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Further study of tris(cyclohexyl)stannane compounds, Cy₃SnX. Syntheses of the compounds with X = Br, I, N₃ and NCS and redetermination of the crystal structures of Cy₃SnX (X = Br and I)

R. Alan Howie^{a,*}, Marcelo V.H. Moura^b, James L. Wardell^b, Solange M.S.V. Wardell^c

^a Department of Chemistry, University of Aberdeen, Old Aberdeen, AB24 3UE, Scotland, UK

^b Departamento de Química Inorgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, CP 68563, 21945-970 Rio de Janeiro, RJ, Brazil ^c Far-Manguinhos, Fiocruz, Rua Sizenando Nabuco 100, Manguinhos, CEP 21041-250, Rio de Janeiro, RJ, Brazil

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Abstract

Methods of preparation and far IR data are presented for various Cy₃SnX compounds. The synthesis of tris(cyclohexyl)tin hydroxide, Cy₃SnOH, is also described. Redeterminations of the crystal structures of tris(cyclohexyl)tin bromide and iodide, Cy₃SnBr and Cy₃SnI, confirm their molecular nature and improve considerably upon the results reported earlier [S. Calogero, P. Ganis, V. Peruzzo, G. Tagliavini, G. Valle, J. Organomet. Chem. 220 (1981) 11] providing, in both cases, lower R-factors and, in particular, a revised estimate of the Sn–I bond length, now 2.7463(6) Å. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Tris(cyclohexyl)tin; Halostannanes; Crystal structure

1. Introduction

Halo- and pseudo-halostannanes of the general form $R_{4-n}SnX_n$, (R = an organic group, X = halide or pseudo halide and n = 1-13), have received much attention. Of interest in compounds of this type, particularly for those with n = 2 and more especially those with n = 1, has been the investigation of the occurrence and nature of secondary Sn–X contacts to establish whether they contribute to the coordination of tin and change its nominal tetrahedral nature to one with a higher coordination number. Typical examples of this are the detailed report

of the temperature dependent order-disorder transition in tris(cyclohexyl)tin chloride, 1 (X = Cl), [1, and references therein], and reports on the structures of 1 (X = F, Br and I) [2] and of various tris(2-methyl-2-phenyl-propyl)stannane derivatives (Neo)₃SnX, 2 (X = Cl, Br, I, N₃ and NCS) [3]. We now report the synthesis of 1 (X = Br, I, N₃ and NCS) and of tris(cyclohexyl)tin hydroxide, along with redeterminations of the structures of 1 (X = Br) and 1 (X = I). Far IR data are also presented for various Cy₃SnX compounds.

2. Experimental

E-mail address: r.a.howie@abdn.ac.uk (R.A. Howie).

Melting points were measured on Melt-Temp-II equipment. Far IR spectra were obtained using a Nicolet

^{*} Corresponding author. Tel.: +44 1224 272907; fax: +44 1224 272921.

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Magna 760 FTIR instrument with samples suspended in Nujol between polythene plates. Cy₃SnCl was a recrystallised commercial sample, m.p. 127-129 °C.

Far IR: v 492, 439, 420, 327, 271, 252, 199 cm⁻¹.

2.1. Preparation of tris(cyclohexyl) tin iodide, I(X = I)

Solutions of Cy₃SnCl (2 mmol) in Me₂CO (15 ml) and NaI (5 mmol) in Me₂CO (15 ml) were mixed. After stirring at RT for 4 h the reaction mixture was filtered and the filtrate evaporated to leave a residue which was extracted into CHCl₃. The chloroform extract was evaporated and the solid residue was recrystallised from EtOH, m.p. 64–66 °C.

Far IR: v: 492, 439, 420, 324, 250(sh), 239, 212, 161 cm⁻¹.

2.2. Preparation of tris(cyclohexyl)tin hydroxide, 1 (X = OH)

A solution of Cy₃SnCl (2 mmol) in Et₂O (15 ml) was added to a solution of NaOH (5%) in H₂O (15 ml) and the mixture was stirred for 1 h, and then filtered. The ether layer in the filtrate was collected, dried and evaporated. The residue from the ether layer was added to the original solid collected by filtration and the combined solids were recrystallised from aqueous EtOH, m.p.174–179 °C. The wide m.p. range is attributed to the presence in trace amounts, and in situ formation, of bis[tris(cyclohexyl)tin] oxide, (Cy₃Sn)₂O, in accord with the previous report [4] that only with great difficulty can pure samples of either the oxide or the hydroxide be obtained, ν (OH) 3623 cm⁻¹.

