



Self-assembly syntheses and crystal structures of triorganotin(IV) pyridinecarboxylate: 1D polymers and a 42-membered macrocycle

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ABSTRACT

A series of new triorganotin(IV) pyridinecarboxylates with 6-hydroxynicotinic acid (6-OH-3-nicH), 5-hydroxynicotinic acid (5-OH-3-nicH) and 2-hydroxyisonicotinic acid (2-OH-4-isonicH) of the types: $[R_3Sn(6-OH-3-nic-L)]_n$ (**I**) (R = Ph, L = Ph-EtOH, **1**; R = Bn, L = H₂O-EtOH, **2**; R = Me, L = O, **3**; R = *n*-Bu, L = O, **4**), $[R_3Sn(5-OH-3-nic)]_n$ (**II**) (R = Ph, **5**; R = Bn, **6**; R = Me, **7**; R = *n*-Bu, **8**), $[R_3Sn(2-OH-4-isonic-L)]_n$ (**III**) (R = Bn, **9**, L = MeOH; R = Me, L = O, **10**; R = Ph, **11**, L = 0.5EtOH) have been synthesized. All the complexes were characterized by elemental analysis, TGA, IR and NMR (¹H, ¹³C, ¹¹⁹Sn) spectroscopy analyses. Among them, except for complexes **5** and **6**, all complexes were also characterized by X-ray crystallography diffraction analysis. Crystal structures show that complexes **1–10** adopt 1D infinite chain structures which are generated by the bidentate *O, O* or *N, O* and the five-coordinated tin centers. Significant O–H···O, and N–H···O intermolecular hydrogen bonds stabilize these structures. Complex **11** is a 42-membered macrocycle containing six tin atoms, and forms a 2D network by intermolecular N–H···O hydrogen.

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1. Introduction

Self-assembly of organotin(IV) pyridinecarboxylates are attracting more and more attention because the ligand with multi-coordination may lead to different specific architectures [1–9]. Recently, considerable advances have been made in this area, mono-, dicarboxylic acids and substituted carboxylic acids have been extensively investigated. Hopfl and co-workers have carried out some very elegant work on such systems, having reported a series of trinuclear macrocyclic organotin complexes by the use of 2,5-pyridine dicarboxylic as ligands [1–3]. Amini and co-workers have reported an interesting complex containing two types of metals tin and sodium by the use of 2,6-pyridine dicarboxylic as ligand [4]. In our previous work, we have also synthesized a series of triorganotin pyridinedicarboxylates by use of 2,6-, 2,5- and 3,5-pyridinecarboxylate [10]. Specially, we reported a novel 18-tin-nuclear macrocyclic complex with 2-mercaptopyridinecarboxylic acid [11].

To continue research in this area, we selected another three fascinating ligands 6-hydroxynicotinic acid, 5-hydroxynicotinic acid, 2-hydroxyisonicotinic acid on the basis of the following considerations: first, all of them have a carboxy group and a hydroxyl group, so they should form strong covalent bonds with organotin

moiety; second, the spatial separation of the two groups attached to the same pyridine ring should induce the formation either of a polymeric chain or of a cyclooligomeric ring structure. Herein, we reported the syntheses and characterizations of 11 new organotin polymers with the three acids.

2. Results and discussion

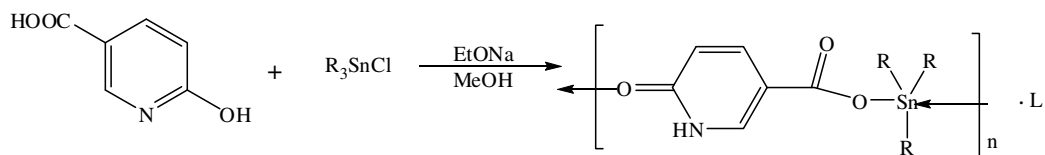
2.1. Syntheses

The syntheses procedures of complexes **1–11** are given in Scheme 1.

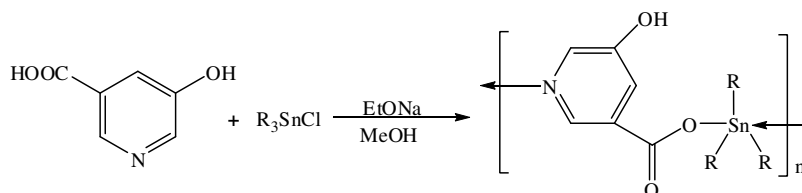
2.2. IR spectra

The stretching frequencies of interest are those associated with the C(O)O, Sn–C and Sn–O groups. The strong absorption appears at about 447–458 cm^{−1} in the respective spectra of all the complexes, which are absent in the free ligand, are assigned to the Sn–O stretching modes of vibration. All these values are consistent with those detected in a number of organotin(IV)-oxygen derivatives [12,13]. Besides, the value of $\Delta\nu$ [$\nu_{AS}(COO) - \nu_s(COO)$] for all the complexes located about 280 cm^{−1} revealing that the carboxylate ligand with monodentate modes [14].

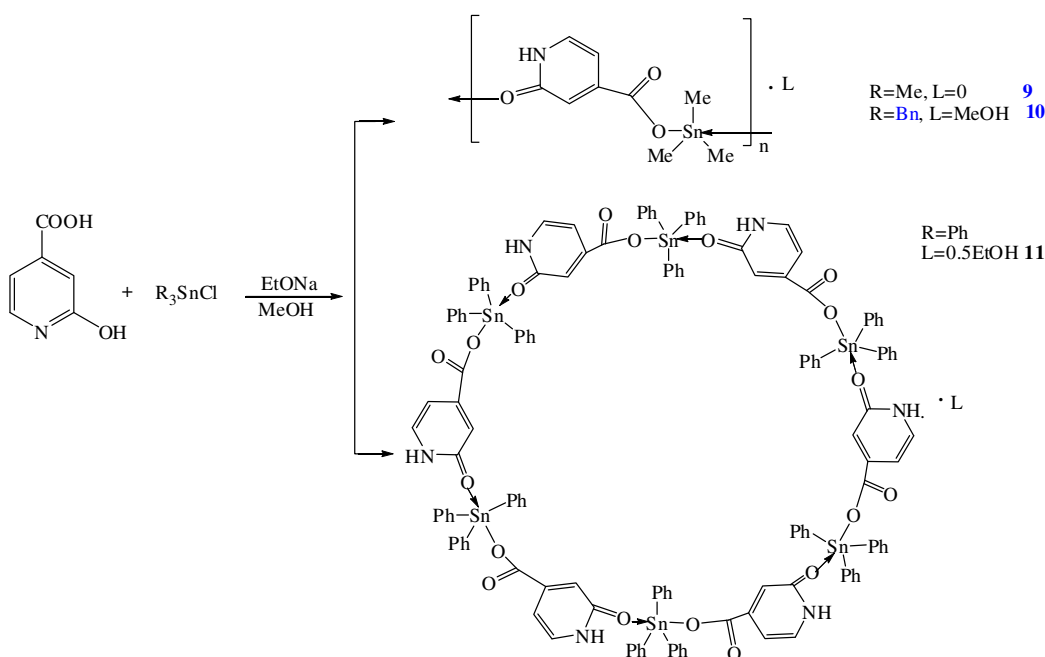
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R=Ph, L=C₆H₆, EtOH, **1**; R=Bn, L=EtOH, H₂O **2**; R=Me, L=0, **3**; R=Bu, L=0, **4**



R=Ph, **5**; Bn, **6**; Me, **7**; Bu, **8**



R=Me, L=0 **9**
R=Bn, L=MeOH **10**

R=Ph
L=0.5EtOH **11**

Scheme 1.

2.3. NMR spectra

The ¹H NMR spectra show the expected integration and peak multiplicities. In the spectra of the free ligands, the resonance observed at about 10.8 ppm, which is absent in the spectra of all the complexes, indicates the replacement of the carboxylic acid protons by organotin moiety on complex formation, while the resonance for the N–H at about 11.5 ppm in complexes **1–4** and **9–11** suggests the interconversions between the keto-form and the enol-form on the ligand. For complexes **5–8**, the resonance at about 9.7 ppm ascribes to the hydroxy groups.

The ¹³C NMR spectra of all complexes show a significant downfield shift of all carbon resonance compared with the free ligands, the shift is a consequence of an electron density transfer from the ligand to the metal atoms. The single resonances at 164.26–168.36 are attributing to the COO groups in all the complexes.

The ¹¹⁹Sn NMR spectroscopic data of all the complexes show only one resonance between –104.8 and –176.2 ppm, typical

five-coordinate species [15], and this can be confirmed by the X-ray crystal structures of the complexes.

2.4. Description of crystal structures

2.4.1. Crystal structure of complex **1**, **2**, **3** and **4**

The molecular structures and 1D infinite chain structures of complexes **1–4** are illustrated in Figs. 1–4, and selected bond lengths and angles are listed in Table 3, respectively. In the crystalline state, these complexes adopt an infinite 1D polymeric chain structures with a five-coordinated tin center, which are generated by the one carboxyl oxygen atom, one keto oxygen atom and the Sn center. The central Sn atom exists in a trigonal bipyramidal environment with two O atoms and three C atoms, which exhibits a *trans*-R₃SnO₂ geometry. The axial position is occupied by two oxygen atoms of the ligand, axial angles: [O(1)–Sn(1)–O(3)#1 = 175.79(10)° (#1 *x* + 1/2, –*y* + 3/2, *z* + 1/2) for complex **1**; O(1)–Sn(1)–O(3) = 168.3(15)° for complex **2**;

Table 1
Crystal data and structure refinement parameters for complexes **1**, **2**, **3**, **4** and **7**.

