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Syntheses and crystal structures of di- and triorganotin(IV) derivatives with 2,4,5-trifluoro-3-methoxybenzoic acid

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Abstract

Eight new organotin(IV) complexes with 2,4,5-trifluoro-3-methoxybenzoic acid $R_nSn(O_2CC_6HF_3OCH_3)_{4-n}$ ($n = 3$: R = Ph (**1**), $PhCH_2$ (**2**), Me (**3**), *n*-Bu (**4**); $n = 2$: R = Ph (**5**), $PhCH_2$ (**6**), Me (**7**), *n*-Bu (**8**)) have been synthesized. All complexes were characterized by elemental, IR, ^1H and ^{13}C NMR spectra analyses, and the structures of complexes **1**, **3**, **7** and **8** were also determined by X-ray crystallography. The geometries at the tin atoms of **1** and **3** are five-coordinated and those of complexes **7** and **8** are six-coordinated. The structures of complexes **1**, **3**, **7** and **8** have been found to consist of 1D chains built up by intermolecular C–H···F weak hydrogen bonding. Intermolecular C–F···F weak non-hydrogen interactions in the crystal lattice of **3** link the molecules into a 2D network.

Keywords: 2,4,5-Trifluoro-3-methoxybenzoic acid; Organotin(IV); Weak hydrogen bonding

1. Introduction

The chemistry of organotin(IV) derivatives is a subject of study with growing interest [1], not only because of the environmental consequences of the widespread use of these complexes [2], but also due to the increasing importance of their medical assays for bactericide and antitumor purposes [3]. Among the organotin derivatives organotin(IV) carboxylates have had increasing interest shown due to their activity against various types of cancer. In fact many dialkyltin(IV) and trialkyltin (IV) complexes display interesting antitumor activities. Recent work also reveals higher antitumor activities for various di- and tri-organotin fluoro-substituted carboxylates than their non-fluorinated analogues [4]. Furthermore, in the literature people have reported that the introduction of fluorine atoms into organic molecules in general causes drastic changes of the physico-chemical properties, chemical reactivity and biological activity in comparison to their non-fluorinated parent complexes [5–7]. Moreover, it was discussed that a C–F bond can function in certain cases as a weak hydrogen bond acceptor [8]. Though these interactions are much weaker than C=O···H–X (X = O, N) interactions they do influence molecular packing in crystals [9].

In view of the above reasons and in connection with our interest in coordination chemistry of organotin(IV) complexes with different carboxylic acids [10], we choose the fluoro-substituted carboxylate ligand: 2,4,5-trifluoro-3-methoxybenzoic acid. To our knowledge, although multi-fluorine substituted organotin(IV) carboxylate derivatives have been studied before [11], no organotin(IV) derivatives of 2,4,5-trifluoro-3-methoxybenzoic acid have been reported.

The above considerations stirred our interest in some detailed syntheses and structures for di- and triorganotin(IV) derivatives of the ligand. Eight complexes $[R_nSn(O_2CC_6HF_3OCH_3)_{4-n}$ ($n = 3$: R = Ph (**1**), $PhCH_2$ (**2**); Me (**3**); *n*-Bu (**4**); $n = 2$: R = Ph (**5**); $PhCH_2$ (**6**); Me

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(**7**); *n*-Bu (**8**))] were obtained by reaction of di- and trialkyltin with 2,4,5-trifluoro-3-methoxybenzoic acid. All the complexes were characterized by elemental, IR, ^{1}H and ^{13}C NMR spectra analyses. Among them, complexes **1**, **3**, **7** and **8** are also characterized by X-ray crystallography diffraction analyses.

2. Experimental

2.1. Materials and measurements

Triphenyltin chloride, trimethyltin chloride, tri-*n*-butyltin chloride, dimethyltin dichloride, di-*n*-butyltin dichloride, diphenyltin dichloride and 2,4,5-trifluoro-3-methoxybenzoic acid were commercially available, and they were used without further purification. Dibenzyltin dichloride and tribenzyltin chloride were prepared by a standard method reported in the literature [12]. The melting points were obtained on a Kofler micro melting point apparatus and are uncorrected. Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Mercury Plus 400 MHz NMR spectrometer. The chemical shifts are reported in ppm with respect to the references and are stated relative to external tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR. Elemental analyses were performed with a PE-2400 II elemental apparatus.

2.2. Syntheses of the complex *1–8*

2.2.1. [$Ph_3SnO_2CC_6HF_3OCH_3$] (*1*)

Under a dry nitrogen atmosphere, 2,4,5-trifluoro-3-methoxybenzoic acid (0.206 g, 1.0 mmol) and sodium ethoxide (0.068 g, 1.0 mmol) were added in benzene (20 ml) to a Schlenk flask and stirred for about 10 min, then triphenyltin chloride (0.385 g, 1.0 mmol) was added to the mixture. The stirring was continued for 12 h at 40 °C and then the solution was filtered. The filtrate was gradually evaporated until a solid product was obtained. The solid was recrystallized from ether–petroleum and a transparent colorless crystal of complex **1** was formed. Yield: 88%; m.p. 109–110. °C. *Anal.* Calc. for $C_{26}H_{19}F_3O_3Sn$: C, 56.25; H, 3.45. Found: C, 56.49; H, 3.34%. IR (KBr, cm^{-1}): ν_{as}(C=O) 1582, ν_s(C–O)1380, ν_{as}(Sn–C) 564, ν_s(Sn–C) 523, ν(Sn–O) 484. ^{1}H NMR ($CDCl_3$, ppm): δ 7.26–7.52 (m, 1H, $C_6HF_3OCH_3$), 7.49–7.80 (m, 15H, Sn–C_6H_5), 4.02 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 168.24 (COO), 113.45, 129.00, 129.32, 129.64, 129.62, 130.61, 130.68, 130.75, 136.92, 137.16, 137.40, 137.80 (Ar–C), 62.36 (OCH_3).

