

# Synthesis and X-ray Crystal Structure of the Novel Organotin Dication $[n\text{-Bu}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+}$ : A Lamellar Layered Structure Assisted by Intermolecular Hydrogen Bonding

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**Summary:** The reaction of  $n\text{-Bu}_2\text{SnO}$  with 2,5-dimethylbenzenesulfonic acid affords the stable monomeric tin complex  $[n\text{-Bu}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+} [2,5\text{-Me}_2\text{-C}_6\text{H}_3\text{SO}_3]^{-2}$ . The solid-state structure of the molecule reveals that the hydrogen-bonding interaction between the coordinated water and the sulfonate anion moieties leads to an unprecedented two-dimensional layered structure with a planar array of tin atoms. Further, the Lewis acidic dication complex is an extremely good catalyst for acylation of alcohols and phenols.

Clusters based on organotin compounds have been of considerable interest in recent years.<sup>1</sup> A surprisingly large structural diversity can be achieved by relatively simple synthetic variations.<sup>2</sup> Thus, several novel cluster types such as ladder,<sup>3a</sup> drum,<sup>3b</sup> O-capped cluster,<sup>3c</sup> cube,<sup>3d</sup> butterfly,<sup>3e</sup> triply and doubly bridged ladders,<sup>4</sup> etc. have been assembled and structurally characterized. Most of these clusters are prepared from the reactions of organotin precursors such as  $\text{R}_3\text{SnOSnR}_3$ ,  $[\text{R}_3\text{SnOH}]_n$ ,  $[\text{R}_2\text{SnO}]_n$ , and  $[\text{RSnOOH}]_n$ , which are hydrolysis products of the corresponding organotin halides.<sup>5</sup> Although there have been speculations on the possibility of hydrated organotin cations such as  $[\text{R}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+}$  and analogous mono- or triorganotin compounds being involved in the hydrolysis of the corresponding organotin halides, there has been only one report dealing with the X-ray structure of  $[\text{Me}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+} [\text{C}_6\text{H}_4(\text{SO}_2)_2\text{N}]^{-2}$  (**1**). The preparative details of **1** have not been published, and it appears that crystals of this compound have been

isolated in a serendipitous manner in a reaction involving  $\text{Me}_2\text{SnCl}_2$  and the silver salt of benzene-1,2-disulfonic imide.<sup>6</sup> Other attempts to isolate such compounds have resulted in the formation of dehydrated hydroxyl-bridged ditin derivatives such as  $[n\text{-BuSn}(\text{OH})(\text{OH}_2\text{Cl}_2)_2]$ ,  $[\text{((CN)}_2\text{C}_2\text{S}_2)_2\text{SnOH}]_2[\text{Et}_4\text{N}]_2$ ,<sup>7</sup> and  $[\text{R}_2\text{SnOH}(\text{H}_2\text{O})_2]^{2+} [\text{OCF}_3\text{SO}_3]^{-2}$  ( $\text{R} = n\text{-Bu}$ ,  $t\text{-Bu}$ , 2-phenylbutyl)<sup>8a,c</sup> or oxo-bridged ladders such as  $[\text{Ph}_2\text{Sn}(\text{Cl})\text{OSn}(\text{Cl})\text{Ph}_2]_2$  and  $[\text{Ph}_2\text{Sn}(\text{Cl})\text{OSn}(\text{OH})\text{Ph}_2]_2$ .<sup>9</sup> In addition, cytotoxic studies of organotin compounds have suggested the possibility of the moieties  $[\text{R}_n\text{Sn}^{\text{IV}}]^{(4-n)+}$  ( $n = 2, 3$ ;  $\text{R} = \text{Et}$ ,  $n\text{-Bu}$ ) being bound to membrane proteins, glycoproteins, or cellular proteins.<sup>10</sup> Further, organotin cations are also important from the point of view of catalytic applications involving organic reactions such as esterification.<sup>8a,b</sup>

We reasoned that weakly coordinating sulfonate ligands containing sterically hindered substituents offer the best possibility of isolating discrete hydrated organotin dications with an effective ion-pair separation in solution and possibly in the solid state as well.<sup>11,12</sup> Accordingly, we report in the following account the isolation and X-ray structural characterization of a stable diorganotin tetrahydrate,  $[n\text{-Bu}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+} [2,5\text{-Me}_2\text{C}_6\text{H}_3\text{SO}_3]^{-2}$ .

