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Synthesis and structural characterization of diorganotin(IV) esters with pyruvic acid isonicotinyl hydrazone and pyruvic acid salicylhydrazone Schiff bases

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Abstract

Eight diorganotin esters of Schiff base ligands formulated as $[R_2SnLY]_2$, where L_1 is 4-$NC_5H_4CON_2C(CH_3)$ CO_2 with Y = H_2O, R = Ph (**1**), $PhCH_2$ (**2**), *m*-$ClC_6H_4CH_2$ (**3**), and L_2 is 2-$HOC_6H_4CON_2C(CH_3)$ CO_2 with Y = CH_3OH, R = $PhCH_2$ (**4**), *o*-$ClC_6H_4CH_2$ (**5**), *m*-$ClC_6H_4CH_2$ (**6**), *o*-$FC_6H_4CH_2$ (**7**), *p*-$FC_6H_4CH_2$ (**8**) have been prepared and characterized by elemental analysis, IR, ^1H and ^{119}Sn NMR spectra. The crystal structures of compounds **1**, **2** and **4** have been determined by X-ray single crystal diffraction. Their structures show that the tin atoms of three compounds are all rendered seven-coordinated in distorted pentagonal bipyramid geometries with a planar SnO_4N unit and two apical aryl carbon atoms. A comparison of the IR spectra of the ligands with those of the corresponding compounds, reveals that the disappearance of the bands assigned to carbonyl unambiguously conforms that the ligands coordinate with tin in the enol form.

Keywords: Schiff base; Hydrazone; Diorganotin; Crystal structure

1. Introduction

The studies of diorganotin(IV) compounds are of current interest owing to their wide range of applications as biocides and homogeneous catalysts in the industry [1]. In recent years, there have been more and more reports on the synthesis, antitumor activities and structural elucidation of various diorganotin(IV) derivatives of carboxylic acid [2–5]. In particular, there has been considerable interest in structural studies of diorganotin(IV) compounds of carboxylic acid, because there are many possible bonding interactions between the oxygen atom of carboxyl group and tin atom. Studies on diorganotin(IV) compounds of carboxylic acid having carboxylate ligands with additional donor atom, such as nitrogen, revealed new structural types which may lead to compounds with different activities [5–10]. In line with these developments, we have recently reported some diorganotin compounds of pyruvic acid isonicotinyl hydrazone [11]. As a continuation of this line of investigation, we now synthesized eight diorganotin esters of Schiff base ligands pyruvic acid isonicotinyl hydrazone and salicylhydrazone by different reaction methods. The details of the structure and spectral characterizations of the compounds **1**–**8** are reported herein. Three of the compounds have been studied by X-ray diffraction, and reveal that these three compounds are all dimers and adopt the same structure. Furthermore, for compounds **1** and **2**, because of the presence of intermolecular hydrogen bonds, their structures show a one-dimensional indefinite chain arrangement. And the Schiff base ligands, pyruvic acid isonicotinyl hydrazone and salicylhydrazone, were both found to be introduced

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into the inner coordination sphere and can thus function as tridentate chelates with O, N and O atoms occupying suitable positions for the coordination.

2. Experimental

2.1. Materials and methods

Triphenyltin hydroxide, isonicotinic acid hydrazide, salicylhydrazide and pyruvic acid were commercially available and used without further purification. Triaryltin chlorides were prepared by a standard method reported in the literature [12]. All the solvents used in the reactions were of AR grade and dried using standard literature procedures. The melting points were obtained with Kolfer micro melting point apparatus and were uncorrected. IR spectra were recorded with a Nicolet-460 spectrophotometer, as KBr discs. ^{1}H and ^{119}Sn NMR spectra were recorded on a Mercury Plus-400 NMR spectrometer in $CDCl_3$, and chemical shifts were given relative to Me_4Si and Me_4Sn. Elemental analyses were performed with a PE-2400 II elemental analyzer.

2.2. Synthesis of Schiff base ligands

2.2.1. Preparation of pyruvic acid isonicotinyl hydrazone

The Schiff base has been prepared with isonicotinic acid hydrazide and pyruvic acid in ethanol according to the literature [13], and a mount of white powder was obtained. Yield: 95%, m.p. 222–223 °C. Anal. Calc. for $C_9H_9N_3O_3$: C, 48.14; H, 5.00; N, 18.38%. Found: C, 48.00; H, 4.89; N, 18.67%.

2.2.2. Preparation of pyruvic acid salicylhydrazone

The Schiff base has been prepared with salicylhydrazide and pyruvic acid in ethanol according to the literature [14], and white acicular crystals were obtained. Yield: 80%, m.p. 216 °C. Anal. Calc. for $C_{10}H_{10}N_2O_4$: C, 54.92; H, 4.54; N, 12.61%. Found: C, 54.72; H, 4.68; N, 12.85%.

