metal-organic papers

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Bis(cyclopentenylacetato)tetraethyldistannoxane dimer

The molecular structure of the title compound, tetra-μ_2-(cyclopent-2-enyl)acetato-1:2κ^2O:O';1:3κ^2O:O';2:4κ^2O:O';-3:4κ^2O:O'-octaethyl-1κ^2C,2κ^2C,3κ^2C,4κ^2C-di-μ_3-oxo-1:2:3κ^3O;-2:3:4κ^3O-tetratin, [Sn$_4$(C$_2$H$_5$)$_8$(C$_7$H$_9$O$_2$)$_4$O$_2$], is composed of two independent centrosymmetric dimers lying about inversion centers. In each dimer, the central Sn$_2$O$_2$ core is fused with two four-membered (Sn$_2$O$_2$) and two six-membered (Sn$_2$O$_3$C) rings. The endocyclic Sn atoms are six-coordinate in a skew-trapezoidal bipyramidal environment. The exocyclic Sn atoms are five-coordinate and show disotorted trigonal–bipyramidal geometry. The cyclopentenylacetate ligand shows different modes of coordination with tin. In both dimers, the Sn—C distances lie in a very narrow range [2.118 (4)–2.134 (4) Å], while the Sn—O distances range between 2.042 (2) and 2.314 (3) Å for strong bonds and between 2.638 (3) and 2.658 (3) Å for relatively weaker Sn—O bonds.

Comment

Organotin compounds have important applications in the chemical industry. They are used in stabilization of PVC to prevent thermal degradation during processing and long-term photodegradation (Ahmad *et al.*, 2000). Dioctyltin compounds are used in PVC for food packing (Davies & Smith, 1982). Dibutyltin dilaurate is widely employed as a catalyst (Al-Allaf *et al.*, 1999). Organotin carboxylates are effective antitumor agents (Davies & Smith, 1982). Continuing our studies on the structural aspects of organotin carboxylates (Parvez, Ali, Mazhar, Bhatti & Khokhar, 1999; Parvez, Ali, Bhatti *et al.*, 1999; Parvez, Ali, Mazhar, Bhatti & Choudhary, 1999; Parvez *et al.*, 2000, 2002; Sadiq-ur-Rehman, Shouldice *et al.*, 2004; Sadiq-ur-Rehman, Abdelrahman *et al.*, 2004), we have synthesized a new compound, bis(cyclopentenylacetato)-tetraethyldistannoxane dimer, (I) the structure of which is reported here.
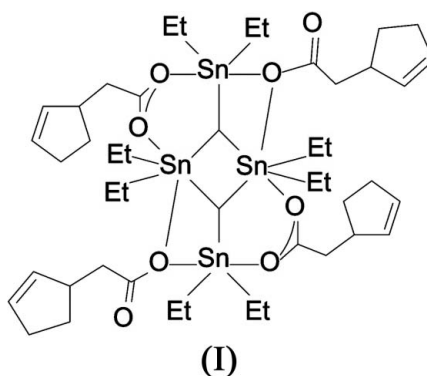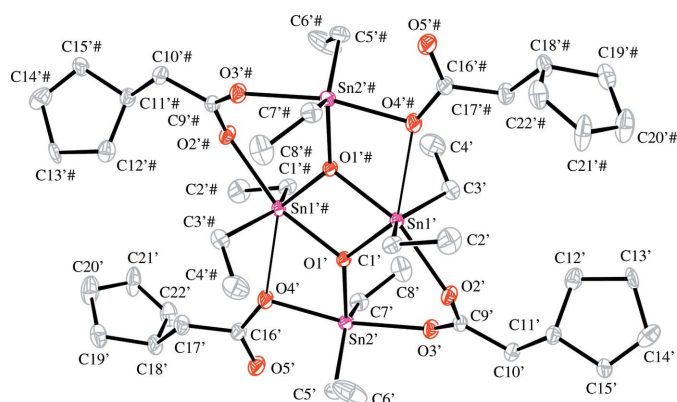

