

α,ω -Bis(trichlorostanny)alkanes: Unravelling the Hydrolysis Pathway to Organotin-oxo Oligomers

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New α,ω -bis(trichlorostanny)alkanes, $\text{Cl}_3\text{Sn}(\text{CH}_2)_n\text{SnCl}_3$ [$n = 3-5, 8$], have been synthesized via tin–phenyl bond cleavage reactions on α,ω -bis(triphenylstanny)alkanes, $\text{Ph}_3\text{Sn}(\text{CH}_2)_n\text{SnPh}_3$ [$n = 3-5, 8$], using either SnCl_4 or concentrated hydrochloric acid. Some key missing links, $(\text{H}_2\text{O})\text{Cl}_3\text{Sn}(\text{CH}_2)_3\text{SnCl}_3(\text{H}_2\text{O})$ (**1a**) and $(\text{H}_2\text{O})_2\text{Cl}_3\text{Sn}(\text{CH}_2)_3\text{SnCl}_3(\text{H}_2\text{O})_2$ (**6**), in the hydrolysis pathway of organotin trichlorides were identified. Crystal structures of the nonassociated di-tin compounds $(\text{H}_2\text{O})\text{Cl}_3\text{Sn}(\text{CH}_2)_3\text{SnCl}_3(\text{H}_2\text{O})$ (**1a**) and $(\text{H}_2\text{O})_2\text{Cl}_3\text{Sn}(\text{CH}_2)_3\text{SnCl}_3(\text{H}_2\text{O})_2$ (**6**, isolated as the 18-crown-6 cocrystal acetonitrile solvate) as well as the polymeric hydrolysis product $[\text{H}_2\text{O}(\text{OH})\text{Cl}_2\text{Sn}(\text{CH}_2)_3\text{SnCl}_2(\text{OH})\text{H}_2\text{O} \cdot 2\text{H}_2\text{O}]_n$ (**7**· $2\text{H}_2\text{O}$) are reported.

Introduction

Oligomers based on organotin-oxo structures are of current interest because of their extensive potential as new materials^{1,2} and their use as mild Lewis acid catalysts^{3–5} for organic reactions. Control over the degree of oligomerization still represents some synthetic challenges. Oligomers have been most usually synthesized by hydrolysis reaction of diorganotin and monoorganotin precursors, R_2SnX_2 and RSnX_3 , respectively. For example, the partial hydrolysis of diorganotin dihalides usually affords dimeric tetraorganodistannoxanes $[\text{R}_2(\text{X})\text{SnOSn}(\text{X})\text{R}_2]_2$, which have the two-dimensional planar $\text{Sn}_4\text{X}_2\text{O}_2$ ladder structure^{6–10} **A** (Chart 1). More recently these organotin-oxo oligomers were accessed by reaction of appropriate precursors with an oxygen transfer source such as $(^t\text{Bu}_2\text{SnO})_3$.^{11–14}

The use of polymethylene bridged di-tin precursors, $\text{RX}_2\text{Sn}(\text{CH}_2)_n\text{SnX}_2\text{R}$, makes it possible to introduce a third dimension by linking two ladder units to give a double ladder type structure^{4,11} **B**. This theme has been repeated with the formation of triple¹⁵ and quadruple¹⁶ ladders from appropriate tri- and tetra-tin precursors.

On the other hand, the hydrolysis reactions of RSnX_3 precursors are more complicated and only relatively few oligomers have been characterized.^{17–22} The most interesting of these is $[(\text{RSn})_{12}\text{O}_{14}(\text{OH})_6]\text{X}_2$ ($\text{R} = ^i\text{Pr}, ^n\text{Bu}$; $\text{X} = \text{Cl}, \text{OH}$)^{22–25} because of their potential for further oligomerization to give new materials. The current trend is to attempt oligomerization/polymerization by use of anions, X , which have functionality, e.g., methacrylate.^{26–27} Our strategy to form new organotin-oxo clusters is to use linked di-tin precursors α,ω -bis-(trichlorostanny)alkanes, $\text{Cl}_3\text{Sn}(\text{CH}_2)_n\text{SnCl}_3$, in place of RSnCl_3 as starting materials for the synthesis of tin-12

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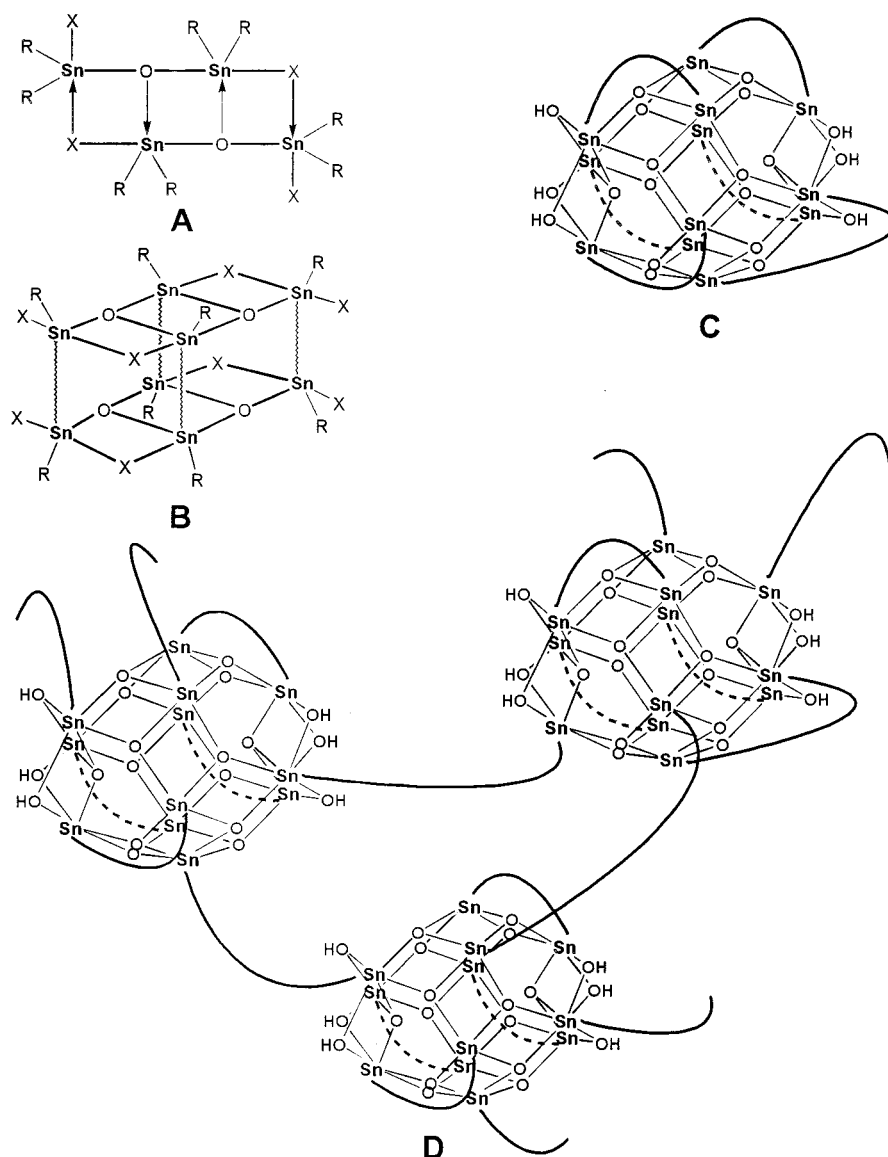
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Chart 1

