

Formation of a Novel Trinuclear Spirostannoxane Tin(IV) Compound. Crystal and Molecular Structure of $[\text{Sn}^n(\text{Bu})(\text{Cl})\{(\text{OCH}_2\text{CH}_2\text{S})_2\text{Sn}^n(\text{Bu})\}_2]$ and the Stannolane $[(n\text{Bu})\text{Sn}(\text{SCH}_2\text{CH}_2\text{O})\text{SCH}_2\text{CH}_2\text{OH}]$

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The reaction of $n\text{BuSnCl}_3$ and the sodium salt of 2-mercaptoethanol (1:1) in ethanol gave the compound $[\text{Sn}^n(\text{Bu})(\text{Cl})\{(\text{OCH}_2\text{CH}_2\text{S})_2\text{Sn}^n(\text{Bu})\}_2]$ (**1**). $[(n\text{Bu})\text{Sn}(\text{SCH}_2\text{CH}_2\text{O})\text{SCH}_2\text{CH}_2\text{OH}]$ (**2**) was initially isolated from the reaction of **1** with $n\text{BuMgCl}$ as a rearrangement product but was also synthesized from $n\text{BuSn}(\text{O})\text{OH}$ and two molar equivalents of 2-mercaptoethanol. Both compounds were characterized by means of IR, ^{119}Sn , ^{13}C , and ^1H NMR, FAB mass spectroscopy, and elemental analyses. The structures were determined by single-crystal X-ray diffraction. **1** crystallizes in the monoclinic Cc space group ($a = 18.492(3)$ Å, $b = 17.329(2)$ Å, $c = 10.787(1)$ Å, $\beta = 111.88(1)^\circ$, $Z = 4$), while **2** crystallizes in the orthorhombic $Pbca$ space group ($a = 14.458(2)$ Å, $b = 10.393(1)$ Å, $c = 16.479(2)$ Å, $Z = 8$). **1** is a trimetallic Tin(IV) compound in which the central atom is in 6-fold coordination, while the two remaining tin atoms show 5-fold coordination. Both pentacoordinated tin atoms are bonded to a butyl group and to the oxygen and the sulfur atoms from two $[\text{OCH}_2\text{CH}_2\text{S}]^{2-}$ ligands forming two stannolanes, which are fused with the hexacoordinated tin atom forming a distannoxane system. This arrangement is quite different from previous ladder or staircase structures. NMR data point to maintenance of this structure in solution. **2** consists of $[(n\text{Bu})\text{Sn}(\text{SCH}_2\text{CH}_2\text{O})\text{SCH}_2\text{CH}_2\text{OH}]$ units, which are associated via intermolecular Sn–O interactions building up a dimer. The tin atom forms two “stannolane” units by interaction with $[\text{OCH}_2\text{CH}_2\text{S}]^{2-}$ and $[\text{HOCH}_2\text{CH}_2\text{S}]^-$ ligands.

Introduction

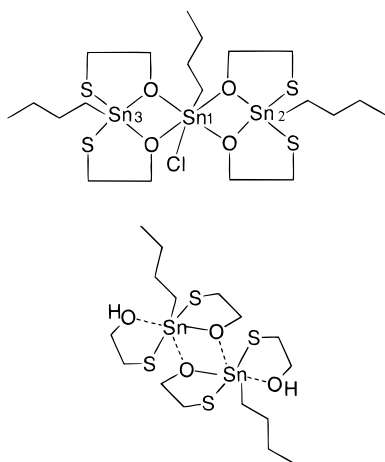
Holmes and co-workers have studied extensively the chemistry of spirocyclic tin compounds containing oxygen, sulfur, and mixed oxygen–sulfur ligands.^{1–7} They have synthesized and structurally characterized by X-ray diffraction a number of anionic five-coordinated tin derivatives containing five-membered ring systems, as well as six-coordinated monomeric and dimeric species. The systematic structural studies by Holmes of tin compounds combined with the structural data for silicon⁸ and germanium⁹ analogues allow comparison with the structural

