

Structures, semi-empirical calculations and thermolyses of some five- and six-membered chelate organotin mercaptide complexes

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Abstract

Characterization of $\text{Ph}_2\text{Sn}(\text{Cl})(\text{MBT})$ (**1**) (HMBT = 2-mercaptobenzothiazole) has been carried out by IR, Mössbauer, ^1H , ^{13}C and ^{119}Sn spectroscopies and by X-ray crystallography for **1** together with that of $\text{Ph}_2\text{Sn}(\text{SCH}_2\text{CH}_2\text{S})$ (**2**). Compound **1**, unexpectedly obtained from the reaction between Ph_2SnCl_2 and KMBT in a 1:2 mole ratio, has a trigonal-bipyramidal geometry, due to intramolecular Sn–N interactions, both in the solid state and in solution; the axial sites are occupied by N and Cl, $\text{N}(24)\text{–Sn–Cl}(4) = 155.27(17)^\circ$, the chelate bite angle, $\text{N}(24)\text{–Sn–S}(15)$, is $64.65(17)^\circ$. Compound **2** is essentially monomeric in the solid state and has a distorted tetrahedral structure; the bond angles at tin vary from $92.50(16)^\circ$ [$\text{S}(2)\text{–Sn–S}(5)$] to $116.4(6)^\circ$ [$\text{C}(6)\text{–Sn–C}(12)$]. The shortest intermolecular Sn \cdots S contact in **2** is 3.885 Å, just within the sum of the van der Waals' radii for Sn and S (4.0 Å). PM3 semi-empirical calculations for **2** indicated that the geometry at the tin center can be accounted for by a high degree of p-character in the tin bonding orbitals to sulfur; PM3 semi-empirical calculations on $\text{Ph}_2\text{Sn}(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})$ (**3**) indicated the geometry at tin to be less distorted from tetrahedral, with a S–Sn–S angle of 99° ; the calculations further indicated that the only stable conformation of the six-membered ring in **3** is the chair form. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Organotin mercaptides; Dithiolates; X-ray structure; Semi-empirical calculations

1. Introduction

Interest in complexes, which incorporate thiolate ligands, has been generated for various reasons. Among these are their relevance to biological systems [1], the potential in C–S bond cleavages and in de-sulfurizations [2], and their use as precursors of ceramic materials [3]: Boudjouk et al. have shown, for example, that

pyrolysis of phenyltin chalcogenides produced SnS [4,5]. We have initiated a study of diorganotin dimer-captides as SnS and/or SnS₂ precursors. This report is concerned with diphenyltin derivatives of the thiolato compounds shown in Fig. 1. The ligand HMBT was chosen in order to determine the effect of using a thiolate, containing an additional N-donor site.

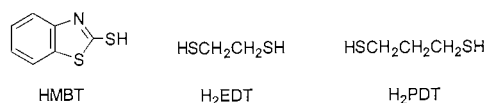


Fig. 1. Ligands used in the present work.

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2. Experimental

2.1. General comments

All operations were carried out under pure dinitrogen, using Schlenk and vacuum techniques. Nitrogen was predried by passing in a column consisting of molecular sieves, calcium chloride and calcium sulfate. Hexane and tetrahydrofuran were distilled from

sodium–benzophenone. All solvents were used immediately following distillation or stored under nitrogen over the appropriate molecular sieves. Ph_2SnCl_2 , ethane-1,2-dithiol (H_2EDT), propane-1,3-dithiol (H_2PDT) and 2-mercaptobenzothiazole (HMBT), from Aldrich, were used as supplied. ^{119}Sn Mössbauer spectroscopy was performed in a constant acceleration equipment moving a CaSnO_3 source kept at room temperature. The samples were cooled at liquid nitrogen temperature. All spectra were computer-fitted assuming Lorentzian lineshape. Infrared spectra were recorded on a Perkin–Elmer 283 spectrophotometer in the $4000\text{--}200\text{ cm}^{-1}$ range in Nujol mulls, on CsI plates. ^1H (200 MHz) and ^{13}C (50 MHz) NMR spectra were recorded on a Bruker AC-200 and referenced to internal SiMe_4 and ^{119}Sn (149.21 MHz) NMR spectra were recorded on a Bruker AC-400 and referenced to internal SnMe_4 . C and H analyses were performed using a Perkin–Elmer PE-2400 CHN microanalyser. Atomic absorption for tin was performed on a Hitachi Z-8200 Polarized Zeeman Atomic Absorption Spectrophotometer. TG analysis was performed on a Mettler Thermobalance TG 50 of TA 4000 System at a flow rate of $10^\circ\text{C min}^{-1}$.

