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Organotin(IV) carboxylates based on amide carboxylic acids: Syntheses, crystal structures and characterizations

Xiao Xiao [a], Xiao Han [a], Zemin Mei [b], Dongsheng Zhu [a,*], Kuizhan Shao [a], Jingwen Liang [a], Min Tian [a], Lin Xu [a]

[a] Department of Chemistry, Northeast Normal University, 5268 Renmin Street, Changchun 130024, PR China
[b] Department of Chemistry, Baicheng Normal University, 9 Zhongxing East Street, Baicheng 137000, PR China

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ABSTRACT

A series of organotin carboxylates based on amide carboxylic acids: $(Ph_3Sn)(L^1)\cdot C_7H_8$ (**1**) (L^1 = (1,3-dioxo-1*H*,3*H*-benzo[de]isoquinolin-2-yl)-acetic acid), $(Ph_3Sn)(L^2)$ (**2**) (L^2 = 3-(1,3-dioxo-1*H*,3*H*-benzo[de]isoquinolin-2-yl)-benzoic acid), $(Ph_3Sn)(L^3)\cdot C_7H_8$ (**3**) (L^3 = N-phenyl-phthalamic acid), $(n\text{-}Bu_2Sn)(L^1)_2\cdot C_7H_8$ (**4**), $(n\text{-}Bu_2Sn)(L^4)_2$ (**5**) (L^4 = 4-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-benzoic acid), $[(n\text{-}Bu_2Sn)_2(L^2)O]_2\cdot C_7H_8$ (**6**), $\{[n\text{-}Bu_2Sn(L^5)]_2O\}_2\cdot C_7H_8$ (**7**) (L^5 = 4-(1,3-dioxo-1*H*,3*H*-benzo[de]isoquinolin-2-yl)-benzoic acid) were synthesized with toluene being used as solvent in the reaction and characterized by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy and X-ray crystallography diffraction analyses. Complexes **1**–**5** are monomers in which **1**–**3** are triphenlytin carboxylates while **4** and **5** are dibutyltin carboxylates possessing crystallographically imposed two-fold symmetry. Complexes **6** and **7** are dimeric carboxylate tetraorganodistannoxanes and show a "ladder-like" molecular structure. Ligands in **1**–**3** and **6** adopt unidentate chelating mode and in **4** and **5** they are bidentate, while for **7** both of the chelate coordination modes exist. Intermolecular hydrogen bonds and $\pi\cdots\pi$ interactions help complexes **1**–**7** build their respective supramolecular structures which are discussed in detail. It is found that amide carboxylic acids are apt to adopt various coordination modes and lead diverse molecular architectures for organotin carboxylates.

1. Introduction

Self-assembly of organic ligands with organotin and the various intriguing topologies of organotin carboxylates have been extensively studied [1–4]. It is well known that the multidimensional architectures of them can be controlled by adjusting the tin-R groups, metal-to-ligand molar ratio and the type of organic ligands [5,6]. In addition to this, intermolecular interaction carries the weight of generating various supramolecular structures [7–9]. It is found that the reaction of monocarboxylic acid with triphenyltin hydroxide is inclined to produce mononuclear carboxylate, however, di-, tetra-nuclear polymeric carboxylates with complicated constructions are easily formed when monocarboxylic acid reacts with dibutyltin oxide [10–12]. To further understand the coordination chemistry and explore the diversiform structures of organotin carboxylate, we have investigated novel carboxylate ligands which have one kind hetero atoms "nitrogen" (amide carboxylic acid) and synthesized seven new organotin carboxylates herein.

2. Experimental section

2.1. General and instrumental

The reagents were used as supplied while the solvents were purified according to standard procedures [13]. The melting point was obtained with Kofler micro-melting point apparatus and was uncorrected. Elemental analyses (C, H, N) were carried out on a Perkin–Elmer PE 2400 CHN instrument. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury operating at 300 and 75 MHz, respectively. IR spectra (KBr pellets) were recorded on an Alpha Centauri FI/IR spectrometer (400–4000 cm^{-1} range).

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* Corresponding author. Tel.: +86 13009010567; fax: +86 0431 85684009.
E-mail address: zhuds206@nenu.edu.cn (D. Zhu).

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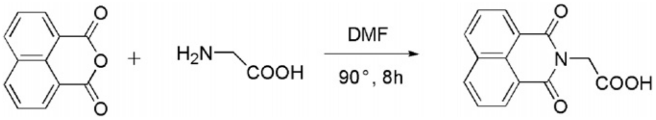
Table 1
Crystal data and structure refinement parameters for **1**–**7**.

	1	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{35}H_{23}NO_4Sn$	$C_{37}H_{25}NO_4Sn$	$C_{39}H_{33}NO_3Sn$	$C_{79}H_{76}N_4O_{16}\ Sn_2$	$C_{38}H_{34}N_2O_8Sn$	$C_{70}H_{92}N_2O_{12}Sn_4$	$C_{122}H_{128}N_4O_{18}\ Sn_4$
M	640.23	666.09	682.35	1574.82	765.36	1628.22	2413.04
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\overline{1}$	$C2/c$	$C2/c$	$P\overline{1}$	$C2/c$	$P2_1/n$	$P\overline{1}$
a (Å)	8.7329(5)	35.3105(16)	31.094(2)	11.3853(5)	16.1847(15)	11.728(3)	13.2350(11)
b (Å)	9.1426(5)	9.7150(4)	10.0610(7)	11.8691(5)	7.2069(7)	23.791(7)	14.0524(12)
c (Å)	19.8833(11)	18.3051(8)	21.3427(15)	14.0419(6)	28.821(3)	13.941(4)	16.6201(14)
α (°)	92.0320(10)	90.00	90.00	97.9050(10)	90.00	90.00	80.1360(10)
β (°)	90.0860(10)	112.3770(10)	103.6560(10)	104.7740(10)	94.554(2)	90.00	88.6990(10)
γ (°)	111.6570(10)	90.00	90.00	104.4930(10)	90.00	90.00	63.7390(10)
V (Å^3)	1474.34(14)	5806.6(4)	6488.0(8)	1734.83(13)	3351.2(6)	3889.7(19)	2726.1(4)
Z	2	8	8	1	4	2	1
μ (mm^{-1})	0.906	0.923	0.826	0.794	0.820	1.323	0.975
Reflections collected	7483	15,149	18,748	9487	10,279	24,112	14,112
Independent reflections	5115	5721	5731	6678	3273	7726	10,476
R_{int}	0.0136	0.0254	0.0541	0.0128	0.0365	0.0605	0.0164
Goodness-of-fit on F^2	1.044	1.052	0.966	1.053	1.069	1.030	1.047
R_1, wR_2 [$I > 2\sigma(I)$]	0.0339, 0.0945	0.0259, 0.0634	0.0383, 0.0722	0.0395, 0.1052	0.0381, 0.0831	0.0921, 0.2464	0.0398, 0.0983
R_1, wR_2 (all data)	0.0370, 0.0967	0.0311, 0.0664	0.0730, 0.0830	0.0431, 0.1091	0.0462, 0.0870	0.1184, 0.2602	0.0500, 0.1048



Scheme 1. Synthesis of ligand L^1.

2.2. X-ray crystallography

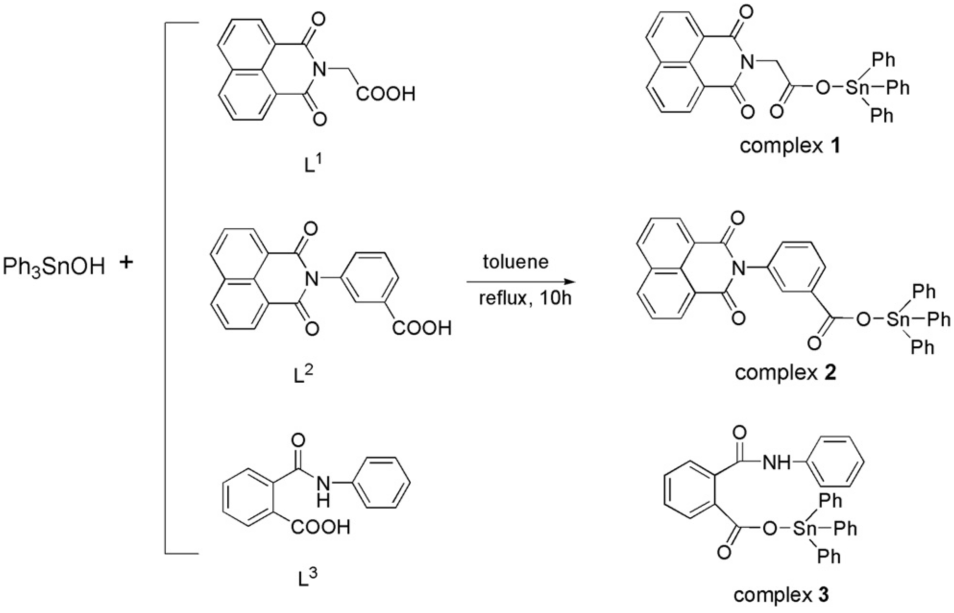
Diffraction intensities for complexes **1**–**7** were collected on a Bruker CCD Area Detector image plate diffractometer by using the ω/φ scan technique with Mo-Kα radiation (λ = 0.71073 Å). Absorption corrections were applied by using multiscan techniques. The structures were solved by direct methods with SHELXS-97 [14] and refined using SHELXL-97 [15]. All non-hydrogen atoms were refined with anisotropic temperature parameters; hydrogen atoms were refined as rigid groups. Crystal data and refinement results for complexes **1**–**7** are listed in Table 1.

