

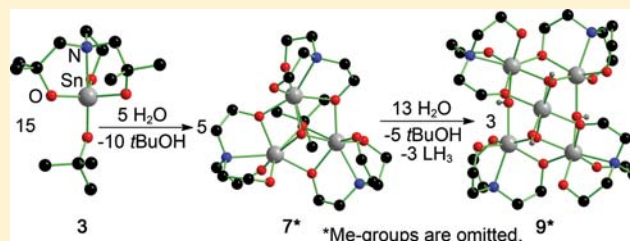
Novel Trialkanolamine Derivatives of Tin of the Type $[N(CH_2CMe_2O)_2(CH_2)_nOSnOR]_m$ ($m = 1, 2$; $n = 2, 3$; $R = t\text{-Bu}, 2,6\text{-Me}_2\text{C}_6\text{H}_3$) and Related Tri- and Pentanuclear Tin(IV) Oxoclusters. Syntheses and Molecular Structures

Thomas Zöllner and Klaus Jurkschat*

Lehrstuhl für Anorganische Chemie II, Technischen Universität Dortmund, D-44221 Dortmund, Germany

Supporting Information

ABSTRACT: The syntheses of the novel alkanolamine $N-(CH_2CMe_2OH)_2(CH_2CH_2CH_2OH)$ (**2**), the novel amino-trialkoxides of tin of the type $[N-(CH_2CMe_2O)_2(CH_2)_nOSnOR]_m$ (**3**: $m = 1, n = 2, R = t\text{-Bu}$; **4**: $m = 2, n = 3, R = t\text{-Bu}$; **5**: $m = n = 2, R = 2,6\text{-Me}_2\text{C}_6\text{H}_3$; **6**: $m = 2, n = 3, R = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) and the related trinuclear tin oxoclusters $[(LSnOSnL)(LSnOR)]$ [$L = N-(CH_2CMe_2O)_2(CH_2CH_2O)$, **7**: $R = t\text{-Bu}$; **8**: $R = 2,6\text{-Me}_2\text{C}_6\text{H}_3$] 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 ($^1H, ^{13}C, ^{119}Sn, ^1H\text{-}^1H$ cosy, $^1H\text{-}^{13}C$ HSQC) NMR spectroscopy, electrospray ionization mass spectrometry, and single crystal X-ray diffraction analyses (**3**, **4**: C_7H_8 , **5**, **7**, **8**: $0.5C_7H_8, 9\cdot 6H_2O$).



INTRODUCTION

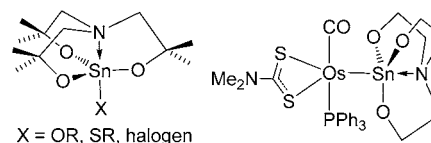
Tin alkoxides find application in sol–gel chemistry for the manufacturing of tin dioxide thin films and related materials. These materials can be used as transparent conductors in solar cells, screens, and gas detection devices.^{1–7} Furthermore, we found that alkanolamine derivatives of tin are excellent 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**) ($R = \text{alkyl, aryl}$; $X = \text{alkoxide, alkanoate, halogen, hydroxide}$) are characterized by a kinetically labile intramolecular $N \rightarrow Sn$ 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 ($X = t\text{-Bu}$).^{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, $PhHgOC(O)CH_2CH_2CH_2CH_2CH_2CMe_3$.¹⁴

Compounds of type **C** are called stannatranes, and the chemistry of the organotin derivatives $N(CH_2CH_2O)_3SnR$ ($R = \text{alkyl, aryl}$) has been extensively studied in the past decades.¹⁵ Among these, the methylstannatranes, 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 $O \rightarrow Sn$ 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 $N(CH_2CH_2O)_3SnR$ ($R = t\text{-Bu}, ^o\text{-}$

$C_6H_4OMe^{18}$) 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 $N-(CH_2CMe_2O)_3SnX$ ($X = Ot\text{-Bu}, Oi\text{-Pr}, 2,6\text{-Me}_2\text{C}_6\text{H}_3O, p\text{-}t\text{-BuC}_6\text{H}_4O, p\text{-}NO_2C_6\text{H}_4O, p\text{-}FC_6\text{H}_4O, p\text{-}PPh_2C_6\text{H}_4O, p\text{-}MeC_6\text{H}_4S, o\text{-}NH_2C_6\text{H}_4O, OCPPh_2CH_2NMe_2, Ph_2P(S)S, p\text{-}t\text{-BuC}_6\text{H}_4C(O)O, p\text{-}N[(CH_2CMe_2O)_3SnOSiMe_2]_2C_6\text{H}_4, \text{halogen}$) (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 configured 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

Received: September 20, 2012

Published: January 31, 2013

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}

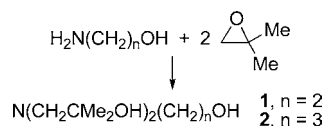
In contrast to a great variety of organotin(IV) oxoclusters,^{25–29} related clusters that lack any Sn–C bonds are scarce and to the best of our knowledge, only the five crystallographically characterized examples Sn₃O(O*i*-Bu)₁₀(HO*i*-Bu)₂,³⁰ [SnO(acac)₂]₃,³¹ Sn₄O₂(OEt)₁₀(acac)₂,¹ [SnO(O*t*-Bu)(OAc)]₆,³² and Sn₁₂O₈(OH)₄(OEt)₂₈(HOEt)₄³³ 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(CH₂CMe₂OH)₂(CH₂CH₂CH₂OH), novel inorganic stannatranes of the type [N(CH₂CMe₂O)₂(CH₂)_nOSnOR]_m (*m* = 1, 2; *n* = 2, 3; R = *t*-Bu, 2,6-Me₂C₆H₃) 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(CH₂CMe₂OH)₂(CH₂CH₂OH) (**1**),^{34a} and bis(2-methyl-2-hydroxypropyl)(3-hydroxypropyl)amine, N(CH₂CMe₂OH)₂(CH₂CH₂CH₂OH) (**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**

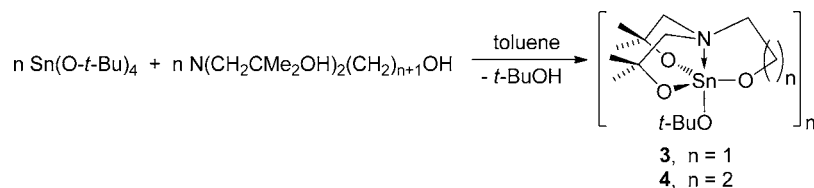


Compound **2** is a colorless oil, that crystallizes upon standing at room temperature for several days. It is well soluble in common organic solvents such as diethylether, tetrahydrofuran, chloroform, dichloromethane, and toluene. Its molecular structure including a graph set analysis of the hydrogen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

The reaction of tin tetra-*t*-butoxide, Sn(O*t*-Bu)₄, with the unsymmetrically substituted aminotrialkohols **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).

