

1,3-Dichloro-1,1-dimethyl-3,3-diisopropyl-distannoxane¹

Yan Lu,* Xuebing Leng, Honggen Wang, Qinglan Xie and Jing Li

National Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Correspondence e-mail: lyane@public.tpt.tj.cn

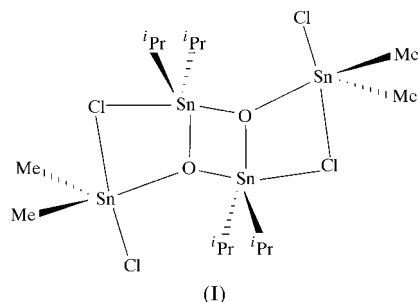
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The title compound, $[\text{Sn}_4(\text{CH}_3)_4(\text{C}_3\text{H}_7)_4\text{Cl}_4\text{O}_2]$ or $\{\text{Cl}[(\text{CH}_3)_2\text{CH}]_2\text{SnOSn}(\text{CH}_3)_2\text{Cl}\}_2$, obtained by the reaction of $[(\text{CH}_3)_2\text{CH}]_2\text{SnO}$ and $(\text{CH}_3)_2\text{SnCl}_2$, exists as centrosymmetric dimers in the solid state. It contains a central planar four-membered Sn_2O_2 ring. The coordinate geometry about the Sn atoms is distorted trigonal pyramidal.

Comment

1,3-Disubstituted-1,1,3,3-tetraorganodistannoxanes are useful catalysts for many reactions (Otera, 1994). A characteristic feature of symmetric tetraorganodistannoxanes is their dimerization, which results in a ladder-type arrangement containing a central planar four-membered Sn_2O_2 ring. Compared with symmetric tetraorganodistannoxanes, the structures of asymmetric tetraorganodistannoxanes have not been fully investigated. From the reported data for asymmetric tetraorganodistannoxanes with mixed *R* groups, it can be seen that larger groups promote linkage with exocyclic Sn atoms because of their hindering effect (Dakternieks *et al.*, 1997; Lu *et al.*, 2000). But the title compound, 1,3-disubstituted-1,1,3,3-tetraorganodistannoxane, (I), is an exception.



The title compound (Fig. 1) exists as ladder-type dimers that are analogous to the traditional structure of symmetric

¹ Systematic name: di- μ -chloro-1:2 κ^2 Cl;3:4 κ^2 Cl-dichloro-1 κ Cl,4 κ Cl-tetraiso-propyl-2 κ^2 C,3 κ^2 C-tetramethyl-1 κ^2 C,4 κ^2 C-di- μ_3 -oxo-1:2:3 κ^3 O;2:3:4 κ^3 O-tetramethin(IV).

distannoxanes, but the larger bulky isopropyl (*i*Pr) groups unusually link to *exo*-Sn atoms, while the smaller Me groups connect to *endo*-Sn atoms. In the asymmetric unit, both Me_2SnCl and $\text{Sn}(\text{iPr})_2$ groups are connected by a Cl and an O atom to form the $\text{Me}_2\text{Sn}(\text{Cl})(\mu_2\text{-Cl})(\mu\text{-O})\text{Sn}(\text{iPr})_2$ fragment. The bridging oxo atom functions as a triple-bond bridge and the internal angles [105.55 (14) and 74.45 (14) $^\circ$; Table 1] of the central Sn_2O_2 are compared with those in other distannoxane systems, such as 104.6 (2) $^\circ$ in $[\text{Cl}(\text{iBu})_2\text{SnOSnMe}_2\text{Cl}]_2$, 104.8 (2) $^\circ$ in $[\text{Cl}(\text{iBu})_2\text{SnOSnPh}_2\text{Cl}]_2$ (Dakternieks *et al.*, 1997) and 105.69 (17) $^\circ$ in $[\text{Cl}(\text{iBu})_2\text{SnOSnPh}_2\text{Cl}]_2$ (Lu *et al.*, 2000). The three $\mu_3\text{-O-Sn}$ bond distances are very similar [$\text{Sn}2\text{-O}1$ 2.053 (3) Å, $\text{Sn}1\text{-O}1$ 2.015 (3) Å and $\text{Sn}2'\text{-O}1$ 2.143 (3) Å; symmetry code: (i) $-x, 2-y, 2-z$], reflecting the strong bridging oxo coordination with Sn atoms in the dimer. All four Sn atoms, the four Cl atoms and two O atoms comprise a fused ring system that is coplanar, with a mean deviation of ± 0.0054 (6) Å.

