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Hydrogen Bond Studies. CXVI. A Neutron Diffraction Study of the Structure of Sodium Perchlorate Monohydrate, $NaClO_4.H_2O$, at 298K

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The structure of sodium perchlorate monohydrate has been determined previously by X-ray diffraction methods [Berglund, Thomas & Tellgren, *Acta Cryst.* (1975), B31, 1842–1846]. The prime aim of the present single-crystal neutron diffraction study is to investigate the geometry, vibrational motion and hydrogen-bond arrangement associated with the water molecule. No conclusive evidence in support of statistical disordering is forthcoming in spite of the anomalously large amplitudes of thermal vibration found for the hydrogen atoms in the plane of the water molecule: largest r.m.s. vibrational amplitudes are 0·53 (1) and 0·46 (1) Å for the hydrogen atoms, and these in directions only 0·4 and 3·7° out of the H_2O plane. Amplitudes perpendicular to the plane are both $\sim$0·26 Å. The H···O hydrogen-bond contacts are long: 2·378 (10) and 2·389 (7) Å for H(1) and 2·152 (8) Å for H(2), confirming the weakness of the hydrogen bonding to the water molecule. The O–H distances [O(*W*)–H(1) 0·905 (6), O(*W*)–H(2) 0·935 (7) Å] are seriously foreshortened as a result of the large librational (or pseudo-librational) motion of the molecule. The H–O–H angle is 105·7 (8)°.

Introduction

An earlier X-ray determination of the structure of sodium perchlorate monohydrate (Berglund, Thomas & Tellgren, 1975) (hereafter BTT) confirmed earlier predictions made on the basis of IR data (Brink & Falk, 1970; Bellamy, Blandamer, Symons & Waddington, 1971) that the water molecule is extremely weakly hydrogen-bonded in the structure. All O(*W*)···O hydrogen-bond interaction distances were found to be in excess of 3·0 Å. On the other hand, the X-ray diffraction study could say little about the hydrogen bonding associated with the water molecule. It is thus the main purpose of the present study to attempt to rectify this situation.

Experimental

Suitably large single crystals were grown as described in BTT. A summary of crystal data is given in Table 1. The crystal chosen for data-collection purposes was sealed into a thin-walled quartz glass tube. It had a somewhat irregular plate-like form and a volume of 35·1 mm^3; crystal shape and dimensions are summarized in Table 2. The intensity measurements were made using a Hilger & Watts four-circle diffractometer controlled by a PDP-8 computer at the R2 reactor at Studsvik, Sweden. The apparatus used is described more fully in Tellgren, Ramanujam & Liminga (1974) and references therein. The intensity of the beam at the crystal is $\sim 10^6$ neutrons cm^{-2}s^{-1} at a wavelength of 1·210 Å. The crystal orientation was such that the χ and φ angles for the $h00$, $0k0$ and $00l$ reflexions were 82·49, −38·60; 1·85, −142·75; and 13·38, −52·31° respectively [symmetrical A setting: Arndt & Willis (1966)]. A complete set of symmetry-independent reflexions was collected out to $\sin\theta/\lambda = 0{\cdot}693$ Å^{-1} using an $\omega/2\theta$ scan mode, with three standard reflexions interspersed at regular intervals throughout the data set. Unlike the X-ray case, where time-dependent extinction effects were observed, only random fluctuations of up to about $\pm 4\sigma(I)_{\text{count}}$ were obtained. The intensity data were corrected for background (by the 'background-peak-background' method), and values of $\sigma(I)_{\text{count}}$ were calculated assuming Poisson counting statistics. The intensities were then reduced to a set of F^2_{obs} values after correction for the Lorentz effect and absorption. The value used for the linear absorption coefficient (μ) was determined experimentally to be 1·45 cm^{-1}. This gives a value of 68·4 barns for the incoherent scattering cross-section for hydrogen. The calculated range of transmission factors was 0·57–0·83. Of the 1248 independent reflexions measured, 285 had intensities less than $2\sigma_{\text{count}}$ and were not included in the refinements.

Table 1. *Crystal data for sodium perchlorate monohydrate at* 25°C

Numbers in parentheses here and throughout the paper give the estimated standard deviations on the least significant digits.

