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Note

Syntheses, characterization and crystal structure of diorganotin and triorganotin heterocyclicdicarboxylates with monomeric, 2D network and 3D framework structures

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Abstract

A series of new diorganotin and triorganotin(IV) heterocyclicdicarboxylates $[(^n\mathrm{Bu_3Sn})_2(2,5\text{-pdc})]_\infty$ (**1**), $\{[(2\text{-}\mathrm{FC_6H_4CH_2})_3\mathrm{Sn}]_2(2,5\text{-pdc})\}_\infty$ (**2**), $\{[(2\text{-}\mathrm{ClC_6H_4CH_2})_3\mathrm{Sn}]_2(2,5\text{-pdc})\}_\infty$ (**3**), $\{[(4\text{-}\mathrm{CNC_6H_4CH_2})_3\mathrm{Sn}]_2(2,5\text{-pdc})\}_\infty$ (**4**), $\{[(4\text{-}\mathrm{ClC_6H_4CH_2})_3\mathrm{Sn}]_2(2,5\text{-pdc})\}_\infty$ (**5**), $[(\mathrm{Ph})_2\mathrm{Sn}(2,6\text{-pdc})(\mathrm{H_2O})]_\infty$ (**6**), $\{[^n\mathrm{Bu_3Sn}(2,6\text{-pdc})\mathrm{Sn}^n\mathrm{Bu_3}]_2(\mathrm{H_2O})_2\}\cdot\mathrm{C_2H_3N}$ (**7**) and $\{[\mathrm{Ph_3Sn}(2,3\text{-pdz})\mathrm{SnPh_3}]_2(\mathrm{H_2O})\}$ (**8**) have been obtained by reactions of diorganotin(IV) and triorganotin (IV) oxide with 2,6 or 2,5-H_2pdc (pdc = pyridinedicarboxylate) or 2,3-H_2pdz (pdz = pyrazinedicarboxylate). Complexes **1**–**8** were characterized by elemental, IR and NMR spectra analyses. The crystal and molecular structures of compounds **1**, **6**, **7** and **8** have been determined by X-ray single crystal diffraction. Compound **1** has 2D network structures. Compound **6** has 1D polymeric chain and 3D framework supramolecular structures due to the coordinated water molecules. Compound **7** has a monomeric structure, but the supramolecular structures are network.

Keywords: Heterocyclicdicarboxylic acid; Diorganotin and triorganotin; Hydrogen bond; X-ray crystallography; Supramolecular structures

1. Introduction

Organotin(IV) carboxylates have attracted much attention owing to their potential biocidal activities [1–4] and cytotoxicities [5] as well as their industrial and agricultural applications [6–11]. Among them, the study of the structural chemistry of triorganotin carboxylates has received considerable attention owing to the various structural types that may be adopted in the solid state [12–19]. Although a large number of structural studies have been carried out on the triorganotin esters of monofunctional carboxylic acids [20], relatively little work has so far been undertaken on the triorganotin esters of dicarboxylic acids [21–24]. The organotin(IV) dicarboxylates have been studied in considerable detail, and in general the reported organotin(IV) dicarboxylates exist as dinuclear [25], one-dimensional zigzag chain [26] and cyclic structures [27]. Recently, our interest has focused on triorganotin(IV) complexes containing dicarboxylate ligands which have an additional hetero-donor atom (e.g., N, O) residing on the R group that is, potentially pentadentate ligands, in order to examine what effect the presence of the heteroatom has on the structure adopted by these complexes [28]. As a part of our continuing program in this area, we have synthesized and structurally characterized diorganotin(IV) and triorganotin(IV) pyridinedicarboxylates of 2,5 or 2,6-pyridinedicarboxylic acid and 2,3-pyrazinedicarboxylic acid and the results of this study are reported herein.

2. Experimental

2.1. Materials and measurements

All the reactions were carried out under nitrogen atmosphere. Ph_2SnO, $[(^n\mathrm{Bu})_3\mathrm{Sn}]_2\mathrm{O}$, $[\mathrm{Ph_3Sn}]_2\mathrm{O}$, 2,5-pyridinedicarboxylic acid, 2,6-pyridinedicarboxylic acid and 2,3-

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pyrazinedicarboxylic acid were used as received. The $[(2\text{-}FC_6H_4CH_2)_3Sn]_2O$, $[(2\text{-}ClC_6H_4CH_2)_3Sn]_2O$, $[(4\text{-}CNC_6H_4CH_2)_3Sn]_2O$, $[(4\text{-}ClC_6H_4CH_2)_3Sn]_2O$ and $[(4\text{-}FC_6H_4CH_2)_3Sn]_2O$, were prepared by the reported method [29]. The melting points were obtained with Kofler micromelting points apparatus and were uncorrected. Infrared spectra were recorded on a Nicole-460 spectrophotometer using KBr discs. ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Mercury Plus-400 NMR spectrometer. Chemical shifts were given in ppm relative to Me_4Si and Me_4Sn in $CDCl_3$ solvent. Elemental analyses were performed on PE-2400-II elemental analyzer.

2.2. Synthesis of the complexes

*2.2.1. $[(^nBu_3Sn)_2(2,5\text{-pdc})]_\infty$ (**1**)*

The reaction was carried out under a nitrogen atmosphere with use of a standard Schlenk technique. A mixture of 2,5-pyridinedicarboxylic acid (0.167 g, 1.0 mmol) and $[^nBu_3Sn]_2O$ (0.596 g, 1.0 mmol) in a 5:1 solvent mixture of benzene and methanol (80 ml) was heated under reflux for 8 h. After cooling down to room temperature, the solution was filtered. The solvent of the filtrate was gradually removed by evaporation under vacuum until a solid product was obtained. The solid was then recrystallized from dichloromethane/methanol and colorless crystals were formed. Yield: 72%. M.p.: 201–203 °C. *Anal.* Calc. for $C_{31}H_{57}NO_4Sn_2$: C, 49.96; H, 7.71; N, 1.88. Found: C, 49.61; H, 7.79; N, 1.93%. IR (KBr, cm^{-1}): $\upsilon_{as}(COO)$, 1622; $\upsilon_s(COO)$, 1445; $\upsilon(Sn–C)$, 578, $\upsilon(Sn–O)$, 486. ^1H NMR ($CDCl_3$, ppm): 0.82 (t, 18H, CH_3), 1.39–1.83 (m, 36H, $CH_2CH_2CH_2$), 7.45–7.95 (pyridine). ^{13}C NMR ($CDCl_3$, ppm): 26.9 (αCH_2, $^1J(^{119}Sn–^{13}C)$, 682 Hz), 26.9 (βCH_2), 25.6 (γCH_2), 13.6 (CH_3), 172.6 (COO), 150.2, 151.6, 125.6, 131.8, 138.9 (Ar–C, pyridine). ^{119}Sn NMR ($CDCl_3$, ppm): δ −129.6.

*2.2.2. $\{[(2\text{-}FC_6H_4CH_2)_3Sn]_2(2,5\text{-pdc})\}_\infty$ (**2**)*

The compound **2** was prepared in the same way as that of compound **1**, by adding $[(2\text{-}FC_6H_4CH_2)_3Sn]_2O$ (0.908 g, 1.0 mmol) to 2,5-pyridinedicarboxylic acid (0.167 g, 1.0 mmol). The solid was then recrystallized from methanol and the colorless crystals were obtained. Yield: 62%. M.p.: 216–218 °C. *Anal.* Calc. for $C_{49}H_{39}F_6NO_4Sn_2$: C, 55.67; H, 3.72; N, 1.32. Found: C, 55.29; H, 3.78; N, 1.36%. IR (KBr, cm^{-1}): $\upsilon_{as}(COO)$, 1634; $\upsilon_s(COO)$, 1466; $\upsilon(Sn–C)$, 572, $\upsilon(Sn–O)$, 476. ^1H NMR ($CDCl_3$, ppm): 3.06 (t, 6H, $J_{Sn–H} = 68$ Hz, $–CH_2–$), 7.16–7.21 (m, 24H, Ph–H), 7.52–7.99 (pyridine). ^{13}C NMR ($CDCl_3$, ppm): δ 32.3 (CH_2Ar, $^1J(^{119}Sn–^{13}C)$, 562 Hz), 172.5 (COO), 35.8 (CH_2Ar), 137.7, 136.4, 135.1, 131.5, 129.6, 125.0, 153.2, 126.8, 137.5 (Ar–C, pyridine). ^{119}Sn NMR ($CDCl_3$, ppm): δ −115.2.