2.2.2. [$(PhCH_2)_3SnO_2CC_6HF_3OCH_3$] (*2*)

The procedure is similar to that of complex **1**. 2,4,5-Trifluoro-3-methoxybenzoic acid (0.206 g, 1.0 mmol), sodium ethoxide (0.068 g, 1.0 mmol) and tribenzyltin chloride (0.427 g, 1.0 mmol) were reacted for 12 h at 40 °C. Recrystallized from ether–petroleum, a transparent colorless crystal was formed. Yield: 77%; m.p. 123–125 °C. *Anal.* Calc. for $C_{29}H_{25}F_3O_3Sn$: C, 58.32; H, 4.22. Found: C, 58.72; H, 4.31%. IR (KBr, cm^{-1}): ν_{as}(C=O), 1590 ν_s(C–O) 1381, ν_{as}(Sn–C) 560, ν_s(Sn–C) 518, ν(Sn–O) 479. ^{1}H NMR ($CDCl_3$, ppm): δ 7.31–7.81 (m, 1H, $C_6HF_3OCH_3$), 7.23–7.52 (m, 15H, Sn–$CH_2C_6H_5$), 3.16 (s, 6H, Sn–$CH_2C_6H_5$), 4.03 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 32.5 ($ArCH_2$), 112.85, 112.92, 129.76, 128.88, 129.15, 129.37, 130.29, 130.35, 136.74, 136.90, 137.20, 137.32 (Ar–C), 168.25(COO), 62.35 (OCH_3).

2.2.3. [$Me_3SnO_2CC_6HF_3OCH_3$] (*3*)

The procedure is similar to that of complex **1**. 2,4,5-Trifluoro-3-methoxybenzoic acid (0.206 g, 1.0 mmol), sodium ethoxide (0.068 g, 1.0 mmol) and trimethyltin chloride (0.199 g, 1.0 mmol) were reacted for 12 h at 40 °C. Recrystallized from ether–petroleum, a transparent colorless crystal was formed. Yield: 87%; m.p. 104–106 °C. *Anal.* Calc. for $C_{11}H_{13}F_3O_3Sn$: C, 35.81; H, 3.55. Found: C, 35.80; H, 3.73. IR (KBr, cm^{-1}): ν_{as}(C=O) 1589, ν_s(C–O) 1372, ν_{as}(Sn–C) 555, ν_s(Sn–C) 530, ν(Sn–O) 488. ^{1}H NMR ($CDCl_3$, ppm): δ 7.25–7.80 (m, 1H, $C_6HF_3OCH_3$), 0.60–0.87 (m, 9H), 4.03 (s, 3H, OCH_3) ppm. ^{13}C NMR ($CDCl_3$, ppm): δ 167.46 (COO), 114.87, 138.75, 145.65, 148.02, 148.34, 152.35 (Ar–C), 62.36 (OCH_3), 14.27 (–CH_3).

2.2.4. [n-$Bu_3SnO_2CC_6HF_3OCH_3$] (*4*)

The procedure is similar to that of complex **1**. 2,4,5-Trifluoro-3-methoxybenzoic acid (0.206 g, 1.0 mmol), sodium ethoxide (0.068 g, 1.0 mmol) and tri-*n*-butyltin (0.325 g, 1.0 mmol) were reacted for 12 h at 40 °C. Recrystallized from ether–petroleum, a transparent colorless crystal was formed. Yield: 78%. m.p. 163–165 °C; *Anal.* Calc. for $C_{20}H_{31}F_3O_3Sn$: C, 48.51; H, 6.31. Found: C, 48.71; H, 6.18%. IR (KBr, cm^{-1}): ν_{as}(C=O) 1586, ν_s(C–O) 1380, ν_{as}(Sn–C) 561, ν_s(Sn–C) 527, ν(Sn–O) 482. ^{1}H NMR ($CDCl_3$, ppm): δ 7.26–7.75 (m, 1H, $C_6HF_3OCH_3$), 0.83–1.54 (m, 27H, Sn–C_4H_9), 4.04 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 167.46 (COO), 113.00, 138.68, 145.46, 145.85, 147.91, 148.02, 153.67 (Ar–C), 62.36 (OCH_3), 22.83, 31.773, 45.57 (–CH_2–), 14.27 (CH_3).

2.2.5. [$Ph_2Sn(O_2CC_6HF_3OCH_3)_2$] (*5*)

The procedure is similar to that of complex **1**. 2,4,5-Trifluoro-3-methoxybenzoic acid (0.412 g, 2.0 mmol), sodium ethoxide (0.136 g, 2.0 mmol) and dimethyltin dichloride (0.219 g, 1.0 mmol) were reacted for 12 h at 40 °C. Recrystallized from ether–petroleum, a transparent colorless crystal was formed. Yield: 83%; m.p. 187–189 °C. *Anal.* Calc. for $C_{28}H_{18}F_6O_6Sn$: C, 49.23; H, 2.66. Found: C, 49.31; H, 2.86%. IR (KBr, cm^{-1}): ν_{as}(C=O) 1586, ν_s(C–O) 1378, ν_{as}(Sn–C) 559, ν_s(Sn–C) 525, ν(Sn–O) 488. ^{1}H NMR ($CDCl_3$, ppm): δ 7.15–7.72 (m, 12H, Sn–C_6H_5 and $C_6HF_3OCH_3$), 4.04 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, ppm): δ168.65 (COO), 112.42, 112.51, 129.56, 128.78, 129.35, 129.47, 130.49, 130.45, 136.64, 136.77, 137.40, 137.68 (Ar–C), 62.36 (OCH_3).

