Synthesis and Crystal Structures of the First Two Novel Dicarboxylate Organotin Polymers Constructed from Dimeric Tetraorganodistannoxane Units

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Assembly of nitroterephthalic acid (H_2NTPA) or diphenic acid (H_2DPA) with trimethyltin chloride under hydrothermal conditions produces a one-dimensional chain polymer $[(Me_2Sn)_2(\mu_3\text{-NTPA})(\mu_3\text{-O})]_n$ (**1**) or a two-dimensional corrugated sheet polymer $[(Me_2Sn)_4(\mu_3\text{-DPA})(\mu_4\text{-DPA})(\mu_3\text{-O})_2]_n$ (**2**), respectively. Both consist of different types of dimeric dicarboxylatotetraorganodistannoxane secondary building units.

The design and synthesis of novel coordination polymers with unusual and tailorable structures are fundamental steps to discover and fabricate various technologically useful materials.[1−4] The majority of such species have been constructed from organic ligands and metal ions by spontaneous self-assembly. Recently, much effort has been devoted to the design and construction of new supramolecular frameworks by using metal clusters[5,6] or metal-organic secondary building units (SBUs)[7−13] as building blocks, and multifunctional organic ligands as linkers. Such assembly has resulted in a host of intriguing structural topologies and an extensive application in material science. For instance, the use of carboxylate-bridged zinc clusters as metal-organic SBUs and 1,4-benzenedicarboxylate or 1,3,5-benzenetricarboxylate as linkers by Yaghi et al. has provided several novel porous metal-organic frameworks which can absorb and desorb small gas molecules.[9−13]

It is well-known that the discrete dimeric dicarboxylatotetraorganodistannoxane complexes $\{[R_2Sn(O_2CR')_2O]_2\}$ have been extensively studied due to their wide application in biology and catalysis; most of them were obtained by the assembly of monofunctional carboxylate ligands and organotin reagents.[14−20] To the best of our knowledge, the crystal structures of only two organotin polymers containing dimeric tetraorganodistannoxane units have been reported.[21,22] It is predictable that extended structures may be obtained by using bifunctional dicarboxylate ligands instead of monofunctional carboxylate ligands as linkers and the dimeric tetraorganodistannoxane as nodes. However, the reported dicarboxylate organotin complexes exist as dinuclear[23−25] and one-dimensional zigzag chain structures.[26−29] With the aim of extending the chemistry of dimeric dicarboxylatotetraorganodistannoxane, we have recently begun to study the reactions of organotin and di- or polycarboxylic acid ligands under hydrothermal conditions. Here we report the syntheses and crystal structures of two novel organotin complexes consisting of dimeric dicarboxylatotetraorganodistannoxane SBUs, $[(Me_2Sn)_2(\mu_3\text{-NTPA})(\mu_3\text{-O})]_n$ (**1**) and $\{(Me_2Sn)_4(\mu_3\text{-DPA})(\mu_4\text{-DPA})(\mu_3\text{-O})_2\}_n$ (**2**), assembled from nitroterephthalic acid (H_2NTPA) or diphenic acid (H_2DPA) with trimethyltin chloride under hydrothermal conditions.

The hydrothermal reaction of H_2NTPA or H_2DPA, 4,4′-bipyridne and trimethyltin chloride in a molar ratio 1:1:2 at 140 °C for three days produced colorless crystals of **1** or **2**, respectively (Scheme 1). These compounds are insoluble in common solvents, such as water, methanol, acetone, acetonitrile, dichloromethane, tetrahydrofuran, *N*,*N*′-dimethylformamide and dimethyl sulfoxide. The presence of the carboxylate group was confirmed by very strong IR absorption peaks in the solid-state spectrum at 1647 and 1365 cm^{-1} for **1** and 1699 and 1680 cm^{-1} for **2**. Signals for the nitro group in **1** were identified at 1549, 1531 and 1340 cm^{-1}; these values are unchanged with respect to those of the starting acid.