*2.2.3. $\{[(2\text{-}ClC_6H_4CH_2)_3Sn]_2(2,5\text{-pdc})\}_\infty$ (**3**)*

The compound **3** was prepared in the same way as that of compound **1**, by adding $[(2\text{-}ClC_6H_4CH_2)_3Sn]_2O$ (1.007 g, 1.0 mmol) to 2,5-pyridinedicarboxylic acid (0.167 g, 1.0 mmol). The solid was then recrystallized from methanol and the colorless crystals were obtained. Yield: 69%. M.p. 211–213 °C. *Anal.* Calc. for $C_{49}H_{39}Cl_6NO_4Sn_2$: C, 50.91; H, 3.40; N, 1.21. Found: C, 50.66; H, 3.46; N, 1.26%. IR (KBr, cm^{-1}): $\upsilon_{as}(COO)$, 1620; $\upsilon_s(COO)$, 1438; $\upsilon(Sn–C)$, 582, $\upsilon(Sn–O)$, 467; ^1H NMR ($CDCl_3$, ppm): 3.01 (t, 6H, $J_{Sn–H} = 61$ Hz, $–CH_2–$), 7.35–7.53 (m, 24H, Ph–H), 7.63–7.86 (pyridine). ^{13}C NMR ($CDCl_3$, ppm): δ 31.3 (CH_2Ar, $^1J(^{119}Sn–^{13}C)$, 586 Hz), 173.8 (COO), 36.6 (CH_2Ar), 127.0, 127.1, 129.2, 131.5, 132.7,137.1, 133.8, 137.6, 152.8 (Ar–C, pyridine). ^{119}Sn NMR ($CDCl_3$, ppm): δ −143.1.

*2.2.4. $\{[(4\text{-}CNC_6H_4CH_2)_3Sn]_2(2,5\text{-pdc})\}_\infty$ (**4**)*

The compound **4** was prepared in the same way as that of complex **1**, by adding $[(4\text{-}CNC_6H_4CH_2)_3Sn]_2O$ (0.950 g, 1.0 mmol) to 2,5-pyridinedicarboxylic acid (0.167 g, 1.0 mmol). The solid was then recrystallized from methanol and the colorless crystals were obtained. Yield: 59%. M.p.: 225–227 °C. *Anal.* Calc. for $C_{55}H_{39}N_7O_4Sn_2$: C, 60.09; H, 3.58; N, 8.92. Found: C, 60.32; H, 3.56; N, 8.99%. IR (KBr, cm^{-1}): 2220 (s, $C{\equiv}N$), $\upsilon_{as}(COO)$, 1636; $\upsilon_s(COO)$, 1458; $\upsilon(Sn–C)$, 571, $\upsilon(Sn–O)$, 478; ^1H NMR ($CDCl_3$, ppm): 3.09 (t, 6H, $J_{Sn–H} = 66$ Hz, $–CH_2–$), 7.27–7.48 (m, 24H, Ph–H), 7.58–7.75 (pyridine). ^{13}C NMR ($CDCl_3$, ppm): δ 32.1 (CH_2Ar, $^1J(^{119}Sn–^{13}C)$, 597 Hz), 172.6 (COO), 36.9 (CH_2Ar), 115.2 (CN), 109.1, 125.1, 127.6 128.8, 130.6, 133.1, 138.5, 147.2, 150.2 (Ar–C, pyridine). ^{119}Sn NMR ($CDCl_3$, ppm): δ −128.9.

*2.2.5. $\{[(4\text{-}ClC_6H_4CH_2)_3Sn]_2(2,5\text{-pdc})\}_\infty$ (**5**)*

The compound **5** was prepared in the same way as that of compound **1**, by adding $[(4\text{-}ClC_6H_4CH_2)_3Sn]_2O$ (1.007 g, 1.0 mmol) to 2,5-pyridinedicarboxylic acid (0.167 g, 1.0 mmol). The solid was then recrystallized from methanol and the colorless crystals were obtained. Yield: 66%. M.p.: 216–218 °C. *Anal.* Calc. for $C_{49}H_{39}Cl_6NO_4Sn_2$: C, 50.91; H, 3.40; N, 1.21. Found: C, 50.66; H, 3.48; N, 1.25%. IR (KBr, cm^{-1}): $\upsilon_{as}(COO)$, 1619; $\upsilon_s(COO)$, 1472; $\upsilon(Sn–C)$, 568, $\upsilon(Sn–O)$, 466; ^1H NMR ($CDCl_3$, ppm): 3.05 (t, 6H, $J_{Sn–H} = 58$ Hz, $–CH_2–$), 7.38–7.61 (m, 24H, Ph–H), 7.51–7.72 (pyridine). ^{13}C NMR ($CDCl_3$, ppm): δ 31.9 (CH_2Ar, $^1J(^{119}Sn–^{13}C)$, 578 Hz), 174.6(COO), 35.2 (CH_2Ar), 151.2, 148.8, 135.4, 136.4, 127.6, 125.5, 111.4 (Ar–C, pyridine). ^{119}Sn NMR ($CDCl_3$, ppm): δ −172.6.

*2.2.6. $[Ph_2Sn(2,6\text{-pdc})(H_2O)]_\infty$ (**6**)*

The compound **6** was prepared in the same way as that of compound **1**, by adding Ph_2SnO (0.289 g, 1.0 mmol) to 2,6-pyridinedicarboxylic acid (0.167 g, 1.0 mmol). The solid was then recrystallized from methanol and the colorless crystals were obtained. Yield: 82%. M.p.: 171–173 °C. *Anal.* Calc. for $C_{38}H_{30}N_2O_{10}Sn_2$: C, 50.04; H, 3.32; N, 3.07. Found: C, 50.39; H, 3.38; N, 3.12%. IR (KBr, cm^{-1}): $\upsilon(H–O–H)$, 3325; $\upsilon_{as}(COO)$, 1628, 1604; $\upsilon_s(COO)$, 1471, 1316; $\upsilon(Sn–C)$, 569; $\upsilon(Sn–N)$, 458; $\upsilon(Sn–O)$, 485. ^1H

NMR ($CDCl_3$, ppm): δ 8.96 (s, H_2O); 7.45–7.78 (m, 20H, Ph–H); 7.62–8.22 (Ar–C, pyridine). ^{13}C NMR ($CDCl_3$, ppm): δ 127.2, 128.7, 130.6, 137.8, 139.8, 141.3, 146.9, (Ar–C, pyridine), 173.6 (COO). ^{119}Sn NMR ($CDCl_3$, ppm): δ −341.5.