2.2.6. *[$(PhCH_2)_2Sn(O_2CC_6HF_3OCH_3)_2$] (**6**)*

The procedure is similar to that of complex **1**. 2,4,5-Trifluoro-3-methoxybenzoic acid (0.412 g, 2.0 mmol), sodium ethoxide (0.136 g, 2.0 mmol) and dibenzyltin dichloride (0.371 g, 1.0 mmol) were reacted for 12 h at 40 °C. Recrystallized from ether–petroleum, a transparent colorless crystal was formed. Yield: 85%; m.p. 192–194 °C. *Anal.* Calc. for $C_{30}H_{22}F_6O_6Sn$: C, 50.66; H, 3.12. Found: C, 50.45; H, 3.24%. IR (KBr, cm^{-1}): ν_{as}(C=O) 1589, ν_s(C–O) 1381, ν_{as}(Sn–C) 588, ν_s(Sn–C) 533, ν(Sn–O) 460. ^{1}H NMR ($CDCl_3$, ppm): δ 7.84–7.36 (m, 12H, $C_6HF_3OCH_3$ and Sn–$CH_2C_6H_5$), 3.29 (s, 4H, Sn–$CH_2C_6H_5$), 4.06 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 168.05 (COO), 112.65, 112.32, 129.46, 128.58, 129.05, 129.17, 130.19, 130.15, 136.54, 136.70, 137.10, 137.22 (Ar–C), 32.6 ($ArCH_2$), 62.52 (OCH_3).

2.2.7. *[$Me_2Sn(O_2CC_6HF_3OCH_3)_2$] (7)*

The procedure is similar to that of complex **1**. 2,4,5-Trifluoro-3-methoxybenzoic acid (0.412 g, 2.0 mmol), sodium ethoxide (0.136 g, 2.0 mmol) and dibenzyltin dichloride (0.371 g, 1.0 mmol) were reacted for 12 h at 40 °C. Recrystallized from ether–petroleum, a transparent colorless crystal was formed. Yield: 85%; m.p. 192–194 °C. *Anal.* Calc. for $C_{18}H_{14}F_6O_6Sn$: C, 38.67; H, 2.52. Found: C, 38.65; H, 2.33%. IR (KBr, cm^{-1}): ν_{as}(C=O) 1587, ν_s(C–O)1379, ν_{as}(Sn–C) 586, ν_s(Sn–C) 532, ν(Sn–O) 461. ^{1}H NMR ($CDCl_3$, ppm): δ 7.26–7.60 (m, 2H, $C_6HF_3OCH_3$), 4.06 (s, 3H, OCH_3), 0.85–1.28 (m, 6H, Sn–CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 170.80 (COO), 113.29, 145.72, 147.10, 148.18, 149.53, 151.83 (Ar–C), 62.49 (OCH_3), 8.87 (–CH_3).

2.2.8. *[n-$Bu_2Sn(O_2CC_6HF_3OCH_3)_2$] (**8**)*

The procedure is similar to that of complex **1**. 2,4,5-Trifluoro-3-methoxybenzoic acid (0.412 g, 2.0 mmol), sodium ethoxide (0.136 g, 2.0 mmol) and di-*n*-butyltin dichloride (0.303 g, 1.0 mmol) were reacted for 12 h at 40 °C. Recrystallized from ether–petroleum, a transparent colorless crystal was formed. Yield: 80%; m.p. 117–119 °C. *Anal.* Calc. for $C_{24}H_{26}F_6O_6Sn$: C, 44.82; H, 4.07. Found: C, 45.0; H, 4.10%. IR (KBr, cm^{-1}): ν_{as}(C=O) 1579, ν_s(C–O)1373, ν_{as}(Sn–C) 586, ν_s(Sn–C) 537, ν(Sn–O) 462. ^{1}H NMR (CDCl, ppm): δ 7.27–7.62 (m, 2H, Sn–$C_6HF_3OCH_3$), 0.88–1.81 (m, 12H, Sn–C_4H_9), 4.06 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 170.10 (COO), 113.19, 145.62, 146.87, 148.08, 149.33, 151.63 (Ar–C), 62.50 (OCH_3), 22.83, 31.75, 45.36 (–CH_2–), 14.28 (CH_3).

