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ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 3922–3930
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis, characterization, and molecular structures of di- and triorganotin(IV) complexes with 9-anthracenecarboxylic acid: The structural diversity in organotin 9-anthracenecarboxylates

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Received 24 March 2007; received in revised form 20 May 2007; accepted 24 May 2007
Available online 9 June 2007

Abstract

The di- and triorganotin(IV) derivatives of anthracenecarboxylic acid, $Ph_2MeSnOC(O)C_{14}H_9$ (**2**), $Me_3SnOC(O)C_{14}H_9$ (**3**), $Me_2Sn[OC(O)C_{14}H_9]_2 \cdot CH_3OH$ (**4**) $Ph_3SnOC(O)C_{14}H_9 \cdot CH_3OH$ (**5**), $Ph_2EtSnOC(O)C_{14}H_9$ (**6**), $Ph_2Sn[OC(O)(C_{14}H_9)]_2$ (**7**) and $PhMe_2SnOC(O)C_{14}H_9$ (**8**) were synthesized by the reaction of Ph_2MeSnI, Me_3SnCl, Me_2SnCl_2, Ph_3SnCl, Ph_2EtSnI, Ph_2SnCl_2, and $PhMe_2SnI$ with 9-anthracenecarboxylic acid, respectively, with the aid of potassium *iso*-propoxide. All complexes were characterized by elemental analysis, mass spectrometry, IR, ^1H, ^{13}C and ^{119}Sn NMR spectroscopes. The molecular structures of complexes **2**, **3** and **4** were determined by single crystal X-ray analysis. The X-ray structures reveal that complex **2** and **3** adopt a polymeric *trans*-C_3SnO_2 trigonal bipyamidal configuration with the oxygen atoms occupying axial positions. Complex **4** adopts a monomeric structure with two carboxylates coordinated to tin in a monodentate form from axial and equatorial positions, and with the coordination number raised to five as the methanol occupies the apical position of the trigonal bipyramid.

Keywords: Anthracenecarboxylic acid; Organotin; Carboxylate; Crystal structure

1. Introduction

The interest in organotin compounds in general and organotin carboxylates in particular continues to grow because of their biological activity and potential antineoplastic and antituberculosis agents [1–3]. Vast studies have been focused on organotin carboxylates and many of them have been characterized recently either by single crystal structure determination or by spectroscopy [4–15]. Organotin carboxylates adopt a wide variety of structure modes including monomers, dimers, tetramers, oligomeric ladders, and hexameric drums [16–19].

The molecular structures of organotin carboxylates depend largely on the types of carboxylate groups and depend less on electro-negativity of substituted group carboxylate and organic moieties on tin. In this regard, in recent years, many organotin complexes of fluorinated carboxylate acids were synthesized, and their biological activities reported were [20]. However, it is well known that the biological activity of organotin compounds decrease with the increasing length of alkyl-substituted groups on tin [21]. Interestingly, tri-*n*-butyltin(IV) benzoate exhibits higher activity than triphenyltin(IV) benzoate against several human tumor cell lines [20]. This clearly demonstrates the significant role of organic substituent groups on tin. Although synthesis and characterization of organotin carboxylates have been widely investigated, there are only a limited number of studies on the preparation of organotin carboxylates with mixed alkyl and aryl substituent groups on tin [22–25]. Probably this is because of the difficulties presented by the syntheses of mixed organic groups on tin entity. By realizing the important role of organic substituent groups on tin in vitro antitumor activity as well as the

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0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.05.049

role of carboxylate group it may be possible to tailor such activity by introducing a certain number of alkyl and aryl groups on tin along with a wide variety of carboxylates. Therefore, synthesis of new organotin carboxylates with different structural features will be beneficial in the development of pharmaceutical organotin and in other properties and application. In this paper, we report synthesis, characterization and structural studies of several new mixed aryl and alkyl triorganotin carboxylates along with their unmixed di- and triorganotin derivatives.

2. Experimental

2.1. Materials

Triphenyltin(IV) chloride, trimethyltin(IV) chloride, dimethyltin(IV) dichloride, diphenyltin(IV) dichloride, ethyl iodide, methyl iodide, and silver acetate were purchased from Merck and used without further purification. All solvents were dried and distilled under nitrogen prior to use according to a standard procedure. Ethyltriphenyltin(IV) was prepared by using a conventional Grignard synthesis with triphenyltin(IV) chloride and ethylmagnesium bromide and purified by recrystallization from methanol (m.p. 51 °C, yield 70%).

2.2. Physical measurements

Melting points were obtained with Electrothermal 9200 melting point apparatus and were not corrected. Infrared spectra from 4000 to 400 cm^{-1} were recorded on a Shimadzu 470 FT-IR instrument, using KBr pellets. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded at room temperature in $CDCl_3$ on a Bruker AVANCE 300-MHz operating at 300.3, 75.4 MHz and 111.9 MHz, respectively. The NMR spectra are referenced to Me_4Si (^{1}H and ^{13}C) or Me_4Sn (^{119}Sn) as external standards. The mass spectroscopy was performed on a Varian MAT 44 instrument (electron impact, 20 eV).

2.2.1. X-ray crystallography

The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo Kα radiation. For $[Ph_2MeSnOC(O)C_{14}H_9]$ (**2**), a colorless prismatic crystal with a dimension of $0.30 \times 0.25 \times 0.10$ mm, for $[Me_3SnOC(O)C_{14}H_9]$ (**3**), a colorless needle crystal with a dimension of $0.60 \times 0.08 \times 0.05$ mm and for $\{Me_2Sn[OC(O)C_{14}H_9]_2 \cdot CH_3OH\}$. CH_3OH (**4**), a colorless block crystal with a dimension of $0.50 \times 0.40 \times 0.35$ mm were mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for the data collection were obtained by least-squares refinement of diffraction data from 5487 for (**2**), 3505 for (**3**) and 5580 for (**4**) unique reflections (Table 1). Data were collected at a temperature of 20 °C to a maximum 2θ value of 55.94° for (**2**), 55.76° for (**3**) and 53.58° for (**4**) and in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA software package [26]. The numerical absorption coefficient, μ, for Mo Kα radiation is 1.141 mm^{-1} for (**2**), 1.593 mm^{-1} for (**3**) and 0.918 mm^{-1}

