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New organotin carboxylates derived from 6-chloro-3-pyridineacetic acid exhibiting discrete molecular, drum-like, linear polymeric and ladder structures constructed from dimeric tetraorganodistannoxane units

Jun-Hong Zhang^{a,c}, Ru-Fen Zhang^{a,*}, Chun-Lin Ma^{a,b}, Da-Qi Wang^a, Hai-Zeng Wang^c

^a Department of Chemistry, Liaocheng University, Liaocheng 252059, PR China

^b Taishan University, Taian 271021, PR China

^c College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, Shandong, PR China

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ABSTRACT

Seven new organotin (IV) carboxylates have been synthesized by the reactions of 6-chloro-3-pyridineacetic acid with triorganotin chloride and diorganotin dichloride. All the complexes were characterized by elemental analysis, IR, ¹H NMR, ¹³C NMR, ¹¹⁹Sn NMR and X-ray crystallography. The structural analyses show that all the complexes present various structures, including monomer, drum, 1D polymers and ladders. It is worth noting that complex **1** is a novel 1D spring-like helical chain containing guest solvent molecules.

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1. Introduction

It is well known that organotin carboxylates have versatile molecular structures, both in the solid state and in solution, such as monomers, dimers, tetramers, oligomeric ladders and hexameric drums, etc. [1–4]. It has also been demonstrated that other structural types are formed due to the presence of additional heteroatom sites (S, N or O, etc.) along with a carboxylate moiety [5-10]. In our previous work, we have reported some new organotin complexes, including a macrocycle containing five tin nuclei with heterocyclic sulfur and nitrogen donor ligands and macrocyclic complexes containing 3 and 18 tin nuclei with 2mercaptonicotinic [11,12], as well as a novel 2D network polymer containing a 60-membered organotin macrocycle [13]. To continue our research on organotin (IV) complexes in this field, we chose another carboxylic acid ligand, 6-chloro-3-pyridineacetic acid, and obtained seven new organotin carboxylates by the use of this ligand with triorganotin chloride and diorganotin dichloride. These complexes have been characterized by elemental analysis, IR, ¹H, ¹³C and ¹¹⁹Sn NMR spectroscopy and X-ray crystallography. In this article, we report the synthesis, characterization and crystal structures of these organotin carboxylates.

2. Results and discussion

2.1. Spectra of complexes 1-7

The main feature in the IR spectra of complexes **1–7** is the absence of bands in the region $3170-2990 \text{ cm}^{-1}$, which appear in the free ligand as CO₂H stretching vibrations, thus indicating metal–ligand bonding through these sites. The typical absorptions for Sn-C, Sn-O vibrations in all the complexes are located in the normal range of similar organotin complexes [14,15].

The ¹H NMR spectra shows the signals of the $-CO_2H$ proton, present in the spectrum of the ligand, are absent in all the complexes, indicating the removal of the $-CO_2H$ proton and the formation of Sn-O bonds. According to the literature [16], signals for complexes **1–2** and **4–6** in the ¹¹⁹Sn NMR spectra indicate the same coordination environments in the solid state and in solution; while for complexes **3** and **7**, the ¹¹⁹Sn NMR spectroscopic data ($\delta = 48.2$ and -18.3 ppm, respectively) show signals in the range of four-coordinated tin complexes, so it can reasonably be assumed that the environments around the tin atoms in complexes **3** and **7** are different in the solid state and in solution.

2.2. Crystal structures of complexes 1-7

2.2.1. { (Ph_3Sn)](COO)(CH₂C₅H₃NCl)]}_n (**1**)

Selected bond lengths and bond angles of complex **1** are shown in Table 1, the repeating unit, 1D chain structure and perspective



^{*} Corresponding author. Tel.: +86 635 8238121; fax: +86 538 6715521. *E-mail address:* yver123@163.com (R.-F. Zhang).

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

		-	
Sn(1)-O(1A)	2.23(3)	Sn(1)-O(2B)	2.24(3)
Sn(2)-O(1B)	2.29(3)	Sn(2)-O(2C)	2.30(3)
Sn(3)-O(1C)	2.22(3)	Sn(3)-O(2D)	2.25(3)
Sn(4)-O(1D)	2.26(3)	Sn(4)-O(2E)	2.28(4)
Sn(5)-O(1E)	2.24(3)	Sn(5)-O(2F)	2.31(3)
Sn(6)-O(2G)	2.28(4)	Sn(6)-O(1F)	2.32(4)
Sn(7)-O(2H)	2.18(4)	Sn(7)-O(1G)	2.27(4)
Sn(8)-O(2I)	2.19(4)	Sn(8)-O(1H)	2.22(5)
Sn(9)-O(1I)	2.23(3)	Sn(9)-O(2J)	2.26(3)
Sn(10)-O(1J)	2.22(3)	Sn(10)-O(2A)#1	2.28(3)
O(1A)-Sn(1)-O(2B)	177.2(10)	O(1B)-Sn(2)-O(2C)	175.6(11)
O(1C)-Sn(3)-O(2D)	176.2(12)	O(1D)-Sn(4)-O(2E)	178.7(12)
O(1E)-Sn(5)-O(2F)	173.8(15)	O(2G)-Sn(6)-O(1F)	179.3(15)
O(2H)-Sn(7)-O(1G)	178.4(17)	O(2I)-Sn(8)-O(1H)	177.1(14)
O(1I)-Sn(9)-O(2J)	175.2(13)	O(1J)-Sn(10)-O(2A)#1	174.2(11)

Symmetry code for complex 1: #1 x - 1, y, z.