2.2.7. *{[^{n}Bu$_3$Sn(2,6-pdc)Sn^{n}Bu$_3$]$_2$(H$_2$O)$_2$} · CH$_3$CN (7)*

The compound **7** was prepared in the same way as that of compound **1**, by adding [(^{n}Bu)$_3$Sn]$_2$O (0.596 g, 1.0 mmol) to 2,6-pyridinedicarboxylic acid (0.167 g, 1.0 mmol). The solid was then recrystallized from acetonitrile and the colorless crystals were obtained. Yield: 62%. M.p. 128–130 °C. *Anal.* Calc. for $C_{64}H_{121}N_3O_{10}Sn_4$: C, 49.04; H, 7.78; N, 2.68. Found: C, 48.71; H, 7.86; N, 2.73%. IR (KBr, cm^{-1}): v(H–O–H), 3327, v_{as}(COO), 1645; v_s(COO), 1336; v(Sn–C), 598, v(Sn–O), 467; ^1H NMR ($CDCl_3$, ppm): δ 8.98 (s, H_2O); 7.56–8.07 (pyridine), 0.86 (t, 36H, CH_3), 1.31–1.86 (m, 72 H, $CH_2CH_2CH_2$), 1.96 (s, 3H, CH_3CN). ^{13}C NMR ($CDCl_3$, ppm): δ 27.7 (αCH_2, $^1J(^{119}Sn–^{13}C)$, 565 Hz), 27.3 (αCH_2, $^1J(^{119}Sn–^{13}C)$, 628 Hz), 27.1 (βCH_2), 26.9 (βCH_2), 26.6 (βCH_2), 26.3 (γCH_2), 25.9 (γCH_2), 25.3 (γCH_2), 13.6 (CH_3), 13.8 (CH_3), 172.6 (COO), 117.8 (CN), 146.7, 128.4, 138.8 (Ar–C, pyridine). ^{119}Sn NMR ($CDCl_3$, ppm): δ −116.8, 82.5.

2.2.8. *{[Ph$_3$Sn(2,3-pdz)SnPh$_3$]$_2$(H$_2$O)} (**8**)*

The compound **7** was prepared in the same way as that of compound **1**, by adding [Ph$_3$Sn]$_2$O (0.716 g, 1.0 mmol) to 2,3-pyrazinedicarboxylic acid (0.168 g, 1.0 mmol). The solid was then recrystallized from methanol and the colorless crystals were obtained. Yield: 52%. M.p.: 131–133 °C. *Anal.* Calc. for $C_{84}H_{66}N_4O_9Sn_4$: C, 57.64; H, 3.80; N, 3.20. Found: C, 57.36; H, 3.82; N, 3.30%. IR (KBr, cm^{-1}): v(H–O–H), 3329, v_{as}(COO), 1667, 1617; v_s(COO), 1486, 1418; v(Sn–C), 576; v(Sn–O), 472; ^1H NMR ($CDCl_3$, ppm): δ 8.97 (s, H_2O); 7.28–7.71 (m, 70H, Ph–H), δ 8.76 (s, 4H, pdz-C–H). ^{13}C NMR ($CDCl_3$, ppm): δ 123.6, 131.8, 138.6, 141.3, 144.5, 146.9, 149.4 (Ar–C, pyrazine), 171.1(COO). ^{119}Sn NMR ($CDCl_3$, ppm): δ −129.1, 48.6.

2.3. *X-ray crystallographic studies*

X-ray crystallographic data for complexes **1**, **6**, **7** and **8** were collected on a Bruker smart-1000 CCD diffractometer using Mo Kα radiations (0.71073 Å). The structures were solved by direct method and difference Fourier map using SHELXL-97 program, and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated

Table 1
Crystal, data collection and structure refinement parameters for complexes **1**, **6**, **7** and **8**

Compound	1	6	7	8
Empirical formula	$C_{31}H_{57}NO_4Sn_2$	$C_{38}H_{30}N_2O_{10}Sn_2$	$C_{64}H_{121}N_3O_{10}Sn_4$	$C_{84}H_{66}N_4O_9Sn_4$
Formula weight	745.16	912.02	1567.40	1750.17
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions				
a (Å)	8.974(2)	9.779(2)	15.783(12)	9.634(12)
b (Å)	19.011(4)	9.807(2)	20.722(16)	10.658(14)
c (Å)	22.223(5)	19.334(4)	25.033(19)	19.61(2)
α (°)	90	90	90	99.41(2)
β (°)	01.507(4)	100.915(3)	100.110(13)	91.16(2)
γ (°)	90	90	90	112.479(18)
Z	4	2	4	1
Absorption coefficient (mm^{-1})	1.374	1.432	1.272	1.413
Crystal size (mm)	0.47 × 0.43 × 0.18	0.48 × 0.45 × 0.39	0.49 × 0.40 × 0.31	0.24 × 0.15 × 0.08
θ Range for data collection (°)	2.14–25.01	2.15–25.01	1.94–25.01	2.10–25.01
Index ranges	$-10 \leqslant h \leqslant 10$, $-22 \leqslant k \leqslant 21$, $-26 \leqslant l \leqslant 14$	$-11 \leqslant h \leqslant 11$, $-11 \leqslant k \leqslant 11$, $-12 \leqslant l \leqslant 22$	$-18 \leqslant h \leqslant 12$, $-23 \leqslant k \leqslant 24$, $-29 \leqslant l \leqslant 29$	$-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-23 \leqslant l \leqslant 20$
Reflections collected	18962	9237	41864	9673
Unique reflections (R_{int})	6530 (0.0907)	3206 (0.0307)	14076 (0.1249)	7780 (0.0430)
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	6530/264/343	3206/0/235	14076/534/731	7780/54/916
Goodness-of-fit on F^2	1.004	1.001	1.006	1.005
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0767$, $\omega R_2 = 0.1857$	$R_1 = 0.0238$, $\omega R_2 = 0.0569$	$R_1 = 0.0715$, $\omega R_2 = 0.1680$	$R_1 = 0.0525$, $\omega R_2 = 0.0984$
R indices (all data)	$R_1 = 0.1786$, $\omega R_2 = 0.2616$	$R_1 = 0.0337$, $\omega R_2 = 0.0628$	$R_1 = 0.2355$ $\omega R_2 = 0.2308$	$R_1 = 0.0933$, $\omega R_2 = 0.1140$

positions and refined isotropically. Further details are given in Table 1.

3. Results and discussion

3.1. Design of organotin (IV) complexes

Reactions of heterocyclicdicarboxylic acid with diorganotin(IV) oxide or bis(triorganotin) oxide in 1:1 stoichiometry in the 5:1 refluxing solvent mixture of benzene and methanol, which afford air stable complexes. The synthesis procedure of compound **1** is shown in Scheme 1. Complexes **2**–**9** are similar to **1**.

