

Fig. 2. Projection of the structure, parallel to the crystallographic *b* axis.

3.41 (2) Å with its corresponding centrosymmetrically related molecule, in position $(-x-1, -y, -z)$, with an overlap estimated as 33%, while phen(2), in position (x, y, z) , is at a distance of 3.43 (1) Å from its centrosymmetrically related molecule, in position $(-x, -y, -z+1)$, with an overlap estimated as 47%. The nitrate anion and water molecule are out of the coordination sphere of the metal ion. The water molecule, however, is strongly associated to the complex cation through the coordinated Cl⁻ ion with a short contact Cl \cdots H(2)—O(1) = 3.209 (4), Cl \cdots H(2)

= 2.286 (1) Å and Cl—H(2)—O(1) = 166.7 (3)°. It also exhibits a short contact with the nitrate ion with O(12) \cdots H(1)—O(1) = 2.909 (6), O(12) \cdots H(1) = 2.198 (6) Å and O(12)—H(1)—O(1) = 153.5 (3)°.

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Structure of Triphenyltin(IV) Methoxyethylxanthate

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Abstract. (*O*-Methoxyethyldithiocarbonato)triphenyltin(IV), [Sn(S₂COCH₂CH₂OCH₃)(C₆H₅)₃], *M_r* = 501.24, triclinic, *P* $\bar{1}$, *a* = 9.400 (1), *b* = 14.277 (3), *c* = 18.506 (5) Å, α = 68.14 (2), β = 83.05 (1), γ = 75.43 (1)°, *U* = 2229.8 (9) Å³, Mo *K* α radiation, λ = 0.71069 Å, *T* = 295 (2) K, *D_x* = 1.493 (1), *D_m* = 1.47 (2) g cm⁻³, *Z* = 4, *F*(000) = 1008, μ = 12.32 cm⁻¹, *R* = 0.044 for 3435 unique reflections [*I* \geq 2 σ (*I*)]. There are two independent molecules per asymmetric unit which differ significantly only in their intermolecular contacts. The xanthate (ROCS₂⁻) moiety

coordinates the tin atom *via* one S atom [Sn—S = 2.456 (3), 2.457 (3) Å] together with a long interaction from the O atom [Sn—O = 3.107 (8), 3.094 (8) Å]. A short intermolecular contact between a methylene H and an ether O [H \cdots O 2.47 (2) Å] is observed.

Introduction. The very rare *S*- and *O*-xanthate coordination mode has been observed for triphenyltin isopropylxanthate [Ph₃Sn(iprxa)] (Tiekink & Winter, 1986). It was therefore of interest to examine whether

Table 1. Fractional atomic coordinates and B_{eq} values for triphenyltin methoxyethylxanthate
$$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

