

Synthesis and structure of a novel trinuclear 18-membered macrocycle of diphenyltin complexes with 2-mercaptionicotinic acid

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Abstract

The 18-membered stereoregular diphenyltin macrocycles: $\{\text{Ph}_2\text{Sn}[\text{S}(\text{C}_6\text{H}_3\text{NO})\text{O}]\}_3$ (**8**), $\{\text{Ph}_2\text{Sn}[\text{S}(\text{C}_6\text{H}_3\text{NO})\text{O}]\}_3 \cdot 2.67\text{H}_2\text{O}$ (**9**) and $\{\text{Ph}_2\text{Sn}[\text{S}(\text{C}_6\text{H}_3\text{NO})\text{O}]\}_3 \cdot 4\text{C}_6\text{H}_6$ (**10**) have been synthesized by the reaction of diphenyltin dichloride with 2-mercaptionicotinic acid. The three complexes were characterized by elemental, IR, ¹H-NMR analyses. The X-ray crystallography analyses of **9** and **10** were also given. Single crystal X-ray diffraction data reveal that both **9** and **10** are highly symmetrical tri-nuclear cyclic complexes with the ligand 2-mercaptionicotinic acid bridging the adjacent tin atoms. The tin environment is distorted *cis*-trigonal bipyramid. Weak interaction $\text{Sn} \cdots \text{O}$ was recognized between tin and exocyclic-oxygen atoms. The potential tridentate of endocyclic sulfur atoms make them interesting ligands.

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Keywords: Macrocycle; Organotin; 2-Mercaptionicotinic acid; Crystal structure

1. Introduction

Recently development in coordination chemistry has produces numerous macrocyclic and supramolecular complexes through appropriate coordination geometry of organometal complexes and certain organic ligands [1–9]. Among them organotin macrocycles are attracting more and more attention for their potential industrial applications and biological activities [10,11]. As reported in these metallo-macrocyclic systems, ligands with multi-coordination or donor atoms and particular stereochemistry may lead to different specific architectures. Especially those carboxylate or mercapto ligands with additional donor atoms, such as a nitrogen atom, available for coordination to Sn, have been revealed to help the construction of interesting macrocyclic structures [5]. Accordingly, it is crucial to choose linking ligands for the construction of specific topologies. In our previous work, we have reported a novel penta-tin-

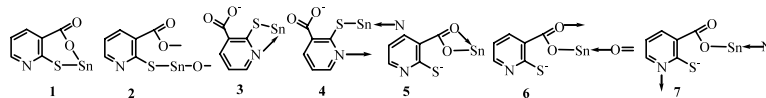
nuclear macrocycle with heterocyclic sulfur and nitrogen donor ligand [12]. To continue our research on organotin (IV) complexes, we choose another fascinating ligand: 2-mercaptionicotinic acid.

This ligand is interesting because of its potential multiplebidentate coordinate possibilities. At least seven bonding modes between ligand and tin are conceivable (Scheme 1). Chelations by both S and O atoms (mode 1) have been found in very few complexes [13,14] and chelations by S and adjacent O atoms (mode 2) are to our knowledge unknown, while S, N chelations and O, O chelations (mode 3 and mode 5) are commonly observed in dialkyltin compounds [12,15–19]. In addition, bridging between different molecules via the heterocycles (modes 4, 6 and 7) rather than chelation and/or distortion from regular geometry is possible [5,20–22].

The above considerations stir our interest in some detail synthesis, structure patterns for diorganotin derivative of the ligand. To our surprise, we obtained three complexes **8**, **9** and **10**, which belong to the same kind of trinuclear 18-member stereoregular macrocycle, by the reaction of diphenyltin dichloride with sodium salt of 2-mercaptionicotinic acid. All three complexes

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Scheme 1.

have been characterized by elemental, IR, $^1\text{H-NMR}$ analyses. Furthermore, we have characterized complexes **9** and **10** by X-ray crystallography analyses. The synthesis procedure was as in the following Scheme 2.

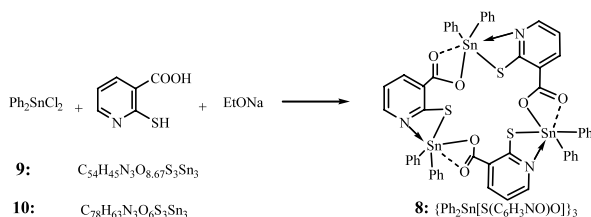
2. Experimental

2.1. Materials and measurements

Diphenyltin dichloride and 2-mercaptopyridone were commercially available, and they were used without further purification. The melting points were obtained with Kofler micro melting point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. $^1\text{H-NMR}$ spectra were obtained on a JEOL-FX-90Q NMR spectrometer, chemical shifts were given in parts per million relative to Me_4Si in CDCl_3 solvent. Elemental analyses were performed with a PE-2400II apparatus.

