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Mono-organotin(IV) and Tin(IV) Derivatives of 2-Mercaptopyridine and 2-Mercaptopyrimidine: X-ray Structures of Methyl-tris(2-pyridinethiolato)tin(IV) and Phenyl-tris(2-pyridinethiolato)tin(IV)·1.5$CHCl_3$

Friedo Huber,[1] Ralf Schmiedgen,[1] Markus Schürmann,[1] Renato Barbieri,[2]† Giuseppe Ruisi[2] and Arturo Silvestri[2]

[1] Fachbereich Chemie, Universität Dortmund, D-44221 Dortmund, Germany
[2] Università di Palermo, Dipartimento di Chimica Inorganica, Via Archirafi 26-28, I-90123 Palermo, Italy

Mono-organotin(IV) and tin(IV) derivatives of 2-mercaptopyridine (HSPy) and 2-mercaptopyrimidine (HSPym), $RSnL_3$ (R = Me, n-Bu, Ph; L = SPy, SPym; R = Bz = benzyl, *o*-ClBz, *o*-ClC_6H_4, *p*-ClC_6H_4, *o*-tolyl, *p*-tolyl; L = SPy), $RSnClL_2$ (R = Me, n-Bu, Ph; L = SPy, SPym), $RSnCl_2L$ (R = Me, n-Bu; L = SPy, SPym) and $SnCl_{4-n}L_n$ (L = SPy, SPym; $n = 2, 4$) were obtained from $RSnCl_3$ or $SnCl_4$ and NaL or by neutralization (R = Ph, *p*-tolyl; L = SPy, SPym). $RSnClL_2$ and $RSnCl_2L$ were better prepared by comproportionation of $RSnCl_3$ and $RSnL_3$.

$MeSn(SPy)_3$ and $PhSn(SPy)_3 \cdot 1.5CHCl_3$ crystals, as determined by single-crystal X-ray diffraction, are monoclinic. In the discrete monomeric $RSn(SPy)_3$ units, three bidentate SPy ligands together with R form a distorted pentagonal bipyramid around tin. One S and the C(R) atom are in the axial positions. Two S atoms and three N atoms form the pentagonal plane.

From ^{119}Sn Mössbauer and IR data, analogous structures are inferred for the other solid $RSnL_3$ compounds, except for R = Bz, *o*-ClBz, *o*-ClC_6H_4 and *o*-tolyl, in which tin would be hexacoordinated. In the compounds $RSnClL_2$ and $RSnCl_2L$, tin is at the center of an octahedron or a trigonal bipyramid, respectively. For $Sn(SPym)_4$ and $SnCl_2(SPym)_2$, the same type of octahedral structure as was previously found for $Sn(SPy)_4 \cdot HSPy$ and $SnCl_2(SPy)_2$ is proposed.

According to IR and ^{1}H, ^{13}C and ^{119}Sn NMR data, the solid-state molecular structures are retained in chloroform and dimethyl sulfoxide solution.

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INTRODUCTION

In the context of studies on the coordination of organotin(IV) moieties by thiol sulfur and heterocyclic nitrogen, diorganotin(IV) complexes of 2-mercaptopyridine (HSPy), $R_2Sn(SPy)_2$ and $R_2SnCl(SPy)$, have been recently synthesized and characterized in the solid state and in the solution phase.[1] The crystal and molecular structure of $Ph_2SnCl(SPy)$ was determined by X-ray crystallography,[1] contributing to the general understanding of the structural characteristics of organotin(IV) coordinated by bidentate ligands containing thiol sulfur and electronegative donor atoms.[1, 2] The structure and dynamics for representative terms of series of $Me_2Sn(IV)$, MeSn(IV) and Sn(IV) complexes with S,N donors, determined by ^{119}Sn Mössbauer spectroscopy, have been reported.[2]

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Continuing our work in the field, a series of complexes $RSnL_3$, $RSnClL_2$, $RSnCl_2L$, $SnCl_2L_2$ and SnL_4 (L = SPy and SPym; HSPym = 2-mercaptopyrimidine) have been prepared and characterized; the structures of $MeSn(SPy)_3$ and $PhSn(SPy)_3 \cdot 1.5CHCl_3$ were determined by X-ray diffractometry. The results are reported in the present paper.

In the context of these studies, it is worth mentioning the relevance of thiol-bound organotins to biological systems and molecules, considering the values of stability constants of Sn–S(thiol) bonds, which are even larger than the related hydrolysis constants;[3,4] as a consequence, thiolated species would be expected to occur in living organisms. Complexes R_nSn–SPy and –SPym in fact interact with deoxyribonucleic acid *in vitro*, provoking the condensation of DNA[5–8] analogous to findings concerning the systems R_nSnCl_{4-n}–DNA.[5–7,9]

EXPERIMENTAL

The mono-organotin halides were prepared according to procedures given in Refs. 10–12. PymS–SPym was synthesized according to Ref. 13; PyS–SPy was obtained analogously. HSPy and HSPym were products of Fluka Chemie AG; other reactants and solvents were commercial products and were purified and dried as usual.[14] All reactions were carried out in dry solvents under stirring in a dry nitrogen atmosphere.

The compounds **1**–**26**, listed in Table 1, were prepared according to the following methods, as specified in Table 1 for the individual compounds.

Method A

NaOMe (3 mmol) in MeOH (0.5 M solution, 6 ml) was added to 3 mmol of HL (L = SPy, SPym). After dissolution, 20 ml MeOH was added and subsequently the solution was dropped into a solution of 1 mmol $RSnCl_3$ in 50 ml $CHCl_3$, over a period of 30 min. After being stirred for 24 h at room temperature, the solvent was removed at 20 °C and the residue was extracted with 50 ml $CHCl_3$. The volume of the filtered extract was reduced to 8 ml. Petroleum ether was added till the solution became turbid, and then the mixture was kept for crystallization at −30 °C. The product was filtered and dried in vacuum.

Method A1

A solution of 22 mmol $HgBz_2$ (Bz = benzyl) in 200 ml benzene was dropped into a solution of 22 mmol $SnCl_4$ in 100 ml benzene. After the mixture had been stirred for 24 h, the solvent was removed in vacuum. The residue was dissolved in 50 ml $CHCl_3$ and then a solution of NaSPy (obtained from 88 mmol HSPy and 88 mmol NaOMe) and 60 ml MeOH were slowly added (see below, Eq. [2]). After stirring for 24 h at room temperature, removal of solvent, treatment of the residue with 100 ml $CHCl_3$ and filtration to remove NaCl, the volume of the solution was reduced to about 50 ml, and petroleum ether (b.p. 30–60 °C) was carefully added in small portions for fractional crystallization of compound **3**; BzHg(SPy) remained in solution.

Method B

$RSnCl_3$ (1 mmol/2 mmol for preparing $RSnClL_2$/$RSnCl_2L$, respectively) and $RSnL_3$ (2 mmol/1 mmol for preparing $RSnClL_2$/$RSnCl_2L$, respectively) were refluxed in 40 ml CCl_4 for 24 h. The solvent was removed, and the solid residue was treated with Et_2O and petroleum ether (b.p. 30–60 °C). The solution was kept at room temperature for crystallization. The product was filtered off and dried in vacuum. Compound **22** was obtained as an oil; residual solvent was removed in high vacuum.

Method B1

The comproportionation procedure was the same as described for Method B, but after the solvent had been removed the residue was treated with a mixture of petroleum ether (b.p. 30–60 °C) and pentane (compound **11**), with a mixture of petroleum ether (b.p. 30–60 °C) and Et_2O (compound **14**) or with Et_2O (compound **19**). The solution was kept at −30 °C for crystallization.

Method B2

The comproportionation procedure was the same as described for Method B, but the volume of the reaction mixture was reduced to about 2 ml. After addition of 10 ml Et_2O the solution was kept at −30 °C for crystallizaton.

Method C

A solution (10 ml) of 2 mmol $SnCl_4$ in CCl_4 was added to a solution of NaSPy (obtained from 8 mmol HSPy and 16 ml of a 0.5 M NaOMe solution; 80 ml MeOH). After the mixture had

Table 1 Analytical data for mono-organotin(IV) and tin(IV) derivatives of 2-mercaptopyridine (HSPy) and 2-mercaptopyrimidine (HSPym)

Compound		Method	Yield (%)	M.p. [dec.] (°C)	Analytical data: Found (calcd.) (%) C	H	N	Molecular weight: Found in $CHCl_3$ (calcd.)
1	$MeSn(SPy)_3$	A	66	138 [193]	41.6 (41.4)	3.3 (3.3)	9.0 (9.1)	434 (464)
2	$n\text{-}BuSn(SPy)_3$	A	60	107 [225]	45.3 (45.1)	4.3 (4.2)	8.2 (8.3)	520 (506)
3	$BzSn(SPy)_3$	A1	30	114 [220]	48.7 (48.9)	3.5 (3.5)	7.6 (7.8)	524 (540)
4	$o\text{-}ClBzSn(SPy)_3$	A	71	173 [331]	45.8 (46.0)	3.2 (3.1)	7.2 (7.1)	571 (575)
5	$PhSn(SPy)_3$	A	71	159 [256]	47.9 (47.9)	3.3 (3.3)	8.0 (8.0)	499 (526)
6	$o\text{-}ClPhSn(SPy)_3$	A	70	201 [291]	44.8 (45.0)	2.9 (2.9)	7.3 (7.5)	534 (561)
7	$p\text{-}ClPhSn(SPy)_3$	A	71	172 [304]	44.9 (45.0)	2.8 (2.9)	7.3 (7.5)	531 (561)
8	$o\text{-}TolSn(SPy)_3$	A	68	146 [285]	48.3 (48.9)	3.5 (3.5)	7.7 (7.8)	537 (540)
9	$p\text{-}TolSn(SPy)_3$	A	73	175 [306]	48.8 (48.9)	3.5 (3.5)	7.8 (7.8)	542 (540)
10	$MeSnCl(SPy)_2$	B	90	172 [213]	33.7 (33.9)	2.8 (2.9)	7.1 (7.2)	377 (389)
11	$n\text{-}BuSnCl(SPy)_2$	B1	78	68 [227]	39.0 (39.0)	3.8 (4.0)	6.5 (6.5)	458 (432)
12	$PhSnCl(SPy)_2$	B	89	134 [185]	42.4 (42.6)	2.8 (2.9)	6.2 (6.2)	446 (452)
13	$MeSnCl_2(SPy)$	B	82	97 [163]	23.0 (22.9)	2.3 (2.2)	4.5 (4.5)	342 (315)
14	$n\text{-}BuSnCl_2(SPy)$	B1	80	56 [158]	30.2 (30.3)	3.7 (3.7)	3.9 (3.9)	380 (357)
15	$MeSn(SPym)_3$	A	69	— [185]	33.2 (33.4)	2.6 (2.6)	17.9 (18.0)	476 (467)
16	$n\text{-}BuSn(SPym)_3$	A	71	188[a] [207]	37.7 (37.7)	3.6 (3.6)	16.5 (16.5)	497 (509)
17	$PhSn(SPym)_3$	A	78	210 [250]	40.7 (40.9)	2.7 (2.7)	15.7 (15.9)	533 (529)
18	$MeSnCl(SPym)_2$	B2	90	143 [226]	27.5 (27.6)	2.3 (2.3)	14.3 (14.3)	403 (391)
19	$n\text{-}BuSnCl(SPym)_2$	B1	67	104 [203]	33.3 (33.3)	3.6 (3.5)	12.8 (12.9)	456 (433)
20	$PhSnCl(SPym)_2$	B	90	165 [243]	36.5 (37.1)	2.4 (2.4)	12.2 (12.4)	476 (454)
21	$MeSnCl_2(SPym)$	B	63	104 [137]	19.0 (19.0)	1.9 (1.9)	8.9 (8.8)	341 (316)
22	$n\text{-}BuSnCl_2(SPym)$	B	98	oil	27.5 (26.9)	3.3 (3.4)	7.7 (7.8)	387 (358)
23	$Sn(SPy)_4$	C	68	120 [173]	43.2 (43.0)	3.0 (2.9)	10.0 (10.0)	d (559)
24	$SnCl_2(SPy)_2$[b]	C	73	— [270]	29.2 (29.3)	2.0 (2.0)	6.7 (6.8)	d (410)
25	$Sn(SPym)_4$	C	71	197 [221]	33.9 (34.1)	2.1 (2.1)	19.7 (19.9)	d (563)
26	$SnCl_2(SPym)_2$[b]	C	75	— [253][c]	23.3 (23.3)	1.4 (1.5)	13.6 (13.5)	d (412)