Molecule 1	x	y	z	$B_{eq}(\text{\AA}^2)$
Sn(1)	0.29720 (8)	0.50208 (5)	0.29915 (4)	3.27
S(11)	0.4658 (4)	0.3404 (2)	0.3726 (2)	4.47
S(12)	0.5312 (4)	0.1297 (2)	0.3726 (2)	5.97
C(1X1)	0.450 (1)	0.2501 (8)	0.3345 (6)	3.63
O(1X1)	0.3682 (8)	0.2934 (5)	0.2712 (4)	4.55
C(1X2)	0.358 (1)	0.230 (1)	0.2287 (8)	5.95
C(1X3)	0.288 (1)	0.299 (1)	0.1532 (7)	5.87
O(1X2)	0.140 (1)	0.3395 (7)	0.1659 (4)	6.13
C(1X4)	0.063 (2)	0.409 (1)	0.0968 (8)	8.69
C(11)	0.075 (1)	0.4927 (8)	0.3317 (6)	3.63
C(12)	0.002 (1)	0.4394 (9)	0.3065 (6)	4.34
C(13)	-0.145 (2)	0.444 (1)	0.3240 (8)	5.79
C(14)	-0.219 (1)	0.499 (1)	0.3679 (7)	5.18
C(15)	-0.152 (1)	0.5526 (9)	0.3951 (7)	4.76
C(16)	-0.002 (1)	0.5480 (8)	0.3778 (6)	4.29
C(17)	0.345 (1)	0.5508 (8)	0.1782 (6)	3.50
C(18)	0.235 (1)	0.6116 (9)	0.1265 (6)	4.29
C(19)	0.271 (2)	0.652 (1)	0.0464 (7)	5.00
C(110)	0.409 (2)	0.629 (1)	0.0203 (8)	6.03
C(111)	0.520 (1)	0.569 (1)	0.0710 (8)	5.63
C(112)	0.490 (1)	0.5297 (9)	0.1503 (6)	4.11
C(113)	0.362 (1)	0.6015 (8)	0.3443 (6)	3.40
C(114)	0.427 (1)	0.6821 (8)	0.2937 (6)	4.63
C(115)	0.476 (1)	0.7442 (9)	0.3222 (8)	5.50
C(116)	0.466 (1)	0.726 (1)	0.4008 (8)	6.61
C(117)	0.403 (1)	0.6477 (9)	0.4496 (6)	6.18
C(118)	0.354 (1)	0.5848 (8)	0.4224 (6)	4.58
Molecule 2				
Sn(2)	-0.04339 (8)	-0.07288 (5)	0.20673 (4)	3.36
S(21)	-0.2096 (4)	0.0969 (2)	0.1482 (2)	4.63
S(22)	-0.2658 (4)	0.2905 (3)	0.1790 (2)	6.03
C(2X1)	-0.183 (1)	0.1689 (8)	0.2013 (6)	3.95
O(2X1)	-0.0917 (8)	0.1144 (5)	0.2600 (4)	4.40
C(2X2)	-0.070 (1)	0.1640 (9)	0.3124 (7)	5.55
C(2X3)	0.008 (2)	0.083 (1)	0.3812 (6)	5.66
O(2X2)	0.155 (1)	0.0530 (7)	0.3576 (5)	5.74
C(2X4)	0.243 (2)	-0.024 (1)	0.4197 (8)	6.61
C(21)	0.176 (1)	-0.0609 (8)	0.1684 (5)	3.40
C(22)	0.249 (1)	-0.0041 (9)	0.1929 (7)	5.00
C(23)	0.395 (2)	0.000 (1)	0.1652 (7)	5.42
C(24)	0.461 (2)	-0.049 (1)	0.1151 (8)	5.71
C(25)	0.387 (2)	-0.102 (1)	0.0901 (7)	5.87
C(26)	0.245 (1)	-0.1097 (9)	0.1181 (6)	4.19
C(27)	-0.087 (1)	-0.1325 (8)	0.3295 (6)	3.42
C(28)	0.024 (1)	-0.1971 (8)	0.3788 (6)	3.84
C(29)	-0.005 (2)	-0.2359 (9)	0.4581 (6)	5.18
C(210)	-0.144 (2)	-0.213 (1)	0.4881 (7)	5.11
C(211)	-0.254 (2)	-0.147 (1)	0.4393 (7)	5.34
C(212)	-0.226 (1)	-0.1084 (9)	0.3601 (6)	4.37
C(213)	-0.117 (1)	-0.1561 (8)	0.1495 (6)	3.55
C(214)	-0.168 (1)	-0.2441 (9)	0.1905 (7)	4.32
C(215)	-0.217 (2)	-0.2985 (9)	0.1537 (8)	5.63
C(216)	-0.215 (2)	-0.263 (1)	0.0745 (9)	6.58
C(217)	-0.164 (2)	-0.176 (1)	0.0299 (7)	6.24
C(218)	-0.114 (1)	-0.1228 (9)	0.0677 (6)	4.87

this mode of coordination is retained when isopropyl is replaced by another substituent. The methoxyethyl moiety was chosen because it has been shown to yield structural types different from those already observed for xanthate complexes of a particular element (Abrahams, Hoskins, Tiekink & Winter, 1988).

Experimental. The compound was prepared by mixing equimolar amounts of triphenyltin chloride and potassium methoxyethylxanthate in dichloromethane. The suspension was stirred and warmed for 1 h. The filtrate was then evaporated to dryness and recrystallized from hot petroleum ether (40–60° fraction). A block-shaped crystal bounded by $\pm(111)$, $\pm(001)$, $\pm(011)$ separated

Table 2. Bond lengths (\AA) and angles ($^\circ$) for triphenyltin methoxyethylxanthate (excluding phenyl rings)

