

CRYSTAL STRUCTURES

R. W. G. WYCKOFF

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Volume IV



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CHAPTER XIII

THE STRUCTURES OF ALIPHATIC COMPOUNDS

INTRODUCTION

Though the number of structures of organic crystals that have been determined has increased rapidly in recent years, they are not yet so numerous that they must be classified according to the systems used in organic chemistry. From the standpoint of crystal analysis the best classification is one that keeps together atomic arrangements that are closely related to one another and in the following discussion an attempt has been made to fulfill this requirement. Accordingly, organic structures will be described in three chapters, one (XIII) dealing with aliphatic chain compounds, the next with aromatic compounds (XIV) and the last with other cyclic compounds (XV).

The classification within these chapters must itself be somewhat arbitrary and open to criticism. For the present chapter, however, it has been most convenient to make use of the following sub-groups:

- A. Alkyl Ammonium and related Compounds
- B. Metallo-alkyl Compounds
- C. Aliphatic Hydrocarbons and their simple Derivatives
- D. Salts of Aliphatic Acids
- E. More Complicated Aliphatic Compounds

A. ALKYL AMMONIUM AND RELATED COMPOUNDS

Practically all the substances of this type (Table XIII A,1) that have been examined with x-rays are either halides or chlorostannates. It is consequently convenient to discuss them under these two headings and in relation to the simpler ammonium salts discussed in preceding chapters which they often resemble.

ALKYL AMMONIUM HALIDES

(XIII, a1). Though *mono methyl ammonium chloride*, $\text{NH}_3\text{CH}_3\text{Cl}$, has a structure different from that of the bromide and iodide, they are all tetragonal. The chloride was originally described in terms of a simple unimolecular cell of the dimensions: $a_0 = 4.28 \text{ \AA}$, $c_0 = 5.13 \text{ \AA}$. A recent reexamination has, however, pointed to a larger bimolecular unit of the dimensions: $a_0 = 6.04 \text{ \AA}$, $c_0 = 5.05 \text{ \AA}$. The originally chosen structure was a CsCl arrangement with a chlorine atom at the origin and the carbon and nitrogen atoms of the (CH_3NH_3) ion in $\frac{1}{2}, \frac{1}{2}, u$ where $u(\text{C})$ was probably at ca. 0.50 and $u(\text{N})$ at ca. 0.24. The new structure found for this compound differs from the foregoing mainly in that whereas in the unimolecular structure all (CH_3NH_3) groups were pointed the same way along the c_0 axis, in the new structure half of them are pointed upwards, the other half downwards. In this structure, which formally is the same as that of PbO (III, e1) and PH_4I (III, b3), atoms are distributed according to the following special positions of D_{4h}^7 (P4/nmm):

Cl: (a) $000; \frac{1}{2}, \frac{1}{2}, 0$

N: (c) $0, \frac{1}{2}, u; \frac{1}{2}, 0, \bar{u}$, with $u = 0.198$

C: (c), with $u' = 0.488$.

In this grouping (Figure XIII A,1), $\text{N} - \text{C} = 1.465 \text{ \AA}$, $\text{C} - \text{Cl} = 3.90 \text{ \AA}$ or 3.97 \AA and $\text{N} - \text{Cl} = 3.18 \text{ \AA}$.

XIII a

XIIIa

As Table XIII A, 3 indicates, all three of the mono-propyl ammonium halides are isomorphous with $\text{CH}_3\text{NH}_3\text{Cl}$; a very recent study indicates that their correct units also are the larger bimolecular prisms of this table. The rotational motion of the cations within these crystals is too complicated to permit a more detailed description of atomic positions.

At reduced temperatures, *propyl ammonium chloride* goes over by a second order transition to a low symmetry form. From photographs made at somewhat below -100°C . it was concluded that this low $(\text{NH}_3\text{C}_3\text{H}_7)\text{Cl}$ has a tetramolecular monoclinic cell of the dimensions:

$$a_0 = 9.06 \text{ \AA}, \quad b_0 = 8.58 \text{ \AA}, \quad c_0 = 7.34 \text{ \AA}, \quad \beta = 98^\circ.$$

The space group has been chosen as $\text{C}_{2h}^3 (\text{C2/m})$ with all atoms except chlorine in (i) $\pm (u0v; \bar{u} + \frac{1}{2}, \frac{1}{2}, v)$. The chloride ions are in (e) $\pm (\frac{1}{4}, \frac{1}{4}, 0; \frac{1}{4}, \frac{3}{4}, 0)$ and approximate positions, corresponding to a non-rotating cation, have been proposed for the carbon and nitrogen atoms.

