



# Synthesis and structural characterization of organotin(IV) compounds derived from the self-assembly of hydrazone Schiff base series and various alkyltin salts

Min Hong, Han-Dong Yin\*, Shao-Wen Chen, Da-Qi Wang

Department of Chemistry, Liaocheng University, Liaocheng 252059, China

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## ABSTRACT

Reactions of pyruvic acid hydrazone series [pyruvic acid thiophenecarbonyl hydrazone (L1), pyruvic acid 4-hydroxybenzoylhydrazone (L2), pyruvic acid salicyloylhydrazone (L3), pyruvic acid benzoylhydrazone (L4)], or salicylaldehyde hydrazone Schiff base ligand [salicylaldehyde isonicotinoylhydrazone (L5)] with different alkyltin salts result in six new organotin(IV) compounds,  $\{(n\text{-Bu})_2\text{Sn}[2\text{-SC}_4\text{H}_3\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2\text{-(HOC}_3\text{H}_7\text{-}i)]_2\}$  (**1**),  $\{[(n\text{-Bu})_2\text{SnCl}(\text{O})(n\text{-Bu})\text{Sn}(\text{O})\text{C}_6\text{H}_4\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2\text{Sn}(n\text{-Bu})_2(\text{HOCH}_3)_2]_\infty\}$  (**2**),  $\{(o\text{-ClBz})_2\text{-Sn}[4\text{-HOC}_6\text{H}_4\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2\text{-(HOC}_2\text{H}_5)_2\}$  (**3**),  $\{(n\text{-C}_8\text{H}_{17})_2\text{Sn}[2\text{-HOC}_6\text{H}_4\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2\text{-(H}_2\text{O)}_2\}$  (**4**),  $\{(n\text{-Bu})_2\text{Sn}[\text{C}_6\text{H}_5\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2\text{[HOSn}(n\text{-Bu})_3]_2\}$  (**5**), and  $\{[(n\text{-C}_4\text{H}_9)\text{SnCl}_2]^- [4\text{-NHC}_5\text{H}_4\text{CON}_2\text{CH}(\text{C}_6\text{H}_4\text{-O-2})]^+\}$  (**6**), which have been characterized by single crystal X-ray diffraction, elemental analysis, IR,  $^1\text{H}$  and  $^{119}\text{Sn}$  NMR. In compounds **1**, **3**, **4**, weak-bridged dimers are found, in which the two tin atoms are linked by a pair of monodentate  $\text{CO}_2^-$  bridges. Each pyruvic acid hydrazone ligand serves as an enolic tridentate ligand. Compound **2** contains dimeric units of  $\{\text{Sn}_6(\text{L}_2)_2(n\text{-Bu})_6(\text{HOCH}_3)_2\}$  that are further connected by two pairs of monodentate  $\text{CO}_2^-$  bridges into a 1D weak-bridged polymeric chain, in which there also exists a fascinating dichlorodistannoxane ladder structure. Studies show that the bulk and steric hindrance of the alkyl groups and the coordinated solvent molecule bonding to Sn center have little effect on the geometry of the weak-bridge for compounds **1–4**. A similar weak-bridged dimeric structure is also found in compound **5**; in this case, however, there is no coordinated solvent molecule and the corresponding coordination site is replaced by the trialkyltin hydroxide. Compound **6** exhibits a rare 1D supermolecular chain constructed from the zwitterionic  $\{\text{Sn}(\text{L}_5)(n\text{-Bu})\text{Cl}_2\}$  units connected by the intermolecular  $\text{N-H}\cdots\text{Cl}$  hydrogen bonds. The thermal stability of compound **1** was also studied.

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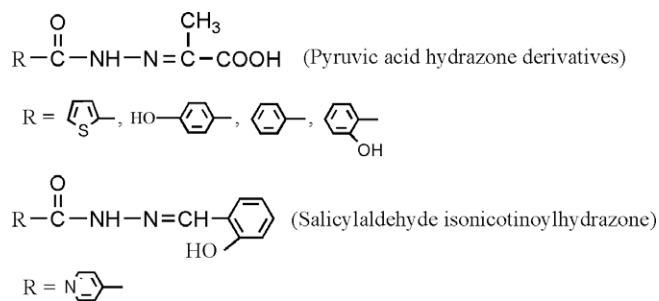
## 1. Introduction

The numerous chemical, physical, and biological properties of organotin(IV) compounds have largely contributed to the development of fundamental synthetic, structural, and reactivity studies as well as of their industrial applications [1]. In general, the biochemical activity of organotin(IV) compounds is influenced greatly by the structure of the molecule and the coordination number of the tin atoms [2–4]. Among these, Schiff base organotin(IV) compounds have received much attention, as such ligands and their metal complexes are reported to exhibit bactericidal and antitumor activities [3–5]. Hydrazone Schiff base has long been paid considerable attention for its fascinating chemical behavior [6–8] and biological essentiality [7–11]. Of interest to structural chemists is the coordination ability of the hydrazone ligand through the nitrogen or oxygen electron-donating atoms that allows it to serve as either a multidentate or a bridging building block in structural assemblies.

Recently, works in our laboratory have focused on the construction and crystallographic characterization of hydrazone Schiff base organotin(IV) compounds under ambient conditions [12–17]. It is well known that the biological activity of organotins is related to the type of alkyl groups attached to the tin atom. The structural characterization of such organotin(IV) compounds may provide important clues to the structure–activity relationship of the ligand and alkyl species and provide an invaluable insight to the reaction mechanism that may, in turn, allow synthetic chemists to further optimize reaction conditions. Thus new rational strategies to construct a variety of types of organotins are required.

As part of our interest to hydrazone Schiff base organotin(IV) compounds, we intend to modify the composition of the hydrazone Schiff base ligands and the alkyl type, as well as adjust different coordination solvent molecules. In this contribution, we outline our work on a series of pyruvic acid or salicylaldehyde hydrazone Schiff bases organotins by using thiophenecarbonyl, isonicotinoyl, salicyloyl, benzoyl or 4-hydroxybenzoyl group as the other part of the ligand (Scheme 1). The isolation and structural characterization of six tin coordination monomer, dimer or polymer by X-ray crystallography are presented. It is expected that the selection

\* Corresponding author. Tel./fax: +866358239121.  
E-mail address: [handongyin@lcu.edu.cn](mailto:handongyin@lcu.edu.cn) (H.-D. Yin).



**Scheme 1.** Pyruvic acid hydrazone series and salicylaldehyde hydrazone Schiff base ligands investigated in this study.

freedom of Schiff bases' components and various alkyltin salts afford opportunities for generating novel topologies. Meanwhile, to obtain a preliminary understanding of the thermal stability of this types of organotin(IV) compounds, thermogravimetric (TG) analysis were determined for compound **1**.

## 2. Results and discussion

### 2.1. Synthesis of organotin(IV) compounds

Compounds **1–5** were obtained by the treatment of pyruvic acid hydrazone with the corresponding alkyltin salt in different solvent under the reflux conditions. The mixture of di-*n*-butyltin chloride, pyruvic acid thiophenecarbonyl hydrazone and sodium ethoxide in the molar ratio of 1:1:1 was found to give the weak-bridged dimer compound **1** with the ligand in an enolization state. However, the similar route, except for the excess sodium ethoxide corresponding to pyruvic acid 4-hydroxybenzoylhydrazone (2:1), resulted in a novel one-dimensional (1D) weak-bridged infinite chain composed by ladder distannoxane dimer units. About this phenomenon, a reasonable reaction mechanism has been proposed (as shown in Scheme 2). Due to the presence of excess sodium ethoxide, the possible intermediate hydroxylated tin salt, (*n*-Bu)<sub>2</sub>Sn(Cl)OH, would

be obtained by the controlled hydrolysis of di-*n*-butyltin chloride, and this contribute to the further reaction of the *para* hydroxyl group in the ligand and realize the final chain structure. The similar reaction mechanism has also been described by previous reports referred to distannoxane compounds [18–20].

To verify the rationality of our proposal, an experiment with the equimolar ratio of pyruvic acid 4-hydroxybenzoylhydrazone, sodium ethoxide and di-*o*-chlorobenzyltin chloride, has been prepared to obtain compound **3**. X-ray crystal diffraction demonstrates that the structure of compound **3** has the identical geometry with **1**, a simple weak-bridged dimer, and the *para* hydroxyl group in the ligand retains intact.

