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Coordination geometry of monomeric, dimeric and polymeric organotin(IV) compounds constructed from 5-bromopyridine-2-carboxylic acid and mono-, di- or tri-organotin precursors

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HIGHLIGHTS

▶ Five new organotin(IV) compounds with 5-bromopyridine-2-carboxylic acid as the ligand were synthesized.

- ► Monomeric, dimeric and polymeric organotin(IV) carboxylates were obtained.
- ► In all compounds, there are three different coordination modes for the ligands.

► For triorganotin(IV) polymers, the intermolecular interaction would rupture in solution.

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ABSTRACT

Reactions of mono-, di-, tri-alkyltin chlorides or oxide with 5-bromopyridine-2-carboxylic acid result in five new organotin(IV) compounds, $[MeSn(O_2CC_5NH_3Br)Cl_2(H_2O)]\cdot(C_2H_5)_2O$ (1), $[(n-Bu)Sn(O_2CC_5NH_3Br)Cl_2(H_2O)]\cdot(C_2H_5)_2O$ (2), $\{[(n-Bu)_2Sn(O_2CC_5NH_3Br)]_2O\}_2$ (3) $[(n-Bu)_3Sn(O_2CC_5NH_3Br)]_n$ (4) and $[Ph_3 Sn(O_2CC_5NH_3Br)]_n$ (5), which have been characterized by single crystal X-ray diffraction, element analysis, IR, ¹H, ¹³C and ¹¹⁹Sn NMR. Three different coordination modes for the ligand are demonstrated in this group of compounds: (1) bidentate mode with the pyridyl nitrogen atom and carboxyl oxygen atom for mono-alkyltin compounds 1 and 2, in which six-coordinated tin center is also bound with two chlorine ions and one water molecule; (2) compound 3 is a tetranuclear centrosymmetric dimer with a central Sn₂O₂ four-membered ring. The four tin atoms are linked by two bridging carboxyl groups while the remaining two act as monodentate ligands to the endo- and exo-cyclic tin atoms; (3) for tri-alkyltin compounds **4** and **5**, the bidentate bridging carboxylate bridge propagates 1D polymeric chains, typical for five coordinate tin. However, in compounds **3**–5, the pyridyl nitrogen atoms do not participate in the coordination. For triorganotin(IV) polymers **4** and **5**, the solution studies show the collapse of the intermolecular interactions observed in the solid state to yield monomeric species.

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1. Introduction

In recent years, organotin(IV) compounds have attracted considerable interests, because of their applications in industry, agriculture, biology, especially in the fields of organic synthesis, catalysts, pharmaceutics and antitumour activities [1–4]. In general, the biochemical activity of organotin(IV) compounds is influenced greatly by their molecular structure and the coordination

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number of tin atoms [5–7]. From the view of coordination chemistry, the bi-dentate or multi-dentate ligands with N, O and S donor atoms may benefit the construction of more complicated and interesting structures that have multiple tin atoms and molecular structure dimension, and increase coordination number as well as diversified coordination modes [8–10]. These aspects have been attracting the attention of a number of researchers and a multitude of structural types have been discovered [11].

A large number of organotin(IV) carboxylates has been prepared and structurally characterized during the last few decades in our laboratory [12,13], and it is well known that the biological activity

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of organotins is related to not only the coordination number, but also the type of alkyl groups attached to the tin atom. The structural characterization of such organotin(IV) compounds may provide important clues to the structure–activity relationship of the ligand and alkyl species and provide an invaluable insight to the reaction mechanism that may, in turn, allow synthetic chemists to further optimize reaction conditions [14–16]. Thus new rational strategies to construct a variety of types of organotins(IV) are required.

Studies reveal that the introduction of halogen atoms into the antitumor agents will have a significan affect on their biological activity [17–19]. As part of our interest to pyridine carboxylic acid ligands, we intend to modify the composition of the organotin(IV) 5-bromopyridine-2-carboxylates with mono-, bi-, tri-alkyltin salts, as well as adjust different coordination solvent molecules. Furthermore, the isolation and structural characterization of five tin coordination monomeric, dimeric or polymeric compounds by X-ray crystallography are presented. From previous reports it is known that the reaction of organotin(IV) groups with 2-pyridinecarboxylate and its derivatives gives complexes with coordinative N \rightarrow Sn bonds and five-membered C₂NOSn chelate rings [20,21]. It is expected that different alkyltin salts afford opportunities for generating novel topologies.

2. Experimental

2.1. Materials and physical measurements

Methyltin trichloride, *n*-butyltin trichloride, di-*n*-butyltin oxide, tri-*n*-butyltin chloride, triphenyltin chloride, 5-bromopyridine-2carboxylic acid were purchased from Sigma–Aldrich Chemical Co. and used without further purification. All the solvents used in the reaction were of AR grade and dried using standard literature procedures.

IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs. ¹H, ¹³C and ¹¹⁹Sn NMR spectra were recorded on a Mercury Plus-400 NMR spectrometer; chemical shifts were given in ppm relative to Me₄Si and Me₄Sn in CDCl₃ solvent, and ¹³C and ¹¹⁹Sn NMR spectra were determined in the decoupling mode. The spectra were acquired at room temperature (25 °C) unless otherwise specified. Elemental analyses were performed with a PE-2400II elemental analyzer.

2.2. Synthesis of the compounds

2.2.1. Synthesis of compound $[MeSn(O_2CC_5NH_3Br)Cl_2(H_2O)] \cdot (C_2H_5)_2O$ (1)

The reaction was carried out under nitrogen atmosphere with the use of the the standard Schlenk technique. 5-Bromopyridine-2-carboxylic acid (0.202 g, 1 mmol) and sodium ethoxide (0.068 g, 1.0 mmol) were added to 20 mL absolute benzene and heated under reflux with stirring for 0.5 h. After the addition of methyltin trichloride (0.24 g, 1.0 mmol) to the reactor, the reaction mixture was refluxed for 10 h more. The reaction solution obtained after filtering was evaporated in vacuum to give a solid, which was then recrystallized from diethyl/petroleum ether to give colorless block crystals suitable for single crystal X-ray diffraction. Yield: 76%. M.p.: 179–180 °C. Anal. Calc. for C₁₁H₁₈BrCl₂NO₄Sn: C 26.54, H 3.65, N 2.81; Found: C 26.73, H 3.52, N 2.75%. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.48–9.24 (*m*, 3H, Py–H), 3.47 (*q*, 4H, -CH₂-), 1.61 (s, 2H, H₂O), 1.22 (t, 6H, -CH₃), 0.83 (s, 3H, Sn-CH₃). ¹³C NMR (100 MHz, CDCl₃, ppm): δ13.8 (-CH₃), 114.1, 138.8, 145.5, 148.3, 159.7 (Py-C), 157.4 (COO). ¹¹⁹Sn NMR (149 MHz, CDCl₃, ppm): δ-358.6. IR (KBr, cm⁻¹): 3327 (s, H–O–H), 1538, 1299 (s, COO), 574 (*m*, Sn–C), 532 (*m*, Sn–O), 429 (*w*, Sn–N), 367 (*m*, Sn–Cl).

2.2.2. Synthesis of compound $[(n-Bu)Sn(O_2CC_5NH_3Br)Cl_2(H_2O)]$ $\cdot(C_2H_5)_2O(\mathbf{2})$

Compound **2** was prepared by the similar method as compound 1. 5-Bromopyridine-2-carboxylic acid (0.202 g, 1 mmol) and sodium ethoxide (0.068 g, 1.0 mmol) were added to dry benzene (20 ml) in a Schlenk flask and stirred for 0.5 h. n-Butyltin trichloride (0.28 g, 1.0 mmol) was then added and the reaction mixture was refluxed for 10 h more and then filtered. The solvent was gradually removed by evaporation under vacuum until a solid product was obtained. The solid was then recrystallized from diethyl/petroleum ether to give colorless crystals suitable for single crystal X-ray diffraction were obtained. Yield 71%. M.p.: 160–162 °C. Anal. Calc. for C14H24BrCl2NO4Sn: C 31.15. H 4.48. N 2.59: Found: C 31.07, H 4.52, N 2.61%. ¹H NMR (400 MHz, CDCl₃, ppm): δ8.56-9.09 (m, 3H, Py-H), 3.47 (q, 4H, -CH₂-), 1.72 (s, 2H, H₂O), 1.57-1.63 (m, 4H, Sn-n-Bu-α, β-CH₂), 1.19-1.36 (m, 2H, Sn-n-Bu- γ -CH₂), 1.11 (*t*, 6H, CH₃), 0.92 (*t*, *J* = 6.8 Hz, 3H, Sn-*n*-Bu- δ -CH₃). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 15.3 (CH₃), 25.7, 26.8, 39.7, (-CH₂-), 120.1, 135.8, 147.5, 150.3, 153.7 (Py-C), 157.4 (COO). ¹¹⁹Sn NMR (149 MHz, CDCl₃, ppm): δ-339.8. IR (KBr, cm⁻¹): 3331 (s, H-O-H), 1512, 1265 (s, COO), 552 (m, Sn-C), 537 (m, Sn-O), 434 (m, Sn-N), 351 (m, Sn-Cl).

