Self-Assembled Triorganotin(IV) Moieties with 1,3,5-Benzenetricarboxylic Acid: Syntheses and Crystal Structures of Monomeric, Helical, and Network Triorganotin(IV) Complexes

Chunlin Ma,*[a,b] Yinfeng Han,[a] Rufen Zhang,[a] and Daqi Wang[a]

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A series of novel triorganotin(IV) complexes of the type $[(R_3Sn)_3(TMA)]\cdot Y\cdot L$ [R = CH_3, Y = $3CH_3OH$ (**1**); R = CH_3, Y = $2CH_3OH$ (**2**); R = $C_6H_5CH_2$ (**3**); R = *o*-F-$C_6H_4CH_2$ (**4**); R = *o*-Cl-$C_6H_4CH_2$ (**5**); R = C_6H_5, L = CH_2Cl_2 (**6**); R = C_6H_5, L = $EtOH\cdot 2H_2O$ (**7**); R = C_6H_5, L = $Et_2O\cdot CH_2Cl_2$ (**8**); H_3TMA = 1,3,5-benzenetricarboxylic acid] and $[(CH_3)_3Sn]_2(HTMA)\cdot H_2O$ (**9**) have been synthesized. All complexes were characterized by elemental analysis and by IR, ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy. Except for **4** and **5**, all complexes were also characterized by X-ray crystallography. Complex **1** possesses a network structure where TMA acts as a tridentate ligand coordinated to three trimethyltin(IV) moieties and three methanol molecules that are involved in a hydrogen-bond system, whereas **2** possesses a helical structure where TMA acts as a tetradentate ligand coordinated to three trimethyltin(IV) ions and two methanol molecules that bend into the helical turn in the intra-helix hydrogen-bond system. Complexes **3**–**8** are monomeric structures where TMA acts as a hexadentate ligand coordinated to triorganotin(IV) ions and **9** possesses a network structure where TMA acts as a tetradentate ligand coordinated to trimethyltin(IV) ions and water molecules in the hydrogen-bond system that links the neighboring layers into a 3D network.

Introduction

In the last years, metal-directed self-assembly[1] has produced fascinating results in two topical areas dealing respectively with the deliberate construction of molecular interlocked/intertwined species, like rotaxanes, catenanes, knots, and helicates,[2,3] and the crystal engineering of extended 2D and 3D networks.[4,5] Conformationally flexible ligands are typical building elements in the former area, while in the latter essentially rigid rod-like organic units are usually employed to connect the metal centers. In particular, multi-benzenecarboxylate ligands have been shown to be good building blocks in the design of self-assembly complexes with desired topologies owing to their rich coordination modes.[6–10] In spite of the rich coordination chemistry exhibited by transition metals with these ligands,[11–17] relatively little is known with respect to the synthesis and the formal coordination of discrete organotin(IV) complexes with these ligands. Therefore, exploring whether organotin(IV) complexes with these ligands can help the construction of novel structure is of interest.

In this work, we selected H_3TMA and the triorganotin(IV) ion on the basis of the following considerations: (a) it has three carboxylic acid groups that may be completely or partially deprotonated, inducing rich coordination modes and allowing interesting structures with higher dimensions; (b) it can act not only as a hydrogen-bond acceptor but also as a hydrogen-bond donor, depending upon the number of deprotonated carboxyl groups; (c) some of the carboxyl groups may not lie in the phenyl ring plane upon complexation to metal ions owing to space hindrance, thus it may connect metal ions in different directions; (d) it possesses high symmetry that may be helpful for the crystal growth of the product formed; (e) triorganotin(IV) ions have a high affinity for hard donor atoms, and ligands containing oxygen atoms, especially carboxylic ligands, are usually employed in the architectures for polymeric complexes. Recently, we began to assemble H_3TMA and triorganotin(IV) ions and hope the rich information stored in H_3TMA will induce novel polymeric structures constructed by tin(IV) centers. Herein we report the syntheses and characterizations of nine triorganotin(IV) complexes constructed from H_3TMA. With a 1:3:3 molar ratio of H_3TMA:EtONa:R_3SnCl we obtained eight trinuclear complexes (**1**–**8**) of the type $[(R_3Sn)_3(TMA)]\cdot Y\cdot L$ [R = CH_3, Y = $3CH_3OH$ (**1**); R = CH_3, Y = $2CH_3OH$ (**2**); R = $C_6H_5CH_2$ (**3**); R = *o*-F-$C_6H_4CH_2$ (**4**); R = *o*-Cl-$C_6H_4CH_2$ (**5**); R = C_6H_5, L = CH_2Cl_2 (**6**); R = C_6H_5, L = $EtOH\cdot 2H_2O$ (**7**); R = C_6H_5, L

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[a] Department of Chemistry, Liaocheng University,
Liaocheng 252059, People's Republic of China
Fax: +86-538-6715521
E-mail: macl@lctu.edu.cn
[b] Taishan University,
Taian 271021, People's Republic of China

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= $Et_2O{\cdot}CH_2Cl_2$ (**8**)], and with a 1:2:2 ratio a 3D network **9** was obtained with the formula $[(CH_3)_3Sn]_2(HTMA){\cdot}H_2O$.

Results and Discussion

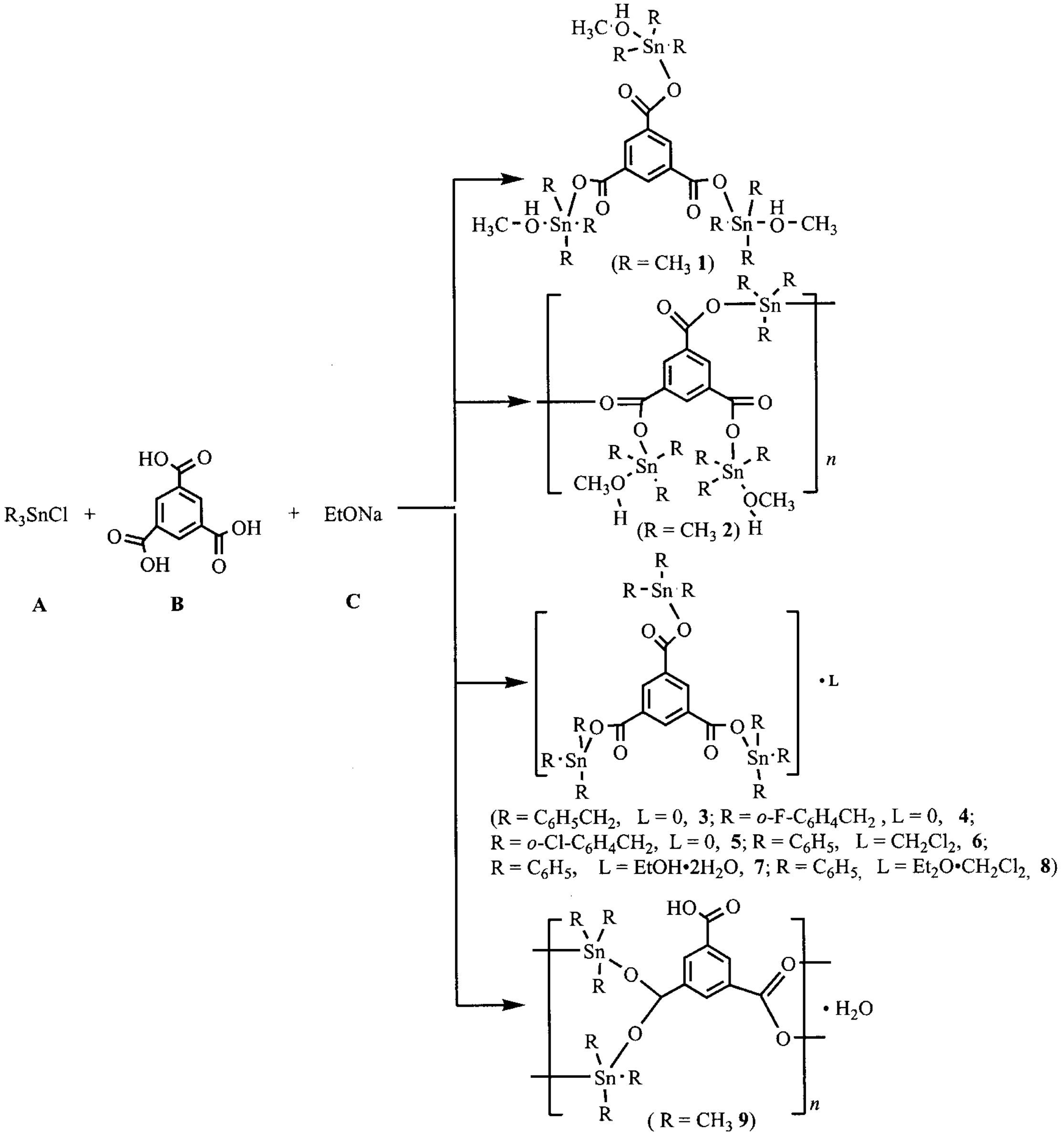
Reactions of H_3TMA and sodium ethoxide with triorganotin(IV) chlorides in a 1:3:3 or 1:2:2 stoichiometry afford the air-stable complexes **1**–**8** or **9**, respectively. The synthetic procedures are shown in Scheme 1.

