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Molecular Receptors for Tin: Structural Studies of Organotin−Coronand Adducts Mediated by Hydrogen-Bonding Interactions

Stephen E. Johnson*

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242-1294

Carolyn B. Knobler

Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California 90024-1569

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Hypervalent organotin−coronand adducts are observed when organotin chloride compounds of the type $Me_{3-n}SnCl_{n+1}$ (n = 0−2) are combined with water in the presence of 1,3-xylyl-18-crown-5 or 2-*n*-butyl-1,3-xylyl-18-crown-5 rather than products of hydrolysis (*i.e.* stannoxanes). The synthesis and characterization of $[Me_3SnCl(H_2O)]_2$·1,3-xylyl-18-crown-5 (**4**), $[Me_2SnCl_2(H_2O)]_2$·1,3-xylyl-18-crown-5 (**5**) and $\{[MeSnCl_3(H_2O)_2]\cdot H_2O$·1,3-xylyl-18-crown-5$\}_n$ (**6**) and the corresponding 2-*n*-butyl-1,3-xylyl-18-crown-5 adducts of Me_2SnCl_2 and $MeSnCl_3$ (**7, 8**) are reported. Compounds **4**−**6** are 2:1 or 1:1 adducts, whereas **7** and **8** are exclusively 1:1 adducts. In all organotin−coronand adducts, the water molecules serve to bind the organotin centers in a pentacoordinate or hexacoordinate manner and provide a link to the coronand via hydrogen-bonding interactions. Hydrolysis products are observed when the organotin compounds are present in excess of either coronand. The solution-state behavior of the organotin−coronand adducts was investigated by ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy. The molecular structures of **6**, **7** and an organodistannoxane derived from the hydrolysis of $MeSnCl_3$ (**9**) have been determined from X-ray crystallographic studies. Compound **6** exhibits an infinite chain structure of $MeSnCl_3(H_2O)_2$ and 1,3-xylyl-18-crown-5 molecules held together via an extensive hydrogen-bonding network. Compound **7** is a discrete 1:1 adduct of 2-*n*-butyl-1,3-xylyl-18-crown-5 and $Me_2SnCl_2(H_2O)$ molecules. Compound **6** crystallized in the monoclinic space group , $P2_{1/c}$ with $a = 9.6360(6)$ Å, $b = 37.7550(9)$ Å, $c = 15.0044(6)$ Å, $\beta = 95.206(5)°$, $V = 4860$ Å^3, $Z = 4$, $R = 0.054$. Compound **7** crystallized in the triclinic space group $P1$ with $a = 9.616(1)$ Å, $b = 9.737(2)$ Å, $c = 16.369(2)$ Å, $\alpha = 100.117(5)°$, $\beta = 76.360(5)°$, $\gamma = 99.927(5)°$, $V = 1453$ Å^3, $Z = 2$, $R = 0.081$. Compound **9** crystallized in the monoclinic space group $C/2_c$ with $a = 13.009(1)$ Å, $b = 6.9883(6)$ Å, $c = 16.937(2)$ Å, $\beta = 98.480(2)°$, $V = 1523$ Å^3, $Z = 4$, $R = 0.018$.

Introduction

Neutral molecule complexes of macrocyclic receptors are thermodynamically much less stable than ionic host-guest complexes of crown ethers.[1] The use of macrocyclic polyethers as receptors in the second-sphere coordination of metals was recognized only in recent years as a means of stabilizing supramolecular architectures.[2] Macrocyclic polyether adducts of aquated inorganic Sn(II) and Sn(IV) compounds have been reported, where the aqua ligands coordinated to tin exhibit an enhanced dipole and increased acidity in the same manner that ammonia or amine ligands on transition metals are activated towards second-sphere coordination of metals.[3] Definite complexes between organotin compounds and macrocyclic polyethers are still relatively unexplored,[4] however, despite advances in the molecular recognition of anions by organotin hosts.[5] In designing receptors for anionic organotin compounds, we have exploited non-covalent forces such as electrostatic attraction, hydrogen-bonding and van der Waals interactions.[6,7] More recently, we have demonstrated that 1,3-xylyl crown ethers are effective receptors for organotin compounds and structurally characterized the first example of a discrete adduct in which coordinated water molecules serve as ligands and link pentacoordinate organotin

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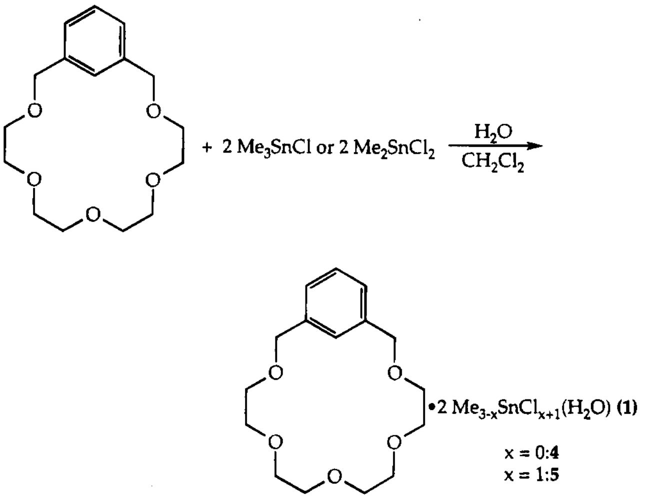
centers to the coronand via hydrogen-bonding interactions.[8] Studies of pentacoordinate tin compounds are of special significance in structural tin chemistry because of their probable role as intermediates in nucleophilic substitution reactions of organotin compounds.[9] An intimate knowledge of structural details, therefore, is crucial in understanding the role that intermolecular forces (*i.e.* hydrogen-bonding interactions) play in the assembly of the organotin–coronand adducts described herein.

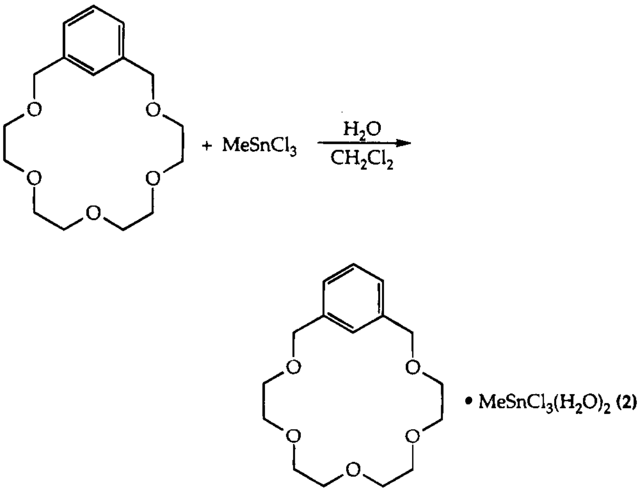
Normally, organotin chlorides undergo hydrolysis to give a variety of organostannoxanes, which are formal intermediates en route to the final products along the hydrolytic pathway.[10] Triorganotin chlorides afford dimeric hydroxides upon hydrolysis, which subsequently condense to form bis(triorganotin)oxides. Hydrolysis of diorganotin dichlorides results in diorganodistannoxanes which exhibit "ladder" structures composed of Sn_2O_2 heterocycles.[11] More complicated cyclic stannoxanes and cage intermediates are observed when monoorganotin trichlorides undergo hydrolysis, termed "extended ladders", "drum" and "football" motifs respectively.[12] In addition, the essential role of water in the solvation of xylyl-substituted crown ethers in chlorinated hydrocarbons was demonstrated, and this complexation ability increases as the ring size becomes larger.[13] The observation of discrete, aquated organotin–coronand compounds instead of polymeric organotin-crown ether adducts with both coordinated and uncoordinated H_2O molecules was unprecedented and required further examination.[8] Specifically, we wanted to understand the effects that functionalization of the intraannular position would have on complexation properties of the coronand. Reinhoudt and co-workers recently reported that 1,3-xylyl crown ethers with intraannular proton-donating substituents provided receptors for urea and water via strong hydrogen bonds.[14] We anticipated that an *n*-butyl group in the intraannular position would alter the stoichiometries of the organotin–coronand adducts.

With these observations in mind, a series of organotin chlorides of the type $Me_{3-n}SnCl_{n+1}$ ($n = 0-2$) were combined with the coronands 1,3-xylyl-18-crown-5 or 2-*n*-butyl-1,3-xylyl-18-crown-5 in different stoichiometric ratios, followed by the addition of water, to afford the organotin–coronand adducts **4**–**8**. Herein we report characterization data, solid-state studies, and solution-state studies for compounds **4**–**9**. The molecular structures of adducts **6** and **7** represent new examples of aquated organotin compounds activated towards second-sphere coordination of coronands. Functionalization of the intraannular position appears to strongly influence the composition and structures of the organotin–coronand adducts, as highlighted in the case of **7**. Hydrogen-bonding interactions in the solid-state were examined using IR spectroscopy and X-ray diffraction. The solution-state behavior of the organotin–coronand adducts was investigated by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy.