Scheme 3. Synthesis of Compounds **3** and **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·C₇H₈, 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 stannatranane **3** resembles those of the parent halogenido- and aryloxido-substituted stannatranes N(CH₂CMe₂O)₃SnX (X = Cl, Br, I, OAr; Ar = *p*-*t*-BuC₆H₄, *p*-FC₆H₄, *p*-NO₂C₆H₄, *p*-Ph₂PC₆H₄, 2,6-Me₂C₆H₃).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 ($\Delta\Sigma(\theta)^{34b} = 56.2^\circ$) 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(CH₂CMe₂O)₃SnX (X = OR, SR, halogen),²³ the compounds **4**·C₇H₈ and **5** form dimers via intermolecular O→Sn coordination to give four-membered planar Sn₂O₂ rings with intracyclic Sn(1)–O(3)/Sn(1)–O(3A) distances of 2.046(2)/2.232(2) Å (**4**·C₇H₈) and 2.059(2)/2.204(1) Å (**5**), respectively. These μ₂-O–Sn distances are comparable with those of dimeric tin(II) aminoalkoxides [MeN(CH₂CR₂O)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(O*i*-Pr)₄(HO*i*-Pr)₂]₂³⁷ (2.080(4)/2.091(4) Å), Sn₃O(O*i*-Bu)₁₀(HO*i*-Bu)₂³⁰ [2.096(3)/2.129(4) Å] and Sn₁₂O₈(OH)₄(OEt)₂₈(HOEt)₄³³ [1.93(1)/2.13(1)]. To the best of our knowledge the compounds **4**·C₇H₈ 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 4. Synthesis of Compounds 5 and 6

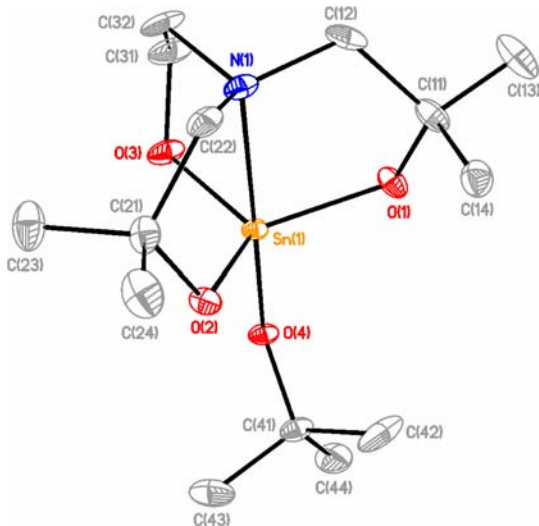
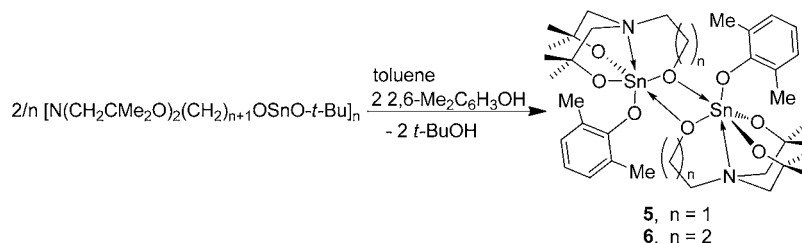


Figure 1. Molecular structure of compound 3 (molecule A, ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). Selected interatomic distances [Å] and angles [deg]: Sn(1)–O(1) 1.965(2), Sn(1)–O(2) 1.976(2), Sn(1)–O(3) 1.985(2), Sn(1)–O(4) 1.949(2), Sn(1)–N(1) 2.275(2); 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] ($4\text{-C}_7\text{H}_8/5$) from 180°. The tin atoms are displayed from the plane $E(O_{\text{atrane}})$ defined by the oxygen atoms O(1)–O(3) by 0.3663(2) Å ($4\text{-C}_7\text{H}_8$) and 0.4663(1) Å (**5**), respectively, in direction to the exocyclic ligand. The N–Sn distances are 2.390(2) Å ($4\text{-C}_7\text{H}_8$) 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 $\text{N}(\text{CH}_2\text{CMe}_2\text{O})_3\text{SnX}$ (X = OR, SR, halogen) (2.232(2)–2.295(3) Å)²³ or monoorgano-stannatranes of the type $[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{SnR}]_n$ (R = Me, $n = 3$, $d(\text{N}–\text{Sn}) = 2.28(1)$ Å;¹⁶ R = *t*-Bu, $n = 1$, $d(\text{N}–\text{Sn}) = 2.324$ Å;¹⁷ R = $\text{C}_6\text{H}_4\text{-}o\text{-OMe}$, $n = 1$, $d(\text{N}–\text{Sn}) = 2.323(7)$ Å¹⁸) are considerable shorter while the only longer N–Sn distance of 2.422(4) Å was found for $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{SnOs}(\eta\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$.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 $4\text{-C}_7\text{H}_8$ adopts a twist-boat conformation. Given

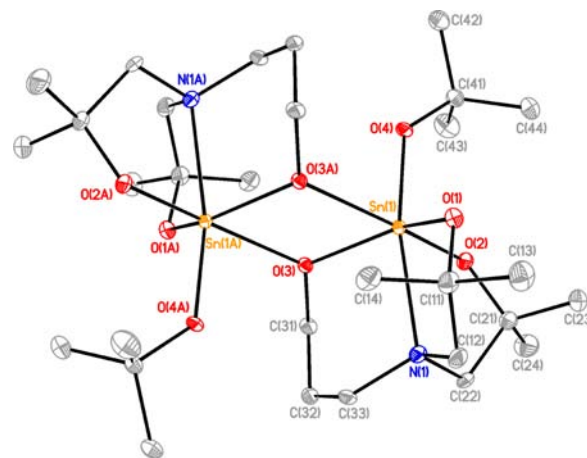


Figure 2. Molecular structure of compound $4\text{-C}_7\text{H}_8$ (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). The asymmetric unit contains a half toluene molecule which is omitted. Selected interatomic distances [Å] and angles [deg]: Sn(1)–O(1) 1.979(2), 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).

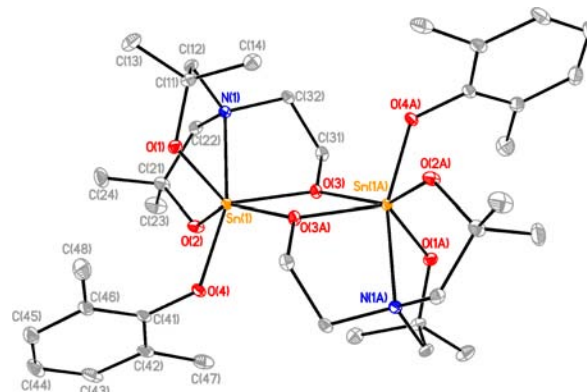


Figure 3. Molecular structure of compound 5 (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). Selected interatomic distances [Å] and angles [deg]: Sn(1)–O(1) 1.978(2), Sn(1)–O(2) 1.993(2), Sn(1)–O(3) 2.059(2), Sn(1)–O(4) 2.024(1), Sn(1)–O(3A) 2.204(1), Sn(1)–N(1) 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 $4\text{-C}_7\text{H}_8$ and **5** is possible (Δ, Δ ; $\Lambda, \Lambda/\Delta, \Lambda$; Λ, Δ). In the unit cells of the single crystals actually measured the stereoisomers $\Delta, \Lambda\text{-4}$ and $\Delta, \Lambda\text{-5}$ are observed.

