

# Self-assembly of organooxotin(IV) clusters with Schiff-base-containing-triazole from hydrolysis or solvothermal synthesis: Crystal structures, hydrogen bonds, C–H··· $\pi$ stacking and S···S interaction

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## Abstract

Eight new organostannoxane-based multiredox assemblies containing-Schiff-base-triazole ligand peripheries have been readily synthesized by hydrolysis or solvothermal synthetic routes. The reactions of the diorganotin dichloride with the Schiff-base-containing-triazole ligand afford the following types:  $[(\text{Me}_2\text{Sn})_2\text{O}_2(\text{Ln})]_2$  ( $n = 1$ , for **1**)  $[(\text{Me}_2\text{Sn})_2\text{O}(\text{RO})(\text{Ln})]_2$  ( $\text{R} = \text{Et}$ ,  $n = 2$ , for **2**;  $\text{R} = \text{Me}$ ,  $n = 3$ , for **3**),  $[(n\text{-Bu}_2\text{Sn})_2\text{O}_2(\text{Ln})]_2$  ( $n = 1$ , for **4**;  $n = 2$ , for **5**;  $n = 3$ , for **6**) and  $[(\text{Me}_2\text{Sn})_2\text{Ln}_2\text{O}]_2 \cdot \text{L}$  ( $n = 2$ ;  $\text{L} = \text{H}_2\text{O}$  for **7**,  $\text{L} = \text{CH}_3\text{OH}$  for **8**). All the complexes were characterized by elemental analysis, IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  spectra analyses. Except for complexes **4** and **6**, the other complexes are also characterized by X-ray crystallography diffraction analyses. Complexes **1–3** and **5** show similar structures containing a  $\text{Sn}_4\text{O}_4$  ladder-shaped skeleton in which the N atom from a corresponding thione-form deprotonated Schiff base coordinated to the exo tin atoms in monodentate chelating agent. Complex **7** and **8** show a novel framework containing a  $\text{Sn}_2\text{O}_2$  symmetrical core with two N atoms from triazole moiety coordinated to tin atoms. Weak but significant intermolecular hydrogen bondings, C–H··· $\pi$  stacking or non-bonded S···S interaction lead to aggregation and self-assembly of these complexes into 1D, 2D or 3D supramolecular frameworks.

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**Keywords:** Organooxotin(IV); Cluster; Schiff-base-containing-triazole; Hydrolysis; Solvothermal

## 1. Introduction

Organooxotin clusters have been attracting considerable attention in recent years because of their novel structures [1], their suitability for construction of supramolecular framework [2], and their efficient catalysis of various organic reactions [3]. Several types of organooxotin clusters, such as ladder [4a], cube [4b], butterfly [4c], drum [4d], among others, have been prepared and their structures

established by X-ray diffraction analysis. The most intriguing aspect of the latter is the notion of being able to manipulate on one day not only the features of specific molecules, but also the bulk, intermolecular characteristic and properties of the entire crystalline aggregate. To date, a plethora of eloquent research has been conducted in this discipline, resulting in an extensive array of 1D coordination polymers, 2D grids and 3D lattices [5]. Typically, these coordination-based systems employ di- or multitopic metal centers and rigid, organic subunits or “spacers”. In this field, a vast majority of reported work is based upon the use of polyfunctional organic ligands to bind to the tin ions through self-assembly processes, leading to the formation of complexes with fascinating topologies and physical

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properties. Ligands with flexible multiply coordinating donor atoms, such as heterocyclic thionate ligands [6], which contain at least one deprotonated heterocyclic thioamide group ( $\text{N}-\text{C}-\text{S}^-$ ) and can act as monodentate, chelating or bridging ligands are particularly important [7]. In our previous work, we studied the ligand 2,5-dimercapto-1,3,4-thiadiazole ( $\text{H}_2\text{dmt}$ ) and obtained a metallomacrocyclic organooxotin cluster [8]; however, much less work has been carried out to investigate organooxotin cluster with Schiff-base ligand. To continue our study in this field, we selected and synthesized the Schiff-base-containing-triazole ligands. Interestingly, we adopted two different synthetic routes of hydrolysis or solvothermal method from that reported before and obtained eight ladder-shaped and N-bridged organooxotin clusters.

Thus, we reported the synthesis of three Schiff-base-containing-triazole ligands ( $\text{L}_1-\text{L}_3$ ) and eight tetranuclear organooxotin clusters of the types:  $[(\text{Me}_2\text{Sn})_2\text{O}_2(\text{Ln})]_2$  ( $n = 1$ , for **1**)  $[(\text{Me}_2\text{Sn})_2\text{O}(\text{RO})(\text{Ln})]_2$  ( $\text{R} = \text{Et}$ ,  $n = 2$ , for **2**;  $\text{R} = \text{Me}$ ,  $n = 3$ , for **3**),  $[(n\text{-Bu}_2\text{Sn})_2\text{O}_2(\text{Ln})]_2$  ( $n = 1$ , for **4**;  $n = 2$ , for **5**;  $n = 3$ , for **6**) and  $[(\text{Me}_2\text{Sn})_2\text{Ln}_2\text{O}]_2 \cdot \text{L}$  ( $n = 2$ ;  $\text{L} = \text{H}_2\text{O}$  for **7**,  $\text{L} = \text{CH}_3\text{OH}$  for **8**), which were obtained by hydrolysis and solvothermal synthetic routes. All the complexes were structurally characterized by elemental analysis, and IR, NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{119}\text{Sn}$ ) spectra. Except for complexes **4** and **6**, the other complexes were also characterized by X-ray crystallography diffraction analyses. Complexes **1–3** and **5** show similar structures containing a  $\text{Sn}_4\text{O}_4$  ladder-shaped skeleton in which the N atom from a corresponding thione-form deprotonated Schiff base coordinated to the exo tin atoms in monodentate chelating agent. Complexes **7** and **8** show a novel framework containing a  $\text{Sn}_2\text{O}_2$  symmetrical core with the two N atoms coordinated to tin atoms. Weak but significant intermolecular hydrogen bondings,  $\text{C}-\text{H} \cdots \pi$  stackings or non-bonded  $\text{S} \cdots \text{S}$  interactions lead to aggregation and self-assembly of these complexes into 1D, 2D or 3D supramolecular frameworks.

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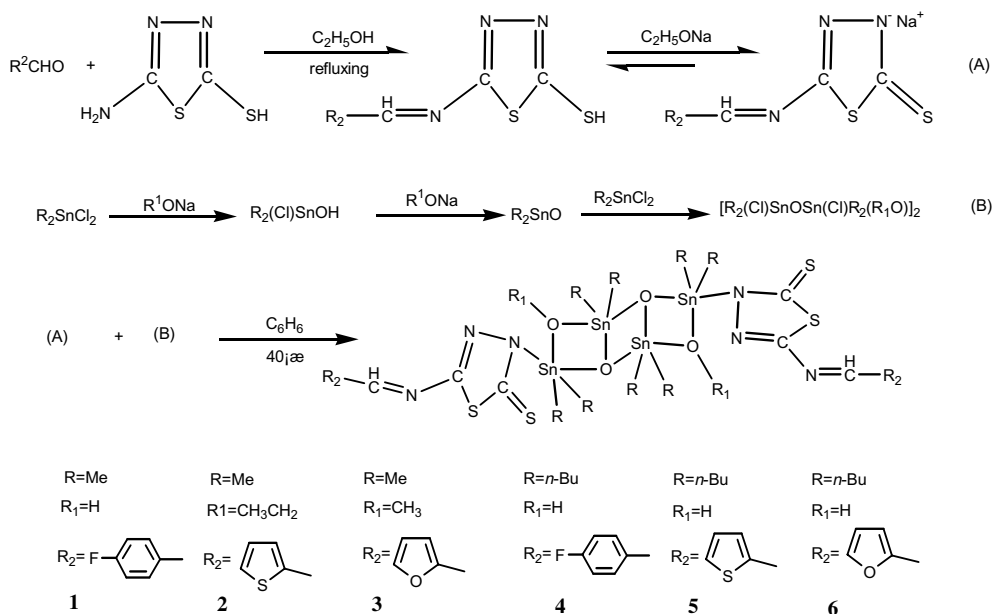
## 2. Results and discussion

### 2.1. Synthetic aspects and spectra

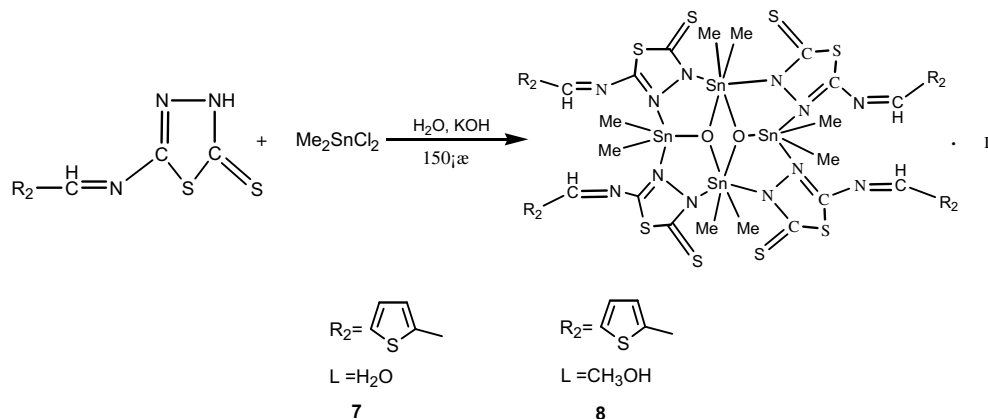
We synthesized three Schiff-base-containing-triazole ligands ( $\text{L}_1-\text{L}_3$ ) with three types of aldehydes and obtained eight tetranuclear organooxotin clusters with diorganotin(IV) chloride by hydrolysis or solvothermal synthetic routes. These reactions afford the following eight tetranuclear clusters of the types:  $[(\text{Me}_2\text{Sn})_2\text{O}_2(\text{Ln})]_2$  ( $n = 1$ , for **1**)  $[(\text{Me}_2\text{Sn})_2\text{O}(\text{RO})(\text{Ln})]_2$  ( $\text{R} = \text{Et}$ ,  $n = 2$ , for **2**;  $\text{R} = \text{Me}$ ,  $n = 3$ , for **3**),  $[(n\text{-Bu}_2\text{Sn})_2\text{O}_2(\text{Ln})]_2$  ( $n = 1$ , for **4**;  $n = 2$ , for **5**;  $n = 3$ , for **6**) and  $[(\text{Me}_2\text{Sn})_2\text{Ln}_2\text{O}]_2 \cdot \text{L}$  ( $n = 2$ ;  $\text{L} = \text{H}_2\text{O}$  for **7**,  $\text{L} = \text{CH}_3\text{OH}$  for **8**). The detail of synthetic experiments are shown in Schemes 1 and 2.