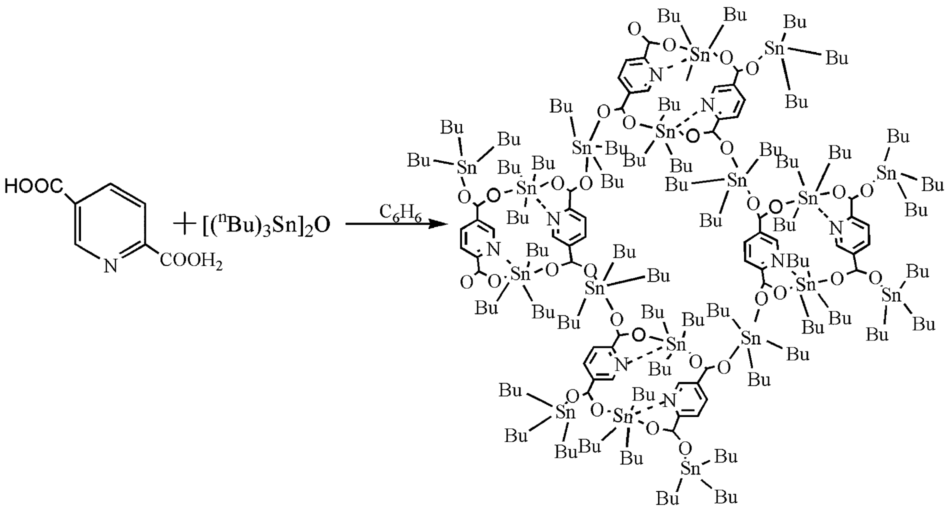
3.2. Spectroscopic studies

The infrared spectrum of the three free ligands show v(C=O) of COOH at 1671, 1662 and 1681 cm^{-1}, respectively, as a strong band, which indicate that there are intermolecular hydrogen bonds of the type C=O…H—O in the uncoordinated 2,5-pyridinedicarboxylic acid, 2,6-pyridinedicarboxylic acid and 2,3-pyrazinedicarboxylic acid molecules. This is commonly observed in the case of carboxylic acids [30]. After deprotonation and coordinated to tin atoms, these bands disappear and are replaced by strong bands in the 1617–1604 and 1316–1486 cm^{-1} regions, which correspond to the asymmetric and symmetric vibrations, respectively, of the COO moiety. Also strong absorption appear at 466–486 cm^{-1} in the respective spectra of the complexes **1**–**8**, which is absent in the spectra of the free ligands, and is assigned to the Sn–O stretching mode of vibration. All these values are consistent with that detected in a number of organotin(IV) derivatives [31–33]. The peak at about 3325–3329 cm^{-1} in the infrared spectrum indicates the existence of the coordinated water molecules in complexes **6**–**8**. Besides, as reported in the literature [34,35], the IR spectra can provide useful information concerning the mode of coordination of the carboxylate in organotin complexes. The magnitude of ($\Delta v = v_{as}(COO) - v_s(COO)$) of about in the band of 147–182 cm^{-1} for complexes **1**–**6** and **8** is comparable to those for the corresponding sodium salts, which indicates the presence of bidentate carboxyl groups [36]. Moreover, the magnitude of Δv also occurring at about 249–312 cm^{-1} for complexes **6** and **8** indicates that the carboxylate ligands function as the type of monodentate except bidentate, which was also confirmed by X-ray structure analyses.

The ^{1}H NMR spectra show the expected integration and peak multiplicities. A single resonance of –OH in the spectra of the free ligands is absent in the spectra of all the complexes **1**–**8** indicating the replacement of the carboxylic acid protons by a organotin moiety on complex formation. In addition, the resonances appear at 8.96–8.98 ppm for **6**–**8** are attributed to the protons of coordinated water molecules in the structures.

The ^{13}C NMR spectra of all complexes show a significant downfield shift of all carbon resonances compared with the free ligands. The shift is a consequence of an electron density transfer from the ligand to the acceptor. The single resonance at 171.1–174.6 is attributed to the COO groups in complexes **1**–**8**. These data are consistent with the structures of **1**–**8**.

^{119}Sn NMR chemical shift values may be used to give tentative indications of the environment around each tin atom. Seven-coordinate Sn has $\delta(^{119}Sn)$ values ranging from about −525 to −786 ppm, six-coordination Sn from −333 to −395 ppm [37,38], five-coordination Sn from −90 to −190 and four-coordination Sn from +200 to −60 in solution [39]. The ^{119}Sn NMR spectra of complexes **1**–**5** exhibit signals between −115.2 and −172.6 ppm., suggesting there is five-coordination in the distannoxane. The value of −341.5 of compound **6** indicates six-coordination other than seven-coordination. The deviation may be because the intermolecular Sn–N or Sn–O interaction probably does not survive in solution. Therefore it can reasonably be assumed that the structure in solution of com-



Scheme 1.

pound **6** is different from that observed in the solid state. Complexes **7**–**8** ($\delta = -116.8$–129.1 ppm) and ($\delta = 48.6$ and 82.5 ppm, respectively) lie between four- and five-coordination. This is confirmed by the X-ray crystal structures of complexes **1**, **6**, **7** and **8**.

3.3. X-ray crystal structures

*3.3.1. Structure of [(^{n}Bu$_3$Sn)$_2$(2,5-pdc)]$_n$ (**1**)*

The molecular structure and cyclic unit are illustrated in Figs. 1 and 2, respectively. It consists of infinite 2D network extending through the cell in the bc plane, as indicated in Fig. 2. Bond lengths and bond angles are given in Table 2. The tributyltin groups are linked by a carboxylate of each pdc ligand in **1**, in turn, employs its two bidentate carboxylic groups to coordinate to two metal centers. Thus, two ligands are linked by two metal centers into a 18-membered macrocycle, which is further linked to four nearest-neighbor tin centers by four 18-membered macrocycle to give rise to a 34-membered macrocycle. The lattice 2D network with two types of cavity can be evaluated by the Sn…Sn and transannular O…O distances, which are 6.722–18.436 and 9.289–15.861 Å, respectively. Similar cavities have been found within the polymeric crystal structures of microporous metal-organic frameworks formed between 2,5-pyridinedicarboxylic acid and Sn centers [40].

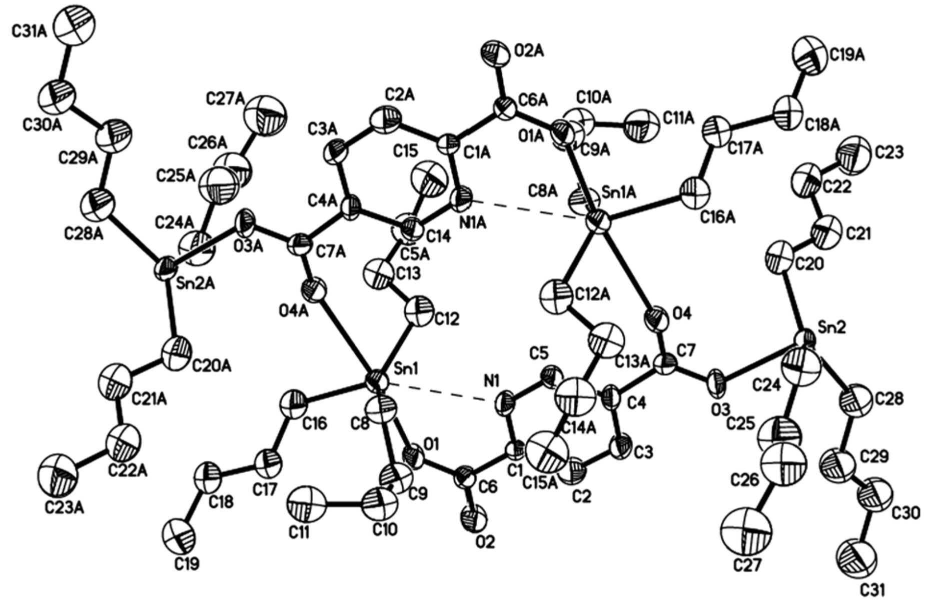


Fig. 1. Molecular structure of compound **1**.

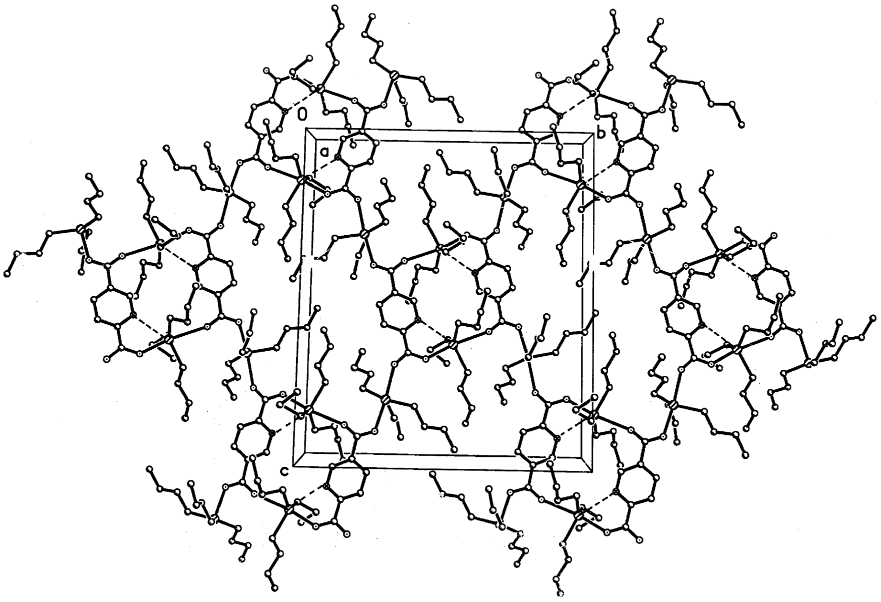


Fig. 2. Packing of the molecules in a unit cell of compound **1**.

