inorganic compounds

Figure 1
The independent components of orthorhombic hydronium perchlorate at 193 K, showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted (see *Comment*). [Symmetry code: (vii) $x, \frac{1}{2} - y, z$.]

Redetermination of hydronium perchlorate at 193 and 293 K

Azhar A. Rahman,[a] Anwar Usman,[a] Suchada Chantrapromma[b] and Hoong-Kun Fun[a]*

[a]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand

Correspondence e-mail: hkfun@usm.my

A sample of hydronium perchlorate, $H_3O^+ \cdot ClO_4^-$, crystallized from ethanol at ambient temperature, was found to be orthorhombic (space group *Pnma*) at both 193 and 293 K, with no phase transition observed in this temperature range. This contrasts with the earlier observation [Nordman (1962). *Acta Cryst.* **15**, 18–23] of a monoclinic phase (space group $P2_1/n$) at 193 K for crystals grown at that temperature from perchloric acid. The hydronium and perchlorate ions lie across a mirror plane but it is not possible to define at either temperature a simple description of the H-atom positions due to the three-dimensional tumbling of the hydronium cation.

Comment

The formation of the hydronium ion in water has been frequently postulated to explain the abnormal mobility of protons through water. Evidence of the existence of these ions in crystals has been obtained by X-ray diffraction methods (Volmer, 1925; Luzzati, 1953); for example, the X-ray diffraction pattern of perchloric acid monohydrate is very similar to that of ammonium perchlorate, implying that the perchloric acid monohydrate reported is, in fact, hydronium perchlorate. This question was investigated by both NMR (Richards & Smith, 1951) and Raman spectroscopy (Taylor & Vidale, 1956), which provided early evidence for the occurrence of the hydronium ion. The early NMR data suggested that the hydronium ion was nearly planar, but subsequent X-ray diffraction studies on a wide variety of salts containing the hydronium ion gave H—O—H angles with an average value of 109.3 (5)° (Lundgren & Williams, 1973).

Richards & Smith (1951) found that the hydronium ions in the perchlorate salt undergo re-orientation at high temperature in the solid state, and a phase transition was observed at 243 K (Taylor & Vidale, 1956). The orientational disorder is also supported by a room-temperature X-ray diffraction analysis (Lee & Carpenter, 1959), in which the hydronium ions are rotating or disordered among several orientations,
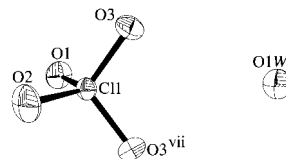
although no direct evidence for the location of the H atoms appeared in electron-density projections and no further attempt was made to locate these atoms. In the low-temperature X-ray study reported by Nordman (1962), it was found that at 193 K, hydronium perchlorate crystallized from perchloric acid in the monoclinic space group $P2_1/n$, while Lee & Carpenter (1959) suggested a transition above 243 K to a space group of higher symmetry, *viz.* orthorhombic *Pnma*, with $a = 9.065$ (8), $b = 5.569$ (4) and $c = 7.339$ (4) Å.

In the present study, we have redetermined the crystal structure of hydronium perchlorate at both 193 K and room temperature (293 K) (Fig. 1) using a sample crystallized at ambient temperature from ethanol solution. We observed no temperature-dependent phase transition, even though we recycled the sample several times through the temperature range 193–293 K; the orthorhombic space group *Pnma* was consistently observed at both 193 and 293 K.

In this orthorhombic phase, perchlorate atoms Cl1, O1 and O2, and hydronium atom O1W lie on the mirror plane at $y = \frac{1}{4}$ (Fig. 2). The geometry of the perchlorate anion is effectively constant, within experimental error, over the temperature range 193–293 K (Tables 1 and 2).
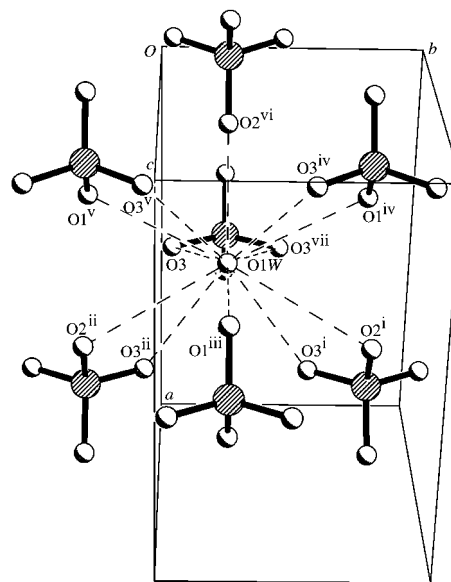

