Crystal Structure of Pyridinium Tetrachlorodimethylstannate(IV)

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The crystal structure of the title compound has been determined by single-crystal *X*-ray diffraction from diffractometer data and refined to a final *R* of 5.3%. Crystals are monoclinic, space group $P2_1/c$ [a = 8.053(2), b = 15.340(6), c = 7.323(2) Å, β = 94.81(2)°, Z = 2] and the structure consists of planar pyridinium ions and *trans*-octahedral $[SnMe_2Cl_4]^{2-}$ anions [Sn–C 2.109(9), Sn–Cl 2.625(2), and 2.603(2) Å].

THE stereochemistry of organotin complexes has been studied by many physical techniques and a recent paper[1] summarizes some of the subtle and confusing problems. Salts of the $[SnMe_2X_4]^{2-}$ anion (X = F, Cl, Br, or I) are well known [2,3] and both vibrational spectroscopy and Mössbauer spectroscopy indicate a *trans* isomer although no *X*-ray work has been reported.

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Beattie *et al.*[3] recently pointed out anomalies in the Raman spectra of the $[SnMe_2Cl_4]^{2-}$ ion and the deuteriated analogue, and reassigned the band at 207 cm^{-1} as a tin–carbon deformation mode. The totally symmetric Sn–Cl mode, normally an intense band in the Raman spectrum, is particularly weak in this species and has been tentatively assigned only.[3] Because this six-co-ordinate ion contains the simplest Sn–C bond, has only two types of ligands, and poses unresolved problems with the vibrational spectra, we felt it was important to establish unambiguously the detailed structure in the solid state. Salts of the $[SnMe_2Cl_4]^{2-}$ ion with various cations have been described (Cs,[3-5] Me_4N,[4,6] Et_4N,[3] C_5H_6N,[7-9] C_9H_8N,[7,10] Ph_4As,[11] and $Me_3NCH_2{\cdot}CH_2{\cdot}OH$ [6]) and we report now the structure of the pyridinium salt.

EXPERIMENTAL

Mixing $CHCl_3$ solutions of pyHCl and $SnMe_2Cl_2$ (py = pyridine) gave over a few minutes very fine needle crystals of $[pyH]_2[SnMe_2Cl_4]$ (m.p. 150—153°, lit.,[9] 151 °C; Found: C, 32.6; H, 3.9; Cl, 31.4. Calc. for $C_{12}H_{18}Cl_4N_2Sn$: C, 31.97; H, 4.02; Cl, 31.46%). Suitable crystals for *X*-ray studies, obtained by slow room-temperature evaporation of $CHCl_3$ solutions, were mounted in Lindeman glass capillaries.

TABLE 1

Final positional parameters with standard deviation in parentheses

	x/*a*	*y*/*b*	*z*/*c*
(*a*) Non-hydrogen atoms (× 10^4) *			
Sn	5 000	0	5 000
Cl(1)	5 143(2)	1 542(1)	3 465(3)
Cl(2)	1 942(3)	−190(1)	3 604(4)
N(1)	8 868(11)	2 176(6)	5 235(10)
C(2)	8 342(10)	2 993(10)	5 447(12)
C(3)	9 443(16)	3 642(6)	5 597(14)
C(4)	11 071(13)	3 473(6)	5 498(12)
C(5)	11 579(10)	2 648(8)	5 237(11)
C(6)	10 476(15)	2 000(6)	5 116(11)
C	4 172(11)	575(6)	7 378(11)
(*b*) Hydrogen atom positions †			
	x/*a*	*y*/*b*	*z*/*c*
H(1)	0.84	0.16	0.54
H(2)	0.73	0.31	0.58
H(3)	0.94	0.43	0.53
H(4)	1.17	0.40	0.55
H(5)	1.28	0.25	0.49
H(6)	1.08	0.13	0.49
H	0.40	0.12	0.76
H′	0.32	0.04	0.76
H″	0.51	0.04	0.81

* The numbering system for the atoms of the pyridinium ring [N(1) and C(2)—C(6)] is systematic. † U set at 7.6 × 10^{-2} for all H atoms; $T = \exp[-8\pi^2 U \sin^2\theta/\lambda^2]$. H(1) to H(6) are bonded to the corresponding numbered atom of the pyridinium ring. H, H′, and H″ are bonded to the methyl carbon atom (C).

