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A Supramolecular Assembly of Organotin Complexes: Syntheses, Characterization and Crystal Structures of Organotin Complexes with *meso*-2,3-Dimercaptosuccinic Acid

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A series of two types of organotin complexes, namely $[(R_3Sn)_4(dmsa)]$ (R = Ph **1**, $PhCH_2$ **2**, CH_3 **3**, *n*Bu **4**; H_4dmsa = *meso*-2,3-dimercaptosuccinic acid) and $[(R_2Sn)_2(dmsa)(Y)]\cdot L$ (R = Ph, Y = $2H_2O$, L = H_2O, Et_2O **5**; R = $PhCH_2$ **6**; R = CH_3 **7**; R = *n*Bu **8**; R = *n*Bu, Y = 0.5MeOH **9**) have been synthesized. All complexes were characterized by elemental analysis and FT-IR and NMR (^1H, ^{13}C and ^{119}Sn) spectroscopy. Among them, the strucrtures of complexes **1**, **3**, **5**, and **9** were also determined by X-ray crystallography. The structural analyses show that complexes **1** and **3** are tetranuclear triorganotin monomers, complex **5** is a dinuclear diphenyltin monomer, and complex **9** is a 3D di-*n*-butyltin coordination polymer with a metal-organic framework structure. The supramolecular structure analyses reveal that the type of organic substituent attached to the tin atoms can apparently affect the supramolecular assembly: when the substituents attached to the tin atom are aromatic groups (**1** and **5**) the supramolecular structures are dominated by intermolecular π–π (C–H···π) weak interactions, whereas when the substituents attached to the tin atom are alkyl groups (**3** and **9**) the supramolecular structures are dominated by intermolecular Sn←X (X = S, O) coordination interactions.

Introduction

Recently, the design and self-assembly of metal compounds into one-, two-, or three-dimensional supramolecular architectures has been attracting considerable attention due to their potential applications and intriguing architectures.[1–9] Two main lines of study are adopted, based on the different nature and bonding energy of the interactions responsible for networking, namely (i) frameworks comprised of metal centers and di- or polydentate ligands connected through chemical (covalent or coordination) bonds, which have been widely studied in the crystal engineering of microelectronic, nonlinear optical, ferromagnetic, and catalytic materials,[2,3] (ii) networks derived by the assembly of mono- or polynuclear metal complexes through intermolecular weak interactions such as hydrogen bonds, π–π interactions, electrostatic interactions, and so on, where it has been found that these weak interactions play vital roles in highly efficient and specific biological reactions and are essential for molecular recognition and the self-organization of molecules in supramolecular chemistry.[4,5]

Both systems mentioned above have recently been widely investigated in the supramolecular chemistry of organometallic complexes[6–9] because the supramolecular structures of such complexes can be more rationally controlled by tailoring the type and number of organic substituents attached to the metal center. Among these complexes, organotin complexes are attracting more and more attention due to their wide industrial applications and antitumor activities,[10] as well as their interesting and varied supramolecular structures.[7–9] In our previous work, we have also reported several interesting supramolecular structures assembled from organotin complexes.[9] To continue our research in this area, we selected another interesting ligand – *meso*-2,3-dimercaptosuccinic acid (H_4dmsa). This ligand was chosen based on the following considerations: first, both the carboxy and thiol groups in this ligand can form strong covalent bonds with the organotin moiety, thus providing sufficient thermodynamic stability for them to be stable in the solid state, including toward corrosive substances such as oxygen and water; second, H_4dmsa is a polyfunctional chelate ligand with two carboxy and two thiol groups, so it has a rich coordination chemistry and can help to construct multidimensional coordination polymers by acting as a multidentate bridging linker; third, the conformational flexibility of this ligand will allow for the formation of various and interesting molecular and supramolecular structures; fourth, H_4dmsa can bond more than one organotin moiety in one discrete molecule, which will increase the opportunities for supramolecular assembly from these complexes through intermolecular weak interactions between substituents (such as π–π interactions); fifth,

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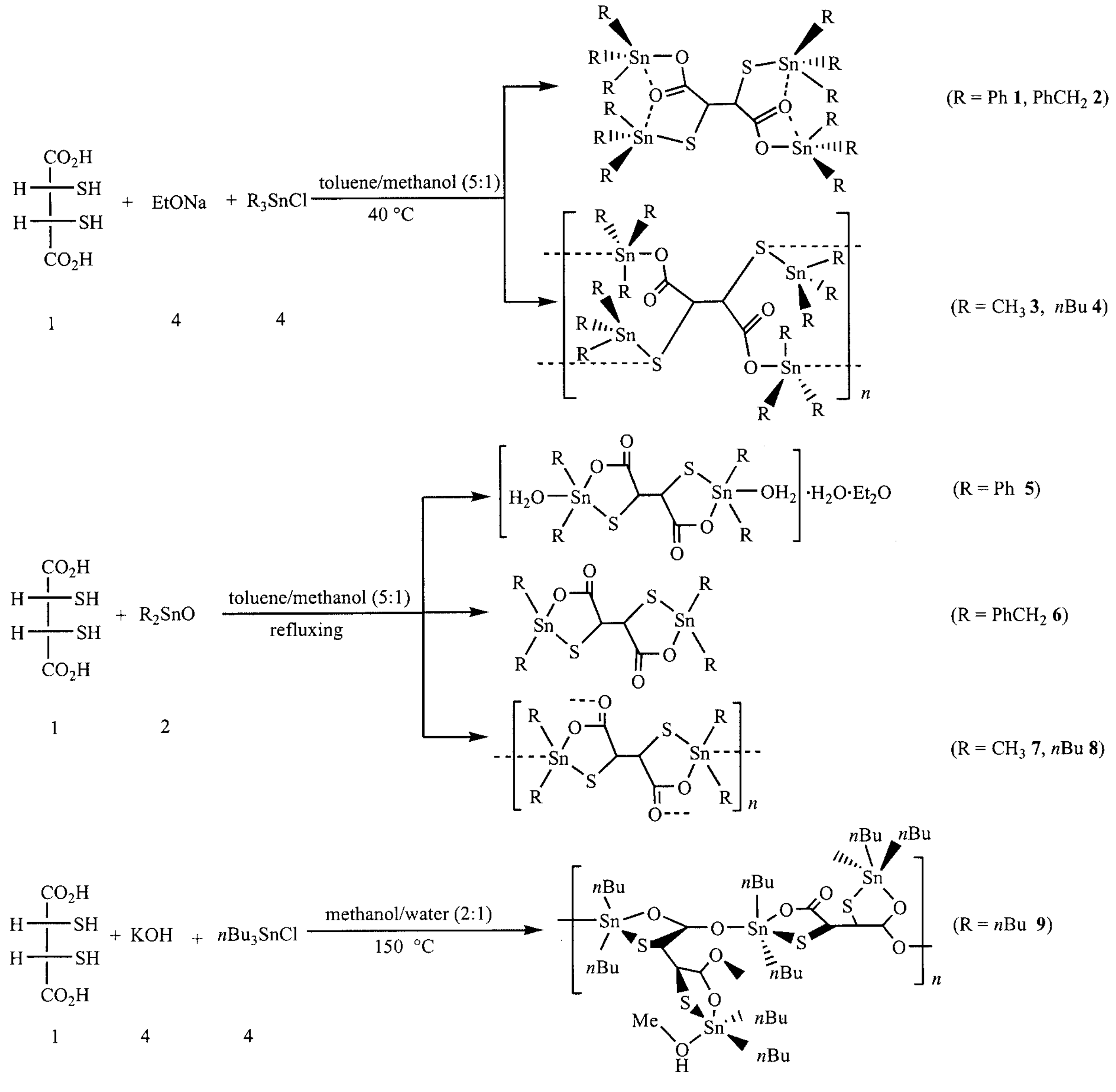
H_4dmsa is a simple linear ligand without a complicated inner structure, which makes it easy to analyze the electronic and steric influence of the organic substituents attached to the tin atom on the supramolecular structure. In addition, although H_4dmsa is a mercapto-containing, water-soluble, nontoxic, orally administered metal chelator that has been used as an antidote to heavy metal (lead, mercury, arsenic, and cadmium) toxicity for more than 50 years,[11] few metal complexes with this ligand have been determined by X-ray crystallography so far.[12] Recently, we began to treat H_4dmsa with organotin compounds with the hope of obtaining interesting supramolecular structures by assembly of this polyfunctional ligand with different organotin compounds. Here we report the detailed syntheses of eight new organotin complexes of *meso*-2,3-dimercaptosuccinic acid of two types: $[(R_3Sn)_4(dmsa)]$ (R = Ph **1**, $PhCH_2$ **2**, CH_3 **3**, *n*Bu **4**) and $[(R_2Sn)_2(dmsa)(Y)]\cdot L$ (R = Ph Y = $2H_2O$ L = H_2O, Et_2O **5**; R = $PhCH_2$ **6**; R = CH_3 **7**; R = *n*Bu **8**; R = *n*Bu Y = 0.5MeOH **9**). All complexes were characterized by elemental analysis and FT-IR and NMR (^1H, ^{13}C, and ^{119}Sn) spectroscopy. The structures of complexes **1**, **3**, **5**, and **9** were also determined by X-ray crystallography.

