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A new “Sn_{12}” oxo-cluster—how to flatten the football

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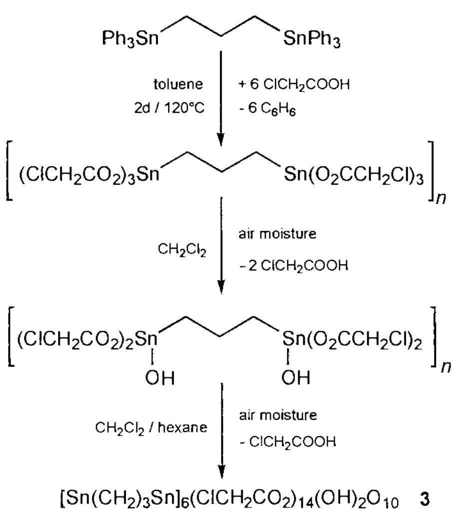
Controlled hydrolysis of $[(ClCH_2CO_2)_3Sn(CH_2)_3Sn(O_2CCH_2Cl)_3]_n$ 1 resulted in the hitherto unknown “Sn_{12}” cluster $\{[Sn(CH_2)_3Sn]_6(ClCH_2CO_2)_{14}(OH)_2O_{10}\}$ 3 with trimethylene “handles”: compound 3 has all twelve tin atoms nearly coplanar, in stark contrast to previously described “Sn_{12}” clusters which have a spherical football structure.

In recent years there has been an increasing interest in preparing well-defined oligomeric organotin clusters as nano-building blocks for the synthesis of hybrid organic–inorganic materials.[1,2] Of particular interest has been the exploitation of the di-cationic “Sn_{12}” compound $[(RSn)_{12}O_{14}(OH)_6]X_2$ ($R = {}^iPr$, ${}^nBu$; $X = Cl$, OH).[3–6] Several general strategies have been suggested for connecting “Sn_{12}” units into larger oligomers: (i) to incorporate unsaturated functions capable of further polymerisation into “Sn_{12}”,[7] (ii) to use bifunctional anions, such as dicarboxylates, which allow assembly of “Sn_{12}” *via* strong electrostatic interactions,[8,9] and (iii) to utilise anions which are capable of further polymerisation (*e.g.* methacrylates).[10]

To the best of our knowledge there are no reports for the use of $X_3Sn(CH_2)_nSnX_3$ (X = halogen, carboxylic acid, alkoxide) as precursors for the preparation of linked “Sn_{12}” or “Sn_{12} with handles”. Furthermore, there are only two reports of the synthesis of precursors of the type $X_3SnCH_2SnX_3$ (X = Cl,[11] OAc[12]).

The lability of tin–phenyl bonds against carboxylic acids[13] is well known and we decided to use this as a starting point for the synthesis of a new type of precursor for the synthesis of linked “Sn_{12}” clusters. Thus, reaction of 1,3-bis(triphenylstannyl)propane, $Ph_3Sn(CH_2)_3SnPh_3$,[14] with 6 equivalents of chloroacetic acid afforded in the first instance a white solid **1**† which is insoluble in common organic solvents. This compound is thought to be $[(ClCH_2CO_2)_3Sn(CH_2)_3Sn(O_2CCH_2Cl)_3]_n$. The insolubility is probably due to intra- and inter-molecular interactions involving the chloroacetic acid functions resulting in the increase of the coordination number at tin and consequently in formation of a polymeric product. Stirring **1** in CH_2Cl_2 under the influence of air moisture afforded a clear solution. This is due to partial hydrolysis of two of the six carboxylic acid groups which gives the oligomeric compound characterised as $[(ClCH_2CO_2)_2(OH)Sn(CH_2)_3Sn(OH)(O_2CCH_2Cl)_2]_n$ **2**‡ based on elemental analysis and on the integration of the proton NMR spectrum. The ^{119}Sn NMR spectrum of **2** in $CDCl_3$ displays 4 signals in the hexacoordinated region δ −497.6 (23%), −520.8 (27%), −549.8 (25%), −591.3 (25%). Repeated crystallisation of **2** from CH_2Cl_2–hexane afforded colourless single crystals of neutral **3**§ (Scheme 1) which were no longer soluble in common organic solvents.



