

Synthesis and structural characterizations of diorganotin(IV) complexes with 2-pyrazinecarboxylic acid

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Abstract

Two types of diorganotin(IV) complexes $\{[R_2Sn(O_2CC_4H_3N_2)]_2O\}_2$ ($R = n$ -octyl **1**, 2- $ClC_6H_4CH_2$ **3**, 2- $FC_6H_4CH_2$ **5**, 4- $FC_6H_4CH_2$ **7**) and $R_2Sn(O_2CC_4H_3N_2)_2$ ($R = n$ -octyl **2**, 2- $ClC_6H_4CH_2$ **4**, 2- $FC_6H_4CH_2$ **6**, 4- $FC_6H_4CH_2$ **8**) were prepared by reactions of diorganotin oxide with 2-pyrazinecarboxylic acid. The complexes **1–8** are characterized by elemental analysis, IR and NMR (1H , ^{13}C , ^{119}Sn) spectroscopies. The complexes $\{[(n-C_8H_{17})_2Sn(O_2CC_4H_3N_2)]_2O\}_2$ (**1**) and $(n-C_8H_{17})_2Sn(O_2CC_4H_3N_2)_2$ (**2**) are also determined by X-ray single crystal diffraction, which reveal that the *endo*-cyclic tin atom of complex **1**, is seven-coordinate, and the *exo*-cyclic tin atom is hexa-coordinated geometry, while the complex **2** is seven-coordinated geometry. The nitrogen atom of the aromatic ring participates in the interactions with the Sn atom.

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Keywords: Diorganotin oxide; 2-Pyrazinecarboxylic acid; Synthesis; Crystal structure

1. Introduction

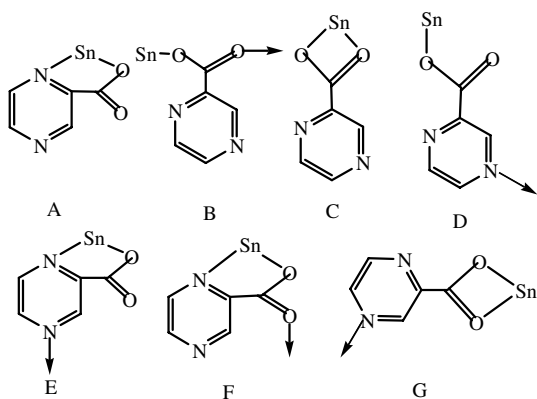
The environmental and biological chemistry of organotin(IV) carboxylates have been the subjects of interest for some time due to their increasingly widespread use in industry and agriculture [1–5]. In particular, a few diorganotin(IV) derivatives have been shown to exhibit *in vitro* antitumour properties against a wide panel of tumoral cell lines of human origin. In general, the biochemical activity of organotin carboxylates is influenced greatly by the structure of the molecule and the coordination number of the tin atoms [6–8]. Recent review on structures of diorganotin carboxylates has demonstrated that when a 1:1 (tin/ligand) ratio is used, five types of structure adopted in the crystalline state. A characteristic feature of these complexes in the solid state is their dimerization that results in the so-called ladder or staircase arrange-

ment that contains a central planar Sn_2O_2 four-membered ring. When a 1:2 ratio is used, a diorganotin dicarboxylate is formed.

Our current interest focuses on how the hetero-atoms (N, O or S) of the carboxylic acids influence the coordination mode and further help the self-assemble of these molecules [9–11]. Based on the above considerations, we have investigated a series of reactions of diorganotin oxide with 2-pyrazinecarboxylic acid. This ligand is interesting because of its potential multiple bidentate coordination possibilities. As exhibited in Scheme 1, at least seven bonding modes between this ligand and tin are conceivable although nobody has investigated its actual coordination mode until now [10]. With 1:1 ratio (tin/ligand), we have obtained four ladder complexes of the type $\{[R_2Sn(O_2CC_4H_3N_2)]_2O\}_2$ ($R = n$ -octyl **1**, 2- $ClC_6H_4CH_2$ **3**, 2- $FC_6H_4CH_2$ **5**, 4- $FC_6H_4CH_2$ **7**). With 1:2 ratio, another four complexes were obtained and the general formula is $R_2Sn(O_2CC_4H_3N_2)_2$ ($R = n$ -octyl **2**, 2- $ClC_6H_4CH_2$ **4**, 2- $FC_6H_4CH_2$ **6**, 4- $FC_6H_4CH_2$ **8**).

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Scheme 1.

2. Experimental

2.1. Materials and measurements

All the reactions were carried out under nitrogen atmosphere. Di-*n*-octyltin oxide and 2-pyrazinecarboxylic acid were used as received. The $(\text{ArCH}_2)_2\text{SnO}$ were prepared by the reported method [12]. The melting points were obtained with Kofler micro-melting 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 are 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 $\{[R_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_3\text{N}_2)]_2\text{O}\}_2$ ($R = n\text{-octyl}$ 1, 2- $\text{ClC}_6\text{H}_4\text{CH}_2$ 3, 2- $\text{FC}_6\text{H}_4\text{CH}_2$ 5, 4- $\text{FC}_6\text{H}_4\text{CH}_2$ 7)

The diorganotin oxide (2.0 mmol) and the 2-pyrazinecarboxylic acid (2.0 mmol) were dissolved in dry benzene (30 ml) and stirred at reflux for 7 h (for complexes 3, 5 and 7 stirred 14 h). After cooling to room temperature, the solvent was evaporated under vacuum. The crude adduct was recrystallized from dichloromethane–hexane to give colorless crystals.