The ^{119}Sn NMR spectrum of **3** in C_6D_6 shows a sharp resonance at $\delta -326$ (**3**) and a signal of low intensity at $\delta -621$ ($^2J(^{119}\text{Sn}-^{117}\text{Sn}) = 217$ Hz) that is assigned to the trinuclear partial hydrolysis product $[(\text{LSn}-\mu_3\text{-OSnL})(\text{LSn}-\mu_3\text{-O}-t\text{-Bu})]$ [$\text{L} = \text{N}(\text{CH}_2\text{CMe}_2\text{O})_2(\text{CH}_2\text{CH}_2\text{O})$] (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 $\delta -621$ 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 $\delta -326$ 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 $\delta -335$ 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 $\delta -400$ ($\delta -395$, $T = 223$ K) (**4**) respectively at $\delta -417$ (**6**). In case of compound **6** there is an additional signal of low intensity (8%) at $\delta -431$ 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 $(\text{CH}_2)\text{O} \rightarrow \text{Sn}$ interactions. This is confirmed by the ^1H and ^{13}C NMR spectra showing strong downfield shifts of the CH_2O and CH_2O resonances for compounds **4** ($\delta^1\text{H}$ 4.28, $\delta^{13}\text{C}$ 68.5) and **6** ($\delta^1\text{H}$ 4.31, $\delta^{13}\text{C}$ 68.8) as compared with **3** ($\delta^1\text{H}$ 3.85, $\delta^{13}\text{C}$ 58.4) and **5** ($\delta^1\text{H}$ 3.89, $\delta^{13}\text{C}$ 58.7), respectively. The assignment of the resonances was supported by ^1H - ^{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).

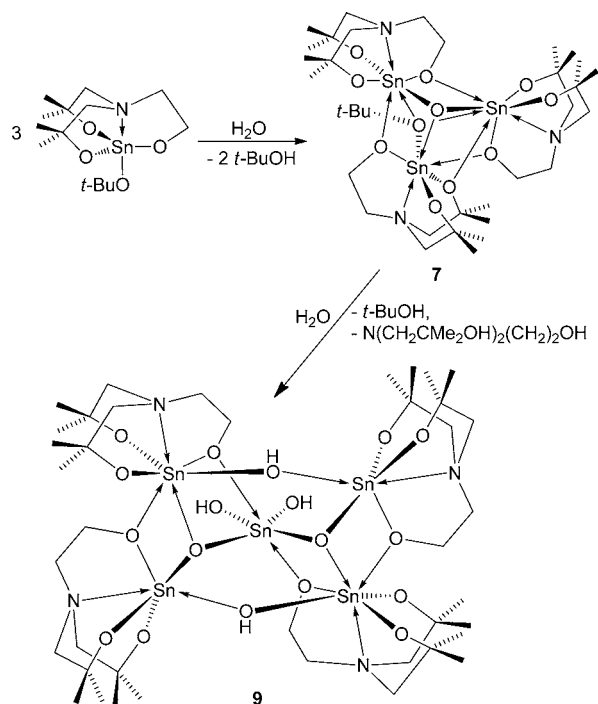
The molecular structures of compounds **7** and **8**, as its toluene solvate $8 \cdot 0.5\text{C}_7\text{H}_8$, as determined by single crystal X-ray diffraction analysis, are shown in Figures 4 and 5, respectively. Selected interatomic distances and angles are summarized in Table 1.

The molecular structures of both compounds can formally be interpreted as being composed of the distannoxane moiety LSnOSnL that is complexed by the alkoxido-stannatranes LSnOR to give the cluster of the type $[(\text{LSnOSnL})(\text{LSnOR})]$ ($\text{L} = \text{N}(\text{CH}_2\text{CMe}_2\text{O})_2(\text{CH}_2\text{CH}_2\text{O})$, $\text{R} = t\text{-Bu}$ (**7**), 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ ($8 \cdot 0.5\text{C}_7\text{H}_8$)). Alternatively, compound **7** can also be seen as $[t\text{-BuO}(\text{LSn})_3\text{O}]$ in which three LSn^+ cations are bridged by one μ_3 -oxido, O^{2-} (O11) and one μ_3 -*tert*-butoxido, $t\text{-BuO}^-$, 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 $8 \cdot 0.5\text{C}_7\text{H}_8$ 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

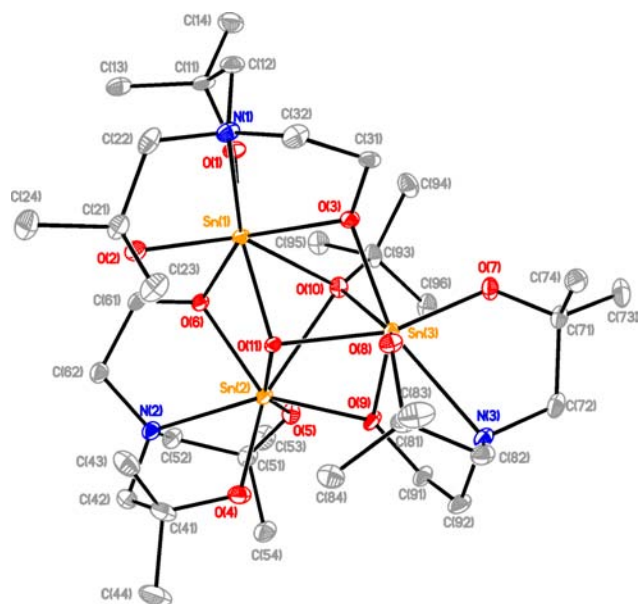
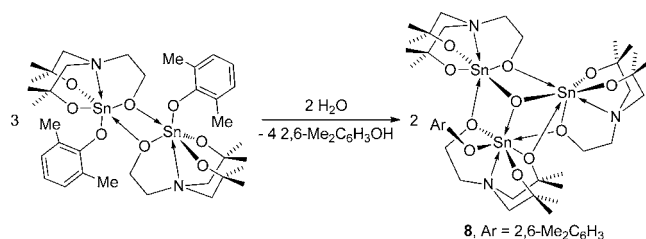


Figure 4. Molecular structure of compound **7** (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme).

