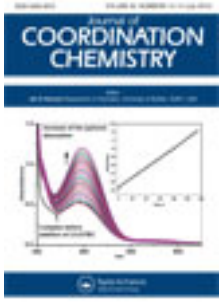

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Syntheses and structural characterization of organotin(IV) complexes derived from reaction of 2,3-diphenylpropionic acid and various alkyltin salts

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Five new organotin(IV) complexes, $[(R_3Sn)(O_2C_{15}H_{13})]_n$ (R = Me: **1**; *n*Bu: **2**), $[RSn(O)(O_2C_{15}H_{13})]_6$ (R = Ph: **3**), $[(R_2Sn)_2(O_2C_{15}H_{13})_2(\mu_3\text{-}O)]_2$ (R = Me: **4**), and $[(R_2Sn)(O_2C_{15}H_{13})_2]$ (R = *n*Bu: **5**), have been prepared by the reaction of 2,3-diphenylpropionic acid and the corresponding organotin chloride with sodium ethoxide in methanol. All the complexes were characterized by elemental analysis, FT-IR, NMR (^{1}H, ^{13}C, ^{119}Sn) spectroscopy, TGA, and X-ray crystallography. The structural analyses reveal that **1** and **2** are 1-D infinite polymeric chains with Sn in *syn–anti* conformation. Complex **3** has a drum structure with six Sn centers. Complex **4** has a supramolecular chain-like ladder through weak intermolecular Sn···O interactions. Complex **5** is a monomer, connected into a 1-D polymer through intermolecular C–H···O interactions. Complexes **1** and **5** crystallize in the orthorhombic space groups *P*212121 and *P*21212, which are chiral space groups.

Keywords: Organotin(IV); 2,3-Diphenylpropionic acid; X-ray crystallography; Structural characterization

1. Introduction

Metal-directed self-assembly has become a powerful tool for the construction of systems containing cavities or possessing intrinsic physical and chemical properties promising for new materials and new metal-based drugs [1, 2]. Organotin derivatives give rise to a wide range of complexes employed in organic synthesis, catalysis, and particularly in biochemical activity [3]. However, the biochemical activity of organotin(IV) complexes is influenced by the molecular structure and coordination number of tin [4–6]. Organotin carboxylates exhibit good bactericidal and antitumor activities [7, 8]. The coordination ability of the carboxylic acid serving as either a multidentate or bridging ligand is of interest to structural chemists.

Recently, work in our laboratory has focused on self-assembly and crystallographic characterization of organotin(IV) carboxylates under ambient conditions [9–11]. Carboxylates can be monodentate or bidentate, intermolecularly bridging or

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intramolecularly chelating ligands. Biological activity of organotin complexes is related to the type of alkyl attached to tin. The structural characterization of such organotin(IV) complexes may provide important clues to structure–activity relationships and provide insight to the reaction mechanism that may, in turn, allow synthetic chemists to further optimize reaction conditions. Thus, new strategies to construct a variety of organotin complexes are required. We selected 2,3-diphenylpropionic acid as bridging ligands and succeeded in obtaining five organotin complexes. Here we report the syntheses, characterization, and crystal structures of these new carboxylate organotin(IV) complexes.

2. Results and discussion

2.1. *Syntheses*

The syntheses of **1**–**5** are given in scheme 1.

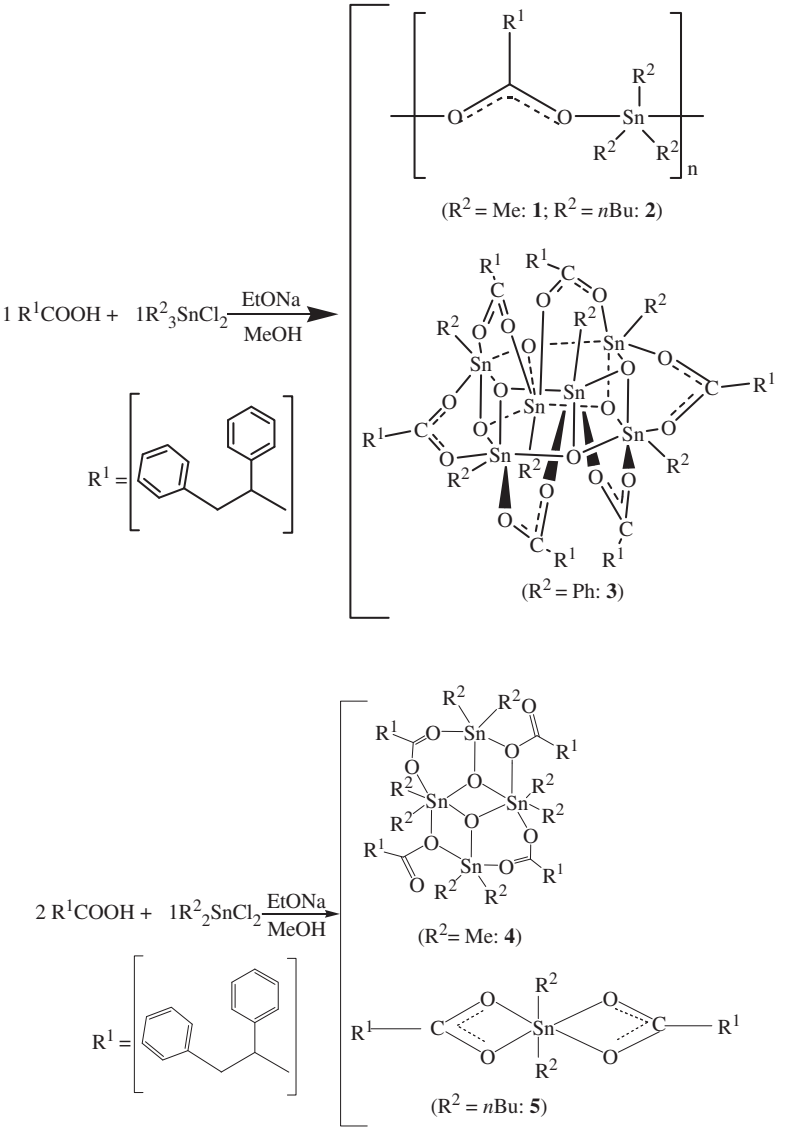
2.2. *IR spectra*

IR spectra of **1**–**5** were recorded from 4000 to 400 cm^{-1}. The stretching frequencies are associated with COO^-, Sn–C, and Sn–O groups. Strong absorption at 416–462 cm^{-1}, which is absent in the spectrum of the free ligand, is assigned to the Sn–O stretching mode. Strong absorptions at 1496–1602 and 1187–1408 cm^{-1} in these spectra are assigned to asymmetric and symmetric vibrations of COO^-, respectively. The $\Delta\nu$ values for **1**–**5** reveal that carboxylate is bidentate, while **4** also has monodentate carboxylate. These values are consistent with those of a number of organotin(IV)–oxygen derivatives [12, 13].