2.2. Synthesis

2.2.1. Alkali metal thiolates

2.2.1.1. NaMBT . A reaction mixture of HMBT (0.400 g, 2.50 mmol) and Na (0.058 g, 2.50 mmol) in THF (20 ml) was stirred for 2 h in a Schlenk flask. To the yellow solution was added hexane; the white KMBT precipitate was collected and dried under vacuo. Yield: 90%. The product was shown to be free of the SH group by the absence of a $\nu(\text{S–H})$ stretch at 2500 cm^{-1} [6]. M.p. $> 300^\circ\text{C}$. Anal. Calc. for $\text{C}_7\text{H}_4\text{S}_2\text{NNa}$: C, 44.44; H, 2.11; N, 7.40. Found: C, 43.67; H, 2.11; N, 6.98%.

2.2.1.2. Na_2EDT . A reaction mixture of H_2EDT (0.600 g, 6.38 mmol) and NaOMe (0.700 g, 12.96 mmol) in THF (20 ml) was stirred for 1 h in a Schlenk flask. The solvent was carefully removed from the white Na_2EDT precipitate using a cannula and the solid was collected and dried under vacuo. The product was shown to be free of the SH group by the absence of $\nu(\text{S–H})$ stretch at 2500 cm^{-1} [6]. M.p. 230°C (dec). Anal. Calc. for $\text{C}_2\text{H}_4\text{S}_2\text{Na}_2$: C, 17.39; H, 2.89. Found: C, 17.27; H, 2.68%.

2.2.1.3. Na_2PDT . This was prepared in a similar manner to that described for Na_2EDT . M.p. 250°C (dec). Anal. Calc. for $\text{C}_3\text{H}_6\text{S}_2\text{Na}_2$: C, 23.68; H, 3.94. Found: C, 23.08; H, 3.92%.

2.2.2. Diphenyltin thiolates

2.2.2.1. $\text{Ph}_2\text{SnCl}(\text{MBT})$ (1). A reaction mixture of Ph_2SnCl_2 (0.30 g, 0.87 mmol) and KMBT (0.35 g, 1.71 mmol) in THF (20 ml) was refluxed in a Schlenk flask under nitrogen for 5 h, cooled and hexane added. The white precipitate of $\text{Ph}_2\text{SnCl}(\text{MBT})$ was collected as an air stable compound and was recrystallized from THF–hexane; yield 61%, m.p. $> 300^\circ\text{C}$. Anal. Found: C, 48.35; H, 2.93; N, 3.41; Sn, 22.48. Calc. for $\text{C}_{19}\text{H}_{14}\text{SnClNS}_2$: C, 48.07; H, 2.95; N, 2.95; Sn, 25.09%. IR (cm^{-1} , Nujol): $\nu(\text{C=N})$ 1620, $\nu(\text{Sn–S})$ 275. $^1\text{H-NMR}$ (δ , CDCl_3): 7.46–7.79 (m, C_6H_5). $^{13}\text{C-NMR}$ (δ , CDCl_3): 112.27, 121.37, 124.70, 127.22, 129.57 (C_6H_5), 140.2 (C=N). $^{119}\text{Sn-NMR}$ (δ , CDCl_3): -177.1 . Mössbauer (mm s^{-1}): $\delta = 0.90 \pm 0.01$, $\Delta = 1.96 \pm 0.01$.

2.2.2.2. $\text{Ph}_2\text{Sn}(\text{EDT})$ (2). This was prepared by a modification of published procedures [7]. A reaction mixture of Ph_2SnCl_2 (0.50 g, 1.45 mmol) and Na_2EDT (0.20 g, 1.45 mmol) in THF (20 ml) was refluxed in a Schlenk flask under nitrogen for 24 h, cooled and hexane added. The white precipitate of $\text{Ph}_2\text{Sn}(\text{EDT})$ was collected and recrystallized from THF–hexane; yield 57%. Anal. Found: Sn, 31.9. Calc. Sn, 32.6%. IR (cm^{-1} , Nujol): $\nu(\text{Sn–S})$ 290 and 275. $^1\text{H-NMR}$ (δ , CDCl_3): 7.76–7.32 (m, 2 C_6H_5), 3.68–3.52 (m, 2 CH_2). $^{13}\text{C-NMR}$ (δ , CDCl_3): 104.89, 112.85, 121.75, 124.99, 127.55 (C_6H_5), 18.78 (s, CH_2). Mössbauer (mm s^{-1}): $\delta = 1.38 \pm 0.01$, $\Delta = 1.56 \pm 0.01$; [lit. values [8] $\delta = 1.37$, $\Delta = 1.67$].