Table 1
Crystal data for compounds **2**, **3** and **4**

	2	**3**	**4**
Formula	$C_{28}H_{22}O_2Sn$	$C_{18}H_{18}O_2Sn$	$C_{34}H_{32}O_6Sn$
Formula weight	509.17	385.01	655.29
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/c$	$P2_1$
Crystal size (mm^3)	$0.30 \times 0.25 \times 0.10$	$0.60 \times 0.08 \times 0.05$	$0.50 \times 0.40 \times 0.35$
a (Å)	10.0715(13)	11.9910(14)	9.010(3)
b (Å)	10.5828(16)	10.1874(9)	12.958(3)
c (Å)	10.9810(15)	13.8854(16)	13.045(4)
β (°)	102.765(10)	108.825(9)	106.20(2)
V ($Å^3$)	1141.5(3)	1605(3)	1462.5(7)
Z	2	4	2
D_{calc} (g cm^{-1})	1.481	1.593	1.488
θ Ranges for data collection	1.90–27.97	2.53–27.88	1.63–26.79
$F(000)$	512	768	668
Absorption coefficient	1.141	1.593	0.918
Index ranges	$-13 \leqslant h \leqslant 13$, $-13 \leqslant k \leqslant 13$, $-14 \leqslant l \leqslant 14$	$-15 \leqslant h \leqslant 14$, $0 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 18$	$-11 \leqslant h \leqslant 11$, $-15 \leqslant k \leqslant 16$, $-16 \leqslant l \leqslant 16$
Data collected	8559	3812	14 138
Unique data [R_{int}]	5487 [0.0182]	3505 [0.0000]	5580 [0.0428]
Parameters, restrains	281, 1	193, 0	381, 3
Final R_1, wR_2^a (Observation data)	0.0209, 0.0463	0.0290, 0.0773	0.0215, 0.0589
Final R_1, wR_2^a (All data)	0.0227, 0.0470	0.0321, 0.0791	0.0216, 0.0590
Absolute structure parameter	−0.050(17)	–	−.0.007(13)
Goodness-of-fit on F^2 (S)	1.069	1.083	1.010
Largest difference in peak and hole (e $Å^3$)	0.361, −0.345	0.611, −1.205	0.769, −1.069

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$.

for (**4**). A numerical absorption correction was applied using X-RED [27] and X-SHAPE software's [28]. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct and subsequent difference Fourier map and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters methods [29]. Subsequent refinement then converged with R factors and parameters errors significantly better than for all attempts to model the solvent disorder. Atomic factors are from International Tables for X-ray Crystallography [30]. All refinements were performed using the X-STEP32 crystallographic software package [31].

2.3. Synthesis of complexes

2.3.1. Synthesis of ethyldiphenyltin(IV)iodide (Ph_2EtSnI) (**1**)

Ethyldiphenyltin(IV) iodide was prepared according to the similar procedure for the preparation of dimethylphenyltin(IV) iodide [32]. The iodine (5.08 g, 40 mmol) was extracted by boiling carbon tetrachloride into ethyltriphenyltin(IV) (7.60 g, 20 mmol) in a Soxhlet apparatus. Then, the iodine was used up after 18 h, the solvent was removed under reduced pressure, and the crude product was vacuum-distilled (85 °C/0.5 torr). ^{1}H NMR (ppm): 1.36–1.44 (3H, t, CH_3), 1.73–1.81 (2H, q, CH_2), 7.39–7.72 (10H, m, C_6H_5). ^{13}C NMR (ppm): 9.3 (CH_3, $^2J^{119}$Sn–^{13}C, 405 Hz, $^2J^{117}$Sn–^{13}C, 387 Hz), 11.2 (CH_2, $^1J^{119}$Sn–^{13}C, 672 Hz, $^1J^{117}$Sn–^{13}C, 653 Hz), 129.1 (C_{meta}, $^3J^{119/117}$Sn–^{13}C, 58 Hz), 129.6 (C_{para}, $^4J^{119/117}$Sn–^{13}C, 13 Hz), 136.2 (C_{ortho}, $^2J^{119/117}$Sn–^{13}C, 46 Hz), 137.2 (C_{ipso}, $^1J^{119}$Sn–^{13}C, 495 Hz, $^1J^{117}$Sn–^{13}C, 474 Hz). ^{119}Sn NMR (ppm): −28.5. Mass spectrum data, tin-bearing fragment: m/e 430 $[(C_6H_5)_2(C_2H_5)SnI]^+$, 401 $[(C_6H_5)_2SnI]^+$, 353 $[(C_6H_5)(C_2H_5)SnI]^+$, 247 $[SnI]^+$, 197 $[(C_6H_5)Sn]^+$, 149 $[(C_2H_5)Sn]^+$, 120 $[Sn]^+$. Mass numbers are based on ^{1}H, ^{12}C, ^{119}Sn and ^{127}I.

2.3.2. Synthesis of methyldiphenyltin(IV) (9-anthracenecarboxylato)[$Ph_2MeSnOC(O)(C_{14}H_9)$] (**2**)

Methyldiphenyltin(IV) iodide was prepared by the method of Davison and Rakita [32]. This reagent (0.83 g, 2 mmol) was treated with potassium isopropoxide (0.19 g, 2 mmol) in isopropanol (20 ml) to produce methyldiphenyltin(IV) isopropoxide and potassium iodide. The potassium iodide precipitate was removed by filtration and then 9-anthracenecarboxylic acid (0.44 g, 2 mmol) in isopropanol (20 ml) was added to the filtrate; the solution was refluxed for 2 h. Evaporation of the solvent gave a yellow solid, which was purified by recrystallization from an isopropanol–methanol (1:1 v/v) mixture at room temperature which presented yellowish crystals (m.p. 134 °C). Anal. Calc. for $C_{28}H_{22}O_2Sn$: C, 66.04; H, 4.32. Found: C, 66.32; H, 4.50%. IR (KBr, cm^{-1}): 420w, 471m, 501w, 525sh, 569w, 638m, 734m, 771m, 797w, 866w, 894m, 1015m, 1147w, 1258s, 1296s, 1385sh, 1415m, 1443w 1485sh, 1579sh, 1646s, 2824w, 2953w. ^{1}H NMR ($CDCl_3$, ppm): 1.14–1.34 (3H, s, CH_3, $^2J^{119}$Sn–H, 59.2), 7.40–8.47 (19H, m, C_6H_5). ^{13}C NMR (ppm): 10.3 (CH_3, $^1J^{119}$Sn–^{13}C, 402 Hz, $^1J^{117}$Sn–^{13}C, 386 Hz), 128.4 (C_{meta}), 129.5 (C_{para}), 136.6 (C_{ortho}, $^2J^{119/117}$Sn–^{13}C, 48 Hz), 139.4 (C_{ispo}), 125.2, 125.6, 126.5, 128.2, 128.5, 128.9, 130.2, 131.1 ($C_{14}H_9$) 175.5 (COO). ^{119}Sn NMR (ppm): −1.3. Mass spectrum data, tin-bearing fragment: m/e 294 $[Sn(C_{14}H_9)]^+$, 374 $[SnPh(C_{14}H_9)]^+$, 389 $[PhSnMe(C_{14}H_9)]^+$, 451, $[Ph_2Sn(C_{14}H_9)]^+$, 495 $[Ph_2SnOCO(C_{14}H_9)]$.

