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Organotin adducts with pyrimidinethione: crystal structure of dimethyldi(pyrimidine-2-thiolato)tin(IV) and diphenyldi(pyrimidine-2-thiolato)tin(IV)

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The complexes dimethyldi(pyrimidine-2-thiolato)tin(IV) (1) and diphenyldi(pyrimidine-2-thiolato)tin(IV) (2) have been structurally characterized by means of X-ray crystallography. Complex 1 exhibits strong π–π stacking interactions and adduct 2 is self-assembled *via* intermolecular hydrogen bonds, C—H–π and π–π stacking interactions. Partial solvolysis occurs in organic solvents for 1 and 2. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

Organotin compounds show a large spectrum of biological activities. In recent years, several investigations to test their antitumour activity have been carried out. It has been observed that several organotin complexes are effective antineoplastic and antiviral agents; therefore, much attention has been focused on their antitumour properties and their implications in antioncogenesis.[1] Also, they are used commercially as bactericides, fungicides, acaricides, and industrial and agriculture biocides.[2] The presence of 2-mercaptopyrimidine nucleotides has been detected in *Escherichia coli* sRNA and yeast tRNA; it was found to inhibit the synthesis of tRNA, and thus it acts as an antitumour and antithyroid agent.[3] A similar inhibitory effect has been found for pyrimidine-2-thione (Hpmt), and the compound also shows pronounced *in vitro* bacteriostatic activity.[4]

Continuing our studies on the co-ordination chemistry of heterocyclic thiones (specifically pyrimidine-2-thione) with transition metal ions[5] and organotin(IV),[6] we report here on the crystal and molecular structure of dimethyl(pyrimidine-2-thiolato)tin(IV), $SnMe_2(Spym)_2$ **1**, and diphenyldi(pyrimidine-2-thiolato)tin(IV), $SnPh_2(Spym)_2$ **2**, complexes.

EXPERIMENTAL

The complexes **1** and **2** were prepared according to the procedure proposed in Ref. 6a. Colourless crystals suitable for X-ray diffraction study were formed by slow evaporation of a methanol/acetonitrile (1:1) solution prepared by dissolving of the title products. X-ray diffraction data were collected on KUMA KM4 κ-geometry diffractometer.[7a] Crystal data and experimental conditions are listed in Table 1. The structures were solved by direct methods using SHELXS86 software[7b] and the refinements were carried out using SHELXL93 software[7c] minimizing on the weighting R factor R^w. Anisotropic thermal parameters were used for all non-hydrogen atoms, whereas hydrogen atoms were inserted in calculated positions and treated as a 'riding model'.

RESULTS AND DISCUSSION

Interatomic distances and bond angles for **1** and **2**

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Table 1 Crystal data and experimental conditions for complexes **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{10}H_{12}N_4S_2Sn$	$C_{20}H_{16}N_4S_2Sn$
Formula weight	371.07	495.22
Crystal system	Monoclinic	Orthorhombic
Space group	*Cm*	*Pbca*
a/Å	7.1360(10)	12.661(3)
b/Å	17.858(4)	17.230(3)
c/Å	6.2210(10)	37.683(8)
α/deg	90	90
β/deg	117.88(3)	90
γ/deg	90	90
V/Å^3	700.8(3)	8221(3)
Z	2	16
D_{calc}/g cm^{-3}	1.758	1.600
F(000)	364	3936
μ(Mo Kα)/cm^{-1}	21.0	14.6
Crystal size/mm	0.10 × 0.20 × 0.20	0.20 × 0.20 × 0.30
Data collection		
Temperature (K)	293	293
Radiation/Å	Mo Kα 0.710 73	Mo Kα 0.710 73
θ range/deg	2.3, 27.0	1.1, 23.0
Range *h*; *k*; *l*	0 to 8; −22 to 22; −7 to 7	−13 to 0; −18 to 0; −41 to 0
Total data	1641	5590
Unique data, *R*(int)	850, 0.181	5587, 0.011
Observed data [$I > 2.0\sigma(I)$]	793	3361
Refinement		
No. of reflections	839	4544
No. of parameters	80	487
R	0.0655	0.0390
R_w	0.1548	0.1340
S	0.97	1.07
Min., max. residual density e/Å^{-3}	−1.60, 2.03	−0.78, 0.56

are compiled in Tables 2 and 3. A perspective view of **1** is shown in Fig. 1.[7d] The crystal structure of **1** consists of a monomer unit in which tin(IV) is coordinated to two methyl groups and to two sulfur and nitrogen atoms from the two deprotonated ligands (Spym). The Sn—C distances [2.17(1) and 2.25(1) Å] and Sn—S distance [2.466(4) Å] are similar to those found in $[SnR_2(Spy)_2]$ [2.133(9)–2.13(1) Å and 2.487 Å respectively. The Sn—S distance is close to the typical length of a single covalent bond.[8a] The Sn—N distance, 2.83(2) Å is longer than that found in $[SnR_2(Spy)_2]$, 2.702(5) Å. The Sn—N bond distance, though less than the sum of the van der Waals radii, 3.75 Å,[8b] is one of the largest reported for organotin compounds, although longer bonds have been reported in other tin species.[8c] The bite angle S(2)—Sn—N(3) of compound **1** [58.5(2) °] is reconcilable with skew-trapezoidal bipyramid geometry. This geometry can be considered as a distortion of a *trans* regular

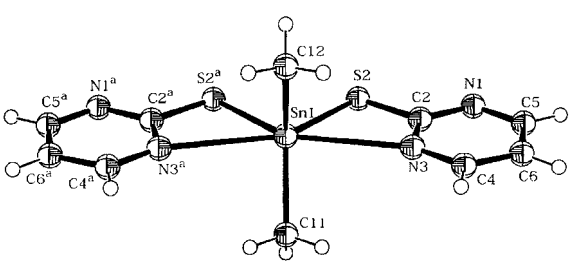

Figure 1 An ORTEP representation of **1** with the atom numbering scheme.

Table 2 Bond lengths (Å) for **1** and **2**

Compound **1**			
Sn(1)—C(11)	2.17(1)	N(1)—C(5)	1.35(2)
Sn(1)—C(12)	2.25(1)	C(5)—C(6)	1.35(2)
Sn(1)—S(2)	2.466(4)	N(3)—C(2)	1.34(2)
Sn(1)—N(3)	2.83(2)	C(4)—C(6)	1.39(3)
S(2)—C(2)	1.72(2)	N(3)—C(4)	1.36(3)
N(1)—C(2)	1.35(2)		
Compound **2**			
Molecule 1		*Molecule 2*	
Sn(1)—C(41)	2.089(8)	Sn(1)—C(31)	2.101(9)
Sn(1)—C(31)	2.112(8)	Sn(1)—C(41′)	2.103(9)
Sn(1)—S(12)	2.464(2)	Sn(1)—S(12′)	2.466(3)
Sn(1)—S(22)	2.466(2)	Sn(1′)—S(22′)	2.474(2)
Sn(1)—N(11)	2.639(6)	Sn(1′)—N(21′)	2.666(7)
Sn(1)—N(21)	2.948(8)	Sn(1′)—N(11′)	2.688(7)
C(12)—S(12)	1.730(9)	C(12′)—S(12′)	1.739(9)
N(13)—C(12)	1.33(1)	N(13′)—C(12′)	1.32(1)
N(23)—C(22)	1.32(1)	N(23′)—C(22′)	1.33(1)
C(24)—C(25)	1.37(2)	C(24′)—C(25′)	1.36(1)
C(32)—C(33)	1.37(2)	C(32′)—C(33′)	1.39(2)
C(41)—C(42)	1.38(1)	C(41′)—C(42′)	1.36(1)
C(44)—C(45)	1.36(2)	C(44′)—C(45′)	1.37(2)
S(22)—C(22)	1.739(9)	S(22′)—C(22′)	1.737(9)
N(13)—C(14)	1.32(1)	N(13′)—C(16′)	1.30(1)
N(23)—C(24)	1.33(2)	N(23′)—C(24′)	1.334(1)
C(25)—C(26)	1.37(2)	C(25′)—C(26′)	1.35(2)
C(33)—C(34)	1.36(2)	C(33′)—C(34′)	1.34(2)
C(41)—C(46)	1.36(1)	C(41′)—C(46′)	1.33(1)
C(45)—C(46)	1.40(1)	C(45′)—C(46′)	1.37(2)
N(11)—C(12)	1.33(1)	N(11′)—C(12′)	1.33(1)
N(21)—C(22)	1.31(1)	N(21′)—C(22′)	1.32(1)
C(14)—C(15)	1.37(2)	C(14′)—C(15′)	1.36(2)
C(31)—C(32)	1.36(1)	C(31′)—C(32′)	1.37(1)
C(34)—C(35)	1.36(2)	C(34′)—C(35′)	1.31(3)
C(42)—C(43)	1.38(1)	C(42′)—C(43′)	1.37(2)
N(11)—C(16)	1.31(1)	N(11′)—C(14′)	1.31(1)
N(21)—C(26)	1.31(1)	N(21′)—C(26′)	1.35(1)
C(15)—C(16)	1.38(1)	C(15′)—C(16′)	1.39(2)
C(31)—C(36)	1.37(1)	C(31′)—C(36′)	1.36(1)
C(35)—C(36)	1.37(1)	C(35′)—C(36′)	1.38(2)
C(43)—C(44)	1.36(1)	C(43′)—C(44′)	1.32(2)

octahedron and it is favoured if the chelate bite angle is small. This structure is also favoured if asymmetric bidentate ligands, such as Spy and Spym, are used in place of symmetric bidentate groups. The same structure was observed in the adduct $SnMe_2(OAc)_2$, where the acetato groups are anisobidentate, with Sn—O distances of 2.106(2) and 2.539(2) Å and a bite angle of 55.14(7) °.[9a] Kepert[9b] predicted the skew-trapezoidal bipyramid structure from ligand–ligand repulsion energy calculations and showed that the one end of a bidentate ligand experiences a greater repulsion than the other. This accounts for the gross asymmetry observed in the bidentate ligands.[9b] The S—C bond distance, 1.72(2) Å, is shorter than that found in $[SnR_2(Spy)_2]$, 1.751(7) Å, and is consistent with increased single-bond character. These values suggest that the ability of HSpy, compared with HSpym, to transform its thione to the thiol form is higher. The pyrimidine rings (1) and (2) are planar, as is the equatorial plane formed by the two pyrimidine rings and the Sn1 atom (3).

Table 3 Bond angles (deg) for **1** and **2**

Compound **1**			
S(2)—Sn(1)—C(11)	116.0(3)	S(2)—Sn(1)—C(12)	106.6(2)
C(11)—Sn(1)—C(12)	120.6(5)	C(11)—Sn(1)—S(2)a	116.0(3)
Sn(1)—S(2)—C(2)	95.1(6)	C(2)—N(1)—C(5)	117(2)
S(2)—C(2)—N(1)	120(1)	S(2)—C(2)—N(3)	116(1)
N(3)—C(4)—C(6)	119(2)	N(1)—C(5)—C(6)	121(2)
S(2)—Sn(1)—S(2)a	85.3(1)		
C(12)—Sn(1)—S(2)a	106.6(2)		
C(2)—N(3)—C(4)	118(2)		
N(1)—C(2)—N(3)	124(2)		
C(4)—C(6)—C(5)	120(2)		
Compound **2**			
S(12)—Sn(1)—S(22)	87.09(8)	S(12′)—Sn(1′)—S(22′)	89.81(9)
S(22)—Sn(1)—C(31)	106.3(2)	S(22′)—Sn(1′)—C(31′)	106.2(2)
Sn(1)—S(12)—C(12)	90.1(3)	Sn(1′)—S(12′)—C(12′)	91.0(3)
C(12)—N(13)—C(14)	114.2(8)	C(12′)—N(13′)—C(16′)	115.2(9)
S(12)—C(12)—N(11)	116.0(6)	S(12′)—C(12′)—N(11′)	116.3(6)
N(13)—C(14)—C(15)	125(1)	N(11′)—C(14′)—C(15′)	123(1)
S(22)—C(22)—N(21)	117.7(6)	S(22′)—C(22′)—N(21′)	115.8(6)
N(23)—C(24)—C(25)	123(1)	N(23′)—C(24′)—C(25′)	123.5(8)
Sn(1)—C(31)—C(32)	118.5(7)	Sn(1′)—C(31′)—C(32′)	122.1(7)
C(31)—C(32)—C(33)	122(1)	C(31′)—C(32′)—C(33′)	119(1)
C(34)—C(35)—C(36)	122(1)	C(34′)—C(35′)—C(36′)	122(1)
Sn(1)—C(41)—C(46)	119.4(7)	Sn(1′)—C(41′)—C(46′)	121.9(7)
C(42)—C(43)—C(44)	120.1(9)	C(42′)—C(43′)—C(44′)	120(1)
S(12)—Sn(1)—C(31)	108.8(2)	S(12′)—Sn(1′)—C(31′)	110.1(2)
S(22)—Sn(1)—C(41)	107.4(2)	S(22′)—Sn(1′)—C(41′)	110.3(2)
Sn(1)—S(22)—C(22)	96.9(3)	Sn(1′)—S(22′)—C(22′)	90.6(3)
C(22)—N(21)—C(26)	117.1(8)	C(22′)—N(21′)—C(26′)	116.7(8)
S(12)—C(12)—N(13)	118.5(7)	S(12′)—C(12′)—N(13′)	117.7(7)
C(14)—C(15)—C(16)	116(1)	C(14′)—C(15′)—C(16′)	114(1)
S(22)—C(22)—N(23)	116.3(7)	S(22′)—C(22′)—N(23′)	117.1(7)
C(24)—C(25)—C(26)	116(1)	C(24′)—C(25′)—C(26′)	117.8(9)
Sn(1)—C(31)—C(36)	124.2(6)	Sn(1′)—C(31′)—C(36′)	119.9(7)
C(32)—C(33)—C(34)	120(1)	C(32′)—C(33′)—C(34′)	121(1)
C(31)—C(36)—C(35)	120.3(9)	C(31′)—C(36′)—C(35′)	120(1)
C(42)—C(41)—C(46)	117.6(8)	C(42′)—C(41′)—C(46′)	116.5(9)
C(43)—C(44)—C(45)	121(1)	C(43′)—C(44′)—C(45′)	120(1)
S(12)—Sn(1)—C(41)	106.6(2)	S(12′)—Sn(1′)—C(41′)	106.6(2)
C(31)—Sn(1)—C(41)	131.6(3)	C(31′)—Sn(1′)—C(41′)	127.4(3)
C(12)—N(11)—C(16)	118.9(8)	C(12′)—N(11′)—C(14′)	116.6(8)
C(22)—N(23)—C(24)	115.7(9)	C(22′)—N(23′)—C(24′)	114.1(8)
N(11)—C(12)—N(13)	125.5(8)	N(11′)—C(12′)—N(13′)	126.0(8)
N(11)—C(16)—C(15)	120.7(9)	N(13′)—C(16′)—C(15′)	124(1)
N(21)—C(22)—N(23)	126.0(8)	N(21′)—C(22′)—N(23′)	127.1(8)
N(21)—C(26)—C(25)	122(1)	N(21′)—C(26′)—C(25′)	120.7(9)
C(32)—C(31)—C(36)	117.2(9)	C(32′)—C(31′)—C(36′)	118.0(9)
C(33)—C(34)—C(35)	118(1)	C(33′)—C(34′)—C(35′)	119(1)
Sn(1)—C(41)—C(42)	123.0(6)	Sn(1′)—C(41′)—C(42′)	121.5(7)
C(41)—C(42)—C(43)	120.9(8)	C(41′)—C(42′)—C(43′)	122(1)
C(44)—C(45)—C(46)	118(1)	C(44′)—C(45′)—C(46′)	119(1)
C(41)—Sn(1)—C(31)	131.6(3)	C(31′)—Sn(1′)—C(41′)	127.4(3)
S(12)—Sn(1)—S(22)	87.08(8)	S(12′)—Sn(1′)—S(22′)	89.81(8)
S(12)—Sn(1)—N(11)	61.2(2)	S(22′)—Sn(1′)—N(21′)	60.6(2)
S(22)—Sn(1)—N(21)	57.1(2)	S(12′)—Sn(1′)—N(11′)	60.8(2)
N(11)—Sn(1)—N(21)	154.4(2)	N(21′)—Sn(1′)—N(11′)	149.0(2)

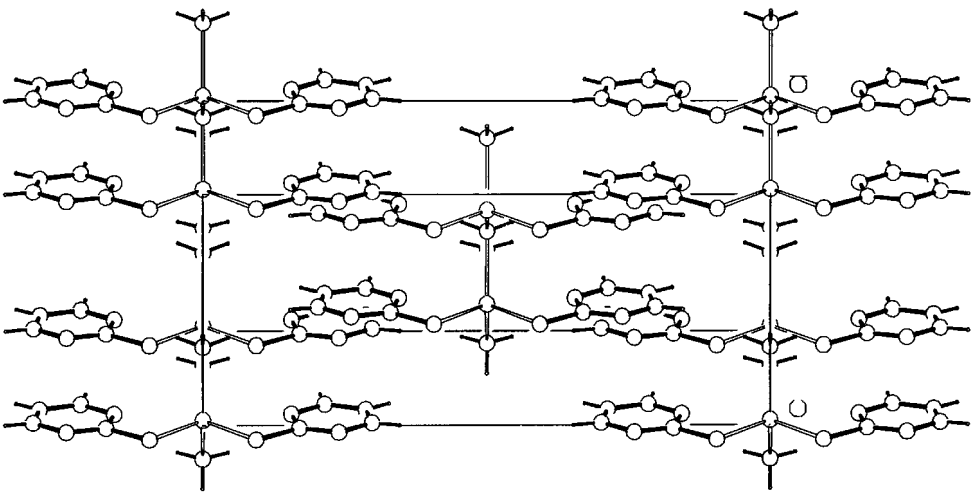

Figure 2 Packing diagram of complex **1** viewed along the *c* axis of the unit cell, showing π–π stacking interactions.

The largest deviation from the best plane (3) is −0.032(5) ° and 0.027(7) ° for S(2) and N(1) respectively. The dihedral angles between the planes of ring (1) and the equatorial plane (3) is 1.2(8) °, indicating that the equatorial plane as a whole does not deviate from planarity.

The observed bond angle of C—Sn—C is 120.6(5) °. This compares with a predicted value of 110 ° based on Mössbauer data (isomer shift 1.30 mm s^{-1}, quadrupole splitting 2.46 mm s^{-1})[6b] and the point-charge approach given by the equation $\Delta E_Q = 4[R](1 - 3\sin^2\theta\cos^2\theta)^{1/2}$, where $(180 - 2\theta)$ is the C—Sn—C bond angle and the partial quadrupole splitting (PQS) contributions from ligands other than R groups are considered to be negligible. The low calculated value (110 °) is due to the fact that sulfur and nitrogen atoms have non-zero PQS values and that contributions other

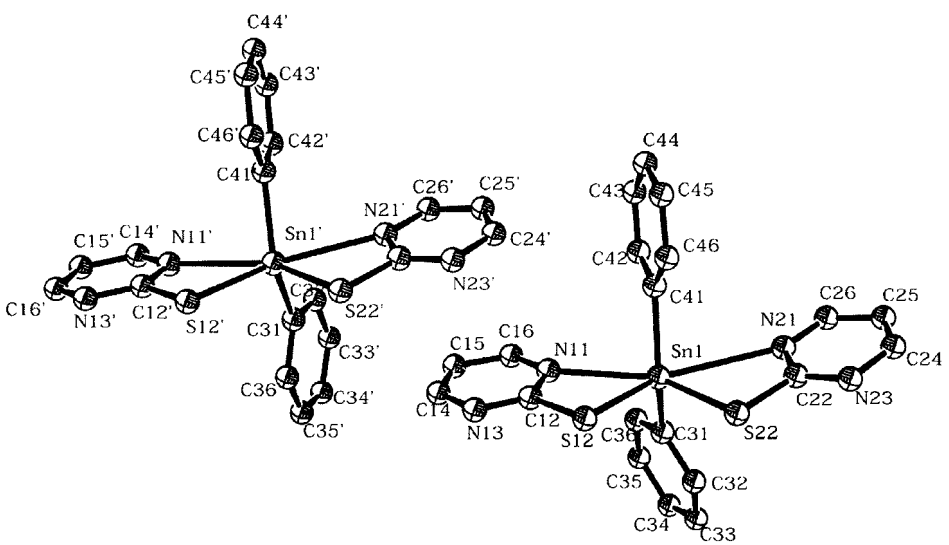

Figure 3 An ORTEP representation of **2** with the atom numbering scheme.

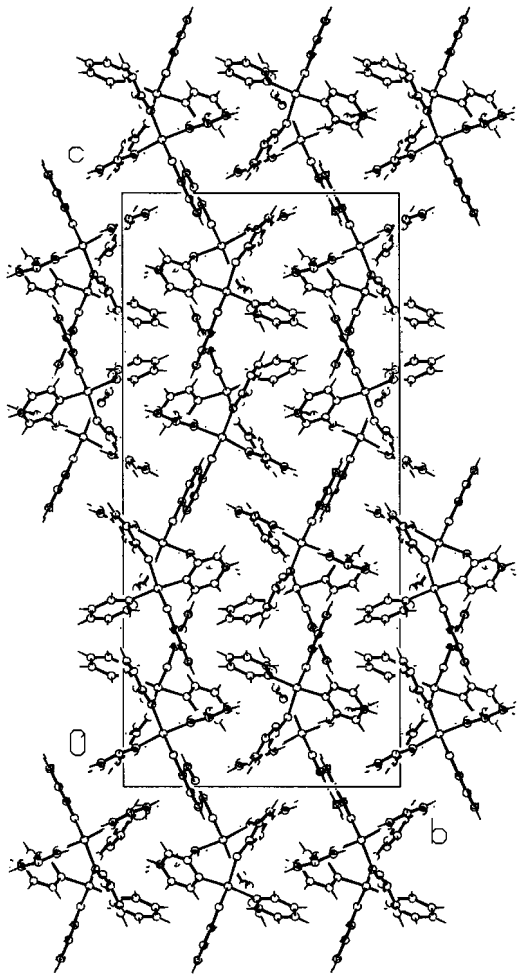

Figure 4 Packing diagram of complex **2** viewed along the *a* axis of the unit cell, showing C—H–π and π–π stacking interactions.

than from the R group are not negligible.[10] From the coupling constant [$^2J(^{119/117}$Sn—C—H)], the angle C—Sn—C was also calculated to be 133 ° in DMSO-d_6 solution, suggesting Sn–DMSO interaction.[6b]

The crystal structure of **1** shows ring-stacking interactions; each Spym group is arrange face-to-face at a distance of 3.66 Å and shows significant π–π stacking interactions.[11,13] The orientation is such that the heterocyclic ring substituents 'face' other heterocyclic rings on neighbouring monomers. A view of the extended network along the *c* axis is shown in Fig. 2.

The molecular structure of compound **2** and the atom numbering scheme is shown in Fig. 3. The unit cell contains two crystallographically independent molecules. The ligand behaves as a bidentate species and chelates the tin atom by means of the aromatic nitrogen and the thiolato sulfur. The Sn—C distances [2.089(8)–2.112(8) Å] and the Sn—S distances [2.464(2)–2.474(2) Å] are similar to those found in other [$SnR_2(chelate)_2$] systems.[12] The four Spym ligands (considering both molecules) differ distinctly from each other with regard to their Sn—N bond distances [2.639(6), 2.948(8) Å] and S—Sn—N bite angles [57.1(2)–60.8(2) °], whereas for $SnPh_2(Spy)_2$ the respective values [Sn—N(mean) is 2.67(4) Å, S—Sn—N is 60.7(8) °] are almost identical.[12b] This co-ordination geometry is also described as skew-trapezoidal bipyramidal. The basal plane is defined by the four atoms (S_2N_2) derived from the two chelating Spym ligands and the axial positions are occupied by the two phenyl groups. The S—C bond distances [1.730(9)–1739(9) Å] are consistent with increased single-bond character. The pyrimidine rings and the phenyl rings are planar. The dihedral angles between the planes of the heterocyclic rings are 12.4(5) ° and 8.5(5) ° for molecules 1 and 2 respectively, indicating that the equatorial plane as a whole deviates significantly from planarity. Also, the dihedral angles between the phenyl groups are 23.4(5) ° and 14.7(5) ° respectively for the two molecules.

The crystal structure of **2** shows ring-stacking interactions. The orientation is such that the heterocyclic ring substituents of molecule 1 'face' the heterocyclic ring of molecule 2 at a distance of 3.665 Å and show significant π–π stacking interactions. Furthermore, C—H–π interactions and intermolecular hydrogen bonds stabilize this structure (Table 4). In this case, complex **2** is self-assembled *via* intermolecular hydrogen bonds, C—H–π and π–π stacking interactions; consequently, a different packing arrangement than complex **1** results.[11,13] A view of the crystal packing along the *a* axis is shown in Fig. 4.

The co-ordination scheme of **1** and **2** is similar to that found in di-*n*-butylbis(5-nitropyridine-2-thiolato)tin(IV) by Domazetis et al.[8d], who described it as a distorted octahedron. However, Ng et al.[12a] consider that the co-ordination polyhedra of this and similar compounds are best described as being skew-trapezoidal bipyramidal.

The observed C—Sn—C bond angles are 127.4(3)–131.6(3) °, whereas the predicted value based on Mössbauer data is 112 ° (isomer shift 1.27 mm s^{-1}, quadrupole splitting 2.53 mm s^{-1}).[6b]

Table 4 C—H–π, π–π interactions and inter-hydrogen bonding in **1** and **2** (Cg = ring centroid)

			Distance (Å)		Angle (deg)
Compound **1**[a]			Cg(*I*)–Cg(*J*)[c]	CgJ_perp[d]	A[e]
Cg(1) → Cg(2)[i]			3.665	3.393	2.10
Cg(2) → Cg(1)[ii]			3.665	3.363	2.10
Compound **2**[b]					
Cg(1) → Cg(4)			3.655	3.455	5.81
Cg(5) → Cg(7)[iii]			4.779	5.004	65.03
Cg(6) → Cg(8)[iii]			4.980	3.131	3.76
Cg(7) → Cg(4)			4.819	4.681	79.92
Cg(7) → Cg(6)[iv]			4.996	4.586	48.32
			H-Cg	X-Cg	C—H-Cg
C(15)—H(15) → Cg(6)			2.948	3.725	142.21
C(24′)—H(24′) → Cg(7)			2.784	3.600	146.85
C(34′)—H(34′) → Cg(7)[vi]			3.109	3.815	134.10
C(35′)—H(35′) → Cg(4)[iii]			3.012	3.893	158.50
C(45)—H(45) → Cg(1)[vii]			3.284	3.958	131.16
C(45)—H(45) → Cg(5)[vii]			3.355	3.987	127.24
C(45′)—H(45′) → Cg(2)[vii]			2.773	3.545	141.14
Donor (D)	—H···	TAcceptor (A)	D···A	H···A	D—H···A
C(43′)—	H(43′)	···N(23)[v]	3.436(14)	2.604(14)	149.3(12)

Symmetry operations: (i) $-\frac{1}{2}+x, \frac{1}{2}-y, z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, z$; (iv) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (v) $-\frac{1}{2}+x, y, \frac{1}{2}-z$; (vi) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vii) $\frac{1}{2}-x, -\frac{1}{2}+y, z$.

[a] Cg(1) and Cg(2) are the centroids of the two rings of compound **1**.

[b] Cg(1) and Cg(2) are the rings N(11)—C(12)—N(13)—C(14)—C(15)—C(16) and N(11′)—C(12′)—N(13′)—C(14′)—C(15′)—C(16′) respectively; Cg(5) and Cg(6) are the phenyl rings C(31)—C(32)—C(33)—C(34)—C(35)—C(36) and C(31′)—C(32′)—C(33′)—C(34′)—C(35′)—C(36′) respectively; Cg(7) and Cg(8) are the phenyl rings C(41)—C(42)—C(43)—C(44)—C(45)—C(46) and C(41′)—C(42′)—C(43′)—C(44′)—C(45′)—C(46′) respectively; Cg(4) is the pyrimidine ring N(21′)—C(22′)—N(23′)—C(24′)—C(25′)—C(26′).

[c] Cg–Cg is the distance between ring centroids.

[d] CgJ_perp is the perpendicular distance of Cg(*J*) on ring *I*.

[e] A is the dihedral angle between planes *I* and *J*.

The structures of **1** and **2** from spectroscopic data were assumed to be *trans*-octahedral, *cis-S*, *cis-N* or skew trapezoidal in the solid state or in solution.[6b,14a] Values of δ (ppm) in ^{119}Sn NMR spectra for **1** and **2** have been reported in Ref. 13 (δ = -107 and -150 in $CDCl_3$ and in $CDCl_3$–DMSO-d_6 respectively for **1** and $\delta = -227$ and -259 7shy;in the same solvents respectively for **2**). Shifts to more negotions fields in $CDCl_3$–DMSO-d_6 could be interpreted in terms of DMSO co-ordination to tin or to a partial solvolysis.[14b] Shifts of δ to higher fields for **1** compared with **2** reflect the decreasing co-ordination number at tin in **1**; dissociation probably occurs in both solvents for **1** and **2**. The fact that **1** interacts more strongly with DMSO-d_6 could be due to a steric effect: methyl groups for **1** instead of phenyl groups for **2**. DMSO-d_6 presumably approaches **1** to the tin centre and the value of the C—Sn—C bond angle increases from 121.1 to 133 °.

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