

cationic water species. The crystal structure of this compound is stabilized by the hydrogen bonds formed between anionic molecules and cationic water species.

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Tetraethylammonium Chloride Monohydrate*

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Abstract. $C_8H_{20}ClN \cdot H_2O$, monoclinic, $C2/c$, $a = 13.684$ (3), $b = 14.144$ (3), $c = 12.372$ (4) Å, $\beta = 110.75$ (2)° at 24°C, $Z = 8$, $D_x = 1.0899$ (5) g cm⁻³. The asymmetric unit consists of one formula unit. Pairs of Cl⁻ ions and water molecules form a centrosymmetric hydrogen-bonded ring. The tetraethylammonium ions lie on a twofold axis and have two different orientations. One conforms to the crystallographic symmetry while the other is in a general orientation with a twofold disorder.

Introduction. Several prismatic crystals grew slowly from a chloroform–ether solution of tetraethylammonium chloride (Et₄NCl) during attempts to grow crystals of Et₄NCl·CHCl₃. The composition of these crystals was established by the present structural analysis. Since dried solvents and vacuum-dried salt were used, the water must have entered from the atmosphere. The crystal used for data collection was placed in a glass capillary from which all solvent was removed prior to sealing.

Data were collected using Mo $K\alpha$ radiation on a Nonius CAD-4 diffractometer fitted with a graphite monochromator. 24 independent reflections were used to determine the lattice parameters by a least-squares fit

with the diffraction angle θ , measured as $4\theta [2\theta - (-2\theta)]$. Systematic extinctions were observed for all reflections with $h + k$ odd and for $h0l$ reflections with h odd. The choice of space group $C2/c$ rather than Cc was made after determination of the structure. All unique reflections (1976) were measured out to $\theta = 25^\circ$ ($\sin \theta/\lambda = 0.595 \text{ \AA}^{-1}$) using a θ – 2θ scan technique. No significant changes were observed in four standard reflections monitored at regular intervals. Background corrections were made using the profile-analysis method of Lehmann & Larsen (1974) following which the data were corrected for Lorentz and polarization effects and for absorption ($\mu = 3.01 \text{ cm}^{-1}$) using the Gaussian integration method with a grid of 360 points. The crystal had faces of the forms $\{110\}$ and $\{111\}$ and measured $0.013 \times 0.013 \times 0.024$ cm with the long axis coinciding with c . Of the 1976 unique reflections measured, 834 with observed intensities greater than $1.5\sigma(I)$ were used in the refinement.

The position of the Cl⁻ ion was found using both heavy-atom and direct methods.† The non-hydrogen

† The program *MULTAN* (Declercq, Germain, Main & Woolfson, 1973) was used for direct methods. All other programs used in this work, including *ORTEP* (Johnson, 1965) used in preparing Fig. 1, are described by Lundgren (1975) or were written by the authors.

* Hydrogen Bond Studies. CXXVIII.

atoms in the $\text{Et}_4\text{N}^+(1)$ ion and the water molecule were found in an electron density map with reflections phased only by the Cl^- ion. The atoms of $\text{Et}_4\text{N}^+(2)$ were not as easily found due to disorder. Untangling of the structures of the members of the disordered pair of cations was based on difference-map peaks with chemically reasonable bond lengths and angles. Following determination of the positions of all heavy atoms, a difference map showed peaks corresponding to all H atoms on water and $\text{Et}_4\text{N}^+(1)$. In $\text{Et}_4\text{N}^+(2)$ only a few peaks could be unambiguously assigned to specific H atoms. For each of the final refinement cycles, H atoms were placed in calculated positions and not refined. In the Et_4N^+ ions C—H distances were assumed to be 1.091 Å and O—H in water 0.990 Å (*International Tables for X-ray Crystallography*, 1968). H—C—H angles were set at 109.5° in methylene and 107.3° in methyl groups, approximating the values determined by neutron diffraction (Kvick, Koetzle & Thomas, 1974). The H atoms were placed on the line between O and Cl^- for water molecules, in the plane bisecting the N—C—C angle and equidistant from the N—C—C plane for CH_2 groups, and using the best fit to peaks in the difference map to determine the rotational orientation for CH_3 groups.

Refinement was carried out using the full-matrix least-squares method. In the final cycles the refinement was based on weighted, observed intensities (F_o^2), minimizing $\sum w(F_o^2 - F_c^2)$, where $w^{-1} = \sigma_{\text{obs}}^2(F_o^2) + (0.025F_o^2)^2$ with σ_{obs} based on counting statistics. Scattering factors as given in *International Tables for X-ray Crystallography* (1968) were used for C, N, O and Cl^- atoms; for H atoms the values given by Stewart, Davidson & Simpson (1965) were used. Anomalous-dispersion corrections to the scattering factors as calculated by Cromer & Liberman (1970) were applied.