2.3. Preparation of tris(cyclohexyl)tin bromide, 1 (X = Br)

Concentrated HBr (2 ml) was added to a solution of Cy_3SnOH (0.5 mmol) in EtOH (20 ml). The mixture was stirred at room temperature for 2 h, the volatiles removed under vacuum and the solid product recrystal-lised from CHCl₃; m.p. 77–79 °C.

Far IR: v: 491, 438, 419, 322, 250(sh), 228(br), 203(sh) cm⁻¹.

2.4. Preparation of tris(cyclohexyl)tin azide, $1 (X = N_3)$

A solution of Cy₃SnCl (2 mmol) in Me₂CO (15 ml) and a suspension of NaN₃ (5 mmol) in Me₂CO (15 ml) were mixed. After stirring at RT overnight, the reaction mixture was filtered. The filtrate was shaken with a further suspension of NaN₃ (5 mmol) in Me₂CO (15 ml) for 4 h, all volatiles removed by rotary evaporation and the residue extracted into CHCl₃. The chloroform extract was dried and rotary evaporated to leave a solid residue. $v(N_3)$ 2071 cm⁻¹: no v(OH)

2.5. Preparation of tris(cyclohexyl)tin isothiocyanate, 1 (X = NCS)

A solution of Cy₃SnCl (2 mmol) in Me₂CO (15 ml) and a suspension of NaNCS (5 mmol) in Me₂CO (15 ml) were mixed. After stirring at RT overnight, the reaction mixture was filtered and the filtrate collected. The filtrate was shaken with a further suspension of NaNCS (5 mmol) in Me₂CO (15 ml) for 4 h, all volatiles removed by rotary evaporation and the residue extracted into CHCl₃. The chloroform extract was dried and rotary evaporated to leave a solid residue which was recrystallised from CH₂Cl₂/hexane, m.p. 120–122 °C.

IR: v: 2071 cm⁻¹. Far IR: v: 570(br), 491, 439, 420, 326, 252, 220, 200 cm⁻¹

2.6. X-ray crystallography

2.6.1. Data collection

Intensity data for 1 (X = Br and I) were obtained with Mo K α radiation, $\lambda = 0.71073$ Å, by means of the Enraf Nonius KappaCCD area diffractometer of the EPSRC's crystallography service at Southampton. For 1 (X = Br), for which the crystal shattered on cooling, the data were obtained at 298 K and at 120 K for 1 (X = I). The entire process of data collection, cell refinement and data reduction was accomplished by means of the programs DENZO [5] and COLLECT [6]. Correction for absorption by a semi-empirical method based upon the variation in intensity of equivalent reflections was achieved with the program SORTAV [7,8]. The transmission factors for each compound (Table 1) are not then on an absolute scale. Unfortunately both data sets have proved to be less than fully complete (see Table 1). This is especially true in the case of 1 (X = Br), where the available crystals were of particularly dubious quality, but is perceived to have no more deleterious effect than to limit the precision with which derived quantities such as bond lengths and bond angles are estimated.

2.6.2. Structure solution and refinement

In both cases initial solution of the structure was obtained by the heavy atom technique with the program SHELXS-86 [9] and completed and refined by full matrix least squares on F^2 with SHELXL-97 [10]. In the case of 1 (X = Br) the structure was finally re-refined with the atomic coordinates from the refinement of 1 (X = I) as starting parameters but with bromine substituted for iodine thus ensuring total equivalence between the labelling schemes of these two refinements. One reflection showing particularly poor agreement due to extinction was omitted from the refinement of 1 (X = Br). Despite a degree of disorder affecting the atoms of the cyclohexyl groups of 1 (X = Br), which was not modelled in detail, anisotropic thermal vibration parameters were refined for all non-H atoms. In all cases the residual electron