A single crystal X-ray diffraction analysis reveals that complex **1** has a one-dimensional chain motif constructed from novel approximately rectangular rings. As shown in Figure 1, each ring is composed of two NTPAs and two dimeric tetraorganodistannoxane units. The dihedral angle of the two phenyl rings in the ring is 91.9° i.e. they are almost perpendicular. NTPA in a μ_3-bridging mode links two dimeric tetraorganodistannoxane units and the dimeric tetraorganodistannoxane units are shared by the approximate rectangular rings to form a one-dimensional chain coordination polymer. This structural feature of **1** is quite different from that of $\{([Me_2Sn(OAc)]_2O)_2\}_n$, the only known one-dimensional organotin polymer, in which the acetate

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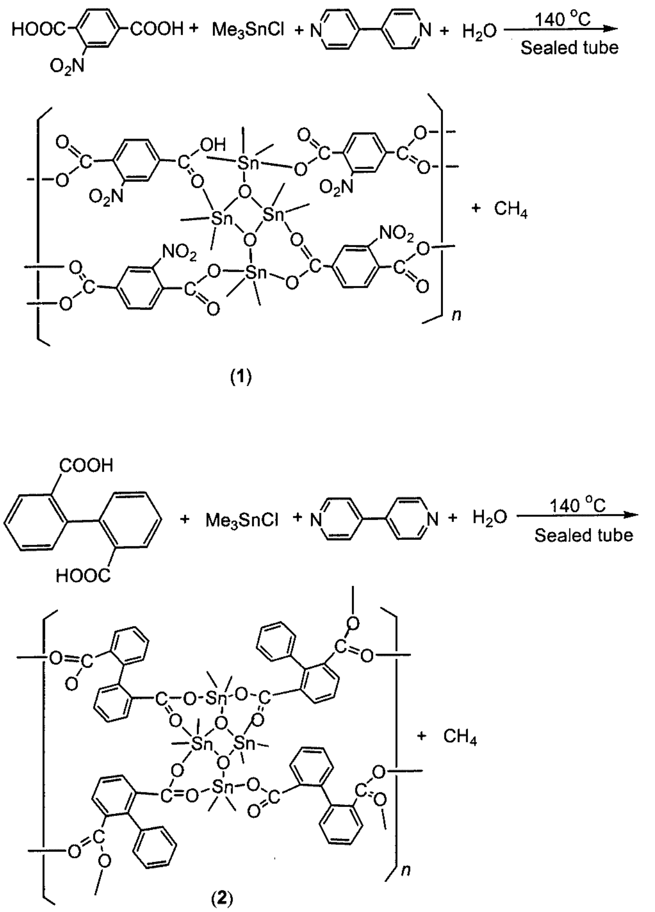

Scheme 1. Synthesis of complexes **1** and **2**

links the dimeric tetraorganodistannoxane units in a tetradentate mode.[21]

The SBU in **1** is the predominant structural form in five types of dimeric dicarboxylatotetraorganodistannoxane in which each Sn atom is in a five-coordinate geometry.[14] It consists of a central planar $(Me_2Sn)_2O_2$ four-membered ring and two peripheral Me_2Sn units attached to two μ_3-oxygen atoms. NTPA acts as a tridentate ligand which coordinates to an outer Sn atom through an oxygen atom of the carboxylate adjacent to NO_2 and chelates between exocyclic and endocyclic Sn atoms forming a stable six-membered ring through the other carboxylate oxygen atoms. The NO_2 in NTPA is not involved in coordination to Sn atoms. Thus, the Sn atoms in the SBU adopt a distorted trigonal bipyramidal geometry. The exocyclic and endocyclic Sn atoms lie 0.1442 and 0.1492 Å out of the plane defined by the three coordinated oxygen atoms, respectively.

Complex **2** is a two-dimensional corrugated sheet polymer made up of the dimeric tetraorganodistannoxane units and bridging DPA ligands. As shown in Figure 2, the SBU in **2** is different from that in complex **1**. The central four-membered ring $(Me_2Sn)_2O_2$ is connected to two independently exocyclic Sn atoms through μ_3-oxygen atoms. The distance between the two Sn atoms in the four-membered ring is 3.325 Å, which is longer than 3.264 Å in complex **1**, but smaller than the sum of the van der Waals radii of Sn^{II} (3.40 Å), suggesting the possible presence of a weak metal-metal interaction. There are two types of DPA ligands which are distinguished by their bridging fashions. One acts as a tetradentate ligand and bridges a pair of exocyclic and endocyclic Sn atoms to form two stable six-membered rings; the other adopts a μ_3-bridging mode through bonding to an exocyclic Sn atom and chelating between exocyclic and endocyclic Sn atoms. Thus, an endocyclic Sn(1) atom adopts a six-coordinate geometry with a deviation of 0.0088 Å from the plane defined by the four coordinated oxygen atoms [O(1) O(2) O(11) and O(41)], two methyl groups occupy the apical positions, with a Me−Sn(1)−Me bond angle of 157.4°, and the other endocyclic Sn(3) atom and two exocyclic Sn atoms (Sn2 and Sn4) are a five-coordinate with deviations of 0.0191, 0.1161 and 0.0110 Å from the plane defined by the coordinated oxygen atoms, respectively.