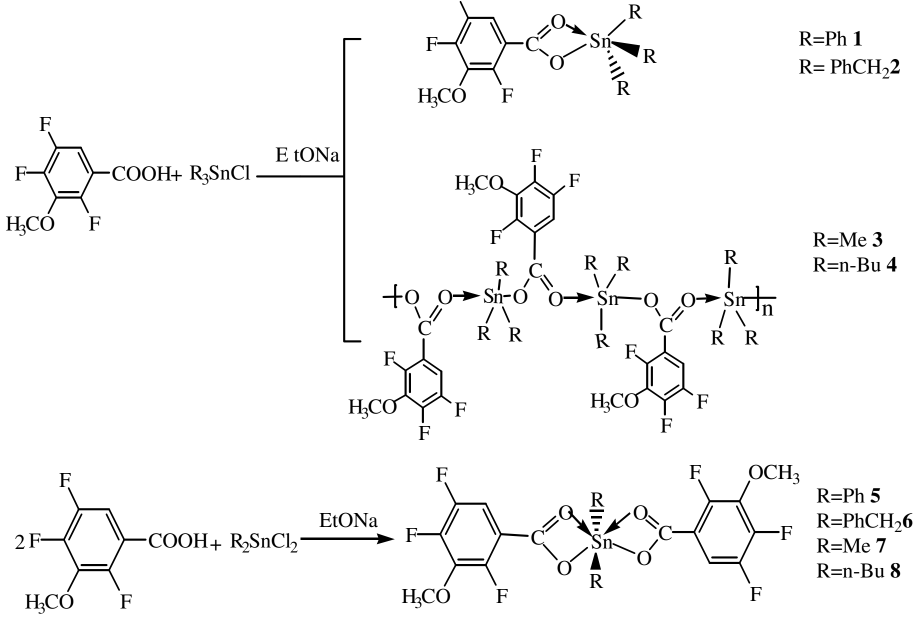
3. Results and discussion

3.1. Syntheses

The syntheses procedure is given in Scheme 1.

3.2. IR spectra

Comparing the IR spectra of the free ligand with complexes **1**–**8**, the explicit feature is the absence of a band in the region 3200–3500 cm^{-1}, which appears in the free ligand as the –OH stretching vibration, thus indicating metal-ligand bond formation through this site. The absorption in the region 460–488 cm^{-1}, which is absent in the spectrum of the free ligand, is assigned to the Sn–O stretching mode. All these values are consistent with those detected in a



Scheme 1.

number of organotin-oxygen derivatives [13,14]. In the organotin carboxylate complexes, IR spectroscopy can provide useful information concerning the coordinate formation of the carboxylate [15]. $\Delta\nu(\nu_{as}(COO)–\nu_{s}(COO))$, 202–217 cm^{-1}, are smaller than that of the free ligand, 341 cm^{-1}, but near to that in the sodium salt of the ligand, 200 cm^{-1}, which suggest the presence of bidentate chelating carboxylate groups [16]. This information is consistent with the analysis of related X-ray crystallography data.

3.3. NMR spectra

The ^1H NMR spectra show that the signal for the OH proton (10.89 ppm) in the spectrum of the ligand is absent in the spectra of the complexes, thus indicating the removal of the OH proton and the formation of Sn–O bonds. This is consistent with the IR data. Signals for the other groups appear in the same positions as in the ligand.

The ^{13}C NMR spectra of all the complexes shown a significant downfield shift of all carbon resonances compared with the free ligand. The shift is a consequence of electron density transfer from the ligand to the acceptor.

3.4. X-ray crystallographic studies

3.4.1. Crystal structure of [$Ph_3SnO_2CC_6HF_3OCH_3$] (**1**)

The molecular structure of complex **1** is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. As can be seen from Fig. 1, the complex possesses a monomeric structure, the Sn(1)–O(1) [2.076(3) Å] bond length lies in the range that has been reported as the Sn–O covalent bond length [2.054(3)–2.083(2) Å for Sn(1)–O(1)] [17a], which proves that the oxygen atoms are coordinated to the tin atoms by a strong chemical bond. The intramolecular distance [Sn(1)···O(2)] is 2.743(4) Å. Although the distance is considerably longer than the normal Sn–O covalent bond length, they lie in the range of Sn···O distances of (2.61–3.02 Å), which have been confidently reported for intramolecular bonds [17b,17c]. As the oxygen atom is involved in a weak coordinative interaction with tin along one of the tetrahedral faces, the structure distortion for the tin atom in complex **1** is best described as a capped tetrahedron.

Table 1
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths			
Sn(1)–C(9)	2.130(4)	Sn(1)–O(1)	2.076(3)
Sn(1)–C(15)	2.123(5)	Sn(1)–O(2)	2.743(4)
Sn(1)–C(21)	2.133(5)		
Bond angles			
O(1)–Sn(1)–C(15)	108.19(16)	C(15)–Sn(1)–C(9)	112.57(19)
O(1)–Sn(1)–C(9)	97.24(16)	C(15)–Sn(1)–C(21)	116.14(19)
O(1)–Sn(1)–C(21)	112.47(15)	C(9)–Sn(1)–C(21)	108.69(18)
O(1)–Sn(1)–O(2)	52.18 (12)	C(9)–Sn(1)–O(2)	149.13(15)

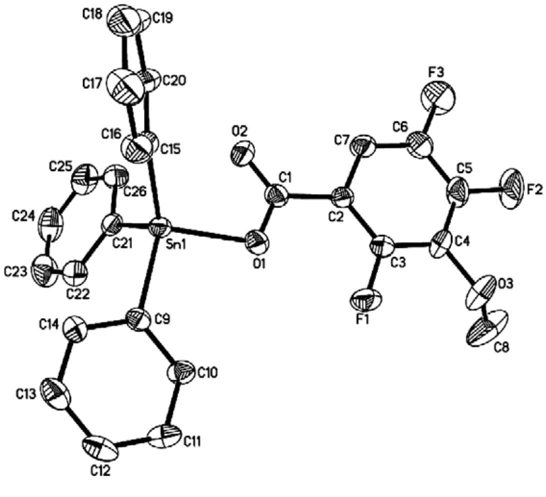


Fig. 1. Molecular structure of complex **1**.

As shown in Fig. 2, a pair of intermolecular C–H···F hydrogen bonds are recognized, which associate the discrete molecule into a dimer. The C–H···F distance is 2.557 Å, which is shorter than the sum of van der waals radii of H and F (2.67 Å) [18]. The C···F distance and the C–H···F angle are 3.343 Å and 142.5°, respectively.

