Hydrogen Bond Studies. CII.* An X-ray Determination of the Crystal Structure of Sodium Perchlorate Monohydrate, NaClO₄.H₂O

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The crystal structure of NaClO₄. H₂O has been determined from three-dimensional single-crystal X-ray diffraction data collected at room temperature using an automatic Stoe-Philips four-circle diffractometer. The unit cell is monoclinic with space group C2/c and contains eight formula units. The cell dimensions are a = 15.5422 (13), b = 5.5399 (5), c = 11.0455 (11) Å, $\beta = 110.666$ (8)°, V = 889.84 Å³. The final conventional R(F) value is 0.025. The structure comprises a three-dimensional network of ClO₄ tetrahedra linked together via weak O-H···O hydrogen bonds from the water molecules and electrostatic Na⁺···O interactions. Both of the hydrogen atoms of the water molecule appear to form weak bifurcated hydrogen-bond interactions, with O···O distances 3.024 (2) and 3.336 (2) Å for H(1) and 3.093 (2) and 3.156 (2) Å for H(2). The Na⁺ ions occupy special positions at (0.25, 0.25, 0.50) and (0, y, 0.25); the packing is such that each ion is approximately octahedrally coordinated with six oxygen atoms (two water oxygens and four oxygens belonging to different ClO₄ groups) with O(W)-Na-O(W) angles of 180 and 164.63 (7)°, and an Na-O(W)-Na angle of 117.80 (5)°.

Introduction

Sodium perchlorate monohydrate ($NaClO_4$, H_2O) has previously been studied using infrared spectroscopic methods by Brink & Falk (1970) and also by Bellamy, Blandamer, Symons & Waddington (1971). The observed O-H stretching frequencies ($\sim 150 \text{ cm}^{-1}$ lower than in a free water molecule) indicate that the water molecule is involved in very weak hydrogen bonding. Furthermore, the environment around the water molecule, while appearing symmetric at room temperature. becomes more asymmetric as the temperature is lowered (Brink & Falk, 1970). These workers suggested that the apparent spectroscopic equivalence of the two OH groups in the water molecule is purely fortuitous. rather than a result of crystal symmetry. It was felt that an X-ray structure determination of NaClO₄. H₂O would assist in resolving the situation around the water molecule. Neutron diffraction and n.m.r. studies of NaClO₄. H₂O are also in progress at this Institute. This work forms part of a series of studies of the water molecule in solid hydrates. The previous paper in the series is a combined n.m.r. and infrared investigation of LiHCOO. H₂O (Berglund, Lindgren & Tegenfeldt, 1974).

Crystal data

Sodium perchlorate monohydrate, NaClO₄. H₂O; F.W. 140.47. Monoclinic, a=15.5422 (13),* b=5.5399 (5), c=11.0455 (11) Å, $\beta=110.666$ (8)°, V=889.84 Å³ at 25°C, Z=8, $D_x=2.097$ g cm⁻³. Space group C2/c (No. 15).

Experimental

Commercially available sodium perchlorate monohydrate (*pro analysi*) was used to grow crystals from an aqueous solution by slow evaporation at room temperature. The flat plate-like crystals were hygroscopic but, in a dry environment, easily lost their water of crystallization. A crystal of dimensions $0.40 \times$ 0.25×0.23 mm was sealed in a thin-walled glass capillary, and its general quality checked by taking a Laue and a series of Weissenberg photographs.

The cell parameters were measured using an XDC 700 Guinier-Hägg powder camera with Cu $K\alpha_1$ radiation ($\lambda = 1.54051$ Å) and Si (a = 5.43054 Å) as an internal standard. A least-squares refinement with 54 observed θ values gave the cell parameters. Diffraction symmetry and systematic absences suggested the monoclinic space group C2/c or Cc. The centrosymmetric alternative C2/c was chosen as the most likely on chemical grounds. This was also supported by the good correspondence between the experimental E distribution and that expected theoretically for a centrosymmetric ric space group (Table 1).

Table 1.	Experie	mental d	and th	eoretical	statistical	distri-
buti	on of th	e norme	alized	structure	factors (E	;)

	Experimental	Centro- symmetric	Non- centrosymmetric
$\langle E ^2 \rangle$	1.001	1.000	1.000
$\langle E^2 - 1 \rangle$	0.982	0.968	0.736
$\langle E \rangle$	0.799	0 ·798	0.886
E > 3	0.2 %	0.3 %	0.01 %
E > 2	4.7 %	5.0%	1.8%
E > 1	31.8%	3 2 ·0 %	37.0%

^{*} Figures in parentheses represent estimated standard deviations of the least significant digits.

