

The C–H distances are calculated using the positions of the hydrogen atoms as obtained from the difference synthesis.

The benzene ring is a slightly distorted regular hexagon and the average C–C distance is 1.387 Å. The least-squares plane defined by the six carbon atoms was calculated using a method described by Blow (1960). The carbon ring is not significantly different from planar. The deviations of the atoms from the plane are shown in Fig. 8. The S–O distances 1.463, 1.442 and 1.459 Å are normal for an aromatic sulphonate group. The orientation of the sulphonate group with respect to the carbon ring is such that atom O(1) lies nearly in the plane of the ring. The angle between the least-squares plane and the plane defined by C(1), S and O(1) is only 2.3°. The average O–S–O and C–S–O angles in the group are 112.5° and 106.2° respectively. These angles are similar to those found in related structures, e.g. 112.4° and 106.4° in ammonium

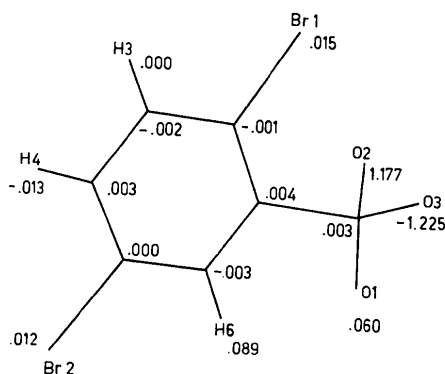


Fig. 8. Deviations of the atoms from the least-squares plane defined by the six carbon atoms of the 2,5-dibromobenzenesulphonate ion (Å).

acid *o*-carboxybenzenesulphonate (Okaya, 1967) and 112.9° and 106.7° in 2-aminoethylsulphonic acid (Okaya, 1966).

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Hydrogen Bond Studies. L. The Crystal Structure of Perchloric Acid Trihydrate

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The crystal structure of $\text{HClO}_4 \cdot 3\text{H}_2\text{O}$ has been determined from three-dimensional single-crystal X-ray diffraction data recorded at -188°C . The crystals are orthorhombic, space group *Pbca*, with eight formula units in a cell of dimensions: $a=8.252$, $b=13.105$, $c=10.218$ Å. Two water molecules are bonded to an H_3O^+ ion by short hydrogen bonds (2.49 and 2.54 Å) to form H_7O_3^+ ions. Longer hydrogen bonds (2.74–2.89 Å) connect these with the ClO_4^- ions and with one another to form a three-dimensional network. The shape of the ClO_4^- ion is almost perfectly tetrahedral with a mean uncorrected Cl–O distance of 1.437 Å.

Introduction

This work is part of a current series of investigations at this Institute directed towards the study of the hydro-

tion of the proton in the solid state. Earlier papers in this series reported the crystal structures of $\text{HCl} \cdot n\text{H}_2\text{O}$, $n=2,3$ (Lundgren & Olovsson, 1967*a,b*), $\text{HBr} \cdot n\text{H}_2\text{O}$, $n=1,2,3,4$ (Lundgren, 1970; Lundgren & Olovsson,

1968) and $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$, $n=1, 2, 4$ (Taesler & Olovsson, 1968, 1969; Kjällman & Olovsson, 1971).

The melting point diagram of the system $\text{HClO}_4\text{-H}_2\text{O}$ indicates the existence of at least nine intermediate phases (Mascherpa, 1965). The structures of $\text{HClO}_4 \cdot \text{H}_2\text{O}$ (Lee & Carpenter, 1959; Nordman, 1962), $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ (Olovsson, 1968), and $\text{HClO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ (Almlöf, Lundgren & Olovsson, 1971) have already been determined, and studies of some of the remaining phases are in progress at this Institute. The present investigation is based on single-crystal X-ray diffraction data recorded at -188°C .

