Self-Assembly of Organotin(IV) Moieties with the Schiff-Base Ligands Pyruvic Acid Isonicotinyl Hydrazone and Pyruvic Acid Salicylhydrazone: Synthesis, Characterization, and Crystal Structures of Monomeric or Polymeric Complexes

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A series of organotin(IV) complexes of the type $[R_2SnLY]_2$ or $[R_2SnL(R_3SnOH)]_2$ [L = $4\text{-}NC_5H_4CON_2C(CH_3)CO_2$ or $2\text{-}HOC_6H_4CON_2C(CH_3)CO_2$, and Y = H_2O or CH_3OH] have been synthesized by the condensation reaction of R_2SnO (R = Ph **1**, nC_8H_{17} **2**) or R_3SnCl (R = *o*-ClBz **3**, *o*-FBz **4**, *p*-FBz **5**, *p*-CNBz **6**) with the Schiff-base ligand pyruvic acid isonicotinyl hydrazone in a 1:1 molar ratio or $(R_3Sn)_2O$ (R = *n*Bu **7**, Bz **8**, *p*-CNBz **9**) or R_3SnCl (R = *o*-ClBz **10**, *p*-ClBz **11**, *p*-CNBz **12**) with the Schiff-base ligand pyruvic acid salicylhydrazone in a 1:1 molar ratio. All complexes were characterized by elemental analysis and IR, ^1H, and ^{119}Sn NMR spectroscopy. The crystal structures of complexes **1**, **2**, **3**, **7**, and **10** have been determined by X-ray single crystal diffraction analyses, which show that the tin atoms of **1**, **2**, **3**, and **10** are all seven-coordinate in distorted pentagonal bipyramid geometries, of which only complex **1** exhibits an asymmetric structure containing two different types of tin atoms. The crystal structure of **7** exhibits a dimeric structure containing distannoxane units with two types of tin atoms, in which one tin atom appears to be seven-coordinate with a distorted pentagonal bipyramid geometry and the other is four-coordinate with a distorted tetrahedral geometry. A comparison of the IR spectra of the ligands with those of the corresponding complexes reveals that the ligands coordinate to tin in the enol form due to the disappearance of the bands assigned to the carbonyl group.

Introduction

Schiff bases still play an important role as ligands in metal coordination chemistry even after almost a century since their discovery.[1–4] Organotin(IV) complexes with Schiff bases have received increasing attention owing to their antitumor activities and potential applications in biotechnology.[5–11] In addition, Schiff base organotin(IV) complexes are of interest for structural reasons. The coordination chemistry of some tridentate ONO- and ONS-donor Schiff bases has been described,[12,13] and we have recently reported some organotin(IV) complexes with the potentially ONO tridentate Schiff-base ligands salicylideneamino acids and pyruvic acid isonicotinyl hydrazone.[14,15] As part of our ongoing project dealing with the study of the interaction of tin(IV) and organotin(IV) species with *O*-donor and *N*-donor ligands, we have now synthesized twelve new organotin(IV) complexes of pyruvic acid isonicotinyl hydrazone and salicylhydrazone by self-assembly of metal ions, utilizing their preference for different coordination geometry, choice of suitable ligands, and intermolecular interactions such as hydrogen bonding. The details of the structural and spectroscopic characterization of complexes **1**–**12** are reported herein. Five of the complexes have been studied by X-ray diffraction, and reveal that there exist five different types of coordinated tin atoms (shown in Scheme 1).

Complexes **2**, **3**, and **10** are coordinated in mode A, and each reveals a highly centrosymmetric dimeric structure containings a distannoxane unit. This is the more usual structure adopted by this class of complexes.[15,16] It is worthwhile to note that crystals containing an *n*-octyl group were obtained by the reaction of pyruvic acid isonicotinyl hydrazone with di-*n*-octyltin oxide and recrystallized from acetone, as structural information for complexes containing *n*-octyl groups was lacking until now. Meanwhile, to our surprise, we obtained an unusual asymmetric linear chain polymer complex **1** containing two different types of tin atom from the reaction of Schiff-base ligand pyruvic acid isonicotinyl hydrazone with diphenyltin oxide. These two types of tin atom contain ligands in mode B. One of the two types is coordinated by tridentate formation of the Schiff base, while the other is not in the same way due to

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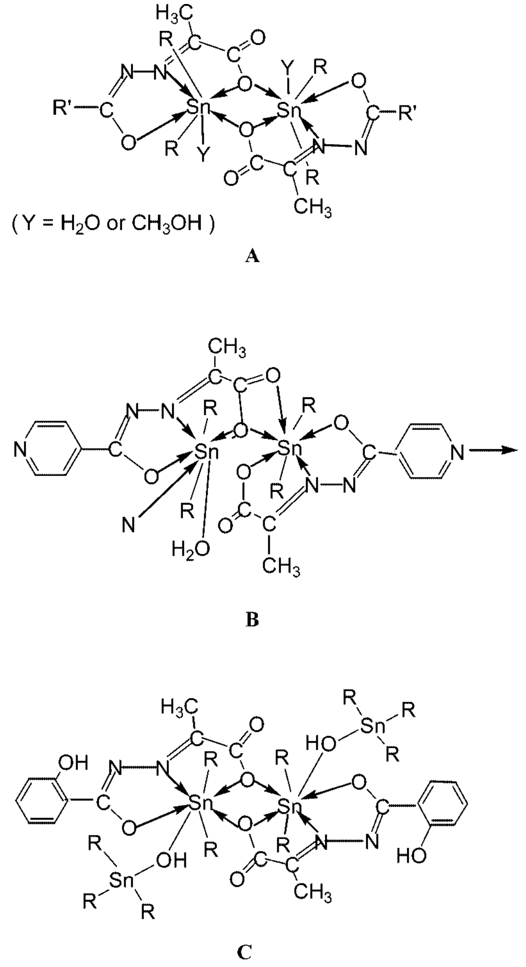


A

B

C

Scheme 1.

coordination between tin and two oxygen atoms derived from the carboxyl group of the adjacent ligand.

Interestingly, we also succeeded in preparing a novel tetranuclear organotin(IV) complex $[(n\mathrm{Bu})_2\mathrm{Sn}\{2\text{-}\mathrm{HOC_6H_4}\text{-}\mathrm{CON_2C(CH_3)CO_2}\}\{(n\mathrm{Bu})_3\mathrm{SnOH}\}]_2$ (**7**) by treatment of $[(n\mathrm{Bu})_3\mathrm{Sn}]_2\mathrm{O}$ with the Schiff-base ligand pyruvic acid salicylhydrazone in a 1:1 molar ratio, which exhibits a dimeric structure containing distannoxane units with two types of tin atoms, of which one tin atom appears to be seven-coordinate with a distorted pentagonal bipyramid geometry and the other is four-coordinate with a distorted tetrahedral geometry (mode C).

Results

IR Spectra

A remarkable difference between the IR spectra of the ligands and those of the corresponding complexes is that the stretching vibration bands of the carbonyl group disappear from the spectra of all the complexes. The absence of the bands assigned to the carbonyls unambiguously confirms that the ligands coordinated to the tin are in their enol form. The characteristic absorptions at 1622–1640 and 1595–1608 $\mathrm{cm^{-1}}$ in the spectra of these complexes indicate the presence of C=N and C=N–N=C groups.[17] The stretching frequencies of interest are those associated with the acid COO and the Sn–O and Sn–N groups. The spectra of all complexes have some common features. The explicit feature in the infrared spectra of all complexes is the strong absorption at about 700 $\mathrm{cm^{-1}}$ in the spectra of the complexes, which is absent in the free ligands, which is assigned to the Sn–O stretching mode of vibration. The weak- or medium-intensity band in the region 476–486 $\mathrm{cm^{-1}}$ can be assigned to the Sn–N stretching vibration. All these values are consistent with those detected in a number of organotin(IV) derivatives.[18,19]

The IR spectra of organotin carboxylate complexes can provide useful information concerning the coordination behavior of the carboxyl groups. The IR spectrum of complex **1** shows that the ν_{as} and ν_{as} bands are assigned to the regions 1603, 1505 $\mathrm{cm^{-1}}$ and 1366, 1312 $\mathrm{cm^{-1}}$, respectively. The magnitude of $\Delta\nu$ [ν_{as}(COO) – ν_s(COO)] is 237 and 193 $\mathrm{cm^{-1}}$, and therefore indicates the presence of mono- and didentate carboxyl groups.[20] Moreover, the magnitude of $\Delta\nu$ (231–285 $\mathrm{cm^{-1}}$) for complexes **2**–**12** indicates that the carboxylate ligand functions as a monodentate ligand in these complexes.[20] These conclusions are supported by the results of X-ray diffraction studies.