2.3. *NMR spectra*

^1H NMR spectra showing signals of $-CO_2H$ in the ligand are absent in these complexes, indicating deprotonation and formation of Sn–O bond, consistent with IR data. ^{13}C NMR spectra of all complexes show a significant downfield shift of all carbon resonances compared with free ligand because of electron–density transfer from the ligands to metal. The single resonances at $\delta = 178.05$–183.27 ppm are attributed to COO^- in **1**–**5**. These data are consistent with the structures of **1**–**5**.

The ^{119}Sn NMR spectra of complexes show resonances between $\delta = -220.78$ and $\delta = 113.81$. As reported [14], δ values for ^{119}Sn NMR spectra from -210 to -400, -90 to -190, and 200 to -60 ppm have been associated with six-, five-, and four-coordinate tin, respectively. On this basis, we conclude that **1** is five-coordinate and **3** is six-coordinate. Complexes **4** and **5** have only one signal at -113.41, -141.94 ppm, respectively, indicating only five-coordination, not in accord with the structures in the solid state. Some Sn–O bonds about the six-coordinate tin in **4** and **5** are much longer than the covalent radii of tin and oxygen; these weak Sn–O bonds may rupture in solution and six-coordinate tin becomes five-coordinate. Tin of **2** becomes four-coordinate, so Sn–O bonds of **2** also ruptured in solution.



Scheme 1. The syntheses of **1–5**.

2.4. *Description of crystal structures*

2.4.1. Crystal structures of 1 and 2. The repeating units and 1-D polymeric chain structures of **1** and **2** are illustrated in figures 1–4; selected bond lengths and angles for these complexes are given in tables 1 and 2. Complexes **1** and **2** adopt infinite 1-D polymeric chain structures with five-coordinate tin, which are generated by the bidentate-bridging carboxylates and Sn. Tin exists in a distorted trigonal bipyramidal environment with two oxygen atoms and three carbon atoms, linked by ligands in *syn–anti* conformation [15]. Axial positions are occupied by oxygen [axial angles: complex **1**,

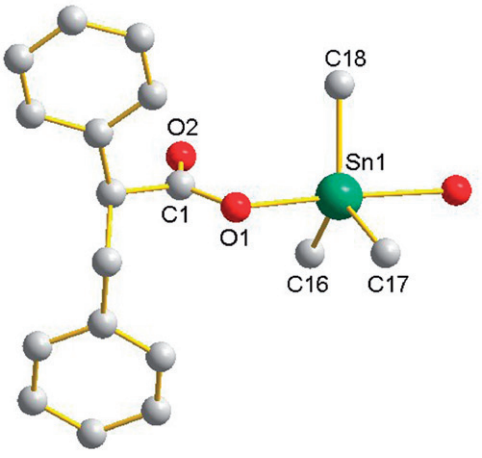


Figure 1. Repeating unit of **1**.

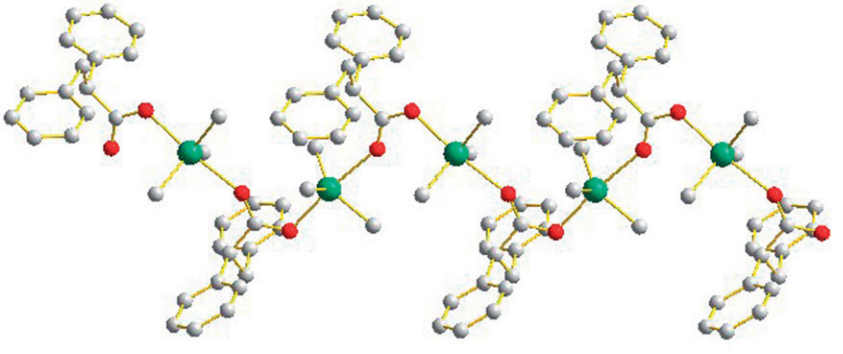


Figure 2. 1-D polymeric chain of **1**.

O(1)–Sn(1)–O(2)#1 = 172.95(15)°, #1: $x+1/2$, $-y+1/2$, $-z$; complex **2**, O(1)–Sn(1)–O(4)#1 = 175.2(8)°, #1: $x+1$, y, z, O(3)–Sn(2)–O(2) = 175.2(11)°]. The axial angles of **1** and **2** are not 180°, showing distortion of the geometry. Three methyl (butyl) carbons occupy the equatorial plane, and the sum of the trigonal C–Sn–C angles approaches 360° [complex **1**, 359.2°; complex **2**, Sn(1) 357.7°, Sn(2) 358.4°]. These Sn–O bond lengths [**1**: Sn(1)–O(1) = 2.204(4) Å, Sn(1)–O(2)#1 = 2.375(4) Å; **2**: Sn(1)–O(1) = 2.24(3), Sn(1)–O(4)#1 = 2.43(3) Å, Sn(2)–O(3) = 2.15(2) Å, Sn(2)–O(2) = 2.44(3) Å] are a little longer than Sn–O covalent bond lengths [2.038–2.115 Å] [16]. The Sn–C distances [1.91(5)–2.24(4) Å] are equal within experimental error and are close to the single-bond value for a trigonal–bipyramidal tin [17]. We have reported similar 1-D polymeric chain structures with substituted benzeneseleninic acid ligands [18, 19].