2.2.2.3. $\text{Ph}_2\text{Sn}(\text{PDT})$ (3). This was similarly prepared to **2** from Ph_2SnCl_2 (0.450 g, 1.32 mmol) and Na_2PDT (0.200 g, 1.32 mmol) in THF (20 ml) on refluxing in a Schlenk flask under nitrogen for 24 h; yield 53%. Anal. Found: Sn, 30.4. Calc. Sn, 31.4%. IR (cm^{-1} , Nujol): $\nu(\text{Sn–S})$ 240. $^1\text{H-NMR}$ (δ , CDCl_3): 0.84 (m, 2H, CH_2), 1.26 (s, 4H, CH_2), 7.45 (m, 10H, C_6H_5). $^{13}\text{C-NMR}$ (δ , CDCl_3): 24.7 (CH_2), 39.3 (CH_2), 129.10, 130.41, 134.74, 135.35 (C_6H_5). $^{119}\text{Sn-NMR}$ (δ , CDCl_3): 25.7. Mössbauer (mm s^{-1}): $\delta = 1.38 \pm 0.01$, $\Delta = 1.80 \pm 0.01$; [lit. values [8]: $\delta = 1.39$, $\Delta = 1.72$].

2.3. X-ray crystal structure elucidation

General operating procedures and listings of programs have been given previously [9]. Data were collected using a standard moving crystal, moving detector technique with fixed background counts at each extreme of the scan. All data were corrected for Lorentz and polarization effects, and equivalent data were then averaged to yield a unique set of intensities. An absorption correction was made, based on the measured dimensions of the crystal. The structures were solved by direct methods and Fourier techniques and refined by full-matrix least-squares. Details of crystallographic

Table 1
Summary of crystallographic data collection for complexes **1** and **2**

Empirical formula	C ₁₉ H ₁₄ ClNS ₂ Sn	C ₁₄ H ₁₄ S ₂ Sn
Formula weight	474.59	365.07
<i>a</i> (Å)	9.146(1)	6.191(1)
<i>b</i> (Å)	9.259(1)	13.000(1)
<i>c</i> (Å)	12.347(1)	17.612(2)
α (°)	74.62(1)	
β (°)	78.89(1)	
γ (°)	67.87(1)	
<i>Z</i>	2	4
<i>V</i> (Å ³)	928.77	1417.46
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ 2 ₁
Radiation	Mo-K α	Mo-K α
	(0.71073)	(0.71073)
<i>D</i> _{calc} (g cm ⁻³)	1.697	1.711
μ (cm ⁻¹)	17.411	20.680
2 θ _{max} (°)	50	45
<i>R</i> , <i>R</i> _w	0.0505, 0.0502	0.0491, 0.0453
GOF	2.220	1.838
Temperature (°C)	–165	–165
No. of parameters refined	212	154
No. reflections (collected/independent)	3560/3258	1146/1109

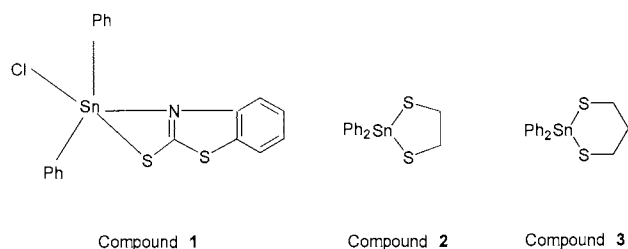


Fig. 2. Compounds studied in the present work.