Table 2
Selected bond distances (Å) and angles (°) for complexes **1**, **6**, **7** and **8**

*Complex **1***			
Sn(1)–C(8)	2.091(17)	Sn(2)–C(24)	2.10(2)
Sn(1)–C(16)	2.137(14)	Sn(2)–C(28)	2.120(16)
Sn(1)–C(12)	2.140(16)	Sn(2)–C(20)	2.132(15)
Sn(1)–O(1)	2.164(9)	Sn(2)–O(3)	2.182(8)
Sn(1)–N(1)	2.889(10)	Sn(2)–O(2)#1	2.405(9)
C(8)–Sn(1)–C(16)	110.1(7)	C(8)–Sn(1)–C(12)	131.0(7)
C(16)–Sn(1)–C(12)	113.3(6)	C(8)–Sn(1)–O(1)	101.9(5)
C(16)–Sn(1)–O(1)	87.9(5)	C(12)–Sn(1)–O(1)	101.5(6)
C(8)–Sn(1)–N(1)	78.2(5)	C(16)–Sn(1)–N(1)	150.8(5)
C(12)–Sn(1)–N(1)	75.2(5)	O(1)–Sn(1)–N(1)	62.9(3)
C(24)–Sn(2)–C(28)	115.3(8)	C(24)–Sn(2)–C(20)	129.3(8)
C(28)–Sn(2)–C(20)	114.2(7)	C(24)–Sn(2)–O(3)	94.6(6)
C(28)–Sn(2)–O(3)	93.5(5)	C(20)–Sn(2)–O(3)	92.9(6)
C(24)–Sn(2)–O(2)#1	84.3(6)	C(28)–Sn(2)–O(2)#1	91.5(6)
C(20)–Sn(2)–O(2)#1	83.9(6)	O(3)–Sn(2)–O(2)#1	174.9(3)
C(6)–O(2)–Sn(2)#2	142.9(9)		
Symmetry code:	#1 x, $-y+1/2$, $z-1/2$	#2 x, $-y+1/2$, $z+1/2$	
*Complex **6***			
Sn(1)–C(8)	2.112(3)	Sn(1)–O(3)	2.449(2)
Sn(1)–C(14)	2.125(3)	Sn(1)–N(1)	2.342(2)
Sn(1)–O(1)	2.223(2)	O(4)–Sn(1)#2	2.383(2)
Sn(1)–O(5)	2.267(2)	Sn(1)–O(4)#1	2.383(2)
C(8)–Sn(1)–C(14)	172.56(13)	O(1)–Sn(1)–N(1)	69.72(7)
C(8)–Sn(1)–O(1)	95.54(12)	O(5)–Sn(1)–N(1)	142.73(7)
C(14)–Sn(1)–O(1)	91.44(10)	C(8)–Sn(1)–O(4)#1	86.57(12)
C(8)–Sn(1)–O(5)	87.04(10)	C(14)–Sn(1)–O(4)#1	86.06(10)
C(14)–Sn(1)–O(5)	92.50(10)	O(1)–Sn(1)–O(4)#1	151.67(7)
O(1)–Sn(1)–O(5)	73.53(7)	O(5)–Sn(1)–O(4)#1	78.39(7)
C(8)–Sn(1)–N(1)	90.44(10)	N(1)–Sn(1)–O(4)#1	138.59(7)
C(14)–Sn(1)–N(1)	94.39(10)	C(8)–Sn(1)–O(3)	87.89(11)
C(14)–Sn(1)–O(3)	88.92(10)	O(1)–Sn(1)–O(3)	135.56(7)
O(5)–Sn(1)–O(3)	150.86(7)	N(1)–Sn(1)–O(3)	65.95(7)
O(4)#1–Sn(1)–O(3)	72.67(7)		
Symmetry code:	#1 $-x+1$, $y-1/2$, $-z+1/2$	#2 $-x+1$, $y+1/2$, $-z+1/2$	
*Complex **7***			
Sn(1)–C(8)	2.041(16)	Sn(1)–C(12)	2.122(17)
Sn(1)–O(1)	2.160(9)	Sn(1)–C(16)	2.169(16)
Sn(1)–O(5)	2.661(9)	Sn(2)–C(24)	2.117(17)
Sn(2)–O(3)	2.125(9)	Sn(2)–C(20)	2.18(2)
Sn(2)–C(28)	2.26(2)	Sn(3)–C(39)	2.06(2)
Sn(3)–C(43)	2.060(16)	Sn(3)–C(47)	2.066(16)
Sn(3)–O(6)	2.203(9)	Sn(3)–O(10)	2.412(8)
Sn(4)–C(59)	1.77(3)	Sn(4)–C(55)	2.10(2)
Sn(4)–O(8)	2.117(11)	Sn(4)–C(51)	2.14(3)
C(8)–Sn(1)–C(12)	120.7(7)	C(8)–Sn(1)–O(1)	96.9(6)
C(12)–Sn(1)–O(1)	100.1(5)	C(8)–Sn(1)–C(16)	113.8(7)
C(12)–Sn(1)–C(16)	121.9(7)	O(1)–Sn(1)–C(16)	91.9(5)
C(8)–Sn(1)–O(5)	86.2(5)	C(12)–Sn(1)–O(5)	83.7(4)
O(1)–Sn(1)–O(5)	172.9(3)	C(16)–Sn(1)–O(5)	81.0(5)
C(24)–Sn(2)–O(3)	92.8(5)	C(24)–Sn(2)–C(20)	117.7(8)
O(3)–Sn(2)–C(20)	103.8(6)	C(24)–Sn(2)–C(28)	123.1(9)
O(3)–Sn(2)–C(28)	100.5(7)	C(20)–Sn(2)–C(28)	112.2(9)
C(39)–Sn(3)–C(43)	108.9(8)	C(39)–Sn(3)–C(47)	128.8(8)
C(43)–Sn(3)–C(47)	120.9(7)	C(39)–Sn(3)–O(6)	97.9(6)
C(43)–Sn(3)–O(6)	89.3(6)	C(47)–Sn(3)–O(6)	94.1(5)
C(39)–Sn(3)–O(10)	87.0(6)	C(43)–Sn(3)–O(10)	86.6(6)
C(47)–Sn(3)–O(10)	84.8(5)	O(6)–Sn(3)–O(10)	174.5(3)
C(59)–Sn(4)–C(55)	119.6(12)	C(59)–Sn(4)–O(8)	99.1(9)
C(55)–Sn(4)–O(8)	94.2(8)	C(59)–Sn(4)–C(51)	120.0(11)
C(55)–Sn(4)–C(51)	110.9(11)	O(8)–Sn(4)–C(51)	107.6(8)

Table 2 (*continued*)