Experimental

Perchloric acid (ca. 73%) was diluted with distilled water to a molar ratio $\text{H}_2\text{O}:\text{HClO}_4=3.00$. The composition was checked by titration with a solution of sodium hydroxide. Samples were sealed in glass capillaries having a diameter of 0.1–0.2 mm and a wall thickness of about 0.02 mm. Single crystals were grown using the zone-melting technique in a Weissenberg camera modified for low-temperature work (Olovsson, 1960). The observed melting point was in good agreement with the value of -40.2°C reported by Mascherpa. The cell dimensions were determined from quartz-calibrated zero-layer oscillation photographs around the [100] and [010] axes. The cell dimensions were fitted to the 46 measured θ -values in a least-squares program and are given in Table 1. Numbers in parenthesis denote e.s.d.'s in the least significant digit throughout this paper. The value 4.9131 Å was used for $a(\text{SiO}_2)$ at 25°C .

Table 1. *Crystallographic and physical data*

$\text{HClO}_4 \cdot 3\text{H}_2\text{O}$	F.W. 154.50
Space group, <i>Pbca</i> (No. 61 in <i>International Tables for X-ray Crystallography</i> , 1952)	
$a = 8.252$ (2) Å (at -188°C)	
$b = 13.105$ (2)	
$c = 10.218$ (2)	
$V = 1105$ Å ³	
$D_x = 1.86$ g.cm ⁻³	
$Z = 8$	
m.p. -40.2°C	
$\mu = 49.6$ cm ⁻¹	

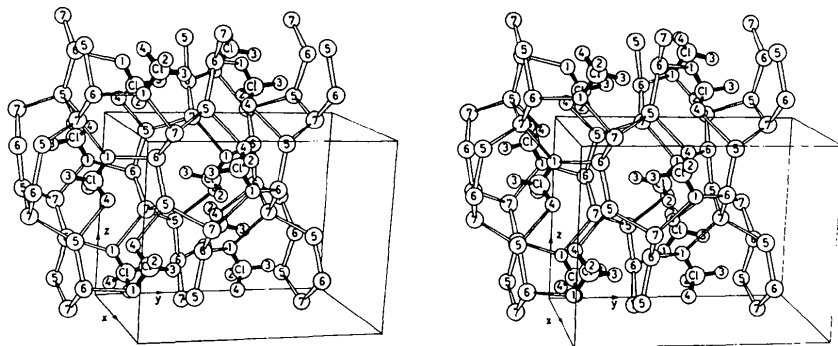


Fig. 1. A stereoscopic pair of drawings showing the structure. The hydrogen atoms are omitted for the sake of clarity. Covalent bonds are filled, hydrogen bonds are open.

Equi-inclination Weissenberg photographs, layers $0 \leq h \leq 7$, were taken at -188°C using unfiltered Cu *K* radiation and employing the multiple film method with five films. The crystal used was cylindrical of radius 0.056 mm, and with its axis tilted 9.2° from the rotation axis. The number of independent reflexions recorded was 1089, corresponding to 88% of the total number of independent reflexions within the copper reflexion sphere. Of these 179 were not significantly different from the background. The relative intensities were estimated visually by comparison with an intensity scale. The whole data set was estimated three times, and the mean values of the intensities were used. The data were corrected for absorption and secondary extinction effects. The cylindrical shape of the crystal was represented approximately by 14 boundary planes in the calculation of the absorption and extinction corrections.

The structure determination

The coordinates of the eight heavy atoms were determined from a three-dimensional Patterson function and refined in a Fourier electron-density synthesis. Atomic coordinates and isotropic temperature factors, together with scale factors for the eight layers, were refined in two cycles of least-squares calculation,

Table 2. *Atomic coordinates* $\times 10^4$
(in the case of hydrogen $\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>
Cl	2466 (1)	781 (1)	1764 (1)
O(1)	2507 (4)	202 (2)	2981 (3)
O(2)	4000 (4)	691 (3)	1133 (4)
O(3)	2116 (5)	1827 (2)	2042 (3)
O(4)	1238 (4)	349 (2)	938 (3)
O(5)	99 (4)	3233 (2)	4045 (3)
O(6)	4560 (4)	3585 (2)	3298 (3)
O(7)	1854 (4)	3369 (2)	64 (3)
H ₂ O(5) {	H(1) 40 (12)	379 (8)	458 (9)
	H(2) 66 (16)	264 (11)	444 (12)
	H(3) 428 (7)	425 (5)	327 (6)
H ₃ O(6)+ {	H(4) 49 (12)	354 (7)	107 (9)
	H(5) 475 (8)	348 (5)	240 (6)
H ₂ O(7) {	H(6) 263 (14)	316 (18)	30 (12)
	H(7) 197 (8)	110 (5)	456 (6)