The dimers of complex **1** are further linked by intermolecular C–H···F hydrogen bonds. As shown in Fig. 3, the C(13A) atom acts as a hydrogen-bond donor via the

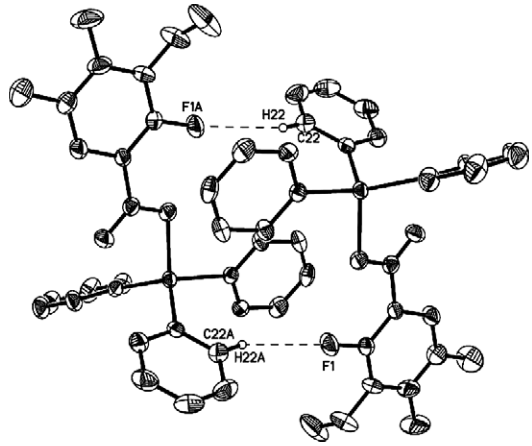


Fig. 2. Dimer structure of complex **1**.

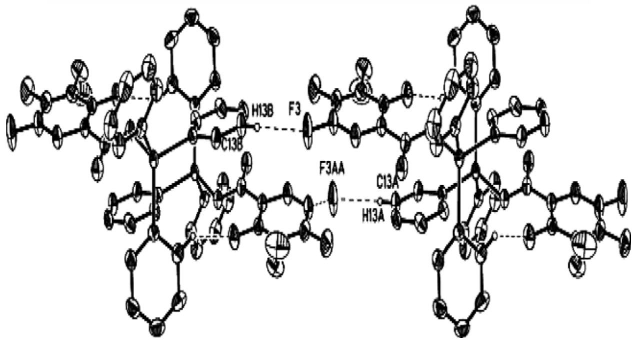


Fig. 3. 1D chain structure of complex **1**, propagation by weak C–H···F interactions.

H(13A) atom to the fluorine F(3AA) atom, and the C(13B) atom acts the same as C(13A), so the dimers form a 1D chain with a head-to-tail arrangement. The C···F and H···F distances and the C–H···F angle are 3.239 Å, 2.556 Å and 130.62°, respectively. The observed C–H···F distances are consistent with phenyl C–H···F interactions reported for various fluorobenzene complexes (2.36–2.86 Å) [19].

3.4.2. *Crystal structure of [$Me_3SnO_2CC_6HF_3OCH_3$] (3)*

The molecular structure of complex **3** is shown in Fig. 4 and selected bond lengths and angles are given in Table 2. As can be seen from Fig. 4, the geometry of the tin center is a distorted trigonal bipyramid and the structure adopted in the solid state is *trans*-R_3SnO_2. The central tin atom is five-coordinated with the two O atoms [O(1) and O(2A)] occupying the axial sites, the angle of the axial ligands [O(1)–Sn(1)–O(2A)] is 174.93(9)°. Three methyl groups define the equatorial plane and the sum of the trigonal C–Sn–C angles is 356.7°. The carboxylate ligand bridges two symmetry-related Sn atoms and gives rise to the unequal Sn–O bond distances. This inequality is reflected in the C(1)–O bond distance, and the longer C(1)–O(1) [1.282(4) Å] is associated with the shorter Sn(1)–O(1) [2.120(3) Å] bond, which is shorter than other reported trimethylorganotin(IV) polymeric structures [2.14(1)–2.208(2) Å] [20a,21] and approaches the covalent radii of Sn and O (2.13 Å) [18]. The Sn(1)–O(2A) distance [2.668(3) Å] is longer than other reported complexes [21], but is far shorter than the sum of the van der Waals radii of Sn and O (3.68 Å) [18]. All these information indicate that Sn(1)–O(2) is a weak coordinate bond. The Sn-C distances [2.103(4)–2.114(4) Å] are consistent with those reported in other triorganotin(IV) carboxylates [17d,20a].

The intermolecular C=O → Sn coordination in **3** leads to infinite zigzag chains containing the tin centers and carboxyl groups [Fig. 5], which is consistent with another organotin(IV) complex that has been reported [20a]. Furthermore, the F(2) atom of the ligand in one chain and the F(2E) atom in another chain form an intermolecular non-bonding F···F interaction [Fig. 6], which is similar to that of the Cl···Cl interaction reported in the literature [21]. The F···F distance (2.820 Å) is a little longer than that has been reported (2.80 Å) [22], but is considerably shorter than the sum of the van der waals radii of two fluorine atoms (2.94 Å)[18]. The C(5)···F(2A) distance and C(5)–F(2)···F(2A) angle is 3.399 Å and 103.98° respectively. These 1D chains are further linked by intermolecular C–H···F hydrogen bonds, as shown in Fig. 7, the C(9) and C(9B) atoms act as a hydrogen-bond donors via H(9C) and H(9CB) atoms to phenyl F(2C) and F(2BA) atoms [Fig. 7] The C···F, F···H distance and the C–H···F angle are 3.522 Å, 2.631 Å and 148.2° respectively. The F···H distance (2.631 Å) and the C–H···F angle are bigger than the same type of measurements that are found in complex **1** (2.557 Å and 142.5°, 2.556 Å and 130.62°), but shorter than the sum of van der waals radii of H and F (2.67 Å) [18]. These intermolecular F···F and C–H···F interactions

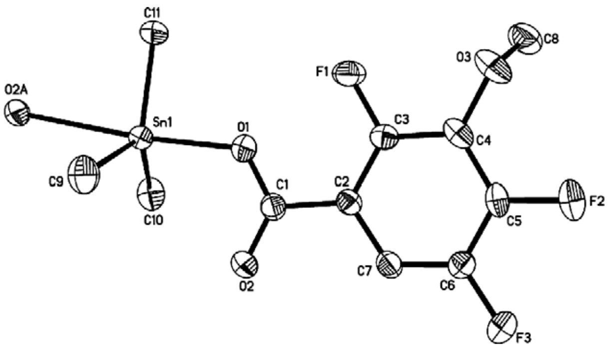


Fig. 4. The molecular structure of complex **3**.

