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**Structural studies of diorganotin(IV) bischelates.  
 Crystallographic evidence of seven-coordinate tin  
 in bis(2-carbomethoxyethyl)bis(*N,N*-  
 dimethyldithiocarbamato)tin(IV),  
 $[\text{MeOC}(\text{O})(\text{CH}_2)_2]_2\text{Sn}[\text{SC}(\text{S})\text{NMe}_2]_2$  \***

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**Abstract**

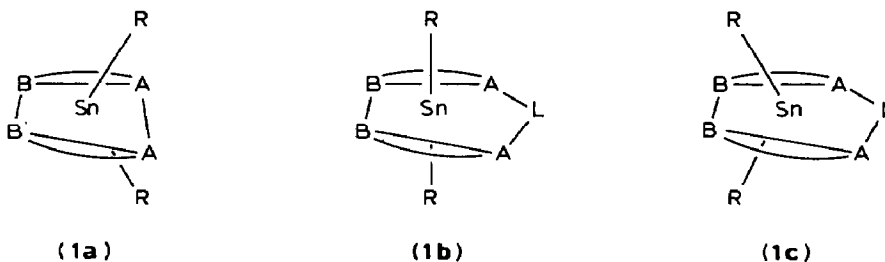
The crystal structure of bis(2-carbomethoxyethyl)bis(*N,N*-dimethyldithiocarbamato)tin(IV) was determined from 2495 observed Mo- $K_\alpha$  reflections and refined to an *R* factor of 0.053 (space group  $P2_1/c$ ; *a* 15.629(4), *b* 10.574(3), *c* 16.118(4) Å;  $\beta$  117.00(2)°; *V* 2373(1) Å<sup>3</sup>; *Z* = 4). The compound is monomeric and the tin is seven-coordinate in a distorted pentagonal bipyramid with the organic groups in apical positions (C–Sn–C 154.3(3)°); the pentagonal girdle is made up of the four sulfur atoms of the anisobidentate dithiocarbamato ligands and the carbonyl oxygen atom of a bent apical organic group (Sn–S (short) 2.571(2), 2.598(2); Sn–S (long) 2.848(2), 2.913(2); Sn–O 2.751(5) Å). The oxygen atom and one sulfur atom are displaced equally but oppositely by 0.24(3) Å from the pentagonal least-squares plane, and the tin atom by 0.054(1) Å. The compound is six-coordinate in  $\text{CDCl}_3$  solution, as shown by ambient <sup>13</sup>C NMR data; the one-bond coupling constant, <sup>1</sup>*J*(<sup>119</sup>Sn–<sup>13</sup>C), has the value 794.2 Hz, consistent with the lower coordination state. There is some evidence, however, of retention of the seven-fold coordination in pyridine solution.

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\* In memoriam Prof. Dr. J.J. Zuckerman.

## Introduction

For six-coordinate  $R_2Sn(A-B)_2$  compounds, where A-B represents an anionic bidentate chelate with the negative charge at the B end, a distorted octahedral geometry with carbon-tin-carbon bond angles in the range  $135$  to  $155^\circ$  has been labeled 'skewed-trapezoidal bipyramid' (STB) [1]. This geometry, intermediate between the *cis*- and *trans*-[ $SnR_2$ ] skeletal configurations, has been viewed as a discrete polytopal form [2] on ligand-ligand repulsion energy grounds, and it appears to be especially favored for chelates with small bite angles [2,3]. A re-interpretation of several distorted *trans*-octahedral geometries as STB has recently been advanced [4]. The STB geometry is characterized by a wide A-Sn-A angle and an inclination of the Sn-R bonds towards the long A-A edge (1a).



