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Self-assembly of diorganotin(IV) moieties and 2-pyrazinecarboxylic acid: syntheses, characterizations and crystal structures of monomeric, polymeric or trinuclear macrocyclic compounds

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A series of diorganotin(IV) compounds of the type $[R_2Sn(pca)Cl]_3$ (R = CH_3 **1**; ${}^nBu$ **2**; C_6H_5 **3**; $C_6H_5CH_2$ **4**; Hpca = 2-pyrazinecarboxylic acid), $R_2Sn(pca)_2(mH_2O)\cdot nH_2O$ (m = 1: R = CH_3, n = 2 **5**, R = ${}^nBu$, n = 0 **6**; m = 0, n = 0: R = ${}^nBu$ **7**, C_6H_5 **8**, $C_6H_5CH_2$ **9**) and $(Et_3NH)^+[R_2Sn(pca)_2Cl]^-\cdot mH_2O$ (m = 0: R = CH_3 **10**, ${}^nBu$ **11**, $C_6H_5CH_2$ **13**; m = 1: R = C_6H_5 **12**) have been obtained by reactions of 2-pyrazinecarboxylic acid with diorganotin(IV) dichloride in the presence of sodium ethoxide or triethylamine. All compounds were characterized by elemental, IR and NMR spectra analyses. Except for compounds **3**, **4**, **7**, **11** and **13**, the others were also characterized by X-ray crystallography diffraction analyses, which revealed that compounds **1** and **2** were trinuclear macrocyclic structures with six-coordinate tin(IV) atoms, compounds **5** and **6** were monomeric structures with seven-coordinate tin(IV) atoms, compounds **8** and **9** were polymeric chain structures with seven-coordinate tin(IV) atoms and compounds **10** and **12** were stannate with seven-coordinate tin(IV) atoms.

Introduction

Metal-directed self-assembly of organic ligands and metal ions or organometallic substances with various intriguing topologies have been extensively studied.[1,2] The increasing interest in this field is due to the potential relevance of such compounds in catalysis.[3] An important objective is also the synthesis of new higher soluble metal complexes 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 found in organic synthesis and catalysis (synthesis of polyesters, polyurethanes, cross-linking of silicons, esterification, transesterification, polymerization, *etc.*) have been reported.[4] Especially, organotin compounds react with the ligands with nitrogen atoms, yielding products characterized by Sn–N bonds.[5] This fact has led to considerable effort being devoted to characterizing model compounds obtained from the ligands which have other donor atoms or groups. A biologically interesting donor is the carboxyl group, which coexists with the nitrogen atom in several relevant species, such as pyridine-2,6-dicarboxylic acid and pyridinecarboxylic acid. In our previous work, we have reported on the chemical, structural, spectroscopic properties of a series of similar organotin(IV) compounds, characterized by different coordinating properties.[6,7] 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-pyrazinecarboxylic acid (Hpca).

This ligand is interesting because of its potential multiple bidentate coordinate possibilities. As exhibited in Scheme 1, at least six bonding modes between this ligand and tin are conceivable although nobody has investigated its actual coordination mode until now. However, its analogical ligands, such as pyridinecarboxylic acid and pyridinedicarboxylic acid systems which commonly possess a coordination atom and additional donor atom, have previously been extensively studied.[8–10] For example, organotin complexes with chelation by both N and O atoms (mode **A**, **B** and **C**) have been reported, the ligand is pyridinecarboxylic acid.[10] The O, O chelations (mode **D** and **E**) are commonly observed in organotin carboxylates.[11] In addition, bridging between different molecules *via* the heterocycles (mode **B**, **C**, **E** and **F**) rather than chelation is possible.[9a,9c]

The above considerations stirred our interest in some detailed syntheses, and structure patterns for diorganotin derivatives of the ligand. To our surprise, we obtained a series of diorganotin(IV) compounds by reaction of diorganotin(IV) dichloride with 2-pyrazinecarboxylic acid in the presence of sodium ethoxide or triethylamine. When using a 1 : 1 : 1 molar ratio of R_2SnCl_2 : Hpca : EtONa, we obtained four trinuclear macrocyclic compounds **1**, **2**, **3** and **4** of the type $[R_2Sn(pca)Cl]_3$ (R = CH_3 **1**; ${}^nBu$ **2**; C_6H_5 **3**; $C_6H_5CH_2$ **4**). With a 1 : 2 : 2 ratio, another five monomeric or polymeric compounds **5–9** compounds are obtained and the general formula is $R_2Sn(pca)_2(mH_2O)\cdot nH_2O$ (m = 1: R = CH_3, n = 2 **5**, ${}^nBu$, n = 0 **6**; m = 0, n = 0: R = ${}^nBu$ **7**, C_6H_5 **8**, $C_6H_5CH_2$ **9**). When using a 1 : 2 : 2 molar ratio of R_2SnCl_2 : Hpca : Et_3N, we obtained four stannate compounds **10–13** of the type $(Et_3NH)^+[R_2Sn(pca)_2Cl]^-\cdot mH_2O$ (m = 0: R = CH_3 **10**, ${}^nBu$ **11**, $C_6H_5CH_2$ **13**; m = 1: R = C_6H_5 **12**). Determinations by elemental, IR and NMR spectra analyses of all the compounds are given and except for compounds **3**, **4**, **7**, **11** and **13**, the others are also characterized by X-ray crystallography diffraction analyses.

Experimental

Materials and methods

Dimethyltin dichloride, di-n-butyltin dichloride, diphenyltin dichloride and 2-pyrazinecarboxylic acid are commercially available, and they are used without further purification. Dibenzyltin dichlorides were prepared by a standard method reported in the literature.[12] The melting points were obtained with Kofler micro-melting point apparatus and were uncorrected. Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ${}^1H$, ${}^{13}C$ and ${}^{119}Sn$ NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer operating at 400, 100.6 and 149.2 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ${}^{13}C$ spectra are broadband proton decoupled. The chemical shifts were reported in ppm with respect to the references and were stated relative to external tetramethylsilane (TMS) for ${}^1H$ and ${}^{13}C$ NMR, and to neat tetramethyltin for ${}^{119}Sn$ NMR. Elemental analyses (C, H, N) were performed with a PE-2400II apparatus.

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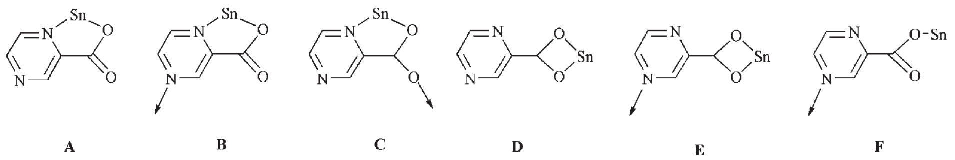


Scheme 1

Syntheses

$[(CH_3)_2Sn(pca)Cl]_3$ 1. The reaction is carried out under a nitrogen atmosphere. The 2-pyrazinecarboxylic acid (0.248 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol) was added to the solution of dry benzene (20 ml) in a Schlenk flask and stirred for 0.5 h. After the dimethyltin dichloride (0.438 g, 2 mmol) was added to the reactor, the reaction mixture was stirred for 12 h at 40 °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 ethanol and the white crystal compound **1** is formed. Yield: 78%. Mp 106–108 °C. Anal. Found: C, 27.27; H, 2.89; N, 9.10. Calc. for $C_{21}H_{27}Cl_3N_6O_6Sn_3$: C, 27.36; H, 2.95; N, 9.12%. IR (KBr, cm^{-1}): ν_{as}(COO), 1627; ν_s(COO), 1451; ν(C=N), 1591; ν(Sn–C), 583; ν(Sn–O), 476; ν(Sn–N), 457; ν(Sn–Cl), 270. ^{1}H NMR ($CDCl_3$, ppm): δ 0.84 (t, 18H, $^2J_{SnH}$ = 94.6 Hz), 8.46 (dd, 3H), 8.90 (d, 3H), 9.42 (d, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 10.2 (^1J(^{119}Sn–^{13}C), 893 Hz), 143.6, 145.4, 147.1, 147.5, 173.5. ^{119}Sn NMR ($CDCl_3$, ppm): −223.1.

