Syntheses and Crystal Structures of Diorganotin Derivatives of 2,5-Dimercapto-1,3,4-thiadiazole

Chunlin Ma,*[a,b] Junhong Zhang,[a] Feng Li,[a] and Rufen Zhang[a]

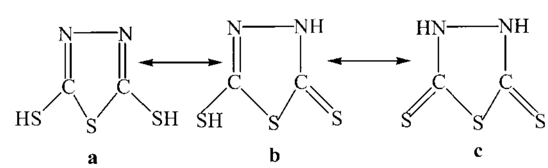
Keywords: Macrocyclic ligands / N ligands / Oxo ligands / S ligands / Tin

Two novel trinuclear tin oxo clusters $[(C_2S_3N_2)R_6Sn_3O(OH)Y]\cdot L$ [R = CH_3, Y = OH, L = $1\cdot 5H_2O$ (**1**); R = $PhCH_2$, Y = OEt, L = 0 (**2**)], a pentanuclear tin macrocycle $[(CH_3)_2Sn(C_2N_2S_3)]_5\cdot CH_2Cl_2\cdot 3H_2O$ (**3**) and $[(PhCH_2)_4Cl_2Sn(C_2S_3N_2)]$ (**4**) have been synthesized by the reaction of 2,5-dimercapto-1,3,4-thiadiazole with dialkyltin dichloride in ethanol (95%) or dichloromethane. Complexes **1**–**4** have been characterized by elemental analysis and IR, ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. The structures of **1**–**3** have been determined by X-ray crystallography. Complexes **1** and **2** display a unique tricyclic structure consisting of fused five-membered Sn_2ON_2 and four-membered Sn_2O_2 rings that form a planar $N_2Sn_3O_2$ skeleton, with a distorted trigonal bipyramidal coordination at tin. Complex **3** is a pentanuclear 35-membered tin macrocycle containing the crown thioether-type ligand in which all five tin atoms bond to the sulfur and nitrogen atoms with distorted octahedral geometries. The structures of complexes **1** and **3** are stabilized by hydrogen bonds or intermolecular non-bonding S···S interactions.

Introduction

Recent developments in coordination chemistry have produced numerous supermolecular and macrocyclic complexes through the appropriate combination of organometallic complexes and various organic ligands.[1−6] Organotin macrocycles are attracting more and more attention for their potential industrial applications and biological activities.[7,8] In these metallomacrocyclic systems, ligands with multiply coordinating donor atoms and particular stereochemistry may lead to different specific architectures. Heterocyclic thionate ligands,[5] which contain at least one deprotonated heterocyclic thioamide group $(N-C-S)^-$ and can act as monodentate, chelating or bridging ligands are particularly important.[9] 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 the tin atoms occurs through sulfur rather than through nitrogen. Moreover, different coordination patterns of the ligand in the thiolic form have been found.[10,11]

To continue our study in this field, we chose another ligand: 2,5-dimercapto-1,3,4-thiadiazole (H_2dmt), which possesses a more complex deprotonated heterocyclic thioamide group $(S-C-N-N-C-S)^{2-}$ than Hmnc. The heterocycle of H_2dmt, with four available donors all of which can be utilized in bonding in varying combinations, as shown in Scheme 1),[12] may act as a fulcrum about which lattice construction is orchestrated in two or more dimensions.



Scheme 1. Tautomeric forms of H_2dmt

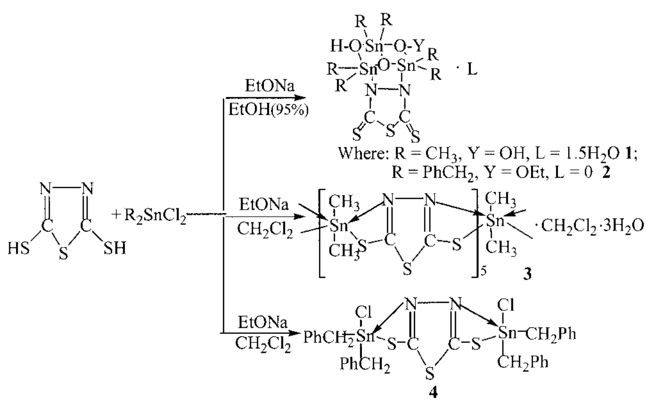
In our previous work we reported a pentanuclear tin macrocycle[13] in which the coordination of H_2dmt is through two sulfur atoms of the thiol (**a**) rather than the thione (**c**) tautomer. While continuing our research on other diorganotin complexes of H_2dmt, we surprisingly obtained four novel complexes $[(C_2S_3N_2)(CH_3)_6Sn_3O(OH)_2]\cdot 1.5H_2O$ (**1**), $[(C_2S_3N_2)\{(PhCH_2)_6Sn_3O(OH)(OEt)\}]$ (**2**) $[(CH_3)_2Sn(C_2N_2S_3)]_5\cdot CH_2Cl_2\cdot 3H_2O$ (**3**) and $[(PhCH_2)_2ClSn(S-C_2SN_2-S)SnCl(PhCH_2)_2]$ (**4**). It is worthwhile to note that complexes **1** and **3** were obtained by the same reactants in different solvents, and the complexes **2** and **4** were obtained by the same reactants in different solvents, too, and that H_2dmt shows different coordination to the tin(IV) atom. All four complexes **1**−**4** were characterized by elemental analysis and IR, ^{1}H, ^{13}C and ^{119}Sn NMR spec-

[a] Department of Chemistry, Liaocheng University, Liaocheng 252059, P. R. China
Fax: +86-538-671-5521
E-mail: macl@lctu.edu.cn
[b] Department of Chemistry, Taishan University, Taian 271021, P. R. China

troscopy and the structures of **1**, **2** and **3** were determined by X-ray crystallography.

Results and Discussion

Complexes **1**−**4** were prepared by the reaction of dimethyltin dichloride or dibenzyltin dichloride with 2,5-dimercapto-1,3,4-thiadiazole in either EtOH (95%) or CH_2Cl_2. The reaction procedures are shown in Scheme 2.



Scheme 2

When the reaction solvent is EtOH (95%), the complexes **1** and **2** were obtained. In view of the results of our present studies[10,14] and those of earlier work,[15] the possible mechanism of formation of complexes **1** and **2** is as follows. Firstly, a hydrolysis reaction of R_2SnCl_2 occurs to form $R_2(Cl)Sn(OH)$, which is then further hydrolyzed to produce $[R_2(OH)SnY]$ (Y = OH or OEt). Two $R_2(Cl)Sn(OH)$ molecules then condense to form $[R_2(Cl)Sn]_2O$, which then reacts with $[R_2(OH)SnY]$ to produce $[R_6Sn_3O(Cl)_2(OH)Y]$.[14] Finally, the two chlorine atoms of $[R_6Sn_3O(Cl)_2(OH)Y]$ are substituted by two nitrogen atoms of the sodium salt of H_2dmt $[Na_2(C_2N_2S_3)]$ to produce the title complexes **1** and **2**. As shown in Scheme 2, the H_2dmt acts as tautomer **c**, bonding to tin(IV) through two nitrogen atoms in both complexes **1** and **2**.