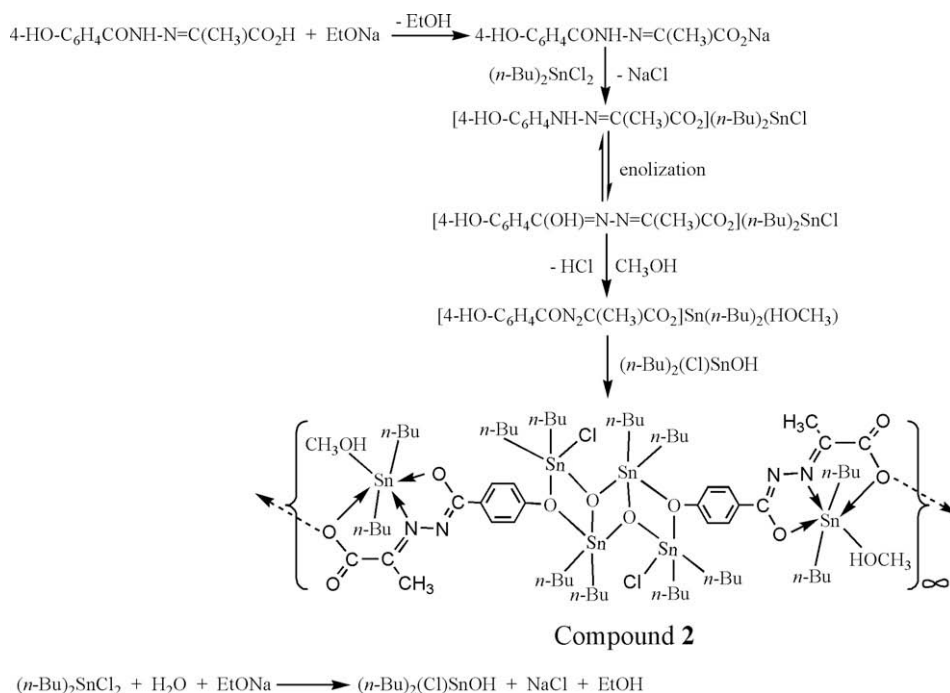
Treatment of di-*n*-octyltin oxide with the pyruvic acid salicyloylhydrazone Schiff base ligand in the benzene/ethanol (3:1, v/v) mixture solution gave compound **4** in a good yield 76%. X-ray crystal diffraction analysis suggested that the structure of **4** is similar to that of compound **1** presenting a weak-bridged dimer.

The self-assembly reaction of pyruvic acid salicyloylhydrazone and [(*n*-Bu)<sub>3</sub>Sn]<sub>2</sub>O in the benzene solution also afforded a weak-bridged dimeric alkyltin compound **5**, but it presents a different geometric topology with that of compounds **1–4**. Its possible reaction mechanism is given in Scheme 3.

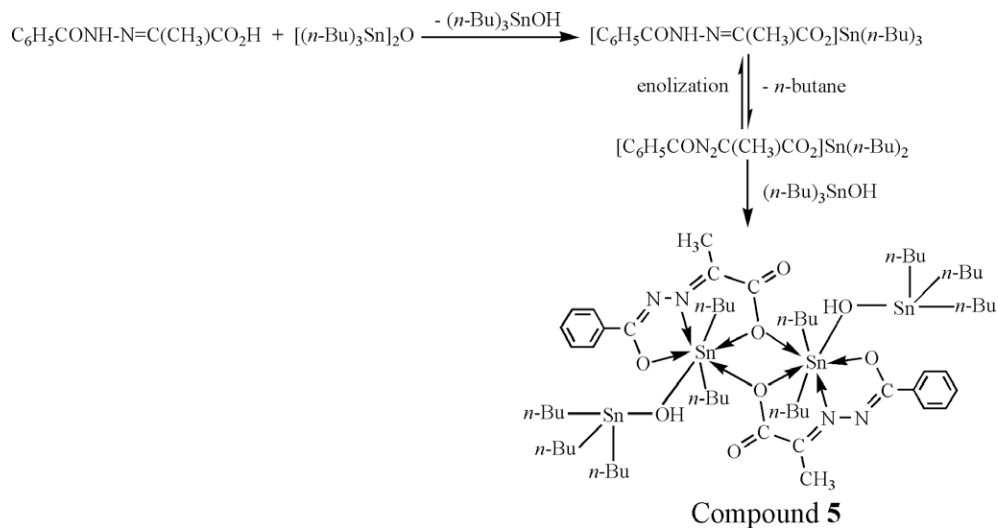
In addition, another type of salicylaldehyde based isonicotinoylhydrazone Schiff base ligand has been synthesized according to the literature. A mixture of this ligand and *n*-butyltin trichloride in the presence of triethylamine yields a rarely reported zwitterionic organotin(IV) compound, **6** (shown in Scheme 4).

### 2.2. IR spectra

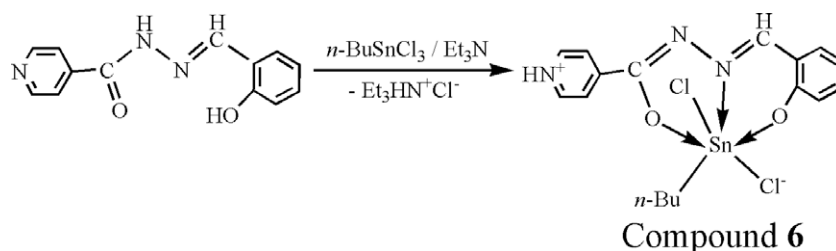
The IR spectra show the metal–ligand bonds formation through –CO<sub>2</sub><sup>-</sup>, –O<sup>-</sup> and –N sites, and the associated Sn–O–Sn, Sn–O, and Sn–N absorption values are also support this. In addition, the Δν [ν<sub>as</sub>(CO<sub>2</sub><sup>-</sup>)–ν<sub>s</sub>(CO<sub>2</sub><sup>-</sup>)] values (230–282 cm<sup>-1</sup>) for compounds **1–5** indicate that the carboxylate groups adopt the monodentate coordination mode [21]. Characteristic absorption at 1596–1615 cm<sup>-1</sup> in the spectra of these compounds indicate the presence of C=N–N=C group [13], thus indicating the ligands coordinate to the tin



**Scheme 2.** Reaction mechanism diagram of compound **2**.



Scheme 3. Reaction mechanism diagram of compound 5.



Scheme 4. Reaction diagram of compound 6.

center in an enolic form, which is in accordance with the X-ray structure analysis and their corresponding reaction mechanism.

### 2.3. $^1\text{H}$ and $^{119}\text{Sn}$ NMR spectra ( $\text{CDCl}_3$ )

All compounds gave good NMR spectra. In the  $^1\text{H}$  NMR spectra of compounds 1–6, the single resonance for the proton of the  $-\text{NHN}=\text{C}$  group is absent at  $\delta = 3.7\text{--}3.9$  ppm [12,14], thus indicating deprotonation of the  $-\text{NHN}=\text{C}$  group and confirming that all ligands coordinate to the Sn center in the enolic form. For all compounds, the spectra show that the chemical shifts of the protons on the aryl group have been assigned reasonably. The Ar–OH resonance,  $\delta = 11.28$  for 3 and 11.31 for 4, appeared as a singlet, which suggest that the phenolic oxygen atom do not participate in coordination to the tin centers; whereas for compound 2, the Ar–OH resonance is absent, which is accordance with X-ray single crystal diffraction structural analysis.

The  $^{119}\text{Sn}$  NMR spectroscopic data show one resonance signal at around  $\delta = -450$  ppm for compounds 1–5 ( $\delta = -459.6$  ppm for 1;  $\delta = -449.4$  ppm for 2;  $\delta = -447.3$  ppm for 3;  $\delta = -463.1$  ppm for 4;  $\delta = -454.1$  ppm for 5) and all of them are in the normal range seven-coordinate tin compounds [22]. Besides, for compound 2, there also exists another two signals,  $\delta = -177.1$  and  $-196.4$  ppm, which are in the range of reported for related five-coordinate di-*n*-butyltin derivatives [23–26], thus indicating the existence of another two different coordination environments around the tin atoms for compound 2 in solution. However, compound 5 show another signal at  $\delta = 107.4$  ppm, which is in the range corresponding to a type of four-coordinate tetrahedral tin atom ( $\delta = 200$  to  $-60$  ppm) [27,28], thus it can reasonably be assumed that there is also one different coordination environment around the tin atom of compound 5 in

solution. The  $^{119}\text{Sn}$  NMR spectroscopic datum of compound 6 ( $\delta = -365.1$  ppm) show signal in the normal range for six-coordinate tin compound, which is similar to that found in the compound bis-(triethylammonium)-bis-(3,5-di-*tert*-butyl-2-oxo-phenyl)-oxamido-bis-(dichlorobutyl-stannate) [29].

