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Synthesis and spectroscopic properties of [*N*-(4-carboxyphenyl) salicylideneiminato] di- and tri-organotin (IV) complexes and crystal structures of $\{[^nBu_2Sn(2\text{-}OHC_6H_4CH{=}NC_6H_4COO)]_2O\}_2$ and $Ph_3Sn(2\text{-}OHC_6H_4CH{=}NC_6H_4COO)$

Han Dong Yin *, Qi Bao Wang, Sheng Cai Xue

Department of Chemistry, Liaocheng University, Liaocheng 252059, China

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Abstract

Reactions of R_2SnO (R: ^{n}Bu, Cy, Ph, $PhCH_2$) and R_3SnCl (R: Ph, Cy, $PhCH_2$, 2-*Cl*-$PhCH_2$, 4-*F*-$PhCH_2$, 4-*Cl*-$PhCH_2$) with *N*-(4-carboxyphenyl)-salicylideneimine (LH_2) in 1:1 stoichiometry afford complexes $\{[R_2Sn(LH)]_2O\}_2$ and $R_3Sn(LH)$. These complexes have been characterized by elemental analyses, IR, ^1H and ^{119}Sn NMR spectroscopy. The crystal structures of $\{[^nBu_2Sn(LH)]_2O\}_2$, **1** and $Ph_3Sn(L)$, **5** are determined by single crystal X-ray diffraction. Results showed that in the solid state the complex **1** is a tetranuclear centrosymmetric dimer with six-coordination being assigned to both the *endo*-cyclic and *exo*-cyclic tin atoms after consideration of close intermolecular tin oxygen contacts, and study show that the imino nitrogen atom do not participate in coordination to the tin atom. The complex **5** is a monomer, and in the molecule the tin atoms are five-coordinated in trigonal bipyramidal geometries with the two oxygen atom of the carboxylate both coordinating to the tin atoms.

Keywords: Organotin (IV) complex; Schiff base; Synthesis; Crystal structure

1. Introduction

Organotin(IV) complexes with Schiff bases have been the focus all the while owing to their anti-tumour activities [1–8], in particular organotin(IV) esters of *N*-arylidene-amino acids have been observed to exhibit a great anti-tumour activity against human tumour cell lines [9]. Recently studies on the coordination chemistry of amio-acid-derived Schiff bases ligating diorganotin(IV) centers have received some attention [10]. Previous studies have shown that the mode of coordination of the Schiff bases in diorganotin(IV) complexes are mostly tridentate [11–13], including the four complexes we have reported [14]. And triorganotin(IV) esters of *N*-arylidene-ω-amino acids are mostly features one-dimensional chain polymeric structure with the carboxylate group bridging both the intra- and intermolecular tin atoms [15]. As an extension of these studies, we synthesized another ten new di- and triorganotin (IV) complexes of *N*-(4-carboxyphenyl) salicylideneiminato with quite different coordination modes. X-ray studies show that complex **1** exhibits a centrosymmetric dimeric structure with an Sn_2O_2 core, while complex **5** confrom to monomeric structure with the carboxylate group bidentate coordinating to the central tin atom. Noteworthy in both structures is the absence of the significant contact between the tin atoms and the imino nitrogen atoms. All the ten complexes have been characterized by elemental analyses, IR, ^1H and ^{119}Sn NMR spectra, and the results of this study are reported herein.

* Corresponding author. Tel./fax: +866358238121.
E-mail address: handongyin@sohu.com (H.D. Yin).

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2. Experimental

2.1. Materials and methods

Diorganotin oxides were commercially available and used without further purification, and triorganotin chlorindes were prepared by the method described in the literature [16]. The melting points were obtained with Kolfer micro melting point apparatus and were uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H and ^{119}Sn NMR spectra were recorded on a Mercury Plus-400 NMR spectrometer, chemical shifts were given in ppm relative to Me_4Si and Me_4Sn in $CDCl_3$ solvent. Elemental analyses were performed in a PE-2400 II elemental analyzer, and tin was estimated as SnO_2.

2.2. Preparation of the ligand

An ethanol solution of salicylidene (10.5, 0.1 ml) was added slowly to an ethanol solution containing *p*-aminobezoic acid (13.7 g, 0.1 mol) under stirring for about 15 min, and the crude product was precipitated. This was washed thoroughly with petroleum ether and recrystallized from methanol to yield pure LH_2 22.4 g. Yield 93%. M.p. 193 °C (dec.) (see Scheme 1).