$[(^nBu)_2Sn(pca)Cl]_3$ 2. Compound **2** is prepared in the same way as that of compound **1**, by adding di-n-butyltin dichloride (0.606 g, 2 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid is then recrystallized from ethanol and the white crystal compound **2** is formed. Yield: 85%. Mp 52–54 °C. Anal. Found: C, 39.81; H, 5.41; N, 7.08. Calc. for $C_{39}H_{63}Cl_3N_6O_6Sn_3$: C, 39.89; H, 5.41; N, 7.16%. IR (KBr, cm^{-1}): ν_{as}(COO), 1621; ν_s(COO), 1447; ν(C=N), 1595; ν(Sn–C), 558; ν(Sn–O), 475; ν(Sn–N), 458; ν(Sn–Cl), 263. ^{1}H NMR ($CDCl_3$, ppm): δ 0.91(t, 18H), 1.28–1.70 (m, 36H), 8.61 (dd, 3H), 8.87 (d, 3H), 9.28 (d, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 13.4, 25.8, 26.5, 27.0, 143.1, 144.8, 147.0, 147.6,173.0. ^{119}Sn NMR ($CDCl_3$, ppm): −341.5.

$[(Ph)_2Sn(pca)Cl]_3$ 3. Compound **3** is prepared in the same way as that of compound **1**, by adding diphenyltin dichloride (0.686 g, 2 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid is then obtained from ethanol. Yield: 84%. Mp 78–80 °C. Anal. Found: C, 47.23; H, 3.14; N, 6.49. Calc. for $C_{51}H_{39}Cl_3N_6O_6Sn_3$: C, 47.33; H, 3.04; N, 6.49%. IR (KBr, cm^{-1}): ν_{as}(COO), 1633; ν_s(COO), 1444; ν(C=N), 1597; ν(Sn–C), 558; ν(Sn–O), 481; ν(Sn–N), 457; ν(Sn–Cl), 267. ^{1}H NMR ($CDCl_3$, ppm): δ 7.35–7.78 (m, 30H), 8.58 (dd, 3H), 8.81 (d, 3H), 9.35 (d, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 129.3, 130.0, 136.9, 148.0, 143.0, 144.5, 147.2, 147.6, 172.5. ^{119}Sn NMR ($CDCl_3$, ppm): −371.4.

$[(PhCH_2)_2Sn(pca)Cl]_3$ 4. Compound **4** is prepared in the same way as that of compound **1**, by adding dibenzyltin dichloride (0.742 g, 2 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid is then obtained from ethanol. Yield: 86%. Mp 112–116 °C. Anal. Found: C, 49.56; H, 3.71; N, 6.01. Calc. for $C_{57}H_{51}Cl_3N_6O_6Sn_3$: C, 49.66; H, 3.73; N, 6.10%. IR (KBr, cm^{-1}): ν_{as}(COO), 1624; ν_s(COO), 1453; ν(C=N), 1601; ν(Sn–C), 528; ν(Sn–O), 478; ν(Sn–N), 463; ν(Sn–Cl), 265. ^{1}H NMR ($CDCl_3$, ppm): δ 3.16 (s, 12H), 7.31–7.58 (m, 30H), 8.64 (dd, 3H), 8.61 (d, 3H), 9.37 (d, 3H). ^{13}C NMR ($CDCl_3$. ppm): δ 38.2, 127.1, 129.3, 141.0, 143.3, 144.1, 146.9, 147.4, 172.5. ^{119}Sn NMR ($CDCl_3$, ppm): −305.2.

$(CH_3)_2Sn(pca)_2(H_2O)\cdot 2H_2O$ 5. The compound **5** is prepared in the same way as that of compound **1**, by adding dimethyltin dichloride (0.219 g, 1 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid is then recrystallized from 95% ethanol and the white crystal compound **5** is formed. Yield: 81%. Mp 156–158 °C. Anal. Found: C, 30.76; H, 4.30; N, 11.92. Calc. for $C_{12}H_{20}N_4O_8Sn$: C, 30.86; H, 4.32; N, 11.99%. IR (KBr, cm^{-1}): ν(O–H), 3346; ν_{as}(COO), 1635; ν_s(COO), 1326; ν(C=N), 1597; ν(Sn–C), 543; ν(Sn–O), 480; ν(Sn–N), 444. ^{1}H NMR ($CDCl_3$–D_2O, ppm): δ 0.82 (s, 6H), 3.01 (s, 2H), 8.56 (dd, 2H), 8.90 (d, 2H), 9.36 (d, 2H). ^{13}C NMR ($CDCl_3$. ppm): δ 11.1, 143.2, 145.1, 146.9, 147.5, 170.1. ^{119}Sn NMR ($CDCl_3$, ppm): −226.7.

$(^nBu)_2Sn(pca)_2(H_2O)$ 6. Compound **6** is prepared in the same way as that of compound **1**, by adding di-n-butyltin dichloride (0.303 g, 1 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid is then recrystallized from 95% ethanol and the white crystal compound **6** is formed. Yield: 80%. Mp 186–188 °C. Anal. Found: C, 43.32; H, 5.11; N, 11.33. Calc. for $C_{18}H_{26}N_4O_5Sn$: C, 43.49; H, 5.27; N, 11.27%. IR (KBr, cm^{-1}): ν(O–H), 3357; ν_{as}(COO), 1640; ν_s(COO), 1333; ν(C=N), 1603; ν(Sn–C), 536; ν(Sn–O), 475, ν(Sn–N), 461. ^{1}H NMR ($CDCl_3$–D_2O, ppm): δ 0.82 (t, 6H), 1.27–1.71 (m, 12H), 3.23 (s, 2H), 8.42 (dd, 2H), 8.97 (d, 2H), 9.31 (d, 2H). ^{13}C NMR ($CDCl_3$. ppm): δ 13.4, 25.8, 26.5, 27.0, 143.3, 145.4, 147.8, 148.0, 173.7. ^{119}Sn NMR ($CDCl_3$, ppm): −201.5.

$(^nBu)_2Sn(pca)_2$ 7. Compound **7** is prepared in the same way as that of compound **1**, by adding di-n-butyltin dichloride (0.303 g, 1 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid is then recrystallized from ethanol and the white crystal compound **7** is formed. Yield: 87%. Mp 112–114 °C. Anal. Found: C, 45.08; H, 5.01; N, 11.59. Calc. for $C_{18}H_{24}N_4O_4Sn$: C, 45.13; H, 5.05; N, 11.69%. IR (KBr, cm^{-1}): ν_{as}(COO), 1651; ν_s(COO), 1439; ν(C=N), 1598; ν(Sn–C), 549; ν(Sn–O), 482; ν(Sn–N), 455. ^{1}H NMR ($CDCl_3$, ppm): δ 0.85 (t, 6H), 1.30–1.77 (m, 12H), 8.58 (dd, 2H), 8.92 (d, 2H), 9.41 (d, 2H). ^{13}C NMR ($CDCl_3$, ppm): δ 13.6, 26.3, 26.5, 27.1, 143.5, 145.2, 147.6, 147.9, 172.1. ^{119}Sn NMR ($CDCl_3$, ppm): −221.3.

$(Ph)_2Sn(pca)_2$ 8. Compound **8** is prepared in the same way as that of compound **1**, by adding diphenyltin dichloride (0.343 g, 1 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid is then recrystallized from ethanol and the white crystal compound **8** is formed. Yield: 84%. Mp > 200 °C (dec.). Anal. Found: C, 50.81; H, 3.10; N, 10.72. Calc. for $C_{22}H_{16}N_4O_4Sn$: C, 50.91; H, 3.11; N, 10.79%. IR (KBr, cm^{-1}): ν_{as}(COO), 1649; ν_s(COO), 1448; ν(C=N), 1607; ν(Sn–C), 550; ν(Sn–O), 471; ν(Sn–N), 451. ^{1}H NMR ($CDCl_3$, ppm): δ 7.34–7.68 (m, 10H), 8.68 (dd, 2H), 8.92 (d, 2H), 9.47 (d, 2H). ^{13}C NMR ($CDCl_3$. ppm): δ 129.2, 130.3, 136.6, 148.1, 143.2, 144.6, 147.2, 147.5, 172.7. ^{119}Sn NMR ($CDCl_3$, ppm): −386.6.

$(PhCH_2)_2Sn(pca)_2$ 9. Compound **9** is prepared in the same way as that of compound **1**, by adding dibenzyltin dichloride (0.371 g, 1 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid is then recrystallized from ethanol and the white crystal compound **9** is formed. Yield: 80%. Mp 100–102 °C. Anal. Found: C, 52.62; H, 3.58; N, 10.21. Calc. for $C_{24}H_{20}N_4O_4Sn$: C, 52.69; H, 3.68; N, 10.24%. IR (KBr, cm^{-1}): ν_{as}(COO), 1647; ν_s(COO), 1434; ν(C=N), 1596; ν(Sn–C), 540; ν(Sn–O), 472; ν(Sn–N), 454. ^{1}H NMR ($CDCl_3$, ppm): δ 3.26 (s, 4H), 7.34–7.68 (m, 10H), 8.65 (dd, 2H), 8.76 (d, 2H), 9.37 (d, 2H). ^{13}C NMR ($CDCl_3$. ppm): δ 38.0, 127.4, 129.7, 141.3, 143.7, 144.1, 147.2, 147.6, 172.8. ^{119}Sn NMR ($CDCl_3$, ppm): −334.9.