Spectroscopic Studies

IR Spectroscopy

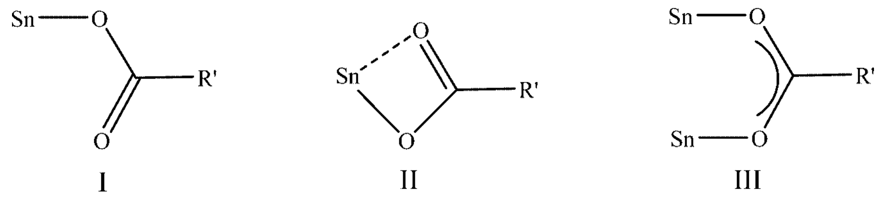
The stretching frequencies of interest are those associated with the C(O)O, Sn–C, and Sn–O groups. The strong absorption in the region 468–496 cm^{-1}, which is absent in the spectrum of the free ligand, is assigned to the Sn–O stretching mode. All these values are consistent with those detected in a number of organotin(IV)–oxygen derivatives.[18,19]

In organotin carboxylate complexes, IR spectroscopy can provide useful information concerning the coordination mode of the carboxyl group. When the carboxylic group coordinates the tin atom in a monodentate manner, the difference between the wavenumbers of the asymmetric and symmetric carboxylic stretching bonds (mode I), $\Delta\nu[\nu_{asC(O)O^-} - \nu_{sC(O)O^-})$ is greater than that observed for ionic complexes. When the ligand chelates (mode II), $\Delta\nu$ is considerably smaller than that for ionic complexes, while for asymmetric bidentate coordination the value is in the



(with **A**:**B**:**C** = 3:1:3, complexes **1–8**; with **A**:**B**:**C** = 2:1:2, complex **9**)

Scheme 1.



Scheme 2. Different coordination modes of the carboxylate group.

range characteristic of monodentate coordination.[20] The characteristic wavenumber difference for mode III is larger than that for chelated ions and nearly the same as observed for ionic complexes (Scheme 2).

Based on the above results, it was possible to distinguish the coordination mode of the C(O)O$^-$ group. The magnitude of $\Delta\nu$ of about 170 cm^{-1}, compared with those for the corresponding sodium salts, reveals that the carboxylate ligands function as bidentate ligands under the conditions employed.[21,22] This is also consistent with the X-ray diffraction study (see below).

NMR Spectroscopy

The ^{1}H NMR spectra show the expected integration and peak multiplicities. In the spectrum of the free ligand, the resonance observed at about δ = 10.51 ppm, which is absent in the spectra of the complexes, indicates the replacement of the carboxylic acid proton on complex formation. The chemical shifts of the signals for the methyl groups (δ = 0.81–1.01 ppm) and the phenyl group (δ = 7.21–7.76 ppm) appear at the same position as in the ligands. The $^2J_{\mathrm{Sn,H}}$ values of trimethyltin derivatives **1** and **2** (68.6 and 69.4 Hz, respectively) are similar to those previously reported for five-coordinate trigonal bipyramidal tin(IV) adducts.[23]

The ^{13}C NMR spectra of all complexes show a significant downfield shift of all carbon resonances compared with the free ligand because of an electron density transfer from the ligand to the acceptor. Although at least two different types of carboxyl groups are present, only a single resonance is observed for the COO group in the ^{13}C NMR spectra. A possible reason for this is that either accidental magnetic equivalence of the carbonyl carbon atoms occurs or the separations between the sets of resonance are too small to be resolved.

The ^{119}Sn NMR spectra of **1** and **2** show only one signal, typical of a five-coordinate species, which is in accordance with their structures in the solid state.[24] However, the chemical shift for **9** (δ = –55.0 ppm) is within the range corresponding to a coordination number of 4 (δ = –60 to +200 ppm),[24] so it can reasonably be assumed that the structure of **9** in solution is probably different from that observed in the solid state.

Crystal Structure of [(Me$_3$Sn)$_3$(TMA)]·3CH$_3$OH (1)

The molecular structure is illustrated in Figures 1 and 2 and selected bond lengths and bond angles are given in Table 1. Complex **1** is a two-dimensional polymer in the crystalline state. All the Sn atoms are five-coordinate with a trigonal bipyramidal structure by coordinating an additional methanol group. The axial ligand–tin–axial ligand angles [O(1)–Sn(1)–O(3) = 172.60(18)°, O(4)–Sn(2)–O(6) = 174.97(19)°, and O(7)–Sn(3)–O(9) = 174.7(2)°] suggest that the structures are near to a normal trigonal bipyramid. Intermolecular hydrogen-bond interactions between the methanol and the oxygen atom of an adjacent molecule [O(3A)–H···O(2) = 2.703 Å, O(6B)–H···O(8) = 2.694 Å, and O(9C)–H···O(5) = 2.608 Å] result in the formation of a two-dimensional network.

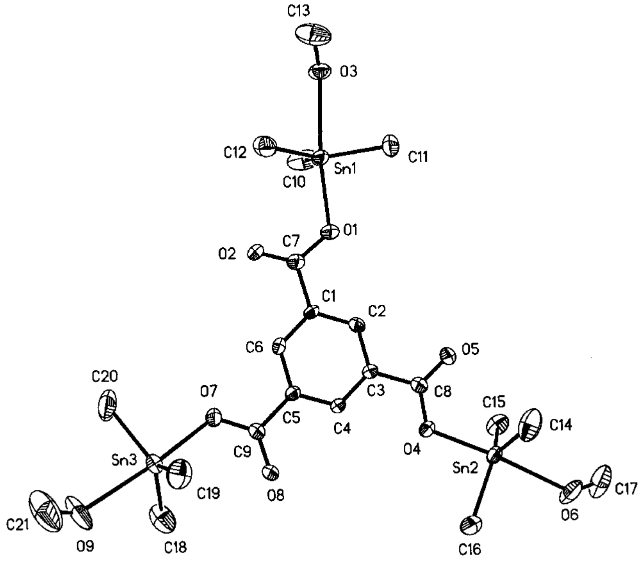


Figure 1. The molecular structure of **1**.

