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Synthesis and characterization of di-*n*-butyltin(IV) complexes with 4′/2′-nitrobiphenyl-2-carboxylic acids: X-ray crystal structures of $[\{(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4')\}_2O]_2$ and $(n\text{-}C_4H_9)_2Sn\{OCOC_{12}H_8NO_2\text{-}4'\}_2$

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Reactions of di-*n*-butyltin(IV) oxide with 4′/2′-nitrobiphenyl-2-carboxylic acids in 1:1 and 1:2 stoichiometry yield complexes $[\{(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4'/2')\}_2O]_2$ (1 and 2) and $(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4'/2')_2$ (3 and 4) respectively. These compounds were characterized by elemental analysis, IR and NMR (^1H, ^{13}C and ^{119}Sn) spectroscopy. The IR spectra of these compounds indicate the presence of anisobidentate carboxylate groups and non-linear C–Sn–C bonds. From the chemical shifts δ (^{119}Sn) and the coupling constants $^1J(^{13}C, ^{119}Sn)$, the coordination number of the tin atom and the geometry of its coordination sphere have been suggested. $[\{(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4')\}_2O]_2$ (1) exhibits a dimeric structure containing distannoxane units with two types of tin atom with essentially identical geometry. To a first approximation, the tin atoms appear to be pentacoordinated with distorted trigonal bipyramidal geometry. However, each type of tin atom is further subjected to a sixth weaker interaction and may be described as having a capped trigonal bipyramidal structure. The diffraction study of the complex $(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4')_2$ (3) shows a six–coordinate tin in a distorted octahedral frame containing bidentate asymmetric chelating carboxylate groups, with the *n*-Bu groups trans to each other. The *n*-Bu–Sn–*n*-Bu angle is 152.8° and the Sn–O distances are 2.108(4) and 2.493(5) Å. The oxygen atom of the nitro group of the ligand does not participate in bonding to the tin atom in 1 and 3. Crystals of 1 are triclinic with space group $P\bar{1}$ and of that of 3 have orthorhombic space group *Pnna*. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: di-*n*-butyltin(IV) 4′/2′-nitrobiphenyl-2-carboxylates; di(4′/2′-nitrobiphenyl-2-carboxylato)tetra-*n*-butyldistannoxanes; X-ray Crystallography; NMR; infrared

INTRODUCTION

The coordination chemistry of diorganotin(IV) dicarboxylates, $R_2Sn(OCOR')_2$, is extensive, with various geometries and coordination numbers.[1–18] The coordination number at tin can increase, usually beyond six, by inter- and/or intra-molecular interactions, especially in compounds where the R′ group contain a donor center.[7,19,20] Molecular and X-ray investigations of several organotin(IV) carboxylates have revealed that the choice of structure is dictated by a subtle combination of steric and electronic effects, along with the crystal packing and hydrogen bonding effects.[21] In this context, we have chosen to prepare di-*n*-butyltin(IV) derivatives of electronegative acid ligands, 4′-nitrobiphenyl-2-carboxylic acid ($pK_a = 4.62$) and 2′-nitrobiphenyl-2-carboxylic acid, with an aim that these compounds may adopt polymeric structures. Further, the presence of another potential donor ligand in the form of an NO_2 group may provide an additional

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coordination site besides the carboxylate ion, leading to supramoluclar association with expansion of coordination number. The degree of flexibility about the C–C bond connecting the two phenyl rings may depend upon the steric requirements and also on the types of interaction of the NO_2 group in the complexes. To investigate these aspects fully, we report in this paper the preparation and molecular and crystal structures of $[\{(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4')\}_2O]_2$ (**1**) and $(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4')_2$ (**3**).

EXPERIMENTAL

Materials

Di-*n*-butyltin(IV) oxide was obtained from Fluka and was pumped dry before use. The solvents used were of AnalaR grade and were purified/dried by standard techniques (chloroform and dichloromethane over P_2O_5, benzene, toluene and methanol over sodium). All glassware was dried in an oven and further flame dried under vacuum before setting the reaction.

Synthesis of 4′/2′-nitrobiphenyl-2-carboxylic acid

Biphenyl-2-carboxylic acid was prepared from 9-fluorenone (Fluka) by a reported method.[22] Nitration of biphenyl-2-carboxylic acid gave a mixture of both 4′- and 2′-nitrobiphenyl-2-carboxylic acids. Recrystallizations from methanol yielded pure 4′-nitrobiphenyl-2-carboxylic acid; m.p. 221 °C. After separation of 4′-nitrobiphenyl-2-carboxylic acid the mother liquor gave impure 2′-nitrobiphenyl-2-carboxylic acid, which, after two to three recrystallizations from chloroform, yielded pure 2′-nitrobiphenyl-2-carboxylic acid, m.p., 167 °C.

