

# Synthesis, spectroscopic properties and crystal structures of $\text{SnBr}_2[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2)_2\text{O}]_2$ , $(4\text{-F-C}_6\text{H}_4\text{CH}_2)_2\text{Sn}(\text{Cl})\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2)_2\text{O}$ and $(2\text{-F-C}_6\text{H}_4\text{CH}_2)_3\text{SnS}_2\text{CN}(\text{CH}_2\text{CH}_2)_2\text{O}$

Handong Yin<sup>\*</sup>, Chuanhua Wang, Mei Hong, Daqi Wang

Department of Chemistry, Liaocheng University, Liaocheng 252059, PR China

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## Abstract

Three organotin(IV) complexes with dithiomorpholinocarbamate ligand:  $\text{SnBr}_2[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2)_2\text{O}]_2$  (**1**),  $(4\text{-F-C}_6\text{H}_4\text{CH}_2)_2\text{Sn}(\text{Cl})\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2)_2\text{O}$  (**2**) and  $(2\text{-F-C}_6\text{H}_4\text{CH}_2)_3\text{SnS}_2\text{CN}(\text{CH}_2\text{CH}_2)_2\text{O}$  (**3**) have been synthesized and characterized by elemental analysis, IR, UV and NMR. Their crystal and molecular structures have been determined by X-ray single crystal diffraction. In the complex **1**, the tin atom is rendered six-coordination in a distorted octahedron configuration. And in the complexes **2** and **3**, the tin atoms are rendered five-coordination in a distorted trigonal bipyramidal structure.  
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**Keywords:** Tin(IV) complex; Dithiomorpholinocarbamate; Synthesis; Crystal structure

## 1. Introduction

Metal *N,N*-dialkyldithiocarbamates have been synthesized by the action of metal halides on sodium *N,N*-dialkyldithiocarbamate in both aqueous and non-aqueous solution [1–3]. More recently, pharmaceutical properties of alkyltin(IV) complexes with dithiocarbamate ligands have been investigated for their antitumour activity [4–9]. Crystallographic studies have revealed that the coordination at the tin atom depends not only on the factors such as R-radical stereochemistry, but also on whether the 1,1-dithiolates behave as monodentate or bidentate ligands and whether the complexes are monomeric or oligomeric. As an extension of our studies of alkyltin(IV) complexes with dithiocarbamate ligands, we have synthesized and structurally characterized three novel organotin(IV) complexes with dithiomorpholinocarbamate ligand:  $\text{SnBr}_2[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2)_2\text{O}]_2$  (**1**),  $(4\text{-F-C}_6\text{H}_4\text{CH}_2)_2\text{Sn}(\text{Cl})\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2)_2\text{O}$  (**2**) and  $(2\text{-F-C}_6\text{H}_4\text{CH}_2)_3\text{SnS}_2\text{CN}(\text{CH}_2\text{CH}_2)_2\text{O}$  (**3**). And the results of this study are reported herein.

## 2. Experimental

### 2.1. General procedure

Anhydrous sodium dithiomorpholinocarbamate was prepared according to the method described in the literature [10]. The solvent dichloromethane was dried over phosphorus(V) oxide prior to use. Infrared spectra were recorded on a Nicolet-460 spectrophotometer, using KBr as discs. <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn-NMR spectra were obtained with Mercury Plus-400 NMR spectrometer and the chemical shifts are given in ppm relative to Me<sub>4</sub>Si, Me<sub>4</sub>Sn in CDCl<sub>3</sub>. Elemental analyses were performed on PE-2400-II elemental analyzer. UV spectra were obtained on a UV 210A spectrometer.

### 2.2. Synthesis of complexes **1**, **2** and **3**

#### 2.2.1. Synthesis of complex **1**

Anhydrous sodium dithiomorpholinocarbamate (2.0 mmol) was added to 30 mL 95% ethanol solution of di(4-fluorobenzyl)tin dibromide (1.0 mmol). Then the mixture was heated under reflux for 6 h. The precipitated sodium bromide was removed by filtration and the filtrate was

<sup>\*</sup> Corresponding author. Tel.: +866358238121; fax: +866358238121.  
E-mail address: [handongyin@sohu.com](mailto:handongyin@sohu.com) (H. Yin).

concentrated to about 5 mL under reduced pressure. When hexane (5 mL) was added to this solution, immediately, a precipitate was formed. The products were recrystallized from ethanol to give red crystals 0.39 g, yield 65%. M.p.: 143–145 °C. UV–Vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$ : 222, 265, 288 nm. <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  4.10 (8H, t,  $J = 7.8$  Hz, OCH<sub>2</sub>), 3.83 (8H, t,  $J = 7.8$  Hz, NCH<sub>2</sub>) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  210.31(CS<sub>2</sub>), 68.32(CH<sub>2</sub>N), 56.29(CH<sub>2</sub>O) ppm. <sup>119</sup>Sn-NMR  $\delta$  -490.46 ppm. IR (KBr, cm<sup>-1</sup>): 1463 (s, C–N), 1121, 995 (s, CS<sub>2</sub>), 457 (m, Sn–S). Anal. Calc. for C<sub>10</sub>H<sub>16</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub>Sn: C, 19.98; H, 2.75; N, 4.68; S, 21.20. Found: C, 19.92; H, 2.67; N, 4.65; S, 21.27%.

