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Novel Trialkanolamine Derivatives of Tin of the Type $[N(CH_2CMe_2O)_2(CH_2)_nOSnOR]_m$ (m = 1, 2; n = 2, 3; R = t-Bu, 2,6-$Me_2C_6H_3$) and Related Tri- and Pentanuclear Tin(IV) Oxoclusters. Syntheses and Molecular Structures

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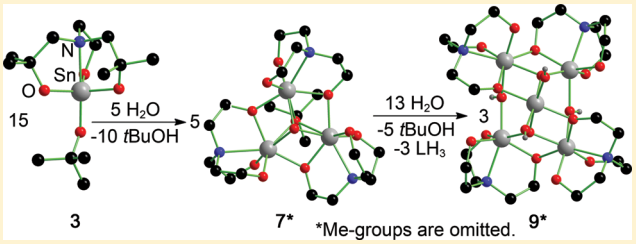
Supporting Information

ABSTRACT: The syntheses of the novel alkanolamine N-$(CH_2CMe_2OH)_2(CH_2CH_2CH_2OH)$ (**2**), the novel aminotrialkoxides of tin of the type $[N(CH_2CMe_2O)_2(CH_2)_nOSnOR]_m$ (**3**: m = 1, n = 2, R = t-Bu; **4**: m = 2, n = 3, R = t-Bu; **5**: m = n = 2, R = 2,6-$Me_2C_6H_3$; **6**: m = 2, n = 3, R = 2,6-$Me_2C_6H_3$) and the related trinuclear tin oxoclusters $[(LSnOSnL)(LSnOR)]$ [L = $N(CH_2CMe_2O)_2(CH_2CH_2O)$, **7**: R = t-Bu; **8**: R = 2,6-$Me_2C_6H_3$] and the pentanuclear tin oxocluster $[LSnOSn(OH)_2OSnL{\cdot}2LSnOH]$, [**9**, L = $N(CH_2CMe_2O)_2(CH_2CH_2O)$] are reported. The compounds are characterized by elemental analyses, multinuclear (^1H, ^{13}C, ^{119}Sn, ^1H-^1H cosy, ^1H-^{13}C HSQC) NMR spectroscopy, electrospray ionization mass spectrometry, and single crystal X-ray diffraction analyses (**3**, **4**·C_7H_8, **5**, **7**, **8**·0.5C_7H_8, **9**·6H_2O).



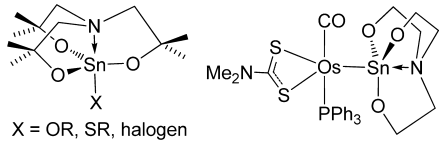
INTRODUCTION

Tin alkoxides find application in sol−gel chemistry for the manufacturing of tin dioxide thin films and related materials. These materials can be used as transparent conductors in solar cells, screens, and gas detection devices.[1−7] Furthermore, we found that alkanolamine derivatives of tin are excellent delayed action catalysts for the formation of polyurethanes.[8,9] These tin aminoalkoxides of the types $(R_2NCH_2CH_2O)_2SnX_2$ (**A**), $RN(CH_2CH_2O)_2SnX_2$ (**B**), or $N(CH_2CH_2O)_3SnX$ (**C**) (R = alkyl, aryl; X = alkoxide, alkanoate, halogen, hydroxide) are characterized by a kinetically labile intramolecular N→Sn coordination which is likely to be responsible for the delayed action activity. The so-called dissociation-inversion mechanism was analyzed in detail for the organically substituted representatives (X = t-Bu).[10−13] There is considerable interest in inorganic, nontoxic tin compounds which might replace the highly toxic, state of the art mercury catalysts, such as phenylmercury neodecanoate, $PhHgOC(O)CH_2CH_2CH_2CH_2CMe_3$.[14]

Compounds of type **C** are called stannatranes, and the chemistry of the organotin derivatives $N(CH_2CH_2O)_3SnR$ (R = alkyl, aryl) has been extensively studied in the past decades.[15] Among these, the methylstannatrane, as its aqua solvate $[N(CH_2CH_2O)_3SnMe]_3{\cdot}6H_2O$,[16] is unique as it is a trimer that is formed by intermolecular O→Sn interactions. The trimerization is the result of insufficient steric protection of the highly Lewis-acidic tin atom by the methyl substituent and the triethanolamine framework. The t-butyl- and o-anisyl-substituted derivatives $N(CH_2CH_2O)_3SnR$ (R = t-Bu,[17] o-C_6H_4OMe[18]) are, however, monomeric both in solution and in the solid state.

Stannatranes without any metal−carbon bond are less studied[19−24a] and only few solid state structures as determined by single crystal X-ray diffraction analysis have been described so far (Scheme 1).[19,23]

Scheme 1. Stannatranes Lacking Sn−C Bonds



Recently we have reported the syntheses and structures in solution and in the solid state of the stannatranes N-$(CH_2CMe_2O)_3SnX$ (X = Ot-Bu, Oi-Pr, 2,6-$Me_2C_6H_3O$, p-t-BuC_6H_4O, p-$NO_2C_6H_4O$, p-FC_6H_4O, p-$PPh_2C_6H_4O$, p-MeC_6H_4S, o-$NH_2C_6H_4O$, $OCPh_2CH_2NMe_2$, $Ph_2P(S)S$, p-t-$BuC_6H_4C(O)O$, p-$N[(CH_2CMe_2O)_3SnOSiMe_2]_2C_6H_4$, halogen) (Scheme 1).[23] Although the tin atoms in these compounds are highly Lewis-acidic and prone to extend their coordination number beyond five, they are monomeric with trigonal-bipyramidally configurated metal atoms. Again, this is the result of steric protection as induced by the methyl-substitution at the carbinol carbon atoms (OC) of the atrane

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framework. On successive replacement of these methyl substituents by hydrogen atoms, control of the degree of association via intermolecular O→Sn coordination should be possible. Such strategy proved to be true in case of related titanatranes.[24b]

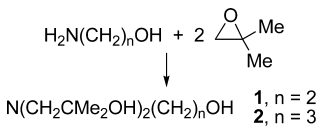
In contrast to a great variety of organotin(IV) oxoclusters,[25−29] related clusters that lack any Sn−C bonds are scarce and to the best of our knowledge, only the five crystallographically characterized examples $Sn_3O(Oi\text{-}Bu)_{10}(HOi\text{-}Bu)_2$,[30] $[SnO(acac)_2]_3$,[31] $Sn_4O_2(OEt)_{10}(acac)_2$,[1] $[SnO(Ot\text{-}Bu)(OAc)]_6$,[32] and $Sn_{12}O_8(OH)_4(OEt)_{28}(HOEt)_4$[33] have been reported so far. One reason for this might be that the hydrolysis of purely inorganic tin alkoxides is very fast with the consequence that oligomeric intermediates are difficult to isolate.[30] Chelating ligands with coordinating donor groups such as aminoalkoxides should be suitable to stabilize such oligomeric intermediates. Again, this was shown to be the case for related titanatranes.[24c,d]

In context with what is stated above, we here report the novel alkanolamine $N(CH_2CMe_2OH)_2(CH_2CH_2CH_2OH)$, novel inorganic stannatranes of the type $[N(CH_2CMe_2O)_2(CH_2)_nOSnOR]_m$ (m = 1, 2; n = 2, 3; R = *t*-Bu, 2,6-$Me_2C_6H_3$) as well as, by controlled hydrolysis of the latter compounds, novel tri- and pentanuclear tin oxoclusters.

RESULTS AND DISCUSSION

The aminoalcohols bis(2-methyl-2-hydroxypropyl)(2-hydroxyethyl)amine, $N(CH_2CMe_2OH)_2(CH_2CH_2OH)$ (**1**),[34a] and bis(2-methyl-2-hydroxypropyl)(3-hydroxypropyl)amine, $N(CH_2CMe_2OH)_2(CH_2CH_2CH_2OH)$ (**2**), were prepared by the reaction of 2-aminoethanol respectively 3-aminopropan-1-ol with two equivalents of 1,1-dimethyloxirane (Scheme 2).

Scheme 2. Synthesis of Aminoalcohols 1 and 2



Compound **2** is a colorless oil, that crystallizes upon standing at room temperature for several days. It is well soluble in common organic solvents such as diethylether, tetrahydrofuran, chloroform, dichloromethane, and toluene. Its molecular structure including a graph set analysis of the hydrogen bonding pattern will be published elsewhere.

The reaction of tin tetra-*t*-butoxide, $Sn(Ot\text{-}Bu)_4$, with the unsymmetrically substituted aminotrialcohols **1** and **2** gave the novel 1-alkoxido-stannatranes **3** and **4**, respectively (Scheme 3).

The acid−base type reactions of the *t*-butoxido-substituted stannatranes **3** and **4** with 2,6-dimethylphenol provided the corresponding aryloxido-substituted stannatranes **5** and **6**, respectively (Scheme 4).

The compounds **3**−**6** are crystalline, colorless solids that are well soluble in dichloromethane, acetone, hot toluene, or benzene. The *t*-butoxido-substituted derivatives **3** and **4** are sensitive toward moisture.

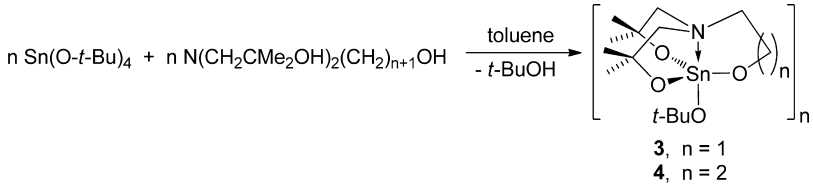
The molecular structures of compounds **3**, **4**, as its toluene solvate **4**·C_7H_8, and **5** as determined by single crystal X-ray diffraction analysis are shown in Figures 1, 2, and 3, respectively. Selected interatomic distances and angles are given in the figure captions. The unit cell of **3** contains two crystallographic independent molecules **A** and **B** whose interatomic distances and angles differ only slightly. Consequently, only those of molecule **A** are discussed. Those of molecule **B** are given in the Supporting Information, Figure S1.

The molecular structure of the *t*-butoxido-substituted stannatrane **3** resembles those of the parent halogenido- and aryloxido-substituted stannatranes $N(CH_2CMe_2O)_3SnX$ (X = Cl, Br, I, OAr; Ar = *p*-*t*-BuC_6H_4, *p*-FC_6H_4, *p*-$NO_2C_6H_4$, *p*-$Ph_2PC_6H_4$, 2,6-$Me_2C_6H_3$).[23] It is monomeric with the shortest intermolecular Sn···O distance being 5.670(2) Å (Sn(1)···O(103)). The Sn(1) atom is five-coordinate by one nitrogen and four oxygen atoms and shows a distorted trigonal bipyramidal configuration ($\Delta\Sigma(\vartheta)$[34b] = 56.2°) with N(1) and O(4) occupying the axial and O(1), O(2), and O(3) occupying the equatorial positions. The Sn(1)−N(1) distance of 2.275(2) Å (molecule **B**: Sn(2)−N(2) 2.306(2) Å) is comparable with the corresponding distances in the stannatranes mentioned above.[23] Interestingly, the Sn(1)−O(4) distance of 1.949(2) Å (molecule **B**: Sn(2)−O(104) 1.949(2) Å) is shorter than the distances to the equatorially bound oxygen atoms ranging between 1.965(2) (Sn(1)−O(1)) and 1.985(2) Å (Sn(1)−O(3)). One possible explanation is that this axial Sn(1)−O(4) bond exhibits high ionic character and that the expected lengthening as induced by the N→Sn coordination is more than compensated for by electrostatic attraction.

