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A pseudosymmetric triclinic modification of triphenyltin isopropylxanthate

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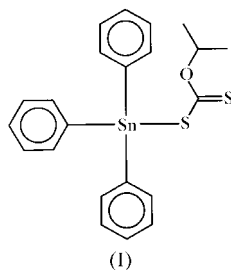
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All three independent molecules in the triclinic modification of (*O*-isopropyl dithiocarbonato-*S*)triphenyltin, [Sn(C₆H₅)₃(C₄H₇OS₂)], show tetrahedral coordination at their Sn atoms. Bond dimensions involving the Sn atoms are similar to those found in the monoclinic modification of the same compound. Two of the independent molecules are related by a pseudo-translation allowing a stacking fault that reduces the intensities of *h* + *k* odd reflections.

Comment

The structure of the title compound, (I), has a 0.8395:0.1605(3) stacking fault over alternative origins (*a* + *b*)/2 apart that causes the *h* + *k* = 2*n* + 1 reflections to be scaled down by a factor of 0.6791 (5). The structure consists of three different layers perpendicular to *c*^{*}, each containing two molecules per



unit cell. The first two layers are related by a crystallographic inversion whereas the third contains inversion-related molecules. The asymmetric unit is one layer at approximately *z* = 1/3 that contains molecule *a* and molecule *b* [related by a pseudo-translation of (*a* + *b*)/2] and a third molecule (molecule *c*) of a different orientation at approximately *z* = 0. A pseudo-inversion at ($\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$) relates the layers at *z* = ± $\frac{1}{3}$, and if it acts on the total substructure on one side of an interface at *z* = $\frac{1}{2}$, the net result is a translation of the structure by (*a* + *b*)/2. The structure factors are changed to [(1 - *a*) + *a*(-1)^{*h+k*}]*F*(*hkl*)_o, where *F*(*hkl*)_o is the structure for the idea-

alized non-stacking-faulted structure and *a* the average fraction of structure that has been stacking faulted. This effect can be modeled by simply using two scale constants.

Bond dimensions involving the Sn atom are not statistically different among the three molecules, and they are similar to those found in the monoclinic modification (Tiekink & Winter, 1986). For both modifications, the tetrahedral geometry at Sn is distorted owing to an intramolecular Sn...O interaction. The interaction is somewhat shorter than those found in the two independent molecules of triclinic (*P* $\bar{1}$) triphenyltin methoxyethylxanthate (Edwards *et al.*, 1988). This structure is ordered with the two molecules related by a pseudo-inversion at (0.127, 0.215, 0.253).

Experimental

Triphenyltin xanthate, (I), synthesized from reaction between triphenyltin chloride and potassium isopropylxanthate in ethanol, was treated with an equimolar quantity of 2,2'-bipyridine *N,N'*-dioxide in an attempt to synthesize triphenyltin isopropylxanthate·2,2'-bipyridine *N,N'*-dioxide in a sequel to the study on the quinoline *N*-oxide complex (Ng *et al.*, 1995). The reagents were dissolved in a small volume of hot ethanol; slow cooling of the solution returned the xanthate. Elemental analysis: found: C 54.50, H 4.55%; calculated for C₂₂H₂₂OS₂Sn: C 54.46, H 4.57%. The starting triphenyltin isopropylxanthate reactant exists as the monoclinic modification when recrystallized from ethanol.

Crystal data

[Sn(C₆H₅)₃(C₄H₇OS₂)]
M_r = 485.21
Triclinic, *P* $\bar{1}$
a = 10.3136 (3) Å
b = 12.124 (1) Å
c = 27.139 (3) Å
 α = 100.346 (9)°
 β = 93.422 (7)°
 γ = 97.605 (7)°
V = 3297.0 (6) Å³

Z = 6
D_x = 1.466 Mg m⁻³
Mo *K*α radiation
Cell parameters from 25 reflections
 θ = 14.5–15.0°
 μ = 1.360 mm⁻¹
T = 298 (2) K
Cube, light yellow
0.43 × 0.43 × 0.43 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
 ω scans
Absorption correction: ψ scan
[North *et al.* (1968) in *WinGX* (Farrugia, 1998)]
*T*_{min} = 0.515, *T*_{max} = 0.557
12 299 measured reflections
11 586 independent reflections

8184 reflections with *I* > 3σ(*I*)
*R*_{int} = 0.013
 θ _{max} = 24.98°
h = 0 → 12
k = -14 → 14
l = -32 → 32
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on *F*
R = 0.050
R = missing
wR = 0.090
S = 1.45
11 586 reflections

271 parameters
Part of **TLX** rigid body motions
w = 1/[σ(*F*)² + (0.04*F*)²]
(Δ/σ)_{max} = 0.3
Δρ_{max} = 1.31 e Å⁻³
Δρ_{min} = -0.83 e Å⁻³

bondtable >

Table 1
Selected geometric parameters (Å, °).

