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Self-Assembly of Dialkyltin Moieties and Mercaptobenzoic Acid into Macrocyclic Complexes with Hydrophobic "Pseudo-Cage" or Double-Cavity Structures: Supramolecular Infrastructures Involving Intermolecular C−H···S Weak Hydrogen Bonds and π–π Interactions

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

Abstract: Four novel organotin complexes of two types—$[R_2Sn(o\text{-}SC_6H_4CO_2)]_6$ (R = Me, **1**·H_2O; *n*Bu, **2**) and $\{[R_2Sn(m\text{-}CO_2C_6H_4S)R_2Sn(m\text{-}SC_6H_4CO_2)SnR_2]O\}_2$ (R = Me, **3**; *n*Bu, **4**)—have been prepared by treatment of *o*- or *m*-mercaptobenzoic acid and the corresponding R_2SnCl_2 (R = Me, *n*Bu) with sodium ethoxide in ethanol (95%). All the complexes were characterized by elemental analysis, FT-IR and NMR (^1H, ^{13}C, ^{119}Sn) spectroscopy, TGA, and X-ray crystallography diffraction analysis. The molecular structure analyses reveal that both **1** and **2** are hexanuclear macrocycles with hydrophobic "pseudo-cage" structures, while **3** and **4** are hexanuclear macrocycles with double-cavity structures. Furthermore, the supramolecular structure analyses show that looser and more intriguing supramolecular infrastructures were also found in complexes **1**–**4**, which exist either as one-dimensional chains of rings or as two-dimensional networks assembled from the organometallic subunits through intermolecular C−H···S weak hydrogen bonds (WHBs) and π–π interactions.

Keywords: macrocycles · organotin · self-assembly · supramolecular chemistry · weak interactions

Introduction

Metal-directed self-assembly has in recent years become a powerful tool for the construction of systems containing cavities or possessing intrinsic physical and chemical properties that are promising for the creation of new materials and new metal-based drugs.[1] More recently, noncovalent weak molecular forces capable of connecting these metallic subunits into looser and more intriguing supramolecular infrastructures (such as hydrogen bonds, van der Waals forces, nonbonded contacts, and π–π interactions) have been widely investigated in structural chemistry, structural biology, and the pharmaceutical sciences.[2]

Although considerable advances have been made in the development of self-assembly chemistry, only a relatively small number of organometallic species with main group elements have so far been reported.[3,4] Among them, organotin complexes are attracting more and more attention not only for their wide industrial applications and biological activities,[5] but also for their interesting and various architectures and topologies.[1a,q,s,4] The latter aspect has been actively investigated by a large number of researchers, and a multitude of structural types, including monomers, dimers, tetramers, oligomeric ladders, and hexameric drums, have been discovered.[6] Recently, many novel and interesting organotin complexes have been obtained by use of appropriate multifunctional ligands. Prabusankar and Murugavel, for example, have reported a hexanuclear macrocyclic organotin complex obtained by the use of 3,5-diisopropylsalicylic acid as ligand,[4e] Chandrasekhar and co-workers have reported a lipophilic hexaporphyrin assembly supported on a stannoxane core,[7] and—in particular—Höpfl and co-workers have carried out some very elegant work on such systems, having reported a series of polymeric and trinuclear macrocyclic organotin complexes obtained through the use of aromatic dicarboxylates as ligands.[4a–c] In our previous work, we have also reported several novel organotin complexes, including a

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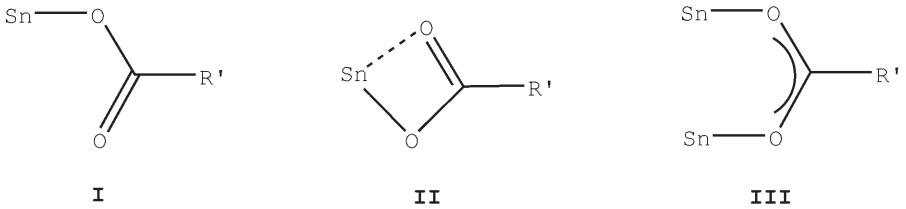
macrocycle containing five tin nuclei with heterocyclic sulfur and nitrogen donor ligands[4m] and macrocyclic complexes containing three and eighteen tin nuclei with 2-mercaptonicotinic acid,[4n,o] as well as an eight-tin macrocyclic complex with 2-mercapto-4-methylthiazol-5-ylacetic acid.[4p] In continuation of our research in this area, we chose two other fascinating ligands: *o*-mercaptobenzoic acid and *m*-mercaptobenzoic acid.

These two ligands were chosen for the following reasons: first, each of them has a carboxy group and a thiol group, so it should form strong covalent bonds with a diorganotin moiety, second, the spatial separation of the two groups attached to the same aromatic ring should induce the formation either of a polymeric chain or of a cyclooligomeric ring structure, and third, these two ligands also present a number of opportunities for the creation of supramolecular arrangements through weak hydrogen bonds (WHBs) from Lewis base sites (O, S) and π–π interactions (face-to-face or edge-to-face) between the adjacent aromatic rings. Here we report the syntheses and characterizations of four novel organotin macrocyclic complexes, obtained by treatment of *o*- or *m*-mercaptobenzoic acid with sodium ethoxide and the corresponding R_2SnCl_2 species (R = Me, *n*Bu) in ethanol (95%).



Scheme 2. Different coordination modes of the carboxylate group.