NMR Spectra

In ^{1}H NMR spectra of the free ligands, the single resonance for the proton of the -NHN= group is observed at either δ = 3.75 or 3.89 ppm, and is absent in the spectra of the complexes, thus indicating deprotonation of the -NHN= group and confirming that the ligand coordinate to the tin in the enol form. For complexes **1**–**6**, the spectra show that the chemical shifts of the protons on the pyridine ring exhibit two sets of signal in the ranges δ = 7.57–8.89 ppm, as a doublet, and δ = 7.22–8.13 ppm, also as a doublet. The coupling constant is equal to 4.80–8.40 Hz. The Ar-OH resonance appears in the region δ = 10.87–11.43 ppm, as a singlet, for the complexes **7**–**12**, which strongly suggests that the phenolic oxygen atoms do not participate in coordination to the tin atoms; this is quite different to the four complexes we have reported previously.[14]

The ^{119}Sn NMR resonance at around δ = –450 ppm is characteristic[21] of the seven-coordinate tin atom observed in the crystalline state for all the complexes. As reported in the literature,[22–24] values of $\delta_{^{119}\mathrm{Sn}}$ in the ranges δ = –210 to –400, –90 to –190, and 200 to –60 ppm have been associated with six-, five-, and four-coordinate tin centers, respectively. On this basis we can conclude that the $\delta_{^{119}\mathrm{Sn}}$ value for the other type of tin atom in **1** is δ = –226.9 ppm in solution, which suggests that the intermolecular Sn–N interaction probably does not survive in solution and that a six-coordinate species is formed. Therefore, it can reasonably be assumed that the structure of complex **1** in solution is different from that observed in the solid state. For complexes **7**–**9**, the ^{119}Sn chemical shifts (δ = 102.3–111.7 ppm) in $CDCl_3$ indicate that there is also a type of four-coordinate tetrahedral tin atom in these complexes.

Description of the Structures

Crystal Structure of {$Ph_2Sn[4\text{-}NC_5H_4CON_2C(CH_3)CO_2]$-($H_2O$)}$_2$ (1)

The molecular structure of complex **1** is shown in Figure 1. Figure 2 shows a particular one-dimensional linear chain polymeric structure. Selected bond lengths and angles are listed in Table 1. The crystal structure of complex **1** reveals a dinuclear complex containing two types of tin atom (mode B), where a one-dimensional chain polymeric structure forms through an interaction between the N atoms of the pyridine ring and the tin atoms of an adjacent molecule. Both of the tin atoms Sn1 and Sn2 have a seven-coordinate geometry in a distorted pentagonal bipyramidal arrangement.

Table 1. Selected bond lengths [Å] and bond angles [°] for complex **1**.

Sn1–C19	2.089(15)	Sn2–C31	2.116(18)
Sn1–C25	2.135(13)	Sn2–C37	2.136(14)
Sn1–O3	2.221(11)	Sn2–O4	2.207(9)
Sn1–N1	2.327(11)	Sn2–O6	2.210(7)
Sn1–O7	2.370(10)	Sn2–N4	2.249(12)
Sn1–O1	2.387(7)	Sn2–O2	2.388(10)
Sn1–N6#1	2.394(9)	Sn2–O1	2.594(8)
C19–Sn1–C25	176.8(6)	C31–Sn2–C37	169.9(6)
C19–Sn1–O3	91.5(4)	C31–Sn2–O4	93.1(5)
C25–Sn1–N1	90.5(5)	C37–Sn2–O6	90.1(5)
C25–Sn1–O7	87.0(5)	C37–Sn2–N4	94.3(5)
C19–Sn1–O1	89.5(4)	C31–Sn2–O2	83.8(6)
C25–Sn1–O1	90.3(5)	C37–Sn2–O2	86.2(5)
N1–Sn1–O1	66.2(3)	O6–Sn2–O2	87.8(3)
C19–Sn1–N6#1	87.8(4)	C31–Sn2–O1	86.5(5)
O3–Sn1–N6#1	72.7(4)	O4–Sn2–O1	77.6(3)
O1–Sn1–N6#1	151.2(3)	O2–Sn2–O1	52.2(2)

The Sn1 atom is rendered seven-coordinate by coordination of the nitrogen atom N6#1 of the 4-pyridinecarbonyl group from an adjacent molecule. The tin atom is surrounded by one water molecule, one tridentate pyruvic acid isonicotinyl hydrazone ligand, two *trans* phenyl groups, and nitrogen atom N6#1 (x – 1/2, –y + 3/2, z). Thus, the atoms O1, N1, O3, N6#1, and O7 are coplanar within ±0.0263 Å,

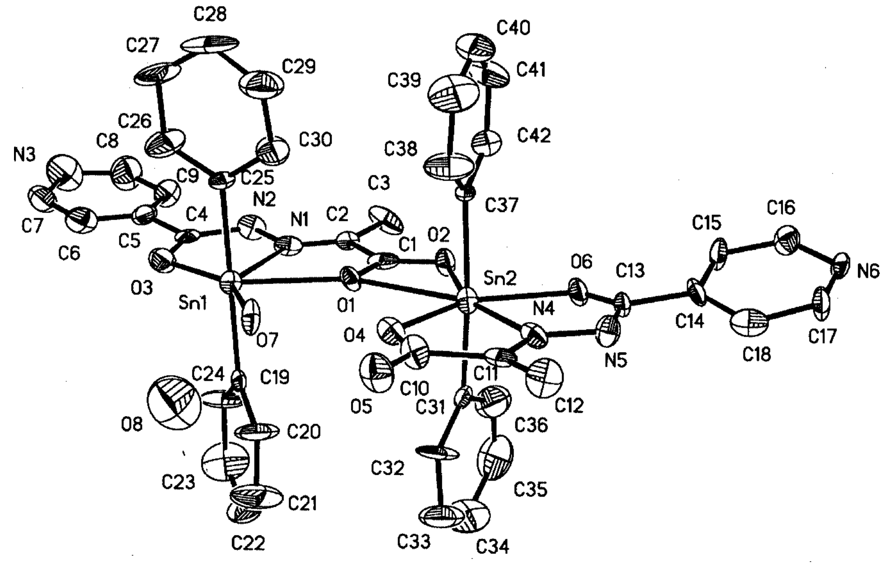


Figure 1. Molecular structure of complex **1**; ellipsoids shown at the 30% probability level.