### 2.2.2. Synthesis of complex 2

Anhydrous sodium dithiomorpholinocarbamate (1.0 mmol) were added to 30 mL dichloromethane solution of di(4-fluorobenzyl)tin dichloride (1.0 mmol). The mixture was stirred for 14 h at 30 °C. The precipitated sodium chloride was removed by filtration and the filtrate was concentrated to about 5 mL under reduced pressure. When hexane (5 mL) was added to this solution, immediately, a precipitate was formed. The products were recrystallized from dichloromethane-ethyl ether to give colorless crystals 0.40 g, yield 75%. M.p.: 133–134 °C. UV–Vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$ : 221, 257, 286. <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  6.80–7.05 (8H, m, ArH), 4.15 (4H, t,  $J = 10.8$  Hz, OCH<sub>2</sub>), 3.85 (4H, t,  $J = 10.5$  Hz, NCH<sub>2</sub>), 2.84 (4H, t,  $J_{\text{Sn–H}} = 70.7$  Hz, ArCH<sub>2</sub>Sn) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  168.45, 148.82, 129.81, 121.32, 29.72 (4-*F*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>), 201.48(CS<sub>2</sub>), 67.62(CH<sub>2</sub>N), 54.85(CH<sub>2</sub>O) ppm. <sup>119</sup>Sn-NMR  $\delta$  -315.82 ppm. IR (KBr, cm<sup>-1</sup>): 1478 (s, C–N), 1131, 998 (s, CS<sub>2</sub>), 554 (m, Sn–C), 455 (m, Sn–S). Anal. Calc. for C<sub>19</sub>H<sub>20</sub>ClF<sub>2</sub>NOS<sub>2</sub>Sn: C, 42.69; H, 3.77; N, 2.62; S, 11.99. Found: C, 42.49; H, 3.58; N, 2.74; S, 12.17%.

### 2.2.3. Synthesis of complex 3

Anhydrous sodium dithiomorpholinocarbamate (1.0 mmol) was added to 30 mL dichloromethane solution of tri(2-fluorobenzyl)tin chloride (1.0 mmol). The mixture was stirred for 18 h at 30 °C. The precipitated sodium chloride was removed by filtration and the filtrate was concentrated to about 5 mL under reduced pressure. When hexane (5 mL) was added to this solution, immediately, a precipitate was formed. The products were recrystallized from dichloromethane-hexane to give colorless crystals 0.47 g, yield 78%. M.p.: 121–122 °C. UV–Vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$ : 223, 262, 280. <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  6.92–7.02 (8H, m, ArH), 4.04 (4H, t,  $J = 11.2$  Hz, OCH<sub>2</sub>), 3.77 (4H, t,  $J = 11.2$  Hz, NCH<sub>2</sub>), 2.62 (4H, t,  $J_{\text{Sn–H}} = 75.3$  Hz, ArCH<sub>2</sub>Sn) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  160.15, 130.25, 126.82, 125.32, 123.69, 117.53, 28.98 (2-*F*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>), 189.23 (CS<sub>2</sub>), 68.76(CH<sub>2</sub>N), 59.60(CH<sub>2</sub>O) ppm. <sup>119</sup>Sn-NMR  $\delta$  -211.35 ppm. IR (KBr, cm<sup>-1</sup>): 1490 (s, C–N), 1142, 1003 (s, CS<sub>2</sub>), 545 (m, Sn–C), 462 (m, Sn–S). Anal. Calc.

for C<sub>26</sub>H<sub>26</sub>F<sub>3</sub>NOS<sub>2</sub>Sn: C, 51.34; H, 4.31; N, 2.30; S, 10.54. Found: C, 51.07; H, 4.20; N, 2.19; S, 10.72%.

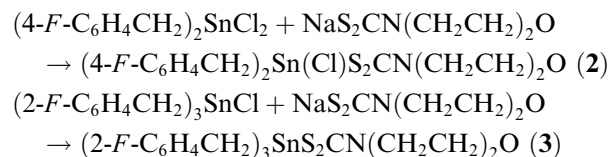
### 2.3. Crystallographic measurements

All X-ray crystallographic data were collected on a Bruker smart-1000 CCD diffractometer with graphite monochromated Mo K $\alpha$  (0.71073 Å) radiation. The structures were solved by direct method and difference Fourier map using SHELXL-97 program, and refined by full-matrix least-squares on  $F^2$ . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically.

