A New Structural Form of Tin in a Double O-Capped Cluster

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Rings, cages, and clusters containing organooxotin motifs in general and distannoxane motifs in particular have been attracting considerable attention in recent years.[1-3] In addition to the interest arising from the potential utility of these assemblies in the preparation of new materials[4] there has also been a significant interest in exploiting the remarkable structural plasticity of these stannoxane motifs. Thus, for example the four-membered distannoxane motif Sn_2O_2 is found in a number of structural forms such as the *ladder*,[5a] *drum*,[5b-d] *cube*,[5e,f] *O-capped cluster*,[5f,g] football cage[6] etc. Although, many structural forms containing the Sn_2O_2 unit have been discovered so far the inter-relationship between these various forms has not been delineated in any great detail. However, some clues do exist. Thus, the partial hydrolysis of an organotin-tricarboxylate, $RSn(O_2CR')_3$ affords first a ladder $[(RSn(O)O_2CR')_2-RSn(O_2CR')_3]_2$, which undergoes further transformation to a drum $[RSn(O)O_2CR']_6$.[7] Trinuclear *O-capped clusters* such as $[\{n\text{-BuSn-}(OH)O_2PPh_2\}_3O][Ph_2PO_2]$ have been isolated in the reaction of *n*-butylstannonic acid and diphenylphosphinic acid.[5f] The structural relationship between the drum and the *O-capped* cluster is that the latter represents a hydrolysis product of the hexameric drum. Two units of the *O-capped* cluster can be joined to each other in a *face–face* manner with a rearrangement in the phosphinate bridges and Sn–O bonds to afford the *drum*. We now report an unprecedented structural form of tin viz., a *double O-capped cluster* $[\{(n\text{-BuSn})_3-(PhO)_3O\}_2\{HPO_3\}_4]$, **1**, where two *O-capped* tin clusters each containing a Sn_3 unit are linked in a back–back manner by the intervention of bridging phosphonate ligands. The synthesis and X-ray crystal structure[8] of this compound are discussed in the following account. The structural relationship of the cage **1** obtained in the present study with that of other structures known, particularly the football cage, is also discussed.

In view of the reported isolation of the double cube $[\{n\text{-BuSnS-}(O_2PPh_2)\}_3O]_2Sn$ in the reaction of $[n\text{-BuSnO(OH)}]$ with $Ph_2P(O)H$ in the presence of sulfur[9] we probed an analogous reaction involving $[n\text{-BuSnO(OH)}]$ and $(PhO)_2P(O)H$ but without the use of sulfur.[10a] We discovered that the reaction proceeds to afford a completely unprecedented product which involves an in situ P–O bond cleavage leading to the generation of a $[HPO_3]^{2-}$ ion along with phenol. Thus, the compound isolated $[\{(n\text{-BuSn})_3(PhO)_3O\}_2-\{HPO_3\}_4]$, **1**, has a Sn:P ratio of 6:4 and Sn:OPh ratio of 1:1. We were also able to obtain **1** in a *direct* route involving the reaction of $[n\text{-BuSnO(OH)}]$ with phenol and phosphorous acid (Scheme 1).[10b] It may be noted that we have recently demonstrated the utility of phosphonate ligands in the assembly of multimetallic clusters involving transition metal ions.[11] Compound **1** is thermally stable and does not decompose until 290 °C. In addition it is quite lipophilic and is soluble in a wide range of organic solvents. The presence of P–H is confirmed by ^{1}H NMR (δ 7.13; [1]J(P–H): 690 Hz) and ^{31}P NMR (δ 0.57). The high negative chemical shifts

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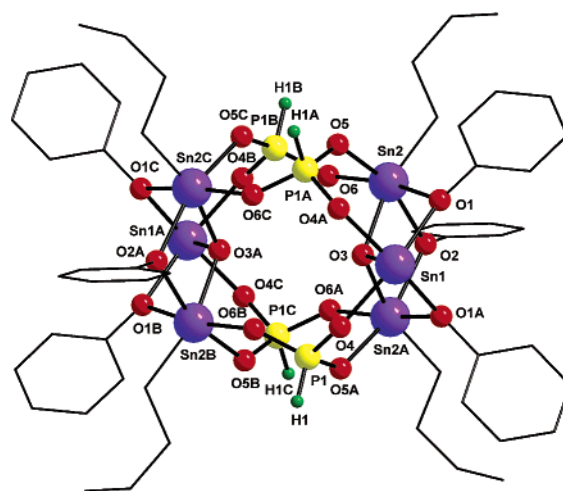‡ National University Of Singapore.

