

# Synthesis and characterization of tri(*o*-fluorobenzyl)tin esters of heteroaromatic carboxylic acid and crystal structures of tri(*o*-fluorobenzyl)tin esters of 4-pyridinecarboxylic acid and 3-pyridinecarboxylic acid

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## Abstract

Reaction of tri(*o*-fluorobenzyl)tin chloride with sodium of heteroaromatic carboxylic acid in 1:1 stoichiometry yielded complexes of the type (2-*F*-Bz)<sub>3</sub>SnOOCR (R = 2-furanyl, 2-furanvinyl, 2-thiophenyl, 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-indolyl, 3-indolmethyl and 3-indolpropyl), respectively. These complexes have been characterized by elemental analyses, IR and <sup>1</sup>H NMR spectroscopy. The crystal structures of tri(*o*-fluorobenzyl)tin esters of 4-pyridinecarboxylic acid (**5**) and 3-pyridinecarboxylic acid (**6**) were determined by single crystal X-ray diffraction. In the crystals of compounds **5** and **6**, the tin atoms are rendered five-coordinate in a trigonal bipyramidal structure by coordinating with pyridine N atom of carboxylate group. The resulting structure is a one-dimensional linear polymer containing Sn–O bond lengths of 2.161(4), 2.202(9) Å and Sn–N bond lengths of 2.518(5), 2.454(10) Å. © 2003 Elsevier B.V. All rights reserved.

**Keywords:** Heteroaromatic carboxylic acid; Tri(*o*-fluorobenzyl)tin; Synthesis; Crystal structure

## 1. Introduction

Organotin esters of carboxylic acid are widely used as biocides, fungicides, and as homogeneous catalysts in industry [1–4]. Recently, pharmaceutical properties of organotin esters of carboxylic acid have been investigated for their antitumour activity [5,6]. In general, the biocidal activity of organotin compounds is influenced greatly by the structure of the molecule and the coordination number of the tin atom(s) [7,8]. Studies on organotin compounds containing carboxylate ligands with additional donor atom (e.g. N, O or S) that are available for coordinating to tin atom, have revealed that new structural types may lead to different activity [9,10]. As an extension of our studies of organotin esters of carboxylic acid with additional donor atoms residing on the carboxylate ligand [11], we have synthesized and structurally characterized a series of tri(*o*-fluoroben-

zyl)tin esters of heteroaromatic carboxylic acid and determined the crystal structures of tri(*o*-fluorobenzyl)tin esters of 4-pyridinecarboxylic acid and 3-pyridinecarboxylic acid. And the results of this study are reported herein.

## 2. Experimental

### 2.1. Materials and methods

All reactants were reagent grade. Infrared spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs. <sup>1</sup>H NMR spectra were obtained on Mercury Plus-400 NMR spectrometer, chemical shifts were given in parts per million relative to Me<sub>4</sub>Si in CDCl<sub>3</sub> solvent. Elemental analyses were performed with a PE-2400 II elemental apparatus. Tin was estimated as SnO<sub>2</sub>. X-ray measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo-K $\alpha$  (0.071073 nm) radiation.

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## 2.2. Synthesis

Anhydrous sodiums of heteroaromatic carboxylic acid (1.2 mmol) were added to benzene solution of tri(*o*-fluorobenzyl)tin chloride (1.0 mmol), respectively. The mixtures were stirred for 15 h at 40 °C. The precipitate salts were removed by filtration. And solvent was gradually removed by evaporation under vacuum until solid products were obtained. The products were recrystallized from acetone–hexane to give a colorless crystal (see Scheme 1).

### 2.2.1. (2-*F-Bz*)<sub>3</sub>SnO<sub>2</sub>CC<sub>4</sub>H<sub>3</sub>O (1)

Yield: 87%, m.p. 112–113 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.42(1H, s, 5-furan-H), 6.90–7.15(12H, m, Ar-H), 6.72(1H, d, 3-furan-H), 6.55(1H, dd, 4-furan-H), 2.63(6H, t, *J*<sub>Sn-H</sub> = 71.35 Hz, ArCH<sub>2</sub>Sn) ppm. IR (KBr, cm<sup>-1</sup>): 1552, 1385(s, CO<sub>2</sub>), 553(w, Sn–C), 453(m, Sn–O). Anal. Calc. for C<sub>26</sub>H<sub>21</sub>O<sub>3</sub>F<sub>3</sub>Sn: C, 56.27; H, 3.91; Sn, 21.18. Found: C, 56.05; H, 3.80; Sn, 21.30%.