Results and Discussion

Synthesis. Trimethyltin chloride (**1**) and dimethyltin dichloride (**2**) react with 1,3-xylyl-18-crown-5 in methylene chloride solution to afford 2:1 pentacoordinate organotin–coronand adducts **4** and **5**, respectively (eq 1). The same adducts are observed when a stoichiometric amount or an excess of water is added. In contrast, methyltin trichloride (**3**) forms a 1:1 hexacoordinate organotin–coronand adduct, **6**, when combined with two equivalents or an excess of water and 1,3-xylyl-18-crown-5 (eq 2). By comparison, trimethyltin hydroxide is obtained from the hydrolysis of **1** and was reported by Okawara and co-workers to exhibit a dimeric structure in solution[15] and a polymeric structure in the solid-





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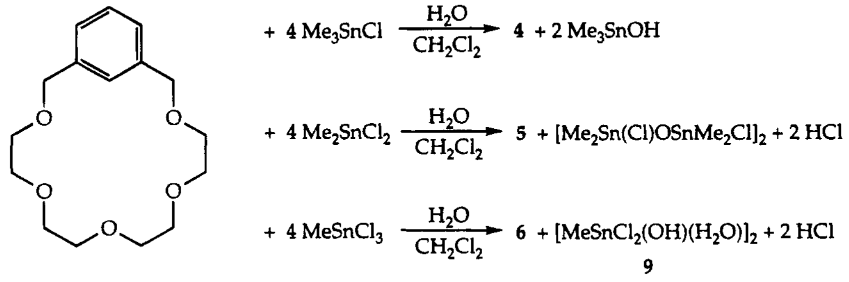
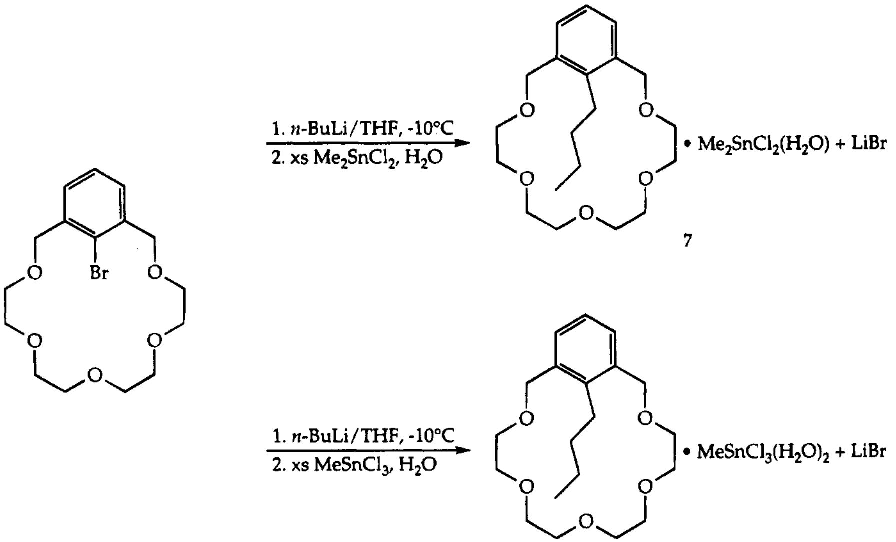
Scheme 1



Scheme 2



state.[16] Moreover, the hydrolysis product of **2** is a dimeric tetraalkyldistannoxane, $[ClMe_2SnOSnMe_2Cl]_2$, from spectroscopic data and X-ray analysis.[17,18] Methyltin trichloride is completely hydrolyzed to afford methyl stannoic acid, MeSn(O)OH,[19] although dimeric intermediates of the type $[RSnCl_2(OH)(H_2O)]_2$ (R = *i*-Pr, *i*-Bu, *n*-Bu, Et)[12d,20,21] have been observed as initial products of the partial hydrolysis of $RSnCl_3$ compounds. In the presence of 1,3-xylyl-18-crown-5, however, discrete organotin–coronand adducts are observed in high yields (> 90%). Hydrolysis products are observed along with organotin–coronand adducts **4–6** when an excess of the respective organotin compound is combined with the coronand upon addition of water, as summarized in Scheme 1. It is interesting to note that the hydrolysis product $[MeSnCl_2(OH)(H_2O)]_2$, **9**, was observed in the reaction of an excess of **3** with the coronand along with **6** and was characterized from spectroscopic data and an X-ray diffraction study.

The organotin adducts of 2-*n*-butyl-1,3-xylyl-18-crown-5 were prepared by first generating the coronand *in situ* and combining it with the appropriate organotin chloride reagent (Scheme 2). Normally bromine to lithium exchange occurs when 2-bromo-1,3-xylyl-18-crown-5 reacts with *n*-BuLi at −78 °C.[14] If the same reaction is carried out at −10 to 0 °C, the Wurtz coupled product, 2-*n*-butyl-1,3-xylyl-18-crown-5 is observed. Subsequent addition of **2** or **3**, followed by the addition of water, affords the crystalline organotin–coronand adducts **7** and **8** in high yields, respectively. In contrast to **5**, a 1:2 adduct, compound **7** is a 1:1 adduct. In addition, whereas **6** is a 1:1 adduct that exhibits a polymeric structure in the solid-state (*vide infra*), compound **8** is a discrete 1:1 adduct. The solution-state behavior of the organotin–coronand adducts **4–8** was investigated by ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy.

NMR Behavior. All organotin adducts were characterized in solution by a combination of ^1H, $^{13}C\{^1H\}$, and $^{119}Sn\{^1H\}$NMR spectroscopy. The ^1H NMR data for adducts **4–8** and their related triorganotin halides (**1–3**) are summarized in Table 1.

Relatively little information can be discerned from the chemicals shifts of the methyl-tin protons. The important information lies in magnitude of the two bond proton-tin coupling constants, $^2J|^1H^{119}Sn|$. Since the coupling constant is related via the Fermi contact term to the *s*-electron density in the bond, their magnitudes are used to infer valence electron distribution in tin-carbon bonds, and indeed have been shown to be directly related to minimal changes occurring in the C–H bonds.[22,23] The increase of $^2J|^1H^{119}Sn|$ for the pentacoordinate or hexacoordinate organotin centers in **4–8** can

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Table 1. ^{1}H NMR Data for Organotin(IV) Compounds

compound	solvent	$\delta(\mathrm{Me}_x\mathrm{Sn})$, ppm	$^2J|^1\mathrm{H}^{119}\mathrm{Sn}|$, Hz	$\delta(\mathrm{H_2O})$, ppm
Me_3SnCl (**1**)	$CDCl_3$	0.65	59	
Me_2SnCl_2 (**2**)	$CDCl_3$	1.21	69	
$MeSnCl_3$ (**3**)	$CDCl_3$	1.68	98	
$2Me_3SnCl(H_2O)\cdot$1,3-xylyl-18-crown-5 (**4**)	$CDCl_3$	0.64	61	5.21
$2Me_2SnCl_2(H_2O)\cdot$1,3-xylyl-18-crown-5 (**5**)	$CDCl_3$	1.14	72	2.36
$MeSnCl_3(H_2O)_2\cdot$1,3-xylyl-18-crown-5 (**6**)	$CDCl_3$	1.31	110	5.36
$Me_2SnCl_2(H_2O)\cdot$2-*n*-butyl-1,3-xylyl-18-crown-5 (**7**)	$CDCl_3$	1.09	74	2.65
$MeSnCl_3(H_2O)_2\cdot$2-*n*-butyl-1,3-xylyl-18-crown-5 (**8**)	$CDCl_3$	1.66	113	2.84

Table 2. ^{13}C NMR Data for Organotin(IV) Compounds

compound	solvent	$\delta(\mathrm{Me}_x\mathrm{Sn})$, ppm	$^1J|^{13}\mathrm{C}^{119}\mathrm{Sn}|$, Hz
Me_3SnCl (**1**)	$CDCl_3$	−0.87	379
Me_2SnCl_2 (**2**)	$CDCl_3$	6.89	468
$MeSnCl_3$ (**3**)	$CDCl_3$	11.04	692
$2Me_3SnCl(H_2O)\cdot$1,3-xylyl-18-crown-5 (**4**)	$CDCl_3$	0.49	414
$2Me_2SnCl_2(H_2O)\cdot$1,3-xylyl-18-crown-5 (**5**)	$CDCl_3$	8.27	539
$MeSnCl_3(H_2O)_2\cdot$1,3-xylyl-18-crown-5 (**6**)	$CDCl_3$	15.7	891
$Me_2SnCl_2(H_2O)\cdot$2-*n*-butyl-1,3-xylyl-18-crown-5 (**7**)	$CDCl_3$	8.89	543
$MeSnCl_3(H_2O)_2\cdot$2-*n*-butyl-1,3-xylyl-18-crown-5 (**8**)	$CDCl_3$	14.0	876

Table 3. ^{119}Sn NMR Data for Organotin(IV) Compounds

compound	solvent	$\delta(^{119}\mathrm{Sn})$, ppm	$\Delta\delta(^{119}\mathrm{Sn})^a$
Me_3SnCl (**1**)	$CDCl_3$	165.7	
Me_2SnCl_2 (**2**)	$CDCl_3$	127.5	
$MeSnCl_3$ (**3**)	$CDCl_3$	6.30	
$2Me_3SnCl(H_2O)\cdot$1,3-xylyl-18-crown-5 (**4**)	$CDCl_3$	120.0	45.7
$2Me_2SnCl_2(H_2O)\cdot$1,3-xylyl-18-crown-5 (**5**)	$CDCl_3$	82.5	45.0
$MeSnCl_3(H_2O)_2\cdot$1,3-xylyl-18-crown-5 (**6**)	$CDCl_3$	−169.2	176.0
$Me_2SnCl_2(H_2O)\cdot$2-*n*-butyl-1,3-xylyl-18-crown-5 (**7**)	$CDCl_3$	78.3	49.2
$MeSnCl_3(H_2O)_2\cdot$2-*n*-butyl-1,3-xylyl-18-crown-5 (**8**)	$CDCl_3$	−171.4	177.7

^{a} $\Delta\delta(^{119}\mathrm{Sn}) = \delta^{119}\mathrm{Sn}$ (precursor) − $\delta^{119}\mathrm{Sn}$ (adduct), $T = 21$ °C.

be interpreted as a redistribution of the *s*-electron density in the Sn−C bonds, as compared to **1**−**3**, with a concomitant increase in the *p*-character of the Sn−X bonds in accordance with Bent's principle.[24] The increase in $^2J|^1\mathrm{H}^{119}\mathrm{Sn}|$ for **4**, **5** and **7** was consistent with pentacoordinate organotin centers,[7] whereas the magnitude of $^2J|^1\mathrm{H}^{119}\mathrm{Sn}|$ for **6** and **8** are within the ranges reported for hexacoordinated organotin compounds.[10] The chemical shifts of the coordinated water molecules in **4**−**8** range from 2.36 to 5.36 ppm. Studies are currently in progress to understand why a range of chemical shifts are observed. Two possible explanations are that the chemical shifts of the solvent molecules are concentration dependent or that differing degrees of dissociation are being expressed.