The reaction of  $n\text{-Bu}_2\text{SnO}$  with 2,5-dimethylbenzenesulfonic acid in a 1:2 stoichiometry in toluene afforded a white solid in about 74% yield, identified as the organotin dication complex  $[n\text{-Bu}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+} [2,5\text{-Me}_2\text{C}_6\text{H}_3\text{SO}_3]^{-2}$  (**2**)<sup>13</sup> (Scheme 1). Consistent with its formulation, conductivity studies on **2** revealed that it is a 1:2 electrolyte with a specific conductivity of  $946 \mu\text{S cm}^{-1}$  and a molar conductivity of  $158 \text{ S cm}^2 \text{ mol}^{-1}$  ( $3 \text{ mmol L}^{-1}$  in  $\text{CH}_3\text{OH}$ ). The  $^{119}\text{Sn}$  NMR of **2** shows a

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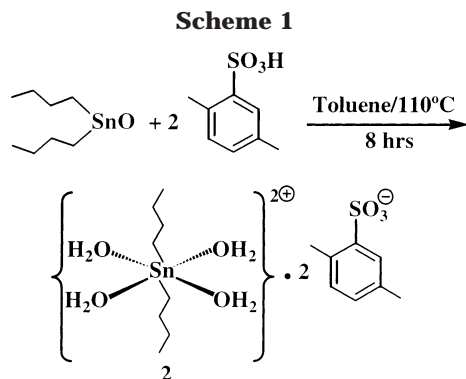
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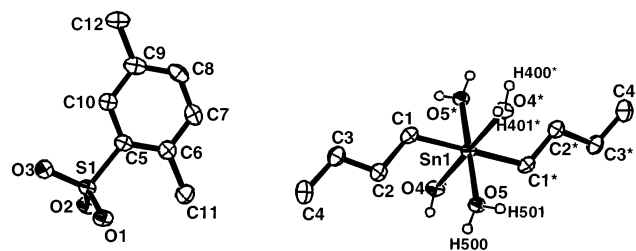
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single resonance at  $-360.0$  ppm, which is characteristic of a  $C_2O_4$  environment around tin.<sup>14</sup>

The X-ray crystal structure<sup>15</sup> of **2** is shown in Figure 1. This reveals that the tin atom is octahedrally coordinated; the organo ligands bind in a trans fashion. The tetraaquo diorganotin dication exhibits crystallographic  $P1$  symmetry. Although the structure is reminiscent of a *Werner type* coordination complex<sup>16</sup> with four classical ligands in the form of water molecules, it also possesses a typical organometallic motif in the form of the Sn–alkyl groups. The average Sn–O bond length observed in **2** is  $2.271(3)$  Å, and the O–Sn–O bond angles observed are typical of a planar coordination environment:  $O4-Sn1-O4^*$ , =  $180.00(10)^\circ$ ,  $O5-Sn1-O5^*$  =  $180.00(14)^\circ$ . These metric parameters are similar to those observed in **1**. Although the sulfonate anions do not coordinate to tin, they are involved in an extensive intermolecular O–H–O hydrogen-bonding interaction with the coordinated water molecules around tin (Figure 2a). Essentially every sulfonate anion is associated in bridging three different tin centers through the tripodal  $RSO_3^-$  motif by means of four O–H–O bonds. While one of the sulfonate oxygens (O31) is involved in a bifurcated hydrogen bond with two water molecules arising from two neighboring



