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Adeninium perchlorate adenine dihydrate

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.138
Data-to-parameter ratio = 13.4

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

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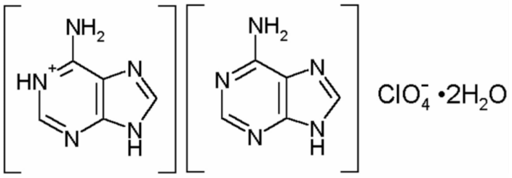
The structure of the title compound, $C_5H_6N_5^+\cdot ClO_4^-\cdot C_5H_5N_5\cdot 2H_2O$, contains both an adeninium cation (AdeH$^+$) and an adenine molecule (Ade). As a result of the protonation, the C—N—C angle at the protonated N atom is larger by 4° than the corresponding angle in the neutral adenine molecule. The crystal packing is governed by classical hydrogen bonds, connecting the Ade and AdeH$^+$ moieties in the crystallographic [101] direction. In addition, AdeH$^+$ and Ade form hydrogen bonds with the water molecules. These hydrogen bonds increase the dimensionality of the system to three-dimensional space. The water molecules are connected to each other by hydrogen bonds in the [001] direction.

Comment

The adeninium cation (1+ or 2+) is known to form a variety of inorganic salts, *e.g.* chloride (Kistenmacher & Shigematsu, 1974), bromide (Langer & Huml, 1978*a*), bistriiodide (Cheng *et al.*, 2002), sulfate (Langer & Huml, 1978*b*), nitrate (Hingerty *et al.*, 1981) or phosphate (Langer *et al.*, 1979). Recently, the structure of the adeninium salt with perchlorate as counter-anion, $(AdeH_2)(ClO_4)_2\cdot H_2O$, has been described (Bendjeddou *et al.*, 2003). We report here the structure of another compound in this family, adeninium perchlorate adenine dihydrate, (I).



(I)

The crystal structure of (I) contains both adeninium cations (AdeH$^+$) and neutral adenine molecules (Ade). The positive charge of the AdeH$^+$ ion is balanced by the perchlorate anion. The asymmetric unit is completed by two water molecules (Fig. 1). A similar architecture comprising an adenine cation and a neutral adenine molecule was reported with tetrafluoroborate as the counterion (Young *et al.*, 1991).

The molecular dimensions in Ade and AdeH$^+$ (Table 1) are comparable with those observed in the free base (Voet & Rich, 1970) and with those in, for example, adenine hydrochloride (Kistenmacher & Shigematsu, 1974). In agreement with the relative basicity of the N atoms in adenine (N9 > N1 > N7 > N3 > N10$_{\text{exocyclic}}$; Lippert, 2000), atoms N9 are protonated in both Ade and AdeH$^+$. In addition, the protonation of atom N1 takes place in the AdeH$^+$ cation. As a result of this

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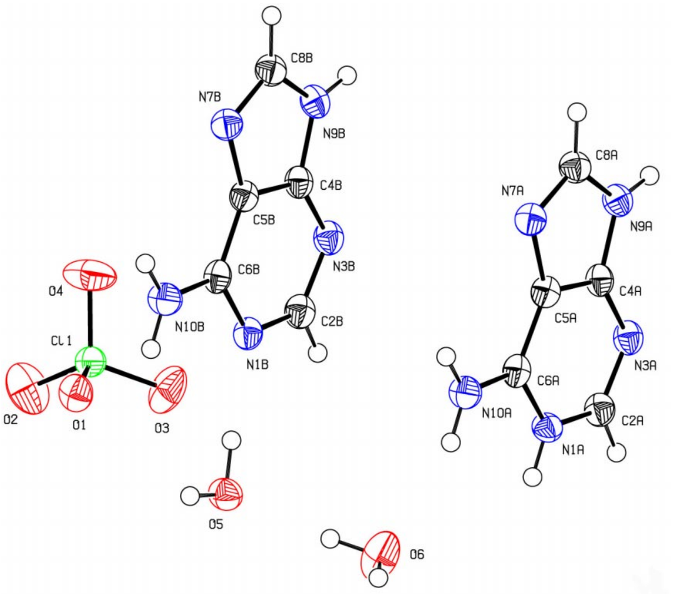

Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

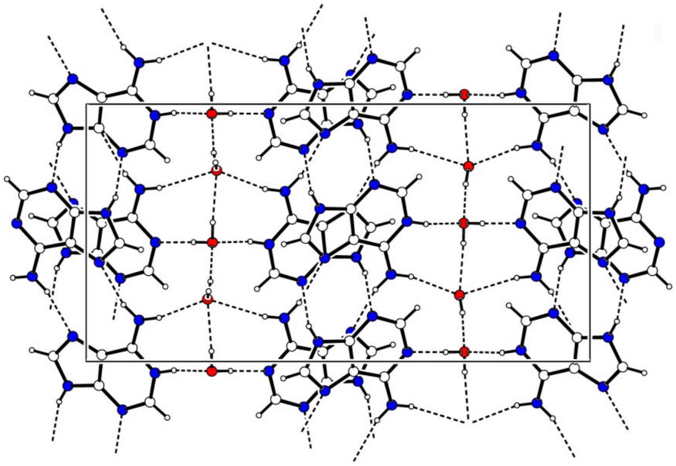

Figure 2
A view, along the *a* axis, of the crystal packing in (I). Hydrogen bonds are shown as dashed lines. The perchlorate anions have been omitted for clarity.

protonation, the C2*A*—N1*A*—C6*A* angle is larger by 4° than the C2*B*—N1*B*—C6*B* angle in the neutral adenine molecule. The Cl—O bond distances and O—Cl—O angles show nearly ideal tetrahedral geometry, and they are comparable with the values reported with perchlorate as the counterion for diprotonated adenine, $(AdeH_2)(ClO_4)_2 \cdot H_2O$ (Bendjeddou *et al.*, 2003).

The crystal packing in (I) is mostly governed by classical hydrogen bonds (Table 2). Atoms N3, N7, N9 and exocyclic N10 of $AdeH^+$ and Ade participate in the formation of hydrogen bonds which connect these residues in the [101] direction. In addition, the exocyclic atom N10, the protonated atom N1*A* (in $AdeH^+$) and atom N1*B* (in Ade) form hydrogen bonds with the water molecules. These hydrogen bonds increase the dimensionality of the system to three-dimensional space (Fig. 2). The water molecules are connected to each other by hydrogen bonds in the [001] direction. The perchlorate anions are connected *via* O—H···O hydrogen bonds to the water O6 molecules, and *via* weak C—H···O interactions to the Ade and $AdeH^+$ molecules (Fig. 3).

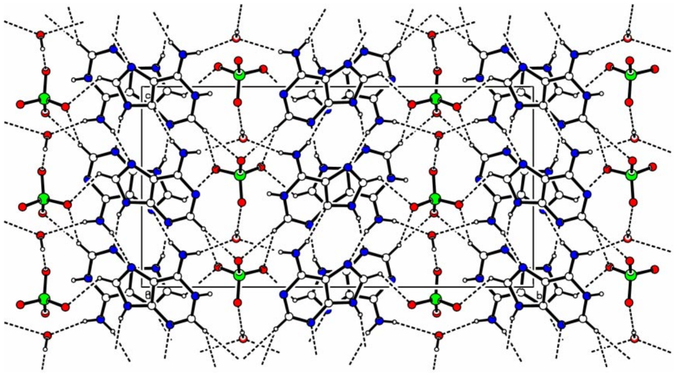

Figure 3
A view of the packing in (I), showing the O—H···O and C—H···O contacts formed by the perchlorate anions. The water O5 molecules have been omitted for clarity.

Experimental

The title compound was isolated from a reaction mixture containing adenine, $Zn(ClO_4)_2$, NaOH and 1,4,7-triazacyclononane (tacn) in the ratio 0.265:0.265:0.800:0.265 mmol. The pH of the solution was adjusted to 5.0 using dilute $HClO_4$. Crystals of (I) grew from the reaction mixture after four weeks.

Crystal data

$C_5H_6N_5^+ \cdot ClO_4^- \cdot C_5H_5N_5 \cdot 2H_2O$
$M_r = 406.77$
Monoclinic, $P2_1/c$
$a = 7.7750$ (2) Å
$b = 20.1180$ (5) Å
$c = 10.5900$ (3) Å
$\beta = 103.8880$ (15)°
$V = 1608.04$ (7) Å^3
$Z = 4$

$D_x = 1.680$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 27 858 reflections
$\theta = 1$–27.5°
$\mu = 0.30$ mm^{-1}
$T = 150$ (2) K
Needle, colourless
0.35 × 0.30 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: none
28 827 measured reflections
3656 independent reflections

