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# Microwave assisted solid-state synthesis of functional organotin carboxylates from sterically encumbered 3,5-di-*tert*-butylsalicylic acid

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ABSTRACT

Microwave assisted solid-state reaction between equimolar quantities of sterically encumbered 3,5-di-*tert*-butylsalicylic acid ($H_2$-DTBSA) and *n*-butylstannoic acid results in the formation of hexameric drum shaped stannoxane [$^n$BuSn(O)(H-DTBSA)]$_6$ (**1**). Synthesis of **1** could not be achieved under normal thermal conditions or mechanical grinding. However, the azeotropic removal of water produced in the reaction of $^n$Bu$_2$SnO with 3,5-di-*tert*-butyl salicylic acid in benzene yielded the tetrameric ladder shaped stannoxane [{$^n$Bu$_2$Sn(H-DTBSA)}$_2$O]$_2$ (**2**), which could also be synthesized in better yields by microwave irradiation as in the case of **1**. Compounds **1** and **2** have been characterized by elemental analysis, IR, MALDI-MS and NMR ($^1$H and $^{13}$C) spectroscopy. The structures of compound **1** and **2** are determined by single crystal X-ray diffraction techniques. Compound **1** is hexameric with a $Sn_6O_6$ drum core while compound **2** forms a ladder structure with three $Sn_2O_2$ rings, both decorated with –OH functionalities on the exterior of the polyhedral structure. While the formation of **1** from *n*-butylstannoic acid is straightforward, the formation of **2** from *n*Bu$_2$SnO (and not a cyclic structure similar to **3**, where the phenolic oxygen also coordinates to tin) can be understood in terms of the increased steric hindrance in DTBSA for the phenolic protons to react with tin.

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## 1. Introduction

Exploring newer and better experimental techniques to carry out chemical transformations has been an important premise of chemical synthesis. Irradiation of microwave on homogenous reaction mixtures and on solid surfaces has been one such technique, which has emerged as a useful method for achieving better yields of the products, significant reduction in reaction time, and reduction or elimination of environmentally detrimental solvents. For these reasons, microwave assisted synthesis has clearly become a rapidly growing field of study especially for various organic transformations [1].

Reactions of organotin oxides with carboxylic acids have been studied in detail because of the industrial [2] and biological [3] applications of the organotin carboxylates. In addition, a wide spectrum of interesting and exotic structural types can be obtained by changing either the stoichiometry of the reactants or changing the additional functionality on the carboxylate ligand [4–9]. Reaction of various carboxylic acids with RSn(O)(OH) has been extensively studied and in most of the cases a drum shaped [RSn(O$_2$CR′)]$_6$ stannoxane with a $Sn_6O_6$ core has been isolated [4a,6]. The only exception where a mono-organotin carboxylate adopts linear chain structure, [SnPh(O$_2$CCCl$_3$)O]$_6$, was obtained via dearylation reaction of Ph$_3$Sn(OH) with Cl$_3$CCOOH [7]. On the other hand, tetrameric tin carboxylates [{R$_2$Sn(R′COO)$_2$}$_2$O]$_2$ (type A–D; Fig. 1) are obtained when the reaction between R$_2$SnO and R′COOH is carried out in strictly 1:1 stoichiometry [8d,9d]. Recently we reported that the presence of other reaction centers on the carboxylate ligand (e.g. 3,5-di-isopropyl salicylic acid) leads to the formation of a hexameric cyclic tin carboxylate of formula [$^n$Bu$_2$Sn(3,5-$^i$Pr$_2$C$_6$H$_2$(O)(COO))]$_6$ [8a]. Later this reaction was generalized by Ma et al. with the synthesis of [$^n$BuSn(*o*-SC$_6$H$_4$COO)]$_6$ [10].

The reaction between an organotin oxide or acid and a carboxylic acid proceeds through the elimination of water to produce oligomeric organotin carboxylate clusters. Traditionally, the water produced in the above reaction is removed from the reaction mixture via simultaneous azeotropic distillation from a benzene or toluene medium, depending on the temperature required for the reaction. Not only these reactions are very slow but often require high temperatures in environmentally detrimental solvents. Considering the industrial and biological utilization of organotin carboxylates, a much faster and environmentally benign method for their synthesis is desired. Chandrasekhar et al. have recently reported the synthesis of organotin carboxylates having most commonly observed structure using a solventless methodology where the starting materials are ground together [11]. The only limitations of this very useful method are the relatively slower rates and the hazards associated with prolonged grinding of the reaction