2.2.3. Synthesis of compound $\{[(n-Bu)_2Sn(O_2CC_5NH_3Br)]_2O\}_2$ (3)

5-Bromopyridine-2-carboxylic acid (0.202 g, 1 mmol) was added to benzene solution (30 ml) of di-n-butyltin oxide (0.2487 g, 1 mmol). The mixture was heated under reflux with stirring for 10 h. The clear solution thus obtained was evaporated under vacuum to form a solid, and recrystallized in dichloromethane/ hexane. Then the colorless crystals suitable for single crystal X-ray diffraction were obtained. Yield: 85%. M.p.: 118-120 °C. Anal. Calc. for C₅₆H₈₄Br₄N₄O₁₀Sn₄: C 38.05, H 4.79, N 3.17; Found: C 38.11, H 4.73, N 3.22%. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.31–9.16 (*m*, 12H, Py-H), 1.60 (t, J = 8.0 Hz, 16H, Sn-n-Bu- α -CH₂), 1.23–1.36 (m, 32H, Sn-*n*-Bu- β , γ -CH₂), 0.91 (*t*, *J* = 7.2 Hz, 24H, Sn-*n*-Bu- δ -CH₃). ¹³C NMR (100 MHz, CDCl₃, ppm): δ14.1 (CH₃), 26.3, 29.1, 42.3 (--CH2--), 113.8, 134.7, 145.6, 146.5, 151.3 (Py--C), 164.7, 169.5 (COO). ¹¹⁹Sn NMR (149 MHz, CDCl₃, ppm): δ -205.3, -220.8. IR (KBr, cm⁻¹): 1635, 1617, 1435, 1391 (s, COO), 636 (m, Sn–O–Sn), 563 (*m*, Sn–C), 462, 541 (*m*, Sn–O).

2.2.4. Synthesis of compound $[(n-Bu)_3Sn(O_2CC_5NH_3Br)]_n$ (4)

Compound **4** was prepared by the similar method as compound 1, 5-bromopyridine-2-carboxylic acid (0.202 g, 1.0 mmol) and sodium ethoxide (0.068 g, 1.0 mmol) were added to dry benzene (20 ml) and stirred for 0.5 h. Tri-n-butyltin chloride (0.325 g, 1.0 mmol) was then added and the reaction mixture was refluxed for 10 h more and then filtered. The solvent was gradually removed by evaporating under vacuum until a solid product was obtained. The solid was then recrystallized from diethyl/petroleum ether and colorless block crystals suitable for X-ray diffraction were obtained. Yield: 72%. M.p.: 156–160 °C. Anal. Calc. for C₁₈H₃₀BrNO₂Sn: C 44.03, H 6.16, N 2.85%; Found: C 44.15, H 6.09, N 2.86%. ¹H NMR (400 MHz, CDCl₃, ppm): δ8.47–9.05 (m, 3H, Py–H), 1.51–1.60 (m, 6H, Sn-n-Bu-α-CH₂), 1.44-1.51 (m, 6H, Sn-n-Bu-β-CH₂) 1.23-1.36 $(pq, 6H, Sn-n-Bu-\gamma-CH_2), 0.90$ $(t, J = 7.2 Hz, 9H, Sn-n-Bu-\delta-CH_3).$ ¹³C NMR (100 MHz, CDCl₃, ppm): δ 13.9 (CH₃), 43.7 (-CH₂-), 115.8, 138.7, 146.6, 148.5, 151.3 (Py-C), 162.4 (COO). ¹¹⁹Sn NMR (149 MHz, CDCl₃, ppm): δ-137.1. IR (KBr, cm⁻¹): 1586, 1384 (s, COO), 562 (w, Sn–C), 485 (m, Sn–O).

2.2.5. Synthesis of compound $[Ph_3Sn(O_2CC_5NH_3Br)]_n$ (5)

Compound **5** was prepared by the similar method as compound 1, 5-bromopyridine-2-carboxylic acid (0.202 g, 1.0 mmol) and sodium ethoxide (0.068 g, 1.0 mmol) were added to dry benzene (20 ml) and stirred for 0.5 h. Triphenyltin chloride (0.385 g, 1.0 mmol) was then added and the reaction mixture was refluxed for 10 h more and then filtered. The solvent was gradually removed by evaporating under vacuum until a solid product was obtained. The solid was then recrystallized from diethyl/petroleum ether and colorless block crystals suitable for X-ray diffraction were obtained. Yield: 83%. M.p.: 172-173 °C. Anal. Calc. for C24H18 BrNO₂Sn: C 52.32, H 3.29, N 2.54%; Found: C 52.39, H 3.22, N 2.47%. ¹H NMR (400 MHz, CDCl₃, ppm): δ8.53–9.25(*m*, 3H, Py–H), 7.49–7.67 (*m*, 15H, Sn–C₆H₅). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 114.3, 125.6, 126.3, 129.9, 131.6, 136.9, 141.4, 146.8, 149.1 (Ar–C), 168.24 (COO). ¹¹⁹Sn NMR (149 MHz, CDCl₂, ppm): δ -126.3. IR (KBr. cm⁻¹): 1558, 1359 (s. COO), 567 (m. Sn–C), 487 (*m*, Sn–O).