2.3. Synthesis of diorganotin compounds

2.3.1. Preparation of $\{Ph_2Sn[4\text{-}NC_5H_4CON_2C(CH_3)CO_2](H_2O)\}_2 \cdot CH_2Cl_2 \cdot H_2O$ (1)

Pyruvic acid isonicotinyl hydrazone (0.5 mmol) was added to a benzene solution (30 ml) of Ph_3SnOH (0.5 mmol). The mixture was heated under reflux with stirring for 6 h. The clear solution thus obtained was evaporated under vacuum to form a yellow sticky material and recrystallized in dichloromethane–hexane to give light yellow crystals. Yield: 63%, m.p. 238 °C. Anal. Calc. for $C_{43}H_{42}Cl_2N_6O_9Sn_2$: C, 47.12; H, 3.84; N, 5.84%. Found: C, 47.31; H, 3.78; N, 5.66%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.21(6H, d, $J = 6.00$ Hz, CH_3), 5.23(2H, s, CH_2Cl_2), 5.51(6H, s, H_2O), 6.72–7.17(20H, m, Ph–H), 8.03(4H, d, $J = 5.20$ Hz, 3,5-pyridine–H), 8.82(4H, d, $J = 5.20$ Hz, 2,6-pyridine–H). ^{119}Sn NMR ($CDCl_3$, ppm): −458.5. IR (KBr, cm^{-1}) ν: 3415(m, H_2O), 2978, 2921(s, Ar–H), 2854(m, C–H), 1609, 1363(m, CO_2), 1618(m, C=N), 1602(s, C=N–N=C), 1204(s, C–O), 678(s, Sn–O), 546(w, Sn–C), 475(m, Sn–N).

2.3.2. Preparation of $\{(PhCH_2)_2Sn[4\text{-}NC_5H_4CON_2C(CH_3)CO_2](H_2O)\}_2$ (2)

Pyruvic acid isonicotinyl hydrazone (0.5 mmol) and tribenzyltin chloride (0.5 mmol) were added to a solution of dry toluene (30 ml) and heated under reflux with stirring for 1 h. After the triethylamine (0.5 mmol) was added to the reactor, the reaction mixture was refluxed for 1 h more. The clear solution thus obtained was evaporated under vacuum to form a white solid and recrystallized in methanol to give colorless crystals. Yield: 81%, m.p. 145 C. Anal. Calc. for $C_{46}H_{46}N_6O_8Sn_2$: C, 52.66; H, 4.39; N, 8.01%. Found: C, 52.81; H, 4.42; N, 7.95%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.21(6H, d, $J = 6.00$ Hz, CH_3), 3.13(8H, t, $J_{Sn-H} = 88.80$ Hz, $PhCH_2Sn$), 5.51(4H, s, H_2O), 6.72–7.17(20H, m, Ph–H), 7.81(4H, d, $J = 5.20$ Hz, 3,5-pyridine–H), 8.79(4H, d, $J = 4.80$ Hz, 2,6-pyridine–H). ^{119}Sn NMR ($CDCl_3$, ppm): −469.5. IR (KBr, cm^{-1}) ν: 3022(m, Ar–H), 2921(s, C–H), 1633(s, C=N), 1604(s, C=N–N=C), 1615, 1334(s, CO_2), 1203(s, C–O), 697(s, Sn–O), 544(m, Sn–C), 479(w, Sn–N).

2.3.3. Preparation of $\{(m\text{-}ClC_6H_4CH_2)_2Sn[4\text{-}NC_5H_4CON_2C(CH_3)CO_2]\}_2$ (3)

Compound **3** was prepared using the same procedure as described for compound **2** and recrystallized from methanol to give yellow crystals. Yield: 82%, m.p. 138 °C. Anal. Calc. for $C_{46}H_{38}Cl_4N_6O_6Sn_2$: C, 48.02; H, 3.31; N, 8.35%. Found: C, 47.81; H, 3.55; N, 8.39%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.26(6H, d, $J = 6.00$ Hz, CH_3), 3.55(8H, t, $J_{Sn-H} = 84.80$ Hz, $PhCH_2Sn$), 6.52–7.11(16H, m, Ph–H), 7.76(4H, d, $J = 6.40$ Hz, 3,5-pyridine–H), 8.81(4H, d, $J = 4.80$ Hz, 2,6-pyridine–H). ^{119}Sn NMR ($CDCl_3$, ppm): −459.5. IR (KBr, cm^{-1}) ν: 3058(m, Ar–H), 2933(s, C–H), 1631(s, C=N), 1598(s, C=N–N=C), 1608, 1355(s, CO_2), 1192(s, C–O), 683(m, Sn–O), 562(w, Sn–C), 487(m, Sn–N).

2.3.4. Preparation of $\{(PhCH_2)_2Sn[2\text{-}HOC_6H_4CON_2C(CH_3)CO_2](CH_3OH)\}_2$ (4)

Pyruvic acid salicylhydrazone (0.5 mmol) and tribenzyltin chloride (0.5 mmol) were added to a solution of dry toluene (30 ml) and heated under reflux with stirring for 1 h. After the triethylamine (0.5 mmol) was added to the reactor, the reaction mixture was refluxed for 1 h more. The clear solution thus obtained was evaporated under vacuum to form a white solid and recrystallized

in methanol to give colorless crystals. Yield: 78%, m.p. 135 °C. Anal. Calc. for $C_{50}H_{52}N_4O_{10}Sn_2$: C, 54.23; H, 4.70; N, 5.06%. Found: C, 53.81; H, 4.79; N, 5.12%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.18(2H, s, Ar–OH), 8.15(2H, s, R–OH), 6.94–7.49(28H, m, Ar–H and Ph–H), 3.35–3.49(8H, m, $PhCH_2Sn$), 1.89(12H, s, CH_3). ^{119}Sn NMR ($CDCl_3$, ppm): −445.5. IR (KBr, cm^{-1}): 3419(m, OH), 3024(s, Ar–H), 2936(s, C–H), 1625(s, C=N), 1608(s, C=N–N=C), 1588, 1322(s, CO_2), 1211(s, C–O), 698(s, Sn–O), 524(w, Sn–C), 489(w, Sn–N).

