

# Diorganotin(IV) complexes of imidazole-2-carbaldehyde thiosemicarbazone (H<sub>2</sub>ImTSC). The crystal and molecular structures of the “free” ligand and of [SnMe<sub>2</sub>(ImTSC)]

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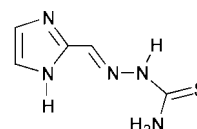
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The compounds [SnR<sub>2</sub>(ImTSC)] (R = Me, <sup>n</sup>Bu or Ph; H<sub>2</sub>ImTSC = imidazole-2-carbaldehyde thiosemicarbazone) were synthesized by treating the appropriate diorganotin(IV) oxide with the ligand in ethanol. The structures of H<sub>2</sub>ImTSC·0.5H<sub>2</sub>O and [SnMe<sub>2</sub>(ImTSC)]·EtOH were determined by X-ray diffractometry. The thiosemicarbazone chain of the former has *E,E,E* configuration and is almost coplanar with the imidazole ring. A rich network of hydrogen bonds involving all potential donor and acceptor groups of H<sub>2</sub>ImTSC and the water molecule stabilizes the crystal lattice. The crystal of the dimethyltin(IV) complex is composed of discrete molecules that are likewise linked by hydrogen bonds. The Sn is bound to the two methyl groups and to an N,N,S-tridentate thiosemicarbazonato dianion (ImTSC<sup>2-</sup>) in a highly distorted trigonal bipyramidal arrangement with the thioamide sulfur and the imidazole nitrogen apical. The Sn–N bond lengths [2.129(5) and 2.174(5) Å] are close to the sum of the covalent radii and dominate the metal–ligand interaction. The Sn–S bond length [2.659(2) Å] suggests a weak bond. The unusual co-ordination mode of the ImTSC<sup>2-</sup> anion creates four- and six-membered stannole rings. The EtOH is bound to the complex *via* hydrogen bonds involving the nitrogen of the imidazole that is not co-ordinated to the tin and the thiosemicarbazone NH<sub>2</sub> group. The IR spectra of the <sup>n</sup>Bu and Ph derivatives suggest that they are structurally similar to the methyl complex. <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR spectroscopy indicates that the structure of the complexes in the solid state persists in CDCl<sub>3</sub> solution. For H<sub>2</sub>ImTSC, <sup>15</sup>N NMR data are presented in addition to IR and <sup>1</sup>H and <sup>13</sup>C NMR data.

The increasing interest in thiosemicarbazones (TSCs)<sup>1</sup> that has arisen in recent decades has to a large extent been prompted by their broad therapeutic activity. Particular attention has been given to the antineoplastic activity displayed both *in vitro* and *in vivo* by α(N)-heterocyclic carbaldehyde thiosemicarbazones.<sup>1</sup> The early hypothesis<sup>2</sup> that this biological behaviour might be associated with the chelation of iron and consequent inhibition of ribonucleotide reductase focused part of this research effort on TSC co-ordination chemistry. The subsequent observation that, in a number of cases, the metal complexes showed even greater antineoplastic activity than the TSC ligand alone<sup>1</sup> further encouraged co-ordination studies involving TSCs. Reviews on the structures of thiosemicarbazonato complexes<sup>3,4</sup> show that TSCs are very versatile ligands, the π delocalization and configurational flexibility of the TSC chain creating the possibility of a variety of co-ordination modes.

In search of new and better therapeutic agents, we have for some time studied interactions between this type of ligand and diorganotin(IV) cations.<sup>5</sup> We report here the synthesis and structural characterization of an α(N)-heterocyclic carbaldehyde thiosemicarbazone that has hitherto received little attention, imidazole-2-carbaldehyde thiosemicarbazone (H<sub>2</sub>ImTSC), and of its complexes with SnR<sub>2</sub><sup>2+</sup> (R = Me, <sup>n</sup>Bu or Ph). This work included determination of the crystal structures of the “free” ligand and its dimethyltin(IV) complex (to our best knowledge, the first X-ray study of H<sub>2</sub>ImTSC or one of its complexes); the latter exhibits a rather unusual co-ordination mode for a TSC ligand.



## Experimental

### General procedures

Thiosemicarbazide (Merck), 2-imidazolecarbaldehyde (Aldrich), dimethyltin dichloride (Alfa), dibutyltin oxide (Aldrich) and diphenyltin dichloride (Aldrich) were used as supplied. The dimethyl- and diphenyl-tin(IV) oxides were obtained by the procedure described in ref. 6. Elemental analyses were performed with a Carlo-Erba 1108 analyser. Melting points were determined with a Büchi apparatus. The mass spectra were obtained using a Kratos MS50TC spectrometer connected to a DS90 data system and operating in electron impact (EI) mode (direct insertion probe, 70 eV, 250 °C); all fragments were identified using DS90 software. IR spectra were recorded on a Bruker IFS-66V spectrometer, <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N and <sup>119</sup>Sn NMR spectra at room temperature on Bruker AMX 300 or AMX 500 instruments and referred to TMS (<sup>1</sup>H, <sup>13</sup>C), pure CH<sub>3</sub>NO<sub>2</sub> (<sup>15</sup>N) and external neat Sn(CH<sub>3</sub>)<sub>4</sub> (<sup>119</sup>Sn); δ in ppm, J in Hz.