2.3.3. Synthesis of trimethyltin(IV) (9-anthracenecarboxylato)[$Me_3SnOCO(C_{14}H_9)$] (**3**)

Trimethyltin(IV) chloride (0.77 g, 2 mmol) was treated with potassium isopropoxide (0.19 g, 2 mmol) in isopropanol (20 ml) to produce trimethyltin(IV) isopropoxide and potassium chloride. The potassium chloride precipitate was removed by filtration and then 9-anthracenecarboxylic acid (0.44 g, 2 mmol) in isopropanol (20 ml) was added to the filtrate; the solution was refluxed for 2 h. Evaporation of the solvent gave a yellow solid, which was purified by recrystallization from a chloroform–methanol (1:1 v/v) mixture at room temperature to furnish yellowish crystals (m.p. 98 °C). Anal. Calc. for $C_{18}H_{18}O_2Sn$: C, 56.14; H, 4.67. Found: C, 56.82; H, 4.45%. IR (KBr, cm^{-1}): 415m, 458m, 548m,575m, 652m, 731s, 767s, 840w, 884m, 1008w, 1190w, 1271m, 1318s, 1392s, 1437s, 1490sh, 1549s, 1620s, 2364sh, 2922w, 3003w. ^{1}H NMR ($CDCl_3$, ppm): 0.74–0.93 (9H, s, CH_3, $^2J^{119}$Sn–H, 57.0 Hz), 7.27–8.47 (9H, m, $C_{14}H_9$). ^{13}C NMR (ppm): −1.9 (CH_3, $^1J^{119}$Sn–^{13}C, 393 Hz, $^1J^{117}$Sn–^{13}C, 375 Hz), 125.2, 125.5, 126.4, 127.9, 128.1, 128.5, 130.4, 131.1 ($C_{14}H_9$), 175.4 (CO). ^{119}Sn NMR (ppm): 163.1.

2.3.4. Synthesis of dimethyltin(IV) di(9-anthracenecarboxylato){$Me_2Sn[OC(O)(C_{14}H_9)]_2 \cdot CH_3OH\}CH_3OH$ (**4**)

Dimethyltin(IV) dichloride (0.44 g, 2 mmol) was treated with potassium isopropoxide (0.39 g, 4 mmol) in isopropanol (20 ml) to produce dimethyltin(IV) diisopropoxide and potassium chloride. The potassium chloride precipitate was removed by filtration and then 9-anthracenecarboxylic acid (0.88 g, 4 mmol) in isopropanol (40 ml) was added to the filtrate; the solution was refluxed for 2 h. Evaporation of the solvent gave a yellow solid, which was purified by recrystallization from a toluene–methanol mixture (1:1 v/v) at room temperature to furnish yellowish crystals (m.p. 150 °C). Anal. Calc. for $C_{34}H_{32}O_6Sn$: C, 62.31; H, 4.88. Found: C, 63.01; H, 4.53%. IR (KBr, cm^{-1}): 460m, 515 m, 547m, 599w, 635m, 724m, 792w, 847w, 889w, 915w, 1005w, 1174w, 1252m, 1291m, 1344w, 1389m, 1404w, 1448sh, 1625s, 1677s, 2854w, 2924w. ^{1}H NMR ($CDCl_3$, ppm): 1.52–1.79 (6H, s, CH_3, $^2J^{119}$Sn–H, 81.2 Hz), 3.50 (3H, s, CH_3OH) 7.48–8.56 (9H, m, C_6H_5). ^{13}C NMR (ppm): 5.4 (CH_3, $^1J^{119}$Sn–^{13}C, 642 Hz, $^1J^{117}$Sn–^{13}C, 625 Hz), 50.3 (CH_3OH), 124.8, 124.9, 126.1, 126.7, 128.1, 128.4, 129.6, 130.5 ($C_{14}H_9$), 178.4 (COO). ^{119}Sn NMR (ppm): −99.5. Mass spectrum data, tin-bearing fragment: m/e 135 $[MeSn]^+$, 150 $[Me_2Sn]^+$, 297 $[Sn(C_{14}H_9)]^+$.

*2.3.5. Synthesis of triphenyltin(IV) (9-anthracenecarboxylato) [$Ph_3SnOC(O)(C_{14}H_9)\cdot CH_3OH$] (**5**)*

Triphenyltin(IV) chloride (0.77 g, 2 mmol) was treated with potassium isopropoxide (0.19 g, 2 mmol) in isopropanol (20 ml) to produce triphenyltin *iso*-propoxide and potassium chloride. The potassium chloride precipitate was removed by filtration and then 9-anthracenecarboxylic acid (0.44 g, 2 mmol) in isopropanol (20 ml) was added to the filtrate; the solution was refluxed for 2 h. Evaporation of the solvent gave a yellow solid, which was purified by recrystallization from a chloroform–methanol (1:1 *v*/*v*) mixture at room temperature to furnish yellowish crystals (m.p. 84 °C). Anal. Calc. for $C_{34}H_{28}O_3Sn$: C, 67.71; H, 4.64. Found: C, 68.05; H, 4.42%. IR (KBr, cm^{-1}): 421w, 447m,495w, 525w, 640m, 695m, 729m, 779m, 866w, 887w, 998w, 1073w, 1295m, 1298m, 1367sh, 1428sh, 1480sh, 1621s, 2091m. ^1H NMR ($CDCl_3$, ppm): 3.5 (3H, s, CH_3O), 7.37–8.48 (24H, m, C_6H_5). ^{13}C NMR (ppm): 50.8 (CH_3OH), 128.4 (C_{meta}), 129.5 (C_{para}), 137.1 (C_{ortho}, $^2J^{119/117}Sn$–C, 49 Hz), 138.1 (C_{ipso}), 125.2, 125.6, 126.6, 128.6, 128.8, 129.0, 130.4, 131.0 ($C_{14}H_9$), 175.0 (COO). ^{119}Sn NMR (ppm): −85.6. Mass spectrum data, tin- bearing fragment: *m*/*e* 197 $[SnPh]^+$, 351 $[SnPh_3]^+$, 451 $[Ph_2Sn(C_{14}H_9)]^+$, 495 $[Ph_2SnOOC(C_{14}H_9)]^+$, 572 $[Ph_3SnOOC(C_{14}H_9)]^+$.

