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# Synthesis, characterisation and thermal decomposition of tin(IV) dithiocarbamate derivatives – single source precursors for tin sulfide powders

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#### Abstract

The reaction of ammonium pyrrolidinedithiocarbamate with  $SnPh_2Cl_2$  and  $SnPh_3Cl$  produced in good yield the compounds  $[Sn\{S_2CN(CH_2)_4\}_2\{C_6H_5\}_2]$  toluene (1) and  $Sn\{S_2CN(CH_2)_4\}\{C_6H_5\}_3$  (2). They were fully characterised by multinuclear NMR  $[{}^{1}H, {}^{13}C\{{}^{1}H\}$  and  ${}^{119}Sn\{{}^{1}H\}$ ] and  ${}^{119}Sn$  Mössbauer spectroscopies. In addition the structure of 1 was determined, and 2 was revised by X-ray crystallographic studies. Finally, thermal decomposition experiments were carried out for both compounds in nitrogen and the residues were characterised by X-ray powder diffraction (XRD), X-ray electron probe microanalysis (EPMA), scanning electron microscopy (SEM) and  ${}^{119}Sn$  Mössbauer spectroscopy. The results clearly indicate the formation of a mixture of  $\gamma$ -Sn<sub>2</sub>S<sub>3</sub> and SnS, both orthorhombic phases.

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# 1. Introduction

Tin sulfides are narrow-bandgap semiconductors with special optical and electronic properties [1]. Tin sulfides have three main phases: (i)  $SnS_2$ , (ii) SnS that exhibit layer structures and (iii)  $Sn_2S_3$  which is a mixed valence Sn(II)/Sn(IV) compound with the same local order as the former sulfide, but with a ribbon-like structure [2]. Tin(II) sulfide displays a distorted rock-salt arrangement which is isostructural to GeS (orthorhombic, *Pbnm* group). Six sulfur atoms surround each tin centre with three short Sn–S bonds within the layer and three long bonds to the sulfur of the next layer [3,4].

Tin sulfides might encounter applications as low-cost green materials for photovoltaic devices either replacing cadmium chalcogenides, which have been banned in many countries because of their toxicity, or else as substitute to the expensive silicon-based sensors. Their preparation methods require high temperature reactions (more than 300 °C) or special reactors [5,6]. Atmospheric pressure chemical vapour deposition (APCVD) and pyrolysis using unsymmetrical organotin dithiocarbamates complexes, like [(CH<sub>3</sub>)<sub>3</sub>Sn(S<sub>2</sub>CN(C<sub>4</sub>H<sub>9</sub>)CH<sub>3</sub>)] and [(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Sn(S<sub>2</sub>CN(C<sub>4</sub>H<sub>9</sub>)CH<sub>3</sub>)]<sub>3</sub>, or heteroleptic thiolate/dithiocarbamate derivatives, (Et<sub>2</sub>NCS<sub>2</sub>)(RS)<sub>2</sub>-Sn (R = Cy, CH<sub>2</sub>CF<sub>3</sub>), have already been reported [7–9].

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However, either the decomposition temperatures are still too high or the process goes on in complicated many step mechanisms. Therefore the search for more appropriate single source precursors for Sn–S based materials is still justified.

The work reported here is part of a more general study performed by our research team concerning precursors for tin sulfide and oxide powders, which is still under investigation [10,11]. So far we have employed organotin derivatives such as  $Sn_4S_4R_6$  and  $Sn_4O_4R_6$ {R = methyl (Me), *n*-butyl or phenyl}. We found those economically attractive not only because of the facile preparation method but also due to their air stability, however, the decomposition temperatures are still high. In order to explore other promising starting materials and check the viability as a good precursor, we have also an interest in tin-containing dithiocarbamates complexes, and herein we describe the first outcomes of our investigations.

