Crystal and Molecular Structure of Quinolinium Trichlorodimethylstannate(IV)

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The structure of $[C_9H_8N][Me_2SnCl_3]$ has been determined by single-crystal X-ray diffraction from photographic data by the heavy-atom method, and refined to R 5.5%. Crystals are triclinic, $a = 9.55(3)$, $b = 12.53(2)$, $c = 7.03(2)$ Å, $\alpha = 109.4(1)$, $\beta = 96.7(3)$, $\gamma = 111.2(2)°$, $Z = 2$, space group $P\bar{1}$. The anion, of approximate C_{2v} symmetry, has a structure intermediate between a trigonal bipyramid and square pyramid. When based on the former, carbon atoms occupy equatorial positions [Sn–Cl 2.560(9), 2.585(9) (ax), 2.407(5) (eq), Sn–C 2.08(3) Å, C–Sn–C 152.2(8)°] whilst with the latter description there is a short (2.407 Å) Sn–Cl(ax) bond. There is a weak Sn ··· Cl interaction between atoms of adjacent anions, giving rise to dimeric units [Sn ··· Cl 3.486(7) Å]. The geometry of the planar cation is as expected.

ORGANOTIN halogeno-species have been extensively studied by both vibrational spectroscopy and X-ray diffraction but no stereochemical models with sound predictive ability have been put forward.[1] The interaction between dimethyltin dichloride and chloride ions yields the $[Me_2SnCl_3]^-$ and $[Me_2SnCl_4]^{2-}$ species and a number of salts with various cations have been prepared.[2-4] The former anion has been characterized by X-ray diffraction in the compound $[(terpy)SnMe_2Cl][Me_2SnCl_3]$.[5]

While studying the interaction between quinoline and dimethyltin dichloride in methanol–hydrochloric acid we isolated $(C_9H_8N)_2Me_2SnCl_4$[6] and a second material which X-ray analysis established as $(C_9H_8N)_2Me_2SnCl_3$. It is not yet known how variable is the geometry of a complex ion, in its solid compounds, as the counter ion is varied. It is thus important for the development of any satisfactory bonding models that various structures containing a particular ion are examined, and therefore useful to compare our results directly with the previous study on the $[Me_2SnCl_3]^-$ ion; we report now our crystallographic studies on $[C_9H_8N][Me_2SnCl_3]$.

EXPERIMENTAL

Dimethyltin dichloride (B.D.H.) was used directly and quinoline was distilled. The method of Pfeiffer[6] was used to synthesize $[C_9H_8N]_2[Me_2SnCl_4]$ by mixing 2 : 1 mol quantities of quinoline and Me_2SnCl_2 in hydrogen chloride saturated anhydrous methanol and allowing the mixture to evaporate in a desiccator (over NaOH pellets). Fine needle crystals were obtained [m.p. 170 °C (lit.)[6] 169° C)] (Found: Cl, 25.4. Calc.: 25.7%), but attempts to obtain single crystals were unsuccessful. In some experiments diamond-shaped crystals of very different habit were observed. X-Ray powder photographs were not the same as for samples of $[C_9H_8N]_2[Me_2SnCl_4]$ and subsequent crystal-structure analysis established the material as $[C_9H_8N][Me_2SnCl_3]$ (m.p. 148 °C) (Found: Cl, 26.5. Calc.: Cl, 27.6%).

Crystal Data.—$C_{11}H_{14}Cl_3NSn$, $M = 385.3$, Triclinic, $a = 9.55(3)$, $b = 12.53(2)$, $c = 7.03(2)$ Å, $\alpha = 109.4(1)$, $\beta = 96.7(3)$, $\gamma = 111.2(2)°$, $U = 712.4$ Å^3, $D_m = 1.73(3)$ (by flotation), $Z = 2$, $D_c = 1.79$ g cm^{-3}. Space group $P1$ (No. 1) or $P\bar{1}$ (No. 2), the latter borne out by the analysis. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 22.5 cm^{-1}.

Preliminary cell dimensions and diffraction symmetry were obtained from Weissenberg and precession photographs. For data collection a crystal ($0.7 \times 0.2_2 \times 0.4_5$ mm) was mounted about the c axis in a Lindemann glass capillary. Multiple-film equi-inclination Weissenberg photographs were obtained by use of zirconium-filtered Mo-K_α radiation for the layers $hk0$—6. For some layers an additional short exposure film was required. The films were scanned automatically by use of an Optronics P 1000 Photoscan densitometer.†

From the initial (provided) indexed reflection for each layer, the reflections were indexed, integrated intensities measured, scaling within each level accomplished, and after rejecting some reflections on various criteria a final list of reflections and integrated intensities was produced. Final comparison of the films with the measured reflections confirmed the satisfactory indexing and intensities and, after averaging equivalent reflections, 768 observed reflections were used in the data set for structure analysis. Lorentz and polarization factors were applied and scattering factors for the neutral atoms carbon, nitrogen, and chlorine, were taken from ref. 7 and for tin from ref. 8. (No absorption correction was applied owing to the irregular shape of the crystal and its enclosure in a glass tube.)

