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Synthesis and characterization of triphenyltin esters of heteroaromatic carboxylic acids and the crystal structure of $[Ph_3SnO_2CC_5H_4N \cdot 0.5H_2O]_{\infty}$

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Abstract

The reaction of triphenyltin hydroxide with 2-furanyl, 2-furanvingl, 2-(5-terbutyl) furanyl, 2-(5-benzoyl) furanyl, 2-pyridinyl, 4pyridinyl, 3-indolyl, 3-indolethyl, 3-indolethyl and 3-indolpropyl carboxylates in 1:1 stoichiometry yields triphenyltin esters of heteroaromatic carboxylic acids Ph_3SnO_2CR . All compounds are characterized by elemental analysis, IR and ¹H NMR. The crystal structure of the triphenyltin ester of 4-pyridinyl carboxylic acid (6) is determined by single crystal X-ray diffraction. In compound (6), the tin atom is rendered five-coordinate in a trigonal bipyramidal structure by coordinating with the 4-pyridinyl carboxlate group. The resulting structure is a linear polymer containing Sn–O bond lengths of 0.2160(5)–0.2166(5) nm and Sn–N bond lengths of 0.2512(6)–0.2612(6) nm.

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Keywords: Heteroaromatic carboxylic acid; Triphenyltin; 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 antitumor 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 an additional donor atom (e.g., N, O or S) that are available for coordinating to the 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 triorganotin compounds derived

from 2-furanyl, 2-furanvingl, 2-(5-terbutyl)furanyl, 2-(5-benzoyl)furanyl, 2-pyridinyl, 4-pyridinyl, 3-indolyl, 3-indolmethyl, 3-indolethyl and 3-indolpropyl carboxylic acids and determined the crystal structure of $[Ph_3SnO_2-CC_5H_4N\cdot0.5H_2O]_{\infty}$. The results of these studies are reported herein.

2. Experimental

2.1. General procedures

All reactants were reagent grade. Infrared spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs. ¹H NMR spectra were obtained on Mercury Plus-400 NMR spectrometer, chemical shifts are given in parts per million relative to Me₄Si in CDCl₃ solvent. Elemental analyses were performed with a PE-2400 II elemental apparatus. Tin was estimated as SnO₂. X-ray measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo K α (0.071073 nm) radiation.

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2.2. Synthesis of triphenyltin esters of heteroaromatic carboxylic acids

Heteroaromatic carboxylic acids (1.2 mmol) were added to a benzene solution of Ph_3SnOH (1.0 mmol). Then the mixture was refluxed for 5 h, with water formed during the reaction being removed azeotropically with a Dean and Stark apparatus. The clear solution obtained after filtration was evaporated in vacuum to give a white solid. The products were recrystallized from acetone–hexane to give colorless crystals (see Scheme 1 for compounds R).

 $Ph_3SnOH + RCOOH \rightarrow Ph_3SnOOCR$

2.3. Crystallographic measurements of $Ph_3SnO_2CC_5H_4$ -N-4 \cdot 0.5 H_2O

A colorless crystal having approximate dimensions of 0.50 mm × 0.50 mm × 0.20 mm was mounted on a glass capillary. All measurements were made on a Bruker Smart 1000 CCD diffractometer with graphite monochromated Mo K α (0.071073 nm) radiation. The data were collected at room temperature (298±2 K) using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 52.9°. The crystal structure belongs to orthorhombic crystal system, with space group $P2_12_12$, a = 1.4882(3), b = 2.3802(5), c = 1.2366(2) nm, $\alpha = \beta = \gamma = 90^\circ$, Z = 4, V = 4.3805(15) nm³, $D_c = 1.459$ g/cm³, $\mu = 1.187$ mm⁻¹, F(000) = 1928. The structure was solved by direct method and differential Fourier map using the SHELXL-97 program, and refined by full-ma-

trix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. The weighting scheme was $w = 1/[s^2(F_o^2) + (0.0720P)^2 + 0.0000P]$, $p = (F_o^2 + 2F_c^2)/3$. The refinement was converged to the final R = 0.0540, wR = 0.1237, $(\Delta/\sigma)_{max} = 0.001$ and S = 0.999. In the final difference map, the residuals are 1.074 and -1.238 e/Å³.