Table 1 Crystal data and structure refinement

Compound	1 (X = Br)	1 (X = I)
Empirical formula	$C_{18}H_{33}BrSn$	C ₁₈ H ₃₃ ISn
Formula weight	448.04	495.03
Temperature (K)	298(2)	120(2)
Crystal system	orthorhombic	orthorhombic
Space group	Pnma	Pnma
Unit cell dimensions		
a (Å)	11.2576(10)	12.2446(8)
b (Å)	16.6583(17)	17.1651(14)
<i>c</i> (Å)	10.2199(9)	9.0044(6)
Volume ($Å^3$)	1916.6(3)	1892.5(2)
Ζ	4	4
Calculated density (Mg/m ³)	1.553	1.737
Absorption coefficient (mm ⁻¹)	3.410	2.973
<i>F</i> (000)	904	976
Crystal ^a size (mm)	$0.22 \times 0.16 \times 0.07$	$0.30 \times 0.20 \times 0.20$
θ range for data collection (°)	2.69–20.97	3.05-27.50
Index ranges	$-10 \leqslant h \leqslant 10, -15 \leqslant k \leqslant 12, -7 \leqslant l \leqslant 10$	$-15 \leq h \leq 13, -19 \leq k \leq 22, -11 \leq l \leq 10$
Reflections collected/unique	1346/741	10576/2179
	$[R_{\rm int} = 0.0955]$	$[R_{\rm int} = 0.0737]$
Completeness to max. θ (%)	69.4	97.1
Absorption correction Tmin/max	0.2059/0.3222	0.7415/0.8258
Data/restraints/parameters	741/0/97	2179/0/97
Goodness-of-fit on F^2	1.026	1.018
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0690, wR_2 = 0.1826$	$R_1 = 0.0402, wR_2 = 0.0763$
<i>R</i> indices (all data)	$R_1 = 0.0930, wR_2 = 0.2085$	$R_1 = 0.0674, wR_2 = 0.0855$
Largest peak and hole $(e/Å^3)$	0.405 and -0.460	1.218 and -1.307

^a Colourless crystals in every case.

density features noted in Table 1 are in the vicinity (within 0.90 Å) of heavy atoms. In the final stages of refinement H atoms were introduced in calculated positions and refined with a riding model. The program OR-TEP-3 for Windows [11] was used in the preparation of the Figures and SHELXL-97 and PLATON [12] for bond length and angle and other molecular geometry calculations. PLATON was used, in particular, for calculations based upon crystallographic data extracted from the Cambridge Structural Database [13]. It is noted here that in Table 4 for those compounds with more than one molecule in the asymmetric unit, e.g. all 2, the bond distances and bond angles and the associated estimated errors are average values. Further details of the data collection and structure refinement processes are available in Table 1.

3. Results and discussion

3.1. General features of the structures

All of the cyclohexyl rings are found to be in the chair conformation with C–C distances and internal C–C–C angles more or less as expected provided that due allowance is made for the disorder in 1 (X = Br) noted above. Apart from this the real significance of the structures presented here lies in the nature of the tin coordination which they reveal which is discussed below.

3.2. Crystal structures of 1 (X = Br and I)

The compounds 1 (X = Br) and 1 (X = I) are isomorphous and it is for this reason that both the drawing of the molecule (Fig. 1) and the layer of molecules shown in Fig. 2, although based on data for 1 (X = I), are applicable to both compounds. In these structures the tin and halogen atoms lie on a crystallographic mirror plane which also bisects one of the cyclohexyl groups and re-



Fig. 1. The molecule of 1 (X = I) showing the labelling scheme. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms as small circles of arbitrary radius. Symmetry code (i) x, 3/2 - y, z.



Fig. 2. A layer of molecules of 1 (X = I). Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms have been omitted for clarity. Only selected atoms are labelled. Symmetry codes (ii) x - 1, y, z; (iii) x, y, 1 + z; (iv) x - 1, y, 1 + z; (v) x - 1/2, y, 1/2 - z.

lates the two remaining cyclohexyl groups by symmetry. Thus the asymmetric unit consists of one complete cyclohexyl group [C(1-6)], four atoms of another cyclohexyl group [C(7-10)] and the tin and halogen atoms (see Fig. 1). In both cases the bond length and bond angle data in Table 2 are consistent with tin in a tetrahedral environment distorted primarily in order to

Table 2 Selected bond lengths and angles $(\text{\AA}, ^{\circ})$ for isomorphous 1 (X = Br and I)

	X = Br	X = I		
Bond lengths				
Sn(1)-C(1) 2.09(2) × 2		$2.167(4) \times 2$		
Sn(1)–C(7)	2.09(2)	2.166(6)		
Sn(1)-X(1)	2.501(4)	2.7463(6)		
Bond angles				
$C(1)-Sn(1)-C(1^{i})$	119.6(16)	115.9(2)		
C(1)-Sn(1)-C(7)	$112.6(7) \times 2$	$114.45(12) \times 2$		
C(1)-Sn(1)-X(1)	$102.5(9) \times 2$	$104.90(10) \times 2$		
C(7)-Sn(1)-X(1)	104.5(6)	99.71(14)		

Symmetry code: (i) x, 3/2 - y, z.

