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Organotin(IV) complexes of 4,6-dimethylpyrimidine-2-thione, Me_2PymtH. Preparation, characterization and crystal structure determination of *cis*-[$Ph_2Sn(Me_2Pymt)_2$] and [$Ph_3Sn(Me_2Pymt)$]

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Abstract

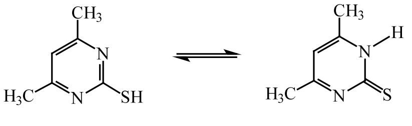
The coordination mode of the ambidentate ligand 4,6-dimethylpyrimidine-2-thione (Me_2PymtH) was investigated with respect to the organotin(IV) compounds, namely Me_2SnCl_2, *n*-Bu_2SnCl_2, Ph_2SnCl_2 and Ph_3SnCl. An X-ray crystal structure determination carried out on *cis*-[$Ph_2Sn(Me_2Pymt)$] (**3**) and [$Ph_3Sn(Me_2Pymt)$] (**4**) revealed that the Me_2Pymt^- ligand is N,S-coordinated in both complexes. The Sn(IV) atom is six-coordinated in **3** and five-coordinated in **4**. The similarities observed in the IR, NMR (^{1}H, ^{13}C) and mass spectroscopy are indicative of a similar behavior of the ligand in all the complexes, thus suggesting a six-coordination in the dimethyltin (**1**) derivative and five-coordination in the dibutyltin (**2**) one. The complexes were characterized by means of elemental analysis, IR, NMR (^{1}H, ^{13}C) and mass spectroscopic methods. © 2002 Published by Elsevier Science Ltd.

Keywords: Organotin(IV) complexes; Dimethylpyrimidinethione; Crystal structures

1. Introduction

The variety of coordination modes of 4,6-dimethylpyrimidine-2-thione (Me_2PymtH) has been demonstrated in a number of complexes [1] and their biological applications have been of considerable interest for years [2]. Insofar as many organotin(IV) complexes are also noteworthy for the same reason [3], a combination of the two chemistry is an interesting topic to pursue.

The present work deals with the preparation and characterization of four new organotin(IV) complexes with the Me_2PymtH ligand, whose structure is shown below.



Me_2PymtH

This ligand was chosen since it has the potential to form four-, five-or hexacoordinate metal complexes which the polyhedral of these compounds assuming structures that are considerably distorted from ideal configuration. These distorted structures in many organotin(IV) complexes are thought to be due to a number of factors, such as steric requirements, electronic effects arising from different electronegativities of the ligands, intermolecular interactions and crystal packing requirements [4]. Pyridines and pyrimidines substituted with an SH or an OH group at the two or four positions are fundamentally tautomeric heterocyclic system and many experimental studies have been reported [5,6]. The complexes were studied by microanalyses, IR, NMR (^{1}H, ^{13}C), mass spectroscopy and crystal X-ray diffraction.

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2. Experimental

Solvents were purified and dried according to standard procedures. Thiourea, pentane-2,4-dione and organotin(IV) chlorides were obtained from Aldrich and used without further purification. IR spectra were recorded on a Bruker IFS-28 spectrophotometer in the 4000–400 cm^{-1} range using KBr pellets. NMR (^1H, ^{13}C) spectra were obtained from a Bruker DPX-200 spectrometer using $CDCl_3$ as the solvent with chemical shifts in parts per million downfield from Me_4Si. The mass spectra were recorded on a Micromass 7070-F instrument, using FAB+Xe at 8 eV and alcohol 3-nitrobenzilic as matrix. Microanalyses were performed in a VARIO EL (Elementar Analysensysteme GmbH) instrument.