3. Results and discussion

3.1. Physical properties

Physical data for compounds 1-10 are listed in Table 1. All compounds are colorless crystals. They are soluble in many organic solvents such as CCl₄, CHCl₃, C₆H₆, (CH₃)₂CO, but are insoluble in hexane, petroleum ether and water.

3.2. Analyses of spectroscopies

3.2.1. IR spectra

The characteristic IR spectral data of compounds 1– 10 are shown in Table 2. The assignment of IR bands of these compounds has been determined by a comparison with the IR spectra of related organotin compounds, carboxylates and Ph₃SnOH. It is worth noting that the difference Δv between $v^{as}(COO)$ and $v^{s}(COO)$ is important because these frequencies can be used to determine the type of bonding between the metal and carboxylate ligand [1,12]. Generally triorganotin esters of carboxylic

$$R = \bigvee_{O} 1, \bigvee_{O} CH=CH-2, \underset{t-Bu}{\longrightarrow} 0 3, \underset{PhCO}{\longrightarrow} 4, \bigvee_{N} 5, \underset{N}{\longrightarrow} 6,$$

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Table 1						
Physical	and	analytical	data	of	compounds	1-10

Compound	Yield (%)	M.p. (°C)	Found (Calc.)%				
			С	Н	Ν	Sn	
1	90	102-104	59.68(59.91)	3.87(3.93)		25.79(25.74)	
2	88	120-122	61.75(61.64)	4.21(4.14)		24.55(24.37)	
3	76	93–95	62.91(62.70)	5.16(5.07)		22.80(22.95)	
4	67	74–76	63.97(63.75)	4.05(3.92)		21.24(21.00)	
5	87	151-152	61.28(61.06)	4.12(4.06)	2.90(2.97)	25.33(25.14)	
6	81	210-212	59.58(59.92)	4.22(4.19)	2.87(2.91)	24.33(24.67)	
7	92	134–135	63.41(63.57)	4.17(4.15)	2.70(2.75)	23.34(23.27)	
8	87	123-125	64.00(64.16)	4.39(4.42)	2.73(2.67)	22.85(22.64)	
9	93	110-112	62.91(62.62)	4.92(4.89)	2.47(2.52)	21.21(21.34)	
10	80	84-85	65.09(65.25)	5.17(4.93)	2.62(2.54)	21.65(21.49)	

Table 2 IR data (cm⁻¹) of compounds 1–10

Compound	v(C–H) (aryl)	v ^{as} (COO)	v ^s (COO)	v(Sn–C)	v(Sn–N) or (N–H)	v(Sn–O)
1	3057w	1541s(1650)	1371s(1357)	562w		453w
2	3050w	1591s(1648)	1401s(1340)	545w		447w
3	3051w	1594s(1650)	1395s(1346)	559w		450m
4	3058m	1654(1657)	1343(1347)	547w		442w
5	3065w	1631s(1639)	1354s(1347)	557w	484w(489)	453w
6	3060w	1658s(1656)	1355s(1352)	552w	483w	460w
7	3052m	1593s(1652)	1396s(1355)	556w	3423s	443w
8	3057w	1588s(1649)	1401s(1340)	554w	3425s	438w
9	3061m	1590s(1646)	1405s(1354)	558w	3423s	435w
10	3054m	1586s(1640)	1400s(1341)	545w	3426s	443m

The parentheses give the vibration of compounds in CCl₄.



acid adopt three types of structures in the solid state (as shown in Scheme 2).