Complex	1	2	3	4	7
Empirical formula	C ₃₂ H ₃₁ NO ₄ Sn	C ₂₉ H ₃₃ NO ₅ Sn	C ₉ H ₁₃ NO ₃ Sn	C ₁₈ H ₃₁ NO ₃ Sn	C ₁₈ H ₂₆ N ₂ O ₆ Sn ₂
Formula weight	612.27	594.25	301.89	428.13	603.79
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>P2(1)/n</i>	<i>P2(1)</i>	<i>Pna2(1)</i>	<i>P2(1)2(1)2(1)</i>	<i>Cc</i>
<i>a</i> (Å)	8.9239(7)	9.1760(12)	14.149(2)	8.6910(16)	17.670(2)
<i>b</i> (Å)	18.146(2)	16.975(3)	10.5466(14)	10.716(4)	8.9461(12)
<i>c</i> (Å)	18.215(3)	9.9575(17)	7.9595(10)	22.502(5)	14.2930(16)
α (°)	90	90	90	90	90
β (°)	91.729(2)	113.052(2)	90	90	90.898(2)
γ (°)	90	90	90	90	90
<i>V</i> (Å ³)	2948.3(6)	1427.2(4)	1187.7(3)	2095.7(9)	2259.2(5)
<i>Z</i>	4	2	4	4	4
<i>D</i> _{calc} (Mg/m ³)	1.379	1.383	1.688	1.357	1.775
μ (mm ⁻¹)	0.902	0.931	2.135	1.232	2.245
<i>F</i> (0 0 0)	1248	608	592	880	1184
Crystal size (mm)	0.28 × 0.13 × 0.10	0.23 × 0.14 × 0.13	0.48 × 0.40 × 0.39	0.26 × 0.21 × 0.18	0.26 × 0.15 × 0.07
Reflections collected	14 592	7226	4666	13 616	5548
Unique reflections (<i>R</i> _{int})	5195 (<i>R</i> _{int} = 0.0395)	4804 (<i>R</i> _{int} = 0.0432)	1830 (<i>R</i> _{int} = 0.0260)	5096 (<i>R</i> _{int} = 0.0329)	2800 (<i>R</i> _{int} = 0.0252)
Data/restraints/parameters	5195/0/364	4804/1/346	1830/1/125	5096/0/210	2800/2/361
Goodness-of-fit on <i>F</i> ²	1.039	1.087	1.069	1.016	1.071
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0376, <i>wR</i> ₂ = 0.0750	<i>R</i> ₁ = 0.0877, <i>wR</i> ₂ = 0.2354	<i>R</i> ₁ = 0.0379, <i>wR</i> ₂ = 0.0958	<i>R</i> ₁ = 0.0376, <i>wR</i> ₂ = 0.0831	<i>R</i> ₁ = 0.0241, <i>wR</i> ₂ = 0.0465
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0643, <i>wR</i> ₂ = 0.0872	<i>R</i> ₁ = 0.1159, <i>wR</i> ₂ = 0.2580	<i>R</i> ₁ = 0.0451, <i>wR</i> ₂ = 0.1029	<i>R</i> ₁ = 0.0673, <i>wR</i> ₂ = 0.0943	<i>R</i> ₁ = 0.0288, <i>wR</i> ₂ = 0.0490

Table 2
Crystal data and structure refinement parameters for complexes **8**, **9**, **10**, and **11**.

Complex	8	9	10	11
Empirical formula	C ₁₈ H ₃₁ NO ₃ Sn	C ₁₄₅ H ₁₁₇ N ₆ O _{18.5} Sn ₆	C ₂₈ H ₂₉ NO ₄ Sn	C ₉ H ₁₃ NO ₃ Sn
Formula weight	428.13	2951.59	562.21	301.89
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Hexagonal	Monoclinic	Monoclinic
Space group	<i>P2(1)/n</i>	<i>R</i> $\bar{3}$	<i>P2(1)/n</i>	<i>C2/c</i>
<i>a</i> (Å)	10.2153(9)	23.3453(19)	10.4698(11)	24.540(2)
<i>b</i> (Å)	14.450(2)	23.3453(19)	16.1420(14)	8.1950(8)
<i>c</i> (Å)	14.3812(19)	23.997(2)	16.1310(15)	14.0910(17)
α (°)	90	90	90	90
β (°)	93.823(2)	90	105.5740(10)	124.077(2)
γ (°)	90	120	90	90
<i>V</i> (Å ³)	2118.1(5)	11326.4(16)	2626.1(4)	2347.2(4)
<i>Z</i>	4	3	4	8
<i>D</i> _{calc} (Mg/m ³)	1.343	1.036	1.422	1.709
μ (mm ⁻¹)	1.219	0.931	1.005	2.160
<i>F</i> (0 0 0)	880	4431	1144	1184
Crystal size (mm)	0.48 × 0.40 × 0.32	0.40 × 0.28 × 0.13	0.22 × 0.20 × 0.08	0.28 × 0.25 × 0.20
Reflections collected	10 207	7226	13 092	5732
Unique reflections (<i>R</i> _{int})	3582 (<i>R</i> _{int} = 0.0781)	4804 (<i>R</i> _{int} = 0.0432)	4624 (<i>R</i> _{int} = 0.0500)	2070 (<i>R</i> _{int} = 0.0187)
Data/restraints/parameters	3582/10/319	4804/1/346	4624/0/309	2070/0/127
Goodness-of-fit on <i>F</i> ²	1.035	1.087	1.097	1.123
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0961, <i>wR</i> ₂ = 0.2489	<i>R</i> ₁ = 0.0394, <i>wR</i> ₂ = 0.0998	<i>R</i> ₁ = 0.0385, <i>wR</i> ₂ = 0.0788	<i>R</i> ₁ = 0.0215, <i>wR</i> ₂ = 0.0499
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1238, <i>wR</i> ₂ = 0.2893	<i>R</i> ₁ = 0.0647, <i>wR</i> ₂ = 0.1124	<i>R</i> ₁ = 0.0661, <i>wR</i> ₂ = 0.0887	<i>R</i> ₁ = 0.0309, <i>wR</i> ₂ = 0.0579

O(1)–Sn(1)–O(3)#1 = 178.87(14)° (#1 *x*, *y* + 1, *z*) for complex **3**, O(1)–Sn(1)–O(3) = 178.2(2)° for complex **4**] are all slightly deviated from the linear arrangement. Three alkyl groups defined the equatorial plane and the sum of the angles subtended at the central Sn atom are 358.8° for complex **1**, 358.7° for complex **2**, 358.7° for complex **3**, 357.2° for complex **4**, respectively. The Sn–O bond lengths [Sn(1)–O(1) = 2.157(3) Å, Sn(1)–O(3)#1 = 2.358(3) Å for complex **1**; Sn(1)–O(1) = 2.140(11) Å, Sn(1)–O(3) = 2.346(11) Å for complex **2**; Sn(1)–O(1) = 2.167(8) Å, Sn(1)–O(3) = 2.367(6) Å for complex **3**; Sn(1)–O(1) = 2.160(3) Å, Sn(1)–O(3)#1 = 2.428(3) Å for complex **4**] are little longer than the sum of the covalent radii of Sn and O (2.13 Å), but much

shorter than the sum of the van der Waals radii of two atoms (3.68 Å) [16]. The bond length of O(3)–C(6) 1.253(4) Å for **1**, O(3)–C(6)#1 1.265(16) Å for **2**, O(3)–C(6)#1 1.263(10) Å for **3**, O(3)–C(3) 1.249(5) Å for **4**, reveal that these bonds should be keto C=O, just for this, intermolecular C=O → Sn coordination in complex leads to the forming of the infinite zigzag chain.

Besides, for complex **1** and **2**, they crystallizes with two solvent molecules of C₆H₆, EtOH and H₂O, EtOH significant N–H···O and O–H···O intermolecular hydrogen bonds were found. Just for that, the supramolecular structure of a 2D network is formed. For complex **3** and complex **4**, a 3D framework and a dimer structure are formed by N–H···O intermolecular hydrogen bonds.

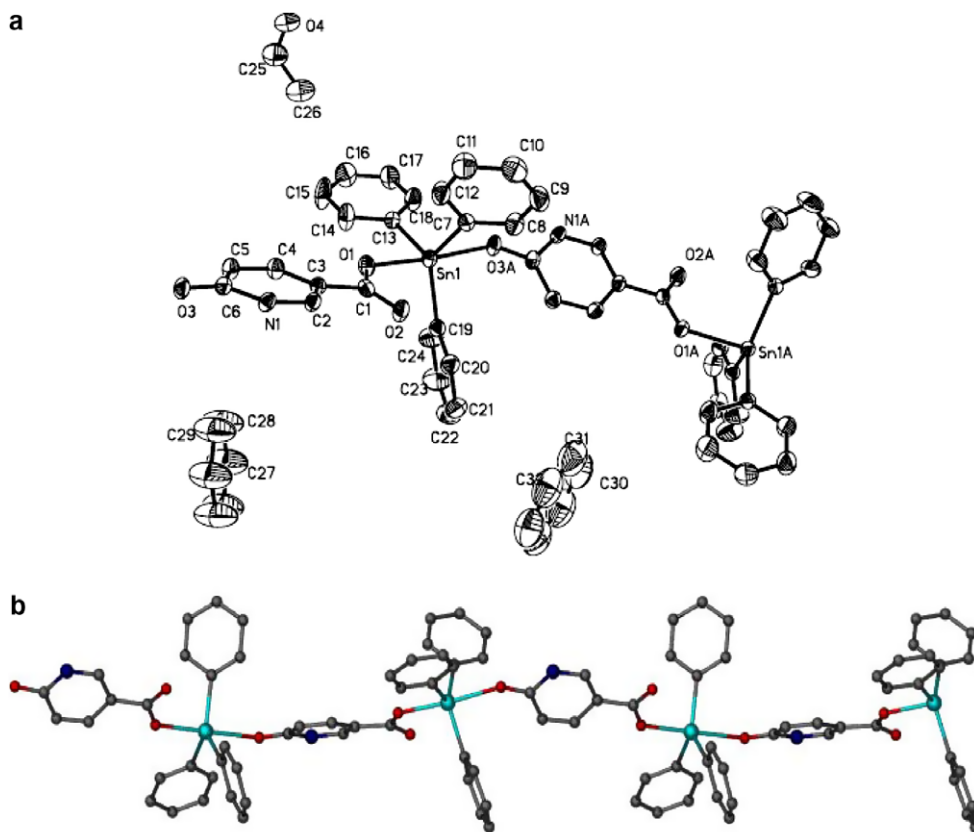


Fig. 1. Perspective views of a–b are showing the molecular structure and the 1D chain structure of complex 1.

