

Polyhedron 21 (2002) 1667-1676



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# Tris(2-methyl-2-phenylpropyl)stannane derivatives, $(Neo)_3SnX$ , revisited. Comparison of crystal structures of $(Neo)_3SnX$ $(X = Cl, Br, I, N_3, NCS and OAc)$

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Received 8 February 2002; accepted 26 April 2002

#### Abstract

The <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR and far-IR spectra of tris(neophyl)stannanes, (PhCMe<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>SnX, (Neo)<sub>3</sub>SnX, [1: X = F, Cl, Br, I, N<sub>3</sub>, NCS, OSn(Neo)<sub>3</sub> and OAc], and the crystal structures of 1 (X = Br, I, N<sub>3</sub>, NCS and OAc) are reported. The compounds 1 (X = Br, I, N<sub>3</sub> and NCS) and the previously reported 1 (X = Cl) all contain four-coordinate tin centers, with distorted tetrahedral geometries in the solid state. In contrast, 1 (X = OAc) is five-coordinate due to the acetate group acting as a chelating ligand. With the exception of 1 (X = Cl), all the compounds have entirely molecular structures with only van der Waals forces controlling the packing of the molecules. The molecules in 1 (X = Cl), with threefold axial symmetry, are packed head to tail in rows with weak C-H···Cl intermolecular contacts. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Organotin; Crystal structures; Halides; N-Thiocyanate; Azide; Acetate

## 1. Introduction

Tris(neophyl)tin compounds, (PhCMe<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>SnX, [1, (Neo)<sub>3</sub>SnX] have attracted both industrial [1] and academic attention [2-12] over the past four decades or so. A major interest has been their acaricidal properties and uses, especially of 1 (X = OSn(Neo)<sub>3</sub>) [fenbutatin, Vendex<sup>®</sup> or Torque<sup>®</sup>] [1]. While the agricultural use of fenbutatin, as with the general use of all triorganotin compounds, is much curtailed currently, interest in such environmental effects as its detection [13], and persistence [14], as well as the developing resistance of targeted insects to the pesticide [15], continue to be areas of much endeavor.

Interest in 1 has also centered on the effects of the bulky organic groups on the reactivities and especially on the geometries at the tin centers [2,3]. Solid state

structures have been probed mainly by Mössbauer spectroscopy [4], and much less so by X-ray diffraction [5–9]. Mössbauer spectral data have been provided for various 1, including X = F, Cl, Br, I, N<sub>3</sub> and OH and the tetraorganotin compound (1: X = Neo), while X-ray structures of 1 (X = Cl [5,6], 1-triazolyl [5], OCO-CH<sub>2</sub>OPh [7] and Neo [8,9]) have been reported. From all these solid state studies, the compounds 1 are indicated to be monomeric with four-coordinate tin centers in all except 1 (X = OCOCH<sub>2</sub>OPh [7]), in which the carboxylate group is weakly chelating, which leads to five-coordinate tin centers. NMR spectral data in solution for 1, mainly <sup>1</sup>H NMR [2,3] but also <sup>119</sup>Sn NMR for 1 (X = OH [10,12], OSn(Neo)<sub>3</sub> [12], OAc [10], F [10] and Cl [10,12]) have been reported.

The crystal structures of 1 (X = Br, I, N<sub>3</sub>, NCS and OAc) are reported here and are compared with those previously reported for 1 (X = Cl) [5,6] and 1 (X =  $O_2CCH_2COPh$ ) [7]. Attempts were also made to determine the crystal structures of 1 (X = F and OSn(Neo)<sub>3</sub>). However, extreme disorder about the Sn–F and Sn–O

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bonds prevented sensible conclusions being obtained, in particular regarding the Sn–X bonds. In addition to the X-ray data, solution <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR and far-IR spectral data are presented.

## 2. Experimental

NMR spectra were run on Bruker 300 and Varian 400 MHz instruments, IR spectra on Nicolet Magna 760 FTIR and Nicolet Fourier-transform spectrometers. Melting points were measured on a Melt-TempII instrument and are uncorrected.

# 2.1. Synthesis

Compound 1 (X = Neo) [9] was obtained by a published procedure and 1 (X =  $OSn(Neo)_3$ ) was a gift from Dow Chemical Co.

Compound 1 (X = Neo). IR (CsI, cm<sup>-1</sup>): v: 462, 391, 259, 158. [1: X = OSn(Neo)<sub>3</sub>]. IR (CsI, cm<sup>-1</sup>): v: 454, 419, 396, 374, 256, 157.

# 2.1.1. 1 (X = Cl)

To a solution of 1 (X = OSn(Neo)<sub>3</sub>) (0.5 mmol) in Et<sub>2</sub>O was added aqueous HCl (2 ml of 1.0 M solution). After sonification for 5 min, the organic phase was collected and evaporated. Crystals of 1 (X = Cl) were obtained by slow evaporation from an Et<sub>2</sub>O solution; m.p. 117–119 °C; lit. [3] value 117.5–118.5 °C.

IR (CsI, cm<sup>-1</sup>): v: 461, 394, 311(Sn-Cl), 266, 160.

2.1.2. 1 (X = Br)

To a solution of 1 (X = Neo) (2.0 mmol) in CHCl<sub>3</sub> was added, dropwise with stirring, a solution of Br<sub>2</sub> (2.0 ml) in CHCl<sub>3</sub> at -10 °C. After addition was complete, the temperature was allowed to rise to ambient. Complete reaction occurred after 2 h as shown by the decoloration of the reaction mixture. The solvent was removed under vacuum to leave a solid, which was washed with cold MeOH. Crystals of 1 (X = Br) were obtained by slow evaporation from an Et<sub>2</sub>O solution; m.p. 112–113 °C; lit. [3] value 109.5–110 °C.