When the reaction solvent was replaced by CH_2Cl_2 we obtained complexes **3** and **4**. In this case the hydrolysis of R_2SnCl_2 does not occur and the ligand coordinates to the tin(IV) center, through two sulfur atoms, as the thiol tautomer (**a**).

Moreover, in complex **4**, the spatial resistances of two benzyl groups are strong enough to prevent another H_2dmt ligand chelating to the central tin atom, which is well consistent with the sequence of steric constraints phenyl ≈ benzyl > *n*-butyl > methyl: the larger the steric constraint of the R groups, the more difficult the substitution of the chlorine atoms.[16]

Description of the Structures

[$(C_2S_3N_2)(CH_3)_6Sn_3O(OH)_2$]·1.5$H_2O$ (1) and [$(C_2S_3N_2)(PhCH_2)_6Sn_3O(OH)(OEt)$] (2)

The molecular structures and unit cells of complexes **1** (Figure 1 and 2) and **2** (Figure 3 and 4) are shown below; selected bond lengths and angles are collected in Table 1 and 2, respectively. Like other trinuclear organotin oxo clusters,[17] complex **1** contains a tricyclic system formed by an N_2Sn_2O ring and two Sn_2O_2 rings, in which the $N_2Sn_3O(OH)_2$ structural motif is almost planar with a mean deviation of ±0.0452 Å. All three tin atoms show severely distorted trigonal bipyramidal configurations.

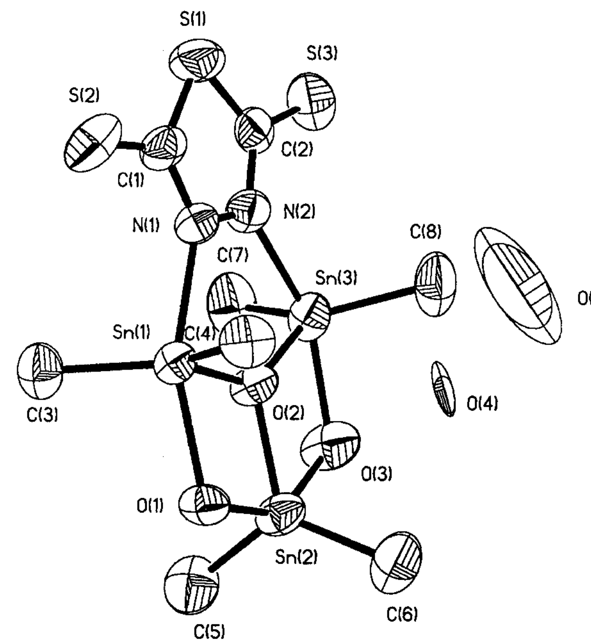


Figure 1. Molecular structure of complex **1**; ellipsoids at 30% probability

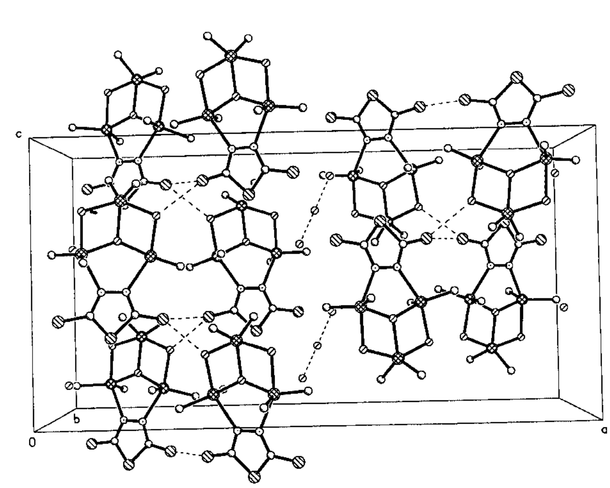


Figure 2. Unit cell of complex **1**

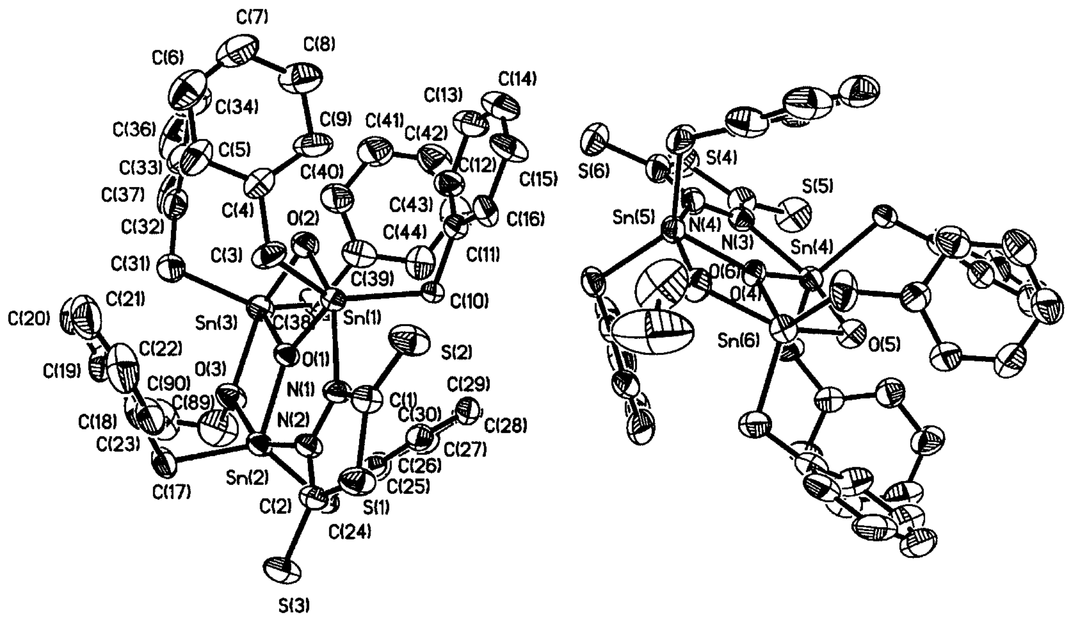


Figure 3. Molecular structure of complex **2**; ellipsoids at 30% probability

Sn(1) and Sn(3) have the same environment, where one μ_3-O atom and two C atoms of the methyl groups occupy the equatorial positions [C(3), C(4) and O(2) for Sn(1); C(7), C(8) and O(2) for Sn(3)], and the axial positions are occupied by one N atom of the H_2dmt and one O atom of the hydroxyl group [N(1) and O(1) for Sn(1); N(2) and O(3) for Sn(3)]. The geometry of Sn(2) is *cis*-R_2SnO_3, in which the axial positions are occupied by the O(3) and O(1) atoms of hydroxyl groups, and two C(5) and C(6) atoms of methyl groups and one μ_3-O(2) atom occupy the equatorial plane. The distortion of the axial angles is very large at the three tin atoms [O(1)−Sn(1)−N(1) 150.4(2)°, O(3)−Sn(3)−N(2) 150.0(2)° and O(3)−Sn(2)−O(1) 144.1(2)° respectively] compared to the ideal angle of 180°.