### Synthesis of compounds

**H<sub>2</sub>ImTSC.** The ligand was prepared by treating 2-imidazolecarbaldehyde and thiosemicarbazide in 1:1 ratio in

ethanol–water following the general procedure previously reported.<sup>7</sup> mp 225 °C. Found: C, 33.8; H, 4.5; N, 39.2%. Calc. for C<sub>7</sub>H<sub>6</sub>N<sub>5</sub>S·0.5H<sub>2</sub>O: C, 33.7; H, 4.5; N, 39.3%. IR spectrum (cm<sup>-1</sup>, KBr): 3300–2800s (br) ν(NH<sub>2</sub>) + ν(NH) + ν(OH); 1624vs (br), δ(NH<sub>2</sub>) + ν(CN); 1548m, δ(NH); 1518s (br), 1474m, 1455m, 1444sh, ν(ring) + ν(NCS); 847m, ν(CS) + γ(CH); 760m, γ(CH); 650m, δ(ring). NMR data (see Fig. 1 for numbering scheme): <sup>1</sup>H (in dms<sub>o</sub>-d<sub>6</sub>) δ[N(4)H] 12.51s br(1); δ[N(2)H] 11.55s br(1); δ[N(1)H<sub>2</sub>] 8.31s(1), 8.03s(1); δ[C(2)H] 7.86s(1); δ[C(4)H] 7.31s br(1); and δ[C(5)H] 7.02s br(1); <sup>13</sup>C (in dms<sub>o</sub>-d<sub>6</sub>) δ[C(1)] 178.3; δ[C(2)] 132.2; δ[C(3)] 143.1; δ[C(4)] 118.5; and δ[C(5)] 129.7; <sup>15</sup>N (in dms<sub>o</sub>-d<sub>6</sub>) δ[N(1)] –270; δ[N(4)] –220; δ[N(5)] –220; and δ[N(2)] –210.

**[SnMe<sub>2</sub>(ImTSC)].** A solution of H<sub>2</sub>ImTSC (0.30 g, 1.8 mmol) in ethanol (50 mL) was added to a suspension of SnMe<sub>2</sub>O (0.29 g, 1.8 mmol) in 20 mL of the same solvent. The mixture was refluxed for 4 days, and a yellow-green crystalline solid was filtered out. mp 223 °C. Found: C, 26.1; H, 3.5; N, 21.7%. Calc. for C<sub>7</sub>H<sub>11</sub>N<sub>5</sub>SSn: C, 26.6; H, 3.5; N, 22.2%. Mass spectrum (*m/z*, %): M<sup>+</sup> (317, 100); M<sup>+</sup> – Me (302, 30); and M<sup>+</sup> – 2Me (287, 75). IR (cm<sup>-1</sup>, KBr): 3405m, 3371m, 3332m, ν(NH<sub>2</sub>); 1656m, 1631m, 1602m, δ(NH<sub>2</sub>) + ν(CN); 1501s (br), 1466m, 1431vs, ν(ring) + ν(NCS); 802m, ν(CS); 816m, γ(CH); 676m, δ(ring); 563m, ν<sub>asym</sub>(Sn–C); 527m, ν<sub>sym</sub>(Sn–C). NMR data (see Fig. 1 for numbering scheme of the ImTSC moiety): <sup>1</sup>H (in dms<sub>o</sub>-d<sub>6</sub>) δ[N(1)H<sub>2</sub>] 8.88s br(1), 8.40s br(1); δ[C(2)H] 7.13s(1); δ[C(4)H] 7.37s(1); δ[C(5)H] 7.23s(1); δ(Sn–R) 0.92s(6); <sup>2</sup>J(<sup>1</sup>H–<sup>117/119</sup>Sn) = 79/82 Hz; (in CDCl<sub>3</sub>) δ[N(1)H<sub>2</sub>] 7.39vbr(1), 6.53vbr(1); δ[C(2)H] 7.02s(1); δ[C(4)H] 7.45s(1); δ[C(5)H] 7.34d(1), *J* = 0.7; δ(Sn–R) 1.01s(6), <sup>2</sup>J(<sup>1</sup>H–<sup>117/119</sup>Sn) = 69/73 Hz; <sup>13</sup>C (in CDCl<sub>3</sub>) δ[C(1)] 178.8; δ[C(2)] 124.5, *J*(<sup>1</sup>H–Sn) = 26; δ[C(3)] 145.4; δ[C(4)] 132.3, *J*(<sup>1</sup>H–Sn) = 15; δ[C(5)] 137.6, *J*(<sup>1</sup>H–Sn) = 19; δ(Sn–R) 3.4, <sup>1</sup>J(<sup>13</sup>C–<sup>117/119</sup>Sn) = 534/559 Hz. <sup>119</sup>Sn (in CDCl<sub>3</sub>) δ –170.1.

Recrystallization from EtOH gave single crystals appropriate for X-ray diffraction studies.

