

## Crystal and Molecular Structure of Trisdimethyltin(IV) Bis(orthophosphate) Octahydrate

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**SUMMARY** The crystal structure of  $(\text{Me}_2\text{Sn})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  shows one tin atom in a regular octahedral environment with *trans*-methyl groups, and the other two tin atoms in a highly distorted ( $\angle \text{C-Sn-C} = 147^\circ, 150^\circ$ ) tetrahedral configuration due to weak co-ordination to two water molecules; all the water molecules are involved in hydrogen bonding to each other and to phosphate oxygen atoms.

STRUCTURAL studies of organotin compounds are increasing,<sup>1</sup> and it is known that  $\text{Me}_2\text{SnX}_2$  derivatives (X = anion of a monobasic acid) usually have associated structures with either octahedral geometry about tin and *trans*-methyl groups (X = F,<sup>2</sup>  $\text{SO}_3\text{F}^3$ ) or strongly distorted tetrahedral structures for compounds with weak intermolecular association ( $\angle \text{C-Sn-C} = \text{ca. } 149^\circ$ , X = CNS,<sup>4</sup> CN;<sup>5</sup>  $\angle \text{C-Sn-C} = \text{ca. } 123^\circ$ , X = Cl<sup>6</sup>). In  $\text{Me}_2\text{Sn}(\text{NO}_3)_2$  the ligands are unsymmetrically bidentate with  $\angle \text{C-Sn-C} = \text{ca. } 145^\circ$ .<sup>7</sup> X-Ray data for compounds in which X = anion of a di- or tri-basic acid are, however, lacking. We report here the first structure determination of a dimethyltin derivative of a tri-basic acid,  $(\text{Me}_2\text{Sn})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , a compound which had

previously been characterised as  $\text{Me}_2\text{SnHPO}_4$ ,<sup>8,9</sup> on the basis of C,H analyses, i.r. spectra, and method of preparation.<sup>†</sup>

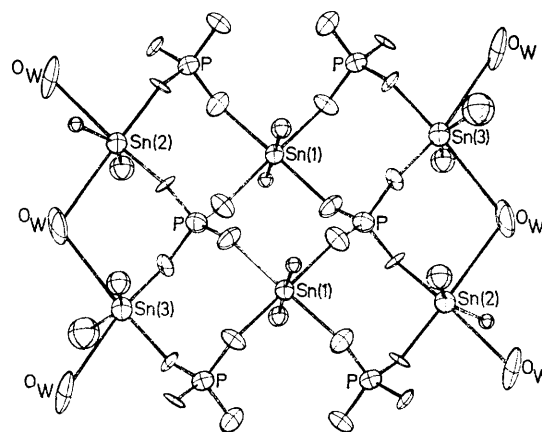


FIGURE. An ORTEP drawing of  $(\text{Me}_2\text{Sn})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . Water molecules bonded to the two outer tin atoms are indicated  $\text{O}_\text{W}$ ; other water molecules have been omitted for clarity.

<sup>†</sup> Crystals of  $(\text{Me}_2\text{Sn})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  were slowly deposited from an aqueous solution containing equimolar quantities of  $\text{Me}_2\text{SnCl}_2$  and  $\text{Na}_2\text{HPO}_4$  (ca. 0.5 M).

**Crystal data:** Crystals of  $(\text{Me}_2\text{Sn})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  are orthorhombic,  $a = 22.578$  (4),  $b = 9.395$  (2),  $c = 11.100$  (2) Å,  $Z = 4$ , space group  $Pnma$  or  $Pn2_1a$  by systematic absences (the former confirmed by intensity statistics). Intensity data were collected with  $\text{Cu-K}\alpha$  radiation ( $\mu = 279 \text{ cm}^{-1}$ ) for 1586 unique reflections [ $604$  with  $I > 3\sigma(I)$ ] using a Picker 4-circle diffractometer in the  $\theta-2\theta$  scan mode with graphite monochromator. Absorption corrections were made by Gaussian quadrature. The structure was solved by Patterson and Fourier techniques and refined to the present  $R$  value of 0.081 by full-matrix least squares using isotropic temperature parameters for the carbon atoms and anisotropic temperature parameters for the other heavy atoms. The hydrogen atoms have not been located.

The structure of  $(\text{Me}_2\text{Sn})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , as shown in the Figure, consists of infinite 'ribbons' extending through the crystal in the  $b$ -direction. The tin atoms lie on mirror planes at  $y = \frac{1}{4}, \frac{3}{4}$  and are linked by phosphate tetrahedra to give eight-membered rings in chair configurations *cf.*  $\text{SnCl}_4 \cdot 2\text{POCl}_3$ .<sup>10</sup> A single water molecule and its symmetry equivalent occupy two co-ordination positions for each of the two outer tin atoms,  $\text{Sn}(2)$  and  $\text{Sn}(3)$ . The other water molecules form a three dimensional network of hydrogen bonds involving the phosphate oxygen atoms (*cf.* ref. 11),

The co-ordination about the inner tin atom  $\text{Sn}(1)$  is distorted only slightly from regular octahedral geometry,  $\angle \text{C-Sn-C} = 178.0$  (1.5)°. The  $\text{Sn}(1)$ -C bond distances, 2.12 (4) Å, are close to the single-bond value for octahedral tin, 2.16 Å,<sup>12</sup> while the  $\text{Sn}(1)$ -O bond lengths, 2.18 (2) Å, are considerably longer than the single-bond value, 2.05 Å.<sup>12</sup> The two outer tin atoms can be considered to be in strongly distorted tetrahedral environments,  $\angle \text{C-Sn-C} = 150^\circ$  and  $147^\circ$ , respectively, due to weak co-ordination to two water molecules. There are significant differences in the relative bond lengths for the two outer tin atoms. For  $\text{Sn}(2)$ , the distances water-Sn, 2.88 (2) Å, and C-Sn, 2.10 (4) Å, are short and O-Sn distances are long, 2.06 (2) Å, while for  $\text{Sn}(3)$ , the water-Sn, 3.05 (2) Å, and C-Sn bonds, 2.18 (4) Å, are long and the O-Sn bonds, 2.02 (2) Å, are short. No obvious explanation can be given for these differences. The P-O bond distances, 1.52-1.57 (2) Å, and the bond angles  $\angle \text{O-P-O} = 105-114$  (1)° of the phosphate groups are unexceptional.

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‡ The configuration about the two outer tin atoms could also be described as a highly distorted octahedron, in which a water molecule occupies two positions in the co-ordination sphere.

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