

The Crystal Structure of N-Methylhydroxylammonium Chloride

LEO TOFT and BODIL JERSLEV

Chemical Laboratory C, The Royal Danish
School of Pharmacy, Copenhagen, Denmark

The crystal structure of $\text{H}_3\text{CNH}_2^+\text{OH}\cdot\text{Cl}^-$ has been determined from three-dimensional visually estimated X-ray data obtained by multiple film Weissenberg techniques. 410 independent reflections were observed. The crystals were obtained from an ethanol-ethylacetate mixture as hygroscopic, orthorhombic needles elongated in the c -direction. M.p. determined on a melting point microscope $84.5-86^\circ\text{C}$, density $\rho_{\text{expt.}} = 1.36 \text{ g}\cdot\text{cm}^{-3}$, the absorption coefficient for $\text{CuK}\alpha$ radiation has the value 65.3 cm^{-1} . Unit cell dimensions are $a = 8.72 \text{ \AA}$, $b = 7.85 \text{ \AA}$, $c = 6.07 \text{ \AA}$. $Z = 4$ corresponds to $\rho_x = 1.34 \text{ g}\cdot\text{cm}^{-3}$. Reflections $0kl$ were observed only for $l = 2n$ and $h0l$ only for $h = 2n$. This indicates the space group to be either the centrosymmetric $Pcam$ or the noncentrosymmetric $Pca2_1$. Attempts to distinguish between these space groups by Wilson statistics gave inconclusive results. No piezoelectric effect could be detected. The decision was finally made after full refinement of the atomic coordinates, which showed small deviations from centrosymmetry. The space group is probably $Pca2_1$, and the following description is based upon that assumption.

Since no piezoelectric effect could be found, the structure must be pseudo-centrosymmetric. This implies that the atoms must be placed in layers that are parallel to the c -plane and are separated by distances of approximately $\frac{1}{2}c$. This was confirmed by the Patterson projections $P(uw)$ and $P(vw)$. Trial x and y coordinates for the Cl, O, N, and C atoms were determined from the isomorphous N-methylhydroxylammonium bromide. The Patterson projection $P(uv)$ of that compound gave bromine coordinates based upon which structure factors $F(hk0)$ were calculated. The phases from these were used for calculation of the centrosymmetric electron density projection $\rho(xy)$ from which fairly accurate x and y coordinates of the bromine atom and of the three light atoms as well were directly measurable.

Table 1. Atomic parameters. Standard deviations in parentheses are multiplied by 10^4 .

	x	y	z
C	-0.1087(10)	0.3262(13)	0.7402(64)
N	0.0382(6)	0.2387(8)	0.7265(36)
O	0.1521(6)	0.3707(7)	0.7559(38)
Cl	0.0719(3)	0.1421(3)	0.2368(0) ^a

^a The z -parameter of the chlorine atom was arbitrarily fixed at the given value.

The x and y coordinates thus obtained were used directly for a calculation of structure factors $F(hk0)$ for the chloride. The three light atoms were all inserted as nitrogen, and an R -value of 0.23 was obtained. The positions found for the light atoms could be distributed between C, N, and O in two ways only, since the nitrogen atom according to the chemical constitution must be the central one. Both possibilities were tested by subsequent structure factor calculations, and the changes in the R -value clearly indicated which was the correct choice.

Refinement proceeded first by means of the R -minimisation method of Bhuiya and Stanley¹ using an ALGOL program written by Danielsen² and finally by Busing, Martin and Levy's least squares full matrix program ORFLS³ at the computing centre NEUCC. Individual, anisotropic thermal parameters were used. Final R -value = 0.14. A subsequent three dimensional $F_o - F_c$ synthesis did not give additional information, e.g. of the hydrogen positions, and it was consequently concluded, that the data were not good enough to give more structural details than already obtained.

The positional parameters found are given in Table 1, the structure is shown in Fig. 1. The dimensions of the N-methylhydroxylammonium ion present no surprises. The chlorine ion is surrounded by

four ions N^+ forming a distorted tetrahedron and similarly each nitrogen makes contact with four chlorine ions, but this arrangement forms a flat, irregular four sided pyramid with nitrogen at the top. Two of the N-Cl contacts connect the N-methylhydroxylammonium ion with a chlorine ion in each of the adjacent layers. These contacts can be regarded from geometrical considerations as N-H...Cl bonds. Furthermore a close contact between chlorine and oxygen in the same layer is interpreted as an

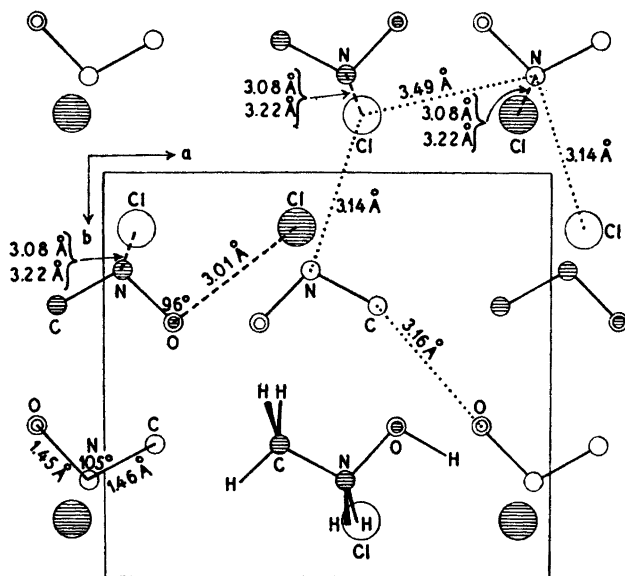


Fig. 1. The structure viewed along the c -axis. Open circles indicate atoms in the layer at $z \approx \frac{1}{4}$, shaded circles indicate atoms with $z \approx \frac{3}{4}$. Molecular dimensions and hydrogen bonds are shown to the left. In the upper row the distribution of ions N^+ around a chlorine ion and *vice versa* is shown. Approximate hydrogen positions are indicated at one ion in the lower part of the figure in order to give an impression of the proposed conformation of the N-methylhydroxylammonium ion.

O—H...Cl bond. This is in accordance with the expected *trans* arrangement of the O—H bond relative to the C—N bond. Within a layer a short intermolecular distance between O and C (3.16 Å, *cf.* Fig. 1) suggests that the oxygen is squeezed in between two methyl hydrogen atoms placed roughly symmetrically on each side of the layer. This description corresponds precisely to the staggered conformation expected around the C—N bond. In the crystal structures of hydroxylammonium chloride⁴ and O-methylhydroxylammonium chloride⁵ as well as in the present structure all hydrogen atoms capable of forming a hydrogen bond do so with a chlorine ion as acceptor. The geometrical arrangements of the hydrogen bonds in

the three structures are similar, but the structure determinations are not accurate enough for detailed comparisons to be made.

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