Table 1 Crystal, data collection and structure refinement parameters for compounds **1**, **2**, **5**, **8–10** and **12**

Compound	**1**	**2**	**5**	**8**	**9**	**10**	**12**
Empirical formula	$C_{21}H_{27}Cl_3N_6O_6Sn_3$	$C_{39}H_{63}Cl_3N_6O_6Sn_3$	$C_{12}H_{20}N_4O_8Sn$	$C_{22}H_{16}N_4O_4Sn$	$C_{24}H_{20}N_4O_4Sn$	$C_{18}H_{28}ClN_5O_4Sn$	$C_{28}H_{34}ClN_5O_5Sn$
M	921.91	1174.37	467.01	519.08	547.13	532.59	674.74
Crystal system	Monoclinic	Hexagonal	Rhombohedral	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2(1)/n$	$P6(3)/m$	$R\text{-}3c$	$Pbca$	$Pbca$	$P\bar{1}$	$P2(1)/c$
a/Å	13.448(4)	13.934(6)	24.920(10)	11.987(6)	12.021(4)	10.156(11)	15.549(6)
b/Å	16.747(6)	13.934(6)	24.920(10)	18.759(9)	18.256(6)	10.445(11)	10.595(4)
c/Å	14.003(5)	16.794(10)	17.486(10)	18.976(10)	20.857(7)	12.309(13)	18.259(7)
α/°	90	90	90	90	90	76.887(14)	90
β/°	92.570(5)	90	90	90	90	78.974(14)	97.649(7)
γ/°	90	120	120	90	90	63.059(13)	90
V/Å^3	3150.5(18)	2824(2)	9404(8)	4267(4)	4577(3)	1128(2)	2981(2)
Z	4	2	18	8	8	2	4
μ/mm^{-1}	2.658	1.499	1.263	1.234	1.155	1.284	0.992
Reflections collected	16317	12186	15861	21358	22896	6007	15502
Independent reflections	5556	1453	1837	3779	4034	3933	5269
R_{int}	0.0544	0.0860	0.0826	0.0851	0.0807	0.0258	0.0862
R1 [$I > 2\sigma(I)$]/R1 (all data)	0.0366, 0.0805	0.0369, 0.0565	0.0470, 0.0941	0.0335, 0.0884	0.0407, 0.0931	0.0366, 0.0477	0.0510, 0.1064
wR1 [$I > 2\sigma(I)$]/wR1 (all data)	0.0724, 0.1025	0.0683, 0.0807	0.1096, 0.1240	0.0652, 0.1029	0.0894, 0.1301	0.0956, 0.1157	0.0931, 0.1075

$(Et_3NH)^+[(CH_3)_2Sn(pca)_2Cl]^-$ 10. Compound **10** is prepared in the same way as that of compound **1**, by adding dimethyltin dichloride (0.219 g, 1 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol) and triethylamine (0.202 g, 2 mmol). The solid is then recrystallized from ethanol and the white crystal compound **10** is formed. Yield: 76%. Mp 122–124 °C. Anal. Found: C, 40.48; H, 5.32; N, 13.11. Calc. for $C_{18}H_{28}ClN_5O_4Sn$: C, 40.59; H, 5.30; N, 13.15%. IR (KBr, cm^{-1}): ν(N–H), 3430; ν_{as}(COO), 1647; ν_s(COO), 1331; ν(C=N), 1602; ν(Sn–C), 576; ν(Sn–O), 474; ν(Sn–N), 458; ν(Sn–Cl), 270. ^{1}H NMR (CDCl$_3$, ppm): δ 0.78 (s, 6H), 1.10 (t, 9H), 2.84 (m, 6H), 8.37 (dd, 2H), 8.80 (d, 2H), 9.41(d, 2H), 11.21(s, 1H). ^{13}C NMR (CDCl$_3$. ppm): δ 7.8, 52.2, 10.9 ($^1J(^{119}Sn–^{13}C)$, 920 Hz), 143.1, 145.3, 147.5, 148.0, 171.6. ^{119}Sn NMR (CDCl$_3$, ppm): −359.1.

$(Et_3NH)^+[(^nBu)_2Sn(pca)_2Cl]^-$ 11. Compound **11** is prepared in the same way as that of compound **1**, by adding di-n-butyltin dichloride (0.303 g, 1 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol) and triethylamine (0.202 g, 2 mmol). The solid is then obtained from ethanol. Yield: 80%. Mp 131–133 °C. Anal. Found: C, 46.69; H, 6.51; N, 11.27. Calc. for $C_{24}H_{40}ClN_5O_4Sn$: C, 46.74; H, 6.54; N, 11.36%. IR (KBr, cm^{-1}): ν(N–H), 3412; ν_{as}(COO), 1652; ν_s(COO), 1326; ν(C=N), 1600; ν(Sn–C), 537; ν(Sn–O), 481; ν(Sn–N), 460; ν(Sn–Cl), 272. ^{1}H NMR (CDCl$_3$, ppm): δ 0.83 (t, 6H), 1.28–1.81 (m, 12H), 1.08 (t, 9H), 2.76 (m, 6H), 8.52 (dd, 2H), 8.90 (d, 2H), 9.37 (d, 2H), 11.32 (s, 1H). ^{13}C NMR (CDCl$_3$. ppm): δ 7.5, 53.1, 13.6, 26.2, 26.6, 27.9, 142.9, 145.4, 147.6, 148.1, 172.0. ^{119}Sn NMR (CDCl$_3$, ppm): −374.8.

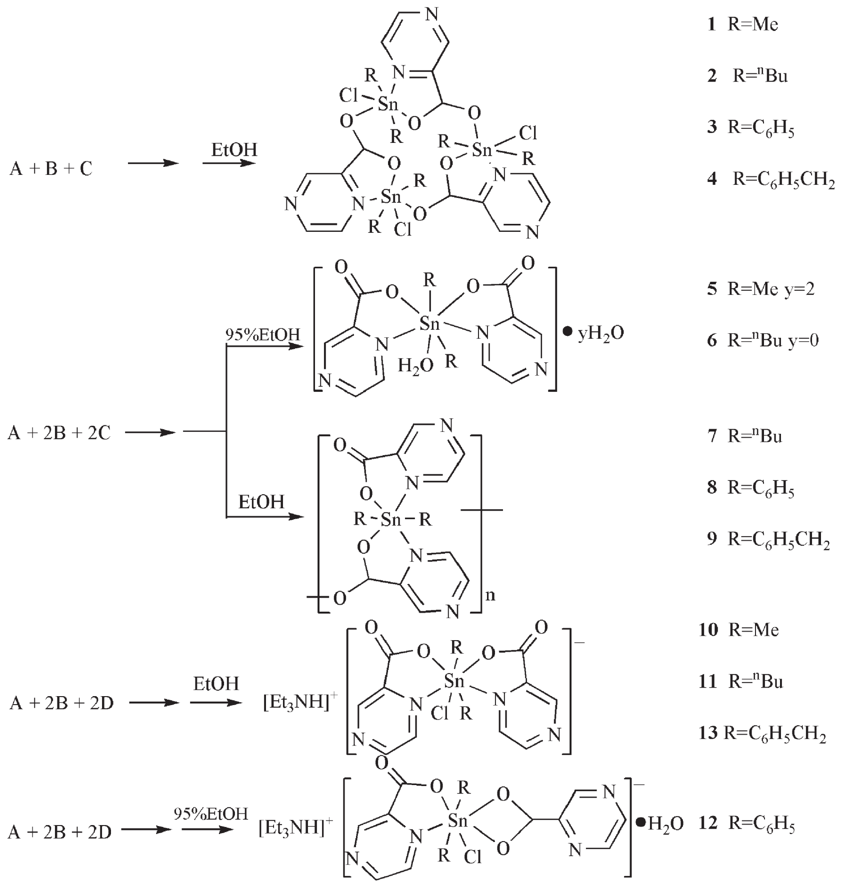
$(Et_3NH)^+[(Ph)_2Sn(pca)_2Cl]^-\cdot H_2O$ 12. Compound **12** is prepared in the same way as that of compound **1**, by adding diphenyltin dichloride (0.343 g, 1 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol) and triethylamine (0.202 g, 2 mmol). The solid is then recrystallized from 95% ethanol and the white compound **12** is formed. Yield: 82%. Mp 146–148 °C. Anal. Found: C, 49.75; H, 5.05; N, 10.29. Calc. for $C_{28}H_{34}ClN_5O_5Sn$: C, 49.84; H, 5.08; N, 10.38%. IR (KBr, cm^{-1}): ν(N–H), 3423; ν(O–H), 3351; ν_{as}(COO), 1642 and 1621; ν_s(COO), 1432 and 1432; ν(C=N), 1597; ν(Sn–C), 536; ν(Sn–O), 479; ν(Sn–N), 451; ν(Sn–Cl), 273. ^{1}H NMR (CDCl$_3$–D$_2$O, ppm): δ 1.15 (t, 9H), 2.81 (m, 6H), 7.26–7.67 (m, 10H), 8.57 (dd, 2H), 8.84 (d, 2H), 9.29 (d, 2H), 11.25 (s, 1H). ^{13}C NMR (CDCl$_3$. ppm): δ 7.7, 52.9, 128.9, 130.2, 136.7, 148.1, 143.2, 144.1, 147.2, 147.9, 172.6. ^{119}Sn NMR (CDCl$_3$, ppm): −421.0.