With regard to the hydrolysis, three $[(CH_3)_2Sn]$ units are bridged by one μ_3-O atom and two O atoms of hydroxyl groups, and thus form a trinuclear complex containing two Sn_2O_2 rings. Three Sn atoms and three O atoms [Sn(1), Sn(3), O(2), Sn(2), O(1), O(3)] comprise a fused ring system and are nearly coplanar, with a mean deviation of ±0.0326 Å, which is similar to traditional hydrolytic products with a ladder-type arrangement,[18] but different from the staircase structure of $[Me_4Sn_2(OSiMe_3)_2O]_2$.[19] The Sn−O distances between μ_3-O atom and the tin atoms are similar [Sn(3)−O(2) 2.037(5) Å, Sn(2)−O(2) 2.051(5) Å and Sn(1)−O(2) 2.032 (5) Å], but other Sn−O lengths between the O atoms of the hydroxyl and the tin atoms [Sn(1)−O(1) 2.150(5) Å, Sn(2)−O(1) 2.106(5) Å, Sn(2)−O(3) 2.094(6) Å, Sn(3)−O(3) 2.129(6) Å] are slightly longer, and similar to the Sn−O bonds in the ladder structure $[Me_2Cl-SnOSnMe_2Cl]_2$ [2.115(9) Å].[20] All of the above indicates that a strong oxo bridge exists in complex **1**.

The two nitrogen atoms of the H_2dmt ligand, which is a five-membered ring, bond to tin atoms to form another five-membered N_2Sn_2O ring. The dihedral angle between the two rings is 1.2°, which indicates that all the atoms of the two rings are almost planar. The Sn−N bond lengths [Sn(1)−N(1) 2.274(6) Å and Sn(3)−N(2) 2.246(7) Å] are similar to the sum of the covalent radii of Sn and N (2.15 Å) and much shorter than the sum of the van der Waals radii of tin and nitrogen atoms (3.74 Å),[21] which proves that the nitrogen atoms coordinate to tin by strong chemical bonds. Furthermore, the C−S bonds [S(2)−C(1) 1.701(10) Å, S(3)−C(2) 1.668(10) Å] are similar to those in thiourea (1.681 Å),[22] suggesting that they are C=S double bonds and therefore retain the thione form. All of above proves

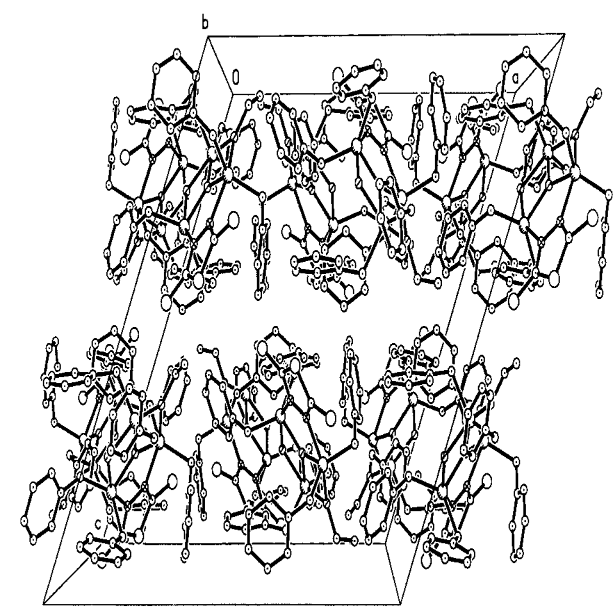


Figure 4. Unit cell of complex **2**

Table 1. Selected bond lengths (Å) and angles (°) for **1**[a]

Sn(1)−O(2)[a]	2.032(5)	Sn(3)−O(2)	2.037(5)
Sn(1)−C(4)	2.079(8)	Sn(3)−C(8)	2.104(10)
Sn(1)−C(3)	2.096(9)	Sn(3)−C(7)	2.107(10)
Sn(1)−O(1)	2.150(5)	Sn(3)−O(3)	2.129(6)
Sn(1)−N(1)	2.274(6)	Sn(3)−N(2)	2.246(7)
Sn(2)−O(2)	2.051(5)	S(1)−C(1)	1.714(9)
Sn(2)−C(6)	2.075(10)	S(1)−C(2)	1.743(10)
Sn(2)−O(3)	2.094(6)	S(2)−C(1)	1.701(10)
Sn(2)−O(1)	2.106(5)	S(3)−C(2)	1.668(10)
Sn(2)−C(5)	2.121(10)	O(1)···S(2)i	3.178
N(1)−C(1)	1.325(9)	O(3)···S(3)ii	3.206
N(1)−N(2)	1.388(8)	O(4)···O(5)iii	2.085
N(2)−C(2)	1.330(9)	S(3)···S(3)	3.274
O(2)−Sn(1)−C(4)	113.8(3)	O(2)−Sn(3)−C(8)	112.7(3)
O(2)−Sn(1)−C(3)	111.0(3)	O(2)−Sn(3)−C(7)	112.8(3)
C(4)−Sn(1)−C(3)	135.2(4)	C(8)−Sn(3)−C(7)	134.3(4)
O(2)−Sn(1)−O(1)	71.77(18)	O(2)−Sn(3)−O(3)	71.3(2)
C(4)−Sn(1)−O(1)	94.0(3)	C(8)−Sn(3)−O(3)	96.5(4)
C(3)−Sn(1)−O(1)	97.6(3)	C(7)−Sn(3)−O(3)	93.7(4)
O(2)−Sn(1)−N(1)	78.8(2)	O(2)−Sn(3)−N(2)	78.8(2)
C(4)−Sn(1)−N(1)	95.2(3)	C(8)−Sn(3)−N(2)	97.3(4)
C(3)−Sn(1)−N(1)	95.6(3)	C(7)−Sn(3)−N(2)	95.5(4)
O(1)−Sn(1)−N(1)	150.4(2)	O(3)−Sn(3)−N(2)	150.0(2)
O(2)−Sn(2)−C(6)	116.6(4)	C(1)−N(1)−Sn(1)	125.5(6)
O(2)−Sn(2)−O(3)	71.8(2)	N(2)−N(1)−Sn(1)	121.4(5)
C(6)−Sn(2)−O(3)	99.1(4)	C(2)−N(2)−N(1)	115.1(7)
O(2)−Sn(2)−O(1)	72.32(18)	C(2)−N(2)−Sn(3)	121.8(6)
C(6)−Sn(2)−O(1)	98.6(3)	N(1)−N(2)−Sn(3)	123.1(5)
O(3)−Sn(2)−O(1)	144.1(2)	Sn(2)−O(1)−Sn(1)	104.64(19)
O(2)−Sn(2)−C(5)	117.4(3)	Sn(1)−O(2)−Sn(3)	138.0(3)
C(6)−Sn(2)−C(5)	126.0(5)	Sn(1)−O(2)−Sn(2)	111.2(2)
O(3)−Sn(2)−C(5)	97.0(4)	Sn(3)−O(2)−Sn(2)	110.9(2)
O(1)−Sn(2)−C(5)	97.5(3)	Sn(2)−O(3)−Sn(3)	105.7(2)
C(1)−N(1)−N(2)	113.1(7)	O(4)−H(3)···O(5)iii	124.44
O(1)−H(1)···S(2)i	174.32	O(3)−H(2)···S(3)ii	158.81

[a] Symmetry transformations used to generate equivalent atoms: (i) x, $-y$, $z + 1/2$; (ii) $-x + 1/2$, y, $z + 1/2$; (iii) $-x + 1$, y, $-z + 3/2$.

