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Syntheses and crystal structures of di- and triorganotin derivatives with 2,5-dimercapto-1,3,4-thiodiazole

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Abstract

A series of organotin(IV) complexes with 2,5-dimercapto-1, 3, 4-thiodiazole (HHdmt) of the type $(R_nSnCl_m)_2(dmt)$ ($m = 0$, $n = 3$, R = Ph **1**, $PhCH_2$ **2**, *n*-Bu 3; $m = 1$, $n = 2$, R = Ph **4**) and $[R_2Sn(dmt) \cdot L]_n$ ($L = 0.5C_6H_6$, $R = CH_3$ **5**; $L = 0$, $n = 5$, R = *n*-Bu **6**) have been synthesized. All complexes 1–6 were characterized by elemental analysis, IR, ^1H and ^{13}C NMR spectra. And except for **3**, complexes **1**, **2**, **4**, **5** and **6** were also determined by X-ray crystallography. The tin atoms of complexes **1**, **2**, **3** and **4** are all five-coordinated. The geometries at tin atoms of **1**, **2**, **3** and **4** are distorted trigonal bipyramidal. The tin atoms of complexes **5** and **6** are six-coordinated and their geometries are distorted octahedral.

Keywords: Organotin(IV) compounds; 2,5-Dimercapto-1,3,4-thiodiazole; Tautomer; Bonding mode

1. Introduction

Increasing investigation of organotin(IV) complexes has been focused on acquiring well-defined solid-state structures to learn the nature of their versatile bonding modes [1], especially that of some organotin(IV) derivatives from heterocyclic thionates [2–5]. Heterocyclic thionates are ligands derived from heterocyclic thiones that contain at least one deprotonated heterocyclic thioamide group $(N–C–S)^-$ and can act as monodentate, chelating and bridging ligands. The aforementioned systems have been extensively studied in the field of coordination chemistry [6]. In our previous work, we studied the ligand 2-mercaptonicotinic acid (Hmnc), which possesses one deprotonated heterocyclic thioamide group $(N–C–S)^-$, and found that the primary bond of the ligand to tin atoms occurs through sulfur but not through nitrogen sites. Moreover, different coordination patterns of the ligand in the thiolic form have been found [7,8].

To continue our study in this field, we chose another ligand: 2,5-dimercapto-1,3,4-thiodiazole (HHdmt), which possesses a more complex deprotonated heterocyclic thoamide group $(S–C–N–N–C–S)^{2-}$ than Hmnc. The heterocycle of HHdmt, with four available donors all of which can be utilized in bonding in varying combinations, may act as a fulcrum about which lattice construction is orghestrated in two or more dimensions. In this paper, we reported the syntheses, crystal and molecular structures of the related organotin derivatives **1**–**6**, which exhibit versatile structures, based upon different coordination modes of HHdmt (Scheme 1).

All complexes **1**–**6** were characterized by elemental analysis, IR, ^1H and ^{13}C NMR spectra. And except for **3**, complexes **1**, **2**, **4**, **5** and **6** were furthermore determined by X-ray crystallography, among which the crystal structure of **6** has been discussed in our previous report [9]. It is worth to note that the coordinates of HHdmt in complexes **1**, **2**, **4** and **6** are through two sulfur atoms via its thiol (**a**), not thione (**b**) tautomer, while in complex **5** the primary bond of the ligand to tin atoms occurs through one sulfur and one nitrogen atoms and the coordination pattern of HHdmt in this reaction is found in the transitional form (**c**) (Scheme 2).

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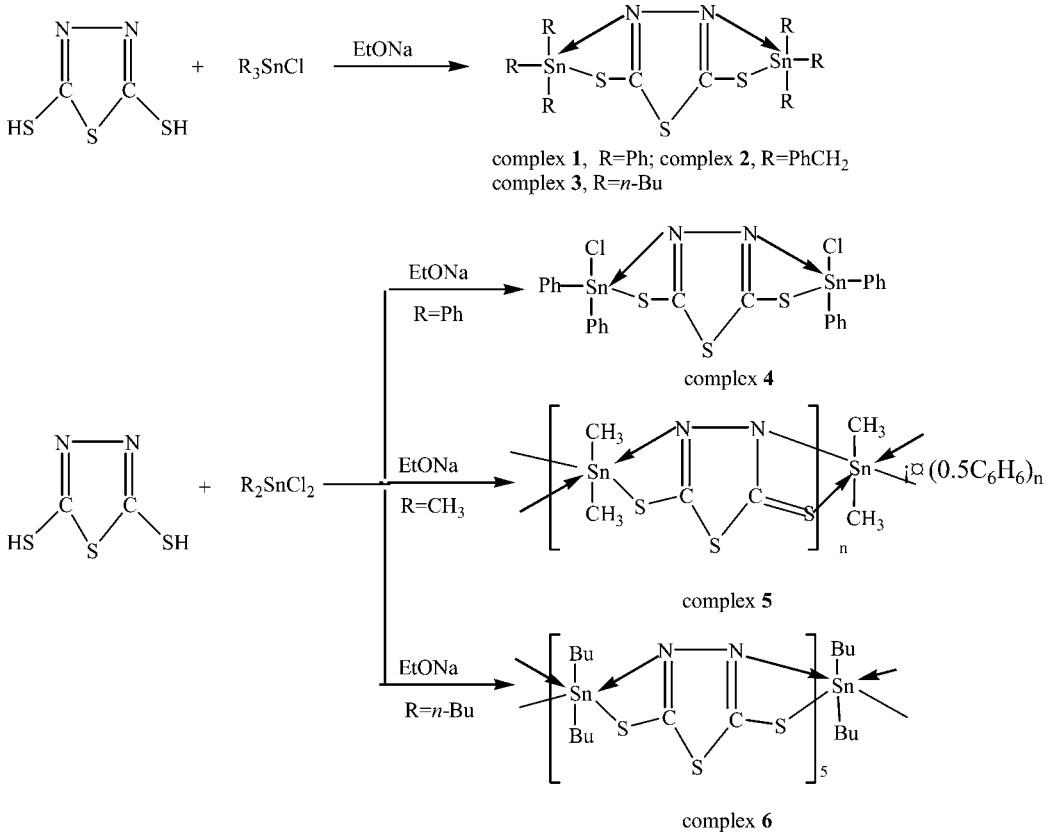
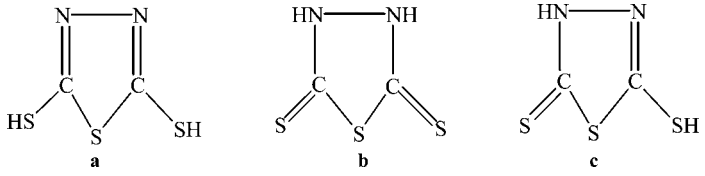


