

Self-assembly of triorganotin(IV) or diorganotin(IV) moieties and 2-methylpyrazine-5-acid: Syntheses, characterizations and crystal structures of monomeric, polymeric or tetranuclear macrocyclic compounds

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Abstract

A series of diorganotin(IV) and triorganotin(IV) compounds of the type $[R_2Sn(pca)_2ClSnR_3]_2$ ($R=PhCH_2$ **1**, 2- $C_6H_4CH_2$ **2**, 2- $FC_6H_4CH_2$ **3**, 4- $FC_6H_4CH_2$ **4**, 4- $CNC_6H_4CH_2$ **5**, 4- $C/C_6H_4CH_2$ **6**, 2,4- $Cl_2C_6H_3CH_2$ **7**; Hpca=2-methylpyrazine-5-acid), $[(^tBu)_3Sn(pca)]_\infty$ **8**, $[(CH_3)_2Cl_2Sn(pca)Sn(CH_3)_2(pca)]_\infty$ **9**, $\{[(^tBu)_2Sn(pca)]_2O\}_2$ **10** and $\{[Ph_2Sn(pca)]_3O_2[Ph_2Sn(OCH_3)]\}$ **11** have been obtained by reactions of 2-methylpyrazine-5-acid with triorganotin(IV) chloride, diorganotin(IV) dichloride, and diorganotin(IV) oxide. All compounds were characterized by elemental, IR, and NMR spectra analyses. The crystal structure of compounds **1**, **8–11** were determined by X-ray single crystal diffraction, which revealed that compound **1** was tetranuclear macrocyclic structures with seven-coordinate and five-coordinate tin atoms, compounds **8** and **9** were polymeric chain structures with five-coordinate and seven-coordinate tin atoms, compounds **10** and **11** were monomeric structures with six-coordinate and five-coordinate tin atoms.

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Keywords: Organotin(IV) compounds; 2-Methylpyrazine-5-acid; Synthesis; Crystal structure

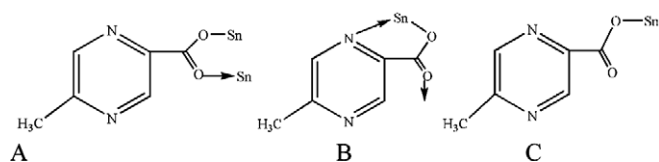
1. Introduction

Metal-directed self-assembly of organic ligands and metal ions or organometallic substances with various intriguing topologies have been extensively studied [1,2]. An important objective is also the synthesis of new higher soluble metal compounds useful for testing the distinctive reactivity patterns of the multimetallic systems. In recent years organotin(IV) derivatives have received much attention, both in academic and applied research, because of the ability of the tin to afford stable bonds with carbons as well as with heteroatoms: a wide range of compounds have been reported in organic synthesis and catalysis [3]. Especially, organotin compounds react with the ligands

with nitrogen atoms, yielding products characterized by Sn–N bonds [4]. This fact has led to considerable effort being devoted to characterizing model compounds obtained from the ligands which have other donor atoms or groups. In previous work, we have reported on the chemical, structural, spectroscopic properties of a series of similar organotin(IV) compounds, characterized by different coordinating properties [5]. As an extension of this research program and in connection with our current interest in the coordination chemistry of organotin compounds with heterocyclic ligands, we choose another fascinating ligand: 2-methylpyrazine-5-acid (Hpca). This ligand is interesting because of its potential multiple coordinate possibilities. As exhibited in Scheme 1, at least three bonding modes between this ligand and tin are conceivable. The above considerations stirred our interest in some detailed syntheses, and structure patterns for diorganotin derivatives of the ligand. Interestingly, we obtained a series of

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Scheme 1.

diorganotin(IV) and triorganotin(IV) compounds by reaction of diorganotin(IV) dichloride or triorganotin(IV) chloride with 2-methylpyrazine-5-acid in the presence of sodium ethoxide. When using a 1:1:1 molar ratio of $R_ySnCl:H_pca:EtONa$ ($R=PhCH_2$ **1**; 2- $C_6H_4CH_2$ **2**, 2- $FC_6H_4CH_2$ **3**, 4- $FC_6H_4CH_2$ **4**, 4- $CNC_6H_4CH_2$ **5**, 4- $C_6H_4CH_2$ **6**, 2,4- $Cl_2C_6H_3CH_2$ **7**, $y=3$), we obtained seven tetranuclear macrocyclic compounds **1–7** of the type $[R_2Sn(pca)_2ClSnR_3]_2$. Although also with a 1:1:1 ratio, another two polymeric compounds **8** and **9** are obtained and the general formula are $[(^nBu)_3Sn(pca)]_\infty$ **8** ($R=Bu$, $y=3$) and $[(CH_3)_2Cl_2Sn(pca)Sn(CH_3)_2(pca)]_\infty$ **9** ($R=CH_3$, $y=2$). When using a 1:1 molar ratio of $R_2SnO:H_pca$ ($R=Bu$ **10**, Ph **11**), we obtained two monomeric compounds $\{[(^nBu)_2Sn(pca)_2O]_2\}$ **10** and $\{[Ph_2Sn(pca)_3O_2[Ph_2Sn(OCH_3)]]\}$ **11**. Determinations by elemental, IR, and NMR spectra analyses of all the compounds are given and except for compounds **2–7**, the others are also characterized by X-ray crystallography diffraction analyses.

2. Experimental

2.1. Materials and measurements

All the reactions were carried out under nitrogen atmosphere. nBu_3SnCl , $(CH_3)_2SnCl_2$, nBu_2SnO , Ph_2SnO , and 2-methylpyrazine-5-acid were used as received. The series of triorganotin(IV) chloride (for **1–7**) were prepared by the reported method [6]. The melting points were obtained with Kofler micro-melting points apparatus and were uncorrected. Infrared spectra were recorded on a Nicole-

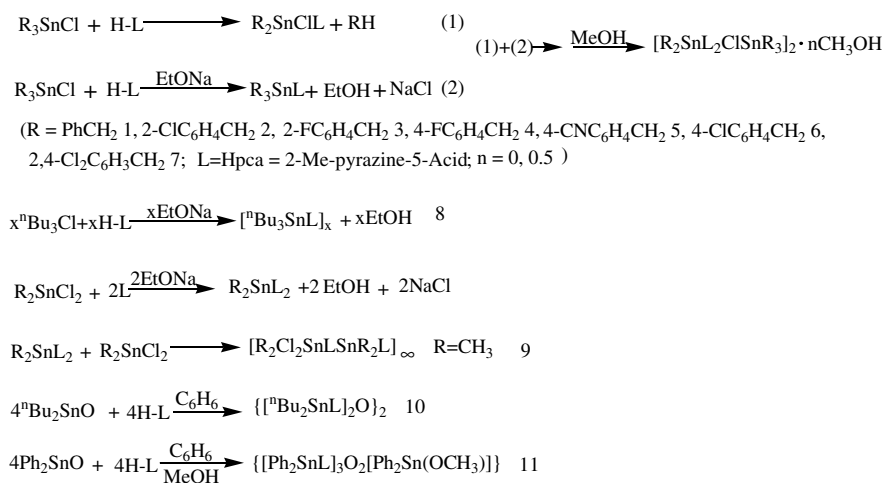
460 spectrophotometer using KBr discs. 1H , ^{13}C , and ^{119}Sn NMR spectra were recorded on a Mercury Plus-400 NMR spectrometer. Chemical shifts are given in ppm relative to Me_4Si and Me_4Sn in $CDCl_3$ solvent. Elemental analyses were performed on PE-2400-II elemental analyzer.

2.2. Synthesis of the complex

The reactions **1–9** are carried out under a nitrogen atmosphere. 2-Methylpyrazine-5-acid (2.0 mmol) was added to the solution of benzene (20 ml) of triorganotin(IV) chloride (or diorganotin(IV) dichloride) (2.0 mmol) in a Schlenk flask and stirred for 0.5 h. After the sodium ethoxide (2.0 mmol) was added to the reactor, the reaction mixture was stirred for 24 h at 50 °C and then filtered. The solvent is gradually removed by evaporation under vacuum until a solid product is obtained. The solid is then recrystallized from methanol to give colorless crystals. The synthesis procedures are shown in Scheme 2, similar to our previous studies [7,8]. The reaction **10** and **11** is of 2-Me-pyrazine-5-Acid (2.0 mmol) with nBu_2SnO (or Ph_2SnO) (2.0 mmol) in refluxing benzene and methyl (60 ml), which afford air-stable solid complexes. The solid is then recrystallized from methanol to give colorless crystals. The synthesis procedures are shown in Scheme 2.