2.2.1. $\{[(n\text{-C}_8\text{H}_{17})_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_3\text{N}_2)]_2\text{O}\}_2$ (1)

Yield: 81%. m.p. 103–104 °C. Anal. Calc. for $\text{C}_{84}\text{H}_{148}\text{N}_8\text{O}_{10}\text{Sn}_4$: C, 52.96; H, 7.83; N, 5.88. Found: C, 52.92; H, 7.80; N, 5.91%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1663, 1639; $\nu_{\text{s}}(\text{COO})$, 1400, 1374; $\nu(-(\text{CH}_2)_n-)$, 725; $\nu(\text{Sn}-\text{C})$, 577; $\nu(\text{Sn}-\text{O})$, 479; $\nu(\text{Sn}-\text{O}-\text{Sn})$, 620; $\nu(\text{Sn}-\text{N})$, 443. ^1H NMR (CDCl_3 , ppm): δ 0.80 (t, 24H, CH_3), 1.34–1.67 (m, 112H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 7.71–8.85 (m, 12H, pyrazine-H). ^{13}C NMR (CDCl_3 , ppm): δ 33.85 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 618 Hz), 34.02 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 780 Hz), 31.87 (βCH_2), 32.21 (βCH_2), 29.64 (γCH_2), 29.39 (γCH_2), 29.20 (δCH_2), 29.14 (δCH_2), 27.36 (ϵCH_2), 25.95 (ϵCH_2), 25.34 (ζCH_2), 22.58, (ζCH_2), 18.41 (ηCH_2), 18.30 (ηCH_2), 14.07 (CH_3), 13.94 (CH_3), 147.64, 147.13,

144.20, 141.71 ($\text{C}_4\text{H}_3\text{N}_2-$), 174.22 (COO). ^{119}Sn NMR (CDCl_3 , ppm): δ -380.5, -250.6.

2.2.2. Synthesis of $\{[(2\text{-ClC}_6\text{H}_4\text{CH}_2)_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_3\text{N}_2)]_2\text{O}\}_2$ (3)

Yield: 54%. m.p. 199–201 °C. Anal. Calc. for $\text{C}_{76}\text{H}_{60}\text{Cl}_8\text{N}_8\text{O}_{10}\text{Sn}_4$: C, 45.55; H, 3.02; N, 5.59. Found: C, 45.56; H, 2.99; N, 5.57%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1671, 1648; $\nu_{\text{s}}(\text{COO})$, 1383, 1377; $\nu(\text{Sn}-\text{C})$, 569; $\nu(\text{Sn}-\text{O})$, 474; $\nu(\text{Sn}-\text{O}-\text{Sn})$, 619, $\nu(\text{Sn}-\text{N})$, 452. ^1H NMR (CDCl_3 , ppm): δ 3.04 (t, 8H, $J_{\text{Sn}-\text{H}} = 80$ Hz, SnCH_2), 3.22 (t, 8H, $J_{\text{Sn}-\text{H}} = 86$ Hz, SnCH_2), 6.59–6.72 (m, 32H, Ph-H), 7.75–8.88 (m, 12H, pyrazine-H). ^{13}C NMR (CDCl_3 , ppm): δ 31.58 (CH_2Ar , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 615 Hz), 32.54 (CH_2Ar , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 844 Hz), 151.63, 150.68, 136.10, 128.47, 125.21, 125.35, 122.73, 122.59 (Ar-C), 147.01, 146.41, 143.85, 141.56 ($\text{C}_4\text{H}_3\text{N}_2-$), 170.26 (COO). ^{119}Sn NMR (CDCl_3 , ppm): δ -344.7, -230.1.

2.2.3. Synthesis of $\{[2\text{-FC}_6\text{H}_4\text{CH}_2]_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_3\text{N}_2)_2\text{O}\}_2$ (5)

Yield: 56%. m.p. 190–192 °C. Anal. Calc. for $\text{C}_{76}\text{H}_{60}\text{F}_8\text{N}_8\text{O}_{10}\text{Sn}_4$: C, 48.76; H, 3.23; N, 5.98. Found: C, 48.71; H, 3.26; N, 5.95%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1637, 1604; $\nu_{\text{s}}(\text{COO})$, 1428, 1379; $\nu(\text{Sn}-\text{C})$, 571; $\nu(\text{Sn}-\text{O})$, 477; $\nu(\text{Sn}-\text{O}-\text{Sn})$, 628, $\nu(\text{Sn}-\text{N})$, 446. ^1H NMR (CDCl_3 , ppm): δ 2.93 (t, 8H, $J_{\text{Sn}-\text{H}} = 80$ Hz, SnCH_2), 3.21 (t, 8H, $J_{\text{Sn}-\text{H}} = 88$ Hz, SnCH_2), 6.62–6.74 (m, 32H, Ph-H), 7.74–8.87 (m, 12H, pyrazine-H). ^{13}C NMR (CDCl_3 , ppm): δ 31.16 (CH_2Ar , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 613 Hz), 33.74 (CH_2Ar , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 853 Hz), 151.73, 148.56, 137.45, 129.65, 127.55, 127.21, 116.13, 115.52 (Ar-C), 147.01, 146.41, 143.85, 141.56 ($\text{C}_4\text{H}_3\text{N}_2-$), 173.85 (COO). ^{119}Sn NMR (CDCl_3 , ppm): δ -373.6, -248.7.

