

## 4-Hydroxyanilinium perchlorate dihydrate

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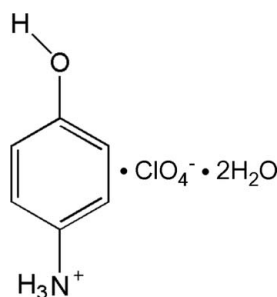
Received 8 May 2010; accepted 28 June 2010

 Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.048;  $wR$  factor = 0.097; data-to-parameter ratio = 13.5.

In the crystal structure of the title compound,  $\text{C}_6\text{H}_8\text{NO}^+\cdot\text{ClO}_4^-\cdot 2\text{H}_2\text{O}$ , intermolecular  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds occur. The protonated amine cations and the perchlorate anions are linked through the water molecules, and the hydroxy groups of the cations and the anions are linked through the water molecules. The cations are connected to the perchlorate anions *via* intermolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds. In addition, the crystal structure exhibits weak intermolecular  $\text{C}-\text{H}\cdots\pi$  interactions.

### Related literature

For background to phase transition materials, see: Li *et al.* (2008); Zhang *et al.* (2009)



### Experimental

#### Crystal data

$\text{C}_6\text{H}_8\text{NO}^+\cdot\text{ClO}_4^-\cdot 2\text{H}_2\text{O}$   
 $M_r = 245.62$   
 Orthorhombic,  $Pna2_1$   
 $a = 24.341$  (5) Å

$b = 5.253$  (1) Å  
 $c = 7.824$  (2) Å  
 $V = 1000.4$  (4) Å<sup>3</sup>  
 $Z = 4$

Mo  $K\alpha$  radiation  
 $\mu = 0.40$  mm<sup>-1</sup>

$T = 298$  K  
 $0.40 \times 0.30 \times 0.20$  mm

#### Data collection

Rigaku SCXmini diffractometer  
 Absorption correction: multi-scan  
 (*CrystalClear*; Rigaku, 2005)  
 $T_{\text{min}} = 0.866$ ,  $T_{\text{max}} = 0.923$

9517 measured reflections  
 2275 independent reflections  
 1986 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.052$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$   
 $wR(F^2) = 0.097$   
 $S = 1.11$   
 2275 reflections  
 168 parameters  
 8 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.21$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.53$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983), 1049 Friedel pairs  
 Flack parameter: 0.00 (7)

**Table 1**

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1–C6 benzene ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1O}\cdots\text{O2W}^i$	0.75 (3)	2.10 (3)	2.801 (3)	156 (4)
$\text{N1}-\text{H1N}\cdots\text{O4}$	0.79 (5)	2.34 (5)	3.016 (4)	144 (4)
$\text{N1}-\text{H2N}\cdots\text{O1W}^{ii}$	0.98 (4)	1.98 (5)	2.951 (4)	168 (4)
$\text{N1}-\text{H3N}\cdots\text{O1W}$	1.00 (5)	1.97 (5)	2.972 (4)	175 (4)
$\text{O1W}-\text{H1AW}\cdots\text{O3}^{iii}$	0.79 (5)	2.40 (7)	3.089 (3)	146 (8)
$\text{O1W}-\text{H1BW}\cdots\text{O5}$	0.83 (4)	2.47 (6)	3.083 (4)	132 (5)
$\text{O2W}-\text{H2AW}\cdots\text{O4}$	0.93 (4)	2.28 (4)	3.068 (4)	143 (4)
$\text{O2W}-\text{H2BW}\cdots\text{O1}^{iv}$	0.77 (3)	2.17 (3)	2.937 (3)	173 (5)
$\text{C2}-\text{H2}\cdots\text{Cg1}^{iv}$	0.93	2.88	3.677 (3)	144

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors are grateful to the starter fund of Southeast University for financial support to purchase the diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LX2151).