2.2. Synthesis of complex $\{\text{Ph}_2\text{Sn}[\text{S}(\text{C}_6\text{H}_3\text{NO})\text{O}]\}_3$ (**8**)

The reaction was carried out under nitrogen atmosphere. The diphenyltin dichloride (0.343 g, 1 mmol) was added to a mixture of 2-mercaptopyridone (0.155 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol) in dichloromethane (30 ml). The reaction mixture was stirred in a Schlenk flask for 14 h at 30°C and then filtered. The filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The solid was dried under vacuum and a kind of white powder **8** was obtained, which was then recrystallized from different solvents. Colorless block-like crystal complex **9** was formed from ethanol (95%), while another colorless block-like crystal complex **10** grew from benzene.



Scheme 2.

2.2.1. The complex **8**

Yield, 91%. M.p. $>200^\circ\text{C}$ (dec.). Anal. Calc. for $\text{C}_{51}\text{H}_{39}\text{N}_3\text{O}_6\text{S}_3\text{Sn}_3$: C, 57.43; H, 3.69; N, 3.94; S, 9.00. Found: C, 57.38; H, 3.61; N, 3.80; S, 9.29%. $^1\text{H-NMR}$ (CDCl_3 , ppm): 6.71–8.13 (m, 39H); IR (KBr, cm^{-1}): $\nu(\text{C-H})$, 3066; $\nu_{\text{as}}(\text{Sn-C})$, 270; $\nu_{\text{s}}(\text{Sn-C})$, 232; $\nu(\text{Sn-S})$, 290; $\nu(\text{Sn-N})$, 337; $\nu(\text{Sn-O})$, 587; $\nu(\text{C=N})$, 1570; $\nu(\text{C=O})$, 1642.

2.2.2. The complex **9**

M.p. $>200^\circ\text{C}$ (dec.). Anal. Calc. for $\text{C}_{54}\text{H}_{45}\text{N}_3\text{O}_{8.67}\text{S}_3\text{Sn}_3$: C, 48.88; H, 3.42; N, 3.17; S, 7.24. Found: C, 49.16; H, 3.55; N, 3.18; S, 6.99%. $^1\text{H-NMR}$ (CDCl_3 , ppm): 6.70–8.06 (m, 39H); IR (KBr, cm^{-1}): $\nu(\text{O-H})$, 3434; $\nu(\text{C-H})$, 3067; $\nu_{\text{as}}(\text{Sn-C})$, 270; $\nu_{\text{s}}(\text{Sn-C})$, 232; $\nu(\text{Sn-S})$, 290; $\nu(\text{Sn-N})$, 337; $\nu(\text{Sn-O})$, 587; $\nu(\text{C=N})$, 1577; $\nu(\text{C=O})$, 1642.

2.2.3. The complex **10**

M.p. $>200^\circ\text{C}$ (dec.). Anal. Calc. for $\text{C}_{78}\text{H}_{63}\text{N}_3\text{O}_6\text{S}_3\text{Sn}_3$: C, 58.90; H, 3.99; N, 2.64; S, 6.04. Found: C, 59.04; H, 3.71; N, 2.80; S, 5.84%. $^1\text{H-NMR}$ (CDCl_3 , ppm): 6.74–8.10 (m, 63H). IR (KBr, cm^{-1}): $\nu(\text{C-H})$, 3066; $\nu_{\text{as}}(\text{Sn-C})$, 270; $\nu_{\text{s}}(\text{Sn-C})$, 232; $\nu(\text{Sn-S})$, 290; $\nu(\text{Sn-N})$, 335; $\nu(\text{Sn-O})$, 587; $\nu(\text{C=N})$, 1564; $\nu(\text{C=O})$, 1642.

2.3. X-ray structure determination

All X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer. Criterion of observability was used for the solution and refinement. The structure was solved by direct methods and refined by a full-matrix least squares procedure based on F^2 using the SHELXL-97 program system. All data were collected at 298(2) K using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$) and the $\omega/2\theta$ scan technique, and corrected for Lorentz and polarization effects but not for absorption. All non-H atoms were included in the model at their calculated positions. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included. For the complexes **9** and **10**, the crystal structures and unit cells in crystal are shown in Figs. 1–4, respectively. Fig. 5 shows the crystal structure of the same component of complexes **9** and **10** with all co-crystallized solvent molecules omitted. Table 1 lists the crystal data and structure refinement parameters, and the selected bond distances and angles are showed in Tables 2 and 3.

