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Synthesis and Structural Characterisation of Diorganotin(IV) and Diphenyllead(IV) Complexes of Pyrimidine-2-thionate Derivatives

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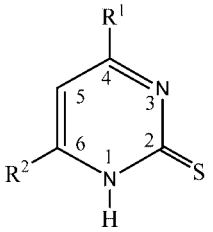
The reaction between the ligands 4-(trifluoromethyl)pyrimidine-2-thione (4-CF_3pymSH) and 6-methyl-4-(trifluoromethyl)pyrimidine-2-thione (6-Me-4-CF_3pymSH) and the corresponding diorganotin(IV) dichloride [R_2SnCl_2] (R = Me, *t*Bu or Ph) or diphenyllead(IV) dichloride in the presence of triethylamine yields the diorganotin(IV) complexes [R_2Sn(4-CF_3pymS)$_2$] and [R_2Sn(6-Me-4-CF_3pymS)$_2$] or diorganolead-(IV) complexes [Ph_2Pb(4-CF_3pymS)$_2$] and [Ph_2Pb(6-Me-4-CF_3pymS)$_2$], respectively. The compounds have been characterised by microanalysis, mass spectrometry and by IR and Mössbauer spectroscopy and, in the case of the compound that was sufficiently soluble, by ^{1}H, ^{13}C, ^{119}Sn and ^{207}Pb NMR spectroscopy. The compounds [Me_2Sn(4-CF_3pymS)$_2$] (**1**), [Ph_2Sn(4-CF_3pymS)$_2$] (**2**), [Ph_2Sn(6-Me-4-CF_3pymS)$_2$] (**5**), [*t*Bu_2Sn(6-Me-4-CF_3pymS)$_2$] (**6**), [Ph_2Pb(4-CF_3pymS)$_2$] (**7**) and [Ph_2Pb(6-Me-4-CF_3pymS)$_2$] (**8**) have also been characterised by X-ray diffraction. The X-ray crystal structures show that the metal centre in all these complexes is in a distorted octahedral environment with bonds to two carbon atoms from the aryl or alkyl substituents and to sulfur and heterocyclic nitrogen atoms from the pyrimidine derivative, which acts a (κ^2-N,S) chelating ligand.

Introduction

The chemistry of metal complexes of heterocyclic thione ligands is receiving increasing attention, largely because of the potential relevance of such compounds as models of active sites in metalloenzymes and also their ability to adopt geometries of variable nuclearity and great structural complexity, which is a result of the tendency of thiolate ligands to bridge metal centres to yield oligomeric or polymeric species.[1–8]

However, in comparison with the coordination chemistry of transition metals, the chemistry of main group metals with sulfur ligands remains much less developed.[9–13] In many cases, the interaction of toxic main group metals with biological systems frequently involves bonding of the metal to the sulfhydryl groups present in enzymes. Hence, an insight into the chemistry of main group thiolate compounds is important in terms of understanding the aforementioned interaction and for the design of detoxifying agents.[14,15] This interest has led us to study organotin and organolead compounds that, in a biological medium, react with thiol groups in relevant molecules to yield products that are characterised by metal–thiolate interactions, which are of interest in the design of sequestering agents; indeed, several papers have been dedicated to the design of specific complexing agents.[15,16] In addition, organotin complexes have been studied more recently in terms of their pharmacological and antitumour activity.[17–22]

As a continuation of our studies into the coordination chemistry of sterically hindered heterocyclic thiones,[23] we report here the synthesis and characterisation of diorganotin(IV) and diphenyllead(IV) complexes with 4-(trifluoromethyl)pyrimidine-2-thione and 6-methyl-4-(trifluoromethyl)-pyrimidine-2-thione ligands, the structures of which are shown in Scheme 1. These ligands, besides having solubilising and bulky groups, belong to one of the most versatile types of sulfur ligand in terms of coordination modes. For example, they can act (a) as a neutral monodentate ligand coordinated through the sulfur atom,[24] through one of the nitrogen atoms,[25] and as a bridging ligand through sulfur[26] or as an N,S-chelating ligand,[27,28] or (b) as an anionic ligand, in which case they can be monodentate through the sulfur atom,[29] an N,S-chelating ligand[30–32] or



R^1 = 4-CF_3; R^2 = H, CH_3

Scheme 1.

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a binuclear bridging ligand through nitrogen and sulfur,[33] or sulfur only,[34] and as a binuclear triply bridging ligand through sulfur and one of the nitrogen atoms,[31,35] or the two nitrogen and sulfur atoms,[36,37] and as a trinuclear triply bridging system.[38]

Moreover, these ligands were chosen because they are unsymmetrical ambidentate systems and can therefore give rise to linkage isomerism when they are coordinated in some of the aforementioned ways.

Results and Discussion

A series of diorganotin(IV) and diphenyllead(IV) complexes of general formulae $[R_2Sn(RpymS)_2]$ and $[Ph_2Pb(RpymS)_2]$ were synthesised in reasonable yields (47–74%) from the appropriate diorganotin(IV) dichloride $[R_2SnCl_2]$ (R = Me, Ph, *t*Bu) or diphenyllead(IV) dichloride (Ph_2PbCl_2) and the corresponding pyrimidine-2-thione derivative in methanol in the presence of triethylamine, according to Scheme 2.

The complexes reported here are air-stable as solids and do not show a tendency to decompose or oxidise. In addition, they have quite high solubility in the reaction medium, so the resulting solutions were concentrated in order to obtain the corresponding solids. Crystals of $[Ph_2Sn(4\text{-}CF_3pymS)_2]$ (**2**), $[Ph_2Sn(6\text{-Me-}4\text{-}CF_3pymS)_2]$ (**5**), $[Ph_2Pb(4\text{-}CF_3pymS)_2]$ (**7**) and $[Ph_2Pb(6\text{-Me-}4\text{-}CF_3pymS)_2]$ (**8**) suitable for X-ray studies were obtained by slow evaporation of the mother liquor at room temperature; $[Me_2Sn(4\text{-}CF_3pymS)_2]$ (**1**) and $[tBu_2Sn(6\text{-Me-}4\text{-}CF_3pymS)_2]$ (**6**) were obtained by recrystallisation of the initial product from ethanol.

Molecular Structures of $[Me_2Sn(4\text{-}CF_3pymS)_2]$ (1), $[Ph_2Sn(4\text{-}CF_3pymS)_2]$ (2), $[Ph_2Sn(6\text{-Me-}4\text{-}CF_3pymS)_2]$ (5) and $[tBu_2Sn(6\text{-Me-}4\text{-}CF_3pymS)_2]$ (6)

The molecular structures of **1**, **2**, **5** and **6** are shown in Figures 1, 2, 3 and 4, respectively, together with the atom labelling scheme adopted. Crystallographic data and a se-

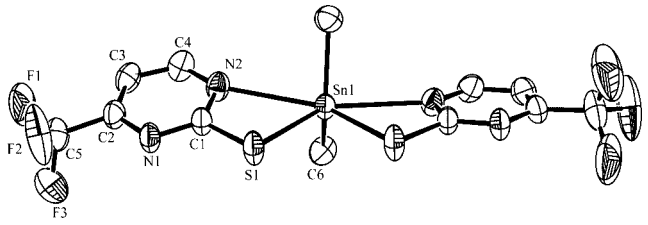


Figure 1. Crystal structure of $[Me_2Sn(4\text{-}CF_3pymS)_2]$ (**1**) (50% probability displacement ellipsoids).

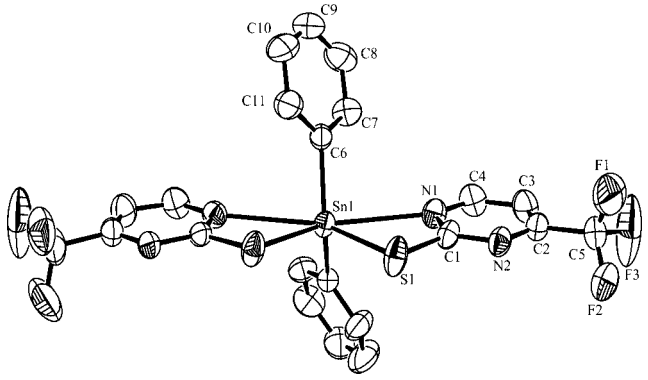
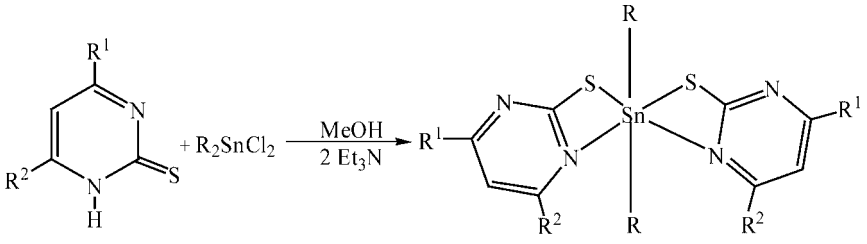
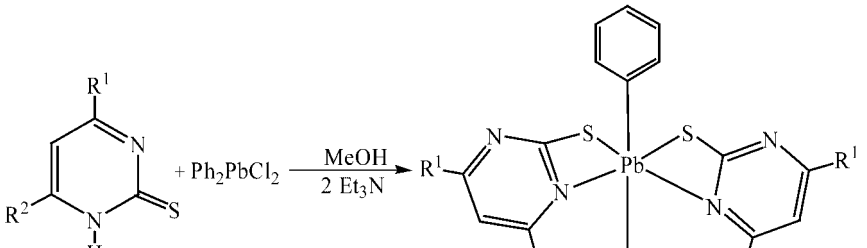


Figure 2. Crystal structure of $[Ph_2Sn(4\text{-}CF_3pymS)_2]$ (**2**) (50% probability displacement ellipsoids).



R = Me, *t*Bu, Ph; $R^1 = CF_3$; R^2 = H, CH_3



$R^1 = CF_3$; R^2 = H, CH_3

Scheme 2. General synthesis of the diorganotin(IV) and diphenyllead(IV) complexes.

lection of bond lengths and angles (with the estimated standard deviations) are given in the Experimental Section and Tables 1, 2, 3 and 4, respectively.

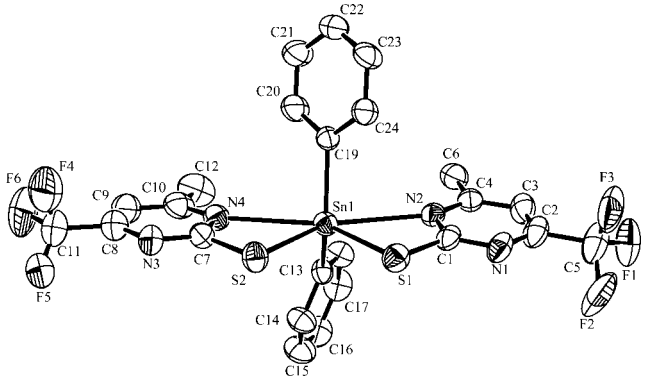


Figure 3. Crystal structure of [Ph_2Sn(6-Me-4-CF_3pymS)$_2$] (**5**) (50% probability displacement ellipsoids).

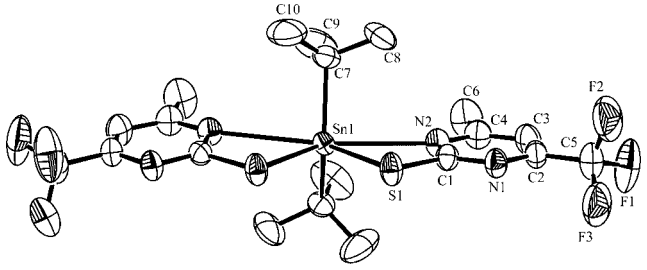


Figure 4. Crystal structure of [tBu$_2$Sn(6-Me-4-CF_3pymS)$_2$] (**6**) (50% probability displacement ellipsoids).

Table 1. Selected bond lengths [Å] and angles [°] for [Me_2Sn(4-CF_3pymS)$_2$] (**1**).[a]

Sn(1)–C(6)	2.108(4)	Sn(1)–S(1)	2.4836(9)
Sn(1)–N(2)	2.770(3)	S(1)–C(1)	1.744(3)
N(1)–C(2)	1.327(4)	N(1)–C(1)	1.335(4)
N(2)–C(4)	1.315(5)	N(2)–C(1)	1.345(5)
C(6)–Sn(1)–C(6)#1	123.0(2)	C(6)–Sn(1)–S(1)#1	113.87(11)
C(6)#1–Sn(1)–S(1)#1	107.02(12)	C(6)–Sn(1)–S(1)	107.02(12)
C(6)#1–Sn(1)–S(1)	113.87(11)	S(1)#1–Sn(1)–S(1)	86.15(4)
C(6)–Sn(1)–N(2)	85.53(13)	C(6)#1–Sn(1)–N(2)	82.66(13)
S(1)#1–Sn(1)–N(2)	145.02(7)	S(1)–Sn(1)–N(2)	59.70(6)
C(6)–Sn(1)–N(2)#1	82.66(13)	C(6)#1–Sn(1)–N(2)#1	85.53(13)
S(1)#1–Sn(1)–N(2)#1	59.70(6)	S(1)–Sn(1)–N(2)#1	145.02(7)
N(2)–Sn(1)–N(2)#1	155.11(12)	C(4)–N(2)–Sn(1)	151.8(3)

C–H–X interactions[b]	D–H	H···A	D–A	D–H···A
C(3)#2–H(3)#2···S(1)	0.930	2.991	3.778	143.34
C(6)–H(6b)···S(1)#3	0.960	3.036	3.984	169.61

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1$, y, $-z + 3/2$. [b] Symmetry codes: #2: $1.5 - x$, $-0.5 + y$, $1.5 - z$; #3: x, $-y$, $0.5 + z$.

The tin atom in **1**, **2** and **6** is located on a twofold rotation axis; accordingly, both methyl, phenyl or *tert*-butyl groups and both pyrimidine-2-thionate derivatives are symmetry equivalent. The molecular structures of **1**, **2**, **5** and **6** consist of neutral monomeric units with the tin atom bonded to two carbon atoms from the alkyl or phenyl groups and two anionic pyrimidinethionate derivatives, which act as chelating ligands through the sulfur atom and

Table 2. Selected bond lengths [Å] and angles [°] for [Ph_2Sn(4-CF_3pymS)$_2$] (**2**).[a]

Sn(1)–C(6)	2.121(2)	Sn(1)–S(1)	2.4599(7)
Sn(1)–N(1)	2.859(2)	S(1)–C(1)	1.734(3)
N(1)–C(4)	1.321(3)	N(1)–C(1)	1.337(3)
N(2)–C(2)	1.321(4)	N(2)–C(1)	1.342(3)
C(6)–Sn(1)–C(6)#1	125.67(13)	C(6)–Sn(1)–S(1)	112.86(6)
C(6)#1–Sn(1)–S(1)	105.14(6)	C(6)–Sn(1)–S(1)#1	105.14(6)
C(6)#1–Sn(1)–S(1)#1	112.86(6)	S(1)–Sn(1)–S(1)#1	89.31(3)
C(6)–Sn(1)–N(1)#1	81.82(7)	C(6)#1–Sn(1)–N(1)#1	86.06(7)
S(1)–Sn(1)–N(1)#1	147.88(5)	S(1)#1–Sn(1)–N(1)#1	58.78(4)
C(6)–Sn(1)–N(1)	86.06(7)	C(6)#1–Sn(1)–N(1)	81.82(7)
S(1)–Sn(1)–N(1)	58.78(4)	S(1)#1–Sn(1)–N(1)	147.88(5)
N(1)#1–Sn(1)–N(1)	153.28(8)	C(4)–N(1)–Sn(1)	154.86(18)

C–H–X interactions[b]	D–H	H···A	D–A	D–H···A
C(7)#1–H(7)#1···S(1)	0.930	2.772	3.573	144.79
C(4)#1–H(4)#1···S(1)	0.930	3.007	3.838	149.52
C(4)#1–H(4)#1···N(2)	0.930	2.929	3.807	157.94

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 2$, y, $-z + 1/2$. [b] Symmetry code #1: x, $-1 + y$, z.

Table 3. Selected bond lengths [Å] and angles [°] for [Ph_2Sn(6-Me-4-CF_3pymS)$_2$] (**5**).

Sn(1)–C(13)	2.126(3)	Sn(1)–C(19)	2.128(3)
Sn(1)–S(2)	2.4665(10)	Sn(1)–S(1)	2.4719(10)
Sn(1)–N(2)	2.801(3)	Sn(1)–N(4)	2.837(3)
S(1)–C(1)	1.753(4)	S(2)–C(7)	1.750(4)
N(1)–C(2)	1.322(5)	N(1)–C(1)	1.335(4)
N(2)–C(4)	1.328(4)	N(2)–C(1)	1.341(4)
N(3)–C(8)	1.309(6)	N(3)–C(7)	1.338(5)
N(4)–C(10)	1.329(5)	N(4)–C(7)	1.333(5)
C(13)–Sn(1)–C(19)	126.76(12)	C(13)–Sn(1)–S(2)	107.90(9)
C(19)–Sn(1)–S(2)	109.24(9)	C(13)–Sn(1)–S(1)	110.91(9)
C(19)–Sn(1)–S(1)	107.45(9)	S(2)–Sn(1)–S(1)	87.55(3)
C(13)–Sn(1)–N(2)	84.73(10)	C(19)–Sn(1)–N(2)	84.11(10)
S(2)–Sn(1)–N(2)	147.22(6)	S(1)–Sn(1)–N(2)	59.70(6)
C(13)–Sn(1)–N(4)	79.38(10)	C(19)–Sn(1)–N(4)	88.51(10)
S(2)–Sn(1)–N(4)	59.00(7)	S(1)–Sn(1)–N(4)	146.38(7)
N(2)–Sn(1)–N(4)	153.45(9)	C(4)–N(2)–Sn(1)	152.1(2)

C–H–X interactions[a]	D–H	H···A	D–A	D–H···A
C(15)#1–H(15)#1···S(1)	0.930	3.056	3.952	162.18
C(6)#2–H(6c)#2···S(2)	0.960	2.767	3.677	158.48

[a] Symmetry codes: #1: $-x + 2$, $-y$, $1 - z$; #2: $x + 0.5$, $-y + 0.5$, $z + 0.5$.

Table 4. Selected bond lengths [Å] and angles [°] for [tBu$_2$Sn(6-Me-4-CF_3pymS)$_2$][a] (**6**).

Sn(1)–C(7)	2.216(4)	Sn(1)–S(1)	2.4886(12)
Sn(1)–N(2)	2.978(4)	S(1)–C(1)	1.746(5)
N(1)–C(2)	1.336(6)	N(1)–C(1)	1.342(6)
N(2)–C(4)	1.326(6)	N(2)–C(1)	1.345(6)
C(7)–Sn(1)–C(7)#1	131.6(2)	C(7)–Sn(1)–S(1)	106.37(13)
C(7)#1–Sn(1)–S(1)	109.09(13)	C(7)–Sn(1)–S(1)#1	109.09(13)
C(7)#1–Sn(1)–S(1)#1	106.37(13)	S(1)–Sn(1)–S(1)#1	84.12(5)
C(7)–Sn(1)–N(2)	87.31(15)	C(7)#1–Sn(1)–N(2)	85.26(15)
S(1)–Sn(1)–N(2)	57.10(8)	S(1)#1–Sn(1)–N(2)	141.05(8)
N(2)–Sn(1)–N(2)#1	161.82(15)	C(4)–N(2)–Sn(1)	154.6(3)

C–H–X interactions[b]	D–H	H···A	D–A	D–H···A
C(6)#1–H(6c)#1···S(1)	0.960	3.165	3.733	119.54
C(6)#1–H(6b)#1···N(1)	0.960	2.955 Å	3.401	109.70

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1$, y, $-z + 1/2$. [b] Symmetry code: #1: x, $-1 + y$, z.

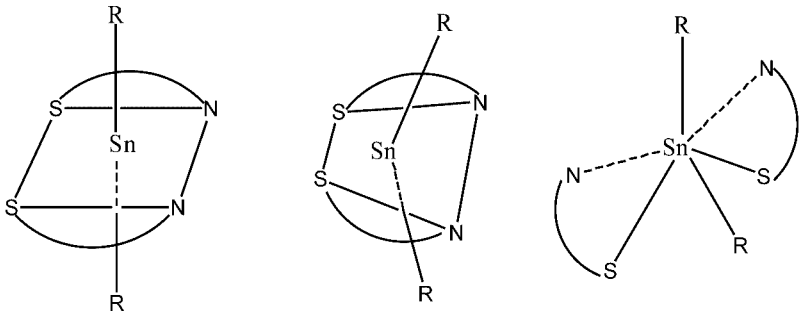
one of the nitrogen atoms. Therefore, this pyrimidinethionate derivative is an example of an unsymmetrical ambidentate ligand whose N,S-bidentate coordination to the tin atom could generate linkage isomerism depending on which nitrogen atom is involved. In the case under discussion, the ligand uses the nitrogen atom with less hindrance (i.e., that in position 1), which is the nitrogen atom farthest from the trifluoromethyl substituent in the pyrimidine ring. This suggests that the nitrogen atom involved in the coordination in **1** and **2** is determined by the steric hindrance introduced by the trifluoromethyl group. In the case of the 6-methyl-4-(trifluoromethyl)pyrimidine-2-thionate ligand, the presence of the CF_3 group in the 4-position produces greater steric hindrance than the methyl group in the 6-position and, once again, the heterocyclic ligand in $[Ph_2Sn(6\text{-Me-}4\text{-}CF_3pymS)_2]$ (**5**) and $[tBu_2Sn(6\text{-Me-}4\text{-}CF_3pymS)_2]$ (**6**) adopts the same coordination mode as the 4-(trifluoromethyl)pyrimidine-2-thionate ligand in **1** and **2**. Naturally, other factors, such as crystal packing and inter- and/or intramolecular interactions, can also play a role in the coordination mode of the 4-(trifluoromethyl)pyrimidine-2-thionate ligand.

These complexes can be considered to be examples of a hexacoordinate bischelate diorganotin(IV) complex in which the environment around the tin atom is highly distorted octahedral. The C–Sn–C bond angle [123.0(2)° for **1**, 125.67(13)° for **2**, 126.76(12)° for **5** and 131.6(2)° for **6**] is intermediate between the ideal value for the *cis* isomer (90°) and the *trans* isomer (180°), a similar situation to that found in the majority of this type of compounds (122–155°), which suggests that the geometry of **1**, **2**, **5** and **6** can be described as a distorted trapezoidal bipyramid[39] in which the equatorial plane is formed by the sulfur and nitrogen atoms (the longest vertices of the trapezium consist of the two nitrogen atoms and the shortest contain the sulfur atoms) and the axial positions are occupied by the two methyl groups. Another possibility is to consider the compound as a bicapped tetrahedron[40,41] defined by the carbon and sulfur atoms, with four tetrahedral angles close to the ideal value [105.14(6)–113.87(11)°] and two C–Sn–C [123.0(2)–131.6(2)°] and S–Sn–S [84.12(5)–89.31(3)°] angles distorted by the influence of the capping atoms.

The Sn–S bond lengths [2.4599(7)–2.4886(12) Å] are slightly longer than the sum of the covalent radii of these elements (2.42 Å). These values are similar to those found in other hexacoordinate diorganotin(IV) compounds with anionic heterocyclic thionate N,S-chelate ligands, which have values in the range 2.4476(10)–2.503(2) Å.[22,42–46] Examples of such complexes include $[Me_2Sn(pyS)_2]$ [2.487(2) Å],[42] $[Ph_2Sn(4,6\text{-}Me_2\text{-}2\text{-}pymS)_2]$ [2.4476(10)],[44] $[(cyclo\text{-}C_6H_{11})_2Sn(pyS)_2]$ [2.503(2) Å][45] and $[Ph_2Sn(pyS)_2]$ [2.485(1) Å].[46] The Sn–C bond lengths [2.108(4)–2.216(4) Å] are similar to those found in the complexes $[R_2Sn(chelate)_2]$ discussed above, which have values in the range 2.046(14)–2.25(1) Å. The Sn–N bond lengths [2.770(3)–2.978(4) Å] are shorter than the sum of the van der Waals radii of these elements (3.75 Å)[47] but are rather longer than those found in other complexes containing Sn–N bonds {e.g., 2.271(9) and 2.256(9) Å in $[Cl_2Sn(pyS)_2]$}.[48] However, the values obtained for **1**, **2**, **5** and **6** are in the range found in the aforementioned $[R_2Sn(chelate)_2]$ complexes [2.639(6)–3.083(3) Å].

Both heterocyclic ligands in complexes **1**, **2** and **6** are essentially planar, with the sulfur atoms lying practically in the plane of the pyrimidine ring to which they are bonded. On the other hand, the tin atom lies out of these planes by 0.265(6) Å for **1** and 0.171(8) Å for **6** and practically in the plane of the pyrimidine ring in **2** [0.064(4) Å]. Each of the pyrimidine rings in compound **5** is also planar. However, whereas the sulfur and tin atoms are in the plane of the pyrimidine ring to which they are bound [deviation of 0.002 Å for S(1) and 0.028 Å for Sn] for one of these ligands, for the other ligand S(2) (0.094 Å) and Sn (0.228 Å) lie out of the plane of the pyrimidine ring. Moreover, the interplanar angle between the pyrimidine rings in **2** is only 0.23°. Consequently, **2** has an arrangement similar to that found in the complex dimethylbis(pyridine-2-thionato)tin(IV)[42] but is very different to that in the complexes dichloridobis(pyridine-2-thionato)tin(IV),[48] in which the planes of the two ligand molecules are almost perpendicular, and in **1**, **5** and **6**, where the thionate ligands form a dihedral angle [20.2(2)°, 6.89° and 9.09°, respectively] intermediate between those found in the aforementioned complexes.

The S–C [1.734(3)–1.753(4) Å] bond lengths in **1**, **2**, **5** and **6** are intermediate between the values observed in the free ligands 4,6-dimethylpyrimidine-2-thione[28] and 4,6-dimethyl-1-phenylpyrimidine-2-thione[27] [1.692(2) and



1.686(4) Å, respectively], which exist in the thione form in the solid state, and the values of 1.781(2) and 1.782(3) Å found in bis(pyrimidyl)-2,2′-disulfide[49] and bis(4,6-dimethylpyrimidyl)-2,2′-disulfide,[50] which possess a simple C–S bond; this suggests that the ligand is coordinated in a form that is closer to the pyrimidine-2-thionate than to the thione form.

Molecular Structures of $[Ph_2Pb(4\text{-}CF_3pymS)_2]$ (7) and $[Ph_2Pb(6\text{-}Me\text{-}4\text{-}CF_3pymS)_2]$ (8)

The molecular structures of **7** and **8** are shown in Figure 5 and Figure 6, respectively, together with the atom labelling scheme adopted. Crystallographic data and selected bond lengths and angles are given in the Experimental Section and Tables 5 and 6, respectively.

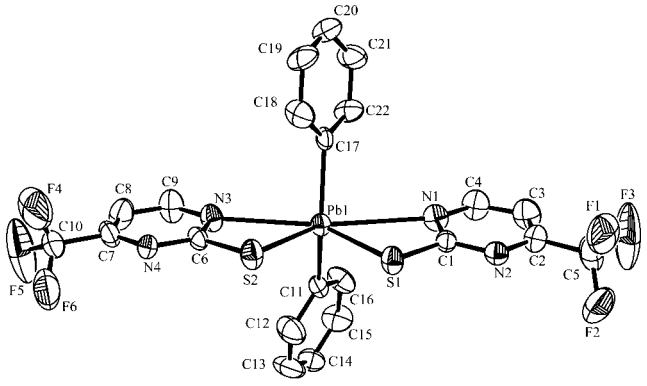


Figure 5. Crystal structure of $[Ph_2Pb(4\text{-}CF_3pymS)_2]$ (**7**) (50% probability displacement ellipsoids).

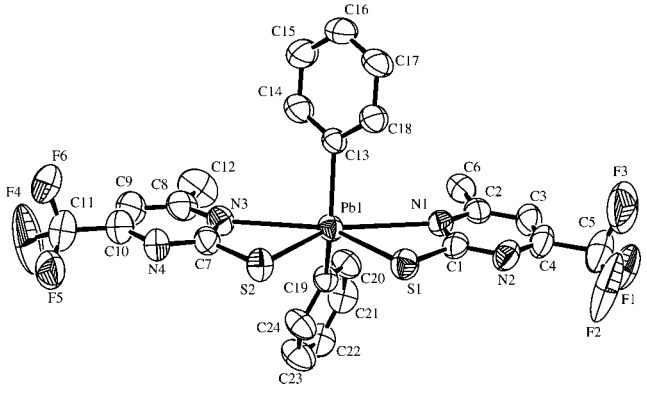


Figure 6. Crystal structure of $[Ph_2Pb(6\text{-}Me\text{-}4\text{-}CF_3pymS)_2]$ (**8**) (50% probability displacement ellipsoids).

The structures determined for these complexes are, as far as we know, the first examples of lead(IV) complexes containing heterocyclic thione ligands, such as pyridine-2-thione or pyrimidine-2-thione. The only previously reported structures containing lead and this type of ligand are the mononuclear complex $[Pb(3\text{-}CF_3pyS)_2]$[9] and trinuclear complex $[Pb_3(3\text{-}Me_3SipyS)_6]$.[51] In both cases the lead atom is in the oxidation state (II). This situation precludes a direct comparison involving the structural parameters of the compounds reported here.

Table 5. Selected bond lengths [Å] and angles [°] for $[Ph_2Pb(4\text{-}CF_3pymS)_2]$ (**7**).

Pb(1)–C(17)	2.189(11)	Pb(1)–C(11)	2.196(11)
Pb(1)–S(2)	2.577(3)	Pb(1)–S(1)	2.582(3)
Pb(1)–N(3)	2.824(9)	Pb(1)–N(1)	2.986(10)
S(1)–C(1)	1.730(11)	S(2)–C(6)	1.732(11)
N(1)–C(4)	1.309(16)	N(1)–C(1)	1.346(13)
N(2)–C(2)	1.309(14)	N(2)–C(1)	1.352(13)
N(3)–C(9)	1.360(16)	N(3)–C(6)	1.362(13)
N(4)–C(6)	1.332(13)	N(4)–C(7)	1.336(15)
C(17)–Pb(1)–C(11)	142.8(4)	C(17)–Pb(1)–S(2)	104.0(3)
C(11)–Pb(1)–S(2)	104.6(3)	C(17)–Pb(1)–S(1)	104.1(3)
C(11)–Pb(1)–S(1)	102.2(3)	S(2)–Pb(1)–S(1)	83.96(10)
C(17)–Pb(1)–N(3)	89.7(3)	C(11)–Pb(1)–N(3)	85.7(3)
S(2)–Pb(1)–N(3)	57.86(19)	S(1)–Pb(1)–N(3)	141.65(19)
C(17)–Pb(1)–N(1)	85.0(3)	C(11)–Pb(1)–N(1)	88.2(3)
S(2)–Pb(1)–N(1)	140.23(19)	S(1)–Pb(1)–N(1)	56.38(19)
N(3)–Pb(1)–N(1)	161.9(2)	C(4)–N(1)–Pb(1)	154.4(9)

C–H–X interactions[a]	D–H	H···A	D–A	D–H···A
C(16)#1–H(16)#1···S(1)	0.930	2.778	3.694	168.38°
C(22)#1–H(22)#1···S(1)	0.930	2.785	3.704	169.80°
C(4)#1–H(4)#1···S(1)	0.930	2.964	3.753	143.65°
C(9)#1–H(9)#1···S(2)	0.930	3.081	3.847	140.79°
C(4)#1–H(4)#1···N(2)	0.930	2.711	3.598	159.66°
C(9)#1–H(9)#1···N(4)	0.930	2.639	3.543	164.16°

[a] Symmetry code: #1: x, $y + 1$, z.

Table 6. Selected bond lengths [Å] and angles [°] for $[Ph_2Pb(6\text{-}Me\text{-}4\text{-}CF_3pymS)_2]$ (**8**).

Pb(1)–C(13)	2.187(5)	Pb(1)–C(19)	2.190(5)
Pb(1)–S(2)	2.5722(1)	Pb(1)–S(1)	2.5723(1)
Pb(1)–N(3)	2.865(5)	Pb(1)–N(1)	2.909(4)
S(1)–C(1)	1.748(6)	S(2)–C(7)	1.747(6)
N(1)–C(1)	1.338(6)	N(1)–C(2)	1.346(6)
N(2)–C(4)	1.331(7)	N(2)–C(1)	1.343(6)
N(3)–C(8)	1.337(7)	N(3)–C(7)	1.341(6)
N(4)–C(10)	1.333(8)	N(4)–C(7)	1.337(6)
C(13)–Pb(1)–C(19)	134.59(19)	C(13)–Pb(1)–S(2)	106.99(13)
C(19)–Pb(1)–S(2)	105.48(14)	C(13)–Pb(1)–S(1)	103.46(13)
C(19)–Pb(1)–S(1)	108.76(14)	S(2)–Pb(1)–S(1)	87.66(5)
C(13)–Pb(1)–N(3)	90.06(15)	C(19)–Pb(1)–N(3)	81.31(16)
S(2)–Pb(1)–N(3)	57.72(10)	S(1)–Pb(1)–N(3)	145.31(10)
C(13)–Pb(1)–N(1)	86.88(14)	C(19)–Pb(1)–N(1)	84.43(15)
S(2)–Pb(1)–N(1)	144.84(10)	S(1)–Pb(1)–N(1)	57.41(10)
N(3)–Pb(1)–N(1)	156.65(13)	C(2)–N(1)–Pb(1)	151.7(4)

C–H–X interactions[a]	D–H	H···A	D–A	D–H···A
C(23)#1–H(23)#1···S(1)	0.930	2.993	3.877	159.47
C(6)#2–H(6c)#2···S(2)	0.960	2.914	3.755	146.89

[a] Symmetry codes: #1: $-x + 2$, $-y$, $-z + 2$; #2: $x + 0.5$, $-y + 0.5$, $z + 0.5$.

The complexes $[Ph_2Pb(4\text{-}CF_3pymS)_2]$ (**7**) and $[Ph_2Pb(6\text{-}Me\text{-}4\text{-}CF_3pymS)_2]$ (**8**) consist of neutral monomeric molecules in which the lead atoms are coordinated by two monoanionic thionate ligands and two phenyl groups. The thionate ligands are coordinated to the lead through their sulfur atoms and, more weakly, to one of the nitrogen atoms of each ligand, in such a way that each thionate ligand acts a bidentate chelate system (κ^2-N,S). In this way, the coordination number for the lead atom is six and the environment around this metal atom can be described as being similar to the analogous tin(IV) complexes **2** and **5**,

i.e., a skewed trapezoidal bipyramid or a bicapped tetrahedron. The C–Pd–C bond angles are 142.8(4) Å for **7** and 134.59(19) Å for **8**, which are larger than those found in the diorganotin(IV) complexes previously described. In addition, in **7** and **8** the heterocyclic ligands adopt, for the same reasons, the same coordination mode as in the tin complexes mentioned previously.

The Pb–S bond lengths, 2.577(3) and 2.582(3) Å for **7** and 2.5722(14) and 2.5723(15) Å for **8**, are close to those found in diorganolead(II) tetracoordinate with thiolate ligands; 2.489(6) Å in $[Ph_3PbSMe]$[52] or 2.523(5) and 2.580(4) Å in $[(Ph_3Pb)_2(dmit)]$,[53] where H_2dmit is 4,5-dimercapto-1,3-dithio-2-thione. However, the values found in **7** and **8** are lower than those found in the hexacoordinate thiolate $\{Ph_2Pb[S_2P(OCH_2Ph)_2]_2\}$,[54] 2.679(6) and 2.957(6) Å. The Pb–N bond lengths, 2.824(9) and 2.986(10) Å for **7** and 2.865(5) and 2.909(4) Å for **8**, are much longer than the sum of the corresponding covalent radii for lead (1.600 Å) and nitrogen (0.700 Å) and also longer than those found in other hexacoordinate diorganolead(IV) complexes containing a Pb–N bond; for example, 2.498(7) and 2.461(7) Å in $[Ph_2PbCl_2(imidazole)_2]$.[55] The fact that these distances are shorter than the sum of the van der Waals radii (3.82 Å) suggests that the Pb···N bonds in complexes **7** and **8** are significantly weaker than a normal intermolecular Pb–N bond, a situation similar to that observed in organotin complexes discussed above.

The phenyl and pyrimidine rings are planar [maximum deviation 0.010(3) Å]. The interplanar angle between the pyrimidine rings is only 4.75° in **7** and 3.76(3)° in **8** whereas the rings of the phenyl groups have interplanar angles of 19.63(8)° and 76.04(2)°, respectively. In compound **7**, the sulfur and lead atoms lie approximately in the plane of the pyrimidine ring to which they are bound. However, in **8** the sulfur atoms are approximately in the plane of the pyrimidine rings to which they are bound; 0.038(6) Å for S(1) and 0.067(7) Å for S(2). The lead atom is also practically in the plane of the pyrimidine to which S(1) is bonded [0.055(8) Å] but is out of the plane of the pyrimidine ring to which S(2) is attached [0.296(9) Å].

The average length of the S–C bond, 1.731(11) Å, is similar to that found in other complexes with pyrimidine-2-thionate derivatives, a fact that suggests that this ligand is coordinated in a form that is closer to the thionate than the thione.

Crystal Packing and Intermolecular Interactions in 1, 2 and 5–8

The crystal packing in compounds **1**, **2** and **5**–**8** is mainly dictated by C–H···X hydrogen-bonding interactions between different C–H groups and the sulfur and nitrogen atoms of the pyrimidine-2-thionate ligands that are not coordinated, as well as interactions involving the CF_3 groups (see Tables 1–6).[56,57]

The way in which these C–H···X interactions propagate in space enables the crystal structures of these compounds to be classified into three groups: (1) interactions that propagate in a direction that gives rise to chains that interact weakly with one another; (2) bidimensional interactions that give rise to layers that interact weakly with one another; (3) interactions that are similar in intensity in all three dimensions.

Compounds with Crystal Packing in Chains

The crystal packing arrangements in $[Ph_2Sn(4\text{-}CF_3pymS)_2]$ (**2**), $[tBu_2Sn(6\text{-}Me\text{-}4\text{-}CF_3pymS)_2]$ (**6**) and $[Ph_2Pb(4\text{-}CF_3pymS)_2]$ (**7**) can be described as chains parallel to the crystallographic *b* axis. The pyrimidine rings and the metal atoms are located approximately in the same plane throughout each of the chains. This arrangement is the result of weak C–H···X interactions that propagate along this direction. In **2** and **7**, this arrangement consists of two C–H···S[58,59] interactions between two C–H groups from the phenyl rings and the same sulfur atom of one of the pyrimidine-2-thionate ligands (**7**; see Figure 7) or with a sulfur atom of a different pyrimidine-2-thionate ligand (**2**). This situation is reflected in the angle between the planes of the phenyl rings, which is 19.63(80)° for **7** and 58.96(10)° for **2**. At the same time, and in the same direction, C–H···N[60,61] interactions are established between the uncoordinated nitrogen atom and the symmetry equivalent C–H *para* to this nitrogen (see Figure 7).

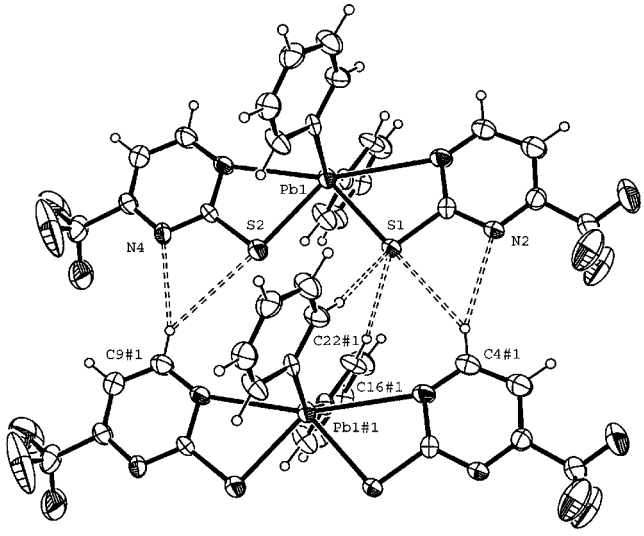


Figure 7. The crystal packing in **7**. Dashed lines show the C–H···S and the C–H···N interactions.

The crystal network of $[tBu_2Sn(6\text{-}Me\text{-}4\text{-}CF_3pymS)_2]$ (**6**) contains the same type of chain along the crystallographic *b* axis, with weak C–H···N and C–H···S interactions similar to those in the two previous cases, although in this case the C–H donor is the methyl group *para* to the uncoordinated nitrogen atom.

In all three cases each of the chains is involved in weak interactions with neighbouring chains in such a way that the planes of the pyrimidine rings along the chain are parallel to one another in the resulting crystal packing. These inter-chain interactions can be classified into two types:

those that involve the phenyl (complexes **2** and **7**) or *tert*-butyl (complex **6**), which are established with other chains located above and below the plane of the pyrimidine-2-thionate ligands, and those that involve CF_3 groups.[56,57] These CF_3 groups are located near to other trifluoromethyl groups in all three cases, a situation that is usual for this type of group.

Compounds with Crystal Packing in Layers

The only compound reported here that shows this type of packing is $[Me_2Sn(4\text{-}CF_3pymS)_2]$ (**1**). Each pyrimidine-2-thionate ligand in this compound establishes two C–H···S interactions between the thionate groups and the C–H groups *para* to the sulfur atoms, as shown in Figure 8. The propagation of these interactions gives rise to layers of molecules parallel to the crystallographic AB plane. Within these layers the CF_3 groups are located very close to other CF_3 groups in such a way that F···F interactions are also formed within each layer; these interactions are not shown in Figure 8.

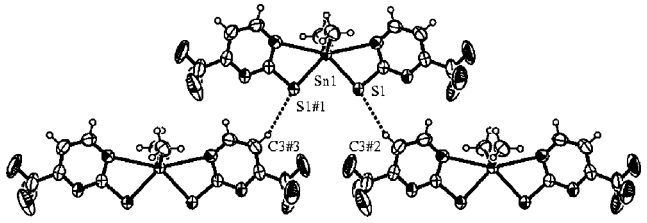


Figure 8. The crystal packing in **1**. Dashed lines show the C–H···S interactions.

The layers that are parallel to the AB planes interact weakly with one another through C–H···S[58,59] interactions between the methyl groups above and below the layers and the sulfur atoms of the pyrimidine-2-thionate ligands in neighbouring layers.

Compounds with Three-Dimensional Crystal Packing

The compounds $[Ph_2Sn(6\text{-Me-}4\text{-}CF_3pymS)_2]$ (**5**) and $[Ph_2Pb(6\text{-Me-}4\text{-}CF_3pymS)_2]$ (**8**) are isomorphous and have identical crystal packing arrangements as a result of interactions of similar strength in three directions in space. The interactions responsible for the packing in these compounds are also C–H···S[58,59] interactions, and each of the thionate groups in the complex is involved in interactions with different C–H groups of other neighbouring complex molecules, as shown in Figure 9.

The S(1) sulfur atom establishes one of these interactions with a C–H group of one of the phenyl rings, while the S(2) sulfur establishes an interaction with a methyl group of a pyrimidine-2-thionate ligand of a neighbouring complex.

There is another type of interaction in addition to the C–H···S interactions, which involves π-π stacking between the phenyl ring not involved in C–H···S interactions and a symmetry equivalent centre of the pyrimidine ring connected to sulfur S(1). This interaction, which is relatively weak, is of the "parallel displaced" type and the centroids of the two rings are separated by 3.920 Å from tin and 3.843 Å from lead. As in the previously discussed complexes, the CF_3 groups are located very close to other CF_3 groups in such a way that F···F interactions are established.[56,57]

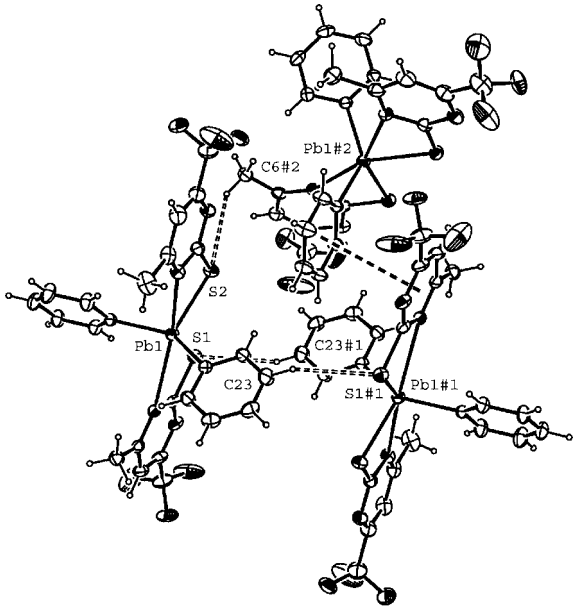


Figure 9. The crystal packing in **8**. Dashed lines show the C–H···S and the π-π stacking interactions.

Spectroscopic Studies

IR Spectroscopy

The IR spectra of the complexes (see the Experimental Section) show that the ν(N–H) bands of the free pyrimidine-2-thione ligands, which appear between 3200–3050 cm^{-1}, are absent from the thionate complexes. This indicates that deprotonation of the thionate group has occurred and therefore that the pyrimidine-2-thione is coordinated in the thionate form. This conclusion is supported by the shift to lower wavenumbers (1580–1550 cm^{-1} in the complexes) of the strong bands due to ν(C=C) and ν(C=N), which appear at 1650–1550 cm^{-1} in the free ligands. The spectra of the complexes also show bands due to the ring breathing vibration in the regions 1110–990 cm^{-1} and 750–620 cm^{-1}, which are at higher wavenumbers than the corresponding bands in the free ligands. These shifts provide evidence for coordination of the ligands through the nitrogen atom.[62] The spectra of the methyl and *tert*-butyl derivatives also show additional medium intensity bands at 3100–2900 cm^{-1}, which correspond to the vibrations of the methyl groups.

NMR Spectra

The main change in the ^1H NMR spectra of the thionate complexes brought about by complexation is the disappearance of the broad signal due to the N–H proton; this confirms that the ligand is in the deprotonated thionate form in the complexes.

The ^{1}H NMR spectra of the complexes show, in addition to the signals corresponding to the protons on the heterocyclic thionate ligand, signals due to the methyl, *tert*-butyl and phenyl groups of the organometallic fragments. The spectra of the dimethyltin(IV) derivatives also contain a signal at high field (δ = 1.1 ppm), which is attributed to the protons on the methyl groups of the Me_2Sn fragment. These signals are accompanied by satellite peaks due to coupling of the proton with ^{119}Sn and ^{117}Sn nuclei. The $^2J_{^1H,^{119}Sn}$ and $^2J_{^1H,^{117}Sn}$ coupling constants are 74 and 72 Hz, respectively, and these values are similar to those found in other compounds containing the Me_2Sn fragment.[22,63] These ^2J coupling constant values can be used to estimate the Me–Sn–Me angle.[64] The values calculated for these angles are 123.9° and 121.8° for **1** and **4**, respectively, and are very similar to one another and also to that found in the solid state for **1** by X-ray diffraction. This suggests that the structures of both compounds in solution are the same as that determined in the solid state for compound **1**.

The ^{1}H NMR spectra of the tBu_2Sn derivatives each contain a singlet at around δ = 1.50 ppm due to the *tert*-butyl protons. Once more, the corresponding satellite peaks can be observed. The $^3J_{^1H,^{119}Sn}$ and $^3J_{^1H,^{117}Sn}$ coupling constants in these cases are 52 and 50 Hz, respectively. The ^{1}H NMR spectra of the Ph_2Sn and Ph_2Pb derivatives contain peaks attributable to the aromatic protons. Two groups of signals can be observed. The first is at δ = 7.8 ppm and is due to the protons *ortho* to the Sn atom. The second group appears at δ = 7.4 ppm and it is attributable to the other ring protons. The signals in the first group, in the case of the Ph_2Sn derivatives, show satellite signals due to ^{1}H-^{119}Sn coupling. In these cases, the $^3J_{^1H,^{119}Sn}$ values are close to 75 Hz.

The ^{13}C NMR spectrum of the free ligand 6-Me-4-CF_3pymSH contains twice the expected number of signals for C(2), C(6), CF_3 and CH_3 as the free ligand exists in two tautomeric forms. This doubling in the number of signals is not observed in the ^{13}C NMR spectra of the metal complexes. This situation provides evidence that the ligand is coordinated to the metal only in the thionate form in solution. The ^{13}C NMR spectra of the other complexes that were sufficiently soluble in $CDCl_3$ show, in addition to the expected signals for the thionate ligand, signals attributable to the methyl group (δ = 6.5–5.5 ppm), phenyl group (δ = 122–140 ppm) and quaternary and primary carbon atoms from the *t*Bu groups (δ = 30–40 ppm) in the organometallic fragment.

The ^{119}Sn NMR spectra of these complexes were recorded at room temperature in $CDCl_3$ using $SnMe_4$ as an external standard. The ^{119}Sn chemical shifts seem to depend more on the nature of the alkyl or aryl groups bonded to the tin atom than on the pyrimidine ligand. Indeed, it appears that these groups do not have a significant effect on the shielding or deshielding of the tin nucleus. Whereas the ^{119}Sn chemical shift for the diphenyltin(IV) derivatives appears at δ = –201.0 ppm for **2** and δ = –179.3 ppm for **5**, the compounds containing alkyl groups show less negative ^{119}Sn chemical shifts. For example, the Me_2Sn derivatives exhibit signals at δ = –70.3 ppm for **1** and δ = –86.4 ppm for **4**. These values are within the range reported for other complexes of diphenyl- or dimethyltin(IV) with pyrimidine or pyrimidine-2-thionate ligands with the same coordination number.[22,47,65] In the spectra of the tBu_2Sn derivatives, the values of the ^{119}Sn chemical shift are δ = –32.1 ppm for **3** and δ = –4.8 ppm for **6**. These seem to indicate that the complexes have a lower coordination number (tetracoordination) in $CDCl_3$ solution than in the solid state.[66] This change can be explained in terms of the breakdown of Sn–N interactions in solution, with these bonds in **6** (obtained from X-ray crystallography) being longer than the others presented in this work.

The ^{207}Pb NMR spectra of diphenyllead(IV) complexes were recorded at room temperature in $CDCl_3$ using $PbMe_4$ as an external standard. The ^{207}Pb chemical shift seems to be particularly sensitive to the electronic environment and is therefore an excellent tool for the study of changes in coordination number.[67] The ^{207}Pb spectra contain a single peak at around δ = –199.0 ppm for **7** and δ = –206.7 ppm for **8**. These values suggest that both complexes of diphenyllead(IV) have the same coordination number in $CDCl_3$ solution (probably hexacoordinate as in the solid state).

Mass Spectra

The tin and lead complexes were also characterised by mass spectrometry using the positive ion FAB technique in 3-nitrobenzyl alcohol (NBA) as matrix. The FAB spectra of dimethyl- and di-*tert*-butyltin with 4-CF_3pymS and dimethyltin with 6-Me-4-CF_3pymS show the molecular ion peak with the appropriate isotope distribution (*m*/*z* 508, 592 and 536, respectively). In these cases, peaks were also observed due to the fragments produced by the loss of one thionate ligand (*m*/*z* 328, 412 and 342, respectively) or one of these ligands and the two alkyl groups. The spectra of the other tin complexes do not show the molecular ion peaks but do show peaks associated with loss of one phenyl group [*m*/*z* 555 for $PhSn(4\text{-}CF_3pymS)_2$ and 582 for $PhSn(6\text{-}Me\text{-}4\text{-}CF_3pymS)_2$] or one thionate ligand [*m*/*z* 453 for $Ph_2Sn(4\text{-}CF_3pymS)$, 467 for $Ph_2Sn(6\text{-}Me\text{-}4\text{-}CF_3pymS)$ and 427 for $tBu_2Sn(4\text{-}CF_3pymS)_2$].

The FAB mass spectrum of $[Ph_2Pb(4\text{-}CF_3pymS)_2]$ shows the molecular ion peak at *m*/*z* = 720. In this compound, and also in the other lead compound, peaks corresponding to fragments of the parent ions due to loss of different groups from the compounds are observed. For example, peaks are observed at *m*/*z* 540 for **7** and 555 for **8** and these are associated with $Ph_2Pb(RpymS)$ formed by loss of one thionate ligand. Peaks due to the fragments produced by the loss of two phenyl groups and one thionate ligand (*m*/*z* 386 when R = CF_3 and 400 when R = 6-Me-4-CF_3) are also seen.

Mössbauer Spectra

As expected from their chemical formulae, the Mössbauer spectra of the reported compounds show only a single, slightly asymmetric, quadrupole split doublet (Table 7).

The linewidths are narrow enough to rule out any doublet overlap, which implies the existence of just a single tin site in each complex. The isomer shift values are rather surprising as they are grouped around two values, both of which are typical for SnR_2 derivatives (1.49 and 1.87 mm s^{-1}), in an unexpected way. In fact, the inductive effects of the organic groups would lead to increasing values in the order Ph >> Me > Bu, and so the only explanation must lie in different geometrical distortions or in varying Sn–N bond lengths. A closer analysis of Tables 2, 3, 4, and 5 shows that the average Sn–N bond length for compounds **1**, **2**, and **5**, which have the lowest isomer shift values, is 2.817 ± 0.039 Å, clearly shorter than that of compound **6** [2.978(4) Å]. This value, even though significantly shorter than the sum of the van der Waals radii of these atoms (3.75 Å), indicates that the two Sn–N bonds are rather weak and so the coordination geometry around the tin centre has a considerable fourfold character. This increases the s-electron density at the tin nucleus and so leads to a larger isomer shift. Moreover, the presence of a methyl group in the ligand does not affect the electron density on the tin atom, as expected. The quadrupole splitting values are also very close to each other and quite low, close to values typical for *cis*-SnR_2 derivatives (1.7–2.2 mm s^{-1}).

Table 7. Mössbauer parameters collected at 80 K. The δ values are quoted relative to SnO_2 at room temperature.

	δ [mm s^{-1}]	ΔE_Q [mm s^{-1}]	Γ [mm s^{-1}]	Γ_2/Γ_1
[$Me_2Sn(4\text{-}CF_3pymS)_2$] (**1**)	1.49	2.46	0.87	0.91
[$Ph_2Sn(4\text{-}CF_3pymS)_2$] (**2**)	1.49	2.68	0.87	0.97
[$tBu_2Sn(4\text{-}CF_3pymS)_2$] (**3**)	1.87	2.74	0.86	0.96
[$Ph_2Sn(6\text{-}Me\text{-}4\text{-}CF_3pymS)_2$] (**5**)	1.49	2.54	0.85	1.03
[$tBu_2Sn(6\text{-}Me\text{-}4\text{-}CF_3pymS)_2$] (**6**)	1.87	2.70	0.92	0.93

Point charge calculations performed by ignoring the influence of the pymS ligand on the electron density around the tin atoms, but taking into account only the experimental C–Sn–C bond angles, afforded values that were too high (2.83–3.14 mm s^{-1}) and strongly dependent on the input values. In fact, the C–Sn–C bond angles [123.0–131.6°] are intermediate between the ideal values for the *cis* (90°) and for the *trans* isomer (180°), a situation similar to that found in the majority of this type of compounds (122–155°). The coordination geometry for these compounds can, in fact, be described as a distorted trapezoidal bipyramid[39] in which the equatorial plane is formed by the sulfur and nitrogen atoms, or as a bicapped tetrahedron. These results point to the inability of the point charge method to reproduce the Mössbauer quadrupole splitting in the case of severely distorted structures.

Conclusions

The work described here involves the synthesis and structural characterisation of a series of compounds obtained by the reaction of the appropriate diorganotin(IV) and diphenyllead(IV) dichlorides with 4-(trifluoromethyl)pyrimidine-2-thione and 6-methyl-4-(trifluoromethyl)pyrimidine-2-thione in methanol in the presence of triethylamine.

The structures of the diorganotin(IV) and diphenyllead(IV) compounds have been investigated and the coordination polyhedron of the metal atom can be described either as a distorted skew-trapezoid or a bicapped tetrahedron, with the heterocyclic thionate acting in a bidentate (κ^2-N,S) manner. In these arrangements the ligands are unsymmetrical ambidentate and therefore the N,S-bidentate coordination to the metallic atom could generate linkage isomerism through one of the two nitrogen atoms. Only one coordination mode is found in these complexes and this involves the sulfur atom and the less hindered nitrogen atom, which is farthest from the group with the highest level of steric hindrance in the heterocyclic rings; in both cases this is the trifluoromethyl group. Furthermore, it is worth noting that the R groups (methyl, *tert*-butyl or phenyl) of the R_2M moiety do not markedly influence the structure of the complex.

Experimental Section

General: 4-(Trifluoromethyl)pyrimidine-2-thione, 1,1,1-trifluoro-2,4-pentanedione, thiourea, triethylamine, dimethyltin(IV) dichloride, diphenyltin(IV) dichloride, bis(*tert*-butyl)tin dichloride and diphenyllead(IV) dichloride were obtained commercially and used as supplied.

Elemental analysis was performed with a Carlo–Erba EA microanalyser. IR spectra were recorded as KBr mulls with a Bruker IFS-66V spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AMX 300 MHz instrument using $CDCl_3$ or [D_6]DMSO as solvent. Chemical shifts are quoted relative to TMS as the internal standard. ^{119}Sn and ^{207}Pb NMR spectra were recorded with a Bruker AMX500 spectrometer in $CHCl_3$ as solvent using $SnMe_4$ and $PbMe_4$ as an external standard, respectively. The Mössbauer spectra were recorded at T = 80 K in a constant acceleration apparatus and are referenced to SnO_2. The mass spectra (FAB) were recorded with a Micromass Autospec spectrometer, with 3-nitrobenzyl alcohol as the matrix material.

Synthesis of 6-Me-4-CF_3pymSH: This compound was obtained by direct reaction between thiourea (2.428 g, 32 mmol) and 1,1,1-trifluoro-2,4-pentanedione (5 g, 32 mmol) in ethanol in the presence of concentrated hydrochloric acid (1 mL) as a catalyst. The mixture was heated under reflux for 2 h and the resulting dusty yellow solid was filtered off. $C_6H_5F_3N_2S$: calcd. C 37.11, H 2.60, N 14.43, S 16.51; found C 36.39, H 2.60, N 14.26, S 16.38. IR (KBr): $\tilde{\nu}$ = 3100–3200 cm^{-1} m, br, 1615 vs, 1590 vs, 1440 m, 1350 vs, 1320 w, 1200 s, br, 1130 m, 1100 m, 1030 w, 970 s, 920 m, 860 w, 850 m, 705 w, 660 w, 595 w, 570 w, 530 m, 510 w, 470 m, 450 m, 370 w. ^{1}H NMR ([D_6]DMSO): δ = 14.40 (s, 1 H, NH), 7.19 (s, 1 H, H-5), 2.39 (s, 3 H, CH_3) ppm. ^{13}C NMR ([D_6]DMSO): δ = 181.00 and 172.13 (s, C-2), 155.86 and 153.72 (q, $^2J_{^{13}C,^{19}F}$ = 35 Hz, C-4), 104.89 (s, C-5), 163.61 (s, C-6), 119.27 and 119.67 (q, $^1J_{^{13}C,^{19}F}$ = 275 Hz, CF_3), 23.45 and 18.46 (s, CH_3). MS (FAB): *m*/*z* (%) 194 (27) [6-Me-4-CF_3pymSH].

Synthesis of [$Me_2Sn(4\text{-}CF_3pymS)_2$] (1): Triethylamine (0.128 mL, 0.700 mmol) was added by syringe to a solution of 4-CF_3pymSH (0.150 g, 0.832 mmol) in methanol (50 mL) and the resulting solution was stirred for 1 h at room temperature. A solution of dimethyltin dichloride (0.091 g, 0.414 mmol) in methanol (15 mL) was then added and the mixture was heated under reflux for about

2.5 h. The solution was filtered and slow evaporation of the solvent gave rise to a cream-coloured solid, which was recrystallised from ethanol to give yellow crystals suitable for X-ray studies. Yield: 0.099 g (47%). $C_{12}H_{10}F_6N_4S_2Sn$ (507.04): calcd. C 28.43, H 1.99, N 11.05, S 12.65; found C 28.44, H 1.65, N 11.03, S 12.71. IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} w, 1550 s, 1420 m, 1340 vs, 1325 vs, 1200 s, 1160 vs, br, 1110 s, 980 w, 840 sh, 830 s, 780 m, 730 m, 665 m, 555 w, 520 w, 460 w, 355 w, 320 w. ^{1}H NMR ($CDCl_3$): δ = 8.7 (d, $^3J_{H,H}$ = 4.9 Hz, 1 H, H-6), 7.3 (d, $^3J_{H,H}$ = 4.9 Hz, 1 H, H-5), 1.1 (s, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 175 (s, C^2), 160 (s, C^6), 150 (q, C^4), 120 (q, C^7), 115 (s, C^5), 5.4 ppm (s, Me). ^{119}Sn NMR ($CDCl_3$): δ = –70.29 ppm. MS (FAB): *m*/*z* (%) 508 (12) [Me_2Sn(4-CF_3pymS)$_2$], 328 (100) [Me_2Sn(4-CF_3pymS)].

Synthesis of [Ph_2Sn(4-CF_3pymS)$_2$] (2): The same procedure as for **1** was used for the synthesis of the diphenyltin derivative. A solution of Ph_2SnCl_2 (0.142 g, 0.413 mmol), 4-CF_3pymSH (0.150 g, 0.832 mmol) and NEt_3 (0.128 mL, 0.700 mmol) in methanol (40 mL) was heated under reflux for 3 h. This solution was concentrated to give single crystals suitable for X-ray studies. Yield: 0.193 g (74%). $C_{22}H_{14}F_6N_4S_2Sn$ (631.18): calcd. C 41.86, H 2.24, N 8.88, S 10.16; found C 42.31, H 2.30, N 8.21, S 10.12. IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} w, 1550 vs, 1470 m, 1420 s, 1330 vs, br, 1200 s, 1140 m, 1110 m, 1060 w, 1015 w, 990 w, 975 w, 960 vw, 910 w, 830 s, 780 vw, 720 s, 690 m, 665 s, 460 w, 440 m, 355 m, 320 m. ^{1}H NMR ($CDCl_3$): δ = 8.38 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H, H-6), 7.8 (br, phenyl H) and 7.4 (br, phenyl H), 7.08 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H, H-5) ppm. ^{13}C NMR ($CDCl_3$): δ = 129–135 ppm (aromatic carbons). NO other signals could be detected due to the poor solubility of this complex. ^{119}Sn NMR ($CDCl_3$): δ = –201 ppm. MS (FAB): *m*/*z* (%) 554.8 (12) [PhSn(4-CF_3pymS)$_2$], 452.9, (54) [Ph_2Sn(4-CF_3pymS)], 298.8 (7) [Sn(4-CF_3pymS)].

Synthesis of [*t*Bu_2Sn(4-CF_3pymS)$_2$] (3): A solution of *t*Bu_2SnCl_2 (0.126 g, 0.414 mmol) in methanol was added to a solution of 4-CF_3pymSH (0.150 g, 0.832 mmol) and NEt_3 (0.128 mL, 0.421 mmol) in methanol (30 mL) and the reaction mixture was stirred and heated under reflux for 3 h. The resulting solution was slowly evaporated at room temperature to give colourless crystals suitable for X-ray studies. Yield: 0.175 g (74%). $C_{18}H_{22}F_6N_4S_2Sn$ (591.20): calcd. C 36.57, H 3.75, N 9.48, S 10.85; found C 36.74, H 3.14, N 9.50, S 10.96. IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} w, 2980 w, 2940 w, 2840 m, 1550 s, 1460 m, 1450 m, 1425 m, 1340 w, 1330 vs,br, 1205 s, 1190 m, 1150 m, 1140 m, 1110 m, 1080 vw, 1010 w, 975 w, 935 w, 830 m, 730 m, 665 m, 460 vw, 350 w, 315 w. ^{1}H NMR ($CDCl_3$): δ = 8.8 (d, $^3J_{H,H}$ = 4.9 Hz, 1 H, H-6), 7.4 (d, $^3J_{H,H}$ = 4.9 Hz, 1 H, H-5), 1.50 (s, 9 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 170 (s, C^2), 160 (s, C^6), 155 (q, C^4), 120 (q, C^7), 95 (s, C^5), 29.7, 30.0 and 31.6 ppm (*t*Bu). ^{119}Sn NMR ($CDCl_3$): δ = –32.16 ppm. MS (FAB): *m*/*z* (%) 592 (14) [*t*Bu_2Sn(4-CF_3pymS)$_2$], 534 (12) [*t*Bu_2Sn(4-CF_3pymS)$_2$ – 3F], 412 (76) [*t*Bu_2Sn(4-CF_3pymS)], 298 (100) [Sn(4-CF_3pymS)].

Synthesis of [Me_2Sn(6-Me-4-CF_3pymS)$_2$] (4): A solution of Me_2SnCl_2 (0.100 g, 0.220 mmol) was added to a solution of (6-Me-4-CF_3pymSH) (0.030 g, 0.157 mmol) and NEt_3 (0.073 g, 0.233 mmol) in methanol (40 mL) with constant stirring at room temperature. This mixture was heated under reflux for 2.5 h. The solution was the concentrated to give single crystals that were not suitable for X-ray studies. Yield: 0.132 g (54%). $C_{14}H_{14}F_6N_4S_2Sn$ (535.09): calcd. C 31.43, H 2.64, N 10.47, S 11.98; found C 31.52, H 2.52, N 10.51, S 11.72. IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} w, 3060 w, 1575 m, 1540 s, 1530 vw, 1390 vs, 1365 m, 1310 w, 1265 vs, 1255 m, 1220 w, 1190 w, 1165 w, 1140 m, 1110 m, 1030 w, 990 w, 980 w, 920 m, 875 w, 855 s, 790 m, br, 710 s, 550 m, 515 w, 480 w, 460 w. ^{1}H NMR ($CDCl_3$): δ = 7.14 (s, 1 H, H-5), 2.55 (s, 3 H, H-8), 1.08 (s, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 176.6 (s, C^2), 155 (q, C^4), 110.6 (s, C^5), 171 (s, C^6), 120 (q, C^7) 24.84 (s, C^8), 5.79 ppm (s, Me). ^{119}Sn NMR ($CDCl_3$): δ = –86.4 ppm. MS (FAB): *m*/*z* (%) 536 (19) [Me_2Sn(6-Me-4-CF_3pymS)$_2$], 342 (100) [Me_2Sn(6-Me-4-CF_3pymS)].

Synthesis of [Ph_2Sn(6-Me-4-CF_3pymS)$_2$] (5): A solution containing diphenyltin dichloride (0.150 g, 0.436 mmol), 6-methyl-4-(trifluoromethyl)pyrimidine-2-thione (0.140 g, 0.721 mmol) and triethylamine (0.110 g, 0.400 mmol) in methanol (30 mL) was heated under reflux for 3 h. It was then evaporated to give white, needle-like crystals that were suitable for X-ray studies. Yield: 0.139 g (52%). $C_{24}H_{18}F_6N_4S_2Sn$ (659.23): calcd. C 43.73, H 2.75, N 8.50, S 9.73; found C 43.12, H 2.49, N 8.38, S 9.62. IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} w, 1575 s, 1530 s, 1470 w, 1440 w, 1425 m, 1385 s, 1360 m, 1305 vw, 1265 vs, 1250 w, 1220 m, 1190 m, 1170 m, 1135 s, 1110 m, 1070 vw, 995 w, 980 vw, 920 w, 845 s, 730 m, 710 s, 690 m, 545 w, 460 w, 440 m. ^{1}H NMR ($CDCl_3$): δ = 7.85 (m, *ortho*-phenyl), 7.3 (m, phenyl) 7.15 (s, 1 H, H-5), 2.5 (s, 3 H, H-8) ppm. ^{13}C NMR ($CDCl_3$): δ = 173.3 (s, C^2), 156.0 (q, C^4), 141.5–122.4 (phenyl carbons), 112.2 (s, C^5), 170.0 (s, C^6), 120 (q, C^7), 24.13 ppm (s, C^8). ^{119}Sn NMR ($CDCl_3$): δ = –179.3 ppm. MS (FAB): *m*/*z* (%) 582 (12) [PhSn(6-Me-4-CF_3pymS)$_2$], 467 (52) [Ph_2Sn(6-Me-4-CF_3pymS)], 312 (15) [Sn(4-Me-6-CF_3pymS)].

Synthesis of [*t*Bu_2Sn(6-Me-4-CF_3pymS)$_2$] (6): The same procedure as for **4** was used for the synthesis of the di-*tert*-butyltin derivative. A solution of 6-Me-4-CF_3pymSH (0.150 g, 0.772 mmol) in methanol (50 mL) was added to a solution containing di-*tert*-butyltin dichloride (0.140 g, 0.461 mmol) and NEt_3 (0.110 g, 0.700 mmol) in methanol (15 mL) and the mixture was stirred and heated under reflux for 4 h. It was then filtered and evaporated to give a white crystalline solid (0.136 g, 57%). Crystallisation from ethanol gave single crystals that were suitable for X-ray studies. $C_{20}H_{26}F_6N_4S_2Sn$ (619.26): calcd. C 38.79, H 4.23, N 9.05, S 10.35; found C 38.76, H 4.11, N 8.98, S 10.08. IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} w, 2980 m, 2940 w, 2840 m, 1570 s, 1530 s, 1450 m, 1430 w, 1390 vs, 1355 w, 1305 m, 1260 vs, br, 1220 m, 1175 m, 1150 vs, br, 1100 w, 1010 w, 970 m, 920 m, 840 s, 800 vw, 780 vw, 655 s, 575 w, 550 m, 480 vw, 450 w. ^{1}H NMR ($CDCl_3$): δ = 7.13 (s, 1 H, H-5), 2.56 (s, 3 H, H-8), 1.49 (s, 9 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 176 (s, C^2), 170.2 (s, C^6), 112.07 (s, C^5), 25.02 (s, C^8), 46 [s, $C(CH_3)_3$], 31.82 ppm [s, $C(CH_3)_3$]. ^{119}Sn NMR ($CDCl_3$): δ = –4.78 ppm. MS (FAB): *m*/*z* (%) 506.9 (13) [Sn(6-Me-4-CF_3pymS)$_2$], 427.0 (72) [*t*Bu_2Sn(6-Me-4-CF_3pymS)], 312.9 (100) [Sn(6-Me-4-CF_3pymS)].

Synthesis of [Ph_2Pb(4-CF_3pymS)$_2$] (7): A solution of 4-CF_3pymSH (0.150 g, 0.832 mmol) and NEt_3 (0.126 g, 0.700 mmol) in methanol (50 mL) was added to a stirred suspension of diphenyllead dichloride (0.179 g, 0.414 mmol) in methanol (15 mL). The reaction mixture was heated under reflux for 4 h and the yellow solid was filtered off, washed with diethyl ether and dried under vacuum. The mother liquor yielded crystals suitable for X-ray studies (0.112 g, 56%). $C_{22}H_{14}F_6N_4PbS_2$ (719.68): calcd. C 36.72, H 1.96, N 7.78, S 8.91; found C 36.70, H 2.03, N 7.78, S 8.90. IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} w, 1555 s, 1465 w, 1430 w, 1415 m, 1340 s, 1330 s, 1205 s, 1170 w, 1140 m, 1115 m, 1010 w, 990 m, 975 w, 835 m, 730 m, 720 m, 680 vw, 670 m, 440 m. ^{1}H NMR ($CDCl_3$): δ = 8.54 (d, $^3J_{H,H}$ = 5.0 Hz, 1 H, H-6), 8.14–7.29 (phenyl H), 7.15 ppm (d, $^3J_{H,H}$ = 5.0 Hz, 1 H, H-5). ^{13}C NMR ($CDCl_3$): δ = 135–130 ppm (phenyl C). ^{207}Pb NMR ($CDCl_3$): δ = –199.0 ppm. MS (FAB): *m*/*z* (%) 720 (6) [Ph_2Pb(4-CF_3pymS)$_2$], 540 (100) [Ph_2Pb(4-CF_3pymS)], 386 (40) [Pb(4-CF_3pymS)], 284 (28) [PhPb].

Synthesis of [Ph_2Pb(6-Me-4-CF_3pymS)$_2$] (8): A similar procedure to that described above was followed, starting from a suspension

of Ph_2PbCl_2 (166 mg) in methanol, and a mixture of 6-Me-4-CF_3pymSH (150 mg, mmol) and NEt_3 (110 mL, mmol) in methanol (50 mL). Concentration of the mother liquor in air at room temperature gave crystals of [Ph_2Pb(6-Me-4-CF_3pymS)$_2$] suitable for X-ray studies (0.175 g, 61%). $C_{24}H_{18}F_6N_4S_2Pb$ (747.74): calcd. C 38.55, H 2.43, N 7.49, S 8.58; found C 38.84, H 2.64, N 7.28, S 8.51. IR (KBr): $\tilde{\nu}$ = 1570 cm^{-1} m, 1560 m, 1535 w, 1465 w, 1425 w, 1385 vs, 1360 w, 1305 vw, 1260 vs, br, 1220 m, 1190 w, 1170 w, 1130 m, 1110 w, 1010 w, 990 m, 915 w, 840 m, 720 m, 710 m, 680 vw, 540 w, 425 w. ^{1}H NMR ($CDCl_3$): δ = 8.14–7.30 (m, phenyl H), 7.00 (s, 1 H, H-5), 2.32 (s, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 135–130 (phenyl C), 25 ppm (s, C^8). ^{207}Pb NMR ($CDCl_3$): δ = –206.7 ppm. MS (FAB): *m*/*z* (%) 555.0 (100) [Ph_2Pb(6-Me-4-CF_3pymS)], 400.4 (45) [Pb(6-Me-4-CF_3pymS)], 285 (37) [PhPb], 207 (11) [Pb].

Caution: *Lead is a highly toxic cumulative poison. Compounds should be handled carefully.*

Crystal Structure Determinations: X-ray data for compounds **1**, **2** and **5**–**8** were collected on a Bruker Smart CCD 1000 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The data were collected at T = 293 K for all structures.

Table 8. Summary of crystal data and structure refinement for ligands and tin and lead compounds.

Compound	[Me_2Sn(4-CF_3pymS)$_2$] (**1**)	[Ph_2Sn(4-CF_3pymS)$_2$] (**2**)	[Ph_2Sn(6-Me-4-CF_3 pymS)$_2$] (**5**)
Empirical formula	$C_{12}H_{10}F_6N_4S_2Sn$	$C_{22}H_{14}F_6N_4S_2Sn$	$C_{24}H_{18}F_6N_4S_2Sn$
Formula weight	507.05	631.18	659.23
Crystal size [mm]	0.35 × 0.25 × 0.20	0.40 × 0.34 × 0.15	0.55 × 0.20 × 0.05
Temperature [K]	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*	$P2_1/n$
a [Å]	17.4481(10)	16.7891(6)	13.2553(2)
b [Å]	11.8154(7)	6.4499(3)	13.4370(3)
c [Å]	11.5926(7)	23.1215(9)	16.4170(3)
α [°]	90	90	90
β [°]	129.9330(10)	91.2600(10)	108.3050(10)
γ [°]	90.00	90.00	90
V [Å^3]	1832.55(19)	2503.18(18)	2776.09(9)
Z	4	4	4
Calcd. density [Mg m^{-3}]	1.838	1.675	1.577
μ [mm^{-1}]	1.682	1.250	1.131
F(000)	984	1240	1304
No. reflections collected	6290	8323	19798
No. of independent reflections	2272 [*R*(int) = 0.0382]	3096 [*R*(int) = 0.0334]	6832 [*R*(int) = 0.0388]
Data/restraints/parameters	2272/0/141	3096/0/187	6832/6/390
Goodness-of-fit	1.024	1.018	1.003
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0394[a]	R_1 = 0.0298	R_1 = 0.0399
	wR_2 = 0.0905[b]	wR_2 = 0.0646	wR_2 = 0.0906
Largest diff. peak and hole [e Å^{-3}]	1.252 and –1.886	0.375 and –0.537	0.500 and –0.524
	[tBu$_2$Sn(6-Me-4-CF_3pymS)$_2$] (**6**)	[Ph_2Pb(4-CF_3pymS)$_2$] (**7**)	[Ph_2Pb(6-Me-4-CF_3pymS)$_2$] (**8**)
Empirical formula	$C_{20}H_{26}F_6N_4S_2Sn$	$C_{22}H_{14}F_6N_4PbS_2$	$C_{24}H_{18}F_6N_4PbS_2$
Formula weight	619.26	719.68	747.73
Crystal size, mm	0.15 × 0.08 × 0.03	0.22 × 0.10 × 0.07	0.49 × 0.19 × 0.03
Temperature [K]	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*	$P2_1/n$
a [Å]	15.1671(11)	47.497(9)	12.8826(18)
b [Å]	7.5778(5)	6.2325(12)	13.707(2)
c [Å]	23.3832(17)	17.665(3)	16.453(2)
α [°]	90	90	90
β [°]	102.7950(10)	108.470(3)	108.732(2)
γ [°]	90	90	90
V [Å^3]	2620.8(3)	4959.8(16)	2751.4(7)
Z	4	8	4
Calcd. density [Mg m^{-3}]	1.569	1.928	1.805
μ [mm^{-1}]	1.192	7.035	6.344
F(000)	1240	2736	1432
No. reflections collected	8267	17872	17498
No. of independent reflections	3230 [*R*(int) = 0.0630]	5039 [*R*(int) = 0.0697]	5623 [*R*(int) = 0.0396]
Data / restraints / parameters	3230 / 0 / 154	5039 / 0 / 316	5623 / 6 / 390
Goodness-of-fit	1.001	1.053	1.043
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0498[a]	R_1 = 0.0449	R_1 = 0.0278
	wR_2 = 0.0896[b]	wR_2 = 0.1013	wR_2 = 0.0506
Largest diff. peak and hole [e Å^{-3}]	0.539 and –1.055	1.225 and –1.609	0.936 and –0.933

[a] $R_1 = \Sigma[|F_o| - |F_c|]/\Sigma[|F_o|]$. [b] $wR_2 = [\Sigma(F_o^2 - F_c^2)^2]/\Sigma(F_o^2)^2]^{1/2}$.

The ω-scan technique was employed to measure intensities for all crystals. Decomposition of the crystals did not occur during data collection. The intensities of all data sets were corrected for Lorentz and polarisation effects. Absorption corrections were carried out using SADABS.[68] All the structures were solved by direct methods and refined[69] by full-matrix least-squares based on F^2. For all the complexes, hydrogen atoms were also included in idealised positions and refined with isotropic displacement parameters. The CF_3 groups of compounds **1**, **2**, **5** and **8** were found to be disordered over two positions with occupancies 73:27 and 52:48 for the groups on C(5) and C(10) in compound **8**, 60:40 for the CF_3 group in compound **1**, 50:50 for the CF_3 group in **2**, and 55:45 and 62:38 for the groups on C(5) and C(10) in compound **5**.

Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from the International Tables for X-ray Crystallography.[70] The crystal data and summary of data collection and structure refinement for these compounds are given in Table 8. ORTEP 3 drawings,[71] along with the numbering schemes used, are provided in the text.

CCDC-622379 to -622384 (for **1**, **2** and **5**–**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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