Abbreviations: Me, methyl; n-Bu, normal butyl; Bz, benzyl; Ph, phenyl; Tol, tolyl; *o*, *ortho*; *p*, *para*.
[a] M.p. 191 °C.[23]
[b] Determination of Cl [Found (calcd.) (%)] in **24**: 17.4 (17.3); in **26**: 17.0 (17.2).
[c] Dec. at 261 °C.[23]
[d] Insufficient solubility (see Results and Discussion section).

been stirred for 24 h at room temperature the solvent was removed in vacuum. NaCl was separated by treating the residue with 50 ml $CHCl_3$ and filtration. The volume of the filtrate was reduced to about 10 ml, then 40 ml of Et_2O was added and the solution was kept at -30 °C for crystallization of **23**. Compound **25** was prepared similarly (HSPym instead of HSPy: 50 ml instead of 80 ml MeOH). The product precipitated during a reaction time of five days and was dried after filtration.

Compounds **24** and **26** were prepared analogously using NaL (L = SPy, SPym; 4 mmol HL; 8 ml 0.5 M NaOMe solution; 20 ml MeOH) and a mixture of 10 ml of a 0.2 M solution of $SnCl_4$ (2 mmol) in CCl_4 and 20 ml MeOH. The product precipitated during stirring for ten days.

Characterization of the compounds

C,H,N analyses were carried out with an Elemental Analyzer 1106 (Carlo Erba, Milano, Italy). Halogens were determined potentiometrically after reaction with sodium peroxide and ethylene glycol in a Parr bomb.[15] IR spectra of solids (KBr pellets) were recorded on a Bruker FTIR spectrometer IFS 113 V, and IR spectra of solutions (cell with KBr plates, 25 μm) on a Perkin–Elmer PE 580 B grating spectrometer. Raman spectra (see discussion of vibrational data) were obtained with a Coderg PHO laser-spectrometer (glass capillaries, 514.5–647.1 nm, according to the sensitivity of the sample). NMR spectra were recorded on Bruker AM 300 or Bruker AC 200 spectrometers at 37 °C. Tetramethylsilane and tetramethylstannane were used as internal standards. The ^{119}Sn Mössbauer spectra of finely ground solid absorber samples (*ca* 0.5 mg $^{119}Sn/cm^2$ thickness) were measured with the apparatus and techniques described in previous papers.[2, 9, 16, 17] Molecular weights were determined osmometrically employing a Knauer vapor-pressure osmometer. Melting points were determined with a Büchi S Mp 20 apparatus, and decomposition temperatures (both uncorrected) by DTA/TG measurements with a Mettler Vacuum-Thermoanalyzer T1 (reference: Al_2O_3, 25 °C; N_2, 6 °C min^{-1}; Pt/PtRh thermoelement).

Single crystals of $MeSn(SPy)_3$ (**1**) and $PhSn(SPy)_3 \cdot 1.5CHCl_3$ (**5a**) were obtained by crystallization from $CHCl_3$; petroleum ether was added at -30 °C until the solution started to become turbid. Crystal data, and structure determination data, are compiled in Table 2. The measured data were corrected for Lorentz polarization but not for absorption effects. The observed reflections with $I \geq 2\sigma(I)$ were used for the structure determination via a Patterson function, $\Delta\rho$ maps and full-matrix least-squares refinements with anisotropic temperature factors for all non-H atoms and a common isotropic temperature factor for H atoms, which were placed in geometrically calculated positions (C–H 0.96 Å). Complex neutral-atom scattering factors and real and imaginary dispersion terms were taken from *International Tables for X-ray Crystallography*.[18] The following programs were used: SHELXL93,[19] SHELXTL PLUS,[20] PLATON[21] and MISSYM.[22]

Final fractional atomic coordinates are listed in Table 3, selected bond distances and angles in Table 4. Full listings of atomic coordinates and thermal parameters are available upon request from the authors and from the Cambridge Crystallographic Data Base.

RESULTS AND DISCUSSION

The compounds $RSnL_3$, **1**, **2**, **5**–**9**, **15**–**17**, listed in Table 1, were prepared by reacting a solution of the appropriate mono-organotin trichloride in $CHCl_3$ with NaL in MeOH according to Eq. [1] (Method A; see Experimental section and Table 1):

$$RSnCl_3 + 3NaL \rightarrow RSnL_3 + 3NaCl \qquad [1]$$

Pure products resulted with yields in the range of about 60–78% (Table 1). Compound **16** was obtained recently by this procedure with a yield of 85% using KSPym, with EtOH as solvent.[23]

$BzSnCl_3$(Bz = $C_6H_5CH_2$) is not readily available. $BzSn(SPy)_3$ (Table 1) was therefore synthesized by an *in situ* reaction of NaSPy with the mixture of products obtained by symmetrization of $SnCl_4$ and $HgBz_2$ according to Eq. [2] (Method A1):

$$(BzSnCl_3 + BzHgCl) + 4NaSPy \rightarrow$$

$$BzSn(SPy)_3 + BzHg(SPy) + 4NaCl \qquad [2]$$

$RSn(SPy)_3$ (R = Ph, *p*-tolyl), **5** and **9**, were also obtained by neutralizing RSnOOH according to

Eq. [3]:

$$RSnOOH + 3HSPy \rightleftharpoons RSn(SPy)_3 + 2H_2O \quad [3]$$

Water of reaction was removed by azeotropic distillation when toluene was used as solvent, or by reaction with 2,2-dimethoxypropane when $CHCl_3$ was used as solvent. This procedure offers no advantages, however, since long reaction times are necessary (60–90 h) and yields, about 70%, are not higher. Compound **16** was prepared recently according to Eq. [3], in EtOH.[23]

Compounds of the type $RSnClL_2$, **10**–**12** and **18**–**20**, and $RSnCl_2L$, **13**, **14**, **21**, **22** (Table 1) could be prepared by metathesis following the procedure of Eq. [1], but according to ^{1}H NMR data the products contained small amounts of more highly substituted products, e.g. $RSnL_3$. Attempts to purify the compounds by fractional crystallization failed, due to similar solubilities. Pure products, however, were readily obtained by comproportionation under reflux in $CHCl_3$ or CCl_4 with good to high yields according to Eqs [4] and [5] (Methods B–B2):

$$RSnCl_3 + 2RSnL_3 \rightarrow 3RSnClL_2 \quad [4]$$

Table 2 Crystal data for $MeSn(SPy)_3$ (**1**) and $PhSn(SPy)_3 \cdot 1.5CHCl_3$ (**5a**)

	1	**5a**
Empirical formula	$C_{16}H_{15}N_3S_3Sn$	$C_{21}H_{17}N_3S_3Sn \cdot 1.5CHCl_3$
Color	Light yellow	Light yellow
Crystal size (mm^3)	$0.16 \times 0.22 \times 0.42$	$0.40 \times 0.48 \times 0.92$
Space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Unit cell dimensions		
a, b, c (Å)	8.211(2), 18.228(2), 12.919(2)	8.972(8), 15.577(11), 19.735(16)
β (deg)	103.93(2)	91.84(7)
Volume (Å^3)	1876.6(7)	2757(4)
Z	4	4
$D_{calc.}$ (g cm^{-3})	1.643	1.699
$F(000)$	920	1396
Radiation; λ (Å)	Mo Kα; 0.71073	Mo Kα; 0.71073
Temperature (K)	293(1)	170(1)
No. of rflns for lattice parameters;		
θ range (deg)	43; 5.1–14.8	40; 7.7–14.6
Diffractometer type	Nicolet R3m/V	Nicolet R3m/V
Absorption correction, type	empirical, Ψ scan	empirical, Ψ scan
Absorption correction (T_{max}/T_{min})	0.990/0.827	1.000/0.569
2θ range (deg)	2.0–50.0	2.0–50.0
Scan speed (deg, min^{-1} in θ)	1.5–15.0	2.5–15.0
No. of std reflections/interval	6/300	6/300
No. of reflections measured	3805	5571
No. of independent reflections	3323	4871
No. of observed reflections	2329 with $1 > 2\sigma(I)$	4035 with $1 > 2\sigma(I)$
$h_{min}/k_{min}/l_{min}$	$-9/-1/-14$	$-10/-1/-23$
$h_{max}/k_{mas}/l_{max}$	0/21/15	0/18/23
R_{int}	0.0230	0.0230
θ_{max} (deg)	25.05	25.06
Variation of stds (%)	$< \pm 3.4$	$< \pm 4.3$
No. of parameters refined	210	327
No. of reflections used in refinement	3317	4863
R	0.0254 with $F > 4\sigma(F)$	0.0583 with $F > 4\sigma(F)$
wR, based on F^2	0.0445	0.1548
S, based on F^2	0.91	1.08
Weighting scheme, with	Calcd $w =$	Calcd $w =$
$P = (F_o^2 + 2F_c^2)/3$	$1/[\sigma^2(F_o^2) + (0.0192P)^2 + 0.0P]$	$1/[\sigma^2(F_o^2) + (0.1312P)^2 + 0.0P]$
$(\Delta/\sigma)_{max}$	0.001	-0.001
$(\Delta/\rho)_{min}$ (e Å^{-3})	-0.329	1.922
Solution	Patterson, difference Fourier	Patterson, difference Fourier

