APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 10, 35–45 (1996)

Synthesis and Characterization of Organotin Complexes with 2-Mercaptopyridine Derivatives

M. D. Couce,*† V. Cherchi,* G. Faraglia,* U. Russo,* L. Sindellari,*§ G. Valle‡ and N. Zancan*

* Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Via Loredan 4, I-35131 Padova, Italy, † Departamento de Química Pura y Aplicada, Universidad de Vigo, Galicia, Spain, and ‡ Centro di Ricerche sui Biopolimeri del CNR, Via Marzolo 1, I-35131 Padova, Italy

By reaction of diphenyltin(IV) chloride and triphenyltin(IV) hydroxide with esters of the 2-mercaptopyridine-5-carboxylic acid NH(CS)CHCHC(COOR)CH (HTNME, R = methyl; HTNEE, R = ethyl; HTNIPE, R = isopropyl) the complexes $Ph_3Sn(L)$, $Ph_2SnCl(L)$ (L = TNME, TNEE and TNIPE) and $Ph_2Sn(TNEE)_2$ have been prepared and characterized by IR, NMR and Mössbauer spectroscopies. Moreover, the Ph_2SnCl_2/2-mercaptopyridine (HMP) system has been found to yield either the $Ph_2SnCl_2(HMP)_2$ adduct or the $Ph_2SnCl(MP)$ complex.

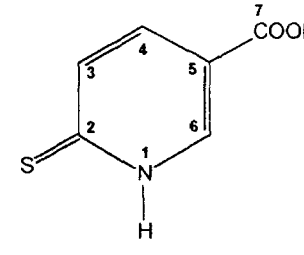
The structures of $Ph_2SnCl(TNEE)$ and $Ph_2SnCl(MP)$ have been determined by X-ray single-crystal diffraction studies. The two structures are similar. Both ligands behave as bidentate chelating groups forming a four-membered ring with an identical small N–Sn–S bite angle of 63.7°. The tin atom is pentacoordinated, presenting a severely distorted trigonal bipyramidal geometry with apical Cl–Sn–N angles of 155.0(2)° [$Ph_2SnCl(TNEE)$] and 155.7(7)° [$Ph_2SnCl(MP)$] and equatorial C–Sn–C angles of 114.9(2)° and 125.0(3)° respectively. On the basis of ^{119}Sn Mössbauer data, all the complexes should present analogous structures except $Ph_2Sn(TNEE)_2$ and $Ph_2SnCl_2(HMP)_2$, for which an octahedral coordination geometry with a *trans* arrangement of the phenyl groups can be proposed. The effect of dimethyl sulphoxide on $Ph_2SnCl(L)$ and $Ph_2SnCl_2(HMP)_2$ is also discussed.

Keywords: organotin; esters of 2-mercaptopyridine-5-carboxylic acid; 2-mercaptopyridine; Mössbauer; IR; NMR; crystal structure

INTRODUCTION

Organotin(IV) complexes are widely studied because, besides their purely chemical interest, they can present cytotoxic activity against a variety of tumours.[1] Among compounds studied so far, the most promising ones are those which contain N–O or N–S donor ligands, a few examples of complexes with bidentate ligands containing both nitrogen and sulphur having been reported.[2–8] The interest in this class of ligands depends on their coordination versatility and on a possible enhancement of the cytotoxic activity with respect to monodentate ligands. Mercaptocarboxylic acid derivatives, sulphur-containing models of purinic and pyrimidinic bases, seem to be particularly interesting because they present antimetastatic and pharmacological properties[8,9] and, when bonded to organotin moieties, they could act as carriers of the metal into biological systems. We believed them to be of interest for studying tin complexes with variously substituted mercaptopyridines, such as 2-mercaptopyridine-5-alkyl esters and related disulphides. The complexes $Ph_3Sn(L)$ and $Ph_2SnCl(L)$, where L = TNIPE, TNEE or TNME, and $Ph_2Sn(TNEE)_2$ have been characterized along with the 2-mercaptopyridine (HMP) derivatives $Ph_2SnCl(MP)$ and $Ph_2SnCl_2(HMP)_2$.

R = methyl HTNME
R = ethyl HTNEE
R = isopropyl HTNIPE



Moreover, the crystal structures of $Ph_2SnCl(L)$

§ Author to whom correspondence should be addressed.

CCC 0268–2605/96/010035–11

Received 31 December 1994
Accepted 6 June 1995

Table 1 Analytical and physical data for the organotin(IV) derivatives

Compound	Colour	M.p. (°C)	Analysis (%): Found (Calcd) C	H	N	S
$Ph_2SnCl(TNME)$	White	168	47.0 (47.9)	3.2 (3.3)	2.6 (2.9)	6.6 (6.7)
$Ph_2SnCl(TNEE)$	White	122	48.0 (48.9)	3.5 (3.7)	2.6 (2.8)	6.4 (6.5)
$Ph_2SnCl(TNIPE)$	White	129	49.6 (49.9)	3.9 (4.0)	2.7 (2.8)	6.6 (6.3)
$Ph_2Sn(TNEE)_2$	White	177	52.3 (52.7)	3.9 (4.0)	4.2 (4.4)	10.4 (10.1)
$Ph_3Sn(TNME)$	White	130	57.2 (57.9)	3.9 (4.0)	2.5 (2.7)	6.2 (6.2)
$Ph_3Sn(TNEE)$	White	114	59.0 (58.6)	4.4 (4.3)	2.7 (2.6)	6.1 (6.0)
$Ph_3Sn(TNIPE)$	White	80	59.3 (59.3)	4.6 (4.7)	2.6 (2.6)	6.0 (5.9)
$Ph_2SnCl_2(HMP)_2$	Yellow	120	46.3 (46.6)	3.4 (3.6)	4.8 (4.9)	11.2 (11.3)
$Ph_2SnCl(MP)$	White	117	48.6 (48.8)	3.4 (3.4)	3.5 (3.4)	7.7 (7.7)

(L = TNEE or MP) were determined. While this work was in progress, the crystal structure of a $Ph_2SnCl(MP)$ sample prepared in $MeOH/CHCl_3$ was published.[3] The structure of our sample prepared in EtOH is reported here owing to some crystallographic differences.

EXPERIMENTAL

Materials

Diphenyltin dichloride (Alfa–Ventron), triphenyltin hydroxide, 2-mercaptopyridine-5-carboxylic acid and triethylamine (Aldrich), thiourea (Sigma) and 2-mercaptopyridine (Fluka) were used as supplied. The solvents were purified according to standard procedures. The alkyl esters of 2-mercaptopyridine-5-carboxylic acid were prepared as reported in the literature.[10,11]

Preparations

The complexes $Ph_2SnCl(L)$ (L = TNME, TNEE or TNIPE) were prepared by adding solid Ph_2SnCl_2 to an ethanol solution, or to a suspension, of the appropriate ligand (molar ratio 1:1). As an example, Ph_2SnCl_2 (1.0 mmol) was reacted with H(TNEE) (1.0 mmol in 5 ml of EtOH). After three days under stirring, the solid was filtered off, washed with EtOH, and dried *in vacuo*. Crystals of $Ph_2SnCl(TNEE)$ suitable for X-ray analysis were obtained by slow evaporation of the filtered solution.