Results and Discussion

Syntheses

Complexes **1**–**4** were obtained by reaction of H_4dmsa/EtONa/R_3SnCl in a 1:4:4 molar ratio in toluene/methanol (5:1) at 40 °C, while complexes **5**–**8** were obtained by reaction of H_4dmsa/R_2SnO in a 1:2 molar ratio in toluene/methanol (5:1) at reflux. Crystals of complex **9** were obtained by solvothermal reaction of H_4dmsa/KOH/R_3SnCl in a 1:4:4 molar ratio in methanol/water (2:1) at 150 °C. The synthetic procedures are shown in Scheme 1.



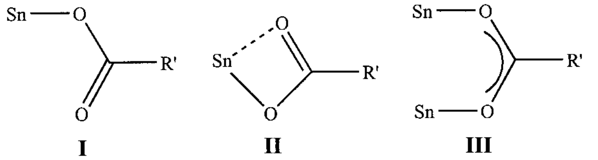
Scheme 1.

Spectroscopic Studies

IR

The main feature in the IR spectra of complexes **1**–**9** is the absence of bands in the region 3120–2980 and 2560–2410 cm^{-1}, which appear in the free ligand as CO_2H and SH stretching vibrations, thus indicating metal–ligand bonding through these sites. The typical absorptions for Sn–C, Sn–O, and Sn–S vibrations in complexes **1**–**9** are all located in the normal range of similar organotin complexes.[13,14]

IR spectroscopy can provide useful information concerning the coordination of the carboxyl groups in organotin carboxylates.[15,16] When the carboxylic group coordinates the tin atom in a monodentate manner (mode **I**), the difference between the wavenumbers of the asymmetric and symmetric carboxylic stretching bonds, $\Delta\tilde{\nu}$ [$\Delta\tilde{\nu} = \tilde{\nu}(\nu_{as}CO_2^-) - \tilde{\nu}(\nu_sCO_2^-)$], is larger than that observed for ionic complexes. When the ligand chelates (mode **II**), $\Delta\tilde{\nu}$ is considerably smaller than that for ionic complexes, while in the asymmetric bidentate coordination mode the value is in the range characteristic of monodentate coordination. The characteristic wavenumber difference for mode **III** is larger than that for chelating groups and nearly the same as that observed for ionic complexes (Scheme 2).



Scheme 2. Different coordination modes of the carboxylate group.

Based on the above results, it was possible to distinguish the coordination mode of the CO_2^- group. The magnitude of $\Delta\tilde{\nu}$ (about 242–268 cm^{-1}) for **1**–**6**, compared with that for the corresponding sodium salts, reveals that the carboxylate ligands are monodentate, while the value of about 200 cm^{-1} for **7**–**9** suggests a bidentate coordination mode. The conclusions drawn from the IR data are consistent with the X-ray crystallography study.

NMR

The ^{1}H NMR spectra show the expected integration and peak multiplicities. In the spectra of the free ligand, the resonances observed at $\delta \approx 10.50$ and 1.65 ppm, which are absent in the spectra of the complexes, indicate removal of the CO_2H and SH protons and formation of Sn–O and Sn–S bonds. This conclusion accords well with the IR data. Moreover, the ^{1}H NMR spectroscopic data show that the chemical shifts of the phenyl groups in complexes **1** and **5** (δ = 7.36–7.79 ppm), the methyl groups in complexes **3** and **7** (δ = 0.84–0.91 ppm), and the methylene groups connected directly to the tin atom in complexes **2**, **4**, **6**, **8**, and **9** (δ = 1.25–3.26 ppm) undergo an upfield shift relative to those of their precursors.

The ^{13}C NMR spectra of all compounds 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 metal atom. Although at least two different types of carboxy groups are present, only one single resonance is observed for the CO_2 group in the ^{13}C spectra. A possible reason for this is that either accidental magnetic equivalence of the carbonyl carbon atoms occurs or the separation between the sets of resonance is too small to be resolved.

The ^{119}Sn NMR spectroscopic data show two signals for complexes **1**–**4** (δ = –95.1, –125.5 ppm for **1**; δ = –93.5, –118.8 ppm for **2**; δ = –96.4, –121.6 ppm for **3**; δ = –98.2, –126.1 ppm for **4**) and both of them are in the normal range for four-coordinate tin complexes,[17] thus indicating the existence of two different coordination environments around the tin atoms for complexes **1**–**4** in solution, which is similar to that found in the complexes [$(Ph_3Sn)_2$(*p*-mpspa)] and [$(Ph_3Sn)_2$(cpa)].[18] The ^{119}Sn NMR spectroscopic data of complexes **5**–**8** (δ = –150.2, –165.8, –175.7, and –173.8 ppm for **5**–**8**, respectively) show signals in the normal range for five-coordinate tin complexes.[17] However, complex **9** shows two signals at δ = –126.8 and –170.5 ppm, which are in the range corresponding to the coordination number 5 (δ = –90 to –190 ppm),[17] thus it can reasonably be assumed that there are also two different coordination environments around the tin atoms of complex **9** in solution.

Crystal Structures

X-ray Crystallographic Study of 1 and 3

Crystals of **1** suitable for an X-ray crystallography study were grown from dichloromethane, while crystals of **3** were grown from diethyl ether. The most relevant crystallographic data for **1** and **3** are summarized in the Experimental Section. Selected bond lengths and bond angles for **1** and **3** are given in Tables 1 and 2, respectively.

Table 1. Selected bond lengths and angles for complex **1**.