*2.3.6. Synthesis of ethyldiphenyltin(IV) (9-anthracenecarboxylato)[$Ph_2EtSnOC(O)(C_{14}H_9)$] (**6**)*

Ethyldiphenyltin(IV) iodide (0.86 g, 2 mmol) was treated with potassium isopropoxide (0.19 g, 2 mmol) in isopropanol (20 ml) to produce ethyldiphenyltin(IV) isopropoxide and potassium iodide. The potassium iodide precipitate was removed by filtration and then 9-anthracenecarboxylic acid (0.44 g, 2 mmol) in isopropanol (20 ml) was added to the filtrate; the solution was refluxed for 2 h. Evaporation of the solvent gave a yellow solid, which was purified by recrystallization from a chloroform–methanol (1:1 *v*/*v*) mixture at room temperature to furnish yellowish crystals (m.p. 123 °C). Anal. Calc. for $C_{29}H_{24}O_2Sn$: C, 66.59; H, 4.58. Found: C, 66.02; H, 4.66%. IR (KBr, cm^{-1}): 465m, 510w, 536sh, 575w, 618s, 663m,731m, 764w, 792w, 843m, 888m, 949m, 1011m, 1175sh, 1275m, 1321s, 1378s, 1436sh, 1479sh, 1520s, 1568s, 1640s, 2869w, 2917w, 3049w. ^1H NMR ($CDCl_3$, ppm): 1.63–1.68 (3H, t, CH_3), 7.37–8.48 (19H, m, C_6H_5). ^{13}C NMR (ppm): 10.0 (CH_3), 10.2 (CH_2), 128.3 (C_{meta}), 129.2 (C_{para}), 136.8 (C_{ortho}, $^2J^{119/117}Sn$–^{13}C, 45 Hz), 139.2 (C_{ispo}), 125.2, 125.6, 126.5, 128.2, 128.4, 128.9, 130.1, 131.1 ($C_{14}H_9$), 175.6 (COO). ^{119}Sn NMR (ppm): −17.0. Mass spectrum data, tin-bearing fragment: *m*/*e* 149 $[EtSn]^+$, 197 $[PhSn]^+$, 374 $[PhSn(C_{14}H_9)]^+$, 403 $[PhEtSn(C_{14}H_9)]^+$, 451 $[Ph_2Sn(C_{14}H_9)]^+$.

*2.3.7. Synthesis of diphenyltin(IV) di-(9-anthracenecarboxylato){$Ph_2Sn[OC(O)(C_{14}H_9)]_2$} (**7**)*

Diphenyltin(IV) dichloride (0.69 g, 2 mmol) was treated with potassium isopropoxide (0.39 g, 4 mmol) in isopropanol (20 ml) to produce diphenyltin(IV) diisopropoxide and potassium chloride. The potassium chloride precipitate was removed by filtration and then 9-anthracenecarboxylic acid (0.88 g, 4 mmol) in isopropanol (40 ml) was added to the filtrate; the solution was refluxed for 2 h. Evaporation of the solvent gave a yellow solid, which was purified by recrystallization from a toluene–methanol–dichloromethane mixture (1:1 *v*/*v*) at 4 °C to furnish yellowish crystals (m.p. 142 °C). Anal. Calc. for $C_{42}H_{28}O_4Sn$: C, 70.54; H, 3.91. Found: C, 70.02; H, 4.12%. IR (KBr, cm^{-1}): 449m, 512m, 556w, 596w, 638m, 726sh, 792m, 845w, 888m, 915m, 1020w, 1143w, 1228s, 1253sh, 1292sh, 1342w, 1424m 1445sh, 1486sh, 1678s, 2824w. ^1H NMR ($CDCl_3$, ppm): 7.30–8.63 (10H, m, C_6H_5 and 9H, m, $C_{14}H_9$). ^{119}Sn NMR (ppm): −49.5. Mass spectrum data, tin-bearing fragment: *m*/*e* 120 $[Sn]^+$, 197 $[SnPh]^+$, 274 $[SnPh_2]^+$, 451 $[Ph_2Sn\ (C_{14}H_9)]^+$, 495 $[Ph_2SnOCO(C_{14}H_9)]$.

*2.3.8. Synthesis of dimethylphenyltin(IV) (9-anthracenecarboxylato)[$PhMe_2SnOC(O)(C_{14}H_9)$] (**8**)*

Dimethylphenyltin(IV) iodide was prepared according to published procedure [32]. This reagent (0.7 g, 2 mmol) was treated with potassium isopropoxide (0.19 g, 2 mmol) in isopropanol (20 ml) to produce methyldiphenyltin(IV) isopropoxide and potassium iodide. The potassium iodide precipitate was removed by filtration and then 9-anthracenecarboxylic acid (0.44 g, 2 mmol) in isopropanol (20 ml) was added to the filtrate; the solution was refluxed for 2 h. Evaporation of the solvent gave a yellow solid, which was purified by recrystallization from a dichloromethane–methanol mixture (1:1 *v*/*v*) at 4 °C to furnish yellowish crystals (m.p. 109 °C). Anal. Calc. for $C_{23}H_{20}O_2Sn$: C, 61.81; H, 4.47. Found: C, 61.22; H, 4.35 %. IR (KBr, cm^{-1}): 415w, 449w, 524w, 555w, 589w, 697m, 729s, 767m, 845w, 865w, 895w, 960w, 1015w, 1077w, 1278m, 1318sh, 1389s, 1429s, 1485sh, 1546s, 1621sh, 2854w, 2924w. ^1H NMR ($CDCl_3$, ppm): 0.93–1.15 (6H, s, CH_3, $^2J^{119}Sn$–H, 64.2 Hz), 7.18–8.46 (5H, m, C_6H_5 and 9H, m, $C_{14}H_9$). ^{13}C NMR (ppm): −4.3 (CH_3, $^1J^{119}Sn$–^{13}C, 428 Hz, $^1J^{117}Sn$–^{13}C, 415 Hz), 128.3 (C_{meta}), 129.5 (C_{para}), 136.1 (C_{ortho}, $^2J^{119/117}Sn$–^{13}C, 48 Hz), 139.2 (C_{ispo}), 124.9, 125.3, 126.4, 128.1, 128.4, 128.7, 130.8, 131.2 ($C_{14}H_9$), 176.1 (COO). ^{119}Sn NMR (ppm): 79.8. Mass spectrum data, tin-bearing fragment: *m*/*e* 120 $[Sn]^+$, 135 $[SnMe]^+$, 150 $[SnMe_2]^+$, 197 $[SnPh]^+$, 227 $[PhSnMe_2]^+$, 294 $[Sn(C_{14}H_9)]^+$, 389 $[PhSnMe(C_{14}H_9)]^+$, 433 $[PhMeSn\ OCO(C_{14}H_9)]$.