### 2.2.2. (2-*F-Bz*)<sub>3</sub>SnO<sub>2</sub>CCHCHC<sub>4</sub>H<sub>3</sub>O (2)

Yield: 75%, m.p. 103–105 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.46(1H, d, 5-furan-H), 7.30(1H, s, C=CHCO<sub>2</sub>), 6.84–7.09(12H, m, Ar-H), 6.76(1H, d, 3-furan-H), 6.59(1H, d, 4-furan-H), 6.37(1H, d, C=CHAr), 2.73(6H, t, *J*<sub>Sn-H</sub> = 69.86 Hz, ArCH<sub>2</sub>Sn) ppm. IR (KBr, cm<sup>-1</sup>): 1592, 1395(s, CO<sub>2</sub>), 545(w, Sn–C), 456(m, Sn–O). Anal. Calc. for C<sub>28</sub>H<sub>23</sub>O<sub>3</sub>F<sub>3</sub>Sn: C, 57.89; H, 3.83; Sn, 20.42. Found: C, 57.67; H, 3.98; Sn, 20.35%.

### 2.2.3. (2-*F-Bz*)<sub>3</sub>SnO<sub>2</sub>CC<sub>4</sub>H<sub>3</sub>S·CH<sub>2</sub>Cl<sub>2</sub> (3)

Yield: 78%, m.p. 134–136 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.81(1H, d, 5-thiophene-H), 7.63(1H, d, 3-thiophene-H), 6.77–7.11(13H, m, Ar-H, 4-thiophene-H), 5.13(2H, s, CH<sub>2</sub>Cl<sub>2</sub>), 2.68(6H, t, *J*<sub>Sn-H</sub> = 73.03 Hz, ArCH<sub>2</sub>Sn) ppm. IR (KBr, cm<sup>-1</sup>): 1601, 1402(s, CO<sub>2</sub>), 548(w, Sn–C), 459(m, Sn–O). Anal. Calc. for C<sub>27</sub>H<sub>23</sub>O<sub>2</sub>F<sub>3</sub>Cl<sub>2</sub>SSn: C, 49.02; H, 3.70; Sn, 18.16. Found: C, 49.28; H, 3.52; Sn, 18.03%.

### 2.2.4. (2-*F-Bz*)<sub>3</sub>SnO<sub>2</sub>CC<sub>5</sub>H<sub>4</sub>N (4)

Yield: 70%, m.p. 125–127 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.31(1H, br, 6-pyridine-H), 7.90(1H, d, 2-pyridine-H), 7.46(1H, d, 4-pyridine-H), 7.25(1H, d, 3-pyridine-H),

6.85–7.15(12H, m, Ar-H), 2.74(6H, t, *J*<sub>Sn-H</sub> = 76.76 Hz, ArCH<sub>2</sub>Sn) ppm. IR (KBr, cm<sup>-1</sup>): 1638, 1360(s, CO<sub>2</sub>), 550(w, Sn–C), 497(w, Sn–N), 450(m, Sn–O). Anal. Calc. for C<sub>27</sub>H<sub>22</sub>NO<sub>2</sub>F<sub>3</sub>Sn: C, 57.31; H, 4.05; N, 2.43; Sn, 20.64. Found: C, 57.08; H, 3.90; N, 2.47; Sn, 20.89%.

### 2.2.5. (2-*F-Bz*)<sub>3</sub>SnO<sub>2</sub>CC<sub>5</sub>H<sub>4</sub>N·0.5CH<sub>2</sub>Cl<sub>2</sub> (5)

Yield: 77%, m.p. 143–145 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.70(2H, d, 2,6-pyridine-H), 7.65(2H, d, 3,5-pyridine-H), 6.88–7.15(12H, m, Ar-H), 4.78(1H, s, CH<sub>2</sub>Cl<sub>2</sub>), 2.70(6H, t, *J*<sub>Sn-H</sub> = 76.84 Hz, ArCH<sub>2</sub>Sn) ppm. IR (KBr, cm<sup>-1</sup>): 1633, 1354(s, CO<sub>2</sub>), 545(w, Sn–C), 494(w, Sn–N), 467(m, Sn–O). Anal. Calc. for C<sub>27.5</sub>H<sub>23</sub>NO<sub>2</sub>F<sub>3</sub>ClSn: C, 53.86; H, 3.69; N, 2.40; Sn, 19.73. Found: C, 54.09; H, 3.80; N, 2.29; Sn, 19.44%.

