

Coordination Behavior of ω -(Trichlorostannyl)alkyl Acetates, $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$ ($n = 3-5$): A Solution and Solid-State Multinuclear NMR and AM1 Quantum-Chemical Study

Monique Biesemans,[†] Rudolph Willem,^{*,†} Said Damoun,[‡] Paul Geerlings,[‡] Mohammed Lahcini,[§] Pascale Jaumier,[§] and Bernard Jousseume^{*,§}

High Resolution NMR Centre (HNMR) and Department of General and Organic Chemistry of the Faculty of Applied Sciences (AOSC) and Eenheid Algemene Chemie (ALGC), Free University of Brussels (VUB), Pleinlaan 2, B-1050 Brussels, Belgium, and Laboratoire de Chimie Organique et Organométallique, URA 35 CNRS, Université Bordeaux I, 351 Cours de la Libération, F-33405 Talence Cedex, France

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The coordination behavior of three ester-functionalized monoorganotin trichlorides of the type ω -(trichlorostannyl)alkyl acetate, $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$ ($n = 3-5$), has been investigated by multinuclear solid- and solution-state NMR, as well as AM1 quantum-chemical calculations. The data reveal basically the existence of a fast equilibrium between two species involved respectively in an intramolecular and intermolecular donor-acceptor interaction between the ester function and the tin atom. In the $n = 3$ case, the species involving the intramolecular interaction is by far the dominant one, with a coordination from the alkoxy oxygen atom to the tin atom, resulting in an interaction of the type $-\text{CH}_2\text{O}(\text{Ac})\rightarrow\text{SnCl}_3$ ($\text{Ac} = \text{CH}_3\text{CO}-$). In contrast, for the $n = 4$ and 5 cases, the species involving the intermolecular interaction prevails, resulting in (cyclo)dimeric or oligomeric species displaying coordinations from the carbonyl oxygen atom to the tin atom of the type $-\text{CH}_2\text{OC}(\text{CH}_3)=\text{O}\rightarrow\text{SnCl}_3$.

Introduction

Organotin halides are important intermediates in both academic¹ and industrial² organotin chemistry. However, most studies on this class of compounds have been devoted to triorganotin and diorganotin halides.³ Recently, monoorganotin trihalides bearing various functional groups on the organic moiety displayed catalytic properties which have been developed for acetalization reactions.⁴ They have been found to be excellent transfer agents of alkyl, aryl,⁵ or allyl⁶ groups to various halogenated or carbonylated compounds, under palladium catalysis or not. They were involved in the preparation of α -methylene ketones and aldehydes through an amine-induced dehydrotrichlorostan-

nation.⁷ From these halogenated organotin compounds, amino acid derivatives could be regioselectively obtained in high yield.⁸ Recently, they have been used as key intermediates for the preparation of monoorganotin trialkoxides which are precursors of hybrid materials.⁹ Some of these compounds, especially those in which the carbon chain was substituted by a fragile ester function, were found to be unstable, their stability being a function of the carbon chain length between the metal and the functional group.^{10a} As coordination of the electrophilic tin by the ester group was anticipated, spectroscopic studies were initiated on model compounds to find evidence for this coordination and to determine its nature in terms of the length of the polymethylene chain between the tin atom and the coordinating function. Such a coordination has been studied for compounds with two¹¹ or three¹² methylene groups between the metal and the carbonyl carbon atom of an acid, ester, or amide. To the best of our knowledge,

[†] HNMR and AOSC, Free University of Brussels.

[‡] ALGC, Free University of Brussels.

[§] Université Bordeaux I.

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no studies have been performed for longer polymethylene chains.

This report presents the results of our NMR investigations on the coordination properties of $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$ compounds, mainly in solution ($n = 3-5$). Our main investigation tools were ^1H , ^{13}C , ^{119}Sn , and ^{17}O 1D NMR,¹³ gradient-assisted¹⁴ $^1\text{H}-^{119}\text{Sn}$ heteronuclear multiple quantum correlation (HMQC) spectroscopy,^{15,16} and, for solid-state measurements (provided for comparison), ^{13}C and ^{117}Sn CP-MAS NMR.^{17,18} The ^{17}O NMR spectral data, complemented by some IR data, have been interpreted in parallel with AM1 quantum-chemical calculations¹⁹ on relative stabilities and charge distributions of structures showing various intra- and intermolecular tin-oxygen interactions.

Experimental Section

Synthesis of the Compounds. The $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$ ($n = 3-5$) compounds were prepared according to a procedure described recently.^{9a}

NMR Experiments. Solid State. All CP-MAS NMR spectra¹⁷ were recorded on a Bruker AC250 spectrometer, operating at 89.15 and 62.93 MHz for ^{117}Sn and ^{13}C nuclei, respectively. The spectrometer is interfaced with an Aspect 3000 computer and equipped with a MAS broad-band probe for solid-state experiments. The matching conditions for Hartmann-Hahn cross-polarization¹⁷ (^1H 90° pulse length: 5 μs) was set with $(\text{C}_6\text{H}_{11})_4\text{Sn}$ for the ^{117}Sn nucleus, as well as the chemical shift reference (-97.35 ppm relative to $(\text{CH}_3)_4\text{Sn}$); adamantane was used (38.3 ppm relative to $(\text{CH}_3)_4\text{Si}$) for the ^{13}C nucleus. ZrO_2 rotors (7 mm o.d.) and a spinning rate of 4 kHz were used for the ^{13}C acquisitions; spectra were obtained by acquiring 4K data points over a spectral width of 15.1 kHz, a 2 ms contact time, and a relaxation delay of 4 s with 100–1000 scans. The ^{117}Sn spectra were typically obtained by acquiring 32K data points over a spectral width of 166.7 kHz, a 2 ms contact time, and a relaxation delay of 2 s with 1000–10 000 scans. In order to find the isotropic chemical shift, spectra were run at two or three different spinning rates.¹⁷

^{117}Sn spectra were recorded instead of the more common ^{119}Sn ones to overcome a local radio interference problem.²⁰ No misinterpretations are to be expected when solid-state ^{117}Sn chemical shift data are compared with solution ^{119}Sn data,

since $^{117}\text{Sn}/^{119}\text{Sn}$ isotopic effects on tin chemical shifts are known to be negligible.²¹

NMR Experiments. Solution State. The samples were prepared by dissolving the appropriate amounts of the compounds in 500 μL of C_6D_6 . All NMR spectra were recorded at 303K on a Bruker AMX500 spectrometer interfaced with a X32 computer and operating at 500.13, 125.77, and 186.50 MHz for the ^1H , ^{13}C , and ^{119}Sn nuclei, respectively. Chemical shifts were referenced to the residual solvent peak (C_6D_6) and converted to the standard Me_4Si scale by adding 7.15 and 128.0 ppm for ^1H and ^{13}C nuclei, respectively. The ^{119}Sn reference frequency was calculated from the absolute ^1H frequency of TMS and the known absolute frequency of Me_4Si , being 37.290 665 MHz²³ at the B_0 field; the absolute frequency of the ^1H nucleus is exactly 100.000 000 MHz.

