Solution- and Solid-State Coordination Behavior of ω-Trichlorostannyl Alcohols, HO(CH₂)ₙSnCl₃ (*n* = 3−5): X-ray Diffraction, Multinuclear NMR, and AM1 Quantum Chemical Studies

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The coordination behavior of ω-trichlorostannyl alcohols of the type HO(CH₂)ₙSnCl₃ (*n* = 3−5) has been investigated by solid-state ¹³C and ¹¹⁷Sn NMR, by ¹H, ¹³C, ¹¹⁹Sn, and ¹⁷O as well as gradient-assisted 2D ¹H−¹¹⁹Sn HMQC and ¹¹⁹Sn EXSY NMR spectroscopy in CD₂Cl₂ and acetone-*d₆* solutions, by X-ray diffraction for the C5 (*n* = 5) alcohol, and AM1 quantum mechanical calculations. The crystal structure of the C5 alcohol reveals a polymeric structure that arises from significant intermolecular HO → Sn interactions of 2.356(6) Å. The tin atom is thus five-coordinate and exists in a distorted trigonal bipyramidal geometry with the oxygen and one of the chloride atoms defining the axial positions. The polymeric nature of the C5 alcohol explains its insolubility, unlike the C3 and C4 alcohols, in CD₂Cl₂ solution. In this solvent, the C3 and C4 alcohols display almost exclusively intramolecular HO → Sn coordination, resulting in five- and six-membered ring structures, respectively. In the C5 alcohol, the solid-state intermolecular HO → Sn interaction is too strong for CD₂Cl₂ to break up the polymer. The acetone-*d₆* NMR data reveal a complex coordination behavior combining five- and six-coordinated species in fast equilibrium in which HO → Sn and (CD₃)₂C=O → Sn interactions are evidenced. This behavior is accompanied by very slow hydrolysis, observed in acetone but not in dichloromethane, ascribed to limited slow acetone autocondensation.

Introduction

Monoorganotin trichlorides with various functional groups on the organic moiety were recently shown to be of interest in catalysis[1] and organic synthesis applications.[2−5] They are also key intermediates for the preparation of monoorganotin trialkoxides, which are precursors of organic−inorganic hybrid materials and clusters containing tin.[6] The stability of such organically functionalized monoorganotin trichlorides depends on the carbon chain length between the tin center and the functional group, as different coordination modes of the functional group to tin may arise upon varying the polymethylene chain length.[7−9] Such coordination has been studied for compounds with two[8] or three[9] methylene groups between the metal and the carbonyl carbon atom of an acid, ester, or amide. Recent NMR and quantum chemical studies devoted to the coordination properties of ω-(trichlorostannyl)alkyl acetates

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$(CH_3COO(CH_2)_nSnCl_3$; $n = 3-5)^{7}$ revealed that such compounds exist in solution as a mixture of a monomer with intramolecular coordination and an oligomer with intermolecular coordination in fast equilibrium on the ^1H, ^{13}C, and ^{119}Sn NMR time scales.

Of interest is the coordination to tin from the alkoxy oxygen in the monomer, as opposed to the coordination from the carbonyl oxygen in the oligomer. Further evidence that the oligomer is the cyclodimer with carbonyl coordination has recently been found in an X-ray diffraction analysis of the C4 ester.[10] It is noted that the different chemical stability of the C3 ester as compared to the C4/C5 esters is related to the observation that in the dynamic equilibrium mixture the monomeric form is predominant for the C3 ester, independent of the concentration, while in the C4/C5 esters the oligomeric form becomes increasingly predominant as the concentration increases.

ω-Trichlorostannyl alcohols of the type $HO(CH_2)_n$-$SnCl_3$ ($n = 3-5$) are likewise important synthons.[6a] The dependence of their chemical properties on the number of methylene groups between the trichlorostannyl and the hydroxy moieties prompted us to investigate their coordination properties. This report presents the results of our findings, which reveal marked differences when compared to the corresponding $CH_3COO(CH_2)_nSnCl_3$ esters. For the C5 ($n = 5$) alcohol, crystals suitable for X-ray diffraction analysis could be obtained. For solution studies, our main investigation tools are, as previously,[7] ^1H, ^{13}C, ^{119}Sn,[11a-c] and ^{17}O 1D NMR,[11d] gradient-assisted[12] $^1H-^{119}Sn$[13] heteronuclear multiple quantum correlation (HMQC) spectroscopy,[14] and for solid-state measurements, provided for comparison, ^{13}C and ^{117}Sn CP-MAS NMR.[15,16] The ^{17}O NMR spectral data are interpreted in parallel, where possible, with AM1 quantum chemical calculations[17] on charge distributions of structures showing intramolecular tin−oxygen interactions.

Table 1. Crystallographic Data and Refinement Details for HO(CH₂)₅SnCl₃

formula	$C_5H_{11}Cl_3OSn$
fw	312.2
cryst size, mm	$0.02 \times 0.24 \times 0.42$
cryst syst	monoclinic
space gp	$P2_1/c$
a, Å	7.385(2)
b, Å	11.434(2)
c, Å	12.000(2)
β, deg	95.08(2)
V, Å³	1009.3(3)
Z	4
D_{calcd}, g cm⁻³	2.054
$F(000)$	600
μ, cm⁻¹	32.65
transmission factors	0.469−1
no. of data collctd	2640
no. of unique data	2460
no. of unique data with $I \geq 3.0\sigma(I)$	1593
R	0.044
R_w	0.050
residual electron density	1.02

Experimental Section

Synthesis of the Compounds. The preparation of the C3−C5 alcohols, synthesized and characterized previously,[6a] was improved as follows. In a Schlenk tube at −20 °C, tin tetrachloride (1.96 g, 7.5 mmol) was added to a solution of 8.3 mmol of (ω-hydroxyalkyl)tricyclohexyltin in dry dichloromethane. The solution was stirred for 1 h at room temperature. After evaporation of the solvent under reduced pressure, the solid was washed five times with 20 mL of dry petroleum ether to give the following: (3-Hydroxypropyl)tin trichloride, mp 71 °C; (4-hydroxybutyl)tin trichloride, mp 52°C; (5-hydroxypentyl)tin trichloride, mp 92°C. Crystals of (5-hydroxypentyl)tin trichloride suitable for X-ray analysis were found in the crude sample.