$NaClO_4.H_2O$, F.W. 140·47
Space group $C2/c$ (No. 15), $Z=8$
a = 15·5422 (13) Å (Berglund *et al.*, 1975)
b = 5·5399 (5)
c = 11·0455 (11)
β = 110·666 (8)°
V = 889·84 Å^3
D_x = 2·097 g cm^{-3}
μ_{obs} = 1·45 cm^{-1}

Table 2. *Distance d of the boundary planes hkl from a point in the surface of the crystal*

$h\ k\ l$	d (mm)
0 0 1	0·00
0 0 $\bar{1}$	1·23
0 1 0	0·00
1 1 0	1·55
1 $\bar{1}$ 0	4·60
$\bar{2}$ $\bar{1}$ 0	2·62
$\bar{9}$ 0 1 (approx.)	0·00

Refinement

A difference Fourier synthesis, calculated following least-squares refinement of the non-hydrogen atoms alone, revealed two negative peaks in positions close to those found for H(1) and H(2) by X-ray diffraction; starting parameters in this refinement were taken from BTT. These peaks, though somewhat extended (Fig. 1), both possessed a single central minimum and, in their general form, gave no suggestion of disordering of the protons. This in no way rules out the possibility of disorder, however; disordered proton sites separated by only a few tenths of an ångström could remain unresolved in the present room-temperature study.

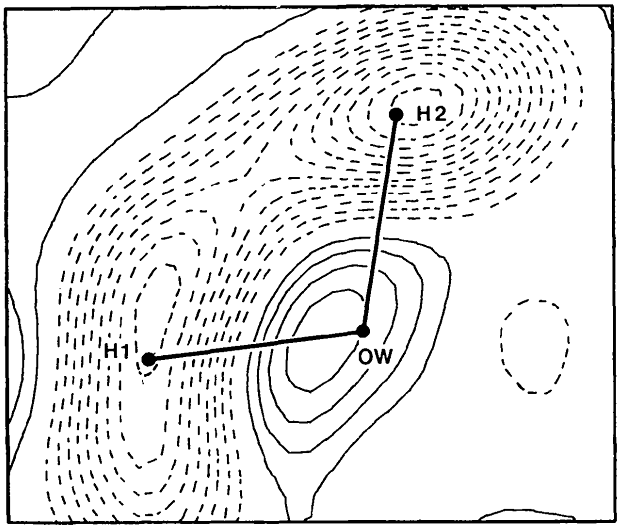

Fig. 1. An N–N difference Fourier synthesis calculated in the H_2O plane, after the final refinement and subsequent removal of H(1) and H(2). No new scale factor was calculated. Contours are plotted at intervals of 0·1 protons Å^{-3}, with dashed lines representing regions of proton excess. The zero-level contour is omitted.

With the rough positions for H(1) and H(2) obtained from the difference synthesis, the whole structure was refined with anisotropic thermal parameters. The function minimized was $\sum w(|F_o^2|-|F_c^2|)^2$, using the full-matrix least-squares refinement program *UPALS*. [This and other programs used in the present work are summarized by Lundgren (1974).] The weight w is given by the expression $w=1/\sigma^2(F^2)$, where $\sigma^2(F^2)=\sigma^2_{\text{count}}(F^2)+(0{\cdot}04F^2)^2$. The second term constitutes a preferential biasing of the weighting scheme to increase the weighting of the weaker reflexions.

It was soon apparent that many of the reflexions in the data set were seriously affected by extinction. First an isotropic and subsequently an anisotropic (type 1 and type 2) Zachariasen secondary extinction model was refined (after Coppens & Hamilton, 1970). A type 2 model was finally chosen on the basis of marginally smaller standard deviations on the refined parameters and slightly ($\sim 0{\cdot}002$) lower R values. The final anisotropic extinction parameters for both type 1 and type 2 models are given in Table 3. In a final series of refinements, an additional 45 reflexions calculated to have y values less than 0·4 were omitted (where $F^2_{\text{obs}}=F^2_{\text{corr}}y$). The final R values for the refinements were $R(F^2)=\sum||F_o^2|-|F_c^2||/\sum|F_o^2|=0{\cdot}079$; and $R_w(F^2)=[\sum w(|F_o^2|-|F_c^2|)^2/\sum w|F_o^4|]^{1/2}=0{\cdot}111$. The more conventional $R(F)$ value was 0·055. A ΔR plot for all reflexions included in the final refinement had a slope of 1·61 and an intercept on the ΔR(expected) axis of $-0{\cdot}15$. The corresponding plot including only those reflexions with $y>0{\cdot}85$ had a slope of 1·52 and a $-0{\cdot}19$ intercept. The range $1{\cdot}00>y>0{\cdot}85$ is a conservative estimate of the range of validity for the Zachariasen model as refined here [provided that a 'sin 2θ' term is added to the formalism: see Becker & Coppens (1974)].

