287. *The Crystal and Molecular Structure of Chloro(trimethyl)-pyridinetin*(IV).

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By *X*-ray diffraction methods the compound $(C_5H_5N)Me_3SnCl$ is shown to be monomeric and covalent. The trigonal bipyramidal molecules contain a five co-ordinate tin atom, the Sn–Cl distance being $2{\cdot}42 \pm 0{\cdot}04$ Å.

OBSERVATIONS and reasoning which suggest the possible occurrence of five co-ordinate tin atoms have already been summarised.[1,2] In particular, Beattie *et al.*,[3,4] arguing from spectroscopic and other observations on several organotin halides, were led to believe that the tin atom in $pyMe_3SnCl$ (py = pyridine) would be five co-ordinate. This paper describes the details of a two-dimensional *X*-ray structure analysis to ascertain the molecular geometry of this compound and the nature of the five-fold co-ordination of groups about the tin atom. Other properties of $pyMe_3SnCl$ crystals are recorded *en passant*.

EXPERIMENTAL

Preparation of the Crystals.—Although Beattie and McQuillan[4] were able to prepare the compound $pyMe_3SnCl$ from pyridine and trimethyltin chloride in the open, it was found that in small quantities on a microscope slide the crystals tended to decompose. Such decomposition could be due to hydrolysis, loss of pyridine, disproportionation, or some combination of these. The initial reaction appears to depend on humidity and is, presumably, hydrolysis although after a while a new crystalline species appears unlike the usual hydrolysis products.

Because of this, the crystals selected were somewhat larger than is usually desirable for *X*-ray work and they were handled throughout in a dry-box designed in this Department for crystallographic purposes.[5] The crystals were rapidly transferred in the dry-box to thin-walled Lindemann glass tubing which was sealed while still in the dry-box. No crystals were used for photography after more than 24 hr. had elapsed from the time of their being sealed. This condition imposes further difficulties in the way of obtaining accurate intensity data, and this is reflected in the magnitude of the final *R* factor for the structure.

X-*Ray Data.*—$C_8H_{14}NSnCl$, $M = 278{\cdot}2$, orthorhombic. $a = 12{\cdot}90 \pm 0{\cdot}05$, $b = 7{\cdot}74 \pm 0{\cdot}03$, $c = 10{\cdot}85 \pm 0{\cdot}04$ Å, as determined from Cu-K_α single-crystal oscillation and zero-layer Weissenberg photographs about the *b*- and the *c*-axis. $D_m = 1{\cdot}5 \sim 1{\cdot}8$, whence $Z = 4$, $D_c = 1{\cdot}706$. $F(000) = 544$. $\mu_{Cu} = 220$ cm.$^{-1}$.

The only systematically absent reflections are $hk0$ when h is odd and $0kl$ when $(k + l)$ is odd. The space group may be either the non-centric $Pn2_1a$ (C_{2v}^9, No. 33) or the centric $Pnma$ (D_{2h}^{16}, No. 62). The results of a statistical analysis of the $h0l$ and hkl intensity data, although not as definite as one might wish, owing to the presence of a heavy atom, suggest a centrosymmetric space group; nothing in the subsequent structure analysis has conflicted with this suggestion. The space group may thus be taken as $Pnma$ (No. 62), which has eight-fold general positions. It follows that with four molecules in the unit cell they must lie in some suitable set of special positions.

Multiple-film Cu-K_α radiation Weissenberg photographs were taken about the *b*- and the *c*-axes. As very small crystals could not be used, the intensity data suffer to some extent from absorption effects. Relative intensities were estimated visually by comparison with standard intensity strips. 38 $hk0$, 62 hkl, and 68 $h0l$ reflections were observed to be non-zero. The corresponding structure amplitudes are recorded in Table 1.

Structure Determination.—The only special position which could accommodate a molecule of $pyMe_3SnCl$ would be one in the plane of symmetry perpendicular to *b*. It seemed appropriate therefore to look at the *c*-axis projection first. The *x,y*-co-ordinates of the tin atom were determined from the $hk0$ Patterson function, from which an electron-density projection was

[1] Beattie and Gilson, *J.*, 1961, 2585.
[2] van der Kerk, Luijten, and Janssen, *Chimica*, 1962, **16**, 10.
[3] Beattie, McQuillan, and Hulme, *Chem. and Ind.*, 1961, 1429.
[4] Beattie and McQuillan, *J.*, preceding paper.
[5] Szymanski, Ph.D. Thesis, London, 1963.

