Preparation and Structure of a Novel Crystalline Adduct of Two Organotin Compounds [Ph$_2$Sn-SnPh$_2$• (μ-PhCO$_2$)$_2$] and (Ph$_3$Sn-SnPh$_3$)

Bin Zhao[1,*], Fan Li Lu[1], Feng Qin Wang[1], Jin Chao Tao[2]

1. Chemistry Department, Qufu Normal University, Qufu, Shangdong 273165, China
2. Department of Chemistry, Zhengzhou University, Zhengzhou, Henan 450052, China
01186-537-4456305 (Phone); 01186-537-4456305 (Fax); bin-zhao@sohu.com

Abstract: A new interesting crystalline adduct was prepared by the radical reaction of triphenyltin hydride and benzoyl peroxide. The crystalline adduct structure was determined. It is found out that the crystalline adduct is formed by two organotin compounds [**1**: Ph$_2$Sn-SnPh$_2$• (μ-PhCOO)$_2$, **2**: Ph$_3$Sn-SnPh$_3$, 1 / 1] which are interacted by intermolecular Van der Walls forces. The Ph$_4$Sn$_2$ units in compound **1** are bridged by two isobidentate benzoates resulting in five-coordinated tin atoms. The Sn-Sn bonds are found in organotin compound **1** and **2** and the Sn-Sn bond lengths in **1** and **2** are 2.6983(10) and 2.8040(11) Å respectively. A possible mechanism of the formation of the crystalline adduct is also suggested. [Nature and Science. 2004;2(4):28-33].

Keywords: organotin compounds; crystalline adduct; preparation; Sn-Sn bond; crystal structure

1. Introduction

Since the synthesis of organotin compounds was first reported by Frankland in 1849, the syntheses and application of organotin compounds have attracted chemists' considerable attention (Pan, 1990; Gielen, 1992; Crowe, 1980; Gielen, 1996). Hutton et al developed a novel route to the preparation of β-alkoxycarbonylethyltin trichlorides, ROCOCH$_2$CH$_2$SnCl$_3$ (1978). The research results show that these compounds have a variety of coordination geometries regarding the tin atom. We have reported the synthesis, structure and transesterification of the derivatives of 2-alkoxycarbonylethyltin trichlorides (Tian, 1998; 1998; 2000). With an attempt to get the derivatives of 2-alkoxycarbonylethyltriphenyltin (Ph$_3$SnCH$_2$CH$_2$CO$_2$R) by the radical reaction of triphenyltin hydride, acrylate and benzoyl peroxide, we got a crystalline adduct of organotin compound **1** and **2** (the structures are shown as follows) instead. In this present paper, this novel mixed single crystal structure is reported, and a possible mechanism for the formation of the crystalline adduct is suggested.
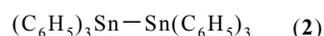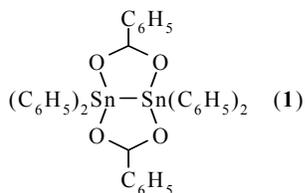
2. Experimental

2.1. Materials and physical measurements

All chemicals were of reagent grade or analytical grade, and used without further purification. The solvents used were dried over CaCl$_2$ and distilled before use. Carbon and hydrogen analyses were carried out with a Perkin-Elmer 2400II elemental analyzer, and tin was determined gravimetrically as SnO$_2$. The results of elemental analyses are in agreement with the theoretical calculations (± 0.5 %). IR spectra were recorded on a Nicolet 470 FT-IR spectrophotometer in KBr pellet. ^{1}H NMR spectra were carried out on a DPX-400 FT NMR spectrometer. Chemical shifts δ are given in ppm relative to that of chloroform (δ = 7.24 ppm). The structure was determined on an R-AXIS-IV diffratometer with graphite monochromated Mo-Kα radiation.

