ELSEVIER

Journal of Organometallic Chemistry 513 (1996) 77–83

Journal of Organometallic Chemistry

Synthesis, characterisation and X-ray crystal structures of diorganotin(IV) complexes with 2-mercaptopyridine derivatives

M.D. Couce [a], G. Faraglia [a], U. Russo [a,*], L. Sindellari [a], G. Valle [b]

[a] *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Via Loredan 4, I-35131 Padova, Italy*
[b] *Centro di Ricerche sui Biopolimeri del CNR, Via Marzolo 1, I-35131 Padova, Italy*

Received 7 July 1995

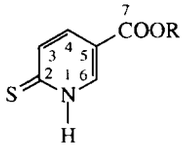
Abstract

By reaction of diorganotin(IV) dihalides with esters of 2-mercapto-pyridine-5-carboxylic acid NH(CS)CHCHC(COOR)CH (R = Et, HTNEE; R = ^{i}Pr, HTNIPE) the complexes $R_2SnX(L)$ and $R_2Sn(L)_2$ (L = TNEE or TNIPE; R = Me, Et, Bu or Ph) have been prepared and characterised by IR, NMR, and Mössbauer spectroscopies. The structures of Et_2SnBr(TNIPE) and Me_2SnCl(TNEE) have been determined by an X-ray single crystal diffraction study. Both ligands behave as bidentate chelating groups forming a four-member ring with very similar and small N–Sn–S bite angles. The tin atom is pentacoordinated in a severely distorted trigonal bipyramidal geometry with apical X–Sn–N angles of 151.9(2)° for Et_2SnBr(TNIPE) and 154.9(1)° for Me_2SnCl(TNEE) and equatorial C–Sn–C angles of 127.4(6)° and 129.8(2)° respectively. On the basis of ^{119}Sn Mössbauer data, analogous structures are proposed for all the complexes.

Keywords: Diorganotin(IV); X-ray structure; Mössbauer; NMR; Esters of 2-mercaptopyridine-5-carboxylic acid

1. Introduction

The studies on organotin complexes with 2-mercaptopyridine (HMP) essentially concern diorganotin derivatives of the type $R_2Sn(MP)_2$ or $R_2SnCl(MP)$ [1–4]. The coordination polyhedron in $Me_2Sn(MP)_2$ can be described as either skew trapezoidal bipyramid or bicapped tetrahedron owing to the strong distortions caused in the coordination octahedron by the elongated Sn–S and Sn–N bonds [1]. The complexes $(cyclohexyl)_2Sn(MP)_2$ and $Ph_2Sn(MP)_2$ present analogous features, the trapezoidal plane of the MP residues contain cis Sn–S and Sn–N bonds, whereas the C–Sn–C angle is strongly bent (about 126° C) [2,3]. Recently, the monosubstituted complex $Ph_2SnCl(MP)$, in which the tin atom is pentacoordinated in a severely distorted trigonal bipyramidal geometry, has been reported [4]. In a previous paper we reported phenyltin complexes with a series of 2-mercaptopyridine-5-alkylesters having general formulae $Ph_3Sn(L)$ and $Ph_2SnCl(L)$ [5].



HL

R = Methyl ⟶ HTNME
R = Ethyl ⟶ HTNEE
R = *iso*Propyl ⟶ HTNIPE

The crystal structure of Ph_2SnCl(TNEE) is extremely similar to that of $Ph_2SnCl(MP)$, no interaction between tin and carboxylato oxygens being observed. The interest in tin complexes with such a class of S, N donors depends on the coordination versatility and on the possible biochemical implications. Despite the minor activity of tin complexes compared with the usual platinum drugs, studies in this field are in progress because tin-based drugs are generally less toxic. Among organotins, antitumour properties are particularly evident for species containing the R_2Sn^{2+} moiety and seem to

* Corresponding author.

0022-328X/96/$15.00 © 1996 Elsevier Science S.A. All rights reserved
SSDI 0022-328X(95)05985-7

depend on the alkyl group (from methyl to *n*-butyl), longer chain derivatives being generally less active [6]. Moreover, the toxicity of organotin complexes with potential S, N donors depends on both ligand and tin substituents [7]. Some $R_2Sn(ox)_2$ (ox = oxinato) derivatives have been found active, whereas the scarce activity of the tiooxinato analogues was supposed to depend on the covalent character of the Sn–S bond [8]. Hydrolytic processes are determinant, and the ligand seems to modulate the release of tin moiety in the site of the action. As the activity tests have generally been carried out on R_2SnL_2 (L = bidentate anion) samples, we thought it would be interesting to characterise R_2SnL_2 and R_2SnXL (X = halide; L = mercaptopyridine ester anion) species containing ligands with pharmacological properties [9,10] and that are supposed to undergo different hydrolytic reactions. Moreover, the presence of variously combined substituents on tin and on the ester moiety could change the sample absorption by different cells. This paper reports the synthesis and characterisation of the complexes $R_2SnX(L)$ and $R_2Sn(L)_2$ (R = Me, Et, Bu or Ph; X = Cl or Br; L = TNEE or TNIPE), along with the X-ray crystal structures of Et_2SnBr(TNIPE) and Me_2SnCl(TNEE).

