Tin Clusters

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Organic–Inorganic Sn_{12} and Organic Sn_6 Oxide–Hydroxide Clusters**

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For many years, it was thought that the hydrolysis of monoorganotin compounds leads only to ill-defined products called organostannonic acids and formulated as $(RSnOOH)_n$. These acids are of industrial importance, as they are used as esterification and transesterification catalysts.[1] Recently, reinvestigation of this reaction showed that it can also give clusters of low molecular weights and variable sizes, which depend on the identity of the organic group linked to the tin atom and on the reaction conditions. A ball-like Sn_{12} cluster bearing two hydroxy groups was formed, together with an undefined oxopolymer, from the hydrolysis of tin halides or alkoxides bearing a simple butyl group as the organic ligand.[2] In this cluster, half of the tin atoms are pentacoordinated and the other half are hexacoordinated. When the very bulky tris(trimethylsilyl)methyl group was used as the ligand in a similar reaction, an adamantane-type Sn_4 cluster containing tetracoordinated tin atoms was isolated. A change in the reaction conditions led to a different result: the use of LiOH instead of Na_2O afforded a small Sn_3 cluster, in which each of the tetracoordinated tin atoms bears a hydroxy group. In this case, the very bulky organic group linked to the tin atom prevented further condensation of the monoorganotin units into distannoxane dimers, which are the building blocks of the Sn_{12} cluster isolated when butyl groups are used as ligands.[3]

Recently, we reported the preparation of trialkynyl tin compounds, which are alternative precursors for organotin oxides and alkoxides.[4] We also demonstrated that the hydrolysis of bis(tripropynylstannyl) derivatives is a facile route to self-assembled hybrid materials with alternating layers of tin oxide and hydrophobic organic chains.[5] The properties of the final materials depend strongly on the identity of the organic groups linked to the tin atoms. To gain deeper insight into the hydrolysis pathway of aryl tin compounds, we investigated monometallic systems such as

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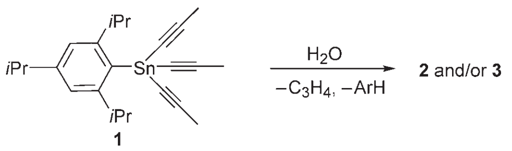
aryl tripropynyltin compounds. Herein, we describe the first mixed organotin compound in which inorganic tin(IV) atoms coexist with monoorganotin(IV) units. To our knowledge, the isolation and structural characterization of tin oxide fragments embedded between two monoorganotin oxide moieties have not been reported previously. Moreover, slight changes in the reaction conditions produced a new hexameric cage composed of a folded strip of poly(organostannoxane).

Treatment of 2,4,6-iPr$_3$C$_6$H$_2$Sn(CCMe)$_3$ (**1**)[4] with 12 equivalents of water under reflux conditions in THF resulted in the cleavage of the tin–propynyl bonds. Colorless crystals of dodecameric [(2,4,6-iPr$_3$C$_6$H$_2$Sn)$_8$(μ_4-O)$_2$(μ_3-O)$_8$(μ_2-O)$_4$(μ_2-OH)$_8${Sn(OH)}$_4$] (**2**) were isolated from the pale yellow solution in fairly good yield (Scheme 1). Compound **2** is stable under atmospheric conditions, soluble in a large number of common organic solvents, including hydrocarbons such as hexane and pentane, and thermally quite stable (m.p. 202–204 °C). The IR spectrum of **2** revealed the presence of associated hydroxy groups as a broad OH-stretching absorption at 3385 cm^{-1}. The ^{1}H NMR spectrum of **2** revealed that there are two different types of Sn-OH hydrogen atoms, which resonate as singlets at $\delta = 4.93$ ($^2J_{\mathrm{HSn}} = 58$ Hz) and 8.83 ppm ($^2J_{\mathrm{HSn}} = 17$ Hz). The observation of two singlets indicates that the chemically non-equivalent hydroxy groups in the molecule do not undergo proton exchange (on the NMR timescale). The upfield signal associated with the largest coupling constant is attributed to the hydrogen atoms of bridging hydroxy groups. The solution ^{119}Sn NMR spectrum of **2** consisted of three resonances with an intensity ratio of 1:1:1 at $\delta = -338.0$, -438.2, and -574.1 ppm, which are attributed to the pentacoordinated aryl tin centers, hexacoordinated aryl tin centers, and dearylated hexacoordinated tin centers, respectively. The solid-state CP-MAS ^{119}Sn NMR spectroscopy investigation of **2** was fully consistent with the solution-state study. The spectrum also consisted of three resonances, at $\delta = -343$, -448, and -576 ppm, corresponding to tin atoms in three different environments.



