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Solvent-controlled assembling by hydrogen bridges and halogen-halogen interactions of novel organotin oxo clusters†

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The crystal structure of the novel methylene-bridged tetraorganodistannoxane {[Ph(HO)SnCH$_2$Sn(I)Ph]O}$_4$ (1) depends on the solvent it is crystallised from and is controlled by hydrogen bridges and interhalogen interactions.

Currently, there are well accepted models used in chemical education helping to understand the way atoms assemble to form molecules of different size and shape and to explain chemical transformations. On the other hand, the factors that control the way molecules assemble in the solid state are much less known and research in the direction of crystal design and crystal engineering is growing. An increase of knowledge in this area will certainly contribute to improve the syntheses of tailor-made materials and catalysts.[1]

Weak intermolecular forces such as donor–acceptor bonds[2] or hydrogen bonds[3] are known to influence the crystallisation process and the reversibility in the formation of hydrogen bonds leads to a better control over the latter. As a result of cooperative effects[4] the resulting hydrogen-bonded networks are usually very robust.

In recent years several discrete organotin oxo clusters have been reported[5] and there is a growing interest to link such tin-containing clusters together.[6] Here we report a simple approach to assemble *via* hydrogen-bonding the novel organotin oxo cluster {[Ph(HO)SnCH$_2$Sn(I)Ph]O}$_4$ (**1**) into one- and two-dimensional polymers. The capability of the solvent to form hydrogen bonds is the structure-determining factor and controls the association of the organotin oxo cluster (**1**) in the solid state.

The organotin oxo cluster {[Ph(HO)SnCH$_2$Sn(I)Ph]O}$_4$ (**1**) has been prepared by hydrolysis of PhI$_2$SnCH$_2$SnI$_2$Ph† ‡ in a MeOH/H$_2$O/Et$_3$N mixture and has subsequently been crystallised from THF to give the discrete building block as the THF-adduct, **1**·4THF (Fig. 1). Similar to previously described double ladder structures,[7] compound **1** consists of two at first approximation planar Sn$_4$O$_4$I$_2$ layers (mean deviation 0.1167 Å) which are linked by four methylene spacers. The exocyclic tin atoms Sn(1) and Sn(4) as well as the endocyclic tin atoms Sn(2) and Sn(3) exhibit trigonal bipyramidal configurations with C(1), C(11), O(1) and C(1A), C(41), O(2), respectively, and C(2), C(21), O(1) and C(3), C(31), O(2), respectively, in the equatorial positions. The axial positions are occupied by I(1), O(3) (for Sn(1)), I(2), O(4) (for Sn(4)), O(2), O(3) (for Sn(2)), and O(1), O(4) (for Sn(3)). The Sn(1)–O(3)–Sn(2) and Sn(3)–O(4)–Sn(4) bridges are unsymmetrical by 0.042 and 0.076 Å, respectively. The THF molecules in **1**·4THF form hydrogen bonds (Sn–O–H···O 2.617(19)/2.698(13) Å) to the OH-groups and thus prevent formation of a polymeric hydrogen-bonded network.

Crystallisation of {[Ph(HO)SnCH$_2$Sn(I)Ph]O}$_4$ (**1**) from CH$_2$Cl$_2$ gave **1**·3CH$_2$Cl$_2$ whereas crystallisation from CH$_3$CN provided solvent-free **1**. In the crystal structure of **1**·3CH$_2$Cl$_2$ the organotin oxo clusters {[Ph(HO)SnCH$_2$Sn(I)Ph]O}$_4$ are linked by intermolecular hydrogen bonds of the type Sn–O–H···I–Sn (O–I distance 3.759(5) Å) to give a one-dimensional polymer (Fig. 2). Noteworthy, only one out of four hydroxy groups and one out of four iodines of each cluster are involved in the hydrogen-bonding. A second iodide of each cluster interacts with two CH$_2$Cl$_2$ molecules *via* intermolecular I···Cl distances of 3.824(2) and 3.926(3) Å, respectively, being close to the sum of the van der Waals radii (3.65–4.02 Å)[8] of these atoms. The third CH$_2$Cl$_2$ molecule is related to one of the iodine-bonded CH$_2$Cl$_2$ molecules by an intramolecular Cl···Cl distance of 3.584(4) Å being close to the sum of the van der Waals radii of two chlorine atoms (3.40–3.80 Å).[8]