The other compounds, $\{R_2Sn[2\text{-}HOC_6H_4CON_2C(CH_3)CO_2]\}_2$ [R=*o*-$ClC_6H_4CH_2$ (**5**), *m*-$ClC_6H_4CH_2$ (**6**), *o*-$FC_6H_4CH_2$ (**7**), *p*-$FC_6H_4CH_2$ (**8**)], were prepared analogously with appropriate trialkyltin chloride and their analytical data are presented below.

2.3.5. $\{(o\text{-}ClC_6H_4CH_2)_2Sn[2\text{-}HOC_6H_4CON_2C(CH_3)CO_2]\}_2$ (**5**)

Compound **5** was recrystallized from methanol to give orange-red precipitate. Yield: 72%, m.p. 131 °C. Anal. Calc. for $C_{48}H_{40}Cl_4N_4O_8Sn_2$: C, 48.84; H, 3.39; N, 4.75%. Found: C, 49.11; H, 3.56; N, 4.72%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.16(2H, s, Ar–OH), 6.83–7.64(24H, m, Ar–H and Ph–H), 3.22–3.50(8H, m, $PhCH_2Sn$), 1.64(6H, s, CH_3). ^{119}Sn NMR ($CDCl_3$, ppm): −448.5. IR (KBr, cm^{-1}): 3417(m, OH), 3021(m, Ar–H), 2916(m, C–H), 1618(m, C=N), 1603(s, C=N–N=C), 1586, 1321(s, CO_2), 1209(m, C–O), 677(m, Sn–O), 525(w, Sn–C), 465(w, Sn–N).

2.3.6. $\{(m\text{-}ClC_6H_4CH_2)_2Sn[2\text{-}HOC_6H_4CON_2C(CH_3)CO_2]\}_2$ (**6**)

Compound **6** was recrystallized from methanol to give orange-red precipitate. Yield: 85%, m.p. 129 °C. Anal. Calc. for $C_{48}H_{40}Cl_4N_4O_8Sn_2$: C, 48.84; H, 3.39; N, 4.75%. Found: C, 49.33; H, 3.36; N, 4.52%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 12.56(2H, s, Ar–OH), 6.55–7.63(24H, m, Ar–H and Ph–H), 3.22–3.41(8H, m, $PhCH_2Sn$), 1.74(6H, s, CH_3). ^{119}Sn NMR ($CDCl_3$, ppm): −465.5. IR (KBr, cm^{-1}): 3421(m, OH), 3019(m, Ar–H), 2933(m, C–H), 1622(s, C=N), 1609(s, C=N–N=C), 1594, 1351(s, CO_2), 1211(m, C–O), 654(m, Sn–O), 547(m, Sn–C), 459(w, Sn–N).

2.3.7. $\{(o\text{-}FC_6H_4CH_2)_2Sn[2\text{-}HOC_6H_4CON_2C(CH_3)CO_2]\}_2$ (**7**)

Compound **7** was recrystallized from methanol to give orange-red precipitate. Yield: 72%, m.p. 131 °C. Anal. Calc. for $C_{48}H_{40}F_4N_4O_8Sn_2$: C, 51.73; H, 3.59; N, 5.03%. Found: C, 51.88; H, 3.52; N, 4.97%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.22(2H, s, Ar–OH), 6.81–7.55(24H, m, Ar–H and Ph–H), 3.30–3.53(8H, m, $PhCH_2Sn$), 1.88(6H, s, CH_3). ^{119}Sn NMR ($CDCl_3$, ppm): −471.5. IR (KBr, cm^{-1}): 3418(m, OH), 3019(s, Ar–H), 2922(m, C–H), 1622(m, C=N), 1602(s, C=N–N=C), 1596, 1333(s, CO_2), 1209(m, C–O), 674(m, Sn–O), 565(w, Sn–C), 475(m, Sn–N).

2.3.8. $\{(p\text{-}FC_6H_4CH_2)_2Sn[2\text{-}HOC_6H_4CON_2C(CH_3)CO_2]\}_2$ (**8**)

Compound **8** was recrystallized from methanol to give orange precipitate. Yield: 86%, m.p. 124 °C. Anal. Calc. for $C_{48}H_{40}F_4N_4O_8Sn_2$: C, 51.73; H, 3.59; N, 5.03%. Found: C, 51.74; H, 3.62; N, 4.96%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.28(2H, s, Ar–OH), 6.91–7.49(24H, m, Ar–H and Ph–H), 3.45–3.57(8H, m, $PhCH_2Sn$), 1.79(6H, s, CH_3). ^{119}Sn NMR ($CDCl_3$, ppm): −455.5. IR (KBr, cm^{-1}): 3387(m, OH), 3026(s, Ar–H), 2925(s, C–H), 1614(m, C=N), 1606(s, C=N–N=C), 1591, 1321(s, CO_2), 1201(m, C–O), 676(m, Sn–O), 545(w, Sn–C), 468(w, Sn–N).