In complex **2**, DPA is a chiral ligand and the dihedral angles of two phenyl rings are 99.4° for the tridentate mode and 87.1° for the tetradentate mode. It is noteworthy that a μ_4-bridging DPA moiety links the dimeric tetraorganodist-

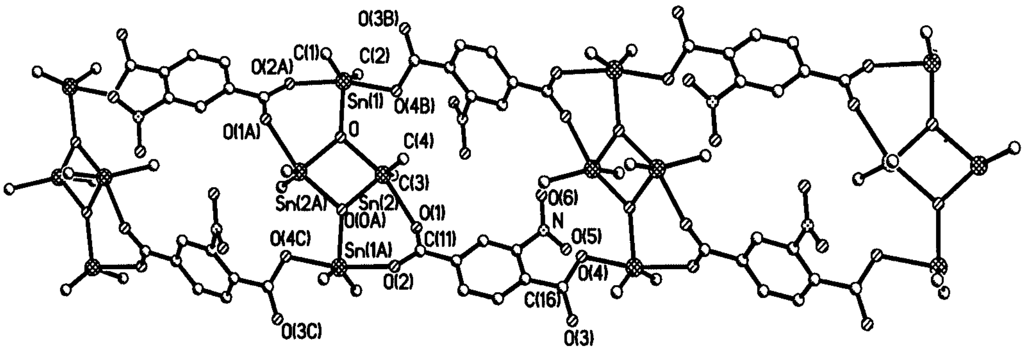

Figure 1. View of the one-dimensional chain in **1** with atomic numbering; selected bond lengths (Å): Sn(1)−C(1) 2.092(7) Sn(1)−C(2) 2.098(7), Sn(1)−O2.045(5), Sn(1)−O(2A) 2.290(5), Sn(1)−O(4B) 2.191(5), Sn(2)−C(3) 2.106(8), Sn(2)−C(4) 2.094(8), Sn(2)−O 2.137(4), Sn(2)−O(1) 2.267(5), Sn(2)−O(0A) 2.042(5), Sn(2)−Sn(2A) 3.2644(9); symmetry code: (A) $-x + 1/2$, $-y + 3/2$, $-z$; (B) $-x + 1$, y, $-z + 1/2$.