The final refinement resulted in $R(F^2) = 0.081$ and $R_w(F^2) = 0.118$ for 834 reflections used and $R(F^2) = 0.142$ for all 1976 reflections. This corresponds to a conventional $R(F) = 0.074$ for the 834 reflections with intensities above $1.5\sigma(I)$. The largest parameter shift in the final cycle was 0.034 times the estimated standard deviation. The total number of refined parameters was 116. The final difference map has a maximum electron density of $0.25 \text{ e } \text{Å}^{-3}$. The location of the residual peaks in the difference map indicates that some disorder of methyl groups and additional disorder of the cation skeleton of $\text{Et}_4\text{N}^+(2)$ may not have been accounted for.*

Discussion. The final coordinates of the atoms are shown in Table 1 and the bond distances and angles given in Table 2. Fig. 1 shows the orientation of the ions in the cell and the way in which they interact. In the crystal the $\text{Et}_4\text{N}^+(1)$ and $\text{Et}_4\text{N}^+(2)$ ions each stack in a zig-zag column in the c direction. The $\text{H}_2\text{O}-\text{Cl}^-$ rings are tilted between the resulting layers of cations in such

Table 1. Atom positions for one asymmetric unit in fractions of the unit-cell vectors $\times 10^4$

For parameters which were varied in the refinement, e.s.d.'s are shown in parentheses. Atoms of the disordered $\text{Et}_4\text{N}^+(2)$ are indicated by an asterisk.

	x	y	z
Cl	1439 (1)	1807 (1)	1126 (1)
O	1620 (3)	6341 (3)	4717 (4)
N(1)	0	9131 (4)	2500
C(1)	978 (4)	8525 (4)	2771 (5)
C(2)	942 (5)	7812 (4)	1839 (5)
C(3)	125 (5)	9735 (4)	3567 (5)
C(4)	1014 (5)	435 (4)	3865 (5)
N(2)*	89 (21)	4159 (5)	2519 (29)
C(5)*	841 (11)	4288 (8)	1918 (12)
C(6)*	1636 (11)	4990 (11)	2423 (13)
C(7)*	9422 (9)	5045 (8)	2451 (11)
C(8)*	8643 (15)	5033 (14)	3082 (17)
C(9)*	9446 (9)	3257 (9)	2059 (12)
C(10)*	8790 (16)	3392 (15)	711 (18)
C(11)*	646 (11)	4035 (10)	3814 (13)
C(12)*	1462 (13)	3223 (12)	4026 (15)
H(1)	1564	6914	5153
H(2)	2212	6483	4460
H(3)	1642	8994	2896
H(4)	1090	8139	3570
H(5)	234	7383	1595
H(6)	955	8161	1058
H(7)	1607	7331	2128
H(8)	9411	128	3409
H(9)	259	9264	4304
H(10)	1771	82	4218
H(11)	1008	833	3107
H(12)	973	946	4508
H(13)*	1229	3612	1924
H(14)*	404	4494	1027
H(15)*	1378	5691	2065
H(16)*	1832	5036	3356
H(17)*	2352	4829	2266
H(18)*	9957	5632	2804
H(19)*	8978	5175	1540
H(20)*	7978	4572	2650
H(21)*	9002	4782	3968
H(22)*	8330	5738	3120
H(23)*	9970	2653	2183
H(24)*	8913	3137	2526
H(25)*	7161	3905	567
H(26)*	9282	3638	242
H(27)*	8431	2728	311
H(28)*	1042	4691	4190
H(29)*	79	3854	4220
H(30)*	1109	2535	4041
H(31)*	1797	3203	3346
H(32)*	2105	3311	4846

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33793 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

a way that all O atoms are close to $\text{Et}_4\text{N}^+(2)$ and all Cl^- to $\text{Et}_4\text{N}^+(1)$.