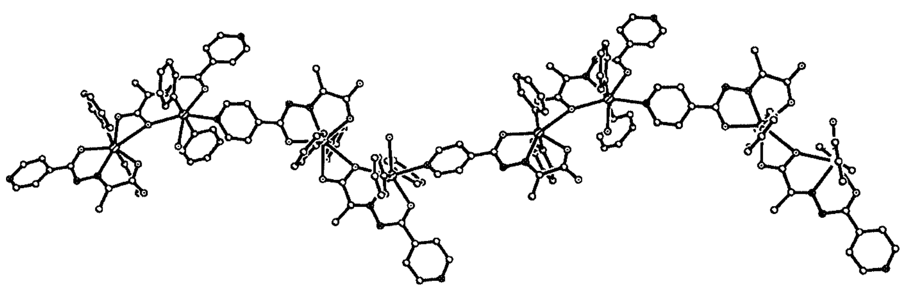


Figure 2. Perspective view of the one-dimensional chain of complex **1**.

and form the equatorial plane. While two *trans* phenyl carbon atoms occupy the axial sites, the angle of the axial C25–Sn1–C19 is 176.8(6)°, which deviates from the linear angle of 180°. These data indicate that the Sn1 atom is in a distorted pentagonal bipyramid geometry. The intermolecular Sn1–N6#1 distance of 2.394(9) Å is longer than the sum of the covalent radii of Sn and N (2.15 Å), but considerably less than the sum of the van der Waals radii (3.75 Å),[25] therefore it should be considered as a bonding interaction. In this connection it is relevant to note the Sn–N bond lengths found in other crystal structures of organotin complexes containing a pyridinecarboxylate ligand.[20,26] For instance, in the dicarboxylate tetraorganostannoxane $\{[(n\text{Bu})_2\text{Sn}(2\text{-pic})]_2\text{O}\}_2$ the two Sn–N bond lengths are 2.550(5) Å and 3.150(5) Å,[26] and in the linear polymer $[(\text{PhCH}_2)_3\text{Sn}(\text{OO}_2\text{CC}_5\text{H}_4\text{N-4})]$ the Sn–N distance is 2.563 Å.[20]

The Sn2 atom is bonded to the carboxyl oxygens O1 and O2, with Sn2–O1 and Sn2–O2 bond lengths of 2.594(8) and 2.388(10) Å, respectively. Thus, the Sn2 atom is surrounded by C31 and C37 of the two *trans* phenyl groups along the axial direction while O1, O2, O6, N4, and O4 form the equatorial plane. The pentagonal bipyramid geometry of Sn2 is distorted, as indicated by the bonding angles of 169.9(6)°, 93.1(5)°, 90.1(5)°, 142.5(4)°, 95.4(5)°, 83.8(6)°, 157.4(3)° and 86.4(4)° for C31–Sn2–C37, C31–Sn2–O4, C37–Sn2–O6, O4–Sn2–O6, C31–Sn2–N4, C31–Sn2–O2, N4–Sn2–O2, and C37–Sn2–O1, respectively.

Crystal Structure of $[(n\text{C}_8\text{H}_{17})_2\text{Sn}\{4\text{-NC}_5\text{H}_4\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2\}(\text{H}_2\text{O})]_2$ *(2)*

The molecular structure of compolex **2** is shown in Figure 3. Figure S2 shows the packing of the molecule in the unit cell as seen in projection on the plane. Selected bond lengths and angles are listed in Table 2. In this complex, the Sn atom exists in a seven-coordinate environment in which one water molecule, two tridentate pyruvic acid isonicotinyl hydrazone ligands, and two *trans n*-octyl groups coordinate to each Sn center (mode A). The atoms O1, O5, O4, O3, and N1 are coplanar within ±0.0244 Å, and form the equatorial plane. Furthermore, the angle of the axial C18–Sn1–C10 is 164.4(10)°, which deviates from the linear angle of 180°. These data indicate that the tin atom of this complex is in a distorted pentagonal bipyramid geometry. The O1 atom of the carboxylate residue also binds the other tin atom, Sn2, generating an Sn_2O_2 four-membered ring. The Sn2–O1#2 (x, $y + 1$, z) distance [2.745(10) Å] is longer than that of Sn1–O1 [2.340(10) Å], but is comparable with those found in related seven-coordinate diorganotin systems.[20,23] The structure of this complex can therefore be described as a dimer, and the coordination geometry of tin can be also described as a *trans*-$\text{C}_2\text{SnO}_4\text{N}$ pentagonal bipyramid with the two *n*-octyl groups occupying *trans* positions [C18–Sn1–C10 = 164.4(10)° and C35–Sn2–C43 = 165.1(8)°]. It also has intradimer hydrogen bonds [O4···O6 = 2.642 Å and O8···O2 = 2.661 Å] and interdimer hydrogen bonds [O4···N6#3 ($x - 1/2$, $-y + 1/2$, z) = 2.718 Å and O8···N3#4 ($x - 1/2$, $-y + 3/2$, z) = 2.756 Å]. Neighboring molecules are held together by hydrogen bonds (O4···N6#3 and O8···N3#4). These hydrogen bonds contribute to the crystal stability and compactness and result in a one-dimensional chain arrangement. It is worthwhile to note that, for organotin(IV) complexes containing straight-chain alkyl groups, there are plenty of *n*-butyl group complexes, while complexes with *n*-octyl groups are lacking until now. This

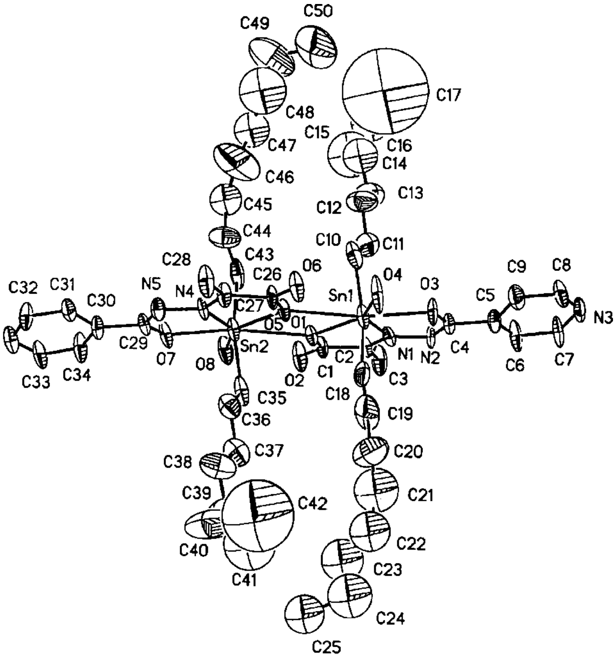


Figure 3. Molecular structure of complex **2**; ellipsoids shown at the 30% probability level.

Table 2. Selected bond lengths [Å] and bond angles [°] for complexes **2** and **3**.

$[(n\text{C}_8\text{H}_{17})_2\text{Sn}\{4\text{-NC}_5\text{H}_4\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2\}(\text{H}_2\text{O})]_2$ **(2)**			
Sn1–C18	2.06(3)	Sn1–O1	2.340(10)
Sn1–C10	2.09(3)	Sn1–O4	2.354(13)
Sn1–O3	2.219(9)	Sn1–O5#1	2.715(10)
Sn1–N1	2.283(16)		
C18–Sn1–C10	164.4(10)	O3–Sn1–O4	77.4(4)
C10–Sn1–O3	94.2(7)	N1–Sn1–O4	147.4(4)
C18–Sn1–N1	98.5(8)	O1–Sn1–O4	143.9(4)
O3–Sn1–N1	70.0(5)	C10–Sn1–O5#1	83.9(7)
C10–Sn1–O1	90.1(7)	O3–Sn1–O5#1	154.8(4)
O3–Sn1–O1	138.6(4)	N1–Sn1–O5#1	135.1(4)
N1–Sn1–O1	68.6(4)	O1–Sn1–O5#1	66.6(3)
C18–Sn1–O4	80.8(9)	O4–Sn1–O5#1	77.4(3)
$[(o\text{ClBz})_2\text{Sn}\{4\text{-NC}_5\text{H}_4\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2\}(\text{H}_2\text{O})]_2$ **(3)**			
Sn1–C17	2.145(9)	Sn1–N1	2.275(6)
Sn1–C10	2.166(8)	Sn1–O4	2.323(6)
Sn1–O3	2.180(5)	Sn1–O1	2.400(5)
Sn1–O1#1	2.614(5)		
C17–Sn1–C10	165.0(3)	C10–Sn1–O1	88.1(3)
C17–Sn1–O3	96.2(3)	O3–Sn1–O1	139.10(18)
C10–Sn1–N1	94.8(3)	N1–Sn1–O1	68.53(18)
O3–Sn1–N1	70.6(2)	C17–Sn1–O1#1	83.0(3)
C17–Sn1–O4	87.3(3)	O3–Sn1–O1#1	155.71(15)
O3–Sn1–O4	76.9(2)	N1–Sn1–O1#1	133.69(17)
N1–Sn1–O4	147.43(19)	O1–Sn1–O1#1	65.19(19)