principles established for pentacoordinated main group 15 compounds.¹⁰ According to this, stannolane structures of this class are in agreement with the principles formulated for phosphoranes and are also applicable to five-coordinated derivatives of other group 14 and 15 elements. These tin compounds prefer Sn–S to Sn–O bonding, and when the tin acidity is increased by replacing ring sulfur atoms with oxygen atoms, higher coordination numbers are observed, for example, $[(\text{C}_6\text{H}_4\text{O}_2)_3\text{Sn}][\text{Et}_3\text{NH}]$.¹ This may arise by formation of $\text{Sn}\cdots\text{O}$ interactions stabilizing dimeric species in the solid state, for example, $[(\text{C}_6\text{H}_4\text{OS})_3\text{Sn}]_2[\text{H}][\text{Et}_4\text{N}]$.¹ The presence of saturated five-membered rings or only one unsaturated ring normally gives TBP (trigonal bipyramidal) structures as in $[(\text{SCH}_2\text{CH}_2\text{S})_2\text{SnPh}][\text{Et}_4\text{N}]$ ² and $[(\text{C}_7\text{H}_6\text{S}_2)\text{SnPh}_2\text{Cl}][\text{Et}_4\text{N}]$.³ Two unsaturated five-membered rings containing like atoms bound to the central atom in each of the rings lead to RP (rectangular-pyramidal) structures, as in $[(\text{CN})_2\text{C}_2\text{S}_2\text{Sn}^n(\text{Bu})][\text{Et}_4\text{N}]$.⁴ Also, the presence of a large, fifth ligand of lower electronegativity favors RP arrangement, as in $[(\text{C}_7\text{H}_6\text{S}_2)\text{SnBr}][\text{MePPH}_3]\cdot 2\text{C}_6\text{H}_6$.¹ Introduc-

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Chart 1. Molecular Structures of **1** (Top) and **2** (Bottom)

tion of dissimilar bonding ring atoms causes displacement back to the more stable TBP structure, for example, $[(C_6H_4OS)_2SnCl] \cdot [Et_4N]^+$.¹

In the course of our studies of the chemistry of heavy main group metalolanes, we obtained an unexpected trinuclear tin(IV) compound, $Sn(^nBu)(Cl)\{(OCH_2CH_2S)_2Sn(^nBu)\}_2$ (**1**), from the reaction of nBuSnCl_3 and 2-mercaptoethanol. In addition, we also identified the spirostannolane $(^nBu)Sn(SCH_2CH_2O)SCH_2CH_2OH$ (**2**). Both compounds were characterized by IR, ^{119}Sn , ^{13}C , and 1H NMR, mass spectroscopy, and elemental analyses. The molecular structures of **1** and **2** were determined using single-crystal X-ray diffraction (Chart 1).

Results and Discussion

The reaction of equimolar quantities of nBuSnCl_3 and the sodium salt of 2-mercaptoethanol in ethanol unexpectedly gave compound **1**. In an attempt to replace the chlorine atom, the reaction of **1** with nBuMgCl yielded compound **2**, which was obtained as the major product from the crystallization of the crude product. Compound **2** was also synthesized by mixing $^nBuSn(O)OH$ with two molar equivalents of 2-mercaptoethanol. Both compounds are air-stable, colorless crystalline solids; **1** was soluble in organic solvents (e.g., CH_2Cl_2 , $CHCl_3$, THF), while **2** was highly soluble in DMSO and slightly soluble in $CHCl_3$ and CH_2Cl_2 .

In the FAB mass spectra, the base peaks for **1** and **2** were $[M^+ - Cl]$ (m/z 831) and $[C_{10}H_{21}O_3S_3Sn_2]^+$ (m/z 523), respectively. Other fragments are associated primarily with ions containing spirostannolane units, that is, $[C_{14}H_{31}O_3S_3Sn_2]$ (only for **1**, m/z 581), $[C_{10}H_{21}O_3S_3Sn_2]$ (m/z 523), $[C_8H_{17}O_2S_2Sn_2]$ (m/z 447), $[C_8H_{17}O_2S_2Sn]^+$ (only for **2**, M^+ , m/z 329), $[C_6H_{13}OSSn]$ (m/z 253), $[C_2H_5OSSn]$ (m/z 197). The isotopic pattern agreed well with the number of the tin atoms in each fragment.