Results and Discussion

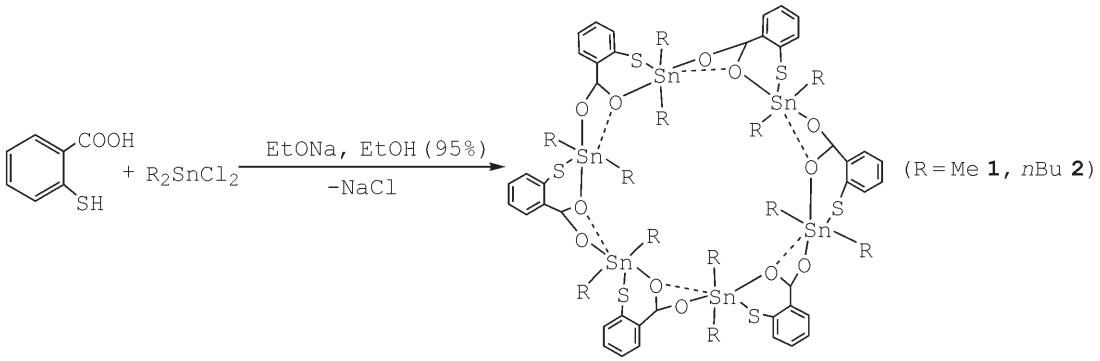
Characterization of dimethyl- and di-*n*-butyltin derivatives of *o*-mercaptobenzoic acid—{[$Me_2Sn(o\text{-}SC_6H_4CO_2)]_6(H_2O)$} (1·$H_2O$) and [$nBu_2Sn(o\text{-}SC_6H_4CO_2)]_6$ (2)

Preparation and spectral characterization: As reported in the literature,[4g] complex **2** has been prepared by condensation of di-*n*-butyltin oxide and *o*-mercaptobenzoic acid in 1:1 molar ratio at 80°C, but we obtained both complex **1**·H_2O and complex **2** by treatment of *o*-mercaptobenzoic acid with sodium ethoxide and the corresponding R_2SnCl_2 species (R = Me, *n*Bu) in ethanol (95%) at 40°C (Scheme 1). Complexes **1**·H_2O and **2** can be dissolved in common polar and nonpolar solvents such as benzene, ether, chloroform, ethanol, methanol, and acetonitrile.

Their IR spectra show metal–ligand bond formation through $-CO_2^-$ and $-S^-$ sites, and the associated Sn–O–Sn, Sn–O, and Sn–S absorption values are all in the ranges reported for other organotin complexes.[8,9] In addition, as reported in the literature,[10,11] IR spectra can provide useful information relating to coordinate formation through carboxylate moieties in organotin complexes (coordination modes shown in Scheme 2). The Δν values for complexes **1** and **2** reveal that the coordinate formation through the carboxylate groups in **1** and **2** is of the mode **III** type.

The ^1H NMR and ^{13}C NMR data for the two complexes are consistent with the formulation of the two products. The ^{119}Sn NMR spectra of both **1** and **2** each exhibit only a sharp signal, at $\delta = -224.6$ and -225.8 ppm, suggesting the equivalence of all six tin atoms. These chemical shift values are also in good agreement with what has been found in similar diorganotin derivatives.[4d,e]

In order also to evaluate the stabilities of the two complexes, both in solution and in the solid state, two different kinds of experiments were carried out. First, molecular weight determination by the cryoscopic freezing point method in benzene provided molecular weights of 650 for **1** and 820 for **2**, suggesting that their molecules exist in solution as dimers and not as hexamers. This is not surprising in view of the fact that the related hexameric compounds



Scheme 1. Preparation of complexes **1** and **2** in ethanol (95%).

$[n\mathrm{Bu_2Sn(OOCCH_2CH_2S)}]_6$ and $[n\mathrm{Bu_2Sn(3,5\text{-}i Pr_2C_6H_2(O)(COO))}]_6$ also exist as dimers in solution.[4d,e] Moreover, TGA shows that weight loss by **1** and **2** begins at 277 and 212 °C (loss of weight by $\mathbf{1}\cdot H_2O$ at 102 °C was disregarded due to the presence of water solvent molecules), close to the values found in DOP (dioctyl phthalate), PVC-DOP [poly(vinyl chloride)-dioctyl phthalate] and PVC-LSN117 [poly(vinyl chloride)-dioctyl tin bis-isooctyl thioglycollate].[13] The data suggest that the dimethyltin derivative has a higher decomposition temperature than the di-*n*-butyl derivative, consistently with what has been reported in $Sn_4R_4O_6$ complexes.[14]

X-ray crystallographic study of $\mathbf{1}\cdot H_2O$ *and* **2**: Crystals of $\mathbf{1}\cdot H_2O$ suitable for X-ray crystallography study were grown from the mother liquor, whilst crystals of **2** suitable for X-ray crystallographic study were grown from ether. The most relevant crystallographic data for $\mathbf{1}\cdot H_2O$ and **2** are summarized in Table 1.

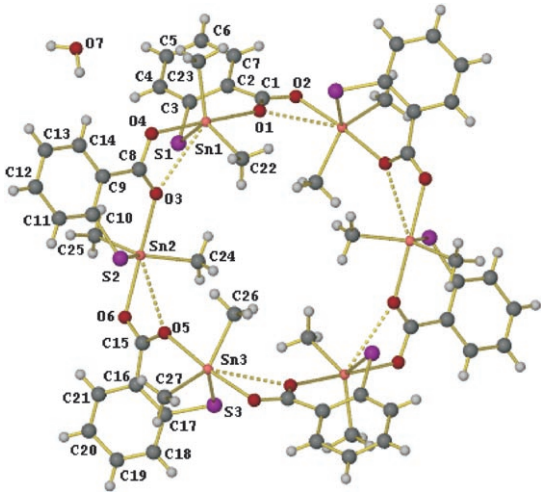


Figure 1. Molecular structure of the complex $\mathbf{1}\cdot H_2O$.

Table 1. Crystallographic data for complexes **1**, **2**, **3**, and **4**.

Complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{54}H_{62}O_{13}S_6Sn_6$	$C_{90}H_{132}O_{12}S_6Sn_6$	$C_{40}H_{52}O_{10}S_4Sn_6$	$C_{76}H_{124}O_{10}S_4Sn_6$
formula weight	1823.72	2310.46	1533.20	2038.32
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	*P* 2(1)/c	*P* 2(1)/c	*P* î	*P* î
unit cell dimension				
a [Å]	17.067(8)	14.007(2)	10.699(7)	13.443(5)
b [Å]	17.370(8)	23.389(4)	11.394(7)	15.331(6)
c [Å]	13.939(6)	17.105(3)	11.545(8)	24.093(8)
α [°]	90	90	106.211(8)	75.075(6)
β [°]	108.893(8)	113.250(3)	100.187(9)	74.484(4)
γ [°]	90	90	102.893(9)	75.284(6)
volume [Å^3]	3909 (3)	5148.9 (15)	1273.6 (14)	4531 (3)
Z	2	2	1	2
absorption coefficient [mm^{-1}]	2.096	1.607	3.110	1.768
crystal size [mm]	0.43×0.19×0.16	0.23×0.18×0.11	0.45×0.37×0.22	0.49×0.41×0.29
ρ_{calcd} [g cm^{-3}]	1.564	1.490	1.999	1.485
θ range for data collection [°]	2.35 to 25.03	1.81 to 25.03	1.90 to 25.03	1.82 to 25.03
reflections collected	19654	25907	6579	23623
unique reflections	6792 (R_{int}=0.1153)	8861 (R_{int}=0.1002)	4393 (R_{int}=0.0149)	15641 (R_{int}=0.0317)
data/restraints/parameters	6792/3/362	8861/72/520	4393/0/271	15641/61/855
final *R* indices [$I>2\sigma$ (*I*)]	R_1=0.0621, wR_2=0.1314	R_1=0.0700, wR_2 =0.1607	R_1=0.0245, wR_2=0.0628	R_1=0.0611, wR_2=0.1315
R indices (all data)	R_1=0.1841, wR_2=0.1857	R_1=0.1837, wR_2=0.2288	R_1=0.0286, wR_2=0.0662	R_1=0.1593, wR_2=0.1825

A perspective view of the molecular structure of $\mathbf{1}\cdot H_2O$ is shown in Figure 1. It should be noted that the macrocyclic component, $[Me_2Sn(o\text{-}SC_6H_4CO_2)]_6$ (**1**), crystallizes with one solvent molecule of H_2O, but the obvious interactions between the **1** moiety and the solvent molecule were not found. The macrocyclic $[Me_2Sn(o\text{-}SC_6H_4CO_2)]_6$ component consists of six Me_2Sn fragments linked together through six bridging $[oSC_6H_4CO_2]$ ligands to afford a hexanuclear Sn_6O_{12} macrocycle, which can be described as a carbon-studded *molecular bangle*.[4e] The overall macrocyclic molecule is held together by covalent Sn–O bonds, thus providing sufficient thermodynamic stability for existence in the solid state (see TGA). To the best of our knowledge, although the tetrameric structure is a very common aggregated form in diorganotin carboxylates,[1a,6] hexameric clusters of diorganotin carboxylates have so far only rarely been reported,[4d,e,g] whilst the six tin atoms and twelve carboxyl oxygen atoms in most reported hexameric macrocycles[4d,e] lie almost in a plane, with the alkyl groups on tin positioned above and below the plane. The associated ligands also lie not far away from the mean plane defined by the tin and oxygen atoms, thus providing an overall planar structure for the macrocyclic molecule. However, there is a striking difference between the two previously reported hexamers—$[n\mathrm{Bu_2Sn(OOCCH_2CH_2S)}]_6$ and $[n\mathrm{Bu_2Sn(3,5\text{-}i Pr_2C_6H_2(O)(COO))}]_6$—and complex **1**, since the macrocycle components in the two previously reported hexamers are almost planar, while their counterpart in complex **1** is twisted. This dramatic difference might be related to steric effects and to the different sorts of coordinated atoms. In fact, Sn1, Sn2, and Sn3 occupy a plane 6.263 Å distant from the plane defined by Sn1#, Sn2#, and Sn3# (symmetry operations: $-x$, $-y+1$, $-z+1$). It is notable that this twisted structural feature gives rise to an interesting hydrophobic "pseudo-cage" in complex **1**. Indeed, the sets of

three inner methyl groups attached to the tin atoms each form a small trigonal cavity (for example: C22–C24# = 4.573 Å, C26–C24# = 5.080 Å, and C22–C26 = 5.520 Å; symmetry operations: $-x$, $-y+1$, $-z+1$), which is apparently smaller than the Sn_6O_{12} cavity (transannular Sn···Sn distance = 9.252–10.388 Å, O···O = 8.930–9.893 Å). The distance between the two C3 cycles is only 3.072 Å (centroid–centroid), so a flat "cage" with two small "openings" has been generated in complex **1**. The hydrophobic character of this "cage" is also evidenced, at least to some extent, by the fact that the H_2O molecule in **1**·H_2O is located not in the "cage" but outside it.

Each of the tin atoms in complex **1** is essentially pentacoordinated (Figure 1), bound to two methyl groups, two carboxyl oxygen atoms, and one thiol sulfur atom, so the geometry of each tin atom can be described as a distorted trigonal bipyramid in which the apical positions are occupied by the oxygen atoms from two carboxylate groups (av O–Sn–O = 174.13°). In addition, there is also a weak sixth coordination for each of the three crystallographically independent tin atoms, between the carboxylate oxygen atoms O1, O3, and O5 and their neighboring tin atoms, shown in Figure 1 as broken lines. If this weak interaction to the metal is included, the *o*-mercaptobenzoic acid in **1** acts as a doubly negative tetradentate chelating bridging ligand. As we know, such ligating behavior was previously unknown in the other metal complexes formed by *o*-mercaptobenzoic acid.

The Sn–O and the Sn–S bond lengths around each tin center are close to those observed in other diorganotin derivatives.[4d,g] Of the Sn–O bonds around each tin atom, the monodentate carboxylic oxygen atoms (O2, O4, O6) form bonds to tin only a little shorter (av 2.191 Å) than those formed by the bidentate bridging carboxylic oxygen atoms O1, O3, and O5 (av 2.278 Å). The carboxylates thus bond to tin in a highly symmetric fashion (the average difference between Sn–O bonds for each tin is only 0.087 Å), whilst the two C–O distances within each carboxylate moiety also show no significant difference (av 0.033 Å), indicating substantial delocalization of the CO_2 π-electron density. This is closely consistent with observations for the similar diorganotin carboxylate $[n\mathrm{Bu_2Sn(OOCCH_2CH_2S)}]_6$.[4d] In fact, the intermonomer Sn–O bonds in this macrocycle are even shorter than the intramonomer ones (av 0.087 Å), so the hexamer can alternatively be viewed as a large macrocycle reinforced by additional intramonomer Sn–carboxylate interactions. Furthermore, the third Sn–O bond, a weaker interaction, is the longest in the molecule (av 3.005 Å) but appreciably shorter than the sum of the van der Waals radii of tin and oxygen atoms (3.70 Å).[15]