### References

- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Li, X. Z., Qu, Z. R. & Xiong, R. G. (2008). *Chin. J. Chem.* **11**, 1959–1962.  
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 Zhang, W., Chen, L. Z., Xiong, R. G., Nakamura, T. & Huang, S. D. (2009). *J. Am. Chem. Soc.* **131**, 12544–12545.

**supplementary materials**

*Acta Cryst.* (2010). E66, o1920 [ doi:10.1107/S1600536810025365 ]

## 4-Hydroxyanilinium perchlorate dihydrate

X. Fu

### Comment

As a continuation of our study of phase transition materials, including organic ligands (Li *et al.*, 2008), metal-organic coordination compounds (Zhang *et al.*, 2009), organic-inorganic hybrids, we studied the dielectric properties of the title compound, unfortunately, there was no distinct anomaly observed from 93 K to 350 K, suggesting that this compound should be not a real ferroelectrics or there may be no distinct phase transition occurred within the measured temperature range. Here, we report the crystal structure of the title compound (Fig. 1).

The asymmetric unit of the title compound is made up of a 4-hydroxyanilinium cation wherein the non-hydrogen atoms are practically co-planar with a mean deviation of 0.015 (2) Å, a perchlorate anion and two solvent molecules of water (Fig. 1). The crystal packing (Fig. 2) is stabilized by intermolecular N—H $\cdots$ O, O—H $\cdots$ O hydrogen bonds and weak intermolecular C—H $\cdots$  $\pi$  interactions. (Table 1). Both the protonated amine cations and the perchlorate anions are linked through the water molecules, and the hydroxy groups of the cations and the anions are linked through the water molecules. Additionally, the cations are connected to the perchlorate anions via intermolecular N—H $\cdots$ O hydrogen bonds.

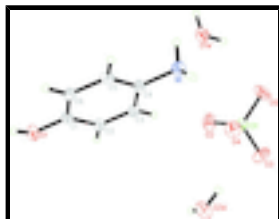
### Experimental

1.09g (10 mmol) 4-aminophenol was firstly dissolved in 10ml ethanol, to which perchloric acid aqueous solution (70% w/w) was then added under stirring until the PH of the solution was ca. 6. Ethanol was added until the precipitated substrates disappeared. Colorless prism single crystal for X-ray was obtained by the acid solution slow evaporated at room temperature after two days.

### Refinement

Aryl H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å.  $U_{iso}(H) = 1.2U_{eq}(C)$ . The other H atoms attached to N and O atoms were found difference maps using restraints for O—H bond distances (O—H = 0.85 (5) Å) and H—O—H angles (H $\cdots$ H = 1.35 (10) Å). Their displacement parameters were freely refined.

### Figures



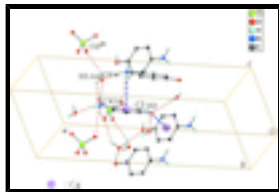


Fig. 2. N—H $\cdots$ O, O—H $\cdots$ O and C—H $\cdots$  $\pi$  interactions (dotted lines) in the crystal structure of the title compound. Cg denotes the ring centroid. [Symmetry codes: (i)  $-x + 1, -y + 2, z + 1/2$ ; (ii)  $x, y + 1, z$ ; (iii)  $x, y, z + 1$ ; (iv)  $-x + 1, -y + 1, z - 1/2$ .]

## 4-Hydroxyanilinium perchlorate dihydrate

### Crystal data

$C_6H_8NO^+ \cdot ClO_4^- \cdot 2H_2O$

$M_r = 245.62$

Orthorhombic,  $Pna2_1$

Hall symbol: P 2c -2n

$a = 24.341 (5) \text{ \AA}$

$b = 5.253 (1) \text{ \AA}$

$c = 7.824 (2) \text{ \AA}$

$V = 1000.4 (4) \text{ \AA}^3$

$Z = 4$

$F(000) = 512$

$D_x = 1.631 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 4523 reflections

$\theta = 3.1\text{--}55.2^\circ$

$\mu = 0.40 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Prism, colourless