2.3. Determination of crystal structures

X-ray diffraction data for crystals were performed with graphite-monochromated Mo K α radiation (0.71073 Å) on the Bruker Smart-1000 CCD diffractometer and collected by the ω -2 θ scan technique at 298(2) K. The crystal structures were solved by direct method and different Fourier syntheses using SHELXL-97 program, and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were put in calculated positions or located from the Fourier maps and refined isotropically with the isotropic vibration parameters related to the non-hydrogen atom to which they are bonded. Crystallographic data and experimental details of the structure determinations are listed in Table 1.

3. Results and discussion

3.1. Synthetic procedures of organotin(IV) compounds 1-5

Compounds **1–5** were obtained by the reactions between equimolar of 5-bromopyridine-2-carboxylic acid with mono-, bi- or trialkyltin salts in different solvents under the reflux conditions in good yields, 71–85%. In the preparation procedures of compounds

Table 1

Crystal data and structure refinement details for compounds 1-5.

1, **2**, **4** and **5**, the ligand should be firstly deprotonated by the addition of sodium ethoxide for further coordinating with organotin(IV) center. Reaction pathway for these compounds is shown in Scheme 1. All five compounds have been characterized by X-ray diffraction analysis, of which both compound **1** and **2** contain one uncoordinated diethyl ether solvent molecule incorporated from the recrystallization.

3.2. IR spectra

The IR spectra of compounds 1-5 reveal similarities. For all compounds, the characteristic absorptions of -COOH belonging to the ligand at 3200–3500 cm⁻¹ disappear, indicating that it coordinates to the tin atom in COO⁻ form. The $\Delta v[v_{as}(CO_2^-) - v_s(CO_2^-)]$ values $(239-247 \text{ cm}^{-1})$ for compounds **1** and **2** indicate that the carboxylate groups adopt the monodentate coordination mode [22]. In compounds **4** and **5** the Δv values are under 200 cm⁻¹, which indicates a bidentate coordination mode for the carboxylate ligand. However, IR spectra reveal strong absorptions at 1635, 1617, 1435 and 1391 cm^{-1} for compound **3**, corresponding to the symmetric and antisymmetric carboxylate stretches, which are typical for tetranuclear diorganotin carboxylates. In the 462-541 cm⁻¹ region, medium absorptions are assigned to ν (Sn–O) [23]. The presence of two Sn–O bands, which is more obvious for compound **3**, reflects different Sn–O bond lengths, as proved by the X-ray analysis. The dichlorotin derivatives 1 and 2 exhibit v(Sn-O) (532 and 537 cm⁻¹) shifted to higher frequencies, reflecting the different effects of Cl⁻ and the organo ligands. Generally, a powerful electron-withdrawing group, such as Cl, increases the strength of the Sn–O bonds. ν (Sn–Cl) for **1** and **2** are at about 360 cm^{-1} . Otherwise, in **1** and **2**, the absorptions at ~430 cm⁻¹ for $\nu(Sn-N)$ have also been observed. A strong absorption at 636 cm⁻¹ for compound **3** is assigned to Sn–O–Sn stretching vibration, indicating that the existence of Sn-O-Sn bridged structure [23].

3.3. ¹H, ¹³C and ¹¹⁹Sn NMR spectra (CDCl₃)

In the ¹H NMR spectra of compounds **1–5**, the single resonance for the proton of —COOH is absent, indicating the carboxylic ligand coordinated to tin atom in COO[–] form. The protons of the pyridyl ring for all compounds give broad signals at 8.31–9.25 ppm, which

Compound	1	2	3	4	5
Empirical formula	C11H18BrCl2NO4Sn	C14H24BrCl2NO4Sn	C ₂₈ H ₄₂ Br ₂ N ₂ O ₅ Sn ₂	C18H30BrNO2Sn	C24H18BrNO2Sn
Formula weight	497.76	539.84	883.84	491.03	550.99
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P2(1)/c	P-1	P2(1)/n	P2(1)/n
a (Å)	7.4621(16)	17.979(2)	11.390(2)	12.726(3)	12.945(3)
b (Å)	9.472(2)	10.0792(16)	13.145(3)	10.727(2)	12.333(3)
<i>c</i> (Å)	14.361(3)	11.7368(18)	13.782(3)	16.007(4)	13.420(3)
α (°)	70.897(2)	90	112.139(2)	90	90
β(°)	89.188(2)	90.1450(10)	111.375(2)	93.409	91.985(3)
γ (°)	70.113(2)	90	94.370(2)	90	90
$V(\dot{A}^3)$	896.5(3)	2126.9(5)	1724.4(6)	2181.3(8)	2141.3(9)
Ζ	2	4	2	4	4
F(000)	484	104	868	984	1080
Dcalc (g cm ⁻³)	1.844	1.686	1.702	1.495	1.709
θ Range (°)	1.51-25.01	2.32-25.00	1.73-25.01	1.99-25.01	2.15-25.01
Number of reflections	4656	10410	8701	11083	9993
Number of paramters	184	208	352	211	262
R factor all	0.0476	0.1148	0.0797	0.1114	0.0372
<i>R</i> factor $[I > 2\sigma(I)]$	0.0395	0.0694	0.0520	0.0606	0.0253
wR_2	0.1132	0.2617	0.1506	0.2068	0.0594
$wR_2 [I > 2\sigma(I)]$	0.1057	0.1983	0.1289	0.1625	0.0550
Goodness-of-fit (GOF)	1.004	1.011	1.041	1.000	1.055



