

## 3-(Ammoniomethyl)pyridinium bis(perchlorate)

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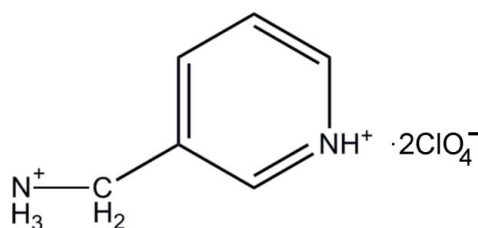
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.051;  $wR$  factor = 0.148; data-to-parameter ratio = 21.5.

In the title molecular salt,  $\text{C}_6\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{ClO}_4^-$ , 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 $\cdots$ O and C—H $\cdots$ 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

$\text{C}_6\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{ClO}_4^-$   
 $M_r = 309.06$   
 Monoclinic,  $P2_1/c$   
 $a = 5.1947$  (1) Å  
 $b = 12.1221$  (3) Å  
 $c = 18.2724$  (5) Å  
 $\beta = 98.067$  (1)°

$V = 1139.24$  (5) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.61$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.44 \times 0.33 \times 0.22$  mm

#### Data collection

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

#### Refinement

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

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O5	0.86	2.16	2.901 (3)	144
N1—H1 $\cdots$ O7 <sup>i</sup>	0.86	2.36	2.945 (3)	125
N2—H2A $\cdots$ O2 <sup>ii</sup>	0.89	2.09	2.866 (3)	146
N2—H2A $\cdots$ O6 <sup>iii</sup>	0.89	2.54	3.166 (3)	128
N2—H2B $\cdots$ O6 <sup>ii</sup>	0.89	2.10	2.925 (3)	155
N2—H2B $\cdots$ O3 <sup>iv</sup>	0.89	2.47	2.922 (4)	112
N2—H2C $\cdots$ O1 <sup>v</sup>	0.89	2.08	2.933 (3)	160
C5—H5 $\cdots$ O1 <sup>vi</sup>	0.93	2.54	3.350 (4)	145
C6—H6A $\cdots$ O8 <sup>vii</sup>	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 data and figures for this paper are available from the IUCr electronic archives (Reference: LR2104).

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## supporting information

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### 3-(Ammoniomethyl)pyridinium bis(perchlorate)

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#### S1. 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 mechanism 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<sub>6</sub>H<sub>10</sub>N<sub>2</sub>)(ClO<sub>4</sub>)<sub>2</sub>.

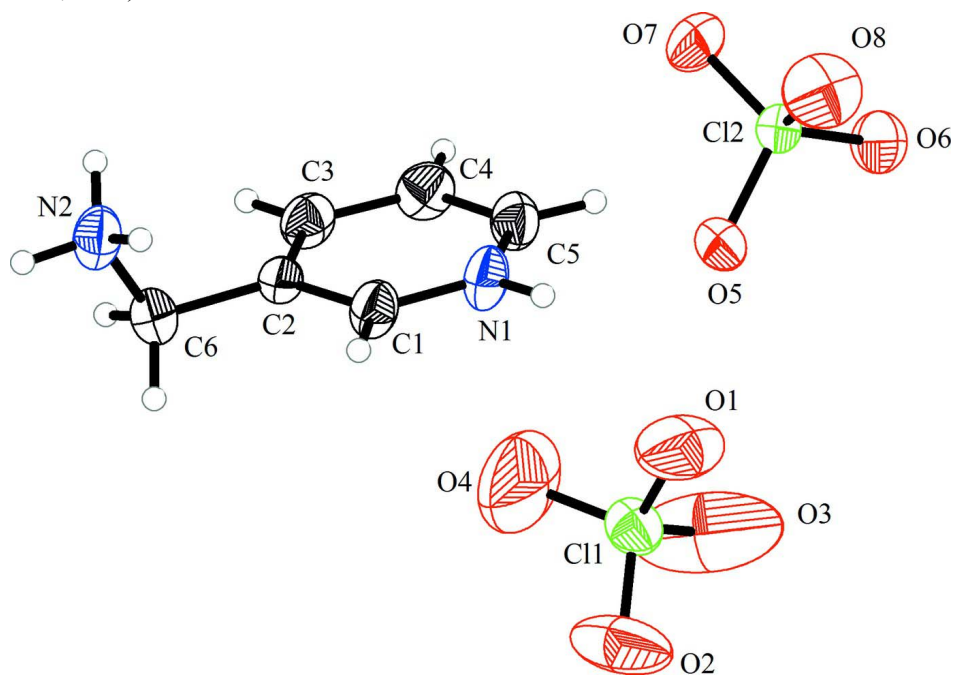
The structure consists of one 3-ammoniomethylpyridinium dication and two perchlorate anions (Fig. 1). In the crystal, the three H atoms of the ammonium group are involved into N—H···Cl and N—H···O hydrogen bonds: N2—H2C···Cl1(v), N2—H2B···Cl2(ii), N2—H2C···O1(v), N2—H2A···(O6vi, O2iv) and N2—H2B···(O6iv, O3vii), the two later are bifurcated (for the symmetry codes, see Table 1). These hydrogen bonds link the ionic units (NH<sub>3</sub><sup>+</sup> and [ClO<sub>4</sub>]<sup>-</sup>) 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  $\pi$ - $\pi$  stacking interactions between the organic rings or C—H··· $\pi$  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 pyridine. 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<sub>4</sub>]<sup>-</sup> 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<sub>4</sub>]<sup>-</sup> anion and from 1.420 (2) to 1.440 (2) Å for [Cl(2)O<sub>4</sub>]<sup>-</sup> anion are comparable to that previously reported for the perchlorate anions (Kaplinger & 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)O<sub>4</sub> 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<sub>4</sub>]<sup>-</sup> tetrahedron.

