Derivatives of Bivalent Germanium, Tin, and Lead. Part XVI.[1] Crystal and Molecular Structure of Tin(II) Bis(*O*-methyl dithiocarbonate)

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The structure of the title compound has been determined from diffractometer data by Patterson and Fourier techniques. Crystals are monoclinic, space group $P2_1/c$, a = 12.3328(9), b = 4.4283(8), c = 19.4710(9) Å, β = 106.799(1)°, Z = 4. Discrete molecules are stacked parallel to the c axis. Each tin atom is chelated by two *O*-methyl dithiocarbonato-groups resulting in pseudo-trigonal bipyramidal geometry at tin, the lone pair occupying an equatorial site. The Sn–S(ax) bond distances are longer [2.817(4) Å] than Sn–S(eq) [2.623(3) Å], and the S–Sn–S(ax) and S–Sn–S(eq) valence-bond angles are reduced from ideality to 140.8(1) and 99.3(1)°.

PREVIOUSLY we have discussed the spectroscopic properties and structures of tin(II) derivatives of the potentially bidentate β-ketoenolato-ligands.[2,3] In all cases studied, the β-ketoenolato-residue did indeed function as a bidentate ligand towards tin, and [Sn(OCPh·CH·COMe)$_2$] was shown to possess a structure involving distorted pseudo-trigonal bipyramidal geometry at the metal with the lone pair of electrons occupying an equatorial site.[3] Such a geometry is, however, by no means universal for all potentially bidentate oxygen ligands towards bivalent tin. Thus, whilst the tin atoms enjoy a three-co-ordinate pyramidal geometry in tin(II) sulphate,[4] co-

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[1] Part XV, A. B. Cornwell, P. G. Harrison, and J. A. Richards, *J. Organometallic Chem.*, 1976, **108**, 47.

[2] P. F. R. Ewings, D. E. Fenton, and P. G. Harrison, *J.C.S. Dalton*, 1975, 821.

[3] P. F. R. Ewings, P. G. Harrison, and T. J. King, *J.C.S. Dalton*, 1975, 1455.

[4] J. D. Donaldson and D. C. Puxley, *Acta Cryst.*, 1972, **B28**, 864.

ordination numbers of up to seven have been observed for carboxylatotin(II) derivatives.[5-7] Both sulphato- and carboxylato-derivatives involve bridging and/or bidentate groups.

To date, the only available structures involving bonds between bivalent tin and sulphur are those of SnS,[8] Sn_2S_3,[9] and $BaSnS_2$,[10] which have distorted NaCl-type lattices, $Sn(tu)_2SO_4$ (tu = thiourea),[11] and bis(diethyldithiocarbamato)tin(II).[12] This latter compound, together with several dithiocarbamato-,[13] *O*-methyl dithiocarbonato-,[14,15] and dithiophosphoridato-lead(II) [16] derivatives,* also has a structure very similar to that of [Sn(OCPh·CH·COMe)$_2$].[3] The pyridine solvate of bis(*O*-isopropyl dithiocarbonato)lead(II) [18] is not strictly comparable, since the Pb–N distance [2.55(4) Å] is short enough to represent a bonding interaction, and hence realise some perturbation on the otherwise pseudo-trigonal bipyramidal geometry at lead. As in the case of bidentate oxygen ligands and divalent tin, other geometries are also possible with bidentate sulphur ligands and divalent lead; and bis(*OO'*-di-isopropyl phosphorodithiolato)lead(II) has a chain structure in which each lead atom is co-ordinated by six sulphur atoms in a pseudo-pentagonal bipyramidal arrangement with the lone pair occupying an equatorial position.[19]

We have previously [20] measured the tin-119m Mössbauer spectra of the two closely related compounds, bis(diethyldithiocarbamato)tin(II) and bis(*O*-methyl dithiocarbonato)tin(II), and, from their quite different isomer shifts and quadrupole splittings, we inferred that the latter compound might possess a substantially different geometry from the dithiocarbamate derivative, the structure of which has already been determined.[12] We therefore undertook an *X*-ray diffraction study of bis(*O*-methyl dithiocarbonato)tin(II), the results of which we now report.