Analysis of the supramolecular infrastructure in the crystal lattice of **1**·H_2O reveals that weak intermolecular C–H···S and C–H···π WHBs play important roles in the supramolecular arrangements. The C–H···π interaction can also be viewed as an edge-to-face (as opposed to point-to-face or T-shape) π–π interaction.[2v] Although both are much weaker than covalent and coordinated interactions, even than typical hydrogen bonds (such as O–H···O, N–H···O, etc.), they clearly govern the assembly of supramolecular structures in many compounds.[2,16] In complex **1**, a series of parallel chains of rings connected by intermolecular C18–H18···S2 and C27–H27B···π (C16-C21) double WHBs running along the *c* axis have been found. Because the macrocycle is highly centrosymmetric (symmetric operation: $-x$, $-y+1$, $-z+1$), similar molecular chains have also been found along the [011] direction. This structural feature gives rise to an interesting and loose two-dimensional network in the *bc* plane. The values for the C–H···S WHB (see Table 2) suggest that it is weaker than an intramolecular C–H···S WHB in (r-2, c-4)-3-benzyl-2,4,5,5-tetraphenyl-1,3-thiazolidine (3.04 Å, 2.55 Å, and 110°),[17] whilst the parameters for the C–H···π interaction (see Table 2) suggest that it is stronger than has been reported for this motif.[2v]

Table 2. C–H···S and C–H···π weak hydrogen bonds of complexes **1**·H_2O, **2**, **3**, and **4** and π–π stacking interactions (face-to-face) of complexes **3** and **4**.

Complex	C–H···S, C–H···π weak hydrogen bonds C–H···X	Lengths [Å]			Angles [°]	π–π stacking interactions Interplanar separation (h) [Å]	Centroid–centroid [Å]	Slip angle (θ) [°]
		C–H	C···X	H···X	C–H···X			
1·H_2O	C18–H18···S2	0.930	3.638	2.908	136.40			
	C27–H27B···π (centroid)	0.960	3.602	2.895	131.29			
2	C21–H21···π (centroid)	0.930	4.014	3.479	119.09			
3	C20–H20···S2	0.960	3.916	2.963	171.60	3.5109	3.695	18.2
4	C60–H60B···S4	0.967	3.804	2.927	152.44	3.7383	3.868	14.9
	C69–H69B···S2	0.969	3.872	2.911	171.13			

The molecular structure of complex **2** is presented in Figure 2 (the somewhat disordered β, γ, and δ carbon atoms of the Sn-butyl groups have been omitted for clarity). The complex is similar to complex **1** and has been reported by Marcel et al.,[4g] so we do not deal with any structural details here, but a comparison of the molecular conformations and configurations of complexes **1** and **2** should be noted: first, the distance between the two planes (6.632 Å) defined by Sn1, Sn2, and Sn3 and by Sn1#, Sn2#, and Sn3# (symmetry operations: $-x+1$, $-y+1$, $-z+1$) in **2** is close to that found in complex **1**, second, the dimensions of the Sn_6O_{12} ring (transannular Sn···Sn = 9.903–10.236 Å, O···O = 9.471–9.825 Å) in complex **2** show no apparent difference from those in complex **1**, and third, the dimensions of the small trigonal cavity (C37–C29# = 4.373 Å, C4–C29# = 4.381 Å, and C37–C41 = 5.148 Å; symmetry operations: $-x+1$, $-y+1$, $-z+1$) are also very close to those found in complex **1**.

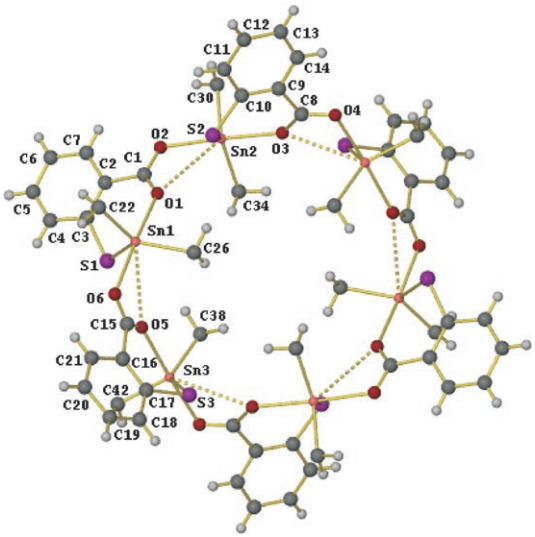


Figure 2. Molecular structure of complex **2** (the somewhat disordered β-, γ-, and δ-carbon atoms of the Sn-butyl groups have been omitted for clarity).

However, the distance between the two C3 cycles in **2** (centroid–centroid = 10.373 Å) is markedly longer than that found in complex **1**, thus producing a relatively spindly "cage".

