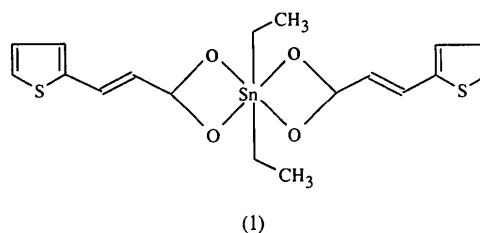Banister, A. J., Luke, A. W., Rawson, J. M., Whitehead, R. J. & Singer, R. (1997). In preparation.
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Diethylbis[3-(2-thienyl)-2-propenoato-O,O']tin(IV)

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Abstract

The crystal structure of $[Sn(C_2H_5)_2(C_7H_5O_2S)_2]$ contains discrete molecules in which hexa-coordinated Sn atoms lie on twofold axes. The Sn atom is coordinated asymmetrically to two symmetry-related propenoates, with Sn—O distances of 2.105 (5) and 2.538 (6) Å, and to two ethyl groups, with Sn—C distances of 2.155 (2) Å.

Comment

Diorganotin carboxylates of general formula R_2SnL_2 (where R = alkyl or aryl, and L = carboxylate anion) usually exist in an octahedral state in the solid phase (Tiekink, 1991; Gielen, Buoalam, Mahieu & Tiekink, 1992; Piret, Buoalam, Willem & Gielen, 1993). However, their geometry in solution cannot be defined with certainty because of the dynamic processes involved with carboxylate O atoms, due to competition in their coordination behaviour with the Sn atom (Danish, Alt *et al.*, 1995; Danish, Ali *et al.*, 1995). We wanted to investigate the contribution of a heteroatom, as part of a five-membered ring, on the geometry of the central Sn atom. In this regard, we have prepared several compounds and have studied their geometry in the solid as well as in the solution phase. It has been observed that a heteroatom which is an integral part of a five-membered ring has no substantial effect on the geometry of the central metal atom either in the solid or the solution phase.

In this paper, we wish to report the crystal structure of the title compound, (1).

(1)

The structure of (1) (Fig. 1) is composed of discrete monomeric molecules in which Sn atoms lie on a crystallographic twofold axis such that only half of the molecule represents the asymmetric unit.
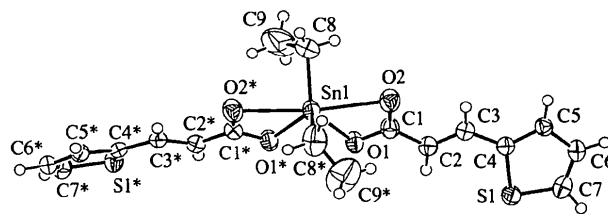

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (1) with the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms have been assigned arbitrary radii; the minor fraction of disordered C9 has been ignored. Symmetry operation for starred atoms: $2 - x$, y, $\frac{3}{2} - z$.

The hexa-coordinated Sn atom is surrounded by four O atoms of the propenoate ligands forming an almost planar base, and the ethyl groups occupy the two remaining positions resulting in a highly distorted octahedral geometry which may best be described as based on a skew-trapezoidal planar geometry. The terminal C atom of the methyl group is disordered over two sites, C9 and C9', with site occupancies 0.78 (2) and 0.22 (2), respectively. The symmetry-related propenoates are asymmetrically coordinated to the Sn atom, with Sn—O bond distances of 2.105 (5) and 2.538 (6) Å; the Sn—C bond distances are 2.155 (2) Å. The angle between the Et_2Sn and $SnCO_2$ planes is 73.0 (2)°, while the $SnCO_2$ and thienyl (S1, C4—C7) rings are inclined at 24.2 (3)° with respect .to each other; both the rings are individually planar, the maximum deviations being 0.024 (5) and 0.019 (4) Å, respectively. The molecules are separated by normal van der Waals contacts in the crystal with no Sn···S interactions. The structures exhibiting similar geometry as found in (1) include $Me_2Sn(OAc)_2$ (Lockhart, Calabrese & Davidson, 1987), $Bu_2Sn(O_2CCH_2SC_6H_5)_2$ (Sandhu, Sharma & Tiekink, 1989), $^nBu_2Sn[O_2C(CH_2Ph)C(H)N(H)C(O)CH_2Cl]_2$ (Sandhu, Hundal & Tiekink, 1991), $Me_2Sn(O_2CPh)_2$ (Tiekink, 1991), $Et_2Sn(O_2CC_4H_3S)_2$ (Vatsa, Jain, Das & Tiekink, 1991) and $Et_2Sn(O_2CC_5H_3NSMe)_2$ (Gie-

len, Khloufi, Biesemans, Willem & Piret, 1992). All of these structures exhibit an anisobidentate mode of co-ordination of the carboxylate ligands accompanied by unequal C—O bond distances, the C—O distances for the weakly coordinated O atoms being shorter than the C—O distances of the strongly bound O atoms which are 1.301 (9) and 1.242 (10) Å, respectively, in (1).

