5644 *Organometallics* **2004,** *23,* 5644−5647

Hexameric Organotincarboxylates with Cyclic and Drum Structures

Ganesan Prabusankar and Ramaswamy Murugavel*

Department of Chemistry, Indian Institute of Technology-Bombay,
Powai, Mumbai 400 076, India

Received June 8, 2004

*Summary: The interaction of 3,5-diisopropylsalicylic acid (DIPSA) with [^{n}Bu$_2$Sn(O)] in benzene proceeds with elimination of water to produce stannoxane [^{n}Bu$_2$Sn(3,5-^{i}Pr$_2$C$_6$H$_2$(O)(COO))]$_6$ (**1**), while an analogous reaction of DIPSA with [^{n}BuSn(O)(OH)] leads to the isolation of [^{n}BuSn(O)(3,5-^{i}Pr$_2$C$_6$H$_2$(OH)(COO))]$_6$ (**2**). The new products have been characterized by elemental analysis and EI-MS, IR, and NMR (^{1}H, ^{13}C, and ^{119}Sn) spectroscopy. The molecular structure of **1** determined by single-crystal X-ray diffraction studies reveals a rare cyclic hexameric structure. The tin atoms are pentacoordinated with distorted trigonal-bipyramidal geometry. Complex **2** is also a hexameric cluster, but existing in a more common drum-like structure where the tin centers are hexacoordinated.*

Introduction

Organotin compounds are of interest in view of their considerable structural diversity.[1−9] Among the organotin compounds, the most ubiquitous are the organotin carboxylates.[2−5] The reactions of organotin precursors with carboxylic acids have been studied in considerable detail. Depending on the carboxylic acid used and the stoichiometry of the reactants, several products such as monomers, dimers, tetramers, oligomeric ladders, and hexameric durms have been isolated.[2−5] It has also been demonstrated that other structural types are formed due to the presence of additional coordinating sites along with a carboxylate moiety.[4−7] Thus, it appears that the preference of a particular tin carboxylate to adopt a given structure stems from a combination of steric and electronic factors.

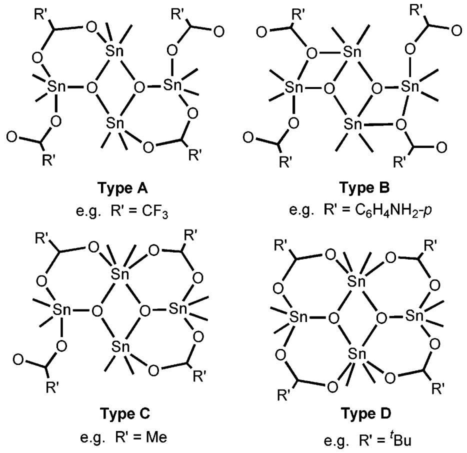

Type A
e.g. R' = CF$_3$
Type B
e.g. R' = C$_6$H$_4$NH$_2$-*p*
Type C
e.g. R' = Me
Type D
e.g. R' = ^{t}Bu

Figure 1. Known structural types of tetrameric diorganotin-oxo-monocarboxylates.

Diorganotin carboxylates have been an extensively investigated class of compounds over the last several decades. The most common reaction product of a reaction between R$_2$SnO (or R$_2$SnX$_2$) and R′COOH (in a 1:2 ratio) is the hexacoordinate mononuclear tin dicarboxylate of formula [R$_2$Sn(OOCR′)$_2$], where the tin center exists in a skewed trapezoidal geometry.[6] The same reaction when carried out with a strict 1:1 stoichiometry of the reactants yields tetrameric compounds [R$_2$(OOCR′)SnOSn(OOCR′)]$_2$, which exist in four different structural types (types A−D) as shown in Figure 1.[4,7] On the other hand, monoorganotin carboxylates are predominately known to exist as drum-shaped hexameric clusters,[8] although a few examples of other structural types are also known.[9] The simultaneous presence

---

* Corresponding author. Fax: +(22) 2572 3480. Tel: +(22) 2576 7163. E-mail: rmv@iitb.ac.in.

(1) Evans, C. J. *Chemistry of Tin*; Smith, P. J., Ed.; Blackie Academic and Professional: London, 1998; p 442.

(2) Holmes, R. R. *Acc. Chem. Res.* **1989**, *22*, 190.