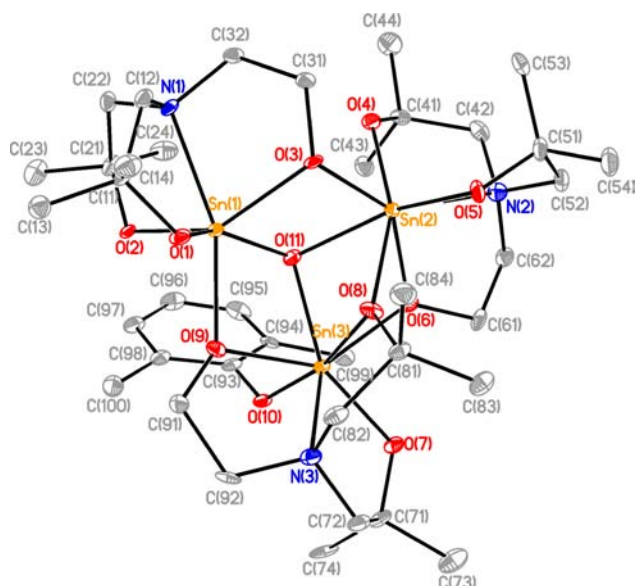


Figure 5. Molecular structure of compound $8 \cdot 0.5C_7H_8$ (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). The solvent molecule was removed by the Squeeze routine of the program Platon.³⁸

bridge, and three atrane- μ_2 -oxygen atoms (O(3), O(6), O(9)). The coordination pattern in compound $8 \cdot 0.5C_7H_8$ slightly differs. The tin(IV) oxocluster $8 \cdot 0.5C_7H_8$ 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 aryloxy substituent being cis to the μ_3 -oxido (O(11)) bridge; in contrast to the *t*-butoxy substituent in **7** (Figure 6).

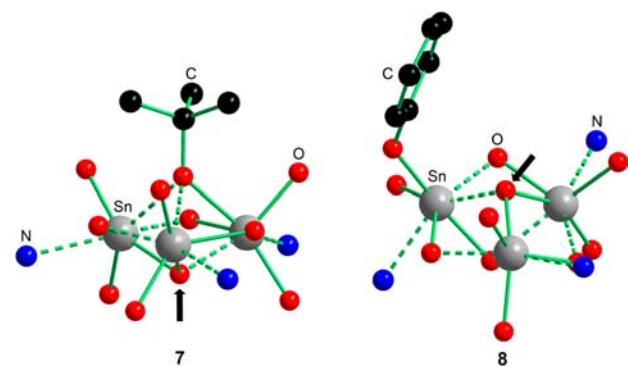


Figure 6. Simplified molecular structures (ball and stick) of compounds **7** (left) and **8** (right) showing the *t*-butoxy substituent in **7** to be trans and the aryloxy substituent in **8** to be cis to the μ_3 -oxido (O(11)) bridge, as indicated by the black arrow. All carbon atoms of the alkanolamine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

The O–Sn distances in compounds $7/8 \cdot 0.5C_7H_8$ 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 ($8 \cdot 0.5C_7H_8$) 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 ($^2J(^{119}Sn-^{117/119}Sn) = 217$ 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 $8 \cdot 0.5C_7H_8$ in $CDCl_3$ shows three equally intense resonances at $\delta -533$ ($^2J(^{119}Sn-^{117/119}Sn) = 309$ Hz, 225 Hz), -634 ($^2J(^{119}Sn-^{117/119}Sn) = 222$ Hz, 90 Hz), and -703 ($^2J(^{119}Sn-^{117/119}Sn) = 306$ Hz, 89 Hz) indicating the cluster to be kinetically inert on the corresponding NMR time scale. The same holds for the 1H and ^{13}C NMR spectra showing the expected resonances for the magnetically non-equivalent CH_2 , $C(Me)_2$, and CMe 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*-butoxy-substituted stannatranane **3** under the experimental conditions employed.

The hydrolysis of the *t*-butoxy-substituted stannatranane **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).

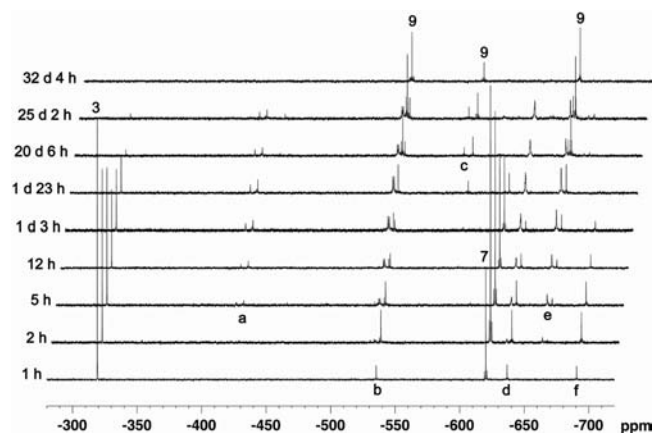


Figure 7. Stacked plot of time-dependent ^{119}Sn NMR spectra of a solution of compound **3** in CD_2Cl_2 to which had been added a droplet of water.

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 $\delta -535$ ($J(^{119}Sn-O-^{117/119}Sn) 248, 300$ Hz; signal b), -637 ($J(^{119}Sn-O-^{117/119}Sn) 125, 245$ Hz; signal d) and -691 ($J(^{119}Sn-O-^{117/119}Sn) 126, 298$ Hz, signal f). With caution and in analogy to the structure of the trinuclear tin oxocluster $8 \cdot 0.5C_7H_8$ (Figures 5, 6), these resonances are assigned to an isomer of **7** in which the *t*-butoxy substituent is cis to the μ_3 -oxido bridge. After 5 h the intensity of the signals (b), (d), and (f) reached a

Table 1. Selected Bond Distances (Å) and Angles (deg) for Compounds 7 and 8·0.5C₇H₈

| | 7 | 8·0.5C ₇ H ₈ | | 7 | 8·0.5C ₇ H 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) |

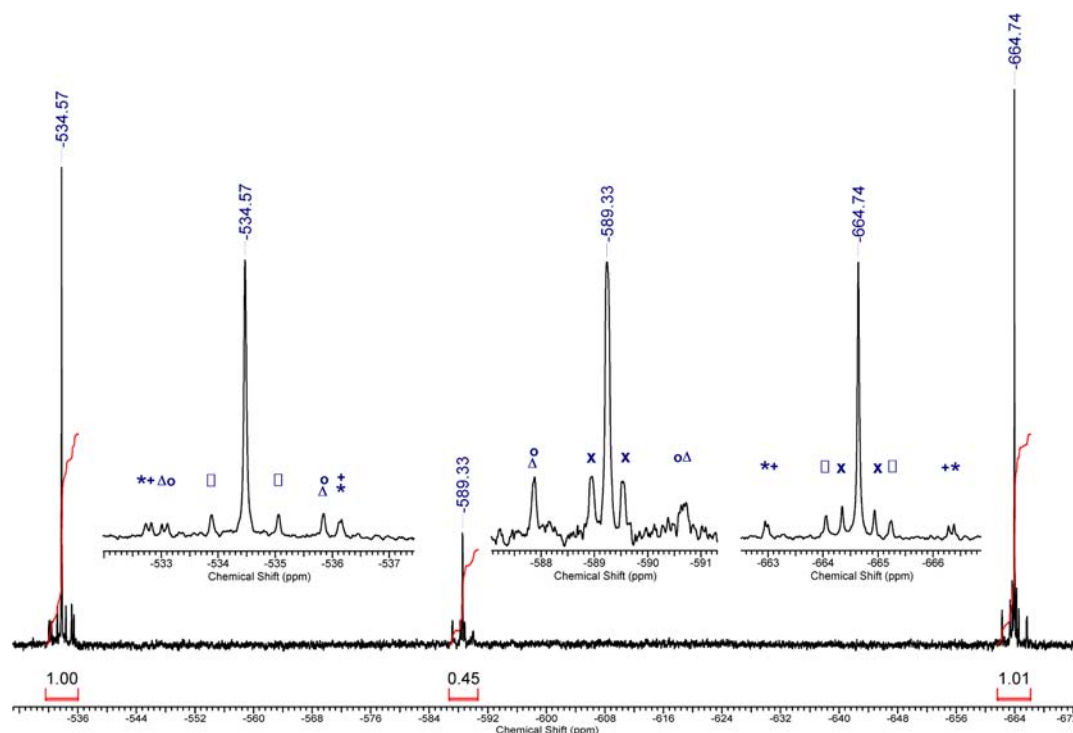


Figure 8. ^{119}Sn NMR spectrum of compound **9** in CD_2Cl_2 . *, +, Δ , o, ϵ , \times assign $J(^{119}\text{Sn-O-}^{117/119}\text{Sn})$ satellites, as discussed in the text.

