# The Crystal Structures of Methylammonium Hexachlorostannate(IV) in the High- and Low-temperature Phases Studied by X-Rays

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(Received June 28, 1978)

The title compound crystallizes in the trigonal space group R$\bar{3}$m with $a=7.171$, $c=21.952$ Å, and $Z=3$ at 298 K. The crystal structures at 298 and 120 K, as well as the lattice parameters in the temperature range 113—298 K, have been determined by X-rays, in order to elucidate the mechanism of the phase transition occurring at $T_t=156$ K. The structure of the high-temperature phase is essentially the same as that determined by Wyckoff, except for the discrimination between C and N atoms. No change in the space group nor in the basic structure was detected over the temperature range studied, in spite of a strong suggestion from previous $^{35}$Cl-NQR measurements. A small but significant anomaly associated with the transition is recognized in the c axis, which retains almost the same length near and below $T_t$. As a result, the lattice shrinkage below $T_t$ becomes increasingly anisotropic as the temperature is lowered, whereas the thermal expansion above it is relatively isotropic.

In a series of hexahalo complexes of quadrivalent metal ions, $A_2MX_6$, the compounds of methylammonium cations, $A=CH_3NH_3^+$, are of much interest, because dumbell-like cations and octahedral anions co-exist in their structures. According to Wyckoff, a crystal of methylammonium hexachlorostannate(IV) has an anti-fluorite type structure which is deformed by elongation of the cubic unit-cell parallel to [111].[1] A phase transition in this compound was found at 156 K from an anomaly in the frequency of chlorine-35 NQR (nuclear quadrupole resonance) measured by Kume *et al.*[2] In our laboratory, molecular motions of both cation and anion have been studied by means of magnetic resonance of $^1$H and $^{35}$Cl nuclei. The results of PMR (proton magnetic resonance) revealed that the total cations are rapidly reorienting about their three-fold axes even at very low temperatures.[3] It was also suggested that the motion of cations makes a minor contribution to the occurrence of the phase transition. On the other hand, the $^{35}$Cl-NQR spin-lattice relaxation time, $T_1$, showed a distinct reduction in the vicinity of the phase transition temperature, $T_t$.[4] This anomalous behavior of $^{35}$Cl-$T_1$ has been explained in terms of the softening of some rotary lattice mode of anion octahedra, $[SnCl_6]^{2-}$, in analogy with $K_2PtBr_6$.[5]

The present X-ray study was undertaken to make clear the change in crystal structure and/or in lattice constants on passing through the phase transition and to check the transition mechanism suggested from the NQR results. Discrimination between C and N atoms of the cation will be accomplished as well.

## Experimental

Polycrystalline $(CH_3NH_3)_2SnCl_6$ was prepared by the same method as in the previous paper.[3] Single crystals were obtained as hexagonal plates by the slow cooling of a 6 mol/dm$^3$ HCl solution.

All single crystals used were sealed in glass capillary tubes to protect them from moisture. Cooling was achieved by blowing a stream of cold nitrogen gas over a crystal. The temperature of a sample was stabilized within $\pm 0.5$ K during measurements of the lattice constants and within $\pm 1.0$ K during exposure of X-ray photographs and also throughout the intensity data collection at 120 K.

A single crystal with dimensions $0.3\times0.3\times0.15$ mm was used throughout the measurements described below. The crystal was mounted on a Rigaku four-circle diffractometer with the a-axis along the $\phi$-axis of the goniostat. Intensity data at 120 and 298 K and the lattice parameters from 113 to 298 K were measured with graphite monochromatized Mo $K\alpha$ radiation. Diffraction peaks were centered automatically in the measurement of the cell constants. The lattice parameters at a given temperature were refined by a least-squares method based on the setting angles ($2\theta$, $\omega$, $\chi$, and $\phi$) of nine reflections. The results are summarized in Table 1.