(3) Tiekink, E. R. T. *Appl. Organomet. Chem.* **1991**, *5*, 1.

(4) Tiekink, E. R. T. *Trends Organomet. Chem.* **1994**, *1*, 71.

(5) Chandrasekhar, V.; Nagendran, S.; Baskar, V. *Coord. Chem. Rev.* **2002**, *235*, 1.

(6) Gielen, M.; El Khloufi, A.; Biesemans, M.; Willem, R.; Meunier-Piret, J. *Polyhedron* **1992**, *11*, 1861. (b) Teoh, S.-G.; Ang, S.-H.; Declercq, J.-P. *Polyhedron* **1997**, *16*, 3729. (c) Teoh, S.-G.; Ang, S.-H.; Looi, E.-S.; Keok, C.-A.; Teo, S.-B.; Declercq, J.-P. *J. Organomet. Chem.* **1996**, *523*, 75. (d) Chandrasekhar, V.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *Inorg. Chem.* **1988**, *27*, 958.

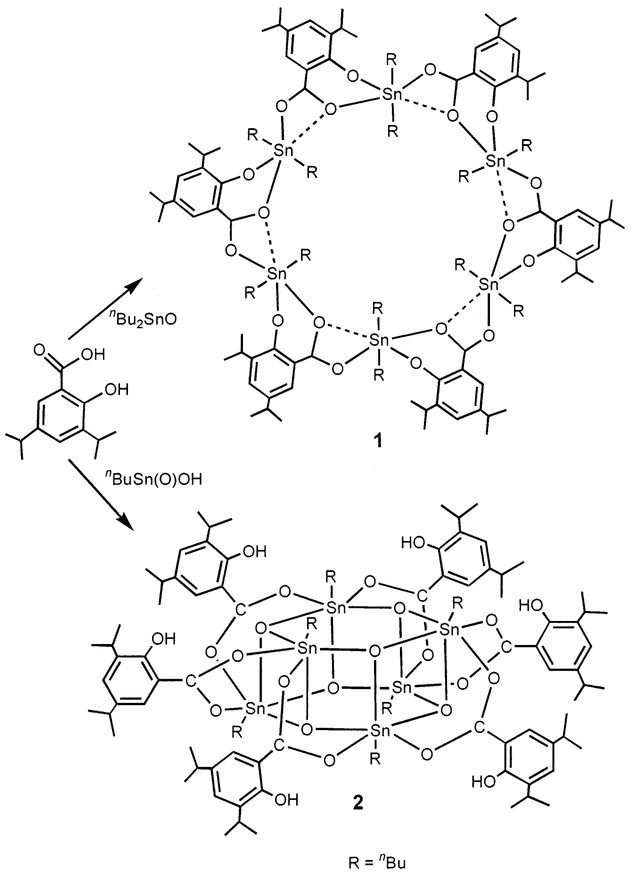
(7) (a) Holmes, R. R.; Schmid, C. G.; Chandrasekhar, V.; Day, R. O.; Holmes, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 1408. (b) Kemmer, M.; Dalil, H.; Biesemans, M.; Martins, J. C.; Mahieu, B.; Horn, E.; de Vos, D.; Tiekink, E. R. T.; Willem, R.; Gielen, M. *J. Organomet. Chem.* **2000**, *608*, 63. (c) Kovala-Demertzi, D.; Kourkoumelis, N.; Koutsodimou, A.; Moukarika, A.; Horn, E.; Tiekink, E. R. T. *J. Organomet. Chem.* **2001**, *620*, 194. (d) Vatsa, C.; Jain, V. K.; Keshavdas, T.; Tiekink, E. R. T. *J. Organomet. Chem.* **1991**, *408*, 157. (e) Tiekink, E. R. T.; Gielen, M.; Bouhdid, A.; Biesemans, M.; Willem, R. *J. Organomet. Chem.* **1995**, *494*, 247. (f) Gielen, M.; Bouhdid, A.; Willem, R.; Bregadze, V. I.; Ermanson, L. V.; Tiekink, E. R. T. *J. Organomet. Chem.* **1995**, *501*, 277. (g) Ribot, F.; Sanchez, C.; Meddour, A.; Gielen, M.; Tiekink, E. R. T.; Biesemans, M.; Willem, R. *J. Organomet. Chem.* **1998**, *552*, 177. (h) Dokorou, V.; Ciunik, Z.; Russo, U.; Kovala-Demertzi, D. *J. Organomet. Chem.* **2001**, *630*, 205. (i) Ng, S. W.; Wei, C.; Kumar Das, V. G. *J. Organomet. Chem.* **1991**, *412*, 39. (j) Vatsa, C.; Jain, V. K.; Das, T. K.; Tiekink, E. R. T. *J. Organomet. Chem.* **1991**, *418*, 329. (k) Xiong, R.-G.; Zuo, J.-L.; You, Z.-Z.; Fun, H.-K.; Raj, S. S. S. *Organometallics* **2000**, *19*, 4183. (l) Lockhart, T. P.; Manders, W. F.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 6611.