2.3. Syntheses

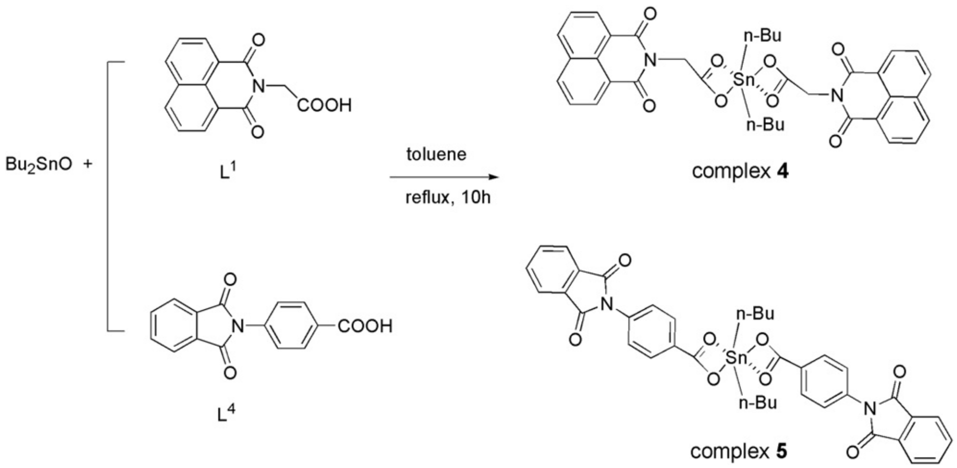
2.3.1. Syntheses of ligands

L^3 is commercially available. L^2, L^4 and L^5 were prepared by a standard method reported in the literature [16]. The preparation of L^1 is similar to that of L^2 and shown in Scheme 1.

L^1: Benzo[de]isochromene-1,3-dione (3.96 g, 0.02 mol) and glycine (1.50 g, 0.02 mol) were added into a three-neck flask with 40 mL DMF in it. The reaction mixture was stirred for 8 h in an oil-bath at 90 °C. After standing overnight, the mixture was filtrated to get the pale yellow powder. After washed with ethanol till the filter liquor turned colorless, the powder was recrystallized in a small portion of DMF. Yield: 89.4%; mp: 270.8–273.4 °C. ^{1}H NMR (dimethyl sulfoxide-d_6, ppm): δ 13.03 (s, 1H, COOH); 8.60 (d, 2H, J = 7.2 Hz, Ar–H); 8.54 (d, 2H, J = 7.1 Hz, Ar–H); 7.93 (dd, 2H, J = 7.4, 7.0 Hz, Ar–H); 4.74 (s, 2H, –CH$_2$–). ^{13}C NMR (dimethyl sulfoxide-d_6, ppm): δ 179.81 (1C, COO); 173.50 (2C, C=O); 137.56 (2C), 135.25 (2C), 130.23 (1C), 127.76 (2C), 125.66 (1C), 121.85 (2C) (carbon protons of aryl groups), 40.78 (1C, –CH$_2$–).



Scheme 2. Syntheses of complexes **1**–**3**.



Scheme 3. Syntheses of complexes **4** and **5**.

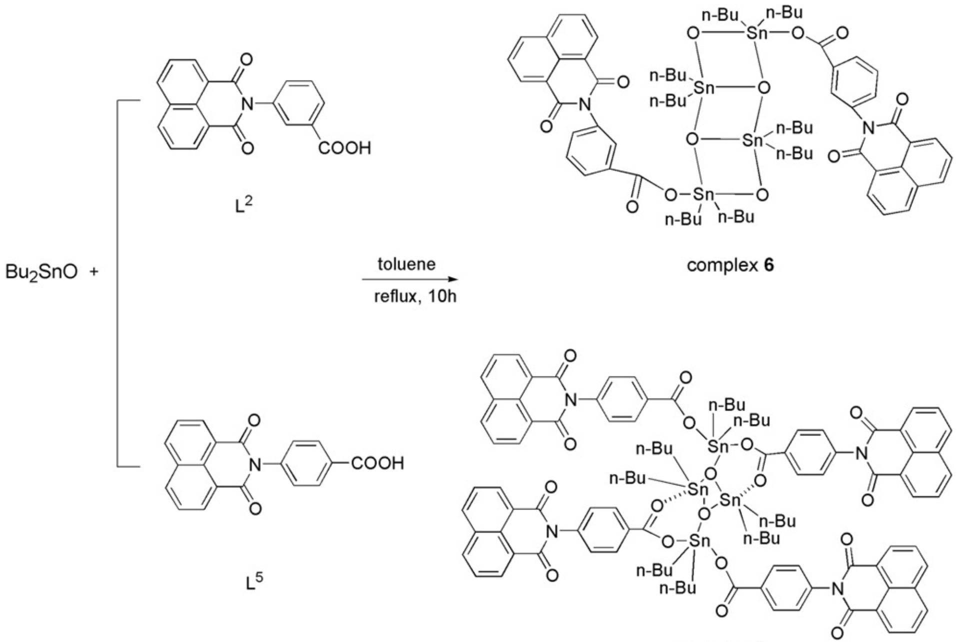
The syntheses of complexes **1**–**3** were shown in Scheme 2.

2.3.2. *Synthesis of (Ph$_3$Sn)(L^1)·C$_7$H$_8$ (**1**)*

A mixture of triphenyltin hydroxide (0.367 g, 1 mmol) and L^1 (0.255 g, 1 mmol) was heated under reflux in toluene (50 mL) for 10 h in a Dean–Stark apparatus for azeotropic removal of the water formed in the reaction. After cooling to room temperature, the solution was filtered. The filtrate was gradually evaporated and the X-ray quality colorless crystals were obtained. Yield: 75%; mp: 255.7–258.0 °C. Anal. Calcd for $C_{32}H_{23}NO_4Sn \cdot C_7H_8$: C, 67.26; N, 2.01; H, 4.49%. Found: C, 67.38; N, 2.08; H, 4.38%. IR (cm^{-1}): ν(O=C) 1714; ν_{as}(COO) 1598; ν_s(COO) 1393; ν(Sn–C) 581; ν(Sn–O) 437. ^{1}H NMR (CDCl$_3$, ppm): δ 8.37–8.31 (m, 4H, Ar–H: H5, H7, H9, H11); 7.66 (dd, 2H, $J = 7.6, 7.0$ Hz, Ar–H: H6, H10); 7.25–7.28 (m, 15H, Ph–H); 4.92 (s, 2H, –CH$_2$–). ^{13}C NMR (CDCl$_3$, ppm): 179.78 (1C, COO); 167.79 (2C, C=O); 135.46 (2C, C5, C11), 133.69 (2C, C7, C9), 132.58 (1C, C8), 129.04 (3C, $^1J_{^{119}Sn-^{13}C} = 424$ Hz, $^2J_{^{119}Sn-^{13}C} = 19$ Hz, $^3J_{^{119}Sn-^{13}C} = 63$ Hz, C15, C21, C27), 128.82 (6C, C16, C20, C22, C26, C28, C32), 128.23 (6C, C17, C19, C23, C25, C29, C31), 127.51 (3C, C18, C24, C30), 125.30 (2C, C6, C10), 124.98 (1C, C13), 123.20 (2C, C4, C12) (carbon protons of aryl groups), 35.92 (1C, –CH$_2$–).

2.3.3. *Synthesis of (Ph$_3$Sn)(L^2) (**2**)*

The preparation of **2** is similar to that of **1** except that L^2 (0.317 g, 1 mmol) was used to replace L^1. Yield: 78%; mp: 159.9–162.3 °C. Anal. Calcd for $C_{37}H_{25}NO_4Sn$: C, 66.70; N, 2.10; H, 3.78%. Found: C, 66.59; N, 2.19; H, 3.83%. IR (cm^{-1}): ν(O=C) 1704; ν_{as}(COO) 1658; ν_s(COO) 1435; ν(Sn–C) 585; ν(Sn–O) 440. ^{1}H NMR (CDCl$_3$, ppm): δ 8.65 (s, 1H, Ar–H: H3); 8.30 (d, 2H, $J = 7.6$ Hz, Ar–H: H10, H16); 8.28 (d, 1H, $J = 7.5$ Hz, Ar–H: H5); 7.89 (d, 2H, $J = 7.6$ Hz, Ar–H: H12, H14); 7.78 (d, 1H, $J = 7.5$ Hz, Ar–H: H7); 7.68 (dd, 1H, $J = 7.8, 7.2$ Hz, Ar–H: H6); 7.63 (dd, 2H, $J = 7.1, 8.1$ Hz, Ar–H: H11, H15); 7.35–7.50 (m, 15H, Ph–H). ^{13}C NMR (CDCl$_3$, ppm): 171.79 (1C, COO); 164.25 (2C, C=O); 138.19 (1C, C4), 136.96 (2C, C10, C16), 136.17 (2C, C12, C14), 135.52 (1C, C2), 134.45 (1C, C13), 133.09 (1C, C6), 131.71 (2C, C11, C15), 131.03 (2C, C9, C17), 130.21 (1C, C19), 129.31



Scheme 4. Syntheses of complexes **6** and **7**.

(3C, $^{1}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 390$ Hz, $^{2}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 23$ Hz, $^{3}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 59$ Hz, C20, C26, C32), 128.95 (6C, C21, C25, C27, C31, C33, C37), 128.53 (6C, C22, C24, C28, C30, C34, C36), 128.05 (3C, C23, C29, C35), 127.08 (1C, C5), 126.58 (1C, C7), 122.66 (1C, C3) (carbon protons of aryl groups).