IR (CsI, cm<sup>-1</sup>): v: 457, 398, 266, 212(Sn-Br), 164.

2.1.3. 1 (X = I)

To a solution of 1 (X = Br) (0.55 mmol) in Me<sub>2</sub>CO was added a solution of KI (1.75 mmol) in warm Me<sub>2</sub>CO. The reaction mixture was stirred at room temperature (r.t.) for 1 h, filtered and the filtrate evaporated. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the extractions were partially evaporated. Colorless crystals of 1 (X = I) were obtained by further slow evaporation; m.p. 117–118 °C; lit. [3] value 116.5–117.5 °C.

IR (CsI, cm<sup>-1</sup>): v: 454, 396, 268, 172(Sn–I).

2.1.4. 1 (X = F)

Solutions of 1 (X = Br) (0.60 mmol) in Et<sub>2</sub>O and NaF (3.66 mmol) in water were mixed. A little decyltrimethylammonium bromide was added and the mixture was sonicated for 10 min. Sodium sulfate was added and the organic phase collected. Slow evaporation of the organic solution gave crystals of 1 (X = F); m.p. 99–100 °C; lit. [3] value 98–100 °C.

IR (CsI,  $cm^{-1}$ ): v: 497(Sn-F), 444, 263, 178.

2.1.5. 1  $(X = N_3)$ 

To a solution of 1 (X = Br) (0.25 mmol) in EtOH was added a solution of NaN<sub>3</sub> (2.5 mmol) in warm EtOH. The reaction mixture was stirred at r.t. for 30 min, filtered and the filtrate evaporated. The residue was extracted with Et<sub>2</sub>O and the extracts gave colorless crystals of  $1 (X = N_3)$  on slow evaporation; m.p. 98– 99.5 °C; lit. [3] value 96–96.5 °C.

IR (CsI, cm<sup>-1</sup>): v: 2069 (N<sub>3</sub>), lit. [3] value 2072, 456, 386, 266, 153.

2.1.6. 1 (X = NCS)

To a solution of 1 (X = Br) (0.3 mmol) in Me<sub>2</sub>CO was added a solution of KNCS (2.2 mmol) in warm acetone. The reaction mixture was stirred at r.t. for 1 h, filtered and the filtrate evaporated. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the extracts gave colorless crystals of 1 (X = NCS) on slow evaporation; m.p. 98–99.5 °C.

IR (CsI, cm<sup>-1</sup>): v: 2021(NC), 459, 399, 303(Sn–N), 268, 167.

2.1.7. 1 (X = OAc)

Compound 1 (X = OSn(Neo)<sub>3</sub>] (0.15 mmol) was dissolved in acetic acid (3 ml, 5.2 mmol). The solution was evaporated under vacuum and gently heated to leave a residue of 1 (X = OAc). This was recrystallized from acetic acid; m.p. 85–88 °C; lit. [3] value 86.5–87 °C.

IR (CsI, cm<sup>-1</sup>): v: 1667 (CO) (lit. [3] value 1660), 456, 402, 292, 266, 160.

Selected <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR spectral data for 1 are displayed in Table 1.

## 2.2. Crystallography

#### 2.2.1. Data collection

Intensity data for 1 (X = Br, I, N<sub>3</sub> and OAc) were obtained, at 150 K in all cases, by means of the Enraf Nonius KappaCCD area detector diffractometer of the EPSRC's crystallography service at Southampton. The entire process of data collection, cell refinement and data reduction was accomplished by means of the programs DENZO [16] and COLLECT [17]. Correction for absorption by a semi-empirical method based upon the variation in intensity of equivalent reflections was achieved with the program SORTAV [18]. Data for 1

Table 1 Selected NMR spectral data for 1 in CDCl<sub>3</sub>

X	$\delta^{119} \mathrm{Sn}$	$\delta^{1}$ H(CH <sub>2</sub> ) [J( <sup>119,117</sup> Sn-H)]	$\delta^{1}$ H(Me) [J( <sup>119,1117</sup> Sn-H)]	$\delta^{13}$ C(CH <sub>2</sub> ) [ $J(^{119,117}$ Sn $^{-13}$ C)]	$\delta^{13}$ C(Me) [ $J(^{119,117}$ Sn $^{-13}$ C)]	$\delta^{13}C(CMe_2)$ [ $J(^{119,117}Sn^{-13}C)$ ]	$\delta$ (others)
F	138.8	1.01	1.18	39.8	38.6	33.8	${}^{1}J(\mathrm{Sn}-\mathrm{F}) = 2301$
	[146] <sup>a</sup>	[48.9]	[ca. 5]	[350]	[20.5]	[44.1]	${}^{3}J(F-CH_{2}) = 3.1$ ${}^{2}J(F-CH_{2}) = 7.6$
		0.95 °	1.22				2/
		[52.4] °	[-]				
Cl	118.4	1.11	1.18	40.4	38.9	33.9	
		[47.2]	[5.8]	[334,319]	[21.3]	[46.4]	
	[118] <sup>a</sup>			• • •			
	[117.7] <sup>b</sup>	1.05 °	1.19 °				
		[47.8] °	[5.8] °				
Br	92.3	1.23	1.19	39.1	38.1	32.9	
		[46.5]	[5.8]	[323,309]	[22.0]	[46.4]	
		1.07 <sup>c</sup>	1.20 °				
		[48.4] <sup>c</sup>	[5.9] °				
Ι	14.7	1.38	1.19	39.3	39.6	34.0	
		[45.1]	[6.2]	[309,295]	[22.0]	[46.3]	
		1.34 °	1.19 °				
		[44.5] °	[6.2] <sup>c</sup>				
NCS	47.9	1.05	1.22	37.5	37.6	32.8	${}^{1}J(\mathrm{Sn}-\mathrm{N}) = 125$
		[49.0]	[6.2]	[354,339]	[22.8]	[46.0]	
$N_3$		1.03	1.19	37.5	37.6	32.8	
		[48]	[6.2]	[-]	[-]	[-]	
OAc	83.4	1.07	1.12	37.3	37.8	32.87	$\delta^{13}\mathrm{C(CO)} = 176.2$
		[50.6]	[5.1]	[356]	[20.1]	[44.1]	$\delta^{13}\mathrm{C(CH_3)} = 22.6$
	[79] <sup>a</sup>						$\delta^1 \mathrm{H}(\mathrm{C}H_2) = 1.89$
		1.04 °	1.25 °				$\delta^1 \mathrm{H}(\mathrm{C}H_2) = 1.82^\circ$
		[51.7] °	[5.2] °				
OH	77.1	0.99	1.20	37.8	37.3	33.1	
	[75.9] <sup>b</sup>	[50.4]	[4.6]	[-]	[-]	[41.9]	
Neo	-52.5	0.80	1.16	31.2	38.5	33.6	
		[47.9]	[-]	[-]	[18.6]	[34.5]	

