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THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIMETHYLTIN(IV) CHLORIDE, A CHLORINE-BRIDGED, LINEAR POLYMER *

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Summary

The crystal and molecular structure of trimethyltin(IV) chloride has been determined by the heavy-atom technique, and refined to a final R value of 0.041 for 1375 independent reflections ($2\theta < 53°$; Mo-K_α radiation $I > 2\sigma(I)$) recorded at 138 ± 2 K on a Nonius CAD-4 counter diffractometer. The crystals are monoclinic with space group $I2/c$; a 12.541(8), b 9.618(11), c 11.015(11) Å, β 92.62(7)°, $Z = 8$, D_{calcd} 1.994 g cm^{-3}. The needle crystals are composed of polymeric chains of chlorine atoms bridging non-planar trimethyltin(IV) units at unequal (2.430(2) and 3.269(2) Å) distances. The zig-zag chains are bent at chlorine (angle Sn–Cl · · · · Sn 150.30(9)°), but nearly linear at tin (angle Cl–Sn · · · · Cl 176.85(6)°) to describe a distorted trigonal bipyramidal geometry at tin with the trimethyltin groups eclipsed. The interchain d(Sn · · · · Cl) distances are greater than 4.1 Å. The angles carbon–tin–carbon (mean 117.1(3)°) are larger than tetrahedral, while the angles carbon–tin–chlorine (mean 99.9(2) Å) are smaller, in accord with isovalent hybridization principles, but more severely distorted than in the gas-phase, monomeric structure. The tin–chlorine distance of 2.430(2) Å is also longer than in the gas phase monomer, and the intermolecular contact of 3.269 Å is shorter than in other organotin chloride bridged systems (sum of Van der Waals radii 3.85 Å).

The organotin(IV) chlorides represent an intriguing middle ground in structural organotin chemistry. These key laboratory starting materials lie between the fluorides which are almost universally bridged polymers and the heavier halides which are often monomeric solids [2]. It is here that the problem of assigning the

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coordination number at the metal center maximizes, and ambiguous molecular structure data must be scrutinized for short intermolecular contact distances and potentially coordinating atoms lying in stereochemically significant positions [3]. Reference to gas phase structural data (electron diffraction or microwave) is useful in providing information on molecular symmetry unaffected by the influence of packing forces or the interactions with donor atoms of neighboring molecules.

A case in point is the structure of triphenyltin(IV) chloride (m.p. 106°C) in which the mean carbon–tin–carbon angle is 112.3°, close to the tetrahedral value, and the shortest tin–chlorine contact distance between the two crystallographically independent molecules of almost identical geometry contained within the unit cell is ca. 6 Å [4]. Here we have a structure apparently composed of truly discrete, non-interacting organotin chloride molecules *. Moving to the structure of diphenyltin(IV) dichloride (m.p. 42°C), considerable distortion from tetrahedral geometry is found [8]. The data have subsequently been interpreted in terms of one chlorine on each molecule being terminal and short at 2.34, and the second longer at 2.35 Å and apparently directed axially to the longer tin–chlorine vector of an adjacent molecule at 3.77 Å. These contacts result in the formation of chains of four molecules with the end-members four- and the two interior members six-coordinated. Thus the crystal contains both tetrahedral and octahedrally coordinated molecules [9]. The original authors, however, interpreted the data in terms of an arrangement of discrete molecules in the solid [8], and in any case the association must be weak. The authors of the report of the dimethyltin(IV) dichloride (m.p. 104°C) structure chose to emphasize the similarities with the difluoride analogue. Here the distortion from tetrahedral toward octahedral symmetry is very severe, and the molecular units are aligned so that double, unsymmetrical, chlorine–tin bridges form at distances of 2.40 and 3.54 Å, with methyl groups projecting above and below the Sn_2Cl_2 plane [10]. In bis(chloromethyl)tin dichloride (m.p. 88.0–89.0°C) this system would be expected to tighten because of the increased Lewis acid character of the tin atom, but instead an alternative structure is adopted in which both the tin-chlorines are directed toward (chelating?) the same tin atom of an adjacent molecule, rather than as in the dimethyltin analogue in which the chlorine atoms of each molecule are directed toward differing tin atoms of two neighboring molecules [9]. This has the effect of lengthening the intermolecular chlorine contact distance to 3.71 Å, but the infinite chains with chloromethyl groups above and below the Sn_2Cl_2 planes are easy to see [9]. The structure of diethyltin(IV) dichloride resembles that of the dimethyl analogue in adopting a similar chlorine bridging arrangement, but here the bridging chlorine–tin distance is still shorter at 3.46 Å. Curiously enough, while diethyltin(IV) dibromide takes a similar structure, the diiodide adopts the chelating arrangement favored in the bis(chloromethyl) solid [11].

