

Table 6 (cont.)

| | |
|-----------------------------|------------|
| C(2)···H(3) ₅₆₅₂ | 2·951 (20) |
| H(1)···H(2) ₅₄₄₃ | 2·598 (20) |
| H(1)···H(2) ₅₅₄₁ | 2·991 (25) |
| H(2)···H(3) ₅₆₅₂ | 2·699 (25) |
| H(2)···H(4) ₅₆₅₁ | 2·818 (32) |
| H(3)···H(4) ₅₆₄₂ | 2·622 (27) |
| H(3)···H(4) ₅₆₅₁ | 2·634 (31) |

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Hydrogen-Bond Studies. XLV. The Crystal Structure of $\text{HClO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$

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The crystal structure of $\text{HClO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ has been determined from three-dimensional single-crystal X-ray diffraction data recorded at -188°C . The structure is monoclinic with space group $P2_1/c$ and contains eight formula units. The cell dimensions are $a=10\cdot960$, $b=7\cdot132$, $c=15\cdot167$ Å, $\beta=124\cdot55^\circ$. The structure contains H_2O molecules and H_3O^+ ions interlinked by hydrogen bonds to form infinite helices. These helices form layers both by hydrogen bond interlinkage and by hydrogen bonding to the perchlorate ions. The two independent perchlorate ions show only minor deviations from tetrahedral symmetry, and the mean Cl-O distances are 1·435 and 1·439 Å.

Introduction

This work is part of a systematic study of the hydrates of strong acids being carried out at this Institute aimed at investigating the hydration of the proton in the solid state. In $\text{HBr} \cdot \text{H}_2\text{O}$ (Lundgren, 1970), $\text{HCl} \cdot \text{H}_2\text{O}$ (Yoon & Carpenter, 1959), $\text{HClO}_4 \cdot \text{H}_2\text{O}$ (Lee & Carpenter, 1959; Nordman, 1962), $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (Taesler & Olovsson, 1968, 1969) the proton occurs as an H_3O^+ ion, whereas H_5O_2^+ has been found in $\text{HCl} \cdot 2\text{H}_2\text{O}$ and $\text{HCl} \cdot 3\text{H}_2\text{O}$ (Lundgren & Olovsson, 1967*a*, *b*), $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ (Olovsson, 1968), $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ (Kjällman & Olovsson, 1971), and in

$\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (Williams & Peterson, 1969*a*). The investigations of $\text{HClO}_4 \cdot 3\text{H}_2\text{O}$ (Almlöf, 1971) and $\text{HBr} \cdot 4\text{H}_2\text{O}$ (Lundgren & Olovsson, 1968) have indicated the existence of H_7O_3^+ . The latter compound has also been suggested to contain H_9O_4^+ ions. The present investigation of $\text{HClO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ is based on single-crystal X-ray diffraction data recorded at -188°C .

Experimental

A solution with the molar ratio $\text{H}_2\text{O}:\text{HClO}_4=2\cdot50$ was prepared by diluting analytical grade perchloric acid (*ca.* 73%) with distilled water and analysed by titration

with sodium hydroxide. Samples were sealed in glass capillaries of diameter 0.2–0.3 mm and wall thickness about 0.02 mm. The compound showed a pronounced tendency to supercool so the samples had to be seeded with quartz powder and treated with liquid nitrogen to induce crystallization.

Single crystals were grown using the zone-melting technique in a Weissenberg camera modified for low-temperature work (Olovsson, 1960). During this procedure the melting point was found to be in good agreement with the value -32.8°C reported by Mascherpa (1965). Equi-inclination Weissenberg photographs, layers $0 \leq l \leq 10$, were taken both at -50°C and -188°C using unfiltered Cu K radiation and employing the multiple-film technique with five films. The two data sets showed only minor differences, apparently caused by the difference in thermal motion at the two temperatures, and only data recorded at the lower temperature were used. 1987 independent reflexions were recorded, corresponding to 89% of the reflexions within the copper reflexion sphere; 216 of these were too weak to be measured. The relative intensities were estimated visually by comparison with an intensity scale. The whole data set was estimated twice and the mean values of the intensities were used. The data were corrected for the Lorentz and polarization effects and for absorption (cylindrical specimen). The linear absorption coefficient for Cu $K\alpha$ radiation is 54.6 cm^{-1} , and the radius of the crystal was 0.012 cm . The intensities were not corrected for secondary extinction effects.