The dimensions in the thienylpropionate ligands in (1) are unexceptional with mean bond distances C=C 1.33 (2) and C_{sp^2}—C_{sp^2} 1.44 (2) Å. The S—C distances are significantly different from each other (Table 2); similar inequivalent distances have been observed in $Me_2Sn(OAc)_2$ (Lockhart *et al.*, 1987).

Experimental

Diethyltin dichloride (0.01 mol) and 3-(2-thienyl)-2-propenoic acid (0.02 mol) were refluxed with constant stirring in dry dichloromethane for 8 h under an inert atmosphere of argon. The reaction mixture was then cooled to room temperature and the solid was removed by filtration under argon. The filtrate was given activated charcoal treatment and concentrated under reduced pressure. The solid mass obtained after 7 d was crystallized from dichloromethane/hexane (80:20) by slow evaporation under argon at room temperature (yield 85%, m.p. 371–373 K).

Crystal data

[Sn(C_2H_5)_2(C_7H_5O_2S)_2]
$M_r = 483.15$
Monoclinic
$C2/c$
$a = 23.910\,(3)$ Å
$b = 5.492\,(4)$ Å
$c = 16.831\,(3)$ Å
$\beta = 112.208\,(12)°$
$V = 2046.3\,(16)$ Å^3
$Z = 4$
$D_x = 1.568$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 10.0–15.0°$
$\mu = 1.471$ mm^{-1}
$T = 200\,(1)$ K
Prismatic
$0.60 \times 0.50 \times 0.26$ mm
Colourless

Data collection

Rigaku AFC-6S diffractom-eter
$\omega/2\theta$ scans
Absorption correction:
  ψ scans (North, Phillips & Mathews, 1968)
  $T_{min} = 0.463$, $T_{max} = 0.682$
2017 measured reflections
1809 independent reflections

1465 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 28$
$k = 0 \rightarrow 6$
$l = -20 \rightarrow 18$
3 standard reflections
  every 200 reflections
  intensity decay: 0.38%

Refinement

Refinement on F^2
$R(F) = 0.0334$
$wR(F^2) = 0.0839$
$S = 1.204$
1787 reflections
111 parameters

H atoms riding, C—H = 0.95 Å

$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 4.5017P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.78$ e Å^{-3}

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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	1	0.19545 (15)	3/4	0.0421 (3)
S1	1.21126 (9)	−0.4388 (4)	1.12277 (12)	0.0453 (5)
O1	1.0486 (2)	−0.0958 (10)	0.8265 (3)	0.0471 (13)
O2	1.0971 (3)	0.2418 (10)	0.8809 (4)	0.055 (2)
C1	1.0924 (3)	0.0176 (15)	0.8858 (5)	0.042 (2)
C2	1.1334 (3)	−0.1313 (14)	0.9564 (5)	0.040 (2)
C3	1.1833 (3)	−0.0378 (13)	1.0140 (4)	0.035 (2)
C4	1.2267 (3)	−0.1608 (13)	1.0873 (4)	0.0332 (15)
C5	1.2841 (3)	−0.0848 (14)	1.1378 (4)	0.037 (2)
C6	1.3144 (3)	−0.2539 (14)	1.2035 (5)	0.042 (2)
C7	1.27945 (14)	−0.4360 (8)	1.2019 (3)	0.047 (2)
C8	1.04905 (14)	0.3434 (8)	0.6769 (3)	0.078 (3)
C9†	1.03965 (14)	0.2075 (8)	0.5969 (3)	0.126 (10)
C9'‡	1.01417 (14)	0.3864 (8)	0.5844 (3)	0.10 (2)

† Site occupancy = 0.78 (3).   ‡ Site occupancy = 0.22 (3).

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

Sn1—O1	2.105 (5)	S1—C4	1.729 (7)
Sn1—O2	2.538 (6)	O1—C1	1.301 (9)
Sn1—C8	2.155 (2)	O2—C1	1.242 (10)
S1—C7	1.670 (5)		
O1—Sn1—O2	55.5 (2)	C8—Sn1—O2^i	89.0 (2)
O1—Sn1—O1^i	81.1 (3)	C8^i—Sn1—O2^i	86.7 (2)
O1—Sn1—O2^i	135.7 (3)	C8—Sn1—C8^i	135.7 (3)
O2^i—Sn1—O2	168.5 (3)	C7—S1—C4	89.7 (3)
O1—Sn1—C8	110.0 (2)	C1—O1—Sn1	101.8 (5)
O1^i—Sn1—C8	103.3 (2)	C1—O2—Sn1	83.2 (4)