data collection, structure refinement and crystal data are given in Table 1. Complex **1** crystallizes in the space group *P* $\bar{1}$. Cell constants were obtained from the refinement of 115 reflections. A total of 3560 reflections were collected of which 3258 were independent and 2717 were flagged as observed ($F > 2.33\sigma(F)$). Their reflections were collected at -165° in $2\theta-\theta$ scan mode with a scan rate of $8.0^\circ \text{ min}^{-1}$. Most hydrogen atoms were visible in a difference Fourier phased on the non-hydrogen atoms and were included in their idealized positions as fixed isotropic contributors in the final cycles of refinement. Compound **2** crystallizes in the space group *P*2₁2₁. Cell constants were obtained from the refinement of 156 reflections. A total of 1146 reflections were collected of which 1109 were independent and 999 were flagged as observed ($F > 2.33\sigma(F)$). Hydrogen atoms were readily located in a difference Fourier phased on the non-hydrogen atoms, and were included as fixed contributions in the final cycles of refinement.

3. Results and discussion

The thiolate ligands used and the complexes, **1–3**, obtained are shown in Figs. 1 and 2, respectively. The salts of the ligands could be handled in air but should be kept under an inert atmosphere because they can suffer hydrolysis in the presence of moisture, after some days. All complexes were soluble in common organic solvents like THF, toluene and CH₂Cl₂. Despite using a 1:2 mole ratio of Ph₂SnCl₂: KMBT, only one chloride was replaced in Ph₂SnCl₂, see Eq. (1):



The retention of a chloride group at tin maintains sufficient Lewis acidity at tin to allow its strong coordination with the hard internal nitrogen center in the thiolato ligand and hence formation of a relatively strong chelate complex [10]. As shown later, the presence of a chelated structure for **1**, with five-coordinate tin, in the solid state is clear from the X-ray study (and also from the Mössbauer data). The $\delta^{119}\text{Sn-NMR}$ value for **1** – 177.1 ppm in solution suggests that the Sn–N interaction probably survives in solution and that a five-coordinate species is maintained. Five-coordinate ClPh₂SnXY compounds (X and Y = electronegative groups) in solution have $\delta^{119}\text{Sn-NMR}$ values in the region – 140 to – 180 ppm, depending on the groups present, e.g. $\delta^{119}\text{Sn-NMR}$ values of -143 ± 3 and -173 ± 3 ppm for five-coordinate anions in [cation][ClPh₂Sn(dmit)] [10] and [cation][ClPh₂Sn(dmio)] [11] complexes, respectively, in solution [$\text{H}_2\text{-dmit} = 4,5\text{-dimercapto-1,3-dithiole-2-thione}$ and $\text{H}_2\text{-dmio} = 4,5\text{-dimercapto-1,3-dithiole-2-one}$]. Complexes **2** and **3** have been previously described in the literature [7]. Their syntheses appear deceptively straight forward; however serious problems were encountered in isolating pure materials from the reaction mixtures. Compound **2** was also particularly sensitive to hydrolysis, as reported by other workers [12]. As described below, the tin center in **2** is essentially four-coordinate in the solid state, from the X-ray study and from the Mössbauer spectrum [13]. The Mössbauer and $^{119}\text{Sn-NMR}$ spectra point to **3** being a four-coordinate species too.

3.1. X-ray crystal structures

Crystals of complex Ph₂Sn(Cl)(MBT) (**1**), suitable for X-ray crystallographic analysis was obtained from a hexane solution that was allowed to evaporate at room temperature. Crystals of Ph₂SnEDT, **2**, were obtained in the same way. Crystallographic data for the complexes are shown in Table 1. Selected bond lengths and bond angle parameters are presented in Tables 2 and 3 for complexes **1** and **2**, respectively. The molecular

structures and labeling schemes are shown in Figs. 3 and 4, respectively.

3.1.1. Compound 1

The geometry about tin in **1** is distorted trigonal-bipyramidal. Tin forms four primary bonds: two to the phenyl groups one to the chloride and sulfur atoms.

