

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 (NaClO₄·H₂O) 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 (~ 150 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).

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

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 × 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 space group (Table 1).

Table 1. *Experimental and theoretical statistical distribution of the normalized 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 %	32.0 %	37.0 %

2) with mean $\text{Na}^+\cdots\text{O}$ distances of 2.371 and 2.391 Å [cf. the Na^+ ion in $\text{NaHC}_2\text{O}_4\cdot\text{H}_2\text{O}$ (Tellgren & Olovsson, 1971)]; this has approximately octahedral

coordination with a mean $\text{Na}^+\cdots\text{O}$ 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 $\text{NaClO}_4\cdot\text{H}_2\text{O}$

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

k	l	$100 F_o $	$100 F_c $	$100E$
0	0	100	100	100
0	1	100	100	100
0	2	100	100	100
0	3	100	100	100
0	4	100	100	100
0	5	100	100	100
0	6	100	100	100
0	7	100	100	100
0	8	100	100	100
0	9	100	100	100
0	10	100	100	100
0	11	100	100	100
0	12	100	100	100
0	13	100	100	100
0	14	100	100	100
0	15	100	100	100
0	16	100	100	100
0	17	100	100	100
0	18	100	100	100
0	19	100	100	100
0	20	100	100	100
0	21	100	100	100
0	22	100	100	100
0	23	100	100	100
0	24	100	100	100
0	25	100	100	100
0	26	100	100	100
0	27	100	100	100
0	28	100	100	100
0	29	100	100	100
0	30	100	100	100
0	31	100	100	100
0	32	100	100	100
0	33	100	100	100
0	34	100	100	100
0	35	100	100	100
0	36	100	100	100
0	37	100	100	100
0	38	100	100	100
0	39	100	100	100
0	40	100	100	100
0	41	100	100	100
0	42	100	100	100
0	43	100	100	100
0	44	100	100	100
0	45	100	100	100
0	46	100	100	100
0	47	100	100	100
0	48	100	100	100
0	49	100	100	100
0	50	100	100	100
0	51	100	100	100
0	52	100	100	100
0	53	100	100	100
0	54	100	100	100
0	55	100	100	100
0	56	100	100	100
0	57	100	100	100
0	58	100	100	100
0	59	100	100	100
0	60	100	100	100
0	61	100	100	100
0	62	100	100	100
0	63	100	100	100
0	64	100	100	100
0	65	100	100	100
0	66	100	100	100
0	67	100	100	100
0	68	100	100	100
0	69	100	100	100
0	70	100	100	100
0	71	100	100	100
0	72	100	100	100
0	73	100	100	100
0	74	100	100	100
0	75	100	100	100
0	76	100	100	100
0	77	100	100	100
0	78	100	100	100
0	79	100	100	100
0	80	100	100	100
0	81	100	100	100
0	82	100	100	100
0	83	100	100	100
0	84	100	100	100
0	85	100	100	100
0	86	100	100	100
0	87	100	100	100
0	88	100	100	100
0	89	100	100	100
0	90	100	100	100
0	91	100	100	100
0	92	100	100	100
0	93	100	100	100
0	94	100	100	100
0	95	100	100	100
0	96	100	100	100
0	97	100	100	100
0	98	100	100	100
0	99	100	100	100
0	100	100	100	100

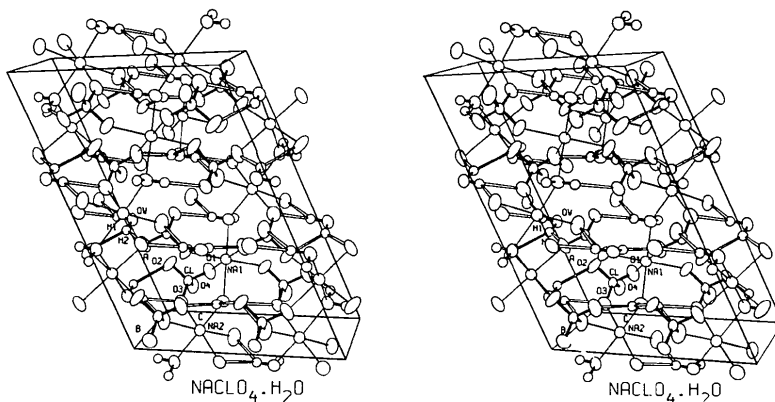


Fig. 1. A stereoscopic illustration of the structure. The labelled atoms represent the chosen asymmetric unit. Covalent bonds: thick solid lines; $\text{H}\cdots\text{O}$ contacts: thick unfilled lines; electrostatic interactions: thin unbroken lines. Here, and in the figures which follow, thermal ellipsoids for non-hydrogen atoms are drawn to include 50% probability. $B(\text{H})$ values are fixed at 1.5 \AA^2 .