Crystal Structure of [(Me$_3$Sn)$_3$(TMA)]·2CH$_3$OH (2)

The molecular structure of complex **2** is illustrated in Figures 3 and 4 and selected bond lengths and bond angles are given in Table 1. The asymmetric unit of **2** consists of [(Me$_3$Sn)$_3$(TMA)]·2CH$_3$OH as the building block. There are two types of independent Sn atoms: the geometry at Sn(1) atom is trigonal bipyramidal with a bridging carboxyl group (O1 and O6A) and the geometries at Sn(2) and Sn(3) are trigonal bipyramidal with coordinating methanol group. The O(1)–Sn(1)–O(6)#1 [$-x$, $-y$, $z + 1/2$; 168.7(3)°], O(3)–Sn(2)–O(7)#2 [x, $y - 1$, z; 175.1(3)°], and O(5)–Sn(3)–O(8) [171.0(3)°] angles suggest that the structures are near to an ideal trigonal bipyramid. There are also two types of carboxylate groups, one of which is bidentate and the other monodentate. Due to the anisobidentate coordination mode of the carboxylate groups to the tin atoms, two groups of

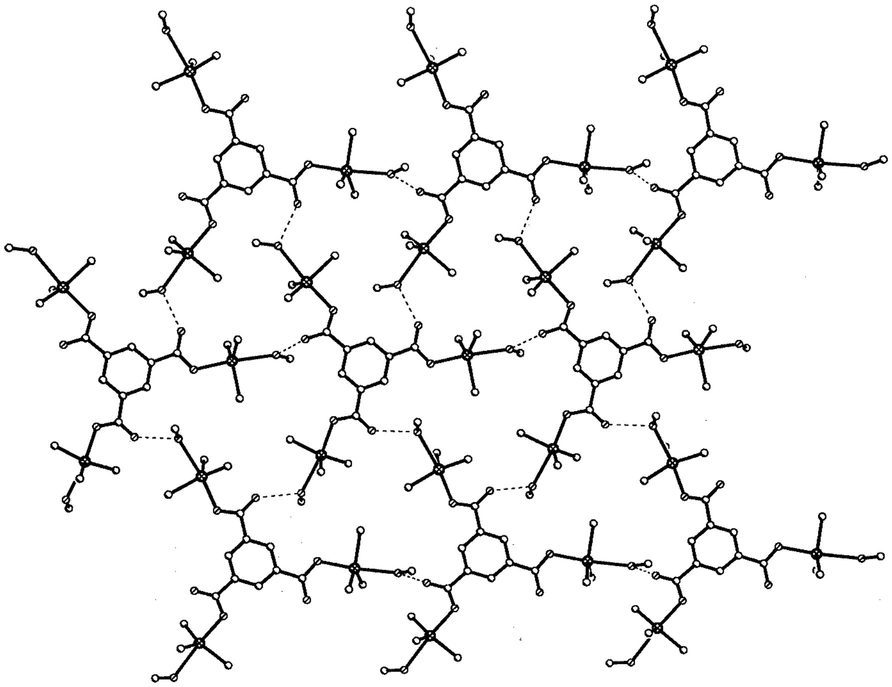


Figure 2. Polymeric network formed through intermolecular OH···O hydrogen-bond interactions in **1**.

Table 1. Selected bond lengths [Å] and bond angles [°] for **1** and **2**. #1: 1 – *x*, –*y*, *z* + 1/2: #2: *x*, *y* – 1, *z*; #3: –*x*, –*y*, *z* – 1/2.

1		**2**	
Sn(1)–O(1)	2.149(5)	Sn(1)–O(1)	2.160(7)
Sn(1)–O(3)	2.493(5)	Sn(1)–O(6)#1	2.549(8)
Sn(1)–C(11)	2.111(9)	Sn(1)–C(11)	2.107(17)
Sn(1)–C(10)	2.096(9)	Sn(1)–C(10)	2.125(13)
Sn(1)–C(12)	2.096(7)	Sn(1)–C(12)	2.135(13)
Sn(2)–C(14)	2.094(9)	Sn(2)–C(14)	2.084(16)
Sn(2)–C(15)	2.118(8)	Sn(2)–C(15)	2.108(12)
Sn(2)–C(16)	2.118(9)	Sn(2)–C(13)	2.158(12)
Sn(2)–O(4)	2.145(5)	Sn(2)–O(3)	2.160(7)
Sn(2)–O(6)	2.509(6)	Sn(2)–O(7)#2	2.569(9)
Sn(3)–C(19)	2.094(8)	Sn(3)–C(16)	2.059(15)
Sn(3)–C(18)	2.100(8)	Sn(3)–C(18)	2.102(14)
Sn(3)–C(20)	2.125(10)	Sn(3)–C(17)	2.118(16)
Sn(3)–O(7)	2.154(5)	Sn(3)–O(5)	2.156(9)
Sn(3)–O(9)	2.477(6)	Sn(3)–O(8)	2.462(9)
		Sn(1)#3–O(6)	2.549(8)
C(11)–Sn(1)–C(10)	120.2(5)	C(11)–Sn(1)–C(10)	115.2(7)
C(11)–Sn(1)–C(12)	118.8(4)	C(11)–Sn(1)–C(12)	127.0(6)
C(10)–Sn(1)–C(12)	118.3(4)	C(10)–Sn(1)–C(12)	114.2(8)
O(1)–Sn(1)–O(3)	172.60(18)	O(1)–Sn(1)–O(6)#1	168.7(3)
C(14)–Sn(2)–C(15)	121.4(4)	C(14)–Sn(2)–C(15)	120.1(6)
C(14)–Sn(2)–C(16)	118.7(4)	C(14)–Sn(2)–C(13)	120.8(6)
C(15)–Sn(2)–C(16)	118.0(4)	C(15)–Sn(2)–C(13)	116.2(6)
O(4)–Sn(2)–O(6)	174.97(19)	O(3)–Sn(2)–O(7)#2	175.1(3)
C(19)–Sn(3)–C(18)	120.9(4)	C(16)–Sn(3)–C(18)	119.3(9)
C(19)–Sn(3)–C(20)	117.8(4)	C(16)–Sn(3)–C(17)	119.1(9)
C(18)–Sn(3)–C(20)	119.6(5)	C(17)–Sn(3)–C(18)	119.2(9)
O(7)–Sn(3)–O(9)	174.7(2)	O(5)–Sn(3)–O(8)	171.0(3)

different Sn–O bond lengths are found, one group corresponding to Sn–O bonds of covalent character [2.156(9)–2.160(7) Å] and the other group corresponding to Sn–O bonds of coordinative character (2.548 Å). Bond lengths of 2.114(3)–2.208(2) Å and 2.381(2)–2.57(1) Å, respectively, have been measured in related trimethyltin carboxylates.[25] Also, there are two methanol molecules in the coordination sphere, with Sn–O bond lengths of 2.462 Å and 2.568 Å, respectively, which are comparable in strength to the intramolecular tin–oxygen bonds and close in length to the sum of the covalent radii of tin and oxygen (2.13 Å),[26] which is recognized as a coordinative bond.