2.1. Synthesis

The ligand was prepared according to the literature [2] and the complexes by the following procedure: 0.28 g (2 mmol) of Me_2PymtH was dissolved in 30 ml of THF (freshly distilled) in a Schlenk tube kept under N_2 atmosphere. To the solution, 0.84 ml (6 mmol) of triethylamine (Et_3N) was added via a syringe and the resulting solution was stirred for 30 min. To this solution was added, during 10 min, 1 mmol of the appropriate organotin(IV) species dissolved in 3 ml of THF, and the mixture was refluxed for about 4 h. A white flocculent precipitate identified as triethylamine chloride (Et_3NHCl) was produced and filtered. Slowly evaporation of the solvent led to the appearance of white amorphous crystalline solids with yields of the order 70%. Well formed crystals suitable for X-ray studies were only obtained for complexes **3** and **4** by recrystallization from a 1:1 (v/v) mixture of dichloromethane–*n*-hexane. The microanalyses were performed in a Perkin–Elmer 2400C analyzer, giving for C, H and N the following results: $[Me_2Sn(Me_2Pymt)_2]$ (**1**): (m.p. 197–199 °C). *Anal*. Found: C, 40.66; H, 4.78; N, 13.55. Calc. for ($C_{14}H_{20}N_4S_2Sn$): C, 39.37; H, 4.72; N, 13.12%. $[Bu_2SnCl(Me_2Pymt)]$ (**2**): (m.p. 212–211 °C). *Anal*. Found: C, 43.32; H, 6.46; N, 6.72. Calc. for ($C_{14}H_{25}ClN_2SSn$): C, 41.26; H, 6.18; N, 6.87%. *cis*-$[Ph_2Sn(Me_2Pymt)_2]$ (**3**): (m.p. 202–204 °C). *Anal*. Found: C, 52.17; H, 4.58; N, 10.62. Calc. for ($C_{24}H_{24}N_4S_2Sn$): C, 52.29; H, 4.39; N, 10.16%. $[Ph_3Sn(Me_2Pymt)]$ (**4**): (m.p. 206–208 °C). *Anal*. Found: C, 58.67; H, 4.57; N, 5.84. Calc. for ($C_{24}H_{22}N_4S_2Sn$): C, 58.92; H, 4.53; N, 5.73%.

2.2. X-ray studies

Colourless single crystals of compounds **3** and **4** which were suitable for X-ray diffractometric studies were selected and data collected on a Bruker Smart CCD for **3** and an Enraf–Nonius MACH3 for **4**. The data were corrected for absorption effects by an empirical correction (SADABS 7b) (**3**) or using ψ-scans 7a (**4**).

Structural solutions were determined by direct methods [8]. Least-squares full-matrix refinement on F2 was performed using the program SHELXL-97 [8]. All non-H atoms were refined anisotropically. H atoms were calculated and refined as ridding atoms (HFIX [8]). Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for Crystallography [9]. Graphics were obtained with ZORTEP [10].

3. Results and discussion

3.1. Infrared spectroscopy

Table 1 shows the assignment of the main IR absorptions of the ligand and its complexes. The Me_2PymtH ligand shows a rather complicated spectrum in the 3100–2600 cm^{-1} range where C–H and N–H stretching absorptions occur. Thus, the spectra of complexes retain those absorptions found in free ligand. The ring stretching vibrations, $\nu(C{=}C)+\nu(C{=}N)$, are shifted to lower frequencies, together with the shift in opposite direction of the ligand band at 1235 cm^{-1}, assigned to mixed $\nu(C{-}S)+\nu(C{-}N)$ absorption bands. These results suggest, in accordance with ^1H NMR, an N,S-chelation of the aromatic Me_2Pymt^- anion around the Sn(IV) ion. Similar results have been reported for tiolate complexes of 2-PySH (2-mercaptopyridine) and 2-PymSH (2-mercaptopyrimidine) and different metal ions such as Ni(II) [11] and Pt(II) [12], as well as with Re(V) complex of Me_2PymtH [13].

In the IR spectrum of $[Me_2Sn(Me_2Pymt)_2]$ the asymmetric Sn–C stretching band at 551 cm^{-1} indicates that this complex has the *trans* arrangement of the methyl groups [14].

3.2. NMR spectroscopy

Table 2 lists ^1H chemical shifts for the free ligand Me_2PymtH and its complexes. The ^{13}C NMR spectrum to complex **1** showed a $^1J(^{119}Sn{-}CH_3)$ coupling constant of 600 Hz and the ^1H NMR spectrum showed one doublet and a singlet in the methyl region occurring at 2.37 and 1.03 [$^2J(^{119}Sn{-}CH_3)$ 83 Hz] due to two magnetically non-equivalent methyl groups bonded in $N{=}CH{-}CH_3$ and $Sn{-}CH_3$, respectively. These ^1J and ^2J coupling constants data can be used to estimate the $CH_3{-}Sn{-}CH_3$ angle in complex **1**, and according to the literature [15,16], two empirical equations can be set up for this estimate:

Table 1
Main IR absorptions (cm^{-1}) for Me_2PymtH and its Sn(IV) complexes

Compound	C.N. [a]	ν(N–H)+ν(C–H)	ν(C=C)+ν(C=N)	ν(C–S)+ν(C–N)
Me_2PymtH		2911	1625, 1569, 1432	1235
$[Me_2Sn(Me_2Pymt)_2]$ (**1**)	6	2916	1578, 1543, 1435	1257
$[Bu_2SnCl(Me_2Pymt)]$ (**2**)	5	2921	1578, 1539, 1437	1257
cis-$[Ph_2Sn(Me_2Pymt)_2]$ (**3**)	6	3038	1579, 1525, 1430	1255
$[Ph_3Sn(Me_2Pymt)]$ (**4**)	5	3038	1584, 1524, 1427	1255

[a] C.N. = coordination number.

Table 2
^1H NMR data in $CDCl_3$ solution[a]

Me_2PymtH	6.49 (s, 1H, C–H); 2.39 (t, 6H, C–CH_3)
$[Me_2Sn(Me_2Pymt)_2]$ (**1**)	6.69 (s, 2H, C–H); 2.37 (d, 12H, C–CH_3); 1.03 (s, 6H, Sn–CH_3) $^2J(^{119}Sn–CH_3)$ = 83/75
$[Bu_2SnCl(Me_2Pymt)]$ (**2**)	(s, 2H, C–H); 2.37 (d, 6H, C–CH_3); 1.64-1.55 (m, 4H, Sn–CH_2–C); 1.42–1.26 (m, 4H, C–CH_2–C); 0.79 (t, 6H, Bu–CH_3)
cis-$[Ph_2Sn(Me_2Pymt)_2]$ (**3**)	7.88–7.26 (m, 10H, Sn–C_6H_5); 6.52 (s, 2H, C–H); 2.18 (s, 6H, C–CH_3)
$[Ph_3Sn(Me_2Pymt)]$ (**4**)	7.80–7.23 (m, 10H, Sn–C_6H_5); 6.55 (s, 2H, C–H); 2.13 (s, 6H, C–CH_3)

[a] s = Singlet, d = doublet, m = multiplet, δ in ppm, J in Hz.

$$^1J(^{119}Sn–^{13}CH_3) = 11.4\theta - 875 \quad (1)$$

$$\theta = 0.0161\{^2J(^{119}Sn–CH_3)\}^2 - 1.32\{^2J(^{119}Sn–CH_3)\} + 133.4 \quad (2)$$

Using ^1J into Eq. (1) and ^2J into Eq. (2), one finds values of θ of 135° and 129°, respectively. These angles values might suggests that in solution the dimethyltin derivative is a distorted *trans* octahedral complex and the basic structural features of the solid-state phase remain in $CDCl_3$ solution. For dibutyl derivative, similar structural considerations in solution might hold.

Similar results were reported for octahedral complexes with analogous *trans* arrangement, namely $[Me_2Sn(dtc)_2]$ [17] [$^2J(^{119}Sn–CH_3)$ 84 Hz and $^1J(^{119}Sn–^{13}CH_3)$ 670 Hz], $[Me_2SnCl_2{\cdot}(DMSO)_2]$ [15] [$^2J(^{119}Sn–CH_3)$ 86 Hz] and $[Me_2Sn(CH_3COO)_2]$ [18] [$^2J(^{119}Sn–CH_3)$ 82 Hz], where Hdtc = ditiocabamic acid and DMSO = dimethylsulfoxide.

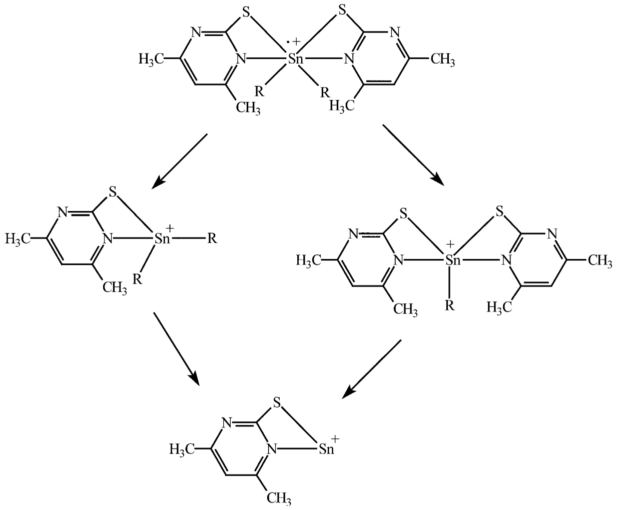

Fig. 1. Fragmentation scheme proposed for complexes **1**–**3**.