1H and ^{13}C NMR Spectra. The 1H and ^{13}C NMR data for **1** and **2** are collected in Table 1. The 1H NMR spectrum of **1** points to maintenance of the solid-state structure in solution. The CH_2-S resonance from the $-SCH_2CH_2O-$ fragment occurs as a series of three broad resonance in the range 2.8–3.25 ppm (8H) and the CH_2-O resonance as a broad signal centered at 3.8 ppm (8H). Cooling led to greater resolution of these broad resonances, and at $-70^\circ C$, there were two groups of three multiplets for the both CH_2 proton groups: 3.09, 2.9, 2.84 [SCH_2] and 4.11, 3.97, 3.72 [CH_2O] ppm. The carbon atoms of the $-SCH_2CH_2O-$ fragment (^{13}C NMR spectra) correspond to the two lowest-field-shifted resonances at 63.2 and 31.3 ppm.

All three butyl groups attached to the tin atoms are equivalent on the 1H NMR time scale but not on the ^{13}C NMR time scale, where there were seven signals. A Hetcor experiment allowed assignments of the butyl carbon atoms and the associated proton shifts. The carbon atoms in all $-CH_2-CH_3$ moieties are equivalent on the ^{13}C NMR time scale. The methylene resonance (CH_2-CH_3) occurs at 26.18 (^{13}C NMR) and as a sextet at 1.42 ppm (1H NMR). The triplet at 0.95 ppm corresponds to the methyl proton resonance with the associated carbon resonance at 13.30 ppm. This latter assignment was originally found by a distortionless enhancement by polarization transfer (DEPT) experiment. The proton resonance from the methylene β to the tin nucleus ($Sn-CH_2-CH_2-$) are at 1.79 (q) ppm. Only two β carbon atoms are magnetically equivalent (27.22 ppm) from the ^{13}C NMR spectrum and correspond to those from butyls attached to the two five-coordinate tin atoms. The remaining β -carbon resonance from butyl bonded to six-coordinate tin atom occurs at 28.11 ppm ($^1J(^{13}C^{119}Sn) = 31$ Hz). The $Sn-CH_2$ proton resonance at 1.58 (t) ppm experiences a relative shielding effect from the presence of the electropositive tin(IV) atoms. The three carbon atoms are nonequivalent; therefore, there are three signal for each $Sn-CH_2$ carbon resonance. Two resonance signals at 25.62 and 25.18 ppm correspond to the carbons attached to the nonequivalent five-coordinated tin atoms (see the ^{119}Sn NMR data). The carbon atom resonance from the $Cl-Sn-CH_2$ moiety is shifted to lower field (28.70 ppm), and it was identified initially from coupling with the tin nucleus ($^1J(^{13}C^{119}Sn) = 1120$ Hz).

The 1H and ^{13}C NMR resonances (Table 1) associated with the butyl and the $-SCH_2CH_2O-$ units for **2** exhibit a pattern similar to those of **1**. Two broad signals in the range 2.6–2.85 and 3.4–3.7 ppm correspond to the $-CH_2-S$ and $-CH_2O-$ resonance, respectively, while the proton signal from the $-SCH_2CH_2OH$ fragment occurs as a broad peak at 5.55 ppm, which disappears on addition of D_2O . Carbon atoms bonded to the oxygen atom in the $-SCH_2CH_2OH$ and the cycle $-SCH_2CH_2O-$ fragments are distinguishable (Table 1).

^{119}Sn NMR Spectra. The ^{119}Sn NMR spectra are straightforward (Table 1). That for **1** contains signals at -39.04 ($^2J(^{119}Sn^{119/117}Sn) = 173.9$ Hz), -42.6 ($^2J(^{119}Sn^{119/117}Sn) = 236.1$ Hz), and -447.00 ($^2J(^{119}Sn^{119/117}Sn) = 173.9$ and 236.1 Hz) ppm for each of the three nonequivalent tin atoms. That at the highest field is associated with the six-coordinated tin center, which carries the chlorine atom. Only one signal at 28.7 ppm is observed in the ^{119}Sn NMR spectrum of **2**, which is within the range for the four-coordinated tin nucleus.¹¹ Therefore, the structure in solution is different from that observed in the solid state. There are probably no intermolecular $Sn \cdots O$ interactions in the solution state.