view along a axis of **1** are shown in Figs. 1–3, respectively. By searching the CSD, we found that although some 1D chain organotin structures have been reported [17-20], such novel 1D springlike helical chains are rare. The crystal structure of complex 1 is constructed from a 1D helical chain consisting of [(Ph₃Sn) (C₇H₅ClNO₂)] entities, Fig. 1 shows a perspective view of the [(Ph₃Sn)(C₇H₅ClNO₂)] entity. In complex **1**, all the tin atoms possess the same coordination environment. The coordination about the tin atom is only slightly distorted from a regular trigonal bipyramidal geometry. As the result of the bidentdate mode of coordination about the carboxylic acid, each tin center is five-coordinated and exists in a trigonal bipyramidal geometry with the coordinated oxygen atoms occupying the axial sites, the Sn-O distances [2.18(3)–2.32(4) Å] are similar to those reported in other organotin complexes [21,22], and approach the sum of the covalent radii of tin and oxygen [23], which prove the oxygen atoms are coordinated to the tin atoms by strong chemical bonds. The O-Sn-O angles [173.8(15)–179.3(15)°] are close to linear arrangements. The Sn–C bond lengths [2.02(6)–2.23(5)Å] are consistent with those reported in other triorganotin carboxylates [24-26]. The repeating [(Ph₃Sn)(C₇H₅ClNO₂)] units are linked by intermolecular Sn–O bonds, thus giving a 1D spring-like helical chain with a columnar channel. It is worth mentioning here that the solvent benzene molecules are captured in this channel (Figs. 2 and 3), and one benzene molecule is included per 10 monomer units.

2.2.2. $\{(Me_3Sn)[(COO)(CH_2C_5H_3NCl)]\}_n$ (2)

Selected bond lengths and bond angles for complex **2** are given in Table 2, and the 1D polymeric chain structure of complex **2** is



Fig. 1. The repeating unit of complex 1.

shown in Fig. 4. Similar to complex **1**, the carboxylic acid adopts a bidentate mode and coordinates to the tin atoms. The geometry of the tin center is a distorted trigonal bipyramid, and the center tin atom is five-coordinated with the two oxygen atoms occupying the axial sites; the O–Sn–O axial angles are O(2)–Sn(1)–O(4)#1 175.3(6)° and O(3)–Sn(2)–O(1) 173.9(6)°. Three Sn-methyl groups define the equatorial plane, and the sum of the trigonal C–Sn–C angles are 359.1° and 358.7°, which illustrates that the three methyl groups and tin atoms are nearly coplanar. As shown in Fig. 4, each deprotonated 6-chloro-3-pyridineacetic acid acts as a bidentate ligand, connecting two adjacent tin atoms and giving rise to an infinite zigzag chain, which is different from complex **1** and consistent with that found in our previous work [27].

2.2.3. { $(PhCH_2)_3Sn$](COO)(CH₂C₅H₃NCl)]}·H₂O (**3**)

Selected bond lengths and bond angles for complex **3** are given in Table 3, and the molecular structure of complex **3** is shown in Fig. 5. Complex **3** is a monomer, which is different from complexes **1** and **2**, and the carboxy group adopts a monodentate mode of coordination to the tin atom in complex **3**, whereas a bidentate mode is adopted in complexes **1** and **2**. The central tin atom of complex **3** is five-coordinated with a distorted trigonal bipyramidal geometry, the carboxylic oxygen atom and an additional water molecule occupying the axial sites, and the axial angle O(1)–Sn(1)– O(3) is 172.37(10)°. The primary bond lengths in complex **3** are: Sn(1)–O(1) 2.141(3) Å and Sn(1)–O(3) 2.430(3) Å. All the Sn–O bonds are comparable with those found in other similar organotin complexes [28].

2.2.4. [PhSn(0)(COO)(CH₂C₅H₃NCl)]₆ (4)

Selected bond lengths and bond angles for complex 4 are given in Table 4, and the molecular structure of complex 4 is shown in Fig. 6. Complex 4 has a typical drum structure. Although we used diphenyltin dichloride as a raw material, in the reaction process one phenyl group was lost and a stable drum structure was formed because of hydrolysis. The centrosymmetric structure is built around a Sn₆O₆ central stannoxane core which contains two puckered six-membered $[Sn_3(\mu_3-0)_3]$ rings as its top and bottom faces. The two $[Sn_3(\mu_3-0)_3]$ rings are connected further by six Sn-O bonds, provided by tri-coordinated O atoms. Thus the side face of the drum is characterized by six puckered four-membered $[Sn_2(\mu_3-O)_2]$ rings. Alternate tin atoms are held together by the coordination action of bidentate carboxylate groups to form a symmetrical bridge between two carboxylate ligands. This represents the signature structural feature of stannoxane clusters. In general, the Sn-O bond lengths inside the core range between 2.08 and 2.14 Å, and these distances are comparatively shorter than the Sn-O bonds to the bridging carboxylate ligands (2.16 (3)-2.21(6)Å) [29]. The Sn–O–Sn bond angles in the six-membered rings, in the ranges 99.4(5)–135.0(6)°, are wider than those found in the four-membered rings. The four-membered $[Sn_2(\mu_3-O)_2]$ rings are not planar, the oxygen atoms being tilted toward the cavity of the drum. Thus the interior of the drum can be considered as a crown made of six oxygen atoms in a trigonal antiprismatic arrangement, and this was approved by the Sn-O bond lengths. The oxygen atoms from the bridging carboxylate ligands occupy two of the coordination sites, and the sixth coordination site is occupied by a carbon atom from the phenyl group, such that the O_5C donor set defines a distorted octahedron. In complex 4, the distance between the planes defined by the six tin atoms is about 2.3 Å, so we can image a center residing in the interior of the cavity. The center is defined by a crown of six oxygen atoms in a trigonalantiprismatic arrangement, where the average O-O distance is 2.63 Å and the average distance from the center of the cavity to the O atoms is 2.12 Å. On the basis of a van der Waals radius of 1.40 Å for oxygen, the interior of the cavity could thus host a spe-



Fig. 2. The 1D spring-like helical chain structure of complex 1 (the phenyl groups are omitted for clarity).