EXPERIMENTAL

Pale yellow crystals of [Sn(S$_2$COMe)$_2$] suitable for intensity measurements were obtained by recrystallisation from hot ethanol–tetrahydrofuran (1 : 1) of the product from the reaction of $SnCl_2$ with two moles of potassium *O*-methyl dithiocarbonate in the same solvent (Found: C, 14.34; H, 1.79%. Calc. for $C_4H_6O_2S_4Sn$: C, 14.42; H, 1.81%). The crystals are air sensitive, but stable to *X*-rays, and a specimen of dimensions *ca.* 0.2 × 0.3 × 0.6 mm was mounted under nitrogen in a Lindemann capillary and used for both the initial photography and subsequent intensity data collection.

Crystal Data.—$C_4H_6O_2S_4Sn$, $M = 333.037$, $a = 12.3328(9)$, $b = 4.4283(8)$, $c = 19.4710(9)$ Å, $\beta = 106.979(1)°$, $U = 1\,017.02$ Å^3, $Z = 4$, $F(000) = 396$. μ(Mo-K_α) = 3.25 cm^{-1}. Space group $P2_1/c$ from systematic absences: $h0l$, $l = 2n$, and $0k0$, $k = 2n$.

The space group and initial cell parameters were determined from oscillation and first- and second-layer Weissenberg photographs obtained on an equi-inclination Weissenberg camera. Relative intensities were collected up to θ 27.50° with monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å) by use of a Hilger and Watts Y 290 four-circle diffractometer. Accurate cell dimensions were obtained by least-squares refinement of *ca.* 20 reflections. Each of 2 689 reflections was counted for 20 s and the two associated background counts for 10 s. The reflections were brought to the same relative intensities by reference reflections monitored every 100 reflections, the orientation of the diffractometer being checked for every 200 reflections recorded. Background counts were low and were subtracted in the usual manner. All reflections with a corrected count of $I < 3\sigma(I)$ were considered unobserved and were not used, reducing the number of reflections from 2 689 to 1 967. Intensities were corrected for Lorentz and polarisation effects; no absorption correction was made due to the low μ value.

Structure Determination and Refinement.—The position of the tin atom in the asymmetric unit was determined from a three-dimensional Patterson synthesis, and the co-ordinates thus obtained were used to phase the initial structure-factor calculation. A Fourier synthesis established three of the four sulphur atom positions, and the positions of these and the tin atom were further refined by two cycles of isotropic block-diagonal least-squares. A second Fourier synthesis at this stage yielded the position of the fourth sulphur atom, and another two cycles of isotropic block-diagonal least-squares refinement followed by a further Fourier synthesis afforded the remaining six non-hydrogen light atom positions. Two cycles of isotropic block-diagonal and four cycles of anisotropic full-matrix least-squares refinement gave *R* 0.087. At this stage the weighting scheme $w = (A/F_o)^2$ where $A = 42.0$ was applied, and two further cycles of anisotropic full-matrix least-squares refinement gave a final *R* of 0.073. Scattering factors used were those for neutral atoms.[21] Final fractional atomic co-ordinates are listed in Table 1, intramolecular bond distances and angles in Tables 2 and 3. Calculations were performed by use of the ' *X*-Ray '70 ' suite of programmes.[22] Final observed and calculated structure factors and anisotropic

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* The partial structure of bis(diethyldithiocarbamato)lead(II) determined by two-dimensional methods [17] bears no relationship to the full structure determination,[10] and is most probably in error.

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[21] ' International Tables for *X*-ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[22] ' *X*-Ray ' system of programs, University of Maryland Report, version of 1970.

thermal parameters are listed in Supplementary Publication No. SUP 21671 (6 pp., 1 microfiche).*

TABLE 1

Final fractional atomic co-ordinates, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Sn(1)	0.777 01(8)	0.468 74(17)	0.247 48(9)
S(1)	0.833 5(2)	0.089 3(7)	0 354 2(2)
S(2)	0.669 8(2)	0.094 8(7)	0.144 1(1)
S(3)	0.603 6(2)	0.354 6(9)	0.310 3(2)
S(4)	0.918 6(2)	0.166 2(8)	0.178 0(2)
C(1)	0.783 5(5)	−0.047 8(20)	0.058 9(3)
O(2)	0.698 1(5)	0.046 1(20)	0.429 2(4)
O(1)	0.793 7(7)	0.065 3(22)	0.123 3(4)
C(2)	0.705 4(7)	0.159 6(23)	0.368 0(4)
C(3)	0.884 4(9)	−0.077 7(35)	0.034 1(6)
C(4)	0.592 7(9)	0.086 3(40)	0.448 0(7)

TABLE 2

Intramolecular bond distances (Å), with estimated standard deviations in parentheses