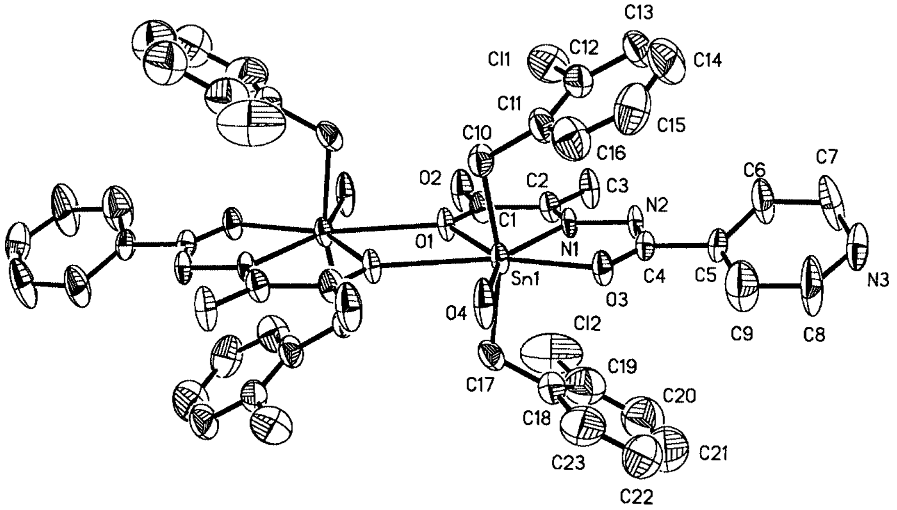


Figure 4. Molecular structure of complex **3**; ellipsoids shown at the 30% probability level.

is possibly because the *n*-octyl group chain is so long that crystals with it are not easy to form.

Although we abtained complex $[(o\text{ClBz})_2\text{Sn}\{4\text{-NC}_5\text{H}_4\text{CON}_2\text{C(CH}_3)\text{CO}_2\}(\text{H}_2\text{O})]_2$ (**3**) by a different method, the structure of **3** (Figure 4) is very similar to complex **2** (mode A), and complex **3** also contains a one-dimensional chain polymer (Figure S2) due to intermolecular hydrogen bonds (O–H···N).

Crystal Structure of $[(n\text{Bu})_2\text{Sn}\{2\text{-HOC}_6\text{H}_4\text{CON}_2\text{C(CH}_3)\text{CO}_2\}\{(n\text{Bu})_3\text{SnOH}\}]_2$ *(7)*

The molecular structure is illustrated in Figure 5 and selected bond lengths and angles are listed in Table 3. The molecular possesses a dimeric structure containing distannoxane units with two types of tin atoms (mode C).

The Sn1 atom lies in a distorted pentagonal bipyramidal coordination environment [Sn1–C11 = 2.087(12) Å, Sn1–C15 = 2.095(12) Å, Sn1–O3 = 2.188(8) Å, Sn1–O5 = 2.259(9) Å, Sn1–N1 = 2.324(11) Å, Sn1–O1 = 2.419(8) Å, Sn1–O1#1 = 2.585(7) Å] in which one tridentate pyruvic acid isonicotinyl hydrazone ligand, two *trans* *n*-butyl groups, and the O5 atom coordinate to each Sn center. The sum of the angles subtended at the tin atom in the pentagonal plane is 378.16°, so O3, O5, N(1), O1, and O1#1 ($-x + 2, -y + 2, -z$) lie almost in the same plane, with the Sn atom only 0.0062 Å away from the equatorial plane, while the two

Table 3. Selected bond lengths [Å] and bond angles [°] for complex **7**.

Sn1–C11	2.087(12)	Sn2–O5	2.024(9)
Sn1–C15	2.095(12)	Sn2–C19	2.073(17)
Sn1–O3	2.188(8)	Sn2–C23	2.088(14)
Sn1–O5	2.259(9)	Sn2–C27	2.116(17)
Sn1–O1	2.419(8)	N1–C2	1.247(14)
Sn1–N1	2.324(11)	N1–N2	1.345(12)
Sn1–O1#1	2.585(7)	N2–C4	1.315(17)
O3–C4	1.274(15)	O2–O5#1	2.545
C11–Sn1–C15	167.5(5)	O5–Sn2–C19	101.6(6)
C11–Sn1–O3	95.5(4)	O5–Sn2–C23	107.8(5)
C11–Sn1–O5	87.9(5)	C19–Sn2–C23	113.9(7)
O3–Sn1–O5	79.7(3)	O5–Sn2–C27	98.9(6)
C11–Sn1–N1	95.3(4)	C19–Sn2–C27	116.7(8)
O5–Sn1–O1#1	77.6(3)	C23–Sn2–C27	115.2(8)
C11–Sn1–O1	87.1(4)	N1–Sn1–O1	67.0(3)
C11–Sn1–O1#1	83.3(4)	O1–Sn1–O1#1	66.6(3)

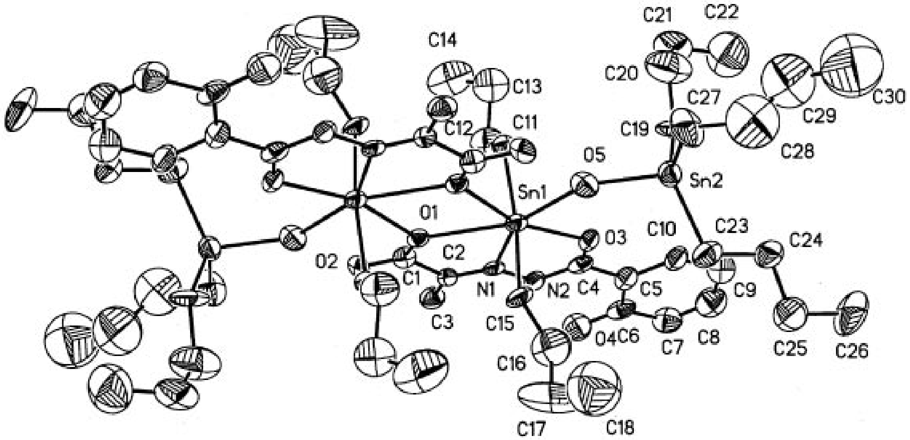


Figure 5. Molecular structure of complex **7**; ellipsoids shown at the 30% probability level.

trans n-butyl carbon atoms take up the axial sites around the Sn1 atom; the angle of the axial C11–Sn1–C15 is 167.5(5)°. The O1 atom of the carboxylate residue also binds the other tin atom, Sn1#1, generating an Sn_2O_2 four-membered ring, therefore the structure of this complex can be described as a dimer.

The coordination at the tin atom Sn2 is distorted tetrahedral, as indicated by bonding angles of 101.6(6)°, 107.8(5)°, 113.9(7)°, 98.9(6)°, 116.7(8)°, and 115.2(8)° for O5–Sn2–C19, O5–Sn2–C23, C19–Sn2–C23, O5–Sn2–C27, C19–Sn2–C27, and C23–Sn2–C27, respectively. In this complex, two different types of tin atom are connected through the bridging O atom, and intramolecular hydrogen bonds O5–H5···O2#1 [2.565(11) Å] and O4–H4···N2 [2.535(15) Å] are also found. The phenolate oxygen atoms do not participate in coordination to the tin atom.