2. Experimental section

2.1. Materials

Dimethyltin dichloride (Ventron), dimethyltin dibromide (Ventron), diethyltin dichloride (Ventron), diethyltin dibromide (Ventron), dibutyltin dichloride (Aldrich), dibutyltin dibromide (Ventron), diphenyltin dichloride (Aldrich), 2-mercaptopyridine-5-carboxylic acid (Aldrich), triethylamine (Aldrich) and thiourea (Sigma) 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 [11,12].

2.2. Preparation of the compounds

The complexes $R_2SnX(L)$ (R = Me, Et, Bu or Ph; X = Cl or Br and L = TNIPE or TNEE) (Table 1) were prepared by addition of R_2SnX_2 (1.0 mmol) to an ethanol solution of triethylamine (1.0 mmol) and ligand (1.0 mmol). After 2 days under stirring, the obtained solid was filtered off, washed with EtOH, and dried in vacuo. Crystals of Et_2SnBr(TNIPE) and Me_2SnCl(TNEE) suitable for X-ray analysis were obtained by slow evaporation of the filtered mother solutions. The $Ph_2SnBr(L)$ complexes were obtained by addition of an acetone solution of Ph_2SnBr_2 (1.0 mmol in 5 ml) to an ethanol solution of H(L) (1.0 mmol in 10 ml). The colourless solution, evaporated in a rotavapour to half the initial volume, separated white microcrystals of the appropriate product.

The $R_2Sn(L)_2$ complexes were prepared by addition of R_2SnX_2 (1.0 mmol) to an ethanol solution of triethylamine (2.0 mmol) and H(L) (2.0 mmol). A white solid was immediately formed, but the suspension was stirred for 2 days. The solid was then filtered off, washed with EtOH, and dried in vacuo.

2.3. Physical measurements

Analytical data, obtained by a Carlo Erba 1108 apparatus, are reported in Table 1. The melting points were measured with a Büchi apparatus. IR spectra were recorded in Nujol mulls or KBr pellets with Nicolet FT IR 5SXC (4000–400 cm^{-1}) and 20F (400–100 cm^{-1}) spectrometers. Mössbauer spectra were recorded at 80.0 K in a Harwell cryostat; the $Ca^{119}SnO_3$ source (NEN)

Table 1
Analytical [a] and physical data

Compound [b]	M.p. (°C)	C (%)	H (%)	N (%)	S (%)
Me_2SnCl(TNIPE)	88	34.8 (34.7)	4.4 (4.2)	3.9 (3.7)	8.2 (8.4)
Me_2SnBr(TNIPE)	101	31.2 (31.1)	3.8 (3.8)	3.3 (3.3)	7.5 (7.5)
Et_2SnBr(TNIPE)	80	34.4 (34.4)	4.4 (4.4)	3.1 (3.1)	7.2 (7.1)
Ph_2SnBr(TNIPE)	127	45.8 (45.9)	3.5 (3.6)	2.4 (2.5)	5.5 (5.8)
$Me_2Sn(TNIPE)_2$	135	44.2 (44.4)	4.8 (4.8)	5.2 (5.2)	11.6 (11.8)
$Et_2Sn(TNIPE)_2$	138	46.5 (46.4)	5.2 (5.3)	4.8 (4.9)	11.2 (11.2)
$Bu_2Sn(TNIPE)_2$	99	49.7 (49.8)	6.6 (6.4)	4.6 (4.5)	10.4 (10.8)
$Ph_2Sn(TNIPE)_2$	181	54.0 (54.1)	4.3 (4.5)	4.1 (4.2)	9.6 (9.6)
Me_2SnCl(TNEE)	123	32.5 (32.8)	3.8 (3.5)	3.8 (3.8)	8.6 (8.7)
Me_2SnBr(TNEE)	115	29.4 (29.2)	3.6 (3.4)	3.4 (3.4)	7.9 (7.8)
Ph_2SnBr(TNEE)	95	44.1 (44.9)	3.4 (3.4)	2.3 (2.6)	6.0 (6.0)
$Me_2Sn(TNEE)_2$	129	42.0 (41.9)	4.4 (4.7)	5.4 (5.4)	12.8 (12.4)
$Et_2Sn(TNEE)_2$	114	44.5 (44.2)	5.2 (5.2)	5.2 (5.2)	12.4 (12.7)
$Bu_2Sn(TNEE)_2$	101	48.0 (48.1)	6.0 (6.0)	4.7 (4.7)	10.9 (10.7)

[a] Required values are given in parentheses. [b] All complexes are white.