*Complex **8***			
Sn(1)–C(19)	2.043(17)	Sn(1)–O(1)	2.100(10)
Sn(1)–C(13)	2.107(15)	Sn(1)–C(7)	2.148(15)
Sn(1)–O(5)	2.518(10)	Sn(2)–O(3)	2.025(11)
Sn(2)–C(37)	2.065(18)	Sn(2)–C(31)	2.117(17)
Sn(2)–C(25)	2.128(17)	Sn(2)–O(4)	2.876(11)
Sn(3)–O(6)	2.042(10)	Sn(3)–C(61)	2.043(17)
Sn(3)–C(49)	2.108(14)	Sn(3)–C(55)	2.116(16)
Sn(3)–O(7)	2.835(11)	Sn(4)–O(8)	2.076(11)
Sn(4)–C(67)	2.082(18)	Sn(4)–C(73)	2.094(16)
Sn(4)–C(79)	2.137(16)	Sn(4)–O(9)	2.661(10)
C(19)–Sn(1)–O(1)	100.2(5)	C(19)–Sn(1)–C(13)	116.9(6)
O(1)–Sn(1)–C(13)	102.4(5)	C(19)–Sn(1)–C(7)	117.2(5)
O(1)–Sn(1)–C(7)	90.5(5)	C(13)–Sn(1)–C(7)	120.5(6)
C(19)–Sn(1)–O(5)	80.7(5)	O(1)–Sn(1)–O(5)	176.6(4)
C(13)–Sn(1)–O(5)	79.9(5)	C(7)–Sn(1)–O(5)	86.2(5)
O(3)–Sn(2)–C(37)	94.5(5)	O(3)–Sn(2)–C(31)	108.3(6)
C(37)–Sn(2)–C(31)	112.3(7)	O(3)–Sn(2)–C(25)	105.5(6)
C(37)–Sn(2)–C(25)	108.2(7)	C(31)–Sn(2)–C(25)	123.8(6)
O(3)–Sn(2)–O(4)	49.6(4)	C(37)–Sn(2)–O(4)	143.6(5)
C(31)–Sn(2)–O(4)	79.6(6)	C(25)–Sn(2)–O(4)	90.0(6)
O(6)–Sn(3)–C(61)	116.4(5)	O(6)–Sn(3)–C(49)	94.3(5)
C(61)–Sn(3)–C(49)	111.1(6)	O(6)–Sn(3)–C(55)	106.7(5)
C(61)–Sn(3)–C(55)	110.8(7)	C(49)–Sn(3)–C(55)	116.8(6)
O(6)–Sn(3)–O(7)	49.7(4)	C(61)–Sn(3)–O(7)	84.0(4)
C(49)–Sn(3)–O(7)	143.1(4)	C(55)–Sn(3)–O(7)	85.9(5)
O(8)–Sn(4)–C(67)	104.0(6)	O(8)–Sn(4)–C(73)	94.7(5)
C(67)–Sn(4)–C(73)	111.3(7)	O(8)–Sn(4)–C(79)	107.8(5)
C(67)–Sn(4)–C(79)	125.2(7)	C(73)–Sn(4)–C(79)	109.2(6)
O(8)–Sn(4)–O(9)	52.5(4)	C(67)–Sn(4)–O(9)	80.2(5)
C(73)–Sn(4)–O(9)	147.2(5)	C(79)–Sn(4)–O(9)	85.2(5)

In other related polymeric systems so far only dimeric [41], hexameric [42], and chainlike [43] motifs have been reported. All the tin atoms in **1** possess a same coordination environment. The coordination about the tin atoms are both distorted from regular trigonal bipyramidal geometry. Associated with the Sn(1)–O(4#) (symmetry code: $-x+1$, $-y+1$, $-z+1$) distance [2.701(2) Å] is a little longer than reported in $[Me_2Sn(pca)Cl]_3$ (2.527 Å) [44]. The Sn(1)–O(1) distance [2.164(9) Å] is close to the distance between coordinated O atom and central tin atom in other organotin complexes [45], but much shorter than the sum of the van der Waals radii of Sn and O (3.68 Å). The angle O(1)–Sn(1)–O(4#) 172.09(6)° is close to a linear arrangement. The sum of the angles subtended at the tin atom in the equatorial plane is 354.3° for Sn(1), so that the atoms Sn(1), C(8), C(12) and C(16) are almost in the same plane. The Sn–C distances [2.091(17)–2.140(16) Å] are equal within experimental error and close to the single-bond value for trigonal bipyramidal tin [46]. It is noteworthy that short contact is recognized between Sn…N (Sn(1)–N(1) 2.889(10) Å) and this distance is significantly less than the sum of the van der Waal's radii for Sn and N of 3.74 Å [47]. If the short contact of tin–nitrogen is considered, the geometry of the Sn(1) is best described as distorted octahedron and the coordinate ligands are quinquidentate. These Sn…N bonds not only contribute to the crystal stability and compactness but also partial result in a macrocycle arrangement (Figs. 1 and 2).

*3.3.2. The structure of $[Ph_2Sn(2,6\text{-}pdc)(H_2O)]_n$ (**6**)*

The Ph_2Sn(2,6-pdc) units are connected in polymeric structures as shown in Figs. 3–5, selected bond lengths (Å) and angles (°) are listed in Table 2. Intermolecular Sn(1)–O(4)#1 (symmetry code: $-x+1$, $y-1/2$, $-z+1/2$) bond [2.383(2) Å] is comparable to the intramolecular tin–oxygen bonds [Sn(1)–O(1), 2.223(2) Å and Sn(1)–

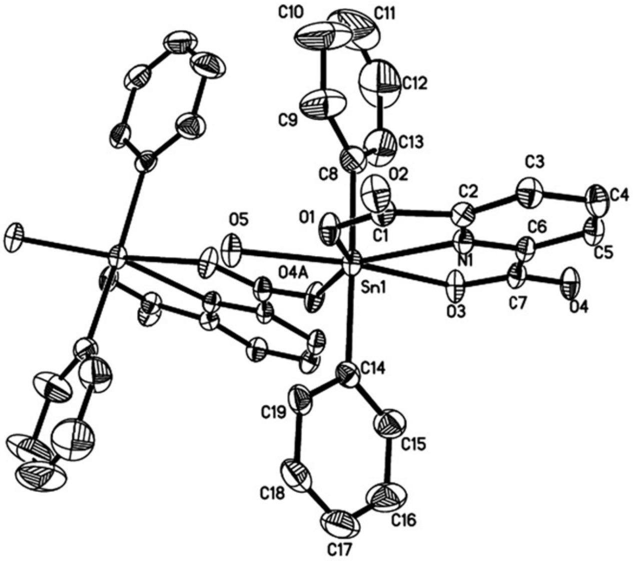


Fig. 3. Molecular structure of compound **6**.

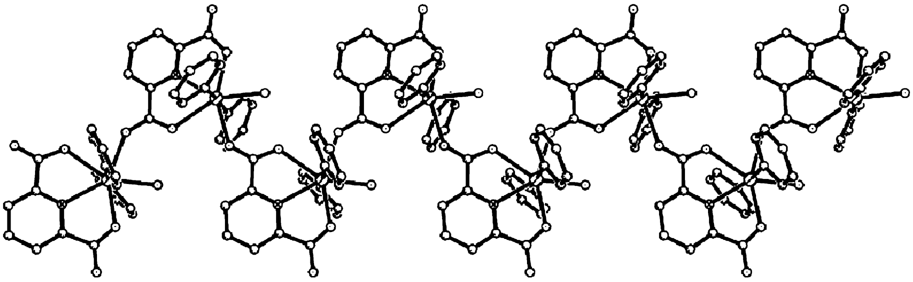


Fig. 4. 1D zigzag structure of compound **6**.

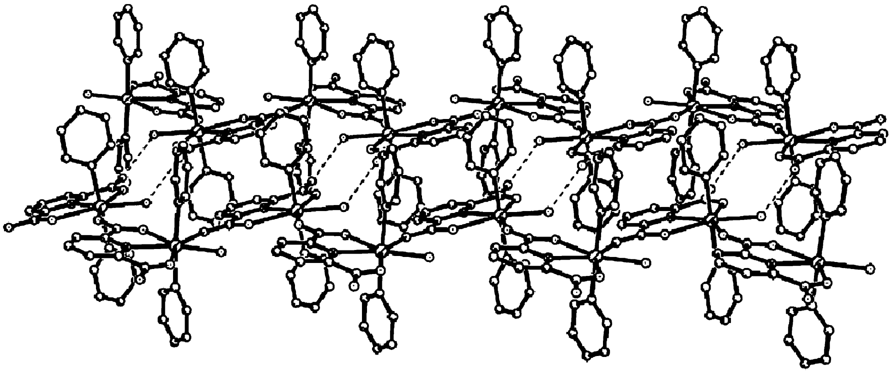


Fig. 5. Perspective view showing the 3D framework of compound **6**.