The magnitude of $\Delta v [v^{as}(COO) - v^{s}(COO)]$ of 170–199 cm^{-1} for compounds 1–3 and 7–10 is approximately equal to that for the corresponding sodium salt of the carboxylic acids. This information indicates the presence of bidentate carboxylate groups [1-4]. So it is impossible for these compounds to be structure A. The IR spectra of these compounds in CCl₄ are also studied in order to find out whether the ligand linkage of the C=O bond to the tin atom is intra-molecular or inter-molecular [1,13]. Because in solution the inter-molecular bond of a fivecoordinated organotin polymer which belongs to structure C is destroyed, the polymeric structure is decomposed into mono-molecules and as a result, the Δv value increases greatly [14,15]. However, the Δv value for compounds with structure **B** and structure **A** do not change obviously when they are determined in solvent [14]. The results showed that the magnitude of Δv 292– 308 cm^{-1} in CCl₄ is much greater than that in KBr for compounds 1-3 and 7-10 (shown in Table 2). This fact reveals that the structure of these compounds might be structure C, not be structure B. The magnitude of 277– 311 cm⁻¹ for compounds **4–6** strongly indicates the unidentate bonding of the carboxylate groups, and the result in KBr is similar to that in CCl₄. But the structures of compounds 5 and 6 are different from structure A. One obvious feature of the IR spectra in the compounds at 484 and 483 cm⁻¹ is the similarity of the stretching band arising from Sn-N [15]. Because the inter-molecular bond of $Sn \leftarrow N$ will break in solvent, while the intra-molecular bond of $Sn \leftarrow N$ is not influenced basically by solvent [14], whether $Sn \leftarrow N$ of an

organotin compound is inter-molecular or intra-molecular may be deduced. It is shown that the N hetero atom on the pyridine group in the carboxylate group coordinates to the tin atom [15]. In CCl₄ solution, this band is not observed in compound **6**. This indicates that the Sn \leftarrow N bond breaks up for the compound in CCl₄ solution, Thus it is proved that compound **6** contains an inter-molecular Sn \leftarrow N bond and exists as a polymer [15]. However, this difference is not observed for compound **5**. Since the intra-molecular coordination bond is not influenced by solvent [14], the Sn \leftarrow N bond existing in the compound with structure **E** can also be observed in solution. So it is possible for compound **6** to be structure **D** and compound **5** to be structure **E** [15] (see Scheme 3).

3.2.2. ¹H NMR spectra

The ¹H NMR spectra of compounds 1-10 are given in Table 3. It is shown that the chemical shifts of the protons on the phenyl groups of compounds 1-10 exhibit signals at about 7.21–7.68 ppm as multiplets.

The chemical shifts of the protons of heteroaromatic rings of compounds 1–10 exhibit signals in the range 6.10-8.82 ppm as multiplets (see Table 3). In compounds 1–4 and 7–10, they are similar to that of the corresponding free heteroaromatic acid but in compounds 5 and 6 they obviously increase to be higher values than that of the corresponding free heteroaromatic acid. This finding may be consistent with previous studies that suggest that only pyridine type N atoms, present in the carboxylate R' group, coordinate to Sn, and there is no evidence of intra- or inter-molecular coordination to Sn by the O atoms of furanyl groups



Table 3				
¹ H NMR	data	(ppm) for	compounds	1 - 10

Compound	¹ H NMR
1	7.25-7.68 (16H, m, Ph-H, 5-furan-H), 7.11 (1H, d, 3-furan-H), 6.53 (1H, d, 4-furan-H)
2	7.19–7.65 (17H, m, Ph-H, 5-furan-H, C=CHCO ₂), 6.91 (1H, d, 3-furan-H), 6.64 (1H, d, 4-furan-H), 6.38 (1H, d, C=CHAr)
3	7.21–7.67 (15H, m, Ph-H,), 6.10 (1H, d, 3-furan-H), 7.87 (1H, d, 4-furan-H), 1.33 (9H, s, CH ₃)
4	7.94 (2H, br, 2,3-furan-H), 7.20–7.64 (20H, m, Ph-H)
5	8.21 (1H, br, 3-pyridine-H), 7.90 (1H, d, 6-pyridine-H), 7.51 (1H, d, 4-pyridine-H), 7.24–7.69 (16H, m, Ph-H, 5-pyridine-H)
6	8.82 (2H, d, 2,6-pyridine-H), 7.84 (2H, d, 3,5-pyridine-H), 7.35–7.75 (15H, m, Ph-H)
7	8.02 (1H, s, N-H), 7.21-7.67 (16H, m, Ph-H, 2-indole-H), 6.84-7.18 (4H, m, indole-H)
8	8.00 (1H, s, N-H), 7.22-7.62 (16H,m, Ph-H, 2-indole-H), 6.78-7.17 (4H, m, indole-H), 3.62 (2H, s, ArCH ₂ CO ₂)
9	7.95 (1H, s, N-H), 7.23-7.66 (16H, m, Ph-H, 2-indole-H), 6.72-7.20 (4H, m, indole-H), 2.91 (2H, br, CH ₂ CO ₂), 2.23 (2H, br,
	ArCH ₂)
10	7.97 (1H, s, N-H), 7.21-7.69 (16H, m, Ph-H, 2-indole-H), 6.75-7.18 (4H, m, indole-H), 2.72 (2H, t, CH ₂ CO ₂), 2.05 (2H, t,
	ArCH ₂), 1.52 (2H, m, CH ₂)