Table 2
Crystal and intensity data

Parameter	Et_2SnBr(TNiPE)	Me_2SnCl(TNEE)
Formula	$C_{13}H_{20}BrNO_2SSn$	$C_{10}H_{14}ClNO_2SSn$
Formula weight	452.8	366.4
a (Å)	19.565(2)	13.614(2)
b (Å)	12.457(2)	12.731(2)
c (Å)	7.380(1)	8.577(1)
α (deg)	—	—
β (deg)	—	106.4(1)
γ (deg)	—	—
Cell volume (Å^3)	1811.7(4)	1426.1(8)
D_c (g cm^{-3})	1.66	1.71
Z	4	4
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
F(000) (elec.)	222	180
μ (cm^{-1})	37.09	21.14
Wavelength (Mo K α) (Å)	0.7107	0.7107
Scan method	θ–2θ	θ–2θ
2θ range (deg)	4.0–56.0	4.5–56.0
Unique reflections	2507	3320
Observed reflections	1205 with $F > [3\sigma(F)]$	2041 with $F > [3\sigma(F)]$
Corrections applied	Lorentz and polarization	
R	0.038	0.034
Rw	0.041	0.035
Weighting scheme	$1.000/[\sigma^2(F) + 0.001308F^2]$	$1.000/[\sigma^2(F) + 0.000943F^2]$
Highest shift/e.s.d.	0.04	0.200
Highest map residual (e Å^{-3})	0.43	0.582

was kept at room temperature and moved at constant acceleration with a triangular wave form. Suitable computer programs were employed in the fitting procedure of the experimental points to Lorentzian lineshapes. ^1H and ^{13}C NMR spectra were recorded on a Jeol FX 90Q spectrometer operating in Fourier transform mode; measurements were performed in a 5 mm spinning tube (reference TMS).

Table 3
Fractional coordinates for Et_2SnBr(TNiPE) with equivalent isotropic thermal parameters (Å^2). U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	x	y	z	U_{eq}
Sn	0.43173(4)	0.46608(6)	0.2067(1)	0.0749(3)
Br	0.41974(6)	0.2684(1)	0.3084(2)	0.1001(5)
S	0.3186(2)	0.4564(3)	0.0612(5)	0.090(1)
O(1)	0.3084(4)	0.9809(6)	−0.052(1)	0.085(3)
O(2)	0.4121(4)	0.9597(6)	0.074(1)	0.114(4)
N(1)	0.3839(4)	0.6341(7)	0.080(1)	0.072(4)
C(1)	0.3943(5)	0.7395(9)	0.066(2)	0.076(5)
C(2)	0.3455(5)	0.8076(8)	0.008(2)	0.063(4)
C(3)	0.2829(5)	0.767(1)	−0.051(2)	0.077(5)
C(4)	0.2726(5)	0.658(1)	−0.035(2)	0.083(5)
C(5)	0.3246(5)	0.5943(9)	0.027(2)	0.068(4)
C(6)	0.3601(7)	0.923(1)	0.013(2)	0.076(5)
C(7)	0.3161(6)	1.0972(9)	−0.040(2)	0.088(5)
C(8)	0.2437(7)	1.138(1)	−0.035(2)	0.116(7)
C(9)	0.3540(9)	1.135(1)	−0.201(3)	0.125(7)
C(10)	0.4347(8)	0.539(2)	0.463(2)	0.139(8)
C(11)	0.379(1)	0.588(2)	0.536(2)	0.17(1)
C(12)	0.5106(8)	0.461(1)	0.011(2)	0.123(7)
C(13)	0.524(1)	0.375(2)	−0.078(4)	0.21(2)

2.4. Determination of the crystal structures of Et_2SnBr(TNIPE) and Me_2SnCl(TNEE)

The X-ray diffraction patterns were recorded at room temperature on a Philips PW1100 four circle diffrac-

Table 4
Fractional coordinates for Me_2SnCl(TNEE) with equivalent isotropic thermal parameters (Å^2). U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	x	y	z	U_{eq}
Sn	0.22022(2)	0.21562(3)	0.25955(4)	0.0498(1)
Cl	0.3745(1)	0.3251(1)	0.3347(2)	0.0701(5)
S	0.1720(1)	0.2751(1)	0.5025(2)	0.0614(5)
O(1)	−0.1729(3)	−0.0654(4)	0.0977(6)	0.090(2)
O(2)	−0.2558(3)	−0.0103(3)	0.2752(5)	0.076(2)
N(1)	0.0648(3)	0.1400(3)	0.2966(5)	0.054(2)
C(1)	0.2917(5)	0.0666(5)	0.2900(8)	0.078(3)
C(2)	0.1393(4)	0.2938(4)	0.0447(8)	0.069(2)
C(3)	0.0662(4)	0.1920(4)	0.4344(7)	0.053(2)
C(4)	−0.0111(4)	0.1791(4)	0.5099(7)	0.059(2)
C(5)	−0.0915(4)	0.1136(4)	0.4379(7)	0.058(2)
C(6)	−0.0932(4)	0.0602(4)	0.2965(6)	0.052(2)
C(7)	−0.0125(4)	0.0767(4)	0.2307(6)	0.056(2)
C(8)	−0.1771(4)	−0.0115(4)	0.2107(7)	0.063(2)
C(9)	−0.3453(5)	−0.0763(6)	0.188(1)	0.095(3)
C(10)	−0.4319(5)	−0.0348(9)	0.238(1)	0.139(5)