^{13}C and ^{119}Sn BB proton-decoupled 1D spectra were recorded using standard pulse sequences and delays from the Bruker program library.

The proton-detected 1D $^1\text{H}-^{119}\text{Sn}$ HMQC correlation spectra with or without ^{119}Sn decoupling were acquired using the pulse sequences of the Bruker program library¹⁵ adapted to include gradient pulses,¹⁴ as proposed recently,^{14e} in addition to phase cycling for coherence pathway selection. This leads to a dramatic improvement in spectrum quality, because of an optimal artifact suppression, as explained and illustrated elsewhere.^{14e} The experiments were optimized to average $^nJ(^1\text{H}-^{119}\text{Sn})$ values ranging from 8 to 4 Hz (delays from 60 to 120 ms). No low-pass J filter was applied.^{15b}

^{17}O NMR spectra were recorded at 313 K on a Bruker AMX500 spectrometer operating at 67.8 MHz resonance frequency. They were acquired at natural-abundance level in C_6D_6 . The signals were referenced to external deionized water at 313 K. Standard instrumental settings were used:²³ a spectral width of 50 kHz, 2K data points, 90° pulse angle, 200 μs acquisition delay, and 40 ms acquisition time with the total number of scans varying between 20 000 and 100 000. Zero-filling to 8K data points and an exponential line broadening of 20 Hz were applied to improve the resolution and signal-to-noise ratio. The reproducibility of the chemical shift is better than ± 0.5 ppm.

Quantum-Chemical Calculations. In view of both the relatively large size of the systems and the presence of a tin atom, a semiempirical method was chosen for the energy and charge distribution calculations. The AM1 method,¹⁹ for which the parameters for Sn were published not so long ago,²⁴ was selected, as it proved to be very efficient in applications to a very wide range of chemical problems.²⁵

Both geometry optimizations and single-point calculations were performed using the GAUSSIAN 92 program²⁶ coupled to the UNICHEM²⁷ software package. The charge distributions were analyzed in terms of the Mulliken atomic populations.²⁸ All calculations were performed on the CRAY Y-MP/116 computer of the Free Universities of Brussels Computer Center.

IR Data. Infrared data were acquired in the Fourier-transform mode on a Perkin-Elmer system 200 FT-IR spectrometer, from CCl_4 solutions or KBr pellets.

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Table 1. Solid-State ^{117}Sn CP-MAS NMR for the $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$ Esters ($n = 3-5$) as well as ^{119}Sn C_6D_6 Solution-State Data for the $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$ Esters ($n = 3-5$) and the Reference Compound $\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$ at Two Concentrations in C_6D_6 Solutions^a

compd	solid ^b	melt ^c	ref 9a ^d	100 mg/ 0.5 mL ^e	10 mg/ 0.5 mL ^e
$\text{CH}_3\text{COO}(\text{CH}_2)_3\text{SnCl}_3$	-80		-38	-42	-32
$\text{CH}_3\text{COO}(\text{CH}_2)_4\text{SnCl}_3$	-168		-47	-35	-4
$\text{CH}_3\text{COO}(\text{CH}_2)_5\text{SnCl}_3$	-168	-99	-67	-33	-2
$\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$				-3	+5

^a Chemical shifts in ppm with respect to tetramethyltin (see Experimental Section). ^b Isotropic ^{117}Sn chemical shift (δ_{iso}) from a ^{117}Sn CP-MAS spectrum of the solid compound. ^c ^{117}Sn chemical shift from a ^{117}Sn MAS spectrum recorded with a sample that melted upon heating because of spinning in the CP-MAS probe. ^d Concentrated solution in CDCl_3 ; data from ref 9a. ^e Concentrations in mg of compound per 0.5 mL of C_6D_6 .

Results and Discussion

^{117}Sn Solid-State and ^{119}Sn Solution NMR Data.

The general structure of the ω -(trichlorostannyl)alkyl acetate compounds investigated can be represented as $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$, with $n = 3-5$. As the main purpose of this work is to elucidate the coordinative properties of the ester function, we also investigated a reference compound in which this function is absent, $\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$.

Table 1 provides an overview of the $^{117/119}\text{Sn}$ chemical shifts obtained for the $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$ esters ($n = 3-5$) and the reference $\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$ compound under several conditions. Data of previous work^{9a} obtained from CDCl_3 solutions are likewise given for comparison. The coordinative properties of the above esters were investigated in benzene- d_6 rather than chloroform- d in order to avoid, as much as possible, potential interference from the solvent on the coordination behavior of the tin atom, taking into account the rather high dipole moment of chloroform.

In the solid state, tin NMR data were acquired with the ^{117}Sn nucleus rather than with the more common ^{119}Sn nucleus in order to overcome RF interference problems from a local radio station (see Experimental Section).^{20,21}

Table 1 reveals that the ^{119}Sn chemical shift in C_6D_6 solution is strongly concentration dependent for the C4/C5 esters, shifting to low frequency by 31 ppm for the C5 and C4 ester upon a 10-fold concentration increase. At higher concentration in CDCl_3 ,^{9a} the low-frequency shift is even more marked. In contrast, the ^{119}Sn chemical shift is less concentration dependent for the C3 ester, shielding occurring only to the extent of 10 ppm upon 10-fold concentration increase. In addition, it is essentially solvent independent.

Solid-state tin chemical shifts are as large as 167 and 163 ppm toward low frequency with respect to those from highly diluted solutions for the C5 and C4 esters, respectively, while this difference remains lower than 50 ppm for the C3 ester.

The ^{119}Sn chemical shift of the reference $\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$ compound is only very slightly concentration dependent, displaying a shift to lower frequency of only 8 ppm upon 10-fold concentration increase, unlike the corresponding $\text{CH}_3\text{COO}(\text{CH}_2)_5\text{SnCl}_3$ ester. The low-frequency ^{119}Sn shifts observed in solution for the $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$ compounds ($n = 3-5$) with respect to

$\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$ indicate a coordination expansion of the tin atom in the esters.²⁹ The presence of a single ^{119}Sn resonance, the chemical shift of which depends on the concentration, is evidence of chemical exchange averaging. This indicates a fast equilibrium between a monomeric and an oligomeric species.