[10]. In addition, the presence of the N–H proton signal in the spectra of compounds 7–10 supports that the indolyl group N atom is not coordinated to the Sn atom.

3.2.3. X-ray crystal structure of $Ph_3SnO_2CC_5H_4N-4 \cdot 0.5H_2O(6)$

Selected bond distances and angles are listed in Table 4. The molecular structure is shown in Fig. 1. Fig. 2 shows the packing of the molecules in the unit cell as seen in a projection onto its face.

In $[Ph_3SnO_2CC_5H_4N \cdot 0.5H_2O]_{\infty}$ 6, two kinds of tin atoms with different chemical environments can be found. Each molecule of compound 6 in the unit cell possesses an unequivocally polymeric structure, but this structure differs from the tributyltin 2-(5-*tert*butyl) furanylcarboxylate [8] and tribenzyltin 2-(5-*tert*butyl)furanylcarboxylate [8]. Each tin atom is rendered five-coordinate in a trigonal bipyramidal structure by coordination of the nitrogen atom from a 4-pyridinyl carboxylate group from an adjacent molecule. The central tin atoms are surrounded axially by one oxygen atom and one nitrogen atom, and equatorially by three carbon atoms of the phenyl groups. The intra-molecular Sn(1)-O(1) and Sn(2)-O(3) bond distances are 0.2166(5) and 0.2160(5) nm, which are longer than that in $\{[^{n}Bu_{2}Sn(2-pic)]_{2}O\}_{2}$ [7] (0.20544 and 0.2110 nm), but are shorter than those in $Me_3SnO_2CC_5H_4N \cdot H_2O$ (0.218 and 0.221 nm) [16]. The Sn(1)-O(2) and Sn(2)-O(4) distances are 0.3237 and 0.3311 nm, which are much greater than the sum of the van der Waals radii for Sn and O of 0.280 nm. It is shown that the O(2) and O(4) atoms do not make any significant contacts with the Sn atom. The Sn(1)-N(2) and Sn(2)-N(1)#1 distances, 0.2512(6) and 0.26612(6) nm, are greater than the sum of the covalent radii of Sn and N (0.215 nm), but are considerably less than the sum of the van der