2.4. X-ray crystallography

Crystallographic data and refinement details are given in Table 1. X-ray crystallographic data for compounds **1**, **2** and **4** were collected on a Bruker SMART CCD 1000 diffractometer at 298(2) K using Mo Kα radiations (0.71073 Å). The structure was solved by direct method and differential Fourier map using SHELXL-97 program, and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms were calculated and refined isotropically. The weighting scheme employed for **1** was of the form $w = 1/[\sigma^2(F_o^2) + (0.0707P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$, $w = 1/[\sigma^2(F_o^2) + (0.1143P)^2 + 1.8551P]$ for **2**, where $P = (F_o^2 + 2F_c^2)/3$, and $w = 1/[\sigma^2(F_o^2) + (0.0743P)^2 + 1.8716P]$ for **4**, where $P = (F_o^2 + 2F_c^2)/3$.

3. Results and discussion

3.1. Preparations

The compounds $[R_2SnLY]_2$ were produced by the reaction from pyruvic acid isonicotinyl hydrazone with triphenyltin hydroxide or triaryltin chloride, and pyruvic acid salicylhydrazone with triaryltin chloride, in the 1:1 molar ratio. It is clear that the existence of enolic proton of ligands leads to the production of dearylation of triaryltin carboxylates, $R_3Sn(C_9H_7N_3O_3)$ and $R_3Sn(C_{10}H_8N_2O_4)$, the major products of R_3SnOH or R_3SnCl with Schiff base ligands, and the seven-coordinate dimeric composition formed as a result of steric effect or solvent effects in the recrystallization. Analogous reactions could also be found in the dearylation of $(R_3Sn)_2O$ or R_3SnOH with other carboxylic acids [15–17], but they do not have the same mechanism as these. Through crystal structure determination, it can be seen that the structures of compounds **1**–**3** were one-dimensional infinite chain polymers because of the presence

Table 1
Crystallographic data of compounds **1**, **2** and **4**

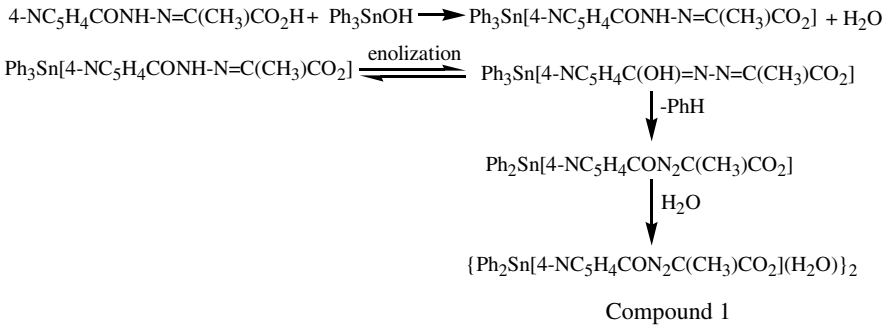
Compound	**1**	**2**	**4**
Empirical formula	$C_{43}H_{42}Cl_2N_6O_9Sn_2$	$C_{46}H_{46}N_6O_8Sn_2$	$C_{50}H_{52}N_4O_{10}Sn_2$
Formula weight	1095.11	1048.27	1106.34
Temperature (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$C2/c$	$P2_1/c$
Unit cell dimensions			
a (Å)	11.3674(17)	32.866(7)	19.124(2)
b (Å)	11.7201(18)	9.8428(18)	18.444(2)
c (Å)	35.127(3)	28.491(5)	15.3732(19)
β(°)	90	95.917(4)	112.699(2)
Volume (Å^3)	4679.8(11)	9168(3)	5002.6(11)
Z	4	8	4
Calculated density (mg/m^3)	1.554	1.519	1.469
F(000)	2192	4224	2240
Crystal size (mm)	$0.45 \times 0.28 \times 0.22$	$0.51 \times 0.43 \times 0.22$	$0.57 \times 0.48 \times 0.42$
Scan range θ (°)	2.1–25.0	1.8–25.0	1.8–25.0
Total/unique/R_{int}	24460/8142/0.065	22817/7990/0.027	25832/8804/0.031
Goodness-of-fit on F^2	1.004	1.004	1.014
Refined parameters	587	571	603
Reflections with $I > n\sigma(I)$	6155, $n = 2$	5897, $n = 2$	5472, $n = 2$
R_1/wR_2	0.052/0.115	0.039/0.124	0.035/0.091
μ (mm^{-1})	1.24	1.148	1.058
ρ_{max}/ρ_{min} (e A^{-3})	0.94 and −0.66	1.13 and −0.50	0.99 and −0.48

of the intermolecular hydrogen bond interactions formed by the coordination water molecule and the pyridine nitrogen atom of the adjacent unit. While the other compounds **4**–**8** with pyruvic acid salicylhydrazone were all monomers.