The ^{13}C NMR data for compounds **1**−**8** are summarized in Table 2. The one bond carbon-tin coupling constant, $^1J|^{13}\mathrm{C}^{119}\mathrm{Sn}|$, is a somewhat more sensitive indicator of the electron distribution changes in tin carbon bonds. A similar increase in $^1J|^{13}\mathrm{C}^{119}\mathrm{Sn}|$ is observed for compounds **4**−**8** as compared to **1**−**3**. The one-bond ^{13}C-^{119}Sn coupling constants, like the two-bond ^{1}H-^{119}Sn couplings, is a relatively accurate way of assessing the coordination number on the organotin center. The non-Fermi contact contributions to the ^{13}C-^{119}Sn couplings increase with increases in the electron donating ability of the coordinated solvent, namely the aqua ligands.[25] The magnitude of $^1J|^{13}\mathrm{C}^{119}\mathrm{Sn}|$ for **4**, **5** and **7** was consistent with pentacoordinate organotin centers,[7] whereas the magnitude of $^1J|^{13}\mathrm{C}^{119}\mathrm{Sn}|$ for **6** and **8** are within the ranges reported for hexacoordinated organotin compounds.[10]

The ^{119}Sn chemical shift data for compounds **1**−**8** are summarized in Table 3. Several points are worth noting. The ^{119}Sn chemical shift data offer the most poignant structural information regarding host-guest complexation for adducts **4**−**8**, since changes in the coordination number at tin can have a dramatic effect upon the shielding. Markedly upfield shifts of $\delta(^{119}\mathrm{Sn})$ are observed for **4**−**8** as compared to their respective uncomplexed organotin compounds, **1**−**3**. The increase in the shielding of the tin nucleus has been interpreted as an increase in the effective electronegativity of the tin atom as the overall number of electronegative substituents increase, which corresponds to a decrease in the *p*-electron imbalance in each bond.[26] The difference in the ^{119}Sn chemical shifts of the organotin compounds and their aquated coronand adducts ($\Delta\delta(^{119}\mathrm{Sn})$) reasonably reflects formation of the host-guest complex and serves to indicate the coordination geometry of the organotin moiety. In addition, the magnitude of $\Delta\delta(^{119}\mathrm{Sn})$, is much greater for **1** and its corresponding anionic derivative [K 18-crown-6][Me_3SnCl_2] (172.4)[7] than $\Delta\delta(^{119}\mathrm{Sn})$ for **1** and **4** (45.7). Although only ambient temperature data are presented, δ ^{119}Sn for **4**−**8** is temperature dependent and at their respective low temperature limits, the structures of adducts **4**, **5** and **7** can be described as pentacoordinated, whereas adducts **6** and **8** can be described as hexacoordinated. Full details of the solution-state behavior and the determination of association constants will be published in a separate paper.

Vibrational Spectra. IR data were measured for compounds **4**−**8** and selected vibrations are summarized in Table 4. The IR data for organotin−coronand ad-

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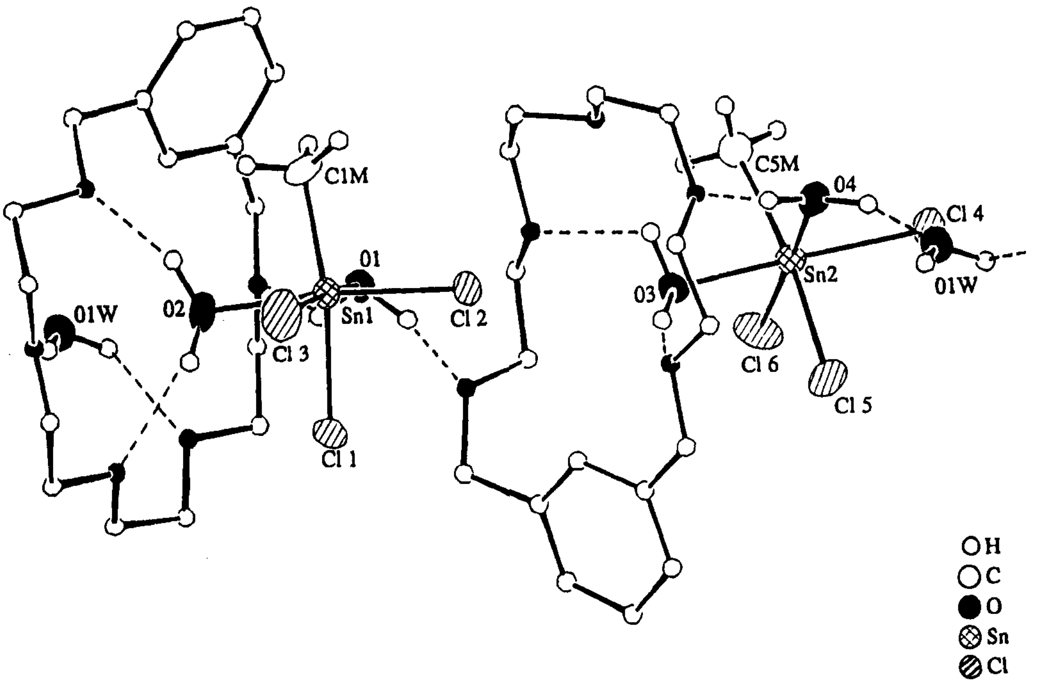

Figure 1. ORTEP representation of **6** showing the numbering scheme. All hydrogen atoms were removed for clarity. Ellipsoids were drawn at the 0.3 probability level.

Table 4. Selected Vibrational Data for Organotin–Coronand Adducts

compound	ν_{OH}, cm^{-1}	ν_{COC}(asymmetric), cm^{-1}
1,3-xylyl-18-crown-5		1104
2-*n*-butyl-1,3-xylyl-18-crown-5		1105
$2Me_3SnCl(H_2O)$·1,3-xylyl-18-crown-5 (**4**)	3350–3590 (br), 3204 (sh)	1100
$2Me_2SnCl_2(H_2O)$·1,3-xylyl-18-crown-5 (**5**)	3300–3600 (br), 3250 (sh)	1101
$MeSnCl_3(H_2O)_2$·1,3-xylyl-18-crown-5 (**6**)	3020–3610 (br)	1086
$Me_2SnCl_2(H_2O)$·2-*n*-butyl-1,3-xylyl-18-crown-5 (**7**)	3300–3583 (br), 3239 (sh)	1102
$MeSnCl_3(H_2O)_2$·2-*n*-butyl-1,3-xylyl-18-crown-5 (**8**)	3000–3634 (br)	1083

ducts **4–8** reflect extensive hydrogen-bonding interactions in the solid-state. All adducts exhibit broad ν(O-H) fundamentals, which range from 3200–3600 cm^{-1}. In addition, all adducts exhibit shifts of the asymmetric C–O stretching fundamental, ν(C–O), to lower frequencies, indicating that the coordinated water molecules on the organotin center(s) or the water molecules of crystallization interact with one (or more) polyether oxygen atoms of the coronands.[4a]

Description of the Molecular Structure of 6. The molecular structure of **6** is presented in Figure 1. The atomic coordinates are summarized in Table 5, and Table 6 lists selected interatomic distances and angles. For clarity, only the organotin compounds are completely labeled. The compound contains two crystallographically independent but similar hexacoordinate $CH_3SnCl_3(H_2O)_2$ molecules linked in chains with the two coronand molecules via an extensive hydrogen-bonded network. The hydrogen-bonds are represented by dashed lines and are evidenced by O(crown)-O(water) contacts that are less than the sum of the van der Waals radii for the two atoms (2.8 Å).[27] A molecule of water per two Sn octahedra also links the coronand and a coordinated water molecule on each organotin center via hydrogen-bonds. The Sn–Cl distances for the Cl trans to the methyl substituent, Cl(1) and Cl(5), are 2.375(4) and 2.357(4) Å, respectively. In each organotin molecule, two Cl ligands, Cl(2), Cl(3) and Cl(4), Cl(6), are trans to the aqua ligands. The two Sn–Cl bond contacts in the direction of the hydrogen-bonded chain, Cl(2) and Cl(4), are 2.405(3) and 2.409(4) Å, respectively, and are somewhat shorter than corresponding Sn(1)–Cl(3) and Sn(2)–Cl(6) distances, 2.434(4) and 2.423(4) Å. The Sn–O bond lengths range from 2.189(9) to 2.265(9) Å. The Sn–C bond distances are 2.121(13) and 2.209(9) Å. The bond angles around tin exhibit small distortions from idealized octahedral geometry.

Description of the Molecular Structure of 7. The molecular structure of **7** is presented in Figure 2. The atomic coordinates are summarized in Table 7, and Table 8 lists selected interatomic distances and angles. The compound crystallizes as a 1:1 adduct and the aquated, hypervalent organotin center is distorted from idealized trigonal bipyramidal geometry. The two Sn–C bond lengths are all within 0.02 Å of the average value of 2.04(2) Å. The equatorial Sn–Cl bond contact, Sn–Cl(1), of 2.446(5) Å is shorter than the axial Sn–Cl(2) bond distance of 2.546(5) Å. The Sn–O(1W) bond length is 2.397(14) Å. The C–Sn–C angle is 148.3(9)° and the C(2M)–Sn–Cl(1) and C(3M)–Sn–Cl(1) bond angles are 104.5(6)° and 96.7(6)°, respectively. The C(2M)–Sn–Cl(2) and C(3M)–Sn–Cl(2) bond angles are 104.0(6)° and 96.1(6)°, respectively, and the Cl–Sn–Cl bond angle is 91.6°. The aqua ligand is trans to Cl (2) and the Cl–Sn–O bond angle is nearly linear, 178.5(4)°. The $Me_2SnCl_2(H_2O)$ molecule is linked to the coronand via hydrogen bonds from the coordinated water ligand (O 1W). The hydrogen-bonds are represented by dashed

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[27] Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; W. A. Benjamin, Inc.: New York, 1968, pp 16, 86–87.