## 2. Experimental

## 2.1. Instrumentation and techniques:

IR spectra were obtained as KBr plates on a Mattson Galaxy Model ST 3000 spectrometer in the 4000–400 cm<sup>-1</sup> range. NMR spectra were record in CDCl<sub>3</sub> at 25 °C on a Brucker Avance DRX 400. The values were referenced to internal SiMe<sub>4</sub> and SnMe<sub>4</sub>. C, H, N analyses were performed using a Perkin–Elmer Model PE 2400 CHN.

Thermal decomposition of 1 and 2 were carried out in a tube furnace in  $N_2$  atmospheres up to 500 °C for 1 and 750 °C for 2 using a heating rate of 5 °C/min and a gas flux of 100 ml/min.

XRD patterns were collected with Rigaku Geigerflex equipment by using Ni-filtered Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) and a graphite monochromator in the diffracted beam. A scan rate of 4 °/min was applied to record a pattern in the 2 $\theta$  range of 4–80°.

<sup>119</sup>Sn Mössbauer measurements were performed on conventional apparatus with the samples at liquid  $N_2$ temperature and a CaSnO<sub>3</sub> source kept at room temperature, for compounds 1 and 2 and both the residues in order to identify the Sn oxidation state and number of different sites.

The scanning electron microscopies (SEM) were taken in JEOL JSM-840A equipment and the samples were previously covered with a thin gold layer. The X-ray electron probe microanalyses (EPMA) were carried out in a JXA 89000 RL wavelength /energy dispersive combined microanalyser with samples covered with a thin film of carbon deposited by sputtering.

The intensity data for the X-ray crystallographic determination of 1 were collected at 293(2) K on an Enraf-Nonius Kappa CCD diffractometer with Mo K $\alpha$ ,  $\lambda$ =0.71073 Å, radiation. Programs used: COLLECT, HKL Denzo-Scalepack, WINGX, SHELXS-97 [12], SHEL-XL-97 and ORTEP-3 [13] and the refinements were carried out on  $F^2$  using SHELXL-97 software [14]. Further details are given in Table 1. All non-H atoms were refined anisotropic. The carbons' H atoms were positioned stereochemically and were refined with fixed individual displacement parameters [ $U_{iso}$  (H)=1.2 $U_{eq}$  (C)] using the SHELXL riding model.

# 2.2. Synthesis of $[Sn \{S_2CN(CH_2)_4\}_2 \{C_6H_5\}_2]$ toluene (1)

[NH<sub>4</sub>][(CH<sub>2</sub>)<sub>4</sub>NCS<sub>2</sub>] (1.32 g, 8 mmol) was dissolved in 20 cm<sup>3</sup> of ethanol and added dropwise to a solution of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SnCl<sub>2</sub> (1.38 g, 4 mmol) in the same solvent. The mixture was stirred for two hours and then the solvent was removed by filtration and a white solid, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Sn[S<sub>2</sub>CN(CH<sub>2</sub>)<sub>4</sub>]<sub>2</sub>, was obtained. The ammonium salt was removed by washing the product with hot water (80 °C). X-ray quality colourless crystals were obtained by cooling a dichloromethane/toluene solution of the compound. Yield: 85%. M.p. 222.5–223.1 °C. IR (cm<sup>-1</sup>, KBr): 990 and 1050 (s, v<sub>C-S</sub>), 1560 (s, v<sub>C-N</sub>). <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 1.95–2.01; 3.60–3.66 (t); 7.23–7.90