<sup>&</sup>lt;sup>a</sup> [10].

(X = NCS) were obtained at 297 K with a Bruker SMART 1000 CCD area detector diffractometer. SMART software [19] was used for data collection and the program SAINT [19] for cell refinement and data reduction. A semi-empirical correction for absorption similar to that noted above was applied by means of the program SADABS [19].

## 2.2.2. Structure solution and refinement

The same procedure was used for all **1**. Structure solutions providing positions for the majority of the non-H atoms were obtained by application of the direct methods procedure of SHELXS-97 [20]. Thereafter difference map calculations to find any missing non-H atoms and completion of the refinement process were carried out with SHELXL-97 [21]. In the final stages of refinement H atoms were placed in calculated positions and refined with a riding model. Further details of the processes of data collection and structure refinement are available in Table 2. The program, ORTEP-3 [22], was used to obtain the Figures.

# 3. Results and discussion

# 3.1. General

The syntheses of the various compounds 1 were achieved by bromo-dealkylation of 1 (X = Neo) or by anion exchange using as reagents either 1 (X = Br), with  $Y^-$  (Y = F, I, NCS or N<sub>3</sub>), or 1 (X = OSn(Neo)<sub>3</sub>), with HCl or HOAc. Complete anion exchanges were indicated from the physical properties, including NMR and far IR spectra.

# 3.2. Crystallography

The solid state structures were not merely studied to determine the coordination at tin, but to investigate the conformations and molecular arrangements in 1, compounds in which there are three relative bulky hydrophobic groups (the neophyl ligands) and a relatively small polar region (the Sn-X fragment).

<sup>&</sup>lt;sup>ь</sup> [12]. ° [3].

Table 2 Crystal data and structure refinement <sup>a</sup> for (1: X = Br, I, N<sub>3</sub>, NCS and OAc)

x	Br	Ι	N <sub>3</sub>	NCS	OAc
Empirical formula	C <sub>30.25</sub> H <sub>39.25</sub> BrCl <sub>0.75</sub> Sn	$C_{30.25}H_{39.25}Cl_{0.75}ISn$	$C_{30}H_{39}N_3Sn$	C31H39NSSn	$\mathrm{C}_{32}\mathrm{H}_{42}\mathrm{O}_{2}\mathrm{Sn}$
M	628.05	675.04	560.33	576.38	577.35
T (K)	150(2)	150(2)	150(2)	297(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Space group	$P2_{1}$	P 21	$P2_1/n$	$P2_1/c$	<i>P</i> 1
Cell dimension					
a (Å)	17.9633(4)	18.0069(3)	18.7224(2)	17.7105(7)	12.2476(2)
b (Å)	17.9225(4)	17.9500(3)	17.2884(2)	18.7575(8)	15.3004(2)
c (Å)	18.3954(6)	18.4313(4)	19.4326(4)	18.3223(8)	16.9444(2)
α (°)	90	90	90	90	104.3450(8)
β (°)	103.9165(9)	103.4000(7)	117.2747(5)	100.7760(10)	103.4030(7)
γ (°)	90	90	90	90	100.7490(6)
$V(Å^3)$	5748.5(3)	5795.25(19)	5590.63(14)	5979.4(4)	2890.50(7)
Ζ	8	8	8	8	4
Calculated density	1.451	1.547	1.331	1.281	1.327
$(Mg m^{-3})$					
Absorption coefficient	2.365	2.032	0.936	0.942	0.909
$(mm^{-1})$					
F(000)	2548	2692	2320	2384	1200
Crystal color	colorless	colorless	colorless	colorless	colorless
Crystal size (mm)	$0.10 \times 0.10 \times 0.10$	$0.35 \times 0.10 \times 0.04$	$0.20 \times 0.20 \times 0.10$	$0.30 \times 0.20 \times 0.20$	$0.20 \times 0.20 \times 0.12$
$\theta$ Range for data	2.91-27.44	3.00-30.83	3.13-27.51	2.08-32.51	2.94 - 30.77
collection (°)					
Index range	-23 < h < 22.	-24 < h < 24.	-24 < h < 21.	-26 < h < 17.	-16 < h < 17.
	-19 < k < 21.	-22 < k < 22.	-20 < k < 21.	-28 < k < 25.	-19 < k < 21.
	-19 < l < 23	-21 < l < 26	-25 < l < 25	-25 < l < 27	-23 < l < 20
Reflections collected/	36214/22983	45 544/26 606	42 274/12 668	61 105/21 502	30 901/22 786
unique					
$[R_{int}]$	0.0754	0.0451	0.0523	0.0533	0.0341
Completeness to $2\theta$	27 44 95 6%	30.83.82.1%	27 51 98 4%	32.51.99.2%	30 77 74 4%
limit (%)	2/11, 9010/0	20102, 0211/0	2,101, 9011/0	02101, 991270	50177,71170
Max and min	0.838 and 0.733	0.995 and 0.908	0.904 and 0.828	0.912 and 0.808	0.910 and 0.846
transmission	ologo und olygo	onyye und onyee	off of and office		
Data/restraints/	22 983/1/1213	26 606/1/1213	12668/0/625	21 502/0/625	22 786/3/1261
narameters	22,703/1/1213	20 000/1/1215	12 000/0/023	21302,0,023	22 /00/3/1201
Goodness-of-fit on $F^2$	1.002	1.010	1.030	0.807	1 103
Final <i>R</i> indices	$R_{\rm c} = 0.0604$	$R_{\rm c} = 0.0470$	$R_{\rm c} = 0.0410$	$R_{\rm c} = 0.0356$	$R_{\rm r} = 0.0374$
$[I > 2\sigma(I)]$	$R_1 = 0.0004,$ $w R_2 = 0.1275$	$R_1 = 0.0470,$ $w R_2 = 0.0947$	$R_1 = 0.0410$ , $w R_2 = 0.0915$	$wR_{2} = 0.0633$	$R_1 = 0.0374,$ $wR_2 = 0.1049$
[I > 20(I)] <i>R</i> indices (all data)	$R_1 = 0.1275$ $R_2 = 0.1199$	$R_1 = 0.0763$	$R_1 = 0.0678$	$R_1 = 0.1258$	$R_1 = 0.0450$
K mulees (an data)	$R_1 = 0.1199$ , $w P_2 = 0.1687$	$K_1 = 0.0703,$ $w P_2 = 0.1081$	$R_1 = 0.0078,$ $w R_2 = 0.1022$	$R_1 = 0.1250,$ $w P_2 = 0.0816$	$R_1 = 0.0430,$ $w R_2 = 0.1200$
Absoluto structuro	$WR_2 = 0.1087$	$wR_2 = 0.1081$ 0.042(15)	$WR_2 = 0.1022$	$WK_2 = 0.0810$	$wR_2 = 0.1209$ 0.047(14)
nosolute sulucture	0.001(11)	-0.042(13)			-0.04/(14)
Largest diff. peak and hole (e $Å^{-3}$ )	0.862  and  -1.050	0.967 and -1.593	0.904  and  -1.074	0.623 and -0.369	0.877  and  -1.362