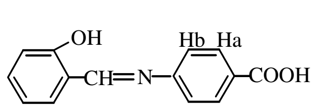
2.3. Preparation of the complexes: general procedure

Complexes **1–4** were prepared using the same procedure as described for complex **1**. The reaction mixture of di-*n*-butyltin oxide (0.248 g, 1.0 mmol) and LH_2 (0.241 g, 1.0 mmol) were added to a solution of absolute benzene (30 ml) and stirred under reflux for 7 h, cooled to room temperature and evaporated under vacuum. The solid was recrystallized from dichloromethane-hexane.

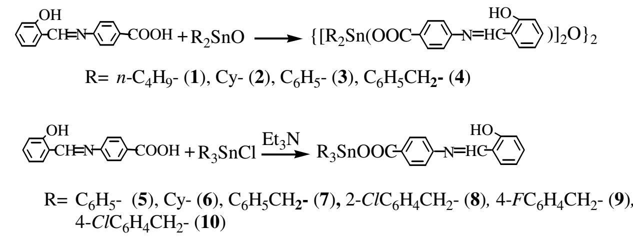
Complexes **5–10** were prepared using the same procedure as described for complex **5**. The solution of LH_2 (0.241 g, 1.0 mmol) in benzene was added triphenyltin(IV) chloride (0.385 g, 1.0 mmol) and Et_3N (1.2 mmol). The mixture was refluxed for 1.5 h and the solvent was removed by evaporation in vacuo. The crude produces were recrystallized from dichloromethane–hexane (see Scheme 2).

2.3.1. *{[^{n}Bu$_2$Sn(LH)]$_2$O}$_2$ (**1**)*

Orange crystals 0.438 g, yield 91%. M.p. 147–149 °C. Anal. Calc. for $C_{88}H_{112}N_4O_{14}Sn_4$: C, 54.92; H, 5.86; N, 2.91; Sn, 24.67. Found: C, 54.89; H, 5.89; N, 2.94; Sn, 24.65%. ^{1}H NMR ($CDCl_3$): 13.02 (4H, d, Ar–OH), 8.68(4H, d, N=C–H), 8.11(8H, d, H(a)), 7.43(8H, d, H(b)), 6.96–7.41(16H, m, Ar–H), 1.25–1.82(48H, m, Sn–$(CH_2)_3$–), 0.78–0.97(24H, m, CH_3); ^{119}Sn NMR ($CDCl_3$): −230.5, −209.6; IR (KBr): *ν*(OH), 3419 cm^{-1}, *ν*(C=N), 1620 cm^{-1}, ν_{as}(COO), 1596,1570, ν_s(COO), 1416, 1399 cm^{-1}, *ν*(Sn–O–Sn), 635 cm^{-1}, *ν*(Sn–C), 545 cm^{-1}, *ν*(Sn–O), 421 cm^{-1}.



Scheme 1.



Scheme 2.

2.3.2. *{[Cy$_2$Sn(LH)]$_2$O}$_2$ (**2**)*

Orange crystals 0.437 g, yield 82%. M.p. 160–161 °C. Anal. Calc. for $C_{104}H_{128}N_4O_{14}Sn_4$: C, 58.56; H, 6.05; N, 2.63; Sn, 22.26. Found: C, 58.75; H, 6.11; N, 2.70; Sn, 22.08%. ^{1}H NMR ($CDCl_3$): 13.05 (4H, d, Ar–OH), 8.77(4H, d, N=C–H), 8.15(8H, d, H(a)), 7.40(8H, d, H(b)), 6.94–7.38(16H, m, Ar–H), 1.16–1.90(88H, m, CH_3); ^{119}Sn NMR ($CDCl_3$): −226.5, −205.4; IR (KBr): *ν*(OH), 3421 cm^{-1}, *ν*(C=N), 1622 cm^{-1}, ν_{as}(COO), 1590, 1576, ν_s(COO), 1411, 1392 cm^{-1}, *ν*(Sn–O–Sn), 632 cm^{-1}, *ν*(Sn–C), 551 cm^{-1}, *ν*(Sn–O), 432 cm^{-1}.