The $Ph_2Sn(TNEE)_2$ complex was prepared by addition of H(TNEE) (2.0 mmol) and Ph_2SnCl_2 (1.0 mmol) to an ethanol solution of triethylamine (2.0 mmol). A white solid was immediately formed, but the suspension was stirred for three days. The solid was filtered off, washed with EtOH, and dried *in vacuo*. Crystals of the same product separated slowly from a solution of $Ph_2SnCl(TNEE)$ in dimethyl sulphoxide. Otherwise they can be obtained by adding dimethyl sulphoxide to a chloroform solution of $Ph_2SnCl(TNEE)$.

The complexes $Ph_3Sn(L)$ (L = TNME, TNEE or TNIPE) were similarly prepared by reaction of Ph_3SnOH with an equimolar amount of the appropriate ligand in ethanol.

$Ph_2SnCl_2(HMP)_2$ and $Ph_2SnCl(MP)$ were prepared by addition of solid Ph_2SnCl_2 (1.0 mmol) to a solution of HMP (2.0 mmol) in ethanol; a yellowish solid was formed in a short time, and after 3 days under stirring was filtered off, washed with the solvent and dried *in vacuo*. This product proved to be $Ph_2SnCl_2(HMP)_2$, while, by slow evaporation of the mother solution, white crystals of $Ph_2SnCl(MP)$ suitable for X-ray study were obtained.

Measurements

Analytical data, obtained with a Carlo Erba 1108 apparatus, are reported in Table 1; melting points were determined on Büchi equipment; infrared (IR) spectra were recorded as Nujol mulls or KBr pellets with Nicolet FT IR 5SXC (4000–400 cm^{-1}) and 20F (400–100 cm^{-1}) spectrometers. ^1H and ^{13}C NMR spectra were recorded at room temperature on a JEOL FX 90Q spectrometer operating in Fourier transform mode; measurements were made in a 5 mm spinning tube. The X-ray diffraction patterns were recorded at room temperature on a Philips PW1100 four-circle diffractometer by using Mo–Kα radiation. Crystal data for $Ph_2SnCl(L)$ (L = TNEE or MP) are listed in

Table 2. The crystal structures were solved using a three-dimensional Patterson–Fourier synthesis. A full-matrix least-squares refinement on F was computed and the function $\Sigma w[|F_0|-|F_c|]^2$ was minimized. The SHELX76 program[12] and the usual scattering factors included therein were used. Lorentz and polarization corrections, but not absorption corrections, were applied. The non-hydrogen atoms were refined anisotropically; the hydrogen atoms were located from a difference Fourier map, but not refined. Mössbauer spectra were recorded at 80.0 K in a Harwell cryostat; the $Ca^{119}SnO_3$ source (NEN) was at room temperature and was moved at constant acceleration with a triangular waveform. Suitable computer programs were employed in the procedure of fitting the experimental points to Lorentzian lineshapes.

RESULTS AND DISCUSSION

The $Ph_2SnCl(L)$ complexes (Table 1) separated as well-shaped white microcrystals from ethanol solutions of Ph_2SnCl_2 and ligand, whereas Ph_3SnCl did not react under the same conditions. For this reason the $Ph_3Sn(L)$ complexes were obtained by reaction of Ph_3SnOH and ligand in ethanol. The reaction of Ph_2SnCl_2 with 2-mercaptopyridine (HMP; molar ratios from 1:1 to 1:2) in ethanol yielded, as a first product, the yellow $Ph_2SnCl_2(HMP)_2$ adduct, whereas the white $Ph_2SnCl(MP)$ complex separated out by slow evaporation of the mother solution.

X-ray results

The atomic parameters for $Ph_2SnCl(TNEE)$ are reported in Table 3 and bond distances and angles in Tables 4 and 5 respectively. The coordination geometry around the tin centre in $Ph_2SnCl(TNEE)$, shown in Fig. 1, is a distorted trigonal bipyramid in which the two phenyl carbon atoms together with the sulphur of the bidentate TNEE ion form the equatorial plane, while the chlorine and the nitrogen atom of the ligand occupy the axial positions. The deviations from ideal geometry are mainly accountable to the small bite of the bidentate ligand which imposes a S(1)–Sn–N(1) bond angle of 63.7(1)°. As a consequence, the angle formed by the two apical atoms decreases from the theoretical 180° to 155.0(2)°. The angles formed by the equatorial ligands are slightly lower than the expected 120°, having an

Table 2 Crystal data for $Ph_2SnCl(TNEE)$ (**1**) and $Ph_2SnCl(MP)$ (**2**)

Parameter	1	2
Formula	$SnC_{20}H_{18}NO_2SCl$	$SnC_{17}H_{14}NSCl$
Mol. wt	490.58	418.51
$F(000)$	488	1648
Crystal dimensions (mm^3)	$0.4\times0.4\times0.6$	$0.2\times0.3\times0.3$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	C_2/c
a (Å)	9.039 (1)	16.397 (2)
b (Å)	13.637 (2)	13.493 (2)
c (Å)	8.852 (1)	17.004 (2)
α (deg)	105.50 (0)	—
β (deg)	90.8 (2)	116.6(2)
γ (deg)	82.40 (0)	—
V (Å^3)	1041.96 (24)	3363.85 (5.93)
Z	2	8
D_c (g cm^{-3})	1.56	1.65
μ (cm^{-1})	14.7	16.5
2θ range (deg)	4–56	4–56
No. of unique reflections	5024	4048
No. of reflections observed $[F>3\sigma(F)]$	4081	2093
R	0.043	0.037
R_w	0.045	0.040
w	$1.0/[\sigma^2(F)+0.008434F^2]$	$1.0/[\sigma^2(F)+0.009473F^2]$

Table 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^4$) defined as one-third of the trace of the orthogonalized U_{ij} tensor for $Ph_2SnCl(TNEE)$