Table 2
X-ray selected bond distances (Å) and angles (°) for complex **1**

Bond distances			
Sn–Cl	2.443(22)	Sn–S(15)	2.485(22)
Sn–N	2.405(7)	Sn–C(2)	2.128(8)
Sn–C(8)	2.119(8)	S(15)–C(16)	1.703(9)
S(17)–C(16)	1.738(8)	S(17)–C(18)	1.767(9)
N–C(16)	1.306(11)	N–C(23)	1.397(11)
Bond angles			
Cl–Sn–S(15)	90.90(8)	Cl–Sn–N	155.27(17)
Cl–Sn–C(2)	96.72(23)	Cl–Sn–C(8)	99.71(24)
S(15)–Sn–N	64.65(17)	S(15)–Sn–C(2)	118.57(22)
S(15)–Sn–C(8)	114.08(23)	N–Sn–C(2)	92.32(28)
N–Sn–C(8)	94.0(3)	C(2)–Sn–C(8)	124.20(3)
Sn–S–C(16)	82.3(3)	C(16)–S(17)–C(18)	89.20(4)

Table 3
X-ray selected bond distances (Å) and angles (°) for complex **2**

Bond distances			
Sn–S(2)	2.424(5)	Sn–S(1)	2.408(5)
Sn–C(6)	2.147(14)	Sn–C(12)	2.155(15)
S(2)–C(4)	1.821(21)	S(1)–C(3)	1.831(18)
Bond angles			
S(2)–Sn–S(1)	92.50(16)	S(1)–Sn–C(12)	111.90(4)
S(2)–Sn–C(6)	107.20(4)	C(6)–Sn–C(12)	116.40(6)
S(2)–Sn–C(12)	111.20(5)	Sn–S(2)–C(4)	95.30(6)
Sn–S(1)–C(3)	95.70(5)	S(1)–Sn–C(6)	114.00(94)
S(2)–C(4)–C(3)	117.00(15)	C(4)–C(3)–S(1)	113.40(12)

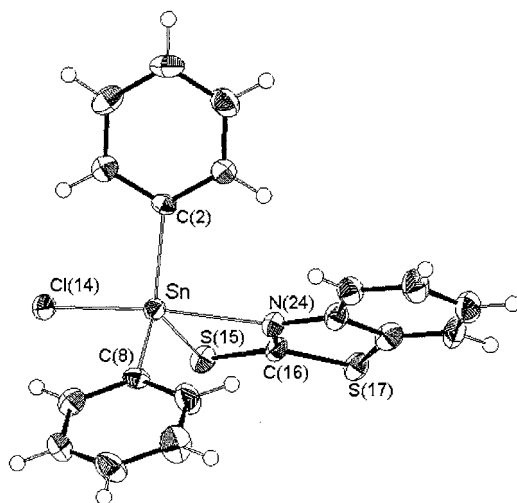


Fig. 3. Atom arrangements and numbering system for compound **1**. Probability ellipsoids drawn at 30%.

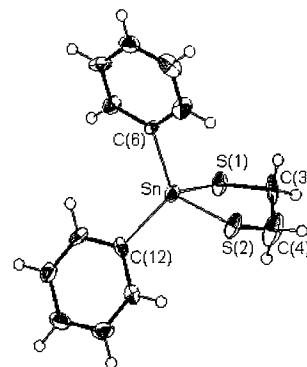


Fig. 4. Atom arrangements and numbering system for compound **2**. Probability ellipsoids drawn at 30%.

There is also an intramolecular Sn–N interaction which produces a four-membered chelate ring and a five-coordinate tin atom. The axial–Sn–axial angle, [N(24)–Sn–Cl(4) = 155.27(17)°], is well removed from the ideal trigonal-bipyramidal angle, but is strongly affected by the small bite angle. The Sn–N(24) distance, 2.4057 Å is greater than the sum of the covalent radii of Sn and N (2.15 Å), but is considerably less than the sum of the van der Waal's radii (3.75 Å) [14] and less than values reported in various five-coordinate triphenyltin heteroareneithiolates [12]; this is as expected from the differences in the Lewis acidities of tin centers in a ClPh₂Sn–thiolate and in Ph₃Sn–thiolates. The Sn–S bond length in **1** is generally also slightly longer than the Sn–S bond lengths in the five-coordinate triphenyltin heteroareneithiolates [12].

