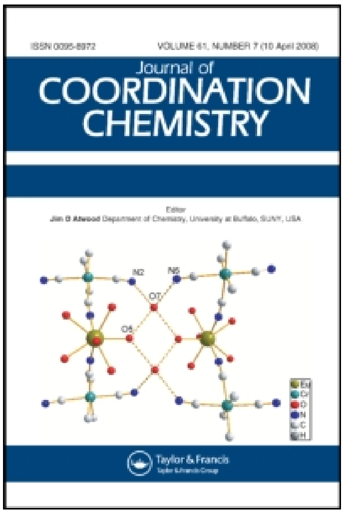

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Syntheses, spectroscopic characterizations and crystal structures of diorganotin(IV)-oxo-carboxylates with 2-pyrazinecarboxylic acid or (2-pyrimidylthio)acetic acid

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Eight diorganotin(IV)-oxo-carboxylates $\{[R_2Sn(O(O)CR')]_2O\}_2 \cdot Y$ ($R' = C_4H_3N_2$ $Y = H_2O$ $R = {}^nBu$ **1**, $Y = 0$ $R = Me$ **2**, $Y = 0$ $R = C_6H_5$ **3**, $Y = 0$ $R = C_6H_5CH_2$ **4**; $R' = CH_2SC_4H_3N_2$-2,6 $Y = 0$ $R = {}^nBu$ **5**, $Y = CH_2Cl_2$ $R = Me$ **6**, $Y = 0$ $R = C_6H_5$ **7**, $Y = 0$ $R = C_6H_5CH_2$ **8**) have been prepared in 1 : 1 molar ratios by reactions of diorganotin(IV) oxide with 2-pyrazinecarboxylic acid or (2-pyrimidylthio)acetic acid, respectively. All the complexes are characterized by elemental analysis, IR, ^1H NMR and ^{13}C NMR spectra. Except for **2**, **4** and **7**, the complexes are also characterized by X-ray crystallography diffraction analyses, which reveal that the complexes adopt the familiar dicarboxylato tetraorganodistannoxane structural mode. Among them, the evident difference is that weak intramolecular interactions between Sn and N atoms are recognized in complexes **1** and **3**. However, for complex **5** two different coordination modes are found in the same lattice.

Keywords: Diorganotin(IV) oxide; 2-Pyrazinecarboxylic acid; (2-Pyrimidylthio)acetic acid; Tetranuclear centrosymmetric dimeric

1. Introduction

Organotin(IV) carboxylate derivatives were extensively studied due to their biological activities [1]. In general, the biochemical activity of organotin(IV) carboxylates is influenced by the structure of the molecule and the coordination number of the tin [2–4]. Crystallographic investigations on these compounds have revealed that the structure depends on the steric bulk of the hydrocarbon groups bonded to tin or the ligand and their electronic effects [5]; with a 1 : 1 (tin/ligand) ratio five types of structures have been observed for organotin(IV) carboxylates assuming that additional coordination to tin originates only from carboxylate oxygen atoms. All structures adopt the dimeric dicarboxylatorganodistannoxanes [6] with a central distannoxane motif [7–9].

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Despite extensive studies being carried out, reports on coordination of additional heteroatoms to Sn are rare [10, 11]. Our current interest is whether the existence of more than one coordination active nitrogen atom influences the coordination mode. We designed a series of experiments of diorganotin(IV) oxide with 2-pyrazinecarboxylic acid or (2-pyrimidylthio)acetic acid and obtained eight diorganotin ladder complexes **1**–**8** of the type $\{[R_2Sn(O(O)CR')]_2O\}_2 \cdot Y$ ($R' = C_4H_3N_2 Y = H_2O R = {}^nBu$ **1**, $Y = 0$ $R = Me$ **2**, $Y = 0 R = C_6H_5$ **3**, $Y = 0 R = C_6H_5CH_2$ **4**; $R' = CH_2SC_4H_3N_2$-2,6$Y = 0$ $R = {}^nBu$ **5**, $Y = CH_2Cl_2 R = Me$ **6**, $Y = 0 R = C_6H_5$ **7**, $Y = 0 R = C_6H_5CH_2$ **8**).

2. Experimental

2.1. *Materials and measurements*

Dimethyltin oxide, di-*n*-butyltin oxide, diphenyltin oxide, dibenzyltin oxide, 2-pyrazinecarboxylic acid and (2-pyrimidylthio)acetic acids are commercially available, and were used without further purification. Melting points were obtained with a 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 and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 400.1 spectrometer at 400 and 100.6 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 external tetramethylsilane (TMS). Elemental analyses were performed with a PE-2400II apparatus.

2.2. *Syntheses*

2.2.1. Synthesis of $\{[^nBu_2Sn(O_2CC_4H_3N_2)]_2O\}_2 \cdot H_2O$ (1). The di-*n*-butyltin oxide (0.496 g, 2 mmol) and 2-pyrazinecarboxylic acid (0.248 g, 2 mmol) in benzene solution (30 mL) in a Schlenk flask gives a clear solution within 15 min. Refluxing was continued for 10 h and then the solvent gradually removed by evaporation under vacuum until solid product is obtained. The solid recrystallized from ethyl ether and white crystal complex **1** is formed. Yield: 81%, m.p. 106–108°C. Anal. Found: C, 42.18; H, 6.00; N, 7.49. Calcd for $C_{52}H_{86}N_8O_{11}Sn_4$: C, 42.37; H, 5.88; N, 7.60%. IR (KBr, cm^{-1}): 3231, 1667, 1601, 1377, 1599, 621, 576, 476, 445. ^1H NMR ($CDCl_3$-D_2O, ppm): δ 0.90(t, 24), 1.34–1.67(m, 48), 3.24(s, 2H), 8.57(dd, 4H), 8.86(d, 4H), 9.49(d, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 26.6, 27.2, 26.3, 26.5, 25.6, 25.5, 12.8, 13.3, 143.2, 146.1, 147.5, 148.1, 174.2.

