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Dimeric dithiocarbamates of stannolane. An example of the presence of secondary bonds in the formation of an inorganic ring. Molecular and crystal structure of 2-^{n}butyl-2-(dimethyldithiocarbamate)-1,3,2-oxathiastannolane and 2-^{n}butyl-2-(piperidyldithiocarbamate)-1,3,2-oxathiastannolane

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Abstract

Two dithiocarbamate derivatives of stannolane, 2-^{n}butyl-2-(dimethyldithiocarbamate)-1,3,2-oxathiastannolane and 2-^{n}butyl-2-(piperidyldithiocarbamate)-1,3,2-oxathiastannolane have been obtained and full characterized. The X-ray single crystal diffraction studies show the presence of a dimer arrangement, through the formation of an inorganic ring. The bond lengths between the tin and all the S and O atoms are in the middle of covalent and secondary bonds, with a remarkable preference toward oxygen atoms. Both oxathiastannolane units present in solid state an equilibrium between conformations, while the arrangement of the three fused rings (oxathiastannolane–distannoxane–oxathiastannolane) is almost planar. © 2002 Published by Elsevier Science B.V.

Keywords: X-ray structure; 1,3,2-Oxathiastannolane; Distannoxane; Dithiocarbamate; Tin(IV)

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1. Introduction

It is known that tin(IV) compounds have the ability to increase their coordination number above 4 [1]. Recently Haiduc [2] suggested that when the preferred coordination number of the central metal in inorganic Main Group compounds is larger than the number of coordination sites occupied by the organic groups and the donor ligands, self-organized supramolecular associations may occur. Some factors that have been related to this behavior are the electronegativity of the ligands around the metallic center [3], the bulky effect of the ligands [4] and the bond angles [5].

In 1,3,2-dioxa, 1,3,2-dithia and 1,3,2-oxathiastannolane systems, these effects are combined to obtain supramolecular associations, in accordance with previous structural studies, the intermolecular interactions are able to stabilize since a dimer system until a polymeric one [6–11].

In this work we present the synthesis and X-ray studies of two dithiocarbamate 1,3,2-oxathiastannolane compounds where secondary interactions exist in the bidentate coordination of dithiocarbamate ligand and in the formation of the inorganic ring. The relation in dihedral angles between the three rings formed shows that the arrangement is almost planar and not staircase or ladder as is usual for compounds with the very common distannoxane unit [8,12–16].

2. Experimental

All operations were carried out under argon atmosphere using standard vacuum line techniques. Solvents were dried by conventional procedures and distilled prior to use. Chemicals of commercial grade were

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purchased from Aldrich and were used as supplied. ^{1}H and ^{13}C spectra were obtained using a Varian Unity spectrometer (299.94 and 75.42 MHz, respectively) in $CDCl_3$ at 20 °C. ^{119}Sn spectra were obtained using a JEOL Unity spectrometer (112.07 MHz) and were processed by Single Exponential Automatic adjustment in $CDCl_3$ at 20 °C. The EI–MS data were collected from a JEOL JMS-AX505HA (70 eV) Unity. Microanalyses were conducted by Galbraith Laboratories (Knoxville, TN).

2.1. Synthesis

The butyltin hydroxide oxide hydrate (**1** 940.2 mg, 4.277 mmol; **2** 626.8 mg, 2.852 mmol) was refluxed 24 h in benzene with 2-mercaptoethanol in a molar ratio 1:1. After that time, a molar amount of the corresponding dithiocarbamate sodium salt (**1** 612 mg, 4.277 mmol; **2** 521.8 mg, 2.852 mmol) was added to the solution and stirred for 1 h (Fig. 1). The solvent was removed by low-pressure distillation, and hexane for crystallization was added. Colorless crystals were obtained by a diffusion crystallization system methylene chloride–hexane. The compounds are stable at room conditions in solid state.

2.1.1. 2-^{n}Butyl-2-(dimethyldithiocarbamate)-1,3,2-oxathiastannolane (*1*)

Mp 162 °C, yield 20.1% (320 mg). Anal. Calc. for $C_9H_{19}NOS_3Sn$: C, 29.05; H, 5.15. Found: C, 28.70; H, 5.20. MS (E.I.+), *m/z*: 316 $[C_5H_{10}NOS_3Sn]^+$, 297 $[C_7H_{15}NS_2Sn]^+$, 240 $[C_3H_6NS_2Sn]^+$, 197 $[C_2H_5OSSn]^+$. IR Data (KBr pellet) cm^{-1}: 2954, 2918, 2851, 1527, 1393, 1277, 1249, 1047, 1010, 978, 571 (Fig. 2).