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 hexaqua solvate $\mathbf{9}\cdot 6\text{H}_2\text{O}$, were isolated from the NMR sample and were analyzed by X-ray diffraction.

Table 2. Selected Bond Distances (Å) for Compound $\mathbf{9}\cdot 6\text{H}_2\text{O}$

| | |
|-------------|----------|
| 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 $\mathbf{9}\cdot 6\text{H}_2\text{O}$ is shown in Figure 9. Selected bond distances and angles are given in Tables 2 and 3, respectively.

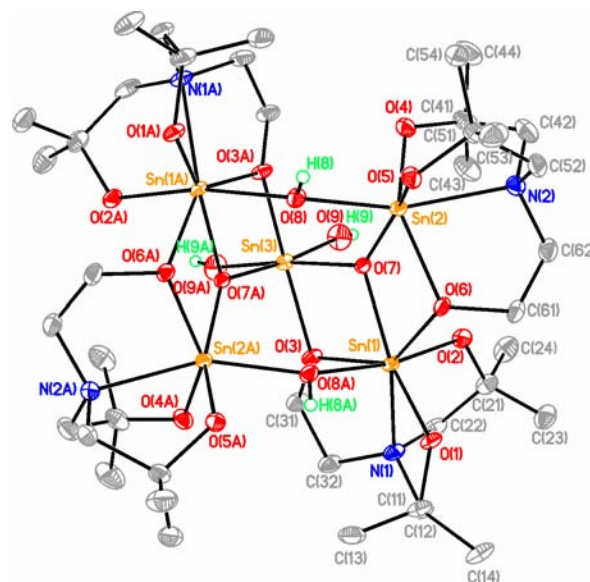


Figure 9. Molecular structure of compound $\mathbf{9}\cdot 6\text{H}_2\text{O}$ (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). The water molecules were removed by the Squeeze routine of the program Platon.³⁸

Compound $\mathbf{9}\cdot 6\text{H}_2\text{O}$ is a centrosymmetric pentanuclear tin oxocluster composed of the tristannoxane moiety $\text{LSnOSn}(\text{OH})_2\text{OSnL}$ (with Sn(2), Sn(3), Sn(2A)) to which two hydroxido-substituted stannatrane moieties LSnOH (with Sn(1), Sn(1A)) associate via $(\text{CH}_2)\text{O}\rightarrow\text{Sn}$ and $(\text{H})\text{O}\rightarrow\text{Sn}$ donor–acceptor interactions.

Table 3. Selected Angles (deg) for Compound 9·6H₂O

| | | | | | |
|------------------|----------|------------------|----------|-------------------|-----------|
| 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**·0.5C₇H₈ 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 ¹¹⁹Sn NMR spectroscopy (Supporting Information, Figure S3). After 10 d, the reaction seems to be finished as only one resonance at δ –432 (ν_{1/2} 13 Hz) is observed that lacks any J(¹¹⁹Sn–O–^{117/119}Sn) couplings. With caution, this and the chemical shift being close to that for compound **4** (δ –400) suggest the formation of [N(CH₂CMe₂O)₂(CH₂)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 stannatranane N-(CH₂CMe₂O)₃SnOC₆H₃Me₂-2,6²³ 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 stannatranane **3** to the corresponding derivative **4**·C₇H₈. 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**·0.5C₇H₈, and **9**·6H₂O. 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*-butoxide³⁷ 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 (¹H, ¹³C) and tetramethylstannane (¹¹⁹Sn). Elemental analyses were performed on a LECO CHNS-932 analyzer. The electrospray mass spectra were recorded on a Thermoquest Finnigan instrument using CH₂Cl₂ 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-*K*α radiation at 110 K. The structures were solved with direct methods using SHELXS-97⁴⁰ and refinements were carried out against F² 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**·0.5C₇H₈ 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**·6H₂O the water molecules could not be located properly and were removed by the Squeeze routine of the program Platon³⁸ to improve the main part of the structure. CCDC-915085 (**3**), CCDC-902025 (**4**·C₇H₈), CCDC-

902026 (5), CCDC-902027 (7), CCDC-902028 (8·0.5 C₇H₈), and CCDC-915086 (9·6H₂O) 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 isobutylene oxide (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 MgSO₄, filtered, 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.

¹H NMR (400.13 MHz, CDCl₃, 298 K): δ 4.07 (s, 2H, CMe₂OH), 3.68 (t, 3H, ³J(H¹-H) = 5.9 Hz, CH₂OH), 2.69 (t, 2H, ³J(H¹-H) = 6.8 Hz, NCH₂CH₂), 2.51 (s, 4H, NCH₂CMe₂), 1.65 (not resolved, 2H, NCH₂CH₂), 1.16 (s, 12H, ¹J(H¹³C) = 125.4 Hz, C(CH₃)₂). ¹³C{¹H} NMR (100.63 MHz, CDCl₃, 298 K): δ 71.1 (s, NCH₂CMe₂), 68.3 (s, C(CH₃)₂), 61.0 (s, NCH₂CH₂), 57.0 (s, CH₂OH), 30.1 (s, NCH₂CH₂), 28.1 (s, C(CH₃)₂). Mp. 53–55 °C. Anal. Calcd. for C₁₁H₂₅NO₃ (%): 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 [C₁₁H₂₄NO₃]⁺, 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.

