Crystal Structure of 4-Chloropyridinium Hexachlorostannate(IV)

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The title compound has been examined by single-crystal *X*-ray crystallography and crystallizes in the space-group $P2_1/c$ with $Z = 2$ in a unit cell of dimensions a = 8·555, b = 16·962, c = 7·122 Å and β = 113·15°. The structure was solved by conventional Fourier techniques and was refined anisotropically by full-matrix least-squares methods to *R* 0·039 using 1600 independent reflections measured by counter methods. The cation is regular and normal. The $SnCl_6^{2-}$ ion is tetragonally distorted with three crystallographically inequivalent Sn–Cl bonds [2·414(4), 2·419(2), and 2·463(3) Å], the source of the distortion being Cl · · · H–N hydrogen bonding between the long Sn–Cl bonds of $SnCl_6^{2-}$ and the cation. These results account very well for the marked splittings in the ^{35}Cl n.q.r. signals observed for this anion.

RECENT n.q.r. measurements on $SnCl_6^{2-}$, $PbCl_6^{2-}$, and $TeCl_6^{2-}$ salts indicate[1] that when the 4-chloropyridinium ion (4-ClpyH) is the counter cation, very large splittings in the chlorine resonance frequencies of the anion appear. N.q.r. spectroscopy can be used to detect chemical and crystallographic inequivalencies of nuclei having quadrupole moments. Crystallographic inequivalence generally leads to small splittings which are rarely >5% of the overall effect. However in $[4\text{-ClpyH}]_2SnCl_6$, for example, resonance multiplets appear that are split by >15% of the overall effect. It is of importance to n.q.r. spectroscopy to know what sorts of interactions can generate such marked splittings in an MCl_6^{2-} salt. To the general chemistry of tin it is important to know whether this cation has distorted the $SnCl_6^{2-}$ ion enough to produce a different anionic arrangement, such as a $SnCl_5^-$, Cl^- ion pair. Finally, in the only crystallographic data available on the $SnCl_6^{2-}$ ion,[2-4] the Sn–Cl bond lengths are either not known or determined approximately to be 2·41 ± 0·05—0·10 Å. We therefore undertook a crystal structure determination of 4-chloropyridinium hexachlorostannate(IV).

EXPERIMENTAL

Crystal Data.—$C_{10}N_2H_{10}SnCl_8$, M = 555·47, Monoclinic, a = 8·555(9), b = 16·962(5), c = 7·122(7) Å, β = 113·15° [cos (β) = −0·3932(18)], U = 950·3 Å^3, D_m = 2·05 ± 0·05 (by flotation), Z = 2, D_c = 1·958, $F(000)$ = 540. Space group $P2_1/c$ (C_{2h}^5, No. 14[5]). Intensity data were collected with Mo-K_α radiation, λ = 0·7107 Å, μ(Mo-K_α) = 25·0 cm^{-1}.

Unit-cell dimensions were obtained from least-squares refinement of 28 2θ diffractometer settings between 15 and 45°, by use of dimensions from precession photographs as the initial parameter values. The prismatic, transparent crystals were stable to *X*-radiation.

Collection and Reduction of Data.—The sample of dimensions 0·13 × 0·08 × 0·07 mm, was mounted on its longest dimension, such that the crystal is mounted on its two-fold (b) axis.

Intensity data were collected by the θ—2θ scanning using a take-off angle of *ca.* 2°. The range of each scan, at a rate of 2° min^{-1}, consisted of a reflection base-width of 2° and an increment, $\Delta(2\theta) = 0{\cdot}285 \tan\theta$, to allow for spectral dispersion. Background counts for 30 s were taken at both limits of the scan.

Intensity data to sin θ/λ 0·9812 were collected in quadrants $+h$, $+k$, $+l$, giving *ca.* 1600 independent reflections. Reflections were considered to be observed, when $F_o \geq 3{\cdot}0\sigma_F$, where σ_F is the standard deviation of F_o computed from scan and back-ground counts corrected for instrumental instability (estimated at 0·5%).