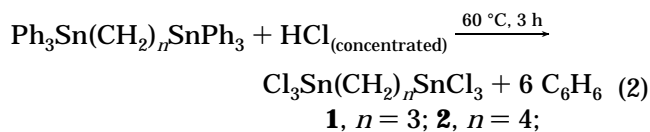
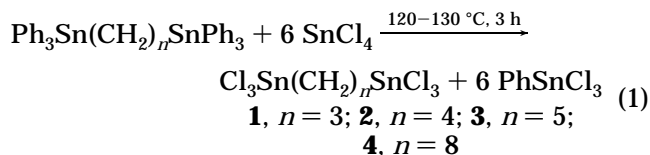


compounds. This strategy could lead to further linkage of tin-12 units, **D**, or afford tin-12 with organic "handles" **C**.

Thus far, $\text{Cl}_3\text{SnCH}_2\text{SnCl}_3$ is the only member of the series of α,ω -bis(trichlorostannyl)alkanes that has been reported.²⁸ It was synthesized via the reaction of $(\text{vinyl})_3\text{SnCH}_2\text{Sn}(\text{vinyl})_3$ with excess SnCl_4 . Since tin-phenyl bonds are even more readily cleaved than tin-vinyl bonds,^{29,30} we decided to use α,ω -bis(triphenylstannyl)alkanes $\text{Ph}_3\text{Sn}(\text{CH}_2)_n\text{SnPh}_3$ as precursors for the synthesis of α,ω -bis(trichlorostannyl)alkanes $\text{Cl}_3\text{Sn}(\text{CH}_2)_n\text{SnCl}_3$. We now report on the synthesis of various polymethylene-bridged di-tin hexahalides and crystal structures of the diaquo adduct $(\text{H}_2\text{O})\text{Cl}_3\text{Sn}(\text{CH}_2)_3\text{SnCl}_3 \cdot (\text{H}_2\text{O})$ (**1a**), the tetraaquo adduct $(\text{H}_2\text{O})_2\text{Cl}_3\text{Sn}(\text{CH}_2)_3\text{SnCl}_3 \cdot (\text{H}_2\text{O})_2$ (**6**), and the partially hydrolyzed polymeric material $[\text{H}_2\text{O}(\text{OH})\text{Cl}_2\text{Sn}(\text{CH}_2)_3\text{SnCl}_2(\text{OH})\text{H}_2\text{O} \cdot 2\text{H}_2\text{O}]_n$ (**7**·**2H**₂O).

Results and Discussion

Synthesis of the Polymethylene Spacer-Bridged Di-tin Compounds (1–5). The reaction of α,ω -bis(triphenylstannyl)alkane $\text{Ph}_3\text{Sn}(\text{CH}_2)_n\text{SnPh}_3$ ^{31,32} ($n = 3–5, 8$) with either SnCl_4 or concentrated hydrochloric acid afforded the related α,ω -bis(trichlorostannyl)alkanes $\text{Cl}_3\text{Sn}(\text{CH}_2)_n\text{SnCl}_3$ (**1–4**) in good to moderate yields (eqs 1 and 2). The reaction according to eq 1 was also used to prepare the known $\text{Cl}_3\text{SnCH}_2\text{SnCl}_3$ for purposes of comparison.



The basic concept of Sn–Ph cleavage with tin tetrahalogenides was successfully extended to the synthesis

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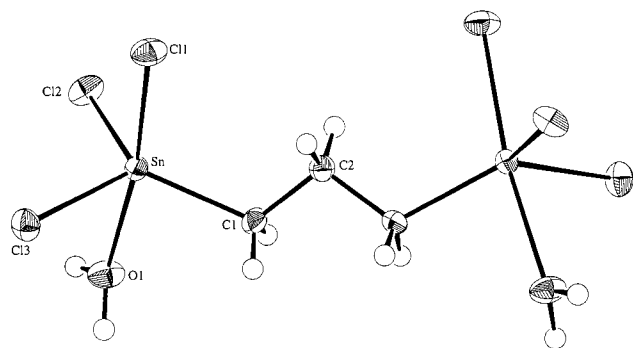
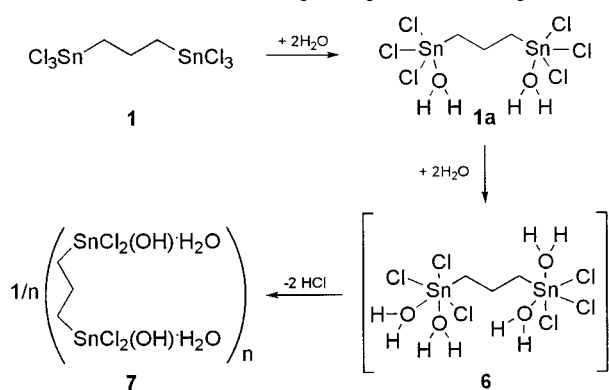


Figure 1. Molecular structure and atomic numbering scheme for $(\text{H}_2\text{O})\text{Cl}_3\text{Sn}(\text{CH}_2)_3\text{SnCl}_3(\text{H}_2\text{O})$ (**1a**).