The structure of trimethyltin(IV) chloride would occupy a central position with regard to the discussion of potentially bridging halogen–tin systems, but experimen-

* The suggestion of a phase transition occurring in triphenyltin(IV) chloride between ambient and liquid nitrogen temperatures [4] is based upon a very low value reported for the NQR coupling constant at 77 K [5]. However, this signal could not be reproduced [6]. The strong similarity of the tin-119m Mössbauer parameters at 80, 110 and 295 K suggests that the solid is isostructural over this temperature range [7].

TABLE 1

THE PHYSICAL PROPERTIES OF TRIMETHYLTIN(IV) CHLORIDE [from ref. 37] GAS-PHASE STRUCTURE

Microwave: Symmetry C_{3v}
Electron diffraction: d(Sn–Cl) 2.106(6); d(Sn–Cl) 2.351(7); d(C–H) 1.125(15) Å; angles C–Sn–C 114.9(1.6)°; C–Sn–Cl 103.2(0.6)°; Sn–C–H 113.4(1.4)° [14]
Dipole moment in solution: 3.46–3.73 D
NMR data:
$\delta((CH_3)_3SnCl)$ 9.34–9.78; 9.06 ppm in pyridine.
$\delta((CH_3)_3SnCl)$ 0.0–0.7 ppm vs. TMS.
$\delta((CH_3)_3SnCl)$ −152 to −166 ppm vs. $(CH_3)_4Sn$.
$|^2J(^{119}Sn–C–^1H)|$ 58.2 Hz, $|^1J(^{13}C–^1H)|$ 132.2 Hz.
NQR data: ^{35}Cl at 77 K; ν 11.40–11.734 MHz.
Tin-119m Mössbauer data [21,22]:
IS 1.64–1.12 mm s^{-1}, QS 3.01–4.24 mm s^{-1}
Vibrational frequencies, cm^{-1} (s, strong; m, medium)

	IR (melt)	IR(CS_2)	Raman (melt)	IR (solid)
$\nu_{asym}(CH_3)$	3002s	2997m	3001m, 2998m	
$\nu_{sym}(CH_3)$	2925s	2920m	2921s, 2923s	
$\delta_{asym}(CH_3)$	1400s	1400m	1401s	
$\delta_{sym}(CH_3)$	1193s	1192m	1198m, 1202m	
$\rho(CH_3)$	787s	782s	790s	
$\nu_{asym}(C_3Sn)$	561m, 545s, 523m	543s	545m, 548m	
$\nu_{sym}(C_3Sn)$	514s	514m	514s, 518s	
δ(SnCl)		331	313m, 318s	288
$\delta(C_3Sn)$			145m, 150m	

He(I) photoelectron data: 9.98, 10.16, 11.33 and 13.95 eV
ESCA data: Sn(3d) 492.36 and 500.81 eV, C(1s) 290.04 eV, Cl(2p) 204.6 and 206.3 eV.
Mass spectral data at 70 eV
$[(CH_3)_3SnCl]^+$ (0.5), $[(CH_3)_2SnCl]^+$ (40.7), $[CH_3SnCl]^+$ (6.6), $[SnCl]^+$ (12.2), $[(CH_3)_3Sn]^+$ (18.6), $[(CH_3)_3SnH]^+$ (0.5), $[(CH_3)_2Sn]^+$ (5.9), $[CH_3Sn]^+$ (8.7), $[CH_2Sn]^+$ (2.5), $[SnH_2^+]$ (1.5) and $[Sn^+]$ (5.7)
Melting point: 34–45°C
Boiling point: 152–157°C/1 atm.
ΔH_{vap} 14 kcal/mol
Conductivity in absolute ethanol: Λ_0 30.8 Ω^{-1} cm^2 val^{-1}
E_0 = −0.140 V (ethanol); −0.139 V (methanol) vs. Ag(AgCl)

tal difficulties probably stood in the way of earlier attempts *. We report here the structure carried out at 138 K of this highly toxic, low melting (m.p. 39.5°C), volatile (b.p. 154°C) material, whose physical properties are listed in Table 1.