2.3.3. *{[Ph$_2$Sn(LH)]$_2$O}$_2$ (**3**)*

Orange crystals 0.432 g, yield 83%. M.p. 175–176 °C. Anal. Calc. for $C_{104}H_{80}N_4O_{14}Sn_4$: C, 59.92; H, 3.87; N, 2.69; Sn, 22.78. Found: C, 59.75; H, 3.90; N, 2.78; Sn, 22.54%. ^{1}H NMR ($CDCl_3$): 13.11 (4H, d, Ar–OH), 8.75(4H, d, N=C–H), 8.08(8H, d, H(a)), 7.45(8H, d, H(b)), 6.68–7.44(56H, m, Ar–H & Ph–H); ^{119}Sn NMR ($CDCl_3$): −224.8, −205.0; IR (KBr): *ν*(OH), 3424 cm^{-1}, *ν*(C=N), 1625 cm^{-1}, ν_{as}(COO), 1604, 1578, ν_s(COO), 1410, 1395 cm^{-1}, *ν*(Sn–O–Sn), 640 cm^{-1}, *ν*(Sn–C), 550 cm^{-1}, *ν*(Sn–O), 431 cm^{-1}.

2.3.4. *{[Bz$_2$Sn(LH)]$_2$O}$_2$ (**4**)*

Orange crystals 0.499 g, yield 91%. M.p. 153–155 °C. Anal. Calc. for $C_{112}H_{96}N_4O_{14}Sn_4$: C, 61.24; H, 4.40; N, 2.55; Sn, 21.61. Found: C, 61.02; H, 4.33; N, 2.62; Sn, 21.49%. ^{1}H NMR ($CDCl_3$): 13.05 (4H, d, Ar–OH), 8.70(4H, d, N=C–H), 8.14(8H, d, H(a)), 7.41(8H, d, H(b)), 6.85–7.42(56H, m, Ar–H & Ph–H), 2.70–2.75(16H, m, $SnCH_2$); ^{119}Sn NMR ($CDCl_3$): −226.6, −208.2; IR (KBr): *ν*(OH), 3416 cm^{-1}, *ν*(C=N), 1622 cm^{-1}, ν_{as}(COO), 1611, 1580, ν_s(COO), 1414, 1392 cm^{-1}, *ν*(Sn–O–Sn), 642 cm^{-1}, *ν*(Sn–C), 546 cm^{-1}, *ν*(Sn–O), 434 cm^{-1}.

*2.3.5. $Ph_3Sn(LH)$ (**5**)*

Orange crystals 0.513, yield 87%. M.p. 125–127 °C. Anal. Calc. for $C_{32}H_{25}NO_3Sn$: C, 65.12; H, 4.27; N, 2.37; Sn, 20.11. Found: C, 65.09; H, 4.28; N, 2.35; Sn, 20.09%. ^1H NMR ($CDCl_3$): 13.01 (1H, s, Ar–OH), 8.62(1H, s, N=C—H), 8.20(2H, d, H(a)), 7.81(6H, t, SnPh–H,), 7.51(2H, d, H(b)), 6.94–7.47(13H, m, Ar–H & SnPh–H);^{119}Sn NMR ($CDCl_3$): −204.7; IR (KBr): ν(OH), 3428 cm^{-1}, ν(C=N), 1620 cm^{-1}, ν_{as}(COO), 1598 cm^{-1}, ν_s(COO), 1408 cm^{-1}; ν(Sn–C), 563 cm^{-1}, ν(Sn–O), 442 cm^{-1}.

*2.3.6. $Cy_3Sn(LH)$ (**6**)*

Orange crystals 0.441 g, yield 73%. M.p. 117–119 °C. Anal. Calc. for $C_{32}H_{40}NO_3Sn$: C, 63.49; H, 6.66; N, 2.31; Sn, 19.61. Found: C, 63.47; H, 6.69; N, 2.35; Sn, 19.59%. ^1H NMR ($CDCl_3$): 13.08 (1H, s, Ar–OH), 8.62(1H, s, N=C—H), 8.12(2H, d, H(a)), 7.43(2H, d, H(b)), 6.93–7.30(4H, m, Ar–H), 1.35–1.97(30H, m, SnCy–H);^{119}Sn NMR ($CDCl_3$): −207.2; IR (KBr): ν(OH), 3393 cm^{-1}, ν(C=N), 1624 cm^{-1}, ν_{as}(COO), 1595 cm^{-1}, ν_s(COO), 1414 cm^{-1}; ν(Sn–C), 533 cm^{-1}, ν(Sn–O), 430 cm^{-1}.