Scheme 1. Possible Hydrolysis Pathway for 1



of $\text{Br}_3\text{Sn}(\text{CH}_2)_3\text{SnBr}_3$ **5** via the reaction of $\text{Ph}_3\text{Sn}(\text{CH}_2)_3\text{SnPh}_3$ with an excess of SnBr_4 .

Compounds **1** and **2** are solids, whereas **3** and **4** are highly viscous oils. The compounds are hygroscopic and require storage in a moisture-free environment. All bis(trichlorostannyl)alkanes are readily soluble in common organic solvents as well as in water.

Hydrolysis Reactions. It is noteworthy that compounds **1** and **2** crystallize as the diaquo adducts $\text{Cl}_3(\text{H}_2\text{O})\text{Sn}(\text{CH}_2)_n\text{Sn}(\text{H}_2\text{O})\text{Cl}_3$ (**1a**, $n = 3$; **2a**, $n = 4$) and appear to be the missing links in the early stages of the hydrolysis pathway of organotin trihalides as illustrated in Scheme 1. It is known that the neutral macrocycles, such as crown ethers, can stabilize organotin halides with respect to hydrolysis reactions.¹⁷ Reaction of **1** with 18-crown-6 in methanol and recrystallization from acetonitrile afforded the tetraaquo adduct **6** (as the 18-crown-6 cocrystal acetonitrile solvate). Compound **6** represents a stabilized example of the second hydrolysis step (Scheme 1). Slow evaporation of a solution of **1** in aqueous solution afforded $[\text{H}_2\text{O}(\text{OH})\text{Cl}_2\text{Sn}(\text{CH}_2)_3\text{SnCl}_2(\text{OH})\text{H}_2\text{O}]_n$, **7**, isolated as a dihydrate ($7 \cdot 2\text{H}_2\text{O}$). The solid-state structures of **1a**, **2a**,³³ **6**, and $7 \cdot 2\text{H}_2\text{O}$ have been determined by X-ray crystallography.

The molecular structure of **1a** is shown in Figure 1, and selected interatomic parameters are collected in Table 1. The molecule has crystallographic 2-fold symmetry and features trigonal bipyramidal tin centers with the Cl(1) and O(1) atoms defining the axial positions. The tin atom lies 0.2943(2) Å out of the CCl_2

Table 1. Selected Interatomic (Å, deg) Parameters for $(\text{H}_2\text{O})\text{Cl}_3\text{Sn}(\text{CH}_2)_3\text{SnCl}_3(\text{H}_2\text{O})$ (**1a**)^a

Sn–Cl(1)	2.405(2)	Sn–Cl(2)	2.321(1)
Sn–Cl(3)	2.337(1)	Sn–O(1)	2.353(2)
Sn–C(1)	2.122(3)	C(1)–C(2)	1.509(3)
Cl(1)–Sn–Cl(2)	93.30(5)	Cl(1)–Sn–Cl(3)	94.00(3)
Cl(1)–Sn–O(1)	172.20(5)	Cl(1)–Sn–C(1)	104.30(8)
Cl(2)–Sn–Cl(3)	109.62(4)	Cl(2)–Sn–O(1)	81.24(7)
Cl(2)–Sn–C(1)	122.46(8)	Cl(3)–Sn–O(1)	82.70(6)
Cl(3)–Sn–C(1)	122.82(8)	O(1)–Sn–C(1)	83.39(9)
Sn–C(1)–C(2)	116.4(2)	C(1)–C(2)–C(1) ⁱ	108.0(3)

^a Symmetry operation i : $-x, y, 0.5 - z$.

Table 2. Temperature Dependence of the ¹¹⁹Sn Chemical Shift and Coupling of **1a** and **5**

compound	solvent	temp	$\delta^{119}\text{Sn}$	$^4J(^{117}\text{Sn}-^{119}\text{Sn})$
1a	CDCl_3	20	−0.9	595
		−25	−4.0	735
		−50	−5.4	898
	toluene- <i>d</i> ₈	80	0.26	n.o.
		20	−0.54	886
		0	−1.28	1020
5	CDCl_3	−20	−2.21	1190
		−40	−3.53	1387
		25	−168.88	497
	CDCl_3	−25	−166.09	590
		−45	−164.59	719

plane in the direction of the Cl(1) atom. The axial Sn–Cl(1) distance is significantly longer than the remaining two Sn–Cl distances (Table 1), and of the equatorially bound chlorides, the Cl(3) atom forms the longer distance. While the difference between the axial and equatorial Sn–Cl bond distances is electronic in origin, an examination of the crystal structure is required to rationalize the disparity in the Sn–Cl(2) and Sn–Cl(3) bonds. In the lattice, the most significant intermolecular contact occurs between centrosymmetrically related pairs of O(1)–H(4) and Cl(3)ⁱ atoms so that H(4)⋯Cl(3)ⁱ is 2.51 Å, O(1)⋯Cl(3)ⁱ is 3.329(3) Å, and O(1)–H(4)⋯Cl(3)ⁱ is 162°; symmetry operation i : $0.5 - x, 0.5 - y, -z$. These associations lead to the formation of kinked chains. The Cl(2) atom does not participate in any significant intermolecular interactions, and hence, the slight elongation of the Sn–Cl(3) distance can be related to the presence of the H⋯Cl(3) contact. Translationally related molecules associate via O(1)–H(5)⋯Cl(1)ⁱⁱ interactions: H(5)⋯Cl(1)ⁱⁱ 2.58 Å, O(5)⋯Cl(1)ⁱⁱ 3.290(2) Å, and O(5)–H(5)⋯Cl(1)ⁱⁱ 136°; symmetry operation ii : $x, 1 + y, z$. These contacts serve to link the aforementioned chains into a two-dimensional array.

The ¹¹⁹Sn NMR shifts for analytically pure samples of **1a** and **2a** in CDCl_3 are δ 1.7 and 6.3, respectively, indicating four coordinated tin centers and that the coordinated water found in the crystal structure has dissociated in solution. The chemical shift for **1a** decreases and the $^4J(^{117}\text{Sn}-^{119}\text{Sn})$ coupling increases as the temperature is lowered (Table 2). The ¹¹⁹Sn NMR shift of **1a** in the solid state is at −42 ppm, but the spectral quality is unable to distinguish $^4J(^{117}\text{Sn}-^{119}\text{Sn})$ coupling. These observations are consistent with W-interactions in which the more favorable bonding component is favored as the temperature is decreased, the most favorable conformer occurring in the solid state. The ¹¹⁹Sn shift for **1a** is not significantly concentration dependent.