$(Et_3NH)^+[(PhCH_2)_2Sn(pca)_2Cl]^-$ 13. Compound **13** is prepared in the same way as that of compound **1**, by adding dibenzyltin dichloride (0.371 g, 1 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol) and triethylamine (0.202 g, 2 mmol). The solid is then obtained from ethanol. Yield: 79%. Mp 166–168 °C. Anal. Found: C, 52.49; H, 5.25; N, 10.11. Calc. for $C_{30}H_{36}ClN_5O_5Sn$: C, 52.62; H, 5.30; N, 10.23%. IR (KBr, cm^{-1}): ν(N–H), 3425; ν_{as}(COO), 1646; ν_s(COO), 1331; ν(C=N), 1601; ν(Sn–C), 534; ν(Sn–O), 469; ν(Sn–N), 450; ν(Sn–Cl), 268. ^{1}H NMR (CDCl$_3$, ppm): δ 1.09 (t, 9H), 2.82 (m, 6H), 3.21 (s, 4H), 7.36–7.71 (m, 10H), 8.52 (dd, 2H), 8.74 (d, 2H), 9.40 (d, 2H), 11.28 (s, 1H). ^{13}C NMR (CDCl$_3$. ppm): δ 7.2, 52.6, 38.1, 127.5, 129.4, 141.5, 143.6, 144.6, 146.9, 147.7, 172.3. ^{119}Sn NMR (CDCl$_3$, ppm): −401.7.

X-ray crystallography

Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Smart CCD area-detector with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). A semiempirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refined against F^2 by full matrix least-squares using SHELXL-97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 1.

CCDC reference numbers 220183 **1**, 222014 **2**, 220176 **5**, 220168 **6**, 220184 **8**, 220171 **9**, 209701 **10** and 220165 **12**.



A=Diorganotin(IV) dichlorides; B=2-pyrazinecarboxylic acid; C=Sodium ethoxide; D=Triethylamine

Scheme 2

See http://www.rsc.org/suppdata/dt/b4/b404477k/ for crystallographic data in CIF or other electronic format.

Results and discussion

Syntheses

Reactions of diorganotin(IV) dichloride with 2-pyrazinecarboxylic acid in 1 : 1 or 1 : 2 stoichiometry depending on the nature of the starting acceptor and reaction condition affords air-stable compounds. The syntheses procedures are shown in Scheme 2.

Spectroscopic studies

IR. The stretching frequencies of interest are those associated with the acid COO, Sn–C, Sn–O and Sn–N groups. The spectra of all the compounds show some common characters. The explicit feature in the infrared spectra of all compounds, strong absorption appearing at about 477 cm^{-1} in the respective spectra of the compounds, which is absent in the free ligand, is assigned to the Sn–O stretching mode of vibration. The ν(C=N) band, occurring at about 1598 cm^{-1}, is considerably shifted towards lower frequencies with respect to that of the free ligand, confirming the coordination of the heterocyclic N to the tin. The stretching frequency is lowered owing to the displacement of electron density from N to Sn atom, thus resulting in the weakening of the C=N bond as reported in the literature.[13] The weak- or medium-intensity band in the region 444–463 cm^{-1} can be assigned to Sn–N stretching vibrations. All these values are consistent with that detected in a number of organotin(IV) derivatives.[14,15]

Some obvious differences among the spectra of the compounds are also observed. A strong band at about 268 cm^{-1} for **1**–**4** and **10**–**13** are assigned to ν(Sn–Cl) stretching mode of vibration. Besides, in organotin carboxylate complexes, the IR spectra can provide useful information concerning the coordinate formation of the carboxyl. The magnitude of $\Delta\nu$ ($\Delta\nu = \nu_{as}(\mathrm{COO}) - \nu_s(\mathrm{COO})$) of about 180 cm^{-1} for compounds **1**–**4** is comparable to those for the corresponding sodium salts, which indicates the presence of bidentate carboxyl groups.[16] Moreover, the magnitude of $\Delta\nu$ occurring at about 315 cm^{-1} for compounds **5**, **6**, **10**, **11** and **13** indicates that the carboxylate ligand functions as monodentate ligand under the conditions employed,[17,18] which was also confirmed by X-ray structure analyses.

NMR. In ^{1}H NMR spectra of the free ligand, single resonances are observed at 7.46 ppm, which are absent in the spectra of the compounds, indicating the replacement of the carboxylic acid proton by a diorganotin moiety. The spectra shows that the chemical shifts of the methyl groups, 0.78–0.82 ppm, 0.82–1.81 ppm for the butyl group, 7.26–7.78 ppm for the phenyl group and the benzyl group in 3.17–3.26 and 7.32–7.86 ppm. All upfield shifts as compared with those of their corresponding precursors. The $^2J_{\mathrm{SnH}}$ of dimethyltin derivative **1** has a value of 95.6 Hz, comparable with those previously reported for six-coordinated octahedral tin(IV) adducts.[19]

The ^{13}C NMR spectra of all compounds show a significant downfield shift of all carbon resonance, compared with the free ligand. The shift is a consequence of an electron density transfer from the ligand to the acceptor. 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 small to be resolved. Complementary information is given by the values of the coupling constant. The $^1J_{\mathrm{SnC}}$ value for **1** is 893 Hz, similar to that of the hexa-coordinate compound, and the calculated θ(C–Sn–C) by the Holeček and Lyčka equation[20] are 163.9°, which are close to the angles observed in the solid state for compound **1**.

The ^{119}Sn NMR data show only one signal for compounds **1**–**4**, typical of a six-coordinate species, and has been found in accordance with the solid state structure.[21] However, The chemical shift for compound **8** shows −386.6 ppm. Although δ(^{119}Sn) is influenced

