

Phenyltin Trichloroacetate Complexes: Preparations and Structures †

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Six phenyltin trichloroacetate complexes have been synthesised and their structures established by X-ray crystallography. The complex $\text{SnPh}_3(\text{O}_2\text{CCl}_3)\cdot\text{MeOH}$ (**1**) ($R = 0.0296$ for 1 770 unique observed reflections) is a five-co-ordinate monomer. Complexes (**2**) and (**4**) are isomers of $\{[\text{SnPh}_2(\text{O}_2\text{CCl}_3)]_2\text{O}\}_2$ ($R = 0.0918$ for 3 185 reflections and $R = 0.0379$ for 3 132 reflections respectively). They are centrosymmetric dimers respectively with all their carboxylate groups bridging, and with half of them unidentate. The complex $\text{Sn}_6\text{Ph}_6(\text{O}_2\text{CCl}_3)_{10}\text{O}_4\cdot 2\text{C}_6\text{H}_6$ (**3**) ($R = 0.0521$ for 2 556 reflections) is a linear hexatin compound containing three $(\text{Sn}-\text{O})_2$ stannoxane rings. Complex (**6**) is also a hexatin compound $[\text{SnPh}(\text{O}_2\text{CCl}_3)\text{O}]_6\cdot 3\text{C}_6\text{H}_6$ ($R = 0.0296$ for 1 921 reflections) with a drum structure. The complex $\text{Sn}_4\text{Ph}_8(\text{O}_2\text{CCl}_3)_6(\text{OH})_2$ (**5**) ($R = 0.0454$ for 3 111 reflections) is a novel linear chain connected by hydroxy and acetate bridges. Compounds (**2**)—(**4**) and (**6**) were all formed by dearylation reactions starting from di- and tri-phenyl tin compounds.

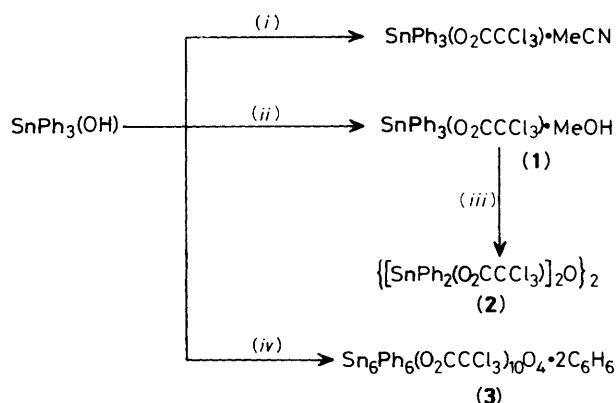
The initial aim of this investigation was to prepare Ph_3Sn carboxylate complexes for comparison to corresponding tellurium compounds.¹ However, when we used $\text{Cl}_3\text{CCO}_2\text{H}$ as the acid we encountered a remarkable range of complexes whose preparations, structures, and (to a certain extent) interconversions are described here. With hindsight, the variety of co-ordination and oligomerisation modes encountered should perhaps not have surprised us, in the light of the range of aryl and alkyl tin carboxylates already reported.^{2,3} However one particular feature has added to the complexity of the trichloroacetate complexes. This is the remarkably facile dearylation, taking place even during recrystallisation. This is presumably mediated by traces of water in the (nominally dry) solvents, interacting with the relatively strong acid used. Such dearylations have previously been reported,⁴ but have not been found to have a role in the interconversion of tin carboxylate complexes.

Results and Discussion

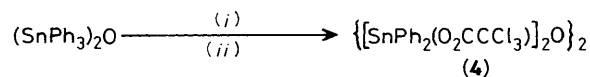
Preparations and Interconversions.—Although the complexes prepared were characterised analytically and spectroscopically, their structural variety has meant that full identification was only possible by crystal structure determination.

The compounds were obtained from triphenyltin hydroxide or oxide, by the routes shown in Schemes 1—3.

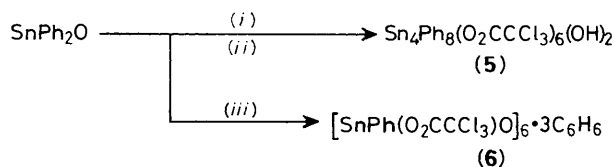
Compounds similar to (**1**) with other co-ordinating ligands (for example MeCN) can easily be prepared by the reaction of $\text{SnPh}_3(\text{OH})$ and the carboxylic acid in the corresponding solvent. Synthesis of $\text{SnPh}_3(\text{O}_2\text{CCl}_3)$ without the attached solvent molecule appears to be unusually difficult, although well known for other carboxylates.^{5,6} In particular, recrystallisation of (**1**) in a non-co-ordinating solvent leads to the diphenyltin compound (**2**). The stannoxane unit structure present in this complex is found in several other tin compounds. A compound of the same formulation is also formed in the dearylation of $(\text{SnPh}_3)_2\text{O}$ (Scheme 2). However, under these conditions (see above) the molecule, (**4**), has a different structure. It is not clear whether this is due to solvent effects in the recrystallisation or to the different reaction route. The structure of (**4**), $\{[\text{SnR}_2(\text{O}_2\text{CR}')]\}_2\text{O}\}_2$, is the most common for this type of compound and has been reported also with $\text{R} = \text{Me}$ or Bu and $\text{R}' = \text{CF}_3$ or CCl_3 for instance.^{7,8} In contrast to (**2**),



Scheme 1. (i) $\text{Cl}_3\text{CCO}_2\text{H}$, MeCN; (ii) $\text{Cl}_3\text{CCO}_2\text{H}$, MeOH; (iii) recrystallisation from CCl_4 -hexane; (iv) $\text{Cl}_3\text{CCO}_2\text{H}$, C_6H_6 , reflux



Scheme 2. (i) $\text{Cl}_3\text{CCO}_2\text{H}$, MeOH; (ii) recrystallisation from CH_2Cl_2 -light petroleum (b.p. 30—40 °C)



Scheme 3. (i) $\text{Cl}_3\text{CCO}_2\text{H}$, MeOH; (ii) recrystallisation from CH_2Cl_2 -light petroleum (b.p. 30—40 °C); (iii) $\text{Cl}_3\text{CCO}_2\text{H}$, C_6H_6 , reflux

it has one pendant carboxylate group in each of the asymmetric units. One intermediate between (**2**) and (**4**) has been reported by Lockhart *et al.*² No analogues to (**2**) could be found in the literature and this would appear to be an energetically less stable structure probably because of the absence of the intermolecular interactions formed by the unidentate carboxylates in the more common structures.

In the formation of (**3**) a double dearylation, Ph_3Sn to PhSn , has taken place, followed by a condensation to give a molecule containing a linear chain of six tin atoms. This structure is analogous to that reported by Holmes *et al.*³ Following

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

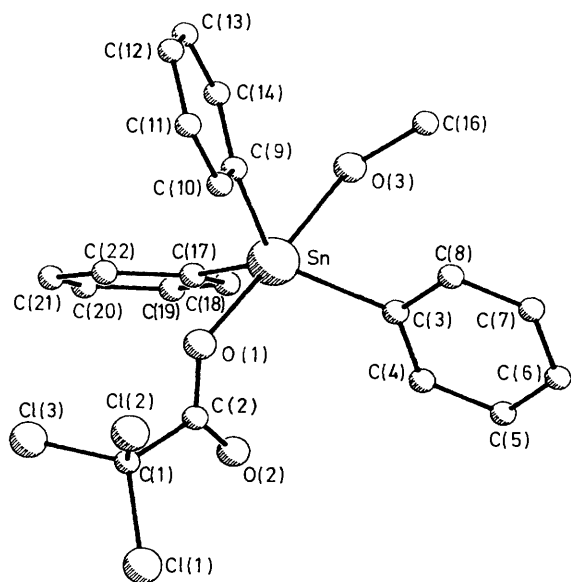


Figure 1. The structure of $\text{SnPh}_3(\text{O}_2\text{CCl}_3)\cdot\text{MeOH}$ (1)

Holmes, hydrolysis of this product (3) was expected to produce the cyclic complex (6), but conclusive evidence for this reaction route was not found. Complex (6) was however produced in the dearylation reaction (iii) (Scheme 3). Analogues of (6) with $\text{R} = \text{Bu}$ or Ph and $\text{R}' = \text{C}_6\text{H}_4\text{NO}_2$, or C_6H_{11} respectively and also with phosphonic acids have been reported.^{3,9,10}

Structure (5) appears to be entirely novel. The product formed does not contain a stannoxane ring but is held together by hydroxide and acetate bridges.