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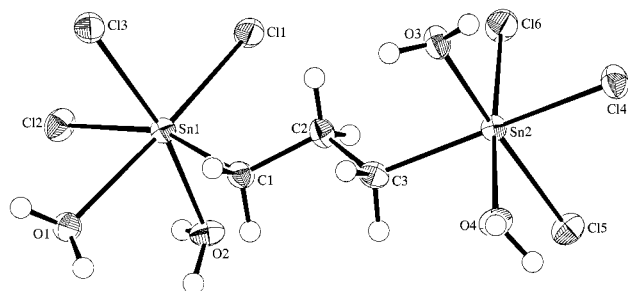


Figure 2. Molecular structure and atomic numbering scheme for $(\text{H}_2\text{O})_2\text{Cl}_3\text{Sn}(\text{CH}_2)_3\text{SnCl}_3(\text{H}_2\text{O})_2$ in $6\cdot 18\text{-crown-6}\cdot\text{CH}_3\text{CN}$.

Table 3. Selected Interatomic (\AA , deg) Parameters for $(\text{H}_2\text{O})_2\text{Cl}_3\text{Sn}(\text{CH}_2)_3\text{SnCl}_3(\text{H}_2\text{O})_2$ ($6\cdot 18\text{-crown-6}\cdot\text{CH}_3\text{CN}$)

Sn(1)–Cl(1)	2.404(1)	Sn(2)–Cl(4)	2.372(2)
Sn(1)–Cl(2)	2.370(1)	Sn(2)–Cl(5)	2.439(2)
Sn(1)–Cl(3)	2.448(2)	Sn(2)–Cl(6)	2.419(1)
Sn(1)–O(1)	2.405(3)	Sn(2)–O(3)	2.242(4)
Sn(1)–O(2)	2.231(4)	Sn(2)–O(4)	2.287(3)
Sn(1)–C(1)	2.137(5)	Sn(2)–C(3)	2.145(5)
C(1)–C(2)	1.522(8)	C(2)–C(3)	1.525(8)

Cl(1)–Sn(1)–Cl(2)	93.79(5)	Cl(4)–Sn(2)–Cl(5)	91.63(5)
Cl(1)–Sn(1)–Cl(3)	94.24(4)	Cl(4)–Sn(2)–Cl(6)	92.66(5)
Cl(1)–Sn(1)–O(1)	174.15(9)	Cl(4)–Sn(2)–O(3)	82.3(1)
Cl(1)–Sn(1)–O(2)	92.84(9)	Cl(4)–Sn(2)–O(4)	83.18(9)
Cl(1)–Sn(1)–C(1)	102.4(1)	Cl(4)–Sn(2)–C(3)	162.3(1)
Cl(2)–Sn(1)–Cl(3)	90.10(5)	Cl(5)–Sn(2)–Cl(6)	93.65(4)
Cl(2)–Sn(1)–O(1)	80.37(9)	Cl(5)–Sn(2)–O(3)	171.2(1)
Cl(2)–Sn(1)–O(2)	81.5(1)	Cl(5)–Sn(2)–O(4)	86.06(8)
Cl(2)–Sn(1)–C(1)	161.3(1)	Cl(5)–Sn(2)–C(3)	98.3(1)
Cl(3)–Sn(1)–O(1)	85.88(8)	Cl(6)–Sn(2)–O(3)	93.0(1)
Cl(3)–Sn(1)–O(2)	169.4(1)	Cl(6)–Sn(2)–O(4)	175.8(1)
Cl(3)–Sn(1)–C(1)	97.8(1)	Cl(6)–Sn(2)–C(3)	101.2(1)
O(1)–Sn(1)–O(2)	86.3(1)	O(3)–Sn(2)–O(4)	86.9(1)
O(1)–Sn(1)–C(1)	83.4(1)	O(3)–Sn(2)–C(3)	86.1(2)
O(2)–Sn(1)–C(1)	88.4(2)	O(4)–Sn(2)–C(3)	83.0(2)
Sn(1)–C(1)–C(2)	115.8(3)	Sn(2)–C(3)–C(2)	117.0(3)
C(1)–C(2)–C(3)	110.5(3)		

On the other hand for **5** both the coupling constant and the chemical shift increase with decreasing temperature (Table 2).

The compound $6\cdot 18\text{-crown-6}\cdot\text{CH}_3\text{CN}$ is not soluble in nondonor solvents such as CDCl_3 , and we were able to obtain the ^{119}Sn NMR shift only for this compound dissolved in CD_3CN (-274 ppm). In such a strong donor solvent, it is likely that all of the originally coordinated water molecules are displaced and that the tin atoms are both six-coordinate under these conditions. Unfortunately it was also not possible to obtain a ^{119}Sn NMR shift for $6\cdot 18\text{-crown-6}\cdot\text{CH}_3\text{CN}$ in the solid state. However, the ^{119}Sn NMR shift for $7\cdot(2\text{H}_2\text{O})$ in the solid state is at -472 ppm, consistent with the six-coordinate tin atoms observed in the crystal structure determination.

The molecular structure of the di-tin molecule in $6\cdot 18\text{-crown-6}\cdot\text{CH}_3\text{CN}$ is shown in Figure 2, and Table 3 collects some selected geometric parameters. The unit cell comprises four molecules of each of **6**, 18-crown-6, and CH_3CN , there being no molecular symmetry associated with any of the components (see Experimental Section). The tin atoms are coordinated by three chlorides, two water molecules, and the carbon atom of the propylene bridges. The geometry about each tin atom is distorted octahedral, the chlorides occupying facial positions. The Sn–Cl distances with chloride trans to a