In contrast to the monomeric stannatranes of the type $N(CH_2CMe_2O)_3SnX$ (X = OR, SR, halogen),[23] the compounds **4**·C_7H_8 and **5** form dimers via intermolecular O→Sn coordination to give four-membered planar Sn_2O_2 rings with intracyclic Sn(1)−O(3)/Sn(1)−O(3A) distances of 2.046(2)/2.232(2) Å (**4**·C_7H_8) and 2.059(2)/2.204(1) Å (**5**), respectively. These μ_2-O−Sn distances are comparable with those of dimeric tin(II) aminoalkoxides $[MeN(CH_2CR_2O)_2Sn]_2$ [R = Me:[35] 2.140(2)/2.259(2) Å, 2.134(2)/2.244(2) Å; R = H:[36] (2.176(9)/2.200(9) Å] and with those of the tin(IV) compounds $[Sn(Oi\text{-}Pr)_4(HOi\text{-}Pr)_2]_2$[37] (2.080(4)/2.091(4) Å), $Sn_3O(Oi\text{-}Bu)_{10}(HOi\text{-}Bu)_2$[30] [2.096(3)/2.129(4) Å] and $Sn_{12}O_8(OH)_4(OEt)_{28}(HOEt)_4$[33] [1.93(1)/2.13(1)]. To the best of our knowledge the compounds **4**·C_7H_8 and **5** are the first examples of crystallographically established dimeric stannatranes.

As result of the dimerization and the intramolecular N→Sn coordination the tin atoms each show a distorted octahedral configuration. The distortion from the ideal geometry is

Scheme 3. Synthesis of Compounds 3 and 4



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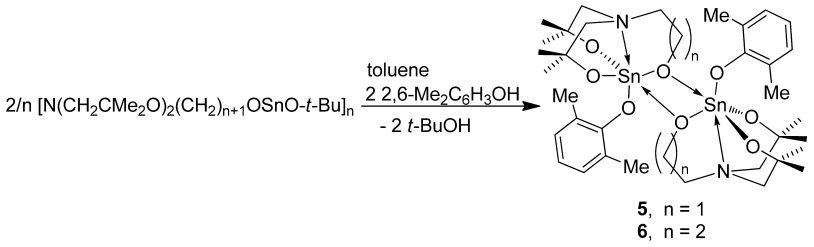
Scheme 4. Synthesis of Compounds 5 and 6



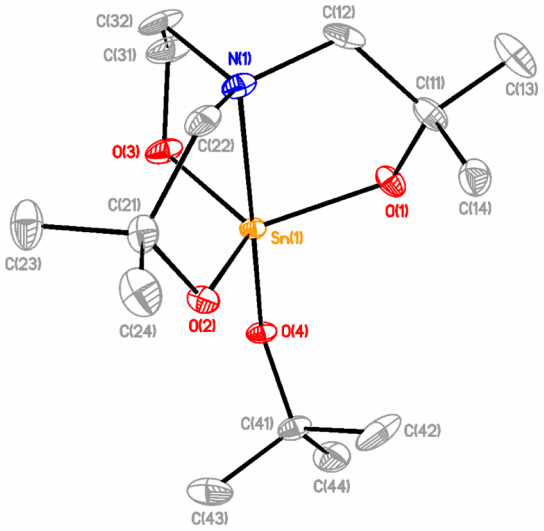


Figure 1. Molecular structure of compound **3** (molecule **A**, ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). Selected interatomic distances [Å] and angles [deg]: Sn(1)−O(1) 1.965(2), Sn(1)−O(2) 1.976(2), Sn(1)−O(3) 1.985(2), Sn(1)−O(4) 1.949(2), Sn(1)−N(1) 2.275(2); O(1)−Sn(1)−O(2) 119.18(7), O(1)−Sn(1)−O(3) 112.78(8), O(1)−Sn(1)−O(4) 98.79(7), O(1)−Sn(1)−N(1) 81.08(8), O(2)−Sn(1)−O(3) 120.85(8), O(2)−Sn(1)−O(4) 102.86(7), O(2)−Sn(1)−N(1) 80.67(8), O(3)−Sn(1)−O(4) 94.95(7), O(3)−Sn(1)−N(1) 81.37(8), O(4)−Sn(1)−N(1) 175.90(8), Sn(1)−O(4)−C(41) 124.6(2). The data for molecule **B** are rather similar and are given in the Supporting Information, Figure S1.

manifested by the strong deviation of the *trans*-angles O(1)−Sn(1)−O(3) [138.78(7)/126.67(6) Å], O(2)−Sn(1)−O(3A) [163.81(7)/151.19(6) Å] and N(1)−Sn(1)−O(4) [167.23(7)/158.50(6) Å] (**4**·C_7H_8/**5**) from 180°. The tin atoms are displayed from the plane $E(O_{atrane})$ defined by the oxygen atoms O(1)−O(3) by 0.3663(2) Å (**4**·C_7H_8) and 0.4663(1) Å (**5**), respectively, in direction to the exocyclic ligand. The N−Sn distances are 2.390(2) Å (**4**·C_7H_8) and 2.401(2) Å (**5**) being among the longest N−Sn distances for stannatranes. The N−Sn distances of comparable stannatranes of the type $N(CH_2CMe_2O)_3SnX$ (X = OR, SR, halogen) (2.232(2)−2.295(3) Å)[23] or monoorgano-stannatranes of the type $[N(CH_2CH_2O)_3SnR]_n$ (R = Me, *n* = 3, *d*(N−Sn) = 2.28(1) Å;[16] R = *t*-Bu, *n* = 1, *d*(N−Sn) = 2.324 Å;[17] R = C_6H_4-*o*-OMe, *n* = 1, *d*(N−Sn) = 2.323(7) Å[18]) are considerable shorter while the only longer N−Sn distance of 2.422(4) Å was found for $N(CH_2CH_2O)_3SnOs(\eta_2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$.[19]

The five-membered atrane rings adopt uniform envelope conformations and make the molecules chiral in terms of Δ and Λ stereochemistry.[23] The six-membered atrane ring in compound **4**·C_7H_8 adopts a twist-boat conformation. Given

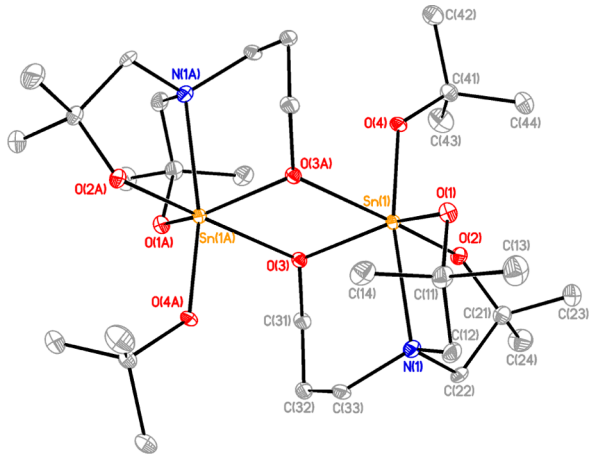


Figure 2. Molecular structure of compound **4**·C_7H_8 (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). The asymmetric unit contains a half toluene molecule which is omitted. Selected interatomic distances [Å] and angles [deg]: Sn(1)−O(1) 1.979(2), Sn(1)−O(2) 2.002(2), Sn(1)−O(3) 2.046(2), Sn(1)−O(4) 1.971(2), Sn(1)−O(3A) 2.232(2), Sn(1)−N(1) 2.390(2); O(1)−Sn(1)−O(3) 138.78(7), O(2)−Sn(1)−O(3A) 163.81(7), N(1)−Sn(1)−O(4) 167.23(7), Sn(1)−O(3)−Sn(1A) 113.21(8), O(3)−Sn(1)−O(3A) 66.79(8).

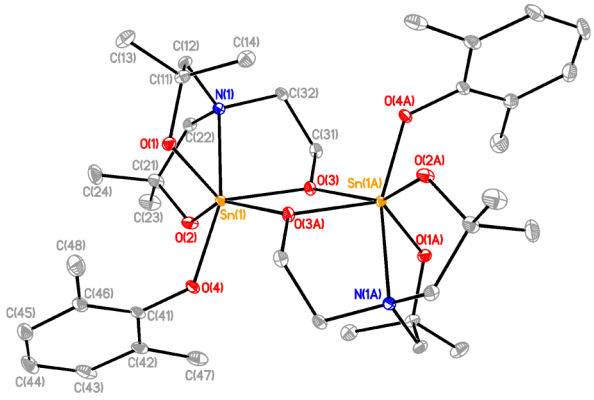


Figure 3. Molecular structure of compound **5** (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). Selected interatomic distances [Å] and angles [deg]: Sn(1)−O(1) 1.978(2), Sn(1)−O(2) 1.993(2), Sn(1)−O(3) 2.059(2), Sn(1)−O(4) 2.024(1), Sn(1)−O(3A) 2.204(1), Sn(1)−N(1) 2.401(2); O(1)−Sn(1)−O(3) 126.67(6), O(2)−Sn(1)−O(3A) 151.19(6), N(1)−Sn(1)−O(4) 158.50(6), Sn(1)−O(3)−Sn(1A) 112.31(7), C(41)−Sn(1)−O(4) 122.26(1).

the dimerization the formation of two pairs of enantiomers for both **4**·C_7H_8 and **5** is possible (Δ,Δ; Λ,Λ/Δ,Λ; Λ,Δ). In the unit cells of the single crystals actually measured the stereoisomers Δ,Λ-**4** and Δ,Λ-**5** are observed.

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The ^{119}Sn NMR spectrum of **3** in C_6D_6 shows a sharp resonance at δ −326 (**3**) and a signal of low intensity at δ −621 ($^2J(^{119}\text{Sn}\text{-}^{117}\text{Sn})$ = 217 Hz) that is assigned to the trinuclear partial hydrolysis product [(LSn-μ_3-OSnL)(LSn-μ_3-O-*t*-Bu)] [L = $N(CH_2CMe_2O)_2(CH_2CH_2O)$] (see also discussion of the ^{119}Sn solution NMR spectrum of **7** below). The strong high field chemical shift indicates higher coordination numbers at the tin atoms. Successive addition of water to the NMR sample causes the resonance at δ −621 to increase and the resonance assigned to compound **3** to decrease and to finally completely disappear. The absence of $^2J(^{119}\text{Sn}\text{-}O^{117}\text{Sn})$ satellites for the resonance at δ −326 indicates compound **3**, as in the solid state, to be monomeric in solution as well.