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

$[(CH_3)_2Sn(pca)Cl]_3$ **1**			
Sn(1)–C(21)	2.109(8)	Sn(3)–C(18)	2.095(7)
Sn(1)–C(20)	2.119(8)	Sn(3)–C(19)	2.105(9)
Sn(1)–O(1)	2.239(5)	Sn(3)–O(5)	2.270(5)
Sn(1)–Cl(1)	2.439(2)	Sn(3)–Cl(3)	2.427(2)
Sn(1)–O(6)	2.440(5)	Sn(3)–O(4)	2.527(5)
Sn(1)–N(5)	2.479(6)	Sn(3)–N(3)	2.507(6)
Sn(2)–C(17)	2.076(8)	O(1)–C(1)	1.265(8)
Sn(2)–C(16)	2.111(8)	O(2)–C(1)	1.241(8)
Sn(2)–O(3)	2.331(5)	O(3)–C(6)	1.247(9)
Sn(2)–Cl(2)	2.447(2)	O(4)–C(6)	1.250(9)
Sn(2)–O(2)	2.453(5)	O(5)–C(11)	1.245(9)
Sn(2)–N(1)	2.477(6)	O(6)–C(11)	1.257(9)
C(21)–Sn(1)–C(20)	159.7(4)	C(17)–Sn(2)–C(16)	161.9(3)
C(21)–Sn(1)–O(1)	90.4(3)	C(17)–Sn(2)–O(3)	92.8(3)
C(20)–Sn(1)–O(1)	88.6(3)	C(16)–Sn(2)–O(3)	87.1(3)
C(21)–Sn(1)–Cl(1)	99.4(2)	C(17)–Sn(2)–Cl(2)	97.9(3)
C(20)–Sn(1)–Cl(1)	100.8(3)	C(16)–Sn(2)–Cl(2)	100.0(2)
O(1)–Sn(1)–Cl(1)	87.94(15)	O(3)–Sn(2)–Cl(2)	81.50(14)
C(21)–Sn(1)–O(6)	79.9(3)	C(17)–Sn(2)–O(2)	82.3(3)
C(20)–Sn(1)–O(6)	83.0(3)	C(16)–Sn(2)–O(2)	83.7(3)
O(1)–Sn(1)–O(6)	119.51(18)	O(3)–Sn(2)–O(2)	128.86(18)
Cl(1)–Sn(1)–O(6)	152.48(14)	Cl(2)–Sn(2)–O(2)	149.64(14)
C(21)–Sn(1)–N(5)	90.3(3)	C(17)–Sn(2)–N(1)	93.0(3)
C(20)–Sn(1)–N(5)	93.0(3)	C(16)–Sn(2)–N(1)	91.9(3)
O(1)–Sn(1)–N(5)	173.2(2)	O(3)–Sn(2)–N(1)	164.0(2)
Cl(1)–Sn(1)–N(5)	85.31(16)	Cl(2)–Sn(2)–N(1)	82.97(16)
O(6)–Sn(1)–N(5)	67.22(19)	O(2)–Sn(2)–N(1)	66.74(19)
C(18)–Sn(3)–C(19)	152.7(4)	O(5)–Sn(3)–N(3)	166.2(2)
C(18)–Sn(3)–O(5)	93.5(3)	Cl(3)–Sn(3)–N(3)	83.86(16)
C(19)–Sn(3)–O(5)	87.6(3)	C(18)–Sn(3)–O(4)	77.7(3)
C(18)–Sn(3)–Cl(3)	101.9(3)	C(19)–Sn(3)–O(4)	80.3(3)
C(19)–Sn(3)–Cl(3)	105.3(3)	O(5)–Sn(3)–O(4)	128.57(19)
O(5)–Sn(3)–Cl(3)	82.85(15)	Cl(3)–Sn(3)–O(4)	148.56(13)
C(18)–Sn(3)–N(3)	93.0(3)	O(4)–Sn(3)–N(3)	64.87(19)
C(19)–Sn(3)–N(3)	92.3(3)		
$[(^nBu)_2Sn(pca)Cl]_3$ **2**			
Sn(1)–C(6)#1	2.090(8)	Sn(1)–Cl(1)	2.412(2)
Sn(1)–C(6)	2.090(8)	Sn(1)–O(1)	2.424(4)
Sn(1)–O(2)#2	2.292(4)	Sn(1)–N(1)	2.442(5)
O(1)–C(1)	1.253(8)	O(2)–C(1)	1.250(7)
C(6)#1–Sn(1)–C(6)	157.2(4)	O(2)#2–Sn(1)–O(1)	124.71(14)
C(6)#1–Sn(1)–O(2)#2	86.29(17)	Cl(1)–Sn(1)–O(1)	150.98(11)
C(6)–Sn(1)–O(2)#2	86.29(17)	C(6)#1–Sn(1)–N(1)	95.77(17)
C(6)#1–Sn(1)–Cl(1)	100.3(2)	C(6)–Sn(1)–N(1)	95.77(17)
C(6)–Sn(1)–Cl(1)	100.3(2)	O(2)#2–Sn(1)–N(1)	168.51(16)
O(2)#2–Sn(1)–O(1)	84.31(11)	Cl(1)–Sn(1)–N(1)	84.20(13)
C(6)#1–Sn(1)–O(1)	83.3(2)	O(1)–Sn(1)–N(1)	66.78(15)
C(6)–Sn(1)–O(1)	83.3(2)		

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), it may be used with a cation to infer the coordination number of the tin atom.[21b] In the case of diphenyltin(IV) compounds, different coordination numbers are clearly associated with different ranges of $\delta(^{119}Sn)$ values, and the chemical shift of compound **8** is well within the range corresponding to coordination number 6, −360 to −540 ppm.[21b] Therefore it can reasonably be assumed that the structure in solution of compound **8** is likely different from that observed in the solid state.

Crystal structures

Crystal structure of $[(CH_3)_2Sn(pca)Cl]_3$ 1 and $[(^nBu)_2Sn(pca)Cl]_3$ 2. The molecular structures are illustrated in Fig. 1 and Fig. 2, respectively. Selected bond lengths (Å) and angles (°) are listed in Table 2. The compounds prove to be trinuclear macrocyclic compounds with 2-pyrazinecarboxylic acid bridging the adjacent tin atoms with a fifteen-member $Sn_3O_6N_3C_3$ ring. The units are $[(CH_3)_2Sn(pca)Cl]$ and $[(^nBu)_2Sn(pca)Cl]$, in which the primary bonds of the ligand to tin occur through its nitrogen atom and two oxygen atoms of the carboxyl (mode **C**). The compounds exist in distorted octahedron geometry about all three tin atoms with six-coordinate tin(IV) atom. Distortion from strict octahedral coordination is partly because of the bonding variance and they occupy *cis* positions in the range of 67.22(19)–119.51(14)°. The Sn–N bond lengths are 2.479(6) Å [Sn(1)–N(5)], 2.477(6) Å [Sn(2)–N(1)], 2.507(6) Å [Sn(3)–N(3)] for **1** and 2.442(5) [Sn(1)–N(1)] Å for **2**. All these values lie in the range recorded in the Cambridge Crystallographic Database from 2.27 to 2.58 Å,[22] slightly greater than the sum of the covalent radii of tin and nitrogen atoms (2.15 Å) but are considerably less than the van der Waal's radii of the two atoms (3.74 Å).[23] 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 three carboxylate ligands being 0.202, 0.122, 0.257 Å for **1** and 0.132 Å for **2**, respectively. Although the Sn–O ranges from 2.239(5) to 2.527(5) Å which is longer than the sum of the covalent radii of the tin and oxygen 2.13 Å,[24] both of which are similar to those reported in the literature.[25] The Sn–Cl bond length [Sn(1)–Cl(1) 2.439(2) Å, Sn(2)–Cl(2) 2.447(2) Å] and 2.427(2) Å for **1** and 2.412(2) Å for **2** lies in the range of the normal covalent radii (2.37–2.60 Å).[22] The Sn–C distances fall in a narrow range from 2.076(8) to 2.119(8) Å, typical of organotin derivatives.

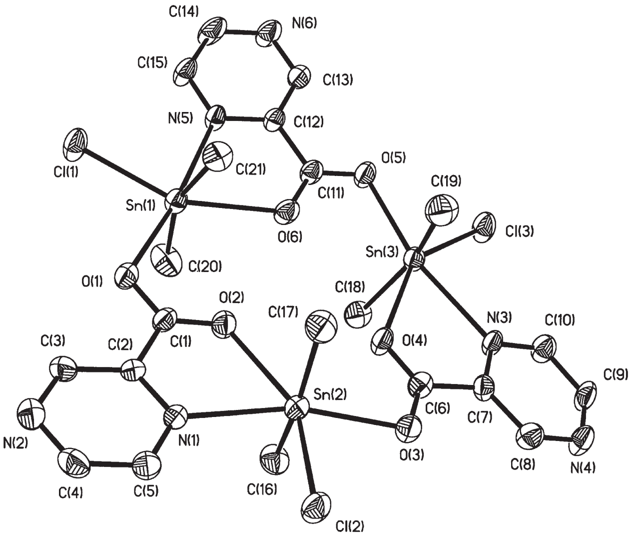


Fig. 1

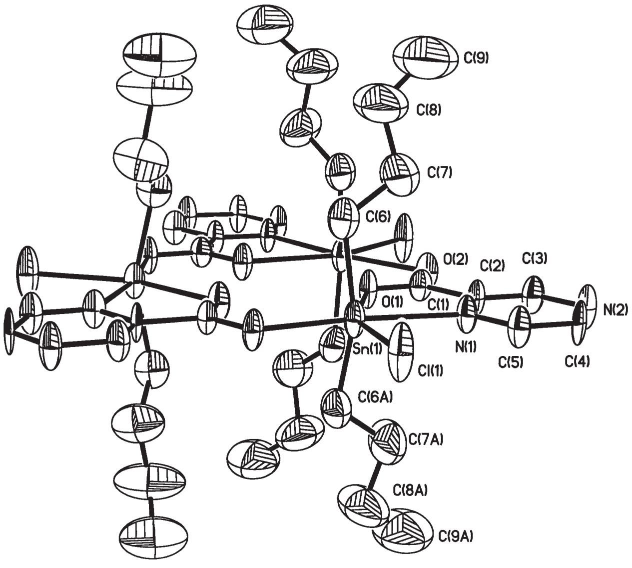


Fig. 2

Furthermore, we investigated the distance between the three endocyclic oxygen atoms and found the separations in compound **1** are 3.358, 3.644 and 3.345 Å for O(2)···O(4), O(4)···O(6) and O(6)···O(2), respectively. The corresponding values in compound **2** are 3.470 Å. It does not mean some significant interactions between these atoms, however, what attracts us is the center cavity formed in these macrocyclic and the potential function of the endocyclic oxygen atoms similar to crown ethers.[26] Out of consideration for molecular design, the compounds may be regarded as a potential ligand for the recognition of special molecules.