Fig. 3. Perspective view along the a axis of complex 1, from this angle of view we can distinctly see the benzene molecules which are captured by the columnar channel of 1.

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

Sn(1)-C(16)	2.06(2)	Sn(1)-C(17)	2.105(16)
Sn(1)-C(15)	2.15(3)	Sn(1)-O(2)	2.191(17)
Sn(1)-O(4)#1	2.370(11)	Sn(2)-C(19)	2.107(17)
Sn(2)-C(18)	2.12(3)	Sn(2)-C(20)	2.131(18)
Sn(2)-O(3)	2.167(19)	Sn(2)-O(1)	2.368(12)
C(16)-Sn(1)-C(17)	125.2(9)	C(16)-Sn(1)-C(15)	116.7(10)
C(17)-Sn(1)-C(15)	117.2(11)	C(16)-Sn(1)-O(2)	93.2(8)
C(17)-Sn(1)-O(2)	95.7(6)	C(15)-Sn(1)-O(2)	90.7(10)
C(16)-Sn(1)-O(4)#1	88.4(7)	C(17)-Sn(1)-O(4)#1	87.0(6)
C(15)-Sn(1)-O(4)#1	84.6(9)	O(2)-Sn(1)-O(4)#1	175.3(6)
C(19)-Sn(2)-C(18)	117.4(10)	C(19)-Sn(2)-C(20)	124.6(8)
C(18)-Sn(2)-C(20)	116.7(9)	C(19)-Sn(2)-O(3)	93.9(8)
C(18) - Sn(2) - O(3)	91.0(9)	C(20)-Sn(2)-O(3)	96.0(8)
C(19)-Sn(2)-O(1)	87.0(7)	C(18)-Sn(2)-O(1)	83.2(8)
C(20)-Sn(2)-O(1)	88.4(7)	O(3)-Sn(2)-O(1)	173.9(6)

Symmetry code for complex **2**: #1 x + 1, y – 1, z.

cies with a radius of approximate 0.70 Å. The entrance to the cavity is defined by three oxygen atoms arranged as an approximate equilateral triangle with an average edge length (oxygen center to oxygen center) of 3.27 Å. Again with 1.40 Å as the van der Waals radius of oxygen, species with radii up to about 0.50 Å could gain entrance to the cavity.

2.2.5. { $(Bu_2Sn)_2(O)[(COO)(CH_2C_5H_3NCI)]_2$ } (**5**), { $(Me_2Sn)_2(O)[(COO)(CH_2C_5H_3NCI)]_2$ } (**6**) and { $[(PhCH_2)_2Sn)]_2$ [$(O)(COO)(CH_2C_5H_3NCI)]$ }·2CH₃OH (**7**)

Selected bond lengths and bond angles for complexes **5**–**7** are given in Table 5; the molecular structures of complexes **5** and **7** are shown in Figs. 7 and 9, respectively; while the 1D chain structure of complex **6** is shown in Fig. 8. In complexes **5–7** the hydrolysis occurred because of the presence of water molecules in the benzene solvent. Complexes **5–7** are all typical organotin ladders



Fig. 4. The 1D infinite zigzag chain structure of complex 2.

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

Sn(1)-C(22)	2.133(4)	Sn(1)-C(15)	2.138(4)
Sn(1)-O(1)	2.141(3)	Sn(1)-C(8)	2.146(4)
Sn(1)-O(3)	2.430(3)	C(22)-Sn(1)-C(15)	119.39(18)
C(22)-Sn(1)-O(1)	91.75(14)	C(15)-Sn(1)-O(1)	94.22(14)
Sn(2)-O(3)	2.167(19)	Sn(2)-O(1)	2.368(12)
C(22)-Sn(1)-C(8)	120.49(19)	C(15)-Sn(1)-C(8)	117.36(16)
O(1)-Sn(1)-C(8)	100.69(14)	C(22)-Sn(1)-O(3)	81.98(13)
C(15)-Sn(1)-O(3)	85.16(14)	O(1)-Sn(1)-O(3)	172.37(10)

Symmetry code for complex **3**: #1 x + 1, y - 1, z.



Fig. 5. The molecular structure of complex 3.

made up of dimeric tetraorganodistannoxane and bridging carboxylate units, but they are not completely the same.

The structure of complex **5** is based on a centrosymmetric Sn_2O_2 unit connected to a pair of exocyclic Sn atoms via bridging oxygen atoms, so that the bridging oxygen atoms are tri-coordinative and cap three tin atoms. There are two diverse carboxylate groups in this structure. One carboxylate ligand is bidentate bridging and bridges both the endocyclic and exocyclic Sn atoms via O(1) and O(2) atoms, and the other carboxylate ligand is monodentate. The endocyclic tin atom, Sn(2), forms five significant bonds in this structure. A coordination number of six is found for the exocyclic

Table 4				
Selected bon	i lengths (Å) and angles	(°) for	complex 4.