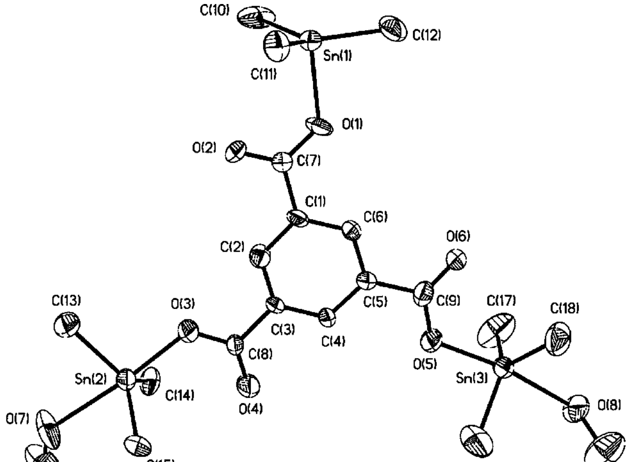


Figure 3. The molecular structure of **2**.

The structure shows that the Sn(1) ion is arranged in an infinite single helix with intervening TMA^{3-} ligands even though the ligand has no intrinsic tendency to form helical structures. The helical structure of **2** is a result of metal–organic ligand interactions coupled with the stereoelectronic characteristics of the ligand and the conditions prevailing during the synthesis. The helix has two distinct

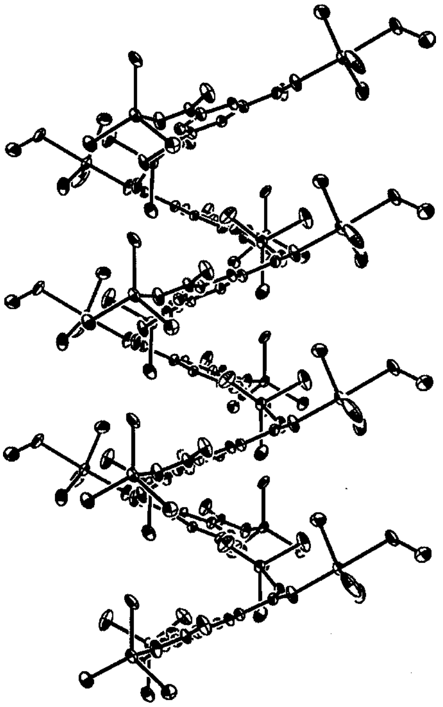


Figure 4. The helical structure of **2**.

Sn···Sn distances of 5.810 and 6.771 Å. The stability of the final helical structure relies on the coordinative bonds that each metal makes with the ligand. The helix is further organized into a metal–organic framework structure through inter-helix hydrogen bonding interactions to form a curved three-dimensional network.

The oxygen–oxygen distances in the crystal are also within the hydrogen-bonding range.[27] Hydrogen bonding is one of the main factors in the construction of supramolecular systems, and there are a variety of such linkages between the oxygen atoms of the carboxylic and coordinated methanol molecules. The packing is such that the oxygen of the coordinated methanol molecule forms two hydrogen bonds with the carboxylic oxygen atom of an adjacent molecule, which means that in the crystal there are a series of parallel helical chains that are linked by hydrogen bonds between coordinated CH_3OH and carboxylic oxygen atoms, which run through each other.

Crystal Structures of $[\{(C_6H_5CH_2)_3Sn\}_3(TMA)]$ (3), $[\{(C_6H_5)_3Sn\}_3(TMA)]\cdot CH_2Cl_2$ (6), $[\{(C_6H_5)_3Sn\}_3(TMA)]\cdot EtOH\cdot 2H_2O$ (7), and $[\{(C_6H_5)_3Sn\}_3(TMA)]\cdot Et_2O\cdot CH_2Cl_2$ (8)

The molecular structures of complexes **3**, **6**, **7**, and **8** are illustrated in Figures 5, 6, 7, and 8, respectively, and se-

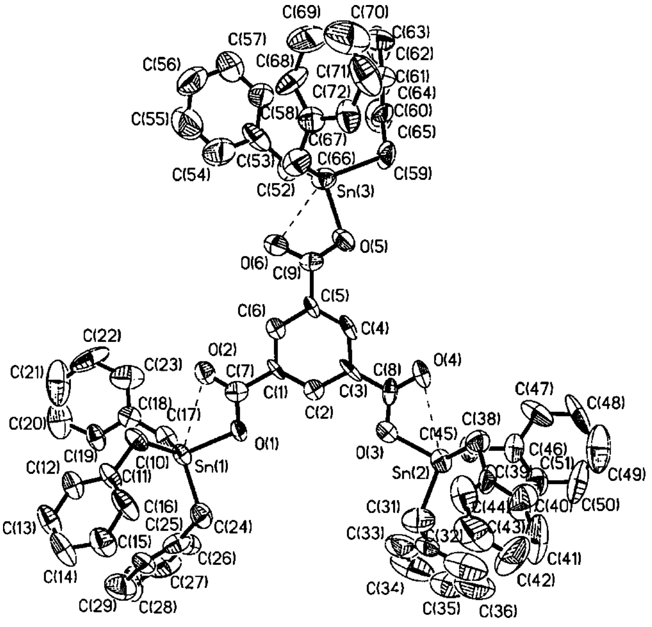


Figure 5. The molecular structure of **3**.

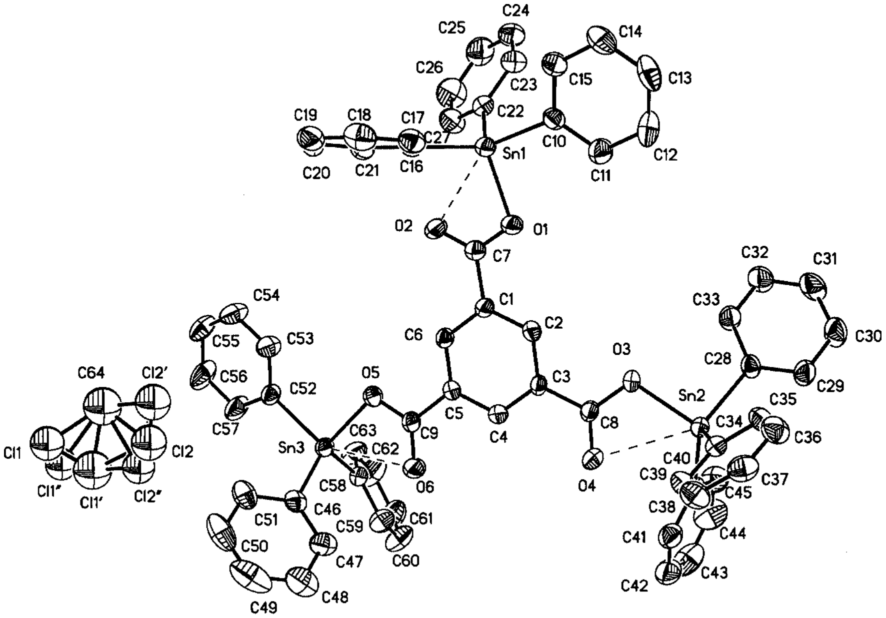


Figure 6. The molecular structure of **6**.