Bond lengths [Å]			
Sn1–C3	2.122(5)	Sn1–C9	2.135(5)
Sn1–C15	2.114(4)	Sn1–S1	2.4373(13)
Sn1–O1	2.071(3)	Sn1–O2	2.838(3)
Sn2–C21	2.152(4)	Sn2–C27	2.154(5)
Sn2–C33	2.130(5)	Sn2–S1	2.4373(13)
Sn2–O2	2.849(3)	C1–O1	1.294(5)
C1–O2	1.224(5)	C2–S1	1.820(4)
Bond angles [°]			
C3–Sn1–C15	120.23(18)	C3–Sn1–O1	108.67(15)
C15–Sn1–O1	107.00(15)	C9–Sn1–O2	150.50(14)
C3–Sn1–C9	110.86(19)	C9–Sn1–C15	106.90(18)
C9–Sn1–O1	101.51(15)	C3–Sn1–O2	76.02(14)
C15–Sn1–O2	92.38(14)	O1–Sn2–O2	50.53(10)
C21–Sn2–C33	114.72(18)	C21–Sn2–S1	114.09(12)
C33–Sn2–S1	116.78(13)	C27–Sn2–O2	164.38(14)
C21–Sn2–O2	84.33(14)	C33–Sn2–O2	77.37(14)
S1–Sn2–O2	70.10(7)	C21–Sn2–C27	108.08(18)
C27–Sn2–C33	104.74(18)	C27–Sn2–S1	95.68(13)

A perspective view of the molecular structure of complex **1** is shown in Figure 1. Complex **1** is a tetranuclear tin moi-

Table 2. Selected bond lengths and angles for complex **3**.

Bond lengths [Å]			
Sn1–C3	2.100(6)	Sn1–C4	2.105(6)
Sn1–C5	2.114(6)	Sn1–O1	2.095(3)
Sn1–O2	3.092(3)	Sn2–C6	2.121(7)
Sn2–C7	2.130(6)	Sn2–C8	2.125(7)
Sn2–S1	2.4384(13)	Sn2–O2	3.164(4)
C1–O1	1.296(5)	C1–O2	1.212(5)
C2–S1	1.834(4)		
Bond angles [°]			
C3–Sn1–C4	121.6(3)	C3–Sn1–C5	117.4(3)
C4–Sn1–C5	115.1(3)	C3–Sn1–O1	100.3(2)
C4–Sn1–O1	101.01(18)	C5–Sn1–O1	92.84(19)
C6–Sn2–C7	116.0(3)	C6–Sn2–C8	109.8(3)
C7 –Sn2–C8	108.4(3)	C6–Sn2–S1	111.5(2)
C7–Sn2–S1	111.30(19)	C8–Sn2–S1	98.3(2)

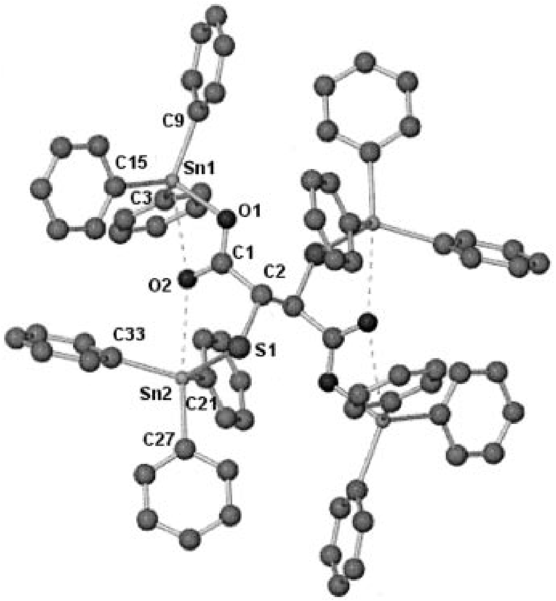


Figure 1. Molecular structure of complex **1** (all hydrogen atoms have been omitted for clarity).

ety containing two symmetrical $(Ph_3Sn)_2(SCHCO_2)$ moieties (inversion center: $-x+2$, $-y+1$, $-z$). Each tin atom in complex **1** forms four primary bonds: three from the phenyl C atoms and one from the O (for Sn1) or S (for Sn2) atom of the bridging ligand. The bond angles around the Sn1 and Sn2 atoms range from 101.51(15) to 120.23(18)° and from 95.68(13) to 116.78(13)°, respectively, suggesting apparent distortion from an ideal tetrahedron. The Sn1–O1 (2.071 Å) and Sn2–S1 [2.4373(13) Å] distances are in the normal range for Sn–O[19] and Sn–S[20] covalent bonds. There are also two weak intramolecular Sn···O interactions in complex **1** [Sn1–O2 = 2.838(3) and Sn2–O2 = 2.849(3) Å]. Although these distances are considerably longer than the normal Sn–O covalent bond, they lie in the range of Sn···O distances of 2.61–3.02 Å that have been confidently reported for intramolecular bonds.[21] As the oxygen atoms of the carboxylate groups in complex **1** are involved in weak coordination interactions with the tin atoms along one of the tetrahedral faces, the structural distortion for the tin atoms in **1** is best described as a capped tetrahedron.

Analysis of the supramolecular structure in the crystal lattice of **1** reveals that weak intermolecular C–H···π interactions 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-shaped) π–π interaction, and now is usually assigned to non-conventional weak hydrogen bonds.[5c,5g] Although this interaction is much weaker than covalent and coordinative interactions, and even than typical hydrogen bonds (such as O–H···O and N–H···O etc.), it clearly governs the supramolecular assembly in many compounds.[5g,22] In complex **1**, a series of parallel molecular chains connected by weak intermolecular C8–H8···Cg1 interactions (Cg1 is the centroid of the phenyl ring C9–C14) is found along the horizontal direction. Interestingly, these parallel molecular chains are further interlinked by weak intermolecular C6–H6···Cg2 interactions (Cg2 is the centroid of phenyl ring C27–C32) to form a 2D network structure in the defined plane (see Figure S1 in the Supporting Information). These C–H···π interactions in complex **1** (C8···Cg1 = 3.270, H8···Cg1 = 3.860 Å, C8–H8···Cg1 = 112.67°; C6···Cg2 = 3.752, H6···Cg2 = 2.867 Å, C6–H6···Cg2 = 159.41°) are close to those found in bis(*N*-pyridoxy-L-amino acidato)cobalt(III) complexes,[23] thereby suggesting they are strong enough to assemble these tetranuclear tin molecules into a 2D network in the solid state.

A perspective view of the molecular structure of **3** is shown in Figure 2. Complex **3** is also a tetranuclear tin moiety containing two symmetrical $(Me_3Sn)_2(SCHCO_2)$ moieties (inversion center: x, $1-y$, $-1/2+z$). The molecular structure of **3** is similar to that of **1**, so we will not deal with many structural details here. However, a comparison of the molecular conformations and configurations of complexes **1** and **3** should be noted: first, the two intramolecular Sn···O weak interactions (Sn1···O2 = 3.092, Sn2···O2 = 3.165 Å) in complex **3** are weaker than in **1** and are out of the range of typical intramolecular Sn–O bonds (2.61–3.02 Å).[21] Therefore, these distances are almost sufficient to make this oxygen atom stereochemically inactive around the two Sn atoms; second, the Sn2 atom in complex **3** displays a distorted tetrahedral coordination sphere, with six angles ranging from 98.3(2) to 116.0(3)°. The bond angles around Sn1 (from 92.84 to 121.6°) show a larger deviation from the ideal value for a tetrahedron (109.5°), thereby indicating that there may be intermolecular contacts around Sn1 in the crystal lattice (vide infra). Finally, all the Sn–C and covalent Sn–O and Sn–S bonds around each tin atom in complex **3** are unremarkable, as expected.