The *tetramethyl ammonium halides*, of which $\text{N}(\text{CH}_3)_4\text{Cl}$ is typical, have a distortion of the CsCl arrangement which is "anti" to the foregoing. This has already been described in connection with the isomorphous PH_4I (III, b3 and Table III, 9). The perchlorate and permanganate, also listed in Table III, 9, have this general structure though their investigation has not been sufficiently detailed to establish the positions of more than the ionic centers. In this "anti" structure the halogen ion is in (c) of D_{4h}^7 with a value of u near that of the center of gravity of the NH_3CH_3 ion in $\text{NH}_3\text{CH}_3\text{Cl}$ while the N atoms at the center of the cations of $\text{N}(\text{CH}_3)_4\text{Cl}$ are in fixed positions (a).

The *tetramethyl ammonium dichloroiodide*, $\text{N}(\text{CH}_3)_4\text{ICl}_2$, has this same type of distorted CsCl arrangement. Its bimolecular tetragonal unit has almost the same length of c_0 axis as $\text{N}(\text{CH}_3)_4\text{I}$; the a_0 axis is longer:

$$a_0 = 9.18 \text{ \AA}, \quad c_0 = 5.80 \text{ \AA}.$$

Atoms have been placed in the space group $V_d^3(P\bar{4}2_1m)$ of lower symmetry with the positions:

N: (b) $0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

I: (c) $0, \frac{1}{2}, w; \frac{1}{2}, 0, \bar{w}$, with $w = 0.106$

Cl: (e) $u, u + \frac{1}{2}, v; \bar{u}, \frac{1}{2} - u, v; u + \frac{1}{2}, \bar{u}, \bar{v}; \frac{1}{2}, -u, u, \bar{v}$,

with $u = 0.181$, $v = 0.106$.

C: (f) $xyz; \bar{x}\bar{y}z; \frac{1}{2} - x, y + \frac{1}{2}, \bar{z}; x + \frac{1}{2}, \frac{1}{2} - y, \bar{z}; \bar{y}x\bar{z}; y\bar{x}\bar{z};$

$y + \frac{1}{2}, x + \frac{1}{2}, z; \frac{1}{2} - y, \frac{1}{2} - x, z,$

with $x = 0.114$, $y = 0.053$, $z = 0.361$.

The origin for this description is displaced $\frac{1}{2} c_0$ with respect to that used above. The similarity between this structure and that of $N(CH_3)_4I$ is nevertheless clear from a comparison of Figures III, 6 and XIII A, 2. The ICl_2^+ ion is linear in this structure as in other dichloroiodides (VI, a7 and a16) with substantially the same I - Cl separation (2.34 Å.).

The *tetraethyl ammonium iodide*, $N(C_2H_5)_4I$, has a tetragonal bimolecular unit of similar shape, with:

$$a_0 = 8.87 \text{ Å.}, \quad c_0 = 6.95 \text{ Å.}$$

The iodine atoms are in special positions (c) $0, \frac{1}{2}, u; \frac{1}{2}, 0, \bar{u}$, but u in this case is very close to 0.25, and these atoms are so heavy that positions of the $N(C_2H_5)_4$ groups could not be established.

(XIII, a2). The bimolecular tetragonal unit found for *mono methyl ammonium iodide*, NH_3CH_3I , has a different shape from that of the chloride, with

$$a_0 = 5.11 \text{ Å.}, \quad c_0 = 8.97 \text{ Å.}$$

XIIIa

The iodine atoms are in positions that can be described by the same special positions of D_{4h}^7 used above:

$$I: (c) \quad 0, \frac{1}{2}, u; \frac{1}{2}, 0, \bar{u}, \text{ with } u = 0.195.$$

In the corresponding bromide the parameters established for the Br' ion is 0.185.

Because of the overwhelming scattering powers of the halogen atoms positions could not be established for the nitrogen and carbon atoms in these crystals, but it was pointed out that satisfactory interatomic distances result if these atoms also are in special positions (c) with $u(N) = \text{ca. } 0.79$ and $u(C) = \text{ca. } 0.64$ for the iodide. Such a structure, as illustrated in Figure XIII A, 3, is a simple distortion of the NaCl (III, a1) rather than of the CsCl arrangement.

All higher mono alkyl halides except the ethyl compounds and the propyl derivatives just discussed appear to be isomorphous with the iodide and to have the bimolecular cell dimensions of Table XIII A, 4. The units of all these crystals have bases that remain constant with increase in chain length and c_0 axes that increase by amounts that are much less than the known C - C = ca. 1.54 Å. The high symmetry and simple unit cells found for these crystals are understandable only if the carbon and nitrogen atoms of their long aliphatic chains do not occupy fixed positions compatible with such simple units but instead have zigzag chains that "rotate" about the c_0 axis.