2.2.1. $[(PhCH_2)_2Sn(pca)_2ClSn(PhCH_2)_3]_2 \cdot 0.5CH_3OH$ **1**

The reaction is carried out under a nitrogen atmosphere. 2-Methylpyrazine-5-acid (0.276 g, 2.0 mmol) was added to the solution of dry benzene (20 ml) of $(PhCH_2)_3SnCl$ (0.855 g, 2.0 mmol) in a Schlenk flask and stirred for 0.5 h. After the sodium ethoxide (0.136 g, 2.0 mmol) was added to the reactor, the reaction mixture was stirred for 12 h at 50 °C and then filtered. The solvent is gradually removed by evaporation under vacuum until a solid product is obtained. The solid is then recrystallized from methanol and the colorless crystal compound **1** is formed. Yield: 68%. Mp 116–117 °C. Anal. Calc. for $C_{94.50}H_{88}Cl_2N_8O_{8.50}$



Scheme 2.

Sn₄: C, 56.25; H, 4.40; N, 5.55. Found: C, 56.52; H, 4.43; N, 5.42%. IR (KBr, cm⁻¹): ν_{as}(COO), 1654; ν_s(COO), 1456; ν(C=N), 1593; ν(Sn–C), 552; ν(Sn–O), 478; ν(Sn–N), 468; ν(Sn–Cl), 268. ¹H NMR (CDCl₃, ppm): δ 3.16 (t, 8H, J_{Sn–H} = 95 Hz, –CH₂–), 3.09 (t, 12H, J_{Sn–H} = 72 Hz, –CH₂–), 6.85–7.10 (m, 50H, Ph–H), 8.76 (br, 4H, *pca*–H), 9.25 (br, 4H, *pca*–H), 2.55 (s, 12H, *pca*–CH₃). ¹³C NMR (CDCl₃, ppm): δ 32.26 (CH₂Ar, ¹J(¹¹⁹Sn–¹³C) = 596 Hz), δ 33.7 (CH₂Ar, ¹J(¹¹⁹Sn–¹³C) = 895 Hz), 28.7, 122.5, 122.3, 127.1, 127.3, 151.7, 152.2, 154.6, 154.8 (Ar–C), 141.2, 142.5, 143.6, 147.4 (C₄H₃N₂–), 171.6 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm): δ –576.6, –56.6.

2.2.2. [(2-ClC₆H₄CH₂)₂Sn(*pca*)₂ClSn(2-ClC₆H₄CH₂)₃]₂ **2**

Compound **2** is prepared in the same way as that of compound **1**. The solid is then recrystallized from methanol. Yield: 62%. Mp 125–127 °C. Anal. Calc. for C₉₄H₇₈Cl₁₂N₈O₈Sn₄: C, 48.08; H, 3.35; N, 4.77. Found: C, 48.34; H, 3.41; N, 4.76%. IR (KBr, cm⁻¹): ν_{as}(COO), 1662; ν_s(COO), 1475; ν(C=N), 1602; ν(Sn–C), 567; ν(Sn–O), 482; ν(Sn–N), 466; ν(Sn–Cl), 267. ¹H NMR (CDCl₃, ppm): δ 3.11 (t, 8H, J_{Sn–H} = 92 Hz, –CH₂–), 3.02 (t, 12H, J_{Sn–H} = 76 Hz, –CH₂–), 7.08–7.21 (m, 40H, Ph–H), 8.68 (br, 4H, *pca*–H), 9.27 (br, 4H, *pca*–H), 2.56 (s, 12H, *pca*–CH₃). ¹³C NMR (CDCl₃, ppm): δ 31.1 (CH₂Ar, ¹J(¹¹⁹Sn–¹³C) = 598 Hz), δ 33.7 (CH₂Ar, ¹J(¹¹⁹Sn–¹³C) = 892 Hz), 28.6, 157.6, 154.6, 129.1, 128.4, 125.2, 125.3, 124.7, 122.6 (Ar–C), 141.1, 142.6, 146.6, 147.8 (C₄H₃N₂–), 172.5 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm): δ –512.5, –55.8.

2.2.3. [(2-FC₆H₄CH₂)₂Sn(*pca*)₂ClSn(2-FC₆H₄CH₂)₃]₂ **3**

Compound **3** is prepared in the same way as that of compound **1**. The solid is then recrystallized from methanol. Yield: 59%. Mp 121–122 °C. Anal. Calc. for C₉₄H₇₈Cl₂F₁₀N₈O₈Sn₄: C, 51.71; H, 3.60; N, 5.13. Found: C, 51.49; H, 3.73; N, 5.07%. IR (KBr, cm⁻¹): ν_{as}(COO), 1668; ν_s(COO), 1478; ν(C=N), 1598; ν(Sn–C), 538; ν(Sn–O), 480; ν(Sn–N), 462; ν(Sn–Cl), 268. ¹H NMR (CDCl₃, ppm): δ 3.19 (t, 8H, J_{Sn–H} = 96 Hz, –CH₂–), 3.08 (t, 12H, J_{Sn–H} = 73 Hz, –CH₂–), 7.09–7.18 (m, 40H, Ph–H), 8.76 (br, 4H, *pca*–H), 9.22 (br, 4H, *pca*–H), 2.55 (s, 12H, *pca*–CH₃). ¹³C NMR (CDCl₃, ppm): δ 31.0 (CH₂Ar, ¹J(¹¹⁹Sn–¹³C) = 598 Hz), δ 33.7 (CH₂Ar, ¹J(¹¹⁹Sn–¹³C) = 894 Hz), 28.5, 161.7, 158.5, 156.4, 129.6, 127.5, 128.5, 116.2, 115.5 (Ar–C), 142.2, 143.1, 144.5, 147.4 (C₄H₃N₂–), 173.1 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm): δ –593.6, –52.2.

2.2.4. [(4-FC₆H₄CH₂)₂Sn(*pca*)₂ClSn(4-FC₆H₄CH₂)₃]₂ **4**

Compound **4** is prepared in the same way as that of compound **1**. The solid is then recrystallized from methanol. Yield: 69%. Mp 134–137 °C. Anal. Calc. for C₉₄H₇₈Cl₂F₁₀N₈O₈Sn₄: C, 51.71; H, 3.60; N, 5.13. Found: C, 51.56; H, 3.65; N, 5.09%. IR (KBr, cm⁻¹): ν_{as}(COO),

1667; ν_s(COO), 1479; ν(C=N), 1591; ν(Sn–C), 576; ν(Sn–O), 481; ν(Sn–N), 463; ν(Sn–Cl), 270. ¹H NMR (CDCl₃, ppm): δ 3.08 (t, 8H, J_{Sn–H} = 94 Hz, –CH₂–), 3.02 (t, 12H, J_{Sn–H} = 79 Hz, –CH₂–), 7.08–7.16 (m, 40H, Ph–H), 8.26 (br, 4H, *pca*–H), 9.13 (br, 4H, *pca*–H), 2.53 (s, 12H, *pca*–CH₃). ¹³C NMR (CDCl₃, ppm): δ 32.1 (CH₂Ar, ¹J(¹¹⁹Sn–¹³C), 610 Hz), δ 33.7 (CH₂Ar, ¹J(¹¹⁹Sn–¹³C), 893 Hz), 28.5, 159.6, 157.5, 153.3, 129.3, 127.7, 125.7, 123.7 (Ar–C), 148.2, 147.2, 143.7, 141.6 (C₄H₃N₂–), 173.5 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm): δ –596.6, –58.7.