Table 3 Comparison table of selected geometric parameters (Å, °) in 1 (X = F, Cl, Br and I)

accommodate the steric requirements of the cyclohexyl groups. Particularly notable in this table is the Sn(1)–I(1) bond length of 2.7463(6) Å which is much more reasonable than the previous published value [2] of 2.54(1) Å. The molecules are found in layers on the crystallographic mirror planes as shown in Fig. 2 within which the next nearest neighbour Sn–X distances are 5.375(5) and 4.8013(7) Å for X = Br and X = I, respectively. The surprisingly shorter next nearest neighbour distance for X = I is attributed primarily to the different temperatures at which the intensity data were collected (see Table 1).

3.3. Structural trends in R_3SnX compounds with X = F, Cl, Br and I

The nature, polymeric or molecular, of the solid state structure of 1 (X = Cl) has been a matter of conjecture for many years. Initial X-ray structural results [14] were taken to be indicative of a molecular structure with four coordinate tin in contrast to earlier results from Mössbauer spectoscopy suggestive of a polymeric structure with five coordinate tin. Means were then found [2] to resolve this disparity in favour of the molecular structural model. Further support for this model was obtained, by comparison of ¹¹⁹Sn chemical shifts in the solid state (CP/MAS) with those found for the compounds in solution, by Harris et al. [15]. The results of this study were considered to be compatible with 1 (X = Cl) existing as a molecular species in the solid state in the same manner as 1 (X = Br) and 3 (X = Cl). Most recently Asadi et al. [1] have investigated the X-ray crystal structure of 1 (X = Cl) over the temperature range 120-298 K. This study reveals, in addition to an order-disorder transition at about 248 K, an inverse and temperature dependent relationship between the nearest, Sn–Cl, and next nearest, $Sn \cdots Cl'$, distances. These distances tend to equality with reducing temperature. Also present are essentially linear Cl-Sn···Cl' and Sn- $Cl \cdots Sn'$ groups (see Table 3). The findings of Asadi et al. support the earlier suggestion [4], based on NMR (solution) and Mössbauer spectroscopy, that 1 (X = CI) is weakly polymeric in the solid state but

Х	Temperature ^a (K)	$Sn-X^{b}$	$Sn{\cdot} \cdot \cdot X'$	$Sn\!\!-\!\!X\!\cdots\!Sn'$	$X\!\!-\!\!Sn\!\cdot\cdot\cdot X'$	Reference
F		2.052(10)	2.302(10)	180	180	[16]
Cl	298	2.415(3)	3.298(3)	178.95(17)	178.95(12)	[1]
Cl	108	2.4657(7)	3.0077(7)	171.95(3)	178.58(3)	[1]
Br	298	2.501(4)	5.375(5)	135.39(15)	116.67(9)	c
Ι	120	2.7463(6)	4.8013(7)	140.03(2)	129.70(2)	с

^a Room temperature unless otherwise stated.

^b Primed and unprimed labels indicate next nearest and nearest neighbour atoms, respectively.

^c Isomorphs, this work.

Comparison of selected interatomic distances (A) in $(Neo)_3$ SnX, 2, and Ph ₃ SnX, 3								
	Ph ₃ Sn–X			(Neo) ₃ Sn–X				
Х	Sn–X ^a	$Sn{\cdot}{\cdot}{\cdot}X'$	Temperature ^b (K)	Reference	Sn–X	$Sn{\cdot}{\cdot}{\cdot}X'$	Temperature (K)	
Cl ^c	2.3548(17)	>5.84		[17]	2.382(3)	>7.31	150	
Cl ^c	2.3605(12)	>5.63	110	[17]				
Br ^c	2.495(2)	>5.79		[18]	2.5444(14)	>5.64	150	
Ι	2.6988(9) ^e	>6.30		[19]	2.7424(6)	>5.67	150	
Ι	$2.7080(7)^{f}$	>6.30		[20]				

[20]

Table 4 C

Primed and unprimed labels indicate next nearest and nearest neighbour atoms, respectively.

b Room temperature unless otherwise stated.