Structural Analysis.—Complex (1). The structure consists of a slightly distorted trigonal bipyramidal molecule of $\text{SnPh}_3(\text{O}_2\text{CCl}_3)\cdot\text{MeOH}$ (Figure 1). The distortion results from the displacement of the tin atom from the plane of the three equatorial phenyl groups by 0.128(2) Å. The phenyl groups have adopted the usual 'paddle wheel' formation to lessen steric hindrance. The tin atom lies closer to the acetate oxygen than the methanol oxygen as would be expected from a simple covalent/dative bond analysis (see Table 1 for bond lengths and angles for all compounds). The molecule is monomeric in solution, but in the solid state the tin atoms are linked in an infinite chain *via* a methanol/acetate hydrogen bond [$\text{O}(2)\cdots\text{O}(3)$ 2.705(4) Å].

Table 1. Selected bond lengths (Å) and angles (°) *

Complex (1)							
Sn—O(1)	2.172(2)	Sn—O(3)	2.400(3)	Sn—C(17)	2.118(4)	C(2)—O(1)	1.272(4)
Sn—C(3)	2.123(4)	Sn—C(9)	2.125(3)	C(2)—O(2)	1.208(4)	O(2)⋯O(3)	2.705(4)
O(1)—Sn—O(3)	178.3(0.1)	O(1)—Sn—C(3)	96.2(0.1)	O(3)—Sn—C(17)	84.5(0.1)	C(3)—Sn—C(9)	117.6(0.1)
O(1)—Sn—C(9)	88.9(0.1)	O(1)—Sn—C(17)	94.7(0.1)	C(3)—Sn—C(17)	127.6(0.1)	C(9)—Sn—C(17)	113.7(0.1)
O(3)—Sn—C(3)	85.5(0.1)	O(3)—Sn—C(9)	90.0(0.1)	O(1)—C(2)—O(2)	127.6(0.3)		
Complex (2)							
Sn(1)—O(2)	2.432(10)	Sn(1)—O(5)	2.138(10)	Sn(1)—C(21)	2.118(14)	Sn(2)—C(31)	2.186(16)
Sn(1)—O(4 ^l)	2.400(14)	Sn(1)—O(5 ^l)	2.131(8)	Sn(2)—C(41)	2.126(16)	O(1)—C(1)	1.202(22)
Sn(2)—O(1)	2.207(11)	Sn(2)—O(3)	2.199(12)	O(2)—C(1)	1.206(22)	O(3)—C(3)	1.251(20)
Sn(2)—O(5)	2.015(9)	Sn(1)—C(11)	2.127(13)	O(4)—C(3)	1.243(24)		
O(2)—Sn(1)—O(5)	91.8(0.4)	O(2)—Sn(1)—O(4 ^l)	99.2(0.4)	Sn(1)—O(5)—Sn(1 ^l)	103.9(0.4)	Sn(2)—O(5)—Sn(1 ^l)	128.3(0.5)
O(2)—Sn(1)—O(5 ^l)	168.0(0.4)	O(5)—Sn(1)—O(4 ^l)	168.9(0.3)	C(11)—Sn(1)—C(21)	153.4(0.5)	C(31)—Sn(2)—C(41)	134.2(0.6)
O(5)—Sn(1)—O(5 ^l)	76.1(0.4)	O(4 ^l)—Sn(1)—O(5 ^l)	92.8(0.4)	O(5)—Sn(2)—C(31)	113.6(0.5)	O(5)—Sn(2)—C(41)	112.2(0.5)
O(1)—Sn(2)—O(3)	171.6(0.5)	O(1)—Sn(2)—O(5)	94.1(0.4)	O(1)—C(1)—O(2)	128.8(1.4)	O(3)—C(3)—O(4)	126.0(2.0)
O(3)—Sn(2)—O(5)	94.3(0.4)	Sn(1)—O(5)—Sn(2)	127.8(0.4)				
Complex (3)							
Sn(1)—O(2)	2.213(12)	Sn(1)—O(3)	2.162(12)	Sn(2)—C(21)	2.080(20)	Sn(3)—C(31)	2.092(19)
Sn(1)—O(11)	2.124(9)	Sn(1)—O(12)	2.094(9)	O(1)—C(1)	1.265(19)	O(2)—C(1)	1.218(20)
Sn(1)—O(12 ^l)	2.030(10)	Sn(2)—O(4)	2.208(12)	O(3)—C(3)	1.227(20)	O(4)—C(3)	1.228(20)
Sn(2)—O(6)	2.126(14)	Sn(2)—O(7)	2.285(12)	O(5)—C(5)	1.260(22)	O(6)—C(5)	1.223(25)
Sn(2)—O(9)	2.080(14)	Sn(2)—O(11)	1.994(10)	O(7)—C(7)	1.255(22)	O(8)—C(7)	1.212(24)
Sn(3)—O(1)	2.156(11)	Sn(3)—O(5)	2.149(10)	O(9)—C(9)	1.109(50)	O(9)—C(9 ^l)	1.301(85)
Sn(3)—O(8)	2.125(11)	Sn(3)—O(11)	2.095(11)	O(10)—C(9)	1.433(72)	O(10 ^l)—C(9 ^l)	0.887(91)
Sn(3)—O(12 ^l)	2.024(10)	Sn(1)—C(11)	2.111(16)				
O(2)—Sn(1)—O(3)	173.5(0.4)	O(2)—Sn(1)—O(11)	85.9(0.4)	O(7)—Sn(2)—C(21)	85.6(0.6)	O(9)—Sn(2)—O(11)	88.5(0.5)
O(2)—Sn(1)—O(12)	97.7(0.4)	O(2)—Sn(1)—O(12 ^l)	85.9(0.4)	O(9)—Sn(2)—C(21)	102.8(0.7)	O(11)—Sn(2)—C(21)	168.6(0.6)
O(2)—Sn(1)—C(11)	86.8(0.6)	O(3)—Sn(1)—O(11)	87.6(0.4)	O(1)—Sn(3)—O(5)	82.0(0.4)	O(1)—Sn(3)—O(8)	168.7(0.4)
O(3)—Sn(1)—O(12)	87.5(0.4)	O(3)—Sn(1)—O(12 ^l)	91.7(0.4)	O(1)—Sn(3)—O(11)	83.5(0.4)	O(1)—Sn(3)—O(12 ^l)	93.9(0.4)
O(3)—Sn(1)—C(11)	96.7(0.6)	O(11)—Sn(1)—O(12)	147.3(0.4)	O(1)—Sn(3)—C(31)	91.2(0.6)	O(5)—Sn(3)—O(8)	89.4(0.4)
O(11)—Sn(1)—O(12 ^l)	74.1(0.4)	O(11)—Sn(1)—C(11)	116.6(0.5)	O(5)—Sn(3)—O(11)	87.1(0.4)	O(5)—Sn(3)—O(12 ^l)	161.9(0.4)
O(12)—Sn(1)—O(12 ^l)	73.8(0.4)	O(12)—Sn(1)—C(11)	96.1(0.5)	O(5)—Sn(3)—C(31)	88.2(0.6)	O(5)—Sn(3)—O(11)	88.8(0.4)
O(12 ^l)—Sn(1)—C(11)	166.6(0.5)	O(4)—Sn(2)—O(6)	168.0(0.5)	O(8)—Sn(3)—O(12 ^l)	92.9(0.4)	O(8)—Sn(3)—C(31)	95.9(0.6)
O(4)—Sn(2)—O(7)	81.1(0.4)	O(4)—Sn(2)—O(9)	92.6(0.5)	O(11)—Sn(3)—O(12 ^l)	74.8(0.4)	O(11)—Sn(3)—C(31)	173.3(0.6)
O(4)—Sn(2)—O(11)	84.6(0.4)	O(4)—Sn(2)—C(21)	93.4(0.7)	O(12 ^l)—Sn(3)—C(31)	109.6(0.5)	O(1)—C(1)—O(2)	130.3(1.5)
O(6)—Sn(2)—O(7)	89.0(0.5)	O(6)—Sn(2)—O(9)	96.2(0.6)	O(3)—C(3)—O(4)	129.6(1.8)	O(5)—C(5)—O(6)	124.7(1.7)
O(6)—Sn(2)—O(11)	87.6(0.5)	O(6)—Sn(2)—C(21)	92.5(0.7)	O(7)—C(7)—O(8)	128.1(1.7)	O(9)—C(9)—O(10 ^l)	104.7(3.9)
O(7)—Sn(2)—O(9)	169.9(0.5)	O(7)—Sn(2)—O(11)	83.0(0.4)				

