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The ionic tin(IV) complex tri-μ_2-methoxy-μ_3-oxo-tris[di-*tert*-butyltin(IV)] tri-μ_2-methoxy-bis[*tert*-butyldimethoxystannate(IV)]

Danielle Ballivet-Tkatchenko,* Romain Burgat, Laurent Plasseraud and Philippe Richard

LSEO UMR 5188 CNRS, Université de Bourgogne, BP 47870, 21078 Dijon Cedex, France

Correspondence e-mail: ballivet@u-bourgogne.fr

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Key indicators

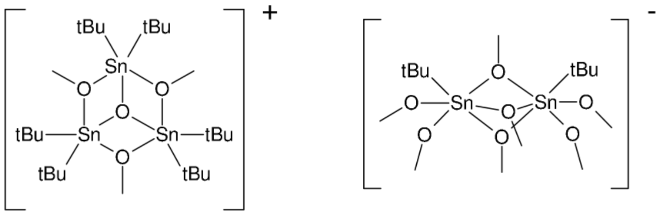
Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.027
wR factor = 0.057
Data-to-parameter ratio = 20.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The solid-state of the title compound, $[Sn_3(C_4H_9)_6(CH_3O)_3O][Sn_2(C_4H_9)_2(CH_3O)_7]$, consists of distinct $[^t\mathrm{Bu}_6\mathrm{Sn}_3(\mu\text{-OCH}_3)_3(\mu_3\text{-O})]^+$ cations and $[^t\mathrm{Bu}_2\mathrm{Sn}_2(\mathrm{OCH}_3)_4(\mu\text{-OCH}_3)_3]^-$ anions, apparently formed as a result of slow hydrolysis of pure di(*tert*-butyl)dimethoxystannane, $^t\mathrm{Bu}_2\mathrm{Sn}(\mathrm{OCH}_3)_2$. In the monocation, the coordination about the Sn atoms is distorted trigonal bipyramidal, and, in the monoanion, distorted octahedral. The trigonal bipyramidal arrangement induces planarity of the Sn_3O_4 motif.

Comment

Our interest in the reactivity of Sn—O*R* bonds of di(*n*-butyl)dialkoxystannanes toward CO_2 insertion (Ballivet-Tkatchenko *et al.*, 2000) has been extended to di(*tert*-butyl)dialkoxystannanes. For this purpose, the synthesis of $^t\mathrm{Bu}_2\mathrm{Sn}(\mathrm{OCH}_3)_2$ was achieved and crystals of the title compound, (I), were formed from liquid $^t\mathrm{Bu}_2\mathrm{Sn}(\mathrm{OCH}_3)_2$ upon standing under argon for one month at room temperature.



(I)

Comparison of the empirical formulae of the two compounds allows us to write a reaction stoichiometry involving hydrolysis due to water in trace amounts:

$$5[^t\mathrm{Bu}_2\mathrm{Sn}(\mathrm{OCH}_3)_2] + \mathrm{H_2O} \rightarrow [^t\mathrm{Bu}_6\mathrm{Sn}_3(\mathrm{OCH}_3)_3\mathrm{O}]^+[^t\mathrm{Bu}_2\mathrm{Sn}_2(\mathrm{OCH}_3)_7]^- + 2^t\mathrm{BuH}.$$

The main features of the reaction are conservation of the Sn:OCH_3 ratio, the presence of an extra O atom in the product, and cleavage of two Sn—^{t}Bu bonds. The X-ray diffraction analysis of (I) reveals an ionic structure with no significant non-ionic intermolecular contacts. The monocation $[^t\mathrm{Bu}_6\mathrm{Sn}_3(\mathrm{OCH}_3)_3\mathrm{O}]^+$ adopts approximate D_{3h} symmetry (Fig. 1). The three Sn atoms are pentacoordinated in a distorted trigonal bipyramidal arrangement (TBP). The equatorial plane is occupied by the two *tert*-butyl groups [C—Sn—C = 119.6 (8)° (mean) and Sn—C = 2.189 (6) Å (mean)] and the μ_3-O atom [C—Sn—O4 = 120 (3)° (mean) and Sn—O4 = 2.016 (2) Å (mean)], while the μ-OCH_3 groups are in the axial positions [O—Sn—O = 136.9 (2)° (mean) and Sn—O = 2.230 (16) Å (mean)]. The three TBPs share the equatorial μ_3-O4 atom, being connected pairwise *via* an O4–OCH_3 edge. The Sn_3O_4 core is planar (seven atoms r.m.s. deviation =