Sn–(S1)	2.603(3)	S(4)–C(1)	1.672(8)
Sn–S(2)	2.644(3)	S(3)–C(2)	1.662(9)
Sn–S(4)	2.813(3)	C(1)–O(1)	1.322(12)
Sn–S(3)	2.802(4)	C(2)–O(2)	1.320(12)
S(1)–C(2)	1.707(10)	O(1)–C(3)	1.467(15)
S(2)–C(1)	1.695(10)	O(2)–C(4)	1.461(15)

TABLE 3

Intramolecular bond angles (°) with estimated standard deviations in parentheses

S(1)–Sn–S(2)	99.3(1)	Sn–S(3)–C(2)	82.4(3)
S(1)–Sn–S(4)	90.4(1)	S(2)–C(1)–S(4)	122.9(5)
S(1)–Sn–S(3)	66.2(1)	S(2)–C(1)–O(1)	114.3(4)
S(2)–Sn–S(4)	65.6(1)	S(4)–C(1)–O(1)	122.8(4)
S(2)–Sn–S(3)	86.8(1)	C(1)–O(1)–C(3)	119.4(7)
S(4)–Sn–S(3)	140.8(1)	S(1)–O(2)–S(3)	122.6(6)
Sn–S(1)–C(2)	87.9(3)	S(1)–C(2)–O(2)	112.6(6)
Sn–S(2)–C(1)	86.8(3)	S(3)–C(2)–O(2)	124.8(7)
Sn–S(4)–C(1)	81.8(3)	C(2)–O(2)–C(4)	118.7(6)

DISCUSSION

Crystals of the title compound are composed of stacks of independent molecules lined parallel to the *c* axis (Figure 1). The geometry about each individual tin atom is remarkably similar to that in [Sn(S$_2$CNEt$_2$)$_2$] [9] (Table 4), and may also be described as pseudo-trigonal bipyramidal with the lone pair being again stereochemically active (Figure 2). The bonding parameters associated with the tin valence shell in both compounds are very similar, and the molecule has an approximate two-fold axis lying on the bisectors of the S(ax)–Sn–S(ax) and S(eq)–Sn–S(eq) bond angles (Figure 3). All the Sn–S bond distances are shorter than the sum of the ionic radii (3.05 Å), and therefore may be considered to represent bonding interactions. The next shortest (intermolecular) Sn ··· S contacts are >3.4 Å. As in other molecules with the same geometry, the Sn–S(ax) bond distances [mean 2.817(4) Å] are significantly longer than the Sn–S(eq) bond distances (mean 2.623 Å), but are longer than those in [BaSnS$_2$] [2.517(6), 2.580(6), and 2.612(6) Å].[10] Such anisobidentate behaviour, however, is not confined to the bivalent derivatives of tin and lead, and unequal Sn–S bond distances have also been observed in the quadrivalent tin derivatives [Me$_3$Sn(S$_2$CNEt$_2$)$_2$] [2.47(1) and 3.16(1) Å],[23] [Me$_2$ClSn(S$_2$CNEt$_2$)]

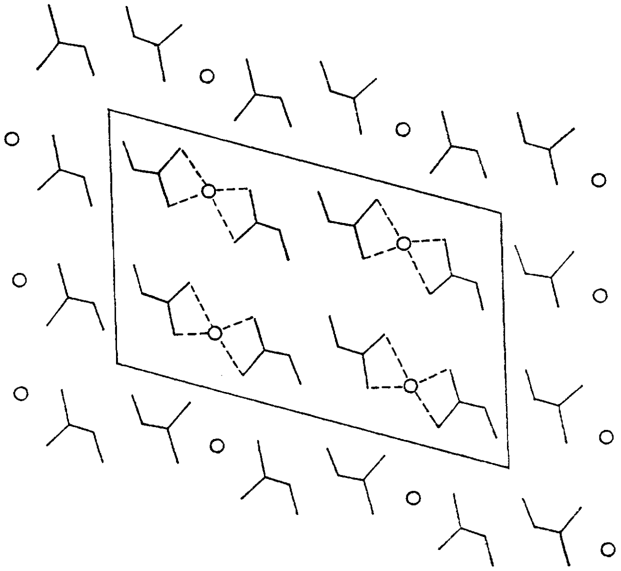

FIGURE 1 Projection of the unit cell onto the *ac* plane

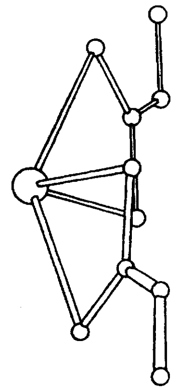

FIGURE 2 Diagram of the molecule illustrating the pseudo-trigonal bipyramidal geometry and the stereochemical activity of the lone pair