2.2.4. Synthesis of $\{[(4\text{-FC}_6\text{H}_4\text{CH}_2)_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_3\text{N}_2)]_2\text{O}\}_2$ (7)

Yield: 51%. m.p. 195–196 °C. Anal. Calc. for $\text{C}_{76}\text{H}_{60}\text{F}_8\text{N}_8\text{O}_{10}\text{Sn}_4$: C, 48.76; H, 3.23; N, 5.98. Found: C, 48.74; H, 3.28; N, 5.94%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1655, 1620; $\nu_{\text{s}}(\text{COO})$, 1439, 1379; $\nu(\text{Sn}-\text{C})$, 571; $\nu(\text{Sn}-\text{O})$, 471; $\nu(\text{Sn}-\text{O}-\text{Sn})$, 617, $\nu(\text{Sn}-\text{N})$, 447. ^1H NMR (CDCl_3 , ppm): δ 2.92 (t, 8H, $J_{\text{Sn}-\text{H}} = 80$ Hz, SnCH_2), 3.22 (t, 8H, $J_{\text{Sn}-\text{H}} = 88$ Hz, SnCH_2), 6.62–6.74 (m, 32H, Ph-H), 7.74–8.87 (m, 12H, pyrazine-H). ^{13}C NMR (CDCl_3 , ppm): δ 31.46 (CH_2Ar , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 607 Hz), 33.27 (CH_2Ar , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 857 Hz), 137.34, 131.15, 129.31, 128.74, 123.79, 122.83 (Ar-C), 148.64, 147.25, 142.74, 141.64 ($\text{C}_4\text{H}_3\text{N}_2-$), 172.55 (COO). ^{119}Sn NMR (CDCl_3 , ppm): δ -359.4, -225.5.

2.3. Synthesis of $R_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_3\text{N}_2)_2$ ($R = n\text{-octyl}$ 2, 2- $\text{ClC}_6\text{H}_4\text{CH}_2$ 4, 2- $\text{FC}_6\text{H}_4\text{CH}_2$ 6, 4- $\text{FC}_6\text{H}_4\text{CH}_2$ 8)

The diorganotin oxide (2.0 mmol) and the 2-pyrazinecarboxylic acid (4.0 mmol) were dissolved in dry benzene (30 ml) and stirred at reflux for 7 h (for complexes 4, 6

and **8** stirred 14 h). After cooling to room temperature, the solvent was evaporated under vacuum. The crude adduct was recrystallized from dichloromethane–hexane to give colorless crystals.

2.3.1. $(n\text{-C}_8\text{H}_{17})_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_3\text{N}_2)_2$ (**2**)

Yield: 79%; m.p. 179–181 °C. Anal. Calc. for $\text{C}_{26}\text{H}_{40}\text{N}_4\text{O}_4\text{Sn}$: C, 52.80; H, 6.82; N, 9.47. Found: C, 52.78; H, 6.83; N, 9.45%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1646, 1598; $\nu_{\text{s}}(\text{COO})$, 1415, 1347; $\nu(-\text{CH}_2)_n$, 723; $\nu(\text{Sn}-\text{C})$, 536; $\nu(\text{Sn}-\text{O})$, 485; $\nu(\text{Sn}-\text{N})$, 467. ^1H NMR (CDCl_3 , ppm): δ 0.82 (t, 24H, CH_3), 1.27–1.70 (m, 28H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 7.73–8.87 (m, 6H, pyrazine-H). ^{13}C NMR (CDCl_3 , ppm): δ 34.54 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 615 Hz), 32.21 (βCH_2), 29.74 (γCH_2), 29.19 (δCH_2), 26.36 (ϵCH_2), 23.17 (ζCH_2), 18.36 (ηCH_2), 13.94 (CH_3), 148.01, 147.23, 144.86, 142.17 ($\text{C}_4\text{H}_3\text{N}_2$), 174.55 (COO). ^{119}Sn NMR (CDCl_3 , ppm): δ -432.5.