Measurements

NMR spectra were recorded in $CDCl_3$ and dimethylsulfoxide-d_6 (DMSO-d_6) solutions on a Bruker AC-300F spectrometer with tetramethylsilane (^1H), $CDCl_3$ (^{13}C) and tetramethyltin (^{119}Sn) as standards. IR spectra were recorded both as KBr pellets and as solution in $CHCl_3$ on a Perkin Elmer model 1720XFT spectrophotometer. Elemental analyses (C, H, N) were performed on a Perkin Elmer model 2400 CHN elemental analyzer. Tin was determined by a gravimetric method.[23] The mass spectrum of **3** was obtained on a VG analytical 11-2505-70 SMS mass spectrometer at 70 eV.

Syntheses of di-*n*-butyltin(IV) 4′/2′-nitrobiphenyl-2-carboxylates

To a suspension of di-*n*-butyltin(IV) oxide (0.55 g, 2.25 mmol) in dry benzene (60 ml) was added 4′-nitrobiphenyl-2-carboxylic acid (0.56 g, 2.25 mmol). The contents were refluxed for about 8 to 10 h and the water liberated in the reaction was removed azeotropically on completion of the reaction. The clear solution on evacuation yielded a white solid (0.85 g) in about 80% yield. It was recrystallized from benzene; m.p. 205 °C. Molar conductance Λ_M^{1000} (Ω^{-1} cm^2 mol^{-1}): 5.84 (methanol). Anal. Found : C, 52.55; H, 4.49; N, 2.76. Calc. for $C_{42}H_{52}N_2O_9Sn_2$: C, 52.21; H, 5.39; N, 2.90%. ^1H NMR: δ, 0.80(m), 1.17(m), 1.44(m) [18H, n-C_4H_9Sn]; 7.30(m), 7.63(m), 8.16(m) ppm [8H, $-OCOC_{12}H_8NO_2$-4′). $^{13}C\{^1H\}$ NMR: δ, 13.08 C(4), 26.28 C(3), 26.12 C(2), 26.51 C(1) (*n*-Bu); 122.4; 127.7; 129.0; 129.9; 130.3; 133.2; 139.0; 146.1; 148.6; 173.5 ppm (ligand). The values for coupling constants $^nJ(^{119}Sn, ^{13}C)$ are: ^1J, 609.1; ^2J, 55.6, ^3J, 143.8 Hz. ^{119}Sn NMR: δ, −210 ppm. Selected IR bands (KBr pellet, cm^{-1}): 1630m, 1600sh,m, 1580m, 1560m [ν_a(COO)], 1520s [$\nu_a(NO_2)$], 1410m [ν_s(COO)], 1340s [$\nu_s(NO_2)$], 630m [ν(O–Sn–O)], 580w [$\nu_a(SnC_2)$], 540w [$\nu_s(SnC_2)$], 480m, 420w [ν(Sn–O)]. The following fragments have been recorded in its mass spectrum, m/z: 476 $[M^{+\bullet}-(OCOC_{12}H_8NO_2\text{-}4')]$ (1.2); 243 $[M^{+\bullet}-\{(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4')\}+H^+]$ (100); 234 $[M^{+\bullet}-(OCOC_{12}H_8NO_2\text{-}4')_2]$ (0.9); 226 $[M^{+\bullet}-\{(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4')\}-(OH)^-]$ (38.1); 197 $[M^{+\bullet}-\{(n\text{-}C_4H_9)_2Sn(OCOH)(OCOC_{12}H_8NO_2\text{-}4')]\}$ (38.7); 177 $[M^{+\bullet}-(n\text{-}C_4H_9)-(OCOC_{12}H_8NO_2\text{-}4')_2]$ (2.4).