Table 1 (continued)

Complex (4)							
Sn(1)-O(1)	2.154(4)	Sn(1)-O(1 ^{II})	2.062(5)	Sn(2)-C(21)	2.129(7)	Sn(2)-C(27)	2.113(8)
Sn(1)-O(22 ^{II})	2.323(6)	Sn(1)-C(11)	2.115(8)	O(11)-C(113)	1.259(11)	O(12)-C(113)	1.209(10)
Sn(1)-C(17)	2.107(8)	Sn(2)-O(1)	2.031(5)	O(21)-C(213)	1.222(11)	O(22)-C(213)	1.219(11)
Sn(2)-O(11)	2.212(5)	Sn(2)-O(21)	2.250(5)				
O(1)-Sn(1)-O(1 ^{II})	76.4(0.2)	O(1)-Sn(1)-O(22 ^{II})	170.0(0.2)	O(1)-Sn(2)-C(21)	107.3(0.3)	O(1)-Sn(2)-C(27)	106.9(0.3)
O(1)-Sn(1)-C(11)	99.2(0.2)	O(1)-Sn(1)-C(17)	99.9(0.2)	O(11)-Sn(2)-O(21)	172.7(0.2)	O(11)-Sn(2)-C(21)	95.6(0.2)
O(1 ^{II})-Sn(1)-O(22 ^{II})	93.6(0.2)	O(1 ^{II})-Sn(1)-C(11)	103.2(0.3)	O(11)-Sn(2)-C(27)	94.3(0.2)	O(12)-Sn(2)-C(21)	87.1(0.2)
O(1 ^{II})-Sn(1)-C(17)	104.1(0.3)	O(22 ^{II})-Sn(1)-C(11)	82.0(0.2)	O(12)-Sn(2)-C(27)	87.3(0.3)	C(21)-Sn(2)-C(27)	145.5(0.3)
O(22 ^{II})-Sn(1)-C(17)	83.3(0.3)	C(11)-Sn(1)-C(17)	149.6(0.3)	O(11)-C(113)-O(12)	126.1(0.7)	O(21)-C(213)-O(22)	127.0(0.7)
O(1)-Sn(2)-O(11)	80.7(0.2)	O(1)-Sn(2)-O(21)	92.0(0.2)				
Complex (5)							
Sn(1)-O(2)	2.361(7)	Sn(1)-O(6)	2.277(6)	Sn(2)-C(25)	2.108(11)	O(1)-C(1)	1.244(12)
Sn(1)-O(7)	2.155(6)	Sn(1)-O(1 ^{II})	2.185(6)	O(2)-C(1)	1.204(11)	O(3)-C(3)	1.255(11)
Sn(1)-C(7)	2.098(10)	Sn(1)-C(13)	2.104(10)	O(4)-C(3)	1.203(11)	O(5)-C(5)	1.220(11)
Sn(2)-O(3)	2.157(6)	Sn(2)-O(5)	2.212(6)	O(6)-C(5)	1.232(10)		
Sn(2)-O(7)	2.021(5)	Sn(2)-C(19)	2.083(12)				
O(2)-Sn(1)-O(6)	98.0(0.2)	O(2)-Sn(1)-O(7)	175.1(0.2)	O(3)-Sn(2)-O(7)	86.3(0.2)	O(3)-Sn(2)-C(19)	95.9(0.3)
O(2)-Sn(1)-O(1 ^{II})	96.9(0.2)	O(2)-Sn(1)-C(7)	84.0(0.3)	O(3)-Sn(2)-C(25)	91.0(0.3)	O(5)-Sn(2)-O(7)	86.9(0.2)
O(2)-Sn(1)-C(13)	86.1(0.3)	O(6)-Sn(1)-O(7)	86.6(0.2)	O(5)-Sn(2)-C(19)	89.8(0.3)	O(5)-Sn(2)-C(25)	88.6(0.3)
O(6)-Sn(1)-O(1 ^{II})	165.0(0.2)	O(6)-Sn(1)-C(7)	86.9(0.3)	O(7)-Sn(2)-C(19)	104.8(0.3)	O(7)-Sn(2)-C(25)	118.7(0.3)
O(6)-Sn(1)-C(13)	87.1(0.3)	O(7)-Sn(1)-O(1 ^{II})	78.4(0.2)	C(19)-Sn(2)-C(25)	136.3(0.4)	O(1)-C(1)-O(2)	126.8(0.9)
O(7)-Sn(1)-C(7)	94.8(0.3)	O(7)-Sn(1)-C(13)	95.7(0.3)	O(3)-C(3)-O(4)	128.0(0.9)	O(5)-C(5)-O(6)	129.6(0.9)
O(1 ^{II})-Sn(1)-C(7)	93.1(0.3)	O(1 ^{II})-Sn(1)-C(13)	95.5(0.3)	Sn(1)-O(7)-Sn(2)	137.8(0.3)		
C(7)-Sn(1)-C(13)	167.6(0.4)	O(3)-Sn(2)-O(5)	172.1(0.3)				
Complex (6)							
Sn(1)-O(1)	2.089(3)	Sn(1)-O(3)	2.183(3)	Sn(1)-O(2 ^{III})	2.191(3)	Sn(1)-C(3)	2.104(13)
Sn(1)-O(1 ^{III})	2.095(7)	Sn(1)-O(1 ^{IV})	2.075(3)	O(2)-C(1)	1.240(11)	O(3)-C(1)	1.244(10)
O(1)-Sn(1)-O(3)	86.6(0.1)	O(1)-Sn(1)-O(1 ^{III})	77.3(0.2)	O(3)-Sn(1)-C(3)	90.4(0.2)	O(1 ^{III})-Sn(1)-O(1 ^{IV})	77.5(0.2)
O(1)-Sn(1)-O(1 ^{IV})	104.6(0.1)	O(1)-Sn(1)-O(2 ^{III})	158.1(0.2)	O(1 ^{III})-Sn(1)-O(2 ^{III})	87.4(0.2)	O(1 ^{III})-Sn(1)-C(3)	176.2(0.1)
O(1)-Sn(1)-C(3)	101.0(0.2)	O(3)-Sn(1)-O(1 ^{III})	86.2(0.2)	O(1 ^{IV})-Sn(1)-O(2 ^{III})	87.0(0.1)	O(1 ^{IV})-Sn(1)-C(3)	106.2(0.2)
O(3)-Sn(1)-O(1 ^{IV})	157.4(0.2)	O(3)-Sn(1)-O(2 ^{III})	76.7(0.1)	O(2 ^{III})-Sn(1)-C(3)	93.3(0.3)	O(2)-C(1)-O(3)	128.6(0.4)

* I 1 - x, 1 - y, 1 - z; II 1 - x, -y, 1 - z; III z, x, y; IV 1 - z, 1 - x, 1 - y

Complex (2). The structure of (2) consists of a centrosymmetric dimer. The asymmetric unit has one five- and one six-coordinate tin atom (Figure 2). The six-coordinate tin is part of a stannoxane ring around the centre of symmetry.