$0.40 \times 0.30 \times 0.20 \text{ mm}$

### Data collection

Rigaku SCXmini  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

Detector resolution:  $13.6612 \text{ pixels mm}^{-1}$

$\omega$  scans

Absorption correction: multi-scan  
(*CrystalClear*; Rigaku, 2005)

$T_{\min} = 0.866, T_{\max} = 0.923$

9517 measured reflections

2275 independent reflections

1986 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$

$\theta_{\max} = 27.5^\circ, \theta_{\min} = 3.1^\circ$

$h = -31 \rightarrow 31$

$k = -6 \rightarrow 6$

$l = -10 \rightarrow 10$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.097$

$S = 1.11$

2275 reflections

168 parameters

8 restraints

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and  
constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.21 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.53 \text{ e \AA}^{-3}$

Absolute structure: Flack (1983), 1049 Friedel pairs

Primary atom site location: structure-invariant direct methods Flack parameter: 0.00 (7)

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor wR and goodness of fit S are based on  $F^2$ , conventional R-factors R are based on F, with F set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.70519 (2)	0.26502 (10)	0.38081 (9)	0.03119 (16)
O1	0.41921 (9)	0.7270 (4)	0.6125 (3)	0.0418 (5)
H1O	0.4080 (14)	0.855 (5)	0.638 (4)	0.041 (10)*
O2	0.65704 (9)	0.1268 (4)	0.4283 (3)	0.0543 (6)
O3	0.72121 (12)	0.1930 (5)	0.2130 (3)	0.0615 (7)
O4	0.69370 (9)	0.5318 (3)	0.3859 (3)	0.0490 (5)
O5	0.74825 (10)	0.2072 (4)	0.4975 (4)	0.0633 (7)
N1	0.64637 (12)	0.7547 (5)	0.7092 (4)	0.0383 (6)
H1N	0.6637 (19)	0.763 (7)	0.624 (7)	0.067 (14)*
H2N	0.6575 (16)	0.911 (8)	0.768 (6)	0.082 (13)*
H3N	0.6580 (18)	0.587 (9)	0.759 (6)	0.102 (16)*
C1	0.47480 (12)	0.7447 (5)	0.6368 (3)	0.0303 (6)
C2	0.50729 (12)	0.5551 (5)	0.5650 (4)	0.0323 (6)
H2	0.4911	0.4256	0.5014	0.039*
C3	0.56328 (12)	0.5591 (5)	0.5878 (4)	0.0347 (6)
H3	0.5852	0.4326	0.5404	0.042*
C4	0.58649 (11)	0.7533 (4)	0.6821 (3)	0.0308 (6)
C5	0.55500 (11)	0.9431 (5)	0.7512 (4)	0.0320 (6)
H5	0.5714	1.0744	0.8124	0.038*
C6	0.49832 (11)	0.9382 (5)	0.7292 (4)	0.0324 (6)
H6	0.4765	1.0651	0.7768	0.039*
O1W	0.68473 (10)	0.2523 (4)	0.8370 (3)	0.0461 (6)
H1AW	0.680 (3)	0.245 (11)	0.937 (6)	0.19 (4)*
H1BW	0.7155 (18)	0.270 (10)	0.793 (8)	0.13 (2)*
O2W	0.62796 (12)	0.7872 (5)	0.0985 (4)	0.0514 (6)
H2AW	0.6577 (16)	0.773 (8)	0.172 (5)	0.079 (15)*
H2BW	0.6131 (18)	0.658 (6)	0.103 (6)	0.070 (14)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

$U^{11}$                        $U^{22}$                        $U^{33}$                        $U^{12}$                        $U^{13}$                        $U^{23}$