* Reports of an earlier X-ray structure by A.G. Davies, H.J. Milledge and D.C. Puxley showing a five-coordinated structure bent at tin have been quoted in the literature [12], but never published.

Crystal data

The crystals are well-formed prismatic needles, which sublime very quickly (15–30 s) in air at room temperature. The extremely volatile nature of the crystals puts severe limitations on crystallographic measurements. After several unsuccessful attempts, a crystal (0.40 × 0.10 × 0.08 mm) was mounted on a diffractometer fitted with a low-temperature device. All X-ray measurements were carried out with the crystal in a cold nitrogen gas stream (temperature ca. 138 K). At this temperature the crystal appeared to be reasonably stable, although there were signs of slow deterioration. In addition, the crystal showed a relatively large mosaic spread (ca. 1.3°). Preliminary diffraction studies showed the crystal to be monoclinic. The intensity distribution indicated several extinction and pseudo-extinction conditions (all $h + k + l = 2n + 1$, absent or weak; $h0l$, $h = 2n + 1$, $l = 2n + 1$, absent or weak), leading to a space group ambiguity. Patterson analyses and subsequent structure determination and refinements failed to give conclusive evidence regarding the space group. All monoclinic data were collected, and a preliminary report of the structure was published (ref. 1) with the lowest symmetry space group, $P2$. The cell parameters were obtained by a least-squares fit to $+2\theta$ and -2θ values of 22 reflections measured at 138 K using Mo-K_α radiation. The crystal data are listed in Table 2.

Intensity measurements

Intensities of all monoclinic reflections within the sphere of $2\theta \leqslant 53°$ were collected using graphite monochromatized Mo-K_α radiation on an Enraf–Nonius CAD-4 counter diffractometer. The method of data collection has been described [13]. Specific parameters relevant to data collection are given in Table 3. The horizontal aperture was kept wide open (5.5 mm) in order to allow for the large crystal mosaic. Of the total scan time, 2/3 was spent scanning the peak and 1/6 time was spent scanning each of the right and the left backgrounds. Even at low temperature the crystal is seen to undergo slow decomposition. The monitor inten-

TABLE 2

CRYSTAL DATA FOR TRIMETHYLTIN CHLORIDE

Molecular formula	C_3H_9ClSn
Formula weight	199.3
Crystal system	Monoclinic
Space group	$I2/c$ [a]
Cell parameters	(at 138 ± 2 K)
a	12.541(8) Å
b	9.618(11) Å
c	11.015(11) Å
β	92.62(7)°
V	1327.2 Å^3
Z	8
D (calc.)	1.994 g cm^{-3}
μ (Mo-K_α)	41.3 cm^{-1}

[a] See text.

TABLE 3

DATA COLLECTION PARAMETERS

Diffractometer	Enraf–Nonius CAD-4
Radiation	Mo-K_α (λ 0.7107 Å)
Temperature	138 ± 2 K
Scan technique	θ–2θ
2θ limit	$0° \leq 2\theta \leq 53°$
Scan time	60 s
Scan angle	$(1.20 + 0.35 \tan\theta)°$
Aperture width	$(5.00 + 0.86 \tan\theta)$ mm
Aperture height	6 mm
Aperture distance	173 mm
Monitor reflection	314
Intensity monitor	1800 s
Max. fluctuation	8%
Orientation monitor	200 reflections[a]
Number of unique data	1375 ($I2/c$)
Number of observed data[b]	1335

[a] New orientation matrix if angular change greater than 0.1°. Orientation matrix based on 15 reflections.
[b] $I > 2\sigma(I)$.

8%, most of it during the last third of data collection. Intensities were scaled by using the monitor reflection and corrected for Lorentz and polarization factors. Partial sublimation of the data crystal prevented the measurement of all the faces correctly, and thus no absorption correction was made. An experimental weight estimated on the basis of counting statistics was assigned to each structure amplitude [13].