Atom	*x*	*y*	*z*	U_{ij}
Sn	3480.4 (3)	2283.9 (2)	4246.9 (3)	437 (1)
Cl	4648 (1)	3529.2 (9)	6188 (1)	688 (4)
S (1)	5675 (1)	1000.2 (8)	4053 (1)	562 (4)
O (1)	874 (5)	−1132 (4)	−1093 (7)	127 (2)
O (2)	2718 (4)	−2404 (3)	−1565 (4)	72 (1)
N (1)	3352 (3)	594 (2)	2367 (4)	47 (1)
C (1)	4735 (4)	184 (3)	2634 (4)	47 (1)
C (2)	5323 (5)	−810 (3)	1815 (5)	57 (2)
C (3)	4481 (5)	−1375 (3)	697 (5)	57 (1)
C (4)	3037 (4)	−950 (3)	411 (5)	51 (1)
C (5)	2522 (4)	34 (3)	1277 (5)	51 (1)
C (6)	2079 (5)	−1491 (3)	−809 (6)	64 (2)
C (7)	1927 (7)	−2990 (4)	−2888 (7)	87 (2)
C (8)	180 (1)	−3972 (6)	−271 (2)	150 (5)
C (9)	1538 (4)	2214 (3)	5506 (4)	48 (1)
C (10)	1161 (6)	1310 (4)	5743 (6)	67 (2)
C (11)	−202 (8)	1340 (6)	6539 (8)	94 (3)
C (12)	−1142 (6)	2248 (6)	7031 (7)	91 (3)
C (13)	−761 (6)	3131 (5)	6814 (6)	80 (2)
C (14)	568 (6)	3126 (4)	6074 (5)	64 (2)
C (15)	3106 (4)	3056 (3)	2465 (4)	46 (1)
C (16)	2160 (5)	2699 (3)	1257 (5)	59 (2)
C (17)	1940 (6)	3168 (4)	51 (6)	72 (2)
C (18)	2663 (8)	4005 (5)	67 (6)	81 (2)

average value 118.3°, indicating that the tin atom is slightly outside the plane (0.29 Å). The other angles are close to the values expected for compounds exhibiting a trigonal bipyramidal structure. The 2-mercaptopyridine ring presents bond angles and distances that are typical for an aromatic system, indicating electron delocalization over the whole ring. The structure of $Ph_2SnCl(TNEE)$ is very similar to that of $Ph_2SnCl(MP)$,[3] the S–Sn–N bond angle being 64.8(1)°. All the other parameters are very close to each other, indicating that the COOEt group in the 2-mercaptopyridine ring does not influence the coordination around the tin atom as no O–Sn contact distances shorter than 2.5 Å have been found.

Table 4 Bond distances (Å) for $Ph_2SnCl(TNEE)$

Atoms	Distance	Atoms	Distance
Sn–Cl	2.411 (3)	Sn–S(1)	2.441 (1)
Sn–N(1)	2.472 (3)	Sn–C(9)	2.119 (5)
Sn–C(15)	2.118 (4)	S(1)–C(1)	1.735 (4)
C(1)–C(2)	1.393 (6)	C(2)–C(3)	1.370 (6)
C(3)–C(4)	1.405 (6)	C(4)–C(5)	1.379 (5)
N(1)–C(5)	1.347 (5)	N(1)–C(1)	1.345 (5)
C(4)–C(6)	1.475 (6)	O(1)–C(6)	1.186 (6)
O(2)–C(6)	1.306 (5)	O(2)–C(7)	1.466 (7)
C(7)–C(8)	1.41 (1)	C(9)–C(10)	1.389 (7)
C(10)–C(11)	1.42 (1)	C(11)–C(12)	1.37 (1)
C(12)–C(13)	1.36 (1)	C(13)–C(14)	1.374 (8)
C(9)–C(14)	1.400 (6)	C(15)–C(16)	1.385 (6)
C(16)–C(17)	1.383 (8)	C(17)–C(18)	1.386 (9)
C(18)–C(19)	1.356 (9)	C(19)–C(20)	1.386 (8)
C(15)–C(20)	1.397 (6)		

The cell parameters of $Ph_2SnCl(MP)$ were determined and correlated with those reported in the literature.[3] The cell parameters together with the crystal system and the space group of the two samples gave different results and this fact prompted us to determine fully the crystal structure. The atomic parameters of our sample are reported in Table 6, while only the bond distances that are different by more than 3σ from the literature values are given in Table 7. A comparison between the torsion angles involving the tin centres of the two structures is reported in Table 8. The crystal structure is shown in Fig. 2. The two structures are nearly identical to each other; the main differences are found in the angles that are slightly smaller. The existence of these two compounds may be due to the preparative methods in different solvents.

NMR results

The proton NMR spectra of ligands and complexes in various deuterated solvents are reported in Table 9. Signal assignments for ring protons are based on coupling constant values, according to literature data for variously substituted mercaptopyridines.[13–15] In $CDCl_3$ the ligands show the signal of the CH proton near nitrogen at *ca* 8.2 ppm, well downfield with respect to the other ring proton resonances at *ca* 7.81 (H_4) and 7.5 ppm (H_3). The presence of a broad NH signal at about 13.6 ppm suggests that this class of molecules exists essentially in the thione form,[16] the ionizable proton being bound to nitrogen. An equilibrium situation between thione and thiol forms can be excluded on the basis of the proton NMR spectra, which do not contain any signal due to the SH proton in the 4–2 ppm region. As shown in Table 9 for HTNIPE, signal values in deuterated acetone are very close to those observed in $CDCl_3$, except for the NH resonance, about 1.1 ppm upfield, whereas in deuterated dimethyl sulphoxide all ring proton resonances are shifted upfield in the order of 0.2 ppm.

Table 5 Bond angles (deg) for $Ph_2SnCl(TNEE)$

Atoms	Angle	Atoms	Angle
C(9)–Sn–C(15)	114.9 (2)	N(1)–Sn–C(15)	92.1 (1)
S(1)–Sn–C(15)	119.4 (1)	S(1)–Sn–C(9)	120.7 (1)
Cl–Sn–C(15)	100.7 (1)	Cl–Sn–C(9)	100.6 (1)
Cl–Sn–S (1)	91.33 (9)	N(1)–Sn–C(9)	93.2 (2)
S(1)–Sn–N(1)	63.7 (1)	Cl–Sn–N(1)	155.0 (2)
Sn–S(1)–C(1)	87.0 (2)	Sn–N(1)–C(1)	95.3 (3)
Sn–N(1)–C(5)	145.4 (4)	S(1)–C(1)–N(1)	114.0 (3)
C(1)–N(1)–C(5)	119.3 (4)	S(1)–C(1)–C(2)	124.6 (5)
C(3)–C(4)–C(6)	123.1 (5)	N(1)–C(5)–C(4)	122.5 (6)
C(1)–C(2)–C(3)	119.2 (6)	N(1)–C(1)–C(2)	121.4 (5)
C(2)–C(3)–C(4)	119.7 (4)	C(3)–C(4)–C(5)	118.0 (5)
C(5)–C(4)–C(6)	118.9 (5)	O(2)–C(6)–C(4)	112.5 (5)
O(1)–C(6)–C(4)	123.9 (6)	O(2)–C(7)–C(8)	110.4 (7)
Sn–C(9)–C(14)	117.5 (4)	C(10)–C(9)–C(14)	118.9 (6)
O(1)–C(6)–O(2)	123.6 (7)	C(6)–O(2)–C(7)	117.8 (6)
C(9)–C(10)–C(11)	118.9 (6)	C(10)–C(11)–C(12)	120.1 (8)
C(11)–C(12)–C(13)	120.8 (8)	C(12)–C(13)–C(14)	120.2 (7)
C(9)–C(14)–C(13)	121.0 (6)	Sn–C(9)–C(10)	123.5 (4)
Sn–C(15)–C(20)	121.6 (3)	Sn–C(15)–C(16)	119.4 (3)
C(16)–C(17)–C(18)	119.4 (5)	C(15)–C(16)–C(17)	120.4 (6)
C(16)–C(15)–C(20)	119.0 (4)	C(17)–C(18)–C(19)	120.9 (6)
C(18)–C(19)–C(20)	120.2 (6)	C(15)–C(20)–C(19)	120.0 (5)