2.2.5. [(4-CNC₆H₄CH₂)₂Sn(*pca*)₂ClSn(4-CNC₆H₄CH₂)₃]₂ **5**

Compound **5** is prepared in the same way as that of compound **1**. The solid is then recrystallized from methanol. Yield: 58%. Mp 130–133 °C. Anal. Calc. for C₁₀₄H₇₈Cl₂N₁₈O₈Sn₄: C, 55.43; H, 3.49; N, 11.19. Found: C, 55.58; H, 3.35; N, 11.06%. IR (KBr, cm⁻¹): ν_{as}(COO), 1671; ν_s(COO), 1491; ν(C=N), 1606; ν(Sn–C), 578; ν(Sn–O), 487; ν(Sn–N), 465; ν(Sn–Cl), 262. ¹H NMR (CDCl₃, ppm): δ 3.15 (t, 8H, J_{Sn–H} = 97 Hz, –CH₂–), 3.04 (t, 12H, J_{Sn–H} = 72 Hz, –CH₂–), 7.11–7.24 (m, 40H, Ph–H), 8.70 (br, 4H, *pca*–H), 9.19 (br, 4H, *pca*–H), 2.53 (s, 12H, *pca*–CH₃). ¹³C NMR (CDCl₃, ppm): δ 32.0 (CH₂Ar, ¹J(¹¹⁹Sn–¹³C) = 603 Hz), δ 33.7 (CH₂Ar, ¹J(¹¹⁹Sn–¹³C) = 891 Hz), 28.6, 158.6, 157.4, 152.5, 127.1, 127.5, 122.1 (Ar–C), 143.5, 141.0, 143.2, 147.6 (C₄H₃N₂–), 170.1 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm): δ –522.8, –51.3.

2.2.6. [(4-ClC₆H₄CH₂)₂Sn(*pca*)₂ClSn(4-ClC₆H₄CH₂)₃]₂ **6**

Compound **6** is prepared in the same way as that of compound **1**. The solid is then recrystallized from methanol. Yield: 52%. Mp 126–128 °C. Anal. Calc. for C₉₄H₇₈Cl₁₂N₈O₈Sn₄: C, 48.08; H, 3.35; N, 4.77. Found: C, 47.88; H, 3.41; N, 4.72%. IR (KBr, cm⁻¹): ν_{as}(COO), 1659; ν_s(COO), 1481; ν(C=N), 1595; ν(Sn–C), 558; ν(Sn–O), 481; ν(Sn–N), 467; ν(Sn–Cl), 268. ¹H NMR (CDCl₃, ppm): δ 3.14 (t, 8H, J_{Sn–H} = 93 Hz, –CH₂–), 3.05 (t, 12H, J_{Sn–H} = 74 Hz, –CH₂–), 7.09–7.22 (m, 40H, Ph–H), 8.68 (br, 4H, *pca*–H), 9.23 (br, 4H, *pca*–H), 2.55 (s, 12H, *pca*–CH₃). ¹³C NMR (CDCl₃, ppm): δ 32.3 (CH₂Ar, ¹J(¹¹⁹Sn–¹³C) = 615 Hz), δ 33.7 (CH₂Ar, ¹J(¹¹⁹Sn–¹³C) = 892 Hz), 28.7, 163.5, 161.4, 158.6, 122.6, 125.3 (Ar–C), 141.1, 142.2, 142.6, 146.6 (C₄H₃N₂–), 173.8 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm): δ –536.5, –63.6.

2.2.7. [(2,4-Cl₂C₆H₃CH₂)₂Sn(*pca*)₂ClSn(2,4-Cl₂C₆H₃CH₂)₃]₂ **7**

Compound **7** is prepared in the same way as that of compound **1**. The solid is then recrystallized from methanol. Yield: 79%. Mp 112–113 °C. Anal. Calc. for C₉₄H₆₈Cl₂₂N₈O₈Sn₄: C, 41.93; H, 2.55; N, 4.16. Found: C, 42.11; H, 2.58; N, 4.03%. IR (KBr, cm⁻¹): ν_{as}(COO), 1668; ν_s(COO), 1471; ν(C=N), 1592; ν(Sn–C), 568; ν(Sn–O), 483; ν(Sn–N), 462; ν(Sn–Cl), 265. ¹H NMR (CDCl₃, ppm): δ 3.21 (t, 8H, J_{Sn–H} = 97 Hz, –CH₂–), 3.01 (t, 12H,

$J_{\text{Sn-H}} = 78$ Hz, $-\text{CH}_2-$), 7.17–7.36 (m, 30H, Ph-H), 8.86 (br, 4H, *pca*-H), 9.26 (br, 4H, *pca*-H), 2.56 (s, 12H, *pca*-CH₃). ¹³C NMR (CDCl₃, ppm): δ 33.8 (CH₂Ar, $^1J(^{119}\text{Sn}-^{13}\text{C}) = 618$ Hz), δ 33.7 (CH₂Ar, $^1J(^{119}\text{Sn}-^{13}\text{C}) = 876$ Hz), 28.5, 169.1, 168.3, 161.8, 158.9, 157.3, 152.1, 152.1, 151.1, 122.5, 122.3 (Ar-C), 142.1, 142.4, 142.6, 146.6 (C₄H₃N₂-), 172.5 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm): δ -572.8, -56.8.

2.2.8. $[(^n\text{Bu})_3\text{Sn}(\text{pca})]_\infty \mathbf{8}$

Compound **8** is prepared in the same way as that of compound **1**. The solid is then recrystallized from methanol and the colorless crystal compound **8** is formed. Yield: 87%. Mp 90–92 °C, Anal. Calc. for C₃₆H₆₄N₄O₄Sn₂: C, 50.61; H, 7.55. Found: C, 50.60; H, 7.55%. IR (KBr, cm⁻¹): $\nu_{\text{as}}(\text{COO})$, 1584; $\nu_{\text{s}}(\text{COO})$, 1423, $\nu(\text{C}=\text{N})$, 1596, $\nu(\text{Sn}-\text{C})$, 534; $\nu(\text{Sn}-\text{O})$, 465. ¹H NMR (CDCl₃, ppm): δ 8.25–9.28 (m, 4H, *pca*), 2.34 (s, 6H, *pca*-CH₃), 1.33–1.56 (m, 36H, $-(\text{CH}_2)_3-$), 0.99 (t, 18H, $-\text{CH}_3$). ¹³C NMR (CDCl₃, ppm): δ 26.7 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 596 Hz), ¹¹⁹Sn NMR (CDCl₃, ppm): δ -46.5.

2.2.9. $[(\text{CH}_3)_2\text{Cl}_2\text{Sn}(\text{pca})\text{Sn}(\text{CH}_3)_2(\text{pca})]_\infty \mathbf{9}$

Compound **9** is prepared in the same way as that of compound **1**. The solid is then recrystallized from methanol and the colorless crystal compound **8** is formed. Yield: 80%. Mp 136–138 °C. Anal. Calc. for C₃₂H₄₄Cl₄N₈O₈Sn₄: C, 29.90; H, 3.45; N, 8.72. Found: C, 29.88; H, 3.48; N, 8.76%. IR (KBr, cm⁻¹): $\nu_{\text{as}}(\text{COO})$, 1620; $\nu_{\text{s}}(\text{COO})$, 1426; $\nu(\text{C}=\text{N})$, 1586, $\nu(\text{Sn}-\text{C})$, 561, $\nu(\text{Sn}-\text{O})$, 479, $\nu(\text{Sn}-\text{N})$, 458, $\nu(\text{Sn}-\text{Cl})$, 271; ¹H NMR (CDCl₃, ppm): δ 0.85 (t, 12H, $J_{\text{Sn-H}} = 96$ Hz, $-\text{CH}_3$), 0.82 (t, 12H, $J_{\text{Sn-H}} = 85$ Hz, $-\text{CH}_3$), 8.70 (br, 4H, *pca*-H), 9.28 (br, 4H, *pca*-H), 2.61 (s, 12H, *pca*-CH₃). ¹³C NMR (CDCl₃, ppm): δ 10.0 (CH₃, $^1J(^{119}\text{Sn}-^{13}\text{C})$, 728 Hz), δ 12.1 (CH₃, $^1J(^{119}\text{Sn}-^{13}\text{C})$, 909 Hz), 143.6, 145.6, 145.6, 147.4 (C₄H₃N₂-), 171.6 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm): δ -375.6, -35.5.

