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Self-Assembly of Triorganotin Complexes: Syntheses, Characterization, and Crystal Structures of Dinuclear, 1D Polymeric Chain, and 2D Network Polymers Containing Chiral (+)-(1*R*,3*S*)-Camphoric Acid and *meso*-*cis*-4-Cyclohexene-1,2-dicarboxylic Acid Ligands

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Eight new chiral triorganotin(IV) complexes, $(R_3Sn)_2[C_8H_{14}(COO)_2]$ (R = C_6H_5: **1**; $PhCH_2$: **2**), $\{(R_3Sn)_2[C_8H_{14}(COO)_2]\}_n$ (R = *n*Bu: **3**; Me: **4**), $(R_3Sn)_2[C_6H_8(COO)_2]$ (R = C_6H_5: **5**; $PhCH_2$: **6**), $\{(R_3Sn)[C_6H_8(COO)_2]\}_n$ (R = *n*Bu: **7**), and $\{(R_3Sn)_2[C_8H_{14}(COO)_2]\}_n$ (R = Me: **8**) have been synthesized by the reaction of (+)-(1*R*,3*S*)-camphoric acid and *meso-cis*-4-cyclohexene-1,2-dicarboxylic acid with triorganotin(IV) chloride in the presence of sodium ethoxide. All of the complexes were characterized by elemental analysis, FT-IR, NMR (^{1}H, ^{13}C and ^{119}Sn) spectroscopy, and TGA. Except for **2**, **5**, and **6**, all of the complexes were also characterized by X-ray crystallography. Complex **1** has a dinuclear structure, and complex **3** has a 1D zigzag chain structure and forms a 3D organotin framework through weak intermolecular O···Sn interactions. Complex **7** also has a 1D zigzag chain structure in which *meso-cis*-4-cyclohexene-1,2-dicarboxylic acid acts as a bidentate ligand coordinated to tri-*n*-butyltin(IV) ions. Complexes **4** and **8** have 2D network structures in which (+)-camphoric acid and *meso-cis*-4-cyclohexene-1,2-dicarboxylic acid act as tetradentate ligands coordinated to trimethyltin(IV) ions.

Introduction

Metal-directed self-assembly has 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] Among them, the self-assembly of organotin complexes is attracting more and more attention in view of their considerable structural diversity and topologies.[2] A multitude of structure types including monomers, dimers, tetramers, oligomeric ladders, and hexameric drums have been discovered.[3] In our previous work, through the self-assembly of organotin moieties with appropriate multifunctional ligands, we obtained numerous novel and interesting organotin complexes. For example, we reported several macrocycles, including a macrocycle containing five tin nuclei with heterocyclic sulfur and nitrogen donor ligands, a 48-membered macrocycle with eighteen tin nuclei and 2-mercaptonicotinic acid, as well as a macrocyclic complex with eight tin nuclei and 2-mercapto-4-methylthiazol-5-ylacetic acid.[4] Furthermore, we also reported some organotin carboxylates with trinuclear, 1D chain, and 2D network structures.[5]

Although considerable advances have been made in the development of the self-assembly of organotin complexes, only a relatively small number of chiral complexes of this type have been reported. Over recent years there has been increased interest in the self-assembly of chiral organotin complexes owing to their potential biocidal activities and cytotoxicities.[6] For example, Metzger et al. as well as Nanni and Curran prepared organotin complexes containing the C_2-symmetric binaphthyl moiety.[7] A series of organotin complexes containing the intramolecularly coordinating chiral 2-[(1*S*)-1-(dimethylamino)ethyl]phenyl ligand (L*) also displayed some enantioselectivity in free radical reductions.[8] During the last few years, some chiral organotin(IV) carboxylates have been prepared, and some structural types have been discovered.[9] To continue the work in this field, we selected the chiral dicarboxylic acid (+)-(1*R*,3*S*)-camphoric acid and the *meso-cis*-4-cyclohexene-1,2-dicarboxylic acid as bridging ligands, and succeeded in obtaining eight chiral triorganotin complexes. Herein we report the studies on the syntheses, characterizations, and crystal structures of these chiral triorganotin complexes.

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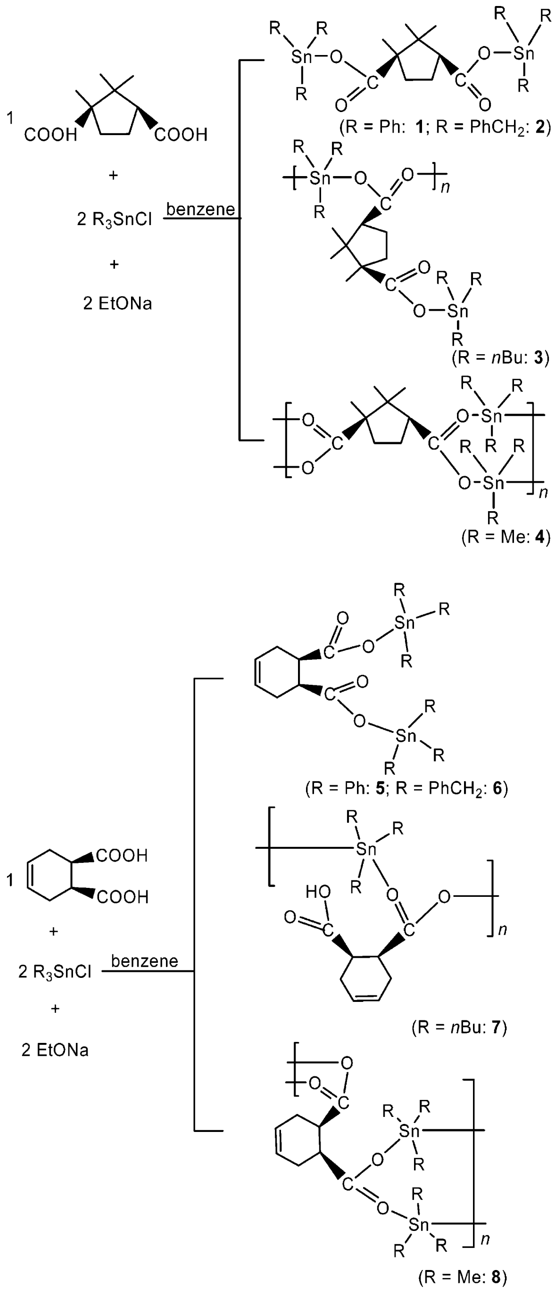
Results and Discussion

Syntheses

The reactions of (+)-(1*R*,3*S*)-camphoric acid or *meso-cis*-4-cyclohexene-1,2-dicarboxylic acid and sodium ethoxide with triorganotin(IV) chloride in a 1:2:2 stoichiometry afford the air-stable complexes **1**–**8**. The synthetic procedures are shown in Scheme 1.



Scheme 1.

