5124 *Organometallics* **1997,** *16,* 5124−5126

Solid-State Coordination Behavior of Trichloro(4-acetoxybutyl)tin

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Received July 14, 1997⊗

Summary: In the solid state, trichloro(4-acetoxybutyl)tin is a centrosymmetric dimer in which the tin shows a distorted trigonal-bipyramidal geometry. Two molecules are linked through coordination bonds between the metal and the carbonyl oxygen of the ester group.

Introduction

Monoorganotin compounds are important intermediates that possess interesting applications.[1−3] In these compounds, tin is sufficiently electrophilic to increase its coordination[4] from four, in the presence of suitable ligands, to five or even six with good coordinating agents. In cases where the organic group contains a potential donor atom separated from the metal by two or three methylene groups, this coordination is usually intramolecular, leading to cyclic adducts.[5−7] A five- or six-membered ring is, thus, formed by internal coordination.

Recently, we have been interested in the preparation of hybrid materials, obtained by hydrolysis−polymerization of functional monoorganotin oxides, which necessitates functionalized trichloroorganotins as intermediates.[8] During this study, we were intrigued by the different behavior of trichloro(ω-acetoxyalkyl)tins which was found to depend on the number of methylene units, three (**1**), four (**2**), or five (**3**), between the tin and the ester group. The compounds **1**, **2**, and **3** have six, seven, or eight bonds between the tin and the carbonyl oxygen, respectively. For instance, the ^{119}Sn NMR chemical shift of ester **1** is insensitive to dilution, while **2** and **3** show an upfield shift of about 30 ppm when going from ~0.06 to ~0.6 N solution. The propensity to spontaneously polymerize by autocondensation of the acryloyl moiety was also higher for trichloro(3-acroyloxypropyl)tin (**4**) than for trichloro(4-acroyloxybutyl)tin (**5**) and trichloro(5-acroyloxypentyl)tin (**6**).[9] Extensive multinuclear solid- and solution-state NMR, as well as AM1 quantum-chemical calculations, showed that these compounds differed in the coordination mode of the ester group. In compounds **2** and **3**, the tin atom is *inter*molecularly bonded to the oxygen of the carbonyl of the ester group, which leads to cyclodimeric or oligomeric aggregate structures. In contrast, in compound **1**, the tin is *intra*molecularly bonded to the alkoxy oxygen atom of the ester group, rather than the carbonyl oxygen, to give a stable five-membered cyclic structure, as shown in Figure 1.[10] Subsequent to the publication of this work, suitable crystals of trichloro(4-acetoxybutyl)tin (**2**) have been obtained and the results of their X-ray crystallographic study are reported herein.

Results and Discussion

Recrystallization of **2** from a toluene solution provided crystals suitable for structure determination. The mo-

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⊗ Abstract published in *Advance ACS Abstracts*, October 15, 1997.

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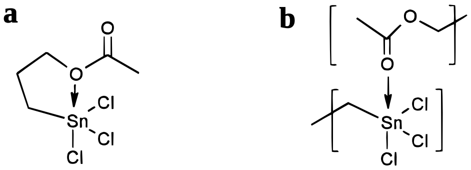

Figure 1. (a) Proposed structure for **1**. (b) Oligomeric or dimeric proposed structure for **2** and **3**.

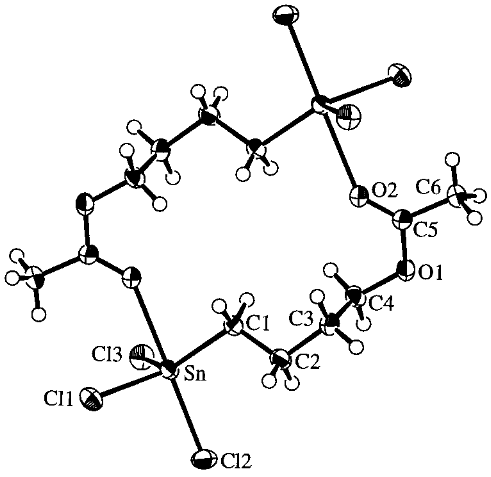

Figure 2. Molecular structure of **2**.

Table 1. Selected Interatomic Parameters (Å, deg) for 2[a]

Sn−Cl(1)	2.332(1)	Sn−Cl(2)	2.389(1)
Sn−Cl(3)	2.324(1)	Sn−O(2)^i	2.463(3)
Sn−C(1)	2.132(4)	O(1)−C(4)	1.460(5)
O(1)−C(5)	1.324(5)	O(2)−C(5)	1.213(4)
Cl(1)−Sn−Cl(2)	93.20(4)	Cl(1)−Sn−Cl(3)	104.24(4)
Cl(1)−Sn−O(2)^i	85.61(7)	Cl(1)−Sn−C(1)^i	125.9(1)
Cl(2)−Sn−Cl(3)	98.04(4)	Cl(2)−Sn−O(2)^i	178.67(7)
Cl(2)−Sn−C(1)	103.6(1)	Cl(3)−Sn−O(2)^i	82.83(7)
Cl(3)−Sn−C(1)	123.1(1)	O(2)^i−Sn−C(1)	76.7(1)
C(4)−O(1)−C(5)	117.8(3)	Sn−O(2)^i−C(5)^i	140.9(3)
Sn−C(1)−C(2)	115.7(3)		