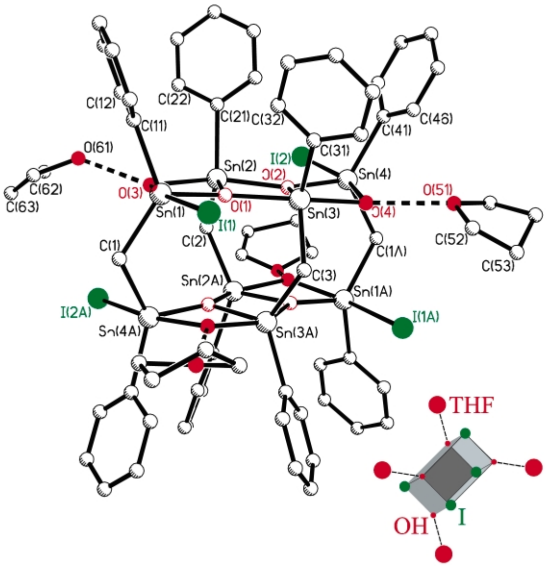

Fig. 1 Molecular structure of {[Ph(HO)SnCH$_2$Sn(I)Ph]O}$_4$·4THF (**1**·4THF) including a schematic representation. In the latter, the twist between the upper and lower Sn$_4$O$_4$I$_2$ layers is not shown.

The crystal structure of the solvent-free organotin oxo cluster **1** (Fig. 3) is characterised by a two-dimensional network being realised by a combination of two intermolecular

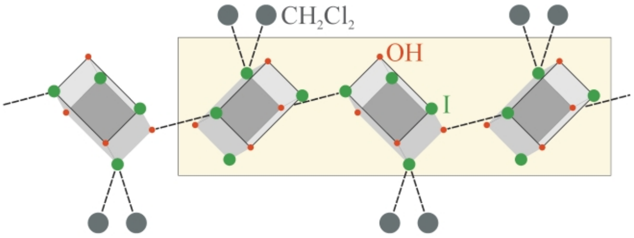

Fig. 2 Schematic representation of the one-dimensional polymer of **1**·3CH$_2$Cl$_2$. The third CH$_2$Cl$_2$ molecule is omitted and the twist between the upper and lower Sn$_4$O$_4$I$_2$ layers is not shown.

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† Electronic supplementary information (ESI) available: Synthesis and analytical data for PhI$_2$SnCH$_2$SnI$_2$Ph. See http://www.rsc.org/suppdata/cc/b1/b111337b/

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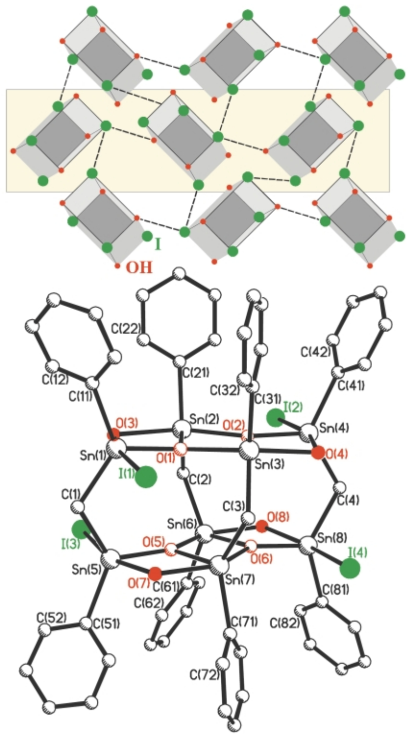

Fig. 3 Molecular structure of $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4$ (**1**) including a schematic representation of the two-dimensional network. In the schematic representation, the twist between the upper and lower $Sn_4O_4I_2$ layers is not shown.

Sn–O–H···I–Sn hydrogen bonds (O–I distance 3.514(7) Å) and three weak intermolecular Sn–I···I–Sn interactions ranging from 4.1296(11)–4.2017(16) Å, the latter being close to the sum of the van der Waals radii of two iodine atoms (3.90–4.24 Å).[8] They are likely to be the result of crystal packing and contribute only little to the crystal energy.[9] Remarkably, the crystal structure of the solvent-free organotin oxo cluster **1** contains a similar chain-type structural motif as observed for **1**·$3CH_2Cl_2$ (Fig. 2).

In contrast to most of the previously reported tetraorganodistannoxanes with double ladder-type structures the two $Sn_4O_4I_2$ layers which are linked by four methylene spacers in **1**·4THF, **1**·$3CH_2Cl_2$ as well as in solvent-free **1** show a twist of 28.02(4), 29.00(2) and 29.15(3)°, respectively. Moreover, the organotin oxo clusters **1**·$3CH_2Cl_2$ and solvent-free **1** lack any symmetry and exhibit chirality (see Fig. 3 as representative) with, however, both enantiomers being present in the corresponding crystal lattice.