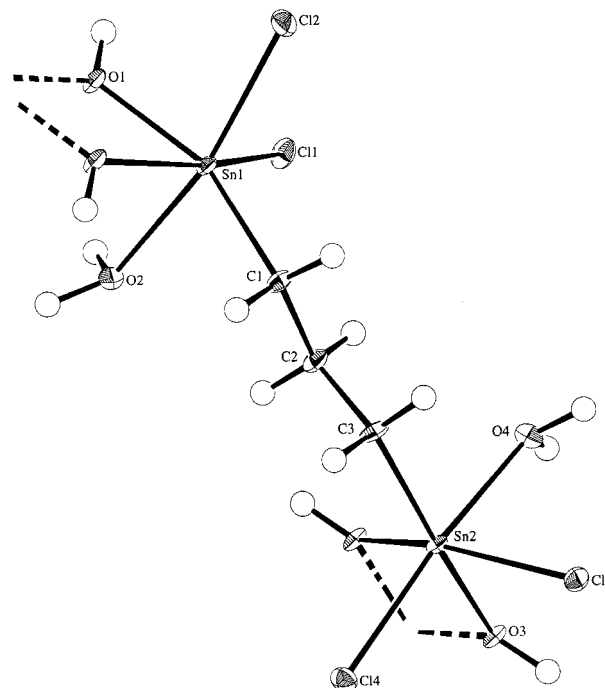


Figure 3. Molecular structure and atomic numbering scheme for $[\text{H}_2\text{O}(\text{OH})\text{Cl}_2\text{Sn}(\text{CH}_2)_3\text{SnCl}_2(\text{OH})\text{H}_2\text{O}]_n$ in $7\cdot 2\text{H}_2\text{O}$.

Table 4. Selected Interatomic (\AA , deg) Parameters for $[\text{H}_2\text{O}(\text{OH})\text{Cl}_2\text{Sn}(\text{CH}_2)_3\text{SnCl}_2((\text{OH})\text{H}_2\text{O}\cdot 2\text{H}_2\text{O})_n$ ($7\cdot 2\text{H}_2\text{O}$)^a

Sn(1)–Cl(1)	2.4248(6)	Sn(2)–Cl(3)	2.4674(7)
Sn(1)–Cl(2)	2.4258(8)	Sn(2)–Cl(4)	2.4689(6)
Sn(1)–O(1)	2.047(2)	Sn(2)–O(3)	2.051(2)
Sn(1)–O(1) ⁱ	2.164(2)	Sn(2)–O(3) ⁱⁱ	2.125(2)
Sn(1)–O(2)	2.361(2)	Sn(2)–O(4)	2.220(2)
Sn(1)–C(1)	2.140(3)	Sn(2)–C(3)	2.136(3)
C(1)–C(2)	1.531(4)	C(2)–C(3)	1.514(4)

Cl(1)–Sn(1)–Cl(2)	93.89(2)	Cl(3)–Sn(2)–Cl(4)	93.00(2)
Cl(1)–Sn(1)–O(1)	91.49(5)	Cl(3)–Sn(2)–O(3)	87.95(5)
Cl(1)–Sn(1)–O(1) ⁱ	159.98(5)	Cl(3)–Sn(2)–O(3) ⁱⁱ	157.55(5)
Cl(1)–Sn(1)–O(2)	82.12(5)	Cl(3)–Sn(2)–O(4)	86.42(5)
Cl(1)–Sn(1)–C(1)	103.70(7)	Cl(3)–Sn(2)–C(3)	99.89(8)
Cl(2)–Sn(1)–O(1)	89.36(6)	Cl(4)–Sn(2)–O(3)	89.30(5)
Cl(2)–Sn(1)–O(1) ⁱ	92.69(6)	Cl(4)–Sn(2)–O(3) ⁱⁱ	92.87(5)
Cl(2)–Sn(1)–O(2)	167.39(5)	Cl(4)–Sn(2)–O(4)	172.98(6)
Cl(2)–Sn(1)–C(1)	103.87(8)	Cl(4)–Sn(2)–C(3)	98.02(7)
O(1)–Sn(1)–O(1) ⁱ	69.69(8)	O(3)–Sn(2)–O(3) ⁱⁱ	70.48(8)
O(1)–Sn(1)–O(2)	78.83(8)	O(3)–Sn(2)–O(4)	83.69(7)
O(1)–Sn(1)–C(1)	158.91(9)	O(3)–Sn(2)–C(3)	169.66(8)
O(1) ⁱ –Sn(1)–O(2)	87.39(7)	O(3) ⁱⁱ –Sn(2)–O(4)	85.13(7)
O(1) ⁱ –Sn(1)–C(1)	93.01(8)	O(3) ⁱⁱ –Sn(2)–C(3)	101.71(9)
O(2)–Sn(1)–C(1)	88.71(9)	O(4)–Sn(2)–C(3)	88.98(9)
Sn(1)–O(1)–Sn(1) ⁱ	110.31(8)	Sn(2)–O(3)–Sn(2) ⁱⁱ	109.52(8)
Sn(1)–C(1)–C(2)	115.8(2)	Sn(2)–C(3)–C(2)	115.3(2)
C(1)–C(2)–C(3)	109.7(2)		

^a Symmetry operation *i*: $-x, -1-y, -z$; *ii*: $1-x, -y, -1-z$.

coordinated water molecule are systematically longer than those with the chloride trans to a carbon atom. There are no significant intermolecular interactions (<4.0 Å) involving the tin center and either of the 18-crown and acetonitrile molecules. The crystal structure is essentially a layer structure being comprised of alternate layers stacked along the crystallographic *a*-direction defined by di-tin and acetonitrile molecules on one hand and 18-crown molecules on the other. All coordinated water molecules are involved in the hydrogen-bonding network in the structure.

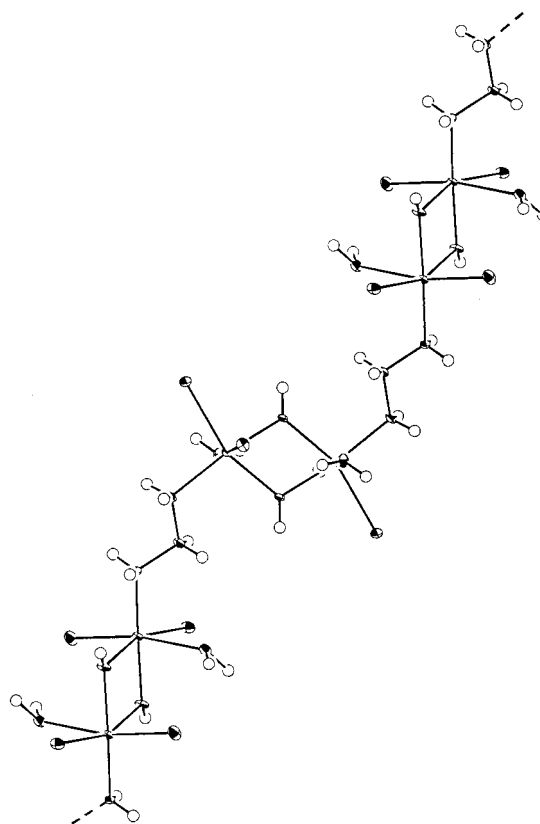
Table 5. Crystallographic Data for (H₂O)Cl₃Sn(CH₂)₃SnCl₃(H₂O) (1a), (H₂O)₂Cl₃Sn(CH₂)₃SnCl₃(H₂O)₂ (6·18-crown-6·CH₃CN), and [H₂O(OH)Cl₂Sn(CH₂)₃SnCl₂((OH)H₂O·2H₂O)]_n (7·2H₂O)

