Novel Supramolecular Frameworks Self-Assembled from a Two-Dimensional Polymeric Network: Synthesis and Crystal Structure of a Macrocyclic Organotin(IV) Complex

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The two-dimensional polymer $[n\mathrm{Bu_2Sn(O_2CC_6H_4)}]_4$ has been synthesized by the self-assembly of di-*n*-butyltin oxide and 4-carboxyphenylboronic acid. The X-ray crystal structure shows that the metal ions display a trigonal bipyramidal coordination geometry to bind the endocyclic oxygen atom. Intermolecular π–π stacking interactions between adjacent phenyl groups of the ligand cause the self-assembly into a 1D chain. In this chain one oxygen atom of the carboxylate group binds to one $[n\mathrm{Bu_2Sn(O_2CC_6H_4)}]_4$ unit to give rise to a 2D architecture.

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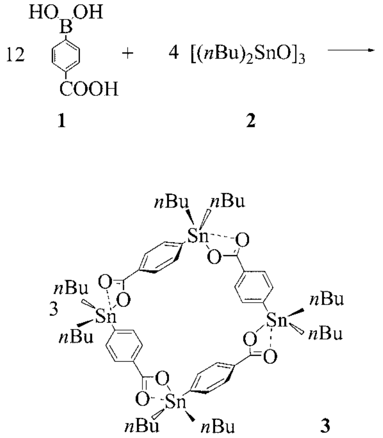
Introduction

Owing to the enormous variety of intriguing structural topologies and their unexpected properties for potential practical applications,[1–4] the chemistry of novel organotin(IV) polymers based on covalent interactions[5–9] or supramolecular contacts (such as hydrogen bonding and/or π–π stacking interactions)[10–13] has been actively investigated. The vast majority of reported work is based upon the use of polyfunctional organic ligands to bind to the tin ions through self-assembly processes, leading to the formation of compounds with fascinating topologies and physical properties. It has also been shown that the careful selection of appropriate multidentate bridging ligands is helpful not only to tailor effectively the polymer architectures but also to realize various applications. In this field, studies have been focused on benzenecarboxylate ligands, such as benzenetricarboxylic acid. However, much less work has been carried out to investigate organotin polymer boronic acid ligands. In this work, we select 4-carboxyphenylboronic acid as the ligand, on the basis of the following considerations: (i) 4-carboxyphenylboronic acid anions have two different groups, and they may act as linkers to connect metal ions into higher dimensional structures by varied coordination modes; (ii) 4-carboxyphenylboronic acid anions may have different effects in the construction of coordination polymers; (iii) the carboxyl and boronic acid occupy *trans* positions, and thus can act as a good bridging ligand and benefit the molecular self-assembly. Therefore, we selected this ligand with the hope of constructing novel organotin(IV) coordination polymers with fascinating structures and/or characteristic properties. To our surprise, we obtained an unprecedented tetranuclear macrocyclic organotin complex $[n\mathrm{Bu_2Sn(O_2CC_6H_4)}]_4$ by B–C cleavage and the new Sn–C bond formation. To the best of our knowledge, this is the first example where organic linkers are incorporated into one metal–organic polymer by B–C bond cleavage and new Sn–C bond formation. The complex has been characterized by elemental analysis and IR, ^{1}H, and ^{13}C NMR spectroscopy. Furthermore, we have also characterized the complex by X-ray crystallography.

Result and Discussion

The synthetic procedure is shown in Scheme 1.



Scheme 1.

The main feature in the IR spectrum is the absence of a band in the region between 2800 and 3320 cm^{-1}, where the