Figure 1. DIAMOND view of **1**. The hydrogen atoms of the *n*- butyl and the phenyl groups have been removed. The disordered carbon atoms on the tin atoms labeled Sn1 and Sn1A have also been omitted for clarity. Selected bond lengths [Å] and bond angles [deg] are: Sn(2)–O(3) 2.053-(1), Sn(2)–O(2) 2.163(1), Sn(2)–O(1) 2.201(2), Sn(2)–O(6) 2.064(2), Sn-(2)–O(5) 2.071(2), Sn(1)–O(3) 2.090(3), Sn(1)–O(1) 2.152(3), Sn(1)–O(4) 2.081(2), P(1)–O(6) 1.515(2), P(1)–O(5) 1.519(2), P(1)–O(4) 1.525(2), O(3)–Sn(2)–O(5) 88.19(7), O(6)–Sn(2)–O(5) 88.40(7), O(6)–Sn(2)–O(2) 88.51(8), O(5)–Sn(2)–O(2) 161.10(7), O(6)–Sn(2)–O(1) 167.31(7), O(5)–Sn(2)–O(1) 85.57(7), Sn(2)–O(3)–Sn(1) 108.32, P(1)–O(4)–Sn(1) 127.91(11), O(4)–P(1)–O(6B) 111.07(11), O(4)–P(1)–O(5A) 112.28(10).

Scheme 1
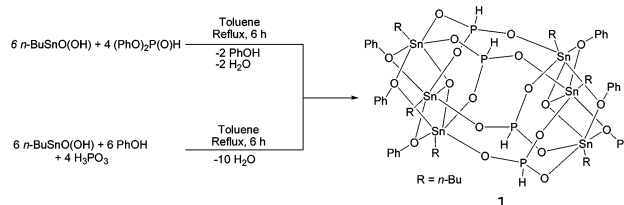
observed in the ^{119}Sn NMR are indicative of the CO_5 coordination environment around tin.

The X-ray crystal structure analysis of **1** shows that it has a cage-type of architecture. A DIAMOND view of **1** is shown in Figure 1. Selected metric parameters are summarized in the figure caption. The molecular structure of **1** consists of two tritin motifs viz., $\{(n\text{-BuSn})_3(PhO)_3O\}$ that are connected to each other by means of four tripodal HPO_3 ligands. The *poles* of the cage comprise of three tin centers held together by a μ_3-oxygen. Further three phenoxides are involved as bridging ligands; a μ_2-oxygen of each phenoxide binds two adjacent tin atoms.

Thus, the tritin subunit of the cage consists of three Sn_2O_2 rings that are nearly perpendicular to each other. This is similar to the molecular structure of the *O-capped cluster* reported earlier.[5f] The most important structural variation comes in the linking of the two
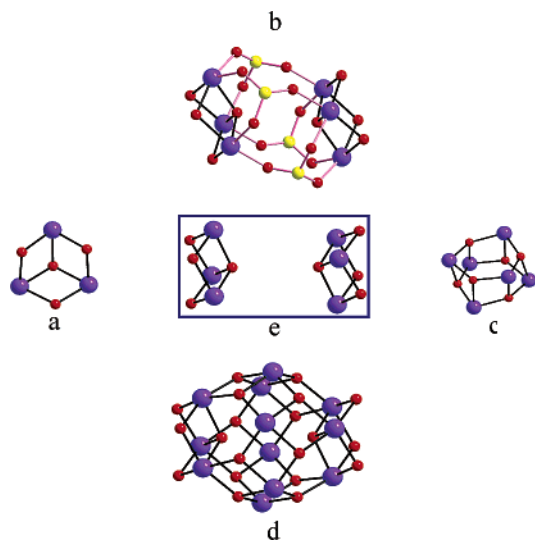
Figure 2. Comparison of the crystal structure of **1**, the *double O-capped* (b) with the *O-capped* (a), the *drum* (c), and the *football cage* (d) In this DIAMOND representation, violet represent the tin atoms, red the oxygens and yellow represents the phosphorus atoms. In all the structures only the tin−oxygen core is shown for clarity.

poles in the present structure by the bridging phosphonate groups. Thus, each phosphonate binds in a bridging mode using two of its oxygens to link two tins from the *same* pole and one tin from the *opposite pole*. All the six tin centers are thus effectively stitched with each other by means of four tripodal HPO$_3$ ligands. Consequently, two cyclic rings each containing six oxygen atoms sandwich a central rim of four phosphorus atoms. The average (μ_3)O−Sn bond length is 2.065 Å, while the average (μ_2)O−Sn bond length is 2.172 Å. These values are comparable to literature precedents.[5f,6] The average Sn−O distance involving the bridging phosphonate is 2.072 Å.