A coordination cavity exists in the trapezoidal plane of the structure and this can be conceivably filled by a 'pointed' donor ligand (L). Consideration of this possibility admits of a widening of the R-Sn-R angle to near-linearity (1b) or even of a backwards skewing of the R groups (1c). These expectations are borne out, for example, by the X-ray results on dimethyltin diacetate [5], which adopts an STB geometry, and the pentagonal bipyramidal anion,  $[Me_2Sn(OAc)_3]^-$  [5] which has the structure 1c. In several seven-coordinate complexes of diphenyltin nitrate with anionic [6,7] and oxygen-donor [8-11] ligands, near linear (1b) and bent (1c)  $Ph_2Sn$  skeletons have been observed. To provide a basis for a more rigorous appraisal of these structural variations, we have studied the title compound,  $[MeOC(O)(CH_2)_2]_2Sn[SC(S)NMe_2]_2$ , which carries a potential intramolecularly-coordinating bonding function in the organic R groups. The parent diorganotin dihalide,  $[MeOC(O)(CH_2)_2]_2SnCl_2$ , has been crystallographically shown to adopt a distorted *trans*-octahedral geometry (C-Sn-C  $144.1^\circ$ ) with the carbonyl oxygens of the 2-carbomethoxyethyl groups engaged in intramolecular coordination [12]. In a previous report [13], we have postulated, on spectroscopic evidence, a chelating bonding mode for the dithiocarbamate group in the title compound, but the carbonyl stretching frequencies in the infrared spectrum were interpreted in terms of negligible carbonyl coordination to tin. A six-coordinate distorted *trans*-octahedral geometry was assigned based on the magnitude of the  $^{119}Sn$  Mössbauer quadrupole splitting ( $3.30\text{ mm s}^{-1}$ ) and the apparent magnetic equivalence of the R groups as probed by  $^1H$  NMR. The 2-carbomethoxyethyl group is a potential internal chelate, and as from considerations of electronegativity and Pearson hardness the carbonyl oxygen, more than thiocarbonyl sulfur, is expected to coordinate to tin, we felt it useful to undertake an X-ray crystal study on the title compound to look for subtle structural features not discernable from solid state spectral investigations.

## X-ray analysis

Crystals of the  $[\text{MeC}(\text{O})\text{O}(\text{CH}_2)_2]_2\text{Sn}[\text{SC}(\text{S})\text{NMe}_2]_2$  [13] were grown by slow evaporation from an ethanol solution of the compound. A needle-shaped, colorless crystal of dimensions  $0.2 \times 0.2 \times 0.4$  mm was chosen and mounted on a Nicolet *P3m* automatic diffractometer with graphite-monochromatized  $\text{Mo-K}_\alpha$  radiation ( $\lambda$  0.71073 Å). Standard centering and autoindexing procedures indicated a monoclinic cell which was confirmed by axial photographs. The orientation matrix and accurate unit cell dimensions were determined from a least-squares fit of 15 reflections ( $30 < 2\theta < 35^\circ$ ) scattered evenly throughout the reciprocal space. Procedures for data collection were as previously described [14]. The intensities of 4 standard reflections ( $\bar{1}11$ , 002, 020, 200) measured after every 97 data showed no evidence of significant crystal decay during the entire data collection. Redundant and equivalent reflections were averaged and converted to unscaled  $|F_o|$  values, following corrections for Lorentz and polarization factors. The structure was solved by direct methods using the MULTAN-82 program. Full-matrix least-squares refinement followed by difference Fourier synthesis revealed the positions of all atoms except two hydrogen atoms on C(14) which experiences vibrational disorder along the O–C bond. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned isotropic temperature factors equal to 1.2 of their respective parent carbon atoms. All computations were performed on a PDP11/73 minicomputer with the TEXRAY program package [15]. The atomic scattering factors were taken from ref. 16. The effects of anomalous dispersion for all non-hydrogen atoms were included in  $|F_o|$  [17,18]. The final *R* indices and data processing parameters are listed in Table 1. Positional and thermal parameters of the nonhydrogen atoms are listed in Table 2 in accordance with the labeling scheme of Fig. 1. Selected bond distances and bond angles are given in Table 3. A complete listing of the bond dimensions along with least-squares planes, tables of hydrogen atom coordinates, anisotropic temperature parameters and structure factors are available from the authors on request.

## Discussion

The atomic labeling for the molecular structure of bis(2-carbomethoxyethyl)bis(*N,N*-dimethyldithiocarbamato)tin is given in Fig. 1. The tin atom is seven-coordinated: the two 2-carbomethoxyethyl groups (Sn–C 2.133(8), 2.136(8) Å) subtend an angle of  $154.3(3)^\circ$  at the metal center and the two negatively charged sulfur atoms make strong bonds to tin (Sn–S 2.571(2), 2.598(2) Å) whereas the other two thiocarbonyl sulfur atoms are less strongly bonded to tin (Sn–S 2.848(2), 2.913(2) Å). The four sulfur atoms and the tin atom comprise a flat trapezoidal plane with apical connectivity of the organic groups. The seventh coordination site is occupied by the carbonyl oxygen, O(3), of one of the two 2-carbomethoxyethyl groups at a distance of 2.751(5) Å from the tin to form a five-membered internally chelated ring. The carbonyl oxygen of the other apical organic groups does not bend back to coordinate. The overall geometry at tin is thus seen to be a distorted pentagonal bipyramid.