Scheme 1. Reaction pathway of compounds 1-5.

are consistent with values reported in other organotin(IV) compounds with pyridyl carboxylic acid as ligands [24–26]. The methyl protons of mono-methyltin(IV) derivative **1** appear as sharp singlets at 0.83 ppm with well-defined satellites. The α -CH₂, β -CH₂ and γ -CH₂ protons of mono-*n*-butyltin compounds appear as multiplets, and δ -CH₃ appears as a triplet with $^{3}J[^{1}H, ^{1}H] = 6.8$ Hz. The α -CH₂ protons of di-*n*-butyltin compounds appear as a triplet at 1.60 ppm with $^{3}J[^{1}H, ^{1}H] = 8.0$ Hz; the β -CH₂ and γ -CH₂ protons appear as multiplets, and δ -CH₃ appears as a triplet with $^{3}J[^{1}H, ^{1}H] = 7.2$ Hz. In the tri-*n*-tributyltin(IV) complex, the δ -CH₃ appears as a triplet at 0.90 ppm with $^{3}J[^{1}H, ^{1}H] = 7.2$ Hz, γ -CH₂ as a pseudoquintet at 1.23–1.36 ppm, and the α -CH₂ and β -CH₂ protons as multiplets at 1.51–1.60 ppm and 1.44–1.51 ppm, respectively. The ¹³C NMR spectral data for the R groups attached to the tin atom, where $R = CH_3$, *n*-Bu and Ph, were assigned by comparison with related analogues as model compounds [24–26]. The positions of the pyridyl carbon signals undergo minor variations in the compounds compared with those observed in the free acid. The carboxylate carbon shifts to a lower field region in all the compounds, indicating participation of the carboxylic group in coordination to tin(IV).

The ¹¹⁹Sn NMR spectra were recorded in CDCl₃ solution, a noncoordinating solvent. The chemical shift values obtained for the monoorganotin(IV) derivatives **1** and **2** (see Section 2) lie in the normal range expected for six-coordinate tin compounds, which is similar to that found in the compound $\{[(n-Bu)SnCl_2]^{-}[4-NHC_5]$



Fig. 1. Dimeric structure (with thermal ellipsoids at 30% probability) of compound 1 linked by intermolecular O-H…O hydrogen bonds (dotted line) among the coordinated water molecule, diethyl ether solvent and the carboxyl oxygen atoms, and its numbering scheme. All H atoms are omitted for clarity.



Fig. 2. Supramolecular structure (with thermal ellipsoids at 30% probability) of compound 2 showing the 1D chain linked by intermolecular O—H···O hydrogen bonds (dotted line) among the coordinated water molecule, diethyl ether solvent and the carboxyl oxygen atoms, and its numbering scheme. All H atoms are omitted for clarity.

Table 2 Selected bond lengths (Å	A) and angles (°) f	or compounds 1 and 2 .	
1			
Sn(1) - C(7)	2.113(6)	Sn(1) - N(1)	2.263(4)
Sn(1) = O(1)	2.124(3)	Sn(1) - Cl(2)	2.413(1)
Sn(1) = O(3)	2.202(4)		2.424(2)
C(7)— $Sn(1)$ — $O(1)$	94.1(2)	N(1)— $Sn(1)$ — $Cl(1)$	88.45(10)
C(7)— $Sn(1)$ — $O(3)$	95.8(2)	C(7)— $Sn(1)$ — $Cl(2)$	100.5(2)
O(1)-Sn(1)-O(3)	79.45(1)	O(1)-Sn(1)-Cl(2)	94.63(1)
O(1)-Sn(1)-N(1)	74.37(1)	N(1)-Sn(1)-Cl(2)	83.80(1)
O(3) - Sn(1) - N(1)	79.30(1)	Cl(1)-Sn(1)-Cl(2)	95.55(5)
C(7) - Sn(1) - Cl(1)	102.1(2)	O(3)-Sn(1)-Cl(1)	85.53(9)
2	.,		
Sn(1)—O(1)	2.110(8)	Sn(1)-N(1)	2.256(9)
Sn(1)—C(7)	2.146(1)	Sn(1)-Cl(2)	2.399(3)
Sn(1)—O(3)	2.199(8)	Sn(1)-Cl(1)	2.406(3)
O(1)-Sn(1)-C(7)	95.2(5)	O(1)-Sn(1)-Cl(2)	89.6(2)
O(1)-Sn(1)-O(3)	83.7(3)	C(7)-Sn(1)-Cl(2)	103.3(4)
C(7)-Sn(1)-O(3)	90.1(5)	N(1)-Sn(1)-Cl(1)	88.4(2)
O(1)—Sn(1)—N(1)	73.7(3)	N(1)—Sn(1)—Cl(2)	86.8(2)
O(3)—Sn(1)—N(1)	79.0(3)	C(7)—Sn(1)—Cl(1)	101.6(5)
O(3)—Sn(1)—Cl(1)	88.8(3)	Cl(2)—Sn(1)—Cl(1)	93.74(1)