### 2.2.6. (2-*F-Bz*)<sub>3</sub>SnO<sub>2</sub>CC<sub>5</sub>H<sub>4</sub>N (6)

Yield: 68%, m.p. 129–131 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.14(1H, d, 2-pyridine-H), 8.77(1H, d, 6-pyridine-H), 7.53(1H, d, 5-pyridine-H), 6.90–7.20(12H, m, Ar-H), 2.73(6H, t, *J*<sub>Sn-H</sub> = 78.04 Hz, ArCH<sub>2</sub>Sn) ppm. IR (KBr, cm<sup>-1</sup>): 1631, 1361(s, CO<sub>2</sub>), 558(w, Sn–C), 503(w, Sn–N), 467(m, Sn–O). Anal. Calc. for C<sub>27</sub>H<sub>22</sub>NO<sub>2</sub>F<sub>3</sub>Sn: C, 57.23; H, 3.97; N, 2.56; Sn, 21.01. Found: C, 57.08; H, 3.90; N, 2.47; Sn, 20.89%.

### 2.2.7. (2-*F-Bz*)<sub>3</sub>SnO<sub>2</sub>CC<sub>8</sub>H<sub>6</sub>N (7)

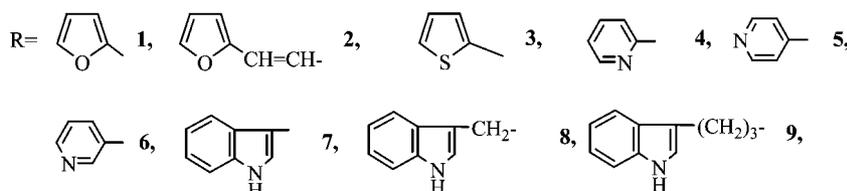
Yield: 80%, m.p. 92–93 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.96(1H, s, N–H), 7.43(1H, br, 2-indole-H), 6.84–7.15(19H, m, Ar-H, indole-H), 2.70(6H, t, *J*<sub>Sn-H</sub> = 73.76 Hz, ArCH<sub>2</sub>Sn) ppm. IR (KBr, cm<sup>-1</sup>): 3432(m, N–H), 1582, 1387(s, CO<sub>2</sub>), 555(w, Sn–C), 458(m, Sn–O). Anal. Calc. for C<sub>30</sub>H<sub>24</sub>NO<sub>2</sub>F<sub>3</sub>Sn: C, 59.20; H, 3.72; N, 2.32; Sn, 19.33. Found: C, 59.44; H, 3.99; N, 2.31; Sn, 19.58%.

### 2.2.8. (2-*F-Bz*)<sub>3</sub>SnO<sub>2</sub>CCH<sub>2</sub>C<sub>8</sub>H<sub>6</sub>N (8)

Yield: 82%, m.p. 81–82 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.05(1H, s, N–H), 7.52(1H, br, 2-indole-H), 6.88–7.23(16H, m, Ar-H, indole-H), 3.62(2H, s, ArCH<sub>2</sub>CO<sub>2</sub>), 2.66(6H, t, *J*<sub>Sn-H</sub> = 72.46 Hz, ArCH<sub>2</sub>Sn) ppm. IR (KBr, cm<sup>-1</sup>): 3428(m, N–H), 1590, 1409(s, CO<sub>2</sub>), 543(w, Sn–C), 452(m, Sn–O). Anal. Calc. for C<sub>31</sub>H<sub>26</sub>NO<sub>2</sub>F<sub>3</sub>Sn: C, 60.27; H, 4.42; N, 2.18; Sn, 19.20. Found: C, 60.03; H, 4.23; N, 2.26; Sn, 19.14%.



1–9



Scheme 1.