O(3), 2.449(2) Å] and close the sum of the covalent radii of tin and oxygen, 2.13 Å, creating a continuous zigzag polymeric chain (Fig. 4). For compound **6**, one ligand is chelate to one tin, bonding through the nitrogen atom and two oxygen atoms from different carboxyl groups. Therefore, the coordinate ligands in this compound is quadridentate. Due to the coordinated water molecule, the overall configuration at tin is best described as pentagonal bipyramidal: tin, the bonded oxygen and nitrogen atoms are nearly coplanar and deviate only slightly from regular pentagonal geometry, mean deviation from plane is 0.0522 Å. The aryl groups occupy the apical position, the axial–Sn–axial, C(8)–Sn(1)–C(14) is 172.56(13)°. The Sn(1)–N(1) distance 2.342(2) Å is in keeping with those reported in Sn–N complexes $Me_2SnCl(2\text{-Pic})$ [48], $Me_2Sn(2\text{-Pic})_2$ [49] and $\{[^nBu_2Sn(2\text{-Pic})]_2O\}_2$ [50]. Through the coordinated water molecules to the tin atoms, the chain structures are associated with each other via hydrogen bonds, so that a 3D framework is formed (Fig. 5). The distances of hydrogen-bonding, O(5)–H…O(2#) (symmetry code: $-x+1$, $-y+1$, $-z$) and O(5)–H…O(3#) (symmetry code: $-x+1$, $y-1/2$, $-z+1/2$) are 2.669 and 2.676 Å, respectively, and the O(5)–H…O(2#) and O(5)–H…O(3#) angles are 166.68° and 165.73°, respectively. This confirms that the water molecules play an important role in the stabilization of the polymer.

3.3.3. Structure of $\{[^nBu_3Sn(2,6\text{-}pdc)Sn^nBu_3]_2(H_2O)_2\}\cdot CH_3CN$ *(7)*

The crystal and the polymeric structures are illustrated in Figs. 6 and 7, respectively, selected bond lengths (Å) and angles (°) are listed in Table 2. For compound **7**, the asymmetric unit contains two monomers A and B (Fig. 7), which are crystallographically nonequivalent. The conformations of the two independent molecules A and B are almost same, with only small differences in bond lengths and bond angles. As can be seen from Fig. 6, compound **7** is a tributyltin ester of 2,6-pyridinedicarboxylic acid. The two monomers structure with four tributyltin centers. Take A for example, each 2,6-pyridinedicarboxylic acid dianion bridges two tin centers via only one O atom derived from the monodentate carboxylate moiety. Obviously, one tin center [Sn(2)] is four-coordination and the other [Sn(1)] is five-coordination due to the coordinated water molecule. The four-coordination central tin atom forms four primary bonds: three to the *n*-butyl groups and one to the oxygen atom derived of the monodentate carboxyl group. Thus, the geometry of the tin center displays a distorted tetrahedral coordinated sphere with six angles ranging from 92.8(5)° to 123.1(9)°. The Sn–C bond lengths [2.117(17)–2.26(2) Å] are consistent with those reported in other triorganotin carboxylates [38]. The Sn(2)–O(3) distance [2.125(9) Å] is a little longer than reported in $[Ph_3Sn(O_2CC_6H_5)]$ (2.073 Å) [46] and approaches the sum of the covalent radii of Sn and O (2.13 Å). The Sn(1) atom is rendered five-coordination by coordinating with the water molecule. It is rendered a distorted trigonal bipyramidal type, surrounded axially by two oxygen atoms and equatorially by three carbon atoms of the *n*-butyl groups. The O atoms occupy the axial sites [Sn(1)–O(1) 2.160(9), Sn(1)–O(5) 2.661(9) Å and O(1)–Sn(1)–O(5) 172.9(3)°]. Despite rather high estimated stan-

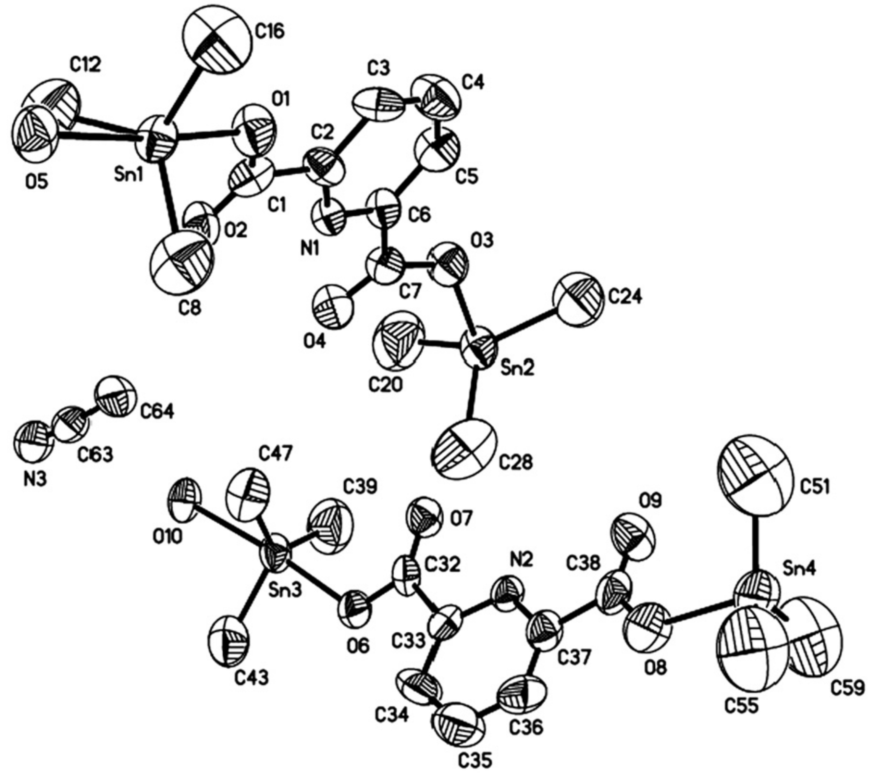


Fig. 6. Molecular structure of compound **7**. (For clarity, only the first carbon atoms of the *n*-butyl chain linked to Sn are shown.)