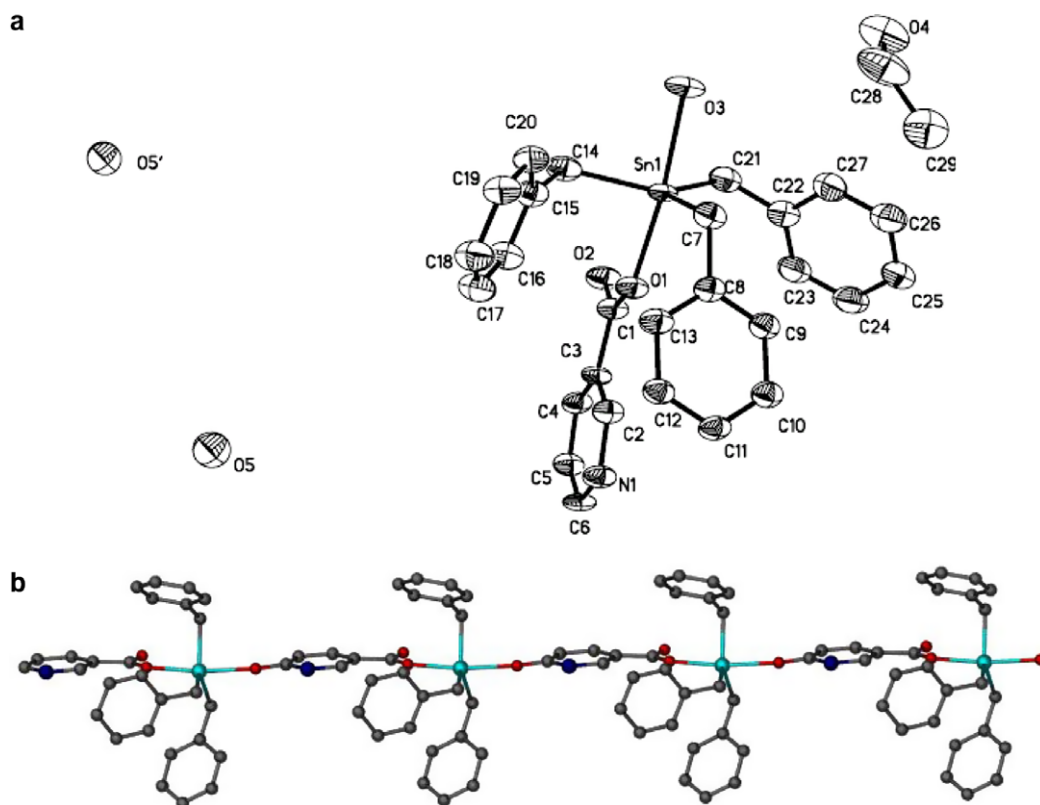


Fig. 2. Perspective views of a–b are showing the molecular structure and the 1D chain structure of complex 2.

Table 3
Selected bond lengths (Å) and angles (°) for complex 1–4.

Complex 1			
Sn(1)–C(7)	2.123(4)	Sn(1)–O(1)	2.157(3)
Sn(1)–C(19)	2.130(4)	Sn(1)–O(3)#1	2.358(3)
Sn(1)–C(13)	2.144(4)		
C(7)–Sn(1)–C(19)	127.16(16)	C(13)–Sn(1)–O(1)	89.94(13)
C(7)–Sn(1)–C(13)	118.58(15)	C(7)–Sn(1)–O(3)#1	85.96(13)
C(19)–Sn(1)–C(13)	112.97(16)	C(19)–Sn(1)–O(3)#1	85.65(13)
C(7)–Sn(1)–O(1)	92.65(13)	C(13)–Sn(1)–O(3)#1	87.24(12)
C(19)–Sn(1)–O(1)	98.34(13)	O(1)–Sn(1)–O(3)#1	175.79(10)
Complex 2			
Sn(1)–C(14)	2.13(4)	Sn(1)–C(21)	2.16(4)
Sn(1)–C(7)	2.136(12)	Sn(1)–O(3)	2.346(11)
Sn(1)–O(1)	2.140(11)		
C(14)–Sn(1)–C(7)	114.8(17)	O(1)–Sn(1)–C(21)	101.6(14)
C(14)–Sn(1)–O(1)	86.7(13)	C(14)–Sn(1)–O(3)	86.8(12)
C(7)–Sn(1)–O(1)	93.1(5)	C(7)–Sn(1)–O(3)	80.8(5)
C(14)–Sn(1)–C(21)	128.8(7)	O(1)–Sn(1)–O(3)	168.3(15)
C(7)–Sn(1)–C(21)	115.1(19)	C(21)–Sn(1)–O(3)	90.1(13)
Complex 3			
Sn(1)–C(8)	2.119(9)	Sn(1)–O(1)	2.167(8)
Sn(1)–C(7)	2.118(8)	Sn(1)–O(3)	2.367(6)
Sn(1)–C(9)	2.135(13)		
C(8)–Sn(1)–C(7)	115.0(5)	C(9)–Sn(1)–O(1)	95.8(4)
C(8)–Sn(1)–C(9)	124.5(4)	C(8)–Sn(1)–O(3)	83.7(3)
C(7)–Sn(1)–C(9)	118.2(4)	C(7)–Sn(1)–O(3)	87.5(3)
C(8)–Sn(1)–O(1)	97.8(4)	C(9)–Sn(1)–O(3)	84.0(5)
C(7)–Sn(1)–O(1)	90.9(3)	O(1)–Sn(1)–O(3)	178.2(2)
Complex 4			
Sn(1)–C(8)	2.127(5)	Sn(1)–O(1)	2.160(3)
Sn(1)–C(16)	2.130(5)	Sn(1)–O(3)#1	2.428(3)
Sn(1)–C(12)	2.142(5)		
C(8)–Sn(1)–C(16)	127.2(2)	C(12)–Sn(1)–O(1)	93.50(16)
C(8)–Sn(1)–C(12)	114.8(2)	C(8)–Sn(1)–O(3)#1	83.08(15)
C(16)–Sn(1)–C(12)	115.2(2)	C(16)–Sn(1)–O(3)#1	83.44(18)
C(8)–Sn(1)–O(1)	95.98(14)	C(12)–Sn(1)–O(3)#1	87.46(17)
C(16)–Sn(1)–O(1)	96.67(17)	O(1)–Sn(1)–O(3)#1	178.87(14)

Symmetry code for complex 1: #1 $x + 1/2, -y + 3/2, z + 1/2$.

Symmetry code for complex 4: #1 $x, y + 1, z$.

2.4.2. Crystal structure of complex 7 and 8

The molecular structures and 1D infinite chain structures of complexes 7 and 8 are illustrated in Figs. 5 and 6, and selected bond lengths and angles are listed in Table 4, respectively. Com-

plexes 7 and 8 are both infinite 1D polymeric chain structures, the central tin atom in the two complexes is essentially five coordinated, bound to three alkyl groups, one carboxylate oxygen atom, and one nitrogen atom, so the geometry of the tin atom can be described as a distorted trigonal bipyramidal geometry in which the apical position is occupied by the oxygen atom and the nitrogen atom. The axial angles [O(1)#1–Sn(1)–N(1) = 172.3(2)° for 7 and O(1)–Sn(1)–N(1) = 175.4(3)° for 8] suggests that the structure are near to normal trigonal bipyramid. The bond lengths of Sn(1)–O(1)#1 = 2.196(5) for 7 and Sn(1)–O(1) = 2.183(8) for 8, are similar to the complex 1–4. The Sn(1)–N(1) bond length 2.445(6) Å for 7 and 2.520(8) Å for 8 lies in the range recorded in the Cambridge Crystallographic Database from 2.27 to 2.58 Å [17], slightly greater than the sum of the covalent radii of tin and nitrogen atoms, but much less than the sum of the van der Waals radii (3.74 Å) [18].

Besides, for complex 7 and 8, significant O–H···O intermolecular hydrogen bonds are found, which link the complexes to 2D network structures. The O···O, H···O distances and the O–H···O angles are 2.644 Å, 1.828 Å and 173.69° for 7 and 2.578 Å, 1.777 Å and 165.31° for 8, respectively.