To our surprise, the common intermolecular C=O→Sn interactions that can give rise to either polymeric or cyclo-oligomeric structures in trimethyltin compounds[24] are not found in complex **3**. In fact, the supramolecular structure of complex **3** is a 2D network linked by weak intermolecular Sn←S coordination interactions. As shown in Figure 3, the asymmetric unit of complex **3** is linked by weak intermolecular Sn1···S1 coordination interactions along the

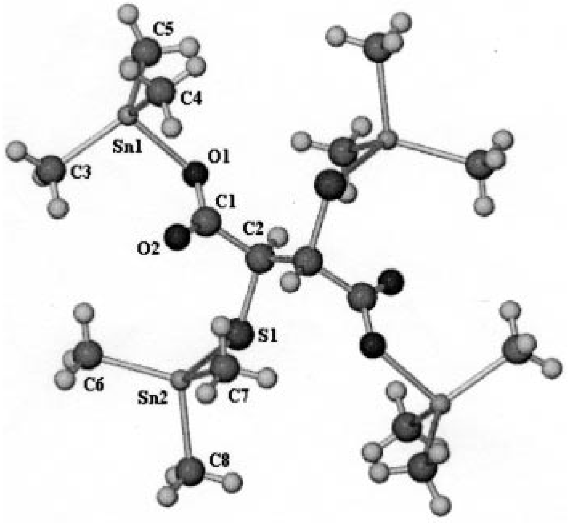


Figure 2. Molecular structure of complex **3**.

b and *c* axes to form a 2D layer with a 24-membered cavity in the *bc* plane. Although the loose cavities provided by these intermolecular Sn–S weak coordination interactions are large enough (7.525 × 11.265 Å) and are not completely filled by the methyl groups on the tin atoms that protrude into the interior, there are no solvent molecules in these cavities. This is not surprising in view of the fact that packing of such layers along the *a* axis produces a genuine no-cavity structure in the crystal lattice of complex **3** (see Figure S2 in the Supporting Information). Although the weak intermolecular Sn···S coordination distance in complex **3** is 3.286 Å, it still falls in the range proposed for secondary Sn···S coordination bonds (2.79–3.81 Å)[6] and is even close to the C=S···Sn distance [3.2274(8) Å] found in (5-mercapto-3-phenyl-1,3,4-thiadiazoline-2-thionato)trimethyltin.[25] If the weak Sn···S interaction is also considered, the coordination environment around the Sn1 atom in complex **3** can best be described as a distorted trigonal bipyramid.

X-ray Crystallographic Study of 5 and 9

Crystals of **5** suitable for an X-ray crystallography study were grown from dichloromethane/diethyl ether, while crystals of **9** were obtained from the mother liquor of the solvothermal reaction. The most relevant crystallographic data for **5** and **9** are summarized in the Experimental Section. Selected bond lengths and bond angles for **5** and **9** are given in Tables 3 and 4, respectively.

Table 3. Selected bond lengths and angles for complex **5**.

Bond lengths [Å]			
Sn1–C11	2.11(2)	Sn1–C5	2.13(2)
Sn1–O1	2.37(1)	Sn1–S1	2.416(4)
Sn1–O5	2.443(6)	Sn2–C23	2.130(9)
Sn2–C17	2.16(2)	Sn2–O3	2.36(1)
Sn2–O6	2.406(7)	Sn2–S2	2.413(4)
Bond angles [°]			
C5–Sn1–C11	121.7(7)	C11–Sn1–S1	118.4(6)
C5–Sn1–S1	116.8(5)	O1–Sn1–O5	167.2(3)
C17–Sn2–C23	118.7(6)	C23–Sn2–S2	122.2(3)
C17–Sn2–S2	116.5(6)	O3–Sn2–O6	167.3(3)

A perspective view of the molecular structure of **5** is shown in Figure 4. The [$(Ph_2Sn)_2(dmsa)\cdot 2H_2O$] asymmetric unit is a dinuclear tin moiety with two coordinated water molecules. The [$(Ph_2Sn)_2(dmsa)$] moiety contains two five-membered SnSCCO chelate metallacycles with an envelope

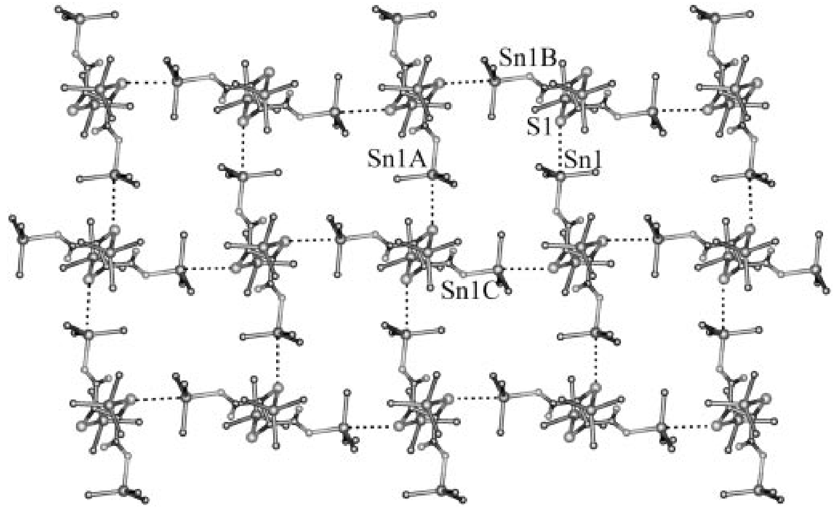


Figure 3. Supramolecular structure of complex **3** showing the 2D network linked by intermolecular Sn1···S1 coordination interactions (dotted line).

Table 4. Selected bond lengths and angles for complex **9**.[a]

Bond lengths [Å]			
Sn1–C9	2.125(18)	Sn1–C13	2.12(2)
Sn1–O1	2.156(13)	Sn1–O9	2.264(15)
Sn1–S1	2.394(5)	Sn2–C17	2.104(182)
Sn2–C21	2.08(2)	Sn2–O3	2.234(10)
Sn2–O8B	2.186(9)	Sn2–S2	2.408(4)
Sn3–C25	2.081(18)	Sn3–C29	2.138(19)
Sn3–O5	2.183(10)	Sn3–O4	2.259(9)
Sn3–S3	2.389(4)	Sn4–C33	2.09(2)
Sn4–C37	2.138(18)	Sn4–O2A	2.239(11)
Sn4–O7	2.241(9)	Sn4–S4	2.402(4)
Bond angles [°]			
C9–Sn1–C13	125.0(10)	C9–Sn1–S1	119.5(6)
C13–Sn1–S1	115.2(8)	O1–Sn1–O9	167.3(5)
C17–Sn2–C21	125.4(8)	C17–Sn2–S2	114.5(6)
C21–Sn2–S2	119.2(5)	O3–Sn2–O8A	164.4(4)
C25–Sn3–C29	123.5(9)	C25–Sn3–S3	119.3(6)
C29–Sn3–S3	117.0(7)	O4–Sn3–O5	162.5(4)
C33–Sn4–C37	118.1(9)	C33–Sn4–S4	114.4(7)
C37–Sn4–S4	127.4(6)	O7–Sn4–O2B	163.6(4)

[a] Symmetry codes: A: $x-1/2$, $-y+1/2$, $z-1/2$; B: x, $-y$, $z+1/2$.