## 3. Results and discussion

### 3.1. The synthetic mechanism of complexes 1–3

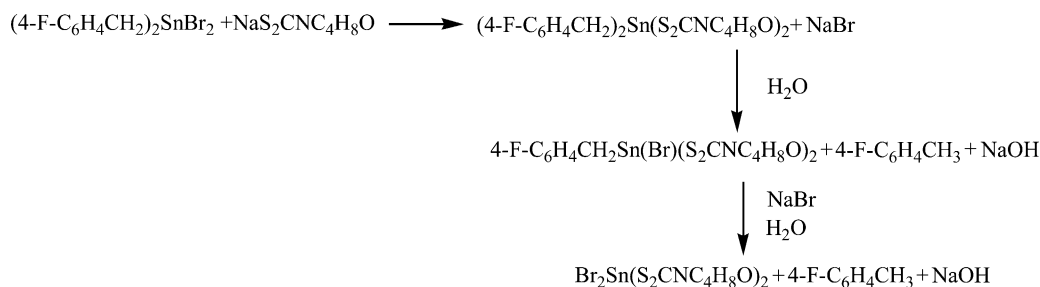
Reaction of (4-*F*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>SnCl<sub>2</sub> and (2-*F*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>3</sub>SnCl with sodium dithiomorpholinocarbamate in 1:1 stoichiometry in dichloromethane gives (4-*F*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>Sn(Cl)S<sub>2</sub>CN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O and (2-*F*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>3</sub>SnS<sub>2</sub>CN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O in 75% and 78% yield after recrystallization:



As we know, a few papers about the synthesis and structural study of SnX<sub>2</sub>(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub> have been reported [10,11]. However, the study on this type compound which was synthesized by the reaction of dialkyltin dihalide with *N,N*-dialkyldithiocarbamate has not been seen in previous literatures. When the reaction of (4-*F*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>SnBr<sub>2</sub> with NaS<sub>2</sub>CN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O in 1:2 molar ratio occurred, an unexpected complex Br<sub>2</sub>Sn[S<sub>2</sub>CN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O]<sub>2</sub> (1) was obtained instead of the expected (4-*F*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>Sn[S<sub>2</sub>CN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O]<sub>2</sub>. A possible mechanism is given in Scheme 1. During the reaction, the little H<sub>2</sub>O in solvent may be major factor which results in dealkylation. The synthetic mechanism of this complex is similar to those of drum organooxotin cluster [12–14]. Moreover, under anhydrous conditions, using dichloromethane or anhydrous ethanol as solvent, we have synthesized the complex (4-*F*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>Sn[S<sub>2</sub>CN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O]<sub>2</sub> at room temperature. The results also make sure of our conclusion for the synthetic mechanism of the complex 1.

### 3.2. Spectroscopic properties

In complexes 1, 2 and 3, as can be shown from UV spectra, the band 1 at  $\lambda_{\text{max}}$  222, 221 and 223 nm which



Scheme 1.

belongs to strong absorption, is a *K* band due to  $\pi\text{-}\pi^*$  transition of dithiomorpholinocarbamate NCS. The band 2 at  $\lambda_{\text{max}}$  265, 257 and 262 nm which belongs to medium absorption due to  $\pi\text{-}\pi^*$  transition of SCS moiety reveals a hypsochromic shift 18–26 nm in comparison with that of the appropriate sodium salt of dithiomorpholinocarbamate acid [10]. The band 3 at  $\lambda_{\text{max}}$  288, 286 and 280 nm which belongs to a weak absorption is attributed to electron-transfer transition  $n\text{-}\pi^*$  in  $\text{CS}_2$  group, exhibiting a hypsochromic shift by 15–23 nm when compared with the corresponding band of salts of dithiomorpholinocarbamate acid [10]. This suggests that sulphur atoms of dithiomorpholinocarbamate groups coordinate to tin atom.

In IR spectra of complexes **1–3**, a new absorption band appears at  $455\text{--}462\text{ cm}^{-1}$  which is the characteristic vibrations of Sn–S bond [7–9]. One obvious feature of the IR spectra is the similarity of the stretching bands arising from the dithiocarbamate ligands. The relatively high value ( $1463\text{--}1490\text{ cm}^{-1}$ ) for  $\nu(\text{C}\text{--}\text{N})$  is similar to that reported for analogous tin complexes [7–9]. This suggests that the dithiomorpholinocarbamate ligand of three complexes are linked to Sn atom in a bidentate fashion [7–9]. In IR spectra the important bands arising from  $\nu(\text{CS}_2)_{\text{asym}}$  and  $\nu(\text{CS}_2)_{\text{sym}}$  appear at  $1121\text{--}1142\text{ cm}^{-1}$  and  $995\text{--}1003\text{ cm}^{-1}$ , respectively. The  $\Delta\nu$  values [ $\nu(\text{CS}_2)_{\text{asym}} - \nu(\text{CS}_2)_{\text{sym}}$ ] ( $126\text{--}139\text{ cm}^{-1}$ ) is much smaller than the  $\Delta\nu^*$  of the  $\text{R}_2\text{NCS}_2\text{R}'$  [10], but it is larger than the  $\Delta\nu'$  of the corresponding sodium dithiomorpholinocarbamate [10]. This information shows the dithiomorpholinocarbamate group in three complexes coordinates to tin in an anisobidentate fashion [4–6], and the analysis is consistent with X-ray single crystal diffraction results.

