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Syntheses and crystal structures of diorganotin(IV) bis(2-pyridinethiolato-*N*-oxide) complexes

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The complexes di-*n*-butyldi(2-pyridinethiolato-*N*-oxide)tin(IV) (1), diphenyldi(2-pyridinethiolato-*N*-oxide)tin(IV) (2) and dibenzyldi(2-pyridinethiolato-*N*-oxide)tin(IV) (3) are synthesized and characterized by elemental analyses, IR, ^{1}H, ^{13}C, ^{119}Sn NMR spectroscopy, and their structures are determined by X-ray crystallography. In complex 1 the coordination geometry at tin is a skew-trapezoidal bipyramid, with *cis*-*S*,*S* and *cis*-*O*,*O* atoms occupying the trapezoidal plane and two *n*-butyl groups occupying the apical positions, which also exhibits strong $\pi-\pi$ stacking interactions. In complexes 2 and 3 the geometry at tin is distorted *cis*-octahedral, with *cis*-*O*,*O* and *cis*-*C*,*C* atoms occupying the equatorial plane and *trans*-*S*,*S* atoms occupying the apical positions. Their *in vitro* cytotoxicity against two human tumour cell lines, MCF-7 and WiDr is reported. The ID_{50} values found are comparable to those found for *cis*-platin, but lower than for many other diorganotin compounds. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: diorganotin; 2-pyridinethiolato-*N*-oxide; X-ray crystal structure; cytotoxicity

INTRODUCTION

Metal thiolato complexes have been extensively studied because of their ability to adopt various nuclearities and their relevance in biology, since they form the inorganic part of the biologically active centers of some metalloproteins and enzymes.[1–4] Recently, attention has been paid to the coordination chemistry of polydentate ligands that incorporate both thiol sulfur and heterocyclic nitrogen donor sites because of their unusual geometries and moderate biological activities against various bacteria and fungi.[5] In this regard, the most studied systems are the proligands, 2-mercaptopyridine (HSPy), $R_2Sn(SPy)_2$ and $R_2SnCl(SPy)$, which have been characterized in solid state and in solution.[6] And some five-coordinated pyridine oxide complexes such as a square pyramidal, $R_3SnCl(SpyO)$, and a trigonal-bipyramidal, $R_2SnCl_2(PyO)$, have also been reported.[7,8] Many of those organotin compounds, similar to those of the platinum,[9–11] exhibit *in vitro* antitumour properties against a wide panel of tumoral cell lines of human origin.[12–14]

Therefore, in order to widen the scope of the investigation on the coordination behaviour of ligands containing {S, O} donors towards organotin(IV) derivatives[15–17] in biological systems, we have synthesized three diorganotin(IV) derivatives from 2-pyridinethiolato-*N*-oxide and characterized them by elemental analyses, IR, ^{1}H, ^{13}C, ^{119}Sn NMR spectroscopy, and determined their structures. Their *in vitro* cytotoxicity against two human tumour cell lines, MCF-7 and WiDr is also reported. The reaction is shown in Scheme 1.

EXPERIMENTAL

Materials and methods

Diphenyltin dichloride, di-*n*-butyltin dichloride and 2-pyridinethiolato-*N*-oxide sodium were commercially available, and they were used without further purification. Dibenzyltin dichloride were prepared by a standard method reported in the literature.[18] The melting points were obtained with Kofler micro melting point apparatus and were uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AMX-300

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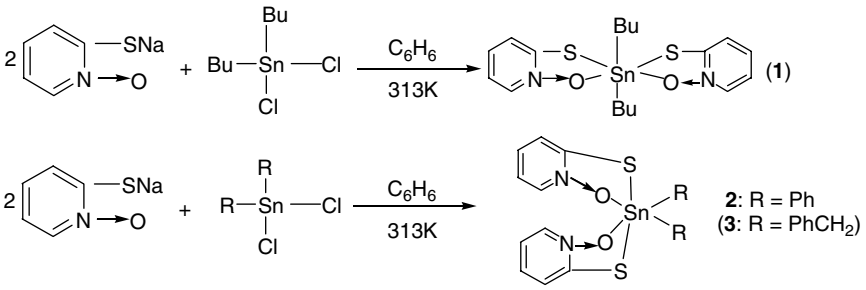

Scheme 1.

spectrometer operating at 300 MHz, 75.3 MHz and 111.9 MHz respectively. The spectra were acquired at room temperature (298 K) unless specified otherwise; ^{13}C spectra are broadband proton decoupled. The chemical shifts are reported in ppm with respect to the references and were stated relative to external tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR, and to neat tetramethyltin for ^{119}Sn NMR. Elemental analyses were performed with PE-2400II apparatus.