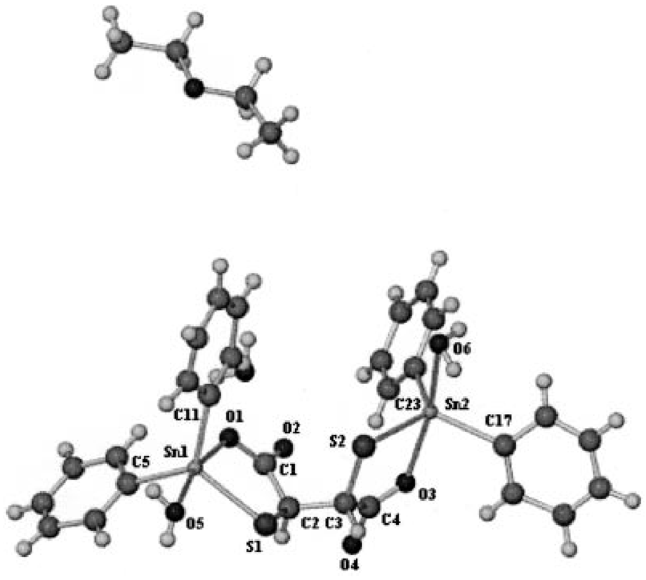


Figure 4. Molecular structure of complex **5**.

conformation, which is similar to the anion of the diorganotin carboxylate $[(n\mathrm{Pr})_3\mathrm{NH}][\mathrm{Me_2Sn}(\mu^2\text{-}\mathrm{SCH_2COO})\mathrm{Cl}]$.[26] Each tin atom in complex **5** is a five-coordinate trigonal bipyramid, with two phenyl groups and the sulfur atom of dmsa occupying the equatorial plane and one of the carboxyl oxygen atoms (O1 or O3) and one coordinated water molecule (O5 or O6) in axial positions. Because there is a strong (O,S) chelate effect (O1–Sn1–S1 = 78.64°, O3–Sn2–S2 = 78.75°), the corresponding axial–Sn–axial angles (167.20° for Sn1 and 167.24° for Sn2) and equatorial angles (116.80°, 118.40°, 121.69° for Sn1 and 116.51°, 118.67°, 122.15° for Sn2) suggest the geometries of both tin atoms in complex **5** are distorted trigonal pyramids. The two coordinative Sn–OH_2 bonds (Sn1–O5 = 2.443, Sn2–O6 = 2.406 Å) are slightly longer than the corresponding covalent Sn–O bonds (Sn1–O1 = 2.367, Sn2–O2 = 2.360 Å) and are in the range of known Sn–OH_2 bonds [2.14(3)–2.47(2) Å].[27] Both Sn–O (Sn1–O1 = 2.367, Sn2–O2 = 2.360 Å) and Sn–S (Sn1–S1 = 2.415, Sn2–S3 = 2.413 Å) bond lengths are close to those found in diorganotin carboxylates and thiolates.[9a] In addition, there are co-crystallized water and diethyl ether molecules in complex **5**.

The supramolecular structure of complex **5** is dominated by a 1D helical molecular chain along the *c* axis linked by intermolecular C–H···π (C3–H3···Cg3, Cg3 is the centroid of phenyl C5–C10) weak hydrogen-bonding interactions (see Figure S3 in the Supporting Information); the pitch of this helix (13.337 Å) is longer than that found in $(\mathrm{Ph_3Sn})_2(\mathrm{SC_6H_4CO_2})$ (9.991 Å).[20b] The corresponding C3···Cg3, H3···Cg3, and C3–H3···Cg3 values (3.866 Å, 3.019 Å, and 145.31°) in complex **5** are close to the C–H···π values in the CH_4/C_6H_6 system[5g] but larger than that found in complex **1**, which is in good agreement with theoretical calculations that predict that C–H···π interactions in aliphatic/aromatic systems are weaker than in aromatic/aromatic systems.[5g]

A perspective view of the molecular structure of **9** is shown in Figure 5; for clarity, the somewhat disordered β, γ and δ carbon atoms of the butyl groups have been omitted. The structure analysis for **9** reveals that it is a 3D metal-organic framework constructed by the S-shaped building block $[(n\mathrm{Bu_2Sn})_2(\mathrm{dmsa})]_2\cdot\mathrm{MeOH}$. The S-shaped asymmetric unit consists of two $[(n\mathrm{Bu_2Sn})_2(\mathrm{dmsa})]$ moieties and one coordinated MeOH molecule. Interestingly, every two five-membered SnSCCO chelate metallacycles in the asymmetric unit that are connected by the same dmsa ligand, such as pSn1 and pSn2, pSn3 and pSn4,[28] are not coplanar (dihedral angles between pSn1 and pSn2 and pSn3 and pSn4 are 71.51° and 60.69°, respectively), while pSn2, pSn3, and the bridging O4 atom are almost in the same plane (largest deviation: 0.071 Å; mean deviation: 0.035 Å). Each $[(n\mathrm{Bu_2Sn})_2(\mathrm{dmsa})]$ moiety in complex **9** also contains two five-membered SnSCCO chelate metallacycles, similar to those found in complex **5**. The coordination environment around each tin atom in complex **9** is also distorted trigonal-bipyramidal, with the equatorial positions occupied by two *n*-butyl groups and one thiol sulfur atom from the dmsa ligand and the axial positions shared by one coordinated oxygen atom from the dmsa ligand and an additional Lewis base, which may be a solvent molecule (for Sn1) or an intermolecular C=O→Sn bond (for Sn2, Sn3, and Sn4). The corresponding axial–Sn–axial skeletons are bent (ranging from 162.51° to 167.51°; av. 164.53°) due to the strong chelate effect of the O and S atoms (O–Sn–S chelate angles ranging from 80.31° to 82.68°; av. 81.36°), which is similar to that found in complex **5**. All the Sn–S and Sn–O distances lie in the range 2.389(4)–2.408(4) and 2.156(13)–2.259(9) Å, respectively, except for Sn1–O9, which is consistent with the situation reported in other organotin compounds.[9a,29] Moreover, the solvent-coordinated Sn–O bond (Sn1–O9) is only 2.264(15) Å, which is close to the corresponding covalent Sn–O bond [Sn1–O1 = 2.156(13) Å] formed with carboxylate groups (the difference between these two Sn–O bonds is only 0.108 Å) and shorter than that found in [$(Me_3Sn)(TMA)$]·2MeOH (2.462 and 2.586 Å),[9b] thus showing the strong coordinative interactions between guest methanol molecules and the host framework.

The supramolecular structure of complex **9** is a 3D metal-organic framework built by {[$(n\mathrm{Bu}_2\mathrm{Sn})_2(\mathrm{dmsa})]_2$·MeOH} units. As shown in Figure 6a, each {[$(n\mathrm{Bu}_2\mathrm{Sn})_2(\mathrm{dmsa})]_2$·MeOH} unit is linked by intermolecular C=O→Sn coordination interactions along the 110 and 0$\bar{1}$1 directions, thus forming a 2D layer with 53-membered organotin rings in the defined plane. Furthermore, these layers are linked to form a 3D framework along the 010 direction to give 56-membered rhombic channels (Figure 6b). The size of the 53-membered ring channel is 26.83 × 11.50 Å (transannular Sn4···Sn4′ and Sn2···Sn3), while the 56-membered ring rhombic channels are only 13.551 × 9.658 Å in size (transannular Sn4···Sn4′′ and Sn2′···Sn3′). The solvent methanol molecules reside in the 53-membered ring channels because they are strongly coordinated to the framework Sn1 atoms. A strong H-bonding interaction is also found between the methanol molecule and the framework oxygen atom O9 (O9···O6 = 2.525 Å). These coordinating and H-bonding interactions between the methanol molecules and the framework are believed to be responsible for the formation of the framework structure. It is worth mentioning here that, although the channels in this complex are ostensibly large enough to capture the guest methanol molecules, they constitute only 4.3 % of the crystal volume and are almost com-