3.3. Mass spectroscopy

Table 3 shows the FAB mass spectra of compounds **1**–**4** and Fig. 1 presents a fragmentation scheme proposed for complexes **1**–**3** compatible with literature data [4,19]. The molecular ion for complexes **1**, **3** and **4** were detectable at m/z 429, 553 and 489, respectively.

The spectra of complexes **1** and **3** showed that the base peaks are the ions $R_2Sn(Me_2Pymt)^+$ (R = Me, Ph), in agreement with reported works [4,19]. This contrasts with the spectra of compounds **2** and **4**, in which the base peaks appeared at m/z 882 (not attributed) and m/z 291 (probably due to the ion $Ph_2Sn(H_2O)^+$), respectively.

Table 3
Fragment-ions observed in the FAB mass spectra of compounds **1**–**4**

Fragment-ion	Me_2Sn (**1**) m/z [a] (abundance)	Bu_2Sn (**2**) m/z [a] (abundance)	Ph_2Sn (**3**) m/z [a] (abundance)	Ph_3Sn (**4**) m/z [a] (abundance)
$R_3Sn(Me_2Pymt)^+$				489(8)
$R_2Sn(Me_2Pymt)_2{}^+$	429(33)		553(15)	
$R_2Sn(Me_2Pymt)^+$	289(100)	373(64)	413(100)	
$RSn(Me_2Pymt)_2{}^+$	413(16)		258(9)	
$Sn(Me_2Pymt)^+$	259(18)	259(22)	259(24)	259(25)
$(Me_2Pymt)_2{}^+$	279(9)	279(16)	279(48)	

[a] Nominal values calculated using the most abundant isotope ^{120}Sn.

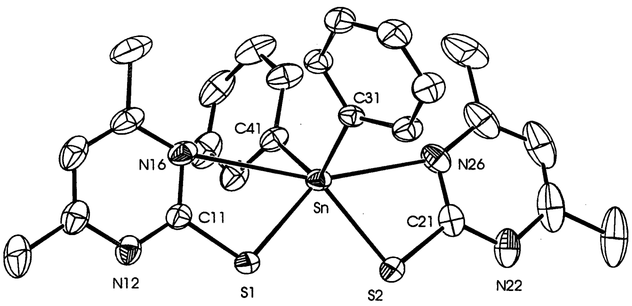

Fig. 2. Perspective view of *cis*-[$Ph_2Sn(Me_2Pymt)_2$] (**3**) showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

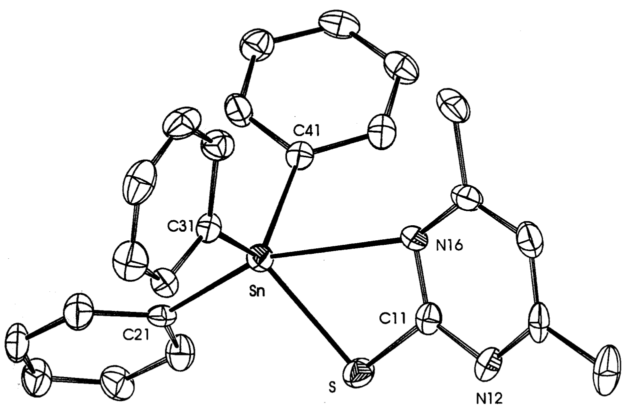

Fig. 3. Perspective view of [$Ph_3Sn(Me_2Pymt)$] (**4**) showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

3.4. X-ray structures of cis-[$Ph_2Sn(Me_2Pymt)_2$] (3) and [$Ph_3Sn(Me_2Pymt)$] (4)

The molecular structures of **3** and **4** are given in Figs. 2 and 3, respectively. Tables 4 and 5 summarize the crystal data and selected bond lengths and bond angles for the two compounds, respectively.

