

## A Unique Macrocyclic Structure of Tetrameric Trimethyltin(IV) Diphenylphosphinate, $[\text{Me}_3\text{SnO}_2\text{PPh}_2]_4$ , containing a Sixteen-membered $\text{Sn}_4\text{O}_8\text{P}_4$ Inorganic Ring

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Trimethyltin(IV) diphenylphosphinate,  $\text{Me}_3\text{SnO}_2\text{PPh}_2$ , is a macrocyclic tetramer containing an  $\text{Sn}_4\text{O}_8\text{P}_4$  ring made up from trigonal bipyramidal  $\text{O}-\text{SnMe}_3-\text{O}$  units interconnected by (nearly) tetrahedral diphenylphosphinato groups,  $\text{O}-\text{PPh}_2-\text{O}$ , through oxygen-sharing.

The structural contrasts between organotin oxo- and thio-phosphorus acid derivatives are well documented.<sup>1</sup> Thus thio compounds  $\text{R}_n\text{Sn}(\text{S}_2\text{PR}'_2)_{4-n}$  ( $n = 1-3$ ,  $\text{R} \neq$  alkyl, aryl, alkoxo) are molecular compounds while oxo analogues  $\text{R}_n\text{Sn}(\text{O}_2\text{PR}'_2)_{4-n}$  are either polycyclic cage compounds, when  $n = 1, 2$  or non-crystalline insoluble materials when  $n = 2$  or  $3$ .<sup>1</sup> In some exceptional cases when suitable crystals could be obtained, X-ray diffraction studies revealed a helical polymeric structure for the phosphonate  $\alpha\text{-Me}_3\text{SnOP}(\text{O})(\text{OH})\text{Ph}$ ,<sup>3</sup> and a hexameric cyclic structures for the phosphate  $\text{Ph}_3\text{SnO}_2\text{P}(\text{OPh})_2$ <sup>4</sup> and the *O*-methyl methylphosphonate  $\text{Ph}_3\text{SnO}_2\text{P}(\text{OMe})\text{Me}$ .<sup>5</sup> Mössbauer spectroscopy suggested that organotin phosphinates,  $\text{R}_n\text{Sn}(\text{O}_2\text{PPh}_2)_{4-n}$  with  $n = 2$  and  $3$  are polymeric containing five-coordinate (when  $n = 3$ ) and six-coordinate (when  $n = 2$ ) tin atoms.<sup>6</sup>

Earlier work<sup>7</sup> reporting molecular mass determinations of some triorganotin phosphonates thereby indicating  $[\text{R}_3\text{SnO}_2\text{PPh}_2]_n$  to be dimeric when  $\text{R} = \text{Pr}^n$  or  $\text{Bu}^n$  but tetrameric when  $\text{R} = \text{Me}$  appears to have been forgotten since no single crystal structure determination by X-ray diffraction was attempted for any of these compounds. After several unsuccessful attempts, we have now obtained single crystals of

$\text{Me}_3\text{SnO}_2\text{PPh}_2$  suitable for X-ray analysis from the reaction of  $\text{Me}_3\text{SnCl}$  and  $\text{NH}_4\text{O}_2\text{PPh}_2$  in benzene.† We are now able to confirm the tetrameric structure of this compound in the solid state.<sup>8</sup> A related tetrameric macrocyclic structure has recently been reported for bismuth(III) 2,2-dimethylpropanoate (pivalate).<sup>9</sup>

The molecular structure of  $[\text{Me}_3\text{SnO}_2\text{PPh}_2]_4$  is shown in Fig. 1. The compound is a macrocyclic tetramer based upon a sixteen-membered ring made up from four trigonal bipyramidal  $\text{OSnMe}_3\text{O}$  units connected through phosphinato groups by sharing the oxygen atoms. The molecule exhibits a crystallographic mirror plane passing through Sn(1) and Sn(2). In the trigonal bipyramidal units the  $\text{O}-\text{Sn}-\text{O}$  sequence is linear,