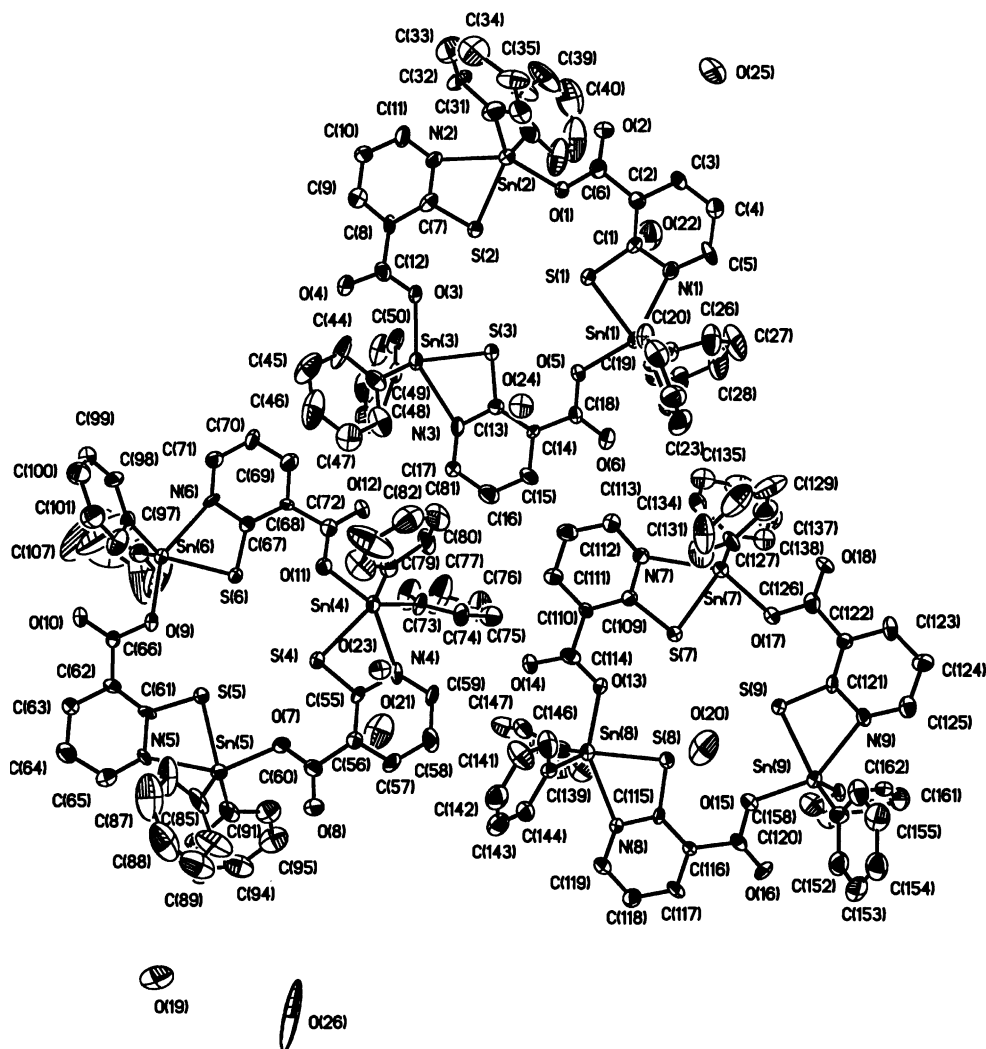


Fig. 1. Molecular structure of the complex **9**.

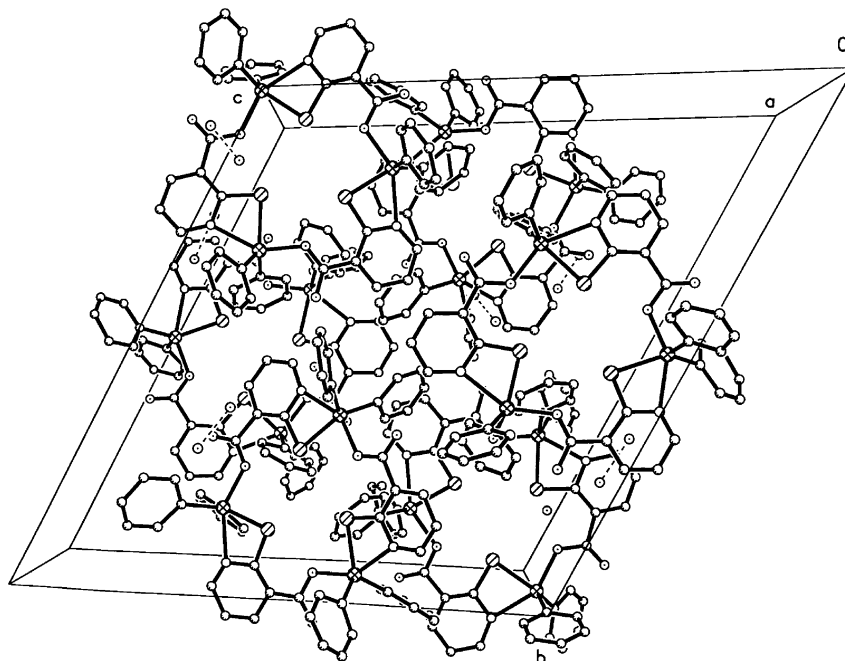
3. Results and discussion

3.1. IR data

For the three complexes **8**, **9** and **10**, there exist many common features. First, their infrared spectra are all absent of the band in the region $2500\text{--}2600\text{ cm}^{-1}$, which appears in the free ligand as $\nu(\text{S-H})$ vibration, thus indicates metal–ligand bond formation through the site. While in the far-infrared spectra, strong absorption appears at 290 cm^{-1} for all three complexes **8**, **9** and **10**, which is absent in the spectrum of the free ligand, and the value is consistent with the Sn–S stretching mode of vibration detected for a number of organotin(IV)-sulfur derivatives [23–25], so that it has been assigned to the Sn–S vibration. Second, the lowering of the C=O stretching frequency from 1681 cm^{-1} in the free ligand to 1642 cm^{-1} in all the three complexes is indicative of