2.4.2. Crystal structure of 3. The molecular structure and framework of the drum of **3** are illustrated in figures 5 and 6, respectively; selected bond lengths and angles are given in table 3. The geometry of the stannoxane framework is shown in figure 5, indicating

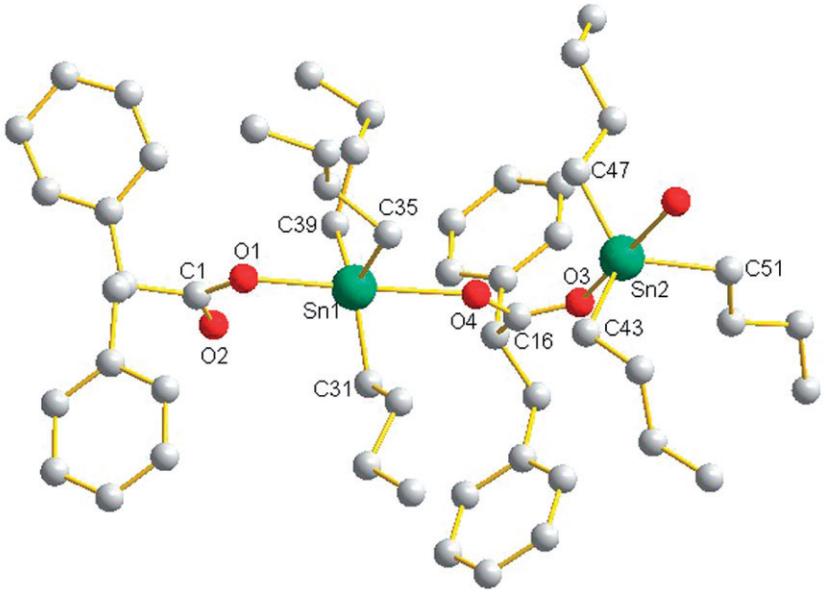


Figure 3. Repeating unit of **2**.

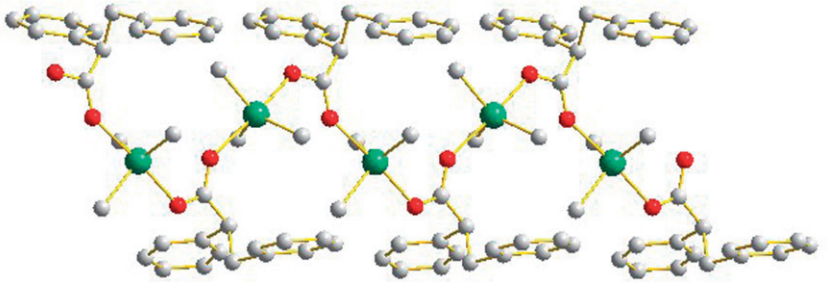


Figure 4. 1-D polymeric chain of **2** (additional carbons of Sn-butyl groups are omitted for clarity).

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

Sn(1)–C(16)	2.101(7)	Sn(1)–O(1)	2.204(4)
Sn(1)–C(17)	2.111(7)	Sn(1)–O(2)#1	2.375(4)
Sn(1)–C(18)	2.121(6)		
C(16)–Sn(1)–C(17)	117.4(4)	C(17)–Sn(1)–O(1)	88.7(2)
C(16)–Sn(1)–C(18)	122.6(3)	C(18)–Sn(1)–O(1)	94.8(3)
C(17)–Sn(1)–C(18)	119.2(4)	C(16)–Sn(1)–O(2)#1	88.7(2)
O(1)–Sn(1)–O(2)#1	172.95(15)	C(17)–Sn(1)–O(2)#1	84.3(2)
C(16)–Sn(1)–O(1)	95.5(3)	C(18)–Sn(1)–O(2)#1	87.6(3)

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

that the six-membered rings have a chair conformation. Two Sn–C bonds ruptured during the reaction, so two benzene rings were lost and only one phenyl was connected with tin in **3**. Each Sn is bonded to three framework oxygen atoms, with Sn–O bonds from 2.094(8) to 2.122(8) Å. Oxygen atoms of the framework are trivalent with the

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

Sn(1)–C(31)	1.91(5)	Sn(2)–C(47)	1.96(4)
Sn(1)–C(39)	2.17(4)	Sn(2)–C(43)	2.08(4)
Sn(1)–C(35)	2.24(4)	Sn(2)–C(51)	2.19(4)
Sn(1)–O(1)	2.24(3)	Sn(2)–O(3)	2.15(2)
Sn(1)–O(4)#1	2.43(3)	Sn(2)–O(2)	2.44(3)
C(31)–Sn(1)–C(39)	126.8(18)	C(47)–Sn(2)–C(43)	125.1(15)
C(31)–Sn(1)–C(35)	113.9(17)	C(47)–Sn(2)–C(51)	119.3(17)
C(39)–Sn(1)–C(35)	117.1(18)	C(43)–Sn(2)–C(51)	114.0(17)
O(1)–Sn(1)–O(4)#1	175.2(8)	O(3)–Sn(2)–O(2)	126.8

Symmetry code: #1: $x+1$, y, z.

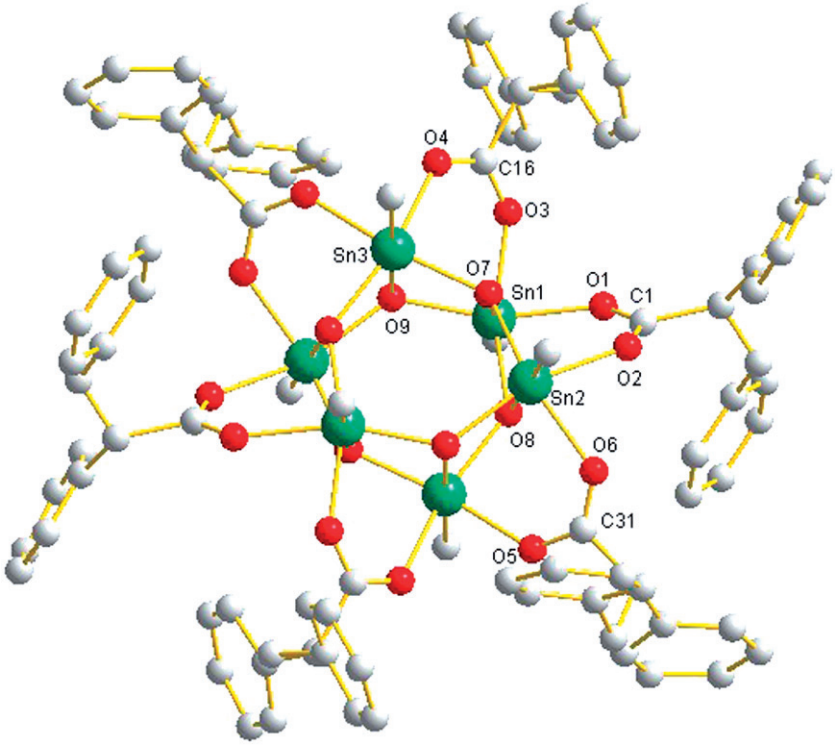


Figure 5. Molecular structure of **3** (the α-carbon of the phenyl ring (Sn–Ph) is drawn, but other atoms are omitted for clarity.