The ^{119}Sn NMR spectrum of compound **5** in CD_2Cl_2 exhibits a single resonance at δ −335 that lacks $^2J(^{119}\text{Sn}\text{-}O^{117}\text{Sn})$ satellites. In agreement with the chemical shift observed for compound **3**, it is assigned to the monomeric structure. A monomer−dimer equilibrium that is fast on the ^{119}Sn NMR time scale and that lies on the monomer site cannot be ruled out, however. This was not investigated further.

The ^{119}Sn NMR spectra in CD_2Cl_2 of compounds **4** and **6** that contain an additional methylene group in the amino-alkoxide framework show resonances at δ −400 (δ −395, T = 223 K) (**4**) respectively at δ −417 (**6**). In case of compound **6** there is an additional signal of low intensity (8%) at δ −431 that is not assigned. The significant highfield shifts as compared to compounds **3** and **5** indicate higher coordination numbers at the tin atoms by dimerization via intermolecular $(CH_2)O\rightarrow Sn$ interactions. This is confirmed by the ^{1}H and ^{13}C NMR spectra showing strong downfield shifts of the CH_2O and CH_2O resonances for compounds **4** (δ ^{1}H 4.28, δ ^{13}C 68.5) and **6** (δ ^{1}H 4.31, δ ^{13}C 68.8) as compared with **3** (δ ^{1}H 3.85, δ ^{13}C 58.4) and **5** (δ ^{1}H 3.89, δ ^{13}C 58.7), respectively. The assignment of the resonances was supported by ^{1}H-^{13}C HSQC NMR experiments.

The partial hydrolysis of the stannatranes **3** and **5** gave the novel tin oxoclusters **7** and **8**, respectively as colorless crystalline materials that show good solubility in dichloromethane and chloroform (Schemes 5, 6).

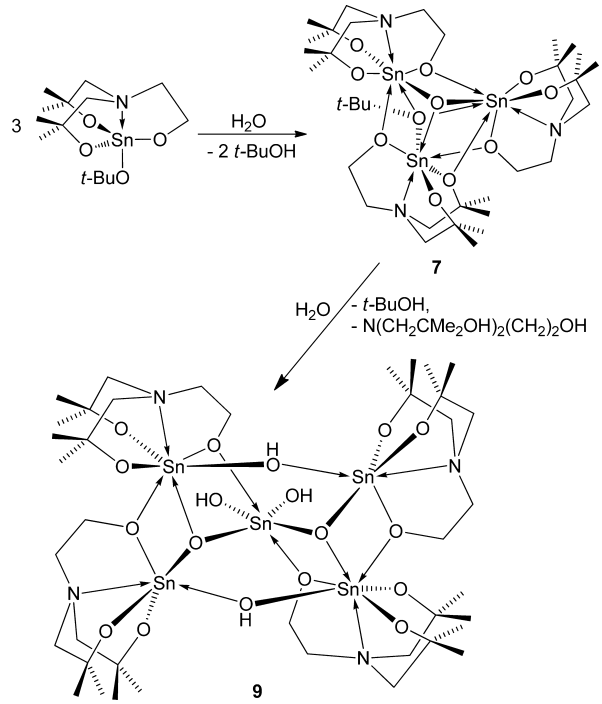
The molecular structures of compounds **7** and **8**, as its toluene solvate **8**·0.5C_7H_8, as determined by single crystal X-ray diffraction analysis, are shown in Figures 4 and 5, respectively. Selected interatomic distances and angles are summarized in Table 1.

The molecular structures of both compounds can formally be interpreted as being composed of the distannoxane moiety LSnOSnL that is complexed by the alkoxido-stannatrane LSnOR to give the cluster of the type [(LSnOSnL)(LSnOR)] (L = $N(CH_2CMe_2O)_2(CH_2CH_2O)$, R = *t*-Bu (**7**), 2,6-$Me_2C_6H_3$ (**8**·0.5C_7H_8)). Alternatively, compound **7** can also be seen as [*t*-BuO$(LSn)_3O$] in which three LSn^+ cations are bridged by one μ_3-oxido, O^{2-} (O11) and one μ_3-*t*-butoxido, *t*-BuO^-, ligand.

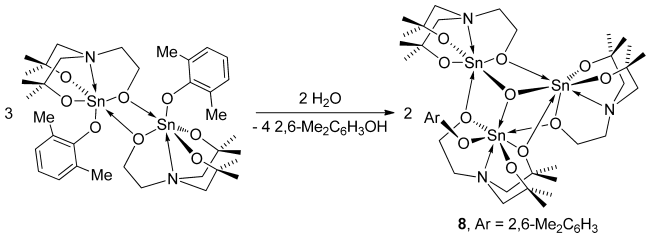
The unit cell of **7** contains four Sn_3-clusters. Two of these clusters contain atrane cages showing Δ, Δ, Δ - and the other two clusters contain atrane cages showing Λ, Λ, Λ -stereochemistry. The situation in **8**·0.5C_7H_8 is analogous with, however, two Sn_3-clusters in the unit cell.

In compound **7** the Sn(1), Sn(2), and Sn(3) atoms are heptacoordinated and adopt distorted pentagonal bipyramidal configurations with O(1)/O(11), O(5)/O(11), and O(7)/O(11), respectively, occupying the axial positions. They are linked by one μ_3-oxido bridge (O(11)), one μ_3-*tert*-butoxido

Scheme 5. Synthesis of Compounds 7 and 9



Scheme 6. Synthesis of Compound 8



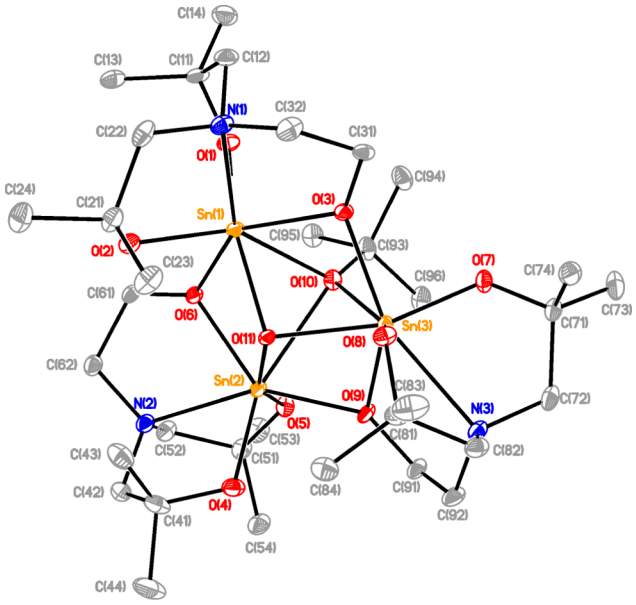


Figure 4. Molecular structure of compound **7** (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme).

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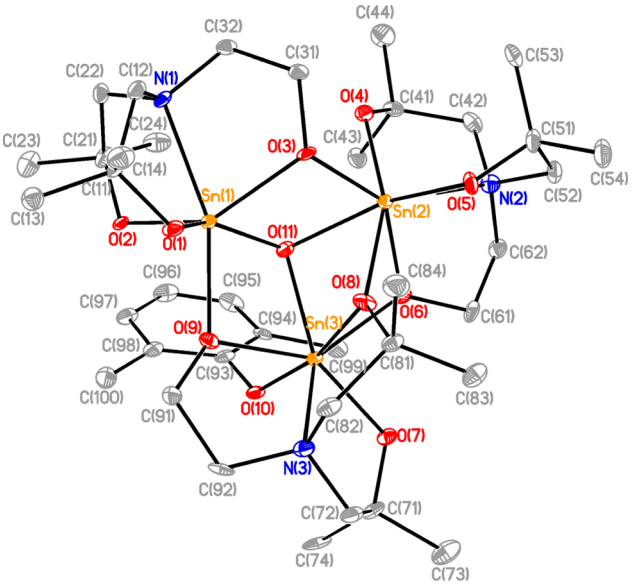

Figure 5. Molecular structure of compound **8**·0.5C_7H_8 (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). The solvent molecule was removed by the Squeeze routine of the program Platon.[38].

bridge, and three atrane-μ_2-oxygen atoms (O(3), O(6), O(9)). The coordination pattern in compound **8**·0.5C_7H_8 slightly differs. The tin(IV) oxocluster **8**·0.5C_7H_8 consists of one hexa- (Sn1) and two hepta-coordinated (Sn(2), Sn(3)) tin atoms which adopt distorted octahedral (Sn(1)) or pentagonal bipyramidal (Sn(2), Sn(3)) configurations, respectively. They are linked by a central μ_3-oxido (O(11)) bridge and four atrane-μ_2-oxygen atoms (O(3), O(6), O(8), O(9)), whereas the aryl-bound oxygen atom is not involved in any bridge. This is the result of the aryloxido substituent being cis to the μ_3-oxido (O(11)) bridge; in contrast to the *t*-butoxido substituent in **7** (Figure 6).

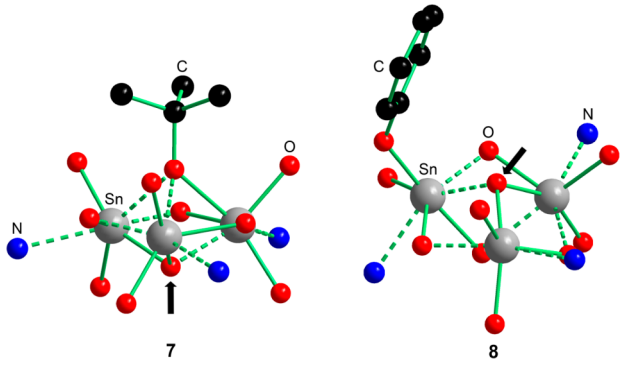

Figure 6. Simplified molecular structures (ball and stick) of compounds **7** (left) and **8** (right) showing the *t*-butoxido substituent in **7** to be trans and the aryloxido substituent in **8** to be cis to the μ_3-oxido (O(11)) bridge, as indicated by the black arrow. All carbon atoms of the alkanolamine ligands and the methyl substituents at the aryloxido group are omitted.

The O–Sn distances in compounds **7**/**8**·0.5C_7H_8 vary between 1.976(2)/1.978(3) Å and 2.430(2)/2.277(3) Å with the bridging O–Sn distances being longer than nonbridging ones. The N–Sn distances vary between 2.306(3) Å and 2.485(4) Å (**8**·0.5C_7H_8) respectively 2.418(2) Å and 2.487(2) Å (**7**) with the latter being the longest N–Sn distance in stannatranes reported so far.