Scheme 1.



Scheme 2. The possible tautomers of HHdmt.

2. Results and discussion

2.1. Synthetic aspects and spectra

We synthesized a series of organotin(IV) complexes with 2,5-dimercapto-1,3,4-thiodiazole (HHdmt) of the type $(R_nSnCl_m)_2(dmt)$ ($m = 0$, $n = 3$, R = Ph **1**, $PhCH_2$ **2**, *n*-Bu **3**; $m = 1$, $n = 2$, R = Ph **4**) and $[R_2Sn(dmt)\cdot L]_n$ ($L = 0.5C_6H_6$, $R = CH_3$ **5**; $L = 0$, $n = 5$, R = *n*-Bu **6**), the details of synthetic experiments were shown in Table 1. Among them, complexes **1**–**4** are dinuclear complexes, complex **5** is a one-dimensional chain, while complex **6** is a pentanuclear macrocyclic complex as reported in our previous work [9]. As shown in Table 1, triorganotin

Table 1
The details of synthetic experiments of complexes **1–6**

Complexes	R_mSnCl_n	R_mSnCl_n: HHdmt:EtONa	Products
1	Ph_3SnCl	2:1:2	$Ph_3Sn(S–C_2SN_2–S)SnPh_3$
2	$(PhCH_2)_3SnCl$	2:1:2	$(PhCH_2)_3Sn(S–C_2SN_2–S)Sn(PhCH_2)_3$
3	$(n\text{-}Bu)_3SnCl$	2:1:2	$(n\text{-}Bu)_3Sn(S–C_2SN_2–S)Sn(n\text{-}Bu)_3$
4	Ph_2SnCl_2	2:1:2	$Ph_2ClSn(S–C_2SN_2–S)SnClPh_2$
		1:1:2	$Ph_2ClSn(S–C_2SN_2–S)SnClPh_2$
5	$(CH_3)_2SnCl_2$	1:1:2	$[(CH_3)_2Sn(S–C_2SN_2–S)]_n$
6	$(n\text{-}Bu)_2SnCl_2$	1:1:2	$[(n\text{-}Bu)_2Sn(S–C_2SN_2–S)]_5$

derivatives from HHdmt are all 2:1 (R_3SnCl:HHdmt) products which can be given the common formula as $R_3Sn(S–C_2SN_2–S)SnR_3$ (R = Ph **1**, $PhCH_2$ **2**, *n*-Bu **3**). In contrast, diorganotin derivatives from HHdmt are more complex. Generally, they are apt to form 1:1 products as the cases in both complexes **5** and **6**. However, complex **4** is an exception. We obtained the same product: $Ph_2ClSn(S–C_2SN_2–S)SnClPh_2$ as 2:1 product with only one chlorine atom of Ph_2SnCl_2 replaced despite using 1:1 molar ratio of Ph_2SnCl_2:HHdmt. The result suggested that the spatial resistances from two phenyl groups are strong enough to prevent another ligand's chelating to the central tin atom. This conclusion is well consistent with the sequence of stereo-constraints, phenyl > *n*-butyl > methyl, the larger the stereo-constraint of R groups, the more difficult the substituent for chlorine atoms [10].

The IR spectra show that the strong absorption at 2650 cm^{-1} in free ligand due to the –SH group is absent in spectra of all six complexes **1**–**6**, while new absorption appears in 315–321 cm^{-1} region. All these values are located within the range for Sn–S vibration observed in common organotin derivatives of thiolate (300–400 cm^{-1}) [11,12], consequently, they can be assigned to *v*(Sn–S). The *v*(Sn–Cl) absorption at 277 cm^{-1} in complex **4** is close to those found in 2-mercapto-6-nitrobenzothiazolyl diphenyltin chloride (266 cm^{-1}) and trichloromethyl-bis(imidazole)tin · H_2O (275 cm^{-1}) [13,14], but is lowered by some 100 cm^{-1} compared to the $\nu_{as,s}$(Sn–Cl) at about 355 cm^{-1} in the spectra of Ph_2SnCl_2[15], which suggests the incomplete substituent of chlorine atoms of Ph_2SnCl_2. The middle intensity bands observed at 1635 cm^{-1} in the spectra of complexes **1**, **2**, **3**, **4** and **6** have been assignable to *v*(C=N) according to literatures [16–18], which suggested the coordinates of dmt to in these complexes is through sulfur atoms via thiol tautomer **a**. Furthermore, the absorption at 1210 cm^{-1} and that at 1635 $cm^{-1}$for complex **5** have been assigned to *v*(C=S) and *v*(C=N), respectively, and their existences indicate that the primarily bonds of the dmt to tin atoms are through one sulfur and one nitrogen sites via transitional form **c**, just as literatures reported [19,20].