(I)

The molecular structure of (I) is composed of two independent centrosymmetric dimers lying about inversion centers
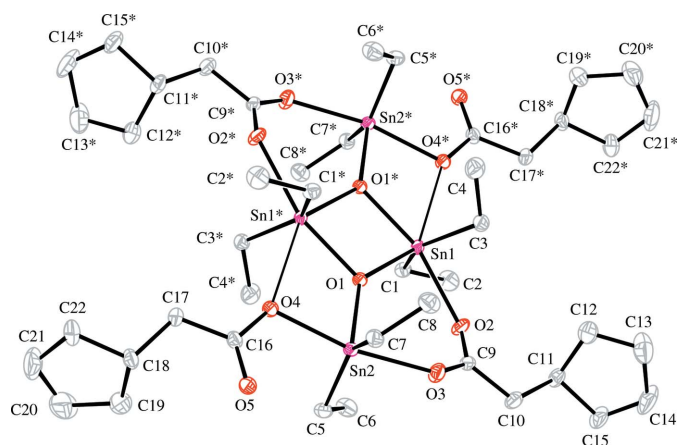
Figure 1
ORTEPII (Johnson, 1976) drawing of a dimer of (I) with displacement ellipsoids plotted at the 30% probability level. H atoms have been omitted for clarity. [symmetry code: (*) $1 - x$, $-y$, $1 - z$].

Figure 2
ORTEPII (Johnson, 1976) drawing of the second dimer of (I) with displacement ellipsoids plotted at the 30% probability level; fractions of disordered C atoms bearing A in the atomic labels of cyclopentenyl rings have been ignored. H atoms have been omitted for clarity. [symmetry code: (#) $1 - x$, $1 - y$, $-z$].

(Figs. 1 and 2). In each dimer, the central Sn_2O_2 core is fused with two four-membered (Sn_2O_2) and two six-membered (Sn_2O_3C) rings. The cyclopentenylacetate ligand shows different modes of coordination with tin. It acts as a monodentate ligand, bridging the two Sn atoms *via* atoms O4 and O4′ in each of the two dimers forming four-membered rings Sn1*/O4/Sn2/O1 [symmetry code: (*) $1 - x$, $-y$, $1 - z$] and Sn1′#/O4′/Sn2′/O1′ [symmetry code: (#) $1 - x$, $1 - y$, $-z$], respectively. The ligand also bridges two Sn atoms in bidentate coordination thus resulting in six-membered rings Sn1/O1/Sn2/O3/C9/O2 and Sn1′/O1′/Sn2′/O3′/C9′/O2′. The endocyclic Sn atoms are six-coordinate in a skew-trapezoidal bipyramidal environment. The exocyclic Sn atoms are five-coordinate and show distorted trigonal–bipyramidal geometry. In both dimers, Sn—C distances lie in a very narrow range [2.118 (4)–2.134 (4) Å], while Sn—O distances range between 2.042 (2) and 2.314 (3) Å for strong bonds and 2.638 (3) and 2.658 (3) Å for relatively weaker Sn—O bonds. The endocyclic Sn—O distances in the central core of the two dimers, Sn1/O1/Sn1*/O1* and Sn1′/O1′/Sn1′#/O1′# lying in the range 2.048 (2)–

2.140 (2) Å, and the exocyclic distances Sn1—O2 and Sn1′—O2′ [2.313 (3) and 2.314 (3) Å, respectively] are similar to those observed in bis[1,1,3,3-tetrabutyl-1,3-bis(picolinato *N*-oxide)]distannoxane hydrate (Ng, 1998), tetrabutylbis(*N*-phthaloylglycinato)distannoxane dimer (Parvez *et al.*, 2000) and tetrabutylbis(*N*-phthaloylphenylalaninato)distannoxane dimer (Hans *et al.*, 2002). However, the Sn1···O4* and Sn1···O4′# interactions of 2.638 (3) and 2.658 (3) Å, respectively, in the two dimers of (I) are significantly shorter than the corresponding interactions observed in tetrabutylbis(*N*-phthaloylphenylalaninato)distannoxane dimer [2.725 (3) Å; Hans *et al.*, 2002] and tetrabutylbis(*N*-phthaloylglycinato)distannoxane dimer [2.746 (3) Å; Parvez *et al.*, 2000].