Fable 3							
Selected	bond	lengths	(Å) and	l angles	(°) for	compound	3.

Selected Bolid lengths (11) di	ia angles () ioi	compound 3.	
Sn(1)-C(17)	2.111(7)	Sn(2)-O(5)	1.991(4)
Sn(1)-O(5)	2.112(4)	Sn(2)-C(25)	2.109(9)
Sn(1)-C(13)	2.127(7)	Sn(2)-C(21)	2.121(8)
Sn(1)-O(5)#1	2.182(5)	Sn(2)-O(3)	2.207(5)
Sn(1)-O(1)	2.347(5)	Sn(2)-O(2)	2.222(6)
Sn(1)-O(3)#1	2.516(5)		
C(17)—Sn(1)—O(5)	102.9(2)	O(1)-Sn(1)-O(3)#1	130.73(2)
O(5) - Sn(1) - C(13)	100.2(2)	O(5)-Sn(2)-C(25)	115.0(3)
C(17)-Sn(1)-O(5)#1	99.2(3)	O(5)-Sn(2)-C(21)	117.9(3)
O(5)-Sn(1)-O(5)#1	74.62(2)	C(25)-Sn(2)-C(21)	127.1(4)
C(13)-Sn(1)-O(5)#1	97.6(2)	O(5)-Sn(2)-O(3)	76.40(2)
C(17) - Sn(1) - O(1)	84.6(3)	C(25)-Sn(2)-O(3)	94.1(3)
O(5) - Sn(1) - O(1)	87.83(2)	C(21) - Sn(2) - O(3)	97.9(3)
C(13) - Sn(1) - O(1)	85.2(3)	O(5)-Sn(2)-O(2)	94.42(2)
C(17)-Sn(1)-O(3)#1	83.9(2)	C(25)-Sn(2)-O(2)	89.3(3)
C(13)-Sn(1)-O(3)#1	85.0(2)	C(21)-Sn(2)-O(2)	86.8(3)
O(5)#1—Sn(1)—O(3)#1	66.83(2)		

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

H₄CON₂CH(C₆H₄O-2)]⁺ we reported previously [27]. The solution ¹¹⁹Sn NMR spectra of **3** shows two peaks at δ = -205.3, -220.8,

suggesting there are either five- or six-coordinate tin atoms in the distannoxane [28,29], which also reveals that the dimeric structure found in the solid state (vide infra) are retained in solution. However, ¹¹⁹Sn NMR spectra of compounds **4** (-137.1)



Fig. 3. The 1D chain structure of compound 3 (with thermal ellipsoids at 30% probability) formed by intermolecular C—H…O hydrogen-bonding interactions along the a-axis, and its numbering scheme. Part hydrogen and *n*-butyl carbon (except Sn—C) atoms are omitted for clarity.



Fig. 4. A perspective view of the 1D chain polymeric structure of compound 4 (with thermal ellipsoids at 30% probability) and its numbering scheme.



Fig. 5. A perspective view of the 1D chain polymeric structure of compound 5 (with thermal ellipsoids at 30% probability) and its numbering scheme.

and 5 (-126.3) are consistent with monomeric structures in solution [29,30], which is characteristic for a tetrahedral geometry.

3.4. X-ray crystallography

3.4.1. Crystal structures of compounds 1 and 2

When the reaction of 5-bromopyridine-2-carboxylic acid with methyltin trichloride or *n*-butyltin trichloride was carried out, compound **1** and **2** were obtained. As illustrated in Figs. 1 and 2, compounds **1** and **2** present the similar crystal structures, both including two parts, the organotin(IV) moieties and one uncoordinated diethyl ether solvent molecule. Selected bond distances and angles of compounds **1** and **2** are listed in Table 2.