In the ^{13}C NMR spectra of all six complexes **1–6**, chemical shifts are quite similar to those of the parent ligand. Only a shift in the positions of two carbon atoms in the deprotonated group $(S–C–N–N–C–S)^{2-}$ of HHdmt are seen, which may be due to the deshielding of the two carbon atoms upon deprotonation of the thiol group and coordination through sulfur atom [21]. The data of complex **5** reflect the differences between thiol-C and thione-C atoms. The thiol-to-thione evolution is responsible for the marked deshielding of thione-C.

2.2. Description of crystal structures

2.2.1. $Ph_3Sn(S–C_2SN_2–S)SnPh_3$ (**1**) and $(PhCH_2)_3Sn(S–C_2SN_2–S)Sn(CH_2Ph)_3$ (**2**)

Selected bond lengths and bond angles for **1** and **2** are given in Table 2 and their molecular structures are shown in Figs. 1 and 2, respectively.

As exhibited in Figs. 1 and 2, both complexes **1** and **2** are dinuclear complexes and the dmt group functions as tetradentate. With rigid symmetry, the two thiol-S atoms and two azole-N atoms of HHdmt bond to different tin atoms. There exists crystallographic two-fold axe in both the compounds **1** and **2**. Thus, two Sn–S, Sn–N bonds are identical, respectively, due to the symmetric operation.

For complex **1**, the two Sn–S bond lengths (2.467(2) Å) lie toward the middle of the range reported for tri-

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **1** and **2**

Complex **1**		Complex **2**	
Sn(1)–C(14)	2.108(6)	Sn(1)–C(9)	2.138(7)
Sn(1)–C(8)	2.116(5)	Sn(1)–C(2)	2.157(6)
Sn(1)–C(2)	2.123(6)	Sn(1)–C(16)	2.172(6)
Sn(1)–S(2)	2.467(2)	Sn(1)–S(2)	2.489(2)
Sn(1)–N(1)	2.987(7)	Sn(1)–N(1)	2.858(5)
N(1)–C(1)	1.287(5)	N(1)–C(1)	1.294(6)
N(1)–N(1A)	1.380(8)	N(1)–N(1A)	1.360(9)
S(1)–C(1)	1.733(5)	S(1)–C(1)	1.736(6)
S(2)–C(1)	1.739(6)	S(2)–C(1)	1.740(6)
C(14)–Sn(1)–C(8)	110.3(2)	C(9)–Sn(1)–C(2)	111.8(3)
C(14)–Sn(1)–C(2)	107.2(2)	C(9)–Sn(1)–C(16)	107.3(2)
C(8)–Sn(1)–C(2)	115.1(2)	C(2)–Sn(1)–C(16)	123.0(2)
C(14)–Sn(1)–S(2)	98.86(18)	C(9)–Sn(1)–S(2)	102.90(19)
C(8)–Sn(1)–S(2)	106.40(16)	C(2)–Sn(1)–S(2)	104.84(18)
C(2)–Sn(1)–S(2)	117.69(15)	C(16)–Sn(1)–S(2)	104.98(17)
C(14)–Sn(1)–N(1)	156.13(3)	C(9)–Sn(1)–N(1)	161.9(2)
C(8)–Sn(1)–N(1)	83.65(5)	C(2)–Sn(1)–N(1)	78.2(2)
C(2)–Sn(1)–N(1)	82.38(2)	C(16)–Sn(1)–N(1)	77.13(19)
S(2)–Sn(1)–N(1)	24.23(3)	S(2)–Sn(1)–N(1)	59.19(9)

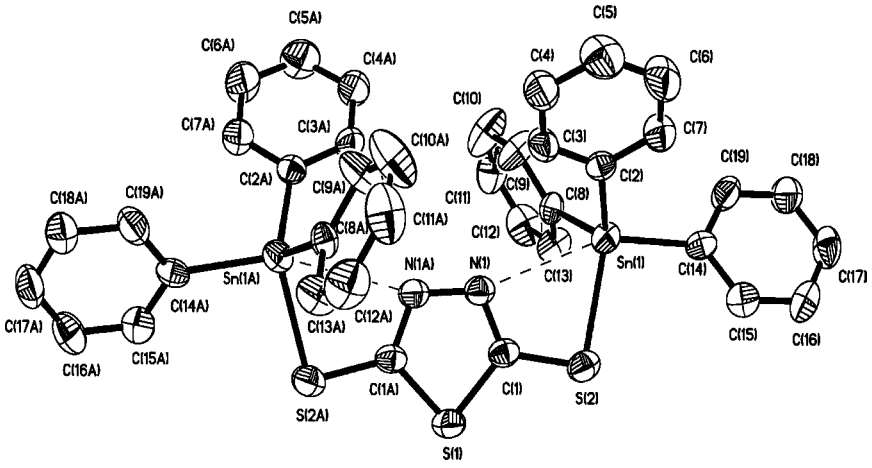


Fig. 1. Molecular structure of complex **1**.