Final positional and thermal parameters are given in Tables 4 and 5.*

Discussion

A stereoscopic view of the structure as refined from neutron diffraction data is given in Fig. 2; the water molecule environment is shown in Fig. 3. It is seen

Table 3. *Refined anisotropic extinction parameters, for a type* 1 (Z'_{ij}) *and a type* 2 (W'_{ij}) *secondary extinction model as proposed by Coppens & Hamilton* (1970)

Type 1	Z'_{11}	Z'_{22}	Z'_{33}	Z'_{12}	Z'_{13}	Z'_{23}
	54 (7)	124 (28)	32 (7)	50 (21)	−68 (13)	−23 (17)

Type 2					
W'_{11}	W'_{22}	W'_{33}	W'_{12}	W'_{13}	W'_{23}
0·029 (7)	0·019 (3)	0·037 (5)	−0·009 (8)	−0·030 (8)	0·023 (6)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31774 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Refined atomic coordinates* ($\times 10^5$)

The neutron values are given above the X-ray values.

	x	*y*	*z*
Na(1)	25000	25000	50000
	25000	25000	50000
Na(2)	0	46481 (68)	25000
	0	46626 (13)	25000
Cl	12545 (6)	−2268 (15)	19349 (8)
	12541 (2)	−2264 (5)	19332 (3)
O(1)	16736 (18)	−1651 (35)	33135 (18)
	16733 (10)	−1625 (19)	33131 (11)
O(2)	19395 (19)	−1156 (39)	13581 (29)
	19400 (11)	−1163 (20)	13541 (16)
O(3)	6632 (19)	17933 (44)	15051 (24)
	6621 (10)	17957 (24)	15087 (12)
O(4)	7566 (16)	−24353 (37)	15702 (19)
	7537 (8)	−24320 (19)	15710 (10)
O(*W*)	37459 (13)	2583 (38)	5020 (17)
	37467 (9)	2392 (25)	5100 (13)
H(1)	39217 (49)	3269 (198)	−1963 (53)
	38000 (200)	2000 (500)	300 (300)
H(2)	35617 (42)	18245 (93)	6118 (77)
	36400 (200)	15300 (800)	4700 (400)

from Table 4 that the only significant discrepancies between the positional parameters derived from neutron and X-ray diffraction occur for atoms of the water molecule (see later). The resulting geometries are given in Table 6. The general description of the structure as formulated in BTT ('a three-dimensional network of Na^+ ions, ClO_4^- ions and water molecules, held together by electrostatic and hydrogen-bond interactions') thus requires no greater modification than a qualification concerning the nature of the hydrogen bonding to the water molecule. It will initially be assumed that the ordered structure (as refined) is the correct one; a discussion of the possibility of disordering of the water molecule will follow later.

Although the modern view (*e.g.* Donohue, 1968) is that a bifurcated hydrogen bond is an extremely rare phenomenon, it would appear that H(1) may well participate in bifurcated (though weak) hydrogen bonding, with H(1)···O contacts 2·378 (10) and 2·389 (7) Å and O(*W*)–H(1)···O angles 135·2 (9) and 140·4 (9)° respectively. The H(1)···O distances are at the currently proposed limit of 2·4 Å for a hydrogen bond (see, for example, Olovsson & Jönsson, 1976). These distances are anomalously large, however, because of the apparent O(*W*)–H shortening produced by the large librational freedom of the water molecule (see below). The second hydrogen atom H(2), on the other hand, participates in a somewhat stronger hydrogen bond to O(1) [O(*W*)···O(1) = 3·028 (3), H(2)···O(1) = 2·152 (8) Å, O(*W*)–H(2)···O(1) = 155·5 (7)°]; the H(2)···O(2) contact [2·733 (7) Å] illustrated in Fig. 3 is well outside the 2·4 Å limit but is included as representing a structurally significant influence on the water molecule.

