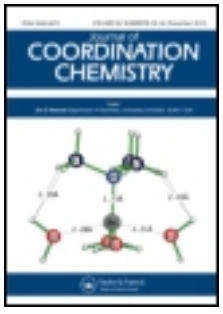

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Syntheses, characterizations, crystal structures, and in vitro antitumor activities of chiral triorganotin(IV) complexes containing (S)-(+)-2-(4-isobutyl-phenyl)propionic and (R)-(+)-2-(4-hydroxyphenoxy)propionic acid ligands

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Syntheses, characterizations, crystal structures, and *in vitro* antitumor activities of chiral triorganotin(IV) complexes containing (S)-(+)-2-(4-isobutyl-phenyl)propionic and (R)-(+)-2-(4-hydroxyphenoxy)propionic acid ligands

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Four new chiral triorganotin(IV) carboxylates, $[(R_3Sn)(O_2C_{13}H_{17})]_n$ (R = Me **1**, Ph **2**), $[(R_3Sn)(O_2C_{13}H_{17})]$ (R = *n*-Bu **3**), and $[(R_3Sn)(O_4C_9H_9)]_n$ (R = Me **4**), have been synthesized by reaction of (S)-(+)-2-(4-isobutyl-phenyl)propionic acid and (R)-(+)-2-(4hydroxyphenoxy)propionic acid with triorganotin(IV) chloride in the presence of sodium ethoxide. The complexes have been characterized by elemental analyses, FT-IR, NMR (^{1}H, ^{13}C, and ^{119}Sn) spectra, and X-ray crystallography diffraction analyses. Structural analyses show that **1** has a 1-D infinite chiral zigzag chain structure. Complexes **2** and **4** have a 1-D spring-like chiral helical chain with a channel, while **3** is a monomer. Antitumor activities of **1**–**4** have been studied.

Keywords: Triorganotin(IV) complexes; Chiral; (S)-(+)-2-(4-Isobutyl-phenyl)propionic acid; (R)-(+)-2-(4-Hydroxyphenoxy)propionic acid; Anticancer activity

1. Introduction

Organotin carboxylates have versatile molecular structures both in the solid state and in solution, such as monomers, dimers, tetramers, oligomeric ladders, and hexameric drums. [1–5], and are reported to exhibit good bactericidal and antitumor activities [6–10]. However, the biochemical activity of organotin(IV) complexes is influenced greatly by the structure of the molecule and the coordination number of tin [11, 12].

A variety of organotin carboxylates have been synthesized [8], but chiral organotin carboxylates have received little attention. Our recent efforts have focused on preparation of chiral organotin complexes; we selected chiral (S)-(+)-2-(4-isobutyl-phenyl)propionic acid and (R)-(+)-2-(4-hydroxyphenoxy)propionic acid as bridging ligands and obtained four new chiral triorganotin complexes. Here, we report the

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syntheses, characterizations, crystal structures, and antitumor activities of these new chiral organotin(IV) carboxylates.

2. Experimental

2.1. *Materials and measurements*

Trimethyltin chloride, triphenyltin chloride, tri-*n*-butyltin chloride, (S)-(+)-2-(4-isobutyl-phenyl)propionic acid, and (R)-(+)-2-(4-hydroxyphenoxy)propionic acid were purchased from Alfa Aesar. Melting points were obtained with a Kofler micro-melting point apparatus and are uncorrected. Elemental analyses were performed with a PE-2400II apparatus. Infrared (IR) spectra were recorded with a Nicolet-5700 spectrometer using KBr discs and NaCl optics. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded with a Varian Mercury Plus 400 spectrometer operating at 400, 100.6, and 149.2 MHz, respectively. The spectra were acquired at room temperature (298 K), unless otherwise specified. ^{13}C NMR spectra are broadband proton-decoupled. 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 and to neat tetramethyltin for ^{119}Sn NMR.

2.2. *Synthesis of 1*

The (S)-(+)-2-(4-isobutyl-phenyl)propionic acid (0.206 g, 1 mmol) and the sodium ethoxide (0.068 g, 1 mmol) were added to the solution of benzene (30 mL) in a Schlenk flask and stirred for 30 min. Then trimethyltin chloride (0.199 g, 1 mmol) was added, the reaction mixture was stirred for 12 h at 45°C, filtered and the solvent of the filtrate gradually removed by evaporation under vacuum until solid product was obtained. The solid was recrystallized from diethyl ether and a transparent colorless crystal formed. Yield: 73%; m.p. 120–123°C. Anal. Calcd for $C_{16}H_{26}O_2Sn$ (%): C, 52.07; H, 7.10. Found (%): C, 52.36; H, 7.32. IR (KBr, cm^{-1}): $\nu(COO)_{as}$ 1561, $\nu(COO)_s$ 1363, ν(Sn–C) 550, ν(Sn–O) 431. ^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.06$–7.21 (m, 4H, Ph–H), 3.67 (q, 1H, CH–COO), 2.44 (d, 2H, CH_2), 1.84 (m, 1H, CH), 1.46 (d, 3H, CH_3), 0.88 (d, 6H, CH_3), 0.49 (s, 9H, CH_3–Sn, $^{2}J_{Sn-H} = 69.5$ Hz). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 180.16$ (COO), 139.85, 139.13, 129.03, 126.98 (Ph–C), 44.97 (CH–COO), 45.65, 30.06, 22.29 (*i*–Bu–C), 19.42 ($\underline{C}H_3$ –CH), −2.59 (CH_3–Sn, $^{1}J_{Sn-C} = 496.4$ Hz). ^{119}Sn NMR ($CDCl_3$, ppm): −167.15.