lected bond lengths [Å] and angles [°] are listed in Table 2. Trinuclear triphenyltin or tribenzyltin carboxylate of H_3TMA possesses a monomeric structure. For the complexes, it can be seen that the Sn(1)–O(1), Sn(2)–O(3), and Sn(3)–O(5) bond lengths (2.052–2.097 Å) lie in the range of 2.038(9)–2.115(6) Å that has been reported as the Sn–O covalent bond length, which proves that the oxygen atoms are coordinated to the tin atoms by a strong chemical bond. The intramolecular distances Sn(1)···O(2), Sn(2)···O(4), and Sn(3)···O(6) are in the range 2.634–2.916 Å. Although these distance are considerably longer than the normal Sn–O covalent bond length, they lie in the range of Sn···O distances of 2.61–3.02 Å which have been confidently reported for intramolecular bonds.[28,29] As the oxygen atoms of the carboxylate are involved in a weak coordinative interaction with tin along one of the tetrahedral faces, the structure distortion for the tin atoms in **3** and **6**–**8** is best described as a capped tetrahedron.

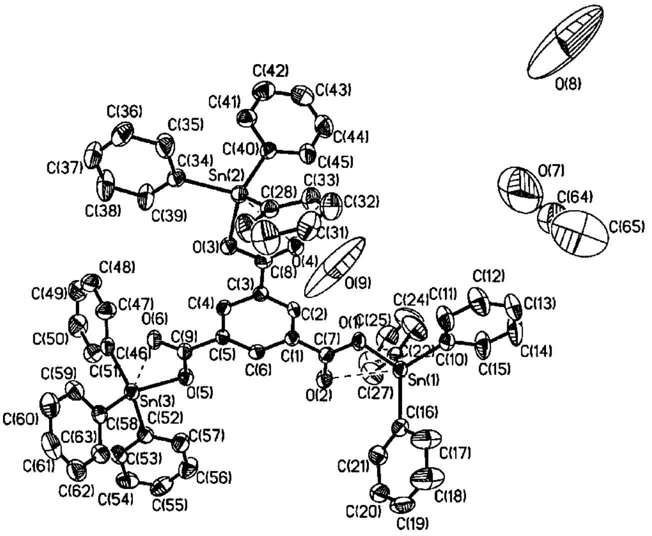


Figure 7. The molecular structure of **7**.

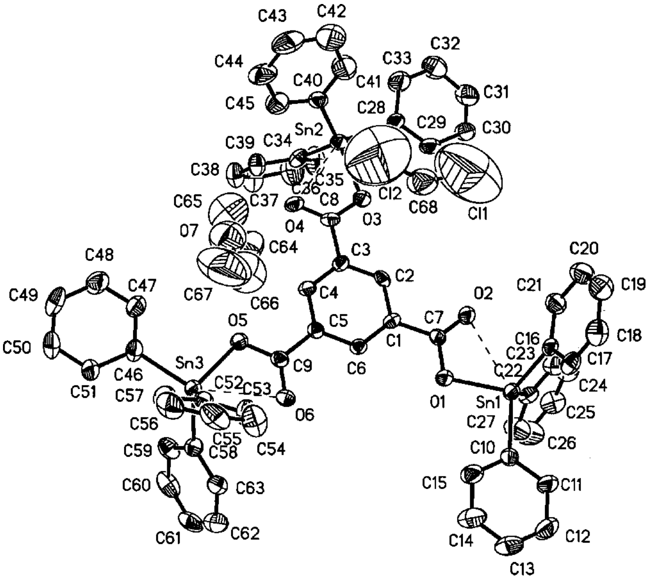


Figure 8. The molecular structure of **8**.

Table 2. Selected bond lengths [Å] and bond angles [°] for **3** and **6**.

3		**6**		**7**		**8**	
Sn(1)–O(1)	2.079(7)	Sn(1)–O(1)	2.070(3)	Sn(1)–O(1)	2.084(3)	Sn(1)–O(1)	2.066(5)
Sn(1)–O(2)	2.855(8)	Sn(1)–O(2)	2.745(3)	Sn(1)–O(2)	2.745(4)	Sn(1)–O(2)	2.783(6)
Sn(1)–C(10)	2.108(11)	Sn(1)–C(10)	2.120(5)	Sn(1)–C(10)	2.120(5)	Sn(1)–C(10)	2.119(8)
Sn(1)–C(24)	2.108(11)	Sn(1)–C(16)	2.122(5)	Sn(1)–C(16)	2.121(6)	Sn(1)–C(16)	2.114(9)
Sn(1)–C(17)	2.133(10)	Sn(1)–C(22)	2.118(5)	Sn(1)–C(22)	2.136(6)	Sn(1)–C(22)	2.115(9)
Sn(2)–O(3)	2.015(9)	Sn(2)–O(3)	2.068(3)	Sn(2)–O(3)	2.068(3)	Sn(2)–O(3)	2.052(5)
Sn(2)–C(38)	2.125(12)	Sn(2)–O(4)	2.801(3)	Sn(2)–O(4)	2.812(4)	Sn(2)–O(4)	2.729(6)
Sn(2)–O(4)	2.916(9)	Sn(2)–C(28)	2.132(5)	Sn(2)–C(28)	2.130(5)	Sn(2)–C(28)	2.112(8)
Sn(2)–C(31)	2.068(14)	Sn(2)–C(34)	2.119(5)	Sn(2)–C(34)	2.136(5)	Sn(2)–C(34)	2.115(9)
Sn(2)–C(45)	2.125(11)	Sn(2)–C(40)	2.120(5)	Sn(2)–C(40)	2.120(6)	Sn(2)–C(40)	2.103(10)
Sn(3)–C(52)	2.052(15)	Sn(3)–O(5)	2.070(3)	Sn(3)–O(5)	2.070(3)	Sn(3)–O(5)	2.058(5)
Sn(3)–C(59)	2.174(10)	Sn(3)–O(6)	2.745(3)	Sn(3)–O(6)	2.769(4)	Sn(3)–O(6)	2.751(6)
Sn(3)–O(5)	2.091(9)	Sn(3)–C(46)	2.122(5)	Sn(3)–C(46)	2.129(6)	Sn(3)–C(46)	2.115(8)
Sn(3)–O(6)	2.633(8)	Sn(3)–C(52)	2.127(5)	Sn(3)–C(52)	2.136(5)	Sn(3)–C(52)	2.125(9)
Sn(3)–C(66)	2.112(12)	Sn(3)–C(58)	2.130(5)	Sn(3)–C(58)	2.134(6)	Sn(3)–C(58)	2.124(9)
C(10)–Sn(1)–C(24)	114.7(4)	C(10)–Sn(1)–C(16)	111.75(19)	C(10)–Sn(1)–C(16)	109.2(2)	C(10)–Sn(1)–C(16)	110.9(3)
C(24)–Sn(1)–C(17)	110.4(5)	C(10)–Sn(1)–C(22)	109.14(19)	C(10)–Sn(1)–C(22)	110.8(2)	C(10)–Sn(1)–C(22)	110.6(3)
C(10)–Sn(1)–C(17)	113.4(5)	C(16)–Sn(1)–C(22)	116.48(18)	C(16)–Sn(1)–C(22)	120.5(2)	C(16)–Sn(1)–C(22)	116.5(3)
O(1)–Sn(1)–O(2)	50.7(3)	O(1)–Sn(1)–O(2)	52.05(11)	O(1)–Sn(1)–O(2)	52.74(11)	O(1)–Sn(1)–O(2)	51.67(18)
C(31)–Sn(2)–C(38)	112.0(5)	C(40)–Sn(2)–C(28)	110.3(2)	C(40)–Sn(2)–C(28)	116.4(2)	C(40)–Sn(2)–C(28)	110.5(4)
C(31)–Sn(2)–C(45)	114.8(5)	C(40)–Sn(2)–C(34)	120.07(19)	C(40)–Sn(2)–C(34)	111.0(2)	C(40)–Sn(2)–C(34)	120.8(3)
C(38)–Sn(2)–C(45)	113.9(4)	C(28)–Sn(2)–C(34)	111.45(18)	C(28)–Sn(2)–C(34)	110.0(2)	C(28)–Sn(2)–(34)	108.7(4)
O(3)–Sn(2)–O(4)	49.4(3)	O(3)–Sn(2)–O(4)	51.43(11)	O(3)–Sn(2)–O(4)	51.61(12)	O(3)–Sn(2)–O(4)	52.33(19)
C(52)–Sn(3)–C(66)	117.1(6)	C(46)–Sn(3)–C(58)	116.61(19)	C(46)–Sn(3)–C(58)	115.5(2)	C(46)–Sn(3)–C(58)	111.1(4)
C(52)–Sn(3)–C(59)	109.5(6)	C(46)–Sn(3)–C(52)	111.9(2)	C(46)–Sn(3)–C(52)	111.2(2)	C(46)–Sn(3)–C(52)	110.6(3)
C(59)–Sn(3)–C(66)	113.8(5)	C(58)–Sn(3)–C(52)	109.92(19)	C(58)–Sn(3)–C(52)	110.4(2)	C(58)–Sn(3)–C(52)	115.7(3)
O(5)–Sn(3)–O(6)	53.6(3)	O(5)–Sn(3)–O(6)	52.22(11)	O(5)–Sn(3)–O(6)	52.13(12)	O(5)–Sn(3)–O(6)	51.74(19)