The difference in concentration dependence of the exchange-averaged ^{119}Sn chemical shift of the C4/C5 esters as compared to the C3 ester indicates, in addition, different equilibrium populations in these species with different coordination patterns. Both the quite strong low-frequency shift of ca. 40 ppm in the ^{119}Sn chemical shift of $\text{CH}_3\text{COO}(\text{CH}_2)_3\text{SnCl}_3$ with respect to $\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$ and the relative insensitivity of this upon concentration changes suggest the fast equilibrium to be dominated by a monomeric species with an *intramolecular* coordination from the ester function toward the tin atom in this C3 ester.

In contrast, the existence of a single, broad, and concentration-dependent ^{119}Sn resonance for the C4/C5 esters, conjugated with the large ^{119}Sn low-frequency shift upon concentration increase, indicates an exchange equilibrium between at least two species which is fast on the ^{119}Sn NMR time scale. At high concentration, an aggregated species resulting from *intermolecular* coordination would be favored in this fast equilibrium, resulting in the exchange-averaged ^{119}Sn resonance appearing at low frequency with respect to the model compound $\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$, while at high dilution a monomeric species would be favored. For this monomeric species, the high similarity in the ^{119}Sn chemical shifts as compared to the reference compound, $\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$, indicates only very weak *intramolecular* coordination, if any, in $\text{CH}_3\text{COO}(\text{CH}_2)_4\text{SnCl}_3$ and $\text{CH}_3\text{COO}(\text{CH}_2)_5\text{SnCl}_3$, unlike $\text{CH}_3\text{COO}(\text{CH}_2)_3\text{SnCl}_3$.

^{13}C NMR Data. Table 2 provides an overview of the ^{13}C chemical shifts and the $^nJ(^{13}\text{C}-^{119/117}\text{Sn})$ coupling constants obtained for the $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$ esters ($n = 3-5$) and the reference $\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$ compound, under several conditions. Data from previous work,^{9a} obtained from CDCl_3 solutions, are again given for comparison.

Concentration-induced shifts, reinforced in the melt and the solid state, are observed for the esters, while the ^{13}C chemical shifts of the reference $\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$ compound are essentially concentration independent.

Most striking is the difference in concentration dependence of the $^1J(^{13}\text{C}-^{119/117}\text{Sn})$ coupling constants of the esters. In the case of the C4/C5 esters, they roughly increase from ca. 660 to 780 Hz as one goes from the most dilute solution to the solid. For the C5 ester in the molten state, the $^1J(^{13}\text{C}-^{119/117}\text{Sn})$ coupling constant has a value intermediate between those of the solid and the concentrated C_6D_6 solution. In contrast, the $^1J(^{13}\text{C}-^{119/117}\text{Sn})$ coupling constants of the C3 ester almost do not depend on concentration and aggregation state, even if a slightly higher value is noted for a concentrated CDCl_3 solution. In C_6D_6 solution, the value of the $^1J(^{13}\text{C}-^{119/117}\text{Sn})$ coupling constant is higher in the C3 ester than in the C4/C5 ones; in the solid state, it is smaller. In the reference $\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$ compound, the $^1J(^{13}\text{C}-^{119/117}\text{Sn})$ coupling constant is lower than in

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Table 2. ^{13}C NMR Data for the $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$ Compounds ($n = 3-5$) in the Solid State as well as for the $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$ ($n = 3-5$) and $\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$ Compounds at Two Concentrations in C_6D_6 Solutions^a

carbon	solid ^b	melt ^c	ref 9a ^d	100 mg/0.5 mL ^e	10 mg/0.5 mL ^e
$\text{CH}_3\text{COO}(\text{CH}_2)_3\text{SnCl}_3$					
α -CH ₂	36.2 [720] ^f		29.9 [746] ^f	29.7 [729/696] ^g	28.5 [723/692] ^g
β -CH ₂	25.3		23.9 [63] ^h	23.7 [65] ^h	23.6 [64] ^h
γ -CH ₂	66.6		64.9 [63] ⁱ	64.5 [64] ⁱ	64.1 [59] ⁱ
COO	175.0		171.9	170.3	169.7
CH ₃	23.6		21.4	21.0	20.9
$\text{CH}_3\text{COO}(\text{CH}_2)_4\text{SnCl}_3$					
α -CH ₂	35.7 [768] ^f		32.9 [724] ^f	32.5 [695/663] ^g	31.0 [665/636] ^g
β -CH ₂	22.0		21.6 [57] ^h	21.5 [57] ^h	21.3 [57] ^h
γ -CH ₂	29.3		30.9 [120] ^j	30.8 [132] ^j	30.8 [126] ^j
δ -CH ₂	66.4		63.5	63.4 [9] ^k	62.7 [9] ^k
COO	177.4		171.1	171.6	170.2
CH ₃	22.9		21.1	20.6	20.3
$\text{CH}_3\text{COO}(\text{CH}_2)_5\text{SnCl}_3$					
α -CH ₂	41.9 [784] ^f	37.7 [747] ^f	35.5 [735] ^f	33.8 [695/675] ^g	31.9 [658/630] ^g
β -CH ₂	28.2	25.3	24.6 [61] ^h	24.5 [62] ^h	24.2 [58] ^h
γ -CH ₂	29.6	28.9	28.5 [128] ^j	28.5 [128] ^j	28.5 [124] ^j
δ -CH ₂	28.8	28.3	27.7	27.8	27.8
ϵ -CH ₂	68.8	66.1	65.1	64.4	63.6
COO	178.7	174.8	173.7	172.1	170.4
CH ₃	22.7	22.1	21.3	20.8	20.5
$\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$					
α -CH ₂				32.7 [649/622] ^g	32.2 [648/620] ^g
β -CH ₂				24.7 [60] ^h	24.6 [59] ^h
γ -CH ₂				32.0 [110] ^j	31.9 [115] ^j
δ -CH ₂				31.0	30.9
ϵ -CH ₂				22.4	22.4
CH ₃				14.0	14.0