2.2. Preparation of triphenyltin hydride (Ph₃SnH) (Kuivila, 1961)

A solution of triphenyltin chloride (Ph₃SnCl, 38.5 g, 0.1 mol) dissolved in ether (150 cm³) was placed in a three-necked, Ar-flashed flask. LiAlH₄ (1.56 g, 0.041 mol) was added slowly under 5°C. The reaction mixture was stirred vigorously at 5°C for 15 minutes and placed at room temperature for 3 hours. Then, 100 cm³ of cool water was added dropwise. The ether layer was separated and the water layer was extracted with ether (2×50 cm³). The mixed extract was washed with water (2×50 cm³), dried with anhydrous sodium sulphate, and then evaporated to dryness to afford a crude oily product. The pure triphenyltin hydride (28 g, 79.8%) was obtained by reduced pressure distillation (162-168°C / 0.5 mmHg) as an oil.

2.3. Preparation of the crystalline adduct {[Ph₂Sn-SnPh₂ • (μ-PhCOO)₂] and (Ph₃Sn-SnPh₃)}

Triphenyltin hydride (0.005 mol) and benzoyl peroxide (0.005 mol) were dissolved in ether (100 cm³). The solution was stirred at 35 °C for 30 hours. The crude solid product was obtained after the removal of the solvent. The pure crystalline adduct was obtained by the recrystallization from chloroform, yield 6.4 g of the crystalline adduct. *Anal*. Found: C, 59.66; H, 4.19, Sn, 31.58 %. Calc. for $C_{74}H_{60}O_4Sn_4$: C, 59.72; H, 4.06, Sn, 31.91 %. IR: 3037(C-H); 1600, 1587 (phenyl ring); 1528, 1410 (COO). ¹H NMR (CDCl₃): δ = 6.78~7.46 (m, 30H, ArH).

2.4. Crystal structure determination of the crystalline adduct

A summary of the fundamental Crystal data for the crystalline adduct is given in Table 1. A colorless crystal of the crystalline adduct with the dimensions 0.30×0.20×0.20 mm was mounted on a R-AXIS-IV diffratometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The cell parameters were refined by least-squares fit of all reflections collected. The structure was solved by heavy-atom method. All refinements were performed by full-matrix least-squares on F^2. The positions of the hydrogen atoms were calculated assuming ideal geometries and refined with isotropic thermal parameters. All non-hydrogen atoms were refined with anisotropic thermal parameters.

3. Results and Discussion

3.1. Preparation of the crystalline adduct

With an attempt to get the derivatives of 2-alkoxycarbonylethyltriphenyltin (Ph₃SnCH₂CH₂CO₂R) by the radical reaction of triphenyltin hydride, acrylate and benzoyl peroxide, a kind of white crystal was obtained. The characterization by EA, IR, ¹H NMR showed that the product was a mixture of organotin compound **1** and **2** with the ratio of 1:1. The mixture was also obtained by the radical reaction of triphenyltin hydride and benzoyl peroxide in ether. The crystalline adduct used for the structure determination was obtained by the recrystallization from chloroform.

3.2. Crystal structure of the novel crystalline adduct

The crystal structures of the crystalline adduct, compound **1** and **2** are shown in Figure 1, Figure 2 and Figure 3. The crystal packing of the crystalline adduct is shown in Figure 4. Bond lengths and bond angles are given in Table 2 and Table 3. It is shown that the organotin compound **1** and **2** are interacted by intermolecular Van der Walls forces. The Ph₂Sn-SnPh₂ units in compound **1** are bridged by two isobidentate benzoates resulting in five-coordinated tin atoms. The bond lengths (in the compound **1**) of Sn(1)-Sn(1A), Sn(1)-O(1), Sn(1)-O(2), Sn(1)-C(6) and Sn(1)-C(19) are 2.6983(10), 2.274(4), 2.312(3), 2.143(5) and 2.157(5) Å respectively, the bond angles of C(6)-Sn(1)-C(19), C(6)-Sn(1)-Sn(1A), O(1)-Sn(1)-Sn(1A), O(1)-Sn(1)-C(6) and O(1)-Sn(1)-O(2) are 115.3(2), 123.39(15), 84.88(10), 93.1(2) and 169.02(13)°, respectively. The bond lengths (in compound **2**) of Sn(2)-Sn(2A) and Sn(2)-C(31) are 2.8040(11) and 2.159 Å, the bond angles of C(31)-Sn(2)-C(37) and C(31)-Sn(2)-Sn(2A) are 106.9(2) and 111.5(2)°. The Sn-Sn bond lengths of the organotin compound **1** and **2** are shorter than the distance between tin atom in the metal crystal (2.82 Å). These results demonstrate that Sn-Sn bond is formed, which is a very valuable result.