¹H NMR (300.13 MHz, CD₂Cl₂, 295 K): δ 3.85 (t, ³J(H¹-H) = 5.4 Hz, ¹J(H¹¹⁹Sn) = 85.2 Hz, ¹J(H¹¹⁷Sn) = 82.0 Hz, 2H, CH₂O), 3.00 (t, ³J(H¹-H) = 5.5 Hz, 2H, NCH₂CH₂), 2.83 (d, ²J(H¹-H) = 13.2 Hz, 2H, NCH–H_ACMe₂), 2.71 (d, ²J(H¹-H) = 13.2 Hz, 2H, NCH–H_BCMe₂), 1.29 (s, 9H, C(CH₃)₃), 1.27 (s, 6H, C(CH₃)₂), 1.26 (s, 6H, C(CH₃)₂). ¹³C{¹H} NMR (75.48 MHz, CD₂Cl₂, 295 K): δ 72.0 (s, C(CH₃)₃), 68.8 (s, ¹J(¹³C-^{117/119}Sn) = 20.7 Hz, C(CH₃)₂), 68.0 (s, ¹J(¹³C-^{117/119}Sn) = 47.6 Hz, NCH₂CMe₂), 61.6 (s, ¹J(¹³C-^{117/119}Sn) = 52.2 Hz, NCH₂CH₂), 58.4 (s, ¹J(¹³C-^{117/119}Sn) = 18.8 Hz, CH₂O), 33.1 (s, ³J(¹³C-^{117/119}Sn) = 26.9 Hz, C(CH₃)₃), 31.7 (s, ¹J(¹³C-^{117/119}Sn) = 29.4 Hz, C(CH₃)₂), 31.2 (s, ¹J(¹³C-^{117/119}Sn) = 30.0 Hz, C(CH₃)₂). ¹¹⁹Sn{¹H} NMR (111.87 MHz, CD₂Cl₂, 294 K): δ –320 (s). Mp. 194–196 °C. MS (ESI +): *m/z* = 170.2 [C₁₀H₂₀NO]⁺, 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·C₇H₈ (3.09 g, 3.40 mmol, 68%) upon storage at –15 °C.

¹H NMR (300.13 MHz, CD₂Cl₂, 295 K): δ 7.32–7.07 (not resolved, 2.5H, toluene), 4.28 (t, ³J(H¹-H) = 5.1 Hz, ¹J(H^{117/119}Sn) = 72.3 Hz, 2H, CH₂O), 3.15 (t, ³J(H¹-H) = 5.1 Hz, 2H, NCH₂CH₂), 2.83 (d, ²J(H¹-H) = 13.1 Hz, 2H, NCH–H_ACMe₂), 2.67 (d, ²J(H¹-H) = 13.1 Hz, 2H, NCH–H_BCMe₂), 2.34 (s, 1.5H, toluene), 1.87–1.74 (not resolved, 2H, CH₂CH₂CH₂), 1.34 (s, ¹J(H¹³C) = 125.3 Hz, 6H, C(CH₃)₂), 1.28 (s, ¹J(H¹³C) = 125.8 Hz, 6H, C(CH₃)₂), 1.26 (s, ¹J(H¹³C) = 124.6 Hz, 9H, C(CH₃)₃). ¹³C{¹H} NMR (75.48 MHz, CD₂Cl₂, 295 K): δ 138.1 (s, toluene), 129.2 (s, toluene), 128.4 (s, toluene), 125.5 (s, toluene), 71.3 (s, ¹J(¹³C-^{117/119}Sn) = 37.6 Hz, C(CH₃)₃), 68.5 (s, ¹J(¹³C-^{117/119}Sn) = 36.4 Hz, C(CH₃)₂), 68.5 (s, ¹J(¹³C-^{117/119}Sn) = 24.8 Hz, CH₂O), 68.4 (s, ¹J(¹³C-^{117/119}Sn) = 45.7 Hz, NCH₂CMe₂), 63.0 (s, NCH₂CH₂), 33.1 (s, ³J(¹³C-^{117/119}Sn) = 26.4 Hz, C(CH₃)₃), 31.8 (s, ¹J(¹³C-^{117/119}Sn) = 32.6 Hz, C(CH₃)₂), 31.2 (s, ¹J(¹³C-^{117/119}Sn) = 33.5 Hz, C(CH₃)₂), 30.5 (s, ¹J(¹³C-^{117/119}Sn) = 48.7 Hz, CH₂CH₂CH₂), 21.4 (s, toluene). ¹¹⁹Sn{¹H} NMR (111.87 MHz, CD₂Cl₂, 295 K): δ –400 (s). Mp.

260–262 °C (decomposition). Anal. Calcd. for C₃₀H₆₂N₂O₈Sn₂ (%): 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 (C H₂ C M e₂ O)₂ (C H₂ C H₂ C H₂ O) S n }₂ O + N - (C H₂ C M e₂ O)₂ (C H₂ C H₂ C H₂ O) S n }⁺, 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%).

¹H NMR (300.13 MHz, CD₂Cl₂, 294 K): δ 6.92 (d, ³J(H¹-H) = 7.3 Hz, 2H, *m*-H), 6.68 (t, ³J(H¹-H) = 7.4 Hz, 1H, *p*-H), 3.89 (t, ²J(H¹-H) = 5.3 Hz, ¹J(H^{117/119}Sn) = 88.3 Hz, 2H, CH₂O), 3.06 (t, ²J(H¹-H) = 5.5 Hz, ¹J(H^{117/119}Sn) = 17.9 Hz, 2H, NCH₂CH₂), 2.90 (d, ²J(H¹-H) = 13.3 Hz, 2H, NCH–H_ACMe₂), 2.77 (d, ²J(H¹-H) = 13.3 Hz, 2H, NCH–H_BCMe₂), 2.26 (s, ¹J(H^{117/119}Sn) = 7.9 Hz, 6H, *o*-CH₃), 1.32 (s, 12H, C(CH₃)₂). ¹³C{¹H} NMR (75.48 MHz, CD₂Cl₂, 294 K): δ 157.0 (s, C_i), 129.4 (s, C_i), 128.2 (s, ¹J(¹³C-^{117/119}Sn) = 11.7 Hz, C_m), 120.0 (s, ¹J(¹³C-^{117/119}Sn) = 11.7 Hz, C_o), 69.5 (s, ¹J(¹³C-^{117/119}Sn) = 20.4 Hz, C(CH₃)₂), 67.0 (s, ¹J(¹³C-^{117/119}Sn) = 47.9 Hz, NCH₂CMe₂), 61.6 (s, NCH₂CH₂), 58.7 (s, ¹J(¹³C-^{117/119}Sn) = 17.7 Hz, CH₂O), 31.6 (s, ¹J(¹³C-^{117/119}Sn) = 30.8 Hz, C(CH₃)₂), 31.1 (s, ¹J(¹³C-^{117/119}Sn) = 31.1 Hz, C(CH₃)₂), 17.2 (s, *o*-(CH₃)). ¹¹⁹Sn{¹H} NMR (111.87 MHz, CD₂Cl₂, 294 K): δ –335 (s). Mp. 194–196 °C. Anal. Calcd. for C₃₆H₅₈N₂O₈Sn₂ (%): 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.