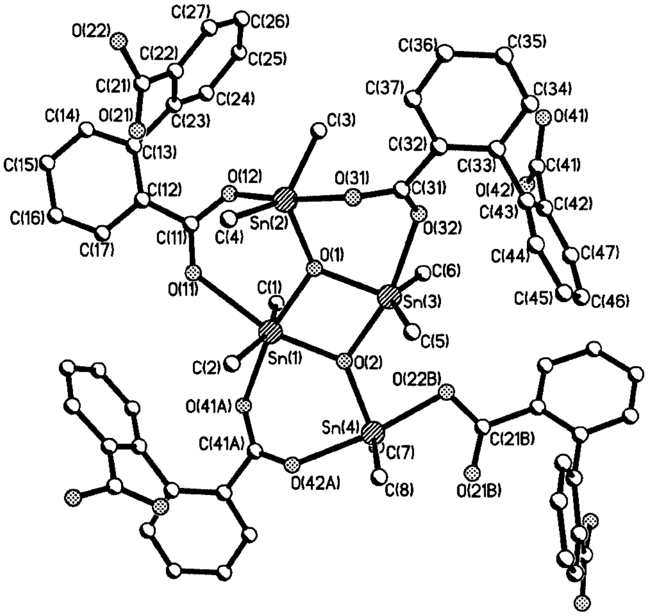

Figure 2. View of the SBU in **2** with atomic numbering; selected bond lengths (Å): Sn(1)−C(1) 2.084(9), Sn(1)−C(2) 2.106(8), Sn(1)−O(1) 2.183(5), Sn(1)−O(2) 2.078(5), Sn(1)−O(11) 2.514(7), Sn(1)−O(41A) 2.326(5), Sn(2)−C(3) 2.083(9), Sn(2)−C(4) 2.104(8), Sn(2)−O(1) 1.997(5), Sn(2)−O(12) 2.139(5), Sn(2)−O(31) 2.270(5), Sn(3)−C(5) 2.107(8), Sn(3)−C(6) 2.096(8), Sn(3)−O(1) 2.047(5), Sn(3)−O(2) 2.129(5), Sn(3)−O(32) 2.318(5), Sn(4)−C(7) 2.093(8), Sn(4)−C(8) 2.086(8), Sn(4)−O(2) 2.012(5), Sn(4)−O(22C) 2.171(5), Sn(4)−O(42A) 2.250(5); symmetry code: (A) $x + 1/2, -y + 1/2, z + 1/2$, (C) $x - 1/2, -y + 1/2, z + 1/2$.

annoxane units, forming a helical chain, and a μ_3-bridging DPA moiety links the helical chains by ligating the remaining coordination sites of the dimeric tetraorganodistannoxane units, forming a curved two-dimensional sheet structure (Figure 3). The main structural feature of **2** is quite different from that of a two-dimensional rhombohedral grid polymer composed of ladder-type dimeric tetraorganodistannoxane units and 4-hydroxyl-3-methoxybenzoic acid dianion.[22] As shown in Figure 4, the two-dimensional sheet is folded in a highly corrugated way with DPA as the turning points when viewed along *c* axis. The distance between adjacent sheets is 9.54 Å.

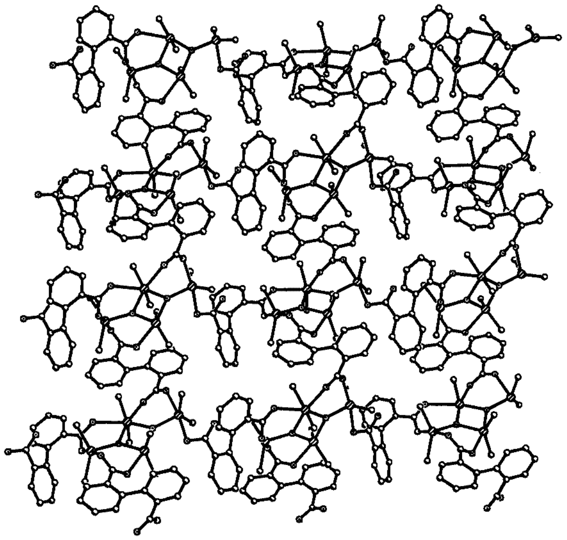

Figure 3. View of the two-dimensional sheet along the *b* axis in **2**

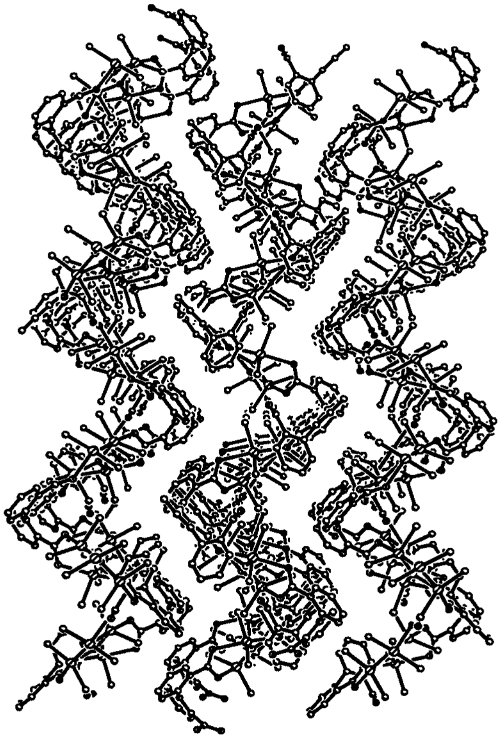

Figure 4. View of the corrugated sheet along the *c* axis in **2**

In summary, this work demonstrates that the assembly of dicarboxylate ligands — such as nitroterephthalic acid and diphenic acid — and trimethyltin chloride allows for the formation of organotin polymers consisting of dimeric dicarboxylatotetraorganodistannoxane units, which act as metal-organic SBUs in the extended structures. To the best of our knowledge, they are the first dicarboxylate polymers consisting of dimeric dicarboxylatotetraorganodistannoxane SBUs of which the crystal structures have been determined. Thus, our report may open a new approach for the assembly of different types of discrete dimeric dicarboxylatotetraorganodistannoxane complexes into extended polymers through using di- or polycarboxylates as linker ligands instead of monofunctional carboxylates. Extension of this work, including more di- or polycarboxylate ligands and other organotin compounds, is in progress.