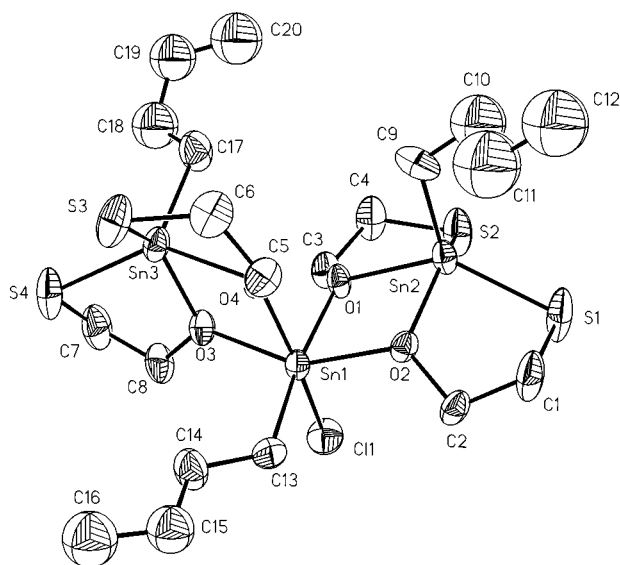
Description of Structures. Compounds **1** and **2** were amenable to study by single-crystal X-ray diffraction, and the structure and the atom numbering scheme are illustrated in Figures 1 and 2. Selected bond lengths and angles for **1** and **2** are listed in Table 2.

The structure of compound **1** consists of discrete trinuclear $[Sn(^nBu)(Cl)\{(OCH_2CH_2S)_2Sn(^nBu)\}_2]$ units in which two of the tin centers are five-coordinated and the other is six-coordinated. Both pentacoordinated tin atoms ($Sn(2)$ and $Sn(3)$) are bonded to a butyl group and to the oxygen and the sulfur

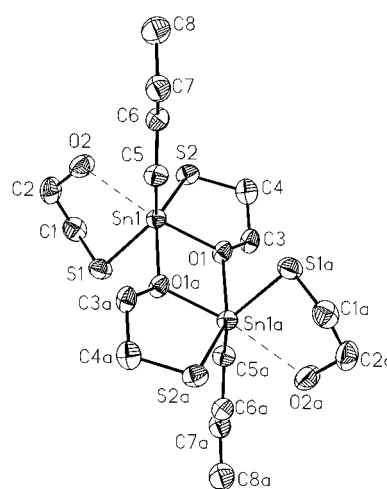
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Table 1. ^{119}Sn , ^{13}C , and ^1H NMR Data for Compounds **1** (in CD_2Cl_2) and **2** (in $(\text{CD}_3)_2\text{SO}$)^a

moiety		compound 1		compound 2		
Sn	^{119}Sn	Sn(1)		^{119}Sn		
	-447 -42.6, -39	Sn(2, 3)		28.7 Sn(1, 2)		
-SCH ₂ CH ₂ O-	^1H (at -70 °C)		^{13}C	^1H		^{13}C
	3.17 (m)	8 H	31.3	2.85–2.6 (bs)	4 H	30.7
	2.9 (m)					
-SCH ₂ CH ₂ O-	2.84 (m)					
	4.11 (m)	8 H	63.2	3.7–3.4 (bs)	4 H	63.4
	3.97 (m)					
-SCH ₂ CH ₂ OH	3.72 (m)					
				5.52 (bs)		59.9
SnCH ₂ CH ₂ CH ₂ CH ₃	0.95 (t)	9 H	13.3	0.84 (t)	3 H	14.1
SnCH ₂ CH ₂ CH ₂ CH ₃	1.42 (sex.)	6 H	26.2	1.32 (bs)	2 H	27.8
SnCH ₂ CH ₂ CH ₂ CH ₃	1.79 (q)	6 H	27.2 Sn(2, 3)	1.5 (bs)	2 H	29.9
			28.1 Sn(1)			
SnCH ₂ CH ₂ CH ₂ CH ₃	1.58 (t)	6 H	25.6 Sn(2)	1.6 (bs)	2 H	26.0
			25.2 Sn(3)			
			28.7 Sn(1)			