Structure Determination.—The structure was determined by conventional methods following the location of the tin atom from the Patterson map. The quinolinium group was initially treated as containing only carbon atoms and least-squares refinement gave R 6.5%. A difference electron-density synthesis at this stage confirmed that there were no atoms unaccounted for. An empirical weighting scheme was developed from an analysis of $\overline{\Delta F^2}$ vs. $\overline{F_o}$ for various ranges of F_o [$w = 1/(A + BF_o + CF_o^2)$ where $A = 24.5$, $B = -0.7$, and $C = 0.0082$]. An analysis of $w\Delta^2$ in terms of F_o and $\sin\theta/\lambda$ confirmed the adequacy of the weighting scheme. At this stage an attempt was made to locate the nitrogen atom of the quinolinium moiety.[9] Electron-density peak heights and isotropic thermal parameters of the carbon atoms were inconclusive. Least-squares refinement of the four possible nitrogen positions (calculated weights,

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† The S.R.C. Microdensitometer Service at the Atlas Computer Laboratory.

[1] See *e.g.* P. G. Harrison, T. J. King, and J. A. Richards, *J.C.S. Dalton*, 1974, 1723.

[2] J. P. Clark and C. J. Wilkins, *J. Chem. Soc.* (*A*), 1966, 871.

[3] I. R. Beattie, F. C. Stokes, and L. E. Alexander, *J.C.S. Dalton*, 1973, 465.

[4] M. K. Das, J. Buckle, and P. G. Harrison, *Inorg. Chim. Acta*, 1972, **6**, 17.

[5] F. W. B. Einstein and B. R. Penfold, *J. Chem. Soc.* (*A*), 1968, 3019.

[6] P. Pfeiffer, *Annalen*, 1910, **376**, 310.

[7] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[8] L. H. Thomas and K. Umeda, *J. Chem. Phys.*, 1957, **26**, 293.

[9] S. L. Lawton, E. R. McAfee, J. E. Benson, and R. A. Jacobson, *Inorg. Chem.*, 1973, **12**, 2939.

all positional and thermal parameters) gave R factors of 0.0654, 0.0654, 0.0649, and 0.0652 compared with 0.0653 with all carbon atoms. Inspection of the refined temperature factors, the residuals, and the intermolecular contacts established that the nitrogen position corresponding to the lowest R factor had the lowest temperature factor for N and the shortest intermolecular distance to neighbouring Cl atoms [see Table 3(c) and the Discussion section]. This was taken to be the correct nitrogen position in subsequent refinement of the model. One further cycle of refinement (positional and isotropic thermal parameters, calc. weights, scale factors, 71 variables) gave a converged R of 6.5% and the introduction of anisotropic thermal parameters for Sn and Cl reduced R to a final value of 5.5%. This decrease in the R factor is highly significant when Hamilton's statistical test is applied.[10] No hydrogen atoms were included in the structure-factor calculations. A final difference electron-density map showed no prominent features, although a number of small peaks (*ca.* 0.5 eÅ^{-3}) were found in positions corresponding to hydrogen atoms of the quinolinium group.

Final positional and thermal parameters, together with the standard deviations derived from the least-squares analysis, are shown in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No SUP 21453 (9 pp., 1 microfiche).*

TABLE 1

Final positional ($\times 10^4$) and isotropic thermal parameters ($\times 10^2$), with standard deviations in parentheses

	x/a	y/b	z/c	$U/\text{Å}^2$
Sn	2 379(2)	824(2)	4 361(3)	*
Cl(1)	1 357(9)	1 616(7)	7 500(11)	*
Cl(2)	3 363(9)	16(6)	1 145(11)	*
Cl(3)	4 830(7)	2 655(6)	5 953(11)	*
N(1)	6 463(24)	2 599(19)	845(37)	4.9(5)
C(2)	5 212(36)	2 821(27)	880(51)	5.6(7)
C(3)	5 409(34)	4 040(25)	1 616(50)	5.8(7)
C(4)	6 838(31)	5 043(24)	2 305(47)	5.0(6)
C(5)	9 689(34)	5 789(26)	2 912(51)	5.9(7)
C(6)	10 939(32)	5 510(25)	2 846(48)	5.4(7)
C(7)	10 687(40)	4 238(30)	2 032(60)	7.5(9)
C(8)	9 253(32)	3 250(25)	1 417(49)	5.4(7)
C(9)	7 940(24)	3 555(18)	1 446(36)	2.9(5)
C(10)	8 139(28)	4 771(22)	2 248(43)	4.4(6)
C(11)	2 686(28)	−542(22)	5 209(41)	4.4(6)
C(12)	1 076(27)	1 417(20)	2 720(39)	3.4(6)

*Anisotropic thermal parameters (Table 2).