The assignment of IR bonds of these complexes has been made by comparison with IR spectra of their related precursors. In the spectra of the organotin(IV) complexes **1–8**, the frequency of  $\nu(\text{S}-\text{H})$  is not observed at 3106 and 2925  $\text{cm}^{-1}$ , and new frequencies occur at about 1242  $\text{cm}^{-1}$  ( $\text{C}=\text{S}$ ), indicating the deprotonation of N–H of the thione form. A new band at  $439 \pm 13 \text{ cm}^{-1}$  in the spectra of organotin(IV) complexes, which is assigned to  $\nu(\text{Sn}-\text{N})$ , showing N atom from the triazole moiety is coordinated to the central tin atom.

In the uncoordinated ligand spectrum two bands at 3347 and 3244  $\text{cm}^{-1}$  are assigned to  $\nu_{\text{as}}(\text{NH}_2)$  and  $\nu_{\text{s}}(\text{NH}_2)$  modes, respectively. But in complexes **1–8**, the frequency is not observed and a new frequency is assigned at about



Scheme 1.



Scheme 2.

1658  $\text{cm}^{-1}$ , showing that the Schiff-base ( $\text{CH}=\text{N}$ ) mode is formed.

#### NMR.

In the  $^1\text{H}$  NMR spectrum of complexes **1–8**, the signal at  $\delta = 1.6$  ppm for the  $-\text{SH}$  proton of the ligand is absent and the new signal at  $\delta = 2.06$  ppm ( $\text{N}-\text{H}$ ) occurs, showing the occurrence of thiol  $\rightarrow$  thione tautomerism in the  $\text{CDCl}_3$  solution. It has been reported [9] that  $\text{N}-\text{H}$  ring in the uncoordinated ligand is clearly observed at  $\delta$  13.2 ppm instead of the aromatic  $\text{SH}$  in the region  $\delta$  2.0–5.0 ppm, indicating that the ligand exists in thione form rather than in the thiol form. Moreover, a new signal appears at 8.4 ppm, showing that the Schiff-base ( $\text{CH}=\text{N}$ ) mode is formed.

In the  $^{13}\text{C}$  NMR spectrum of uncoordinated ligand  $\text{C}(\text{C}=\text{S})$  atom is reported at  $\delta$  181.2 ppm, respectively. Further, in the  $^{13}\text{C}$  NMR spectra of the organotin(IV) complexes the signal of  $\text{C}(\text{C}=\text{S})$  is shifted to higher field upon complexation, as expected for a process involving deprotonation of  $\text{N}(\text{N}-\text{H})$  and a partial evolution of the thione form at  $\text{C}(\text{C}=\text{S})$  into a thiolate form [10]. A new single resonance is observed at about 154.2 ppm for the  $\text{CH}=\text{N}$  groups in the  $^{13}\text{C}$  spectra. All magnetically non-equivalent protons and carbons of the alkyl or phenyl groups attached to tin have been identified and their chemical shift values are in close agreement with the reported values [11].

The  $^{119}\text{Sn}$  NMR spectrum of complexes **1–6** in  $\text{CDCl}_3$  solution reveals two equally intense  $^{119}\text{Sn}$  resonances near  $-173.88$  and  $-190.2$  ppm, with the latter being broad, in good agreement with literature data ( $-174.4$  and  $-190.0$  ppm) [12]. These solution chemical shifts clearly favour the type, in which both the endo-cyclic tin atoms are five-coordinated and display trigonal bipyramidal geometry. While in complexes **7** and **8**, the low frequency isotropic chemical shifts near  $-298$  and  $-287$  ppm can be assigned to six-coordinate tin atoms, the high frequency ones,  $-209$  and  $-178$  ppm, can be assigned to five-coordinate tin atoms. Both are isotropic chemical shift domains, ca.  $-290$  and  $-190$  ppm. These values of  $\delta$  ( $^{119}\text{Sn}$ ) are in accordance with that reported in the literatures [13].

## 2.2. Description of crystal structures

### 2.2.1. Crystal structures of complexes **1–3** and **5**

Complexes **1–3** and **5** possess similar symmetrical  $\text{Sn}_4\text{O}_4$  ladder structures. Crystals of **1** suitable for an X-ray crystallography study were grown from moist diethyl ether. The most relevant crystallographic data for **1–3** and **5** are summarized in Section 3. Selected bond lengths and bond angles for **1–3** and **5** are given in Tables 1–4.

A perspective view of the molecular structure and unit cell of complexes **1** is shown in Figs. 1 and 2, respectively; it consists of  $\text{Sn}_4\text{O}_4$  ladders with one N atom of Schiff-base ligand coordinating to the exo tin atom. This situation is reminiscent of that in a previously reported double *O*-capped organooxotin cluster [14]. The four tin atoms and four O atoms are basically coplanar with the deviation 0.0219 Å. Each of the ladders consists of four tin centers held together by two  $\mu_3$ -oxygen atoms. According to their

Table 1  
Selected bond lengths and angles for complex **1**

Bond	Distance (Å)	Bond	Distance (Å)
O(1)–Sn(1)	1.996(4)	Sn(1)–N(1)	2.323(6)
O(1)–Sn(2)#1	2.089(4)	Sn(2)–O(1)#1	2.089(4)
O(1)–Sn(2)	2.100(4)	Sn(2)–C(10)	2.089(7)
Sn(1)–C(13)	2.099(8)	Sn(2)–C(11)	2.096(7)
Sn(1)–C(12)	2.101(7)	Sn(2)–O(2)	2.329(5)
Sn(1)–O(2)#1	2.138(5)	Sn(2)–N(2)	2.657(6)
O(2)–Sn(1)#1	2.138(5)		
Angle	Amplitude (°)	Angle	Amplitude (°)
Sn(1)–O(1)–Sn(2)#1	111.5(2)	O(1)#1–Sn(2)–O(2)	72.09(17)
Sn(1)–O(1)–Sn(2)	142.4(2)	O(1)#1–Sn(2)–N(2)	147.05(18)
Sn(2)#1–O(1)–Sn(2)	105.92(18)	O(1)–Sn(2)–N(2)	73.02(17)
O(1)–Sn(1)–O(2)#1	78.12(18)	O(2)–Sn(2)–N(2)	140.82(18)
O(1)–Sn(1)–N(1)	84.1(2)	Sn(1)#1–O(2)–Sn(2)	98.15(19)
O(2)#1–Sn(1)–N(1)	162.2(2)	O(1)–Sn(2)–O(2)	146.16(17)
O(1)#1–Sn(2)–O(1)	74.08(18)		

#1  $-x + 1, -y, -z$ .

Table 2  
Selected bond lengths and angles for complex 2

Bond	Distance (Å)	Bond	Distance (Å)
Sn(1)–O(1)	2.006(7)	Sn(2)–C(11)	2.099(13)
Sn(1)–C(8)	2.101(13)	Sn(2)–O(1)#1	2.120(8)
Sn(1)–C(9)	2.107(13)	Sn(2)–C(10)	2.134(14)
Sn(1)–O(2)	2.157(11)	Sn(2)–O(2)#1	2.332(10)
Sn(1)–N(1)	2.299(10)	O(1)–Sn(2)#1	2.120(8)
Sn(2)–O(1)	2.098(8)	O(2)–Sn(2)#1	2.332(10)
Angle	Amplitude (°)	Angle	Amplitude (°)
C(8)–Sn(1)–C(9)	132.0(6)	O(2)–Sn(1)–N(1)	160.4(4)
O(1)–Sn(1)–C(8)	114.5(5)	C(8)–Sn(1)–N(1)	92.5(5)
O(1)–Sn(1)–C(9)	113.5(5)	C(9)–Sn(1)–N(1)	92.7(5)
O(1)–Sn(1)–O(2)	75.9(4)	O(2)–Sn(2)–N(2)	140.82(18)
O(1)–Sn(1)–N(1)	84.5(3)	O(1)–Sn(2)–C(11)	98.8(5)
C(8)–Sn(1)–O(2)	95.2(6)	O(1)–Sn(2)–O(1)#1	105.8(5)
C(9)–Sn(1)–O(2)	95.5(5)	O(1)–Sn(2)–O(2)#1	144.8(4)
C(11)–Sn(2)–O(2)#1	90.5(5)	O(1)#1–Sn(2)–O(2)#1	70.1(3)
C(10)–Sn(2)–O(2)#1	87.2(5)	Sn(1)–O(1)–Sn(2)	141.1(4)
Sn(1)–O(1)–Sn(2)#1	113.6(4)	Sn(2)–O(1)–Sn(2)#1	105.3(3)
C(12)–O(2)–Sn(1)	135.6(10)	C(12)–O(2)–Sn(2)#1	120.1(10)
Sn(1)–O(2)–Sn(2)#1	100.5(4)		

#1  $-x, -y, -z + 2$ .

Table 3  
Selected bond lengths and angles for complex 3

Bond	Distance (Å)	Bond	Distance (Å)
Sn(1)–O(2)	2.014(5)	Sn(2)–C(11)	2.100(8)
Sn(1)–C(9)	2.096(9)	Sn(2)–O(2)#1	2.116(5)
Sn(1)–C(8)	2.118(9)	Sn(2)–O(3)	2.247(5)
Sn(1)–O(3)	2.132(6)	Sn(2)–O(2)	2.063(5)
Sn(1)–N(1)	2.288(7)	Sn(2)–C(10)	2.089(8)
Angle	Amplitude (°)	Angle	Amplitude (°)
O(2)–Sn(1)–C(9)	116.3(4)	C(9)–Sn(1)–N(1)	93.8(4)
O(2)–Sn(1)–C(8)	110.1(3)	C(8)–Sn(1)–N(1)	93.3(4)
C(9)–Sn(1)–C(8)	133.5(4)	O(3)–Sn(1)–N(1)	159.0(2)
O(2)–Sn(1)–O(3)	74.9(2)	O(2)–Sn(2)–C(10)	106.5(3)
C(9)–Sn(1)–O(3)	93.6(3)	O(2)–Sn(2)–C(11)	106.6(3)
C(8)–Sn(1)–O(3)	95.8(4)	C(10)–Sn(2)–C(11)	145.0(4)
O(2)–Sn(1)–N(1)	84.1(2)	O(2)–Sn(2)–O(2)#1	74.5(2)
C(10)–Sn(2)–O(2)#1	99.5(3)	C(11)–Sn(2)–O(2)#1	100.0(3)
O(2)–Sn(2)–O(3)	71.6(2)	C(10)–Sn(2)–O(3)	89.4(3)
C(11)–Sn(2)–O(3)	90.5(3)	O(2)#1–Sn(2)–O(3)	146.0(2)
C(1)–N(1)–Sn(1)	123.6(6)	N(2)–N(1)–Sn(1)	122.3(5)
Sn(1)–O(2)–Sn(2)	112.1(2)	Sn(1)–O(2)–Sn(2)#1	142.0(3)
Sn(2)–O(2)–Sn(2)#1	105.5(2)	C(12)–O(3)–Sn(1)	129.0(7)
C(12)–O(3)–Sn(2)	129.8(7)	Sn(1)–O(3)–Sn(2)	101.1(2)

#1  $-x + 1, -y + 1, -z + 1$ .