The  $^1\text{H-NMR}$  spectra of complexes **2** and **3** show that the chemical shifts of the protons on the benzyl group exhibit two signals about 6.80–7.05 ppm as multiplet and 2.84, 2.62 ppm as a triplet which is caused by the tin ( $^{119}\text{Sn}$ ) hydrogen coupling. And the spin-spin coupling constant  $J_{\text{Sn-H}}$  is equal 70.7 and 75.3 Hz. In the  $^1\text{H-NMR}$  spectra of complexes **1–3**, the  $\text{NCH}_2$  and  $\text{OCH}_2$  protons give rise to triplet signals at 3.83, 4.10; 3.85, 4.15 and 3.77, 4.04 ppm, as expected.

A comparison of the  $^{13}\text{C-NMR}$  spectra of the ligand. With the corresponding organotin complexes shows a

downfield shift in the position of  $\text{C}_{\text{C-N}}$  and  $\text{C}_{\text{C-O}}$  signals and an upfield shift in the position of  $\text{C}_{\text{CSS}}$  signal. These shifts indicate the bidentate behaviour of the dithiomorpholinocarbamate moieties in the complexes.

The  $^{119}\text{Sn}$  chemical shift values in three complexes are found to be in the range of  $-211.35$  to  $490.46$  ppm. The appearance of chemical shift values in this region indicates five- and six-coordination environment [19] around the central tin atoms in these complexes.

### 3.3. Molecular structures of complexes **1–3**

Crystallographic data, together with refinement details of complexes **1**, **2** and **3** are given in Table 1. The selected bond distances and angles are given in Tables 2–4, their molecular structures were illustrated in Figs. 1–3.

#### 3.3.1. Complex **1**

As was showed in Fig. 1, the coordination at the tin atom is octahedral geometry, surrounded by four sulphur atoms and two bromine atoms. So the tin atom is rendered six-coordinate for complex  $\text{SnBr}_2[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2)_2\text{O}]_2$  (**1**). Thus, the structure is similar to those of the complexes:  $\text{SnCl}_2[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$  [7] and  $\text{SnBr}_2(\text{S}_2\text{COC}_2\text{H}_5)_2$  [11].

The tin atom has a highly distorted octahedral configuration. The distortion is reflected in the *cis* angles which vary from  $70.57(4)^\circ$  to  $103.14(4)^\circ$ , the range of *trans* angles is from  $156.76(7)^\circ$  to  $163.62(3)^\circ$ . These *trans* angles result from the necessity for the two bidentate dithiomorpholinocarbamate ligands to have a smaller bite than usual (i. e. in the order of  $63\text{--}71^\circ$ ) [15–17]. The binding of the dithiomorpholinocarbamate group is found to be in an anisobidentate fashion in many structures. However, the Sn–S distances [ $0.25184(17)$ ,  $0.25636(17)$  nm] in this structure show much smaller anisobonding. Though this can be attributed to the presence of non-bulky bromine groups in the coordination sphere, the observation that in the structure of dibenzyltin bis(dithiotetrahydropyrrolocarbamate) [18], the reported Sn–S bond distances [ $0.25209(12)$  and  $0.29083(13)$  nm] show both the packing forces and coordination geometry most probably play a vital role in the very near isobonding

