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Bis(adeninium) chloranilate dihydrate

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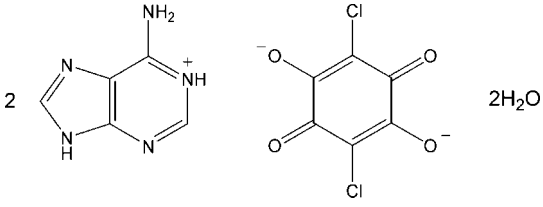
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.035; wR factor = 0.089; data-to-parameter ratio = 15.5.

In the crystal structure of the title compound, $2C_5H_6N_5^+\cdot C_6Cl_2O_4^{2-}\cdot 2H_2O$, two adeninium cations, one chloranilate dianion and two water molecules are held together by O—H···O, N—H···O, O—H···Cl and C—H···O hydrogen bonds, forming a centrosymmetric unit. The chloranilate dianion resides on an inversion centre. The anion and two cations are approximately coplanar, the dihedral angle between the planes of the adeninium cation and the chloranilate dianion being 3.25 (3)°. The crystal structure is stabilized by inter-unit N—H···N, N—H···O, N—H···Cl and O—H···N hydrogen bonds, forming a three-dimensional hydrogen-bonding network.

Related literature

For related compounds, see: Gotoh *et al.* (2006); Jai-nhuknan *et al.* (1997); Ojala *et al.* (1994); Young *et al.* (1991).



Experimental

Crystal data

$2C_5N_5H_6^+\cdot C_6Cl_2O_4^{2-}\cdot 2H_2O$
M_r = 515.27
Monoclinic, $P2_1/c$
a = 7.7080 (4) Å
b = 7.1460 (3) Å
c = 17.9718 (9) Å
β = 95.366 (2)°
V = 985.57 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.39 mm^{-1}
T = 100 (2) K
0.30 × 0.25 × 0.13 mm

Data collection

Rigaku R-AXIS RAPID-II diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.854, T_{max} = 0.950
10874 measured reflections
2876 independent reflections
2560 reflections with $I > 2\sigma(I)$
R_{int} = 0.058

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.089
S = 1.08
2876 reflections
186 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H2···O2^{i}	0.938 (17)	2.357 (17)	3.1004 (16)	136.0 (15)
N1—H1···O1	0.89 (2)	1.91 (2)	2.7913 (15)	168 (2)
N3—H3···Cl1^{ii}	0.90 (2)	2.81 (2)	3.3038 (12)	115.4 (17)
N3—H3···O2^{ii}	0.90 (2)	1.88 (2)	2.7682 (14)	166 (2)
N5—H5···N4^{iii}	0.89 (2)	2.06 (2)	2.9044 (16)	158 (2)
N5—H6···O3	0.90 (2)	1.87 (2)	2.7358 (16)	160 (2)
O3—H7···Cl1	0.85 (3)	2.66 (3)	3.2311 (11)	126 (2)
O3—H7···O1	0.85 (3)	1.98 (3)	2.7681 (14)	155 (3)
O3—H8···N2^{iv}	0.94 (3)	1.93 (3)	2.8628 (15)	174 (2)

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

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2052).

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supplementary materials

Acta Cryst. (2007). E**63**, o4433 [**doi:10.1107/S1600536807052087**]

Bis(adeninium) chloranilate dihydrate

K. Gotoh, R. Ishikawa and H. Ishida

Comment

The title compound, (I), was prepared in order to extend our studies on D—H···A hydrogen bonding (*D* = N, O, or C; *A* = N, O or Cl) in the pyridine–chloranilic acid system (Gotoh *et al.*, 2006). Adenine, one of the nucleotide building blocks, is a strong base and some crystal structures of its organic salts have been reported (Jai-Nhuknan *et al.*, 1997; Ojala *et al.*, 1994; Young *et al.*, 1991).

The asymmetric unit in (I) contains one adeninium cation, one half chloranilate dianion and a water molecule; these three molecules are held together by O3—H7···O1, N1—H1···O1, N5—H6···O3, O3—H7···Cl1 and C5—H2···O2^{i} hydrogen bonds (Table 1), forming a centrosymmetric unit (Fig. 1). The neighboring units related by an inversion center are connected by an N5—H5···N4^{iii} hydrogen bond (Table 1), resulting in an approximately planar tape running along the [2$\bar{1}$0] direction (Fig. 2). The tapes are further connected by N3—H3···Cl1^{ii}, N3—H3···O2^{ii} and O3—H8···N2^{iv} hydrogen bonds (Table 1), forming a three-dimensional hydrogen-bond network.

Experimental

Crystals were obtained by slow evaporation from a methanol solution (100 ml) of chloranilic acid with adenine in a 1:2 molar ratio (37 and 48 mg for chloranilic acid and adenine, respectively).