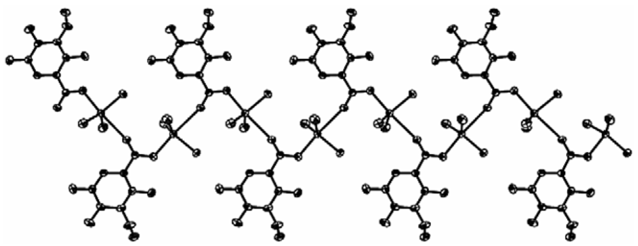


Fig. 5. The 1D chain structure of complex **3**, propagation via O → Sn coordination.

Table 2
Selected bond lengths (Å) and angles (°) for **3**

Bond lengths			
Sn(1)1–C(9)	2.109(4)	Sn(1)–O(1)	2.120(3)
Sn(1)–C(10)	2.114(4)	Sn(1)–O(2A)	2.668(3)
Sn(1)–C(11)	2.103(4)	C(1)–O(1)	1.282(4)
C(2)–O(2)	1.227(4)		
Bond angles			
C(11)–Sn(1)–C(9)	118.8(2)	C(11)–Sn(1)–O(1)	91.15(15)
C(11)–Sn(1)–C(10)	115.4(2)	C(9)–Sn(1)–O(1)	99.16(15)
C(9)–Sn(1)–C(10)	122.50(19)	C(10)–Sn(1)–O(1)	97.56(15)
O(1)–Sn(1)–O(2A)	174.93(9)	C(9)–Sn(1)–O(2A)	82.21(14)
C(10)–Sn(1)–O(2A)	85.71(15)	C(11)–Sn(1)–O(2A)	83.94(15)
O(1)–Sn(1)–O(2A)	174.93(9)		

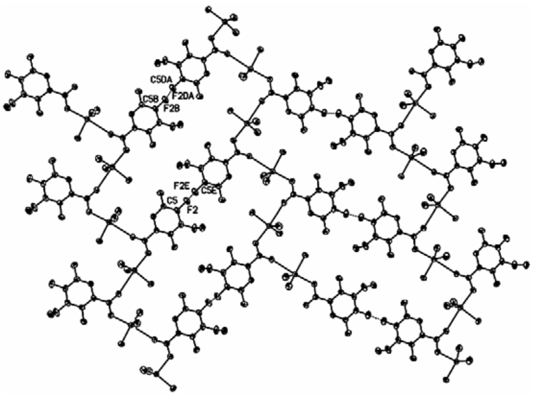


Fig. 6. The 2D network structure of complex **3**.

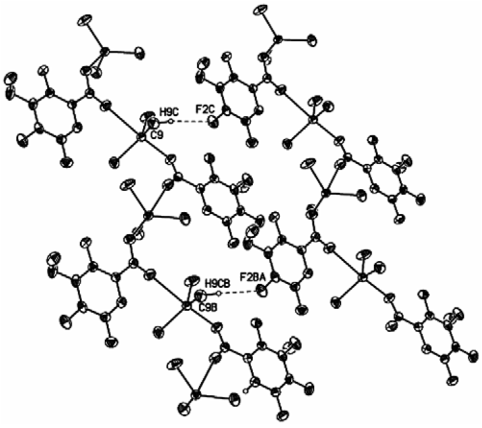


Fig. 7. The 2D network structure of complex **3**.

lead to an expansion of the supramolecular structure of **3** and make it form a 2D network.

*3.4.3. Crystal structures of [$Me_2Sn(O_2CC_6HF_3OCH_3)_2$] (7) and [n-$Bu_2Sn(O_2CC_6HF_3OCH_3)_2$] (**8**)*

The molecular structures of complexes **7** and **8** are shown in Figs. 8 and 10, and selected bond lengths and angles are given in Tables 3 and 4. The geometry at the central Sn atoms in both complexes of **7** and **8** is a skew-trapezoidal bipyramidal geometry. The four O atoms, which derive from two chelate carboxylate ligands, define the basal plane. The C–Sn–C angle [142.4(4)° for **7**, 147.5(2)° for **8**] lies in the range of C–Sn–C angles of 122.6–156.9° found for diorganotin derivatives in which the organo substituents do not adopt *cis*- or *trans*-geometries about the tin atom [23]. The carboxylate ligands chelate the Sn center with asymmetric Sn–O bond distances and this asymmetry is related to the shorter Sn–O bonds. The degree of asymmetry in the Sn–O bond distances is not equal to the difference between the Sn–O bond distances for two carboxylate

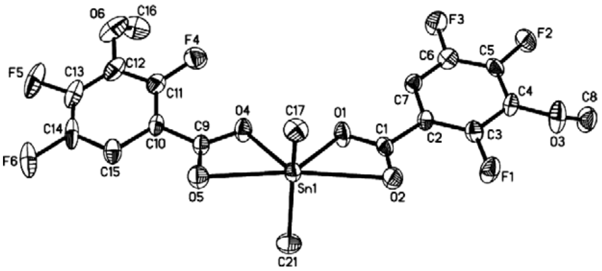


Fig. 8. The molecular structure of complex **7**.