Figure 2
A view of the O···O contacts around hydronium atom O1W at 193 K. Symmetry codes are as given in Table 3.

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Detailed scrutiny of an extensive series of difference-map sections in different planes adjacent to the O1W atom shows that the electron density associated with the three H atoms forms a fairly uniform and nearly spherical shell (of approximate radius 1 Å) around the water O atom. This implies that the hydronium cation is actually tumbling with nearly spherical symmetry at both 193 and 293 K. This tumbling of the hydronium cation is consistent with the rather long (>2.94 Å) contact distances between O1W and the surrounding O atoms of the anions (Table 3 and Fig. 2). Even at 193 K, the O1W···O distances may not be short enough for the formation of hydrogen bonds strong enough to tether the cations firmly to the anions; thus, the hydronium cations may still be tumbling with nearly spherical symmetry. In view of these findings, it is not possible to say anything about the shape and dimensions of the hydronium cation or anything about the details of the hydrogen bonding at both 193 and 293 K. This study concurs with the 293 K study of the orthorhombic phase (Lee & Carpenter, 1959) and confirms the disordered nature of the hydronium cation. By contrast, in the monoclinic phase, there are three O···O contact distances between a given cation and three neighbouring anions lying in the range 2.63 (1)–2.71 (1) Å, and the H atoms were explicitly located in fully ordered sites, leading to the identification of three cation–anion O—H···O hydrogen bonds (Nordman, 1962).

The persistence at 193 K of the orthorhombic phase is in contrast to the observation by Nordman (1962) of a monoclinic phase below 243 K, and two possible interpretations suggest themselves. The sample employed here may be much purer than that used by Nordman and may thus lack the specific trace impurities required to initiate the phase transformation. Alternatively, the monoclinic phase may, in fact, be a disappearing polymorph (Bernstein & Henck, 1998).

Experimental

The sample of hydronium perchlorate used was an adventitious by-product from the attempted synthesis of a copper(II) macrocyclic complex by the [2+2]-cyclocondensation between sodium 2,6-diformyl-4-methylphenolate (0.1863 g, 1 mmol) and 1,4-phenylenediamine (0.1081 g, 1 mmol) in ethanol (30 ml) *via* the sodium template method (Gou & Fenton, 1994). A yellow solid was obtained (0.195 g, 0.38 mmol) and transmetallated with $Cu(ClO_4)_2·6H_2O$ (0.292 g, 0.76 mmol) in ethanol (25 ml). The solution was refluxed under nitrogen for 1 h. The resulting clear solution was filtered hot and left to cool in air. After several days, colourless crystals of hydronium perchlorate were deposited.

$H_3O^+·ClO_4^-$ at 193 K

Crystal data

$H_3O^+·ClO_4^-$	Mo $K\alpha$ radiation
$M_r = 118.47$	Cell parameters from 1600
Orthorhombic, $Pnma$	reflections
$a = 9.1517 (9)$ Å	$\theta = 3.5–28.3°$
$b = 5.7886 (6)$ Å	$\mu = 0.86$ mm^{-1}
$c = 7.4034 (8)$ Å	$T = 193 (2)$ K
$V = 392.20 (7)$ Å^3	Block, colorless
$Z = 4$	$0.28 \times 0.24 \times 0.14$ mm
$D_x = 2.006$ Mg m^{-3}	

Data collection

Siemens SMART CCD area-detector diffractometer	532 independent reflections
ω scans	490 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.018$
(*SADABS*; Sheldrick, 1996)	$\theta_{max} = 28.2°$
$T_{min} = 0.795$, $T_{max} = 0.889$	$h = -9 \rightarrow 12$
2301 measured reflections	$k = -7 \rightarrow 7$
	$l = -9 \rightarrow 8$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 1.0711P]$
$wR(F^2) = 0.117$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
532 reflections	$\Delta\rho_{max} = 0.53$ e Å^{-3}
34 parameters	$\Delta\rho_{min} = -0.47$ e Å^{-3}
H atoms not located (see *Comment*)	

Table 1
Selected geometric parameters (Å, °) for (I).