Reaction in a 1 : 2 mole ratio between $(n\text{-}C_4H_9)_2SnO$ (0.64 g, 2.59 mmol) and 4′-nitrobiphenyl-2-carboxylic acid (1.26 g, 5.18 mmol) in benzene yielded a clear solution, which, on evacuation, gave $(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4')_2$ (**3**; 1.57 g) in about 85% yield. It was also recrystallized from benzene; m.p. 146 °C. Anal. Found: C, 57.24; H, 3.56; N, 3.90. Calc. for $C_{34}H_{34}N_2O_8Sn$: C, 56.93; H, 4.74; N, 3.91%. Molar conductance Λ_M^{1000}(Ω^{-1} cm^2 mol^{-1}): 2.85 (methanol). ^1H NMR: δ, 0.77(m), 1.25(m), 1.53(m) [18H, n-C_4H_9Sn)]; 7.20(m), 7.44(m), 8.0(m) ppm [16H, –ligand]. $^{13}C\{^1H\}$ NMR: δ, 13.55 C(4), 26.30 C(3), 26.58 C(2), 25.19 C(1) (*n*-Bu); 123.1; 128.5; 129.2; 129.6; 129.9; 130.6; 131.3; 132.1; 132.6; 141.2; 147.0; 148.7; 176.5 ppm (ligand). The values for coupling constants $^nJ(^{119}Sn, ^{13}C)$ are: ^1J, 571.3; ^2J, 37.1; ^3J, 99.4 Hz. ^{119}Sn NMR: δ, −294.6 ppm. Selected IR bands (KBr pellet, cm^{-1}): 1700vs, 1600vs, 1570sh [ν(C=O)], 1510vs [$\nu_a(NO_2)$]), 1370m [ν_a(C–O)], 1340vs [$\nu_s(NO_2)$], 570m [$\nu_a(SnC_2)$], 510m [$\nu_s(SnC_2)$], 480m, 430m [ν(Sn–O)].

Complexes **2** and **4** were obtained by reactions of di-*n*-butyltin(IV) oxide with 2′-nitrobiphenyl-2-carboxylic acid under identical conditions as employed for **1** and **3**. The compounds were precipitated out from the solvent mixture and were filtered and vacuum dried. Complex **2**: m.p. 175–177 °C. Anal. Found: C, 51.91; H, 4.97; N, 2.34. Calc. for $C_{42}H_{52}N_2O_9Sn_2$: C, 52.20; H, 5.38; N, 2.90%. ^1H NMR: δ, 0.79(m), 1.15(m), 1.40(m) [18H, n-C_4H_9Sn]; 7.32(m), 7.60(m), 8.11(m) ppm [8H, $-OCOC_{12}H_8NO_2$-4′)]. Selected IR bands (KBr pellet, cm^{-1}): 1632m, 1600sh,m, 1569m [ν_a(COO)], 1527m [$\nu_a(NO_2)$], 1404m [ν_s(COO)], 1348s [$\nu_s(NO_2)$], 540w [$\nu_s(SnC_2)$], 480m, 428w [ν(Sn–O)]. Complex **4**: m.p. 82–84 °C. Anal. Found: C, 54.40; H, 5.9; N, 3.2. Calc. for $C_{34}H_{34}N_2O_8Sn$: C, 56.92; H, 4.74; N, 3.90% ^1H NMR: δ, 0.79(m), 1.24(m), 1.56(m) [18H, n-C_4H_9Sn)]; 7.25(m), 7.48(m), 8.4(m) ppm [16H, –ligand]. Selected IR bands

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(KBr pellet, cm^{-1}): 1703m, 1608vs, 1582m [$\nu(C{=}O)$], 1500m [$\nu_a(NO_2)$], 1353s [$\nu_a(C{-}O)$] and [$\nu_s(NO_2)$], 587m [$\nu_a(SnC_2)$], 544m [$\nu_s(SnC_2)$].

Structure determination and refinement

Crystallization of $[\{(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4')\}_2O]_2$ (**1**) and $(n\text{-}C_4H_9)_2Sn\{OCOC_{12}H_8NO_2\text{-}4'\}_2$ (**3**) by slow evaporation of their saturated solutions in benzene yielded good single crystals. Numerous attempts to grow single crystals of **2** and **4** for a structural study have been unsuccessful. Intensity data were collected on a Siemens P4 single-crystal diffractometer equipped with molybdenum sealed tube ($\lambda = 0.710\,73$ Å) and highly oriented graphite monochromator using crystals of dimensions $0.32 \times 0.24 \times 0.17$ mm^3 for **1** and $0.33 \times 0.28 \times 0.21$ mm^3 for **3** mounted in Lindemann glass capillaries. For **1**, the lattice parameters and standard deviations were obtained by least-squares fit to 6002 reflections ($9.70 < 2\theta < 29.98^o$). The data were collected by $2\theta{-}\theta$ scan mode with a variable scan speed ranging from 2.0° to a maximum of 45.0° min^{-1}. Three reflections were used to monitor the stability and orientation of the crystal and were measured after every 97 reflections. Their intensities showed only statistical fluctuations during 78.6 h X-ray response time. The data were collected for Lorentz and polarization factors and an empirical absorption correction based on the psi scan method was applied.

Both the structures were solved by direct methods using SHELX-97[24] and also refined on F^2 using the same program. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the ideal positions with fixed isotropic U values and were riding with their respective non-hydrogen atoms. A weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $a = 0.0600$ and $b = 2.28$ was used. The refinement converged to a final R value of 0.0397 ($wR_2 = 0.104$ for 4902 reflections) [$I > 2\sigma(I)$]. The final difference map was featureless.