2.2.2. Synthesis of $\{[(CH_3)_2Sn(O_2CC_4H_3N_2)]_2O\}_2$ (2). Complex **2** is prepared in the same way as complex **1**, by adding dimethyltin oxide (0.330 g, 2 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol). The solid is then obtained from ethyl ether. Yield: 79%, m.p. 157–159°C. Anal. Found: C, 30.13; H, 3.04; N, 10.09. Calcd for $C_{28}H_{36}N_8O_{10}Sn_4$: C, 30.04; H, 3.24; N, 10.01%. IR (KBr, cm^{-1}): 1647, 1611, 1374, 1587, 620, 572, 479, 444. ^1H NMR ($CDCl_3$-D_2O, ppm): δ 0.98(s, 24H), 8.62(dd, 4H), 8.81(d, 4H), 9.48(d, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 10.2, 143.6, 145.4, 147.1, 147.5, 173.5.

2.2.3. Synthesis of $\{[(C_6H_5)_2Sn(O_2CC_4H_3N_2)]_2O\}_2$ (3). Complex **3** is prepared in the same way as complex **1**, by adding diphenyltin oxide (0.598 g, 2 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol). The solid is then recrystallized from ethyl ether and the white crystal complex **3** is formed. Yield: 90%, m.p. >210°C (dec.). Anal. Found: C, 50.71; H, 3.09; N, 7.12. Calcd for $C_{68}H_{52}N_8O_{10}Sn_4$: C, 50.54; H, 3.24; N, 6.93%. IR (KBr, cm^{-1}): 1654, 1618, 1612, 1409, 1382, 619, 586, 493, 455. ^{1}H NMR ($CDCl_3$, ppm): δ 7.26–7.82(m, 40H), 8.69(dd, 4H), 8.91(d, 4H), 9.39(d, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 128.5, 131.1, 136.4, 148.3, 143.7, 144.8, 147.2, 147.9, 173.1.

2.2.4. Synthesis of $\{[(C_6H_5CH_2)_2Sn(O_2CC_4H_3N_2)]_2O\}_2$ (4). Complex **4** is prepared in the same way as complex **1**, by adding dibenzyltin oxide (0.634 g, 2 mmol) to 2-pyrazinecarboxylic acid (0.248 g, 2 mmol). The solid is then obtained from ethyl ether. Yield: 91%, m.p. > 210°C (dec.). Anal. Found: C, 52.73; H, 3.79; N, 6.34. Calcd for $C_{76}H_{68}N_8O_{10}Sn_4$: C, 52.82; H, 3.97; N, 6.48%. IR (KBr, cm^{-1}): 1635, 1615, 1393, 1381, 622, 579, 484, 461. ^{1}H NMR ($CDCl_3$, ppm): δ 3.12(s, 16H), 7.30–7.64(m, 40H), 8.61(dd, 4H), 8.83(d, 4H), 9.36(d, 4H). ^{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.

2.2.5. Synthesis of $\{[^nBu_2Sn(O_2CCH_2SN_2H_3C_4\text{-}2,6)]_2O\}_2$ (5). Complex **5** is prepared in the same way as complex **1**, by adding di-*n*-butyltin oxide (0.496 g, 2 mmol) to (2-pyrimidylthio)acetic acid (0.340 g, 2 mmol). The solid is then recrystallized from ethyl ether giving light-yellow crystals of complex **5**. Yield: 81%, m.p. 86–88°C. Anal. Found: C, 40.96; H, 5.62; N, 6.64. Calcd for $C_{56}H_{92}N_8O_{10}S_4Sn_4$: C, 41.00; H, 5.65; N, 6.83%. IR (KBr, cm^{-1}): 1653, 1608, 1414, 1384, 640, 558, 492. ^{1}H NMR ($CDCl_3$, ppm): δ 0.87–0.94(t, 24H), 1.16–1.61(m, 48H), 3.65(s, 8H), 7.10(m, 4H), 8.95(d, 8H).^{13}C NMR ($CDCl_3$, ppm): δ 27.5, 27.4, 27.0, 26.8, 225.0, 23.8, 14.1, 13.6, 169.7.

2.2.6. Synthesis of $\{[(CH_3)_2Sn(O_2CCH_2SN_2H_3C_4\text{-}2,6)]_2O\}_2 \cdot CH_2Cl_2$ (6). Complex **6** is prepared in the same way as complex **1**, by adding dimethyltin oxide (0.330 g, 2 mmol) to (2-pyrimidylthio)acetic acid (0.340 g, 2 mmol). The solid is then recrystallized from ethyl ether and light-yellow **6** is formed. Yield: 85%, m.p. 196–198°C. Anal. Found: C, 28.26; H, 3.42; N, 8.24. Calcd for $C_{33}H_{46}N_8O_{10}S_4Sn_4$: C, 28.54; H, 3.34; N, 8.07%. IR (KBr, cm^{-1}): 1648, 1601, 1410, 1376, 637, 541, 479. ^{1}H NMR ($CDCl_3$, ppm): δ 0.74(s, 24H), 3.72 (s, 8H), 7.26(m, 4H), 8.55(d, 8H). ^{13}C NMR ($CDCl_3$, ppm): δ 12.0, 54.2, 172.4.