Sn(1)-O(1)	2.118(12)	Sn(1)-O(3)#1	2.120(13)
Sn(1)-O(2)	2.124(12)	Sn(1)-O(5)	2.211(13)
Sn(1)-Sn(2)	3.2461(17)	Sn(2)-O(2)	2.113(13)
Sn(2)-O(3)	2.121(12)	Sn(2)-O(1)	2.123(12)
Sn(2)-O(7)	2.192(15)	Sn(2)-O(6)	2.199(13)
Sn(3)-O(3)	2.126(12)	Sn(3)-O(2)#1	2.131(12)
Sn(3)-O(1)	2.139(11)	Sn(3)-O(8)	2.184(15)
O(1)-Sn(1)-O(3)#1	107.0(5)	O(1)-Sn(1)-O(2)	78.3(5)
O(3)#1-Sn(1)-O(2)	79.0(5)	O(1)-Sn(1)-O(10)#1	157.1(5)
O(2)-Sn(1)-O(10)#1	87.4(5)	O(1)-Sn(1)-O(5)	84.6(5)
O(2)-Sn(1)-O(5)	88.3(5)	O(2)-Sn(2)-O(3)	103.5(5)
O(2)-Sn(2)-O(1)	78.4(5)	O(3)-Sn(2)-O(1)	78.3(5)
O(2)-Sn(2)-O(7)	161.3(5)	O(3) - Sn(2) - O(7)	85.4(5)
O(1)-Sn(2)-O(7)	87.6(5)	O(2)-Sn(2)-O(6)	89.6(5)
O(3) - Sn(2) - O(6)	155.1(5)	O(1)-Sn(2)-O(6)	83.9(5)
O(3)-Sn(3)-O(8)	86.4(5)	O(1)-Sn(3)-O(8)	86.9(5)
O(3)-Sn(3)-O(9)	88.8(5)	O(1)-Sn(3)-O(9)	161.8(5)

Symmetry code for complex **4**: #1 - x + 2, -y + 1, -z + 1.



Fig. 6. The molecular structure of complex 4 (the phenyl groups are omitted for clarity).

Table 5
Selected bond lengths (Å) and angles (°) for complexes 57

Complex 5			
Sn(1) - O(5)	2.059(9)	Sn(1)-C(15)	2.075(18)
Sn(1)-O(5)#1	2.125(9)	Sn(1) - C(19)	2.132(19)
Sn(1) - O(1)	2.321(11)	Sn(1) - Sn(1) # 1	3.2898(18)
Sn(2) - O(5)	2.029(10)	Sn(2) - C(23)	2.071(19)
Sn(2) - C(27)	2.086(19)	Sn(2) = O(3)	2.203(9)
O(5) - Sn(1) - O(5) # 1	76.3(4)	O(5) - Sn(1) - O(1)	87.4(4)
O(5)#1-Sn(1)-O(1)	162.8(4)	O(5)-Sn(2)-O(3)	77.5(4)
O(5) - Sn(2) - O(2)	91.5(4)	O(3)-Sn(2)-O(2)	167.9(4)
C(27) - Sn(2) - O(2)	92.8(6)	C(23)-Sn(2)-O(3)	92.3(6)
Complex 6			
$S_{p}(1) O(1)$	2.071(4)	$S_{p}(1) C(20)$	2100(7)
Sn(1) = O(1) Sn(1) = O(2)	2.071(4)	Sn(1) - C(29)	2.100(7)
SII(1) = O(3) Sp(1) = O(8) # 1	2.215(5)	SII(1) = O(9)	2.290(3)
SII(1) = O(0) # 1 Sp(2) = C(21)	2.313(3)	SII(2) = O(2)	2.076(4)
SII(2) = C(SI) SII(2) = O(5)	2.100(8)	SII(2) = O(1)	2.132(4)
SII(2) = O(3) Sn(2) = O(2)	2.314(0) 2.001(4)	Sn(2) = O(4)	2.430(3)
Sn(3) = O(2) Sn(3) = O(7)	2.001(4) 2.246(5)	Sn(4) O(1)	2.233(3)
Sn(3) = O(7) Sn(4) = O(2)	2.240(3) 2.125(4)	Sn(4) = O(1)	2.039(4) 2.205(5)
O(1) Sp(1) O(2)	2.123(4) 0472(19)	O(1) Sp(1) O(0)	2.293(3)
O(1) - 3I(1) - O(3) O(2) Sp(1) O(0)	$\frac{54.72(10)}{170.19(10)}$	O(1) - SI(1) - O(3)	33.10(18) 17154(18)
O(3) = 3II(1) = O(3) O(2) = Sn(1) = O(3) #1	76 92(19)	O(1) - SI(1) - O(8) + 1 O(2) Sp(2) O(1)	76 77(17)2
O(3) = 3II(1) = O(3) # 1 O(3) = Sn(3) = O(5)	70.82(18) 97.05(10)	O(2) - SI(2) - O(1) O(1) Sp(2) O(5)	162 72(10)
O(2) - Sn(2) - O(3)	163 /1(17)	O(1) - Sn(2) - O(3)	86 66(16)
O(2) - Sn(2) - O(4)	100.41(17)	O(2) - Sn(2) - Sn(4)	30.54(12)
O(3) - Sn(2) - Sn(4)	37 50(11)	O(2) - Sn(2) - Sn(4)	12622(15)
O(1) - Sn(2) - Sn(4)	97.30(11)	O(2) - Sn(2) - O(7)	70.27(17)
O(2) Sn(3) O(0) O(1) - Sn(4) - O(10)	88 07(18)	O(1) - Sn(4) - Sn(2)	39 52(12)
0(1) 51(4) 0(10)	00.07(10)	O(1) SI(4) SI(2)	55.52(12)
Complex 7			
Sn(1) - O(3)	2.034(3)	Sn(1) - C(15)	2.142(6)
Sn(1) - C(8)	2.148(6)	Sn(1) - O(1)	2.158(4)
Sn(1) - O(4)	2.262(4)	Sn(2) - O(3)	2.048(3)
Sn(2)-C(22)	2.122(6)	Sn(2) - O(4)	2.126(4)
Sn(2)–O(3)#1	2.138(3)	Sn(2)-C(29)	2.156(6)
O(3) - Sn(1) - O(1)	82.95(14)	O(3) - Sn(1) - O(4)	71.16(13)
O(1)-Sn(1)-O(4)	153.82(14)	O(3) - Sn(2) - O(4)	73.78(13)
O(3)-Sn(2)-O(3)#1	73.86(14)	C(22)-Sn(2)-O(3)#1	95.9(2)
O(4)-Sn(2)-C(29)	97.5(2)	O(3)#1-Sn(2)-C(29)	98.6(2)