Table 3 Fractional coordinates and equivalent isotropic displacement parameters (Å^2) for MeSn(SPy)$_3$ (**1**) and PhSn(SPy)$_3$·1.5CHCl$_3$ (**5a**)

$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a_i} \cdot \mathbf{a_j}$

	1					**5a**			
	x	*y*	*z*	U_{eq} (Å^2)		*x*	*y*	*z*	U_{eq} (Å^2)
Sn(1)	0.11409(3)	0.22980(1)	0.14436(2)	0.03639(7)	Sn(1)	0.17746(3)	0.21880(2)	0.20733(2)	0.0265(2)
S(1)	0.33850(12)	0.17320(6)	0.07228(7)	0.0509(3)	S(1)	0.27007(15)	0.14039(9)	0.31031(8)	0.0377(3)
S(2)	−1.2258(13)	0.17186(6)	0.00082(7)	0.0532(3)	S(2)	0.04845(15)	0.08950(9)	0.15064(8)	0.0386(3)
S(3)	0.08068(12)	0.34748(5)	0.02940(7)	0.0469(2)	S(3)	0.39029(14)	0.18307(9)	0.12743(7)	0.0369(3)
C(11)	0.4478(4)	0.1625(2)	0.2050(3)	0.0405(9)	C(11)	0.2055(6)	0.2294(3)	0.3549(3)	0.0360(12)
N(11)	0.3587(3)	0.18199(15)	0.2759(2)	0.0384(7)	N(11)	0.1457(5)	0.2911(3)	0.3147(2)	0.0295(9)
C(13)	0.4323(5)	0.1790(2)	0.3803(3)	0.0493(10)	C(13)	0.0883(6)	0.3614(3)	0.3435(3)	0.0347(12)
C(14)	0.5940(5)	0.1556(2)	0.4176(3)	0.0606(11)	C(14)	0.0907(7)	0.3742(4)	0.4123(3)	0.050(2)
C(15)	0.6828(5)	0.1350(2)	0.3459(4)	0.0715(13)	C(15)	0.1553(9)	0.3113(5)	0.4538(4)	0.061(2)
C(16)	0.6119(5)	0.1379(2)	0.2397(4)	0.0617(11)	C(16)	0.2126(8)	0.2380(5)	0.4246(3)	0.054(2)
C(21)	−0.0871(4)	0.0954(2)	0.0830(3)	0.0409(9)	C(21)	−0.0987(6)	0.1130(3)	0.2032(3)	0.0332(12)
N(21)	0.0296(3)	0.10632(15)	0.1750(2)	0.0386(7)	N(21)	−0.707(4)	0.1790(3)	0.2456(2)	0.0314(10)
C(23)	0.0623(5)	0.0528(2)	0.2480(3)	0.0487(10)	C(23)	−0.1757(5)	0.2023(4)	0.2901(3)	0.0332(12)
C(24)	−0.0184(5)	−0.0136(2)	0.2333(3)	0.0601(11)	C(24)	−0.3092(6)	0.1602(4)	0.2921(3)	0.0421(14)
C(25)	−0.1355(5)	−0.0258(2)	0.1377(4)	0.0644(12)	C(25)	−0.3387(6)	0.0936(3)	0.2484(3)	0.0395(13)
C(26)	−0.1711(5)	0.0284(2)	0.0629(3)	0.0590(11)	C(26)	−0.2348(6)	0.0692(3)	0.2024(3)	0.0380(13)
C(31)	0.2681(4)	0.3785(2)	0.1129(3)	0.0406(8)	C(31)	0.4819(6)	0.2676(3)	0.1691(3)	0.0305(11)
N(31)	0.3345(3)	0.3327(2)	0.1933(2)	0.0433(7)	N(31)	0.4052(4)	0.3011(3)	0.2204(2)	0.0275(9)
C(33)	0.4816(5)	0.3506(2)	0.2598(3)	0.0560(10)	C(33)	0.4668(5)	0.3649(3)	0.2581(3)	0.0306(11)
C(34)	0.5674(5)	0.4129(2)	0.2486(3)	0.0622(11)	C(34)	0.6050(6)	0.3983(3)	0.2456(3)	0.0330(11)
C(35)	0.4988(5)	0.4601(2)	0.1665(3)	0.0670(12)	C(35)	0.6829(5)	0.3641(4)	0.1915(3)	0.0372(13)
C(36)	0.3473(5)	0.4434(2)	0.0984(3)	0.0568(11)	C(36)	0.6222(6)	0.2990(4)	0.1537(3)	0.0355(12)
C(1)	0.0018(4)	0.2679(2)	0.2660(3)	0.0499(9)	C(41)	0.3889(7)	0.8841(4)	0.0210(3)	0.0458(14)
					C(1)	0.0807(5)	0.3234(3)	0.1511(3)	0.0277(10)
					C(2)	0.1053(5)	0.4091(3)	0.1712(3)	0.0317(11)
					C(3)	0.0407(6)	0.4765(4)	0.1345(3)	0.0381(12)
					C(4)	−0.0469(6)	0.4607(4)	0.0781(3)	0.0411(13)
					C(5)	−0.0696(6)	0.3769(4)	0.0565(3)	0.0431(14)
					C(6)	−0.0058(6)	0.3089(4)	0.0936(3)	0.0338(12)
					Cl(1)	0.3772(3)	0.78658(14)	0.0652(2)	0.0957(8)
					Cl(2)	0.4125(3)	0.96997(14)	0.07790(9)	0.0729(6)
					Cl(3)	0.2278(2)	0.89753(13)	−0.02966(10)	0.0656(5)
					C(51)[a]	0.5316(17)	0.4914(10)	0.0255(7)	0.058(3)
					Cl(4)[a]	0.4991(18)	0.5973(5)	0.0015(8)	0.230(9)
					Cl(5)[a]	0.3733(7)	0.4511(10)	0.0579(5)	0.176(5)
					Cl(6)[a]	0.5680(14)	0.4386(10)	−0.0473(7)	0.215(6)

[a] Site occupancy factor (s.o.f.) of the chloroform molecule 0.5.

$$2RSnCl_3 + RSnL_3 \rightarrow 3RSnCl_2L \quad [5]$$

Attempts to prepare and isolate $PhSnCl_2L$ (L = SPy, SPym) according to Eq. [5] failed; only undefined, colorless, insoluble products were obtained. However, treatment of NaL with $PhSnCl_3$ in petroleum ether afforded a product which was soluble in $CHCl_3$ or acetone and was identified as $PhSnCl_2$(SPy) and $PhSnCl_2$(SPym), respectively, by ^{1}H NMR spectroscopy.

The inorganic tin(IV) compounds **23**–**26** (Table 1) were prepared by metathesis, Method C, in analogy to Eq. [1]; the products precipitated slowly after dropping the appropriate stoichiometric amount of NaL in $CHCl_3$ to a solution of $SnCl_4$ in MeOH at room temperature. The amount of MeOH used has to be large enough to keep NaCl in solution. Compound **23** was prepared recently from PySSPy and elemental tin in refluxing toluene,[24] and **24** was obtained, *inter alia*, from PySSPy and $SnCl_2$.[25] Compound **26** was recently reported to be formed from $SnCl_2 \cdot 2H_2O$ and HSPym at room temperature under evolution of H_2 with a yield of 60%,[23] in

Table 4 Selected bond distances (Å) and bond angles (deg) in $MeSn(SPy)_3$ (**1**) and $PhSn(SPy)_3 \cdot 1.5CHCl_3$ (**5a**) (standard deviations in parentheses)[a]

Bond distances	**1**	**5a**		**1**	**5a**
Sn(1)–C(1)	2.121(3)	2.139(5)	N(11)–C(13)	1.340(4)	1.344(7)
Sn(1)–N(11)	2.457(3)	2.425(5)	C(21)–N(21)	1.350(4)	1.344(7)
Sn(1)–N(21)	2.416(3)	2.453(5)	C(21)–C(26)	1.395(5)	1.398(7)
Sn(1)–N(31)	2.577(3)	2.419(4)	N(21)–C(23)	1.338(4)	1.358(7)
Sn(1)–S(1)	2.4805(10)	2.491(2)	C(31)–N(31)	1.342(4)	1.347(7)
Sn(1)–S(2)	2.5681(11)	2.562(2)	C(31)–C(36)	1.386(5)	1.393(7)
Sn(1)–S(3)	2.5858(10)	2.576(2)	N(31)–C(33)	1.343(4)	1.348(7)
S(1)–C(11)	1.744(4)	1.751(6)	C(41)–Cl(3)	—	1.743(7)
S(2)–C(21)	1.734(4)	1.743(6)	C(41)–Cl(2)	—	1.755(6)
S(3)–C(31)	1.747(3)	1.745(5)	C(41)–Cl(1)	—	1.756(7)
C(1)–C(6)	—	1.372(8)	C(51)[b]–Cl(6)[b]	—	1.69(2)
C(1)–C(2)	—	1.409(7)	C(51)[b]–Cl(5)[b]	—	1.70(2)
C(11)–N(11)	1.350(4)	1.347(7)	C(51)[b]–Cl(4)[b]	—	1.74(2)
C(11)–C(16)	1.388(5)	1.381(9)			
Bond angles	**1**	**5a**		**1**	**5a**
C(1)–Sn(1)–N(11)	91.88(11)	92.5(2)	S(1)–Sn(1)–S(3)	96.61(3)	99.15(7)
N(21)–Sn(1)–N(11)	77.03(9)	73.5(2)	S(2)–Sn(1)–S(3)	88.24(3)	84.05(6)
C(1)–Sn(1)–N(21)	89.49(12)	89.7(2)	N(31)–Sn(1)–S(3)	60.55(7)	62.60(11)
C(1)–Sn(1)–N(31)	89.10(12)	88.8(2)	C(11)–S(1)–Sn(1)	86.02(11)	85.1(2)
N(21)–Sn(1)–N(31)	148.24(9)	150.79(15)	C(21)–S(2)–Sn(1)	84.39(12)	85.2(2)
N(11)–Sn(1)–N(31)	71.31(9)	77.47(15)	C(31)–S(3)–Sn(1)	87.58(12)	84.0(2)
S(1)–Sn(1)–N(31)	81.59(7)	85.09(12)	C(13)–N(11)–Sn(1)	143.7(2)	143.7(4)
S(2)–Sn(1)–N(31)	147.25(7)	146.26(11)	C(11)–N(11)–Sn(1)	96.4(2)	97.3(3)
C(1)–Sn(1)–S(1)	155.37(10)	156.33(14)	C(23)–N(21)–Sn(1)	141.0(2)	141.9(4)
N(21)–Sn(1)–S(1)	86.70(7)	84.67(12)	C(21)–N(21)–Sn(1)	99.5(2)	98.9(3)
N(11)–Sn(1)–S(1)	63.55(7)	63.91(12)	C(31)–N(31)–Sn(1)	97.6(2)	99.5(3)
C(1)–Sn(1)–S(2)	106.34(10)	101.6(2)	C(33)–N(31)–Sn(1)	143.5(3)	141.2(3)
N(21)–Sn(1)–S(2)	62.47(7)	62.21(12)	Cl(3)–C(41)–Cl(2)	—	110.8(4)
N(11)–Sn(1)–S(2)	134.75(7)	133.05(11)	Cl(3)–C(41)–Cl(1)	—	109.1(4)
S(1)–Sn(1)–S(2)	93.40(4)	96.02(4)	Cl(2)–C(41)–Cl(1)	—	110.5(3)
C(1)–Sn(1)–S(3)	98.54(10)	98.25(14)	Cl(6)[b]–C(51)[b]–Cl(5)[b]	—	109.0(10)
N(21)–Sn(1)–S(3)	150.69(7)	146.25(11)	Cl(6)[b]–C(51)[b]–Cl(4)[b]	—	105.4(9)
N(11)–Sn(1)–S(3)	130.35(7)	138.21(11)	Cl(5)[b]–C(51)[b]–Cl(4)[b]	—	108.6(10)

[a] Atomic numbering according to Fig. 1 (**1**) and Fig. 2 (**5a**). The other bond distances and bond angles of the aromatic rings correspond to the usual values.
[b] S.o.f. 0.5 (see Table 3).

what appears to us to be a remarkable reaction.

