

Synthesis, Structure and Reactivity of Hydrated and Dehydrated Organotin Cations

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Monomeric organotin dications $\{[n\text{Bu}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+} \cdot 2\text{C}_6\text{H}_5\text{SO}_3^-\}$ and $\{[n\text{Bu}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+} \cdot 1,5\text{-C}_{10}\text{H}_6(\text{SO}_3^-)_2\}$ have been synthesized by the reaction of $[n\text{Bu}_2\text{SnO}]_n$ and the corresponding arylsulfonic acid. Dodecanuclear organooxotin macrocations $\{[(n\text{BuSn})_{12}(\mu_3\text{-O})_{14}(\mu_2\text{-OH})_6]^{2+} \cdot 2\text{RSO}_3^-\}$ ($\text{R} = \text{C}_6\text{H}_5$; 2,5- $\text{Me}_2\text{C}_6\text{H}_3$) have been synthesized by the reaction of $n\text{BuSn}(\text{O})(\text{OH})$ and the corresponding arylsulfonic acid.

The X-ray crystal structure of one of the dodecanuclear cages is reported. These organotin cations have been shown to be effective catalysts in acetylation and transacetylation reactions.

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Introduction

Organotin oxides $[(\text{R}_3\text{Sn})_2\text{O}]$; $(\text{R}_2\text{SnO})_n$, hydroxides $[\text{R}_3\text{SnOH}]$ and oxide hydroxides $[\{\text{RSn}(\text{O})(\text{OH})\}_n]$ are important precursors for the synthesis of a large number of organotin compounds.^[1] These precursors are the eventual hydrolysis products of the corresponding organotin halides. Initial hydrolysis of organotin halides leads to the formation of hydrated organotin cations.^[2] In spite of their apparent simplicity there have been very few reports on the isolation of such species in the solid state.^[3] In most cases, dehydrated hydroxide-bridged compounds^[4a] or oxo-bridged ladders^[4b] are the products. In preliminary communications we have recently reported that arylsulfonic acids are effective in stabilizing $\{[n\text{Bu}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+} \cdot 2 \cdot 2,5\text{-Me}_2\text{C}_6\text{H}_3\text{SO}_3^-\}$ (**1**)^[5a] and $\{[n\text{Bu}_2\text{Sn}(\text{H}_2\text{O})_3]_2[\mu\text{-}1,5\text{-C}_{10}\text{H}_6(\text{SO}_3^-)_2]^{2+} \cdot 1,5\text{-C}_{10}\text{H}_6(\text{SO}_3^-)_2\}$ (**2**).^[5b] Herein we report the general applicability of this synthetic procedure. Accordingly, the hydrated organotin cations, $\{[n\text{Bu}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+} \cdot [x\text{Y}]^{2-}\}$, where $x = 2$, $\text{Y} = \text{C}_6\text{H}_5\text{SO}_3^-$ (**3**); $x = 1$, $\text{Y} = 1,5\text{-C}_{10}\text{H}_6(\text{SO}_3)_2$ (**4**) have been prepared and characterized. Attempts to prepare hydrated monoorganotin cations resulted in the macromeric dodecanuclear organooxotin cages (*foot-ball cages*), $\{[(n\text{BuSn})_{12}(\mu_3\text{-O})_{14}(\mu_2\text{-OH})_6]^{2+} \cdot 2\text{RSO}_3^-\}$, where $\text{R} = \text{C}_6\text{H}_5$ (**5**); 2,5- $\text{Me}_2\text{C}_6\text{H}_3$ (**6**). The X-ray crystal structure of **6** is reported and compared with other members of this structural type. In view of the interest in neutral and cationic organotin

compounds in esterification and transesterification reactions we have explored the catalytic activity of **1–6** towards acetylation of alcohols and phenols.