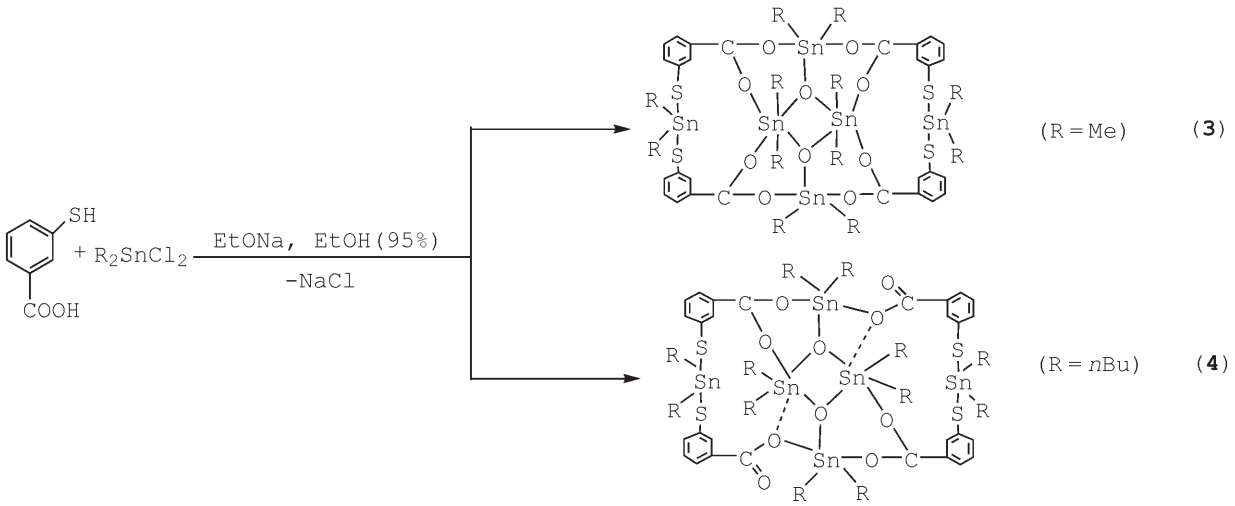
The supramolecular structure of complex **2** is a two-dimensional network in the *bc* plane, similar to that found in complex **1**, but there are certain differences between the supramolecular structures of the two complexes, one being that the macrocyclic molecules of complex **2** are only connected by intermolecular C21–H21···π (C2–C7) interactions in complex **2** and the other being that the molecular chains of rings in complex **2** are running along the [011] and [01–1] directions. In addition, the butyl groups are crowded between the adjacent macrocyclic molecules, thus resulting in a long distance (4.014 Å) between C27 and centroid, markedly longer than that found in complex **1** but close to that found in $[\alpha\text{-NaiEtH}]^+[PF_6]^-$ (C–centroid = 4.090 Å, H–centroid = 3.149 Å, C–H–centroid = 167.088°).[18]

Characterization of dimethyl- and di-*n*-butyltin derivatives of *m*-mercaptobenzoic acid—{[$Me_2Sn(m\text{-}SC_6H_4CO_2)MeSnMe(m\text{-}SC_6H_4CO_2)SnMe_2]O\}_2$ (3) and {[$nBu_2Sn(m\text{-}SC_6H_4CO_2)nBuSnnBu(m\text{-}SC_6H_4CO_2)\ nBu_2Sn]O\}_2$ (4)

Preparation and characterization: Complexes **3** and **4** were prepared analogously to complexes **1** and **2** by treatment of *m*-mercaptobenzoic acid and the corresponding R_2SnCl_2 species (R = Me, **3**; R = *n*Bu, **4**) with sodium ethoxide in ethanol (95%) at 40°C (Scheme 3). Both complexes **3** and **4** can be dissolved in common polar and nonpolar solvents such as benzene, ether, chloroform, ethanol, methanol, and acetonitrile.

The IR spectra show metal–ligand bond formation through $-CO_2^-$ and $-S^-$ sites, and the associated Sn–O–Sn, Sn–O, and Sn–S absorption values are also support this. In addition, the Δν values for complexes **3** and **4** indicate that the carboxylate coordination modes of **3** and **4** can be regarded as modes **III** and **II**. The ^{1}H NMR and ^{13}C NMR data for the two complexes are consistent with the formulation of the two products. The ^{119}Sn NMR spectra of **3** and **4** each show three types of tin atoms: signals at $\delta = 70.6$ ppm (for **3**) and $\delta = 75.8$ ppm (for **4**) are due to tetracoordinate tin atoms, signals at $\delta = -180.5$ ppm (**3**) and $\delta = -185.2$ ppm (**4**) are due to pentacoordinate tin atoms, and signals at $\delta = -228.1$ ppm (**3**) and $\delta = -235.6$ ppm (**4**) are due to hexacoordinate tin atoms,[19] so it can reasonably be assumed that the environments around the tin atoms in **3** and **4** in solution should not be markedly different.

Moreover, molecular weight determination by the cryoscopic freezing point method in benzene provided the molecular weights of 1580 for **3** and 2130 for **4**, suggesting that



Scheme 3. Preparation of complexes **3** and **4** in ethanol (95%).

the structures of both complexes in solution are similar to those observed in the solid state. TGA showed weight loss of **3** and **4** starting at 213 and 174 °C, slightly low in relation to that found in DOP, PVC-DOP, and PVC-LSN117.[13] The data suggest that the dimethyltin derivative has a higher decomposition temperature than the di-*n*-butyl derivative, which is consistent with what has been reported for $Sn_4R_4O_6$ complexes.[14]

*X-ray crystallographic study of **3** and **4***: Crystals of **3** suitable for X-ray crystallographic study were grown from the mother liquor, whilst crystals of **4** suitable for X-ray crystallographic study were grown from ether/petroleum. The most relevant crystallographic data for **3** and **4** are summarized in Table 1.

A perspective view of the molecular structure of **3** is shown in Figure 3 a. This complex is a hexanuclear macrocycle containing a four-membered Sn_2O_2 ring, which features

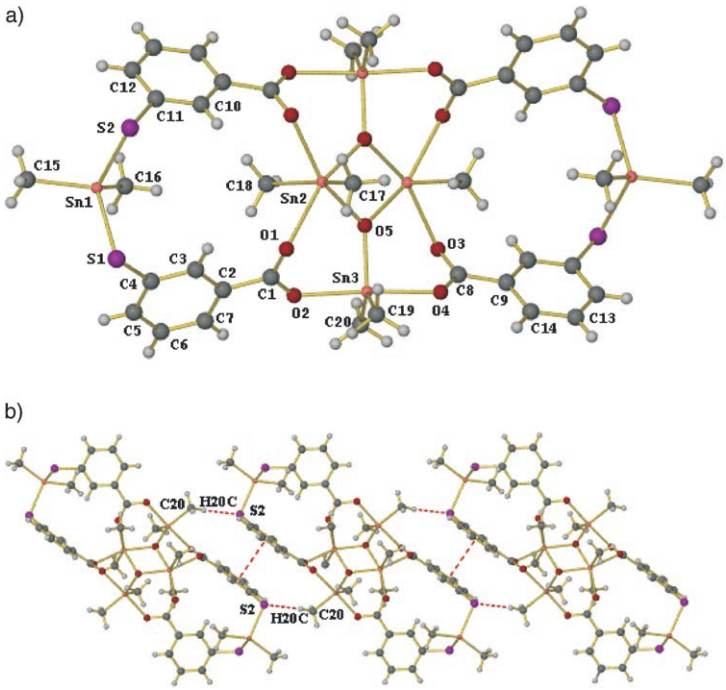


Figure 3. a) Molecular structure of complex **3**. b) Supramolecular structure of complex **3**, showing a chain of rings connected by intermolecular C–H···S WHBs with a head-to-tail arrangement and π···π stacking interactions between the adjacent aryl rings (shown with broken lines).