distorted pyramidal geometry. The Sn–O–Sn bond angles in the six-membered rings, 99.3(3)–134.6(4) Å, are larger than those found in four-membered rings [20]. The six tins are chemically equivalent, as are the six trivalent oxygen atoms. The Sn–O framework can be described as a drum with top and bottom faces comprised of a six-membered $(–Sn–O–)_3$ tri-stannoxane ring. The drum faces are joined by six Sn–O bonds containing tri-coordinate oxygen. The sides of the drum are thus comprised of six four-membered $(–Sn–O–)_2$ distannoxane rings, each of which is spanned by a carboxylate that forms a symmetrical bridge between two tins. The Sn–O bonds to the bridging carboxylates are

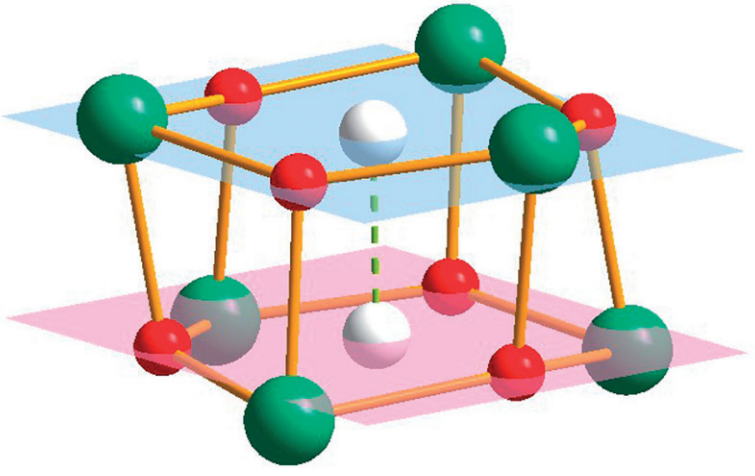


Figure 6. Framework of the drum structure (except tin and oxygen, all other atoms are omitted for clarity).

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

Sn(1)–O(1)	2.186(10)	Sn(2)–O(9)#1	2.122(8)
Sn(1)–O(3)	2.168(12)	Sn(3)–O(4)	2.190(11)
Sn(1)–O(7)	2.106(8)	Sn(3)–O(5)#1	2.182(11)
Sn(1)–O(8)	2.097(8)	Sn(3)–O(7)	2.103(8)
Sn(1)–O(9)	2.096(8)	Sn(3)–O(8)#1	2.112(8)
Sn(2)–O(2)	2.181(11)	Sn(3)–O(9)	2.094(8)
Sn(2)–O(6)	2.187(11)	Sn(1)–C(46)	2.129(15)
Sn(2)–O(7)	2.111(8)	Sn(2)–C(52)	2.115(14)
Sn(2)–O(8)	2.107(8)	Sn(3)–C(58)	2.133(14)
O(1)–C(1)	1.25(2)	O(2)–C(1)	1.25(2)
O(3)–C(16)	1.26(2)	O(4)–C(16)	1.28(2)
O(5)–C(31)	1.26(2)	O(6)–C(31)	1.26(2)
O(7)–Sn(1)–C(46)	177.0(5)	O(7)–Sn(2)–O(2)	87.2(4)
O(3)–Sn(1)–O(1)	77.1(4)	O(7)–Sn(2)–O(9)#1	103.6(3)
O(9)–Sn(1)–O(3)	87.3(4)	O(9)–Sn(3)–C(58)	177.6(4)
O(8)–Sn(1)–O(1)	86.6(4)	O(7)–Sn(3)–O(4)	87.9(4)
O(9)–Sn(1)–O(8)	104.9(3)	O(7)–Sn(3)–O(8)#1	102.9(3)
O(8)–Sn(2)–C(52)	177.2(5)	O(8)#1–Sn(3)–O(5)#1	87.8(4)
O(9)#1–Sn(2)–O(6)	88.2(4)	O(5)#1–Sn(3)–O(4)	77.2(4)
O(2)–Sn(2)–O(6)	76.8(4)	Sn(1)–O(8)–Sn(2)	99.7(3)
Sn(3)–O(7)–Sn(1)	99.6(3)	Sn(1)–O(8)–Sn(3)#1	133.7(4)
Sn(3)–O(7)–Sn(2)	134.6(4)	Sn(2)–O(8)–Sn(3)#1	99.6(3)
Sn(1)–O(7)–Sn(2)	99.3(3)	Sn(3)–O(9)–Sn(1)	100.2(3)
Sn(3)–O(9)–Sn(2)#1	99.7(3)	Sn(1)–O(9)–Sn(2)#1	132.3(4)

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

longer than the core bonds, ranging from 2.168(12) to 2.190(11) Å. Similar metal-organic frameworks have been reported recently [21]. Concomitant with the equivalence of the Sn–O bonds to a particular carboxylate is the corresponding equivalence of the pairs of C–O carboxylate bond lengths.