Results and Discussion

Synthesis of Organotin Cations

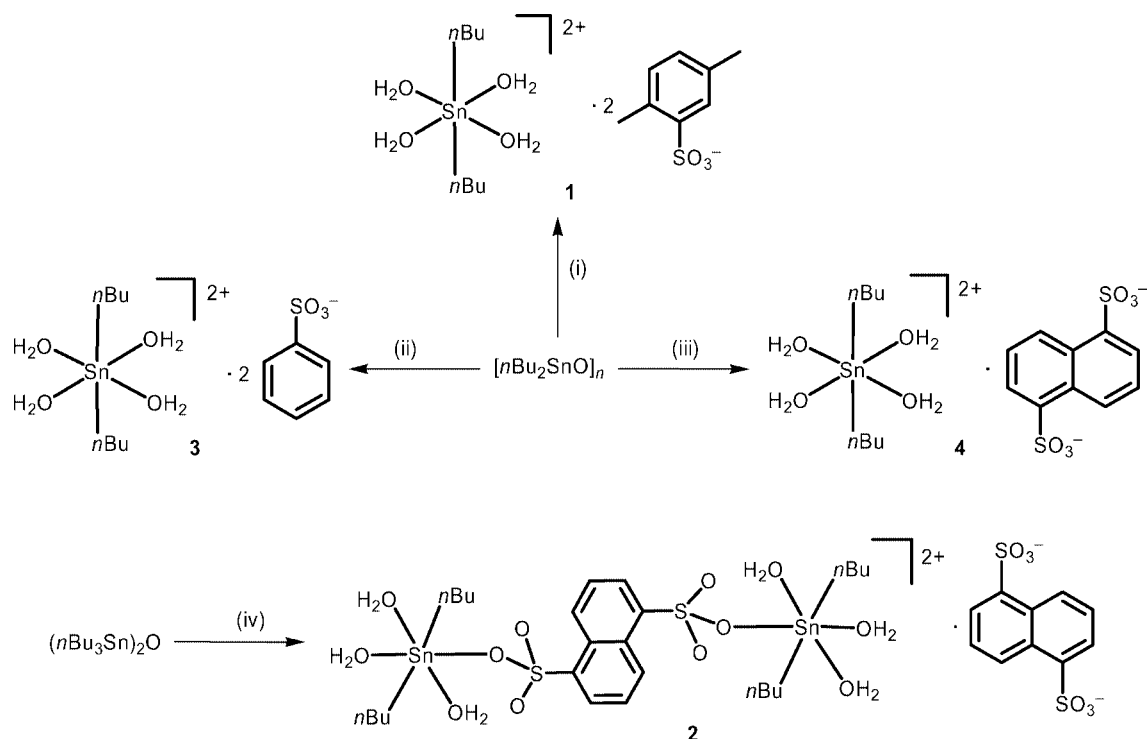
The synthesis of the organotin cations has been accomplished in high yields by the reaction of an organotin oxide with an arylsulfonic acid. The work-up of the reaction mixture and subsequent crystallization in open air allows the isolation of the compounds **1–4**. All of these organotin cations are air-stable solids. Compounds **3** and **4** are prepared by a reaction of the polymeric $[n\text{Bu}_2\text{SnO}]_n$ with the corresponding sulfonic acids (Scheme 1). This procedure is similar to that reported by us recently for the synthesis of **1** (Scheme 1).^[5a] Compound **2**, which contains two tin units bridged by a disulfonate, is synthesized by the dealkylation reaction involving a 1:1 reaction of $(n\text{Bu}_3\text{Sn})_2\text{O}$ with naphthalene-1,5-disulfonic acid.^[5b] The dodecanuclear organooxotin cages **5** and **6** are assembled by the reaction of *n*-butylstannonic acid, $n\text{BuSn}(\text{O})(\text{OH})$ with the corresponding sulfonic acids (Scheme 2).^[6]

Solution Studies

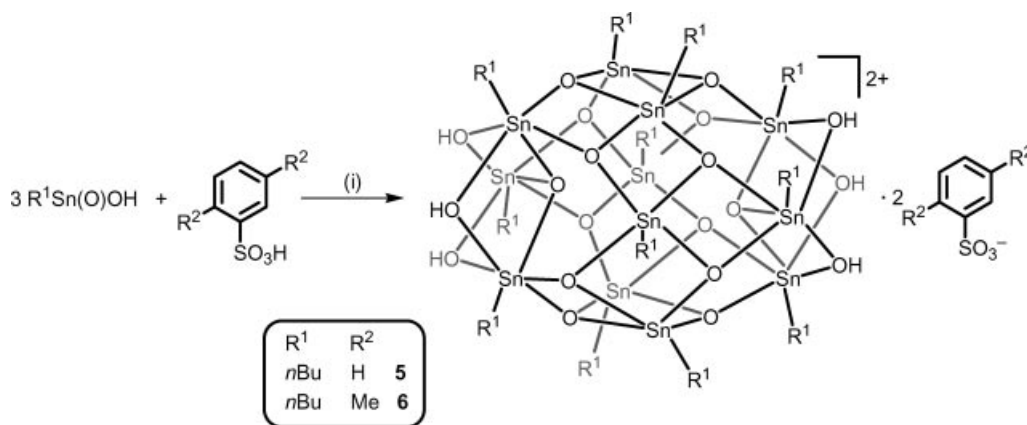
All of these compounds have been characterized by analytical and spectroscopic techniques (see experimental section). Consistent with the above formulation; conductivity studies on **3** and **4** revealed that these compounds are 1:2 electrolytes. While the specific and molar conductivities of **3** are $1811 \mu\text{Scm}^{-1}$ and $300 \text{Scm}^2\text{mol}^{-1}$ (3 mmol/L in

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Scheme 1. Synthesis of diorganotin cations **1–4**. (i) 2 2,5-Me₂C₆H₃SO₃H, toluene, reflux, 8 h. (ii) 2 C₆H₅SO₃H, toluene, reflux, 8 h. (iii) 1,5-C₁₀H₆(SO₃H)₂, toluene, reflux, 8 h. (iv) 2 1,5-C₁₀H₆(SO₃H)₂, toluene, reflux, 6 h.



Scheme 2. Synthesis of monoorganotin macrocations **5** and **6**. (i) toluene, reflux, 72 h.

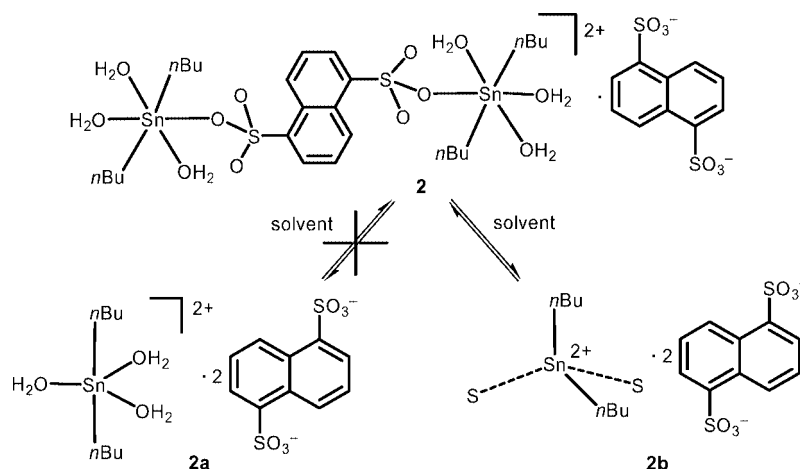
CH₃OH), **4** has a specific conductivity of 898 μScm^{-1} and a molar conductivity of 150 $\text{Scm}^2\text{mol}^{-1}$ (3 mmol/L in DMF) (Table 1). The increased ionic conductivity of **3** when compared to **1** [specific conductivity 946 μScm^{-1} ; molar conductivity 158 $\text{Scm}^2\text{mol}^{-1}$ (3 mmol/L in CH₃OH)]^[5a] and **4** is attributed to the increased acidic nature of **3** which arises due to the benzenesulfonate ligand. The ¹¹⁹Sn NMR spectra of **3** and **4** show a single resonance at –360.6 and –384.9 ppm, respectively (Table 1), which are comparable to that observed for **1** (a single resonance at $\delta = -360.0$ ppm)^[5a] which is characteristic of a C₂O₄ environment around tin atoms.^[1b]