The data collection procedure, structure solution and refinement for **3** were essentially the same as that for **1**; 2276 reflections ($10.20 < 2\theta < 28.79^o$) for accurate cell parameter determinations, a total of 34.53 h of X-ray exposure time, $R = 0.0528$, $wR_2 = 0.1413$, $a = 0.0792$ and $b = 3.85$ (in the weighting scheme) were the parameters associated with this structure. All other relevant information about the data collection and the refinement are presented in Table 1.

Table 1. Crystal data, data collection and structure refinement parameters for compounds **1** and **3**

	1	3
Empirical formula	$C_{42}H_{52}N_2O_9Sn_2$	$C_{17}H_{17}O_4NSn_{0.50}$
Formula weight	966.24	358.66
Crystal system, space group	Triclinic, $P\overline{1}$	Orthorhombic, *Pnna*
Unit cell dimensions		
a (Å)	12.483(1)	7.776 (1)
b (Å)	13.479(1)	29.562(2)
c (Å)	13.645(1)	14.286(1)
α (°)	88.10(1)	90
β (°)	81.01(1)	90
γ (°)	72.62(1)	90
Volume (Å^3)	2163.9(3)	3284.0(5)
Z, calculated density (Mg m^{-3})	2, 1.483	8, 1.451
Absorption coefficient (mm^{-1})	1.208	0.831
$F(000)$	980	1464
Max. and min. transmission	0.928, 0.761	0.966, 0.783
θ range for data collection (°)	1.97 to 23.00	2.85 to 22.99
Reflections collected	6332	2276
Independent reflections	6002 ($R_{int} = 0.015$)	2276 ($R_{int} = 0.000$)
Data/restraints/parameters	6002/12/496	2276/3/205
Goodness-of-fit on F^2	1.042	1.068
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.0600P)^2 + 2.28P]$, $P = (\max(F_o^2, 0){+}2F_c^2)/3$	$1/[\sigma^2(F_o^2) + (0.0792P)^2 + 3.85P]$, $P = (\max(F_o^2, 0){+}2F_c^2)/3$
Data to parameter ratio	12.1 : 1	11.1 : 1
Final R indices, [$I > 2\sigma(I)$]	$R_1 = 0.039$, $wR_2 = 0.104$ 4902 reflections	$R_1 = 0.052$, $wR_2 = 0.141$ 1543 reflections
R indices (all data)	$R_1 = 0.051$, $wR_2 = 0.114$	$R_1 = 0.085$, $wR_2 = 0.157$
Largest diff. peak and hole (e^- Å^{-3})	0.692 and −0.436	0.760 and −0.575
CCDC number	199841	199842

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RESULTS AND DISCUSSION

Compounds **1**–**4** were prepared by reaction of 4′/2′-nitrobiphenyl-2-carboxylic acids with di-*n*-butyltin(IV) oxide. All these newly synthesized complexes were off-white air- and moisture-stable solids and were identified and characterized with melting points and elemental analyses, IR data and ^{1}H, ^{13}C and ^{119}Sn NMR data. The compounds **1** and **3** were soluble in organic solvents. They behave as non-electrolytes in methanol.[25] Compounds **2** and **4** were insufficiently soluble in organic solvents to permit ^{13}C and ^{119}Sn NMR studies to be carried out.

In the IR spectra of compounds **1**–**4**, the appearance of bands in the carboxy region and the shift of ν(C=O) to lower frequencies with respect to that found in the free ligand, suggest that the ligand is coordinated to tin in the bidentate mode. Bands assignable to the nitro group have been observed in **1**–**4** at about the same frequencies as observed in the free ligand, thus suggesting that the nitro group is not coordinated to tin. The carboxyl stretching region for these compounds in the solid- and solution-state spectra is quite complex, suggesting more than one type of carboxylate coordination (different C–O bond lengths to tin). The $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ bands were assigned to the regions 1700–1510 cm^{-1} and 1400–1350 cm^{-1} respectively. The non-linearity of the C–Sn–C fragment (and confirmed by diffraction structure of **1** reported below) is shown by the presence of ν_a and ν_s(Sn–C$_2$) in the IR spectra of all four compounds. A strong band at 630 cm^{-1} is assigned to vibrations associated with the Sn–O–Sn stretch.[8,19,26–29] The IR spectra of **1** and **3** in CHCl$_3$ solution showed CO$_2$ antisymmetric stretching bands (**1**: 1597s, 1579s, 1551s; **3**: 1685m, 1598 cm^{-1}) and a single CO$_2$ symmetric stretching band (**1**: 1396s, **3**: 1350 cm^{-1}) that were identical to the spectra of the solid compounds. It is suggested that the solid-state structures of **1** and **3** are maintained in solution.