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

Sn(1)−O(1)	2.047(5)	Sn(2)−O(1)	2.054(5)
Sn(1)−O(2)	2.186(6)	Sn(2)−O(3)	2.223(6)
Sn(1)−C(10)	2.170(8)	Sn(2)−C(24)	2.143(9)
Sn(1)−C(3)	2.136(9)	Sn(2)−C(17)	2.134(9)
Sn(1)−N(1)	2.224(7)	Sn(2)−N(2)	2.230(7)
Sn(3)−O(1)	2.053(5)	S(1)−C(2)	1.747(10)
Sn(3)−O(3)	2.137(6)	S(1)−C(1)	1.755(9)
Sn(3)−O(2)	2.139(6)	S(2)−C(1)	1.672(10)
Sn(3)−C(38)	2.163(12)	S(3)−C(2)	1.687(9)
Sn(3)−C(31)	2.127(11)	N(2)−C(2)	1.317(10)
N(1)−C(1)	1.333(11)	N(1)−N(2)	1.389(9)
C(3)−Sn(1)−C(10)	134.8(4)	C(17)−Sn(2)−C(24)	130.6(4)
O(1)−Sn(1)−C(3)	112.8(3)	O(1)−Sn(2)−C(17)	114.1(3)
O(1)−Sn(1)−C(10)	112.2(3)	O(1)−Sn(2)−C(24)	115.0(3)
O(2)−Sn(1)−C(3)	96.7(3)	O(3)−Sn(2)−C(17)	94.2(3)
O(2)−Sn(1)−C(10)	93.5(3)	O(3)−Sn(2)−C(24)	96.0(3)
O(1)−Sn(1)−O(2)	71.7(2)	O(1)−Sn(2)−O(3)	71.3(2)
O(1)−Sn(1)−N(1)	79.4(2)	O(1)−Sn(2)−N(2)	79.5(2)
O(2)−Sn(1)−N(1)	151.1(2)	O(3)−Sn(2)−N(2)	150.9(2)
C(3)−Sn(1)−N(1)	94.1(3)	C(17)−Sn(2)−N(2)	98.7(3)
C(10)−Sn(1)−N(1)	97.7(3)	C(24)−Sn(2)−N(2)	95.3(3)
C(38)−Sn(3)−C(31)	125.0(5)	Sn(2)−O(1)−Sn(3)	112.4(2)
O(1)−Sn(3)−O(2)	72.7(2)	Sn(2)−O(3)−Sn(3)	103.0(3)
O(1)−Sn(3)−O(3)	73.2(2)	Sn(1)−O(1)−Sn(2)	135.6(3)
O(2)−Sn(3)−O(3)	145.9(2)	Sn(1)−N(1)−N(2)	123.3(5)
C(38)−Sn(3)−O(2)	100.0(3)	Sn(2)−N(2)−N(1)	122.2(5)
C(38)−Sn(3)−O(1)	119.8(4)	N(2)−N(1)−C(1)	114.8(7)
C(38)−Sn(3)−O(3)	97.5(3)	N(1)−N(2)−C(2)	114.3(7)
C(31)−Sn(3)−O(1)	115.2(4)	N(1)−C(1)−S(2)	124.6(7)
C(31)−Sn(3)−O(3)	97.4(4)	N(2)−C(2)−S(3)	124.8(7)
C(31)−Sn(3)−O(2)	96.3(4)	C(1)−S(1)−C(2)	90.6(4)

indirectly that H_2dmt bonds to tin as the nitrogen tautomer **c** and not the sulfur tautomer.

As can be seen in Figure 2, molecules of **1** are joined into a network of 2D dimers in a head-to-tail fashion by intermolecular hydrogen bonds. Each monomeric unit forms two weak hydrogen bonds between the O atom of the hydroxyl and the uncoordinated S atom of a neighboring molecule of H_2dmt [O(1)−H(1) 0.897 Å, H···S(2) 2.302 Å, O(1)···S(2) 3.178, O(1)−H(1)···S(2) 174.32°; O(3)−H(2) 0.886 Å, H···S(3) 2.364 Å, O(3)···S(3) 3.206 Å, O(3)−H(2)···S(3) 158.81°]. Moreover, S···S weak intermolecular non-bonding interactions also help to stabilize the structure. The S(3)···S(3) distance of 3.274 Å is significantly shorter than the sum of the van der Waals radii of two sulfur atoms (3.7 Å).[23] Therefore in these two cases hydrogen bonds and intermolecular non-bonding interactions lead to aggregation and formation of a supramolecular assembly.[24]

The tin environment in complex **2** is the same as that of complex **1**. The Sn−N distance [Sn(1)−N(1) 2.224(7) Å, Sn(2)−N(2) 2.230(7) Å], the C−S bonds [S(2)−C(1) 1.673(9) Å, S(3)−C(2) 1.688(9) Å] and the Sn−O distance [from 2.047 Å to 2.224(6) Å] are all similar to those found in complex **1**, which indicates that the $(PhCH_2)_2SnCl_2$ was also hydrolyzed and the ligand coordinates to tin(IV) through two nitrogen atoms as the tautomer **c**. The difference between complexes **1** and **2** lies in the co-ligands formed during the hydrolysis reaction. As shown in Figure 1 and 3 the products of the hydrolysis reaction are $[(CH_3)_2Sn(OH)_2]$ for complex **1** and $[(PhCH_2)_2Sn(OH)(OEt)]$ for complex **2**, respectively. Such a difference may be due to the larger steric constraints of $PhCH_2$ groups than CH_3.

$[(CH_3)_2Sn(C_2N_2S_3)]_5\cdot CH_2Cl_2\cdot 3H_2O$ (3)

The molecular structure and unit cell of complex **3** are shown in Figure 5 and 6, respectively; Figure 7 shows the crystal structure of the same component with all co-crystallized solvent molecules omitted. Selected bond lengths and angles are listed in Table 3.

As shown in Figure 5, the coordination of H_2dmt in complex **3** is different from that in complex **1**, but is similar to our previously reported complex $(Bu_2SnC_2N_2S_3)_5$;[13] the ligand is found as the thiol tautomer **a** when bonded to tin. The pentanuclear tin complex is characterized by a 35-membered $C_{10}S_{10}N_{10}Sn_5$ macrocycle ring system with all ten sulfur atoms pointing to the exterior of the cavity, thereby acting as a crown thioether.[25] All five tin atoms have the same arrangement — they are hexacoordinate with