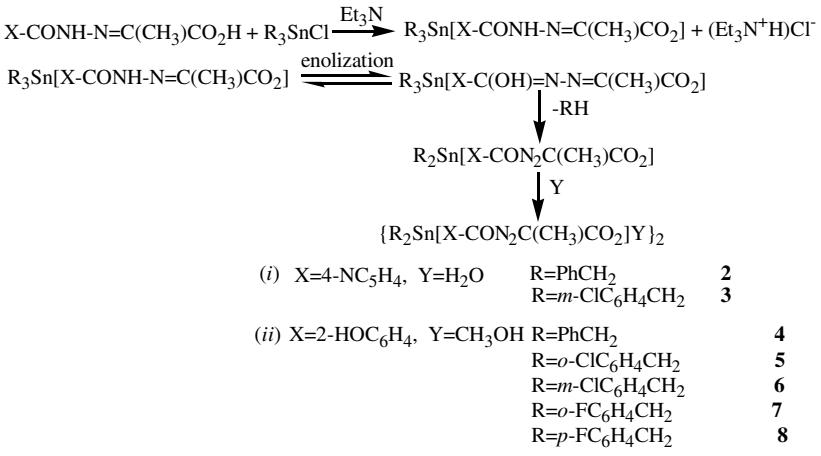
A possible mechanism is given in Schemes 1 and 2.

3.2. IR data

A remarkable difference between the IR spectra of the ligands and those of the corresponding compounds is that the stretching vibration bands of carbonyl disappear from the spectra of the compounds. The disappearance of the bands assigned to carbonyls unambiguously confirms that the ligands coordinated with the tin are in the enol form. The characteristic absorptions at 1614–1633 and 1598–1609 cm^{-1} in the spectra of these compounds indicate the presence of C=N and C=N–N=C groups [18]. The stretching frequencies of interest are those associated with the COO, 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 680 cm^{-1} in the respective spectra of the compounds, which is absent in the free ligands, is assigned to the Sn–O stretching mode of vibration. The weak- or medium-intensity band in the region 459–489 cm^{-1} can be assigned to Sn–N stretching vibration. All these values are consistent with that detected in a number of organotin(IV) derivatives [19,20], and the infrared spectra of compounds **4**–**8** show strong typical broad bands at 3387–3421 cm^{-1} related to the phenolic hydrogen



Scheme 1.



Scheme 2.

stretching vibration according to the previous report [21], which strongly indicates that in these compounds the phenolic oxygen atoms do not participate in coordination to the atoms.

In organotin carboxylates, the IR spectra can provide useful information concerning the coordinate form of the carboxyl. The IR spectra of compounds **1**–**8** show that the ν_{as} and ν_s bands are assigned to the regions 1588–1615 and 1321–1363 cm^{-1}, respectively. The magnitude of $\Delta\nu[\nu_{as}(COO) - \nu_s(COO)]$ occurring at 243–281 cm^{-1} indicates that the carboxylate ligands function as monodentate ligand under the conditions employed [9], respectively. These conclusions are supported by the results of X-ray diffraction studies.

3.3. ^1H NMR spectra

In ^1H NMR spectra of the two free ligands, a single resonance for the proton in –NHN= group is observed at 1487 and 1495 ppm, which are absent in the spectra of the compounds, indicating the deprotonation of the –NHN= group, and confirming that the ligands coordinate with the tin in the enol form. For compounds **1**–**3**, the spectra show that the chemical shifts of the protons on the pyridine ring exhibited two sets of signals in δ 7.79–8.82 as a doublet and in δ 7.76–8.03 as a doublet, too, and the coupling constant is equal to 4.80–5.20 Hz. The Ar–OH resonance appeared in the region 11.16–12.56 ppm as singlet for the compounds **4**–**8** strongly suggests that the phenolic oxygen atoms do not participate in coordination to the tin atoms, and this is quite different from that of the four compounds we have reported [22].

3.4. ^{119}Sn NMR spectra

Although $\delta(^{119}Sn)$ is influenced by several factors, including the aromatic 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 [23]. The ^{119}Sn NMR data show only one signal around –455 ppm for compounds **1**–**8**, typical of a seven-coordinate species, and have been found in accordance with the crystalline state structure [24]. This further confirms the dimeric structures for all compounds.

3.5. X-ray crystallography

3.5.1. Structures of $\{Ph_2Sn[4\text{-}NC_5H_4\text{-}(O)N_2C(CH_3)CO_2](H_2O)\}_2 \cdot CH_2Cl_2 \cdot H_2O$ (**1**) and $\{(PhCH_2)_2Sn[4\text{-}NC_5H_4\text{-}C(O)N_2C(CH_3)CO_2](H_2O)\}_2$ (**2**)

The crystal structures of compounds **1** and **2** have been determined. The structures conform to the same motif. The $[R_2SnL(H_2O)]_2$ units are connected in polymeric structures as shown in Figs. 1–4, respectively, selected bond lengths (Å) and angles (°) are listed in

