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New Structural Forms of Organostannoxane Macrocycle Networks

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Summary: The reaction of pyrazole-3,5-dicarboxylic acid with dibenzyltin dichloride in the presence of potassium hydroxide affords a novel 2D network containing rectangular box type hexatin units interconnected by two Bz_2SnCl bridging groups. Hydrolysis of the latter affords a polymeric tape containing alternate hexatin macrocycle and tetratin ladder motifs.

Organostannoxanes are a very interesting class of compounds which have been attracting interest in view of their remarkable structural diversity[1] as well as their utility as catalysts in organic reactions.[2] More recently, organostannoxane platforms have also been used to support electroactive[3] and photoactive[4] as well as multisite coordinating ligands.[5] Organostannoxanes can be synthesized by many methods. Hydrolysis reactions of organotin precursors are potent synthetic routes. Reactions of organotin oxides/hydroxides with protic acids such as carboxylic,[3−5] phosphinic,[6a−d] seleninic,[6e] sulfonic,[7] and phosphonic acids[8] is another powerful synthetic method for assembling a variety of organostannoxanes. In contrast to the reactions of organotin precursors with monocarboxylic acids, those involving dicarboxylic acids have been much less investigated. However, the utility of the latter in the assembly of metal−organic frameworks (MOFs)[9] certainly warrants a serious investigation of the reactions of dicarboxylic acids with appropriate organotin precursors. Already, from the limited literature available, some interesting results are discernible. Höpfl and co-workers have reported the self-assembly of supramolecular architectures in the reactions of 2,5-pyridinedicarboxylic acid and R_2SnO ($R =$ Me, nBu, Ph).[10] In contrast, polymeric or discrete trinuclear macrocyclic forms were obtained in the reactions of R_2SnO with isophthalic or phthalic acid.[10b] Ma and co-workers have reported the isolation of a mixed-valent tin−oxygen cluster in the reaction of $n$$Bu_2SnO$ and ferrocenedicarboxylic acid.[3a] Intrigued by such reports, we chose to investigate the reactions of dibenzyltin dichloride with pyrazole-3,5-dicarboxylic acid, LH_3. The deprotonated form of the latter, $[L]^{3-}$, is a potentially hexadentate ligand capable of binding multiple metal sites (Chart 1).

Chart 1. Pyrazole-3,5-dicarboxylic Acid and Its Deprotonated Forms

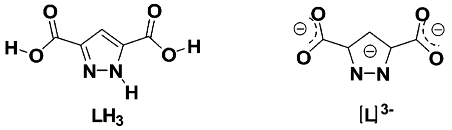
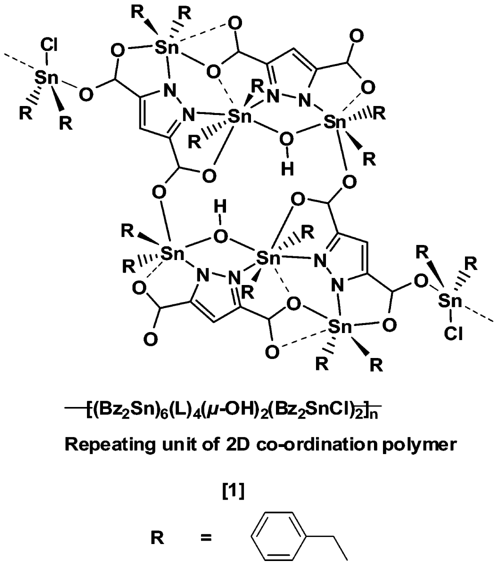

LH_3   **$[L]^{3-}$**

Chart 2. Line Diagram of 1



$-[(Bz_2Sn)_6(L)_4(\mu\text{-}OH)_2(Bz_2SnCl)_2]_n-$

Repeating unit of 2D co-ordination polymer

[1]

The reaction of pyrazole-3,5-dicarboxylic acid with $(Bz)_2SnCl_2$ in the presence of KOH in ethanol/water afforded **1**, a novel organostannoxane macrocycle network, in excellent yield (Chart 2).[11] In spite of its limited solubility in organic solvents single

