

Hydrolysis products of diorganotin dihalides. I. Bis[1,3-dihydroxo-1,1,3,3-tetrakis(2-methyl-2-phenylpropyl)-distannoxane]

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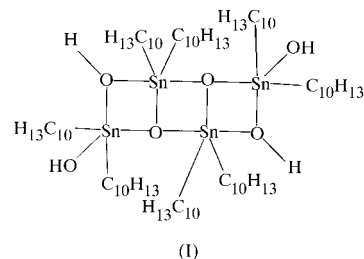
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In the solid state, the title compound, di- μ -hydroxo-1:2 κ^2 O;-3:4 κ^2 O-dihydroxo-1 κ O,4 κ O-octakis(2-methyl-2-phenylpropyl)-1 κ^2 C,2 κ^2 C,3 κ^2 C,4 κ^2 C-di- μ_3 -oxo-1:2:3 κ^3 O;2:3:4 κ^3 O-tetra-tin(IV), [Sn₄O₂(OH)₄(C₁₀H₁₃)₈], forms centrosymmetric dimeric [(Neophyl₂SnOH)(Neophyl₂SnOH)O]₂ molecules (Neophyl = 2-methyl-2-phenylpropyl), with an almost planar Sn–O framework that adopts a ladder-type structure consisting of three four-membered rings. The hydroxyl groups are shielded by the organic groups, which prevent them from further condensation and from the formation of hydrogen bonds.

Comment

Although the first step in the hydrolysis of diorganotin dihalides, R₂SnX₂, (1) (X = Cl, Br or I), namely the formation of a dimeric ‘hydroxide halide’ R₂Sn(OH)X, (2) (Puff *et al.*, 1985), is common to all kinds of organic groups R, further hydrolysis products depend on the size of the two organic ligands. Thus, the complete hydrolysis of (1) with bulky organic groups such as *tert*-butyl (Puff, Schuh *et al.*, 1981) or mesityl (Weber *et al.*, 1982) results in the formation of soluble trimeric ‘oxides’ (R₂SnO)₃, (3), with tetrahedrally coordinated Sn. In the case of small organic groups such as isopropyl or phenyl, however, complete hydrolysis leads to the formation of insoluble polymeric ‘oxides’ (R₂SnO)_n, (4), the structures of which are unknown. On the way to this final product, three intermediates can be isolated, all showing the so-called ‘ladder-type structure’, because their inorganic frameworks consist of three four-membered rings, with fivefold trigonal-bipyramidally coordinated Sn atoms. According to the degree of hydrolysis and condensation one can distinguish between the so-called ‘dihalides’ [(R₂SnX)(R₂SnX)O]₂, (5), ‘hydroxide halides’ [(R₂SnX)(R₂SnOH)O]₂, (6) and ‘dihydroxides’ [(R₂SnR₂SnOH)O]₂, (7). Although in the literature there are numerous examples of compounds of types (5) (Harrison *et al.*, 1980; Puff, Friedrichs & Visel, 1981; Graziani *et al.*, 1983;

Dakternieks *et al.*, 1984; Vollano *et al.*, 1984; Hamalainen & Turpeinen, 1987; Beckmann *et al.*, 1998) and (6) (Vollano *et al.*, 1984; Puff *et al.*, 1983; Tiekink, 1991; Kresinski *et al.*, 1994; Cox & Tiekink, 1994), only one compound with R = trimethylsilylmethyl (Puff, Friedrichs & Visel, 1981) is known to be of type (7), because this step in the course of the hydrolysis is difficult to prepare. Only by chance we found, in our study of tris(2,2-dimethyl-2-phenylethyl)tin halides (Neophyl₃SnX; X = F, Cl, Br or I; Neophyl = 2-methyl-2-phenylpropyl), a second compound of this type (7), namely the title compound, (I).