Table 5. Positional and Equivalent Isotropic Thermal Parameters for 6[a]

atom	x	y	z	$\langle U^2\rangle$, Å^2
Sn(1)	0.06033(10)	0.33820(3)	0.74345(6)	0.0256(5)
Cl(1)	0.25991(37)	0.29713(10)	0.74045(23)	0.0456(23)
Cl(2)	0.07332(36)	0.33573(10)	0.90421(21)	0.0406(21)
Cl(3)	−0.09047(44)	0.28092(13)	0.71448(27)	0.0568(27)
O(1)	0.2135(9)	0.38791(25)	0.76103(54)	0.0299(51)
O(2)	0.0985(10)	0.34516(29)	0.59751(56)	0.0487(63)
C(1)	−0.0996(14)	0.38110(45)	0.7199(10)	0.027(8)
Sn(2)	0.41201(9)	0.43444(3)	1.22763(6)	0.0246(5)
Cl(4)	0.46064(38)	0.46156(11)	1.37570(23)	0.0410(22)
Cl(5)	0.49442(42)	0.37133(12)	1.27417(26)	0.0490(25)
Cl(6)	0.63246(40)	0.45060(12)	1.17066(28)	0.0375(22)
O(3)	0.3356(9)	0.39972(25)	1.10657(56)	0.0400(57)
O(4)	0.2116(9)	0.41626(29)	1.27226(56)	0.0258(51)
C(5M)	0.3103(10)	0.48685(27)	1.16222(62)	0.0466(64)
O(1W)	0.2131(10)	0.37521(27)	1.41962(58)	0.0469(61)
O(1W′)	0.2131(10)	0.37521(27)	0.41962(58)	0.0469(61)
C(1C)	0.0474(14)	0.4432(4)	0.5428(9)	0.033(4)
C(2C)	−0.0958(15)	0.4429(4)	0.5257(9)	0.036(4)
C(3C)	−0.1741(16)	0.4669(5)	0.5764(10)	0.044(4)
C(4C)	−0.1114(16)	0.4909(5)	0.6408(10)	0.047(4)
C(5C)	0.0311(16)	0.4912(5)	0.6579(10)	0.041(4)
C(6C)	0.1129(14)	0.4674(4)	0.6089(9)	0.032(3)
C(7C)	0.2673(15)	0.4674(5)	0.6219(10)	0.042(4)
O(8C)	0.3204(9)	0.4275(3)	0.6285(6)	0.031(2)
C(9C)	0.4643(14)	0.4262(4)	0.6168(10)	0.036(4)
O(11C)	0.4508(9)	0.3608(3)	0.5517(6)	0.036(2)
C(12C)	0.5022(17)	0.3204(5)	0.5528(11)	0.048(4)
C(13C)	0.4315(16)	0.2979(5)	0.4810(10)	0.048(4)
O(14C)	0.2892(10)	0.2934(3)	0.4950(6)	0.039(2)
C(15C)	0.2197(17)	0.2676(5)	0.4320(11)	0.056(5)
C(16C)	0.0701(17)	0.2685(5)	0.4401(11)	0.057(5)
O(17C)	0.0193(11)	0.3074(3)	0.4180(7)	0.046(3)
C(18C)	−0.1267(18)	0.3103(6)	0.4222(12)	0.066(5)
C(19C)	−0.1717(19)	0.3502(5)	0.4004(12)	0.061(5)
O(20C)	−0.1226(9)	0.3767(3)	0.4740(6)	0.036(2)
C(21C)	−0.1621(16)	0.4159(5)	0.4553(10)	0.044(4)
C(1D)	0.4640(14)	0.3207(4)	1.0029(8)	0.025(3)
C(2D)	0.4805(14)	0.2997(4)	1.0817(9)	0.029(3)
C(3D)	0.6096(14)	0.2816(4)	1.1076(9)	0.031(3)
C(4D)	0.7176(16)	0.2845(5)	1.0535(10)	0.043(4)
C(5D)	0.7016(14)	0.3066(4)	0.9750(9)	0.033(4)
C(6D)	0.5739(13)	0.3251(4)	0.9499(9)	0.026(3)
C(7D)	0.5580(15)	0.3481(4)	0.8621(9)	0.036(4)
O(8D)	0.4645(9)	0.3813(3)	0.8645(6)	0.029(2)
C(9D)	0.5139(13)	0.4114(4)	0.9239(9)	0.028(3)
C(10D)	0.4140(14)	0.4461(4)	0.9124(9)	0.032(4)
O(11D)	0.2838(9)	0.4340(3)	0.9414(6)	0.030(2)
C(12D)	0.1767(14)	0.4626(4)	0.9196(9)	0.036(4)
C(13D)	0.0418(15)	0.4467(5)	0.9386(9)	0.039(4)
O(14D)	0.0401(11)	0.4381(3)	1.0316(7)	0.053(3)
C(15D)	−0.0852(20)	0.4162(6)	1.0461(12)	0.069(6)
C(16D)	−0.0798(20)	0.4007(6)	1.1322(13)	0.074(6)
O(17D)	0.0376(10)	0.3763(3)	1.1588(6)	0.040(3)
C(18D)	0.0171(14)	0.3350(4)	1.1460(9)	0.032(3)
C(19D)	0.1459(15)	0.3133(5)	1.1783(10)	0.039(4)
O(20D)	0.2562(9)	0.3212(3)	1.1237(6)	0.030(2)
C(21D)	0.3635(14)	0.2930(4)	1.1397(9)	0.035(4)

[a] Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter.

Table 6. Selected Interatomic Distances and Angles for 6

Distances (Å)			
Sn1−Cl1	2.375(4)	O1−O8D	2.761(12)
Sn1−O1	2.235(8)	O2−O20C	2.897(13)
Sn2−Cl4	2.409(4)	O3−O20D	2.778(12)
Sn2−O3	2.230(8)	O1W′−O11C	2.930(13)
O1−O8C	2.678(12)	Sn1−Cl3	2.434(4)
O3−O11D	2.739(12)	Sn1−C1M	2.121(14)
O4−O17D	2.647(13)	Sn2−Cl6	2.423(4)
O1W′−O17C	2.954(14)	Sn2−C5M	2.209(9)
Sn1−Cl2	2.405(3)	O2−O14C	3.051(13)
Sn1−O2	2.265(9)	O2−O14C	3.051(13)
Sn2−Cl5	2.357(4)	O4−O1W	2.608(12)
Sn2−O4	2.189(9)		
Angles (deg)			
Cl1−Sn1−Cl2	91.7(1)	Cl1−Sn1−Cl3	90.2(1)
Cl1−Sn1−O1	85.0(2)	Cl1−Sn1−O2	80.8(3)
Cl1−Sn1−C1M	166.7(4)	Cl2−Sn1−Cl3	97.3(1)
Cl2−Sn1−O1	86.2(2)	Cl2−Sn1−O2	167.1(3)
Cl2−Sn1−C1M	99.3(4)	Cl3−Sn1−O1	174.2(2)
Cl3−Sn1−O2	93.2(3)	Cl3−Sn1−C1M	95.7(4)
O1−Sn1−O2	82.7(3)	O1−Sn1−C1M	88.2(4)
O2−Sn1−C1M	87.0(5)	Cl4−Sn2−Cl5	92.2(1)
Cl4−Sn2−Cl6	97.8(1)	Cl4−Sn2−O3	166.7(2)
Cl4−Sn2−O4	85.8(3)	Cl4−Sn2−C5M	98.4(3)
Cl5−Sn2−Cl6	91.5(1)	Cl5−Sn2−O3	81.0(2)
Cl5−Sn2−O4	86.5(3)	Cl5−Sn2−C5M	168.4(3)
Cl6−Sn2−O3	93.8(2)	Cl6−Sn2−O4	175.9(3)
Cl6−Sn2−C5M	91.8(3)	O3−Sn2−O4	82.3(3)
O3−Sn2−C5M	87.6(3)	O4−Sn2−C5M	89.6(3)

lines and are evidenced by O(crown)-O(water) contacts (2.85(2) and 2.80(2) Å) that are on the order of the van der Waals radii for the two oxygen atoms (2.8 Å).[27]

Description of the Molecular Structure of 9. The molecular structure of **9** is presented in Figure 3. The atomic coordinates are summarized in Table 9, and Table 10 lists selected interatomic distances and angles. The compound contains two $CH_3SnCl_2(H_2O)$ moieties bridged by two OH groups in a centrosymmetric dimeric structure. The two tin centers of the dimer are distorted from idealized octahedral geometry. The Sn−C bond distance is 2.115(4) Å. The axial Cl ligand, Cl(1) is trans to an aqua ligand and this Sn−Cl bond distance is 2.474(1) Å, somewhat longer than the equatorial Sn−Cl(2) bond contact, 2.452(1) Å. The Cl(1)−Sn−O(1W) bond angle is 173.2(1)°. The O(2)−Sn−O(2) is 72.0(1)°, while the C(1M)−Sn−O(2) and C(1M)−Sn−Cl(2) bond angles are 98.7(1)° and 101.0(1)°, respectively. The Sn−O(2) distances (2.127(2) and 2.051(2) Å) are not equal for the hydroxyl ligands bonded to tin. The Sn−O(2)−Sn bond angle is 108.0(1)°. The Sn−O distance for the aqua ligand is 2.208(2) Å. The bond parameters discussed are all consistent with derivatives of the type $[RSnCl_2(OH)(H_2O)]_2$ (R = *i*-Pr, *i*-Bu, *n*-Bu, Et).[12d,20,21] In contrast to these derivatives, three molecules of water are associated per dimeric unit of **9**. Water molecules of crystallization are hydrogen-bonded to both aqua ligands and the hydroxyl ligands of the tin centers, forming a network throughout the crystal, as shown in Figure 4. The hydrogen-bonding interactions are evidenced by O(hydroxyl)-O(water) or O(water)-O(water) interactions that are less than or on the order of the van der Waals radii for the two appropriate oxygen atoms (2.8 Å).[27] By comparison, derivatives of the type $[RSnCl_2(OH)(H_2O)]_2$ are associated by OH⋯Cl hydrogen-bonds to chains which are linked by layers.[12d]

Structural Comparisons. It is of interest to compare the structural parameters for **6** and **7** with the X-ray data reported for related organotin-macrocyclic ether adducts (**5**, **10**−**12**), as summarized in Table 11. As mentioned in the introductory remarks, the presence of water in the coordination sphere of organotin compounds is not a completely new feature.[4] The axial Sn−Cl distances range from 2.583(2) Å to 2.446(5) Å and the equatorial Sn−Cl contacts range from 2.472(2) Å to 2.393(1) Å in the adducts with pentacoordinate organotin centers (**5**, **7**). The corresponding axial Sn−Cl distances range from 2.546(5) Å to 2.405(2) Å and the equatorial Sn−Cl contacts range from 2.375(4) Å to 2.364(2) Å in the adducts with hexacoordinate organotin centers (**6**, **10**−**12**). There appears to be little variation in the Sn−O bond lengths for adducts **5** and **7** and all