### 2.4. X-ray crystallography

#### 2.4.1. Crystal structure of compound 1

The molecular structure of compound 1 is illustrated in Fig. 1. Selected bond distances and angles are listed in Table 1. For compound 1, central Sn atom is coordinated by one isopropyl alcohol O atom, one N atom and two O atoms from tridentate pyruvic acid Schiff base ligand, and two C atoms of *trans* *n*-butyl groups. The

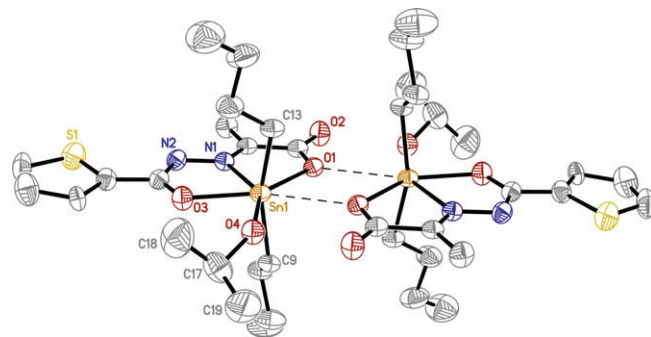


Fig. 1. X-ray single crystal structure of compound 1 (the thermal ellipsoids are drawn at 30% probability). All H atoms are omitted for clarity.

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

Sn1–O3	2.174(4)	Sn1–O4	2.486(4)
Sn1–N1	2.251(4)	Sn1–O1	2.305(3)
C9–Sn1–C13	158.4(2)	C9–Sn1–O3	95.2(2)
C13–Sn1–O3	98.1(2)	C9–Sn1–N1	101.7(2)
O3–Sn1–N1	70.15(15)	N1–Sn1–O1	69.36(14)
O1–Sn1–O1#1	65.65(13)	C9–Sn1–O1#1	81.97(18)
C9–Sn1–O4	83.83(19)	O3–Sn1–O4	77.63(14)

Symmetry code: #1 2 – x, 1 – y, –z.

O1 atom of the carboxylate residue also binds the other neighboring tin atom, Sn1#1 [#1: 2 – x, 1 – y, –z], generating a Sn<sub>2</sub>O<sub>2</sub> four-membered ring. The distance of Sn1#1...O1, 2.805(4) Å, is greater than the sum of the covalent radii of Sn and O (2.56 Å), but is considerably less than the sum of the van der Waals radii (3.68 Å) and should be considered as a weak bonding interaction. Thereby the structure of compound **1** can be described as a weak-bridged dimer with Sn...O weak interactions, and the coordination geometry of tin center can be also described as a *trans*-C<sub>2</sub>SnO<sub>4</sub>N pentagonal bipyramid with the two *n*-butyl groups occupying *trans* positions [C9–Sn1–C13 is 158.4(2)°]. The atoms O3, N1, O1, O1#1 and O4 are coplanar within ±0.0242 Å, which form the equatorial plane. These data indicate that the tin atom of compound **1** is in a distorted pentagonal bipyramidal configuration.

In compound **1**, there also exists intramolecular hydrogen bond, O4–H4...O2#1, which contributes to the crystal stability and compactness.

#### 2.4.2. Crystal structure of compound **2**

Compound **2** crystallizes in triclinic space group *R*-1. Due to the bad quality of crystals of compound **2**, the diffraction for it is quite weak. Therefore, the *R* factor of compound **2** is bad in crystallography.

Compound **2** is a dimer containing a central planar Sn<sub>2</sub>O<sub>2</sub> four-membered ring (Fig. 2a). Selected bond distances and angles are listed in Table 2. In the dimeric structure, the geometries of all the tin atoms can be classified into three types, of which the geom-

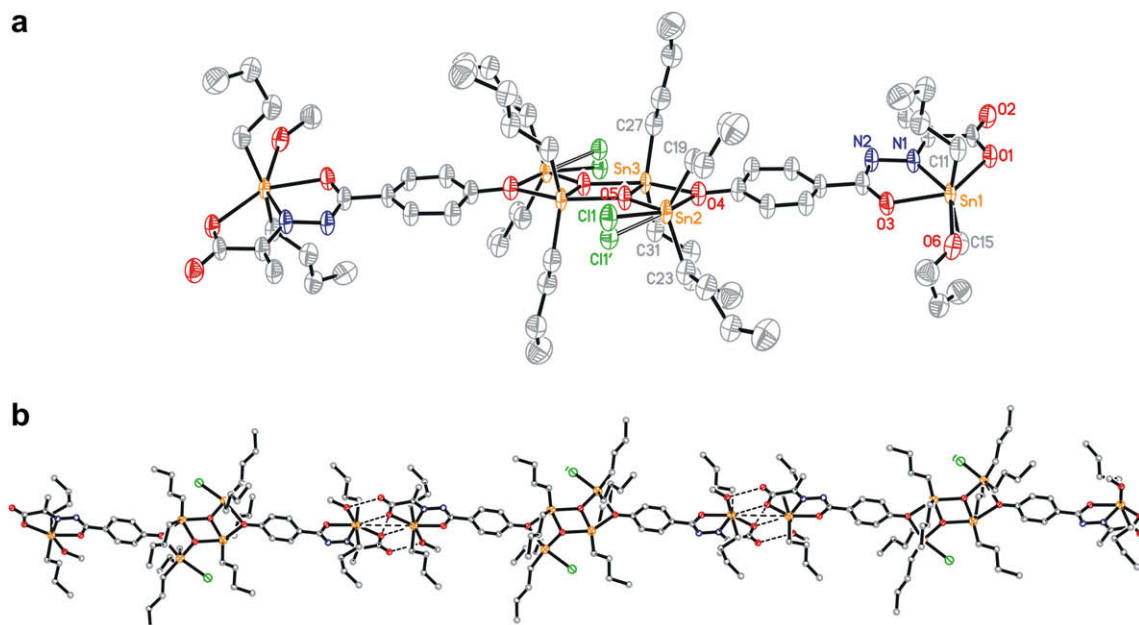
**Table 2**  
Selected bond lengths (Å) and angles (°) for compounds **2**.

Sn1–N1	2.166(19)	Sn2–O4	2.297(13)
Sn1–O3	2.169(13)	Sn3–O5	2.020(13)
Sn1–O1	2.313(15)	Sn3–O5#2	2.133(12)
Sn1–O6	2.496(17)	Sn3–O4	2.247(14)
Sn2–O5	2.021(13)	Cl1...Sn3#2	3.577
C11–Sn1–C15	162.0(9)	C23–Sn2–Cl1	102.4(8)
C11–Sn1–N1	99.6(8)	O4–Sn2–Cl1	158.2(8)
C11–Sn1–O3	94.3(7)	C27–Sn3–O5	113.7(8)
N1–Sn1–O3	69.7(6)	C27–Sn3–C31	133.5(9)
C15–Sn1–O1	89.1(8)	O5–Sn3–O5#2	72.3(6)
N1–Sn1–O1	70.4(6)	C27–Sn3–O5#2	99.1(8)
C15–Sn1–O6	82.8(8)	O5–Sn3–O4	72.4(5)
C23–Sn2–O5	111.5(8)	C27–Sn3–O4	97.0(8)
C23–Sn2–C19	129.9(9)	O4–Sn3–O5#2	144.6(5)
O4–Sn2–O5	71.3(5)	Sn3–O5–Sn3#2	107.7(6)
O5–Sn2–Cl1	88.0(8)		

Symmetry code: #2: 1 – x, 1 – y, 1 – z.

etry composed by two types of cyclic atoms is similar to the 1,3-disubstituted distannoxane compound with the 'ladder' structure [20]. The third type of tin center is weak-bridged by the oxygen atom from the carboxylate group of the neighboring dimer, this make compound **2** present a weak-bridged 1D supermolecular polymer in the lattice (Fig. 2b).