X-ray Diffraction Analysis. Intensity data for a crystal of $HO(CH_2)_5SnCl_3$ with dimensions $0.02 \times 0.24 \times 0.42$ mm were collected at room temperature on a Rigaku AFC6R diffractometer employing the ω:2θ scan technique. Graphite monochromatized Mo Kα radiation (λ 0.710 73 Å) was used such that θ_{max} was 27.5°. The data set was corrected for Lorentz and polarization effects,[18] and an empirical absorption correction[19] was applied (range of transmission factors: 0.469−1). Crystal data are presented in Table 1. The structure was solved by direct methods[20] and refined by a full-matrix least-squares procedure based on F.[18] Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms included in the model at their calculated positions (C−H 0.97 Å); the O-H atom was not located. A σ weighting scheme was applied, i.e., $w = 1/\sigma^2(F)$, and the refinement continued until convergence. Neutral scattering factors em-

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ployed were as included in teXsan,[18] and the numbering scheme is shown in Figure 2, which was drawn with ORTEP[21] at the 50% probability level. Final refinement details are given in Table 1.

NMR Experiments. Solid State. All CP-MAS NMR spectra[15,16] were recorded on a Bruker AC250 spectrometer, operating at 89.15 and 62.93 MHz for [117]Sn and ^{13}C nuclei, respectively, under the same experimental conditions as described previously.[7]

[117]Sn rather than the more common [119]Sn spectra were recorded in order to overcome local radio interferences around 93.2 MHz.[22] Comparing [117]Sn and ^{119}Sn NMR data is no problem, since [117]Sn/[119]Sn isotopic effects are negligible.[23]

NMR Experiments. Solution State. The samples were prepared by dissolving 10 or 100 mg of compound in 500 μL of CD_2Cl_2 or $(CD_3)_2CO$. Because the $HO(CH_2)_nSnCl_3$ compounds ($n = 3-5$) are very hygroscopic, the solutions were prepared *in vacuo* under moisture-free conditions with solvents from freshly opened ampules, in NMR tubes that were subsequently sealed. Even with these precautions, the NMR spectra of all solutions tend to display spurious resonances from decomposition products upon aging, especially in acetone. All ^{1}H, ^{13}C, ^{119}Sn, and ^{17}O NMR spectra were recorded at 303 K, unless otherwise indicated, on a Bruker AMX500 spectrometer as previously described.[7,14,24-27] Chemical shifts were referenced to the residual solvent peak and converted to the standard Me_4Si scale by adding 5.32 and 53.8 ppm for ^{1}H and ^{13}C nuclei, respectively, in the case of CD_2Cl_2 and 2.04 and 29.8 ppm, respectively, in the case of $(CD_3)_2CO$. For [119]Sn chemical shifts, $\Xi = 37.290\,665$ MHz[24] was used. [17]O chemical shifts were referenced to external deionized water at 313 K. The gradient-pulsed proton-detected 1D [1]H$-$[119]Sn HMQC correlation spectra were acquired as illustrated recently.[7,12,14,25] The [119]Sn EXSY spectra[26a-c] were recorded with mixing times of 3, 10, 30, and 100 ms, as described earlier.[26d]

Quantum Chemical Calculations. The AM1 method[17a] was selected with the parameters for tin published previously[17b] for energy and charge distribution calculations, as it proved to be very efficient in applications to relatively large systems[28] containing tin atoms.[7]

Geometry optimizations were performed using the GAUSS-IAN 92 program[29] coupled to the UNICHEM[30] software package. The charge distributions were analyzed in terms of the Mulliken atomic populations.[31] All calculations were per-

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Table 2. Selected Geometric Parameters (Å, deg) for HO(CH₂)₅SnCl₃

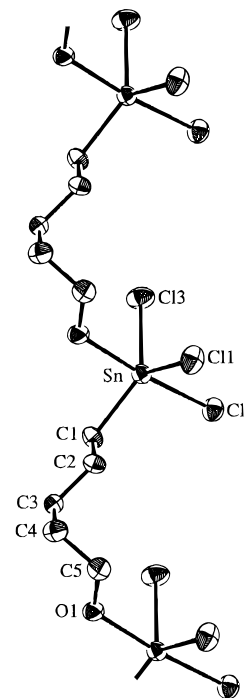|			
Sn$-$Cl(1)	2.343(2)	Sn$-$Cl(2)	2.447(2)
Sn$-$Cl(3)	2.310(2)	Sn$-$O(1)$'^a$	2.356(6)
Sn$-$C(1)	2.121(8)	O(1)$-$C(5)	1.44(1)
Cl(1)$-$Sn$-$Cl(2)	91.64(8)	Cl(1)$-$Sn$-$Cl(3)	106.05(9)
Cl(1)$-$Sn$-$O(1)$'$	84.1(2)	Cl(1)$-$Sn$-$C(1)	116.8(2)
Cl(2)$-$Sn$-$Cl(3)	94.90(8)	Cl(2)$-$Sn$-$O(1)$'$	174.7(2)
Cl(2)$-$Sn$-$C(1)	100.5(2)	Cl(3)$-$Sn$-$O(1)$'$	83.2(1)
Cl(3)$-$Sn$-$C(1)	133.7(2)	O(1)$-$Sn$-$C(1)	84.4(3)
Sn$-$O(1)$-$C(5)	127.7(5)	Sn$-$C(1)$-$C(2)	111.5(5)

^{a} Symmetry operation: $1 + x, y, z$.