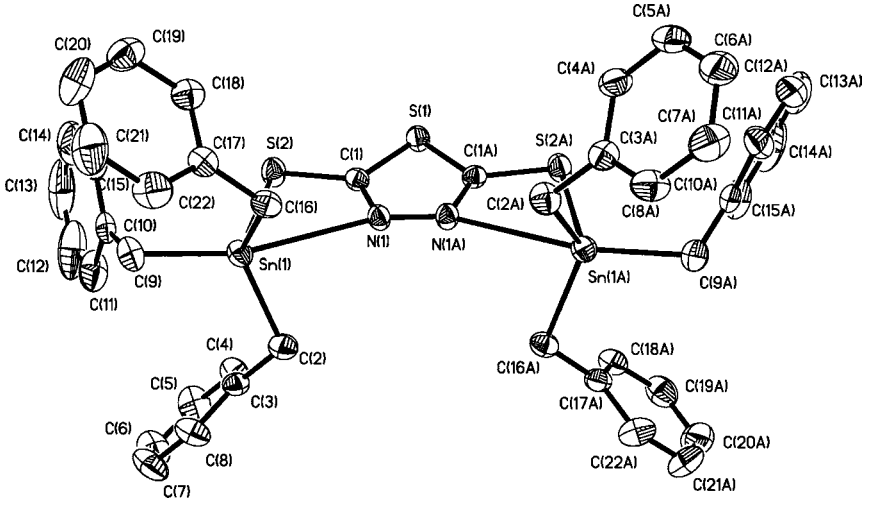


Fig. 2. Molecular structure of complex **2**.

phenyltin heteroarenethiolates (2.405–2.481 Å) and approach the sum of the covalent radii of tin and sulfur (2.42 Å) [22,23]. Besides, there exist intramolecular Sn–N interactions, common observed in triphenyltin heteroarenethiolates [24]. The distance of two Sn–N bonds (2.95(5) Å) are midway between the sums of the van der Waals radii and covalent radii of tin and nitrogen (2.15–3.74 Å) [25] and can be regarded as weak coordination bonds. All above information suggests that the primary bonds of the HHdmt to tin atoms are through sulfur atoms via its thiol tautomer **a**. The same coordination mode occurs in complex **2**. But what is different between complexes **1** and **2** lies in that the Sn–S and the Sn–N bond lengths are average at 2.489(2) and 2.858(5) Å, respectively, with the former longer and the latter shorter than the corresponding values in complex **1**. Such differences in bond lengths may attribute to the fact that the stereo-constraints of $PhCH_2$-groups are smaller than that of Ph-groups. Consequently, it can be concluded that the decrease of stereo-constraints may benefit the coordination of nitrogen atoms.

The C–S bond distances of complexes **1** and **2** (1.739(6) and 1.740(6) Å) are consistent with C–S single bond (1.730 Å) in triphenyltin derivatives with thiolate ligands [24], which indicates C–S existing as single bond and further proves indirectly the HHdmt bonding to tin atoms via thiol isomer **a**, which keeps accordance with the result from the IR spectral data.

Including the tin–nitrogen interactions, the geometry at tin atoms in both complexes **1** and **2** become distorted *cis*-trigonal bipyramidal with the axial-tin-axial angles N(1)–Sn(1)–C(14) of 157.4(4)° for complex **1** and N(1)–Sn(1)–C(9) of 161.9(2)° for complex **2**.

2.2.2. $Ph_2ClSn(S–C_2SN_2–S)SnClPh_2$ (**4**) and $\{[(CH_3)_2Sn(S–C_2SN_2–S)]\cdot 0.5C_6H_6\}_n$ (**5**)

Selected bond lengths and bond angles for **4** and **5** are given in Table 3 and the molecular structures of **4** and **5**