Table 1

	Crystal data f	or [(C	$_{6}H_{5})_{2}Sn$	S <sub>2</sub> CN(C	H_2)4}2]	· toluene
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	23
Empirical formula	$C_{22}H_{26}SnN_2S_4$
Molecular weight	581.38
<i>T</i> (K)	100(2)
$\lambda$ (Å)	0.71073
Crystal system	triclinic
Space group	$P\overline{1}$
Unit cell dimensions	
a (Å)	8.7355(11)
b (Å)	9.1326(7)
<i>c</i> (Å)	16.72.88(17)
α (°)	83.704(4)
β (°)	84.318(6)
γ (°)	88.979(5)
$V(\text{\AA}^3)$	1320.0(2)
Ζ	2
$\rho_{\text{calc}} (\text{Mg/m}^3)$	1.463
Absorption coefficient (mm <sup>-1</sup> )	1.300
<i>F</i> (000)	588
Crystal size (mm <sup>3</sup> )	$0.18 \times 0.08 \times 0.04$
$\theta$ Range for data collection (°)	3.23-25.00
Reflections collected	28756
Independent reflections $(R_{int})$	4634 (0.0392)
Completeness to $\theta = 25.00^{\circ}$ (%)	99.7
Maximum and minimum transmission	0.9498 and 0.7997
Refinement method	full-matrix least-squares
	on $F^2$
Data/restraints/parameters	4634/0/282
Goodness-of-fit on $F^2$	0.999
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0503, wR_2 = 0.1168$
R indices (all data)	$R_1 = 0.0555, wR_2 = 0.1209$
Largest difference peak and hole (e $Å^{-3}$ )	2.859 and -1.520
CCDC reference	236258

(m, 2 C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR ( $\delta$ , CDCl<sub>3</sub>): 26.7; 54.9; 128.1; 128.3 [<sup>1</sup>J(<sup>119</sup>Sn<sup>-13</sup>C)=811 Hz]; 134.3 [<sup>2</sup>J(<sup>119</sup>Sn<sup>-13</sup>C)=621 Hz]; 151.6; 194.5. <sup>119</sup>Sn NMR ( $\delta$ , CHCl<sub>3</sub>): -500 [<sup>1</sup>J(<sup>119</sup>Sn<sup>-13</sup>C)=811 Hz, <sup>2</sup>J(<sup>119</sup>Sn<sup>-13</sup>C)=621 Hz]. *Anal.* Calc. for C<sub>22</sub>H<sub>26</sub>SnN<sub>2</sub>S<sub>4</sub>: C, 46.75; H, 4.60; N, 4.95. Found: C, 46.62; H, 4.54; N, 4.84%.

# 2.3. Synthesis of $Sn \{S_2 CN(CH_2)_4\} \{C_6 H_5\}_3$ (2)

Prepared accordingly using  $[NH_4][(CH_2)_4NCS_2]$ (0.56 g, 4 mmol) and  $SnCl_2(C_6H_5)_2$  (1.54 g, 4 mmol) dissolved in 20 cm<sup>3</sup> of ethanol. Yield: 89%. M.p. 171–171.4 °C. IR (cm<sup>-1</sup>, KBr): 990 and 1060 ( $v_{C-S}$ ), 1460 and 1570( $v_{C-N}$ ). <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 1.85–1.97 (m); 3.59–3.70 (t); 7.28–7.90 (m, 2 C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR ( $\delta$ , CDCl<sub>3</sub>): 26.64; 55.05; 128.45 [<sup>2</sup>J(<sup>119</sup>Sn–<sup>13</sup>C)=62 Hz]; 129.06; 136.71 [<sup>3</sup>J(<sup>119</sup>Sn–<sup>13</sup>C)=51 Hz]; 142.07 [<sup>1</sup>J(<sup>119</sup>Sn–<sup>13</sup>C) = 606 Hz]; 191.57. <sup>119</sup>Sn NMR ( $\delta$ , CHCl<sub>3</sub>): -174 [<sup>1</sup>J(<sup>119</sup>Sn–<sup>13</sup>C)=606 Hz, <sup>2</sup>J(<sup>119</sup>Sn–<sup>13</sup>C)=62 Hz, <sup>3</sup>J(<sup>119</sup>Sn–<sup>13</sup>C)=51 Hz]. *Anal.* Calc. for C<sub>23</sub>H<sub>23</sub>SnNS<sub>2</sub>: C, 55.67; H, 4.64; N, 2.82. Found: C, 55.47; H, 4.73; N, 2.81%.

