3-(Ammoniomethyl)pyridinium bis(perchlorate)

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In the title molecular salt, $C_6H_{10}N_2^{2+} \cdot 2ClO_4^-$, the Cl—O bond lengths [anion 1: 1.369 (3)–1.415 (3); anion 2: 1.420 (2)–1.441 (2) Å] and the O—Cl—O angles [anion 1: 105.4 (2)–111.8 (4); anion 2: 107.8 (1)–110.3 (1)°] indicate a slight distortion of the perchlorate anions from regular tetrahedral symmetry. In the crystal, the components are linked into columns along the a-axis direction via N—H⋯O and C—H⋯O hydrogen bonds, with stacks of the organic molecules being surrounded by stacks of perchlorate anions.

Related literature

For general background to perchlorate salts with organic cations, see: Czarnecki *et al.* (1994); Czupinski *et al.* (2002, 2006). For related structures, see: Kapplinger & Keutel (1999); Ye *et al.* (2002)
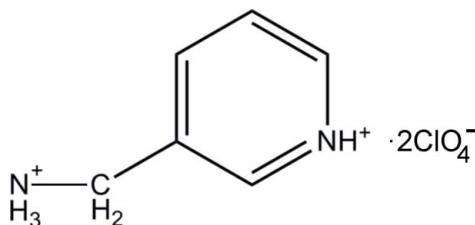
Experimental

Crystal data

$C_6H_{10}N_2^{2+} \cdot 2ClO_4^-$	$V = 1139.24$ (5) Å^3
$M_r = 309.06$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 5.1947$ (1) Å	$\mu = 0.61$ mm^{-1}
$b = 12.1221$ (3) Å	$T = 293$ K
$c = 18.2724$ (5) Å	$0.44 \times 0.33 \times 0.22$ mm
$\beta = 98.067$ (1)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	26338 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	3509 independent reflections
$T_{min} = 0.765$, $T_{max} = 0.875$	3007 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$	163 parameters
$wR(F^2) = 0.148$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{max} = 0.70$ e Å^{-3}
3509 reflections	$\Delta\rho_{min} = -0.75$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O5	0.86	2.16	2.901 (3)	144
N1—H1⋯O7[i]	0.86	2.36	2.945 (3)	125
N2—H2A⋯O2[ii]	0.89	2.09	2.866 (3)	146
N2—H2A⋯O6[iii]	0.89	2.54	3.166 (3)	128
N2—H2B⋯O6[ii]	0.89	2.10	2.925 (3)	155
N2—H2B⋯O3[iv]	0.89	2.47	2.922 (4)	112
N2—H2C⋯O1[v]	0.89	2.08	2.933 (3)	160
C5—H5⋯O1[vi]	0.93	2.54	3.350 (4)	145
C6—H6A⋯O8[vii]	0.97	2.50	3.137 (3)	123

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

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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supplementary materials

3-(Ammoniomethyl)pyridinium bis(perchlorate)

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Comment

Studies of perchlorate salts containing organic cations have had a great deal of attention in recent years, because of their ferroelectric and dielectric behaviour (Czupinski *et al.*, 2002; Czupinski *et al.*, 2006). It was shown that dynamics of pyridinium cations contributes mainly to the mecanism of solid-solid phase transition and leads ferroelectricity in these molecular-ionic crystals (Czarnecki *et al.*, 1994) Here, we report the synthesis and the crystal structure of the title compound (I), $(C_6H_{10}N_2)(ClO_4)_2$.