It is interesting to note that in each dimer, one of the ligands is coordinated to both Sn atoms with C—O distances lying between a single and a double bond representing a delocalized system. In the other ligand the distances O—C clearly indicate a single and a double bond (details are in Table 1). A search of the Cambridge Structural Database (2006 Release; Allen, 2002) for similar fused-ring systems resulted in 80 hits, only three of which contained diethyl Sn units (refcodes JIPMIE, JUSJEM and REWXOG).

Experimental

Crystal data

$[Sn_4(C_2H_5)_8(C_7H_9O_2)_4O_2]$	$V = 2497.7$ (10) Å^3
$M_r = 1239.81$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.649$ Mg m^{-3}
$a = 11.736$ (3) Å	Mo $K\alpha$ radiation
$b = 12.201$ (3) Å	$\mu = 2.03$ mm^{-1}
$c = 19.503$ (4) Å	$T = 173$ (2) K
$\alpha = 72.674$ (14)°	Prism, colorless
$\beta = 73.357$ (12)°	$0.12 \times 0.12 \times 0.08$ mm
$\gamma = 73.937$ (13)°	

Data collection

Bruker–Nonius KappaCCD diffractometer	21463 measured reflections
ω and φ scans	11338 independent reflections
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)	8414 reflections with $I > 2\sigma(I)$
$T_{min} = 0.793$, $T_{max} = 0.855$	$R_{int} = 0.033$
	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0161P)^2 + 3.54P]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.073$	$(\Delta/\sigma)_{max} = 0.02$
$S = 1.07$	$\Delta\rho_{max} = 0.67$ e Å^{-3}
11338 reflections	$\Delta\rho_{min} = -0.91$ e Å^{-3}
556 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Sn1—O1	2.056 (2)	Sn1′—O1′	2.048 (2)
Sn1—C3	2.125 (4)	Sn1′—C1′	2.118 (4)
Sn1—C1	2.128 (4)	Sn1′—C3′	2.132 (4)
Sn1—O1^i	2.140 (2)	Sn1′—O1′^{ii}	2.139 (2)
Sn1—O2	2.313 (3)	Sn1′—O2′	2.314 (3)
Sn1—O4^i	2.638 (3)	Sn1′—O4′^{ii}	2.658 (3)
Sn2—O1	2.042 (2)	Sn2′—O1′	2.047 (3)
Sn2—C7	2.126 (4)	Sn2′—C5′	2.122 (4)
Sn2—C5	2.134 (4)	Sn2′—C7′	2.124 (4)
Sn2—O4	2.210 (3)	Sn2′—O4′	2.212 (3)
Sn2—O3	2.229 (3)	Sn2′—O3′	2.251 (3)
O2—C9	1.252 (5)	O2′—C9′	1.249 (5)
O3—C9	1.258 (4)	O3′—C9′	1.266 (5)
O4—C16	1.300 (4)	O4′—C16′	1.298 (5)
O5—C16	1.222 (5)	O5′—C16′	1.221 (5)
O1—Sn1—C3	105.98 (13)	O1′—Sn1′—C1′	111.57 (13)
O1—Sn1—C1	108.74 (12)	O1′—Sn1′—C3′	104.41 (14)
C3—Sn1—C1	141.62 (15)	C1′—Sn1′—C3′	140.28 (16)
O1—Sn1—O1^i	76.13 (10)	O1′—Sn1′—O1′^{ii}	75.89 (11)