Structure determination, refinements and space group

The structure was determined by heavy atom technique, and refined by full-matrix, least-squares routine. Space group ambiguity was resolved by making a detailed analysis of the intensity data (summarized in Table 4) and by refining the structure in five different space groups, $P2$, $P2/a$, $P2_1/c$, $P2_1/a$ and $I2/c$. In both $P2$ and $P2/a$ the temperature factors of two of the methyl carbons behaved erratically. The final R factor was also higher than that obtained for the other three space groups (0.069 for $P2$, and 0.080 for $P2/a$). Refinements in space groups $P2_1/c$, $P2_1/a$ and $I2/c$ went smoothly. Temperature factors of all the atoms shifted normally, and the final discrepancy factor was much lower (0.055 for $P2_1/c$, 0.051 for $P2_1/a$ and 0.041 for $I2/c$). Of the three space groups, $I2/c$ gave the most desirable convergence with the lowest R factor and cleanest final difference Fourier map (max. peak height 0.7 e/Å^3). Space group $I2/c$ was, therefore, preferred over the others, although the final results of all three space groups are presented in this report for comparison. In choosing $I2/c$, a difficulty arose owing to some 300 reflections with $h + k + l = 2n + 1$ whose $|F_0|$ ranges between 10–30 e (see Table 4). A close look at the diffractometer output of these reflections showed that all of these reflections lie between very strong $h + k + l = 2n$ reflections (average $|F_0|$ is 67.5 e), and invariably they have unusually high background. These are indications that the measured

TABLE 4

SUMMARY OF INTENSITY DATA ANALYSES (Total number of reflections measured: 2933)

	Space group		
	$I2/c$ ($h+k+l=2n+1$, $h0l$, $l=2n+1$)	$P2_1/a$ ($0k0$, $k=2n+1$, $h0l$, $h=2n+1$)	$P2_1/c$ ($0k0$, $k=2n+1$, $h0l$, $l=2n+1$)
No. of reflections affected by space group extinctions	1558	177	177
$S = I/\sigma(I)$ of these reflections			
$S \leqslant 3$	832	124	129
$3 < S \leqslant 5$	187	13	13
$5 < S \leqslant 10$	266	29	26
$10 < S \leqslant 20$	253	9	8
$20 < S \leqslant 25$	20	2	1
$\|F_0\|$ range of these reflections			
$\|F_0\| \leqslant 5$	1249	117	132
$5 < \|F_0\| \leqslant 10$		56	42
$10 < \|F_0\| \leqslant 15$	189	4	3
$15 < \|F_0\| \leqslant 30$	141	–	–
Least-squares refinements			
No. of reflections excluding space group extinctions	1375	2756	2756
Average $\|F_0\|$	67.5	42.0	43.0
No. of unobserved ($I \leqslant 2\sigma(I)$) Excluded from least squares sum	40	649	638
No. of Reflections Included in least squares sum	1335	2107	2118
R-factor	0.041	0.051	0.055

TABLE 5

POSITIONAL PARAMETERS OF NON-HYDROGEN ATOMS (Estimated standard deviations in parentheses.)

	x	y	z
Sn	0.70372(3)	0.48688(5)	0.35566(4)
Cl	0.69781(15)	0.42418(22)	0.14172(13)
C(1)	0.8699(6)	0.4709(9)	0.3984(8)
C(2)	0.5981(5)	0.3334(8)	0.4198(6)
C(3)	0.6406(5)	0.6899(7)	0.3438(5)

TABLE 6

ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) (Standard deviations of the last digits are within parentheses.)

	U_{11}	U_{12}	U_{33}	U_{23}	U_{13}	U_{12}
Sn	198(4)	290(4)	184(4)	24(1)	19(2)	−27(1)
Cl	559(11)	514(12)	193(8)	−32(7)	24(7)	−104(9)
C(1)	215(34)	397(41)	488(48)	80(36)	−40(30)	−5(31)
C(2)	298(31)	386(39)	388(33)	61(30)	86(26)	−102(28)
C(3)	299(31)	367(37)	263(28)	12(26)	72(24)	148(27)

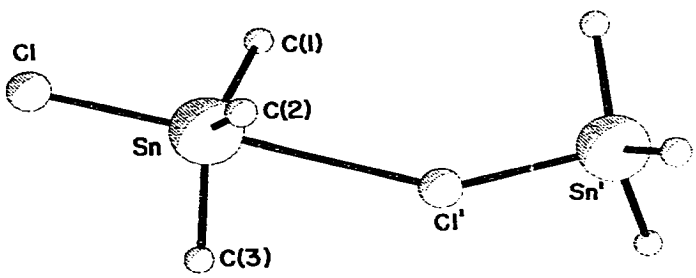

Fig. 1. The asymmetric unit of trimethyltin(IV) chloride with the atomic labeling. The interchain d(Sn···Cl) values are greater than 4.1 Å.

intensities for $h + k + l = 2n + 1$ reflections could be due to diffused scattering or perhaps background streaks and are erroneously "present".