TABLE 1.

Observed structure amplitudes, $|F_o|$, and calculated structure factors, F_c.

(*a*) *hk*0 data, $B = 3{\cdot}8$, $R = 19{\cdot}0\%$.

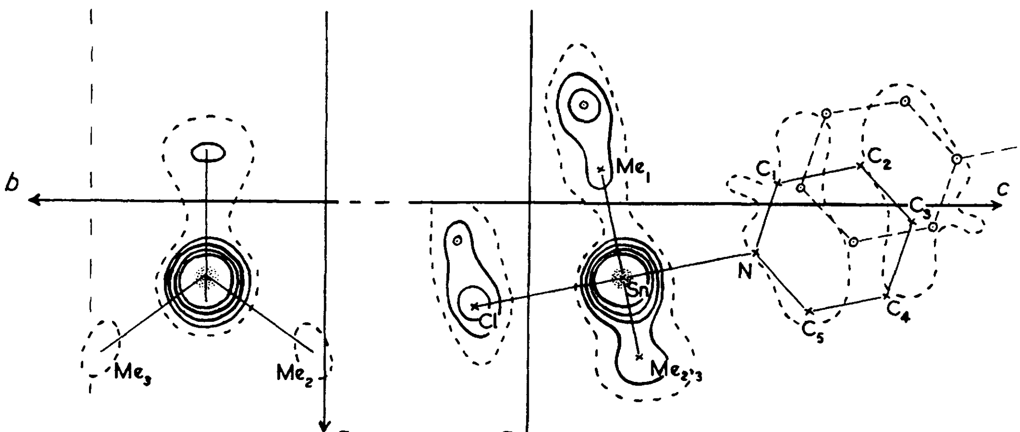
*hk*0	$\|F_o\|$	F_c	*hk*0	$\|F_o\|$	F_c	*hk*0	$\|F_o\|$	F_c	*hk*0	$\|F_o\|$	F_c	*hk*0	$\|F_o\|$	F_c	*hk*0	$\|F_o\|$	F_c
200	110	115	610	78	106	620	132	100	830	77	−71	10.40	30	30	460	44	54
4	123	−143	8	89	87	8	<20	−35	10	<20	2				6	42	42
6	100	−85	10	<20	2	10	50	−26				250	100	−114			
8	<20	9	12	30	−27	12	29	−2				4	54	−32	270	32	56
10	40	45	14	26	−15				040	205	213	6	21	50	4	29	29
12	17	−2							2	58	58	8	44	48	6	<20	−36
			020	247	−287	230	156	164	4	98	−86				8	26	−26
210	190	−245	2	138	−138	4	96	74	6	79	−56	060	86	−108	080	32	60
4	72	−74	4	139	129	6	73	−90	8	<20	10	2	30	−44			

(*b*) *hkl* data, $B = 4{\cdot}1$, $R = 18{\cdot}6\%$.

hkl	$\|F_o\|$	F_c	*hkl*	$\|F_o\|$	F_c	*hkl*	$\|F_o\|$	F_c	*hkl*	$\|F_o\|$	F_c	*hkl*	$\|F_o\|$	F_c	*hkl*	$\|F_o\|$	F_c
101	60	70	111	62	−74	221	46	65	331	80	76	541	60	−53	651	50	40
2	109	−125	2	57	−70	3	37	37	4	58	−44	6	<19	13	7	22	28
3	80	−79	3	83	−93	4	100	87	5	<16	−6	7	<20	−14	8	<21	12
4	42	−44	4	57	54	5	99	95	6	99	−70	8	48	50	9	16	15
5	72	−81	5	<14	10	6	12	−40	7	51	−50	9	<22	22			
6	<15	15	6	109	85	7	24	12	8	<20	−8	10	16	22	161	21	−25
71	16	−23	7	52	59	8	77	−66	9	25	−18				2	29	29
8	70	78	8	18	18	9	20	−32	10	26	28	051	62	−71	3	<21	17
9	14	32	9	42	26	10	16	−22				1	26	−38	4	30	30
10	27	34	10	49	−38	11	29	−21	141	47	49	2	18	−25	5	23	37
11	26	29	11	<21	−11				2	66	−66	3	38	−44	6	<22	−14
12	22	−26	12	22	−20	031	89	94	3	32	−39	4	32	26	7	<22	6
						1	48	47	4	51	−33	5	<20	5	8	16	−30
011	127	−156	121	34	−54	2	52	60									