The unit-cell dimensions were determined from quartz-calibrated zero-layer oscillation photographs. Data were collected from three crystals, rotated around [100], [101] and [110] and the cell dimensions were fitted to the measured θ -values by a least-squares procedure. Parameters used were $a_{\text{SiO}_2} = 4.9131\text{ \AA}$ at 25°C , $\lambda(\text{Cu } K\alpha_1) = 1.54051$, $\lambda(\text{Cu } K\alpha_2) = 1.54433$, $\lambda(\text{Cu } K\beta) = 1.39217\text{ \AA}$.

The cell dimensions (with e.s.d.'s in the least significant digit) at -188°C are;

$$\begin{aligned} a &= 10.960 (3) \text{ \AA} \\ b &= 7.132 (1) \\ c &= 15.167 (2) \\ \beta &= 124.55^\circ (1) \\ V &= 976.5 \text{ \AA}^3. \end{aligned}$$

The density was estimated to be 1.92 g.cm^{-3} at -80°C by determining the volume and weight of the polycrystalline mass in a number of sealed glass tubes. Assuming eight formula units in the cell the calculated density at -188°C is 1.979 g.cm^{-3} .

Space group and structure determination

The diffraction symmetry and systematic absences suggest the space group $P2_1/c$ (No. 14 in *International Tables for X-ray Crystallography*, 1952). The coordinates of the chlorine atoms were determined from a

three-dimensional Patterson synthesis and those of oxygen from electron-density maps based on the chlorine positions.

Coordinates and individual isotropic thermal parameters for the heavy atoms and scale factors for the eleven layers were refined in a series of least-squares calculations. The function $\sum w(|F_o| - |F_c|)^2$ was minimized using the full-matrix program *LALS*. After two cycles of refinement the discrepancy index $R = \sum |F_o| - |F_c| / \sum |F_o|$ for observed reflexions was 0.14. Anisotropic thermal parameters were then refined together with an overall scale factor. The inter-layer scale factors were set to the values obtained in the isotropic refinement. The total number of parameters increased from 71 to 136 and the R value dropped to 0.095 after two more cycles of refinement. 16 strong reflexions with low θ values and $F_o \ll |F_c|$ were then given zero weight in all further calculations. These were probably subject to secondary extinction and some might also have been incorrectly measured because of spot deformation. Further series of refinement, first isotropic and then anisotropic, lowered R to 0.081. The shifts in the positional parameters were all less than 0.5σ , but some of the thermal parameters increased significantly.

In order to locate the hydrogen atoms a three-dimensional difference Fourier synthesis was calculated using only data with $\sin \theta / \lambda$ less than 0.5 \AA^{-1} . Peaks with heights between 0.4 and 0.6 e.\AA^{-3} were found at expected hydrogen atom positions. Another peak of height 0.4 e.\AA^{-3} was also found but was situated close to a chlorine atom and could be definitely excluded as a possible hydrogen atom position. When the hydrogen atoms were included with fixed coordinates and fixed Debye–Waller factors of 3.0 \AA^2 , the R value in the final anisotropic refinement decreased to 0.075. The parameter shifts in the final cycle were all less than one tenth of the corresponding estimated standard deviations. The weighting scheme used in the final cycle was $w = (7.2 + |F_o| + 0.017|F_o|^2)^{-1}$ for observed and $w = 0$ for unobserved reflexions. An analysis of the weighting scheme suggested that these weights were suitable.

The atomic coordinates and thermal parameters with e.s.d.'s from the final refinement are listed in Tables 1 and 2. Observed and calculated structure factors are listed in Table 3.