Sn1a–S1a	2.443 (1)	Sn1b–C7b	2.131 (3)
Sn1a–C1a	2.148 (3)	Sn1b–C13b	2.133 (3)
Sn1a–C7a	2.131 (3)	Sn1c–S1c	2.444 (2)
Sn1a–C13a	2.134 (3)	Sn1c–C1c	2.136 (4)
Sn1b–S1b	2.444 (1)	Sn1c–C7c	2.135 (4)
Sn1b–C1b	2.148 (3)	Sn1c–C13c	2.135 (4)
S1a–Sn1a–C1a	98.3 (2)	C1b–Sn1b–C13b	109.8 (2)
S1a–Sn1a–C7a	106.3 (2)	C7b–Sn1b–C13b	116.7 (2)
S1a–Sn1a–C13a	113.5 (2)	S1c–Sn1c–C1c	97.2 (2)
C1a–Sn1a–C7a	114.8 (2)	S1c–Sn1c–C7c	108.1 (1)
C1a–Sn1a–C13a	110.4 (2)	S1c–Sn1c–C13c	114.5 (1)
C7a–Sn1a–C13a	112.8 (2)	C1c–Sn1c–C7c	114.0 (2)
S1b–Sn1b–C7b	105.9 (2)	C1c–Sn1c–C13c	111.9 (2)
S1b–Sn1b–C13b	110.5 (2)	C7c–Sn1c–C13c	110.6 (2)
C1b–Sn1b–C7b	113.4 (2)		

Table 2
Refinement statistics.

Class ^a	Number	<i>R</i> (<i>F</i>)	<i>R</i> (<i>F</i> ²)	<i>wR</i>	GoF	$\langle F^2 \rangle^b$
1	4741	0.040	0.088	0.056	1.18	1000
2	2927	0.088	0.138	0.110	1.82	145
1 and 2	7668	0.050	0.093	0.075	1.46	676
3	3918	0.674	0.984	0.453	1.28	7

† Notes: an uncorrelated 4% error in $|F(h)|$ was included along with counting statistics for evaluating weights. (a) Class 1: reflections with $h + k = 2n$ and $I(h) > 3\sigma[I(h)]$; class 2: reflections with $h + k = 2n + 1$ and $I(h) > 3\sigma[I(h)]$; class 3: reflections with $I(h) < 3\sigma[I(h)]$. (b) Scaled relative to 1000 for class 1.

Two scale constants were used in the refinement to allow for a stacking fault over origins $(a + b)/2$ apart. Difference maps were calculated with the effects of a stacking fault removed by setting $F_o = [Y_o/Y_c]^{1/2} \times F_c$, where F_c is the calculated structure factor for the prototype, and Y_o and Y_c are the observed and calculated values of the intensity. Because reflections are weak for $h + k$ odd, constraints and restraints were used in a refinement that only behaved when two scale constants were used. The modeling for the least-squares refinement used refineable local orthonormal coordinates available in *RAELS96* (Rae, 1975, 1996) to describe the atoms in the unit cell. All phenyl groups were restrained to have a common set of local coordinates and to maintain local *mm2* symmetry. Restraints were used to minimize differences in bond lengths involving molecule *a* and molecule *b*. Twelve different 15-parameter **TLX** parameterizations (Rae, 1984) were used for the ligand thermal motions, one set per ligand, and librations were initially centered on the relevant Sn atoms. Because of the pseudo translation relationship between molecule *a* and molecule *b*, the **TLX** thermal parameterizations were constrained to retain this relationship (Rae, 1984). These constraints

were later removed but reimposed when it was found that variations in **TLX** parameters were relatively large, had little effect on the statistics and were of no apparent physical meaning. Individual anisotropic displacement parameters were used for the Sn atoms. The stacking fault creates a Sn1c atom at $(\frac{1}{2} - x, \frac{1}{2} - y, -z)$ which lies near atoms C20c and C22c, distorting the apparent geometry in an unconstrained ligand. The distances and angles involving C20c were therefore restrained to minimize their differences from the corresponding features of molecules *a* and *b* with little apparent consequence for refinement statistics. In the final cycle, 271 independent variables were used, and the shift/error ratio was less than 0.1 for all but the libration parameters of one ligand. The refinement was stable, the shift/error ratio being an artifact of considering variables one at a time. There is a well recognized singularity in the equations for **TLX** motion for atoms on a conic section, which is retained should a **TLX** model of 6 phenyl C atoms have its center of action at the center of the ring. H atoms were included in geometrically sensible positions which were updated each refinement cycle. The thermal parameters of H atoms were evaluated using the **TLX** parameters associated with the atoms to which they are attached. Quoted errors are conditional on the appropriateness of the various constraints and restraints. Refinement statistics are presented in Table 2.

Data collection: *CAD-4/PC* (Kretschmar, 1994); cell refinement: *CAD-4/PC* (Enraf–Nonius, 1988); data reduction: *XCAD4* (Harms, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *RAELS96* (Rae, 1996); software used to prepare material for publication: *RAELS96* (Rae, 1996).

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