Owing to ligand deprotonation, the spectra of the complexes do not contain the NH signal, ring proton resonances being shifted downfield with respect to those of the corresponding free ligands. The effect is particularly evident for the H_6 signal (about 0.4 ppm downfield), whereas the H_3 resonance is generally obscured by the phenyl proton multiplet in the 7.3–7.5 ppm range. The $Ph_3Sn(TNIPE)$ spectra in the solvents examined do not change with time, whereas the behaviour of the $Ph_2SnCl(L)$ species clearly depends on the solvent. As an example, $Ph_2SnCl(TNEE)$ crystals used for the structural work show in deuterated chloroform one signal for each proton group, the

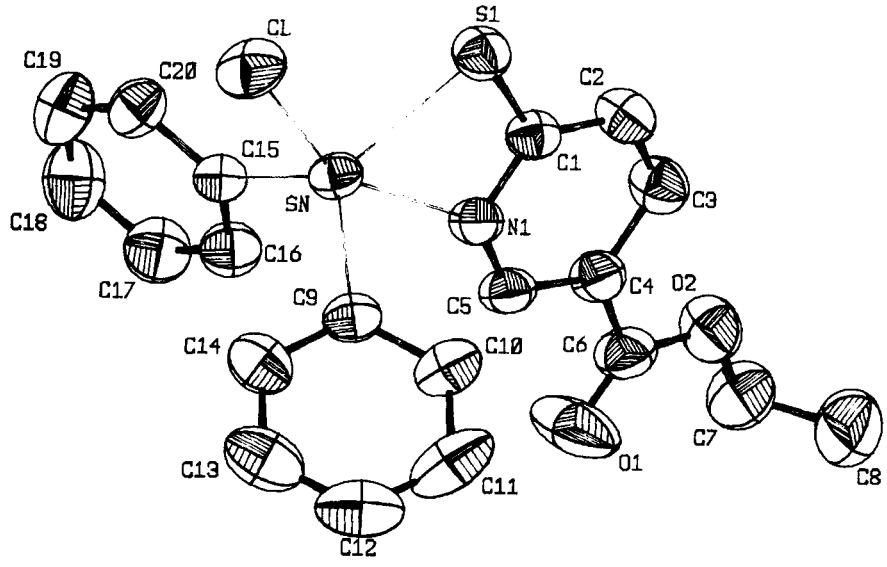


Figure 1 Molecular structure of $Ph_2SnCl(TNEE)$ with the atom numbering scheme.

Table 6 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^4$) defined as one-third of the trace of the orthogonalized U_{ij} tensor for $Ph_2SnCl(MP)$

Atom	x	y	z	U_{ij}
Sn	2206.7 (3)	326.3 (3)	1285.7 (3)	457 (2)
Cl	2936 (1)	−1222 (1)	1171 (1)	82 (1)
S(1)	888 (1)	−599 (1)	1205 (1)	546 (7)
N	1039 (3)	1322 (4)	1380 (3)	48 (2)
C(1)	774 (4)	2263 (5)	1444 (4)	57 (3)
C(2)	−46 (4)	2468 (5)	1424 (4)	60 (3)
C(3)	−632 (4)	1685 (6)	1341 (4)	66 (3)
C(4)	−373 (4)	737 (5)	1291 (4)	58 (3)
C(5)	471 (4)	569 (4)	1296 (3)	45 (2)
C(6)	2055 (4)	987 (4)	86 (4)	48 (2)
C(7)	2557 (4)	618 (5)	−330 (5)	61 (3)
C(8)	2422 (7)	1007 (6)	−1136 (6)	85 (5)
C(9)	1771 (7)	1731 (6)	−1534 (5)	82 (4)
C(10)	1283 (6)	2100 (5)	−1141 (4)	71 (4)
C(11)	1408 (5)	1726 (5)	−334 (4)	55 (3)
C(12)	3224 (4)	734 (5)	2578 (4)	47 (2)
C(13)	3034 (5)	1333 (5)	3115 (5)	63 (3)
C(14)	3717 (6)	1609 (6)	3967 (5)	75 (4)
C(15)	4558 (6)	1178 (7)	4268 (6)	83 (4)
C(16)	4742 (6)	554 (8)	3735 (6)	89 (4)
C(17)	4077 (5)	320 (6)	2899 (5)	67 (4)

spectrum being unchanged within one week. In deuterated acetone the same complex presents initially one set of signals, whereas after one day additional weak peaks are observed, being particularly evident for the ester proton groups. The effect is more marked in dimethyl sulphoxide, the spectrum recorded after one day showing in particular a weak H_6 signal at 8.94 ppm, well downfield with respect to the corresponding resonance in freshly prepared solutions (8.57 ppm). Such behaviour could be due to the interaction of the

Table 7 Bond distances (Å) and angles (deg) for $Ph_2SnCl(MP)$ that deviate by more than 3σ from those reported in Ref. 3

Atoms	Distance	Atoms	Distance
Sn–Cl	2.458 (2)	Sn–S	2.447 (2)
Sn–C(12)	2.152 (7)		
Atoms	**Angle**	**Atoms**	**Angle**
C(6)–Sn–C(12)	125.0 (3)	N–Sn–C(12)	93.8 (2)
N–Sn–C(6)	94.3 (2)	S–Sn–C(12)	116.7 (2)
S–Sn–C(6)	115.9 (2)	Cl–Sn–C(12)	96.7 (2)
Cl–Sn–S	90.65 (9)	Cl–Sn–C(6)	97.6 (2)
Sn–C(6)–C(11)	121.5 (6)	Sn–C(6)–C(7)	119.5 (5)
Sn–S–C(5)	84.6 (2)		

Table 8 Relevant torsion angles (deg) for $Ph_2SnCl(MP)$ calculated from the present data (a) and from the data reported in Ref. 3(b)