**[SnBu<sub>2</sub>(ImTSC)].** A solution of H<sub>2</sub>ImTSC (0.29 g, 1.7 mmol) in 40 mL of absolute ethanol was added to a stirred suspension of SnBu<sub>2</sub>O (0.42 g, 1.7 mmol) in 20 mL of the same solvent. The mixture was refluxed for 4 days, and a yellow-green solid was filtered out. mp 157 °C. Found: C, 39.7; H, 5.9; N, 17.5%. Calc. for C<sub>13</sub>H<sub>23</sub>N<sub>5</sub>SSn: C, 39.0; H, 5.8; N, 17.5%. Mass spectrum (*m/z*, %): M<sup>+</sup> (401, 46); M<sup>+</sup> – Bu (344, 57); and M<sup>+</sup> – 2Bu (287, 100); IR (cm<sup>-1</sup>, KBr): 3470m (br); 3305m, ν(NH<sub>2</sub>); 1640m, 1617m, 1602m, δ(NH<sub>2</sub>) + ν(CN); 1496s (br), 1462m, 1429vs, ν(ring) + ν(NCS); 799m, ν(CS); 813m, γ(CH); 677m, δ(ring). NMR data (see Fig. 1 for numbering scheme of the ImTSC moiety): <sup>1</sup>H (in dms<sub>o</sub>-d<sub>6</sub>) δ[N(1)H<sub>2</sub>] 8.83s br(1), 8.34s br(1); δ[C(2)H] 7.12s(1); δ[C(4)H] 7.32s(1); δ[C(5)H] 7.20s(1); butyl fragment [δ(H<sub>α</sub> and H<sub>γ</sub>) 1.52m(8); δ(H<sub>β</sub>) 1.19q(4); δ(H<sub>δ</sub>) 0.76t(6)]; (in CDCl<sub>3</sub>) δ[N(1)H<sub>2</sub>] 7.34s br(1), 6.14s br(1); δ[C(2)H] 7.03s(1); δ[C(4)H] 7.42s(1); δ[C(5)H] 7.34d(1), *J* = 0.7 Hz; butyl fragment [δ(H<sub>α</sub> and H<sub>γ</sub>) 1.65m(8); δ(H<sub>β</sub>) 1.32q(4); δ(H<sub>δ</sub>) 0.88(6)]; <sup>13</sup>C (in CDCl<sub>3</sub>) δ[C(1)] 178.7; δ[C(2)] 124.6; δ[C(3)] 145.4; δ[C(4)] 131.9; δ[C(5)] 137.3; butyl fragment [δ(C<sub>α</sub>) 27.2; δ(C<sub>β</sub>) 26.1; δ(C<sub>γ</sub>) 23.3; δ(C<sub>δ</sub>) = 19.3]; <sup>119</sup>Sn (in CDCl<sub>3</sub>) δ –178.5.

**[SnPh<sub>2</sub>(ImTSC)]·EtOH.** To a suspension of SnPh<sub>2</sub>O (0.17 g, 0.6 mmol) in absolute ethanol (50 mL) was added a solution of ligand (0.10 g, 0.6 mmol) in 30 mL of the same solvent. After refluxing for 4 days the yellow-green solid formed was filtered out and vacuum dried. mp 203 °C. Found: C, 46.1; H, 4.4; N, 14.5%. Calc. for C<sub>19</sub>H<sub>21</sub>N<sub>5</sub>OSSn: C, 46.0; H, 4.3; N, 14.4%. Mass spectrum (*m/z*, %): M<sup>+</sup> (441, 56); M<sup>+</sup> – Ph (364, 27); M<sup>+</sup> – 2Ph (287, 6); and C<sub>5</sub>H<sub>7</sub>N<sub>5</sub> (137, 100). IR (cm<sup>-1</sup>, KBr): 3424(sh), 3312m, ν(NH<sub>2</sub>); 1630m, 1610(sh), 1597m (br), δ(NH<sub>2</sub>) + ν(CN); 1502s (br), 1467m, 1429vs, ν(ring) + ν(NCS);

800m, ν(CS); 812m, γ(CH); 673m, δ(ring); 279m, ν(Sn–C); 253m, ν(Sn–C). NMR data (see Fig. 1 for numbering scheme of the ImTSC moiety): <sup>1</sup>H (in dms<sub>o</sub>-d<sub>6</sub>) δ[N(1)H<sub>2</sub>] 9.27s(1), 8.77s(1); δ[C(2)H] 7.28s(1); δ[C(4)H] 7.45 (overlapping phenyl signals); δ[C(5)H] 7.36s(1); phenyl fragment [δ(H<sub>o</sub>) 7.61dd(4); δ(H<sub>m</sub> and H<sub>p</sub>) 7.44]; EtOH signals [δ(CH<sub>3</sub>) 1.05t(3); δ(CH<sub>2</sub>) 3.43cd(2); δ(OH) 4.36t(1)]; (in CDCl<sub>3</sub>) δ[N(1)H<sub>2</sub>] 7.43 (overlapping phenyl signals), 6.38s br(1); δ[C(2)H] 7.21s(1); δ[C(4)H] 7.53s(1); δ[C(5)H] 7.43 (overlapping phenyl signals); phenyl fragment [δ(H<sub>o</sub>) 7.62d(4), δ(H<sub>m</sub> and H<sub>p</sub>) 7.43m]; EtOH signals [δ(CH<sub>3</sub>) 1.25t(3); δ(CH<sub>2</sub>) 3.72c(2)]; <sup>13</sup>C (in CDCl<sub>3</sub>) δ[C(1)] 178.6; δ[C(2)] 126.1; δ[C(3)] 146.4; δ[C(4)] 131.9; δ[C(5)] 137.3; phenyl fragment [δ(C<sub>i</sub>) 143.3, δ(C<sub>o</sub>) 134.8, δ(C<sub>m</sub>) 130.0, δ(C<sub>p</sub>) 130.5]; EtOH signals [δ(CH<sub>3</sub>) 17.4; δ(CH<sub>2</sub>) 57.5]; <sup>119</sup>Sn (in CDCl<sub>3</sub>) δ –293.5.