where the function $\sum w(|F_o| - |F_c|)^2$ was minimized. The discrepancy index R at this stage was 0.098 excluding zero weight data. Two cycles of anisotropic refinement lowered R to 0.086. The inter-layer scale factors were here fixed to the values obtained in the isotropic refinement. The hydrogen atoms could then be located from a three-dimensional Fourier difference synthesis where only data with $\sin \theta/\lambda$ less than 0.5 \AA^{-1} were used. The heights of the hydrogen peaks were

0.55–0.84 e.Å⁻³. There were also a small number of spurious peaks with heights up to 0.5 e.Å⁻³, but these could all be excluded as possible hydrogen peaks on the basis of distance and angle considerations. Further cycles of refinement, first isotropic and then anisotropic, including the hydrogen atoms with fixed parameters, lowered R to 0.080. The weighted R value $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}$ at this stage was 0.116. Since several strong reflexions with low θ appeared to

Table 3. Thermal parameters ($\times 10^4$)

The form of the temperature factor is $\exp(-h^2\beta_{11} - \dots - hk\beta_{12} - \dots)$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	31 (2)	14 (1)	18 (1)	-2 (1)	1 (2)	2 (1)
O(1)	52 (6)	17 (2)	26 (3)	-12 (6)	10 (3)	10 (3)
O(2)	40 (6)	36 (2)	50 (3)	3 (5)	37 (7)	12 (4)
O(3)	73 (6)	21 (2)	33 (3)	-7 (5)	-18 (7)	2 (3)
O(4)	42 (6)	25 (2)	31 (3)	-8 (5)	-28 (6)	-8 (4)
O(5)	48 (6)	23 (2)	30 (3)	-2 (5)	3 (6)	-2 (3)
O(6)	63 (6)	20 (2)	25 (3)	2 (5)	5 (6)	-5 (3)
O(7)	57 (7)	17 (2)	25 (3)	1 (4)	-7 (6)	7 (3)

Table 4. Observed and calculated structure factors

The three columns are, in order I , $10|F_o|$, $10|F_c|$. Unobserved reflexions have $|F_o|=0$.