Data collection was carried out at $\sim 25^{\circ}$ C using a four-circle Stoe-Philips X-ray diffractometer operating in an $\omega/2\theta$ scan mode and controlled by a PDP8/I computer. Graphite-monochromated molybdenum radiation was used ($\lambda = 0.71069$ Å). During the first week of data collection the intensity of the strongest of the three standard reflexions increased steadily. This was probably brought about by radiation damage increasing the mosaicity and hence decreasing the extinction in the crystal. When this trend disappeared the data collection was restarted; from then on only small random fluctuations were observed. The integrated peak intensities so obtained were then corrected for background and assigned standard deviations $\sigma_{\rm count}(I)$ based on Poisson counting statistics. The reflexions were corrected for Lorentz, polarization and absorption effects (transmission factors: 0.822-0.864) to give F_o^2 and $\sigma_{\text{count}}(F_o^2)$ values. Of the 1287 independent reflexions collected (out to sin $\theta/\lambda = 0.704 \text{ Å}^{-1}$) 1175 were in excess of $3\sigma_{count}(F^2)$ and were used in the final refinements.

Structure determination and refinement

The approximate position of the chlorine atom was obtained from a three-dimensional Patterson synthesis. The positions of all other atoms were obtained subsequently from a series of Fourier difference syntheses.

The structure was refined with the full-matrix leastsquares program UPALS (Lundgren, 1974). The function minimized was $\sum w(|F_o^2| - |F_c^2|)^2$, where $w = 1/\sigma^2(F^2)$ and $\sigma^2(F^2) = \sigma_c^2(F^2) + (kF^2)^2$. The constant k was given the value 0.02. In the final cycles of refinement the parameters varied were: one scale factor, one isotropic extinction parameter, 25 atomic positional parameters, 46 anisotropic temperature factors for the non-hydrogen atoms and two isotropic temperature factors for the hydrogen atoms. The final shifts were all smaller than 0.3 σ . The final agreement indices were:

and

J

$$R_w(F^2) = \left[\sum w(|F_o^2| - |F_c^2|)^2 / \sum w|F_o^4|\right]^{1/2} = 0.068.$$

 $R(F^2) = \sum ||F_o^2| - |F_c^2|| / \sum |F_o^2| = 0.033$

The conventional agreement index R(F) was 0.025. The refined value of the isotropic extinction parameter g was 1300 (288) (Coppens & Hamilton, 1970).

The parameters after the last cycle are given in Tables 2 and 3. Observed and calculated structure factors are given in Table 4. The atomic scattering factors used for Na⁺, Cl and O were those suggested by Hanson, Herman, Lea & Skillman (1964). For H the spherical scattering factors proposed by Stewart, Davidson & Simpson (1965) were used. Values for the anomalous dispersion terms ($\Delta f'$ and $\Delta f''$) for Na and Cl were taken from Cromer (1965).

Table 2. Atomic coordinates for non-hydrogen atoms $(\times 10^5)$ and for hydrogen atoms $(\times 10^3)$

X	у	Z
Na(1) 25000	25000	50000
Na(2) 0	46626 (13)	25000
CI 12541 (2	2) $-2264(5)$	19332 (3)
O(1) 16733 (1	10) - 1625 (19)	33131 (11)
D(2) 19400 (1	-1163 (20)	13541 (16)
O(3) 6621 (1	10) 17957 (24)	15087 (12)
O(4) 7537 (8	-24320 (19)	15710 (10)
O(W) = 37467 (9)	2392 (25)	5100 (13)
H(1) 380 (2	2) 20 (5)	3 (3)
H(2) 364 (2	2) 153 (8)	47 (4)

Description of the structure

General

The atomic arrangement is illustrated in Fig. 1; interatomic distances and angles of interest are given in Table 5. The structure comprises a three-dimensional network of Na⁺ ions, ClO_4^- ions and water molecules, held together by electrostatic and hydrogenbond interactions. The latter are extremely weak and apparently bifurcated. A more definitive description of the hydrogenbond scheme awaits the findings of a current neutron diffraction study.

The sodium ion

The asymmetric unit includes two Na⁺ ions occupying the special positions (0.25, 0.25, 0.50) and (0, y, 0.25). The packing is such that the coordination around each ion approximates to regular octahedral (see Fig.

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

The form of the temperature factor is $\exp \left[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)\right]$. The r.m.s. components $(R_i \times 10^3 \text{ Å})$ of thermal displacement along the principal axes of the thermal vibration ellipsoids are also given along with the isotropic temperature factors (B, A^2) for the hydrogen atoms.