Spectroscopic Studies

IR

The stretching frequencies of interest are those associated with the COO$^–$, Sn–C, and Sn–O groups. The strong absorption bands that appear at 437–458 cm^{-1} in the IR spectra of the complexes **1**–**8**, which are absent in the spectra of the free ligands, are assigned to the Sn–O stretching mode of vibration. Also, the strong absorption bands that appear at 1600–1686 and 1342–1466 cm^{-1} in these spectra are assigned to the asymmetric and symmetric vibrations of the COO$^–$ moiety, respectively. All of these values are consistent with those detected in a number of organotin(IV) derivatives.[10]

NMR

The ^{1}H NMR spectra show the expected integrations and peak multiplicities. The ^{13}C NMR spectra of all of the complexes show a significant downfield shift for all of the carbon resonances compared with those of the free ligands; this shift is a consequence of an electron-ensity transfer from the ligand to the acceptor. The single resonances at δ = 168.7–178.7 ppm are attributed to the COO$^–$ groups in complexes **1**–**8**. These data are consistent with the structures of **1**–**8**. The ^{119}Sn NMR spectra of the complexes show resonances between δ = –39.4 and –143.8 ppm. As reported in the literature,[11] δ values for ^{119}Sn NMR spectra in the –210 to –400, –90 to –190, and 200 to –60 ppm ranges have been associated with hexa-, penta-, and tetracoordinated tin centers, respectively. On this basis, we can conclude that complexes **1**, **2**, **5**, and **6** are typically tetracoordinate and that complexes **4**, **7**, and **8** are typically pentacoordinate. Complex **3** has two signals at δ = –118.5 and –39.4 ppm, which thus indicate the existence of two different coordination environments around the tin atoms for this complex. These coordination assignments are confirmed by the X-ray crystal structures of complexes **1**, **3**, **4**, **7**, and **8**.

Crystal Structures

X-ray Crystallographic Study of Complex 1

The molecular structure of complex **1** is illustrated in Figure 1, and selected bond lengths and bond angles are given in Table 1. As can be seen from Figure 1, complex **1** is a triphenyltin ester of (+)-(1*R*,3*S*)-camphoric acid possessing an unequivocal structure. Both tin atoms [Sn(1) and Sn(2)] have different environments. For Sn(2), there are four primary bonds to the central tin atom: three to the phenyl groups and one to the oxygen atom. The Sn(2)–O(3) bond length is 2.051(6) Å and approaches that which has been reported as the Sn–O covalent bond length (2.13 Å),[12] which proves that the O(3) atom is coordinated to the tin atom by a strong chemical bond. The Sn(2)···O(4) distance (2.805 Å) is considerably shorter than the sum of the van der Waals radii of the Sn and O atoms (3.68 Å),[12] but the oxygen atom is not involved in any intramolecular interactions with tin. Thus, the geometry of Sn(2) is best described as monocapped-tetrahedral. For Sn(1), there are five primary bonds to the central tin atom: three to the phenyl groups and two to the oxygen atoms. The Sn(1)–O(1) bond length is 2.063(6) Å, which is a little longer than

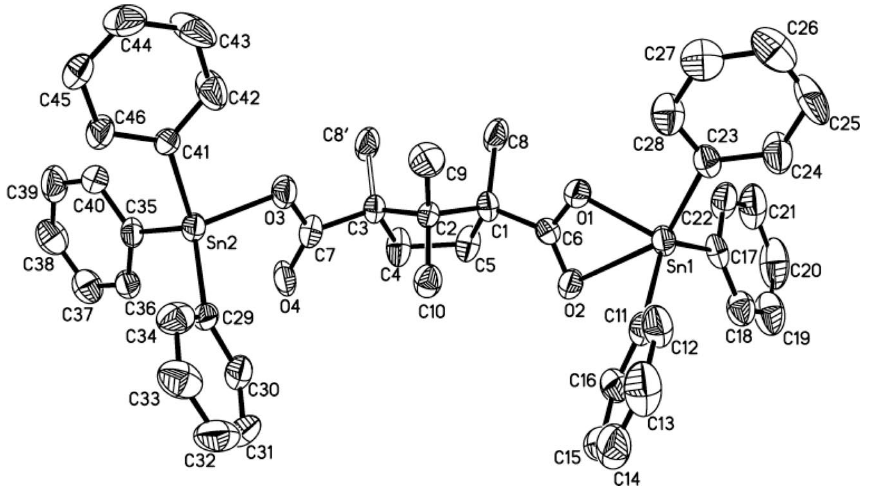


Figure 1. Molecular structure of complex **1**.

the Sn(2)–O(3) bond [2.051(6) Å] and approaches the Sn–O covalent bond length (2.13 Å); thus, it is also a strong chemical bond. The Sn(1)–O(2) bond length is 2.690(6) Å, which is longer than the Sn–O covalent bond length (2.13 Å) but considerably shorter than the sum of the van der Waals radii of the two atoms (3.68 Å).[12] Therefore, if the Sn(1)–O(2) interaction is included, the geometry at Sn(1) is a distorted *cis*-trigonal bipyramid with one of the phenyl carbon atoms [C(23)] and the O(2) atom in the axial sites. Another two phenyl carbon atoms [C(11) and C(17)] occupy the equatorial plane. Because it is part of a chelating carboxylate group, the O(1)–Sn(1)–O(2) angle is not 90° but 52.9(2)° and the C(23)–Sn(1)–O(2) angle is 150.5(3)°; this proves the distortion of the geometry.

Table 1. Selected bond lengths [Å] and angles [°] for complex **1**.

Sn(1)–O(1)	2.063(6)	Sn(2)–O(3)	2.051(6)
Sn(1)–O(2)	2.690(6)	Sn(2)–C(41)	2.108(7)
Sn(1)–C(17)	2.115(9)	Sn(2)–C(35)	2.128(9)
Sn(1)–C(23)	2.134(9)	Sn(2)–C(29)	2.145(9)
Sn(1)–C(11)	2.146(10)		
O(1)–Sn(1)–C(17)	106.9(3)	C(23)–Sn(1)–O(2)	150.5(3)
O(1)–Sn(1)–C(23)	97.6(3)	C(11)–Sn(1)–O(2)	85.9(3)
C(17)–Sn(1)–C(23)	110.5(3)	O(3)–Sn(2)–C(41)	94.3(3)
O(1)–Sn(1)–C(11)	110.2(3)	O(3)–Sn(2)–C(35)	111.6(3)
C(17)–Sn(1)–C(11)	120.0(4)	C(41)–Sn(2)–C(35)	109.8(3)
C(23)–Sn(1)–C(11)	109.3(4)	O(3)–Sn(2)–C(29)	109.2(3)
O(1)–Sn(1)–O(2)	52.9(2)	C(41)–Sn(2)–C(29)	110.9(3)
C(17)–Sn(1)–O(2)	80.7(3)	C(35)–Sn(2)–C(29)	118.4(3)