In the dimer **2**, the part of dichlorodistannoxane adopts the most common structural type found for compounds of the general formula [R<sub>2</sub>(Cl)SnOSn(μ<sub>3</sub>-O)R<sub>2</sub>]<sub>2</sub> and exists as ladder structure that contains two *endo*- and two *exo*-cyclic Sn atoms. The *n*-butyl groups are the same for both the *endo*- and the *exo*-Sn atoms, so they can be viewed as the centrosymmetric dimers with centrosymmetric units held in a two-dimensional polymeric lattice by oxo-bridges. Of the center Sn<sub>2</sub>O<sub>2</sub> ring, the bridge-oxo atom serves as tridentate and the internal angles [O5–Sn3–O5#2: 72.3(6); Sn3–O5–Sn3#2: 107.7(6)] [#2: 1 – x, 1 – y, 1 – z] are consistent with those in other distannoxane systems, such as 72.09, 107.9 of [(PhCH<sub>2</sub>)<sub>2</sub>(Cl)SnOSn(OEt)(CH<sub>2</sub>Ph)<sub>2</sub>]<sub>2</sub>, 73.16, 106.84 of [(PhCH<sub>2</sub>)<sub>2</sub>(Cl)SnOSn(Cl)(CH<sub>2</sub>Ph)<sub>2</sub>]<sub>2</sub> [20] and 74.2, 106.0 of [Ph<sub>2</sub>(Cl)SnOSn(OH)Ph<sub>2</sub>]<sub>2</sub> [18]. The distance of μ<sub>3</sub>-O to the *endo*- and *exo*-cyclic



**Fig. 2.** Structure of segments of the 1D chain of compound **2**. Thermal ellipsoids are shown at the 30% probability level (a). A perspective view of the 1D chain via the weak-bridged interaction and intramolecular hydrogen bonds (b). All H atoms are omitted for clarity.



Sn atoms are extremely similar: Sn2–O5 2.021(13) Å, Sn3–O5 2.020(13) Å and Sn3–O5#2 2.133(12) Å, reflecting the strong coordination of bridge-oxo with tin atoms in the dimer.

The ladder structure of compound **2** is different from the staircase structure of [MeSn<sub>2</sub>(OSiMe<sub>3</sub>)<sub>2</sub>O]<sub>2</sub> [30] (three four-membered rings are not coplanar), as evidenced by the near coplanarity of the atoms comprising the fused ring system. Eight atoms O4, Sn2, O5, Sn3, O4#2, Sn2#2, O5#2 and Sn3#2 are coplanar to an extent within ±0.0128 Å. This near coplanarity is also seen in the dihedral angle between the planes defined by the central and terminal four-atom rings, which is 2.2°. The geometries at the *endo*- and *exo*-cyclic tin atoms are essentially similar in compound **2**, all of which are pentacoordinated and arranged in distorted trigonal bipyramids. The trigonal plane is defined by two carbon atoms of *n*-butyl groups and O5. The axial angles O4–Sn2–C11 [158.2(8)°] and O4–Sn3–O5#2 [144.5(6)°] for compound **2**, are all smaller than the ideal value (180°) of trigonal bipyramid, which is possible due to the presence of weak interaction between the chlorine atom and the *endo*-cyclic tin atom. The distance of Cl1···Sn3#2 is 3.577 Å, which is less than the sum of the van der Waals radii of Sn and Cl (4.0 Å), so there is weak interaction between the two atoms. In addition, the disorder phenomenon has been observed for the terminal chlorine atom.

In the structure of compound **2**, central Sn1 atom is coordinated by one methanol O atom, one N atom and two O atoms from pyru-

vic acid Schiff base ligand, and two C atoms of *trans n*-butyl groups. The carboxylic O1 atom of the carboxylate residue also binds the other tin atom, Sn1#1 [#1:  $-x, 2-y, -z$ ], generating a Sn<sub>2</sub>O<sub>2</sub> four-membered ring. The distance of Sn1···O1#1, 2.734(15) Å, is greater than the sum of the covalent radii of Sn and O (2.56 Å), but is considerably less than the sum of the van der Waals radii (3.68 Å) and should be considered as a weak bonding interaction. Thereby the structure of compound **2** can be described as a weak-bridged polymer with weak interactions of Sn···O bonding, and the coordination geometry of the Sn1 atom can be also described as a *trans*-C<sub>2</sub>SnO<sub>4</sub>N pentagonal bipyramid with the two *n*-butyl groups occupying *trans* positions [C11–Sn1–C15 is 162.0(9)°]. The atoms O3, N1, O1, O1#1 and O6 are coplanar within ±0.0585 Å, which form the equatorial plane. These data indicate that the Sn1 atom of compound **2** is in a distorted pentagonal bipyramidal configuration.

In the polymeric structure of compound **2**, there also exists intramolecular hydrogen bond between the coordinated methanol oxygen atom and the O2 from the carboxylic group of ligand, O6–H6···O2#1 (see Table 3), which contributes to the crystal stability and compactness undoubtedly.

#### 2.4.3. Crystal structures of compounds **3** and **4**

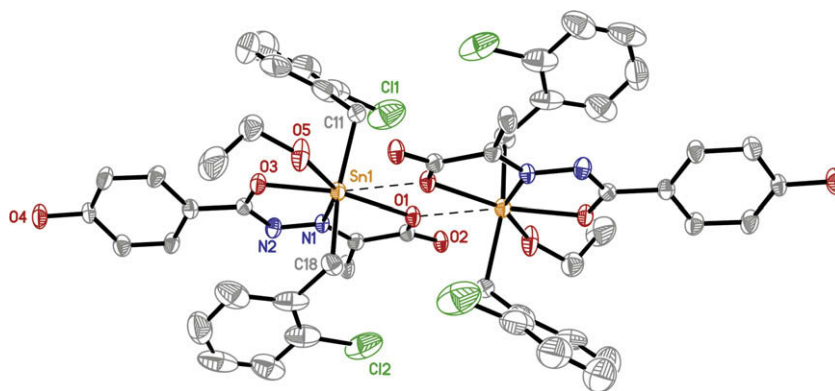
When the reaction of pyruvic acid hydrazone ligand with di-*o*-chlorobenzyltin chloride or di-*n*-octyltin oxide was carried out, compounds **3** and **4** were obtained. As illustrated in Figs. 3 and 4, compounds **3** and **4** have the similar weak-bridged dimeric structure, which also present the identical structure geometry of *trans*-C<sub>2</sub>SnO<sub>4</sub>N pentagonal bipyramid with that of compound **1** for the central tin atom, except for the different coordinated solvent molecule, isopropyl alcohol for **1**, ethanol for **3** and water for **4**, as well as the different alkyl groups, *n*-butyl group for **1**, *o*-chlorobenzyl group for **3** and *n*-octyl group for **4**. That is to say, the nature the alkyl group and the coordinated solvent molecule bonding to the Sn center does not exert a great influence on the overall structural topology of weak-bridged dimers. Selected bond distances and angles of compounds **3** and **4** are listed in Table 4. Different from the structure of compound **2**, in compounds **3** and **4**, the *para*- or *ortho*-position phenolate oxygen atoms of the ligand do not participate in coordination to the tin atom.

Table 5 shows the comparison of the bond length of Sn1···O1#1 in the crystal structure of compound **1–4**. From the structure description of each compound, it can be seen that pyruvic acid hydrazone Schiff base series ligand generally coordinate to tin center in a tridentate fashion, an enolic O atom, a Schiff base group N atom and one carboxylic O atom. Besides, the carboxylic O atom can also coordinate to the neighboring molecular tin atom as a weak interaction. Thus, all compounds can be described as weak-

**Table 3**  
Hydrogen bonding geometries for compounds **1–6**.

D–H···A	H···A	D···A	D–H···A
<b>Compound 1</b>			
O4–H4···O2#1	0.85	2.678(6)	171.6
<b>Compound 2</b>			
O6–H6···O2#1	0.82	2.67(2)	165.2
<b>Compound 3</b>			
O5–H1···O2#1	0.85(2)	2.700(8)	133(10)
O4–H4···O2#2	0.82	2.795(8)	176.5
<b>Compound 4</b>			
O4–H4···N2	0.82	2.543(8)	144.4
O5–H2···O2#1	0.80(10)	2.673(9)	162(10)
O5–H1···O4#2	0.86(10)	2.836(9)	166(10)
<b>Compound 5</b>			
O4–H4C···O2#1	0.82	2.663(11)	168.2
<b>Compound 6</b>			
N3–H3···Cl1#1	0.86	3.170(14)	145.4

Symmetry code: (#1 for **1**)  $2-x, 1-y, -z$ ; (#1 for **2**)  $-x, 2-y, -z$ ; (#1 for **3**)  $2-x, 1-y, -z$ ; (#2 for **3**)  $x-1/2, 1/2-y, z+1/2$ ; (#1 for **4**)  $1/2-x, 1/2-y, -z$ ; (#2 for **4**)  $1/2-x, 1/2+y, 1/2-z$ ; (#1 for **5**)  $-x, -y, 2-z$ ; (#1 for **6**)  $1+x, y, z$ .



**Fig. 3.** X-ray single crystal structure of compound **3** (the thermal ellipsoids are drawn at 30% probability). All H atoms are omitted for clarity.