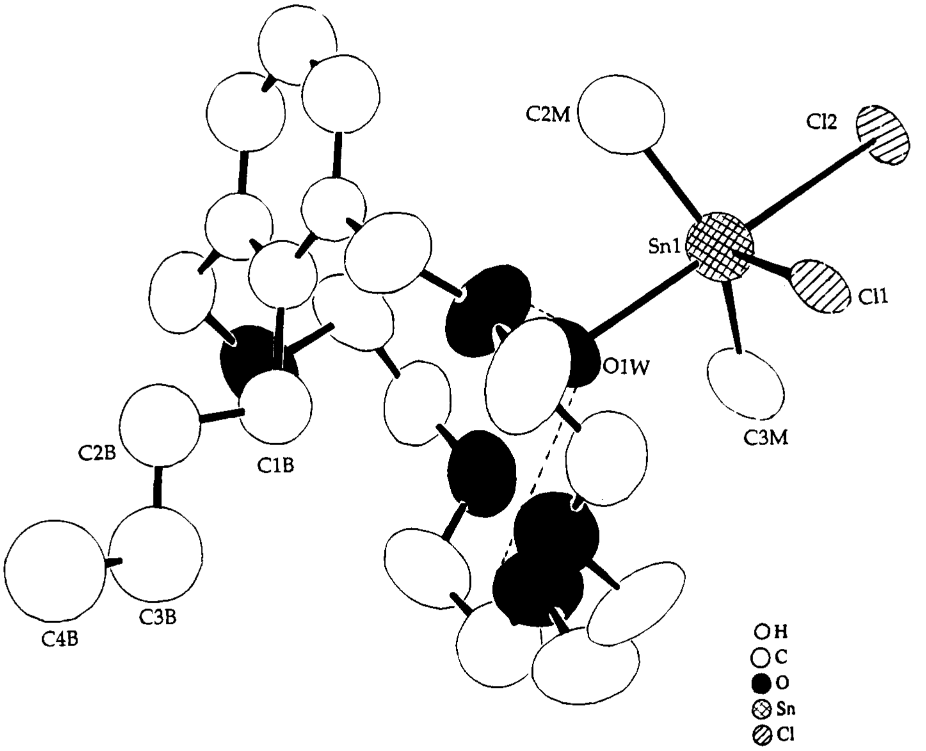

Figure 2. ORTEP representation of **7** showing the numbering scheme. All hydrogen atoms were removed for clarity. Ellipsoids were drawn at the 0.5 probability level.

Table 7. Positional and Equivalent Isotropic Thermal Parameters for 7[a]

atom	*x*	*y*	*z*	$\langle U^2 \rangle$, Å^2
Sn(1)	1.1241(2)	0.3405(2)	0.0288(1)	0.064(1)
Cl(1)	1.2655(5)	0.1570(5)	−0.0534(3)	0.066(4)
Cl(2)	1.0815(5)	0.4086(5)	−0.1056(3)	0.058(4)
O(1W)	1.1626(16)	0.2821(15)	0.1573(9)	0.091(12)
C(2M)	1.2751(23)	0.5105(22)	0.0514(16)	0.080(17)
C(3M)	0.9251(23)	0.2359(23)	0.0656(14)	0.084(18)
C(1C)	1.5328(25)	0.3577(25)	0.2155(17)	0.066(17)
O(2C)	1.4429(17)	0.2576(18)	0.1681(12)	0.081(12)
C(3C)	1.4909(34)	0.1236(31)	0.1474(20)	0.117(26)
C(4C)	1.3810(35)	0.0160(31)	0.1229(19)	0.100(26)
O(5C)	1.2530(25)	0.0078(18)	0.1913(12)	0.126(17)
C(6C)	1.1256(34)	−0.0773(28)	0.1656(23)	0.099(25)
C(7C)	0.9974(36)	−0.0672(29)	0.2314(21)	0.122(28)
O(8C)	0.9749(21)	0.0778(18)	0.2513(13)	0.101(15)
C(9C)	0.8425(37)	0.0889(33)	0.3081(19)	0.134(30)
C(10C)	0.8299(33)	0.2401(31)	0.3446(17)	0.135(27)
O(11C)	0.8396(21)	0.3262(22)	0.2840(11)	0.143(17)
C(12C)	0.8286(32)	0.4656(29)	0.3166(17)	0.131(27)
C(13C)	0.9732(28)	0.5597(27)	0.3245(16)	0.105(23)
O(14C)	1.0128(19)	0.5272(18)	0.3984(10)	0.094(14)
C(15C)	1.1415(26)	0.6189(27)	0.4210(15)	0.084(19)
C(3P)	1.331(2)	0.730(1)	0.312(1)	0.10(1)
C(4P)	1.452(2)	0.729(1)	0.246(1)	0.09(1)
C(5P)	1.517(2)	0.607(1)	0.217(1)	0.09(1)
C(6P)	1.459(2)	0.485(1)	0.254(1)	0.06(1)
C(1P)	1.338(2)	0.486(1)	0.320(1)	0.07(1)
C(2P)	1.273(2)	0.609(1)	0.349(1)	0.07(1)
C(1B)	1.276(3)	0.346(2)	0.362(1)	0.08(1)
C(2B)	1.361(3)	0.356(3)	0.438(2)	0.10(1)
C(3B)	1.297(4)	0.218(4)	0.477(2)	0.14(1)
C(4B)	1.403(5)	0.212(5)	0.539(3)	0.16(2)
C(5B)	1.340(10)	0.122(9)	0.443(6)	0.09(3)

[a] Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter.

Table 8. Selected Interatomic Distances and Angles for 7

	Distances (Å)		
Sn(1)−Cl(1)	2.446(5)	Sn(1)−Cl(2)	2.546(5)
Sn(1)−C(2M)	2.05(2)	Sn(1)−C(3M)	2.02(2)
Sn(1)−O(1W)	2.397(14)	O(8C)−O(1W)	2.85(2)
O(1W)−O(2C)	2.80(2)		
	Angles (deg)		
Cl(1)−Sn(1)−Cl(2)	91.6(2)	C(2M)−Sn(1)−C(3M)	148.3(9)
Cl(1)−Sn(1)−C(2M)	104.5(6)	Cl(1)−Sn(1)−O(1W)	89.8(4)
Cl(2)−Sn(1)−O(1W)	178.5(4)	Cl(1)−Sn(1)−C(3M)	104.0(6)
Cl(2)−Sn(1)−C(3M)	96.7(6)	Cl(2)−Sn(1)−C(2M)	96.1(6)
O(1W)−Sn(1)−C(3M)	83.4(7)	O(1W)−Sn(1)−C(2M)	83.1(7)
O(2C)−O(1W)−O(8C)	106.3(7)		

are within 0.004 Å from the average value of 2.404(10) Å. The corresponding Sn−O bond lengths are within 0.078 Å from the average length of 2.205(6) Å for adducts **6**, **10**−**12**. The Sn−C bond distances are within 0.03 Å from the average value of 2.08(1) Å for adducts **5** and **7** while the corresponding Sn−C bond lengths for adducts **6** and **10** are within 0.038 Å from the average length of 2.134(7) Å. The O−Sn−Cl bond angles are essentially linear for adducts **5** and **7**, deviating only 0.8° from the average value of 177.7(3)°. The corresponding O−Sn−Cl bond angles for adducts **6**, **10** and **12** are within 2.9° from the average value of 172.1(2)°. The structural parameters for the trigonal bipyramidal organotin adducts **5** and **7** are essentially the same, however, they differ in the number of hydrogen bonding-interactions the aquated organotins form with the coronand. While both compounds are discrete molecular adducts, the effect of functionalizing the intraannular position with an *n*-butyl substituent appears to limit the number of hydrogen-bonding interactions possible with the organotin in the latter case. As a consequence, the *n*-butyl group appears to prevent formation of a 1:2 adduct, as observed for **5**.

The compounds **5** and **7** represent the *only* examples to date of discrete organotin adducts of xylyl crown ethers. By contrast, the adduct **10** differs from **5** only in the macrocyclic polyether (18-crown-6 vs. 1,3-xylyl-18-crown-5), yet the former exhibits hexacoordinated organotins and a polymeric structure, with the organ-

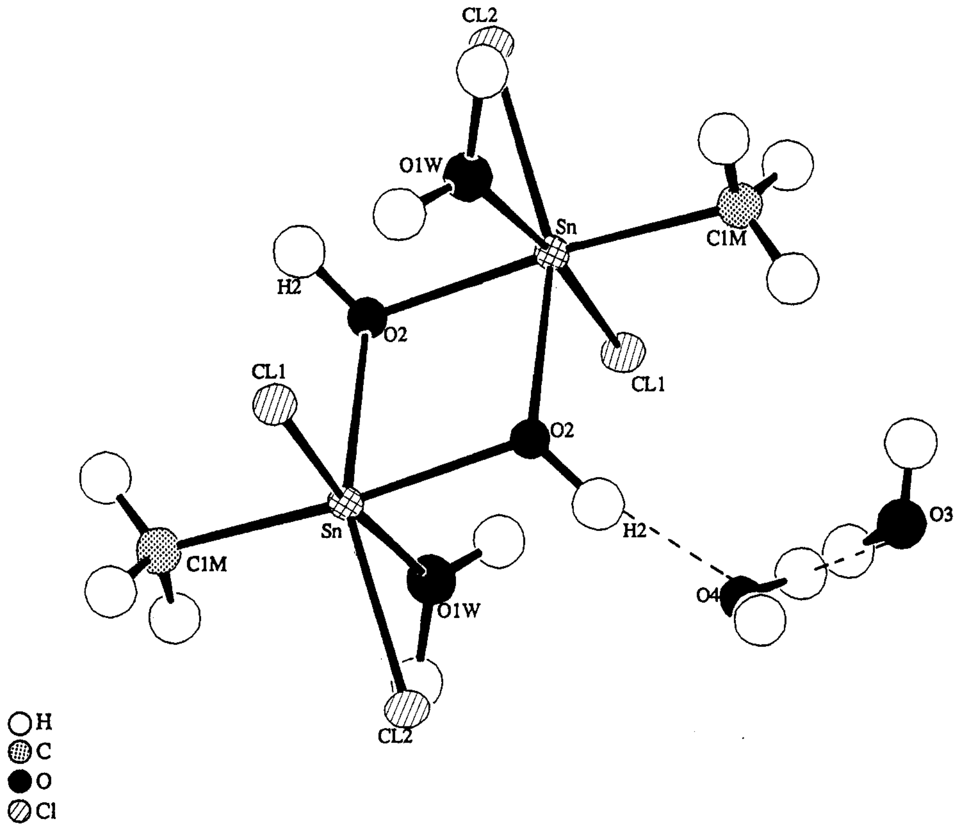

Figure 3. ORTEP representation of **9** showing the numbering scheme. All hydrogen atoms were removed for clarity. Ellipsoids were drawn at the 0.2 probability level.