This tin atom has an octahedral geometry with four equatorial oxygens and two axial carbon atoms. Its geometry is somewhat distorted by the small angle (Table 1) in the stannoxane ring, affecting the equatorial angles. Steric effects between the phenyl groups across the stannoxane ring cause the rings to bend away from the centre of the molecule [C-Sn-C 153.4(0.5)°] and also to twist relative to each other. The five-coordinate tin atom has a trigonal bipyramidal co-ordination with the two acetate oxygens in the axial positions, and the phenyl rings and stannoxane oxygen occupying the equatorial plane. As with the six-coordinate tin atom, the C-Sn-C angle increases from 120° to 134.2(0.6)° by phenyl-phenyl interactions, though this time the groups are on the same tin atom. An unusual feature here is that although the acetate bridges are symmetrical [difference in C-O bond lengths is 0.010(20) Å], the Sn-O bond lengths are not equal [difference of 0.213(12) Å]. This is probably due to the *trans* effect from the strongly bound stannoxane ring oxygen, as first suggested by Graziani *et al.*⁷

Complex (3). The molecule is a dimer, the two halves being related by a centre of symmetry, and it contains three crystallographically distinct tin atoms (Figure 3). All have geometries based on an octahedron, bonded to five oxygen atoms and one carbon. Distortions in the octahedra are again due to the small angle in the stannoxane rings (Table 1). Of the five trichloroacetate groups in the structure, four are sym-

metrically bidentate bridging, while the fifth, connected to Sn(2), is unidentate. All other bond lengths and angles are as expected.

Complex (4). Molecule (4) has the same composition as (2), but has crystallised as a different isomer. The molecule still possesses a centre of symmetry, but here one of the acetate groups is 'hanging' rather than bridging (Figure 4). This is the more usual structure adopted by this class of compounds.^{9,10}

The tin atoms both have five primary bonds and one long-range interaction. However, one adopts a geometry based on an octahedron and the other a trigonal bipyramid.

The geometry around Sn(1), the stannoxane ring tin, is essentially the same as its counterpart in (2). The vacant site and consequent long-range interaction, caused by the hanging acetate, make very little difference to the geometry. This is, no doubt, due to the strong stannoxane ring bonding governing the geometry.

The geometry around Sn(2) is similar to that in (2) except for a slight narrowing of the O(1)-Sn(2)-O(11) angle (Table 1) to accommodate the long Sn(2)-O(12) bond. The different modes of bonding of the acetates, *i.e.* bridging or hanging, are easily distinguishable from the relevant bond lengths. The unidentate acetate has a difference of 0.05(1) Å between its C-O bonds while for the bidentate acetate this difference is only 0.003(10) Å. The bidentate acetate shows the same asymmetry in its Sn-O bond lengths as noted for (2).

Complex (5). The molecule has a centre of symmetry giving two crystallographically distinct tin atoms. One has octahedral geometry, the other trigonal bipyramidal (Figure 5). Distortions arise due to the uneven bridges between the tin atoms. This is

Table 2. Crystal data and data collection parameters

Compound	(1)	(2)	(3)	(4)	(5)	(6)
Formula	$C_{20}H_{15}Cl_3O_2Sn_2 \cdot CH_3OH$	$C_{36}H_{40}Cl_2O_{10}Sn_4$	$C_{36}H_{30}Cl_3O_{2.4}Sn_6 \cdot 2C_6H_6$	$C_{36}H_{40}Cl_2O_{10}Sn_4$	$C_{60}H_{42}Cl_{18}O_{14}Sn_4$	$C_{48}H_{30}Cl_{18}O_{18}Sn_6 \cdot 3C_6H_6$
<i>M</i>	544.48	1773.33	3019.66	1773.33	2100.38	2402.12
<i>D_c</i>	1.563	1.850	1.932	1.895	1.787	1.881
<i>Z</i>	4	2	2	2	1	2
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Trigonal
Systematic absences	$h0l = 2n + 1$ $0k0 = 2n + 1$	$h0l = 2n + 1$ $0k0 = 2n + 1$	$h0l = 2n + 1$ $0k0 = 2n + 1$	$h0l = 2n + 1$ $0k0 = 2n + 1$	None	$hk/h + k = 2n + 1$ $h0l/h, l = 2n + 1$
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$R\bar{3}c$
<i>a</i> /Å	10.196(2)	13.172(3)	15.714(4)	12.818(3)	10.008(4)	21.770(4)
<i>b</i> /Å	12.672(2)	12.697(5)	14.054(4)	18.241(4)	10.696(4)	
<i>c</i> /Å	17.913(3)	19.561(5)	23.575(4)	13.651(3)	18.878(7)	42.35(1)
$\alpha/^\circ$	91.59(2)	103.32(2)	94.59(2)	103.24(2)	80.71(3)	
$\beta/^\circ$					78.30(3)	
$\gamma/^\circ$					85.89(3)	
<i>U</i> /Å ³	2313.6(8)	3183.5(1.7)	5189.8(2.3)	3107.0(1.1)	1951.3(1.3)	4240.0(1.8)
μ/cm^{-1}	14.74	21.19	22.69	21.71	19.48	23.81
<i>F</i> (000)	1076	1720	2896	1720	1018	2388
Crystal size	$0.2 \times 0.2 \times 0.4$	$0.1 \times 0.2 \times 0.5$	$0.1 \times 0.3 \times 0.2$	$0.3 \times 0.3 \times 0.3$	$0.2 \times 0.1 \times 0.3$	$0.2 \times 0.2 \times 0.4$
Max. transmission	0.7915	0.8120	0.7971	0.78	0.8653	0.6914
Min. transmission	0.7464	0.6115	0.7540	0.66	0.7109	0.5486
Scan range	± 0.95	± 1.0	± 1.1	± 1.0	± 1.5	± 0.95
Scan rate/ $^\circ$	4.0	2.0	3.5	3.0	2.0	2.0
Max. $2\theta/^\circ$	50	50	45	50	45	50
Reflections collected	4440	5353	7301	5925	5140	8449
Reflections observed [$I \geq 2\sigma(I)$]	1770	3185	2556	3132	3111	1921
<i>w</i>	0.00041	0.00235	0.00114	0.00072	0.00049	0.00057
<i>R</i>	0.0296	0.0918	0.0521	0.0379	0.0454	0.0296
<i>R'</i>	0.0327	0.1017	0.0509	0.0385	0.0451	0.0330
Max. on final Fourier/ $e \text{ \AA}^{-3}$	± 0.3	± 3.2	± 0.8	± 0.5	± 0.7	± 0.7
Max. δ/σ	0.105	0.08	0.075	0.013	0.030	0.003
No. of parameters	259	382	555	370	433	164