## Crystallography

**X-Ray data collection, structure solution and refinement.** All X-ray crystallographic measurements were carried out at 293 K using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu-Kα (H<sub>2</sub>ImTSC·0.5H<sub>2</sub>O) or Mo-Kα radiation (λ = 1.54184 and 0.71073 Å, respectively). Data were obtained with the ω–2θ scan technique and corrected for Lorentz and polarization effects. Sources of scattering factor data are named in ref. 8. Most calculations were performed and graphics produced with SHELX 97<sup>9</sup> and SCHAKAL.<sup>10</sup> Table 1 summarizes the crystal data, experimental details and refinement results. The structures were solved by Patterson and Fourier methods and refined on *F*<sup>2</sup> by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms.<sup>9</sup>

**Structure solution and refinement.** H<sub>2</sub>ImTSC·0.5H<sub>2</sub>O. Hydrogen atoms were located in the last Fourier map and refined isotropically. Inspection of *F*<sub>c</sub> and *F*<sub>o</sub> values indicated that a correction for secondary extinction was required.

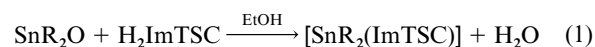
**[SnMe<sub>2</sub>(ImTSC)]·EtOH.** An empirical absorption correction was made.<sup>11</sup> The carbon atoms of the ethanol molecule were refined with common anisotropic parameters. All hydrogen atoms were calculated and refined using a riding model,<sup>9</sup> except that the hydroxyl H of the ethanol was located in the last Fourier map.

CCDC reference number 186/1997.

See <http://www.rsc.org/suppdata/dt/b0/b002286/> for crystallographic files in .cif format.

## Results and discussion

The three complexes were prepared by the general procedure of treating a suspension of the appropriate organotin oxide in ethanol with a solution of the ligand in the same solvent, eqn. (1). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of these compounds in



solution are consistent with the proposed formulae, showing, in particular, the solvation of [SnPh<sub>2</sub>(ImTSC)] by a molecule of ethanol. [SnMe<sub>2</sub>(ImTSC)] acquired an EtOH molecule during crystallization.

## Description of the structures

Fig. 1 shows the two molecules of H<sub>2</sub>ImTSC and the water molecule that are included in each asymmetric unit, together with the numbering scheme adopted. Selected bond lengths and bond angles are listed in Table 2. The very small differences between the structural parameters of the two H<sub>2</sub>ImTSC molecules probably derive from differences in packing forces

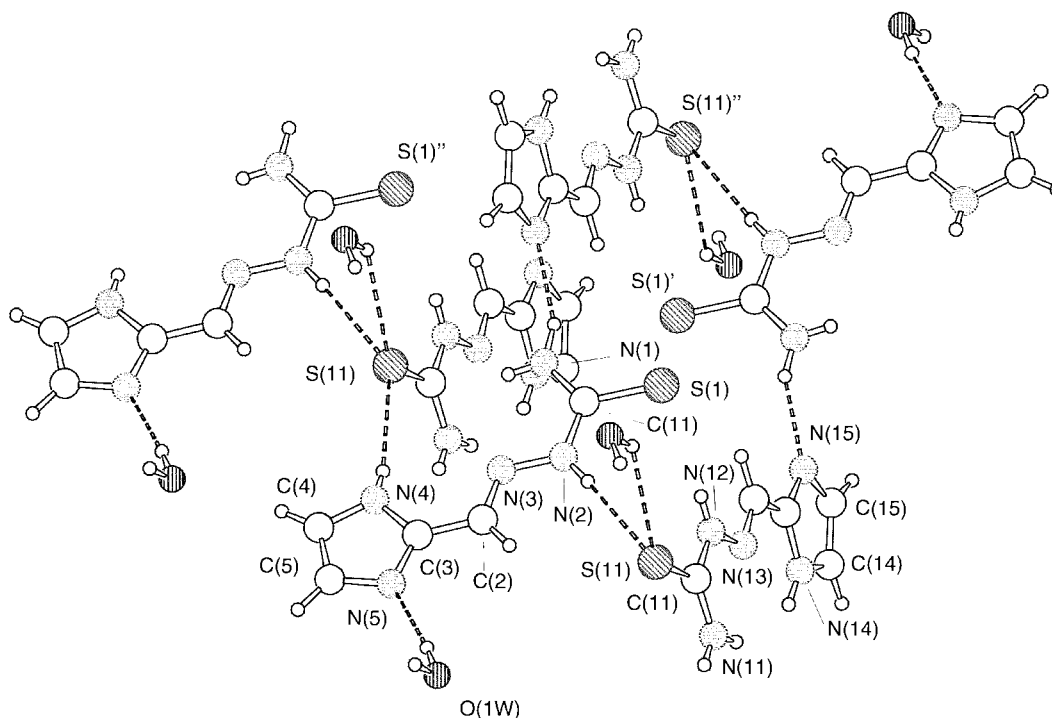


Fig. 1 SCHAKAL diagram of  $\text{H}_2\text{ImTSC}\cdot 0.5\text{H}_2\text{O}$  showing the intermolecular association by hydrogen bonding.