Table 5
Bond distances (Å) and angles (deg) for $Et_2SnBr(TNiPE)$

Sn–Br	2.602(2)	Sn–S	2.462(3)
Sn–N(1)	2.488(9)	Sn–C(10)	2.10(2)
Sn–C(12)	2.11(2)	S–C(5)	1.75(1)
O(1)–C(6)	1.34(2)	O(1)–C(7)	1.47(1)
O(2)–C(6)	1.20(2)	N(1)–C(1)	1.34(1)
N(1)–C(5)	1.32(1)	C(1)–C(2)	1.35(2)
C(2)–C(3)	1.40(1)	C(2)–C(6)	1.48(2)
C(3)–C(4)	1.39(2)	C(4)–C(5)	1.37(2)
C(7)–C(8)	1.51(2)	C(7)–C(9)	1.48(2)
C(10)–C(11)	1.36(3)	C(12)–C(13)	1.29(3)
C(10)–Sn–C(12)	127.4(6)	N(1)–Sn–C(12)	92.5(5)
N(1)–Sn–C(10)	88.8(5)	S–Sn–C(12)	110.9(5)
S–Sn–C(10)	116.0(5)	S–Sn–N(1)	62.7(2)
Br–Sn–C(12)	103.5(5)	Br–Sn–C(10)	99.1(4)
Br–Sn–N(1)	151.9(2)	Br–Sn–S	89.86(9)
Sn–S–C(5)	87.4(4)	C(6)–O(1)–C(7)	116.0(9)
Sn–N(1)–C(5)	97.0(7)	Sn–N(1)–C(1)	143.9(7)
C(1)–N(1)–C(5)	118.7(9)	N(1)–C(1)–C(2)	123(1)
C(1)–C(2)–C(6)	118(1)	C(1)–C(2)–C(3)	119(1)
C(3)–C(2)–C(6)	122(1)	C(2)–C(3)–C(4)	117(1)
C(3)–C(4)–C(5)	120(1)	N(1)–C(5)–C(4)	122(1)
S–C(5)–C(4)	125.1(9)	S–C(5)–N(1)	112.8(8)
O(2)–C(6)–C(2)	123(1)	O(1)–C(6)–C(2)	112(1)
O(1)–C(6)–O(2)	125(1)	O(1)–C(7)–C(9)	108(1)
O(1)–C(7)–C(8)	104.0(9)	C(8)–C(7)–C(9)	113(1)
Sn–C(10)–C(11)	122(1)	Sn–C(12)–C(13)	121(1)

Table 6
Bond distances (Å) and angles (deg) for $Me_2SnCl(TNEE)$

Sn–Cl	2.451(2)	Sn–S	2.473(2)
Sn–N(1)	2.426(4)	Sn–C(1)	2.114(6)
Sn–C(2)	2.110(6)	S–C(3)	1.750(5)
O(1)–C(8)	1.202(8)	O(2)–C(8)	1.337(8)
O(2)–C(9)	1.495(8)	N(1)–C(3)	1.351(7)
N(1)–C(7)	1.319(6)	C(3)–C(4)	1.392(9)
C(4)–C(5)	1.376(7)	C(5)–C(6)	1.385(8)
C(6)–C(7)	1.386(8)	C(6)–C(8)	1.485(7)
C(9)–C(10)	1.46(1)		
C(1)–Sn–C(2)	129.8(2)	N(1)–Sn–C(2)	92.4(2)
N(1)–Sn–C(1)	90.9(2)	S–Sn–C(2)	113.2(2)
S–Sn–C(1)	113.1(2)	S–Sn–N(1)	64.1(1)
Cl–Sn–C(2)	99.2(2)	Cl–Sn–C(1)	98.5(2)
Cl–Sn–N(1)	154.9(1)	Cl–Sn–S	90.90(6)
Sn–S–C(3)	85.6(2)	C(8)–O(2)–C(9)	115.0(5)
Sn–N(1)–C(7)	143.7(4)	Sn–N(1)–C(3)	97.0(3)
C(3)–N(1)–C(7)	119.1(5)	S–C(3)–N(1)	113.3(4)
N(1)–C(3)–C(4)	121.6(5)	S–C(3)–C(4)	125.2(4)
C(3)–C(4)–C(5)	118.2(5)	C(4)–C(5)–C(6)	120.3(5)
C(5)–C(6)–C(8)	123.8(5)	C(5)–C(6)–C(7)	117.6(5)
C(7)–C(6)–C(8)	118.6(5)	N(1)–C(7)–C(6)	123.1(5)
O(2)–C(8)–C(6)	112.5(5)	O(1)–C(8)–C(6)	123.0(6)
O(1)–C(8)–O(2)	124.4(6)	O(2)–C(9)–C(10)	105.2(6)

tometer by using Mo Kα radiation. Crystal data for $Et_2SnBr(TNIPE)$ and $Me_2SnCl(TNEE)$ are listed in Table 2. The crystal structures were solved by using a

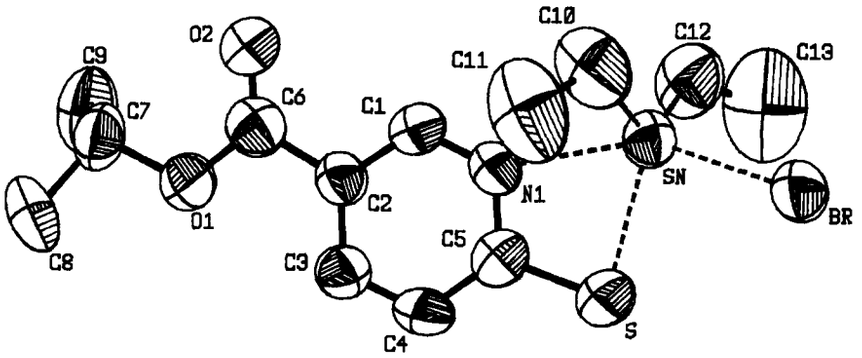


Fig. 1. Molecular structure of $Et_2SnBr(TNIPE)$ with the atom numbering scheme.