as a centrosymmetric core in this macrocycle. Each bridging oxygen atom in the Sn_2O_2 ring is attached to three Me_2Sn units, and as a result these oxygen atoms are tricoordinate. Although the diorganotin carboxylate moiety in this complex is very common in organotin complexes,[6,20] to the best of our knowledge, no macrocycle with a double cavity in a discrete molecule was known previously among the organotin complexes, except for the case of $\{[n\mathrm{Bu}_2\mathrm{Sn}(O_2CCH_2C_4H_3NS)SS(C_4H_3NSCH_2CO_2)\mathrm{Sn}n\mathrm{Bu}_2]O\}_2$.[21]

This macrocycle is divided into two 14-membered small cycles by the ladder part, so the effective space of the cavity (each small cycle: Sn2–Sn2# = 6.967 Å, C10–C3 = 5.002 Å) in this macrocyclic derivative is evidently reduced in relation to the overall macrocyclic dimensions (Sn1–Sn1# = 6.616 Å, Sn3–Sn3# = 16.980 Å).

The geometries of all the tin atoms in complex **3** can be classified into three types: tetracoordinated exocyclic tin (Sn1), pentacoordinated exocyclic tin (Sn3), and hexacoordinated endocyclic tin (Sn2). Each of the tetracoordinated tin atoms—Sn1, for example—forms four primary bonds: two to the methyl groups and the others to the sulfur atoms, and so displays a distorted tetrahedral coordination sphere with six angles ranging from 104.31(14) to 120.7(2)°. The Sn–C bond and the Sn–S bond lengths are consistent with those reported in other diorganotin thiolates.[22] Each of the pentacoordinated exocyclic tin atoms—Sn3 for example—forms three short Sn–O bonds with three oxygen atoms: one from the Sn_2O_2 moiety and the other two from two different carboxylate groups. Together with the two bonds to methyltin groups, the Sn3 atom may be viewed as a slightly distorted trigonal bipyramid with the axial site occupied by the O2 and O4 atoms (O2–Sn3–O4 = 176.42(10)°). Each of the hexacoordinated endocyclic tin atoms—Sn2, for example—has an octahedral geometry with four equatorial oxygen atoms and two axial carbon atoms, the geometry being somewhat distorted by the small angles in the stannoxane rings, affecting the equatorial angles. Steric effects between the methyl groups across the stannoxane ring cause the rings to bend away from the center of the molecule (C17–Sn2–C18 = 153.60(16)°) and also to twist relative to each other. An unusual feature here is that although the acetate bridges are symmetrical [differences in C–O bond lengths are 0.029 and 0.008 Å], the Sn–O bond lengths are unequal (differences of 0.124 and 0.259 Å). This is probably due to the *trans* effect from the strongly bound stannoxane ring oxygen, as first suggested by Graziani et al.[23]

The supramolecular structure of complex **3** is a linear chain connected by intermolecular C–H···S WHBs and π–π (face-to-face) interactions. As shown in Figure 3 b, every pair of adjacent macrocyclic molecules are linked by a pair of intermolecular C20–H20C···S2 WHBs with a head-to-tail arrangement, thus forming a loose cavity between the two adjacent molecules (C20–C20# = 10.601 Å, centroid–centroid = 3.695 Å). This loose structure is further stabilized by the presence of a π–π interaction established between the adjacent phenyl groups. The C–H···S value (see Table 2) suggests that it is weaker than that found in $\mathbf{1}\cdot H_2O$, whilst the value of the π–π interaction (see Table 2) in this complex is closely in agreement with what has been reported in the literature.[24]

A perspective view of molecular structure **4** is shown in Figure 4 (the somewhat disordered β, γ, and δ carbon atoms of the Sn-butyl groups have been omitted for clarity). Complex **4** is also a hexanuclear centrosymmetric macrocycle containing one centrosymmetric ladder, but not completely identical to that found in complex **3**. Two of the acetate

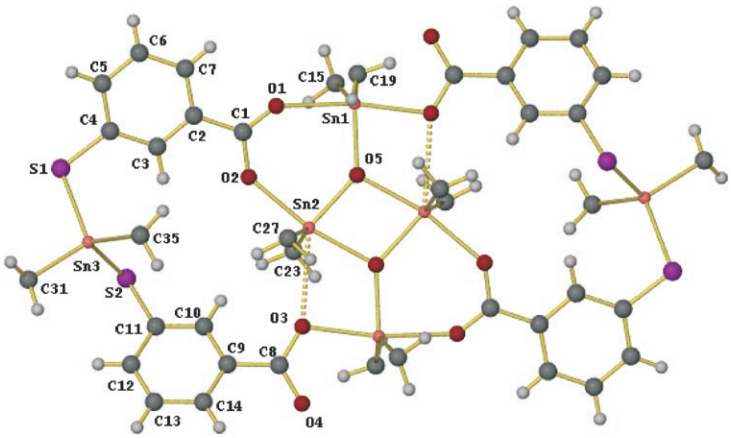


Figure 4. Molecular structure of complex **4**; the somewhat disordered β-, γ-, and δ-carbon atoms of the Sn-butyl groups have been omitted for clarity.

groups in **4** are "hanging" rather than bridging, which is the more usual structure in organotin carboxylates.[20]

