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*Review*

# Organotin compounds containing four-membered distannoxane $[Sn(\mu\text{-}OH)]_2$ units†

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**Compounds containing the distannoxane core $[Sn(\mu\text{-}OH)]_2$ are reviewed. Synthesis and structural aspects of these compounds are summarized in this article. Copyright © 2007 John Wiley & Sons, Ltd.**

**KEYWORDS:** organotin compounds; organotin hydroxide; distannoxane; organostannoxane; bridging hydroxide ligand

## INTRODUCTION

The hydroxides of silicon are very well studied.[1–4] Compounds where the silicon atom contains one, two or three–OH groups are well known (Fig. 1), and can be prepared by utilizing a large number of preparative methods.[1] Such compounds are also of interest because of their utility as precursors for the preparation of metallosiloxanes.[1,3–5] In contrast to the situation in silicon, organotin compounds containing the -OH group are not common. For example, the trihydroxide, $RSn(OH)_3$ is not known.[6] Even among dihydroxides, only one example of $R_2Sn(OH)_2$ has been reported which has been structurally characterized.[7] Trioganotin hydroxides, $R_3SnOH$ are known in certain instances (R = Me, Ph, *cyc*-$C_6H_{11}$).[8] One of the reasons for the rarity of organotin compounds with Sn-OH groups is their ready condensation to afford organotin oxides, hydroxides and oxide-hydroxides.[8–12] Representative examples of organotin oxides, hydroxides and oxide-hydroxides are shown in Fig. 2.

Organotin oxides, -oxide-hydroxides as well as -hydroxides serve as excellent precursors for the preparation of organotin clusters.[8,9] Another facet of the hydroxide ligand, in the context of organotin compounds, is the role it plays in bridging two tin centers together to afford $[Sn(\mu\text{-}OH)]_2$ motifs (thus, such compounds can be considered as dimeric forms of organotin monohydroxides).[9] These can exist as independent chemical entities or they can be part of large tin clusters (Fig. 3).[9] Compounds containing the four-membered $[Sn(\mu\text{-}OH)]_2$ ring can be isolated in a number of diverse chemical reactions. Surprisingly there has been no attempt, thus far, to review the existing literature on these compounds. This short account is an effort to fill this gap. Only those compounds that have been unambiguously characterized by X-ray crystallography are included in this article. A summary of the synthetic routes and structural details of distannoxanes containing the $[Sn(\mu\text{-}OH)]_2$ structural unit are listed in Table 1. The following is a brief description of the material given in Table 1. Most of the compounds containing the $[Sn(\mu\text{-}OH)]_2$ motif are diorganotin compounds. A few examples of monoorganotin compounds are also known.

## DIORGANOTIN COMPOUNDS

A number of neutral and ionic distannoxanes containing various nitrate, halide and hydroxide terminal ligands are known (Table 1, entries 1–9). The reaction of dimethyltin oxide with nitric acid affords $[Me_2Sn(\mu\text{-}OH)(NO_3)]_2$ (Table 1, entry 1).[13] Each nitrate group acts as a monodentate ligand. The geometry around each tin is distorted trigonal bipyramidal. Two types of Sn–O bond distances are found, a short distances of 2.06(3) Å and a longer distance of 2.18(3) Å. In general, most of the distannoxanes display such asymmetry in Sn–O bond distances.

The reaction of $[t\text{-}Bu_2SnO]_3$ with HCl, that of $t\text{-}Bu_2SnCl_2$ with aqueous NaOH (followed by KF) or that of $t\text{-}Bu_2SnBr_2$ with aqueous NaOH affords distannoxanes containing reactive terminal halide groups (Table 1, entries 3–5).[14,15]

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E-mail: vc@iitk.ac.in
†Dedicated to the memory of Professor Des Cunningham and to the ICCOC-GTL-12 Galway meeting.
Contract/grant sponsor: Department of Science and Technology, New Delhi.

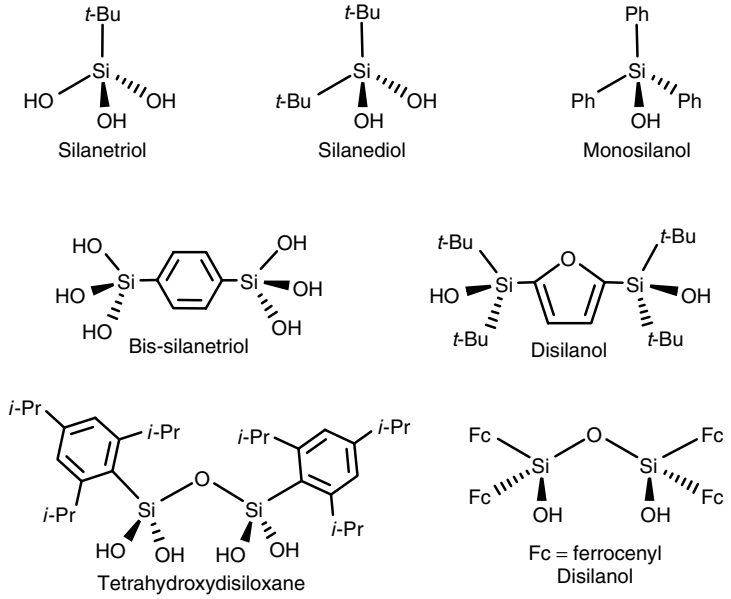


**Figure 1.** Various types of silanols.

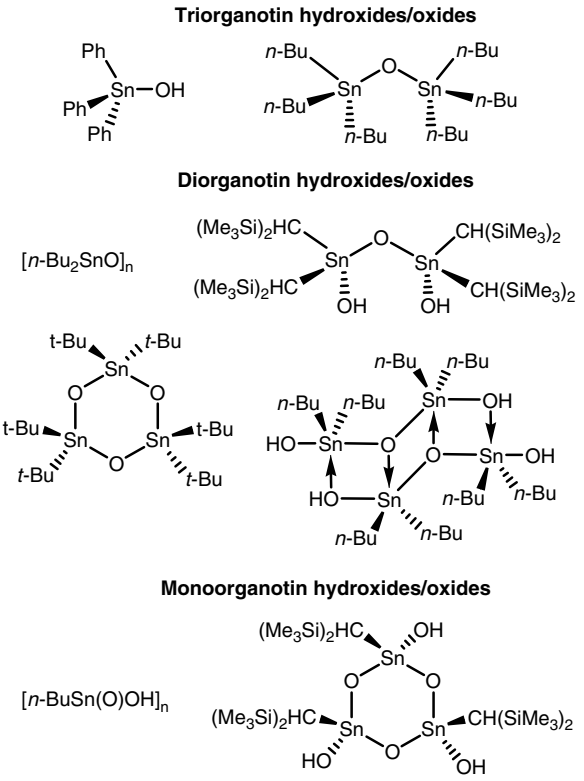


**Figure 2.** Representative examples of organotin oxides and hydroxides.

Such compounds can be utilized for further elaboration. For example, $[t\text{-}Bu_2Sn(\mu\text{-}OH)Cl]_2$ reacts with $AgNO_3$ by a substitution of chlorine to afford $[t\text{-}Bu_2Sn(\mu\text{-}OH)(NO_3)]_2$.[14]

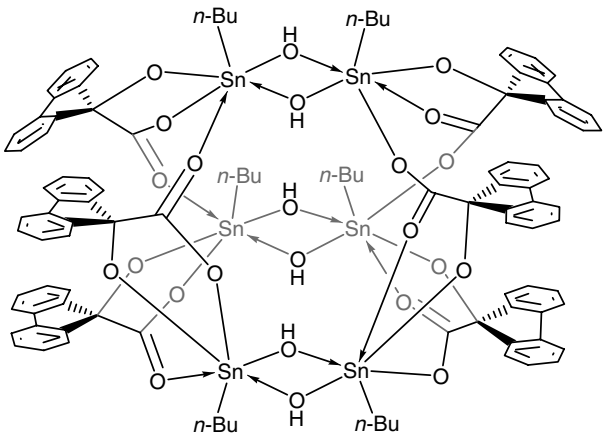

**Figure 3.** Trimeric four-membered $[Sn(\mu\text{-}OH)]_2$ ring containing organotin compound.

The nitrate ligand coordinates in a chelating mode (Table 1, entry 2). Mild hydrolysis of $Ph_2SnCl_2$ in presence of quinoline affords $[Ph_2Sn(\mu\text{-}OH)Cl]_2 \cdot 2C_9H_7N$ (Table 1, entry 6).[16] The bridging hydroxide ligands in the latter are involved in O–H–N hydrogen bonding interactions with non-coordinated quinoline molecules.