с Isomorphous pairs of compounds.

d Isomorphous pairs of compounds.

e Triclinic polymorph with Z = 4.

^f Triclinic polymorph with Z = 2.

monomeric in solution. Thus in the context of compounds of the form R_3 SnCl (R = alkyl or aryl) 1 (X = Cl) is perceived as being polymeric but intermediate in this respect between, on the one hand, such as polymeric Me₃ SnCl and on the other, for example, molecular Ph_3 SnCl, 3 (X = Cl).

With the information now available the status of various 1 can be considered further in terms of the nature of X as well as R. Thus from the data in Table 3 1 (X = Fand Cl), with $Sn \cdot \cdot X'$ distances much shorter than the sums of the contact radii of the relevant atoms (PLATON contact radii 2.26, 1.47, 1.75, 1.85 and 1.98 Å for Sn, F, Cl, Br and I, respectively) and essentially linear X- $Sn \cdots X'$ groups, are clearly polymeric. The remainder, 1 (X = Br and I) with $Sn \cdots X'$ distances greater than the relevant contact radii sums and non-linear X- $Sn \cdots X'$ groups, are equally clearly molecular species. Table 4 shows Sn-X and Sn $\cdot \cdot \cdot X'$ distances for compounds of the form R_3 SnX, R = Neo, 2, and R = Ph, 3, with, in both cases, X = Cl, Br and I. All of these compounds are molecular species as shown by the $Sn \cdots X'$ distances, all much greater than the sums of the contact radii. For 2 this is largely because of the bulk of the nonhalogen substituents. For 3 it comes about because the molecules occur in stacks in such a way as to permit large numbers of C–H– π intermolecular contacts. The Sn-X bonds of successive molecules in the stack are then directed in opposite directions away from the mid-line of the stack. In other words, in the case of 3 (X = Cl, Br and I), the stacking of the molecules favours interactions between the phenyl groups rather than $Sn \cdots X'$ intermolecular contacts.

Three notable features arise from comparison of Tables 3 and 4. First, whereas in 3 (X = CI), the only case for which the necessary data are available in Table 4, reduced temperature has virtually no effect on the Sn-Cl distance but shortens the $Sn \cdot \cdot Cl'$ contact dramatically, in 1 (X = Cl) both types of distance are temperature dependent but in opposite senses. Second, the Sn-Cl distance is longer in polymeric 1 (X = Cl) than in either of the corresponding, but molecular, 2 and 3 in which last two this distance is very similar. Third, for all molecular 1, 2 and 3 (X = Br and I) the Sn-X distances are much the same for any particular X. The implication of the above is that, at least for X = halogen, a polymeric compound of the form R₃Sn-X will display temperature dependency of the type noted above for 1 (X = Cl), more or less linear X–Sn···X' groups and an Sn–X distance longer than that found in a molecular compound with the same X but, obviously, a different R. In general terms it appears that the formation of polymeric species with bridging X in R_3SnX (X = halogen) in the solid state is favoured for more electronegative and smaller X and disfavoured by large R. On the other hand, as in the case of 3 (X = Cl, Br and I), polymerisation with bridging X may be supplanted by other intermolecular interactions.

The structures for 1 (X = Br and I) presented here improve upon those previously reported [2] not only because they are better determined but also, in the case of 1 (X = I), because the data derived from the original structure determination are very similar to those obtained both here and previously for 1 (X = Br). Likewise the previously reported [2] structure of 1 (X = F) has been ignored in favour of that of Tudela et al. [16] because the data derived from the original determination closely resembled that of 1 (X = CI). There is, therefore, doubt as to the authenticity of the samples used in the original structure determinations [2] of 1 (X = F and I).

4. Supplementary material

Supplementary data, including atomic coordinates, anisotropic thermal parameters and bond lengths and angles are available from the Cambridge Crystallographic Data Centre with reference codes CCDC 231208 and 231209 for 1 (X = I) and 1 (X = Br), respectively. Copies of this information may be obtained, free of charge, from the Director, CCDC, 12 Union Road,

Reference

[21]

[3]^d

[3]^d

Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk) or via http://www. ccdc.cam.ac.uk/conts/retrieving.html.

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