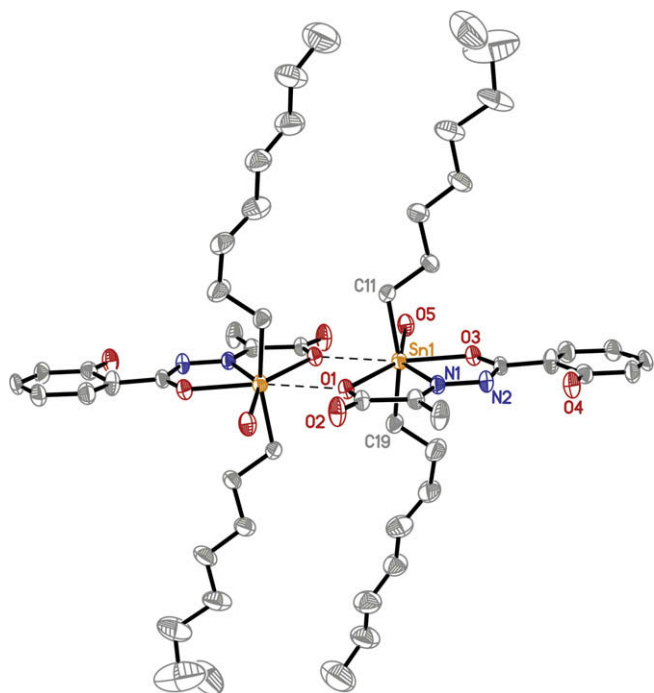


Fig. 4. X-ray single crystal structure of compound **4** (the thermal ellipsoids are drawn at 30% probability). All H atoms are omitted for clarity.

Table 4  
Selected bond lengths (Å) and angles (°) for compounds **3** and **4**.

Compound <b>3</b>			
Sn1–O3	2.133(5)	Sn1–O5	2.504(6)
Sn1–N1	2.220(6)	Sn1–O1	2.337(5)
C11–Sn1–C18	158.6(3)	C11–Sn1–O1	89.7(3)
C11–Sn1–O3	95.9(3)	O3–Sn1–N1	71.35(19)
C11–Sn1–O5	84.0(3)	N1–Sn1–O1	70.00(19)
C11–Sn1–O1#1	80.2(2)	O3–Sn1–O5	76.17(19)
C11–Sn1–N1	104.3(3)	O1–Sn1–O1#1	64.57(18)
Compound <b>4</b>			
Sn1–O3	2.185(5)	Sn1–O5	2.378(6)
Sn1–N1	2.296(6)	Sn1–O1	2.386(5)
C11–Sn1–C19	163.8(3)	C11–Sn1–O1	88.6(3)
C11–Sn1–O3	97.7(3)	O3–Sn1–N1	69.4(2)
C11–Sn1–O5	82.8(3)	N1–Sn1–O1	67.80(19)
C11–Sn1–O1#1	83.0(2)	O3–Sn1–O5	77.3(2)
C11–Sn1–N1	94.4(3)	O1–Sn1–O1#1	66.2(2)

Symmetry code: (#1 for **3**)  $2-x, 1-y, -z$ ; (#1 for **4**)  $1/2-x, 1/2-y, -z$ .

bridged dimers (for compound **1**, **3**, **4**) or polymer (for compound **2**). But due to the overall effect of bulk and steric hindrance of the alkyl groups and the coordinated solvent molecule bonding to the Sn center, *o*-chlorobenzyl > *n*-octyl > *n*-butyl, and isopropyl alcohol > ethanol > methanol > water, the distances between the tin atom and the corresponding neighboring carboxylic O1#1 have obvious differences, which have been listed in the Table 5.

In compounds **3** and **4**, there also exist intra- and intermolecular hydrogen bonds formed with the O–H of coordinated solvent molecule or ligand phenol group and the corresponding acceptor oxygen or nitrogen atoms, which are listed in the Table 3.

#### 2.4.4. Crystal structure of compound **5**

Single crystal X-ray analyses reveal that compound **5** also presents a weak-bridged dimer. However, it shows a complete different

Table 5

Comparison of the bond length of Sn1...O1#1 in compounds **1–4**, when different alkyl group and coordinated solvent molecule bonding to the tin center.

Compound	Alkyl group	Solvent molecule	Distance of Sn1...O1#1 (Å)
<b>1</b>	<i>n</i> -Butyl group	Isopropanol	2.805(4)
<b>2</b>	<i>n</i> -Butyl group	Methanol	2.734(15)
<b>3</b>	<i>o</i> -Chlorobenzyl group	Ethanol	2.748(5)
<b>4</b>	<i>n</i> -Octyl group	Water	2.620(5)

Table 6

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

Sn1–N1	2.279(9)	Sn1–O4	2.253(8)
Sn1–O3	2.190(7)	Sn2–O4	2.016(7)
Sn1–O1	2.397(7)		
C11–Sn1–C15	164.6(5)	O1–Sn1–O1#1	67.0(3)
C11–Sn1–N1	97.6(4)	O4–Sn1–O1#1	77.7(2)
C11–Sn1–O3	95.2(4)	O4–Sn2–C19	104.3(6)
C11–Sn1–O1	88.2(4)	O4–Sn2–C23	104.5(5)
C11–Sn1–O1#1	82.5(4)	C19–Sn2–C23	111.7(7)
C11–Sn1–O4	86.8(4)	O4–Sn2–C27	101(8)
N1–Sn1–O3	68.9(3)	C19–Sn2–C27	113(6)
N1–Sn1–O1	68.1(3)	C23–Sn2–C27	120(5)
O4–Sn1–O3	78.3(3)		

Symmetry code: #1  $-x, -y, 2-z$ .

structure from that compound **1**, **3** or **4**. The asymmetric unit of **5** consists of two different types of tin atoms, which are linked by the hydroxyl group derived from the decomposition of the reactant 'bis(tri-*n*-butyltin) oxide'. The Sn1 atom lies in a distorted pentagonal bipyramidal coordination environment, in which one tridentate pyruvic acid benzoyl hydrazone ligand, two *trans* *n*-butyl groups, the hydroxyl oxygen atom O4, and the carboxylate O1 from the neighboring molecule, coordinate to the central Sn1 atom. The sum of the angles subtended at the Sn1 atom in the pentagonal plane is 360.1°, so O3, O4, N1, O1, and O1#1 [ $\#1: -x, -y, 2-z$ ] lie almost in the same plane, with the Sn1 atom only 0.0018 Å away from the equatorial plane, while the two *trans* *n*-butyl carbon atoms take up the axial sites around the Sn1 atom; the angle of the axial C11–Sn1–C15 is 164.6(5)°. O1 atom of the carboxylate residue also binds the other tin atom, Sn1#1, generating a Sn<sub>2</sub>O<sub>2</sub> four-membered ring. The distance of Sn1#1...O1, 2.671(7) Å, is greater than the sum of the covalent radii of Sn and O (2.56 Å), but is considerably less than the sum of the van der Waals radii (3.68 Å) and should be considered as a weak bonding interaction. Therefore, the structure of compound **5** can also be described as a weak-bridged dimer (selected bond lengths and angles see Table 6).

The coordination configuration at the tin atom Sn2 is distorted tetrahedron, as indicated by bonding angles of 104.3(6)°, 104.5(5)°, 111.7(7)°, 101(8)°, 113(6)°, and 120(5)° for O4–Sn2–C19, O4–Sn2–C23, C19–Sn2–C23, O4–Sn2–C27, C19–Sn2–C27, and C23–Sn2–C27, respectively. In particular, as can be seen from the Fig. 5, the somewhat disordered β-, γ-, and δ-carbon atoms of the *n*-butyl groups occurred for all of the five *n*-butyl groups coordinated with the two types of tin atoms. Meanwhile, an intramolecular hydrogen bond has also been observed between the bridging hydroxyl group and the carboxylate oxygen atom O2#1 (see Table 3).