#### S2. Experimental

3-ammoniomethylpyridinium (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%).

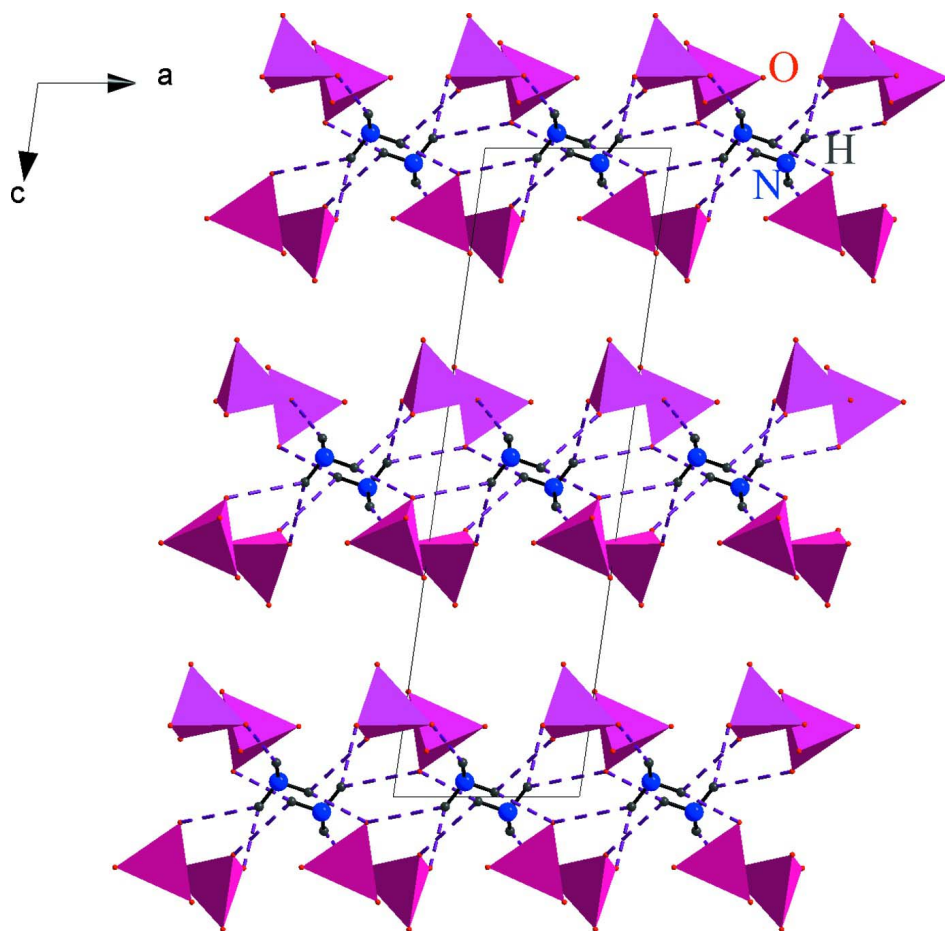
### S3. Refinement

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

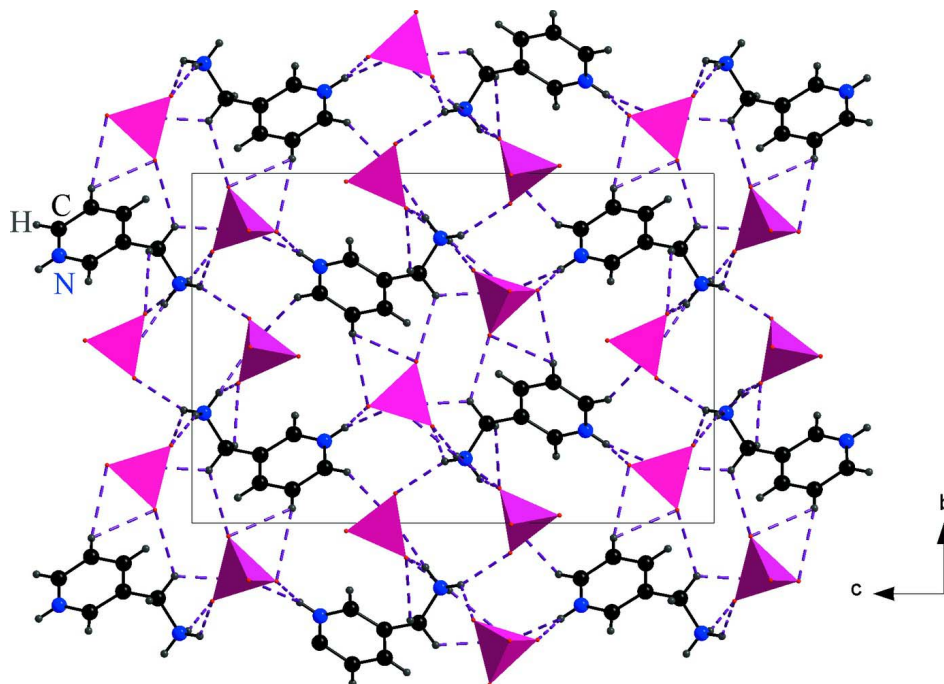


**Figure 1**

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

$C_6H_{10}N_2^{2+} \cdot 2ClO_4^-$

$M_r = 309.06$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 5.1947 (1) \text{ \AA}$

$b = 12.1221 (3) \text{ \AA}$

$c = 18.2724 (5) \text{ \AA}$

$\beta = 98.067 (1)^\circ$

$V = 1139.24 (5) \text{ \AA}^3$

$Z = 4$

$F(000) = 632$

$D_x = 1.802 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 5314 reflections

$\theta = 2.3\text{--}30.6^\circ$

$\mu = 0.61 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Block, colourless

$0.44 \times 0.33 \times 0.22 \text{ mm}$

#### Data collection

Bruker APEXII CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 2003)

$T_{\min} = 0.765$ ,  $T_{\max} = 0.875$

26338 measured reflections

3509 independent reflections

3007 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 30.6^\circ$ ,  $\theta_{\min} = 2.0^\circ$

$h = -7 \rightarrow 7$

$k = -17 \rightarrow 17$

$l = -26 \rightarrow 26$

Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.148$   
 $S = 1.06$   
 3509 reflections  
 163 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0782P)^2 + 0.9452P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.70 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.75 \text{ e } \text{\AA}^{-3}$