Elucidation and Refinement of the Structure.—Because of the symmetry-fixed tin locations, it was possible to go

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[1] T. B. Brill and W. A. Welsh, preceding paper.

[2] G. Engel, *Z. Krist.*, 1935, **90**, 341.

[3] L. Pauling, *Z. Krist.*, 1930, **72**, 482.

[4] See R. W. G. Wyckoff, 'Crystal Structures,' vol. III, Interscience, New York, 1965.

[5] 'International Tables for *X*-Ray Crystallography,' vol. I, Kynoch Press, Birmingham, 1968.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses

	x	y	z
Sn [a]	0(0)	0(0)	0(0)
Cl(1)	−458(2)	1273(1)	−1662(2)
Cl(2)	2863(2)	388(1)	2150(2)
Cl(3)	−1057(2)	529(1)	2502(2)
N	2358(7)	3829(5)	1227(9)
C(2)	3952(8)	4052(5)	2424(11)
C(3)	5197(8)	3476(6)	3180(11)
C(4)	4808(7)	2712(5)	2708(9)
Cl(4)	6340(2)	2006(2)	3645(4)
C(5)	3150(7)	2492(5)	1450(9)
C(6)	1947(7)	3068(6)	739(10)
H(1) [b]	1384	4272	639
H(2) [b]	4238	4664	2798
H(3) [b]	6483	3643	4142
H(5) [b]	2831	1880	1052
H(6) [b]	655	2912	225

[a] Sn is in a symmetry-fixed special position. [b] Hydrogen positions are calculated such that each hydrogen is 1·08 Å from its nearest ring atom.

TABLE 2

Isotropic and anisotropic [a] ($\times 10^4$) thermal parameters with estimated standard deviation in parentheses [b]

Atom type	B	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	2·4	262(3)	238(7)	337(2)	9(2)	80(2)	17(2)
Cl(1)	3·2	405(8)	308(18)	539(8)	60(8)	180(6)	107(8)
Cl(2)	3·0	287(7)	387(18)	497(7)	−5(7)	56(5)	−80(8)
Cl(3)	2·8	339(7)	411(19)	383(6)	23(7)	139(5)	−38(7)
N	3·4	393(29)	303(71)	552(30)	79(31)	186(22)	36(33)
C(2)	4·2	453(38)	218(72)	715(44)	−127(37)	235(32)	−63(40)
C(3)	3·3	309(32)	447(88)	600(36)	15(36)	177(25)	−64(40)
C(4)	2·1	339(29)	211(75)	425(27)	100(32)	150(21)	−6(32)
Cl(4)	4·9	484(10)	537(23)	859(13)	211(10)	166(9)	146(12)
C(5)	3·0	389(30)	171(67)	519(31)	−43(33)	137(24)	−4(32)
C(6)	2·6	321(31)	486(95)	458(30)	54(35)	82(22)	37(36)

[a] Anistropic thermal parameters are root-mean square amplitude displacements expressed in Å, ($\times 10^4$). The form of the anisotropic temperature factor expression is: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* \cos\gamma^* + 2U_{13}hla^*c^* \cos\beta^* + 2U_{23}klb^*c^* \cos\alpha^*)]$. [b] Hydrogen thermal parameters were set uniformly at B 4·0.

directly to a three-dimensional Fourier synthesis [6] with tin atoms in place. This lead immediately to placement of the chlorine atoms about the tin; a third synthesis led to location of the non-hydrogen atoms of the chloropyridinium ring.

Full-matrix least-squares refinement of the non-hydrogen atom positional parameters and isotropic thermal parameters, using unit weights, led to a convergence at R 8%. Hydrogen atoms were then introduced by calculation [7] and the 21 non-hydrogen atoms then refined anisotropically by use of a weighting scheme derived from the relationship between F_o and ΔF for this data set. The weighting function used was, $w = 1/\overline{|\Delta F|}^2$, where $\overline{|\Delta F|} = A + B\overline{|F_o|}$. $\overline{\Delta F}$ and $\overline{F_o}$ were plotted against each other for 20 groups of reflections, each group containing approximately equal numbers of observed reflections. The resulting plot was linear and gave 1·50 and 0·0359 for A and B, respectively.