Figure 1. Crystallographic numbering scheme for HO-(CH₂)₅SnCl₃ showing the polymeric nature of the compound.

formed on the CRAY Y-MP/116 computer of the Free Universities of Brussels' Computer Center.

Results and Discussion

X-ray Diffraction Analysis of HO(CH₂)₅SnCl₃. Selected interatomic parameters are collected in Table 2, and the numbering scheme employed is shown in Figure 1, which highlights the polymeric nature of the structure. The tin atom is coordinated by three chlorine atoms, the C(1) atom of the tin-bound $-(CH_2)_5OH$ substituent as well as a hydroxy oxygen atom of a symmetry-related molecule; this latter interaction leads to a linear polymer propagated by translational symmetry along the crystallographic *a*-axis. This arrangement results in a five-coordinate geometry best described as being based on a trigonal bipyramid. In this description, the trigonal, equatorial plane is defined by the Cl(1), Cl(3), and C(1) atoms with the Cl(2) and O(1) atoms occupying the axial positions; Cl(2)$-$Sn$-$O(1) is 174.7(2)°, and the tin atom lies 0.2387(6) Å out of the trigonal plane in the direction of the Cl(2) atom. As a consequence of this coordination geometry, the Sn$-$Cl(2) bond distance of 2.447(2) Å, i.e., with Cl(2) *ca.* trans to the O(1) atom, is significantly longer than the remaining

Table 3. NMR Data of HO(CH$_2$)$_n$SnCl$_3$ in CD$_2$Cl$_2$ (n = 3, 4)[a] and in the Solid State (n = 3−5)

	HO(CH$_2$)$_3$SnCl$_3$		HO(CH$_2$)$_4$SnCl$_3$	
	concd[b]	diluted[c]	concd[b]	diluted[c]
^{1}H NMR				
CH$_2$(α)	2.11 (t, 6.7)[d] [94][e]	2.10 (m)[d] [94][e]	2.49 (t, 6.2)[d] [96][e]	2.48 (t, 6.2)[d] [96][e]
CH$_2$(β)	2.17 (m)[d] [262][e]	2.17 (m)[d] [264][e]	2.23 (m)[d] [323][e]	2.15 (t, 6.2)[d] [328][e]
CH$_2$(γ)	3.87 (t, 6)[d]	3.87 (m)[d]	1.84 (m)[d]	1.84 (m)[d]
CH$_2$(δ)			4.12 (t, 5.5)[d]	4.12 (t, 5.4)[d]
OH	3.54 (bs)[d]	3.20 (t, 4)[d] [4][e]	3.96 (bs)[d]	3.40 (t, 6.2)[d]
^{13}C NMR				
CH$_2$(α)	25.8 [832/793][f]	26.1 [831/795][f]	39.2 [842/803][f]	39.5 [861/820][f]
CH$_2$(β)	24.9 [67][g]	25.6 [67][g]	25.4 [76][g]	25.8 [76][g]
CH$_2$(γ)	61.9 [82][g]	62.5 [78][g]	30.8 [33][g]	30.7 [23][g]
CH$_2$(δ)			68.2	68.5
^{119}Sn NMR[h]	−137	−131	−172	−174
^{17}O NMR[i]	17.4		34.7	

solid-state CP-MAS NMR	HO(CH$_2$)$_3$SnCl$_3$	HO(CH$_2$)$_4$SnCl$_3$	HO(CH$_2$)$_5$SnCl$_3$
^{13}C CP-MAS NMR			
CH$_2$(α)	28.6 [788][j]	45.0 [850][j]	42.5 [800][j]
CH$_2$(β)	24.8	26.4	24.8
CH$_2$(γ)	62.5	31.6	26.1
CH$_2$(δ)		70.6	30.7
CH$_2$(ϵ)			63.2
^{117}Sn CP-MAS NMR	−174	−224	−230

[a] Chemical shifts as referenced in the Experimental Section. [b] 100 mg/0.5 mL. [c] 10 mg/0.5 mL. [d] $^3J(^1\text{H}-^1\text{H})$ multiplet patterns in parentheses; bs: broad singlet; t = triplet; m = complex pattern; $^3J(^1\text{H}-^1\text{H})$ coupling constant in Hz. [e] $^nJ(^1\text{H}-^{119}\text{Sn})$ coupling constants in Hz (in brackets), as determined from 1D $^1\text{H}-^{119}\text{Sn}$ HMQC spectra. [f] $^1J(^{13}\text{C}-^{119}\text{Sn})$ and $^1J(^{13}\text{C}-^{117}\text{Sn})$ coupling constants in Hz. [g] Unresolved $^nJ(^{13}\text{C}-^{119}\text{Sn})$ and $^nJ(^{13}\text{C}-^{117}\text{Sn})$ coupling constants in Hz. [h] ^{119}Sn chemical shifts of reference compounds: HexSnCl$_3$, −3 (100 mg/0.5 mL), +5 (10 mg/0.5 mL); BuSnCl$_3$, −2 (100 mg/0.5 mL), +1 (10 mg/0.5 mL). [i] With respect to water; ^{17}O chemical shift of butanol in CD$_2$Cl$_2$: 1.0 ppm. [j] Unresolved $^1J(^{13}\text{C}-^{119}\text{Sn})$ and $^1J(^{13}\text{C}-^{117}\text{Sn})$ coupling constants in Hz.