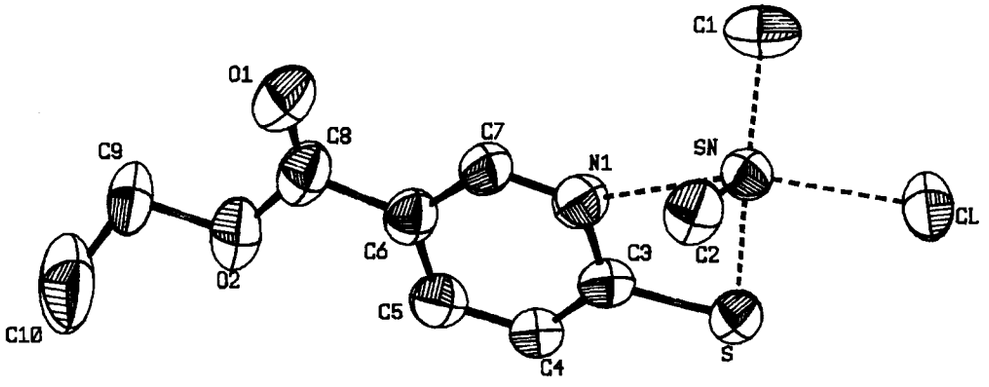


Fig. 2. Molecular structure of $Me_2SnCl(TNEE)$ with the atom numbering scheme.

Table 7
Selected IR data for ligands and complexes (cm^{-1})

	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
Me_2SnCl(TNIPE)	1720s	1589s	1460m	395w, 345w, 304m, 285s, 270m
Me_2SnBr(TNIPE)	1715s	1589s, 1551w	1461m	397w, 291ms, 274w, 254w, 226w
Et_2SnBr(TNIPE)	1710s	1588s	1458m	288m, 278mbr, 247m
Ph_2SnBr(TNIPE)	1703s	1591s	1454w	295s, 276s, 258w, 227sh, 225m
$Me_2Sn(TNIPE)_2$	1711s	1564s, 1542vvw	1455m	384m, 286s, 265m, 254sh
$Et_2Sn(TNIPE)_2$	1713s	1562s	1455m	387w, 347w, 284s, 266w, 255w
$Bu_2Sn(TNIPE)_2$	1713s	1588s	1458m	386m, 344m, 282ms, 262m
$Ph_2Sn(TNIPE)_2$	1710s	1584s	1456m	281m, 269w, 251m
Me_2SnCl(TNEE)	1717s	1588s	1471w, 1452s	371w, 278sbr
Me_2SnBr(TNEE)	1717s	1589s	1470w, 1460m	283sbr, 234vw
Ph_2SnBr(TNEE)	1713s	1591s	1454m	302w, 291w, 272s, 227s, 200w
$Me_2Sn(TNEE)_2$	1718, 1710s	1585s	1451w	290s, 270s, 243w, 213w
$Et_2Sn(TNEE)_2$	1716s, 1705sh	1585s	1456w	391m, 369w, 290s, 274s
$Bu_2Sn(TNEE)_2$	1714s	1586s, 1547vw	1456m	382, 289w, 272s

three-dimensional Patterson–Fourier synthesis. A full-matrix least squares refinement on F was computed and the function $\Sigma w[|F_o| - |F_c|]^2$ was minimised. The SHELX76 program [13] and the usual scattering factors therein enclosed were used. Lorentz and polarisation, but not absorption, corrections were applied. The non-hydrogen atoms were refined anisotropically; the hydrogen atoms were located from a difference Fourier map, and not refined.

3. Results and discussion

The complexes Ph_2SnBr(L) formed easily in ethanol–acetone by reaction of Ph_2SnBr_2 and ligand in equimolar ratio, as observed previously for Ph_2SnCl(L) [5]. Conversely, no reaction was observed when dialkyltin dihalides and ligand were mixed in ethanol or in ethanol–acetone mixtures. The synthesis of the $(alkyl)_2SnX$(L) and $R_2Sn(L)_2$ species required the presence of a base (in this case triethylamine) to favour ligand deprotonation.