The solution ionic conductivity measurement on **2** shows that the observed specific and molar conductivities are 2257 μScm^{-1} and 376 $\text{Scm}^2\text{mol}^{-1}$ (3 mmol/L in CH₃OH), respectively. These values suggest that in solution **2** does not exist as a 1:2 electrolyte but presumably undergoes an unsymmetrical disproportionation of the tin–sulfonate oxygen bond and thereby producing different kinds of cationic species. Support for such a hypothesis also comes from the ¹¹⁹Sn NMR chemical shifts of the compound **2**. ¹¹⁹Sn NMR spectrum of a [D₆]DMSO solution of **2** shows two resonances at –385.7 and 8.3 ppm (Table 1). Whereas, the signal at $\delta = -385.7$ ppm corresponds to the six-coordinate

Table 1. Solution studies of some of the selected organotin compounds.

Entry	Compound	Specific conductivity [μScm^{-1}]	Molar conductivity [$\text{Scm}^2\text{mol}^{-1}$]	^{119}Sn NMR [δ , ppm]	Ref.
1	$\{n\text{Bu}_2\text{Sn}(\mu\text{-OH})(\text{H}_2\text{O})(\text{O}_3\text{SCF}_3)\}_2$	870 ^[a]	43.5 ^[a]	−203.2 ^[h] (−209.7 ^[i])	[3c]
2	$\{[n\text{Bu}_2\text{Sn}(\mu\text{-OH})(\text{H}_2\text{O})]^+\cdot\text{CF}_3\text{SO}_3^-\}_2$	994 ^[a]	49.7 ^[a]	−249.7 ^[h] (−249.6 ^[i])	[3c]
3	$\{[(2\text{-C}_6\text{H}_5\text{-C}_4\text{H}_8)_2\text{Sn}(\mu\text{-OH})(\text{H}_2\text{O})]^+\cdot\text{CF}_3\text{SO}_3^-\}_2$	805 ^[a]	40.0 ^[a]	−188.4 ^[i]	[3d]
4	1	946 ^[b]	158 ^[b]	−360.04 ^[i]	[5a]
5	3	1811 ^[b]	300 ^[b]	−360.61 ^[i]	this work
6	4	898 ^[c]	150 ^[c]	−384.91 ^[k]	this work
7	2	2257 ^[b]	376 ^[b]	−385.7, +8.3 ^[k]	this work
8	5	1503 ^[b]	250 ^[b]	−284.28, −463.8 ^[l]	this work
9	6	971 ^[b]	162 ^[b]	−283.97, −462.77 ^[l]	this work
10	$[\text{Me}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2]^{2+}\cdot 2\text{CF}_3\text{SO}_3^-$	714 ^[d]	—	−296.4 ^[l] (−343.9 ^[i])	[3e]
11	$[n\text{Bu}_2\text{Sn}(\text{H}_2\text{O})_2(\text{OPPh}_3)_2]^{2+}\cdot 2\text{CF}_3\text{SO}_3^-$	705 ^[d]	—	−302.1 ^[l] (−363.5 ^[i])	[3e]
12	<i>foot-ball cage</i> ^[n]	5 ^[e]	—	−282.8, −461.8 ^[m]	[6]
		200 ^[f] –1210 ^[g]			

[a] 10 mmol/L in CH_3CN . [b] 3 mmol/L in CH_3OH . [c] 3 mmol/L in DMF. [d] 3.3 mmol/L in CH_3CN . [e] 5 mmol/L in CD_2Cl_2 (for pure CD_2Cl_2 , $5\text{ }\mu\text{Scm}^{-1}$). [f] 5 mmol/L in DMSO. [g] 50 mmol/L in DMSO. [h] $[\text{D}_6]\text{acetone}$. [i] CD_3CN . [j] CD_3OD . [k] $[\text{D}_6]\text{DMSO}$. [l] CDCl_3 . [m] CD_2Cl_2 . [n] Anion: 2 4-MeC₆H₄SO₃[−].

Scheme 3. Solution equilibrium exhibited by the cation **2**. S: more polar solvents (CH_3OH or $[\text{D}_6]\text{DMSO}$).

C_2O_4 environment around tin, the value of +8.3 ppm is quite unusual for a diorganotin oxo species and could be attributed to a tetracoordinate tin containing two coordinated DMSO molecules.^[7] If a very dilute solution is used only the signal at +8.3 ppm is seen. This could presumably be due to the highly polar nature of the solvent DMSO which displaces all the ligated (water and sulfonate) groups of tin and thereby producing a $[n\text{Bu}_2\text{Sn}(\text{DMSO})_2]^{2+}$ species **2b** (Scheme 3).