Final atomic parameters, both positional and thermal ($I2/c$) are listed in Tables 5 and 6, respectively. The molecular unit, with atomic labeling, is diagramed

TABLE 7

INTERATOMIC DISTANCES (Å) (estimated standard deviations in parentheses)

	$P2_1/c$		$P2_1/a$		$I2/c$		$P2$ [1]
		Mean		Mean		Mean	
Sn–Cl	2.434(2)	2.431(2)	2.425(2)	2.428	2.430(2)		2.434(5)
	2.428(2)		2.431(2)				
Sn–Cl	3.266(2)	3.267	3.268(2)	3.270	3.269(2)		3.259(5)
	3.268(2)		3.272(2)				
Sn–C	2.135(13)		2.100(10)		2.121(8)		2.14(2)
	2.138(11)		2.138(9)		2.126(7)	2.119	
	2.105(11)	2.120	2.111(9)	2.118	2.109(7)		
	2.120(10)		2.115(10)				
	2.117(8)		2.114(9)				
	2.104(9)		2.115(9)				

TABLE 8

INTERATOMIC ANGLES (Estimated standard deviations in parentheses)

Angle	$P2_1/c$			$P2_1/a$			$I2/c$		$P2$ (average value)
		Mean			Mean		Mean		
Sn–Cl–Sn	150.3(1) 150.6(1)	150.5		150.5(1) 150.3(1)	150.4		150.30(9)		150.9(4)
Cl–Sn–Cl	177.10(10) 176.65(8)	176.88		176.62(8) 176.90(8)	176.76		176.85(6)		176.8(2)
Cl–Sn–C(1)	101.6(4) 100.2(2)	100.9		101.6(3) 100.1(3)	100.9		100.6(2)		
Cl–Sn–C(2)	99.9(3) 99.4(2)	99.7	100.1	99.4(3) 99.0(2)	99.2	100.1	99.1(2)	99.9	99.5(5)
Cl–Sn–C(3)	100.6(2) 98.5(2)	99.6		100.5(3) 99.9(2)	100.2		100.1(2)		
Cl′–Sn–C(1)	81.3(4) 83.1(2)	82.2		81.7(3) 83.0(3)	82.4		82.6(2)		
Cl′–Sn–C(2)	79.0(3) 78.7(2)	78.9	80.0	79.2(3) 79.7(2)	79.5	79.9	79.6(2)	80.1	80.5(5)
Cl′–Sn–C(3)	77.5(2) 80.0(2)	78.8		77.5(2) 78.3(2)	77.9		78.0(1)		
C(1)–Sn–C(2)	118.7(4) 115.5(3)	117.1		119.6(4) 120.0(4)	119.8		119.8(3)		
C(1)–Sn–C(3)	117.2(4) 120.8(3)	119.0	117.0	115.6(4) 116.4(4)	116.0	117.0	116.3(3)	117.1	117.2(8)
C(2)–Sn–C(3)	114.0(4) 115.9(3)	115.0		115.0(3) 115.2(3)	115.1		115.2(3)		