TABLE 2

Heavy atom anisotropic temperature factors * ($\times 10^3$; for Sn $\times 10^4$), with standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	256(9)	303(9)	306(58)	118(7)	92(6)	135(7)
Cl(1)	62(5)	58(4)	45(7)	38(4)	28(4)	28(4)
Cl(2)	65(5)	39(4)	49(7)	29(4)	30(4)	17(3)
Cl(3)	36(4)	40(3)	53(7)	7(3)	7(3)	10(3)

* In the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^*\cos\gamma^* + 2U_{13}hla^*c^*\cos\beta^* + 2U_{23}klb^*c^*\cos\alpha^*)]$.

All calculations, except for the drawing program ORTEP, were carried out on an ICL 1906A computer at the S.R.C. Atlas Laboratory by use of the X-Ray system of programs.[11]

DISCUSSION

The structure consists of quinolinium cations and five-co-ordinate $[\text{Me}_2\text{SnCl}_3]^-$ anions with evidence of a weak association of two anions to form a dimeric unit. Calculated bond lengths and angles are shown in Table 3 together with selected intermolecular distances and the equation of the plane passing through the quinolinium cation. The anion is illustrated in Figure 1, and Figure 2 shows the molecular packing arrangement in the unit cell.

TABLE 3

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

(*a*) Anion

Sn–Cl(1)	2.560(9)	Sn–C(11)	2.09(3)
Sn–Cl(2)	2.585(9)	Sn–C(12)	2.08(3)
Sn–Cl(3)	2.407(5)		
Cl(1)–Sn–Cl(2)	178.9(3)	C(11)–Sn–Cl(2)	87.1(8)
Cl(1)–Sn–Cl(3)	90.9(3)	C(11)–Sn–Cl(3)	106.0(6)
Cl(2)–Sn–Cl(3)	89.9(2)	C(12)–Sn–Cl(1)	88.5(8)
C(11)–Sn–C(12)	152.2(8)	C(12)–Sn–Cl(2)	90.6(8)
C(11)–Sn–Cl(1)	93.5(8)	C(12)–Sn–Cl(3)	101.7(6)

(*b*) Cation *

N(1)–C(2)	1.32(5)	C(8)–C(9)	1.44(4)
C(2)–C(3)	1.37(5)	C(9)–C(10)	1.37(4)
C(3)–C(4)	1.37(3)	C(9)–N(1)	1.38(3)
C(5)–C(6)	1.36(5)	C(10)–C(4)	1.40(5)
C(6)–C(7)	1.42(5)	C(10)–C(5)	1.45(3)
C(7)–C(8)	1.37(4)		

* C–C–C, N–C–C, C–N–C internal angles range 116.1(3.0) – 123.4(3.3).

(*c*) Intermolecular distances

N(1) ··· Cl(2$^{\text{I}}$)	3.181(25)	C(5) ··· Cl(1$^{\text{II}}$)	3.816(40)
N(1) ··· Cl(2)	3.599(23)	C(8) ··· Cl(2$^{\text{I}}$)	3.590(24)
C(4) ··· Cl(1$^{\text{II}}$)	3.855(31)	Sn ··· Cl(1$^{\text{III}}$)	3.486(7)

(*d*) Equation of the least squares plane passing through the atoms of the quinolinium group:

$$-0.427\,13x - 4.162\,33y + 7.007\,92z = -0.776\,71$$

where x, y, z are the fractional co-ordinates in direct space.

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x, y, z:

I $1 - x, -y, -z$ III $-x, -y, 1 - z$
II $1 - x, 1 - y, 1 - z$

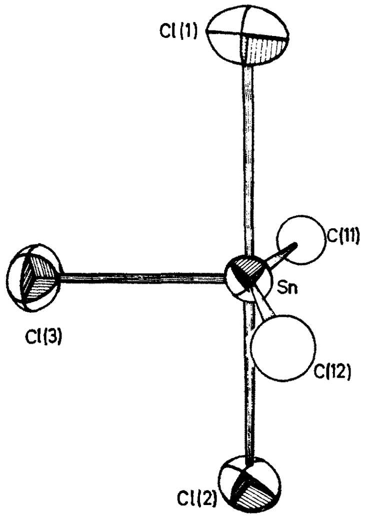

FIGURE 1 The isolated $[\text{Me}_2\text{SnCl}_3]^-$ anion

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

[10] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

[11] 'X-Ray' program system, University of Maryland Technical Report TR 192, version of June 1972.

