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Triorganotin(IV) Complexes Containing Multifunctional *meso*-Dimercaptosuccinic Acid Ligand: Syntheses, Characterizations, and Crystal Structures

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ABSTRACT: *Four triorganotin complexes of the types* $[(R_3Sn)_2(C_2H_2S_2)(COOH)_2]\cdot 2Et_2O$ *(R = Ph,* **1***) and* $(R_3Sn)_2(C_2H_2S_2)(COOH)_2$ *(R = Me* **2***, R = n-Bu* **3***, and R = PhCH₂* **4***) have been obtained by the reaction of meso-dimercaptosuccinic acid and sodium ethoxide with triorganotin(IV) chloride in 1:2:2 stoichiometry. All the complexes were characterized by elemental analyses, IR spectroscopy, and NMR spectroscopy. Furthermore, complexes* **1** *and* **2** *were characterized by X-ray diffraction analyses, which revealed that complexes* **1** *and* **2** *are mononuclear structures and further interlinked by intermolecular C—H···O and O—H···O hydrogen bonds, respectively.* © 2009 Wiley Periodicals, Inc. Heteroatom Chem 20:50–55, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20511

INTRODUCTION

Organotin complexes have attracted more and more attention in recent years, partly owing to their determinately or potentially pharmaceutical value, which have been reported several times before [1–9], as well as the versatile molecular structure and supramolecular architecture exhibited by these complexes [10–14]. It is well known that organotin carboxylates have versatile molecular structures both in solid and in solution, such as monomers, dimers, tetramers, oligomeric ladders, hexameric drums, etc [15]. It has also been demonstrated that other structural types are formed owing to the presence of additional heteroatom sites (S, N, or O) along with a carboxylate moiety [10–12,16]. In our previous work, we have reported several new molecular structures of triorganotin complexes by the reaction of *meso*-dimercaptosuccinic acid (H_4dmsa) and sodium ethoxide with triorganotin(IV) chloride in 1:4:4 stoichiometry [17]. Now, we synthesize other four triorganotin complexes by the reaction of H_4dmsa and sodium ethoxide with triorganotin(IV) chloride in 1:2:2 stoichiometry. In this paper, we report syntheses and characterization of these triorganotin(IV) complexes.

EXPERIMENTAL

Materials and Measurements

All reagents were commercially available, and they were used without further purification. The melting points were obtained with X-4 digital micro melting point apparatus and were uncorrected. Infrared spectra were recorded on a Nicolet-5700

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spectrophotometer by using KBr discs and sodium chloride optics. ^{1}H and ^{119}Sn NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer operating at 400 and 149.2 MHz, respectively. The spectra were obtained at 298 K. Chemical shift values were reported in ppm with respect to references and were expressed relative to external tetramethylsilane for ^{1}H NMR and neat tetramethyltin for ^{119}Sn NMR. Elemental analyses (C and H) were performed with a PE-2400II apparatus.

Syntheses of Complexes **1–4**

$[(Ph_3Sn)_2(C_2H_2S_2)(COOH)_2]\cdot 2Et_2O$ **1**. The reaction was carried out under nitrogen atmosphere. H_4dmsa (0.182 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol), and Ph_3SnCl (0.770 g, 2 mmol) were added to ethanol (20 ml), continuing the reaction for 12 h at 40°C. The solid was recrystallized from ether, and colorless crystals were obtained. Yield: 79%. m.p. 160°C–162°C. Anal. found: C 56.77%, H 5.03%. Calc. for $C_{48}H_{54}O_6S_2Sn_2$: C 56.06%, H 5.29%. IR (KBr, cm^{-1}): ν(COO—H) 3227, ν(C—O—C) 944, ν(Sn—C) 522, ν(Sn-S) 331. ^{1}H NMR ($CDCl_3$, ppm): δ 1.11 (t, 12H, CH_3), 3.53 (m, 8H, CH_2), 4.22 (s, 2H, CH), 7.35–7.72 (m, 30H, Ar—H), 12.63 (s, 2H, COOH). ^{13}C NMR ($CDCl_3$, ppm): 174.2 (COOH), 136.5 (*i*-C, $^1J_{SnC} = 542$ Hz), 132.4 (*o*-C, $^2J_{SnC} = 40.4$ Hz), 129.2 (*m*-C, $^3J_{SnC} = 57.2$ Hz), 128.7 (*p*-C), 66.5 (O-CH_2), 52.4 (C—S), 15.3 (CH_3). ^{119}Sn NMR ($CDCl_3$, ppm): 76.5.