2.2.7. Synthesis of $\{[(C_6H_5)_2Sn(O_2CCH_2SN_2H_3C_4\text{-}2,6)]_2O\}_2$ (7). Complex **7** is prepared in the same way as complex **1**, by adding diphenyltin oxide (0.598 g, 2 mmol) to (2-pyrimidylthio)acetic acid (0.340 g, 2 mmol). The solid is then obtained from ethyl ether. Yield: 75%, m.p. 190–192°C. Anal. Found: C, 47.86; H, 3.59; N, 6.54. Calcd for $C_{72}H_{60}N_8O_{10}S_4Sn_4$: C, 48.03; H, 3.36; N, 6.33%. IR (KBr, cm^{-1}): 1643, 1623, 1603, 1384, 634, 572, 488. ^{1}H NMR ($CDCl_3$, ppm): δ 3.61(s, 8H), 7.24–7.73(m, 40H), 3.87 (s, 8H), 7.23(m, 4H), 8.62(d, 8H). ^{13}C NMR ($CDCl_3$, ppm): δ 128.5, 131.1, 136.4, 173.1.

2.2.8. Synthesis of {[$(C_6H_5CH_2)_2Sn(O_2CCH_2SN_2H_3C_4\text{-}2,6)$]$_2$O}$_2$ (8). Complex **8** is prepared in the same way as complex **1**, by adding dibenzyltin oxide (0.634 g, 2 mmol) to (2-pyrimidylthio)acetic acid (0.340 g, 2 mmol). The solid is then recrystallized from ethyl ether and the light-yellow crystal complex **8** is formed. Yield: 76%, m.p. 112–114°C. Anal. Found: C, 49.99; H, 4.02; N, 5.65. Calcd for $C_{80}H_{76}N_8O_{10}S_4Sn_4$: C, 50.24; H, 4.01; N, 5.86%. IR (KBr, cm^{-1}): 1642, 1611, 1548, 1501, 1452, 1376, 635, 567, 481. ^{1}H NMR ($CDCl_3$, ppm): δ 3.19(s, 16H), 7.31–7.58(m, 40H), 3.66 (s, 8H). ^{13}C NMR ($CDCl_3$, ppm): δ 34.4, 125.6, 128.6, 129.7, 139.3, 172.8.

2.3. *X-ray crystallographic studies*

Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Smart CCD area-detector with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ 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.

3. Results and discussion

3.1. *Synthetic aspects*

Reactions of diorganotin oxide with 2-pyrazinecarboxylic acid or (2-pyrimidylthio) acetic acid, respectively, in 1 : 1 stoichiometry in refluxing benzene afford air-stable complexes **1**–**8**, respectively. The synthetic procedure is shown in scheme 1.

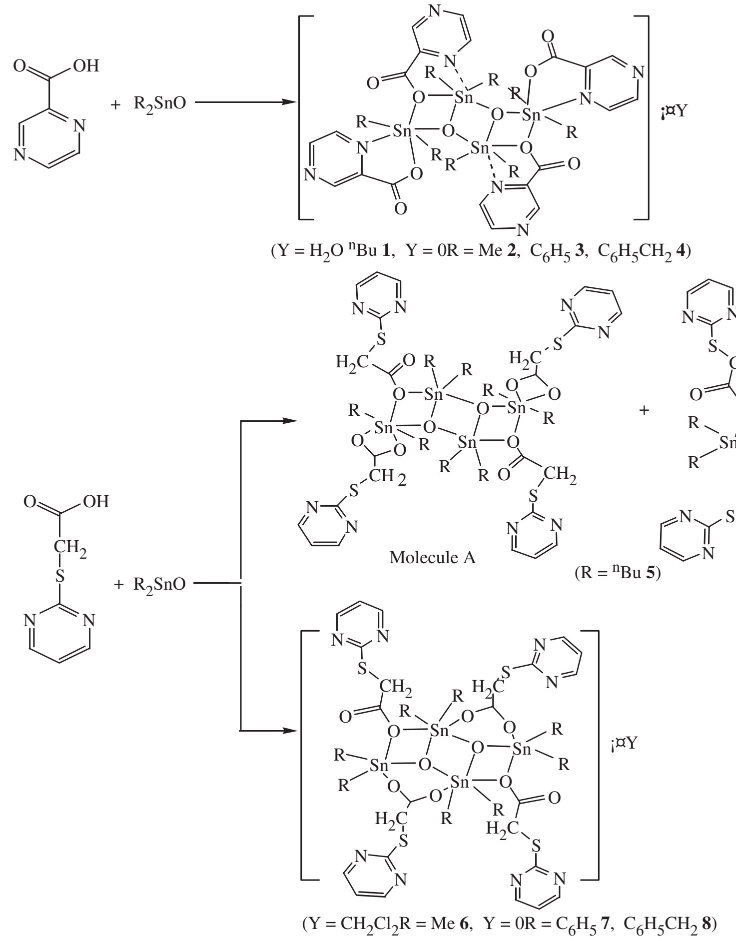
3.2. *Spectroscopic studies*

3.2.1. IR spectroscopy. The stretching frequencies of interest are those associated with the carboxylate (COO), Sn–C and Sn–O groups. The strong absorption in the region of 476–493 cm^{-1} in spectra of complexes **1**–**8**, which is absent in the spectrum of the free ligand, is assigned to the Sn–O stretch. These values are consistent with those for a number of organotin(IV)-oxygen derivatives [12, 13]. The observation of two Sn–C absorption bands in the 558–586 cm^{-1} regions reveals a non-linear trans configuration of the C–Sn–C moiety [14]. A strong band in the region of 619–640 cm^{-1} is assigned to ν(Sn–O–Sn), indicating Sn–O–Sn bridged structure.