two Sn−Cl distances of 2.343(2) and 2.310(2) Å, respectively. In the lattice there are a number of weak interchain contacts. Notably, there is a Sn⋯Cl(2)$^\text{i}$ contact of 3.588(2) Å (symmetry operation i: −x, −y, −z) and a contact of 3.206(6) Å between Cl(2) and O(1)$^\text{ii}$ (symmetry operation ii: −1 + x, 0.5 − y, −0.5 + z), presumably indicative of a Cl⋯H interaction (the O*H* atom was not located in the refinement).

Solubility of HO(CH$_2$)$_n$SnCl$_3$ Alcohols. The C3/C4 alcohols are quite soluble in standard solvents as benzene, dichloromethane, and chloroform, while the C5 alcohol is not soluble at all.[6a] All three alcohols are, however, soluble in acetone. Accordingly, the solution NMR studies of the HO(CH$_2$)$_n$SnCl$_3$ alcohols were conducted in both CD$_2$Cl$_2$ and (CD$_3$)$_2$CO solutions, and these revealed extremely solvent-dependent coordination patterns. Therefore, the results will be presented separately. On the other hand, the different solubilities are indicative of different coordinations for the C3/C4 alcohols as compared to the C5 alcohol. The C5 alcohol shows a polymeric association in the solid-state, which cannot be dissociated by CH$_2$Cl$_2$, and the C3/C4 alcohols are expected to show a lower degree of association.

Coordination Behavior of HO(CH$_2$)$_3$SnCl$_3$ and HO(CH$_2$)$_4$SnCl$_3$ in Dichloromethane. A survey of the NMR data obtained for the C3 and C4 alcohols in CD$_2$Cl$_2$ is given in Table 3. Solid-state NMR data on the three alcohols, C3, C4, and C5, are also provided.

Similar to CH$_3$COO(CH$_2$)$_3$SnCl$_3$, the NMR data of HO(CH$_2$)$_3$SnCl$_3$ and HO(CH$_2$)$_4$SnCl$_3$ are essentially concentration independent at the level of both chemical shifts and coupling constants. The strong low frequency shift of the ^{119}Sn chemical shift, lying around −135 and −173 ppm for the C3 and C4 compounds, respectively, as compared to the model compounds BuSnCl$_3$ and HexSnCl$_3$[7] (around 0 ppm) and to the CH$_3$COO(CH$_2$)$_n$-
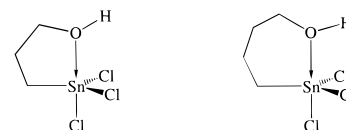
Figure 2. Structures of HO(CH$_2$)$_3$SnCl$_3$ (left) and HO(CH$_2$)$_4$SnCl$_3$ (right) in CD$_2$Cl$_2$ solution.

SnCl$_3$ esters (0 to −42 ppm)[7] indicates a strong coordination of the tin atom by the OH group. The concentration independence of the NMR data strongly suggests that this coordination is intramolecular, resulting in a five-membered ring for the C3 alcohol and a six-membered ring for the C4 alcohol (Figure 2). ^{17}O NMR data, coupled to AM1 calculations, and 1D $^1\text{H}-^{119}\text{Sn}$ HMQC experiments confirm this view.

Taking butanol ($\delta^{17}\text{O}$ = 1.0) as a reference compound for further assessing the HO → Sn interaction, the ^{17}O chemical shift of the C4 alcohol ($\delta^{17}\text{O}$ = 34.7) appears at a frequency almost twice as high as that of the C3 alcohol ($\delta^{17}\text{O}$ = 17.4) (see Table 3). Given that an increase in pure σ-electron density at oxygen induces high frequency ^{17}O shifts,[32] these data can be explained by a Gutmann pileup effect[33] at the oxygen atom.[34] However, ring formation and the resulting presence of electronegative substituents in β position relative to the oxygen atom can also result in a high frequency shift.[11e]

In order to evaluate the relative contribution of a change in electron density upon cyclization, AM1 cal-

(32) (a) Orsini, F.; Severini Ricca, G. *Org. Magn. Reson.* **1984**, *22*, 653. (b) Jaccard, G.; Carrupt, P.-A.; Lauterwein, J. *Magn. Reson. Chem.* **1988**, *26*, 239.

(33) (a) Kollman, P. A. In *Applications of Electronic Structure Theory;* Schaeffer, H. F., III, Ed.; Plenum Press: New York, 1977; Chapter 3. (b) Gutmann, V. *The Donor−Acceptor Approach to Molecular Interactions;* Plenum Press: New York, 1978.

(34) It should be remembered that when dominating π-electronic density is involved, such a pileup effect induces an opposite low frequency shift of the ^{17}O chemical shift.

Table 4. Charge Distributions, Based on Mulliken Populations, on Selected Atoms for HO(CH$_2$)$_n$SnCl$_3$ (n = 3−5), As Calculated by the AM1 Method

compd	O	Sn	Cl	d_{SnO} (Å)
HO(CH$_2$)$_5$SnCl$_3$ (open chain form)	−0.328	+1.048	−0.323 −0.327 −0.335	5.849
HO(CH$_2$)$_4$SnCl$_3$ (6-membered ring)	−0.353	+1.105	−0.341 −0.363 −0.382	2.600
HO(CH$_2$)$_3$SnCl$_3$ (5-membered ring)	−0.346	+1.114	−0.322 −0.357 −0.377	2.606

culations were performed. Table 4 gives an overview of charge distributions, based on Mulliken populations, as obtained from AM1 calculations[17] on the three alcohols.