X-ray single-crystal structural analyses reveal that both **1** and **2** are simple mononuclear compounds. In these two compounds, the Sn center is six-coordinated, being bound to one alkyl carbon atom, two chlorine atoms and one water oxygen atom, as well as one nitrogen and one oxygen atom from the bidentate ligand. The geometry around the tin atom is distorted octahedral, with the al-kyl carbon atom and the pyridyl nitrogen atom being in *trans* position, the two chlorine atoms and two oxygen atoms lying in the molecular plane. The bond lengths of Sn–O, Sn–N, Sn–Cl, and Sn–C, and their corresponding angles between two neighboring bonds (listed in Table 2) are consistent with those of similar mono-*n*-butyltin compound $\{[(n-Bu)SnCl_2]^-[4-NHC_5H_4CON_2CH (C_6H_4O-2)]^+$ we reported previously [27].

 Table 4

 Selected bond lengths (Å) and angles (°) for compounds 4 and 5.

4			
Sn(1)-C(7)	2.116(2)	Sn(1)-O(1)	2.266(7)
Sn(1)-C(15)	2.121(2)	Sn(1)-O(2)#1	2.336(8)
Sn(1)-C(11)	2.136(2)		
C(7)—Sn(1)—C(15)	123.8(6)	C(11) - Sn(1) - O(1)	85.3(5)
C(7) - Sn(1) - C(11)	117.2(6)	C(7)—Sn(1)—O(2)#1	89.5(6)
C(15)— $Sn(1)$ — $C(11)$	119.0(6)	C(15)—Sn(1)—O(2)#1	96.8(5)
C(7) - Sn(1) - O(1)	94.4(5)	C(11)-Sn(1)-O(2)#1	83.5(5)
C(15) - Sn(1) - O(1)	89.8(5)		
5			
Sn(1)-C(19)	2.128(3)	Sn(1)-O(1)	2.205(2)
Sn(1)-C(7)	2.131(3)	Sn(1)-O(2)#1	2.396(2)
Sn(1)-C(13)	2.144(3)		
C(19) - Sn(1) - C(7)	138.61(1)	C(13) - Sn(1) - O(1)	87.36(1)
C(19)—Sn(1)—C(13)	106.56(1)	C(19)-Sn(1)-O(2)#1	85.53(9)
C(7)—Sn(1)—C(13)	113.42(1)	C(7)—Sn(1)—O(2)#1	86.59(1)
C(19) - Sn(1) - O(1)	96.44(9)	C(13)-Sn(1)-O(2)#1	86.49(1)
C(7) - Sn(1) - O(1)	95.66(1)		

Symmetry code: (#1 for **4**) 3/2 - x, 1/2 + y, 1/2 - z; (#1 for **5**) 3/2 - x, -1/2 + y, 1/2 - z.

Intermolecular hydrogen-bonding interactions among the water molecules, uncoordinated solvent diethyl ether molecules and carboxyl oxygen atoms result in a dimeric structure for compound **1** (see Fig. 1) or a 1D infinite supramolecular chain for

compound **2** (see Fig. 2) [hydrogen bonding data: $O3 \cdots O4\#1$, 2.693 Å for **1** and 2.680 Å for **2**; $O3 \cdots O2\#2$, 2.648 Å for **1** and 2.659 Å for **2**; (#1 for **1**) 2 - x, 1 - y, 1 - z; (#2 for **1**) 2 - x, 1 - y, 2 - z; (#1 for **2**) x, 3/2 - y, -1/2 + z; (#2 for **2**) x, 3/2 - y, 1/2 + z].

3.4.2. Crystal structure of compound 3

Molecular structure of compound **3** is shown in Fig. 3; for clarity, the β , γ and δ carbon atoms of the *n*-butyl groups have been omitted. Selected bond distances and angles are listed in Table 3. As is the case of the other known carboxystannoxanes [28,30], the complex is a tetranuclear centrosymmetric dimer with a central Sn₂O₂ four-membered ring. The four tin atoms are linked by two bridging carboxyl groups while the remaining two act as monodentate ligands to the endo- and exo-cyclic tin atoms. Consideration of the axial angles O(2)—Sn(1)—O(3)#1 [#1: -x + 1, -y + 1, -z + 1 [130.73(17)°] and O(2)–Sn(2)–O(3) [170.81(18)°] and the Sn-O distances lead to the conclusion that the two tin atoms are in different environments. Both tin atoms are coordinated by two *n*-butyl moieties which form C–Sn–C angles of 154.3(3)° and $127.1(4)^\circ$, respectively. In the case of the exocyclic Sn(2) atom, the coordination is completed by O(2), O(3) and O(5) with distances of 2.222(6), 2.207(5) and 1.991(4) Å, respectively. For the endocyclic Sn(1) atom, the O(1), O(5) and O(5) #1 atoms all coordinate at distances of 2.347(5), 2.112(4) and 2.182(5) Å, and there is a longer but significant interaction of 2.516(5) Å to O(3)#1. In the case of Sn(2), O(1) is 3.603 Å from the tin atom. However, O(4) is appreciably closer at 3.361 Å, but it appears that the interaction is very weak. Thus it may be concluded that the exocyclic tin atom Sn(1) is best described as five-coordinated, and the endocyclic Sn(2) as pseudo-six-coordinated. As we know, this chemistry structure is very common for the other diorganotin(IV) pyridine-2-carboxylates [28,30], but is thoroughly different from those of diorganotin(IV) pyridyl 3- or 4-carboxylates. The place of carboxyl group on the pyridyl ring has an important effect on the coordination geometry of the central tin atoms, such as in the previous reported dibutyltin or dimethyltin 5-bromopyridine-3-carboxylates, the tin atoms are coordinated by four carboxyl oxygen atoms and one pyridyl nitrogen atom besides two alkyl carbon atoms, and the infinite one-dimensional polymeric chain structures have been formed by the bridging of the pyridine-3-carboxyl ligands [31,32].