Symmetry code for complex **5**: #1 - x + 1, -y + 1, -z + 1; symmetry code for complex **6**: #1 - x + 1, -y + 1, -z + 1; symmetry code for complex **7**: #1 - x + 1, -y + 1, -z + 1.

tin atom, Sn(1), which exists in a octahedral geometry with the carboxylate oxygen atoms in *trans* positions. As a consequence, the endocyclic and exocyclic tin atoms are six-coordinated and fivecoordinated, respectively.

The predominant structural form of complex **6** is a dimeric dicarboxylatotetraorganodistannoxane, which consists of a central planar (Me₂Sn)₂O₂ four-membered ring and two peripheral Me₂Sn units. Each bridging oxygen atom in the Sn₂O₂ ring is attached to three Me₂Sn units and as a result these oxygen atoms are threecoordinated. The geometries of all the tin atoms in complex 6 can be classified into two types: pentacoordinated tin (Sn(1) and Sn(3)), and hexacoordinated tin (Sn(2) and Sn(4)). Each of the pentacoordinated tin atoms, Sn(1) for example, forms three short Sn-O bonds with three oxygen atoms: one from the Sn₂O₂ moiety and the other two from two different carboxylate groups. Together with the two bonds to methyl groups, the geometry of the Sn(1)atom may be viewed as a slightly distorted trigonal bipyramid with the axial site occupied by two different carboxylic oxygen atoms. Each of the hexacoordinated tin atoms, Sn(2) for example, has an octahedral geometry with four equatorial oxygen atoms and two axial carbon atoms, the geometry being somewhat distorted by the small angles in the stannoxane rings, affecting the equatorial angles. As shown in Fig. 8, complex 6 forms a one-dimensional infinite chain linked by bidentate carboxylic oxygen atoms. This structural feature of complex 6 is quite different from that of $\{(Me_2Sn(OAc)_2O)_2\}_n$, a one-dimensional organotin polymer in which the acetate links the dimeric tetraorganodistannoxane units in a tetradentate mode [30].

The structure of complex **7** is different from complexes **5** and **6**. In complex **7** only two carboxylate ligands coordinate to the tin atoms, and all the ligands are monodentate. Furthermore, two solvent methanol molecules coordinate to the tin atoms, together with the two bonds of benzyl groups and the tri-coordinative oxygen atoms, so all the tin atoms in complex **7** are five-coordinated and the geometry of the tin atoms is trigonal bipyramidal. All the bond lengths and bond angles are similar those in complexes **5** and **6**.

3. Conclusion

In summary, we have obtained a series of new organotin (IV) carboxylates by the reactions of 6-chloro-3-pyridineacetic acid with triorganotin chloride and diorganotin dichloride. In our work, various structures are found, including 1D spring-like helical chain, infinite zigzag chain, drum, monomer and ladders. Especially, in complex **1** a novel spring-like helical chain containing guest solvent molecules is observed, which has not been reported previously in the literature. It should be noted that although the carboxylic acid ligand has a heterocyclic nitrogen atom, the nitrogen atom does not show any obvious interaction to the tin atoms; maybe spatial hindrance from the organic groups blocks the nitro-



Fig. 7. The molecular structure of complex 5 (only one carbon atom of the butyl group is shown for clarity).



Fig. 8. The 1D infinite chain structure of complex 6 (the methyl groups are omitted for clarity).



Fig. 9. The molecular structure of complex **7** (only one carbon atom of the benzyl group is shown for clarity).

gen atom from coordinating to the tin atoms. These organotin structures reported in this paper further enrich organotin chemistry in the structural field.

4. Experimental details

4.1. Materials and measurements

Triorganotin chloride, diorganotin dichloride and 6-chloro-3pyridineacetic acid are commercially available and they were used without further purification. The melting points were obtained with an X-4 digital micro melting-point apparatus and were uncorrected. Infrared-spectra were recorded on a Nicolet-5700 spectrophotometer using KBr discs and sodium chloride optics. ¹H, ¹³C and ¹¹⁹Sn NMR spectra were recorded on 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; the ¹³C NMR spectra are broadband proton decoupled. The chemical shifts were reported in ppm with respect to the references and were stated relative to external tetramethylsilane (TMS) for ¹H and ¹³C NMR spectra, and to neat tetramethyltin for ¹¹⁹Sn NMR spectra [31]. Elemental analyses (C, H and N) were performed with a PE-2400II apparatus.