**Figure 1.** ORTEP diagram of **2**. All the hydrogens have been omitted, except those present on the water molecules. Selected bond lengths (Å) and angles (deg): Sn1–O4 =  $2.272(4)$ , Sn1–O5 =  $2.270(3)$ ; O4–Sn1–O5 =  $95.55(9)$ , O4–Sn1–O5\* =  $84.45(9)$ , C–Sn1–C1\* =  $179.99(13)$ .

tin centers (O42 and O53), the other two oxygens (O11 and O21) are involved in hydrogen bonds with two water molecules from the *same* tin center (O41' and O51') (Figure 2b). The metric parameters involved in these hydrogen bonds are summarized in Figure 2 and point to the fact that these are essentially strong hydrogen bonds. Further, all the hydrogen bonds are nearly linear, with the O–H–O bond angles being very close to  $180^\circ$ . The overall result of the hydrogen bonding between the coordinated water molecules around tin and the sulfonate anion is the formation of a two-dimensional layered structure containing a series of rings. Thus, each tin is at the center of four rings: viz., two eight-membered  $Sn_2O_6$  (A and A'; Figure 2a) and two six-membered  $SnO_4S$  rings (B and B'; Figure 2a). In addition, two other eight-membered rings  $S_2O_6$  (C and C'; Figure 2a) are formed, which connect different rows to afford the two-dimensional layered structure. Within any given row containing the tins, a continuous array of eight-membered  $Sn_2O_6$  rings is present. The arrangement of individual sulfonate anions is such that they are alternately above and below a triangular array of tins in a given layer (Figure 2). Another interesting feature of the supramolecular organization in compound **2** is that the rings C and C' of alternate two-dimensional layers eclipse each other to form tubular columns with an average diameter of  $5.743$  Å (Figure 2c). Further, all the tins in a given layer are in a completely planar array. Such an architecture is unknown in organotin compounds, although recently there has been a report on a graphite-like structure being adopted by the oxonium ion  $[(Me_3Sn)_3O]Cl$ .<sup>17</sup> Compound **2** represents the first example of the utilization of sulfonates for the formation of layered structures in organotin compounds. It is of interest to note that previously Ward and co-workers have utilized organodisulfonates along with guanidinium cations for the assembly of pillared structures,<sup>18</sup> while Shimizu and Squattrito have utilized various organosulfonates in coordinative interactions with various metal ions to afford layered and nonlayered structures.<sup>19,20</sup>

Compound **2** has been tested for its catalytic activity in esterification reactions involving acylation of alcohols and phenols. It is observed that even with very low molar concentrations of **2** acylation reactions occur rapidly at room temperature, affording the products in

(13) Synthesis of **2**: a mixture of  $n\text{-Bu}_2\text{SnO}$  (0.33 g, 1.34 mmol) and 2,5-dimethylbenzenesulfonic acid (0.50 g, 2.68 mmol) in toluene (60 mL) was heated under reflux for 8 h using a Dean–Stark apparatus to remove the water formed in the reaction by azeotropic distillation. A white puffy solid formed in the reaction was filtered by a sintered funnel and dried. This was analytically pure and was shown to be **2**. Crystals suitable for single-crystal X-ray diffraction were obtained by the slow evaporation of a solution of **2** in a mixture of  $CH_2Cl_2$  and  $CH_3OH$  (1:1) at room temperature. Yield: 0.66 g (74%). Mp:  $273^\circ C$ . Anal. Calcd for  $C_{24}H_{44}O_{10}S_2Sn$  (675.40): C, 42.68; H, 6.56. Found: C, 42.90; H, 6.15. IR (KBr,  $cm^{-1}$ ): 3427 (br,  $\nu(H_2O)$ ), 1265 (s,  $\nu(SO_3^-)$  asym str), 1195 (s,  $\nu(SO_3^-)$  asym str), 1095 (s,  $\nu(SO_3^-)$  sym str), 1030 (s,  $\nu(SO_3^-)$  ionic), 630 (m,  $\nu(C-S)$  str).  $^1H$  NMR (200 MHz,  $CD_3OD$ ):  $\delta$  0.87 (t,  $J = 7.25$  Hz, 6H,  $CH_3$ ), 1.33 (m, 8H,  $CH_2CH_2$ ), 1.66 (m, 4H,  $SnCH_2$ ), 7.17 (s, 4H, aromatic), 7.73 (s, 2H, aromatic), 2.33 (s, 6H,  $Ar-CH_3$ ), 2.59 (s, 6H,  $Ar-CH_3$ ).  $^{119}Sn$  NMR (150 MHz,  $CD_3OD$ ):  $\delta$   $-360.04$  (s).