<sup>a</sup> In all cases, absorption correction was semi-empirical from equivalents and refinement by full-matrix least-squares on  $F^2$ .

The crystals used in the crystallography were grown by evaporation of CHCl<sub>3</sub> solutions. Unsolvated compounds were obtained for 1 (X = N<sub>3</sub>, NCS and OAc), while solvates,  $[1 \cdot 1/4$ CHCl<sub>3</sub>] were isolated for 1 (X = Br and I).

As well as the structures of  $1 (X = Br, I, N_3, NCS and OAc)$ , the structure of the previously reported compound 1 (X = Cl) [6] at 150 K is also discussed here. All these molecules are themselves not inconsiderable in size requiring the placement, in the absence of coincident crystallographic and molecular symmetry, of at least 32 non-H atoms per molecule. The situation is further

complicated by the fact that the asymmetric unit of 1 (X = N<sub>3</sub>) and 1 (X = NCS) contains two complete molecules and that of 1 (X = Br), 1 (X = I) and 1 (X = OAc) no less than four. This has prompted the following labeling convention. The atoms of every neophyl group have been labeled numerically in the same manner (Fig. 1), e.g. in every case C1 is bonded to Sn1 and the methyl and phenyl groups are C3 and C4 and C5 to C10, respectively. There is not, however, complete consistency in the numbering of the atoms of the methyl and phenyl groups in relation to their orientation with respect to the molecule as a whole.



Fig. 1. The general atom numbering scheme used for the carbon atoms of the neophyl groups in 1, see text. The example shown is the asymmetric unit of 1 (X = Cl) omitting the Cl atom. Non-H atoms are shown as 30% ellipsoids and H atoms as small circles.

For 1 ( $X = N_3$ ) and 1 (X = NCS), the two independent molecules are termed I and II: in molecule I, the tin atom is Sn1a, the three neophyl ligands/their constituent atoms are identified by the suffices A/a, B/b and C/c, while in molecule II, the tin atom is Sn1b and the suffixes used for the three neophyl groups/atoms are D/ d, E/e and F/f. In each of 1 (X = Br), 1 (X = I) and 1 (X = OAc), which have four independent molecules in the asymmetric unit, a similar system is utilized. The four independent molecules are termed I, II, III and IV, having tin atoms Sn1a, Sn1b, Sn1c and Sn1d, respectively. The neophyl group suffices are here A, B and C (in molecule I), D, E and F (in molecule II), G, H and I (in molecule III) and J, K and L (in molecule IV): the atoms within each neophyl ligand take the appropriate lower case suffix. A similar strategy as used for Sn has been applied to the labeling of the halide, X, in molecules of 1 (X = Br) and 1 (X = I). The general numbering of the other X group atoms are (Sn1)-N1-N2-N3 in 1 (X = N<sub>3</sub>), and (Sn1)-N1-C11-S1 in 1 (X = NCS) and (Sn1)-O1-C11(O2)-C12 in 1 (X =OAc).