The structure consists of one 3-ammoniomethylpyrinidinium dication and two perchlorate anions (Fig. 1). In the crystal, the three H atoms of the ammonium group are involved into N—H···Cl and N—H···O hydrogen bonds: N2—H2C···Cl1(v), N2—H2B···Cl2(ii), N2—H2C···O1(v), N2—H2A··· (O6vi, O2iv) and N2—H2B··· (O6iv, O3vii), the two laters are bifurcated (for the symmetry codes, see Table 1). These hydrogen bonds link the ionic units (NH_3^+ and $[ClO_4]^-$) to form columns running along the *a*-axis direction (Fig.2) and situated at $y = z = 1/2$ (Fig.3). The organic groups are located between these columns *via* two kinds of hydrogen bonds: a bifurcated N—H···O and two C—H···O: N1—H1 (O5, O7viii), C6—H6A···O8(iii) and C5—H5···O1(vi) (Fig. 3, Table 1). No π-π stacking interactions between the organic rings or C—H···π interactions towards them are observed. It is worth noting that the C—N—C angles of pyridine are very sensitive to protonation: a pyridinium cation always has an expanded angle of the C—N—C in comparison with the parent pydidine. The angle C(5)—N(1)—C(1) [123.4 (2)°] is consistent with the type of pyridinium cation. The hydrogen atom HN(1), which is deprived from its parent, attaches the nitrogen atom. As expected, the $[ClO_4]^-$ anion has typical tetrahedral geometry where the Cl—O bond lengths and O—Cl—O angles are not equal to one another but vary with the environment around the O atoms. In the title compound, the Cl—O bond lengths vary from 1.369 (3) to 1.415 (3) Å for $[Cl(1)O_4]^-$ anion and from 1.420 (2) to 1.440 (2) Å for $[Cl(2)O_4]^-$ anion are comparable to that previuosly reported for the perchlorate anions (Kapplinger & Keutel, 1999). The O—Cl—O angles range from 105.4 (2) to 111.8 (4)° for the first anion and from 109.04 (15) to 110.33 (13)° for the second one. These values, which are characteristic of perchlorate anions (Ye *et al.*, 2002), clearly indicate that the coordination geometry of the Cl(2) atom can be regarded as being a less distorted tetrahedron than the one of the Cl(1). However, for the Cl(2)O4 tetrahedron, all the oxygen atoms are involved in hydrogen bonds, while only three oxygen atoms act as acceptors of hydrogen bonds for the $[Cl(1)O_4]$ tetrahedron.

### Experimental

3-ammoniomethylpyrinidinium (1 mmol, 0.108 g) was dissolved in a mixture of distilled water (10 ml) and perchloric acid (0.5 ml).The resultant solution was evaporated at room temperature. Crystals of the title compound, which remained stable under normal conditions of temperature and humidity, were isolated after several days and subjected to X-ray diffraction analysis (yield 64%).

Refinement

All the H-atoms were located in difference Fourier synthesis maps and refined as riding on their parent atoms, using *SHELXL97*(Sheldrick, 2008) defaults.

Computing details

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).
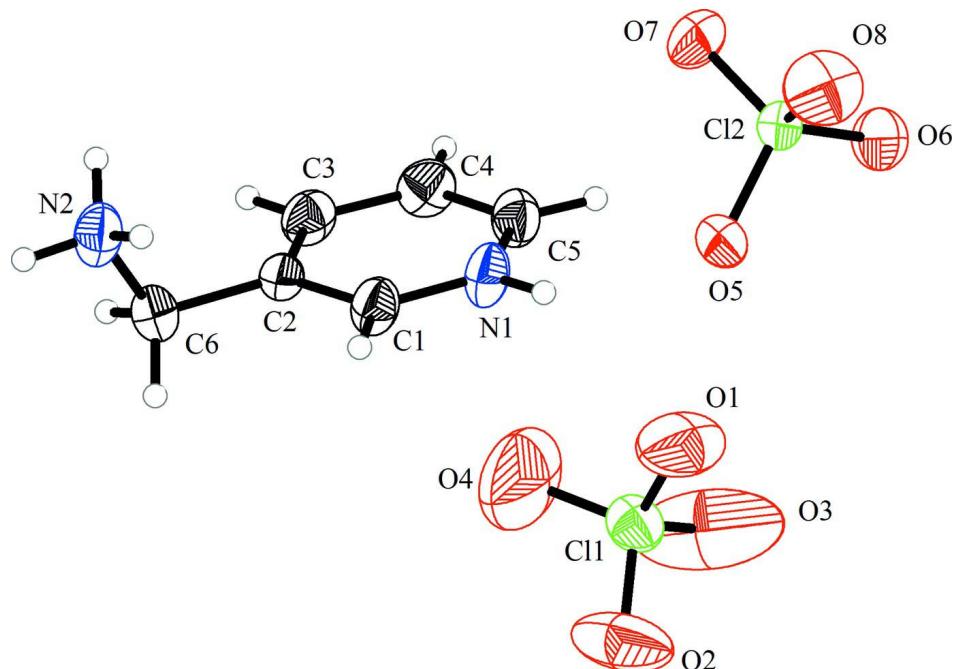
Figure 1