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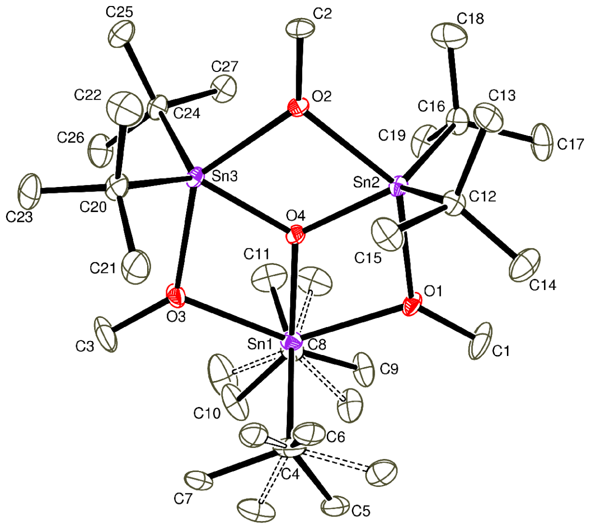

Figure 1
*ORTEP*III (Burnett & Johnson, 1996) view of the cationic moiety of the title compound (30% probability displacement ellipsoids). For clarity, the H atoms are not shown. Both disordered components are shown.

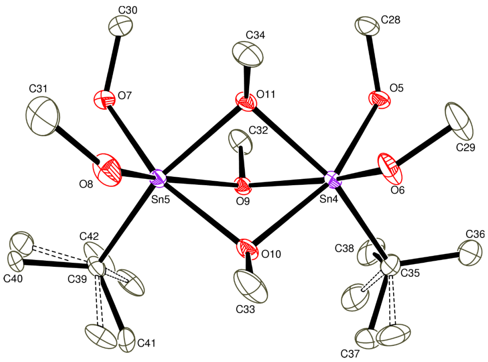

Figure 2
*ORTEP*III (Burnett & Johnson, 1996) view of the anionic moiety of the title compound (30% probability displacement ellipsoids). For clarity, the H atoms are not shown. Both disordered components are shown.

0.04 Å). Interestingly, in the compound $\{[(CH_3)_3Sn]_3O\}Cl$ described as a tritin oxonium salt, the $Sn_3\mu_3$-O core is also planar with pentacoordination about Sn atoms (Räke *et al.*, 1999). The O-capped structure has been observed for neutral tritin compounds in which Sn atoms are hexacoordinated, as, for example, $\{[n\text{-}BuSn(OH)O_2PPh_2]_3O\}\{Ph_2PO_2\}$ (Day *et al.*, 1987) and $Sn_3(O^iBu)_7(\mu\text{-}O^iBu)_3(\mu_3\text{-}O)\cdot 2^iBuOH$ (Reuter & Kremser, 1992). The monoanion $[^tBu_2Sn_2(OCH_3)_7]^-$ in (I) adopts approximate C_s symmetry (Fig. 2). It is formed by face-sharing distorted octahedra built about Sn4 and Sn5, with no significant Sn—Sn bonding interaction [Sn4···Sn5 = 3.1762 (3) Å]. The three μ-OCH$_3$ ligands are equidistant from the two Sn atoms, as in the monocation, with similar Sn—O mean bond lengths of 2.166 (12) and 2.230 (16) Å, respectively. That with the terminal OCH$_3$ is shorter [2.022 (6) Å], as expected. The two *tert*-butyl groups adopt a *syn* configuration. The Sn—C mean bond length is very similar to that of the cation, 2.182 (3) and 2.189 (6) Å, respectively. The $[^tBu_2Sn_2(OCH_3)_4(\mu\text{-}OCH_3)_3]^-$ fragment can be visualized as a variant of the ionic structure $[I_6Sn_2(\mu\text{-}O^iC_3H_7)_3]^-$ (Veith *et al.*, 1997).

Experimental

The title compound separated as clear transparent crystals from liquid $^tBu_2Sn(OCH_3)_2$ upon storage in a Schlenk tube under argon atmosphere over a period of two months at room temperature. A single crystal of (I) was selected for X-ray structure determination at 110 K. The precursor compound, $^tBu_2Sn(OCH_3)_2$, was prepared from $^tBu_2SnCl_2$ (Kandil & Allred, 1970) and sodium methoxide according to an adapted procedure (Ballivet-Tkatchenko *et al.*, 2000). Final purification by vacuum distillation (2×10^{-2} mbar) at 313 K led to the colorless oil $^tBu_2Sn(OCH_3)_2$. Analysis calculated for $C_{10}H_{24}O_2Sn$: C 40.72, H 8.20%; found: C 40.79, H 8.09%. NMR (CDCl$_3$, 300 K, p.p.m.): $^{13}C\{^1H\}$ (75.46 MHz, $^{13}CDCl_3$ = 77.00): 54.70 (OCH$_3$), 39.77 [$^1J^{13}C$, ^{119}Sn = 470 Hz, $^1J^{13}C$, ^{117}Sn = 450 Hz, C(CH$_3$)$_3$], 29.88 [C(CH$_3$)$_3$]; $^{119}Sn\{^1H\}$ [111.92 MHz, $^{119}Sn(CH_3)_4$ = 0], −108; ^1H (300.13 MHz, CHCl$_3$ = 7.24), 3.81 (OCH$_3$), 1.37 [C(CH$_3$)$_3$] (1:3).