^a Chemical shift data in ppm.**Figure 1.** ORTEP plot of $[\text{Sn}(\text{Bu})(\text{Cl})\{(\text{OCH}_2\text{CH}_2\text{S})_2\text{Sn}(\text{Bu})\}_2]$ (**1**). The atoms were drawn with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

atoms from two $[\text{OCH}_2\text{CH}_2\text{S}]^{-2}$ ligands forming two stannolanes, which are fused with the central six-coordinated tin atom [Sn(1)]. This atom carries a butyl group, a chlorine atom, and oxygen atoms from each of the four stannolane units. Therefore, the Sn(1)O₄ core is the bridge between the stannolane systems to form a spirodistannoxane system, Sn(2)O₂Sn(1)O₂Sn(3). The average Sn–O and the Sn–S bonds lengths in the stannolane units, 2.152 and 2.414 Å, respectively, are close to the sum of the appropriate covalent radii^{12a} and similar to those in previous stannolane structures.^{1–7,13} The Sn–O bond in stannolane units are longer than those in distannoxanes (ave Sn–O = 2.128 Å).

**Figure 2.** ORTEP plot of $[(\text{Bu})\text{Sn}(\text{SCH}_2\text{CH}_2\text{O})(\text{SCH}_2\text{CH}_2\text{OH})]$ (**2**). The atoms were drawn with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

In each $(\text{OCH}_2\text{CH}_2\text{S})_2\text{Sn}(\text{Bu})$ moiety, the five-coordinated tin atoms exhibit very distorted square pyramidal geometry with the butyl group in the apical position. This distortion may be a consequence of the constraints imposed by the fused five- and four-membered systems. The five-membered rings adopt an envelope conformation with the carbon atoms (C(3) and C(7)) attached to the sulfur atom at the lap.

The six-coordinate Sn(1) atom exhibits octahedral geometry highly distorted from constraints imposed by the two four-membered distannoxane ring system. The mean Sn–O bond distance and internal O–Sn–O angle are 2.12(2) Å and 71.3(9)°, respectively, values close to those from previously reported distannoxane structures.^{7,13b,14,15} Since in this compound the two distannoxane rings form a spirostannoxane system, the present structure represents a totally different type from the common ladder or staircase structures observed previously for trinuclear distannoxanes, for example, $[(\text{R}_2\text{Sn})(\text{R}_2\text{SnO})(\text{R}_2\text{SnOH})(\text{HONZO})-(\text{ONZO})]^{15}$ (R = Me, ⁿBu; HONZO = *o*-HON=CHC₆H₄O–; and ONZO = *o*-(–ON=CHC₆H₄O–)), and for other related compounds.^{7,14a–d}

The structure of compound **2** consists of $[(\text{Bu})\text{Sn}(\text{SCH}_2\text{CH}_2\text{O})(\text{SCH}_2\text{CH}_2\text{OH})]$ units associated into dimers via intermolecular Sn–O interactions. The tin atom is bonded to a butyl group and to the sulfur and oxygen atoms from one