Scheme 1 Synthesis pathway towards the new “Sn_{12}” structure **3**.

The X-ray structure analysis of **3**¶ (Fig. 1) revealed a completely new motif for “Sn_{12}” clusters. The lower view of Fig. 1 shows the tin-oxo core and is used as a starting point to describe the structure. The centrosymmetric central Sn_4O_2 core (*i.e.* containing the Sn(2) and Sn(4) atoms) is as found in the ubiquitous distannoxanes[15] and forms the building block for the rest of the structure. The molecule features a twisted concatenation of three Sn_2O_2 parallelograms linked at Sn(2) atom apices. The chain is terminated at each end by two Sn(OH) units linked to a SnO edge leading to a sub-structure comprising six tin atoms and five Sn_2O_2 units. On either side of the central chain are linked two pairs of SnO resulting in the formation of two six-membered Sn_3O_3 rings. The remaining tin atoms bridge the O(5) and O(6) atoms to form two more Sn_2O_2 units. In addition to the tricoordinate oxo-bridges, a complicated network of bridges serve to connect the tin atoms in **3**. The propylene handles link the Sn(1,3), Sn(2,4) and Sn(5,6) atoms. Carboxylic acid bridges link the Sn(1,6′), Sn(3,4), Sn(3,5) [twice] and Sn(4,5) atoms. The four remaining carboxylate groups coordinate the Sn(1) and Sn(6) atoms in a monodentate fashion. In this description, the tin atoms occupying positions on the perimeter of the SnO core are linked by a combination of hydroxyl, propylene and carboxylate bridges. Whereas the Sn(2) atom exists in a distorted trigonal bipyramidal geometry, the remaining tin atoms are distorted octahedral.

The relationship between **3** and the Sn_{12} balls[3–6] is relatively simple given the above description. In the Sn_{12} ball, the central chain in **3** becomes of girth of corner-shared (at tin) Sn_2O_2 units. Spanning the girth, both above and below, forming alternating four- ($3 \times Sn_2O_2$) and six-membered ($3 \times Sn_3O_3$) rings are three tin atoms. The latter sets of three tin atoms are in turn connected by OH bridges forming a crown. The presence of covalent links between the tin atoms in the precursor **2** precludes the molecule to fold back upon itself during the

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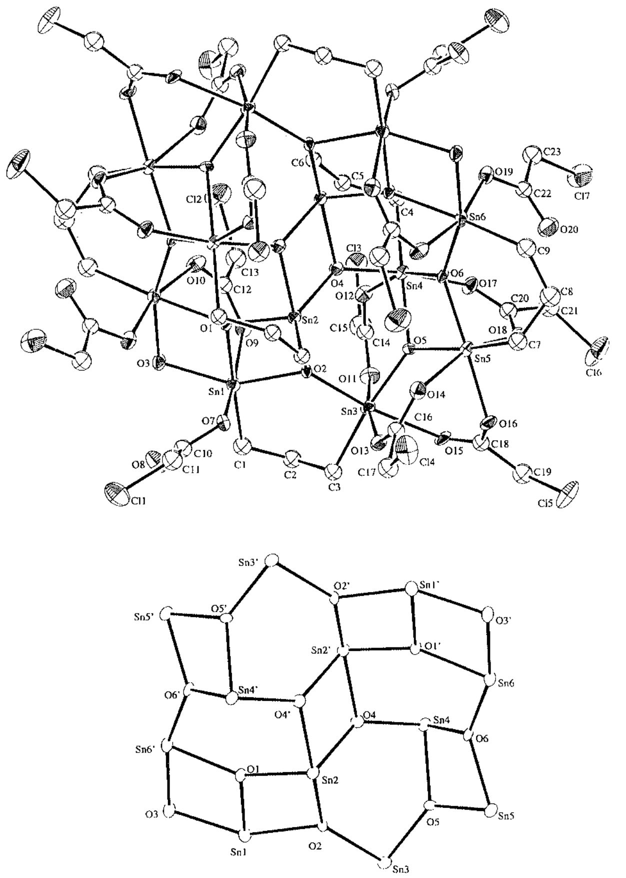

Fig. 1 Molecular structure and crystallographic numbering scheme for **3** (upper view). Note that O(3) is an hydroxyl oxygen atom. The lower view shows the SnO core.

hydrolysis pathway resulting in the formation of a flattened molecule as opposed to the ball structure formed by the hydrolysis of monomeric organotin precursors.[3–6]

These results reveal that the use of propylene bridged ditin hexacarboxylate **1** as a precursor for the controlled hydrolysis allows the formation of a new type of monoorgano tin oxygen cluster. Studies on the use of different bridging chain length and functional groups in the precursors $X_3Sn(CH_2)_nSnX_3$ (X = halogen, carboxylic acid, alkoxide) are currently under way.