(8) (a) Kumara Swamy, K. C.; Said, M. A.; Nagabrahmanandachari, S.; Poojary, D. M.; Clearfield, A. *J. Chem. Soc., Dalton Trans.* **1998**, 1645. (b) Chandrasekhar, V.; Nagendran, S.; Bansal, S.; Kozee, M. A.; Powell, D. R. *Angew. Chem., Int. Ed.* **2000**, *39*, 1833. (c) Chandrasekhar, V.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1985**, *24*, 1970. (d) Chandrasekhar, V.; Schmid, C. G.; Burton, S. D.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1987**, *26*, 1050. (e) Day, R. O.; Chandrasekhar, V.; Kumara Swamy, K. C.; Holmes, J. M.; Burton, S. D.; Holmes, R. R. *Inorg. Chem.* **1988**, *27*, 2887.

(9) Allcock, N. W.; Roe, S. M. *J. Chem. Soc., Dalton Trans.* **1989**, 1589.

10.1021/om049584u CCC: $27.50

Scheme 1. Synthesis of $[^n\mathrm{Bu}_2\mathrm{Sn}(3{,}5\text{-}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_2(\mathrm{O})(\mathrm{COO}))]_6$ (1) and $[^n\mathrm{BuSn}(\mathrm{O})(3{,}5\text{-}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_2(\mathrm{OH})(\mathrm{COO}))]_6$ (2)



of functional groups, i.e., $-$OH, $-$NH$_2$, etc. (in addition to carboxylate functionality), in the ligand framework has also been investigated,[10] and it has been found that the acidic protons of these groups, in general, do not react with tin, although they play an important role in the formation of supramolecular frameworks in the solid state, through X$-$H$\cdots$O hydrogen bonds.

Continuing our studies on the reactions of main group metal cations with substituted benzoic acids such as amino, hydroxyl, and mercapto benzoic acids,[11] and with the aim to unravel the effect of bulky carboxylic acids on the formation of the final structures as well as the role of additional functional groups, we have chosen the sterically encumbered 3,5-diisopropylsalicylic acid (DIPSA) as ligand and investigated its reaction with organotin derivatives $[^n\mathrm{Bu}_2\mathrm{Sn}(\mathrm{O})]$ and $[^n\mathrm{BuSn}(\mathrm{O})(\mathrm{OH})]$.

Results and Discussion

Synthesis and Spectral Characterization of $[^n\mathrm{Bu}_2\mathrm{Sn}(3{,}5\text{-}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_2(\mathrm{O})(\mathrm{COO}))]_6$ (1). The reaction between di-*n*-butyltin oxide and DIPSA, by azeotropic removal of water generated in benzene, generates the new organotin complex $[^n\mathrm{Bu}_2\mathrm{Sn}(3{,}5\text{-}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_2(\mathrm{O})(\mathrm{COO}))]_6$ (**1**) (Scheme 1). The reaction is likely to have proceeded through the generation of the $[^n\mathrm{Bu}_2\mathrm{Sn}(3{,}5\text{-}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_2(\mathrm{O})(\mathrm{COO}))]$ unit, which then oligomerizes through carboxylate bridging to afford the hexameric cyclic compound **1**. Quite surprisingly, either a monomeric diorganotin dicarboxylate $[\mathrm{R}_2\mathrm{Sn}(\mathrm{OOCR}')_2]$ or any of the oligomeric diorganotin-oxo-carboxylate types shown in Figure 1 do not form in the present case. The formation of the hexameric cyclic cluster **1** is probably due to the rejection of a second sterically overcrowded DIPSA ligand in the coordination sphere of tin as well as the ability of the ligand to utilize its phenolic proton for reaction with the metal to form a chelate ring.