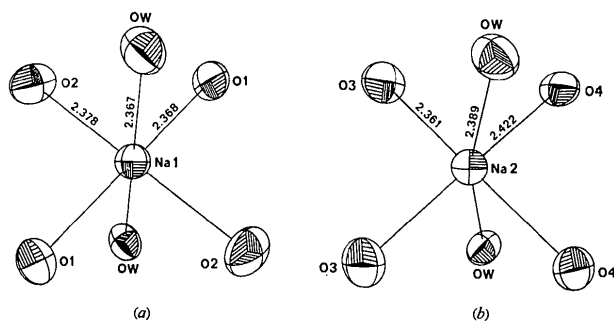


Fig. 2. The environments of the two independent sodium ions: (a) Na(1) at (0.25, 0.25, 0.50) and (b) Na(2) at (0, y , 0.25).

further four oxygens belonging to different ClO_4^- ions. In the $\cdots\text{O}(W)\cdots\text{Na}(1)\cdots\text{O}(W)\cdots\text{Na}(2)\cdots\text{O}(W)\cdots$ zigzag chains which arise, the $\text{O}(W)\text{--Na}(1)\text{--O}(W)$ angle is required by symmetry to be 180° , and the $\text{O}(W)\text{--Na}(2)\text{--O}(W)$ angle is $164.63(7)^\circ$. The $\text{Na}(1)\text{--O}(W)\text{--Na}(2)$ angle is $117.80(5)^\circ$.

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 ($^\circ$)*

The symmetry operations implied by the subscripts are the following:

<i>a</i>	$\frac{1}{2}-x,$	$\frac{1}{2}+y,$	$\frac{1}{2}-z$	<i>b</i>	$x,$	$1+y,$	z
<i>c</i>	$\frac{1}{2}-x,$	$\frac{1}{2}-y,$	$-z$	<i>d</i>	$x,$	$-y,$	$-\frac{1}{2}+z$
<i>e</i>	$x,$	$-y,$	$\frac{1}{2}+z$	<i>f</i>	$-\frac{1}{2}+x,$	$\frac{1}{2}+y,$	z
<i>g</i>	$-x,$	$1+y,$	$\frac{1}{2}-z$	<i>h</i>	$-x,$	$y,$	$\frac{1}{2}-z$
<i>i</i>	$\frac{1}{2}+x,$	$-\frac{1}{2}+y,$	z	<i>j</i>	$\frac{1}{2}-x,$	$\frac{1}{2}-y,$	$-z$

(a) ClO_4^- ion

Cl–O(1)	1.431 (1)	O(1)–Cl–O(2)	110.21 (9)
Cl–O(2)	1.425 (1)	O(1)–Cl–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)–Cl–O(4)	110.93 (9)

Table 5 (cont.)

(b) Na^+ ion

Na(1) $\cdots\text{O}(W)_a$	2.367 (1)	$\text{O}(W)_e\cdots\text{Na}(1)\cdots\text{O}(1)$	87.66 (5)
Na(1) $\cdots\text{O}(1)$	2.368 (1)	$\text{O}(W)_e\cdots\text{Na}(1)\cdots\text{O}(2)_e$	86.84 (5)
Na(1) $\cdots\text{O}(2)_a$	2.378 (1)	$\text{O}(1)\cdots\text{Na}(1)\cdots\text{O}(2)_e$	86.08 (5)
Mean Na(1) $\cdots\text{O}$	2.371		
Na(2) $\cdots\text{O}(W)_a$	2.389 (1)	$\text{O}(3)\cdots\text{Na}(2)\cdots\text{O}(3)_h$	95.46 (7)
Na(2) $\cdots\text{O}(3)$	2.361 (1)	$\text{O}(3)\cdots\text{Na}(2)\cdots\text{O}(W)_f$	90.60 (5)
Na(2) $\cdots\text{O}(4)_b$	2.422 (1)	$\text{O}(3)\cdots\text{Na}(2)\cdots\text{O}(W)_a$	99.75 (5)
Mean Na(2) $\cdots\text{O}$	2.391	$\text{O}(3)\cdots\text{Na}(2)\cdots\text{O}(4)_b$	84.00 (5)
		$\text{O}(W)_a\cdots\text{Na}(2)\cdots\text{O}(4)_b$	86.66 (5)
		$\text{O}(W)_f\cdots\text{Na}(2)\cdots\text{O}(4)_b$	83.14 (4)
		$\text{O}(4)_g\cdots\text{Na}(2)\cdots\text{O}(4)_b$	96.69 (6)

