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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

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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, ^{1}H NMR, ^{13}C NMR, ^{119}Sn 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.

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 2-mercaptonicotinic [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, ^{1}H, ^{13}C and ^{119}Sn 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 cm^{-1}, which appear in the free ligand as CO_2H 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 ^{1}H 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 ^{119}Sn NMR spectra indicate the same coordination environments in the solid state and in solution; while for complexes **3** and **7**, the ^{119}Sn 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. $\{(Ph_3Sn)[(COO)(CH_2C_5H_3NCl)]\}_n$ (**1**)

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

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Table 1
Selected 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 spring-like helical chains are rare. The crystal structure of complex **1** is constructed from a 1D helical chain consisting of [$(Ph_3Sn)(C_7H_5ClNO_2)$] entities, Fig. 1 shows a perspective view of the [$(Ph_3Sn)(C_7H_5ClNO_2)$] 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 [$(Ph_3Sn)(C_7H_5ClNO_2)$] 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 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].

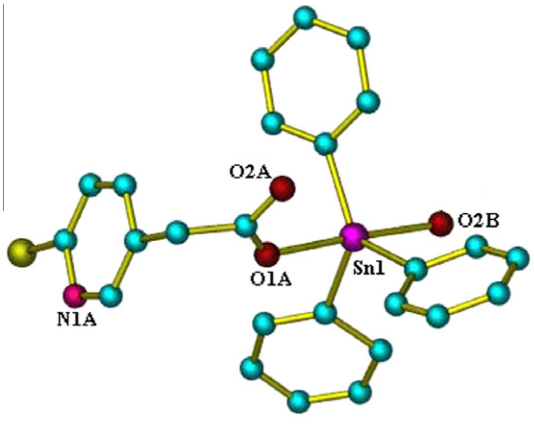

Fig. 1. The repeating unit of complex **1**.

2.2.3. {$(PhCH_2)_3Sn)[(COO)(CH_2C_5H_3NCl)]$}$\cdot H_2O$ (**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. $[PhSn(O)(COO)(CH_2C_5H_3NCl)]_6$ (**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 Sn_6O_6 central stannoxane core which contains two puckered six-membered [$Sn_3(\mu_3\text{–}O)_3$] rings as its top and bottom faces. The two [$Sn_3(\mu_3\text{–}O)_3$] 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 [$Sn_2(\mu_3\text{–}O)_2$] 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 [$Sn_2(\mu_3\text{–}O)_2$] 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 trigonal-antiprismatic 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-