X-ray Crystallographic Study of Complexes 3 and 7

The repeating unit, 1D infinite zigzag chain, and 3D supermolecular structure of complex **3** are illustrated in Figures 2, 3, and 4, respectively; the repeating unit and 1D infinite zigzag chain of complex **7** are illustrated in Figures 5 and 6, respectively; selected bond lengths and bond angles for these complexes are given in Table 2. The geometries of all the tin atoms in complex **3** can be classified into two types: tetracoordinate [Sn(2)] and pentacoordinate [Sn(1)]. Each of the tetracoordinate tin atoms – Sn(2), for example – forms three short Sn–C bonds as part of the Sn–butyl groups and one Sn–O bond as part of the monodentate carboxylate groups; the geometry of the tin center displays a distorted tetrahedral coordination environment with six angles ranging from 95.2(7)° to 121.2(10)°. Furthermore, it is noteworthy that a weak intermolecular Sn···O interaction is recognized between the Sn(2) and O(4A) atoms [O(4A) is part of the adjacent monodentate carboxylate group]. The Sn(2)···O(4A) distance (2.953 Å) is considerably shorter

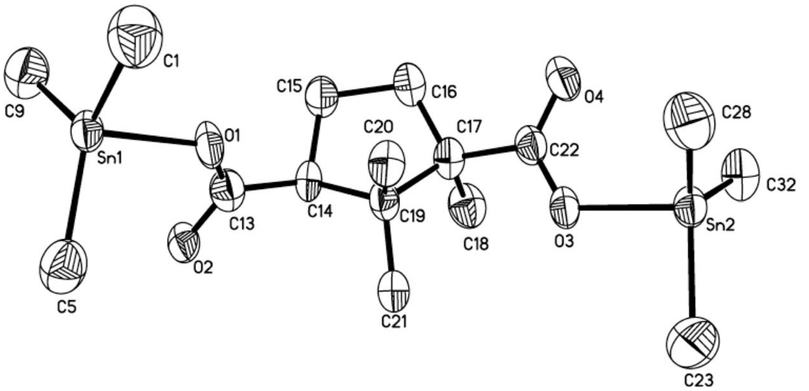


Figure 2. Repeating unit of complex **3** (the additional carbon atoms of the Sn–*n*-butyl groups are omitted for clarity).

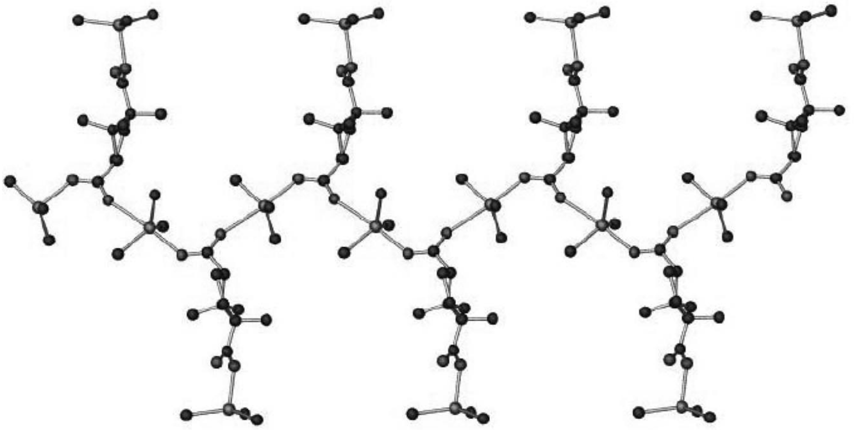


Figure 3. 1D polymeric chain of complex **3** (the additional carbon atoms of the Sn–*n*-butyl groups are omitted for clarity).

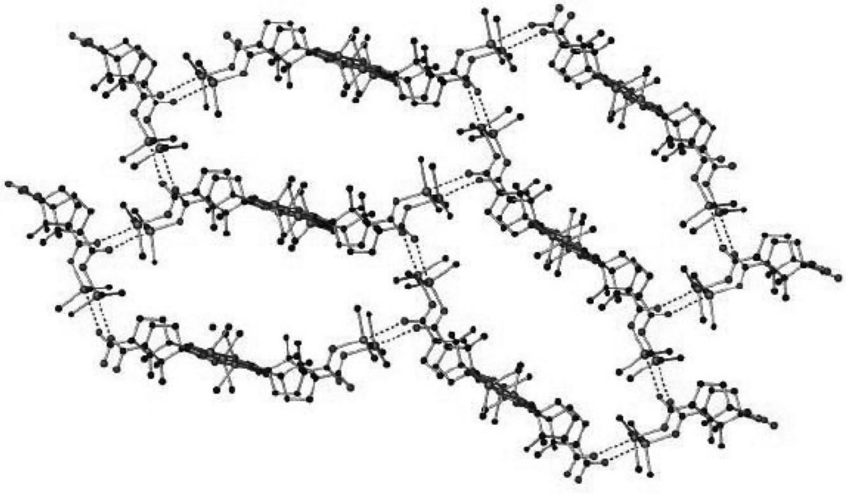


Figure 4. 3D metal framework of complex **3** made up of intermolecular weak Sn···O interactions.

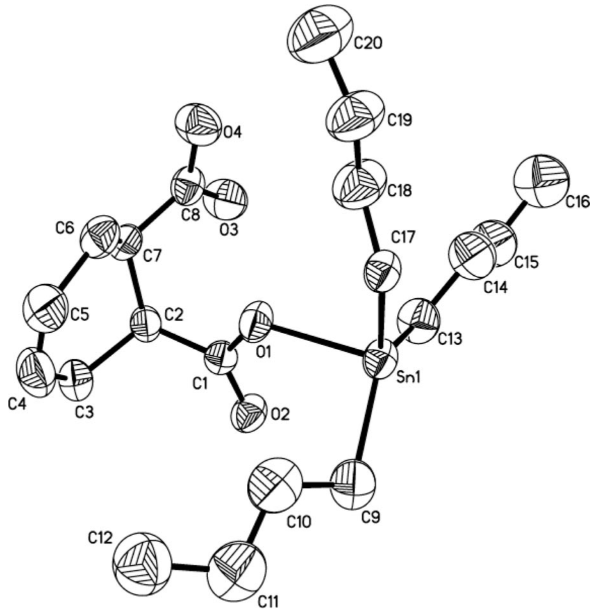


Figure 5. Repeating unit of complex **7**.