$(Me_3Sn)_2(C_2H_2S_2)(COOH)_2$ **2**. The procedure is similar to that reported for complex **1**. H_4dmsa (0.182 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol), and Me_3SnCl (0.398 g, 2 mmol) were added to ethanol (20 ml), continuing the reaction for 12 h at 40°C. The solid was recrystallized from ether, and colorless crystals were formed. Yield: 73%. m.p. 153°C–155°C. Anal. found: C 23.85%, H 4.12%. Calc. for $C_{10}H_{22}O_4S_2Sn_2$: C 23.65%, H 4.37%. IR (KBr, cm^{-1}): ν(COO—H) 3146, ν(Sn—C) 503, ν(Sn—S) 342. ^{1}H NMR [$(CD_3)_2SO$, ppm]: δ 0.85 (s, 18H, CH_3, $^2J_{SnH} = 62.4$ Hz), 4.37 (s, 2H, CH), 12.59 (s, 2H, COOH). ^{13}C NMR ($CDCl_3$, ppm): 172.8 (COOH), 54.1 (C—S), 13.8 (CH_3, $^1J_{SnC} = 420$ Hz). ^{119}Sn NMR ($CDCl_3$, ppm): 63.9.

$[(n\text{-}Bu)_3Sn]_2(C_2H_2S_2)(COOH)_2$ **3**. The procedure is similar to that reported for complex **1**. H_4dmsa (0.182 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol), and Me_3SnCl (0.650 g, 2 mmol) were added to ethanol (20 ml), continuing the reaction for 12 h at 40°C. The solvent is gradually removed by evaporation under vacuum until solid product is obtained. Yield: 76%. m.p. 131°C–134°C. Anal. found: C 44.51%, H 7.87%. Calc. for $C_{28}H_{58}O_4S_2Sn_2$: C 44.24%, H 7.69%. IR (KBr, cm^{-1}): ν(COO—H) 3197, ν(Sn—C) 515, ν(Sn—S) 328. ^{1}H NMR [$(CD_3)_2SO$, ppm]: δ 0.91 (s, 18H, CH_3), 1.29–1.58 (m, 36H, CH_2-CH_2-CH_2, $^2J_{SnH} = 76.8$ Hz), 4.05 (s, 2H, CH), 12.61 (s, 2H, COOH). ^{13}C NMR ($CDCl_3$, ppm): 169.4 (COOH), 53.3 (C—S), 28.7 (γCH_2, $^3J_{SnC} = 68$ Hz), 26.4 (βCH_2, $^2J_{SnC} = 22.4$ Hz), 25.6 (αCH_2, $^1J_{SnC} = 364.8$ Hz), 14.6 (CH_3). ^{119}Sn NMR ($CDCl_3$, ppm): 82.7.

$[(PhCH_2)_3Sn]_2(C_2H_2S_2)(COOH)_2$ **4**. The procedure is similar to that reported for complex **1**. H_4dmsa (0.182 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol), and Me_3SnCl (0.650 g, 2 mmol) were added to ethanol (20 ml), continuing the reaction for 12 h at 40°C. The solvent is gradually removed by evaporation under vacuum until solid product is obtained. Yield: 84%. m.p. 182°C–185°C. Anal. found: C 57.01%, H 4.52%. Calc. for $C_{46}H_{46}O_4S_2Sn_2$: C 57.29%, H 4.81%. IR (KBr, cm^{-1}): ν(COO—H) 3273, ν(Sn—C) 526, ν(Sn—S) 335. ^{1}H NMR [$(CD_3)_2SO$, ppm]: δ 2.72 (s, 12H, Ar—CH_2, $^2J_{SnH} = 67.2$ Hz), 4.63 (s, 2H, CH), 7.15–7.69 (m, 30H, Ar—H), 12.68 (s, 2H, COOH). ^{13}C NMR ($CDCl_3$, ppm): 170.5 (COOH), 137.3 (*i*-C, $^2J_{SnC} = 41.2$ Hz), 133.5 (*o*-C, $^3J_{SnC} = 19.2$ Hz), 130.8 (*m*-C), 128.9 (*p*-C), 51.7 (C—S), 24.3 (Ar—CH_2, $^1J_{SnC} = 320.8$ Hz). ^{119}Sn NMR ($CDCl_3$, ppm): 68.6.