Compounds containing both chelating and terminally coordinating nitrate ligands are also found. Thus, an ionic compound $\{[Me_2Sn(\mu\text{-}OH)(NO_3)_2]_2^{2-}[ImH_2^+]_2\}$ is formed in the reaction of $[Me_2Sn(\mu\text{-}OH)(NO_3)]_2$ with imidazole and aqueous $HNO_3$ (Table 1, entry 7).[17] The former contains two nitrate ligands around each tin. While one nitrate binds in chelating mode, the other interacts in an $\eta^1$ fashion in a monodentate coordination. A similar type of compound



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**Table 1.** Summary of organostannoxanes containing [Sn($\mu$-OH)]$_2$ unit

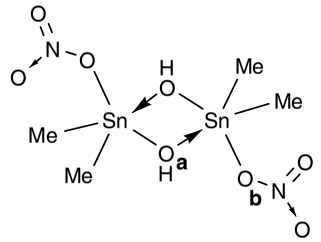
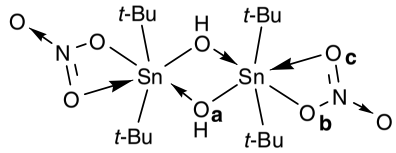
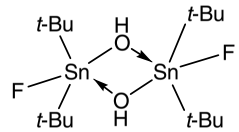
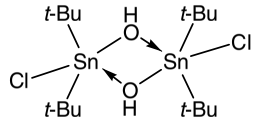
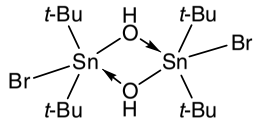
| Entry | Reaction | Structure | Description of structure | Reference |
|---|---|---|---|---|
| 1 | • $[Me_2SnO]_n + HNO_3$<br>• Reaction in aqueous medium<br>• Crystals grown from MeOH |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted trigonal bipyramidal (axial ligands: $O_b$ and longer $O_a$); monodentate coordination of $NO_3$<br>*3. Bonding parameters:* Sn–$O_a$ 2.06(3) and 2.18(3) Å; Sn–$O_b$ 2.30(3) Å | 13 |
| 2 | • [*t*-$Bu_2Sn(\mu$-OH)Cl]$_2 + AgNO_3$<br>• Reaction in $Me_2CO$ at room temperature<br>• Crystals grown from THF<br>• $^{119}$Sn NMR: $\delta$ − 293.6 ppm |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* hexacoordinate ($C_2O_4$); distorted octahedral; bidentate (chelating) coordination of $NO_3$<br>*3. Bonding parameters:* Sn–$O_a$ 2.048(3) and 2.187(2) Å; Sn–$O_b$ 2.224(2) Å; Sn–$O_c$ 3.060(2) Å | 14 |
| 3 | • *t*-$Bu_2SnCl_2$ + NaOH followed by KF<br>• Reaction in $Et_2O$ and $H_2O$ at room temperature<br>• Crystals obtained by sublimation |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_2F$); distorted trigonal bipyramidal (axial ligands: F and longer O)<br>*3. Bonding parameters:* Sn–O 2.012(5) and 2.199(5) Å; Sn–F 2.049(5) Å | 15 |
| 4 | • [*t*-$Bu_2SnO]_3$ + HCl<br>• Reaction in a mixture of $H_2O$ and $Me_2CO$<br>• Crystallized from $Me_2CO$ |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_2Cl$); distorted trigonal bipyramidal (axial ligands: Cl and longer O)<br>*3. Bonding parameters:* Sn–O 2.036(6) and 2.237(9) Å; Sn–Cl 2.506(3) Å | 15 |
| 5 | • *t*-$Bu_2SnBr_2$ + NaOH<br>• Reaction in $Me_2CO$ and $H_2O$ |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_2Br$); distorted trigonal bipyramidal (axial ligands: Br and longer O)<br>*3. Bonding parameters:* Sn–O 2.048(10) and 2.257(16) Å; Sn–Br 2.624(3) Å | 15 |




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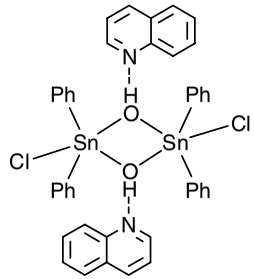
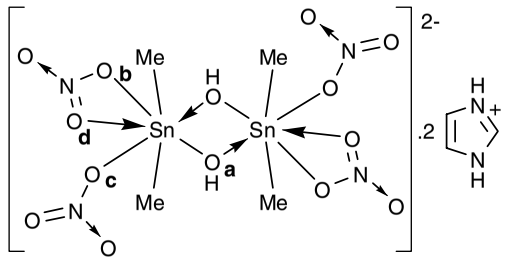
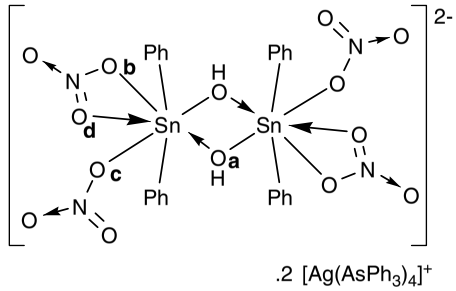
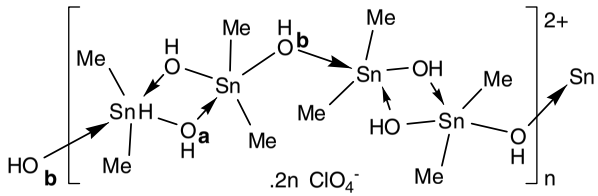
**Table 1.** (*Continued*)

| Entry | Reaction | Structure | Description of structure | Reference |
|---|---|---|---|---|
| 6 | • $Ph_2SnCl_2$ + quinoline<br>• Reaction in $Et_2O$ at 10 °C<br>• Crystals obtained from the partial elimination of the solvent |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_2Cl$); distorted trigonal bipyramidal (axial ligands: Cl and longer O)<br>3. Quinoline involved in O–H–N hydrogen bonding<br>*4. Bonding parameters:* Sn–O 2.020(2) and 2.184(2) Å; Sn–Cl 2.465(1) Å | 16 |
| 7 | • $[Me_2Sn(\mu\text{-}OH)(NO_3)]_2$ + Imidazole + aq. $HNO_3$<br>• Reaction in aqueous medium<br>• Crystals obtained from the partial elimination of the solvent<br>• Alternative method: $Me_2SnCl_2$ + $AgNO_3$ + imidazole + $HNO_3$<br>• Reaction in aqueous medium<br>• Crystals obtained from the partial elimination of the solvent |  | *1. Overall structure:* molecular, ionic<br>*2. Coordination around tin:* heptacoordinate ($C_2O_5$); distorted pentagonal bipyramidal (axial ligands: two methyl groups); mono- and bidentate (chelating) coordination of $NO_3$<br>*3. Bonding parameters:* Sn–$O_a$ 2.129(4) and 2.162(4) Å; Sn–$O_b$ 2.415(4) Å; Sn–$O_c$ 2.569(5) Å; Sn–$O_d$ 2.765(5) Å | 17 |
| 8 | • $Ph_3SnNO_3$ + $Ag(AsPh_3)_2NO_3$<br>• Reaction in $Me_2CO$/MeCN<br>• Crystals grown from the slow evaporation of the above solution |  | *1. Overall structure:* molecular, ionic<br>*2. Coordination around tin:* heptacoordinate ($C_2O_5$); distorted pentagonal bipyramidal (axial ligands: two phenyl groups); mono- and bidentate (chelating) coordination of $NO_3$<br>*3. Bonding parameters:* Sn–$O_a$ 2.108(5) and 2.138(5) Å; Sn–$O_b$ 2.359(6) Å; Sn–$O_c$ 2.423(6) Å; Sn–$O_d$ 2.752(6) Å | 18 |
| 9 | • $[Me_2SnO]_n$ + $HClO_4$ + $NaClO_4$<br>• Reaction in aqueous medium at pH = 4.5<br>• Crystals grown from the slow evaporation of the above solution |  | *1. Overall structure:* One-dimensional coordination polymer, ionic<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted trigonal bipyramidal (axial ligands: $O_b$ and longer $O_a$); $\mu$-bridging of OH and anionic $ClO_4$<br>*3. Bonding parameters:* Sn–$O_a$ 2.030(4) and 2.220(3) Å; Sn–$O_b$ 2.132(3) and 2.139(3) Å<br>4. Hydroxyl bridged distannoxanes | 19 |