2.3. *Synthesis of 2*

The procedure is similar to that of **1** using (S)-(+)-2-(4-isobutyl-phenyl)propionic acid (0.206 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), and triphenyltin chloride (0.385 g, 1 mmol). Recrystallizing from ether, transparent colorless crystals formed. Yield: 80%; m.p. 72–75°C. Anal. Calcd for $C_{31}H_{32}O_2Sn$ (%): C, 67.05; H, 5.81. Found (%): C, 67.36; H, 5.56. IR (KBr, cm^{-1}): $\nu(COO)_{as}$ 1573, $\nu(COO)_s$ 1359, ν(Sn–C) 550, ν(Sn–O) 457. ^{1}H NMR $CDCl_3$, ppm): $\delta = 7.01$–7.64 (m, 19H, Ph–H), 3.82 (q, 1H, CH–COO),

2.43 (d, 2H, CH_2), 1.81 (m, 1H, CH), 1.48 (d, 3H, CH_3), 0.87 (d, 6H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 180.01$ (COO), 138.22, 136.72, 129.98, 129.10, 128.76, 127.28 (Ph–C), 45.01 (CH–COO), 45.18, 30.17, 22.37 (*i*–Bu–C), 19.18 ($\underline{C}H_3$–CH). ^{119}Sn NMR ($CDCl_3$, ppm): −137.50.

2.4. *Synthesis of 3*

The procedure is similar to that of **1** using (S)-(+)-2-(4-isobutyl-phenyl)propionic acid (0.206 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), and tri-*n*-butyltin chloride (0.325 g, 1 mmol). Recrystallizing from ether, transparent colorless crystals formed. Yield: 79%; m.p. 154–156°C. Anal. Calcd for $C_{25}H_{44}O_2Sn$ (%): C, 60.62; H, 8.95. Found (%): C, 60.95; H, 8.69. IR (KBr, cm^{-1}): $\nu(COO)_{as}$ 1563, $\nu(COO)_s$ 1290, ν(Sn–C) 548, ν(Sn–O) 427. ^1H NMR ($CDCl_3$, ppm): $\delta = 7.07$–7.24 (m, 4H, Ph–H), 3.69 (q, 1H, CH–COO), 2.43 (d, 2H, CH_2), 1.83 (m, 1H, CH), 1.45 (d, 3H, CH_3), 1.19–1.28 (m, 18H, CH_2), 0.88 (m, 15H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 180.02$ (COO), 139.81, 139.29, 128.97, 127.07 (Ph–C), 45.12 (CH–COO), 45.87, 30.14, 22.34 (*i*–Bu–C), 19.17 ($\underline{C}H_3$–CH), 27.69, 26.98, 16.35, 13.59 (Bu–C). ^{119}Sn NMR ($CDCl_3$, ppm): −149.03.

2.5. *Synthesis of 4*

The procedure is similar to that of **1** using (R)-(+)-2-(4-hydroxyphenoxy)propionic acid (0.182 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol), and trimethyltin chloride (0.199 g, 1 mmol). Recrystallizing from ether, transparent colorless crystals formed. Yield: 77%; m.p. 177–179°C. Anal. Calcd for $C_{12}H_{18}O_4Sn$ (%): C, 41.78; H, 5.26. Found (%): C, 41.50; H, 5.58. IR (KBr, cm^{-1}): $\nu(COO)_{as}$ 1598, $\nu(COO)_s$ 1365, ν(Sn–C) 547, ν(Sn–O) 449, ν(O–H) 3575, δ(O–H) 1633. ^1H NMR ($CDCl_3$, ppm): $\delta = 6.58$–7.31 (m, 4H, Ar–H), 4.57 (q, 1H, CH), 1.55 (d, 3H, CH_3–CH), 5.10 (s, 1H, –OH), 0.52 (s, 9H, CH_3–Sn, $^2J_{Sn-H} = 68.8$ Hz). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 177.39$ (COO), 150.98, 136.83, 119.81, 115.78 (Ph–C), 73.84 (CH), 18.80 (CH_3). −1.55 (CH_3–Sn, $^1J_{Sn-C} = 488.5$ Hz). ^{119}Sn NMR ($CDCl_3$, ppm): −100.24.