Table 4 Selected bond distances (nm) and angles (°) for compound **6**

Bond distances					
Sn(1)–O(1)	0.2166(5)	Sn(1)-N(2)	0.2512(6)	Sn(1)–C(19)	0.2129(8)
Sn(2)–N(1)#1	0.26612(6)	Sn(1)-C(7)	0.2142(9)	Sn(2)–C(37)	0.2130(7)
Sn(1)-C(13)	0.2125(8)	Sn(2)–C(31)	0.2125(8)	Sn(2)–O(3)	0.2160(5)
Sn(2)–C(43)	0.2115(8)	O(2)–C(1)	0.1208(10)	O(3)–C(25)	0.1245(9)
O(1)–C(1)	0.1276(10)	N(1)–C(4)	0.1338(11)	N(1)–C(5)	0.1300(10)
O(4)–C(25)	0.1206(9)	N(2)-C(28)	0.1336(10)	N(2)–C(29)	0.1289(9)
Pond angles					
$C(12)$ $S_{\pi}(1)$ $C(7)$	120.2(4)	C(12) = C(10)	115 0(4)	$C(7) = S_{22}(1) - C(10)$	124.0(2)
C(13) = Sn(1) = C(7)	120.2(4)	C(13) = Sn(1) = C(19)	115.0(4)	C(7) = SII(1) = C(19)	124.0(3)
C(13) - Sn(1) - O(1)	96.2(3)	C(7) - Sn(1) - O(1)	93.2(3)	C(19) - Sn(1) - O(1)	89.9(3)
C(13)-Sn(1)-N(2)	88.0(2)	C(19)–Sn(1)–N(2)	88.2(3)	C(7)-Sn(1)-N(2)	84.9(3)
O(1)-Sn(1)-N(2)	175.8(2)	C(37)–Sn(2)–O(3)	88.4(2)	C(43)–Sn(2)–O(3)	99.5(3)
C(31)-Sn(2)-N(1)#1	84.5(2)	C(37)-Sn(2)-N(1)#1	84.8(2)	C(43)-Sn(2)-N(1)#1	84.4(3)
O(3)-Sn(2)-N(1)#1	173.1(2)	C(31)–Sn(2)–O(3)	97.8(3)	C(28)-N(2)-Sn(1)	119.8(5)
C(1)-O(1)-Sn(1)	120.9(5)	C(29)-N(2)-Sn(1)	124.7(5)	C(12)-C(7)-Sn(1)	123.4(7)
C(8)-C(7)-Sn(1)	120.1(7)	C(14)-C(13)-Sn(1)	119.2(8)	C(18)-C(13)-Sn(1)	124.0(9)
C(24)-C(19)-Sn(1)	126.8(8)	C(20)-C(19)-Sn(1)	116.8(6)	C(36)–C(31)–Sn(2)	116.9(6)
C(32)-C(31)-Sn(2)	124.0(6)	C(25)–O(3)–Sn(2)	115.1(5)	C(42)-C(37)-Sn(2)	120.9(7)
C(44)-C(43)-Sn(2)	123.0(6)	C(38)–C(37)–Sn(2)	120.9(6)	C(4)-N(1)-C(5)	116.7(7)
C(48)-C(43)-Sn(2)	120.4(6)	O(2)–C(1)–O(1)	127.1(8)	O(1)-C(1)-C(2)	113.9(7)
N(1)-C(4)-C(3)	123.6(8)	N(1)-C(5)-C(6)	124.0(8)	O(2)-C(1)-C(2)	118.9(8)



Fig. 1. The molecular structure of compound 6.



Fig. 2. Projection of compound 6.

Waals radii (0.375 nm) [17] and should be considered as bonding interactions. In this connection it is relevant to note the Sn-N bond distances found in three other crystal structures of organotin compounds containing the pyridine carboxylate ligand. In polymeric $[Me_2SnCl(2-pic)]_n$ [18] the two unique Sn–N bond distances are 0.250(3) and 0.247(2) nm, in polymeric $[Me_2Sn(2-pic)_2]_n$ [9] the two Sn–N bond distances are 0.2507(4) and 0.2477(4) nm and in dicarboxylato tetraorganostannoxane $\{ [^{n}Bu_{2}Sn(2-pic)]_{2}O \}_{2}$ [7] the two Sn-N bond distances are 0.2550(5) and 0.3150(5) nm. In compound 6, the distortions from true trigonal bipyramidal symmetry are reflected in the interatomic angles. For instance around the Sn(1) atom of compound 6 the angles of C(7)–Sn(1)–O(1) 93.2(3)°, C(13)–Sn(1)–O(1) 96.2(3)°, C(19)–Sn(1)–O(1) 89.9(3)°, C(7)–Sn(1)–N(2) 84.9(3)°, C(13)-Sn(1)-N(2) 88.0(2)°, C(19)-Sn(1)-N(2)

 $88.2(3)^\circ$, all are not 90° , and only one approximates to 90° . The angle of O(1)–Sn(1)–N(2), 175.8(2)°, shows that the atoms O(1), Sn(1) and N(2) are nearly linear. The Sn(2) atom is similar to the Sn(1) atom and it has a distorted trigonal bipyramidal structure too.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 200373 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, or www: http://www.ccdc.cam.ac.uk).

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