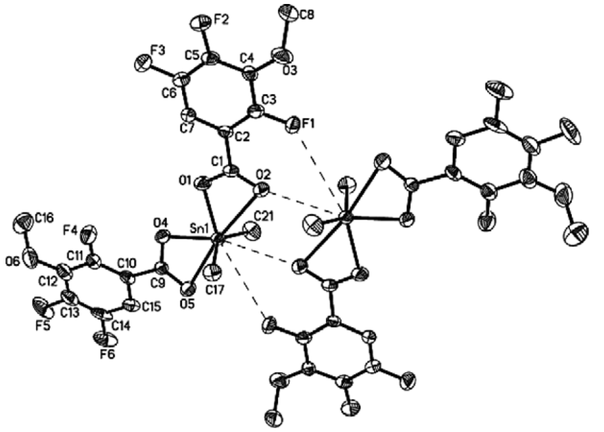


Fig. 9. The dimer structure of complex **7**.

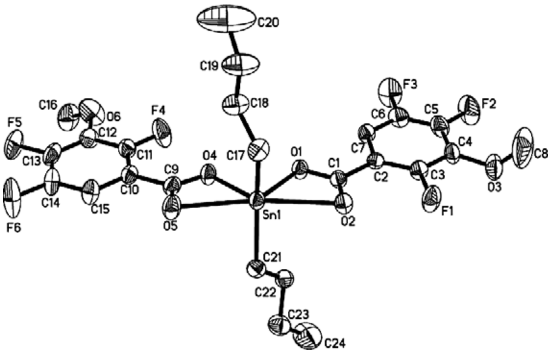


Fig. 10. The molecular structure of complex **8**.

Table 3
Selected bond lengths (Å) and angles (°) for **7**

Bond lengths			
Sn(1)–C(21)	2.090(9)	Sn(1)–O(4)	2.118(5)
Sn(1)–C(17)	2.091(8)	Sn(1)–O(5)	2.506(6)
Sn(1)–O(1)	2.115(6)	Sn(1)–O(2)	2.656(6)
C(1)–O(1)	1.262(9)	C(1)–O(2)	1.234(10)
C(9)–O(4)	1.288(10)	C(9)–O(5)	1.229(10)
Bond angles			
C(21)–Sn(1)–C(17)	142.2(4)	C(17)–Sn(1)–O(4)	103.1(3)
C(21)–Sn(1)–O(1)	105.2(4)	O(1)–Sn(1)–O(4)	80.3(2)
C(17)–Sn(1)–O(1)	103.9(3)	C(21)–Sn(1)–O(5)	86.3(3)
C(21)–Sn(1)–O(4)	105.1(3)	C(17)–Sn(1)–O(5)	89.4(3)
O(1)–Sn(1)–O(5)	135.8(2)	O(4)–Sn(1)–O(5)	55.6(2)
C(21)–Sn(1)–O(4)	105.1(3)	C(17)–Sn(1)–O(2)	88.4(3)
O(1)–Sn(1)–O(2)	53.0(2)	O(4)–Sn(1)–O(2)	133.3(2)
O(5)–Sn(1)–O(2)	171.17(18)		

Table 4
Selected bond lengths (Å) and angles (°) for **8**

Bond lengths			
Sn(1)–C(21)	2.109(5)	Sn(1)–O(4)	2.141(3)
Sn(1)–C(17)	2.107(5)	Sn(1)–O(5)	2.531(4)
Sn(1)–O(1)	2.128(3)	Sn(1)–O(2)	2.562(3)
C(1)–O(1)	1.287(6)	C(1)–O(2)	1.226(6)
C(9)–O(4)	1.281(6)	C(9)–O(5)	1.245(6)
Bond angles			
C(17)–Sn(1)–C(21)	147.5(2)	C(17)–Sn(1)–O(4)	102.97(19)
C(17)–Sn(1)–O(1)	99.8(2)	O(1)–Sn(1)–O(4)	82.60 (13)
C(21)–Sn(1)–O(1)	105.04(17)	C(17)–Sn(1)–O(5)	88.02(19)
C(21)–Sn(1)–O(4)	100.69(17)	C(21)–Sn(1)–O(5)	87.41(18)
O(1)–Sn(1)–O(5)	137.80(12)	O(4)–Sn(1)–O(5)	55.31(12)
C(17)–Sn(1)–O(2)	88.60(19)	C(21)–Sn(1)–O(2)	89.06(17)
O(1)–Sn(1)–O(2)	54.58(12)	O(4)–Sn(1)–O(2)	137.08(12)
O(5)–Sn(1)–O(2)	167.61(12)		

ligands (0.541 Å and 0.388 Å for **7**, 0.434 Å and 0.390 Å for **8**). The anisobidente mode of coordination of the carboxylate is also reflected in the disparity of the associated carbon–oxygen bonds. Although the Sn(1)–O(2) (2.656 Å for **7** and 2.562(3) Å for **8**) and Sn(1)–O(5) (2.506 Å for **7** and 2.531(4) Å for **8**) bonds are longer than the sum of the covalent radii of Sn and O (2.13 Å), they are nevertheless significantly below the sum of the van der waals radii of these atoms (3.68Å) [18].