2.6. *X-ray crystallographic studies*

Diffraction data were collected on a Smart CCD area-detector with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). 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 listed in table 1.

2.7. *Cell lines and culture conditions*

Human liver cancer cell line (SMMC-7721) and human breast cell line (MCF-7) were used for screening. Cell lines were maintained in the logarithmic phase at 37°C in a 5% carbon dioxide atmosphere using the following culture media containing 10% fetal

Table 1. Crystal, data collection, and structure refinement parameters for **1–4**.

Complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{16}H_{26}O_2Sn$	$C_{31}H_{32}O_2Sn$	$C_{25}H_{44}O_2Sn$	$C_{12}H_{18}O_4Sn$
Formula weight	369.06	555.26	495.29	344.95
Temperature (K)	298(2)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Tetragonal	Monoclinic	Orthorhombic
Space group	*p*21	*p*43	*p*21/*n*	*p*212121
Unit cell dimensions (Å, °)				
a	6.5542(5)	12.8058(15)	15.376(14)	6.721(6)
b	10.0132(11)	12.8058(15)	10.422(10)	11.2930(12)
c	13.9896(13)	17.1366(18)	17.409(16)	18.8513(15)
α	90	90	90	90
β	95.7990(10)	90	101.188(16)	90
γ	90	90	90	90
Volume (Å^3), *Z*	913.42(15), 2	2810.2(6), 4	2737(4), 4	1430.9(13), 4
Calculated density (Mg m^{-3})	1.342	1.312	1.202	1.601
Absorption coefficient (mm^{-1})	1.396	0.933	0.949	1.786
F(000)	376	1136	1040	688
Crystal size (mm^3)	0.48 × 0.36 × 0.35	0.41 × 0.16 × 0.12	0.42 × 0.19 × 0.11	0.40 × 0.30 × 0.19
θ range for data collection (°)	1.46–25.02	2.25–25.01	2.38–25.02	2.81–25.02
Reflection collected	4536	12,822	13,600	5751
Unique reflection	2991 [*R*(int) = 0.0252]	4932 [*R*(int) = 0.0822]	4820 [*R*(int) = 0.2360]	2507 [*R*(int) = 0.1643]
Data/restraints/parameters	5561/1/433	4932/621/310	4820/576/247	2507/0/158
Goodness-of-fit on F^2	0.923	1.211	1.093	1.047
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0369$, $wR_2 = 0.1025$	$R_1 = 0.0703$, wR2 = 0.1284	$R_1 = 0.2074$, $wR_2 = 0.4515$	$R_1 = 0.0936$, $wR_2 = 0.2014$
R indices (all data)	$R_1 = 0.0503$, $wR_2 = 0.1247$	$R_1 = 0.1380$, $wR_2 = 0.1409$	$R_1 = 0.3731$, $wR_2 = 0.5507$	$R_1 = 0.1445$, $wR_2 = 0.2419$

bovine serum and 1% antibiotics (50 units mL^{-1} penicillin and 50 μg mL^{-1} streptomycin): RPMI-1640 medium for SMMC-7721 and MCF-7 cells.