The water molecule

As indicated earlier, the acquisition of structural and dynamical information relating to the water molecule is the major motivation for the present study. It is immediately clear from Fig. 3, however, that the situation remains partially unresolved even after a room-temperature neutron diffraction experiment. The exceptionally large orientational freedom of the water molecule [as evidenced by the sizes of the thermal ellipsoids for H(1) and H(2)] results in an anomalously severe 'shortening' of the O(*W*)–H lengths [O(*W*)–H(1) = 0·905 (6), O(*W*)–H(2) = 0·935 (7) Å]. The H(1)–O(*W*)–H(2) angle [105·7 (8)°] is likely to be less seriously affected by thermal motion (or statistical disorder). The H–O–H angle in free water is 104·5°.

Table 5. *Anisotropic thermal parameters* ($\times 10^4$ Å^2)

The form of the temperature factor is $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{12}a^*b^*hk + \ldots)]$. For the non-hydrogen atoms, the neutron determined values are given above the X-ray determined values. The r.m.s. components R_i($\times 10^3$ Å) along the principal axes of thermal vibration are also given.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	R_1	R_2	R_3
Na(1)	301 (16)	302 (17)	318 (15)	5 (12)	63 (13)	−6 (13)	166 (4)	174 (5)	196 (5)
	353 (3)	341 (4)	337 (3)	−11 (3)	89 (3)	−16 (3)	176 (1)	187 (1)	199 (1)
Na(2)	343 (17)	346 (17)	339 (15)	0	118 (13)	0	184 (4)	186 (5)	186 (5)
	393 (4)	380 (4)	353 (4)	0	134 (3)	0	187 (1)	195 (1)	198 (1)
Cl	333 (5)	210 (5)	265 (5)	−19 (3)	143 (4)	−38 (3)	137 (2)	157 (2)	186 (1)
	362 (2)	254 (2)	278 (2)	−18 (1)	153 (1)	−35 (1)	148 (1)	164 (1)	193 (1)
O(1)	715 (14)	412 (11)	313 (8)	−124 (9)	39 (9)	−72 (7)	158 (3)	210 (3)	293 (3)
	774 (8)	489 (6)	313 (5)	−127 (5)	62 (5)	−74 (4)	165 (1)	223 (1)	301 (2)
O(2)	672 (14)	497 (12)	839 (16)	−148 (9)	579 (13)	−188 (10)	162 (3)	206 (3)	328 (3)
	713 (8)	548 (7)	856 (10)	−121 (5)	591 (8)	−156 (6)	171 (1)	222 (1)	329 (2)
O(3)	793 (16)	490 (14)	578 (13)	335 (11)	303 (12)	123 (9)	165 (3)	230 (3)	318 (3)
	855 (9)	548 (7)	605 (7)	343 (7)	324 (7)	116 (5)	180 (1)	235 (1)	328 (2)
O(4)	630 (12)	431 (12)	381 (9)	−267 (9)	198 (9)	−95 (7)	156 (3)	191 (3)	286 (3)
	673 (7)	479 (6)	410 (5)	−277 (5)	200 (5)	−101 (4)	167 (1)	201 (1)	295 (1)
O(*W*)	382 (9)	444 (11)	334 (8)	−110 (7)	55 (7)	51 (7)	172 (2)	178 (2)	246 (2)
	455 (6)	468 (6)	380 (6)	−99 (4)	98 (5)	42 (4)	189 (1)	192 (1)	248 (1)
H(1)	861 (37)	2532 (111)	532 (23)	−597 (49)	272 (25)	267 (40)	189 (6)	267 (6)	532 (12)
	–	–	–	–	–	–	–	–	–
H(2)	869 (34)	472 (27)	1415 (59)	−15 (23)	−177 (37)	206 (29)	205 (6)	260 (6)	461 (9)
	–	–	–	–	–	–	–	–	–

The grossly extended form of the thermal ellipsoids for H(1) and H(2) suggests that the conventional second-rank cumulant tensor formalism as used here (*i.e.* the ellipsoidal model) gives an inadequate description of the probability density functions (p.d.f.'s) for the protons in the water molecule. An attempt was therefore made to refine the additional ten elements of a third-rank 'skewness tensor' for each proton (see *International Tables for X-ray Crystallography*, 1974) but no satisfactory convergence could be obtained.