## supplementary materials

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Cl1	0.0311 (3)	0.0332 (3)	0.0292 (3)	0.0050 (2)	0.0005 (3)	-0.0030 (3)
O1	0.0300 (11)	0.0394 (11)	0.0560 (14)	0.0019 (10)	-0.0011 (10)	-0.0022 (11)
O2	0.0455 (12)	0.0505 (11)	0.0667 (15)	-0.0075 (10)	0.0107 (11)	0.0084 (11)
O3	0.0783 (17)	0.0697 (15)	0.0365 (14)	0.0053 (14)	0.0176 (13)	-0.0112 (11)
O4	0.0573 (13)	0.0358 (9)	0.0541 (12)	0.0082 (9)	-0.0003 (13)	0.0001 (11)
O5	0.0484 (15)	0.0774 (16)	0.0640 (17)	0.0242 (13)	-0.0244 (13)	-0.0038 (13)
N1	0.0317 (14)	0.0414 (15)	0.0419 (17)	0.0010 (12)	0.0015 (12)	0.0017 (13)
C1	0.0319 (14)	0.0327 (13)	0.0262 (14)	-0.0010 (12)	-0.0009 (12)	0.0064 (11)
C2	0.0337 (15)	0.0293 (13)	0.0341 (14)	-0.0031 (12)	-0.0005 (12)	-0.0067 (11)
C3	0.0357 (16)	0.0277 (12)	0.0405 (16)	0.0041 (11)	0.0070 (13)	-0.0073 (11)
C4	0.0292 (13)	0.0301 (13)	0.0331 (14)	0.0011 (12)	0.0000 (11)	0.0044 (11)
C5	0.0383 (15)	0.0287 (11)	0.0290 (13)	-0.0009 (11)	-0.0045 (12)	-0.0015 (11)
C6	0.0358 (14)	0.0295 (13)	0.0320 (15)	0.0087 (11)	-0.0014 (11)	-0.0040 (12)
O1W	0.0394 (12)	0.0513 (12)	0.0477 (18)	-0.0040 (12)	-0.0053 (10)	0.0005 (11)
O2W	0.0401 (15)	0.0486 (14)	0.0654 (17)	0.0015 (12)	-0.0133 (12)	0.0038 (13)

### *Geometric parameters (Å, °)*

Cl1—O3	1.421 (2)	C2—C3	1.375 (4)
Cl1—O5	1.423 (2)	C2—H2	0.9300
Cl1—O2	1.428 (2)	C3—C4	1.379 (4)
Cl1—O4	1.4297 (18)	C3—H3	0.9300
O1—C1	1.370 (3)	C4—C5	1.369 (4)
O1—H1O	0.75 (3)	C5—C6	1.391 (4)
N1—C4	1.473 (4)	C5—H5	0.9300
N1—H1N	0.79 (5)	C6—H6	0.9300
N1—H2N	0.98 (4)	O1W—H1AW	0.79 (5)
N1—H3N	1.00 (5)	O1W—H1BW	0.83 (4)
C1—C6	1.372 (4)	O2W—H2AW	0.93 (4)
C1—C2	1.391 (4)	O2W—H2BW	0.77 (3)
O3—Cl1—O5	109.51 (18)	C3—C2—H2	120.0
O3—Cl1—O2	109.27 (17)	C1—C2—H2	120.0
O5—Cl1—O2	109.22 (16)	C2—C3—C4	119.1 (2)
O3—Cl1—O4	109.90 (17)	C2—C3—H3	120.4
O5—Cl1—O4	109.61 (14)	C4—C3—H3	120.4
O2—Cl1—O4	109.31 (13)	C5—C4—C3	121.4 (2)
C1—O1—H1O	105 (3)	C5—C4—N1	119.6 (2)
C4—N1—H1N	114 (3)	C3—C4—N1	119.1 (2)
C4—N1—H2N	110 (2)	C4—C5—C6	119.6 (2)
H1N—N1—H2N	102 (4)	C4—C5—H5	120.2
C4—N1—H3N	109 (3)	C6—C5—H5	120.2
H1N—N1—H3N	103 (4)	C1—C6—C5	119.5 (2)
H2N—N1—H3N	119 (4)	C1—C6—H6	120.2
O1—C1—C6	122.4 (3)	C5—C6—H6	120.2
O1—C1—C2	117.2 (2)	H1AW—O1W—H1BW	124 (7)
C6—C1—C2	120.4 (3)	H2AW—O2W—H2BW	106 (4)
C3—C2—C1	120.0 (3)		
O1—C1—C2—C3	-178.6 (2)	C3—C4—C5—C6	1.3 (4)
C6—C1—C2—C3	0.7 (4)	N1—C4—C5—C6	-178.4 (3)