	1a	6·18-crown-6·CH ₃ CN	7·2H ₂ O
formula	C ₃ H ₁₀ Cl ₆ O ₂ Sn ₂	C ₁₇ H ₄₁ Cl ₆ NO ₁₀ Sn ₂	C ₃ H ₁₆ Cl ₄ O ₆ Sn ₂
fw	528.2	869.6	527.4
cryst size, mm	0.08 × 0.23 × 0.36	0.11 × 0.13 × 0.29	0.11 × 0.12 × 0.14
color	colorless	colorless	colorless
temp, K	173	173	173
cryst syst.	monoclinic	monoclinic	triclinic
space group	<i>C2/c</i>	<i>Cc</i>	<i>P1</i>
<i>a</i> , Å	11.859(3)	15.374(1)	7.2652(1)
<i>b</i> , Å	6.261(5)	11.641(2)	9.6400(2)
<i>c</i> , Å	18.686(8)	20.283(3)	10.2992(2)
α, deg			90.323(1)
β, deg	90.46(3)	115.051(8)	103.169(1)
γ, deg			94.047(1)
<i>V</i> , Å ³	1387(1)	3288.5(7)	700.43(2)
<i>Z</i>	4	4	2
<i>D</i> _{calcd} , g cm ⁻³	2.528	1.756	2.500
<i>F</i> (000)	984	1728	500
μ, cm ⁻¹	47.24	20.49	43.30
transmn factors	0.942–1	0.660–1	0.483–0.692
no. of data coll'd	4630	5105	13956
θ _{max} , deg	27.5	30.0	30.1
no. of unique data with <i>I</i> ≥ 3.0σ(<i>I</i>)	1347	4233	3675
<i>R</i>	0.026	0.024	0.031
<i>R</i> _w	0.024	0.023	0.046
residual electron density, e Å ⁻³	1.25	0.52	0.87

Within the *bc*-plane, hydrogen bonds serve to link the di-tin and acetonitrile molecules with the most notable interactions formed between O(1)–H and N(1) [H⋯N(1) 1.97 Å, O(1)⋯N(1) 2.888(6) Å, and O(1)–H⋯N(1) 160°] and O(4)–H⋯O(1)^{*i*} [2.29 Å, 2.847(4) Å, 152°, and symmetry operation *i*: *x*, –*y*, 0.5 + *z*]. Connections between the layers are afforded by six hydrogen bonds formed between the coordinated water molecules and each of the ether oxygen atoms of the 18-crown.

Slow evaporation of a solution of **1** in aqueous solution afforded [H₂O(OH)Cl₂Sn(CH₂)₃SnCl₂(OH)H₂O]_{*n*}, **7**, isolated as a dihydrate (7·2H₂O). The solid state ¹¹⁹Sn NMR shift of this material occurs at –472 ppm, consistent with the six-coordinate structure determined by the X-ray structure analysis.

The structure is comprised of hydrated polymeric chains of [H₂O(OH)Cl₂Sn(CH₂)₃SnCl₂(OH)H₂O] with the repeat unit illustrated in Figure 3; important geometric parameters are listed in Table 4. The repeat unit comprises two tin centers linked via a propylene bridge in which each tin atom is also coordinated by two chloride atoms and an oxygen atom derived from a water molecule. The remaining positions in the distorted octahedral coordination geometry about each tin atom are occupied by two μ₂-hydroxide groups. The crystallographic asymmetric unit is completed by two water molecules of crystallization, i.e., O(5) and O(6). The nature of the bridging is such that centrosymmetrically related pairs of Sn(1) atoms and of Sn(2) atoms are linked with the result that an infinite polymeric chain is generated as shown in Figure 4. The major distortions in the tin atom geometries may be traced to the acute angles induced by the Sn₂(OH)₂ rings, i.e., O(1)–Sn(1)–O(1)^{*i*} 69.69(8)° and O(3)–Sn(2)–O(3)^{*ii*} 70.48(8)°; symmetry operations *i*: –*x*, –1 – *y*, –*z* and *ii*: 1 – *x*, –*y*, –1 – *z*. The Sn–O distances within the four-membered rings are not symmetrical, with the bond trans to a carbon atom shorter than that trans to a chloride. While for each tin center the Sn–Cl distances are equivalent,

**Figure 4.** Polymeric structure for [H₂O(OH)Cl₂Sn(CH₂)₃SnCl₂(OH)H₂O]_{*n*} (7·2H₂O).

the Sn(1)–Cl bonds are significantly shorter than the Sn(2)–Cl bonds. The reason for this disparity is not obvious; however, it is noted that the Sn(1)–O_{water} bond distance is significantly longer than the comparable bond involving Sn(2). As expected, there is a complicated network of hydrogen-bonding interactions in the lattice and the important contacts are summarized below.

The hydroxides each form a hydrogen bond. For the first, O(1)–H \cdots Cl(3)ⁱⁱⁱ is 2.26 Å, O(1) \cdots Cl(3)ⁱⁱⁱ is 3.158(2) Å, and the O(1)–H \cdots Cl(3)ⁱⁱⁱ angle is 165°; symmetry operation *iii*: $-1 + x, -1 + y, z$. For the other hydroxide, O(3)–H \cdots O(5) is 1.88 Å, O(2) \cdots O(5) is 2.778(3) Å, and O(2)–H \cdots O(5) is 169°, where H₂O(5) is one of the water molecules of crystallization. The coordinated water bound to Sn(1) forms two contacts, namely, to a lattice water O(6) (1.63, 2.749(3), 167) and, albeit weaker, to Cl(2) (2.49, 3.206(2), 129.2; $-x, -1 - y, -z$). The coordinated O(4) water molecule forms a contact with O(6) (1.78, 2.718(3), 169; $x, 1 + y, z$) via the H(11) atom and a weaker one to Cl(4) (2.54, 3.221(2), 148; $1 - x, -y, -1 - z$) via H(12).