Crystal Structure of [{$(CH_3)_3Sn$}$_2$(HTMA)]·H_2O (9)

The molecular structure of **9** is illustrated in Figure 9. It consists of infinite ribbons extending through the cell in the *b* direction, as indicated in Figure 10. Bond lengths and bond angles are given in Table 3. The trimethyltin(IV) groups are situated in special positions in the crystallographic mirror planes and are linked by a carboxylate; each TMA ligand in **9**, in turn, employs its two bidentate carboxylic groups to coordinate to four metal centers. Thus, four ligands are linked by four metal centers into a 24-membered macrocycle, which is further linked to eight nearest-neighbor Sn centers by four independent TMA ligands to give rise to a lattice plane with a cavity of 10.441–10.445 Å. All the tin atoms possess the same coordination environment. The coordination about the tin atom is only slightly distorted from a regular trigonal bipyramidal geometry. The angles O(3)#1–Sn(1)–O(1) 169.62(15)° and O(2)–Sn(2)–O(4)#2 171.48(16)° are close to a linear arrangement. The sum of the angles subtended at the tin atom in the trigonal plane is 358.3° for Sn(1) and 359.9° for Sn(2), so that the atoms Sn(1), C(10), C(11), and C(12) and Sn(2), C(13), C(14), and C(15) are almost in the same plane. The Sn–C distances [2.100(6)–2.118(7) Å] are equal within experimental error and close to the single-bond value for trigonal bipyramidal tin.[30]

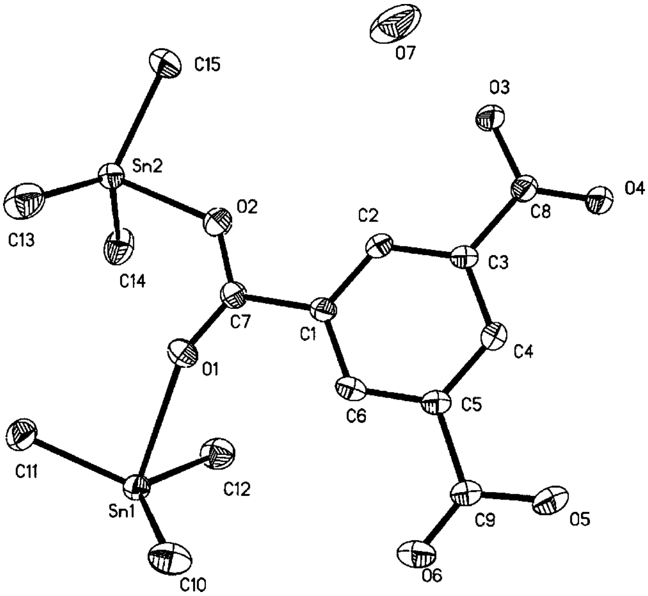


Figure 9. The molecular structure of **9**.

Interestingly, the [{$(CH_3)_3Sn$}$_2$(HTMA)]·H_2O groups are joined together by hydrogen bonds to form a three-dimensional network. The crystallization water molecule is linked to the O(3) atom to form a hydrogen bond [O(7)–H···O(3)] and to the O(5) and O(6) atoms from the neighboring [$(CH_3)_3Sn$]$_2$(HTMA)·H_2O group to form a further two hydrogen bonds [O(7)–H···O(6A) and O(7)···O(5A)–H(5A), respectively]. Viewed along the *a* axis, each layer [$(CH_3)_3$-Sn]$_2$(HTMA)·H_2O is linked to an adjacent [$(CH_3)_3Sn$]$_2$-(HTMA)·H_2O unit leading to an infinite network of intermolecular O···H–O hydrogen bonds. Thus, these networks are further organized into metal–organic framework structures through inter-network hydrogen bonding interactions that form a curved three-dimensional network.

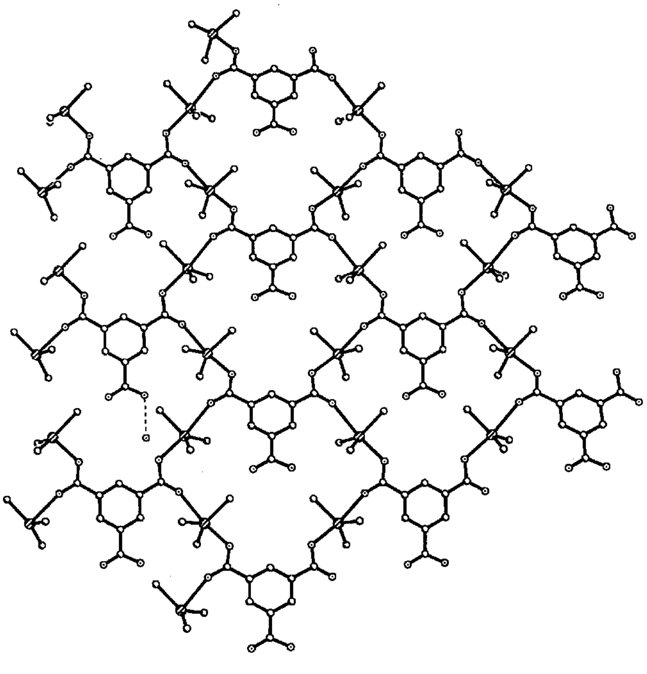


Figure 10. The network structure of **9**.