Crystal Data.—$C_{12}H_{18}Cl_4N_2Sn$, $M = 450.8$, Monoclinic, $a = 8.053(2)$, $b = 15.340(6)$, $c = 7.323(2)$ Å, $\beta = 94.81(2)°$, $U = 901.4$ Å^3, $D_m = 1.67(3)$ g cm^{-3} (by flotation), $Z = 2$, $D_c = 1.661$ g cm^{-3}, $F(000) = 444$. Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 20.01 cm^{-1}. Systematic absences $h0l$ for $l = 2n + 1$, and $0k0$ for $k = 2n + 1$ established space group $P2_1/c$ (No. 14).

TABLE 2

Bond lengths (Å) and angles (°) and selected intermolecular distances (Å), with standard deviation in parentheses

(*a*) Anion			
Sn–Cl(1)	2.625(2)	Cl(1)–Sn–Cl(2)	90.39(6)
Sn–Cl(2)	2.603(2)	Cl(1)–Sn–C	90.30(26)
Sn–C	2.109(9)	Cl(2)–Sn–C	90.97(25)
(*b*) Cation			
N(1)–C(2)	1.34(2)	N(1)–C(2)–C(3)	119.7(9)
C(2)–C(3)	1.33(2)	C(2)–C(3)–C(4)	119.7(10)
C(3)–C(4)	1.34(2)	C(3)–C(4)–C(5)	119.9(9)
C(4)–C(5)	1.35(2)	C(4)–C(5)–C(6)	120.1(9)
C(5)–C(6)	1.33(2)	C(5)–C(6)–N(1)	119.4(9)
C(6)–N(1)	1.33(2)	C(6)–N(1)–C(2)	121.1(9)
(*c*) Intermolecular distances			
N(1) · · · Cl(1)	3.312(9)	N(1) · · · Cl(2^{I})	2.243(10)

[Atom Cl(2^{I}) is at $1 - x, -y, 1 - z$]

(*d*) Equation of least-squares plane passing through the pyridinium group (x, y, z are fractional co-ordinates in direct space)

$$0.268\,21x - 1.934\,40y + 7.214\,39z = 3.584\,60$$

(*e*) Equation of least-squares plane passing through the 4 Cl atoms of the anion

$$-3.224\,13x + 6.459\,19y + 6.184\,59z = 1.480\,23$$

Preliminary cell dimensions and diffraction symmetry were obtained from Weissenberg and precession photographs. Most of the crystals were twinned (100 plane) and it was necessary to collect the data from a crystal (0.9 × 0.2_5 × 0.2_5 mm) which consisted mainly of a single crystal but with a small part of the twin. Diffracted intensities from the larger twin were collected on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[12] Of the total of 1 600 independent reflections (complete for $2.9 < 2\theta < 50.0°$), 1 376 were considered observed according to the criterion $I > 2.5\sigma(I)$. No significant deterioration in the diffracted intensities of monitored reflections was observed over the period of the data collection.

A Patterson synthesis gave a solution in which the tin atoms occupy sites 2(*d*) of space group $P2_1/c$, while all other atoms occupy general positions 4(*e*). Data were corrected for absorption and the structure was refined by full-matrix least-squares techniques. Hydrogen atoms were incorporated into the structure-factor calculations at positions estimated from the electron-density syntheses but neither their positional nor thermal parameters were refined (Table 1). Atomic scattering factors for chlorine, nitrogen, and carbon were taken from ref. 13, for tin(2+) from ref. 14, and for hydrogen from ref. 15; those for tin and chlorine were corrected for anomalous dispersion effects.[14] The nitrogen atom of the pyridinium ring was

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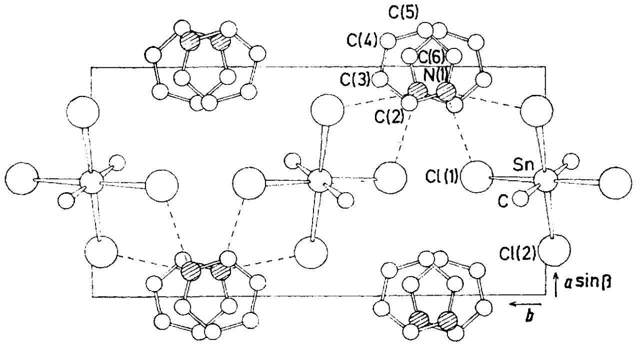
chosen on the basis of the refined isotropic temperature factor when all the atoms of the ring were treated as carbon and this conclusion received additional support from inspection of the intermolecular contact distances (see Discussion section). Weights were applied according to the scheme $w = 1/(\sigma^2 + DF_o)$ where D (0.2) was chosen from an analysis of the variation of $w\Delta^2$ with F_o and with $\sin\theta$. In the final stages of refinement, all non-hydrogen atoms were given anisotropic thermal parameters. The refinement converged (88 refined parameters) at R 0.053 (R' 0.076) for 1 376 reflections with shift-to-error of <0.001. A final electron-density difference synthesis showed no peaks >0.4 or <-0.4 eÅ^{-3}, except for a region close to the tin atom.