Compound **1** is a stable colorless crystalline solid melting at 203$-$205 °C. Analytically pure **1** has been characterized by elemental analysis and EI-MS, IR, and multinuclear NMR spectroscopy (^{1}H, ^{13}C, and ^{119}Sn). The heaviest ion appearing in the EI-MS of **1** (70 eV) at *m/z* 1303 is attributable to the loss of an *n*-butyl group from the trimeric unit ($\mathrm{M}^+/2 - {}^n\mathrm{Bu}$ fragment). Molecular weight determination by the cryoscopic freezing point method in benzene provided a molecular weight of 972 for **1**, suggesting that the molecule exists as a dimer and not as a hexamer in solution. This is not surprising in view of the fact that the related hexameric compound $[^n\mathrm{Bu}_2\mathrm{Sn}(\mathrm{OOCCH}_2\mathrm{CH}_2\mathrm{S})]_6$ also exists as monomer, dimer, or trimer in solution.[12]

In the IR spectrum of **1**, the absence of broad $\bar{\nu}_{\mathrm{OH}}$ absorption of DIPSA in the range 2500$-$3400 cm^{-1} indicates a double deprotonation of the ligand during coordination to the tin atom. The IR spectrum of compound **1** exhibits an unsymmetrical doublet for the carboxylate asymmetric stretching, $\bar{\nu}_{\mathrm{COO}}$, centered at 1530 cm^{-1}.[13] The $\bar{\nu}_{\mathrm{Sn-O}}$ is observed at 680 cm^{-1}.[14] The ^{1}H NMR spectral integration and the ^{13}C NMR spectral pattern are consistent with the formulation of the product. The ^{119}Sn NMR spectrum exhibits a sharp singlet at δ -225.8 ppm, suggesting the equivalence of all six tin atoms. This chemical shift value also indicates that the molecular structure of **1** is quite different from any of the four well-known types of diorganotin carboxylates listed in Figure 1, which actually show two separate resonances in the ^{119}Sn NMR spectrum for the exo ($\mathrm{Sn}_2\mathrm{O}_2$) and endo tin centers between -175 and -225 ppm.[5]

Structure of $[^n\mathrm{Bu}_2\mathrm{Sn}(3{,}5\text{-}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_2(\mathrm{O})(\mathrm{COO}))]_6$ (1). Crystals of **1** suitable for X-ray diffraction were obtained from a petroleum ether/dichloromethane solution at 0 °C. A perspective view of the molecular structure **1** is shown in Figure 2. The molecule consists of six $^n\mathrm{Bu}_2\mathrm{Sn}$ fragments linked together by six bridging $3{,}5\text{-}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_2(\mathrm{O})(\mathrm{COO})$ ligands to afford a hexanuclear $\mathrm{Sn}_6\mathrm{O}_{18}$ macrocycle, which can be best described as a

---

[10] (a) Narula, S. P.; Bharadwaj, S. K.; Sharma, H. K.; Mairesse, G.; Barbier, P.; Nowogrocki, G. *J. Chem. Soc., Dalton Trans.* **1988**, 1719. (b) Narula, S. P.; Kaur, S.; Shankar, R.; Bharadwaj, S. K.; Chadha, R. K. *J. Organomet. Chem.* **1996**, *506*, 181. (c) Smith, P J.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M.; Holmes, R. R. *Inorg. Chem.* **1986**, *25*, 2495.

[11] (a) Murugavel, R.; Karambelkar, V. V.; Anantharaman, G.; Walawalkar, M. G. *Inorg. Chem.* **2000**, *39*, 1381. (b) Murugavel, R.; Baheti, K.; Anantharaman, G. *Inorg. Chem.* **2001**, *40*, 6870. (c) Murugavel, R.; Banerjee, S. *Inorg. Chem. Commun.* **2003**, *6*, 810. (d) Murugavel, R.; Anantharaman, G.; Sathiyendiran, M.; Krishnamurthy, D.; Walawalkar, M. G. *Proc. Ind. Acad. Sci. (Chem. Sci.)* **2000**, *112*, 273. (e) Murugavel, R.; Karambelkar, V. V.; Anantharaman, G. *Ind. J. Chem., Sect. A* **2000**, *39*, 843.