than the sum of the van der Waals radii of the Sn and O atoms (3.68 Å). Thus, if the weak Sn···O interaction is considered, the geometry of Sn(2) is best described as distorted trigonal-bipyramidal. The Sn–C bond lengths [2.07(2)–2.10(2) Å] are consistent with those reported in other triorganotin carboxylates.[13] The Sn(2)–O(3) distance [2.106(9) Å] is a little longer than the Sn–O distance reported in [$Ph_3Sn(O_2CC_6H_5)$][14] and approaches the sum of the covalent radii of Sn and O (2.13 Å) but is much shorter than the sum of the van der Waals radii of Sn and O (3.68). Each of the pentacoordinate tin atoms – Sn(1), for example – forms three short Sn–C bonds as part of the Sn–butyl groups and two Sn–O bonds as part of the carboxylate groups. Thus, the tin atom is at the center of a distorted trigonal bipyramid and is surrounded axially by two oxygen atoms and equatorially by three carbon atoms of the Sn–butyl groups. The angle formed by the axial ligands [O(1)–Sn(1)–O(2A)] is 173.3(3)°. Three Sn–butyl groups define the equatorial plane, and the sum of the trigonal C–Sn–C angles is 356.1°. The carboxylate ligand bridges two symmetry-related Sn atoms and gives rise to the unequal Sn–O bond lengths. This inequality is reflected in the C(13)–O

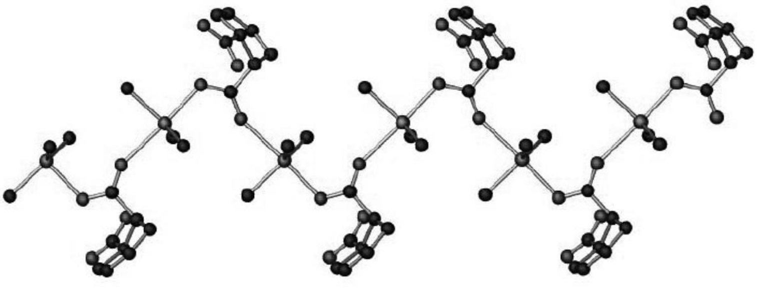


Figure 6. 1D polymeric chain of complex **7** (the additional carbon atoms of the Sn–*n*-butyl groups are omitted for clarity).

bond length, and the longer C(13)–O(1) length [1.24(2) Å] is associated with the shorter Sn(1)–O(1) length [2.144(9) Å], which is similar to other reported triorganotin polymeric structures.[15] The Sn(1)–O(2A) distance [2.512(9) Å] is longer than in other reported triorganotin complexes.[5b] All of this information indicates that the Sn(1)–O(2A) interaction is a coordinate bond.

Table 2. Selected bond lengths [Å] and angles [°] for complexes **3** and **7**.

Complex **3**			
Sn(1)–C(9)	2.08(2)	Sn(2)–C(28)	2.10(2)
Sn(1)–C(1)	2.11(2)	Sn(2)–C(32)	2.092(19)
Sn(1)–C(5)	2.14(2)	Sn(2)–O(3)	2.106(9)
Sn(1)–O(1)	2.144(9)	Sn(2)–C(23)	2.18(2)
Sn(1)–O(2A)	2.512(9)	O(2)–Sn(1B)	2.512(9)
C(9)–Sn(1)–C(1)	111.9(10)	C(5)–Sn(1)–O(2A)	84.8(6)
C(9)–Sn(1)–C(5)	122.5(9)	O(1)–Sn(1)–O(2A)	173.3(3)
C(1)–Sn(1)–C(5)	121.4(10)	C(28)–Sn(2)–C(32)	122.6(9)
C(9)–Sn(1)–O(1)	98.4(7)	C(28)–Sn(2)–O(3)	102.1(7)
C(1)–Sn(1)–O(1)	92.8(7)	C(32)–Sn(2)–O(3)	98.7(6)
C(5)–Sn(1)–O(1)	99.1(7)	C(28)–Sn(2)–C(23)	115.3(10)
C(9)–Sn(1)–O(2A)	84.0(7)	C(32)–Sn(2)–C(23)	116.8(11)
C(1)–Sn(1)–O(2A)	80.5(7)	O(3)–Sn(2)–C(23)	93.9(7)
Complex **7**			
Sn(1)–C(17)	2.133(8)	Sn(1)–O(1)	2.189(5)
Sn(1)–C(13)	2.134(9)	Sn(1)–O(2A)	2.479(6)
Sn(1)–C(9)	2.140(11)		
C(17)–Sn(1)–C(13)	119.9(4)	C(9)–Sn(1)–O(1)	97.1(3)
C(17)–Sn(1)–C(9)	112.1(4)	C(17)–Sn(1)–O(2A)	87.1(3)
C(13)–Sn(1)–C(9)	127.3(4)	C(13)–Sn(1)–O(2A)	87.8(3)
C(17)–Sn(1)–O(1)	89.4(3)	C(9)–Sn(1)–O(2A)	86.5(3)
C(13)–Sn(1)–O(1)	91.7(3)	O(1)–Sn(1)–O(2A)	175.7(2)

The intermolecular C=O→Sn coordination in complex **3** leads to 1D infinite zigzag chains containing the tin centers and carboxylate groups, which is consistent with another organotin(IV) complex that has been reported.[16] The 1D infinite zigzag chains are further interlinked to form a 3D metal framework with weak intermolecular Sn···O interactions (Figure 4).

In complex **7**, only one carboxylate group from *meso-cis*-4-cyclohexene-1,2-dicarboxylic acid coordinates to the tin atoms, and the other carboxylate groups do not coordinate to them; thus, *meso-cis*-4-cyclohexene-1,2-dicarboxylic acid acts as a bidentate ligand coordinated to tri-*n*-butyltin(IV) ions. Similarly to complex **3**, the geometry of the tin center is distorted trigonal-bipyramidal,and the center tin atom is pentacoordinate with the two O atoms [O(1) and O(2A)] occupying the axial sites. The angle defined by the axial ligands [O(1)–Sn(1)–O(2A)] is 175.7(2)°. Three Sn–butyl groups define the equatorial plane, and the sum of the trigonal C–Sn–C angles is 359°, which illustrates that the three methyl groups and the Sn atom are nearly coplanar. The carboxylate ligand bridges two symmetry-related Sn atoms and gives rise to the unequal Sn–O bond lengths. This inequality is reflected in the C(1)–O bond length, and the longer C(1)–O(1) bond [1.274(11) Å] is associated with that of the shorter Sn(1)–O(1) bond [2.189(5) Å], which is similar to other reported triorganotin polymeric structures.[5b,5c] The Sn(1)–O(2A) distance [2.479(6) Å] is shorter than the Sn(1)–O(2A) distance in complex **3** and a little longer than the sum of the covalent radii of the Sn and O atoms (2.13 Å). As shown in Figure 6, each deprotonated *meso-cis*-4-cyclohexene-1,2-dicarboxylic acid acts as a bidentate ligand by connecting two adjacent tin atoms to give rise to an infinite zigzag chain, which is consistent with the type of structure found in complex **3**.