A view of the title compound, showing 50% probability displacement ellipsoids and arbitrary spheres for the H atoms.
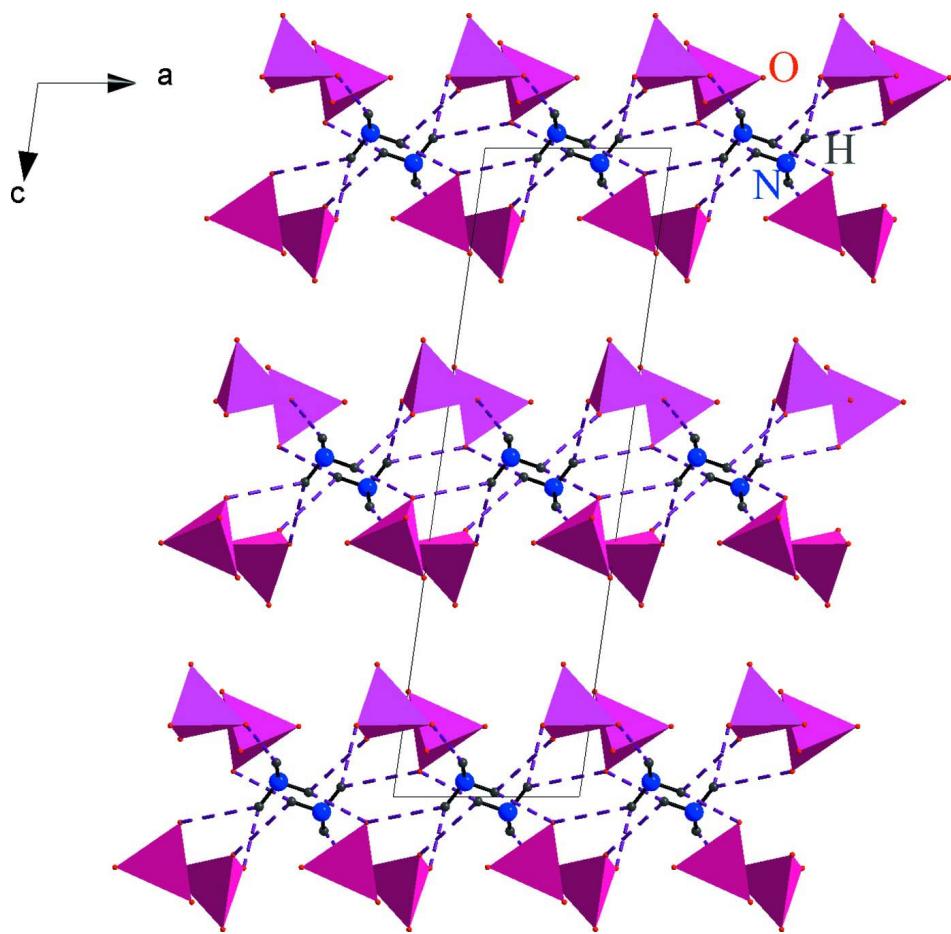
Figure 2