The geometries of all the tin atoms in complex **4** can also be classified into three types: tetracoordinate exocyclic tin (Sn3), pentacoordinate exocyclic tin (Sn1), and hexacoordinate endocyclic tin (Sn2). The tetracoordinate tin atoms—Sn3, for example—also form four primary bonds: two to the butyl groups and the others to the sulfur atoms, thus adopting a distorted tetrahedral geometry similar to that found in complex **3**. The pentacoordinated atoms—Sn1, for example—in this complex each have five primary bonds, and the geometry around Sn1 is similar to that in **3** except for a slight narrowing of the O3#-Sn1-O5 angle (80.75°; symmetry operations: $-x+1$, $-y$, $-z+1$) to accommodate the long Sn1···O4# (symmetry operations: $-x+1$, $-y$, $-z+1$) weak interaction (2.920 Å). The hexacoordinate Sn2 atom, the stannoxane ring tin, is essentially the same as its counterpart in complex **3**. Although the Sn2···O3 distance (2.820 Å) is apparently longer than that found in **3** (2.464 Å), it makes very little difference to the geometry of the Sn2 atom, no doubt due to the strong stannoxane ring bonding governing the geometry and the large bulk of the *n*-butyl groups.

To our surprise, although there are two "hanging" carboxyl oxygen atoms in complex **4**, no intermolecular C=O···Sn interaction—which may give rise to polymeric or cyclooligomeric structures (such as in complexes **1** and **2**) in organotin carboxylates—was found in the supramolecular structure.[4a–e,g] In fact, the supramolecular structure of complex **4** is a two-dimensional network in the *bc* plane, in which the discrete molecules are connected through two types of C–H···S WHBs from two adjacent macrocyclic molecules: one is a intermolecular C60–H60C···S4 WHB with head-to-tail arrangements accompanied by π–π stacking interactions, similar to that found in complex **3**, whilst the other is an intermolecular C69–H69B···S2 WHB (see Supporting Information). The loose cavities provided by these weak interactions are of 30.189 Å (S4–S4)×8.667 Å (Sn3–Sn3) and are completely filled by the butyl groups on tin atoms that protrude into each interior.

Conclusion

In conclusion, this contribution has shown that the self-assembly of a diorganotin moiety and an appropriately substituted benzoic acid such as *o*-mercaptobenzoic acid or *m*-mercaptobenzoic acid can result in the formation of interesting macrocyclic organotin complexes. Steric effects are apparent in the self-assembly process: when the mercapto group is *ortho* to the carboxyl group it can assist the carboxyl group in the same ligand in forming a hexanuclear macrocycle through intermolecular C=O···Sn interactions, while a mercapto group *meta* to the carboxyl group provided no assistance to the carboxyl group in the same ligand, due to spatial remoteness, but was able to form cyclooligomeric structures through S–Sn–S and O–Sn–O covalent linkage.

The supramolecular structures described in this paper demonstrate that weak intermolecular interactions have enormous potential for assembling discrete molecular systems in which the subunits are organometallic complexes. This contribution adds several new features to the rapidly developing field of WHBs and supramolecular assembly and aids in the fundamental understanding of molecular recognition and interpretation of supramolecular aggregation in crystal engineering.

Experimental Section

Materials and measurements: Dimethyltin dichloride, di-*n*-butyltin dichloride, *o*-mercaptobenzoic acid, *m*-mercaptobenzoic acid, and solvents were commercially available and were used without further purification. The melting points were obtained with a Kofler micro melting point apparatus and are uncorrected. Elemental analyses were performed with a PE-2400II apparatus. The FT-IR spectra were recorded on a Nicolet-460 spectrophotometer with use of KBr discs and sodium chloride optics. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Varian VXR 400S spectrometer operating at 400, 75.3, and 186.5 MHz, respectively. The ^{13}C spectra are broadband proton decoupled, and all the NMR chemical shifts are given in ppm in $CDCl_3$ solvent at room temperature (298 K) unless otherwise specified. Molecular weight measurements were carried out in benzene by the cryoscopic freezing point method.[25] The FAB-mass spectra were obtained with a Finnigan MAT 95 spectrometer, with the use of 3-nitrobenzylalcohol (3-NBA) as the matrix material. TGA was carried out with a Perkin–Elmer Pyris-1 instrument with a heating rate of 10 °C min^{-1} from 50 to 560 °C and with a 20.0 cm^3 min^{-1} nitrogen gas flow.

Preparations

$[Me_2Sn(o\text{-}SC_6H_4CO_2)]_6\cdot H_2O$} (1·H$_2$O): The reaction was carried out under nitrogen atmosphere by use of standard Schlenk techniques. The *o*-mercaptobenzoic acid (0.154 g, 1 mmol) was added to the solution of ethanol (95%, 40 mL) together with sodium ethoxide (0.136 g, 2 mmol), and the mixture was stirred for 10 min. Me_2SnCl_2 (0.220 g, 1 mmol) was then added to the mixture, and the reaction was allowed to continue for 12 h at 40 °C. After cooling down to room temperature, the solution was filtered. The solvent was gradually removed from the filtrate by evaporation under vacuum until solid product was obtained. The solid was then crystallized from the mother liquor. Colorless crystals were formed. Yield, 0.266 g, 88%. m.p. 208–210 °C (decomp); ^{1}H NMR ($CDCl_3$, D_2O):

$\delta = 7.78$–7.25 (m, 4H; Ar–H), 0.91 (s, 36H; CH_3) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 6.8$ (Sn*C*H$_3$), 125.7 (*C*5-Ar), 130.5 (*C*4-Ar), 131.4 (*C*1-Ar), 133.5 (*C*6-Ar), 136.5 (*C*3-Ar), 138.7 (*C*2-Ar), 172.9 (*C*OO) ppm; ^{119}Sn NMR ($CDCl_3$): $\delta = -224.6$ ppm; IR (KBr): $\tilde{\nu} = 1617$, 1545 (ν_{as}(COO)); 1398, 1331 (ν_s(COO)); 676 (ν(O-Sn-O)); 547 (ν(Sn–C)); 438 (ν(Sn–O)); 325 (ν(Sn–S)) cm^{-1}; FAB-MS (3-NBA): *m*/*z*: 1806 $[M-H_2O]^+$ (^{119}Sn); elemental analysis calcd (%) for $C_{54}H_{62}O_{13}S_6Sn_6$: C 35.56, H 3.43; found: C 35.58, H 3.45.