The geometry about all the Sn atoms can be described as distorted trigonal bipyramidal. With regard to Sn1, one $\mu_3\text{-O}$ and two methyl C atoms are in equatorial positions. The axial Cl-Sn-Cl angle of 163.48 (5) $^\circ$ deviates from the ideal value of 180 $^\circ$. This deviation may be due to the interaction of the Cl atoms with the endocyclic Sn atoms. For Sn2, the axial O-Sn-Cl angle is 150.80 (9) $^\circ$. Both kinds of Sn atoms are pentacoordinated. Atom Cl2 has a close intermolecular contact with Sn2, which may be viewed as a weak bonding interaction; the Sn...Cl2 distance is 3.3613 (19) Å, compared with the van der Waals radii sum of 4.0 Å. This is different from the case in asymmetric tetraorganodistannoxanes $[\text{Cl}(\text{iBu})_2\text{SnOSnR}_2\text{Cl}]_2$ (*R* = Me, Bu), in which both Cl atoms interact with the endocyclic Sn atom, making the *endo*-Sn atom six-coordinate, while the *exo*-Sn atom is still five-coordinate [the *endo*-Sn-Cl and *exo*-Sn-Cl bond lengths are 2.802 (2) and 2.675 (2) Å for *R* = Me, and 2.907 (2) and 2.598 (2) Å, respectively, for *R* = "Bu"]. The reason for this may be attributable to the fact that the Sn2 atom is connected to

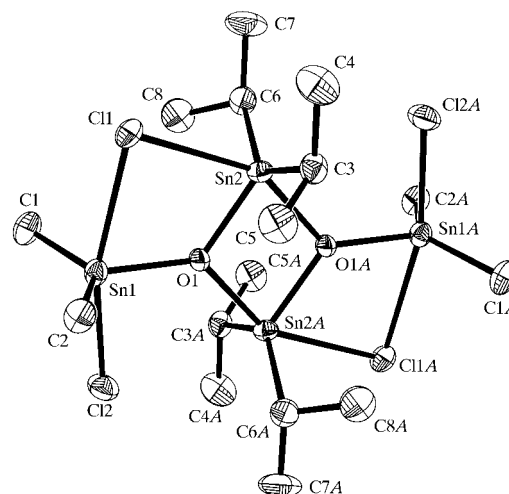


Figure 1

A view of (I) showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

the larger *exo*-butyl groups while the *endo*-Sn atom is connected to the smaller groups in the dimer.

Experimental

The synthesis of the title compound was carried out by reaction of equimolar amounts of $[(\text{CH}_3)_2\text{CH}]_2\text{SnO}$ and $(\text{CH}_3)_2\text{SnCl}_2$ by refluxing an acetone solution for 1 h until the solution became clear. Recrystallization from acetone yielded colourless crystals of (I) suitable for X-ray analysis (yield 67%). Analysis calculated for $\text{C}_{16}\text{H}_{40}\text{Cl}_4\text{O}_2\text{Sn}_4$: C 21.81, H 4.58%; found: C 21.73, H 4.62%; FT-IR data (KBr pellet, cm^{-1}): 2965 (s), 2859 (m), 1382 (m), 1355 (s), 1197 (m), 1153 (s), 797 (s), 607 (s), 546 (s).

Crystal data

$[\text{Sn}_4(\text{CH}_3)_4(\text{C}_3\text{H}_7)_4\text{Cl}_4\text{O}_2]$	$D_x = 1.989 \text{ Mg m}^{-3}$
$M_r = 881.04$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 52 reflections
$a = 10.268 (4) \text{ \AA}$	$\theta = 2.8\text{--}25.3^\circ$
$b = 9.529 (3) \text{ \AA}$	$\mu = 3.73 \text{ mm}^{-1}$
$c = 15.315 (5) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 101.023 (6)^\circ$	Rhombic, colorless
$V = 1470.8 (9) \text{ \AA}^3$	$0.20 \times 0.10 \times 0.10 \text{ mm}$
$Z = 2$	

Data collection

Bruker CCD area-detector diffractometer	1825 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.038$
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)	$\theta_{\text{max}} = 25.0^\circ$
$T_{\text{min}} = 0.646$, $T_{\text{max}} = 0.689$	$h = -12 \rightarrow 11$
5966 measured reflections	$k = -9 \rightarrow 11$
2591 independent reflections	$l = -18 \rightarrow 12$
	Intensity decay: none

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.029$	$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2]$
$wR(F^2) = 0.068$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.92$	$(\Delta/\sigma)_{\text{max}} = 0.002$
2591 reflections	$\Delta\rho_{\text{max}} = 0.43 \text{ e \AA}^{-3}$
118 parameters	$\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$

All H atoms were located geometrically (C–H = 0.96 Å) and neither their positional nor displacement parameters were refined.

Table 1

Selected geometric parameters (Å, °).

Sn1–O1	2.015 (3)	Sn2–O1	2.053 (3)
Sn1–Cl2	2.474 (2)	Sn2–O1 ⁱ	2.143 (3)
Sn1–Cl1	2.757 (2)	Sn2–Cl1	2.724 (2)
O1–Sn1–Cl2	87.31 (10)	O1–Sn2–Cl1	76.43 (10)
C2–Sn1–Cl2	95.87 (17)	O1 ⁱ –Sn2–Cl1	150.81 (9)
C1–Sn1–Cl2	95.63 (17)	Sn2–Cl1–Sn1	82.34 (4)
O1–Sn1–Cl1	76.21 (10)	Sn1–O1–Sn2	125.01 (17)
Cl2–Sn1–Cl1	163.48 (5)	Sn1–O1–Sn2 ⁱ	129.36 (16)
O1–Sn2–O1 ⁱ	74.45 (14)	Sn2–O1–Sn2 ⁱ	105.55 (14)

Symmetry code: (i) $-x, 2 - y, 2 - z$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1147). Services for accessing these data are described at the back of the journal.

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