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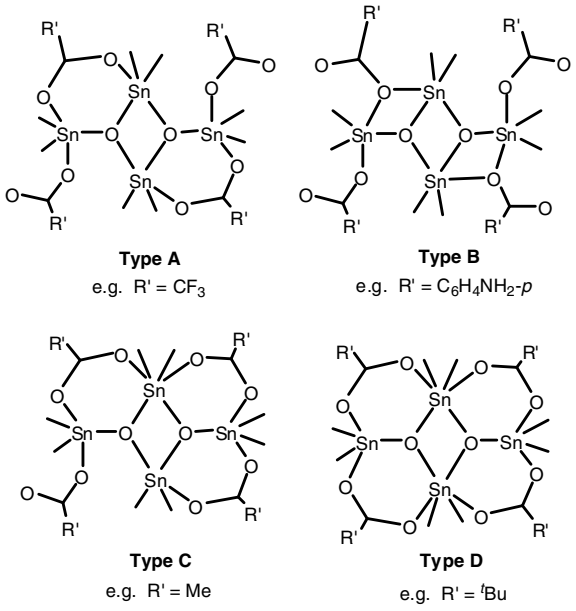



**Fig. 1.** Four different structural types of $[\{R_2Sn(R'COO)_2\}_2O]_2$.

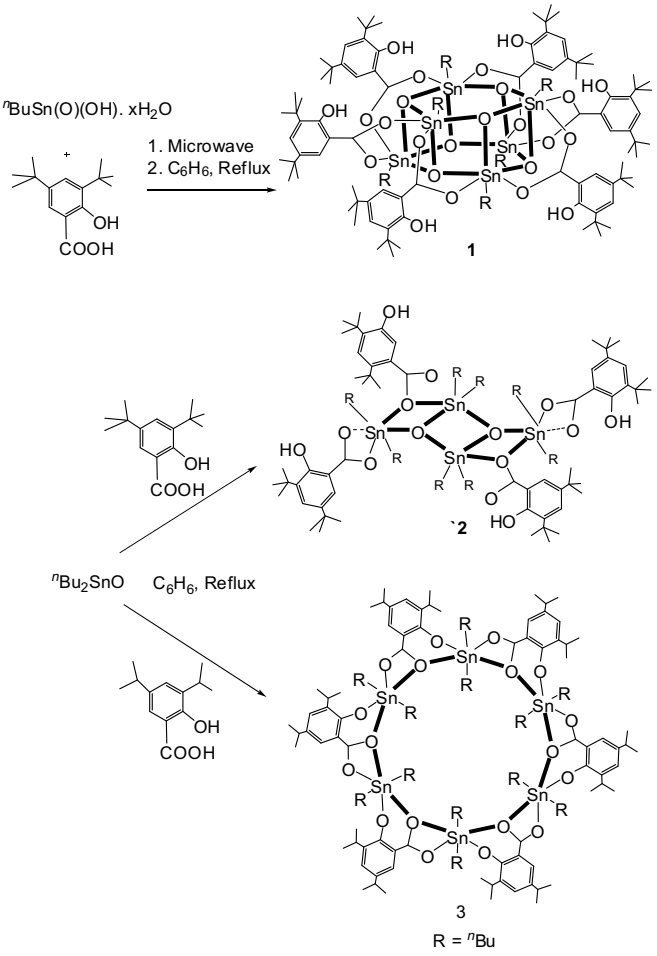
mixture (organotin carboxylates are known to have anti-neoplastic properties) [12]. Continuing our earlier studies on tin carboxylates derived from bulkier carboxylic acids [8a] we wish to report in this contribution a synthetic strategy that utilizes both grinding and microwave irradiation to efficiently remove the water produced in the condensation reaction between an organotin acid/oxide and 3,5-di-*tert*-butylsalicylic acid.

## 2. Results and discussion

### 2.1. Synthesis and characterization of $[^nBuSn(O)(H\text{-}DTBSA)]_6$ (**1**)

The reaction between *n*-butylstannoic acid and $H_2$-DTBSA in refluxing benzene or toluene did not yield **1**, but an insoluble powder which could not be characterized. Similarly, the use of grinding methodology described by Chandrasekhar et al. [11] also did not lead to product formation in this case. Hence this reaction was attempted using microwave irradiation. Initially the solid reactants were ground together in a mortar to obtain a homogeneous mixture and transferred to a Petri dish. The homogeneous mixture was covered with another Petri dish and placed inside a microwave oven and irradiated for 2 min at 400 W. The irradiation was repeated three times during which time water produced from the reaction condensed on the lid. In order to completely remove the water from the product formed, the contents of the Petri dish were dissolved in benzene and heated under reflux using a Dean–Stark apparatus. After all the water has been removed as azeotrope, the clear benzene solution was left for crystallization to obtain single crystals of $[^nBuSn(O)(H\text{-}DTBSA)]_6$ (**1**) in good yield (Scheme 1). Compound **1** is a stable colorless solid that melts at 200–203 °C.