C1—C2—C3—C4	-0.2 (4)	O1—C1—C6—C5	179.1 (2)
C2—C3—C4—C5	-0.8 (4)	C2—C1—C6—C5	-0.2 (4)
C2—C3—C4—N1	178.9 (3)	C4—C5—C6—C1	-0.8 (4)

*Hydrogen-bond geometry (Å, °)*

Cg1 is the centroid of the C1—C6 benzene ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1O...O2W <sup>i</sup>	0.75 (3)	2.10 (3)	2.801 (3)	156 (4)
N1—H1N...O4	0.79 (5)	2.34 (5)	3.016 (4)	144 (4)
N1—H2N...O1W <sup>ii</sup>	0.98 (4)	1.98 (5)	2.951 (4)	168 (4)
N1—H3N...O1W	1.00 (5)	1.97 (5)	2.972 (4)	175 (4)
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Fig. 1

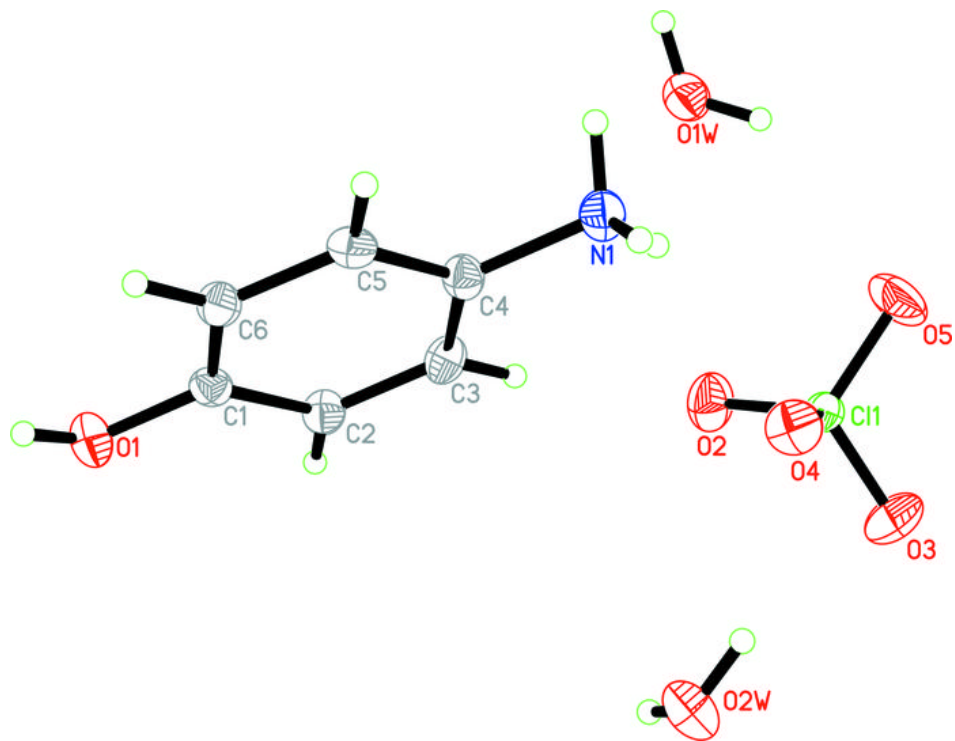




Fig. 2