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Notes and references

† A solution of $Ph_3Sn(CH_2)_3SnPh_3$ (1.23 g, 1.66 mmol) and chloroacetic acid (980 mg, 10.37 mmol) in 10 mL of toluene was refluxed for 2 d at 120 °C. Cooling the reaction mixture to room temperature resulted in the precipitation of a brownish oil and some white solid. The toluene was removed *in vacuo* and the resulting oily residue stirred for 12 h with 50 mL CH_2Cl_2 under the exclusion of air moisture affording a white suspension of **1** which appeared to be completely insoluble.

‡ Stirring the white suspension of **1** for a further 3 h under the influence of air moisture resulted in a clear solution. The solvent was removed *in vacuo* to afford a yellowish solid which was kept for several hours at 80–100 °C and 10^{-3} Torr to remove chloroacetic acid. This procedure resulted in a yellowish solid (1.13 g, 99%) mp 250–270 °C with the basic composition of $[(ClCH_2CO_2)_2(OH)Sn(CH_2)_3Sn(OH)(O_2CCH_2Cl)_2]_n$. Anal. Calcd. for $C_{11}H_{16}Cl_4O_{10}Sn_2$ **2**: C, 19.22; H, 2.34. Found: C, 19.28; H, 2.19%. ^1H NMR (299.98 MHz, $CDCl_3$): **2**, δ 1.21–2.89 (mm, 6H, $CH_2CH_2CH_2$); 4.17 (s, 8H, CH_2Cl). $^{119}Sn\{^1H\}$ NMR (111.85 MHz, $CDCl_3$): **2**, δ −497.6 (s, 23%), −520.8 (s, 27%), −549.8 (s, 25%), −591.3 (s, 25%).

§ After dissolving **2** in 20 mL CH_2Cl_2 and adding 2 mL hexane the solvents were allowed slowly to evaporate providing 60 mg of white single crystals (mp 275–280 °C) which were no longer soluble in organic solvents and a yellow oil. Repeated (5 times) recrystallisation of the yellow oil from CH_2Cl_2–hexane afforded a further 280 mg of the white insoluble crystalline material and *ca.* 600 mg of the yellow oil. The combined yield from six crystallisations was 340 mg, 39%. Anal. Calcd. for $C_{46}H_{66}Cl_{14}O_{40}Sn_{12}$ **3**: C, 17.38; H, 2.09. Found: C, 17.43; H, 2.07%.

¶ Crystal data for $C_{46}H_{66}Cl_{14}O_{40}Sn_{12}$ **3**: $M = 3179.85$, monoclinic $P2_1/n$, $a = 12.059(2)$, $b = 24.484(1)$, $c = 14.4170(4)$, $\beta = 103.797(3)°$, $U = 4133.7(1)$ Å^3, $Z = 2$, $D_c = 2.554$ g cm^{-3} and $\mu = 40.96$ cm^{-1}. Data were collected at 173 K on a Rigaku/MSC Mercury CCD coupled with a Rigaku AFC8 goniometer employing Mo-Kα radiation in the range $1.5 < \theta < 31.5°$. The structure was solved by and refined with the teXsan Structure Analysis Package (Molecular Structure Corporation, 1998) of crystallographic programs. Of the 49099 reflections measured, 6985 with $I \geq 3.0\sigma(I)$ were used in the refinement (on F) which converged with $R = 0.047$ and $Rw = 0.049$. The C(2) atom of the propylene bridge was found to be disordered over two positions of equal weight—H atoms were not included for this group. The O–*H* atoms were not located in the study. CCDC reference number 186/2201. See http://www.rsc.org/suppdata/dt/b0/b007896o/ for crystallographic files in .cif format.

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