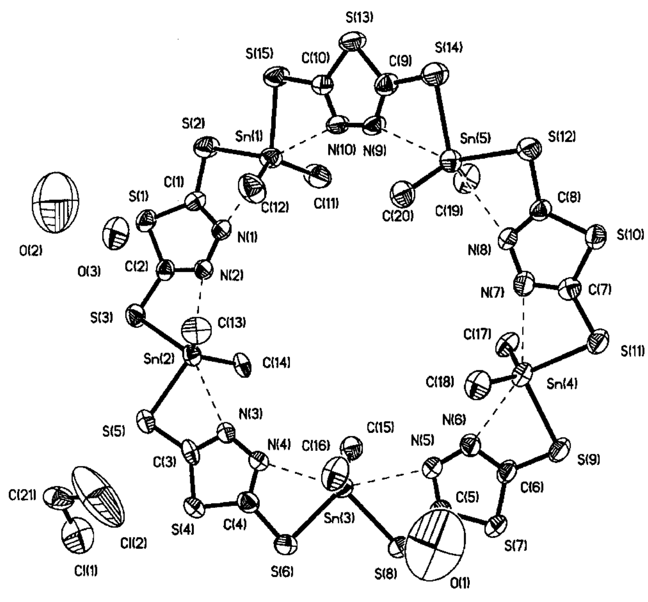


Figure 5. Molecular structure of complex **3**; ellipsoids at 30% probability

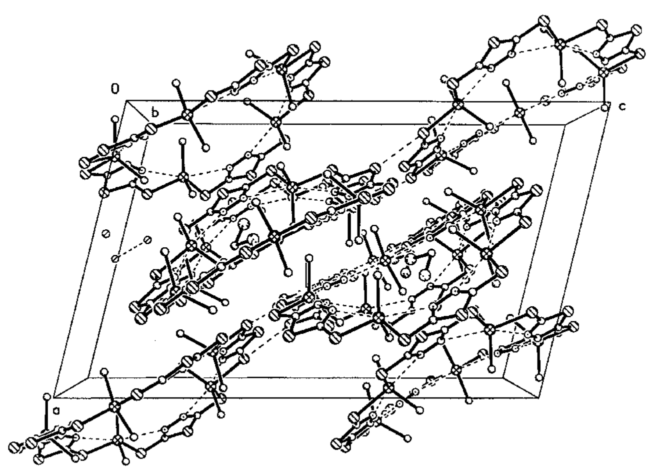


Figure 6. Unit cell of complex **3**

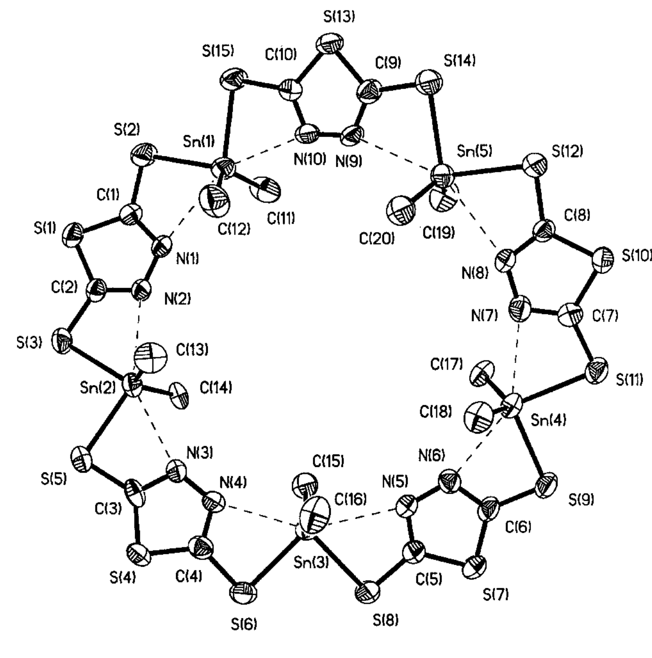


Figure 7. Molecular structure of complex **3** (all solvent molecules omitted)

distorted octahedral geometries. Two sulfur atoms and two carbon atoms occupy the equatorial positions and the axial positions are occupied by two azole-N atoms. The deviation from an ideal octahedron is manifested by the bond angles N(1)−Sn(1)−N(10) [149.5(2)°], N(2)−Sn(2)−N(3) [148.7(2)°], N(4)−Sn(3)−N(5) [150.3(2)°], N(6)−Sn(4)−N(7) [147.0(3)°] and N(8)−Sn(5)−N(9) [149.0(2)°], all of which deviate from the ideal value of 180°.

The Sn···S (from 2.483 Å to 2.502 Å) and Sn···N distances (from 2.701 Å to 2.890 Å) are similar to those in the reported complex $(Bu_2SnC_2N_2S_3)_5$ (average value: 2.494 Å and 2.762 Å, respectively).[13] The longest Sn−S distance is slightly longer than the sum of the covalent radii of Sn and S (2.44 Å),[26] but consistent with Sn−S in $t$$Bu_2Sn(S_2CNEt_2)_2$ (2.554 Å),[27] and is much shorter than the sum of the van der waals radii of 4.0 Å.[28] This proves that the sulfur atoms coordinate to the tin atoms by strong chemical bonds. The average Sn−N bond length (2.778 Å) is much longer than that in complex **1**, but is similar to the Sn←N (2.787 Å) intermolecular bond found in the trimeric $[Me_3SnSCN_4Ph]_3$ unit.[29] All the Sn−N distances are midway between the covalent radii and the sums of the van der Waals of Sn and N (2.15 and 3.74 Å)[21] and can be regarded as weak coordination bonds. Thus the coordination number of the tin atom is increased to six through Sn←N intermolecular bonds. All above information suggests that the primary bonds of the H_2dmt ligand to tin atoms are through sulfur atoms with the ligand appearing as the thiol tautomer **a**. This situation is similar to that in the reported complex $(Bu_2SnC_2N_2S_3)_5$.[13]

The C−S bond lengths are in the range from 1.695 to 1.750 Å with an average value of 1.723 Å for the chelating ligands, similar to the C−S single bond (1.724 Å) in triphenyltin benzoxazole-2-thiolate,[30] thereby confirming the above proposal.

It is worthwhile to note that the critical cross-ring interatomic distances of the cavity are 10.904 Å [N(1)···Sn(4)] and 10.897 Å [N(4)···Sn(5)], which are larger than those found in dimethyl- and di-*n*-butyltin(IV) complexes with phthalic and isophthalic acid.[8] Furthermore, as shown in Figure 5, there are weak intermolecular non-bonding S···S interactions between the coordinated S atom and the uncoordinated S atom of the neighboring ligand. The S···S distances [S(1)···S(8) 3.489 and S(9)···S(15) 3.449] are all shorter than the sum of the Van der Waals radii of two sulfur atoms (3.7 Å),[23] which indicate that these intermolecular non-bonding interactions lend the crystal stability and compactness and result in a one-dimensional supramolecular polymers arrangement.[5]