Table 1 Crystallographic data and details of the structure determination of  $\text{H}_2\text{ImTSC}\cdot 0.5\text{H}_2\text{O}$  and  $[\text{SnMe}_2(\text{ImTSC})]\cdot \text{EtOH}$

	$\text{H}_2\text{ImTSC}\cdot 0.5\text{H}_2\text{O}$	$[\text{SnMe}_2(\text{ImTSC})]\cdot \text{EtOH}$
Chemical formula	$\text{C}_5\text{H}_8\text{N}_5\text{O}_{0.5}\text{S}$	$\text{C}_9\text{H}_{17}\text{N}_5\text{OSSn}$
Formula weight	178.25	315.96
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2$
$\mu/\text{mm}^{-1}$	3.08	1.838
$a/\text{\AA}$	7.7676(9)	22.920(8)
$b/\text{\AA}$	7.8401(9)	6.3651(7)
$c/\text{\AA}$	15.873(2)	10.488(4)
$\alpha^\circ$	81.828(9)	
$\beta^\circ$	81.140(10)	101.655(16)
$\gamma^\circ$	61.146(9)	
$V/\text{\AA}^3$	836.44(17)	1498.5(7)
$T/\text{K}$	293(2)	293(2)
$Z$	4	4
No. reflections measured	3637	2465
No. unique reflections/ $R(\text{int.})$	2968/0.0798	2350/0.0202
Final $R1, wR2$ ( $I > 2\sigma(I)$ )	0.0498, 0.1365	0.0422, 0.1064
(all data)	0.0512, 0.1378	0.0395, 0.1040

(see below), so discussion will be centred on the molecule with the lowest-numbered atoms (molecule A), with only occasional reference to the other (molecule B).

The bond lengths in the TSC chain [C(2)N(3)N(2)C(1)S(1)-N(1)] (Table 2) are similar to those of other free unsubstituted TSCs, although all except  $d[\text{C}(1)-\text{S}]$  and  $d[\text{C}(11)-\text{S}]$  are smaller than in the average TSC chain recorded in the Cambridge Structural Database.<sup>4</sup> This suggests that significant  $\pi$ -charge delocalization occurs along the  $\text{H}_2\text{NC}(\text{S})\text{NNC}$  backbone. As is usual in free unsubstituted TSCs, the S atom is *trans* to the azomethine N atom; that is, the molecule adopts an *E* configuration about the C(1)-N(2) bond. The same configuration is also adopted about the N(2)-N(3) and N(3)-C(2) bonds. This *E,E,E*-configuration sequence places the N(2)-H group in an unsuitable position for intramolecular hydrogen bonding with the pyridine-like nitrogen atom of the imidazole ring (it has been suggested that some <sup>1</sup>N-substituted derivatives of this ligand feature this N(2)-H...N(5) bond in solution).<sup>12</sup>

The thiosemicarbazone chain and the imidazole ring are both planar (r.m.s. deviations 0.0041 and 0.0015 Å, respectively, in molecule A) and are almost coplanar (dihedral angle 6.1(1)° in

Table 2 Bond lengths (Å) and angles (°) for  $\text{H}_2\text{ImTSC}\cdot 0.5\text{H}_2\text{O}$

Molecule A		Molecule B	
S(1)-C(1)	1.694(2)	S(11)-C(11)	1.684(2)
N(1)-C(1)	1.313(3)	N(11)-C(11)	1.312(3)
N(2)-C(1)	1.338(3)	N(12)-C(11)	1.338(3)
N(2)-N(3)	1.362(3)	N(12)-N(13)	1.361(2)
N(3)-C(2)	1.269(3)	N(13)-C(12)	1.266(3)
C(1)-N(2)-N(3)	119.23(17)	C(11)-N(12)-N(13)	118.95(17)
C(2)-N(3)-N(2)	117.06(17)	C(12)-N(13)-N(12)	116.96(18)
N(1)-C(1)-N(2)	117.77(19)	N(11)-C(11)-N(12)	117.92(19)
N(1)-C(1)-S(1)	123.86(17)	N(11)-C(11)-S(11)	123.64(17)
N(2)-C(1)-S(1)	118.37(15)	N(12)-C(11)-S(11)	118.44(15)
N(3)-C(2)-C(3)	119.01(19)	N(13)-C(12)-C(13)	118.47(18)

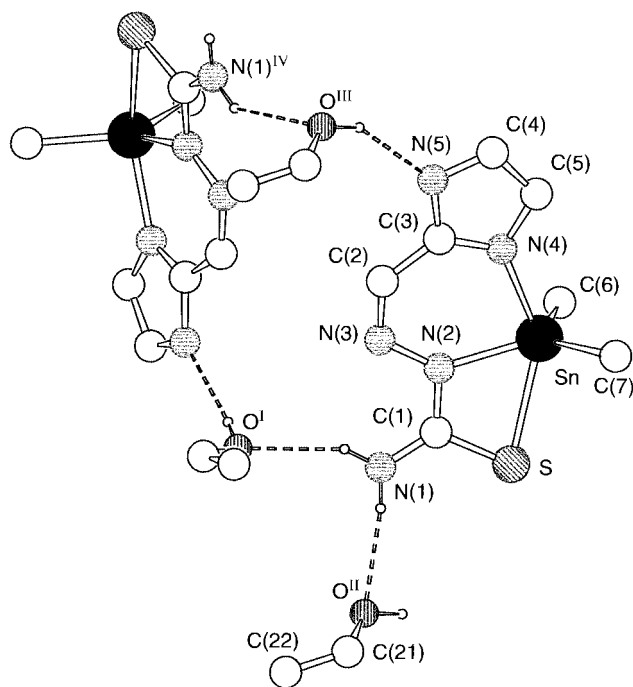
molecule A and 4.7(2)° in molecule B). The mutual orientation of molecules A and B is indicated by the dihedral angle of 68.5(1)° between their TSC chains.