4.2. Syntheses of complexes 1-7

4.2.1. { $(Ph_3Sn)[(COO)(CH_2C_5H_3NCl)]$ }_n (**1**)

6-Chloro-3-pyridineacetic acid (0.172 g, 1 mmol) and sodium ethoxide (0.068 g, 1 mmol) were added to a solution of benzene (30 ml) in a Schlenk flask, and the mixture was stirred for 10 min. Then triphenyltin chloride (0.385 g, 1.00 mmol) was added to the mixture, and the reaction mixture was stirred for 12 h at 40 °C. The solution was filtered and the filtrate was gradually removed by evaporation under vacuum until a solid product was obtained. Crystals of complex **1** were obtained by recrystallisation from dichloromethane. Yield: 70%. M.p. 144–146 °C. Anal. Calc. for C₂₆₈H₂₁₈Cl₁₀N₁₀O₂₀Sn₁₀: C, 59.17; H, 4.04; N, 2.57. Found: C, 59.48; H, 4.33; N, 2.24%. IR (KBr, cm⁻¹): 1622 v_{as}(COO), 1419 v_s(COO), 511 v(Sn-C), 442 v(Sn-O). ¹H NMR (CDCl₃) δ (ppm): 7.24–8.29 (m, 198H, Ar-H), 3.58 (s, 20H, CH₂). ¹³C NMR (CDCl₃) δ (ppm): 174.6 (COO), 124.1–150.9 (Ar-C), 37.6 (CH₂). ¹¹⁹Sn NMR δ (ppm): –118.5.

4.2.2. $\{(Me_3Sn) | (COO) (CH_2C_5H_3NCl) \}_n$ (2)

Complex **2** was prepared in a similar way to complex **1**, using 6chloro-3-pyridineacetic acid (0.172 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), trimethyltin chloride (0.199 g, 1 mmol) and benzene (30 ml). Crystals of complex **2** were obtained on recrystallisation from dichloromethane. Yield: 75%. M.p. 156–158 °C. *Anal.* Calc. for C₂₀H₂₈Cl₂N₂O₄Sn₂: C, 35.92; H, 4.22; N, 4.19. Found: C, 36.17; H, 4.51; N, 3.95%. IR (KBr, cm⁻¹): 1628 v_{as} (COO), 1433 v_{s} (COO), 508 v(Sn-C), 462 v(Sn-O). ¹H NMR (CDCl₃) δ (ppm): 7.01–8.66 (m, 6H, Ar-H), 3.32 (s, 4H, CH₂), 0.88 (s, 18H, CH₃). ¹³C NMR (CDCl₃) δ (ppm): 175.3 (COO), 122.8–150.1 (Ar-C), 38.3 (CH₂), 13.8 (CH₃). ¹¹⁹Sn NMR δ (ppm): –133.7.

4.2.3. { $(PhCH_2)_3Sn$](COO)(CH₂C₅H₃NCl)]}·H₂O (**3**)

Complex **3** was prepared in a similar way to complex **1**, using 6chloro-3-pyridineacetic acid (0.172 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), tribenzyltin chloride (0.427 g, 1 mmol) and, benzene (30 ml). Crystals of complex **3** were obtained on recrystallisation from dichloromethane. Yield: 69%. M.p. 137–139 °C. *Anal.* Calc. for C₂₈H₂₈ClNO₃Sn: C, 57.91; H, 4.86; N, 2.41. Found: C, 57.63; H, 4.59; N, 2.68%. IR (KBr, cm⁻¹): 1657 ν_{as} (COO), 1403 ν_{s} (COO), 523 ν (Sn-C), 435 ν (Sn-O). ¹H NMR (CDCl₃) δ (ppm): 7.17–8.28 (m, 18H, Ar-H), 3.67 (s, 2H, CH₂), 2.35 (s, 6H, Sn-CH₂). ¹³C NMR (CDCl₃) δ (ppm): 172.8 (COO), 127.5–149.7 (Ar-C), 37.9 (CH₂), 26.8 (CH₂–Sn). ¹¹⁹Sn NMR δ (ppm): 48.2.

4.2.4. [PhSn(O)(COO)(CH₂C₅H₃NCl)]₆ (4)

Complex **4** was prepared in a similar way to complex **1**, using 6chloro-3-pyridineacetic acid (0.172 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), diphenyltin dichloride (0.343 g, 1 mmol) and methanol (30 ml). Crystals of complex **4** were obtained on recrystallisation from diethyl ether. Yield: 67%. M.p. 211–213 °C. *Anal.* Calc. for C₇₈H₆₀C₁₆N₆O₁₈Sn₆: C, 40.83; H, 2.64; N, 3.66. Found: C, 40.57; H, 2.45; N, 3.86%. IR (KBr, cm⁻¹): 1586 v_{as} (COO), 1382 v_{s} (COO), 648 v(O-Sn-O), 515 v(Sn-C), 452 v(Sn-O). ¹H NMR (CDCl₃) δ (ppm): 7.18–8.42 (m, 48H, Ar-H), 3.45 (s, 12H, CH₂). ¹³C NMR (CDCl₃) δ (ppm): 173.1 (COO), 124.1–150.1 (Ar-C), 37.5 (CH₂). ¹¹⁹Sn NMR δ (ppm): –340.6.

4.2.5. $\{(Bu_2Sn)_2(0)|(COO)(CH_2C_5H_3NCl)|_2\}$ (5)

Complex **5** was prepared in a similar way to complex **1**, using 6chloro-3-pyridineacetic acid (0.172 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), dibutyltin dichloride (0.303 g, 1 mmol) and methanol (30 ml). Crystals of complex **5** were obtained by recrystallisation from diethyl ether. Yield: 78%. M.p. 182–184 °C. *Anal.* Calc. for C₆₀H₉₂C₁₄N₄O₁₀Sn₄: C, 43.78; H, 5.63; N, 3.40. Found: C, 43.95; H, 5.32; N, 3.64%. IR (KBr, cm⁻¹): 1673, 1589 v_{as} (COO), 1412, 1391 v_s (COO), 653 v(O-Sn-O), 524 v(Sn-C), 437 v(Sn-O). ¹H NMR (CDCl₃) δ (ppm): 7.28–8.29 (m, 12H, Ar-H), 3.50 (s, 8H, Ar-CH₂), 1.21–1.58 (m, 48H, CH₂–CH₂–CH₂), 0.87 (t, 24H, CH₃). ¹³C NMR (CDCl₃) δ (ppm): 177.5 (COO), 121.9–150.4 (Ar-C), 37.6 (Ar-CH₂), 25.4–29.1 (Sn-CH₂–CH₂–CH₂), 13.6 (CH₃). ¹¹⁹Sn NMR δ (ppm): –263.8, –137.2.