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

Sn(1)−C(11)	2.086(11)	Sn(4)−C(18)	2.116(9)
Sn(1)−C(12)	2.090(10)	Sn(4)−C(17)	2.117(9)
Sn(1)−S(15)	2.484(3)	Sn(4)−S(11)	2.492(3)
Sn(1)−S(2)	2.487(3)	Sn(4)−S(9)	2.500(3)
Sn(1)−N(10)	2.722(8)	Sn(4)−N(7)	2.727(8)
Sn(1)−N(1)	2.890(8)	Sn(4)−N(6)	2.770(8)
Sn(2)−C(13)	2.092(9)	Sn(5)−C(19)	2.098(9)
Sn(2)−C(14)	2.124(9)	Sn(5)−C(20)	2.109(9)
Sn(2)−S(3)	2.483(3)	Sn(5)−S(14)	2.489(3)
Sn(2)−S(5)	2.495(3)	Sn(5)−S(12)	2.495(3)
Sn(2)−N(3)	2.777(8)	Sn(5)−N(9)	2.780(8)
Sn(2)−N(2)	2.781(8)	Sn(5)−N(8)	2.797(8)
Sn(3)−C(15)	2.088(9)	S(1)−C(2)	1.735(9)
Sn(3)−C(16)	2.140(9)	S(1)−C(1)	1.743(9)
Sn(3)−S(8)	2.492(3)	S(2)−C(1)	1.742(9)
Sn(3)−S(6)	2.502(3)	S(3)−C(2)	1.733(9)
Sn(3)−N(4)	2.701(8)	S(4)−C(3)	1.695(10)
Sn(3)−N(5)	2.835(8)	S(4)−C(4)	1.719(10)
N(1)−C(1)	1.293(10)	S(5)−C(3)	1.745(10)
N(1)−N(2)	1.373(9)	S(6)−C(4)	1.729(11)
N(2)−C(2)	1.280(10)	S(7)−C(6)	1.707(10)
N(3)−C(3)	1.297(10)	S(7)−C(5)	1.727(10)
N(3)−N(4)	1.330(9)	S(8)−C(5)	1.730(10)
N(4)−C(4)	1.310(10)	S(9)−C(6)	1.715(10)
N(5)−C(5)	1.319(10)	S(10)−C(7)	1.724(9)
N(5)−N(6)	1.371(9)	S(10)−C(8)	1.726(9)
N(6)−C(6)	1.327(10)	S(11)−C(7)	1.715(9)
N(7)−C(7)	1.332(10)	S(12)−C(8)	1.747(9)
N(7)−N(8)	1.377(9)	S(13)−C(9)	1.723(10)
N(8)−C(8)	1.303(10)	S(13)−C(10)	1.727(9)
N(9)−C(9)	1.290(10)	S(14)−C(9)	1.728(10)
N(9)−N(10)	1.357(9)	S(15)−C(10)	1.750(10)
N(10)−C(10)	1.283(10)	O(2)···O(3)	2.361
S(1)···S(8)	3.489	S(9)···S(15)	3.449
C(11)−Sn(1)−C(12)	128.8(5)	N(4)−Sn(3)−N(5)	150.3(2)
C(11)−Sn(1)−S(15)	107.3(3)	S(6)−Sn(3)−N(5)	148.06(18)
C(12)−Sn(1)−S(15)	110.3(3)	S(8)−Sn(3)−N(5)	59.96(18)
C(11)−Sn(1)−S(2)	105.7(3)	C(16)−Sn(3)−N(5)	81.7(3)
C(12)−Sn(1)−S(2)	108.2(3)	C(15)−Sn(3)−N(5)	85.1(3)
S(15)−Sn(1)−S(2)	89.37(10)	S(6)−Sn(3)−N(4)	61.57(18)
C(11)−Sn(1)−N(10)	85.9(4)	S(8)−Sn(3)−N(4)	149.64(18)
C(12)−Sn(1)−N(10)	82.8(3)	C(18)−Sn(4)−C(17)	130.0(4)
S(15)−Sn(1)−N(10)	61.37(19)	C(18)−Sn(4)−S(11)	105.8(3)
S(2)−Sn(1)−N(10)	150.70(19)	C(17)−Sn(4)−S(11)	109.2(3)
C(11)−Sn(1)−N(1)	88.3(3)	C(18)−Sn(4)−S(9)	107.8(3)
C(12)−Sn(1)−N(1)	77.7(3)	C(17)−Sn(4)−S(9)	105.5(3)
S(15)−Sn(1)−N(1)	148.08(17)	S(11)−Sn(4)−S(9)	91.99(9)
S(2)−Sn(1)−N(1)	59.24(16)	C(18)−Sn(4)−N(7)	83.8(3)
N(10)−Sn(1)−N(1)	149.5(2)	C(17)−Sn(4)−N(7)	83.1(3)
C(13)−Sn(2)−C(14)	127.0(4)	S(11)−Sn(4)−N(7)	61.01(19)
C(13)−Sn(2)−S(3)	108.2(3)	S(9)−Sn(4)−N(7)	152.89(19)
C(13)−Sn(2)−S(5)	107.0(3)	C(18)−Sn(4)−N(6)	81.6(3)
C(14)−Sn(2)−S(5)	108.9(3)	C(17)−Sn(4)−N(6)	83.9(3)
S(3)−Sn(2)−S(5)	91.18(9)	S(11)−Sn(4)−N(6)	151.85(19)
C(13)−Sn(2)−N(3)	86.6(3)	S(9)−Sn(4)−N(6)	60.10(19)
C(14)−Sn(2)−N(3)	79.2(3)	N(7)−Sn(4)−N(6)	147.0(3)
S(3)−Sn(2)−N(3)	150.79(17)	C(19)−Sn(5)−C(20)	129.1(4)
S(5)−Sn(2)−N(3)	60.01(17)	C(19)−Sn(5)−S(14)	109.8(3)
C(13)−Sn(2)−N(2)	81.2(3)	C(20)−Sn(5)−S(14)	106.0(3)
C(14)−Sn(2)−N(2)	85.4(3)	C(19)−Sn(5)−S(12)	105.1(3)
S(3)−Sn(2)−N(2)	60.27(17)	C(20)−Sn(5)−S(12)	109.4(3)
S(3)−Sn(2)−N(2)	60.27(17)	S(14)−Sn(5)−S(12)	90.75(9)
S(5)−Sn(2)−N(2)	151.25(18)	C(19)−Sn(5)−N(9)	83.0(3)
N(3)−Sn(2)−N(2)	148.7(2)	C(20)−Sn(5)−N(9)	84.9(3)
C(15)−Sn(3)−C(16)	133.5(4)	S(12)−Sn(5)−N(9)	150.45(18)
C(15)−Sn(3)−S(8)	104.5(3)	S(14)−Sn(5)−N(9)	60.03(18)
C(16)−Sn(3)−S(8)	106.7(3)	C(19)−Sn(5)−N(8)	80.6(3)
C(15)−Sn(3)−S(6)	108.8(3)	C(20)−Sn(5)−N(8)	85.3(3)
C(16)−Sn(3)−S(6)	105.7(3)	S(12)−Sn(5)−N(8)	60.11(18)
S(8)−Sn(3)−S(6)	88.39(10)	S(14)−Sn(5)−N(8)	150.85(18)
C(15)−Sn(3)−N(4)	82.9(3)	N(9)−Sn(5)−N(8)	149.0(2)
C(16)−Sn(3)−N(4)	87.1(3)		