For complexes **1**–**4**, the ν(C=N) band, occurring at about 1601, 1611, 1612, 1615, 1608, 1601, 1603 and 1601 cm^{-1} for complex **1**–**8**, respectively, is considerably shifted towards lower frequency with respect to that of the free ligand (1620 cm^{-1}), confirming coordination of the heterocyclic N to the tin. The stretching frequency is lowered due to

Table 1. Crystal, data collection and structure refinement parameters for complexes **3**, **5**, **6** and **8**.

Complex	**3**	**5**	**6**	**8**
Empirical formula	$C_{68}H_{52}N_8O_{10}Sn_4$	$C_{56}H_{92}N_8O_{10}S_4Sn_4$	$C_{33}H_{46}Cl_2N_8O_{10}S_4Sn_4$	$C_{80}H_{76}N_8O_{10}S_4Sn_4$
Formula weight	1615.94	1638.36	1388.68	1912.49
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimension				
a (Å)	13.949(5)	13.884(12)	7.303(4)	11.323(3)
b (Å)	16.458(6)	14.345(12)	11.466(7)	15.044(4)
c (Å)	14.432(5)	21.369(18)	15.646(10)	23.665(6)
α (°)	90	98.273(13)	90.522(8)	90.172(4)
β (°)	104.273(5)	104.156(12)	94.703(8)	92.093(4)
γ (°)	90	113.619(11)	107.889(8)	91.432(4)
Z	2	2	1	2
Absorption coefficient (mm^{-1})	1.603	1.525	2.321	1.577
Crystal size (mm^3)	0.34 × 0.26 × 0.20	0.42 × 0.29 × 0.22	0.47 × 0.39 × 0.24	0.47 × 0.41 × 0.28
θ range for data collection (°)	2.34 to 25.03	1.61 to 25.03	1.87 to 25.03	1.72 to 25.03
Index ranges	$-15 \leq h \leq 16$; $-19 \leq k \leq 11$; $-16 \leq l \leq 17$	$-16 \leq h \leq 16$; $-17 \leq k \leq 9$; $-24 \leq l \leq 25$	$-8 \leq h \leq 8$; $-13 \leq k \leq 13$; $-15 \leq l \leq 18$	$-8 \leq h \leq 13$; $-15 \leq k \leq 17$; $-28 \leq l \leq 25$
Reflections collected	16,550	19,168	6491	21,091
Unique reflections	5673($R_{int} = 0.0366$)	12657($R_{int} = 0.0247$)	4314($R_{int} = 0.0157$)	13967($R_{int} = 0.0294$)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5673/0/406	12657/26/739	4314/4/286	13967/168/955
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0303$, $wR_2 = 0.0539$	$R_1 = 0.0424$, $wR_2 = 0.0911$	$R_1 = 0.0261$, $wR_2 = 0.0664$	$R_1 = 0.0505$, $wR_2 = 0.1025$
R indices (all data)	$R_1 = 0.0539$, $wR_2 = 0.0600$	$R_1 = 0.0910$, $wR_2 = 0.1161$	$R_1 = 0.0368$, $wR_2 = 0.0752$	$R_1 = 0.1196$, $wR_2 = 0.1396$



(Y = H_2O ^{n}Bu **1**, Y = 0R = Me **2**, C_6H_5 **3**, $C_6H_5CH_2$ **4**)

(R = ^{n}Bu **5**)

(Y = CH_2Cl_2R = Me **6**, Y = 0R = C_6H_5 **7**, $C_6H_5CH_2$ **8**)

Scheme 1. Synthetic procedure of complexes **1**–**8**.

displacement of electron density from N to Sn atom, resulting in weakening of the C=N bond as reported in the literature [15]. The weak- or medium-intensity band at about 450 cm^{-1} can be assigned to Sn–N stretch. All these values are consistent with a number of organotin(IV) derivatives [16, 17].

In organotin carboxylate complexes, the IR spectra provide useful information concerning the coordination of the carboxylate. The magnitude of $\Delta\nu$ ($\Delta\nu = \nu_{as}(COO) - \nu_s(COO)$) of about 242–290 cm^{-1} for compounds **1**–**4** is larger than those for the corresponding sodium salts (236 cm^{-1}), which indicates monodentate carboxylate [18]. Moreover, the magnitude of $\Delta\nu$ of 239 and 279 cm^{-1} for complex **5**, 238 and 272 cm^{-1} for complex **6**, 239 and 259 for complex **7**, 190 and 266 for complex **8**, indicating both monodentate and bidentate carboxylate [19, 20].

3.2.2. NMR spectra. The ^{1}H NMR spectra show the expected integration and peak multiplicities. In the spectra of the free ligands, a single resonance at 7.46 and

8.51 ppm, respectively, absent in the spectra of the complexes indicates the replacement of the carboxylic acid proton by a diorganotin moiety on complex formation. In addition, the resonance at 3.65 ppm for complexes **5–8** is attributed to the protons of $-S-CH_2$.

The ^{13}C 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 electron density transfer from the ligand to the tin. Although at least two different types of carboxylate are present, only a single resonance in the ^{13}C spectra may indicate fast site exchange of the carboxylates.

