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Diprotonated adeninium diperchlorate hydrate at 120 K

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Key indicators

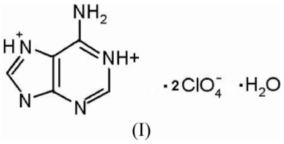
Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
Disorder in solvent or counterion
R factor = 0.036
wR factor = 0.105
Data-to-parameter ratio = 22.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_5H_9N_5^{2+}\cdot 2ClO_4^{-}\cdot H_2O$, the structure can be described as alternating layers of $C_5H_9N_5^{2+}$ and ClO_4^{-} ions along the *a* axis. Layers of adeninium cations and perchlorate anions are linked by strong anion–cation and anion–water hydrogen bonds *via* the sandwiched water molecules. This three-dimensional complex network of hydrogen bonds (N—H···O) reinforces the cohesion of the ionic structure.

Comment

Structure elucidation of components of nucleic acids and their derivatives are of interest, because of their widespread biological occurrence (Richards *et al.*, 1972; Perutz & Ten Eyck, 1972). Adenine is one of the precursors of DNA and RNA nucleotides, along with cytosine, guanine, thymine, and uracil. The crystal structures of adenine hydrochloride hemihydrate (Cunane & Taylor, 1997), adenine hydrobromide hemihydrate (Langer & Huml, 1978*a*), adenine dihydrochloride (Kistenmacher & Shigematsu, 1974), adeninium dinitrate (Hardgrove *et al.*, 1983), adeninium phosphate (Langer *et al.*, 1979), adeninium sulfate (Langer & Huml, 1978*b*), and adeninium hemisulfate hydrate (Langer *et al.*, 1978) have been reported. In several crystal structures of compounds with organic bases, amino acids and inorganic acids, the structural cohesion is assured by strong hydrogen bonds, as was observed in *m*-carboxyphenylammonium nitrate (Benali-Cherif, Cherouana *et al.*, 2002) and L-histidinium dinitrate (Benali-Cherif, Benguedouar *et al.*, 2002), *m*-carboxyphenylammonium phosphate (Benali-Cherif, Bendheif *et al.*, 2002), *p*-carboxyphenylammonium dihydrogenmonophosphate monohydrate (Benali-Cherif, Abouimrane *et al.*, 2002), guaninium dinitrate dihydrate (Bouchouit *et al.*, 2002), guaninium sulfate monohydrate (Cherouana *et al.*, 2003) and L-valinium monohydrogenphosphite (Bendheif *et al.*, 2003). The main purpose of the present study is to examine the hydrogen bonding engineered in crystals of diprotonated adeninium diperchlorate hydrate, (I), at 120 K.



(I)

The structure determination reveals that the imidazolyl and pyrimidine rings are coplanar. The perchlorate ions are slightly disordered at 120 K, but remain tetrahedral in shape with Cl—O distances and O—Cl—O angles ranging from

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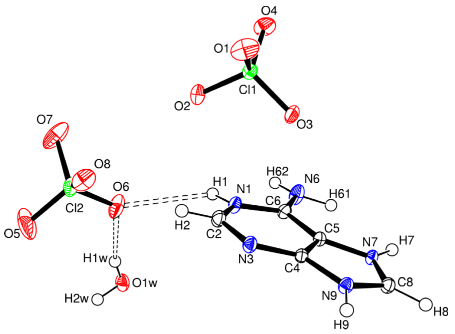

Figure 1
An *ORTEP*-3 (Farrugia, 1997) view of the title compound, with the atom-numbering scheme and 50% probability displacement ellipsoids.

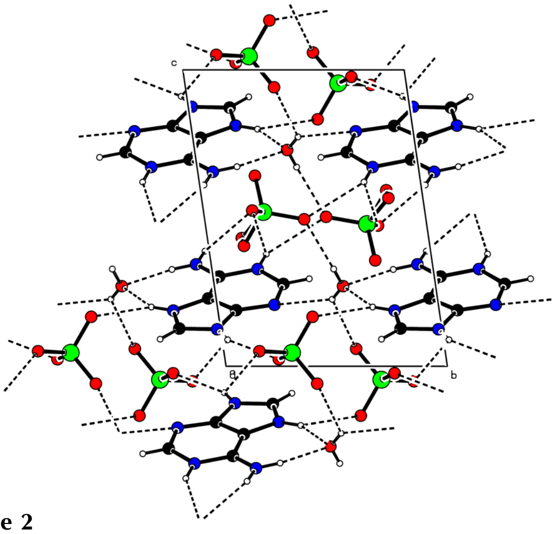

Figure 2
PLUTON (Spek, 1990) view of the ionic structure, showing the immediate hydrogen-bonded surroundings of anions and cation.