3.3. Mechanism for the formation of the crystalline adduct

The formation of the crystalline adduct is very

interesting. So, the formation mechanism for the crystalline adduct is studied. The formation reaction of the crystalline adduct undergoes a radical mechanism, and a possible mechanism of the formation is suggested (Figure 1). The homolysis of benzoyl peroxide gives two benzoyloxy radicals, which abstract two hydron atoms from two triphenyltin hydride, producing two triphenyltin radicals and two molecules of benzoic acid. And then, these two triphenyltin radicals combine to form hexaphenyl distannane (**2**). Finally, the substitution of two phenyl groups in hexaphenyl distannane by two benzoate anions, producing tetraphenyl distannane dibenzoate complex (**1**).
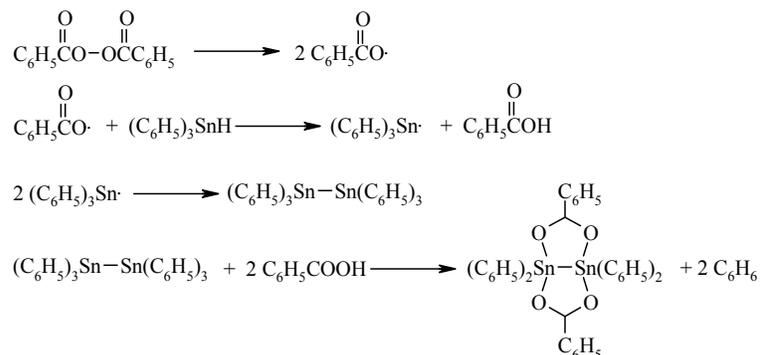
Figure 1. A possible mechanism for the formation of the crystalline adduct

Table 1. Crystal data for the crystalline adduct {[Ph$_2$Sn-SnPh$_2$• (µ-PhCOO)$_2$] & (Ph$_3$Sn-SnPh$_3$)}

Empirical formula	C$_{74}$H$_{60}$O$_4$Sn$_4$
Formula weight	1487.98
Temperature (K)	291(2)
Crystal system	triclinic system
Space group	P-1
Unit cell dimensions	
a (Å)	9.242(2)
b (Å)	12.248(2)
c (Å)	14.511(3)
α (°)	95.73(3)
β (°)	95.07(3)
γ (°)	94.71(3)
V (Å^3)	1621.2(6)
Dc (Mg mm^{-3})	1.524
Z	1
F(000)	736
Absorption coefficient μ (mm^{-1})	1.570
λ (Å)	0.71073
Crystal size (mm)	0.30 × 0.20 × 0.20
Theta range for data collection (°)	1.42 ≤ θ ≤ 27.58
Index ranges	-12 ≤ h ≤ 11, 0 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	5343
Independent reflections	5343
R$_{int}$	0.0000
Refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	5343 / 0 / 371
Goodness-of-fit on F^2	1.114
final R indices [$I>2\sigma(I)$]	R$_1$ = 0.0712[a], wR$_2$ = 0.2050[b]
R indices (all data)	R$_1$ = 0.0850[a], wR$_2$ = 0.2258[b]
Extinction coefficient	0.0155(12)
Largest difference peak and hole (e Å^{-3})	1.778 and −1.478