*2.3.7. $Bz_3Sn(LH)$ (**7**)*

Orange crystals 0.480 g, yield 76%. M.p. 123–125 °C. Anal. Calc. for $C_{35}H_{31}NO_3Sn$: C, 66.48; H, 4.94; N, 2.22; Sn, 18.77. Found: C, 66.46; H, 4.91; N, 2.25; Sn, 18.76%. ^1H NMR ($CDCl_3$): 13.03 (1H, s, Ar–OH), 8.66(1H, s, N=C—H), 8.08(2H, d, H(a)), 7.42(2H, d, H(b)), 6.81–7.38(19H, m, Ar–H & Ph–H), 2.69(6H, t, $SnCH_2$, $J_{Sn–H}$ = 69.63);^{119}Sn NMR ($CDCl_3$): −210.3; IR (KBr): ν(OH), 3387 cm^{-1}, ν(C=N), 1608 cm^{-1}, ν_{as}(COO), 1596 cm^{-1}, ν_s(COO), 1402 cm^{-1}; ν(Sn–C), 528 cm^{-1}, ν(Sn–O), 455 cm^{-1}.

*2.3.8. $(2\text{-Cl-PhCH}_2)_3Sn(LH)$ (**8**)*

Orange crystals 0.632 g, yield 86%. M.p. 119–121 °C. Anal. Calc. for $C_{35}H_{28}Cl_3NO_3Sn$: C, 57.14; H, 3.84; N, 1.90; Sn, 16.14. Found: C, 57.12; H, 3.86; N, 1.91; Sn, 16.11%. ^1H NMR ($CDCl_3$): 13.03 (1H, s, Ar–OH), 8.66(1H, s, N=C—H), 8.05(2H, d, H(a)), 7.45(2H, d, H(b)), 6.75–7.41(16H, m, Ar–H & Ph–H), 2.79(6H, t, $SnCH_2$, $J_{Sn–H}$ = 68.75); ^{119}Sn NMR ($CDCl_3$): −205.8; IR (KBr): ν(OH), 3431 cm^{-1}, ν(C=N), 1618 cm^{-1}, ν_{as}(COO), 1597 cm^{-1}, ν_s(COO), 1398 cm^{-1}; ν(Sn–C), 563 cm^{-1}, ν(Sn–O), 458 cm^{-1}.

*2.3.9. $(4\text{-F-PhCH}_2)_3Sn(LH)$ (**9**)*

Orange crystals 0.528 g, yield 77%. M.p. 127–129 °C. Anal. Calc. for $C_{35}H_{28}F_3NO_3Sn$: C, 61.25; H, 4.11; N, 2.04; Sn, 17.30. Found: C, 61.24; H, 4.13; N, 2.06; Sn, 17.27%. ^1H NMR ($CDCl_3$): 12.98 (1H, s, Ar–OH), 8.66(1H, s, N=C—H), 8.06(2H, d, H(a)), 7.43(2H, d, H(b)), 6.61–7.36(16H, m, Ar–H & Ph–H), 2.69(6H, t, $SnCH_2$, $J_{Sn–H}$ = 71.45);^{119}Sn NMR ($CDCl_3$): −207.7; IR (KBr): ν(OH), 3408 cm^{-1}, ν(C=N), 1614 cm^{-1}, ν_{as}(COO), 1598 cm^{-1}, ν_s(COO), 1411 cm^{-1}; ν(Sn–C), 562 cm^{-1}, ν(Sn–O), 460 cm^{-1}.