Compounds **1**–**26** (Table 1) are colorless to light-yellow solids (except **22**, which is an oil) which are not decomposed by air or light and can be stored at room temperature. Compounds **1**–**22** are soluble in CH_2Cl_2, $CHCl_3$, acetone and coordinating solvents, e.g. dimethyl sulfoxide (DMSO); they are moderately soluble in CCl_4 and MeOH, and only slightly soluble to insoluble in Et_2O or non-polar solvents, such as petroleum ether. The compounds are insoluble in water, and they are not hydrolyzed. The complexes $SnCl_2L_2$ and $Sn(SPym)_4$, **24**–**26**, are only slightly soluble in non-polar and polar solvents so that no data in solution phase could be determined here. In contrast, **23** proved to be soluble in $CHCl_3$, acetone and MeOH.

The molecular weights measured in $CHCl_3$ solution (Table 1) correspond quite well with calculated values; thus, the presence of monomeric species may be safely inferred. The molecular weights of **1**, **5**, **10**, **13**, **15** and **17** in DMSO solution were found to be 222, 259, 208, 219, 259 and 290, respectively; these values would indicate dissociation. Since the measurements of the solutions in DMSO were made for technical reasons at 90 °C, and since ^{1}H, ^{13}C and ^{119}Sn NMR spectra of the compounds (*vide infra*) obtained at room temperature indicate the presence of monomeric species, it is assumed that dissociation occurs only at higher temperatures. Data for compounds **1**, **18**, **25** and **26** (Table 1) correspond to values from independent syntheses.[2]

Structures in the solid state

$MeSn(SPy)_3$ (**1**) and $PhSn(SPy)_3 \cdot 1.5CHCl_3$ (**5a**) crystallize in a monoclinic space group. According to the X-ray structure determination, discrete monomeric units of the $RSn(SPy)_3$ moieties (R = Me, Ph, respectively) are present in both complexes (Figs 1 and 2). The unit cells are shown in Figs 3 and 4. Compound **5a** crystallizes from the $CHCl_3$ solution of **5** at −30 °C incorporating six $CHCl_3$ molecules (two disordered with site occupancy factor (s.o.f.) 0.5, four not disordered) in the unit cell (Fig. 4), corresponding to the overall formula $PhSn(SPy)_3 \cdot 1.5CHCl_3$. On being warmed to room temperature the crystals decay, giving off $CHCl_3$ and leaving amorphous **5**. In both compounds the three bidentate SPy ligands form a distorted pentagonal bipyramid around tin, with two S atoms and three N atoms in the pentagonal plane and C and one S atom in axial positions. The heavy distortion of the pentagonal bipyramid is evident considering, e.g., the angle S(1)–Sn–C(1), with 155.4(1)° (in **1**) and 156.3(1)° (in **5**) (Table 4). The molecular structures of **1** and **5** fully correspond to structures found in *p*-$TolSn(SPy)_3$(**9**)[26] and *n*-$BuSn(SPym)_3$

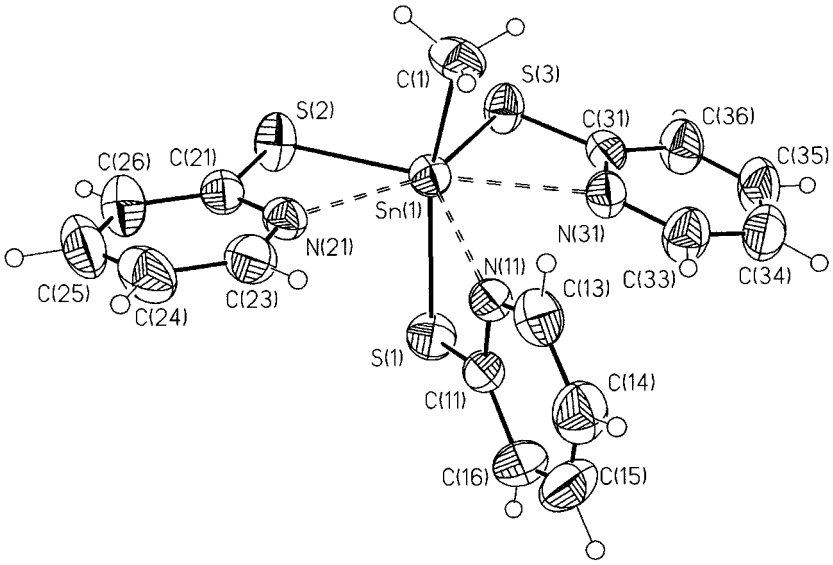


Figure 1 General view of a molecule of $MeSn(SPy)_3$ (**1**) showing 50% probability displacement ellipsoids and atom numbering.

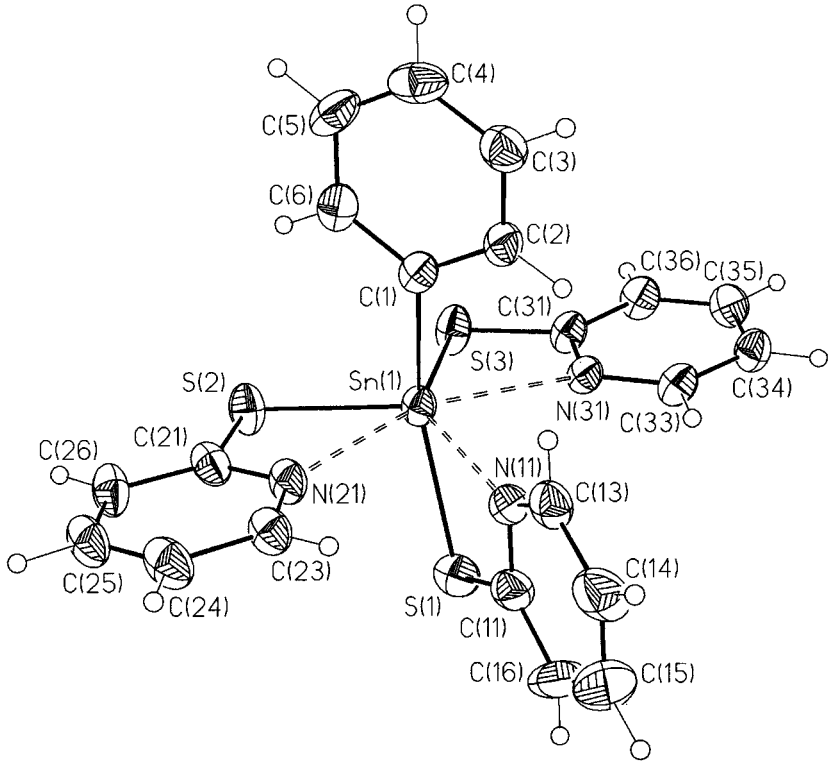


Figure 2 General view of a molecule of $PhSn(SPy)_3$ (**5**) as part of the unit cell of **5a** showing 50% probability displacement ellipsoids and atom numbering.

(**16**).[27, 28] It seems noteworthy that in contrast to **1** and **5**, in which all SPy ligands are bidentate rendering tin heptacoordinated, in $Sn(SPy)_4 \cdot 2H$-SPy only two of the four SPy ligands are bidentate and tin as center of the molecular unit **23** is only hexacoordinated.[24] In accordance with the spectroscopic results (*vide infra*) it is evident that the thiol-thione equilibria of HSPy and HSPym[29–32] (Fig. 5) are shifted to the thiol form on complex formation.

The ^{119}Sn Mössbauer isomer shift parameters, δ (mm s^{-1}) (Table 5) for mono-organotin(IV) (**1**–**21**) and tin(IV) (**23**–**26**) complexes sit well in the δ ranges reported in the literature (RSn^{IV}: $\delta = 0.40$–2.00;[34, 35] Sn^{IV}: $\delta = -0.48$–1.40,[34, 35] mm s^{-1}). The general narrowness of linewidths

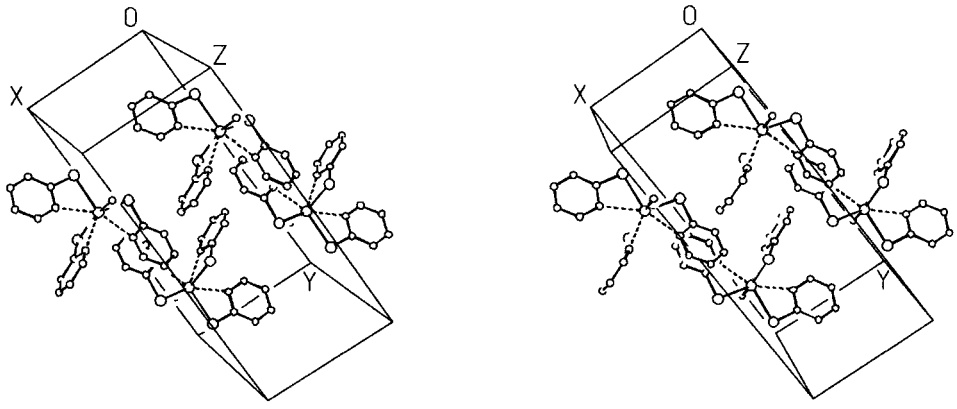


Figure 3 Structure of $MeSn(SPy)_3$ (**1**): stereoscopic view (*SHELXTL Plus* graphic) of the unit cell.