^a Chemical shifts in ppm with respect to TMS; ⁿ $J(^{13}\text{C}-^{119/117}\text{Sn})$ given in brackets, in Hz (see below). ^b Solid-state CP-MAS ^{13}C spectrum of the solid compound. ^c MAS ^{13}C spectrum resulting from a sample that melted upon heating because of spinning in the CP-MAS probe. ^d Concentrated solution in CDCl_3 ; data from ref 9a. ^e Concentrations in mg of compound per 0.5 mL of C_6D_6 . ^f Averaged coupling value from the unresolved $^1J(^{13}\text{C}-^{119}\text{Sn})$ and $^1J(^{13}\text{C}-^{117}\text{Sn})$ satellites. ^g Coupling values from the resolved $^1J(^{13}\text{C}-^{119}\text{Sn})$ and $^1J(^{13}\text{C}-^{117}\text{Sn})$ satellites. ^h Averaged coupling value from the unresolved $^2J(^{13}\text{C}-\text{C}-^{119}\text{Sn})$ and $^2J(^{13}\text{C}-\text{C}-^{117}\text{Sn})$ satellites. ⁱ Averaged coupling value from the combination of unresolved $^3J(^{13}\text{C}-\text{C}-\text{C}-^{119}\text{Sn})$ and $^3J(^{13}\text{C}-\text{C}-\text{C}-^{117}\text{Sn})$ satellites and unresolved $^2J(^{13}\text{C}-\text{O}-^{119}\text{Sn})$ and $^2J(^{13}\text{C}-\text{O}-^{117}\text{Sn})$ satellites (see text). ^j Averaged coupling value from the unresolved $^3J(^{13}\text{C}-\text{C}-\text{C}-^{119}\text{Sn})$ and $^3J(^{13}\text{C}-\text{C}-\text{C}-^{117}\text{Sn})$ satellites. ^k Averaged coupling value from the unresolved $^4J(^{13}\text{C}-\text{C}-\text{C}-\text{C}-^{119}\text{Sn})$ and $^4J(^{13}\text{C}-\text{C}-\text{C}-\text{C}-^{117}\text{Sn})$ satellites.

the esters and is independent of the concentration. These observations are in agreement with the ^{119}Sn NMR data, confirming dynamic equilibria between monomeric and oligomeric species, dominated by monomeric, intramolecular coordination in the C3 ester and by oligomeric intermolecular coordination in the C4/C5 esters at high concentration.

The $^2J(^{13}\text{C}-^{119/117}\text{Sn})$ and $^3J(^{13}\text{C}-^{119/117}\text{Sn})$ coupling constants associated with the β - and γ -carbon atoms of the C4/C5 esters are both poorly solvent and concentration dependent. They display the usual relationship $|^3J| > |^2J|$.²⁹ The same holds for the $^2J(^{13}\text{C}-^{119/117}\text{Sn})$ coupling constant associated with the β -carbon atom of the C3 ester. Roughly, the same value of *ca.* 60 Hz is found for the reference $\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$ compound. In contrast, the value of the $^3J(^{13}\text{C}-^{119/117}\text{Sn})$ coupling associated with the γ -carbon atom of the C3 compound is unusually of the same order of magnitude, *ca.* 60 Hz, as the $^2J(^{13}\text{C}-^{119/117}\text{Sn})$ coupling constant of the β -carbon atom, about half as large as the value of *ca.* 120 Hz found for the γ -carbon atoms of all other compounds, including the reference one. This strongly suggests the γ -carbon-tin coupling in the C3 ester arises from two coupling pathways having coupling constant values of opposite sign, the usual $^3J(^{13}\text{C}-^{119/117}\text{Sn})$ coupling pathway through the carbon chain and one involving some intramolecular coordination between the ester function and the tin atom.

1D $^1\text{H}-^{119}\text{Sn}$ Heteronuclear Multiple Quantum Correlation Spectroscopy ($^1\text{H}-^{119}\text{Sn}$ HMQC). Pro-

ton chemical shifts are concentration dependent, in the expected range.^{9a,10b} The only spectral data worth outlining are the $^3J(^1\text{H}-^{119}\text{Sn})$ coupling constants which increase slightly upon 10-fold concentration increase, from 184 to 191 Hz for $\text{CH}_3\text{COO}(\text{CH}_2)_4\text{SnCl}_3$, from 191 to 200 Hz for $\text{CH}_3\text{COO}(\text{CH}_2)_5\text{SnCl}_3$, and from 190 to 204 Hz for $\text{CH}_3(\text{CH}_2)_5\text{SnCl}_3$, the reference compound. In contrast, the $^3J(^1\text{H}-^{119}\text{Sn})$ coupling constant, as high as 269 and 264 Hz for the C3 ester $\text{CH}_3\text{COO}(\text{CH}_2)_3\text{SnCl}_3$, supports a major conformation difference resulting from the essentially concentration independent intramolecular coordination evidenced by the ^{13}C and ^{119}Sn NMR data.

In order to gain information on the sites of coordination in the $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$ esters, we performed various 1D $^1\text{H}-^{119}\text{Sn}$ heteronuclear multiple quantum correlation spectroscopy ($^1\text{H}-^{119}\text{Sn}$ HMQC) experiments.^{15,16,30} We introduced recently the application of 1D and 2D HMQC spectroscopy¹⁵ to the ^{119}Sn nucleus^{16,30} and demonstrated the power of this technique in structure elucidation in organotin chemistry, especially with regard to weak intramolecular coordination from Lewis bases to the tin atom leading to its coordination expansion.^{30,31} In order to increase the sensitivity by ensuring optimal minimization of artifacts due to imperfect suppression of the parent signals, we performed

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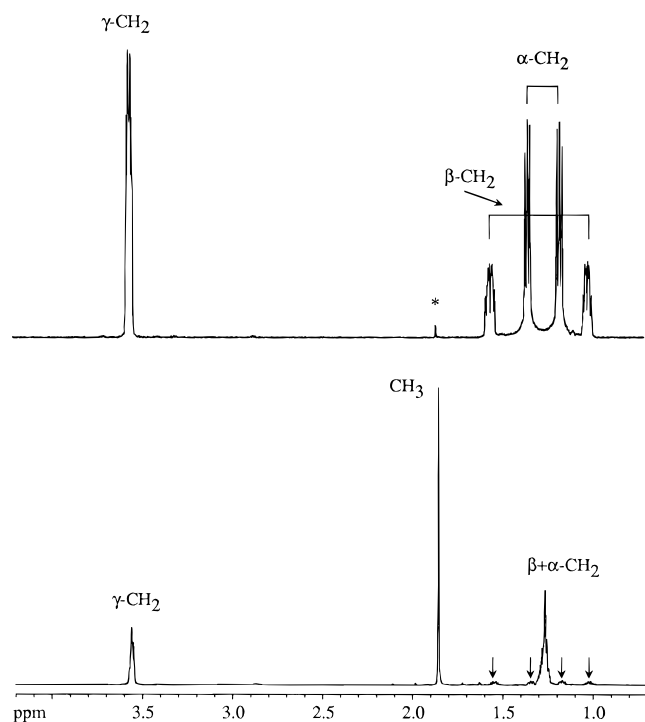


Figure 1. Gradient-assisted 1D ^1H - ^{119}Sn HMQC spectrum (top) of a concentrated solution (100 mg in 0.5 mL of C_6D_6 ; delay 120 ms) of the C3 ester $\text{CH}_3\text{COO}(\text{CH}_2)_3\text{SnCl}_3$. Assignment of the different ^{119}Sn edited ^1H nuclei is given. The asterisk denotes a small peak arising from the CH_3 group (see text). A standard 1D NMR spectrum is given for comparison (bottom). Arrows in the standard 1D spectrum indicate the $^nJ(^1\text{H}-^{119}\text{Sn})$ coupling satellites edited in the 1D ^1H - ^{119}Sn HMQC spectrum (top).

the experiments with gradient pulses,^{14a-d} as introduced recently for the ^{119}Sn nucleus.^{14e}

Figure 1 displays the gradient-assisted 1D ^1H - ^{119}Sn HMQC spectrum of a concentrated solution (100 mg in 0.5 mL C_6D_6) of the C3 ester, $\text{CH}_3\text{COO}(\text{CH}_2)_3\text{SnCl}_3$. A dilute solution displays essentially the same pattern, with a poorer signal to noise ratio; a longer recording time is needed.