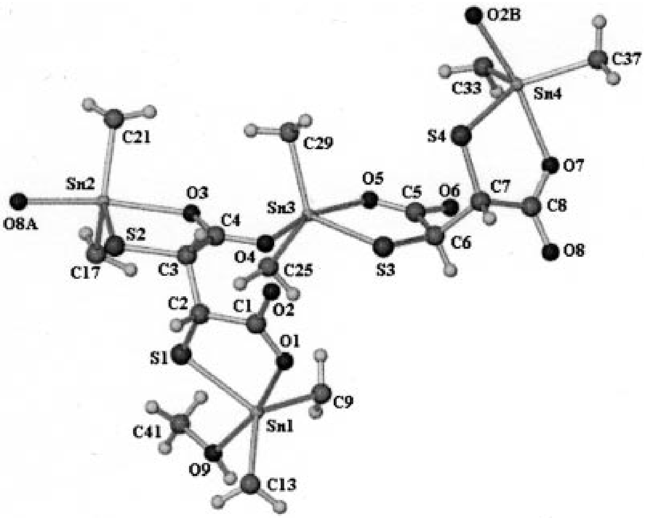


Figure 5. Molecular structure of complex **9** (the β, γ, and δ carbon atoms of the butyl groups on the tin atom have been omitted for clarity).

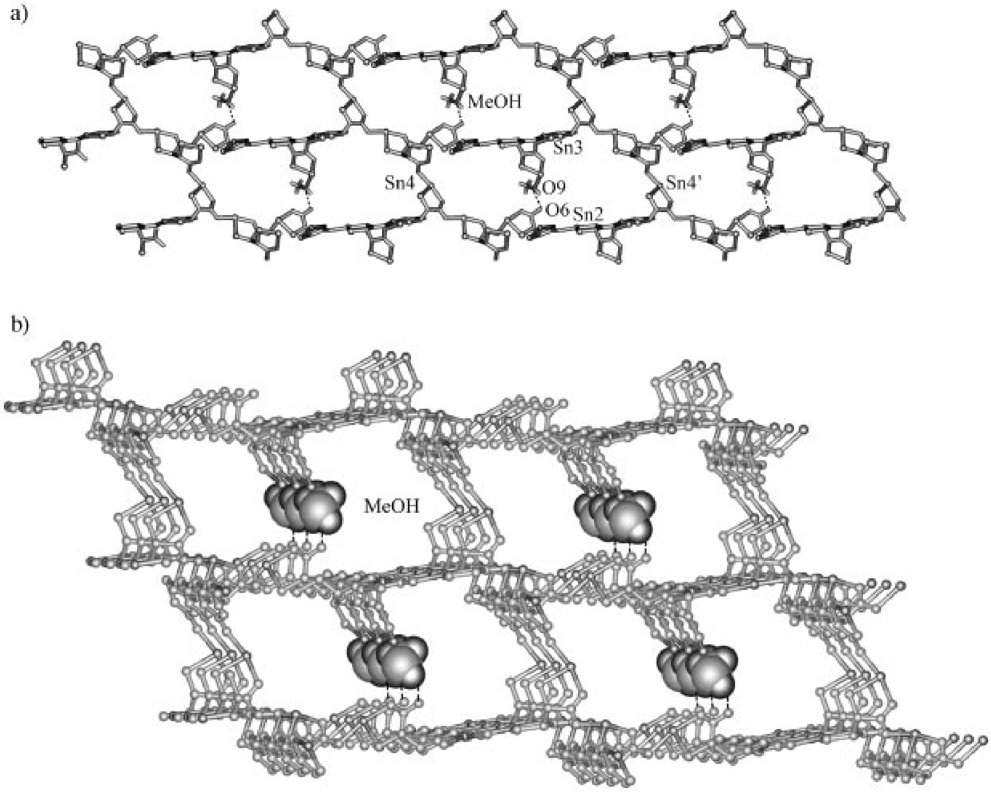


Figure 6. a) 2D "wall-like" layer and b) 3D metal-organic framework of complex **9**. The O–H···O hydrogen bonds between guest methanol molecules and the host organotin framework are shown with a broken line (the *n*-butyl groups on the tin atoms have been omitted for clarity).

pletely filled by the butyl groups on the tin atoms that protrude into the interior (if *n*Bu groups are omitted they constitute up to 69.7%; see Figure S4, Supporting Information).[30] This is apparently different to ionic complexes with a 3D open-framework structure, such as $[\{Mn(dcbp)\}\cdot 2H_2O]_n$ (dcbp = 4,4′-dicarboxylato-2,2′-bipyridine)[31] and $[Co(bix)_2(H_2O)_2](SO_4)\cdot 7H_2O$ [bix = 1,4-bis(imidazol-1-ylmethyl)benzene],[32] which all have a large pore aperture for guest molecules (18.2% and 27%, respectively) and show reversible "desorption-adsorption" processes.

The TGA of **9** shows a continuous weight loss (found: 2.7%) from 77 to 135 °C, which is attributed to the loss of guest methanol molecules (calcd. 2.5%); the host framework is stable up to 280 °C, at which point decomposition starts. However, during thermal treatment under vacuum the crystal lattice collapses at relatively low temperatures (< 100 °C). X-ray crystallography proved that the crystalline 3D framework is transformed into an amorphous material, which is similar to that found in the organotin complex $[\{(n\mathrm{Bu})_2Sn(2,5\text{-pdc})(H_2O)\}_3\cdot 3H_2O\cdot y\mathrm{EtOH}]_n$.[8a] To evaluate the porosity of this material, crystals of **1** were thermally treated for a period of 1 h (100 °C at 10 Torr) and then exposed to vapors of H_2O, EtOH, MeOH, and NH_3. In all cases no solvent molecules were found by elemental analysis or integration of the ^1H NMR spectrum in CD_3COCD_3, thus showing the irreversibility of the removal of the enclathrated guest molecule within the host framework. This is well in agreement with the crystal structure analysis.

Conclusions

In summary, a series of organotin complexes based on *meso*-2,3-dimercaptosuccinic acid have been synthesized. All complexes were characterized by elemental analysis and FT-IR and NMR (^1H, ^{13}C and ^{119}Sn) spectroscopy. The structures of complexes **1**, **3**, **5**, and **9** have also been determined by X-ray diffractomety. Both the spectra and crystal structures show that when *meso*-2,3-dimercaptosuccinic acid reacts with triorganotin compounds it can form tetranuclear monomers, whereas when it reacts with diorganotin compounds it can form dinuclear monomers or 3D polymers with a metal-organic framework structure.

The supramolecular structures described in this paper demonstrate that the type of substituent attached to the tin atom has an influence on the supramolecular arrangement: when the groups attached to the tin atom are aromatic groups (**1** and **5**), the supramolecular structures are dominated by intermolecular C–H···π weak interactions, whereas when the groups attached to the tin atom are alkyl groups (**3** and **9**), the supramolecular structures are dominated by intermolecular Sn←X (X = S, O) coordination interactions. In diorganotin complexes, it also shows that the number of solvent molecules coordinated to the tin atom is crucial for the supramolecular assembly. This contribution adds several new features to the fast developing field of supramolecular chemistry and aids the fundamental understanding of molecular recognition and systematic rationalization of molecular aggregation in crystal engineering of organometallic complexes.