Let us consider then the possibility of an unresolved disorder in the water molecule. As pointed out earlier, the absence of double-peaking in the difference maps at the proton sites (Fig. 1) in no way rules out the presence of a statistical disordering of the water molecule. Evidence more suggestive of disorder, however, can be found from a crude analysis of the refined ellipsoids of thermal vibration for the atoms of the water molecule (Table 5). The directional cosines of the principal axes of these ellipsoids with respect to a coordinate system in the frame of the (refined) water molecule are given in Table 7. The directions of maximum amplitude of thermal vibration for H(1) and H(2) lie only 0·4 and 3·7°, respectively, out of the H_2O plane. At this stage it would normally be instructive to derive the **T**, **L** and **S** tensors which can be defined (Schomaker & Trueblood, 1968) to describe the rigid-body motion of a molecule, and hence deduce corrections to the refined water geometry. Refinement of these tensors does not converge to produce meaningful quantities in the case of a water molecule, however. Instead, a crude empirical approach is used tantamount to assuming $\mathbf{S}=0$ in the Schomaker & Trueblood approach, *i.e.* no coupling exists between the translational and librational motion. We assume then that the water molecule moves as a rigid body with libration axes passing through the water oxygen atom. The librational contribution to the motion of H(1) and

Table 6. *Comparison of interatomic distances* (Å) *and angles* (°) *determined by neutron and X-ray diffraction*

Symmetry code

(i)	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$	(ii)	x,	$1+y$,	z
(iii)	$\frac{1}{2}-x$,	$\frac{1}{2}-y$,	$-z$	(iv)	x,	$-y$,	$-\frac{1}{2}+z$
(v)	x,	$-y$,	$\frac{1}{2}+z$	(vi)	$-\frac{1}{2}+x$,	$\frac{1}{2}+y$,	z
(vii)	$-x$,	$1+y$,	$\frac{1}{2}-z$	(viii)	$-x$,	y,	$\frac{1}{2}-z$
(ix)	$\frac{1}{2}+x$,	$-\frac{1}{2}+y$,	z	(x)*	$\frac{1}{2}-x$,	$-\frac{1}{2}-y$,	$-z$

(*a*) ClO_4^- ion

	Neutron	X-ray
Cl–O(1)	1·430 (2)	1·431 (1)
Cl–O(2)	1·422 (2)	1·425 (1)
Cl–O(3)	1·419 (2)	1·420 (1)
Cl–O(4)	1·428 (2)	1·428 (1)
Mean Cl–O	1·425	1·426
O(1)–Cl–O(2)	110·15 (18)	110·21 (9)
O(1)–Cl–O(3)	109·59 (15)	109·30 (8)
O(1)–Cl–O(4)	108·59 (12)	108·53 (6)
O(2)–Cl–O(3)	108·35 (16)	108·56 (8)
O(2)–Cl–O(4)	109·13 (13)	109·31 (7)
O(3)–Cl–O(4)	111·02 (17)	110·93 (9)