The distannoxane rings of the sides of the drum are not planar but folded along the Sn–Sn vectors so that the oxygen atoms are directed towards the interior of the

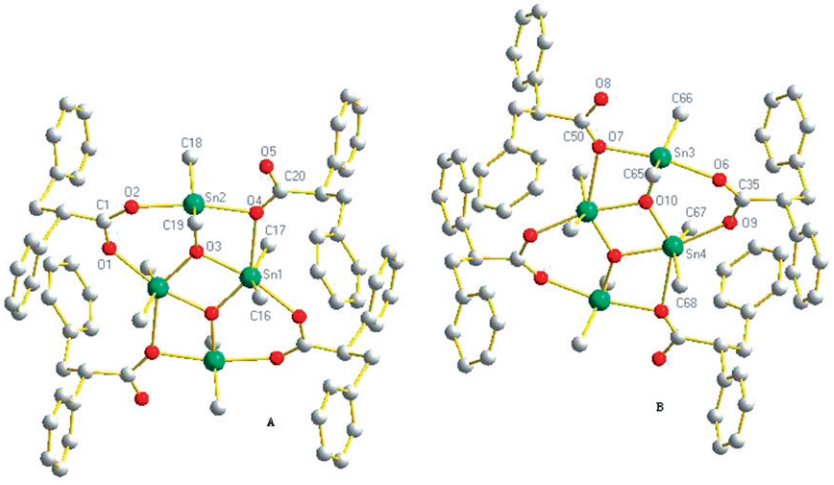


Figure 7. Molecular structure of **4**.

cavity (figure 6). Similarly, the tristannoxane ring faces of the drum are not planar but have oxygen atoms directed toward the interior of the cavity, relative to Sn. Thus, the interior of the cavity is defined by a crown of six oxygen atoms, in a trigonal-antiprismatic arrangement, and the entrance to the cavity is defined by three oxygen atoms from three μ_3-atoms arranged as an equilateral triangle. The coordination geometry about each Sn is completed by a carbon of the phenyl which occupies a position *trans* to a framework oxygen. Thus, each Sn is coordinated by three framework oxygen atoms, two carboxylate oxygen atoms, and a carbon such that the O_5C donor set defines a distorted octahedron.

2.4.3. Crystal structure of 4. The molecular structure and 1-D ladder structure of **4** are illustrated in figures 7 and 8, respectively; selected bond lengths and angles are given in table 4. The asymmetric unit contains two monomers **A** and **B** (figure 7), which are different from a crystallographic point of view. The conformations of the two independent molecules are almost the same, with only slight differences in bond lengths and angles. We describe the details of **4** with molecule **A** as an example. The predominant structural form of **4** is dimeric carboxylatotetraorganodistannoxane, which consists of a central planar $(Me_2Sn)_2O_2$ four-membered ring and two peripheral Me_2Sn units; each bridging oxygen in Sn_2O_2 is attached to three Me_2Sn units and these oxygen atoms are three-coordinate. Endocyclic and exocyclic tins are six- and five-coordinate, respectively (figure 7). For Sn(1), there are six primary bonds to tin, two to methyl molecules, two to μ_3-oxygen atoms, and two to the carboxyl oxygen atoms. Two methyl molecules occupy axial positions with the axial angle [C(16)–Sn(1)–C(17)] of 149.3(8)° deviating from linear; the basal plane is defined by four oxygen atoms. Sn(2) is bound to two methyl molecules and three oxygen atoms, two carboxyl molecules from two ligands and one μ_3-oxygen. The geometry of Sn(2) can be described as a distorted trigonal bipyramid in which the apical positions are occupied by oxygen atoms from two carboxylate molecules [O(2)–Sn(2)–O(4) = 168.7(5)°]. In this complex, a stable

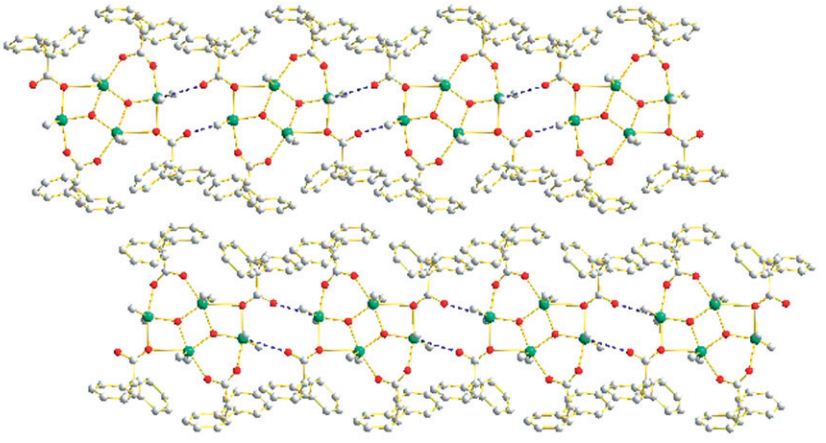


Figure 8. The 1-D supramolecular chain-like ladder structure of **4** made up of intermolecular weak Sn···O interactions.

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

Sn(1)–C(16)	2.082(17)	Sn(2)–C(18)	2.101(17)
Sn(1)–C(17)	2.088(19)	Sn(2)–C(19)	2.081(17)
Sn(1)–O(1)	2.266(16)	Sn(2)–O(2)	2.180(13)
Sn(1)–O(3)	2.036(11)	Sn(2)–O(3)	2.049(11)
Sn(1)–O(3)#1	2.115(12)	Sn(2)–O(4)	2.211(13)
Sn(3)–C(65)	2.142(18)	Sn(4)–C(67)	2.096(18)
Sn(3)–C(66)	2.084(18)	Sn(4)–C(68)	2.124(17)
Sn(3)–O(6)	2.206(13)	Sn(4)–O(7)	2.668(13)
Sn(3)–O(7)	2.213(14)	Sn(4)–O(9)	2.250(14)
Sn(3)–O(10)#2	2.049(12)	Sn(4)–O(10)	2.023(11)
Sn(4)–O(10)#2	2.127(12)	Sn(1)–O(4)#1	2.644(13)
C(16)–Sn(1)–C(17)	149.3(8)	C(19)–Sn(2)–C(18)	146.0(8)
O(3)–Sn(1)–O(3)#1	75.6(5)	O(6)–Sn(3)–O(7)	168.4(5)
O(3)–Sn(1)–O(1)	91.0(5)	O(10)#2–Sn(3)–C(66)	107.1(7)
O(3)#1–Sn(1)–O(4)#1	67.0(4)	O(10)#2–Sn(3)–C(65)	108.8(6)
O(1)–Sn(1)–O(4)#1	126.3(5)	C(66)–Sn(3)–C(65)	143.9(8)
O(2)–Sn(2)–O(4)	168.7(5)	C(67)–Sn(4)–C(68)	148.9(9)
O(3)–Sn(2)–C(19)	107.1(6)	O(10)–Sn(4)–O(9)	90.0(5)
O(3)–Sn(2)–C(18)	106.9(7)	O(10)–Sn(4)–O(10)#2	76.0(5)
O(10)#2–Sn(4)–O(7)	67.0(4)	O(9)–Sn(4)–O(7)	127.0(5)

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

six-membered ring was formed in which the endocyclic tins lay on the plane and exocyclic tins lay 0.302 Å out of the plane defined by three-coordinate oxygen atom. The Sn–O bond lengths in **4** range from 2.023(11) to 2.668(13) Å, consistent with the literature [22]. The Sn–C distances, which are almost identical, lie within the narrow range of 2.081(17)–2.142(18) Å, in agreement with the reported values [23].