Although in comparison with other 3-oxopropyltin compounds  $[\text{ROC}(\text{O})-(\text{CH}_2)_2]_n\text{SnCl}_{4-n}$  ( $n = 2, 3$ ) [12,19,20], the Sn–O distance of 2.751(5) Å in the title compound is 0.2–0.4 Å longer, it is nevertheless well within the van der Waals limit

Table 1

Data processing parameters for bis(2-carbomethoxyethyl)bis(*N,N*-dimethyldithiocarbamato)tin

Molecular formula	C <sub>14</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub> S <sub>4</sub> Sn
Molecular weight	533.32
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Cell constants	<i>a</i> 15.629(4) Å <i>b</i> 10.574(3) Å <i>c</i> 16.118(4) Å $\beta$ 117.00(2)° <i>V</i> 2373(1) Å <sup>3</sup>
<i>Z</i>	4
<i>D</i> <sub>m</sub>	1.46 g cm <sup>-3</sup> (flotation in KI/H <sub>2</sub> O)
<i>D</i> <sub>c</sub>	1.49 g cm <sup>-3</sup>
Temperature	23 ± 1 °C
$\mu$	14.38 cm <sup>-1</sup>
Collection range	<i>h</i> : -20 to 13; <i>k</i> : 0 to 14; <i>l</i> : 0 to 22
Unique reflections	6676
Unobserved reflections	4181; criterion $ F_o  < 3\sigma( F_o )$
Variables	226
<i>R</i>	0.053
<i>R</i> <sub>w</sub>	0.064
$\omega$	$4(F_o)^2/[\sigma(F_o)]^2$
Max. shift/error	0.59
Final difference Fourier map	max. 0.81 e Å <sup>-3</sup> ; min. -0.48 e Å <sup>-3</sup>
<i>F</i> (000)	1080

of 3.70 Å. As carbonyl donors are generally weak Lewis bases compared to other oxygen donor ligands such as phosphine oxides, sulfoxides or amine oxides, a limiting tin–oxygen distance is to be expected for carbonyl systems that are least able to disperse the positive charge on carbon [21]. The question of whether a carbonyl oxygen is engaged in coordination to tin in organotin structures is often enigmatic. Thus, whereas a distance of 3.206 Å is claimed as a bonding interaction in Ph<sub>3</sub>SnOAc [22], a contact of 2.929 Å in Cyh<sub>3</sub>Sn(indolyl-3-acetate) [23] is not. Also, values in the range 2.564 to 2.861 Å found for substituted benzoates of triphenyltin [24], wherein the carbonyl oxygens are proximately located on the tetrahedral face of the coordination polyhedron, have been viewed as essentially non-bonding [25,26]. An even shorter contact of 2.463 Å in a triorganotin arylazo-benzoate, originally reported as an equatorial Sn–O bonding interaction in a *cis*-C<sub>3</sub>SnO<sub>2</sub> trigonal bipyramidal configuration [27], has been similarly discounted [28]. For two tricyclohexyltin carboxylates, the intermolecular Sn–O distance [29,30] exceeds the sum of the van der Waals radii of the two atoms, but the structures have been classified as weak polymers [27,31]. Clearly, the parameter that is more important than Sn–O distance in deciding whether a carbonyl oxygen is engaged in coordination or not is the spatial orientation of this atom in the coordination polyhedron around the tin center. Given the constraints of an internal chelate, we note that the Sn–O bond distance in our compound is only about 0.1 Å larger than that found in the salicylaldehyde adduct of Me<sub>2</sub>SnCl<sub>2</sub> [32]. In six-coordinate [MeOC(O)(CH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>SnCl<sub>2</sub>, the chelating 2-carbomethoxyethyl group makes Sn–O bonds of 2.52 Å [12], whereas in five coordinate MeOC(O)(CH<sub>2</sub>)<sub>2</sub>SnCl<sub>3</sub>, the Sn–O

Table 2

Positional and thermal parameters for bis(2-carbomethoxyethyl)bis(*N,N*-dimethyldithiocarbamato)tin