X-ray Crystallography

Data were collected at 298 K on a Bruker SMART CCD 1000 diffractometer equipped with the Mo Kα radiation. The structures were solved by direct methods and refined by a full-matrix least-squares procedure based on $F2$ by using the SHELXL-97 program system. All nonhydrogen atoms were included in the model at their calculated positions. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included. Crystal data and experimental details of the structure determination are listed in Table 1.

RESULTS AND DISCUSSION

Syntheses of Complexes **1–4**

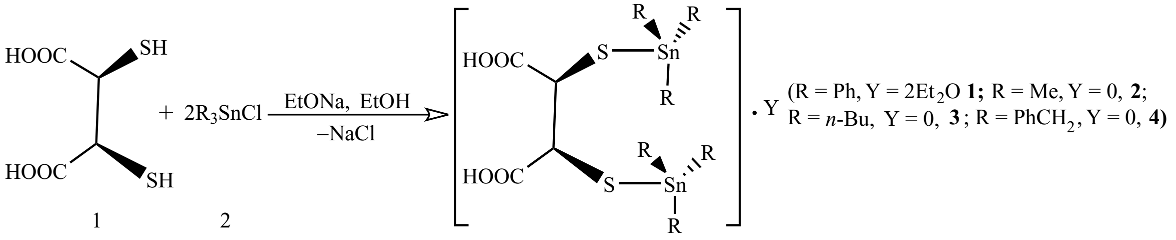
The synthetic procedure is shown in Scheme 1.

IR Spectroscopic Studies of Complexes **1–4**

The explicit features in the infrared spectra of complexes **1**–**4**, that is, strong absorption appearing in the range from 328 to 342 cm^{-1} for the complexes, which are absent in the free ligand, are assigned to

TABLE 1 Crystal Data and Refinement Details for Complexes **1** and **2**

	*Complex **1***	*Complex **2***
Empirical formula	$C_{48}H_{54}O_6S_2Sn_2$	$C_{10}H_{22}O_4S_2Sn_2$
Formula weight	1028.41	507.78
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/n$
Unit cell dimensions		
a (Å)	13.2002(12)	7.5434(12)
b (Å)	16.670(2)	14.390(2)
c (Å)	11.7247(10)	9.1840(16)
α (°)	90	90
β (°)	111.090(2)	110.822(2)
γ (°)	90	90
V (Å^3)	2407.1(4)	931.8(3)
Z	2	2
D_c (mg m^{-3})	1.419	1.810
Absorption coefficient (mm^{-1})	1.169	2.907
F (0 0 0)	1044	492
Crystal size (mm)	0.40 × 0.36 × 0.34	0.49 × 0.45 × 0.44
θ range (°)	2.06–25.01	2.76–25.01
Reflections collected	11,861	4552
Independent reflections	4236	1635
Data/restraints/parameters	4236/0/284	1635/0/85
Goodness-of-fit on $F2$	1.079	1.093
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0377$, $wR2 = 0.0845$	$R1 = 0.0347$, $wR2 = 0.0709$
R indices (all data)	$R1 = 0.0674$, $wR2 = 0.1044$	$R1 = 0.0477$, $wR2 = 0.0752$



SCHEME 1

the Sn—S stretching mode [18]. While the broad absorption band at 3100–3300 cm^{-1} is present in complexes **1–4**, which are assigned to the —COOH groups [19], indicating that the —COOH groups are not coordinate to the tin atoms. Moreover, a strong absorption band at about 944 cm^{-1} in complex **1** is assigned to the C—O—C stretching mode, which indicates the presence of ether molecules in complex **1**.