The conductivity values of **5** and **6** suggest that these compounds are 1:2 electrolytes in solution. While the observed specific and molar conductivities of **5** are $1503\text{ }\mu\text{Scm}^{-1}$ and $250\text{ Scm}^2\text{mol}^{-1}$ (3 mmol/L in CH_3OH), the respective values observed for **6** are $971\text{ }\mu\text{Scm}^{-1}$ and $162\text{ Scm}^2\text{mol}^{-1}$ (3 mmol/L in CH_3OH), respectively (Table 1). The ^{119}Sn NMR spectra of **5** and **6** show two resonances around −280 and −460 ppm. The chemical shift value of $\delta = -280$ ppm is characteristic of the five-coordinate tin situated at the equator of the molecule whereas the signal at $\delta = -460$ ppm is due to the presence of six-coordinate tins at the poles.^[6]

Molecular Structure

Whereas the molecular structures of **1** and **2** have been determined previously,^[5] that of **6** is reported here. The molecular structure of **6** (dioxane) is shown in Figure 1 (a). The macrocation is composed of a centrosymmetric $[(n\text{BuSn})_{12}(\mu_3\text{-O})_{14}(\mu_2\text{-OH})_6]^{2+}$ moiety with the asymmetric unit possessing two symmetry-related “half molecules”. The structure of this cationic tin cage was described previously by the use of anions such as chloride,^[8a] hydroxide^[8b] or phosphinate.^[8c] There has been one report on the structure of this macrocation where *p*-toluenesulfonate is the counter anion.^[6] The structure of the macrocation in **6** is like a “football” consisting of twelve tin atoms which are linked by μ_3 -oxo and μ_2 -hydroxo bridges. All the *n*-butyl chains situated on the tin atom are pointing outside the cage core. The bonding parameters found in this cage are given in Table 2 and are comparable with the literature values.^[6,8] The structure of the molecule can be understood as follows. Among the twelve tin atoms present in the molecule, six are situated at the two poles of the cage and the remaining six

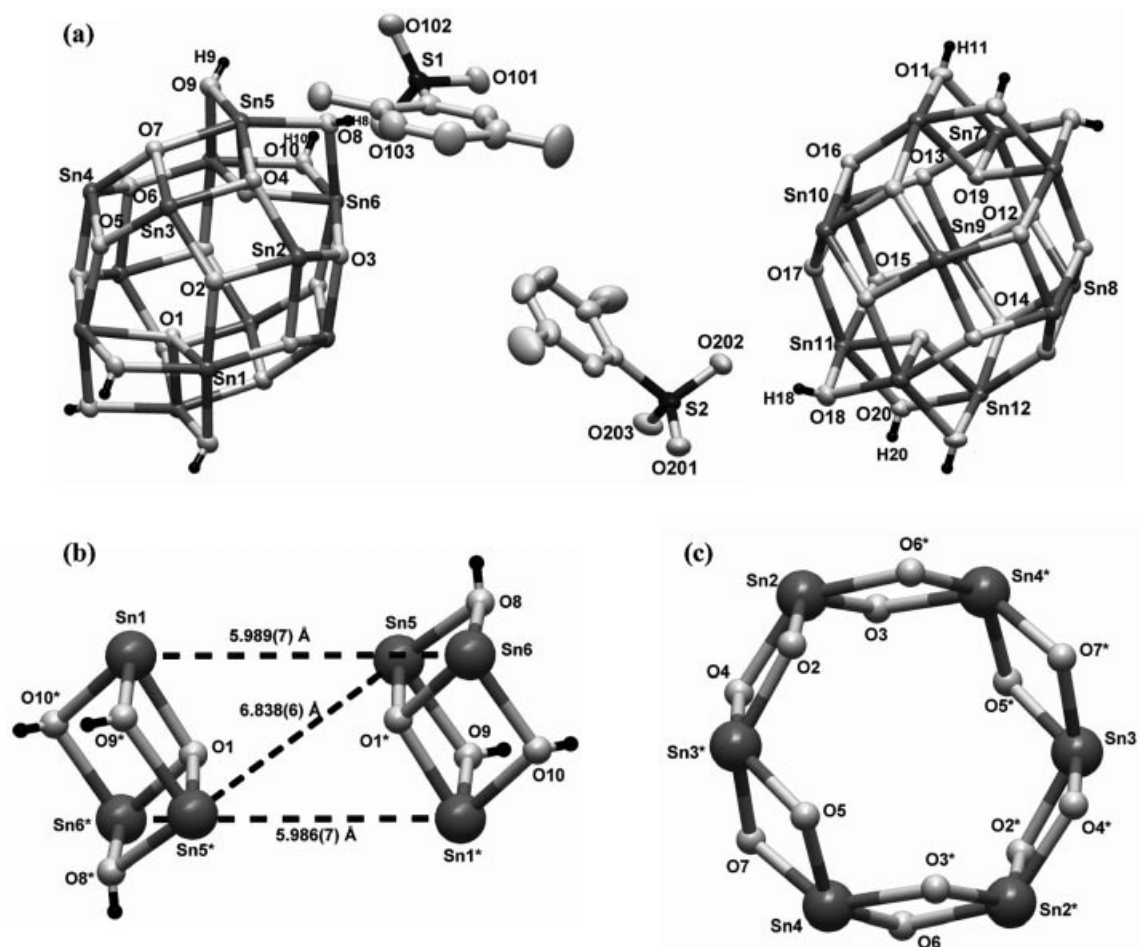


Figure 1. (a) View of the two molecules of **6** present in its asymmetric unit (at 50% ellipsoidal probability level). The unlabeled atoms are symmetric counterparts of the labeled atoms. All the *n*-butyl groups on tin atoms along with their protons and protons in the sulfonate moieties are removed. (b) View of the two *poles* consist of two trimeric O-capped subunits of $\text{Sn}_3(\mu_3\text{-O})(\mu_2\text{-OH})_3$. (c) View of the *equator* is spanned by a hexameric oxotin cycle $\text{Sn}_6(\mu_3\text{-O})_{12}$.