The ^{119}Sn NMR spectrum in C_6D_6 of single crystals of **7** the purity of which had been confirmed by powder X-ray diffraction analysis (see Supporting Information, Figure S2) and elemental analysis shows a resonance at −621 ($^2J(^{119}\text{Sn}\text{-}^{117/119}\text{Sn})$ = 217 Hz). The satellite-to-signal-to-satellite integral ratio of 7.7:84.6:7.7 is consistent with the trimeric structure of **7** to be retained in solution.

The ^{119}Sn NMR spectrum of **8**·0.5C_7H_8 in $CDCl_3$ shows three equally intense resonances at δ −533 ($^2J(^{119}\text{Sn}\text{-}^{117/119}\text{Sn})$ = 309 Hz, 225 Hz), −634 ($^2J(^{119}\text{Sn}\text{-}^{117/119}\text{Sn})$ = 222 Hz, 90 Hz), and −703 ($^2J(^{119}\text{Sn}\text{-}^{117/119}\text{Sn})$ = 306 Hz, 89 Hz) indicating the cluster to be kinetically inert on the corresponding NMR time scale. The same holds for the ^{1}H and ^{13}C NMR spectra showing the expected resonances for the magnetically non-equivalent CH_2, $C(Me)_2$, and C*Me* protons and carbon atoms, respectively.

The ESI MS spectra of **7** and **8** show mass clusters centered at *m*/*z* = 527.2, 846.3, and 978.2 which are assigned to [**1** + LSn]$^+$, [LSnLHSnL + H]$^+$, and [$(LSn)_2O$ + LSn]$^+$ (L = $N(CH_2CMe_2O)_2(CH_2CH_2O)$), respectively. The latter mass cluster is also present in the ESI MS spectrum of the *t*-butoxido-substituted stannatrane **3** under the experimental conditions employed.

The hydrolysis of the *t*-butoxido-substituted stannatrane **3** in CD_2Cl_2 solution to which had been added one droplet of water was studied in more detail by time-dependent ^{119}Sn NMR spectroscopy (Figure 7).

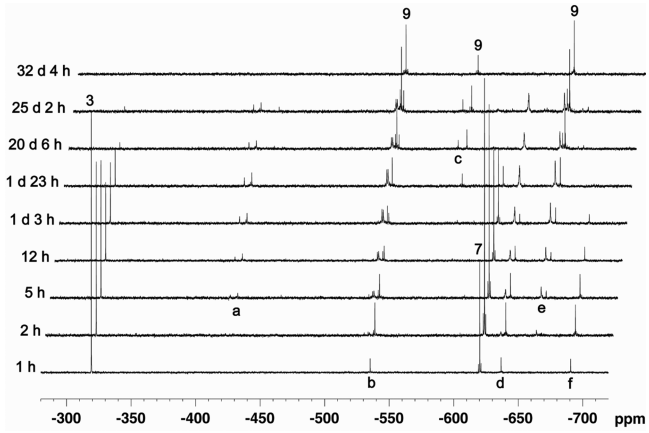

Figure 7. Stacked plot of time-dependent ^{119}Sn NMR spectra of a solution of compound **3** in CD_2Cl_2 to which had been added a droplet of water.

In contrast to the hydrolysis in benzene that exclusively gave the trinuclear tin oxocluster **7** (see discussion above), the hydrolysis in CD_2Cl_2 appears to be more complex. Thus, the spectrum recorded after 1 h showed, in addition to the signal assigned to **7**, three equally intense resonances at δ −535 ($J(^{119}\text{Sn-O-}^{117/119}\text{Sn})$ 248, 300 Hz; signal b), −637 ($J(^{119}\text{Sn-O-}^{117/119}\text{Sn})$ 125, 245 Hz; signal d) and −691 ($J(^{119}\text{Sn-O-}^{117/119}\text{Sn})$ 126, 298 Hz, signal f). With caution and in analogy to the structure of the trinuclear tin oxocluster **8**·0.5C_7H_8 (Figures 5, 6), these resonances are assigned to an isomer of **7** in which the *t*-butoxido substituent is cis to the μ_3-oxido bridge. After 5 h the intensity of the signals (b), (d), and (f) reached a

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Table 1. Selected Bond Distances (Å) and Angles (deg) for Compounds 7 and 8·0.5C_7H_8

	7	8·0.5C_7H_8		7	8·0.5C_7H_8
Sn(1)−O(1)	1.981(2)	1.993(3)	Sn(2)−O(10)	2.430(2)	
Sn(1)−O(2)	2.015(2)	1.977(3)	Sn(2)−O(11)	2.054(2)	2.087(2)
Sn(1)−O(3)	2.119(2)	2.142(3)	Sn(2)−N(2)	2.431(2)	2.485(3)
Sn(1)−O(6)	2.122(2)		Sn(3)−O(3)	2.109(2)	
Sn(1)−O(9)		2.109(3)	Sn(3)−O(6)		2.209(3)
Sn(1)−O(10)	2.411(2)	2.033(3)	Sn(3)−O(7)	1.981(2)	2.013(3)
Sn(1)−O(11)	2.047(2)	2.306(3)	Sn(3)−O(8)	2.012(2)	2.081(3)
Sn(1)−N(1)	2.418(2)	2.124(3)	Sn(3)−O(9)	2.090(2)	2.193(3)
Sn(2)−O(3)		2.004(3)	Sn(3)−O(10)	2.297(2)	2.010(3)
Sn(2)−O(4)	2.003(2)	1.978(3)	Sn(3)−O(11)	2.089(2)	2.100(3)
Sn(2)−O(5)	1.976(2)	2.103(3)	Sn(3)−N(3)	2.487(2)	2.389(3)
Sn(2)−O(6)	2.110(2)	2.277(3)	Sn(1)···Sn(2)	3.198(3)	
Sn(2)−O(8)		2.078(3)	Sn(1)···Sn(3)	3.1835(3)	
Sn(2)−O(9)	2.108(2)		Sn(2)···Sn(3)	3.187(3)	3.1403(5)
O(1)−Sn(1)−O(2)	105.9(1)	108.2(1)	O(5)−Sn(2)−O(11)	155.0(1)	150.8(1)
O(1)−Sn(1)−O(3)	101.6(1)	92.6(1)	O(5)−Sn(2)−N(2)	78.3(1)	75.0(1)
O(1)−Sn(1)−O(6)	89.7(1)		O(6)−Sn(3)−O(7)		79.1(1)
O(1)−Sn(1)−O(9)		87.4(1)	O(6)−Sn(2)−O(8)		73.4(1)
O(1)−Sn(1)−O(10)	91.7(1)		O(6)−Sn(2)−O(9)	136.5(1)	
O(1)−Sn(1)−O(11)	156.5(1)	146.9(1)	O(6)−Sn(2)−O(10)	69.1(1)	
O(1)−Sn(1)−N(1)	79.1(1)	81.1(1)	O(6)−Sn(2)−O(11)	76.7(1)	70.7(1)
O(2)−Sn(1)−O(3)	131.2(1)	142.3(1)	O(6)−Sn(2)−N(2)	71.9(1)	71.2(1)
O(2)−Sn(1)−O(6)	83.8(1)		O(8)−Sn(2)−O(11)		70.9(1)
O(2)−Sn(1)−O(9)		89.0(1)	O(8)−Sn(2)−N(2)		126.1(1)
O(2)−Sn(1)−O(10)	147.8(1)		O(9)−Sn(2)−O(10)	69.1(1)	
O(2)−Sn(1)−O(11)	91.6(1)	99.5(1)	O(9)−Sn(2)−O(11)	84.0(1)	
O(2)−Sn(1)−N(1)	75.0(1)	78.1(1)	O(9)−Sn(2)−N(2)	151.4(1)	
O(3)−Sn(1)−O(6)	136.2(1)		O(10)−Sn(2)−O(11)	65.2(1)	
O(3)−Sn(1)−O(9)		123.9(1)	O(10)−Sn(2)−N(2)	136.2(1)	
O(3)−Sn(1)−O(10)	68.2(1)		O(10)−Sn(2)−N(2)		
O(3)−Sn(1)−O(11)	77.0(1)	75.3(1)	O(11)−Sn(2)−N(2)	123.1(1)	129.5(1)
O(3)−Sn(1)−N(1)	71.6(1)	74.5(1)	O(3)−Sn(3)−O(7)	89.4(1)	
O(6)−Sn(1)−O(10)	69.3(1)		O(3)−Sn(3)−O(8)	85.4(1)	
O(6)−Sn(1)−O(11)	76.6(1)		O(3)−Sn(3)−O(9)	139.6(1)	
O(6)−Sn(1)−N(1)	152.0(1)		O(3)−Sn(3)−O(10)	70.6(1)	
O(9)−Sn(1)−O(11)		75.0(1)	O(3)−Sn(3)−O(11)	76.3(1)	
O(9)−Sn(1)−N(1)		159.0(1)	O(3)−Sn(3)−N(3)	149.8(1)	
O(10)−Sn(1)−O(11)	65.7(1)		O(6)−Sn(3)−O(8)		75.2(1)
O(10)−Sn(1)−N(1)	135.9(1)		O(6)−Sn(3)−O(9)		138.8(1)
O(11)−Sn(1)−N(1)	121.4(1)	123.1(1)	O(6)−Sn(3)−O(10)		106.3(1)
O(3)−Sn(2)−O(4)		84.1(1)	O(6)−Sn(3)−O(11)		68.3(1)
O(3)−Sn(2)−O(5)		90.7(1)	O(6)−Sn(3)−N(3)		135.6(1)
O(3)−Sn(2)−O(6)		141.1(1)	O(7)−Sn(3)−O(8)	107.0(1)	103.2(1)
O(3)−Sn(2)−O(8)		78.7(1)	O(7)−Sn(3)−O(9)	106.6(1)	141.2(1)
O(3)−Sn(2)−O(11)		74.8(1)	O(7)−Sn(3)−O(10)	91.3(1)	88.7(1)
O(3)−Sn(2)−N(2)	74.9(1)	147.6(1)	O(7)−Sn(3)−O(11)	157.2(1)	146.9(1)
O(4)−Sn(2)−O(5)	107.5(1)	110.3(1)	O(7)−Sn(3)−N(3)	76.6(1)	75.4(1)
O(4)−Sn(2)−O(6)	129.9(1)	115.3(1)	O(8)−Sn(3)−O(9)	122.6(1)	84.4(1)
O(4)−Sn(2)−O(8)		159.2(1)	O(8)−Sn(3)−O(10)	149.7(1)	168.0(1)
O(4)−Sn(2)−O(9)	84.0(1)		O(8)−Sn(3)−O(11)	89.7(1)	74.4(1)
O(4)−Sn(2)−O(10)	147.8(1)		O(8)−Sn(3)−N(3)	73.8(1)	76.0(1)
O(4)−Sn(2)−O(11)	91.9(1)	93.6(1)	O(9)−Sn(3)−O(10)	72.1(1)	87.1(1)
O(4)−Sn(2)−N(2)	74.9(1)	74.3(1)	O(9)−Sn(3)−O(11)	75.5(1)	71.2(1)
O(5)−Sn(2)−O(6)	101.2(1)	111.1(1)	O(9)−Sn(3)−N(3)	70.6(1)	69.6(1)
O(5)−Sn(2)−O(8)		81.6(1)	O(10)−Sn(3)−O(11)	67.4(1)	94.9(1)
O(5)−Sn(2)−O(9)	90.3(1)		O(10)−Sn(3)−N(3)	135.2(1)	108.9(1)
O(5)−Sn(2)−O(10)	90.5(1)		O(11)−Sn(3)−N(3)	124.1(1)	133.1(1)