X-ray Crystallographic Study of Complexes 4 and 8

The repeating unit and 2D network structure of complex **4** are illustrated in Figures 7 and 8, respectively; the repeating unit and 2D network structure of complex **8** are illustrated in Figures 9 and 10, respectively; selected bond lengths and bond angles for these complexes are given in Table 3. In complex **4**, the trimethyltin(IV) groups are linked by a carboxylate group of each deprotonated (+)-(1*R*,3*S*)-camphoric acid ligand, which, in turn, employs its two bidentate carboxylate groups to coordinate to four metal centers. Thus, four ligands are linked by four metal centers into a 32-membered macrocycle, which is further linked to eight nearest-neighbor tin centers by four independent deprotonated (+)-(1*R*,3*S*)-camphoric acid ligands to give rise to a 2D network with two types of cavities with widths of 10.836–12.552 and 7.318–7.373 Å. Similar cavities have been found within the polymeric crystal structure of microporous metal–organic frameworks formed between 1,3,5-benzenetricarboxylic acid and tin.[5d] In other related polymeric systems, so far only dimeric,[17] hexameric,[18] and chain-like[19] motifs have been reported.

In complex **4**, all of the tin atoms possess the same coordination environment. The coordination around the tin atom is only slightly distorted from the regular trigonal-

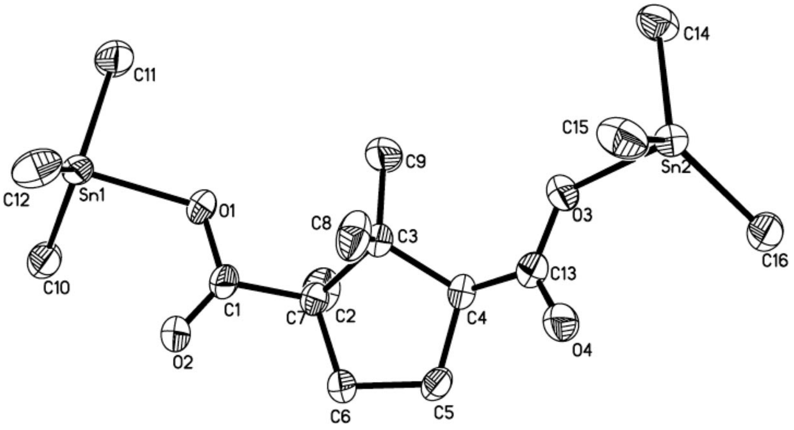


Figure 7. Repeating unit of complex **4**.

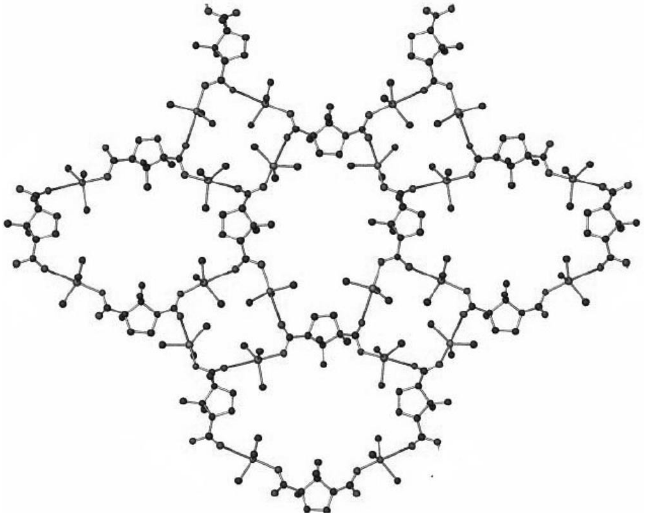


Figure 8. 2D network structure of complex **4**.

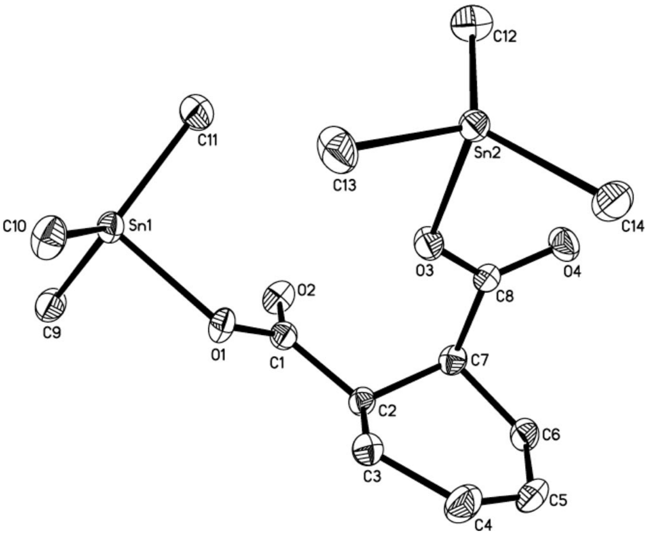


Figure 9. Repeating unit of complex **8**.

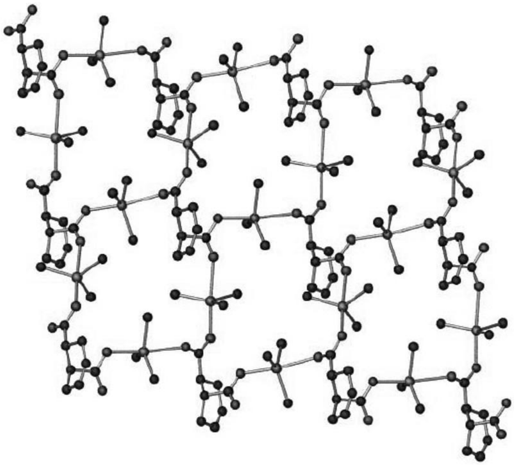


Figure 10. 2D network structure of complex **8**.

bipyramidal geometry. As a result of the bidentate mode of coordination of the deprotonated dicarboxylic acid, each Sn center is pentacoordinate and exhibits a trigonal-bipyramidal geometry with the coordinated O atoms occupying the axial sites. The Sn(1)–O(1) distance [2.098(6) Å] is a little shorter than that reported in $[Me_3Sn(O_2CC_4H_3S)]$ (2.149 Å).[20] The Sn(1)–O(4A) distance [2.682 Å] is close to the distance between a coordinated O atom and a central tin atom in other organotin complexes,[21] but is much shorter than the sum of the van der Waals radii of Sn and O (3.68 Å). The Sn(1)–O(1)–O(4A) angle of 178.22° indicates that these atoms are nearly arranged in a linear fashion. The sum of the angles subtended at the tin atom in the equatorial plane is 356.52° for Sn(1), so that the Sn(1), C(10), C(11), and C(12) atoms are almost in the same plane. The Sn–C distances [2.081(10)–2.135(10) Å] are equal within experimental error and close to the single-bond value for a trigonal-bipyramidal tin atom.[12]

Similarly to complex **4**, in complex **8** the trimethyltin(IV) groups are linked by a carboxylate group of each deprotonated *meso*-*cis*-4-cyclohexene-1,2-dicarboxylic acid ligand, which, in turn, employs its two bidentate carboxylate groups to coordinate to four metal centers. Thus, four li-

Table 3. Selected bond lengths [Å] and angles [°] for complexes **4** and **8**.