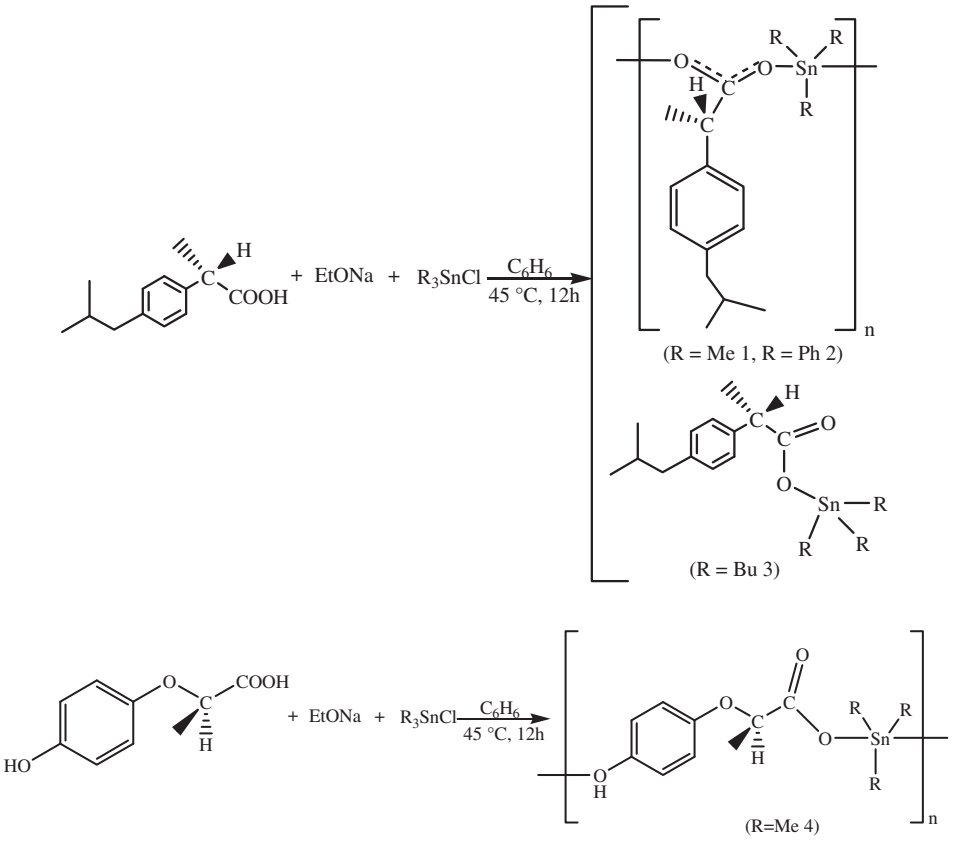
3. Results and discussion

3.1. *Syntheses*

The syntheses of **1–4** are given in scheme 1.

3.2. *Spectral characterization*

By comparing IR spectra of the free ligands with those of the complexes, the stretch of carboxylic O–H disappears, supporting deprotonation of the ligands during coordination. The appearance of new bands at 427–457 cm^{-1}, assigned to ν(Sn–O), supports the bonding of oxygen to tin. These values are consistent with a number of organotin(IV) derivatives [13–15]. IR spectroscopy can provide useful information relating to bond formation through carboxylates in organotin carboxylates [16, 17], distinguishing the



Scheme 1. The syntheses of **1–4**.

coordination mode of $-CO_2$ group. The $\Delta\nu$ ($\Delta\nu = \nu_{as}(COO) - \nu_s(COO)$) for **1** and **2** (198 cm^{-1} and 214 cm^{-1}), while **3** and **4** (273 cm^{-1} and 233 cm^{-1}), compared with those for the corresponding sodium salts, reveal bidentate carboxylates in **1** and **2**, while **3** and **4** are monodentate. The conclusions are consistent with the X-ray crystallography study.

The ^1H NMR spectrum of the complexes shows that the signal for –OH in the spectrum of the ligand is absent, indicating removal of –OH and formation of Sn–O in all the complexes, consistent with the IR data. In ^{13}C NMR spectra, the position of the carboxylate carbon moved to lower field, as compared with the free ligands, indicating participation of carboxylate in coordination to tin [18].

The ^{119}Sn NMR spectra of the complexes show resonances between $\delta = -100.24$ and $\delta = -167.15$. As reported [19], δ values for ^{119}Sn NMR spectra at -210 to -400, -90 to -190, and 200 to -60 ppm have been associated with six-, five-, and four-coordinate tin, respectively. Thus, **1–4** are typically five-coordinate in solution. The coordination environments of **1**, **2**, and **4** in the solid state are consistent with that in solution, but **3** is four-coordinate in the solid state. Weak intermolecular Sn···O coordination may exist in solution of **3**.

Table 2. Half maximal inhibitory concentration ($\mu g\,mL^{-1}$) of **1–4** against tumor cell lines.

	IC_{50} ($\mu g\,mL^{-1}$)	
Complex	SMMC-7721	MCF-7
1	2 ± 0.6	9 ± 0.24
2	11 ± 0.2	35 ± 0.4
3	19 ± 0.6	13 ± 0.7
4	$12 \pm 0.6\,ng\,mL^{-1}$	$51 \pm 0.11\,ng\,mL^{-1}$
CPT	13.7	0.699

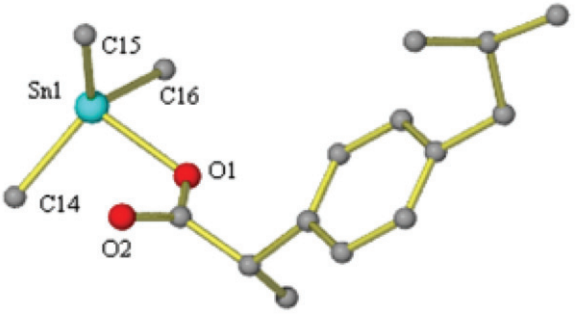


Figure 1. The molecular structure of **1**.