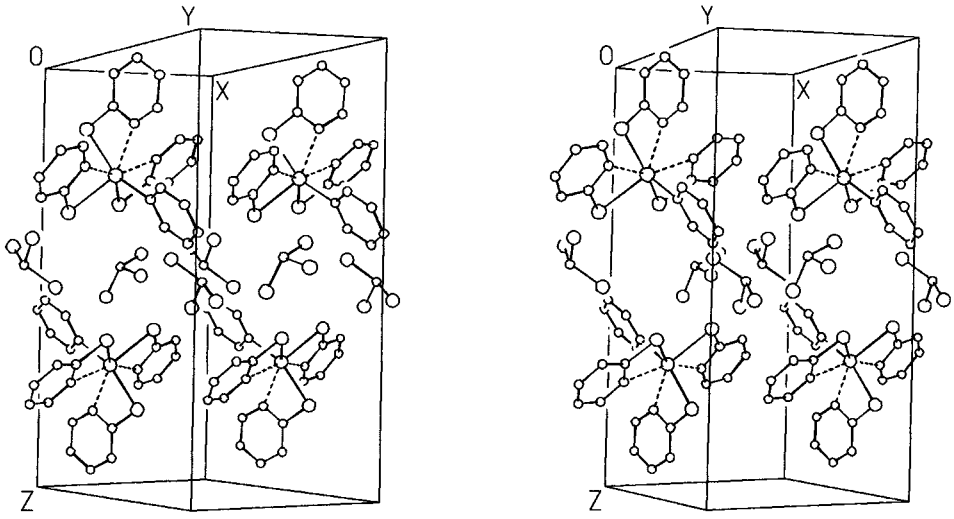


Figure 4 Structure of $PhSn(SPy)_3 \cdot 1.5CHCl_3$ (**5a**): stereoscopic view (*SHELXTL Plus* graphic) of the unit cell.

Γ (mm s^{-1}) as well as the mutual correspondence of Γ values in two-line spectra (Table 5) suggest the occurrence of a single coordination site in each complex.

Structural assignments, inherent to the environment of tin atoms, may be effected on the basis of the experimental nuclear quadrupole splitting parameters ΔE (mm s^{-1}) listed in Table 5, by both fingerprint attribution[34, 35] and point-charge model calculations,[1, 2, 34, 35] accounting for the rule $|\Delta E_{exp} - \Delta E_{calcd}| \leqslant 0.4$ mm s^{-1} for a given configuration in the latter context.[36] By these procedures and criteria, the idealized (regular) structures for RSn^{IV} complexes with S_{thiol} and N_{het} donor atoms, discussed below and reported in Table 6, have been attributed to complexes **1**–**26**, on the basis of the data and parameters summarized in Table 6 and related notes.

Pentagonal bipyramidal structures are assigned to $RSnL_3$ complexes **1**, **2**, **15** and **16**, and **5**, **7**, **9** and **17**, in line with the crystal and molecular structures of members of the series discussed above. Octahedral structures can be assigned to the complexes $RSnClL_2$, according to a general bidentate (chelating) behaviour of ligands L. By fingerprint (Table 6), octahedral structures can be attributed to the complexes of inorganic Sn^{IV}, in conformity with X-ray studies carried out for $Sn(SPy)_4 \cdot HSPy$[24] and $SnCl_2(SPy)_2$.[39]

The structure of $Sn(SPym)_4$, **23**, could also correspond to that proposed for the 8-oxyquinoline complex $SnOx_4$, where Sn is possibly eight-coordinated,[40] showing $\Delta E_{exp} = 0.00$ mm s^{-1}.[41]

As far as the complexes $RSn(SPy)_3$ (**3**, **4**, **6**, **8**; Tables 5 and 6) are concerned, the octahedral structure (III), Table 6, could be assigned to *o*-$TolSn(SPy)_3$, **8**, where one ligand would act in a monodentate sense, coordinating Sn through the S atom.

Tin centers in the complexes $BzSn(SPy)_3$ (**3**), *o*-$ClBzSn(SPy)_3$ (**4**) and *o*-$ClPhSn(SPy)_3$ (**6**) may

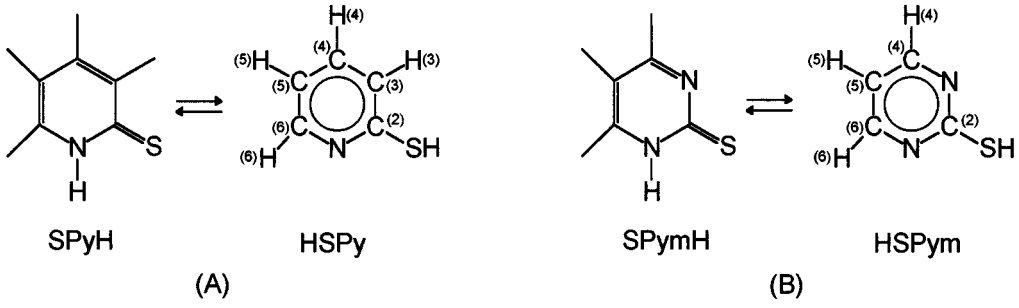


Figure 5 Thiol–thione equilibria of 2-mercaptopyridine (A) and 2-mercaptopyrimidine (B).[29–32] Labelling of H atoms and C atoms related to ^1H NMR and ^{13}C NMR spectral data.

be assumed both as six- or five-coordinated (Table 6); also, tetrahedral tin configurations $RSnS_3$ could be advanced for these compounds [ΔE_{exp} range[34, 35] = 0.00–3.35; ΔE_{calcd} = 1.64 (R = alkyl) and 1.42 (R = aryl), mm s^{-1}]. On the other hand, *o*-$ClBzSn(SPy)_3$ (**4**) has been determined to assume the octahedral structure VI (Table 6) by X-ray crystallographic study (M. Schürmann, F. Huber and R. Barbieri, unpublished results), and the same type of structure could then be assumed to occur also for $BzSn(SPy)_3$ and *o*-$ClPhSn(SPy)_3$ (**3** and **6**, Tables 5 and 6). It could be concluded that steric hindrance in complexes **3**, **4**, **6** and **8** requires one SPy to act as a monodentate ligand through the S atom, producing a lack of attainment of seven-coordination at tin centres. The behavior of SPy as monodentate in $Sn(SPy)_4 \cdot HSPy$[24] (structure VIII in Table 6) have been discussed above.

The general behavior of ligands SPy and SPym as S,N bidentate chelating agents in the thiol form towards RSn^{IV} in complexes **1**, **2**, **5**, **7** and **9**–**21** has been inferred here from the ^{119}Sn Mössbauer ΔE parameters, extending the struc-

Table 5 ^{119}Sn Mössbauer parameters, at T = 77.3 K, of mono-organotin(IV) and -tin(IV) derivatives of 2-mercaptopyridine and 2-mercaptopyrimidine

Compound[a]		δ[b] (mm s^{-1})	ΔE[c] (mm s^{-1})	Γ_1[d] (mm s^{-1})	Γ_2[d] (mm s^{-1})
1	$MeSn(SPy)_3$	1.15[e]	2.23[e]	0.96[e]	0.87[e]
2	$n\text{-}BuSn(SPy)_3$	1.27	2.08	0.84	0.82
3	$BzSn(SPy)_3$	1.18	1.24	0.93	0.86
4	*o*-$ClBzSn(SPy)_3$	1.15	1.12	0.85	0.89
5	$PhSn(SPy)_3$	1.04	1.89	1.00	0.94
6	*o*-$ClPhSn(SPy)_3$	0.99[e]	1.10[e]	0.93[e]	0.83[e]
7	*p*-$ClPhSn(SPy)_3$	1.08[e]	1.92[e]	0.77[e]	0.83[e]
8	*o*-$TolSn(SPy)_3$	1.02	1.57	0.87	0.90
9	*p*-$TolSn(SPy)_3$	1.11	1.94	0.88	0.94
10	$MeSnCl(SPy)_2$	1.00	1.55	0.94	0.84
11	$n\text{-}BuSnCl(SPy)_2$	1.16	1.62	0.89	0.82
12	$PhSnCl(SPy)_2$	1.01	1.56	0.97	0.86
13	$MeSnCl_2(SPy)$	1.22	2.12	1.01	0.91
14	$n\text{-}BuSnCl_2(SPy)$	1.28	2.02	0.90	0.86
15	$MeSn(SPym)_3$	1.28	2.22	0.89	0.78
16	$n\text{-}BuSn(SPym)_3$	1.30	2.22	0.97	0.85
		1.30[f]	2.24[f]	1.00[f]	1.00[f]
17	$PhSn(SPym)_3$	1.15	2.13	1.12	0.94
18	$MeSnCl(SPym)_2$	1.03[e]	1.54[e]	0.91[e]	0.90[e]
19	$n\text{-}BuSnCl(SPym)_2$	1.41	2.21	0.99	0.85
20	$PhSnCl(SPym)_2$	1.00	1.51	0.92	0.84
21	$MeSnCl_2(SPym)$	1.15	2.45	1.05	0.90
23	$Sn(SPy)_4$	0.83	0.00	1.66	—
	(two lines fit)	0.82	0.69	1.29	1.29
24	$SnCl_2(SPy)_2$	0.79	0.89	0.84	0.90
		0.81[g]	0.93[g]	1.04[g]	0.74[g]
25	$Sn(SPym)_4$	0.95[e]	0.00[e]	1.11[e]	—
	(two lines fit)	0.96	0.21	1.07	1.07
26	$SnCl_2(SPym)_2$	0.82	0.98	0.99	0.85
		0.73[h]	0.94[h]	0.91[h]	0.79[h]
		0.73[f]	0.87[f]	1.12[f]	1.12[f]

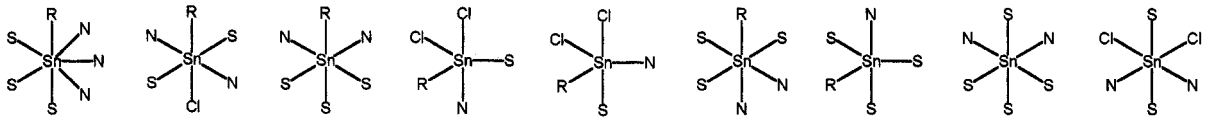
[a] See Table 1. [b] Isomer shift relative to room temp. $Ca^{119}SnO_3$. [c] Nuclear quadrupole splitting. [d] Full width at half-height of the resonant peaks, at lower and higher velocity than the spectrum centroid, respectively. [e] Values corresponding to average data in T ranges 77.3–145/170 K; Ref. 2, and unpublished results (A. Silvestri *et al.*). [f] Data reported in Ref. 23. [g] Data reported in Ref. 33. [h] Average data in the T range 77.3–200.5 K, Ref. 2.

tural findings from *X*-ray diffractometry (structures in Table 6). These assumptions, and the structural differences regarding the complexes **3**, **4**, **6** and **8**, were also checked by vibrational spectroscopy. Modes of the coordinated SPy and SPym ligands in the solid state are reported in Table 7. The IR absorptions A, G and H of the mercaptopyridine derivatives **1**–**14**, **23** and **24**, and of the mercaptopyrimidine derivatives **15**–**22**, **25** and **26** (and to a lesser extent bands C also, as well as D for SPy complexes) are found at higher wavenumbers in comparison