The ^{1}H NMR spectra of the compounds showed the expected integration and peak multiplicities. The ^{13}C NMR spectrum for **1** displayed only a single set of *n*-Bu$_2$Sn resonances, and not the two sets that have generally been observed in the spectra of dicarboxylatotetraorganodistannoxanes[8,19,20] for the exocyclic and endocyclic *n*-Bu$_2$Sn carbon atoms. Probably, the separation between the two sets of resonances was too small to be resolved. The $^{1}J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ values are in the expected region for these compounds.[30] The C–Sn–C angles θ have been calculated by applying the Holecek equation,[30] and these values suggest a non-linear arrangement. Only a single peak is observed for the COO group in the ^{13}C spectrum of **1**. Single resonances at −210.0 ppm and −294.6 ppm in the ^{119}Sn NMR spectra of **1** and **3** respectively suggest that the tin atom in these compounds exhibits hexacoordination[30] (*cf.* X-ray structures).

The mass spectrum of **3** shows the absence of the molecular ion peak at m/z 718. The ionization of the molecular ion proceeds in two different ways. In organometallic-type fragmentation, it gives cluster of species at m/z 476 [$M^{+\bullet}$–(OCOC$_{12}$H$_8$NO$_2$-4′)], 234 [$M^{+\bullet}$–(OCOC$_{12}$H$_8$NO$_2$-4′)$_2$] and 177 [$M^{+\bullet}$ – {(C$_4$H$_9$)(OCOC$_{12}$H$_8$NO$_2$-4′)$_2$}] with poor relative abundance of about 1–2%. The organic-type fragmentation begins with the fast decomposition of the molecular ion to a fragment at m/z 243 (base peak). This is due to (HOCOC$_{12}$H$_8$NO$_2$-4′) formed from $M^{+\bullet}$ via Mclafferty rearrangement. It further fragments to m/z 226 (38) with the loss of a hydroxyl radical. The latter can also be formed from m/z 476 due to the neutral loss of O=Sn(n-C$_4$H$_9$)$_2$. Interestingly, a loss of the formyl radical has also been noticed to give a fragment ion at m/z 197 (38). The non-observation of a molecular ion peak is consistent with some earlier observations on organotin(IV) compounds;[31,32] the loss is attributed to the non-existence of the tin(V) oxidation state.[33]

Crystal structures of [{(n-C$_4$H$_9$)$_2$Sn(OCOC$_{12}$H$_8$NO$_2$-4′)}$_2$O]$_2$ (1) and (n-C$_4$H$_9$)$_2$Sn(OCOC$_{12}$H$_8$NO$_2$-4′)$_2$ (3)

Perspective views of **1** and **3** with the atom numbering scheme are given in Figs 1 and 2 respectively. Selected bond distances and angles are given in Table 2. As observed for a number of related structures, the core geometry of the molecules of **1** consist of a tetranuclear centrosymmetric dimer with a central four-membered ring defined by Sn(1)–O(5)–Sn(1)$^{\#1}$–O(5)$^{\#1}$ (#1 symmetry transformations used to generate equivalent

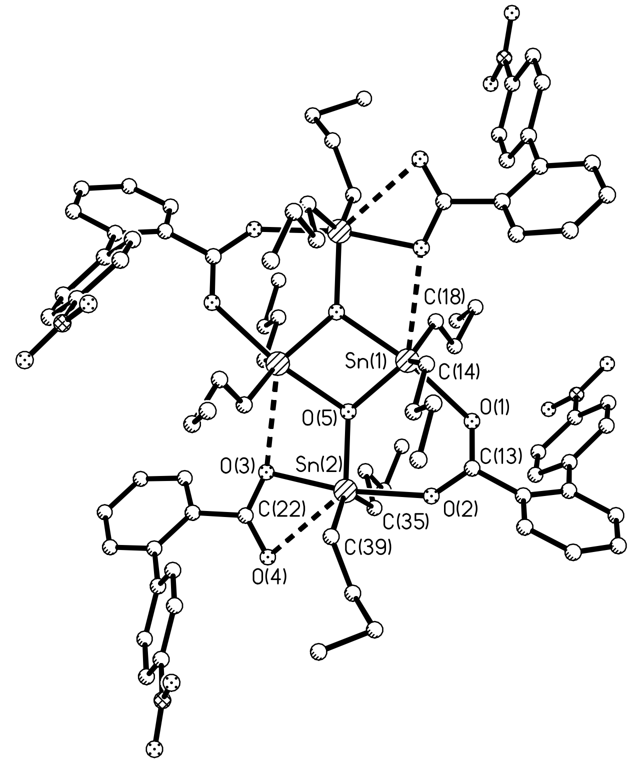

Figure 1. Molecular structure and crystallographic numbering scheme employed for [{(n-C$_4$H$_9$)$_2$Sn(OCOC$_{12}$H$_8$NO$_2$-4′)}$_2$O]$_2$ (**1**).