2.2.10. $\{[(^n\text{Bu})_2\text{Sn}(\text{pca})]_2\text{O}\}_2 \mathbf{10}$

The reaction is carried out under nitrogen atmosphere. 2-Methylpyrazine-5-acid (0.276, 2.0 mmol) are added to the solution of dry benzene and methanol (5:1) of di-*n*-butyltin oxide (0.498 g, 2.0 mmol) in a Schlenk flask. The mixture gives a clear solution within 10–15 min. Refluxing was continued for 10 h, the solvent is gradually removed by evaporation under vacuum until solid product is obtained. The solid is then recrystallized from methanol and the colorless crystal is obtained. Yield: 86%. Mp 145–147 °C. Anal. Calc. for C₅₆H₉₀N₈O₁₀Sn₄: C, 44.54; H, 6.01; N, 7.42. Found: C, 44.27; H, 6.11; N, 7.38%. IR (KBr, cm⁻¹): $\nu_{\text{as}}(\text{COO})$, 1665, 1617; $\nu_{\text{s}}(\text{COO})$, 1388, 1464; $\nu(\text{C}=\text{N})$, 1598, $\nu(\text{Sn}-\text{C})$, 571; $\nu(\text{Sn}-\text{O}-\text{Sn})$, 627; $\nu(\text{Sn}-\text{O})$, 489; ¹H NMR (CDCl₃, ppm): δ 9.56 (br, 4H, *pca*-H), 9.19 (br, 4H, *pca*-H), 2.83 (s, 12H, ArCH₃), δ 0.87 (t, 24H, CH₃), 1.10–1.58 (m, 48H, CH₂CH₂CH₂), ¹³C NMR (CDCl₃, ppm): δ 26.7 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 655 Hz), 27.3 (αCH_2 , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 772 Hz), 26.5

(βCH_2), 26.7 (βCH_2), 25.3 (γCH_2), 25.1 (γCH_2), 13.5 (CH₃), 13.6 (CH₃), 141.1, 142.2, 142.6, 146.6 (C₄H₂N₂-), 30.4 (CH₃Ar), 167.2 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm): δ -286.6, -202.6.

2.2.11. $\{[\text{Ph}_2\text{Sn}(\text{pca})]_3\text{O}_2[\text{Ph}_2\text{Sn}(\text{OCH}_3)]\} \mathbf{11}$

The complex **11** is prepared in the same way as that of complex **10**. The solid is then recrystallized from methanol and the colorless crystal is obtained. Yield: 82%. Mp 91–92 °C. Anal. Calc. for C₆₇H₅₈N₆O₉Sn₄: C, 51.39; H, 3.73; N, 5.37. Found: C, 51.30; H, 3.82; N, 5.51%. IR (KBr, cm⁻¹): $\nu_{\text{as}}(\text{COO})$, 1669, 1604; $\nu_{\text{s}}(\text{COO})$, 1384; 1471; 1565, 1480, 1438 (m, Ph); $\nu(\text{C}=\text{N})$, 1602, $\nu(\text{Sn}-\text{O}-\text{Sn})$, 681; $\nu(\text{Sn}-\text{C})$, 579; $\nu(\text{Sn}-\text{O})$, 447. ¹H NMR (CDCl₃, ppm): δ 9.61 (br, 3H, *pca*-H), 9.23 (br, 3H, *pca*-H), 7.32–8.45 (m, 40H, Ph-H); 3.92 (d, 3H, CH₃O), 2.74 (s, 9H, ArCH₃); ¹³C NMR (CDCl₃, ppm): δ 159.7, 159.2, 158.5, 152.1, 137.9, 137.3, 136.6, 136.4, 131.5, 131.2, 130.8, 130.3, 130.0, 129.8, 129.4, 129.2 (C₆H₅-), 51.3 (CH₃O), 30.4 (CH₃Ar), 173.2 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm): δ -480.5, -183.3.

2.3. X-ray crystallographic studies

X-ray crystallographic data for compounds **1** and **8–11** were collected on a Bruker smart-1000 CCD diffractometer using MoK 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 leastsquares 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 stretching frequencies of interest are those associated with the acid COO, Sn-C, Sn-O, and Sn-N groups. Above all, there are absorption peaks near 478 cm⁻¹ and 436–458 cm⁻¹, which indicate that there are Sn-O and Sn-N bonds in all compounds. All these values are consistent with that detected in a number of organotin(IV) derivatives [9,10]. Besides, in organotin carboxylate compounds, the IR spectra can provide useful information concerning the coordinate formation of the carboxyl. The magnitude of ($\Delta\nu = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$) of about in the band of 133–198 cm⁻¹ for compounds **1–11** is comparable to those for the corresponding sodium salts, which indicates the presence of bidentate carboxyl groups [11]. Moreover, the magnitude of $\Delta\nu$ also occurring at about 280 cm⁻¹ for compounds **10** and **11** indicates that the carboxylate ligands function as the type of monodentate except bidentate, which was also confirmed by X-ray structure analyses.

Table 1
Crystal, data collection and structure refinement parameters for compounds **1** and **8–11**

Compound	1	8	9	10	11
Empirical formula	C _{94.50} H ₈₈ Cl ₂ N ₈ O _{8.50} Sn ₄	C ₃₆ H ₆₄ N ₄ O ₄ Sn ₂	C ₃₂ H ₄₄ Cl ₄ N ₈ O ₈ Sn ₄	C ₅₆ H ₉₀ N ₈ O ₁₀ Sn ₄	C ₆₇ H ₅₈ N ₆ O ₉ Sn ₄
Formula weight	2017.39	854.29	1285.31	1510.12	1565.95
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Orthorhombic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pna</i> ₂₁	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimension					
<i>a</i> (Å)	12.427(2)	10.6572(14)	30.205(7)	12.176(3)	12.220(3)
<i>b</i> (Å)	14.184(2)	11.5515(15)	10.824(3)	12.630(3)	27.210(7)
<i>c</i> (Å)	15.843(3)	18.860(3)	7.2092(16)	13.292(3)	21.423(6)
α (°)	114.255(2)	82.867(2)	90	70.662(4)	90
β (°)	103.927(2)	78.588(2)	90	69.435(3)	100.186(5)
γ (°)	95.997(2)	71.823(2)	90	65.545(3)	90
<i>Z</i>	1	2	2	1	4
Absorption coefficient (mm ⁻¹)	1.138	1.194	2.373	1.507	1.464
Crystal size (mm)	0.45 × 0.32 × 0.21	0.41 × 0.30 × 0.22	0.58 × 0.43 × 0.11	0.39 × 0.18 × 0.12	0.45 × 0.38 × 0.29
θ Range for data collection (°)	2.31–25.01	1.86–25.03	2.00–25.01	1.90–25.03	1.78–25.01
Index ranges	–14 ≤ <i>h</i> ≤ 9, –16 ≤ <i>k</i> ≤ 15, –15 ≤ <i>l</i> ≤ 18	–12 ≤ <i>h</i> ≤ 11, –13 ≤ <i>k</i> ≤ 11, –22 ≤ <i>l</i> ≤ 22	–29 ≤ <i>h</i> ≤ 35, –12 ≤ <i>k</i> ≤ 10, –8 ≤ <i>l</i> ≤ 8	–14 ≤ <i>h</i> ≤ 14, –15 ≤ <i>k</i> ≤ 9, –15 ≤ <i>l</i> ≤ 15	–14 ≤ <i>h</i> ≤ 14, –32 ≤ <i>k</i> ≤ 32, –14 ≤ <i>l</i> ≤ 25
Reflections collected	12620	11137	11833	9036	35672
Unique reflections (<i>R</i> _{int})	8334(0.0179)	7395(0.0267)	4154(0.0769)	5947(0.0303)	12062(0.1100)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	8334/421/596	7395/234/416	4154/1/253	5947/62/352	12062/36/779
Goodness of fit on <i>F</i> ²	1.056	1.001	1.002	1.031	1.003
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0395, ωR_2 = 0.0924	<i>R</i> ₁ = 0.0518, ωR_2 = 0.1320	<i>R</i> ₁ = 0.0448, ωR_2 = 0.1079	<i>R</i> ₁ = 0.0555, ωR_2 = 0.1287	<i>R</i> ₁ = 0.0647, ωR_2 = 0.1450
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0695, ωR_2 = 0.1127	<i>R</i> ₁ = 0.0620, ωR_2 = 0.1407	<i>R</i> ₁ = 0.0530, ωR_2 = 0.1146	<i>R</i> ₁ = 0.1097, ωR_2 = 0.1591	<i>R</i> ₁ = 0.1760, ωR_2 = 0.2062

3.1.2. NMR spectroscopic

In ¹H NMR spectra of the free ligand, single resonances are observed at 7.02 ppm, which are absent in the spectra of the compounds, indicating the replacement of the carboxylic acid proton by a organotin moiety. The ¹H NMR of compounds **1–7** show that the chemical shifts of the protons of methylene bound to tin atom (ArCH₂Sn) exhibit two signals at the region 3.01–3.21 ppm as triplets and indicates that there are two different types of tin atoms, which is also indicated by tin (¹¹⁹Sn)–hydrogen coupling [5,12,13].

The ¹³C NMR spectra of all compounds show a significant downfield shift of all carbon resonances, compared with the free ligand. The shift is a consequence of an electron density transfer from the ligand to the acceptor.