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub> (Å <sup>2</sup> ) <sup>a</sup>
Sn	0.72525(4)	0.30460(6)	0.05104(4)	4.52(1)
S(1)	0.7685(2)	0.4855(2)	-0.0297(1)	5.50(6)
S(2)	0.5792(2)	0.3632(3)	-0.1308(2)	6.28(7)
S(3)	0.9039(2)	0.3320(3)	0.1726(2)	6.33(7)
S(4)	0.7869(2)	0.1492(3)	0.2176(2)	7.00(7)
O(1)	0.7692(6)	-0.0578(9)	-0.1191(7)	18.8(3)
O(2)	0.8937(5)	0.0307(7)	-0.1130(5)	9.7(2)
O(3)	0.5570(4)	0.1926(6)	0.0280(4)	6.8(2)
O(4)	0.4427(4)	0.2448(8)	0.0679(5)	8.7(2)
N(1)	0.6377(6)	0.5563(7)	-0.1975(4)	6.2(2)
N(2)	0.9708(5)	0.1968(9)	0.3277(5)	7.5(2)
C(1)	0.6562(6)	0.4754(8)	-0.1299(5)	4.9(2)
C(2)	0.5501(8)	0.548(1)	-0.2835(6)	8.8(4)
C(3)	0.7021(9)	0.655(1)	-0.1939(7)	9.0(4)
C(4)	0.8943(6)	0.2213(9)	0.2481(5)	5.9(2)
C(5)	1.0615(8)	0.257(1)	0.3565(8)	9.8(4)
C(6)	0.9665(8)	0.104(1)	0.3953(7)	9.4(4)
C(7)	0.7450(6)	0.1361(9)	-0.0110(6)	5.7(2)
C(8)	0.7995(7)	0.149(1)	-0.0654(6)	6.3(2)
C(9)	0.8199(7)	0.030(1)	-0.0989(6)	7.5(3)
C(10)	0.9182(9)	-0.084(1)	-0.1471(8)	11.1(4)
C(11)	0.6549(6)	0.421(1)	0.1099(6)	6.4(3)
C(12)	0.5898(6)	0.355(1)	0.1404(6)	6.7(3)
C(13)	0.5298(6)	0.257(1)	0.0721(6)	6.0(2)
C(14)	0.3602(8)	0.167(1)	-0.0171(9)	16.3(4)

$$^a B_{\text{iso}} = \frac{4}{3}[a^2 B_{1,1} + b^2 B_{2,2} + c^2 B_{3,3} + ab \cos \gamma B_{1,2} + ac \cos \beta B_{1,3} + bc \cos \alpha B_{2,3}]$$

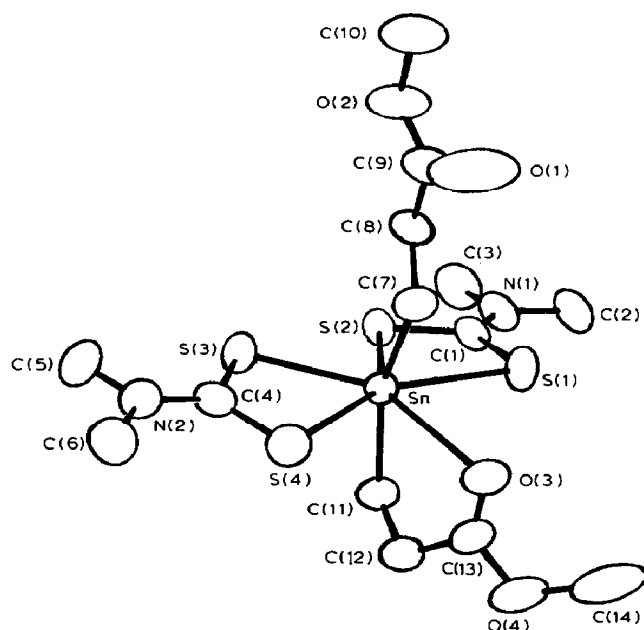
Fig. 1. Molecular structure of [MeOC(O)(CH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Sn[SC(S)NMe<sub>2</sub>]<sub>2</sub>.