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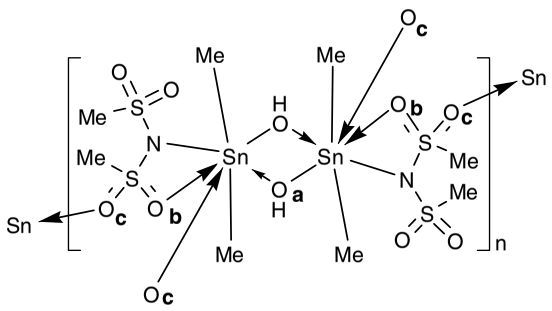
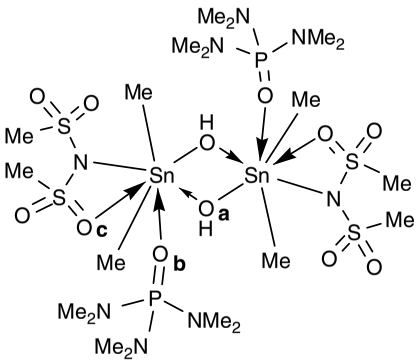
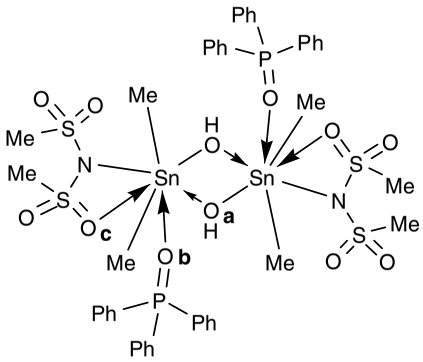
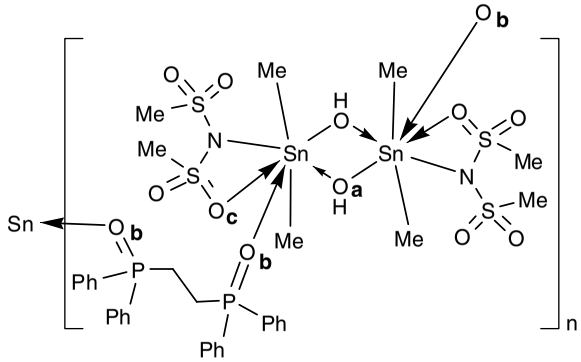
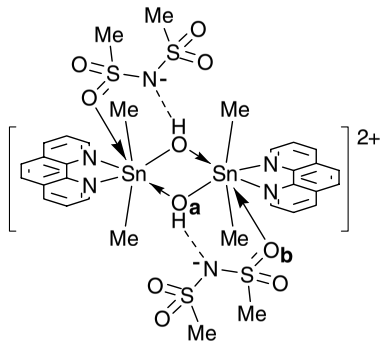
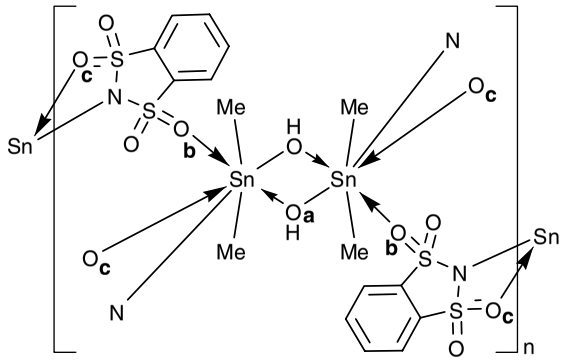
|---|---|---|---|---|
| 10 | • $Me_2Sn[N(SO_2Me)_2]_2 + H_2O$<br>• Reaction in MeCN at 50 °C<br>• Crystals grown from $CH_2Cl_2$/pet-ether<br>• Alternative method: $[Me_2SnO]_n + HN(SO_2Me)_2$<br>• Reaction in MeCN at 20 °C |  | *1. Overall structure:* Two-dimensional coordination polymer, neutral<br>*2. Coordination around tin:* heptacoordinate ($C_2O_4N$); distorted pentagonal bipyramidal (axial ligands: two methyl groups); mono- and bidentate (chelating) coordination of $N(SO_2Me)_2$<br>*3. Bonding parameters:* Sn–$O_a$ 2.073(2) and 2.151(2) Å; Sn–N 2.475(2) Å; Sn–$O_b$ 2.906(2) Å; Sn–$O_c$ 2.677(2) Å<br>4. Sulfonimide bridged distannoxanes | 20,21 |
| 11 | • $\{Me_2Sn(\mu\text{-}OH)[N(SO_2Me)_2]\}_2 + 2$ HMPA<br>• Reaction in MeCN at room temperature<br>• Crystals grown from MeCN |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* heptacoordinate ($C_2O_4N$); distorted pentagonal bipyramidal (axial: two methyl groups); monodentate coordination of HMPA and bidentate (chelating) coordination of $N(SO_2Me)_2$<br>*3. Bonding parameters:* Sn–$O_a$ 2.061(2) and 2.132(2) Å; Sn–N 2.893(2) Å; Sn–$O_b$ 2.225(2) Å; Sn–$O_c$ 3.087(2) Å | 21 |
| 12 | • $\{Me_2Sn(\mu\text{-}OH)[N(SO_2Me)_2]\}_2 +$ 2 $Ph_3P{=}O$<br>• Reaction in MeCN at room temperature<br>• Crystals grown from MeCN |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* heptacoordinate ($C_2O_4N$); distorted pentagonal bipyramidal (axial ligands: two methyl groups); monodentate coordination of $Ph_3P{=}O$ and bidentate (chelating) coordination of $N(SO_2Me)_2$<br>*3. Bonding parameters:* Sn–$O_a$ 2.085(13) and 2.121(13) Å; Sn–N 2.673(1) Å; Sn–$O_b$ 2.326(12) Å; Sn–$O_c$ 2.979(1) Å | 21 |




DOI: 10.1002/aoc

**Table 1.** (*Continued*)

| Entry | Reaction | Structure | Description of structure | Reference |
|---|---|---|---|---|
| 13 | • $\{Me_2Sn(\mu\text{-}OH)[N(SO_2Me)_2]\}_2$ $+[O{=}P(Ph)_2CH_2]_2$<br>• Reaction in MeCN at room temperature<br>• Crystals grown from MeCN |  | *1. Overall structure:* One-dimensional coordination polymer, neutral<br>*2. Coordination around tin:* heptacoordinate ($C_2O_4N$); distorted pentagonal bipyramidal (axial ligands: two methyl groups); monodentate/bridging coordination of $[O{=}P(Ph)_2CH_2]_2$ and bidentate (chelating) coordination of $N(SO_2Me)_2$<br>*3. Bonding parameters:* Sn–$O_a$ 2.080(13) and 2.121(12) Å; Sn–$O_b$ 2.312(26) Å; Sn–$O_c$ 2.900(22) Å; Sn–N 2.781(7) Å | 22 |
| 14 | • $\{Me_2Sn(\mu\text{-}OH)[N(SO_2Me)_2]\}_2 + 2$ 1,10-phenanthroline<br>• Reaction in MeCN at room temperature<br>• Crystals grown from MeCN<br>• Alternative method: $Me_2Sn[N(SO_2Me)_2]_2 + 2$ 1,10-phenanthroline<br>• Reaction in MeCN at room temperature |  | *1. Overall structure:* molecular, ionic<br>*2. Coordination around tin:* heptacoordinate ($C_2O_3N_2$); distorted pentagonal bipyramidal (axial ligands: two methyl groups); bidentate (chelating) coordination of 1,10-phenanthroline ligands<br>*3. Bonding parameters:* Sn–$O_a$ 2.066(2) and 2.248(2) Å; Sn–N 2.365(2) and 2.567(2) Å; Sn–$O_b$ 3.565(3) Å | 23,24 |
| 15 | • 2 $[Me_2SnO]_n + 2\ C_6H_4(SO_2)_2NH$<br>• Reaction in MeCN under reflux<br>• Crystals grown from MeCN |  | *1. Overall structure:* two-dimensional coordination polymer, neutral<br>*2. Coordination around tin:* heptacoordinate ($C_2O_4N$); distorted pentagonal bipyramidal (axial ligands: two methyl groups); mono- and bidentate (chelating) coordination of $C_6H_4(SO_2)_2N$<br>*3. Bonding parameters:* Sn–$O_a$ 2.088(2) and 2.091(2) Å; Sn–N 2.782(2) Å; Sn–$O_b$ 2.537(2) Å; Sn–$O_c$ 2.978(2) Å<br>4. Sulfonimide bridged distannoxanes | 23 |

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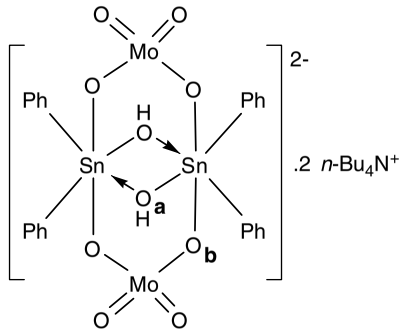
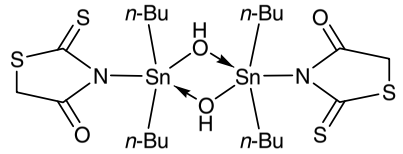
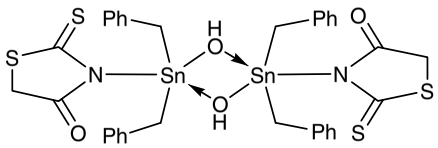
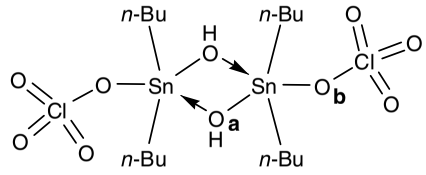
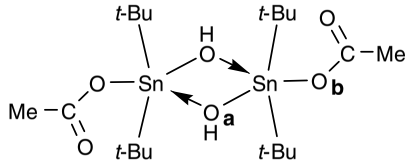
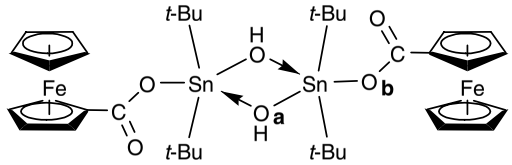
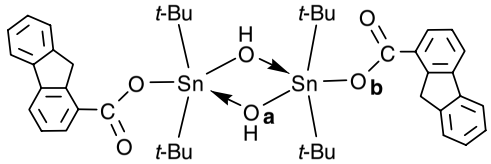
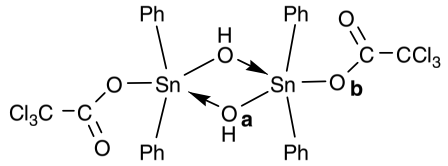
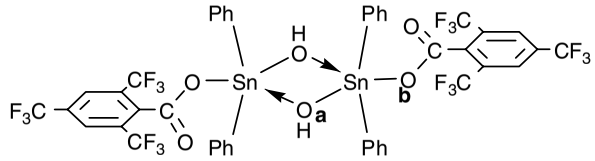
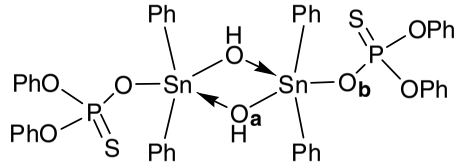
|---|---|---|---|---|
| 16 | • $Ph_2SnCl_2$ + $n$-$Bu_4NOH$ + $[n\text{-}Bu_4N^+]_2[Mo_2O_7]^{2-}$<br>• Reaction in MeCN at room temperature<br>• Crystals grown from $CH_2Cl_2$/PhMe |  | *1. Overall structure:* molecular, ionic<br>*2. Coordination around tin:* hexacoordinate ($C_2O_4$); distorted octahedral; bidentate (chelating) coordination of $MoO_4$ ligands<br>*3. Bonding parameters:* Sn–$O_a$ 2.176(4) and 2.188(4) Å; Sn–$O_b$ 2.115(4) and 2.130(4) Å | 25 |
| 17 | • $n$-$Bu_2SnCl_2$ + rhodanine + 95% NaOEt<br>• Reaction in EtOH at 50 °C<br>• Crystals grown from $Et_2O$/pet-ether (2 : 1) |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_2N$); distorted trigonal bipyramidal (axial ligands: N and OH)<br>*3. Bonding parameters:* Sn–O 2.040(5) and 2.190(5) Å; Sn–N 2.374(5) Å | 26 |
| 18 | • $(PhCH_2)_2SnCl_2$ + rhodanine + 95% NaOEt<br>• Reaction in EtOH at 50 °C<br>• Crystals grown from $Et_2O$/pet-ether (2 : 1) |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_2N$); distorted trigonal bipyramidal (axial ligands: N and OH)<br>*3. Bonding parameters:* Sn–O 2.026(3) and 2.282(4) Å; Sn–N 2.277(4) Å | 26 |
| 19 | • [$n$-$Bu_2SnO$]$_n$ + $HClO_4$ |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted trigonal bipyramidal (axial ligands: $O_b$ and longer $O_a$)<br>*3. Bonding parameters:* Sn–$O_a$ 2.079(9) and 2.130(8) Å; Sn–$O_b$ 2.425(5) Å | 27 |
| 20 | • $t$-$Bu_2Sn(O_2CMe)_2$ + NaOH<br>• Reaction in $Me_2CO$ at room temperature<br>• Crystallized from $CHCl_3/Me_2CO$<br>• Alternative method: [$t$-$Bu_2SnO$]$_3$ + 3 $MeCO_2H$<br>• Reaction in benzene at room temperature<br>• $^{119}$Sn NMR: $\delta$ − 267 ppm |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted trigonal bipyramidal (axial ligands: longer $O_a$ and $O_b$); monodentate coordination of carboxylate ligand<br>*3. Bonding parameters:* Sn–$O_a$ 2.046(2) and 2.204(2) Å; Sn–$O_b$ 2.156(2) Å | 28 |