3. Results and discussion

3.1. Synthesis

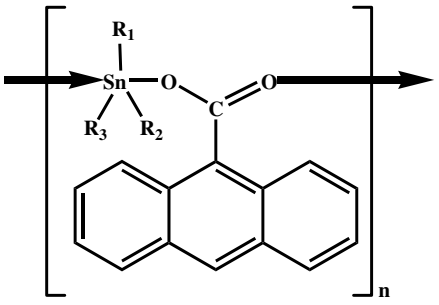
A new methodology has been used to synthesize organotin carboxylates. Organotin carboxylates are usually prepared by reacting organotin hydroxide or di-alkyltin oxide to corresponding carboxylic acid. However, organotin hydroxides or oxides are limited and other routes are needed for the preparation of organotin carboxylate,

specifically organotin carboxylates with mixed alkyl and aryl groups on tin. Several authors have used various approaches for synthesis of organotin carboxylates, including reacting organotin chloride to carboxylic acid in the presence of sodium hydroxide or sodium salt of carboxylic acids. Alternatively, they were prepared by reacting organotin iodide to silver acetates [24]. However, in the latter approach, cleavage of aryl groups present some difficulties, consequently a milder synthetic approach has been used. In the present study, we have replaced halogens of di- or triorganotin with isopropoxide group by reacting them to potassium isopropoxide. The triorganotin isopropoxide was isolated and reacted to anthracenecarboxylic acid. This procedure provides a clean reaction for the preparation of organotin carboxylates without any side product.

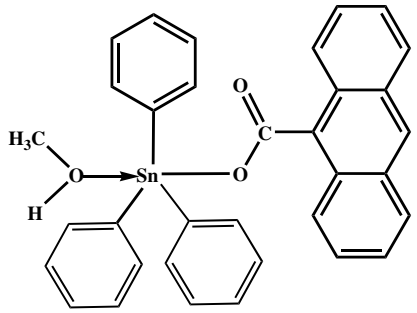
3.2. General characterization

3.2.1. Infrared spectroscopy

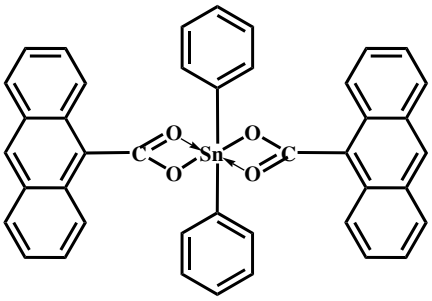
The infrared data of di- and triorganotin carboxylates are usually used to predict their solid-state structures. In the simplest triorganotin carboxylates, trimethyltin acetate, the oxygen atom of the acetate, and the carbonyl oxygen of the acetate occupy the apical positions in the C_3SnO_3 polyhedron, which is a common feature in triorganotin compounds [33], to form a polymer with zigzag configuration. The bridging carboxylate in organotin compounds is simply followed by infrared spectroscopy with shift of $\upsilon(CO_2)$ bands, as compared to the parent carboxylic acid. In the infrared spectra of $Ph_2MeSnOCO(C_{14}H_9)$ (**2**), $Me_3SnOCO(C_{14}H_9)$ (**3**), $Me_2Sn[OCO(C_{14}H_9)]_2$ (**4**), $Ph_3SnOCO(C_{14}H_9)$ (**5**), $Ph_2EtSnOCO(C_{14}H_9)$ (**6**), $Ph_2Sn[OCO(C_{14}H_9)]_2$ (**7**), and $PhMe_2SnOCO(C_{14}H_9)$ (**8**), the $\upsilon_{sym}(CO_2)$ and $\upsilon_{asym}(CO_2)$ modes appear at 1385, 1579; 1392, 1549; 1389, 1677; 1367, 1621; 1378, 1568; 1486, 1678; 1389, 1546 cm^{-1}, respectively. The shift of those bands to red for **2**–**8** with respect to free acid confirms formation of organotin carboxylates. The magnitude of $\upsilon_{asym} - \upsilon_{sym}$ ($\Delta\upsilon$) separation has been used to explain the type of carboxylate structure present [34]. The magnitude of $\upsilon_{asym} - \upsilon_{sym}$ ($\Delta\upsilon$) for **2**, **3**, **6**, and **8** are in the expected range (below 200 cm^{-1}) for the bridged triorgnotin carboxylates (Scheme 1). Furthermore, the observation of two Sn–C absorption bands in the 524–575 cm^{-1} region for the above-mentioned triorganotin carboxylates rules out an exactly planar arrangement of the three Sn–C bonds and therefore a precisely symmetrical *trans*-trigonal bipyramidal geometry around the tin. Infrared assignments are confirmed by single crystal structure determination of **2**, **3**, and **4.**



Scheme 1. $R^1 = CH_3$, $R^2 = R^3 = C_6H_5$ (**2**); $R^1 = R^2 = R^3 = CH_3$ (**3**); $R^1 = C_2H_5$, $R^2 = R^3 = C_6H_5$ (**6**); $R^1 = R^1 = CH_3$, $R^3 = C_6H_5$ (**8**).



Scheme 2. Proposed structure for complex **5**.



Scheme 3. Proposed structure for complex **7**.

In contrast, for the complexes **4** and **5**, the values of $\Delta\upsilon$ exceed 230 cm^{-1}; this clearly shows that these complexes adopt the monodentate carboxylate structure. A five-coordinated tin is expected for the triphenyltin derivative **5**, by considering that the carboxylate group is monodentate and the coordinated methanol is present in the complex (Scheme 2). Interestingly, triphenyltin arylcarboxylates are generally monomeric molecules with tetrahedral tin [35,36], the aryl group prefers to be conjugated to the carboxylate group so that those two planes can remain coplanar, but this orientation prevents the carbonyl oxygen from approaching the tin [37]. Apparently, similar behavior is intact for the complex **5**, however, orientation of aryl groups should be different to some extent in order to allow methanol to coordinate to tin. The infrared spectrum of complex **7** exhibited single $\upsilon_{sym}(CO_2)$ and $\upsilon_{asym}(CO_2)$ peaks which indicate that both carboxylate groups have similar bonding mode. The magnitude of $\Delta\upsilon$, 192 cm^{-1}, is on the broader-line of monodentate and bidentate carboxylates; therefore, one can conclude a four- or six-coordinated tin for this complex (Scheme 3). However, a $\Delta\upsilon$ value of 200 ± 10 cm^{-1}, is attributed to the chelated carboxyl groups [38].