4.2.6. $\{(Me_2Sn)_2(0)[(COO)(CH_2C_5H_3NCl)]_2\}_n$ (6)

Complex **6** was prepared in a similar way to complex **1**, using 6chloro-3-pyridineacetic acid (0.172 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), dimethyltin dichloride (0.219 g, 1 mmol) and methanol (30 ml). Crystals of complex **6** were obtained by recrystallisation from diethyl ether. Yield: 75%. M.p. 150–152 °C. *Anal.* Cacl. for C₃₆H₄₄Cl₄N₄O₁₀Sn₄: C, 33.02; H, 3.39; N, 4.28. Found: C, 33.34; H, 3.65; N, 4.02%. IR (KBr, cm⁻¹): 1590 v_{as} (COO), 1384 v_s (COO), 649 v(O-Sn-O), 520 v(Sn-C), v(Sn-O) 446. ¹H NMR (CDCl₃) δ (ppm): 7.26–8.27 (m, 12H, Ar-H), 3.55 (s, 8H, Ar-CH₂), 0.97 (s,

Table 6

Crystal data and structure refinement parameters for complexes 1-4

Complex	1	2	3	4
Empirical formula	C ₂₆₈ H ₂₁₈ C ₁₁₀ N ₁₀ O ₂₀ Sn ₁₀	$C_{20}H_{28}C_{12}N_2 O_4Sn_2$	C28H28CINO3Sn	C78H60Cl6N6 O18Sn6
Formula weight	5443.70	714.39	580.65	2294.16
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	Сс	ΡĪ	P2(1)/c	ΡĪ
a (Å)	15.3106(14)	6.7992(11)	13.8291(14)	11.7306(10)
b (Å)	51.192(5)	9.9628(15)	11.8991(12)	14.1721(14)
c (Å)	35.568(3)	10.8971(16)	17.5097(16)	14.3501(15)
α (°)	90	68.2320(10)	90	70.4470(10)
β(°)	99.814(2)	76.676(2)	109.9180(10)	74.576(2)
γ(°)	90	71.0100(10)	90	72.3780(10)
V (Å ³)	27470(4)	643.13(17)	2708.9(5)	2106.3(4)
Ζ	4	1	4	1
$\mu (\mathrm{mm}^{-1})$	1.048	2.176	1.070	2.011
Reflections collected	35 718	3279	13 300	10 070
Independent reflections	33 261	2679	4772	7058
Goodness-of-fit (GOF) on F^2	1.036	1.034	1.085	1.078
$R_1[I > 2\sigma(I)]/R_1(all date)$	0.1339, 0.3355	0.0557, 0.1322	0.0325, 0.0614	0.0910, 0.2329
$wR_2[I > 2\sigma(I)]/wR_2(all date)$	0.2673, 0.4086	0.0697, 0.1446	0.0639, 0.0789	0.1549, 0.2989

Table 7

Crystal data and structure refinement parameters for complexes 5-7.

Complex	5	6	7
Empirical formula	$C_{60}H_{92}Cl_4N_4O_{10}Sn_4$	$C_{36}H_{44}Cl_4N_4O_{10}Sn_4$	C72H72Cl2N2O8Sn4
Formula weight	1645.94	1309.31	1638.98
Crystal system	triclinic	triclinic	triclinic
Space group	ΡĪ	ΡĪ	ΡĪ
a (Å)	12.1092(13)	11.1222(12)	12.2782(12)
b (Å)	13.1921(12)	14.9057(14)	12.5445(13)
<i>c</i> (Å)	14.4226(16)	14.9836(16)	13.5161(15)
α (°)	116.025(2)	93.4660(10)	106.8910(10)
β(°)	112.733(2)	96.8020(10)	104.0540(10)
γ(°)	90.7050(10)	107.617(2)	112.305(2)
$V(Å^3)$	1863.0(3)	2338.7(4)	1690.0(3)
Ζ	1	2	1
μ (mm ⁻¹)	1.519	2.394	1.596
Reflections collected	8820	12 078	8695
Independent reflections	6095	8077	5806
Goodness-of-fit (GOF) on F ²	1.076	1.020	1.124
$R_1[I > 2\sigma(I)]/R_1(all date)$	0.0772, 0.1834	0.0453, 0.1083	0.0346, 0.0704
$wR_2[I > 2\sigma(I)]/wR_2(all date)$	0.1470, 0.2590	0.0811, 0.1360	0.0597, 0.0901

24H, CH₃). ¹³C NMR (CDCl₃) δ (ppm): 173.3 (COO), 124.1–150.2 (Ar-C), 37.7 (Ar-CH₂), 14.1 (CH₃). ¹¹⁹Sn NMR δ (ppm): –253.7, –149.5.