3.1.2. Compound 2

The two Sn–S bond lengths in **2** (Table 3) are shorter than the Sn–S bond length in **1**: the Sn–C bonds lengths in the expected region. The geometry about tin is distorted tetrahedral. The distortion away from ideal tetrahedral geometry is apparent from the range of bond angles at tin: –92.50(16)° [S(2)–Sn–S(1)] to 116.4(6)° [C(6)–Sn–C(12)]. Both the bond lengths and range of bond angles in **2** are similar to those in other diorganotin ethanedithiolates, R₂Sn(EDT); R = Me {89.55(3)° [S–Sn–S] to 121.73(18)° [C–Sn–C] [16], Bu {90.5° [S–Sn–S] to 122.6° [C–Sn–C] [15] and 'Bu {92.2(1)° [S–Sn–S] to 118.5(3)° [C(6)–Sn–C(12)] [18]. However, diorganotin dithiolates are coordinatively unsaturated species and will tend to extend their coordination numbers, at least in the solid state, beyond four, if steric effects allow. This is frequently achieved by intermolecular Sn–S associations [17], as for examples in Bu₂Sn(EDT) and Bu₂Sn(EDT) [17] and Me₂Sn(EDT) [16]. The closest intermolecular Sn···S distance in **2** is 3.885 Å and is just within the sum of the van der Waals' radii of Sn and S (4.0 Å) [15]. It is apparent, that the presence or absence of the additional inter-

Table 4
Semi-empirical PM3 geometrical parameters for complexes **2** and **3**

Bond distances (Å)	Complex 2		Complex 3		
	Complex 2	Complex 3	Complex 2	Complex 3	
Sn–S(2)	2.52(7)	2.52(9)	S(2)–Sn–S(1)	89	99
Sn–S(1)	2.52(8)	2.52(7)	S(2)–Sn–C(4)	112	110
Sn–C(4)	2.08(6)	2.09(2)	S(2)–Sn–C(5)	114	111
Sn–C(5)	2.08(3)	2.08(3)	S(1)–Sn–C(4)	114	111
S(2)–C(26)	1.82(4)	1.82(5)	S(1)–Sn–C(5)	112	110
S(1)–C(27)	1.82(4)	1.82(4)	C(4)–Sn–C(5)	112	111
C(26)–C(27)	1.51(5)		Sn–S(2)–C(26)	97	104
C(26)–C(32)		1.52(0)	Sn–S(1)–C(27)	97	104
Torsion angles (°)					
SnS(2)C(26)–C(27)	–41				
SnS(2)C(26)–C(32)		55			
SnS(2)C(26)–H(28)	85	175			
SnS(2)C(26)–H(29)	198	–71			
SnS(1)C(27)–C(26)	–41				
SnS(1)C(27)–C(32)		–56			
SnS(1)C(27)–H(31)	85	184			
SnS(1)C(27)–H(30)	198	71			
S(2)C(26)C(27)–S(3)	61				
S(1)C(27)C(32)–C(26)		87			
S(2)SnC(4)–C(11)	–94	2.7			
S(2)SnC(4)–C(12)	85	–177			
S(1)SnC(4)–C(11)	5.6	112			
S(1)SnC(4)–C(12)	–175	–68			
S(2)SnC(5)–C(6)	–135	–131			
S(2)SnC(5)–C(7)	45	48			
S(1)SnC(5)–C(6)	123	119			
S(1)SnC(5)–C(7)	–56	–62			
S(2)SnC(5)–C(6)	–136	–131			

molecular Sn \cdots S interactions have only a small effect on the molecular geometry of the R₂Sn(EDT) compounds. If any trend is detected it is that the greater the strength of the intermolecular Sn \cdots S interaction, i.e. the smaller the Sn \cdots S separation, the smaller is the S–Sn–S intramolecular angle. In all cases this intramolecular angle is very close to 90° and suggests the importance of p-orbitals in the bonding in these 1,2-dithiolates. As a comparison, the S–Sn–S bond angle in Ph₂Sn(SPh)₂ is 110.8(1)° [19].

3.2. Semi-empirical calculations

We could not obtain crystals of good quality of complex **3** to solve the structure by X-ray, therefore, PM3 semi-empirical calculations [20] were performed in order to determine a equilibrium molecular geometry for this complex. To allow a comparison with experimental data obtained from the X-ray investigation, PM3 semi-empirical calculations were also carried out on **2**. The data obtained for these complexes are shown in Table 4 and Fig. 5. As can be observed, Table 4, the

computed Sn–S bond distances were, on average, about 0.1 Å longer than the values obtained in the X-ray determination and the calculated S(2)–Sn–S(1) bond angle for complex **2** was 89.2°, a figure close to the value determined by X-ray, Table 3.