It is interesting to compare the *double-O-capped* structure found in the present instance with that of the *foot-ball cage* and the *drum* (Figure 2). As noted vide supra the fusion of two *O-capped clusters* in a *face-face* manner affords the hexameric drum. The *football cage* on the other hand is dodecanuclear. Both **1** and the football cage have exactly identical *pole* structures comprising of two Sn$_3$ motifs. Whereas in the *football cage* structure the two *poles* are connected to each other by means of an *equator* made up of the {(RSn)$_6$O$_{12}$} motif, in the present instance it is replaced by an inorganic phosphonate (HPO$_3$)$_4$ motif where each phosphorus is tetrahedral and contains a HO$_3$ coordination environment. Interestingly, despite the diverse *equator* motifs the cage dimensions in **1** and the football cage are similar. Thus, the distance between the diametrically opposite tin atoms (in the *equator*) in the *football cage* is 6.407 Å. In **1** the corresponding atoms P1 and P1B are separated by a distance of 6.337 Å. Also the interpolar μ_3-O distances in **1** and in the *football* are 3.778 and 3.984 Å, respectively. In **1** the presence of μ_2-OPh represents a situation where the polar hydroxyls of the *O-capped cluster* or the *football cage*[6e] are completely replaced by a phenoxide. In this regard this is the first instance where such a replacement has been unambiguously recorded.

Thus, in conclusion, we have isolated and structurally characterized a *double O-capped* cluster, which represents a new structural form. The current synthetic methodology also opens up possibilities for assembling nanobuilding blocks for the design of tin-based hybrid organic−inorganic materials through the use of biphenols. These studies are currently in progress.

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(8) Crystal data for **1**. The structure was solved by direct methods and refined by using full-matrix least-squares on F^2 (SHELX97[12]). Monoclinic, space group $C2/m$, $a = 16.9713(7)$ Å, $b = 15.6743(6)$ Å, $c = 14.2523(6)$ Å, $\beta = 105.5550°$, $V = 3652.4(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.787$ Mg/m^3, $T = 223(2)$ K, reflections collected = 14858, 5373 independent reflections [R(int) = 0.0242], Mo Kα radiation, $\lambda = 0.71073$ Å, θ range for data collection = 1.80−30.00°, absorption correction − Sadabs(Sheldrick, 1996), final R indices [$I > 2\sigma(I)$] R1 = 0.0282, wR2 = 0.0615, R indices (all data) R1 = 0.0349, wR2 = 0.0630, largest diff. peak and hole = 1.125 and −0.394 e· Å^{-3}. The hydrogen on the phosphorus atom was located from the difference maps and the positions were refined. All the other hydrogens were fixed at calculated positions.
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(10) Synthesis: Compound **1** has been prepared by two synthetic routes. (a) *n*-Butylstannonic acid (2.20 g, 10.5 mmol) and diphenyl phosphite (1.64 g, 7.00 mmol) were taken in 100 mL of toluene and heated under reflux. After about 45 min the solution became clear. Heating was continued for a further period of 5 h. At this stage the reaction mixture was allowed to cool to room temperature and filtered. The filtrate was reduced to one-tenth of its initial volume (10 mL) *in vacuo* and kept for crystallization at room temperature. Within a period of 3−4 weeks colorless blocklike crystals were formed which were separated by filtration. The crystals were purified further by quickly washing them with chloroform (3 mL). Yield 0.70 g (20%). Mp 290−292 °C dec; ^{1}H NMR (CDCl$_3$, ppm) 0.50−0.73 (m, 18H, CH$_3$ of *n*-Bu), 0.80−1.46 (m, 36H, CH$_2$ of *n*-Bu), 6.83−7.35 (m, 30H, phenyl), 7.13 (d, 4H, ^1J(H−P) = 690 Hz); ^{31}P NMR (CDCl$_3$, ppm) 0.57 (d, ^1J(P−H) = 688 Hz); ^{119}Sn NMR (CDCl$_3$, ppm) −532.7 (m), −551.3 (m), −563.6 (m); elemental analysis Calcd for C$_{60}$H$_{88}$O$_{20}$P$_4$-Sn$_6$: C 36.66%, H 4.51%; found: C 36.11%, H 4.09%. (b) *n*-Butylstannonic acid (0.93 g, 4.45 mmol), phenol (0.42 g, 4.46 mmol), and phosphorous acid (0.24 g, 2.92 mmol) were taken in 60 mL of toluene and refluxed. A Dean−Stark apparatus was used to remove the water formed in the reaction by azeotropic distillation. Workup of the reaction mixture as described in the previous preparation afforded a white solid. Yield 0.45 g (31%). The spectroscopic and analytical data for the compound obtained in this preparation matched with those given in the above procedure.
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