Partial packing of the title compound, viewed down the *b* axis, showing columns formed between perchlorate anions and ammonium groups.
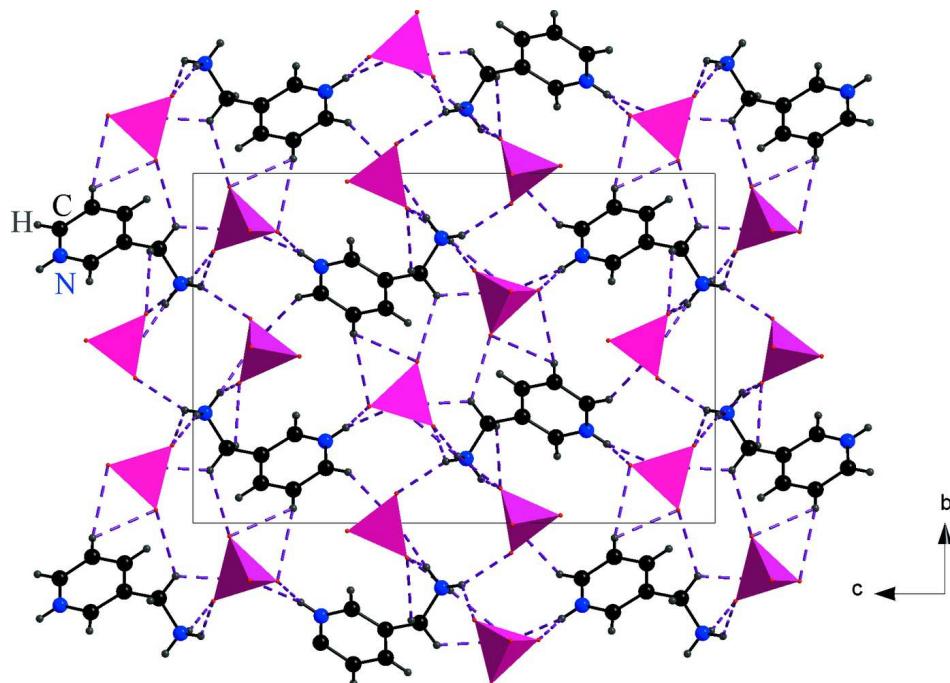
Figure 3

The crystal packing of the title compound viewed along the *a* axis.

3-(Ammoniomethyl)pyridinium bis(perchlorate)

Crystal data
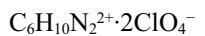
$C_6H_{10}N_2^{2+}\cdot 2ClO_4^-$	$F(000) = 632$
$M_r = 309.06$	$D_x = 1.802$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 5314 reflections
$a = 5.1947$ (1) Å	$\theta = 2.3$–$30.6°$
$b = 12.1221$ (3) Å	$\mu = 0.61$ mm^{-1}
$c = 18.2724$ (5) Å	$T = 293$ K
$\beta = 98.067$ (1)°	Block, colourless
$V = 1139.24$ (5) Å^3	$0.44 \times 0.33 \times 0.22$ mm
$Z = 4$	