Refinement

H atoms were found in a difference Fourier map and refined isotropically [refined distances: O—H = 0.85 (3)–0.94 (3), N—H = 0.88 (2)–0.90 (2) and C—H = 0.939 (19)–0.965 (19) Å].

Figures

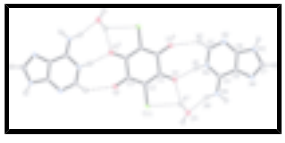

Fig. 1. A view of the centrosymmetric unit of the title compound, with the atom numbering. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. N—H···O, O—H···O O—H···Cl and C—H···O hydrogen bonds are indicated by dashed lines [symmetry code (i) is as given in Table 1].

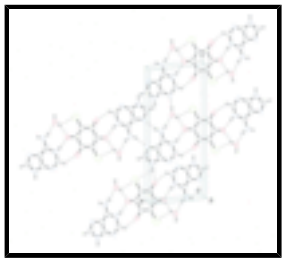

Fig. 2. A partial packing diagram, approximately viewed down the *b* axis, showing the hydrogen-bonded molecular tape and the hydrogen-bonding scheme. Dashed lines show N—H···O, N—H···N, O—H···O, O—H···N, C—H···O, N—H···Cl and O—H···Cl hydrogen bonds.

Bis(adeninium) chloranilate dihydrate

Crystal data

$2C_5N_5H_6^+ \cdot C_6Cl_2O_4^{2-} \cdot 2H_2O$	$F_{000} = 528.00$
$M_r = 515.27$	$D_x = 1.736$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71075$ Å
Hall symbol: -P 2ybc	Cell parameters from 12221 reflections
$a = 7.7080$ (4) Å	$\theta = 3.1$–$30.1°$
$b = 7.1460$ (3) Å	$\mu = 0.39$ mm^{-1}
$c = 17.9718$ (9) Å	$T = 100$ (2) K
$\beta = 95.366$ (2)°	Plate, purple
$V = 985.57$ (8) Å^3	0.30 × 0.25 × 0.13 mm
$Z = 2$	

Data collection

Rigaku R-AXIS RAPID-II diffractometer	2560 reflections with $I > 2\sigma(I)$
Detector resolution: 10.00 pixels mm^{-1}	$R_{int} = 0.058$
$T = 100$(2) K	$\theta_{max} = 30.0°$
ω scans	$\theta_{min} = 3.1°$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$h = -10 \rightarrow 10$
$T_{min} = 0.854$, $T_{max} = 0.950$	$k = -10 \rightarrow 9$
10874 measured reflections	$l = -25 \rightarrow 24$
2876 independent reflections	

Refinement

Refinement on F^2	All H-atom parameters refined
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 0.5544P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.089$	$\Delta\rho_{max} = 0.39$ e Å^{-3}
$S = 1.08$	$\Delta\rho_{min} = -0.37$ e Å^{-3}
2876 reflections	Extinction correction: none
186 parameters	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > 2\text{sigma}(F^2)$ 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	0.19323 (4)	0.42773 (4)	0.660836 (15)	0.01354 (9)
O1	0.32479 (12)	0.34900 (15)	0.51288 (5)	0.0162 (2)
O2	−0.16665 (12)	0.57064 (14)	0.62314 (5)	0.01537 (19)
O3	0.54421 (14)	0.20531 (15)	0.62976 (6)	0.0187 (2)
N1	0.53807 (15)	0.21786 (16)	0.40694 (6)	0.0140 (2)
N2	0.59010 (15)	0.16074 (16)	0.28044 (6)	0.0152 (2)
N3	0.87954 (15)	0.02622 (16)	0.27282 (6)	0.0138 (2)
N4	0.97050 (14)	0.00942 (16)	0.39558 (6)	0.0137 (2)
N5	0.73247 (16)	0.13676 (17)	0.51095 (6)	0.0155 (2)
C1	0.17542 (16)	0.41976 (17)	0.50991 (7)	0.0115 (2)
C2	0.08698 (16)	0.46508 (18)	0.57219 (6)	0.0115 (2)
C3	−0.08301 (16)	0.53768 (17)	0.56819 (7)	0.0113 (2)
C4	0.69243 (16)	0.14470 (18)	0.43820 (7)	0.0126 (2)
C5	0.49359 (17)	0.2210 (2)	0.33161 (7)	0.0160 (2)
C6	0.74616 (17)	0.09277 (18)	0.31014 (7)	0.0125 (2)
C7	1.00994 (17)	−0.02156 (19)	0.32668 (7)	0.0149 (2)
C8	0.80350 (16)	0.08175 (17)	0.38542 (7)	0.0122 (2)
H1	0.462 (3)	0.269 (3)	0.4356 (12)	0.029 (5)*
H2	0.384 (2)	0.273 (3)	0.3169 (10)	0.016 (4)*
H3	0.876 (3)	0.011 (3)	0.2228 (13)	0.032 (5)*
H4	1.120 (3)	−0.071 (3)	0.3134 (11)	0.019 (4)*
H5	0.833 (3)	0.085 (3)	0.5277 (12)	0.025 (5)*
H6	0.661 (3)	0.182 (3)	0.5434 (14)	0.038 (6)*
H7	0.461 (4)	0.262 (4)	0.6051 (16)	0.055 (8)*
H8	0.553 (3)	0.256 (4)	0.6781 (17)	0.056 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01460 (15)	0.01792 (15)	0.00795 (13)	0.00072 (11)	0.00021 (9)	0.00064 (10)
O1	0.0136 (4)	0.0241 (5)	0.0110 (4)	0.0042 (4)	0.0015 (3)	0.0002 (4)
O2	0.0157 (4)	0.0209 (5)	0.0100 (4)	0.0019 (4)	0.0040 (3)	0.0002 (4)
O3	0.0187 (5)	0.0243 (5)	0.0133 (4)	0.0044 (4)	0.0019 (4)	−0.0020 (4)
N1	0.0141 (5)	0.0159 (5)	0.0123 (5)	0.0024 (4)	0.0028 (4)	−0.0011 (4)
N2	0.0159 (5)	0.0178 (5)	0.0119 (5)	0.0003 (4)	0.0007 (4)	0.0000 (4)
N3	0.0160 (5)	0.0163 (5)	0.0095 (4)	−0.0004 (4)	0.0026 (4)	−0.0003 (4)
N4	0.0135 (5)	0.0153 (5)	0.0123 (5)	0.0000 (4)	0.0017 (4)	0.0000 (4)
N5	0.0165 (5)	0.0208 (5)	0.0094 (5)	0.0020 (4)	0.0023 (4)	−0.0005 (4)
C1	0.0132 (5)	0.0126 (5)	0.0089 (5)	−0.0014 (4)	0.0018 (4)	0.0000 (4)