[*n*Bu$_2$Sn(*o*-SC$_6$H$_4$CO$_2$)]$_6$ (2): The preparation procedure was the same as used for **1**. *o*-Mercaptobenzoic acid (0.154 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol), and (nBu)$_2$SnCl$_2$ (0.304 g, 1 mmol), reaction time 12 h, temperature 40 °C. Recrystallized from ethyl ether; colorless crystal was formed. Yield, 0.331 g, 86 %. M.p. 205–206 °C; ^{1}H NMR ($CDCl_3$): $\delta =$ 7.78–7.25 (m, 4H; Ar–H), 1.77–1.41 (m, 72H; $CH_2CH_2CH_2$), 0.91–0.75 (t, 36H; CH_3) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 13.6$ (*C*H$_3$), 26.2 (γ*C*H$_2$), 26.6 (β*C*H$_2$), 27.8 (α*C*H$_2$), 126.2 (*C*5-Ar), 129.8 (*C*4-Ar), 131.5 (*C*1-Ar), 132.9 (*C*6-Ar), 136.9 (*C*3-Ar), 138.5 (*C*2-Ar), 171.5 (*C*OO) ppm; ^{119}Sn NMR ($CDCl_3$): $\delta = -225.8$ ppm; IR (KBr): $\tilde{\nu} = 1621$, 1538 ($\nu_{as}(CO_2)$); 1395, 1295 ($\nu_s(CO_2)$); 668 ν(O–Sn–O); 552 (ν(Sn–C)); 445 (ν(Sn–O)); 336 (ν(Sn–S)) cm^{-1}; FAB-MS (3-NBA): *m*/*z*: 2310 $[M]^+$ (^{119}Sn); elemental analysis calcd (%) for $C_{90}H_{132}O_{12}S_6Sn_6$: C 46.78, H 5.76; found: C 46.75, H 5.69.

{[Me$_2$Sn(*m*-O$_2$CC$_6$H$_4$S)MeSnMe(*m*-SC$_6$H$_4$CO$_2$)SnMe$_2$]O}$_2$ (3): The preparation procedure was the same as used for **1**. *m*-Mercaptobenzoic acid (0.154 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol), and Me_2SnCl_2 (0.220 g, 1 mmol), reaction time 12 h, temperature 40 °C. The solid was then crystallized from mother liquid; colorless crystals were formed. Yield, 0.314 g, 82 %. m.p. 218–220 °C; ^{1}H NMR ($CDCl_3$): $\delta = 7.66$–7.26 (m, 16H; Ar–H), 0.95 (s, 36H; CH_3) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 9.5$ (SnCH_3), 126.5 (*C*6-Ar), 129.2 (*C*5-Ar), 130.5 (*C*2-Ar), 131.8 (*C*1-Ar), 134.8 (*C*4-Ar), 138.4 (*C*3-Ar), 168.8 (CO_2) ppm; ^{119}Sn NMR ($CDCl_3$): $\delta =$ 70.6, −180.5, −228.1 ppm; IR (KBr): $\tilde{\nu} = 1626$, 1545 (ν_{as}(COO)); 1388, 1331 (ν_s(COO)); 645 (ν(O–Sn–O)); 547 (ν(Sn–C)); 485 (ν(Sn–O)); 318 (ν(Sn–S)) cm^{-1}; FAB-MS (3-NBA): *m*/*z*: 1534 $[M]^+$ (^{119}Sn); elemental analysis calcd (%) for $C_{40}H_{52}O_{10}S_4Sn_6$: C 31.33, H 3.42; found: C 31.29, H 3.45.

{[*n*Bu$_2$Sn(*m*-O$_2$CC$_6$H$_4$S)*n*BuSn*n*Bu(*m*-SC$_6$H$_4$CO$_2$)*n*Bu$_2$Sn]O}$_2$ (4): The preparation procedure was the same as used for **1**. *m*-Mercaptobenzoic acid (0.154 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol), and (nBu)$_2$SnCl$_2$ (0.304 g, 1 mmol), reaction time 12 h, temperature 40 °C. Recrystallized from ether/petroleum; colorless crystals were formed. Yield: 0.431 g, 85 %. m.p. 212–214 °C; ^{1}H NMR ($CDCl_3$): $\delta = 7.60$–7.15 (m, 16H; Ar–H), 1.82–1.31 (m, 72H; $CH_2CH_2CH_2$), 0.92 (t, 36H; CH_3) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 13.8$ (*C*H$_3$), 25.3 (γ*C*H$_2$), 26.5 (β*C*H$_2$), 27.1 (α*C*H$_2$), 126.3 (*C*6-Ar), 129.5 (*C*5-Ar), 130.7 (*C*2-Ar), 132.1 (*C*1-Ar), 133.6 (*C*4-Ar), 137.9 (*C*3-Ar), 169.3 (*C*O$_2$) ppm; ^{119}Sn NMR ($CDCl_3$): $\delta =$ 75.8, −185.2, −235.6 ppm; IR (KBr): $\tilde{\nu} = 1603$, 1540 (ν_{as}(COO)); 1409, 1356 (ν_s(COO)); 653 (ν(O–Sn–O)); 545 (ν(Sn–C)); 478 (ν(Sn–O)); 325 (ν(Sn–S)) cm^{-1}; FAB-MS (3-NBA): *m*/*z*: 2038 $[M]^+$ (^{119}Sn); elemental analysis calcd (%) for $C_{76}H_{124}O_{10}S_4Sn_6$: C 44.78, H 6.13; found: C 44.73, H 6.10.

X-ray crystallography: Crystals were mounted in Lindemann capillaries under nitrogen. All X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 298(2) K. Semiempirical absorption correction was applied to the data. The structure was solved by direct methods by use of SHELXS-97 and refined against F^2 by full-matrix, least squares with use of SHELXL-97. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions with use of a riding model. The molecular and supramolecular structures in this paper were created with the X-Seed software package.[26]

CCDC-254170, CCDC-271964, CCDC-238963, and CCDC-254167 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.

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