### 2.2.9. (2-*F-Bz*)<sub>3</sub>SnO<sub>2</sub>C(CH<sub>2</sub>)<sub>3</sub>C<sub>8</sub>H<sub>6</sub>N (**9**)

Yield: 74%, m.p. 68–70 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.94(1H, s, N–H), 7.46(1H, br, 2-indole-H), 6.81–7.25(16H, m, Ar–H, indole-H), 2.78(2H, t, CH<sub>2</sub>CO<sub>2</sub>), 2.65(6H, t, *J*<sub>Sn–H</sub> = 74.12 Hz, ArCH<sub>2</sub>Sn), 2.13(2H, t, ArCH<sub>2</sub>), 1.47(2H, m, CH<sub>2</sub>) ppm. IR (KBr, cm<sup>-1</sup>): 3430(m, N–H), 1574, 1410(s, CO<sub>2</sub>), 547(w, Sn–C), 455(m, Sn–O). Anal. Calc. for C<sub>33</sub>H<sub>30</sub>NO<sub>2</sub>F<sub>3</sub>Sn: C, 60.93; H, 4.58; N, 2.32; Sn, 18.53. Found: C, 61.14; H, 4.66; N, 2.16; Sn, 18.31%.

### 2.3. Crystallographic measurements

All X-ray crystallographic data were collected on a Bruker smart-1000 CCD diffractometer with graphite monochromated Mo-Kα (0.071073 nm) radiation. The structures were solved by direct method and difference Fourier map using SHELXL-97 program, and refined by full-matrix least-squares on *F*<sup>2</sup>. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically.

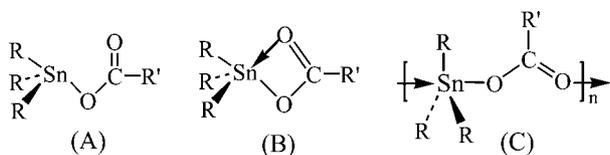
## 3. Results and discussion

### 3.1. Physical properties

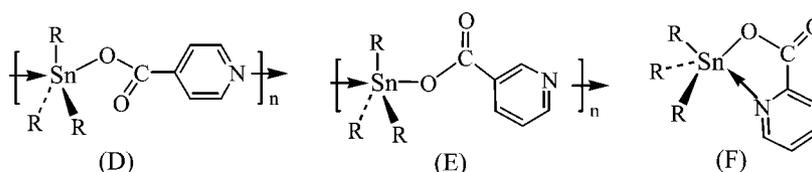
All compounds are colorless crystal. They are soluble in many organic solvents such as CCl<sub>4</sub>, CHCl<sub>3</sub>, C<sub>6</sub>H<sub>6</sub>, (CH<sub>3</sub>)<sub>2</sub>CO, but are insoluble in hexane, petroleum ether, water and so on.

### 3.2. IR spectra

The assignment of IR bands of these compounds has been compared with the IR spectra related compounds [carboxylate and tri(*o*-fluorobenzyl)tin chloride]. It is to be noted that the difference Δ*v* of *v*<sup>as</sup>(coo) and *v*<sup>s</sup>(coo) is of importance because these frequencies can be useful



Scheme 2.



Scheme 3.

for determining the type of bonding between metal and carboxyl [1,12]. Generally triorganotin esters of carboxylic acid adopt three structure type in the solid state (as shown in Scheme 2):

The magnitude of Δ*v* [*v*<sup>as</sup>(coo) – *v*<sup>s</sup>(coo)] of 164–199 cm<sup>-1</sup> for compounds **1–3**, **7–9** is approximate with those of the corresponding sodium of carboxylic acids. This indicates the presence of bidentate carboxylate groups [1–4]. So it is impossible for these compounds to be structure A. Moreover, in order to know whether the linkage of C=O bond and tin atom is intra-molecular or inter-molecular [1], IR spectra of these compounds in CCl<sub>4</sub> were characterized. The result showed that the magnitude of Δ*v* 288–308 cm<sup>-1</sup> in CCl<sub>4</sub> is much greater than the magnitude of Δ*v* in KBr. The fact revealed that the structure of these compounds might be structure C, not be structure B. The magnitude of 239–279 cm<sup>-1</sup> for compounds **3–6** strongly indicates the carboxylate groups are not bidentate. The result in KBr is similar to that in CCl<sub>4</sub>. But the structures of these compounds are different from structure A. One obvious feature of the IR spectra in these compounds at 494–503 cm<sup>-1</sup> is the similarity of stretching band arising from Sn–N [13]. It is showed that N hetero atom on the pyridine group in carboxylate group coordinate to tin atom [14]. In CCl<sub>4</sub> solution, this band is not observed in compounds **5** and **6**. This indicates that the Sn ← N bond broke up for these compounds in CCl<sub>4</sub> solution. However, this difference is not observed for compounds **4**. So it is possible for compounds **5** and **6** to be structure D and E, and compound **4** to be structure F (see Scheme 3).