Table 1. Lattice parameters for $(CH_3NH_3)_2SnCl_6$ at various temperatures

| $T$/K | $a$/Å | $c$/Å | $V$/Å$^3$ |
|---|---|---|---|
| 298 | 7.171 | 21.952 | 977.6 |
| 293 | 7.169 | 21.944 | 976.7 |
| 233 | 7.137 | 21.859 | 964.3 |
| 213 | 7.130 | 21.828 | 961.0 |
| 193 | 7.119 | 21.810 | 957.2 |
| 173 | 7.108 | 21.790 | 953.4 |
| 153 | 7.098 | 21.790 | 950.7 |
| 133 | 7.090 | 21.791 | 948.6 |
| 120 | 7.082 | 21.790 | 946.5 |
| 113 | 7.077 | 21.789 | 945.1 |

e.s.d.'s for $a$ and $c$ are less than 0.004 and 0.009 Å, respectively. Space group : R$\bar{3}$m (throughout the temperature range). $Z=3$, $F.W.=395.54$ g mol$^{-1}$, $F(000)=570$ e cell$^{-1}$, $\rho_{obsd}=1.989$ g cm$^{-3}$ (at 293 K), $\rho_{calcd}=2.018$ g cm$^{-3}$ (at 293 K).

The intensity data at the two temperatures were collected in a $2\theta$ range of 0—60° by using the $2\theta$-$\omega$ scan technique. Of 402 independent reflections at 298 K and of 392 ones at 120 K, 383 reflections at 298 K and 364 ones at 120 K were observable ($F_o>3\sigma_{CS}$); these were used in the present analysis and refinement. No correction was made for absorption ($\mu$ for Mo $K\alpha=31.3$ cm$^{-1}$).

## Structure Determination and Refinement

Weissenberg and precession photographs of zero- and upper-layers showed that the space group is either R32, R3m, or R$\bar{3}$m at both 120 and 298 K, and that no change in crystal symmetry occurs on passing through the phase transition. By judging from the solutions of the structure, the space group was determined to be R$\bar{3}$m

for both phases.

The positional parameters of the Cl atom reported by Wyckoff,[1] together with the isotropic thermal parameters of the Sn and Cl atoms, were refined by least-squares methods with the intensity data collected at 298 K. Using the intensity data phased with these coordinates, three-dimensional electron density maps were calculated. The position of the C atom was clearly distinguished from that of the N atom; the peaks assigned to C and N atoms were as high as 8.0 and 11.0 e/Å$^3$, respectively. Successive difference Fourier syntheses did not yield any hydrogen position. The block-diagonal least-squares refinement with anisotropic thermal parameters was continued until the maximum shift of any parameter was less than one-fifth of its associated e.s.d. The structure in the low-temperature phase was determined at 120 K by almost the same procedure as described above.

The atomic scattering factors for $Sn^{4+}$, $Cl^-$, C, and N and the anomalous dispersion corrections $f'$ and $f''$ for Sn and Cl were taken from the International Tables for X-Ray Crystallography, Vol. IV.[6] The quantity minimized in the refinement was $\sum w(|F_o|-k|F_c|)^2$ with unit weight for all reflections. The final residual values, $R[=\sum||F_o|-|F_c||/\sum|F_o|]$, of 0.052 and 0.062 were obtained at 298 and 120 K, respectively. The final positional and thermal parameters of non-hydrogen atoms at the two temperatures are presented in Table 2. The coordinates for all H atoms were calculated by assuming their existence on the crystallographic mirror planes, the staggered conformation of the $CH_3NH_3^+$ ions, and the bond lengths and angles: N–H=1.03 Å, C–H=1.09 Å, C–N–H=109.47°, and N–C–H=109.47°. Thus the assumed positions are also included in Table 2. The main interatomic distances and angles are given in Table 3. A list of the observed and calculated structure factors at 120 and 298 K has been deposited with the Chemical Society of Japan (Document No. 7904).