3.3. *Biological activity*

Complexes **1–4** were screened for *in vitro* tumor-inhibiting activity against SMMC-7721 and MCF-7 cell lines. The IC_{50} inhibitory concentrations have been assayed for **1–4** and are listed in table 2. Complexes **1**, **2**, and **4** exhibit higher activities than *cis*-platin (**CPT**) against SMMC-7721 [20] with **4** the most efficient antitumor agent for MCF-7; its antitumor activity is much higher than that of the clinically used *cis*-platin (**CPT**) [20]. Based on the data analysis, possible structure–activity relationships could be recognized as follows: (1) all compounds exhibit *in vitro* cytotoxicities toward two cancer lines which in some cases are identical to, or even higher than, that of "*cis*-platin." The activity mechanism of these compounds is not clear now, but from the structural characterization we can see that it is related to several factors, such as their structures or the length of the organic groups bound with tin. (2) As observed in previous studies [21], R plays an important role. Indeed, the trimethyltin complexes exhibit stronger antitumor activity than triphenyltin or tributyltin complexes, which can be explained by their low solubility in DMSO.

3.4. *X-ray crystal structures of 1 and 2*

The molecular and 1-D infinite zigzag chain structure of **1** are illustrated in figures 1 and 2, respectively; the repeating unit and 1-D infinite helical chain structure of **2** are illustrated in figures 3 and 4, respectively; and selected bond lengths and angles are listed in tables 3 and 4.

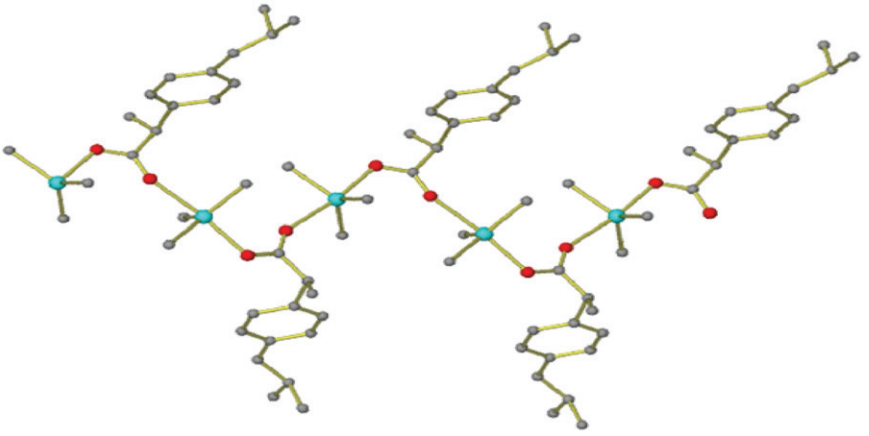


Figure 2. The 1-D infinite zigzag chain of **1**.

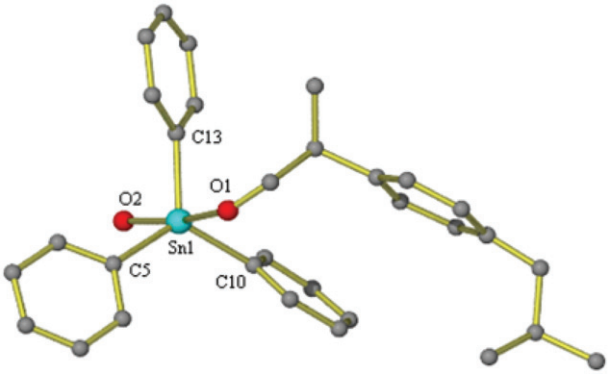


Figure 3. The molecular structure of **2**.

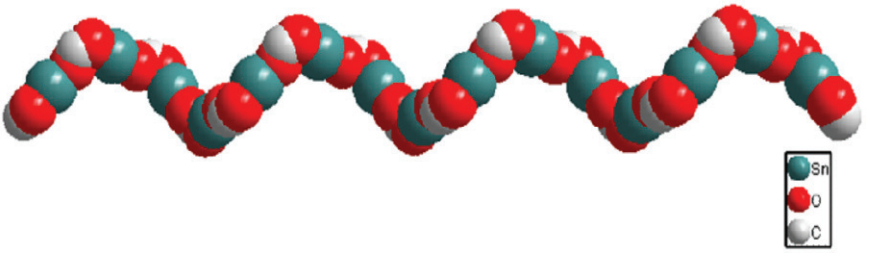


Figure 4. The 1-D spring-like helical chain of **2** (only carboxyl and tin are shown for clarity).

In **1**, five primary bonds are formed around tin, three methyl groups, and two carboxyl oxygen atoms with all tins possessing the same coordination. The geometry of tin can be described as a distorted trigonal bipyramid with three methyls lying in the equatorial plane and oxygen occupying the apical positions. The coordination mode of carboxylate in **1** is bidentate. The O–Sn–O, with a value of 172.13°, approaching that

Table 3. Selected bond lengths (Å) and angles (°) for **1**.