### 3.3. <sup>1</sup>H NMR Spectra

The <sup>1</sup>H NMR spectra of compounds **1–9** show that the chemical shifts of the protons on the benzyl group exhibit two signals about 6.81–7.25 ppm as multiplet and about 2.63–2.74 ppm as a triplet which is caused by the tin(<sup>119</sup>Sn) hydrogen coupling. And the spin–spin coupling constant *J*<sub>Sn–H</sub> is equal 69.86–78.04 Hz.

The chemical shift of the protons of heteroaromatic ring exhibit signals at 6.55–9.14 ppm as multiplet. In compounds **1–3**, **7–9**, this is similar to that of corresponding free heteroaromatic acid, but that of compounds **4–6** obviously increase in comparison with that of corresponding free heteroaromatic acid. This result may be consistent with previous conclusion. This suggest that

only pyridine type N atoms, present in the carboxylate R' group, coordinate to Sn, but there is no evidence of intra- or inter-molecular coordination to Sn by the S or O atoms of the thiophenyl and furanyl groups [10]. In addition, the presence of the N–H proton signal in the compounds 7–9 reveals the indolyl group's N atom does not coordinate to Sn.

### 3.4. X-ray crystal structures

Crystallographic data, together with refinement details are given in Table 1. Atom arrangement and numbering system for tri(*o*-fluorobenzyl)tin esters of 4-pyridinecarboxylic acid and 3-pyridinecarboxylic acid are shown in Figs. 1 and 2, respectively.

#### 3.4.1. Compound (5)

Tri(*o*-fluorobenzyl)tin ester of 4-pyridinecarboxylic acid possesses an unequivocally polymeric structure, but this structure differs from the  $\text{Cy}_3\text{SnO}_2\text{CC}_3\text{H}_7$  [15] and  $(\text{PhCH}_2)_3\text{SnO}_2\text{CCH}_3$  [16]. Each tin atom is rendered five-coordinate by coordinating with the nitrogen atom of 4-pyridine carboxylate group from an adjacent molecule. The tin atom is rendered a distorted trigonal bipyramidal type, surrounded axially by one oxygen atom, one nitrogen atom and equatorially by three  $\alpha$ -carbon atoms of the *o*-fluorobenzyl groups (see Fig. 1).

The intramolecular Sn(1)–O(1) bond length of 2.202(9) Å is longer than those of  $\{[\text{Bu}_2\text{Sn}(2\text{-pic})]_2\text{O}\}_2$  (2.0544 and 2.110 Å) [17] and  $(\text{PhCH}_2)_3\text{SnOO}_2\text{CC}_5\text{H}_4\text{N-4}$  (2.142 Å) [18], but is shorter than that of  $\text{Me}_3\text{SnO}_2\text{CC}_5\text{H}_4\text{N} \cdot \text{H}_2\text{O}$  (2.18 and 2.21 Å) [19]. The