Table 1. Atomic coordinates with estimated standard deviations ($\times 10^4$)

| | <i>x</i> | <i>y</i> | <i>z</i> |
|-------|----------|----------|----------|
| Cl(1) | 2762 (1) | 1661 (1) | 942 (1) |
| O(11) | 3143 (4) | 2589 (5) | 306 (3) |
| O(12) | 1313 (4) | 860 (5) | 241 (3) |
| O(13) | 3809 (3) | 175 (4) | 1562 (2) |
| O(14) | 2766 (4) | 2997 (5) | 1654 (3) |
| Cl(2) | 7491 (1) | 3067 (1) | 1708 (1) |
| O(21) | 6463 (4) | 4397 (4) | 932 (2) |
| O(22) | 8681 (4) | 4084 (4) | 2632 (3) |
| O(23) | 8090 (4) | 1917 (4) | 1267 (3) |
| O(24) | 6792 (4) | 1879 (5) | 2066 (3) |
| O(1) | 112 (3) | 4992 (4) | 1266 (2) |

Table 1 (*cont.*)

| | x | y | z |
|------|----------|----------|----------|
| O(2) | 1485 (3) | 2888 (4) | 2930 (2) |
| O(3) | 4394 (3) | 3612 (4) | 4077 (2) |
| O(4) | 5701 (3) | 1164 (4) | 3735 (2) |
| O(5) | 8628 (3) | 1855 (4) | 4516 (2) |

Hydrogen coordinates from the difference maps ($\times 10^3$)

| | x | y | z |
|----------------------------------|-----|-----|-----|
| H ₃ O(1) ⁺ | 911 | 66 | 377 |
| | 945 | 420 | 61 |
| | 74 | 414 | 186 |
| H ₂ O(2) | 140 | 159 | 271 |
| | 73 | 298 | 308 |
| H ₃ O(3) ⁺ | 331 | 311 | 365 |
| | 492 | 277 | 385 |
| | 424 | 479 | 367 |
| H ₂ O(4) | 502 | 111 | 295 |
| | 563 | 998 | 398 |
| H ₂ O(5) | 754 | 167 | 416 |
| | 886 | 318 | 467 |

Description of the structure

The structure is shown in Figs. 1–3. Bond distances and angles are listed in Tables 4 and 5 and are illustrated in Figs. 4 and 5. The corrections to the bond distances for anisotropic thermal riding motion are all less than 0.011 Å. Assuming independent motion, the corresponding corrections are less than 0.026 Å. Since inter-layer scale factors were refined these corrections are rather uncertain. Only uncorrected values are therefore listed. Standard deviations of 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 cycle of refinement. The uncer-

Table 2. Thermal parameters with *e.s.d.*'s ($\times 10^4$)The form of the temperature factor is $\exp(-\beta_{11}h^2 - \dots - \beta_{12}hk - \dots)$.

| | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|--------------|--------------|--------------|--------------|--------------|--------------|
| Cl(1) | 15 (1) | 18 (2) | 13 (1) | 0 (2) | 14 (1) | -1 (1) |
| O(11) | 60 (4) | 55 (6) | 24 (2) | -19 (8) | 45 (5) | -5 (6) |
| O(12) | 32 (4) | 61 (6) | 36 (2) | -9 (8) | 17 (5) | 6 (6) |
| O(13) | 32 (4) | 29 (5) | 18 (2) | 12 (7) | 19 (4) | 3 (5) |
| O(14) | 46 (4) | 52 (6) | 24 (2) | 20 (8) | 43 (5) | -4 (5) |
| Cl(2) | 15 (1) | 20 (2) | 11 (1) | 1 (2) | 13 (1) | 2 (1) |
| O(21) | 36 (3) | 44 (5) | 17 (2) | 11 (7) | 19 (4) | 4 (5) |
| O(22) | 31 (4) | 46 (6) | 19 (2) | -13 (7) | 17 (4) | -9 (5) |
| O(23) | 47 (4) | 49 (6) | 24 (2) | 3 (8) | 43 (5) | -12 (5) |
| O(24) | 42 (4) | 61 (6) | 26 (2) | -30 (8) | 33 (5) | -4 (5) |
| O(1) | 24 (3) | 33 (5) | 16 (2) | 4 (6) | 11 (4) | -1 (5) |
| O(2) | 33 (4) | 30 (5) | 21 (2) | -4 (7) | 27 (4) | -2 (5) |
| O(3) | 24 (4) | 51 (5) | 18 (2) | 0 (7) | 23 (4) | 3 (5) |
| O(4) | 22 (4) | 35 (5) | 15 (2) | -7 (6) | 16 (4) | -5 (5) |
| O(5) | 22 (4) | 32 (5) | 16 (2) | 7 (6) | 13 (4) | 2 (5) |