4.2.7. {[(PhCH₂)₂Sn)]₂ [(0)(COO)(CH₂C₅H₃NCl)]}·2CH₃O (**7**)

Complex **7** was prepared in a similar way to complex **1**, using 6chloro-3-pyridineacetic acid (0.172 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), dibenzyltin dichloride (0.219 g, 1 mmol) and methanol (30 ml). Crystals of complex were obtained by recrystallisation from diethyl ether. Yield: 72%. M.p. 164–166 °C. *Anal.* Cacl. for C₇₂H₇₂Cl₂N₂O₈Sn₄: C, 52.76; H, 4.43; N, 1.71. Found: C, 52.51; H, 4.71; N, 1.53%. IR (KBr, cm⁻¹): 1654 v_{as}(COO), 1407 v_s(COO), 651 v(O-Sn-O), 515 v(Sn-C), 438 v(Sn-O). ¹H NMR (CDCl₃) δ (ppm): 7.16–8.28 (m, 46H, Ar-H), 3.67 (s, 4H, CH₂), 3.18 (s, 16H, Sn-CH₂). ¹³C NMR (CDCl₃) δ (ppm): 172.5 (COO), 123.9–150.1 (Ar-C), 38.2 (Ar-CH₂). ¹¹⁹Sn NMR δ (ppm): –18.3.

4.3. X-ray crystallographic studies

X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer with graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 298(2) K. 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. Figures in this paper were created by the X-Seed software packages. Crystal data and experimental details of the structure determinations are listed in Tables 6 and 7.

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Appendix A. Supplementary data

CCDC 739402, 737072, 742568, 740790, 737073, 737074 and 755877 contain the supplementary crystallographic data for complexes **1–7**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] E.R.T. Tiekink, Trends Organomet. Chem. 1 (1994) 71.
- [2] E.R.T. Tiekink, Appl. Organomet. Chem. 5 (1991) 1.
- [3] V. Chandrasekhar, S. Nagendran, V. Baskar, Coord. Chem. Rev. 235 (2002) 1.
 [4] V. Chandrasekhar, K. Gopal, P. Sasikumar, R. Thirumoorthi, Coord. Chem. Rev. 249 (2005) 1745.
- [5] G.K. Sandhu, R. Hundal, E.R.T. Tiekink, J. Organomet. Chem. 412 (1991) 31.
- [6] R. Garcýa-Zarracino, H. Höpfl, J. Am. Chem. Soc. 127 (2005) 3120.
- [7] T.P. Lockhart, F. Davidson, Organometallics 6 (1987) 2471.
- [8] H. Preut, B. Mundus, F. Huber, R. Barbieri, Acta Crystallogr., Sect. C 42 (1986) 536.
- [9] K.C. Molloy, T.G. Purcell, M.F. Mahon, E. Minshall, Appl. Organomet. Chem. 1 (1987) 507.
- [10] P.J. Smith, R.O. Day, V. Chandrasekhar, J.M. Holmes, R.R. Holmes, Inorg. Chem. 25 (1986) 2495.
- [11] C.L. Ma, F. Li, D.Q. Wang, H.D. Yin, J. Organomet. Chem. 667 (2003) 5.
- [12] C.L. Ma, Q. Jiang, R.F. Zhang, D.Q. Wang, J. Chem. Soc., Dalton Trans. (2003) 2975.
- [13] C.L. Ma, Q.F. Wang, R.F. Zhang, Inorg. Chem. 47 (2008) 7060.
- [14] T.A. George, J. Organomet. Chem. 31 (1971) 233.
- [15] J.R. May, W.R. McWhinnie, R.C. Poller, Spectrochim. Acta, Part A 27 (1971) 969.
- [16] J. Holecek, M. Nadvornik, K. Handlir, A. Lycka, J. Organomet. Chem. 315 (1986) 299.
- [17] H.I. Beltran, L.S. Zamudio-Rivera, T. Mancilla, R. Santillan, N. Farfan, Chem. Eur. J. 9 (2003) 2291.
- [18] S. Hadjikakou, M.A. Demertzis, J.R. Miller, D. Kovala-Demertiz, J. Chem. Soc., Dalton Trans. (1999) 663.
- [19] C.D. Nicola, A.G. Galindo, J.V. Hanna, F. Marchetti, C. Pettinari, R. Pettinari, E.
- Rivarola, B.W. Skelton, A.H. White, Inorg. Chem. 44 (2005) 3094.
- [20] S.W. Ng, Acta Crystallogr., Sect. C 55 (1999) 1447.
 [21] G.K. Sandhu, S.P. Verma, J. Organomet. Chem. 393 (1990) 195.
- [22] R. Willem, A. Bouhdid, B. Mahieu, L. Ghys, M. Biesemans, E.R.T. Tiekink, D. de Vos, M. Gielen, J. Organomet, Chem. 531 (1997) 151.
- [23] A. Bondi, J. Phys. Chem. 68 (1964) 441.
- [24] D.R. Smyth, E.R. Tiekink, Z. Kristallogr. 213 (1998) 605.
- [25] R.G. Swisher, J.F. Vollano, V. Chandrasekhar, R.O. Day, R.R. Holmes, Inorg. Chem. 23 (1984) 3147.
- [26] J.F. Vollano, R.O. Day, D.N. Rau, V. Chandrasekhar, R.R. Holmes, Inorg. Chem. 23 (1984) 3153.
- [27] C.L. Ma, J.S. Sun, R.F. Zhang, J. Organomet. Chem. 691 (2006) 5873.
- [28] G.K. Sandhu, R. Hundal, J. Organomet. Chem. 412 (1991) 31.
- [29] R.O. Day, V. Chandrasekhar, K.C. Kumara Swamy, J.M. Holmes, S.D. Burton, R.R. Holmes, Inorg. Chem. 27 (1988) 2887.
- [30] T.P. Lockhart, W.F. Manders, E.M. Holt, J. Am. Chem. Soc. 108 (1986) 6611.
- [31] R. Shankar, M. Kumar, S.P. Narula, R.K. Chadha, J. Organomet. Chem. 671 (2003) 35.