C3—Sn1—O1^i	105.38 (12)	C1′—Sn1′—O1′^{ii}	99.07 (13)
C1—Sn1—O1^i	98.38 (12)	C3′—Sn1′—O1′^{ii}	105.60 (14)
O1—Sn1—O2	88.21 (9)	O1′—Sn1′—O2′	87.59 (10)
C3—Sn1—O2	83.22 (12)	C1′—Sn1′—O2′	80.83 (13)
C1—Sn1—O2	82.04 (12)	C3′—Sn1′—O2′	84.50 (14)
O1^i—Sn1—O2	163.65 (9)	O1′^{ii}—Sn1′—O2′	162.27 (9)
O1—Sn1—O4^i	142.10 (8)	O1′—Sn1′—O4′^{ii}	140.42 (9)
C3—Sn1—O4^i	81.54 (12)	C1′—Sn1′—O4′^{ii}	82.62 (13)
C1—Sn1—O4^i	81.10 (12)	C3′—Sn1′—O4′^{ii}	80.19 (14)
O1^i—Sn1—O4^i	66.15 (8)	O1′^{ii}—Sn1′—O4′^{ii}	65.23 (9)
O2—Sn1—O4^i	129.68 (8)	O2′—Sn1′—O4′^{ii}	131.84 (9)
O1—Sn2—C7	111.03 (12)	O1′—Sn2′—C5′	109.32 (14)
O1—Sn2—C5	109.19 (13)	O1′—Sn2′—C7′	111.87 (14)
C7—Sn2—C5	139.76 (15)	C5′—Sn2′—C7′	138.81 (17)
O1—Sn2—O4	76.65 (9)	O1′—Sn2′—O4′	75.88 (10)
C7—Sn2—O4	94.54 (12)	C5′—Sn2′—O4′	95.12 (14)
C5—Sn2—O4	95.47 (13)	C7′—Sn2′—O4′	95.25 (14)
O1—Sn2—O3	91.45 (10)	O1′—Sn2′—O3′	90.49 (10)
C7—Sn2—O3	87.62 (13)	C5′—Sn2′—O3′	90.30 (14)
C5—Sn2—O3	90.49 (13)	C7′—Sn2′—O3′	88.83 (14)
O4—Sn2—O3	167.90 (10)	O4′—Sn2′—O3′	166.33 (10)
Sn2—O1—Sn1	136.02 (12)	Sn2′—O1′—Sn1′	135.34 (12)
Sn2—O1—Sn1^i	119.67 (11)	Sn2′—O1′—Sn1′^{ii}	119.99 (11)
Sn1—O1—Sn1^i	103.87 (10)	Sn1′—O1′—Sn1′^{ii}	104.11 (11)
C9—O2—Sn1	134.1 (2)	C9′—O2′—Sn1′	131.4 (2)
Sn1—O2—Sn2	76.78 (7)	Sn1′—O2′—Sn2′	77.29 (7)
C9—O3—Sn2	134.4 (3)	C9′—O3′—Sn2′	130.8 (3)
C16—O4—Sn2	111.2 (2)	C16′—O4′—Sn2′	111.9 (2)

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x + 1, -y + 1, -z$.

Both cyclopentenyl rings of the second dimer (Fig. 2) were disordered, with C10′–C15′ and C10A–C15A both having 0.50 site-occupancy factors, while C18′–C22′ and C18A–C22A had site-occupancy factors of 0.774 (9) and 0.226 (9), respectively. The pairs of disordered C atoms were allowed the same anisotropic displacement parameters (EADP command). Moreover, the same coordinates were used for the pairs of atoms C10′/C10A, C11′/C11A and C18′/C18A in order to model the cyclopentenyl rings and determine the positions of H atoms (EXYZ command). H atoms were included in the refinement at geometrically idealized positions with C—H = 0.95–1.00 Å and U_{iso} = 1.5 (methyl) and 1.2 (the rest) times U_{eq} of the atoms to which they were bonded. The final difference map was free of any chemically significant features.

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