(*b*) Na^+ ion

	Neutron	X-ray
Na(1)···O(*W*)^{i}	2·374 (2)	2·367 (1)
Na(1)···O(1)	2·369 (2)	2·368 (1)
Na(1)···O(2)^{i}	2·382 (2)	2·378 (1)
Mean Na(1)···O	2·375	2·371
Na(2)···O(*W*)^{i}	2·397 (2)	2·389 (1)
Na(2)···O(3)	2·360 (3)	2·361 (1)
Na(2)···O(4)^{ii}	2·429 (3)	2·422 (1)
Mean Na(2)···O	2·395	2·391
O(*W*)^{v} ···Na(1)···O(1)	87·34 (8)	87·66 (5)
O(*W*)^{v} ···Na(1)···O(2)^{v}	86·87 (7)	86·84 (5)
O(1) ·····Na(1)···O(2)^{v}	86·12 (9)	86·08 (5)
O(3) ·····Na(2)···O(3)^{viii}	95·86 (19)	95·46 (7)
O(3) ·····Na(2)···O(*W*)^{vi}	90·72 (9)	90·60 (5)
O(3) ·····Na(2)···O(*W*)^{i}	100·16 (10)	99·75 (5)
O(3) ·····Na(2)···O(4)^{ii}	83·84 (9)	84·00 (5)
O(*W*)^{i} ···Na(2)···O(4)^{ii}	86·43 (10)	86·66 (5)
O(*W*)^{vi}···Na(2)···O(4)^{ii}	82·80 (9)	83·14 (4)
O(4)^{vii} ···Na(2)···O(4)^{ii}	96·61 (17)	96·69 (6)

* In BTT (*j*) should be as (x) here. Also, H(1) and H(2) must be interchanged in the text.

Table 7. *Direction cosines* (*cos* α_1, *cos* α_2 *and cos* α_3) *for the eigenvectors of the vibrational tensors associated with the atoms of the water molecule*

The orthonormal system with respect to which the cosines are defined has its origin at O(*W*) and its *y* axis in the direction of the bisector of H(1)–O(*W*)–H(2); *x* and *z* axes are in and perpendicular to the H_2O plane respectively.

		cos α_1	cos α_2	cos α_3
O(*W*)	R_1	0·1894 (614)	0·0844 (2416)	−0·9783 (110)
	R_2	−0·2343 (541)	0·9714 (216)	0·0385 (2434)
	R_3	−0·9535 (83)	−0·2219 (310)	−0·2038 (248)
H(1)	R_1	0·6146 (124)	−0·7856 (102)	0·0717 (521)
	R_2	−0·0497 (350)	0·0521 (444)	0·9974 (37)
	R_3	−0·7873 (96)	−0·6165 (123)	−0·0071 (221)
H(2)	R_1	0·4481 (213)	0·8906 (103)	0·0783 (799)
	R_2	−0·0929 (424)	−0·0407 (732)	0·9948 (65)
	R_3	−0·8891 (102)	0·4531 (196)	−0·0645 (267)

Table 6 (*cont.*)

(*c*) H_2O molecule

	O(*W*)···O			H···O	
	Neutron	X-ray	O(*W*)–H	Neutron	∠O(*W*)–H···O
O(*W*)–H(1)···O(3)^{iii}	3·141 (3)	3·156 (2)	0·905 (6)	2·389 (7)	140·4 (9)
O(*W*)–H(1)···O(4)^{x}	3·087 (3)	3·093 (2)	0·905 (6)	2·378 (10)	135·2 (9)
O(*W*)–H(2)···O(1)^{i}	3·028 (3)	3·034 (2)	0·935 (7)	2·152 (8)	155·5 (7)
O(*W*)–H(2)···O(2)^{iii}	3·325 (3)	3·336 (2)	0·935 (7)	2·733 (7)	122·0 (7)

Angle H(1)–O(*W*)–H(2) = 105·7 (8)°.

H(2) is thus obtained (see Table 8) by subtracting the translational motion of O(W) from the refined thermal ellipsoids for H(1) and H(2). This is done by considering the in-plane and out-of-plane vibrational components ($\langle l^2_{\rm in}\rangle$ and $\langle l^2_{\rm out}\rangle$) perpendicular to the respective O–H directions. Subtraction of the O(W) from the H values gives an in-plane rocking mode component $\langle \mathbf{L}^2_{\rm in}\rangle$ and a combination of an out-of-plane twisting and an out-of-plane wagging mode $\langle \mathbf{L}^2_{\rm out}\rangle$.