2.3.4. Synthesis of $(Ph_3Sn)(L^3)\cdot C_7H_8$ (**3**)

The preparation of **3** is similar to that of **1** except that L^3 (0.241 g, 1 mmol) was used to replace L^1. Yield: 72%; mp: 150.1–152.8 °C. Anal. Calcd for $C_{32}H_{25}NO_3Sn\cdot C_7H_8$: C, 68.64; N, 2.05; H, 4.87%. Found: C, 68.68; N, 2.08; H, 4.81%. IR (cm^{-1}): ν(O=C) 1708; ν_{as}(COO) 1598; ν_{s}(COO) 1345; ν(Sn–C) 571; ν(Sn–O) 443. ^{1}H NMR (CDCl$_3$, ppm): δ 8.07 (d, 1H, J = 7.3 Hz, Ar–H: H7); 8.01 (s, 1H, NH); 7.97 (d, 1H, J = 7.2 Hz, Ar–H: H4); 7.81 (dd, 1H, J = 6.9, 7.7 Hz, Ar–H: H5); 7.68 (dd, 1H, J = 7.1, 7.3 Hz, Ar–H: H6); 7.61–7.34 (m, 20H, Ph–H). ^{13}C NMR (CDCl$_3$, ppm): 172.01 (1C, COO); 168.90 (2C, C=O); 138.21 (1C, C9), 137.78 (1C, C3), 137.23 (1C, C5), 136.59 (1C, C6), 132.09 (1C, C7), 131.32 (1C, C2), 130.19 (2C, C11, C13), 129.33 (1C, C4), 129.11 (3C, $^{1}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 402$ Hz, $^{2}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 22$ Hz, $^{3}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 60$ Hz, C21, C31, C41), 128.94 (6C, C22, C26, C32, C36, C42, C46), 128.47 (6C, C23, C25, C33, C35, C43, C45), 128.24 (3C, C24, C34, C44), 124.16 (1C, C12), 119.92 (2C, C10, C14) (carbon protons of aryl groups).

The syntheses of complexes **4** and **5** were shown in Scheme 3.

2.3.5. Synthesis of $(n\text{-}Bu_2Sn)(L^1)_2\cdot C_7H_8$ (**4**)

The preparation of **4** is similar to that of **1** except that dibutyltin oxide (0.124 g, 0.5 mmol) was used to replace triphenyltin hydroxide. Yield: 69.5%; mp: 264.7–267.6 °C. Anal. Calcd for $C_{36}H_{34}N_2O_8Sn\cdot C_7H_8$: C, 61.96; N, 3.36; H, 5.08%. Found: C, 61.89; N, 3.42; H, 5.12%. IR (cm^{-1}): ν(O=C) 1705; ν_{as}(COO) 1589; ν_{s}(COO) 1390; ν(Sn–C) 531; ν(Sn–O) 435. ^{1}H NMR (CDCl$_3$, ppm): δ 8.47 (d, 4H, J = 7.3 Hz, Ar–H: H5, H11, H19, H25); 8.13 (d, 4H, J = 7.2 Hz, Ar–H: H7, H13, H21, H27); 7.69 (dd, 4H, J = 7.6, 7.0 Hz, Ar–H: H6, H12, H20, H26); 4.97 (s, 4H, –CH$_2$–); 1.75 (t, 4H, J = 6.8 Hz, Bu–H: –CH$_2$–), 1.39–1.57 (m, 8H, Bu–H: –CH$_2$–); 0.96 (t, 6H, J = 6.9 Hz, Bu–H: –CH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 178.10 (2C, COO), 163.25 (4C, C=O), 133.77 (4C, C5, C11, C19, C25), 130.68 (4C, C7, C13, C21, C27), 129.03 (2C, C8, C22), 128.22 (2C, C9, C23), 126.41 (4C, C6, C12, C20, C26), 121.40 (4C, C4, C10, C18, C24) (carbon protons of aryl groups), 41.48 (2C, –CH$_2$–); 26.61 (2C, –CH$_2$–), 26.38 (2C, –CH$_2$–), 13.63 (2C, –CH$_3$), 7.05 (2C, –CH$_2$–, $^{1}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 767$ Hz, $^{2}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 35$ Hz, $^{3}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 89$ Hz) (carbon protons of butyl groups).

2.3.6. Synthesis of $(n\text{-}Bu_2Sn)(L^4)_2$ (**5**)

The preparation of **5** is similar to that of **4** except that L^4 (0.267 g, 1 mmol) was used to replace L^1. Yield: 63.7%; mp: 102.2–104.7 °C. Anal. Calcd for $C_{38}H_{34}N_2O_8Sn$: C, 59.63; N, 3.66; H, 4.48%. Found: C, 59.68; N, 3.61; H, 4.46%. IR (cm^{-1}): ν(O=C) 1711; ν_{as}(COO) 1605; ν_{s}(COO) 1465; ν(Sn–C) 582; ν(Sn–O) 476. ^{1}H NMR (CDCl$_3$): δ 8.29 (d, 4H, J = 7.0 Hz, Ar–H: H11, H14); 7.98 (d, 4H, J = 6.9 Hz, Ar–H: H3, H7); 7.83 (dd, 4H, J = 6.8, 7.0 Hz, Ar–H: H12, H13); 7.62 (d, 4H, J = 7.0 Hz, Ar–H: H4, H6); 1.79 (t, 4H, J = 6.8 Hz, Bu–H: –CH$_2$–); 1.34–1.48 (m, 8H, Bu–H: –CH$_2$–); 0.91 (t, 6H, J = 6.7 Hz, Bu–H: –CH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 175.27 (2C, COO), 166.81 (4C, C=O), 136.09 (2C, C5), 134.67 (4C, C10, C15), 131.58 (4C, C12, C13), 131.39 (4C, C3, C7), 130.85 (2C, C11, C14), 125.92 (4C, C2), 123.94 (4C, C4, C6) (carbon protons of aryl groups), 26.77 (2C, –CH$_2$–), 26.30 (2C, –CH$_2$–), 13.61 (2C, –CH$_3$), 7.95 (2C, –CH$_2$–, $^{1}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 664$ Hz, $^{2}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 34$ Hz, $^{3}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 88$ Hz) (carbon protons of butyl groups).

The syntheses of complexes **6** and **7** were shown in Scheme 4.

2.3.7. Synthesis of $\{[n\text{-}Bu_2Sn(L^2)]_2O\}_2\cdot C_7H_8$ (**6**)

The preparation of **6** is similar to that of **4** except that L^2 (0.079 g, 0.25 mmol) was used to replace L^1. Yield: 66.4%; mp: 253.5–256.3 °C. Anal. Calcd for $C_{70}H_{92}N_2O_{12}Sn_4\cdot C_7H_8$: C, 53.75; N, 1.63; H, 5.86%. Found: C, 53.68; N, 1.61; H, 5.80%. IR (cm^{-1}): ν(O=C) 1708; ν_{as}(COO) 1583; ν_{s}(COO) 1352; ν(Sn–C) 548; ν(Sn–O) 447. ^{1}H NMR (CDCl$_3$, ppm): δ 8.71 (s, 2H, Ar–H: H3); 8.66 (d, 4H, J = 7.4 Hz, Ar–H: H10, H16); 8.30 (d, 4H, J = 7.5 Hz, Ar–H: H12, H14); 7.99 (d, 2H, J = 7.1 Hz, Ar–H: H5); 7.81 (dd, 4H, J = 7.9, 6.9 Hz, Ar–H: H11, H15); 7.63 (dd, 2H, J = 7.4, 6.8 Hz, Ar–H: H6); 7.20 (d, 2H, J = 7.3 Hz, Ar–H: H7); 1.72 (t, 16H, J = 7.0 Hz, Bu–H: –CH$_2$–); 1.37–1.46 (m, 32H, Bu–H: –CH$_2$–); 0.92 (t, 24H, J = 6.8 Hz, Bu–H: –CH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 173.03 (2C, COO), 164.17 (4C, C=O); 137.70 (2C, C4), 134.34 (4C, C10, C16), 133.85 (4C, C12, C14), 131.62 (2C, C2), 130.77 (2C, C13), 129.59 (2C, C6), 129.04 (4C, C11, C15), 128.49 (4C, C9, C17), 128.23 (2C, C19), 127.06 (2C, C7), 125.31 (2C, C5), 122.70 (2C, C3) (carbon protons of aryl groups), 27.49 (8C, –CH$_2$–), 26.82 (8C, –CH$_2$–), 13.63 (8C, –CH$_3$), 8.01 (8C, –CH$_2$–, $^{1}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 618$ Hz, $^{2}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 31$ Hz, $^{3}J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 81$ Hz) (carbon protons of butyl groups).

2.3.8. Synthesis of $\{[n\text{-}Bu_2Sn(L^5)]_2O\}_2\cdot C_7H_8$ (**7**)

The preparation of **7** is similar to that of **4** except that L^5 (0.159 g, 0.5 mmol) was used to replace L^1. Yield: 61.4%; mp: 254.1–256.9 °C. Anal. Calcd for $C_{108}H_{112}N_4O_{18}Sn_4\cdot C_7H_8$: C, 59.51; N, 2.41; H, 5.21%. Found: C, 59.58; N, 2.48; H, 5.19%. IR (cm^{-1}): ν(O=C) 1711; ν_{as}(COO)

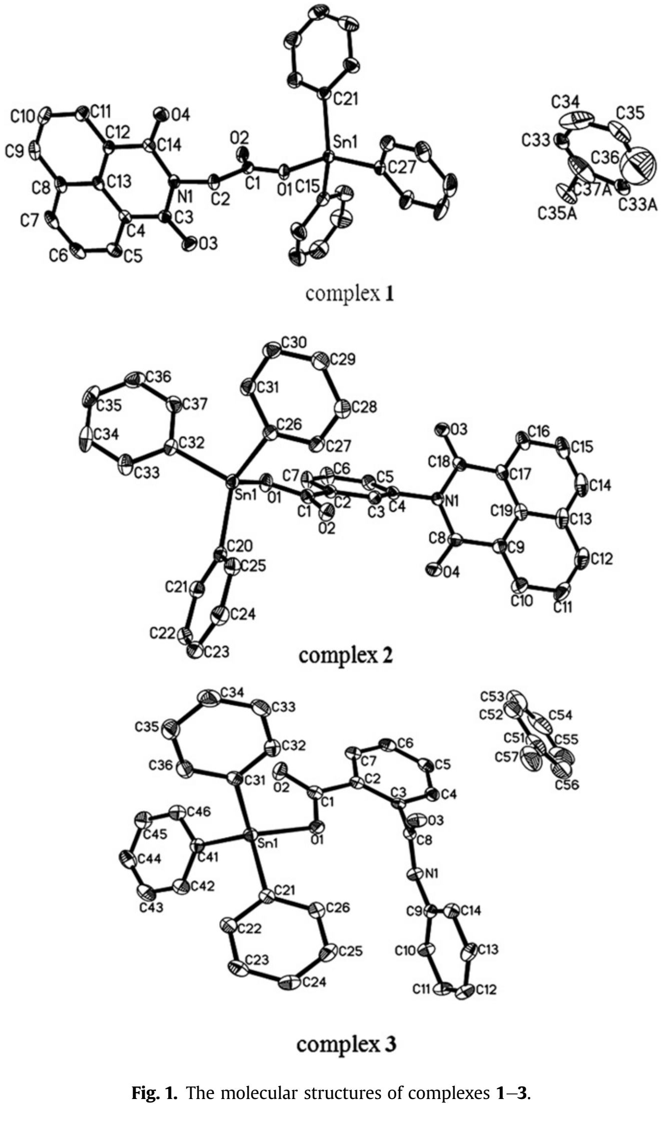


Fig. 1. The molecular structures of complexes **1**–**3**.