2.4.3. Crystal structure of complex 9 and 10

The molecular structures and 1D infinite chain structures of complexes 9 and 10 are illustrated in Figs. 7 and 8, and selected bond lengths and angles are listed in Table 5, respectively. As complexes 1–4, the central Sn atoms for complexes 7 and 8 are also five-coordinate with trigonal bipyramidal geometry, bound to three alkyl groups, one carboxylate oxygen atom, one keto oxygen atom. Intermolecular C=O → Sn coordination in complex leads to the forming of the infinite zigzag chain. The Sn–O bond lengths [Sn(1)–O(1) = 2.154(3) Å, Sn(1)–O(3) = 2.407(3) Å for 1; Sn(1)–O(1) = 2.182(2) Å, Sn(1)–O(3) = 2.334(3) Å for 2] and axial angles [O(1)–Sn(1)–O(3) = 174.30(10)° for complex 1; O(1)–Sn(1)–O(3) = 168.38(9)° for complex 2] are similar to the complexes 1–4.

Besides, it should be noted, complex 9 crystallizes with one solvent molecule of H₂O, just for that, significant O–H···O and N–H···O intermolecular hydrogen bonds are found, which link the complex into a 2D network structure. For complex 10, the supramolecular structure of a 2D network is also formed by intermolecular N–H···O hydrogen bond.

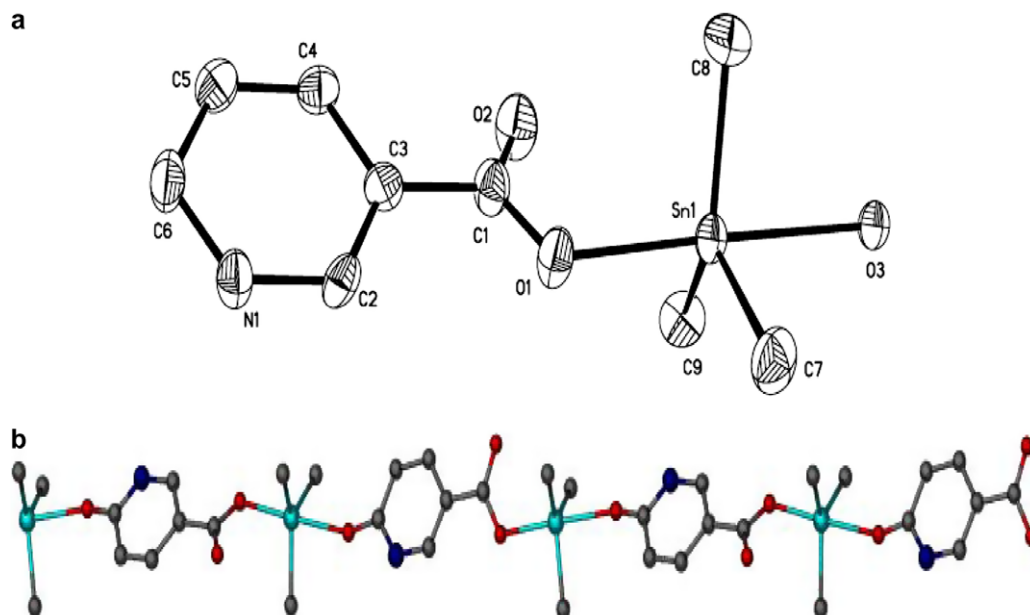


Fig. 3. Perspective views of a–b are showing the molecular structure and the 1D chain structure of complex 3.

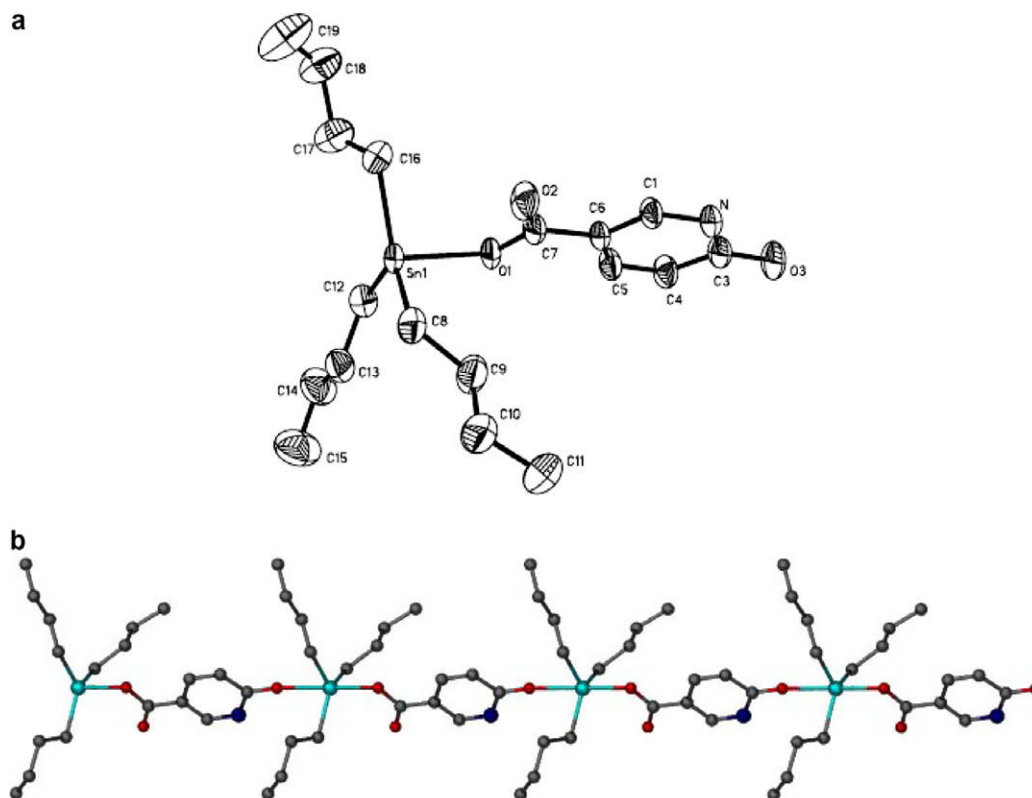


Fig. 4. Perspective views of a–b are showing the molecular structure and the 1D chain structure of complex 4.

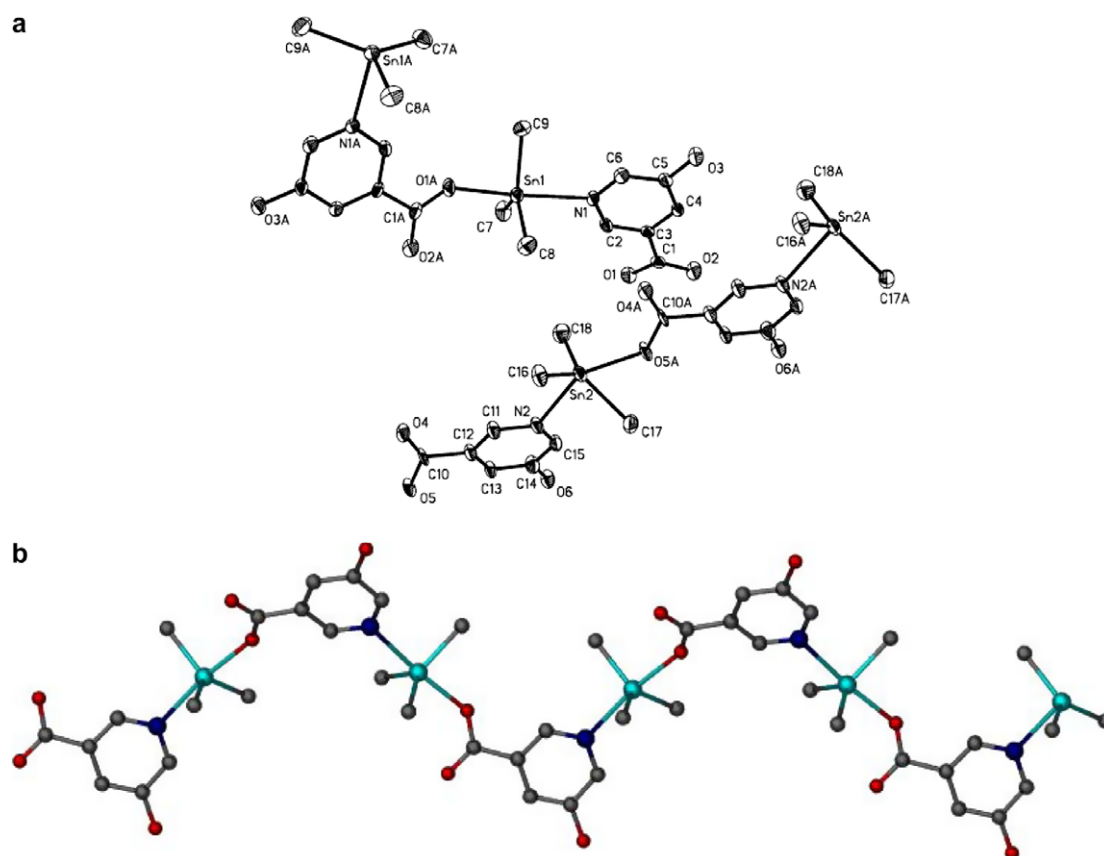


Fig. 5. Perspective views of a–b are showing the molecular structure and the 1D chain structure of complex 7.