Scheme 1. Reaction of **1** with water to produce **2** and/or **3**.

The molecular structure of **2**, which crystallizes as a solvate with 12 molecules of THF, is shown in Figure 1.[6] The oval-shaped cluster consists of 12 tin and 26 oxygen atoms. An adamantane-type inorganic (SnO$_{3/2}$OH)$_4$ core of tin oxide hydroxide is capped by two identical, perpendicular (2,4,6-iPr$_3$C$_6$H$_2$SnO(OH))$_4$ organostannoxane-type arcs. The four inorganic tin atoms are hexacoordinated and each bear a hydroxy group. The aryl stannoxane arc consists of two hexacoordinated tin units that are linked to two pentacoordinated fragments. There are five different types of oxygen environments in cluster **2**: two tetra-, eight tri-, and four dicoordinated oxygen bridges, eight oxygen atoms in bridging hydroxy groups, and four oxygen atoms in terminal hydroxy groups on the stannonic acid tin atoms. The terminal hydroxy groups participate in intramolecular hydrogen bonding with bridging oxygen atoms.

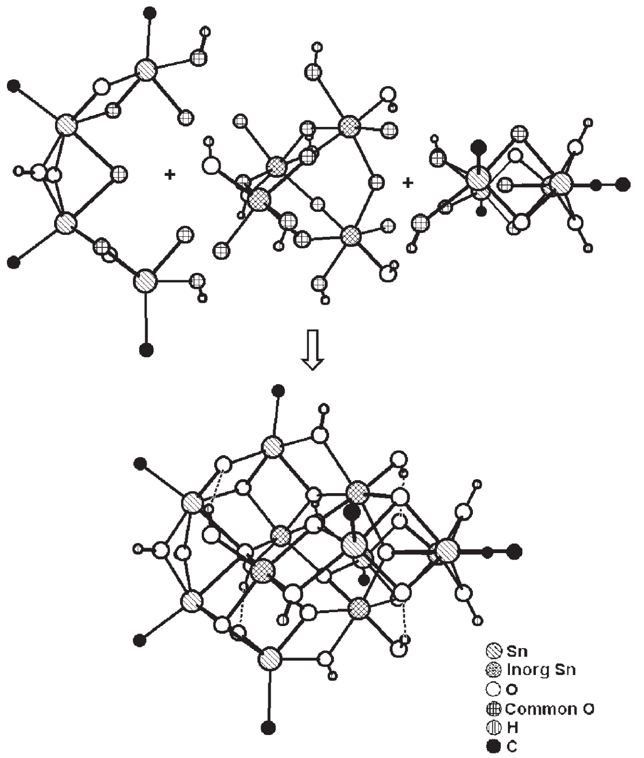


Figure 1. Molecular structure of **2**, showing the tin oxide core. Solvent THF molecules and the noncoordinated atoms of the 2,4,6-iPr$_3$C$_6$H$_2$ ligands are omitted for clarity.

The formation of the stannonic acid unit in **2** may occur through the partial dearylation of **1** by water during the hydrolysis of the alkynyl groups.[7] The low reactivity of the alkynyl groups in **1** towards hydrolysis (no reaction after 2 months at 20 °C), which is due to the steric hindrance of the bulky 2,4,6-iPr$_3$C$_6$H$_2$ group, led to the use of more severe reaction conditions (65 °C, 9 days), which favored the dearylation. No dearylation was observed for less bulky aryl groups (20 °C, 6 days).[5] Another explanation for the formation of the stannonic acid unit involves the redistribution of the monoaryl tin compound into diaryl tin and dearylated tin compounds.[8] This possibility was ruled out, as the diaryl tin compound was not detected in the reaction mixture. The reaction mixture did, however, contain some 2,4,6-iPr$_3$C$_6$H$_3$ formed through the cleavage of the tin–aryl bond.