2.3.2. $(2\text{-ClC}_6\text{H}_4\text{CH}_2)_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_3\text{N}_2)_2$ (**4**)

Yield: 49%; m.p. 212–214 °C. Anal. Calc. for $\text{C}_{24}\text{H}_{18}\text{Cl}_2\text{N}_4\text{O}_4\text{Sn}$: C, 46.79; H, 2.95; N, 9.09. Found: C, 46.76; H, 2.99; N, 9.07%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1642, 1615; $\nu_{\text{s}}(\text{COO})$, 1435, 1388; $\nu(\text{Sn}-\text{C})$, 532; $\nu(\text{Sn}-\text{O})$, 482; $\nu(\text{Sn}-\text{N})$, 468. ^1H NMR (CDCl_3 , ppm): δ 2.96 (t, 4H, $J_{\text{Sn}-\text{H}} = 96$ Hz, SnCH_2), 6.63–6.71 (m, 8H, Ph-H), 7.70–8.90 (m, 6H, pyrazine-H). ^{13}C NMR (CDCl_3 , ppm): δ 33.58 (CH_2Ar , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 889 Hz), 138.18, 135.42, 131.98, 121.92, 117.85, 115.43 (Ar-C), 150.16, 147.36, 145.74, 143.65 ($\text{C}_4\text{H}_3\text{N}_2$), 172.23 (COO). ^{119}Sn NMR (CDCl_3 , ppm): δ -412.7.

2.3.3. $(2\text{-FC}_6\text{H}_4\text{CH}_2)_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_3\text{N}_2)_2$ (**6**)

Yield: 56%; m.p. 218–220 °C. Anal. Calc. for $\text{C}_{24}\text{H}_{18}\text{F}_2\text{N}_4\text{O}_4\text{Sn}$: C, 49.43; H, 3.11; N, 9.61. Found: C, 49.40; H, 3.14; N, 9.58%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1630, 1588; $\nu_{\text{s}}(\text{COO})$, 1412, 1331; $\nu(\text{Sn}-\text{C})$, 551; $\nu(\text{Sn}-\text{O})$, 492; $\nu(\text{Sn}-\text{N})$, 464. ^1H NMR (CDCl_3 , ppm): δ 2.13 (t, 4H, $J_{\text{Sn}-\text{H}} = 97$ Hz, SnCH_2), 6.73–6.82 (m, 8H, Ph-H), 7.81–8.99 (m, 6H, pyrazine-H). ^{13}C NMR (CDCl_3 , ppm): δ 34.58 (CH_2Ar , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 889 Hz), 138.98, 130.15, 129.01, 124.13, 118.05, 116.43 (Ar-C), 147.01, 146.41, 143.85, 141.56 ($\text{C}_4\text{H}_3\text{N}_2$), 172.86 (COO). ^{119}Sn NMR (CDCl_3 , ppm): δ -441.8.

2.3.4. $(4\text{-FC}_6\text{H}_4\text{CH}_2)_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_3\text{N}_2)_2$ (**8**)

Yield: 56%; m.p. 215–218 °C. Anal. Calc. for $\text{C}_{24}\text{H}_{18}\text{F}_2\text{N}_4\text{O}_4\text{Sn}$: C, 49.43; H, 3.11; N, 9.61. Found: C, 49.41; H, 3.15; N, 9.57%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1645, 1611; $\nu_{\text{s}}(\text{COO})$, 1423, 1350; $\nu(\text{Sn}-\text{C})$, 558; $\nu(\text{Sn}-\text{O})$, 484; $\nu(\text{Sn}-\text{N})$, 459. ^1H NMR (CDCl_3 , ppm): δ 2.16 (t, 4H, $J_{\text{Sn}-\text{H}} = 85$ Hz, SnCH_2), 6.75–6.86 (m, 8H, Ph-H), 7.84–9.05 (m, 6H, pyrazine-H). ^{13}C NMR (CDCl_3 , ppm): δ 35.41 (CH_2Ar , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 889 Hz), 135.34, 126.55, 125.98, 116.43 (Ar-C), 147.01, 146.41, 143.85, 141.56 ($\text{C}_4\text{H}_3\text{N}_2$), 173.47 (COO). ^{119}Sn NMR (CDCl_3 , ppm): δ -450.3.

Table 1

Crystal data collection and structure refinement parameters for complexes **1** and **2**

	1	2
Empirical formula	$\text{C}_{84}\text{H}_{148}\text{N}_8\text{O}_{10}\text{Sn}_4$	$\text{C}_{26}\text{H}_{40}\text{N}_4\text{O}_4\text{Sn}$
<i>M</i>	1904.86	591.31
<i>T</i> (K)	298(2)	298(2)
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	<i>Pbca</i>
<i>a</i> (Å)	11.942(6)	12.123(4)
<i>b</i> (Å)	21.513(10)	18.819(6)
<i>c</i> (Å)	21.520(10)	26.004(8)
β (°)	104.830(7)	90
<i>V</i> (Å ³)	4969(4)	5932(3)
<i>Z</i>	2	8
Calculated density (Mg/m ³)	1.273	1.324
<i>F</i> (000)	1976	2448
μ (mm ⁻¹)	1.046	0.896
Scan range θ (°)	1.92–25.03	2.15–25.02
Reflections collected	25512	28636
Unique data	17026	5094
Date/restraints/parameters	17026, 214, 796	5094, 68, 316
Maximum/minimum transmission	0.6620, 0.5920	0.7940, 0.6680
GOF	0.999	1.072
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0793, 0.1334	0.0680, 0.1588
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.2233, 0.1759	0.1205, 0.2098
Largest difference peak, hole (e Å ⁻³)	1.138, -0.478	1.263, -2.310

2.4. X-ray crystallographic studies

X-ray crystallographic data for complexes **1** and **2** were collected on a Bruker smart-1000 CCD diffractometer using Mo K α 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 positions and refined isotropically. Further details are given in Table 1.