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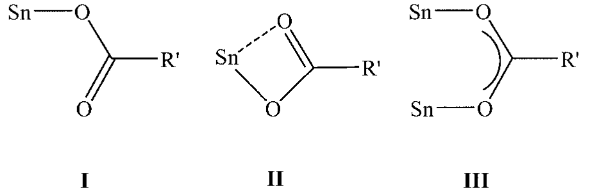
ν(O–H) vibration in the free ligand appears, which indicates metal–ligand bond formation. In organotin carboxylate complexes, the IR spectra can provide useful information concerning the coordination mode of the carboxylate. When the carboxylate group coordinates to the atom in a monodentate manner, the difference between the wavenumbers of the (mode I) asymmetric and symmetric carboxylate stretching bonds, $\Delta\nu$ ($\nu_{\mathrm{asCOO^-}} - \nu_{\mathrm{symCOO^-}}$), is larger than that observed for ionic compounds. When the ligand chelates (mode II), $\Delta\nu$ is considerably smaller than that for ionic compounds, while for asymmetric bidentate coordination the value is in the range characteristic of monodentate coordination.[14] The characteristic wavenumber difference, $\Delta\nu$, for mode III is larger than that for chelated ions and nearly the same as that observed for ionic compounds (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 COO⁻ group. The magnitude of $\Delta\nu$ of about 273 cm^{-1}, compared with that for the corresponding sodium salt, reveals that the carboxylate ligands are monodentate under the conditions employed.[15,16]

The ^{1}H NMR spectrum of the complex shows that the signal for the OH proton in the spectrum of the ligand is absent in that of the complex, thus indicating the removal of the OH proton and the formation of Sn–O bonds. This consistent with the IR data. The ^{13}C NMR spectroscopic data for the complex are consistent with organotin carboxylate structures. Although at least four different types of carboxylate groups are present, only single resonance are observed for the COO group in the ^{13}C NMR spectrum. This is either due to accidental magnetic equivalence of the carbonyl carbon atoms or the separations between the four peaks of resonance are too small to be resolved.

The molecular structure and a fragment of the crystal lattice are illustrated in Figure 1 and Figure 2, respectively. A crystallographic study of complex **3** shows that the tetranuclear complex is characterized by a 28-membered $C_{20}O_4Sn_4$ macrocyclic ring system with all four oxygen atoms directed into the interior of the cavity and the eight *n*-butyl groups attached to the tin centers approximately perpendicular to the molecular plane (Figure 1). All the tin atoms possess the same ligand environments, with only minor differences in bond lengths and bond angles. For Sn(1), for example, the geometry of the tin atom is distorted tetrahedral and the tin atom forms four primary bonds: two to the butyl groups, one to phenyl, and one to an oxygen atom. Around the tin atom, the angles O(1)–Sn–C(29) [100.9(8)°], C(29)–Sn–C(33) [128.7(9)°], and C(26)–Sn–C(33) [116.4(8)°] are wider while O(1)–Sn–C(26) [93.8(5)°], C(29)–Sn–C(26) [109.1(9)°], and O(1)–Sn–C(33) [98.6(7)°] are narrower than the ideal tetrahedral angle. Also, the weak Sn···O bond [2.906 Å for Sn(1)···O(4′)] between tin and the exocyclic oxygen atoms of adjacent molecules is less than the sum of the van der Waal's radii of tin oxygen atoms (3.68 Å),[17] all of which are similar to those reported in the literature.[18] Therefore, if considering the Sn···O weak interaction, the structural distortion for the tin atom is best described as a trigonal bipyramidal geometry with O(1) and O(4′) atoms occupying the axial sites and an axial-Sn-axial [O(1)–Sn–O(4′)] angle of 175.36°. Sn(1), C(26), C(29), and C(33) are almost completely coplanar with the tin atom. The sum of angles between the tin atom and the equatorial atoms is 354.2°, consistent with the ideal value of 360°.