Complex **4**			
Sn(1)–C(12)	2.081(10)	Sn(2)–O(3)	2.098(6)
Sn(1)–O(1)	2.098(6)	Sn(2)–C(15)	2.122(10)
Sn(1)–C(10)	2.111(10)	Sn(2)–C(16)	2.127(9)
Sn(1)–C(11)	2.135(10)	Sn(2)–C(14)	2.134(9)
C(12)–Sn(1)–O(1)	99.6(4)	O(3)–Sn(2)–C(15)	101.1(4)
C(12)–Sn(1)–C(10)	122.9(5)	O(3)–Sn(2)–C(16)	96.8(3)
O(1)–Sn(1)–C(10)	97.2(3)	C(15)–Sn(2)–C(16)	123.8(4)
C(12)–Sn(1)–C(11)	117.5(5)	O(3)–Sn(2)–C(14)	90.6(3)
O(1)–Sn(1)–C(11)	91.5(4)	C(15)–Sn(2)–C(14)	116.4(4)
C(10)–Sn(1)–C(11)	116.0(5)	C(16)–Sn(2)–C(14)	116.2(4)
Complex **8**			
Sn(1)–C(9)	2.119(3)	Sn(2)–C(14)	2.120(4)
Sn(1)–C(11)	2.123(3)	Sn(2)–C(13)	2.125(3)
Sn(1)–O(1)	2.158(2)	Sn(2)–O(3)	2.152(2)
Sn(1)–O(4A)	2.534(2)	Sn(2)–O(2B)	2.520(2)
Sn(1)–C(10)	2.111(3)	Sn(2)–C(12)	2.113(3)
C(10)–Sn(1)–C(9)	116.97(15)	C(12)–Sn(2)–C(14)	125.01(16)
C(10)–Sn(1)–C(11)	114.45(16)	C(12)–Sn(2)–C(13)	120.60(16)
C(9)–Sn(1)–C(11)	126.32(16)	C(14)–Sn(2)–C(13)	113.41(17)
C(10)–Sn(1)–O(1)	91.81(11)	C(12)–Sn(2)–O(3)	94.43(12)
C(9)–Sn(1)–O(1)	96.18(11	C(14)–Sn(2)–O(3)	95.25(12)
C(11)–Sn(1)–O(1)	96.61(12)	C(13)–Sn(2)–O(3)	89.90(12)
C(10)–Sn(1)–O(4A)	83.57(11)	C(12)–Sn(2)–O(2B)	84.62(11)
C(9)–Sn(1)–O(4A)	85.91(11)	C(14)–Sn(2)–O(2B)	90.57(12)
C(11)–Sn(1)–O(4A)	85.39(12)	C(13)–Sn(2)–O(2B)	85.05(12)
O(1)–Sn(1)–O(4A)	175.38(8)	O(3)–Sn(2)–O(2B)	173.47(8)

gands are linked by four metal centers into a 22-membered macrocycle, which is further linked to eight nearest-neighbor tin centers by four independent deprotonated *meso*-*cis*-4-cyclohexene-1,2-dicarboxylic acid ligands to give rise to a 2D network with a cavity whose size can be evaluated by the Sn···Sn distances, which are 7.872–8.692 Å. Similar cavities have been found within the polymeric crystal structures of microporous metal–organic frameworks formed between 3,5-pyridinedicarboxylic acid and tin atoms.[5a]

All of the tin atoms in complex **8** possess the same coordination environment. The coordination around the tin atom is only slightly distorted from the regular trigonal-bipyramidal geometry. As a result of the bidentate mode of coordination of the deprotonated dicarboxylic acid, each Sn center is pentacoordinate and exists in a trigonal-bipyramidal geometry with the coordinated O atoms occupying the axial sites. The Sn–O distances [Sn(1)–O(1) 2.158(2), Sn(2)–O(2A) 2.520(2) Å] are similar to the distances between bonding O atoms and central Sn atoms in other organotin complexes[5a] but are much shorter than the sum of the van der Waals radii of Sn and O.[12] The O–Sn–O angles [O(1)–Sn(1)–O(4A) 175.38(8), O(3)–Sn(2)–O(2B) 173.47(8)°] indicate that these atoms are nearly in a linear arrangement.

TGA Studies

To study the stability of complexes **1**–**8**, thermogravimetric analysis (TGA) was performed in the 50–550 °C temperature range under N_2. The TGA shows that the decomposition temperatures of all of the complexes are between 150 and 350 °C, and these are all relatively high. In general, all of these organotin complexes exhibit good thermal stability.

Conclusions

A series of chiral triorganotin complexes based on the chiral (+)-(1*R*,3*S*)-camphoric acid and *meso*-*cis*-4-cyclohexene-1,2-dicarboxylic acid ligands have been synthesized. Both the spectra and crystal structures show that when (+)-(1*R*,3*S*)-camphoric acid and *meso*-*cis*-4-cyclohexene-1,2-dicarboxylic acid react with triorganotin compounds, they can form dinuclear complexes, 1D polymeric chains, and 2D network polymers with metal–organic structures. In general, trimethyltin dicarboxylate compounds mainly assume 2D network structures (such as in complexes **4** and **8**), and tributyltin dicarboxylate compounds often assume 1D polymeric chain structures (such as in complexes **3** and **7**), whereas triphenyltin dicarboxylate compounds form discrete monomers (such as in complex **1**). This phenomenon may be related to the spatial hindrance of the triorganotin group.

Experimental Section

Materials and Measurements: Trimethyltin chloride, tri-*n*-butyltin chloride, triphenyltin chloride, (+)-(1*R*,3*S*)-camphoric acid, and *meso*-*cis*-4-cyclohexene-1,2-dicarboxylic acid are commercially available, and tribenzyltin chloride was prepared by a standard method reported in the literature.[21] These were all used without further purification. Melting points were obtained with a Kofler micro-melting point apparatus and are reported uncorrected. Infrared spectra were recorded with a Nicolet-5700 spectrometer using KBr discs and NaCl optics. ^{1}H, ^{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 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. Elemental analyses (C and H) were performed with a PE-2400II apparatus. TGA was carried out with a Perkin–Elmer Pyris-1 instrument with a heating rate of 10 °C min^{-1} from 50 to 550 °C and with a 20.0 cm^{3} min^{-1} nitrogen gas flow.