3. Results and discussion

3.1. Spectroscopic studies

3.1.1. IR spectra

The infrared spectra of the diorganotin(IV) carboxylates are listed above. The $\Delta\nu(\nu_{\text{as}}(\text{CO}_2)-\nu_{\text{s}}(\text{CO}_2))$ value can be used to determine the type of bonding between metal and carboxyl group [13,14]. It is generally believed that the difference in $\Delta\nu$ between asymmetric $\nu_{\text{asym}}(\text{CO}_2)$ and symmetric $\nu_{\text{sym}}(\text{CO}_2)$ absorption frequencies below 200 cm^{-1} for the bidentate carboxylate moiety, but greater than 200 cm^{-1} for the monodentate carboxylate moiety [15–18]. For complexes **1**, **3**, **5** and **7** the values of $\Delta\nu$ are between 210 and 300 cm^{-1} and this strongly indicates that these complexes adopt the monodentate carboxylate structure. In complexes **2**, **4**, **6** and **8**, the magnitudes of $\Delta\nu^1[\nu_{\text{as}}(\text{CO}_2)^1-\nu_{\text{s}}(\text{CO}_2)^1]$ and $\Delta\nu^2[\nu_{\text{as}}(\text{CO}_2)^2-\nu_{\text{s}}(\text{CO}_2)^2]$ are 254–299 and 174–188 cm^{-1} which indicate the presence of

bidentate and monodentate carboxylate groups in these complexes. A strong absorption appears at 471–492 cm^{-1} in the respective spectra of the complexes **1–8**, which is absent in the spectra of the free ligand. This is assigned to the Sn–O stretching mode of vibration. The observation of two Sn–C absorption bands in the 532–577 cm^{-1} region reveals a non-linear *trans* configuration of the C–Sn–C moiety. New vibrations, which appear in the 443–468 cm^{-1} , are attributed to Sn–N bonds. For complexes **1**, **3**, **5** and **7**, a strong band near 620 cm^{-1} , which is absent in the other four complexes, is assigned to $\nu(\text{Sn–O–Sn})$, indicating a Sn–O–Sn bridged structure. These assignments are also confirmed by the X-ray diffraction studies of complexes **1** and **2**.

3.1.2. NMR spectroscopic

The ^1H NMR spectra show the expected integration and peak multiplicities. In the spectra of the free ligand, single resonance are observed at 11.46 ppm, which is absent in the spectra of the complexes indicating the replacement of the carboxylic acid proton by a diorganotin moiety on complex formation. The ^1H NMR of complexes **3**, **5**, **7** show that the chemical shifts of the protons of methylene bound to tin atom (ArCH_2Sn) exhibit two signals at the region 2.91–3.30 ppm as triplets and indicates that there are two different types of tin atoms, which is also indicated by tin (^{119}Sn)–hydrogen coupling. The coupling constant $J_{\text{Sn–H}}$ are equal 76–80 and 82–89 Hz, which would be in agreement with the decrease of the s-character of the C(Bz)–Sn bonds on going from 5- to 6-coordination [19,20].

Although at least two different types of carboxyl groups are present, only single resonances are observed for the COO group in the ^{13}C spectra. The possible reason is that either accidental magnetic equivalence of the carbonyl carbon atoms or the separations between the two sets of resonance are too small to be resolved. The ^{13}C NMR data for the complexes **1**, **3**, **5** and **7** are consistent with a dimeric tetraorganostannoxane structure. The $^1J_{\text{SnC}}$ values for **1**, **3**, **5** and **7** are 590–626 and 831–870 Hz, are similar to that of the dimeric organotin complex $\{[{}^n\text{Bu}_2\text{Sn}(2\text{-Py})_2\text{O}]_2\}$ [21,22].

The ^{119}Sn NMR of complexes **1**, **3**, **5** and **7** showed two well separated resonances, characteristic of the tetraorganodistannoxane structure [23]. The low- and high-field resonances observed for these complexes are attributed to the *exo*-cyclic and *endo*-cyclic tin atoms, respectively [23]. Single resonances at the regions –225.5 to –250.6 and –344.7 to –230.5 ppm in the ^{119}Sn NMR spectra of complexes suggest that the tin atoms exhibit hexa-coordination [23]. The ^{119}Sn chemical shift values in complexes **2**, **4**, **6** and **8** are found to be in the range of –412.7 to –450.3 ppm. The appearance of chemical shift values in this region indicates seven-coordination environment [23] around the central tin atoms in these complexes.