† Crystal data:  $\text{C}_{60}\text{H}_{76}\text{O}_8\text{P}_4\text{Sn}_4$ ;  $M_r = 1523.92$ ; orthorhombic, space group  $Pnma$  (No. 62),  $a = 15.249$ ,  $b = 29.178$ ,  $c = 14.501$  Å,  $V = 6451.8$  Å<sup>3</sup>,  $Z = 8$ ;  $D_c = 1.569$  g cm<sup>-3</sup>; radiation Cu-Kα,  $F(000) = 3040$ ,  $T = 23 \pm 1$  °C, final  $R = 0.068$ , 5215 unique reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

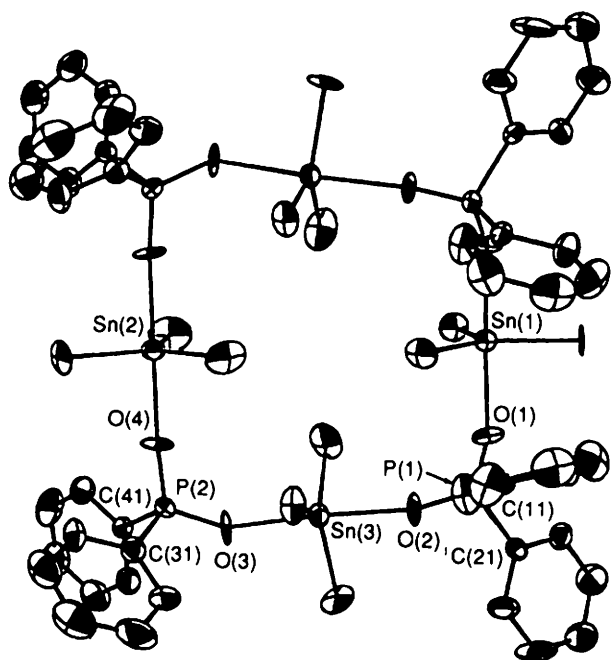


Fig. 1 ORTEP diagram of  $[\text{Me}_3\text{SnOPPh}_2]_4$

e.g.  $\text{O}(3)\text{--Sn}(3)\text{--O}(2)$   $176.2(3)^\circ$ , and symmetrical:  $\text{Sn}(3)\text{--O}(3)$   $2.243(5)$  Å and  $\text{Sn}(3)\text{--O}(2)$   $2.245(6)$  Å. The P–O bond lengths are slightly different, e.g.  $\text{P}(1)\text{--O}(1)$   $1.509(6)$  Å,  $\text{P}(1)\text{--O}(2)$   $1.486(6)$  Å,  $\text{P}(2)\text{--O}(3)$   $1.494(6)$  Å, and  $\text{P}(2)\text{--O}(4)$   $1.483$  Å, thus retaining some O=P=O character. The oxygen bond angles are rather large and non-identical:  $\text{Sn}(1)\text{--O}(1)\text{--P}(1)$   $134(4)^\circ$ ,  $\text{Sn}(3)\text{--O}(2)\text{--P}(1)$   $158.7(5)^\circ$ ,  $\text{Sn}(3)\text{--O}(3)\text{--P}(2)$   $140.4(4)^\circ$ , and  $\text{Sn}(2)\text{--O}(4)\text{--P}(2)$   $176.2(5)^\circ$ . The O–P–O bond angles are larger than tetrahedral, i.e.  $\text{O}(1)\text{--P}(1)\text{--O}(2)$   $117.3(4)^\circ$  and  $\text{O}(3)\text{--P}(2)\text{--O}(4)$   $117.2(4)^\circ$ .

The formation of the tetrameric ring is unexpected since it was suggested<sup>1</sup> that a pentamer would best fit the geometric

criteria for ring closure with linear O–Sn–O units interconnected by tetrahedral fragments. Two of the three methyl groups at each tin atom (Fig. 1) are seen to protrude into the ring. Larger groups such as phenyl require the formation of a hexameric macrocycle with enough room inside to accommodate the phenyl groups.<sup>4,5</sup> However, for the trimethyltin derivative there appears enough room for the small methyl groups in a tetrameric macrocycle. An analogous pentameric macrocyclic structure can be anticipated for  $[\text{R}_3\text{SnO}_2\text{PPh}_2]_n$  derivatives with substituents of intermediate size between methyl and phenyl groups.

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