Crystal structure of $(CH_3)_2Sn(pca)_2(H_2O)\cdot 2H_2O$ 5. The molecular structures are illustrated in Fig. 3 and Fig. 4, selected bond lengths (Å) and angles (°) are listed in Table 3. The molecule possesses a monomeric structure, but this structure differs from those of $Me_2Sn(2\text{-}Pic)_2$ and $Et_2Sn(O_2CC_4H_3S)_2$.[27,28] The compound contains a seven-coordinated tin atom and has a pentagonal bipyramidal environment with C(6) and C(6)#1 atoms occupying the axial sites and the axial–Sn–axial, C(6)–Sn–C(6)#1 [$-x + 4/3, -x + y + 2/3, -z + 7/6$] is 172(6)°. The tin atom lies on a crystallographic 2-fold structure, Sn(1), O(1), O(1)#1, O(3), N(1) and N(1)#1 [$-x + 4/3, -x + y + 2/3, -z + 7/6$] are completely coplanar with the tin atom existing in the plane. The sum of angles between the tin atom and the equatorial atoms is 360°, consistent with the ideal value of 360°. In the structure, two carbon atoms and two nitrogen atoms of 2-pyrazinecarboxylic acid and the oxygen atom of water are covalently linked to the tin. The Sn–O bond lengths (2.22(8) Å) are longer than those in $\{[^nBu_2Sn(2\text{-}pic)]_2O\}_2$ (2.0544 and 2.110 Å), near to the sum of the covalent radii of Sn and O (2.13 Å).[24] The Sn–N bond lengths [Sn(1)–N (1) and Sn(1)–N(1)#1, 2.55 (9) Å] are longer than those in $^nBu_2Sn(pca)_2(H_2O)$ [2.2522(6) Å],[29] similar to those in $Me_2Sn(2\text{-}Pic)_2$ (2.507 and 2.477 Å),[27] but much shorter than the sum of the van der Waal's radii of Sn and N, 3.74 Å,[23] and Sn–O(3) 2.33(10) Å is also below the sum of the van der Waal's radii of these atoms, 3.68 Å.[24] The intermolecular interactions exist between the coordinate water and two adjacent molecules and result in hydrogen bonds O(3)–H···O(2)(2.674 Å). Through these, a two-dimensional hydrogen bonded network is formed. Besides, co-crystallization is found in the crystals and the co-crystallized solvent is water with the molar ratio $(CH_3)_2Sn(pca)_2(H_2O):H_2O$ of 1 : 2. It is worthwhile to note that the co-crystallized waters do not participate in the interaction with the units, but six neighboring co-crystallized waters form a six-member ring through the hydrogen bonds O–H···O.

The structure of compound **6** is similar to compound **5**. Although we obtained compound **6** by a different method, its structure has been reported in our previous work.[30]

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

$(CH_3)_2Sn(pca)_2(OH_2)\cdot 2H_2O$ **5**			
Sn(1)–C(6)	2.09(11)	Sn(1)–O(3)	2.33(10)
Sn(1)–C(6)#1	2.09(10)	Sn(1)–N(1)#1	2.55(9)
Sn(1)–O(1)#1	2.22(8)	Sn(1)–N(1)	2.55(9)
Sn(1)–O(1)	2.22(8)		
C(6)–Sn(1)–C(6)#1	172(6)	C(6)–Sn(1)–N(1)	90(3)
C(6)#1–Sn(1)–O(1)	94(4)	O(1)–Sn(1)–N(1)	68(3)
C(6)–Sn(1)–O(1)	92(3)	O(1)#1–Sn(1)–N(1)	142(3)
C(6)#1–Sn(1)–O(1)#1	92(3)	O(3)–Sn(1)–N(1)	75(2)
C(6)–Sn(1)–O(1)#1	94(4)	C(6)#1–Sn(1)–N(1)#1	90(3)
O(1)#1–Sn(1)–O(1)	74(4)	C(6)–Sn(1)–N(1)#1	88(3)
C(6)#1–Sn(1)–O(3)	86(3)	O(1)–Sn(1)–N(1)#1	142(3)
C(6)–Sn(1)–O(3)	86(3)	O(1)#1–Sn(1)–N(1)#1	68(3)
O(1)–Sn(1)–O(3)	142.9(19)	O(3)–Sn(1)–N(1)#1	75(2)
O(1)#1–Sn(1)–O(3)	142.9(19)	N(1)#1–Sn(1)–N(1)	150(4)
C(6)#1–Sn(1)–N(1)	88(3)		

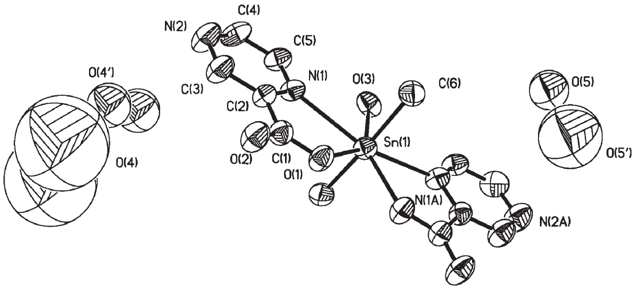


Fig. 3

Crystal structure of $(Ph)_2Sn(pca)_2$ 8 and $(PhCH_2)_2Sn(pca)_2$ 9. The $R_2Sn(pca)_2$ units are connected in polymeric structures as shown in Fig. 5–8, respectively, selected bond lengths (Å) and angles (°) are listed in Table 4. Intermolecular tin–oxygen bonds [2.319(4) for **8** and 2.312(4) Å for **9**] that are comparable in strength to the intramolecular tin–oxygen bonds and close in length to the sum of the covalent radii of tin and oxygen, 2.13 Å,[24] create a continuous polymeric chain.

For compounds **8** and **9**, both ligands chelate to one tin, bonding through one carboxyl oxygen and the nitrogen atom; an additional intermolecular Sn(1)···O(2)#1 [$x + 1/2, y, -z + 3/2$] interaction between each tin and the carboxylic oxygen of a neighboring molecule gives rise to the polymeric structure (mode **C**). Therefore, there are two distinct coordinate ligands in the compounds, one is bidentate and the other is tridentate. The overall configuration at tin is best described as pentagonal bipyramidal: tin and the bonded oxygen and nitrogen atoms are nearly coplanar and deviate only slightly from regular pentagonal geometry, mean deviation from plane is 0.0783 Å for **8** and 0.0344 Å for **9**. The alkyl groups occupy the apical position, the axial–Sn–axial, C(17)–Sn–C(11) is 171.2(2)° for **8** and C(18)–Sn–C(11) is 174.0(3)° for **9**. The Sn–N distances 2.393(5) and 2.638(4) Å for **8**, 2.422(6) and 2.632(5) Å for **9**, are in keeping with those reported in Sn–N compounds $Me_2SnCl(2\text{-}Pic)$,[31] $Me_2Sn(2\text{-}Pic)_2$[27] and $\{[^nBu_2Sn(2\text{-}Pic)]_2O\}_2$.[32]