Table 4  
Selected bond lengths and angles for complex 5

Bond	Distance (Å)	Bond	Distance (Å)
Sn(1)–C(15)	2.103(11)	Sn(2)–C(17)	2.119(17)
Sn(1)–C(16)	2.107(12)	Sn(2)–N(2)#1	2.299(12)
Sn(1)–O(2)	2.115(7)	Sn(2)–N(2)	2.299(12)
Sn(1)–O(1)	2.127(7)	Sn(3)–O(2)	2.025(10)
Sn(1)–N(1)	2.447(10)	Sn(3)–C(19)	2.112(19)
Sn(1)–N(4)	2.504(9)	Sn(3)–C(20)	2.144(18)
Sn(1)–Sn(1)#1	3.275(2)	Sn(3)–N(5)#1	2.307(9)
Sn(2)–O(1)	2.020(11)	Sn(3)–N(5)	2.307(9)
Sn(2)–C(18)	2.083(19)		
Angle	Amplitude (°)	Angle	Amplitude (°)
C(15)–Sn(1)–C(16)	156.9(6)	C(16)–Sn(1)–N(1)	84.7(4)
C(15)–Sn(1)–O(2)	96.8(4)	O(2)–Sn(1)–N(1)	160.5(4)
C(16)–Sn(1)–O(2)	100.5(5)	O(1)–Sn(1)–N(1)	81.8(4)
C(15)–Sn(1)–O(1)	101.0(5)	C(15)–Sn(1)–N(4)	84.2(4)
C(16)–Sn(1)–O(1)	97.3(5)	C(16)–Sn(1)–N(4)	83.1(4)
O(2)–Sn(1)–O(1)	78.9(3)	O(2)–Sn(1)–N(4)	82.1(3)
C(15)–Sn(1)–N(1)	84.1(4)	O(1)–Sn(1)–N(4)	160.7(3)
O(1)–Sn(2)–C(18)	111.3(7)	O(1)–Sn(2)–C(17)	111.6(7)
C(18)–Sn(2)–C(17)	137.1(9)	O(2)–Sn(3)–C(19)	108.5(6)
O(1)–Sn(2)–N(2)#1	85.7(3)	O(2)–Sn(3)–C(20)	109.2(8)
C(18)–Sn(2)–N(2)#1	93.7(3)	C(19)–Sn(3)–C(20)	142.3(9)
C(17)–Sn(2)–N(2)	89.4(3)	O(2)–Sn(3)–N(5)#1	86.7(2)
N(2)#1–Sn(2)–N(2)	170.2(6)	C(19)–Sn(3)–N(5)#1	93.3(3)
C(20)–Sn(3)–N(5)	88.9(3)	Sn(2)–O(1)–Sn(1)	127.0(3)
N(5)#1–Sn(3)–N(5)	171.8(5)	Sn(2)–O(1)–Sn(1)#1	127.0(3)
Sn(1)–O(1)–Sn(1)#1	100.7(4)	Sn(3)–O(2)–Sn(1)#1	127.7(2)
Sn(3)–O(2)–Sn(1)	127.7(2)	Sn(1)#1–O(2)–Sn(1)	101.5(4)

#1  $-x + 2, -y + 1, -z + 1$  #2  $-x + 1, -y, -z$ .

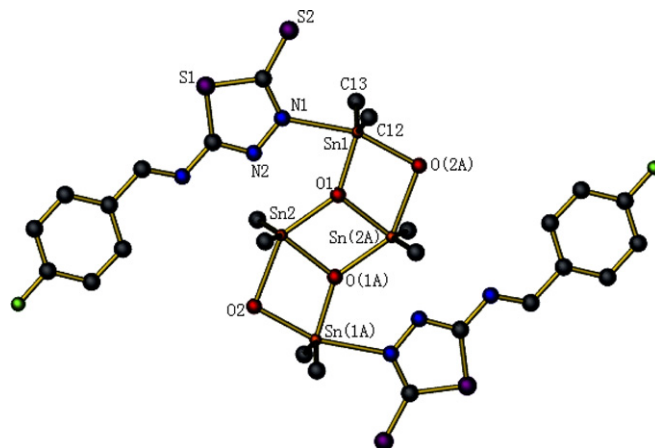


Fig. 1. Molecular structure of complex 1.

different coordination environments, the four tin atoms can be divided into two types. The four tin atoms Sn1, Sn1A, Sn2, Sn2A are each bonded to one  $\mu$ 3-oxygen atom, one  $\mu$ 2-oxygen atom, and one nitrogen atom derived from the Schiff-base ligand. All of the tin atoms are of five-coordinated distorted trigonal bipyramidal coordination environment. For Sn1, two methyl groups and one O atom occupy the equatorial position [C12, C13, O1]. The N atom from

Schiff base ligand and one O atom [N1, O2#1 (symmetry operation:  $1 - x, -y, -z$ )] lie in an apical position with the angle  $162.2(2)^\circ$  of N1–Sn1–O2#1 (symmetry operation:  $1 - x, -y, -z$ ). For Sn2, two methyl groups and one  $\mu$ 3-oxygen atom occupy the equatorial position [C10, C11, O1#1 (symmetry operation:  $1 - x, -y, -z$ )]. One

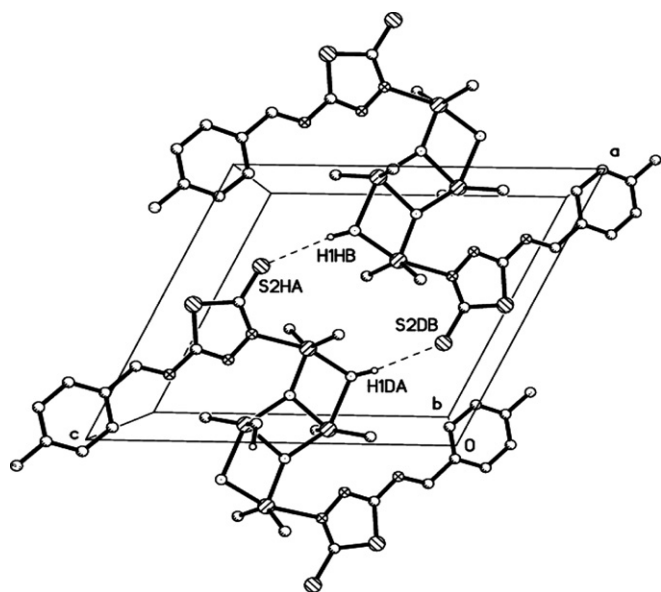


Fig. 2. The unit cell of complex **1**, forming a 12-membered macrocyclic framework via intermolecular C–H···S hydrogen bond.

$\mu$ 3-oxygen atom and one  $\mu$ 2-oxygen [O1, O2] lie in an apical position with the angle of O1–Sn2–O2 [146.16 (17)°], showing the considerable deviation from 180°. These two axis angles lie in the range 95.68° to 116.78°, suggesting apparent distortion from an ideal trigonal bipyramidal geometry. The bond length of Sn(1)–N(1) is 2.323(6) Å, approaching the sum of the covalent radii of tin and nitrogen (2.15 Å) [15], which prove that nitrogen atom coordinated to tin atom by strong covalent bonds. Con-

cerning the distance of Sn(2)–N(2) [2.657(6) Å] is midway between the sum of the van der Waals and covalent radii of Sn and N (3.75 and 2.15 Å, respectively) [15], but shorter than that reported [16] and can be regarded as weak coordination bonds. Thus the environment of Sn2 is increased to six-coordinated distorted octahedral geometries, which is similar to that in the reported complex [(C<sub>2</sub>S<sub>3</sub>N<sub>3</sub>)(CH<sub>3</sub>)<sub>6</sub>Sn<sub>3</sub>O(OH)<sub>2</sub>]·1.5H<sub>2</sub>O [16]. In addition, the C–S distance of 1.665 Å is similar to the reported C=S bond length [14]. All the above information show that the thiol form quickly tautomerizes to the thione form in the presence of diorganotin dichloride.

In Fig. 3 the supramolecular structure of complex **1** is dominated by a 1D infinite chain along *a* axis direction, which is linked by intermolecular O–H···S hydrogen bonding between hydrogen atom from  $\mu$ 2-oxygen and sulfur atom from Schiff-base moiety, giving a 12-membered ring. These rings were connected via the molecular ladder-shaped structure into a 1D chain. The distances of H1···S2 and O1···S2 are 2.818 Å and 3.714 Å, respectively, the angle of O1–H1···S2 is 170.82°, which is similar to our previously reported complex in the laboratory [16]. Moreover, in Fig. 4, the supramolecular framework in complex **1** reveals that weak intermolecular C–H··· $\pi$  stacking interaction plays important roles in the supramolecular arrangement. The C–H··· $\pi$  interaction can also be viewed as an edge-to-face (as opposed to point-to-face or T-shaped)  $\pi$ – $\pi$  interaction, and now is usually assigned to non-conventional weak hydrogen bonds [17]. The corresponding C···Cg, H···Cg, and C–H···Cg values (3.597°, 3.228°, and 104.91°) in complex **1** are close to the

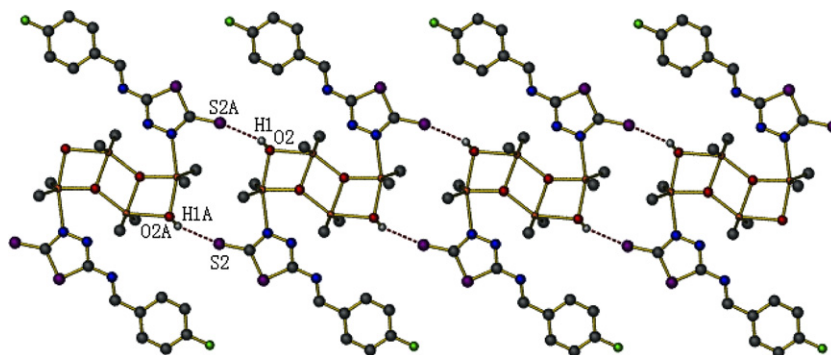


Fig. 3. The supramolecule of complex **1**, showing a 1D infinite chain framework via intermolecular O–H···N hydrogen bonding.