DOI: 10.1002/aoc

**Table 1.** (*Continued*)

| Entry | Reaction | Structure | Description of structure | Reference |
|---|---|---|---|---|
| 21 | • $[t\text{-}Bu_2SnO]_3 + 3FcCO_2H$<br>• Reaction in toluene under reflux<br>• Alternative method: $[t\text{-}Bu_2SnO]_3 + 3\ FcCO_2H$<br>• Reaction in solvent-free grinding method<br>• $^{119}$Sn NMR: $\delta - 271.1$ ppm<br>• $E_{1/2} = +0.69$ V |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted trigonal bipyramidal (axial ligands: $O_a$ and $O_b$); monodentate coordination of carboxylate ligand<br>*3. Bonding parameters:* Sn–$O_a$ 2.036(18) and 2.173(18) Å; Sn–$O_b$ 2.155(16) Å | 29 |
| 22 | • $[t\text{-}Bu_2SnO]_3 + 3\ RCO_2H$<br>• Reaction in toluene under reflux<br>• $^{119}$Sn NMR: $\delta - 212.6$ ppm<br>• Absorbance: λ 265, 313 nm<br>• Emission: λ 355 nm (solution), 410 nm (solid-state) |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted trigonal bipyramidal (axial ligands: longer $O_a$ and $O_b$); monodentate coordination of carboxylate ligand<br>*3. Bonding parameters:* Sn–$O_a$ 2.036(1) and 2.191(1) Å; Sn–$O_b$ 2.172(1) Å | 30 |
| 23 | • $[Ph_2SnO]_n + Cl_3CCO_2H$ |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted trigonal bipyramidal (axial ligands: $O_b$ and longer $O_a$)<br>*3. Bonding parameters:* Sn–$O_a$ 2.023(5) and 2.163(17) Å; Sn–$O_b$ 2.156(14) Å | 31 |
| 24 | • $[Ph_3Sn]_2O + 2\ R_fCO_2H$<br>• Reaction in benzene under reflux<br>• $^{119}$Sn NMR: $\delta - 316.4$ ppm |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted trigonal bipyramidal (axial ligands: $O_a$ and $O_b$); monodentate coordination of carboxylate ligand<br>*3. Bonding parameters:* Sn–$O_a$ 2.042(2) and 2.157(2) Å; Sn–$O_b$ 2.174(2) Å | 32 |
| 25 | • $Ph_2Sn[O(S)P(OPh)_2]_2 + H_2O$<br>• Reaction in $Et_2O$ under reflux<br>• Recrystallized from MeOH |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted trigonal bipyramidal (axial ligands: $O_a$ and $O_b$); monodentate coordination of thiophosphate ligand<br>*3. Bonding parameters:* Sn–$O_a$ 2.032(2) and 2.198(2) Å; Sn–$O_b$ 2.151(2) Å | 33 |



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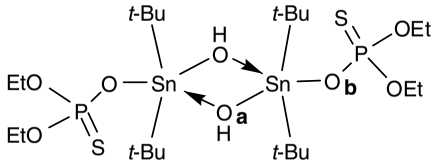
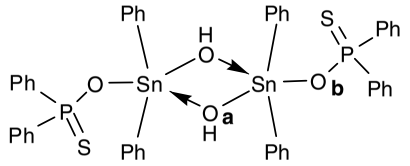
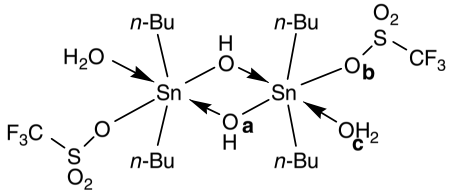
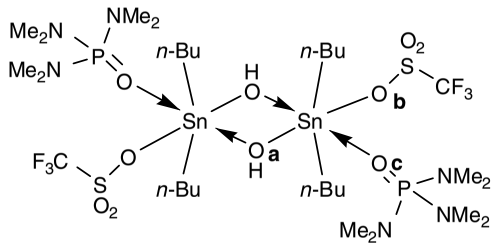
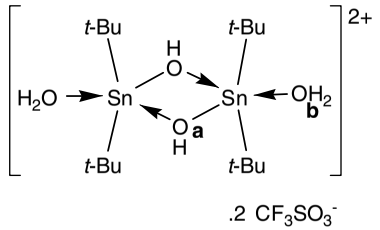
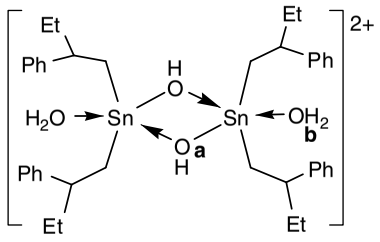
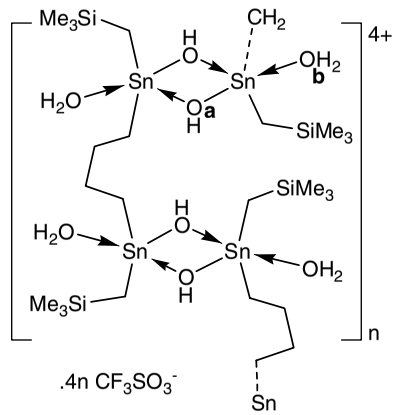
| | | | | |
|---|---|---|---|---|
| 26 | • $t$-$Bu_2Sn[O(S)P(OEt)_2]_2$ + aq. NaOH<br>• Reaction in $Me_2CO$ at room temperature<br>• Recrystallized from EtOH-hexane mixture (1 : 1)<br>• $^{119}$Sn NMR: $\delta$ − 289 ppm |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted trigonal bipyramidal (axial ligands: longer $O_a$ and $O_b$); monodentate coordination of thiophosphate ligand<br>*3. Bonding parameters:* Sn–$O_a$ 2.018(6) and 2.197(6) Å; Sn–$O_b$ 2.121(7) Å | 34 |
| 27 | • $Ph_3SnCl + NH_4[O(S)PPh_2]\cdot xH_2O$<br>• Reaction in $CHCl_3$ or benzene at room temperature<br>• Recrystallized from $CHCl_3$ |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted trigonal bipyramidal (axial ligands: $O_a$ and $O_b$); monodentate coordination of thiophosphinate ligand<br>*3. Bonding parameters:* Sn–$O_a$ 2.024(3) and 2.174(3) Å; Sn–$O_b$ 2.089(3) Å | 35 |
| 28 | • $[n\text{-}Bu_2SnO]_n$ + TfOH<br>• Reaction in MeCN at room temperature<br>• Recrystallized from $CH_2Cl_2$<br>• Alternative method: $\{[n\text{-}Bu_2SnCl]_2O\}_2 + AgOTf + H_2O$<br>• Reaction in $Me_2CO$ at room temperature<br>• Alternative method: $n$-$Bu_2Sn(OTf)_2$<br>• Refluxed in $CH_2Cl_2$<br>• $^{119}$Sn NMR: $\delta$ − 209.7 ppm |  | *1. Overall structure:* molecular; neutral [ionic dissociation in solution (1 : 2 electrolyte)]<br>*2. Coordination around tin:* hexacoordinate ($C_2O_4$); distorted octahedral; monodentate coordination of OTf and $H_2O$ ligands<br>*3. Bonding parameters:* Sn–$O_a$ 2.085(3) and 2.147(3) Å; Sn–$O_b$ 2.622(4) Å; Sn–$O_c$ 2.409(3) Å | 14,36 |
| 29 | • $[n\text{-}Bu_2Sn(\mu\text{-}OH)(OH_2)(O_3SCF_3)]_2$ + HMPA<br>• Reaction in $CHCl_3$ at room temperature<br>• Recrystallized from $CHCl_3$<br>• $^{119}$Sn NMR: $\delta$ − 224.4 ppm |  | *1. Overall structure:* molecular; neutral<br>*2. Coordination around tin:* hexacoordinate ($C_2O_4$); distorted octahedral; monodentate coordination of OTf and HMPA ligands<br>*3. Bonding parameters:* Sn–$O_a$ 2.07(1) and 2.15(2) Å; Sn–$O_b$ 2.82(1) Å; Sn–$O_c$ 2.10(1) Å | 14 |