All computations were made on a NEAC 2200/700 at the computer center, Osaka University, using local modifications of RSSFR-5, HBLS-IV, and RSDA-4 in the UNICS program system,[7] and the stereoscopic drawing program ORTEP.[8]

Table 2. Positional ($x_j$) and thermal parameters ($B_{ij}$/Å$^2$) for $(CH_3NH_3)_2SnCl_6$ in hexagonal coordinate system

Estimated standard deviations are given in parentheses. The anisotropic thermal factors are of the form: $T=\exp[-1/4(h^2a^{*2}B_{11}+\ldots+2klb^*c^*B_{23})]$.

| Atom | Wyckoff notation | | 120 K | 298 K |
|---|---|---|---|---|
| Sn | 3 a | $x=y=z=0$ | | |
| | | $B_{11}(=B_{22}=2B_{12})$ | 0.32(4) | 1.98(5) |
| | | $B_{33}$ | 1.20(5) | 4.17(7) |
| | | $B_{13}=B_{23}=0$ | | |
| Cl | 18 h | $x(=-y)$ | 0.1617(4) | 0.1599(4) |
| | | $z$ | 0.0632(1) | 0.0628(1) |
| | | $B_{11}(=B_{22})$ | 2.29(16) | 3.52(17) |
| | | $B_{33}$ | 1.40(7) | 4.59(11) |
| | | $B_{12}$ | 1.90(9) | 2.37(10) |
| | | $B_{13}(=-B_{23})$ | −0.07(6) | −0.32(9) |
| N | 6 c | $x=y=0$ | | |
| | | $z$ | 0.2738(8) | 0.2729(9) |
| | | $B_{11}(=B_{22}=2B_{12})$ | 5.14(71) | 7.74(84) |
| | | $B_{33}$ | 5.21(69) | 8.56(92) |
| | | $B_{13}=B_{23}=0$ | | |
| C | 6 c | $x=y=0$ | | |
| | | $z$ | 0.2039(9) | 0.2051(11) |
| | | $B_{11}(=B_{22}=2B_{12})$ | 4.51(121) | 5.69(126) |
| | | $B_{33}$ | 0.95(61) | 4.10(102) |
| | | $B_{13}=B_{23}=0$ | | |
| H(N)[a] | 18 h | $x(=-y)$ | −0.0792 | −0.0782 |
| | | $z$ | 0.2895 | 0.2885 |
| H(C)[a] | 18 h | $x(=-y)$ | 0.0838 | 0.0827 |
| | | $z$ | 0.1872 | 0.1886 |

a) This position is assumed. See text.

Table 3. Interatomic distances ($l$/Å) and angles ($\theta$/°)

| | | 120 K | 298 K |
|---|---|---|---|
| (a) $[SnCl_6]^{2-}$ octahedron | | | |
| Sn–Cl | *6 times* | 2.415(2) | 2.417(3) |
| Cl–Sn–Cl$^{i}$ | *6 times* | 90.71(6) | 90.72(7) |
| Cl–Sn–Cl$^{ii}$ | *6 times* | 89.29(6) | 89.28(7) |
| Cl–Cl$^{i}$ | *6 times* | 3.436(2) | 3.439(3) |
| Cl–Cl$^{iii}$ | *6 times* | 3.394(3) | 3.396(2) |
| (b) $CH_3$–$NH_3^+$ ion | | | |
| C–N | | 1.522(25) | 1.487(30) |
| (c) Between ions | | | |
| Cl···Cl$^{iv}$ | *twice* | 3.646(16) | 3.732(19) |
| C···Cl | *3 times* | 3.652(16) | 3.703(20) |
| C···Cl$^{vi}$ | *6 times* | 3.824(7) | 3.863(9) |
| N···Cl$^{v}$ | *3 times* | 3.404(13) | 3.458(14) |
| N···Cl$^{vi}$ | *6 times* | 3.542(2) | 3.587(2) |
| N–C···Cl | *3 times* | 147.09(17) | 147.57(20) |
| C–H(C)···Cl | *3 times* | 129.0 | 128.6 |
| N–C···Cl$^{vi}$ | *6 times* | 67.82(27) | 68.17(33) |
| C–H(C)···Cl$^{vi}$ | *6 times* | 113.3 | 113.6 |
| C–N···Cl$^{v}$ | *3 times* | 141.80(17) | 141.46(19) |
| N–H(N)$^{vii}$···Cl$^{v}$ | *3 times* | 135.4 | 136.1 |
| C–N···Cl$^{vi}$ | *6 times* | 88.73(27) | 89.19(29) |
| N–H(N)$^{vii}$···Cl$^{vi}$ | *6 times* | 132.4 | 133.3 |
| Symmetry code | | | |
| none | $x$, | $-x$, | $z$, |
| i | $x$, | $2x$, | $z$, |
| ii | $-x$, | $-2x$, | $-z$, |
| iii | $2x$, | $x$, | $-z$, |
| iv | $x$, | $-1+2x$, | $z$, |
| v | $2/3-2x$, | $1/3-x$, | $1/3+z$, |
| vi | $2/3-x$, | $1/3+x$, | $1/3-z$, |
| vii | $-2x$, | $-x$, | $z$, |