[a] R = $\Sigma(||Fo|-|Fc||)/\Sigma|Fo|$. 　　　[b] R = $[\Sigma w(|Fo|-|Fc|)^2/\Sigma w(|Fo|^2)]^{1/2}$, where $w=1/\alpha^2(|Fo|)$.
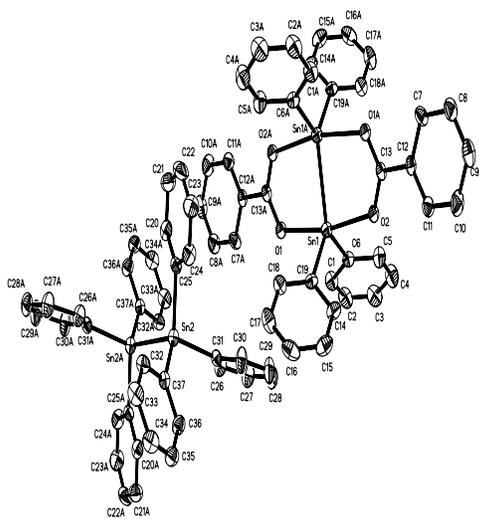
Figure 1. Molecular Structure of the Crystalline adduct
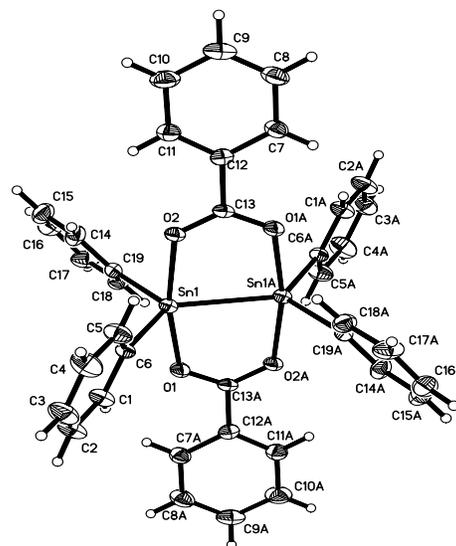
Figure 2. Molecular structure and atomic numbering scheme of A
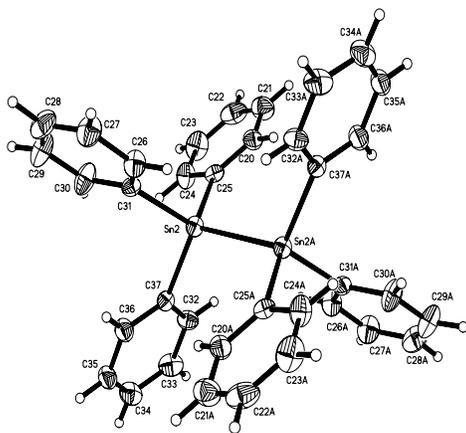
Figure 3. Molecular structure and atomic numbering scheme of B
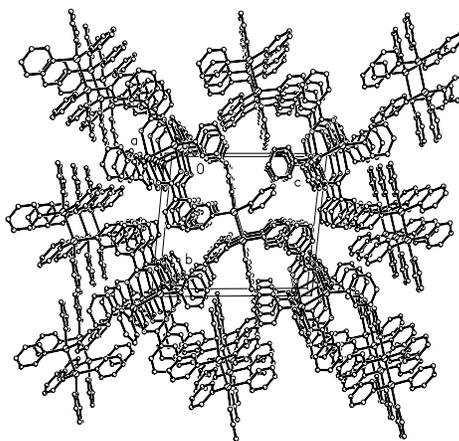
Figure 4. The crystal packing of the crystalline adduct

Table 2. Selected bond lengths (Å)