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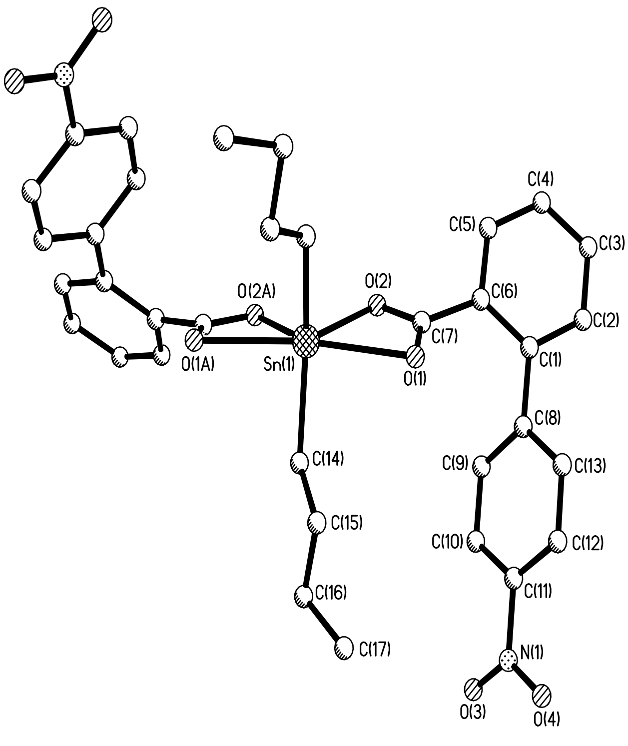

Figure 2. Molecular structure and crystallographic numbering scheme employed for $(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4')_2$ (**3**).

atoms for **1**: $-x+1$, $-y+2$, $-z+1$) with two additional $(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4')$ units attached at each of the bridging oxygen atoms O(5) and O(5)$^{\#1}$, with the result that the oxygen atoms of this ring are three-coordinate. This six-atom core is nearly planar (±0.087).

Molecules of **1** contain two distinct types of carboxylate group. One is defined by O(1) and O(2) and forms nearly symmetrical bridges [C(13)–O(1) = 1.229(7) and C(13)–O(2) = 1.253(7) Å] between the two tin atoms, and the other is defined by O(3) and O(4) and coordinates essentially as an anisobidentate ligand [C(28)–O(4) = 1.225(7) and C(28)–O(3) = 1.292(7) Å]. The Sn–O bond lengths for the symmetrical bridges range from 2.288(4) to 2.294(4) Å. The pendant carboxylate ligands have one normal ester linkage [Sn(2)–O(3) = 2.176(4) Å] and two weaker interactions: one from the acyl oxygen atom to the same tin atom [Sn(2)–O(4) = 2.763(4) Å] and one from the ester oxygen atom to an adjacent tin atom [Sn(1)$^{\#1}$–O(3) = 2.967(4) Å. These longer Sn···O contacts are outside the normal Sn–O covalent (1.9–2.1 Å bond length,[34] but are considerably shorter than the van der Waals sum of 3.68 Å.[34] Intramolecular Sn···O contacts in the range of 2.363(6)–3.071(2) Å have been confidently reported to indicate Sn–O bonding.[35–39] Although there are two types of tin atom in **1**, the geometry about these two types is essentially identical. At first sight, both tin atoms appear to be pentacoordinated with a distorted trigonal bipyramidal arrangement, being bonded to two carbon atoms (both equatorial) and three oxygen atoms [Sn(1)–O(5), 2.031(3)

Table 2. Interatomic distances and angles for compounds **1** and **3**[a]