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

Based on the systematic absences of *hkl*, $h + k = 2n + 1$ and *h0l*, $l = 2n + 1$, statistical analyses of intensity distributions and successful solution and refinements of the structures, the space group was determined to be $C2/c$. H atoms were included at geometrically idealized positions with C—H = 0.95 Å. The terminal C atom of the ethyl group bonded to the Sn atom is disordered over two sites, C9 and C9'. The C—C distance in the ethyl group was constrained at 1.48 Å. The site occupancy factors refined to 0.78 (3) and 0.22 (3) for C9 and C9', respectively; the latter site was allowed an isotropic displacement parameter.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL93*.

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Two Heteroleptic Cobalt(III) Cyclopentadienyl/Dithiolene Complexes

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Abstract

The crystal structure determinations of (η^5-cyclopentadienyl)(4,5-dimercapto-1,3-dithiole-2-thionato)cobalt(III), [Co(C_5H_5)(C_3S_5)], and (4,5-dimercapto-1,3-dithiole-2-thionato)(η^5-pentamethylcyclopentadienyl)cobalt(III), [Co($C_{10}H_{15}$)(C_3S_5)], show that Cp* substitution does not significantly modify the geometric features of these complexes, which are characterized by a perpendicular arrangement of the planar Cp or Cp* and (CoS_2C_2) moieties.

Comment

In the course of our work on electroactive materials built from heteroleptic cyclopentadienyl/dithiolene complexes with Ti, Nb and Mo (Fourmigué & Coulon, 1994; Fourmigué, Lenoir, Coulon, Guyon & Amaudrut, 1995; Guyon, Fourmigué, Audebert & Amaudrut, 1995; Guyon, Lenoir, Fourmigué, Larsen & Amaudrut, 1990), we have been interested in the corresponding Co complexes of general formula CpCo(dithiolene), where Cp is the cyclopentadienyl ligand. The structures of such Co^{III} complexes with various dithiolenes have been reported, e.g. $S_2C_2(CN)_2$ (Churchill & Fennessey, 1968), $S_2C_2(CF_3)_2$ (Baird & White, 1966), $S_2C_6H_4$ (Miller, Brill, Rheingold & Fultz, 1983); complexes with nitrogen-containing dithiolenes have also been reported (Werner, Xiaolan & Nurnberg, 1992; Armstrong *et al.*, 1993). More recently, sulfur-rich dithiolene ligands such as dmit^{2-} or dddt^{2-} (where dmit^{2-} is 4,5-dimercapto-1,3-dithiole-2-thionate and dddt^{2-} is 5,6-dihydro-1,4-dithiine-2,3-dithiolate) have been used (Ushijima *et al.*, 1990, 1991) and the electrochemical properties of the complexes investigated. These latter ligands have been shown to be particularly versatile in homoleptic paramagnetic complexes as, for example, in Ni(dmit)$_2^-$, since they promote a solid-state organization with strong intermolecular S$\cdots$S interactions, a prerequisite for the setting of collective electronic properties such as conductivity, superconductivity and magnetism (Canadell, Ravy, Pouget & Brossard, 1990).

In this paper, the crystal structures of CpCo(dmit), (I), and Cp*Co(dmit), (II), are reported. The geometry of the cyclopentadienyl complex, (I), is compared with that of previously reported complexes as well as with the Cp* analogue, (II), for which no crystal structure with any dithiolene ligand has been reported previously.

(I)   (II)
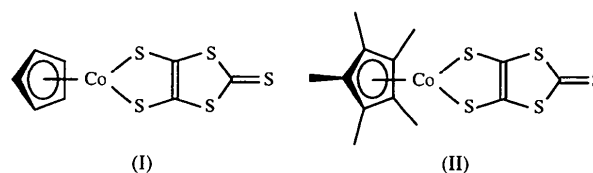
In both compounds, the Co(S_2C_2) moiety is nearly planar and perpendicular to the Cp [88.4 (2)°] and the Cp* [87.8 (2)°] moieties. The dimensions of the [(η-C_5H_5)Co(S_2C_2)] moiety in (I) are similar to those of each of the five structurally characterized molecules of this type. With the Cp* ligand, a slight elongation of the Co—S bonds was observed, which might be attributable to the more electron-rich character of the Cp* ligand when compared with the Cp ligand.

In the solid state, short S$\cdots$S contacts are identified in (I) [S4$\cdots$S1^i 3.608 (3), S2$\cdots$S1^i 3.655 (3) and S4$\cdots$S3^i 3.733 (3) Å; symmetry code: (i) $x - 1$, y, z], thus linking the parallel dmit moieties of neighbouring molecules obtained by translation along the a axis. These short