The crystal structure of (I) consists of centrosymmetric [Neophyl₂SnOH)(Neophyl₂SnOH)O]₂ molecules with an almost planar Sn–O framework. This is characterized by a central four-membered Sn–O ring with a small O1–Sn1–O1ⁱ angle [73.19 (9)°] and a broadened Sn1–O1–Sn1ⁱ angle [106.81 (9)°] [symmetry code: (i) 2 – x, 2 – y, 1 – z]. These values are typical for such a building unit and are also found, for example, in (5) and (6), as well as in cassiterite, SnO₂ (Bolzan *et al.*, 1997). The two outer four-membered Sn–O rings differ from this geometry because only the O1 atom is of the μ_3 -type; the other O atom belongs to a μ_2 -OH function and therefore the bond lengths and angles are different. In particular, the bridging OH group shows great differences in bond lengths: 2.325 (3) Å to the outer and 2.110 (2) Å to the

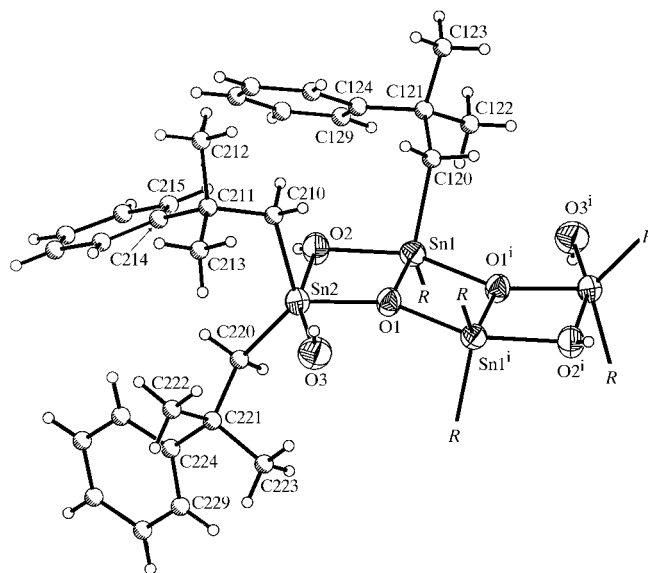


Figure 1
A perspective view of the asymmetric unit of (I) and the centrosymmetric atoms of the Sn–O framework. Sn and O atoms are plotted with displacement ellipsoids at the 50% probability level; other atoms are shown as small spheres of arbitrary radii. Some of the neophyl groups are shown simply as R for clarity [symmetry code: (i) 2 – x, 2 – y, 1 – z].

inner Sn atom. The bond angles are O1—Sn1—O2 = 74.57 (19) and O1—Sn2—O2 = 70.34 (9), Sn1—O2—Sn2 = 100.87 (19)° at the μ_3 -O atom and Sn2—O1—Sn1 = 114.13 (11)° at the μ_2 -OH group.

Both Sn atoms have a distorted trigonal bipyramidal coordination, with two O atoms in axial positions and two C and one further O atom in equatorial positions. However, the axes of these trigonal bipyramids are to some extent bent, as shown by the angles O2—Sn1—O1ⁱ = 147.75 (9)° and O2—Sn2—O3 = 159.0 (1)°. Similar distortion can also be found in the ladder-type structures of (5) and (6). The mean Sn—C distance is 2.152 Å, which is slightly shorter than the Sn—C distance in the corresponding tetraorganotin compound (2.186 Å; Reuter & Pawlak, 1998).

The organic groups in (I) shield the Sn—O framework and prevent it from further condensation and from the formation of intermolecular hydrogen bonding.

Experimental

The title compound was obtained by chance during the preparation of trineophyltin iodide, Neophyl₃SnI, from trineophyltin chloride *via* the corresponding distannoxane. For this purpose, the chloride was hydrolyzed with concentrated potassium hydroxide solution in a heated toluene–water mixture. Most of the organic layer containing the distannoxane was decanted and worked up; the aqueous reaction mixture, which also contained a small amount of the organic solution, was left aside. After some weeks, most of the solvent had evaporated and some clear transparent crystals of (I) had formed. It is known (Davies, 1997) that tetraorganotin distannoxanes often separate from samples of triorganotin halides when stored for long periods. A single crystal of (I) was selected using a polarization microscope and mounted on top of a Lindemann capillary with a cyanoacrylate adhesive.