Table 9. Positional and Equivalent Isotropic Thermal Parameters for 9[a]

atom	*x*	*y*	*z*	$\langle U^2 \rangle$, Å^2
Sn	0.28951(2)	0.19058(3)	0.41250(1)	0.0142(2)
Cl(1)	0.10786(6)	0.11803(12)	0.35466(5)	0.0163(4)
Cl(2)	0.35230(6)	−0.12779(12)	0.38174(5)	0.0231(4)
O(1W)	0.44592(18)	0.24890(43)	0.47809(14)	0.0169(12)
O(2)	0.26004(16)	0.08078(31)	0.51922(12)	0.0200(11)
O(3)	0.50000	−0.00491(50)	0.75000	0.0297(19)
O(4)	0.39783(18)	−0.16474(34)	0.60558(14)	0.0197(12)
C(1M)	0.32794(28)	0.35104(53)	0.31510(21)	0.0277(18)
H(1M1)	0.2925	0.2899	0.2650	0.060[b]
H(1M2)	0.4049	0.3453	0.3161	0.030[b]
H(1M3)	0.3055	0.4877	0.3169	0.030[b]
H(1W1)	0.4678(36)	0.2712(79)	0.5363(7)	0.030[b]
H(1W2)	0.5129(22)	0.2017(69)	0.4632(32)	0.030[b]
H(2)	0.3086(28)	−0.0123(56)	0.5500(25)	0.030[b]
H(3)	0.4612(34)	0.1020(44)	0.7711(30)	0.030[b]
H(4A)	0.3700(39)	−0.2963(31)	0.6114(32)	0.030[b]
H(4B)	0.4271(35)	−0.1032(74)	0.6572(17)	0.030[b]

[a] Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. [b] Denotes an atom refined isotropically.

otins linked to the crown ethers through an extensive hydrogen-bonded network. Adducts **6**, **11** and **12**, in fact, exhibit polymeric structures, with the organotins associated with their respective macrocyclic polyethers through H-bonded networks. The total number of H-bonds varies, depending on the amount of water molecules associated with the organotin moieties as ligands and as solvent of crystallization (if any). The macrocyclic polyethers and coronands of all structurally characterized adducts adopt the normal all-*gauche* conformations. Adducts **6** and **12** are unique in that, although the aqua ligands on the hexacoordinate tin centers are *cis* to each other, they still support a hydrogen-bonded polymeric structure by involving noncoordinated water molecules bound to each face of their respective macrocyclic polyether ligands.

Table 10. Selected Interatomic Distances and Angles for 9

	Distances (Å)		
Sn−Cl(1)	2.474(1)	H(1W2)−O(4)	1.78(4)
Sn−O(2)	2.051(2)	O(4)−H(4B)	1.00(3)
O(2)−O(4)	2.743(3)	Sn−O(1W)	2.208(2)
O(1W)−O(4)	2.708(3)	Sn−O(2)	2.127(2)
O(3)−O(4)	2.835(3)	H(2)−O(4)	1.75(4)
Sn−Cl(2)	2.452(1)	O(1W)−H(1W2)	1.00(3)
Sn−C(1M)	2.115(4)	H(4B)−O(3)	1.84(4)
O(2)−H(2)	1.00(4)		
	Angles (deg)		
Cl(1)−Sn−Cl(2)	93.4(0)	Cl(1)−Sn−O(1W)	173.2(1)
Cl(1)−Sn−O(2)	88.9(1)	Cl(1)−Sn−C(1M)	97.0(1)
Cl(1)−Sn−O(2)	91.2(1)	Cl(2)−Sn−O(1W)	87.9(1)
Cl(2)−Sn−O(2)	87.7(1)	Cl(2)−Sn−C(1M)	101.0(1)
Cl(2)−Sn−O(2)	159.1(1)	O(1W)−Sn−O(2)	84.5(1)
O(1W)−Sn−C(1M)	89.3(1)	O(1W)−Sn−O(2)	85.3(1)
O(2)−Sn−C(1M)	169.2(1)	O(2)−Sn−O(2)	72.0(1)
C(1M)−Sn−O(2)	98.7(1)	O(2)−H(2)−O(4)	177(4)
O(1W)−H(1W2)−O(4)	153(4)	O(4)−H(4B)−O(3)	171(4)

Conclusions

The structural analyses of **6** and **7** confirm the conclusions drawn from the spectroscopic data, namely, that complexation of organotin compounds occurs with 1,3-xylyl-crown ethers upon addition of water in preference to products of hydrolysis, with the molecules of hydration serving as ligands to form hypervalent tin derivatives. Although it can be argued that the second-sphere coordination interaction is indirect and mediated by the molecules of hydration, to our knowledge, the formation of discrete molecular adducts **4**, **5** and **7** represents a new feature in structural organotin chem-

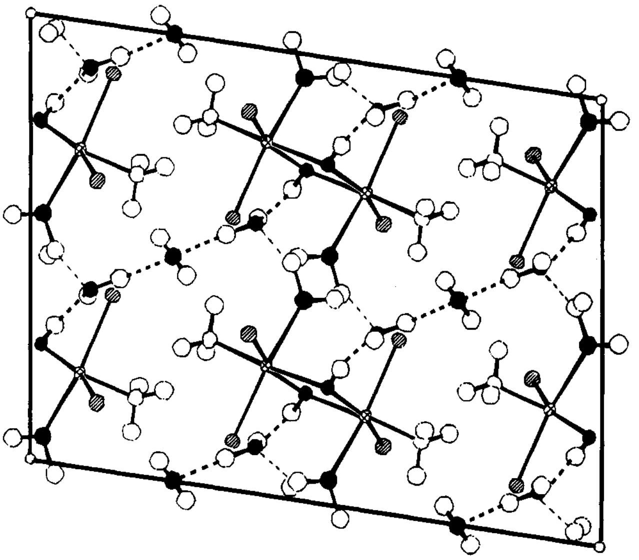

Figure 4. Unit cell of **9** along the *b* direction, indicating hydrogen-bonding network.

istry and the general phenomenon of second-sphere coordination in molecular receptor design. This is in contrast to structural data for **6** and **10**–**12**, where octahedral geometry for tin and coordination polymers are observed. Moreover, the intrinsic duality of hydrogen-bonding interactions is highlighted: stabilization of the Lewis-acid coronand interaction, while imparting changes in the geometry of the hypervalent state for tin. Determination of thermodynamic parameters for these and analogous derivatives (*i.e.* equilibrium constants) by ^{119}Sn NMR spectroscopic and calorimetric methods are under active investigation. It is conceivable that such interactions play an important role in the biological activity of organotin compounds or the design of new types of molecular receptors for organotin compounds.[28] The results suggest that novel macrocyclic polyether or coronand hosts could be developed incorporating a Lewis acidic site along with a crown ether moiety. One could envision that these novel inorganic hosts would exhibit interesting cooperative binding of both cations and anions. Research efforts in this direction are currently in progress.

Experimental Section

General Considerations. Standard glove box, Schlenk and vacuum line techniques were employed for all manipulation of air and moisture-sensitive compounds. Reaction solvents were reagent grade and were distilled from appropriate drying agents under argon before use. Methylene chloride and hexane were dried over CaH_2. Deuterated solvents were obtained from Cambridge Isotope Laboratories or Aldrich. The compound 1,3-xylyl-18-crown-5 was generously donated by Prof. D. J. Cram. Trimethyltin chloride (**1**), dimethyltin dichloride (**2**), methyltin trichloride (**3**) were purchased from Aldrich and were used as received. The compound 2-bromo-1,3-xylyl-18-crown-5 was prepared by literature methods.[14]

Physical Measurements. NMR spectra were obtained on Bruker AF 200, AM 360 and 500 MHz spectrometers. ^{1}H and ^{13}C chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced to deuterated solvents as internal standards. Chemical shift values for ^{119}Sn spectra were referenced relative to external Me_4Sn (0.00 ppm). Resonances observed upfield of the references were assigned negative chemical shift values in all cases. Infrared spectra were obtained as Nujol mulls or KBr pellets and were recorded on a Perkin-Elmer FT-IR instrument. Xenon FAB mass spectra were obtained on an AEI Ltd. Model MS-9 spectrometer. Elemental analyses were performed at the Gailbraith microanalysis laboratories.

Preparation of Adduct 4. Two equivalents of **1** (1.03 g, 5.17 mmol) and water (0.09 g, 5.17 mmol) were combined with one equivalent of 1,3-xylyl-18-crown-5 (0.77 g; 2.58 mmol) in CH_2Cl_2 (30 mL) at ambient temperature with stirring. The mixture was allowed to stir overnight. After stirring for 24 h, the solvent was removed *in vacuo* to afford a colorless crystalline material. Recrystallization from a mixture of CH_2Cl_2 and hexane afforded 1.70 g of **4** in 90% yield: mp 53–56 °C. This compound is somewhat hygroscopic and should be stored in moisture-free environment. The same product is obtained when using an excess of water. ^{1}H NMR ($CDCl_3$): 0.663 (s, 18 H, Me_3Sn-, $^2J_{^1H^{119}Sn} = 61$ Hz), 3.71 (s, 16 H, $-OCH_2CH_2O-$), 4.59 (s, 4 H, $ArCH_2O-$), 5.21 (br s, 4 H, H_2O), 7.12–7.73 (m, 4 H, ArH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 0.49 (s, Me_3Sn-, $^1J_{^{13}C^{119}Sn} = 414$ Hz), 69.0 (s, $-OCH_2CH_2O-$), 70.0 (s, $-OCH_2CH_2O-$), 72.5 (s, $ArCH_2O-$), 127.2 (s, Ar C), 127.7 (s, *p*-Ar C), 138.2 (s, *o*-Ar C). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): 120.0. **Anal.** Calcd for $C_{22}H_{46}O_7Sn_2Cl_2$: C, 36.15; H, 6.36. Found: C, 35.77; H, 6.01. FAB MS: *m/e* 297 $(C_{16}H_{24}O_5)^+$, *m/e* 217 $(C_3H_{11}OClSn)^+$, *m/e* 164 $(C_3H_9Sn)^+$.