DOI: 10.1002/aoc

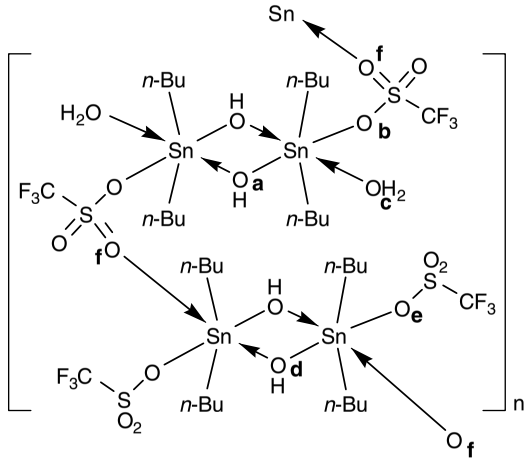
**Table 1.** (*Continued*)

| Entry | Reaction | Structure | Description of structure | Reference |
|---|---|---|---|---|
| 30 | • $[t\text{-}Bu_2SnO]_3 + TfOH$<br>• Reaction in MeCN at room temperature<br>• Recrystallized from $CH_2Cl_2$<br>• $^{119}Sn$ NMR: $\delta -249.6$ ppm |  | *1. Overall structure:* molecular, ionic<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted trigonal bipyramidal (axial ligands: $O_a$ and $O_b$); monodentate coordination of $H_2O$ ligand<br>*3. Bonding parameters:* Sn–$O_a$ 2.044(4) and 2.181(4) Å; Sn–$O_b$ 2.294(5) Å | 14 |
| 31 | • $[(2\text{-}Ph\text{-}n\text{-}Bu)_2SnO]_n + TfOH$<br>• Reaction in MeCN at room temperature<br>• Recrystallized from $CH_2Cl_2$<br>• $^{119}Sn$ NMR: $\delta -188.4$ ppm |  | *1. Overall structure:* molecular, ionic<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted trigonal bipyramidal (axial ligands: longer $O_a$ and $O_b$); monodentate coordination of $H_2O$ ligand<br>*3. Bonding parameters:* Sn–$O_a$ 2.035(7) and 2.193(6) Å; Sn–$O_b$ 2.255(8) Å | 14 |
| 32 | • $[Me_3SiCH_2Sn(OTf)_2(CH_2)_2]_2$ in $CH_3CN/CHCl_3$ was kept in open air<br>• Crystallization from $CH_3CN/CHCl_3$<br>• $^{119}Sn$ NMR: $\delta -166.5, -185.7$ ppm |  | *1. Overall structure:* one-dimensional coordination polymer; ionic<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted octahedral (axial ligands: longer $O_a$ and $O_b$); monodentate coordination of $H_2O$ ligand<br>*3. Bonding parameters:* Sn–$O_a$ 2.024(9) and 2.179(8) Å; Sn–$O_b$ 2.250(9) Å<br>4. Alkyl $[CH_2CH_2CH_2CH_2]$ bridged distannoxanes | 37 |




DOI: 10.1002/aoc

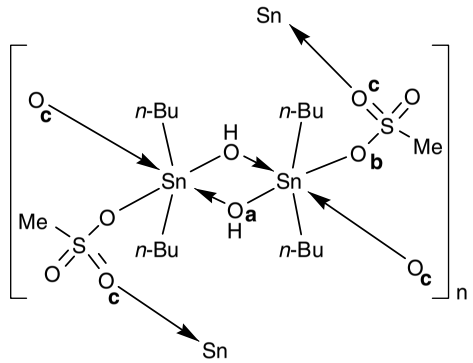
33
- [*n*-$Bu_2SnO]_n$ + TfOH
- Reaction in $CH_2Cl_2$ at room temperature
- Crystals grown by slow diffusion of *n*-hexane into the $CH_2Cl_2$ solution of the solid
- $^{119}$Sn NMR: $\delta$ − 156.3 ppm



*1. Overall structure:* one-dimensional coordination polymer; neutral
*2. Coordination around tin:* hexacoordinate ($C_2O_4$); distorted octahedral; monodentate coordination of $H_2O$ and bidentate coordination of OTf ligand
*3. Bonding parameters:* Sn–$O_a$ 2.064(4) and 2.138(4) Å; Sn–$O_d$: 2.090(4) and 2.120(4) Å; Sn–$O_b$ 2.863(3) Å; Sn–$O_e$ 2.492(5) Å; Sn–$O_c$ 2.364(5) Å; Sn–$O_f$ 2.630(4) Å
4. OTf bridged distannoxanes

38

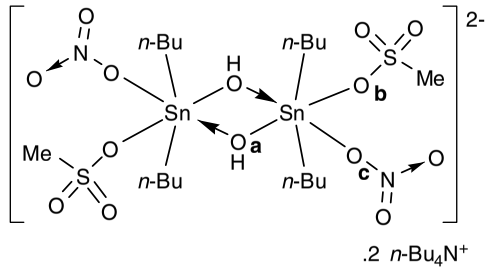
34
- *n*-$Bu_2Sn(OMe)(O_3SMe)$
- Reaction in moist MeOH (95 : 5) at room temperature
- Crystallization from $CH_2Cl_2$/*n*-hexane
- $^{119}$Sn NMR: $\delta$ − 189.3, −182.9, −175.3, −172.8, −168.3, −162.7 ppm



*1. Overall structure:* two-dimensional coordination polymer; neutral
*2. Coordination around tin:* hexacoordinate ($C_2O_4$); distorted octahedral; bidentate coordination of OTf ligands
*3. Bonding parameters:* Sn–$O_a$ 2.086(4) and 2.112(4) Å; Sn–$O_b$ 2.429(4) Å; Sn–$O_c$ 2.489(4) Å
4. $MeSO_3$ bridged distannoxanes
5. Coordination polymer with 20-membered macrocyclic repeating units

39

35
- [*n*-$Bu_2Sn(\mu$-OH)$(O_3SMe)]_2$ + 2 *n*-$Bu_4NNO_3$
- Reaction in $CH_2Cl_2$ at room temperature
- Crystals grown from $CH_2Cl_2$
- $^{119}$Sn NMR: $\delta$ − 234, −194, −159, −157 ppm



*1. Overall structure:* molecular; ionic
*2. Coordination around tin:* hexacoordinate ($C_2O_4$); distorted octahedral; monodentate coordination of $NO_3$ and OTf ligands
*3. Bonding parameters:* Sn–$O_a$ 2.118(5) and 2.130(5) Å; Sn–$O_b$ 2.451(6) Å; Sn–$O_c$ 2.418(5) Å

40


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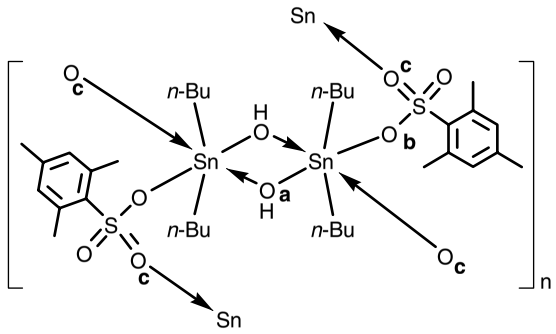
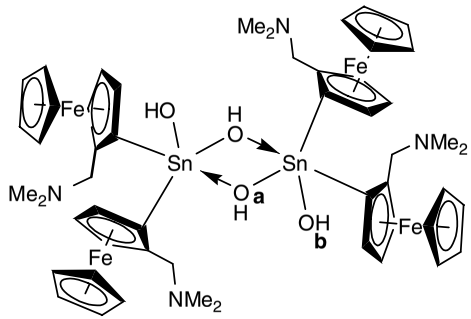
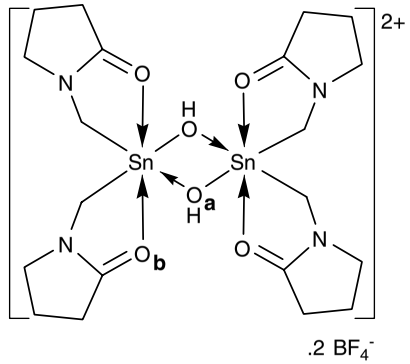
**Table 1.** (*Continued*)

| Entry | Reaction | Structure | Description of structure | Reference |
|---|---|---|---|---|
| 36 | • Crystallization of $[n\text{-}Bu_2Sn(O_3SMes)_2]_n$ in 50 : 50 v/v MeOH/$CHCl_3$ upon keeping it for 35 days at 25 °C<br>• $^{119}Sn$ NMR: $\delta$ − 324.1 ppm |  | *1. Overall structure:* one-dimensional coordination polymer; neutral<br>*2. Coordination around tin:* hexacoordinate ($C_2O_4$); distorted octahedral bidentate coordination of $O_3SMes$ ligands<br>*3. Bonding parameters:* Sn–$O_a$ 2.066(17) and 2.107(17) Å; Sn–$O_b$ 2.399(2) Å; Sn–$O_c$ 2.783(2) Å<br>4. $MesSO_3$ bridged distannoxanes<br>5. One-dimensional coordination polymer with 12-membered macrocyclic repeating units | 41 |
| 37 | • $SnCl_2$ + 2 $FcCH_2NMe_2$<br>• Crystals grown from $CHCl_3$ |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* pentacoordinate ($C_2O_3$); distorted trigonal bipyramidal (axial ligands: $O_b$ and longer $O_a$)<br>*3. Bonding parameters:* Sn–$O_a$ 2.021(12) and 2.230(9) Å; Sn–$O_b$ 2.018(5) Å | 42 |
| 38 | • $L_2SnCl_2$ + $AgBF_4$<br>• Crystals grown from dioxane |  | *1. Overall structure:* molecular, ionic<br>*2. Coordination around tin:* hexacoordinate ($C_2O_4$); distorted octahedral; bidentate (chelating) coordination of (2-oxopyrrolidino)methyl ligands<br>*3. Bonding parameters:* Sn–$O_a$ 2.107(4) and 2.119(5) Å; Sn–$O_b$ 2.294(7) and 2.307(8) Å | 43 |