¹H NMR (500.13 MHz, CD₂Cl₂, 303 K): δ 6.88 (d, ³J(H¹-H) = 7.4 Hz, 2H, *m*-H), 6.68 (t, ³J(H¹-H) = 7.4 Hz, 1H, *p*-H), 4.31 (t, ²J(H¹-H) = 5.0 Hz, ¹J(H^{117/119}Sn) = 75.6 Hz, 2H, CH₂O), 3.23 (t, ²J(H¹-H) = 4.7 Hz, 2H, NCH₂CH₂), 2.91 (d, ²J(H¹-H) = 13.1 Hz, 2H, NCH–H_ACMe₂), 2.76 (d, ²J(H¹-H) = 13.2 Hz, 2H, NCH–H_BCMe₂), 2.25 (s, 4H, *o*-(CH₃)), 2.23 (s, 2H, *o*-(CH₃)), 1.91–1.82 (not resolved, 2H, CH₂CH₂CH₂), 1.38 (s, 6H, C(CH₃)₂), 1.32 (s, 6H, C(CH₃)₂). ¹³C{¹H} NMR (125.77 MHz, CD₂Cl₂, 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(CH₃)₂), 68.8 (s, CH₂O), 68.6 (s, ¹J(¹³C-^{117/119}Sn) = 46.8 Hz, NCH₂CMe₂), 63.0 (s, NCH₂CH₂), 31.7 (s, ¹J(¹³C-^{117/119}Sn) = 34.1 Hz, C(CH₃)₂), 30.5 (s, ¹J(¹³C-^{117/119}Sn) = 34.4 Hz, C(CH₃)₂), 30.5 (s, CH₂CH₂CH₂), 17.4 (s, *o*-CH₃), 15.9 (s, *o*-CH₃). ¹¹⁹Sn{¹H} NMR (111.87 MHz, CD₂Cl₂, 294 K): δ –418 (s, integral 1), –431 (s, integral 0.08). Mp. 217–220 °C. Anal. Calcd. for C₃₈H₆₂N₂O₈Sn₂ (%): 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(CH₂CMe₂OH)₂ + Na]⁺, 202.1 [2 – OH]⁺, 220.1 [2 + H]⁺, 555.3 [N(CH₂CMe₂O)₂(CH₂CH₂CH₂O)Sn + 2]⁺, 685.2 [N(CH₂CMe₂O)₂(CH₂CH₂CH₂O)Sn]₂O + H]⁺, 1020.3 [{ N (C H₂ C M e₂ O)₂ (C H₂ C H₂ C H₂ O) S n }₂ O + N - (C H₂ C M e₂ O)₂ (C H₂ C H₂ C H₂ O) S n }⁺, 1074.8.

Synthesis of (μ₃-oxido)(μ₃-tert-butanolato)-tris(2,8,9-trioxa-5-aza-3,3,7,7-tetramethyl-1-stanna-tricyclo[3.3.3.0^{1,5}]undecane) [(μ₃-O)(μ₃-Ot-Bu){Sn(OCH₂CH₂)(OCMe₂CH₂)N₃} (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.

^1H 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). $^{119}\text{Sn}\{^1\text{H}\}$ 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 $\text{C}_{34}\text{H}_{69}\text{N}_3\text{O}_{11}\text{Sn}_3$ (%): C 38.8, H 6.6, N 4.0. Found: C 38.7, H 6.6, N 3.9. MS (ESI +): $m/z = 170.1$ [$\text{C}_{10}\text{H}_{20}\text{NO}$] $^+$, 188.2 [$1 - \text{OH}$] $^+$, 206.2 [$1 + \text{H}$] $^+$, 527.2 [$1 + \text{LSn}$] $^+$, 846.3 [$\text{LSnLHSnL} + \text{H}$] $^+$, 978.2 [$(\text{LSn})_2\text{O} + \text{LSn}$] $^+$, 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 $_2$ C $_6$ H $_3$ -O){Sn(OCH $_2$ CH $_2$)-(OCMe $_2$ CH $_2$) $_2$ 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 $_7$ H $_8$ in the form of colorless plates.

^1H 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 $_3$) $_2$). $^{119}\text{Sn}\{^1\text{H}\}$ 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 $\text{C}_{38}\text{H}_{69}\text{N}_3\text{O}_{11}\text{Sn}_3\cdot 0.5\text{C}_7\text{H}_8$ (%): C 43.5, H 6.4, N 3.7. Found: C 43.7, H 6.3, N 3.8. MS (ESI +): $m/z = 188.2$ [$1 - \text{OH}$] $^+$, 206.2 [$1 + \text{H}$] $^+$, 339.1 [$1 + \text{HN}(\text{CH}_2\text{CMe}_2\text{OH})(\text{CH}_2\text{CH}_2\text{OH}) + \text{H}$] $^+$, 527.2 [$1 + \text{LSn}$] $^+$, 846.5 [$\text{LSnLHSnL} + \text{H}$] $^+$, 978.3 [$(\text{LSn})_2\text{O} + \text{LSn}$] $^+$.

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 $^{119}\text{Sn}\{^1\text{H}\}$ 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 . $^{119}\text{Sn}\{^1\text{H}\}$ 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 $_2$ O, 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 $_2$ O are given below.

^1H 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, $\text{NCH}-\text{H}_\text{A}\text{CMe}_2$, 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, $\text{NCH}_\text{A}\text{H}_\text{B}\text{CMe}_2$, 9), 2.60 (s, NCH_2CMe_2 , 1), 2.63–2.49 (not resolved, 10H, $\text{NCH}_\text{A}\text{H}_\text{B}\text{CMe}_2$, 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*-BuOH, 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, SnOH). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, CD_2Cl_2 , 303 K): δ 71.3 (s, C(CH $_3$) $_2$, 1), 69.7 (s, NCH_2CMe_2 , 9), 69.3 (s, NCH_2CMe_2 , 1), 69.1 (s, *t*BuOH), 68.2 (s, CH_2O , 9), 67.6 (s, CH_2O , 9), 67.1 (s, CH_2O , 9), 66.5 (s, NCH_2CMe_2 , 9), 63.3 (s, NCH_2CMe_2 , 9), 61.9 (s, NCH_2CH_2 , 1), 61.0 (s, CH_2O , 1), 60.4 (s, NCH_2CH_2 , 9), 58.2 (s, CH_2O , 9), 57.6 (s, NCH_2CH_2 , 9), 56.1 (s, CH_2O , 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). $^{119}\text{Sn}\{^1\text{H}\}$ 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, $J(^{119}\text{Sn}-\text{O}-^{119/117}\text{Sn}) = 65$ Hz), Sn(1)). MS (ESI +): $m/z = 188.2$ [$1 - \text{OH}$] $^+$, 206.2 [$1 + \text{H}$] $^+$, 228.1 [$1 + \text{Na}$] $^+$, 278.2, 527.2 [$1 + \text{LSn}$] $^+$, 848.3, 978.2 [$(\text{LSn})_2\text{O} + \text{LSn}$] $^+$, 1316.7, 1386.4, 1465.4, 1485.5 [$9 - \text{OH}$] $^+$, 1591.8 [$9 + 5\text{H}_2\text{O} + \text{H}$] $^+$, 1634.5, 1805.2. Because only rather small amounts of 9·6H $_2$ O 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>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: klaus.jurkschat@tu-dortmund.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

T.Z. is grateful to the Fonds der Chemischen Industrie for a scholarship. We thank Mrs. S. Marzian for recording the ESI mass spectra and the anonymous reviewers for valuable hints.