Cluster **2** is not the only product that can be isolated from the hydrolysis of **1**. The compound [(2,4,6-iPr$_3$C$_6$H$_2$Sn)$_6$(OH)$_4$(μ_3-O)$_4$(μ_2-O)$_2$(μ_2-OH)$_2$] (**3a**) was isolated in low yield after evaporation of the solvent from the final reaction mixture, extraction of the solid with chloroform, and crystallization (Scheme 1). An analogous compound, **3b**, was obtained in 56 % yield when the hydrolysis of **1** was conducted in *tert*-amyl alcohol (TAA). The IR spectrum of **3a** revealed the presence of hydroxy groups as an absorption band at

3404 cm^{-1}, but the solution ^{1}H NMR spectrum was not very informative, owing to the presence of more than 20 signals of varying intensity. The solution ^{1}H and ^{119}Sn NMR spectra recorded for **3b** were also very complex. The CP-MAS ^{119}Sn NMR spectrum of **3b** showed only two sets of resonances at $\delta = -213$ and -355 ppm.

The molecular structure of **3a** is depicted in Figure 2.[6] The $\{Sn_6O_8\}$ core of cluster **3a** is composed of six puckered four-membered $\{Sn_2O_2\}$ rings, in a cagelike arrangement. It can also be described as a double-twist Möbius band of stannoxane units (see Scheme 2). All six tin atoms in **3a** are pentacoordinated. Two tin atoms (Sn_a) are coordinated by three bridging oxygen atoms (two μ_3 and one μ_2), one hydroxy group, and one 2,4,6-iPr$_3$C$_6$H$_2$ fragment. Two tin atoms (Sn_b) are surrounded by two μ_3-bridging oxygen atoms, one μ_2-bridging hydroxy group, one terminal hydroxy group, and one 2,4,6-iPr$_3$C$_6$H$_2$ fragment. The remaining two tin atoms are bonded to three bridging oxygen atoms (two μ_3 and one μ_2), one μ_2-bridging hydroxy group, and one 2,4,6-iPr$_3$C$_6$H$_2$ group. There are four different oxygen environments in **3a**: four tri- and two dicoordinated oxygen bridges, two oxygen atoms in bridging hydroxy groups, and four oxygen atoms in terminal hydroxy groups. The tin oxide inorganic core is completely wrapped by the hydrophobic bulky aryl moiety (2,4,6-iPr$_3$C$_6$H$_2$), which leads to the absence of intermolecular hydrogen-bonding interactions in **3a**. However, intramolecular hydrogen bonding occurs between the terminal hydroxy groups and the bridging hydroxy groups. The molecular structure of **3b**, which crystallizes as a solvate with four molecules of TAA, has an identical cage arrangement.[6] The structures of **3a** and **3b** differ mainly in the additional intermolecular hydrogen bonding that occurs between the hydroxy groups of the cage and those of the TAA solvent molecules in **3b** . Unlike **2**, compounds **3a** and **3b** are kinetically labile in solution, as evidenced by the appearance of many signals, which were not assigned, in their ^{119}Sn NMR spectra. However, their decomposition is reversible, as **3a** and **3b** are quantitatively recovered upon crystallization. Thus, the bulky aryl substituent on the tin atom does not allow the formation of the large, soluble NMR-inactive oxopolymers observed for butyltin compounds,[9] but leads to the formation of detectable discrete species.

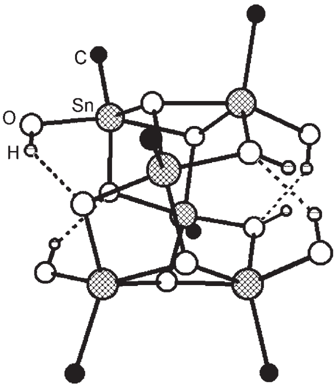
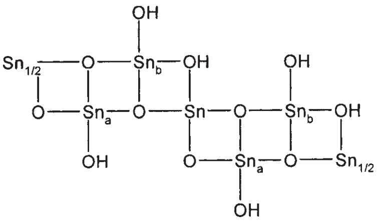


Figure 2. Molecular structure of **3a**. The noncoordinated atoms of the 2,4,6-iPr$_3$C$_6$H$_2$ ligands are omitted for clarity.



Scheme 2. Strip schematic representation of **3**. The 2,4,6-iPr$_3$C$_6$H$_2$ ligands have been omitted for clarity.