Data collection

Bruker APEXII CCD area-detector diffractometer	26338 measured reflections
Radiation source: fine-focus sealed tube	3509 independent reflections
Graphite monochromator	3007 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.032$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	$\theta_{max} = 30.6°$, $\theta_{min} = 2.0°$
$T_{min} = 0.765$, $T_{max} = 0.875$	$h = -7 \rightarrow 7$
	$k = -17 \rightarrow 17$
	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.051$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.148$	
$S = 1.06$	H-atom parameters constrained
3509 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0782P)^2 + 0.9452P]$
163 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.70$ e Å^{-3}
	$\Delta\rho_{min} = -0.75$ e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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	0.11942 (12)	0.50919 (5)	0.12761 (3)	0.04193 (16)
Cl2	0.82533 (9)	0.14688 (4)	0.09563 (2)	0.03098 (14)
O1	−0.1534 (5)	0.4964 (2)	0.1114 (2)	0.0912 (10)
O2	0.2513 (6)	0.4146 (3)	0.10993 (17)	0.0916 (10)
O3	0.1869 (7)	0.5993 (4)	0.0893 (4)	0.172 (3)
O4	0.1865 (11)	0.5226 (5)	0.2043 (2)	0.169 (2)
O5	0.5608 (3)	0.16338 (19)	0.10859 (10)	0.0499 (5)
O6	0.8768 (4)	0.22306 (18)	0.03930 (11)	0.0523 (5)
O7	0.9987 (4)	0.16608 (18)	0.16220 (10)	0.0530 (5)
O8	0.8562 (5)	0.03757 (18)	0.07037 (15)	0.0673 (6)
N1	0.4671 (4)	0.26538 (17)	0.24604 (10)	0.0400 (4)
H1	0.4241	0.2266	0.2068	0.048*
N2	0.3730 (4)	0.18501 (18)	0.47673 (11)	0.0429 (5)
H2A	0.2868	0.1768	0.5152	0.064*
H2B	0.5421	0.1917	0.4928	0.064*
H2C	0.3466	0.1263	0.4474	0.064*
C1	0.3473 (5)	0.24549 (19)	0.30466 (12)	0.0377 (4)
H1A	0.2182	0.1919	0.3022	0.045*
C2	0.4155 (4)	0.30457 (18)	0.36882 (10)	0.0318 (4)
C3	0.6048 (5)	0.38511 (19)	0.36950 (12)	0.0385 (4)
H3	0.6529	0.4269	0.4119	0.046*
C4	0.7224 (5)	0.4036 (2)	0.30740 (14)	0.0417 (5)
H4	0.8501	0.4575	0.3079	0.050*
C5	0.6497 (5)	0.3420 (2)	0.24510 (12)	0.0392 (5)
H5	0.7267	0.3537	0.2028	0.047*
C6	0.2791 (5)	0.2852 (2)	0.43480 (13)	0.0443 (5)

H6A	0.3051	0.3487	0.4673	0.053*
H6B	0.0939	0.2781	0.4185	0.053*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0443 (3)	0.0361 (3)	0.0473 (3)	0.0052 (2)	0.0129 (2)	0.0049 (2)
Cl2	0.0309 (2)	0.0361 (3)	0.0261 (2)	0.00110 (17)	0.00438 (16)	−0.00042 (15)
O1	0.0420 (11)	0.0839 (18)	0.152 (3)	0.0086 (11)	0.0271 (14)	0.0586 (18)
O2	0.0762 (17)	0.104 (2)	0.0872 (19)	0.0430 (16)	−0.0138 (14)	−0.0469 (16)
O3	0.078 (2)	0.132 (3)	0.295 (6)	−0.031 (2)	−0.009 (3)	0.148 (4)
O4	0.190 (5)	0.245 (6)	0.066 (2)	0.104 (4)	−0.003 (2)	−0.048 (3)
O5	0.0325 (8)	0.0816 (14)	0.0368 (8)	0.0027 (8)	0.0089 (6)	−0.0020 (8)
O6	0.0490 (10)	0.0643 (12)	0.0455 (9)	−0.0003 (9)	0.0130 (8)	0.0202 (9)
O7	0.0437 (9)	0.0765 (13)	0.0356 (8)	−0.0043 (9)	−0.0061 (7)	−0.0026 (8)
O8	0.0796 (16)	0.0426 (11)	0.0782 (15)	0.0089 (10)	0.0055 (12)	−0.0173 (10)
N1	0.0520 (11)	0.0437 (10)	0.0241 (7)	−0.0097 (8)	0.0048 (7)	−0.0045 (7)
N2	0.0466 (11)	0.0530 (12)	0.0296 (8)	−0.0131 (9)	0.0066 (7)	0.0008 (8)
C1	0.0407 (11)	0.0434 (11)	0.0284 (9)	−0.0099 (9)	0.0028 (8)	−0.0009 (8)
C2	0.0318 (9)	0.0379 (10)	0.0256 (8)	0.0052 (7)	0.0037 (7)	−0.0005 (7)
C3	0.0416 (11)	0.0383 (10)	0.0337 (10)	−0.0002 (9)	−0.0009 (8)	−0.0066 (8)
C4	0.0400 (11)	0.0409 (11)	0.0430 (11)	−0.0087 (9)	0.0016 (9)	0.0012 (9)
C5	0.0428 (11)	0.0441 (12)	0.0318 (9)	−0.0024 (9)	0.0089 (8)	0.0049 (8)
C6	0.0426 (12)	0.0597 (14)	0.0325 (10)	0.0077 (10)	0.0116 (9)	0.0003 (10)