C=O group weak coordination. Thus the band at 587 cm^{-1} can be assigned to Sn–O vibration. Similarly, the $\nu(\text{C=N})$ band, occurring at 1570 cm^{-1} for **8**, 1576 cm^{-1} for **9** and 1577 cm^{-1} for **10**, is considerably shifted towards lower frequencies with respect to that of the free ligand (1622 cm^{-1}), confirming the coordination of the heterocyclic N to the tin. The stretching frequency is lowered owing to the displacement of electron density from N to Sn atom, thus resulting in the weakening of the C=N bond as reported in the literature [26]. Accordingly, the weak- or medium-intensity band at 337 cm^{-1} for complexes **8** and **9**, 335 cm^{-1} for complex **10**, can be assigned to Sn–N stretching vibrations. Furthermore, medium-intensity bands at 270 and 232 cm^{-1} have been assigned to $\nu_{\text{as}}(\text{Sn-C})$ and $\nu_{\text{s}}(\text{Sn-C})$, respectively.

The only difference among spectra of the three complexes attributes to the specific vibrations of the

Fig. 2. Unit cell of the complex **9**.

co-crystallized solvent molecules. For complex **9**, a very strong-intensity band at 3434 cm^{-1} was assigned to the vibration of O–H.

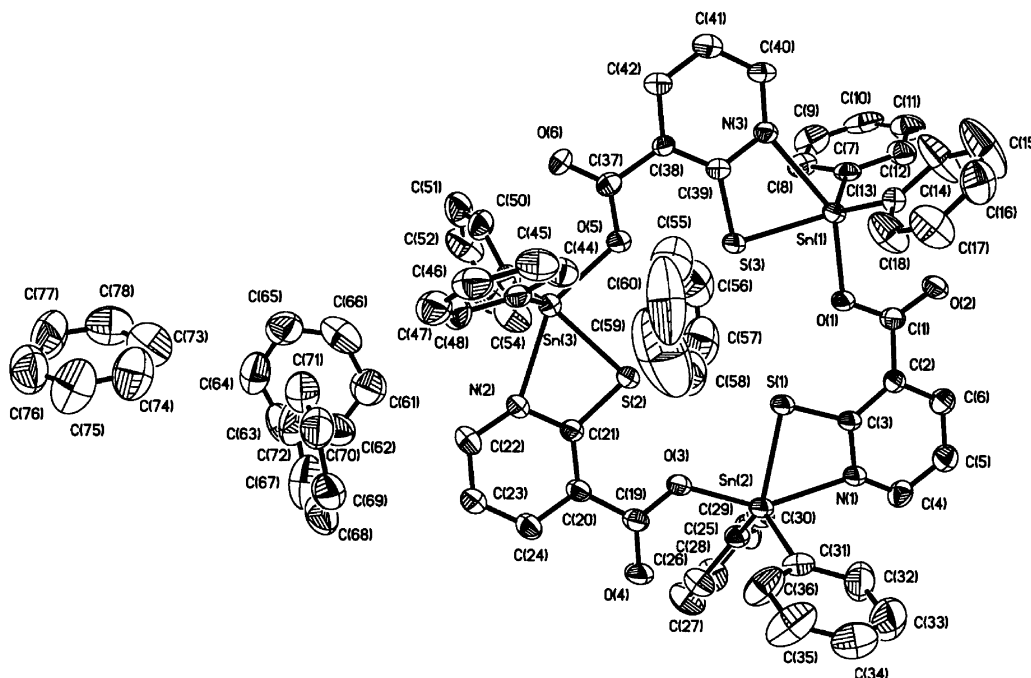
3.2. $^1\text{H-NMR}$ data

$^1\text{H-NMR}$ data showed the signal δ (1.6 ppm) of the –SH protons in the spectrum of the ligand are absent in all the three complexes **8**, **9** and **10**, indicating the removal of the SH proton and the formation of Sn–S

bond. And the –OH protons is absent for both complexes **8** and **10** but appears in complex **9**, which further proves the difference of their guest molecules. The information well accords with what the IR data have revealed.

3.3. Molecular structures

Our attempt at preparation of suitable crystal from complex **8** was unsuccessful due to the co-crystallization

Fig. 3. Molecular structure of the complex **10**.