Final positional parameters are given in Table 1 and bond lengths and angles with their standard deviations in Table 2. All calculations were carried out at the University of London Computing Centre using the '*X*-Ray' system of programs.[16] Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 21733 (9 pp., 1 microfiche).*

DISCUSSION

The structure consists of discrete pyridinium ions and *trans*-$[\mathrm{SnMe_2Cl_4}]^{2-}$ ions (see Figure). The mean C–C bond length in the pyridinium ring is 1.34(2) Å and the bond angles vary between 119.4 and 121.1°. These dimensions agree well with those from earlier studies.[17] The pyridinium ion is planar with a maximum deviation from the least squares plane of 0.01 Å and a mean deviation of 0.006 Å. The $[\mathrm{SnMe_2Cl_4}]^{2-}$ anion is centrosymmetric with *trans*-methyl groups and Table 2 shows that to a good approximation the ion has D_{4h} symmetry (excluding H atoms). In general as the co-ordination number of a metal in a fixed oxidation state increases from 4 to 5 to 6, it might be expected that the bond length would increase, owing to the decrease in the percentage of *s* (and *p*) character per bond. This is observed for series such as $\mathrm{SnCl_4}$, $[\mathrm{SnCl_5}]^-$, and $[\mathrm{SnCl_6}]^{2-}$ (ref. 2) where the increased negative charge will also enhance the lengthening of the Sn–Cl bond. The Sn–C distance for the methyl ligand is 2.109(9) Å, fairly short for such a bond. By contrast the Sn–Cl bonds [2.625(2) and 2.603(2) Å] are considerably longer than those found in the majority of related compounds.[1] In the series $\mathrm{SnMe_2Cl_2}$,[18] $[\mathrm{SnMe_2Cl_3}]^-$ (refs. 10, 19), and $[\mathrm{SnMe_2Cl_4}]^{2-}$ there is a progressive lengthening of the Sn–Cl bond. The effects can be rationalized in terms of a preferential concentration of the *s* orbital electrons in the Sn–C bonds,[1-3] leading in the limit to a linear *sp* $[\mathrm{SnMe_2}]^{2+}$ ion, and chloride ions, as originally suggested by Beattie.[20] We also note that the shortest N $\cdots$ Cl intermolecular distances are 3.312(9) and 3.243(10) Å, to Cl(1) and Cl(2) respectively, which are typical for a Cl $\cdots$ H–N bond,[17,21] in this case producing a bifurcated hydrogen bond. This also helps to account for the long Sn–Cl bond lengths observed. A view of the unit cell is shown in the Figure and illustrates the way in which the anion and cation pack together. All (non-hydrogen) intermolecular distances are >3.6 Å other than those already described.



Projection of the structure from $z = -\frac{1}{4}$ to $+\frac{3}{4}$ viewed from the positive c direction towards the origin. Dotted lines indicate N(H) $\cdots$ Cl interactions

The Raman spectrum of the compound showed three rather broad bands at *ca.* 200 cm^{-1}, but attempts at single-crystal studies to aid the vibrational assignment have so far been unsuccessful. This is largely due to difficulties in obtaining both suitably sized untwinned crystals and spectra for all the required orientations, together with the unfavourable orientation of the anions in the unit cell. The crystallographic *c* direction has pseudo-tetragonal symmetry, making depolarization of the laser beam incident along this direction the source of complications [5 145 Å line from Ar$^+$ laser with Cary 82 Raman spectrometer gave bands at 504(110), 399(4), 225(6), 194(17), 162(3) Δ cm^{-1} in the 100—600 cm^{-1} range; approximate relative intensity in parentheses].

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