3.2. Crystal structure of $\{[(n\text{-C}_8\text{H}_{17})_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_3\text{N}_2)]_2\text{O}\}_2$ (**1**)

In the crystal of complex **1**, the asymmetric unit contains two independent molecules that are practically superimpos-

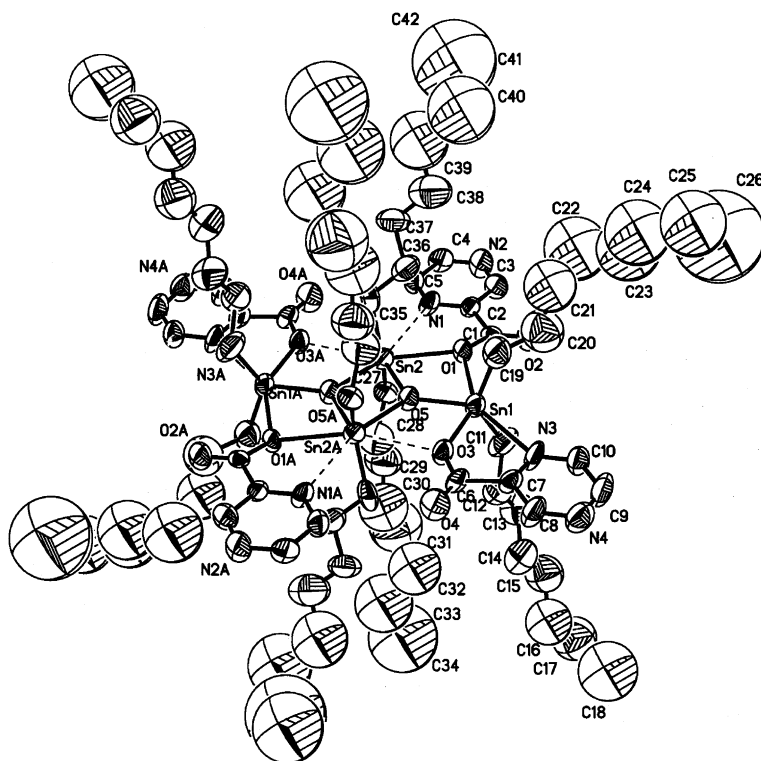
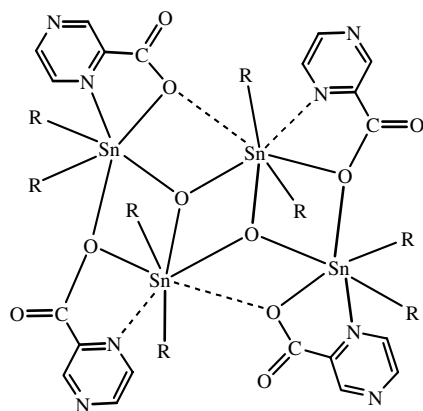


Fig. 1. Molecular structure of complex **1**.

able. In fact, a computer fitting of molecules A and B shows only a very marginal difference in the bond lengths and angles. One of the two molecules is represented in Fig. 1, the chemical structure diagram is represented in Scheme 2, selected bond lengths and angles are listed in Table 2. There are significant intra- and inter-molecular contracts in the crystal lattice. As observed for the related



Scheme 2.

structure [2,17,22], the core geometry of the molecule consists of a centrosymmetric planar four-membered Sn_2O_2 ring with two additional $(n\text{-C}_8\text{H}_{17})_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_3\text{N}_2)$ unit attached to each bridging oxygen atom, with the result that these oxygen atoms are three coordinate. The two crystallographically unique 2-pyrazinecarboxylic ligands coordinate in different ways. The ligand contains the O(1) and O(2) atoms bridging two tin atoms via the O(1) atom, $\text{Sn}(1)\text{--O}(1)$ 2.412(7) Å and $\text{Sn}(2)\text{--O}(1)$ 2.450(6). Although the O(2) oxygen is 3.615 Å from the Sn(1) atom, a distance is slightly less than the sum of the van der Waal's radii for Sn and O of 3.74 Å [20], it is not indicative of a significant bonding interaction. The C–O bond distance which associates with the oxygen atom bridging the two tin atoms of 1.294(11) Å is significantly longer than the other C–O bond distance of 1.211(14) Å that suggests a partial localization of π -electron density in the C(1)–O(1) bond. The nitrogen atom from the 2-pyrazine ring of this ligand a even close contact with Sn(2) at 2.920(9) Å, and another nitrogen atom from the 2-pyrazine ring of another ligand makes a even closer contact to Sn(1) at 2.730(10) Å, which are significantly less than the sum of the van der Waal's radii for Sn and N of 3.74 Å [17] and should be considered as a bonding interaction. The O(3) of the second ligand in