Table 6 Literature ranges of experimental values of ^{119}Sn Mössbauer quadrupole splittings, ΔE, for RSn^{IV} and Sn^{IV} derivatives, and point-charge model calculations of ΔE for RSn^{IV} complexes of 2-mercaptopyridine and 2-mercaptopyrimidine, as functions of the structure of the tin environment

		Complexes with SPy, SPym[b]			
				Point-charge model estimate[e]	
Geometry	Range of ΔE_{exp}[a] (mm s^{-1})	Class[c]	ΔE_{exp}, or range of ΔE_{exp}[d] (mm s^{-1})	ΔE_{calcd} (mm s^{-1})	Structure[f]
(A) RSn^{IV}					
Pentagonal bipyramidal	1.70–2.23	$AlkylSnL_3$ (**1**, **2**, **15**, **16**)	2.08–2.24	2.44(5)[g]	**I**
		$ArylSnL_3$ (**5**, **7**, **9**, **17**)	1.90–2.13	2.35	**I**
Octahedral	1.38–2.50	$AlkylSnClL_2$ (**10**, **11**, **18**, **19**)	1.53–2.18	(−)1.76[h]	**II**
		$ArylSnClL_2$ (**12**, **20**)	1.56; 1.51	(−)1.70	**II**
		o-$TolylSn(SPy)_3$ (**8**)	1,57	1.70	**III**
Trigonal bipyramidal	1.18–2.69	$AlkylSnCl_2L$ (**13**, **14**, **21**)	2.02–2.45	2.48	**IV**
				(−)2.29	**V**
Octahedral or trigonal bipyramidal	—	$BenzylSn(SPy)_3$ (**3**, **4**)	1.24; 1.12	(−)0.93 (R = Alkyl)	**VI**
				(−)0.86 (R = Aryl)	**VI**
		o-$ClPhSn(SPy)_3$ (**6**)	1.09	1.41 (R = Alkyl)	**VII**
				1.13 (R = Aryl)	**VII**
(B) Sn^{IV}					
Octahedral	0.00–1.21	SnL_4 (**23**, **25**)	0.00 or 0.69 0.00 or 0.21	—[i]	**VIII**
		$SnCl_2L_2$ (**24**, **26**)	0.89; 0.98	—[i]	**IX**

[a] From Refs 34 and 35, and refs cited therein. [b] See Table 1. [c] L = SPy or SPym; numbers in parentheses refer to individual complexes according to the labeling in the Tables, e.g. 1 and 5. [d] From Table 5. [e] Effected according to the procedures and partial quadrupole splitting (p.q.s.) data reported in Refs 1, 2, 34 and 35, and refs cited therein; p.q.s. $[Cl]^{tbe} = +0.20$ mm s^{-1}. [f] Idealized regular structures, inherent to complexes with S_{thiol} and N_{het} ligands. Selected according to X-ray crystallographic data: **I**, this work and Refs 26–28; **VIII**, Ref. 24; **IX**, Ref. 39. Assumed on the basis of point-change model calculations: **II**–**VII**. [g] $V_{zz} = (-)2.31$ is reported in Ref. 2. [h] Ref. 2. [i] Not applicable; see Ref. 2.



Structure **II**: at variance with crystallographic data for a series of $R_2Sn(SPy)_2$ and related complexes, where N,N and S,S atoms have been determined to be in *cis* positions.[1] Structures **IV** and **VII**: obey the rule of Muetterties and Schunn,[37] concerning the location in axial positions of the most electronegative groups in trigonal bipyramidal configurations, which has been determined to hold for SPy and related complexes.[38]

Table 7 Infrared spectral data for mono-organotin(IV) and tin(IV) derivatives of 2-mercaptopyridine and 2-mercaptopyrimidine, and of PySSPy and PymSSPym

		ν(C–C/C–N) (cm^{-1})				δ(C–H) (cm^{-1})			Ring (cm^{-1})
Compound[a]		A	B	C	D	E	F	G	H
1	$MeSn(SPy)_3$	1578 vs 1573 vs	1551 vs	1440 s 1445 s	1420 vs 1425 vs	760 vs	753 vs	728 vs	638 m 633 m
2	n-$BuSn(SPy)_3$	1579 vs	1552 s	1444 vs	1419 vs 1416 vs	754 vs	748 vs	727 vs	639 w 634 m
3	$BzSn(SPy)_3$	1575 vs 1568 vs	1545 m	1438 vs	1415 vs 1405 vs	762 m	750 s	729 m 715 s	630 w
4	*o*-$ClBzSn(SPy)_3$	1575 vs 1567 vs	1545 m	1443 vs 1438 vs	1418 vs 1408 vs	760 s	742 s	720 m 722 s	638 w
5	$PhSn(SPy)_3$	1576 vs	1554 m 1551 m	1442 vs	1419 vs	763 m	752 s	738 m 729 s	637 w
6	*o*-$ClPhSn(SPy)_3$	1578 vs 1575 vs	1550 m	1443 vs	1418 vs 1410 vs	760 s	748 s	725 m	634 w 620 w
7	*p*-$ClPhSn(SPy)_3$	1577 vs	1549 m	1442 vs 1440 vs	1419 vs	760 s	752 s 750 vs	725 m	637 w 630 w
8	*o*-$TolSn(SPy)_3$	1575 vs	1550 m 1540 w	1442 vs	1418 vs	760 m	750 s	728 m	631 w
9	*p*-$TolSn(SPy)_3$	1576 vs	1549 m	1442 vs 1439 vs	1419 vs	760 m	749 s	724 m	630 w
10	$MeSnCl(SPy)_2$	1581 vs	1550 s	1443 vs	1424 vs	755 vs	741 vs	726 vs	644 s 649 m
11	n-$BuSnCl(SPy)_2$	1579 vs	1551 s 1547 vs	1445 vs 1437 vs	1422 vs	758 vs	751 vs	726 vs	645 s 648 m
12	$PhSnCl(SPy)_2$	1583 vs	1549 s	1439 vs	1423 vs	757 vs	733 s	726 vs	649 m 648 m
13	$MeSnCl_2(SPy)$	1585 vs	1559 s	1449 vs	1428 vs	778 s	763 vs	724 s	643 s
14	n-$BuSnCl_2(SPy)$	1585 vs	1556 s	1450 vs	1426 vs	760 vs	724 s		642 s
15	$MeSn(SPym)_3$	1570 vs 1563 vs	1545 vs	1376	—	800 s 786 s	769 s	751 s 746 s	648 s 643 s
16	n-$BuSn(SPym)_3$[b]	1565 s	1550 s 1542 vs	1376 vs	—	803 m	769 s	746 s	648 w 643 m
17	$PhSn(SPym)_3$	1565 vs	1548 s 1542 vs	1377 vs	—	799 w 791 w	769 s	749 s 743 w	648 m 645 m
18	$MeSnCl(SPym)_2$	1576 vs	1545 vs	1374 vs	—	797 m 778 m	762 s	748 s	656 m
19	n-$BuSnCl(SPym)_2$	1560 vs	1546 vs	1375 vs	—	809 m	773 m 767 m	747 s	651 m 635 m
20	$PhSnCl(SPym)_2$	1575 s 1570 s	1542 vs	1376 vs	—	805 w 793 w	767 m 759 m	747 m 738 m	656 m 652 m
21	$MeSnCl_2(SPym)$	1568 sh	1556 vs	1382 vs	—	783 m	761 s	747 s	653 s
22	n-$BuSnCl_2(SPym)$	1566 vs	1551 vs	1381 vs	—	803 m	767 m	749 m	648 m
23	$Sn(SPy)_4$	1591 vs 1575 vs	1550 s 1545 s	1450 vs 1444 vs 1439 vs	1426 vs 1419 vs 1414 vs	782 s 767 vs	749 s 742 s 730 m	735 m 732 s 726 s	644 m 628 m 622 w
24	$SnCl_2(SPy)_2$[b]	1579 vs	1551 s	1441 vs	1426 vs	776 vs	759 vs	724 vs	649 s
25	$Sn(SPym)_4$	1573 s	1554 s 1545 s	1376 vs	—	809 w 800 m	779 w 761 s	746 s 738 s	657 m 628 m
26	$SnCl_2(SPym)_2$[b]	1561 s	1538 s	1372 vs	—	808 m	761 s	745 s	657 m
—	PySSPy[b]	1569 vs	1556 vs	1443 vs	1417 vs	766 sh	754 vs	715 vs	616 s
—	PymSSPym	1560 vs	1550 vs	1384 vs 1373 vs	—	795 s 807 s	767 s 774 s	742 vs	627 vs

[a] See Table 1. Abbreviations: w, weak; m, medium; s, strong; v, very. A–H: classes of vibrational bands, tentatively assigned here in relation to Ref. 32. [b] PySSPy: Ref. 1. The vibrational data determined here and reported essentially correspond to literature values for: **16**, Ref. 23; **24**, Refs 25, 33; **26**. Ref. 23; PySSPy, Ref. 25.

with PySSPy and PymSSPym, respectively, indicating N→Sn coordination according to literature reports.[1, 42, 43] The absorptions of $RSnClL_2$ **10**–**12** and **18**–**20**, and $RSnCl_2L$ **13**, **14**, **21** and **22**, show in part a stronger shift to higher wavenumbers than $RSnL_3$ derivatives **1**–**9** and **15**–**17**. This is especially evident when considering the bands A, C and D of the series $MeSn(SPy)_3$–$MeSnCl(SPy)_2$–$MeSnCl_2(SPy)$ (**1**, **10**, **13**), and can be related with an increase in the Lewis acidity of Sn and of the strength of N→Sn coordination on substitution of SPy by Cl. The splitting of bands observed with SnL_4 (**23**, **25**), $RSnL_3$ (**1**–**9**; **15**–**17**) and $RSnClL_2$ (**10**–**12**; **19**, **20**) may be correlated with differences in the coordination strength of ligands L, the higher (lower) wavenumbers of A to H being characteristic for more (less) strongly coordinated ligands. However, the lowest value of the split bands of **23** and **25** do not exclude a non-chelating monodentate ligand L being present. Raman lines of derivatives of the type $RSnClL_2$ were observed in the range around 280 cm^{-1} which is characteristic for ν(SnCl) of compounds with non-bridging Cl ligands.[44] Comparable lines were found in derivatives $R_2SnCl(SPy)$ for which non-bridging Cl ligands were proposed, and this was corroborated by the X-ray structure determination of $Ph_2SnCl(SPy)$.[1]

In the class of $RSn(SPy)_3$ complexes, in the *o*-substituted aryl derivatives **6** and **8** splitting of bands is distinctly greater than in the *p*-substituted heptacoordinated derivatives **7** and **9**; as shown for **9** by an X-ray structure determination, all three SPy ligands are bidentately bonded to tin, and the Sn–N as well as the S–C distances are not significantly different.[26] In the benzyl derivatives **3** and **4**, splitting similar to that in the *o*-substituted aryl derivatives is observed. Thus, in comparison with the other $RSn(SPy)_3$ compounds, marked differences in bonding of SPy ligands in **3**, **4**, **6** and **8** should be expected (*vide infra*).