Atoms	(a)	(b)
C(6)–Sn–N–C(5)	115.6 (5)	115.6 (1)
C(12)–Sn–N–C(5)	−118.8 (5)	−122.0 (1)
Cl–Sn–N–C(5)	−3.5 (9)	5.3 (1)
C(12)–Sn–C(6)–C(7)	87.0 (7)	69.2 (1)
Cl–Sn–C(6)–C(7)	−16.7 (7)	−33.8 (1)
Cl–Sn–C(12)–C(13)	−158.1 (6)	−169.6 (1)
C(6)–Sn–C(12)–C(17)	−84.5 (7)	−92.5 (1)
S–Sn–C(12)–C(17)	113.7 (6)	105.5 (1)
N–Sn–C(12)–C(17)	177.6 (6)	170.7 (1)
S–Sn–C(6)–C(7)	−111.1 (6)	−128.9 (1)
N–Sn–C(6)–C(7)	−175.4 (6)	168.6 (1)
N–Sn–S–C(5)	0.8 (3)	3.6 (1)
Sn–C(12)–C(13)–C(14)	178.3 (7)	−177.3 (1)
Sn–C(6)–C(7)–C(8)	176.3 (7)	176.9 (1)

O-donor solvent with the tin coordination sphere forming fairly stable adducts. In order to clarify the solvent effect, dimethyl sulphoxide was added to a saturated solution of $Ph_2SnCl(TNEE)$ in deuterated chloroform. Well-shaped white crystals separated overnight, which were filtered and washed with n-pentane. Elemental analysis data suggest the formation of the $Ph_2Sn(TNEE)_2$ species, the NMR spectrum in deuterated chloroform being identical to that of $Ph_2Sn(TNEE)_2$ samples prepared by reaction of Ph_2SnCl_2, H(TNEE) and triethylamine in ethanol (molar ratio 1:2:2).

The proton NMR spectrum of 2-mercaptopyridine in acetone agrees with the thione tautomeric form, the NH proton signal being at 12.8 ppm and the ring CH resonances at 7.72 (H_6), 6.81 (H_2), and in the 7.38–7.42 ppm range (H_3 and H_4). The spectrum of $Ph_2SnCl_2(HMP)_2$ in deuterated acetone contains all ring resonances shifted downfield with respect to free HMP [8.01 (H_6), 7.02 (H_2), and in the 7.40–7.52 ppm range (H_3 and H_4)] the NH resonance not being observed. Conversely, the spectrum in deuterated dimethyl sulphoxide shows all free-ligand signals [13.4 (NH), 7.89 (H_6), 6.73 (H_2) and *ca* 7.32 ppm (H_3 and H_4)], due to solvent interaction with parallel HMP release from the tin coordination sphere.

The ^{13}C NMR spectra of ligands in deuterated chloroform (Table 10) contain the CS carbon signal at about 180 ppm, the carboxylic carbon signal being observed at about 163 ppm. The CH (near nitrogen) resonance is at about 140 ppm,

whereas the ring carbon bound to carboxyl gives rise to the signal at about 117 ppm.

The Ph_3Sn(TNIPE) spectra in the solvents examined show a marked upfield shift (about 14 ppm) of the CS signal, the carboxyl carbon being unaffected by coordination, as for the OR carbons. As regards ring CH groups, the C_4 signal is unchanged, whereas the carbon (near nitrogen) resonance undergoes a downfield shift of about 10 ppm. The opposite shifts of the C_3 (upfield) and C_5 (downfield) signals cause closeness and, in some cases, superimposition of the corresponding resonances, whose assignments are therefore given tentatively. The $Ph_2SnCl(L)$ spectra in acetone contain, along with the main signal set, a series of weak resonances whose intensity increases with time. It was impossible to measure the spectra in dimethyl sulphoxide. In fact samples of those products dissolved at first in this solvent with subsequent slow separation of white crystals of the corresponding $Ph_2Sn(L)_2$ complex. The resulting dilute solution shows broad weak signals even after prolonged accumulation. The $Ph_2Sn(TNEE)_2$ spectrum in deuterated chloroform is very close to that of Ph_2SnCl(TNEE) apart for a downfield shift (about 6 ppm) of the C_4 carbon signal.

Infrared results

Some significant absorptions in the infrared spectra of ligands and complexes are reported in Table 11. The strong absorption in the 1700–1720 cm^{-1} interval is due to the asymmetric stretch of the carboxylato group, whereas the bands in the 1560–1620 cm^{-1} range originate from strongly mixed ν(CN), δ(CH) and δ(NH) modes.[17,18] The medium-intensity absorption at about 1620 cm^{-1}, which is absent in the complexes, is probably due to NH vibrations, ring vibrations giving rise to the sharp bands in the 1425–1480 cm^{-1} range. All triphenyltin complexes show in the far-IR region a strong ligand absorption at about 260 cm^{-1}, which shifts to higher energy (275 cm^{-1}) in the diphenyltin complexes. The $Ph_2SnCl(L)$ spectra should contain one Sn–Cl absorption, as observed for the maltolato (Ma) analogues Ph_2SnCl(Ma) (278 cm^{-1}) and Me_2SnCl(Ma) (281 cm^{-1}).[19] Accordingly, the ν(Sn–Cl) band is found at 295 cm^{-1} in

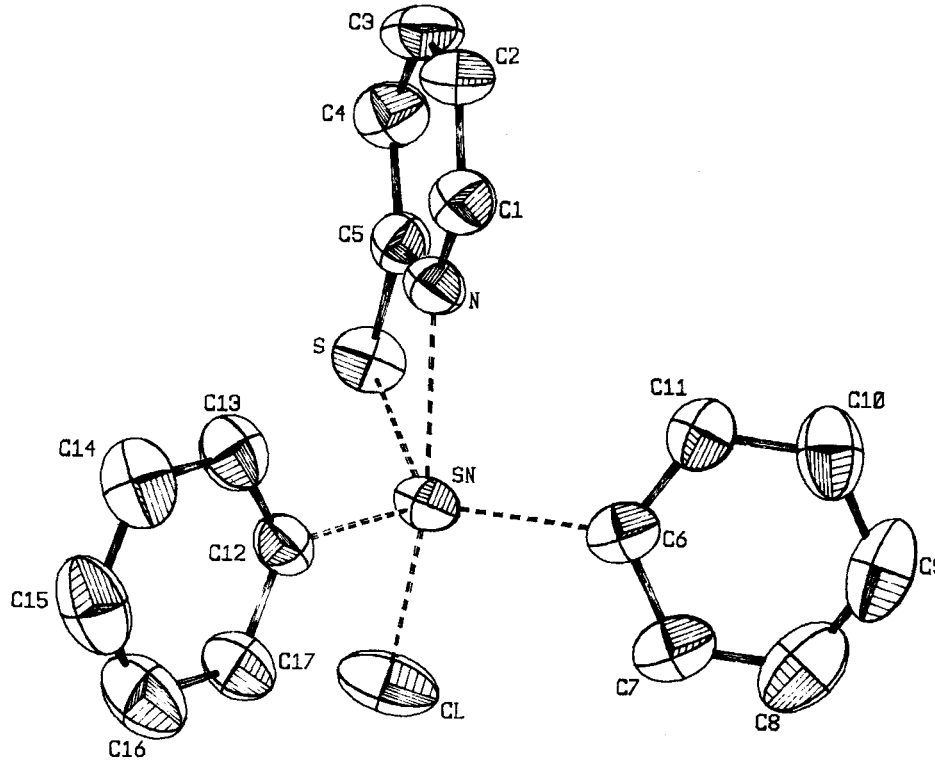


Figure 2 Molecular structure of Ph_2SnCl(MP) with the atom numbering scheme.