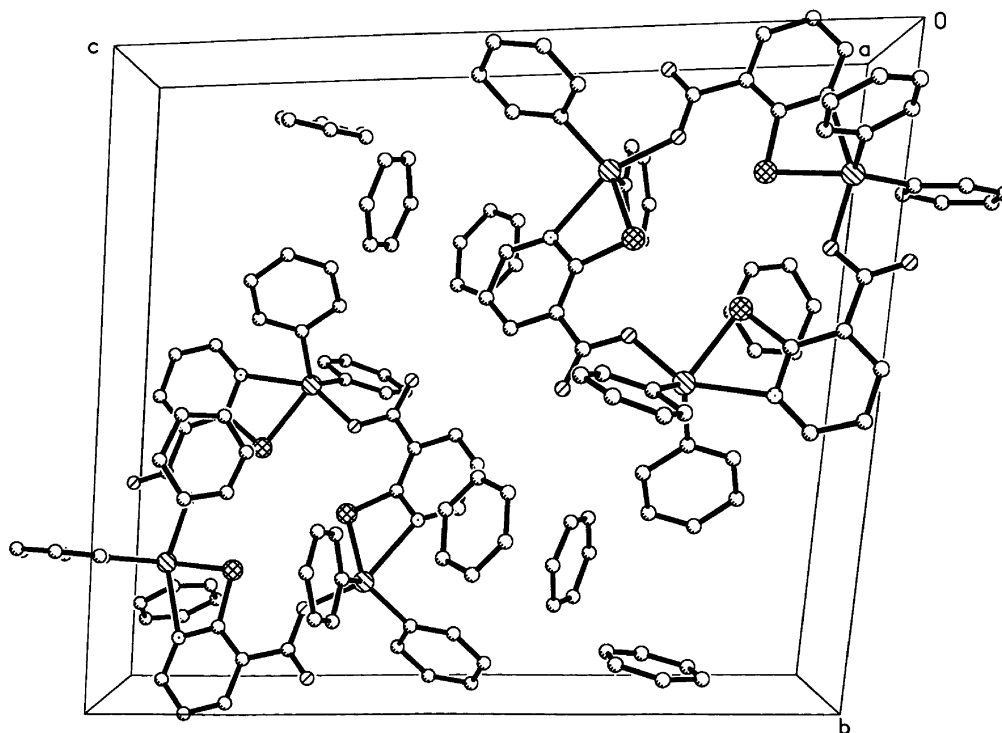


Fig. 4. Unit cell of the complex 10.

of the complex **8** and solvent molecules, so that no crystallographic information for this complex has been reported. Crystals suitable for X-ray diffraction studies of complexes **9** and **10** were obtained upon recrystallization from ethanol (95%) and benzene, respectively. When the complex **8** crystallized from 95% ethanol, it absorbed water molecules and the molar ratio of $\{\text{Ph}_2\text{Sn}[\text{S}(\text{C}_6\text{H}_3\text{NO})\text{O}]\}_3 \cdot \text{H}_2\text{O}$ is 1:2.67. And when it crystallized from benzene, it absorbed benzene molecules and the molecular ratio is 1:4. It is obvious that various solvents have a different influence on the entire crystal-topology. The selected co-crystallization may be realized by face-to-face/edge-to-face π - π interactions and aromatic $\text{C}-\text{H} \cdots \text{O}$ (for benzene) or by $\text{C}=\text{O} \cdots \text{H}$ (for H_2O) weak hydrogen-bonding interactions as reported in literature [27–29].

That different structures are found in crystal units of **9** and **10** is of interest but not unprecedented. Both complexes **9** and **10** contain the same molecular component that can be given the same molecular formula as complex **8** ($\{\text{Ph}_2\text{Sn}[\text{S}(\text{C}_6\text{H}_3\text{NO})\text{O}]\}_3$). The component ($\{\text{Ph}_2\text{Sn}[\text{S}(\text{C}_6\text{H}_3\text{NO})\text{O}]\}_3$) proved to be a highly symmetrical tri-nuclear macrocyclic complex with the ligand 2-mercaptonicotinic acid bridging the adjacent tin atoms (as shown in Fig. 5). The repeated unit is $\text{Ph}_2\text{Sn}[\text{S}(\text{C}_6\text{H}_3\text{NO})\text{O}]$, in which the primary bondings of the ligand to tin occur through its sulfur atom and endocyclic carboxyl oxygen atom (as mode **3**), while nitrogen atom of the ligand is involved in a fifth weaker bonding interaction with tin (as mode **7**).

Table 1
Crystal data and structure refinement parameters for **9** and **10**

Complexes	9	10
Empirical formula	$\text{C}_{54}\text{H}_{45}\text{N}_3\text{O}_{8.67}\text{S}_3\text{Sn}_3$	$\text{C}_{78}\text{H}_{63}\text{N}_3\text{O}_6\text{S}_3\text{Sn}_3$
Formula weight	1326.85	1590.56
Temperature (K)	293(2)	298(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
<i>a</i> (Å)	17.810(6)	9.746(5)
<i>b</i> (Å)	24.177(8)	18.603(9)
<i>c</i> (Å)	24.312(8)	20.830(11)
α (°)	60.855(5)	82.656(8)
β (°)	69.622(5)	82.111(9)
γ (°)	79.945(6)	75.248(9)
<i>V</i> (Å ³)	8571(5)	3600(3)
<i>Z</i>	6	2
<i>D</i> _{calc} (g cm ⁻³)	1.542	1.467
μ (mm ⁻¹)	1.464	1.173
<i>F</i> (0 0 0)	3944	1593
θ range (°)	1.71–26.81	1.43–26.46
Reflections collected	40 220	16 536
Independent reflections	31 806	13 227
<i>R</i> _{int}	0.0716	0.0268
Data/restraints/parameters	31 806/0/1937	13 227/0/838
Goodness-of-fit on <i>F</i> ²	0.777	0.820
Final <i>R</i> indices	<i>I</i> > 2 σ (<i>I</i>)	
<i>R</i> ₁	0.0648	0.0472
<i>wR</i> ₂	0.0903	0.0805
<i>R</i> indices (all data)		
<i>R</i> ₁	0.2172	0.1088
<i>wR</i> ₂	0.1289	0.0952
Largest difference peak and hole (e Å ⁻³)	0.956 and -1.033	0.812 and -0.328