Experimental Section

Materials and Measurements: Commercially available starting materials and solvents were used. Tribenzyltin chloride,[33]dimethyltin oxide, and dibenzyltin oxide[34]were prepared by standard methods reported in the literature. The melting points were obtained with a Kofler micro-melting point apparatus and are uncorrected. IR spectra were recorded with a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^1H, ^{13}C, and ^{119}Sn NMR spectra were recorded with a 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 NMR spectra were broadband-proton-decoupled. The chemical shifts are reported in ppm with respect to the references and are quoted relative to external tetramethylsilane (TMS) for ^1H and ^{13}C NMR, and to neat tetramethyltin for ^{119}Sn NMR spectroscopy. Elemental analyses were performed with a PE-2400II apparatus.

$[(Ph_3Sn)_4(dmsa)]$ (1): This reaction was carried out under nitrogen. *meso*-2,3-Dimercaptosuccnic acid (0.182 g, 1 mmol) and sodium ethoxide (0.272 g, 4 mmol) were added to a mixed solution of toluene and methanol (5:1) in a Schlenk flask and stirred for 0.5 h. After the addition of triphenyltin chloride (1.542 g, 4 mmol), the mixture was stirred at 40 °C for 12 h and then filtered. The solvent was gradually removed by evaporation under vacuum until a solid product was obtained. This solid was then recrystallized from dichloromethane to give colorless crystals of **1**. Yield: 1.294 g (82%). M.p. 212–214 °C. $C_{76}H_{62}O_4S_2Sn_4$ (1578.1): calcd. C 57.84, H 3.96, S 4.06; found C 57.75, H 4.05, S 4.00. IR (KBr): $\tilde{\nu}$ = 1594 cm^{-1} $\nu(COO)_{as}$, 1352 $\nu(COO)_s$, 560 ν(Sn–C), 447 ν(Sn–O), 320 ν(Sn–S). ^1H NMR ($CDCl_3$): δ = 4.25 (s, 2 H, CH), 7.46–7.79 (m, 60 H, C_6H_5) ppm. ^{13}C NMR ($CDCl_3$): δ = 53.1, 128.1, 129.3, 136.5, 148.6, 177.4 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –95.1, –125.5 ppm.

$[\{(PhCH_2)_3Sn\}_4(dmsa)]$ (2): Complex **2** was prepared in the same way as compound **1**, by adding tribenzyltin chloride (1.710 g, 4 mmol) to *meso*-2,3-dimercaptosuccinic acid (0.182 g, 1 mmol) and sodium ethoxide (0.272 g, 4 mmol). The solvent was gradually removed by evaporation under vacuum until a solid product was obtained. Yield: 1.484 g (85%). M.p. 200–202 °C. $C_{88}H_{86}O_4S_2Sn_4$ (1746.6): calcd. C 60.51, H 4.96, S 3.70; found C 60.55, H 5.00, S 3.75. IR (KBr): $\tilde{\nu}$ = 1595 cm^{-1} $\nu(COO)_{as}$, 1358 $\nu(COO)_s$, 575 ν(Sn–C), 438 ν(Sn–O), 335 ν(Sn–S). ^1H NMR ($CDCl_3$): δ = 3.24 (s, 24 H, CH_2), δ = 4.25 (s, 2 H, CH), 7.25–8.05 (m, 60 H, C_6H_5) ppm. ^{13}C NMR ($CDCl_3$): δ = 34.8, 54.2, 126.6, 128.7, 129.7, 134.2, 135.0, 176.3 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –93.5, –118.8 ppm.

$[(Me_3Sn)_4(dmsa)]$ (3): Complex **3** was prepared in the same way as compound **1**, by adding trimethyltin chloride (0.800 g, 4 mmol) to *meso*-2,3-dimercaptosuccinic acid (0.182 g, 1 mmol) and sodium ethoxide (0.272 g, 4 mmol). The solvent was gradually removed by evaporation under vacuum until a solid product had formed. The solid was then recrystallized from ethanol to give colorless crystals of **3**. Yield: 0.733 g (88%). M.p. 108–110 °C. $C_{16}H_{38}O_4S_2Sn_4$ (833.34): calcd. C 23.06, H 4.60, S 7.69; found C 23.10, H 4.65, S 7.65. IR (KBr): $\tilde{\nu}$ = 1598 cm^{-1} $\nu_{as}(COO)$, 1360 $\nu_s(COO)$, 583 ν(Sn–C), 476 ν(Sn–O), 357 ν(Sn–S). ^1H NMR ($CDCl_3$): δ = 0.84 (s, 36 H, CH_3), 4.25 (s, 2 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = –5.0, 2.5, 53.4, 175.5 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –96.4, –121.6 ppm.

$[(n\mathrm{Bu}_3Sn)_4(dmsa)]$ (4): Complex **4** was prepared in the same way as compound **1**, by adding tri-*n*-butyltin chloride (1.302 g, 4 mmol) to *meso*-2,3-dimercaptosuccinic acid (0.182 g, 1 mmol) and sodium ethoxide (0.272 g, 4 mmol). The solvent was gradually removed by evaporation under vacuum until a solid product was obtained. Yield: 1.137 g (85%). M.p. 152–154 °C. $C_{52}H_{110}O_4S_2Sn_4$ (1338.4): calcd. C 46.70, H 8.25, S 4.75; found C 46.66, H 8.28, S 4.79. IR (KBr): $\tilde{\nu}$ = 1590 cm^{-1} ν_{as}(COO), 1358 ν_s(COO), 575 ν(Sn–C), 450 ν(Sn–O), 365 ν(Sn–S). ^{1}H NMR ($CDCl_3$): δ = 0.92 (t, $^3J_{H,H}$ = 7.2 Hz, 36 H, CH_3), 1.25–1.71 (m, 72 H, $CH_2CH_2CH_2$), 4.27 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.4, 25.8, 26.5, 27.0, 54.0, 177.2 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –98.2, –126.1 ppm.

[$(Ph_2Sn)_2$(dmsa)($2H_2O$)]·H_2O·Et_2O (5): A mixture of *meso*-2,3-dimercaptosuccinic acid (0.182 g, 1 mmol) and Ph_2SnO (0.580 g, 2 mmol) in toluene/methanol (5:1) was refluxed in a Dean–Stark trap for 10 h. After cooling to room temperature, the solvent was removed under vacuum to give **5** as a colorless solid. This solid was then recrystallized from diethyl ether to give colorless crystals of **5**. Yield: 0.732 g (86%). M.p. > 300°C (dec.). $C_{32}H_{38}O_8S_2Sn_2$ (852.1): calcd. C 45.10, H 4.50, S 7.55; found C 45.08, H 4.45, S 7.60. IR (KBr): $\tilde{\nu}$ = 1585 cm^{-1} ν_{as}(COO), 1352 ν_s(COO), 558 ν(Sn–C), 460 ν(Sn–O), 375 ν(Sn–S). ^{1}H NMR ($CDCl_3$): δ = 7.68–7.36 (m, 20 H, C_6H_5), 4.26 (s, 2 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 51.8, 128.4, 128.8, 131.5, 150.8, 176.5 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –150.2 ppm.