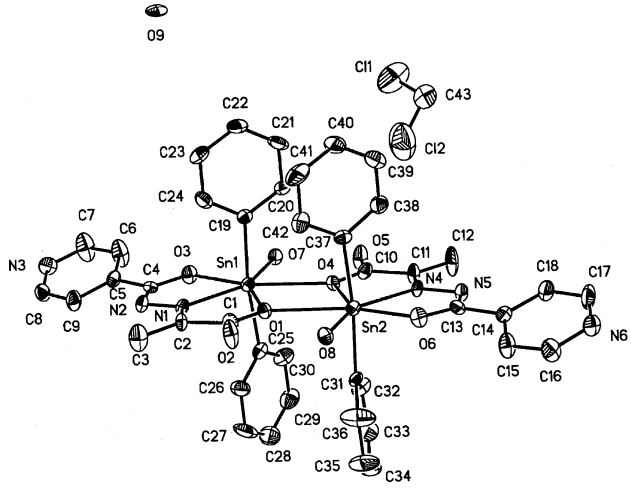


Fig. 1. Molecular structure of compound **1**.

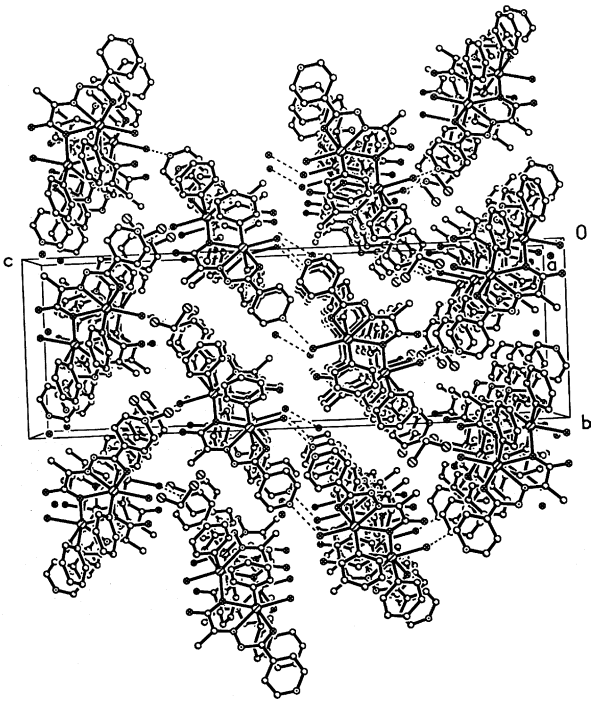


Fig. 2. Packing of the molecules in a unit cell of compound **1**.

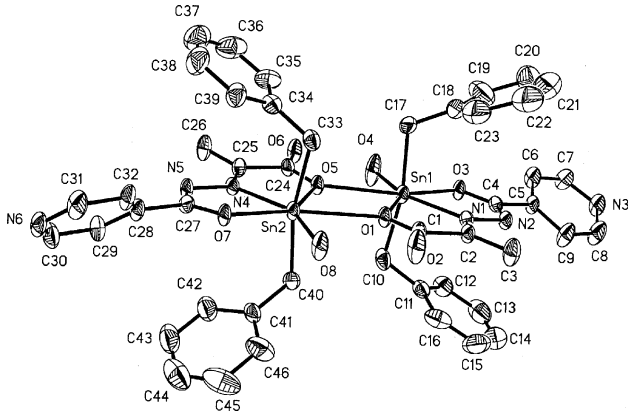


Fig. 3. Molecular structure of compound **2**.

Tables 2 and 3. Intermolecular hydrogen bonds [2.808, 2.785 Å for **1** and 2.651, 2.804 Å for **2**] create a continuous one-dimensional polymeric chain.

For compounds **1** and **2**, all Sn atoms are chelated by the tridentate ligands, and molecular structures reveal dinuclear dimers with a central Sn_2O_2 four-membered ring. Every tin atom exists in a distorted pentagonal bipyramidal coordination environment in which one water molecule, one tridentate pyruvic acid isonicotinyl hydrazone ligand, and two *trans* aryl groups coordinate to Sn center. Tin and the bonded oxygen and nitrogen atoms are nearly coplanar and deviate only slightly from regular pentagonal geometry, mean deviations from plane are 0.0041, 0.0111 Å for **1** and 0.0220, 0.0358 Å