Sn(1)-C(6)	2.413(5)	C(14)-C(15)	1.367(9)
Sn(1)-C(19)	2.157(5)	C(15)-C(19)	1.383(8)
Sn(1)-O(1)	2.274(4)	C(15)-C(16)	1.397(11)
Sn(1)-O(2)	2.312(3)	C(16)-C(17)	1.358(12)
Sn(1)-Sn(1A)	2.6983(10)	C(17)-C(18)	1.421(9)
Sn(2)-C(31)	2.159(6)	C(18)-C(19)	1.361(8)
Sn(2)-C(37)	2.159(6)	C(20)-C(25)	1.345(9)
Sn(2)-C(25)	2.169(6)	C(20)-C(21)	1.432(11)
Sn(2)-Sn(2A)	2.8040(11)	C(21)-C(22)	1.385(12)
O(1)-C(13A)	1.285(6)	C(22)-C(23)	1.359(13)
O(2)-C(13)	1.265(6)	C(23)-C(24)	1.393(11)
C(1)-C(6)	1.396(8)	C(24)-C(25)	1.396(9)
C(1)-C(2)	1.408(9)	C(26)-C(31)	1.389(9)
C(2)-C(3)	1.362(11)	C(26)-C(27)	1.423(10)
C(3)-C(4)	1.374(12)	C(27)-C(28)	1.362(12)
C(4)-C(5)	1.383(10)	C(28)-C(29)	1.400(13)
C(5)-C(6)	1.395(8)	C(29)-C(30)	1.382(11)
C(7)-C(8)	1.411(9)	C(30)-C(31)	1.393(9)
C(7)-C(12)	1.415(8)	C(32)-C(33)	1.383(10)
C(8)-C(9)	1.375(10)	C(32)-C(37)	1.392(9)
C(9)-C(10)	1.397(11)	C(33)-C(34)	1.399(11)
C(10)-C(11)	1.402(9)	C(34)-C(35)	1.376(11)
C(11)-C(12)	1.362(8)	C(35)-C(36)	1.389(10)
C(12)-C(13)	1.503(7)	C(36)-C(37)	1.384(9)
C(13)-O(1A)	1.285(6)		

Table 3. Selected bond angles (º)

C(6)-Sn(1)-C(19)	115.3(2)	O(2)-C(13)-C(12)	117.9(5)
C(6)-Sn(1)-O(1)	93.1(2)	O(1A)-C(13)-C(12)	117.0(5)
C(19)-Sn(1)-O(1)	92.2(2)	C(15)-C(14)-C(19)	120.4(6)
C(6)-Sn(1)-O(2)	93.8(2)	C(14)-C(15)-C(16)	119.5(7)
C(19)-Sn(1)-O(2)	92.6(2)	C(17)-C(16)-C(15)	120.9(7)
O(1)-Sn(1)-O(2)	169.02(13)	C(16)-C(17)-C(18)	119.0(7)
C(6)-Sn(1)-Sn(1A)	123.39(15)	C(19)-C(18)-C(17)	119.7(6)
C(19)-Sn(1)-Sn(1A)	121.33(15)	C(18)-C(19)-C(14)	120.5(5)
O(1)-Sn(1)-Sn(1A)	84.88(10)	C(18)-C(19)-Sn(1)	119.7(4)
O(2)-Sn(1)-Sn(1A)	84.20(9)	C(14)-C(19)-Sn(1)	119.7(4)
C(31)-Sn(2)-C(37)	106.9(2)	C(25)-C(20)-C(21)	120.5(7)
C(31)-Sn(2)-C(25)	109.6(2)	C(22)-C(21)-C(20)	118.7(8)
C(37)-Sn(2)-C(25)	104.3(2)	C(23)-C(22)-C(21)	120.8(8)
C(31)-Sn(2)-Sn(2A)	111.5(2)	C(22)-C(23)-C(24)	119.7(8)

Continue Table3:

C(37)-Sn(2)-Sn(2A)	113.73(15)	C(23)-C(24)-C(25)	120.7(7)
C(25)-Sn(2)-Sn(2A)	110.4(2)	C(20)-C(25)-C(24)	119.5(6)
C(13A)-O(1)-Sn(1)	122.8(3)	C(20)-C(25)-Sn(2)	121.7(5)
C(13)-O(2)-Sn(1)	122.3(3)	C(24)-C(25)-Sn(2)	118.9(5)
C(6)-C(1)-C(2)	119.2(6)	C(31)-C(26)-C(27)	120.5(7)
C(3)-C(2)-C(1)	120.7(7)	C(28)-C(27)-C(26)	119.8(8)
C(2)-C(3)-C(4)	120.6(7)	C(27)-C(28)-C(29)	120.3(7)
C(3)-C(4)-C(5)	119.7(7)	C(30)-C(29)-C(28)	119.4(8)
C(4)-C(5)-C(6)	121.2(7)	C(29)-C(30)-C(31)	121.7(8)
C(5)-C(6)-C(1)	118.6(6)	C(26)-C(31)-C(30)	118.2(6)
C(5)-C(6)-Sn(1)	121.3(4)	C(26)-C(31)-Sn(2)	122.8(5)
C(1)-C(6)-Sn(1)	120.1(4)	C(30)-C(31)-Sn(2)	118.9(5)
C(8)-C(7)-C(12)	119.7(6)	C(33)-C(32)-C(37)	121.0(6)
C(9)-C(8)-C(7)	120.0(7)	C(32)-C(33)-C(34)	120.2(7)
C(8)-C(9)-C(10)	120.8(7)	C(35)-C(34)-C(33)	118.8(7)
C(9)-C(10)-C(11)	118.4(7)	C(34)-C(35)-C(36)	120.8(7)
C(12)-C(11)-C(10)	122.4(6)	C(37)-C(36)-C(35)	120.8(7)
C(11)-C(12)-C(7)	118.7(6)	C(36)-C(37)-C(32)	118.4(6)
C(11)-C(12)-C(13)	121.2(5)	C(36)-C(37)-Sn(2)	120.9(5)
C(7)-C(12)-C(13)	120.1(5)	C(32)-C(37)-Sn(2)	120.8(4)
O(2)-C(13)-O(1A)	125.1(5)		

Correspondence to:
Bin Zhao
Chemistry Department
Qufu Normal University
Qufu, Shangdong 273165, China
Telephone: (01186) 537-4456305
Email: bin-zhao@sohu.com

References

[1] Deb BK, Ghosh AK. *β*-Alkoxycarbonyl alkyl tin chelates-I. Oxinates and substituted oxinates: Preparation and spectroscopic studies. Polyhedron. 1986;*5*:863-870.

[2] Gielen M, Lelieveld P, Vos D, Pan H, Willem R, Biesemans M, Fiebig H. *In vitro* effect of organotin-substituted steroids in human tumor cell lines. Inorganica Chimica Acta, 1992, *196*:115-117.

[3] Gielen M. Tin-based antitumour drugs. Coordination Chemistry Reviews 1996;151:41-51.

[4] Hutton RE, Burley JW, Oakes V. *β*-Substituted alkyltin halides: I. Monoalkyltin trihalides: Synthetic, methanistic and spectroscopic aspects. Journal of Organometallic Chemistry 1978;156:369-382.

[5] Howie RA, Paterson ES, Wardell JL, Burley JW. Further study of estertin trichlorides, $Cl_3SnCH_2CH_2CO_2R$. Lewis acidity towards acetonitrile. Crystal structure of $Cl_3SnCH_2CH_2CO_2Pr$-*i*. Journal of Organometallic Chemistry 1986;*304*:301-308.

[6] Kuivila HG, Baumel OF. Reduction of some Aldehydes and Ketones with Organotin Hydrides. Journal of the American Chemical Society 1961;*83*:1246-1250.4-estren-17-ol: evidence by x-ray diffraction analysis and iodo demetalation. Organometallics 1990;9:2199-201.

[7] Pan H, Willem R, Meunier-piret J, Gielen M. Intramolecular O.fwdarw.Sn coordination in (Z)-17-[2-(triphenylstannyl)vinyl] -phenolato(2-)-N,O,O'}-2-methoxycarbonylethyltin trichloride. Main Group Metal Chemistry 1998; 21:735-740.

[8] Tian L, Zhou Z, Zhao B, Su Y, Zhang, C. Synthesis, structure and transesterification of {2-[2-hydroxyphenyliminomethyl] $SnCl_3$·(*n*-C_4H_9)$_2$SO. Polyhedron 1998;17:1275-1279.

[9] Tian L, Zhou Z, Zhao B, Yu W. Synthesis and characterization of β-alkoxycarbonylethyltin trichloride complexes with dibutylsulfoxide. Crystal structure of $CH_3CH_2OCOCH_2CH_2$

[10] Tian L, Zhao B, Zhou Z, Xia M, Yu W, Yang P. Synthesis, structure and transesterification of the derivatives of β-alkoxycarbonylethyltin trichlorides with diethyldithiocarbamate. Chinese Chemical Letters 2000;11:517-520.