C2	0.0138 (5)	0.0138 (5)	0.0069 (5)	−0.0007 (4)	0.0003 (4)	0.0004 (4)
C3	0.0133 (5)	0.0116 (5)	0.0091 (5)	−0.0020 (4)	0.0013 (4)	−0.0001 (4)
C4	0.0135 (5)	0.0128 (5)	0.0115 (5)	−0.0016 (4)	0.0014 (4)	−0.0005 (4)
C5	0.0152 (6)	0.0187 (6)	0.0137 (5)	0.0014 (5)	−0.0004 (4)	0.0007 (5)
C6	0.0151 (5)	0.0129 (5)	0.0100 (5)	−0.0016 (4)	0.0029 (4)	−0.0006 (4)
C7	0.0155 (6)	0.0170 (6)	0.0123 (5)	−0.0003 (5)	0.0024 (4)	−0.0004 (5)
C8	0.0135 (5)	0.0133 (5)	0.0098 (5)	−0.0009 (4)	0.0009 (4)	−0.0002 (4)

Geometric parameters (Å, °)

Cl1—C2	1.7423 (12)	N4—C7	1.3210 (17)
O1—C1	1.2540 (15)	N4—C8	1.3833 (16)
O2—C3	1.2512 (15)	N5—C4	1.3163 (16)
O3—H7	0.85 (3)	N5—H5	0.88 (2)
O3—H8	0.94 (3)	N5—H6	0.90 (2)
N1—C5	1.3653 (17)	C1—C2	1.4019 (16)
N1—C4	1.3709 (17)	C1—C3^{i}	1.5437 (17)
N1—H1	0.90 (2)	C2—C3	1.4049 (17)
N2—C5	1.3085 (17)	C3—C1^{i}	1.5437 (17)
N2—C6	1.3593 (17)	C4—C8	1.4096 (17)
N3—C6	1.3645 (16)	C5—H2	0.939 (19)
N3—C7	1.3718 (17)	C6—C8	1.3857 (17)
N3—H3	0.90 (2)	C7—H4	0.965 (19)
H7—O3—H8	106 (2)	O2—C3—C2	125.17 (11)
C5—N1—C4	122.71 (11)	O2—C3—C1^{i}	116.91 (11)
C5—N1—H1	116.5 (14)	C2—C3—C1^{i}	117.92 (10)
C4—N1—H1	120.8 (14)	N5—C4—N1	122.51 (12)
C5—N2—C6	112.45 (11)	N5—C4—C8	123.64 (12)
C6—N3—C7	106.02 (11)	N1—C4—C8	113.85 (11)
C6—N3—H3	125.2 (14)	N2—C5—N1	125.80 (12)
C7—N3—H3	128.7 (14)	N2—C5—H2	119.2 (11)
C7—N4—C8	103.40 (11)	N1—C5—H2	115.0 (11)
C4—N5—H5	118.1 (14)	N2—C6—N3	127.68 (11)
C4—N5—H6	121.8 (15)	N2—C6—C8	126.40 (12)
H5—N5—H6	120 (2)	N3—C6—C8	105.90 (11)
O1—C1—C2	124.90 (11)	N4—C7—N3	113.70 (12)
O1—C1—C3^{i}	117.51 (10)	N4—C7—H4	125.2 (12)
C2—C1—C3^{i}	117.58 (11)	N3—C7—H4	121.1 (12)
C1—C2—C3	124.42 (11)	N4—C8—C6	110.98 (11)
C1—C2—Cl1	118.20 (9)	N4—C8—C4	130.29 (12)
C3—C2—Cl1	117.37 (9)	C6—C8—C4	118.72 (12)
O1—C1—C2—C3	−177.45 (13)	C7—N3—C6—N2	178.54 (13)
C3^{i}—C1—C2—C3	3.3 (2)	C7—N3—C6—C8	0.03 (14)
O1—C1—C2—Cl1	2.04 (18)	C8—N4—C7—N3	0.08 (15)
C3^{i}—C1—C2—Cl1	−177.18 (9)	C6—N3—C7—N4	−0.07 (16)
C1—C2—C3—O2	176.49 (12)	C7—N4—C8—C6	−0.05 (15)
Cl1—C2—C3—O2	−3.01 (18)	C7—N4—C8—C4	−178.86 (13)