Crystal Structure of [(oClBz)$_2$Sn{2-HOC$_6$H$_4$CON$_2$C(CH$_3$)CO$_2$}(CH$_3$OH)]$_2$ (10)

The crystal structure of complex **10** is shown in Figure 6. All hydrogen atoms have been omitted for the purpose of clarity. Table 4 lists selected bond lengths and angles.

Table 4. Selected bond lengths [Å] and bond angles [°] for complex **10**.

Sn1–O3	2.138(7)	N1–C2	1.266(15)
Sn1–N1	2.270(9)	N1–N2	1.377(12)
Sn1–O1	2.331(7)	N2–C4	1.304(13)
Sn1–O5	2.394(7)	O1–C1	1.297(12)
Sn1–O1#1	2.647(7)	O3–C4	1.252(12)
C11–Sn1–C18	163.8(4)	C11–Sn1–O5	82.6(4)
C11–Sn1–O3	92.9(4)	N1–Sn1–O5	148.0(3)
O3–Sn1–N1	70.7(3)	O1–Sn1–O5	142.1(3)
C11–Sn1–N1	95.5(4)	O3–Sn1–O1#1	153.8(2)
O3–Sn1–O1	140.4(3)	C11–Sn1–O1#1	85.3(3)
C18–Sn1–O1	90.2(4)	N1–Sn1–O1#1	135.5(3)
N1–Sn1–O1	69.8(3)	O1–Sn1–O1#1	65.7(3)
O3–Sn1–O5	77.5(3)	O5–Sn1–O1#1	76.4(2)

The crystal structure of **10** is also very similar to that of complex **2**. In this complex, the Sn atom exists in a distorted pentagonal bipyramidal coordination environment in which one methanol molecule, two tridentate pyruvic acid salicylhydrazone ligands, and two *trans o*-chlorobenzyl groups coordinate to each Sn center. The atoms O1, O1#1, O5, O3, and N1 are coplanar within ±0.0334 Å, and form the equatorial plane. Furthermore, the angles of the axial C18–Sn1–C11 is 163.8(4)°, which deviates from the linear angle of 180°. The O1 atom of the carboxylate residue also binds the other tin atom Sn1#1 ($-x + 2$, $-y + 1$, z), generating an Sn_2O_2 four-membered ring. Thereby the molecular structure of this compound can be described as a dimer, and the coordination geometry of tin can be also described as a *trans*-C_2SnO_4N pentagonal bipyramid, with the two *o*-chlorobenzyl groups occupying *trans* positions. From these data we can see that the crystal structure of complex **10** is very similar to those of **2** and **3**. Obviously, the nature of the alkyl group bonding to the Sn center does not exert a great influence on the overall structural motif. The Sn1–O5 bond length is 2.394(7) Å, which is longer than those in analogous complexes[20,27] due to the formation of intradimeric hydrogen bonds (O2···O5#1 = 2.583 Å). There are also strong intramolecular O–H···N hydrogen bonds (O4···N2 = 2.537 Å) involving atom N2 and the phenolic hydroxyl oxygen atom O4, which does not coordinate to the Sn center. Undoubtedly, these hydrogen bonds contribute to the compactness of the dimer.

Discussion

The complexes $[R_2SnLY]_2$ and $[R_2SnL(R_3SnOH)]_2$ (mode A, B, or C) are produced by the reaction between pyruvic acid isonicotinyl hydrazone and dialkyltin oxide or triaryltin chloride and pyruvic acid salicylhydrazone and triaryltin chloride or bis(trialkyltin) oxide, in a 1:1 molar ratio. It is clear that the presence of the enolic proton of the ligands leads to the dealkylation of the trialkyltin carboxylates $[R_3Sn\{4\text{-}NC_5H_4C(O)NHN{=}C(CH_3)CO_2\}]$ and $[R_3Sn\{2\text{-}HOC_6H_4C(O)NHN{=}C(CH_3)CO_2\}]$, which are the

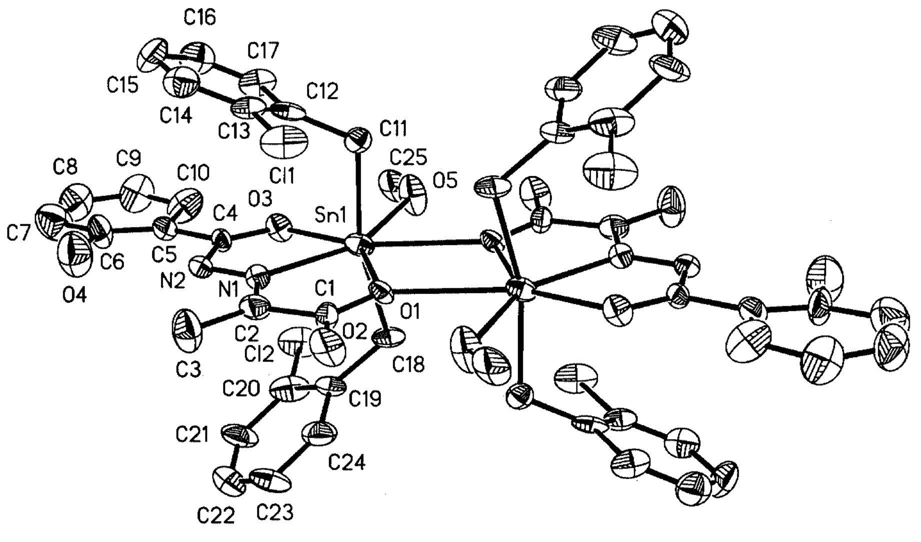
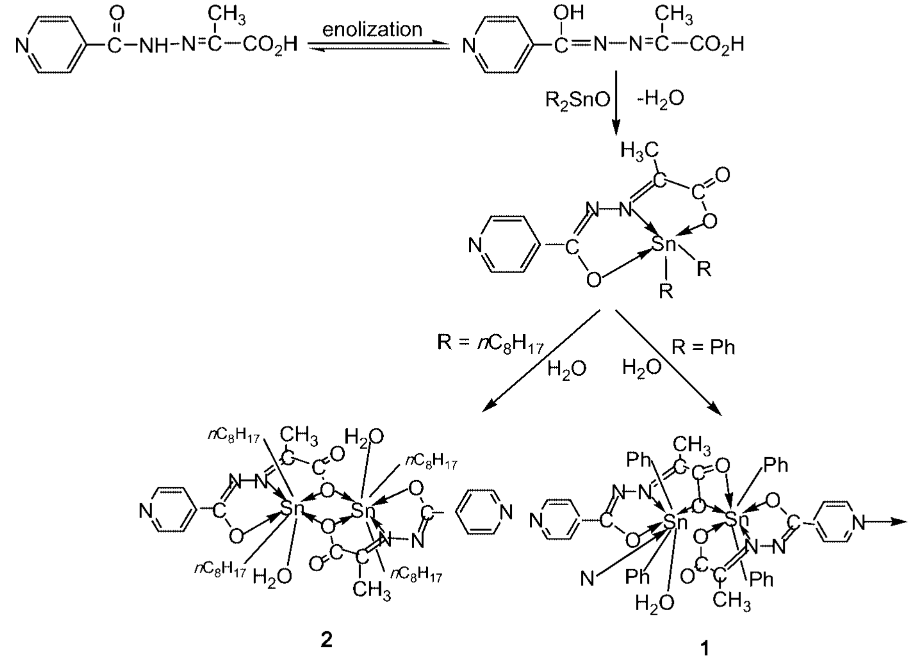
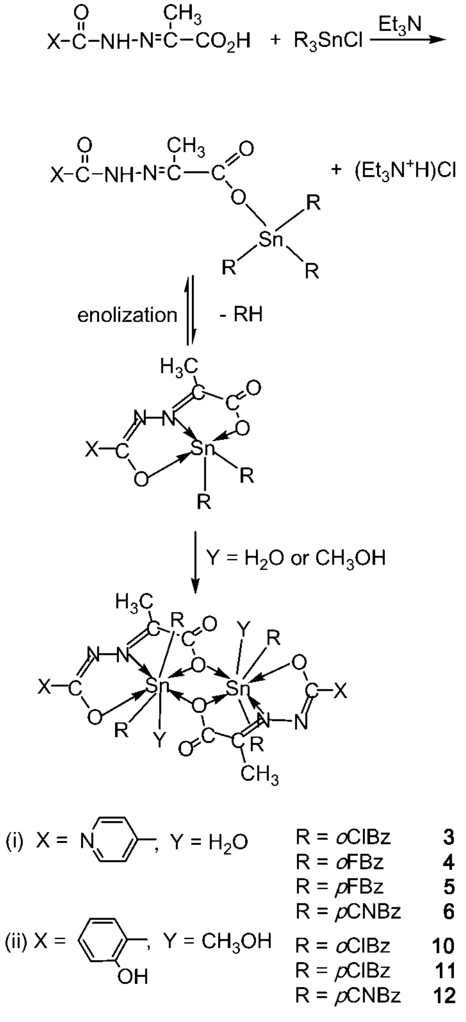