#### 3. Results and discussion

Compounds 1 and 2 were isolated as mixture-free derivatives and after re-crystallisation they showed acceptable melting points, as well as satisfactory elemental analyses. They were obtained as air- and moisture-stable white crystalline solids, readily soluble in polar organic solvents.

Compound 1 was studied by X-ray crystallography and the results are displayed in Table 1. It is shown that the crystalline compound possesses a very disordered molecule of toluene in its structure (Fig. 1).

Table 2 comprises selected bond lengths and angles. A similar derivative,  $[Sn \{S_2CN(CH_2)_4\}_2Me_2]$ , previously published, crystallises as orthorhombic in the Pmmn space group [15]. In this compound, the Sn atom lies at the centre of an almost perfect octahedron with a plane of symmetry, containing the R group and the metal centre, and dividing equally the two ligands. Compound 1 has kept the hexacoordination and the pseudo-octahedral geometry, but the crystals have grown in the triclinic system with the space group  $P\overline{1}$ . Unlike the published derivative, which displays two sets of Sn-S bonds, 2.518(1) and 2.9938(1) Å, all four Sn-S distances in 1 are different. There are three slightly different short bonds, S(22)-Sn 2.5727(13), S(12)-Sn 2.5864(14) and S(11)-Sn 2.6850(17) Å, and a long one S(21)-Sn 2.9495(16) A, which seems not to remain in solution as will be discussed later. Apart from the longer bond, the former bonds correlate very well with those observed for the methyl derivative. Because of the lack



Fig. 1. The Molecular structure of 1 and the atom numbering scheme.

of symmetry, two Sn–C bond lengths are observed, Sn–C(41) 2.166(5) Å and Sn–C(41) 2.156(6) Å, for the Sn–phenyl interactions. The S–Sn–S angles, S(22)–Sn– S(12) 89.77(5)°, S(22)–Sn–S(11) 157.20(5)°, S(12)–Sn– S(11) 67.55(5)° are close to those found in the literature. We have also reviewed the X-ray crystallographic structure of **2** and the data does not differ from the reported structure [16]. The Sn(IV) displays a geometric arrangement between tetrahedral and bipyramidal trigonal.

The <sup>1</sup>H NMR of **1** and **2** revealed signals for the organic groups. Besides the expected resonances for the R groups the <sup>13</sup>C spectra revealed first and second-order <sup>119</sup>Sn–<sup>13</sup>C couplings. Unlike other reported examples found in the literature, which normally describe more than one isomer in solution, detected by <sup>119</sup>Sn NMR experiments, in our case only one signal was observed,  $\delta$ –500 <sup>1</sup>J(<sup>13</sup>C–<sup>19</sup>Sn)=811Hz for **1** and –174 <sup>1</sup>J(<sup>119</sup>Sn– <sup>13</sup>C)=606 Hz for **2**. The latter signal appeared upfield compared to the former because of the higher coordination number of the Sn(IV) centre in compound **2**.

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

		• • • •	
C(31)–Sn	2.156(6)	S(12)–Sn	2.5864(14)
C(41)–Sn	2.166(5)	S(21)–Sn	2.9495(16)
S(11)–Sn	2.6850(17)	S(22)–Sn	2.5737(13)
C(31)–Sn–C(41)	107.58(19)	C(41)-Sn-S(11)	92.66(14)
C(31)–Sn–S(12)	152.82(14)	C(41)-Sn-S(22)	91.18(14)
C(31)–Sn–S(22)	105.35(14)	C(41)-Sn-S(12)	94.29(14)
C(31)–Sn–S(11)	94.87(14)	S(12)–Sn–S(11)	67.55(5)
S(22)–Sn–S(12)	89.77(5)	S(22)–Sn–S(11)	157.20(5)