Table 3
Selected bond lengths (Å) and bond angles (°) for **4** and **5**

Complex **4**		Complex **5**			
Molecule A		Molecule B			
Sn(3)–C(29)	2.065(11)	Sn(1)–C(3)	2.122(9)	Sn(1)–C(3)	2.093(7)
Sn(3)–C(35)	2.099(9)	Sn(1)–C(9)	2.084(10)	Sn(1)–C(4)	2.103(7)
Sn(3)–Cl(3)	2.360(3)	Sn(1)–Cl(1)	2.367(2)	Sn(1)–N(1)	2.152(5)
Sn(3)–S(5)	2.452(3)	Sn(1)–S(2)	2.476(3)	Sn(1)–N(2A)	2.736(5)
Sn(3)–N(3)	2.753(8)	Sn(1)–N(1)	2.570(8)	Sn(1)–S(2)	3.126(2)
Sn(4)–C(41)	2.080(12)	Sn(2)–C(15)	2.099(9)	Sn(1)–S(3A)	2.491(2)
Sn(4)–C(47)	2.138?(10)	Sn(2)–C(21)	2.097(10)	C(1)–S(2)	1.666(6)
Sn(4)–Cl(4)	2.375(3)	Sn(2)–Cl(2)	2.366(3)	N(1)–C(1)	1.317(8)
Sn(4)–S(6)	2.450(3)	Sn(2)–S(3)	2.436(3)	N(1)–N(2)	1.355(7)
Sn(4)–N(4)	2.597(8)	Sn(2)–N(2)	2.774(8)	N(2)–C(2)	1.293(8)
N(3)–C(27)	1.282(11)	N(1)–C(1)	1.301(10)	S(1)–C(2)	1.730(7)
N(4)–C(28)	1.317(11)	N(2)–C(2)	1.323(11)	S(1)–C(1)	1.745(6)
S(5)–C(27)	1.762(10)	S(1)–C (1)	1.716(10)	S(3)–C(2)	1.728(6)
S(6)–C(28)	1.713(11)	S(3)–C (2)	1.721(10)	S(3)–Sn(1B)	2.491(2)
C(29)–Sn(3)–C(35)	121.4(5)	C(9)–Sn(1)–C(3)	131.9(4)	C(3)–Sn(1)–C(4)	134.7(3)
C(35)–Sn(3)–Cl(3)	104.6(3)	C(9)–Sn(1)–Cl(1)	100.5(3)	C(3)–Sn(1)–N(1)	101.8(2)
C(29)–Sn(3)–Cl(3)	105.9(3)	C(3)–Sn(1)–Cl(1)	102.0(3)	C(4)–Sn(1)–N(1)	107.6(3)
C(35)–Sn(3)–S(5)	122.3(3)	C(9)–Sn(1)–S(2)	107.2(3)	C(3)–Sn(1)–S(3A)	108.8(2)
C(29)–Sn(3)–S(5)	104.9(3)	C(3)–Sn(1)–S(2)	112.2(3)	C(4)–Sn(1)–S(3A)	105.9(2)
Cl(3)–Sn(3)–S(5)	92.51(11)	Cl(1)–Sn(1)–S(2)	95.44(9)	N(1)–Sn(1)–S(3A)	88.20(15)
C(35)–Sn(3)–N(3)	86.1(3)	C(9)–Sn(1)–N(1)	86.2(3)	C(3)–Sn(1)–N(2A)	84.9(2)
C(29)–Sn(3)–N(3)	89.3(3)	C(3)–Sn(1)–N(1)	88.4(3)	C(4)–Sn(1)–N(2A)	87.4(2)
Cl(3)–Sn(3)–N(3)	152.1(2)	Cl(1)–Sn(1)–N(1)	157.9(2)	N(1)–Sn(1)–N(2A)	148.43(17)
S(5)–Sn(3)–N(3)	60.5(2)	S(2)–Sn(1)–N(1)	62.5(2)	S(3A)–Sn(1)–N(2A)	60.69(13)
C(47)–Sn(4)–C(41)	127.2(4)	C(21)–Sn(2)–C(15)	117.2(4)	C(3)–Sn(1)–S(2)	85.0(2)
C(47)–Sn(4)–Cl(4)	99.3(3)	C(21)–Sn(2)–Cl(2)	103.0(3)	C(4)–Sn(1)–S(2)	83.7(2)
C(41)–Sn(4)–Cl(4)	100.7(3)	C(15)–Sn(2)–Cl(2)	105.6(2)	N(1)–Sn(1)–S(2)	56.17(14)
C(47)–Sn(4)–S(6)	114.2(3)	C(21)–Sn(2)–S(3)	122.5(3)	S(3A)–Sn(1)–S(2)	144.12(6)
C(41)–Sn(4)–S(6)	112.0(3)	C(15)–Sn(2)–S(3)	109.9(3)	N(2A)–Sn(1)–S(2)	155.19(12)
Cl(4)–Sn(4)–S(6)	95.16(10)	Cl(2)–Sn(2)–S(3)	93.86(10)		
C(47)–Sn(4)–N(4)	91.8(3)	C(21)–Sn(2)–N(2)	90.3(3)		
C(41)–Sn(4)–N(4)	86.5(3)	C(15)–Sn(2)–N(2)	86.5(3)		
Cl(4)–Sn(4)–N(4)	157.8(2)	Cl(2)–Sn(2)–N(2)	154.7(2)		

are shown in Figs. 3 and 4, the unit cell of **5** is shown in Fig. 5.

Different from those triorganotin chlorides, diorganotin dichlorides have two chlorine atoms that can be substituted. Together with the particular stereochemistry of the HHdmt, their reaction may form special cyclic or polymeric complexes such as the cases for complex **5**, a one-dimensional linear polymer as shown in Fig. 4 and for complex **6**, a 35-membered macrocycle as reported in our previous work [9]. However, when large stereo-constraint functions, the situation may change and this is the case of complex **4**, which is a dinuclear complex consisting of discrete molecules as shown in Fig. 3. Besides, for complex **5**, co-crystallization is found owing to the weak interaction between $[(CH_3)_2Sn(S–C_2SN_2–S)]_n$ and C_6H_6 (benzene) molecules (see Fig. 4) and the co-crystallized molar ratio of $[(CH_3)_2Sn(S–C_2SN_2–S)]$: C_6H_6 is 2:1. So that it is better to think $\{[(CH_3)_2Sn(S–C_2SN_2–S)]\cdot 0.5C_6H_6\}_n$ as a kind of compound. The co-crystallization in compound **5** may attribute to face-to-face/edge-to-face π–π interactions between the main chain component $[(CH_3)_2Sn(S–C_2SN_2–S)]_n$ and C_6H_6 (benzene) molecules as reported in the literature [25]. The following are some details on the structures of complexes **4** and **5**.

For complex **4**, also due to the symmetric operation, two Sn–S, Sn–N bonds are basically identical, respectively. Both of the Sn–S bond lengths (Sn(1)–S(2) 2.476(3) Å and Sn(2)–S(3) 2.436(3) Å) approach the covalent radii of Sn and S (2.42 Å) [26]. Concerning the Sn–N bonds lengths, though Sn(1)–N(1) 2.570(8) Å is a little shorter than Sn(2)–N(2) 2.774(8) Å, they are both midway between the sums of the covalent radii and van der Waals radii of tin and nitrogen (2.15–3.74 Å)[26]. As the cases for complexes **1** and **2**, the primary bonds of dmt to the tin atoms in complex **4** are through sulfur atoms and the HHdmt appears mainly as thiol tautomer **a** when reacting with diphenyltin dichloride. There are also two Sn–Cl bonds (Sn(1)-Cl(1) 2.367(2) Å, Sn(2)-Cl(2) 2. 366(3) Å) in complex **4**, which are typical Sn–Cl bond lengths (2.32–2.58 Å) found in chloroorganotin(IV) complexes in general [27,28]. Thus, the geometry at tin atoms of complex **4** become distorted trigonal bipyramidal with C(15), C(21), S(3) atoms occupying the equatorial plane and the axial angle, Cl(1)-Sn(1)-N(1) is 157.9(2)°.