# 3.2.1. Geometry at tin

Selected bond lengths and angles for 1 (X = Cl, Br, I, N<sub>3</sub> and NCS) are listed in Tables 3 and 4, while selected geometric data for 1 (X = OAc) are provided in Table 5. Molecules of 1 (X = Cl, Br, I, N<sub>3</sub> and NCS) clearly contain four-coordinate tin centers, with distorted tetrahedral geometries. Each independent molecule of each compound 1 (X = Cl, Br, I, N<sub>3</sub> and NCS) has a very similar geometry, with relatively small differences in the C-Sn-X and C-Sn-C bond angles for each X. In each molecule, the three smallest angles subtended at tin are the C-Sn-X angles. The bulk of the neophyl groups results in the opening up of the C-Sn-C angles. The average C-Sn-X angles are 99.67°, 101.6°, 102.5°, 100.6° and 99.7° in 1 (X = Cl, Br, I, N<sub>3</sub> and NCS) and

are influenced by both the size of the ligand X and the length of the Sn-X bond. The Sn-X bond lengths, averages for all but 1 (X = Cl), are 2.382(3), 2.545(2), 2.714(8) Å for X = Cl, Br and I, respectively, and are close to the appropriate sums of the covalent radii of 2.39, 2.54 and 2.73 Å [23].

The average Sn-N bond lengths in 1 (X = NCS) and 1 (X = N<sub>3</sub>) are 2.119(2) and 2.247(12) Å, respectively, compared with the sum of the covalent radii for Sn and N of 2.15 Å [24]. There are no intermolecular Sn···N contacts in 1 (X = N<sub>3</sub>) or Sn···S contacts in 1 (X = NCS) less than 4.0 Å. The closest intermolecular contacts in a particular molecule of 1 (X = NCS) are S...S at 3.6429(16) Å—that is close to the sum of the van der Waals radii. Smaller triorganotin N-thiocyanates, such as Me<sub>3</sub>SnNCS {Sn-N and Sn-S = 2.15(6)and 3.13(2) Å} [24], Ph<sub>3</sub>SnNCS {Sn-N and Sn-S = 2.199(11)-2.248(10), and 2.897(4)-2.952(4) Å} [25,26] and  $(p-MeC_6H_4)_3SnNCS$  {Sn-N and Sn-S = 2.195(5) and 3.0255(2) Å} [26], exist in the solid state as zig-zag polymers due to NCS bridging with five-coordinate tin atoms. The more hindered compounds, Me<sub>2</sub>[(PhMe<sub>2</sub>- $Si_{3}C$ [SnNCS {Sn-N = 2.12(3) Å} [27] and (*o*- $MeC_6H_4)_3SnNCS$  {Sn-N = 2.067(6) and 2.066(6) Å} [26], on the other hand, are monomeric in the solid state with four-coordinate tin centers. Compound (o- $MeOC_6H_4$ <sub>3</sub>SnNCS {Sn-N = 2.090(5) Å} [26], is also molecular, but here there is a suggestion of a weak intramolecular Sn–O interaction [Sn–O 2.961(4) Å,  $\angle$  $N-Sn-O = 152.19(17)^{\circ}$  and hence an increase in the coordination number at Sn to 5, but this clearly has little effect on the Sn-N bond length.

The Sn–N bond length in monomeric *t*-Bu<sub>3</sub>SnN<sub>3</sub> [28] is a little shorter, at 2.101(4) Å, than those found in 1 (X = N<sub>3</sub>). Smaller triorganotin azides, e.g. Me<sub>3</sub>SnN<sub>3</sub> [29], are N-bridged in the solid state. The Sn–N bond lengths in [(1: X = triazole) $\cdot 0.5H_2O$ ] [5] are 2.123(6) and 2.105(7) Å.

Compound 1 (X = OAc) was the only trineophyltin compound studied here that was other than fourcoordinate, as a result of the acetate group tending to be a bidentate chelating ligand and the tin centers becoming five-coordinate (Fig. 2). As shown by the Sn-O distances, there is a strong asymmetry in the acetate chelate bonding, with one strong and one weak bond: the primary Sn–O1 bond lengths fall in the range 2.070(5)-2.117(4) Å with the Sn-O2 separations between 2.963 and 3.069 Å. These values can be compared with sums of covalent radii and van der Waals radii of 2.15 and 3.70 Å [23]. Noticeably too, the primary C-Sn-O1 angles fall into three distinct groupings, with ranges of  $93.84^{\circ} \pm 0.82^{\circ}$ ,  $103.13^{\circ} \pm 1.33^{\circ}$  and  $107.75^{\circ} \pm$  $0.55^{\circ}$ , see Table 5. The C-Sn-C angles in 1 (X = OAc) also show a slightly greater variation than those in 1  $(X = Cl, Br, I, N_3 and NCS)$ . The geometry at tin is best described as being on the pathway from tetrahedral to

Х	Mol	Sn1-X1	Sn1-C1(n)				
			[n]	[n]	[n]		
Cl		2.382(3)	2.149(5)	2.149(5)	2.149(5)		
Br	Ι	2.5473(14)	2.150(12) [a]	2.157(10) [c]	2.172(9) [b]		
	II	2.5427(13)	2.147(12) [e]	2.147(10) [f]	2.171(9) [d]		
	III	2.5440(15)	2.151(11) [g]	2.170(11) [h]	2.172(10) [i]		
	IV	2.5438(14)	2.170(10) [j]	2.173(10) [1]	2.184(11) [k]		
Ι	Ι	2.7496(6)	2.154(6) [b]	2.162(7) [a]	2.164(6) [c]		
	II	2.7333(6)	2.159(6) [f]	2.160(7) [d]	2.163(7) [e]		
	III	2.7441(6)	2.143(7) [g]	2.156(7) [h]	2.163(6) [i]		
	IV	2.7424(6)	2.161(6) [1]	2.166(6) [j]	2.166(6) [k]		
N3	Ι	2.259(5)	2.147(3) [b]	2.150(3) [a]	2.156(3) [c]		
	II	2.235(3)	2.143(3) [e]	2.150(3) [f]	2.150(3) [d]		
NCS	Ι	2.117(3)	2.138(3) [b]	2.142(2) [a]	2.147(2) [c]		
	II	2.121(3)	2.141(2) [e]	2.141(2) [f]	2.149(2) [d]		