Table 3. Atom co-ordinates ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
Complex (1)							
Sn(1)	1 712.3(3)	7 372.2(2)	7 467.4(3)	C(10)	4 282(3)	6 356(3)	7 001(3)
Cl(1)	3 309.6(16)	11 432.6(10)	6 369.7(13)	C(11)	5 088	5 570	6 719
Cl(2)	5 040.0(13)	9 671.1(13)	6 248.0(14)	C(12)	4 576	4 572	6 559
Cl(3)	2 665(2)	9 769(2)	5 347(2)	C(13)	3 256	4 360	6 681
O(1)	2 880(3)	8 479(2)	6 845(2)	C(14)	2 450	5 146	6 963
O(2)	1 733(3)	9 907(3)	7 145(3)	C(9)	2 963	6 144	7 123
C(1)	3 389(5)	10 054(4)	6 227(4)	C(18)	-1 236(4)	7 669(3)	7 074(3)
C(2)	2 574(4)	9 461(4)	6 811(4)	C(19)	-2 340	7 746	6 600
C(4)	1 470(4)	8 948(3)	8 756(4)	C(20)	-2 201	7 715	5 827
C(5)	1 770	9 381	9 456	C(21)	-958	7 608	5 530
C(6)	2 711	8 903	9 925	C(22)	146	7 531	6 005
C(7)	3 351	7 992	9 693	C(17)	7	7 562	6 777
C(8)	3 050	7 559	8 993	O(3)	399(3)	6 113(3)	8 117(3)
C(3)	2 110	8 037	8 525	C(16)	841(6)	5 523(5)	8 760(4)
Complex (2)							
Sn(1)	5 046.0(8)	5 331.6(7)	4 176.2(4)	C(13)	4 376(22)	2 010(14)	3 642(11)
Sn(2)	2 415.1(9)	5 271.9(7)	4 582.7(5)	C(14)	4 493(18)	1 918(18)	2 966(11)
C(2)	2 233(5)	5 336(6)	2 261(3)	C(15)	4 786(20)	2 801(15)	2 623(11)
Cl(11)	1 997(5)	4 013(6)	2 053(3)	C(16)	4 927(18)	3 787(14)	2 988(10)
Cl(12)	3 038(5)	5 857(6)	1 755(3)	C(21)	5 251(12)	6 987(11)	4 210(7)
Cl(13)	1 057(5)	6 020(6)	2 090(3)	C(22)	6 294(14)	7 425(12)	4 367(8)
Cl(14)	896(5)	5 523(6)	2 149(3)	C(23)	6 384(16)	8 491(11)	4 425(8)
Cl(15)	2 457(5)	4 087(6)	1 966(3)	C(24)	5 505(16)	9 129(12)	4 354(10)
Cl(16)	2 729(5)	6 281(6)	1 782(3)	C(25)	4 572(16)	8 741(13)	4 201(10)
Cl(21)	2 759(6)	5 572(8)	7 575(3)	C(26)	4 405(14)	7 679(11)	4 129(8)
Cl(22)	1 772(7)	3 688(8)	6 998(4)	C(31)	1 581(13)	3 777(12)	4 545(8)
Cl(23)	848(5)	5 656(7)	6 542(3)	C(32)	1 750(18)	3 036(14)	4 033(10)
O(1)	2 297(10)	5 075(8)	3 446(5)	C(33)	1 253(19)	2 119(14)	4 006(12)
O(2)	3 642(9)	5 820(9)	3 184(5)	C(34)	614(19)	1 905(15)	4 497(14)
O(3)	2 286(11)	5 508(10)	5 673(6)	C(35)	500(16)	2 627(15)	4 959(13)
O(4)	3 511(11)	4 556(9)	6 378(6)	C(36)	1 008(14)	3 581(14)	4 983(10)
O(5)	3 980(7)	5 117(7)	4 839(4)	C(41)	1 943(14)	6 870(12)	4 416(9)
C(1)	2 783(15)	5 434(12)	3 050(8)	C(42)	1 323(15)	7 155(14)	3 764(10)
C(3)	2 676(17)	5 055(14)	6 241(9)	C(43)	1 031(21)	8 155(19)	3 643(12)
C(4)	2 039(19)	5 081(18)	6 810(9)	C(44)	1 319(25)	8 916(19)	4 138(16)
C(11)	4 849(14)	3 848(10)	3 657(7)	C(45)	1 985(25)	8 670(19)	4 794(16)
C(12)	4 558(17)	2 977(11)	3 987(8)	C(46)	2 284(17)	7 607(13)	4 917(13)
Complex (3)							
Sn(1)	4 586.4(7)	5 942.8(8)	4 664.7(6)	C(1)	3 898(10)	6 792(11)	5 749(8)
Sn(2)	2 410.8(8)	6 378.8(9)	3 993.0(7)	C(2)	3 803(13)	7 695(12)	6 095(10)
Sn(3)	3 037.9(7)	4 966.9(9)	5 283.2(6)	C(3)	3 985(10)	5 304(12)	3 469(8)
Cl(11)	4 756(4)	8 367(4)	6 184(3)	C(4)	4 209(11)	4 872(14)	2 904(9)
Cl(12)	3 402(4)	7 521(5)	6 753(3)	C(5)	1 367(10)	6 231(14)	5 057(9)
Cl(13)	3 044(4)	8 401(4)	5 670(4)	C(6)	598(12)	6 593(12)	5 326(9)
Cl(21)	3 837(4)	3 864(4)	2 979(3)	C(7)	2 226(10)	4 051(12)	4 199(10)
Cl(22)	4 806(5)	5 726(5)	2 553(3)	C(8)	2 106(11)	3 132(15)	3 818(10)
Cl(23)	3 283(4)	4 622(6)	2 453(3)	C(9)	2 950(28)	8 403(32)	3 846(24)
Cl(31)	-315(3)	6 411(5)	4 883(4)	C(9 ^l)	3 303(44)	7 950(51)	3 590(36)
Cl(32)	726(4)	7 764(4)	5 520(3)	C(11)	5 156(10)	7 171(11)	4 345(8)
Cl(33)	441(5)	5 947(5)	5 958(4)	C(12)	5 105(11)	7 403(14)	3 798(10)
Cl(41)	1 664(4)	2 253(4)	4 236(4)	C(13)	5 565(16)	8 205(20)	3 619(13)
Cl(42)	1 434(4)	3 341(5)	3 204(3)	C(14)	6 029(20)	8 724(18)	3 959(13)
Cl(43)	3 115(4)	2 802(4)	3 652(3)	C(15)	6 144(12)	8 452(14)	4 536(11)
C(10)	3 105(5)	9 344(5)	3 911(5)	C(16)	5 699(12)	7 690(14)	4 738(10)
Cl(51)	4 029(5)	9 403(5)	4 376(5)	C(21)	1 482(12)	6 575(14)	3 324(9)
Cl(52)	2 217(5)	9 640(5)	4 279(5)	C(22)	1 738(13)	6 909(17)	2 823(12)
Cl(53)	3 190(5)	10 145(5)	3 350(5)	C(23)	1 144(16)	7 041(18)	2 376(14)
Cl(54)	2 338(5)	10 247(5)	3 830(5)	C(24)	364(25)	6 847(26)	2 386(16)
Cl(55)	3 653(5)	9 268(5)	3 295(5)	C(25)	55(21)	6 465(26)	2 855(16)
Cl(56)	3 828(5)	9 603(5)	4 494(5)	C(26)	644(13)	6 359(18)	3 352(13)
O(1)	3 312(7)	6 195(7)	5 815(5)	C(31)	2 779(10)	4 148(12)	5 990(8)
O(2)	4 516(6)	6 740(7)	5 469(5)	C(32)	2 981(17)	4 437(16)	6 537(11)
O(3)	4 500(6)	5 145(7)	3 878(5)	C(33)	2 793(16)	3 850(18)	6 976(14)
O(4)	3 360(7)	5 833(8)	3 433(5)	C(34)	2 370(13)	3 049(16)	6 887(11)
O(5)	1 761(6)	5 520(8)	5 271(6)	C(35)	2 131(16)	2 755(18)	6 375(11)
O(6)	1 526(8)	6 621(9)	4 614(6)	C(36)	2 367(12)	3 302(14)	5 911(11)
O(7)	2 004(7)	4 817(9)	3 957(6)	C(41)	1 470(21)	4 875(32)	1 287(20)

Table 3 (continued)