Preparation of Adduct 5. Two equivalents of **2** (0.99 g, 4.52 mmol) and water (0.08 g, 4.52 mmol) were combined with one equivalent of 1,3-xylyl-18-crown-5 (0.67 g; 2.26 mmol) in CH_2Cl_2 (30 mL) at ambient temperature with stirring. The mixture was allowed to stir overnight. After stirring for 24 h, the solvent was removed *in vacuo* to afford a colorless crystalline material. Recrystallization from a mixture of CH_2Cl_2 and hexane afforded 1.20 g of **5** in 96% yield: mp 87–90 °C. This compound is somewhat hygroscopic and should be stored in moisture-free environment. The same product is obtained when using an excess of water. ^{1}H NMR ($CDCl_3$): 1.14 (s, 12 H, Me_2Sn-, $^2J_{^1H^{119}Sn} = 72$ Hz), 2.36 (br s, 4 H, H_2O), 3.68 (m, 16 H, $-OCH_2CH_2O-$), 4.60 (s, 4 H, $ArCH_2O-$), 7.11–7.74 (m, 4 H, ArH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 8.27 (s, Me_2Sn-, $^1J_{^{13}C^{119}Sn} = 539$ Hz), 69.4 (s, $-OCH_2CH_2O-$), 70.3 (s, $-OCH_2CH_2O-$), 72.9 (s, $ArCH_2O-$), 126.7 (s, Ar C), 127.9 (s, *p*-Ar C), 138.4 (s, *o*-Ar C). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): 82.5. **Anal.** Calcd for $C_{20}H_{40}O_7Sn_2Cl_4$: C, 31.12; H, 5.23. Found: C, 30.88; H, 5.07. FAB MS: *m/e* 297 $(C_{16}H_{24}O_5)^+$, *m/e* 238 $(C_2H_8OCl_2Sn)^+$.

Preparation of Adduct 6. One equivalent of **3** (0.50 g, 2.08 mmol) and water (0.15 g, 8.32 mmol) were combined with one equivalent of 1,3-xylyl-18-crown-5 (0.62 g; 2.08 mmol) in CH_2Cl_2 (30 mL) at ambient temperature with stirring. The mixture was allowed to stir overnight. After stirring for 24 h, the solvent was removed *in vacuo* to afford a colorless crystalline material. Recrystallization from a mixture of CH_2Cl_2 and hexane afforded 1.08 g of **6** in 91% yield: mp 89–91 °C. This compound is somewhat hygroscopic and should be stored in moisture-free environment. The same product is obtained when using an excess of water. ^{1}H NMR ($CDCl_3$): 1.39 (s, 6 H, $MeSn-$, $^2J_{^1H^{119}Sn} = 109$ Hz), 3.70 (s, 32 H, $-OCH_2CH_2O-$), 4.58 (s, 8 H, $ArCH_2O-$), 5.28 (br s, 10 H, H_2O), 7.12–7.71 (m, 8 H, ArH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 15.7 (s, $MeSn-$, $^1J_{^{13}C^{119}Sn} = 891$ Hz), 69.1 (s, $-OCH_2CH_2O-$), 69.4 (s, $-OCH_2CH_2O-$), 69.9 (s, $-OCH_2CH_2O-$), 73.0 (s, $ArCH_2O-$), 127.6 (s, Ar C), 128.2 (s, *p*-Ar C), 137.7 (s, *o*-Ar C). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): -169.2. **Anal.** Calcd for $C_{17}H_{30}O_7SnCl_3$: C, 35.72; H, 5.30. Found: C, 39.98; H, 6.27. FAB MS: *m/e* 296 $(C_{16}H_{24}O_5)^+$, *m/e* 276 $(CH_7OCl_3Sn)^+$.

Preparation of Adduct 7. One equivalent of a 2.5 M solution of *n*-BuLi (1.17 mL; 2.93 mmol) was added at −10 °C to a stirred solution of 2-bromo-1,3-xylyl-18−crown-5[14] (1.10 g; 2.93 mmol) in THF (50 mL). The solution was warmed to 0 °C and 2.2 equivalents of **2** (1.41 g, 6.45 mmol) and water (0.12 g, 6.45 mmol) were combined at ambient temperature with stirring. The mixture was allowed to stir overnight.

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(28) Selwyn, M. L. In *The Chemistry of Tin*; Harrison, P. G., Ed.; Blackie: London, 1989.

Table 11. Structural Parameters for Organotin–Coronand Compounds

compound	Sn–Cl, Å	Sn–O, Å	Sn–C, Å	∠O–Sn–Cl, deg	H-bonds	structure
$2Me_2SnCl_2(H_2O)\cdot$1,3-xylyl-18-crown-5 (**5**)[a]	2.583(2) 2.535(2) 2.472(2) 2.459(2)	2.409(9) 2.405(9)	2.139(14) 2.110(13) 2.094(13) 2.096(14)	176.9(2)	5	discrete adduct Sn, CN = 5
$MeSnCl_3(H_2O)_2\cdot$1,3-xylyl-18-crown-5 (**6**)[b]	2.405(3) 2.375(4) 2.409(4) 2.357(4) 2.434(4) 2.423(4)	2.235(8) 2.230(8) 2.265(9) 2.189(9)	2.209(9) 2.121(14)	174.2(2) 167.1(3) 166.7(2) 175.9(3)	10	network polymer Sn, CN = 6
$Me_2SnCl_2(H_2O)\cdot$2-*n*-butyl-1,3-xylyl-18-crown-5 (**7**)[b]	2.446(5) 2.546(5)	2.397(14)	2.05(2) 2.02(2)	178.5(4)	2	discrete adduct Sn, CN = 5
$Me_2SnCl_2(H_2O)_2\cdot$18-crown-6 (**10**)[c]	2.393(1) 2.536(1) 2.524(1) 2.419(1) 3.050(1) 3.311(1)	2.360(3) 2.313(3)	2.104(3) 2.112(3)	172.5(1)	7	network polymer Sn, CN = 6
$SnCl_4(H_2O)_2\cdot$15-crown-5 (**11**)[d]	2.364(2) 2.379(1) 2.386(2) 2.391(2)	2.107(4) 2.125(4)		179.0(2)[f]	4	network polymer Sn, CN = 6
$SnCl_4(H_2O)_2\cdot$18-crown-6 (**12**)[e]	2.400(3) 2.392(3) 2.393(3) 2.391(3)	2.113(6) 2.115(6)		175.9(2) 172.2(2)	8	network polymer Sn, CN = 6

[a] Reference 8. [b] This work. [c] Reference 4b. [d] Reference 3d. [e] References 3a,b. [f] ∠O–Sn–O, deg.

After stirring for 24 h, the solvent was removed *in vacuo* to afford a colorless crystalline material. Recrystallization from a mixture of CH_2Cl_2 and hexane afforded 1.31 g of **7** in 78% yield: mp 81–84 °C. The same product is obtained when using an excess of water. ^1H NMR ($CDCl_3$): 0.96 (m, 3 H, CH_3–), 1.09 (s, 6 H, Me_2Sn–, $^2J_{^1H^{119}Sn}$ = 74 Hz), 1.25 (m, 4 H, –CH_2-CH_2–), 1.47 (m, 2 H, $ArCH_2$–), 2.65 (br s, 2 H, H_2O), 3.67 (m, 16 H, –OCH_2CH_2O–), 4.60 (m, 4 H, $ArCH_2O$–), 7.07–7.70 (m, 3 H, ArH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 8.89 (s, Me_2Sn–, $^1J_{^{13}C^{119}Sn}$ = 539 Hz), 11.3 (s, CH_3–), 29.1 (s, –CH_2–), 54.3 (s, $ArCH_2$–), 67.4 (s, –OCH_2CH_2O–), 70.0 (s, –OCH_2CH_2O–), 70.5 (s, –OCH_2CH_2O–), 71.0 (s, –OCH_2CH_2O–), 71.3 (s, –OCH_2CH_2O–), 71.7 (s, –OCH_2CH_2O–), 72.0 (s, –OCH_2-CH_2O–), 73.9 (s, $ArCH_2O$–), 75.0 (s, $ArCH_2O$–), 127.9 (s, *p*-Ar C), 128.4 (s, *m*-Ar C), 128.9 (s, *m*-Ar C), 145.0 (s, *o*-Ar C), 145.4 (s, *i*-Ar C). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): 49.2. **Anal.** Calcd for $C_{22}H_{40}O_6SnCl_2$: C, 44.77; H, 6.84. Found: C, 45.98; H, 6.97. FAB MS: *m/e* 353 $(C_{20}H_{32}O_5)^+$, *m/e* 238 $(C_2H_8OCl_2Sn)^+$.

Preparation of Adduct 8. One equivalent of a 2.5 M solution of *n*-BuLi (1.07 mL; 2.66 mmol) was added at –10 °C to a stirred solution of 2-bromo-1,3-xylyl-18–crown-5[14] (1.00 g; 2.66 mmol) in THF (50 mL). The solution was warmed to 0 °C and 2.2 equivalents of **3** (1.41 g, 5.86 mmol) and water (0.11 g, 5.86 mmol) were combined at ambient temperature with stirring. The mixture was allowed to stir overnight. After stirring for 24 h, the solvent was removed *in vacuo* to afford a colorless crystalline material. Recrystallization from a mixture of CH_2Cl_2 and hexane afforded 1.26 g of **8** in 75% yield: mp 84–88 °C. The same product is obtained when using an excess of water. ^1H NMR ($CDCl_3$): 0.88 (m, 3 H, CH_3–), 1.29 (m, 4 H, –CH_2CH_2–), 1.66 (s, 3 H, MeSn-, $^2J_{^1H^{119}Sn}$ = 113 Hz), 1.76 (m, 2 H, $ArCH_2$–), 2.84 (br s, 4 H, H_2O), 3.60 (m, 16 H, –OCH_2CH_2O–), 4.51 (m, 4 H, $ArCH_2O$–), 7.08–7.53 (m, 3 H, ArH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 14.0 (s, MeSn–, $^1J_{^{13}C^{119}Sn}$ = 876 Hz), 11.1 (s, CH_3–), 27.4 (s, –CH_2–), 33.7 (s, –CH_2–), 55.0 (s, $ArCH_2$–), 68.3 (s, –OCH_2CH_2O–), 68.4 (s, –OCH_2-CH_2O–), 68.6 (s, –OCH_2CH_2O–), 68.0 (s, -OCH_2CH_2O–), 68.7 (s, –OCH_2CH_2O–), 69.6 (s, –OCH_2CH_2O–), 69.8 (s, –OCH_2-CH_2O–), 72.5 (s, $ArCH_2O$–), 72.9 (s, $ArCH_2O$–), 125.6 (s, *p*-Ar C), 126.0 (s, *m*-Ar C), 127.0 (s, *m*-Ar C), 135.9 (s, *o*-Ar C), 138.4 (s, *o*-Ar C), 143.6 (s, *i*-Ar C). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): –171.4. **Anal.** Calcd for $C_{21}H_{39}O_7SnCl_3$: C, 40.12; H, 6.27. Found: C, 39.98; H, 5.99. FAB MS: *m/e* 353 $(C_{20}H_{32}O_5)^+$, *m/e* 276 $(CH_7O_2Cl_3Sn)^+$.