Bond lengths (Å)		Bond angles (°)	
Compound **1**			
Sn(1)–O(5)	2.031(3)	O(5)–Sn(1)–C(18)	114.8(3)
Sn(1)–O(1)	2.288(4)	O(5)–Sn(1)–C(14)	109.0(2)
Sn(2)–O(3)	2.176(4)	C(14)–Sn(1)–C(18)	136.2(3)
Sn(1)–O(5)$^{\#1}$	2.178(3)	O(5)–Sn(1)–O(5)$^{\#1}$	76.29(14)
Sn(1)–O(3)$^{\#1}$	2.967(4)	O(5)$^{\#1}$–Sn(1)–C(18)	94.4(2)
Sn(2)–O(5)	2.042(3)	O(5)$^{\#1}$–Sn(1)–C(14)	97.5(3)
Sn(2)–O(2)	2.294(4)	O(5)–Sn(1)–O(1)	93.90(15)
Sn(2)–O(4)	2.763(4)	O(1)–Sn(1)–C(18)	86.6(2)
Sn(1)–C(14)	2.105(7)	O(1)–Sn(1)–C(14)	88.9(3)
Sn(2)–C(35)	2.073(8)	O(5)$^{\#1}$–Sn(1)–O(1)	169.60(15)
Sn(1)–C(18)	2.094(6)	O(5)–Sn(2)–C(35)	110.1(3)
Sn(2)–C(39)	2.105(7)	O(5)–Sn(2)–C(39)	114.1(2)
O(1)–C(13)	1.229(7)	C(39)–Sn(2)–C(35)	133.7(3)
O(3)–C(28)	1.292(7)	O(5)–Sn(2)–O(3)	81.62(13)
O(5)–Sn(1)$^{\#1}$	2.178(3)	O(3)–Sn(2)–C(35)	99.4(3)
O(2)–C(13)	1.253(7)	O(3)–Sn(2)–C(39)	99.7(2)
O(4)–C(28)	1.225(7)	O(2)–Sn(2)–O(2)	88.55(15)
O(6)–N(2)	1.227(11)	O(2)–Sn(2)–C(35)	85.8(3)
O(8)–N(1)	1.212(10)	O(2)–Sn(2)–C(39)	82.4(3)
N(1)–C(10)	1.510(11)	O(3)–Sn(2)–O(2)	169.96(16)
O(7)–N(2)	1.211(10)	Sn(1)–O(1)–C(13)	126.7(4)
O(9)–N(1)	1.207(11)	Sn(2)–O(2)–C(13)	137.2(4)
N(2)–C(32)	1.470(11)	Sn(2)–O(3)–C(28)	106.0(3)
		Sn(1)–O(5)–Sn(2)	133.13(17)
		Sn(1)–O(5)–Sn(1)$^{\#1}$	103.71(14)
		Sn(2)–O(5)–Sn(1)$^{\#1}$	122.43(16)
		O(9)–N(1)–O(8)	127.0(10)
Compound **3**			
O(2)$^{\#1}$–Sn(1)	2.108(4)	O(2)$^{\#1}$–Sn(1)–O(2)	85.8(2)
Sn(1)–O(2)	2.108(4)	O(2)$^{\#1}$–Sn(1)–C(14)	93.9(4)
Sn(1)–C(14)	2.234(13)	O(2)–Sn(1)–C(14)	106.0(4)
Sn(1)–C(14)$^{\#1}$	2.234(13)	O(1)–Sn(1)–O(1)$^{\#1}$	164.2(2)
Sn(1)–O(1)	2.493(5)	C(7)–O(1)–Sn(1)	84.0(4)
Sn(1)–O(1)$^{\#1}$	2.493(5)	C(14)$^{\#1}$–Sn(1)–C(14)	152.8(8)
C(7)–O(1)	1.213(7)	O(2)$^{\#1}$–Sn(1)–O(1)	140.28(17)
C(7)–O(1)	1.283(7)	C(14)–Sn(1)–O(1)	89.7(4)
N(1)–O(3)	1.205(8)	C(14)$^{\#1}$–Sn(1)–O(1)	86.6(4)
N(1)–O(4)	1.204(7)	O(2)$^{\#1}$–Sn(1)–O(1)$^{\#1}$	55.36(16)
N(1)–C(11)	1.465(8)	C(7)–O(2)–Sn(1)	100.2(4)
C(1)–C(2)	1.391(8)	O(4)–N(1)–O(3)	123.1(7)
C(1)–C(6)	1.412(8)	O(4)–N(1)–C(11)	117.9(7)
		O(3)–N(1)–C(11)	118.9(6)
		O(1)–C(7)–O(2)	120.2(6)
		O(1)–C(7)–C(6)	122.2(6)
		O(2)–C(7)–C(6)	117.6(6)
		C(12)–C(11)–N(1)	120.0(6)
		C(10)–C(11)–N(1)	118.1(6)
		C(15)–C(14)–Sn(1)	122.8(11)

[a] #1. Symmetry transformations used to generate equivalent atoms for **1**: $-x+1$, $-y+2$, $-z+1$; symmetry transformations used to generate equivalent atoms for **3**; $-x+1/2$, −y, z.