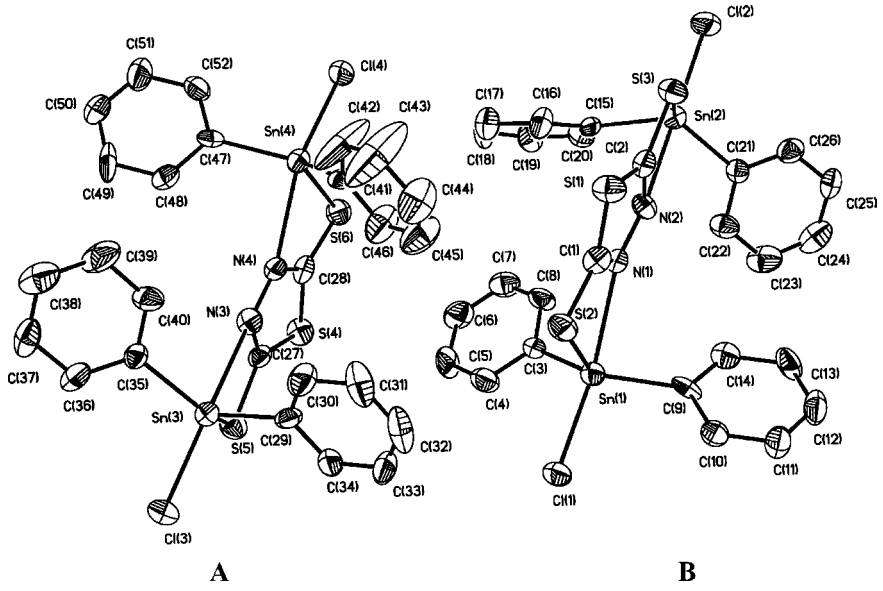


Fig. 3. Molecular structure of complex **4**.

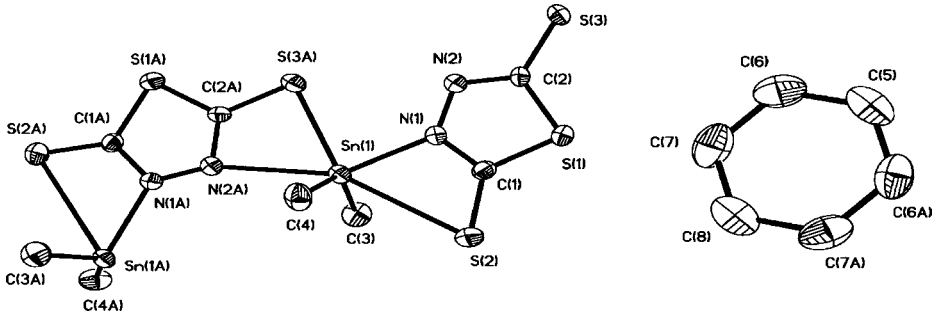


Fig. 4. Molecular structure of a molecular unit of complex **5**.

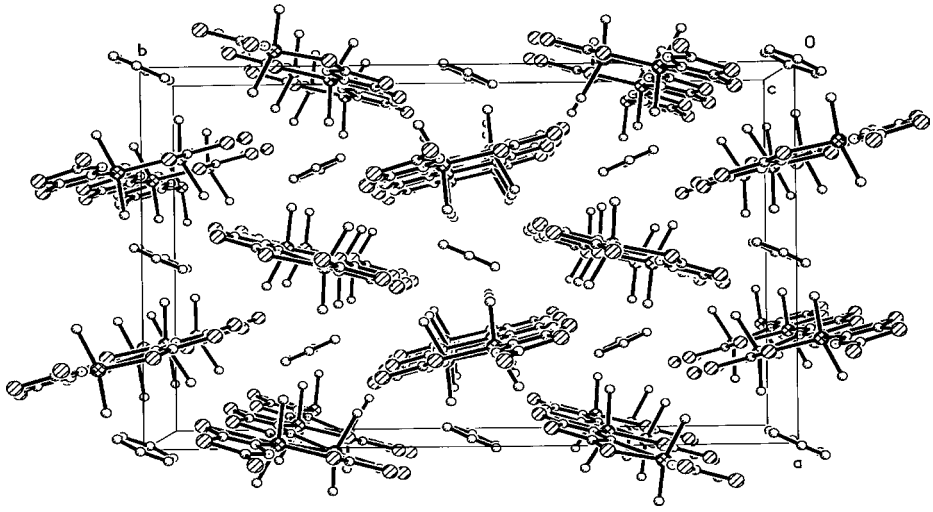


Fig. 5. Cell packing of complex **5**.

As for as the main component $[(CH_3)_2Sn(S–C_2SN_2–S)]_n$ of the compound **5** is concerned, it is a infinite one-dimensional chain whose basic repeated unit is $[(CH_3)_2Sn(S– C_2SN_2–S)]$. As is shown in Fig. 4, the geometry at tin atom in the unit $[(CH_3)_2Sn(S–C_2SN_2–S)]$ is distorted octahedroal. Two Sn–S bonds and two Sn–N bonds form around each tin atom but the two Sn–S bond lengths are much distinct and the