Atom	x	y	z	Atom	x	y	z
O(8)	2 606(7)	3 941(7)	4 663(5)	C(42)	1 239(26)	4 726(37)	767(22)
O(9)	2 995(9)	7 705(10)	4 065(7)	C(43)	592(15)	4 252(18)	631(14)
O(10)	2 300(26)	8 320(32)	4 236(22)	C(44)	111(17)	4 086(30)	1 046(22)
O(10 ¹)	3 107(25)	8 190(29)	3 257(20)	C(45)	117(30)	4 116(25)	1 587(26)
O(11)	3 231(6)	5 920(7)	4 622(5)	C(46)	919(28)	4 653(25)	1 658(22)
O(12)	5 730(6)	5 219(6)	4 886(5)				
Complex (4)							
Sn(1)	4 560(1)	171(1)	3 783(1)	C(113)	7 124(7)	743(4)	2 658(6)
Sn(2)	7 431(1)	514(1)	4 787(1)	O(11)	6 497(4)	579(3)	3 212(4)
Cl(11)	7 361(3)	1 415(2)	952(2)	O(12)	8 074(5)	862(4)	2 937(4)
Cl(12)	5 294(2)	1 071(2)	1 263(2)	C(114)	6 632(7)	806(5)	1 508(6)
Cl(13)	6 719(3)	-76(2)	1 001(2)	C(21)	7 530(6)	1 667(4)	5 029(6)
Cl(21)	10 072(2)	485(2)	7 990(2)	C(22)	7 426(8)	1 938(5)	5 934(7)
Cl(22)	8 601(2)	151(2)	9 216(2)	C(23)	7 481(10)	2 680(6)	6 138(8)
Cl(23)	9 296(4)	-973(1)	8 042(2)	C(24)	7 620(9)	3 159(5)	5 412(9)
O(1)	5 981(4)	183(3)	4 986(3)	C(25)	7 756(9)	2 903(5)	4 514(8)
C(11)	4 200(6)	1 304(4)	3 719(5)	C(26)	7 722(7)	2 182(5)	4 337(7)
C(12)	4 895(8)	1 848(5)	3 617(7)	C(27)	8 272(6)	-441(4)	4 546(6)
C(13)	4 632(10)	2 580(6)	3 688(9)	C(28)	9 196(7)	-656(5)	5 223(7)
C(14)	3 668(10)	2 764(6)	3 883(9)	C(29)	9 704(7)	-1 300(5)	5 070(7)
C(15)	2 956(8)	2 229(5)	4 023(7)	C(210)	9 317(8)	-1 717(5)	4 262(8)
C(16)	3 220(7)	1 509(5)	3 937(6)	C(211)	8 428(8)	-1 524(5)	3 594(8)
C(17)	4 823(7)	-805(4)	3 049(5)	C(212)	7 899(7)	-879(5)	3 711(7)
C(18)	5 202(9)	-1 399(5)	3 581(7)	C(213)	7 997(7)	99(4)	7 183(6)
C(19)	5 352(9)	-2 058(6)	3 142(8)	O(21)	8 190(5)	388(3)	6 437(4)
C(110)	5 113(8)	-2 132(6)	2 150(7)	O(22)	7 127(5)	-107(4)	7 294(4)
C(111)	4 704(10)	-1 551(6)	1 569(7)	C(214)	8 963(7)	-36(4)	8 080(5)
C(112)	4 558(9)	-893(6)	2 012(7)				
Complex (5)							
Sn(1)	9 508.8(7)	347.8(6)	6 332.9(3)	C(7)	7 577(10)	-413(9)	6 492(5)
Sn(2)	9 122.1(7)	-638.9(6)	8 440.7(3)	C(8)	7 438(11)	-1 674(10)	6 828(6)
Cl(1)	8 059(5)	3 694(3)	5 347(2)	C(9)	6 165(12)	-2 189(11)	6 990(7)
Cl(2)	9 576(5)	4 147(3)	3 896(3)	C(10)	5 033(12)	-1 472(12)	6 834(7)
Cl(3)	6 947(4)	3 191(4)	4 180(3)	C(11)	5 206(13)	-268(12)	6 503(7)
Cl(4)	11 619(4)	-4 493(3)	9 406(2)	C(12)	6 436(11)	261(11)	6 336(6)
Cl(5)	10 569(5)	-5 182(3)	8 244(3)	C(13)	11 251(10)	1 449(9)	6 048(5)
Cl(6)	13 361(4)	-4 596(4)	8 030(2)	C(14)	12 112(12)	1 496(12)	5 383(6)
Cl(7)	6 164(5)	3 066(4)	8 644(2)	C(15)	13 225(13)	2 231(12)	5 200(7)
Cl(8)	7 792(5)	4 437(3)	7 409(3)	C(16)	13 500(14)	2 931(12)	5 685(8)
Cl(9)	5 603(4)	3 112(5)	7 251(3)	C(17)	12 693(12)	2 893(11)	6 359(8)
O(1)	9 423(7)	1 399(6)	3 970(3)	C(18)	11 557(11)	2 159(10)	6 549(6)
O(2)	9 071(7)	1 197(6)	5 164(4)	C(19)	10 374(12)	458(8)	8 828(5)
O(3)	10 299(7)	-2 392(6)	8 612(4)	C(20)	11 788(15)	423(11)	8 553(7)
O(4)	11 833(8)	-2 326(7)	7 586(4)	C(21)	12 643(15)	1 128(13)	8 777(8)
O(5)	7 899(7)	1 087(6)	8 118(3)	C(22)	12 144(18)	1 907(13)	9 252(8)
O(6)	8 453(7)	1 927(6)	6 948(3)	C(23)	10 811(18)	2 001(11)	9 543(6)
O(7)	9 944(6)	-581(5)	7 366(3)	C(24)	9 914(12)	1 275(10)	9 311(5)
C(1)	9 039(9)	1 787(9)	4 568(5)	C(25)	7 286(11)	-1 580(10)	8 868(5)
C(2)	8 466(10)	3 161(9)	4 503(5)	C(26)	7 253(12)	-2 873(11)	8 957(7)
C(3)	11 266(10)	-2 832(9)	8 175(5)	C(27)	6 069(16)	-3 476(14)	9 242(8)
C(4)	11 739(11)	-4 213(10)	8 456(6)	C(28)	4 901(15)	-2 781(14)	9 452(8)
C(5)	7 856(9)	1 900(9)	7 588(5)	C(29)	4 898(15)	-1 532(17)	9 382(8)
C(6)	6 920(11)	3 093(9)	7 735(5)	C(30)	6 104(12)	-912(11)	9 076(7)
Complex (6)							
Sn(1)	3 673.1(2)	5 519.0(2)	6 404.4(2)	C(3)	3 803(4)	5 837(4)	7 003(4)
Cl(1)	1 676.2(15)	4 086.0(16)	10 031.8(12)	C(4)	3 743(6)	5 198(6)	7 974(5)
Cl(2)	2 641.2(17)	2 237.5(13)	10 037.7(12)	C(5)	3 882(7)	5 370(7)	8 357(6)
Cl(3)	1 025.0(14)	3 887.1(20)	9 455.3(16)	C(6)	3 986(7)	6 222(7)	7 813(7)
O(1)	4 878(2)	4 101(2)	6 473(2)	C(7)	4 071(9)	6 813(8)	6 889(8)
O(2)	3 316(3)	3 384(2)	7 874(2)	C(8)	3 982(7)	6 623(6)	6 470(6)
O(3)	2 767(2)	4 722(3)	7 919(2)	C(9)	-276(9)	5 552(9)	2 559(9)
C(1)	2 800(3)	3 913(4)	8 291(4)	C(10)	586(9)	4 969(9)	2 624(7)
C(2)	2 072(4)	3 539(4)	9 416(4)	C(11)	1 117(10)	4 143(11)	2 573(14)

the only structure reported here that does not contain stannoxane bridges between the tin atoms.

A further distortion in the geometry of Sn(2) can be traced to a hydrogen bond between O(4), on the hanging acetate, and O(7), the bridging hydroxide, thus narrowing the O(5)–Sn(2)–O(7) angle. The hydrogen atom could not be located on the final difference Fourier and was not included in the refinement.

The trichloroacetate groups in the molecule show all three possible types of bonding: unidentate, *syn-syn* and *syn-anti* bidentate bridging.¹¹ As expected the *syn-syn* bridge is symmetrical while the other two have asymmetrical bond lengths.

Complex (6). The molecule is formed from six identical PhSnO₂CCl₃ units arranged in a drum-shaped formation

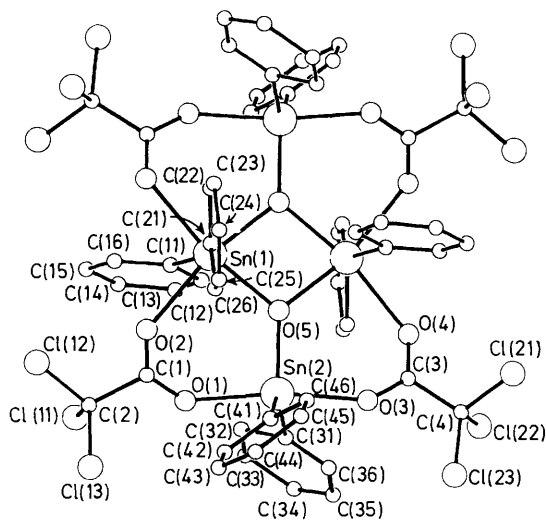


Figure 2. The structure of $\{[\text{SnPh}_2(\text{O}_2\text{CCCl}_3)_2]_2\}_2$ (2)

(Figure 6). The sides are constructed from Sn₂O₂ stannoxane rings and the faces from Sn₃O₃ planes. An *S*₆ axis passes through the centre of the faces of the molecule. The two solvent molecules also lie around this axis, above and below the molecule itself.

The faces themselves are puckered into a chair conformation such that the planes of tin atoms lie further apart than the oxygen planes, by 0.454(2) Å. The acetate group is symmetrically bridging. All dimensions are normal.

Tin Co-ordination.—Table 4 shows the co-ordination of the tin atoms ordered by the number of bonded carbon atoms and by geometry. The Sn–C bond length appears invariant to both these changes although the Sn–O(stannoxane) bond length decreases slightly from C₂Sn to C₁Sn. The Sn–O(bidentate acetate) bond lengths are both longer and more variable than those for Sn–O(unidentate acetate).