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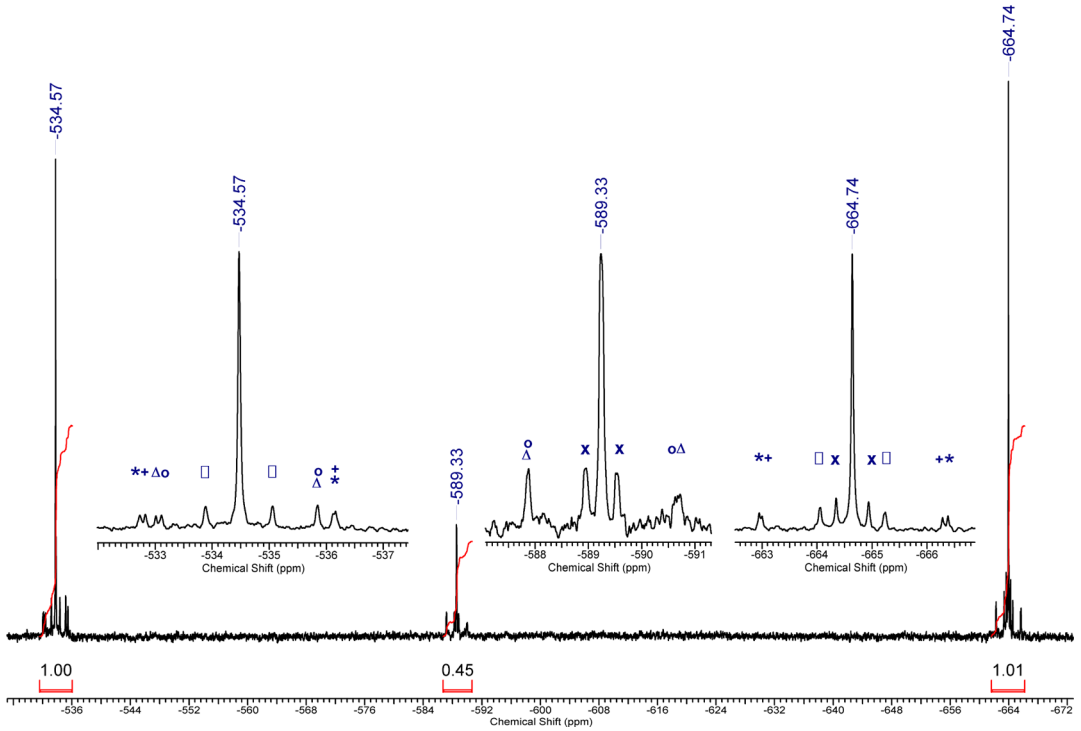

Figure 8. ^{119}Sn NMR spectrum of compound **9** in CD_2Cl_2. $^{*,+,\Delta,o,\varepsilon,\times}$ assign $J(^{119}\text{Sn-O-}^{117/119}\text{Sn})$ satellites, as discussed in the text.

maximum but had almost disappeared after 1 d and 23 h. Instead, a number of new signals (a), (c), and (e) appeared that are not assigned. Most interestingly, the spectrum had simplified after 32 d and 4 h leaving three resonances (Figures 7, 8) at δ −535 (integral 2; $J(^{119}\text{Sn-O-}^{119}\text{Sn})$ = 384, 318 Hz, $J(^{119}\text{Sn-O-}^{117}\text{Sn})$ = 369, 308 Hz, $J(^{119}\text{Sn-O-}^{119/117}\text{Sn})$ = 131 Hz), −589 (integral 1; $J(^{119}\text{Sn-O-}^{119}\text{Sn})$ = 317 Hz, $J(^{119}\text{Sn-O-}^{117}\text{Sn})$ = 306 Hz, $J(^{119}\text{Sn-O-}^{119/117}\text{Sn})$ = 65 Hz), and −665 (integral 2; $J(^{119}\text{Sn-O-}^{119}\text{Sn})$ = 384 Hz, $J(^{119}\text{Sn-O-}^{117}\text{Sn})$ = 368 Hz, $J(^{119}\text{Sn-O-}^{119/117}\text{Sn})$ = 133 Hz), $J(^{119}\text{Sn-O-}^{119/117}\text{Sn})$ = 65 Hz)).

These resonances are assigned to the pentanuclear tin oxocluster **9** (Scheme 5) a few single crystals of which, as its hexaaqua solvate **9**·6H_2O, were isolated from the NMR sample and were analyzed by X-ray diffraction.

Table 2. Selected Bond Distances (Å) for Compound 9·6H_2O

Sn(1)−O(1)	2.039(3)
Sn(1)−O(2)	1.997(3)
Sn(1)−O(3)	2.160(3)
Sn(1)−O(6)	2.189(3)
Sn(1)−O(7)	2.077(3)
Sn(1)-O(8A)	2.119(3)
Sn(1)−N(1)	2.377(4)
Sn(2)−O(4)	1.989(3)
Sn(2)−O(5)	2.026(3)
Sn(2)−O(6)	2.101(3)
Sn(2)−O(7)	2.019(3)
Sn(2)−O(8)	2.075(3)
Sn(2)−N(2)	2.316(4)
Sn(3)−O(3)	2.075(3)
Sn(3)−O(7)	2.048(3)
Sn(3)−O(9)	2.013(3)

The molecular structure of the pentanuclear tin oxocluster 9·6H_2O is shown in Figure 9. Selected bond distances and angles are given in Tables 2 and 3, respectively.

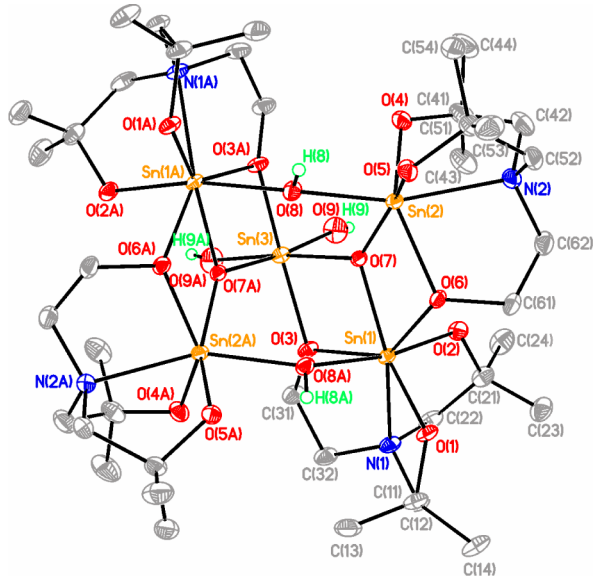

Figure 9. Molecular structure of compound **9**·6H_2O (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). The water molecules were removed by the Squeeze routine of the program Platon.[38].

Compound **9**·6H_2O is a centrosymmetric pentanuclear tin oxocluster composed of the tristannoxane moiety LSnOSn-$(OH)_2$OSnL (with Sn(2), Sn(3), Sn(2A)) to which two hydroxido-substituted stannatrane moieties LSnOH (with Sn(1), Sn(1A)) associate via (CH_2)O→Sn and (H)O→Sn donor−acceptor interactions.

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Table 3. Selected Angles (deg) for Compound 9·6H_2O

O(1)−Sn(1)−O(2)	104.4(1)	O(6)−Sn(1)−N(1)	147.5(1)	O(7)−Sn(2)−N(2)	119.4(1)
O(1)−Sn(1)−O(3)	133.9(1)	O(7)−Sn(1)−O(8A)	84.9(1)	O(8)−Sn(2)−N(2)	153.8(1)
O(1)−Sn(1)−O(6)	78.4(1)	O(7)−Sn(1)−N(1)	136.7(1)	Sn(1)−O(6)−Sn(2)	103.8(1)
O(1)−Sn(1)−O(7)	147.5(1)	O(8A)-Sn(1)−N(1)	110.6(1)	Sn(1)−O(7)−Sn(2)	111.05(1)
O(1)−Sn(1)−O(8A)	82.3(1)	O(4)−Sn(2)−O(5)	107.9(1)	Sn(1A)−O(8)−Sn(2)	141.1(2)
O(1)−Sn(1)−N(1)	75.8(1)	O(4)−Sn(2)−O(6)	142.1(1)	Sn(1)−O(3)−Sn(3)	104.3(1)
O(2)−Sn(1)−O(3)	99.4(1)	O(4)−Sn(2)−O(7)	94.7(1)	Sn(1)−O(7)−Sn(3)	108.4(1)
O(2)−Sn(1)−O(6)	88.8(1)	O(4)−Sn(2)−O(8)	99.4(1)	Sn(2)−O(7)−Sn(3)	135.1(1)
O(2)−Sn(1)−O(7)	85.4(1)	O(4)−Sn(2)−N(2)	78.4(1)	O(3)−Sn(3)−O(3A)	156.9(1)
O(2)−Sn(1)−O(8A)	169.7(1)	O(5)−Sn(2)−O(6)	77.9(1)	O(3)−Sn(3)−O(7)	74.7(1)
O(2)−Sn(1)−N(1)	78.9(1)	O(5)−Sn(2)−O(7)	154.5(1)	O(3)−Sn(3)−O(7A)	88.8(1)
O(3)−Sn(1)−O(6)	141.4(1)	O(5)−Sn(2)−O(8)	78.0(1)	O(3)−Sn(3)−O(9)	96.8(1)
O(3)−Sn(1)−O(7)	72.3(1)	O(5)−Sn(2)−N(2)	77.9(1)	O(3)−Sn(3)−O(9A)	99.8(1)
O(3)−Sn(1)−O(8A)	80.7(1)	O(6)−Sn(2)−O(7)	73.7(1)	O(7)−Sn(3)−O(7A)	89.6(2)
O(3)−Sn(1)−N(1)	70.9(1)	O(6)−Sn(2)−O(8)	115.3(1)	O(7)−Sn(3)−O(9)	91.5(1)
O(6)−Sn(1)−O(7)	70.8(1)	O(6)−Sn(2)−N(2)	76.8(1)	O(7)−Sn(3)−O(9A)	174.4(1)
O(6)−Sn(1)−O(8A)	84.9(1)	O(7)−Sn(2)−O(8)	86.7(1)	O(9)−Sn(3)−O(9A)	88.0(2)

The Sn(1) atom is seven-coordinate and adopts a distorted pentagonal-bipyramidal configuration with the O(2) and O(8A) atoms occupying the apical and the N(1), O(1), O(3), O(6) and O(7) atoms occupying the equatorial positions. The distortion from the ideal geometry is manifested by the apical O(2)−Sn(1)−O(8A) angle of 169.7(1)° and the equatorial angles ranging between 70.8(1) (O(6)−Sn(1)−O(7)) and 78.4(1)° (O(1)−Sn(1)−O(6)). The Sn(2) atom is six-coordinate by N(2), O(4), O(5), O(6), O(7), and O(8) and shows a strongly distorted octahedral configuration with trans angles ranging between 142.1(1) (O(4)−Sn(2)−O(6)) and 163.8(1)° (N(2)−Sn(2)−O(8)). The Sn(3) atom is six-coordinate as well with the O(3), O(3A), O(7), O(7A), O(9), and O(9A) occupying the edges of a distorted octahedron. The trans angles range between 156.9(1) (O(3)−Sn(3)−O(3A)) and 174.4(1)° (O(7)−Sn(3)−O(9A)).