The 1D ^1H - ^{119}Sn HMQC spectrum of Figure 1 exhibits mainly only the $^nJ(^1\text{H}-^{119}\text{Sn})$ satellites, with conservation of the $^nJ(^1\text{H}-^1\text{H})$ coupling multiplets, of all the ^1H nuclei having a detectable coupling to the ^{119}Sn nucleus. Accordingly, the splitting separating the centers of the satellites correspond to $^nJ(^1\text{H}-^{119}\text{Sn})$ coupling constants which are not contaminated by the $^nJ(^1\text{H}-^{117}\text{Sn})$ coupling constants. When $^nJ(^1\text{H}-^{119}\text{Sn})$ couplings are of the same order of magnitude as the $^nJ(^1\text{H}-^1\text{H})$ ones associated with a given proton, because they are of long-range nature or result from weaker bonds, e.g. coordination to tin, the $^nJ(^1\text{H}-^{119}\text{Sn})$ coupling splittings interfere with the $^nJ(^1\text{H}-^1\text{H})$ ones.

In view of these preliminary considerations, the spectrum of Figure 1 is straightforwardly interpreted. The two pairs of satellite multiplets centered at ca. 1.25 ppm, with one large (269 Hz) and one smaller (89 Hz) $^nJ(^1\text{H}-^{119}\text{Sn})$ coupling splitting, are assigned to the accidentally isochronous β - CH_2 and α - CH_2 protons, respectively, on the basis of the well-known relation $|\beta^3J|$

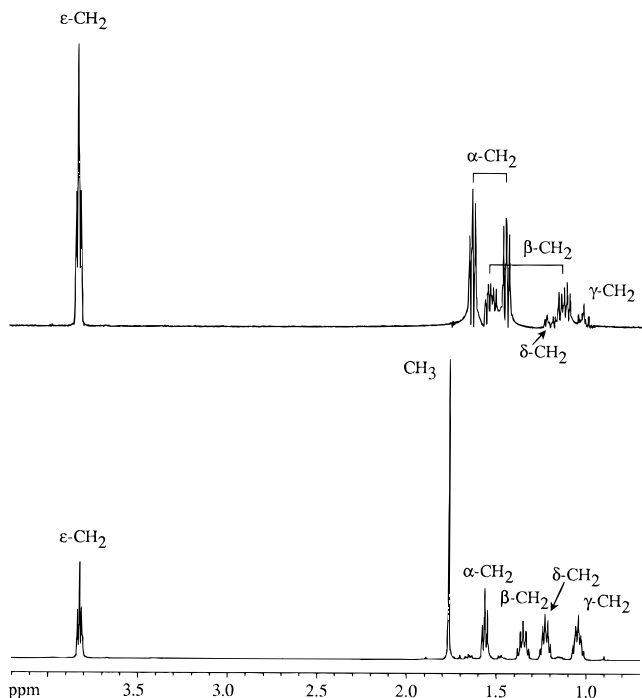


Figure 2. Gradient-assisted 1D ^1H - ^{119}Sn HMQC spectrum (top) of a concentrated solution (100 mg in 0.5 mL of C_6D_6 ; delay 120 ms) of the C5 ester $\text{CH}_3\text{COO}(\text{CH}_2)_5\text{SnCl}_3$. Assignment of the different ^{119}Sn edited ^1H nuclei is given. A standard 1D spectrum is given for comparison (bottom).

$> |\beta^2J|$.²⁹ The pseudoquartet-like pattern, centered at 3.55 ppm, assigned to the γ - CH_2 protons, is interpreted as the $^3J(^1\text{H}-^1\text{H})$ triplet of 5.5 Hz, being duplicated by ca. 6 Hz likewise as a consequence of J coupling with the ^{119}Sn nucleus. The very weak signal marked by a star in Figure 1 at 1.85 ppm, assigned to the methyl protons of the acetoxy group, is likely to reflect an artifactual residue of main signal suppression, common for intense methyl singlets, rather than a real, extremely weak $^nJ(^1\text{H}-^{119}\text{Sn})$ coupling correlation peak.

Figure 2 displays the gradient-assisted 1D ^1H - ^{119}Sn HMQC spectrum of a concentrated solution of the C5 ester, $\text{CH}_3\text{COO}(\text{CH}_2)_5\text{SnCl}_3$.

The 1D ^1H - ^{119}Sn HMQC spectrum reveals intense correlations between the ^{119}Sn nucleus and the α - CH_2 and β - CH_2 protons, corresponding to respectively $^2J(^1\text{H}-^{119}\text{Sn})$ and $^3J(^1\text{H}-^{119}\text{Sn})$ coupling splittings, both conserving their $^3J(^1\text{H}-^1\text{H})$ multiplet patterns. Weak correlation peaks are observed at the frequencies of the γ - CH_2 and δ - CH_2 protons. In contrast, the ϵ - CH_2 protons give an intense correlation peak, appearing as a triplet. The latter is the normal $^3J(^1\text{H}-^1\text{H})$ triplet pattern observed in the standard 1D ^1H spectrum. This indicates that the $^nJ(^1\text{H}-^{119}\text{Sn})$ coupling between the ϵ - CH_2 protons and the ^{119}Sn nucleus is so small that the resulting doublet splitting is unresolved. The fact, however, that an intense ϵ - CH_2 / ^{119}Sn correlation peak is observed makes the existence of such a long-range coupling indisputable. No correlation peak with the acetoxy methyl group is observed, as confirmed by other 1D ^1H - ^{119}Sn HMQC spectra recorded with other delay parameters. Analogous observations were made for the C5 ester in dilute solution as well as for the C4 ester in concentrated and dilute solutions.

While strong correlations were found between the tin-119 nucleus and the ϵ - CH_2 protons of the C5 ester, CH_3 -

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COO(CH₂)₅SnCl₃, significant correlations were found only up to the γ -CH₂ protons of the model C5 compound, CH₃(CH₂)₅SnCl₃, a very weak correlation was found for the δ -CH₂ protons, and no evidence could be found for either the ϵ -CH₂ or the terminal methyl protons.