2.1.2. 2-^{n}Butyl-2-(piperidyldithiocarbamate)-1,3,2-oxathiastannolane (*2*)

Mp 137 °C, yield 31.9% (356 mg). Anal. Calc. for $C_{12}H_{23}NOS_3Sn$: C, 34.96; H, 5.62. Found: C, 34.6; H, 5.7 MS (E.I.+), *m/z*: 356 $[C_8H_{14}NOS_3Sn]^+$, 337 $[C_{10}H_{19}NS_2Sn]^+$, 280 $[C_6H_{10}NS_2Sn]^+$, 197 $[C_2H_5OSSn]^+$. IR Data (KBr pellet) cm^{-1}: 2943, 2918, 2853, 1499, 1441, 1279, 1240, 1047, 1007, 977, 571 (Fig. 3).

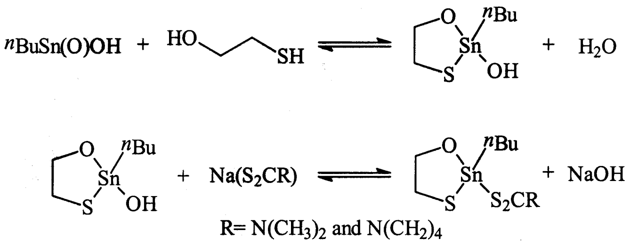


Fig. 1. Reaction scheme for 1,3,2-oxathiastannolane derivatives.

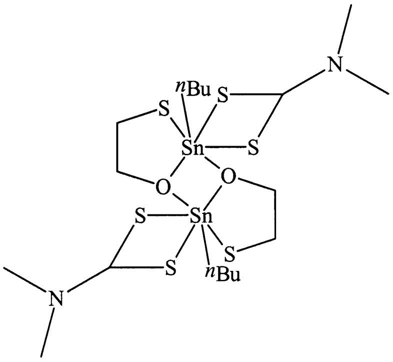


Fig. 2. Scheme for [2-^{n}butyl-2-(dimethyldithiocarbamate)-1,3,2-oxathiastannolane] **1**.

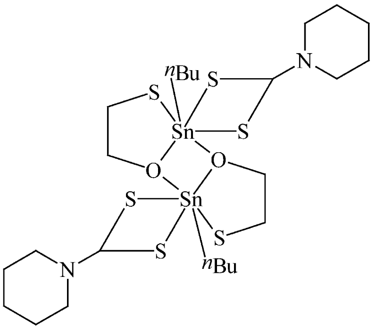


Fig. 3. Scheme for [2-^{n}butyl-2-(piperidyldithiocarbamate)-1,3,2-oxathiastannolane] **2**.

2.2. X-ray measurements

Crystallographic data are summarized in Table 1. Colorless crystals were mounted on a Siemens P4/PC diffractometer at 293(2) K using graphite monochro-

Table 1
Crystal data and refinement details for compounds **1** and **2**

	Compound **1**	Compound **2**
Empirical formula	$C_{18}H_{38}N_2O_2S_6Sn_2$	$C_{24}H_{46}N_2O_2S_6Sn_2$
Formula weight	744.24	824.36
Size (mm)	0.40 × 0.34 × 0.16	0.30 × 0.20 × 0.10
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a (Å)	11.613(2)	12.030(3)
b (Å)	12.279(2)	13.277(3)
c (Å)	11.693(2)	12.087(5)
β°	116.42(1)	116.49(2)
V (Å^3)	1493.2(4)	1727.9(9)
Z	2	2
μ (cm^{-1})	21.09	18.31
Reflections collected	2763	3195
Independent reflections	2627 ($R_{int} = 0.0425$)	3044 ($R_{int} = 0.0700$)
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0408$, [a] $wR_2 = 0.0924$ [b]	$R_1 = 0.0434$, $wR_2 = 0.0942$
GooF (*S*)	0.864	0.833

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

matic Mo-Kα radiation (0.71073 Å). The data were collected for XSCANS 2.1 program and the structures were solved by SHELXL-97 [17] and refined by full-matrix least-squares on F^2. Hydrogen atoms were not refined. Selected bond lengths, bond angles and torsion angles for **1** and **2** are listed in Table 3.

3. Results and discussion

3.1. ^1H and ^{13}C

The ^1H, ^{13}C and ^{119}Sn data for compounds **1** and **2** are collected in Table 2.