Table 2
Selected bond lengths (Å) and angles (°) for **1**–**3**.

Complex **1**			
Bond lengths			
Sn(1)–O(1)	2.050(2)	Sn(1)–C(15)	2.118(3)
Sn(1)–C(21)	2.117(3)	Sn(1)–C(27)	2.127(3)
Bond angles			
O(1)–Sn(1)–C(21)	108.79(11)	C(21)–Sn(1)–C(15)	118.50(14)
O(1)–Sn(1)–C(15)	105.33(12)	C(21)–Sn(1)–C(27)	110.54(13)
O(1)–Sn(1)–C(27)	98.06(11)	C(15)–Sn(1)–C(27)	113.35(13)
Complex **2**			
Bond lengths			
Sn(1)–O(1)	2.0597(14)	Sn(1)–C(32)	2.121(2)
Sn(1)–C(20)	2.118(2)	Sn(1)–C(26)	2.126(2)
Bond angles			
O(1)–Sn(1)–C(20)	113.05(7)	C(20)–Sn(1)–C(32)	113.49(8)
O(1)–Sn(1)–C(32)	97.59(7)	C(20)–Sn(1)–C(26)	114.26(8)
O(1)–Sn(1)–C(26)	108.24(7)	C(32)–Sn(1)–C(26)	108.87(8)
Complex **3**			
Bond lengths			
Sn(1)–O(1)	2.059(2)	Sn(1)–C(41)	2.123(4)
Sn(1)–C(31)	2.117(4)	Sn(1)–C(21)	2.135(3)
Bond angles			
O(1)–Sn(1)–C(31)	109.19(12)	C(31)–Sn(1)–C(41)	113.06(13)
O(1)–Sn(1)–C(41)	113.79(12)	C(31)–Sn(1)–C(21)	112.87(14)
O(1)–Sn(1)–C(21)	96.17(11)	C(41)–Sn(1)–C(21)	110.64(14)

1629, 1551; ν_s(COO) 1412, 1377; ν(Sn–C) 588; ν(Sn–O) 443. ^{1}H NMR (CDCl$_3$, ppm): δ 8.65 (d, 8H, J = 7.6 Hz, Ar–H: H15, H17, H35, H37); 8.29 (d, 8H, J = 7.4 Hz, Ar–H: H2, H8, H22, H28); 8.19 (d, 8H, J = 7.6 Hz, Ar–H: H4, H6, H24, H26); 7.82 (dd, 8H, J = 7.1, 7.9 Hz, Ar–H: H3, H7, H23, H27); 7.19 (d, 8H, J = 7.4 Hz, Ar–H: H14, H18, H34, H38); 1.77 (t, 16H, J = 6.9 Hz, Bu–H: –CH$_2$–); 1.41–1.50 (m, 32H, Bu–H: –CH$_2$–); 0.94 (t, 24H, J = 6.7 Hz, Bu–H: –CH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 173.56 (4C, COO); 164.18 (8C, C=O), 138.21 (4C, C13, C33), 137.78 (8C, C2, C8, C22, C28), 137.23 (8C, C4, C6, C24, C26), 134.41 (4C, C5, C25), 131.72 (8C, C15, C17, C35, C37), 131.09 (8C, C3, C7, C23, C27), 128.55 (4C, C10, C30), 127.05 (4C, C16, C36), 125.72 (8C, C1, C9, C21, C29), 122.68 (8C, C14, C18, C34, C38) (carbon protons of aryl groups), 27.92 (8C, –CH$_2$–), 26.87 (8C, –CH$_2$–), 13.71 (8C, –CH$_3$), 8.20 (8C, –CH$_2$–, $^1J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}}$ = 755 Hz, $^2J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}}$ = 42 Hz, $^3J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}}$ = 91 Hz) (carbon protons of butyl groups).

3. Results and discussion

3.1. IR spectra

Comparing the IR spectra of the free ligands with complexes **1**–**7**, the explicit feature is the absence of a broad band in the region 3400–2800 cm^{-1}, which appears in the free ligands owing to COOH

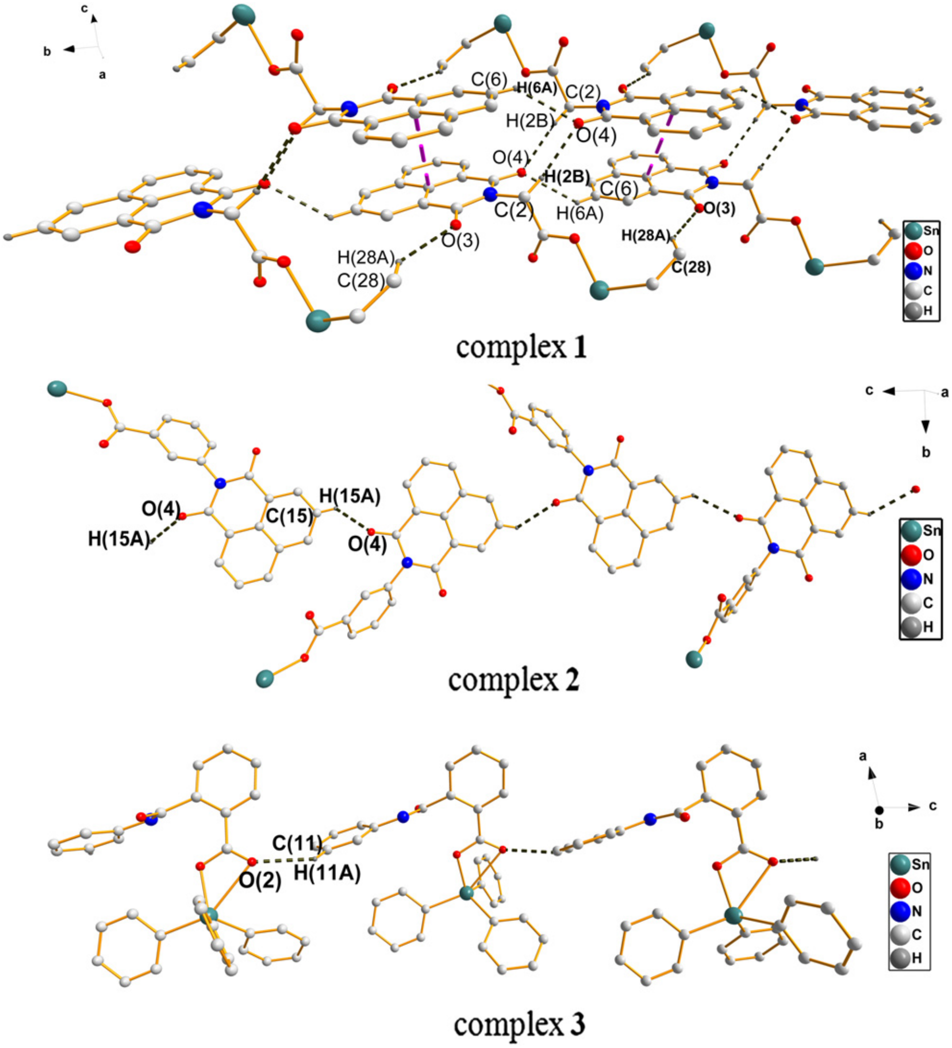


Fig. 2. 1D chain structures of complexes **1**–**3**. Part of phenyl groups and H atoms are omitted for clarity.

group, indicating the removal of COOH protons and the formation of Sn–O bonds through this site [1,17,18]. The $\Delta\nu$ ($\nu_{as}COO - \nu_{s}COO$) values for complexes **1**–**3** and **6** are 205, 223, 253 and 231 cm^{-1} respectively larger than 200 cm^{-1}. This is representative of the unidentate chelating mode for the carboxyl ligands in them [19–21]. For complexes **4** and **5**, they are 199 and 140 cm^{-1} smaller than 200 cm^{-1}, standing for the bidentate chelate coordination of the carboxylate group. For **7**, the values are 217 and 174 cm^{-1} indicating both of the bidentate and unidentate chelate coordination modes exist in the carboxylate group. All of the coordination modes proved by IR spectra of **1**–**7** are totally consistent with the X-ray structures. A band in 531–588 cm^{-1} region is assigned to the stretching frequency associated with Sn–C bond [22,23]. A strong band in 435–476 cm^{-1} for complexes **1**–**7** is assigned to ν(Sn–O), indicative of a Sn–O coordinated structure [24,25].