The major question is that of the coordination modes of the ester function toward the tin atom. The ¹H–¹¹⁹Sn HMQC correlation experiments point to coordination by the alkoxy oxygen atom of the ester function, rather than by its carbonyl one. We consider the strong correlation resonance between the γ -CH₂ protons of the C3 ester and the ¹¹⁹Sn resonance, with a ⁿJ(¹H–¹¹⁹Sn) coupling constant of 6 Hz, to support our proposal. An objection can be raised that such a coupling could arise from a “pure” long range ⁴J(¹H–¹¹⁹Sn) coupling pathway through the carbon chain. Against this objection, we note, however, the very low intensity of such a correlation for the γ -CH₂ protons in the C4/C5 esters. Although the ¹¹⁹Sn chemical shift dependence on concentration of the C4/C5 esters suggests that an intermolecular coordination prevails at higher concentrations, our ¹H–¹¹⁹Sn HMQC data clearly establish the existence at low concentration of an intramolecular correlation between the δ -CH₂ and ϵ -CH₂ protons and the tin-119 nucleus for the C4 and C5 esters, respectively, occurring through the alkoxy oxygen, since any significant such correlation is absent for the acetoxy methyl protons. This illustrates again the power of ¹H–¹¹⁹Sn HMQC spectroscopy to detect weak coordinations, as outlined previously for functionalized triphenylvinyltin compounds.¹⁶

It should be stressed that ¹H–¹¹⁹Sn HMQC spectra provide “snap-shot” resonances from solely those species where an observable ⁿJ(¹H–¹¹⁹Sn) exists, even if this species has very low concentration. Therefore, the species where no such coupling is observable are “edited away” from the spectrum in a ¹H–¹¹⁹Sn HMQC experiment. While the standard ¹H spectrum of the C4/C5 esters reflects an average of a monomeric, intramolecularly coordinating species and an oligomeric one with intermolecular coordination, a ¹H–¹¹⁹Sn HMQC spectrum specifically edits only the species where the coordination between the alkoxy oxygen atom and the tin atom gives rise to a visible coupling. This result suggests a different coordination mode for the oligomeric species. The following ¹⁷O NMR data and AM1 calculations, supported by a few IR data, provide evidence for this.

¹⁷O NMR Data. We measured the ¹⁷O chemical shifts¹³ of both the carbonyl and alkoxy ¹⁷O resonances of CH₃COO(CH₂)_nSnCl₃ with respect to those of butyl acetate, CH₃COO(CH₂)₃CH₃, taken as a reference compound. Acquisitions at high concentration (100 mg/0.5 mL) only could be performed, because of the low sensitivity of ¹⁷O NMR.¹³ Spectra were recorded at slightly higher temperatures (313 K), in order to minimize the unfavorable line-width features of quadrupolar nuclei such as ¹⁷O. The results are reviewed in Table 3.

The chemical shifts of both the carbonyl and alkoxy ¹⁷O nuclei are in agreement with literature data for comparable compounds.³²

Table 3. ¹⁷O Chemical Data at 313 K of C₆D₆ Solutions^a of CH₃COO(CH₂)_nSnCl₃ Esters (n = 3–5) and the Reference CH₃COO(CH₂)₃CH₃ Compound^b

compd	C= ¹⁷ O	– ¹⁷ O–R
CH ₃ COO(CH ₂) ₃ SnCl ₃	367.5 (+3.9) ^c	162.6 (–2.6)
CH ₃ COO(CH ₂) ₄ SnCl ₃	359.3 (–4.3)	166.5 (+1.3)
CH ₃ COO(CH ₂) ₅ SnCl ₃	357.4 (–6.2)	167.8 (+2.6)
CH ₃ COO(CH ₂) ₃ CH ₃	363.6	165.2

^a 100 mg in 0.5 mL of C₆D₆, recorded at 67.8 MHz. ^b Chemical shift (in ppm) referenced to external H₂¹⁷O at natural abundance. ^c Values in parentheses represent the ¹⁷O chemical shift difference with respect to CH₃COO(CH₂)₃CH₃.

The ¹⁷O NMR data likewise outline the different nature of the coordinative properties of the C4/C5 esters with respect to the C3 ester. In comparison with CH₃COO(CH₂)₃CH₃, the carbonyl ¹⁷O chemical shift of the C4/C5 esters is shifted to low frequency by –4.3 and –6.2 ppm, respectively. The alkoxy ¹⁷O resonance is high-frequency-shifted by respectively +1.3 and +2.6 ppm. For the C3 ester, the shifts are in opposite directions, to low frequency for the alkoxy ¹⁷O resonance (–2.6 ppm) and to high frequency for the carbonyl ¹⁷O resonance (+3.9 ppm).

It is well recognized that interactions of oxygen lone pairs with electrophiles, either protons in hydrogen bridges^{23,33} or metals in Lewis donor–acceptor interactions,^{35bc} systematically cause a low-frequency shift of the ¹⁷O resonance of the oxygen atom at which it occurs. Furthermore, it is well-known that a global electron density increase at the oxygen atom is accompanied by a shielding effect (low frequency shift) at the ¹⁷O resonance,^{32b,33b} at least for oxygen atoms where increases in electron density are dominated by π -charge transfers;^{35c} it should indeed be pointed out that pure σ -electron density increases appear to induce high-frequency ¹⁷O shifts.^{32a,33b}

So far, all NMR data, including the ¹⁷O chemical shifts, converge for the C3 ester to indicate a fast equilibrium mixture with the predominant species having an intramolecular coordination of the tin atom by the alkoxy oxygen atom of the ester function, rather than by its carbonyl one. In the case of the C4/C5 esters, the equilibrium mixture favors a monomeric species at high dilution and aggregation at high concentration. At high dilution the ¹H–¹¹⁹Sn HMQC data clearly establish the existence of an intramolecular correlation; this is not, however, reflected by the ¹⁷O NMR data, since they were acquired with concentrated solutions favoring aggregation. Under these conditions, the ¹⁷O chemical shifts, in opposite directions, as compared to the C3 ester, indicate a coordination by the carbonyl oxygen rather than by the alkoxy one.