As shown in Fig. 3, an infinite 1D chain is formed along *a* axis direction via the intermolecular C—H···O hydrogen bonds between oxygen atom O4 of the monodentate ligand and the hydrogen atom of pyridinyl ring (hydrogen bonding data: C4···O4#2, 3.189 Å; #2 1 - x, 2 - y, 1 - z).

3.4.3. Crystal structures of compounds 4 and 5

One-dimensional chain polymers **4** and **5** have been synthesized by the reaction of 5-bromopyridine-2-carboxylic acid with tri-*n*-butyltin chloride or tri-phenyltin chloride. The 1D polymeric chain solid state structures **4** and **5** are shown in Figs. 4 and 5. Selected geometric parameters are collected in Table 4. Due to the identical coordination geometry for **4** and **5**, structural analysis would be carried out by taking compound **4** for example.

The polymeric structure of **4** arises as the carboxylate ligands are typical bidentate bridging, albeit forming the relative symmetric bond distances of approximately 2.266(7) and 2.336(8) Å, which is comparable with literature reports [2.214(3)-2.410(3) Å]for the polymeric structure resulting from bridging coordination of the mono-carboxyl ligand [23], but is different obviously from the values of two asymmetric Sn—O bonds [2.160(3) and2.64.0(3) Å] in the cyclotetrameric tri-*n*-butyltin(IV) carboxylate derived from (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoic acid [19]. The individual tin atom coordination geometry is based on a *trans*-R₃SnO₂ trigonal bipyramid with the above-mentioned disparity in the Sn-O bond distances not withstanding. The axial positions are occupied by O1 and O2#1 [#1: -x + 3/2, y + 1/2, -z + 1/2] and axial angle is 168.8(2)°. The sum of the angles subtended at the tin atom in the equatorial plane is 360.18°, so that the atoms Sn1, C7, C11 and C15 are almost in the same plane.

As mentioned before there are a considerable number of crystal structure determinations for compounds of the general formula $R_3Sn(O_2CR')$ for triorganotin(IV) mono-carboxylates, and these are known to adopt a variety of coordination geometries [30]. The overwhelming majority of structures are monomeric, and these may be described as *cis*- R_3SnO_2 , depending on the magnitude of the intramolecular $Sn \cdots O$ interaction; or polymeric with *trans*- R_3SnO_2 geometry as the carboxylate ligands are bidentate bridging. The cyclo-oligomeric species have also been reported, such as cyclotetrameric or cyclohexameric structures [29], which depend on the steric factors associated the tin- and carboxylate-bound R groups and global crystal packing considerations, and may be thought as being intermediate between the monomeric and polymeric extremes described above.

4. Conclusion

In conclusion, this work has shown that 5-bromopyridine-2-carboxylic acid and different alkyltin salts can result in the formation of various topological organotin(IV) compounds. When mono-alkyltin chlorides and the ligand are used as the starting materials, novel mono-organotin compounds 1 and 2 are produced, in which the ligand present bidentate, one oxygen atom of $-CO_2^$ ion and one pyridyl nitrogen atom. When di-n-butyltin oxide is used as the starting material, a typical dimeric tetranuclear compound 3 results, which contains two different coordination environment tin atoms; and the two types of tin atoms are linked by the bridging bidentate and the monodentate $-CO_2^-$ oxygen atoms. For tri-organotin compounds 4 and 5, the bidentate carboxylic group connects contiguous tin atoms, which result in the formation of 1D bridging infinite polymeric chains. In addition, in compounds 1, 2 and 3 independent units are connected by the intermolecular O-H···O or C-H···O hydrogen bonds into the dimer or infinite supermolecular chain. The effect of the introduction of bromine atom to the pyridyl group in organotin(IV) compounds on their antitumor activities is in progress.

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Appendix A. Supplementary material

CCDC-871010 (for 1), -871009 (for 2), -871011 (for 3), -871013 (for 4), and -871012 (for 5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, 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 http://dx.doi.org/ 10.1016/j.molstruc.2012.11.052.

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