Table 3

Material	Sn site	IS $(mm s^{-1})$	QS (mm $s^{-1}$ )	Area (%)	Width (mm s <sup>-1</sup> )
1	Sn(IV)	1.09	1.72	100	0.90
2	Sn(IV)	1.26	1.65	100	0.90
Residue of 1	Sn(II)	3.31	1.03	88	0.90
	Sn(IV)	0.17	0.59	12	0.90
Residue of 2	Sn(II)	3.08	1.07	77	0.90
	Sn(IV)	0.14	0.56	21	0.90

<sup>119</sup>Sn Mössbauer parameters<sup>a</sup> (isomer shift (IS), quadrupole splitting (QS), area and width) obtained at liquid nitrogen temperature for the compounds 1 and 2 and their respective residues obtained in  $N_2$ 

<sup>a</sup> The errors associated to IS, QS and width are  $\pm 0.05$  mm s<sup>-1</sup> and 1% for the area.

It is possible to estimate the C–Sn–C bond angle employing methods encountered in the literature, which correlates the angle with the first-order coupling constant between <sup>119</sup>Sn and <sup>13</sup>C, in solution [17]. The methods have provided a C–Sn–C angle for compound **1** ranging from 154.57° to 157.34°, in disagreement with the experimental data, 107.58(19)°. Either because the structure of **1** in solution differs drastically from that in the solid state, or the reported methods do not apply to this system. The latter could be justified by the dissociation of the long Sn–S bond, discussed in the X-ray results, effecting a change in the coordination of the metal.

The <sup>119</sup>Sn Mössbauer parameters, isomer shift (IS) and quadrupolar splitting (QS) obtained for compounds **1** and **2** indicate a strong dependence upon the coordination number, hybridisation and symmetry around the Sn(IV) nucleus. The IS for **1**, 1.09 mm s<sup>-1</sup> is smaller than that for **2**, 1.65 mm s<sup>-1</sup>, Table 3, suggesting higher coordination, as attested by the X-ray and <sup>119</sup>Sn-NMR spectroscopic results. It is consistent with a smaller contribution of *s* electrons to the hybridisation scheme at the tin atom in **1** as compared to **2**. The quadrupole splitting parameters 1.30 and 1.80 mm s<sup>-1</sup> points to a lower symmetry for complex **1**. These data match perfectly with other known values for penta and hexacoordinated Sn(IV) derivatives [18].

# 3.1. Thermal decomposition of **1** and **2** and characterisation of the residues

The thermogravimetric curves of 1 and 2, Fig. 2, shows that the decomposition processes begin at 207 and 233 °C ( $\pm 2$  °C), respectively, and at about 350 °C both materials have been consumed. The presence of one more phenyl group in the structure of 2 increases its  $T_d$  (temperature of decomposition) by approximately 26 °C. In both cases, the decomposition take place in a pseudo-single step and the decomposition temperatures are lower than those found for organotin sulfides, reported by us, which have been considered a promising single source precursor [10a].

The residue obtained after the pyrolysis of 1 and 2 carried out in a tube furnace in  $N_2$  were chemically and

structurally characterised. The EPMA results, Fig. 3, clearly indicate the presence of Sn and S as major elements in the residues. However, a tiny amount of oxygen has also been revealed, which might be due to the formation of  $SnO_2$  as a much lesser product. It has possibly originated from the N<sub>2</sub>, which was not completely free from moisture or oxygen, however, it is much smaller than the quantity of carbon, employed to cover the sample.

The diffraction patterns of the residues, Fig. 4, suggested the formation of  $\gamma$ -Sn<sub>2</sub>S<sub>3</sub> and SnS, both orthorhombic phases, in view of the diffraction lines. The lines of SnO<sub>2</sub>, which is quite sensitive to this technique, were not detected. A poor crystallinity of the sample has rendered low quality XRD patterns for residue **1**. Nevertheless, lines at  $2\theta/^{\circ}$  27.19, 31.80, 31.46 and 38,99 assigned to  $\gamma$ -Sn<sub>2</sub>S<sub>3</sub> and SnS were identified. A better diffractogram was obtained for **2** and it was possible to connect the lines at  $2\theta/^{\circ}$  31.61 (201), 31.86 (131), 25.94 (101), 27.22 (140) and 38.94 (301) to  $\gamma$ -Sn<sub>2</sub>S<sub>3</sub> (JCPDS-ICCD 1996 card no. 39-0354). Likewise, those diffractions at  $2\theta/^{\circ}$  31.50 (111), 31.73 (040), 25.94 (110), 27.36 (021), 30.46 (101) and 39.24 (131) were attributed to SnS (JCPDS-ICCD 1996 card no.