Geometric parameters (Å, º)

Cl1—O3	1.369 (3)	N2—H2B	0.8900
Cl1—O2	1.397 (2)	N2—H2C	0.8900
Cl1—O4	1.405 (4)	C1—C2	1.377 (3)
Cl1—O1	1.415 (3)	C1—H1A	0.9300
Cl2—O8	1.420 (2)	C2—C3	1.385 (3)
Cl2—O7	1.4272 (18)	C2—C6	1.500 (3)
Cl2—O6	1.4357 (18)	C3—C4	1.380 (3)
Cl2—O5	1.4406 (18)	C3—H3	0.9300
N1—C5	1.329 (3)	C4—C5	1.369 (3)
N1—C1	1.334 (3)	C4—H4	0.9300
N1—H1	0.8600	C5—H5	0.9300
N2—C6	1.482 (3)	C6—H6A	0.9700
N2—H2A	0.8900	C6—H6B	0.9700
O3—Cl1—O2	111.6 (3)	N1—C1—C2	119.7 (2)
O3—Cl1—O4	111.8 (4)	N1—C1—H1A	120.1
O2—Cl1—O4	105.4 (2)	C2—C1—H1A	120.1
O3—Cl1—O1	107.49 (19)	C1—C2—C3	118.16 (19)
O2—Cl1—O1	111.8 (2)	C1—C2—C6	120.6 (2)
O4—Cl1—O1	108.8 (3)	C3—C2—C6	121.2 (2)
O8—Cl2—O7	110.04 (14)	C4—C3—C2	120.2 (2)
O8—Cl2—O6	109.04 (15)	C4—C3—H3	119.9
O7—Cl2—O6	110.33 (13)	C2—C3—H3	119.9

O8—Cl2—O5	109.69 (14)	C5—C4—C3	119.5 (2)
O7—Cl2—O5	109.86 (11)	C5—C4—H4	120.2
O6—Cl2—O5	107.84 (12)	C3—C4—H4	120.2
C5—N1—C1	123.42 (19)	N1—C5—C4	119.0 (2)
C5—N1—H1	118.3	N1—C5—H5	120.5
C1—N1—H1	118.3	C4—C5—H5	120.5
C6—N2—H2A	109.5	N2—C6—C2	112.65 (19)
C6—N2—H2B	109.5	N2—C6—H6A	109.1
H2A—N2—H2B	109.5	C2—C6—H6A	109.1
C6—N2—H2C	109.5	N2—C6—H6B	109.1
H2A—N2—H2C	109.5	C2—C6—H6B	109.1
H2B—N2—H2C	109.5	H6A—C6—H6B	107.8
C5—N1—C1—C2	−1.3 (4)	C2—C3—C4—C5	0.3 (4)
N1—C1—C2—C3	1.3 (3)	C1—N1—C5—C4	0.7 (4)
N1—C1—C2—C6	178.6 (2)	C3—C4—C5—N1	−0.2 (4)
C1—C2—C3—C4	−0.8 (3)	C1—C2—C6—N2	78.7 (3)
C6—C2—C3—C4	−178.1 (2)	C3—C2—C6—N2	−104.1 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O5	0.86	2.16	2.901 (3)	144
N1—H1···O7[i]	0.86	2.36	2.945 (3)	125
N2—H2*A*···O2[ii]	0.89	2.09	2.866 (3)	146
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N2—H2*B*···O6[ii]	0.89	2.10	2.925 (3)	155
N2—H2*B*···O3[iv]	0.89	2.47	2.922 (4)	112
N2—H2*B*···Cl2[ii]	0.89	2.96	3.600 (2)	131
N2—H2*C*···O1[v]	0.89	2.08	2.933 (3)	160
N2—H2*C*···Cl1[v]	0.89	2.97	3.654 (2)	135
C5—H5···O1[vi]	0.93	2.54	3.350 (4)	145
C6—H6*A*···O8[vii]	0.97	2.50	3.137 (3)	123

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