Table 1  
Crystallographic data of complexes **1**, **2** and **3**

	<b>1</b>	<b>2</b>	<b>3</b>
Molecular formula	C <sub>10</sub> H <sub>16</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>2</sub> S <sub>4</sub> Sn	C <sub>19</sub> H <sub>20</sub> ClF <sub>2</sub> NOS <sub>2</sub> Sn	C <sub>26</sub> H <sub>26</sub> F <sub>3</sub> NOS <sub>2</sub> Sn
Formula weight	605.01	534.62	608.29
Crystal system	Tetragonal	Orthorhombic	Triclinic
Space group	I4(1)/a	Pbca	P1
Unit cell dimensions			
<i>a</i> (nm)	1.7567(8)	1.3637(17)	1.0745(16)
<i>b</i> (nm)	1.7567(8)	1.1710(15)	1.383(2)
<i>c</i> (nm)	1.7596(11)	2.768(3)	1.952(3)
$\alpha$ (°)	90	90	99.62(2)
$\beta$ (°)	90	90	103.83(2)
$\gamma$ (°)	90	90	104.13(2)
<i>V</i> (nm <sup>3</sup> )	5.430(5)	4.421(10)	2.651(7)
<i>Z</i>	8	8	4
<i>D</i> <sub>cal</sub> (kg/cm <sup>3</sup> )	1.480	1.606	1.524
<i>F</i> (000)	2336	2128	1224
Crystal size (mm)	0.50 × 0.30 × 0.20	0.27 × 0.23 × 0.15	0.50 × 0.40 × 0.15
Scan range $\theta$ (°)	2.84 ≤ $\theta$ ≤ 26.37	1.47 ≤ $\theta$ ≤ 25.03	2.39 ≤ $\theta$ ≤ 25.03
Index ranges	−21 ≤ <i>h</i> ≤ 21, −21 ≤ <i>k</i> ≤ 6, −21 ≤ <i>l</i> ≤ 21	−8 ≤ <i>h</i> ≤ 16, <i>l</i> − 13 ≤ <i>k</i> ≤ 13, −31 ≤ <i>l</i> ≤ 32	−9 ≤ <i>h</i> ≤ 12, −16 ≤ <i>k</i> ≤ 14, −23 ≤ <i>l</i> ≤ 23
Total/unique/ <i>R</i> <sub>int</sub>	13895/2618/0.0369	21875/3902/0.0525	8717/7177/0.0243
$\mu$ (mm <sup>−1</sup> )	4.194	1.491	1.161
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub>	0.0398/0.0884	0.0362/0.0848	0.0464/0.1161
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.033	0.957	0.954
$\rho_{\max}/\rho_{\min}$ (e nm <sup>−3</sup> )	0.663/−392	0.509/−493	0.828/−838

Table 2  
Selected bond distances (nm) and angles (°) of complex **1**

Sn(1)–Br(1)	0.27107(12)	S(1)–C(1)	0.1731(5)
Sn(1)–S(1)	0.25184(17)	S(2)–C(1)	0.1711(5)
Sn(1)–S(2)	0.25636(17)	N(1)–C(1)	0.1300(6)
N(1)–C(5)	0.1477(8)	N(1)–C(2)	0.1463(7)
S(1)–Sn(1)–S(1A)	156.76(7)	S(2)–Sn(1)–Br(1A)	90.96(6)
S(1)–Sn(1)–S(2)	70.57(4)	S(2A)–Sn(1)–Br(1A)	163.62(3)
S(1A)–Sn(1)–S(2)	93.04(4)	S(1)–Sn(1)–Br(1)	93.20(4)
S(1A)–Sn(1)–S(2A)	70.57(4)	S(1A)–Sn(1)–Br(1)	103.14(4)
S(2)–Sn(1)–S(2A)	92.09(8)	S(2)–Sn(1)–Br(1)	163.62(3)
Br(1A)–Sn(1)–Br(1)	90.64(6)	C(1)–S(1)–Sn(1)	86.70(17)
N(1)–C(1)–S(2)	121.9(4)	C(1)–S(2)–Sn(1)	85.66(18)
N(1)–C(1)–S(1)	121.1(4)	C(1)–N(1)–C(2)	123.7(5)
S(2)–C(1)–S(1)	117.0(3)	C(1)–N(1)–C(5)	121.4(4)
C(3)–O(1)–C(4)	108.4(6)	C(2)–N(1)–C(5)	114.4(5)

nature of the dithiomorpholinocarbamate group. The bond distance, Sn–Br [0.27107(12) nm] is much larger than that found in Br<sub>2</sub>Sn(S<sub>2</sub>COC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> [11] [0.2537(2) nm], which suggests that the halogenides are weakly coordinated in this complex. We believe that the weak coordination of the halogenide should be the result of packing forces and the presence of bulky hydrophobic groups. The N(1)–C(1) distance of 0.1300(6) nm is similar to those reported for other dialkyldithiocarbamate moieties [7–9]. This distance suggest that the C(sp<sup>2</sup>)–N(sp<sup>2</sup>) bond has a high double bond character, an observation consistent with the IR data. The N(1)–C(2) and N(1)–C(5) bond distance are 0.1463(7) and 0.1477(8) nm, respectively and approximate from the N–C single bond distance (0.148 nm).