Table 3

Selected bond lengths (Å) and bond angles (°) in bis(2-carbomethoxyethyl)bis(*N,N*-dimethyldithiocarbamate)tin

Sn–S(1)	2.571(2)	Sn–S(2)	2.848(2)	Sn–S(3)	2.598(2)
Sn–S(4)	2.913(2)	Sn–O(3)	2.751(5)	Sn–C(7)	2.133(8)
Sn–C(11)	2.136(8)				
S(1)–Sn–S(2)	65.74(6)	S(1)–Sn–S(3)	81.92(7)		
S(1)–Sn–S(4)	146.45(7)	S(1)–Sn–O(3)	135.0(1)		
S(1)–Sn–C(7)	104.9(2)	S(1)–Sn–C(11)	96.0(2)		
S(2)–Sn–S(3)	146.80(7)	S(2)–Sn–S(4)	147.81(7)		
S(2)–Sn–O(3)	71.6(1)	S(2)–Sn–C(7)	85.3(2)		
S(2)–Sn–C(11)	89.9(2)	S(3)–Sn–S(4)	64.88(7)		
S(3)–Sn–O(3)	141.6(1)	S(3)–Sn–C(7)	96.4(2)		
S(3)–Sn–C(11)	101.2(2)	S(4)–Sn–O(3)	77.1(1)		
S(4)–Sn–C(7)	84.4(2)	S(4)–Sn–C(11)	86.3(2)		
O(3)–Sn–C(7)	84.8(2)	O(3)–Sn–C(11)	69.8(2)		
C(7)–Sn–C(11)	154.3(3)	Sn–S(1)–C(1)	92.2(3)		
Sn–S(2)–C(1)	84.8(3)	Sn–S(3)–C(4)	92.7(3)		
Sn–S(4)–C(4)	83.3(3)	Sn–O(3)–C(13)	104.5(4)		
Sn–C(7)–C(8)	116.3(5)	Sn–C(11)–C(12)	116.6(6)		

bond is 2.347 Å [12] \*. The relatively longer Sn–O bond in the title compound is thus not inconsistent with the higher coordination status envisaged at tin.

Keperť [33] in the semi-theoretical treatment of seven-coordination in metal complexes has described three major stereochemistries for the system [M(unidentate)(bidentate)<sub>3</sub>], defined as follows:

Stereochemistry A:  $\phi_C \gg \phi_B$ ;  $\phi_E \gg \phi_D$ ;  $\phi_G \gg \phi_F$

Stereochemistry B:  $\phi_C \sim \phi_B$ ;  $\phi_E \gg \phi_D$ ;  $\phi_G \gg \phi_F$

Stereochemistry C:  $\phi_C \sim \phi_B$ ;  $\phi_E \gg \phi_D$ ;  $\phi_G \sim \phi_F$

The unidentate ligand A is placed at  $\phi = 0$ , and the bidentate ligands are labeled BC, DE and FG, with  $|\phi_D - \phi_E| \gg |\phi_F - \phi_G| \gg |\phi_B - \phi_C|$ . In this model, the  $\phi$  parameters for the title complex are  $\phi_B = 96.4$ ,  $\phi_C = 84.4$ ,  $\phi_D = 84.8$ ,  $\phi_E = 154.3$ ,  $\phi_F = 85.3$  and  $\phi_G = 104.9^\circ$ , where A = C(7), B = S(3), C = S(4), D = O(3), E = C(11), F = S(2) and G = S(1). The order is closest to stereochemistry C which contains a mirror plane through C(7)–O(3)–C(11), and which is intermediate between a pentagonal bipyramid and a capped trigonal prism. This stereochemistry appears to be favored for normalized bites *b* between 1.0 and 1.1 (*b* for S(1)–S(2) is 1.09, for S(3)–S(4) is 1.08 and for C(11)–O(3) is 1.16). A gross description of the overall geometry as a distorted pentagonal bipyramid thus appears appropriate.

The least-squares planes data for the title compound reveal that the plane made up of the S(1), S(2), S(3), S(4) and O(3) atoms is not flat, but is folded along the S(2)–S(4) edge into the shape of an envelope. The dihedral angle between the S(1), S(2), S(3), S(4) and S(2), S(4), O(3) planes is 15.8(8)°. Consideration of the OS<sub>4</sub> pentagonal least-squares plane shows that the O(3) and S(2) atoms are equally but oppositely displaced out of it by 0.24(3) Å and the Sn atom by 0.054(1) Å.