The IR spectrum of compound **1** shows a broad band centered at 3239 $cm^{-1}$, indicating the presence of unreacted phenolic –OH group on the carboxylate ligand. The symmetrical double absorption observed for **1** at 1566 and 1531 $cm^{-1}$ is due to the antisymmetric stretching vibrations of the carboxylate ligands, which bridge the tin centers in the drum structure. The $^1H$ and $^{13}C$ NMR data obtained are consistent with the formulation of compound **1**. In particular, the presence of a broad resonance at 10.62 ppm is indicative of the non-participation of the phenolic group of the ligand in the reaction with the tin acid.




**Scheme 1.** Synthesis of **1**–**3**.

### 2.2. Molecular structure of **1**

Colorless rectangular crystals of **1** obtained directly from the reaction mixture were found to be suitable for single crystal X-ray diffraction measurements. The compound crystallizes in the centrosymmetric triclinic $P\bar{1}$ space group with four molecules of benzene. The final refined molecular structure of compound **1** is shown in Fig. 2 while important bond lengths and bond angles are listed in Table 2. The centrosymmetric structure of **1** is built around a drum shaped $Sn_6O_6$ central stannoxane core that is made up of two hexameric $Sn_3O_3$ rings. These hexameric $Sn_3O_3$ rings exist in a puckered chair conformation and form the upper and lower lids of the drum polyhedron. The two $Sn_3O_3$ rings are connected further by six Sn–O bonds containing tri-coordinate O atoms and thus the side faces of the drum are characterized by six four-membered $Sn_2O_2$ rings. It can be seen from Fig. 2 that the four-membered $Sn_2O_2$ rings are not planar; the oxygen atoms are tilted toward the cavity of the drum. Thus the interior of the drum can be considered as a crown made of six oxygen atoms in a trigonal antiprismatic arrangement. The two tin atoms in each of the six $Sn_2O_2$ rings are bridged by a carboxylate ligand to form a symmetrical bridge between two carboxylate ligands. The Sn–O bond lengths inside the core range between 2.072(3) and 2.157(4) Å. These distances are comparatively shorter than the Sn–O bonds to the bridging carboxylate ligands (2.145(3)–2.197(4) Å). All the six tin atoms are chemically equivalent and are six coordinate with three of the coordination sites occupied by bridging tri-coordinate oxygen atoms. While oxygen atoms from the bridging carboxylate

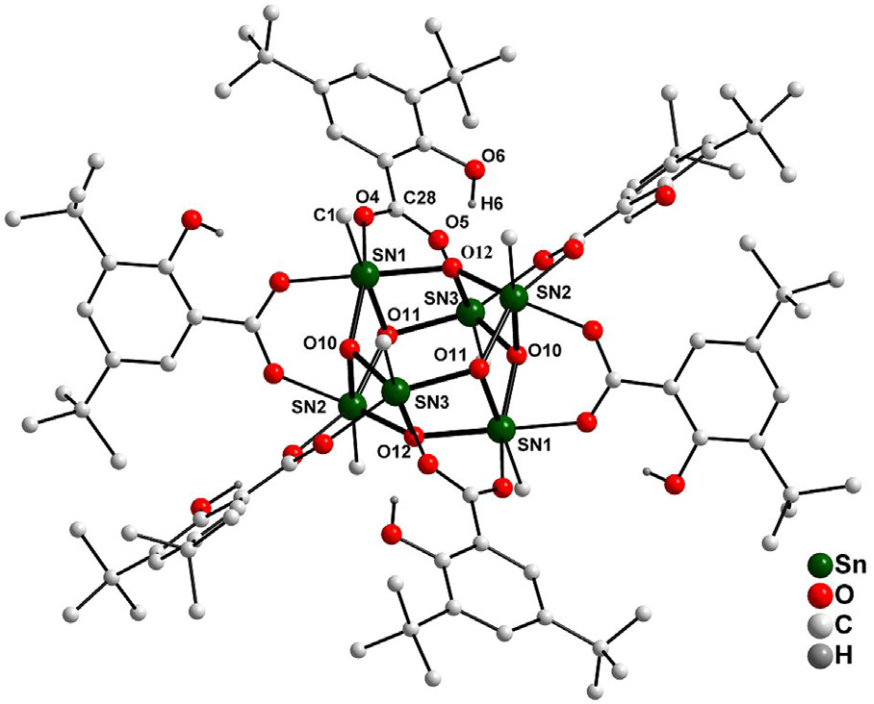



**Fig. 2.** Molecular structure of **1**.

ligands occupy two of the coordination sites, the sixth coordination site is occupied by the *n*-butyl group. The most interesting feature of the structure of **1** is the presence of the free phenolic –OH group on each of the DTBSA ligand. Thus the total of six –OH functionalities on the surface of the tin cluster offer excellent opportunities for further reactions with other metal centers.