Syntheses

Di-n-*butylbis(2-pyridinethiolato*-N-*oxide)tin(IV)* (**1**)

The reaction was carried out under nitrogen atmosphere. The sodium 2-pyridinethiolato-*N*-oxide (0.298 g, 2 mmol) was added to the solution of absolute benzene (20 ml) in a Schlenk flask and stirred for 10 min. After the di-*n*-butyltin dichloride (0.304 g, 1 mmol) was added to the reactor, the reaction mixture was stirred for 12 h at 40 °C. After cooling down to room temperature, the mixture was filtered. The filtered solution was gradually removed by evaporation under vacuum until a solid product was obtained. The solid was then recrystallized from dichloromethane–hexane. Colourless crystal complex **1** was formed: yield, 89%; m.p. 98–100 °C. Anal. Found: C, 44.23; H, 5.07; N, 5.56. Calc. for $C_{18}H_{26}N_2O_2S_2Sn$: C, 44.56; H, 5.40; N, 5.78%. IR (ν_{max}):[12] 1593 (m, C=N); 1460 (s, C–N); 1207 (s, N–O); 750 (s, C–S); 340 (w, Sn–O); 305, 270 ν_{as},ν_s(Sn–C); 309 (m, Sn–S). ^{1}H NMR ($CDCl_3$, 90 MHz): δ 8.1 (d, 2H), 7.4 (d, 2H), 7.3 (d, 2H), 6.92 (d, 2H), 1.57–1.70 (m, 12H, $^{2}J_{SnH} = 80$ Hz), 0.81 (t, 6H). ^{13}C NMR ($CDCl_3$): δ (C_5H_4NS) 118.7, 128.5, 129.2, 137.2, 157.3, 13.6, 26.4, 27.6, 29.7 (^{n}Bu, $^{1}J_{SnC} = 691$ Hz, $^{2}J_{SnC} = 38$ Hz, $^{3}J_{SnC} = 106$ Hz). ^{119}Sn NMR ($CDCl_3$): δ −121.2.

Diphenylbis(2-pyridinethiolato-N-*oxide)tin(IV)* (**2**)

The synthesis procedure was the same as for compound **1**. Ph_2SnCl_2 (0.343 g, 1 mmol) and Na(2-SPyO) (0.298 g, 2 mmol), reaction time 10 h. Recrystallized from ether–hexane: Yield, 81%; m.p. 106–108 °C. Anal. Found: C, 50.08; H, 3.16; N, 4.97. Calc. for $C_{22}H_{18}N_2O_2S_2Sn$: C, 50.31; H, 3.45; N, 5.33%. IR (ν_{max}):[12] 1594 (m, C=N); 1460 (s, C–N); 1214 (m, N–O); 731 (s, C–S); 350 (w, Sn–O); 325, 280 ν_{as},ν_s(Sn–C); 310 (m, Sn–S). ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.26–7.40 (m, 8H), 7.62–7.95 (m, 2H, $^{2}J_{SnH} = 63$ Hz), 8.11 (d, 2H), 7.35–7.40 (m, 4H), 6.78 (d, 2H). ^{13}C NMR ($CDCl_3$): δ (C_5H_4NS) 119.5, 128.1, 128.5, 137.0, 154.3, 128.1 ($^{3}J_{SnC} = 67$ Hz, *m*-C), 129.3 ($^{4}J_{SnC} = 18$ Hz, *p*-C), 136.5 ($^{2}J_{SnC} = 48$ Hz, *o*-C), 148.6 ($^{1}J_{SnC} = 480$ Hz, *i*-C). ^{119}Sn NMR ($CDCl_3$): δ −228.2.

Dibenzylbis(2-pyridinethiolato-N-*oxide)tin(IV)* (**3**)