hkl	$10 F_o $	$10 F_c $	$10 F_o $	$10 F_c $	$10 F_o $	$10 F_c $
0, 0, 0	0	0	0	0	0	0
2, 782, 781	1	0	1	0	1	0
4, 681, 656	1	0	1	0	1	0
6, 701, 711	1	0	1	0	1	0
8, 509, 563	1	0	1	0	1	0
10, 751, 754	1	0	1	0	1	0
12, 425, 407	1	0	1	0	1	0
0, 2, 1	1	0	1	0	1	0
1, 945, 959	2	1	2	1	2	1
2, 608, 652	2	1	2	1	2	1
3, 360, 376	3	1	3	1	3	1
4, 616, 612	4	1	4	1	4	1
5, 299, 325	5	1	5	1	5	1
6, 219, 220	6	1	6	1	6	1
7, 291, 274	7	1	7	1	7	1
8, 303, 312	8	1	8	1	8	1
9, 312, 345	9	1	9	1	9	1
10, 109, 111	10	1	10	1	10	1
11, 10, 211	11	1	11	1	11	1
12, 80, 71	12	1	12	1	12	1
13, 63, 69	13	1	13	1	13	1
0, 4, 1	1	0	1	0	1	0
0, 815, 815	1	0	1	0	1	0
0, 1608, 1606	1	0	1	0	1	0
0, 186, 49	1	0	1	0	1	0
3, 1065, 1069	1	0	1	0	1	0
4, 63, 59	1	0	1	0	1	0
5, 500, 521	1	0	1	0	1	0
6, 603, 641	1	0	1	0	1	0
7, 156, 147	1	0	1	0	1	0
8, 0, 54	1	0	1	0	1	0
9, 336, 349	1	0	1	0	1	0
10, 75, 86	1	0	1	0	1	0
11, 116, 102	1	0	1	0	1	0
12, 293, 287	1	0	1	0	1	0
0, 6, 1	1	0	1	0	1	0
0, 521, 505	1	0	1	0	1	0
1, 1087, 1119	1	0	1	0	1	0
2, 339, 352	1	0	1	0	1	0
3, 583, 555	1	0	1	0	1	0
4, 252, 228	1	0	1	0	1	0
5, 303, 313	1	0	1	0	1	0
6, 115, 203	1	0	1	0	1	0
7, 306, 291	1	0	1	0	1	0
8, 275, 285	1	0	1	0	1	0
9, 368, 321	1	0	1	0	1	0
10, 83, 20	1	0	1	0	1	0
12, 147, 164	1	0	1	0	1	0
0, 8, 1	1	0	1	0	1	0
0, 918, 4019	1	0	1	0	1	0
1, 299, 326	1	0	1	0	1	0
2, 76, 68	1	0	1	0	1	0
3, 79, 20	1	0	1	0	1	0
4, 294, 288	1	0	1	0	1	0
5, 370, 406	1	0	1	0	1	0
6, 99, 91	1	0	1	0	1	0
7, 449, 425	1	0	1	0	1	0
8, 129, 117	1	0	1	0	1	0
9, 0, 16	1	0	1	0	1	0
10, 29, 269	1	0	1	0	1	0
11, 170, 190	1	0	1	0	1	0
0, 10, 1	1	0	1	0	1	0
0, 219, 224	1	0	1	0	1	0
1, 463, 465	1	0	1	0	1	0
2, 260, 280	1	0	1	0	1	0
3, 393, 395	1	0	1	0	1	0
4, 78, 84	1	0	1	0	1	0
5, 520, 498	1	0	1	0	1	0
6, 0, 38	1	0	1	0	1	0
7, 575, 570	1	0	1	0	1	0
8, 170, 163	1	0	1	0	1	0
9, 92, 78	1	0	1	0	1	0
10, 0, 9	1	0	1	0	1	0
0, 12, 1	1	0	1	0	1	0
0, 720, 670	1	0	1	0	1	0
1, 86, 14	1	0	1	0	1	0
2, 158, 153	1	0	1	0	1	0
3, 278, 259	1	0	1	0	1	0
4, 0, 19	1	0	1	0	1	0
5, 81, 85	1	0	1	0	1	0
6, 407, 411	1	0	1	0	1	0
7, 126, 135	1	0	1	0	1	0
8, 183, 162	1	0	1	0	1	0
9, 2, 75	1	0	1	0	1	0
0, 14, 1	1	0	1	0	1	0
0, 222, 178	1	0	1	0	1	0
1, 102, 106	1	0	1	0	1	0
2, 107, 265	1	0	1	0	1	0
3, 135, 136	1	0	1	0	1	0
4, 155, 17	1	0	1	0	1	0
5, 201, 171	1	0	1	0	1	0
6, 2, 95	1	0	1	0	1	0
7, 244, 232	1	0	1	0	1	0

suffer from secondary extinction effects, a correction was applied according to Zachariasen's (1967) formula. This led to a lowering of R to 0.064 and of R_w to 0.081 in the final anisotropic refinement, where the positional coordinates of the hydrogen atoms were also refined. The isotropic temperature factors B for hydrogen were set to 2.5 \AA^2 . The parameter shifts in the final cycle were all less than one tenth of the corresponding e.s.d.'s. The weighting scheme used in the final cycle was $w = (16.32 + |F| + 0.0036|F|^2 + 0.0001|F|^3)^{-1}$ for observed and $w = 0$ for unobserved reflexions. A weight analysis suggested that this weighting scheme was appropriate.