Upon geometry optimization, attempts to force the C5-alcohol to converge to a cyclic structure failed, indicating that the open-chain form is preferred *in vacuo.* The calculated σ-electron density at oxygen in this open chain form was revealed to be identical to that of butanol. This result indicates that the seven-membered ring is unstable, a finding that matches the observation that the C5 alcohol is less soluble than the C3/C4 ones because it finally adopts a coordination pattern leading to the observed polymeric structure in the crystalline state (Figure 1). By contrast, the geometries of the C3 and C4 alcohols show minima, in the energy−geometry hypersurface for cyclic structures, with the σ-electron density at oxygen (Table 4) revealing the expected Gutmann pileup effect[33] in the C4 and the C3 alcohol as well as the corresponding spillover effect[33] at the chlorine atoms.[7] The optimized geometries of the C3 and C4 alcohols correspond to a distorted trigonal bipyramidal geometry, with the most negatively charged chlorine and the oxygen atoms in apical positions. On the basis of the small difference in calculated Mulliken populations and the similar Sn−O distance in the C3 and the C4 alcohol, a comparable interaction between tin and oxygen is suggested in the cyclic form of both compounds.

The 1D ^{1}H−^{119}Sn HMQC spectra of the C3 and C4 alcohols confirm this interpretation, especially in diluted solutions, where intense long-range $^nJ(^1$H−^{119}Sn) coupling correlations can be identified for the OH and the OCH$_2$ proton resonances (Table 3). As an example, Figure 3 gives the 1D ^{1}H−^{119}Sn HMQC spectrum of the C3 alcohol in diluted solution, with the assignment of the different $^nJ(^1$H−^{119}Sn) coupling splittings. The intense long-range coupling correlations for the OH and the OCH$_2$ proton resonances further support the high strength of the intramolecular HO $\rightarrow$ Sn interaction evidenced by the ^{119}Sn, ^{17}O NMR data and the AM1 calculations.

The C4 alcohol gives comparable ^{1}H−^{119}Sn HMQC correlation patterns with, however, a correlation "gap" at the CH$_2(\gamma)$ protons, where no significant cross-peak satellites are observed for HMQC mixing times for which the correlation at the CH$_2(\delta)$ protons is intense. The broad OH resonance of the C4 alcohol at both high and low concentration prevents the corresponding ^{1}H−^{119}Sn HMQC correlation from being visible.

The comparable values of the $^3J(^1$H−^{119}Sn) coupling constants (260−270 Hz) in CH$_3$COO(CH$_2$)$_3$SnCl$_3$[7] and
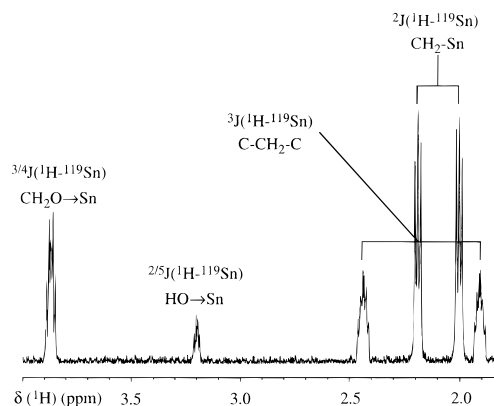
Figure 3. ^{1}H−^{119}Sn HMQC spectrum of HO(CH$_2$)$_3$SnCl$_3$ in diluted CD$_2$Cl$_2$ solution (10 mg/0.5 mL) with proton and $^nJ(^1$H−^{119}Sn) correlation assignment (HMQC delay: 50 ms).

HO(CH$_2$)$_3$SnCl$_3$ are in agreement with the similar five-membered ring structures for both compounds. The higher value of this constant for the C4 alcohol ($\sim$325 Hz) is associated with the different conformation to be expected in the six-membered ring, as compared to a linear chain (180−190 Hz) in, *e.g.,* CH$_3$(CH$_2$)$_5$SnCl$_3$[7] or the five-membered ring above. The higher $^1J(^{13}$C−^{119}Sn) coupling constants in HO(CH$_2$)$_{3/4}$SnCl$_3$ (840−860 Hz) than in CH$_3$COO(CH$_2$)$_3$SnCl$_3$ (720−730),[7] and in the CH$_3$COO(CH$_2$)$_{4/5}$SnCl$_3$ compounds (660−695)[7] as well as in the BuSnCl$_3$ and HexSnCl$_3$ model compounds (640−650),[7] are in agreement with a stronger five-coordinate character of the tin atom in the alcohols as compared to the other compounds, in agreement with the stronger O $\rightarrow$ Sn interaction in the alcohols than in the esters.[7] Last, the abnormally low $^3J(^{13}$C−^{119}Sn) coupling constants in the C3 ($\sim$80 Hz) and especially the C4 alcohol ($\sim$30 Hz), as compared to the reference compounds (110−120 Hz), can be interpreted by the presence of the ring structure altering the carbon chain conformation. Therefore, the usual sequence[11a,c] $|^1J(^{13}$C−^{119}Sn)| >> $|^3J(^{13}$C−^{119}Sn)| > $|^2J(^{13}$C−^{119}Sn)| valid for open chains, *e.g.,* n-butyl groups, is not applicable.