3.1. Description of the structures of Et_2SnBr(TNIPE) and Me_2SnCl(TNEE)

Fractional coordinates, together with equivalent isotropic thermal parameters, are reported in Tables 3 and 4 respectively; bond distances and angles are given in Tables 5 and 6. As shown in Figs. 1 and 2, the two complexes Et_2SnBr(TNIPE) and Me_2SnCl(TNEE) present very similar structures: the coordination geometry about Sn(IV) is a severely distorted trigonal bipyramid in which the two alkyl groups and a sulphur atom form the equatorial plane, while the halogen and the ligand nitrogen occupy the apical positions. In this way the ligand behaves as a bidentate and chelates the tin atom by means of the aromatic nitrogen and the thiolic sulphur. The consequent formation of a four member ring with a very narrow S–Sn–N bond angle (62.7(2)° for Et_2SnBr(TNIPE) and 64.1(1)° for Me_2SnCl(TNEE)) is the main reason for the distortion in these compounds. In fact, similar structures have been reported for diorganotin(IV)halide complexes with closely related ligands, such as differently substituted thionicotinic esters [5] or thiopyridines [3]. In every case the three equatorial angles fall in a narrow range around 120° and the angle formed by the apical ligands varies from 156.9 to 156.1°. Very similar values are also reported for $R_2Sn(MP)_2$ adducts in which the tin atom is octahedrally coordinated [1–3].

3.2. Vibrational spectra

Characteristic IR bands for ligands and complexes are listed in Table 7. All compounds exhibit a strong absorption in the 1700–1720 cm^{-1} range, caused by the

Table 8
Mössbauer effect spectral data at 80.0 K

Compound	δ [a] ($mm\ s^{-1}$)	ΔE_Q ($mm\ s^{-1}$)	Γ ($mm\ s^{-1}$)	A_2/A_1 [b]
Me_2SnCl(TNIPE)	1.49	2.86	0.86	0.86
Me_2SnBr(TNIPE)	1.57	2.90	0.92	0.89
Et_2SnBr(TNIPE)	1.71	3.03	0.91	1.06
Ph_2SnBr(TNIPE)	1.46	2.48	0.82	0.92
$Me_2Sn(TNIPE)_2$	1.55	2.74	0.96	1.09
$Et_2Sn(TNIPE)_2$	1.70	2.67	0.81	0.97
$Bu_2Sn(TNIPE)_2$	1.66	2.74	0.79	0.91
$Ph_2Sn(TNIPE)_2$	1.52	2.40	1.04	0.79
Me_2SnCl(TNEE)	1.55	3.03	0.89	1.05
Me_2SnBr(TNEE)	1.56	2.85	0.88	0.89
Ph_2SnBr(TNEE)	1.48	2.38	0.88	0.94
$Me_2Sn(TNEE)_2$	1.57	2.74	0.83	1.16
$Et_2Sn(TNEE)_2$	1.69	2.86	0.82	0.96
$Bu_2Sn(TNEE)_2$	1.70	2.95	0.78	0.92

[a] Relative to room temperature SnO_2. [b] Area ratio between the high and low velocity component.

Table 9
^{1}H-NMR spectra for ligands and complexes (T = 25°C, δ = ppm; $CDCl_3$)

Compound	Ligand					R_2Sn
	NH [a]	H_6	H_4	H_3	CO_2R	
HTNIPE	13.6	8.20	7.86	7.52	5.15 [b], 1.27 [c]	
HTNEE	13.7	8.17	7.81	7.48	4.30 [d], 1.31 [c]	
Me_2SnCl(TNIPE)		8.53	8.14	7.36	5.26 [b], 1.35 [c]	1.12
Me_2SnBr(TNIPE)		8.53	8.15	7.37	5.26 [b], 1.36 [c]	1.21
Et_2SnBr(TNIPE)		8.56	8.14	7.36	5.26 [b], 1.35 [c]	1.73, 1.37 [e]
Ph_2SnBr(TNIPE)		8.65	8.17	— [f]	5.24 [b], 1.34 [c]	7.9–7.6, 7.5–7.3
Me_2Sn(TNIPE)$_2$		8.68	8.01	7.35	5.26 [b], 1.36 [c]	1.06
Et_2Sn(TNIPE)$_2$		8.71	8.05	7.38	5.26 [b], 1.37 [c]	1.64, 1.33 [e]
Bu_2Sn(TNIPE)$_2$		8.70	8.01	7.36	5.26 [b], 1.37 [c]	1.66, 1.40–1.35 [g], 0.82
Ph_2Sn(TNIPE)$_2$		8.64	8.04	— [f]	5.26 [b], 1.36 [c]	7.9–7.7, 7.5–7.3
Me_2SnCl(TNEE)		8.55	8.16	7.38	4.39 [d], 1.40 [c]	1.12
Me_2SnBr(TNEE)		8.55	8.15	7.37	4.36 [d], 1.38 [c]	1.21
Ph_2SnBr(TNEE)		8.66	8.19	— [f]	4.38 [d], 1.39 [c]	7.95–7.6, 7.5–7.3
Me_2Sn(TNEE)$_2$		8.70	8.02	7.36	4.37 [d], 1.39 [c]	1.05
Et_2Sn(TNEE)$_2$		8.73	8.01	7.36	4.37 [d], 1.39 [c]	1.65, 1.29
Bu_2Sn(TNEE)$_2$		8.71	8.01	7.35	4.38 [d], 1.40 [c]	1.66, 1.48, 1.33, 0.81

[a] Broad signal. [b] CH. [c] CH_3. [d] CH_2. [e] This signal overlaps the ligand methyl resonance. [f] Obscured by the phenyl proton signals. [g] Superimposed signals of β-CH_2 and γ-CH_2.