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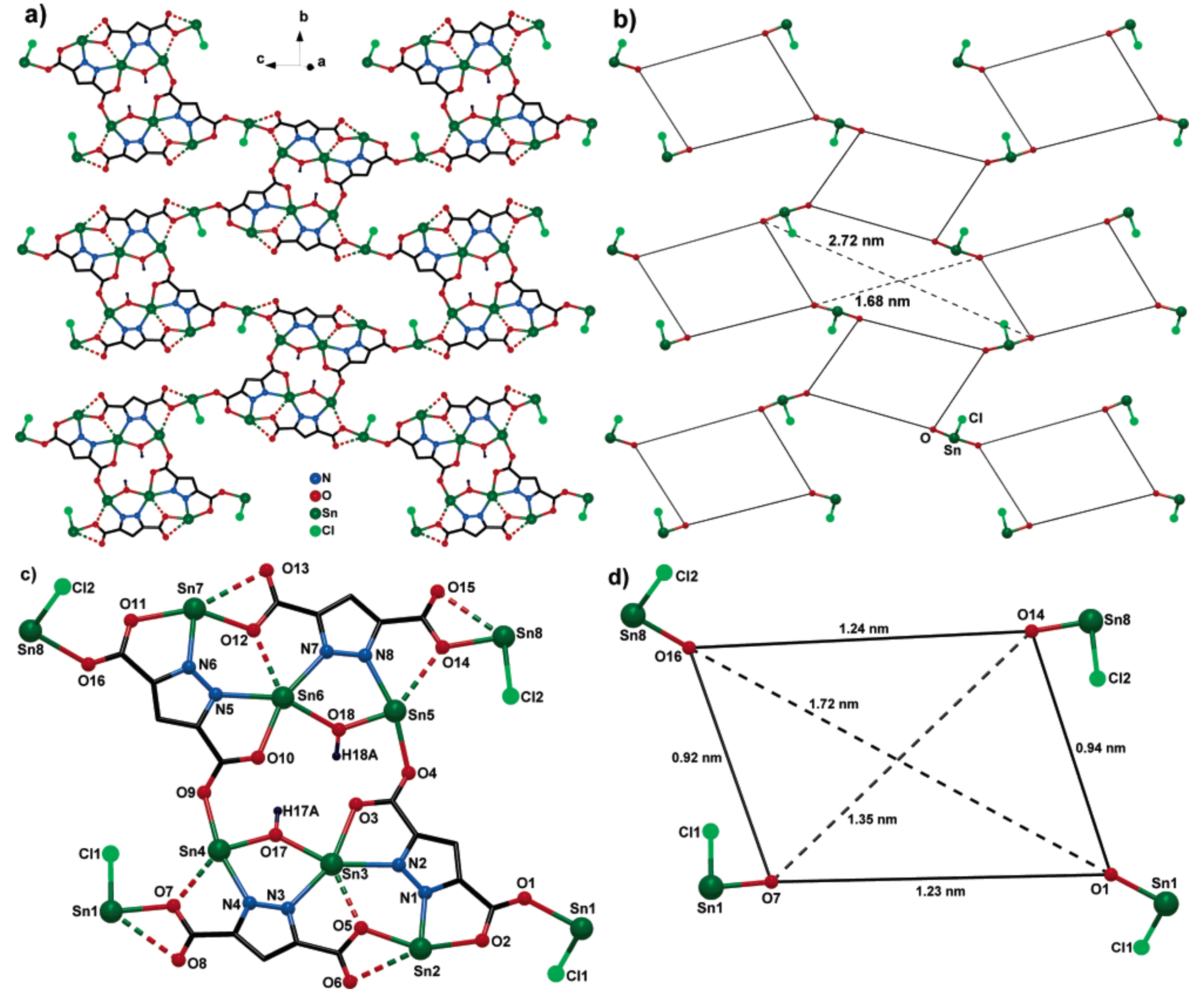
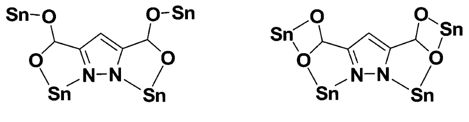


Figure 1. (a) A view of the 2-D network of **1**, showing that each rectangular hexatin unit is interconnected to four other units by Bz_2SnCl bridging groups. The 44-membered macrocyclic cavities in the 2-D network are shown. Benzyl groups have been omitted for clarity. (b) Cartoon representation of **1** showing the relative orientation of the individual columns of the 2-D network. The dimensions of the 44-membered macrocyclic cavity are also shown. (c) Repeating rectangular box unit of the 2D network **1** along with two additional Bz_2SnCl groups. Benzyl groups have been omitted for clarity. (d) Cartoon representation of the rectangular box of **1**. The edge and diagonal dimensions of the rectangular box are shown.

crystals of **1** could be obtained from its solution in a 4:2:1 mixture of tetrahydrofuran, ethanol, and methanol.[12] The bulk product was identical with the single crystals, as inferred by their powder XRD (Supporting Information). By an analysis of the powder XRD pattern of the most intense line (9.2594°), it was possible to ascertain that the particle size in the bulk product corresponds to a size of 15.95 nm.