	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Na(1)	33 (1)	219 (2)	62 (1)	-3(1)	12(1)	-6(1)	176 (1)	187 (1)	199 (1)
Na(2)	37 (1)	245 (2)	65 (Ì)	0 ``	18 (1)	0	187 (1)	195 (1)	198 (1)
CI	34 (1)	163 (Ì)	51 (Ì)	-5(1)	20 (1)	-12(1)	148 (1)	164 (1)	193 (1)
O(1)	72 (1)	314 (4)	58 (1)	-31(1)	8 (1)	-25(1)	165 (1)	223 (1)	301 (2)
O(2)	67 (1)	352 (4)	158 (2)	- 30 (1)	78 (1)	-54(2)	171 (1)	222 (1)	329 (2)
O(3)	80 (1)	352 (4)	112 (Ì)	84 (2)	43 (1)	40 (2)	180 (1)	235 (1)	328 (2)
O(4)	63 (1)	308 (4)	76 (l)	-68(1)	26 (1)	-35(1)	167 (1)	201 (1)	295 (1)
O(W)	42 (1)	301 (4)	70 (l)	-24(1)	13 (1)	14 (1)	189 (1)	192 (1)	248 (1)
H(1)	6.7 (10)				. ,				
H(2)	10·9 (12)								

2) with mean Na⁺...O distances of 2.371 and 2.391 Å [cf. the Na⁺ ion in NaHC₂O₄. H₂O (Tellgren & Olovsson, 1971); this has approximately octahedral

coordination with a mean $Na^+ \cdots O$ distance of 2.390 Å]. It will be observed that each Na^+ ion has two water-oxygen nearest neighbours together with a

Table 4. Observed and calculated X-ray structure factors for NaClO₄. H₂O

The five columns are, in order: k, l, $100|F_o|$, $100|F_c|$ and 100E, where E is the extinction correction factor multiplying F_o . Asterisks mark reflexions not included in the final refinement.

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Fig. 1. A stereoscopic illustration of the structure. The labelled atoms represent the chosen asymmetric unit. Covalent bonds: thick solid lines; $H \cdots O$ contacts: thick unfilled lines; electrostatic interactions: thin unbroken lines. Here, and in the figures which follow, thermal ellipsoids for non-hydrogen atoms are drawn to include 50 % probability. B(H) values are fixed at 1.5 Å².



Fig. 2. The environments of the two independent sodium ions: (a) Na(1) at (0.25, 0.25, 0.50) and (b) Na(2) at (0, y, 0.25).

further four oxygens belonging to different ClO₄ ions. In the $\cdots O(W) \cdots Na(1) \cdots O(W) \cdots Na(2) \cdots$ $O(W) \cdots$ zigzag chains which arise, the O(W)-Na(1)-O(W) angle is required by symmetry to be 180°, and the O(W)-Na(2)-O(W) angle is 164.63 (7)°. The Na(1)-O(W)-Na(2) angle is 117.80 (5)°.

The perchlorate ion

The conformation of the ClO_4^- ion is close to tetrahedral (see Fig. 3 and Table 5) with a mean Cl-O distance of 1.426 Å. Mean Cl-O distances for related compounds are listed in Table 6. It will be noted that

Table 5. Interatomic distances (Å) and angles (°)

The symmetry operations implied by the subscripts are the following:

a c e g i	$\begin{array}{c} \frac{1}{2} - x, \\ \frac{1}{2} - x, \\ x, \\ -x, \\ \frac{1}{2} + x, \end{array}$	$\frac{\frac{1}{2} + y, \frac{1}{2} - z}{\frac{1}{2} - y, -z} - y, \frac{1}{2} + z} \\ 1 + y, \frac{1}{2} - z - \frac{1}{2} + y, z$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$-\frac{1}{2} + z$ z $\frac{1}{2} - z$ $-z$
(a) Cl	O₄ ion			
	Cl-O(1)	1.431 (1)	O(1)-Cl-O(2)	110.21 (9)
	Cl-O(2)	1.425 (1)	O(1) - C1 - O(3)	109.30 (8)
	Cl-O(3)	1.420(1)	O(1) - Cl - O(4)	108.53 (6
	Cl-O(4)	1.428 (1)	O(2) - Cl - O(3)	108.56 (8)
Mean	Cl-O	1.426	O(2) - Cl - O(4)	109.31 (7)
			O(3) - C1 - O(4)	110.93 (9)

the smallest mean Cl-O distances arise in the two metal salts (LiClO₄.3H₂O and NaClO₄.H₂O). This is in good agreement with the fact that, in both compounds, the ClO₄ tetrahedra form only very weak hydrogen bonds to the water molecules. It has been noted earlier that, within a ClO_4^- group, a correlation can be found between the coordination around a given perchlorate oxygen atom and its Cl-O distance (Olovsson, 1968; Almlöf, 1972).