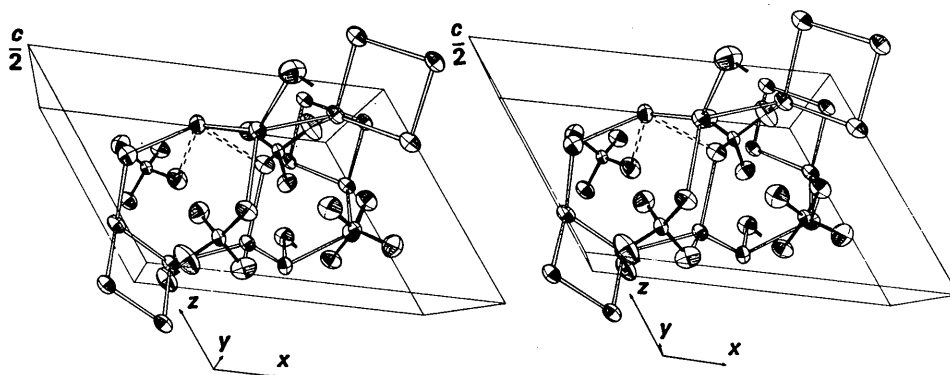


Fig. 1. A stereoscopic pair of drawings showing the hydrogen bond system. Covalent bonds are filled. Full lines represent O–O distances corresponding to normal hydrogen bonds and broken lines represent bifurcated hydrogen bonds. Only one half of the unit cell is drawn in the *c* direction. For notation, see Fig. 4.

Table 3. Observed and calculated structure factors

The three columns are, in order, I, 10|F_o|, 10|F_c|. Unobserved reflexions are marked with*, the values of F_o given correspond to half the minimum observable intensities. Strong reflexions excluded from the refinement are marked with**.

Table with multiple columns containing numerical data for structure factors. The data is organized in a grid-like format with various numerical values and some asterisks indicating unobserved or strong reflexions.

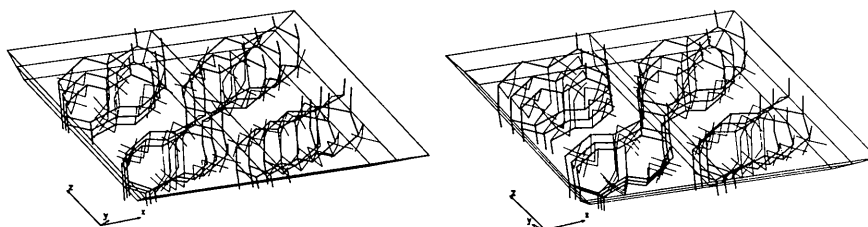


Fig. 2. A stereoscopic pair of drawings showing the packing of the structure. Four unit-cells are drawn, two in the *a* and two in the *b* direction.

tainties in the cell dimensions have also been taken into account.