Table 1
Crystal date and details of structure refinement for $\{[^nBu_2Sn(LH)]_2O\}_2$ (**1**) and $Ph_3Sn(LH)$ (**5**)

Complex	**1**	**5**
Empirical formula	$C_{88}H_{112}N_4O_{14}Sn_4$	$C_{32}H_{25}NO_3Sn$
Formula weight	1924.58	590.22
Crystal size (mm)	0.39 × 0.34 × 0.27	0.42 × 0.35 × 0.09
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions		
a (Å)	12.352(9)	6.8950(14)
b (Å)	12.875(10)	46.350(3)
c (Å)	15.267(11)	8.7250(17)
β (°)	102.559(11)	95.472(3)
D_{calc} density (mg/m^3)	1.358	1.412
F(000)	980	1192
Scan range *θ* (°)	1.59–25.02	1.76–25.03
Total/unique/R_{int}	11959/8128/0.0238	10364/3922/0.1001
Goodness-of-fit on F^2	0.963	1.017
R_1/wR_2	0.0471/0.1085	0.0748/0.1602
μ (mm^{-1})	1.107	0.953
ρ_{max}/ρ_{min} (e Å^{-3})	0.897/−0.480	0.699/−1.335

*2.3.10. $(4\text{-Cl-PhCH}_2)_3Sn(LH)$ (**10**)*

Orange crystals 0.617 g, yield 84%. M.p. 124–126 °C. Anal. Calc. for $C_{35}H_{28}Cl_3NO_3Sn$: C, 57.14; H, 3.84; N, 1.90; Sn, 16.14. Found: C, 57.15; H, 3.83; N, 1.93; Sn, 16.12%. ^1H NMR ($CDCl_3$): 12.92 (1H, s, Ar–OH), 8.66(1H, s, N=C—H), 8.06(2H, d, H(a)), 7.44(2H, d, H(b)), 6.77–7.42(16H, m, Ar–H & Ph–H), 2.70(6H, t, $SnCH_2$, $J_{Sn–H}$ = 67.61);^{119}Sn NMR ($CDCl_3$): −208.2; IR (KBr): ν(OH), 3420 cm^{-1}, ν(C=N), 1620 cm^{-1}, ν_{as}(COO), 1601 cm^{-1}, ν_s(COO), 1418 cm^{-1}; ν(Sn–O), 557 cm^{-1}, ν(Sn–C), 451 cm^{-1}.

2.4. X-ray crystallography

X-ray crystallographic data for the complexes **1** and **5** were collected on a Bruker smart-1000 CCD diffractometer at 293(2) K using Mo Kα radiations (0.71073 Å). The structures were solved by direct method and difference Fourier map using SHELXL-97 program, and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically. Further details are given in Table 1.

3. Results and discussion

3.1. Crystal structures

The ORTEP drawings of complexes **1** and **5** are shown in Figs. 1 and 2. The selected bond lengths and angles are listed in Tables 2 and 3.

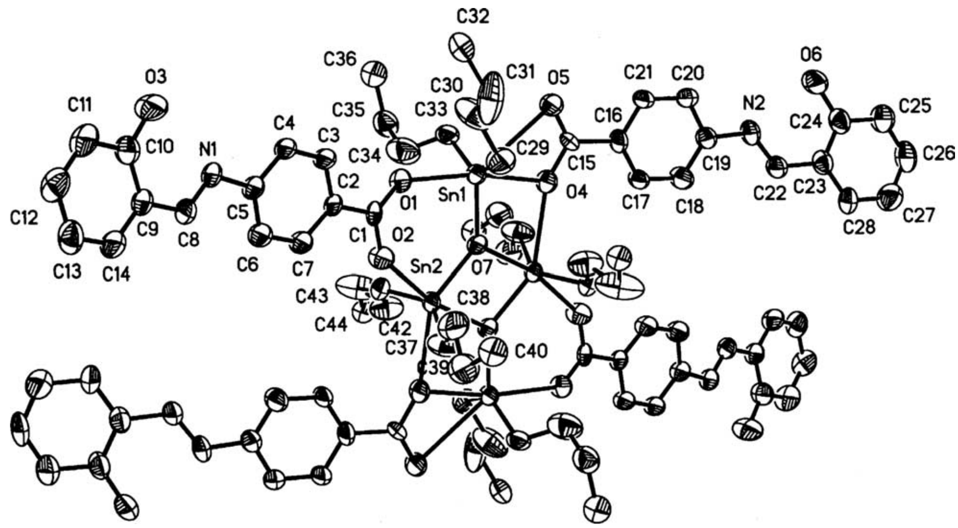


Fig. 1. ORTEP drawing of complex **1**.