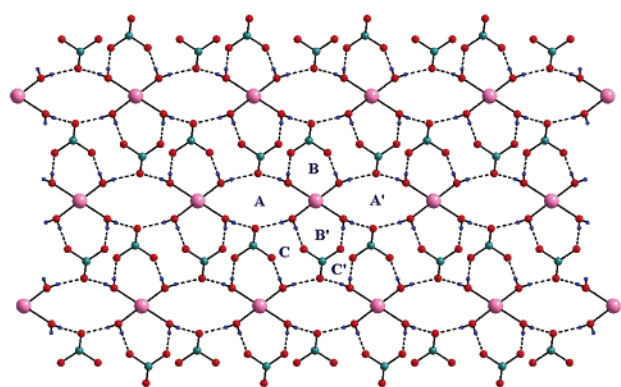
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(15) Crystal data for **2**: crystal dimensions  $0.3 \times 0.15 \times 0.11$  mm, molecular formula  $C_{24}H_{44}O_{10}S_2Sn$ ,  $M_r = 675.40$ , triclinic, space group  $P1$ ,  $a = 7.804(9)$  Å,  $b = 7.9960(10)$  Å,  $c = 14.3421(17)$  Å,  $\alpha = 95.784(2)^\circ$ ,  $\beta = 98.359(2)^\circ$ ,  $\gamma = 118.976(2)^\circ$ ,  $V = 759.34(16)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 150(2)$  K,  $D_{\text{calcd}} = 1.477$  mg  $m^{-3}$ , Bruker AXS Smart Apex CCD diffractometer, Mo  $K\alpha$  radiation, 3895 reflections collected, 2629 independent reflections ( $R_{\text{int}} = 0.0189$ ),  $R1 = 0.0379$ ,  $wR2 = 0.0979$  ( $I > 2\sigma(I)$ ),  $R1 = 0.0387$ ,  $wR2 = 0.0986$  (all data),  $GOF = 1.057$ . The maximum and minimum electron densities are  $2.294$  and  $-1.250$  e Å<sup>-3</sup>, respectively. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least squares on  $F^2$  using SHELXL-97. All the hydrogens of the water molecule were located from the difference map and refined.

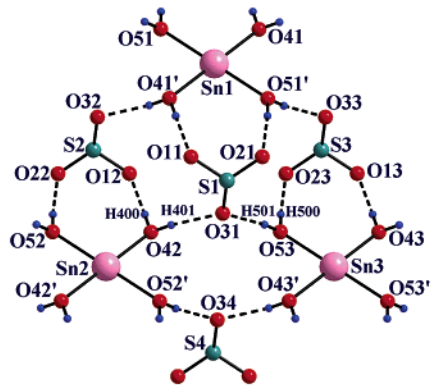
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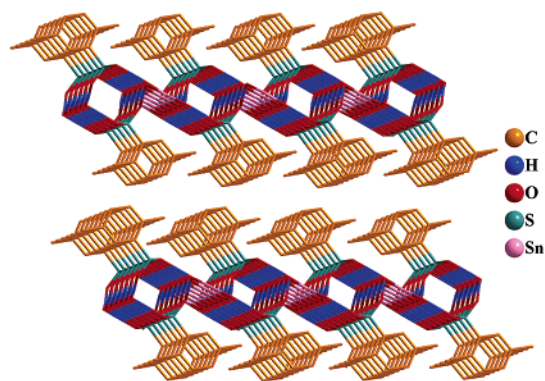
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(a)



(b)



(c)