The crystal lattice features a rich network of intermolecular hydrogen bonds involving practically all the potential donor

**Table 3** Hydrogen bonds for H<sub>2</sub>ImTSC·0.5H<sub>2</sub>O (lengths in Å and angles in °)<sup>a</sup>

D-H...A	d(D-H)	d(H...A)	d(D...A)	DHA
N(1)-H(1N1)...N(15) <sup>i</sup>	0.90(4)	2.10(4)	2.936(3)	155(3)
N(1)-H(2N1)...S(11) <sup>ii</sup>	0.80(3)	2.72(3)	3.443(2)	150(3)
N(2)-H(2)...S(11)	0.86(3)	2.53(3)	3.3887(18)	174(3)
N(4)-H(4)...S(11) <sup>iii</sup>	0.74(3)	2.65(3)	3.375(2)	170(3)
N(11)-H(1N2)...O(1W) <sup>iiii</sup>	0.79(3)	2.14(3)	2.851(3)	150(2)
N(11)-H(2N2)...S(1) <sup>iv</sup>	0.89(3)	2.71(3)	3.495(2)	148(3)
N(12)-H(12)...S(1)	0.81(3)	2.53(3)	3.3301(19)	170(2)
N(14)-H(14)...S(1) <sup>v</sup>	0.84(3)	2.54(3)	3.378(2)	173(2)
O(1W)-H(1W)...S(11) <sup>v</sup>	0.85(5)	2.77(5)	3.4035(19)	132(4)
O(1W)-H(2W)...N(5) <sup>vi</sup>	0.86(5)	1.96(5)	2.818(3)	171(4)

<sup>a</sup> Symmetry transformation used to generate equivalent atoms: i  $-x, -y + 1, -z + 1$ ; ii  $x - 1, y + 1, z$ ; iii  $-x + 1, -y, -z + 1$ ; iv  $x, y - 1, z$ ; v  $-x + 1, -y + 1, -z + 1$ ; vi  $x, y + 1, z - 1$ .

**Fig. 2** SCHAKAL diagram of [SnMe<sub>2</sub>(ImTSC)]·EtOH showing the intermolecular association by hydrogen bonding (hydrogen atoms not involved in the interactions are omitted for clarity).

and acceptor groups (Table 3). As is usual in N-non-substituted TSCs,<sup>4</sup> there is also an intramolecular hydrogen-bond-like interaction between the NH<sub>2</sub> group and the lone pair of N(3) which stabilizes the *E* configuration about the C(1)–N(2) bond. Molecules A and B differ as regards the hydrogen bonds involving the S atom: both sulfurs form bonds with the amino and imino groups of neighbouring TSC chains and with the NH group of the imidazole ring, but S(11) is also hydrogen bonded to the water molecule. This latter is linked *via* its other hydrogen to the unprotonated N atom of the imidazole ring of a type A molecule. The hydrogen bonds of the NH<sub>2</sub> groups of A and B also differ; the former group is linked to the sulfur and N(15) atoms of two different type B molecules, and the latter to S(1) and the H<sub>2</sub>O oxygen.

The molecular structure of [SnMe<sub>2</sub>(ImTSC)]·EtOH is shown in Fig. 2 together with the numbering scheme used. Selected bond lengths and bond angles are listed in Table 4. The tin atom is bound to the two methyl groups, to the S and N(2) atoms of the TSC chain and to one of the N atoms of the imidazole ring, defining a highly distorted trigonal bipyramid with the sulfur and the imidazole nitrogen apical. Although the equatorial angles are reasonably close to the ideal 120° and the equatorial plane is fairly flat {the r.m.s. deviation of C(6), C(7), N(2) and Sn from the least-squares plane fitted to them is 0.0775 Å} and

**Table 4** Bond lengths (Å) and angles (°) for [SnMe<sub>2</sub>(ImTSC)]·EtOH

Sn–C(6)	2.123(8)	C(1)–N(1)	1.329(8)
Sn–C(7)	2.125(7)	C(1)–N(2)	1.342(7)
Sn–N(2)	2.129(5)	C(2)–C(3)	1.451(8)
Sn–N(4)	2.174(5)	N(2)–N(3)	1.398(7)
Sn–S	2.659(2)	N(3)–C(2)	1.277(8)
S–C(1)	1.707(7)		
C(6)–Sn–C(7)	122.2(4)	C(1)–S–Sn	77.2(2)
C(6)–Sn–N(2)	112.8(3)	N(1)–C(1)–N(2)	123.0(6)
C(7)–Sn–N(2)	124.3(3)	N(1)–C(1)–S	123.9(4)
C(6)–Sn–N(4)	100.4(3)	N(2)–C(1)–S	113.0(5)
C(7)–Sn–N(4)	96.1(3)	C(1)–N(2)–N(3)	115.7(5)
N(2)–Sn–N(4)	81.37(19)	C(1)–N(2)–Sn	106.6(4)
C(6)–Sn–S	100.4(2)	N(3)–N(2)–Sn	137.7(4)
C(7)–Sn–S	97.5(2)	C(2)–N(3)–N(2)	117.2(5)
N(2)–Sn–S	63.22(13)	C(3)–N(4)–Sn	126.2(4)
N(4)–Sn–S	143.74(19)	C(4)–N(4)–Sn	128.1(5)

is perpendicular to the least-squares plane through S, C(1), N(2), N(3), C(2), C(3) and N(4) (fitted with an r.m.s. of 0.0535 Å), the small bite of the ligand makes the S–Sn–N(4) angle 143.74(19)° instead of the ideal 180°.