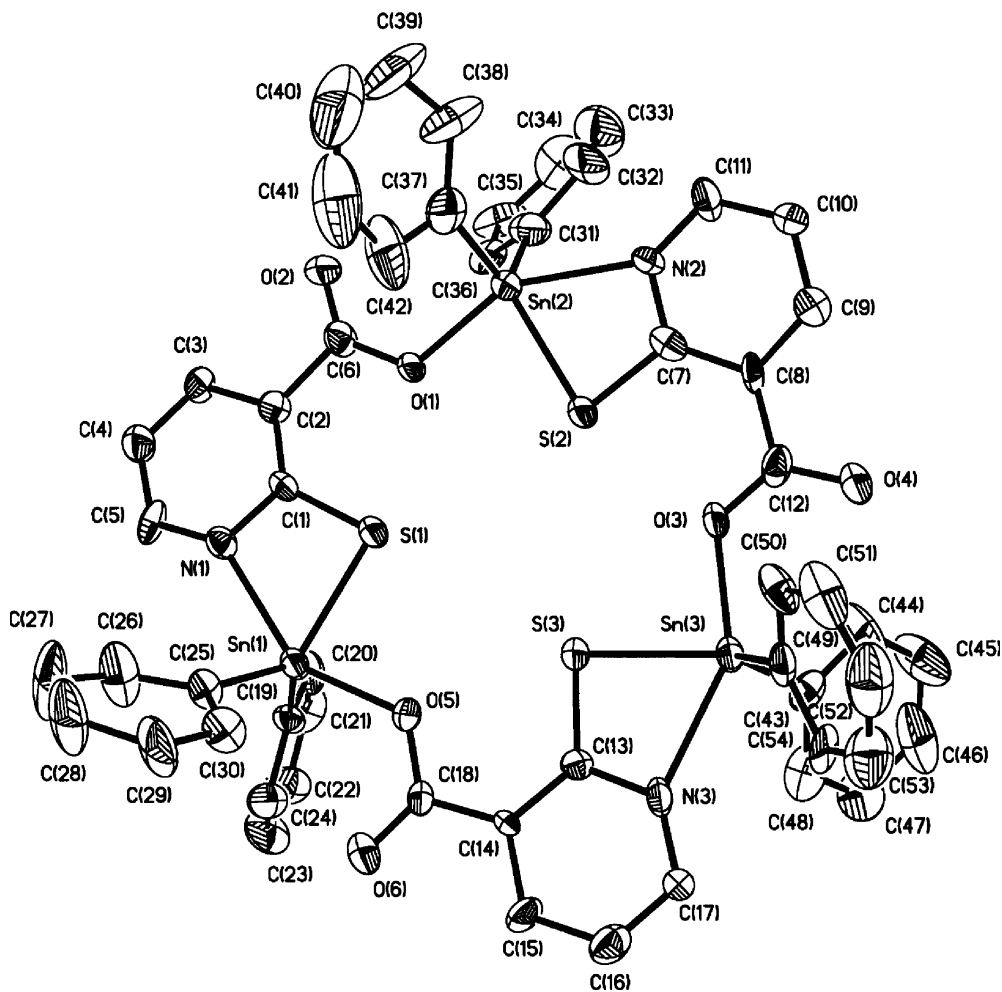


Fig. 5. The same molecular component of complexes **9** and **10** (all solvent molecules omitted).

The Sn–N bond lengths are 2.415(9) (Sn(2)–N(2)), 2.421(9) (Sn(1)–N(1)), 2.444(9) (Sn(3)–N(3)) for complex **9**, and 2.407(4) (Sn(3)–N(2)), 2.441(5) (Sn(2)–N(1)), 2.488(5) (Sn(1)–N(3)) for complex **10**. All these values lie in the range recorded in the Cambridge Crystallographic Database from 2.27 to 2.58 Å [30], slightly greater than the sum of the covalent radii of tin and nitrogen atoms (2.15 Å) but are considerably less than the van der Waals radii of the two atoms (3.75 Å) [31]. As a consequent, the geometry at tin atom becomes distorted *cis*-trigonal bipyramidal with the endocyclic oxygen and nitrogen atoms in axial sites while two phenyl carbon and sulfur atoms occupying the equatorial plane. The sum of the angles subtended at the tin atoms in the trigonal plane is a little smaller than 360° with the average value 356.4° for complex **9** and 356.7° for complex **10**. The Sn atom is slightly displaced out of the basal plane in the direction of the apical oxygen atom. The distortion is mainly due to the rigidity of 4-member chelate ring containing nitrogen atom, together with the large covalent radius of tin (IV).