asymmetric stretching of the uncoordinated carboxylato group. The main feature in complexes is the absence of the δ(NH) absorption, at about 1620 cm^{-1} in free ligands, whereas the strong band in the 1560–1590 cm^{-1} range belongs mainly to ν(CN) [14,15]. In the far IR region the $R_2Sn(L)_2$ species generally show a strong absorption in the 290–270 cm^{-1} range, due to coordinated ligand. Such an absorption is also present in the $R_2SnCl(L)$ complexes; in some cases this overlaps the Sn–Cl band, observed in the 295–305 cm^{-1} range for $Ph_2SnCl(L)$ [5] and at about 280 cm^{-1} in the maltolato (Ma) analogues $R_2SnCl(Ma)$ (R = Me or Ph [16]).

3.3. Mössbauer results

The Mössbauer spectra of all the prepared compounds present slightly asymmetric quadrupole split doublets, with parameters that are typical for these kinds of complex (Table 8). The octahedral compounds with general formula $R_2Sn(L)_2$ present the expected trend for the isomer shift: it slightly increases on going

Table 10
^{13}C-NMR spectra for ligands and complexes (T = 25°C; δ = ppm; $CDCl_3$)

Compound	Ligand							R_2Sn
	C_2	C_3 [a]	C_4	C_5 [b]	C_6	C_7	OR	
HTNIPE	180.6	133.2	136.4	117.9	139.6	162.7	69.5 [c], 21.8 [d]	
HTNEE	180.7	133.4	136.3	117.5	139.9	163.3	61.7 [b], 14.2 [d]	
Me_2SnCl(TNIPE)	169.3	123.2	139.1	122.6	147.1	163.8	69.4 [c], 21.9 [d]	6.3
Me_2SnBr(TNIPE)	169.3	123.0	139.2	122.7	147.1	164.0	69.4 [c], 21.9 [d]	7.1
Et_2SnBr(TNIPE)	169.9	123.1	138.9	122.4	147.3	163.8	69.4 [c], 21.9 [d]	18.5, 10.3
Ph_2SnBr(TNIPE)	169.8	123.1	139.4	122.7	148.0	163.7	69.5 [c], 21.8 [d]	140.2, 135.2, 130.5, 129.1
Me_2Sn(TNIPE)$_2$	169.1	124.0	137.3	121.1	147.8	164.6	68.7 [c], 21.8 [d]	7.1
Et_2Sn(TNIPE)$_2$	169.8	123.9	137.3	121.3	148.0	164.6	68.9 [c], 21.9 [d]	19.0, 10.3
Bu_2Sn(TNIPE)$_2$	170.2	124.5	137.6	121.7	148.6	165.3	69.7 [c], 22.3 [d]	28.6, 27.0, 26.7, 14.0
Ph_2Sn(TNIPE)$_2$	169.0	123.4	137.8	121.6	147.0	164.4	68.9 [c], 21.8 [d]	145.5, 134.4, 129.1, 128.6
Me_2SnCl(TNEE)	169.4	123.2	139.9	122.2	147.0	164.3	61.6 [b], 14.2 [d]	6.3
Me_2SnBr(TNEE)	169.5	123.1	139.2	122.3	147.1	164.4	61.6 [b], 14.3 [d]	7.1
Ph_2SnBr(TNEE)	169.4	123.3	139.3	123.2	148.0	164.2	61.8 [b], 14.3 [d]	140.2, 135.2, 130.5, 129.2
Me_2Sn(TNEE)$_2$	169.7	124.4	137.8	121.5	148.4	165.7	61.6 [b], 14.7 [d]	7.6
Et_2Sn(TNEE)$_2$	170.5	124.6	137.7	121.4	148.5	165.7	61.6 [b], 14.7 [d]	19.6, 10.9
Bu_2Sn(TNEE)$_2$	170.4	124.6	137.6	121.4	148.6	165.7	61.6 [b], 14.7 [d]	28.6, 27.0, 26.7, 14.0

[a] The C_3 and C_5 carbon signals are very close in the complexes. Tentative assignement. [b] CH_2. [c] CH. [d] CH_3.

from the methyl to the ethyl or butyl derivatives, while the diphenyl adducts present the lowest values. ΔE_Q is, in every case, around the values calculated by the point charge model for octahedral geometry (2.80 and 2.48 mm s^{-1} for the alkyl and aryl derivatives respectively) calculated by using already reported p.q.s. data [4,17].

Similar considerations also hold for the $R_2SnX(L)$ pentacoordinated compounds. In fact the δ values increase on going from methyl to ethyl and from chloride to bromide derivatives and the ΔE_Q are close to the calculated 2.94 mm s^{-1}. This value is calculated for an ideal trigonal bipyramidal geometry, while X-ray results show very distorted structures, at least for the two compounds examined here. This discrepancy once more outlines the limits of the point charge calculations in the determination of unknown structures. However, the similarity of the Mössbauer data supports the hypothesis that all the reported complexes present the same structure and very similar distortions.