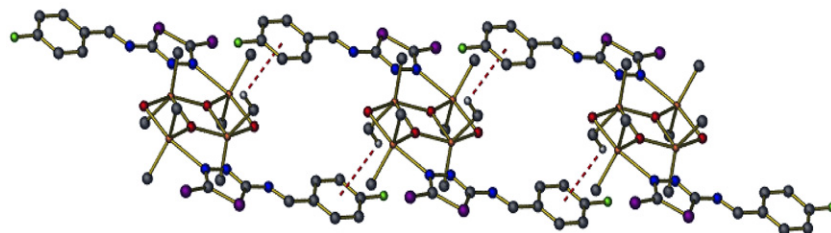


Fig. 4. The supramolecule of complex **1**, showing a 1D infinite chain framework via intermolecular C–H··· $\pi$  stacking interaction.



C–H··· $\pi$  values in the CH<sub>4</sub>/C<sub>6</sub>H<sub>6</sub> system [15], which is in good agreement with theoretical calculations that predict that C–H··· $\pi$  interactions in aliphatic/aromatic systems

are weaker than in aromatic/aromatic systems [17], thereby suggesting that they are strong enough to assemble these tetranuclear tin molecules into a 1D chain framework along *b* axis in the solid state.

For complexes **2** and **3**, the molecular structures and unit cell are shown in Figs. 5, 6, 9 and 10, respectively, the ladder-shaped structures are similar to complex **1**, the bond lengths and bond angles are listed in Table 1. Suitable crystal for X-ray diffraction was obtained by recrystallization from ethanol for **2** and methanol for **3**. The ligands are not different only in the aldehyde moiety and the amine substituent in the triazole is the same with a slight difference in bond lengths and bond angles. The bond length of Sn1–N1 is 2.299 Å for **2** and 2.288 Å for **3**, slightly shorter than that of **1** (2.323 Å), which evidences the stereo-constraints of the ligand moiety strongly affecting the coordination ability of N atom. In this situation, the stereo-constraint of Schiff-base ligand with phenyl group moiety is larger than that of furan or thiophene moiety, showing that the Sn–N bond of complexes **2** and **3** is stronger than that of complex **1**.

As shown in Figs. 8 and 11, the supramolecular structures of complexes **2** and **3** are similar to complex **1**, exhibiting an infinite 1D chain via intermolecular head-to-tail C–H···S hydrogen bonding in the direction of *a* axis, which involve the H atoms from furan or thiophene ring and the tautomerized S(C=S) atoms. The distances of C···S and H···S are 3.648 Å, 2.843 for **2** and 3.827 Å, 2.921 Å for **3**, respectively, close to that in complex **1**. The 32-membered macrocycle was formed with the C–H···S hydrogen bonding and the typical ladder-shaped tetra-organodistannoxane unit for **2** and another 18-membered ring was formed via the C–H···S hydrogen bonding for **3** with the Schiff-base ligand. Moreover, another intermolecular C–H··· $\pi$  interaction is shown in Fig. 7, involving the H atom of methyl group and the core of 5-membered triazole moiety (C1, C2, N1, N2, S1) and formed a 1D chain structure in the direction of *b* axis. The C–H atom is directed towards the symmetry related ring core. The distances of C···C<sub>g</sub> and H···C<sub>g</sub> are 3.529 and 3.028 Å, respectively, shorter than that reported in the previous literature [18], indicating that it is stronger than that found in

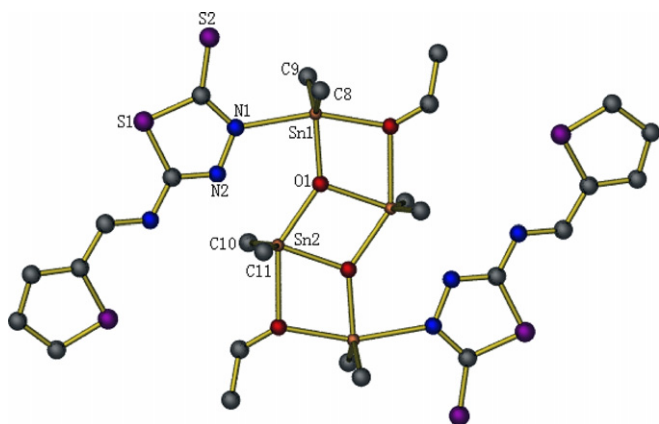


Fig. 5. The molecular structure of complex **2**.

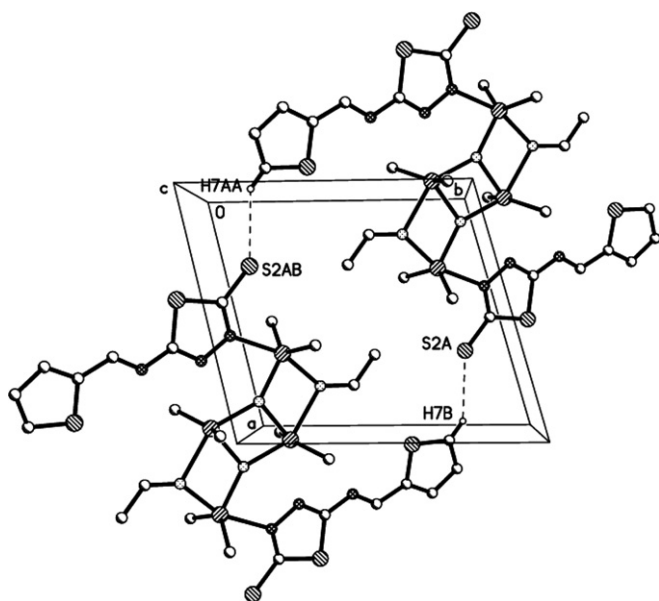


Fig. 6. The unit cell of complex **2**, forming a 34-membered macrocyclic framework via intermolecular C–H···S hydrogen bonding.

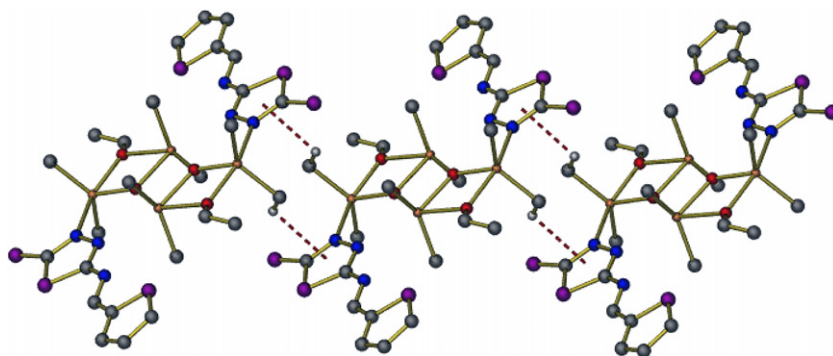


Fig. 7. The supramolecule of complex **2**, showing a 1D infinite chain framework via C–H··· $\pi$  stacking interaction.

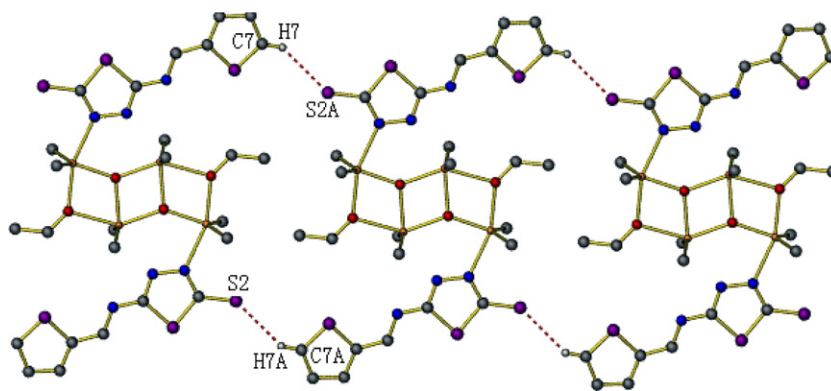


Fig. 8. The supramolecule of complex 2, showing a 1D chain framework via intermolecular C–H···S hydrogen bonding.

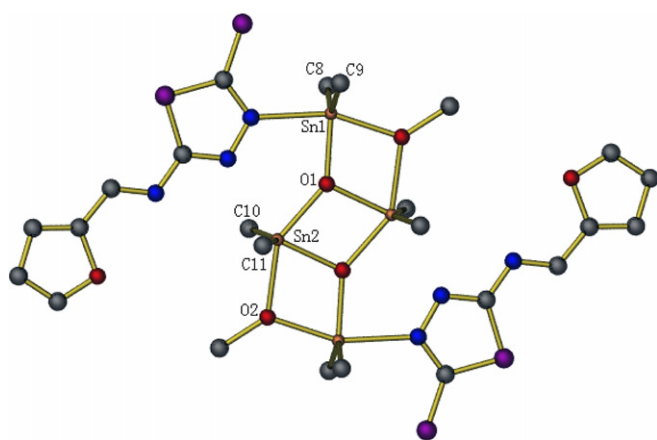


Fig. 9. Molecular structure of complex 3.

complex 1. The angle of C–H···Cg is 113.94°. So a 2D framework was formed via these intermolecular C–H···S hydrogen bonding and C–H··· $\pi$  stacking interaction in the direction of *ab* axis.

For complex 5, a perspective view of the molecular structure is shown in Fig. 12, and selected bond lengths

and bond angles are listed in Table 1. There exist twin molecules in the asymmetric unit. The average bond lengths of Sn1–N1 (2.352 Å) in one molecule that of Sn3–N4 (2.341 Å) in another molecule, which are larger than that of complexes 1–3 (2.323 Å for 1, 2.299 Å for 2, 2.288 Å for 3) due to the larger stereo-constraint of butyl groups than methyl groups from 1–3. Each tin atom exhibits a distorted trigonal bipyramidal geometry with the equatorial positions being occupied by two carbon atoms from *n*-butyl groups and three oxygen atoms, and the axial positions by two oxygen atoms for Sn1 and one N atom from triazole moiety and one  $\mu$ 2-oxygen atom.