Table 3. Selected bond lengths [Å] and bond angles [°] for **9**. #1: *x* + 1/2, –*y* + 3/2, *z* – 1/2; #2: *x* – 1/2, –*y* + 3/2, *z*– 1/2; #3: *x* – 1/2, –*y* + 3/2, *z* + 1/2.

Sn(1)–C(11)	2.100(6)	Sn(2)–C(13)	2.106(7)
Sn(1)–C(10)	2.107(7)	Sn(2)–C(15)	2.108(7)
Sn(1)–C(12)	2.118(7)	Sn(2)–C(14)	2.114(7)
Sn(1)–O(3)#1	2.199(4)	Sn(2)–O(2)	2.128(4)
Sn(1)–O(1)	2.515(4)	Sn(2)–O(4)#2	2.569(4)
O(3)–Sn(1)#3	2.199(4)		
C(11)–Sn(1)–C(10)	113.5(3)	C(13)–Sn(2)–C(15)	122.3(3)
C(11)–Sn(1)–C(12)	122.6(3)	C(13)–Sn(2)–C(14)	121.2(3)
C(10)–Sn(1)–C(12)	122.2(3)	C(15)–Sn(2)–C(14)	114.4(4)
O(3)#1–Sn(1)–O(1)	169.62(15)	O(2)–Sn(2)–O(4)#2	171.48(16)

Conclusions

In summary, by carefully controlling the reaction conditions we have found that H_3TMA is a versatile building block for the construction of metal–organic complexes by complete or partial deprotonation of its carboxyl groups. Despite using a 1:3:3 molar ratio of H_3TMA, EtONa, and $(PhCH_2)_3SnCl$ (or Ph_3SnCl), we couldn't obtain a product similar to the polymeric structure of complex **2**. In general, in the crystalline state these complexes generally adopt either a polymeric structure with a five-coordinate tin atom or a discrete five-coordinate form.[21,31] Trimethyltin benzoates mainly assume one-dimensional associated arrangements, whereas triphenyltin benzoates generally exist in a discrete five-coordinate form. A delicate energy balance is present between the two forms, although the greater electronegativity of a phenyl group than a methyl group has been cited as a factor influencing the formation of the discrete form, as it gives more access to an axial position of a trigonal bipyramid.[31] A polymeric structure for tribenzyl or triphenyl carboxylates is associated with an electron-withdrawing R group. The contribution of either steric or electronic factors has been discussed by Holmes et al.[31] From structural data accumulated so far, the relative ligand electronegativity appears to be an important factor in determining whether the discrete structural form or the chain form is observed.[32] The axial tin–ligand bond lengths in both forms are subject to variations depending on the substitute electronegativity, ring strain, hydrogen bonds, and steric interactions.

Experimental Section

Materials and Measurements: Trimethyltin chloride, triphenyltin chloride, and 1,3,5-benzenetricarboxylic acid are commercially available and were used without further purification. Tribenzyltin chloride, tri(*o*-chlorobenzyl)tin chloride, and tri(*o*-fluorobenzyl)tin chloride were prepared by a standard method reported in the literature.[33] The melting points were obtained with Kofler micro-melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on Varian Mercury Plus 400 spectrometer operating at 400, 100.6, and 149.2 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ^{13}C spectra are broadband proton decoupled. The chemical shifts are reported in ppm with respect to the references and are stated relative to external tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR, and to neat tetramethyltin for ^{119}Sn NMR spectroscopy. Elemental analyses were performed with a PE-2400II apparatus.

Synthesis of $[\{(CH_3)_3Sn\}_3(TMA)]\cdot 3CH_3OH$ (1) and $[\{(CH_3)_3Sn\}_3(TMA)]\cdot 2CH_3OH$ (2): The reaction was carried out under nitrogen. H_3TMA (0.210 g, 1 mmol) and sodium ethoxide (0.204 g, 3 mmol) were added to a Schlenk flask and stirred for 0.5 h. Trimethyltin chloride (0.600 g, 3 mmol) was then added and the reaction mixture was stirred for 10 h at 40 °C. After filtration, the solvent was evaporated in vacuo. Yield: 78%. Rhombic crystals of **1** and block crystals of **2** were obtained from methanol solution.
1: M.p. 198–200 °C (dec.). $C_{21}H_{42}O_9Sn_3$ (794.62): calcd. C 31.74, H 5.33; found C 31.57, H 5.06. IR (KBr): $\tilde{\nu}$ = 3227, 1618, 1554, 1537, 1475, 1464, 1418, 583, 472 cm^{-1}. ^{1}H NMR ($CDCl_3/D_2O$): δ = 0.81–0.92 (s, $^2J_{Sn,H}$ = 68.6 Hz, 36 H), 1.78 (s, 3 H), 7.17 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.7 [$^1J_{^{119}Sn-^{13}C}$) = 471 Hz], 135.9, 136.4, 170.7 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –111.2 ppm.
2: M.p. > 220 °C (dec.). $C_{20}H_{38}O_8Sn_3$ (762.57): calcd. C 31.50, H 5.02; found C 31.31, H 4.87. IR (KBr): $\tilde{\nu}$ = 3204, 1626, 1565, 1532, 1481, 1479, 1440, 581, 476 cm^{-1}. ^{1}H NMR ($CDCl_3/D_2O$): δ = 0.85–0.88 (s, $^2J_{Sn,H}$ = 69.4 Hz, 27 H), 1.56 (s, 2 H), 3.37 (m, 6 H), 7.26 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.3 [$^1J_{^{119}Sn-^{13}C}$) = 492 Hz], 136.2, 136.6, 170.4 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –92.4 ppm.

Synthesis of $[\{(C_6H_5CH_2)_3Sn\}_3(TMA)]$ (3): Yield: 84%. M.p. 130–132 °C. $C_{72}H_{66}O_6Sn_3$ (1383.32): calcd. C 62.51, H 4.81; found C 62.26, H 4.87. IR (KBr): $\tilde{\nu}$ = 1627, 1551, 1512, 1461, 1432, 580, 479 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.24 (s, 18 H), 7.25–8.05 (m, 45 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 34.8, 126.6, 128.7, 129.7, 134.2, 135.0, 171.5 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –54.8 ppm.

Synthesis of $[\{(o\text{-}F\text{-}C_6H_4CH_2)_3Sn\}_3(TMA)]$ (4): Yield: 81%. M.p. 142–144 °C. $C_{72}H_{57}F_9O_6Sn_3$ (1545.33): calcd. C 55.96, H 3.72; found C 60.16, H 3.87. IR (KBr): $\tilde{\nu}$ = 1614, 1543, 1509, 1432, 1411, 576, 464 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.04 (s, 18 H), 6.64–7.58 (m, 36 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 34.6, 126.5, 128.1, 129.2, 134.1, 134.9, 171.0 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –55.6 ppm.

Synthesis of $[\{(o\text{-}Cl\text{-}C_6H_4)_3Sn\}_3(TMA)]$ (5): Yield: 78%. M.p. 150–154 °C. $C_{72}H_{57}Cl_9O_6Sn_3$ (1693.44): calcd. C 51.07, H 3.39; found C 51.26, H 3.21. IR (KBr): $\tilde{\nu}$ = 1621, 1549, 1512, 1439, 1408, 575, 470 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.24 (s, 18 H), 6.86–7.74 (m, 36 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 34.5, 126.6, 128.3, 129.4, 134.4, 135.2, 171.3 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –55.1 ppm.