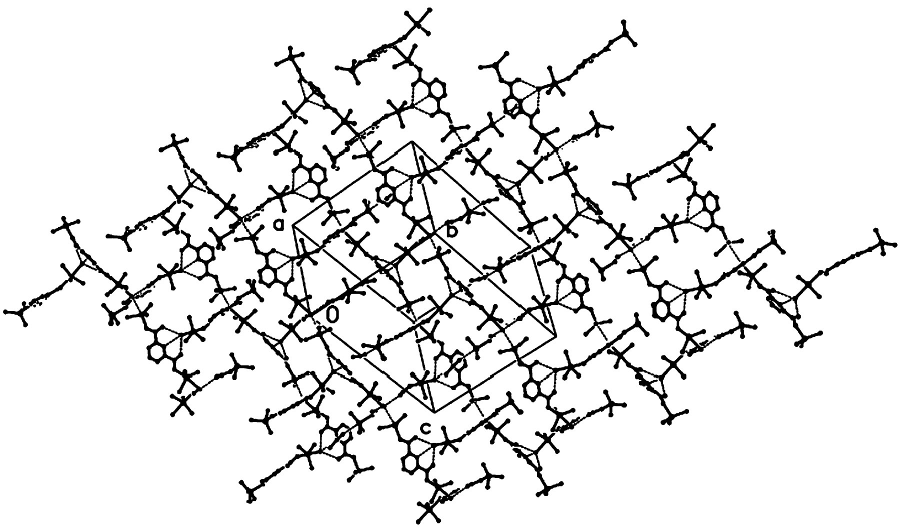


Fig. 7. Perspective view showing the 2D network of compound **7**. (For clarity, only the first carbon atoms of the *n*-butyl chain linked to Sn are shown.)

dard deviations in the C–O bond distances, a clear trend in these parameters may be discerned. As expected, the C–O bond distances [C(1)–O(2) 1.208(15) Å, C(7)–O(4) 1.223(14) Å] associated with the non-coordinating O atoms are shorter than the coordinating C–O bond distances [C(1)–O(1) 1.248(14) Å, C(7)–O(3) 1.295(14) Å]. Although not involved in coordination to tin, the O(2), O(4) [for A] and O(7), O(9) [for B] atoms form significant intermolecular contacts in the crystal lattice. Through the coordinated water molecules and N atoms, the monomeric structures are associated with each other via hydrogen bonds, which A 2D network is formed (Figs. 6 and 7). The distances of hydrogen-bondings, O(5)–H…O(9#) (symmetry code: $x-1/2$, $-y+3/2$, $z+1/2$), O(5)–H…O(7#) (symmetry code: $x-1/2$, $-y+3/2$, $z+1/2$), O(5)–H…N(2#) (symmetry code: $x-1/2$, $-y+3/2$, $z+1/2$), O(10)–H…O(4#) (symmetry code: $-x+1$, $-y+1$, $-z+1$) and O(10)–H…O(2#) (symmetry code: $-x+1$, $-y+1$, $-z+1$) are 2.867, 2.738, 2.936, 2.843 and 2.832 Å, respectively. Also, for compound **7**, cocrystallization is found in the crystals and the co-crystallized solvent is acetonitrile with the molar ratio of $\{[^n\mathrm{Bu}_3\mathrm{Sn}(2,6\text{-pdc})\mathrm{Sn}^n\mathrm{Bu}_3]_2(\mathrm{H_2O})_2\}$: C_2H_3N is 1:1.

3.3.4. Structure of $\{[Ph_3Sn(2,3\text{-}pdz)SnPh_3]_2(H_2O)\}$ (**8**)

The crystal and the polymeric structures are illustrated in Figs. 8 and 9, respectively, selected bond lengths (Å) and angles (°) are listed in Table 2. For compound **8**, the asymmetric unit also contains two crystallographically nonequivalent monomers A and B (Fig. 8). In the case of A, the structure is similar to that in compound **7**. One tin center [Sn(2)] is four-coordination and the other [Sn(1)] is five-coordination due to the coordinated water molecule. For the four-coordination central tin atom forms four primary bonds: three to the phenyl groups and one to the oxygen atom derived from the monodentate carboxyl group. Thus, the geometry of the tin center also displays a distorted tetrahedral. The other tin atom is rendered a distorted trigonal bipyramidal type, surrounded axially by two oxygen atoms and equatorially by three carbon atoms of the *n*-butyl groups. Furthermore, it is noteworthy that a weak intramolecular Sn…O interaction is recognized between the Sn(2) and O(4), O(4) derived from the monodentate carboxyl group. The Sn(2)…O(4) distance [2.876(11) Å] is considerably less than the sum of the van der Waals radii (3.68 Å) (Fig. 8). The **B** structure is similar to the A but have no water molecular coordinate to tin atom. Interestingly, the two tin atoms in B possess different coordination environ-

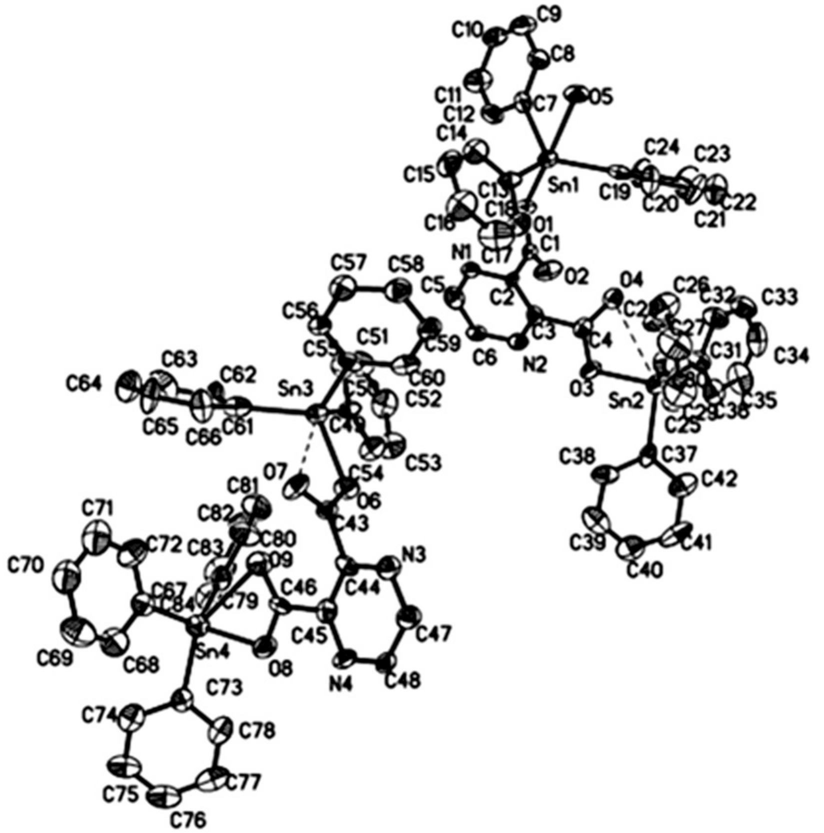


Fig. 8. Molecular structure of complex **8**.

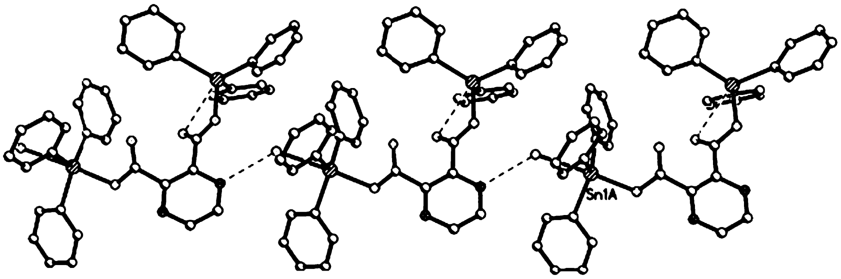


Fig. 9. The polymeric chain in the lattice.

ment. There are two distinct coordinate carboxyl groups, one is monodentate and the other is didentate, which make the overall configurations at tin are distorted tetrahedral and distorted trigonal bipyramidal, respectively.

The salient feature of the supramolecular of compound is that of an 1D chain polymer (Fig. 9) arising from A, in which the chain structure molecules are connected through intermolecular weak interacrions of the N atoms and the water oxygen atoms from adjacent sides.

4. Conclusions

From the crystal structures mentioned above, we can conclude that it is crucial to form bridging O–Sn–O or O–Sn–N linkages for the formation of multiform cyclooligomeric and polymeric chain structure. Meanwhile, these ligands with multi-coordination may lead to different architectures and those dicarboxylate ligands with additional donor atoms among most common ligands are very useful for constructing the complexes with polymeric chain or cyclooligomeric structures.

Acknowledgements

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Appendix A. Supplementary material

CCDC 291170, 291173, 610972 and 291172 contain the supplementary crystallographic data for **1**, **6**, **7** and **8**. 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.ica.2006.12.012.

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