The Sn–S bond lengths in complex **9** are ranging from 2.423 (3) to 2.427(3) Å and the range for complex **10** is from 2.4292 (18) to 2.4362 (17) Å. All these values are close to the sum of the covalent radii of tin and sulfur atoms (2.42 Å) [32], within the range from 2.41 to 2.48 Å that reported in triphenyltin heteroareneithiolates [33], similar to that of Ph₂SnCl(MBT) (2.48) [24] and those reported in trimeric complex [Me₃SnSCN₄Ph]₃ (2.56 Å) [34]. The Sn–O bond lengths in complex **9** rang from 2.082(6) to 2.096(7) and the range for complex **10** is from 2.074(4) to 2.113(4), both of which are similar to those reported in literature (2.00–2.12 Å) [32]. The Sn–C distances fall in a narrow range from 2.050 (11) to 2.180 (12) Å for complex **9** and from 2.106(6) to 2.141(7) Å for complex **10**, typical for organotin derivatives.

Besides, weak interaction Sn···O was recognized between tin and those exocyclic-oxygen atoms. For complex **9**, the Sn···O distances are (3.22, 3.17 and 3.27 Å for Sn(1)···O(6), Sn(2)···O(2) and Sn(3)···O(4), respectively) too long to make the weak interaction regarded as bonding interaction. The same case occurs

Table 2
Selected bond lengths (Å) and angles (°) for **9**

<i>Bond lengths</i>			
Sn(1)–O(5)	2.096(7)	Sn(1)–C(25)	2.050(11)
Sn(1)–C(19)	2.093(12)	Sn(1)–S(1)	2.427(3)
Sn(1)–N(1)	2.421(9)	Sn(2)–O(1)	2.082(6)
Sn(2)–C(37)	2.097(15)	Sn(2)–C(31)	2.170(13)
Sn(2)–S(2)	2.425(3)	Sn(2)–N(2)	2.415(9)
Sn(3)–O(3)	2.093(7)	Sn(3)–C(43)	2.085(7)
Sn(3)–C(49)	2.180(12)	Sn(3)–S(3)	2.423(3)
Sn(3)–N(3)	2.444(9)	N(1)–C(5)	1.318(11)
N(1)–C(1)	1.361(11)	N(2)–C(11)	1.336(12)
N(2)–C(7)	1.341(12)	N(3)–C(17)	1.354(12)
N(3)–C(13)	1.381(11)	S(1)··S(2)	3.842
S(2)··S(3)	3.84	S(1)··S(3)	3.83
Sn(1)··O(6)	3.22	Sn(2)··O(2)	3.17
Sn(3)··O(4)	3.27		
<i>Bond angles</i>			
O(5)–Sn(1)–C(25)	101.4(4)	O(5)–Sn(1)–C(19)	103.6(4)
C(19)–Sn(1)–C(25)	122.4(4)	O(5)–Sn(1)–S(1)	83.7(2)
C(25)–Sn(1)–S(1)	118.5(3)	C(19)–Sn(1)–S(1)	115.2(19)
O(5)–Sn(1)–N(1)	148.0(3)	C(25)–Sn(1)–N(1)	93.4(4)
C(19)–Sn(1)–N(1)	91.7(4)	S(1)–Sn(1)–N(1)	64.4(2)
O(1)–Sn(2)–C(37)	100.3(4)	O(1)–Sn(2)–C(31)	101.8(4)
C(37)–Sn(2)–C(31)	118.5(5)	O(1)–Sn(2)–S(2)	84.5(2)
C(37)–Sn(2)–S(2)	118.8(4)	C(31)–Sn(2)–S(2)	119.9(4)
O(1)–Sn(2)–N(2)	149.3(3)	C(37)–Sn(2)–N(2)	94.6(4)
C(31)–Sn(2)–N(2)	94.1(4)	S(2)–Sn(2)–N(2)	64.9(2)
C(43)–Sn(3)–O(3)	105.2(4)	C(43)–Sn(3)–C(49)	118.6(4)
O(3)–Sn(3)–C(49)	100.7(4)	C(43)–Sn(3)–N(3)	95.3(4)
O(3)–Sn(3)–N(3)	147.9(3)	C(49)–Sn(3)–N(3)	90.4(4)
C(43)–Sn(3)–S(3)	120.4(3)	O(3)–Sn(3)–S(3)	83.9(2)
C(49)–Sn(3)–S(3)	117.0(3)	N(3)–Sn(3)–S(3)	64.4(2)
C(5)–N(1)–C(1)	121.3(10)	C(5)–N(1)–Sn(1)	141.2(8)
C(1)–N(1)–Sn(1)	97.4(7)	C(11)–N(2)–C(7)	119.6(10)
C(11)–N(2)–Sn(2)	144.3(8)	C(7)–N(2)–Sn(2)	96.1(7)
C(17)–N(3)–C(13)	123.9(9)	C(13)–N(3)–Sn(3)	95.2(6)
C(17)–N(3)–Sn(3)	140.9(7)	C(6)–O(1)–Sn(2)	119.8(7)
C(12)–O(3)–Sn(3)	124.1(7)	C(18)–O(5)–Sn(1)	121.9(7)
C(1)–S(1)–Sn(1)	87.2(4)	C(7)–S(2)–Sn(2)	85.6(4)
C(13)–S(3)–Sn(3)	87.6(4)		

in complex **10**. The intermolecular Sn(1)··O(2) interaction is weak at 3.08 Å. And the values for Sn(2)··O(4) and Sn(3)··O(6) are 3.28 and 3.22 Å, respectively. These distances, while within the sum of the van der Waals radii for these atoms (3.7 Å) [35], are debatable whether or not they represent significant bonding interactions between the respective pairs of atoms.