\* Note added in proof: A chelating 2-carbomethoxyethyl group (Sn–O: 2.847(4) Å) has also been observed in bis(2-carbomethoxyethyl)chlorotinolate [S.W. Ng, Chen Wei, V.G. Kumar Das, J.-P. Charland and F.E. Smith, *J. Organomet. Chem.*, 364 (1989) 363].

Table 4

Structural data for seven-coordinate diorganotin compounds

Diorganotin compound <sup>a</sup>	Sn-C (Å)	C-Sn-C (°)	Angles in pentagonal plane (°)	Sum of angles (°)	Ref.
[Me <sub>2</sub> Sn(OAc) <sub>3</sub> ][NMe <sub>4</sub> ]·2CHCl <sub>3</sub>	2.113, 2.129	165.8	53.7, 54.2, 78.2, 84.6, 89.1	359.8	5
Me <sub>2</sub> Sn(O <sub>2</sub> CC <sub>5</sub> H <sub>4</sub> N-2) <sub>2</sub>	2.100, 2.112	174.5	66.2, 69.8, 72.4, 74.6, 77.5	360.5	<sup>b</sup>
[Ph <sub>2</sub> Sn(NO <sub>3</sub> ) <sub>2</sub> Cl][Ag(PPh <sub>3</sub> ) <sub>4</sub> ]	2.08, 2.14	164.2	49.7, 51.7, 82.1, 86.5, 90.3	360.3	6
[Ph <sub>2</sub> Sn(NO <sub>3</sub> ) <sub>2</sub> Cl][Ag(AsPh <sub>3</sub> ) <sub>4</sub> ]	2.13, 2.14	159.3	48.0, 50.2, 85.2, 85.5, 91.2	360.1	7
[Ph <sub>2</sub> Sn(n-Pr <sub>2</sub> SO)(NO <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	2.115, 2.116	176.8	53.0, 73.0, 73.2, 79.2, 81.6	360.0	8
Ph <sub>2</sub> Sn(NO <sub>3</sub> ) <sub>2</sub> ·Ph <sub>3</sub> PO	2.07, 2.124	178.0	54.4, 54.7, 80.5, 85.1, 85.4	360.1	9
Ph <sub>2</sub> Sn(NO <sub>3</sub> ) <sub>2</sub> ·Ph <sub>3</sub> AsO	2.107, 2.110	156	50.6, 51.6, 79.3, 81.5, 97.0	360.0	11
Ph <sub>2</sub> Sn(NO <sub>3</sub> ) <sub>2</sub> ·cdppoet·CHCl <sub>3</sub>	2.120, 2.130	169.2	51.6, 67.9, 72.2, 78.0, 90.2	359.9	10
[Ph <sub>2</sub> Sn(NO <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> ·tdppoet·2H <sub>2</sub> O	2.101, 2.109	173.3	54.6, 54.7, 79.5, 81.3, 89.8	359.9	10
Ph <sub>2</sub> Sn(NO <sub>3</sub> ) <sub>2</sub> ·dppom	2.103, 2.113	178.7	51.9, 72.1, 74.1, 79.5, 82.5	360.1	<sup>c</sup>
Ph <sub>2</sub> Sn(daps)	2.170, 2.182	176.4	67.5, 68.0, 69.2, 69.6, 85.8	360.1	<sup>d</sup>
[Ph <sub>2</sub> Sn(Me <sub>2</sub> SO) <sub>3</sub> (NO <sub>3</sub> )][NO <sub>3</sub> ]	2.15, 2.16	172.1	51.7, 72.5, 77.0, 78.3, 80.5	360.0	<sup>e</sup>
Me <sub>2</sub> Sn(NCS) <sub>2</sub> ·terpy	2.091, 2.119	173.7	64.5, 65.3, 76.5, 76.8, 78.3	359.4	<sup>f</sup>
Et <sub>2</sub> SnCl <sub>2</sub> ·L'	2.125, 2.138	150.4	55.8, 57.4, 78.8, 80.5, 87.6	360.1	34
n-Pr <sub>2</sub> Sn(daps)	2.11, 2.14	170.4	66.7, 67.8, 67.9, 68.2, 89.3	359.9	<sup>g</sup>
n-Bu <sub>2</sub> SnCl <sub>2</sub> ·AIP	2.13, 2.18	158.3			<sup>h</sup>
[MeOC(O)(CH <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub>	2.133(8)	154.3(3)	64.88(7), 65.74(6), 71.6(1),	361.2(5)	this
Sn[SC(S)NMe <sub>2</sub> ] <sub>2</sub>	2.136(8)		77.1(1), 81.92(7)		work