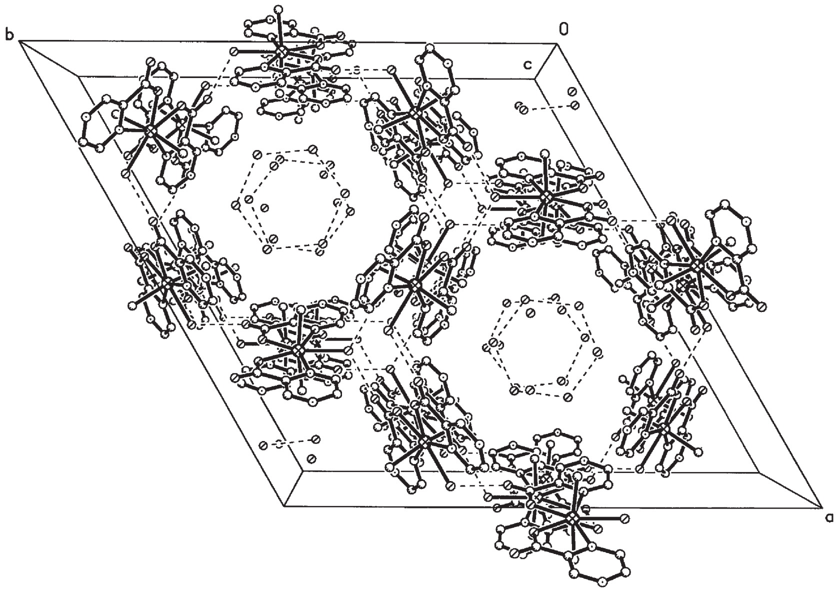


Fig. 4

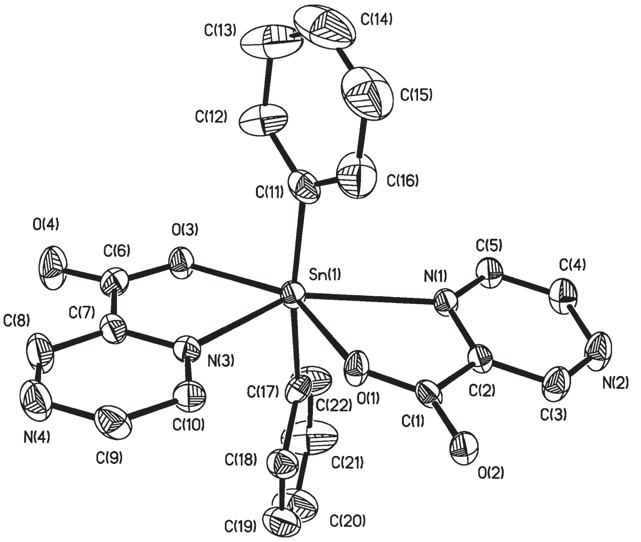


Fig. 5

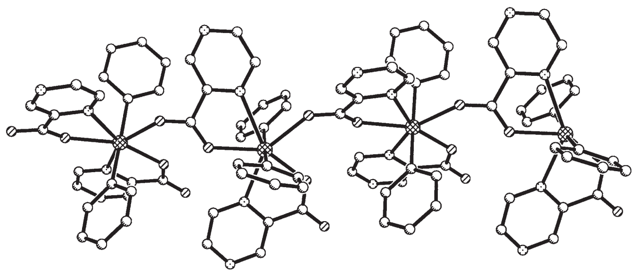


Fig. 6

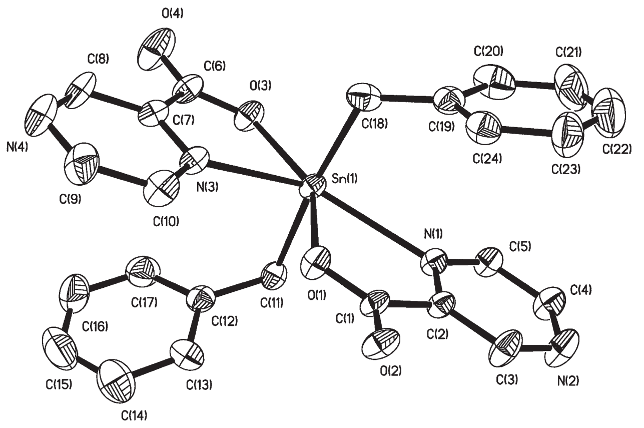


Fig. 7

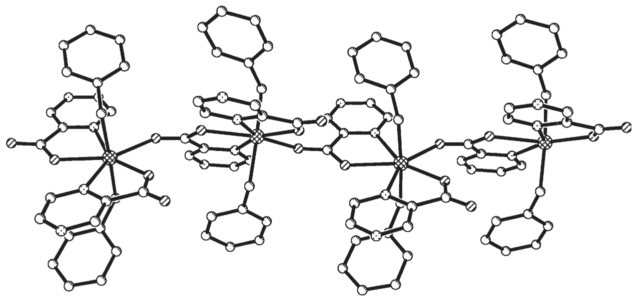


Fig. 8

Table 4 Selected bond lengths (Å) and bond angles (°) for compounds **8** and **9**

(Ph)$_2$Sn(pca)$_2$ **8**			
Sn(1)–C(17)	2.106(6)	Sn(1)–O(2)#1	2.319(4)
Sn(1)–C(11)	2.116(7)	Sn(1)–N(3)	2.396(5)
Sn(1)–O(3)	2.180(4)	Sn(1)–N(1)	2.638(4)
Sn(1)–O(1)	2.260(4)	Sn(1)#2–O(2)	2.319(4)
C(17)–Sn(1)–C(11)	171.2(2)	C(11)–Sn(1)–N(3)	93.2(2)
C(17)–Sn(1)–O(3)	91.41(19)	O(3)–Sn(1)–N(3)	70.85(16)
C(11)–Sn(1)–O(3)	93.4(2)	O(1)–Sn(1)–N(3)	72.75(15)
C(17)–Sn(1)–O(1)	89.54(19)	O(2)#1–Sn(1)–N(3)	150.96(15)
C(11)–Sn(1)–O(1)	90.9(2)	C(17)–Sn(1)–N(1)	82.13(18)
O(3)–Sn(1)–O(1)	143.51(14)	C(11)–Sn(1)–N(1)	90.1(2)
C(17)–Sn(1)–O(2)#1	91.22(19)	O(3)–Sn(1)–N(1)	150.67(14)
C(11)–Sn(1)–O(2)#1	82.3(2)	O(1)–Sn(1)–N(1)	65.38(13)
O(3)–Sn(1)–O(2)#1	80.76(14)	O(2)#1–Sn(1)–N(1)	70.68(13)
O(1)–Sn(1)–O(2)#1	135.69(13)	N(1)–Sn(1)–N(3)	138.05(15)
C(17)–Sn(1)–N(3)	95.4(2)		
(PhCH$_2$)$_2$Sn(pca)$_2$ **9**			
Sn(1)–C(18)	2.129(7)	Sn(1)–O(1)	2.327(5)
Sn(1)–C(11)	2.138(7)	Sn(1)–N(3)	2.422(6)
Sn(1)–O(3)	2.191(5)	Sn(1)–N(1)	2.632(5)
Sn(1)–O(2)#1	2.312(4)	Sn(1)#2–O(2)	2.312(4)
C(18)–Sn(1)–C(11)	174.0(3)	C(11)–Sn(1)–N(3)	94.8(2)
C(18)–Sn(1)–O(3)	93.4(2)	O(3)–Sn(1)–N(3)	70.04(18)
C(11)–Sn(1)–O(3)	92.2(2)	O(2)#1–Sn(1)–N(3)	149.02(18)
C(18)–Sn(1)–O(2)#1	93.3(2)	O(1)–Sn(1)–N(3)	74.69(17)
C(11)–Sn(1)–O(2)#1	85.7(2)	C(18)–Sn(1)–N(1)	88.1(2)
O(3)–Sn(1)–O(2)#1	79.01(17)	C(11)–Sn(1)–N(1)	86.0(2)
C(18)–Sn(1)–O(1)	89.1(2)	O(3)–Sn(1)–N(1)	149.99(17)
C(11)–Sn(1)–O(1)	87.6(2)	O(2)#1–Sn(1)–N(1)	70.98(15)
O(3)–Sn(1)–O(1)	144.58(16)	O(1)–Sn(1)–N(1)	65.34(15)
O(2)#1–Sn(1)–O(1)	136.15(15)	N(1)–Sn(1)–N(3)	139.96(18)
C(18)–Sn(1)–N(3)	89.1(2)		

Crystal structure of (Et$_3$NH)$^+$[(CH$_3$)$_2$Sn(pca)$_2$Cl]$^-$ 10 and (Et$_3$NH)$^+$[(Ph)$_2$Sn(pca)$_2$Cl]$^-$·H$_2$O 12. The molecular structures are illustrated in Fig. 9 and Fig. 10, selected bond lengths (Å) and angles (°) are listed in Table 5. X-ray crystal structure analysis reveals that compound **10** is a stannate and contains a seven-coordinate tin atom. The geometry of the tin atom of the anion [(CH$_3$)$_2$Sn(pca)$_2$Cl]$^-$ is distorted pentagonal bipyramidal with C(11) and C(12) occupying the axial sites and the C(11)–Sn–C (12) is 174.6(3)°. Two oxygen atoms, two nitrogen atoms and one chlorine atom occupy the equatorial plane. The sum of the angles subtended at the tin atom in the pentagonal plane is 360.04°, so the atoms Sn(1), N(1), O(1), N(3), O(3) and Cl(1) are almost in the same plane where the Sn atom is only 0.0086 Å away from the equatorial plane. The Sn–Cl bond length is longer than those in C$_5$H$_4$C(SiMe$_2$)$_2$NSnCl (2.440 Å),[33] but much shorter than the sum of the van der Waal's radii of Sn and Cl(3.85 Å).[24] The Sn–N bond lengths (2.552(4) and 2.577(5) Å) are appreciably greater than those for the pentagonal bipyramidal neutral compounds [(CH$_3$)$_2$Sn(C$_3$H$_2$N$_2$Me$_2$)$_2$] (Sn–N 2.378 Å)[34] and [(CH$_3$)$_2$SnS$_2$(C$_3$H$_3$N$_2$Me)$_2$] (Sn–N 2.351 Å),[35] but much shorter than the sum of the van der Waal's radii of Sn and N, 3.74 Å,[23] indicating the coordination at these sites.