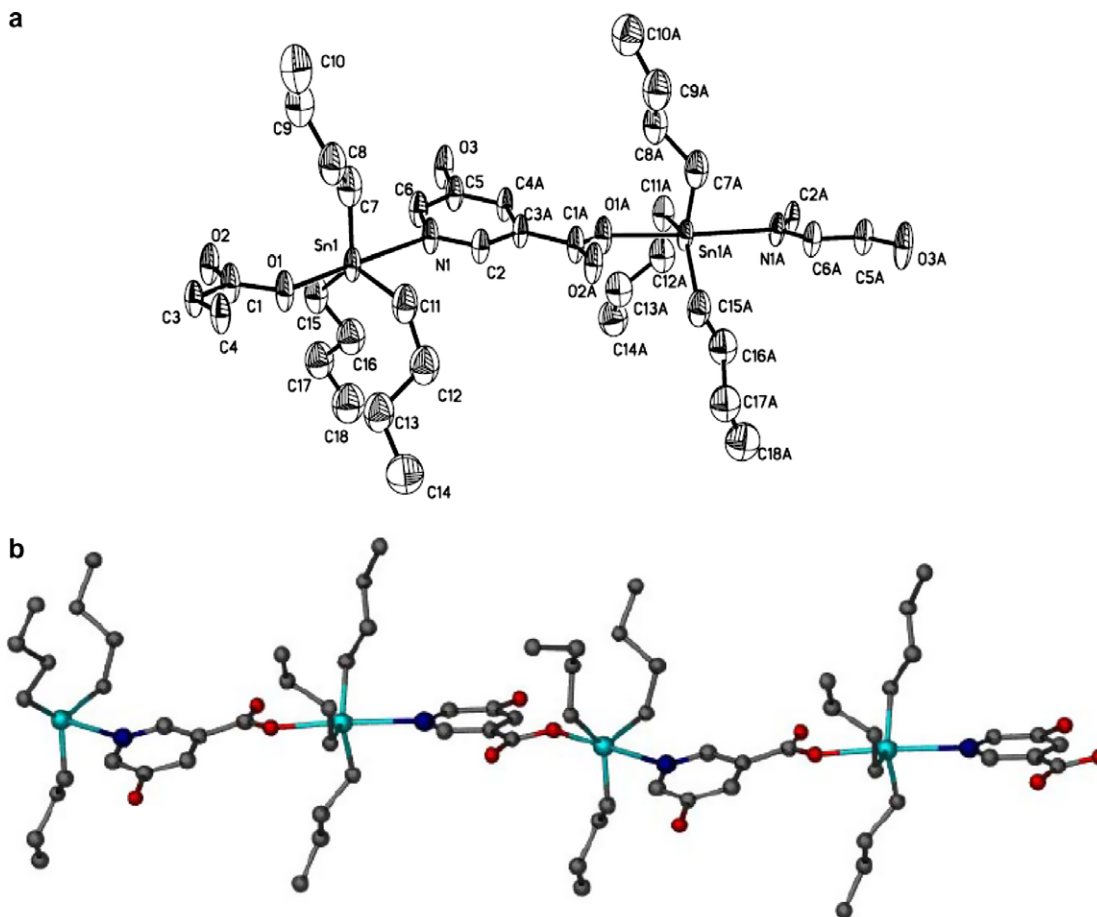


Fig. 6. Perspective views of a–b are showing the molecular structure and the 1D chain structure of complex 8.

Table 4

Selected bond lengths (Å) and angles (°) for complex 7–8.

Complex 7			
Sn(1)–C(7)	2.114(7)	Sn(2)–C(18)	2.111(8)
Sn(1)–C(9)	2.117(7)	Sn(2)–O(5')#2	2.131(10)
Sn(1)–C(8)	2.118(7)	Sn(2)–O(5)#2	2.155(10)
Sn(1)–O(1)#1	2.118(7)	Sn(2)–C(17)	2.198(14)
Sn(1)–N(1)	2.445(6)	Sn(2)–C(16')	2.213(14)
Sn(2)–C(16)	2.009(13)	Sn(2)–N(2)	2.512(11)
Sn(2)–C(17')	2.028(14)	Sn(2)–N(2')	2.532(12)
C(7)–Sn(1)–C(9)	116.8(3)	C(8)–Sn(1)–O(1)#1	91.2(2)
C(7)–Sn(1)–C(8)	119.6(3)	C(7)–Sn(1)–N(1)	91.6(2)
C(9)–Sn(1)–C(8)	123.6(3)	C(9)–Sn(1)–N(1)	89.7(3)
C(7)–Sn(1)–O(1)#1	95.9(2)	C(8)–Sn(1)–N(1)	86.8(2)
C(9)–Sn(1)–O(1)#1	85.1(3)	O(1)#1–Sn(1)–N(1)	172.3(2)
Complex 8			
Sn(1)–C(7)	1.89(9)	Sn(1)–C(11)	2.13(19)
Sn(1)–C(15)	2.07(5)	Sn(1)–O(1)	2.183(8)
Sn(1)–C(15')	2.11(10)	Sn(1)–C(7')	2.22(7)
Sn(1)–C(11')	2.1(3)	Sn(1)–N(1)	2.520(8)
C(15)–Sn(1)–C(11)	133(5)	C(11)–Sn(1)–O(1)	83(3)
C(7)–Sn(1)–C(15)	122(3)	C(7)–Sn(1)–N(1)	85(2)
C(7)–Sn(1)–C(11)	104(5)	C(15)–Sn(1)–N(1)	89(2)
C(7)–Sn(1)–O(1)	94(2)	C(11)–Sn(1)–N(1)	93(3)
C(15)–Sn(1)–O(1)	95(2)	O(1)–Sn(1)–N(1)	175.4(3)

Symmetry code for complex 7: #1 $x, -y + 1, z - \frac{1}{2}$ and #2 $x, y - 1, z$.

2.4.4. Crystal structure of complex 11

A perspective view of the molecular structure is shown in Fig. 9, and selected bond lengths and angles are listed in Table 5, respectively. It should be noted that the macrocyclic component, $[(\text{Ph}_3\text{Sn}(o\text{-OC}_5\text{H}_4\text{NCO}_2))_6]$, crystallizes with solvent molecule of

EtOH, but the obvious interactions between the **11** moiety and the solvent molecule are not found. The macrocyclic $[(\text{Ph}_3\text{Sn}(o\text{-OC}_5\text{H}_4\text{NCO}_2))_6]$ component consists of six Ph_3Sn fragments linked together through six bridging $[o\text{-OC}_5\text{H}_4\text{NCO}_2]$ ligands to afford a hexanuclear Sn_6O_{12} macrocycle, which can be described as a carbon-studded *molecular b angle* [4]. As can be seen from Fig. 9, complex **11** is a 42-membered macrocycle, each of the tin atom is essentially penta-coordinated, bounded to three phenyl groups, one carboxyl oxygen atom and one keto oxygen, so the geometry of the tin atom can be described as a distorted trigonal bipyramid. The axial position is occupied by O(1) and O(3), which forms an angle of $175.75(12)^\circ$ for Sn(1), the basal plane is defined by C(7), C(13) and C(19) and the sum of the angles subtended at the tin atom is 359.2° , so that the atoms Sn(1), C(7), C(13) and C(19) are almost in the same plane. The bond lengths of Sn(1)–O(1), Sn(1)–O(3) are $2.156(3)$ Å and $2.303(3)$ Å, respectively. The size of cavity in this macrocycle can be evaluated from the Sn...Sn and transannular O...O distances, which are 14.207 Å and 13.976 Å, respectively, larger than our previous reported on $[(\text{Ph}_3\text{Sn})_6(\text{O}_3\text{POPh})_3]_2$ [19]. Worth mentioning here is that although the dimensions of the cavity in this complex are ostensibly large enough to capture guest molecules, they are almost completely occupied by the phenyl groups on tin atoms. Besides, may be related to steric effects and to the different sorts of coordinated atoms, the macrocycle is twisted, in fact, Sn1, Sn1A and Sn1B occupy a plane 4.977 Å distant from the plane which the rest three tin atoms defined by.

Furthermore, significant N–H...O intermolecular hydrogen bond stabilize these structure, the H...O, N...O distance and the N–H...O angle are 1.874 Å, 2.732 Å and 174.85° , respectively. Just

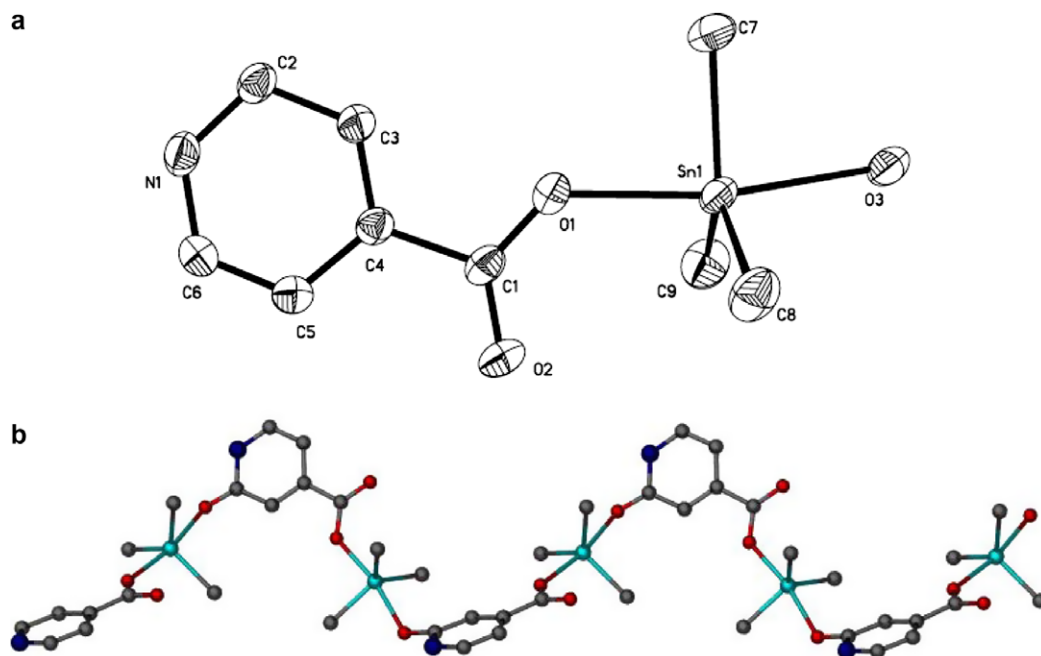


Fig. 7. Perspective views of a–b are showing the molecular structure and the 1D chain structure of complex 9.