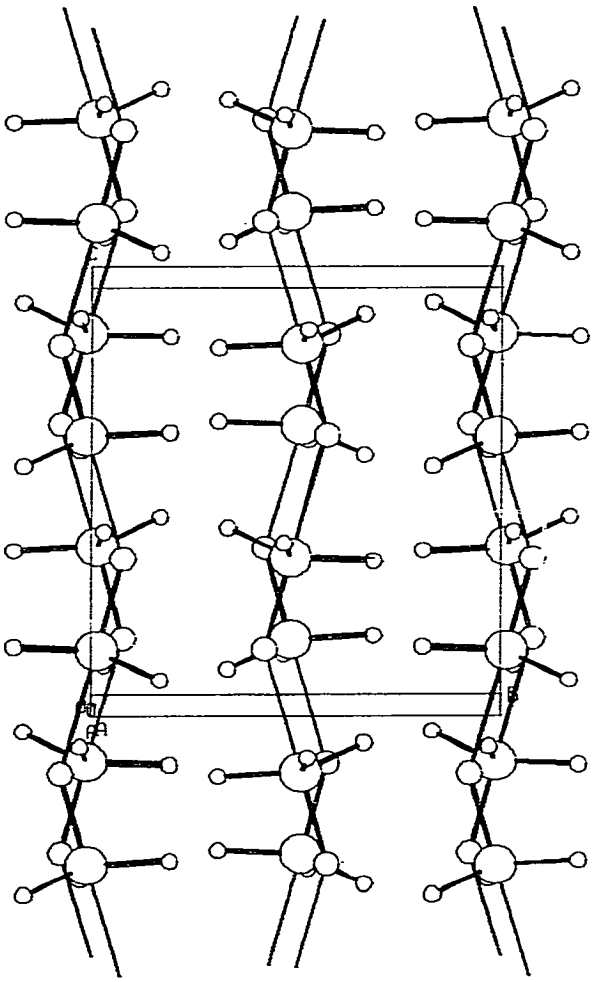

Fig. 2. The contents of the unit cell of trimethyltin(IV) chloride.

in Fig. 1; Fig. 2 shows the contents of the unit cell. Bond distances and angles are given in Tables 7 and 8.

Discussion

Trimethyltin(IV) chloride, which crystallizes in a needle habit, consists of a polymeric lattice with chlorine atoms bridging non-planar trimethyltin groups at unequal distances. The chain is nearly linear at tin (angle Cl–Sn–Cl 176.85(6)°), but bent at chlorine (angle Sn–Cl · · · · Sn = 150.30(9)°), imposing a zig-zag character to the polymeric backbone along which the trimethyltin groups are eclipsed (see Fig. 3). The shortest interchain tin–chlorine contact distances are greater than 4.1 Å.

Data from a recent gas-phase electron diffraction study of trimethyltin(IV) chloride [14] along with those from the X-ray study of the related $[(CH_3)_3SnCl_2]^-$ anion [15] are available for comparison. Despite experimental difficulties, the values

for the five independent parameters Sn–Cl, Sn–C, C–H, angles Cl–Sn–C and Sn–C–H serve to fix C_{3v} geometry for $(CH_3)_3SnCl$ in the gas-phase monomer. The predictions of isovalent hybridization are borne out in the relative opening of the carbon–tin–carbon (mean 114.9°) and closing of the carbon–tin–chlorine (mean 103.2°) angles, and the tin–carbon (2.106 Å) and tin–chlorine (2.351 Å) distances [14] can be taken as the reference points for subsequent comparison. The change in these distances and angles from those found in the vapor to those we have measured for the solid reflects the change from the roughly tetrahedral monomer to the trigonal bipyramidal, polymeric solid. For example, the C–Sn–C angle opens from 114.9° (mean) in the tetrahedral monomer to 117.3° in the associated solid, towards a value of 120° for carbon atoms occupying the equatorial sites of an ideal trigonal bipyramid. Adding a chloride ion to form the $[(CH_3)_3SnCl_2]^-$ anion should relax all the bond lengths, and this is indeed the case with the tin–carbon at 2.12 Å and the