Chart 3. Harris Notation of the Coordination Action of Pyrazole-3,5-dicarboxylate in 1



4.111111 **4.122111**

Single-crystal X-ray structure analysis of **1** showed that it possesses a remarkable network structure formed by the interlinking of macrocyclic tin frameworks (Figure 1a,b). The basic repeating unit of the two-dimensional network is a hexatin framework in a rectangular box type arrangement (Figure 1c,d). The structural descriptors of the individual rectangular boxes are as follows. The box is nanodimensional (edge 1, O16−O14 = 1.24 nm; edge 2, O7−O1 = 1.23 nm; edge 3, O16−O7 = 0.92 nm; edge 4, O14−O1 = 0.94 nm; diagonal 1, O16−O1 =

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(11) Synthesis of **1**: pyrazole-3,5-dicarboxylic acid (0.039 g, 0.22 mmol) was added to a solution of KOH (0.037 g, 0.67 mmol) in a 30 mL mixture of ethanol and water (2:1), and this mixture was stirred for 5 min to obtain a clear solution. At this stage $(Bz)_2SnCl_2$ (0.33 g, 0.89 mmol) was added. The reaction mixture was stirred for a further 3 h at room temperature and then heated to reflux for 3 h. It was cooled and filtered. The solid precipitate that was obtained was washed with water (3 × 10 mL). This was sparingly soluble in organic solvents and could be recrystallized from a mixture of tetrahydrofuran, ethanol, and methanol (4:2:1) to afford colorless crystals of **1** (0.18 g, 92% yield). Mp: >250 °C dec. Anal. Calcd for $C_{132}H_{126}Sn_8O_{22}Cl_2N_8$ (**1**): C, 49.59; H, 3.97; N, 3.50. Found: C, 49.52; H, 3.86; N, 2.98.

(12) Crystal data for **1**: monoclinic; $P2_1/c$; $a = 23.398(5)$ Å, $b = 17.539(5)$ Å, $c = 32.266(5)$ Å; $\beta = 107.938(5)°$; $V = 12598(5)$ Å^3; $T = 100(2)$ K; $Z = 4$; $D_{calcd} = 0.422$ mg m^{-3}; crystal dimensions 0.2 × 0.3 × 0.2 mm; $2\theta_{max} = 25.03°$; 65 147 reflections measured; 22 138 unique reflections ($I > 2\sigma(I)$); 1472 parameters; R1 = 0.0696; wR2 = 0.1512. Crystal data for **2**: triclinic; $P\bar{1}$; $a = 13.717(2)$ Å, $b = 17.571(3)$ Å, $c = 19.095(3)$ Å; $\alpha = 96.546(4)$, $\beta = 93.933(4)$, $\gamma = 93.317(4)°$; $V = 4551.7(13)$ Å^3; $T = 100(2)$ K; $Z = 1$; $D_{calcd} = 0.792$ mg m^{-3}; crystal dimensions 0.2 × 0.3 × 0.2 mm; $2\theta_{max} = 25.03°$; 23 865 reflections measured; 15 769 unique reflections ($I > 2\sigma(I)$); 1028 parameters; R1 = 0.0793; wR2 = 0.1680.