Table 3 Selected bond lengths (Å) for 1 (X = Cl, Br, I, N<sub>3</sub> and NCS) <sup>a</sup>

<sup>a</sup> The three Sn-C1(n) bond lengths in each molecule have been placed in order of increasing bond length. The particular C1(n) atom involved in each bond has been indicated by the lower case letter, a, b, c etc., which, as indicated in the text, are associated with neophyl ligands, A, B, C etc.

trigonal bipyramidal, with the carbonyl oxygens, O2, in quasi axial positions and O1 in the quasi equatorial sites. A similar situation of a *cis*- $R_3SnO_2$  arrangement pertains in 1 (X = O<sub>2</sub>CCH<sub>2</sub>OPh) [7] and in other hindered triorganotin carboxylates [30]. The most frequently found structural type, however, for unhindered triorganotin carboxylates is a carboxylate bridged polymeric chain with *trans*- $R_3SnO_2$  cores [31], for example, as found in Me<sub>3</sub>SnOAc [32].

## 3.2.2. The existence of rotamers

In all of the structures discussed here the molecules are propeller shaped (Fig. 3) and as a consequence can, and do, exist in two rotameric forms. In one form (type R), when viewed along the Sn-X bond from X to Sn,

the phenyl groups of the neophyl substituents are displaced in a clockwise direction. In the other (type L) the displacement is anticlockwise. In 1 (X = Cl), the example shown in Fig. 3, both forms are present due to the operation of the crystallographic bar4 (fourfold rotary inversion axis) and equivalently the *d*-glide of the cubic space group *I*-43*d* and the structure is racemic. It is, however, polar because the space group lacks a center of symmetry and the bar4 creates a molecular arrangement with the overall symmetry of a regular tetrahedron whose orientation relative to the unitcell edges can differ from one crystal to another. The structures of 1 (X = N<sub>3</sub>) and 1 (X = NCS), being centrosymmetric, are of course racemic and non-polar. By accident of choice in both cases both molecules of the bimolecular asym-

Table 4 Selected bond angles (°) <sup>a</sup> in 1 (X = Cl, Br, I, N<sub>3</sub> and NCS)

Х	Mol	Cl(n)-Sn1-X1			C1(n)-Sn1-C1(n')		
		[n]	[n]	[n]	[n,n′]	[n,n']	[n,n']
Cl		99.67(15)	99.67(15)	99.67(15)	117.24(8)	117.24(8)	117.24(8)
Br	Ι	99.6(3) [c]	102.2(4) [a]	103.2(3) [b]	115.0(4) [c,b]	115.7(4) [a,c]	B117.3(4) [a,b]
	II	100.9(3) [e]	101.4(3) [f]	102.5(3) [d]	115.3(4) [e,f]	116.2(4) [e,d]	116.7(4) [f,d]
	III	100.2(4) [h]	101.8(3) [g]	102.9(3) [i]	114.7(4) [g,h]	116.5(4) [g,i]	116.9(4) [h,i]
	IV	100.3(4) [1]	101.4(3) [j]	102.8(3) [k]	115.4(4) [j,1]	115.5(4) [l,k]	117.4(4) [j,k]
Ι	Ι	100.7(2) [c]	102.8(2) [a]	104.41(18) [b]	114.8(3) [a,c]	115.3(2) [b,c]	116.0(2) [b,a]
	II	101.14(19) [e]	101.90(19) [f]	103.13(18) [d]	115.6(3) [f,d]	115.7(2) [f,e]	116.0(2) [d,e]
	III	102.24(17) [g]	C103.2(2) [h]	I04.2(2) [i]	114.9(3) [g,h]	114.9(3) [h,i]	115.0(3) [g,i]
	IV	100.8(2) [1]	102.71(18) [j]	102.78(19) [k]	115.3(2) [1,j]	115.9(2) [j,k]	116.0(2) [l,k]
N3	Ι	98.72(15) [c]	102.18(15) [a]	102.49(16) [b]	115.69(12) [b,c]	115.92(11) [b,a]	117.50(12) [a,c]
	II	100.39(12) [f]	100.58(12) [d]	101.04(12) [e]	115.68(12) [e,d]	117.10(12) [e,f]	117.18(12) [f,d]
NCS	Ι	99.65(11) [b]	99.92(11) [c]	100.72(12) [a]	116.38(10) [b,a]	116.56(10) [a,c]	118.05(10) [b,c]
	II	98.09(12) [e]	99.28(11) [d]	100.70(12) [f]	116.67(10) [f,d]	117.48(10) [e,f]	118.09(10) [e,d]

<sup>a</sup> The three C1(n)—Sn1—X1, and three C1(n)—Sn—C1(n') bond angles in each molecule have been placed in order of increasing size. The particular C1(n) and C1(n') atoms involved have been indicated by the lower case letter, a, b, c etc., which, as indicated in the text, are associated with neophyl ligands, A, B, C etc.

