DALTON
COMMUNICATION

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

Bernhard Zobel,[a] Jason Costin,[a] Beverly R. Vincent,[b] Edward R. T. Tiekink[c] and Dainis Dakternieks*[a]

[a] *Centre for Chiral and Molecular Technologies, Deakin University, Geelong, Victoria 3217, Australia. E-mail: dainis@deakin.edu.au*
[b] *Molecular Structure Corporation, 9009 New Trails Drive, The Woodlands, Texas 77381-5290, USA*
[c] *Department of Chemistry, The University of Adelaide, S.A. 5005, Australia*

Received 29th September 2000, Accepted 29th September 2000

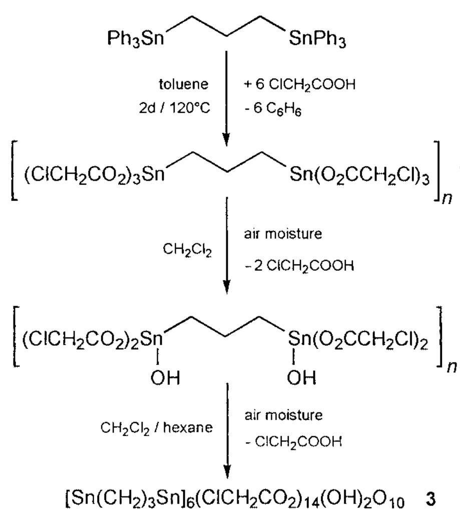
Controlled hydrolysis of $[(ClCH_2CO_2)_3Sn(CH_2)_3Sn(O_2CCH_2Cl)_3]_n$ 1 resulted in the hitherto unknown “Sn_{12}” cluster $\{[Sn(CH_2)_3Sn]_6(ClCH_2CO_2)_{14}(OH)_2O_{10}\}$ 3 with trimethylene “handles”: compound 3 has all twelve tin atoms nearly coplanar, in stark contrast to previously described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

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.



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

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 × Sn_2O_2) and six-membered (3 × 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

DOI: 10.1039/b007896o

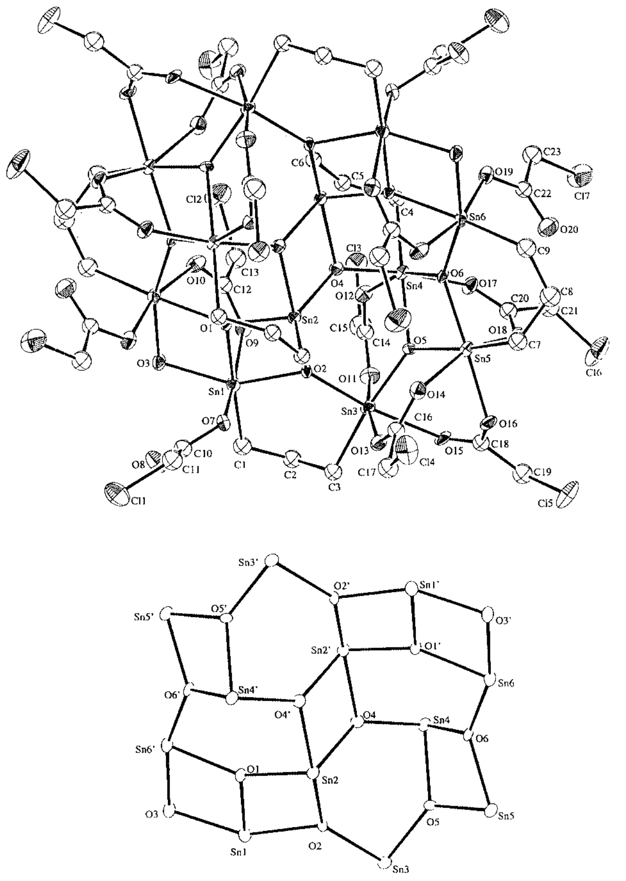


Fig. 1 Molecular structure and crystallographic numbering scheme for **3** (upper view). Note that O(3) is an hydroxyl oxygen atom. The lower view shows the SnO core.

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.

We thank the Australian Research Council for financial support.

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.

1 F. Ribot and C. Sanchez, *Comments Inorg. Chem.*, 1999, **20**, 327 and references therein.

2 F. Ribot, C. Eychenne-Baron and C. Sanchez, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1999, **150–151**, 41 and references therein.

3 H. Puff and H. Reuter, *J. Organomet. Chem.*, 1989, **373**, 173.

4 D. Dakternieks, H. Zhu, E. R. T. Tiekink and R. Colton, *J. Organomet. Chem.*, 1994, **476**, 33.

5 F. Banse, F. Ribot, P. Toledano, J. Maquet and C. Sanchez, *Inorg. Chem.*, 1995, **34**, 6371.

6 C. Eychenne-Baron, F. Ribot and C. Sanchez, *J. Organomet. Chem.*, 1998, **567**, 137.

7 F. Ribot, F. Banse and C. Sanchez, *Mater. Res. Soc. Symp. Proc.*, 1994, **346**, 121.

8 F. Ribot, F. Banse, F. Diter and C. Sanchez, *New J. Chem.*, 1995, **19**, 1145.

9 F. Ribot, C. Eychenne-Baron and C. Sanchez, *Mater. Res. Soc. Symp. Proc.*, 1996, **435**, 43.

10 F. Ribot, F. Banse, C. Sanchez, M. Lahcini and B. Joussaume, *J. Sol-Gel Sci. Technol.*, 1997, **8**, 529.

11 T. J. Karol, J. P. Hutchinson, J. R. Hyde, H. G. Kuivila and J. A. Zubieta, *Organometallics*, 1983, **2**, 106.

12 M. Gielen and K. Jurkschat, *J. Organomet. Chem.*, 1984, **273**, 303.

13 R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Rev.*, 1960, **60**, 459.

14 D. Dakternieks, K. Jurkschat and D. Schollmeyer, *J. Organomet. Chem.*, 1995, **492**, 145.

15 E. R. T. Tiekink, *Appl. Organomet. Chem.*, 1991, **5**, 1; E. R. T. Tiekink, *Trends Organomet. Chem.*, 1994, **1**, 74.