3.4. NMR studies

The proton NMR spectra (Table 9) suggest the presence of free ligands in the thione form [18–21]. In fact the NH proton originates the broad signal at about 13.6 ppm, absent in the complexes. The resonance of the CH proton near nitrogen, at ca. 8.2 ppm in free ligands, undergoes a downfield shift in the complexes, more evident for the $(alkyl)_2Sn(L)_2$ (ca. 8.7 ppm) than for the $(alkyl)_2SnX(L)$ species (ca. 8.55 ppm). A less marked shift is observed for the ring proton in position four, the $(alkyl)_2Sn(L)_2$ values (ca. 8.02 ppm) being in this case upfield with respect to those of the $(alkyl)_2SnX(L)$ complexes (ca. 8.15 ppm). Conversely, a general upfield shift is observed for the ring CH in position three, whose resonance, at ca. 7.5 ppm in free ligands, goes to ca. 7.35 ppm in the complexes. The signals of the ester substituents are unaffected by coordination, as expected on the basis of structural data, which support the absence of Sn...O interactions in the solid state. The Me_2Sn signal position depends on either the halide or the complex geometry, being observed at 1.05 ppm in $Me_2Sn(L)_2$, upfield with respect to $Me_2SnCl(L)$ (1.12 ppm) and $Me_2SnBr(L)$ (1.21 ppm).

The ^{13}C NMR spectra in deuterated chloroform (Table 10) follow the trend observed previously for the $Ph_3Sn(L)$ and $Ph_2SnCl(L)$ complexes [5]. Coordination causes an evident upfield shift of the CS resonance (ca. 180.6 ppm in free ligands against ca. 170 ppm in the complexes), an opposite shift being observed for the N–CH resonance (ca. 140 ppm against ca. 147 ppm). The C_4 resonance is nearly unchanged, whereas the C_3 and C_5 signals, at ca. 133.3 and 117.7 ppm respectively in free ligands, are very close in the complexes (ca. 123 ppm). As for the proton spectra, the signals of the ester substituents have nearly equal values in ligand and complexes.

Acknowledgements

M.D.C. gratefully acknowledges support from Fundación Provigo, Galicia, Spain for financial support.

References

[1] 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).
[2] M. Bouâlam, J. Meunier-Piret, M. Biesemans, R. Willem and M. Gielen, *Inorg. Chim. Acta, 198* (1992) 249.
[3] R. Schmiedgen, F. Huber and H. Preut, *Acta Crystallogr. Sect. C:, 49* (1993) 1735.
[4] R. Schmiedgen, F. Huber, H.Preut, G. Ruisi and R. Barbieri, *Appl. Organomet. Chem., 8* (1994) 397.
[5] M.D. Couce, V. Cherchi, G. Faraglia, U.Russo, L. Sindellari, G. Valle and N. Zancan, *Appl. Organomet. Chem.*, in press.
[6] J.M. Tsangaris and D.R. Williams, *Appl. Organomet. Chem., 6* (1992) 3.
[7] F. Huber, G. Roge, L. Carl, G. Atassi, F. Spreafico, S. Filippeschi, R. Barbieri, A. Silvestri, E. Rivarola, G. Ruisi, F. Di Bianca and G. Alonzo, *J. Chem. Soc. Dalton Trans.*, (1985) 523.
[8] M. Gielen, R. Willem, J. Holecek and A. Lycka, *Main Group Met. Chem., 16* (1993) 29.
[9] S. D'Ancona, G. Magnolfi, G. Guidetti, G. Toffoli, A. Lazzarini, M. Carrara, M. Magon, S. Luciani and T. Berti, *Chemioterapia, V* (1986) 219.
[10] D.R. Grassetti, *Cancer Lett., 31* (1986) 187.
[11] R. Lejeune, L. Thunus and C.L. Lapierre, *J. Pharm. Belg., 35* (1980) 12.
[12] R. Lejeune and L. Thunus, *J. Pharm. Belg., 35* (1980) 98.
[13] G.M. Sheldrick, SHELX76, *A Program for Crystal Structure Determination*, University of Cambridge, UK, 1976.
[14] E. Spinner, *J. Chem. Soc.*, (1960) 1237.
[15] D.N. Sathyanarayana and S.V. Kasmir Raja, *Spectrochim. Acta Part A:, 41* (1985) 809.
[16] D. Fregona, Z. Guo, G. Faraglia and S. Sitran, *J. Coord. Chem., 28* (1993) 73.
[17] R.V. Parish, Structure and bonding in tin compounds, in G.J. Long (ed.), *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, Vol. 1, Plenum, New York, 1984, p. 527.
[18] A. Schanck, J.M. Dereppe and M. Van Meerssche, *Bull. Soc. Chim. Belg., 92* (1983) 199.
[19] M. Gelbcke, R. Grimée, R. Lejeune, L.Thunus and J.V. Dejardin, *Bull. Soc. Chim. Belg., 92* (1983) 39.
[20] M. Gelbcke, R. Grimée, R. Lejeune and L.Thunus, *Spectrochim. Acta Part A:, 41* (1985) 567.
[21] S. Stoyanov, I. Petkov, L. Antonov and T. Stoyanova, *Can. J. Chem., 68* (1990) 1482.