Table 2. Comparison of (bond) distances in the core structures of selected monoorgano oxotin cages.

Compound	Average Sn–O(μ_3) [Å]	Average Sn–OH(μ_2) [Å]	Average Sn–O(X) [Å]	Average Sn...Sn ^[e] [Å]	Inter pole [O(μ_3)...O(μ_3)] [Å]	Ref.
<i>Foot-ball cage</i> 6 ^[a]	2.087(4) ^[f] 2.117(4) ^[g] 2.059(4) ^[h] 2.086(4) ^[i] 2.112(4) ^[j] 2.063(4) ^[k]	2.110(5) 2.109(4)	–	6.366(5) 6.386(6)	3.955(5) 3.938(4)	this work
<i>Foot-ball cage</i> ^[b]	2.080(2) ^[f] 2.115(2) ^[g] 2.057(8) ^[h]	2.119(2)	–	6.379(3)	3.984(2)	[6]
<i>Foot-ball cage</i> ^[c]	2.091(7) ^[f] 2.054(8) ^[g] 2.140(8) ^[h]	2.096(8)	–	6.331(6)	3.899(6)	[8b]
<i>Foot-ball cage</i> ^[d]	2.117(2) ^[f] 2.098(2) ^[g] 2.060(2) ^[h]	2.142(2)	–	6.373(3)	3.996(3)	[8a]
<i>O-Capped cluster</i>	2.075(5)	2.128(6)	2.122(6), X = P	–	–	[9b]
<i>Double O-capped cluster</i>	2.065(3)	2.172(2)	2.072(2), X = P	6.337(1) ^[l]	3.778(4)	[9a]
<i>Drum</i>	2.101(5)	–	2.155(5), X = C	–	–	[9c]

[a] Two crystallographically independent molecules are present; anion: two 2,5-Me₂C₆H₃SO₃[–]. [b] Anion: two 4-MeC₆H₄SO₃[–]. [c] Anion: two OH[–]. [d] Anion: two Cl[–]. [e] Average distance between the diametrically opposite tin atoms present in the equator. [f] Sn is bonded with μ_3 -capped oxygen (O-capped) in the poles. [g] Pole tin atoms bonded with μ_3 -oxygens which are part of the equator. [h] Equator tin atoms bonded with μ_3 -oxygens which are part of the equator. [i] Sn is bonded with μ_3 -capped oxygen (O-capped) in the poles. [j] Pole tin atoms bonded with μ_3 -oxygens which are part of the equator. [k] Equator tin atoms bonded with μ_3 -oxygens which are part of the equator. [l] Average distance between the diametrically opposite phosphorus atoms present in the equator.

tin atoms occupy the equator of the cage. The poles consist of two trimeric *O-capped* subunits of $[(n\text{BuSn})_3(\mu_3\text{-O})(\mu_2\text{-OH})_3]$ (Figure 1, b).^[9a] Within these subunits the tin atoms are hexa-coordinate and possess bridging oxo and hydroxo groups.

The shorter and longer Sn...Sn distances between the two poles are given in Figure 1 (b). The equator of the cage is spanned by a hexameric cycle $[(n\text{BuSn})_6(\mu_2\text{-O})_{12}]$ (Figure 1, c).^[9a] In this sub-unit the tins are five-coordinate and are nearly square pyramidal. This hexameric cycle is stitched by means of six distannoxane motifs (Sn_2O_2) with the average diameter of the cycle being 6.366(5) Å. Thus, it is possible to envisage the construction of the cage by capping each side of the hexameric cycle by the two trimeric tin units.

Supramolecular Assembly

In compound **6**, two molecules of the 2,5-dimethylbenzenesulfonate anion interact with three hydroxy groups at the poles through intermolecular O–H...O hydrogen bonding to generate a one-dimensional chain structure (Figure 2). The bonding parameters involved in these hydrogen bonds point to the fact that these are essentially strong hydrogen bonds. Hydrogen-bonding interactions among these

cages have resulted in the formation of two different rings; a seven-membered $\text{Sn}_2\text{O}_4\text{S}$ ring and a 12-membered $\text{Sn}_2\text{O}_8\text{S}_2$ ring. The average O...O distance observed in this molecule is 2.72 Å and are comparable with the *p*-toluenesulfonate derivative.^[6] The distance between two such polymeric sheets is 11.11 Å. Ribot et al. have utilized a similar type of cage as versatile nanobuilding blocks for the design of tin-based organic–inorganic hybrid materials.^[10]

Catalysis

In solution all the organotin cations behave as 1:2 electrolytes (Table 1). In view of their anticipated Lewis acidity, these compounds were tested as catalysts for acetylation of alcohols. All the organotin cations are very effective in the acetylation reactions of alcohols (Table 3 and Table 4). These reactions are completed much faster than those catalyzed by neutral tetraorganodistannoxanes.^[11] Thus, acetylation of menthol (**7d**) and cholesterol (**7e**) are completed only in 15 min (Table 3; Entries 19–25 and 26–32). Interestingly, inspite of low positive charge, the macrocations **5** and **6** are also reasonably effective although the reaction times are slightly longer.^[3d] The dications **1** and **3** are the most effective, in keeping with their increased Lewis acidity.