A unit cell has been determined for one longer-chained compound which is not isomorphous with the foregoing, normal *mono octadecyl ammonium chloride*, $NH_4 \cdot n C_{18}H_{37}Cl$. This crystal has an orthorhombic pseudotetragonal cell of the dimensions:

$$a_0 = 5.45 \text{ Å.}, \quad b_0 = 5.40 \text{ Å.}, \quad c_0 = 69.4 \text{ Å.}$$

Its double lengthed cell, compared with those of Table XIII A, 4, would contain four molecules; and its low sym-

metry has been interpreted as evidence that in this case the chain need not be rotating.

XIIIa

A preliminary study has been made of these long chain substituted ammonium halides at lowered temperatures where "rotation" of the chains might be expected to be more or less completely arrested. In the course of this it was found that at -80° C. the *amyl ammonium chloride*, $\text{NH}_4 \cdot n \text{C}_5\text{H}_{11}\text{Cl}$ has a large tetramolecular unit with the dimensions:

$$a_0 = 7.03 \text{ A.}, \quad c_0 = 16.70 \text{ A.}$$

(XIII, a3). The *monoethyl ammonium halides* have low symmetry and structures that apparently are unrelated to those described above. Their monoclinic cells, each containing two molecules, have the dimensions:

$$\text{For } \text{NH}_4\text{C}_2\text{H}_5\text{Br: } a_0 = 8.32 \text{ A.}, \quad b_0 = 6.24 \text{ A.}, \quad c_0 = 4.63 \text{ A.}, \quad \beta = 86^{\circ}59'$$

$$\text{For } \text{NH}_4\text{C}_2\text{H}_5\text{I: } a_0 = 8.68 \text{ A.}, \quad b_0 = 6.63 \text{ A.}, \quad c_0 = 4.81 \text{ A.}, \quad \beta = 87^{\circ}54'.$$

It was shown that the halogen atoms for these crystals have the coordinates: $xyz; \bar{x}, y+\frac{1}{2}, \bar{z}$, with $x = 0.15$, $z = 0.11$ for the bromide and $x = 0.16$, $z = 0.12$ for the iodide.

(XIII, a4). No work has yet been done on di-alkyl ammonium halides. The trimethyl ammonium salts have low symmetry (Table XIIIA, 2) but the triethyl compounds have hexagonal symmetry and a structure which is somewhat related to that already described for $\text{LiI} \cdot 3\text{H}_2\text{O}$ (X, c1). Their bimolecular units have the dimensions:

$$\text{For } \text{NH}(\text{C}_2\text{H}_5)_3\text{Br: } a_0 = 8.56 \text{ A.}, \quad c_0 = 7.49 \text{ A.}$$

$$\text{For } \text{NH}(\text{C}_2\text{H}_5)_3\text{Cl: } a_0 = 8.38 \text{ A.}, \quad c_0 = 7.08 \text{ A.}$$

$$\text{For } \text{NH}(\text{C}_2\text{H}_5)_3\text{I: } a_0 = 8.78 \text{ A.}, \quad c_0 = 7.74 \text{ A.}$$

XIIIIa

Ionic centers have been placed in the following special positions of C_{6v}^4 ($C6mc$):

$$(b) \quad 1/3, 2/3, z; \quad 2/3, 1/3, z+1/2$$

For the halogen atoms, z has been taken as 0, and for nitrogen atoms as the centers of the $NH(C_2H_5)_3$ ions it has been given a value which for the chloride lies between 0.58 and 0.42. One set of carbon atoms (CH_2) may be in (c) $u\bar{u}v$; etc. with $u = ca \ 0.27$ and $v = ca \ 0.50$, but in view of the fact that the ethyl groups are undoubtedly "rotating" nothing definite can be considered as known about them or the CH_3 carbons. A projection of this structure is shown in Figure XIIIIA,4.

This is the ionic distribution originally proposed for $(Li.3H_2O)I$, but in the more recent study of this trihydrated lithium salt, the cation has been considered to be in (a) $00u$; $0,0,u+\frac{1}{2}$ of C_{6v}^4 . If this is correct its analogy to the present structure is limited to halogen positions.