In conclusion, we have shown that the organotin oxo cluster $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4$ shows a strong tendency to form intermolecular hydrogen bonds. The assembling process of the clusters is controlled by the identity of the solvent.[10] By crystallisation from a chiral solvent such as Bu^{s}OH the synthesis of enantiopure self-assembled networks might be possible. The supramolecular structures reported here represent three out of eight obtained so far. A detailed description will be given in a forthcoming paper.

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Notes and references

‡ *Synthesis*: To a solution of $PhI_2SnCH_2SnI_2Ph$ (1.95 g, 2.135 mmol) in methanol (4.7 mL) was added dropwise under magnetical stirring a solution of Et_3N (0.94 mL) in water (28.1 mL) to give a suspension. The stirring was continued for 1 h and the waxy-type precipitate was allowed to settle. The supernatent solution was decanted and the residue was washed with water and then recrystallized from CH_3CN, THF and CH_2Cl_2 to give $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4$ (**1**) (mp > 250 °C), **1**·4THF, and **1**·$3CH_2Cl_2$, respectively. ^1H NMR of **1** (400 MHz, $CDCl_3$) δ 2.04 (s, 4H, $^2J(^1H–^{119}Sn)$ 76 Hz, CH_2), 2.52 (s, 4H, $^2J(^1H–^{119}Sn)$ 70 Hz, CH_2), 3.74 (s, 4H, OH), 6.80–7.26 (complex pattern, 24H, H_{aryl}), 7.30 (d, 8H, $^3J(^1H–^{119}Sn)$ 87 Hz, H_{ortho}), 7.65 (d, 8H, $^3J(^1H–^{119}Sn)$ 87 Hz, H_{ortho}). ^{119}Sn NMR (149.2 MHz, $CDCl_3$) δ −222 ($^2J(^{119}Sn–^{117/119}Sn)$ 140 Hz), −244 ($^2J(^{119}Sn–^{117/119}Sn)$ 140 Hz). IR (KBr) ν(OH) 3300–3550 cm^{-1}. Anal. Found: C, 27.7; H, 2.3. Calc. for **1**: C, 27.6; H, 2.3%.

Crystal data for **1**: $C_{52}H_{52}I_4O_8Sn_8$, M = 2262.06, monoclinic, space group $P2_1/n$ (no. 14), Z = 4, a = 15.8313(4), b = 18.5471(5), c = 21.8859(7), β = 105.5531(9), V = 6190.9(3) Å^3, D_c = 2.427 g cm^{-3}, μ(Mo-Kα) = 5.213 mm^{-1}, T = 171(1) K. 11147 unique reflections (R_{int} = 0.061) [5688 with $I > 2\sigma(I)$]. Final $R1$ = 0.0538, $wR2$ (all data) = 0.0923.

Crystal data for **1**·4THF: $C_{68}H_{84}I_4O_{12}Sn_8$, M = 2550.47, monoclinic, space group $C2/c$ (no. 15), Z = 4, a = 27.7234(13), b = 20.1467(11), c = 15.6854(10), β = 114.5854(17), V = 7966.6(8) Å^3, D_c = 2.126 g cm^{-3}, μ(Mo-Kα) = 4.068 mm^{-1}, T = 171(1) K. 6985 unique reflections (R_{int} = 0.049) [3892 with $I > 2\sigma(I)$]. Final $R1$ = 0.0723, $wR2$ (all data) = 0.1878.

Crystal data for **1**·$3CH_2Cl_2$: $C_{55}H_{58}Cl_6I_4O_8Sn_8$, M = 2516.83, monoclinic, space group $P2_1/n$ (no. 14), Z = 4, a = 17.8847(2), b = 19.7039(3), c = 21.2582(2), β = 105.4481(8), V = 7220.71(15) Å^3, D_c = 2.315 g cm^{-3}, μ(Mo-Kα) = 4.697 mm^{-1}, T = 171(1) K. 16361 unique reflections (R_{int} = 0.057) [9885 with $I > 2\sigma(I)$]. Final $R1$ = 0.0462, $wR2$ (all data) = 0.0908.

CCDC reference numbers 178297–178299. See http://www.rsc.org/suppdata/b1/b111337b/ for crystallographic data in CIF or other electronic format.

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