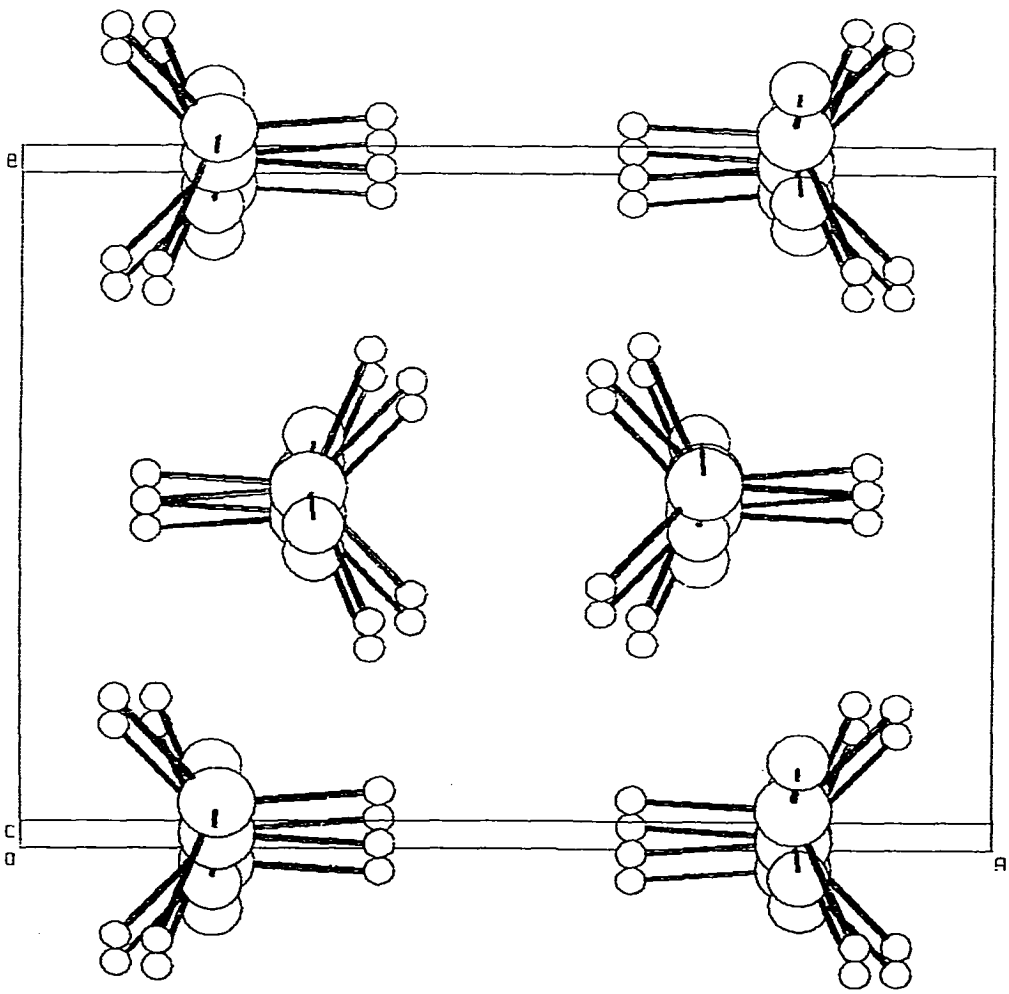

Fig. 3. A view down the chains in the unit cell showing the eclipsed trimethyltin groups.

tin–chlorine distance at a mean of 2.634 Å. However, this axially-distorted, trigonal bipyramidal structure has one short (2.572 Å) and one long tin–chlorine distance at 2.696 Å [15], the latter being the longest such intramolecular length yet reported [2]. The tin–chlorine distance of 2.430(2) Å within the identifiable molecular unit of the title compound is longer than in the gas-phase monomer [14], but shorter than in the $[(CH_3)_3SnCl_2]^-$ anion [15]. The angles are also more distorted from tetrahedral than in the monomer. The direction of approach of the incoming chlorine is along the rearside extension of the Sn–Cl vector, minimizing steric repulsion from the methyl groups. The intermolecular contact distance at 3.269(2) Å is shorter than in the solid dimethyl- (3.54 Å) [10] diphenyl- (3.77 Å) [8] or bis(chloromethyl)-tin(IV) (3.71 Å) [9] dichloride analogues, and substantially shorter than the sum of the tin and chlorine Van der Waals radii of 3.85 Å [19]. The zig-zag axis which can be perceived running through the lattice (see Fig. 2) establishes the polymeric nature of the solid through single chlorine bridges.

Since the structure of the homologous trimethyltin(IV) fluoride cannot be solved because of disorder [16,17] * or tunnel transfer [17] of the fluorine atoms, the widely quoted singly bridging halide structure for $(CH_3)_3SnX$ compounds is being confirmed here for the first time [18]. Comparison data for the structures of tetramethyltin(IV), tin(IV) chloride and other organotin(IV) chlorides are presented in Table 9.

A similar zig-zag axis runs through the structure of trimethyltin(IV) methoxide, but in the latter the trimethyltin groups are staggered (the methoxyl methyl group eclipses an intermolecularly attached methyltin moiety) [20]. Figure 3 is a view down the chain showing the eclipsed nature of the methyl groups in the title compound.