Table 3  
Selected bond distances (nm) and angles (°) of complex **2**

Sn(1)–C(6)	0.2141(6)	S(1)–C(1)	0.1743(5)
Sn(1)–C(13)	0.2157(6)	S(2)–C(1)	0.1694(6)
Sn(1)–Cl(1)	0.2491(3)	N(1)–C(1)	0.1324(7)
Sn(1)–S(1)	0.2466(2)	N(1)–C(2)	0.1475(7)
Sn(1)–S(2)	0.2684(2)	N(1)–C(5)	0.1468(7)
F(1)–C(10)	0.1359(8)	O(1)–C(3)	0.1566(9)
F(2)–C(17)	0.1368(8)	O(1)–C(4)	0.1561(9)
C(6)–Sn(1)–C(13)	129.5(3)	S(1)–Sn(1)–S(2)	69.54(10)
C(6)–Sn(1)–S(1)	111.34(19)	Cl(1)–Sn(1)–S(2)	157.29(6)
C(13)–Sn(1)–S(1)	117.63(19)	S(2)–C(1)–S(1)	117.8(3)
C(6)–Sn(1)–Cl(1)	94.3(2)	N(1)–C(1)–S(2)	123.4(4)
C(13)–Sn(1)–Cl(1)	98.83(18)	N(1)–C(1)–S(1)	118.8(4)
S(1)–Sn(1)–Cl(1)	87.75(10)	C(1)–S(1)–Sn(1)	88.8(2)
C(6)–Sn(1)–S(2)	94.3(2)	C(1)–S(2)–Sn(1)	82.8(2)
C(13)–Sn(1)–S(2)	91.75(18)	C(7)–C(6)–Sn(1)	113.7(4)
C(9)–C(10)–F(1)	118.7(7)	C(14)–C(13)–Sn(1)	117.1(4)
C(11)–C(10)–F(1)	118.5(7)	N(1)–C(2)–C(3)	110.2(6)
C(2)–C(3)–O(1)	110.7(7)	C(5)–C(4)–O(1)	110.8(7)

### 3.3.2. Complex 2

The tin atom is five-coordinated [Sn(1)–S(1) 0.2466(2), Sn(1)–S(2) 0.2684(2), Sn(1)–Cl(1) 0.2491(3), Sn(1)–C(6) 0.2141(6), Sn(1)–C(13) 0.2157(6) nm], with a distorted trigonal bipyramid. The structure differs from those of the complexes (PhCH<sub>2</sub>)<sub>2</sub>SnCl(S<sub>2</sub>CNC<sub>5</sub>H<sub>10</sub>) [19], (PhCH<sub>2</sub>)<sub>2</sub>SnCl(S<sub>2</sub>CNMe<sub>2</sub>) [20] and (PhCH<sub>2</sub>)<sub>2</sub>SnCl(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>O) [21], But it is similar to that of the complex Ph<sub>2</sub>SnCl(S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>) [22].

The geometry is approximately based on a trigonal bipyramid, with atom C(6), S(1) and C(13) occupying equatorial positions. As an indication the sum of the

Table 4  
Selected bond distances (nm) and angles (°) of complex 3

Sn(1)–C(6)	0.2146(7)	Sn(2)–C(39)	0.2144(8)
Sn(1)–C(13)	0.2163(6)	Sn(2)–C(32)	0.2161(7)
Sn(1)–C(20)	0.2187(8)	Sn(2)–C(46)	0.2185(8)
Sn(1)–S(1)	0.2464(4)	Sn(2)–S(3)	0.2463(4)
Sn(1)–S(2)	0.3122(5)	Sn(2)–S(4)	0.3054(4)
S(1)–C(1)	0.1745(8)	S(3)–C(27)	0.1766(7)
S(2)–C(1)	0.1697(7)	S(4)–C(27)	0.1673(7)
C(6)–Sn(1)–C(13)	113.3(3)	C(39)–Sn(2)–C(32)	115.6(3)
C(6)–Sn(1)–C(20)	108.6(3)	C(39)–Sn(2)–C(46)	108.2(3)
C(13)–Sn(1)–C(20)	109.5(3)	C(32)–Sn(2)–C(46)	108.1(3)
C(6)–Sn(1)–S(1)	114.2(2)	C(39)–Sn(2)–S(3)	113.3(2)
C(13)–Sn(1)–S(1)	114.3(2)	C(32)–Sn(2)–S(3)	113.9(2)
C(20)–Sn(1)–S(1)	95.4(2)	C(46)–Sn(2)–S(3)	95.6(2)
C(6)–Sn(1)–S(2)	82.1(2)	C(39)–Sn(2)–S(4)	82.1(2)
C(13)–Sn(1)–S(2)	81.5(2)	C(32)–Sn(2)–S(4)	81.36(19)
C(20)–Sn(1)–S(2)	158.6(2)	C(46)–Sn(2)–S(4)	159.9(2)
S(1)–Sn(1)–S(2)	63.23(6)	S(3)–Sn(2)–S(4)	64.29(8)

equatorial angles ( $358.47^\circ$ ) at the tin atom by the two coordinated carbon atoms and one sulfur atom [C(13)–Sn(1)–S(1)  $117.63(19)^\circ$ , C(6)–Sn(1)–S(1)  $111.34(19)^\circ$ , C(6)–Sn(1)–C(13)  $129.5(3)^\circ$ ] deviates at most by  $1.53^\circ$  from the  $360^\circ$ , so the atoms C(6), S(1), C(13) and Sn(1) are almost in a same plane. The Cl atom occupies approximately one apical position of the trigonal bipyramid. Conversely, due to the constraint of the chelate [the angle [S(1)–Sn(1)–S(2)] is not  $90^\circ$  but only  $69.54(10)^\circ$ ], the S(2) atom cannot exactly occupy the corresponding *trans* axial position of the trigonal bipyramid, the angle Cl(1)–Sn(1)–S(2) being  $157.29(6)^\circ$ .