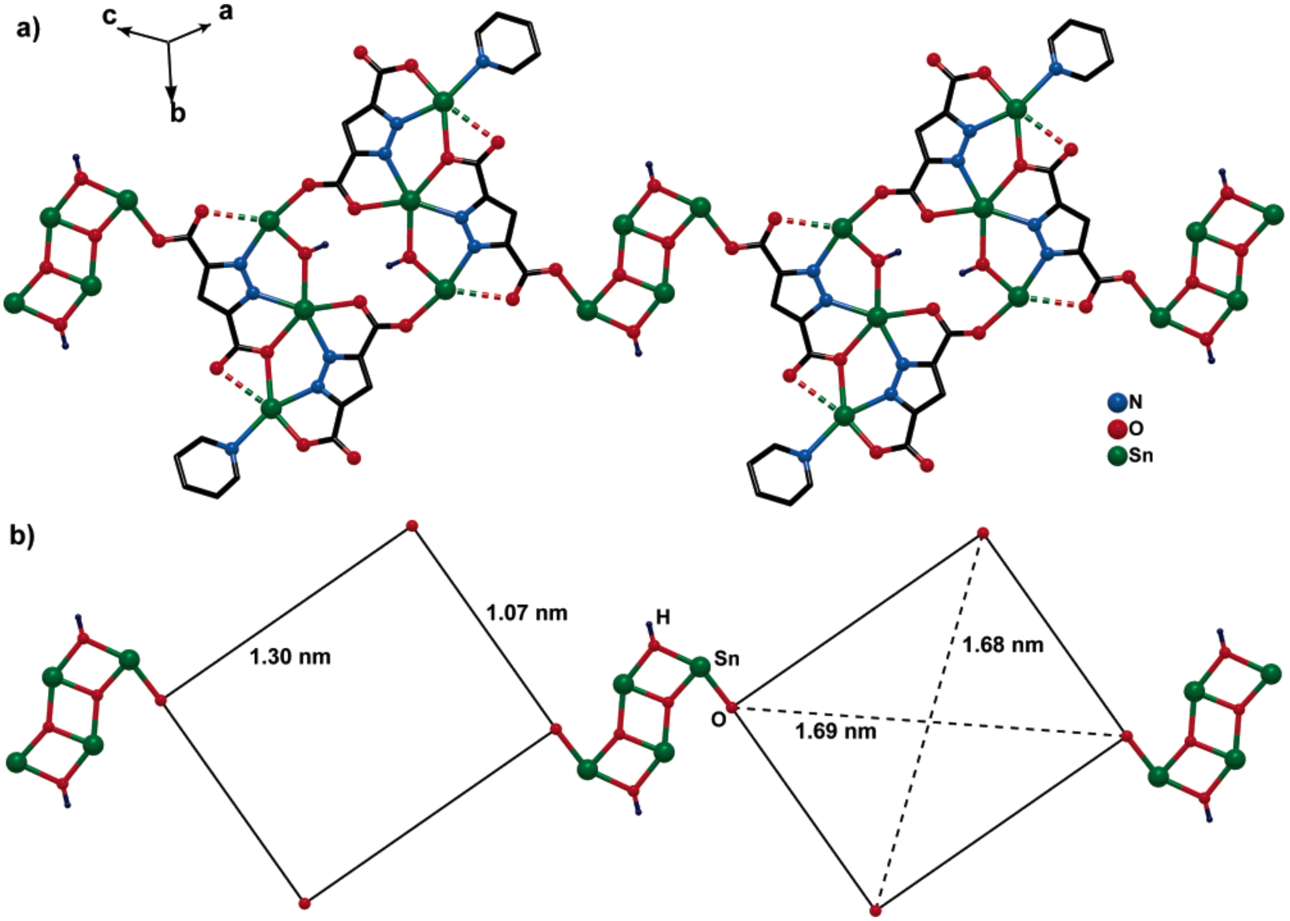
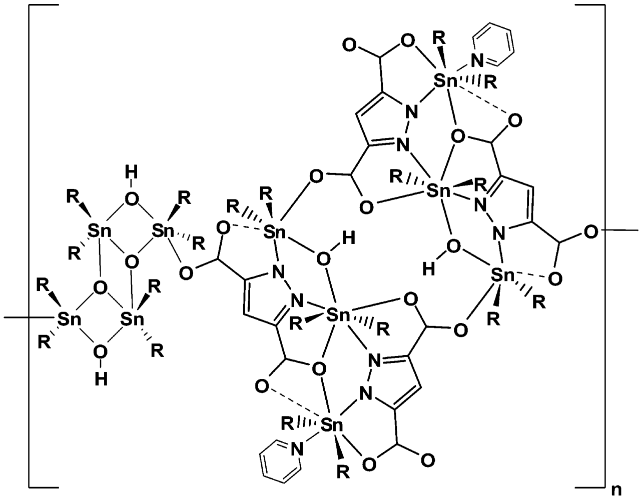


Figure 2. (a) 1D polymeric tape of **2** showing alternate macrocycle−ladder connectivity. Benzyl groups have been omitted for clarity. (b) Cartoon representation of the polymeric tape. The macrocycle dimensions are also shown.