(c) H_2O molecule

$\text{O}(W)\cdots\text{O}(1)_a$	$\left\{ \begin{array}{l} 3.034 (2) \\ 3.336 (2) \end{array} \right.$	$\text{O}(W)\cdots\text{O}(4)_j$	$\left\{ \begin{array}{l} 3.093 (2) \\ 3.156 (2) \end{array} \right.$
$\text{O}(W)\cdots\text{O}(2)_c$		$\text{O}(W)\cdots\text{O}(3)_c$	
$\text{Na}(1)_a\cdots\text{O}(W)\cdots\text{Na}(2)_i$	117.80 (5)		

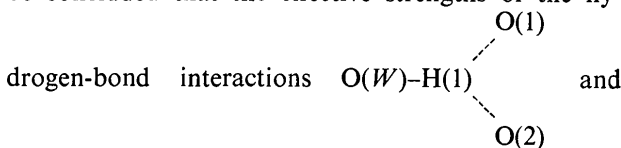
the smallest mean Cl–O distances arise in the two metal salts ($\text{LiClO}_4\cdot 3\text{H}_2\text{O}$ and $\text{NaClO}_4\cdot \text{H}_2\text{O}$). This is in good agreement with the fact that, in both compounds, the ClO_4^- tetrahedra form only very weak hydrogen bonds to the water molecules. It 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
$\text{NaClO}_4\cdot \text{H}_2\text{O}$	1.426 (2)	This work
$\text{HClO}_4\cdot 3\text{H}_2\text{O}$	1.437 (2)	Almlöf (1972)
$\text{HClO}_4\cdot 2\text{H}_2\text{O}$	1.438 (3)	Olovsson (1968)
$\text{HClO}_4\cdot 2\frac{1}{2}\text{H}_2\text{O}$	1.435 (2)	Almlöf, Lundgren & Olovsson (1971)
	1.439 (2)	
$\text{N}_2\text{H}_5\text{ClO}_4\cdot \frac{1}{2}\text{H}_2\text{O}$	1.431 (2)	Liminga (1967)
$\text{LiClO}_4\cdot 3\text{H}_2\text{O}$	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 NaO_6 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 hydrogen-bond participation of the two hydrogen atoms, it may be concluded that the effective strengths of the hy-



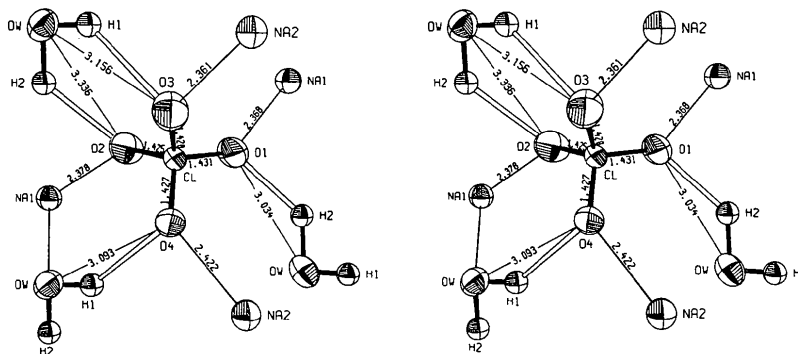


Fig. 3. A stereoscopic illustration of the environment of the ClO_4^- ion. $B(\text{H})$ values are fixed at 1.5 \AA^2 ; hydrogen atom positions are adjusted to give O-H distances of 1.0 \AA .

$\text{O}(W)\text{-H}(2)$ are roughly the same. A note of caution, however: the extremely high isotropic temperature factors and very short O-H distances (0.57 and 0.73 \AA) associated with both hydrogen atoms suggest that the water molecule may well be subject to some form of disordering.

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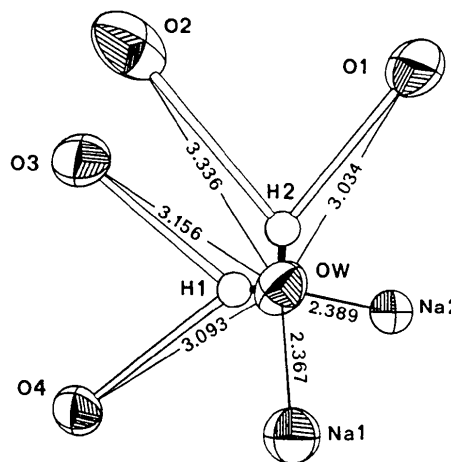


Fig. 4. The bonding situation around the water molecule.