Sn(1)–C(14)	2.103(8)	Sn(1)–C(15)	2.114(13)
Sn(1)–C(16)	2.118(9)	Sn(1)–O(1)	2.176(10)
Sn(1)–O(2)#1	2.413(7)	O(2)–Sn(1)#2	2.413(7)
C(14)–Sn(1)–C(15)	115.2(7)	C(14)–Sn(1)–C(16)	124.0(5)
C(15)–Sn(1)–C(16)	119.2(6)	C(14)–Sn(1)–O(1)	97.8(6)
C(15)–Sn(1)–O(1)	88.6(3)	C(16)–Sn(1)–O(1)	95.4(4)
C(14)–Sn(1)–O(2)#1	85.2(6)	C(15)–Sn(1)–O(2)#1	83.5(5)
C(16)–Sn(1)–O(2)#1	88.9(3)	O(1)–Sn(1)–O(2)#1	172.1(3)

Symmetry transformations: #1: $-x+2, y-1/2, -z+1$; #2: $-x+2, y+1/2, -z+1$.

Table 4. Selected bond lengths (Å) and angles (°) for **2**.

Sn(1)–O(1)	2.312(8)	Sn(1)–O(2)	2.189(8)
Sn(1)–C(13)	2.063(14)	Sn(1)–C(5)	2.093(12)
Sn(1)–C(10)	2.132(11)	C(13)–Sn(1)–C(5)	120.2(5)
C(13)–Sn(1)–C(10)	117.3(5)	C(5)–Sn(1)–C(10)	122.4(5)
C(13)–Sn(1)–O(2)	84.1(4)	C(5)–Sn(1)–O(2)	92.2(4)
C(10)–Sn(1)–O(2)	96.9(4)	C(13)–Sn(1)–O(1)	89.6(4)
C(5)–Sn(1)–O(1)	85.6(4)	C(10)–Sn(1)–O(1)	91.5(4)
O(2)–Sn(1)–O(1)	171.2(3)		

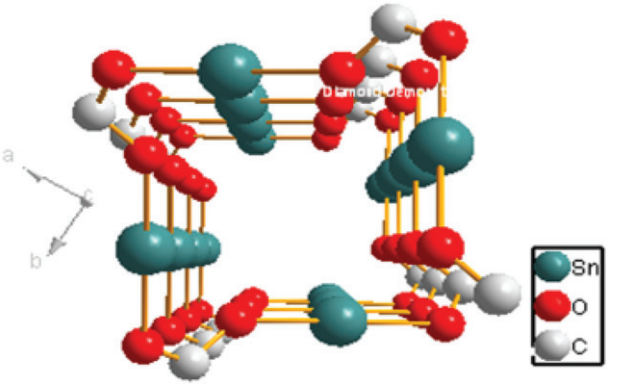


Figure 5. Perspective view along a *c*-axis of **2** (only carboxyl and tin are shown for clarity).

reported on [$EtPh_2SnOC(O)CH_3$] [22], is bent and slightly larger than that of di- and triorganotin carboxylates [23]. The Sn–O distance [2.176(10)–2.413(7) Å] is a little shorter than that reported in other organotin complexes [24], approaching Sn–O covalent bond length (2.13 Å), but much shorter than the sum of the van der Waals radii of Sn and O (3.68 Å) [25], proving that oxygen is coordinated to tin by a strong chemical bond.

Complexes **1** and **2** almost have the same structure; the only difference is that **1** is a 1-D infinite zigzag chain, but **2** is a 1-D infinite helical chain. As seen from figure 4, the repeating units are linked by intermolecular Sn–O bonds, thus giving a 1-D spring-like helical chain. From the *c*-axis direction, **2** has a quadrate cavity (figure 5), which has a chiral space group as determined by X-ray diffraction. Unfortunately, solvent is not captured in this cavity like our previously reported $[(Ph_3Sn)(nap)]_n$ [26].

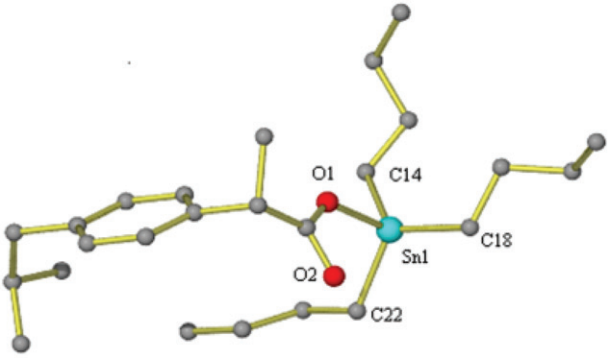


Figure 6. The molecular structure of **3**.

Table 5. Selected bond lengths (Å) and angles (°) for **3**.