The atomic coordinates and thermal parameters with estimated standard deviations are listed in Tables 2 and 3. Observed and calculated structure factors are given in Table 4.

The atomic scattering factors used in the refinement were those given for neutral Cl and O in *International Tables for X-ray Crystallography* (1962), and the spherical scattering factor for hydrogen suggested by Stewart, Davidson & Simpson (1965).

All calculations were made on the CDC 3600 computer in Uppsala using programs described by Liminga (1967).

Description of the structure

The structure is shown in Figs. 1 and 2. Bond distances and angles are listed in Tables 5 and 6 and are illustrated in Fig. 2(b). The bond distances in the perchlorate ion after correction for thermal riding motion have also been calculated. Since inter-layer scale factors have been refined, the thermal parameters and the corresponding corrections must be viewed with a certain amount of scepticism, and only uncorrected values are therefore listed. All corrections are, however, less than 0.013 \AA .

Standard deviations for the distances and angles have been estimated from the errors in the atomic coordinates obtained in the form of a variance-covariance matrix from the final least-squares cycle. The uncertainties in the cell dimensions have also been taken into account.

In the present structure, one H_3O^+ ion and two H_2O molecules are connected together by short hydrogen bonds (2.49 and 2.54 \AA) to form unsymmetric H_7O_3^+ ions. Longer hydrogen bonds (2.74 – 2.89 \AA) connect these to one another and to the ClO_4^- ions to form a three-dimensional network (cf. Fig. 1). The distance $[\text{O}(7) \cdots \text{O}(3)]$ is only 2.87 \AA , but has not here been interpreted as a hydrogen bond since the bond angles are most unfavourable for such a situation. Also no peak has been found in the corresponding region of the difference map. No other $\text{O} \cdots \text{O}$ distance is shorter than 3.0 \AA .

The ClO_4^- ion is almost tetrahedral. The mean uncorrected Cl–O distance is $1.437(2) \text{ \AA}$, in good agreement with the values $1.438(3) \text{ \AA}$ in $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ and $1.434(2)$ and $1.439(2)$ in $\text{HClO}_4 \cdot 2.5\text{H}_2\text{O}$. The longest

Cl–O distance, Cl–O(1), is 1.456 \AA ; 0.019 \AA longer than the mean value. It is significant that this corresponds to the highest coordination for an oxygen atom, and that the second longest distance (1.435 \AA) is found for O(4) which also accepts a hydrogen bond.

Table 5. Bond distances

(a) Cl–O distances (\AA). The values have not been corrected for thermal riding motion.

Cl–O(1)	1.456 (3)
–O(2)	1.426 (4)
–O(3)	1.430 (3)
–O(4)	1.435 (3)

(b) O–H distances (\AA). Hydrogen coordinates from refinement (I) and from difference maps (II).

	I	II
O(5)–H(1)	0.95 (10)	1.03
–H(2)	0.99 (13)	1.05
O(6)–H(3)	0.90 (6)	1.02
–H(4)	1.00 (9)	0.94
–H(5)	0.94 (6)	0.97
O(7)–H(6)	0.74 (12)	0.89
–H(7)	0.87 (7)	0.91

(c) Hydrogen bond distances (\AA)

O(5) \cdots O(4)	2.841 (4)
O(5) \cdots O(7)	2.755 (4)
O(6) \cdots O(1)	2.739 (4)
O(6) \cdots O(5)	2.479 (4)
O(6) \cdots O(7)	2.543 (5)
O(7) \cdots O(1)	2.886 (4)
O(7) \cdots O(5)	2.833 (5)

Table 6. Bond angles ($^\circ$)

(a) O–Cl–O angles

O(1)–Cl–O(2)	108.8 (2)
O(1)–Cl–O(3)	109.5 (2)
O(1)–Cl–O(4)	108.3 (2)
O(2)–Cl–O(3)	110.3 (2)
O(2)–Cl–O(4)	109.2 (2)
O(3)–Cl–O(4)	110.6 (2)