NMR Data of Complexes **1–4**

^{1}H NMR data show that the signal of the —SH proton in the spectrum of the free ligand is absent in complexes **1–4**, indicating the removal of the —SH proton and the formation of Sn—S bonds. ^{13}C NMR spectra show a downfield shift of all carbon resonances compared with the free ligand; the shift is a consequence of an electron density transfer from the ligand to the

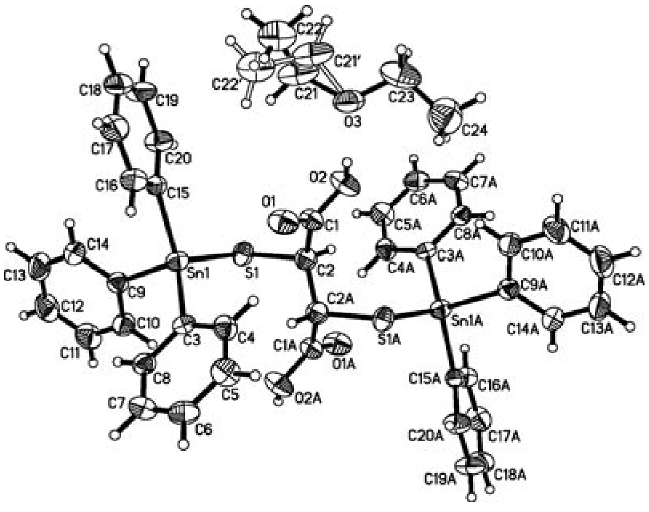


FIGURE 1 Molecular structure of complex **1**.

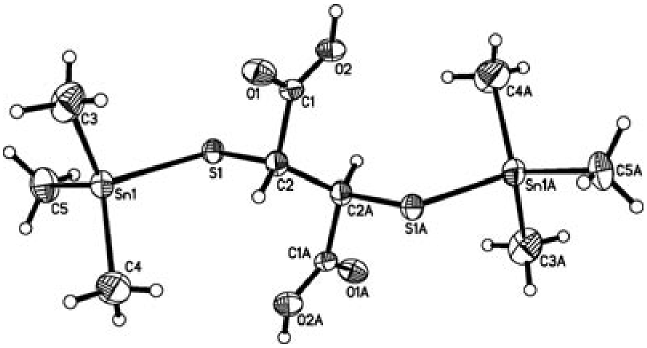


FIGURE 2 Molecular structure of complex **2**.

metal atoms. ^{119}Sn NMR spectra show resonances between 63 and 83 ppm. As reported in the literature [20], values of δ (^{119}Sn) in the ranges -210 to -400, -90 to -190, and 200 to -60 ppm have been associated with six-, five-, and four-coordinated tin centers, respectively. On the basis of these data, we can conclude that complexes **1–4** are typical of four-coordinated tin complexes, and these data are confirmed by the X-ray crystal structures of complexes **1** and **2**.

Crystal Structure of Complexes **1** *and* **2**

The molecular structures of complexes **1** and **2** are illustrated in Figs. 1 and 2, respectively; the two-dimensional and one-dimensional structures of complexes **1** and **2** are illustrated in Figs. 3 and 4, respectively; and selected bond lengths and bond angles are given in Tables 2 and 3, respectively. Both complexes **1** and **2** are dinuclear monomers, with one ligand coordinated to two triphenyltin moieties or trimethyl moieties. The ligand adopts its thiol sulfur atom to coordinate to the central tin atom. The central tin atom forms four primary bonds: three to the phenyl or methyl groups and one to the thiol sulfur atom. Thus, the geometry of the tin center displays a distorted tetrahedral coordinated sphere, with six angles ranging from 95.47(14)° to 118.60(13)° for **1** and 107.7(2)° to 113.6(3)° for **2**. The Sn—C bond lengths [2.129–2.147 Å for **1** and 2.121–2.135 Å for **2**, respectively] are consistent with those of our other reported organotin mercaptocarboxylate complexes [17,21]. The Sn—S bond lengths [2.4258(14) Å for **1** and 2.4421(13) Å for **2**, respectively] are little longer than those found in other triorganotin complexes [22] and approach the sum of