Both Et_4N^+ ions have a configuration close to point symmetry 222 (D_2). In $\text{Et}_4\text{N}^+(1)$ the crystallographic axis coincides with the ionic axis to which the methyl C atoms are closest (*i.e.* the long axis of the ion, see Fig. 1). The analogous ionic axis in the $\text{Et}_4\text{N}^+(2)$ ion is perpendicular to the crystallographic twofold axis which also approximately bisects the angle between the other two ionic pseudosymmetry axes. The N atom in $\text{Et}_4\text{N}^+(2)$ lies 0.116 Å off the twofold axis. If one were to inscribe a cube with its center at the N atom and methylene C atoms near the corners, the ions would have their pseudosymmetry axes coincidental with the fourfold cube axes. $\text{Et}_4\text{N}^+(2)$ is oriented so that the crystallographic axis passes through opposite edges of the cube and is disordered so that the four methylene C atoms statistically occupy the two tetrahedral sets of cube corners. The methyl C positions are however quite close for the two alternative orientations [C(10)–C(12^b) or C(12)–C(10^b) = 0.60 (2) Å and C(6)–C(8^b) or C(8)–C(6^b) = 0.61 (2) Å]. In the anion solvent ring the Cl...O...Cl angle is 103.8 (1)° providing ideal geometry for hydrogen bonding using the two H atoms which are 104° apart in the free water molecule. The O...Cl distances are 3.204 (4) and 3.247 (4) Å. These are slightly longer than those between water and Cl^- ions in $\text{HCl}\cdot 3\text{H}_2\text{O}$ (Lundgren & Olovsson, 1967) where the O lone-pair electrons also participate in hydrogen bonding with H_5O_2^+ ions. In this case there is little possibility for similar lone-pair utilization since all the remaining H atoms in the crystal are on tetraethylammonium ions which would not be expected to interact

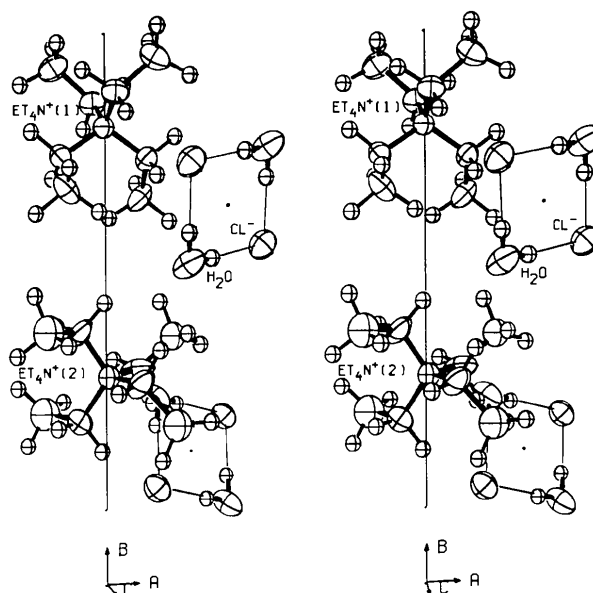


Fig. 1. A stereoscopic view of part of a unit cell. Only one member of the $\text{Et}_4\text{N}^+(2)$ disordered pair is shown. The other is related by the twofold crystallographic axis shown by the vertical line.

strongly. The closest contacts between O and atoms in $\text{Et}_4\text{N}^+(2)$ are: H(28)...O, 2.447; H(19)...O, 2.214; and H(16)...O, 2.584 Å, with H(28)...O having the most favorable geometry. The closest contacts between Cl^- and $\text{Et}_4\text{N}^+(1)$ are not significantly shorter than the sum of the van der Waals radii.

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Table 2. *Interatomic distances (Å) and angles (°) involving the heavy atoms*

Anion–solvent			
Cl...O	3.204 (4)	Cl...O...Cl ^b	103.8 (1)
Cl ^b ...O	3.247 (4)	O...Cl...O ^b	76.2 (1)
$\text{Et}_4\text{N}^+(1)$			
N(1)–C(1)	1.523 (6)	C(1)–N(1)–C(1 ^b)	111.5 (6)
N(1)–C(3)	1.530 (6)	C(1)–N(1)–C(3)	107.7 (3)
C(1)–C(2)	1.520 (8)	C(1)–N(1)–C(3 ^b)	109.0 (3)
C(3)–C(4)	1.510 (7)	C(3)–N(1)–C(3 ^b)	112.1 (5)
		N(1)–C(1)–C(2)	114.6 (4)
		N(1)–C(3)–C(4)	114.2 (4)
$\text{Et}_4\text{N}^+(2)$			
N(2)–C(5)	1.48 (3)	C(5)–N(2)–C(7)	112 (1)
N(2)–C(7)	1.53 (2)	C(5)–N(2)–C(9)	109 (2)
N(2)–C(9)	1.54 (2)	C(5)–N(2)–C(11)	112 (2)
N(2)–C(11)	1.52 (3)	C(7)–N(2)–C(9)	114 (2)
C(5)–C(6)	1.44 (2)	C(7)–N(2)–C(11)	103 (2)
C(7)–C(8)	1.53 (2)	C(9)–N(2)–C(11)	108 (1)
C(9)–C(10)	1.60 (2)	N(2)–C(5)–C(6)	115 (1)
C(11)–C(12)	1.56 (2)	N(2)–C(7)–C(8)	118 (2)
		N(2)–C(9)–C(10)	109 (2)
		N(2)–C(11)–C(12)	109 (1)