3.3. *Molecule structure*

3.3.1. Structure of $\{[(C_6H_5)_2Sn(O_2CC_4H_3N_2)]_2O\}_2 \cdot$ (3). The molecular structure is illustrated in figure 1; selected bond lengths (Å) and angles (°) are listed in table 2. There are significant intramolecular contacts in the crystal lattice. The core geometry of the molecule consists of a centrosymmetric, planar, four-membered Sn_2O_2 ring with two additional $(C_6H_5)_2Sn(O(O)CC_4H_3N_2)$ units attached at each bridging oxygen atom, with the result that these oxygen atoms are three-coordinated. The two crystallographically unique 2-pyrazinecarboxylate ligands coordinate in different ways. The ligand containing the O(1) and O(2) atoms bridge two tin atoms only via O(1), Sn(1)–O(1) 2.358(2) Å and Sn(2)–O(1) 2.335(3) Å. The bond lengths Sn(1)–O(5)

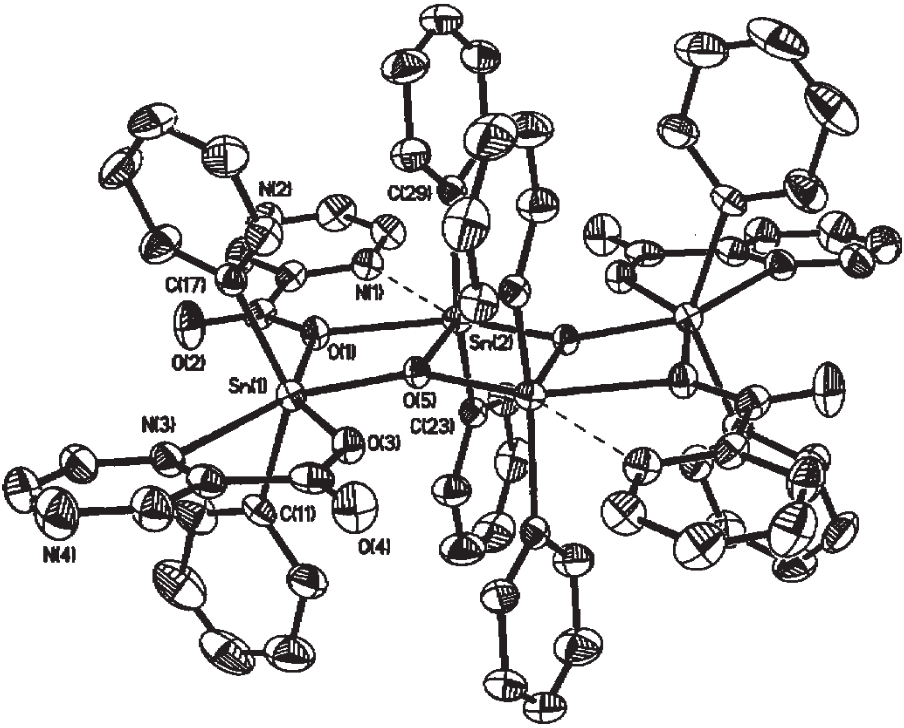


Figure 1. Molecular structure of complex **3**.

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

Sn(1)–O(5)	2.020(2)	Sn(1)–C(17)	2.117(4)
Sn(1)–C(11)	2.131(4)	Sn(1)–O(3)	2.148(2)
Sn(1)–O(1)	2.358(2)	Sn(1)–N(3)	2.720(3)
Sn(2)–O(5)	2.057(2)	Sn(2)–C(29)	2.113(4)
Sn(2)–C(23)	2.119(4)	Sn(2)#1–O(5)	2.128(2)
Sn(2)–O(1)	2.335(3)	Sn(2)–N(1)	2.927(3)
Sn(2)#1–O(3)	2.987(3)	O(1)–C(1)	1.310(4)
O(2)–C(1)	1.193(5)		
C(17)–Sn(1)–C(11)	139.64(17)	C(29)–Sn(2)–C(23)	142.65(15)
O(5)–Sn(1)–O(1)	69.58(9)	O(5)–Sn(1)–O(3)	77.41(9)
O(5)–Sn(1)–N(3)	143.08(10)	O(3)–Sn(1)–O(1)	146.99(9)
O(1)–Sn(1)–N(3)	147.25(10)	O(3)–Sn(1)–N(3)	65.72(10)
O(5)–Sn(2)–O(5)#1	73.01(10)	O(5)–Sn(2)–O(1)	69.49(8)
O(5)#1–Sn(2)–O(1)	142.49(8)	O(5)–Sn(2)–N(1)	130.00(9)
O(5)#1–Sn(2)–N(1)	156.83(9)	O(1)–Sn(2)–N(1)	60.55(9)
O(5)–Sn(2)–O(3)#1	131.46(8)	O(5)#1–Sn(2)–O(3)#1	58.46(8)
O(1)–Sn(2)–O(3)#1	159.04(7)	N(1)–Sn(2)–O(3)#1	98.49(9)

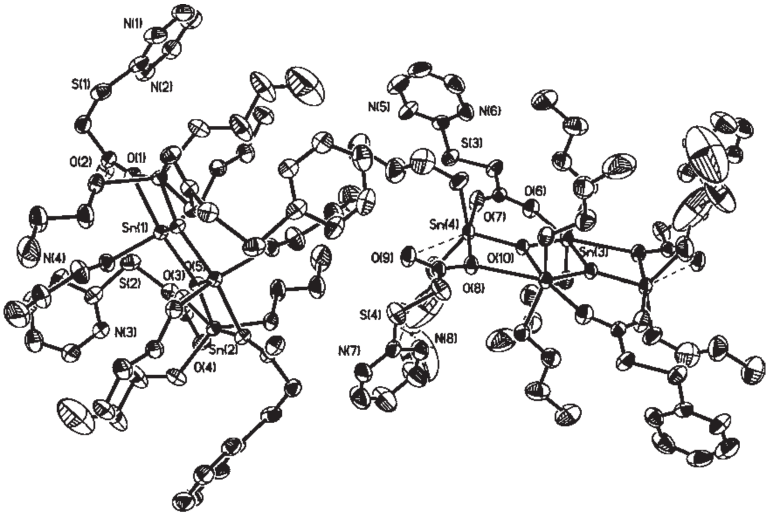
2.020(2) Å and Sn(2)–O(5) 2.057(2) Å are similar to those in $\{[^n\mathrm{Bu}_2\mathrm{Sn}(2\text{-pic})]_2\mathrm{O}\}_2$ (2.0544 and 2.110 Å) [21], near the sum of the covalent radii of Sn and O (2.13 Å) [22]. The nitrogen atom from the 2-pyrazine ring of this ligand makes close contact with Sn(1) at 2.720(3) Å, approaching the range recorded in the Cambridge Crystallographic Database from 2.27 to 2.58 Å [23] and significantly less than those in $\{[^n\mathrm{Bu}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CN}_2\mathrm{H}_3\mathrm{C}_4)]_2\mathrm{O}\}_2 \cdot \mathrm{H}_2\mathrm{O}$ [24]. Although the O(2) oxygen is 3.501 Å from Sn(1), a distance is slightly less than the sum of the Van der Waal's radii for Sn and O (3.68 Å) [22], it is not indicative of a significant bonding interaction.