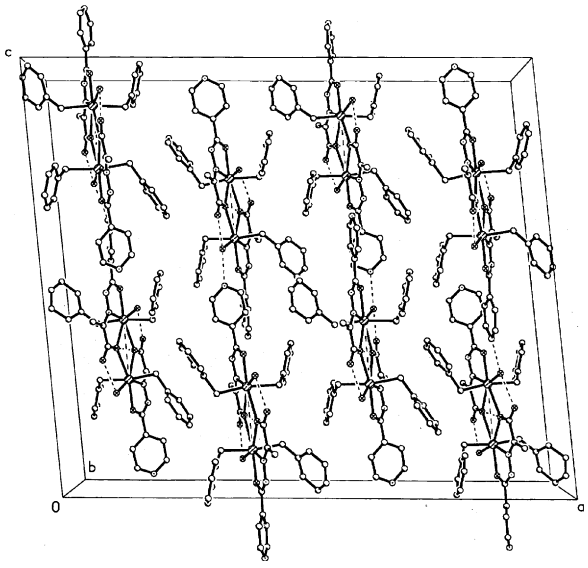


Fig. 4. Packing of the molecules in a unit cell of compound **2**

for **2**. The aryl groups occupy the apical position, the axial–Sn–axial, C19–Sn1–C25 is 172.7(3)° and C31–Sn2–C37 is 174.2(3)° for **1**, C10–Sn1–C17 is 168.5(2)° and C33–Sn2–C40 is 167.5(2)° for **2**. The structures are very similar to that of derivatives reported previously [11]. The bond distances of Sn1–O7 and Sn2–O8 are 2.288(6) and 2.274(6) Å, respectively, for **1**, Sn1–O4 and Sn2–O8 are 2.291(5) and 2.327(4) Å for **2**, which are relatively longer than those in the analogous [5,9,18,25], due to the formation of intradimeric hydrogen bonds, O7···O5 (2.619 Å) and O8···O2 (2.643 Å) for **1**, O4···O6 (2.583 Å) and O8···O2 (2.652 Å) for **2**, and interdimeric hydrogen bonds, O7···N3#1 [$-x+1$, $y+1/2$, $-z+3/2$] (2.808 Å) and O8···N6#2 [$x-1/2$, $-y+3/2$, $-z+2$] (2.785 Å) for **1**, O4···N6#1 [x, $-y+2$, $z+1/2$] (2.651 Å) and O8···N3#2 [x, $-y+1$, $z-1/2$] (2.804 Å) for **2**. Neighboring molecules are held together by hydrogen bonds O7···N3#1 and O8···N6#2 for **1**, O4···N6#1 and O8···N3#2 for **2**. These hydrogen bonds contribute to the crystal stability and compactness and result in a one-dimensional linear chain arrangement from the intermolecular bonds (Figs. 2 and 4). Furthermore, for compound **1**, the crystal consists of discrete dimeric compound and solvent (H_2O and CH_2Cl_2) molecules in the ratio of 1:1:1. The solvent molecules do not have any obvious interaction with the dimer.

*3.5.2. Structure of {$(PhCH_2)_2Sn[2\text{-}HOC_6H_4\text{–}C(O)N_2C(CH_3)CO_2](CH_3OH)\}_2$ (**4**)*

The crystal structure and unit cell of compound **4** are shown in Figs. 5 and 6, respectively. All hydrogen atoms have been omitted for the purpose of clarity. Tables 2 lists the selected bond lengths and angles for compound **4**.

Table 2
Selected bond distances (Å) and angles (°) for compounds **1**, **2** and **4**

1			
Sn1–O3	2.177(6)	Sn2–O6	2.191(6)
Sn1–N1	2.288(7)	Sn2–O8	2.274(6)
Sn1–O7	2.288(6)	Sn2-N4	2.282(7)
Sn1–O1	2.385(6)	Sn2–O4	2.360(6)
Sn1–O4	2.538(5)	Sn2–O1	2.552(5)
C19-Sn1–C25	172.7(3)	C31–Sn2–C37	174.2(3)
C19-Sn1–O3	92.3(3)	C31–Sn2–O6	91.9(3)
C19-Sn1–N1	93.5(3)	C31–Sn2–O8	88.7(3)
C19-Sn1–O7	88.4(3)	C31–Sn2-N4	92.0(3)
C19-Sn1–O4	87.1(2)	C31–Sn2–O1	87.6(2)
2			
Sn1–O3	2.165(4)	Sn2–O7	2.168(3)
Sn1–N1	2.260(4)	Sn2-N4	2.272(4)
Sn1–O4	2.291(5)	Sn2–O8	2.327(4)
Sn1–O1	2.383(3)	Sn2–O5	2.414(3)
Sn1–O5	2.597(3)	Sn2–O1	2.637(3)
C17–Sn1–C10	168.5(2)	C40–Sn2–C33	167.5(2)
C17–Sn1–O3	93.8(2)	C40–Sn2–O7	98.00(17)
C17–Sn1–N1	95.5(2)	C40–Sn2-N4	93.4(2)
C17–Sn1–O4	88.8(3)	C40–Sn2–O8	88.2(2)
C17–Sn1–O1	89.2(2)	C40–Sn2–O5	87.29(19)
4			
Sn1–O3	2.158(3)	Sn1–O5	2.403(4)
Sn1–N1	2.227(4)	Sn1–O1#1	2.816(3)
Sn1–O1	2.296(3)		
C11–Sn1–C18	164.5(2)	C11–Sn1–O5	82.88(18)
C11–Sn1–O3	94.03(17)	C11–Sn1–O1#1	85.92(15)
C11–Sn1–N1	99.81(17)	C11–Sn1–O1	91.02(16)

Symmetry transformations used to generate equivalent atoms: #1: $-x$, $-y+1$, $-z+1$.