	$n = 1$	$n = 2$
Sn(n)—S(n1)	2.456 (3)	2.457 (3)
Sn(n)—C(n1)	2.13 (1)	2.126 (9)
Sn(n)—C(n7)	2.11 (1)	2.14 (1)
Sn(n)—C(n13)	2.13 (1)	2.13 (1)
Sn(n)—O(nX1)	3.107 (8)	3.094 (8)
S(n1)—C(nX1)	1.73 (1)	1.74 (1)
S(n2)—C(nX1)	1.61 (1)	1.63 (1)
C(nX1)—O(nX1)	1.34 (1)	1.34 (1)
O(nX1)—C(nX2)	1.43 (2)	1.45 (2)
C(nX2)—C(nX3)	1.49 (2)	1.48 (2)
C(nX3)—O(nX2)	1.39 (1)	1.41 (2)
O(nX2)—C(nX4)	1.44 (2)	1.43 (2)
S(n1)—Sn(n)—C(n1)	110.6 (4)	108.9 (3)
S(n1)—Sn(n)—C(n7)	112.7 (4)	109.8 (4)
S(n1)—Sn(n)—C(n13)	97.7 (4)	98.7 (4)
C(n1)—Sn(n)—C(n7)	115.0 (5)	117.4 (5)
C(n1)—Sn(n)—C(n13)	110.9 (5)	109.1 (5)
C(n7)—Sn(n)—C(n13)	108.6 (5)	111.2 (5)
Sn(n)—S(n1)—C(nX1)	105.7 (5)	104.1 (5)
S(n1)—C(nX1)—S(n2)	121.6 (6)	121.1 (6)
S(n1)—C(nX1)—O(nX1)	111.8 (7)	113.4 (7)
S(n2)—C(nX1)—O(nX1)	126.6 (7)	125.5 (7)
C(nX1)—O(nX1)—C(nX2)	118.0 (7)	118.4 (7)
O(nX1)—C(nX2)—C(nX3)	108.0 (8)	108.2 (8)
C(nX2)—C(nX3)—O(nX2)	110.2 (9)	107.6 (8)
C(nX3)—O(nX2)—C(nX4)	114.6 (8)	113.0 (9)
Sn(n)—C(n1)—C(n6)	118.1 (8)	118.3 (7)
Sn(n)—C(n1)—C(n2)	123.3 (8)	121.4 (7)
Sn(n)—C(n7)—C(n8)	120.9 (8)	120.1 (8)
Sn(n)—C(n7)—C(n12)	120.2 (8)	120.7 (8)
Sn(n)—C(n13)—C(n14)	119.4 (8)	121.7 (8)
Sn(n)—C(n13)—C(n18)	122.1 (8)	120.8 (8)

by 0.078, 0.143 and 0.243 mm respectively was selected. Oscillation and Weissenberg photographs showed the crystal to be triclinic. The density was measured by flotation in aqueous zinc bromide solution.

An Enraf-Nonius CAD-4F diffractometer and graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) were used. Cell dimensions were obtained by least-squares refinement of angular values obtained for 25 reflections with $13 \leq 2\theta \leq 27.5^\circ$.

Intensity data were collected using the $\omega:2\theta$ scan technique ($2 \leq 2\theta \leq 50^\circ$; $-1 \leq h \leq 11$, $-16 \leq k \leq 16$, $-21 \leq l \leq 21$); the crystal was relatively weakly scattering and no significant data could be measured beyond $2\theta = 50^\circ$. No decomposition of the crystal was detected on the basis of three check reflections (422, 143, 153) remeasured every 3600 s throughout the data collection. Corrections were applied for Lorentz and polarization effects and for absorption (Sheldrick, 1976); maximum and minimum transmission factors 0.9181 and 0.8379 respectively; no correction was made for extinction. Equivalent reflections of the 9553 measured intensities were merged ($R_{int} = 0.030$) giving 7831 unique reflections of which 3435 had $I \geq 2\sigma(I)$.

Tin and sulfur positions were obtained by direct methods (SHELXS86; Sheldrick, 1985) and remaining non-hydrogen atoms were located in subsequent difference maps. All non-hydrogen atoms were refined using full-matrix least squares based on F (SHELX76; Sheldrick, 1976) with anisotropic thermal parameters. Evidence of H atoms (maximum electron density 1.3 e \AA^{-3}) was observed and all H atoms were included

in the model at calculated positions with a common isotropic thermal parameter refined for each H type. A weighting scheme of the form $w = k/[\sigma^2 F_o + 0.001 F_o^2]$ was used and refinement of 490 parameters converged at $R = 0.044$, $wR = 0.044$, $k = 0.8903$, $S = 1.058$, max. $\Delta/\sigma = 0.001$, residual electron density in the range -0.543 to $+1.098 \text{ e \AA}^{-3}$. An analysis of variance showed no special features. The neutral-atom scattering factors used were those incorporated in *SHELX76* (Sheldrick, 1976) and all calculations were performed on the University of Melbourne VAX 11/780 and 11/8650 computers. Fractional atomic coordinates are listed in Table 1* and bond distances and angles (excluding phenyl-ring geometry) are given in Table 2.