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

compound 1		compound 1		compound 2	
Sn(1)–Cl(1)	2.428(4)	Sn(2)–S(2)	2.407(5)	Sn(1)–O(1)	2.081(4)
Sn(1)–O(1)	2.079(12)	Sn(2)–O(2)	2.133(12)	Sn(1)–O(2)	2.679(6)
Sn(1)–O(2)	2.109(9)	Sn(2)–C(9)	2.139(20)	Sn(1)–O(1a)	2.327(4)
Sn(1)–O(3)	2.109(8)	Sn(3)–S(3)	2.415(4)	Sn(1)–S(1)	2.394(2)
Sn(1)–O(4)	2.122(8)	Sn(3)–O(3)	2.153(10)	Sn(1)–S(2)	2.473(2)
Sn(1)–C(13)	2.132(20)	Sn(3)–O(4)	2.155(8)	Sn(1)–C(5)	2.149(6)
Sn(2)–S(1)	2.419(4)	Sn(3)–S(4)	2.417(6)		
Sn(2)–O(1)	2.166(8)	Sn(3)–C(17)	2.156(30)		
compound 1		compound 1		compound 2	
Cl(1)–Sn(1)–O(1)	88.9(3)	S(1)–Sn(2)–S(2)	98.7(2)	O(1)–Sn(1)–O(2)	161.6(2)
Cl(1)–Sn(1)–O(2)	99.4(2)	S(1)–Sn(2)–C(9)	118.3(7)	S(2)–Sn(1)–O(1a)	150.6(1)
Cl(1)–Sn(1)–O(3)	95.6(3)	S(2)–Sn(2)–O(1)	82.8(3)	S(1)–Sn(1)–C(5)	133.2(2)
Cl(1)–Sn(1)–O(4)	165.7(3)	S(2)–Sn(2)–O(2)	136.2(3)	O(2)–Sn(1)–O(1a)	128.3(2)
Cl(1)–Sn(1)–C(13)	96.7(4)	S(2)–Sn(2)–C(9)	112.8(8)	S(2)–Sn(1)–C(5)	111.1(2)
O(1)–Sn(1)–O(2)	72.4(4)	O(3)–Sn(3)–O(4)	70.5(3)	S(1)–Sn(1)–O(1)	108.1(2)
O(1)–Sn(1)–O(3)	83.2(4)	O(3)–Sn(3)–C(17)	103.8(6)	O(1)–Sn(1)–C(5)	105.8(2)
O(1)–Sn(1)–O(4)	82.7(4)	O(4)–Sn(3)–C(17)	99.3(6)	S(1)–Sn(1)–S(2)	104.33(7)
O(1)–Sn(1)–C(13)	168.2(5)	S(3)–Sn(3)–O(3)	137.9(4)	C(5)–Sn(1)–O(1a)	84.9(2)
O(2)–Sn(1)–O(3)	151.0(5)	S(3)–Sn(3)–O(4)	83.2(2)	O(2)–Sn(1)–C(5)	84.6(2)
O(2)–Sn(1)–O(4)	89.1(3)	S(3)–Sn(3)–S(4)	100.2(2)	S(2)–Sn(1)–O(1)	82.95(12)
O(2)–Sn(1)–C(13)	96.3(5)	S(3)–Sn(3)–C(17)	112.7(6)	S(2)–Sn(1)–O(2)	79.1(2)
O(3)–Sn(1)–O(4)	72.0(3)	S(4)–Sn(3)–O(3)	81.2(3)	S(1)–Sn(1)–O(1a)	78.46(14)
O(3)–Sn(1)–C(13)	106.5(6)	S(4)–Sn(3)–O(4)	139.2(4)	S(1)–Sn(1)–O(2)	72.9(2)
O(4)–Sn(1)–C(13)	93.7(5)	S(4)–Sn(3)–C(17)	116.0(5)	O(1)–Sn(1)–O(1a)	68.7(2)
O(1)–Sn(2)–O(2)	70.3(4)	Sn(1)–O(1)–Sn(2)	108.5(4)	Sn(2)–O(1)–Sn(2a)	111.3(2)
O(1)–Sn(2)–C(9)	96.3(7)	Sn(1)–O(2)–Sn(2)	108.7(4)		
O(2)–Sn(2)–C(9)	104.2(8)	Sn(1)–O(3)–Sn(3)	109.0(4)		
S(1)–Sn(2)–O(1)	140.7(3)	Sn(1)–O(4)–Sn(3)	108.4(3)		
S(1)–Sn(2)–O(2)	82.9(3)				