2341 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\rm max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -26 \rightarrow 26$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.138$
$S = 1.05$
3656 reflections
272 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0721P)^2 + 0.3603P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.52$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1*A*—C2*A*	1.357 (2)	C6*B*—N10*B*	1.333 (2)
N1*A*—C6*A*	1.362 (2)	Cl1—O4	1.4287 (15)
C6*A*—N10*A*	1.316 (2)	Cl1—O2	1.4311 (15)
N1*B*—C2*B*	1.348 (2)	Cl1—O1	1.4325 (15)
N1*B*—C6*B*	1.355 (2)	Cl1—O3	1.4362 (16)
C2*A*—N1*A*—C6*A*	123.71 (16)	N1*B*—C6*B*—C5*B*	117.27 (16)
N3*A*—C2*A*—N1*A*	125.33 (17)	O4—Cl1—O2	108.54 (12)
N10*A*—C6*A*—N1*A*	120.27 (17)	O4—Cl1—O1	109.60 (8)
N1*A*—C6*A*—C5*A*	113.95 (15)	O2—Cl1—O1	109.30 (8)
C2*B*—N1*B*—C6*B*	119.72 (16)	O4—Cl1—O3	109.63 (9)
N3*B*—C2*B*—N1*B*	127.93 (17)	O2—Cl1—O3	109.61 (9)
N10*B*—C6*B*—N1*B*	119.08 (17)	O1—Cl1—O3	110.15 (10)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*A*—H1*A*···O5^{i}	0.86	1.87	2.715 (2)	169
N9*A*—H9*A*···N3*B*^{ii}	0.86	2.01	2.847 (2)	163
N10*A*—H10*A*···O6	0.89 (2)	2.18 (2)	3.049 (2)	165 (2)
N10*A*—H10*B*···N7*B*^{iii}	0.88 (2)	2.06 (2)	2.885 (2)	156 (2)
N9*B*—H9*B*···N3*A*^{ii}	0.86	2.09	2.918 (2)	161
N10*B*—H10*C*···O6^{iv}	0.87 (2)	2.48 (2)	3.322 (2)	164 (2)
N10*B*—H10*D*···N7*A*^{iii}	0.85 (2)	2.15 (2)	2.969 (2)	160 (2)
O5—H1*W*···O6^{iv}	0.88 (2)	2.08 (2)	2.897 (2)	156 (2)
O5—H2*W*···N1*B*	0.91 (2)	1.79 (2)	2.700 (2)	177 (2)
O6—H3*W*···O3^{v}	0.84 (2)	2.21 (2)	2.999 (2)	157 (3)
O6—H4*W*···O5	0.88 (2)	1.88 (2)	2.763 (3)	174 (2)
C2*A*—H2*A*···O1^{vi}	0.93	2.49	3.405 (2)	167
C2*A*—H2*A*···O4^{vi}	0.93	2.47	3.205 (2)	136
C2*B*—H2*B*···O1^{i}	0.93	2.50	3.412 (2)	166
C2*B*—H2*B*···O2^{i}	0.93	2.59	3.349 (2)	139
C8*A*—H8*A*···O2^{vii}	0.93	2.39	3.045 (2)	127
C8*B*—H8*B*···O4^{viii}	0.93	2.43	3.032 (2)	122

Symmetry codes: (i) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $-x, 1-y, 1-z$; (iii) $1-x, 1-y, 2-z$; (iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $1+x, y, z$; (vi) $x, y, z-1$; (vii) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (viii) $-x, 1-y, 2-z$.

All H atoms were located in difference Fourier maps. During the refinement, the H atoms of Ade and AdeH$^+$ were treated as riding on the parent C and N atoms, with C—H = 0.93 and N—H = 0.86 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N). The positions of the amine H atoms were refined freely along with their isotropic displacement parameters. The water H atoms were refined with the restraint O—H = 0.88 (2) Å. Analysis of the crystal structure by *PLATON* (Spek, 2003) showed pseudo-symmetry ($P2_1/m$). The test did not take into account the reflection file, where a number of well observed reflections with $l = 2n + 1$ and $F^2 > 3\sigma(F^2)$, and even with $F^2 > 40\sigma(F^2)$, are present, forbidding the possibility of halving the *c* parameter. As the positions of the heavy atoms follow closely the pseudo-translational symmetry $(0,0,\frac{1}{2})$, this symmetry was also imposed on the positions of the H atoms in the first stages of the solution. Therefore, two models of protonation were tested. In the first model, the protonating H atom was disordered and attached to both atoms N1*A* and N1*B* with an occupancy of 0.5, leading to wR_2 = 0.140 and S = 1.06. In the second model, described in this paper, the protonating H atom was attached only to atom N1*A,* resulting in wR_2 = 0.138 and S = 1.05. The latter model is also in agreement with the molecular geometry, where the protonated adenine molecule has a larger C2—N1—C6 angle than the neutral one.

Data collection: *COLLECT* (Nonius, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97, *enCIFer* (Allen *et al.*, 2004) and *WinGX* (Farrugia, 1999).

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