¹¹⁹Sn NMR chemical shift values may be used to give tentative indications of the environment around tin atoms. Seven-coordinate Sn has δ (¹¹⁹Sn) values ranging from about –525 to –786 ppm, six-coordinate from –333 to –395 ppm [14,15], five-coordinate from –90 to –190 and

four-coordinate from +200 to –60 in solution [16]. The ¹¹⁹Sn NMR spectrum of compounds **1–7** exhibit two signals at about δ –51.3 to –63.6 and –512.5 to 593.6 ppm, suggesting there are either 4- and 7-coordinate. The deviation may be because the ¹¹⁹Sn NMR is influenced by several factors, including the aromatic or aliphatic of the R group bound to the tin atom (and possibly the type of donor atoms of the ligand) [17]. Therefore it can reasonably be assumed that the intermolecular Sn–N or Sn–O interaction of compounds **1–7** probably does not survive in solution.

3.2. Crystal structures

3.2.1. Crystal structure of [(PhCH₂)₂Sn(pca)₂ClSn-(PhCH₂)₃]₂ · 0.5CH₃OH **1**

The molecular structure is illustrated in Fig. 1. Selected bond lengths (Å) and angles (°) are listed in Table 2. The compound prove to be tetranuclear macrocyclic compound

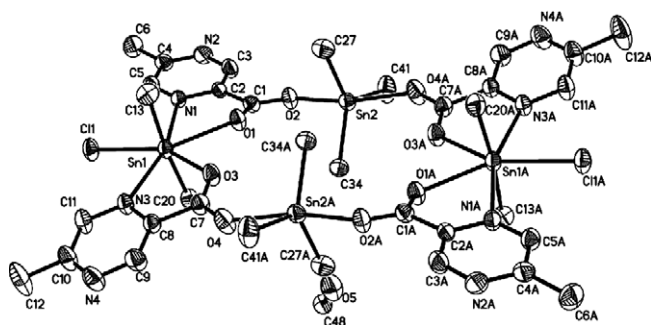


Fig. 1. Molecular structure of compound 1. For clarity, only the first carbon atoms of the benzyl chains linked to Sn are shown.

Table 2
Selected bond distances (Å) and angles (°) for compound 1

Sn(1)–O(3)	2.307(4)	Sn(1)–Cl(1)	2.5402(16)
Sn(1)–O(1)	2.381(4)	Sn(2)–O(4)#1	2.312(4)
Sn(1)–C(20)	2.144(7)	Sn(2)–C(34)	2.139(6)
Sn(1)–C(13)	2.145(7)	Sn(2)–C(27)	2.144(7)
Sn(1)–N(3)	2.504(5)	Sn(2)–C(41)	2.150(7)
Sn(1)–N(1)	2.606(5)	Sn(2)–O(2)	2.216(4)
O(1)–C(1)	1.239(7)	O(2)–C(1)	1.251(7)
O(3)–C(7)	1.238(7)	O(4)–C(7)	1.222(7)
O(1)–Sn(1)–N(1)	65.12(14)	O(3)–Sn(1)–N(1)	133.23(15)
N(3)–Sn(1)–N(1)	159.14(15)	C(13)–Sn(1)–N(1)	92.9(2)
C(20)–Sn(1)–C(13)	174.3(3)	O(3)–Sn(1)–N(3)	67.46(15)
C(20)–Sn(1)–O(3)	90.3(2)	O(1)–Sn(1)–N(3)	135.52(15)
C(13)–Sn(1)–O(3)	86.8(2)	C(20)–Sn(1)–Cl(1)	92.74(19)
C(20)–Sn(1)–O(1)	85.5(2)	C(13)–Sn(1)–Cl(1)	92.3(2)
C(13)–Sn(1)–O(1)	88.9(2)	O(3)–Sn(1)–Cl(1)	147.52(11)
O(3)–Sn(1)–O(1)	68.11(14)	O(1)–Sn(1)–Cl(1)	144.36(11)
C(20)–Sn(1)–N(3)	92.6(2)	N(3)–Sn(1)–Cl(1)	80.10(12)
C(13)–Sn(1)–N(3)	90.8(2)	C(20)–Sn(1)–N(1)	85.5(2)
O(3)–Sn(1)–N(3)	79.25(11)	C(34)–Sn(2)–C(27)	118.2(3)
Cl(1)–Sn(1)–N(1)	119.3(3)	C(27)–Sn(2)–C(41)	121.6(3)
C(34)–Sn(2)–C(41)	97.7(2)	C(27)–Sn(2)–O(2)	91.9(3)
C(41)–Sn(2)–O(2)	90.1(2)	C(34)–Sn(2)–O(4)#1	95.0(2)
C(27)–Sn(2)–O(4)#1	87.7(3)	C(41)–Sn(2)–O(4)#1	78.1(3)
O(2)–Sn(2)–O(4)#1	165.78(16)		

with 2-methylpyrazine-5-acid bridging the adjacent tin atoms with a twenty-member $\text{Sn}_4\text{O}_8\text{N}_4\text{C}_4$ ring. The unit is $[(\text{PhCH}_2)_2\text{Sn}(\text{pca})\text{ClSn}(\text{PhCH}_2)_3]$, in which the primary bonds of the two ligands to tins occur through their nitrogen atoms and four oxygen atoms of the carboxyl (mode B). The compound exist in distorted pentagonal bipyramidal about all four tin atoms with seven-coordinated tin(IV) atom. The Sn–N bond lengths [Sn(1)–N(1)], 2.606(5) and [Sn(1)–N(3)], 2.504(5) are totally in agreement with the valence extension of the tin atom and lie within the sum of their respective Van der Waal's radii of the two atoms (3.74 Å) [18]. The carboxylate ligand chelates two Sn atoms with asymmetric Sn–O bond distances and this asymmetry is reflected in the association with the shorter Sn–O bonds. The degree of asymmetry in the Sn–O bond distances is not equal, with the difference between Sn–O bond distance for the two carboxylate ligands being 0.165, 0.096 Å, respectively. Although the Sn–O ranges from 2.216(4) to 2.381(4) Å which is longer than the sum of the covalent

radii of the tin and oxygen 2.13 Å [19] both of which are similar to those reported in the literature [20]. The Sn–Cl bond length [Sn(1)–Cl(1)] 2.5402(16) Å lies in the range of the normal covalent radii (2.37–2.60 Å) [21]. The Sn–C distances fall in a narrow range from 2.139(6) to 2.150(7) Å, typical of organotin derivatives.

3.2.2. Crystal structure of $[(^n\text{Bu})_3\text{Sn}(\text{pca})]_\infty$ **8** and $[(\text{CH}_3)_2\text{Cl}_2\text{Sn}(\text{pca})\text{Sn}(\text{CH}_3)_2(\text{pca})]_\infty$ **9**

The molecular structure of compounds **8** and **9** are illustrated in Figs. 2–4, selected bond lengths (Å) and angles (°) are listed in Tables 3 and 4. As shown from Fig. 2, the crystal structure of compound **8** possesses a continuous meander-shaped polymeric chain structure and the asymmetric molecular contains two independent tin atoms that are practically superimposable. In fact correlative data of the two tin atoms show only a very marginal difference in the bond lengths and angles. Obviously, the tin atoms are considered as distorted trigonal bipyramidal with the axial site occupied by the O atoms and the basal plane defined by three C atoms from the R groups. The tin–oxygen bond lengths of 2.300(4) and 2.304(4) Å are the evidence of the

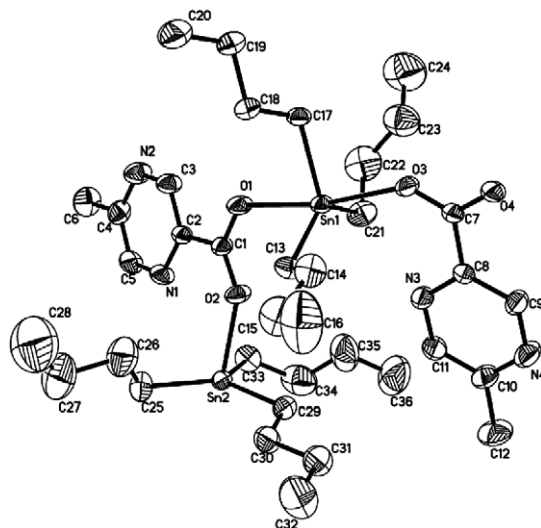


Fig. 2. Molecular structure of compound 8.