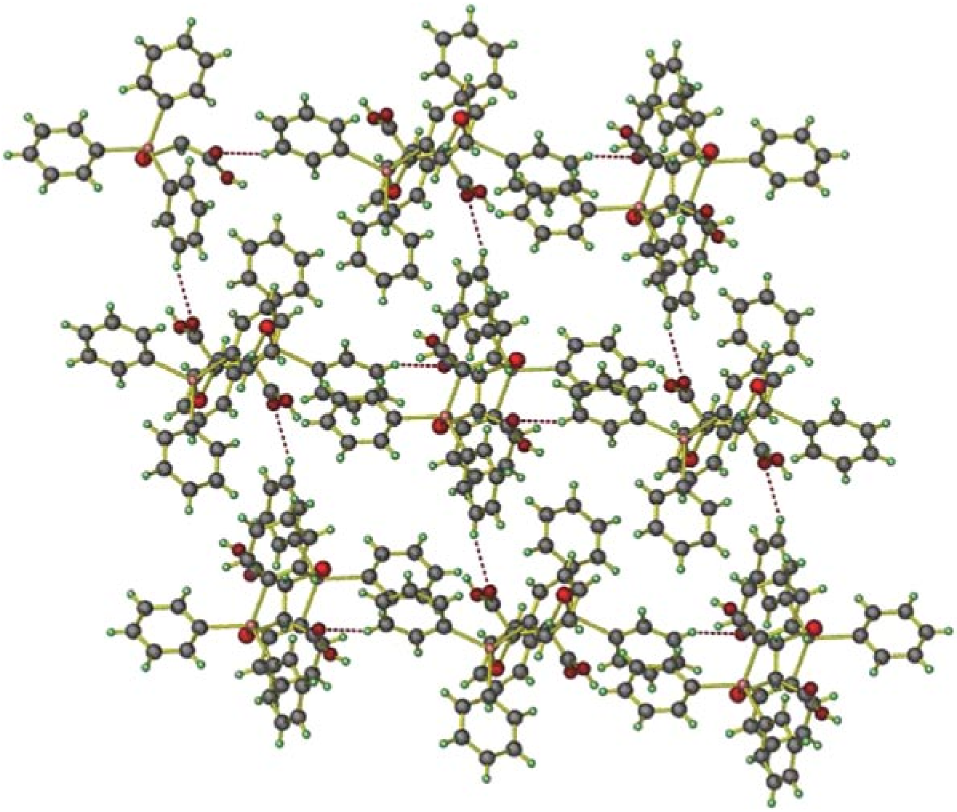


FIGURE 3 Two-dimensional network of complex **1** interlinked by intermolecular C—H···O hydrogen bonds (the disordered ether molecules are omitted for clarity).