The *triethyl sulfonium iodide*, $S(C_2H_5)_3I$, has an orthorhombic structure which may be a slight distortion of this hexagonal arrangement. Its tetramolecular unit has the dimensions:

$$a_0 = 15.81 \text{ \AA.}, \quad b_0 = 8.69 \text{ \AA.}, \quad c_0 = 7.35 \text{ \AA.}$$

The space group probably is V_h^{16} ($Pnma$) or C_{2v}^9 (Pna). The relation to the ammonium salt becomes clear by expressing the hexagonal unit of $NH(C_2H_5)_3I$ in orthohexagonal axes to yield for it the dimensions:

$$a_0' = \sqrt{3} \times a_0 = 15.21 \text{ \AA.}, \quad b_0 = 8.78 \text{ \AA.}, \quad c_0 = 7.74 \text{ \AA.}$$

ALKYL-SUBSTITUTED AMMONIUM CHLOROSTANNATES, ETC.

XIIIa

Nearly all of the numerous alkyl substituted ammonium chlorostannates and related compounds that have been studied have structures that closely resemble the cubic K_2PtCl_6 arrangement (IX,c1). Most of these compounds have cubic symmetry but a few have cations of such a shape as to impress a lower symmetry on the crystalline solid.

(XIII,a5). The various chlorostannates and chloroplatinates that have cubic symmetry are collected in Table XIII A, 5. All these crystals have four molecules in the unit cube with atoms of the $SnCl_6$ and $PtCl_6$ ions occupying more or less exactly the same positions as in K_2PtCl_6 (IX,c1).

For *tetramethyl ammonium chlorostannate*, $[N(CH_3)_4]_2SnCl_6$, the space group can be O_h^5 (Fm3m) as with K_2PtCl_6 and corresponding atoms can occupy the same sets of coordinate positions:

Sn: (a) 000; F.C.

Cl: (e) $\pm(u00; 0u0; 00u)$; F.C., with $u = 0.19$

N: (c) $\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$; F.C.

Probably the carbon atoms, tetrahedrally distributed about the nitrogen atoms, are in:

(f) $\pm(uuu; u\bar{u}\bar{u}; \bar{u}u\bar{u}; \bar{u}\bar{u}u)$; F.C., with $u = \text{ca. } 0.31$.

A packing drawing of this undistorted CaF_2 grouping is shown in Figure XIII A, 5.

A less complete determination has been made of the structure of *trimethyl ethyl ammonium chlorostannate*, $[N(CH_3)_3C_2H_5]_2SnCl_6$. Its chlorine atoms can be given the same coordinates as in the tetramethyl compound with $u = \text{ca. } 0.18$. The true symmetry is undoubtedly less than

XIIIa

holohedral, however, and a partial structure based on $T_h^o(Pa3)$ has been suggested; but there is undoubtedly "rotation" of the ethyl radical in the $[N(CH_3)_3C_2H_5]$ ion and without knowledge of its details a more detailed assignment of atomic positions is meaningless.

The foregoing remarks apply with even greater force to the structures of $[NCH_3(C_2H_5)_3]_2SnCl_6$ and $[PCH_3(C_2H_5)_3]_2SnCl_6$ whose symmetry is probably no more than tetartohedral and whose chlorine atoms are probably in general positions of $T^4(P2_13)$.

Substantially the same structure as that of $[N(CH_3)_3C_2H_5]_2SnCl_6$ has been proposed for *trimethyl ammonium chlorostannate*, $[NH(CH_3)_3]_2SnCl_6$ and for $[S(CH_3)_3]_2SnCl_6$. For the former it has been concluded that the chlorine atoms probably are in general positions of $T_h^o(Pa3)$ with $x = 0.05$, $y = 0.19$, $z = -0.04$. This corresponds to a slight rotation of the $SnCl_6$ ions around three-fold axes from the symmetrical positions prevailing in the crystals with holohedral symmetry. No atomic positions have been fixed for the trimethyl sulfonium compound nor for $[S(CH_3)_2C_2H_5]_2SnCl_6$.

(XIII,a6). The *monomethyl ammonium chlorostannate*, $(NH_3CH_3)_2SnCl_6$, and the corresponding chloroplatinate, have structures that are rhombohedral distortions of the K_2PtCl_6 structure. The unimolecular rhombohedral cells of these two crystals have the dimensions:

For $[NH_3CH_3]_2SnCl_6$: $a_0 = 8.42 \text{ \AA}$, $\alpha = 50^\circ 14'$

For $[NH_3CH_3]_2PtCl_6$: $a_0 = 8.31 \text{ \AA}$, $\alpha = 48^\circ 46'$.

Metal atoms are in the origin (a) 000 and chlorine atoms in the following positions of $D_{3d}^5(R\bar{3}m)$:

(h) $\pm(uuv; uvu; vuu)$, with $u = 0.22$ and $v = -0.26$,

for the chlorostannate. The positions of the light atoms were not determined experimentally because of the over-