

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

By J. PATRICK ASHMORE, TRISTRAM CHIVERS, K. ANN KERR and JOHANNES H. G. VAN ROODE

(Department of Chemistry, The University of Calgary, Calgary T2N 1N4, Alberta, Canada)

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,¹ and it is known that Me_2SnX_2 derivatives (X = anion of a monobasic acid) usually have associated structures with either octahedral geometry about tin and *trans*-methyl groups (X = F,² SO_3F^3) or strongly distorted tetrahedral structures for compounds with weak intermolecular association ($\angle \text{C-Sn-C} = \text{ca. } 149^\circ$, X = CNS,⁴ CN;⁵ $\angle \text{C-Sn-C} = \text{ca. } 123^\circ$, X = Cl⁶). In $\text{Me}_2\text{Sn}(\text{NO}_3)_2$ the ligands are unsymmetrically bidentate with $\angle \text{C-Sn-C} = \text{ca. } 145^\circ$.⁷ 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 $\text{Me}_2\text{SnHPO}_4$ ^{8,9} on the basis of C,H analyses, i.r. spectra, and method of preparation.[†]

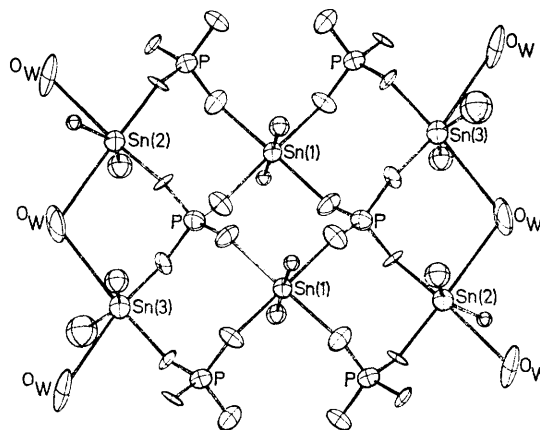


FIGURE. An ORTEP drawing of $(\text{Me}_2\text{Sn})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. Water molecules bonded to the two outer tin atoms are indicated O_w ; other water molecules have been omitted for clarity.

[†] 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 Me_2SnCl_2 and Na_2HPO_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.* $\text{SnCl}_4 \cdot 2\text{POCl}_3$.¹⁰ A single water molecule and its symmetry equivalent occupy two co-ordination positions for each of the two outer tin atoms, Sn(2) and 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 Sn(1) is distorted only slightly from regular octahedral geometry, $\angle \text{C-Sn-C} = 178.0$ (1.5)°. The Sn(1)-C bond distances, 2.12 (4) Å, are close to the single-bond value for octahedral tin, 2.16 Å,¹² while the Sn(1)-O bond lengths, 2.18 (2) Å, are considerably longer than the single-bond value, 2.05 Å.¹² The two outer tin atoms can be considered to be in strongly distorted tetrahedral environments, $\angle \text{C-Sn-C} = 150^\circ$ and 147° , 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 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 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.

We are grateful to the National Research Council of Canada for financial support in the form of operating grants (T.C. and K.A.K.) and a scholarship (J.H.G.v.R.)

(Received, 16th May 1974; Com. 563.)

‡ 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.

¹ B. Y. K. Ho and J. J. Zuckerman, *J. Organometallic Chem.*, 1973, **49**, 1.

² E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, 1966, **5**, 995.

³ F. H. Allen, J. A. Lerbscher, and J. Trotter, *J. Chem. Soc. (A)*, 1971, 2507.

⁴ R. A. Forder and G. M. Sheldrick, *J. Organometallic Chem.*, 1970, **22**, 611; Y. M. Chow, *Inorg. Chem.*, 1970, **9**, 794.

⁵ J. Konnert, D. Britton, and Y. M. Chow, *Acta Cryst. B*, 1972, **28**, 180.

⁶ A. G. Davies, H. J. Milledge, D. C. Puxley, and P. J. Smith, *J. Chem. Soc. (A)*, 1970, 2862.

⁷ J. Hilton, E. K. Nunn, and S. C. Wallwork, *J.C.S. Dalton*, 1973, 173.

⁸ D. Seyferth and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1957, **79**, 515.

⁹ T. Chivers, J. H. G. Van Roode, J. N. Ruddick, and J. R. Sams, *Canad. J. Chem.*, 1973, **51**, 3702.

¹⁰ D. Moras, A. Mitschler, and R. Weiss, *Acta Cryst. B*, 1969, **25**, 1720.

¹¹ G. R. Clark and J. D. Orbell, *J.C.S. Chem. Comm.*, 1974, 139.

¹² L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, pp. 229, 251.