The bideprotonated ligand is bound in a rather unusual tridentate chelating mode. Like the “free” ligand it adopts the *E* configuration about the C(1)–N(2) and N(2)–N(3) bonds, but the configuration about the N(3)–C(2) bond has changed to *Z*. The usual TSC co-ordination mode, through the thioamide sulfur and azomethine nitrogen [N(3)], is not possible; instead, chelation *via* N(2) and S forms a four-membered metallacycle that has formerly been found in (*p*-anisaldehyde thiosemicarbazonato)dimethylthallium(III)<sup>13</sup> and in polymetallic thiosemicarbazones of Al, Ga and In,<sup>4</sup> while the N(4)–Sn bond closes a six-membered metallacycle. There is thus one four- and one six-membered stannole ring instead of the *a priori* more favourable arrangement of two five-membered rings that would have resulted from a *Z* configuration about the C(1)–N(2) bond and *E* configuration about N(3)–C(2).

Note that if the structure of the “free” ligand in solution is as has been suggested on the basis of NMR experiments for <sup>1</sup>N-substituted derivatives [that is, with *E* configuration about C(1)–N(2) and N(2)–N(3) but *Z* configuration about N(3)–C(2)],<sup>12</sup> then the structure and co-ordination scheme adopted by ImTSC<sup>2-</sup> in solid [SnMe<sub>2</sub>(ImTSC)]·EtOH is the same as would result from the ligand being captured by the organometallic cation immediately after deprotonation of the two H–N groups. However, one would normally expect a hypothetical initial co-ordination mode of this kind to evolve rapidly to a more usual chelating scheme; the presence of a significant concentration of the isomer shown in Fig. 2 in a reaction mixture refluxed for 4 days (see the Experimental section) is unexpected and hard to explain. Some inkling may nevertheless be provided by an analysis of bond lengths. It is noteworthy that *d*(Sn–N(4)) is close to, and *d*(Sn–N(2)) [= 2.129(5) Å] even

shorter than, the sum of the covalent radii (2.15 Å<sup>14</sup>), which indicates strong bonds. By contrast, the Sn–S distance, 2.659(2) Å, though much shorter than the sum of the van der Waals radii (4.0 Å<sup>14</sup>), is suggestive of a weak bond, being longer than in five-co-ordinated dimethyltin(IV) thiosemicarbazonato complexes such as [SnMe<sub>2</sub>(FPT)Cl]·0.5H<sub>2</sub>O (HFPT = pyridine-2-carbaldehyde thiosemicarbazone) or [SnMe<sub>2</sub>(STSC)] (H<sub>2</sub>ST-SC = salicylaldehyde thiosemicarbazone), in which *d*(Sn–S) is 2.478(2) Å<sup>15</sup> and 2.5425(8) Å,<sup>16</sup> respectively. The weakness of the Sn–S bond is also indicated by the small magnitude of the changes in the bond parameters of the thiocarbamide group upon co-ordination: the increase in the C(1)–S bond length, just 0.013 Å, indicates very little of the thione-to-thiol evolution usually associated with strong metal–sulfur bonds in this type of complex,<sup>4</sup> and the C(1)–N(2) distance is barely altered {1.338(3) Å in H<sub>2</sub>ImTSC, 1.342(7) Å in [SnMe<sub>2</sub>(ImTSC)]·EtOH}, although the C(1)–N(1) distance increases slightly from 1.313(3) to 1.329(8) Å. Thus the relevant bond lengths suggest that the ligand remains frozen in its initial co-ordination mode because of the formation of very strong Sn–N bonds, maintenance of which must be thermodynamically favourable even though it entails a weak Sn–S bond.

The EtOH molecule is bound in the crystal lattice by a rich network of hydrogen bonds involving the imidazole N(5) atom of one [SnMe<sub>2</sub>(ImTSC)] molecule and the N(1)H<sub>2</sub> groups of two others (see Fig. 2). Together with the intramolecular hydrogen-bond-like interaction between N(3) and the N(1)H<sub>2</sub> group, these interactions probably saturate all the acceptor and donor centres, and there are no other weak intermolecular bonds.

### IR spectra

The most significant IR bands are listed in the Experimental section. The proposed assignment is based on previous studies of thiosemicarbazone and imidazole ligands in metal complexes.<sup>5,12,15–18</sup> The data suggest that the co-ordination mode of ImTSC is in all the complexes the same as was shown for the methyl derivative by the X-ray diffraction study.

The spectrum of the “free” ligand shows a very broad band from 3300 to 2800 cm<sup>-1</sup> which includes the stretching vibrations of the groups NH<sub>2</sub>, OH and NH, all of which are involved in hydrogen bonds. The position of a ν(NH<sub>2</sub>) band at 3400 cm<sup>-1</sup> or higher wavenumbers in the spectra of the complexes is in keeping with the non-co-ordination of this group.<sup>5,15–17</sup> The co-ordination of the deprotonated imidazole N is shown<sup>12,18</sup> by the shift to higher wavenumbers of the γ(CH) and δ(ring) bands at 760 and 650 cm<sup>-1</sup> of the “free” ligand, and S-co-ordination by the shift to lower wavenumbers<sup>12</sup> of the ν(CS) band at 847 cm<sup>-1</sup> of the “free” ligand.