same case occurs for Sn–N bond lengths. The shorter Sn–S bond (Sn(1)-S(3A): 2.491(2) Å) is close to the sum of the covalent radii of tin and sulfur atoms (2.42 Å) [23], while the longer one (Sn(1)-S(2): 3.126(2) Å) is near to the sum of the van der Waals radii of the two atoms (4.0 Å) [29]. Similarly, the shorter and the longer Sn–N bond lengths (Sn(1)-N(1): 2.152(5) Å and Sn(1)-N(2A): 2.736 Å) approach to the sum of the covalent radii (2.15 Å) and the van der Waals radii of tin and nitrogen atoms (3.74 Å), respectively [26]. Furthermore, there are differences between two C–S bonds (C(1)–S(2): 1.666(6) Å and C(2)-S(3): 1.728(6) Å). The shorter C–S bond length is near to that in thioureas (1.681 Å), suggesting its role as C=S double bond. While the longer is close to that in triphenyltin benzoxazole-2-thiolate (1.724 Å) [24] so that it can be regarded as C–S single bond. All these remarkable differences in Sn–S, Sn–N and C–S bond lengths reveal that the thiol and thione forms may be concurrent in one molecule of HHdmt when it reacts with dimethyltin dichloride and as a result, leads to the asymmetry coordination in the basic repeated unit $[(CH_3)_2Sn(S–C_2SN_2–S)]$ via sulfur and nitrogen sites, respectively. That is, the HHdmt seems to exist in the transitional form **c** during the reaction. This conclusion is also proved by the IR data of compound **5**.

3. Experimental details

3.1. Materials and measurements

Triphenyltin chloride, tribenzyltin chloride, di-*n*-butyltin dichloride, dimethyltin dichloride and 2,5-dimercapto-1,3,4-thiodiazole were commercially available, and they were used without further purification. The melting points were obtained with Kofler micro-melting point apparatus and were uncorrected. Infrared spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^1H and ^{13}C spectra were recorded on a Bruker AMX-300 spectrometer operating at 300 and 75.3 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ^{13}C spectra are broadband proton decoupled. The chemical shifts were reported in ppm with respect to the references and were stated relative to external tetramethylsilane (TMS) for ^1H and ^{13}C NMR. Elemental analyses were performed with a PE-2400II apparatus.

3.2. Synthesis of complex $Ph_3Sn(S–C_2SN_2–S)SnPh_3$ (**1**)

The 2,5-dimercapto-1,3,4-thiodiazole (0.15 g, 1 mmol) was added to the solution of ethanol 20 ml with sodium ethoxide (0.136 g, 2 mmol), and the mixture was stirred for 30 min, then add $(Ph)_3SnCl$ (0.770 g, 2 mmol) to the mixture, continuing the reaction for 12 h at 45 °C. After cooling down to room temperature, filtered it. The solvent of the filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The solid was then recrystallized from ether-dichloromethane. Colourless crystal was formed. m.p. 207–209 °C. Yield, 85%. *Anal.* Calc. for $C_{38}H_{30}N_2S_3Sn_2$: C, 53.81; H, 3.56; N, 3.30. Found: C, 53.71; H, 3.59; N, 3.33%. IR (KBr, cm^{-1}): 1632 (C=N), 701 (s, C–S), 560 (m, Sn–C), 317 (m, Sn–S). ^1H NMR (90 MHz, $CDCl_3$): δ 7.46–7.79 (m, 30H). ^{13}C NMR ($CDCl_3$): δ 168.5 (C-1), 168.5 (C-1′), 128.1 (*m*-C), 129.3 (*p*-C), 136.5 (*o*-C), 148.6 (*i*-C).

3.3. Synthesis of complex $(PhCH_2)_3Sn(S–C_2SN_2–S)Sn(PhCH_2)_3$ (**2**)

The synthesis procedure was the same as Section 3.2. HHdmt (0.15 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol), and $(PhCH_3)_3SnCl$ (0.854 g, 2 mmol), reaction time 12 h, temperature 45 °C. Recrystallized from hexane-dichloromethane. m.p. 148–150 °C. Yield, 88%. *Anal.* Calc. for $C_{44}H_{42}N_2S_3Sn_2$: C, 56.68; H, 4.54; N, 3.00. Found: C, 56.60; H, 4.60; N 3.03%. IR (KBr, cm^{-1}): 1631(C=N), 702 (s, C–S), 562 (m, Sn–C), 315 (m, Sn–S). ^1H NMR (90 MHz, $CDCl_3$): δ 7.46–7.79 (m, 30H), 3.26 ($^2J_{SnH} = 66$ Hz, 12H, CH_2–Ph). ^{13}C NMR: δ 168.4 (C-1), 168.4 (C-1′), 37.5 (CH_2–Ph), 127.4 (*m*-C), 128. 2(*p*-C), 127.3 (*o*-C), 124.2 (*i*-C).

3.4. Synthesis of complex $(n\text{-}Bu)_3Sn(S–C_2SN_2–S)Sn(n\text{-}Bu)_3$ (**3**)

The synthesis procedure was the same as Section 3.2. HHdmt (0.15 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol), and $(n\text{-Bu})_3SnCl$ (0.650 g, 2 mmol), reaction time 12 h, temperature 45 °C. Recrystallized from hexane-dichloromethane. m.p. 98–100 °C. Yield, 78%. *Anal.* Calc. for $C_{26}H_{54}N_2S_3Sn_2$: C, 42.88; H, 7.47; N, 3.85. Found: C, 52.87; H, 7.45; N 3.87%. IR (KBr, cm^{-1}): 1631(C=N), 700 (s, C–S), 569 (m, Sn–C), 317 (m, Sn–S). ^1H NMR (90 MHz, $CDCl_3$): δ 1.57–1.70 (m, 36H, $^2J_{SnH} = 80$ Hz), 0.81 (t, 18H). ^{13}C NMR ($CDCl_3$): δ 168.0 (C-1), 168.0 (C-1′), 13.6, 26.4, 27.6, 29.7 (^{n}Bu).