■ DEDICATION

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

■ REFERENCES

- Verdenelli, M.; Parola, S. p.; Hubert-Pfalzgraf, L. G.; Lecocq, S. *Polyhedron* **2000**, *19*, 2069–2075.
- Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33–72.
- Kim, C. G.; Chung, T.-M.; Lee, Y. K.; An, K.-S.; European Patent EP 2105444 A1, 2009.
- Schubert, U.; Huesing, N.; Lorenz, A. *Chem. Mater.* **1995**, *7*, 2010–2027.
- Severin, K. G.; Ledford, J. S. *Langmuir* **1995**, *11*, 2156–2162.
- Huang, R.; Hou, L.; Zhou, B.; Zhao, Q.; Ren, S. *J. Non-Cryst. Solids* **2005**, *351*, 23–28.
- Bulut, G.; Kayan, A. *Open Macromol. J.* **2008**, *2*, 38–42.
- Krause, J.; Richter, S.; Lindner, S.; Schmidt, A.; Jurkschat, K.; Schürmann, M.; Bradtmöller, G.; Patent DE 10 2008 021 980 A1, 2009.
- Zöllner, T.; Iovkova-Berends, L.; Dietz, C.; Berends, T.; Jurkschat, K. *Chem.—Eur. J.* **2011**, *17*, 2361–2364.
- Zschunke, A.; Tzschach, A.; Jurkschat, K. *J. Organomet. Chem.* **1976**, *112*, 273–278.
- Jurkschat, K.; Mügge, C.; Tzschach, A.; Zschunke, A.; Larin, M. F.; Pestunovich, V. A.; Voronkov, M. G. *J. Organomet. Chem.* **1977**, *139*, 279–282.
- Swisher, R. G.; Holmes, R. R. *Organometallics* **1984**, *3*, 365–369.
- Shiryayev, V. I.; Stepina, E. M.; Tandura, S. N.; Kovaleva, E. A.; Grachev, A. A.; Androsenko, S. I. *Russian Chem. Bull.* **1994**, *43*, 666–670.
- Stengel, B. F. International Patent WO/2005/058996, 2005.
- Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233–295.

- (16) Swisher, R. G.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1983**, *22*, 3692–3695.
- (17) Tzschach, A.; Jurkschat, K. *Comments Inorg. Chem.* **1983**, *3*, 35–50.
- (18) Ovcinnikov, Y.; Struchkov, Y.; Baryshok, V.; Voronkov, M. J. *Struct. Chem.* **1994**, *35*, 750–753.
- (19) (a) Mehrotra, R. C.; Gupta, V. D. *Indian J. Chem.* **1967**, *5*, 643–645. (b) E. F. Rickard, C.; R. Roper, W.; J. Woodman, T.; James Wright, L. *Chem. Commun.* **1999**, 837–838.
- (20) Karlov, S. S.; Tyurin, D. A.; Zabalov, M. V.; Churakov, A. V.; Zaitseva, G. S. *J. Mol. Struct. (Theochem)* **2005**, *724*, 31–37.
- (21) Kolosova, N. D. Z., N. N.; Shiro, V. S.; Kocheskov, K. A.; Barminova, N. P. Patent SU 643508 A1 19790125, 1979.
- (22) Li, J.; Tang, Y.-J.; Liu, H.; Dong, S.-P.; Xie, Q.-L. *Gaodeng Xuexiao Huaxue Xuebao* **1998**, *19*, 1074–1077.
- (23) Zöllner, T.; Dietz, C.; Iovkova-Berends, L.; Karsten, O.; Bradtmöller, G.; Wiegand, A.-K.; Wang, Y.; Jouikov, V.; Jurkschat, K. *Inorg. Chem.* **2012**, *51*, 1041–1056.
- (24) (a) Li, J.; Liao, R.-A.; Xie, Q.-L. *Prog. Nat. Sci.* **1994**, *4*, 68–72. (b) Mun, S.-d.; Kim, S. H.; Lee, J.; Kim, H.-J.; Do, Y.; Kim, Y. *Polyhedron* **2010**, *29*, 379–383. (c) Sudhakar, P.; Amburose, C. V.; Sundararajan, G.; Nethaji, M. *Organometallics* **2004**, *23*, 4462–4467. (d) Kemmitt, T.; Al-Salim, N. I.; Gainsford, G. J. *Inorg. Chem.* **2000**, *39*, 6067–6071.
- (25) Chandrasekhar, V.; Nagendran, S.; Baskar, V. *Coord. Chem. Rev.* **2002**, *235*, 1–52.
- (26) Davies, A. G. In *Organotin Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2004; pp 179–202.
- (27) Jurkschat, K. In *Tin Chemistry: Fundamentals, Frontiers, and Applications*; Gielen, M., Davies, A. G., Pannell, K. H., Tiekink, E. R. T., Eds.; John Wiley and Sons, Ltd: Chichester, U.K., 2008; pp 201–231.
- (28) Ribot, F. In *Tin Chemistry: Fundamentals, Frontiers, and Applications*; Gielen, M., Davies, A. G., Pannell, K. H., Tiekink, E. R. T., Eds.; John Wiley and Sons, Ltd.: Chichester, U.K., 2008; pp 69–92.
- (29) Chandrasekhar, V.; Singh, P.; Gopal, K. In *Tin Chemistry: Fundamentals, Frontiers, and Applications*; Gielen, M., Davies, A. G., Pannell, K. H., Tiekink, E. R. T., Eds.; John Wiley and Sons, Ltd: Chichester, U.K., 2008; pp 93–116.
- (30) Reuter, H.; Kremser, M. Z. *Anorg. Allg. Chem.* **1992**, *615*, 137–142.
- (31) Verdenelli, M.; Parola, S.; Lecocq, S.; Hubert-Pfalzgraf, L. G. Z. *Kristallogr.-New Cryst. Struct.* **2001**, *216*, 295.
- (32) Caruso, J.; Hampden-Smith, M. J.; Rheingold, A. L.; Yap, G. J. *Chem. Soc., Chem. Commun.* **1995**, 157–158.
- (33) Ribot, F.; Martinez-Ferrero, E.; Boubekeur, K.; Hendrickx, P. M. S.; Martins, J. C.; Van Lokeren, L.; Willem, R.; Biesemans, M. *Inorg. Chem.* **2008**, *47*, 5831–5840.
- (34) (a) Mun, S.-d.; Lee, J.; Kim, S. H.; Hong, Y.; Ko, Y.-h.; Shin, Y. K.; Lim, J. H.; Hong, C. S.; Do, Y.; Kim, Y. *J. Organomet. Chem.* **2007**, *692*, 3519–3525. (b) Kolb, U.; Dräger, M.; Dargatz, M.; Jurkschat, K. *Organometallics* **1995**, *14*, 2827–2834.
- (35) Iovkova-Berends, L.; Berends, T.; Zöllner, T.; Schollmeyer, D.; Bradtmöller, G.; Jurkschat, K. *Eur. J. Inorg. Chem.* **2012**, 3463–3473.
- (36) Berends, T.; Iovkova, L.; Bradtmöller, G.; Opper, I.; Schürmann, M.; Jurkschat, K. *Z. Anorg. Allg. Chem.* **2009**, *635*, 369–374.
- (37) Hampden-Smith, M. J.; Wark, T. A.; Rheingold, A.; Huffman, J. C. *Can. J. Chem.* **1991**, *69*, 121–129.
- (38) Spek, A. L. *Acta Crystallogr.* **2009**, *D65*, 148.
- (39) Amarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann: Oxford, U.K., 2003.
- (40) Sheldrick, G. M. *Acta Crystallogr. A* **2008**, *64*, 112.