The question of the strength of the intermolecular association in trimethyltin(IV) chloride can be discussed with respect to the tin-119m Mössbauer data for relevant compounds. The quadrupole splitting (QS) values for the trimethyltin(IV) fluoride [16,17] (3.60–4.02) [21,22], cyanide [23] (3.17 for the triethyl derivative) [22], hydroxide [24,25] (2.71–2.97) [21,22] and azide [26,27] (3.23–3.67) [21,22] mm s^{-1}, all known to be associated through single-atom bridges into polymers [2], can be compared with 3.14–4.24 mm s^{-1} reported in different determinations [21,22] for the chloride. Thus the chloride behaves like other five-coordinated trimethyltin(IV) polymers, and the range of QS values reported for the $[(CH_3)_3SnCl_2]^-$ anion (3.23–3.47 mm s^{-1}) [21,22] is corroboratory.

However, the intermolecular tin–chlorine association is apparently disrupted on melting or dissolving in carbon disulfide as shown by ν(Sn–Cl) values which fall from 331 in CS_2 solution to 315 in the melt to 288 cm^{-1} in the solid [28]. Both ν_{asym}- and $\nu_{sym}(SnC_3)$ modes absorb in the infrared and Raman spectra [28–30], in accord with a non-planar arrangement of the methyl groups about the tin atom [28].

Calculations based upon a stereochemical model that takes into account the spatial requirements of atoms have been carried out for trimethyltin(IV) chloride, and yield the angles Cl–Sn–C 99° and C–Sn–C 118° and an intermolecular contact distance of 3.54 Å. The results are listed in Table 9 for a predicted five-coordinated geometry in the solid [31].

* A semiempirical calculation predicts that trimethyltin(IV) fluoride will be ordered below 53 K [17].

TABLE 9. COMPARISON DATA FOR ORGANOTIN(IV) CHLORIDE STRUCTURES

(Figures within the parentheses refer to the standard deviation of a single observation and the r.m.s. deviation of the four independent measurements, respectively)

Compound	Ref.	d(Sn–C) (Å)	d(Sn–Cl) (Å)	Angle (C–Sn–C) (°)	Angle (C–Sn–Cl) (°)	d(Sn···Cl) (Å)	Angle (Cl–Sn···Cl) (°)
$(CH_3)_3SnCl$	This work						
X-ray at 138 K		2.119(7)	2.430(2)	117.1(3)	99.9(2) intra- 80.1(2) inter-	3.269(2)	176.85(6)
predicted	[31]	–	–	118	99	3.54	–
e.d. at 90°C	[31]	2.106(5)	2.351(7)	114.9(1.6)	103.2(6)	–	–
$[(CH_3)_3SnCl_2]^-$		2.12	2.572(4)				
X-ray at r.t.	[15]		2.696(3)	*a*	*a*		
$(CH_3)_3SnCl \cdot py$		*a*	2.42(4)	*a*	*a*	–	–
X-ray at r.t.	[32]						
$(C_6H_5)_3SnCl$		2.12	2.31	112.3	–	–	–
X-ray at r.t.	[4]		2.32				
$(CH_3)_2SnCl_2$		2.21(8)	2.40(4)	123.5(4.5)	109.0(4.5)	3.54(5)	
X-ray at r.t.	[10]						
e.d. at 85–88°C	[33]	2.109(9)	2.327(3)	–	109.8(1.2)	–	–
$[(CH_3)_2SnCl_3]^-$		2.11(5)	2.32(1) eq	140(2)	107		
X-ray at r.t. [b]		2.12(4)	2.53(2) ax		113		
[c]		2.08(3)	2.560(9)	152.2(8)	101.7(6)		
		2.09(3)	2.585(9)		106.0(6)		
$(C_6H_5)_2SnCl_2$		2.114(3)	2.346(2)	125.5	107	3.77	101.7
X-ray at r.t.	[8]						
$(ClCH_2)_2SnCl_2$		2.18(7)	2.37(2)	135	105	3.71	
X-ray at r.t.	[9]						
CH_3SnCl_3		2.105(16)	2.304(3)	–	113.9(7)	–	–
e.d. at 80°C	[14]	–	2.281(2)	–	–	–	–
$SnCl_4$							
e.d. at 0°C [a]	[35]						
$(CH_3)_4Sn$		2.134(3)	–	–	–	–	–
e.d. at 80°C	[36]						

[a] Not given. [b] With gegenion = $[Mo(h^5\text{-}C_5H_5)_3Sn]^+$ in ref. 15. [c] With gegenion = $[(CH_3)_2SnCl \cdot terpy]^+$ in ref. 34.

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