Table 2
Selected bond lengths (Å) and angles (°) for complex 1 and 2

Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
<i>Complex 1</i>					
Sn(1)–O(5)	2.040(6)	C(19)–Sn(1)–C(11)	134.8(6)	O(5)–Sn(2)–O(1)	69.1(2)
Sn(1)–C(19)	2.049(13)	O(5)–Sn(1)–O(3)	75.6(3)	C(35)–Sn(2)–O(1)	95.0(4)
Sn(1)–C(11)	2.104(13)	C(19)–Sn(1)–O(3)	102.7(4)	C(27)–Sn(2)–O(1)	92.8(4)
Sn(1)–O(3)	2.190(7)	C(11)–Sn(1)–O(3)	109.4(5)	O(5A)–Sn(2)–O(1)	141.0(2)
Sn(1)–O(1)	2.412(7)	O(5)–Sn(1)–O(1)	69.8(2)	O(5)–Sn(2)–N(1)	127.7(3)
Sn(1)–N(3)	2.730(10)	C(19)–Sn(1)–O(1)	86.7(4)	C(35)–Sn(2)–N(1)	76.5(4)
Sn(2)–O(5)	2.032(6)	C(11)–Sn(1)–O(1)	84.7(5)	C(27)–Sn(2)–N(1)	74.8(4)
Sn(2)–C(35)	2.052(13)	O(3)–Sn(1)–O(1)	145.3(2)	O(5A)–Sn(2)–N(1)	160.3(3)
Sn(2)–C(27)	2.076(14)	O(5)–Sn(1)–N(3)	140.0(3)	O(1)–Sn(2)–N(1)	58.7(3)
Sn(2)–O(5A)	2.108(6)	C(19)–Sn(1)–N(3)	83.0(5)	O(5)–Sn(2)–O(3A)	85.65(19)
Sn(2)–O(1)	2.450(6)	C(11)–Sn(1)–N(3)	83.0(5)	C(35)–Sn(2)–O(3A)	58.9(3)
Sn(2)–N(1)	2.920(9)	O(3)–Sn(1)–N(3)	64.4(3)	C(27)–Sn(2)–O(3A)	119.3(3)
Sn(2)–O(3A)	2.798(8)	O(1)–Sn(1)–N(3)	150.2(3)	O(5A)–Sn(2)–O(3A)	139.56(19)
		O(5)–Sn(2)–C(35)	111.7(4)	O(1)–Sn(2)–O(3A)	36.11(17)
		O(5)–Sn(2)–C(27)	107.3(4)	N(1)–Sn(2)–O(3A)	53.4(2)
		C(35)–Sn(2)–C(27)	140.5(5)	Sn(1)–O(1)–Sn(2)	96.0(2)
		O(5)–Sn(2)–O(5A)	71.9(3)	Sn(2)–O(5)–Sn(1)	125.0(3)
		C(35)–Sn(2)–O(5A)	98.3(3)	Sn(2)–O(5)–Sn(2A)	108.1(3)
		C(27)–Sn(2)–O(5A)	99.6(4)	Sn(1)–O(5)–Sn(2A)	126.9(3)
<i>Complex 2</i>					
Sn(1)–C(11)	2.044(11)	C(11)–Sn(1)–C(19)	169.6(6)	C(19)–Sn(1)–N(1)	93.2(4)
Sn(1)–C(19)	2.121(9)	C(11)–Sn(1)–O(1)	92.0(5)	O(1)–Sn(1)–N(1)	70.1(2)
Sn(1)–O(1)	2.195(6)	C(19)–Sn(1)–O(1)	95.9(3)	O(3)–Sn(1)–N(1)	151.7(2)
Sn(1)–O(3)	2.317(6)	C(11)–Sn(1)–O(3)	88.5(4)	O(4A)–Sn(1)–N(1)	73.1(2)
Sn(1)–O(4A)	2.352(6)	C(19)–Sn(1)–O(3)	86.0(3)	C(11)–Sn(1)–N(3A)	82.3(5)
Sn(1)–N(1)	2.429(7)	O(1)–Sn(1)–O(3)	81.8(2)	C(19)–Sn(1)–N(3A)	87.6(3)
Sn(1)–N(3A)	2.684(8)	C(11)–Sn(1)–O(4A)	92.6(4)	O(1)–Sn(1)–N(3A)	152.2(2)
		C(19)–Sn(1)–O(4A)	85.1(3)	O(3)–Sn(1)–N(3A)	70.9(2)
		O(1)–Sn(1)–O(4A)	143.2(2)	O(4A)–Sn(1)–N(3A)	64.5(2)
		O(3)–Sn(1)–O(4A)	134.8(2)	N(1)–Sn(1)–N(3A)	137.4(2)
		C(11)–Sn(1)–N(1)	95.9(5)		

$\{[(C_8H_{17})_2Sn(O_2CN_2H_3C_4)]_2O\}_2$ forms a strong bond to Sn(1), 2.190(7) and 2.796(4) Å from Sn(2A). Atom O(4) does not make any significant contacts with the tin atoms. As for the second ligand, the C(6)–O(4) bond at 1.120(12) Å is shorter than the C(6)–O(3) bond at 1.265(11) Å. A weak Sn···N interactions exist between the Sn atom and the adjacent nitrogen atom, thereby forming a chelate with a five-membered ring.