Further support for the interpretation of the ¹⁷O spectra comes from literature data, indicating that the

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Table 4. Charge Distribution (Based on Mulliken Populations) on Selected Atoms for Some of the Possible Structures, As Calculated by the AM1 Method

compd	C=O	-O-R	Sn	Cl
CH ₃ COO(CH ₂) ₃ SnCl ₃ (open chain form)	-0.351	-0.284	+1.062	-0.321 -0.321 -0.321
CH ₃ COO(CH ₂) ₃ SnCl ₃ (five-membered ring)	-0.335	-0.325	+1.101	-0.334 -0.343 -0.360
CH ₃ COO(CH ₂) ₅ SnCl ₃ (cyclodimer, Sn←O=C)	-0.397	-0.231	+1.124	-0.339 -0.339 -0.423
CH ₃ COO(CH ₂) ₅ SnCl ₃ (dimer, octahedral tin with bidentate ester interaction)	-0.351	-0.208	+1.109	-0.275 -0.446 -0.485
CH ₃ COO(CH ₂) ₃ CH ₃	-0.356	-0.284		

interaction complex between PhCOOPh-¹⁷O₂ and AlBr₃, suggested^{35a} by infrared data to involve the carbonyl oxygen atom rather than the alkoxy one, causes strong ¹⁷O chemical shifts to *low* frequency (*ca.* 120 ppm) for the carbonyl oxygen and weaker, though still important, ones to *high* frequency (*ca.* 30 ppm) for the alkoxy oxygen. Besides, considering the extent of these shifts with respect to ours, which amount to only a few ppm, it can be concluded that the -CH₂O→SnCl₃ interaction is considerably weaker than the C=O→AlBr₃ one. This can be traced back to the larger atomic radius and the higher polarizability of the valence electron shell of the Sn atom with respect to the Al one.

Quantum-Chemical AM1 Calculations. In order to interpret properly the ¹⁷O chemical shifts, AM1 calculations¹⁹ have been performed on the CH₃COO-(CH₂)_{*n*}SnCl₃ esters (*n* = 3–5) as well as on CH₃COO-(CH₂)₃CH₃, taken as a reference compound, because ¹⁷O shielding is directly correlated to the charge density on this atom.^{32,33}

In all cases, calculations were performed for an open-chain structure, without any Sn←O interaction, together with cyclic structures involving intra- or intermolecular Sn←O interactions. For *n* = 3, a five-membered ring involving a Sn←OCH₂ interaction was studied together with a seven-membered ring with a Sn←O=C(CH₃)O- interaction. For *n* = 4 (5), a six(seven)-membered ring involving a Sn←OCH₂ interaction was selected; moreover, for *n* = 5, a head-to-tail dimeric form was studied.

A selection of calculated charge densities on oxygen and tin is reviewed in Table 4.

Table 4 reveals an excellent agreement between the charge densities of the reference compound CH₃COO-(CH₂)₃CH₃ and of the open-chain form of CH₃COO-(CH₂)₃SnCl₃ without any interaction between oxygen and tin. In contrast, a decrease in negative charge on the carbonyl oxygen, accompanied by an increase of negative charge on the alkoxy oxygen, is observed in a cyclic conformation of the C3 ester involving an interaction between tin and the alkoxy oxygen. Attempts to find a potential minimum for another cyclic structure of the C3 ester involving intramolecular coordination by the carbonyl oxygen, thus giving rise to a seven-membered ring, failed. Analogous calculations on the C4 and C5 esters, involving an intramolecular interaction between tin and the alkoxy oxygen in a six-

seven-membered ring, respectively, likewise did not converge to an energy minimum.

An intermolecular Sn←O=C(CH₃)O- interaction for the C5 ester gives rise to an increase in negative charge on the carbonyl oxygen, accompanied by a decrease on the alkoxy oxygen. Analogous calculations, assuming a chelating interaction between the tin atom of one molecule and both oxygen atoms of another molecule, giving rise to an octahedral tin atom with a *trans* configuration of the oxygen and chlorine atoms,³⁴ did not converge to an energy minimum. Here, a single-point calculation gave rise to a different charge distribution, indicating less charge transfer from the coordinating oxygen to the acceptor tin atom (see Table 4; compare with the increasing negative charge on the carbonyl oxygen atom and the positive charges on the tin atom (see below)).

Coordination Mode in the C3 Ester. The comparison of AM1 charge distributions in the open chain and cyclic structures of the C3 ester can be interpreted in terms of an electron transfer from the CH₃COO group to the SnCl₃ group, leading to an increase of electronic population on the chlorine and the alkoxy oxygen atoms, accompanied by a decrease on the tin and the carbonyl oxygen atoms. This charge redistribution upon O→Sn interaction is completely analogous to hydrogen bond formation in the unit R-B→H-A, in which the proton donor H-A accepts electrons from the proton acceptor R-B. Quantum-chemical calculations invariably show that, upon interactions of this type, a decrease in the electronic population on the hydrogen atom occurs. In contrast, an increase on atom B of the proton acceptor (Gutman's pileup effect) is found together with an increase in negative charge at the peripheries (A) of the proton donor molecule AH (spillover effect).^{38,39}

In view of these considerations, there is little doubt that the interaction between the tin atom and the ester function in the dominant solution species of the C3 ester occurs at the alkoxy oxygen atom. The Lewis donor-acceptor interaction indeed causes the usual low-frequency shift^{23,33,35} which we observe at the ¹⁷O chemical shift of the alkoxy oxygen atom rather than the carbonyl one. The high-frequency shift at the ¹⁷O resonance of the carbonyl group is completely in agreement with the above-mentioned -CH₂O→SnCl₃ electron flow evidenced by the AM1 calculations. In agreement with this interpretation is the increase of 19 cm⁻¹ in the C=O stretch frequency observed in the FT-IR spectrum in CCl₄ solution for the C3 ester, CH₃COO-(CH₂)₃SnCl₃, with respect to butyl acetate, CH₃COO-(CH₂)₃CH₃. These data³⁶ are in contrast with the strong decrease of 65 cm⁻¹ observed when a strong coordination exists between the carbonyl oxygen and the tin atom of the trichlorostannyl moiety.⁴⁰ Likewise, the decrease in the ³J(¹³C-^{119/117}Sn) coupling value by *ca.* 50% (Table 2) can be rationalized, if the well-known property^{29a} that ²J(X-¹¹⁹Sn) and ³J(X-¹¹⁹Sn) coupling constants (X = ¹H, ¹³C) have opposite signs is exploited. If so, the proposed -CH₂O→SnCl₃ interaction should give rise to a composite J(¹³C-^{119/117}Sn) coupling for the γ -CH₂

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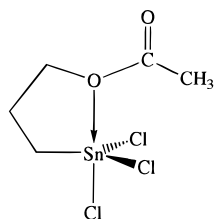


Figure 3. Main structure proposed for the C3 ester $\text{CH}_3\text{COO}(\text{CH}_2)_3\text{SnCl}_3$, in both dilute and concentrated solutions.

carbon atom resulting from the sum of contributions with opposite sign from one 3J pathway, the usual carbon chain $^3J(^{13}\text{C}-\text{C}-^{119}\text{Sn})$ coupling pathway contributing *ca.* 110–130 Hz (see the other compounds) and the special $^2J(^{13}\text{C}-\text{O}\rightarrow^{119}\text{Sn})$ coupling pathway that accordingly decreases the total coupling constant to the value of *ca.* 60 Hz actually observed.

