—C(17)—C(18)	113.1 (5)
Sn—C(19)—C(20)	120.5 (7)	C(19)—C(20)—C(21)	124.3 (11)
S(1)—C(1)—S(2)	119.3 (2)	C(20)—C(21)—C(22)	114.8 (10)
S(3)—C(8)—S(4)	119.6 (3)		

square-planar geometry (*cis* S—Sn—S angles range from 63.9 to 148.6°). The small (but significant) deviations from planarity of the Sn—S_2CN ligand fragments are indicative of a small twist (< 2°) about the C—S bonds.

The crystal structure consists of relatively isolated molecules; all intermolecular distances are greater than 3.6 Å. The abnormal bond lengths and angles in one butyl ligand [C(20)—C(21)—C(22)] may be caused by the high thermal motion of corresponding atoms. The other C—C distances and angles are in keeping with those expected for single bonds.

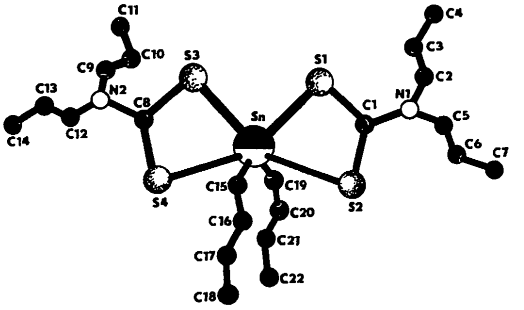

Fig. 1. Molecular structure of [$(n\text{-Bu})_2Sn(S_2CNPr_2)_2$] showing the atomic numbering scheme.

The bond angles in the dtc ligands are not unusual and are in keeping with near sp^2 hybridization of the N atoms, and C(1) and C(8). There is the usual contraction from 120° of the angles opposite the C(1)—N(1) and C(8)—N(2) bonds indicative of the high multiple bond character in these bonds. The C(1)—N(1) and C(8)—N(2) distances of 1.334 (5) and 1.337 (6) Å respectively are intermediate between the sum of the single-bond radii (Pauling, 1960) and the sum of the double-bond radii, 1.29 Å.

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5-(η-*p*-Cymene)-6-ethoxy-5-ruthena-*nido*-decaborane(12)

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Abstract. (1) $C_{12}H_{31}B_9ORu$, $M_r = 389.3$, orthorhombic, $P2_12_12_1$, $a = 11.310$ (3), $b = 18.146$ (11), $c = 18.926$ (4) Å, $V = 3884$ (3) Å^3, two independent molecules per asymmetric unit, $Z = 8$, $D_x = 1.331$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.786$ mm^{-1}, $F(000) = 1600$, $T = 291$ (1) K, $R =$

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