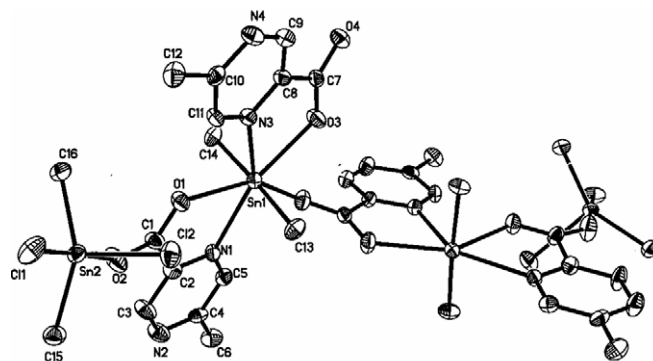


Fig. 3. Molecular structure of compound 9.

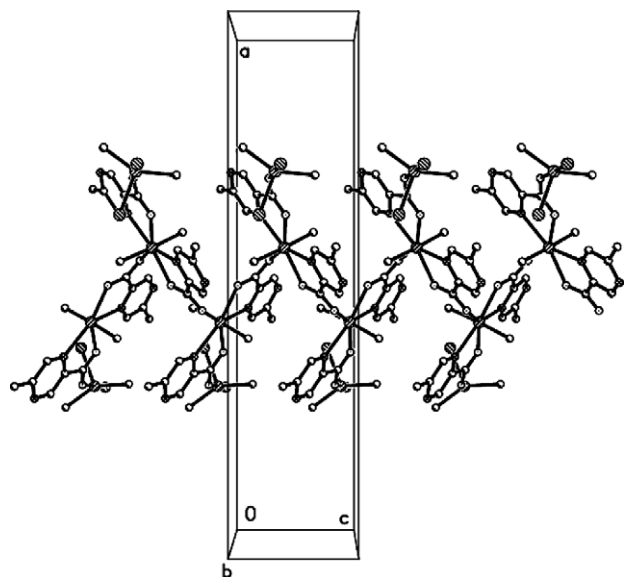


Fig. 4. The helical chain structure of compound **9**, which are linked by bridged carboxyl groups and the chain propagate through along the two-fold screw axis.

Table 3
Selected bond distances (Å) and angles (°) for compound **8**

Sn(1)–C(13)	2.121(6)	Sn(2)–C(29)	2.130(5)
Sn(1)–C(21)	2.137(7)	Sn(2)–C(33)	2.133(6)
Sn(1)–C(17)	2.144(5)	Sn(2)–O(2)	2.303(4)
Sn(1)–O(1)	2.300(4)	Sn(2)–O(4)#1	2.307(4)
Sn(1)–O(3)	2.304(4)	Sn(2)–O(4)	9.040(4)
Sn(2)–C(25)	2.106(6)		
C(13)–Sn(1)–C(21)	130.7(3)	O(4)–Sn(2)#2	2.307(4)
C(13)–Sn(1)–C(17)	114.0(2)	C(29)–Sn(2)–O(2)	85.59(19)
C(21)–Sn(1)–C(17)	115.0(2)	C(33)–Sn(2)–O(2)	93.1(2)
C(13)–Sn(1)–O(1)	91.1(2)	C(25)–Sn(2)–O(4)#1	91.7(2)
C(21)–Sn(1)–O(1)	87.3(2)	C(29)–Sn(2)–O(4)#1	85.57(19)
C(17)–Sn(1)–O(1)	85.16(18)	C(33)–Sn(2)–O(4)#1	87.2(2)
C(13)–Sn(1)–O(3)	94.9(2)	O(2)–Sn(2)–O(4)#1	170.36(14)
C(21)–Sn(1)–O(3)	94.3(2)	C(25)–Sn(2)–O(4)	116.4(2)
C(17)–Sn(1)–O(3)	85.60(18)	C(29)–Sn(2)–O(4)	45.30(16)
O(1)–Sn(1)–O(3)	170.42(14)	C(33)–Sn(2)–O(4)	102.4(2)
C(25)–Sn(2)–C(29)	115.0(3)	O(2)–Sn(2)–O(4)	41.09(10)
C(25)–Sn(2)–C(33)	129.3(3)	O(4)#1–Sn(2)–O(4)	129.50(11)
C(29)–Sn(2)–C(33)	115.4(3)	C(25)–Sn(2)–O(2)	95.5(2)

evenness about bonds. The oxygen–tin–oxygen skeleton is bent ($170.42(14)^\circ$) and the distortion from idealized geometry is also seen in the sum of the carbon–tin–carbon angles (359.7°). Although the nitrogen atom from the pyrazine ring of this ligand makes a close contact with Sn(2) at 3.258 \AA , and another nitrogen atom from the pyrazine ring of another ligand makes a even closer contact to Sn(1) at 3.219 \AA , a distance is slightly less than the sum of the van der Waal's radii for Sn and N of 3.74 \AA [18]. Although the weak Sn–N is not indicative of a significant bonding interaction, it is perhaps the reason that the polymeric chain take on meander-shaped but not linear.

The molecular structure of compound **9** is shown in Figs. 3 and 4, selected bond lengths and angles are listed in Table

Table 4
Selected bond distances (Å) and angles (°) for compound **9**

Sn(1)–C(14)	2.095(9)	Sn(1)–N(3)	2.496(7)
Sn(1)–C(13)	2.100(9)	Sn(2)–C(15)	2.087(10)
Sn(1)–O(1)	2.287(5)	Sn(2)–C(16)	2.117(10)
Sn(1)–O(4)#1	2.311(6)	Sn(2)–O(2)	2.330(6)
Sn(1)–O(3)	2.327(6)	Sn(2)–Cl(2)	2.393(3)
Sn(1)–N(1)	2.487(7)	Sn(2)–Cl(1)	2.480(2)
O(4)–Sn(1)#2	2.311(6)		
C(14)–Sn(1)–C(13)	177.2(4)	C(13)–Sn(1)–N(3)	87.2(3)
C(14)–Sn(1)–O(1)	89.5(3)	O(1)–Sn(1)–N(3)	74.1(2)
C(13)–Sn(1)–O(1)	88.0(3)	O(4)#1–Sn(1)–N(3)	141.8(2)
C(14)–Sn(1)–O(4)#1	87.9(3)	O(3)–Sn(1)–N(3)	67.2(2)
C(13)–Sn(1)–O(4)#1	93.2(3)	N(1)–Sn(1)–N(3)	142.9(2)
O(1)–Sn(1)–O(4)#1	144.1(2)	C(15)–Sn(2)–C(16)	144.5(4)
C(14)–Sn(1)–O(3)	87.1(3)	C(15)–Sn(2)–O(2)	83.1(3)
C(13)–Sn(1)–O(3)	95.7(3)	C(16)–Sn(2)–O(2)	86.0(4)
O(1)–Sn(1)–O(3)	140.9(2)	C(15)–Sn(2)–Cl(2)	106.6(3)
O(4)#1–Sn(1)–O(3)	74.8(2)	C(16)–Sn(2)–Cl(2)	106.3(3)
C(14)–Sn(1)–N(1)	87.8(3)	O(2)–Sn(2)–Cl(2)	86.60(19)
C(13)–Sn(1)–N(1)	90.0(3)	C(15)–Sn(2)–Cl(1)	95.4(3)
O(1)–Sn(1)–N(1)	68.8(2)	C(16)–Sn(2)–Cl(1)	96.1(3)
O(4)#1–Sn(1)–N(1)	75.3(2)	O(2)–Sn(2)–Cl(1)	177.9(2)
O(3)–Sn(1)–N(1)	149.8(2)	Cl(2)–Sn(2)–Cl(1)	92.40(10)
C(14)–Sn(1)–N(3)	93.5(3)	C(7)–O(4)–Sn(1)#2	132.5(6)