## Results and Discussion

*Crystal Structure.* The structure described by Wyckoff[1] was confirmed to be essentially correct. The present study showed that there is no change in the basic structure in moving between the high- and low-temperature phases. This finding is an important piece of structural information about the phase transition which will be discussed later.

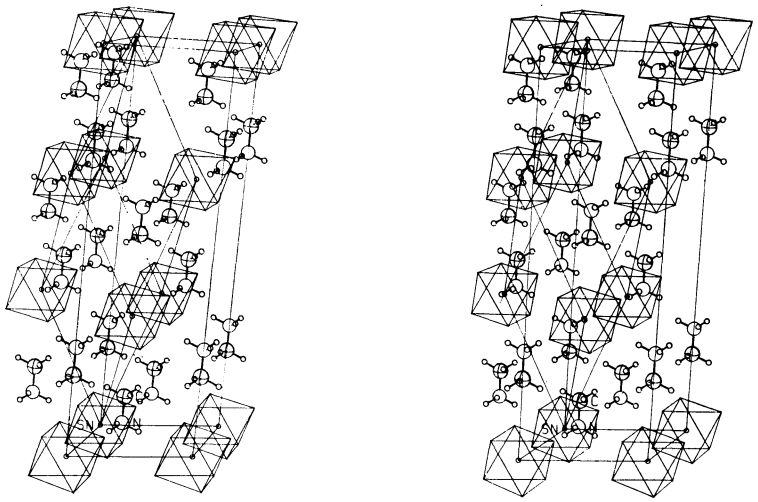

Fig. 1. Stereoscopic drawings of the crystal structure of $(CH_3NH_3)_2SnCl_6$.

The crystal consists of dumbell-like $CH_3NH_3^+$ ions and octahedral $[SnCl_6]^{2-}$ ions. These ions are arranged, in principle, in an antifluorite-type structure like $K_2PtCl_6$, but the real unit cell is deformed rhombohedrally by elongation along one body-diagonal of the cube. The C–N axes of cations are parallel to the hexagonal c-axis thus obtained. The packing of both ions and the relation between the unit cell in the hexagonal coordinate system ($Z=3$) and that in the rhombohedral coordinate system ($Z=1$) are illustrated in Fig. 1. It is clear that each ion species forms separate layers parallel to the hexagonal basal plane. The octahedron layer seems to be stabilized by electrostatic interaction between the negatively charged octahedra and the positively charged $NH_3^+$ groups of cations. Then the layers of octahedra are held together by van der Waals interactions between $CH_3$ residues and Cl atoms. Because the locations of the Cl atoms do not deviate largely from a close-packing of Cl atoms, the stacking sequence of chlorine sheets can be regarded as ABCABC along the hexagonal c-axis.

In the crystal lattice, each cation is tetrahedrally surrounded by four complex anions, while each anion has eight cation neighbors. The $CH_3$ group of a cation faces the triangle of Cl atoms coming from the same octahedron. The equivalent three C···Cl distances (3.70 Å) are shorter than the van der Waals distance (2.0+1.8=3.8 Å), and much shorter than the corresponding value (3.90 Å) found in $CH_3NH_3Cl$.[9] However, a reasonable assumption of tetrahedral angles around a methyl carbon atom leads us to speculate that the C–H bond should deviate greatly from the C···Cl direction; the C–H···Cl angle is estimated to be 129° from the coordinates given in Table 2. Therefore, the methyl group of a cation only has contact with three Cl atoms, and can scarcely form C–H···Cl type hydrogen bonds.