[12] Lockhart, T. B. *Organometallics* **1988**, *7*, 1438.

[13] An unsymmetrical doublet for the carboxylate asymmetric stretching around 1550 cm^{-1} in the IR spectrum is interpreted as a ladder structure (and probably other structures as well, where the carboxylate ligands asymmetrically bridge tin centers), whereas a symmetrical doublet is observed for the drum structure in the same region (cf. ref 15a).

[14] Socrates, G. *Infrared Characteristic Group Frequencies*; Wiley-VCH: Great Britain, 1980.

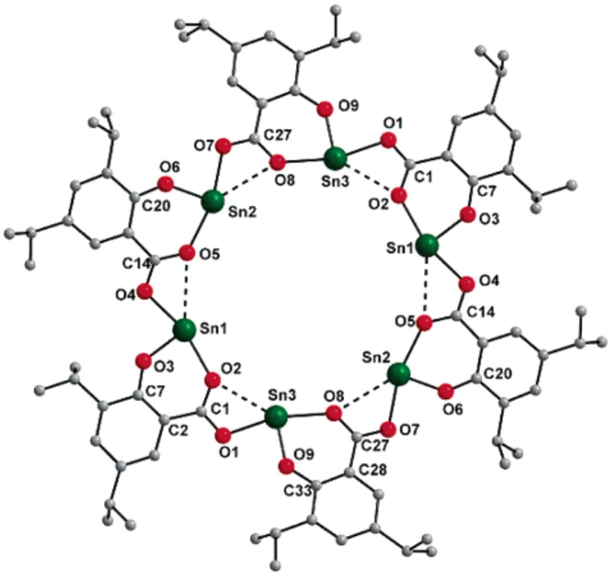
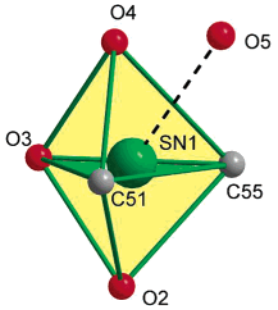


Figure 2. Molecular structure of $[^{n}Bu_2Sn(3,5\text{-}^{i}Pr_2C_6H_2(O)(COO))]_6$ (**1**) (the ^{n}Bu groups on tin are omitted for clarity). Selected bond distances (Å): Sn(1)−O(3) 1.987(4), Sn(1)−O(4)[a] 2.162(4), Sn(1)−O(2) 2.225(4), Sn(1)···O(5) 2.983(4), Sn(1)−C(51) 2.137(7), Sn(1)−C(55) 2.115(6), Sn(2)···O(8) 2.958(5), Sn(3)···O(2) 2.825(3); *a* = 1−*x*, 2−*y*, 1−*z*.

carbon-studded *molecular bangle* (Figure 2). As described vide supra, hexameric clusters are unknown among diorganotin carboxylates, except for $[^{n}Bu_2Sn(OOCCH_2CH_2S)]_6$,[12] and a tetrameric structure is the most preferred form of aggregation for these compounds. Similarly, the bridging-oxo ligand (μ_3-O) and the central Sn_2O_2 moiety, which are very common in diorganotin carboxylate chemistry,[3−5] are absent in **1**.

The role commonly played by the μ_3-O ligand in diorganotin carboxylate chemistry is taken care of in the present case by the phenoxy oxygen which is present in the position ortho to the carboxyl group of the DIPSA ligand. Thus DISPA acts as a di-negative ligand through both carboxylate and phenoxy functionalities. In addition, the second oxygen atom of the carboxylate group (which is not involved in chelation to the metal) bridges a neighboring $[^{n}Bu_2Sn(3,5\text{-}^{i}Pr_2C_6H_2(O)(COO))]$ unit in a concerted fashion to complete a cyclic hexameric structure. These six tin atoms and the 18 oxygen atoms in the macrocycle almost lie in a plane. The aryl ring of the DIPSA ligands also lies not far away from the mean plane formed by the tin and oxygen atoms, thus providing an overall planar structure for the molecule. The *n*-butyl groups on tin and the isopropyl groups on DIPSA are, however, positioned above and below the plane defined by the tin and oxygen atoms.