In summary, the hydrolysis of **1** differs substantially from the hydrolyses of tri(*tert*-amyloxy)phenyltin or tri(propynyl)phenyltin, in which the formation of a ball-like Sn$_{12}$ compound (minor) and an oxopolymer (major) was detected by solution ^{119}Sn NMR spectroscopy.[10] In the present study, either the unprecedented dodecameric oval-shaped cluster **2** or the hexameric cage **3** are formed from the hydrolysis of **1**. The structure of **2** consists of functionalized stannonic acid fragments, derived from **1** through cleavage of the tin–aryl bond, and organotin oxide arcs. The structure of **3** can be described as a circular doubly twisted strip of polystannoxane. In addition, the presence of hydroxy groups on the surfaces of molecules **2** and **3** could allow their further functionalization for use as building blocks in organic–inorganic materials or for solid-acid catalysis. The presence of reactive sites in **2** with different Lewis acidities, corresponding to inorganic tin atoms and organotin moieties, should enhance the catalytic properties of the compound.

Experimental Section

2: A mixture of **1** (2 g, 4.6 mmol) and H$_2$O (0.98 g, 54.6 mmol) was heated at reflux in THF (30 mL). A large amount of white solid was formed after 24 h, and slowly dissolved within 4 days. The pale yellow reaction mixture became clear after 9 days, and the reaction mixture was then slowly brought to room temperature. Colorless crystals of **2** were obtained at 5 °C (0.32 g, 20 %).[6] M.p. 202–204 °C; ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.35$–1.47 (m, 144H; iPr-CH_3), 1.76–1.81 (m, 48H; THF-CH_2), 2.61–2.82 (m), 3.06–3.17 (m), 3.49–3.54 (m, 24H; iPr-CH), 3.65–3.68 (m, 48H; THF-CH_2), 4.93 (s, $^{2}J_{\mathrm{HSn}} = 58$ Hz, 8H; Sn-OH), 6.62–7.06 (m), 7.53 (s, 16H; aryl-CH), 8.83 ppm (s, $^{2}J_{\mathrm{HSn}} = 17$ Hz, 4H; Sn-OH); ^{119}Sn NMR (CDCl$_3$, 74.6 MHz): $\delta = -338.0$ (4Sn; C-Sn_p), -438.2 (4Sn; C-Sn_h), -574.1 ppm (4Sn; HO-Sn_h); CP-MAS ^{119}Sn NMR: $\delta = -343, -448, -576$ ppm; IR (KBr): $\tilde{\nu} = 3385$(w), 2961(vs), 2927(s), 2868(m), 1594(w), 1560(w), 1460(m), 1420(w), 1383(w), 1362(w), 1100(w), 876(w), 717(w), 648(w), 553(m), 496(w), 468 cm^{-1} (m); elemental analysis (%) calcd for C$_{120}$H$_{196}$O$_{26}$Sn$_{12}$·12C$_4$H$_8$O (4344.30): C 46.44, H 6.77, Sn 32.79; found: C 46.10, H 6.22, Sn 31.12.

3a: Compound **3a** was synthesized by the same procedure described for **2**. However, the final reaction mixture was concentrated under vacuum to yield a pale yellow solid, which was extracted with chloroform. Filtration, concentration to approximately 5 mL, and storage at 15 °C afforded colorless crystals of **3a**.[6] ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.29$–1.30 (m, 108H; iPr-CH_3), 2.50–2.60 (m, 18H; iPr-

CH), 6.50–7.08 ppm (m, 12H; aryl-CH); IR (KBr): $\tilde{\nu}$ = 3404(w), 3040(w), 2960(vs), 2924(s), 2868(m), 1594(w), 1561(w), 1462(m), 1419(m), 1383(m), 1362(m), 1261(w), 1100(m), 1056(w), 1020(w), 937(w), 876(m), 803(w), 649(w), 554 cm^{-1} (m).