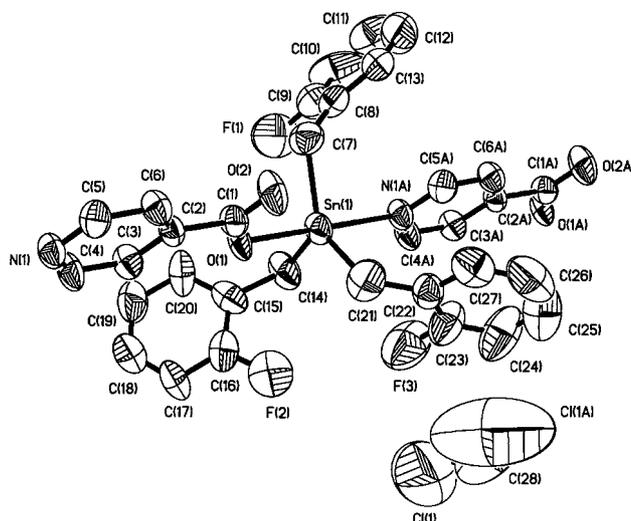


Fig. 1. Molecular structure of tri(*o*-fluorobenzyl)tin ester of 4-pyridinecarboxylic acid (5) Sn(1)–C(14), 2.151(9) Å; Sn(1)–C(21), 2.153(9) Å; Sn(1)–C(7), 2.166(10) Å; Sn(1)–O(1), 2.202(9) Å; Sn(1)–N(1A), 2.454(10) Å; Sn(1)–O(2), 3.252(9) Å; C(14)–Sn(1)–C(21), 116.6(4)°; C(14)–Sn(1)–C(7), 119.6(3)°; C(21)–Sn(1)–C(7), 123.8(3)°; C(14)–Sn(1)–O(1), 92.2(3)°; C(21)–Sn(1)–O(1), 89.0(3)°; C(7)–\*Sn(1)–O(1), 89.0(3)°; C(14)–Sn(1)–N(1A), 86.8(3)°; C(21)–Sn(1)–N(1A), 92.1(3)°; C(7)–Sn(1)–N(1A), 90.9(3)°; O(1)–Sn(1)–N(1A), 178.7(2)°; C(8)–C(7)–Sn(1), 120.7(6)°; C(1)–O(1)–Sn(1), 120.3(5)°; C(1)–O(2)–Sn(1), 69.5(5)°; C(15)–C(14)–Sn(1), 116.6(5)°; C(22)–C(21)–Sn(1), 120.6(7)°.

Sn(1)–O(2) distance of 3.252 Å is much greater than the sum of the van der Waals radii for Sn and O of 2.80 Å. It is shown that the O(2) atom does not make any significant contacts with the Sn(1) atom. The Sn(1)–N(1) distance, 2.454(10) Å is greater than the sum of the covalent radii of Sn and N (2.15 Å), but is considerably

Table 1  
Crystallographic data of compounds 5 and 6

	5	6
Molecular formula	$\text{C}_{27}\text{H}_{23}\text{ClF}_3\text{NO}_2\text{Sn}$	$\text{C}_{27}\text{H}_{22}\text{F}_3\text{NO}_2\text{Sn}$
Formula weight	610.61	568.15
Crystal system	Monoclinic	Orthorhombic
Space group	$C2/c$	$Pbca$
Unit cell dimensions		
<i>a</i> (Å)	2.793(9)	16.556(13)
<i>b</i> (Å)	9.67(3)	14.932(13)
<i>c</i> (Å)	21.78(7)	19.359(16)
$\beta$ (°)	117.60(5)	90
Volume (Å <sup>3</sup> )	5211(8)	4786(7)
<i>Z</i>	8	8
$D_{\text{cal}}$ (kg/cm <sup>3</sup> )	1.557	1.577
$F(000)$	2440	2272
Crystal size (mm)	0.30 × 0.12 × 0.06	0.30 × 0.2 × 0.08
Diffractometer	Bruker Smart-1000 CCD	Bruker Smart-1000 CCD
Scan range $\theta$ (°)	$2.65 \leq \theta \leq 25.02$	$2.10 \leq \theta \leq 25.03$
Index ranges	$-33 \leq h \leq 6, -10 \leq k \leq 10, -21 \leq l \leq 24$	$-19 \leq h \leq 17, -17 \leq k \leq 11, -23 \leq l \leq 20$
Total/unique/ $R_{\text{int}}$	6537/3611/0.0611	23847/4225/0.0654
$\mu$ (mm <sup>-1</sup> )	1.130	1.115
$R_1/wR_2$	0.0496/0.0856	0.0352/0.0910
Goodness-of-fit on $F^2$	0.827	0.912
$\rho_{\text{max}}/\rho_{\text{min}}$ (e · Å <sup>-3</sup> )	0.645/–0.420	0.972/–0.506