Table 8. *Analysis of rigid-body motion for the water molecule in terms of in-plane and out-of-plane librational modes (see text)*

	$\langle l^2_{\rm in}\rangle$	$\langle l^2_{\rm out}\rangle$
(*a*) O(W)-H(1)		
H(1)	0·2684	0·0714
O(W)	0·0483	0·0308
Difference	0·2201 Å^2 ($\langle \mathbf{L}^2_{\rm in}\rangle$)	0·0406 Å^2 ($\langle \mathbf{L}^2_{\rm out}\rangle$)
(*b*) O(W)-H(2)		
H(2)	0·1781	0·0680
O(W)	0·0361	0·0308
Difference	0·1420 Å^2 ($\mathbf{L}^2_{\rm in}$)	0·0372 Å^2 ($\mathbf{L}^2_{\rm out}$)

$\overline{\langle \mathbf{L}^2_{\rm in}\rangle}=0{\cdot}1810$ Å^2 $\overline{\langle \mathbf{L}^2_{\rm out}\rangle}=0{\cdot}0389$ Å^2

$\bar{\nu}_{\rm in}=142$ cm^{-1} $\bar{\nu}_{\rm out}$(twisting) $=\bar{\nu}_{\rm out}$(wagging) $=513$ cm^{-1}

It is seen from Table 8 that the magnitudes of the out-of-plane components for H(1) and H(2) are quite similar (0·0406 and 0·0372 Å^2), giving a mean value $\overline{\langle \mathbf{L}^2_{\rm out}\rangle}$ of 0·0389 Å^2. Applying the quantum statistical expression for a harmonic oscillator (see, for example, Cyvin, 1968), $\langle \mathbf{L}^2_{\rm out}\rangle=(16{\cdot}86/\mu\bar{\nu})[\coth\,(hc\bar{\nu}/2kT)]$, we find that this corresponds to an out-of-plane librational frequency ($\bar{\nu}$) of 513 cm^{-1}. The units of $\langle \mathbf{L}^2\rangle$ are Å^2, and μ is here 2·0 atomic mass units. We have here also assumed equal contributions to the observed m.s. amplitudes from the twisting and wagging modes.

An estimate of the in-plane rocking librational frequency can be obtained in a similar manner by taking the mean of the here considerably differing $\langle \mathbf{L}^2_{\rm in}\rangle$ values for H(1) and H(2) (0·2201 and 0·1420 Å^2), to give a $\overline{\langle \mathbf{L}^2_{\rm in}\rangle}$ value of 0·1810 Å^2. It is interesting to note that, in the ground state, the corresponding calculated in-plane frequency ($\bar{\nu}_{\rm in}$) is 46 cm^{-1} – a value well outside the generally accepted range of 300–900 cm^{-1} for the librational frequency of a water molecule in a crystalline hydrate, and distinctly indicative of disorder. However, the quantum-statistical treatment applied at room temperature results in the much higher value for $\bar{\nu}_{\rm in}$ of 142 cm^{-1}; a value which can no longer be adjudged as unrealistically low (in view of the many

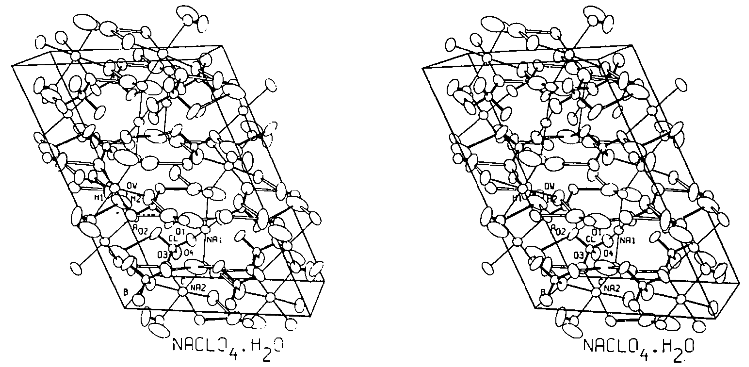

Fig. 2. A stereoscopic illustration of the structure of NaClO$_4$.H$_2$O. Unfilled bonds represent H···O contacts. All thermal ellipsoids are drawn to 50% probability.