3.2.2. NMR spectroscopy

For the determination of structural features of organotin carboxylates in solution, their ^1H, ^{13}C, and ^{119}Sn

NMR have been recorded in $CDCl_3$. The ^1H NMR spectra of all complexes show the expected aliphatic and aromatic peaks with right integration and multiplicities. For those that resolved the $^2J(^{119}Sn–C–^1H)$, namely, **2** (59.2 Hz), **3** (57.0 Hz), **4** (81.0 Hz) and **8** (64.2 Hz), their values indicate tetrahedral geometries for complexes **2**, **3** and **8**, and octahedral for **4**. The magnitude of the two-band coupling, $^2J(^{119}Sn–C–^1H)$, for compounds **2**, **3**, **4** and **8** are 59.2, 57.0, 81.2 and 64.2 Hz, respectively. The estimated value of C–Sn–C angle in **2**, **3**, **4** and **8** is 112°, 110°, 132° and 115°, respectively [39]. The estimated value for compound **4** is in good agreement with the C–Sn–C angle found in the solid state. Apparently, polymeric organotin carboxylates, **2**, **3**, **6** and **8** do not retain a solid-state structure in solution in contrast to complex **4** with $^2J(^{119}Sn–C–^1H)$ of 81.0 Hz. When ^1H NMR spectra of **2**, **3**, **6**, and **8** was recorded in CD_3OD, the $^2J(^{119}Sn–C–^1H)$ values increased to around 70–72 Hz. The increase in the $^2J(^{119}Sn–C–^1H)$ coupling constant from 57–64 Hz in $CDCl_3$ to about 70–72 Hz in CD_3OD reveals a five-coordinated tin atom in a coordinating solvent for the latter-mentioned complexes. Similar to other polymeric triorganotin carboxylates [40], their solid-state structures in solution depolymerize to monomers and four-coordinated species, and then the solvent coordinate to the tin and return them to the five-coordinated status. The increase of coupling constants, $^2J^{119}Sn–C–^1H$, is in agreement with the decrease of the s-character of the CH_3–Sn bonds from four- to five-coordinated tin [4].

The COO resonance in the ^{13}C NMR spectra of complexes **2**, **3**, **4**, **5**, **6** and **8** were observed at 175.5, 175.4, 178.4, 175.0, 175.6 and 176.1 ppm, respectively. By considering that the polymeric organotin carboxylates, **2**, **3**, **6** and **8** do not retain solid-state structure and the carboxylate groups become monodentate in solution; similar ^{13}C chemical shifts are expected for the COO groups in all complexes. The insufficient solubility of complex **7** in chloroform did not allow us to record the ^{13}C NMR spectrum and reach a similar conclusion. Furthermore, C_{ipso} resonances were observed for the complexes **2** (139.4 ppm), **3** (138.1 ppm), **6** (139.2 ppm) and **8** (139.2 ppm) these values are consistent with the four-coordinated organotin structures [41,42]. The C–Sn–C angles for compounds **2** (112°), **3** (111°), **4** (133°) and **8** (114°) is also estimated from their magnitude of $^1J^{119}Sn–^{13}C$ [39]. The estimated value for compound **4** is in good agreement with the C–Sn–C angle found in the solid state and also with the value estimated from magnitude of $^2J(^{119}Sn–C–^1H)$. The ^{13}C NMR spectra of all organotin carboxylates did not show a shift to anthracene ring carbon atoms in comparison with the free anthracenecarboxylic acid, however, as expected, their COO resonances slightly shifted downfield.

All ^{119}Sn NMR spectra were recorded in noncoordinating solvents in order to preclude possible changes in the coordination number of tin. The solution ^{119}Sn NMR spectra of all complexes consists of only one resonance, the chemical shifts of complexes **2**, **3**, **6** and **8** (−1.3, 163.1, −17.0 and 79.8 ppm), and those of complexes **4** and **5** in noncoordinating solvents (−99.5 and −85.6 ppm) falling within the range of four- and five-coordinated organotin compounds, respectively [43,44]. Although by considering that the ^{119}Sn chemical shift in addition to the tin coordination number is influenced by the type of aromatic and aliphatic groups or donor atoms bound to the tin [45], the ^{119}Sn chemical of complex **7**, −49.5 ppm, is far from the range noted for the six-coordinated tin. Therefore, it is reasonable to assume that the complex **7**, similar to polymeric triorganotin carboxylates, do not retain solid-state structure in solution.

3.3. Crystal structures

3.3.1. Crystal structure of $[Ph_2MeSnOC(O)(C_{14}H_9)]$ (2)

Selected bond angles and distances for complex **2** are given in Table 2 and the molecular structure is shown in Fig. 1. This complex is a one-dimensional polymer

Table 2
Selected bond lengths (Å) and angels (°) for $[Ph_2MeSnOC(O)(C_{14}H_9)]$ (**2**)

Bond lengths			
Sn(1)–C(1)	2.116(3)	C(14)–O(2)	1.247(3)
C(14)–O(1)	1.268(3)	C(14)–C(15)	1.501(3)
Sn(1)–C(2)	2.124(2)	Sn(1)–O(1)	2.2231(18)
Sn(1)–C(8)	2.143(2)	Sn(1)–O(2)#1	2.3800(18)
Bond angles			
C(1)–Sn(1)–C(2)	119.36(11)	C(13)–C(8)–Sn(1)	118.8(2)
C(1)–Sn(1)–C(8)	131.74(11)	O(1)–C(14)–C(15)	116.1(2)
C(2)–Sn(1)–C(8)	108.61(9)	C(1)–Sn(1)–O(1)	88.88(10)
C(2)–Sn(1)–O(1)	99.64(8)	C(8)–Sn(1)–O(1)	88.19(8)
C(1)–Sn(1)–O(2)#1	82.82(9)	C(2)–Sn(1)–O(2)#1	96.27(8)
C(8)–Sn(1)–O(2)#1	87.26(8)	O(1)–Sn(1)–O(2)#1	164.08(7)
C(7)–C(2)–Sn(1)	119.84(18)	O(2)–C(14)–O(1)	123.6(2)
O(2)–C(14)–C(15)	120.3(2)	C(9)–C(8)–Sn(1)	123.02(19)
C(3)–C(2)–Sn(1)	122.11(19)		

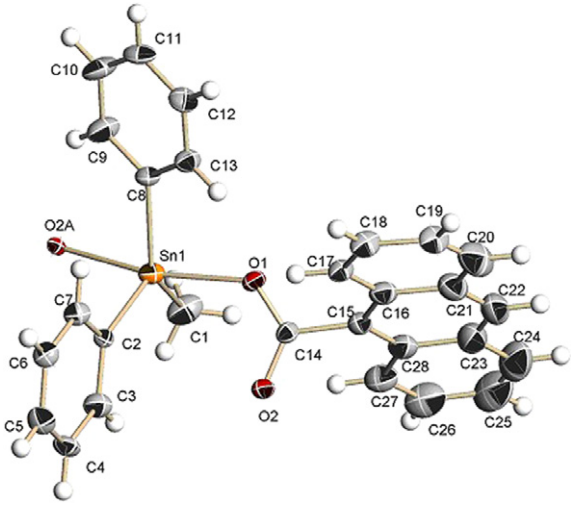


Fig. 1. Molecular structure of methyldiphenyltin (9-anthracenecarboxylate)$[Ph_2MeSnOC(O)C_{14}H_9]$ (**2**).