The endocyclic tin atom, Sn(2), is five-coordinate to a first approximation and exists in a distorted trigonal bipyramidal environment, with two phenyl groups and the centrosymmetrically related bridging oxygen atom defining an approximate trigonal plane. The apical position is occupied by C(23) and C(29) from the ligand. The angle C(23)–Sn–C(29) is 142.65(15)°. If the weakly bonded Sn ⋯ N(1)#1 interaction $[-x+1, -y+1, -z+1]$ is included in the coordination polyhedron, the geometry about the tin atom can be considered as distorted octahedral. The exocyclic tin atom, Sn(1), forms six bonds including a longer bond to O(1). The geometry is highly distorted and the coordination sphere can be thought of as distorted octahedral, similar to Sn(2).

The crystal structure of **1** is similar to **3** and has been reported in our previous work [24].

3.3.2. Structure of $\{[^n\mathrm{Bu}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CSCH}_2\mathrm{C}_4\mathrm{H}_3\mathrm{N}_2\text{-}2,6)]_2\mathrm{O}\}_2$ (5). The crystal structure of **5** is illustrated in figure 2 and selected bond lengths (Å) and bond angles (°) are listed in table 3. There exist two monomers **A** and **B** in the asymmetric unit, with different structural types arising from coordination of the carboxylate ligand. The complex is a centrosymmetric dimer built up on the central cyclic $\mathrm{Sn}_2\mathrm{O}_2$ units. Two tin atoms are linked to this four-membered ring with two additional $^n\mathrm{Bu}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CCH}_2\mathrm{SC}_4\mathrm{H}_3\mathrm{N}_2\text{-}2,6)$ units attached at each bridging oxygen atom, with the result that the oxygen atoms of this ring are three-coordinated.

For molecule **A**, there are two types of tin. The endocyclic, Sn(1), is five-coordinate to a first approximation and exists in a distorted trigonal bipyramidal environment,



Molecule **A** Molecule **B**

Figure 2. Molecular structure of complex **5**.

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

Molecule **A**		Molecule **B**	
Sn(1)–O(5)#1	2.052(4)	Sn(3)–O(10)	2.066(4)
Sn(1)–C(17)	2.122(7)	Sn(3)–C(41)	2.112(7)
Sn(1)–C(13)	2.131(6)	Sn(3)–C(45)	2.131(7)
Sn(1)–O(5)	2.174(4)	Sn(3)–O(10)#2	2.173(4)
Sn(1)–O(1)	2.269(4	Sn(3)–O(6)	2.284(5)
Sn(1)–O(2)	3.126(5)	Sn(3)–O(8)#2	2.682(5)
Sn(2)–O(5)	2.019(4)	Sn(4)–O(10)	2.023(4)
Sn(2)–C(21)	2.104(6)	Sn(4)–C(49)	2.090(9)
Sn(2)–O(3)	2.115(4)	Sn(4)–O(8)	2.192(5)
Sn(2)–C(25)	2.116(7)	Sn(4)–C(53)	2.205(12)
Sn(2)–O(1)#1	2.539(4)	Sn(4)–O(7)	2.238(5)
Sn(2)–O(4)	2.896(5)	Sn(4)–O(9)	3.045(5)
C(17)–Sn(1)–C(13)	131.1(3)	C(41)–Sn(3)–C(45)	144.0(3)
O(5)#1–Sn(1)–O(5)	73.95(15)	O(10)–Sn(3)–O(10)#2	76.39(17)
O(5)#1–Sn(1)–O(1)	73.93(15)	O(10)–Sn(3)–O(6)	90.46(18)
O(5)–Sn(1)–O(1)	147.88(15)	O(10)#2–Sn(3)–O(6)	166.81(16)
O(5)#1–Sn(1)–O(2)	119.04(14)	O(10)–Sn(3)–O(8)#2	142.42(15)
O(1)–Sn(1)–O(2)	45.19(14)	O(10)#2–Sn(3)–O(8)#2	66.03(14)
C(21)–Sn(2)–C(25)	134.5(3)	O(6)–Sn(3)–O(8)#2	127.11(17)
O(5)–Sn(2)–O(3)	82.97(16)	C(49)–Sn(4)–C(53)	134.2(4)
O(5)–Sn(2)–O(1)#1	68.59(14)	O(10)–Sn(4)–O(8)	78.82(17)
O(3)–Sn(2)–O(1)#1	151.48(14)	O(10)–Sn(4)–O(7)	90.95(18)
O(5)–Sn(2)–O(4)	132.27(15)	O(8)–Sn(4)–O(7)	169.61(18)
O(3)–Sn(2)–O(4)	49.34(15)	O(10)–Sn(4)–O(9)	125.48(16)
O(1)#1–Sn(2)–O(4)	158.80(14)	O(8)–Sn(4)–O(9)	46.78(16)
		O(7)–Sn(4)–O(9)	143.53(17)

with the two n-butyl groups and the centrosymmetrically related bridging oxygen atom defining an approximate trigonal plane. The apical positions are occupied by C(11) and C(15) from the ligand. The C(13)–Sn–C(17), is 131.1(3)°. The exocyclic tin atom, Sn(2), forms four short bonds and two Sn–O bonds from two oxygen atoms of the ligand chelating the Sn. The longest Sn–O bond is 2.896(5) Å. The geometry is highly distorted, the coordination sphere can be thought of as distorted octahedral.