The most interesting aspect of the structure concerns intermolecular Sn···O interactions, which help in construction of the supramolecule. As shown in figure 8, **A** and **B** are connected *via* intermolecular interactions Sn(2)···O(5)#3 (#3: $2-x, 2-y, -z$) and Sn(3)···O(8)#4 (#4: $1-x, 1-y, 1-z$) into a supramolecular

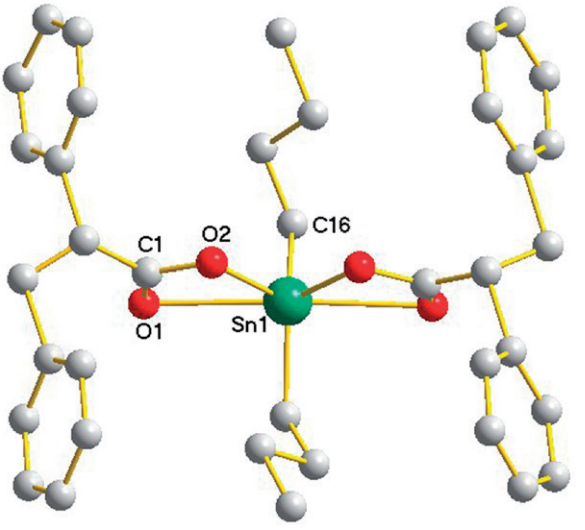


Figure 9. Molecular structure of **5**.

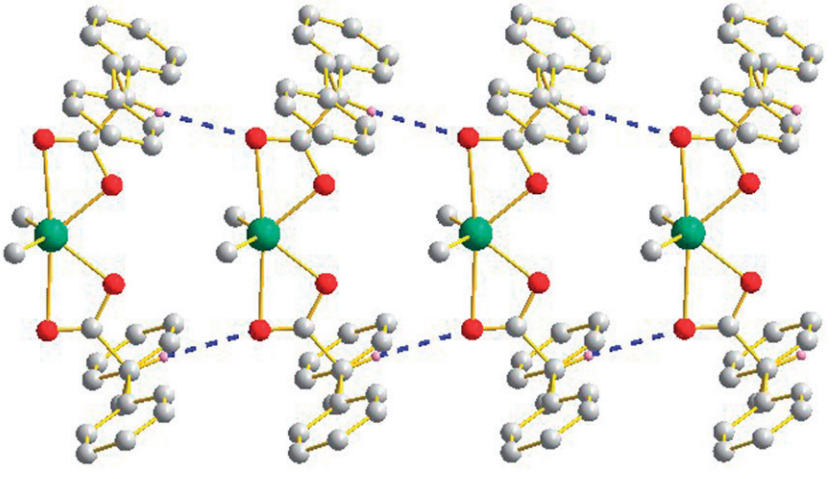


Figure 10. The 1-D polymeric chain structure of **5** made up of intermolecular weak C–H···O interactions (additional carbons of Sn-*n*-butyl groups are omitted for clarity).

chain-like ladder structure. The Sn(2)···O(5)#3 (3.226 Å) and Sn(3)···O(8)#4 (3.219 Å) distances are considerably shorter than the sum of the van der Waals radii of Sn and O (3.68 Å) [17]. Thus, if weak Sn···O interactions are considered, the geometry of Sn(2) and Sn(3) is best described as distorted octahedral.

2.4.4. Crystal structure of 5. The molecular structure and 1-D polymeric chain of **5** are illustrated in figures 9 and 10, respectively; selected bond lengths and angles are given in table 5. Sn exists in a skew-trapezoidal planar geometry in which the basal

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

Sn(1)–O(1)	2.620(8)	Sn(1)–C(16)	2.100(13)
Sn(1)–O(2)	2.112(7)	C(1)–O(1)	1.193(18)
C(1)–O(2)	1.347(17)	C(16)#1–Sn(1)–O(2)	108.0(6)
C(16)–Sn(1)–C(16)#1	131.9(13)	C(16)–Sn(1)–O(2)	108.8(6)
O(2)–Sn(1)–O(2)#1	78.4(4)	C(16)–Sn(1)–O(1)#1	89.3(5)
O(2)#1–Sn(1)–O(1)#1	54.1(3)	C(16)#1–Sn(1)–O(1)#1	87.9(5)
O(1)#1–Sn(1)–O(1)	173.3(4)	O(2)–Sn(1)–O(1)	54.1(3)

Symmetry code: #1: $-x+1, -y+1, z$.

plane is defined by the four oxygen atoms derived from two chelating carboxylate molecules. The two remaining positions are occupied by organic substituents which lie over the Sn–O bonds. The sum of the angles about the basal plane is 360° with angles subtended at Sn in the rather large range 87.9(5)–108.8(6)°. The carboxylate molecules chelate Sn with asymmetric Sn–O bond distances and this asymmetry is reflected in the associated C–O bond distances; as expected, the longer C–O distances are associated with shorter Sn–O bonds (table 5). The Sn–O bond distances are not equal, however, with the difference between Sn–O bond distance for the two carboxylate moleculess being 0.508 and 0.154 Å, respectively. Similar structures have been found in $[Me_2Sn(O_2CC_6H_5)_2]$ [24] and $[Et_2Sn(O_2CC_4H_3S)_2]$ [25]. The bond distances of Sn–C and Sn–O in **5** [Sn1–C16, 2.100(13) Å; Sn1–O1, 2.620(8) Å; Sn1–O2, 2.112(7) Å] are in the normal range of organotin complexes [26].