The assignment for proton and the corresponding carbon atoms in both compounds was made by DEPT and HETCOR experiments.

For compound **1**, the $-SCH_2CH_2O-$ fragment occurs as two broad signals in 3.980 (2H) and 2.947 (2H) ppm associated by a Hetcor experiment with two carbon signals in 64.473 and 33.068 ppm respectively. The assignments are attributed to $-CH_2O-$ and the $-CH_2S-$ moiety in accordance with chemical shift. Correspondence between the triplet at 0.931 ppm (3H) for the methyl protons in the butyl group and the singlet at 3.404 (6H) ppm for the methyl protons in the methyl dithiocarbamate with the carbon signals at 13.578 and 45.918 ppm first assignment by DEPT was confirmed by Hetcor experiment.

The assignment of the butyl fragment is made under the consideration that the carbon nuclei attached to electropositive tin(IV) atom is expected to experience a shielding effect [11]. Two methylene proton broad signals centered in 1.767 and 1.440 ppm (6H) are correlated with three independent carbon atoms α, β and γ to tin in 27.751, 30.745 and 25.987 ppm. No remarkable differences are observed between compounds **1** and **2** in ^1H and ^{13}C resonance of the $-SCH_2CH_2O-$ moiety and butyl group. About the dithiocarbamate fragment, there are three carbon signals corresponding with α 53.832 ppm, β 25.615 ppm and γ 22.645 ppm carbon atoms to N(1) corresponding in the Hetcor spectrum with two proton signals, one in 3.893 ppm (4H) for α hydrogens and other for β and γ in 1.731 ppm (6H) respectively.

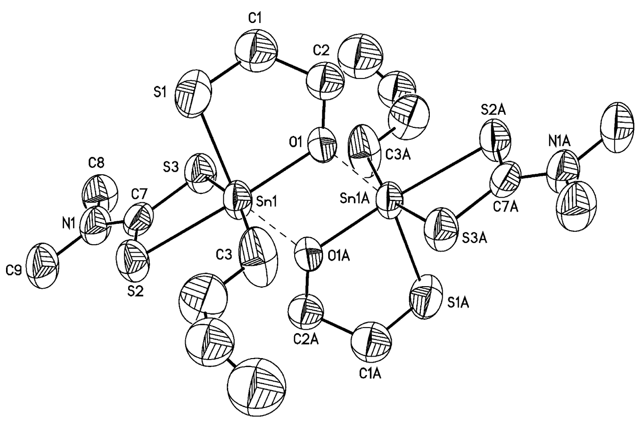
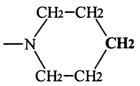
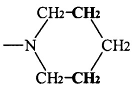
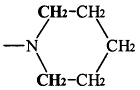


Fig. 4. ORTEP plot of [2-^{n}butyl-2-(dimethyldithiocarbamate)-1,3,2-oxathiastannolane] **1**. The atoms were drawn with 50% probability ellipsoids. Hydrogen and disordered carbon atoms are omitted by clarity.

Table 2
NMR results for compound **1** and **2** in $CDCl_3$

moiety	Compound **1**		Compound **2**	
	^{119}Sn		^{119}Sn	
Sn	-251.11		-230.66	
	^1H	^{13}C	^1H	^{13}C
$SnCH_2CH_2CH_2\mathbf{CH_3}$	0.931 (t) 3H	13.578	0.935 (t) 3H	13.590
$SnCH_2CH_2\mathbf{CH_2}CH_3$	1.440 (bs) 2H	25.987	1.448 (q) 2H	25.995
$SnCH_2\mathbf{CH_2}CH_2CH_3$	1.767 (bs) 4H	30.745	1.793 (bs) 4H	29.936
$Sn\mathbf{CH_2}CH_2CH_2CH_3$		27.751		27.784
$-S\mathbf{CH_2}CH_2O-$	2.947 (bs) 2H	33.068	2.938 (bs) 2H	33.351
$-SCH_2\mathbf{CH_2}O-$	3.980 (bs) 2H	64.473	3.979 (bs) 2H	64.700
$-N(\mathbf{CH_3})_2$	3.404 (s) 6H	45.918		
			1.731 (bs) 6H	22.645
				25.615
			3.893 (bs) 4H	53.832
$-CS_2-$		198.35		195.137

bs: broad signal; q: quartet; s: singlet; t: triplet.