The tin atoms in **1** are essentially pentacoordinated (Figure 3). Each of the tin atoms is bound to two *n*-butyl groups, two carboxylate oxygen atoms, and a phenoxide oxygen. A weak sixth coordination also exists for all three crystallographically independent tin atoms, which originates from the carboxylate oxygen atoms O(2), O(5), and O(8) to the neighboring tin atoms, as shown in Figure 2 as broken lines. Including this weak interaction to the metal, the DIPSA acts as a di-negative tetradentate chelating-bridging ligand in **1**. Such a ligating behavior, to the best of our knowledge, is unknown among the coordination compounds formed by DIPSA. The geometry around the tin atoms can be best described as distorted trigonal bipyramidal. Figure 3 shows that there are six angles close to 90° (80.5(2)−97.4(2)°), three angles close to 120° (109.1(2)−137.7(3)°), and one angle close to 180° (163.4(2)°).



O(4)[a]–Sn(1)–O(2)	163.4(2)
O(3)–Sn(1)–C(55)	112.4(2)
O(3)–Sn(1)–C(51)	109.1(2)
C(55)–Sn(1)–C(51)	137.7(3)
O(3)–Sn(1)–O(4)	80.5(2)
C(55)–Sn(1)–O(4)	97.4(2)
C(51)–Sn(1)–O(4)	96.6(2)
O(3)–Sn(1)–O(2)	83.0(2)
C(55)–Sn(1)–O(2)	87.5(2)
C(51)–Sn(1)–O(2)	90.2(2)

Figure 3. Geometry around one of the tin atoms in $[^{n}Bu_2Sn(3,5\text{-}^{i}Pr_2C_6H_2(O)(COO))]_6$ (**1**) and related bond angles (deg). The other two tin atoms have similar geometrical parameters.

The four Sn−O bond lengths around each of the tin centers are nonequivalent and vary over a wide range. Among the Sn−O bonds around each tin, the Sn−O(phenoxide) bond is the shortest (av 1.993(4) Å). The monodentate carboxylate oxygen atoms (O(1), O(4), O(7)) form shorter bonds to tin (av 2.168 Å) compared to the bidentate bridging carboxylate oxygen atoms O(2), O(5), and O(8) (av 2.231 Å). The fourth Sn−O bond, which is a weak interaction, is the longest in the molecule (av 2.992 Å). In general, the observed bond lengths and angles of **1** are comparable with those of the only other hexanuclear cyclic diorganotin carboxylate, $[^{n}Bu_2Sn(OOCCH_2CH_2S)]_6$.[12]

Synthesis and Spectral Characterization of $[^{n}BuSn(O)(3,5\text{-}^{i}Pr_2C_6H_2(OH)(COO))]_6$ (2). Unlike the reaction between $^{n}Bu_2SnO$ and DISPA, the reaction between the mono-organotin precursor *n*-butylstannoic acid and DIPSA in benzene proceeds via azeotropic removal of water to afford $[^{n}BuSn(O)(3,5\text{-}^{i}Pr_2C_6H_2(OH)(COO))]_6$ (**2**) with a drum structure (Scheme 1). Analytically pure **2** has been obtained by crystallization of the sample from the dichloromethane/petroleum ether mixture (v/v, 1:1) at 0 °C. Molecular weight measurement for **2** by the cryoscopic freezing point method gave a value of 2374, which is in reasonable agreement with the expected value of 2478.6 for the drum structure.

The presence of unreacted phenolic protons on the DIPSA ligand in **2** is deduced from the $\bar{\nu}_{OH}$ absorption band observed in the IR spectrum at 3266 cm^{-1}. The doublet observed for **2** at 1533 and 1566 cm^{-1} is due to the antisymmetric stretching vibration of the carboxylate ligands, which bridge the tin centers in the drum structure.[7a,13] The $\bar{\nu}_{Sn-O}$ stretching vibration appears at 676 cm^{-1}. The definitive structural assignment for **2** comes from the ^{119}Sn NMR spectrum of the compound, which gives a single resonance at δ −479 ppm, indicating the presence of only one type of tin atom. All structurally characterized monoalkyl organotin oxocarboxylates show a single resonance in the ^{119}Sn NMR spectrum in the δ −480 to −520 ppm region[8] (see Supporting Information), which clearly supports the formulation of a drum structure for **2** in the absence of a single-crystal diffraction study (due to the poor quality of the single crystals obtained). The major difference between the structurally characterized drum compounds in the literature and compound **2** is the presence of six phenolic protons on the surface of **2**.