($R_1 = CH_3$, $R_2 = R_3 = C_6H_5$ in Scheme 1) with five-coordinated tin with electronegative oxygen atoms occupying the apical position of the trigonal bipyramid, a feature common in five-coordinated triorganotin compounds [34,46]. The tin–oxygen bond lengths of 2.2231(2) and 2.3800(2) Å is attributed to the unevenness in bonding; the latter value is in the range of Sn–O bond lengths, which have been reported for intramolecular bonds in triorganotin carboxylates [47]. The intramolecular tin–oxygen bond length [Sn(1)–O(2), 2.3800 Å] is similar to those of trimethyltin(IV) and dimethylphenyltin(IV) acetates [24,48] but is slightly longer than that of triphenyltin acetate(IV) [49]. Although the oxygen–tin–oxygen skeleton is bent, 164.08(7)°, the sum of the carbon–tin–carbon angles (359.71°) is consistent with the ideal value of 360°. One of the phenylmethyltin angle, C(1)–Sn(1)–C(8), is significantly larger than the other, C(1)–Sn(1)–C(8), and both are larger than the diphenyltin angle [108.61(9)°]. It seems that the carbonyl oxygen is opens up the carbon–tin–carbon angle nearest to it. Furthermore, the smaller diphenyltin angle in complex **2** in comparison with those of ethyldiphenyltin(IV) chloroacetate [115.2(1)°] [50] and ethyldiphenyltin(IV) dichloroacetate [115.6(1)°] [35] is probably imposed by anthracene group to minimize steric interactions. Furthermore, torsion angles of C(1)–Sn(1)–C(2)–C(7) and C(8)–Sn(1)–C(2)–C(7) with values of 174.9(2)° and −0.4(2)° show that phenyl rings are twisted and become almost perpendicular to the equatorial plane to decrease steric interaction further. In complex **2**, which carries two phenyl groups, the phenyl groups that occupy the equatorial position are farthest from the intramolecular carbonyl oxygen. The bond length of C(14)–O(1) is almost equivalent to the bond length of C(14)–O(2), which is associated with the oxygen bridging the two tin atoms; the bond length of C(14)–O(1) suggests delocalization of π-electron density in it.

3.3.2. Crystal structure of $[Me_3SnOC(O)(C_{14}H_9)]$ (3)

Selected bond angles and distances for complex **3** are listed in Table 3 and the molecular structure is shown in Fig. 2. This complex, which is similar to complex **2** adapt a carboxylate bridged motif in which the tin center shows *trans*-C_3SnO_2 trigonal–bipyramidal coordination ($R^1 = R^2 = R^3 = CH_3$ in Scheme 1), with one axial tin–oxygen bond much longer than the other axial tin–oxygen bond [2.4010(17) and 2.2214(16) Å]. The oxygen–tin–oxygen skeleton in comparison with complex **2** is less bent [170.87(6)°] and is very similar to that of trimethyltin(IV) acetate [48]. The carbon–tin–carbon angles and tin–carbon bond lengths of complex **3** are almost identical with those of trimethyltin acetate. Comparison of carbon–tin–carbon angles with such angles in complex **2** clearly shows that distortion of triorganotin carboxylates from ideal geometry is influenced by type of organic group on tin to a great extent and by steric interactions of bulkier ones with anthracene group to a less extent. As expected, other structural features of complex **2** and **3** are similar.

Table 3
Selected bond lengths (Å) and angels (°) for $[Me_3SnOC(O)C_{14}H_9]$ (**3**)

Bond lengths			
Sn(1)–C(3)	2.123(2)	C(4)–O(1)	1.247(3)
Sn(1)–C(1)	2.126(3)	Sn(1)–O(1)	2.4010(17)
Sn(1)–C(2)	2.126(3)	Sn(1)–O(2)	4.5933(17)
Sn(1)–O(2)#1	2.2214(16)	C(4)–O(2)	1.271(3)
C(4)–C(5)	1.507(3)	C(5)–C(6)	1.403(3)
Bond angles			
C(3)–Sn(1)–C(1)	121.46(11)	C(1)–Sn(1)–O(1)	92.00(9)
C(3)–Sn(1)–C(2)	118.60(12)	C(2)–Sn(1)–O(1)	83.78(8)
C(1)–Sn(1)–C(2)	119.33(12)	C(3)–Sn(1)–O(2)	81.57(7)
C(3)–Sn(1)–O(2)#1	93.20(8)	C(1)–Sn(1)–O(2)	91.81(8)
C(1)–Sn(1)–O(2)#1	95.97(9)	C(2)–Sn(1)–O(2)	88.92(8)
C(2)–Sn(1)–O(2)#1	88.42(9)	O(1)–C(4)–O(2)	123.5(2)
C(3)–Sn(1)–O(1)	86.41(8)	O(1)–C(4)–C(5)	119.87(19)
O(2)–C(4)–C(5)	116.63(19)	C(4)–O(1)–Sn(1)	141.48(14)

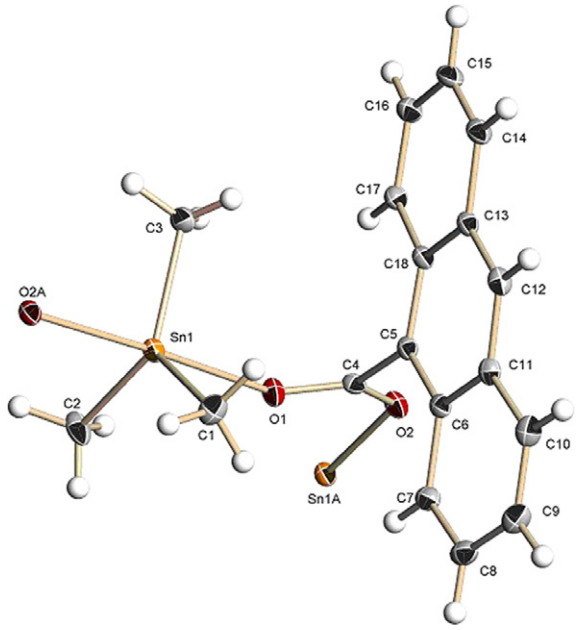


Fig. 2. Molecular structure of trimethyltin(IV) (9-anthracenecarboxylato)$[Me_3SnOCO(C_{14}H_9)]$ (**3**).