Cl1—O2	1.431 (3)	Cl1—O3	1.446 (2)
Cl1—O1	1.441 (3)		
O1—Cl1—O2	110.72 (19)	O3—Cl1—O1	108.91 (10)
O2—Cl1—O3	109.77 (11)	O3^{vii}—Cl1—O3	108.73 (17)

Symmetry code: (vii) $x, \frac{1}{2} - y, z$.

Table 2
Selected geometric parameters (Å, °) for (II).

Cl1—O2	1.429 (3)	Cl1—O3	1.442 (2)
Cl1—O1	1.437 (3)		
O1—Cl1—O2	110.9 (2)	O3—Cl1—O1	108.85 (12)
O2—Cl1—O3	109.77 (13)	O3^{vii}—Cl1—O3	108.68 (18)

Symmetry code: (vii) $x, \frac{1}{2} - y, z$.

Table 3
O···O contacts (Å) involving the hydronium O atom.

	193 K	293 K
O1W···O3^i	2.946 (3)	2.977 (4)
O1W···O3^{ii}	2.946 (3)	2.977 (4)
O1W···O1^{iii}	2.966 (4)	2.982 (4)
O1W···O3^{iv}	2.971 (3)	2.994 (4)
O1W···O3^v	2.971 (3)	2.994 (4)
O1W···O2^{vi}	3.025 (4)	3.055 (5)
O1W···O3	3.059 (3)	3.088 (4)
O1W···O3^{vii}	3.059 (3)	3.088 (4)
O1W···O1^{iv}	3.214 (2)	3.248 (2)
O1W···O1^v	3.214 (2)	3.248 (2)
O1W···O2^i	3.542 (3)	3.542 (3)
O1W···O2^{ii}	3.542 (3)	3.542 (3)

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, 1 - z$; (ii) $1 - x, -y, 1 - z$; (iii) $x, y, 1 + z$; (iv) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (v) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (vi) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (vii) $x, \frac{1}{2} - y, z$.

$H_3O^+·ClO_4^-$ at 293 K

Crystal data

$H_3O^+·ClO_4^-$	Mo $K\alpha$ radiation
$M_r = 118.47$	Cell parameters from 1439
Orthorhombic, $Pnma$	reflections
$a = 9.2343 (15)$ Å	$\theta = 3.5–28.3°$
$b = 5.8178 (9)$ Å	$\mu = 0.84$ mm^{-1}
$c = 7.4606 (12)$ Å	$T = 293 (2)$ K
$V = 400.81 (11)$ Å^3	Block, colorless
$Z = 4$	$0.28 \times 0.24 \times 0.14$ mm
$D_x = 1.963$ Mg m^{-3}	

Data collection

Siemens SMART CCD area-detector diffractometer	545 independent reflections
	483 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.019$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 28.3°$
	$h = -12 \rightarrow 10$
$T_{min} = 0.799$, $T_{max} = 0.891$	$k = -7 \rightarrow 7$
2348 measured reflections	$l = -8 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.6383P]$
$R[F^2 > 2\sigma(F^2)] = 0.047$	
$wR(F^2) = 0.130$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{max} < 0.001$
545 reflections	$\Delta\rho_{max} = 0.47$ e Å^{-3}
34 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}
H atoms not located (see *Comment*)	

The H atoms were not included in the refinements (see *Comment*). The indicated temperature of 193 K for the sample was measured with the low-temperature attachment supplied with the Bruker 1K CCD diffractometer. The measured temperature was at the nozzle of the cold N_2 stream and, according to Bruker's specification, the temperature at the sample would be, at most, 2–3 K higher.

For both temperature determinations, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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