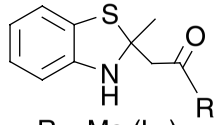
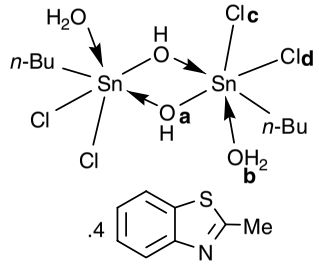
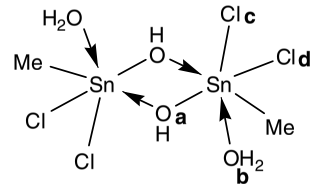
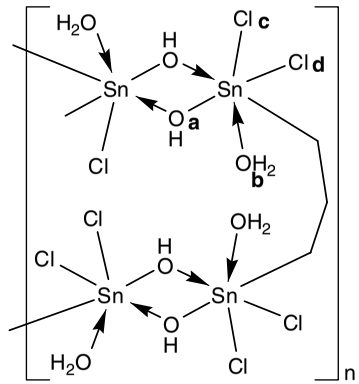

DOI: 10.1002/aoc

| | | | |
|---|---|---|---|
| 39 | Hydrolysis of $EtSnCl_3$ |  | 44 |
| | | | *1. Overall structure*: molecular; neutral<br>*2. Coordination around tin*: hexacoordinate ($CO_3Cl_2$); distorted octahedral; monodentate coordination of $H_2O$ and Cl ligands<br>*3. Bonding parameters*: $Sn–O_a$ 2.067(11) and 2.153(11) Å; $Sn–O_b$ 2.347(20) Å; $Sn–Cl_c$ 2.420(8) Å; $Sn–Cl_d$ 2.427(8) Å |
| 40 | • *n*-$BuSnCl_3$ kept in open air; crystals found after 1 week<br>• $^{119}Sn$ NMR: $\delta$ − 408.6 ppm (major signal) |  | 45 |
| | | | *1. Overall structure*: molecular; neutral<br>*2. Coordination around tin*: hexacoordinate ($CO_3Cl_2$); distorted octahedral; monodentate coordination of $H_2O$ and Cl ligands<br>*3. Bonding parameters*: $Sn–O_a$ 2.047(4) and 2.169(4) Å; $Sn–O_b$ 2.243(5) Å; $Sn–Cl_c$ 2.484(2) Å; $Sn–Cl_d$ 2.419(2) Å |
| 41 | • Hydrolysis of *i*-$PrSnCl_3$ |  | 46 |
| | | | *1. Overall structure*: molecular; neutral<br>*2. Coordination around tin*: hexacoordinate ($CO_3Cl_2$); distorted octahedral; monodentate coordination of $H_2O$ and Cl ligands<br>*3. Bonding parameters*: $Sn–O_a$ 2.046(4) and 2.117(4) Å; $Sn–O_b$ 2.260(4) Å; $Sn–Cl_c$ 2.412(2) Å; $Sn–Cl_d$ 2.507(1) Å |
| 42 | • Hydrolysis of *i*-$BuSnCl_3$ |  | 46 |
| | | | *1. Overall structure*: molecular; neutral<br>*2. Coordination around tin*: hexacoordinate ($CO_3Cl_2$); distorted octahedral; monodentate coordination of $H_2O$ and Cl ligands<br>*3. Bonding parameters*: $Sn–O_a$ 2.052(6) and 2.192(6) Å; $Sn–O_b$ 2.261(7) Å; $Sn–Cl_c$ 2.424(2) Å; $Sn–Cl_d$ 2.478(3) Å |




DOI: 10.1002/aoc

**Table 1.** (*Continued*)

| Entry | Reaction | Structure | Description of structure | Reference |
|---|---|---|---|---|
| 43 | • *n*-BuSnCl$_3$ + **L$_1$** or **L$_2$**<br>• Reaction in $CH_2Cl_2$ at room temperature<br>• Crystals obtained by slow evaporation of the above solvent<br>  <br>R = Me ($L_1$)<br>R = Ph ($L_2$) |  | *1. Overall structure:* molecular, neutral<br>*2. Coordination around tin:* hexacoordinate ($CO_3Cl_2$); distorted octahedral; monodentate coordination of $H_2O$ and Cl ligands<br>*3. Bonding parameters:* Sn–O$_a$ 2.122(3) and 2.038(3) Å; Sn–O$_b$ 2.216(4) Å; Sn–Cl$_c$ 2.483(3) Å; Sn–Cl$_d$ 2.418(3) Å | 47,48 |
| 44 | • MeSnCl$_3$ + $H_2O$ (excess) + 1, 3-xylyl-18-crown-5<br>• Reaction in $CH_2Cl_2$ at room temperature<br>• Crystallized from MeOH<br>• $^{119}$Sn NMR: $\delta$ − 175.9 ppm |  | *1. Overall structure:* molecular; neutral<br>*2. Coordination around tin:* hexacoordinate ($CO_3Cl_2$); distorted octahedral; monodentate coordination of $H_2O$ and Cl ligands<br>*3. Bonding parameters:* Sn–O$_a$ 2.051(2) and 2.127(2) Å; Sn–O$_b$ 2.208(2) Å; Sn–Cl$_c$ 2.474(1) Å; Sn–Cl$_d$ 2.452(1) Å | 49 |
| 45 | • Crystals obtained from slow evaporation of a mixture of $Cl_3Sn(CH_2)_3SnCl_3$ + $H_2O$ (excess) in a watch glass<br>• $^{119}$Sn NMR: $\delta$ − 472 ppm (solid state) |  | *1. Overall structure:* one-dimensional coordination polymer; neutral<br>*2. Coordination around tin:* hexacoordinate ($CO_3Cl_2$); distorted octahedral; monodentate coordination of $H_2O$ and Cl ligands<br>*3. Bonding parameters:* Sn–O$_a$ 2.047(2) and 2.164(2) Å; Sn–O$_b$ 2.361(2) Å; Sn–Cl$_c$ 2.426(8) Å; Sn–Cl$_d$ 2.425(6) Å<br>4. Alkyl [$CH_2CH_2CH_2$] bridged distannoxanes | 50 |



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| | | | |
|---|---|---|---|
| 46 | • $L_3SnCl_3$ + Hg(dmap)Cl<br>• Reaction in $Me_2CO$ at room temperature<br>• Crystallized from $Me_2CO$ |  | *1. Overall structure:* molecular; neutral<br>*2. Coordination around tin:* hexacoordinate ($CO_2Cl_2N$); distorted octahedral; monodentate coordination of Cl and bidentate (chelating) coordination of phenyl-azo ($L_3$) ligands<br>*3. Bonding parameters:* Sn–$O_a$ 2.027(3) and 2.193(2) Å; Sn–$Cl_b$ 2.381(2) Å; Sn–$Cl_c$ 2.402(2) Å; Sn–N 2.463(4) Å |
| 47 | • $L_4SnCl_3$ + 1,2-dianilinoethane<br>• Reaction in $CH_2Cl_2$ at room tempearure<br>• Crystallized from dioxane |  | *1. Overall structure:* molecular; neutral<br>*2. Coordination around tin:* hexacoordinate ($CO_3Cl_2$); distorted octahedral; monodentate coordination of Cl and bidentate (chelating) coordination of alkylacetate ($L_4$) ligands<br>*3. Bonding parameters:* Sn–$O_a$ 2.008(3) and 2.193(2) Å; Sn–$O_b$ 2.387(4) Å; Sn–$Cl_c$ 2.394(1) Å; Sn–$Cl_d$ 2.392(2) Å |




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**Table 1.** (*Continued*)

| Entry | Reaction | Structure | Description of structure | Reference |
|---|---|---|---|---|
| 48 | • $L_5SnCl_3 + H_2O$<br>• Reaction in $Et_2O$ at room temperature<br>• Crystallized from $Et_2O$ |  | *1. Overall structure:* molecular; neutral<br>*2. Coordination around tin:* hexacoordinate ($CO_3Cl_2$); distorted octahedral; monodentate coordination of Cl and bidentate (chelating) coordination of alkylacetate ($L_5$) ligands<br>*3. Bonding parameters:* Sn–$O_a$ 2.023(3) and 2.122(3) Å; Sn–$O_b$ 2.022(3) Å; Sn–$Cl_c$ 2.411(2) Å; Sn–$Cl_d$ 2.375(1) Å | 53 |
| 49 | • $L_6SnCl_3 + KF$<br>• Reaction in $CH_2Cl_2$-$H_2O$ at room temperature<br>• Crystallized from a mixture of $CH_2Cl_2$/toluene/hexane<br>• $^{119}Sn$ NMR: $\delta$ − 602 ppm |  | *1. Overall structure:* molecular; neutral<br>*2. Coordination around tin:* hexacoordinate ($CO_3F_2$); distorted octahedral; monodentate coordination of F and bidentate (chelating) coordination of aromatic phosphonate ($L_6$) ligands<br>*3. Bonding parameters:* Sn–$O_a$ 2.069(4) and 2.157(4) Å; Sn–$O_b$ 2.186(3) Å; Sn–$F_c$ 1.951(3) Å; Sn–$F_d$ 1.947(4) Å | 54 |