IV

C11 C2j

Table 5 Selected geometric parameters for $1 (X = OAc)^{a}$						
Molecule	I	II	III			
C1	C1c	C1d	C1I			
C2	C2b	C2f	C2h			
C3	C3a	C3e	C3g			

C3	C3a	C3e	C3g	C3k				
Bond lengths								
Sn1-O1	2.070(5)	2.117(4)	2.086(4)	2.074(4)				
Sn1-O2	3.069(7)	3.052(5)	3.004(5)	2.963(4)				
Sn1-C1	2.137(6)	2.142(6)	2.151(5)	2.147(5)				
Sn1-C2	2.143(6)	2.145(5)	2.152(5)	2.150(5)				
Sn1-C3	2.163(5)	2.155(5)	2.170(5)	2.164(5)				
C11-O1	1.266(8)	1.266(8)	1.279(8)	1.295(7)				
C11-O2	1.221(10)	1.202(8)	1.214(9)	1.221(7)				
C11-C12	1.498(10)	1.489(10)	1.5222(9)	1.489(8)				
Bond angles	Bond angles							
Equatoriallequatorial								
O1-Sn1-C1	108.3(2)	107.2(2)	107.79(19)	104.46(18)				
O1-Sn1-C2	102.6(2)	102.0(2)	101.8(2)	107.68(17)				
C1-Sn1-C2	115.0(2)	118.7(2)	118.5(2)	119.63(19)				
Axial/equatorial	( <i>C3</i> )							
C3-Sn1-O1	93.3(2)	93.11(19)	94.65(19)	93.02(19)				
C3-Sn1-C1	116.3(2)	115.1(2)	114.2(2)	114.1(2)				
C3-Sn1-C2	117.2(2)	115.7(2)	115.6(2)	113.6(2)				
Axial/equatorial (O2)								
O2-Sn1-O1	45.2(2)	45.45(15)	47.30(16)	47.94(13)				
O2-Sn1-C1	77.2(3)	79.10(19)	78.08(18)	84.36(16)				
O2-Sn1-C2	87.4(2)	85.4(2)	84.9(2)	81.26(16)				
Trans axial								
O2-Sn1-C3	137.1(2)	137.93(19)	141.11(19)	140.78(17)				

<sup>a</sup> Distance and angle table for bidentate acetate anion comprising carboxyl O1, O2 and C11 and methyl group C12 which creates a trigonal bipyramidal coordination around Sn1 with equatorial O1, C1 and C2 (Sn1-C1  $\leftarrow$ Sn1-C2) and axial O2 and C3.



Fig. 2. Trineophyltin carboxylates (1: X = OAc or  $O_2CCH_2COPh$ ).



(a)



Fig. 3. Two molecules of 1 (X = Cl) displaying (a) the 'clockwise' type R rotamer and (b) the 'anticlockwise' type L rotamer. Non-H are shown as 30% ellipsoids and H have been omitted for clarity. Selected atoms are labeled with symmetry codes for (a) 1: *z*, *x*, *y*; 2: *y*, *z*, *x* and (b) 3: 1/4+x, 1/4+z, 1/4+y; 4: 1/4+y, 1/4+x, 1/4+z and 5: 1/4+z, 1/4+z, 1/4+x.



Fig. 4. A portion of a linear chain of head to tail molecules, as indicated by PLATON [39] of 1 (X = Cl) propagated in the direction of a diagonal of the cubic unitcell [111]. Non-H are shown as 30% ellipsoids and H7, involved in C—H···Cl intermolecular contacts (dashed lines), is the only H shown. The molecules in the portion of the chain shown alternate in terms of rotameric type as R at the extremes and L in the center. The parameters associated with the C7—H7···Cl contacts are C—H, H···Cl and C···Cl 0.95, 2.79 and 3.622(8) Å, respectively, and C—H···Cl 146.47°.

metric unit are of the same hand but of type L for 1  $(X = N_3)$  and type R for 1 (X = NCS). In each of 1 (X = Br), 1 (X = I) and 1 (X = OAc) all of the molecules in the asymmetric unit are of the same hand, type R for 1 (X = Br) and isostructural 1 (X = I) and type L for 1 (X = OAc). Since all of these last three structures lack a center of symmetry or any other form of crystallographic symmetry, all of the molecules in a particular crystal must then be of the same hand. However, since there is no element of handedness in the synthesis of the compounds, and no evidence of disorder, a bulk sample of any one of them must contain crystals of one hand in admixture with crystals of the other in equal parts by volume which allows for variation in crystal size.

#### 3.2.3. Molecular packing

With one slight exception, all of the compounds have entirely molecular structures with only van der Waals forces controlling the packing of the molecules and three situations arise. The first is the exception namely 1 (X =Cl). Here the molecules, with crystallographic threefold axial symmetry, are packed head to tail in rigorously linear rows (Fig. 4). This arrangement permits weak Hbond like intermolecular contacts of the form C7- $H7 \cdots Cl'$  with, for the 150 K structure [6] (CSD ref. code FOZRER) [33], symmetry code 5/4 - y, 3/4 - x, z - y1/4 and C-H, H···Cl and C···Cl 0.95, 2.79 and 3.622(8) Å, respectively, and C–H···Cl 146.47°. The second case is that of 1 (X = OAc) in which the molecules can be perceived as forming layers parallel to (001) with molecules II and III forming one layer centered approximately on z = 0.15 and molecules I and IV forming the other centered on z = 0.65 (Fig. 5). The third and last case applies to all of the other structures. The molecules are now found in columns in which all of the molecules are the same (all molecule I or all molecule II etc. but never mixed) and all of the same rotameric type (R or L, see above) because each molecule is related to the next by the operation of a crystallographic twofold screw axis propagating the columns in the direction of b (Fig. 6).

In all of 1 (X = Br, I, N<sub>3</sub> and NCS), four such columns pass through the unit cell and in 1 (X = Br) and 1 (X = I) all of the molecules in all of the columns are of the same type and, as it happens, of type R. In centrosymmetric and therefore racemic 1 (X = N<sub>3</sub>) and 1 (X = NCS), however, it is the all-molecule I or all-molecule II columns which are related in pairs by the crystallographic centers of symmetry and hence there is still no mixture of R and L type molecules within a single column. The chloroform solvate molecules of 1 (X = Br) and 1 (X = I), simply occupy cavities between the columns.