The linking of the tin atoms via four-membered Sn₂OH₂ rings observed in the structure of **7** is analogous to that found in the dimeric structures of (R₂SnCl₂(OH)OH)₂^{17–20} (R = methyl, ethyl, isopropyl, butyl, isobutyl).

Conclusion

While we have demonstrated that Cl₃Sn(CH₂)_{*n*}SnCl₃ does undergo stepwise hydrolysis to give new oligomers, these oligomers do not yet resemble the linked tin-12 or the tin-12 with handles motif. We are currently investigating use of di-tin compounds linked by larger spacers as precursors, which could yield new organotin-oxo clusters derived from the tin-12 motif. Furthermore, the influence of the functional X group X₃Sn(CH₂)_{*n*}SnX₃ (X = halogen, carboxylic acid, alkoxide) on the structural outcome of the hydrolysis will be investigated.

Experimental Section

All solvents were dried and purified by standard procedures. NMR spectra were obtained using a Varian 300 MHz Unity Plus NMR spectrometer. ¹H, ¹³C, and ¹¹⁹Sn chemical shifts δ are given in ppm and are referenced against Me₄Si and Me₄Sn, respectively. If not indicated differently, CDCl₃ was used as the NMR solvent. The melting points reported are uncorrected. Microanalyses were performed using an elemental analyzer MOD 1106 from Carlo Erba Strumantazione.

General Procedure for the Synthesis of α,ω -Bis(trichlorostannyl)alkanes (1–4). Method A. The α,ω -bis(triphenylstannyl)alkane (10.00 mmol) and SnCl₄ (18.24 g, 8.20 mL, 70.00 mmol) were placed in a 50 mL one-neck flask and heated for 3 h to 120–130 °C. The resulting mixture was distilled to give the corresponding α,ω -bis(trichlorostannyl)alkanes.

1,1-Bis(trichlorostannyl)methane: 2.5 g clear oil (54% yield); bp 70–100 °C, 5×10^{-3} Torr.

1,3-Bis(trichlorostannyl)propane, 1: 3.7 g colorless solid (75% yield); bp 120–130 °C, 10^{-3} Torr; recrystallization from CHCl₃ gave the diaquo adduct **1a**, mp 97–98 °C. Anal. Calcd for C₃H₆Cl₆Sn₂·2H₂O: C, 6.82; H, 1.91. Found: C, 7.01; H, 1.87.

1,4-Bis(trichlorostannyl)butane, 2: 3.37 g colorless solid (67% yield); bp 130–150 °C, 10^{-3} Torr; recrystallization from CHCl₃ gave the diaquo adduct **2a**, mp 99–101°. Anal. Calcd for C₄H₈Cl₆Sn₂·2H₂O: C, 8.86; H, 2.23. Found: C, 8.85; H, 1.84.

1,5-Bis(trichlorostannyl)pentane, 3: 3.90 g clear oil (75% yield); bp 140–180 °C, 2×10^{-3} Torr. Anal. Calcd for C₅H₁₀Cl₆Sn₂: C, 11.54; H, 1.94. Found: C, 12.10; H, 1.91.

1,8-Bis(trichlorostannyl)octane, 4: 4.46 g clear oil (80% yield); bp 200–240 °C, 5×10^{-3} Torr. Anal. Calcd for C₈H₁₆Cl₆Sn₂: C, 17.09; H, 3.10. Found: C, 17.61; H, 2.93.

Method B. The appropriate α,ω -bis(triphenylstannyl)alkane (5.00 mmol) was mixed with 40 mL of concentrated

hydrochloric acid and heated at 60 °C for 24 h under magnetic stirring. The reaction mixture was cooled to room temperature and the solvent removed under reduced pressure to provide a brown solid. Recrystallization from toluene yielded the diaquo adducts **1a** (2.01 g 81% yield) and **2a** (2.10 g 83% yield).

1,1-Bis(trichlorostannyl)methane: ¹H NMR δ 2.37 (s, ²*J*(^{117/119}Sn–¹H) = 92/96 Hz, 1H, CH₂); ¹³C{¹H} NMR δ 21.28 (s, ¹*J*(^{117/119}Sn–¹³C) = 635/664 Hz, 1C, CH₂); ¹¹⁹Sn{¹H} NMR (111.85 MHz, CDCl₃) concentration dependent, range from δ –7.0 to –16.0.

1a: ¹H NMR δ 2.34–2.44 (m, ²*J*(^{117/119}Sn–¹H) 87 Hz 2H, SnCH₂); 2.36–2.58 (m, ³*J*(^{117/119}Sn–¹H) 144 Hz, 1H, CH₂); ¹³C{¹H} NMR δ 20.66 (²*J*(^{117/119}Sn–¹³C) 44 Hz); δ 32.31 (¹*J*(^{117/119}Sn–¹³C) 647/679 Hz, ³*J*(^{117/119}Sn–¹³C) 160/168 Hz); ¹¹⁹Sn{¹H} δ 1.7 (s) ⁴*J*(¹¹⁷Sn–¹¹⁹Sn) 595 Hz).

2a: ¹H NMR δ 2.02–2.16 (m, ³*J*(^{117/119}Sn–¹H) 164 Hz, 1H, CH₂); 2.26–2.44 (m, ²*J*(^{117/119}Sn–¹H) 86/90 Hz, 1H, CH₂); ¹³C{¹H} NMR δ 27.15 (²*J*(^{117/119}Sn–¹³C) 53 Hz, ³*J*(^{117/119}Sn–¹³C) 133 Hz); δ 30.41 (¹*J*(^{117/119}Sn–¹³C) 648/680 Hz); ¹¹⁹Sn{¹H} δ 6.3 (s).