The other end of the cation, *i.e.* the $NH_3$ group, has nine Cl neighbors, three from each of the three $[SnCl_6]^{2-}$ ions. The nine N···Cl distances (three 3.46 and six 3.59 Å) are rather long compared with those in such chloride compounds as: $CH_3NH_3Cl$ (N···Cl=3.18 Å),[9] $NH_4Cl$ (3.35 Å),[10] $NH_4HgCl_3\cdot H_2O$ (3.31—3.41 Å),[11] $C_4N_2O_3H_9Cl\cdot H_2O$ (3.18—3.30 Å),[12] and $C_5H_{10}O_4N\cdot Cl$ (3.16—3.21 Å).[13] On the other hand, the N···Cl distances in the present $(CH_3NH_3)_2SnCl_6$ are comparable to the 3.55 Å reported for $(NH_4)_2SnCl_6$.[14] As evidenced by the Sn–Cl distance of 2.417 Å at 298 K, as well as the $^{35}$Cl-NQR frequency of 15.815 MHz at 300 K,[2] the Sn–Cl bond nature is far less ionic and, consequently the effective charge on the $Cl^-$ ion may be appreciably reduced. Furthermore, each hydrogen atom of an $NH_3$ group is probably pointed toward nearly the center of a triangle of Cl atoms, forming a trifurcated hydrogen-bond. However the average H···Cl distance (2.75 Å) is too large, and also the average N–H···Cl angle (134°) is too small, for a significant hydrogen-bond interaction. Such an arrangement of the H atoms or a very weak hydrogen-bonding scheme is supported by the PMR results described previously.[3] Thus, the $CH_3NH_3^+$ ion can exhibit the reorientation about its three-fold axis as a whole, instead of the individual or uncorrelated motions of $CH_3$ and $NH_3$ groups with different activation energies which are recognized in typical $CH_3NH_3Cl$ and other related compounds.[15,16]

The C–N distances were determined to be 1.49 and 1.52 Å at 298 and 120 K, respectively. Each value, especially the room temperature one, is quite usual for normal single-bond lengths between carbon and quaternary nitrogen atoms, in comparison with those in $(CH_3NH_3)_2MnCl_4$,[17] $(CH_3NH_3)_2ZnCl_4$,[18] and $CH_3NH_3Cl$.[9] It may be noted that the C–N distance in the high-temperature phase is a little shorter than in the low-temperature one. Such a tendency has been established in chloride perovskite-layer-compounds and interpreted in terms of a change in motion of methylammonium ions.[17,19] But a tilting motion of the C–N bond relative to the c-axis expected above $T_t$ cannot be confirmed by the present study, because the difference in C–N distance is only twice the associated e.s.d. (Table 3).

*Thermal Expansion.* The lattice constants and the unit-cell volumes are plotted against temperature in Fig. 2, where the ordinate scales are normalized to the

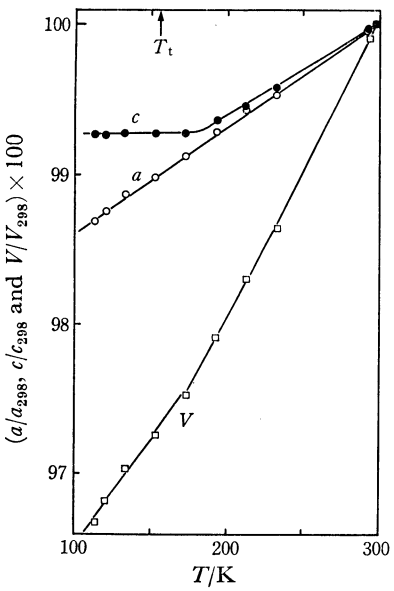


Fig. 2. Variation of $a/a_{298}$, $c/c_{298}$ and $V/V_{298}$ with temperature, where $a_{298}$ *etc.* stand for the lattice constants at 298 K.

respective values at 298 K. The a-axis length increases steadily with a thermal expansion coefficent $(1/a)da/dT$ of $0.7\times10^{-5}$ over the whole temperature range. On the other hand, the c-axis remains at almost the same length between 120 and 180 K (across $T_t$), above which it starts to increase with a linear coefficient $(1/c)dc/dT$ of $0.6\times10^{-5}$. Although this anomaly should be reflected in the volume change, its effect may be largely masked by the more effective expansion of the a-axis. Consequently the unit-cell volume appears to change continuously near $T_t$, indicating that the phase transition is approximately of a higher order. It is therefore concluded that the detectable change in structure on the phase transition is only the anomaly of the c-axis length. This finding may help us to understand the mechanism of the phase transition.

