

A Redetermination of the Crystal Structure of Tetramethylammonium Hexachlorostannate(IV) at 160 K and at 295 K in the $Fd\bar{3}c$ Space Group

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Due to the existence of "forbidden" reflections it has recently been shown^{1,2} that the crystal structures of some tetramethylammonium hexahalometallate(IV) salts, $((\text{CH}_3)_4\text{N})_2\text{MX}_6$, where MX_6 is PtCl_6 or TeBr_6 , are better described in the cubic space group $Fd\bar{3}c$ (O_h^8) rather than in the $Fm\bar{3}m$ (O_h^h) space group. The crystal structure of $((\text{CH}_3)_4\text{N})_2\text{SnCl}_6$ has been solved in space group $Fm\bar{3}m$.³⁻⁵ The authors³ suggested that the high thermal parameters for C and Cl could be due to "some disorder in the crystal, particularly in the position of the $[(\text{CH}_3)_4\text{N}]^+$ ions". In view of our previous results,^{1,2} together with the observed birefringence,⁶ forbidden X-ray reflections ascribed as due to crystal imperfections⁴ and spectroscopic indications of a non- $Fm\bar{3}m$ symmetry,^{7,8} a redetermination of the crystal structure of $((\text{CH}_3)_4\text{N})_2\text{SnCl}_6$ has been carried out at 160 K and at 295 K.

Experimental. Weissenberg photographs proved the existence of $Fm\bar{3}m$ -forbidden reflections, and the space group was found to be consistent with $Fd\bar{3}c$

Table 1. Crystal data of $((\text{CH}_3)_4\text{N})_2\text{SnCl}_6$ at 295 K and 160 K. $M=479.70$. Cubic, $Fd\bar{3}c$ (O_h^8 , No. 228). $Z=32$. $D_o=1.508$ (290 K),⁹ 1.507,⁴ 1.468⁶ g/cm³.

Temperature (K)	295	160
$a(\text{\AA})$	25.699(3)	25.550(10)
$V(\text{\AA}^3)$	16972.6	16679.1
No. of observed reflections, $I > 2\sigma(I)$	194	280
$D_c(\text{g/cm}^3)$	1.502	1.528
$\mu(\text{MoK}\alpha)$ (cm ⁻¹)	19.4	19.8
$R = \Sigma \ F_o - F_c \ / \Sigma F_o $	0.044	0.041
$R_w = (\Sigma w(F_o - F_c)^2 / \Sigma w F_o ^2)^{1/2}$	0.052	0.057

(No. 228). The method of data collection and the refinement technique were similar to those of Ref. 2. However, no correction for absorption was applied, and only unique sets of intensities were measured. Crystal data and some experimental details are given in Table 1, atomic coordinates and thermal parameters are listed in Table 2. A list of observed and calculated structure factors may be obtained from the authors on request.

Results and discussion. Bond lengths and bond angles are given in Table 3, and are close to commonly accepted values. The difference between the C1-N1 and C2-N2 distances is insignificant. The deformations of the present compound from $Fm\bar{3}m$ symmetry resemble those observed for $[(\text{CH}_3)_4\text{N}]_2\text{TeBr}_6$.² The angles between the Sn-Cl bonds and the cubic translation axes are 8.5 (295 K) and 9.2° (160 K). The rotations of the SnCl_6^{2-} ions

Table 2. Positional and thermal parameters (U_{ij} in units of 10^{-4}\AA^2) with standard deviations in parentheses. The temperature factor expression is of the form $\exp[-2\pi^2 \Sigma h_i h_j a_i^* a_j^* U_{ij}]$ or $\exp[-8\pi^2(\sin^2 \theta / \lambda^2) U]$. The first and second line refer to results at 295 and 160 K, respectively.

Atom	Site symmetry	x/a	y/b	z/c	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	$\bar{3}$	0.0	0.0	0.0	495(7)	495	495	1(15)	1	1
		0.0	0.0	0.0	330(5)	330	330	8(5)	8	8
Cl	1	0.0933(1)	0.0100(3)	-0.0098(3)	522(17)	759(51)	792(55)	-61(18)	18(18)	77(16)
		0.0937(1)	0.0106(1)	-0.0108(1)	340(12)	546(20)	601(21)	-32(10)	21(10)	90(9)
N1	23	0.125	0.125	0.125	944(312)					
		0.125	0.125	0.125	576(120)					
N2	$\bar{4}$	0.375	0.125	0.125	467(51)					
		0.375	0.125	0.125	303(30)					
C1	3	0.159(1)	0.159	0.159	1158(168)					
		0.159(1)	0.159	0.159	1351(135)					
C2	1	0.110(1)	0.171(1)	0.407(1)	725(44)					
		0.1090(4)	0.1713(4)	0.4079(4)	455(26)					

Table 3. Interatomic distances (Å) and angles (°) of the $((\text{CH}_3)_4\text{N})_2\text{SnCl}_6$ structure.