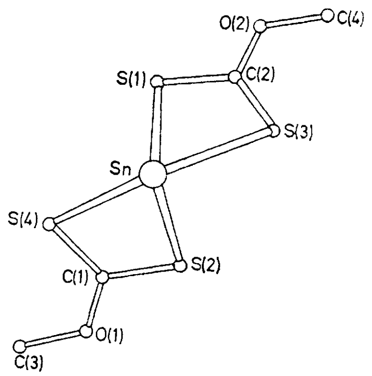

FIGURE 3 Diagram of the molecule showing the approximate two-fold axis and atom numbering system used

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[23] G. M. Sheldrick and W. S. Sheldrick, *J. Chem. Soc.* (*A*), 1970, 490.

TABLE 4

Comparison of geometry in $Sn(S_2COMe)_2$ and structurally related compounds, with estimated standard deviations in parentheses

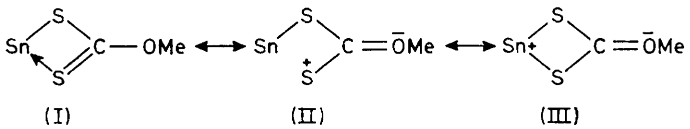
(*a*) Bond distances (Å)

		M–S(ax)	M–S(eq)	S–C	S_2C–ER	S_2CE–R
$[Sn(S_2COMe)_2]$	1	2.802(4)	2.603(3)	1.662(9), 1.707(10)	1.320(12)	1.461(15)
	2	2.813(3)	2.644(3)	1.672(8), 1.695(10)	1.322(12)	1.467(15)
$[Sn(S_2CNEt_2)_2]$	1	2.765(3)	2.574(2)	1.723(8), 1.725(8)	1.346(12)	1.488(12)
	2	2.819(3)	2.592(3)	1.682(9), 1.718(9)	1.370(12)	1.484(12)
$[Pb(S_2COEt)_2]$	1	2.838(25)	2.742(25)	1.70(11), 1.68(11)	1.30(12)	1.52(14)
	2	2.950(30)	2.785(30)	1.78(10), 1.66(10)	1.28(14)	1.44(18)
$[Pb(S_2COBu^n)_2]$	1	2.77(9)	2.83(4)	1.86(19), 1.62(20)	1.25(26)	1.37(35)
	2	3.03(8)	2.76(8)	1.66(19), 1.58(20)	1.25(26)	1.41(35)
$[Pb(S_2CNEt_2)_2]$	1	2.885(11)	2.744(9)	1.709(31), 1.724(24)	1.38(5)	1.49(5)
	2	2.940(10)	2.786(9)	1.635(27), 1.745(27)	1.36(3)	1.49(4)
$[Pb\{S_2P(OEt)_2\}_2]$	1	2.996(5)	2.754(6)			
	2	3.022(6)	2.790(6)			
$[Sn(OCPh{\cdot}CH{\cdot}COMe)_2]$		2.290(6)	2.135(1)			
$[Me_3Sn(S_2CNMe_2)]$		2.47(1)	3.16(1)	1.80(2), 1.70(3)	1.35(3)	1.42(3), 1.52(3)
$[Me_2ClSn(S_2CNEt_2)]$		2.48(1)	2.79(1)	1.68(4), 1.74(4)	1.32(5)	1.51(6), 1.57(6)
$[Ph_2Sn(S_2CNEt_2)_2]$	1	2.613(5)	2.637(5)			
	2	2.578(5)	2.790(6)			

(*b*) Valence bond angles (°)

		S(ax)–M–S(eq)	S(ax)–M–S(ax)	S(eq)–M–S(eq)
$[Sn(S_2COMe)_2]$	1	66.18(9)	140.81(10)	99.28(9)
	2	65.56(8)		
$[Sn(S_2CNEt_2)_2]$	1	67.4(2)	139.6(2)	96.2(2)
	2	65.9(2)		
$[Pb(S_2COEt)_2]$		not given	137.2(10)	98.2(9)
$[Pb(S_2COBu^n)_2]$	1	65.8(20)	141.2(26)	91.7(15)
	2	58.6(20)		
$[Pb(S_2CNEt_2)_2]$	1	64.1(3)	133.2(4)	96.2(2)
	2	61.9(2)		
$[Pb\{S_2P(OEt)_2\}_2]$	1	71.1(2)	138.2(2)	94.1(2)
	2	70.6(2)		
$[Sn(OCPh{\cdot}CH{\cdot}COMe)_2]$		81.2(1)	150.4(2)	94.7(1)
$[Me_3Sn(S_2CNMe_2)]$		63(1)		
$[Me_2ClSn(S_2CNEt_2)]$		68.2(3)		