C1—C2—C3—C1^{i}	−3.3 (2)	N2—C6—C8—N4	−178.52 (12)
Cl1—C2—C3—C1^{i}	177.16 (9)	N3—C6—C8—N4	0.01 (14)
C5—N1—C4—N5	−177.86 (13)	N2—C6—C8—C4	0.4 (2)
C5—N1—C4—C8	2.88 (18)	N3—C6—C8—C4	178.97 (11)
C6—N2—C5—N1	−0.4 (2)	N5—C4—C8—N4	−2.8 (2)
C4—N1—C5—N2	−1.6 (2)	N1—C4—C8—N4	176.46 (13)
C5—N2—C6—N3	−177.25 (13)	N5—C4—C8—C6	178.47 (12)
C5—N2—C6—C8	0.96 (19)	N1—C4—C8—C6	−2.27 (17)

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H2···O2^{i}	0.938 (17)	2.357 (17)	3.1004 (16)	136.0 (15)
N1—H1···O1	0.89 (2)	1.91 (2)	2.7913 (15)	168 (2)
N3—H3···Cl1^{ii}	0.90 (2)	2.81 (2)	3.3038 (12)	115.4 (17)
N3—H3···O2^{ii}	0.90 (2)	1.88 (2)	2.7682 (14)	166 (2)
N5—H5···N4^{iii}	0.89 (2)	2.06 (2)	2.9044 (16)	158 (2)
N5—H6···O3	0.90 (2)	1.87 (2)	2.7358 (16)	160 (2)
O3—H7···Cl1	0.85 (3)	2.66 (3)	3.2311 (11)	126 (2)
O3—H7···O1	0.85 (3)	1.98 (3)	2.7681 (14)	155 (3)
O3—H8···N2^{iv}	0.94 (3)	1.93 (3)	2.8628 (15)	174 (2)

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) *x*+1, −*y*+1/2, *z*−1/2; (iii) −*x*+2, −*y*, −*z*+1; (iv) *x*, −*y*+1/2, *z*+1/2.

Fig. 1

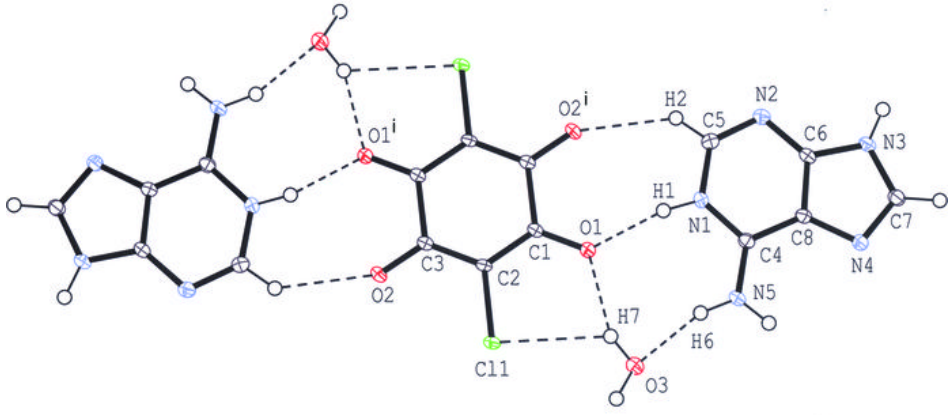

Fig. 2