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Bis(*O*-cyclohexyl dithiocarbonato)dimethyltin(IV)

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Abstract

In $[Sn(CH_3)_2(C_7H_{11}OS_2)_2]$, the environment about the Sn atom is distorted tetrahedral, defined by the donor S atoms of the two monodentate dithiocarbonato (xanthate) ligands and by the two methyl C atoms. The second S atom of each xanthate ligand is twisted towards the Sn atom, in the so-called *S,S* orientation.

Comment

The solid-state structures of metal xanthates have been reviewed (Tiekink & Winter, 1992; Winter, 1980). An interesting feature of the dithiocarbonato (xanthate) ligand (—S_2COR) is shown in its monodentate coordination mode. The second non-coordinating S atom has two possible orientations: towards the central metal atom (the *S,S* mode) or away from it (by a rotation about the coordinated S—C bond), in which case the xanthate O atom is directed towards the central metal atom (the *S,O* mode). Structural studies of gold(I) xanthates have suggested that the presence of bulky substituents on the central atom would favour the former mode of orien-

tation while in cases where there is little or no steric hindrance, the latter mode would be adopted (Siasios & Tiekink, 1993). This paper reports the structure of an organotin xanthate complex, (I), in which the monodentate xanthate ligands adopt the *S,S* orientation even though the two methyl groups are not sterically demanding.

(I)
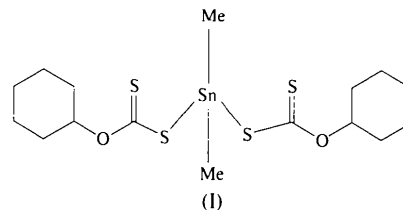
A displacement ellipsoid plot of the molecule with the atom-numbering scheme is shown in Fig. 1. The molecule is symmetrical about the C1—Sn—C2 plane, one half being related to the other by a mirror plane normal to **b**. This is in contrast to other diorganotin bis(xanthate) compounds which have no imposed symmetry (Dakternieks, Hoskins, Tiekink & Winter, 1984; Donoghue & Tiekink, 1991; Donoghue, Tiekink & Webster, 1993). The Sn atom has distorted tetrahedral coordination with angles of 134.7(1) and 87.2(1)°. Both these angles are significantly larger than those of previously reported structures. The large difference in the C3—S2 [1.630(7) Å] and C3—S1 [1.731(7) Å] bond lengths suggests that the xanthate is essentially monodentate. In the present structure, the second S atom of each xanthate ligand is directed towards the central Sn atom in the *S,S* orientation. The Sn⋯S2 distance of 3.072(2) Å is greater than the sum of the covalent radii (2.42 Å) of the Sn and S atoms, but less than the sum of the van der Waals radii (4.00 Å) (Bondi, 1964), indicating a weak interaction. This *S,S* mode is unexpected as the Sn^{IV} ion, being a 'hard' acid, would be expected to be attracted to the 'hard' O atom rather than the 'soft' S atom. Futhermore, the methyl groups on the central Sn atom are not expected to offer substantial steric hindrance so as to force an *S,S* orientation mode.

The remaining parameters defining the xanthate ligands are normal and agree with those of previous examples. The C—C bond distances in the cyclohexyl ring [1.45(1)–1.51(1) Å] are less than the normal values; their apparent shortness may be attributed to high thermal vibrations. The cyclohexyl ring adopts a chair
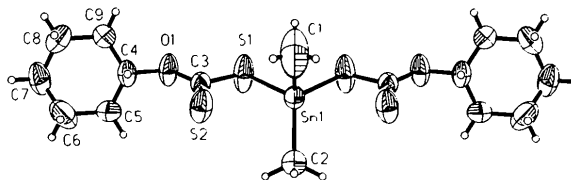

Fig. 1. A 50% probability displacement ellipsoid plot of the title molecule with the atom-numbering scheme.

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conformation; the other atoms in the xanthate skeleton (S_2CO) lie in one plane and the Sn atom deviates by 0.231 (7) Å from this plane. The dihedral angle between the best plane through the atoms in the cyclohexyl ring and the xanthate moiety is 66.3 (2)°. The molecules have linear configurations and lie parallel to the b axis. The crystal structure is stabilized by van der Waals interactions.

Experimental

Crystals suitable for X-ray analysis were obtained from slow evaporation of an n-heptane solution.