Solid-State ^{117}Sn and ^{13}C NMR Data. The ^{117}Sn isotropic chemical shifts of the C3 and C4 alcohols in the solid-state parallel those of the solution state, being low frequency shifted by *ca.* 40−50 ppm. Hence, the HO $\rightarrow$ Sn interaction in C3 and C4 is somewhat enhanced in the solid-state. The exclusive intermolecular nature of the HO $\rightarrow$ Sn interaction in the C5 alcohol, evidenced by the X-ray structure described above, is responsible for its high insolubility and its failure to decompose into monomers exhibiting intramolecular coordination. By contrast, the high solubility of the C4 and C3 alcohol can be explained by the intramolecular HO $\rightarrow$ Sn interaction, evidenced in the solution state, being also present in the solid-state and causing most of the shielding of its tin atom in the solid-state likewise. This is supported by the relatively low shielding of the tin atom in the solid-state as compared to solution (*ca.* 40 ppm) *versus* the obviously large shielding (*ca.* 150 ppm) caused by the intramolecular coordination in solution as compared to model compounds, *e.g.,* BuSnCl$_3$, where no such coordination is possible.

The unresolved $^1J(^{13}$C−$^{119/117}$Sn) coupling constants of the C3- (788 Hz), the C4- (850 Hz), and the C5-alcohol

Table 5. NMR Data of $HO(CH_2)_3SnCl_3$, $HO(CH_2)_4SnCl_3$, $HO(CH_2)_5SnCl_3$, and $BuSnCl_3$ in Acetone-$d_6{}^{a,b}$

compd	$HO(CH_2)_3SnCl_3$	$HO(CH_2)_4SnCl_3$	$HO(CH_2)_5SnCl_3$	$BuSnCl_3$
^1H NMR				
$CH_2(\alpha)$	1.93 [107]^c	2.43 [108]^c	2.42 [108]^c	2.46 [96]^c
$CH_2(\beta)$	2.15 [274]^c	2.23 [341]^c	1.96 [246]^c	1.87 [209]^c
$CH_2(\gamma)$	3.83	1.81	1.59	1.48
$CH_2(\delta)$		4.10	1.70	0.94^d
$CH_2(\epsilon)$			3.74	
OH	7.75	7.46	5.75	
^{13}C NMR				
$CH_2(\alpha)$	29.0 [989/939]^e	42.1 [962/923]^e	38.5 [864/826]^e	38.6 [847/811]^e
$CH_2(\beta)$	25.1 [72]^f	26.4 [78]^f	25.2 [67]^f	27.8 [65]^f
$CH_2(\gamma)$	60.5 [102]^f	30.7 [31]^f	28.8 [114]^f	25.7 [148]^f
$CH_2(\delta)$		67.9	30.7	13.9^d
$CH_2(\epsilon)$			63.5	
^{119}Sn NMR^g	−235	−252	−179	−169
^{17}O NMR^h	13.7	34.6	20.4/10.9	

^{a} Chemical shifts as referenced in the Experimental Section. ^{b} In solutions of 100 mg of substance per 0.5 mL of solvent in sealed tubes. ^{c} $^nJ(^1H-^{119}Sn)$ coupling constants in Hz (in brackets), as determined from 1D $^1H-^{119}Sn$ HMQC, except for $BuSnCl_3$, where it represents averaged, nonresolved $^nJ(^1H-^{119/117}Sn)$ couplings. ^{d} CH_3 group. ^{e} $^1J(^{13}C-^{119}Sn)$ and $^1J(^{13}C-^{117}Sn)$ coupling constants in Hz. ^{f} Unresolved $^nJ(^{13}C-^{119/117}Sn)$ coupling constants in Hz. ^{g} For fresh solutions in sealed tubes, see text, in ppm, Ξ = 37.290 665 MHz. ^{h} With respect to water, in ppm. δ ^{17}O for butanol in acetone-d_6: −2.2. Resonance of free acetone at 570 ppm.

(800 Hz) differ insufficiently to evidence clear structural differences in the solid-state.

Coordination Behavior of $HO(CH_2)_nSnCl_3$ (n = 3−5) in Acetone. A survey of the NMR data relevant to $HO(CH_2)_nSnCl_3$ (n = 3−5) in acetone-d_6 is given in Table 5. Data on $BuSnCl_3$ taken as a reference are given for comparison. These data are basically concentration independent.

Most ^1H and ^{13}C chemical shifts in acetone-d_6 for the C3 and C4 alcohols are comparable to those in CD_2Cl_2 and those for the C5 alcohol as previously given.[6a] Coupling constants ($^nJ(^1H-^{119}Sn)$ and $^nJ(^{13}C-^{119/117}Sn)$), about 5−20% higher in acetone-d_6 than in dichloromethane-d_2, as well as ^{119}Sn chemical shifts at lower frequency, indicate a global higher coordination degree for the three alcohols in acetone.

All three $HO(CH_2)_nSnCl_3$ alcohols in acetone-d_6 exhibit significant $^1H-^{119}Sn$ HMQC correlations between the ^{119}Sn nucleus and the protons of the CH_2O resonances, indicating the existence of a species with intramolecular coordination of the type $HO \rightarrow Sn$.

^{17}O NMR data of the C3 and C4 alcohols in acetone-d_6 confirm the existence of a species with a $HO \rightarrow Sn$ coordination because the ^{17}OH resonances have nearly the same resonance frequencies as in CD_2Cl_2.