The most interesting aspect of the structure concerns the intermolecular weak Sn···O and Sn···F interactions, which help in the construction of the dimer as shown in Figs. 9 and 11. The two weak Sn···O bond lengths are equal (3.121 Å for **7** and 3.097 Å for **8**), which is less than the sum of the van der Walls radii of Sn and O (3.68 Å) [18] and between those that have been reported in [$Et_2Sn(O_2CC_4H_3S)$] (2.891 Å) and $Ph_2Sn(O_2CCH_2Cl)_2$ (3.552 Å) [24,25]. The interaction of Sn···F is similar to the Sn···Cl interaction that has been reported [26] and the distance is 3.635 Å for **7** and 3.638Å for **8**.

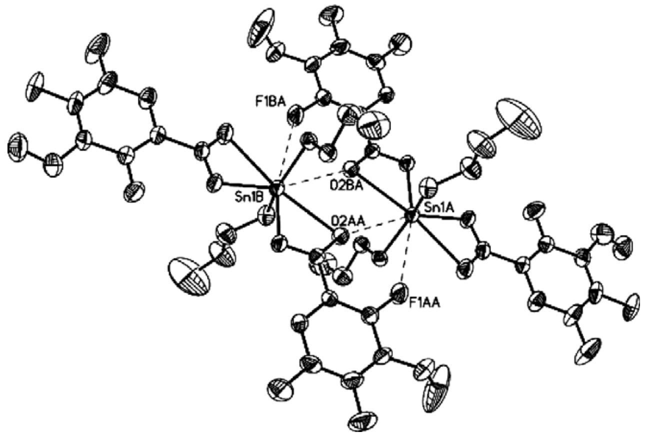


Fig. 11. The dimer structure of complex **8**.

Moreover, for complex **7** the dimers are connected into a 1 D chain through C–H···F hydrogen bonding. The C···F and H···F distances and the C–H···F angle are 3.312 Å, 2.612 Å and 130.01° respectively, these data are consistent with those found in the literature [19]. For complex **8**, we can find two types of shorter distances that are formed by the phenyl F and the methyl H. One is a little longer than the other. For the longer one, its C···F and H···F distances and the C–H···F angle are 3.511 Å, 2.607 Å and 157.06° respectively; and for the shorter one, its C···F and H···F distances and the C–H···F angle are 3.297 Å, 2.517 Å and 138.34° respectively. So a 1D chain structure in the solid state is propagated by two types of C–H···F weak interactions. Further, the C–H···F distance (2.517 Å) is the shortest among the above mentioned in this article.

4. X-ray crystallography

Crystals were mounted in Lindemann capillaries under nitrogen. All X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at

Table 5
Crystal data collection and structure refinement parameters for **1**, **3**, **7** and **8**

Complex	**1**	**3**	**7**	**8**
Empirical formula	$C_{26}H_{19}F_3O_3Sn$	$C_{11}H_{13}F_3O_3Sn$	$C_{18}H_{14}F_6O_6Sn$	$C_{24}H_{26}F_6O_6Sn$
Formula weight	555.10	368.90	558.98	643.14
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	*P*2 (1)/c	P2 (1)/c	$P\bar{1}$	*P*2 (1)/c
Unit cell dimensions				
a (Å)	11.805(4)	10.970(8)	7.684(4)	9.3711(15)
b (Å)	8.705(3)	10.132(7)	9.530(6)	19.609(3)
c (Å)	22.985(8)	13.235(9)	14.285(8)	14.772(2)
α (°)	90	90	84.725(8)	90
β (°)	98.804(5)	113.691(9)	75.599(8)	103.894(2)
γ (°)	90	90	77.605(5)	90
Z	4	4	2	4
D_{calc} (Mg m^{-3})	1.580	1.819	1.878	1.621
Absorption coefficient (mm^{-1})	1.143	1.929	1.382	1.048
F (000)	1104	720	548	1288
Crystal size (mm)	0.52 × 0.48 × 0.43	0.53 × 0.48 × 0.43	0.45 × 0.38 × 0.29	0.58 × 0.43 × 0.41
θ Range for data collection (°)	1.75–25.00	2.62–25.00	2.19–25.01	2.08–25.01
Index ranges	$-14 \leqslant h \leqslant 11$	$-12 \leqslant h \leqslant 13$	$-9 \leqslant h \leqslant 9$	$-10 \leqslant h \leqslant 11$
	$-10 \leqslant k \leqslant 10$	$-12 \leqslant k \leqslant 11$	$-11 \leqslant k \leqslant 11$	$-23 \leqslant k \leqslant 23$
	$-18 \leqslant l \leqslant 27$	$-15 \leqslant l \leqslant 15$	$-14 \leqslant l \leqslant 16$	$-15 \leqslant l \leqslant 17$
Reflections collected	11816	6664	5047	13586
Unique reflections (R_{int})	4111 (0.0459)	2361 (0.0327)	3382 (0.0304)	4644 (0.0367)
Data/restraints/parameters	4111/0/299	2361/0/163	3382/0/282	4644/290/334
Goodness-of-fit on F^2	1.000	1.006	1.001	1.006
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0469$, $wR_2 = 0.1135$	$R_1 = 0.0296$, $wR_2 = 0.0760$	$R_1 = 0.0625$, $wR_2 = 0.1626$	$R_1 = 0.0402$, $wR_2 = 0.1011$
R indices (all data)	$R_1 = 0.0631$, $wR_2 = 0.1304$	$R_1 = 0.0366$, $wR_2 = 0.0825$	$R_1 = 0.0754$, $wR_2 = 0.1736$	$R_1 = 0.0644$, $wR_2 = 0.1188$

298(2) K. A semi-empirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS–97 and refined against F^2 by full-matrix least squares using SHELXL–97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are list in Table 5.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure analysis of the compounds have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 600461 **1**, 600462 **3**, 600459 **7**, 600460 **8**. Copies of these information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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