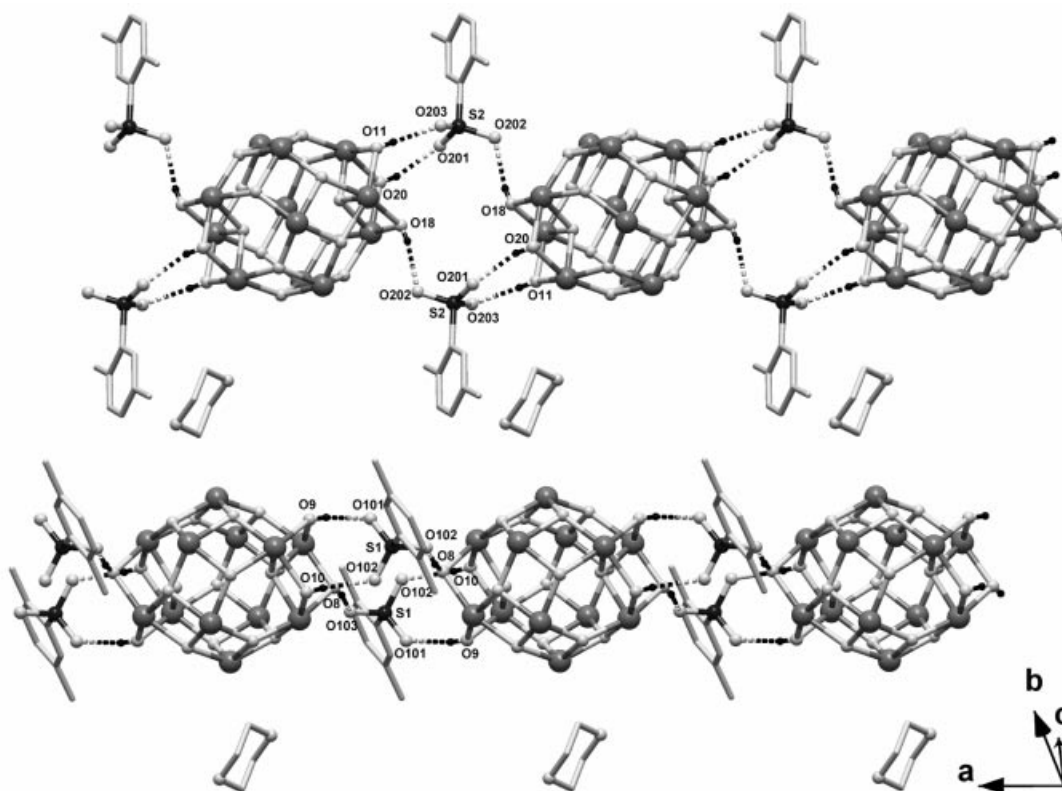
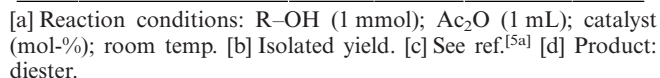
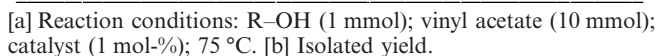


Figure 2. O–H...O hydrogen-bond-mediated one-dimensional supramolecular assembly in compound **6**. All the *n*-butyl groups on tin atoms along with their protons and protons in the sulfonate moieties are removed. Bonding parameters for hydrogen bonding are: O8–H8 0.701(1), H8...O103 2.027(2), O8...O103 2.701(1) Å, O8–H8...O103 161.45(3)°; O9–H9 0.680(4), H9...O101 2.104(3), O9...O101 2.757(3) Å, O9–H9...O101 161.21(4)°; O10–H10 0.688(2), H10...O102 2.043(4), O10...O102 2.725(5) Å, O10–H10...O102 171.22(1)°; O11–H11 0.696(6), H11...O203 1.985(4), O11...O203 2.681(8) Å, O11–H11...O203 178.18(5)°; O18–H18 0.696(1), H18...O202 2.053(3), O18...O202 2.736(8) Å, O18–H18...O202 167.44(1)°; O20–H20 0.690(1), H20...O201 2.058(3), O20...O202 2.721(5) Å, O20–H20...O201 161.45(2)°.

Table 3. Acetylation of alcohols catalyzed by organotin cations.^[a]

In order to assess if the organotin cations can be used for transacetylation reactions, two test cases were examined, using the reaction of the alcohols **7a** and **7b** with vinyl acetate (**10**) (Table 5). Transacetylation was completed in all cases quantitatively, although higher catalyst loadings were

[a] For reaction Scheme, see Table 3; Reaction conditions: R-OH (1 mmol); Ac₂O (1 mL); catalyst (mol-%); room temp. [b] Isolated yield. [c] See ref.^[5a]

Table 5. Transacetylation reactions using organotin cations.^[a]

In summary, we report a series of organotin cations with varying nuclearity and charge and have shown their efficacy in acetylation and in transacetylation reactions. All of the

organotin cations are air-stable solids that can be prepared in excellent yields in a one-step synthesis, thus making them as potentially useful reagents.