The Sn(1)−N(1) distance of 2.377(4) Å is longer than the Sn(2)−N(2) distance of 2.316(4) Å. Both distances are shorter than the corresponding Sn−N distances in the trinuclear tin oxoclusters 7 and 8·0.5C_7H_8 as well as in compounds **4** and **5**, but longer than in compound **3**. The Sn−O distances vary between 1.989(3) (Sn(2)−O(4)) and 2.189(3)° (Sn(1)−O(6)).

The hydrolysis of compound **4** was also studied by time-dependent ^{119}Sn NMR spectroscopy (Supporting Information, Figure S3). After 10 d, the reaction seems to be finished as only one resonance at δ −432 ($\nu_{1/2}$ 13 Hz) is observed that lacks any $J(^{119}\text{Sn-O-}^{117/119}\text{Sn})$ couplings. With caution, this and the chemical shift being close to that for compound **4** (δ −400) suggest the formation of $[N(CH_2CMe_2O)_2(CH_2)_3OSnOH]_2$. However, no single crystalline material suitable for X-ray diffraction analysis could be isolated yet to confirm this hypothesis.

CONCLUSION

We have shown that the degree of self-assembly in the solid state of inorganic stannatranes can in general be controlled by modification of the steric hindrance and/or the chain length of the aminoalkoholate moiety as well as by the identity of the axial substituents. In particular, reducing the 6-fold methyl-substitution in the monomeric stannatrane N-$(CH_2CMe_2O)_3SnOC_6H_3Me_2$-2,6[23] to 4-fold methyl-substitution in compound **5** gives a dimeric structure for the latter. The same effect of dimerization is observed on going from the monomeric *t*-butoxido-substituted stannatrane **3** to the corresponding derivative **4**·C_7H_8. The latter differs in its composition from **3** by only one methylene group. It can be envisaged that further reducing the methyl-substitution to 2-fold and/or by having other chain-length combinations might give oligo- or even polymeric stannatranes.

Furthermore, we demonstrated that the controlled hydrolysis of the *t*-butoxido- as well as the aryloxido-substituted stannatranes gives access to novel tri- and pentanuclear tin oxoclusters such as **7**, 8·0.5C_7H_8, and 9·6H_2O. Apparently, aminoalkoholates are suitable ligands for stabilizing oligomeric intermediates along the hydrolysis pathway of tin alkoxides. With this approach a deeper insight into the mechanism of tin alkoxide hydrolysis should be possible and will be part of further studies.

EXPERIMENTAL SECTION

General Procedures. All experimental manipulations with tin compounds were carried out under argon atmosphere using Schlenk techniques. All solvents were purified by distillation under argon from appropriate drying agents according to standard procedures.[39] 1,1′-(2-Hydroxyethylazanediyl)bis(2-methylpropan-2-ol)[34] and tin tetra-*t*-butoxide[37] were prepared according to literature methods. The NMR spectra were recorded, unless otherwise stated, at room temperature on Bruker DRX 500, Bruker DRX 400, and Bruker DPX 300 spectrometers. Chemical shifts δ are given in ppm and are referenced to the solvent peaks with the usual values calibrated against tetramethylsilane (^{1}H, ^{13}C) and tetramethylstannane (^{119}Sn). Elemental analyses were performed on a LECO CHNS-932 analyzer. The electrospray mass spectra were recorded on a Thermoquest Finnigan instrument using CH_2Cl_2 as a mobile phase. Melting points are uncorrected and were measured on a Büchi M-560.

Crystallography. All intensity data were collected with an Xcalibur2 CCD diffractometer (Oxford Diffraction) using Mo−Kα radiation at 110 K. The structures were solved with direct methods using SHELXS-97[40] and refinements were carried out against F^2 by using SHELXL-97.[40] All non-hydrogen atoms were refined using anisotropic displacement parameters. The C−H hydrogen atoms were positioned with idealized geometry and refined using a riding model. In compound 8·0.5C_7H_8 the solvate molecule was found severely disordered and was removed by Squeeze (Platon)[38] to improve the main part of the structure. In compound 9·6H_2O the water molecules could not be located properly and were removed by the Squeeze routine of the program Platon[38] to improve the main part of the structure. CCDC-915085 (**3**), CCDC-902025 (**4**·C_7H_8), CCDC-

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902026 (**5**), CCDC-902027 (**7**), CCDC-902028 (**8**·0.5 C_7H_8), and CCDC-915086 (**9**·6H_2O) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Bis(2-methyl-2-hydroxypropyl)(3-hydroxypropyl)amine (2). A mixture of 3-aminopropan-1-ol (2.09 g, 27.8 mmol) and isobutylenoxide (4.10 g, 57.0 mmol, 2.05 equiv) was stirred in a Teflon sealed glass vessel and heated at 110 °C for 48 h. The reaction mixture was diluted with diethyl ether, dried with $MgSO_4$, filtrated, and the volatiles of the filtrate were removed under reduced pressure. Compound **2** was obtained as colorless oil (5.85 g, 26.7 mmol, 96%) that crystallized upon standing.

^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K): δ 4.07 (s, 2H, CMe_2OH), 3.68 (t, 3H, $^3J(^1H\text{-}^1H)$ = 5.9 Hz, CH_2OH), 2.69 (t, 2H, $^3J(^1H\text{-}^1H)$ = 6.8 Hz, NCH_2CH_2), 2.51 (s, 4H, NCH_2CMe_2), 1.65 (not resolved, 2H, NCH_2CH_2), 1.16 (s, 12H, $^1J(^1H\text{-}^{13}C)$ = 125.4 Hz, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$, 298 K): δ 71.1 (s, NCH_2CMe_2), 68.3 (s, $C(CH_3)_2$), 61.0 (s, NCH_2CH_2), 57.0 (s, CH_2OH), 30.1 (s, NCH_2CH_2), 28.1 (s, $C(CH_3)_2$). Mp. 53−55 °C. Anal. Calcd. for $C_{11}H_{25}NO_3$ (%): C 60.2, H 11.5, N 6.4. Found: C 59.8, H 11.5, N 6.4. MS (ESI +): m/z = 202.2 $[C_{11}H_{24}NO_2]^+$, 220.2 [**2** + H]$^+$.

Synthesis of 1-*tert*-Butanolato-(2,8,9-trioxa-5-aza-3,3,7,7-tetramethyl-1-stanna-tricyclo[3.3.3.0^{1,5}]undecane) (3). To a stirred solution of tin(IV)-*tert*-butoxide (2.65 g, 6.45 mmol) in dry toluene (120 mL) was added within 10 min at room temperature a solution of **1** (1.33 g, 6.48 mmol) in dry toluene (80 mL). After concentrating the mixture by azeotropic distillation the remaining volatiles were removed under reduced pressure. Compound **3** (2.54 g, 3.23 mmol, quantitative) was obtained as colorless solid. Single crystals were obtained from its toluene solution at 4 °C.

^{1}H NMR (300.13 MHz, CD_2Cl_2, 295 K): δ 3.85 (t, $^3J(^1H\text{-}^1H)$ = 5.4 Hz, $J(^1H\text{-}^{119}Sn)$ = 85.2 Hz, $J(^1H\text{-}^{117}Sn)$ = 82.0 Hz, 2H, CH_2O), 3.00 (t, $^3J(^1H\text{-}^1H)$ = 5.5 Hz, 2H, NCH_2CH_2), 2.83 (d, $^2J(^1H\text{-}^1H)$ = 13.2 Hz, 2H, NCH−H_ACMe$_2$), 2.71 (d, $^2J(^1H\text{-}^1H)$ = 13.2 Hz, 2H, NCH−H_BCMe$_2$), 1.29 (s, 9H, $C(CH_3)_3$), 1.27 (s, 6H, $C(CH_3)_2$), 1.26 (s, 6H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 295 K): δ 72.0 (s, $C(CH_3)_3$), 68.8 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 20.7 Hz, $C(CH_3)_2$), 68.0 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 47.6 Hz, NCH_2CMe_2), 61.6 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 52.2 Hz, NCH_2CH_2), 58.4 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 18.8 Hz, CH_2O), 33.1 (s, $^3J(^{13}C\text{-}^{117/119}Sn)$ = 26.9 Hz, $C(CH_3)_3$), 31.7 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 29.4 Hz, $C(CH_3)_2$), 31.2 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 30.0 Hz, $C(CH_3)_2$). $^{119}Sn\{^1H\}$ NMR (111.87 MHz, CD_2Cl_2, 294 K): δ −320 (s). Mp. 194−196 °C. MS (ESI +): m/z = 170.2 $[C_{10}H_{20}NO]^+$, 188.2 [**1** − OH]$^+$, 206.2 [**1** + H]$^+$, 978.2 $[(LSn)_2O + LSn]^+$, 1466.8.

Synthesis of Bis{1-*tert*-butanolato-(2,9,10-trioxa-6-aza-8,8,11,11-tetramethyl-1-stanna-tricyclo-[4.3.3.0^{1,6}]dodecane)} (4). To a stirred solution of tin(IV)-*tert*-butoxide (4.10 g, 9.97 mmol) in dry toluene (120 mL) was added within 10 min at room temperature a solution of **2** (2.19 g, 9.99 mmol) in dry toluene (80 mL). After concentrating the mixture by azeotropic distillation and recrystallization from toluene, compound **4** crystallized as its toluene solvate **4**·C_7H_8 (3.09 g, 3.40 mmol, 68%) upon storage at −15 °C.