3b: H_2O (0.98 g 54.6 mmol) was added dropwise to a stirred solution of **2** (1 g, 2.3 mmol) in TAA (35 mL) at room temperature. Then the reaction mixture was heated to 60 °C. A large amount of white solid was formed within 3 h. After 9 days, the reaction temperature was raised from 60 to 90 °C. The white precipitate slowly dissolved into the solution, and the reaction mixture became clear. At this stage, the reaction was stopped, and the reaction mixture was slowly brought to 15 °C to afford a large amount of colorless crystals of **3b** (0.53 g, 56 %).[6] M.p. 182–184 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.27–1.38 (m, 152 H; *i*Pr-CH_3, TAA-CH_3, and TAA-CH_2), 1.99 (s, $^2J_{HSn}$ = 40 Hz, 6 H; Sn-OH), 2.58–2.67 (m, 18 H; *i*Pr-CH), 6.57–7.08 ppm (m, 12 H; aryl-CH); ^{119}Sn NMR ($CDCl_3$, 111.92 MHz): $\delta = -309.5, -321.8, -340.0, -342.6, -350.3, -351.3, -367.0, -375.1, -426.8, -538.7$ ppm; CP-MAS ^{119}Sn NMR: $\delta = -213, -355$ ppm; IR (KBr): $\tilde{\nu}$ = 3384(w), 3044(w), 2961(vs), 2928(s), 2870(m), 1595(w), 1561(w), 1463(m), 1412(m), 1384(m), 1363(m), 1101(w), 1070(w), 1057(w), 938(w), 876(m), 743(w), 666(m), 544 cm^{-1} (m); elemental analysis (%) calcd for $C_{90}H_{144}O_{12}Sn_6\cdot 4\,C_5H_{12}O$ (2483.00): C 53.21, H 7.79, O 10.31, Sn 28.69; found: C 52.09, H 7.73, O 8.29, Sn 28.69.

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[6] Crystals of **2**, **3a**, and **3b** were grown from THF (5 °C), chloroform (15 °C), and TAA (15 °C), respectively. In the cases of **2** and **3a**, suitable crystals were covered with mineral oil (Aldrich), mounted onto glass fibers, and transferred directly to the 150-K N_2 stream of a Nonius Kappa CCD diffractometer; in the case of **3b**, a crystal was mounted onto a 1.0-mm glass capillary at room temperature. Structures were solved by direct methods by using SHELXS-97[11] and refined against F^2 by full-matrix least squares by using SHELXL-97.[12] All non-hydrogen atoms were refined anisotropically, with the exception of disordered atoms in the solvent molecules in **2** (THF) and **3b** (TAA). Hydroxy hydrogen atoms were located through difference Fourier synthesis and fixed at these positions during the structure refinements. The largest peaks in the final difference Fourier map were of no chemical significance. **2**: $C_{168}H_{292}O_{38}Sn_{12}$, $M_r = 4344.30$, monoclinic, space group $P2_1/c$, $a = 18.2384(2)$, $b = 26.6625(4)$, $c = 38.7506(5)$ Å, $\beta = 96.161(1)°$, $V = 18734.8(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.540$ g cm^{-3}, $T = 150(2)$ K, $F(000) = 8784$, $\mu(Mo_{K\alpha}) = 1.637$ mm^{-1}, block crystal, 93163 reflections measured, 44564 unique ($R_{int} = 0.022$), 1874 parameters, $R_1 = 0.0414$ ($I > 2\sigma(I)$), $wR_2 = 0.0964$ ($I > 2\sigma(I)$), GOF = 1.062. **3a**: $C_{90}H_{146}O_{12}Sn_6$, $M_r = 2132.2$, monoclinic, space group $C2/c$, $a = 42.6871(13)$, $b = 10.0677(8)$, $c = 30.2690(14)$ Å, $\beta = 134.642(2)°$, $V = 9255.6(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.530$ g cm^{-3}, $T = 150(2)$ K, $F(000) = 4312$, $\mu(Mo_{K\alpha}) = 1.650$ mm^{-1}, plate crystal, 15026 reflections measured, 5789 unique ($R_{int} = 0.1194$), 488 parameters, $R_1 = 0.0828$ ($I > 2\sigma(I)$), $wR_2 = 0.1702$ ($I > 2\sigma(I)$), GOF = 1.052. **3b**: $C_{110}H_{192}O_{16}Sn_6$, $M_r = 2483.00$, monoclinic, space group $C2/c$, $a = 14.9388(2)$, $b = 29.6680(4)$, $c = 28.0134(2)$ Å, $\beta = 91.772(1)°$, $V = 12409.7(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.329$ g cm^{-3}, $T = 296(2)$ K, $F(000) = 5112$, $\mu(Mo_{K\alpha}) = 1.243$ mm^{-1}, plate crystal, 21087 reflections measured, 13136 unique ($R_{int} = 0.0242$), 525 parameters, $R_1 = 0.0548$ ($I > 2\sigma(I)$), $wR_2 = 0.1457$ ($I > 2\sigma(I)$), GOF = 1.013. CCDC-286921 (**2**), CCDC-286922 (**3a**), and CCDC-286923 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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