Discussion. Crystals of triphenyltin methoxyethylxanthate [$\text{Ph}_3\text{Sn}(\text{moexa})$] are molecular, there being two independent molecules per asymmetric unit. The numbering scheme used, together with the orientation of the two molecules with respect to each other, is shown in Fig. 1; molecular packing is illustrated in Fig. 2. There are no major conformational differences between the two molecules. Differences between the corresponding bond lengths and angles are within 3σ . The only significant difference between the molecules is

* Tables of anisotropic thermal parameters, calculated H-atom coordinates, observed and calculated structure factors, phenyl-ring geometry, selected intermolecular contacts and mean planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51001 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

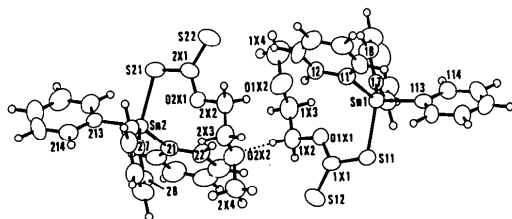


Fig. 1. The asymmetric unit of $\text{Ph}_3\text{Sn}(\text{moexa})$ showing the numbering scheme employed (*ORTEP*; Johnson, 1971). The proposed hydrogen bond $\text{O}(2\text{X}2)\cdots\text{H}(122)$ is indicated.

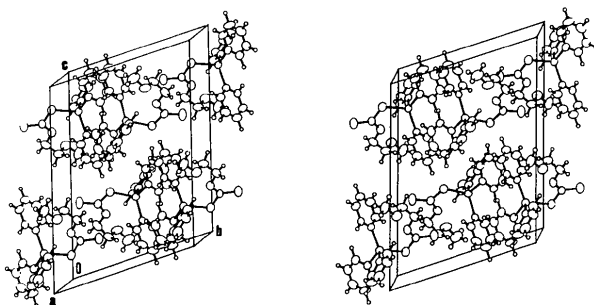


Fig. 2. The packing of $\text{Ph}_3\text{Sn}(\text{moexa})$ molecules in the unit cell (*ORTEP*; Johnson, 1971).

in the intermolecular contacts. Within the asymmetric unit, the contact distance between $\text{O}(2\text{X}2)\cdots\text{H}(122)$ of $2.47(2) \text{ \AA}$ is significantly less than the analogous distance $\text{O}(1\text{X}2)\cdots\text{H}(222)$ of $2.68(1) \text{ \AA}$. The former contact is substantially less than the sum of van der Waals radii [2.7 \AA (Bondi, 1964)] and together with the $\text{C}(1\text{X}2)\text{—H}(122)\cdots\text{O}(2\text{X}2)$ angle of 170° suggest hydrogen bonding (Taylor & Kennard, 1982). The shortest intermolecular contact between non-hydrogen atoms is for $\text{S}(22)\cdots\text{C}(112^i)$ (i denotes the transformation $-1+x, y, z$) at $3.50(1) \text{ \AA}$, this distance being significantly shorter than the comparable $\text{S}(12)\cdots\text{C}(212^i)$ distance of $3.66(1) \text{ \AA}$. This non-equivalence is almost certainly a result of crystal packing.

The Sn atoms of the two independent molecules of $\text{Ph}_3\text{Sn}(\text{moexa})$ are in a distorted tetrahedral environment consisting of three bonded phenyl carbons and an S atom of the xanthate moiety. The bond angles $\text{S}(11)\text{—Sn}(1)\text{—C}(113)$ and $\text{S}(21)\text{—Sn}(2)\text{—C}(213)$ of $97.7(4)$ and $98.7(4)^\circ$ respectively are well below the value expected for ideal tetrahedral geometry, but are comparable to the $100.6(7)^\circ$ reported for the analogous angle in $\text{Ph}_3\text{Sn}(\text{iprx})$ (Tiekink & Winter, 1986). The distances $\text{Sn}(1)\cdots\text{O}(1\text{X}1)$ and $\text{Sn}(2)\cdots\text{O}(2\text{X}1)$ are $3.107(8)$ and $3.094(8) \text{ \AA}$; these values are also similar to that reported for $\text{Ph}_3\text{Sn}(\text{iprx})$ [$2.950(3) \text{ \AA}$] and substantially below the sum of van der Waals radii [3.7 \AA (Bondi, 1964)]. The angles $\text{S}(11)\text{—C}(1\text{X}1)\text{—O}(1\text{X}1)$ and $\text{S}(21)\text{—C}(2\text{X}1)\text{—O}(2\text{X}1)$ of $126.6(7)$ and $125.5(7)^\circ$ are substantially greater than the ideal trigonal value of 120° . This distortion is attributed to the Sn—O interaction. The Sn—C bond distances [range $2.11(1)$ to $2.14(1) \text{ \AA}$] are as expected. The non-equivalence of the S—C bond lengths reflects the non-equivalence of the S atoms, the longer S—C bond involving the coordinated S atom. The C—C and C—O bond lengths in the methoxyethylxanthate moiety are as expected.

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