Lowering the temperature shifts the ^{119}Sn resonance of the C3 alcohol to lower frequency by typically −25 to −30 ppm per 20 K down to 243 K. In parallel, a minor ^{119}Sn resonance around −640 ppm sharpens out to a maximum of 2% in intensity with respect to the main resonance, and the $^1J(^{13}C-^{119/117}Sn)$ coupling constant increases by about 100 Hz. At 223 K, the broad resonance, now at −346 ppm, starts decoalescing to several resonances, as shown in the spectrum at 203 K given in Figure 4.

At 183 K, the spectrum reveals two major (at −353 and −405 ppm, A and D) and two minor sharp resonances (B and E) and a broader weak one C. A ^{119}Sn EXSY spectrum reveals that the major species A and D are in mutual chemical exchange.

All these changes are fully reversible, as raising back the temperature to 303 K completely restores the original $^1J(^{13}C-^{119/117}Sn)$ coupling constant and single ^{119}Sn resonance around −260 ppm. Only the species
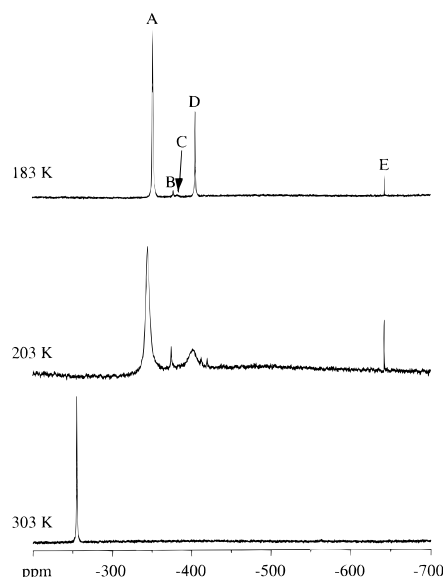

Figure 4. ^{119}Sn spectra of $HO(CH_2)_3SnCl_3$ in acetone-d_6 (100 mg/0.5 mL) at various temperatures. Top: 183 K. Middle: 203 K. Bottom: 303 K.

associated with the major resonances A and D are discussed further here, being the only clearly identifiable ones.[35]

(35) (a) There is no correlation with the γ-CH_2 protons, most likely because of cancelling of coupling contributions of opposite sign through the organic chain ($^4J(^1H-C-C-C-^{119}Sn)$) and the $HO \rightarrow Sn$ coordination ($^3J(^1H-C-O \rightarrow ^{119}Sn)$). (b) Temperature lowering also causes the sharpening of the γ-COH ^1H resonance and the appearance of two other OH resonances, a broad one ranging from 6 to 8 ppm and another smaller sharp one at about 10 ppm. The hydroxylic nature of the corresponding protons was checked by the absence of 2D $^1H-^{13}C$ HMQC correlations at 213 K and supported by exchange cross-peaks between all three OH resonances in a ^1H NOESY spectrum at 273 K. At 243 K, a 2D $^1H-^{119}Sn$ HMQC experiment reveals correlations between the main ^{119}Sn resonance and the γ-COH (8 Hz), α-CH_2 (112 Hz), and β-CH_2 (275 Hz) protons of the C3 alcohol,[35a] as well as between the small ^{119}Sn resonance at −642 ppm and the minor OH resonance at 10.1 ppm, while for the latter ^{119}Sn resonance no correlation with carbon-linked protons was observed. This leads to the conclusion that the broad signal between 6 and 8 ppm is due to water present in the sample (see text) and that the minor OH ^1H signal and ^{119}Sn resonance E arise from a product containing an SnOH moiety. Species E is also observed at low temperature in CD_2Cl_2 solutions. Since the ^{119}Sn EXSY experiment indicates that it is not involved in the equilibria revealed in acetone, and it is only present for no more than 2%, no further attempts were made to identify this minor (mineral?) species.

The low frequency shift of the averaged ^{119}Sn resonance from 303 to 243 K on temperature lowering is in agreement with a fast equilibrium between several species shifting from predominant five-coordination to predominant six-coordination. The room-temperature ^{119}Sn resonance is representative of averaged five-coordinate species in a fast equilibrium between a ring structure involving a HO → Sn coordination (species I) and an open structure involving a $(CD_3)_2C=O →$ Sn coordination (species II). Species I is evidenced by the existence of strong $^1H-^{119}Sn$ HMQC correlations between the ^{119}Sn and the CH_2O and OH ^{1}H resonances. Species II is evidenced by the fact that the averaged ^{119}Sn resonance appears at much lower frequency in the acetone than in the dichloromethane solution. As the temperature is lowered, further coordination by acetone is favored. This causes depletion of the pool of five-coordinated species I and II in favor of a pool of fast equilibrating six-coordinated species. This coordination increase undoubtedly arises from acetone and not the $HO(CH_2)_n$ moiety, as a similar behavior holds for $BuSnCl_3$.

A phenomenon complicating the interpretation of the acetone-d_6 data is the observation, at 303 K, of a slow low-frequency drift of the ^{119}Sn resonance upon solution aging (*ca.* 25 ppm in 5 months for the C3 and C4 alcohols and 75 ppm for the C5 alcohol). A similar drift is also observed for $BuSnCl_3$ in acetone (*ca.* 15 ppm in 10 months). These drifts are likewise accompanied by an increase in $^1J(^{13}C-^{119/117}Sn)$ coupling constant. No such drift occurs in CD_2Cl_2 solutions.