### 2.3. Synthesis and characterization of [{$^n$Bu$_2$Sn(H-DTBSA)}$_2$O]$_2$ (**2**)

We had earlier reported that the reaction of one equivalent of $^n$Bu$_2$SnO with one equivalent of 3,5-di-*iso*-propyl salicylic acid (DIPSA) leads to the formation of an unprecedented hexameric cyclic diorganotin carboxylate **3** where both the carboxylate and phenoxide terminals of the DIPSA ligand bind to the tin atoms through chelating and bridging modes of coordination (Scheme 1) [8a]. In order to establish the generality of this reaction for other substituted salicylic acids and further evaluate the effect of even larger substituents on the salicylic acid [13], the reaction of dibutyltin oxide with H$_2$-DTBSA was carried out in the present study. Unlike in the case of reaction leading to the formation of **1** where the use of microwave radiation was absolutely necessary, the reaction between $^n$Bu$_2$SnO and H$_2$-DTBSA proceeds in benzene under reflux conditions with simultaneous azeotropic removal of water to result in **2** in 81% yield (Scheme 1). Interestingly, the use of microwave irradiation for the synthesis of **2** resulted in better yields in much shorter time (92 %).

Stable colorless crystalline sample of **2**, which melt at 242–245 °C, has been characterized with the aid of elemental analysis, infrared, mass, and NMR spectroscopic techniques. The IR spectrum of **2** shows strong absorptions at 2960 and 2866 cm$^{-1}$ due to the C–H stretching vibrations of the *n*- and *t*-butyl groups. In addition, the $\upsilon(COO)_{asym}$ vibration is observed as a doublet centered at 1531 cm$^{-1}$ while $\upsilon(COO)_{sym}$ vibration is also observed as a doublet centered at 1414 cm$^{-1}$. Occurrence of two different signals both for $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ vibrations reveal that compound **2** contains carboxylate ligands in two different coordination mode unlike in the case of **3**. The $^1$H NMR spectral pattern and the integrated intensities are also consistent with a different formulation for compound **2** compared to the earlier reported **3** [8a]. Further, the presence of a singlet resonance for the phenolic OH group at $\delta$ 11.81 ppm confirms that compound **2** has a different structure and stoichiometry.

### 2.4. Molecular structure of **2**

Colorless rectangular crystals of **2** that are suitable for X-ray measurements were obtained from a $CH_2Cl_2$/ petroleum ether mixture at 5 °C after 1 week. Single crystal X-ray diffraction measurements indicate that the compound crystallizes in centrosymmetric triclinic $P\bar{1}$ space group with two molecules of $CH_2Cl_2$. A perspective view of the molecular structure of compound **2** shown in Fig. 3 indicates that compound **2** falls into the category of structural type B (Fig. 1) where a central cyclic four-membered $Sn_2O_2$ core is linked to two terminal $^n$Bu$_2$Sn entities through the $\mu_3$-O atoms (O(7)). Each pair of the central and terminal tin atoms are asymmetrically bridged by the H-DTBSA ligand through the carboxylate oxygen. Thus the central $Sn_2O_2$ core is linked to the two outer $Sn_2O_2$ rings to result a ladder-like structure as shown in Fig. 3. In addition, the two terminal tin atoms are bonded to a terminal H-DTBSA ligand (O(1)).