**Figure 2.** (a) View of a single layer of **2** along the “c” axis showing the two-dimensional supramolecular lamellar network. (b) Repeating structural motif of the supramolecular network of **2**. The metric parameters are as follows: O41'–H400 = 0.803(43) Å, H400...O11 = 1.869(43) Å, O41'–O11 = 2.672(4) Å, O41'–H400...O11 = 178.96(382)°, symmetry  $-x, -y, 1 - z$ , O42–H401 = 0.796(37) Å, H401...O31 = 1.925(40) Å, O42–O31 = 2.717(5) Å, O42–H401...O31 = 173.61(451)°, symmetry  $-1 + x, -1 + y, -1 + z$ , O51'–H500 = 0.809(41) Å, H500...O21 = 1.872(40) Å, O51'–O21 = 2.626(5) Å, O51'–H500...O21 = 172.12(381)°, symmetry  $-x, -y, 1 - z$ , O53–H501 = 0.806(53) Å, H501...O31 = 1.911(53) Å, O53–O31 = 2.713(4) Å, O53–H501...O31 = 172.93(484)°, symmetry  $x, -1 + y, -1 + z$ . The butyl and the aromatic substituents on tin and sulfonate are not shown for clarity. (c) View of the tubular array of two different layers of **2** formed by rings C and C' along the “a” axis. The aromatic ring and the butyl chains occupy the interlayer region. The butyl groups on tin atoms are not shown for clarity.

nearly quantitative yields (Table 1). Although esterification reactions are catalyzed by neutral organotin compounds, these involve longer reaction times (~24 h).<sup>21</sup> In this regard the catalytic behavior of **2** is

**Table 1.** Acetylation of Alcohols and Phenols<sup>a</sup>

		ROH $\xrightarrow[30^\circ\text{C}]{\text{Ac}_2\text{O}/\text{cat.}}$ ROAc		
Entry	Substrate	Cat. Conc.(mol %) <sup>b</sup>	Rxn. time <sup>c</sup>	Yield (%) <sup>d</sup>
1		0.1	140 min.	96
		0.05	145 min.	98
2		0.1	140 min.	95
		0.05	4 h	90
3		0.1	145 min.	83
		0.2	140 min.	93
4		0.1	70 min.	85
		0.2	50 min.	98

<sup>a</sup> Reaction conditions: ROH (3 mmol); Ac<sub>2</sub>O (1 mL). <sup>b</sup> Neutral distannoxane catalysts with general formula R<sub>2</sub>(X)SnO<sub>2</sub>Sn(Y)R<sub>2</sub> (X = Cl, –NCS; Y = Cl, OH, –NCS) catalyses the reaction with higher molar concentrations and longer reaction times.<sup>14</sup> <sup>c</sup> Recently, cationic organotin triflate complexes such as [R<sub>2</sub>Sn(OH)(OTf)(H<sub>2</sub>O)]<sub>2</sub> were found to be efficient catalysts for acetylation of alcohols.<sup>8a,b</sup> <sup>d</sup> Isolated yields.

reminiscent of the recently reported organotin cationic complexes by Otera and co-workers.<sup>8a,b</sup> Thus it appears that the Lewis acidic nature of the tin center in **2** is accentuated by the dipositive charge on the complex, allowing it to function as a better catalyst.

In conclusion we have assembled and structurally characterized the novel organotin dication complex [n-Bu<sub>2</sub>Sn(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup>[2,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub>]<sup>−2</sup>, containing two alkyl groups and four water molecules attached to tin. The sulfonate anion is noncoordinating to tin but is involved in extensive hydrogen bonding with the coordinated water molecules to afford a two-dimensional layered structure containing a planar array of tin atoms. The organotin dication complex is also catalytically active for esterification reactions involving the acylation of alcohols as well as phenols. It is expected that by adopting this strategy hydrated organotin compounds with even higher charges can be stabilized.

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**Supporting Information Available:** Figure S1, showing the planar array of tin atoms, and text and tables giving X-ray crystal structure data for **2**, including detailed bond length and bond angle parameters (Tables S1–S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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