Table 4. Bond distances with *e.s.d.*'s $\times 10^3$

The distances have not been corrected for thermal motion.

| Covalent bonds | | Hydrogen bonds | |
|----------------|-------------|----------------|-------------|
| Cl(1)–O(11) | 1·414 (4) Å | O(1)···O(5) | 2·634 (4) Å |
| Cl(1)–O(12) | 1·436 (3) | O(1)···O(5') | 2·555 (5) |
| Cl(1)–O(13) | 1·449 (3) | O(1)···O(2) | 2·565 (4) |
| Cl(1)–O(14) | 1·439 (3) | O(3)···O(2) | 2·677 (5) |
| | | O(2)···O(22) | 2·819 (5) |
| Cl(2)–O(21) | 1·432 (3) | O(3)···O(4) | 2·493 (4) |
| Cl(2)–O(22) | 1·456 (3) | O(3)···O(24) | 2·750 (5) |
| Cl(2)–O(23) | 1·431 (3) | O(3)···O(13) | 2·860 (5) |
| Cl(2)–O(24) | 1·440 (4) | O(4)···O(13) | 2·812 (4) |
| | | O(5)···O(4) | 2·762 (4) |
| | | O(4)···O(11) | 2·852 (4) |
| | | O(5)···O(12) | 2·876 (5) |

The water molecules are bonded together by hydrogen bonds to form infinite helices. The helices, which run in the *b* direction, are interconnected by rather short hydrogen bonds to form layers parallel to (10 $\bar{2}$) (see Fig. 2).

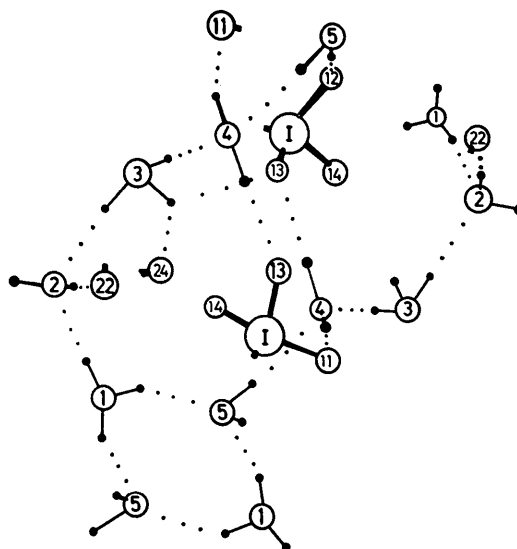


Fig. 3. The hydrogen atom positions found from the difference maps, and the corresponding hydrogen-bond system. The orientation is the same as in Fig. 4.

Table 5. Angles with *e.s.d.*'s $\times 10$

| Angle | | Angle | |
|-------------------|------------|----------------------|-----------|
| O(11)–Cl(1)–O(12) | 108·1 (2)° | O(5)···O(1)···O(5') | 88·9 (1)° |
| O(11)–Cl(1)–O(13) | 110·7 (2) | O(5)···O(1)···O(2) | 125·0 (2) |
| O(11)–Cl(1)–O(14) | 109·0 (2) | O(5')···O(1)···O(2) | 113·1 (2) |
| O(12)–Cl(1)–O(13) | 109·0 (2) | O(1)···O(2)···O(3) | 110·1 (2) |
| O(12)–Cl(1)–O(14) | 110·5 (2) | O(1)···O(2)···O(22) | 111·3 (1) |
| O(13)–Cl(1)–O(14) | 109·5 (2) | O(3)···O(2)···O(22) | 103·4 (1) |
| | | O(2)···O(3)···O(4) | 110·0 (2) |
| O(21)–Cl(2)–O(22) | 108·6 (2) | O(2)···O(3)···O(24) | 78·0 (1) |
| O(21)–Cl(2)–O(23) | 110·6 (2) | O(4)···O(3)···O(24) | 125·7 (2) |
| O(21)–Cl(2)–O(24) | 111·1 (2) | O(2)···O(3)···O(13) | 130·9 (2) |
| O(22)–Cl(2)–O(23) | 109·7 (2) | O(4)···O(3)···O(13) | 67·5 (1) |
| O(22)–Cl(2)–O(24) | 107·9 (2) | O(24)···O(3)···O(13) | 68·6 (1) |
| O(23)–Cl(2)–O(24) | 108·8 (2) | O(3)···O(4)···O(5) | 116·8 (2) |
| | | O(3)···O(4)···O(13) | 106·9 (1) |
| | | O(5)···O(4)···O(13) | 116·9 (2) |
| | | O(3)···O(4)···O(11) | 131·4 (2) |
| | | O(5)···O(4)···O(11) | 82·4 (1) |
| | | O(11)···O(4)···O(13) | 101·1 (1) |
| | | O(1)···O(5)···O(1') | 91·1 (1) |
| | | O(4)···O(5)···O(1) | 119·7 (1) |
| | | O(4)···O(5)···O(1') | 104·7 (1) |
| | | O(4)···O(5)···O(12) | 99·7 (1) |
| | | O(1)···O(5)···O(12) | 125·4 (2) |
| | | O(1')···O(5)···O(12) | 115·1 (1) |