(*c*) *h*0*l* data, $B = 5{\cdot}5$, $R = 16{\cdot}6\%$.

*h*0*l*	$\|F_o\|$	F_c	*h*0*l*	$\|F_o\|$	F_o	*h*0*l*	$\|F_o\|$	F_c	*h*0*l*	$\|F_o\|$	F_c	*h*0*l*	$\|F_o\|$	F_c	*h*0*l*	$\|F_o\|$	F_c
002	29	26	203	<8	−8	402	<10	−10	602	<13	20	803	33	42	11.02	<17	−17
4	182	−176	4	72	−52	3	31	−22	3	<14	8	4	<16	1	3	40	−33
6	21	39	5	125	130	4	61	69	4	59	60	5	36	−49	4	<17	7
8	25	25	6	<13	8	5	55	49	5	16	−30				5	<17	3
10	21	−28	7	12	−12	6	<14	−8	6	28	−32	901	14	28	6	<16	6
			8	17	24	7	<16	2	7	<16	−15	2	64	64	7	26	26
101	60	71	9	58	−48	8	<16	−6	8	19	−28	3	18	−30			
2	80	−85				9	23	−26				4	<16	−9	12.00	17	−1
3	126	−123	301	80	−78				701	16	−21	5	<17	−7	1	<17	−20
4	90	76	2	62	−89	501	72	−77	2	60	52	6	19	−20	2	<17	−13
5	20	−44	3	52	59	2	20	−28	3	40	38				3	<17	−9
6	45	42	4	60	48	3	77	72	4	17	−23	10.00	40	35	4	16	−10
7	58	41	5	12	10	4	15	−26	5	<16	2	1	27	28			
8	32	−40	6	67	62	5	30	41	6	31	−33	2	<17	−18	13.01	<16	1
9	<16	−5	7	<15	−15	6	<15	4	7	24	−24	3	<17	24	2	36	−32
			8	39	−39	7	48	−41				4	33	−31			
200	110	113							800	<14	8	5	<17	−8	14.00	<16	−9
1	109	−124	400	123	−137	600	100	−77	1	70	67				1	12	12
2	16	20	1	42	−42	1	<13	14	2	<15	22	11.01	26	23			



Projections of electron density on to (001) and (010). Contours are at equal arbitrary intervals except round the tin atom. One molecule is indicated in full line, atomic positions being indicated by × with label and number. Atomic positions of neighbouring molecules are indicated by O, neighbouring molecules being in broken line.

obtained which located two methyl groups (Me_2, Me_3) either side of the mirror planes, the remaining atoms lying in the mirror planes at $y = \frac{1}{4}$ and $y = \frac{3}{4}$.

The *h0l* Patterson function served to give the *z*-co-ordinate of tin which in turn made possible the calculation of an electron-density projection. This indicated the positions of the chlorine atom and the three methyl groups, and the approximate location of the pyridine group. After three rounds of refinement by difference synthesis the customary agreement index, *R*, was 16·6%. The corresponding *hk0* data needed only one round of refinement to make $R = 19{\cdot}0\%$. For *hkl* data *R* is 18·6%. It is not considered significant to reduce *R* much further with the present data, suffering as they do from absorption and extinction effects. The *R* factors, $\Sigma(F_o \sim F_c)/\Sigma F_o$, were calculated with the inclusion of unobserved reflections in comparable $\sin\theta$ range in the following manner. When F_c exceeded the locally observed minimum *F*, $({}_mF_o)$, a term $({}_mF_o \sim F_c)$ was included in the numerator without a corresponding addition to the denominator. When $F_c < {}_mF_o$, no terms were included in either numerator or denominator. In each case the structure factors, recorded in Table 1, were calculated by using the atomic co-ordinates recorded in Table 2 and the atomic scattering factors recorded in the International Tables, modified in

TABLE 2.