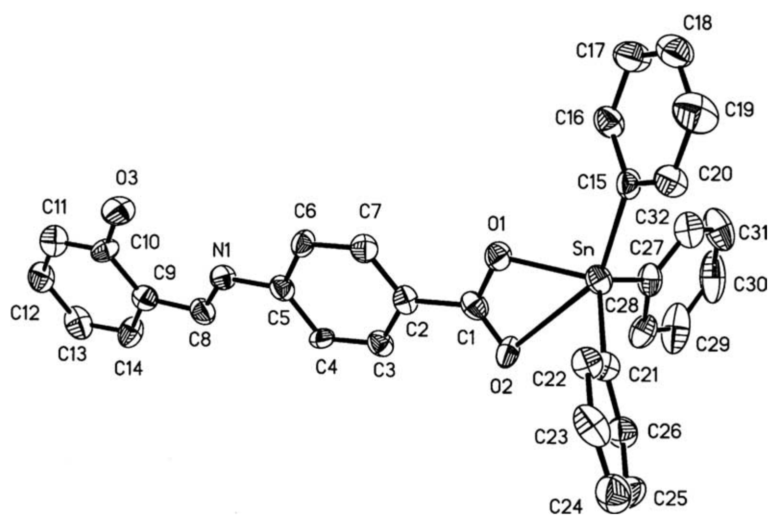


Fig. 2. ORTEP drawing of complex **5**.

Complex $\{[^n\text{Bu}_2\text{Sn(LH)}]_2\text{O}\}_2$ (**1**), possesses teranuclear centrosymmetric dimeric structure with a four-membered planar Sn_2O_2 ring with the Sn–O bond distances 2.040(4) Å for Sn(2)–O(7), 2.151(3) Å for Sn(2)–O(7A) and 2.020(4) Å for Sn(1)–O(7), which are similar to the corresponding distances of the complex $\{[^n\text{Bu}_2\text{Sn(2-MeOC}_6\text{H}_4\text{COO)}]_2\text{O}\}_2$ [17]. In the molecule, the four carboxylate ligands are divided into two different types according to their coordinating fashion. Two of them are bidentate and connect with each of of *exo*- and *endo*-cyclic tin atoms by using both oxygen atoms, whereas the other two are tridentate with one oxygen atom bridging to both of the *exo*- and *endo*-cyclic tin atoms and the other oxygen atom to the *exo*-cyclic tin atom. The bond distances of Sn(1)–O(1), Sn(2)–O(2), Sn(1)–O(5), Sn(1)–O(4) and Sn(2)–O(4A) are 2.263(4), 2.253(4), 2.863(5), 2.200(4), 2.674(4) Å, respectively, which are close to that found in the literature [17]. The *exo*-cyclic tin atom Sn(1) forms five primary bonds: one to the O(7) atom, two to the carboxylate oxygen atoms O(1) and O(4), and two to the tin-bound *n*-butyl groups. In addition the Sn(1) atom makes a close contact of 2.863 Å with the O(5) atom. The contact is significantly less than 3.68 Å, the sum of the van der Waals radii for Sn and O atoms [18,19]. The Sn(1) atom is therefore best be described as six-coordinated in a monocapped trigonal bipyramid geometry with the O(7), C(29) and C(33) atoms occupying the equatorial positions, and the O(1) and O(4) atoms taking up the axial positions. The *endo*-cyclic tin atom Sn(2) is six-coordinated in a distorted octahedral geometry, with the atoms C(37), C(41), O(4A) and O(7) occupying

Table 2
Selected bond distances (Å) and angles (°) of $\{[^{n}Bu_2Sn(LH)]_2O\}_2$ (**1**)