The final refinement cycle converged to a conventional R 3·9% and a weighted value R' 5·5%.

Further refinement cycles and/or adjustments to the weights were deemed unnecessary due to the insensitivity of the positional parameters of the $SnCl_6^{2-}$ ion to such changes. A final difference Fourier synthesis revealed no feature greater than 1 eÅ^{-3} and was adjudged to be free of errors in the determined structure. Atomic positions are collected in Table 1; atomic thermal parameters are listed in Table 2. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20557 (8 pp., 1 microfiche).†

RESULTS AND DISCUSSION

The structure consist of discrete $SnCl_6^{2-}$ and 4-ClpyH$^+$ ions. Figure 1 shows the geometry and thermal ellipsoids of the atoms in these ions, and Figure 2 is a stereoscopic view of the unit cell.

Tables 1 and 2 contain atomic positions in the unit cell and the thermal parameters. Intramolecular and selected intermolecular bond lengths and angles are given in Table 3. All other distances are equal to or greater than van der Waals contacts. For the 4-ClpyH$^+$ ion all distances and angles are regular and normal,[8] and the ion is very uniformly shaped. Within the $SnCl_6^{2-}$ ion, however, there are three pairs of crystallographically inequivalent chlorine atoms. From an angular point of view the ion is an almost perfect octahedron, but it is tetragonally distorted. Two sets of Sn–Cl bonds are similar in length and a third set is markedly longer.

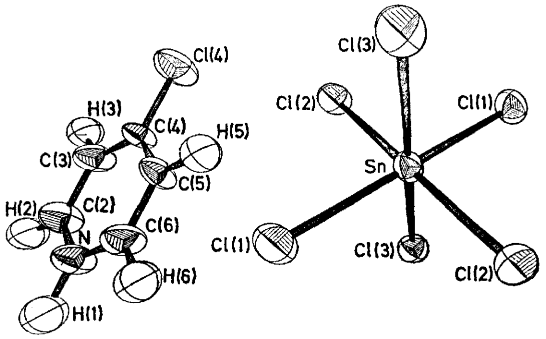

FIGURE 1 ORTEP plot of the 4-chloropyridinium and hexachlorostannate(IV) ions showing 50% probability thermal ellipsoids

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† For details see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[6] All structures refinements were done using '*X*-Ray '70' of J. M. Stewart, F. A. Kundell, and J. C. Baldwin, University of Maryland.

[7] Hydrogen positional parameters were calculated with ATMCAL, adapted from a general hydrogen position calculating program supplied by Dr. Lloyd Guggenberger, The du Pont, Co., Wilmington, Delaware.

[8] Ref. 5, vol. III, 1968.

The crystal structure accurately accounts for the n.q.r. data in the following way. Neglecting π bonding in the Sn–Cl bond, which is reasonable,[9] the two closely spaced high-frequency n.q.r. signals (17·52 and 17·32 MHz) can be assigned to the shorter Sn–Cl bonds (2·414 and 2·419 Å). The lower-frequency n.q.r. signal (14·97 MHz) is associated with the long (2·463 Å) Sn–Cl bond. In this instance a 0·05 Å difference in the bond lengths yields a splitting in the signals in the same ion of *ca.* 15% of the overall n.q.r. effect. Similar large changes in ^{35}Cl n.q.r. frequencies for small changes in bond lengths are observed in square-planar platinum compounds [10] and in chloromercuric salts,[11] although in the platinum and mercury studies, compounds having different lattice symmetries were compared. It is clear, however, that ^{35}Cl n.q.r. frequencies are very sensitive to small bond-length changes.