3.2. *NMR spectra*

^{1}H NMR spectra show that signal for COOH proton (12–14 ppm) of free ligands is absent in the spectra of complexes **1**–**7**. This indicates carboxylate groups participate in the coordination to the Sn atoms [17,18]. The expected integration and peak multiplicities for the hydrogen protons on aromatic rings of ligands in **1**–**7** are also observed. They appear almost in the same positions as in the ligand at 8.71–7.19 ppm. The chemical shifts for "–CH$_2$–" groups of L^1 in **1** and **4**, and "–NH–" group of L^3 in **3** are at 4.92, 4.97 and 8.01 as single peak respectively [26]. Signals for the hydrogen protons on phenyl groups of tin in complexes **1**–**3** are revealed as multiplets at 7.25–7.61 ppm. Butyl groups of **4**–**7** can also be appropriately attributed [8,18].

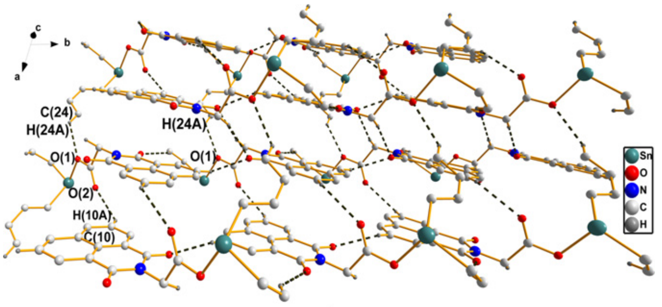
The carbon protons of all the complexes show a significant downfield shift of carbon resonances compared with free ligands. The shift is a consequence of electron density transfer from the ligand to the acceptor Sn atoms [17]. Single resonances at 171.79–179.78 and 163.25–168.90 ppm are attributed to COO and C=O groups [8,17,18]. The carbon protons of phenyl groups in **1**–**3** present four kinds of chemical environment, and give four peaks at 127.51–128.24, 128.23–128.53, 128.82–128.95 and 129.04–129.31 ppm respectively. Chemical shifts for "–CH$_2$–" of **1** and **4** are at 35.92 and 41.48 ppm [26]. The peaks of aromatic rings and butyl groups can also be appropriately attributed. These data are consistent with the structures of **1**–**7**. For **1**–**3**, with the $^1J_{Sn-C}$ values being 390–424 Hz and by the use of the Holecek and Lycka equation [27], C–Sn–C values of 110.9°–114.0° were calculated, which correspond to the geometry of Sn atoms in **1**–**3** (108.87°–118.50°). For **4**–**7**, the values are 618–767 Hz, and C–Sn–C angles of 130.9°–144.0° were calculated which are in accord with the X-ray structures of them (129.20°–149.61°).

3.3. *Crystal structures*

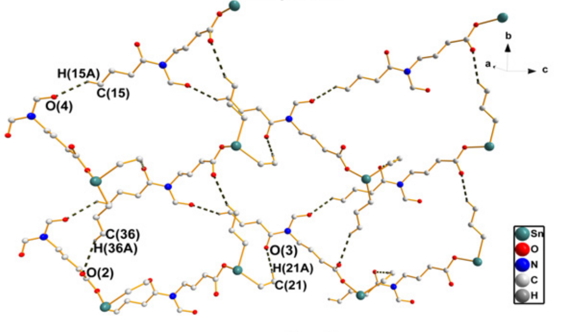
3.3.1. *Crystal structures of* **1**–**3**

The molecular structures of **1**–**3** are shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. **1**–**3** exist as monomers in the solid state with the tin atoms four coordinated. Each tin atom demonstrates a distorted tetrahedral geometry coordinated with one carboxylate oxygen atom from ligand and three carbon atoms of phenyl groups. The related C–Sn–C angles of **1**–**3** among 108.87°–118.50° and O–Sn–C angles sphering from 96.17° to 113.79° prove the distorted geometry. Sn–C bond lengths [2.117(4)–2.135(3) Å] are in the range of those found in other triphenyltin carboxylates [12]. Strong chemical bonds exist between carboxylate oxygen and tin atoms evidenced by the Sn–O bond lengths [2.0500(2)–2.0597(14) Å] which lie in the range of Sn–O covalent bond length reported [28]. In addition to that, intramolecular distances [Sn(1)···O(2) for **1**: 2.943 Å; **2**: 2.950 Å; **3**: 2.735 Å] although longer than Sn–O covalent bond length are much shorter than the sum of the van der Waals radii of tin and oxygen (3.7 Å). They lie in the range of intramolecular Sn–O bond distances of 2.61–3.02 Å [29,30]. Therefore the oxygen atoms [O(2) of **1**–**3**] are involved in a weak coordinative interaction with tin along one of the tetrahedral faces, and the structure distortion for the tin atoms in complex **1**–**3** is best described as a capped tetrahedron.

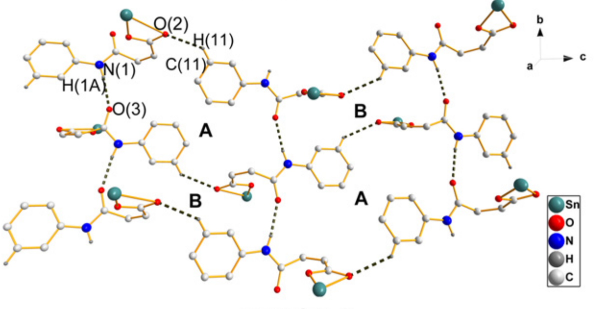
Intermolecular H-bonds of complexes **1**, **2** and **3** [**1**: C(2)–H(2B)···O(4) (2.341 Å), C(6)–H(6A) ···O(4) (2.520 Å), C(28)–H(28A)···O(3) (2.552 Å); **2**: C(15)–H(15A)···O(4) (2.490 Å); **3**: C(11)–H(11A)···O(2) (2.564 Å)] link them into 1D infinite chains (Fig. 2). The oxygen atoms O(3), O(4) in **1** and O(4) in **2** are from amide groups while O(2) in **3** is carboxylate oxygen atom. H(2B) and H(28A) belong to methylene and butyl groups respectively in **1**. H(6A) of **1**, H(15A) of **2** and H(11A) of **3** are from aromatic groups of ligands. For **1**, the adjacent planes of ligands (L^1) in the chain are almost paralleled with dihedral angle 1.49°. Distance between them is 3.461 Å and $\pi\cdots\pi$ interactions (offset face-to-face) exist [31]. Besides these interactions, hydrogen bonds [**1**: C(10)–H(10A)···O(2) (2.718 Å), C(24)–H(24A)···O(1) (2.675 Å); **2**: C(36)–H(36A)···O(2) (2.653 Å), C(21)–H(21A)···O(3) (2.619 Å); **3**: N(1)–H(1A)···O(3) (2.113 Å)] also connect the chains into 2D networks



complex 1



complex 2



complex 3

Fig. 3. 2D network structures of complexes **1**–**3**. Only relevant C and H atoms are drawn for clarity.

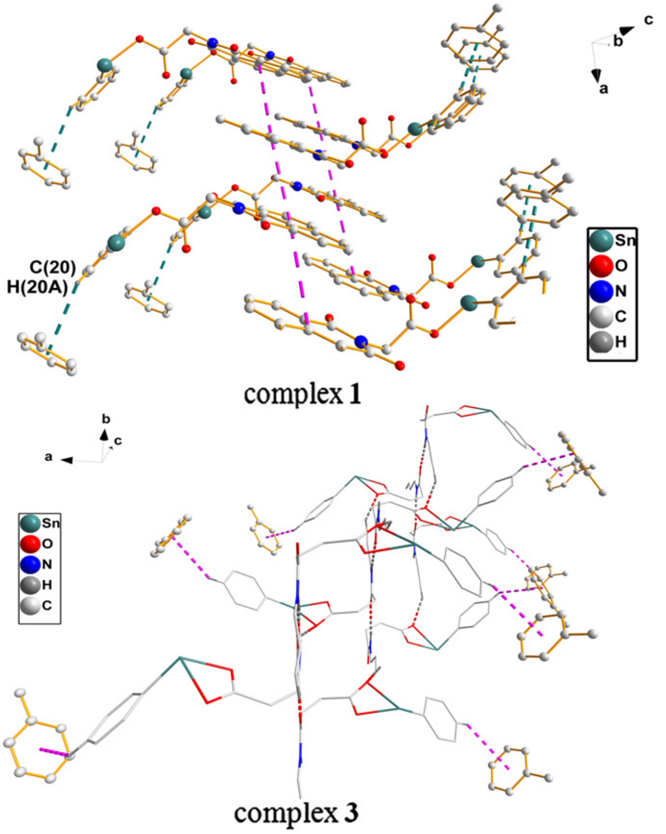


Fig. 4. 2D networks of complexes **1** and **3** interact with free toluene. Part of phenyl groups and H atoms are omitted for clarity.

(Fig. 3). O(3), O(4) in **2** are derived from the amide groups. O(1), O(2) of **1** and O(2) of **2** are the carboxylate oxygens and that H(24A) in **1**, H(36A), H(21A) of **2** are from the phenyl groups on tin. H(10A) of **1**, H(15A) in **2** are hydrogen atoms of aromatic ring. For **3**, N(1), H(1A) and O(3) are all from amide group. With the H-bonds, complex **3** forms two kinds of irregular ring (A and B). A is 28-membered while B is 24-membered. In the crystal lattice of **1** and **3**, free toluene molecules are situated on both sides of the network and stabilized by edge-to-face π⋯π interactions (Fig. 4). The pi electrons are from the phenyl ring of toluene and phenyl group on tin atom. In the stacking format of **2** (Fig. 5), each pair of the networks are connected with each other by π⋯π interactions with the plane of aromatic rings of ligands face-to-face. Compared the supramolecular structures of **1** and **2** (Figs. 4 and 5), it is found that though ligands L^1 and L^2 contain the same part in structure (benzo[de]isoquinoline-1,3-dione), there are more π⋯π interactions among layers of the 2D networks in **1**. That is caused by the steric hindrance from rigid construction of ligand L^2.