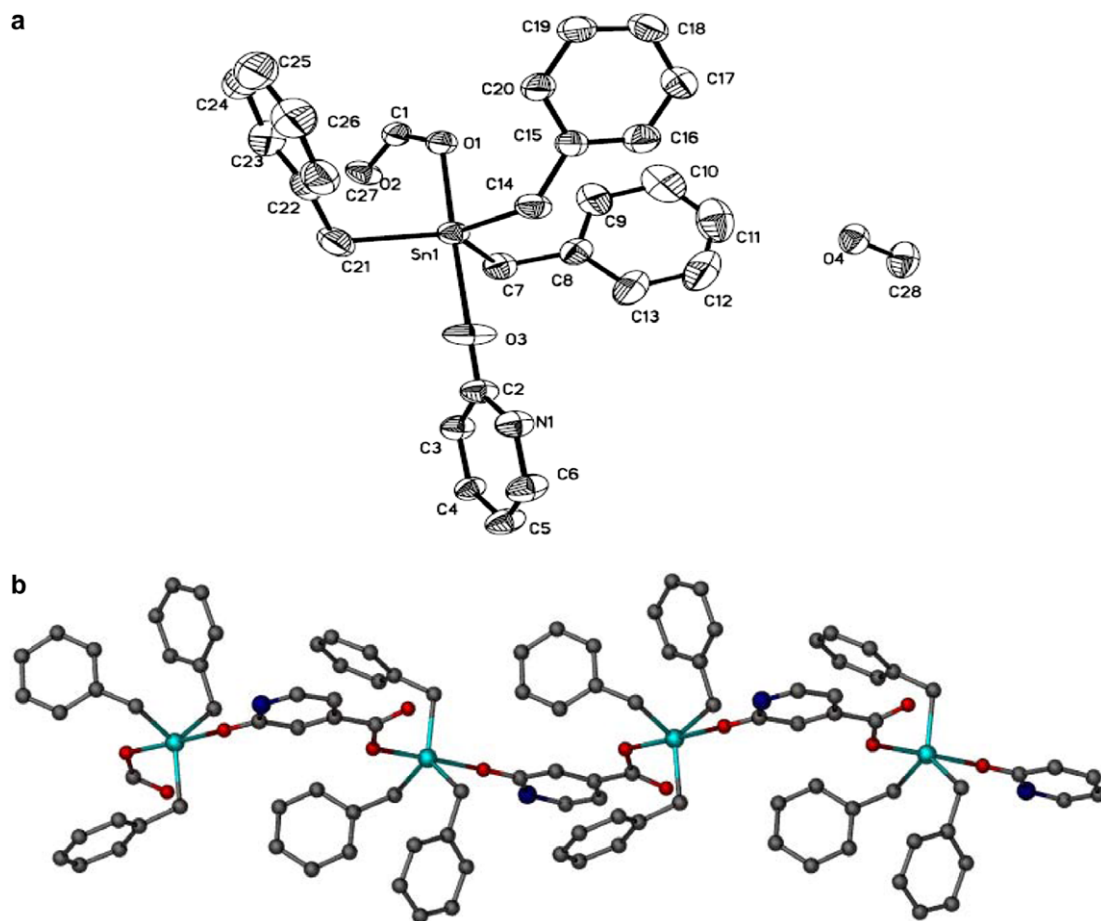


Fig. 8. Perspective views of a–b are showing the molecular structure and the 1D chain structure of complex 10.

Table 5
Selected bond lengths (Å) and angles (°) for complex **9–11**.

Complex 9			
Sn(1)–C(7)	2.113(4)	Sn(1)–O(1)	2.182(2)
Sn(1)–C(9)	2.114(4)	Sn(1)–O(3)	2.334(3)
Sn(1)–C(8)	2.125(4)	O(3)–C(2)#1	1.268(4)
C(7)–Sn(1)–C(9)	123.00(18)	C(8)–Sn(1)–O(1)	95.56(13)
C(7)–Sn(1)–C(8)	118.86(18)	C(7)–Sn(1)–O(3)	84.28(13)
C(9)–Sn(1)–C(8)	117.97(18)	C(9)–Sn(1)–O(3)	87.13(14)
C(7)–Sn(1)–O(1)	86.29(13)	C(8)–Sn(1)–O(3)	94.93(13)
C(9)–Sn(1)–O(1)	92.35(14)	O(1)–Sn(1)–O(3)	168.38(9)
Complex 10			
Sn(1)–C(7)	2.139(4)	Sn(1)–O(1)	2.154(3)
Sn(1)–C(14)	2.145(4)	Sn(1)–O(3)	2.407(3)
Sn(1)–C(21)	2.150(5)		
C(7)–Sn(1)–C(14)	116.48(17)	C(21)–Sn(1)–O(1)	95.33(16)
C(7)–Sn(1)–C(21)	128.05(18)	C(7)–Sn(1)–O(3)	89.30(15)
C(14)–Sn(1)–C(21)	113.47(19)	C(14)–Sn(1)–O(3)	81.80(13)
C(7)–Sn(1)–O(1)	95.33(14)	C(21)–Sn(1)–O(3)	84.37(17)
C(14)–Sn(1)–O(1)	93.13(13)	O(1)–Sn(1)–O(3)	174.30(10)
Complex 11			
Sn(1)–C(13)	2.119(5)	Sn(1)–O(1)	2.156(3)
Sn(1)–C(19)	2.122(5)	Sn(1)–O(3)	2.303(3)
Sn(1)–C(7)	2.133(5)	O(3)–C(2)	1.260(5)
C(13)–Sn(1)–C(19)	120.9(2)	C(7)–Sn(1)–O(1)	87.55(15)
C(13)–Sn(1)–C(7)	119.8(2)	C(13)–Sn(1)–O(3)	84.21(15)
C(19)–Sn(1)–C(7)	118.59(19)	C(19)–Sn(1)–O(3)	88.53(16)
C(13)–Sn(1)–O(1)	95.97(16)	C(7)–Sn(1)–O(3)	88.68(16)
C(19)–Sn(1)–O(1)	95.00(16)	O(1)–Sn(1)–O(3)	175.75(12)

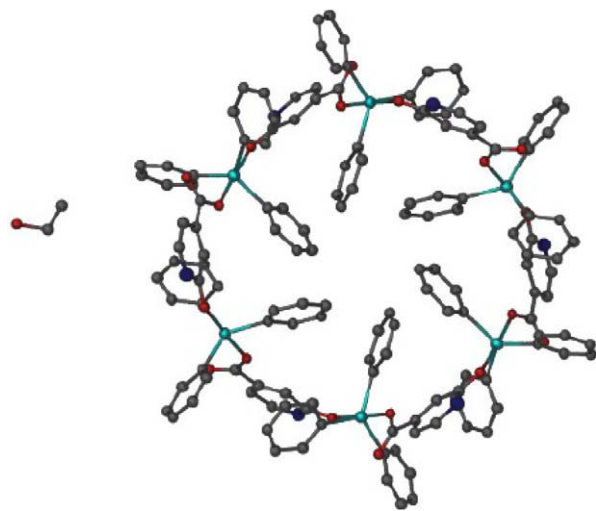


Fig. 9. The molecular structure of **11**.

for that, the supramolecular structure of a 2D network is formed (Fig. 10).

2.5. TGA studies

To study the stability of complexes **1–11**, thermogravimetric analysis (TGA) was performed in the temperature range of 50–600 °C under N₂ atmosphere. The TGA curves of these complexes exhibit one primary continuous weight loss stages in the range of 50–600 °C. In general, all these complexes exhibit good thermal stability. Specially, we analyze the TGA curve of complex **11** in detail. The TGA of **11** (Fig. 11) show a continuous loss (found: 5.222%) from 134.72 °C to 207.73 °C, which is attributed to the loss of the 0.5CH₃OH and C₆H₄NO₃ (calc: 5.341%). Then the host framework begins to decompose from 207.73 °C to 490.82 °C (found: 33.10%), corresponding to 2Ph₃Sn and 2C₆H₄NO₃ (calc: 33.07%).

3. Experimental details

3.1. Materials and measurements

Trimethyltin chloride, triphenyltin chloride, tri-*n*-butyltin chloride, 6-hydroxynicotinic acid, 5-hydroxynicotinic acid and 2-hydroxyisonicotinic acid were commercially available, and they were used without purification. Tribenzyltin(IV) chloride was prepared by a standard method reported in the literature [20]. 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 Varian mercury Plus 400 spectrometer operating 400, 100.6 and 149.2 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ¹³C 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 ¹H and ¹³C NMR and Me₄Sn for ¹¹⁹Sn NMR. Elemental analyses (C, H and N) were performed with a PE-2400II apparatus.