The geometry about Sn(IV) in **3** is best described as a distorted octahedral with the two Me_2Pymt^- anions acting as bidentate ligands with *cis* Ph–Sn–Ph [117.42(13)°] and *cis* S–Sn–S [84.50(3)°] arrangements. The bond distances [2.4476(10); 2.4515(10) Å] in the Sn–S bond lengths found in **3** are shorter than the Sn–S bond distances [2.476(2); 2.485(1) Å], [2.477(3) Å] and [2.487(2) Å] found in [$Ph_2Sn(2\text{-}SPy)_2$] [20], [$n\text{-}Bu_2Sn(2\text{-}SPy\text{-}5\text{-}NO_2)_2$] [4] and [$Me_2Sn(2\text{-}SPy)_2$] [21], respectively, where 2-SPyH is 2-pyridinethione and 2-SPyH-5-NO_2 is 5-nitropyridinethione.

The Sn–N bond distances [2.754(3) and 3.083(3) Å] found in complex **3** are shorter than the sun of the van der Waals radii (3.75 Å) [20] indicating the bidentate nature of the Me_2Pymt^- ligand. However, these distances are longer than the Sn–N distances [2.636(4); 2.698(3) Å] and [2.702(5) Å] found in [$Ph_2Sn(2\text{-}SPy)_2$] [20] and [$Me_2Sn(2\text{-}SPy)_2$] [21], respectively. Although conclusions are drawn with caution, it would appear most reasonable that the disparate Sn–N bond distances in **3** versus [$Ph_2Sn(2\text{-}SPy)_2$] and [$Me_2Sn(2\text{-}SPy)_2$] [21] is probably due to the electronic effects caused by uncomplexed N(12) and N(22) atoms in complex **3**. The Sn–C bond distances (mean value of 2.12 Å) is typical, and compares favorably with the analogous bond in related compounds, in particular [$Ph_2Sn(2\text{-}SPy)_2$] [20] (2.13 Å) and [$Me_2Sn(2\text{-}SPy)_2$] [21] (2.13 Å), with which it shows striking structural similarities.

Table 4
Crystallographic data for the X-ray diffraction studies for **3** and **4**

	3	**4**
Formula	$C_{24}H_{24}N_4S_2Sn$	$C_{24}H_{22}N_2SSn$
Formula weight	551.28	498.19
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pbca$
Z	4	8
A (Å)	9.6990(3)	8.7994(14)
B (Å)	17.0580(5)	17.513(3)
C (Å)	15.9182(4)	28.826(5)
β (°)	106.0652(8)	90
V (Å^3)	2528.14(13)	4442.2(13)
D_{calc} (g cm^{-3})	1.448	1.463
Crystal size (mm)	0.45 × 0.30 × 0.20	0.48 × 0.16 × 0.08
Index ranges	$-12 \leq h \leq 12$	$0 \leq h \leq 10$
	$-18 \leq k \leq 22$	$0 \leq k \leq 21$
	$-21 \leq l \leq 21$	$0 \leq l \leq 35$
μ (mm^{-1})	1.194	1.255
T (K)	293(2)	293(2)
F(000)	1112	1968
Reflections collected	16755	4477
Independent reflections	6151	4477
Reflections observed	4230	1507
R [$I > 2\sigma(I)$]	0.0397	0.0525
R_w	0.0852	0.0881
Goodness-of-fit	1.016	0.894

The geometry about Sn(IV) in **4** is best described as a strongly distorted trigonal bipyramid (TBP) configuration where two phenyl groups and a S atom are at the equatorial plane while N(16) atom and other phenyl group occupy the axial position.

The Sn–S bond distance [2.433(2) Å] found in **4** is within the range (2.405–2.481 Å) [22,23] recently reported for triphenyltin(IV) thiolates compounds R_3SnL, containing potentially bidentate ligand. Similarly, the Sn–C distances [mean 2.14 Å] agree well with those previously reported [22,23].