Experimental Section

General Remarks: Solvents were dried with sodium benzophenone ketyl and were collected from the still at the time of reaction. (*n*Bu₃Sn)₂O, [*n*Bu₂SnO]_{*n*}, *n*BuSn(O)(OH), 1,5-C₁₀H₆(SO₃H)₂·4H₂O (Aldrich), L-menthol (Lancaster), cholesterol (Acro chemicals), cinnamyl alcohol (Fluka), C₆H₅SO₃H (75% w/w water solution), phenol, *p*-cresol, acetic anhydride, vinyl acetate and β-naphthol (sd-fine, India) were purchased and used as such without any further purification. 2,5-Me₂C₆H₃SO₃H,^[12] 1-phenylethanol,^[12] 1,3-diphenyl-2-propen-1-ol^[12] and organotin cations **1**^[5a] and **2**^[5b] were prepared by literature methods. Melting points were measured with a JSGW melting point apparatus and are uncorrected. Elemental analyses were carried out with a Thermoquest CE instruments model EA/110 CHNS-O elemental analyzer. Infrared spectra were recorded in dichloromethane solution as well as neat liquid or as KBr pellets with a FT-IR Bruker-Vector Model. ¹H and ¹¹⁹Sn NMR spectra were obtained with a JEOL-JNM LAMBDA 400 model spectrometer using CDCl₃, CD₃OD and (CD₃)₂SO solutions with shifts referenced to tetramethylsilane (for ¹H NMR) and tetramethyltin (for ¹¹⁹Sn NMR), respectively. ¹¹⁹Sn NMR spectra were recorded under broad-band decoupled conditions. Conductivity measurements were done with a Century Digital Conductivity Meter Model CC-601.

Synthesis of [*n*Bu₂Sn(H₂O)₄]²⁺·2C₆H₅SO₃[−] (3**):** A mixture of [*n*Bu₂SnO]_{*n*} (0.42 g, 1.68 mmol) and C₆H₅SO₃H (75% w/w water solution) (0.70 g, 3.34 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 (G-4), dried (in air) and identified as **3** (0.87 g, 87% yield). M.p. 270 °C (dec.). C₂₀H₃₆O₁₀S₂Sn (619.33): calcd. C 38.78, H 5.85; found C 37.94, H 5.61. IR (KBr, cm^{−1}): $\tilde{\nu}$ = 3420 (br., H₂O), 1251 (s, SO₃ assym. str.), 1192 (s, SO₃ assym. str.), 1070 (s, SO₃ sym. str.), 1022 (s, SO₃ ionic) and 624 (m, C–S). ¹H NMR (400 MHz, CD₃OD, ppm): δ = 0.83 (t, *J* = 7.31 Hz, 6 H, butyl CH₃), 1.25 (q, *J* = 7.31 Hz, 4 H, Sn–CH₂), 1.58–1.64 (m, 4 H, butyl CH₂), 1.75–1.80 (m, 4 H, butyl CH₂), 7.43–7.51 (m, 6 H, aromatic) and 7.82–7.85 (m, 4 H, aromatic). ¹¹⁹Sn NMR (150 MHz, CD₃OD, ppm): δ = −360.61 (s).

Synthesis of [*n*Bu₂Sn(H₂O)₄]²⁺·1,5-C₁₀H₆(SO₃[−])₂ (4**):** A mixture of [*n*Bu₂SnO]_{*n*} (0.30 g, 1.20 mmol) and 1,5-C₁₀H₆(SO₃H)₂·4H₂O (0.43 g, 1.20 mmol) was taken in toluene (60 mL) and heated under reflux for 8 h using a Dean–Stark apparatus to remove the water formed in the reaction by azeotropic distillation. A white solid formed in the reaction was filtered by a sintered funnel (G-4) and dried (in air) to obtain **4** in good yield (0.66 g, 93% yield). M.p. > 280 °C (dec.). C₁₈H₃₂O₁₀S₂Sn (591.91): calcd. C 36.56, H 5.45; found C 36.29, H 5.19. IR (KBr, cm^{−1}): $\tilde{\nu}$ = 3454 (br., H₂O), 1206 (s, SO₃ assym. str.), 1161 (s, SO₃ assym. str.), 1044 (s, SO₃ ionic) and 613 (s, C–S). ¹H NMR (400 MHz, [D₆]DMSO, ppm): δ = 0.86 (t, *J* = 7.2 Hz, 6 H, butyl CH₃), 1.28 (q, *J* = 7.2 Hz, 4 H, Sn–CH₂), 1.47–1.49 (m, 8 H, butyl CH₂CH₂), 7.44 (t, *J* = 7.2 Hz, 2 H, aromatic), 7.95 (d, *J* = 6.8 Hz, 2 H, aromatic) and 8.86 (d, *J* = 8.4 Hz, 2 H, aromatic). ¹¹⁹Sn NMR (150 MHz, [D₆]DMSO, ppm): −384.91(s).

Synthesis of [(*n*BuSn)₁₂(μ₃-O)₁₄(μ₂-OH)₆]²⁺·2C₆H₅SO₃[−] (5**):** A mixture of *n*BuSn(O)(OH) (1.80 g, 8.62 mmol) and C₆H₅SO₃H (75%

w/w water solution) (0.45 g, 2.87 mmol) in toluene (150 mL) was heated under reflux for 72 h using a Dean–Stark apparatus to remove the water formed in the reaction by azeotropic distillation. The reaction mixture was cooled and filtered through a sintered funnel (G-4) and the clear filtrate was evaporated in vacuo to yield **5** as a white amorphous solid (1.88 g, 95% yield). M.p. 196 °C. C₆₀H₁₂₄O₂₆S₂Sn₁₂ (2750.26): calcd. C 26.20, H 4.54; found C 26.09, H 4.24. IR (KBr, cm^{−1}): $\tilde{\nu}$ = 3214 (br., OH), 1258 (s, SO₃ assym. str.), 1194 (s, SO₃ assym. str.), 1126 (s, SO₃ sym. str.), 1035 (s, SO₃ ionic) and 618 (m, C–S). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 0.79–0.89 (m, 36 H, butyl CH₃), 1.05–1.69 (m, 72 H, Sn–CH₂CH₂CH₂) and 6.88–7.79 (m, 10 H, aromatic). ¹¹⁹Sn NMR (150 MHz, CDCl₃, ppm): δ = −284.28 [s, ²*J*(^{117/119}Sn–¹³C) = 204, 208 Hz] and −463.8 [s, ²*J*(^{117/119}Sn–¹³C) = 204 Hz].