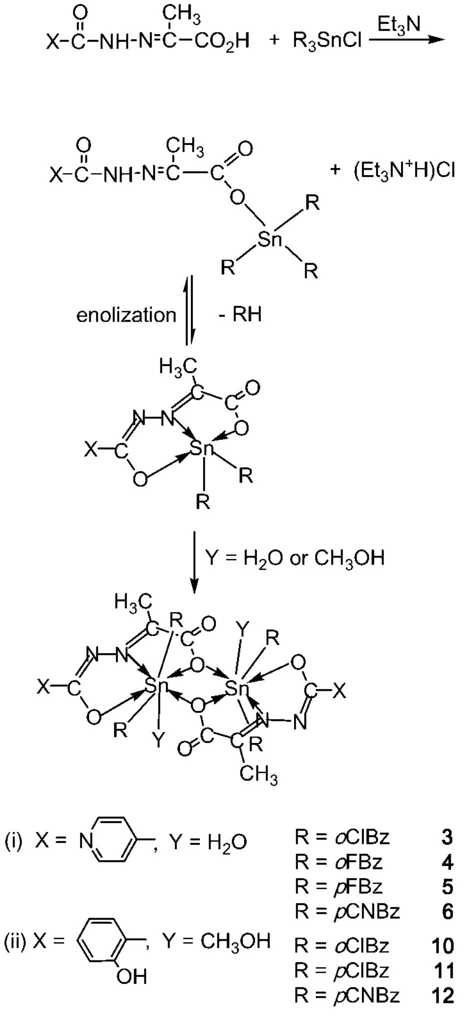
Figure 6. Molecular structure of complex **10**; ellipsoids shown at the 30% probability level.



Scheme 2.



Scheme 3.



Scheme 4.

major products of the reaction of R_3SnCl or $(R_3Sn)_2O$ with Schiff-base ligands. Seven-coordinate dimers are formed as a result of steric or solvent effects in the recrystallization. The crystal-structure determinations show that the structures of complexes **1**–**3** are one-dimensional infinite chain polymers due to intermolecular hydrogen-bond interactions between the coordinated water molecule and the pyridine nitrogen atom of the adjacent unit. Complexes **7** and **10**, which contain pyruvic acid salicylhydrazone, are monomers. Their possible reaction mechanisms are shown in Schemes 2, 3, and 4.

Conclusions

The pyruvic acid hydrazone ligands have been shown to be able to form monomeric or polymeric complexes. The nuclearity and stereochemistry are found to be dependent on the nature of the starting acceptor and the reaction conditions. The ligand chelates to tin atoms, bonding through the oxygen of the carboxyl or enolic hydroxy group and the nitrogen atoms. In the polymeric complex, the dimers are connected through intermolecular hydrogen bonds or interactions between the nitrogen atoms of the pyridine ring and the tin atoms of an adjacent molecule. The monomeric complexes possess a highly centrosymmetric dimeric structure containing a distannoxane unit. The reaction of $[(n\text{Bu})_3\text{Sn}]_2\text{O}$ with pyruvic acid salicylhydrazone gives a novel tetranuclear organotin complex, which exhibits a dimeric structure containing a distannoxane unit with two types of tin atoms that are seven- or four-coordinate.

Experimental Section

Diphenyltin oxide, di-*n*-octyltin oxide and bis(tri-*n*-butyltin) oxide are commercially available, and were used without further purification. The ligands, bis(triaryltin) oxide and triaryltin chloride were prepared by the methods reported in the literature.[28–30] The melting points were obtained with a Kolfer micro melting point apparatus and are uncorrected. IR spectra were recorded with a Nicolet-460 spectrophotometer, as KBr discs. ^1H and ^{119}Sn NMR spectra were recorded with a Mercury Plus-400 NMR spectrometer in $CDCl_3$. The spectra were acquired at room temperature (298 K) unless otherwise specified. The chemical shifts are reported in ppm with respect to the references and are stated relative to external tetramethylsilane (TMS) for ^1H, and to neat tetramethyltin for ^{119}Sn NMR spectroscopy. Elemental analyses were performed with a PE-2400II elemental analyzer.

Pyruvic Acid Isonicotinyl Hydrazone: This Schiff base was prepared from isonicotinic acid hydrazide and pyruvic acid in ethanol according to the literature.[28] A white powder was obtained. Yield: 95% (864.2 mg). M.p. 222–223 °C. $C_9H_9N_3O_3$ (207.19): calcd. C 48.14, H 5.00, N 18.38; found C 48.00, H 4.89, N 18.67.

Pyruvic Acid Salicylhydrazone: This Schiff base was prepared from salicylhydrazide and pyruvic acid in ethanol according to the literature.[29] White, needle-shaped crystals were obtained. Yield: 80% (931.6 mg). M.p. 216 °C. $C_{10}H_{10}N_2O_4$ (222.19): calcd. C 54.92, H 4.54, N 12.61; found C 54.72, H 4.68, N 12.85.

$[Ph_2Sn\{4\text{-}NC_5H_4CON_2C(CH_3)CO_2\}(H_2O)]_2$ (1): Pyruvic acid isonicotinyl hydrazone (2.0 mmol) was added to a benzene/ethanol (3:1, v/v) solution (50 mL) of Ph_2SnO (2.0 mmol). The mixture was heated under reflux with stirring for 6 h. The clear solution thus obtained was evaporated under vacuum to form a brown solid and recrystallized from dichloromethane/hexane to give red crystals. Yield: 78% (113.2 mg). M.p. 165–167 °C. $C_{42}H_{38}N_6O_8Sn_2$ (992.16): calcd. C 50.81, H 3.73, N 8.47; found C 50.73, H 3.69, N 8.52. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.66 (s, 6 H, CH_3), 5.31 (s, 4 H, H_2O), 7.44–7.79 (m, 20 H, Ph-H), 8.13 (d, J = 6.00 Hz, 4 H, 3,5-pyridine-H), 8.84 (d, J = 5.20 Hz, 4 H, 2,6-pyridine-H) ppm. ^{119}Sn NMR ($CDCl_3$): δ = –226.9, –451.0 ppm.