#### 3.3. Spectroscopy

NMR spectral data obtained for 1 in this study were in agreement with those reported in the literature. In the humid atmosphere of Rio de Janeiro,  $1 [X = OSn(Neo)_3]$ in solution was rapidly hydrolyzed to 1 (X = OH), as shown by the  $\delta^{119}Sn$  value 77.1 ppm, obtained after several minutes in solution. Lockhart [12] reported values of 54.8 and 75.9 ppm for  $1 (X = OSn(Neo)_3)$ and 1 (X = OH), respectively, in CDCl<sub>3</sub> solution. The



Fig. 5. Molecules of 1 (X = OAc) in layers parallel to (001) comprising (a) molecules I and IV in a layer centered on z = 0.65 and (b) molecules II and III in a layer centered on z = 0.15. Non-H are shown as 50% ellipsoids and H have been omitted for clarity. Labels on selected Sn and O and group suffices (see text) identify the molecules and neophyl groups.



Fig. 6. A portion of a chain of molecules I in 1 (X = Br) propagated in the direction of b. Non-H atoms are shown as 50% ellipsoids and H have been omitted for clarity. In addition to labeled Sn and Br atoms, neophyl groups are identified by group suffices, A, B and C. Symmetry codes for primed atoms: -x, y+1/2, 1-z (left) and -x, y-1/2, 1-z (right).

product isolated from solutions, however, was always  $1 [X = OSn(Neo)_3]$ . Lockhart also indicated similar effects [12].

Triorganotin chlorides, bromides and iodides, R<sub>3</sub>SnX (R = unfunctionalised organyl group; X = Cl, Br or I),are generally monomeric four-coordinate species in noncoordinating solvents and in the solid state [34]. Hence there are much data available on spectral parameters for such species in solution. On the other hand, R<sub>3</sub>SnF, except the most hindered compounds, such as (2.4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>3</sub>SnF [35], Ph<sub>2</sub>[(Me<sub>3</sub>Si)<sub>3</sub>C]SnF [36], Me<sub>2</sub>[(Ph- $Me_2Si_3CSnF$  [36] and 1 (X = F), are aggregated species in the solid state and are poorly soluble in organic solvents. Reported NMR data for triorganotin fluorides in solution are thus limited. The  ${}^{1}J({}^{119}\text{Sn}-{}^{19}\text{F})$  value for 1 (X = F) = 2301 ppm in CDCl<sub>3</sub> solution is similar to the reported values for other monomeric R<sub>3</sub>SnF compounds, Ph<sub>2</sub>[(Me<sub>3</sub>Si)<sub>3</sub>C]SnF, Me<sub>2</sub>[(PhMe<sub>2</sub>Si)<sub>3</sub>C]SnF and Me<sub>2</sub>[(Me<sub>3</sub>Si)<sub>3</sub>C]SnF [24] [ ${}^{1}J({}^{119}Sn - {}^{19}F) = 2376$ , 2374 and 2463 ppm, respectively]. The  $\delta^{119}Sn$  values for the monomeric trialkyltin fluorides are also similar:  $\delta^{119}$ Sn values for 1 (X = F), Me<sub>2</sub>[(PhMe<sub>2</sub>Si)<sub>3</sub>C]SnF and Me<sub>2</sub>[(Me<sub>3</sub>Si)<sub>3</sub>C]SnF are 138.8, 124.5 and 146.9 ppm, respectively. The  ${}^{1}J({}^{119}\text{Sn}{}^{-14}\text{N})$  values in 1 (X = NCS) and Me<sub>2</sub>[(PhMe<sub>2</sub>Si)<sub>3</sub>C]SnNCS [27] are very close, 125 and 123 Hz, respectively, and are appreciably greater than those  $[90\pm4 \text{ Hz}]$  quoted for  $(o-\text{MeC}_6\text{H}_4)_3$ SnNCS and  $(o-MeOC_6H_4)_3SnNCS$  [26]. The v(NC) = 2021 $cm^{-1}$  value in 1 (X = NCS) is lower than quoted values for four-coordinate triorganotin N-thiocyanates, e.g.  $Me_2[(PhMe_2Si)_3C]SnNCS \{2066 \text{ cm}^{-1}\}$  [27] and (o- $MeC_6H_4$ )<sub>3</sub>SnNCS {2045 cm<sup>-1</sup>} [26].

Values of v(Sn-X) in simple R<sub>3</sub>SnX (e.g. R = Me, Et, Bu, Ph) are generally in the regions: 170–210 (X = I), 220–265 (X = Br), and 325–385 cm<sup>-1</sup> (X = Cl), irrespective of phase [37], whereas values for R<sub>3</sub>SnF depend on the phase, due to differences in aggregation. Gas phase values for R<sub>3</sub>SnF (e.g. R = Me, Et, Bu, Ph) (i.e. for monomeric species) have been reported to be in the range 555–590 cm<sup>-1</sup>, while values for the aggregated species as solids are quoted as  $340-380 \text{ cm}^{-1}$  [37]. The v(Sn-X) values for 1 (X = Cl, Br or I) in CsI, viz. 311, 212 and 172 cm<sup>-1</sup> respectively, fall in the expected regions. The v(Sn-F) value [497 cm<sup>-1</sup>] in molecular 1 (X = F) can be compared with the values, 535 and 537 cm<sup>-1</sup>, found in (2.4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>3</sub>SnF [35] and (*o*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnF [38], respectively, both shown by X-ray crystallography to be monomeric. The latter compound, just like (*o*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnNCS [26], has indications of S–O intramolecular interaction and hence a higher coordination.

#### 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC numbers 178628–178632 for compounds (1: X = Br, I, N<sub>3</sub>, NCS and OAc), respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk).

#### Acknowledgements

The authors thank the ESPSRC X-ray service at the University of Southampton for data collection, and CPNq and FAPERJ, Brazil for financial support. We acknowledge the use of the Chemical Database of EPSRC at Daresbury.

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