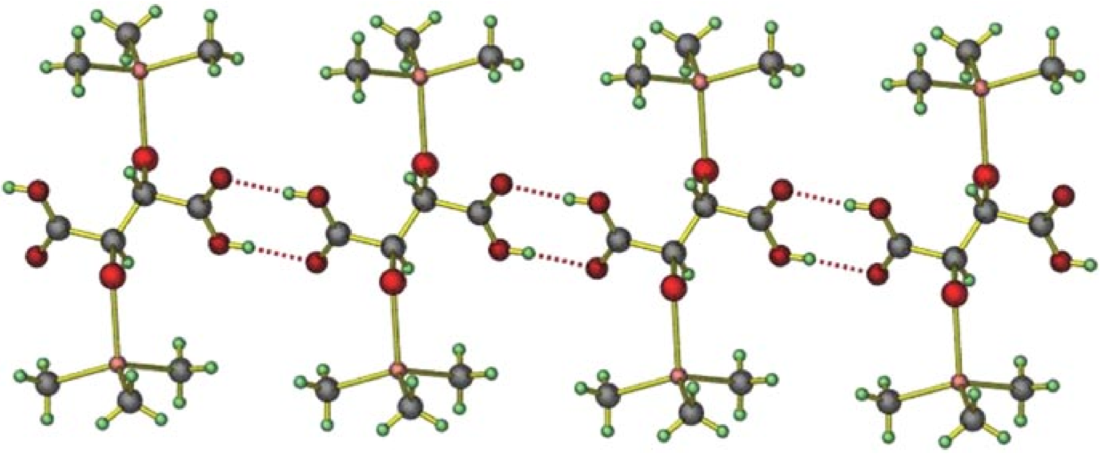


FIGURE 4 One-dimensional infinite chain of complex **2** interlinked by intermolecular O—H···O hydrogen bonds.

TABLE 2 Selected Bond Lengths (Å) and Bond Angles (°) for Complex **1**

Bond lengths			
Sn(1)–C(15)	2.129(4)	Sn(1)–C(3)	2.141(4)
Sn(1)–C(9)	2.147(5)	Sn(1)–S(1)	2.4258(14)
Bond angles			
C(15)–Sn(1)–C(3)	112.88(17)	C(15)–Sn(1)–C(9)	107.66(17)
C(3)–Sn(1)–C(9)	107.91(18)	C(15)–Sn(1)–S(1)	112.24(13)
C(3)–Sn(1)–S(1)	118.60(13)	C(9)–Sn(1)–S(1)	95.47(14)

TABLE 3 Selected Bond Lengths (Å) and Bond Angles (°) for Complex **2**

Bond lengths			
Sn(1)–C(4)	2.121(7)	Sn(1)–C(3)	2.135(7)
Sn(1)–C(5)	2.135(6)	Sn(1)–S(1)	2.4421(13)
Bond angles			
C(4)–Sn(1)–C(3)	113.6(3)	C(4)–Sn(1)–C(5)	113.0(3)
C(3)–Sn(1)–C(5)	113.4(3)	C(4)–Sn(1)–S(1)	107.27(19)
C(3)–Sn(1)–S(1)	107.7(2)	C(5)–Sn(1)–S(1)	100.7(2)

the covalent radii of tin and sulfur atoms (2.42 Å) [23], which proves that the sulfur atom is coordinated to the tin atom by a strong chemical bond.

Typical C—H···O hydrogen bonds are found between C(19)—H(19) and uncoordinated O(1) atom in complex **1**,which connect the adjacent molecules to give a two-dimensional network, the C(19)—H(19) and H(19)···O(1) distances are 0.930 Å and 2.670 Å, respectively, and the C—H···O angle is 158.40°. While typical O—H···O hydrogen bonds are found between O(2)—H(2) and uncoordinated O(1) atom in complex **2**, which connect the adjacent molecules to give rise to a one-dimensional linear chain, the O(2)—H(2) and H(2)···O(1) distances are 0.820 Å and 1.847 Å, respectively, and the O—H···O angle is 163.30°. These weak but significant stacking interactions stabilize these crystal structures.

CONCLUSIONS

A series of triorganotin complexes derived from H_4dmsa have been synthesized and characterized. The results showed that when H_4dmsa and sodium ethoxide react with triorganotin(IV) chloride in 1:2:2 stoichiometry, the thiol protons are more easily deprotonated and coordinate to tin atoms. This results can enlighten us to design and synthesize some purposeful organotin complexes in different stoichiometry.

SUPPLEMENTARY DATA

Atomic coordinates, thermal parameters, and bond lengths and angles for complexes **1** and **2** have been deposited in the Cambridge Crystallographic Data Center, CCDC nos. CCDC 691662 and 691663. Copies of this information may be obtained free of charge from the Director, CCDC, 2 Union Road, Cambridge CB2 1EZ, UK, on request (fax: +44-1223-336-033, e-mail: deposit@ccdc.cam.ac.uk, or URL: http://www.ccdc.cam.ac.uk).

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