$[(nC_8H_{17})_2Sn\{4\text{-}NC_5H_4CON_2C(CH_3)CO_2\}(H_2O)]_2$ (2): Complex **2** was prepared in the same way as complex **1** by adding di-*n*-octyltin oxide (2.0 mmol) to pyruvic acid isonicotinyl hydrazone (2.0 mmol). Unlike the analogous reaction mixtures with di-*n*-butyl-[15] or diphenyltin(IV) oxide, crystallization from dichloromethane/hexane failed to generate the desired crystals of **2**, which is the di-*n*-octyltin analog of the di-*n*-butyltin complex.[15] However, when acetone was used as crystallization solvent colorless crystals of **3** were obtained. Yield: 88% (121.0 mg). M.p. 77 °C. $C_{25}H_{43}N_3O_4Sn$ (568.31): calcd. C 52.73, H 7.57, N, 7.39; found C 52.81, H 7.42, N 7.35. IR (KBr): $\tilde{\nu}$ = 2924 cm^{-1}, 2854 (s, C–H), 1640 (s, C=N), 1606 (s, C=N–N=C), 1619, 1334 (s, CO_2), 1207 (s, C–O), 694 (s, Sn–O), 541 (w, Sn–C), 476 (w, Sn–N). ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.85 (t, J = 10.0 Hz, 6 H, CH_3), 1.22–1.31 [m, 8 H, $Sn(CH_2)_2$ (α,β)], 1.64–1.75 [m, 20 H, CH_2 (ω)], 2.65 (s, 3 H, CH_3), 7.99 (d, J = 5.60 Hz, 2 H, 3,5-pyridine-H), 8.77 (d, J = 5.20 Hz, 2 H, 2,6-pyridine-H) ppm. ^{119}Sn NMR ($CDCl_3$): δ = –460.6 ppm.

$[(o\text{ClBz})_2Sn\{4\text{-}NC_5H_4CON_2C(CH_3)CO_2\}(H_2O)]_2$ (3): Pyruvic acid isonicotinyl hydrazone (2.0 mmol) and tri-*o*-chlorobenzyltin chloride (2.0 mmol) were added to a solution of absolute toluene (30 mL) and heated under reflux with stirring for 1 h. After the addition of triethylamine (2.0 mmol) 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 from methanol to give colorless crystals. Yield: 81% (104.8 mg). M.p. 151 °C. $C_{46}H_{42}Cl_4N_6O_8Sn_2$ (1186.0): calcd. C 46.54, H 3.54, N, 7.08; found C 46.66, H 3.51, N 7.05. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.46 (s, 6 H, CH_3), 3.19 (s, 8 H, $ArCH_2Sn$), 7.05–7.54 (m, 16 H, Ar-H), 7.72 (d, J = 6.60 Hz, 4 H, 3,5-pyridine-H), 8.70 (d, J = 4.80 Hz, 4 H, 2,6-pyridine-H) ppm. ^{119}Sn NMR ($CDCl_3$): δ = –457.2 ppm.

$[(o\text{FBz})_2Sn\{4\text{-}NC_5H_4CON_2C(CH_3)CO_2\}]_2$ (4): Complex **4** was prepared in the same way as **3** by adding tri-*o*-fluorobenzyltin chloride (2.0 mmol) to pyruvic acid isonicotinyl hydrazone (2.0 mmol). The solid was then obtained from methanol. Yield: 80% (90.6 mg). M.p. 145 °C. $C_{46}H_{38}F_4N_6O_6Sn_2$ (1084.24): calcd. C 50.96, H 3.53, N 7.75; found C 50.84, H 3.48, N 7.88. IR (KBr): $\tilde{\nu}$ = 3007 cm^{-1} (m, Ar–H), 2937, 2738 (s, C–H), 1622 (s, C=N), 1608 (s, C=N–N=C), 1618, 1334 (s, CO_2), 1229 (s, C–O), 694 (s, Sn–O), 480 (w, Sn–N). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.20 (s, 6 H, CH_3), 3.15 (s, 8 H, $ArCH_2Sn$), 6.60–7.27 (m, 16 H, Ph-H), 7.78 (d, J = 5.60 Hz, 4 H, 3,5-pyridine-H), 8.74 (d, J = 5.80 Hz, 4 H, 2,6-pyridine-H) ppm. ^{119}Sn NMR ($CDCl_3$): δ = –456.3 ppm.

$[(p\text{FBz})_2Sn\{4\text{-}NC_5H_4CON_2C(CH_3)CO_2\}]_2$ (5): Complex **5** was prepared in the same way as **3** by adding tri-*p*-fluorobenzyltin chloride (2.0 mmol) to pyruvic acid isonicotinyl hydrazone (2.0 mmol). The solid was then obtained from methanol. Yield: 86% (98.4 mg). M.p. 138 °C. $C_{46}H_{38}F_4N_6O_6Sn_2$ (1084.24): calcd. C 50.96, H 3.53, N 7.75; found C 50.91, H 3.61, N 7.61. IR (KBr): $\tilde{\nu}$ = 3021 cm^{-1} (s, Ar–H), 2944 (s, C–H), 1620 (s, C=N), 1605 (m, C=N–N=C), 1617, 1341 (s, CO_2), 1233 (s, C–O), 688 (m, Sn–O), 491 (w, Sn–N). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.25 (s, 6 H, CH_3), 3.23 (s, 8 H,

$ArCH_2Sn$), 6.63–7.39 (m, 16 H, Ph-H), 7.78 (d, J = 4.80 Hz, 4 H, 3,5-pyridine-H), 8.89 (d, J = 6.40 Hz, 4 H, 2,6-pyridine-H) ppm. ^{119}Sn NMR ($CDCl_3$): δ = –449.8 ppm.

[(pCNBz)$_2$Sn{4-NC$_5$H$_4$CON$_2$C(CH$_3$)CO$_2$}]$_2$ (6): Complex **6** was prepared in the same way as **3** by adding tri-p-cyanobenzyltin chloride (2.0 mmol) to pyruvic acid isonicotinyl hydrazone (2.0 mmol). The solid was then obtained from methanol. Yield: 91% (115.8 mg). M.p. 210 °C. $C_{50}H_{38}N_{10}O_6Sn_2$ (1112.3): calcd. C 53.98, H 3.42, N 12.60; found C 53.62, H 3.41, N 12.77. IR (KBr): $\tilde{\nu}$ = 3007 cm^{-1} (m, Ar–H), 2922, 2852 (s, C–H), 1630 (m, C=N), 1619, 1385 (m, CO_2), 1602 (m, C=N–N=C), 1200 (m, C–O), 692 (m, Sn–O), 540 (w, Sn–C), 478 (w, Sn–N). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.42 (s, 6 H, CH_3), 3.08 (s, $ArCH_2Sn$), 7.21–7.35 (m, 16 H, Ph-H), 7.22 (d, J = 8.00 Hz, 4 H, 3,5-pyridine-H), 7.57 (d, J = 8.40 Hz, 4 H, 2,6-pyridine-H) ppm. ^{119}Sn NMR ($CDCl_3$): δ = –453.9 ppm.

[(nBu)$_2$Sn{2-HOC$_6$H$_4$CON$_2$C(CH$_3$)CO$_2$}{(nBu)$_3$SnOH}]$_2$ (7): Pyruvic acid salicylhydrazone (1.0 mmol) was added to a benzene suspension (30 mL) of bis(tri-n-butyltin) oxide (1.0 mmol), then the mixture was stirred and heated at reflux for 6 h. The clear solution obtained after fliteration was evaporated in vacuo to give a solid, which was then recrystallized from dichloromethane/hexane to give colorless crystals. Yield: 83% (71.5 mg). M.p. 101 °C. $C_{30}H_{54}N_2O_5Sn_2$ (759.12): calcd. C 47.40, H 7.16, N 3.68; found C 47.32, H 7.15, N 3.77. IR (KBr): $\tilde{\nu}$ = 3423 cm^{-1} (m, OH), 2955 (s, Ar–H), 2922, 2853 (s, C–H), 1627 (m, C=N), 1608, 1334 (s, CO_2), 1583 (m, C=N–N=C), 1205 (s, C–O), 672 (m, Sn–O), 560 (w, Sn–C), 502 (w, Sn–N). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.83 (t, J = 6.40 Hz, 15 H, CH_3), 1.19–1.61 (m, 30 H, $SnCH_2CH_2CH_2$), 2.38 (s, 3 H, CH_3), 6.88–7.35 (m, 4 H, Ph-H), 11.22 (s, 1 H, Ar-OH) ppm. ^{119}Sn NMR ($CDCl_3$): δ = 102.3, –453.9 ppm.