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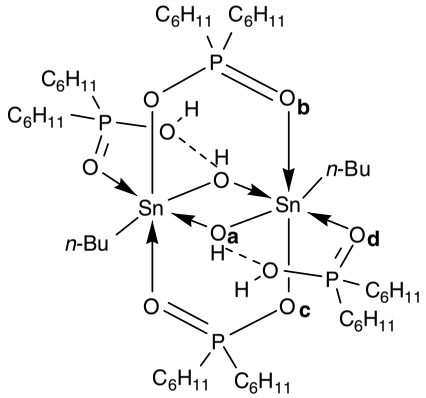
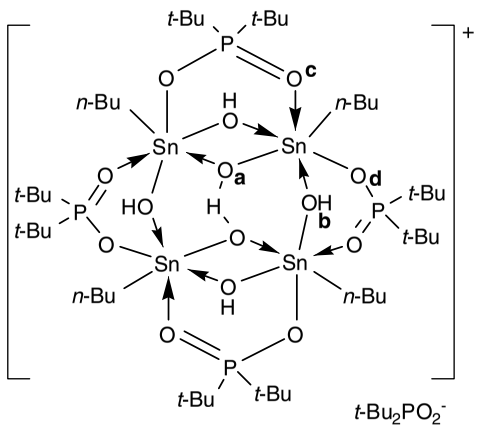
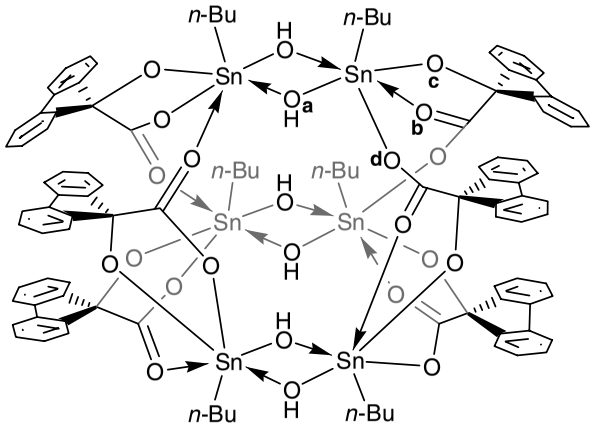
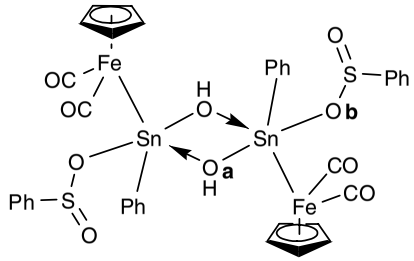
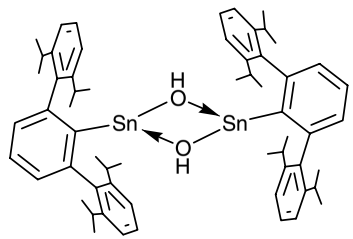
| | | | | |
|---|---|---|---|---|
| 50 | • [*n*-BuSn(O)OH]$_n$ + $(C_6H_{11})_2PO_2H$<br>• Reaction in toluene under reflux<br>• Crystallized from a mixture of $CH_2Cl_2$/hexane<br>• Alternative method:<br>*n*-$BuSnCl_3$ + $(C_6H_{11})_2PO_2Ag$<br>• Reaction in $CHCl_3$ under reflux<br>• Crystallized from a mixture of $CH_2Cl_2$, hexane and $Et_2O$<br>• $^{119}$Sn NMR: $\delta$ − 547.5 ppm |  | *1. Overall structure:* molecular; neutral<br>*2. Coordination around tin:* hexacoordinate ($CO_5$); distorted octahedral; mono- and bidentate coordination of phosphinate ligands<br>*3. Bonding parameters:* Sn–$O_a$ 2.047(3) and 2.128(3) Å; Sn–$O_b$ 2.115(3) Å; Sn–$O_c$ 2.162(3) Å; Sn–$O_d$ 2.061(3) Å | 55 |
| 51 | • [*n*-BuSn(O)OH]$_n$ + *t*-$Bu_2PO_2H$<br>• Reaction in benzene under reflux<br>• Recrystallized from $CH_2Cl_2$ and MeOH<br>• Alternative method:<br>[*n*-$BuSn(O)O_2CMe]_6$ + *t*-$Bu_2PO_2H$<br>• Reaction in toluene under reflux<br>• $^{119}$Sn NMR: $\delta$ − 560.9, −556.7, −541.4, −535.5, −491.2 ppm |  | *1. Overall structure:* molecular; ionic<br>*2. Coordination around tin:* hexacoordinate ($CO_5$); distorted octahedral; bidentate coordination of phosphinate ligands<br>*3. Bonding parameters:* Sn–$O_a$ 2.062(7) and 2.110(7) Å; Sn–$O_b$ 2.122(7) Å; Sn–$O_c$ 2.131(7) Å; Sn–$O_d$ 2.114(7) Å | 56,57 |

**Table 1.** (*Continued*)

| Entry | Reaction | Structure | Description of structure | Reference |
|---|---|---|---|---|
| 52 | • $[n\text{-BuSn(O)OH}]_n + L_7(OH)CO_2H$<br>• Reaction in toluene under reflux<br>• Recrystallized from $CHCl_3$<br>• Alternative method: $[n\text{-BuSn(O)OH}]_n + L_7(OH)CO_2H$ + 4-I-$C_6H_4OH$<br>• Reaction in toluene under reflux<br>• $^{119}$Sn NMR: $\delta$ − 466.6 ppm |  | *1. Overall structure:* molecular; neutral<br>*2. Coordination around tin:* hexacoordinate ($CO_5$); distorted octahedral; alternative mono- and bidentate (chelating) coordination of $L_7(O)CO_2$ ligands<br>*3. Bonding parameters:* Sn–$O_a$ 2.092(3) and 2.107(3) Å; Sn–$O_b$ 2.153(2) Å; Sn–$O_c$ 2.037(3) Å; Sn–$O_d$ 2.161(2) Å | 58 |
| 53 | • Hydrolysis of $CpFe(CO)_2SnPh(O_2SPh)_2$<br>• Recrystallized from EtOH<br>• Alternative method: $CpFe(CO)_2SnPhCl_2 + NaO_2SPh$<br>• Reaction in EtOH under reflux<br>• Recrystallized from EtOH |  | *1. Overall structure:* molecular; neutral<br>*2. Coordination around tin:* pentacoordinate ($CO_3Fe$); distorted trigonal bipyramidal (axial: longer $O_a$ and $O_b$); monodentate coordination of $CpFe(CO)_2$ and $PhSO_2$ ligands<br>3. M–M bonded compound (Sn–Fe)<br>*4. Bonding parameters:* Sn–$O_a$ 2.054(2) and 2.231(2) Å; Sn–$O_b$ 2.206(2) Å; Sn–Fe 2.499(1) Å | 59 |
| 54 | • $[Ar'Sn]_2$ + 2 Tetramethylpiperidine oxide (TEMPO)<br>• Reaction in toluene at 25 °C; Recrystallized from toluene at −18 °C<br>• Alternative method: $[Ar'Sn]_2 + 2\ N_2O$<br>• Reaction in toluene at 25 °C;<br>• $^{119}$Sn NMR: $\delta$ 216.4 ppm |  | *1. Overall structure:* molecular; neutral (organotin (II))<br>*2. Coordination around tin:* tricoordinate ($CO_2$); trigonal planar<br>*3. Bonding parameters:* Sn–$O_{av}$ 2.143(3) Å | 60 |

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$\{[Ph_2Sn(\mu\text{-}OH)(NO_3)_2]_2^{2-}\ [Ag(AsPh_3)_4^+]_2\}$ is obtained as a result of a Sn–C bond cleavage that happens when $Ph_3SnNO_3$ reacts with $Ag(AsPh_3)_2NO_3$ in presence of moisture (Table 1, entry 8).[18]

A polymeric product, where the $[Sn(\mu\text{-}OH)]_2$ units are interlinked by bridging hydroxide ligands, is formed in the reaction of $[Me_2SnO]_n$, $HClO_4$ and $NaClO_4$ (Table 1, entry 9).[19] Diorganotin compounds react with sulfonimides to afford distannoxanes (Table 1, entries 10–15). The reaction of $[Me_2SnO]_n$ with $HN(SO_2Me)_2$ in acetonitrile leads to the exclusive formation of $[Me_2Sn(\mu\text{-}OH)(N(SO_2Me)_2)]_2$.[20,21] The anionic $[N(SO_2Me)_2]^-$ ligand binds to the tin through a nitrogen and an oxygen atom in a chelating fashion. This compound, however, assumes a polymeric structure because of the coordination action of the oxygen atoms, labeled 'c' (Table 1, entry 10). This coordination polymer is readily disrupted by the addition of ligands such as $(Me_2N)_3P{=}O$ or $Ph_3P{=}O$ (Table 1, entries 11 and 12).[21] On the other hand, use of difunctional phosphine oxide, $Ph_2(O)P(CH_2)_2P(O)Ph_2$, affords a one-dimensional coordination polymer (Table 1, entry 13).[22] In the presence of chelating nitrogenous ligand such as 1,10-phenanthroline, the $[N(SO_2Me)_2]^-$ is formally displaced from the coordination sphere of the tin (Table 1, entry 14).[23,24] Interestingly, the reaction of $[Me_2Sn(\mu\text{-}OH)(N(SO_2Me)_2)]_2$ with other nitrogen bases such as pyridine or 4-dimethylaminopyridine results in hydrolysis and $[Me_2SnO]_n$ is liberated. The reaction of $[Me_2SnO]_n$ and $C_6H_4(SO_2)_2NH$ (benzene-1,2-sulfonimide) leads to the formation of a coordination polymer containing the $[Sn(\mu\text{-}OH)]_2$ moiety (Table 1, entry 15).[23]

An interesting example of an A-frame type compound containing bridging molybdate ligand is obtained in the reaction of $Ph_2SnCl_2$ with $[n\text{-}Bu_4N]_2[Mo_2O_7]$ in presence of $n\text{-}Bu_4NOH$ (Table 1, entry 16).[25] On the other hand, reactions of diorganotin halides involving the nitrogen base rhodanine in presence of NaOEt afford N-coordinated organostannoxanes (Table 1, entries 17 and 18).[26] A similar type of framework containing organostannoxane can be isolated from the reaction of $[n\text{-}Bu_2SnO]_n$ with perchloric acid (Table 1, entry 19).[27] In the latter, the perchlorate anion is bound to tin by an $\eta^1$ coordination mode.