The coordination geometry around each of the tin atoms is best described as distorted trigonal bipyramidal. Distortion from ideal trigonal bipyramidal geometry in the case of Sn(1) arises primarily due to the close proximity of the sixth, but weak, ligation through O(2) atom. The acyl O(2) atom is located only 2.652(2) Å away from Sn(1), which is significantly below the sum of the van der Waals radii for these atoms (3.70 Å). If this interaction is considered significant enough, then the Sn(1) atom would be best described to have a skew-trapezoidal bipyramidal geometry with the $^n$Bu groups disposed over the four Sn–O bonds. The O(1), O(2), O(4) and O(7) atoms comprise a trapezoidal plane which is almost perpendicular to the plane passing through C(1), Sn(1) and C(5). The Sn(1)···O(2) distance in **2** (2.652(2) Å) is shorter compared to those observed for similar skew-trapezoidal bipyramid complexes reported earlier,

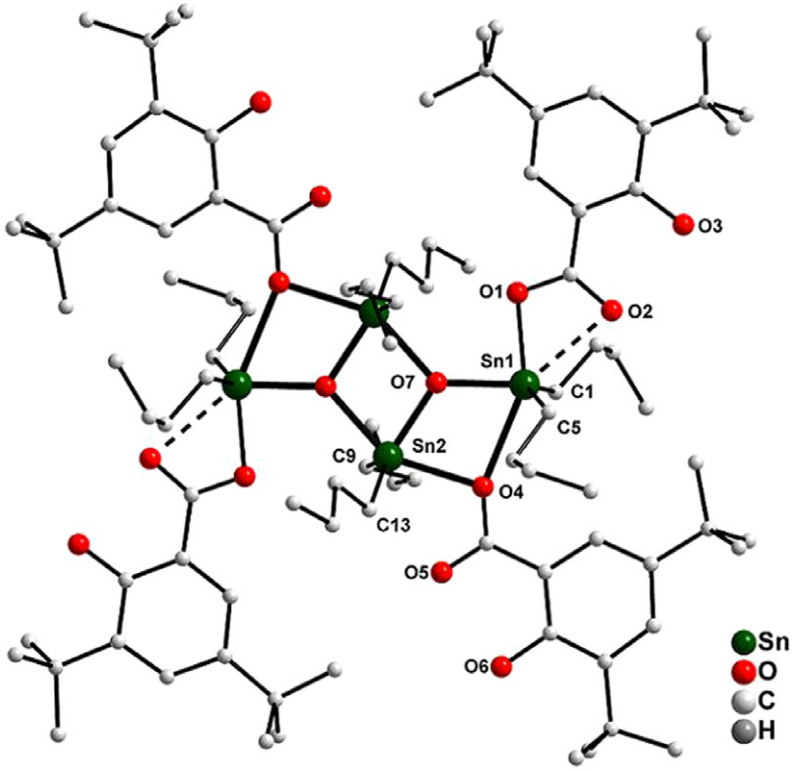



**Fig. 3.** Molecular structure of **2**.

$[\{^nBu_2SnO_2CCH_2CH_2C(O)C_6H_5\}_2O]_2$ (2.746(7) Å) [8d] and $[\{^nBu_2Sn(O_2CCH_2\text{-}C_6H_4F\text{-}p)\}_2O]_2$ (2.746(7) Å) [9e] but longer than that observed for $[\{Me_2Sn(O_2CC_6H_4\text{-}p\text{-}NH_2)\}_2O]_2$ (2.573(6) Å) [8g].

As in the case of **1**, compound **2** also contains phenolic functional groups on each of the DTBSA ligand in the complex thus rendering this compound as a useful starting material for further reactions at the –OH terminal to build multimetallic systems.

## 3. Conclusion

We have shown in this contribution that the reaction between 3,5-di-*tert*-butyl salicylic acid and $^nBuSn(O)(OH)\cdot xH_2O/^nBu_2SnO$ proceeds the best under microwave irradiation conditions followed by the complete removal of water produced in the reaction by azeotropic distillation. It is further shown that the change of the substituent on the aryl ring of the salicylic acid from *iso*-propyl to *tert*-butyl has brought about interesting differences both in the reactivity and the type of products formed. The significant outcome of the present investigation is the isolation of two oligomeric tin carboxylates with surface phenolic –OH groups. This opens up further potential for using these two compounds as starting materials for cluster expansion by exploiting the highly acidic nature of the phenolic protons. Especially interesting would be the reaction of **1** with catalytically useful transition metal precursors. Currently we are investigating this aspect.

## 4. Experimental

### 4.1. Apparatus

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 maintained at <1 ppm of $O_2$ and $H_2O$. All the chemicals used are procured from commercial sources and used as received without any further purification. Solvents were purified by conventional techniques and distilled prior to use. The $^1H$ (using $Me_4Si$ as the internal standard) and $^{13}C$ NMR spectra were recorded on a Varian VSR 400S spectrometer operated at 400 and 100 MHz, respectively. Infrared spectra were obtained from a Perkin Elmer FT-IR spectrophotometer with use of KBr disc. Microanalyses were performed on a Thermo Finnigan (FLASH EA 1112) microanalyzer. Microwave synthesis was carried out on a 1000 W Samsung kitchen microwave oven operating at 40% of the power. Mass spectra were collected using an Axima-CFR MALDI-TOF-MS (Kratos Analytical, Manchester, UK), in the reflectron positive ion mode.