In Fig. 13, the supramolecule of complex 5 exhibits a 1D chain structure via intermolecular C–H···S hydrogen bonds. Every pair of molecule is linked by a pair of intermolecular C–H···S hydrogen bonding with the H atom from thiophene ring and S atom from the triazole moiety. The distances of H···S and C···S are 2.983 Å and 3.844 Å, respectively, and the angle of C–H···S is 154.61° which is close to that of complex 3. Moreover, another infinite chain is stabilized by intermolecular C–H··· $\pi$  stacking interaction which is shown in Fig. 14.

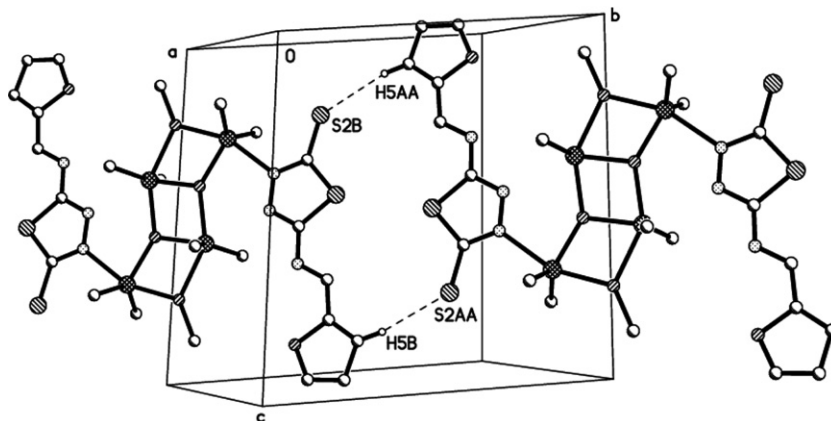


Fig. 10. The unit cell of complex 3, forming an 18-membered macrocyclic framework via intermolecular C–H···S hydrogen bonding.

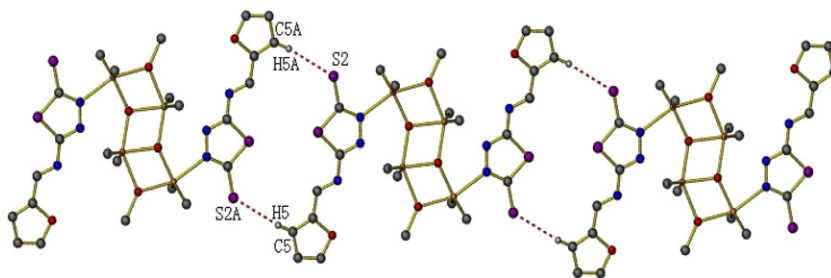


Fig. 11. The supramolecule of complex **3**, showing a 1D chain framework via intermolecular C–H···S hydrogen bonding.

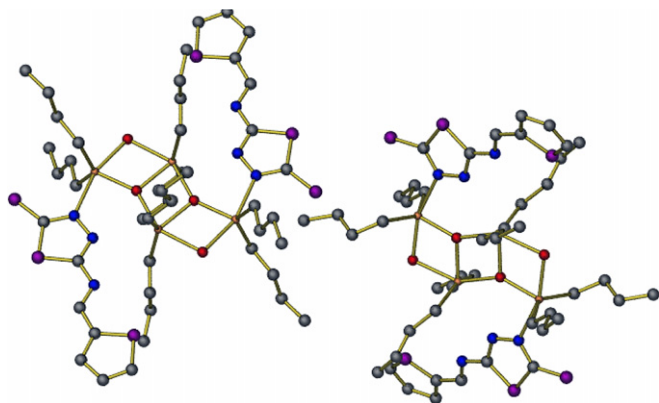


Fig. 12. The molecular structure of complex **5**.

2.2.2. Crystal structures of  $[(\text{Me}_2\text{Sn})_2\text{L}_2\text{O}]_2 \cdot \text{H}_2\text{O}$  (**7**) and  $[(\text{Me}_2\text{Sn})_2\text{L}_2\text{O}]_2 \cdot \text{CH}_3\text{OH}$  (**8**) ( $\text{L} = 4\text{-thiophenylidene-amino-1,3,4-thiadiazole-2-thione}$ )

A perspective view of the molecules of **7** and **8** is shown in Figs. 15 and 19. Selected bonds lengths and bond angles are listed in Tables 5 and 6. Complexes **7** and **8** show the

similar structure except for the different solvent molecules  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$ . Both have a tetranuclear tin moiety containing four highly axis-symmetrical units ( $\text{Me}_2\text{SnL}_2$ ) and a central  $\text{Sn}_2\text{O}_2$  unit with two  $\text{Me}_2\text{Sn}$  groups connected by bridging oxygen atoms. Each pair of exo- and endo-cyclic tin atoms is linked by an almost symmetrically bridging two N atoms from triazole moiety of the Schiff-base ligand. The four tin atoms ( $\text{Sn1}$ ,  $\text{Sn1A}$ ,  $\text{Sn2}$ ,  $\text{Sn3}$ ) are almost in planar with the slight deviation of 0.0283 Å for **7** and 0.0252 Å for **8**. Five rings, each containing two tin atoms, are present in the dimeric tetra-organodistannoxanes, the environment of  $\text{Sn}(1)$  exhibits a distorted octahedral geometry with the N atom from the triazole moiety and two  $\mu_3$ -oxygen atoms occupying the equatorial position. Two methyl groups occupied the axial apical position. The deviation from the standard octahedron environment is also confirmed by the value of the  $\text{C}(15)\text{--}\text{Sn}(1)\text{--}\text{C}(16)$  angle,  $156.9(6)^\circ$  for **7** and  $(8)\text{--}\text{Sn}(1)\text{--}\text{C}(9)$ ,  $138.2(9)^\circ$  for **8**, showing the extent of distortion from an ideal axial angle of  $180^\circ$ . The atom of  $\text{Sn}(2)$  is a five-coordinated distorted trigonal bipyramidal geometry with two methyl-C atoms and a  $\mu_3$ -oxygen atom occupying the equatorial position. Two N atoms from the triazole moiety lie in the axial apical position. The bond

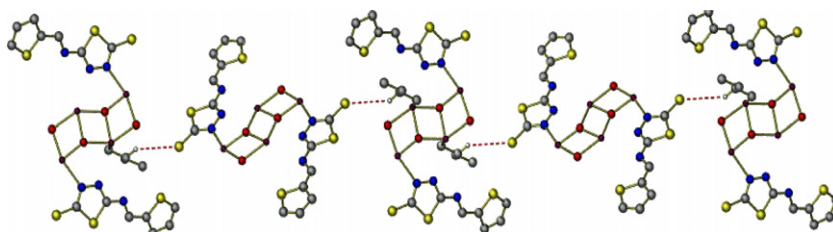


Fig. 13. The supramolecule of 1D chain structure for complex **5**, assembled by the intermolecular C–H···S hydrogen bonding.

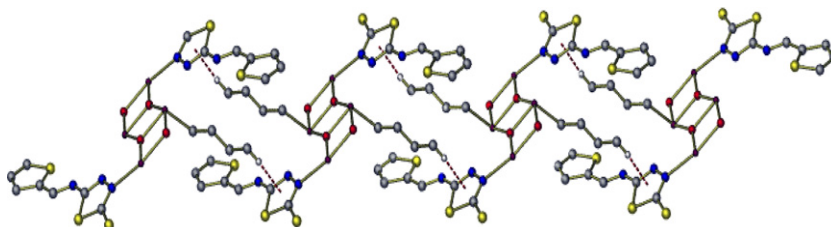


Fig. 14. The supramolecular structure of complex **5**, showing the stair-shaped 1D chain via intermolecular C–H··· $\pi$  stacking interaction.



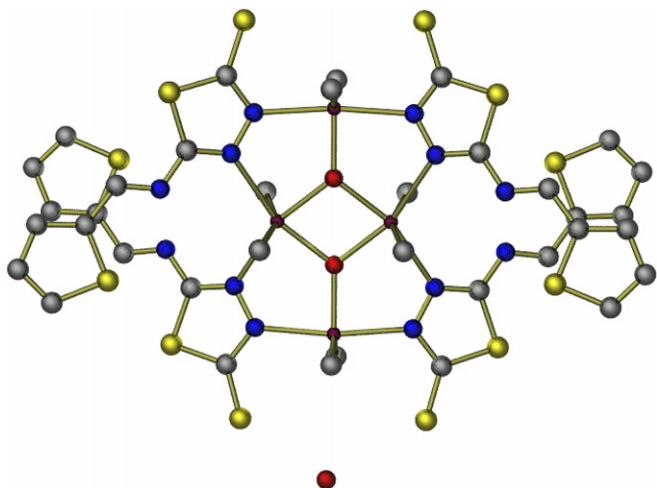


Fig. 15. Molecular structure of complex 7.

length of Sn(2)–N(2) is 2.299(12) Å for 7, basically equal to that of complex 8 (2.291(10) Å), showing a strong coordination interaction.

The supramolecule of complex 7 exhibits a 1D chain structure via intermolecular C–H···S hydrogen bonding. As shown in Fig. 16, every pair of molecules is linked by intermolecular C–H···S hydrogen bonding with the H atom from thiophene ring and S atom from the triazole moiety. The distances of H···S and C···S are 2.983 and 3.844 Å, respectively, and the angle of C–H···S is 154.61° which is close to that reported in the literature [18].

Intermolecular non-bonded S···S interactions were recognized in the crystallographic analysis of complex 7. In Fig. 17, the supramolecular structure of complex 7 shows a 2D rhombohedral grid unit representation via intermolecular non-bonded S···S interaction along *ab* directions. The distance of S···S is 3.370 Å, longer than those reported in the literature [19], but shorter than the sum of the van der Waals radii (S and S) (3.70 Å) [20]. These units are linked by intermolecular S···S interaction, as shown in Fig. 18, forming a 2D “wall-like” rhombic layer with 28-membered parallelogrammatic organotin rings in the defined plane.

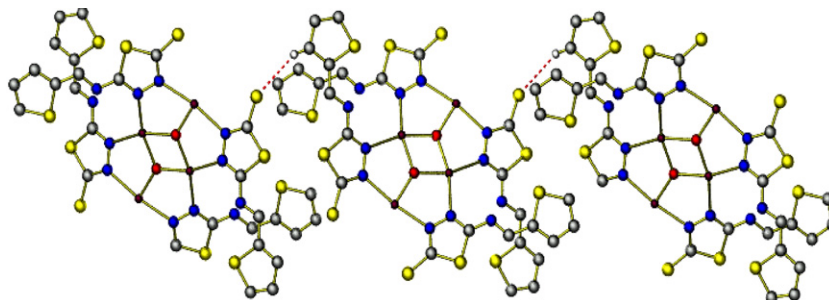


Fig. 16. The supramolecule of 1D chain structure of complex 7 is shown via intermolecular C–H···S hydrogen bonding. (The methyl groups and the solvent molecules have been omitted for clarity.)

