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The Crystal and Molecular Structure of Trimethyltin Chloride at 135 K. A Highly Volatile Organotin Polymer

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Trimethyltin chloride is a key laboratory starting material and has been studied extensively by spectroscopic methods, yet the solid state structure of this highly toxic, low melting (m. 39.5 °C), volatile (b. 154 °C) material has never been determined because of experimental difficulties. The structure of the homologous trimethyltin fluoride [1], which is associated through bridging fluorines, is perhaps the most widely quoted organotin structure of all [2], yet disorder within and between the –F–Sn–F–Sn– chains prevents a satisfactory solution to the anomalous electron density projections recorded at ambient temperatures [3]. Triphenyltin chloride [4] and bromide [5], on the other hand, exist as discrete, monomeric molecules in the crystal [6].

Crystals of trimethyltin chloride are monoclinic, a = 12.541(8), b = 9.618(11), c = 11.015(11) Å, β = 92.62(7)°, space group P2, and Z = 2. Each asymmetric unit consists of four molecules. The structure was solved from 2183 independent reflections [$2\theta \leqslant 53°$, MoKα radiation $I > 2\sigma(I)$] recorded at 135 ± 2 K on a Nonius CAD-4 counter diffractometer by the heavy-atom technique, and refined to a final R value of 0.069 (weighted = 0.058). Sublimation of the crystals prevented the measurement of all faces, and thus no corrections for absorption could be made. The calculated density is 1.994 g/cm^3.

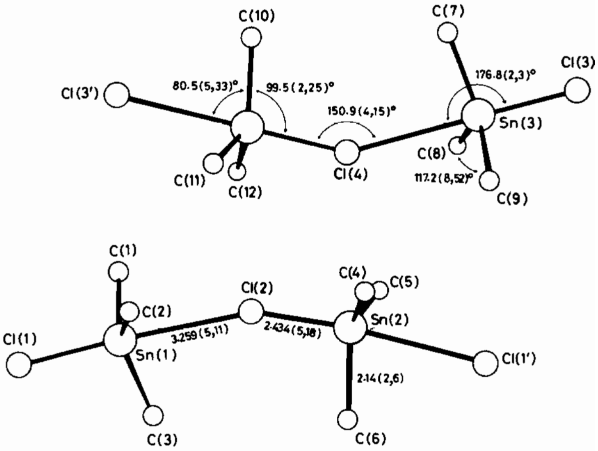

Fig. 1. The asymmetric unit in the trimethyltin chloride structure. The interchain d(Sn····Cl) values are greater than 4.1 A.

The stereochemistry of the asymmetric unit is shown in Fig. 1, along with mean values of the bond distances and angles. The two tin–chlorine distances are not equivalent, with the intramolecular bond [mean value 3.259(5,11) Å], although the latter is significantly shorter than the sum of the respective van der Waals radii (3.85 Å) [11]. Comparison with the parameters of the recent gas-phase electron diffraction study [12] is shown in Table I along with data from the analogous $[(CH_3)_3SnCl_2]^-$ anion (gegen ion $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+$) which takes an axially distorted, trigonal bipyramidal structure with one Sn–Cl the longest such intramolecular distance yet reported [13].

The Cl–Sn–Cl–Sn fragment is nearly linear at tin [mean Cl–Sn–Cl angle 176.8(2,3)°] [10], but bent at chlorine [mean angle 150.9(45)°], imposing a zig-

TABLE I. Comparison with Gas-phase Electron Diffraction

	d(Sn–C)	*d(Sn–Cl)*	*<C–Sn–C*	*<C–Sn–Cl*	*d(Sn——Cl)*	*<(Cl–Sn——Cl)*
$(CH_3)_3SnCl^a$ X-ray at 135 K	2.14(2,6) A	2.434(5, 18) A	117.2(8,52)°	99.5(5,25)° intra- 80.5(5,33)° inter-	3.259(5,11) A	176.8(2,3)°
predicted^b	–	–	118°	99°	3.54	–
e.d. at 90 °C^c	2.106 ± 0.006	2.351 ± 0.007	114.9 ± 1.6°	103.2 ± 0.6°	–	–
$[(CH_3)_3SnCl_2]^-$ X-ray at R.T.^{d}	2.12	2.572(4) 2.696(3)	–	–	–	–

^{a}This work. ^{b}R. F. Zahrobsky, *J. Solid State Chem.*, *8*, 101 (1973). ^{c}Ref. 12. ^{d}Ref. 13.

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zag character to the polymeric backbone, as in trimethyltin methoxide. However, in the latter case the trimethyltin moieties are staggered [the methoxyl methyl group eclipses an intermolecularly attached $(CH_3)_3Sn$ methyl] [14], while the trimethyltin units in the $(CH_3)_3SnCl$ chain are eclipsed. Single –Sn–Cl–Sn bridges such as those found here may also appear in the structure of diphenyltin dichloride [15] which has been reinterpreted in terms of chlorine asymmetrically bridging four- and six-coordinated tin atoms (intra- 2.353, inter- 3.78 Å) [16].

The intermolecular tin–chlorine association in $(CH_3)_3SnCl$ is apparently disrupted on melting or dissolving in carbon disulfide, as shown by reduced infrared and Raman ν(Sn–Cl) values [17, 18].

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