### 4.2. Synthesis of $\mathbf{1}\cdot(C_6H_6)_4$

In a mortar $^nBuSn(O)(OH)\cdot(H_2O)_x$ (0.417 g, 2 mmol) and 3,5-di-*tert*-butyl salicylic acid (0.500 g, 2 mmol) were mixed together and then transferred to a Petri dish and covered with another Petri dish and then placed in a microwave oven (400 W) and heated three times for 2 min. The reaction mixture was transferred to a Schlenk flask and benzene (100 mL) was added and under reflux for 6 h using Dean–Stark apparatus for the compete removal of water. The colorless solution obtained was kept at room temperature to yield colorless needle shaped crystals of $[\mathbf{1}\cdot(C_6H_6)_4]$ after 24 h. Yield 0.780 g, 88%, m.p.: 200–203 °C. Elemental Anal. Calc. For $C_{114}H_{180}O_{24}Sn_6$: C, 51.73; H, 6.85. Found: C, 51.77; H, 7.41%. IR (KBr pallets, $cm^{-1}$): 3239(br), 2959(s), 2871(m), 1617(m), 1566(s), 1531(s), 1447(vs), 1389(vs), 1280(m), 1260(m), 1240(m), 1096(m), 1023(m), 896(w), 804(m), 674(w), 551(w), 491(w). $^1H$ NMR ($CDCl_3$, ppm): δ 10.62(s, 1H, OH), 7.73–7.80 (m, 1H, Ar–H), 7.36–7.48(m, 1H, Ar–H), 1.18–1.34(m, 24H, $CH_2$ & $(CH_3)_3C$), 0.77–0.91(m, 3H, $CH_3$). $^{13}C$ NMR ($CDCl_3$, ppm): δ 175.53 (C=O), 158.76 (Ar–C2), 140.61 (Ar–C5), 137.19 (Ar–C3), 130.74 (Ar–C4), 125.74

(Ar–C6), 114.39 (Ar–C1), 35.31($C(CH_3)_3$), 31.51($CH_3$), 29.72($\alpha CH_2$), 27.84 ($\beta CH_2$), 27.02 ($\gamma CH_2$), 13.85 ($CH_3$). $^{119}$Sn NMR($CDCl_3$, 300 MHz) δ: −483. Mass spectra (MALDI-MS) *m/z*: 884 (100%) $[(DTBSA\text{-}H)_2Bu_2Sn_2O(H_2O)]^+$, 843 $[(DTBSA\text{-}H)_2BuSn_2O_2(H_2O)]^+$, 770 $[(DTBSA\text{-}H)_2Sn_2O(H_2O)]^+$.

### 4.3. Synthesis of **2** · $2CH_2Cl_2$

#### 4.3.1. Thermal synthesis

To a suspension of $^nBu_2SnO$ (0.634 g, 2.54 mmol) in benzene (150 mL) is added 3,5-di-*tert*-butylsalicylic acid (0.637 g, 2.54 mmol) and heated under reflux for 6 h using Dean–Stark apparatus during this time water produced in the reaction separated out. The resulting solution was then dried under vacuum to obtain a white solid which is dissolved in $CH_2Cl_2$ (20 mL)/petroleum ether (40 mL) mixture and filtered. The filtrate was concentrated under vacuum and dissolved in minimum amount of $CH_2Cl_2$. Colorless crystals of [**2** · $(CH_2Cl_2)_2$] were obtained from the filtrate at 10 °C after 1 week. Yield 1.10 g (81%).