In Fig. 20, the supramolecular framework of complex 8 is similar to that of complex 7 along *ab* axis direction. It is worth mentioning here that the disordered solvent methanol molecule resides between interplanar by the intermolecular C–H···O hydrogen bond along *c* axis direction with the O atom from the disordered methanol molecule and the H atom from the methyl group, thus giving another 3D rhombic “pseudo-channels” framework with *out-of-plane* fashion.

### 3. Experimental

#### 3.1. Materials and methods

Di-methyltin dichloride, di-*n*-butyltin dichloride and 5-amino-1,3,4-thiadiazole-2-thiol are commercially available, and they are used without further purification. The melting points were obtained with Kofler micro-melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. <sup>1</sup>H and <sup>13</sup>C NMR spectra

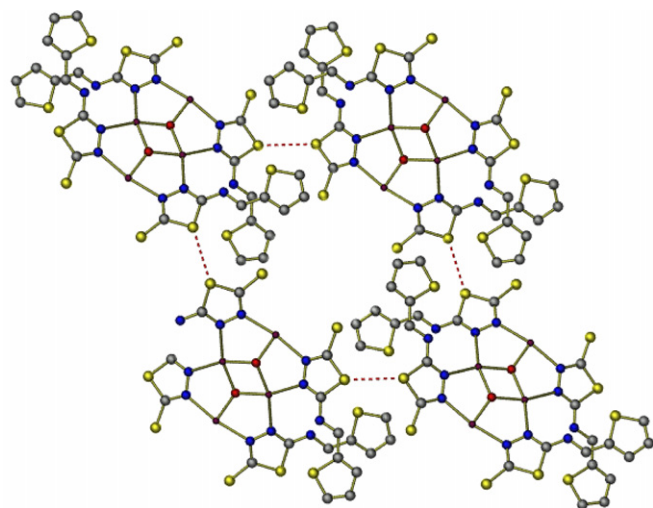


Fig. 17. The supramolecular framework of complex 7, showing rhombohedral grid unit representation via intermolecular non-bonded S···S interaction. (For clarity, the methyl groups and solvent water molecules have been deleted.)

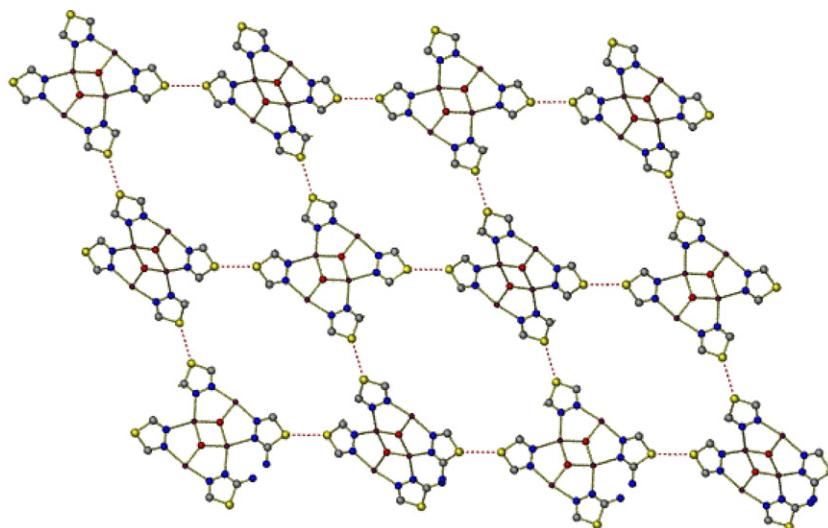


Fig. 18. The supramolecular framework of complex 7, showing a 2D rhombic diagram via intermolecular non-bonded S...S interaction. (For clarity, the methyl groups and the Schiff-base moiety have been deleted, except the triazole moiety.)

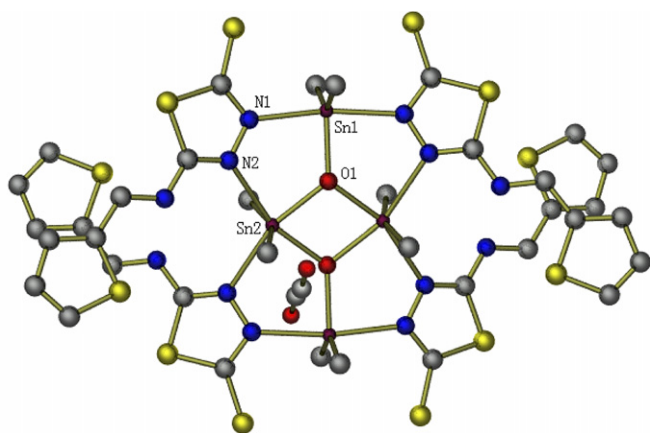


Fig. 19. The molecular structure of complex 8.

were recorded on Varian Mercury Plus 400 spectrometer operating at 400, 100.6 and 149.2 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified;  $^{13}\text{C}$  spectra are broadband proton decoupled. Elemental analyses (C,H,N) were performed with a PE-2400II apparatus.

### 3.2. Synthesis of Schiff-base ligands

#### 3.2.1. Synthesis of 4-*o*-fluorophenylideneamino-1,3,4-thiadiazole-2-thione

The reaction was carried out under nitrogen atmosphere. The 4-amino-1,3,4-thiadiazole-2-thione and 2-furaldehyde were added to the solution of ethanol (30 ml) in a Schlenk flask in the ratio of 1:1. Refluxing was continued for 8 h. After filtration the solvent was evaporated in vacuum and the residue crystallized from dichloromethane and the yellow crystals were obtained Yield: 76%. M.p. 181–183 °C. IR (KBr,  $\text{cm}^{-1}$ ): 1659 (m, C=N), 3108, 2923 (s, N–H) 2622, 2542 (m, S–H).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):

Table 5  
Selected bond lengths and bond angles for complex 7

Bond	Distance (Å)	Bond	Distance (Å)
Sn(1)–C(15)	2.103(11)	Sn(2)–C(17)	2.119(17)
Sn(1)–C(16)	2.107(12)	Sn(2)–N(2)#1	2.299(12)
Sn(1)–O(2)	2.115(7)	Sn(2)–N(2)	2.299(12)
Sn(1)–O(1)	2.127(7)	Sn(3)–O(2)	2.025(10)
Sn(1)–N(1)	2.447(10)	Sn(3)–C(19)	2.112(19)
Sn(1)–N(4)	2.504(9)	Sn(3)–C(20)	2.144(18)
Sn(1)–Sn(1)#1	3.275(2)	Sn(3)–N(5)#1	2.307(9)
Sn(2)–O(1)	2.020(11)	Sn(3)–N(5)	2.307(9)
Sn(2)–C(18)	2.083(19)		
Angle	Amplitude (°)	Angle	Amplitude (°)
C(15)–Sn(1)–C(16)	156.9(6)	C(16)–Sn(1)–N(1)	84.7(4)
C(15)–Sn(1)–O(2)	96.8(4)	O(2)–Sn(1)–N(1)	160.5(4)
C(16)–Sn(1)–O(2)	100.5(5)	O(1)–Sn(1)–N(1)	81.8(4)
C(15)–Sn(1)–O(1)	101.0(5)	C(15)–Sn(1)–N(4)	84.2(4)
C(16)–Sn(1)–O(1)	97.3(5)	C(16)–Sn(1)–N(4)	83.1(4)
O(2)–Sn(1)–O(1)	78.9(3)	O(2)–Sn(1)–N(4)	82.1(3)
C(15)–Sn(1)–N(1)	84.1(4)	O(1)–Sn(1)–N(4)	160.7(3)
O(1)–Sn(2)–C(18)	111.3(7)	O(1)–Sn(2)–C(17)	111.6(7)
C(18)–Sn(2)–C(17)	137.1(9)	O(2)–Sn(3)–C(19)	108.5(6)
O(1)–Sn(2)–N(2)#1	85.7(3)	O(2)–Sn(3)–C(20)	109.2(8)
C(18)–Sn(2)–N(2)#1	93.7(3)	C(19)–Sn(3)–C(20)	142.3(9)
C(17)–Sn(2)–N(2)	89.4(3)	O(2)–Sn(3)–N(5)#1	86.7(2)
N(2)#1–Sn(2)–N(2)	170.2(6)	C(19)–Sn(3)–N(5)#1	93.3(3)
C(20)–Sn(3)–N(5)	88.9(3)	Sn(2)–O(1)–Sn(1)	127.0(3)
N(5)#1–Sn(3)–N(5)	171.8(5)	Sn(2)–O(1)–Sn(1)#1	127.0(3)
Sn(1)–O(1)–Sn(1)#1	100.7(4)	Sn(3)–O(2)–Sn(1)#1	127.7(2)
Sn(3)–O(2)–Sn(1)	127.7(2)	Sn(1)#1–O(2)–Sn(1)	101.5(4)

#1  $x, -y + 3/2, z$ .

$\delta$  13.18 (s, 1H, N–H);  $\delta$  2.08–5.06 (s, 1H, S–H);  $\delta$  7.95–8.42 (m, 1H, CH=N);  $\delta$  6.94–7.31 (m, 4H, Ph–H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  182.1, 168.2, 163.7, 160.8, 132.7, 127.3, 115.6.

Table 6  
Selected bond lengths and bond angles for complex **8**

Bond	Distance (Å)	Distance (Å)	Bond
Sn(1)–C(8)	2.07(2)	2.07(2)	Sn(2)–C(10)
Sn(1)–C(9)	2.092(18)	2.092(18)	Sn(1)–N(1)#1
Sn(2)–O(1)#2	2.093(8)	2.093(8)	Sn(2)–C(10)#3
Sn(1)–O(1)	2.060(13)	2.060(13)	O(1)–Sn(2)#2
Sn(1)–N(1)	2.291(10)	2.291(10)	Sn(2)–O(1)
Sn(2)–N(2)	2.474(11)	2.474(11)	
Angle	Amplitude (°)	Amplitude (°)	Angle
O(1)–Sn(1)–C(8)	111.9(8)	111.9(8)	O(1)–Sn(1)–C(9)
C(8)–Sn(1)–C(9)	138.2(9)	138.2(9)	O(1)–Sn(1)–N(1)
C(8)–Sn(1)–N(1)	89.6(3)	89.6(3)	C(9)–Sn(1)–N(1)
O(1)–Sn(1)–N(1)#1	85.6(4)	85.6(4)	C(8)–Sn(1)– N(1)#1
C(9)–Sn(1)–N(1)#1	93.5(3)	93.5(3)	N(1)–Sn(1)– N(1)#1
O(1)–Sn(2)–O(1)#2	77.2(6)	77.2(6)	O(1)–Sn(2)–C(10)
O(1)#2–Sn(2)–C(10)	98.4(5)	98.4(5)	O(1)–Sn(2)– C(10)#3
C(10)–Sn(2)– C(10)#3	156.4(7)	156.4(7)	O(1)–Sn(2)–N(2)
O(1)#2–Sn(2)–N(2)	160.4(4)	160.4(4)	O(1)–Sn(2)– N(2)#3
O(1)#2–Sn(2)– N(2)#3	83.4(4)	83.4(4)	N(2)–Sn(2)– N(2)#3

#1  $-x + 1, y, z$  #2  $-x + 1, -y + 1, -z + 1$ .