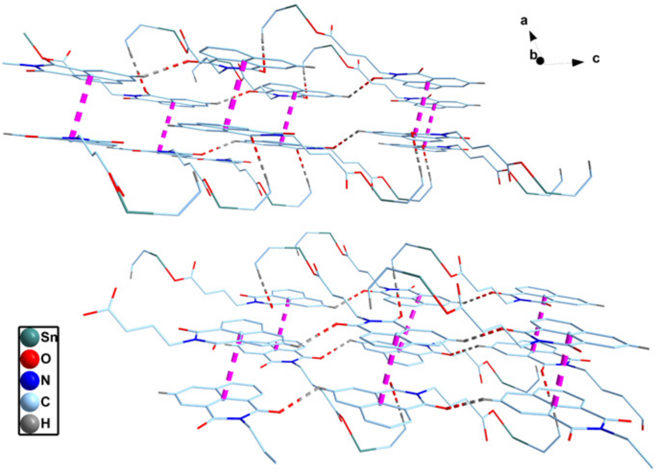


Fig. 5. Packing configuration of complex **2**. Only relevant atoms are drawn for clarity.

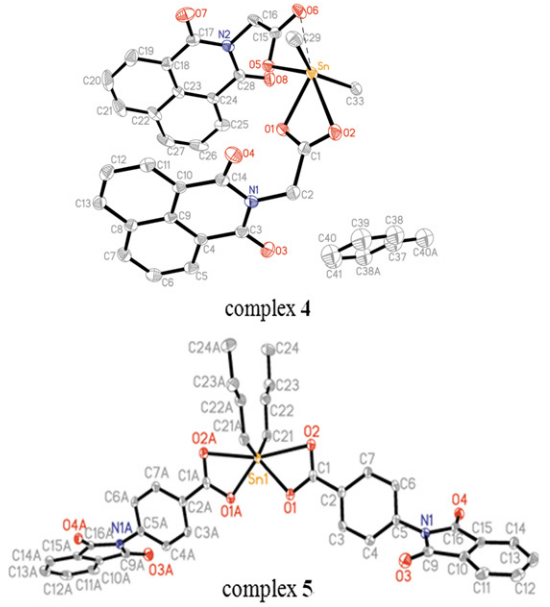


Fig. 6. The molecular structures of complexes **4** and **5**.

3.3.2. *Crystal structures of **4** and **5***

The molecular structures of complexes **4** and **5** are shown in Fig. 6. Selected bond lengths and angles are given in Table 3. Both the

Table 3
Selected bond lengths (Å) and angles (°) for **4** and **5**.

Complex **4**			
Bond lengths			
Sn–O(1)	2.136(2)	Sn–O(2)	2.552(3)
Sn–O(5)	2.140(2)		
Sn–C(33)	2.119(3)	Sn–C(29)	2.130(4)
Bond angles			
O(1)–Sn–O(5)	80.93(8)	C(29)–Sn–O(1)	103.05(12)
O(1)–Sn–O(2)	55.01(8)	C(33)–Sn–O(5)	99.32(12)
O(5)–Sn–O(2)	135.83(8)	C(29)–Sn–O(5)	107.02(13
C(33)–Sn–C(29)	146.41(14)	C(33)–Sn–O(2)	87.60(11)
C(33)–Sn–O(1)	101.33(11)	C(29)–Sn–O(2)	87.77(13)
Complex **5**			
Bond lengths			
Sn(1)–O(1)	2.113(2)	Sn(1)–C(21)	2.109(3)
Sn(1)–O(2)	2.511(2)	Sn(1)–C(1)	2.663(3)
Bond angles			
O(1)–Sn(1)–O(2)	56.04(7)	O(2)–Sn(1)–C(1)#1	168.45(9)
O(1)–Sn(1)–O(2)#1	140.25(7)	C(21)#1–Sn(1)–O(1)	103.67(10)
O(1)–Sn(1)–O(1)#1	84.62(11)	C(21)–Sn(1)–O(1)	110.13(10)
O(2)–Sn(1)–O(2)#1	163.66(10)	C(21)#1–Sn(1)–O(2)	86.81(10)
C(21)#1–Sn(1)–C(21)	133.79(18)	C(21)–Sn(1)–O(2)	86.80(10)
C(21)#1–Sn(1)–C(1)	94.69(11)	O(1)–Sn(1)–C(1)	28.43(9)
C(21)–Sn(1)–C(1)	100.24(11)	O(1)–Sn(1)–C(1)#1	112.99(9)
C(1)–Sn(1)–C(1)#1	141.40(14)	O(2)–Sn(1)–C(1)	27.65(8)

crystal structures of **4** and **5** are composed of discrete molecules in which six-coordinated Sn atoms are bonded by two n-butyl groups and two ligands (L^1 and L^4). The C—Sn—C angles of **4** (146.43°) and **5** (133.80°) are in the range of 122.6°–156.9° found for the diorganotin complexes in which the organo substituents neither adopt cis- nor trans-geometries on the tin atom [32], and the O—Sn—O angles of them are 53.50° [O(5)—Sn—O(6)], 55.01° [O(1)—Sn—O(2)] for **4** and 56.04° [O(1)—Sn(1)—O(2) and O(1A)—Sn(1)—O(2A)] for **5**. The carboxylate groups of ligands coordinate with tin in an anisobidentate mode and form two types of Sn—O bond distances: the short Sn—O distance (2.113–2.140 Å) [Sn—O(1) and Sn—O(5) for **4**; Sn(1)—O(1) and Sn(1)—O(1A) for **5**] and long ones (2.511–2.632 Å) [Sn—O(2) and Sn—O(6) for **4**; Sn(1)—O(2) and Sn(1)—O(2A) for **5**]. This coordination mode is also reflected in the disparity of the associated carboxylate C—O bonds: the C—O bond distances for the weakly coordinated oxygen atoms (1.229–1.245 Å) are shorter than the ones with the strong bonds (1.281–1.291 Å). This type of structure and relevant bond lengths and angles are close to the complexes reported in the literature [6,10,11]. The geometry of tin atom in both **4** and **5** is best described as a skew-trapezoidal bipyramid or bicapped tetrahedron. For the flexibility of L^1 in **4**, two naphthalene rings in the structure are almost paralleled with the dihedral angle 3.50° and distance 6.86 Å, which makes the molecule demonstrate as an "U" shape. While L^4 in **5** is rigid, this leads to the small radian in the line of the molecule structure.

In **4**, intermolecular π···π interactions as shown in Fig. S1 arrange the molecules staggered up and down and link into a 1D infinite chain. In Fig. 7, an extensive set of weak intermolecular Sn···O(6) interactions (2.887 Å) (significantly shorter than the sum of the van der Waals radii for tin and oxygen atoms) help the molecules compose a Sn_2O_2 distannoxane unit [Sn···O(6)···Sn···O(6) 2.632 Å × 2.887 Å] which is highly distorted as evidenced by the difference in O—Sn—O bond angle 63.24° and Sn—O—Sn bond angle 116.78°. Through these Sn···O interactions, the chains build a 2D network. Considering the above, the coordination geometry of tin atom is best described as a skew-pentagonal bipyramid.

Intermolecular H-bonds also help the molecules form a 3D architecture. As shown in Fig. S2, H(12A) from aromatic ring and O(7) of amide group are interacted with each other via C(12)—H(12A)···O(7) bonds with reasonable distance 2.47 Å. Besides that, C(2)—H(2A)···O(2) (2.62 Å) and C(16)—H(16A)···O(3) (2.64 Å) bonds are also formed. H(2A) and H(16A) are from the methylene groups. O(2) is carboxylate oxygen atom and O(3) is from amide group. With these H-bonds, the molecular structure can be described as a 3D architecture with large cavities occupied by free toluene molecules (Fig. S2).

For complex **5**, intermolecular π···π interactions between the aromatic rings of ligands make the structure demonstrate as a zigzag chain (Fig. S3). Except that, the hydrogen bonds C(6)—H(6A)···O(4) (2.575 Å) and C(7)—H(7A)···O(4) (2.695 Å) extend the chains into different directions around. H(6A) and H(7A) are from the aromatic ring of ligand while O(4) is from the amide group. With the connections mentioned above, the molecules form a kind of intermolecular cavity (A) [Fig. 8(a)] and present a 3D architecture as it can be seen in Fig. 8(b). Fig. 8(c) shows the 3D pack configuration on ac-plane.

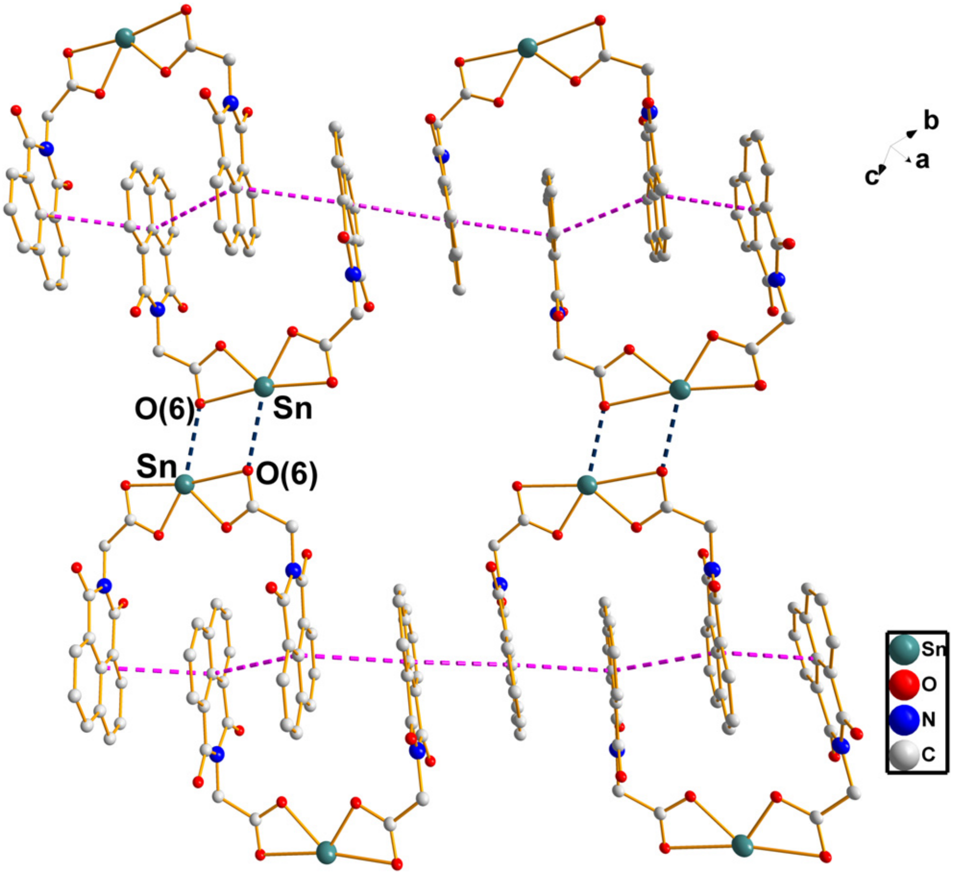


Fig. 7. 2D structure of **4**. Butyl groups and H atoms are omitted for clarity.