3.5. Synthesis of complex $Ph_2SnCl(S–C_2SN_2–S)SnClPh_2$ (**4**)

The synthesis procedure was the same as Section 3.2. HHdmt (0.30 g, 2 mmol), sodium ethoxide (0.272 g, 4 mmol), and Ph_2SnCl_2 (0.686 g, 2 mmol), reaction time 12 h, temperature 55 °C. Recrystallized from ether-dichloromethane. m.p.138–140 °C. Yield, 72%. *Anal.*

Table 4
Crystal data and structure refinement parameters for **1**, **2**, **4** and **5**

	Complex **1**	Complex **2**	Complex **4**	Complex **5**
Empirical formula	$C_{38}H_{30}N_2S_3Sn_2$	$C_{44}H_{42}N_2S_3Sn_2$	$C_{26}H_{20}Cl_2N_2S_3Sn_2$	C_7 $H_9N_2S_3Sn$
Formula weight	848.20	932.36	764.90	336.03
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	C2/c	C2/c	P2(1)/c	Fdd2
Unit cell dimensions				
a (Å)	11.939(3)	20.080(13)	19.412(7)	17.549(9)
b (Å)	16.433(4)	6.487(4)	18.113(6)	26.740(11)
c (Å)	19.245(5)	32.92(2)	17.698(6)	9.830(4)
α (°)	90	90	90	90
β (°)	106.311(4)	106.758(10)	112.440(7)	90
γ (°)	90	90	90	90
Z	4	4	8	16
V (Å^3)	3623.8(16)	4106(5)	5751(3)	4613(4)
μ (mm^{-1})	1.580	1.402	2.159	2.716
$F(000)$	1680	1872	2976	2608
θ range (°)	2.17 to 23.30	1.29 to 26.37	1.60 to 26.37	2.49 to 26.37
Reflections collected	8172	11224	29729	6536
Independent reflections	2612 ($R_{int} = 0.0567$)	4190 ($R_{int} = 0.0526$)	11623($R_{int} = 0.1380$)	2359 ($R_{int} = 0.1711$)
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0348$	$R_1 = 0.0401$	$R_1 = 0.0488$	$R_1 = 0.0306$
	$wR_2 = 0.0514$	$wR_2 = 0.0839$	$wR_2 = 0.0570$	$wR_2 = 0.0740$
R indices (all data)	$R_1 = 0.0820$	$R_1 = 0.0790$	$R_1 = 0.2212$	$R_1 = 0.0356$
	$wR_2 = 0.0603$	$wR_2 = 0.1259$	$wR_2 = 0.0837$	$wR_2 = 0.0759$

Calc. for $C_{26}H_{20}Cl_2N_2S_3Sn_2$: C, 53.81; H, 3.56; N, 3.30; S, 11.34. Found: C, 53.71; H, 3.59; N, 3.33; S, 11.30%. IR (KBr, cm^{-1}): 1635(C=N), 701 (s, C–S), 561 (m, Sn–C), 321 (m, Sn–S), 277 (m, Sn–Cl). ^{1}H NMR (90 MHz, $CDCl_3$): δ 7.46–7.79 (m, 20H). ^{13}C NMR ($CDCl_3$): δ 168.5 (C-1), 168.5 (C-1′), 128.7 (*m*-C), 129.3 (*p*-C), 134.8 (*o*-C), 148.6 (*i*-C).

3.6. Synthesis of $\{[(CH_3)_2Sn(S–C_2SN_2–S)]\cdot 0.5C_6H_6\}_n$ (**5**)

The synthesis procedure was the same as Section 3.2. HHdmt (0.30 g, 2 mmol), sodium ethoxide (0.272 g, 4 mmol), and $(CH_3)_2SnCl_2$ (0.438 g, 2 mmol), reaction time 12 h, temperature 30 °C. Recrystallized from benzene. m.p. 137–139 °C. Yield, 85%. *Anal.* Calc. for $(C_7H_9N_2S_3Sn)_n$: C, 25.02; H, 2.69; N, 8.34. Found: C, 25.04; H, 2.66; N, 8.38%. IR (KBr, cm^{-1}): 1635(m, C=N), 1150(w, C=S), 700 (s, C–S), 564 (m, Sn–C), 315 (m, Sn–S). ^{1}H NMR (90 MHz, $CDCl_3$): δ 7.30 (s, 3H), δ 0.91 (t, 6H). ^{13}C NMR ($CDCl_3$): δ 168.2 (C-1), 173.4 (C-1′), 128.5 (C_6H_6), 10.6 (CH_3).

3.7. Synthesis of complex $[(n\text{-}Bu)_2Sn(S–C_2SC_2N_2–S)]_5$ (**6**) [9]

The synthesis procedure was the same as Section 3.2. HHdmt (0.30 g, 2 mmol), sodium ethoxide (0.272 g, 4 mmol), and $(n\text{-}Bu)_2SnCl_2$ (0.607 g, 2 mmol), reaction time 12 h, temperature 30 °C. Recrystallized from ether-dichloromethane. m.p. 248 °C (dec.). Yield, 74%. *Anal.* Calc. for $C_{50}H_{90}N_{10}S_{15}Sn_5$: C, 31.51; H, 4.76; N, 7.35. Found: C, 31.46; H, 4.78; N, 7.34%. IR (KBr, cm^{-1}): 1635 (m, C=N), 1151 (w, C=S), 701 (s, C–S), 561 (m, Sn–C), 317 (m, Sn–S). ^{1}H NMR (90 MHz, $CDCl_3$): δ 1.10–1.75 (m, $–CH_2CH_2CH_2$); 0.95 (t, $–CH_3$). ^{13}C NMR ($CDCl_3$): δ 13.6, 26.4, 27.6, 29.7 (^{n}Bu).

3.8. X-ray structure analysis of **1**, **2**, **4**, **5**

Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Smart CCD area-detector with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A semi-empirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refined against F^2 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 Table 4.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper (**1**, **2**, **4**, **5**) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-183594, 211513, 209700, 211512. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road,

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

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