Intermolecular C–H $\cdots$ O interactions help construct the supramolecule. As shown in figure 10, **5** is connected *via* intermolecular interactions C(2)–H(2) $\cdots$ O(1)#2 [C(2) $\cdots$ O(1)#2, 3.58(2) Å; H(2) $\cdots$ O(1)#2, 2.62 Å; C(2)–H(2) $\cdots$ O(1)#2, 167.2°] into a 1-D infinite polymeric chain. The hydrogen bond data are consistent with the literature [20].

2.5. *TGA studies*

To evaluate the thermal stability of **1**–**5**, thermogravimetric analyses (TGA) were performed from 30°C to 500°C under N_2. The TGA shows that the decomposition temperatures of all the complexes are between 170°C and 350°C, relatively high. In general, all of these organotin complexes exhibit good thermal stability [27].

3. Experimental details

3.1. *Materials and measurements*

Trimethyltin chloride, tri-*n*-butyltin chloride, triphenyltin chloride, dimethyltin dichloride, di-*n*-butyltin dichloride, 2,3-diphenylpropionic acid, and solvents were commercially available and were used without purification. The melting points were obtained with a Kofler micro melting point apparatus and are uncorrected. Elemental analyses were performed with a PE-2400II apparatus. Infrared 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. TGA was carried out with a Perkin-Elmer Pyris-1 instrument with a heating rate of $10^{\circ}C\,min^{-1}$ from 50°C to 550°C and with a $20.0\,cm^{3}\,min^{-1}$ nitrogen gas flow.

3.2. *Syntheses of 1–5*

3.2.1. $[(Me_3Sn)(O_2C_{15}H_{13})]_n$ (1). The reaction was carried out under nitrogen using standard Schlenk techniques. The 2,3-diphenylpropionic acid (0.226 g, 1 mmol) was added to the solution of methanol (30 mL) together with sodium ethoxide (0.068 g, 1 mmol), and the mixture was stirred for 0.5 h. After addition of trimethyltin chloride (0.199 g, 1 mmol), the mixture was stirred at 50°C for 12 h and filtered. The solvent was gradually removed by evaporation under vacuum until a solid was obtained. The solid was then recrystallized from diethyl ether and colorless crystals of **1** were recovered. Yield: 82%. m.p. 119–121°C. Anal. Calcd for $C_{18}H_{22}O_2Sn$ (%): C 55.57, H 5.70; Found (%): C 55.22, H 6.01. IR (KBr, cm^{-1}): ν_{as}(COO), 1590; ν_{s}(COO), 1408; ν(Sn–C), 548; ν(Sn–O), 416. ^{1}H NMR ($CDCl_3$, ppm): δ 7.12–7.33 (m, 10H, Ph), 3.84–3.88 (m, 1H, CH), 2.98–3.40 (m, 2H, CH_2), 0.44 (s, $^{2}J_{SnH} = 69.3$ Hz, 9H, Sn–CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 178.05 (COO); 53.92 (CH); 40.32 (CH_2); 126.13–139.40 (Ar–C); −2.61 ($^{1}J_{SnC} = 483.88$ Hz, Sn–CH_3). ^{119}Sn NMR ($CDCl_3$, ppm): δ −113.75.

3.2.2. $[(Bu_3Sn)(O_2C_{15}H_{13})]_n$ (2). Complex **2** was prepared in the same way as **1**; tri-*n*-butyltin chloride (0.325 g, 1 mmol) was added to 2,3-diphenylpropionic acid (0.226 g, 1 mmol) and sodium ethoxide (0.068 g, 1 mmol). The solid was then recrystallized from diethyl ether and colorless crystals of **2** were recovered. Yield: 80%. m.p. 82–84°C. Anal. Calcd for $C_{54}H_{80}O_4Sn_2$ (%): C 62.93, H 7.82; Found (%): C 63.26, H 7.53. IR (KBr, cm^{-1}): ν_{as}(COO), 1577; ν_{s}(COO), 1378; ν(Sn–C), 564; ν(Sn–O), 454. ^{1}H NMR ($CDCl_3$, ppm): δ 7.15–7.36 (m, 20H, Ph), 3.86–3.90 (m, 2H, CH), 2.79–3.41 (m, 4H, CH_2), 0.82–0.94 (m, 18H, CH_3), 1.12–1.66 (m, 36H, Sn-$CH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$, ppm): δ 178.24 (COO); 54.43 (CH); 40.40 (CH_2); 125.96–140.24 (Ar–C); 13.48, 26.55, 27.17, 27.64 (butyl-C). ^{119}Sn NMR ($CDCl_3$, ppm): δ 113.81.

3.2.3. $[PhSn(O)(O_2C_{15}H_{13})]_6$ (3). Complex **3** was prepared in the same way as **1**; triphenyltin chloride (0.385 g, 1 mmol) was added to 2,3-diphenylpropionic acid (0.226 g, 1 mmol) and sodium ethoxide (0.068 g, 1 mmol). The solid was recrystallized from diethyl ether and colorless crystals of **3** were recovered. Yield: 79%. m.p. 167–169°C. Anal. Calcd for $C_{126}H_{108}O_{18}Sn_6$ (%): C 57.71, H 4.15; Found (%): C 57.39, H 4.50. IR (KBr, cm^{-1}): ν_{as}(COO), 1602; ν_{s}(COO), 1385; ν(Sn–C), 566; ν(Sn–O), 442; ν(O–Sn–O), 613. ^{1}H NMR ($CDCl_3$, ppm): δ 6.95–7.26 (m, 90H, Ph), 3.60–3.79 (m, 6H, CH), 2.49–3.31 (m, 12H, CH_2). ^{13}C NMR ($CDCl_3$, ppm): δ 180.96 (COO); 56.03 (CH); 39.94 (CH_2); 125.84–140.18 (Ar–C). ^{119}Sn NMR ($CDCl_3$, ppm): δ −220.78.