Sn(1)–O(1)	1.998(18)	Sn(1)–C(14)	2.025(18)
Sn(1)–C(18)	2.037(19)	Sn(1)–C(22)	2.068(18)
O(1)–Sn(1)–C(14)	102.7(14)	O(1)–Sn(1)–C(18)	103.0(13)
C(14)–Sn(1)–C(18)	116.6(15)	O(1)–Sn(1)–C(22)	98.3(11)
C(14)–Sn(1)–C(22)	127.5(19)	C(18)–Sn(1)–C(22)	104.3(18)

3.5. *X-ray crystal structure of 3*

Molecular structure of **3** is illustrated in figure 6. Selected bond lengths and angles are given in table 5. Complex **3** is a tributyltin ester of (S)-(+)-2-(4isobutyl-phenyl)propionic acid possessing an unequivocal monomer structure. The carboxylate are monodentate. Each tin in **3** forms four primary bonds: three from the butyl carbons and one from oxygen of the bridging ligand. Owing to steric effects between butyl groups, Sn may be viewed as distorted tetrahedral geometry. The Sn(1)–O(1) bond length is 1.998(18) Å, shorter than the Sn–O covalent bond length (2.13 Å), proving that O(1) is coordinated by a strong bond.

Analysis of the supramolecular structure in the crystal lattice of **3** reveals that weak intermolecular Sn···O interactions play important roles in the supramolecular arrangements. In fact, supramolecular structure of **3** is a 1-D chain-like structure linked by weak intermolecular Sn···O coordination (figure 7). The Sn(1)···O(2) [O(2) is part of the adjacent monodentate carboxylate] distance (2.813 Å) is considerably shorter than the sum of the van der Waals radii of Sn and O (3.68 Å) [25]. Thus, if the weak Sn···O interaction is considered, the geometry of Sn(1) is best described as distorted trigonal-bipyramidal.

3.6. *X-ray crystal structure of 4*

Molecular and helical structures of **4** are illustrated in figures 8 and 9, respectively. Selected bond lengths and angles are shown in table 6. The structure of **4** is very similar to the structure of **2**, with only minor differences in two aspects. The first aspect is that carboxylates in **4** are monodentate and the other aspect lies in the two oxygen atoms of

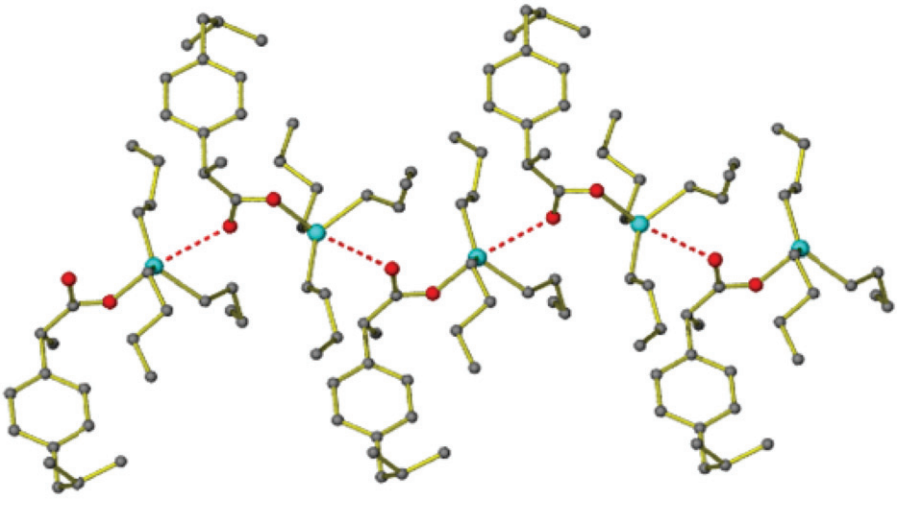


Figure 7. The chain-like structure along the crystallographic formed as a result of Sn···O interactions in the crystal lattice of **3**.

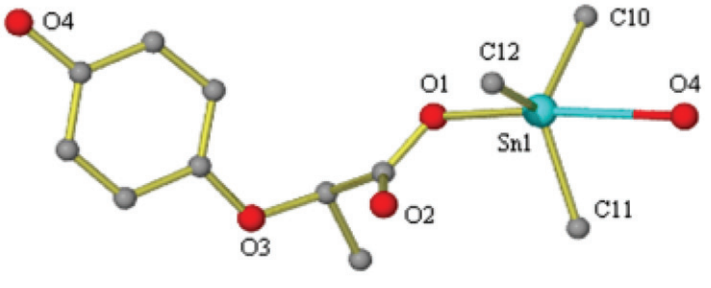


Figure 8. The molecular structure of **4**.

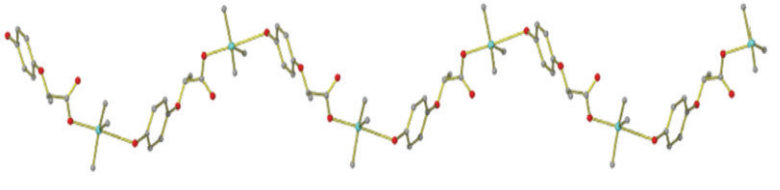


Figure 9. The 1-D spring-like helical chain of **4**.

axial angle O–Sn–O. One oxygen atom comes from carboxylate and the other from hydroxyl. In **2**, both come from carboxylates.