As water was suspected to originate these drifts (despite the use of *in vacuo* sealed tubes), spectra of fresh C3 alcohol solutions to which small amounts of D_2O were added were recorded. Addition of D_2O in a molar ratio of 3:10 causes a low-frequency ^{119}Sn shift of about 15 ppm at 303 K. At 183 K, decoalescence to the major resonances A (-353 ppm) and D (-405 ppm) remains the main feature, with, however, the area of resonance D being increased by *ca.* 10% at the expense of resonance A. Further addition of D_2O up to a molar ratio 1:1 causes an additional ^{119}Sn low frequency shift of *ca.* 40 ppm at 303 K, with only the resonance D remaining observed as major species at 183 K. Concomitantly, the $^1J(^{13}C-^{119/117}Sn)$ coupling constant increases from 989/939 Hz to 1088/1040 Hz at 303 K and to 1202/1146 Hz at 223 K.

A comparable behavior both at low temperature and upon addition of small aliquots of D_2O was observed for the C4/C5 alcohols and the reference compound $BuSnCl_3$.

The only possible source of water in sealed tubes is a slow self-condensation of acetone,[36] according to eq 1, activated by the trichlorotin moiety, which is a good Lewis acid.

$$2(CH_3)_2C=O \rightleftharpoons (CH_3)_2C=CH(C=O)CH_3 + H_2O \quad (1)$$
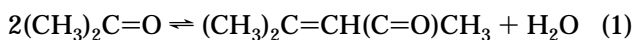
Evidence that this reaction is occuring is as follows: (i) the observation of small resonances in the ^{13}C spectrum that are unambiguously assigned to mesityl oxide; ii) the complete disappearance of the ^{119}Sn resonance A at -353 ppm in favor of resonance D at -405 ppm when the acetone solution of the C3-alcohol is heated at 50 °C for 10 days, accompanied by the parallel growth of mesityl oxide ^{13}C resonances; thus, the same species D is generated upon external addition of water and acetone autocondensation; (iii) importantly, the similar behavior of $BuSnCl_3$ indicating that this drift phenomenon is again not especially due to the organic hydroxy function of the $HO(CH_2)_nSnCl_3$ compounds; and (iv) the absence of ^{119}Sn chemical shift drift in dichloromethane, pointed out earlier.

This information allows a further refinement of the equilibrium model proposed above. At 183 K, the pool **X** of structures ($\delta^{119}Sn = -353$ ppm, resonance A), consisting mainly of fast equilibrating six-coordinated species, is in equilibrium—as evidenced by the ^{119}Sn EXSY spectrum—with another pool **Y** of structures ($\delta^{119}Sn = -405$ ppm, resonance D). This equilibrium between the two pools is slowly drifting to pool **Y** as more water is generated upon slow self-condensation of acetone and concomitant formation of mesityl oxide. Determinant support to this is the external addition of 1 equiv of water causing the ^{119}Sn resonance of only the pool **Y** species to remain visible as the major resonance. Therefore, we propose that the pool **Y** structures result from the substitution of one chlorine atom in the pool **X** structures for a hydroxy group:

$$RSnCl_3 + H_2O \rightarrow RSnCl_2OH + HCl$$
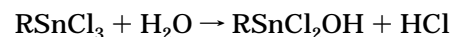
The substitution of a chlorine atom for a more electronegative OH group also explains the increase in the $^1J(^{13}C-^{119/117}Sn)$ coupling constant at room temperature since more s-character is now forced into the Sn−C bond. The increase of this coupling constant upon temperature lowering is due to the resulting higher relative population of six-coordinated species. The same holds for the C4 and C5 alcohols, as well as $BuSnCl_3$, given the similar spectral behaviors.

Finally, the above interpretation is supported by various literature data. Papers by Holmes[37] and Puff[38] describe dichlorohydroxyorganotin compounds. In acetone,[37] two different species with very different coordinations are likewise evidenced by a minor ^{119}Sn resonance at -208.7 and a major one at -408.6 ppm, *i.e., ca.* 200 ppm to low frequency. Comparable observations with several resonances are likewise reported by Blunden *et al.*[39] for $BuSnCl_2(OH)(H_2O)$ in D_2O solution and explained by the simultaneous presence of the basic compound and more advanced hydrolysis products. More importantly, Wardell *et al.*[8e,f] describe equilibria for $CH_3O(C=O)CH_2CH_2SnCl_3$ between species with intramolecular coordination by the C=O group and intermolecular coordination by a CH_3CN or pyridine unit from the solvent.

Conclusion

Multinuclear solid- and solution-state NMR investigations of hydroxy-functionalized monoorganotin trichlorides revealed coordination behaviors depending on both

(36) Carey, F. A. *Organic Chemistry*; McGraw Hill: New York, 1996; pp 746−756.

(37) Holmes, R. R.; Shafieezad, S.; Chandrasekhar, V.; Holmes, J. M.; Day, R. O. *J. Am. Chem. Soc.* **1988**, *110*, 1174.
(38) Puff, H.; Reuter, H. *J. Organomet. Chem.* **1989**, *364*, 57.
(39) Blunden, S. J.; Smith, P. J.; Gillies, D. G. *Inorg. Chim. Acta* **1982**, *60*, 105.

the length of the alkyl chain and the solvent. In a non-coordinating solvent, the compounds with three and four carbons between the tin and the hydroxy group show a cyclic structure resulting from intramolecular coordination between the hydroxy group and the electrophilic tin atom. With five carbons, the corresponding intramolecular coordination leads to an unstable seven-membered ring, explaining that a poorly soluble polymeric form is favored. AM1 quantum-chemical calculations and an X-ray crystallographic study support these proposals. They provide insight into differentiated behavior of the compounds as a function of solvent. The power of combining several NMR techniques to address solution-state coordination of electrophilic organotin compounds is hereby illustrated.

Supporting Information Available: Further details of the structure determination including tables of atomic coordinates, bond distances and angles, and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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