Experimental

The compound SnPh₃(OH) was prepared by the method of Kushlefsky *et al.*,¹² (SnPh₂O)_n by the method of Syutkina *et al.*¹³

Triphenyltin Trichloroacetate–Methanol (1/1) (1).—The compound SnPh₃(OH) (0.554 g, 1.511 mmol) and Cl₃CCO₂H (0.247 g, 1.511 mmol) were stirred in aqueous MeOH (30 cm³) for 3 h. The solution slowly cleared over this period. It was filtered then reduced in volume under vacuum until precipitation started. The flask was left at 0 °C for 24 h. Clear block crystals formed and were used directly for structure determination (Found: C, 44.5; H, 3.2; Cl, 20.0. C₂₁H₁₉Cl₃O₃Sn requires C, 46.3; H, 3.5; Cl, 19.5%). The i.r. spectrum (Nujol) showed peaks at 1 685s and 1 335s cm⁻¹, interpreted as being the *v*_{sym} and *v*_{asym} stretches of the carboxylate. The difference of 350 cm⁻¹ indicates the carboxylate is bridging.

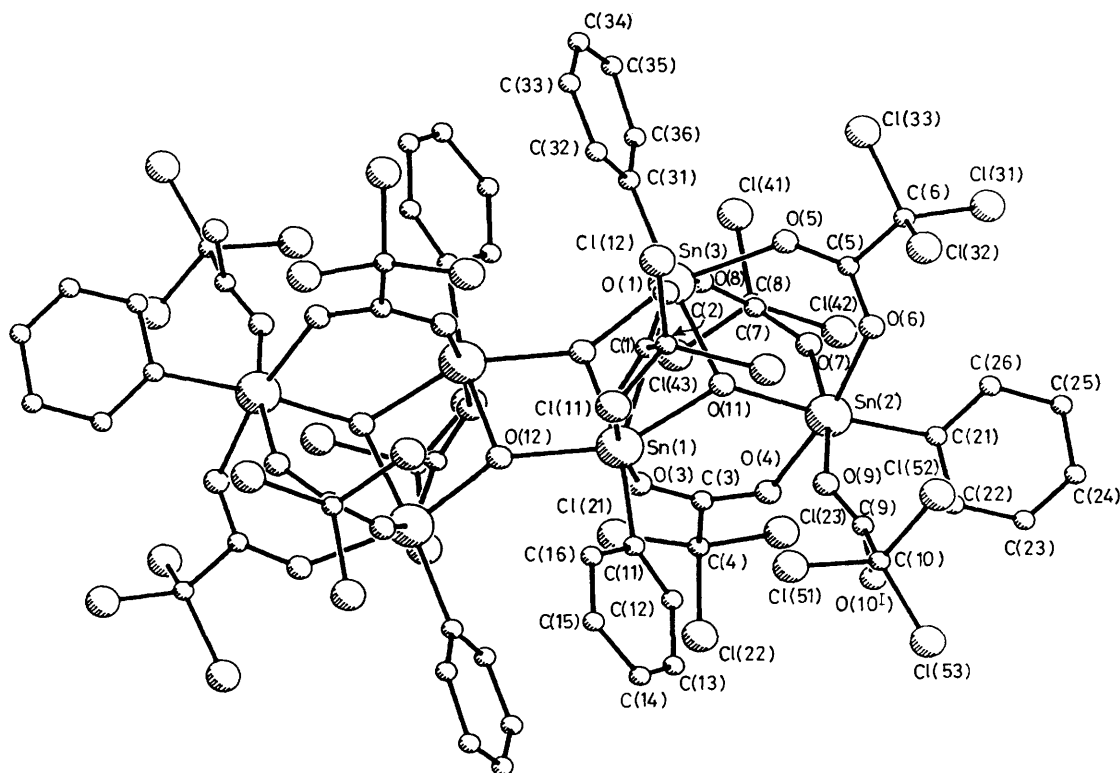


Figure 3. The structure of $\text{Sn}_6\text{Ph}_6(\text{O}_2\text{CCCl}_3)_{10}\text{O}_4 \cdot 2\text{C}_6\text{H}_6$ (3)

Triphenyltin Trichloroacetate-Acetonitrile (1/1).—This complex was prepared as above with MeCN (30 cm³). Clear needles formed in solution after being left at 0 °C for 12 h (Found: C, 47.35; H, 3.2; Cl, 19.25; N, 2.5. C₂₂H₁₈Cl₃NO₂Sn requires C, 47.8; H, 3.2; Cl, 19.3; N, 2.5%). The i.r. spectrum (Nujol) showed a doublet at 2 285 and 2 320 cm⁻¹ corresponding to the CN stretch. Proton n.m.r. (solvent CDCl₃): δ 7.5–8.0 (15) and 2.0 (3).

Dimeric μ₃-Oxo-bis(diphenyl-μ-trichloroacetato-tin) (2).—The compound SnPh₃(O₂CCl₃)·MeOH was prepared as above. The product was recrystallised from CCl₄-hexane solution by the liquid diffusion method. Clear crystals appeared at the interface after 12 h. These were used directly for structure refinement (Found: C, 39.4; H, 2.5; Cl, 23.8; Sn, 26.7).

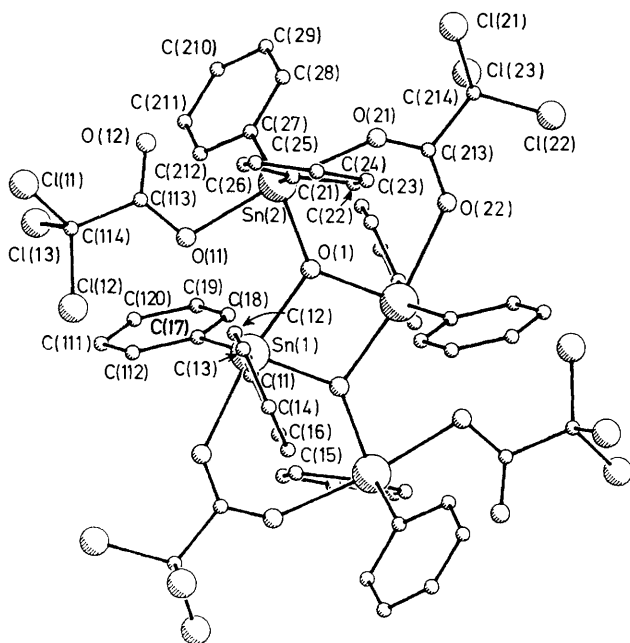


Figure 4. The structure of $\{[\text{SnPh}_2(\text{O}_2\text{CCCl}_3)_2\text{O}]\}_2$ (4)

C₅₆H₄₀Cl₁₂O₁₀Sn₄ requires C, 37.9; H, 2.3; Cl, 24.0; Sn, 26.75%.

Dimeric Di-μ₃-oxo-tetra-μ-trichloroacetato-trichloroacetato-tris(phenyltin)-Benzene (1/1) (3).—The compound SnPh₃(OH) (1.056 g, 2.88 mmol) and Cl₃CCO₂H (0.49 g, 3 mmol) were refluxed in benzene (50 cm³) with a Dean-Stark separator. After 24 h the solution was filtered and reduced to 20 cm³. Hexane was added until precipitation started to occur. The solution was left at 0 °C for 24 h, whereupon crystals formed. Examination under a microscope revealed two distinct crystal types, small clear rhomboids and larger cloudier cubes. The former proved to be identical to (4) by analysis of the unit-cell dimensions. A full structure determination was carried out on the latter only. The unidentate acetate on Sn(2) was disordered and refined equally over two sites.