Figure 3 gives the structure resulting from these data for the dominant solution species of the C3 ester. It exhibits the usual trigonal-bipyramidal structure characteristic for this type of five-coordinate organotin compound.⁴¹ Accordingly, the oxygen atom is proposed to span an apical position, because of the apicophilicity of this element;³⁴ consequently, the α - CH_2 group of the carbon chain occupies an equatorial position. This structure is the one obtained from the geometry optimization by the AM1 computations, giving an Sn–O distance of 2.78 Å. In this structure, the apical chlorine has the most negative charge of the three chlorine atoms, although apical (2.29 Å) and equatorial (2.28 Å) chlorine–tin bond lengths hardly differ.

The only weak dependence of several NMR parameters of the C3 ester on concentration indicates that in the fast equilibrium between the monomeric intramolecularly coordinating species and the oligomeric one with intermolecular coordination, the former is favored by far at both low and high concentration. In the solid state, IR data confirm at least the participation of intermolecular aggregation, by Sn–O=C interaction, as a low-frequency shift of the carbonyl stretching (-38 cm^{-1}) and a high-frequency shift ($+47\text{ cm}^{-1}$) of the acetate band is observed, as compared to butyl acetate in CCl_4 .

Coordination Mode in the C4 and C5 Esters. For the C4/C5 esters, the $^1\text{H}-^{119}\text{Sn}$ HMQC correlation confirms the presence of an intramolecular coordination at high dilution, but it is extremely weak when compared to the C3 ester. The shielding in ^{119}Sn chemical shift between the C4/C5 esters and the nonfunctionalized esters hardly amounts to 10 ppm, in contrast with the C3 ester, where it is larger than 35 ppm. The IR data in dilute CCl_4 solution indicate likewise a weak intramolecular interaction, of the same kind as observed for the C3 ester, to exist in the C4/C5 esters; thus, frequency shifts in the same direction, although much smaller ($+4$ to $+6\text{ cm}^{-1}$ for the C=O and -10 to -12 cm^{-1} for C–O stretches in the C4/C5 esters *versus* $+19\text{ cm}^{-1}$ for the C=O and -33 cm^{-1} for C–O stretches in the C3 ester), are observed when compared with the

reference $\text{CH}_3\text{COO}(\text{CH}_2)_3\text{CH}_3$. Finally, the $^1J(^{13}\text{C}-^{119}\text{Sn})$ coupling constant undoubtedly confirms a weak coordination to exist, being about 10–15 Hz larger than in the nonfunctionalized esters. Taking into account this experimental evidence, we propose the coordination mode for the C4/C5 esters at high dilution to be analogous to the C3 mode. The considerably weaker coordination is ascribed to the expected higher flexibility of the six- and seven-membered rings generated, respectively, in the C4 and C5 esters, which is anticipated to destabilize the intramolecular coordination to a larger extent than in the C3 ester. Attempts to optimize a six-membered ring involving the alkoxy oxygen by AM1 calculations led by no means to a minimum in energy. Exploratory single-point calculations reveal that the charge distribution is close to the open-chain case, with only an extremely weak electron transfer (and resulting stabilization) from the alkoxy oxygen toward the tin atom, as evidenced by the NMR and IR data. Although these calculations refer, strictly speaking, to the gas phase and neglect solvent effects, they confirm at least that the strength of the intramolecular Sn–O interaction decreases upon increase of the polymethylene chain length.

The dramatic low-frequency shift of the ^{119}Sn chemical shift and the increasing $^1J(^{13}\text{C}-^{119}\text{Sn})$ coupling constant upon 10-fold concentration increase in both C4 and C5 esters support an interpretation based on a fast equilibrium favoring aggregation through intermolecular coordination. The low-frequency ^{17}O shift observed at the carbonyl oxygen atom is in accordance with the charge distribution that results from a AM1 calculation, performed on a structure having a Sn–O=C interaction. Geometry optimization of this structure resulted in a trigonal-bipyramidal tin atom, having one oxygen and one chlorine atom in apical positions, with a distance of 2.67 Å between the Sn and O atoms. The latter distance, somewhat shorter than the distance of 2.78 Å found for the intramolecular Sn–OCH₂– coordination of the C3 ester, confirms the intermolecular coordination of the C4/C5 esters to be slightly stronger than the intramolecular one of the C3 ester, in agreement with tin NMR data. An alternative coordination, with the ester in the bidentate mode, is rejected, because AM1 calculations do not converge to an energy minimum and charge distributions resulting from a single-point calculation are in disagreement with the ^{17}O chemical shift data.

We propose the dominant solution species at high concentration, and tentatively also in the solid state, of the C4/C5 esters to be (cyclo)dimeric, in a head-to-tail arrangement, or oligomeric through coordination of the trichlorostannyl moiety by the carbonyl atom of the ester functions. Figure 4 gives a representation of such an intermolecular Sn–O=C interaction.

Conclusion

The difference in coordination modes of the oxygen atoms toward tin, in the C3 ester as compared to the C4/C5 ones, is only apparent, since both coexist in solution in fast chemical equilibrium in all three esters. Thus, whenever coordination expansion is possible through generation of a stable cyclic structure, as in the C3 ester, the latter species is favored. In contrast, whenever intramolecular coordination leads to overly

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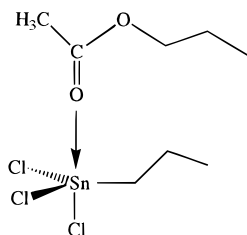


Figure 4. Intermolecular Sn←O=C interaction leading to (cyclo)dimeric or oligomeric aggregate structures in the esters $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$, at high concentration, as well as in pure molten and solid states ($n = 4, 5$).

flexible cycles, made fragile by thermal motions as in the C4/C5 esters, an oligomeric species based on an intermolecular coordination mode is favored. The present investigation on these ω -(trichlorostannyl)alkyl acetates, $\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3$ ($n = 3-5$) reveals how combining ^{17}O NMR, $^1\text{H}-^{119}\text{Sn}$ HMQC NMR spectroscopy, and AM1 calculations allows discrimination between alkoxy and carbonyl oxygen coordination to tin, the latter solely having been reported so far.^{11,12,40,42} Last but not least, the present work provides a firm

understanding of the more pronounced chemical instability of 3-(trichlorostannyl)propyl acrylate as compared to its 5-(trichlorostannyl)pentyl analog, because the stronger intramolecular coordination in the former activates the double bond more toward polymerization.^{10a}

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