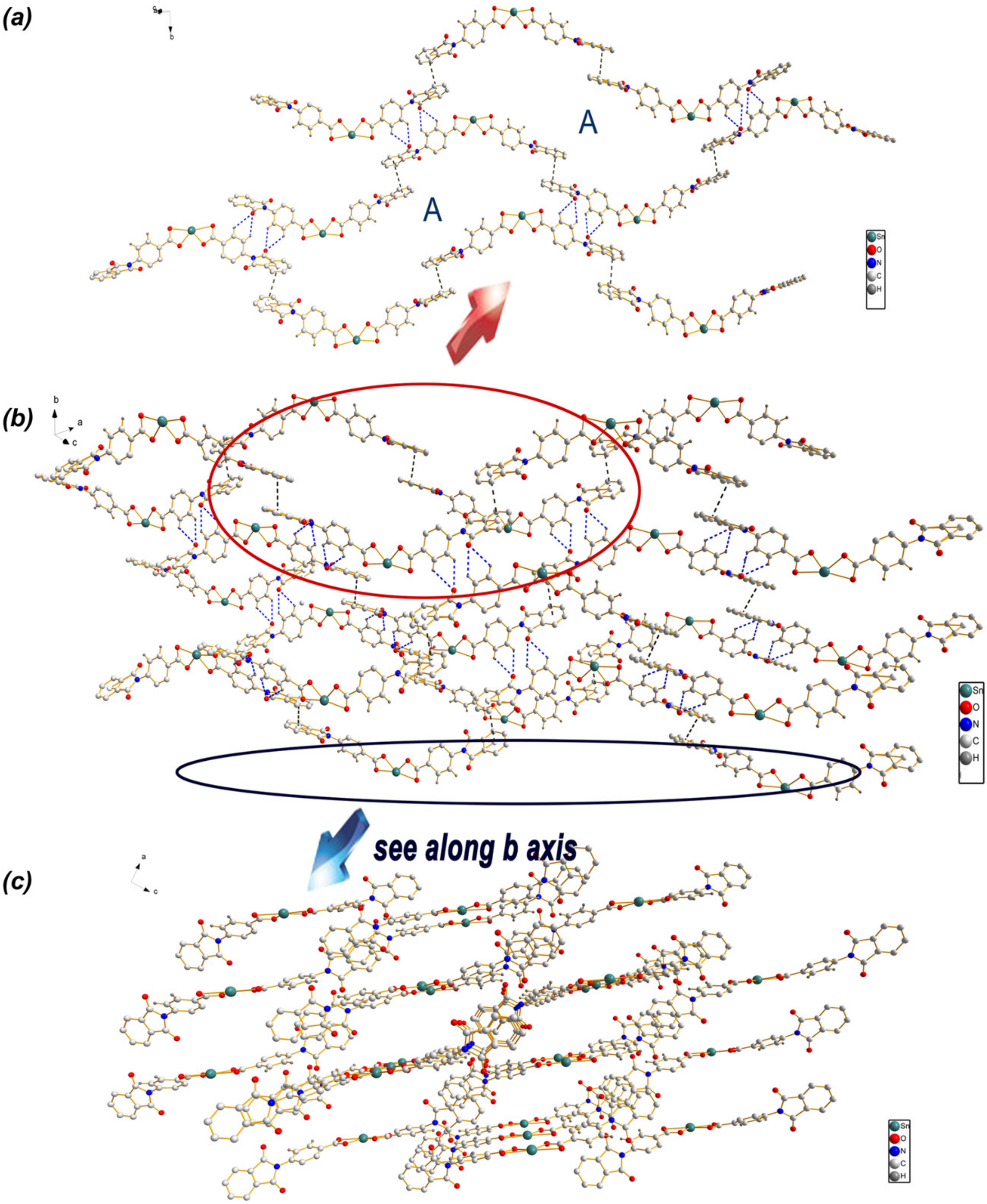
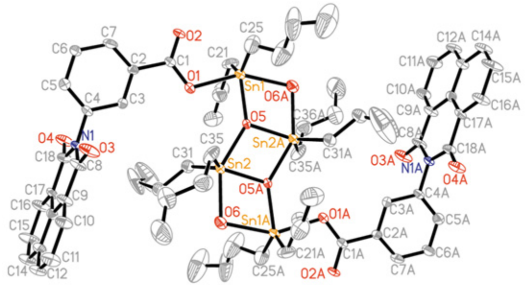


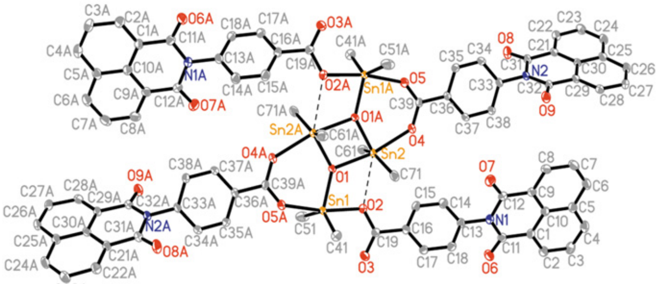
Fig. 8. 3D structure of **5**. Only relevant C and H atoms are drawn for clarity.

3.3.3. *Crystal structures of **6** and **7***

The crystal structures of **6** and **7** are shown in Fig. 9. Selected bond lengths and angles are listed in Table 4. The dominating structural form of **6** and **7** is dimeric tetraorganodistannoxane which is composed of a central planar $(Bu_2Sn)_2O_2$ four-membered ring and two peripheral Bu_2Sn units. Each bridging oxygen atom of the center Sn_2O_2 ring is bound by three Bu_2Sn units. Therefore these oxygen atoms are three-coordinated and adopt planar trigonal geometry. Tin atoms in **6** and **7** are all pentacoordinated coordinated by three oxygen and two carbon atoms of butyl groups. They can be divided into two types in each of the complexes by chemical environments. In **6**, three O atoms connected



complex 6



complex 7

Fig. 9. The molecular structures of complexes **6** and **7**.

with Sn(1) and Sn(1A) are μ_3-O from Sn_2O_2 moiety, μ_2-O [O(6) and O(6A)] and carboxylate O atom respectively. While for Sn(2) and Sn(2A), two of the three O atoms are μ_3-O of Sn_2O_2 ring and the other one is μ_2-O atom. In **7**, for Sn(1) and Sn(1A), two of them are from different carboxylate groups and the other is μ_3-O atom [O(1) and O(1A)]. While Sn(2) and Sn(2A) are chelated with two μ_3-O and a carboxylate O atom. The Sn–O bonds formed are among 2.008(6)–2.261(2) Å. Together with two bonds to butyl groups, the Sn atoms can be viewed as a distorted trigonal bipyramid with the axial angles O–Sn–O [**6**: 147.3(3)° and 152.7(3)°; **7**: 168.67(9)° and 170.43(10)°]. Besides the bonds mentioned above, intramolecular Sn···O bonds [**6**: Sn(1)···O(2) and Sn(1A)···O(2A) (2.943 Å); **7**: Sn(2)···O(2) and Sn(2A)···O(2A) (2.743 Å)] should be taken into account. Thus the coordination of Sn(1) in **6** and Sn(2) in **7** can also be described as distorted tetragonal bipyramid with four equatorial oxygen atoms and two axial carbon atoms and the stannoxane framework in the constructures (Sn_4O_4) of **6** and **7** seems like a short "ladder". All the relevant bond lengths and distances are similar to those found in this type of structures [12,22,23]. The molecular structure of **6** can be revealed as a "ladder" skeleton enclosed by two invert ligands L^2 with monodentate chelating, while the skeleton in **7** is rounded by four ligands L^5 extending into two flanks adopting mono- and bi-dentate coordination modes alternately.

Table 4
Selected bond lengths (Å) and angles (°) for **6** and **7**.