N(2)-Co-ordination must affect the range 1650–1450 cm<sup>-1</sup>, but there is interference from N(4)-co-ordination because the stretching vibrations of the ring are also located in this region. The very broad band at 1624 cm<sup>-1</sup> of the “free” ligand splits into several medium bands close to this position for the complexes, the band at 1548 cm<sup>-1</sup> of the “free” ligand disappears [showing it to be δ(NH)], the 1518 cm<sup>-1</sup> band shifts to slightly lower wavenumbers, and the other two bands, at 1474 and 1455 cm<sup>-1</sup>, merge into a medium band at about 1466 cm<sup>-1</sup>. In this range the spectra of all the complexes resemble that of (*p*-anisaldehyde thiosemicarbazonato)dimethylthallium(III),<sup>13</sup> which an X-ray diffraction study showed to be N(2)-co-ordinated like [SnMe<sub>2</sub>(ImTSC)]. In spite of the impossibility of precise assignment, this similarity suggests that ImTSC is also N(2)-co-ordinated in the butyl and phenyl complexes.

With respect to the vibrations of the SnC<sub>2</sub>N<sub>2</sub>S kernel, the ν(SnC) bands are close to the positions found for other diorganotin(IV) compounds.<sup>16</sup> However, ν(SnS) and ν(SnN) could not rigorously be identified due to the complexity of the spectra.

### NMR spectra

The main parameters of the <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR spectra, and of the <sup>15</sup>N NMR spectrum of the “free” ligand, are collected in the Experimental section. The ligand is very poorly soluble in CDCl<sub>3</sub> and its spectra were recorded in dmsO-d<sub>6</sub>, but it was possible to perform most of the NMR studies of the complexes in the former, less co-ordinating solvent. Some of the spectra of the complexes were also recorded in dmsO-d<sub>6</sub> in order to ascertain the influence of the solvent. In the <sup>13</sup>C NMR spectra changing the solvent switches the positions of the C(2) and C(4) signals [C(2), δ 125.2 in CDCl<sub>3</sub> and 130.5 in dmsO-d<sub>6</sub>; C(4), δ 132.5 in CDCl<sub>3</sub> and 125.5 in dmsO-d<sub>6</sub>], but the positions of the other signals are hardly affected. All assignments (made using <sup>1</sup>H–<sup>13</sup>C and <sup>1</sup>H–<sup>15</sup>N heteronuclear correlation, HMQC experiments and deuteration procedures, and taking into account reports on related ligands<sup>12,19</sup>) are in general agreement with previous work on N<sup>1</sup>-substituted 2-imidazole-2-carbaldehyde TSC ligands,<sup>12</sup> except as regards the C(2) and C(4) signals in the <sup>13</sup>C NMR spectra.

The N(4)H and N(2)H proton signals of the ligand fail to appear in the <sup>1</sup>H NMR spectra of the complexes due to the double deprotonation of H<sub>2</sub>ImTSC. Nevertheless, the most prominent feature of these spectra is the behaviour of the N(1)H<sub>2</sub> group. The two protons of this group are usually magnetically non-equivalent in free N<sup>1</sup>-unsubstituted TSCs but become equivalent upon formation of the complexes, probably because the C(1)–N(1) bond order diminishes when the thioamide group undergoes the usual thione-to-thiol evolution, and also because the N(1)–H···N(3) hydrogen-bond-like interaction that is present in the “free” ligand disappears when the configuration of the C(1)–N(2) bond changes from *E* to *Z* upon complexation. In the spectra of these H<sub>2</sub>ImTSC complexes, however, the two N(1)H<sub>2</sub> signals not only do not merge, but are more separated than in that of the “free” ligand, both in dmsO-d<sub>6</sub> and in CDCl<sub>3</sub>. This is a clear indication that the [SnR<sub>2</sub>(ImTSC)] complexes retain their solid state structures in solution, since maintenance of the *E* configuration about C(1)–N(2) allows maintenance of the N(1)–H···N(3) interaction, and maintenance of the weak Sn–S bond prevents further thione-to-thiol evolution. In keeping with the foregoing, the position of the C(1) signal in the <sup>13</sup>C NMR spectra hardly changes upon complexation.

For [SnMe<sub>2</sub>(ImTSC)], substitution of the coupling constants <sup>2</sup>*J*(<sup>1</sup>H–<sup>119</sup>Sn) and <sup>1</sup>*J*(<sup>13</sup>C–<sup>119</sup>Sn) (82 and 558.5 Hz, respectively) in the corresponding Lockhart–Manders equations<sup>20</sup> (empirical relationships between the coupling constants and the C–Sn–C angle) gives values of 123 and 125° respectively. Their similarity indicates that they are reliable,<sup>20</sup> and their proximity to the value obtained in the X-ray study [122.2(4)°] further supports maintenance of the solid state structure in solution.

Finally, for the methyl and butyl compounds δ(<sup>119</sup>Sn) –170.1 and –178.5 respectively is well inside the range for five-co-ordinated complexes.<sup>21</sup> The value for [SnPh<sub>2</sub>(ImTSC)] (δ –293.5) probably reflects the greater shielding ability of the phenyl groups, not a different co-ordination number.

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