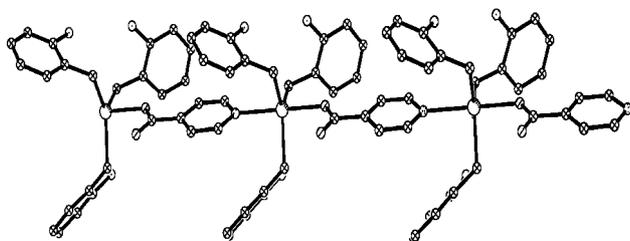


Fig. 2. One-dimensional chain network of tri(*o*-fluorobenzyl)tin ester of 4-pyridinecarboxylic acid (**5**).

less than the sum of the van der Waals radii (3.75 Å) [20] and should be considered as bonding interaction. In this connection it is relevant to note the Sn–N bond distances found in other crystal structures of organotin compounds containing the pyridine carboxylate ligand. In the polymer [Me<sub>2</sub>SnCl(2-pic)]<sub>n</sub> the two unique Sn–N bond distances are 2.50(3) and 2.47(2) Å [14], but in the

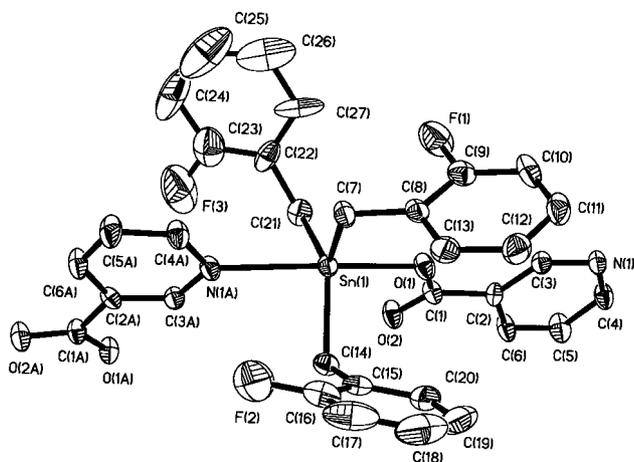


Fig. 3. Molecular structure of tri(*o*-fluorobenzyl)tin ester of 3-pyridinecarboxylic acid (**6**) Sn(1)–C(14), 2.157(6) Å; Sn(1)–C(21), 2.145(6) Å; Sn(1)–C(7), 2.159(6) Å; Sn(1)–O(1), 2.161(4) Å; Sn(1)–N(1A), 2.518(5) Å; Sn(1)–O(2), 3.031(5) Å; C(21)–Sn(1)–C(14), 131.0(2)°; C(21)–Sn(1)–C(7), 115.0(2)°; C(14)–Sn(1)–C(7), 112.6(2)°; C(21)–Sn(1)–O(1), 94.9(2)°; C(14)–Sn(1)–O(1), 92.4(2)°; O(1)–Sn(1)–N(1A), 176.58(14)°; C(8)–C(7)–Sn(1), 114.2(4)°; C(1)–O(1)–Sn(1), 114.0(4)°; C(1)–O(2)–Sn(1), 73.6(3)°; C(7)–Sn(1)–O(1), 94.40(18)°; C(21)–Sn(1)–N(1A), 83.6(2)°; C(14)–Sn(1)–N(1A), 86.4(2)°; C(7)–Sn(1)–N(1A), 89.02(19)°; C(15)–C(14)–Sn(1), 109.7(4)°; C(22)–C(21)–Sn(1), 114.8(4)°.

polymer [Me<sub>2</sub>Sn(2-pic)<sub>2</sub>]<sub>n</sub> the two Sn–N bond distances are 2.507(4) and 2.477(4) Å [9] and dicarboxylato tetraorganostannoxane {[<sup>n</sup>Bu<sub>2</sub>Sn(2-pic)]<sub>2</sub>O}<sub>2</sub> the two Sn–N bond distances are 2.550(5) and 3.150(5) Å [17]. In linear polymer (PhCH<sub>2</sub>)<sub>3</sub>SnOO<sub>2</sub>CC<sub>5</sub>H<sub>4</sub>N-4 the Sn–N distance is 2.563 Å [18].