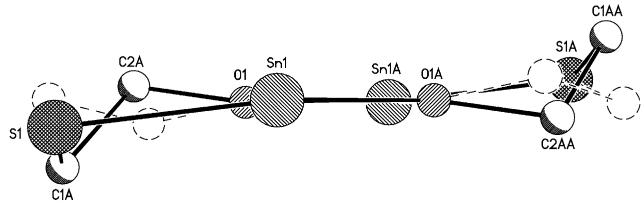


Fig. 5. ORTEP plot of [2-^{n}butyl-2-(piperidyldithiocarbamate)-1,3,2-oxathiastannolane] **2.** The atoms were drawn with 50% probability ellipsoids. Hydrogen and disordered carbon atoms are omitted for clarity.

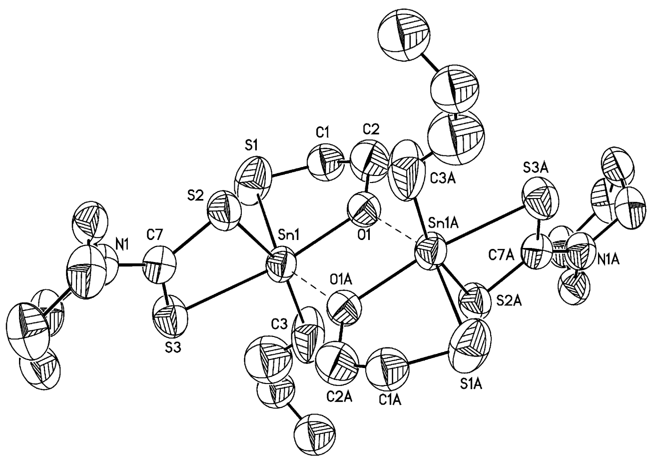


Fig. 6. ORTEP plot of relation between the three fused rings for compound **1**. Disordered carbon atoms are shown as dotted lines.

3.2. ^{119}Sn spectra

Both compounds are monomeric in solution because no coupling constant $^2J(^{119-117}\text{Sn}-^{119-117}\text{Sn})$ were observed. The values obtained from ^{119}Sn spectra for compound **1** (−251.11 ppm) and **2** (−230.66 ppm) are in agreement with a five coordination number [18–20]; this number is easily explained if both ligands were on a bidentate pattern linked at the tin atom.

3.3. Description of the structures

The atom numbering schemes are illustrated in Figs. 4 and 6 for the single-crystal X-ray structures of **1** and **2** respectively. Selected bond lengths and angles are listed in Table 3.

The molecular structure of compound **1** is dimeric, connected through a Sn(1)–O(1a) secondary interaction forming a distannoxane unit. The central atom is also attached by a butyl group (Sn(1)–C(3) 2.163(7)) with a length slightly larger than normal covalent distance [2,21], and two bidentate ligands asymmetrically bonded raising the coordination number to six. A preference of coordination is observed for oxygen over sulfur as donor atom when distances are compared. While Sn(1)–O(1) distance is shorter than the sum of covalent radii (2.111(4) Å), three Sn–S secondary interactions are found: Sn(1)–S(1) 2.466(3) Å, Sn(1)–S(2) 2.6043(19) Å and Sn(1)–S(3) 2.6379(19) Å. The geometry around the tin(IV) atom is highly distorted octahedral due to constraints imposed for the three ring systems around the center (stannolane, distannoxane and bidentade dithiocarbamate ligand).

Table 3
Selected bond lengths (Å), angles (°) and torsion angles (°) for **1** [a] and **2** [a]

	Compound **1**	Compound **2**
Bond lengths		
Sn(1)–S(1)	2.466(3)	2.479(2)
Sn(1)–S(2)	2.6046(19)	2.606(2)
Sn(1)–S(3)	2.6379(19)	2.615(2)
Sn(1)–C(3)	2.163(7)	2.152(9)
Sn(1)–O(1)	2.111(4)	2.117(5)
Sn(1)–O(1a)	2.180(5)	2.189(5)
Bond angles		
S(2)–Sn(1)–S(3)	68.24(6)	68.29(6)
S(1)–Sn(1)–S(3)	91.51(8)	101.98(9)
S(1)–Sn(1)–S(2)	101.87(8)	94.14(9)
O(1)–Sn(1)–S(3)	90.95(14)	160.50(16)
O(1)–Sn(1)–S(2)	158.61(15)	92.56(15)
O(1)–Sn(1)–S(1)	82.83(15)	82.35(15)
C(3)–Sn(1)–S(3)	161.1(3)	93.5(3)
C(3)–Sn(1)–S(2)	95.9(2)	157.3(4)
C(3)–Sn(1)–S(1)	102.3(3)	103.1(4)
C(3)–Sn(1)–O(1)	103.5(2)	104.1(3)
O(1a)–Sn(1)–S(3)	82.77(14)	102.40(14)
O(1a)–Sn(1)–S(2)	101.65(13)	82.32(14)
O(1a)–Sn(1)–S(1)	151.67(13)	152.00(15)
O(1a)–Sn(1)–O(1)	69.6(2)	70.1(2)
O(1a)–Sn(1)–C(3)	90.7(3)	88.9(4)
Torsion angles		
S(1)–Sn(1)–O(1)–C(2a)	16.0 (8)	−9.4(7)
S(1)–Sn(1)–O(1)–C(2b)	−6.5(9)	
O(1)–Sn(1)–S(1)–C(1a)	17.1(7)	24.3(7)
O(1)–Sn(1)–S(1)–C(1b)	−10.3(7)	−5.9(7)