Crystal data

$[Sn(CH_3)_2(C_7H_{11}OS_2)_2]$	Mo $K\alpha$ radiation
$M_r = 499.31$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 25
$Pnma$	reflections
$a = 10.224\,(1)$ Å	$\theta = 8-15°$
$b = 21.514\,(2)$ Å	$\mu = 1.512$ mm^{-1}
$c = 10.230\,(1)$ Å	$T = 293\,(2)$ K
$V = 2250.2\,(4)$ Å^3	Prism
$Z = 4$	$0.54 \times 0.44 \times 0.36$ mm
$D_x = 1.474$ Mg m^{-3}	Very pale brown

Data collection

Siemens $P4$ diffractometer	$R_{int} = 0.0243$
$\theta/2\theta$ scans	$\theta_{max} = 30°$
Absorption correction:	$h = -1 \rightarrow 14$
ψ scans (Siemens, 1994)	$k = -30 \rightarrow 1$
$T_{min} = 0.777$, $T_{max} =$	$l = -1 \rightarrow 14$
0.962	3 standard reflections
4240 measured reflections	monitored every 97
3344 independent reflections	reflections
2814 observed reflections	intensity decay: $<3\%$
$[I > 2\sigma(I)]$	

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.61$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.0668$	$\Delta\rho_{min} = -1.00$ e Å^{-3}
$wR(F^2) = 0.1605$	Extinction correction:
$S = 1.157$	$SHELXL93$ (Sheldrick,
3343 reflections	1993)
118 parameters	Extinction coefficient:
H-atom parameters not	0.0028 (2)
refined	Atomic scattering factors
$w = 1/[\sigma^2(F_o^2) + 18.4913P]$	from International Tables
where $P = (F_o^2 + 2F_c^2)/3$	for Crystallography (1992,
$(\Delta/\sigma)_{max} < 0.001$	Vol. C, Tables 4.2.6.8 and
	6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sn1	0.20453 (7)	3/4	0.88278 (7)	0.0510 (2)
S1	0.3641 (2)	0.67059 (10)	0.9560 (4)	0.1009 (11)
S2	0.1299 (2)	0.61348 (10)	0.8358 (3)	0.0799 (8)
O1	0.3441 (5)	0.5559 (2)	0.9142 (7)	0.075 (2)
C1	0.205 (4)	3/4	0.6786 (18)	0.197 (19)
C2	0.0564 (17)	3/4	1.0295 (19)	0.102 (6)
C3	0.2750 (7)	0.6074 (3)	0.9006 (8)	0.053 (2)
C4	0.2915 (7)	0.4961 (3)	0.8712 (8)	0.056 (2)
C5	0.2269 (10)	0.4652 (4)	0.9820 (9)	0.079 (3)
C6	0.1823 (10)	0.4009 (4)	0.9432 (13)	0.103 (4)
C7	0.2876 (9)	0.3624 (4)	0.8935 (11)	0.085 (3)
C8	0.3552 (11)	0.3943 (4)	0.7824 (10)	0.091 (3)
C9	0.4022 (9)	0.4584 (4)	0.8210 (9)	0.074 (2)

Table 2. *Selected geometric parameters (Å, °)*

Sn1—C1	2.09 (2)	S2—C3	1.630 (7)
Sn1—C2	2.13 (2)	O1—C3	1.322 (8)
Sn1—S1	2.478 (2)	O1—C4	1.462 (8)
S1—C3	1.731 (7)		
C1—Sn1—C2	134.7 (13)	O1—C3—S2	126.6 (5)
C1—Sn1—S1	107.6 (8)	O1—C3—S1	110.1 (5)
C2—Sn1—S1	104.8 (4)	S2—C3—S1	123.3 (4)
S1^i—Sn1—S1	87.18 (10)	O1—C4—C5	109.3 (7)
C3—S1—Sn1	95.5 (2)	O1—C4—C9	107.8 (6)
C3—O1—C4	120.6 (5)		

Symmetry code: (i) $x, \frac{3}{2} - y, z$.

Although the unit cell is metrically tetragonal ($a \simeq c$), the Laue symmetry is *mmm* and the structure orthorhombic. Averaging the intensities, assuming $4/m$ symmetry, produces an unacceptably large merging R factor (0.32).

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*. Geometric calculations: *PARST* (Nardelli, 1983).

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