Spectroscopic Data

IR Spectra

The strong broad bands in the IR spectra of complexes **1−3** in the region 3440−3000 can be attributed to the O−H stretching vibration. A medium-strength band of δ(H−O−H) is also present at about 1650 cm^{-1} in complexes **1** and **3**; the strong absorption at 1286 cm^{-1} in complex **2** is attributed to the C−O vibration of the EtO group. The main feature in the infrared spectra of complexes **1−4** is the absence of a band in the region 2550−2430 cm^{-1}, which appear in the free ligand as the ν(S−H) vibration. In complexes **1** and **2**, the absorption at 1210 cm^{-1} is assigned to the C=S vibration[31] and the new medium-strength band at 445 cm^{-1} for **1** and 480 cm^{-1} for **2** is assigned to the Sn−N stretching,[32] both of which indicate that the $(dmt)^{2-}$ coordinates to tin through its nitrogen atoms as tautomer **c**. The strong absorptions at 597 cm^{-1} for **1** and 627 cm^{-1} for **2** are assigned to Sn−O−Sn stretching. In the far-infrared spectra a strong absorption at 317 cm^{-1} for **3** and 321 cm^{-1} for **4**, which are absent in the spectrum of the ligand, are assigned to the Sn−S stretching vibration. These values are consistent with those reported for a number of organotin(IV) sulfur derivatives.[16,33] The ν(Sn−Cl) absorption at 277 cm^{-1} in complex **4** is close to that found in trichloromethylbis(imidazole)tin·H_2O (275 cm^{-1}).[34] The middle-intensity bands observed at 1635 cm^{-1} in complexes **3** and **4** are assignable to ν(C=N) according to the literature,[35] which suggests that the coordination of dmt to tin is through the sulfur atoms of the thiol tautomer **a**, as reported previously.[36]

NMR Spectra

In the ^{1}H NMR spectra of complexes **1−4** the signal at δ = 1.6 ppm for the -SH protons of the ligand are absent, thus demonstrating that the ligand is deprotonated.

In the ^{13}C NMR spectra of complexes **1−4** the chemical shifts of the signals 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 H_2dmt are seen; these data reflect the differences between the thiol-C and thione-C atoms. The thiol-to-thione evolution is responsible for the marked deshielding of thione-C,[37] which further proves that the coordination between complexes **1**, **2** and **3**, **4**.

For the methyl derivatives **1** and **3**, substitution of the $^{2}J_{^{119}\mathrm{Sn},^{1}}$ (83.2 and 78.1 Hz, respectively) and $^{1}J^{119}{}_{\mathrm{Sn},}{}^{13}\mathrm{C}$ values (618.4 and 595.0 Hz, respectively) into the corresponding Lockhart−Manders equations[38] (empirical relationship between the coupling constants and the C−Sn−C angle) gives C−Sn−C angles of 135.0° and 131.5° for complex **1** and 128.5° and 129.0° for complex **3**. These values indicate that the data are reliable.

The ^{119}Sn chemical shifts of tin complexes appear to depend not only on coordination number, but also on the type of donor atoms bonded to the metal ion.[39] As reported in the literature,[40] chemical shifts in the range $\delta = -210$ to

−400 ppm, −90 to −190 ppm and 200 to −60 ppm have been associated with six-, five- and four-coordinate tin centers, respectively. The value of $\delta = -121.2$ ppm for complex **1**, $\delta = -179.6$ ppm for **2** and $\delta = -187.8$ ppm for **4** are within the range expected for five-coordinate complexes. The chemical shift for complex **3** in $CDCl_3$ indicates a change to a lower coordination than in the solid state, as the value of $\delta = -83.6$ ppm seems to indicate tetracoordination (Me_2S_2)[41] instead of hexacoordination. This change could be explained by the rupture of the weak Sn−N bonds in solution, these bonds being longer than those in other previously published complexes with S,N ligands.[42]

Experimental Section

Materials and Methods: Dimethyltin dichloride (Aldrich) and 2,5-dimercapto-1,3,4-thiadiazole (H_2dmt) were used as received. Dibenzyltin dichloride was prepared by a standard method reported in the literature.[43] The melting points were obtained with a Kofler micro melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H, ^{13}C and ^{119}Sn spectra were recorded on a Bruker AMX-300 spectrometer operating at 300, 75.3 and 111.9 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ^{13}C spectra are broadband proton decoupled. The chemical shifts are reported in ppm with respect to the references (external tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR and neat tetramethyltin for ^{119}Sn). Elemental analyses were performed with a PE-2400II apparatus.

[{$C_2S_3N_2(CH_3)_2Sn$}$_2$O$(CH_3)_2$Sn$(OH)_2$]·1.5H_2O (1): Sodium ethoxide (0.136 g, 2 mmol) was added to a solution of 2,5-dimercapto-1,3,4-thiadiazole (0.150 g, 1 mmol) in 95% ethanol (25 mL) and the mixture was stirred for 30 min. $(CH_3)_2SnCl_2$ (0.659 g, 3 mmol) was then added to the mixture, continuing the reaction for 10 h at 40 °C. After cooling to room temperature, the mixture was filtered and the solvent was gradually removed by evaporation under vacuum to give the solid product. The solid was then recrystallized from ethanol to give colorless crystals of **1**. Yield, 80%. m.p. > 220 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3410 (s, O−H), 2923 (m, C−H), 1210 (w, C=S), 561 (m, Sn−C), 597 (s, Sn−O−Sn), 445 (m, Sn−N) cm^{-1}. ^{1}H NMR ($CDCl_3/D_2O$, 300 MHz): δ = 5.15 (s, 2 H, O−H), 0.96 (s, 18 H, CH_3, $^{2}J_{^{119}Sn,^{1}}$ = 83.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 173.2 (C-1), 173.2 (C-1′), 6.3 [CH_3, $^{1}J_{^{119}Sn,^{13}C}$ = 618.4 Hz] ppm. ^{119}Sn NMR ($CDCl_3$): δ = −121.2 ppm. $C_8H_{23}N_2O_{4.5}S_3Sn_3$ (671.53): calcd. C 14.31, H 3.45, N 4.20; found C 14.34, H 3.42, N 4.17.

[{$C_2S_3N_2(PhCH_2)_2Sn$}$_2$O$(PhCH_2)_2$Sn(OH)(OEt)] (2): The synthesis procedure was the same as complex **1**. H_2dmt (0.150 g, 1 mmol), sodium ethoxide (0.272 g, 4 mmol), and $(PhCH_2)_2SnCl_2$ (1.116 g, 3 mmol) in 95% ethanol (30 mL); reaction time 10 h; temperature 40 °C. Recrystallized from ethanol as colorless crystals. Yield, 89%. m.p. >200 °C(dec.). IR (KBr): $\tilde{\nu}$ = 3420 (O−H), 3021 (w, Ph−H), 2923 (m, C−H), 1631, 1597, 1491, 1451 (m, Ph), 1286 (s, C−O), 561 (m, Sn−C), 627 (s, Sn−O−Sn), 513 (s, Sn−OR), 480 (m, Sn−N). ^{1}H NMR ($CDCl_3$): δ = 7.15−7.56 (m, 30 H, Ph), 5.15 (s, 1 H, O−H), 3.75 [q, $^{3}J(^{119}Sn-^{1}H)$ = 5.8 Hz, 2 H, O−CH_2], 2.28 (m, 12 H, CH_2−Ph, $^{2}J_{^{119}Sn,^{1}}$ = 86 Hz,), 1.25 [t, $^{4}J(^{119}Sn-^{1}H)$ = 1.2 Hz, 3 H, CH_3] ppm. ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 173.4 (C-1), 173.4 (C-1′), 37.5 [CH_2−Ph, $^{1}J_{^{119}Sn,^{13}C}$ = 624.1 Hz], 127.4 (*m*-C), 128.2 (*p*-C), 129.3 (*o*-C), 135.2 (*i*-C) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −179.6 ppm. $C_{46}H_{48}N_2O_3S_3Sn_3$ (1129.1): calcd. C 48.93, H 4.29, N 2.48; found C 48.82, H 4.28, N 2.50.