<sup>a</sup> cdppoet = *cis*-1,2-bis(diphenylphosphoryl)ethylene; tdppoet = *trans*-1,2-bis(diphenylphosphoryl)ethylene; dppom = bis(diphenylphosphoryl)methane; L' = 2-(5-methyl-1,2,4-oxadiazol-3-yl)-1,10-phenanthroline; terpy = 2:2', 6':2''-terpyridine, daps = 2,6-diacetylpyridine bis(salicyloylhydrazone); AIP = 2-(2'-pyridyl)-3-(*N*-2-picolylimino)-4-oxo-1,2,3,4-tetrahydroquinazoline. <sup>b</sup> T.P. Lockhart and F. Davidson, *Organometallics*, 6 (1987) 2471. <sup>c</sup> S. Dondi, M. Nardelli, C. Pelizzi, G. Pelizzi and G. Predieri, *J. Organomet. Chem.*, 308 (1986) 195. <sup>d</sup> C. Pelizzi, G. Pelizzi and G. Predieri, *J. Organomet. Chem.*, 263 (1984) 9. <sup>e</sup> L. Coghi, C. Pelizzi and G. Pelizzi, *Gazz. Chim. Ital.*, 104 (1974) 1315; *J. Organomet. Chem.*, 114 (1976) 53. <sup>f</sup> D.V. Naik and W.R. Scheidt, *Inorg. Chem.*, 12 (1973) 272. <sup>g</sup> C. Pelizzi and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, (1972) 1970. <sup>h</sup> C. Pelizzi, G. Pelizzi and P. Tarasconi, *Polyhedron*, 2 (1983) 145.

A comparison of the structural data of the title compound with those of other pentagonal bipyramidal diorganotin structures (Table 4), however, indicates that the distortion cannot be regarded as being particularly severe. The sum of the angles subtended at tin in the pentagonal girdle is largest for the title compound; nevertheless, the angles do not deviate much from the idealized value of 72°. In Et<sub>2</sub>SnCl<sub>2</sub>·[2-(5-MeC<sub>2</sub>N<sub>2</sub>O)-1,10-phen], the three Sn-N bonds are very long (2.86, 2.95 and 3.01 Å) [34], so that the pentagonal girdle is even more unsymmetrical.

In solution, the ambient-temperature <sup>13</sup>C NMR spectrum of the title compound, [C<sup>4</sup>H<sub>3</sub>OC<sup>3</sup>(O)C<sup>2</sup>H<sub>2</sub>C<sup>1</sup>H<sub>2</sub>]<sub>2</sub>Sn[SC<sup>5</sup>(S)N(C<sup>6</sup>H<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, revealed only one set of carbon resonances (C<sup>1</sup> 31.9, C<sup>2</sup> 30.8, C<sup>3</sup> 176.1, C<sup>4</sup> 51.9, C<sup>5</sup> 201.8, C<sup>6</sup> 44.6 ppm) and a value of 794.2 Hz for the one-bond coupling constant, <sup>1</sup>J(<sup>119</sup>Sn-<sup>13</sup>C). This value compares closely to that obtained (790 Hz) for [n-BuOC(O)(CH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>SnCl<sub>2</sub>, for which a six-coordinate *trans*-[SnR<sub>2</sub>] octahedral geometry was proposed [35]. A retention of octahedral geometry in solution has also been proposed for [MeOC(O)(CH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>SnCl<sub>2</sub> based on IR and <sup>1</sup>H NMR evidence [12,36]. In deuterated pyridine (C<sub>5</sub>D<sub>5</sub>N), the resonances associated with the C<sup>1</sup>, C<sup>2</sup> and C<sup>3</sup> carbons in the title compound are split, but the one-bond coupling could not be discerned: C<sup>1</sup> 31.6, 31.7; C<sup>2</sup> 33.1, 33.3; C<sup>3</sup> 176.3, 176.5; C<sup>4</sup> 52.1; C<sup>5</sup> 202.0; C<sup>6</sup> 44.7 ppm. This feature suggests a

possible seven-coordinate tin environment in the pyridine medium, although, however, the influence of solvent anisotropy cannot be excluded in the absence of more detailed, variable-temperature, spectral studies.

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