3.2. Syntheses of the complex **1–11**

3.2.1. Synthesis of complex **1**

The 6-hydroxynicotinic acid (0.139 g, 1 mmol) and the sodium ethoxide (0.068 g, 1 mmol) were added to the solution of methanol (30 ml) in a Schlenk flask and stirred for 30 min. Then the triphenyltin chloride (0.385 g, 1 mmol) was added to the reactor, the reaction mixture was stirred for 12 h at 40 °C. Then filtrated, the solvent of the filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The solid was recrystallized from benzene and a transparent colorless crystal was formed. Yield: 77%. m.p. > 250 °C. Anal. Calc. for C₃₂H₃₁NO₄Sn: C, 62.77; H, 5.10; N, 2.29. Found: C, 62.93; H, 5.38; N, 2.01%. IR (KBr, cm⁻¹): ν_{as}(COO), 1653; ν_s(COO), 1370; ν(Sn–C), 558; ν(Sn–O), 447. ¹H NMR [(CD₃)₂SO, ppm]: δ = 7.28–7.49 (m, 21H, –Ph), 7.75–8.37 [m, 3H, pyridine (=CH)], 11.55 (s, 1H, N–H). ¹³C NMR [(CD₃)₂SO, ppm]: δ 164.26 (COO); 112.15, 118.57, 138.71, 140.45, 162.31 [pyridine (=C)], 130.41–137.48 (Ar–C). ¹¹⁹Sn NMR [(CD₃)₂SO, ppm]: –124.8.

3.2.2. Synthesis of complex **2**

The procedure is similar to that of complex **1**, 6-hydroxynicotinic acid (0.139 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and tribenzyltin chloride (0.427 g, 1 mmol) were reacted for 12 h at 40 °C. Recrystallized from ether, a transparent colorless crystal was formed. Yield: 73%. m.p. > 250 °C. Anal. Calc. for C₂₉H₃₃NO₅Sn: C, 58.61; H, 5.60; N, 2.36. Found: C, 58.33; H, 5.92; N, 2.07%. IR (KBr, cm⁻¹): ν_{as}(COO), 1655; ν_s(COO), 1371; ν(Sn–C), 571; ν(Sn–O), 453. ¹H NMR [(CD₃)₂SO, ppm]: δ = 11.72 (s, 1H, N–H), 8.19 (s, 2H, H–O–H), 7.62–8.09 [m, 3H, pyridine (=CH)], 7.00–7.34 (m, 15H, –Ph), 4.87 (1H, EtO–H), 3.33 (–CH₂), 2.54 (6H, Ph–CH₂), 1.25 (–CH₃). ¹³C NMR [(CD₃)₂SO, ppm]: δ 165.56 (COO); 112.84, 118.03, 127.92, 140.52, 163.09 [pyridine (=C)]; 128.52–137.65 (Ar–C); 58.31 (–OCH₂); 27.23 (Ph–CH₂); 17.9 (–CH₃). ¹¹⁹Sn NMR [(CD₃)₂SO, ppm]: –138.4.

3.2.3. Synthesis of complex **3**

The procedure is similar to that of complex **1**, 6-hydroxynicotinic acid (0.139 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and trimethyltin chloride (0.199 g, 1 mmol) were reacted for 12 h at 40 °C. Recrystallized from ether, a transparent colorless crystal was formed. Yield: 73%. m.p. > 250 °C. Anal. Calc. for C₉H₁₃NO₃Sn: C, 35.80; H, 4.34; N, 4.64. Found: C, 35.53; H, 4.59; N, 4.35%. IR (KBr, cm⁻¹): ν_{as}(COO), 1656; ν_s(COO), 1373; ν(Sn–C), 571; ν(Sn–O), 449. ¹H NMR [(CD₃)₂SO,

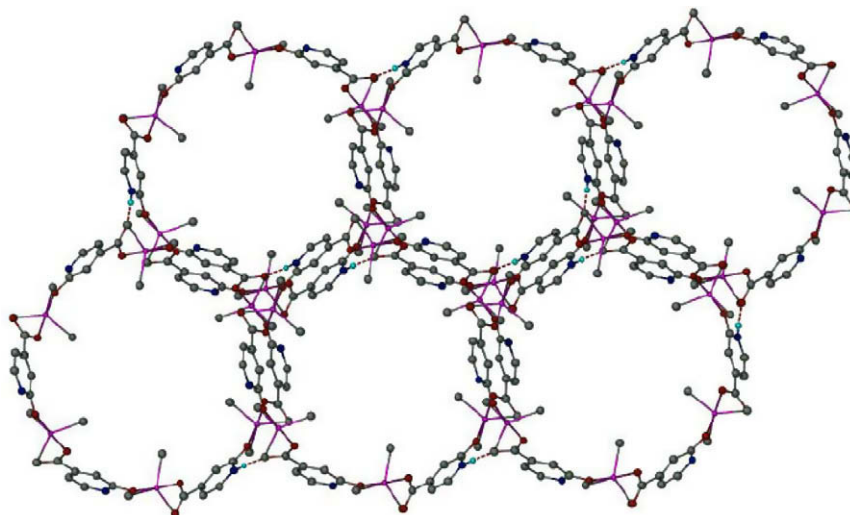


Fig. 10. The 2D network structure of complex **11** connected by intermolecular N–H...O hydrogen bond (the α -carbon of phenyl ring is reserved, and the other carbons are omitted for clarity).

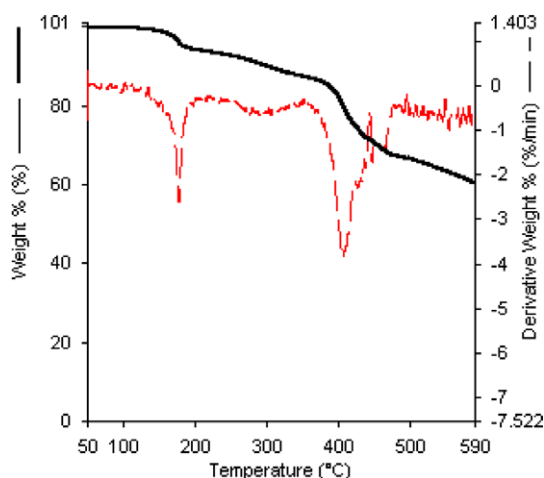


Fig. 11. TGA curve of complex **11**.

ppm]: δ = 11.71 (s, 1H, N–H), 7.78–8.11 (m, 3H, pyridine), 0.88 (t, 9H, CH₃, $^2J_{\text{Sn-H}}$ = 67.6 Hz). ^{13}C NMR [(CD₃)₂SO, ppm]: δ 166.34 (COO); 113.04, 118.13, 138.51, 140.66, 162.67 [pyridine (=C)]; 14.2 (–CH₃, $^1J_{\text{Sn-C}}$ = 652 Hz). ^{119}Sn NMR [(CD₃)₂SO, ppm]: –159.3.

3.2.4. Synthesis of complex **4**

The procedure is similar to that of complex **1**, 6-hydroxynicotinic acid (0.139 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and tri-*n*-butyltin chloride (0.325 g, 1 mmol) were reacted for 12 h at 40 °C. Recrystallized from ether, a transparent colorless crystal was formed. Yield: 77%. m.p. 176–178 °C. Anal. Calc. for C₁₈H₃₁NO₃Sn: C, 50.49; H, 7.30; N, 3.27. Found: C, 50.18; H, 7.59; N, 3.01%. IR (KBr, cm⁻¹): $\nu_{\text{as}}(\text{COO})$, 1653; $\nu_{\text{s}}(\text{COO})$, 1370; $\nu(\text{Sn-C})$, 574; $\nu(\text{Sn-O})$, 458. ^1H NMR [(CD₃)₂SO, ppm]: δ = 11.67 (s, 1H, N–H), 7.79–8.05 [m, 3H, pyridine (=CH)], 1.30–1.41 (m, 18H, CH₂CH₂CH₂), 0.95 (t, 9H, CH₃). ^{13}C NMR [(CD₃)₂SO, ppm]: δ 168.07 (COO); 113.04, 118.13, 138.51, 140.77, 162.67 [pyridine (=C)]; 13.74, 18.74 ($^1J_{\text{Sn-C}}$ = 452 Hz), 26.54, 27.69 (*n*-Bu). ^{119}Sn NMR [(CD₃)₂SO, ppm]: –141.9.

3.2.5. Synthesis of complex **5**

The procedure is similar to that of complex **1**, 5-hydroxynicotinic acid (0.139 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol)

and triphenyltin chloride (0.325 g, 1 mmol) were reacted for 12 h at 40 °C. Recrystallized from ether, a transparent colorless crystal was formed. Yield: 85%. m.p. > 250 °C. Anal. Calc. for C₃₂H₃₁NO₃Sn: C, 59.05; H, 3.92; N, 2.87. Found: C, 58.71; H, 4.17; N, 2.61%. IR (KBr, cm⁻¹): $\nu_{\text{as}}(\text{COO})$, 1647; $\nu_{\text{s}}(\text{COO})$, 1363; $\nu(\text{Sn-C})$, 554; $\nu(\text{Sn-O})$, 457. ^1H NMR [(CD₃)₂SO, ppm]: δ = 9.76 (s, 1H, –OH); 8.01–8.54 [m, 3H, pyridine (=CH)]; 7.48–7.80 (m, 15H, Ph). ^{13}C NMR [(CD₃)₂SO, ppm]: 168.32 (COO); 122.74, 125.57, 138.71, 140.44, 159.31 [pyridine (=C)]; 132.41–138.36 (Ar-C). ^{119}Sn NMR [(CD₃)₂SO, ppm]: –104.8.