Fractional co-ordinates, with some e.s.d. in Å in parentheses (for numbering see Figure).

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn	0·0950 (0·0085)	$\frac{1}{4}$ (0)	0·1410 (0·0059)	C_1	−0·034	$\frac{1}{4}$	0·373
Cl	0·1310 (0·035)	$\frac{1}{4}$ (0)	−0·0785 (0·026)	C_2	−0·044	$\frac{1}{4}$	0·504
Me_1	−0·045	$\frac{1}{4}$	0·103	C_3	0·025	$\frac{1}{4}$	0·584
Me_2	0·191	0·025	0·166	C_4	0·120	$\frac{1}{4}$	0·544
Me_3	0·191	0·475	0·166	C_5	0·135	$\frac{1}{4}$	0·435
N	0·059	$\frac{1}{4}$	0·345				

the case of the tin atom by Hönl's correction.[6] Hydrogen atoms have been ignored, but partly to compensate for this methyl groups have been treated as equivalent to nitrogen atoms. The value of *B* chosen for use in isotropic temperature factors was 3·8, 4·1, and 5·5, for the *hk0*, *hkl*, and *h0l* reflections, respectively.

The final co-ordinates obtained from the two projections are listed in Table 2, the numbering of the atoms being indicated in the Figure. Standard deviations, calculated by Cruickshank's method,[7] are also recorded for the tin and chlorine atoms. No standard deviations are recorded for the lighter atoms and they should be regarded as only very roughly determined.

DISCUSSION

The final electron-density projections are shown in the Figure. It is apparent that the molecule is covalent and several alternative suggestions[8] for the structure of such organotin compounds seem to be excluded. The molecule contains a 5-covalent tin atom, the stereochemistry approximating to a trigonal bipyramid with three methyl groups in the equatorial plane and an almost linear Cl–Sn–N arrangement perpendicular to it. This result appears to support the interpretation of kinetic data on organotin halides in terms of a 5-covalent intermediate.[9] The Sn–Cl distance is $2{\cdot}42 \pm 0{\cdot}04$ Å, and no distance between non-bonded atoms is less than 3·5 Å. The Sn–Cl distance lies within the range of published values[10] for octahedral Sn–Cl (2·39–2·45 Å) but is 0·05 Å greater than the tetrahedral Sn–Cl distance of 2·37 Å in Me_3SnCl itself.[11] This increase, being about equal to the e.s.d. of the two bonds, has little significance. However, similar but larger differences

[6] Bragg, "The Crystalline State," Bell, London, 1948, Vol. II, Appendix III.
[7] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.
[8] Kraus and Greer, *J. Amer. Chem. Soc.*, 1923, **45**, 2946; Kocheshkov, *Uchenuie Zapiski* (*Wiss. Ber. Moscow Staats Univ.*), 1934, **3**, 297 (*Chem. Abs.*, 1936, **30**, 8184); Thomas and Rochow, *J. Inorg. Nuclear Chem.*, 1957, **4**, 205; Seyferth and Grim, *J. Amer. Chem. Soc.*, 1961, **83**, 1610.
[9] Prince, *J.*, 1959, 1783 and refs. therein.
[10] Engel, *Z. Krist.*, 1935, **90**, 341.
[11] Skinner and Sutton, *Trans. Faraday Soc.*, 1944, **40**, 164.

in the same sense are observed between the electronically equivalent structures[12,13] $SbCl_3$ and Me_3SbCl_2 (2·36 ⟶ 2·49 Å) as well as[14,15] ICl and pyICl (2·32 ⟶ 2·51 Å). A smaller difference still in the same sense is obtained by comparing ICl and[16] ICl_2^- (2·32 ⟶ 2·36 Å). The difference may thus have some meaning in terms of the orbitals employed.[17] The smaller force constant reported[3] for the Sn–Cl bond also points to some change in the nature of the bonding.

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