The structure of $SnCl_2(SPy)_2$, **24**, was shown by X ray determination[39] and by Mössbauer measurements[33] to be characterized by hexacoordination of Sn and by *cis*-Sn–Cl, *cis*-Sn–N and *trans*-Sn–S bonds [(IX), Table 6]. Since compounds **24** and **26** [$SnCl_2(SPym)_2$] show similar shifts of the IR bands in comparison with the appropriate disulfides, we propose the same type of molecular structure for **26**.[23]

Structures in solution

Vibrational bands in $CDCl_3$ solutions, types A–D, for the complexes **1**–**22**, fully correspond to data determined in the solid state (Table 7). As a consequence, chelation of the ligands L through N and S donors will persist in $CDCl_3$, analogously to findings for R_2Sn^{IV}–SPy complexes.[1] In contrast to a part of the solid-state spectra of the mono-organotin complexes, splitting of bands A–D in the solution-state spectra is not observed, and only one, though broadened, band appears, which suggests the presence of uniformly bonded ligands. This, however, seems not to be true for $Sn(SPy)_4$ (**23**); splitting of bands is observed in the solid (Table 7), and in the solution state and, in addition, bands shift on going from the solid to solution state. Therefore, different bonding of ligands may be inferred [e.g. structure (VIII), Table 6, and further dissociation of N→Sn bonds].

The occurrence of N→Sn coordination in the RSn^{IV} complexes **1**–**22** in $CDCl_3$ solution is also inferred by NMR spectroscopy. The comparison of the $\delta(^1H)$ shift values of the H atoms of the ligands L and those of the appropriate disulfides (Table 8) allows us to interpret the variations in terms of N→Sn coordination[1] of the ligands in the thiol form. It is observed that $\delta(^1H)$ values of H(6) in SPy derivatives **1**–**14**, and of H(4,6) in SPym complexes **15**–**22**, are consistently shifted to high field; minor shifts are detected for H(4) (L = SPy) and H(5) in $RSnL_3$ (L = SPy, SPym), **1**–**9** and **15**–**17**, and for H(5) in $RSnCl(SPy)_2$, **10**–**12** (Table 8). Since H(6) of SPy and H(4,6) in SPym are nearest to the coordinating N in the chelated species (Fig. 5), these data would suggest the persistence of N→Sn coordination in $CDCl_3$ solutions.[1] The $\delta(^1H)$ signals of **23** in $CDCl_3$ are very broad, even at low temperature; the shift value of H(6) of 8.04 ppm would indicate the presence of chelating SPy ligands (*vide infra*).

When the ^{13}C NMR data of the complexes and of the disulfides are compared, the same inference results as for the ^1H NMR data: Sn in **1**–**22** in $CDCl_3$ solution is chelated by SPy and SPym in the thiol form. Analogously to $\delta(^{13}C)$ values for R_2Sn^{IV}–SPy complexes,[1] δ values of C(6) in RSn–SPy complexes **1**–**14** and of C(4,6) in RSn–SPym complexes **15**–**22** are consistently shifted upfield, while C(2) in SPy and SPym derivatives and C(3) in SPy complexes show downfield shifts (Table 9); variations are quite

limited in the $RSnCl_2(SPym)$ complexes **21** and **22**, C(2) and C(6) being the nearest neighbors to N (Fig. 5). It is inferred that the δ variations described above reflect the occurrence of N→Sn coordination.[1]

The representative ^1H and ^{13}C data, measured for $RSnL_3$ complexes **1**, **5**, **15** and **17** (Tables 8 and 9) in DMSO solutions, correspond to data obtained from $CDCl_3$ solutions. This suggests that the chelated species are present in DMSO also, and that DMSO itself does not coordinate to Sn[1].

Table 8 ^1H HMR spectral data [δ (PPM) with respect to TMS] for mono-organotin(IV) derivatives of 2-mercaptopyridine and 2-mercaptopyrimidine, and of PySSPy and PymSSPym

			SPy, SPym[b]				
Compound		R[a]	H(3)	H(4)	H(5)	H(6)	Solvent
1	$MeSn(SPy)_3$[c]	1.28 s	7.34 d	7.46 t	6.89 t	7.93 d	$CDCl_3$
		1.24 s	7.37 d	7.65 t	7.07 t	7.77 d	DMSO-d_6
2	n-$BuSn(SPy)_3$	0.80 t, 1.29 sex, 1.56–1.67 m, 1.87–1.96 m	7,31 d	7.44 t	6.87 t	7.99 d	$CDCl_3$
3	$BzSn(SPy)_3$	6.86–7.14 m, 3.24 s	7.28 d	7.42 t	6.82 t	7.84 d	$CDCl_3$
4	*o*-$ClBzSn(SPy)_3$	6.85–7.20 m, 3.41 s	7.25 d	7.40 t	6.81 t	7.93 d	$CDCl_3$
5	$PhSn(SPy)_3$	7.26–7.30 m, 7.74–7.77 m	7.32 d	7.42 t	6.84 t	7.93 d	$CDCl_3$
		7.25–7.98 m	(d)	(d)	7.06 t	(d)	DMSO-d_6
6	*o*-$ClPhSn(SPy)_3$	7.04–7.25 m, 7.72–7.86 m	7.30 d	7.40 t	6.83 t	8.09 b	$CDCl_3$
7	*p*-$ClPhSn(SPy)_3$	7.22 d, 7.70 d	7.31 d	7.42 t	6.84 t	7.90 d	$CDCl_3$
8	*o*-$TolSn(SPy)_3$	2.65 s	7.28 d	7.37 t	6.80 t	8.08 d	$CDCl_3$
		7.06–7.17 m, 7.67–7.72 m					
9	*p*-$TolSn(SPy)_3$	2.26 s, 7.07 d, 7.65 d	7.31 d	7.41 t	6.81 t	7.90 d	$CDCl_3$
10	$MeSnCl(SPy)_2$	1.30 s	7.38 d	7.60 t	7.01 t	8.08 d	$CDCl_3$
11	n-$BuSnCl(SPy)_2$	0.88 t, 1.38 sex, 1.57–1.74 m 1.77–1.89 m	7.38 d	7.59 t	6.99 t	8.09 d	$CDCl_3$
12	$PhSnCl(SPy)_2$	7.34–7.37 m, 7.77–7.80 m	7.41 d	7.58 t	7.00 t	8.15 d	$CDCl_3$
13	$MeSnCl_2(SPy)$	1.49 s	7.38 d	7.56 t	7.22 t	7.97 d	$CDCl_3$
14	n-$BuSnCl_2(SPy)$	0.94 t, 1.49 sex, 1.72–1.95 m 2.10–2.18 m	7.37 d	7.74 t	7.21 t	7.98 d	$CDCl_3$
15	$MeSn(SPym)_3$[c]	1.57 s	—	8.39 d	6.98 t	8.39 d	$CDCl_3$
		1.58 s	—	8.47 d	7.26 t	8.47 d	DMSO-d_6
16	n-$BuSn(SPym)_3$[e]	0.86 t, 1.38 sex, 1.68–1.84 m, 2.18–2.26 m	—	8.39 d	6.97 t	8.39 d	$CDCl_3$
17	$PhSn(SPym)_3$	7.32–7.35 m, 7.86–7.89 m	—	8.35 d	6.91 t	8.35 d	$CDCl_3$
		7.52–7.66 m, 7.84–7.89 m	—	8.42 d	7.21 t	8.42 d	DMSO-d_6
18	$MeSnCl(SPym)_2$	1.46 s	—	8.47 d	7.10 t	8.47 d	$CDCl_3$
19	n-$BuSnCl(SPym)_2$	0.91 t, 1.43 sex, 1.66–1.99 m, 2.03 t	—	8.47 d	7.08 t	8.47 d	$CDCl_3$
20	$PhSnCl(SPym)_2$	7.34–7.52 m, 7.72–7.80 m	—	8.49 t	7.08 t	8.49 d	$CDCl_3$
21	$MeSnCl_2(SPym)$	1.56 s	—	8.47 d	7.25 t	8.47 d	$CDCl_3$
22	n-$BuSnCl_2(SPym)$	0.96 t, 1.51 sex, 1.81–1.89 m, 2.18–2.24 m	—	8.45 d	7.22 t	8.45 d	$CDCl_3$
23	$Sn(SPy)_4$	—	6,89 s, b	7.38–7.42 m, b		8.04 s, b	$CDCl_3$
—	PySSPy[f]	—	7.54–7.64 m		7.11 t	8.45 d	$CDCl_3$
			7.64 d	7.81 t	7.29 t	8.51 d	DMSO-d_6
—	PymSSPym		—	8.59 d	7.14 t	8.59 d	$CDCl_3$
				8.73 d	7.39 t	8.73 d	DMSO-d_6

Abbreviations: s, singlet; d, doublet; t, triplet; sex, sextet; m, multiplet; b, broad.
Compounds **24**–**26**: data not determined owing to insufficient solubility (see Results and Discussion section).
[a] δ of protons in the organic group R bound to Sn. See Table 1. [b] δ of protons in SPy and SPym, respectively; see Table 1. For numbering of protons, see Fig. 5. Assignments according to data for MeSPy and MeSPym in Ref. 45. [c] Coupling constants $^2J(^{119}Sn–^1H)$ in $CDCl_3$/DMSO-d_6 (Hz): **1**, 98.2/104; **15**, 97.3/107. [d] Overlap. [e] Ref. 23, data in DMSO-d_6. [f] Ref. 1.