bonds (2.56 and 2.63 Å) to form an almost perfect square (angles 89 and 91°). The arrangement is also required by symmetry to be perfectly planar.

The bonding situation in the present compound in no way resembles that in $\text{HClO}_4 \cdot \text{H}_2\text{O}$ or in $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ so a detailed comparison would be of little relevance.

The perchlorate ions

The structure contains two independent perchlorate ions bonded to the water chains by hydrogen bonds with lengths between 2.75 and 2.88 Å. No other O...O distance is shorter than 2.96 Å.

The mean values of the uncorrected Cl-O distances in the two ClO_4^- ions are 1.435 (2) and 1.439 (2) Å. These are in good agreement with the results from $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ (Olovsson, 1968), $\text{HClO}_4 \cdot 3\text{H}_2\text{O}$ (Almlöf, 1971), and $\text{N}_2\text{H}_5\text{ClO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (Liminga, 1967b), where the mean values of the uncorrected distances are 1.438 (3), 1.437 (2) and 1.431 (2) Å.

The eight independent Cl-O distances show significant differences although none is sufficiently serious to challenge the assumption that the protons of HClO_4 have been transferred to water molecules. In $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{HClO}_4 \cdot 3\text{H}_2\text{O}$, it is found that the Cl-O distances are correlated with the hydrogen-bond coordination around the perchlorate oxygen atoms. Oxygen atoms accepting two hydrogen bonds have the longest Cl-O distance in both cases, followed by those accepting one hydrogen bond. No such conclusions can be drawn in the present case, however, since the oxygen atom with the shortest Cl-O distance [O(11), 1.414 (4) Å], apparently accepts a hydrogen bond.

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Die Kristallstruktur von $\alpha\text{-Li}_3\text{BO}_3$

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$\alpha\text{-Li}_3\text{BO}_3$ is monoclinic, space group $P2_1/c$ with four molecules in a unit cell of dimensions $a=3.265$, $b=9.180$, $c=8.316$ Å, $\beta=101.05^\circ$. The structure was solved by conventional Patterson and electron-density synthesis. Least-squares refinement on three-dimensional data yielded a residual $R=5.7\%$. The results reveal an unusual type of framework containing 'single' BO_3 triangles [$d(\text{B-O})=1.376$ Å]. The lithium atoms, linking the BO_3 groups, show a very distorted tetrahedral coordination by oxygen [$d(\text{Li-O})=1.99$ Å]; two of the lithium atoms have a fifth oxygen at 2.5 Å. The structure contains large holes and $(\text{Li-O})_3$ rings.

Einleitung

Mehrere Alkalimetallborate sind bereits an Einkristallen untersucht worden, bislang sind jedoch die

Strukturen von 'kationenreichen' (Hoppe, 1967) Boraten unbekannt. Dargestellt wurde bisher von Zintl & Morawietz (1938) Na_3BO_3 sowie von Rollett & Bouaziz (1955) Li_3BO_3 , das nach Lehmann & Wöckel