The angles of C(14)–Sn(1)–O(1) [92.2(3)°], C(7)–Sn(1)–N(1A) [90.9(3)°] and C(21)–Sn(1)–N(1A) [92.1(3)°] are greater than 90°; In contrast, the angles of C(7)–Sn(1)–O(1) [89.0(3)°], C(21)–Sn(1)–O(1) [89.0(3)°] and C(14)–Sn(1)–N(1A) [86.8(3)°] are less than 90°. The angle O(1)–Sn(1)–N(1A) is 178.7(2)°, which deviates from linear angle 180°. These data indicate that tin atom is distorted pentagonal bipyramidal geometry.

### 3.4.2. Compound (6)

The structure of tri(*o*-fluorobenzyl)tin ester of 3-pyridinecarboxylic acid (**6**) is similar to tri(*o*-fluorobenzyl)tin ester of 4-pyridinecarboxylic acid (**5**). The coordination at the tin atom is also distorted trigonal bipyramidal, surrounded axially by one oxygen atom, one nitrogen atom and equatorially by three  $\alpha$ -carbon atoms of the *o*-fluorobenzyl groups (Fig. 4).

The intramolecular Sn(1)–O(1) bond length of 2.161(4) Å is longer than that of (PhCH<sub>2</sub>)<sub>3</sub>SnOO<sub>2</sub>CC<sub>5</sub>H<sub>4</sub>N-3 (2.132 Å) [21] but is shorter than those of Me<sub>3</sub>SnO<sub>2</sub>CC<sub>5</sub>H<sub>4</sub>N · H<sub>2</sub>O (2.18 and 2.21 Å) [19] and tri(*o*-fluorobenzyl)tin ester of 4-pyridinecarboxylic acid (**5**). The Sn(1)–N(1A) distance, 2.518(5) Å is greater than of tri(*o*-fluorobenzyl)tin ester of 4-pyridinecarboxylic acid (**5**), but is shorter than that of (PhCH<sub>2</sub>)<sub>3</sub>SnOO<sub>2</sub>CC<sub>5</sub>H<sub>4</sub>N-3 (2.640(2) Å) [21].

The distortions from true trigonal bipyramidal symmetry are reflected in the interatomic angles. The angles of C(14)–Sn(1)–O(1) [94.9(2)°], C(14)–Sn(1)–O(1) [92.4(2)°], C(7)–Sn(1)–O(1) [94.40(18)°], are greater than 90°. In contrast, the angles of C(21)–Sn(1)–N(1A) [83.6(2)°], C(14)–Sn(1)–N(1A) [86.4(2)°], C(7)–Sn(1)–N(1A) [89.02(19)°] are less than 90°. So on the side of the Sn–O bond the *o*-fluorobenzyl groups are moved away from carboxylate group. The angle of O(1)–Sn(1)–N(1A) [176.58(14)°] is less than angle of O(1)–Sn(1)–N(1) [177.7(3)°] in compound [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnO<sub>2</sub>CC<sub>8</sub>H<sub>6</sub>N-4] [22] and the angle in tri(*o*-fluorobenzyl)tin ester of 4-pyridinecarboxylic acid

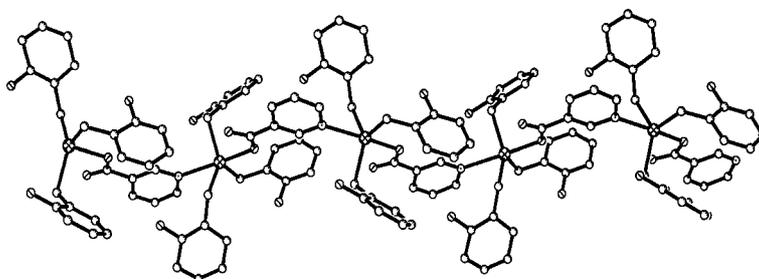


Fig. 4. One-dimensional chain network of tri(*o*-fluorobenzyl)tin ester of 3-pyridinecarboxylic acid (**6**).

(5). These data indicate that tin atom is also distorted pentagonal bipyramidal geometry.

As can be seen from Fig. 3, the nitrogen atom of 3-pyridinyl carboxylate groups coordinates to tin in the crystal lattice. This is different from the compound  $\{[{}^n\text{Bu}_2\text{Sn}(2\text{-pic})]_2\text{O}\}_2$  [17] in which the nitrogen atom of pyridine group coordinate to tin atom by intra-molecular interaction.

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 220121 for compound **5** and CCDC No. 220123 for compound **6**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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