Experimental Section

Synthesis of $[(Me_2Sn)_4(\mu_3\text{-}O)_2(\mu_3\text{-}NTPA)_2]_n$ (1): A mixture of H_2NTPA (0.11 g, 0.5 mmol), 4,4′-bipyridne (0.08 g, 0.5 mmol) and trimethyltin chloride (0.20 g, 1 mmol) in 16 mL of H_2O was placed in a Parr Teflon-lined stainless steel vessel and heated to 140 °C for 72 h, then cooled to room temperature during 5 hours. Colorless crystals were obtained and collected by filtration and washed with water. Yield: 56%. $C_{12}H_{15}NO_7Sn_2$ (522.6): calcd. C 27.58, H 2.87, N 2.68; found C 27.23, H 2.67, N 2.54. IR (KBr pellet): $\tilde{\nu}$ = 3456 (w), 3084 (vw), 2918 (vw), 1647 (s), 1591 (s), 1549 (m), 1531 (s), 1491 (m), 1412 (s), 1365 (s), 1340 (s), 1304 (m), 1254 (w), 1147 (vw), 1066 (vw), 928 (vw), 825 (w), 796 (m), 783 (m), 633 (m), 577 (m), 499 (m) cm^{-1}.

Synthesis of $\{(Me_2Sn)_4(\mu_3\text{-}O)_2(\mu_3\text{-}DPA)(\mu_4\text{-}DPA)\}_n$ (2): The procedure is similar to the synthesis of complex **1** except that H_2DPA (0.12 g, 0.5 mmol) was used instead of H_2NTPA. Yield: 70%. $C_{36}H_{40}O_{10}Sn_4$ (1107.5): calcd. C 39.04, H 3.61; found C 39.32, H 3.43%. IR (KBr pellet): $\tilde{\nu}$ = 3061 (w), 2864 (m), 2825 (m), 1699 (s), 1680 (s), 1599 (s), 1572 (m), 1539 (w), 1475 (w), 1452 (w), 1412 (w), 1360 (s), 1250 (s), 1213 (s), 1140 (m), 1099 (w), 1063 (m), 1003 (m), 939 (w), 822 (vw), 808 (m), 796 (m), 758 (m), 708 (w), 625 (m), 584 (vw) cm^{-1}.

X-ray crystallography: The crystal data and structure determination summary for **1** and **2** are listed in the Table 1. Intensity data for **1** and **2** were measured on a Siemens Smart CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 298 K. Empirical absorption corrections were applied with the SADABS program. The structures were solved by direct methods and all calculations were performed using the SHELXL PC program. The positions of the H-atoms were generated geometrically (C−H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. The structures were refined by full-matrix least-squares minimization of $\Sigma(F_o - F_c)^2$ with anisotropic thermal parameters for all atoms except the H-atoms.
CCDC-181351 (**1**) and -181352 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic data for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{12}H_{15}NO_7Sn_2$	$C_{36}H_{40}O_{10}Sn_4$
Mol. wt.	522.63	1107.44
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$
a, Å	15.1164(4)	13.9872(3)
b, Å	12.6447(1)	19.0810(4)
c, Å	17.4594(5)	16.0374(4)
β, deg	90.549(2)	107.295(1)
V, Å^3	3337.08(13)	4086.69(16)
Z	8	4
D_c, g cm^{-3}	2.080	1.800
μ, cm^{-1}	30.24	24.67
$R1$ [$I > 2\sigma(I)$][a]	0.0419	0.0471
$wR2$ (all data)[b]	0.1150	0.1099

[a] $R = \|F_0| - |F_c\|/|F_0|$. [b] $wR = [w(F_0^2 - F_c^2)^2/w(F_0^2)^2]^{1/2}$.

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