Table 9 ^{1}H NMR spectra for 2-mercaptopyridine-5-alkyl esters and related organotin(IV) complexes ($T = 25$ °C; δ, ppm)

Compound	Solvent	Ligand					Ph_nSn
		NH[a]	H_6	H_4	H_3	CO_2R	
HTNIPE[b]	$CDCl_3$	13.6	8.20	7.86	7.52	5.15(CH), 1.27(CH_3)	
HTNIPE	$(CD_3)_2CO$	12.5	8.22	7.72	7.35	5.17(CH), 1.30(CH_3)	
HTNIPE	$(CD_3)_2SO$	13.8	8.03	7.69	7.31	5.07(CH), 1.27(CH_3)	
HTNEE[c]	$CDCl_3$	13.7	8.17	7.81	7.48	4.30(CH_2), 1.31(CH_3)	
HTNME[d]	$CDCl_3$	n.o.	8.15	7.79	7.47	3.85(CH_3)	
HMP[e]	$(CD_3)_2CO$	12.8	7.72	7.42–7.38			
Ph_3Sn(TNIPE)	$CDCl_3$		8.63	7.99	f	5.20(CH), 1.32(CH_3)	7.73–7.63, 7.45–7.30
Ph_3Sn(TNIPE)	$(CD_3)_2CO$		8.66	8.06	7.56	5.51(CH), 1.29(CH_3)	7.78–7.64, 7.48–7.35
Ph_3Sn(TNIPE)	$(CD_3)_2SO$		8.51	7.90	7.48	5.06(CH), 1.26(CH_3)	7.78–7.62, 7.45–7.30
Ph_2SnCl(TNIPE)	$CDCl_3$		8.68	8.17	f	5.24(CH), 1.34(CH_3)	7.90–7.70, 7.50–7.33
Ph_2SnCl(TNIPE)	$(CD_3)_2CO$		8.93	8.31	7.65	5.24(CH), 1.34(CH_3)	7.95–7.80, 7.57–7.40
Ph_3Sn(TNEE)	$CDCl_3$		8.66	7.98	f	4.34(CH_2), 1.36(CH_3)	7.75–7.60, 7.45–7.30
Ph_2Sn(TNEE)$_2$[g]	$CDCl_3$		8.58	7.98	f	4.30(CH_2), 1.33(CH_3)	7.85–7.77, 7.50–7.30
Ph_2SnCl(TNEE)	$CDCl_3$		8.69	8.19	f	4.39(CH_2), 1.38(CH_3)	7.85–7.75, 7.50–7.30
Ph_2SnCl(TNEE)[h]	$(CD_3)_2CO$		8.96	8.29	7.61	4.33(CH_2), 1.32(CH_3)	7.96–7.82, 7.55–7.40
Ph_2SnCl(TNEE)[i]	$(CD_3)_2SO$		8.57	8.23	7.54	4.27(CH_2), 1.27(CH_3)	7.95–7.80, 7.51–7.25
Ph_3Sn(TNME)	$CDCl_3$		8.67	7.99	f	3.88(CH_3)	7.78–7.60, 7.46–7.35
Ph_2SnCl(TNME)[l]	$CDCl_3$		8.70	8.17	f	3.91(CH_3)	7.85–7.70, 7.50–7.30
Ph_2SnCl_2(HMP)$_2$[e]	$(CD_3)_2CO$	n.o.	8.01	7.52–7.40			8.1–7.3
Ph_2SnCl_2(HMP)$_2$[e]	$(CD_3)_2SO$	13.4	7.89	e	e		8.1–7.2
Ph_2SnCl(MP)$_2$[e]	$(CD_3)_2SO$		8.44	e	e		8.1–7.3

[a] Broad signal whose position depends on concentration; n.o., not observed.
[b] $J_{H_3\text{-}H_4}$, 9.0 Hz; $J_{H_3\text{-}H_6}$, 0.7 Hz; $J_{H_4\text{-}H_6}$, 2.1 Hz.
[c] $J_{H_3\text{-}H_4}$, 9.1 Hz; $J_{H_3\ H_6}$, 0.8 Hz; $J_{H_4\text{-}H_6}$, 2.1 Hz.
[d] The NH signal is hardly detectable and falls in the 13–14 ppm range; $J_{H_3\text{-}H_4}$, 9.1 Hz; $J_{H_3\text{-}H_6}$, 0.5 Hz; $J_{H_4\text{-}H_6}$, 1.7 Hz.
[e] The H_5 proton signal is observed at 6.81 ppm (HMP), 7.02 ppm [Ph_2SnCl_2(HMP)$_2$ in $(CD_3)_2CO$], 6.73 ppm [Ph_2SnCl_2(HMP)$_2$ in $(CD_3)_2SO$] and 6.98 ppm [Ph_2SnCl(MP) in $(CD_3)_2SO$].
[f] Obscured by the phenyl proton signals.
[g] The spectrum is identical to that of a Ph_2SnCl(TNEE) sample recrystallized from $CDCl_3$/dimethyl sulphoxide.
[h] The spectrum registered one day after dissolution contains weak signals at 4.34 and 1.34 ppm.
[i] Weak signals at 8.94, 4.33 and 1.30 ppm are also present, whose intensity increases overnight; saturated solution.
[l] The spectrum contains weak signals at 3.95 and 9.18 ppm.

Ph_2SnCl(TNIPE), whereas the corresponding absorption in Ph_2SnCl(TNEE) is observed at 305 cm^{-1}. The Ph_2SnCl(TNME) spectrum contains, along with the strong band of the coordinated ligand at 272 cm^{-1}, two medium-intensity absorptions at 306 and 296 cm^{-1}. The proton NMR spectrum of the same sample in $CDCl_3$ shows one signal for each proton group of the ligand molecule, supporting the absence of Ph_2Sn(TNME)$_2$ as a side product, which could be the origin of the band at 296 cm^{-1}. Owing to this ambiguity, the Sn–Cl band has not been assigned.