1.4413 (11) to 1.471 (5) Å and 107.9 (3) to 121.6 (2)°. Two imino groups of the imidazolyl and pyrimidine moieties of the adenine base are protonated at positions N1 and N7, as already reported in various crystal structures containing adenine cations (adeninium sulfate, adenine dihydrochloride and adeninium dinitrate). This is evident from the increase in the ring angle at the sites of protonation, namely N1 and N7. The internal angles at N1 and N7 [C6—N1—C2 = 124.02 (15)° and C8—N7—C5 = 108.31 (14)°] have increased from the reported 119.8° and 104.4° values in the unprotonated adenine (Voet & Rich, 1970). The diprotonated adenenium cation and perchlorate anion are linked by hydrogen bonds (Table 2 and Fig. 2). N1, N6, N7 and N9 atoms are involved in the strongest intramolecular and intermolecular N—H···O hydrogen bonds with perchlorate anions. We also observed that the water molecule forms five hydrogen bonds with the adeninium and perchlorate ions, in two modes, as donor with the perchlorate anion and adeninium ion, respectively, and as acceptor with the adeninium ion (Table 2).

Experimental

The title compound was obtained as colorless crystals, after a few days, by slow evaporation of an aqueous solution of adenine and perchloric acid in the stoichiometric ratio of 1:2.

Crystal data

$C_5H_7N_5^{2+}\cdot 2ClO_4^{2-}\cdot H_2O$
$M_r = 354.07$
Triclinic, $P\overline{1}$
$a = 7.7777$ (2) Å
$b = 8.5114$ (2) Å
$c = 11.0871$ (3) Å
$\alpha = 88.703$ (2)°
$\beta = 70.074$ (2)°
$\gamma = 64.789$ (2)°
$V = 617.78$ (3) Å^3
$Z = 2$
$D_x = 1.903$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14891 reflections
$\theta = 2.0$–33.1°
$\mu = 0.59$ mm^{-1}
$T = 120$ K
Needle, colorless
0.3 × 0.2 × 0.1 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
Absorption correction: none
14891 measured reflections
4647 independent reflections
3520 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\rm max} = 33.1°$
$h = -10 \rightarrow 11$
$k = -11 \rightarrow 13$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.105$
$S = 1.10$
4647 reflections
207 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.48$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.60$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—O1	1.4413 (11)	Cl2—O7	1.4511 (13)
Cl1—O3	1.4426 (10)	Cl2—O5*B*	1.483 (6)
Cl1—O2	1.4437 (11)	N1—C6	1.3605 (17)
Cl1—O4	1.4480 (11)	N1—C2	1.3681 (17)
Cl2—O5*A*	1.410 (6)	N7—C8	1.3138 (17)
Cl2—O8	1.4293 (12)	N7—C5	1.3784 (16)
Cl2—O6	1.4483 (11)		
O1—Cl1—O3	109.82 (7)	O5*A*—Cl2—O7	99.8 (2)
O1—Cl1—O2	109.39 (7)	O8—Cl2—O7	108.92 (7)
O3—Cl1—O2	109.11 (6)	O6—Cl2—O7	108.68 (8)
O1—Cl1—O4	109.38 (7)	O8—Cl2—O5*B*	100.2 (2)
O3—Cl1—O4	109.56 (6)	O6—Cl2—O5*B*	110.7 (3)
O2—Cl1—O4	109.57 (7)	O7—Cl2—O5*B*	118.7 (2)
O5*A*—Cl2—O8	121.7 (2)	C6—N1—C2	124.11 (12)
O5*A*—Cl2—O6	107.8 (3)	C8—N7—C5	108.34 (11)
O8—Cl2—O6	109.12 (7)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O7$^{\rm i}$	0.86	2.16	2.909 (2)	146
N1—H1···O6	0.86	2.46	3.025 (2)	124
N7—H7···O1*W*$^{\rm ii}$	0.86	1.91	2.686 (2)	150
N7—H7···O2$^{\rm iii}$	0.86	2.40	2.963 (2)	123
N9—H9···O4$^{\rm iv}$	0.86	2.09	2.849 (2)	146
N9—H9···O3$^{\rm v}$	0.86	2.33	2.868 (2)	121
N6—H6*A*···O7$^{\rm i}$	0.86	2.22	2.941 (2)	141
N6—H6*B*···O1*W*$^{\rm ii}$	0.86	1.97	2.799 (2)	161
O1*W*—H1*W*···O6	0.80 (1)	2.03 (1)	2.798 (2)	160 (2)
O1*W*—H2*W*···N3$^{\rm vi}$	0.78 (1)	2.25 (2)	2.907 (2)	142 (2)
O1*W*—H2*W*···O1$^{\rm vii}$	0.78 (1)	2.47 (2)	3.002 (2)	127 (2)

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

H atoms bonded to carbon and nitrogen atoms were placed and fixed at calculated positions, with isotropic displacement parameters, using a riding model. H atoms associated with the water molecule were located from Fourier difference maps and refined freely. In the initial refinement of the title compound, atom O5 of one perchlorate anion showed large anisotropy of apparent thermal motion. The final refinement was carried out with a model in which O5 is distributed over two sites with equal occupancy (O5*A* and O5*B*), to simulate a disorder that occurs by a twist around the Cl2—O5 bond.

Data collection: *KappaCCD Software* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR*2002 (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *PLUTON* (Spek, 1990); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST* (Nardelli, 1995).

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