[OCH₂CH₂S]²⁻ ligand, forming a stannolane. A second five-membered ring is formed via an Sn–S bond and a weak, secondary Sn–O bond with an [HOCH₂CH₂S]⁻² ligand. This weak intramolecular Sn–O₂ bond [2.679(6) Å] is longer than a normal covalent Sn–O bond^{12a} but shorter than the sum of van der Waals radii, ca. 3.3 Å.^{12b} In addition, there is a stronger intermolecular Sn–O interaction, approximately trans to S(2), with a symmetry-related oxygen [Sn–O(1a) = 2.327(4) Å] whose length is marginally longer than the covalent radii sum (2.13 Å).^{12a} This produces a distannoxane (Sn₂O₂ unit), and in the dimers so formed, the tin coordination is raised to 6. The internal stannolane angles are 82.9(1)° and 72.9(2)° with the smallest angle corresponding to that containing the longest Sn–O₂ bond; this is substantially lower than those usually found for S–Sn–O stannolane angles (81.2–83.2°).^{1,6,7,13d}

Crystal packing of **2** consists of dimeric [(ⁿBu)Sn(SCH₂CH₂O)(SCH₂CH₂OH)]₂ units interconnected by S2–H1b–O2b hydrogen bridges of 2.31(8) Å between the alcohol group and symmetry-related sulfur atoms.

Table 3. Crystallographic Data for **1** and **2**

	1	2
chemical formula	C ₂₀ H ₄₃ ClO ₄ S ₄ Sn ₃	C ₈ H ₁₈ O ₂ S ₂ Sn
formula mass	867.3	329.07
λ, Mo Kα [Å]	0.710 73	0.710 73
temp [K]	293(2)	293(2)
cryst syst	monoclinic	orthorhombic
space group	Cc (No. 9)	Pbca (No. 61)
a [Å]	18.492(3)	14.468(2)
b [Å]	17.329(2)	10.393(1)
c [Å]	10.787(2)	16.479(2)
α [deg]	90	90
β [deg]	111.88(1)	90
γ [deg]	90	90
V [Å ³]	3207.7(7)	2477.9(5)
Z	4	8
ρ _{calcd} [mg/cm ³]	1.796	1.764
μ [cm ⁻¹]	26.89	23.70
R1(F _o) ^a	0.0374	0.0393
wR2(F _o) ^b	0.0893	0.0907

$$^a R1 = \sum |F_o| - |F_c| / \sum |F_o|. \quad ^b wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

It is clear that many factors are involved in determining the formation and the structure of stannolane systems,^{1–7,13} and the behavior of the new compounds (**1** and **2**) reported here exemplify well some of the points mentioned in the Introduction. Clearly, the presence of oxygen donor atoms promoted higher tin coordination numbers, leading both to stabilization of the trinuclear compound **1** in solution and the solid state and to dimer formation for **2** in the solid state. However, the most remarkable feature is that the arrangement of **1** is quite different from previous ladder or staircase analogous structures.

Experimental Section

All operations were carried out under argon atmosphere using standard vacuum line techniques. Solvents were dried by conventional procedures and distilled prior to use. Chemicals of commercial grade were purchased from Aldrich and were used as supplied. ¹¹⁹Sn, ¹H,

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and ^{13}C NMR spectra were obtained using a Varian Unity spectrometer (111.8, 299.94, and 75.42 MHz, respectively) in CD_2Cl_2 (**1**) and $(\text{CD}_3)_2\text{SO}$ (**2**) at 20 °C unless otherwise noted. The external references were $\text{Sn}(\text{CH}_3)_4$ and $\text{Si}(\text{CH}_3)_4$. The FAB⁺ MS (3-nitrobenzyl alcohol support) data were collected from a JEOL JMS-SX102A operating in the positive-ion mode. IR spectra (KBr-pellet) were obtained from a Perkin-Elmer 283B. Microanalyses were conducted by Galbraith Laboratories (Knoxville, TN).