The IR spectrum of Ph_2SnCl(MP) is very close to that of Ref. 3, the ν(Sn–Cl) absorption appearing as a shoulder (about 290 cm^{-1}) of a strong ligand band (274 cm^{-1}). Along with the strong absorption at 1589 cm^{-1}, the Ph_2SnCl_2(HMP)$_2$ spectrum contains a medium band at 1610 cm^{-1}, present in free HMP at 1614 cm^{-1} and assigned to δ(NH). As expected for a distorted octahedral geometry, this compound shows two Sn–Cl absorptions at 328 and 287 cm^{-1}.

Mössbauer results

The Mössbauer effect parameters for all the prepared compounds, reported in Table 12, are typical for di- and tri-aryltin(IV) derivatives. The spectra present a single quadrupole split doublet which sometimes is very asymmetric and good fits could in general be obtained only if both the linewidth and the area of the two absorption peaks were allowed to vary independently.

The diphenyltin chloride derivatives with

TNME, TNEE, TNIPE and MP present isomer shift values that decrease on increasing the steric hindrance of the ester group, probably as a consequence of small increases of the tin-to-ligand bond distances. However, the quadrupole splitting remains nearly constant. The similarity of all the parameters is indicative of structures which are very similar to each other. Therefore, on the basis of the crystal structure obtained for $Ph_2SnCl(TNEE)$, a trigonal bipyramidal structure is proposed for all three complexes. The calculation of ΔE_Q by means of the point charge model[20] using the p.q.s. values previously published[3] supports this hypothesis, even if the results must be interpreted with great care due to deviations from the ideal structure imposed by the bidentate ligand.

The Mössbauer spectrum of $Ph_2Sn(TNEE)_2$ presents a δ value slightly higher than that found for $Ph_2SnCl(TNEE)$ as a consequence of the substitution of a chlorine with a TNEE group, with a possible increase in the tin coordination number. The ΔE_Q value is indicative either of pentacoordination or of a very distorted octahedral geometry. On the basis of the crystal structures already reported for similar compounds,[4,5] a hexacoordinated environment around the tin atom with two chelating TNEE ligands may be proposed.

The three triphenyltin derivatives present virtually identical Mössbauer spectra, so they are presumed to have the same coordination around the tin atom. The substitution of a chlorine atom with a phenyl group causes an increase in the isomer shift due to an increase in the *s*-electron density on the tin nucleus, and also a large decrease in the quadrupole splitting.

The diphenyltin dichloride complex containing two undissociated mercaptopyridines is clearly octahedral with two apical phenyl groups and two chlorine and two sulphur atoms in the equatorial plane. By means of point charge calculations, only a structure with sulphur-bonded ligands in *cis* positions can be excluded, because the calculated quadrupole splitting values for the sulphur-

Table 10 ^{13}C NMR spectra for 2-mercaptopyridine-5-alkyl esters and related organotin(IV) complexes (in $CDCl_3$; $T = 25$ °C; δ, ppm)

	Ligand							Ph_nSn			
Compound	C_2	C_3[a]	C_4	C_5[a]	C_6	C_7	OR	C_1	C_2	C_3	C_4
H(TNIPE)	180.6	133.2	136.4	117.9	139.6	162.7	69.5 (CH) 21.8 (CH_3)				
H(TNEE)	180.7	133.4	136.3	117.5	139.9	163.3	61.7 (CH_2) 14.2 (CH_3)				
H(TNME)	181.3	133.8	136.0	117.0	139.7	163.8	52.6 (CH_3)				
$Ph_3Sn(TNIPE)$	166.2	122.5	137.0	122.0	149.2	164.6	68.7 (CH) 21.8 (CH_3)	140.1	136.5	128.6	129.3
$Ph_3Sn(TNIPE)$[b]	166.7	123.8	136.8	121.3	148.6	163.9	68.4 (CH) 21.5 (CH_3)	141.2	136.1	128.6	129.1
$Ph_3Sn(TNIPE)$[c]	166.7	124.0	138.3	123.3	149.8	164.8	69.4 (CH) 21.9 (CH_3)	140.9	137.2	129.6	130.3
$Ph_2SnCl(TNIPE)$	169.2	123.1	139.3	123.1	147.9	163.7	69.5 (CH) 21.8 (CH_3)	140.4	135.2	129.1	130.5
$Ph_3Sn(TNEE)$	166.5	123.0	136.5	121.6	149.2	165.2	61.2 (CH_2) 14.2 (CH_3)	140.1	136.5	128.6	129.3
$Ph_2Sn(TNEE)_2$	169.1	123.5	145.4	121.3	146.9	164.8	61.2(CH_2) 14.2 (CH_3)	137.9	134.4	128.6	129.2
$Ph_2SnCl(TNEE)$	169.2	123.1	139.3	122.7	147.9	164.1	61.7 (CH_2) 14.2 (CH_3)	140.4	135.1	129.1	130.5
$Ph_2SnCl(TNEE)$[c,d]	168.9	124.2	141.3	124.1	149.1	164.5	62.2 (CH_2) 14.4 (CH_3)	140.8	136.0	130.0	131.4
$Ph_3Sn(TNME)$	166.6	123.0	137.0	121.3	149.2	165.5	52.0 (CH_3)	140.1	136.5	128.6	129.3

[a] The C_3 and C_5 carbon signals are very close in complexes and in some cases they overlap.
[b] In DMSO-d_6.
[c] In acetone-d_6.
[d] Weak signals are observed at 61.9, 120.0, 138.0 and 151.3 ppm (see text).

Table 11 Selected IR data for ligands and complexes (cm^{-1})[a]

	ν(C=O)	ν(CN) + δ(CH) + δ(NH)	Ring	Far-IR
HTNIPE	1715sh, 1704s	1620m, 1586m	1469w, 1458w, 1432m	337w, 264s
HTNEE	1716s	1624m, 1579m, 1548m	1467w, 1453w, 1428w	337w, 294w, 279w, 266w
HTNME	1720w, 1690s	1610m, 1565m	1444m, 1430m	323w, 292w, 273w
Ph_3Sn(TNIPE)	1707s	1586s	1479w, 1454m, 1429m	288m, 270m, 263s
Ph_2SnCl(TNIPE)	1701s	1591s	1479w, 1454m, 1429m	305sh, 295s, 274m, 258m
Ph_3Sn(TNEE)	1710s	1586s	1478w, 1454w, 1429m	300w, 270sh, 264s
$Ph_2Sn(TNEE)_2$	1713s, 1700m	1584s	1456s, 1432w	305sh, 292m, 276s
Ph_2SnCl(TNEE)[b]	1713s	1592s	1480w, 1453m, 1431m	305s, 291sh, 273s
Ph_3Sn(TNME)	1722s	1586s	1478w, 1462w, 1429m	315w, 271m, 257s
Ph_2SnCl(TNME)[c]	1715s	1592s, 1576sh	1461w, 1456m, 1436w	306m, 296ms, 272s, 254sh
$Ph_2SnCl_2(HMP)_2$		1610m, 1589vs	1514m, 1477w, 1443w, 1418s	328s, 287ms, 279sh
Ph_2SnCl(MP)		1586, 1548w	1449m, 1430m, 1418s	290sh, 274s

[a] ν(Sn–Cl) are underlined.
[b] Crystals used for the structural work.
[c] See text.

bonded *trans* isomer (3.30 mm s^{-1}) and for nitrogen-bonded *cis* (3.60 mm s^{-1}) and *trans* isomers (3.61 mm s^{-1}) are all acceptable.