#### 2.4.5. Crystal structure of compound **6**

In contrast to compounds **1–5** reported here, compound **6** is isolated from reaction of salicylaldehyde isonicotinoyl hydrazone with *n*-butyltin trichloride in ethanol in the presence of triethylamine. X-ray single crystal structure analysis reveals that **6** is a

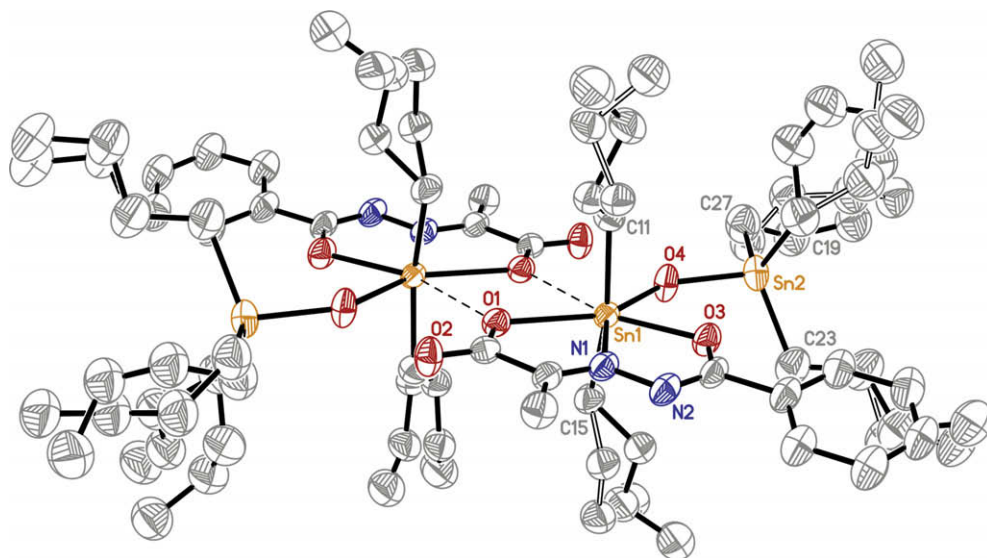


Fig. 5. X-ray single crystal structure of compound **5** (the thermal ellipsoids are drawn at 30% probability). All H atoms are omitted for clarity.

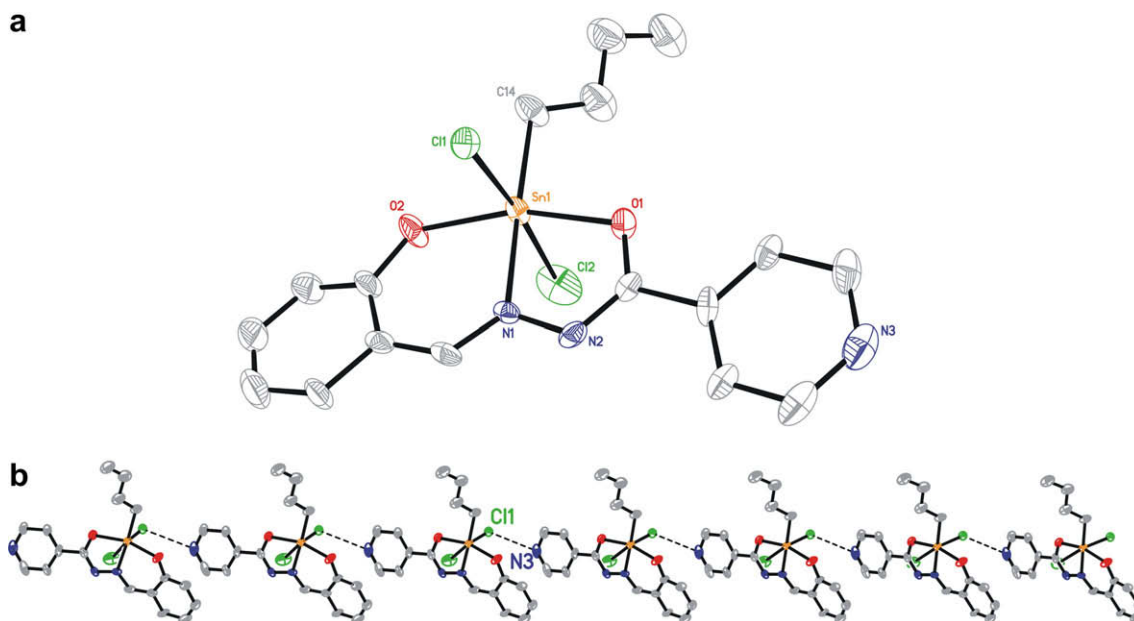


Fig. 6. (a) Coordination environment around the tin(IV) atom in **6** with hydrogen atoms omitted for clarity (the thermal ellipsoids are drawn at 30% probability). (b) 1D infinite linear chain structure in **6** by intermolecular hydrogen bonds between the chlorine atom and proton of pyridyl cycle with the atom labeling scheme.

simple mononucleic compound (Fig. 6a). But interestingly, for keep the neutral nature, compound **6** present in the form of zwitterion with the ionization of nitrogen atom of pyridine cycle in the Schiff base ligand. In the crystal structure of **6**, Sn center is six-coordinate, being bound to one *n*-butyl group, two chlorine atoms, as well as one nitrogen atom and two oxygen atoms from the enolic hydrazone ligand. The geometry around the tin atom is distorted octahedron, with the organyl group lying in the molecular plane, the two chlorine atoms being in *trans* position (selected bond lengths and angles are listed in Table 7). The two Sn–Cl distances in **6** are not equivalent [Sn1–Cl1 2.600(3) and Sn1–Cl2 2.437(4) Å], one of the chlorine atoms has a longer bond length due to a N3–H3...Cl1#1 (#1: 1 + *x*, *y*, *z*) hydrogen bond interaction as is shown in Fig. 6b. Organotin(IV) compounds with the same Sn coordination environment have been reported previously [29,31], and

Table 7  
Selected bond lengths (Å) and angles (°) for compound **6**.

Sn1–N1	2.189(8)	Sn1–Cl4	2.137(12)
Sn1–O1	2.143(8)	Sn1–Cl1	2.600(3)
Sn1–O2	2.056(8)	Sn1–Cl2	2.437(4)
Cl1–Sn1–Cl2	169.77(14)	N1–Sn1–O1	73.5(3)
Cl1–Sn1–N1	81.7(2)	N1–Sn1–O2	85.7(3)
Cl1–Sn1–O1	87.3(2)	C14–Sn1–O1	101.4(4)
Cl1–Sn1–O2	89.1(3)	C14–Sn1–O2	99.1(5)
Cl1–Sn1–Cl4	91.2(5)		

the distances of Sn–Cl lie in the similar range, such as the ionic compound 'bis-(triethylammonium)-bis-(3,5-di-tert-butyl-2-oxophenyl)-oxamido-bis-(dichlorobutyl-stannate)' [Sn–Cl1 2.593(1)

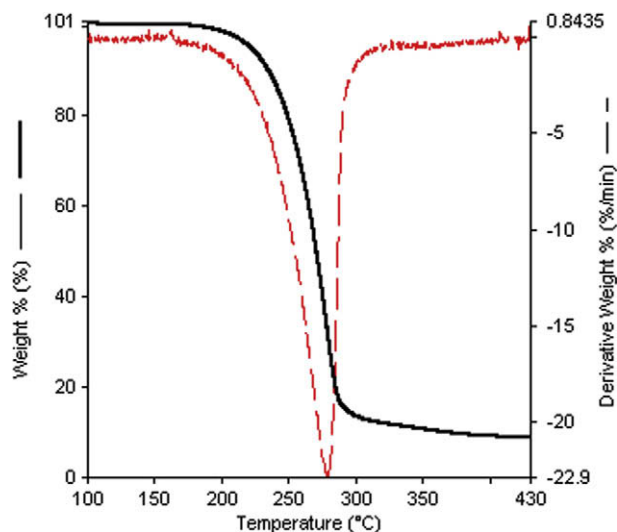


Fig. 7. TGA curve for the thermal decomposition of compound **1**.

and Sn–Cl2 2.429(1) Å [29]. The compound units are linked together through the hydrogen bonds, resulting in a 1D supermolecular chain.

### 2.5. TG analysis of compound **1**

In order to analyze the thermal stability of organotin(IV) compound coordinated with hydrazone Schiff base ligand, TG analysis of the representative compound **1** was performed on powder samples in the range of 100–430 °C. From Fig. 7, it can be seen that compound **1** experiences an obvious weight loss between 200 °C and 300 °C, which attributes to the decomposition of the hydrazone ligand and the collapse of the whole structure. The remainder is SnO<sub>2</sub>, about 17% (calcd 16.2%).