The N(1)–C(1) distance of  $0.1324(7)$  nm is similar to those of complexes  $(\text{PhCH}_2)_2\text{SnCl}(\text{S}_2\text{CNMe}_2)$  [20] and  $(\text{PhCH}_2)_2\text{SnCl}(\text{S}_2\text{CNC}_5\text{H}_{10})$  [19], but longer than that of complex 1. The S(1)–C(1) [ $0.1743(5)$  nm] and S(2)–C(1) [ $0.1694(6)$  nm] bond lengths appear to be charac-

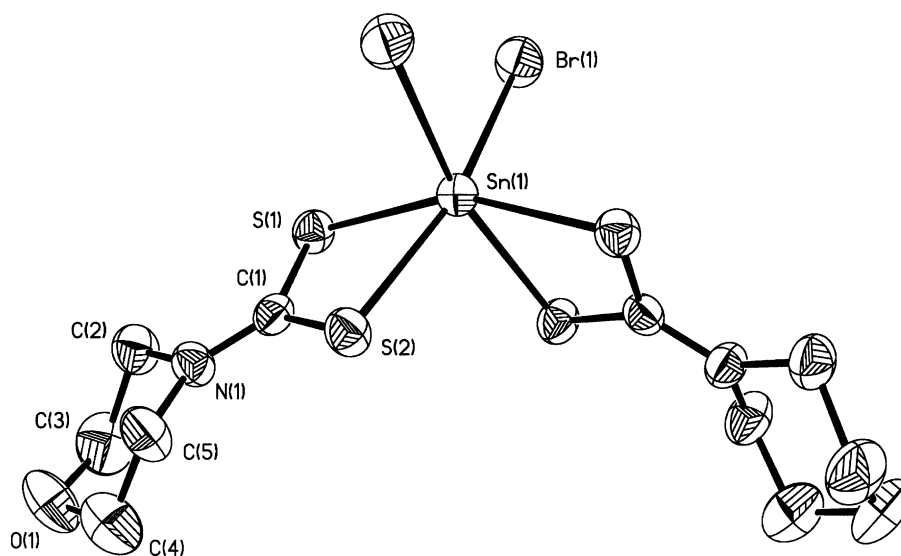


Fig. 1. The molecular structure of complex 1.

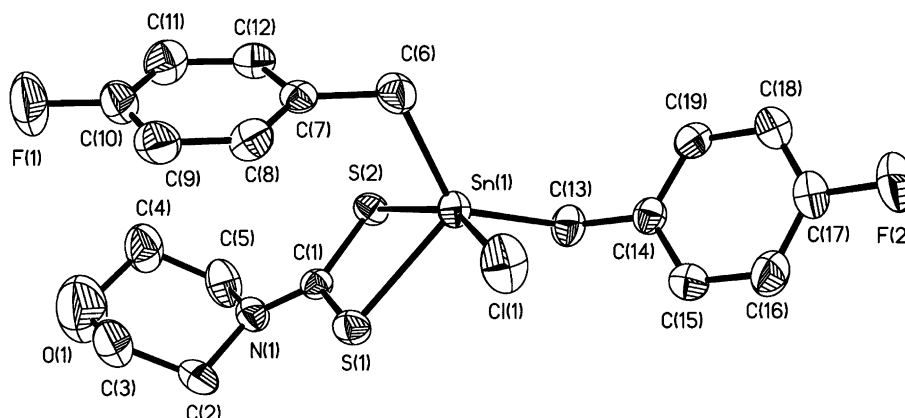


Fig. 2. The molecular structure of complex 2.