3.2.4. $[(Me_2Sn)_2(O_2C_{15}H_{13})_2(\mu_3\text{-}O)]_2$ (4). Complex **4** was prepared in the same way as **1**; dimethyltin dichloride (0.219 g, 1 mmol) was added to 2,3-diphenylpropionic acid (0.452 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid was then recrystallized from diethyl ether and colorless crystals of **4** were recovered. Yield: 84%. m.p. 137–139°C. Anal. Calcd for $C_{68}H_{76}O_{10}Sn_4$ (%): C 53.44, H 5.01; Found (%): C 53.78, H 4.69. IR (KBr, cm^{-1}): ν_{as}(COO), 1595, 1496; ν_s(COO), 1385, 1187; ν(Sn–C), 528; ν(Sn–O), 462; ν(O–Sn–O), 648. ^{1}H NMR ($CDCl_3$, ppm): δ 7.12–7.33 (m, 40H, Ph), 3.90–3.94 (m, 4H, CH), 2.98–3.35 (m, 8H, CH_2), 0.64 (s, $^2J_{SnH} = 80$ Hz, 24H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 183.27 (COO); 53.47 (CH); 40.32 (CH_2); 126.36–139.01 (Ar–C); 4.04 ($^1J_{SnC} = 493$ Hz, Sn–CH_3). ^{119}Sn NMR ($CDCl_3$, ppm): δ −113.46.

3.2.5. $[(Bu_2Sn)(O_2C_{15}H_{13})_2]$ (5). Complex **5** was prepared in the same way as **1**; di-*n*-butyltin dichloride (0.304 g, 1 mmol) was added to 2,3-diphenylpropionic acid (0.452 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid was then recrystallized from diethyl ether and colorless crystals of **5** were recovered. Yield: 81%. m.p. 153–155°C. Anal. Calcd for $C_{38}H_{44}O_4Sn$ (%): C 66.78, H 6.49; Found (%): C 66.40, H 6.81. IR (KBr, cm^{-1}): ν_{as}(COO), 1602; ν_s(COO), 1385; ν(Sn–C), 527 ν(Sn–O), 417. ^{1}H NMR ($CDCl_3$, ppm): δ 7.10–7.37 (m, 20H, Ph), 3.85–3.95 (m, 2H, CH), 3.01–3.41 (m, 4H, CH_2), 0.66–1.53 (m, 18H, *n*Bu). ^{13}C NMR ($CDCl_3$, ppm): δ 182.36 (COO); 53.29 (CH); 39.84 (CH_2); 126.34–139.03 (Ar–C); 13.27, 26.09, 27.17, 29.64 (butyl-C). ^{119}Sn NMR ($CDCl_3$, ppm): δ −141.94.

3.3. *X-ray crystallographic studies*

Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected with a Smart CCD area detector with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A semiempirical 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 [28]. Hydrogen atoms were placed in the calculated positions. Crystal data and experimental details of the structure determinations are listed in table 6.

4. Conclusion

A series of organotin complexes based on 2,3-diphenylpropionic acid have been synthesized. Spectra and crystal structures show 1-D polymeric chains, drum structures, chain-like ladder with metal-organic structures and monomers. In general, trimethyltin carboxylate and tributyltin carboxylate mainly assume 1-D polymeric chains (such as **1** and **2**). Triphenyltin carboxylate adopts a drum structure (**3**) where two Sn–C bonds ruptured during the reaction, leaving only one phenyl connected with tin in **3**. Dibutyltin carboxylate often assumes monomer structures (such as in **5**), whereas dimethyltin carboxylate (**4**) forms chain-like ladders. This may be related to the spatial hindrance of the organotin group. To design organotin complexes with desired structures and high anti-tumor activities, more work is required to explore new complexes using deprotonated carboxylic acids attached with different tin salts.

Table 6. Crystallographic data and structure refinement parameters for **1–5**.

Complex	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{18}H_{22}O_2Sn$	$C_{54}H_{80}O_4Sn_2$	$C_{126}H_{108}O_{18}Sn_6$	$C_{68}H_{76}O_{10}Sn_4$	$C_{18}H_{22}O_2Sn$
Formula weight	389.05	1030.56	2622.26	1528.05	683.42
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P212121$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P21212$
Unit cell dimensions (Å, °)					
a	9.9898(9)	10.1935(8)	27.171(3)	11.5448(11)	16.2419(17)
b	10.1263(11)	12.9231(11)	16.0763(18)	16.4384(15)	18.7261(18)
c	17.8530(15)	22.9307(18)	26.418(3)	19.9552(18)	5.6280(5)
α	90	86.455(2)	90	107.465(2)	90
β	90	83.6760(10)	100.664(2)	101.6210(10)	90
γ	90	67.9670(10)	90	99.6530(10)	90
Volume (Å^3), Z	1806.0(3), 4	2782.4(4), 2	11340(2), 4	3431.3(5), 2	1711.7(3), 2
Calculated density (Mg m^{-3})	1.431	1.230	1.536	1.479	1.326
Absorption coefficient (mm^{-1})	1.417	0.936	1.367	1.492	0.783
$F(000)$	784	1072	5232	1528	708
Crystal size (mm^3)	$0.44 \times 0.36 \times 0.33$	$0.32 \times 0.10 \times 0.08$	$0.34 \times 0.22 \times 0.15$	$0.24 \times 0.15 \times 0.08$	$0.47 \times 0.34 \times 0.30$
Reflections collected	8866	14,332	28,025	17,579	8850
Independent reflections	3161 [R(int) = 0.0355]	9695 [R(int) = 0.1962]	9992 [R(int) = 0.1006]	11,945 [R(int) = 0.1337]	3036 [R(int) = 0.0687]
Goodness-of-fit on F^2	1.055	1.102	1.109	0.938	1.060
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0405$, $wR_2 = 0.0830$	$R_1 = 0.2216$, $wR_2 = 0.4552$	$R_1 = 0.0861$, $wR_2 = 0.2055$	$R_1 = 0.1095$, $wR_2 = 0.2529$	$R_1 = 0.0670$, $wR_2 = 0.1682$
R indices (all data)	$R_1 = 0.0575$, $wR_2 = 0.0945$	$R_1 = 0.4125$, $wR_2 = 0.5490$	$R_1 = 0.1385$, $wR_2 = 0.2630$	$R_1 = 0.2190$, $wR_2 = 0.3322$	$R_1 = 0.1013$, $wR_2 = 0.1906$

Supplementary material

CCDC 865664 (**1**), 865665 (**2**), 865666 (**3**), 865667 (**4**) and 865668 (**5**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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