Fig. 2. The thermogravimetric curves of 1 (a) and 2 (b) in nitrogen.



Fig. 3. The X-ray electron probe microanalysis (EPMA) of the residue of 1 (a) and 2 (b).



Fig. 4. The X-ray powder diffraction patterns of the residue 1 (a) and 2 (b).

30-13790). The respective Miller indexes are indicated in parenthesis.

The <sup>119</sup>Sn Mössbauer spectra were important to confirm the results of XRD and EPMA, Fig. 5. The experiments have clearly shown the presence of two Sn sites corresponding to Sn(II) and Sn(IV) in the residues, in the form of SnS and  $Sn_2S_3$ . Since the amount of  $SnO_2$ is not detectable, it is not absurd to assume that all the Sn nuclei exist as tin-sulfides. For the residue of 1 there are two sets of signals, IS 3.31 mm s<sup>-1</sup>, QS  $1.03 \text{ mm s}^{-1}$  and IS 0.17 mm s<sup>-1</sup>, QS 0.59 mm s<sup>-1</sup>. Similarly, for 2 IS 3.08 mm s<sup>-1</sup>, QS 1.07 mm s<sup>-1</sup> and IS 0.14 mm s<sup>-1</sup>, QS 0.56 mm s<sup>-1</sup> are observed. The Mössbauer parameters for both residues are in good agreement with similar data reported in one of our previous works [10a]. It is important to observe that a smaller amount of Sn(II) was produced in the decomposition of 2 (area = 77%) compared to the residue of 1 (area = 88%). In either case there is more SnS than the required amount to match the Sn<sub>2</sub>S<sub>3</sub> stoichiometry. It is possible that a mixture of the two sulfides is present, which the <sup>119</sup>Sn Mössbauer experiments cannot reveal. We have also performed the same study on a standard of  $Sn_2S_3$ and the same pattern of two set of signals with  $IS=3.35 \text{ mm s}^{-1}$ ,  $QS=0.97 \text{ mm s}^{-1}$  for Sn(II) and  $IS=0.46 \text{ mm s}^{-1}$ ,  $QS=0.88 \text{ mm s}^{-1}$  for Sn(IV) was encountered.

The scanning electron micrographs showed that layered and ribbon-like crystals basically compose the residues, Fig. 6. It is a very common characteristic of SnS and  $Sn_2S_3$  systems. The SEM images have revealed the particle size of microns and also confirmed the low crystallinity of the samples, as pointed out by the XRD diffractograms.



Fig. 5. The  $^{119}$ Sn Mössbauer spectra and the respective quadrupole distribution of the residue of 1 (a) and 2 (b).



Fig. 6. The scanning electron microscopy (SEM) image of the residue of **1**.

#### 4. Conclusions

We have described in this paper the synthesis, characterisation and thermal decomposition of two dithiocarbamate tin-based derivatives. The versatility of compounds **1** and **2** has been proved as single source precursor for SnS and Sn<sub>2</sub>S<sub>3</sub>. They were obtained by a pyrolysis experiment in N<sub>2</sub> in sharp steps at a much lower temperature compared to other compounds. Only a negligible amount of SnO<sub>2</sub> was revealed by EPMA, and was not detected in the XRD or in <sup>119</sup>Sn Mössbauer experiments.

# 5. Supplementary data

Crystallographic data for the structural analysis for complex 1 have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, and are available on request quoting the deposition number CCDC-236258.

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