$[\text{Sn}(\text{nBu})(\text{Cl})\{\text{OCH}_2\text{CH}_2\text{S}\}_2\text{Sn}(\text{nBu})_2]$ (**1**). Amounts of 6.348 g (81.3 mmol) of 2-mercaptoethanol and 3.74 g (162.6 mmol) of metallic sodium were mixed in 150 mL of ethanol with stirring, and the solution was refluxed for 1 h. After the solution was cooled, 22.93 g (81.3 mmol) of *n*-butyltrichloride tin(IV) was added, leading to formation of an immediate white precipitate. The mixture was refluxed for another 4 h. The solid was filtered off in vacuum and washed with ethanol. The residue was stirred with distilled water for 1 h, and the residue after filtration was recrystallized from CH_2Cl_2 (mp 124 °C). Yield: 16.45 g (93.3%). MS (FAB⁺, CHCl_3 , for ^{120}Sn), m/z : 831 $[\text{M} - \text{Cl}]^+$, 581 $[\text{C}_{14}\text{H}_{31}\text{O}_3\text{S}_3\text{Sn}_2]^+$, 523 $[\text{C}_{10}\text{H}_{21}\text{O}_3\text{S}_3\text{Sn}_2]^+$, 447 $[\text{C}_8\text{H}_{17}\text{O}_2\text{S}_2\text{Sn}_2]^+$, 253 $[\text{C}_6\text{H}_{13}\text{OSSn}]^+$, 197 $[\text{C}_2\text{H}_5\text{OSSn}]^+$. Anal. Calcd for $\text{C}_{20}\text{H}_{47}\text{ClO}_4\text{S}_4\text{Sn}_3$ (867.3): C, 27.57; H, 5.02. Found: C, 27.69; H, 5.00.

$[(\text{nBu})\text{Sn}(\text{SCH}_2\text{CH}_2\text{O})(\text{SCH}_2\text{CH}_2\text{OH})]$ (**2**). (a) This compound was obtained initially from a reaction at -78 °C in which 0.5 mL of 0.7 M nBuMgCl in THF was added dropwise with stirring to 0.303 g (0.35 mmol) of **1** in 50 mL of THF. The reaction mixture was then allowed to reach room temperature. After removal of the solvent, 50 mL of hexane was added and the mixture was stirred for 12 h. The resulting solid was filtered off and dissolved in 50 mL of CH_2Cl_2 . After filtration, the solvent was removed in a vacuum to give white crystals of the product. Yield: 64 mg (37.2%).

(b) An amount of 0.277 g (3.56 mmol) of 2-mercaptoethanol was

added to a solution of 0.371 g (1.78 mmol) of *n*-butyltin hydroxide oxide in 50 mL of toluene and the mixture refluxed for 5 h. After removal of the solvent, the residue was extracted with CH_2Cl_2 and filtered. Evaporation of the solution then gave the required compound (mp 120 °C). Yield: 0.327 g (55.9%). MS (FAB⁺, CHCl_3 , for ^{120}Sn), m/z : 523 $[\text{C}_{10}\text{H}_{21}\text{O}_3\text{S}_3\text{Sn}_2]^+$, 447 $[\text{C}_8\text{H}_{17}\text{O}_2\text{S}_2\text{Sn}_2]^+$, 253 $[\text{C}_6\text{H}_{13}\text{OSSn}]^+$, 197 $[\text{C}_2\text{H}_5\text{OSSn}]^+$. Anal. Calcd for $\text{C}_8\text{H}_{18}\text{O}_2\text{S}_2\text{Sn}$ (329.0): C, 29.20; H, 5.51. Found: C, 29.20; H, 5.62.

X-ray Crystallographic Study. Crystals of **1** suitable for X-ray diffraction were obtained by solvent diffusion from a benzene/*n*-hexane mixture at room temperature, while those of **2** were obtained by slow evaporation of a CH_2Cl_2 solution. Data were collected at room temperature on a Siemens P4 four-circle diffractometer with graphite monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). Data collections and refinements are summarized in Table 3. Structures were resolved by direct methods and refined by full-matrix least-squares calculations using SHELXTL-97.¹⁶ Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were calculated as a riding model with a fixed isotropic $U = 0.06$ Å². Absorption effects were corrected by semiempirical methods (ψ scan) for both compounds. The calculated absolute structure parameter for **1** was $\eta = 1.1(2) \times 269$.¹⁷

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Supporting Information Available: IR data and X-ray crystallographic file in CIF format for structure determination of compounds **1** and **2** (structure factors are available only from the authors). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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