Sn(1)–O(7)	2.020(4)	Sn(2)–O(7)	2.040(4)
Sn(1)–C(33)	2.098(8)	Sn(2)–C(37)	2.083(9)
Sn(1)–C(29)	2.100(9)	Sn(2)–C(41)	2.098(7)
Sn(1)–O(4)	2.200(4)	Sn(2)–O(7A)	2.151(3)
Sn(1)–O(1)	2.263(4)	Sn(2)–O(2)	2.253(4)
Sn(1)–O(5)	2.863(5)	Sn(2)–O(4A)	2.674(4)
O(7)–Sn(1)–C(33)	110.5(2)	O(7)–Sn(2)–C(37)	109.9(3)
O(7)–Sn(1)–C(29)	112.1(3)	O(7)–Sn(2)–C(41)	105.2(2)
C(33)–Sn(1)–C(29)	137.2(3)	C(37)–Sn(2)–C(41)	143.3(3)
O(7)–Sn(1)–O(4)	78.25(14)	O(7)–Sn(2)–O(7A)	76.61(15)
C(33)–Sn(1)–O(4)	94.7(2)	C(37)–Sn(2)–O(7A)	97.4(3)
C(29)–Sn(1)–O(4)	97.6(3)	C(41)–Sn(2)–O(7A)	100.9(2)
O(7)–Sn(1)–O(1)	91.13(14)	O(7)–Sn(2)–O(2)	89.99(15)
C(33)–Sn(1)–O(1)	89.1(2)	C(37)–Sn(2)–O(2)	85.4(3)
C(29)–Sn(1)–O(1)	86.2(3)	C(41)–Sn(2)–O(2)	84.2(2)
O(4)–Sn(1)–O(1)	169.38(15)	O(7A)–Sn(2)–O(2)	166.48(15)
O(7)–Sn(1)–O(5)	127.18(13)	O(7)–Sn(2)–O(4A)	142.69(12)
C(33)–Sn(1)–O(5)	79.2(2)	C(37)–Sn(2)–O(4A)	76.9(3)
C(29)–Sn(1)–O(5)	78.6(3)	C(41)–Sn(2)–O(4A)	81.8(2)
O(4)–Sn(1)–O(5)	48.94(13)	O(7A)–Sn(2)–O(4A)	66.09(12)
O(1)–Sn(1)–O(5)	141.67(14)	O(2)–Sn(2)–O(4A)	127.31(13)

Symmetry equivalent positions: A, $2 - x$, $1 - y$, $-z$.

Table 3
Selected bond distances (Å) and angles (°) of $Ph_3Sn(LH)$ (**5**)

Sn–O(1)	2.078(6)	N(1)–C(8)	1.297(11)
Sn–C(21)	2.116(9)	N(1)–C(5)	1.408(11)
Sn–C(27)	2.145(8)	O(1)–C(1)	1.324(9)
Sn–C(15)	2.156(8)	O(2)–C(1)	1.221(10)
Sn–O(2)	2.732(6)	O(3)–C(10)	1.335(10)
O(1)–Sn–C(21)	108.3(3)	C(21)–Sn–O(2)	85.1(3)
O(1)–Sn–C(27)	110.0(3)	C(27)–Sn–O(2)	84.1(3)
C(21)–Sn–C(27)	121.3(4)	C(15)–Sn–O(2)	149.9(3)
O(1)–Sn–C(15)	97.1(3)	C(8)–N(1)–C(15)	122.2(7)
C(21)–Sn–C(15)	111.9(3)	C(1)–O(1)–Sn	106.4(5)
C(27)–Sn–C(15)	105.5(4)	C(1)–O(2)–Sn	78.5(5)
O(1)–Sn–O(2)	53.06(19)	O(2)–C(1)–O(1)	122.0(8)

equatorial positions as indicated by the sum of the bond angles (373.8°) around the tin formed by these atoms. The axial positions are occupied by O(2) and the O(7A) atoms, and the bond angle, O(2)–Sn(2)–O(7A), of 166.48(15)° deviates significantly from linearity. There is no evidence showing that the phenolate oxygen and the imino nitrogen atom have any bonding interaction to the tin atom.