The quinolinium ion has been characterized by *X*-ray diffraction previously (see ref. 9 and refs. therein), and is numbered as in ref. 9. The ion is to a good approximation planar, the maximum displacement from the least-squares plane being 0.03 Å, with two quinolinium groups packing parallel (Figure 2). The N(H) · · · Cl contact distance has frequently been used as evidence for hydrogen bonding. In $[(C_9H_8N)_2CdCl_4]$ the minimum such distance is 3.07 Å,[12] and more recently distances of 3.27 and 3.34 Å were found to have pronounced effects in the n.q.r. spectra of the $[SnCl_6]^{2-}$ ion.[13] Of equal, importance, but less frequently discussed in crystallographic studies, is the angle formed at hydrogen by the other two atoms involved in the hydrogen bond. Thus in the present structure the shortest distance from atoms of the quinolinium group to other non-bonded atoms is 3.18(3) Å from N(1) to Cl(2), and assuming a plausible position for the hydrogen atom we have a very approximately linear N–H · · · Cl group indicative of hydrogen bonding. Inspection of other contact distances between carbon atoms and neighbouring groups shows that where these are short (*e.g.* there are two <3.5 Å) the angle subtended at hydrogen is unreasonable and incompatible with the existence of hydrogen bonding.

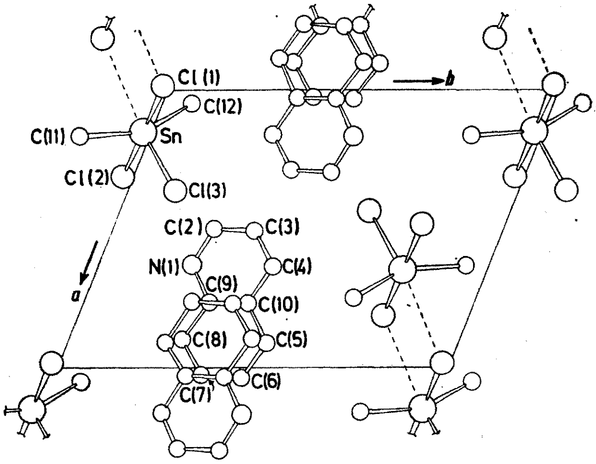

FIGURE 2 View of unit-cell contents looking from the positive c^* direction

The anion present in the structure is $[Me_2SnCl_3]^-$ in which the angle subtended by the carbon atoms at the tin (152°) is midway between that of a trigonal bipyramid (120°) and square pyramid (180° for an axial–basal angle of 90°). A discussion of the anion structure in terms of a distorted co-ordination polyhedron is largely one of semantics. However if we choose to regard the anion as a distorted trigonal bipyramid to aid comparison with an earlier structure we find two axial chlorine atoms with longer bonds [2.560(9) and 2.585(9) Å] than the equatorial Sn–Cl bond [2.407(5)]. The C(11)–Sn–C(12) angle is 152.2° rather larger than the value found in the previous study [5] of the anion [140(2)°]. The anion has to a good approximation C_{2v} symmetry and in general terms agrees with the earlier study of this anion.[5]

The only remaining feature of interest is the way in which two anions are arranged to form a dimeric unit. At a distance of 3.486(7) Å from the tin atom there is a further chlorine atom from an adjacent anion. The environment around the tin atom is very similar to that found [14] for In in Me_2InCl [In · · · Cl 3.450(9); In–Cl 2.673(9) 2.945(6), 2.954(6); In–C 2.179(7) (twice); C–In–C 167.3°]. A similar interaction is also found [15] in solid Me_2SnCl_2 (Sn · · · Cl 3.54 Å; C–Sn–C 123.5°) but not in Ph_2SnCl_2 (mean C–Sn–C 125.5).[16] Authors differ on the significance attached to these long bonds and the C–Sn–C angle (see *e.g.* ref. 16). It would appear in the present example that the electrostatic packing of quinolinium and $[Me_2SnCl_3]^-$ ions would not place two anions together unless there were some gain in stability associated with dimer formation.

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[12] H. Paulus, *Acta Cryst.*, 1966, **21**, A148.

[13] R. C. Gearhart, T. B. Brill, W. A. Welsh, and R. H. Wood, *J.C.S. Dalton*, 1973, 359.

[14] H. D. Hanson, K. Mertz, E. Veigel, and J. Weidlein, *Z. anorg. Chem.*, 1974, **410**, 156.

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

[16] P. T. Greene and R. F. Bryan, *J. Chem. Soc.* (*A*), 1971, 2549.