4. Its absolute configuration was successfully determined by refining the Flack parameter [22]. This structure is made up of infinite 1D zigzag chains. The chains propagate through along the two-fold screw axis. If viewed down the screw axis, it will show the symmetry quite well, which propagate parallel for every other asymmetric units. In every asymmetric unit, there exist two distinct tin environments and one kind of multi-coordination mode for ligands chelated to tin (mode B). The coordination environment of the Sn(1) center are distorted pentagonal bipyramid, in which the deprotonated carboxylate groups bond to the tin center in anisobidentate fashion. The compound contains a seven-coordinated tin atom and the pentagonal bipyramidal environment with C(13) and C(14) atoms occupying the axial sites and the axial–Sn–axial, C(14)–Sn(1)–C(13) is $177.2(4)^\circ$. Sn(1), N(1) and N(3), O(1), O(3), O(4)#1 are completely coplanar with the tin atom existing in the plane. The two chelating nitrogens occupy trans positions. The sum of angles between the tin atom and the equatorial atoms is 360.2° , consistent with the ideal value of 360° . In the structure, two carbon atoms and one oxygen atoms of 2-methylpyrazine-5-acid are covalently linked to the Sn(1). The Sn–O bond length ($2.327(6) \text{ \AA}$) are longer than those in $\{[{}^n\text{Bu}_2\text{Sn}(2\text{-pic})_2\text{O}]\}_2$ (2.0544 and 2.110 \AA), near to the sum of the covalent radii of Sn and O (2.13 \AA) [19]. The Sn–N bond lengths [Sn(1)–N(1) and Sn(1)–N(3), $2.487(7)$, $2.496(7) \text{ \AA}$, respectively] are longer than those in ${}^n\text{Bu}_2\text{Sn}(\text{pca})_2(\text{H}_2\text{O})$ [$2.2522(6) \text{ \AA}$] [23], but much shorter than the sum of the van der Waal's radii of Sn and N, 3.74 \AA [18]. The Sn–O bond lengths [Sn(1)–O(1) and Sn(1)–O(4)#1 $[-x, -y + 1, z - 1/2]$, $2.287(5)$, $2.311(6) \text{ \AA}$] are also below the sum of the van der Waal's radii of these atoms, 3.68 \AA [18]. The overall configuration at Sn(2) is best described as distorted trigonal bipyramid:

tin and the bonded oxygen and chlorine atoms are nearly coplanar and deviate only slightly from regular trigonal bipyramid geometry, mean deviation from plane is 0.0133 Å. The methyl groups occupy the apical position, the axial–Sn–axial, C(13)–Sn(1)–C(14) is 177.2(4)°. The Sn–O distance 2.330(6) Å, is in keeping with those reported in Sn–O compounds [19] Me₂SnCl(2-Pic) [24], Me₂Sn(2-Pic)₂ [25] and {[ⁿBu₂Sn(2-Pic)]₂O}₂ [26].

It should be noted here that the compounds are inherently chiral [27], moreover, in our case we can speak about a significant helical twist in the coordination geometry, since the angle between the two planes formed by the adjacent assymetry units is 76.1°.

3.2.3. Crystal structure of {[ⁿBu)₂Sn(pca)]₂O}₂ **10** and {[Ph₂Sn(pca)]₃O₂[Ph₂Sn(OCH₃)]} **11**

The molecular structure of compounds **10** and **11** are illustrated in Figs. 5 and 6, selected bond lengths (Å) and angles (°) are listed in Tables 5 and 6. There have being significant intramolecular contacts in the crystal lattice. As observed for the related structure [28–30], the core geometry of the molecule consists of a centrosymmetric planar four-membered Sn₂O₂ ring with two additional ⁿBu₂Sn(pca) units attach at each bridging oxygen atom, with the result that these oxygen atoms are three coordination. The two crystallographically unique 2-methylpyrazine-5-acid ligands coordinate in different ways (modes A and C). The ligand contains the O(1) and O(2) atoms bridging two tin atoms only via the O(1) atom. There are two types of tin atom. For compound **10** (Fig. 5), the Sn(1) atom is bonded to two carbon and four oxygen atoms, the longest Sn–O bond is 2.487(6) Å, Sn(1)–O(1), while the others are between 2.096(5) and 2.386(6) Å. Two of the carboxylates ligands are bidentate and bridge a pair of tin atoms and the two other carboxylates are monodentate and coordinate each exocyclic tin atom. The coordination geometry of the tin atom Sn(1) is a distorted octahedron. C(13) and C(17) atoms occupy the apical sites and C(13)–Sn(1)–C(17), is 152.3(4)°. Sn(1), O(1), O(5)#1, O(5), and O(3) are almost coplanar with

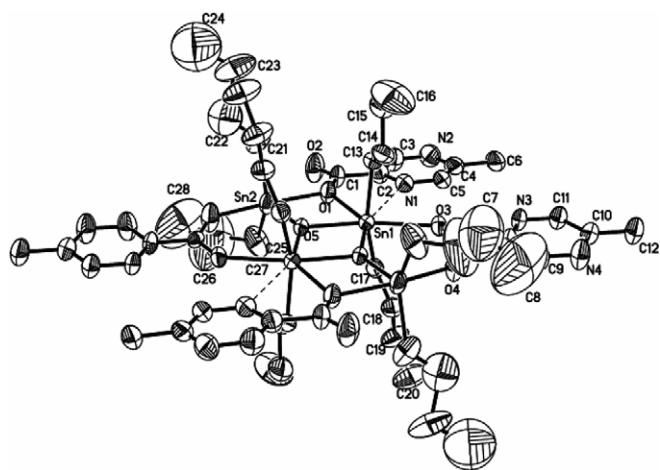


Fig. 5. Molecular structure of compound **10**.

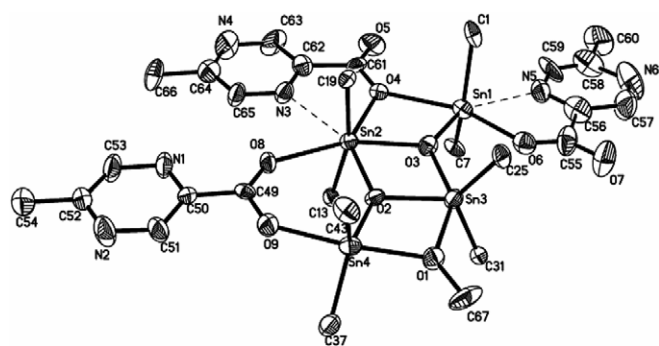


Fig. 6. Molecular structure of compound **11**. For clarity, only the first carbon atoms of the phenyls linked to Sn are shown.

the tin atom deviating from the best plane by 0.0221 Å. The sum of angles between the tin atom and the equatorial atoms is 360.07°. Compared to the ideal octahedral value of 360°, this further testifies the atoms in the same plane. The distortion from trigonal planar geometry is clearly also related to the relatively short Sn1–N1 contacts. At 2.936(8) Å, it is much shorter than the sum of the Van der Waal's radii of Sn and N, 3.74 Å [18]. The coordination sphere of Sn(2) consists of two carbon and three oxygen atoms, with Sn(1)–O bond lengths of 1.993(5)–2.198(6) Å. The angles in the central Sn₂O₂ ring are 75.1(2)° and 104.9(2)°.

For compound **11** (Fig. 6), there are three distinct coordinate ligands. Partial similar to the compound **10**, one of the carboxylates ligands is bidentate and bridge a pair of tin atoms and the two other carboxylates are monodentate. Differently, one of the two monodentate carboxylates ligands bridge a pair of tin atoms through O(4) atom resembling that of in compound **10**, the other only coordinates a exocyclic tin atom. Interestingly, on