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(equatorial); Sn(1)–O(1), 2.288(4) (axial) and Sn(1)–O(5)$^{\#1}$, 2.178(3) Å (axial)] with O(5)$^{\#1}$–Sn(1)–O(1) = 169.60(15)°. The Sn–C bond lengths are similar, but the Sn–O distances differ. The equatorial Sn–O bond length is close to a normal Sn–O covalent bond, whereas the axial Sn–O bonds are slightly longer than the normal Sn–O covalent bond. Each type of tin atom is further subjected to a sixth weaker interaction, in the form of a carboxyl oxygen atom approaching one of the faces of the trigonal bipyramid. The weakly coordinating oxygen atom O(3)$^{\#1}$ approaches the coordinating sphere of tin through one of the trigonal bipyramidal faces, making an angle of 62.7° [O(5)$^{\#1}$–Sn(1)–O(3)$^{\#1}$] with the apical oxygen atom, O(5)$^{\#1}$. As a consequence, the equatorial atoms move apart to provide space for O(3)$^{\#1}$ for such an approach, and thus the C(14)–Sn(1)–C(18) bond angle is substantially increased to 136.2° from an ideal value of 120°, allowing a more efficient electronic interaction between Sn(1) and the O(3)$^{\#1}$ atom.

The exocyclic Sn(2) atom forms Sn–O bonds with the bridging O(2) and the monodentate carboxylate group O(3), as well as with the bridging O(5) atom of the Sn_2O_2 moiety. In addition, there are bonds to two carbon atoms, making the Sn(2) atom five-coordinate. However, the Sn(2) atom forms a weak interaction with O(4) (2.763(4) Å), derived from the monodentate carboxylate group. Interestingly, the directionality of this weak interaction involving the exocyclic tin atom Sn(2) almost mimics that of Sn(1). However, the angle of approach is marginally reduced (51.4°), and this is reflected in the lesser degree of deviation in the C–Sn–C angle (133.7°). The weak nature of this interaction is also suggested by the carbon–oxygen bond distances in the COO moiety. The C–O bond distances [C(28–O(3) = 1.292(7) and C(28)–O(4) = 1.225(7) Å] suggest a partial localization of π-electron density in the C(28)–O(4) bond. The exocyclic Sn(2) atom may be visualized to be six-coordinate.

The crystal structure of **3** shows that $(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4')_2$ consists of discrete molecules with the tin atom acquiring hexa-coordination. The Sn(1) and the four oxygen atoms [O(1), O(1)$^{\#1}$, O(2), O(2)$^{\#1}$ (#1 symmetry transformations used to generate equivalent atoms: $-x + 1/2$, $-y$, z)] are nearly coplanar. The maximum deviation out of the SnO_4 plane is zero for tin. The C–Sn–C angle [C(14)–Sn–C(14)$^{\#1}$ = 152.8(8)°] lies in the range (122.6 to 156.9°) generally observed in diorganotin(IV) compounds with chelating ligands[40,41] and is significantly different from that predicted from the solution NMR data [131.8° obtained from $|^1J|$]. This reduction of bond angle in solution strongly suggests that DMSO has approached the tin atom in the coordination polyhedra. The 4′-nitrobiphenyl-2-carboxylato group coordinates in an asymmetric mode, forming both short [Sn(1)–O(2) = 2.108(4) Å] and long Sn–O bonds [Sn(1)–O(1) = 2.493(5) Å]. The anisobidentate mode of coordination of the carboxylato group is also reflected in the disparity of the associated carbon–oxygen bonds [C(7)–O(2) = 1.283(7) and C(7)–O(1) = 1.213(7) Å]. Although the Sn(1)–O(1) bond distance of 2.493(5) Å is longer than the sum of the covalent radii of tin and oxygen 2.13 Å), it is nevertheless significantly below the sum of the van der Waals radii of these atoms (3.68 Å[35–39]); therefore, this oxygen atom must be considered as bonding. The geometry of this compound is best described as a severely distorted octahedron.

This structure determination, along with many others on diorganotin(IV) derivatives of monocarboxylic acids,[1–4] has clearly establish that these compounds preferably adopt monomeric structures rather than polymeric structures arising from bridging carboxylate groups. On the other hand, diorganotin(IV) sulfonates invariably exhibit polymeric structures by employing bridging bidentate sulfonate groups.[31,32,42] An interlinking feature of these structures concerns the non-coordination of the oxygen of the nitro group to the tin atom. As seen from Figs 1 and 2, the nitro group is directed away from the tin atom. The nitro group also does not make close intermolecular contacts to tin in the crystal lattice. Diorganotin species are known to acquire coordination numbers greater than six, and it appears that the presence of bulky diphenyl rings with free rotation around the C–C bond takes the nitro group away from the neighboring centers.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 199 841 for $[\{(n\text{-}C_4H_9)_2Sn(OCOC_{12}H_8NO_2\text{-}4')\}_2O]_2$ (**1**) and CCDC no. 199842 for $(n\text{-}C_4H_9)_2Sn\{OCOC_{12}H_8NO_2\text{-}4'\}_2$ (**3**).

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