Syntheses of $[\{(C_6H_5)_3Sn\}_3(TMA)]\cdot CH_2Cl_2$ (6), $[\{(C_6H_5)_3Sn\}_3(TMA)]\cdot Et_2OH\cdot 2H_2O$ (7), and $[\{(C_6H_5)_3Sn\}_3(TMA)]\cdot Et_2O\cdot CH_2Cl_2$ (8): A white powder was obtained, which was then recrystallized from different solvents. Colorless crystals of complex **6** were obtained from CH_2Cl_2, while colorless crystals of complexes **7** and **8** grew from 95% EtOH and Et_2O/CH_2Cl_2, respectively.
6: Yield: 81%. M.p. 112–114 °C. $C_{64}H_{50}Cl_2O_6Sn_3$ (1342.01): calcd. C 57.27, H 3.76; found C 57.06, H 3.89. IR (KBr): $\tilde{\nu}$ = 1634, 1587, 1530, 1479, 1450, 587, 496 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 5.33 (s, 2 H), 7.21–7.59 (m, 45 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 53.4, 128.6, 130.3, 132.1, 136.7, 136.7, 170.9 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –57.0 ppm.
7: Yield: 72%. M.p. 125–127 °C. $C_{65}H_{58}O_9Sn_3$ (1839.18): calcd. C 58.29, H 4.37; found C 58.27, H 4.12. IR (KBr): $\tilde{\nu}$ = 1612, 1561, 1537, 1476, 1451, 593, 491 cm^{-1}. ^{1}H NMR ($CDCl_3/D_2O$): δ = 1.20 (t, 3 H), 2.61 (t, $J_{H,H}$ = 4.8 Hz, 1 H), 3.12 (s, 4 H), 3.59 (m, 2 H), 7.24–7.56 (m, 45 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.4, 58.3, 128.3, 130.5, 131.7, 136.8, 136.9, 171.1 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –57.1 ppm.
8: Yield: 77%. M.p. 131–133 °C. $C_{68}H_{60}O_7Sn_3$ 1416.13): calcd. C 57.67, H 4.27; found C 57.44, H 4.35. IR (KBr): $\tilde{\nu}$ = 1634, 1577, 1542, 1480, 1459, 593, 485. ^{1}H NMR ($CDCl_3/D_2O$): δ = 1.21 (t, $J_{H,H}$ = 7.0 Hz, 6 H), 3.48 (m, 4 H), 5.28 (s, 2 H), 7.23–7.76 (m, 45 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.7, 53.4, 67.9, 128.9, 130.4, 131.5, 136.4, 136.8, 171.2 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –57.1 ppm.

Synthesis of $[\{(CH_3)_3Sn\}_2(HTMA)]\cdot H_2O$ (9): Yield: 75%. M.p. >220 °C (dec.). $C_{15}H_{24}O_7Sn_2$ (553.72): calcd. C 32.53, H 4.37; found C 32.37, H 4.34. IR (KBr): $\tilde{\nu}$ = 1702, 1627, 1595, 1521, 1469, 1440, 1359, 567, 472. ^{1}H NMR ($CDCl_3/D_2O$): δ = 1.01 (s, $^2J_{Sn,H}$ = 65.1 Hz, 18 H), 3.24 (s, 2 H), 7.28 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 [$^1J_{^{119}Sn-^{13}C}$ = 456 Hz], 136.4, 136.7, 171.0, 172.0 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –55.0 ppm.

X-ray Crystallographic Studies: Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Smart CCD area-detector with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). A semi-empirical absorption correction was applied to the data. The structures were solved by direct methods using SHELXS-97 and refined against F^2 by full-matrix least-squares using SHELXL-97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 4.
CCDC-256334 (for **1**), -249847 (for **2**), -226854 (for **3**), -248292 (for **6**), -230982 (for **7**), -236567 (for **8**), and -252043 (for **9**) 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.

Table 4. Crystal, data-collection, and structure-refinement parameters for **1**–**3** and **6**–**9**.

Complex	**1**	**2**	**3**	**6**	**7**	**8**	**9**
Empirical formula	$C_{21}H_{42}O_9Sn_3$	$C_{20}H_{38}O_8Sn_3$	$C_{72}H_{66}O_6Sn_3$	$C_{64}H_{50}Cl_2O_6Sn_3$	$C_{65}H_{58}O_9Sn_3$	$C_{68}H_{60}Cl_2O_7Sn_3$	$C_{15}H_{24}O_7Sn_2$
Formula mass	794.62	762.57	1383.32	1342.01	1339.18	1416.13	553.72
Crystal system	monoclinic	orthorhombic	triclinic	triclinic	triclinic	triclinic	monoclinic
Space group	$Pna2_1$	$Pna2_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a [Å]	19.215(8)	41.14(3)	40.08(4)	13.061(6)	12.859(13)	12.759(6)	10.1357(13)
b [Å]	13.024(5)	10.815(7)	11.519(11)	13.913(7)	14.755(14)	14.716(7)	13.013(3)
c [Å]	13.420(6)	6.771(4)	28.12(3)	18.156(9)	19.617(19)	19.513(9)	18.227(4)
α [°]	90	90	90	111.607(6)	110.565(13)	110.923(6)	90
β [°]	97.298(6)	90	91.617(19)	104.883(7)	105.626(13)	105.558(6)	90.160(4)
γ [°]	90	90	90	91.009(7)	93.453(14)	93.646(7)	90
Z	4	4	8	2	2	2	2
Absorption coefficient [mm^{-1}]	2.268	2.502	1.196	1.404	1.174	1.278	2.102
θ range for data collection [°]	1.89 to 25.03	1.95 to 25.03	1.45 to 25.03	1.60 to 25.03	1.50 to 25.03	1.18 to 25.03	2.30 to 25.06
Reflections collected	16796	14435	32303	15452	17262	16263	11946
Unique reflections	5864 ($R_{int} = 0.0825$)	5236 ($R_{int} = 0.0330$)	11461 ($R_{int} = 0.1832$)	10237 ($R_{int} = 0.0180$)	11385 ($R_{int} = 0.0334$)	10841 ($R_{int} = 0.0434$)	4135 ($R_{int} = 0.0386$)
Data/restraints/parameters	5864/3/307	5236/5/288	11461/38/730	10237/4/677	11385/9/703	10841/50/721	4135/3/223
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0429$ $wR_2 = 0.0915$	$R_1 = 0.0535$ $wR_2 = 0.1513$	$R_1 = 0.0540$ $wR_2 = 0.0873$	$R_1 = 0.0357$ $wR_2 = 0.0968$	$R_1 = 0.0405$ $wR_2 = 0.0770$	$R_1 = 0.0631$ $wR_2 = 0.1532$	$R_1 = 0.0398$ $wR_2 = 0.1004$
R indices (all data)	$R_1 = 0.0775$ $wR_2 = 0.1120$	$R_1 = 0.0552$ $wR_2 = 0.1528$	$R_1 = 0.2750$ $wR_2 = 0.1286$	$R_1 = 0.0572$ $wR_2 = 0.1095$	$R_1 = 0.0846$ $wR_2 = 0.0903$	$R_1 = 0.1097$ $wR_2 = 0.1091$	$R_1 = 0.0575$ $wR_2 = 0.1113$

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