Table 9 ^{13}C NMR spectral data [δ ppm) with respect to TMS] for mono-organotin(IV) derivatives of 2-mercaptopyridine and 2-mercaptopyrimidine, and of PySSPy and PymSSPym

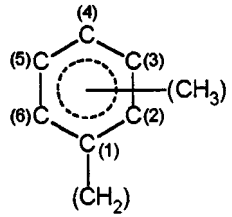
		R[a]				SPy, SPym[b]						
Compound		C(1)	C(2)	C(3)	C(4)	C(2)	C(3)	C(4)	C(5)	C(6)	Solvent	$^1J(^{119}Sn-^{13}C)$ (Hz)
1	$MeSn(SPy)_3$	18.6	—	—	—	165.8b	125.5	137.7	117.7	144.0	$CDCl_3$	—
		19.2	—	—	—	164.0	123.9	138.5	118.0	144.4	DMSO-d_6	—
2	n-$BuSn(SPy)_3$	38.1	28.2	25.7	13.7	165.5	124.8	137.7	117.9	144.6	$CDCl_3$	—
3	$BzSn(SPy)_3$[c]	139.7	127.9	128.2	124.6	165.0	124.8	137.8	117.9	144.6	$CDCl_3$	654/682
4	*o*-$ClBzSn(SPy)_3$[d]	138.1	132.7	128.6	125.9	164.9	124.6	137.9	118.0	144.6	$CDCl_3$	610/638
5	$PhSn(SPy)_3$	151.2	132.5	128.3	128.8	164.9	124.8	137.9	118.1	144.5	$CDCl_3$	1071
		151.3	131.9	128.4	128.8	163.9	124.0	138.9	118.9	144.5	DMSO-d_6	—
6	*o*-$ClPhSn(SPy)_3$[e]	150.3	139.1	135.0	126.7	163.9	124.7	137.8	118.3	144.6	$CDCl_3$	—
7	*p*-$ClPhSn(SPy)_3$	149.7	133.9	128.2	134.8	164.7	124.6	138.1	118.3	144.4	$CDCl_3$	—
8	*o*-$TolSn(SPy)_3$[f]	150.5	142.6	133.3	125.3	163.7	124.8	137.7	118.3	144.6	$CDCl_3$	—
9	*p*-$TolSn(SPy)_3$[g]	147.8	132.4	129.0	138.5	165.0	124.6	137.7	118.0	144.4	$CDCl_3$	—
10	$MeSnCl(SPy)_2$	19.7	—	—	—	166.4	123.8	139.9	118.5	142.8	$CDCl_3$	760
11	n-$BuSnCl(SPy)_2$	38.7	27.9	25.4	13.6	166.5	124.3	139.6	118.4	142.8	$CDCl_3$	791
12	$PhSnCl(SPy)_2$	151.0	132.3	128.6	129.6	166.0	124.1	140.1	118.7	142.9	$CDCl_3$	—
13	$MeSnCl_2(SPy)$	11.7	—	—	—	161.0	122.6	140.6	120.5	144.9	$CDCl_3$	—
14	n-$BuSnCl_2(SPy)$	32.3	27.0	25.3	13.4	161.0	122.7	140.5	120.4	145.2	$CDCl_3$	704
15	$MeSn(SPym)_3$	15.5	—	—	—	175.4	—	156.6	115.9	156.6	$CDCl_3$	—
		17.8	—	—	—	174.2	—	157.1	116.3	157.1	DMSO-d_6	—
16	n-$BuSn(SPym)_3$[h]	35.8	28.1	25.7	13.7	175.8	—	156.6	115.8	156.6	$CDCl_3$	755
17	$PhSn(SPym)_3$	149.3	132.7	128.8	129.5	176.0	—	156.4	115.7	156.4	$CDCl_3$	—
		149.4	131.9	128.9	129.5	174.5	—	157.0	116.5	157.0	DMSO-d_6	—
18	$MeSnCl(SPym)_2$	16.8	—	—	—	175.7	—	156.7	116.2	156.7	$CDCl_3$	—
19	n-$BuSnCl(SPym)_2$	36.7	27.8	25.4	13.5	176.0	—	156.6	116.1	156.6	$CDCl_3$	—
20	$PhSnCl(SPym)_2$	148.6	132.4	129.0	130.3	176.9	—	156.6	116.0	156.6	$CDCl_6$	—
21	$MeSnCl_2(SPym)$	12.1	—	—	—	172.3	—	157.4	117.5	157.4	$CDCl_3$	727

Table 9 Continued

Compound		R[a]				SPy, SPym[b]						
		C(1)	C(2)	C(3)	C(4)	C(2)	C(3)	C(4)	C(5)	C(6)	Solvent	$^1J(^{119}Sn-^{13}C)$ (Hz)
22	n-$BuSnCl_2$(SPym)	32.8	27.4	25.4	13.4	172.8	—	157.5	117.3	157.5	$CDCl_3$	—
23	$Sn(SPy)_4$	—	—	—	—	162.5b	123.5b	137.7	119.0b	145.1b	$CDCl_3$	—
—	PySSPy	—	—	—	—	158.5	120.9	137.2	119.3	149.3	$CDCl_3$	—
						157.3	121.6	137.9	119.4	149.6	DMSO-d_6	—
—	PymSSPym	—	—	—	—	169.1	157.6	118.0	—	157.6	$CDCl_3$	—
						167.8	158.4	119.4	—	158.4	DMSO-d_6	—

Compounds **24**–**26**: insufficient solubility (see Results and Discussion section).

[a] δ values for C atoms of the group R bound to tin (see Table 1). For R = Ph or *p*-substituted phenyl: C(2) = C(6), C(3) = C(5). [b] δ values (b = broad signal) for C atoms of SPy and SPym, respectively; for numbering of C, see Fig. 5; assignments according to data for MeSPy and MeSPym in Refs 30, 45–47. [c] $\delta(CH_2)$: 45.5 ppm. [d] $\delta(CH_2)$: 41.3 ppm; δ(C(5)): 126.1; δ(C(6)): 130.1 ppm. [e] δ(C(5)): 128.8; δ(C(6)): 129.6 ppm. [f] $\delta(CH_3)$: 23.1 ppm; δ(C(5)): 129.9 ppm; δ(C(6)): 126.6 ppm. [g] $\delta(CH_3)$: 21.3 ppm. [h] Ref. 23, data in DMSO-d_6.



The coordination at Sn may be estimated also through $\delta(^{119}Sn)$ values by fingerprinting. In fact, for example, the following $\delta(^{119}Sn)$ ranges (in ppm) have been reported to hold for RSn^{IV}: seven-coordinated Sn, -525 to -786 ppm;[48] six coordinated Sn, -333 to -395 ppm.[49] The $\delta(^{119}Sn)$ range $+25$ to -329 ppm has been reported for R_2Sn^{IV} and R_3Sn^{IV} complexes with five-coordinated Sn.[49] From the δ (^{119}Sn) values in Table 10, it appears that the values for nominally seven-coordinated tin in the $RSnL_3$ complexes **1**–**9** and **15**–**17** are consistently shifted to higher fields with respect to the reported range. Instead, δ values for the $RSnClL_2$ compounds **10**–**12** and **18**–**20** with six-coordinated tin, and for $RSnCl_2L$ compounds **13**, **14**, **21** and **22** with five-coordinated tin, insert into the above literature ranges. Besides, the expected δ difference between R = alkyl and R = Ph[49, 50] is observed to occur in the class of SPym complexes listed in Table 10. The trend detected for $RSnL_3$ (Table 10) corresponds to findings for $R_2Sn(SPy)_2$ and $R_2SnCl(SPy)$[1] and has been ascribed to the electronic effects of S→Sn coordination.[1] In comparison with SPy derivatives **1**–**14**, the appropriate SPym derivatives **15**–**22** show generally a shift of $\delta(^{119}Sn)$ to lower field. This is related to weaker coordination strength of the SPym ligands; also the low-field shift observed on going from hexacoordinated $RSnCl(SPym)_2$ **18**–**20** to heptacoordinated $RSn(SPym)_3$ **15**–**17** is suggested to be correlated with a labilization of N→Sn coordination of the SPym ligand.

Table 10 ^{119}Sn NMR spectral data [δ (ppm), with respect to $SnMe_4$] of mono-organotin(IV) derivatives of 2-mercaptopyridine and 2-mercaptopyrimidine in $CDCl_3$ (if not otherwise indicated)

Compound[a]		δ (^{119}Sn)
1	$MeSn(SPy)_3$	-398
		-469[b]
2	n-$BuSn(SPy)_3$	-387
3	$BzSn(SPy)_3$	-414
4	*o*-$ClBzSn(SPy)_3$	-405
5	$PhSn(SPy)_3$	-448
		-504[b]
6	*o*-$ClPhSn(SPy)_3$	-420
7	*p*-$ClPhSn(SPy)_3$	-445
8	*o*-$TolSn(SPy)_3$	-400
9	*p*-$TolSn(SPy)_3$	-446
10	$MeSnCl(SPy)_2$	-375
11	n-$BuSnCl(SPy)_2$	-368
12	$PhSnCl(SPy)_2$	-429
13	$MeSnCl_2(SPy)$	-167
14	n-$BuSnCl_2(SPy)$	-172
15	$MeSn(SPym)_3$	-267
		-372[b]
16	n-$BuSn(SPym)_3$	-280
17	$PhSn(SPym)_3$	-402
		-491[b]
18	$MeSnCl(SPym)_2$	-318
19	n-$BuSnCl(SPym)_2$	-327
20	$PhSnCl(SPym)_2$	-425
21	$MeSnCl_2(SPym)$	-152
22	n-$BuSnCl_2(SPym)$	-159
23	$Sn(SPy)_4$	-497

[a] See Table 1. Compounds **24**–**26**: insufficient solubility (see Results and Discussion section). [b] DMSO-d_6 as solvent.

The $\delta(^{119}Sn)$ values obtained from solutions of **1**, **5**, **15** and **17** in DMSO are at higher field in comparison with shifts in $CDCl_3$; however, the extent of shifting is too small to assume appreciable additional coordination by solvent molecules (Table 10).

The $\delta(^{119}Sn)$ signal of $Sn(SPy)_4$ (**23**) in CH_2Cl_2 was found at -516 ppm,[24] in $CDCl_3$ we measured a value of -497 ppm (Table 10). In accordance with Ref. 24, a coordination number greater than four is suggested for tin. From the ^{13}C NMR shift values it was concluded that the SPy ligands are equivalent, or are made equivalent by an averaging process.[24] Since tin in solid **23** was found to be hexacoordinated,[24] and considering the observation that tin in organotin mercaptopyridine compounds, whose solid-state structure is known, generally retains its coordination number in non-coordinating solvents, it seems reasonable to propose that in **23** tin has formally a coordination number of six.

Conclusions

The molecular structures of $MeSn(SPy)_3$ (Fig. 1) and $PhSn(SPy)_3$ (Fig. 2), where SPy acts as a bidentate ligand coordinating Sn through chelation by S and N atoms, according to point-charge model rationalization of the ^{119}Sn nuclear quadrupole splitting ΔE, holds for the $RSnL_3$ complexes investigated here in the solid state, except for benzyltin and *o*-aryltin compounds which are octahedral instead of pentagonal bipyramidal. By the same procedure, analogous coordination modes are inferred for octahedral $RSnClL_2$ and trigonal bipyramidal $RSnCl_2L$. The solid-state monomeric species (according also to the dynamics of ^{119}Sn nuclei determined for

representative terms[2]) persist in $CDCl_3$ and $CHCl_3$, as well as in DMSO for some $RSnL_3$ complexes selected as examples; according to IR and ^1H, ^{13}C and ^{119}Sn NMR spectroscopic data, ligands SPy and SPym act as chelating agents in solution phases, and RSn(IV) complexes mainly maintain the solid-state structure also in solution.

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