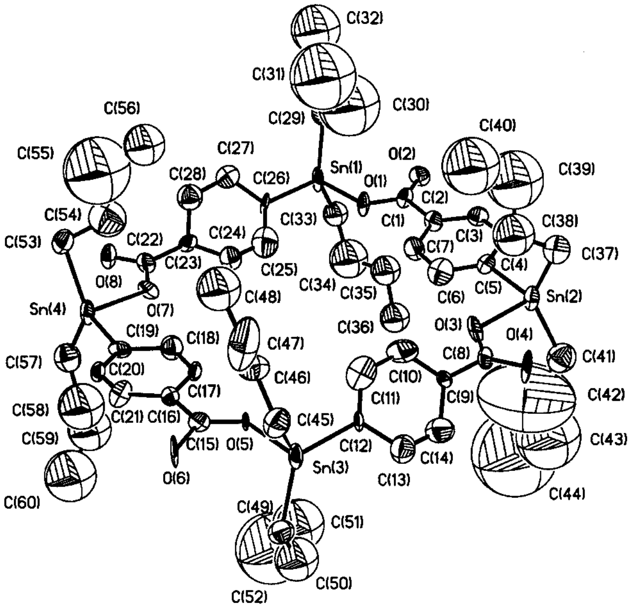


Figure 1. ORTEP plot of the molecular structure of $[n\mathrm{Bu_2Sn(O_2CC_6H_4)}]_4$ (**3**). Thermal ellipsoids are drawn with 30% probability. Selected bond lengths [Å] and angles [°]: Sn(1)–O(1) 2.072(10), Sn(1)–C(29) 2.08(2), Sn(1)–C(26) 2.091(15), Sn(1)–C(33) 2.15(2), Sn(1)···O(2) 3.191, Sn(1)···O(4A) 2.905, Sn(2)–O(3) 2.084(11), Sn(2)–C(37) 2.11(3), Sn(2)–C(41) 2.15(3),Sn(2)–C(5) 2.201(19), Sn(2)···O(4) 3.049, Sn(2)···O(6A) 2.769, Sn(3)–O(5) 2.065(10), Sn(3)–C(49) 2.12(2), Sn(3)–C(12) 2.137(15), Sn(3)–C(45) 2.18(2), Sn(3)···O(6) 3.209, Sn(3)···O(8A) 2.898, Sn(4)–O(7) 2.103(12), Sn(4)–C(57) 2.10(3), Sn(4)–C(19) 2.105(18), Sn(4)–C(53) 2.26(2), Sn(4)···O(8) 3.023, Sn(4)···O(2A) 2.751; C(29)–Sn(1)–C(26) 109.1(9), C(49)–Sn(3)–C(12) 116.1(8), C(26)–Sn(1)–C(33) 116.4(8), C(12)–Sn(3)–C(45) 112.9(8), O(1)–C(1)–O(2) 122.1(14), O(5)–C(15)–O(6) 123.1(14), C(37)–Sn(2)–C(41) 133.1(10), C(57)–Sn(4)–C(19) 109.8(9), C(37)–Sn(2)–C(5) 111.5(9), C(57)–Sn(4)–C(53) 135.9(9), C(41)–Sn(2)–C(5) 108.7(10), C(19)–Sn(4)–C(53) 110.0(8), O(3)–C(8)–O(4) 124.1(19), O(7)–C(22)–O(8) 119.8(17).

The size of cavity in this macrocycle can be evaluated from the Sn···Sn and transannular O···O distances, which are 9.181–9.214 Å and 7.219–7.341 Å, respectively, similar to those in di-*n*-butyltin(IV) isophthalate.[19] From the X-ray structure, we found that the tetranuclear macrocyclic rings are linked into a 1D chain through face-to-face π–π stacking and weak Sn···O interactions. In the case of the stacking

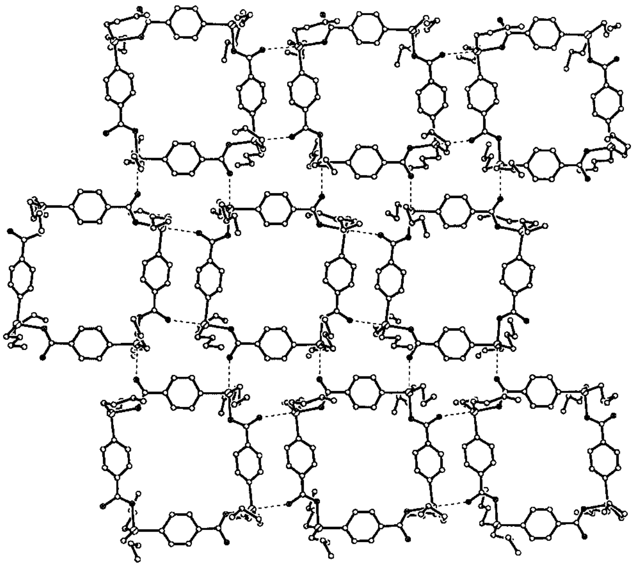


Figure 2. Polymeric network formed through intermolecular Sn···O′ and π–π stacking interactions.