Isolation of Hydrolysis Product 9. Four equivalents of **3** (2.00 g, 8.33 mmol) and an excess of water (0.30 g, 16.6 mmol) were combined with one equivalent of 1,3-xylyl-18-crown-5 (0.62 g; 2.08 mmol) in CH_2Cl_2 (30 mL) at ambient temperature with stirring. The mixture was allowed to stir overnight. After stirring for 24 h, a white precipitate had formed, which was filtered off. Recrystallization from methanol and water afforded **9** in 48% yield (based on **3**): mp 189–192 °C. The solvent was removed *in vacuo* to afford a colorless crystalline material. Recrystallization from a mixture of CH_2Cl_2 and hexane afforded 0.95 g of **6** in 80 % yield (based on the coronand): mp 87–91 °C. This compound is somewhat hygroscopic and should be stored in moisture-free environment. ^1H NMR ($CDCl_3$): 1.32 (s, 6 H, MeSn–, $^2J_{^1H^{119}Sn}$ = 111 Hz), 2.44 (br s, 2 H, SnOH), 3.90 (br s, 6 H, H_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 15.0 (s, MeSn–, $^1J_{^{13}C^{119}Sn}$ = 902 Hz). ^{119}Sn-$\{^1H\}$ NMR ($CDCl_3$): –175.9. **Anal.** Calcd for $C_2H_{12}O_4$-Sn_2Cl_4: C, 2.88; H, 1.45. Found: C, 2.65; H, 1.51.

Collection and Reduction of X-ray Data for 6. A colorless parallelepiped, obtained from a methylene chloride/hexane solution, was cut and mounted on a fiber and placed on a Huber diffractometer constructed by Professor C. E. Strouse of this department. Unit cell parameters were determined from a least-squares fit of 24 accurately centered reflections ($9.6 < 2\theta < 20.2°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table 12. Data were collected at –117 °C in the θ-2θ scan mode. Three intense reflections (3 3 –2, 1 –6 2, 1 6 2) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay during the course of the experiment (35.6 h). Of the 6364 unique reflections measured, 4425 were considered observed ($F^2 > 3\,\sigma(F^2)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects but not for absorption or for secondary extinction. Programs used in this work include locally modified versions of crystallographic programs listed in ref 29.

Solution and Refinement of the Structure of 6. Atoms were located by use of heavy atom methods. All calculations were performed on a VAX 3100 computer. Sn, Cl, O (water), C (methyl) atoms were refined with anisotropic parameters. All other non-hydrogen atoms were refined with isotropic parameters. With the exception of hydrogen atoms on O (water), all hydrogen atoms were included in calculated

Table 12. Details of the Crystallographic Data Collection for 6, 7, and 9

	6	**7**	**9**
T, °C	−117	25	−117
cryst size, mm	0.22 × 0.14 × 0.27	0.04 × 0.15 × 0.32	0.12 × 0.12 × 0.38
normal to faces	100, 01T, 011	001, 010, 100	001, 100, 010
appearance	colorless parallelepiped	colorless plate	colorless needle (cut)
radiation (graphite monochromator)	Mo Kα	Mo Kα	Mo Kα
wavelength, Å	0.7107	0.7107	0.7107
space group	$P2_1/c$	$P\bar{1}$	$C2/c$
a, Å	9.636(1)	9.616(1)	13.009(1)
b, Å	33.755(5)	9.737(2)	6.9883(6)
c, Å	15.004(2)	16.369(2)	16.937(2)
α, deg		100.117(5)	
β, deg	95.206(5)	76.360(5)	98.480(2)
γ, deg		99.927(5)	
V, Å^3	4860	1453	1523
Z	4	2	4
ϱ(calcd), g cm^{-3}	1.58	1.35	2.25
μ, cm^{-1}	14.2	10.96	40.0
scan width			
below Kα_1	1.3	1.3	1.3
above Kα_2	1.6	1.6	1.6
scan rate deg min^{-1}	12.0	4.5	9.0
no. of unique rflns	6364	3810	1338
no. of observed ($F^2 > 3\sigma(F^2)$) rflns	4425	2057	1211
2θ (max), deg	45	45	50
data collected	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of parameters refined	310	229	90
R, R_w, GOF[a]	0.054, 0.088, 2.75	0.081, 0.098, 2.67	0.018, 0.027, 1.17

[a] GOF = $[\Sigma w(|F_o| - |F_c|)^2/(N_O - N_V)]^{1/2}$, where $w = 1/(\sigma^2|F_o|)$. $R = \Sigma||F_o| - |F_c||/|F_c|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

positions as members of rigid groups, C−H = 1.0 Å, H−C−H = 109.5°. All water molecules are involved in hydrogen bonding interactions to oxygen atoms of the crown ether. H atoms were assigned u values based approximately on the U value of the attached atom. Scattering factors for H were obtained from Stewart, *et al.*,[30] and for other atoms were taken from ref 31. Anomalous dispersion terms were applied to the scattering of Cl and Sn. The maximum and minimum peaks on a final difference electron density map were 0.6 e Å^{-3}, located in the region of the crown ether. Final positional and thermal parameters for non-hydrogen atoms are given in Table 5.

Collection and Reduction of X-ray Data for 7. A colorless crystal, obtained from a hexane solution, was sealed in a capillary and placed on a Huber diffractometer constructed by Professor C. E. Strouse of this department. Unit cell parameters were determined from a least-squares fit of 32 accurately centered reflections (9.3 < 2θ < 20.3°). These dimensions and other parameters, including conditions of data collection, are summarized in Table 12. Data were collected at 25 °C in the θ-2θ scan mode. Three intense reflections (0 1 3, 1 −2 6, 2 1 1) were monitored every 97 reflections to check stability. Intensities of these reflections decayed 3% during the course of the experiment (48.7 h). Of the 3810 unique reflections measured, 2057 were considered observed ($F^2 > 2\ \sigma\ (F^2)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for secondary extinction and absorption. Other conditions for collection and reduction were the same as those that were applied to **6**.

Solution and Refinement of the Structure of 7. Atoms were located by use of heavy atom methods (SHELX86 and SHELX76). All calculations were performed on a VAX 3100 computer. The methyl carbon of the n-butyl group is disordered and has been represented by 2 atoms of occupancy 0.7 and 0.3 (C 4B and C 5B), respectively. With the exception of the n-butyl group and the benzene ring carbon atoms, all non-hydrogen atoms were refined with isotropic parameters. No hydrogen atoms were included for the butyl group. Only one hydrogen atom was located for the water ligand. All other hydrogen atoms were included in calculated positions as members of rigid groups, C−H = 1.0 Å, H−C−H = 109.5° (methyl and methylene). H atoms were assigned U values based approximately on the U value of the attached atom. Scattering factors for H were obtained from Stewart, *et al.*,[30] and for other atoms were taken from ref 31. Anomalous dispersion terms were applied to the scattering of Cl and Sn. The largest peak on a final difference electron density map were 0.7 eÅ^{-3}, located near Sn. Final positional and thermal parameters for non hydrogen atoms are given in Table 7.

Collection and Reduction of X-ray Data for 9. A colorless crystal, obtained from a methanol/water solution was sealed in a capillary and placed on a Picker FACS-1 diffractometer constructed by Professor C. E. Strouse of this department. Unit cell parameters were determined from a least-squares fit of 51 accurately centered reflections (8.5 < 2θ < 20.3°). These dimensions and other parameters, including conditions of data collection, are summarized in Table 12. Data were collected at −117 °C in the θ-2θ scan mode. Three intense reflections (2 0 −4, 2 0 2, 3 3 −2) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay during the course of the experiment (9.8 h). Of the 1338 unique reflections measured, 1211 were considered observed ($F^2 > 3\ \sigma\ (F^2)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for secondary extinction and absorption. Other conditions for collection and reduction were the same as those that were applied to **6**.

Solution and Refinement of the Structure of 9. Atoms were located by use of direct methods (SHELXS92). All calculations were performed on a VAX 3100 computer. Two $CH_3SnCl_2(H_2O)$ moieties are bridged by two hydroxyl groups in a centrosymmetric arrangement. Three molecules of water per dinuclear cluster are also present in the crystal. All non-hydrogen atoms were refined with anisotropic parameters. Methyl hydrogens were included in calculated positions as members of rigid groups, C−H = 1.0 Å, H−C−H = 109.5°. The six H atoms attached to O(water) were constrained to remain 1.0 Å from O. H atoms were assigned U values based approximately on the U value of the attached atom. Scattering factors for H were obtained from Stewart, *et al.*,[30] and for other atoms were taken from ref 31. Anomalous dispersion terms were applied to the scattering of Cl and Sn. The largest peak on a final difference electron density map were 0.2 eÅ^{-3}, located near Sn. Final positional and thermal parameters for non hydrogen atoms are given in Table 9.

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Supplementary Material Available: Tables of positional and thermal parameters and complete interatomic distances and angles and additional ORTEP views of **6**, **7**, and **9** (13 pages). Ordering information is given on any current masthead page.

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(29) CARESS (Broach, Coppens, Becker and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin and Levy), structure factor calculation and full-matrix least-squares refinement, ORTEP (Johnson) figure plotting, SHELX76 (Sheldrick) crystal structure package and SHELX86 (Sheldrick) crystal structure solution package.

(30) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(31) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV.