Diorganotin(IV) Complexes of a Cyclic Thiosemicarbazone Ligand: Crystal Structures of $[SnPh_2(C_{15}H_{10}N_3S)Cl]$ and $[SnMe_2(C_{15}H_{10}N_3S)_2]$

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Treatment of 5-methoxy-5,6-diphenyl-4,5-dihydro-2*H*-[1,2,4]triazine-3-thione (LH_2OCH_3) with compounds SnR_2X_2 (R = Me and Ph; X = Cl and NO_3) afforded, for the first time, metal derivatives of a cyclic thiosemicarbazone. Treatment of LH_2OCH_3 with the appropriate diorganotin(IV) chloride in dichloromethane provided 1:1 complexes, but 1:2 derivatives were isolated when the nitrate salts in distilled water were used. The complexes were studied by mass spectrometry, IR and multinuclear (^1H, ^{13}C and ^{119}Sn) NMR in solution, and also by ^{119}Sn CP/MAS NMR spectroscopy and by X-ray diffraction in the solid state. In all the complexes, the thiosemicarbazone had been modified by formation of a new C=N bond. In addition, the ligand LH had lost a hydrogen atom, acting as an anion. The crystal structures of $[SnPh_2(C_{15}H_{10}N_3S)Cl]$ (**1**) and $[SnMe_2(C_{15}H_{10}N_3S)_2]$ (**4**) each consist of discrete molecules with the tin atom bonded to the sulfur and amine nitrogen atoms to give a four-membered chelate ring with the [1,2,4]triazine modified. For phenyl derivative **1**, the tin atom is in a trigonal-bipyramidal environment with the phenyl rings in equatorial positions, and for complex **4** it is in an octahedral arrangement, with the methyl groups in axial positions. The ^{119}Sn CP/MAS NMR spectra of the complexes are in accordance with these structures. The values obtained indicate a five-coordinate geometry for $[SnMe_2(C_{15}H_{10}N_3S)Cl]$ (**2**) and suggest a coordination number of six for complex **3**. The ^{119}Sn spectra of complexes in solution depend on the coordinating capacity of the solvents.

Introduction

The increasing interest in thiosemicarbazones (TSCs) that has arisen in the last decades is related to their wide range of biological properties as, for example, antiviral, antibacterial and anticancer agents.[1−8] In particular, the National Cancer Institute (USA) has requested from us a sample of the molecule studied in this work in order to test it against a full panel of 60 human tumours (NSC no. 711635-Y). From the data obtained, this molecule seems to be active against breast cancer. Moreover, octahedral Sn^{IV} complexes are potential anti-tumour and anti-viral agents, a number of them having been shown to be active. Diorganotin(IV) derivatives appear to be the most active.[9,10]

A combination of the ligand and the metal chemistry is therefore an interesting topic to pursue, since it involves organotin and C=S moieties, both of which should have good biological activity. The mechanism of the activity of these complexes requires understanding of their structures and isomerism. In attempts to correlate anti-tumour activity with structure, it has generally been assumed that the organic ligand should facilitate the transport of the complex across cell membranes, while the actual anti-tumour activity would be exerted by the dissociated diorganotin(IV) moieties.[11−13] Moreover, TSC ligands are very versatile as the π delocalisation (enhanced upon deprotonation) and the presence of different types of donor atoms, such as sulfur, imine and amine nitrogen atoms, makes several coordination modes possible.[14,15]

In previous work, we have studied the synthesis and characterisation of macroligands with common functional groups, but containing different numbers of donor atoms and variable structures. In particular, we have prepared open-chain [1+2] and cyclic [1+1] molecules derived from the reaction between benzil and thiosemicarbazide.[19,20] A macrocyclic [2+2] condensation product was obtained in methanol from the cyclic [1+1] species in the presence of copper(II) chloride, through a metal template macrocyclization.[21] We have also studied their complexation reactions with metal ions, in order to ascertain the structural features of the complexes relating to biological systems and to evaluate their potential use in determination of toxic metals.[22−26] Previously, the cyclic [1+1] compound 5-methoxy-5,6-diphenyl-4,5-dihydro-2*H*-[1,2,4]triazine-3-thi-

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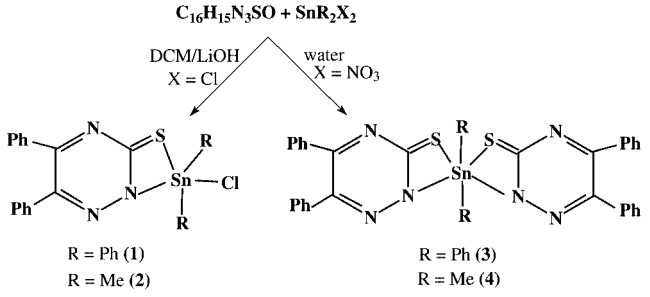
one (LH_2OCH_3) had been observed to undergo a macrocyclization process in the presence of copper(II) nitrate and mercury salts, yielding macrocyclic complexes.[21,27] In this paper we report the synthesis and characterisation of the first complexes from a cyclic thiosemicarbazone obtained by treatment of LH_2OCH_3 with diorganotin(IV) compounds (SnR_2X_2: R = Me, Ph; X = Cl, NO_3). We have observed that the nature of the anionic ligand (Cl and NO_3), results in complexes of different stoichiometry and geometry for the tin atom: 1:1 with a coordination number of five for chloride and 1:2 with a coordination number of six for nitrate derivatives.

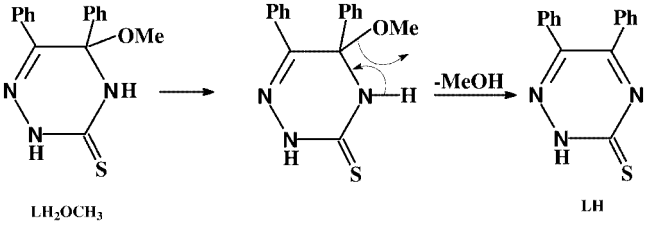
Solid-state ^{119}Sn NMR is known to provide insight into the local symmetry properties of the central tin(IV) atom and, in combination with solution ^{119}Sn NMR spectroscopic data, to provide information about the structural changes occurring upon dissolution of the organotin compounds.[12,16–18] The availability of X-ray data for two structurally related complexes prompted us to complement this work with the solid-state and solution NMR spectroscopic data.

Results and Discussion

Tin complexes were prepared by the general procedure outlined in Scheme 1. The reactions with chlorides were carried out in dichloromethane in the presence of a basic medium and those from nitrates in distilled water. The presence of basic medium or of water induces the loss of methanol, probably due to acid-base reaction with the relatively highly acidic N–H bond, yielding LH (Scheme 2), which has an additional C=N bond.[20]



Scheme 1



Scheme 2

Analytical data for the complexes show metal/ligand 1:1 stoichiometries for the chloride derivatives **1** and **2**, and 1:2 stoichiometries, with the absence of nitrate groups, for complexes **3** and **4**. Conductivity measurements for complex **2** in dimethylformamide and dichloromethane indicate the presence of non-ionic species in these solvents. Mass spectra confirm the molecular mass and also show fragments corresponding to the loss of R (Me or Ph), chlorine ligand or $C_{15}H_{10}N_3S$ (L^-). Experimentally measured isotopic distributions showed the same patterns as the theoretical ones in all compounds.

Crystallography

The crystal structure of **1** consists of discrete molecules of $[SnPh_2(C_{15}H_{10}N_3S)Cl]$. A perspective view of the complex, together with the atom-labelling scheme, is given in Figure 1 (hydrogen atoms are omitted for better clarity, and the thermal ellipsoids are shown at 40% probability) and selected bond angles and distances are given in Table 1. The coordination sphere of the tin atom is made up of the sulfur, amine nitrogen, chloro atoms and two phenyl rings, giving a pentacoordinate geometry. The Sn–L distances are in the range expected for this kind of complexes.[14,33] The three heteroatoms are in the same plane, with a maximum deviation of 0.1611 Å for Cl(1). The coordination mode of the ligand produces a four-membered chelate ring with the phenyl rings in the equatorial positions and the third position occupied by the sulfur atom. As is to be expected, the axial positions are occupied by nitrogen and chlorine atoms, in agreement with the polarity rule. The distortion from the ideal trigonal-bipyramidal configuration is manifested by the Cl(1)–Sn(1)–N(1) angle of 154.4°, which deviates from the ideal value of 180°, probably due to the ligand constraint. An alternative estimate of the geometry is given by the structural parameter τ introduced by Addison et al.[34] to analyse degrees of distortion from tetragonal-pyramidal (τ = 0.00) to trigonal-bipyramidal geometries (τ = 1.00). In this complex τ is 0.61. The phenyl rings form dihedral angles of 69.12, 74.14, 40.38 and 49.53° with respect to the equatorial plane for C(1)–C(6), C(7)–C(12), C(16)–C(21) and C(22)–C(27), respectively. An important change is observed with respect to LH_2OCH_3, where the dihedral angles are 36.94 [C(16)–C(21)] and 95.07° [C(22)–C(27)].[20] This change in one of the phenyl rings can be explained by the loss of the OMe group.

The crystal structure of **4** consists of discrete molecules of $[SnMe_2(C_{15}H_{10}N_3S)_2]$. A perspective view of the complex, together with the atom-labelling scheme, is given in Figure 2 (hydrogen atoms are omitted for better clarity, and thermal ellipsoids shown at 30% probability) and selected bond angles and distances are given in Table 2. Within the complex the tin(IV) ion is hexacoordinate in a distorted octahedral arrangement, four of the coordination positions belonging to the deprotonated ligands, which occupy the equatorial positions through the amine nitrogen atoms N(1) and N(4) and the sulfur atoms S(1) and S(2). The Sn–N distances are longer than in complex **1** and in other related

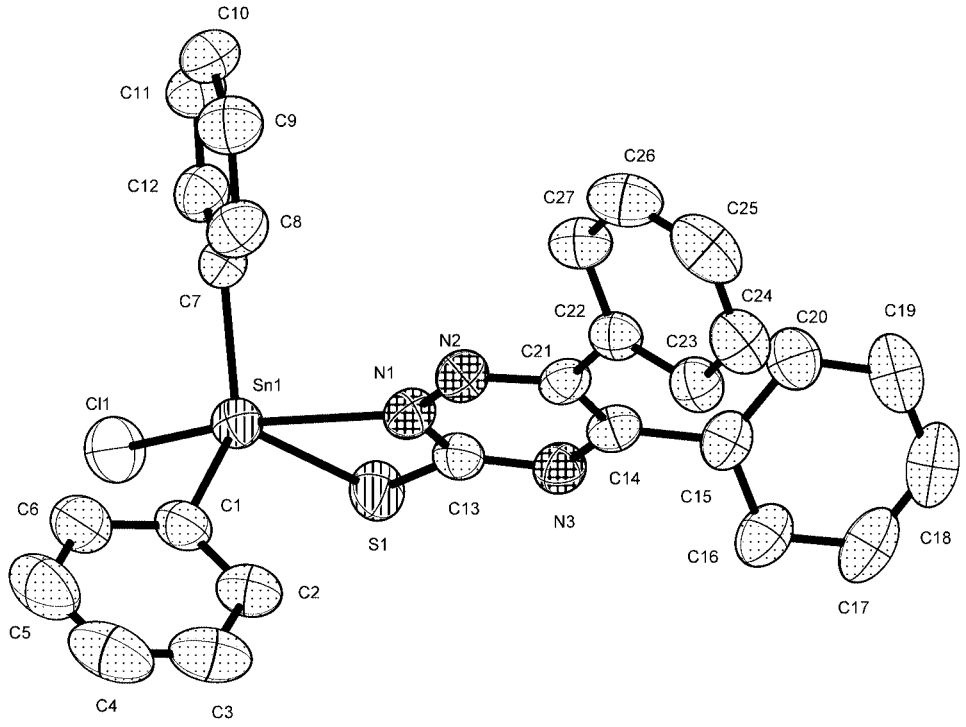


Figure 1. XSHELL view of $[SnPh_2(C_{15}H_{10}N_3S)Cl]$ (**1**)

Table 1. Selected bond lengths [Å] and angles [°] for complex **1**

S(1)−C(13)	1.746(3)	S(1)−Sn(1)	2.4597(8)
Sn(1)−C(1)	2.118(3)	Sn(1)−C(7)	2.125(2)
Sn(1)−Cl(1)	2.4113(8)	Sn(1)−N(1)	2.461(2)
C(13)−N(3)	1.328(3)	C(13)−N(1)	1.338(3)
C(14)−N(3)	1.333(3)	C(14)−C(15)	1.425(3)
C(14)−C(22)	1.484(4)	C(15)−N(2)	1.330(3)
C(15)−C(16)	1.483(3)	N(1)−N(2)	1.331(3)
C(13)−S(1)−Sn(1)	86.91(9)	C(1)−Sn(1)−C(7)	117.71(10)
C(1)−Sn(1)−Cl(1)	102.22(8)	C(7)−Sn(1)−Cl(1)	102.23(7)
C(1)−Sn(1)−S(1)	114.81(8)	C(7)−Sn(1)−S(1)	120.69(7)
Cl(1)−Sn(1)−S(1)	91.64(3)	C(1)−Sn(1)−N(1)	93.59(9)
C(7)−Sn(1)−N(1)	87.68(8)	Cl(1)−Sn(1)−N(1)	154.40(6)
S(1)−Sn(1)−N(1)	63.27(5)	C(13)−N(3)−C(14)	116.1(2)
N(3)−C(13)−S(1)	121.74(19)	N(3)−C(13)−N(1)	125.38(2)
N(3)−C(14)−C(15)	119.8(2)	N(1)−C(13)−S(1)	112.92(18)
N(2)−C(15)−C(14)	120.5(2)	N(2)−N(1)−C(13)	119.6(2)
C(13)−N(1)−Sn(1)	96.90(15)	C(15)−N(2)−N(1)	118.6(2)

compounds.[14,33] The two remaining positions in the octahedral geometry are occupied by two methyl groups, with a deviation from the expected angle of 24.4°.

The coordination mode of the ligand gives rise to two four-membered chelate rings. The core formed by the two thiosemicarbazone backbones and the tin atom can be considered planar, with a maximum deviation from the mean plane of 0.1104 Å for N(1), while the phenyl rings form dihedral angles of 41.46, 39.64, 48.2 and 42.53° with respect to this plane for C(6)−C(11), C(12)−C17), C(21)−C(26) and C(27)−C(32), respectively. These values are modified with respect to LH_2OCH_3 in the same way as in complex **1**.

Bond lengths in both complexes agree well with an iminethione form of the ligand, as does the NMR spectroscopy (see below), but with considerable electronic delocalisation through the thiosemicarbazone backbone, owing to the deprotonation of the ligands. As a consequence of this delocalisation, all the C−N bonds have almost the same length (Tables 1 and 2), which does not occur in LH_2OCH_3 (1.284−1.459 Å).[20] The thione bonds in both complexes (Tables 1 and 2) are longer than in the precursor molecule (1.628 Å in LH_2OCH_3) and are intermediate between the theoretical C−S single and double bonds,[35] as is also the case with the N−N bonds. Both S−C−N angles are also modified, especially that in which the nitrogen atom is involved in the bond to the tin atom. In addition, the N(2)−C(15)−C(14) angle in LH_2OCH_3 is 108.5°, corresponding to sp^3 hybridisation, while those in the complexes are close to 120°, as would be expected for sp^2 hybridisation. The remaining bond lengths and angles are similar to those found in similar organotin(IV) complexes and do not merit further comment.[14,33]

IR Spectroscopy

The IR assignment of LH_2OCH_3 is reported in the Exp. Sect. The absence of any band in the 2600 cm^{-1} region in all complexes suggests the absence of any thiol tautomer.[36] There are no bands in the 3000−3300 cm^{-1} region, indicating the absence of N−H bonds. In complexes **3** and **4** the absence of any band attributable to the nitrate group confirms that the organic fragment acts as an anion. The coordination through the sulfur atom can be observed in a decrease of the ν(C=S) frequency in the spectra of all the

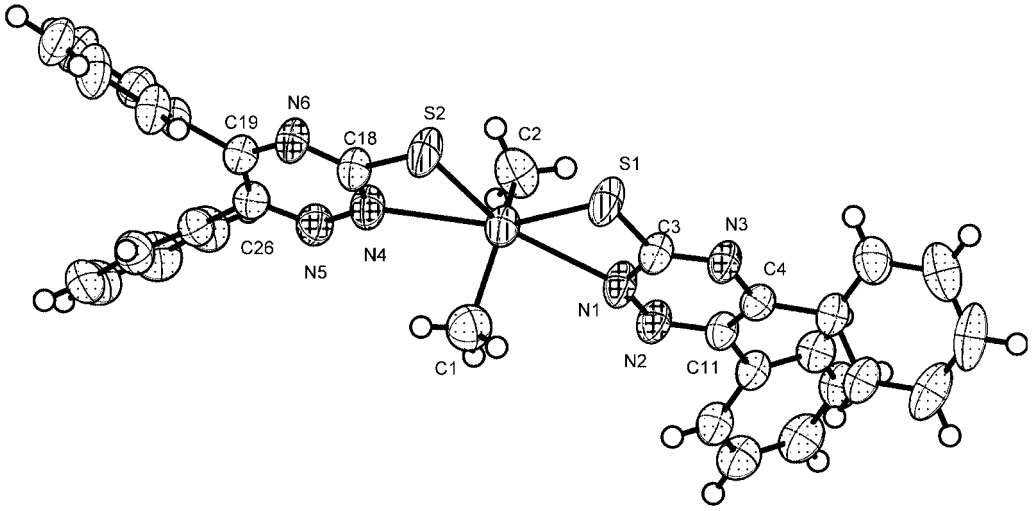


Figure 2. XSHELL view of $[SnMe_2(C_{15}H_{10}N_3S)_2]$ (**4**)

Table 2. Selected bond lengths [Å] and angles [°] for complex **4**

Sn(1)−C(1)	2.117(5)	Sn(1)−C(2)	2.123(5)
Sn(1)−S(2)	2.4938(10)	Sn(1)−S(1)	2.5091(10)
Sn(1)−N(1)	2.593(3)	Sn(1)−N(4)	2.7424(3)
S(1)−C(3)	1.733(4)	S(2)−C(18)	1.745(4)
C(3)−N(3)	1.339(4)	C(3)−N(1)	1.340(4)
C(4)−C(5)	1.423(4)	C(5)−N(2)	1.327(4)
C(4)−N(3)	1.333(4)	C(18)−N(6)	1.346(4)
C(18)−N(4)	1.324(4)	C(19)−C(20)	1.415(5)
C(19)−N(6)	1.333(4)	C(20)−N(5)	1.333(4)
[N(1)−N(2)	1.333(4)	N(4)−N(5)	1.346(4)
C(1)−Sn(1)−C(2)	131.2(3)	C(1)−Sn(1)−S(2)	107.1(2)
C(2)−Sn(1)−S(2)	103.3(2)	C(1)−Sn(1)−S(1)	107.29(18)
C(2)−Sn(1)−S(1)	108.1(19)	S(2)−Sn(1)−S(1)	92.76(3)
C(1)−Sn(1)−N(1)	84.1(2)	C(2)−Sn(1)−N(1)	85.2(2)
S(2)−Sn(1)−N(1)	153.67(7)	S(1)−Sn(1)−N(1)	60.95(7)
C(1)−Sn(1)−N(4)	80.44(19)	C(2)−Sn(1)−N(4)	82.8(2)
S(2)−Sn(1)−N(4)	60.02(7)	S(1)−Sn(1)−N(4)	152.62(7)
N(1)−Sn(1)−N(4)	146.31(9)	C(3)−S(1)−N(4)	89.25(12)
C(18)−S(2)−Sn(1)	91.25(13)	N(3)−C(3)−N(1)	124.6(3)
N(3)−C(3)−S(1)	121.2(3)	N(1)−C(3)−S(1)	114.2(3)
N(3)−C(4)−C(5)	119.7(3)	N(3)−C(4)−C(12)	116.1(3)
N(4)−C(18)−N(6)	124.9(3)	N(2)−C(5)−C(4)	120.1(3)
N(6)−C(18)−S(2)	118.6(3)	N(4)−C(18)−S(2)	116.4(3)
N(5)−C(20)−C(19)	120.2(3)	N(6)−C(19)−C(20)	120.1(3)
C(32)−C(27)−C(19)	119.0(3)	N(5)−C(20)−C(21)	114.5(3)
N(2)−N(1)−Sn(1)	144.6(2)	N(2)−N(1)−C(3)	119.1(3)
C(5)−N(2)−N(1)	119.5(3)	C(3)−N(1)−Sn(1)	95.5(2)
C(18)−N(4)−N(5)	119.3(3)	C(4)−N(3)−C(3)	116.6(3)
N(5)−N(4)−Sn(1)	148.0(2)	C(18)−N(4)−Sn(1)	92.2(2)
C(19)−N(6)−C(18)	116.2(3)	C(20)−N(5)−N(4)	118.9(3)

complexes. The presence of two bands attributable to C=N bonds indicates the formation of a new imine group, due to the loss of the methoxy group of the ligand. These moieties are non-coordinate to the tin atom. In complexes **1** and **3**, a new band at 729 cm^{-1} corresponding to phenyl rings appears. In all complexes the ν(Sn−C) bands are in the same region found in other diorganotin(IV) complexes.[37]

NMR Spectroscopy

The NMR assignments for LH_2OCH_3 are listed in the Exp. Sect. The ^1H NMR spectra of complexes **1** and **3** each show only a multiplet in the aromatic carbon atom region, corresponding to phenyl rings bonded to the tin atom and to the ligand. In each of the complexes **2** and **4** a singlet corresponding to the methyl group bonded to the metal atom can be observed, together with the multiplet for the phenyl rings of the ligand. In all complexes the absence of any signal corresponding to amine protons supports the presence of L. The loss of the methoxy group is confirmed by the absence of the singlet corresponding to the OCH_3 moiety (δ = 3.3 ppm).

In the ^{13}C NMR spectra the signals corresponding to the methoxy group carbon atoms and to the tetrasubstituted carbon atoms have disappeared and two signals attributable to imine carbon atoms have appeared. These groups are not bonded to the metal ion, as established by the X-ray diffraction. In addition, the thione group carbon atoms are deshielded in all complexes, due to the presence of metal−sulfur bonds, suggesting that the ligand retains the thione form. The numbers of signals corresponding to the phenyl carbon atoms are as expected for the proposed structures.

For methyl derivatives **2** and **4**, substitution of $^2J(^{119}Sn-^1H)$ values (72.20 and 75.02 Hz, respectively) and $^1J(^{119}Sn-^{13}C)$ values (518.69 and 557.00 Hz, respectively) into the corresponding Lockhart-Manders equations[38] (empirical relationship between the coupling constants and the C−Sn−C angle) gives C−Sn−C angle values of 122.0 and 124.4° for complex **2** and 125.0 and 125.5° for complex **4**. These similarities indicate that the data are reliable.

The ^{119}Sn chemical shifts of tin complexes appear to depend not only on coordination number, but also on the type of donor atoms bonded to the metal ion.[16,39,40] To bridge the information gap between X-ray diffraction and solution NMR spectroscopic data, solid-state NMR is an important

routine technique.[17b] ^{119}Sn chemical shifts are summarised in Table 3. The values for the ^{119}Sn chemical shift in the solid state for complexes **1** and **4** are those expected for penta- and hexacoordinate environments for the tin atom. That obtained for complex **2** agrees with a five-coordinate structure as suggested by other measurements. The ^{119}Sn CP/MAS NMR spectrum of complex **3** is of lower resolution than the other complexes, but seems to show a δ(^{119}Sn) from −280 to δ = −335 ppm. This value corresponds to hexacoordination for the tin atom and, in comparison with the methyl derivative with the same stoichiometry, it is in the range expected.

Table 3. ^{119} Sn NMR spectroscopic data for the complexes (δ in ppm)

Compound	Solid	$CDCl_3$	[D_6]DMSO
1	−199	−181.5	−224.8
2[a]	−170	−24.5	−213.5
3	−280 to −335[b]	−206.8	−220.9
4	−251	− 84.3	−108.7

[a] −160.7 in dimethylformamide. [b] Low-resolution spectrum.

Holecek[16] established for *n*-butyl derivatives that four-coordinate compounds have δ(^{119}Sn) values in solution ranging from δ = +200 to −60 ppm, five-coordinate compounds δ = −90 to −190 ppm, and six-coordinate compounds δ = −210 to −400 ppm. The value of δ = −181.5 ppm for complex **1** is within the range expected for five-coordinate complexes, which agrees with the environment of the tin atom persisting in solution (Table 3). The value of δ = −24 ppm for complex **2** in $CDCl_3$ correlates well with a four-coordinate complex, which indicates a strong change in the coordination sphere of the metal atom, probably due to the rupture of one (Sn−L) bond (the complex is a non-electrolyte in CH_2Cl_2). The spectrum in DMF, however, shows a signal at δ = −160.7 ppm, as would be expected for pentacoordination (slightly shifted from the value in the solid state), so the five-coordination for the tin atom remains in DMF. The ^{119}Sn values observed for complex **3** are smaller than those seen in the solid state (Table 3), and could reflect a coordination number of either five or six, depending on the atoms bonded to the tin atom. For a particular geometry, relatively lower δ(Sn) values are observed with higher electronegativity of the atom directly bonded to the metal atom.[41] In comparison with complex **1** (five-coordinate by Ph_2SNCl) the elimination of the chlorine ligand and the addition of a new Sn−L bond will give a slightly more negative δ value. On the other hand, replacement of methyl by phenyl, with the same geometry, should shift the signal to a more negative value. If these factors are taken into account, the δ value in complex **3** suggests five-coordination for the tin atom in chloroform.

The chemical shift for complex **4** in $CDCl_3$ indicates a change to a lower coordination than in the solid state (Table 3). Since a value of δ = −181 ppm in solution for complex **1** corresponds to five-coordination, a value of δ = −84.3 ppm seems to indicate tetracoordination (Me_2S_2)[42] instead of hexacoordination. This change could be explained by the rupture of the weak Sn−N bonds in solution, these bonds being longer than those in other previously published complexes with related ligands[14,33] and in those presented in this work.

The ^{119}Sn chemical shift values in [D_6]DMSO are more negative than in $CDCl_3$ and − for complexes **1** and **2** − than in the solid state, as would be expected for this coordinating solvent. [D_6]DMSO can increase the coordination sphere of the tin atom and/or substitute Sn−L bonds, increasing the coordination number to six for complexes **1**−**3** and to five for complex **4**.

Conclusions

The cyclic thiosemicarbazone LH_2OCH_3 reacts with diorganotin species to give non-electrolyte complexes (**1**−**4**). The stoichiometry of the complexes depends on the organotin compound used (chloride or nitrate). X-ray diffraction studies of complexes **1** and **4** revealed that the tin atoms in both are bonded to the sulfur and to the deprotonated amine nitrogen atoms, giving a four-membered chelate ring, with the organic molecule modified. In complex **1** the tin atom is in a trigonal-bipyramid environment with the phenyl rings in equatorial positions, and in complex **4** it is in an octahedral arrangement, with the methyl groups in axial positions. We have also studied the structural changes accompanying the dissolution of the complexes by ^{119}Sn CP/MAS and multinuclear solution NMR spectroscopy. These complexes are promising from the biological point of view, because they contain organotin, the precursor molecule appearing to be active against human tumours, and also contain the C=S moiety, which displays good antimicrobial activity.

Experimental Section

Physical Measurements: Microanalyses were carried out with a Perkin−Elmer 2400 II CHNS/O Elemental Analyser. IR spectra in the 4000−400 cm^{-1} range were recorded on KBr pellets with a Jasco FT/IR-410 spectrophotometer. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded with a Bruker AMX 300 spectrophotometer in $CDCl_3$, [D_6]DMSO and DMF as solvents and with TMS (^{1}H, ^{13}C) and $SnMe_4$ (^{119}Sn) as internal references. Fast atom bombardment mass spectra were recorded with a VG Auto Spec instrument with Cs as the fast atom and *m*-nitrobenzyl alcohol (*m*NBA) as the matrix. ^{119}Sn MAS and CP/MAS NMR spectra were obtained at room temperature with a Bruker MSL 400 spectrometer. The external magnetic field was 9.4 T and samples were spun at 10 kHz around an axis inclined at 54°44′ with respect to this field. The spectrometer frequency was set to 149.11 MHz. For spectra recorded with use of a standard single-pulse sequence, a π/2 pulse of 6 μs and a period between successive accumulations of 10 s were used. In CP-MAS conditions, a contact time of 1 ms was used. The number of scans was 800. Chemical shift values were referenced to $Sn(CH_3)_4$. The analysis of ^{119}Sn NMR spectra was done with the WINFIT Program.

Crystallography: Single crystals, prismatic in shape, of complexes **1** and **4** were obtained by recrystallisation from ethanol. Measurements were carried out with a Bruker SMART 6 K CCD area detector three-circle diffractometer with a Rigaku Rotating Anode (Cu-K_α radiation). For complexes **1** and **4**, the substantial redundancy in the data allows empirical absorption corrections (SADABS)[28] to be applied by use of multiple measurements of symmetry-equivalent reflections. The unit cell parameters were obtained by full-matrix, least-squares refinements of 8312 and 5730 reflections for complexes **1** and **4**, respectively. Crystallographic details are reported in Table 4. The crude intensity data frames were integrated by use of the SAINT[29] program, which also applied corrections for Lorentz and polarisation effects. The SHELXTL[30] software package, version 6.10, was used for space group determination, structure solution and refinement. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed by the structure solution. The structure was solved by direct methods (SHELXS-97),[31] completed with difference Fourier syntheses, and refined by full-matrix, least squares by use of SHELXL-97,[32] with minimisation of $\omega(F_o^2 - F_c^2)^2$. Weighted R factors (R_w) and all goodnesses of fit S are based on F^2; conventional R factors (R) are based on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersions factors are contained in the SHELXTL 6.10 program library. The high quality of the data set allowed all hydrogen atoms to be located by difference maps and refined isotropically in both complexes. CCDC-188698 (**4**) and -188699 (**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 4. Crystal data and structure refinement for complexes **1** and **4**

	1	**4**
Empirical formula	$C_{27}H_{20}ClN_3SSn$	$C_{32}H_{26}N_6S_2Sn$
Formula mass	572.66	677.40
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 9.72620(10) Å	a = 14.8222(2) Å
	b = 27.0583(2) Å	b = 11.62080(10) Å
	c = 9.82690(10) Å	c = 18.3507(2) Å
	β = 105.7710(10)°	β = 105.7700(10)°
Volume	2488.83(4) Å^3	3041.86(6) Å^3
Z	4	4
Absorption coefficient	10.088 mm^{-1}	8.215 mm^{-1}
Reflections collected	4543	5422
Independent reflections	4543	5422
Final R indices	$R1$ = 0.0283,	$R1$ = 0.0333,
[$I > 2\sigma(I)$]	$wR2$ = 0.0755	$wR2$ = 0.0722

Syntheses: $SnMe_2Cl_2$ and $SnPh_2Cl_2$ were used as provided by Aldrich. Dichloromethane was dried by standard procedures.

5-Methoxy-5,6-diphenyl-4,5-dihydro-2*H*-[1,2,4]triazine-3-thione (LH_2OCH_3):[20] A solution of thiosemicarbazide (1.14 g, 12.50 mmol) in methanol (150 mL), hydrochloric acid (25 mL, 2 M), concd. HCl (1 mL) and a solution of benzil (2.63 g, 12.50 mmol) in methanol (100 mL) were alternatively added dropwise and slowly, with strong stirring, to methanol (75 mL). After completion of the addition of all reactants, the mixture was stirred for 8 h. Overnight a crystalline solid formed, which was filtered off, washed and dried in vacuo (yield 95%), m.p. 222 °C. $C_{16}H_{15}N_3OS$ (297.4): calcd. C 64.64, H 5.05, N 14.14; found C 64.45, H 5.09, N 14.05. MS (FAB+): m/z (%) = 298 (35) [$C_{16}H_{15}N_3SO + 1$]$^+$. Selected spectroscopic data: IR: $\tilde{\nu}$ = 3184 s, 3131 s (NH); 1608 w (C=N); 1550 s (thioamide I); 846 w (thioamide IV) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.1 (s, 3 H, OCH_3), 7.2−7.4 (m, 8 H, Ph), 7.5 (m, 2 H, Ph), 10.0 (d, 1 H, NH), 12.1 (d, 1 H, NH) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 169.7 (C=S); 142.4 (C=N); 126.5, 129.3, 133.7, 141.7 (Ph); 83.2 (CH_3O); 50.7 (CR_3) ppm.

[$SnPh_2(C_{15}H_{10}N_3S)Cl$] (1): LH_2OCH_3 (0.50 g, 1.68 mmol) and $LiOH{\cdot}H_2O$ (0.071 g, 1.68 mmol) were stirred in dried dichloromethane (50 mL) at room temperature for 15 min. $SnPh_2Cl_2$ (0.58 g, 1.68 mmol), dissolved in the same solvent (10 mL), was then added. After the mixture had been heated at reflux for 7 d, it was filtered, and the clear yellow solution was concentrated until a yellow solid was formed (yield 95%), m.p. 170 °C. $C_{27}H_{20}ClN_3SSn$ (572.66): calcd. C 56.63, H 3.49, N 7.34, S 5.59; found C 56.44, H 3.76, N 7.14, S 5.52. MS (FAB+): m/z (%) = 537.9 (35) [$SnPh_2(C_{15}H_{10}N_3S)$]$^+$, 574.3 (5) [$SnPh_2(C_{15}H_{10}N_3S)Cl + 1$]$^+$. Selected spectroscopic data: IR (KBr): $\tilde{\nu}$ = 1598 w, 1578 w (C=N); 1489 s (thioamide I); 819 w (thioamide IV); 729 m (Ph) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.31−8.07 (m, Ph). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 128.5, 128.7, 129.3, 129.7, 129.9, 130.0, 130.6, 131.7, 134.3, 134.4, 135.8, 139.8 (Ph); 153.8, 159.8 (C=N); 175.0 (C=S) ppm; $^2J(^{119}Sn-^{13}C)$ = 60.0 Hz; $^3J(^{119}Sn-^{13}C)$ = 17.4 Hz. ^{119}Sn NMR (300 MHz, $CDCl_3$, 25 °C): δ = −181.5 ppm. ^{119}Sn NMR (300 MHz, [D_6]DMSO, 25 °C): δ = −224.8 ppm. ^{119}Sn CP/MAS NMR: δ = −199 ppm.

[$SnMe_2(C_{15}H_{10}N_3S)Cl$] (2): A solution of $SnMe_2Cl_2$ (0.37 g, 1.68 mmol) in dried dichloromethane (10 mL) was added to a boiling mixture of LH_2OCH_3 (0.80 g, 2.69 mmol) and $LiOH.H_2O$ (0.071 g, 1.68 mmol) in the same solvent (80 mL). The mixture was stirred at reflux for 10 days. The white solid was filtered off and discarded. The yellow solution was concentrated until a yellow solid was produced. Yield 90%. m.p. 186 °C. $C_{17}H_{16}ClN_3SSu$ (448.15): calcd. C 45.52, H 3.57, N 9.37, S 7.14; found C 45.29, H 3.71, N 9.12, S 6.95. MS (FAB+): m/z (%) = 414.1 (100) [$SnMe_2(C_{15}H_{10}N_3S)$]$^+$, 450.1 (9) [$SnMe_2(C_{15}H_{10}N_3S)Cl + 1$]$^+$. Selected spectroscopic data: IR (KBr): $\tilde{\nu}$ = 1597 w, 1578 w (C=N); 1489 s (thioamide I); 790 w (thioamide IV); 562 w (ν_{asy} Sn−C); 520 w (ν_{sym} Sn−C) cm^{-1}. Λ_M (DMF) = 4.5 Ω^{-1}cm^{2}mol^{-1}; Λ_M (CH_2Cl_2) = 0.7 Ω^{-1}cm^{2}mol^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.23 [s, 6 H, CH_3, $^2J(^{119}Sn-^1H)$ = 72.2 Hz]; 7.30−7.53 (m, 10 H, Ph) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.8 [CH_3, $^1J(^{119}Sn-^{13}C)$ = 518.6 Hz]; 128.6, 128.8, 129.1, 129.8, 130.0, 131.6, 134.4, 134.5 (Ph); 153.7, 159.1 (C=N); 174.7 (C=S) ppm. ^{119}Sn NMR (300 MHz, $CDCl_3$, 25 °C): δ = −24.5 ppm. ^{119}Sn NMR (300 MHz, DMF, 25 °C): δ = −160.7 ppm. ^{119}Sn NMR (300 MHz, [D_6]DMSO, 25 °C): δ = −213.5 ppm. ^{119}Sn CP/MAS NMR: δ = −170 ppm.

[$SnPh_2(C_{15}H_{10}N_3S)_2$] (3) and [$SnMe_2(C_{15}H_{10}N_3S)_2$] (4): A solution of $AgNO_3$ (3.37 mmol) in distilled water (10 mL) was added to a suspension of SnR_2Cl_2 (1.68 mmol) in the same solvent (10 mL). The mixture was stirred for 30 min and filtered. The filtrate was added slowly, with stirring, to a suspension of LH_2OCH_3 (3.36 mmol) in distilled water (50 mL). After the mixture had been heated at reflux for 3 d, the solid was filtered off, washed with methanol and vacuum dried.

Complex 3: Yield 98%, m.p. 180 °C. $C_{42}H_{30}N_6S_2Sn$ (801): calcd. C 62.90, H 3.75, N 10.49, S 7.99; found C 62.58, H 3.88, N 10.81, S 8.14. MS (FAB+): m/z (%) = 538.1 (100) [$SnPh_2(C_{15}H_{10}N_3S)$]$^+$,

725.1 (15) $[SnPh(C_{15}H_{10}N_3S)_2]^+$, 803 (10) $[SnPh_2(C_{15}H_{10}N_3S)_2 + 1]^+$. Selected spectroscopic data: IR (KBr): $\tilde{\nu}$ = 1597 w, 1578 w (C=N); 1486 s (thioamide I); 806 w (thioamide IV); 729 m (Ph) cm^{-1}. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 128.2, 128.4, 128.8, 129.2, 129.3, 129.7, 129.8, 130.6, 134.8, 134.9, 135.5, 141.1 (Ph); 153.1, 156.6 (C=N); 173.3 (C=S); $^2J(^{119}Sn-^{13}C)$ = 56.1 Hz. ^{119}Sn NMR (300 MHz, $CDCl_3$, 25 °C): δ = −206.8 ppm; (300 MHz, $[D_6]$DMSO, 25 °C): δ = −220.9 ppm.

Complex 4: Yield 79%, m.p. 224 °C. $C_{32}H_{26}N_6SSn$ (677.40): calcd. C 56.74, H 3.84, N 12.41, S 9.45; found C 56.45, H 4.04, N 12.30, S 9.50. MS (FAB+): *m/z* (%) = 413.9 (25) $[SnMe_2(C_{15}H_{10}N_3S)]^+$, 662.8 (5) $[SnMe(C_{15}H_{10}N_3S)_2]^+$, 678.9 (5) $[SnMe_2(C_{15}H_{10}N_3S)_2 + 1]^+$. Selected spectroscopic data: IR (KBr): $\tilde{\nu}$ = 1597 w, 1578 w (C=N); 1485 s (thioamide I); 820 w (thioamide IV); 557 w (ν_{asy} Sn−C); 511 w (ν_{sym} Sn−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.29 [s, 6 H, CH_3, $^2J(^{119}Sn-^1H)$ = 75.0 Hz], 7.30−7.55 (m, 20 H, Ph) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.2 [CH_3, $^1J(^{119}Sn-^{13}C)$ = 557.0]; 128.4, 128.6, 129.2, 129.3, 129.8, 130.9, 135.0, 135.1 (Ph); 153.0, 157.2 (C=N); 174.2 (C=S) ppm. ^{119}Sn NMR (300 MHz, $CDCl_3$, 25 °C): δ = −84.3 ppm. ^{119}Sn NMR (300 MHz, $[D_6]$DMSO, 25 °C): δ = −108.7 ppm. ^{119}Sn CP/MAS NMR: δ = −251 ppm.

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[1] D. X. West, A. E. Liberta, S. B. Padhye, R. C. Chikate, P. B. Sonawane, A. S. Kumbhar, R. G. Yeranda, *Coord. Chem. Rev.* **1993**, *123*, 49−71 and refs. therein.
[2] A. E. Liberta, D. X. West, *Biometals* **1992**, *5*, 121−126.
[3] D. X. West, S. B. Padhye, P. B. Sonawane, *Struct. Bonding* **1991**, *76*, 1−50.
[4] J. G. Cory, A. H. Cory, Eds.; *International Encyclopaedia of Pharmacology and Therapeutics*, Pergamon Press, New York, **1989**.
[5] D. L. Klayman, J. P. Scovill, J. F Bartosevich, J. Bruce, *J. Med. Chem.* **1983**, *26*, 35−59.
[6] J. Easmon, G. Purstinger, G. Heinish, T. Roth, H. H. Fiebig, W. Holzer, W. Jager, M. Jenny, J. Hofman, *J. Med. Chem.* **2001**, *44*, 2164−2171.
[7] Z. Iakovidou, A. Papageorgiou, M. A. Demertzis, E. Mioglou, D. Mourelatos, A. Kostis, P. N. Yadav, D. Kovala-Demertzi, *Anticancer Drugs* **2001**, *12*, 65−70.
[8] M. C. Miller III, C. N. Stineman, J. R. Vance, D. X. West, I. H. Hall, *Anticancer Res.* **1998**, *18*, 4131−4139.
[9] M. Gielen, *Coord. Chem. Rev.* **1996**, *151*, 41−51.
[10] M. Gielen, *Appl. Organomet. Chem.* **2002**, *16*, 481−494.
[11] L. Ronconi, C. Marzano, U. Russo, R. Graziani, D. Fregona, *J. Inorg. Biochem.* **2002**, *91*, 413−420.
[12] L. Pellerito, L. Nagy, *Coord. Chem. Rev.* **2002**, *224*, 111−150.
[13] J. S. Casas, A. Castiñeiras, M. C. Rodríguez-Argüelles, A. Sánchez, J. Sordo, A. Vázquez-López, S. Pinelli, P. Lunghi, P. Ciancianaini, A. Bonati, P. Dall'Aglio, R. Albertini, *J. Inorg. Biochem.* **1999**, *76*, 277−284.
[14] J. S. Casas, A. Castiñeiras, M. C. Rodríguez-Argüelles, A. Sánchez, J. Sordo, A. Vázquez-López, E. M. Vázquez-López, *J. Chem. Soc., Dalton Trans.* **2000**, 2267−2272.
[15] J. S. Casas, M. S. Tasende, J. Sordo, *Coord. Chem. Rev.* **2000**, *209*, 197−261.
[16] J. Holecek, N. Nádvorník, K. Handlír, A. Lycka, *J. Organomet. Chem.* **1986**, *315*, 299−308.
[17] [17a] B. Wrackmeyer in: M. Gielen, R. Willem, B. Wrackmeyer (Eds.), *Physical Organometallic Chemistry*, Wiley, London, **1996**, vol. 1, p. 87−96. [17b] A. Sebald in: M. Gielen, R. Willem, B. Wrackmeyer (Eds.), *Physical Organometallic Chemistry*, Wiley, London, **1996**, vol. 1, p. 123−157.
[18] B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.* **1999**, *38*, 203−264.
[19] P. Souza, M. A. Mendiola, A. Arquero, V. Fernández, E. Gutiérrez-Puebla, C. Ruíz-Valero, *Z. Naturforsch., Teil B* **1994**, *49*, 263−271.
[20] A. Arquero, M. Cañadas, M. Martínez-Ripoll, M. A. Mendiola, A. Ruiz-Valero, *Tetrahedron* **1998**, *54*, 11271−11284.
[21] E. Franco, E. López-Torres, M. A. Mendiola, M. T. Sevilla, *Polyhedron* **2000**, *19*, 441−451.
[22] A. Arquero, M. A. Mendiola, P. Souza, M. T. Sevilla, *Polyhedron* **1996**, *15*, 1657−1665.
[23] Z. Duracková, M. A. Mendiola, M. T. Sevilla, A. Valent, *Bioelectrochem. Bioenerg.* **1999**, *48*, 109−116.
[24] M. J. Gismera, M. A. Mendiola, J. Rodríguez-Procopio, M. T. Sevilla, *Anal. Chim. Acta* **1999**, *385*, 143−150.
[25] M. Cañadas, E. López-Torres, A. Martínez-Arias, M. A. Mendiola, M. T. Sevilla, *Polyhedron* **2000**, *19*, 2059−2068.
[26] E. López-Torres, M. A. Mendiola, J. Rodríguez-Procopio, M. T. Sevilla, E. Colacio, J. M. Moreno, I. Sobrados, *Inorg. Chim. Acta* **2001**, *323*, 130−138.
[27] M. A. Blanco, E. López-Torres, M. A. Mendiola, E. Brunet, M. T. Sevilla, *Tetrahedron* **2002**, 1525.-1531.
[28] G. M. Sheldrick, SADABS version 2.03, *Program for Empirical Absorption Correction*, Universität Göttingen, **1997−2001**.
[29] G. M. Sheldrick, *SAINT+NT (version 6.04) SAX Area-Detector Integration Program*, Bruker AXS, Madison, WI, **1997−2001**.
[30] Bruker, *AXS SHELXTL (version 6.10) Structure Determination Package*, Bruker AXS, Madison, WI, **2000**.
[31] *SHELXS-97, Program for Structure Solution:* G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
[32] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, Universität Göttingen, **1997**.
[33] J. S. Casas, A. Castiñeiras, M. C. Rodríguez-Argüelles, A. Sánchez, J. Sordo, A. Vázquez-López, E. Vázquez-López, *J. Chem. Soc., Dalton Trans.* **2000**, 4056−4063.
[34] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.
[35] L. E. Sutton, *Tables of Interatomic Distances and Configuration in Molecules and Ions*, supplement, The Chemical Society, London, **1965**.
[36] D. E. Fenton, D. H. Cook, *J. Chem. Soc., Chem. Commun.* **1977**, 714−716.
[37] J. S. Casas, A. Sánchez, J. Sordo, A. Vázquez-López, E. E. Castellano, J. Zukerman-Schpector, M. C. Rodríguez-Argüelles, U. Russo, *Inorg. Chim. Acta* **1994**, *216*, 169−175.
[38] T. P. Lockhart, W. F. Manders, *Inorg. Chem.* **1986**, *25*, 892−895.
[39] J. Otera, *J. Organomet. Chem.* **1981**, *221*, 57−61.
[40] C. H. Yoder, L. A. Margolis, J. M. Horne, *J. Organomet. Chem.* **2001**, *633*, 33−38.
[41] A. Deák, L. Radics, A. Kálmán, L. Párkányi, I. Haiduc, *Eur. J. Inorg. Chem.* **2001**, 2849−2856.
[42] A. Tarassoli, T. Sedaghat, B. Neumüller, M. Ghassemzadeh, *Inorg. Chim. Acta* **2001**, *318*, 15−22.

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