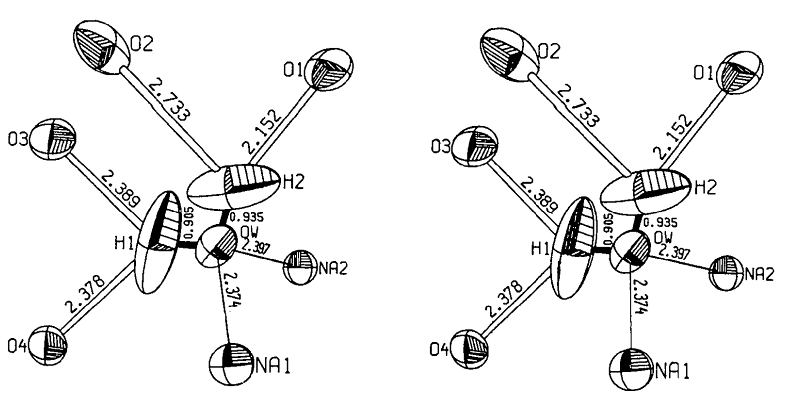

Fig. 3. A stereoscopic view of the water molecule and its immediate environment. Note the inclusion of H(2)···O(2) as a structurally significant interaction. All thermal ellipsoids are drawn to 50% probability.

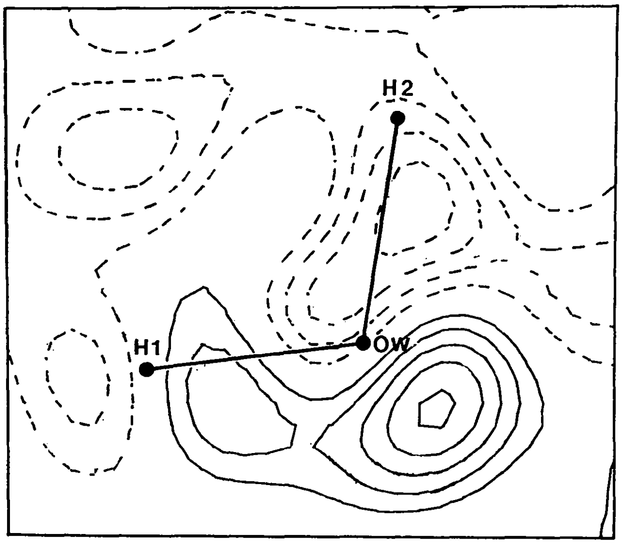

Fig. 4. An X–N difference electron density map calculated in the plane of the H_2O molecule. Contours are plotted at intervals of 0·05 e Å^{-3}, with solid lines representing regions of electron excess. The zero-level contour is omitted.

approximations made), and consequently cannot be interpreted as evidence suggestive of disorder. A neutron diffraction study at low temperature would clearly produce more definitive information; an unequivocal answer to the disorder question cannot be reached on the basis of the present evidence.

It may here be noted that the IR study of both normal and deuterated $NaClO_4.H_2O$ (Brink & Falk, 1970) indicates very small half-widths for the OH and OD stretching bands, and, moreover, that the force fields experienced by H(1) and H(2) [or D(1) and D(2)] are essentially identical. These conditions must be satisfied despite possible disordering of the water molecule for the neutron diffraction and IR results to be compatible.

It can also be mentioned that preliminary NMR studies at room temperature on deuterated single crystals of $NaClO_4.H_2O$ have shown that the D_2O molecule undergoes a fast flipping motion about its twofold axis (Berglund & Tegenfeldt, 1977). The angle between the z principal axis of the quadrupole coupling tensor and the normal to the water molecule plane is 1·6°, and the angle between the y principal axis and the D–D line is 2·9°. These findings are in good general agreement with other neutron diffraction and NMR spectroscopic studies of simple hydrates, *e.g.* Soda & Chiba (1969), Weiss & Wüst (1973).

In conclusion, it can be remarked that the present study was also intended to yield positional and thermal parameters which could be used in combination with earlier X-ray data to produce so-called X–N deformation electron density maps of the structure (see, for example, Coppens, 1974). Here again the main interest was in the electron distribution associated with the water molecule. The X–N map in the H_2O plane, calculated in the same manner as described in Almlöf, Kvick & Thomas (1973), is shown in Fig. 4. Although a well-developed region of electron density appears in the vicinity of O(W), the region of the hydrogen atoms must inevitably suffer from the inadequacy of the neutron-diffraction-determined positional and thermal parameters to describe the detail in the structure. Here again, low-temperature data can produce a significant improvement in the situation.

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