Table 3
Hydrogen-bonding geometry (Å, °)

D-H···*A*	*D*-H	H···*A*	*D*···*A*	*D*-H···*A*
Compound **1**				
O7-H43···O5	0.845	1.846	2.619	151.58
O7-H44···N3#1	0.848	2.02	2.808	154.17
O8-H45···O2	0.849	1.81	2.643	166.5
O8-H46···N6#2	0.847	1.998	2.785	154.36
Compound **2**				
O4-H1···N6#1	0.897	2.142	2.651	115.19
O4-H2···O6	0.899	1.706	2.583	164.21
O8-H3···N3#2	0.898	1.951	2.804	158.19
O8-H4···O2	0.896	1.783	2.652	162.83
Compound **4**				
O5-H51···O2#1	0.898	1.764	2.639	164.31

Symmetry transformations used to generate equivalent atoms: compound **1**: #1 $-x+1$, $y+1/2$, $-z+3/2$; #2 $x-1/2$, $-y+3/2$, $-z+2$. compound **2**: #1 x, $-y+2$, $z+1/2$; #2 x, $-y+1$, $z-1/2$. compound **3**: #1 $-x$, $-y+1$, $-z+1$.

For compound **4**, the asymmetric unit contains two monomers, which are different from a crystallographic point of view. The conformations of the two independent molecules are almost the same, with only small differences in bond lengths and bond angles. In this compound, the Sn atom exists in a distorted pentagonal

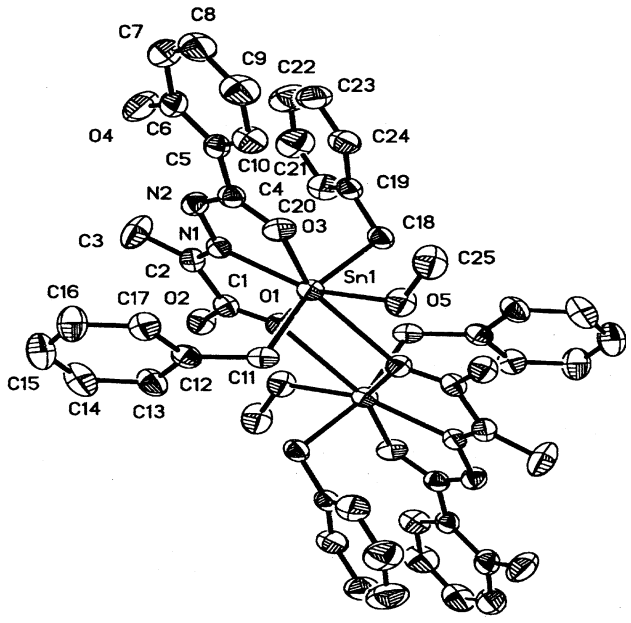


Fig. 5. Molecular structure of compound **4**.

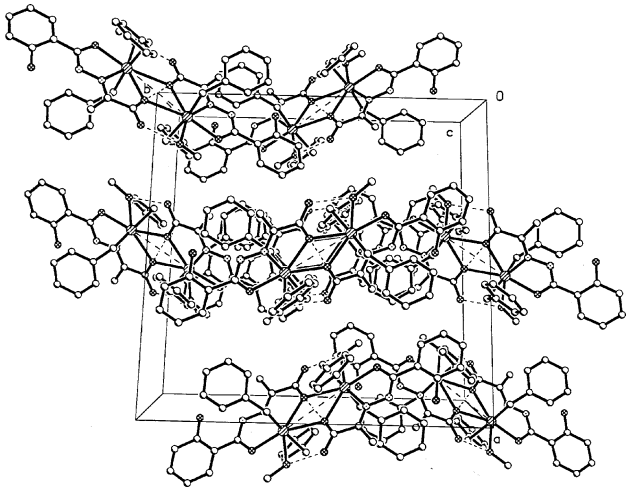


Fig. 6. Packing of the molecules in a unit cell of compound **4**.

bipyramidal coordination environment in which one methanol molecule, one tridentate pyruvic acid salicylhydrazone ligand, and two *trans* benzyl groups coordinate to each Sn center. The atoms O1, O1#1, O5, O3 and N1 are coplanar within 0.0485 Å, which form the equatorial plane. Furthermore, the angle of the axial C18–Sn1–C11 is 164.5(2)°, which deviates from the linear angle of 180°. The O1 atom of the carboxylate residue also binds the other tin atom, Sn1#1, generating a Sn_2O_2 four-membered ring. The distance of Sn1–O1#1 [$-x$, $-y+1$, $-z+1$] (2.816(3) Å) is relatively longer than that of Sn1–O1 (2.296(3) Å), but is comparable with those found in related seven-coordinate diorganotin systems [5,9]. Thereby, the molecular structure of this compound can be described as a dimer, and the coordination geometry of tin can also be described as a

trans-C_2SnO_4N pentagonal bipyramid with the two benzyl groups occupying *trans* positions. Furthermore, in the dimeric structure there also exist intramolecular hydrogen bonds between another carboxyl oxygen atom O2 without coordinating to Sn atom and hydroxyl hydrogen atoms of the coordinated methanol molecule, O2···O5#1 (2.639 Å). Undoubtedly, these hydrogen bonds contribute to the compactness of the dimer. Meanwhile, studies show that the phenolate oxygen atoms are also in nonparticipation in coordination to the tin atom.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 257091 for compound **1**, CCDC No. 257092 for compound **2** and CCDC No. 257093 for compound **4**. Copies of this information may be obtained 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).

Acknowledgements

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