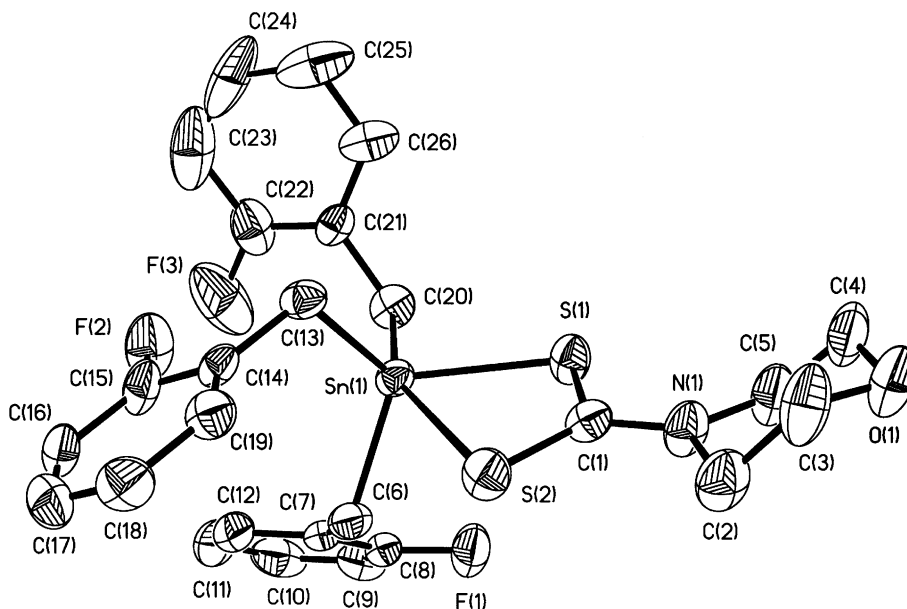


Fig. 3. The molecular structure of complex 3.

teristic of the dithiocarbamate group that these two distances are both intermediate between the values expected “single” and “double” bond [23].

### 3.3.3. Complex 3

In crystal of complex 3, the unit cell contains two independent molecules that are practically superimposable. In fact a computer fitting of molecules A and B shows only a very marginal difference in the bond lengths and angles. One of the two molecules is represented in Fig. 3 with its numbering scheme. The molecule A is discussed in this paper. In complex 3, the coordination at the tin atom is trigonal bipyramidal, surrounded axially by two sulphur atoms and three carbon atoms. Thus, the structure is similar to those of the complexes  $(\text{PhCH}_2)_3\text{S}_2\text{CNC}_4\text{H}_8\text{O}$  [24] and  $(\text{PhCH}_2)_3\text{S}_2\text{CNC}_5\text{H}_{10}$  [25].

The Sn(1)–S(1) bond length is 0.2464(4) nm, it is almost equal to the bond distance of complexes  $\text{Me}_3\text{SnS}_2\text{CNMe}_2$  (0.246 nm) [23] and  $(\text{PhCH}_2)_3\text{SnS}_2\text{CNC}_5\text{H}_{10}$  (0.2481 nm) [22] but shorter than that of  ${}^t\text{Bu}_2\text{Sn}(\text{S}_2\text{CNEt}_2)_2$  (0.255 nm) [22]. The Sn(1)–S(2) distance is 0.3122(5) nm, which is well within the sum of the van der Waals radii of 4.00 nm for Sn and S atoms. It is almost equal to the bond distance of complex  $\text{Me}_3\text{SnS}_2\text{CNMe}_2$  (0.316 nm) [23] but slightly longer than that of complex  $(\text{PhCH}_2)_3\text{S}_2\text{CNC}_5\text{H}_{10}$  (0.3027 nm) [25]. The information showed the two S atoms coordinate to Sn atom. So the tin atom could be considered five coordinate within a trigonal bipyramidal environment.

The geometry of complex 3 is loosely based on a trigonal bipyramid, with atom C(6), S(1) and C(20) occupying equatorial positions. Distortions from true

trigonal bipyramidal symmetry are reflected in the interatomic angles. The sum of equatorial angles C(6)–Sn(1)–S(1) (114.2(2)°), C(13)–Sn(1)–C(20) (109.5(3)°) and C(13)–Sn(1)–S(1) (114.3(2)°) is equal to 338°, which shows that these atoms are not co-planar. The angles C(6)–Sn(1)–S(2) 82.1(2)°, C(13)–Sn(1)–S(2) 81.5(2)° and S(1)–Sn(1)–S(2) 63.23(6)° are all less than 90°. In contrast, the angles C(6)–Sn(1)–C(20) 108.6(3)°, C(13)–Sn(1)–C(20) 109.5(3)° and C(20)–Sn(1)–S(1) 95.4(2)° are greater than 90°, because the 2-fluorobenzyl group is on the side of the plane having more sterical hindrance than the S(2) atom on the other side. The C(20) atom occupies approximately one apical position of the trigonal bipyramid. Conversely, due to the constraint of the chelate [the angle [S(1)–Sn(1)–S(2)] is not 90° but only 62.7(5)°], the S(2) atom cannot exactly occupy the corresponding trans axial position of the trigonal bipyramid, and the angle C(18)–Sn(1)–S(2) only is 158.6(2)° deviating from linear angle 180°. From this, the tin atom of this complex is distorted trigonal bipyramid configuration.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 221746 for complex 1, CCDC No. 221748 for complex 2 and CCDC No. 221747 for compound 3. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1233-336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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