[$\{(PhCH_2)_2Sn\}_2$(dmsa)] (6): Complex **6** was prepared in the same way as complex **5**, by refluxing $(PhCH_2)_2SnO$ (0.634 g, 2 mmol) and *meso*-2,3-dimercaptosuccinic acid (0.182 g, 1 mmol). After cooling to room temperature, the solvent was removed under vacuum to give **6** as a colorless solid. Yield: 0.647 g (83%). M.p. 205–207 °C. $C_{32}H_{30}O_4S_2Sn_2$ (780.13): calcd. C 49.27, H 3.88, S 8.22; found C 49.30, H 3.85, S 8.20. IR (KBr): $\tilde{\nu}$ = 1578 cm^{-1} ν_{as}(COO), 1310 ν_s(COO), 552 ν(Sn–C), 460 ν(Sn–O), 336 ν(Sn–S). ^{1}H NMR ($CDCl_3$): δ = 3.26 (s, 8 H, CH_2), 4.27 (s, 2 H, CH), 7.24–7.58 (m, 20 H, C_6H_5) ppm. ^{13}C NMR ($CDCl_3$): δ = 56.3, 125.8, 128.7, 129.3, 143.7, 177.1 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –165.8 ppm.

[$(Me_2Sn)_2$(dmsa)] (7): Complex **7** was prepared in the same way as complex **5**, by refluxing Me_2SnO (0.330 g, 2 mmol) and *meso*-2,3-dimercaptosuccinic acid (0.182 g, 1 mmol). After cooling to room temperature, the solvent was removed under vacuum to give **7** as a colorless solid. Yield: 0.418 g (88%). M.p. 221–223 °C. $C_8H_{14}O_4S_2Sn_2$ (475.74): calcd. C 20.20, H 2.97, S 13.48; found C 20.25, H 3.00 S 13.55. IR (KBr): $\tilde{\nu}$ = 1635 cm^{-1} ν_{as}(COO), 1326 ν_s(COO), 543 ν(Sn–C), 480 ν(Sn–O), 345 ν(Sn–S). ^{1}H NMR ($CDCl_3$): δ = 0.91 (s, 12 H), 4.27 (s, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = –0.6, 54.8, 177.5 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –175.7 ppm.

[$(n\mathrm{Bu})_2Sn]_2$(dmsa) (8): Complex **8** was prepared in the same way as complex **5**, by refluxing $(n\mathrm{Bu})_2SnO$ (0.498 g, 2 mmol) and *meso*-2,3-dimercaptosuccinic acid (0.182 g, 1 mmol). After cooling to room temperature, the solvent was removed under vacuum to give **8** as a colorless product. Yield: 0.515 g (80%). M.p. 310–312 °C. $C_{20}H_{38}O_4S_2Sn_2$ (644.1): calcd. C 37.30, H 5.95, S 9.96; found C 37.32, H 5.80, S 10.00. IR (KBr): $\tilde{\nu}$ = 1632 cm^{-1} ν_{as}(COO), 1330 ν_s(COO), 558 ν(Sn–C), 464 ν(Sn–O), 328 ν(Sn–S). ^{1}H NMR ($CDCl_3$): δ = 0.80–0.93 (t, $^3J_{H,H}$ = 6.8 Hz, 12 H, CH_3), 1.35–1.82 (m, 24 H, $CH_2CH_2CH_2$), 4.22 (s, 2 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.5, 25.8, 26.3, 27.5, 52.0, 175.4 ppm. ^{119}Sn NMR ($CDCl_3$): δ = –173.8 ppm.

$\{[(n\mathrm{Bu})_2Sn]_4(\mathrm{dmsa})_2(\mathrm{MeOH})\}_n$ (9): A mixture of *meso*-2,3-dimercaptosuccinic acid (0.091 g, 0.5 mmol), KOH (0.112 g, 2 mmol), tri-*n*-butyltin chloride (0.651 g, 2 mmol), CH_3OH (10 mL) and H_2O (5 mL) was heated in a Teflon-lined autoclave at 150 °C for 3 d. After cooling to room temperature, colorless crystals of **9** were collected and washed with hexane. Yield: 0.280 g (85%). M.p. 298°C (dec.). $C_{41}H_{81}O_9S_4Sn_4$ (1320.5): calcd. C 37.30, H 6.11, S 9.72; found C 37.25, H 6.20, S 9.70. IR (KBr): $\tilde{\nu}$ = 3195 cm^{-1} ν_{as}(OH), 1625, 1555 ν_{as}(COO), 1532, 1326 ν_s(COO), 556 ν(Sn–C) 470 ν(Sn–O), 330 ν(Sn–S). ^{1}H NMR (CD_3COCD_3, D_2O): δ = 0.82–0.96 (t, $^3J_{H,H}$ = 7.0 Hz, 24 H, CH_3), 1.33–1.85 (m, 48 H, $CH_2CH_2CH_2$), 4.25 (s, 4 H, CH) ppm. ^{13}C NMR (CD_3COCD_3): δ = 13.8, 25.5, 26.2, 27.1, 52.4, 176.8 ppm. ^{119}Sn NMR (CD_3COCD_3): δ = –126.8, –170.5 ppm.

X-ray Crystallography: Crystals were mounted in Lindemann capillaries under nitrogen. All X-ray crystallographic data were collected with a Bruker SMART CCD 1000 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 298(2) K. A

Table 5. Crystallographic data for complexes **1**, **3**, **5**, and **9**.

Complexes	1	3	5	9
Empirical formula	$C_{76}H_{62}O_4S_2Sn_4$	$C_{16}H_{38}O_4S_2Sn_4$	$C_{32}H_{38}O_8S_2Sn_2$	$C_{41}H_{80}O_9S_4Sn_4$
Formula mass	1578.14	833.34	852.12	1320.05
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$	$Pna2(1)$	Cc
a [Å]	11.027(2)	18.556(3)	9.431(2)	23.733(9)
b [Å]	12.329(3)	13.3144(14)	37.063(10)	13.087(5)
c [Å]	12.733(3)	13.0162(14)	13.337(4)	18.598(7)
α [°]	80.690(3)	90	90	90
β [°]	86.406(3)	105.2910(15)	90	102.383(6)
γ [°]	77.944(3)	90	90	90
Volume [Å^3]	1669.7(6)	3103.7(7)	4662(2)	5642(4)
Z	1	4	4	4
Absorption coefficient [mm^{-1}]	1.590	3.330	1.196	1.941
Crystal size [mm]	0.42×0.35×0.19	0.51×0.43×0.17	0.31×0.27×0.12	0.19×0.15×0.12
$D_{\mathrm{calcd.}}$ [g cm^{-3}]	1.569	1.809	1.214	1.554
θ range for data collection [°]	1.62–25.03	1.91–25.03	2.23–25.01	1.76–25.03
Reflections collected	8855	7895	23091	14550
Unique reflections	5842 (R_{int} = 0.0196)	2742 (R_{int} = 0.0306)	8071 (R_{int} = 0.0794)	7029 (R_{int} = 0.0553)
Data/restraints/parameters	5842/0/338	2742/0/118	8071/610/394	7029/141/516
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0326, wR_2 = 0.0733	R_1 = 0.0286, wR_2 = 0.0669	R_1 = 0.0882, wR_2 = 0.2255	R_1 = 0.0525, wR_2 = 0.1159
R indices (all data)	R_1 = 0.0560, wR_2 = 0.0886	R_1 = 0.0416, wR_2 = 0.0768	R_1 = 0.1448, wR_2 = 0.2683	R_1 = 0.1007, wR_2 = 0.1408

semiempirical 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. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions using a riding model. Crystal data and experimental details of the structure determinations are listed in Table 5. The molecular and supramolecular structures in this paper were created with the X-Seed software package.[35] CCDC-238964 (**1**), -254168 (**3**), -254166 (**5**), and -254171 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Supromolecular structures of complexes **1**, **3**, **5**, and **9** (Figures S1–S4).

Acknowledgments

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