Synthesis of [(*n*BuSn)₁₂(μ₃-O)₁₄(μ₂-OH)₆]²⁺·2 2,5-Me₂C₆H₃SO₃[−] (6**):** A mixture of *n*BuSn(O)(OH) (3.36 g, 16.10 mmol) and 2,5-Me₂C₆H₃SO₃H (1.0 g, 5.37 mmol) in toluene (150 mL) was heated under reflux for 72 h using a Dean–Stark apparatus to remove the water formed in the reaction by azeotropic distillation. The reaction mixture was cooled and filtered through a sintered funnel (G-4) and the clear filtrate was evaporated in vacuo to yield **6** as a white amorphous solid (3.62 g, 96% yield). Crystals suitable for single-crystal X-ray diffraction were obtained by recrystallizing compound **6** in dioxane with 0.5% water. M.p. 158 °C. C₆₄H₁₃₂O₂₆S₂Sn₁₂ (2806.39): calcd. C 27.39, H 4.74; found C 26.97, H 4.85. IR (KBr, cm^{−1}): $\tilde{\nu}$ = 3198 (br., OH), 1193 (s, SO₃ assym. str.), 1195 (s, SO₃ assym. str.), 1088 (s, SO₃ sym. str.), 1021 (s, SO₃ ionic) and 616 (m, C–S). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 0.80 (t, *J* = 7.32 Hz, 18 H, butyl CH₃), δ = 0.88 (t, *J* = 7.36 Hz, 18 H, butyl CH₃), 1.19–1.32 (m, 24 H, Sn–CH₂), 1.38–1.70 (m, 48 H, butyl CH₂CH₂), 2.23 (s, 6 H, Ar–CH₃), 2.55 (s, 6 H, Ar–CH₃), 7.00 (s, 2 H, aromatic), 7.09 (s, 2 H, aromatic) and 7.69 (s, 2 H, aromatic). ¹¹⁹Sn NMR (150 MHz, CDCl₃, ppm): δ = −283.97 [s, ²*J*(^{117/119}Sn–¹³C) = 204, 207 Hz] and −462.77 [s, ²*J*(^{117/119}Sn–¹³C) = 205 Hz].

General Procedure for Acetylation of Alcohols and Phenols:^[5a] A mixture of the alcohol or phenol (**7a–h**) (1 mmol), acetic anhydride (**8**) (1 mL) and catalytic amount (mol%) of the organotin catalyst **1–6** were stirred at room temperature. The progress of the reaction was monitored by TLC. At the end of the reaction excess acetic anhydride was removed in vacuo. The residual portion was dissolved in minimum amount of dichloromethane and filtered through a short column (in some cases the compound was eluted with ethyl acetate and hexane) to yield the corresponding acetate **9a–h**. All the acetates were characterized by ¹H NMR spectra and compared with authentic samples.

General Procedure for trans-Acetylation Reactions: A mixture of alcohol (**7a–b**) (1 mmol), vinyl acetate (**10**) (10 mmol) and catalytic amount (1 mol%) of the tin catalyst **1–6** were refluxed at 75 °C. The progress of the reaction was monitored by TLC. After the reaction was complete, excess vinyl acetate was evaporated and the residue was subjected to column chromatography on silica gel to give acetates **9a–b** in good yields. All the acetates were characterized by ¹H NMR spectra and compared with authentic samples.

X-ray Crystallographic Study: Colorless block-like crystal of **6** suitable for single-crystal X-ray diffraction was loaded on a Bruker AXS Smart Apex CCD diffractometer. The details pertaining to the data collection and refinement for **6** are as follows: size 0.4 × 0.4 × 0.3 mm³; empirical formula C₆₆H₁₃₆O₂₇S₂Sn₁₂; *M_w* = 2850.15; triclinic; space group *P* $\bar{1}$; *a* = 12.6693(11) Å; *b* = 16.4765(14) Å; *c* = 24.8100(2) Å; *a* = 77.131(2)°; *β* = 86.091(2)°; *γ* = 69.637(2)°; *V* = 4733.1(7) Å³; *Z* = 2; *T* = 150(2) K; *D*_{calcd.} = 2.000 Mg·m^{−3}; Mo-

K_{α} radiation; θ range 1.35 to 25.03°; 24859 reflections collected, 16441 independent reflections ($R_{\text{int}} = 0.0180$); $R_1 = 0.0271$, $wR_2 = 0.0688$ [for $I > 2\sigma(I)$]; $R_1 = 0.0314$, $wR_2 = 0.0715$ (for all data); GOF = 1.015. The maximum and minimum electron densities are 0.964 and $-0.727 \text{ e} \cdot \text{\AA}^{-3}$, respectively. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXL-97.^[13] The hydrogen atoms attached to oxygen atoms in the hydroxy groups were located from the difference map and their position were refined. All other hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. A 1,4-dioxane molecule was also present in the asymmetric unit of **6** as a solvate.

CCDC-296001 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Figure 1 and 2 and its bonding parameters were obtained from DIAMOND 3.0 software package.^[14]

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