Conclusion

It has been demonstrated from that 3,5-disopropylsalicylic acid behaves quite differently from other aromatic carboxylic acids bearing additional functional groups (salicylic acid, anthranilic acid, 2,4-dihydroxybenzoic acid, etc.) in its reactions with organotin precursors. The formation of unexpected cyclic hexamer **1** could be explained on the basis of the presence of a highly acidic −OH group on DISPA as well as the steric congestion that would result for the formation of a monomeric 1:2 product, due to the presence of bulky isopropyl rings on the aryl rings. The stannoxane ring and the attached aryl rings in **1** remarkably lie on a plane. Although, the 1:1 reaction between *n*-butylstannoic acid and DIPSA produced one of the quite well-studied structures in tin chemistry, viz., a drum structure for **2**, the presence of surface hydroxyl groups on the aromatic rings makes this compound a useful starting material for cluster expansion through suitable reactions at the surface by exploiting the highly acidic nature of the phenolic protons. Our present investigations are currently directed toward studying the reactivity of **2**, apart from unraveling the reactions of other benzoic acids with bulky substituents.

Experimental Section

Apparatus. All reactions were carried out under an inert atmosphere of purified nitrogen using standard Schlenk line techniques, and samples for characterization were prepared in a nitrogen-filled MBraun (UniLab) glovebox. The ^{1}H, ^{13}C (Me_4Si internal standard), and ^{119}Sn (Ph_4Sn external standard) NMR spectra were recorded on a Varian VXR 400S spectrometer. Infrared spectra were obtained from a Nicolet Impact-400 FT-IR spectrometer. Microanalyses were performed on a Thermo Finnigan (FLASH EA 1112) or a Carlo Eraba 1106 microanalyzer. The EI mass spectra of the solid samples were obtained on a Finnigan MAT System 8230 mass spectrometer. Molecular weight measurements have been carried out by using the cryoscopic freezing point method in benzene.[15]

Synthesis of 1. To a suspension of $^{n}Bu_2SnO$ (1.24 g, 5 mmol) in dry benzene (150 mL) was added DIPSA (1.11 g, 5 mmol), and the mixture was heated under reflux for 5−6 h using a Dean-Stark apparatus for azeotropic removal of the water. The resulting solution was dried under high vacuum for 2 h, dissolved in petroleum ether (40 mL)/CH_2Cl_2 (20 mL), and filtered. The clear filtrate was concentrated to 3 mL, and CH_2Cl_2 (0.5 mL) was added to obtain colorless crystals of **1** at 0 °C. Yield: 0.72 g (53%). Mp: 203−205 °C. Anal. Calcd. for $C_{126}H_{204}O_{18}Sn_6$ (mol wt 2719.04): C, 55.65; H, 7.56. Found: C, 54.88; H, 7.18. Mass spectrum (EI, 70 eV): *m/z* 1303 ($M^+/2 - {}^{n}Bu$), 1188 ($M^+/2 - 3{}^{n}Bu$), 1016 ($M^+/2 - 5{}^{n}Bu$), 850 ($M^+/3 - {}^{n}Bu$, 100%). IR (KBr, cm^{-1}): $\bar{\nu}$ 2958(vs), 2926(s), 2867(m), 1617(w), 1564(m), 1514(vs), 1436(vs), 1397(s), 1310(w), 1229(s), 1176(w), 1078(w), 1022(w), 894(w), 809(m), 759(w), 632(w), 423(w). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.77−0.94 (m, 36H, ^{n}Bu-CH_3), 1.26−1.44 (m, 96H, CH_3 and CH_2), 1.63−1.85 (m, 24H, CH_2), 1.83−1.87 (m, 24H, CH_2), 2.87−2.91 (m, 24H, CH_2), 3.35−3.38 (m, 12H, C*H*), 7.26−7.50 (m, 6H, *p*-Ar), 7.72 (d, 6H, *o*-Ar), 10.81 and 11.58 (s, OH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.74, 13.86 (^{n}Bu-*C*H_3 and ^{i}Pr-*C*H_3), 22.80 (^{n}Bu-CH_2), 24.43 (^{n}Bu-*C*H_2), 26.66, 27.03 (Sn-*C*H_2), 33.71 (*C*H), 114.44, 126.02, 130.59, 136.72, 139.70, 159.60 (Ar), 176.26 (*C*═O). ^{119}Sn NMR (186.50 MHz, $CDCl_3$): δ −225.8 (s) ppm.