For molecule **B**, Sn(3) atom is bonded to two carbon and four oxygen atoms, the longest Sn–O bond is 2.682(5) Å, Sn(3)–O(8)#2 [$-x+1$, $-y$, $-z+1$], while the others are between 2.066(4) and 2.284(5) Å. Two of the carboxylate ligands are bidentate and bridge a pair of tin atoms; the other two carboxylates are monodentate and coordinate to each exocyclic tin atom. The coordination geometry of Sn(3) is a distorted octahedron. The C(21) and C(25) atoms occupy the apical sites and C(21)–Sn(2)–C(25) is 144.0(3)°. The coordination sphere of Sn(4) consists of two carbon and three oxygen atoms, with Sn(1)–O bond lengths of 2.023(4) to 2.238(5) Å. There is, in addition, a weak intramolecular interaction, Sn(4)–O(9), 3.045(5) Å, which derives from the monodentate carboxylate group. Interestingly, the directionality of this weak interaction involving the exocyclic tin almost mimics that of the endocyclic tin. The angles in the central Sn_2O_2 ring are 76.39(17)° and 103.61(17)°.

3.3.3. Structures of $\{[(CH_3)_2Sn(O_2CSCH_2C_4H_3N_2\text{-}2,6)]_2O\}_2 \cdot CH_2Cl_2$ (6) and $\{[(C_6H_5CH_2)_2Sn(O_2CSCH_2C_4H_3N_2\text{-}2,6)]_2O\}_2$ (8). The crystal structures of complexes **6** and **8** are illustrated in figures 3 and 4, respectively. Selected bond lengths (Å) and bond angles (°) are in table 4. For complex **8**, the conformations of the two independent molecules **A** and **B** are almost the same, with only small differences in bond lengths and bond angles. For both complexes **6** and **8**, similar to molecule **B** of **5**, the Sn atoms are bonded to two carbon and four oxygen atoms, the longest Sn–O bonds are Sn(1)–O(3)

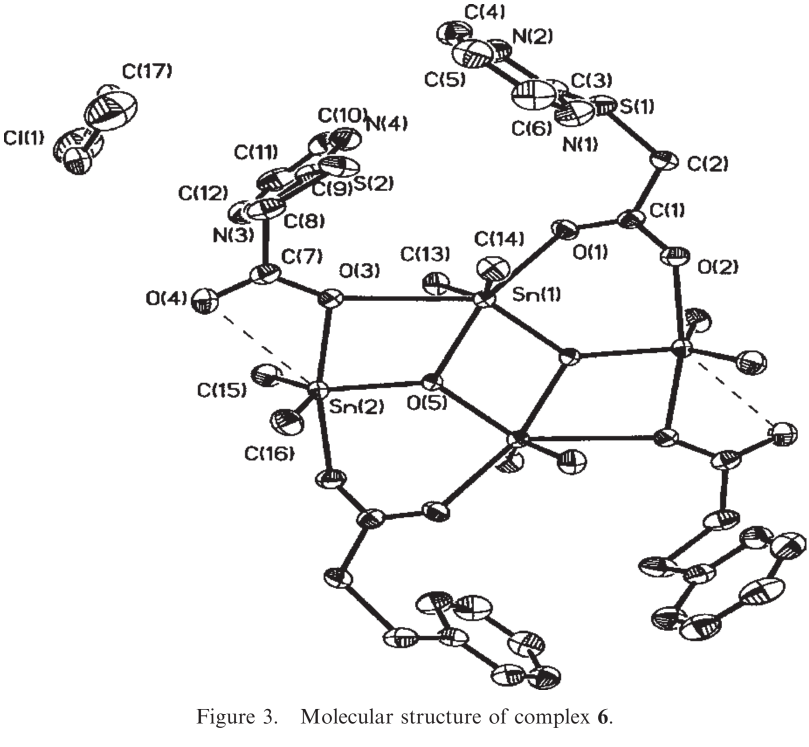
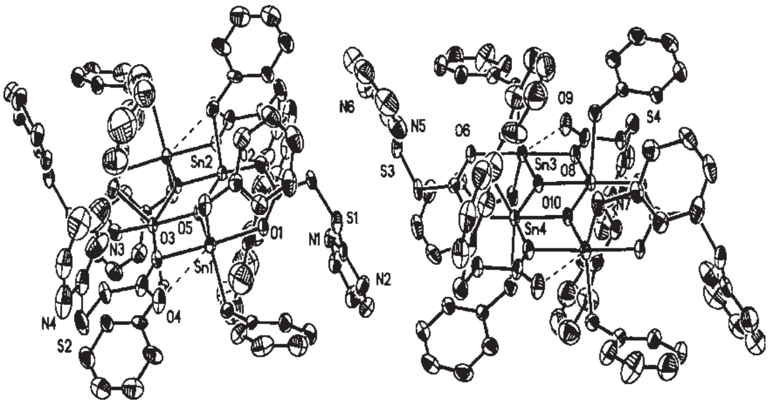


Figure 3. Molecular structure of complex **6**.



Molecule **A** Molecule **B**

Figure 4. Molecular structure of complex **8**.

Table 4. Selected bond lengths (Å) and angles (°) for complexes **6** and **8**.