Crystal data

$[Sn_3(C_4H_9)_6(CH_3O)_3O]$-
$[Sn_2(C_4H_9)_2(CH_3O)_7]$
M_r = 1376.79
Monoclinic, $P2_1/c$
a = 11.5912 (1) Å
b = 21.7257 (2) Å
c = 22.9487 (2) Å
β = 90.7188 (4)°
V = 5778.65 (9) Å^3
Z = 4
D_x = 1.582 Mg m^{-3}
Cell parameters from 23 813 reflections
θ = 1–27.5°
μ = 2.18 mm^{-1}
T = 110 (2) K
Prism, colorless
0.5 × 0.4 × 0.4 mm

Data collection

Nonius KappaCCD diffractometer
φ scans (κ = 0) + additional ω scan
Absorption correction: none
39 184 measured reflections
13 216 independent reflections
10 643 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 27.5°
$h = -15 \rightarrow 15$
$k = -28 \rightarrow 27$
$l = -21 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.057
S = 1.02
13216 reflections
644 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2 + 5.4899P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.011
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.97 e Å^{-3}

Table 1
Selected bond distances (Å).

Sn1—O4	2.0145 (19)	Sn3—O3	2.243 (2)
Sn1—C8	2.193 (3)	Sn4—O6	2.018 (2)
Sn1—C4	2.198 (3)	Sn4—O5	2.028 (2)
Sn1—O3	2.205 (2)	Sn4—O10	2.153 (2)
Sn1—O1	2.240 (2)	Sn4—O9	2.162 (2)
Sn2—O4	2.0144 (19)	Sn4—C35	2.181 (4)
Sn2—C12	2.179 (3)	Sn4—O11	2.184 (2)
Sn2—C16	2.185 (3)	Sn4—Sn5	3.1763 (3)
Sn2—O2	2.2231 (19)	Sn5—O8	2.016 (2)
Sn2—O1	2.248 (2)	Sn5—O7	2.027 (2)
Sn3—O4	2.0180 (19)	Sn5—O11	2.157 (2)
Sn3—C24	2.188 (3)	Sn5—O9	2.1641 (19)
Sn3—C20	2.189 (3)	Sn5—O10	2.174 (2)
Sn3—O2	2.2156 (19)	Sn5—C39	2.178 (3)

Three *tert*-butyl groups (two for the cation and one for the anion) were found to be disordered over two positions [occupancies: C5,C6,C7/C5*A*,C6*A*,C7*A* 0.489 (5):0.511 (5); C9,C10,C11/C9*A*, C10*A*,C11*A* 0.56 (1):0.44 (1); C40,C41,C42/C40*A*,C41*A*,C42*A* 0.60 (1):0.40 (1)]. Two C atoms of the anion exhibit large displacement ellipsoids; each of these atomic positions was then split over two sites [C37,C38/C37*A*,C38*A*; 0.67 (1)/0.33 (1)]. All H atoms were placed in idealized positions (C—H = 0.96 Å) and refined using a riding model [U_{iso}(H) = 1.5U_{eq}(C)]. The torsion angle of the methyl groups in the methoxy groups was refined.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97 and *WinGX* (Farrugia, 1999)

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References

Ballivet-Tkatchenko, D., Douteau, O. & Stutzmann, S. (2000). *Organometallics*, **19**, 4563–4567.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Day, R. O., Holmes, J. M., Chandrasekhar, V. & Holmes, R. R. (1987). *J. Am. Chem. Soc.* **109**, 940–941.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Kandil, S. A. & Allred, A. L. (1970). *J. Chem. Soc. A*, pp. 2987–2992.

Nonius (1997). *KappaCCD Server Software*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Räke, B., Müller, P., Roesky, H. W. & Uson, I. (1999). *Angew. Chem. Int. Ed.* **38**, 2050–2052.

Reuter, H. & Kremser, M. (1992). *Z. Anorg. Allg. Chem.* **615**, 137–142.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Veith, M., Mathur, S. & Huch, V. (1997). *Chem. Commun.* pp. 2197–2198.