Compound **12** is similar to compound **10**, but there are some differences between the two compounds. The biggest difference exists in the coordinate formation of the ligand. In compound

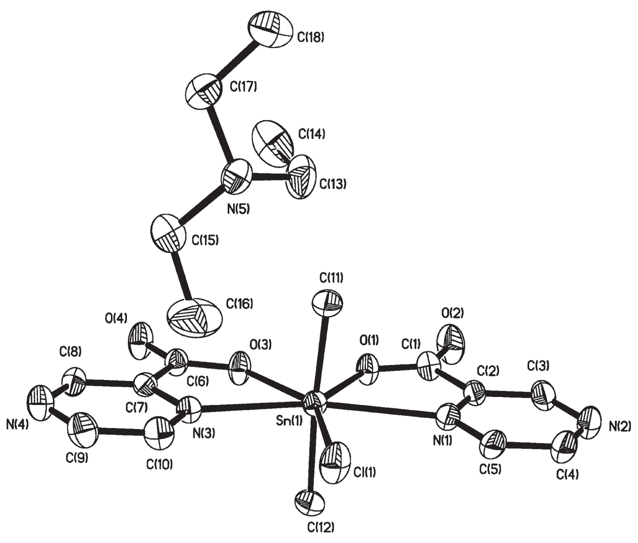


Fig. 9

Table 5 Selected bond lengths (Å) and bond angles (°) for compounds **10** and **12**

$[Et_3H]^+[(CH_3)_2Sn(pca)_2Cl]^-$ **10**			
Sn(1)–C(12)	2.092(6)	Sn(1)–N(3)	2.552(4)
Sn(1)–C(11)	2.104(6)	Sn(1)–N(1)	2.577(5)
Sn(1)–O(1)	2.256(4)	Sn(1)–Cl(1)	2.687(3)
Sn(1)–O(3)	2.204(3)		
C(12)–Sn(1)–C(11)	174.6(3)	C(11)–Sn(1)–N(1)	87.8(2)
C(12)–Sn(1)–O(3)	92.3(2)	O(3)–Sn(1)–N(1)	138.34(13)
C(11)–Sn(1)–O(3)	93.2(2)	O(1)–Sn(1)–N(1)	66.44(14)
C(12)–Sn(1)–O(1)	91.0(2)	N(3)–Sn(1)–N(1)	154.11(14)
C(11)–Sn(1)–O(1)	90.8(2)	C(12)–Sn(1)–Cl(1)	87.4(2)
O(3)–Sn(1)–O(1)	71.90(14)	C(11)–Sn(1)–Cl(1)	88.1(2)
C(12)–Sn(1)–N(3)	92.5(2)	O(3)–Sn(1)–Cl(1)	144.17(10)
C(11)–Sn(1)–N(3)	89.5(2)	O(1)–Sn(1)–Cl(1)	143.92(10)
O(3)–Sn(1)–N(3)	67.51(13)	N(3)–Sn(1)–Cl(1)	76.71(10)
O(1)–Sn(1)–N(3)	139.36(12)	N(1)–Sn(1)–Cl(1)	77.48(11)
C(12)–Sn(1)–N(1)	88.2(2)		
$[Et_3H]^+[(Ph)_2Sn(pca)_2Cl]^-\cdot H_2O$ **12**			
Sn(1)–C(11)	2.128(6)	Sn(1)–O(1)	2.323(4)
Sn(1)–C(17)	2.131(6)	Sn(1)–O(2)	2.465(4)
Sn(1)–O(3)	2.281(4)	Sn(1)–Cl(1)	2.4793(19)
Sn(1)–N(3)	2.566(5)		
C(11)–Sn(1)–C(17)	169.6(2)	C(17)–Sn(1)–Cl(1)	94.43(17)
C(11)–Sn(1)–O(3)	89.09(19)	O(3)–Sn(1)–Cl(1)	82.50(10)
C(17)–Sn(1)–O(3)	89.45(19)	O(1)–Sn(1)–Cl(1)	83.70(12)
C(11)–Sn(1)–O(1)	92.65(18)	O(2)–Sn(1)–Cl(1)	137.92(12)
C(17)–Sn(1)–O(1)	91.14(19)	C(11)–Sn(1)–N(3)	85.23(19)
O(3)–Sn(1)–O(1)	166.19(16)	C(17)–Sn(1)–N(3)	84.69(18)
C(11)–Sn(1)–O(2)	86.9(2)	O(3)–Sn(1)–N(3)	67.23(15)
C(17)–Sn(1)–O(2)	87.5(2)	O(1)–Sn(1)–N(3)	126.56(16)
O(3)–Sn(1)–O(2)	139.58(15)	O(2)–Sn(1)–N(3)	72.36(16)
O(1)–Sn(1)–O(2)	54.22(15)	N(3)–Sn(1)–Cl(1)	149.71(13)
C(11)–Sn(1)–Cl(1)	95.66(19)		

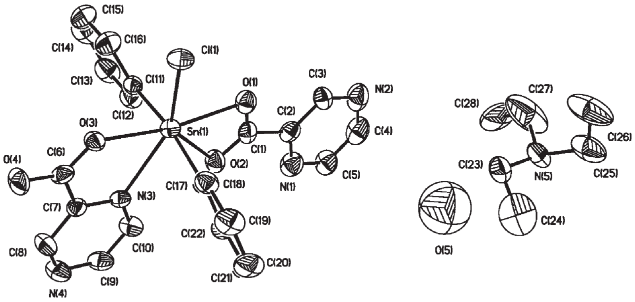


Fig. 10

10, both ligands chelate to one tin, bonding through one carboxylic oxygen atom and the nitrogen atom (mode **A**). However, for compound **12**, one ligand chelates to tin through one carboxylic oxygen atom and the nitrogen atom, the other through two oxygen atoms of the carboxyl (mode **D**). The result suggests that in the presence of $(Et_3NH)^+$ the spatial resistances from two phenyl groups are strong enough to prevent the other five-member metallacyclic systems forming through oxygen and the nitrogen atom chelating to the central tin atom, producing the less steric effect four-member metallacyclic system through two oxygen atoms of one carboxyl. The geometry of the tin atom in the anion $[(Ph)_2Sn(pca)_2Cl]^-$ is distorted pentagonal bipyramidal with C(11) and C(12) occupying the axial sites and the C(11)–Sn–C(17) is 169.6(2)°. Three oxygen atoms, one nitrogen atom and one chlorine atom occupy the equatorial plane. The sum of the angles between the tin atom and the pentagonal plane is 360.01°, so the atoms Sn(1), N(1), O(1), O(3), O(3) and Cl(1) are almost in the same plane with mean deviation from plane of 0.01196 Å.

However, co-crystallization is found in the crystals and the co-crystallized solvent is water with the molar ratio $[(Ph)_2Sn(pca)_2Cl] : H_2O$ of 1 : 1. The interaction between anion and the ammonium cation results in hydrogen bond N(5)H···O(4) 2.747 Å. The oxygen atom O(5) of the water molecule interacts with the two anions to give hydrogen bonds O(5)H···O(4) 2.834 Å and O(5)H–O(2)#1 2.912 Å [$x, y, z - 1$], forming a zigzag polymeric chain.

Conclusion

The 2-pyrazinecarboxylic acid has been shown to be able to form monomeric, stannate, polymeric and trinuclear macrocyclic compounds. The nuclearity and stiochiometry 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 and stannate compounds, the ligand is bidentate and the coordinate number of the tin atom is seven. The trinuclear macrocyclic compounds possess six-coordinate tin atoms and the ligand is tridentate. In the polymeric compounds, the seventh coordinate atoms are not held in the coordination sphere of tin as part of a bi- or tridentate ligand system. Preliminary studies show that 2-pyrazinecarboxylic acid has potential for the design of heteromulti-metallic systems containing both transition and post-transition metals.

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