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4-Hydroxyanilinium perchlorate dihydrate

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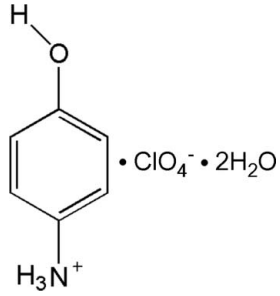
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.048; wR factor = 0.097; data-to-parameter ratio = 13.5.

In the crystal structure of the title compound, $C_6H_8NO^+\cdot ClO_4^-\cdot 2H_2O$, intermolecular N—H···O and O—H···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 N—H···O hydrogen bonds. In addition, the crystal structure exhibits weak intermolecular C—H···π interactions.

Related literature

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



Experimental

Crystal data

$C_6H_8NO^+\cdot ClO_4^-\cdot 2H_2O$
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^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 298 K
0.40 × 0.30 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
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_{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
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}
Absolute structure: Flack (1983), 1049 Friedel pairs
Flack parameter: 0.00 (7)

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C1–C6 benzene ring.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O*···O2*W*^{i}	0.75 (3)	2.10 (3)	2.801 (3)	156 (4)
N1—H1*N*···O4	0.79 (5)	2.34 (5)	3.016 (4)	144 (4)
N1—H2*N*···O1*W*^{ii}	0.98 (4)	1.98 (5)	2.951 (4)	168 (4)
N1—H3*N*···O1*W*	1.00 (5)	1.97 (5)	2.972 (4)	175 (4)
O1*W*—H1*AW*···O3^{iii}	0.79 (5)	2.40 (7)	3.089 (3)	146 (8)
O1*W*—H1*BW*···O5	0.83 (4)	2.47 (6)	3.083 (4)	132 (5)
O2*W*—H2*AW*···O4	0.93 (4)	2.28 (4)	3.068 (4)	143 (4)
O2*W*—H2*BW*···O1^{iv}	0.77 (3)	2.17 (3)	2.937 (3)	173 (5)
C2—H2···*Cg*1^{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

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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.

supporting information

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4-Hydroxyanilinium perchlorate dihydrate

Xue-qun Fu

S1. 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 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···O , O—H···O hydrogen bonds and weak intermolecular C—H···π 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···O hydrogen bonds.

S2. 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.

S3. 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···H =1.35 (10) Å). Their displacement parameters were freely refined.

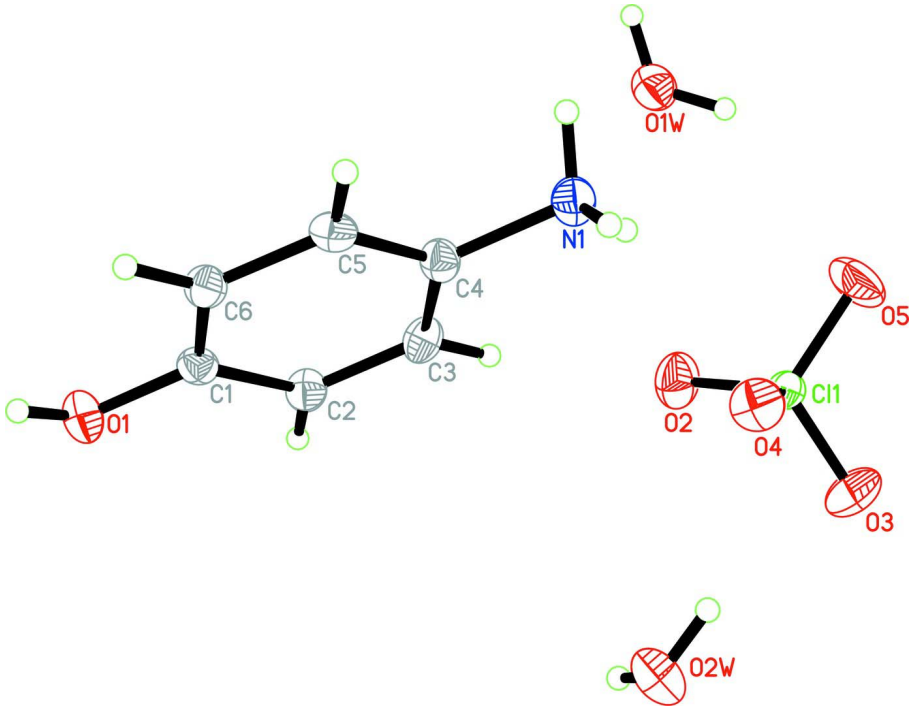

Figure 1

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are presented as a small cycles of arbitrary radius.

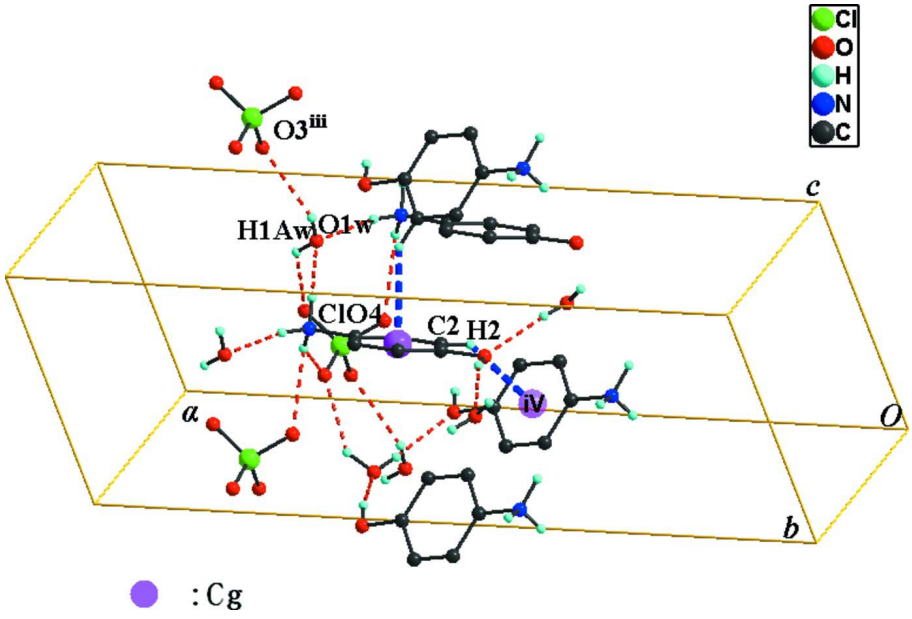

Figure 2

N—H···O, O—H···O and C—H···π 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

$C_6H_8NO^+·ClO_4^-·2H_2O$
$M_r = 245.62$
Orthorhombic, $Pna2_1$
Hall symbol: P 2c -2n
$a = 24.341$ (5) Å
$b = 5.253$ (1) Å
$c = 7.824$ (2) Å
$V = 1000.4$ (4) Å^3
$Z = 4$
$F(000) = 512$
$D_x = 1.631$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4523 reflections
$\theta = 3.1$–$55.2°$
$\mu = 0.40$ mm^{-1}
$T = 298$ K
Prism, colourless
0.40 × 0.30 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 13.6612 pixels mm^{-1}
ω 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 $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
$h = -31 \rightarrow 31$
$k = -6 \rightarrow 6$
$l = -10 \rightarrow 10$

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
Primary atom site location: structure-invariant direct methods
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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}
Absolute structure: Flack (1983), 1049 Friedel pairs
Absolute structure 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	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 (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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, º)

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, º)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O2*W*^{i}	0.75 (3)	2.10 (3)	2.801 (3)	156 (4)
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