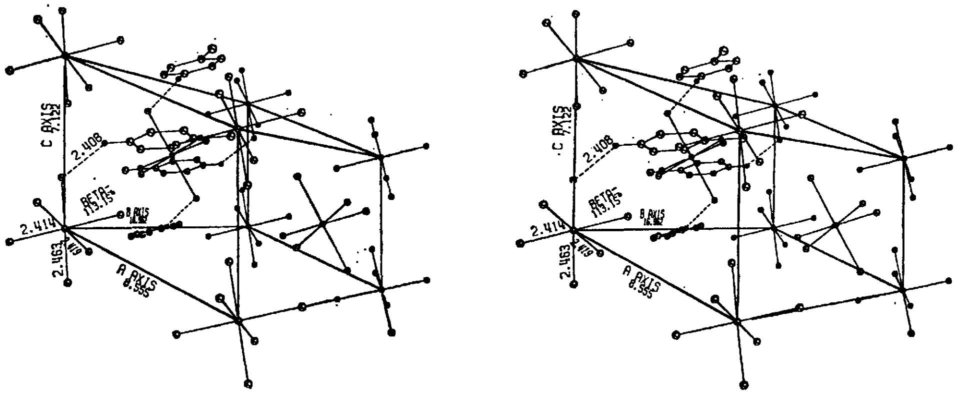

FIGURE 2 Stereoscopic pair reproduction of the unit cell

TABLE 3

(i) Bond distances (Å) with their standard deviations in parentheses

(*a*) Intramolecular

Sn–Cl(1)	2·419(2)	C(3)–C(4)	1·348(14)
Sn–Cl(2)	2·414(4)	C(4)–Cl(4)	1·705(8)
Sn–Cl(3)	2·463(3)	C(4)–C(5)	1·398(8)
N–C(2)	1·341(8)	C(5)–C(6)	1·364(11)
C(2)–C(3)	1·394(12)	C(6)–N	1·346(13)

(*b*) Intermolecular

N · · · Cl(3)	3·266	Cl(3) · · · H(1)	2·408
N · · · Cl(3′)	3·342 [a]	Cl(3′) · · · H(1)	2·583 [a]

(ii) Bond angles (°) with their standard deviations in parentheses

(*a*) Intramolecular

Cl(1)–Sn–Cl(2)	90·15(7)	C(3)–C(4)–C(5)	120·4(7)
Cl(2)–Sn–Cl(3)	90·63(9)	C(3)–C(4)–Cl(4)	120·1(4)
Cl(1)–Sn–Cl(3)	89·27(8)	Cl(4)–C(4)–C(5)	119·6(7)
C(6)–N–C(2)	122·1(7)	C(4)–C(5)–C(6)	118·3(8)
N–C(2)–C(3)	118·7(8)	C(5)–C(6)–N	120·6(6)
C(2)–C(3)–C(4)	120·0(6)		

(*b*) Intermolecular

Cl(3) · · · H(1)–N	135·66	Cl(3) · · · H(1)–N	126·84

[a] Cl(3′) refers to a crystallographically equivalent Cl(3) atom in the adjacent $SnCl_6^{2-}$ ion which is next closest to the N–H group.

The source of the distortion of the $SnCl_6^{2-}$ ion is readily revealed as a Cl · · · H–N intermolecular hydrogen bond. The shortest Cl(3) · · · N(1) contact is 3·244 Å. If a hydrogen atom is placed on the pyridinium nitrogen at a distance of 1·080 Å, the Cl · · · H distance is 2·408 Å, which is a typical Cl · · · H–N bond.[12] As is frequently the case in amino-acid salts, this hydrogen bond seems to be dominant in the packing of the unit cell, which is otherwise a very open structure. Although the hydrogen atom could not be located crystallographically, a hydrogen position 1·08 Å from nitrogen and in the plane of the ring would be close (2·58 Å) to a second crystallographically equivalent chlorine atom in a different anion. Bifurcation of the hydrogen bond cannot be ruled out for this reason.

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[9] R. V. Parish and R. M. Platt, *J. Chem. Soc.* (*A*), **1969**, 2145.

[10] C. W. Fryer, *Chem. Comm.*, 1970, 902.

[11] D. E. Scaife, *Austral. J. Chem.*, 1971, **24**, 1753.

[12] W. Fuller, *J. Phys. Chem.*, 1959, **63**, 1705.