Synthesis of 2. To a suspension of *n*-butylstannoic acid (1.04 g, 5 mmol) in dry benzene (150 mL) was added DIPSA (1.11 g, 5 mmol), and the mixture was heated under reflux for 5−6 h, as above. The dried crude product was dissolved in petroleum ether (40 mL) and filtered. The clear filtrate was concentrated to 3 mL, and CH_2Cl_2 (0.5 mL) was added to obtain colorless crystals of **2** at 0 °C. Yield: 0.97 g (47%). Mp: 258−260 °C. Anal. Calcd for $C_{102}H_{156}O_{24}Sn_6$ (mol wt 2478.58): C, 49.43; H, 6.34. Found: C, 49.09; H, 6.54. Mass spectrum (EI, 70 eV): *m/z* 1744, 1129 ($M^+/2 - 3{}^{n}Bu$), 1073 ($M^+/2 - 4{}^{n}Bu$), 1016 ($M^+/2 - 5{}^{n}Bu$), 678 (100%). IR (KBr, cm^{-1}): $\bar{\nu}$ 3266(m), 3039(w), 2960(s), 2929(s), 2869(m), 1620(m), 1566(s), 1533(s), 1465(vs), 1392(vs), 1321(w), 1300(w), 1235(m), 1174(w), 804(m), 743(w), 676(m), 623(s), 546(w), 459(m). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.91−0.95 (t, 3H, ^{n}Bu-CH_3), 1.16−1.25 (m, 12H, CH_3), 1.40−1.55 (m, 2H, CH_2), 1.83−1.87 (m, 2H, CH_2), 2.83−2.88 (m, 2H, CH_2), 3.35−3.49 (m, 2H, C*H*), 7.18−7.19 (d, 1H, *p*-Ar), 7.68−7.69 (d, 1H, *o*-Ar), 10.36 (s, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 11.07 (^{n}Bu-*C*H_3), 13.87 (^{i}Pr-*C*H_3), 22.72 (^{n}Bu-*C*H_2), 24.13 and 24.27 (^{n}Bu-*C*H_2), 26.58, 26.78, 27.65, 27.97 (Sn-*C*H_2), 33.54 (*C*H), 114.16 (*C*4-Ar), 125.82 (*C*3-Ar), 131.06 (*C*5-Ar), 136.27 (*C*6-Ar), 138.84 (*C*2-Ar), 156.79 (*C*1-Ar), 174.81 (*C*═O). ^{119}Sn NMR (186.50 MHz, $CDCl_3$): δ −479.0 (s) ppm.

Single-Crystal X-ray Studies. Crystals suitable for X-ray diffraction were grown from a petroleum ether/dichloromethane mixture of **1** at 0 °C. Intensity data were collected on a Bruker CCD diffractometer and corrected for absorption effects. All calculations were carried out using the programs in the WinGX module.[16] The structure solution was achieved by direct methods as implemented in SIR-92.[17] The final refinement of the structure was carried out using full matrix least-squares methods on F^2 using SHELXL-97.[18] The crystallographic data for **1** are provided in the Supporting Information.

Acknowledgment. This work was supported by CSIR, New Delhi. This work was also supported by the equipment procured through the Swarnajayanti Fellowship of DST, New Delhi, to R.M. The authors thank the RSIC, IIT-Bombay, for the NMR spectroscopic and analytical data. G.P. thanks CSIR, New Delhi, for a Senior Research Fellowship.

Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters (CIF format), and additional figures and tables (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM049584U

---

[15] Wilson, J. M.; Newcombe, R. J.; Denaro, A. R.; Rickett, R. M. W. *Experiments in Physical Chemistry*; Pergamon Press: Oxford, 1962; p 18.

[16] WinGX, Version 1.64.05. Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

[17] Altomare, A.; Cascarano, G.: Giacovazzo, C.; Gualardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

[18] Sheldrick, G. M. *SHELXL-97*, Program for Structure Refinement; University of Göttingen: Germany, 1997.