[$(CH_3)_2Sn(C_2N_2S_3)]_5$·CH_2Cl_2·3H_2O (3): The reaction was carried out under nitrogen atmosphere with use of standard Schlenk techniques. H_2dmt (0.30 g, 2 mmol) was added to a solution of dichloromethane (40 mL) and sodium ethoxide (0.272 g, 4 mmol), and the mixture was stirred for 30 minutes. $(CH_3)_2SnCl_2$ (0.439 g, 2 mmol) was then added to the mixture, continuing the reaction for 16 h at 30 °C. After cooling to room temperature the mixture was filtered. The solvent of the filtrate was gradually removed by evaporation under vacuum until a solid product was obtained. The solid was then recrystallized from dichloromethane/ethanol (95%) to give colorless crystals of **3**. Yield, 72%. m.p. > 240 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3430 (s, O−H), 2923 (m, C−H), 1635 (m, C=N), 701 (s, C−S), 563 (m, Sn−C), 317 (m, Sn−S) cm^{-1}. ^{1}H NMR ($CDCl_3/D_2O$): δ = 0.95 [t, 30 H, CH_3, $^{2}J_{^{119}Sn,^{1}}$ = 78.1 Hz] ppm. ^{13}C NMR ($CDCl_3$): δ = 168.0 (C-1), 168.0 (C-1′), 5.8 [CH_3, $^{1}J_{^{119}Sn,^{13}C}$ = 595.0 Hz]. ^{119}Sn ($CDCl_3$): δ = −83.6 ppm. $C_{26}H_{38}Cl_2N_{10}O_3S_{15}Sn_5$ (1683.9): calcd. C 18.55, H 2.27, N 8.32; found C 18.52, H 2.25, N 8.31.

[$(PhCH_2)_2$SnCl(S-C_2SN_2-S)SnCl$(PhCH_2)_2$] (4): The synthesis procedure was the same as that of complex **3**. H_2dmt (0.30 g, 2 mmol) was added to a solution of dichloromethane (40 mL) and sodium ethoxide (0.272 g, 4 mmol), and the mixture was stirred for 30 minutes. $(PhCH_2)_2SnCl_2$ (0.744 g, 2 mmol) was then added; reaction time 16 h; temperature 30 °C. Recrystallized from ether/dichloromethane. M.p. 196−198 °C. Yield, 72%. IR (KBr): $\tilde{\nu}$ = 1635 (C=N), 701 (s, C-S), 561 (m, Sn−C), 321 (m, Sn−S), 277 (m, Sn−Cl) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.32−7.86 (m, 20 H, aromatic-H), 3.26 [s, 8 H, CH_2−Ph, $^{2}J_{^{119}Sn,^{1}}$ = 79.0 Hz] ppm. ^{13}C NMR ($CDCl_3$): δ = 168.5 (C-1), 168.5 (C-1′), 38.5 (CH_2−Ph, $^{1}J_{^{119}Sn,^{13}C}$ = 546 Hz), 125.4 ($^{4}J_{^{119}Sn,^{13}C}$ = 30 Hz, *m*-C), 127.0 ($^{5}J_{^{119}Sn,^{13}C}$ = 26 Hz, *p*-C), 130.5 ($^{3}J_{^{119}Sn,^{13}C}$ = 44 Hz, *o*-C), 139.0 ($^{2}J_{^{119}Sn,^{13}C}$ = 36 Hz, *i*-C) ppm. ^{119}Sn NMR ($CDCl_3$): δ = −187.8 ppm. $C_{30}H_{28}Cl_2N_2S_3Sn_2$ (821): calcd. C 43.89, H 3.43, N 3.07; found C 43.86, H 3.40, N 3.05.

Crystal Structures of Complexes 1, 2 and 3: All X-ray crystallographic data were collected on a Bruker SMART-1000-CCD diffractometer. A 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. All data were collected at 298(2) K using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) 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 the hydrogen atoms were calculated, and their contributions in structural factor calculations were included. Table 4 lists the crystal data and structure refinement parameters.
CCDC-215777 (for **1**), -183604 (for **2**) and -215778 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of the charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank the National Natural Science Foundation of China (20271025) and the Natural Science Foundation of Shandong Province for financial support.

Table 4. Crystal data and structure refinement parameters for **1**, **2** and **3**

Empirical formula	$C_8H_{23}N_2O_{4.5}S_3Sn_3$	$C_{46}H_{48}N_2O_3S_3Sn_3$	$C_{26}H_{38}Cl_2N_{10}O_3S_{15}Sn_5$
Formula mass	671.53	1129.11	1683.91
Temperature (K)	298(2)	293(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pcca*	$P2_1/c$	$P2_1/n$
a (Å)	27.831(15)	20.036(3)	15.856(5)
b (Å)	11.259(6)	23.284(3)	15.207(5)
c (Å)	14.492(8)	22.212(3)	25.173(8)
β (°)	90	114.523(2)	103.611(5)
V (Å^3)	4541(4)	9427(2)	5899(3)
Z	8	8	4
D_c (Mg·m^{-3})	1.964	1.591	1.896
μ (mm^{-1})	3.562	1.750	2.746
F(000)	2552	4480	3248
Crystal size (mm)	0.29 × 0.20 × 0.13	0.40 × 0.30 × 0.20	0.32 × 0.18 × 0.12
θ limits (°)	2.72–25.03	1.33–24.83	2.68–25.03
Index ranges	$-30 \le h \le 33$	$-23 \le h \le 23$	$-11 \le h \le 18$
	$-13 \le k \le 13$	$-18 \le k \le 27$	$-18 \le k \le 18$
	$-17 \le l \le 16$	$-26 \le l \le 24$	$-29 \le l \le 27$
Max., min. transmission	0.6546,0.4248	0.7210,0.5412	0.7340,0.4736
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Reflections collected	22346	48195	30356
Unique reflections	3989 (R_{int} = 0.0686)	16226 (R_{int} = 0.0546)	10294 (R_{int} = 0.0675)
Data, restraints, parameters	3989, 6, 194	16226, 0, 1031	10294, 9, 522
Goodness of fit on F^2	0.914	1.000	0.824
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0420, $wR_2$0.0914	R_1 = 0.0500, wR_2 = 0.1195	R_1 = 0.0472, wR_2 = 0.0920
R indices (all data)	R_1 = 0.0913, wR_2 = 0.1094	R_1 = 0.1204, wR_2 = 0.1537	R_1 = 0.1334, wR_2 = 0.1139
Largest peak, hole difference (e·Å^{-3})	0.616, −0.483	0.875, −0.696	0.960, −0.867

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Received November 22, 2003
Early View Article
Published Online April 26, 2004