$(Ph_3Sn)_2[C_8H_{14}(COO)_2]$ (1): The reaction was carried out under nitrogen. (+)-(1*R*,3*S*)-Camphoric acid (0.200 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol) were added to a solution of dry benzene (20 mL) in a Schlenk flask, and the mixture was stirred for 0.5 h. After triphenyltin chloride (0.771 g, 2 mmol) was added to the reaction mixture, it 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. The solid was then recrystallized from diethyl ether, and colorless crystals of complex **1** were recovered. Yield: 79%. M.p. 179–181 °C. $C_{46}H_{44}O_4Sn_2$ (868.2): calcd. C 61.51, H 4.94; found C 61.72, H 4.76. IR (KBr): $\tilde{\nu}$ = 1632 [ν_{as}(COO)], 1456 [ν_s(COO)], 555 [ν(Sn–C)], 447 [ν(Sn–O)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 0.94 (m, 9 H, CH$_3$), 3.89–4.01 (d, 4 H, CH$_2$), 4.22 (s, 1 H, CH), 7.27–7.38 (m, 30 H, Ph) ppm. ^{13}C NMR (CDCl$_3$): δ = 20.7–21.4 (ring-CH$_3$); 32.9, 39.9, 47.1, 52.7, 56.1 (ring-C); 128.5–138.6 (Ar-C); 171.2, 173.4 (COO) ppm. ^{119}Sn NMR (CDCl$_3$): δ = –43.7 ppm.

[(PhCH$_2$)$_3$Sn]$_2$[C$_8$H$_{14}$(COO)$_2$] (2): Complex **2** was prepared in the same way as complex **1**; tribenzyltin chloride (0.854, 2 mmol) was added to (+)-(1*R*,3*S*)-camphoric acid (0.200 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The reaction mixture was stirred at 40 °C for 12 h and then filtered. The solvent was gradually removed by evaporation under vacuum until the solid product was obtained. Yield: 77%. M.p. 212–214 °C. $C_{52}H_{56}O_4Sn_2$ (982.5): calcd. C 63.57, H 5.75; found C 63.81, H 5.52. IR (KBr): $\tilde{\nu}$ =1625 [ν_{as}(COO)], 1466 [ν_s(COO)], 544 [ν(Sn–C)], 452 [ν(Sn–O)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 0.85 (m, 9 H, CH$_3$), 4.35–4.48 (m, 4 H, ring-CH$_2$), 4.86 (s, 1 H, CH), 3.78 (d, $^2J_{SnH}$ = 67.4 Hz, 12 H, SnCH$_2$), 7.44–7.82 (m, 30 H, Ph). ^{13}C NMR (CDCl$_3$): δ = 20.6–22.2 (ring-CH$_3$); 33.8 (Ar-CH$_2$); 34.6, 39.4, 45.7, 51.9, 57.8 (ring-C); 124.5–137.3 (Ar-C); 170.1, 172.5 (COO) ppm. ^{119}Sn NMR (CDCl$_3$): δ = –48.1 ppm.

{(*n*Bu$_3$Sn)$_2$[C$_8$H$_{14}$(COO)$_2$]}$_n$ (3): Complex **3** was prepared in the same way as complex **1**; tri-*n*-butyltin chloride (0.651 g, 2 mmol) was added to (+)-(1*R*,3*S*)-camphoric acid (0.200 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid was then recrystallized from dichloromethane, and colorless crystals of complex **3** were recovered. Yield: 75%. M.p. 101–103 °C. $C_{34}H_{68}O_4Sn_2$ (778.3): calcd. C 52.47, H 8.81; found C 52.69, H 8.65. IR (KBr): $\tilde{\nu}$ = 1611 [ν_{as}(COO)], 1461 [ν_s(COO)], 524 [ν(Sn–C)], 458 [ν(Sn–O)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 0.82–0.91 (m, 27 H, CH$_3$), 4.13–4.28 (d, 4 H, ring-CH$_2$), 4.37 (s, 1 H, CH), 1.47–1.93 (m, $^2J_{SnH}$ = 72.6 Hz, 36 H, SnCH$_2$CH$_2$CH$_2$) ppm. ^{13}C NMR (CDCl$_3$): δ = 20.3–21.9 (ring-CH$_3$); 14.2, 25.5, 27.3, 28.4 (butyl-C); 32.1, 39.7, 45.8, 53.1, 58.7 (ring-C); 168.7, 169.4 (COO) ppm. ^{119}Sn NMR (CDCl$_3$): δ = –118.5, –39.4 ppm.

{(Me$_3$Sn)$_2$[C$_8$H$_{14}$(COO)$_2$]}$_n$ (4): Complex **4** was prepared in the same way as complex **1**; trimethyltin chloride (0.398 g, 2 mmol) was added to (+)-(1*R*,3*S*)-camphoric acid (0.200 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid was then recrystallized from diethyl ether, and colorless crystals of complex **4** were recovered. Yield: 85%. M.p. 198–201 °C. $C_{16}H_{32}O_4Sn_2$ (525.8): calcd. C 36.55, H 6.13; found C 36.31, H 6.32. IR (KBr): $\tilde{\nu}$ = 1600 [ν_{as}(COO)], 1458 [ν_s(COO)], 545 [ν(Sn–C)], 451 [ν(Sn–O)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 0.82–0.89 (m, $^2J_{SnH}$ = 83.2 Hz, 27 H, CH$_3$), 4.47–4.62 (s, 4 H, CH$_2$), 5.53 (d, 1 H, CH) ppm. ^{13}C NMR (CDCl$_3$): δ = 12.5 (SnCH$_3$); 21.3–23.7 (ring-CH$_3$); 33.9, 38.8, 40.1, 51.7, 56.5 (ring-C); 173.4, 175.8 (COO) ppm. ^{119}Sn NMR (CDCl$_3$): δ = –143.8 ppm.

[(Ph$_3$Sn)$_2$[C$_6$H$_8$(COO)$_2$] (5): Complex **5** was prepared in the same way as complex **1**; triphenyltin chloride (0.771 g, 2 mmol) was added to *meso*-*cis*-4-cyclohexene-1,2-dicarboxylic acid (0.170 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The reaction mixture was stirred at 40 °C for 12 h and then filtered. The solvent was gradually removed by evaporation under vacuum until the solid product was obtained. Yield: 81%. M.p. 172–174 °C. $C_{44}H_{38}O_4Sn_2$ (868.2): calcd. C 60.87, H 4.41; found C 60.68, H 4.65. IR (KBr): $\tilde{\nu}$ = 1637 [ν_{as}(COO)], 1388 [ν_s(COO)], 552 [ν(Sn–C)], 446 [ν(Sn–O)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 5.54 (s, 2 H, γ-H), 2.15 (d, 4 H, β-H), 2.91 (d, 2 H, α-H), 7.37–7.78 (m, 30 H, Ph) ppm. ^{13}C NMR (CDCl$_3$): δ = 25.6, 40.9, 124.6 (ring-C); 173.6 (COO); 129.5–135.7 (Ar-C) ppm. ^{119}Sn NMR (CDCl$_3$): δ = –46.6 ppm.