Table 6. Mean Cl–O distances observed in ClO_{4}^{-} ions

Compound	Distance (Å)	Reference
NaClO ₄ .H ₂ O	1.426 (2)	This work
HClO ₄ .3H ₂ O	1.437 (2)	Almlöf (1972)
HClO ₄ .2H ₂ O	1.438 (3)	Olovsson (1968)
$HClO_4.2\frac{1}{2}H_2O$	1.435 (2)	Almlöf, Lundgren & Olovsson
	1.439 (2)	(1971)
$N_2H_5ClO_4$. $\frac{1}{2}H_2$	O 1.431 (2)	Liminga (1967)
LiClO ₄ .3H ₂ O	1.426 (4)	Datt, Rannev & Ozerov (1968)

The water molecule

The environment of the water molecule is illustrated in Fig. 4. The water-oxygen atom constitutes a common corner in the two different NaO₆ octahedra, as well as being involved in weak hydrogen bonding to three different ClO_4^- tetrahedra. The environments around the two O-H bonds are clearly not crystallographically equivalent; both hydrogens appear to participate in weak bifurcated hydrogen-bond interactions: H(1) with O(1) and O(2), and H(2) with O(3)and O(4). Earlier infrared experiments (see Introduction) suggest the two O-H groups to be spectroscopically equivalent. Since the O-H stretching frequencies can be taken to reflect the strength of the hydrogenbond participation of the two hydrogen atoms, it may be concluded that the effective strengths of the hy-

O(1) drogen-bond interactions O(W)-H(1)and O(2)



(b) Na	a ⁺ ion				
	$Na(1)\cdots O(W)_a$ Na(1)\cdots O(1)	2·367 (1) 2·368 (1)		$\begin{array}{l} O(W)_e \cdots Na(1) \cdots O(1) \\ O(W)_e \cdots Na(1) \cdots O(2)_e \end{array}$	87·66 (5) 86·84 (5)
Mean	$\operatorname{Na}(1)\cdots \operatorname{O}(2)_a$ $\operatorname{Na}(1)\cdots \operatorname{O}$	2·378 (1) 2·371		$O(1)\cdots Na(1)\cdots O(2)_e$	86.08 (5)
	$Na(2)\cdots O(W)_a$ $Na(2)\cdots O(3)$	2.389(1) 2.361(1)		$O(3)\cdots Na(2)\cdots O(3)_h$ $O(3)\cdots Na(2)\cdots O(W)_f$	95·46 (7) 90·60 (5)
Mean	$Na(2) \cdots O(4)_b$ $Na(2) \cdots O$	2·422 (1) 2·391		$O(3) \cdots Na(2) \cdots O(W)_a$ $O(3) \cdots Na(2) \cdots O(4)_b$	99·75 (5) 84·00 (5)
				$\begin{array}{c} \mathcal{O}(W)_a \cdots \mathcal{N}a(2) \cdots \mathcal{O}(4)_b \\ \mathcal{O}(W)_f \cdots \mathcal{N}a(2) \cdots \mathcal{O}(4)_b \end{array}$	86·66 (5) 83·14 (4)
പ	O molecula			$O(4)_g \cdots Na(2) \cdots O(4)_b$	96.69 (6)
(C) H ₂	U molecule				
	$O(W) \cdots O(1)_a$ $O(W) \cdots O(2)_c$ $Na(1)_d \cdots O(W) \cdots$	$\begin{cases} 3.034 (2) \\ 3.336 (2) \\ Na(2)_{l} \end{cases}$	117.80 (5)	$O(W)\cdots O(4)_{J}$ $O(W)\cdots O(3)_{c}$	$\begin{cases} 3.093 (2) \\ 3.156 (2) \end{cases}$

Table 5 (cont.)



Fig. 3. A stereoscopic illustration of the environment of the ClO₄⁻ ion. B(H) values are fixed at 1.5 Å²; hydrogen atom positions are adjusted to give O-H distances of 1.0 Å.

O(3) O(W)-H(2) are roughly the same. A note of O(4)

caution, however: the extremely high isotropic temperature factors and very short O-H distances (0.57 and 0.73 Å) associated with both hydrogen atoms suggest that the water molecule may well be subject to some form of disordering.

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Fig. 4. The bonding situation around the water molecule.

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