## 3. Conclusion

In conclusion, this contribution has shown that the self-assembly of two types of hydrazone Schiff base ligands and different alkyltin salts can result in the formation of various topological organotin(IV) compounds. When dialkyltin chlorides or oxide and the pyruvic acid series Schiff base ligands are used as the starting materials, weak-bridged dimer compounds **1**, **3** and **4**, are produced, in which the –CO<sub>2</sub><sup>-</sup> ion functions as the bridge chelating the two neighboring tin atom. It is interesting that compound **2** with a weak-bridged polymeric chain structure can be obtained through changing the amount of sodium ethoxide by using di-*n*-butyltin chloride and pyruvic acid 4-hydroxybenzoylhydrazone as the starting materials, in which the *ortho*-hydroxyl group has been deprotonized and this contribute to the formation of the dichlorodistannoxane ladder structure. When bis(tri-*n*-butyltin) oxide is used as the starting materials, a fascinating dimeric compound **5** results, which contains two different coordination environment tin atoms, and the two types of tin center are linked by the hydroxyl group derived from the decomposition of bis(tri-*n*-butyltin) oxide. Compound **6** is a novel zwitterion trigonal bipyramidal framework with the ionization of nitrogen atom of pyridine cycle in the Schiff base ligand, in which independent units are connected by the intermolecular hydrogen bonds into an infinite supermolecular chain. The TG analysis of compound **1** show that it can keep the stability until about 200 °C, and the final residue is SnO<sub>2</sub>.

## 4. Experimental

### 4.1. Materials and physical measurements

Di-*n*-butyltin chloride, bis(tri-*n*-butyltin) oxide, di-*n*-octyltin oxide, *n*-butyltin trichloride, thiophenecarbonyl hydrazide, 4-hydroxybenzoyl hydrazide, benzoyl hydrazide, salicyloylhydrazide, isonicotinoyl hydrazide, salicylaldehyde and pyruvic acid were commercially available and used without further purification. Schiff base ligands and di-*o*-chlorobenzyltin chloride were prepared by the methods reported in the literature [13,14,32–34]. All the solvents used in the reaction were of AR grade and dried using standard literature procedures.

IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs. <sup>1</sup>H and <sup>119</sup>Sn NMR spectra were recorded on a Mercury Plus-400 NMR spectrometer; chemical shifts were given in ppm relative to Me<sub>4</sub>Si and Me<sub>4</sub>Sn in CDCl<sub>3</sub> solvent. Thermal decomposition was measured on Pyris 1 thermogravimetric analyzer. Elemental analyses were performed in a PE-2400 II elemental analyzer.

### 4.2. Synthesis of the compounds

#### 4.2.1. Preparation of {(*n*-Bu)<sub>2</sub>Sn[2-SC<sub>4</sub>H<sub>3</sub>CON<sub>2</sub>C(CH<sub>3</sub>)CO<sub>2</sub>](HOC<sub>3</sub>H<sub>7</sub>-*i*)}<sub>2</sub> (**1**)

The reaction was carried out under nitrogen atmosphere with the use of standard Schlenk technique. Pyruvic acid thiophenecarbonyl hydrazone (0.21 g, 1.0 mmol) and sodium ethoxide (0.05 g, 1.0 mmol) were added to a solution of absolute isopropyl alcohol (20 ml) and heated under reflux with stirring for 0.5 h. After the addition of di-*n*-butyltin chloride (0.30 g, 1.0 mmol) to the reactor, the reaction mixture was refluxed for 10 h more. The reaction solution thus obtained was filtered and evaporated under vacuum to form a yellow solid, and then recrystallized from dichloromethane/hexane to give yellow single crystals of compound **1**. Yield 59%. Anal. Calc. for C<sub>19</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub>Sn: C, 45.34; H, 6.40; N, 5.57. Found: C, 44.21; H, 6.29; N, 5.49%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm): 1.04 (t, 15H, –CH<sub>3</sub>), 1.29–1.76 (m, 12H, SnCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.12 (m, 1H, –OCH), 4.90 (s, 1H, *i*-Pr–OH), 7.17–7.37 (m, 3H, –C<sub>4</sub>H<sub>3</sub>S). <sup>119</sup>Sn NMR (CDCl<sub>3</sub>, δ ppm): –459.6. IR (KBr, cm<sup>-1</sup>): 3044 (s, Ar–H), 3001 (s, C–H), 1615 (s, C=N–N=C), 1636 (s, C=N), 1586, 1356 (s, CO<sub>2</sub>), 1202 (m, C–O), 561 (m, Sn–O), 537 (w, Sn–C), 469 (w, Sn–N).

#### 4.2.2. Preparation of [ {(*n*-Bu)<sub>2</sub>SnCl(O)(*n*-Bu)<sub>2</sub>Sn(O) [C<sub>6</sub>H<sub>4</sub>CON<sub>2</sub>C(CH<sub>3</sub>)CO<sub>2</sub>]Sn(*n*-Bu)<sub>2</sub>(HOCH<sub>3</sub>)} ]<sub>∞</sub> (**2**)

Compound **2** was prepared by the similar method as compound **1**. Pyruvic acid 4-hydroxybenzoylhydrazone (0.22 g, 1.0 mmol) and sodium ethoxide (0.11 g, 2.0 mmol) were added to dry benzene (20 ml) in a Schlenk flask and stirred for 0.5 h. Di-*n*-butyltin chloride (0.30 g, 1.0 mmol) was then added and the reaction mixture was refluxed for 10 h more and then filtered. The solvent was gradually removed by evaporation under vacuum until a solid product was obtained. The solid was then recrystallized from methanol and colorless block crystals suitable for X-ray diffraction were obtained. Yield 67%. Anal. Calc. for C<sub>70</sub>H<sub>130</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>12</sub>Sn<sub>6</sub>: C, 41.98; H, 6.49; N, 2.81. Found: C, 41.87; H, 6.47; N, 2.93%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm): 0.99 (t, *J* = 15.2 Hz, 36H, –CH<sub>3</sub>), 1.24–1.78 (m, 72H, Sn–CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.68 (s, 6H, CH<sub>3</sub>), 3.31 (s, 6H, CH<sub>3</sub>–O), 6.26–7.65 (m, 8H, Ph–H), 8.17 (s, 2H, R–OH). <sup>119</sup>Sn NMR (CDCl<sub>3</sub>, δ ppm): –449.4, –177.1, –196.4. IR (KBr, cm<sup>-1</sup>): 3039 (s, Ar–H), 2989 (s, C–H), 1636 (s, C=N), 1613 (s, C=N–N=C), 1566, 1326 (s, CO<sub>2</sub>), 1211 (m, C–O), 651 (m, O–Sn–O), 568 (m, Sn–O), 544 (w, Sn–C), 475 (m, Sn–N).



#### 4.2.3. Preparation of $\{(o\text{-ClBz})_2\text{Sn}[4\text{-HOC}_6\text{H}_4\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2](\text{HOC}_2\text{H}_5)\}_2$ (**3**)

Compound **3** was prepared by the same method as compound **2** except for the molar ratio of each reactant is 1:1:1, that is pyruvic acid 4-hydroxybenzoylhydrazone (0.22 g, 1.0 mmol), sodium ethoxide (0.05 g, 1.0 mmol), and di-*o*-chlorobenzyltin chloride (0.44 g, 1.0 mmol). Colorless block crystals suitable for X-ray diffraction were obtained by recrystallized from ethanol. Yield 71%. Anal. Calc. for  $\text{C}_{52}\text{H}_{52}\text{Cl}_4\text{N}_4\text{O}_{10}\text{Sn}_2$ : C, 48.84; H, 3.39; N, 4.75. Found: C, 48.93; H, 3.47; N, 4.63%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 1.70–1.80 (m, 6H,  $\text{CH}_3$ ), 3.44–3.66 (m, 12H,  $-\text{CH}_2-$  &  $\text{PhCH}_2\text{Sn}$ ), 6.41–7.35 (m, 24H, Ar-H & Ph-H), 8.53 (s, 2H, R-OH), 11.28 (s, 2H, Ar-OH).  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): –447.3. IR (KBr,  $\text{cm}^{-1}$ ): 3432 (m, O-H), 3033 (s, Ar-H), 2982 (s, C-H), 1622 (m, C=N), 1601 (s, C=N=N=C), 1577, 1321 (s,  $\text{CO}_2$ ), 1206 (m, C-O), 597 (m, Sn-O), 553 (m, Sn-C), 470 (w, Sn-N).

#### 4.2.4. Preparation of $\{(n\text{-C}_8\text{H}_{17})_2\text{Sn}[2\text{-HOC}_6\text{H}_4\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2](\text{H}_2\text{O})\}_2$ (**4**)

Pyruvic acid salicyloylhydrazone (0.22 g, 1.0 mmol) was added to a benzene/ethanol (3:1, v/v) solution (30 mL) of di-*n*-octyltin oxide (0.36 g, 1.0 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 acetone to give colorless crystals. Yield 76%. Anal. Calc. for  $\text{C}_{52}\text{H}_{88}\text{N}_4\text{O}_{10}\text{Sn}_2$ : C, 53.53; H, 7.60; N, 4.80. Found: C, 53.71; H, 7.72; N, 4.65%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 0.83 (t,  $J = 12.0$  Hz, 12H,  $\text{CH}_3$ ), 1.12–1.39 [m, 16H,  $\text{Sn}(\text{CH}_2)_2$  ( $\alpha$ ,  $\beta$ )], 1.53–1.79 [m, 40H,  $\text{CH}_2$  ( $\omega$ )], 2.65 (s, 6H,  $\text{CH}_3$ ), 7.01–7.36 (m, 8H, Ph-H), 11.31 (s, 2H, Ar-OH).  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): –463.1. IR (KBr): 3113 (s, Ar-H), 2911 (s, C-H), 1644 (s, C=N), 1606 (s, C=N=N=C), 1619, 1337 (s,  $\text{CO}_2$ ), 1203 (s, C-O), 594 (s, Sn-O), 542 (w, Sn-C), 476 (w, Sn-N)  $\text{cm}^{-1}$ .