#### 4.3.2. Microwave route

An equimolar mixture of $^nBu_2SnO$ (0.499 g, 2 mmol) and 3,5-di-*tert*-butylsalicylic acid (0.500, 2 mmol) was ground together to obtain a homogenous mixture. It was then transferred to a Petri dish and covered with another Petri dish and was heated in a microwave at 400 W for 2 min and then cooled for 2 min. The microwave heating cycle was repeated for two times and the resultant thick gelatinous product was extracted with benzene (60 mL) and refluxed for 6 h using a Dean–Stark apparatus in order to distill out the water produced in the reaction. Solvent was removed under vacuo and the residue was dissolved in 20 mL $CH_2Cl_2$–Petry ether (2:1) mixture and filtered. White crystalline [**2** · $(CH_2Cl_2)_2$] were obtained from the filtrate at 0 °C after 1 day. Yield: 0.986 g, 92 %, m.p.: 238–240 °C. Elemental analysis for $C_{94}H_{160}O_{14}Cl_4Sn_4$: Calc.: C, 52.98; H, 7.56. Found: C, 53.51; H, 8.29%. IR (KBr pallets, $cm^{-1}$): 3449(br), 2960(m), 2866(w), 1615(w), 1552(m), 1432(m), 1392(m), 1254(m), 1094(s), 1025(s), 807(s), 683(w), 630(w). $^1$H NMR($CDCl_3$, ppm): δ 11.81 (s, 1H, OH). 7.56–7.62 (m, 1H, Ar–H), 7.44 (s, 1H, Ar–H), 1.20–1.77 (m, 26H, CH2 and $(CH_3)_3C$), 0.72–0.80 (m, 6H, $CH_3$). $^{13}$C NMR ($CDCl_3$, ppm): δ 177.27 (C=O), 163.71/159.34 (Ar–C2), 142.00/140.14 (Ar–C5), 138.82/137.19 (Ar–C3), 130.82/130.09 (Ar–C4), 127.18/124.92 (Ar–C6), 114.92/113.86 (Ar–C1), 35.88/34.47 ($C(CH_3)_3$), 31.76 ($CH_3$), 30.10/29.71 ($\alpha CH_2$), 27.09/26.89 ($\beta CH_2$), 26.75/25.91 ($\gamma CH_2$), 13.70/13.95 ($CH_3$). $^{119}$Sn NMR($CDCl_3$, 300 MHz) δ: (−203)–(−201) (quintet), −189(m), (−182)–(−183) (m). Mass spectra (MALDI-MS) *m/z*: 884 $[(DTBSA\text{-}H)_2Bu_2Sn_2O(H_2O)]^+$, 770 $[(DTBSA\text{-}H)_2Sn_2O(H_2O)]^+$, 650 (100%) $[(DTBSA\text{-}H)_2SnO(OH)]^+$.

### 4.4. X-ray structure determination of **1** and **2**

The intensity data collection for **1** and **2** were carried out on an Oxford Diffraction XCalibur-S diffractometer equipped with a CCD system. Intensity data collection and cell determination protocols were carried out using a graphite-monochromatized Mo Kα radiation ($\lambda$ = 0.71073 Å). Structure solution for each of the compound was obtained using direct methods (SHELXS-97) [14] and refined using full-matrix least square methods on $F^2$ using SHELXL-97 [15]. The positions of hydrogen atoms were either located in the successive difference maps or were geometrically placed and refined using a riding model. All non-hydrogen atoms were refined anisotropically. No disorder or symmetry related problems were encountered for both the compounds. Further details of the crystal data and refinement convergence are listed in Table 1. Additional supporting information available contains the CIF details for both **1** and **2**.

**Table 1**
Crystal data and structure refinement parameters for compounds **1** and **2**

| Compound | [**1** · $(C_6H_6)_4$] | [**2** · $(CH_2Cl_2)_2$] |
|---|---|---|
| Empirical formula | $C_{138}H_{204}O_{24}Sn_6$ | $C_{94}H_{160}Cl_4O_{14}Sn_4$ |
| Formula weight | 2959.15 | 2130.78 |
| Temperature (K) | 150(2) | 150(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| *a* (Å) | 14.344(3) | 12.606(3) |
| *b* (Å) | 16.3354(15) | 13.396(4) |
| *c* (Å) | 16.3561(11) | 17.7186(14) |
| α (°) | 83.292(6) | 76.557(14) |
| β (°) | 80.200(10) | 73.378(14) |
| γ (°) | 73.621(13) | 65.14(3) |
| Volume ($Å^3$) | 3613.7(9) | 2579.5(10) |
| *Z* | 1 | 1 |
| $D_{calc}$ ($mg/m^3$) | 1.360 | 1.372 |
| Absorption coefficient ($mm^{-1}$) | 1.084 | 1.116 |
| *F*(000) | 1524 | 1104 |
| Crystal size ($mm^3$) | 0.33 × 0.26 × 0.11 | 0.22 × 0.15 × 0.10 |
| θ Range for data collection (°) | 2.93–25.00 | 3.09–25.00 |
| Reflections collected | 31535 | 25898 |
| Independent reflections | 12608 [$R_{(int)}$ = 0.0727] | 9045 [$R_{(int)}$ = 0.0395] |
| Completeness of θ (%) | 99.1 | 99.7 |
| Absorption coefficient | 0.8901 and 0.7163 | 0.8966 and 0.7913 |
| Refinement method | Full matrix least square on $F^2$ | Full matrix least squares on $F^2$ |
| Data/restraints/parameters | 12608/0/769 | 9045/0/563 |
| Goodness-of-fit on $F^2$ | 0.888 | 1.048 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1$ = 0.0467, $wR_2$ = 0.0826 | $R_1$ = 0.0337. $wR_2$ = 0.0723 |
| *R* indices (all data) | $R_1$ = 0.1002, $wR_2$ = 0.0923 | $R_1$ = 0.0546, $wR_2$ = 0.0745 |
| Largest difference in peak and hole (e $Å^{-3}$) | 0.849 and −0.855 | 1.183 and −1.240 |