#3  $x, -y + 1, -z + 1$  #4  $-x + 1, -y + 2, -z + 1$ .

### 3.2.2. Synthesis of 4-thiophenylideneamino-1,3,4-thiadiazole-2-thione

The reaction was similar to **1**. Yield: 82%. M.p. 174–178 °C. IR (KBr,  $\text{cm}^{-1}$ ): 1654 (m, C=N), 3138, 2927 (s, N–H) 2616, 2537 (m, S–H).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  13.06 (s, 1H, N–H);  $\delta$  2.01–4.80 (s, 1H, S–H);  $\delta$  7.81–8.47

(m, 1H, CH=N).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  181.7, 165.6, 162.8, 157.9, 133.6, 128.8, 119.2.

### 3.2.3. Synthesis of 4-furfuralideneamino-1,3,4-thiadiazole-2-thione

The reaction was similar to **1**. Yield: 71%. M.p. 165–168 °C. IR (KBr,  $\text{cm}^{-1}$ ): 1640 (m, C=N), 1152 (w, C=S) 3105, 2919 (s, N–H) 2618, 2538 (m, S–H).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  13.12 (s, 1H, N–H);  $\delta$  2.1–5.2 (s, 1H, S–H);  $\delta$  7.69–8.41 (m, 1H, CH=N);  $\delta$  7.58–7.74 (m, 4H, Ph–H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  185.3, 163.2, 163.1, 158.6, 131.5, 128.0, 117.6.

## 3.3. The synthesis of complexes

### 3.3.1. Synthesis of $[(\text{Me}_2\text{Sn})_2\text{O}(\text{HO})(\text{LI})]_2$ (**1**)

The reaction was carried out under a nitrogen atmosphere. HL1 (0.239 g, 1 mmol) and sodium methoxide were added to a Schlenk flask and stirred for 0.5 h. Di-methyltin dichloride (0.439 g, 2 mmol) was then added and the reaction mixture was stirred for 12 h at 40 °C. After cooling down to room temperature, it was filtered. The solvent of the filtrate was gradually removed by evaporation under vacuum until a solid product was obtained. It was then recrystallized from ether–dichloromethane. Yellow crystal was obtained. Yield: 78%. M.p. 186–188 °C. Anal. Calc. for  $\text{C}_{26}\text{H}_{36}\text{F}_2\text{N}_6\text{O}_4\text{S}_4\text{Sn}_4$ : C, 27.45; H, 3.19; N, 7.39%. Found: C, 27.11; H, 2.96; N, 7.58. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$  1641,  $\nu(\text{C}=\text{S})$  1154,  $\nu(\text{Sn}–\text{C})$  559,  $\nu(\text{Sn}–\text{O})$  449,  $\nu(\text{Sn}–\text{O}–\text{Sn})$  636.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  7.50–7.71 (m, 1H),  $\delta$  7.48–7.82 (m, 15H), 0.82 (t,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  182.2, 178.5, 157.3, 154.8, 139.5, 132.0, 123.8, 79.1, 61.2, 10.23 ( $\text{CH}_3$ ).  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  –196.5, –187.4 ppm.

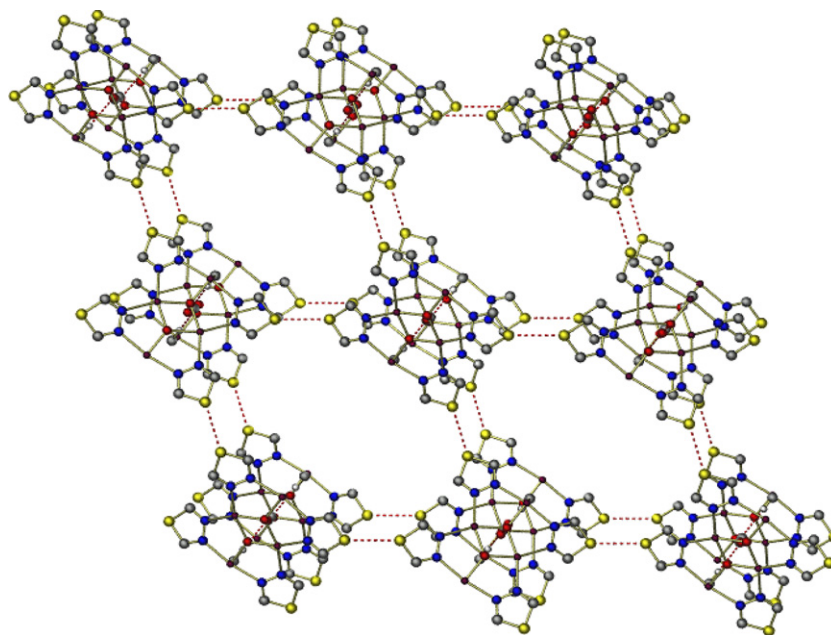


Fig. 20. The supramolecule of open framework of complex **8** exhibits a 3D “wall-like” layer, which was assembled by guest disordered methanol molecules via intermolecular C–H···O hydrogen bonding.

### 3.3.2. Synthesis of $[(Me_2Sn)_2O(EtO)(L2)]_2$ (2)

The synthesis procedure was the same as complex 1. Recrystallized from ether–dichloromethane. Yellow crystal was obtained. Yield: 82%. M.p. 178–181 °C. Anal. Calc. for  $C_{26}H_{42}N_6O_4S_6Sn_4$ : C, 26.69; H, 3.62; N, 7.18%. Found: C, 26.38; H, 3.86; N, 7.41. IR (KBr,  $cm^{-1}$ ):  $\nu(C=N)$  1638,  $\nu(C=S)$  1146,  $\nu(Sn-C)$  554,  $\nu(Sn-O)$  441,  $\nu(Sn-O-Sn)$  629.  $^1H$  NMR ( $CDCl_3$ , ppm):  $\delta$  7.50–7.71 (m, 1H),  $\delta$  7.48–7.82 (m, 15H).  $^{13}C$  NMR ( $CDCl_3$ , ppm):  $\delta$  167.2, 137.5, 136.5, 130.6, 129.4, 114.3.  $^{119}Sn$  NMR ( $CDCl_3$ ): –194.1, –186.2 ppm.

### 3.3.3. Synthesis of $[(Me_2Sn)_2O(MeO)(L3)]_2$ (3)

The synthesis procedure was the same as complex 1. Recrystallized from ether–dichloromethane. Yellow crystal was obtained. Yield: 75%. M.p. 175–177 °C. Anal. Calc. for  $C_{24}H_{38}N_6O_6S_4Sn_4$ : C, 25.98; H, 3.45; N, 7.57%. Found: C, 25.73; H, 3.71; N, 7.72. IR (KBr,  $cm^{-1}$ ):  $\nu(C=N)$  1635,  $\nu(C=S)$  1148,  $\nu(Sn-C)$  551,  $\nu(Sn-O)$  443,  $\nu(Sn-O-Sn)$  626.  $^1H$  NMR ( $CDCl_3$ , ppm):  $\delta$  7.50–7.71 (m, 1H),  $\delta$  7.48–7.82 (m, 15H).  $^{13}C$  NMR ( $CDCl_3$ , ppm):  $\delta$  166.8, 141.3, 139.2, 132.4, 130.6, 115.3, 11.5.  $^{119}Sn$  NMR ( $CDCl_3$ ): –190.4, –184.1 ppm.

### 3.3.4. Synthesis of $[n-Bu_2Sn(L1)_2O]_2$ (4)

The synthesis procedure was the same as complex 1. Recrystallized from ether–dichloromethane. Yellow crystal was obtained. Yield: 76%. M.p. 183–185 °C. Anal. Calc. for  $C_{38}H_{60}F_2N_6O_4S_4Sn_4$ : C, 34.95; H, 4.63; N, 6.43%. Found: C, 34.72; H, 4.86; N, 6.58. IR (KBr,  $cm^{-1}$ ):  $\nu(C=N)$  1644,  $\nu(C=S)$  1156,  $\nu(Sn-C)$  563,  $\nu(Sn-O)$  451,  $\nu(Sn-O-Sn)$  643.  $^1H$  NMR ( $CDCl_3$ , ppm):  $\delta$  7.50–7.71 (m, 1H),  $\delta$  7.48–7.82 (m, 15H),  $\delta$  0.921 (t, 12H, 4CH<sub>3</sub>); 1.460 (m, 8H, 4CH<sub>2</sub>); 1.891 (m, 16H, 4CH<sub>2</sub>CH<sub>2</sub>);  $^{13}C$  NMR ( $CDCl_3$ , ppm):  $\delta$  182.2, 178.5, 157.3, 154.8, 139.5, 132.0, 123.8, 79.1, 61.2, 28.7, 27.3, 26.6, 13.2 (CH<sub>3</sub>).  $^{119}Sn$  NMR ( $CDCl_3$ ): –189.6, –185.3 ppm.

### 3.3.5. Synthesis of $[n-Bu_2Sn(L2)_2O]_2$ (5)

Recrystallized from ether–dichloromethane. Yellow crystal was obtained. Yield: 74%. M.p. 187–189 °C. Anal. Calc. for  $C_{92}H_{160}N_{12}O_8S_{12}Sn_8$ : C, 38.15; H, 5.57; N, 5.80%. Found: C, 38.41; H, 5.32; N, 5.66. IR (KBr,  $cm^{-1}$ ):  $\nu(C=N)$  1641,  $\nu(C=S)$  1154,  $\nu(Sn-C)$  559,  $\nu(Sn-O)$  449,  $\nu(Sn-O-Sn)$  636.  $^1H$  NMR ( $CDCl_3$ , ppm):  $\delta$  7.50–7.71 (m, 1H),  $\delta$  7.48–7.82 (m, 15H),  $\delta$  0.889 (t, 12H, 4CH<sub>3</sub>); 1.460 (m, 8H, 4CH<sub>2</sub>); 1.891 (m, 16H, 4CH<sub>2</sub>CH<sub>2</sub>).  $^{13}C$  NMR ( $CDCl_3$ , ppm):  $\delta$  168.8, 136.4, 131.5, 130.1, 126.4, 117.7, 29.1, 27.6, 26.8, 13.6.  $^{119}Sn$  NMR ( $CDCl_3$ ): –188.5, –184.7 ppm.