The most interesting aspect of the structure concerns the intermolecular O–H···O interactions, which help in the construction of the supramolecule. As shown in figure 10, the 44-membered macrocycles are connected *via* intermolecular hydrogen-bonding [O(4)–H(4)···O(2)] into a 3-D metal framework. The distances of H(4)···O(2) and O(4)···O(2) are 2.054 Å and 2.610 Å, respectively, and the angle of O(4)–H(4)···O(2) is 124.62°, which are consistent with the literature [27].

Table 6. Selected bond lengths (Å) and angles (°) for **4**.

Sn(1)–C(11)	2.12(2)	Sn(1)–O(1)	2.145(11)
Sn(1)–C(12)	2.15(2)	Sn(1)–C(10)	2.188(19)
Sn(1)–O(4)#1	2.712(15)	C(11)–Sn(1)–O(1)	99.9(7)
C(11)–Sn(1)–C(12)	115.6(10)	O(1)–Sn(1)–C(12)	93.3(6)
C(11)–Sn(1)–C(10)	120.6(9)	O(1)–Sn(1)–C(10)	95.7(6)
C(12)–Sn(1)–C(10)	120.2(9)	C(11)–Sn(1)–O(4)#1	86.9(7)
O(1)–Sn(1)–O(4)#1	172.5(5)	C(12)–Sn(1)–O(4)#1	86.5(6)
C(10)–Sn(1)–O(4)#1	78.0(6)		

Symmetry transformation: #1: $-x+3/2$, $-y$, $z-1/2$.

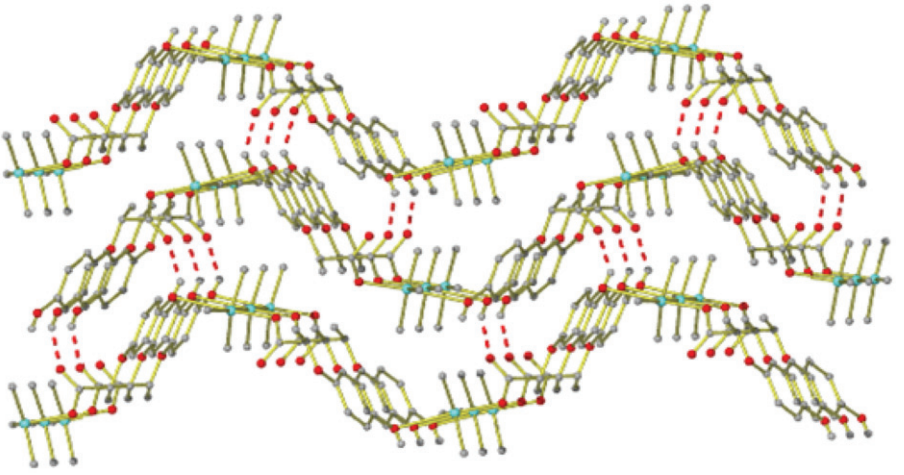


Figure 10. Complex **4** can form a 44-membered macrocycle and further interlink into a 3-D metal framework with intermolecular hydrogen bonds. (Some hydrogen atoms are deleted for clarity.)

4. Conclusion

Four new chiral triorganotin(IV) carboxylate complexes based on (S)-(+)-2-(4-isobutyl-phenyl)propionic acid and (R)-(+)-2-(4-hydroxyphenoxy)propionic acid were synthesized and characterized by IR, ^{1}H NMR, ^{13}C NMR, ^{119}Sn NMR, elemental analyses, and X-ray diffraction. Both spectra and crystal structures show that when (S)-(+)-2-(4-isobutyl-phenyl)propionic acid and (R)-(+)-2-(4-hydroxyphenoxy)propionic acid react with triorganotin complexes, they can form 1-D infinite zigzag chain, 1-D spring-like helical chain, or monomer. Trimethyltin carboxylate complexes usually assume 1-D chain structures (such as in **1**, **2**, and **4**), and tributyltin carboxylate complex often assume discrete monomers (such as in **3**). This may be related to the spatial hindrance of the triorganotin group. Antitumor activities of **1**–**4** have also been tested and **4** exhibits high activities toward MCF-7 cell lines. These data suggest that **1**–**4** have better *in vitro* biological activities than *cis*-platin when screened for antitumor studies. Most antitumor activity of the complexes is higher than those reported [28–30]. We can see that chiral carboxylate organotin complexes have higher activities compared with other complexes.

Supplementary material

Crystallographic data for the structure analysis of the complexes have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos 819854 (**1**), 819856 (**2**), 819859 (**3**), and 819861 (**4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (http://www.ccdc.cam.ac.uk; Fax: +44-1223-336033).

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