**Table 2**
Selected bond lengths (Å) and angles (°) in **1** and **2**

| | | | |
|---|---|---|---|
| [$^nBuSn(O)(H\text{-}DTBSA)]_6$ (**1**) | | | |
| Sn(1)–O(10) | 2.081(4) | Sn(2)–O(2) | 2.145(3) |
| Sn(1)–O(11) | 2.083(4) | Sn(2)–O(7) | 2.181(4) |
| Sn(1)–O(12) | 2.092(3) | Sn(3)–O(12) | 2.079(4) |
| Sn(1)–O(4) | 2.157(4) | Sn(3)–O(10)#1 | 2.083(3) |
| Sn(1)–O(1) | 2.176(3) | Sn(3)–O(11) | 2.098(3) |
| Sn(2)–O(11) | 2.072(3) | Sn(3)–C(9) | 2.121(6) |
| Sn(2)–O(10) | 2.083(4) | Sn(3)–O(8) | 2.159(4) |
| Sn(2)–O(12)#1 | 2.090(3) | Sn(3)–O(5) | 2.197(4) |
| O(10)–Sn(1)–O(11) | 77.80(14) | O(11)–Sn(2)–O(10) | 77.99(14) |
| O(10)–Sn(1)–O(12) | 104.84(13) | O(11)–Sn(2)–O(12)#1 | 104.85(13) |
| O(11)–Sn(1)–O(12) | 77.91(13) | O(10)–Sn(2)–O(12)#1 | 77.70(13) |
| O(10)–Sn(1)–O(4) | 157.96(14) | O(2)–Sn(2)–O(7) | 77.81(14) |
| O(11)–Sn(1)–O(4) | 86.74(14) | O(11)–Sn(2)–Sn(1) | 39.84(10) |
| O(12)–Sn(1)–O(4) | 86.86(13) | O(10)–Sn(2)–Sn(1) | 39.85(10) |
| O(10)–Sn(1)–O(1) | 86.30(13) | O(12)–Sn(3)–O(10)#1 | 77.94(14) |
| O(11)–Sn(1)–O(1) | 87.60(14) | O(12)–Sn(3)–O(11) | 77.88(13) |
| O(12)–Sn(1)–O(1) | 159.18(15) | O(10)#1–Sn(3)–O(11) | 104.81(13) |
| [{$^nBu_2Sn(H\text{-}DTBSA)$}$_2O]_2$ (**2**) | | | |
| Sn(1)–O(7)#1 | 2.011(2) | Sn(2)–C(9) | 2.118(4) |
| Sn(1)–O(1) | 2.110(3) | Sn(2)–C(13) | 2.132(4) |
| Sn(1)–C(1) | 2.125(4) | Sn(2)–O(7) | 2.166(2) |
| Sn(1)–C(5) | 2.134(4) | Sn(2)–O(4) | 2.264(2) |
| Sn(2)–O(7)#1 | 2.046(2) | | |
| O(7)#1–Sn(1)–O(1) | 84.66(9) | O(7)#1–Sn(1)–C(1) | 106.72(13) |
| O(7)#1–Sn(2)–O(7) | 73.63(10) | O(1)–Sn(1)–C(1) | 103.17(12) |
| O(7)#1–Sn(2)–O(4) | 74.89(9) | O(7)#1–Sn(1)–C(5) | 107.85(13) |
| O(7)–Sn(2)–O(4) | 148.48(9) | O(1)–Sn(1)–C(5) | 101.05(13) |
| Sn(1)#1–O(7)–Sn(2)#1 | 122.01(12) | C(1)–Sn(1)–C(5) | 139.16(16) |
| Sn(1)#1–O(7)–Sn(2) | 131.54(11) | O(7)#1–Sn(2)–C(9) | 113.02(13) |
| Sn(2)#1–O(7)–Sn(2) | 106.37(10) | O(7)#1–Sn(2)–C(13) | 115.34(13) |

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.04.001.

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