The spectral parameters for Ph_2SnCl(MP), whose spectrum has been collected from the crystals used for the determination of the structure, present a different isomer shift and identical quadrupole splitting with respect to the literature data.[3] As the main differences between the two structures are due to the bond angles, variations in the ΔE_Q value were expected instead. This surprising result may be attributed to a rearrangement of the *p*-electrons with a consequent increase of the *s*-electron density at the tin nucleus because of the screening effect.

CONCLUSIONS

The reaction of mercaptopyridine derivatives with diphenyltin chloride and triphenyltin hydroxide could yield the species $Ph_3Sn(L)$, $Ph_2Sn(L)_2$ or $Ph_2SnCl(L)$. The species containing only the anionic ligand are stable in most of the solvents in which they dissolve, whereas the $Ph_2SnCl(L)$ complexes interact with strong oxygen-donors, such as dimethyl sulphoxide, yielding the corresponding $Ph_2Sn(L)_2$ species and Ph_2SnCl_2. Along with Ph_2SnCl(MP), mercaptopyridine forms the $Ph_2SnCl_2(HMP)_2$ complex, which releases the ligand molecules in dimethyl sulphoxide. Owing to the versatility of this class

Table 12 Mössbauer effect spectral data at 80.0 K

Compound	δ[a] (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ (mm s^{-1})	Γ_2/Γ_1[b]	A_2/A_1[c]
Ph_3Sn(TNIPE)	1.39	1.60	0.94	0.93	0.92
Ph_2SnCl(TNIPE)	1.26	2.35	0.82	1.00	0.88
Ph_3Sn(TNEE)	1.39	1.67	0.98	0.92	1.00
$Ph_2Sn(TNEE)_2$	1.37	2.38	1.08	0.74	0.57
Ph_2SnCl(TNEE)	1.30	2.38	0.99	1.00	0.78
Ph_3Sn(TNME)	1.39	1.67	0.98	0.93	1.01
Ph_2SnCl(TNME)	1.34	2.36	0.89	0.96	0.70
$Ph_2SnCl_2(HMP)_2$	1.50	3.40	0.93	0.88	0.93
$Ph_2SnCl(MP)_2$	1.37	2.58	0.86	0.97	0.96

[a] Relative to room-temperature SnO_2.
[b] Linewidth ratio between the high- and low-velocity components.
[c] Area ratio between the high- and low-velocity components.

of ligands, it seems interesting to extend the study to inorganic tin complexes containing neutral or ionic mercaptopyridine derivatives. In this way it should be possible to obtain new information on the eventual role of the solvent in determining the reaction products and to look for possible correlations among solvents, the nature of donors and acceptors, and the structures of the products.

Acknowledgements M.D.C. gratefully acknowledges support from the Xunta de Galicia (Spain). L.S. thanks the Italian C.N.R. (C.T. 92 3 038 995) for financial support.

REFERENCES

1. A. J. Crowe, P. J. Smith and G. Atlassi, *Inorg. Chim. Acta* **93**, 179 (1984).
2. R. Barbieri, A. Silvestri, A. Barbieri and G. Ruisi, *Gazz. Chim. Ital.* **124**, 187 (1994).
3. R. Schmiedgen, F. Huber, H. Preut, G. Ruisi and R. Barbieri, *Appl. Organomet. Chem.* **8**, 397 (1994).
4. R. Schmiedgen, F. Huber and H. Preut, *Acta Crystallogr. Sect. C* **49**, 1735 (1993).
5. M. Bouâlam, J. Meunier-Piret, M. Biesemans, R. Willem and M. Gielen, *Inorg. Chim. Acta* **198**, 249 (1992).
6. M. V. Castaño, A. Macias, A. Castiñeiras, A. S. González, E. G. Martinez, J. S. Casas, J. Sordo, W. Hiller and E. E. Castellano, *J. Chem. Soc., Dalton Trans.* 1001 (1990).
7. S. Wen Ng, C. Wei, V. G. Kumar Das and T. C. W. Mak, *J. Org. Chem.* **326**, C61 (1987).
8. S. D'Ancora, G. Magnolfi, G. Guidetti, G. Toffoli, A. Lazzarini, M. Carrara, M. Magon, S. Luciani and T. Berti, *Chemioterapia* **V**, 219 (1986).
9. D. R. Grassetti, *Cancer Lett.* **31**, 187 (1986).
10. R. Leujeune, L. Thunus and C. L. Lapierre, *J. Pharm. Belg.* **35**, 12 (1980).
11. R. Leujeune and L. Thunus, *J. Pharm. Belg.* **35**, 98 (1980).
12. G. M. Sheldrick, SHELX76, *A Program for Crystal Structure Determination*, University of Cambridge, UK, 1976.
13. A. Schank, J. M. Dereppe and M. Van Meerssche, *Bull. Soc. Chim. Belg.* **92**, 199 (1983).
14. M. Gelbcke, R. Grimée, R. Leujeune, L. Thunus and J. V. Dejardin, *Bull. Soc. Chim. Belg.* **92**, 39 (1983).
15. M. Gelbcke, R. Grimée, R. Lejeune and L. Thunus, *Spectrochim. Acta* **41A**, 567 (1985).
16. S. Stoyanov, I. Petkov, L. Antonov and T. Stoyanova, *Can. J. Chem.* **68**, 1482 (1990).
17. E. Spinner, *J. Chem. Soc.* 1237 (1960).
18. D. N. Sathyanarayana and S. V. Kasmir Raja *Spectrochim. Acta* **41A**, 809 (1985).
19. D. Fregona, Z. Guo, G. Faraglia and S. Sitran, *J. Coord. Chem.* **28**, 73 (1993).
20. R. V. Parish, Structure and bonding in tin compounds. In: *Mössbauer Spectroscopy applied to Inorganic Chemistry*, Vol. 1, Long, G. J. (ed.), Plenum Press, New York, 1984.