Complex $Ph_3Sn(LH)$ (**5**) is a monomer as shown in Fig. 2. The molecule of the title complex conforms to the chelated monomeric structure with the central tin atom five-coordinated to three tin-bounded phenyl groups and the chelated carboxylate group. As is frequently the case, the carboxylate is unsymmetrically bidentate, the long Sn–O contact comprising significant perturbations on a basically four-coordinate array about the central tin atom. The Sn–O bond lengthes 2.078(6) Å for Sn–O(1) and 2.732(6) Å for Sn–O(2) are similar to those of the $Ph_3(4\text{-}C_2H_5OC_6H_4COO)$ (2.050(4), 2.837(4) Å) [20]. The sum of the bond angles C(21)–Sn–C(27) 121.3(4)°, C(21)–Sn–C(15) 111.9(3)°, C(27)–Sn–C(15) 105.5(4)° is 338.7°, which indicates that the Sn, C(15), C(21) and C(27) atoms are almost in the same plane. Studies show that the phenolate oxygen and the imino nitrogen atoms are also in nonparticipation in coordination to the tin atoms, which is similar to that of the complex **1**. In the molecular structure of the title complex, the O(3) forms two hydrogen bonds with the intramolecular N(1) and the intermolecular O(3^i) (*i*: $-x - 1$, $-y$, $-z$) atoms. The hydrogen bond distances of O(3)–H(3A)···N(1) and O(3)–H(3A)···O(3^i) are 2.678 and 3.147, and the hydrogen bond angles of O(3)–H(3A)···N(1) and O(3)–H(3A)···O(3^i) are 131.21° and 125.47°.

3.2. Infrared spectra

The infrared spectra of all the organotin(IV) complexes have been recorded and some important assignments are shown above. The infrared spectra of all the ten complexes show strong typical broad bands at 3387–3431 cm^{-1} related to the phenolic hydrogen stretching vibration according to the previous report [21], which strongly indicates that in the complexes the phenolic oxygen atoms do not participate in coordination to the tin atoms. The bands appearing at 1608–1624 cm^{-1} for all the complexes can be assigned as ν(C=N) vibration according to the previous reports [22–24] show that the amino nitrogen atoms are not participating in coordination to the tin atom.

The $\Delta\nu(\nu_{as}(CO_2) - \nu_s(CO_2))$ value is used to determine the nature of bonding of carboxylate to tin(IV) complexes [25]. It is generally believed that the difference in $\Delta\nu$ between asymmetric ($\nu_{as}(CO_2)$) and symmetric ($\nu_s(CO_2)$) absorption frequencies below 200 cm^{-1} for the bidentate carboxylate moiety, but greater than 200 cm^{-1} for the unidentate carboxylate moiety. All the values of $\Delta\nu$ of the ten complexes are between 154 and 199 cm^{-1}, and this indicate that all the seven title complexes adopt bidentate carboxylate structure. For complexes **1**–**4**, The peak appearing at 632–642 cm^{-1} can be assigned to the ν (Sn–O–Sn) mode [26–28].

3.3. ^1H NMR spectra

The Ar–OH resonance appeared in the region 1.92–13.11 ppm as singlet for all the complexes strongly suggest that the phenolic oxygen atoms do not participate in coordination to the tin atoms for all the ten title complexes, and this is quite different from that of the four complexes we have reported [14]. The chemical shift of the protons of azomethine (HC=N) proton resonances exhibit signals in the region 8.62–8.77 ppm for all the ten complexes, the figures are similar to the uncoordinated ligand [15], and this show that the azomethine nitrogen atoms do not participate in coordinating to the tin atoms for all of the ten complexes. The result is different from the complexes reported in the literature [29–31], but is similar to organotin(IV) complexes of 5-[(E)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acid [32]. This may relevant to the spatial environment around the azomethine nitrogen atoms. As to complexes **1**–**4**, the azomethine (HC═N) proton exhibits signal at 8.68–8.77 ppm as doublet, and this suggest that the different coordination mode of the ligands have slight effect on the chemical shift of the azomethine (HC═N) protons [12].

3.4. ^{119}Sn NMR spectra

The ^{119}Sn NMR of complexes **1**–**4** showed two well separated resonances, characteristic of the tetraorganodistannoxane structure [32]. The low- and high-field resonances observed for these complexes are attributed to the *exo*-cyclic and *endo*-cyclic tin atoms, respectively [33]. Single resonances at the regions −205.0 to −209.6 and −224.8 to −230.5 ppm in the ^{119}Sn NMR spectra of complexes suggest that the tin atoms exhibit hexa-coordination [32].

The ^{119}Sn chemical shift values in complexes (**5**–**10**) are found to be in the range of −204.7 to −210.3 ppm. The appearance of chemical shift values in this region indicates six-coordination environment [32] around the central tin atoms in these complexes.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 238875 for complex **1** and CCDC No. 238876 for complex **5**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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