Table 5
Selected bond distances (Å) and angles (°) for compound **10**

Sn(1)–O(5)#1	2.096(5)	O(5)–Sn(1)#1	2.096(5)
Sn(1)–C(13)	2.111(8)	Sn(2)–O(5)	1.993(5)
Sn(1)–C(17)	2.119(8)	Sn(2)–C(25)	2.096(13)
Sn(1)–O(5)	2.166(5)	Sn(2)–C(21)	2.170(12)
Sn(1)–O(3)	2.386(6)	Sn(2)–O(4)#1	2.182(7)
Sn(1)–O(1)	2.487(6)	Sn(2)–O(1)	2.198(6)
Sn(1)–N(1)	2.936(8)	O(4)–Sn(2)#1	2.182(7)
O(5)#1–Sn(1)–C(13)	102.9(3)	C(13)–Sn(1)–N(1)	76.6(3)
O(5)#1–Sn(1)–C(17)	102.5(3)	C(17)–Sn(1)–N(1)	75.7(3)
C(13)–Sn(1)–C(17)	152.3(4)	O(5)–Sn(1)–N(1)	125.2(2)
O(5)#1–Sn(1)–O(5)	75.1(2)	O(3)–Sn(1)–N(1)	72.0(2)
C(13)–Sn(1)–O(5)	97.0(3)	O(1)–Sn(1)–N(1)	58.0(2)
C(17)–Sn(1)–O(5)	99.8(3)	O(5)–Sn(2)–C(25)	113.7(4)
O(5)#1–Sn(1)–O(3)	87.7(2)	O(5)–Sn(2)–C(21)	114.2(4)
C(13)–Sn(1)–O(3)	84.8(3)	C(25)–Sn(2)–C(21)	130.9(5)
C(17)–Sn(1)–O(3)	85.6(3)	O(5)–Sn(2)–O(4)#1	93.3(2)
O(5)–Sn(1)–O(3)	162.7(2)	C(25)–Sn(2)–O(4)#1	93.7(4)
O(5)#1–Sn(1)–O(1)	142.4(2)	C(21)–Sn(2)–O(4)#1	93.6(4)
C(13)–Sn(1)–O(1)	83.7(3)	O(5)–Sn(2)–O(1)	76.2(2)
C(17)–Sn(1)–O(1)	82.8(3)	C(25)–Sn(2)–O(1)	92.8(4)
O(5)–Sn(1)–O(1)	67.27(19)	C(21)–Sn(2)–O(1)	88.6(4)
O(3)–Sn(1)–O(1)	130.0(2)	O(4)#1–Sn(2)–O(1)	169.2(2)
O(5)#1–Sn(1)–N(1)	159.6(2)		

Table 6
Selected bond distances (Å) and angles (°) for compound **11**

Sn(1)–O(3)	2.013(7)	Sn(2)–O(2)	2.184(7)
Sn(1)–C(7)	2.100(12)	Sn(2)–O(4)	2.363(7)
Sn(1)–O(6)	2.121(10)	Sn(2)–O(8)	2.393(7)
Sn(1)–C(1)	2.161(14)	Sn(2)–N(3)	2.618(10)
Sn(1)–O(4)	2.380(8)	Sn(3)–O(3)	2.052(8)
Sn(1)–N(5)	2.614(12)	Sn(3)–O(2)	2.063(7)
Sn(2)–C(19)	2.133(11)	Sn(3)–C(25)	2.113(12)
Sn(2)–O(3)	2.136(8)	Sn(3)–C(31)	2.131(12)
Sn(2)–C(13)	2.147(11)	Sn(3)–O(1)	2.244(8)
Sn(4)–O(2)	1.993(7)	Sn(4)–C(37)	2.121(13)
Sn(4)–O(1)	2.108(8)	Sn(4)–O(9)	2.179(9)
Sn(4)–C(43)	2.112(13)	C(13)–Sn(2)–O(4)	91.9(4)
O(3)–Sn(1)–C(7)	108.3(4)	O(2)–Sn(2)–O(4)	141.0(3)
O(3)–Sn(1)–O(6)	80.2(3)	C(13)–Sn(2)–O(8)	83.5(3)
C(7)–Sn(1)–O(6)	102.4(5)	O(2)–Sn(2)–O(8)	81.2(3)
O(3)–Sn(1)–C(1)	108.6(4)	O(4)–Sn(2)–O(8)	137.8(3)
C(7)–Sn(1)–C(1)	138.9(5)	O(2)–Sn(2)–N(3)	154.9(3)
O(6)–Sn(1)–C(1)	101.1(4)	O(4)–Sn(2)–N(3)	64.0(3)
O(3)–Sn(1)–O(4)	70.7(3)	O(8)–Sn(2)–N(3)	73.8(3)
C(7)–Sn(1)–O(4)	89.2(4)	O(3)–Sn(3)–O(2)	76.2(3)
O(6)–Sn(1)–O(4)	150.7(3)	O(3)–Sn(3)–C(25)	104.1(4)
C(1)–Sn(1)–O(4)	86.4(4)	O(2)–Sn(3)–C(25)	116.6(4)
O(3)–Sn(1)–N(5)	148.3(4)	O(3)–Sn(3)–C(31)	101.8(4)
C(7)–Sn(1)–N(5)	77.3(4)	O(2)–Sn(3)–C(31)	115.3(4)
O(6)–Sn(1)–N(5)	68.2(4)	C(25)–Sn(3)–C(31)	126.0(5)
C(1)–Sn(1)–N(5)	80.8(4)	O(3)–Sn(3)–O(1)	147.2(3)
O(4)–Sn(1)–N(5)	141.0(4)	O(2)–Sn(3)–O(1)	71.0(3)
C(19)–Sn(2)–N(3)	85.8(4)	C(25)–Sn(3)–O(1)	90.6(4)
O(3)–Sn(2)–N(3)	133.1(3)	C(31)–Sn(3)–O(1)	92.4(4)
C(13)–Sn(2)–N(3)	83.2(4)	O(2)–Sn(4)–O(1)	75.2(3)
C(19)–Sn(2)–O(8)	84.4(4)	O(2)–Sn(4)–C(43)	114.0(4)
O(3)–Sn(2)–O(8)	153.1(3)	O(1)–Sn(4)–C(43)	98.2(5)
C(19)–Sn(2)–O(3)	95.6(4)	O(2)–Sn(4)–C(37)	121.7(4)
C(19)–Sn(2)–C(13)	165.5(4)	O(1)–Sn(4)–C(37)	95.2(4)
O(3)–Sn(2)–C(13)	98.9(4)	C(43)–Sn(4)–C(37)	124.3(5)
C(19)–Sn(2)–O(2)	94.1(4)	O(2)–Sn(4)–O(9)	91.7(3)
O(3)–Sn(2)–O(2)	72.0(3)	O(1)–Sn(4)–O(9)	166.1(3)
C(13)–Sn(2)–O(2)	91.9(4)	C(43)–Sn(4)–O(9)	91.3(5)
C(19)–Sn(2)–O(4)	91.8(4)	C(37)–Sn(4)–O(9)	87.7(4)
O(3)–Sn(2)–O(4)	69.1(3)		

another place, a methanol molecule replace the carboxylates ligand as a unique ligand. The Sn(2) and Sn(3) atoms are bonded to two carbon and to four oxygen atoms, two carbon and to three oxygen atoms, resulting in the coordination geometries of the tin atom Sn(2) and Sn(3) are distorted octahedron and trigonal bipyramidal, respectively. The longest Sn–O bonds are 2.393(7) Å, Sn(2)–O(8) and 2.244(8) Å, Sn(3)–O(1). The exocyclic tin atoms, take Sn(1) for example, forms three short Sn–O bonds with three oxygen atoms. Together with the two bonds to phenyltin groups, the Sn(1) atoms may be considered as distorted trigonal bipyramidal with the axial site (O(6)–Sn(1)–O(4), 150.7(3)°) occupied by the O(4) and O(6) atoms and the basal plane defined by O(3), C(1), and C(7). It is noteworthy that short contacts are recognized between Sn–N derived from the monodentate carboxyl group (2.618(10) Å, Sn(2)–N(3) and 2.614(12) Å, Sn(1)–N(5)) [18]. If the short contacts of tin–nitrogen is considered, the geometry of the Sn(1) is best described as distorted octahedron and the two coordinate ligands

are bidentate. The directionality of this interaction involving the exocyclic tin atom Sn or the endocyclic tin almost mimics that of in compound **10**. The angles in the central Sn₂O₂ ring are 72.0(3)° and 107.0(3)°.

3.3. Conclusion

2-Methylpyrazine-5-acid has been shown to be able to form monomeric, polymeric and tetranuclear macrocyclic compounds. The nuclearity and stoichiometry were found to depend on the nature of the starting acceptor and reaction conditions. The ligand chelates to one tin, bonding through the oxygen of carboxyl and the nitrogen atoms. In the monomeric compounds, the ligand is bidentate or monodentate and the coordinate numbers of the tin atom is five or six. When using a series of benzyl triorganotin(IV) chloride react with it, we can obtain the corresponding tetranuclear macrocyclic compounds possess seven-coordinate and five-coordinate tin atoms and the ligand is tridentate. It is noteworthy that dealkylation reaction often occurred. In the polymeric compounds, in view of the highly variable coordination numbers and geometries of tin centers the synthesis of helical chain organotin(IV) architectures, where the building units are linked via dative bonds represent an excellent challenge.

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Appendix A. Supplementary material

CCDCs 606715 (1), 287658 (8), 287659 (9), 606713 (10), and 606714 (11) contain the supplementary crystallographic data for **1**, **8**, **9**, **10**, and **11**. The 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.jorgchem.2006.10.061](https://doi.org/10.1016/j.jorgchem.2006.10.061).

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