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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.0443 (3)	0.0361 (3)	0.0473 (3)	0.0052 (2)	0.0129 (2)	0.0049 (2)
C12	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, °)*

C11—O3	1.369 (3)	N2—H2B	0.8900
C11—O2	1.397 (2)	N2—H2C	0.8900
C11—O4	1.405 (4)	C1—C2	1.377 (3)
C11—O1	1.415 (3)	C1—H1A	0.9300
C12—O8	1.420 (2)	C2—C3	1.385 (3)
C12—O7	1.4272 (18)	C2—C6	1.500 (3)
C12—O6	1.4357 (18)	C3—C4	1.380 (3)
C12—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—C11—O2	111.6 (3)	N1—C1—C2	119.7 (2)
O3—C11—O4	111.8 (4)	N1—C1—H1A	120.1
O2—C11—O4	105.4 (2)	C2—C1—H1A	120.1
O3—C11—O1	107.49 (19)	C1—C2—C3	118.16 (19)
O2—C11—O1	111.8 (2)	C1—C2—C6	120.6 (2)
O4—C11—O1	108.8 (3)	C3—C2—C6	121.2 (2)

O8—C12—O7	110.04 (14)	C4—C3—C2	120.2 (2)
O8—C12—O6	109.04 (15)	C4—C3—H3	119.9
O7—C12—O6	110.33 (13)	C2—C3—H3	119.9
O8—C12—O5	109.69 (14)	C5—C4—C3	119.5 (2)
O7—C12—O5	109.86 (11)	C5—C4—H4	120.2
O6—C12—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, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O5	0.86	2.16	2.901 (3)	144
N1—H1...O7 <sup>i</sup>	0.86	2.36	2.945 (3)	125
N2—H2A...O2 <sup>ii</sup>	0.89	2.09	2.866 (3)	146
N2—H2A...O6 <sup>iii</sup>	0.89	2.54	3.166 (3)	128
N2—H2B...O6 <sup>ii</sup>	0.89	2.10	2.925 (3)	155
N2—H2B...O3 <sup>iv</sup>	0.89	2.47	2.922 (4)	112
N2—H2B...C12 <sup>ii</sup>	0.89	2.96	3.600 (2)	131
N2—H2C...O1 <sup>v</sup>	0.89	2.08	2.933 (3)	160
N2—H2C...C11 <sup>v</sup>	0.89	2.97	3.654 (2)	135
C5—H5...O1 <sup>vi</sup>	0.93	2.54	3.350 (4)	145
C6—H6A...O8 <sup>vii</sup>	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)  $-x+1, y+1/2, -z+1/2$ .