The synthesis procedure was the same as for compound **1**. $(PhCH_2)_2SnCl_2$ (0.371 g, 1 mmol) and Na(2-SPyO) (0.298 g, 2 mmol), reaction time 12 h. Recrystallized from ether–hexane: Yield, 85%; m.p. 113–115 °C. Anal. Found: C, 51.87; H, 3.75; N, 4.86. Calc. for $C_{24}H_{22}N_2O_2S_2Sn$: C, 52.10; H, 4.00; N, 5.06%. IR (ν_{max}):[12] 1596 (m, C–N); 1459 (s, C–N); 1216 (m, N–O); 753 (s, C–S); 355 (m, Sn–O); 340, 290 ν_{as},ν_s(Sn–C); 310 (m, Sn–S). ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.68–7.26 (m, 10H), 8.10 (d, 2H), 7.37–7.42 (m, 4H), 6.76 (d, 2H), 3.26 ($^{2}J_{SnH} = 66$ Hz, 4H, CH_2–Ph). ^{13}C NMR ($CDCl_3$): δ (C_5H_4NS) 119.9, 128.5, 136.6, 141.5, 153.8, 37.5 (CH_2–Ph, $^{1}J_{SnC} = 510$ Hz), 127.4 ($^{4}J_{SnC} = 31$ Hz, *m*-C), 128.2 ($^{5}J_{SnC} = 25$ Hz, *p*-C), 127.3 ($^{3}J_{SnC} = 48$ Hz, *o*-C), 124.2 ($^{2}J_{SnC} = 34$ Hz, *i*-C). ^{119}Sn NMR ($CDCl_3$): δ −219.3.

Crystal and molecular structures of 1, 2 and 3

Data were collected at 298 K on a Bruker SMART CCD 1000 diffractometer using Mo Kα radiation. The structures were solved by direct methods and refined by a full-matrix least-squares procedure based on F^2 using the SHELXL-97 program system. All data were collected at 298(2) K using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) and the ω–2θ scan technique, and corrected for Lorentz and polarization effects but not for absorption. All non-hydrogen atoms were included in the model at their calculated positions. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included.

In vitro cytotoxicity tests

The samples of cytotoxicity against the cell lines was performed according to the PIT method described elsewhere.[19]

RESULTS AND DISCUSSION

IR

The IR medium-intensity bands at 305 and 270 cm^{-1} for complex **1**, 325 and 280 cm^{-1} for complex **2**, and 340 and

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290 cm^{-1} for complex **3** can be assigned to ν_{as}(SnC) and ν_s(SnC). The frequencies ν(Sn–S) appear at 309 cm^{-1} for **1**, 310 cm^{-1} for **2** and 310 cm^{-1} for **3**, and agree with those detected for some organotin(IV)–sulfur derivation.[20] A weak or medium-intensity band in the range 340–355 cm^{-1} has been assigned to Sn–O stretching vibrations. The N–O stretching frequency decreases as a consequence of the decrease in double-bond character of the N–O bond. The magnitude of the shift ($\Delta\nu = 24–33$ cm^{-1}) with respect to the free ligand (1240 cm^{-1}) is in agreement with that observed in other tin or organotin complexes.[21]

NMR data

The $^2J(^{119}Sn–C–^1H)$ value for complex **1** in $CDCl_3$ is 80 Hz, a value intermediate between values recorded for *cis*-*n*-$Bu_2Sn(ox)_2$ (68.1 Hz) and *trans*-*n*-$Bu_2Sn(dbzm)_2$ (98.1 Hz).[22] The $^2J(^{119}Sn–C–^1H)$ values for complexes **2** and **3** are 63 Hz and 66 Hz respectively, and these are constant with those *cis*-octahedral dialkyltin(IV) complexes.[22] A monodentate bonding mode for (2-SpyO) in solution could be ruled out since the coupling constant is unchanged in the presence of added pyridine. The predicted C–Sn–C angle for **1** from the measured $^1J(^{119}Sn–^{13}C)$ value of 691 Hz is 137.7°.[22] Thus, the C_2Sn skeletal configuration, and by inference the skew-trapezoidal geometry, apparently survives in solution. In contrast, the $^1J(^{119}Sn–^{13}C)$ values for **2** and **3** are 480 Hz and 510 Hz respectively, which are considered to be a *cis*-R_2 octahedral-type structure.

From the data of the chemical shift of ^{119}Sn, we can see that all complexes are consistent with the six-coordinated tin(IV) compounds,[23] suggesting that the coordination is asymmetrical, with two oxygen atoms and two sulfur atoms. The ^{119}Sn NMR value for **1** at −121.2 ppm is very different from **2** (228.2 ppm) and **3** (219.3 ppm), which indicates that the chemical shift for the *trans* structure has a lower potential energy than the *cis* geometry,[22] and the shifts are normally higher for phenyl or benzyl substituents compared with alkyl substituents.[24]

Biological activity measurement

The *in vitro* activities of complexes **1**, **2**, and **3**, expressed as ID_{50} values, against the two human tumour cells MCF-7 and WiDr are given in Table 1. They are compared with the ID_{50} values obtained for some reference compounds,[25–28] i.e. diorganotin dicarboxylates, steroidcarboxylates, fluorine-substituted, and polyoxaalkyl moieties.

The screening results indicate that the activities of complexes **1**, **2** and **3** are greater than *cis*-platin and comparable to diorganotin(IV) pyridine-2,6-dicarboxylates, but they are all less than those of the fluorinated aromatic carboxylates and polyoxaalkyltin compounds. Complex **1**, the most active among the three complexes, is comparable to or slightly better than doxorubicin against MCF-7 and tin fluorine-substituted aromatic carboxylates against WiDr.[25–28]

Table 1. ID_{50} values against two human tumour cells, MCF-7 and WiDr, of complexes and reference compounds

	ID_{50} (ng ml^{-1})	
Complex	MCF-7	WiDr
1	56	209
2	296	1185
3	299	930
n-Bu_2Sn(pyridine-2,6-dicarboxylate)[25]	60	106
Ph_2Sn(pyridine-2,6-dicarboxylate)[25]	170	372
$(3\text{-}FC_6H_4COO)_2Sn(n\text{-}Bu)_2$[25]	39	271
$(2,3\text{-}F_2C_6H_3COO)_2Sn(n\text{-}Bu)_2$[25]	23	283
$(n\text{-}Bu)_2Sn$(steroidcarboxylate)[25]	18	36
Polyoxaalkyltin[25]	27	70
cis-Platin[26–28]	850	624
Doxorubicin[26–28]	63	31

X-ray studies

The crystal data and refinement details are given in Table 2 and selected bond distances and angles are given in Table 3. The labelling of the atoms of complexes **1**, **2** and **3** are shown in Fig. 1, Fig. 2 and Fig. 3 respectively. Figure 4, Fig. 5 and Fig. 6 show the molecular packing of complexes **1**, **2** and **3** respectively.

Structure of [*n*-$Bu_2Sn(2\text{-}SpyO)_2$] (1)

The crystal structure of **1** (*trans*-di-*n*-butyl-*cis*-*O*,*O*′-*cis*-*S*,*S*′-bis(2-pyridinethiolato-*N*-oxide)tin(IV)) is shown in Fig. 1. The *n*-butyl groups subtend an angle of 137.8(3)° at tin, and the C_2Sn plane is orthogonal to the plane containing the tin and the two sets of oxygen and sulfur atoms (dihedral angle 89.3°). The dihedral angles between the equatorial plane and heterocyclic rings (1) and (2) are 27.2° and 27.7°

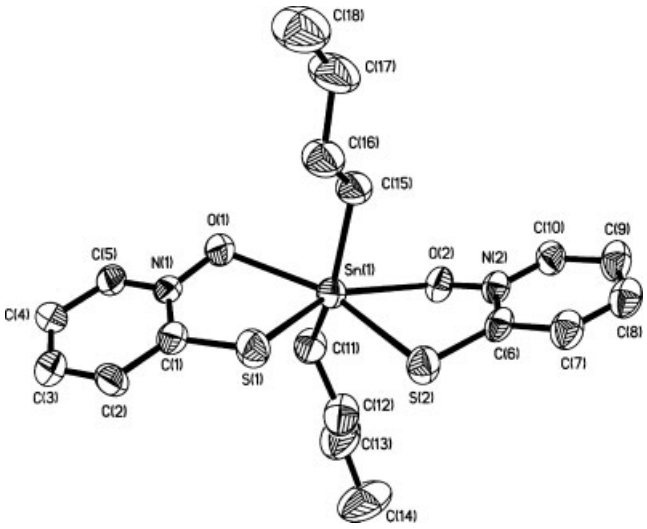

Figure 1. Molecular structure of the compound **1** with thermal ellipsoids at 30% probability level.

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Table 2. Crystal data and refinement details for complexes **1**, **2** and **3**

	1	**2**	**3**
Chemical formula	$C_{18}H_{26}N_2O_2S_2Sn$	$C_{22}H_{18}N_2O_2S_2Sn$	$C_{24}H_{22}N_2O_2S_2Sn$
Formula weight	485.22	525.19	553.25
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$C2/c$	$P\overline{1}$
a (Å)	10.019(16)	17.765(11)	10.993(2)
b (Å)	20.718(12)	9.876(6)	11.087(2)
c (Å)	10.214(6)	13.311(8)	11.406(2)
α (°)	90	90	63.826(2)
β (°)	95.380(9)	115.821(9)	68.950(2)
γ (°)	90	90	75.154(2)
V (Å^3)	2111(2)	2102(2)	1156.4(4)
D_c (g cm^{-3})	1.527	1.659	1.589
Z	4	4	2
F(000)	984	1048	556
Crystal size (mm^3)	0.10 × 0.20 × 0.25	0.10 × 0.15 × 0.30	0.30 × 0.40 × 0.40
θ range (°)	2.0 to 25.0	2.4 to 25.0	2.0 to 23.3
Absorption (mm^{-1})	1.422	1.435	1.31
Reflections collected/unique (R_{int})	9611/3524 (0.050)	5040/1797 (0.040)	5185/3292 (0.013)
Goodness-of-fit on F^2	0.92	1.03	1.04
R indices (all data)	$R_1 = 0.101$, $wR_2 = 0.104$	$R_1 = 0.044$ $wR_2 = 0.081$	$R_1 = 0.027$ $wR_2 = 0.055$
Largest diff. peak and hole (e^{-1} Å^{-3})	0.83 and −0.35	0.68 and −0.86	0.49 and −0.28

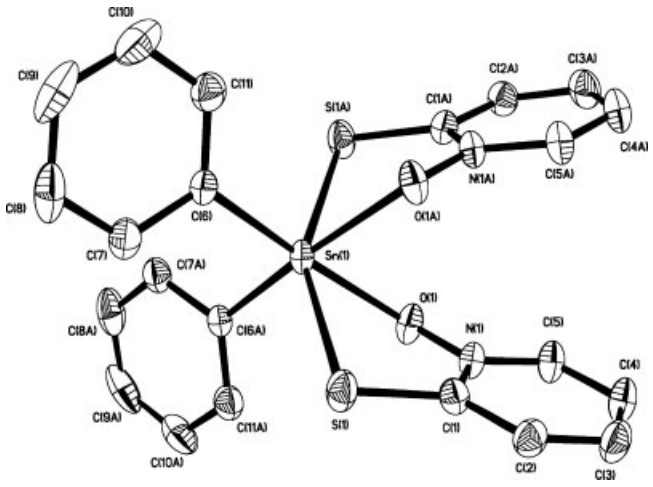

Figure 2. Molecular structure of the compound **2** with thermal ellipsoids at 30% probability level.

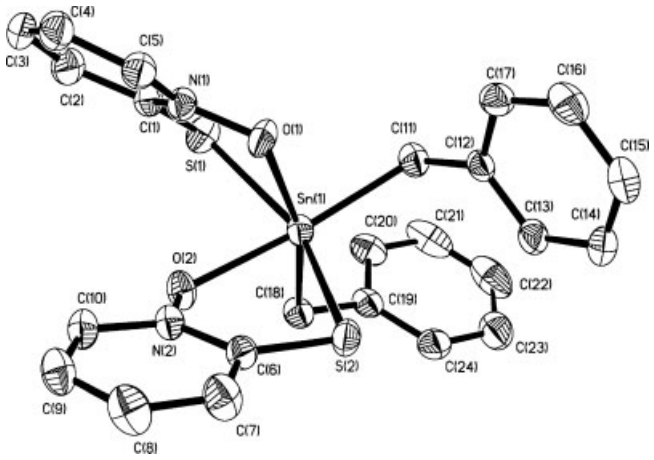

Figure 3. Molecular structure of the compound **3** with thermal ellipsoids at 30% probability level.

respectively, and the dihedral angle of the two pyridine rings is 14.4°. The S(1)–Sn(1)–S(2) angle is 78.84(8)°, but the O(1)–Sn(1)–O(2) angle is opened to 137.86(14)° as a consequence of the intruding *n*-butyl groups. The bite angles of the ligand [72.61(11) and 70.81(10)°] are reconcilable with skew-trapezoidal bipyramid geometry. This geometry can be considered as a distortion of a *trans* regular octahedron and it is favoured if the chelated bite angle is small. This structure is also favoured if asymmetric bidentate ligands, such as Spy and SpyO, are used in place of symmetric bidentate groups. A similar structure was observed in the adduct $SnMe_2(OAc)_2$:[29] the acetato groups are anisobidentate, with Sn–O distances of 2.106(2) and 2.539(2) Å, and the predicted skew-trapezoidal bipyramid structure from ligand–ligand repulsion energy calculations shows that one end of the bidentate ligand experiences a greater repulsion than the other. This accounts for the gross asymmetry observed in the bidentate ligands. The S–C bond distances, 1.714(6) and 1.705(6) Å, are shorter than that found in $[SnR_2(Spy)_2]$,

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Table 3. Selected bond lengths (Å) and bond angles (°) for complexes **1**, **2** and **3**

1		**2**		**3**	
Bond lengths					
Sn(1)–O(1)	2.365(4)	Sn(1)–O(1)	2.191(3)	Sn(1)–O(1)	2.237(2)
Sn(1)–O(2)	2.436(4)	Sn(1)–O(1A)	2.191(3)	Sn(1)–O(2)	2.203(2)
Sn(1)–S(1)	2.519(2)	Sn(1)–S(1)	2.5411(18)	Sn(1)–S(1)	2.5716(9)
Sn(1)–S(2)	2.538(2)	Sn(1)–S(1A)	2.5411(18)	Sn(1)–S(2)	2.5832(9)
Sn(1)–C(11)	2.126(7)	Sn(1)–C(6)	2.139(4)	Sn(1)–C(11)	2.193(3)
Sn(1)–C(15)	2.116(7)	Sn(1)–C(6A)	2.139(4)	Sn(1)–C(18)	2.212(3)
N(1)–O(1)	1.309(6)	N(1)–O(1)	1.340(4)	N (1)–O(1)	1.354(3)
N(2)–O(2)	1.308(5)	N(1A)–O(1A)	1.340(4)	N (2)–O(2)	1.343(3)
Bond angles					
O(1)–Sn(1)–O(2)	137.86(14)	O(1)–Sn(1)–O(1A)	81.84(14)	O(2)–Sn(1)–O(1)	80.77(8)
S(1)–Sn(1)–S(2)	78.84(8)	S(1)–Sn(1)–S(1A)	152.71(6)	S(1)–Sn(1)–S(2)	152.74(3)
C(15)–Sn(1)–O(1)	83.5(2)	C(6)–Sn(1)–O(1)	167.71(11)	C(11)–Sn(1)–O(1)	86.65(11)
C(11)–Sn(1)–O(1)	83.8(2)	C(6A)–Sn(1)–O(1A)	167.71(11)	O(2)–Sn(1)–C(18)	86.71(11)
C(15)–Sn(1)–O(2)	82.3(2)	C(6)–Sn(1)–O(1)	88.84(14)	C(11)–Sn(1)–O(2)	166.66(11)
C(11)–Sn(1)–O(2)	80.7(2)	C(6A)–Sn(1)–O(1A)	88.84(14)	C(18)–Sn(1)–O(1)	164.27(11)
C(15)–Sn(1)–S(1)	108.1(2)	C(6)–Sn(1)–S(1)	96.37(11)	C(11)–Sn(1)–S(1)	99.78(10)
C(11)–Sn(1)–S(1)	106.1(2)	C(6A)–Sn(1)–S(1A)	96.37(11)	C(18)–Sn(1)–S(1)	93.37(12)
C(15)–Sn(1)–C(11)	137.8(3)	C(6)–Sn(1)–C(6A)	101.4(2)	C(11)–Sn(1)–C(18)	106.43(13)
O(1)–Sn(1)–S(1)	72.61(11)	O(1)–Sn(1)–S(1)	74.86(8)	O(1)–Sn(1)–S(1)	75.54(5)
O(2)–Sn(1)–S(1)	149.48(10)	O(1A)–Sn(1)–S(1A)	74.86(8)	O(2)–Sn(1)–S(1)	81.60(5)
C(15)–Sn(1)–S(2)	102.7(2)	C(6)–Sn(1)–S(1A)	100.82(12)	C(11)–Sn(1)–S(2)	99.44(9)
C(11)–Sn(1)–S(2)	107.6(2)	C(6)–Sn(1)–S(1A)	100.82(12)	C(18)–Sn(1)–S(2)	99.51(12)
O(1)–Sn(1)–S(2)	151.26(11)	O(1)–Sn(1)–S(1)	74.86(8)	O(2)–Sn(1)–S(2)	75.34(5)
O(2)–Sn(1)–S(2)	70.81(10)	O(1A)–Sn(1)–S(1A)	74.86(8)	O(1)–Sn(1)–S(2)	86.48(6)
O(1)–N(1)–C(5)	115.9(5)	C (1)–N(1)–O(1)	120.8(3)	C(5)–N(1)–O(1)	116.3(2)
O(1)–N(1)–C(1)	121.2(5)	C(5)–N(1)–O(1)	116.5(3)	O(1)–N(1)–C(1)	121.0(6)
O(2)–N(2)–C(10)	119.5(5)	C(1)–N(1)–C(5)	122.7(3)	O(2)–N(2)–C(10)	116.8(2)
O(2)–N(2)–C(6)	119.2(5)	O(1A)–N(1A)–C(5A)	116.5(3)	O(2)–N(2)–C(6)	120.8(2)
C(10)–N(2)–C(6)	121.3(5)	C(1A)–N(1A)–C(5A)	122.7(3)	C(10)–N(2)–C(6)	122.3(3)
N(1)–O(1)–Sn(1)	116.4(3)	N (1)–O(1)–Sn(1)	115.7(2)	N(1)–O(1)–Sn(1)	116.00(15)
N(2)–O(2)–Sn(1)	117.1(3)	N(1A)–O(1A)–Sn(1)	115.7(2)	N(2)–O(2)–Sn(1)	118.54(14)
C(1)–S(1)–Sn(1)	100.0(2)	C(1)–S(1)–Sn(1)	95.42(15)	C(1)–S(1)–Sn (1)	95.60(10)
C(6)–S(2)–Sn(1)	101.6(2)	C(1A)–S(1A)–Sn(1)	95.42(15)	C(6)–S(2)–Sn(1)	96.84(10)
N(2)–C(6)–S(2)	120.2(4)	N(1)–C(1)–S(1)	119.6(3)	N(2)–C(6)–S(2)	120.1(3)
C(12)–C(11)–Sn(1)	113.1(5)	C(11)–C(6)–Sn(1)	123.5(3)	C(12)–C(11)–Sn(1)	116.8(3)
C(16)–C(15)–Sn(1)	116.3(5)	C(7)–C(6)–Sn(1)	118.1(3)	C(19)–C(18)–Sn(1)	111.4(2)

i.e. 1.751(7) Å.[6] These values suggest that, compared with HSpyO, the ability of HSpy to transform its thione to the thiol form is higher. The Sn–C distances [2.126(7) and 2.116(7) Å] and Sn–S distances [2.519(2) and 2.538(2) Å] are similar to those found in $[Me_2Sn(S_2COMe)_2]$, i.e. 2.10(2), 2.14(1) Å and 2.482(1), 2.538(2) Å respectively.[30] The Sn–O distances [2.365(4) and 2.436(4) Å] are shorter than the *trans*-$[SnR_2]$ octahedral complexes $[SnMe_2Cl_2{\cdot}2PyO]$ 2.251.[31] And the N–O bond distances, 1.308(5) and 1.309(6) Å, are comparable to those found in (pyridine-*N*-oxide) tin derivatives.[8]

The crystal structure of **1** shows ring-stacking interactions: each SpyO group is arranged face-to-face at a distance of 3.511 Å and shows significant $\pi-\pi$ stacking interactions.[32] The orientation is such that the heterocyclic ring substituents 'face' another heterocyclic ring on neighbouring monomers, as shown in Fig. 4.

Structures of $[Ph_2Sn(2\text{-}SpyO)_2]$ (2) and $[(PhCH_2)_2Sn(2\text{-}SpyO)_2]$ (3)

The molecular structures of complexes **2** and **3** are shown in Figs 2 and 3, with the geometry of the coordination polyhedron around tin being described as distorted *cis*-octahedral, as observed in the literature,[33–35] and are different from **1**. The ligand behaves as a bidentate species and chelates the tin atom by means of the oxygen and sulfur atoms. The basal plane is defined by two oxygen atoms of the ligands

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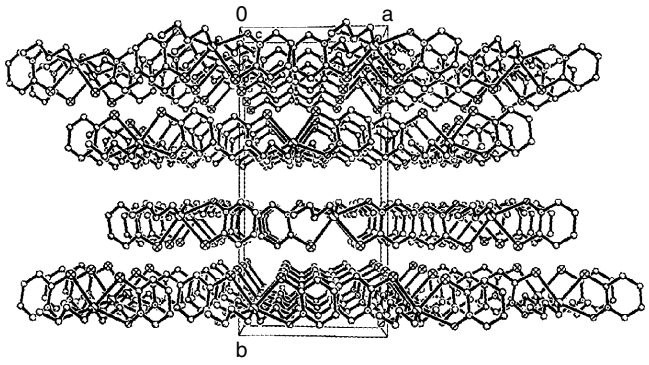

Figure 4. Molecular packing diagram in unit cell of **1** showing $\pi-\pi$ stacking interactions.

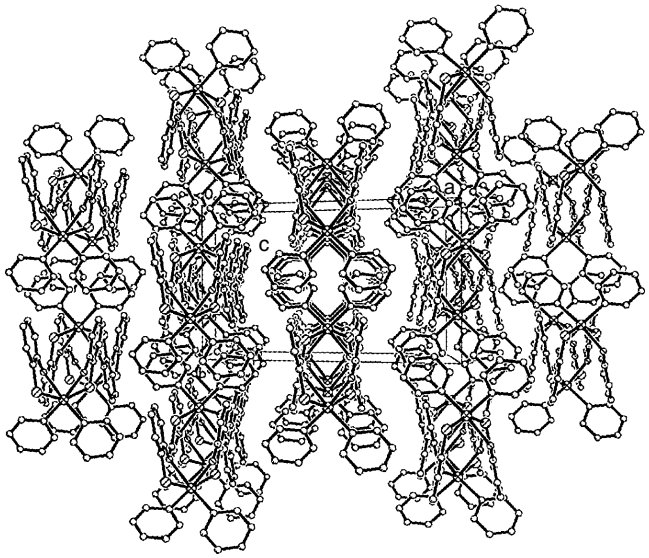

Figure 5. Molecular packing diagram in unit cell of **2**.

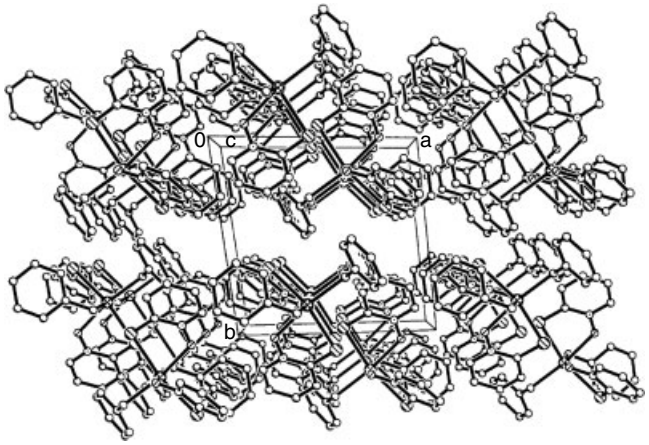

Figure 6. Molecular packing diagram in unit cell of **3**.

and the carbon atoms of the phenyl or benzyl groups, and the apical positions are occupied by two sulfur atoms of the ligands. For **2**, the structure consists of discrete monomeric molecules with crystallographic twofold symmetry, through the tin atom, as found in $Ph_2Sn(S_2COMe)_2$.[30] The sulfur atom subtends an angle of 152.71(6)° at tin, and the S_2Sn plane is orthogonal to the plane containing the tin and the two sets of oxygen and phenyl groups (dihedral angle 91.5°). The pyridine rings (1) and (2) are symmetrical, and the dihedral angle between the two pyridine rings is 22.0°; the dihedral angles between the equatorial plane and this heterocyclic rings (1) and (2) are 64.7°, whereas that of the S_2Sn plane and the heterocyclic rings is 29.3°. The C(1)–Sn(1)–C(2) angle is 101.4(2)°, and the O(1)–Sn(1)–O(2) angle is 81.84(14)°, as a consequence of *cis-C,C* and *cis-O,O*. The bite angle of the ligand is 74.86(8)°. The Sn–O distance [2.191(3) Å] is shorter than that in **1**, and the Sn–C distance (2.139 Å) and the Sn–S distance [2.5411(18) Å] are consistent with those found in $[(cyclo\text{-}C_6H_{11})_2Sn(Spy)_2]$, i.e. [2.200(6) and 2.503(2) Å].[36]

Compound **3** has a structure similar to **2**, in which the tin atom is displaced by 0.05 Å from the geometric centre of the equatorial plane of O(1), O(2), C(11) and C(18). The dihedral angle between the basal plane and the S_2Sn plane is 88.6°. The axial angle S(1)–Sn(1)–S(2) is 152.74° with chelate bite angles of 75.54° and 75.34°. The dihedral angle of the pyridine rings (1) and (2) is 34.2°, and is bigger than that in **2**. Sn–C bond lengths [2.193(3) and 2.212(3) Å], Sn–S [2.5716(9) and 2.5832(9) Å], Sn–O [2.237(2) and 2.203(2) Å] are comparable to those found in **2**. The S–C bond distances [1.707(4) Å for **2**] and [1.716(3) Å and 1.722(3) Å for **3**] are shorter than those found in the above-mentioned $[SnR_2(Spy)_2]$.[6]

From the data, we can see that complexes **2** and **3** have a *cis* configuration; clearly, the combined effect of the bulk of the phenyl or benzyl groups and small bite angles force their complexes to adopt the energetically favoured *cis* configuration.

Supplementary material

Crystallographic data (excluding structure factors) for the structure analysis of compounds **1**, **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos 192502 (**1**), 192506 (**2**) and 183611 (**3**). Copies of this information may be obtained free of charge from The Director, CCDC, 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).

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