3.3.3. Crystal structure of $\{Me_2Sn[OC(O)(C_{14}H_9)]_2 \cdot CH_3OH\}CH_3OH$ (4)

Selected bond lengths and angles for complex **4** are given in Table 4. Complex **4**, as shown in Fig. 3, with trigonal bipyramid geometry possessing a monomeric structure. Two carboxylates are coordinated to tin in monodentate form from axial and equatorial positions and the coordination number is raised to five as the methanol occupies the apical position of the trigonal bipyramid. Apparently, because of the anthracene steric demand, coordination of the preparation solvent, CH_3OH, is preferred to bridge carboxylate. Such a steric control over the molecular structure for diorganotin carboxylates has been noticed previously [51]. Although, several monomeric diorganotin carboxylates with general formula of $R_2Sn(O_2CR')_2$ exist in which the carboxylate ligands are chelated to tin as a bidentate

Table 4
Selected bond lengths (Å) and angels (°) for $Me_2Sn[OC(O)C_{14}H_9]_2 \cdot CH_3OH$ (**4**)

Sn1–O3	2.0637(15)	O3–Sn1–C1	121.07(9)
Sn1–C1	2.108(2)	O3–Sn1–C2	100.94(9)
Sn1–C2	2.120(2)	C1–Sn1–C2	137.12(10)
Sn1–O1	2.1562(16)	O3–Sn1–O1	81.61(7)
Sn1–O5	2.3056(17)	C1–Sn1–O1	97.15(9)
O1–C3	1.290(3)	C2–Sn1–O1	97.11(8)
O2–C3	1.245(3)	O3–Sn1–O5	82.34(7)
C3–C4	1.511(3)	C1–Sn1–O5	88.00(9)
O3–C18	1.309(3)	C2–Sn1–O5	89.52(8)
O4–C18	1.219(3)	O1–Sn1–O5	163.54(7)
O5–C33	1.443(3)	C3–O1–Sn1	112.33(14)
O6–C34	1.424(3)	O1–Sn1–O5 1	63.54(7)

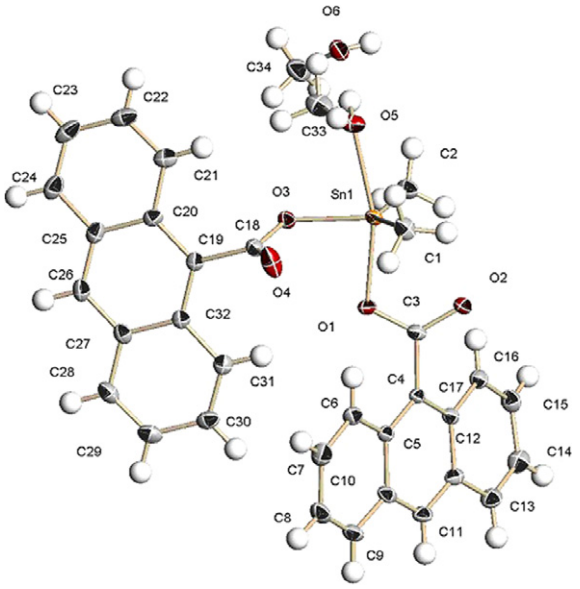


Fig. 3. Molecular structure of dimethyltin(IV) (9-anthracenecarboxylate)$[Me_2Sn(OCOC_{14}H_9)_2 \cdot CH_3OH]$ (**4**).

ligand [17], to the best of our knowledge the structure of complex **4** is the first example of a five-coordinated monomeric diorganotin carboxylate among rich and diverse organotin carboxylate structures [17]. It seems that the extensive crowding imposed by anthracene prevents carboxylate groups to coordinate to tin by inter- or intramolecular interaction. The equatorial tin–oxygen bond length, 2.0637(15) Å, somewhat is quite shorter than the axial tin–oxygen bond length, 2.1562(16) Å, which associates with the oxygen atom of carboxylates, and both bond length are shorter than tin–oxygen bond that arises from the coordination of methanol. The later mentioned tin–oxygen bond length, 2.1562(16) Å, is much shorter than the similar tin–oxygen bond length in organotin carboxylates with a general formula of $R_2Sn(O_2CR')_2$. The oxygen–tin–oxygen angle, which associated with the carboxylate and methanol oxygen, bends 163.54(7)°, and the distortion from idealized geometry is also seen in the sum of the equatorial plane angles (359.13°).

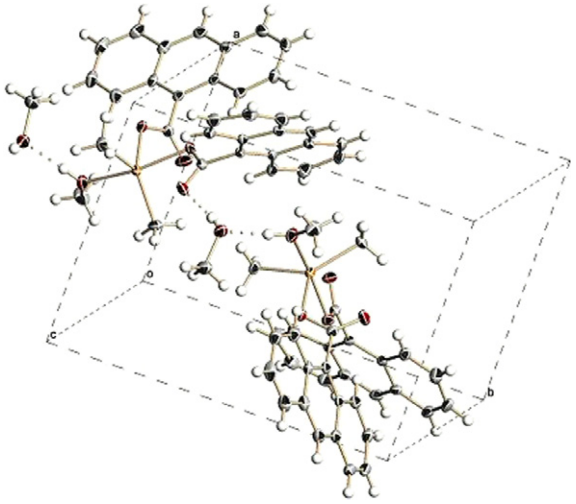


Fig. 4. The molecular packing of complex **4** showing intermolecular hydrogen bonding though solvated CH_3OH.

As shown in Fig. 3, a solvent molecule, methanol, is associated with the coordinated methanol and both methanol molecules, as illustrated in Fig. 4, are engaged in hydrogen bonding. The O(5) atom of coordinated methanol acts as a hydrogen-bond donor by H(5) to the O(6) atom of solvated methanol (O5–H5, 0.849 Å; O5–H···O6, 1.729 Å; O5···O6, 2.575 Å; and an angle at H 173.97°) and O(6) acts as a hydrogen-bond donor by H(6) to Ó(2), a coordinated carboxylate oxygen. The O6–H6, O6–H···Ó(2), and O6···O2 distances are 0.783 Å, 1.941 Å and 2.718 Å, respectively, at angle of 171.8°.

4. Conclusion

This contribution has shown that the combination of di- and triorganotin(IV) moiety with anthracenecarboxylic acid result in the formation of polymeric or discrete complexes. The steric demand of anthracene group influences the coordination geometry of tin. Low coordinated tin is dominant in the majority of di- and trioganotin(IV) derivatives of 9-anthracenecarboxylic acid. For the entire mixed aryl and alkyl groups of triorganotin complexes, carboxylate-bridged motifs were observed, in contrast to discrete triphenyltin derivative which is highly steric demanding.

Acknowledgements

The authors thank the Vice-President's Office for Research Affairs of Shahid Beheshti University for supporting this work.

Appendix A. Supplementary material

CCDC 639904, 639906, and 639905 contain the supplementary crystallographic data for **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2

1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.05.049.

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