Complex **6**			
Bond lengths			
Sn(1)–O(5)	2.008(6)	Sn(1)–O(6)#1	2.237(8)
Sn(1)–O(1)	2.154(7)	O(5)–Sn(2)#1	2.043(6)
Sn(2)–O(5)	2.126(6)	Sn(2)–O(6)	2.146(8)
Sn(1)–C(21)	2.145(15)	Sn(1)–C(25)	2.086(14)
Sn(2)–C(35)	2.117(13)	Sn(2)–C(31)	2.084(13)
Bond angles			
O(5)–Sn(1)–O(1)	80.6(3)	O(5)–Sn(1)–O(6)#1	72.2(3)
O(1)–Sn(1)–O(6)#1	152.7(3)	O(5)#1–Sn(2)–O(5)	73.9(3)
O(5)#1–Sn(2)–O(6)	73.5(3)	O(5)–Sn(2)–O(6)	147.3(3)
O(5)–Sn(1)–C(25)	113.0(6)	O(5)–Sn(1)–C(21)	111.4(4)
C(25)–Sn(1)–O(1)	97.7(6)	C(21)–Sn(1)–O(1)	97.4(5)
C(25)–Sn(1)–O(6)#1	94.6(5)	C(21)–Sn(1)–O(6)#1	91.0(5)
O(5)#1–Sn(2)–C(31)	116.2(4)	O(5)#1–Sn(2)–C(35)	114.5(5)
C(31)–Sn(2)–O(5)	96.1(4)	C(35)–Sn(2)–O(5)	96.4(5)
C(31)–Sn(2)–O(6)	96.8(4)	C(35)–Sn(2)–O(6)	98.4(5)
C(25)–Sn(1)–C(21)	134.7(7)	C(31)–Sn(2)–C(35)	129.2(5)
Complex **7**			
Bond lengths			
Sn(1)–O(1)	2.018(2)	Sn(2)–O(4)	2.261(2)
Sn(1)–O(2)	2.171(3)	Sn(1)–C(41)	2.124(4)
Sn(1)–O(5)#1	2.219(3)	Sn(1)–C(51)	2.122(5)
Sn(2)–O(1)#1	2.045(2)	Sn(2)–C(71)	2.143(4)
Sn(2)–O(1)	2.184(2)	Sn(2)–C(61)	2.125(4)
Bond angles			
O(1)–Sn(1)–O(2)	79.89(10)	C(41)–Sn(1)–O(2)	95.51(14)
O(1)–Sn(1)–O(5)#1	90.67(10)	C(51)–Sn(1)–O(5)#1	87.9(2)
O(2)–Sn(1)–O(5)#1	170.43(10)	C(41)–Sn(1)–O(5)#1	88.91(14)
O(1)#1–Sn(2)–O(1)	76.37(10)	O(1)#1–Sn(2)–C(61)	104.03(14)
O(1)#1–Sn(2)–O(4)	92.31(9)	O(1)#1–Sn(2)–C(71)	106.35(15)
O(1)–Sn(2)–O(4)	168.67(9)	C(61)–Sn(2)–O(1)	93.89(14)
O(1)–Sn(1)–C(51)	112.01(16)	C(71)–Sn(2)–O(4)	89.99(13)
O(1)–Sn(1)–C(41)	108.51(14)	C(71)–Sn(2)–O(1)	93.64(13)
C(51)–Sn(1)–O(2)	94.2(2)	C(61)–Sn(2)–C(71)	149.61(18)
C(61)–Sn(2)–O(4)	88.32(14)	C(51)–Sn(1)–C(41)	139.38(18)

Comparing the structures of **6** and **7**, two more ligands chelate with the molecular center frame employing bidentate coordination mode. This is due to the constructures of ligands L^2 and L^5. Meta-benzo[de]isoquinoline-1,3-dione group of L^2 obstructs other ligand to coordinate with Sn(2) and Sn(2A) in **6**, while the para of L^5 without this hindrance permits more coordination. In **7**, two bidentate ligands make the distances between the coordinated tin atoms [Sn(1) and Sn(2A); Sn(1A) and Sn(2)] shorter than those of Sn(1)···Sn(2) and Sn(1A)···Sn(2A) in **6**. Consequently the 'ladder' structure of **7** is more distorted. Distances of Sn(2)···O(2) and Sn(2A)···O(2A) are beyond the rage of Sn–O covalent bond length, which relieves the tensile force of the stannoxane center unite. For this reason, the C–Sn–C angles across the stannoxane center in **7** [139.38(18)° and 149.61(18)°] are larger than those in **6** [129.2(5)° and 134.7(7)°].

Complexes **6** and **7** have one-dimensional chain structure (Fig. 10) linked by hydrogen bonds [**6**: C(14)–H(14A)···O(2) (2.630 Å); **7**: C(3)–H(3A)···O(8) (2.680 Å)]. H(14A) of **6** and H(3A) in **7** are from the aromatic rings. O(2) is carboxylate oxygen and O(8) is derived from the amide group. Intermolecular rings (**6**: A; **7**: B) are constructed by these bonds. A is 40-membered and B is 44-membered. In Fig. S4, it can be seen that cavity B is like a channel made up by four L^5 ligands which are pairwise paralleled. Two free toluene molecules are located in B stabilized by the π···π interactions with the aromatic groups of ligands L^5.

On the both sides of 1D chain of complex **6**, H(11A), H(14A), H(15A) of aromatic groups and O(4), O(3) from amide groups are connected by the H-bonds C(11)–H(11A)···O(4) (2.522 Å), C(14)–H(14A)···O(3) (2.663 Å) and C(15)–H(15A)···O(3) (2.336 Å) (Fig. S5). These bonds extend the chain into four different directions and help to build the 3D architecture of **6** which is filled with large cavities (Fig. 11). For **7**, C(24)–H(24A)···O(6) (2.612 Å) and C(26)–H(26A)···O(6) (2.468 Å) link the chains into a 2D network, and intermolecular irregular rings C and D are formed as shown in Fig. S6. H(24A), H(26A) are from aromatic rings of ligands and O(6) is from amide group.

It can be seen from complexes **1** and **4**, **2** and **6** that, even if complexes contain the same ligands and obtained under reflux in the same solvent, different organotins will lead different molecular structures. Simple monomers **1** and **2** are obtained when ligands L^1 and L^2 react with triphenyltin hydroxide, while bicapped structure **4** and "ladder" like architecture **6** are built when they coordinate with dibutyltin oxide. And the relevant Sn–O bonds in **1** and **2** (triphenyltin carboxylate) are shorter than those in **4** and **6** (dibutyltin carboxylate).

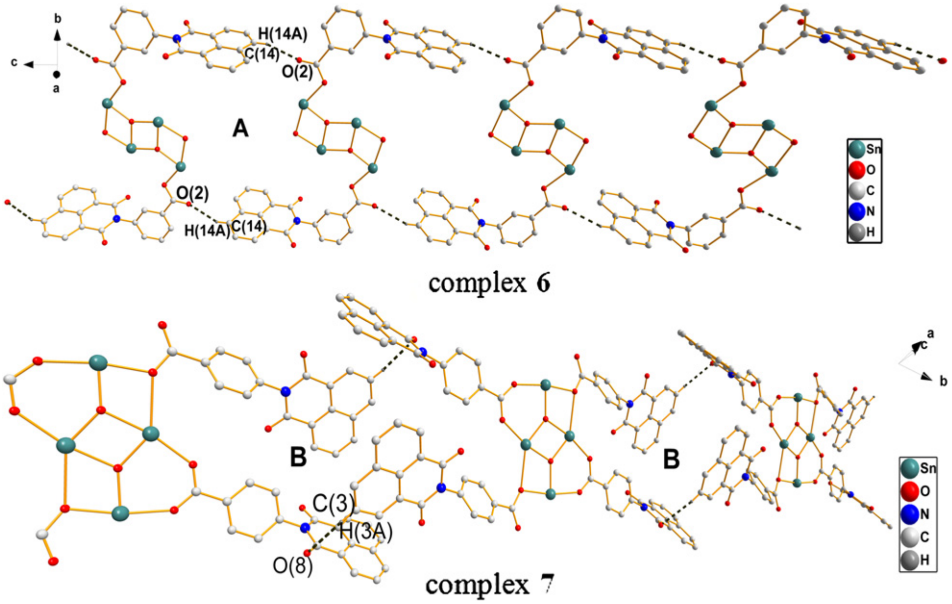


Fig. 10. 1D chain structures of complexes **6** and **7**. Butyl groups and part of H atoms are omitted for clarity.

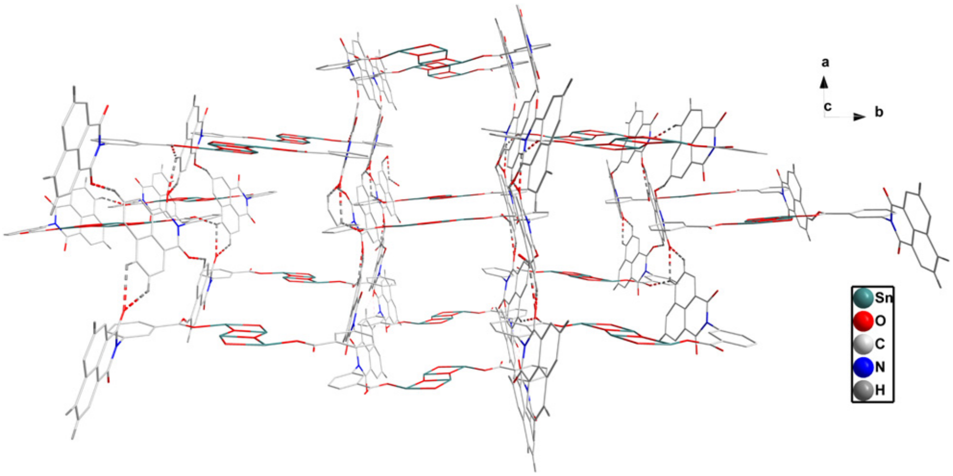


Fig. 11. 3D structure of **6**. Only relevant C and H atoms are drawn for clarity.

4. Conclusion

In summary, a series of organotin(IV) carboxylates complexes based on amide carboxylic acids have been synthesized. They demonstrate diverse molecular structures and possess esthetic supramolecular architectures which supplement the group of organotin carboxylate to help us know better.

Acknowledgments

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Appendix A. Supplementary material

CCDC 916676, 850159, 827596, 916677, 835953, 916678 and 827594 for complexes **1**–**7** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.cccdc.cam.ac.uk/data-request/cif.

Appendix B. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.jorganchem.2013.01.017.

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