^{1}H NMR (300.13 MHz, CD_2Cl_2, 295 K): δ 7.32−7.07 (not resolved, 2.5H, toluene), 4.28 (t, $^3J(^1H\text{-}^1H)$ = 5.1 Hz, $J(^1H\text{-}^{117/119}Sn)$ = 72.3 Hz, 2H, CH_2O), 3.15 (t, $^3J(^1H\text{-}^1H)$ = 5.1 Hz, 2H, NCH_2CH_2), 2.83 (d, $^2J(^1H\text{-}^1H)$ = 13.1 Hz, 2H, NCH−H_ACMe$_2$), 2.67 (d, $^2J(^1H\text{-}^1H)$ = 13.1 Hz, 2H, NCH−H_BCMe$_2$), 2.34 (s, 1.5H, toluene), 1.87−1.74 (not resolved, 2H, $CH_2CH_2CH_2$), 1.34 (s, $^1J(^1H\text{-}^{13}C)$ = 125.3 Hz, 6H, $C(CH_3)_2$), 1.28 (s, $^1J(^1H\text{-}^{13}C)$ = 125.8 Hz, 6H, $C(CH_3)_2$), 1.26 (s, $^1J(^1H\text{-}^{13}C)$ = 124.6 Hz, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 295 K): δ 138.1 (s, toluene), 129.2 (s, toluene), 128.4 (s, toluene), 125.5 (s, toluene), 71.3 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 37.6 Hz, $C(CH_3)_3$), 68.5 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 36.4 Hz, $C(CH_3)_2$), 68.5 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 24.8 Hz, CH_2O), 68.4 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 45.7 Hz, NCH_2CMe_2), 63.0 (s, NCH_2CH_2), 33.1 (s, $^3J(^{13}C\text{-}^{117/119}Sn)$ = 26.4 Hz, $C(CH_3)_3$), 31.8 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 32.6 Hz, $C(CH_3)_2$), 31.2 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 33.5 Hz, $C(CH_3)_2$), 30.5 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 48.7 Hz, $CH_2CH_2CH_2$), 21.4 (s, toluene). $^{119}Sn\{^1H\}$ NMR (111.87 MHz, CD_2Cl_2, 295 K): δ −400 (s). Mp. 260−262 °C (decomposition). Anal. Calcd. for $C_{30}H_{62}N_2O_8Sn_2$ (%): C 44.1, H 7.7, N 3.4. Found: C 44.5, H 7.3, N 3.3. MS (ESI +): m/z = 202.1 [**2** − OH]$^+$, 220.1 [**2** + H]$^+$, 818.4 [M+H]$^+$, 1020.3 $[\{N(CH_2CMe_2O)_2(CH_2CH_2CH_2O)Sn\}_2O$ + N-$(CH_2CMe_2O)_2(CH_2CH_2CH_2O)Sn]^+$, 1074.2.

Synthesis of Bis{1-(2,6-dimethylphenolato)-(2,8,9-trioxa-5-aza-3,3,7,7-tetramethyl-1-stanna-tricyclo[3.3.3.0^{1,5}]undecane)} (5). To a stirred solution of **3** (2.168 g, 5.50 mmol) in dry toluene (100 mL) was added a toluene solution (50 mL) of 2,6-dimethylphenol (0.672 g, 5.50 mmol). The mixture was concentrated to the half by azeotropic distillation of *t*-BuOH/toluene. Cooling to room temperature provided a colorless amorphous solid that was filtered. Recrystallization from toluene and subsequent washing with cold toluene gave colorless block-like crystals of **5** (1.799 g, 2.03 mmol, 74%).

^{1}H NMR (300.13 MHz, CD_2Cl_2, 294 K): δ 6.92 (d, $^3J(^1H\text{-}^1H)$ = 7.3 Hz, 2H, *m*-H), 6.68 (t, $^3J(^1H\text{-}^1H)$ = 7.4 Hz, 1H, *p*-H), 3.89 (t, $^2J(^1H\text{-}^1H)$ = 5.3 Hz, $J(^1H\text{-}^{117/119}Sn)$ = 88.3 Hz, 2H, CH_2O), 3.06 (t, $^2J(^1H\text{-}^1H)$ = 5.5 Hz, $J(^1H\text{-}^{117/119}Sn)$ = 17.9 Hz, 2H, NCH_2CH_2), 2.90 (d, $^2J(^1H\text{-}^1H)$ = 13.3 Hz, 2H, NCH−H_ACMe$_2$), 2.77 (d, $^2J(^1H\text{-}^1H)$ = 13.3 Hz, 2H, NCH−H_BCMe$_2$), 2.26 (s, $J(^1H\text{-}^{117/119}Sn)$ = 7.9 Hz, 6H, *o*-CH_3), 1.32 (s, 12H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 294 K): δ 157.0 (s, C_i), 129.4 (s, C_p), 128.2 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 11.7 Hz, C_m)), 120.0 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 11.7 Hz, C_o), 69.5 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 20.4 Hz, $C(CH_3)_2$), 67.0 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 47.9 Hz, NCH_2CMe_2), 61.6 (s, NCH_2CH_2), 58.7 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 17.7 Hz, CH_2O), 31.6 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 30.8 Hz, $C(CH_3)_2$), 31.1 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 31.1 Hz, $C(CH_3)_2$), 17.2 (s, *o*-(CH_3)). $^{119}Sn\{^1H\}$ NMR (111.87 MHz, CD_2Cl_2, 294 K): δ −335 (s). Mp. 194−196 °C. Anal. Calcd. for $C_{36}H_{58}N_2O_8Sn_2$ (%): C 48.9, H 6.6, N 3.2. Found: C 49.1, H 6.8, N 3.1. MS (ESI +): m/z = 188.2 [**1** − OH]$^+$, 206.2 [**1** + H]$^+$, 1416.5.

Synthesis of Bis{1-(2,6-dimethylphenolato)-(2,9,10-trioxa-6-aza-8,8,11,11-tetramethyl-1-stanna-tricyclo-[4.3.3.0^{1,6}]-dodecane)} (6). In analogy to the procedure for the synthesis of compound **5**, the reaction of **4** (1.00 g, 2.45 mmol) with 2,6-dimethylphenol (0.30 g, 2.45 mmol) provided compound **6** (0.90 g, 0.99 mmol, 81%) as colorless microcrystalline solid.

^{1}H NMR (500.13 MHz, CD_2Cl_2, 303 K): δ 6.88 (d, $^3J(^1H\text{-}^1H)$ = 7.4 Hz, 2H, *m*-H), 6.68 (t, $^3J(^1H\text{-}^1H)$ = 7.4 Hz, 1H, *p*-H), 4.31 (t, $^2J(^1H\text{-}^1H)$ = 5.0 Hz, $J(^1H\text{-}^{117/119}Sn)$ = 75.6 Hz, 2H, CH_2O), 3.23 (t, $^2J(^1H\text{-}^1H)$ = 4.7 Hz, 2H, NCH_2CH_2), 2.91 (d, $^2J(^1H\text{-}^1H)$ = 13.1 Hz, 2H, NCH−H_ACMe$_2$), 2.76 (d, $^2J(^1H\text{-}^1H)$ = 13.2 Hz, 2H, NCH−H_BCMe$_2$), 2.25 (s, 4H, *o*-(CH_3)), 2.23 (s, 2H, *o*-(CH_3)), 1.91−1.82 (not resolved, 2H, $CH_2CH_2CH_2$), 1.38 (s, 6H, $C(CH_3)_2$), 1.32 (s, 6H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125.77 MHz, CD_2Cl_2, 303 K): δ 157.8 (s, C_i), 152.6 (s, C_i), 129.6 (s, C_p), 128.8 (s, C_m), 128.0 (s, C_m), 123.4 (s, C_p), 120.3 (s, C_o), 119.2 (s, C_o), 69.1 (s, $C(CH_3)_2$), 68.8 (s, CH_2O), 68.6 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 46.8 Hz, NCH_2CMe_2), 63.0 (s, NCH_2CH_2), 31.7 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 34.1 Hz, $C(CH_3)_2$), 30.5 (s, $J(^{13}C\text{-}^{117/119}Sn)$ = 34.4 Hz, $C(CH_3)_2$), 30.5 (s, $CH_2CH_2CH_2$), 17.4 (s, *o*-CH_3), 15.9 (s, *o*-CH_3). $^{119}Sn\{^1H\}$ NMR (111.87 MHz, CD_2Cl_2, 294 K): δ −418 (s, integral 1), −431 (s, integral 0.08). Mp. 217−220 °C. Anal. Calcd. for $C_{38}H_{62}N_2O_8Sn_2$ (%):C 50.0, H 6.9, N 3.1. Found: C 49.6, H 6.5, N 3.1. MS (ESI +): m/z = 184.1 $[HN(CH_2CMe_2OH)_2$ + Na]$^+$, 202.1 [**2** − OH]$^+$, 220.1 [**2** + H]$^+$, 555.3 $[N(CH_2CMe_2O)_2(CH_2CH_2CH_2O)Sn$ + **2**]$^+$, 685.2 $[\{N(CH_2CMe_2O)_2(CH_2CH_2CH_2O)Sn\}_2O$ + H]$^+$ 1020.3 $[\{N(CH_2CMe_2O)_2(CH_2CH_2CH_2O)Sn\}_2O$ + N-$(CH_2CMe_2O)_2(CH_2CH_2CH_2O)Sn]^+$, 1074.8.

Synthesis of (μ_3-oxido)(μ_3-*tert*-Butanolato)-tris(2,8,9-trioxa-5-aza-3,3,7,7-tetramethyl-1-stanna-tricyclo[3.3.3.0^{1,5}]-undecane) [(μ_3-O)(μ_3-Ot-Bu){Sn(OCH$_2$CH$_2$)(OCMe$_2$CH$_2$)$_2$N}$_3$] (7). To a solution of **3** (1.12 g, 2.85 mmol) in dichloromethane water (slight excess) was added to form a two-phase system. Crystallization of the product began at the phase boundary and within hours compound **7** (0.41 g, 0.39 mmol, 41%) crystallized as colorless blocks which assembled at the bottom of the flask. The crystalline material was isolated, dried under reduced pressure, and the homogeneity of the bulk material was confirmed by elemental analysis and powder X-ray diffraction analysis.

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^{1}H NMR (400.13 MHz, CD_2Cl_2, 300 K): δ 4.09−3.92 (m, 1H, OCH_2), 3.92−3.66 (not resolved, 4H, OCH_2), 3.66−3.52 (m, 1H, OCH_2), 3.15−2.30 (not resolved, 18H, NCH_2), 1.50−1.00 (not resolved, 45H, CH_3). ^{119}Sn{^{1}H} NMR (111.86 MHz, C_6D_6, 298 K): δ −621 (s, $^2J(^{119}\text{Sn-}^{117/119}\text{Sn})$ = 217 Hz). Mp. 252−253 °C (decomposition). Anal. Calcd. for $C_{34}H_{69}N_3O_{11}Sn_3$ (%): C 38.8, H 6.6, N 4.0. Found: C 38.7, H 6.6, N 3.9. MS (ESI +): m/z = 170.1 $[C_{10}H_{20}NO]^+$, 188.2 [**1** − OH]$^+$, 206.2 [**1** + H]$^+$, 527.2 [**1** + LSn]$^+$, 846.3 [LSnLHSnL + H]$^+$, 978.2 [$(LSn)_2O$ + LSn]$^+$, 1455.3, 1467.5, 1806.7, 1825.6.