Furthermore, we had an investigate on the distances between the three endocyclic sulfur atoms and found the separations in the complex **9** are 3.84, 3.84 and 3.83 Å for S(1)··S(2), S(2)··S(3) and S(3)··S(1), respectively. The corresponding values in the complex **10** are 3.81, 3.91 and 3.93 Å, respectively. These distances all fall in the range found in three examples of Sn(SR)₄ for which S··S (short/long) from 3.79 to 4.04 Å [31] but longer than the sum of the van der Waals radii of two sulfur atoms (3.7 Å) [36]. It does not mean some significant interaction between these atoms, however, what attracts

Table 3
Selected bond lengths (Å) and angles (°) for **10**

<i>Bond lengths</i>			
Sn(1)–O(1)	2.074(4)	Sn(1)–C(13)	2.114(6)
Sn(1)–C(7)	2.117(6)	Sn(1)–S(3)	2.4292(18)
Sn(1)–N(3)	2.488(5)	Sn(2)–O(3)	2.109(4)
Sn(2)–C(25)	2.138(6)	Sn(2)–C(31)	2.141(7)
Sn(2)–S(1)	2.4362(17)	Sn(2)–N(1)	2.441(5)
Sn(3)–O(5)	2.113(4)	Sn(3)–C(43)	2.106(6)
Sn(3)–C(49)	2.135(6)	Sn(3)–S(2)	2.4354(18)
Sn(3)–N(2)	2.407(4)	N(1)–C(3)	1.335(6)
N(1)–C(4)	1.351(7)	N(2)–C(21)	1.354(6)
N(2)–C(2)	1.367(6)	N(3)–C(40)	1.342(6)
N(3)–C(39)	1.355(6)	S(1)··S(2)	3.81
S(2)··S(3)	3.91	S(1)··S(3)	3.93
Sn(1)··O(2)	3.08	Sn(2)··O(4)	3.28
Sn(3)··O(6)	3.22		
<i>Bond angles</i>			
O(1)–Sn(1)–C(13)	102.4(2)	O(1)–Sn(1)–C(7)	104.62(18)
C(13)–Sn(1)–C(7)	121.9(2)	O(1)–Sn(1)–S(3)	82.84(11)
C(13)–Sn(1)–S(3)	114.69(17)	C(7)–Sn(1)–S(3)	119.01(19)
O(1)–Sn(1)–N(3)	146.38(14)	C(13)–Sn(1)–N(3)	93.96(19)
C(7)–Sn(1)–N(3)	90.81(19)	S(3)–Sn(1)–N(3)	63.60(10)
O(3)–Sn(2)–C(25)	101.3(2)	O(3)–Sn(2)–C(31)	101.9(2)
C(25)–Sn(2)–C(31)	123.9(2)	O(3)–Sn(2)–S(1)	83.98(11)
C(25)–Sn(2)–S(1)	118.81(17)	C(31)–Sn(2)–S(1)	113.87(17)
O(3)–Sn(2)–N(1)	147.94(15)	C(25)–Sn(2)–N(1)	92.5(2)
C(31)–Sn(2)–N(1)	93.8(2)	S(1)–Sn(2)–N(1)	64.06(12)
C(43)–Sn(3)–O(5)	98.7(2)	C(43)–Sn(3)–C(49)	128.1(2)
O(5)–Sn(3)–C(49)	99.39(19)	C(43)–Sn(3)–N(2)	94.06(19)
O(5)–Sn(3)–N(2)	149.98(16)	C(49)–Sn(3)–N(2)	93.8(2)
C(43)–Sn(3)–S(2)	115.40(16)	O(5)–Sn(3)–S(2)	85.35(11)
C(49)–Sn(3)–S(2)	114.3(2)	N(2)–Sn(3)–S(2)	64.63(12)
C(3)–N(1)–C(4)	120.8(5)	C(3)–N(1)–Sn(2)	96.5(3)
C(4)–N(1)–Sn(2)	142.5(4)	C(21)–N(2)–C(22)	121.1(5)
C(21)–N(2)–Sn(3)	97.2(3)	C(22)–N(2)–Sn(3)	141.7(4)
C(40)–N(3)–C(39)	121.1(5)	C(40)–N(3)–Sn(1)	143.2(4)
C(39)–N(3)–Sn(1)	95.7(3)	C(1)–O(1)–Sn(1)	118.7(3)
C(19)–O(3)–Sn(2)	125.5(4)	C(37)–O(5)–Sn(3)	122.5(4)
C(3)–S(1)–Sn(2)	86.41(18)	C(21)–S(2)–Sn(3)	86.2(2)
C(39)–S(3)–Sn(1)	88.14(18)		

us is the center cavity formed in these macrocycles and the potential coordination function of the endocyclic sulfur atoms similar as crown thioether [37]. Out of consideration for molecular design, complex **8** may be regarded as a potential ligand for the recognition of special molecules.

4. Supplementary material

Atomic coordinates, thermal parameters and bond lengths and angles for complexes **9** and **10** have been deposited at the Cambridge Crystallographic Data Center (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference numbers CCDC 192513 and CCDC 200316. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union

Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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