The Sn–N bond length [2.835(7) Å] is equal to the length of Sn–N bond [2.836(3) Å] found in [Ph_3Sn(o-quinolinylthiolate)] [22], in which sulfur and nitrogen atoms are bonded to the Sn(IV) atom forming five-membered chelate ring. On the other hand, the Sn–N length in **4** is smaller than that of the Sn–N bond [2.88(5) Å] found in [$Ph_3Sn(2\text{-}Pymt)$] [24], where 2-PymtH is 2-pyrimidinethione, suggesting that the methyl group, C(151), does not cause steric effect. In contrast,

Table 5
Selected bond distances (Å) and angles (°) for **3** and **4**

	3		**4**
Bond distances			
Sn–S(1)	2.4515(10)	Sn–S	2.433(2)
Sn–S(2)	2.4476(10)	Sn–N(16)	2.835(7)
Sn–C(31)	2.124(3)	Sn–C(21)	2.159(8)
Sn–C(41)	2.116(3)	Sn–C(31)	2.117(8)
Sn–N(16)	3.083(3)	Sn–C(41)	2.134(9)
Sn–N(26)	2.754(3)	S–C(11)	1.752(9)
C(11)–N(12)	1.327(5)	C(11)–N(12)	1.334(10)
C(11)–N(16)	1.334(4)	C(11)–N(16)	1.320(10)
C(21)–N(22)	1.341(5)	C(13)–N(12)	1.326(11)
C(21)–N(26)	1.331(5)	C(15)–N(16)	1.344(11)
S(1)–C(11)	1.755(4)	C(13)–C(14)	1.359(13)
S(2)–C(21)	1.740(4)	C(14)–C(15)	1.371(11)
Bond angles			
C(41)–Sn–C(31)	117.42(13)	C(31)–Sn–C(41)	116.8(3)
C(41)–Sn–S(1)	108.81(11)	C(31)–Sn–C(21)	106.9(3)
C(41)–Sn–S(2)	116.30(10)	C(41)–Sn–C(21)	104.3(3)
C(41)–Sn–N(16)	80.65(12)	C(31)–Sn–N(16)	83.3(3)
C(41)–Sn–N(26)	88.44(13)	C(41)–Sn–N(16)	85.7(3)
C(31)–Sn–N(16)	85.23(11)	C(21)–Sn–N(16)	159.7(3)
C(31)–Sn–N(26)	85.04(12)	C(31)–Sn–S	111.0(2)
C(31)–Sn–S(1)	111.93(9)	C(41)–Sn–S	115.2(3)
C(31)–Sn–S(2)	113.03(10)	C(21)–Sn–S	100.7(2)
S(1)–Sn–S(2)	84.50(3)	S–Sn–N(16)	59.03(17)
N(16)–Sn–N(26)	160.02(10)	C(11)–S–Sn	94.6(3)
N(16)–Sn–S(1)	55.75(6)	N(12)–C(11)–N(16)	127.7(9)
N(26)–Sn–S(2)	59.71(8)	N(16)–C(11)–S	116.3(7)
N(16)–Sn–S(2)	140.25(6)	N(12)–C(11)–S	115.9(8)
N(26)–Sn–S(1)	144.21(8)	N(12)–C(13)–C(131)	117.9(11)
N(16)–C(11)–S(1)	117.3(3)	N(16)–C(15)–C(151)	115.5(9)
N(26)–C(21)–S(2)	117.6(4)	C(13)–C(14)–C(15)	118.3(11)

the Sn···N interaction [2.920(3) Å], found in [Ph$_3$Sn(mimt)] [22], where mimtH is 1-methyl-2(3H)-imidazolinethione, slightly distorts the Sn(IV) coordination geometry from that a perfect tetrahedron.

Around the Sn(IV) atom, the S–Sn–C(31), C(31)–Sn–C(41) and C(41)–Sn–S equatorial angles of 110.0(2)°, 116.8(3)°, 115.2(3)° and the N–Sn–C(21) axial angle of 159.7(3)°, are smaller than the ideal trigonal bipyramid angles.

The bite angle of the chelating ligand is similar for both complexes and quite acute, 59.71(8)° for **3** and 59.03(17)° for **4**. In both cases, the phenyl groups (C31 and C41) bend away the coordinate Sn–S bonds, generating an Ph–Sn–Ph angle of 117.42(13)° in the case **3** and 116.8(3)° in **4**.

4. Supplementary data

Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. 167994 (**3**) and 167995 (**4**). Copies of the data can be obtained, free of change, on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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