6			
Sn(1)–O(5)#1	2.044(3)	Sn(2)–O(5)	2.024(3)
Sn(1)–C(14)	2.102(4)	Sn(2)–C(16)	2.095(5)
Sn(1)–C(13)	2.107(4)	Sn(2)–C(15)	2.106(5)
Sn(1)–O(5)	2.143(3)	Sn(2)–O(3)	2.167(3)
Sn(1)–O(3)	2.805(3)	Sn(2)–O(2)#1	2.245(3)
Sn(1)–O(1)	2.282(3)	Sn(2)–O(4)	2.937(3)
C(14)–Sn(1)–C(13)	144.13(19)	C(16)–Sn(2)–C(15)	138.1(2)
O(5)#1–Sn(1)–O(5)	75.46(11)	O(5)–Sn(2)–O(3)	78.84(10)
O(5)#1–Sn(1)–O(1)	88.12(11)	O(5)–Sn(2)–O(2)#1	89.25(11)
O(5)–Sn(1)–O(1)	162.27(10)	O(5)–Sn(2)–O(4)	126.90(10)
O(5)–Sn(1)–O(3)	63.50(9)	O(3)–Sn(2)–O(2)#1	166.59(11)
O(3)–Sn(1)–O(1)	133.41(10)	O(3)–Sn(2)–O(4)	48.43(10)
O(5)#1–Sn(1)–O(3)	138.43(9)		
8			
Molecule **A**		Molecule **B**	
Sn(1)–O(5)	2.028(5)	Sn(3)–O(10)	2.035(5)
Sn(1)–C(20)	2.117(8)	Sn(3)–C(53)	2.136(8)
Sn(1)–C(13)	2.152(7)	Sn(3)–C(60)	2.148(8)
Sn(1)–O(3)	2.182(5)	Sn(3)–O(8)	2.174(5)
Sn(1)–O(1)	2.198(5)	Sn(3)–O(6)	2.229(5)
Sn(1)–O(4)	3.051(7)	Sn(3)–O(9)	2.998(6)
Sn(2)–O(5)	2.062(5)	Sn(4)–O(10)	2.063(5)
Sn(2)–C(27)	2.129(8)	Sn(4)–C(74)	2.142(8)
Sn(2)–C(34)	2.153(8)	Sn(4)–C(67)	2.152(8)
Sn(2)–O(2)	2.319(5)	Sn(4)–O(7)	2.312(6)
Sn(2)–O(5)#1	2.129(4)	Sn(4)–O(10)#2	2.125(4)
Sn(2)–O(3)#1	2.620(6)	Sn(4)–O(8)#2	2.657(6)
C(20)–Sn(1)–C(13)	128.2(7)	C(53)–Sn(3)–C(60)	129.4(4)
O(5)–Sn(1)–O(3)	76.9(2)	O(10)–Sn{3}–O(8)	76.7(2)
O(5)–Sn(1)–O(1)	89.27(19)	O(10)–Sn(3)–O(6)	89.47(19)
O(3)–Sn(1)–O(1)	165.2(2)	O(8)–Sn(3)–O(6)	165.0(2)
O(5)–Sn(1)–O(4)	123.38(18)	O(10)–Sn(3)–O(9)	123.95(18)
O(3)–Sn(1)–O(4)	46.46(19)	O(8)–Sn(3)–O(9)	47.24(18)
O(1)–Sn(1)–O(4)	146.78(19)	O(6)–Sn(3)–O(9)	146.34(19)
C(27)–Sn(2)–C(34)	139.4(4)	C(67)–Sn(4)–C(74)	137.0(3)
O(5)–Sn(2)–O(5)#1	75.2(2)	O(10)–Sn(4)–O(10)#2	74.5(2)
O(5)–Sn(2)–O(2)	86.1(2)	O(10)–Sn(4)–O(7)	85.4(2)
O(5)#1–Sn(2)–O(2)	159.5(2)	O(10)#2–Sn(4)–O(7)	157.6(2)
O(5)–Sn(2)–O(3)#1	140.95(17)	O(10)–Sn(4)–O(8)#2	138.75(17)
O(5)#1–Sn(2)–O(3)#1	66.07(17)	O(10)#2–Sn(4)–O(8)#2	65.18(17)

2.805(3) Å for **6** and Sn(1)–O(4) 3.051(7) Å for **8**. Although the distances are considerably longer than the normal Sn–O covalent bond distance, they are smaller than the sum of the van der Waals radii of the tin and oxygen (3.70 Å) and lie in the range of Sn···O distances of 2.61–3.08 Å reported for intramolecular bonds [25–27]. Considering the weak interactions, all the carboxylates are bidentate. The coordination geometry of the tin atoms is a distorted octahedron. The angles in the central Sn_2O_2 ring are 75.46(11)° and 104.54(11)° for **6**, 75.2(2)° and 104.8(2)° for **8**. Also, co-crystallization is found in the crystals for complex **6** with a 1 : 1 molar ratio $\{[(CH_3)_2Sn(O_2CSCH_2C_4H_3N_2\text{-}2,6)]_2O\}_2 : CH_2Cl_2$.

In summary, different coordination modes were derived from the position of the heteroatoms. For 2-pyrazinecarboxylic acid, the nitrogen atom exists the carboxylate and forms a five-membered ring with the oxygen atom of the carboxylate. However, for (2-pyrimidylthio)acetic acids, the nitrogen atom is away from the linear carboxylate preventing chelation. The conclusion is consistent with our previous work [24].

Supplementary material

Crystallographic data (excluding structure factors) for the structure analysis of complexes **1**, **3**, **5**, **6** and **8** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 220167 **1**, 220174 **3**, 235025 **5**, 252849 **6** and 252848 **8**. Copies of these information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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