### 3.3.6. Synthesis of $[n-Bu_2Sn(L3)_2O]_2$ (6)

Recrystallized from ether–dichloromethane. Yellow crystal was obtained. Yield: 77%. M.p. 190–192 °C. Anal. Calc. for  $C_{92}H_{160}N_{12}O_{16}S_8Sn_8$ : C, 27.57; H, 2.83; N, 10.72%. Found: C, 27.31; H, 2.65; N, 10.54. IR (KBr,  $cm^{-1}$ ):  $\nu(C=N)$  1641,  $\nu(C=S)$  1154,  $\nu(Sn-C)$  559,  $\nu(Sn-O)$  449,

$\nu(Sn-O-Sn)$  636.  $^1H$  NMR ( $CDCl_3$ , ppm):  $\delta$  7.48–7.75 (m, 1H),  $\delta$  7.43–7.84 (m, 15H),  $\delta$  0.910 (t, 12H, 4CH<sub>3</sub>); 1.460 (m, 8H, 4CH<sub>2</sub>); 1.891 (m, 16H, 4CH<sub>2</sub>CH<sub>2</sub>).  $^{13}C$  NMR ( $CDCl_3$ , ppm):  $\delta$  167.8, 137.1, 135.8, 131.6, 129.9, 113.9, 29.3, 27.8, 26.3, 13.9.  $^{119}Sn$  NMR ( $CDCl_3$ ): –189.2, –183.9 ppm.

### 3.3.7. Synthesis of $[(Me_2Sn)_2L_2O]_2H_2O$ (7)

The reaction was carried out under a nitrogen atmosphere. Di-methyltin dichloride (0.219 g, 1 mmol) and HL (0.227 g, 1 mmol) and KOH (0.056 g, 1 mmol) were added to water solution (30 ml) in an airtight vessel at 150 °C for 3 days. After filtration the solvent was evaporated in vacuo and the residue crystallized from dichloromethane and a yellow crystal was obtained. Yield: 68%. M.p. 194–

Table 7

Crystal data collection and structure refinement parameters of complexes 1–3 and 5

Complex	1	2	3
Empirical formula	$C_{26}H_{36}F_2N_6O_4S_4Sn_4$	$C_{26}H_{42}N_6O_4S_6Sn_4$	$C_{24}H_{38}N_6O_6S_4Sn_4$
Formula weight	1137.61	1169.78	1109.60
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	10.7986(19)	9.922(12)	8.208(3)
<i>b</i> (Å)	16.830(3)	10.707(13)	11.309(4)
<i>c</i> (Å)	11.741(2)	10.707(13)	13.002(4)
$\alpha$ (°)	90	88.01	96.989(4)
$\beta$ (°)	114.864(3)	75.173(10)	107.247(4)
$\gamma$ (°)	90	75.173(10)	110.700(4)
<i>V</i> (Å <sup>3</sup> )	4460.3(17)	1062.0(2)	1043.0(6)
<i>Z</i>	2	2	1
<i>D</i> <sub>calc</sub> (Mg m <sup>−3</sup> )	1.951	1.829	1.767
<i>F</i> (000)	1096	568	536
$\mu$ (mm <sup>−1</sup> )	2.814	2.655	1.594
Crystal size (mm)	0.19 × 0.16 × 0.14	0.37 × 0.25 × 0.20	0.49 × 0.20 × 0.08
$\theta$ Range	1.15–25.01	1.97–25.01	1.99–25.01
Index ranges	−12 ≤ <i>h</i> ≤ 10 −20 ≤ <i>k</i> ≤ 19 −13 ≤ <i>l</i> ≤ 13	−11 ≤ <i>h</i> ≤ 10 −12 ≤ <i>k</i> ≤ 8 −10 ≤ <i>l</i> ≤ 12	−8 ≤ <i>h</i> ≤ 9 −13 ≤ <i>k</i> ≤ 13 −15 ≤ <i>l</i> ≤ 13
Reflections collected	10054	5283	54701
Unique reflections [ <i>R</i> <sub>int</sub> ]	3414 [0.0448]	3593 [0.0310]	3637 [0.0225]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max./min. transmission	0.6941, 0.6170	0.6188, 0.4400	0.8186, 0.3616
Data, restraints, parameters	3414, 2, 211	3593, 44, 208	3637, 96, 199
Goodness-of-fit	1.005	1.008	1.006
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0364 <i>wR</i> <sub>2</sub> = 0.0787	<i>R</i> <sub>1</sub> = 0.0633 <i>wR</i> <sub>2</sub> = 0.1734	<i>R</i> <sub>1</sub> = 0.0432 <i>wR</i> <sub>2</sub> = 0.1123
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0723 <i>wR</i> <sub>2</sub> = 0.0994	<i>R</i> <sub>1</sub> = 0.0808 <i>wR</i> <sub>2</sub> = 0.1873	<i>R</i> <sub>1</sub> = 0.0691 <i>wR</i> <sub>2</sub> = 0.1321



196 °C. Anal. Calc. for  $C_{36}H_{44}N_{12}O_4S_{12}Sn_4$ : C, 27.57; H, 2.83; N, 10.72%. Found: C, 27.31; H, 2.65; N, 10.54. IR (KBr,  $cm^{-1}$ ):  $\nu(Sn-C)$ , 559,  $\nu(Sn-O)$ , 449,  $\nu(m, Sn-O-Sn)$  636.  $^1H$  NMR ( $CDCl_3$ , ppm):  $\delta$  7.50–7.71 (m, 1H),  $\delta$  7.48–7.82 (m, 15H).  $^{13}C$  NMR ( $CDCl_3$ , ppm):  $\delta$  166.8, 137.8, 136.8, 131.4, 130.1, 114.7, 14.3.  $^{119}Sn$  NMR ( $CDCl_3$ ):  $-288.3, -187.1$  ppm.

### 3.3.8. Synthesis of $[(Me_2Sn)_2(L2)O]_2CH_3OH$ (8)

The reaction was carried out in the same way with complex 7. It was recrystallized from methanol and a yellow crystal was obtained. Yield: 71%. M.p. 205–207 °C. Anal. Calc. for  $C_{38}H_{48}N_{12}O_4S_{12}Sn_4$ : C, 28.59; H, 3.03; N, 10.53%. Found: C, 28.31; H, 3.25; N, 10.64. IR (KBr,  $cm^{-1}$ ):  $\nu(Sn-C)$ , 563,  $\nu(Sn-O)$ , 454,  $\nu(m, Sn-O-Sn)$  624.

Table 8  
Crystal, data collection and structure refinement parameters of complexes 5, 7 and 8

Complex	5	7	8
Empirical formula	$C_{92}H_{160}N_{12}O_8S_{12}Sn_8$	$C_{36}H_{44}N_{12}O_4S_{12}Sn_4$	$C_{38}H_{48}N_{12}O_4S_{12}Sn_4$
Formula weight	2896.56	1568.31	1596.36
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$Pnma$	$P2_1/c$
<i>a</i> (Å)	11.534(2)	14.313(9)	24.270(5)
<i>b</i> (Å)	14.343(3)	24.290(14)	14.295(3)
<i>c</i> (Å)	20.496(4)	16.665(10)	16.666(3)
$\alpha$ (°)	85.784(3)	90	90
$\beta$ (°)	84.382(3)	90	90
$\gamma$ (°)	67.539(3)	90	90
<i>V</i> (Å <sup>3</sup> )	3115.9(10)	5782(2)	5782(2)
<i>Z</i>	1	4	4
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	1.544	1.798	1.834
<i>F</i> (000)	1452	3136	3136
$\mu$ (mm <sup>-1</sup> )	1.827	2.184	2.190
Crystal size (mm)	0.48 × 0.45 × 0.37	0.29 × 0.28 × 0.19	0.19 × 0.15 × 0.12
$\theta$ Range	1.92–25.01	1.48–25.01	2.06–25.01
Index ranges	$-13 \leq h \leq 10$ $-17 \leq k \leq 15$ $-24 \leq l \leq 16$	$-17 \leq h \leq 17$ $-28 \leq k \leq 28$ $-12 \leq l \leq 19$	$-26 \leq h \leq 28$ $-16 \leq k \leq 14$ $-19 \leq l \leq 19$
Reflections collected	16334	28768	14507
Unique reflections [ <i>R</i> <sub>int</sub> ]	10798 [0.0318]	5212 [0.0468]	2601 [0.1312]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max./min. transmission	0.5514, 0.4743	0.6817 and 0.5700	0.7791 and 0.6810
Data, restraints, parameters	10798, 444, 603	5212/0/322	2601/421/168
Goodness-of-fit	1.005	1.001	0.999
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0476 <i>wR</i> <sub>2</sub> = 0.1109	<i>R</i> <sub>1</sub> = 0.0529, <i>wR</i> <sub>2</sub> = 0.1592	<i>R</i> <sub>1</sub> = 0.0633, <i>wR</i> <sub>2</sub> = 0.1368
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0900 <i>wR</i> <sub>2</sub> = 0.1375	<i>R</i> <sub>1</sub> = 0.0992, <i>wR</i> <sub>2</sub> = 0.2684	<i>R</i> <sub>1</sub> = 0.1824, <i>wR</i> <sub>2</sub> = 0.1867

$^1H$  NMR ( $CDCl_3$ , ppm):  $\delta$  7.50–7.71 (m, 1H),  $\delta$  7.48–7.82 (m, 15H).  $^{13}C$  NMR ( $CDCl_3$ , ppm):  $\delta$  167.8, 138.3, 136.8, 131.2, 129.8, 113.1, 14.8.  $^{119}Sn$  NMR ( $CDCl_3$ ):  $-289.1, -191.6$  ppm.

### 3.3.9. X-ray crystallographic studies

Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Smart-1000 CCD area-detector with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). A semi-empirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXLS-97 and refined against *F*<sup>2</sup> by full matrix least squares using SHELXL-97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Tables 7 and 8.

## 4. Supplementary material

CCDC 623056, 623058, 623059, 630655, 623060 and 623057 contain the supplementary crystallographic data for 1, 2, 3, 5, 7 and 8. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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