Very recently, we have found a similar structural phase transition in the trigonal phase of the tellurium-(IV) complex, $(CH_3NH_3)_2TeCl_6$, which is isomorphous with the tin(IV) complex.[20]

*Phase Transition.* The present X-ray work showed that the basic structures are identical above and below $T_t$. Among the three space groups allowed for a diffraction symmetry of $\bar{3}$m, only R$\bar{3}$m was preferred for both phases. The $^{35}$Cl-NQR results, however, suggested the softening of some rotary phonon of the anion octahedra as a mechanism of the phase transition.[2,4] If this is the case, the appearance of a superstructure and/or a small deviation from the space group R$\bar{3}$m would be expected in the low-temperature phase. The first possibility was easily excluded because no extra spot nor superstructure spot was detected on the X-ray photographs in spite of long exposure. On the other hand, the second possibility is likely to happen if the rotary mode of $[SnCl_6]^{2-}$ octahedra about the c-axis, *i.e.* their three-fold axes, softens at the $\Gamma$ point of the Brillouin zone.

Hence, this possibility was checked by permitting the lowering of the diffraction symmetry. It is evident that all the Cl atoms are equivalent even below $T_t$, because a single $^{35}$Cl-NQR line is observable in the low-temperature phase.[2] Accordingly, the diffraction symmetry should be $\bar{3}$ and then the space group is limited to R$\bar{3}$. Actually the refinement of the low-temperature structure in R$\bar{3}$ yielded a rather poor $R$-value of 0.066. In this trial, however, the Cl atom is displaced only by 0.004 Å, which corresponds to a 0.13° rotation of the $[SnCl_6]^{2-}$ octahedra about the c-axis. Such a very small displacement is of no significance, since it is less than twice of its associated e.s.d. Additionally, taking into account the thermal ellipsoid of the Cl atom, which was rather spherical in the low-temperature phase, we cannot pick out the rotation of $[SnCl_6]^{2-}$ octahedra, at least positively.

In this connection, there arose a new question of whether or not the single crystal might be twinned when it was cooled down below $T_t$. The shift of the Cl position to either side of the mirror plane in R$\bar{3}$m will produce the identical structure, regardless of its orientation. If such twinning occurs, both individual crystals must be related to each other by a 180° rotation about the [210] direction, followed by a 180° rotation about the c-axis. The diffraction intensity in this case can be expressed by $xF^2(hkl)+yF^2(\bar{k}\bar{h}l)$ instead of the usual $F^2(hkl)$, where $x$ and $y$ stand for the volume fractions of both individuals. Therefore, when the twin effect is neglected, the refinement of the low-temperature structure may lead us to unreasonable positional parameters or incredible thermal parameters, especially for the Cl atom. However, as described previously, the results refined in R$\bar{3}$m (Table 2) as well as the electron density maps are good enough to exclude the occurrence of any twinning.

In conclusion, the X-ray study cannot provide any evidence to support the transition mechanism which has been ascribed to a softening of some rotary lattice mode of the anion octahedra. It is therefore conceivable that the rotation angle of the $[SnCl_6]^{2-}$ ion expected for the low-temperature phase is too small to be detected by the present X-ray experiments. On the other hand, an alternative mechanism was proposed from the structural anomaly in the c-spacing. That is, the phase transition in this compound may be primarily triggered by softening of some acoustic mode at the zone center, because it is accompanied by the bulk deformation but not by any change in the structure.

The authors wish to express their thanks to Professor Emeritus Ryôiti Kiriyama for his continuous encouragement and fruitful discussion. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education (No. 154141).

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