(b) Hydrogen bond angles

O(5) \cdots O(6) \cdots O(7)	118.8 (2)
O(5) \cdots O(6) \cdots O(1)	98.1 (1)
O(7) \cdots O(6) \cdots O(1)	128.8 (1)
O(7) \cdots O(5) \cdots O(7)	115.1 (1)
O(7) \cdots O(5) \cdots O(6')	97.4 (2)
O(7) \cdots O(5) \cdots O(4')	93.0 (1)
O(7) \cdots O(5) \cdots O(6)	126.9 (2)
O(7) \cdots O(5) \cdots O(4)	93.9 (1)
O(4) \cdots O(5) \cdots O(6)	126.5 (2)
O(5) \cdots O(7) \cdots O(1)	108.3 (1)
O(5) \cdots O(7) \cdots O(1')	95.8 (1)
O(5) \cdots O(7) \cdots O(6)	86.7 (2)
O(5) \cdots O(7) \cdots O(6')	119.9 (2)
O(5) \cdots O(7) \cdots O(5')	124.8 (1)
O(6) \cdots O(7) \cdots O(1)	123.5 (2)

A similar effect is found in $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$, where the longest Cl–O distance deviates 0.022 \AA from the mean and where the corresponding oxygen atom accepts two hydrogen bonds. There is only one more hydrogen

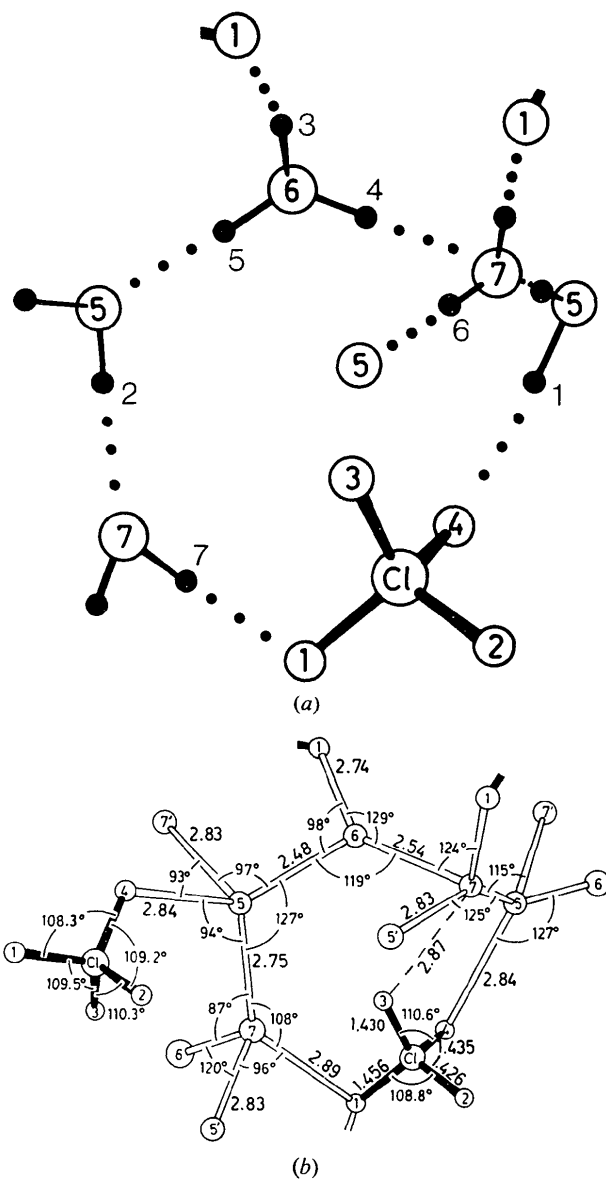


Fig. 2. (a) The hydrogen positions and the corresponding hydrogen bond system. (b) Bond distances and angles.

bond in the dihydrate, and here again it corresponds to the second longest Cl–O distance. This effect cannot be interpreted as being due entirely to a lengthening of the Cl–O bond, however, since a stabilizing effect on the thermal motion of the oxygen atom would have the same qualitative effect on the observed Cl–O distance.

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