[2.48(1) and 2.79(1) Å],[24] and $[Ph_2Sn(S_2CNEt_2)_2]$ [2.548(5) and 2.790(6) Å] (Table 4).[25] The Sn–S distances in the *O*-methyl dithiocarbonate derivative are slightly shorter than the corresponding distances in $[Sn(S_2CNEt_2)_2]$, but the angle subtended at tin by the ligand, and the axial and equatorial S–Sn–S bond angles are essentially the same, the largest deviation lying in the latter angle. The deviation of the axial and equatorial bond angles from the ideal values will be largely determined by the intra-ligand geometry, but some contribution may also arise from ' lone-pair–bond-pair ' repulsions. The shortest Sn–S bond is associated with the longest C–S bond, and *vice versa*, in both ligands, whilst the shortening of the S_2C–OMe bond distance [mean 1.321(12) Å] from that of the S_2CO–Me bond [mean 1.464(15) Å] indicates some contribution from the three canonical forms (I)—(III) to the overall distribution of electrons.



(I) (II) (III)

Similar delocalisation of electron density into S_2C–E bonds also occurs in $[Sn(S_2CNEt_2)_2]$ and in the *O*-methyl dithiocarbonato- and dithiocarbamato-derivatives of lead(II). The two *O*-methyl dithiocarbonate skeletons are essentially planar although the tin atom lies substantially out of both planes (Table 5).

TABLE 5

Equations of least-squares planes,* and, in square brackets, deviations (Å) of relevant atoms from these planes. Equations are in the forms $PI + QJ + RK = S$, where I, J, K are orthogonal co-ordinates in Å related to the monoclinic co-ordinates as: $I = X\cos\theta$, $J = Y$, and $K = Z\sin\theta$

	P	Q	R	S
Plane (1): C(3), O(1), C(1), S(2), S(4)	0.017 7	−0.926 4	0.367 2	0.758 6
[C(3) −0.010 9, O(1) 0.015 5, C(1) −0.001 3, S(2) −0.006 3, S(4) 0.003 0, Sn −0.802 8]				
Plane (2): C(4), O(2), C(2), S(1), S(5)	0.243 1	0.848 8	0.474 1	5.399 2
[C(4) −0.004 6, O(2) 0.007 7, C(2) −0.003 3, S(1) −0.001 9, S(5) 0.002 1, Sn 0.461 2]				

* According to: V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

The tin-119m Mössbauer data for both $[Sn(S_2COMe)_2]$ and $[Sn(S_2NEt_2)_2]$ are presented in Table 6. The higher isomer shift and lower quadrupole splitting for the *O*-methyl dithiocarbonato-derivative reflect, in valence-bond terminology, a greater contribution of the canonical form $[Sn^{2+}]2[S_2COMe^-]$ for this compound. Alternatively, a molecular orbital approach would localise the

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[25] P. F. Lindley and P. Carr, *J. Mol. Cryst. Struct.*, 1974, **4**, 173.

Table 6

Tin-119m Mössbauer data for $[Sn(S_2COMe)_2]$ and $[Sn(S_2CNEt_2)_2]$ (mm s^{-1}) [a,b]

Compound	*I. S.*	*Q. S.*
$[Sn(S_2COMe)_2]$	3.60	0.56
$[Sn(S_2CNEt_2)_2]$	3.26	1.20

[a] Data from ref. 17. [b] Relative to $BaSnO_3$.

lone pair in the 5*s* orbital for the *O*-methyl dithiocarbonate, and the metal would use more *p* and *d* character in the bonds formed to sulphur, producing a lengthening of the Sn–S bonds, as is actually observed, although the differences are small. The effect of such a rehybridisation on the valence-bond angles is perhaps surprisingly small, although it is to be expected that the ' bite ' of both ligands would be the same since that depends primarily on the geometry of the ligand and the size of the metal atom. The two compounds do emphasise, however, that in bivalent tin chemistry differing Mössbauer parameters do not necessarily exclude isostructurality, and *vice versa.*

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