[a] Symmetry tranformations used to generate equivalent atoms: **1**, $x+1$, $-y$, $-z+2$; **2**, x, $-y$, $-z+1$.

The methylene groups in the stannolane ring exhibit a dynamic equilibrium between two half-chair conformations (torsion angles in Table 3) with C(1) in a width range of mobility with respect to the carbon atom linked to O(1). The relation between the three fused rings (two oxathiastannolane and distannoxane rings) is almost planar in accord with the close angles obtained between the planes (i) and (ii), 7.3(4)° and (i) and (iii), 7.2(4)° defining the planes (i) Sn(1)–O(1)–Sn(1a)–O(1a), (ii) S(1)–Sn(1)–O(1)–C(2a) and (iii) S(1)–Sn(1)–O(1)–C(2b) whose mean deviations are 0.0, 0.0968 and 0.0331 Å, respectively (Fig. 5).

The piperidyl derivative **2** is also a dimer and the center tin atom six-coordinated, presents some differences on the coordination sphere in regard to compound **1** described as follows. The coordination of the oxygen and sulfur atoms in the stannolane ring presents

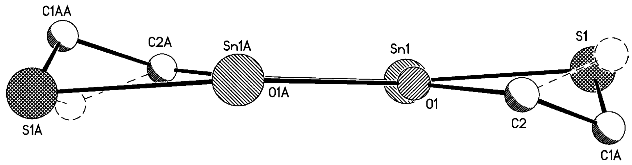


Fig. 7. ORTEP plot of relation between the three fused rings for compound **2**. Disordered carbon atoms are shown as dotted lines.

elongation in both bonds (Sn(1)–O(1) 2.117(5) Å and Sn(1)–S(1) 2.479(3) Å) and the sulfur atoms of the dithiocarbamate fragment are symmetrically linked (Sn(1)–S(2) 2.606(2) Å and Sn(1)–S(3) 2.615(2) Å). The geometry around the tin(IV) atom is distorted octahedral where the central atom is 0.2059 Å out of the plane (O(1)–S(3)–S(2)–C(3), mean deviation plane 0.2059 Å).

The oxathiastannolane ring presents an envelope conformation, the carbon attached to sulfur is disordered above or below the plane of the other four atoms of the ring. The angle between the plane formed by S(1)–Sn(1)–O(1)–C(2) (mean deviation from plane 0.0524 Å) and the distannoxane is just 5.1(3)°, showing an almost planar arrangement (Fig. 7).

A relaxation in the strain of the internal distannoxane angle is observed when compounds are compared (O(1)–Sn(1)–O(1a) **1**, 69.6(2)°; **2**, 70.1(2)° and can be clearly related to the elongation of the Sn–O bonds (**1** Sn(1)–O(1) 2.111(4) Å and Sn(1)–O(1a) 2.180(5) Å; **2** Sn(1)–O(1) 2.117(5) Å and Sn(1)–O(1a) 2.189(5) Å).

4. Conclusions

The effect of the electronegative attached atoms and the angles imposed by the ring systems promoted the secondary interactions and the dimer arrangement is observed in solid state compared in solution where mononuclear compounds observed.

In general, a preference of Sn–O over Sn–S bond is observed [8] in solid state, where bonds Sn–O are in the range of covalent bonds while Sn–S links are all larger than the covalent radii sum but shorter than the van der Waals radii sum.

The small angles between rings (**1** 7.24(36)° average of angles, **2** 5.11(27)°) show an almost planar arrangement of the three fused rings.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 166875 for compound **1** and CCDC no. 166876 for compound **2**. Copies of the available material can be obtained, free of charge, on application to CDCC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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