3: ¹H NMR δ 1.58–1.80 (m, 1H, CH₂); 1.90–2.14 (m, ³*J*(^{117/119}Sn–¹H) 170 Hz, 2H, CH₂); 2.31–2.46 (m, ²*J*(^{117/119}Sn–¹H) 86 Hz, 2H, CH₂); ¹³C{¹H} δ 24.1 (²*J*(^{117/119}Sn–¹³C) 56 Hz); δ 31.9 (¹*J*(^{117/119}Sn–¹³C) 636/666 Hz) δ 34.6 (²*J*(^{117/119}Sn–¹³C) 117/123 Hz); ¹¹⁹Sn{¹H} δ 4.7 (s).

4: ¹H NMR δ 1.24–1.62 (m, 2H, CH₂, CH₂); 1.94 (tt, ³*J*(^{117/119}Sn–¹H) 195 Hz, ³*J*(¹H–¹H) 7.6 Hz, ³*J*(¹H–¹H) 7.6 Hz, 1H, CH₂); 2.38 (t, ²*J*(^{117/119}Sn–¹H) 81/85 Hz, 1H, ³*J*(¹H–¹H) 7.6 Hz, CH₂); ¹³C{¹H} δ 24.63 (²*J*(^{117/119}Sn–¹³C) 60 Hz); δ 28.22; δ 32.07 (³*J*(^{117/119}Sn–¹³C) 106/111 Hz); δ 33.24, (¹*J*(^{117/119}Sn–¹³C) 619/648 Hz); ¹¹⁹Sn{¹H} δ 6.7 (s).

Synthesis of 1,3-Bis(tribromostannyl)propane (5). A mixture of (Ph₃SnCH₂)₂CH₂ (4.65 g, 6.27 mmol) and SnBr₄ (19.00 g, 43.35 mmol) was placed in a 50 mL one-neck flask and heated at 120 °C for 48 h. The resulting yellow mixture was distilled (bp 200–220 °C, 2×10^{-3} Torr) to give **5** (4 g 84% yield), mp 50–70 °C. Anal. Calcd for C₃H₆Br₆Sn₂: C, 4.75; H, 0.80. Found: C, 5.34; H, 0.85. ¹³C{¹H} NMR (75.44 MHz, CDCl₃): δ 22.29 (²*J*(^{117/119}Sn–¹³C) 40 Hz); δ 33.52 (¹*J*(^{117/119}Sn–¹³C) 555/582 Hz, ³*J*(^{117/119}Sn–¹³C) 151/158 Hz). ¹¹⁹Sn{¹H} NMR (111.85 MHz, CDCl₃): δ –168.9 (s) ⁴*J*(¹¹⁷Sn–¹¹⁹Sn) 499 Hz.

Synthesis of 6·18-crown-6·H₂O. To a solution of **1** (95 mg, 0.193 mmol) in 3 mL of MeOH was added 18-crown-6 (102 mg, 0.386 mmol) to afford a clear solution. After 24 h the solvent was removed and the solid residue recrystallized from 18 mL of CH₂Cl₂/hexane (5:1) to give 105 mg (64%) of colorless solid, mp 109–113 °C. Anal. Calcd for C₁₅H₃₈Cl₆O₁₀Sn₂·H₂O: C, 21.28; H, 4.76. Found: C, 21.25; H, 4.75. Crystals suitable for X-ray analysis were grown from acetonitrile (mp 111–116 °C). ¹H NMR δ 2.30–2.48 (m, 2H, CH₂); 2.48–2.64 (m, ³*J*(^{117/119}Sn–¹H) 199 Hz, 1H, CH₂); 3.76 (s, 12H, CH₂-crown); ¹³C{¹H} NMR (CD₃CN) δ 23.15 (²*J*(^{117/119}Sn–¹³C) 54 Hz); δ 43.23 (¹*J*(^{117/119}Sn–¹³C) 895/938 Hz, ³*J*(^{117/119}Sn–¹³C) 202 Hz); 71.34 (s, 6C, CH₂-crown); ¹¹⁹Sn{¹H} (CD₃CN) δ –274.1 (s, *W*_{1/2} approximately 800 Hz).

Synthesis of (7·2H₂O). A solution of **1** (50 mg, 0.102 mmol) in 1 mL of H₂O was placed on a watch glass and slowly evaporated to give 47 mg (94%) of a crystalline solid, mp 110–135 °C. Anal. Calcd for C₃H₁₂Cl₄O₄Sn₂·2H₂O: C, 6.83; H, 3.06. Found: C, 6.95; H, 3.02.

X-ray Crystallography. Data were collected at 173 K employing graphite-monochromatized Mo K α radiation, λ = 0.71073 Å, on a Rigaku AFC7R diffractometer for **1a** and **6·18-crown-6·CH₃CN** and a Nonius CCD for **7·2H₂O**. Corrections were made for Lorentz and polarization effects (**1a**, **6·18-crown-6·CH₃CN**,³⁴ ⁷³⁵) as well as for absorption employing an

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empirical method³⁶ for **1a** and **6**·18-crown-6·CH₃CN and a numerical method for **7**·2H₂O.³⁷ The structures were solved by direct-methods³⁸ and each refined by a full-matrix least-squares procedure based on F_o .³⁴ Non-hydrogen atoms were refined with anisotropic displacement parameters, and H atoms were included in the model in their calculated positions (C–H 0.95 Å); O–H atoms were located from difference maps except for one H of a lattice water molecule (with the O(6) atom) in **7**·2H₂O. The structure of **6**·18-crown-6·CH₃CN was modeled in the noncentrosymmetric space group Cc . Support for this choice is found in the distribution of the E-statistics and well as in the successful refinement. The use of the PLATON program³⁹ shows the presence of pseudosymmetry in the lattice, but several atoms did not comply to the higher

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symmetry required by $C2/c$, perhaps indicating disorder not evident in the low-symmetry space group. The absolute structure was not determined. The refinements were continued until convergence with the application of a weighting scheme of the form $w = 1/[\sigma^2(F_o) + g|F_o|^2]$; $g = 0.00002$, 0.00002 , and 0 for **1a**, **6**·18-crown-6·CH₃CN, and **7**·2H₂O, respectively. Diagrams of the molecules were drawn with ORTEP⁴⁰ plotted at the 50% probability level.

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Supporting Information Available: Further details of the structure determination including atomic coordinates, bond distances and angles, and thermal parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM010202J

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