[Bz$_2$Sn{2-HOC$_6$H$_4$CON$_2$C(CH$_3$)CO$_2$}{Bz$_3$SnOH}]$_2$ (8): Complex **8** was prepared in the same way as **7** by adding bis(tribenzyltin) oxide (1.0 mmol) to pyruvic acid salicylhydrazone (1.0 mmol). The solid was then obtained from dichloromethane/hexane. Yield: 91% (82.2 mg). M.p. 215 °C. $C_{45}H_{43}N_2O_5Sn_2$ (929.25): calcd. C 58.10, H 4.77, N 3.01; found C 58.25, H 4.53, N 3.11. IR (KBr): $\tilde{\nu}$ = 3411 cm^{-1} (m, OH), 3035 (s, Ph–H), 2952, 2859 (s, C–H), 1630 (s, C=N), 1596, 1347 (s, CO_2), 1579 (m, C=N–N=C), 1202 (s, C–O), 679 (m, Sn–O), 555 (m, Sn–C), 477 (w, Sn–N). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.65 (d, J = 5.60 Hz, 3 H, CH_3), 2.81 (t, $J_{Sn,H}$ = 68.88 Hz, 6 H, $ArCH_2Sn$), 3.16 (s, 4 H, $ArCH_2Sn$), 6.93–7.28 (m, 29 H, Ar-H and Ph-H), 11.43 (s, 1 H, Ar-OH) ppm. ^{119}Sn NMR ($CDCl_3$): δ = 111.7, –449.5 ppm.

[(pCNBz)$_2$Sn{2-HOC$_6$H$_4$CON$_2$C(CH$_3$)CO$_2$}{(pCNBz)$_3$SnOH}]$_2$ (9): Complex **9** was prepared in the same way as **7** by adding bis(tri-p-cyanobenzyltin) oxide (1.0 mmol) to pyruvic acid salicylhydrazone (1.0 mmol). The solid was then obtained from dichloromethane/hexane. Yield: 93% (99.7 mg). M.p. 218 °C. $C_{50}H_{38}N_7O_5Sn_2$ (1054.30): calcd. C 56.91, H 3.72, N 9.29; found C 57.15, H 3.55, N 9.21. IR (KBr): $\tilde{\nu}$ = 3423 cm^{-1} (s, OH), 3017 (s, Ph–H), 2988, 2889 (m, C–H), 1621 (m, C=N), 1606, 1367 (s, CO_2), 1542 (s, C=N–N=C), 1211 (s, C–O), 674 (m, Sn–O), 547 (w, Sn–C), 485 (w, Sn–N). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.44 (d, J = 5.40 Hz, 3 H, CH_3), 2.79 (t, $J_{Sn,H}$ = 65.48 Hz, 6 H, $ArCH_2Sn$), 3.22 (s, 4 H, $ArCH_2Sn$), 6.81–7.42 (m, 24 H, Ar-H and Ph-H), 10.91 (s, 1 H, Ar-OH) ppm. ^{119}Sn NMR ($CDCl_3$): δ = 109.5, –452.3 ppm.

[(oClBz)$_2$Sn{2-HOC$_6$H$_4$CON$_2$C(CH$_3$)CO$_2$}(CH$_3$OH)]$_2$ (10): Pyruvic acid salicylhydrazone (2.0 mmol) and tri-o-chlorobenzyltin chloride (2.0 mmol) were added to a solution of absolute toluene (30 mL) and heated under reflux, with stirring, for 1 h. After the addition of triethylamine (2.0 mmol) 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 from methanol to give colorless crystals. Yield: 85% (111.8 mg). M.p. 131 °C. $C_{50}H_{48}Cl_4N_4O_{10}Sn_2$ (1244.1): calcd. C 48.27, H 3.89, N, 4.49; found C 48.36, H 3.71, N 4.55. IR (KBr): $\tilde{\nu}$ = 3417 cm^{-1} (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). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.66 (s, 12 H, CH_3), 3.39 (s, 8 H, $ArCH_2Sn$), 6.84–7.59 (m, 24 H, Ar-H and Ph-H), 8.09 (s, 2 H, R-OH), 11.16 (s, 2 H, Ar-OH) ppm. ^{119}Sn NMR ($CDCl_3$): δ = –445.8 ppm.

[(pClBz)$_2$Sn{2-HOC$_6$H$_4$CON$_2$C(CH$_3$)CO$_2$}]$_2$ (11): Complex **11** was prepared in the same way as **10** by adding tri-p-chlorobenzyltin chloride (2.0 mmol) to pyruvic acid salicylhydrazone (2.0 mmol). The solid was then obtained from methanol. Yield: 87% (115.3 mg). M.p. 144 °C. $C_{48}H_{40}Cl_4N_4O_8Sn_2$ (1179.6): calcd. C 48.84, H 3.39, N 4.75; found C 48.91, H 3.47, N 4.62. IR (KBr): $\tilde{\nu}$ = 3379 cm^{-1} (s, OH), 3023 (m, Ar–H), 2916 (m, C–H), 1633 (m, C=N), 1602 (s, C=N–N=C), 1594, 1367 (s, CO_2), 1202 (m, C–O), 685 (m, Sn–O), 525 (w, Sn–C), 474 (w, Sn–N). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.66 (s, 6 H, CH_3), 3.26 (s, 8 H, $ArCH_2Sn$), 6.26–7.63 (m, 24 H, Ar-H and Ph-H), 11.18 (s, 2 H, Ar-OH) ppm. ^{119}Sn NMR ($CDCl_3$): δ = –443.5 ppm.

[(pCNBz)$_2$Sn{2-HOC$_6$H$_4$CON$_2$C(CH$_3$)CO$_2$}]$_2$ (12): Complex **12** was prepared in the same way as **10** by adding tri-p-cyanobenzyltin chloride (2.0 mmol) to pyruvic acid salicylhydrazone (2.0 mmol). The solid was then obtained from methanol. Yield: 72% (92.1 mg). M.p. 215 °C. $C_{52}H_{40}N_8O_8Sn_2$ (1142.3): calcd. C 54.67, H 3.53, N 9.81; found C 54.81, H 3.44, N 9.72. IR (KBr): $\tilde{\nu}$ = 3411 cm^{-1} (m, OH), 3102 (m, Ar–H), 2922 (m, C–H), 1612 (m, C=N), 1600 (m, C=N–N=C), 1588, 1352 (s, CO_2), 1206 (m, C–O), 677 (w, Sn–O), 523 (m, Sn–C), 459 (w, Sn–N). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.52 (s, 6 H, CH_3), 3.35 (s, 8 H, $ArCH_2Sn$), 6.35–7.61 (m, 24 H, Ar-H and Ph-H), 10.87 (s, 2 H, Ar-OH) ppm. ^{119}Sn NMR ($CDCl_3$): δ = –452.8 ppm.

X-ray Crystallographic Study: All measurements were made on a Bruker Smart 1000 CCD diffractometer at 298(2) K with graphite-monochromated Mo-K_α (λ = 0.71073 Å). Semi-empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and difference Fourier maps using SHELXL-97,[31] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were included in the model at their calculated positions.
CCDC-250084 (**1**), -255498 (**2**), -255497 (**3**), -269987 (**7**), and -269988 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Figures S1, S2, S3, and S4 show the unit cell of complexes **2**, **3**, **7**, and **10**, respectively Crystal data and details of the structure determinations are listed in Tables S1 and S2.

Acknowledgments

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