Synthesis of (μ_3-oxido)-(2,6-Dimethylphenolato)-tris(2,8,9-trioxa-5-aza-3,3,7,7-tetramethyl-1-stanna-tricyclo[3.3.3.0$^{1.5}$]-undecane) [(μ_3-O)(2,6-$Me_2C_6H_3$-O){Sn(OCH_2CH_2)-($OCMe_2CH_2$)$_2$N}$_3$] (8). A solution of **5** (1.16 g, 1.31 mmol) in toluene was stored at −20 °C in a Schlenk flask that had not been closed properly. Within several weeks and after diffusion of water, the tin oxocluster **8** (0.54 g, 0.47 mmol, 54%) crystallized as its toluene solvate **8**·0.5C_7H_8 in the form of colorless plates.

^{1}H NMR (300.13 MHz, $CDCl_3$, 294 K): δ 7.30−7.21 (not resolved, 2.5H, toluene), 6.78 (d, $^3J(^1\text{H-}^1\text{H})$ = 7.4 Hz, 2H, *m*-H), 6.49 (t, $^3J(^1\text{H-}^1\text{H})$ = 7.3 Hz, 1H, *p*-H), 4.69−4.48 (not resolved, 1H, CH_2), 4.12−3.74 (not resolved, 1H, CH_2), 4.12−3.74 (not resolved, 1H, CH_2), 3.67−3.51 (not resolved, 1H, CH_2), 3.50−3.35 (not resolved, 1H, CH_2), 3.34−3.20 (not resolved, 1H, CH_2), 3.18−2.51 (not resolved, 16H, CH_2), 2.37 (s, 6H, *o*-CH_3), 2.24 (s, 1.5H, toluene), 1.44 (s, 3H, C(CH_3)$_2$), 1.38 (s, 3H, C(CH_3)$_2$), 1.32 (s, 6H, C(CH_3)$_2$), 1.24 (s, 3H, C(CH_3)$_2$), 1.17 (s, 6H, C(CH_3)$_2$), 1.10 (s, 6H, C(CH_3)$_2$), 0.97 (s, 3H, C(CH_3)$_2$), 0.92 (s, 3H, C(CH_3)$_2$), 0.89 (s, 3H, C(CH_3)$_2$). ^{119}Sn{^{1}H} NMR (111.85 MHz, $CDCl_3$, 295 K): δ −533 ($^2J(^{119}\text{Sn-}^{117/119}\text{Sn})$ = 309 Hz; 225 Hz), −634 ($^2J(^{119}\text{Sn-}^{117/119}\text{Sn})$ = 222 Hz; 90 Hz), −703 ($^2J(^{119}\text{Sn-}^{117/119}\text{Sn})$ = 306 Hz; 89 Hz). Mp. 243−245 °C (decomposition). Anal. Calcd. for $C_{38}H_{69}N_3O_{11}Sn_3$·0.5$C_7H_8$ (%): C 43.5, H 6.4, N 3.7. Found: C 43.7, H 6.3, N 3.8. MS (ESI +): m/z = 188.2 [**1** − OH]$^+$, 206.2 [**1** + H]$^+$, 339.1 [**1** + HN(CH_2CMe_2OH)(CH_2CH_2OH) + H]$^+$, 527.2 [**1** + LSn]$^+$, 846.5 [LSnLHSnL + H]$^+$, 978.3 [$(LSn)_2O$ + LSn]$^+$.

Synthesis of Bis(μ_3-oxido)-bis(μ_3-hydroxido)-tetrakis(2,8,9-trioxa-5-aza-3,3,7,7-tetramethyl-1-stanna-tricyclo[3.3.3.0$^{1.5}$]-undecane)-stannanediol (9). (A) To a solution of **3** in CD_2Cl_2 in a NMR tube was added a droplet of water. The hydrolysis of compound **3** was monitored by ^{119}Sn{^{1}H} NMR measurements, which showed that the conversion to compound **9** was completed within 32 days.

(B) In a NMR tube compound **7** was dissolved in nondried CD_2Cl_2. ^{119}Sn{^{1}H} NMR data showed that the conversion to compound **9** was completed within 10 days. A few crystals of compound **9** crystallized, as its hexaqua solvate **9**·6H_2O, as colorless blocks that proved being suitable for single crystal X-ray diffraction analysis. The NMR data of the solution before isolation of the crystals of **9**·6H_2O are given below.

^{1}H NMR (500.13 MHz, CD_2Cl_2, 303 K): δ 4.25−4.16 (not resolved, 4H, CH_2O, **9**), 3.90 (dt, $^2J(^1\text{H-}^1\text{H})$ = 10.5 Hz, $^3J(^1\text{H-}^1\text{H})$ = 4.8 Hz, 2H, CH_2O, **9**), 3.62 (dt, $^2J(^1\text{H-}^1\text{H})$ = 11.8 Hz, $^3J(^1\text{H-}^1\text{H})$ = 2.6 Hz, 2H, CH_2O, **9**), 3.60 (t, $^3J(^1\text{H-}^1\text{H})$ = 11.0 Hz, CH_2O, **1**), 3.53 (dt, $^2J(^1\text{H-}^1\text{H})$ = 11.4 Hz, $^3J(^1\text{H-}^1\text{H})$ = 4.8 Hz, 2H, NCH_2CH$_2$, **9**), 3.18 (dt, $^2J(^1\text{H-}^1\text{H})$ = 11.7 Hz, $^3J(^1\text{H-}^1\text{H})$ = 6.7 Hz, 2H, NCH_2CH$_2$, **9**), 3.07 (d, $^2J(^1\text{H-}^1\text{H})$ = 13.2 Hz, 2H, NCH−H_ACMe$_2$, **9**), 2.93−2.82 (not resolved, 4H, NCH_2CH$_2$, **9**), 2.79 (t, $^3J(^1\text{H-}^1\text{H})$ = 11.0 Hz, NCH_2CH$_2$, **1**), 2.81−2.72 (not resolved, 4H, NC$H_A H_B$CMe$_2$, **9**), 2.60 (s, NCH_2CMe$_2$, **1**), 2.63−2.49 (not resolved, 10H, NC$H_A H_B$CMe$_2$, **9**), 1.54 (s, 6H, C(CH_3)$_2$, **9**), 1.35 (s, 6H, C(CH_3)$_2$, **9**), 1.25 (s, 6H, C(CH_3)$_2$, **9**), 1.23−1.22 (not resolved, 21H, *t*-*Bu*OH, C(CH_3)$_2$, **9**), 1.22 (s, 6H, C(CH_3)$_2$, **9**), 1.17 (s, C(CH_3)$_2$, **1**), 1.17 (s, 6H, C(CH_3)$_2$, **9**), 1.15 (s, 6H, C(CH_3)$_2$, **9**), 1.12 (s, 6H, C(CH_3)$_2$, **9**), 0.30 (s, $J(^1\text{H-}^{119/117}\text{Sn})$ = 59.0 Hz, SnO*H*). ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2, 303 K): δ 71.3 (s, C(CH$_3$)$_2$, **1**), 69.7 (s, NCH$_2$CMe$_2$, **9**), 69.3 (s, NCH$_2$CMe$_2$, **1**), 69.1 (s, *t*BuOH), 68.2 (s, CH$_2$O, **9**), 67.6 (s, CH$_2$O, **9**), 67.1 (s, CH$_2$O, **9**), 66.5 (s, NCH$_2$CMe$_2$, **9**), 63.3 (s, NCH$_2$CMe$_2$, **9**), 61.9 (s, NCH$_2$CH$_2$, **1**), 61.0 (s, CH$_2$O, **1**), 60.4 (s, NCH$_2$CH$_2$, **9**), 58.2 (s, CH$_2$O, **9**), 57.6 (s, NCH$_2$CH$_2$, **9**), 56.1 (s, CH$_2$O, **9**), 33.6 (s, C(CH$_3$)$_2$, **9**), 33.2 (s, C(CH$_3$)$_2$, **9**), 32.8 (s, C(CH$_3$)$_2$, **9**), 32.2 (s, C(CH$_3$)$_2$, **9**), 31.4 (s, *t*BuOH), 31.1 (s, C(CH$_3$)$_2$, **9**), 30.4 (s, C(CH$_3$)$_2$, **9**), 28.5 (C(CH$_3$)$_2$, **1**, **9**). ^{119}Sn{^{1}H} NMR (111.87 MHz, CD_2Cl_2, 294 K): δ −535 (s, integral 2, $J(^{119}\text{Sn-}^{119}\text{Sn})$ = 384 Hz, $J(^{119}\text{Sn-}^{117}\text{Sn})$ = 369 Hz, $J(^{119}\text{Sn-}^{119}\text{Sn})$ = 318 Hz, $J(^{119}\text{Sn-}^{117}\text{Sn})$ = 308 Hz, $J(^{119}\text{Sn-}^{119/117}\text{Sn})$ = 131 Hz, Sn(2)), −589 (s, integral 1, $J(^{119}\text{Sn-}^{119}\text{Sn})$ = 317 Hz, $J(^{119}\text{Sn-}^{117}\text{Sn})$ = 306 Hz, $J(^{119}\text{Sn-}^{119/117}\text{Sn})$ = 65 Hz, Sn(3)), −665 (s, integral 2, $J(^{119}\text{Sn-}^{119}\text{Sn})$ = 384 Hz, $J(^{119}\text{Sn-}^{117}\text{Sn})$ = 368 Hz, $J(^{119}\text{Sn-}^{119/117}\text{Sn})$ = 133 Hz, $J(^{119}\text{Sn-O-}^{119/117}\text{Sn})$ = 65 Hz), Sn(1)). MS (ESI +): m/z = 188.2 [**1** − OH]$^+$, 206.2 [**1** + H]$^+$, 228.1 [**1** + Na]$^+$, 278.2, 527.2 [**1** + LSn]$^+$, 848.3, 978.2 [$(LSn)_2O$ + LSn]$^+$, 1316.7, 1386.4, 1465.4, 1485.5 [**9** − OH]$^+$, 1591.8 [**9** + 5H_2O + H]$^+$, 1634.5, 1805.2. Because only rather small amounts of **9**·6H_2O were isolated, no elemental analysis was performed.

■ ASSOCIATED CONTENT

Supporting Information

Molecular structure of compound **3** (Figure S1). X-ray powder diffraction pattern of compound **7** (Figure S2). ^{119}Sn NMR spectra showing the hydrolysis of compound **4** (Figure S3). CIF file and tables showing crystal data and structure refinement. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor Kieran Molloy on the occasion of his 60th birthday.

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