	295 K	160 K
Sn—Cl	2.424(3)	2.425(3)
Sn—C1	> 5.1	> 5.1
Sn—C2	4.75(2)	4.75(1)
Cl—Cl	3.415(8), 3.442(8)	3.405(4), 3.453(4)
Cl—C2	3.70(2), 3.90(2), 3.91(2)	3.68(1), 3.82(1), 3.88(1)
	4.00(2), 4.06(2), 4.19(2)	3.94(1), 4.04(1), 4.16(1)
Cl—N1	4.625(7)	4.605(3)
Cl—N2	4.262(7), 4.635(7), 4.970(7)	4.207(3), 4.601(3), 4.968(3)
C1—N1	1.53(2)	1.51(2)
C2—N2	1.49(2)	1.51(1)
C1—C1	2.49(3)	2.46(3)
C1—C2	4.77(1)	4.71(1)
C2—C2	2.40(2), 2.50(2), 4.09(2)	2.44(1), 2.50(1), 4.07(2)
Cl—Sn—Cl	89.5(2), 90.5(2)	89.2(1), 90.8(1)
C1—N1—C1	109.5(7)	109.5(6)
C2—N2—C2	107.2(9), 114.2(8)	108.1(5), 112.2(5)

Table 4. *R*-values between different sets of symmetry related reflections (cubic symmetry). $R = (\sum w_{ij}(F_{ij}^2 - \langle F_i^2 \rangle)^2 / \sum w_{ij} F_{ij}^4)^{1/2}$, where $w_{ij} = \sigma_{ij}^{-2}$ and $\langle F_i^2 \rangle = \sum w_{ij} F_{ij}^2 / \sum w_{ij}$. In the summations *j* and *i* run over related and independent reflections, respectively.

Set	No. of reflections	<i>R</i> -value
All	42	0.150
Same <i>h</i>	32	0.109
Same <i>k</i>	32	0.150
Same <i>l</i>	32	0.067

around {111}-type vectors amount to 10.4 (295 K) and 11.2° (160 K). The structural differences between the *Fm3m* and the *Fd3c* space groups (which have a subgroup-supergroup relationship) are described and depicted in Refs. 1 and 2.

A comparison of the results at 295 K and at 160 K (above the phase transition occurring at 149 ± 7 K)⁷ shows that the thermal motions of all atoms, except C1, decrease at lower temperatures, whereas the changes in the interatomic distances and angles are small. In the crystal structure of $((\text{CH}_3)_4\text{N})_2\text{TeBr}_6$ short (3.69 Å) and long (3.82 Å) distances were found from Br to C2 and C1, respectively.² This difference between C1 and C2 is less pronounced in the present structure (Table 3). The larger value of the thermal parameter for C1 [$U(160 \text{ K}) = 0.135 \text{ \AA}^2$, $U(295 \text{ K}) = 0.116 \text{ \AA}^2$], whether apparent or real, is in agreement with what was found in the room temperature structure of $((\text{CH}_3)_4\text{N})_2\text{TeBr}_6$ ($U(\text{C1}) = 0.182 \text{ \AA}^2$).

In an attempt to obtain indications of the mechanism of the phase transition the crystal was cooled to 115 K, and a data set with $\theta < 10^\circ$ and positive indices *h*, *k* and *l* was collected. The unit

cell dimensions obtained from optimum diffractometer settings were $a = 25.39(3) \text{ \AA}$, $b = 25.35(4) \text{ \AA}$, $c = 25.51(5) \text{ \AA}$, $\alpha = 90.1(1)^\circ$, $\beta = 90.0(1)^\circ$ and $\gamma = 90.1(1)^\circ$. The width of the reflections range from 1.2 to 2.0°. Of the 304 reflections measured, only those with *h*, *k* and *l* equal to $4n$ or $4n + 2$ had $I > 2\sigma(I)$. Thus, the reflections allowed in the *Fd3c* space group but forbidden in the *Fm3m* space group are not significantly different from zero, indicating that the periodic translations in the three directions are halved. The differences in the cell dimensions at 115 K are accompanied by changes in the intensities. Table 4 shows the *R*-values obtained between different sets of symmetry related reflections (cubic symmetry). Of these, the *R*-value of symmetry related reflections of same *l* is much lower than the others, indicating that the symmetry below the transition temperature is not higher than tetragonal.

1. Berg, R. W. and Sætøfte, I. *Acta Chem. Scand. A* 32 (1978) 241.
2. Berg, R. W. and Nielsen, K. *Acta Chem. Scand. A* 33 (1979) 157.
3. Brill, T. B., Gearhart, R. C. and Welsh, W. A. *J. Magn. Reson.* 13 (1974) 27.
4. Wyckoff, R. W. G. and Corey, R. B. *Am. J. Sci.* 18 (1929) 437.
5. Brill, T. B. and Welsh, W. A. *J. Chem. Soc. Dalton Trans.* (1973) 357.
6. Staritzky, E. and Singer, J. *Acta Crystallogr.* 5 (1952) 536.
7. Ohe, W. von der *J. Chem. Phys.* 62 (1975) 3933; 63 (1975) 2949; *Ph.D. Diss.*, U.C.L.A., Los Angeles 1974.
8. Berg, R. W. *J. Chem. Phys.* 69 (1978) 1325.
9. Ries, A. Z. *Kristallogr.* 49 (1911) 513.

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