#### 4.2.5. Preparation of $\{(n\text{-Bu})_2\text{Sn}[\text{C}_6\text{H}_5\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2](\text{HOSn}(n\text{-Bu})_3)\}_2$ (**5**)

Pyruvic acid benzoylhydrazone (0.20 g, 1.0 mmol) was added to a benzene suspension (20 mL) of bis(tri-*n*-butyltin) oxide (0.61 g, 1.0 mmol), then the mixture was stirred and heated at reflux for 6 h. The clear solution obtained after filtering was evaporated in vacuum to give a solid, which was then recrystallized from dichloromethane/hexane to give colorless crystals. Yield 55%. Anal. Calc. for  $\text{C}_{30}\text{H}_{54}\text{N}_2\text{O}_4\text{Sn}_2$ : C, 48.38; H, 7.26; N, 3.76. Found: C, 48.30; H, 7.19; N, 3.77%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 0.91 (t,  $J = 6.40$  Hz, 15H,  $\text{CH}_3$ ), 1.15–1.51 (m, 30H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ), 2.32 (s, 3H,  $\text{CH}_3$ ), 6.84–7.36 (m, 5H, Ph-H).  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 107.4, –454.1. IR (KBr): 2989 (s, Ar-H), 2931, 2856 (s, C-H), 1633 (m, C=N), 1605, 1330 (s,  $\text{CO}_2$ ), 1601 (m, C=N=N=C), 1207 (s, C-O), 665 (m, O-Sn-O), 589 (m, Sn-O), 558 (w, Sn-C), 496 (m, Sn-N)  $\text{cm}^{-1}$ .

#### 4.2.6. Preparation of $\{(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2\}^+ [4\text{-NHC}_5\text{H}_4\text{CON}_2\text{CH}(\text{C}_6\text{H}_4\text{O}-2)]^-$ (**6**)

A 50 ml three-necked flask was charged with 1.0 mmol of salicylaldehyde isonicotinoylhydrazone (0.24 g), 1.0 ml triethylamine and 20 ml ethanol. *n*-Butyltin trichloride (0.28 g, 1.0 mmol) in 10 ml ethanol was added dropwise into the flask with stirring at room temperature. The solution turned yellow and a white precipitate formed. This solution was stirred for 4 h. The white deposit, which is  $\text{Et}_3\text{N-HCl}$  formed in the reaction, was filtered off, washed with 20 ml ether. Several days later, colorless prism crystals suitable for X-ray diffraction were obtained from the solvent directly at room temperature. Yield 34%. Anal. Calc. for  $\text{C}_{17}\text{H}_{19}\text{Cl}_2\text{N}_3\text{O}_2\text{Sn}$ : C, 41.89; H, 3.90; N, 8.63. Found: C, 41.81, H, 3.77; N, 8.58%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 8.89 (m, 1H, N=CH), 7.91 (d, 2H,  $J = 6.4$  Hz, 2,6-pyridine-H), 7.43 (d, 2H,  $J = 4.8$  Hz, 3,5-pyridine-H), 7.26–6.70 (m, 4H, Ph-H), 1.15–1.51 (m, 6H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2$ ), 0.92 (t,  $J =$

6.0 Hz, 3H,  $\text{CH}_3$ ).  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): –365.1. IR (KBr): 3200 (s, Ar-H), 2831 (s, C-H), 1614 (s, C=N), 1596 (s, C=N=N=C), 1211 (s, C-O), 599 (s, Sn-O), 544 (m, Sn-C), 486 (w, Sn-N)  $\text{cm}^{-1}$ .

### 4.3. Determination of crystal structures

X-ray diffraction data for crystals were performed with graphite-monochromated Mo K $\alpha$  radiation (0.71073 Å) on the Bruker Smart-1000 CCD diffractometer and collected by the  $\omega$ -2 $\theta$  scan

**Table 8**  
Crystal data and structure refinement details for compounds **1–3**.

Compound	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	$\text{C}_{19}\text{H}_{32}\text{N}_2\text{O}_4\text{SSn}$	$\text{C}_{70}\text{H}_{130}\text{Cl}_2\text{N}_4\text{O}_{12}\text{Sn}_6$	$\text{C}_{26}\text{H}_{26}\text{Cl}_2\text{N}_2\text{O}_5\text{Sn}$
Formula weight	503.22	2002.82	636.08
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2(1)/c$	$P\bar{1}$	$P2(1)/n$
<i>a</i> (Å)	12.276(3)	9.4653(10)	12.086(10)
<i>b</i> (Å)	9.3224(19)	12.7335(132)	12.251(10)
<i>c</i> (Å)	20.601(4)	20.134(2)	18.133(15)
$\alpha$ (°)	90	99.8510(10)	90
$\beta$ (°)	93.356(3)	97.7370(10)	90.453(11)
$\gamma$ (°)	90	103.517(2)	90
<i>V</i> (Å <sup>3</sup> )	2353.7(8)	2285.8(4)	2685(4)
<i>Z</i>	4	1	4
<i>F</i> (0 0 0)	1032	1008	1280
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.198	1.455	1.574
$\theta$ Range (°)	1.98–25.01	1.68–25.01	2.01–25.03
Number of reflections	11 970	11 673	13 490
Number of parameters	244	434	328
<i>R</i> factor all	0.0674	0.2206	0.0926
<i>R</i> factor [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0437	0.1129	0.0684
<i>wR</i> <sub>2</sub>	0.1380	0.2933	0.2084
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.1163	0.2333	0.1766
Goodness-of-fit (GOF)	1.014	1.028	1.009

**Table 9**  
Crystal data and structure refinement details for compounds **4–6**.

Compound	<b>4</b>	<b>5</b>	<b>6</b>
Empirical formula	$\text{C}_{52}\text{H}_{88}\text{N}_4\text{O}_{10}\text{Sn}_2$	$\text{C}_{30}\text{H}_{54}\text{N}_2\text{O}_4\text{Sn}_2$	$\text{C}_{17}\text{H}_{19}\text{Cl}_2\text{N}_3\text{O}_2\text{Sn}$
Formula weight	1166.64	744.13	486.94
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2(1)/c$
<i>a</i> (Å)	26.8573(16)	9.6414(18)	10.235(4)
<i>b</i> (Å)	11.6043(13)	9.6652(18)	14.945(5)
<i>c</i> (Å)	21.129(2)	20.176(2)	13.627(5)
$\alpha$ (°)	90	77.533(2)	90
$\beta$ (°)	116.953(2)	81.097(2)	110.727(4)
$\gamma$ (°)	90	85.681(3)	90
<i>V</i> (Å <sup>3</sup> )	5869.8(10)	1811.9(5)	1949.5(12)
<i>Z</i>	4	2	4
<i>F</i> (0 0 0)	2432	760	968
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.320	1.364	1.659
$\theta$ Range (°)	2.03–25.03	2.09–25.10	2.53–25.00
Number of reflections	14 334	9258	9439
Number of parameters	311	494	226
<i>R</i> factor all	0.0838	0.1120	0.1037
<i>R</i> factor [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0567	0.0956	0.0897
<i>wR</i> <sub>2</sub>	0.1730	0.2458	0.2503
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.1477	0.2309	0.2384
Goodness-of-fit (GOF)	1.018	1.144	1.076

technique at 298(2) K. The crystal structures were solved by direct method and different Fourier syntheses using SHELXL-97 program, and refined by full-matrix least-squares on  $F^2$ . All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were put in calculated positions or located from the Fourier maps and refined isotropically with the isotropic vibration parameters related to the non-hydrogen atom to which they are bonded. Crystallographic data and experimental details of the structure determinations are listed in Tables 8 and 9.

### Supplementary material

CCDC 293406, 745102, 744121, 745101, 744023 and 744122 contains the supplementary crystallographic data for **1**, **2**, **3**, **4**, **5** and **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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