Crystal data

[Sn₂O₂(OH)₄(C₁₀H₁₃)₈]

$M_r = 1640.42$

Triclinic, *P* $\bar{1}$

$a = 10.878$ (2) Å

$b = 11.598$ (3) Å

$c = 17.077$ (2) Å

$\alpha = 73.19$ (2)°

$\beta = 81.944$ (19)°

$\gamma = 66.91$ (2)°

$V = 1896.4$ (7) Å³

$Z = 1$

$D_x = 1.436$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 20 reflections

$\theta = 5.07$ – 12.52 °

$\mu = 1.351$ mm⁻¹

$T = 293$ (2) K

Block, colourless

$0.43 \times 0.29 \times 0.25$ mm

Data collection

Siemens P4 diffractometer

$2\theta/\omega$ scans

Absorption correction: ψ -scan

(*SHELXTL*; Sheldrick, 1997a)

$T_{\min} = 0.652$, $T_{\max} = 0.713$

7739 measured reflections

6615 independent reflections

5394 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\text{max}} = 25$ °

$h = -12 \rightarrow 1$

$k = -13 \rightarrow 12$

$l = -20 \rightarrow 20$

3 standard reflections

every 97 reflections

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.072$

$S = 1.029$

6615 reflections

408 parameters

H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 0.3893P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.011$

$\Delta\rho_{\text{max}} = 0.62$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.51$ e Å⁻³

Extinction correction: *SHELXL97* (Sheldrick, 1997b)

Extinction coefficient: 0.0007 (2)

Table 1

Selected geometric parameters (Å, °).

Sn1—O1	2.049 (2)	Sn2—O1	2.029 (2)
Sn1—O2	2.110 (2)	Sn2—O3	2.043 (3)
Sn1—C110	2.151 (4)	Sn2—C220	2.149 (4)
Sn1—C120	2.155 (4)	Sn2—C210	2.151 (4)
Sn1—O1 ⁱ	2.168 (2)	Sn2—O2	2.325 (3)
O1—Sn1—O2	74.57 (10)	O3—Sn2—C220	104.28 (15)
O1—Sn1—C110	123.75 (15)	O1—Sn2—C210	109.07 (12)
O2—Sn1—C110	102.28 (14)	O3—Sn2—C210	99.93 (15)
O1—Sn1—C120	112.75 (12)	C220—Sn2—C210	127.61 (16)
O2—Sn1—C120	97.29 (13)	O1—Sn2—O2	70.34 (9)
C110—Sn1—C120	123.19 (16)	O3—Sn2—O2	159.00 (10)
O1—Sn1—O1 ⁱ	73.19 (9)	C220—Sn2—O2	84.83 (14)
O2—Sn1—O1 ⁱ	147.75 (9)	C210—Sn2—O2	88.70 (14)
C110—Sn1—O1 ⁱ	94.94 (14)	Sn2—O1—Sn1	114.13 (11)
C120—Sn1—O1 ⁱ	95.71 (12)	Sn2—O1—Sn1 ⁱ	139.02 (12)
O1—Sn2—O3	88.71 (11)	Sn1—O1—Sn1 ⁱ	106.81 (9)
O1—Sn2—C220	117.14 (14)	Sn1—O2—Sn2	100.87 (10)

Symmetry code: (i) $2 - x, 2 - y, 1 - z$.

The positions of the H atoms on the OH groups were found in difference Fourier maps and were refined riding on the coordinates of the O atoms (O—H 0.82 Å). All other H atoms were placed in calculated positions (C—H 0.93–0.97 Å).

Data collection and cell refinement: *XSCANS* (Siemens, 1996); data reduction: *SHELXTL* (Sheldrick, 1997a); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b); molecular graphics and 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: NA1470). Services for accessing these data are described at the back of the journal.

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