Dimeric μ³-Oxo-μ-trichloroacetato-trichloroacetatobis(diphenyltin) (4).—The compound SnPh₃Cl (1.094 g, 2.84 mmol) in

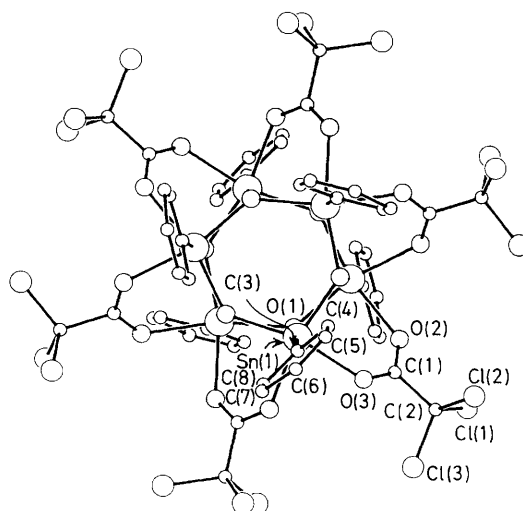


Figure 6. The structure of $[\text{SnPh}(\text{O}_2\text{CCCl}_3)_2\text{O}]_2 \cdot 3\text{C}_6\text{H}_6$ (6)

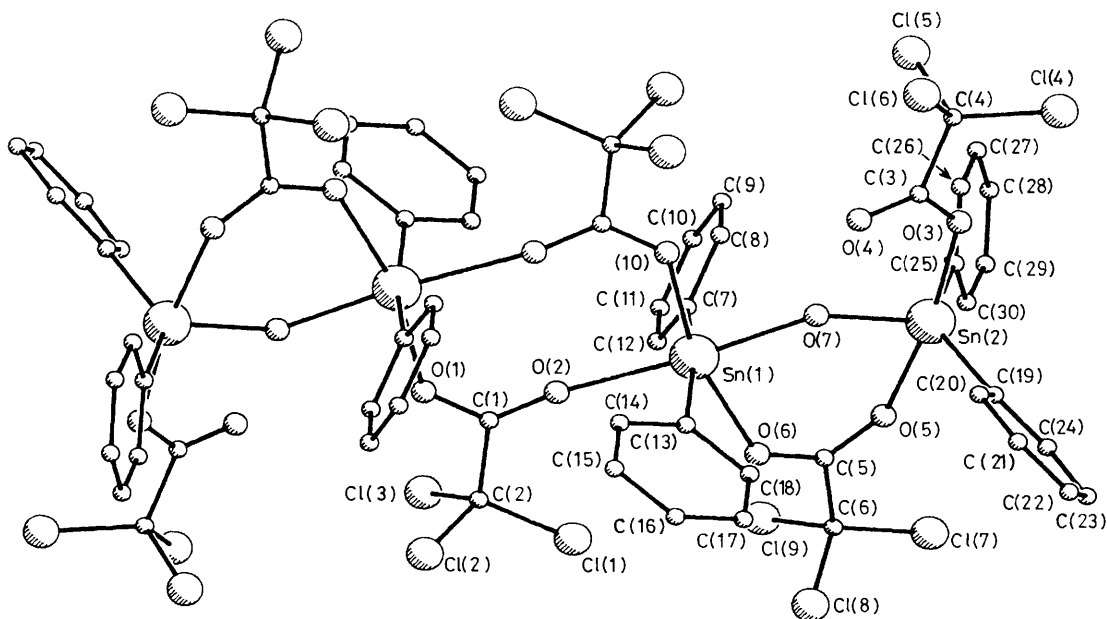


Figure 5. The structure of $\text{Sn}_4\text{Ph}_8(\text{O}_2\text{CCCl}_3)_6(\text{OH})_2$ (5)

Table 4. Tin co-ordination

Number of Carbons	Geometry	Cmpd	Distance/Å			
			Sn-C	Sn-O Stannoxane	Sn-O Unidentate acetate	Sn-O Bidentate acetate
3	tbp	(1)	2.123(4)		2.172(2)	
			2.125(3)			
			2.118(4)			
2	tbp	(2)	2.186(16)	2.015(9)		2.207(11)
			2.126(16)			2.199(12)
2	tbp	(5)	2.083(12)		2.157(6)	2.212(6)
			2.108(11)			
2	tbp(+1)	(4)	2.129(7)	2.031(5)	2.212(5)	2.250(5)
			2.113(8)			[2.902(5)]
2	tbp(+1)	(4)	2.115(8)	2.154(4)		2.323(6)
			2.107(8)	2.062(5)		[2.866(5)]
2	oct	(2)	2.127(13)	2.138(10)		2.432(10)
			2.118(14)	2.131(8)		2.400(14)
2	oct	(5)	2.098(10)			2.361(7)
			2.104(10)			2.277(6)
1	oct	(3)	2.111(16)	2.124(9)		2.185(6)
				2.094(9)		2.213(12)
1	oct	(6)	2.080(20)	1.994(10)	2.080(14)	2.162(12)
						2.208(12)
1	oct	(3)	2.092(19)	2.095(11)		2.126(14)
				2.024(10)		2.285(12)
1	oct	(6)	2.104(13)	2.089(3)		2.156(11)
				2.095(7)		2.149(10)
1	oct	(6)		2.075(3)		2.125(11)
						2.183(3)
						2.191(3)

tbp = Trigonal bipyramidal, oct = octahedral.

CHCl_3 was shaken with NaOH (0.205 g, 5.12 mmol) in water (5 cm^3). The resulting organic layer was separated and the solvent removed under reduced pressure. The product, $(\text{SnPh}_3)_2\text{O}$, was stirred with $\text{Cl}_3\text{CCO}_2\text{H}$ (0.2195 g, 1.34 mmol) in aqueous MeOH (30 cm^3) for 3 h. The solvent was removed and the product recrystallised from CH_2Cl_2 -light petroleum (30–40 °C). The crystals produced were used directly for structure determination.

Dimeric μ -Hydroxo-bis(μ -trichloroacetato)-trichloroacetato-bis(diphenyltin) (5).—The compound $(\text{SnPh}_2\text{O})_n$ (4.33 g, 15 mmol) and $\text{Cl}_3\text{CCO}_2\text{H}$ (5 g, 30 mmol) were stirred in hexane (30 cm^3) for 3 h. The solvent was removed under reduced pressure and the product recrystallised from dichloromethane-light petroleum solution. Large colourless blocks formed after 12 h. These were used directly for structure determination (Found: C, 37.3; H, 2.2; Cl, 29.1. $\text{C}_{60}\text{H}_{42}\text{Cl}_{18}\text{O}_{14}\text{Sn}_4$ requires C, 34.3; H, 2.0; Cl, 30.4%).

Hexameric μ_3 -Oxo-phenyl- μ -trichloroacetato-tin-Benzene (2/1) (6).—The compound $(\text{SnPh}_2\text{O})_n$ (1.6 g, 5.5 mmol) and $\text{Cl}_3\text{CCO}_2\text{H}$ (1.87 g, 11.5 mmol) were refluxed in benzene (100 cm^3) with a Dean-Stark separator for 12 h. Well formed rhombohedral crystals suitable for structure elucidation grew on the side of the reaction vessel. Complex (6) was also obtained by a repetition of the reaction originally used for (2); crystals grown from CCl_4 -hexane solution by liquid diffusion proved to be rhombohedral ($a = 15.6$ Å, $\alpha = 91.4^\circ$, unrefined). They are believed to be an unsolvated form of (6), as recrystallisation from hot benzene gave rhombohedral crystals ($a = 21.3$ Å, $\alpha = 43.2^\circ$, unrefined) clearly identical to (6).

X-Ray Crystallography.—Accurate unit-cell dimensions were determined by least-squares fits to 15 high-angle reflections ($20 < \theta < 22^\circ$) measured on a Syntex $P2_1$ four-circle diffractometer. Intensities were measured using Mo- K_α radiation (graphite-crystal monochromator, $\lambda = 0.71069$ Å). Three check reflections were monitored every 200 reflections, the data being rescaled to account for any variation. Intensities were corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method. Crystal data and a summary of the data-collection parameters are given in Table 2.

Structure determination and refinement. All structures were solved using the heavy-atom method, the positions of the tin atoms being determined from Patterson maps. The remaining non-hydrogen atoms were determined from successive Fourier difference syntheses. Hydrogen atoms were included at calculated positions (C-H 0.96 Å, $U = 0.07$ Å²). A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ was used. Anisotropic thermal parameters were used for non-hydrogen atoms wherever possible, though some atoms had to be refined isotropically. In complex (2) the Cl atoms of one Cl_3CCO_2 were disordered between two equally occupied positions. In (3) one acetate was disordered. It was included as two half-occupancy groups (apart from the co-ordinated O atom); however residual electron density in this area suggests that its disorder may be more complex. All calculations were made with SHELXTL¹⁴ on a Data General DG30 computer. Scattering factors were taken from ref. 15. Selected bond lengths and angles are listed in Table 1 and final atomic co-ordinates in Table 3. Structures are shown in Figures 1–6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

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