Chart 4. Line Diagram of 2



$-[\{(Bz_2Sn)_6(L)_4(\mu\text{-}OH)_2(Py)_2\}\{(Bz_2Sn)_2(O)(\mu\text{-}OH)\}_2]_n-$

[2]

1.72 nm; diagonal 2, O14−O7 = 1.36 nm) (Figure 1d). The hexatin framework of the rectangular box consists of two symmetry-related tritin subunits (Figure 1c). The fusion of these 2 subunits also generates a central 12-membered macrocyclic ring (4Sn, 6O, 2C) within the rectangular box. A further interesting feature of the rectangular box is that it comprises a bewildering number of 16 5-membered rings (8 in each half) apart from the aforementioned 12-membered ring. The 3 tin atoms present in the subunit (Sn7, Sn6, and Sn5) are fully bound by the multiple coordination action (4.111111 and 4.122111, Harris notation;[13] Chart 3) of the pyrazole-3,5-dicarboxylate ligand. In addition, Sn6 and Sn5 are also held together by a μ-OH group. The three independent tin atoms of the tritin subunit possess different coordination environments. While Sn7 and Sn5 are hexacoordinate (1N, 3O, 2C), Sn6 is heptacoordinate (2N, 3O, 2C). The individual coordination environments of the various tin atoms of **1** are given in the Supporting Information.

In spite of the large size of the rectangular box type hexatin macrocycles, these are nearly planar. From the mean plane defined by the six tin atoms (Sn2, Sn3, Sn4, Sn5, Sn6, and Sn7) Sn2 and Sn7 deviate by −0.11 and −0.13 Å, respectively. Every rectangular box is connected to four others by bridging $(Bz)_2SnCl$ units to afford a two-dimensional network, the formation of which generates 44-membered macrocyclic cavities (Figure 1a). A closer inspection of the two-dimensional network reveals that adjacent columns within it are tilted away from each other, giving a wavy zigzag corrugated appearance (Supporting Information). The nanosized 44-membered macrocyclic cavities alternate in a given column while being continuous in a diagonal (Figure 1a). In a given column adjacent rectangular boxes are arranged like steps of a ladder and are separated by a distance of 6.983 Å. Within a diagonal the dihedral angle between the mean planes of the two rectangular boxes is 46.922(6)°.

Realizing that the two−dimensional network of **1** has hydrolyzable Sn−Cl groups in the bridging $(Bz)_2SnCl$ segments,

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we performed a mild hydrolysis of **1** in the presence of pyridine.[14] We were able to isolate **2**, a polymeric tape, in which the robust rectangular framework is retained and the bridging $(Bz)_2SnCl$ units have been transformed into bridging tetranuclear ladder $\{(Bz_2Sn)_2(O)(\mu\text{-}OH)\}_2$ units (Chart 4 and parts a and b of Figure 2).[12] The transformation of **1** into **2** is accompanied by the following events. (a) The rectangular boxes remain interconnected to each other (Sn4, Sn4′), but in one dimension, by a tetranuclear oxo/hydroxo tin cluster (Figure 2; see also the Supporting Information). (b) The coordinative unsaturation of one tin atom (Sn1) of each of the subunits of the rectangular box is fulfilled by a coordinating pyridine unit. (c) The heptacoordinate nature of Sn2 is undisturbed. The individual coordination environments of the various tin atoms of **2** are given in the Supporting Information. Due to the coordination of pyridine to Sn1, the dimensions of the rectangular box are slightly altered in **2**: the edge distances are 1.38 and 1.07 nm, while the diagonal distances are 1.68 and 1.69 nm. In fact, in **2** the rectangle is more symmetric than that found in **1**. Another interesting feature of **2** is that two independent organostannoxane structural types alternate with each other in the one-dimensional coordination polymer.

In conclusion, we report two unprecedented structural forms in organostannoxanes. The self-assembly type synthesis of **1** is clearly a result of the concerted multisite coordination action of pyrazole-3,5-dicarboxylic acid. The transformation of **1** into the one-dimensional polymer **2** is the result of the oxophilicity of tin and the stability of distannoxane-based structural entities among organostannoxane compounds. The ready synthesis of complicated structural types such as **1** and **2** demonstrates the enormous potential of multisite coordination ligands in the construction of nanoarchitectures containing organostannoxane building blocks. These studies are in progress.

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Supporting Information Available: CIF files giving crystal data for **1** and **2** and Figures S1−S6 giving additional structural information. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] Synthesis of **2**: **1** (0.1 g) was added to a mixture of pyridine (5 mL) and water (10 μL), and this mixture was stirred for 30 min to afford a clear solution. Within 1 week colorless crystals of **2** were obtained (0.04 g, 30% yield). Mp: >250 °C dec. Anal. Calcd for $C_{185}H_{171}Sn_{10}O_{22}N_{13}$ (**2**): C, 53.99; H, 4.19; N, 4.42. Found: C, 53.85; H, 4.07; N, 4.30. ^{119}Sn NMR (149 MHz, pyridine-d_5, 20 °C): δ −302.40, −313.88, −422.83 ppm.