3.2.6. Synthesis of complex **6**

The procedure is similar to that of complex **1**, 5-hydroxynicotinic acid (0.139 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and tribenzyltin chloride (0.427 g, 1 mmol) were reacted for 12 h at 40 °C. Recrystallized from ether, a transparent colorless crystal was formed. Yield: 73%. m.p. > 250 °C. Anal. Calc. for C₂₇H₂₅NO₃Sn: C, 61.16; H, 4.75; N, 2.64. Found: C, 60.88; H, 4.97; N, 2.47%. IR (KBr, cm⁻¹): $\nu_{\text{as}}(\text{COO})$, 1645; $\nu_{\text{s}}(\text{COO})$, 1375; $\nu(\text{Sn-C})$, 528; $\nu(\text{Sn-O})$, 475. ^1H NMR [(CD₃)₂SO, ppm]: δ = 9.80 (s, 1H, –OH), 7.79–8.38 [m, 3H, pyridine (=CH)], 7.28–7.49 (m, 15H, Ph), 2.69 (s, 6H, Ph-CH₂). ^{13}C NMR [(CD₃)₂SO, ppm]: δ 167.36 (COO); 118.84, 124.23, 138.67, 140.75, 153.09 [pyridine (=C)]; 131.16–137.31 (Ar-C), 27.11 (Ph-CH₂). ^{119}Sn NMR [(CD₃)₂SO, ppm]: –126.7.

3.2.7. Synthesis of complex **7**

The procedure is similar to that of complex **1**, 5-hydroxynicotinic acid (0.139 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and trimethyltin chloride (0.199 g, 1 mmol) were reacted for 12 h at 40 °C. Recrystallized from ether, a transparent colorless crystal was formed. Yield: 83%. m.p. > 250 °C. Anal. Calc. for C₉H₁₃NO₃Sn: C, 35.80; H, 4.34; N, 4.64. Found: C, 35.56; H, 4.63; N, 4.38%. IR (KBr, cm⁻¹): $\nu_{\text{as}}(\text{COO})$, 1649; $\nu_{\text{s}}(\text{COO})$, 1371; $\nu(\text{Sn-C})$, 550; $\nu(\text{Sn-O})$, 446. ^1H NMR [(CD₃)₂SO, ppm]: δ = 9.66 (s, 1H, O–H), 7.99–8.46 [m, 3H, pyridine (=CH)], 0.91 (t, 9H, CH₃, $^2J_{\text{Sn-H}}$ = 67.6 Hz). ^{13}C NMR [(CD₃)₂SO, ppm]: δ 168.16 (COO); 119.04, 122.13, 138.51, 140.66, 152.67 [pyridine (=C)]; 13.3 (–CH₃, $^1J_{\text{Sn-C}}$ = 439 Hz). ^{119}Sn NMR [(CD₃)₂SO, ppm]: –119.3.

3.2.8. Synthesis of complex **8**

The procedure is similar to that of complex **1**, 5-hydroxynicotinic acid (0.139 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and tri-*n*-butyltin chloride (0.325 g, 1 mmol) were reacted for

12 h at 40 °C. Recrystallized from ether, a transparent colorless crystal was formed. Yield: 77%. m.p. 155–157 °C. Anal. Calc. for $C_{18}H_{31}NO_3Sn$: C, 50.49; H, 7.30; N, 3.27. Found: C, 50.18; H, 7.61; N, 2.99%. IR (KBr, cm^{-1}): $\nu_{as}(COO)$, 1651; $\nu_s(COO)$, 1372; $\nu(Sn-C)$, 536; $\nu(Sn-O)$, 471. 1H NMR [$(CD_3)_2SO$, ppm]: δ = 9.71 (s, 1H, -OH), 8.00–8.54 [m, 3H, pyridine (=CH)], 1.26–1.39 (m, 18H, $CH_2CH_2CH_2$); 0.91 (t, 9H, CH_3). ^{13}C NMR [$(CD_3)_2SO$, ppm]: δ 166.02 (COO); 118.14, 122.37, 139.75, 141.31, 152.95 [pyridine (=C)]; 14.02, 18.21 ($^1J_{Sn-C}$ = 377 Hz), 27.51, 29.38 (*n*-Bu). ^{119}Sn NMR [$(CD_3)_2SO$, ppm]: –129.6.

3.2.9. Synthesis of complex 9

The procedure is similar to that of complex 1, 2-hydroxyisonicotinic acid (0.139 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), and trimethyltin chloride (0.199 g, 1 mmol) were reacted for 12 h at 40 °C. Recrystallized from methanol and a transparent colorless crystal was formed. Yield: 81%. m.p. 188–190 °C. Anal. Calc. for $C_9H_{13}NO_3Sn$: C, 35.80; H, 4.34; N, 4.64. Found: C, 35.54; H, 4.61; N, 4.36%. IR (KBr, cm^{-1}): $\nu_{as}(COO)$, 1655; $\nu_s(COO)$, 1372; $\nu(Sn-C)$, 568; $\nu(Sn-O)$, 457. 1H NMR [$(CD_3)_2SO$, ppm]: δ = 0.64 (s, 9H, $Sn-CH_3$, $^2J_{Sn-H}$ = 72.2 Hz), 7.77–8.12 [m, 3H, pyridine (=CH)], 11.75 (s, 1H, N-H). ^{13}C NMR [$(CD_3)_2SO$, ppm]: δ 167.34 (COO); 113.04, 122.10, 138.51, 140.66, 162.67 [pyridine (=C)], 11.13 (CH_3 , $^1J_{Sn-C}$ = 640 Hz). ^{119}Sn NMR [$(CD_3)_2SO$, ppm]: –151.2.

3.2.10. Synthesis of complex 10

The procedure is similar to that of complex 1, 2-hydroxyisonicotinic acid (0.139 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), and tribenzyltin chloride (0.427 g, 1 mmol) were reacted for 12 h at 40 °C. Recrystallized from methanol and a transparent colorless crystal was formed. Yield: 81%. m.p. 97–99 °C. Anal. Calc. for $C_{28}H_{29}NO_4Sn$: C, 59.81; H, 5.20; N, 2.49. Found: C, 60.18; H, 4.97; N, 2.27%. IR (KBr, cm^{-1}): $\nu_{as}(COO)$, 1654; $\nu_s(COO)$, 1372; $\nu(Sn-C)$, 571; $\nu(Sn-O)$, 453. 1H NMR [$(CD_3)_2SO$, ppm]: δ = 11.49 (s, 1H, N-H), 7.69–8.19 [m, 3H, pyridine (=CH)], 7.28–7.49 (m, 15H, Ph), 4.83 (–OH), 3.61 (– OCH_3), 2.75 (s, 6H, Ph- CH_2). ^{13}C NMR [$(CD_3)_2SO$, ppm]: δ 170.75 (COO); 112.84, 118.63, 138.67, 140.75, 158.09 [pyridine (=C)]; 131.07–138.51 (Ar-C), 58.31 (– OCH_3), 28.13 (Ph- CH_2), 17.9 (– CH_3). ^{119}Sn NMR [$(CD_3)_2SO$, ppm]: –136.8.

3.2.11. Synthesis of complex 11

The procedure is similar to that of complex 1, 2-hydroxyisonicotinic acid (0.139 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), and triphenyltin chloride (0.385 g, 1 mmol) were reacted for 12 h at 40 °C. Recrystallized from methanol and a transparent colorless crystal was formed. Yield: 78%. m.p. 188–190 °C. Anal. Calc. for $C_{145}H_{117}N_6O_{18.5}Sn_6$: C, 59.00; H, 4.00; N, 2.85. Found: C, 58.69; H, 4.21; N, 2.58%. IR (KBr, cm^{-1}): $\nu_{as}(COO)$, 1659; $\nu_s(COO)$, 1372; $\nu(Sn-C)$, 572; $\nu(Sn-O)$, 446. 1H NMR [$(CD_3)_2SO$, ppm]: δ = 7.26–7.51 (s, 90H, $Sn-Ph$), 7.74–8.13 [m, 3H, pyridine (=CH)], 11.67 (s, 6H, N-H). ^{13}C NMR [$(CD_3)_2SO$, ppm]: δ 168.15 (COO); 113.58, 122.37, 135.99, 141.31, 159.61 [pyridine (=C)], 129.33–138.68 (Ar-C). ^{119}Sn NMR [$(CD_3)_2SO$, ppm]: –176.2.

3.3. X-ray crystallographic studies

Diffraction data were collected on a Smart CCD area-detector with graphite monochromated Mo $K\alpha$ radiation (λ = 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. Hydrogen

atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Tables 1 and 2.

4. Conclusions

In summary, a series new triorganotin(IV) pyridinecarboxylates have been synthesized and characterized. Detailed studies on the structures of these complexes indicate that the complexes based on 6-hydroxynicotinic acid and 2-hydroxyisonicotinic acid, the carboxylate oxygen atoms and the keto oxygen atoms coordinate to Sn centers forming a chain/cycle. However, in the complexes based on 5-hydroxynicotinic acid, instead of the keto oxygen atoms, the N atoms and carboxylate oxygen atoms coordinate to Sn centers.

Acknowledgment

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Appendix A. Supplementary material

CCDC 681949, 681953, 681951, 740924, 740928, 740927, 707748, 742093, and 707749 contains the supplementary crystallographic data for complexes 1, 2, 3, 4, 7, 8, 9, 10, and 11. 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.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.09.001.

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