[(PhCH$_2$)$_3$Sn]$_2$[C$_6$H$_8$(COO)$_2$] (6): Complex **6** was prepared in the same way as complex **1**; tribenzyltin chloride (0.854, 2 mmol) was added to *meso*-*cis*-4-cyclohexene-1,2-dicarboxylic acid (0.170 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solvent was gradually removed by evaporation under vacuum until the solid product was obtained. Yield: 72%. M.p. 163–167 °C. $C_{50}H_{50}O_4Sn_2$ (951.3): calcd. C 63.06, H 5.29; found C 63.31, H 5.03. IR (KBr): $\tilde{\nu}$ = 1642 [ν_{as}(COO)], 1351 [ν_s(COO)], 538 [ν(Sn-C)], 439 [ν(Sn–O)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 5.62 (s, 2 H, γ-H), 2.23 (d, 4 H, β-H), 2.89 (d, 2 H, α-H), 3.15 (d, $^2J_{SnH}$ = 65.5 Hz, 12 H, SnCH$_2$), 7.22–7.74 (m, 30 H, Ph) ppm. ^{13}C NMR (CDCl$_3$): δ = 169.2 (COO); 127.5–137.6 (Ar-C); 25.8, 39.4, 123.6 (ring-C); 35.3 (Ar-CH$_2$) ppm. ^{119}Sn NMR (CDCl$_3$): δ = –51.2 ppm.

{[(*n*Bu)$_3$Sn][C$_6$H$_8$(COO)$_2$]}$_n$ (7): Complex **7** was prepared in the same way as complex **1**; tri-*n*-butyltin chloride (0.651 g, 2 mmol) was added to *meso*-*cis*-4-cyclohexene-1,2-dicarboxylic acid (0.170 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid was then recrystallized from dichloromethane, and colorless crystals of complex **7** were recovered. Yield: 83%. M.p. 86–87 °C. $C_{20}H_{36}O_4Sn$ (459.2): calcd. C 52.31, H 7.90; found C 52.59, H 7.64. IR (KBr): $\tilde{\nu}$ =1686 [ν_{as}(COO)], 1342 [ν_s(COO)], 563 [ν(Sn–C)], 437 [ν(Sn–O)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 5.23 (s, 2 H, γ-H), 2.05 (t, 4 H, β-H), 2.74 (d, 2 H, α-H), 1.12–1.75 (m, $^2J_{SnH}$ = 74.7 Hz, 18 H, SnCH$_2$CH$_2$CH$_2$), 0.87 (s, 9 H, CH$_3$), 11.74 (s, 1 H, OH) ppm. ^{13}C NMR (CDCl$_3$): δ = 178.7 (COO); 25.1, 44.6, 125.9 (ring-C); 13.9, 24.2, 26.8, 28.3 (butyl-C) ppm. ^{119}Sn NMR (CDCl$_3$): δ = –126.4 ppm.

{[(CH$_3$)$_3$Sn]$_2$[C$_6$H$_8$(COO)$_2$]}$_n$ (8): Complex **8** was prepared in the same way as complex **1**; trimethyltin chloride (0.398 g, 2 mmol) was added to *meso*-*cis*-4-cyclohexene-1,2-dicarboxylic acid (0.170 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid was then recrystallized from dichloromethane, and colorless crystals of complex **8** were recovered. Yield: 80%. M.p. 202–205 °C. $C_{14}H_{26}O_4Sn_2$ (495.7): calcd. C 33.92, H 5.29; found C 33.71, H 5.03. IR (KBr): $\tilde{\nu}$ =1659 [ν_{as}(COO)], 1357 [ν_s(COO)], 548 [ν(Sn–C)], 449 [ν(Sn–O)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 5.92 (d, 2 H, γ-H), 2.18 (t, 4 H, β-H), 3.13 (d, 2 H, α-H), 0.96 ($^2J_{SnH}$ = 87.6 Hz, 18 H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ = 173.1 (COO); 125.3, 40.2, 24.6 (ring-C); 12.8 (Sn-CH$_3$) ppm. ^{119}Sn NMR (CDCl$_3$): δ = –133.8 ppm.

X-ray Crystallography: Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected with a Smart CCD area detector with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). A semiempirical absorption correction was

Table 4. Crystallographic data and structure refinement parameters for complexes **1**, **3**, and **4**.

Complex	1	3	4
Empirical formula	$C_{46}H_{44}O_4Sn_2$	$C_{34}H_{68}O_4Sn_2$	$C_{16}H_{32}O_4Sn_2$
Formula mass [g mol^{-1}]	898.19	778.26	525.80
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	*C*2/*c*	*P*2(1)2(1)2(1)	*P*2(1)2(1)2
a [Å]	31.351(7)	10.488(2))	19.5005(7)
b [Å]	9.6682(18)	10.839(2)	19.6857(7)
c [Å]	30.073(6)	35.183(7)	6.7171(3)
α [°]	90	90	90
β [°]	116.215(5)	90	90
γ [°]	90	90	90
V [Å^3]	8178(3)	3999.4(14)	2578.57(17)
Z	8	4	4
μ [mm^{-1}]	1.459	1.279	1.947
Reflections collected	20847	19974	29370
Independent reflections	7213	3835	2611
R_{int}	0.11 0.0505	0.0591	0.0328
R_1 [$I > 2\sigma(I)$], R_1 (all data)	0.0535, 0.1368	0.0590, 0.1466	0.0305, 0.1214
$wR2$ [$I > 2\sigma(I)$], $wR2$ (all data)	0.1071, 0.1684	0.0951, 0.1825	0.0324, 0.1241

applied to the data. The structure was solved by direct methods using SHELXS-97 and refined against F^2 by full-matrix least-squares using SHELXL-97.[22] Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Tables 4 and 5. CCDC-663480 (**1**), -663482 (**3**), -663481 (**4**), -663484 (**7**), and -663483 (**8**) 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 5. Crystallographic data and structure refinement parameters for complexes **7**–**8**.

Complex	7	8
Empirical formula	$C_{20}H_{36}O_4Sn$	$C_{14}H_{26}O_4Sn_2$
Formula mass [g mol^{-1}]	459.18	495.73
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [Å]	11.1132(17)	9.9322(17)
b [Å]	9.8314(16)	14.702(2)
c [Å]	21.455(2)	12.906(2)
α [°]	90	90
β [°]	103.175(2)	98.174(2)
γ [°]	90	90
V [Å^3]	2282.4(6)	1865.5(5)
Z	4	4
μ [mm^{-1}]	1.138	1.765
Reflections collected	10231	7641
Independent reflections	3869	3278
R_{int}	0.0436	0.0199
R_1 [$I > 2\sigma(I)$], R_1 (all data)	0.0529, 0.1277	0.0272, 0.0539
$wR2$ [$I > 2\sigma(I)$], $wR2$ (all data)	0.1045, 0.1667	0.0581, 0.1535

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