[a] Symmetry operation i: $1 - x$, $1 - y$, $-z$.

lecular structure and crystallographic numbering scheme is shown in Figure 2, and selected geometric parameters are collected in Table 1. The structure of **2** exists as a centrosymmetric dimer in the solid state as a result of intermolecular coordination between the tin and the carbonyl O(2) atom. The coordination geometry is distorted trigonal bipyramidal with the tin atom being 0.3373(3) Å out of the C(1)/Cl(1)/Cl(3) plane in the direction of the Cl(2) atom. The axial positions are defined by the Cl(2) and O(2)^i atoms such that Cl(2)−Sn−O(2)^i is 178.67(7)°; symmetry operation $i = 1 - x$, $1 - y$, $-z$. The Sn−O(2) separation of 2.463(3) Å is indicative of a significant interaction, and it is noteworthy that the Cl(2) atom, *trans* to O(2), forms the longest Sn−Cl bond, i.e., 2.389(1) Å *cf.* 2.332(1) and 2.324(1) Å. The cyclodimer comprises a 16-membered ring which adopts an extended chair conformation such that the tin polyhedra are above and below the alkyl-rich centers.

There are similarities between the tin-atom geometry in **2** and the tin geometry in trichloro(2-(methoxycarbonyl)ethyl)tin[7d] (**7**), trichloro(2-(*i*-propoxycarbonyl)ethyl)tin[7g] (**8**), and trichloro(3-(methoxycarbonyl)propyl)tin[7f] (**9**). The trigonal bipyramidal geometries are common, with O−Sn−Cl axial coordination (**2** 178.67(7)°; **7** 176.7(2)°; **8** 175.3(1)°; **9** 174.4(2)°) and $SnCl_2$ equatorial planes. They all show almost identical patterns in tin−chlorine bond lengths with the apical bond being consistently longer than the equatorial bonds. The distinguishing feature of the structures is the length of the tin−oxygen bonds. In intramolecularly coordinated **7**, **8**, and **9**, the tin−oxygen bond lengths are, respectively, 2.347(5), 2.337(5), and 2.405(8) Å, which reveals a weakening in coordination when going from a five-membered to a six-membered chelate. This decrease in coordination was confirmed by a study of the formation constants of adducts **7**[7g] and **9**[7f] with various ligands. In **2**, the tin−oxygen bond distance of 2.463(3) Å is even larger, which shows a marked decrease of the strength of the tin−oxygen interaction, and explains the IR shift of the carbonyl stretching bands in the solid state, -85 cm^{-1} in **4** and -62 cm^{-1} in **6** versus -40 cm^{-1} in **2** with respect to butyl acetate as the reference ester.

When intramolecular coordination can lead to five- or six-membered rings, monomers are usually formed.[5] In **2**, this type of internal coordination would give rise to an eight-membered ring. This study demonstrates that large chelate rings are not favored. It also confirms that structural differentiation between intramolecular and intermolecular coordination is possible by combined multinuclear NMR studies and AM1 quantum-chemical calculations. Recently, similar strategies on trichloro(ω-(hydroxyalkyl))tins agreed with the X-ray structure determination with trichloro(5-(hydroxypentyl))tin showing, as predicted, an oligomeric structure.[11]

Experimental Section

Compound **2** was prepared as described previously.[8a] Intensity data for a colorless crystal (0.11 × 0.19 × 0.40 mm) were measured at 200 K on an AFC6R diffractometer fitted with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) employing the $\omega-2\theta$ scan technique. Corrections were applied for Lorentz and polarization effects[12] and for absorption using an empirical procedure (range of transmission factors 0.741−1).[13] Of the 2869 data measured, 2704 were unique and 2131 satisfied the $I \geq 3.0\sigma(I)$ criterion and were used in the subsequent analysis.

Crystal data for **2**: $C_{12}H_{22}Cl_6O_4Sn_2$, $M = 680.4$, monoclinic, space group $P2_1/c$, $a = 8.827(1)$ Å, $b = 9.952(2)$ Å, $c = 12.565(2)$ Å, $\beta = 90.65(1)°$, $V = 1103.6(2)$ Å^3, $Z = 2$, $D_c = 2.047$ g cm^{-3}, $F(000) = 656$, $\mu = 30.01$ cm^{-1}.

The structure was solved by direct methods[14] and refined by a full-matrix least-squares method based on F. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included in the model in their calculated positions (C−H = 0.97 Å). After the inclusion of the weighting scheme of the form $w = 1/\sigma^2(F)$, the refinement was continued until convergence when $R = 0.029$ and $R_w = 0.037$. The maximum residual in the final difference map was 0.57 e Å^{-3}, and the analysis of the variance showed no special features. Neutral scattering factors, corrected for f' and f'', were as incorporated in teXsan[12] with which all

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calculations were conducted. The numbering scheme is given in Figure 2 which was drawn with ORTEP[15] at 50% probability ellipsoids.

Acknowledgment. The Australian Research Council is thanked for support of the crystallographic facility. We are indebted to Sipcam-Phyteurop for the generous gift of chemicals.

Supporting Information Available: Tables of atomic coordinates, bond distances and angles, and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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