A Mulliken populational analysis showed that the electron density left on the s, px, py and pz tin atomic

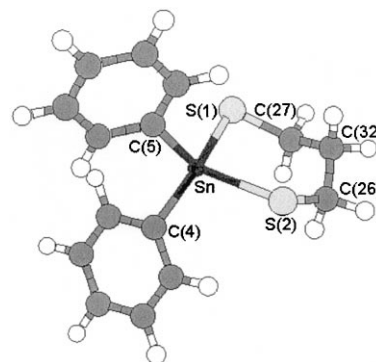


Fig. 5. Proposed molecular structure for compound **3** according to PM3 calculations.

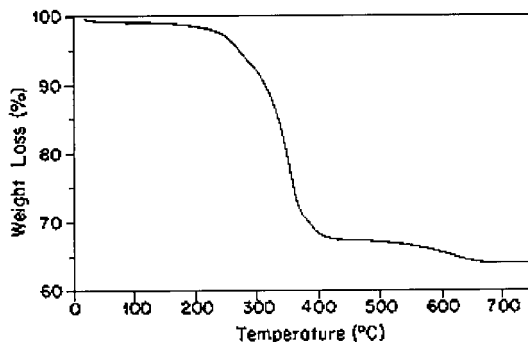


Fig. 6. TGA curve, in nitrogen, for compound **1**.

orbitals makes an excess of 41% of s orbital character and a reduction of 15% of p orbital character, as compared with pure sp^3 hybrid orbitals. This 15% atomic p orbital reduction leads to an increase of 5% per p atomic tin orbital to the molecular bond orbitals, what corresponds to a total of 90% p character, instead of the 75% pure sp^3 hybrid orbitals. On the other hand, the Sn–S and Sn–C bond Mulliken populations analysis showed tin using more p orbitals to form bonds with the S atoms, whereas the density population over the Sn–C bonds are more uniformly distributed among the s and p orbitals. Therefore, according to these results, one should expect a deviation of the S–Sn–S bond angle to be less than the sp^3 109° bond angle; found 89.2°, Table 4, while the remaining two S–Sn–C and C–Sn–C bond angles were expected to be less sensitive, staying slightly larger than 109°.

In complex **3**, tin forms a six-membered ring with the $[PDT]^{-2}$ ligand, and, among others, boat and chair minimum energy conformations, could be expected for the chelate ring. The PM3 results however, showed that only the chair conformation is stable, Fig. 5; an initial boat conformation always leads to a chair form. In **3** the geometry around tin is found to be less distorted from an ideal tetrahedral arrangement, with bonding angles close to those expected from the ‘pure’ sp^3 hybrid orbitals. The larger S–Sn–S bond angle in **3**, as compared with that of **2**, is accounted for by the decrease in the tension energy of the six-membered ring. The Mulliken population analysis for this complex parallels the results found for **2**. The analysis confirms that the formation of the chelate ring is very favorable and it predicts the orbitals used to form the bonds in order to diminish the ring tension.

3.3. Thermogravimetric analyses

The thermogravimetric (TG) analysis was carried out under an inert atmosphere of dry nitrogen. Of the three complexes analyzed, only **1** originated SnS. The TG curve for **1**, in nitrogen, is shown in Fig. 6. The first stage of the decomposition corresponds to the forma-

tion of SnS. The experimental yield, 31.23%, agreed very well with the calculated yield, 31.82%. The identity and phase purity of the residue was determined by comparison of the X-ray diffractogram with that found in the ICDD Powder Diffraction File (21-1250). Complex **2**, in the first stage of decomposition, formed $(C_6H_5)_2SnS$; yields: 84.29 (exp.) and 83.56 (calc.) and complex **3**, $(C_6H_5)_2SnS_2$; yields: 91.24 (exp.) and 89.89 (calc.)

4. Conclusions

PM3 semi-empirical calculations on **2** were in basic agreement with parameters obtained in an X-ray crystallographic study. In particular, the calculations predicted the near 90° S–Sn–S bond angle. The calculations indicated different orbital contributions to the Sn–S bonding in **2** and **3**.

The *N,S*-chelate **1** was found to be a better source of SnS on thermolysis than either of the *S,S*-chelates **2** and **3**.

5. Supplementary material

A table of complete crystallographic data, tables of fractional atomic coordinates for all atoms, complete list of bond distances and angles and tables of anisotropic displacement parameters are available, free of charge, from The Director, Cambridge Crystallographic Data Center, 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>) quoting codes 132683 and 132684 for compounds **1** and **2**, respectively.

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