Reactions of organotin oxides with carboxylic acids can also result in the formation of $\mu$-OH containing distannoxanes. This is particularly true for $[t\text{-}Bu_2SnO]_3$. Thus, the reaction of $[t\text{-}Bu_2SnO]_3$ with $RCO_2H$ affords $[t\text{-}Bu_2Sn(\mu\text{-}OH)O_2CR]_2$ (R = methyl, ferrocenyl, 1-fluorenyl and $CCl_3$) (Table 1, entries 20–23).[28–31] In all of these cases the carboxylate group binds to tin in a monodentate fashion. In an unusual example, the reaction of $(Ph_3Sn)_2O$ with $R_fCO_2H$ leads to an Sn–C bond cleavage and the isolation of $[Ph_2Sn(\mu\text{-}OH)O_2CR_f]_2$ (Table 1, entry 24).[32] The crucial role of $R_fCO_2H$ in determining the course of the reaction can be gauged by the fact that the reaction of $(Ph_3Sn)_2O$ with 2,4,6-$Me_3C_6H_2CO_2H$ gives the *normal* product, viz. $Ph_3SnO_2CC_6H_2$-2,4,6-$Me_3$.[32]

Distannoxanes supported by $R_2P(S)O^-$ ligands are also known (Table 1, entries 25–27). These compounds are formed by the hydrolysis of $t\text{-}Bu_2Sn[OP(S)(OEt)_2]_2$ or $Ph_2Sn[OP(S)(OPh)_2]_2$ (Table 1, entries 25 and 26).[33,34] In one case the hydrolysis event is accompanied by Sn–C bond cleavage (Table 1, entry 27).[35]

Reaction of diorganotin compounds with sulfonic acids is a facile process of generating distannoxanes (Table 1, entries 28–35). Thus, the reaction of the ladder compound $\{[n\text{-}Bu_2SnCl]_2O\}_2$ with AgOTf ($OTf^- = CF_3SO_3^-$) in presence of moisture affords the non-ionic compound $[n\text{-}Bu_2Sn(\mu\text{-}OH)(H_2O)(OTf)]_2$.[14,36] The OTf group binds to tin in a monodentate fashion (Table 1, entry 28). A water molecule completes the coordination environment around tin. The lability of the coordinated water is gauged by the fact that it can be readily replaced by hexamethylphosphorus triamide (HMPA) affording $[n\text{-}Bu_2Sn(\mu\text{-}OH)(OP(NMe_2)_3)(OTf)]_2$.[14] The ligand exchange does not involve any other structural change in the distannoxane (Table 1, entry 29).

In contrast to neutral compounds as described above, cationic distannoxanes $\{[R_2Sn(\mu\text{-}OH)(H_2O)]_2^{2+}[OTf^-]_2\}$ [R = *t*-Bu, $EtCH(Ph)CH_2$] are obtained in the reactions of the corresponding diorganotin oxides with HOTf (Table 1, entries 30 and 31).[14] These organotin cations were found to be highly active in the acetylation reactions of alcohols.[36] In an interesting example, hydrolysis of the alkyl-bridged compound $[Me_3SiCH_2Sn(OTf)_2(CH_2)_2]_2$ afforded a cationic one-dimensional coordination polymer with the repeat unit consisting of distannoxane cores (Table 1, entry 32).[37]

Coordination polymers containing interconnected distannoxanes are obtained in the reaction of $[n\text{-}Bu_2SnO]_n$ with HOTf (Table 1, entry 33). The compounds $\{[n\text{-}Bu_2Sn(\mu\text{-}OH)(OH_2)(OTf)]_2$ and $[n\text{-}Bu_2Sn(\mu\text{-}OH)(OTf)]_2\}_n$ have been found to catalyze the transesterification reaction involving dimethylcarbonate and phenol to produce diphenylcarbonate.[38] Diorganotin oxides react with dimethylsulfite to afford methoxydiorganotin methanesulfonate, $R_2Sn(OMe)O_3SMe$ (R = *n*-Pr, *n*-Bu, *i*-Bu, cyclohexyl). These reactions proceed via an Arbuzov-type rearrangement which occurs at the sulfur center.[39] Methoxy diorganotin methanesulfonates undergo a facile hydrolysis to afford $\{[R_2Sn(\mu\text{-}OH)(O_3SMe)]_2\}_n$ (Table 1, entry 34). The sulfonate ligand is involved in a bridging coordination action leading to the formation of polymeric sheets containing 20-membered macrocycles as repeat units. Each repeat unit contains two four-membered $[Sn(\mu\text{-}OH)]_2$ rings. The coordination polymer is broken up by the reaction of $n\text{-}Bu_4NNO_3$ to afford $[n\text{-}Bu_2Sn(\mu\text{-}OH)(NO_3)(O_3SMe)]_2$ (Table 1, entry 35).[40] Both nitrate and sulfonate ligands bind to the tin in a monodentate manner. A direct reaction involving hydrolysis of the disulfonate, $n\text{-}Bu_2Sn(O_3SC_6H_2$-2,4,6-$Me_3)_2$ also affords a coordination polymer $\{[n\text{-}Bu_2Sn(\mu\text{-}OH)(O_3SC_6H_2$-2,4,6-$Me_3)]_2\}_n$ (Table 1, entry 36).[41] However, in this case, the coordination polymer is one-dimensional where two sulfonate ligands are involved in bridging adjacent distannoxanes units.

An interesting example of an $R_2Sn(OH)_2$ dimer compound containing a bridging hydroxyl group is obtained in the reaction of $SnCl_2$ with $FcCH_2NMe_2$.[42] This results in an



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oxidative addition reaction and is accompanied by hydrolysis to afford $[(FcCH_2NMe_2)_2Sn(\mu\text{-}OH)(OH)]_2$ (Table 1, entry 37). The $NMe_2$ group present in the ferrocenyl ligand is not involved in coordination to tin. However, distannoxanes containing chelating coordination action involving N,O donor centers can be isolated (Table 1, entry 38).[43]

## MONOORGANOTIN COMPOUNDS

Controlled hydrolysis of a number of monoorganotin halides affords distannoxanes (Table 1, entries 39–49). This can occur even in the absence of any additional ligands. Thus, exposure of solutions of $RSnCl_3$ to ambient humid atmosphere leads to the isolation of products $[RSn(\mu\text{-}OH)(H_2O)Cl_2]_2$ (R = Et, *i*-Pr, *n*-Bu, *i*-Bu) (Table 1, entries 39–42).[44–46] In each of these cases the tin atom is hexacoordinate and has a $CO_3Cl_2$ coordination environment. Hydrolysis of *n*-$BuSnCl_3$ or $MeSnCl_3$ in the presence of additional ligands also leads to the formation of similar type of distannoxanes as mentioned above (Table 1, entries 43 and 44).[47–49] In an interesting example, hydrolysis of the alkyl bridged compound $Cl_3Sn(CH_2)_3SnCl_3$ afforded a one-dimensional coordination polymer with the repeat unit consisting of two alkyl bridged distannoxane units.[50] Chelating ligands displace the water molecule in the coordination sphere of tin, as evidenced in the examples shown in entries 46–49 of Table 1.[51–54]

In general, the reactions of $[n\text{-}BuSn(O)OH]_n$ with phosphorus-based acids such as phosphinic acids afford a variety of complex cluster types including *drum*, *cube*, *O-capped cluster*, *double O-capped cluster*, etc.[8–11] Interestingly in the reactions of $[n\text{-}BuSn(O)OH]_n$ with $(C_6H_{11})_2P(O)OH$ as well as *t*-$Bu_2P(O)OH$, phosphinate-bridged distannoxane compounds could be isolated (Table 1, entries 50 and 51). Thus, in the reaction with $(C_6H_{11})_2P(O)OH$, the distannoxane unit is supported by two bridging phosphinate ligands in an A-frame-type structure.[55] Additional phosphinic acids are also held together by hydrogen bonding interactions. The product isolated with *t*-$Bu_2P(O)OH$ is more complex (Table 1, entry 51).[56,57] Two distannoxanes are bridged to each other by the $\mu$-OH group. Four phosphinate ligands provide further structural support, each of them involving a $\mu$-coordination mode. In an extremely interesting example, three distannoxanes are stitched together by a tridentate dianionic oxy-carboxylate ligand (Table 1, entry 52).[58] Each of the tin atoms in this hexanuclear cluster occupies the vertex of a perfect trigonal prism. An interesting aspect of this family of compounds is that they form guest-assisted columnar network structures through hydrogen bonding interactions. An interesting distannoxane involving the presence of an organometallic substituent is provided by entry 53, Table 1.[59]

A rare example of a distannoxane where the tin atom is in a formal oxidation state of +2 is given in entry 54 of Table 1.[60] The bulky terphenyl groups provide steric protection around tin. Interestingly the coordination geometry around tin is trigonal planar.

## CONCLUDING REMARKS

The four-membered distannoxane ring $[Sn(\mu\text{-}OH)]_2$ appears to be a robust structural motif among organostannoxanes Remarkably, hexanuclear cages containing up to three distannoxane units, $[Sn(\mu\text{-}OH)]_2$, are also now known. Also, the ubiquitous nature of the $[Sn(\mu\text{-}OH)]_2$ is evidenced by its occurrence in compounds formed in a variety of reaction conditions. It is of interest to note that such a structural motif is absent in organosilicon hydroxides, underscoring some of the important differences between these main-group elements. In addition to noticing the presence of the $[Sn(\mu\text{-}OH)]_2$ ring in organostannoxanes, the possibility of utilizing the bridging hydroxide ligands in well-designed hydrogen bonding interactions to generate porous structures should attract the attention of researchers in this area.

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