The endocyclic tin atom, Sn(2), is seven-coordinate to a first approximation and exists in a distorted pentagonal bipyramidal environment, with the two "Octyl groups and the centrosymmetrically related bridging oxygen atom defining an approximate pentagonal plane. The apical position is occupied by C(27) and C(35) atom from the ligand. The C(27)–Sn–C(35), is 140.5(5)°. The exocyclic tin atom, Sn(1), forms four short bonds; a longer bond to O(5) is a weak interaction. The geometry is highly distorted, the

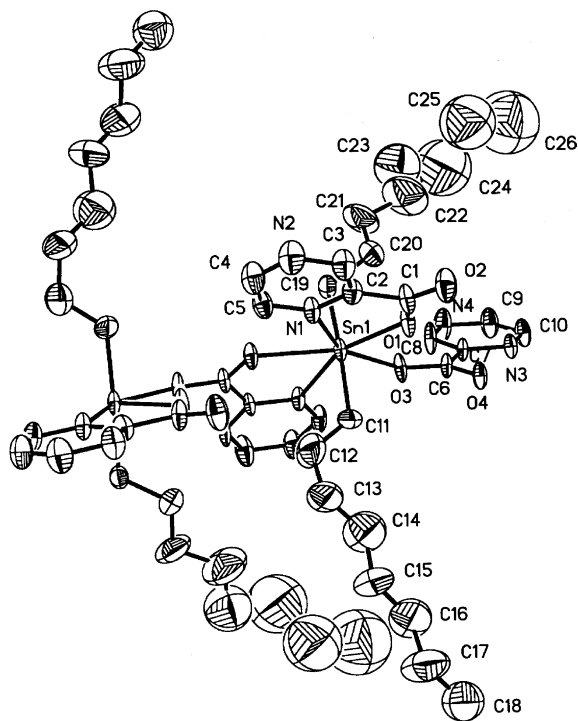
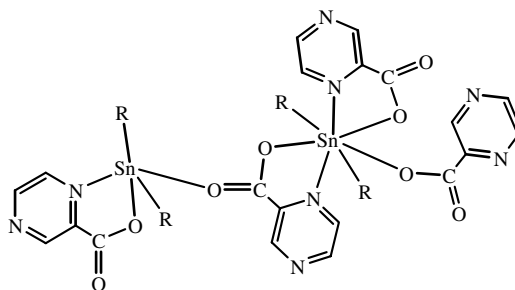


Fig. 2. Molecular structure of complex 2.

coordination sphere can be thought of as a distorted octahedron.

3.3. Crystal structure of $(n-C_8H_{17})_2Sn(O_2CC_4H_3N_2)_2$ (2)

The crystal structure of complex 2 is shown in Fig. 2 and the one-dimensional chain structure is illustrated in Fig. 3. A structural line diagram is shown in Scheme 3. Selected bond distances and bond angles are listed in Table 2. Complex 2 contains a seven-coordinated tin atom and has a pentagonal bipyramidal environment with the C(11) and C(19) atoms occupying the axial sites and the axial–Sn–axial angle, C(11)–Sn(1)–C(19) of 169.6(2)°. The tin atom lies on a crystallographic twofold structure. Atoms Sn(1), O(1), O(3), N(3A), O(4A), N(1) are completely coplanar with the tin atom lying in the plane. The sum of angles between the tin atom and the equatorial atoms is 360.4°, consistent with the ideal value of 360°. In the structure, two carbon atoms and two nitrogen atoms of 2-pyrazine-carboxylic acid and an oxygen atom of the other 2-pyrazine-carboxylic acid are covalently linked to the tin. The Sn–N bond length (Sn(1)–N(1) 2.429(7) Å and Sn(1)–N(4)#1, 2.553(4) Å) is longer than those in $nBu_2Sn(OOCC_5H_4N-2)_2(H_2O)$ (2.2522(6) Å) [24,25], but much shorter than the sum of the vander Waals radii of Sn and N, 3.74 Å [25,26]. The bond Sn(1)–O(4A) 2.352(6) Å also approaches the sum of the covalent radii of Sn and O (2.13 Å) [26]. These carboxylate groups are bidentate and use both oxygen atoms to bridge between two tin atoms, thus the complex becomes a one-dimensional chain polymer as shown in



Scheme 3.

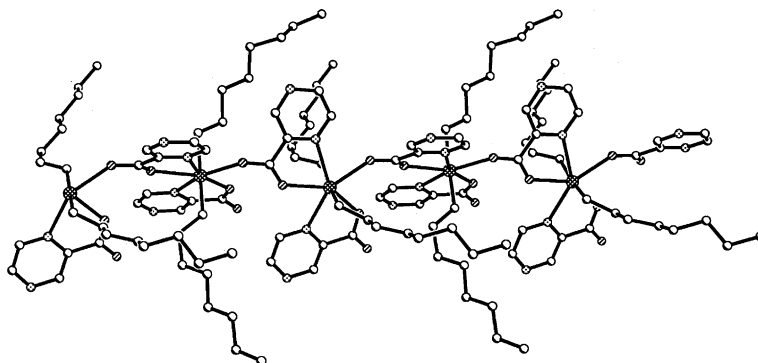


Fig. 3. One-dimensional chain work of complex 2.

Fig. 3. This is not the same as ${}^n\text{Bu}_2\text{Sn}(\text{O}_2\text{CN}_2\text{H}_3\text{C}_4)_2$ [27] which forms a three-dimensional hydrogen bonded network by hydrogen bonds.

4. Supplementary material

Crystallographic data for complexes **1** and **2** have been deposited at the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 284268 and 284269, respectively. The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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