phenyl rings, the centroid–centroid distance is 4.178 Å, which is much shorter than that of the optimized structure for parallel displaced stacking benzene dimer in the gas phase (4.50 Å)[20] and those of other reported stacking aryl groups (4.6 Å[21] and 4.83 Å[22]), thus indicating that the π–π stacking interactions are very strong and it is these interactions that stabilize the 1D chain in the crystal. Therefore, self-assembly occurs through weak Sn···O interactions and helps the molecules form a 2D architecture (Figure 2).

In summary, from the crystal structure described above we can conclude that the B–C cleavage and the new Sn–C bond formation are crucial for the formation of the macrocyclic structure. This discovery may cast light on the reactivity of alkyltin(IV) compounds. That is, we can intentionally design and synthesize alkyltin(IV) compounds to obtain valuable compounds with specific topologies.

Experimental Section

Materials and Measurements: Di-*n*-butyltin oxide and 4-carboxyphenylboronic acid are commercially available, and they were used without further purification. The melting points were obtained with a Kofler micro-melting point apparatus and were uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on Varian Mercury Plus 400 spectrometer operating at 400, 100.6, and 149.2 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ^{13}C spectra are broadband proton decoupled. The chemical shifts are reported in ppm with respect to the references (external tetramethylsilane for ^{1}H and ^{13}C NMR, and neat tetramethyltin for ^{119}Sn NMR). Elemental analyses (C,H) were performed with a PE-2400II apparatus.

[nBu$_2$Sn(O$_2$CC$_6$H$_4$)]$_4$ (3): The reaction was carried out under a nitrogen atmosphere. Di-*n*-butyltin oxide (0.497 g, 2 mmol) and 4-carboxyphenylboronic acid (0.332 g, 2 mmol) were added to a solution of dry toluene (50 mL) in a Schlenk flash. Refluxing was continued for 10 h. After filtration the solvent was evaporated in vacuo and the residue crystallized from dichloromethane to give complex **3** as white crystals. Yield: 81%. M.p. 110–112 °C. $C_{60}H_{88}O_8Sn_4$ (1412.18): calcd. C 51.04, H 6.28; found C 51.01, H 6.21. IR (KBr): $\tilde{\nu}$ = 3067, 2960, 2924, 2855, 1634, 1605, 1582, 1448, 1361, 1342, 561, 546, 471 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 0.89 (t, CH$_3$), 1.34–1.72 (m, $^2J_{\mathrm{Sn,H}}$ = 75.1 Hz, CH$_2$CH$_2$CH$_2$), 7.64 (d, C$_6$H$_4$), 8.13 (d, C$_6$H$_4$) ppm. ^{13}C NMR (CDCl$_3$): δ = 27.1 (α-CH$_2$, $^1J_{^{119}\mathrm{Sn},^{13}\mathrm{C}}$ = 607 Hz), 28.5 (β-CH$_2$), 26.3 (γ-CH$_2$), 13.5 (CH$_3$), 172.1 (COO) ppm. ^{119}Sn NMR (CDCl$_3$): δ = –57.2 ppm.

X-ray Crystallography. Crystal Data for 3: Monoclinic, $P2_1/n$, a = 14.288(18), b = 28.66(3), c = 19.17(2) Å; β = 110.11(2)°, V = 7371 Å^3, T = 293 K, Z = 4, μ = 1.381 mm^{-1}, 34 071 reflections measured, 11 795 unique (R_{int} = 0.2467) which were used in all calculations. Final R indices were R_1 = 0.0978, wR_2 = 0.1692 [$I > 2\sigma(I)$], R_1 = 0.2967 wR_2 = 0.2391 (all data).
CCDC-225030 contains 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.

Acknowledgments

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