

DL-Piperidinium-2-carboxylate bis(hydrogen peroxide): unusual hydrogen-bonded peroxide chains

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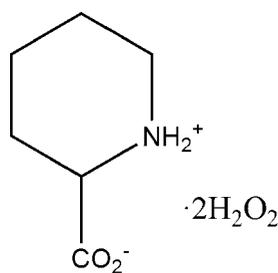
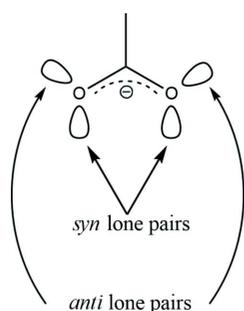
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The title compound, $C_6H_{11}NO_2 \cdot 2H_2O_2$, is the richest (by molar ratio) in hydrogen peroxide among the peroxosolvates of aliphatic α -amino acids. The asymmetric unit contains a zwitterionic pipercolinic acid molecule and two hydrogen peroxide molecules. The two crystallographically independent hydrogen peroxide molecules form a different number of hydrogen bonds: one forms two as donor and two as acceptor ([2,2] mode) and the other forms two as donor and one as acceptor ([2,1] mode). The latter hydrogen peroxide molecule forms infinite hydrogen-bonded hydroperoxo chains running along the *c*-axis direction, which is unusual for aliphatic α -amino acid peroxosolvates.

1. Chemical context

Peroxosolvates are crystalline adducts of hydrogen peroxide with various organic or inorganic compounds. Since they are convenient solid sources of active oxygen, some of them have become widely used commercial bleaching, disinfection and oxidation reagents (Jakob *et al.*, 2012; Cronin *et al.*, 2017). It is well known that their stability is strongly dependent on the hydrogen-bonded motifs formed by hydrogen peroxide (Chernyshov *et al.*, 2017). On other hand, H_2O_2 is one of the most important signalling molecules in biological systems (Li *et al.*, 2020; To *et al.*, 2020). The structures of amino acid peroxosolvates have been studied intensively as simple models of hydrogen peroxide binding with proteins (Prihodchenko *et al.*, 2011; Kapustin *et al.*, 2014). Peroxide and water–peroxide clusters are now of special interest since they may simulate cooperative hydrogen-bonded switching in the transportation of hydrogen peroxide species through cell membranes (Grishanov *et al.*, 2017; Varadaraj & Kumari, 2020; Wang *et al.*, 2020). Recently, several structures of organic peroxosolvates with peroxide hydrogen-bonded 1D-aggregates have been reported (Chernyshov *et al.*, 2017; Navasardyan *et al.*, 2017, 2018).



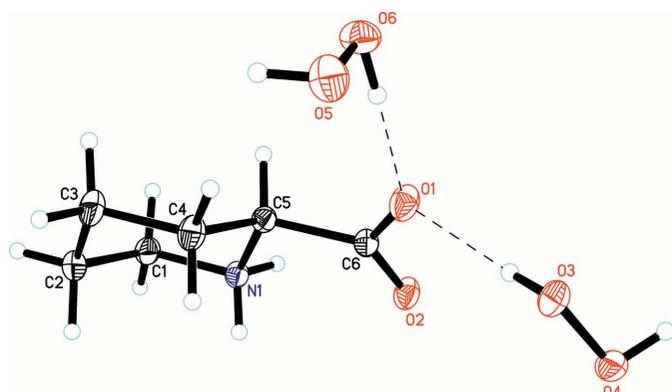


Figure 1
The asymmetric unit of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

2. Structural commentary

The asymmetric unit of the title compound (I) comprises a pipicolinic acid molecule and two crystallographically independent peroxide molecules (Fig. 1). As expected, the amino acid cofomer exhibits the zwitterionic form with almost equal C—O distances [1.2429 (11) and 1.2639 (11) Å]. All bond lengths and angles in the organic cofomer are close to those observed in the structures of pure pipicolinic acid [(II);

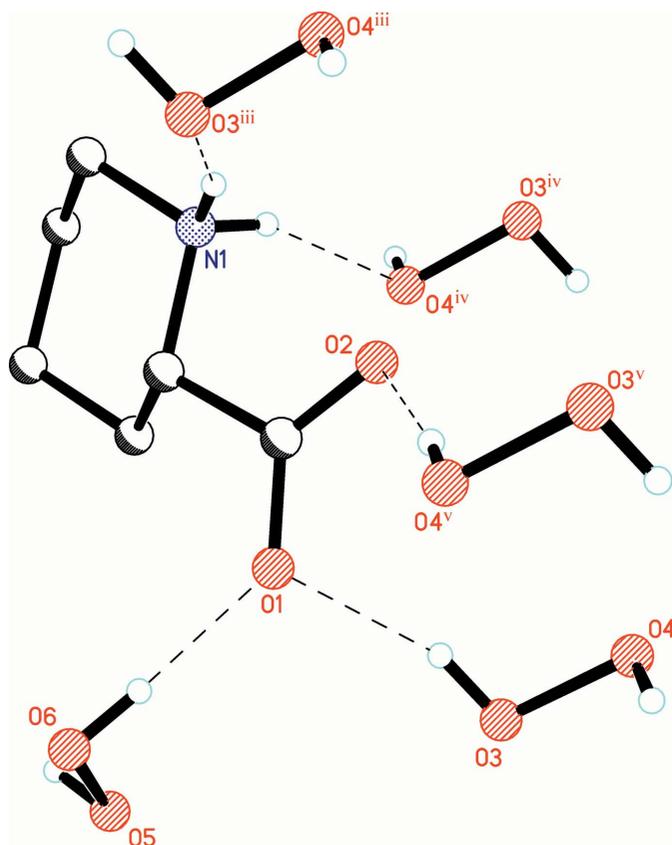


Figure 2
Pipicolinic acid with neighbouring hydrogen-bonded molecules. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (iii) $-1 + x, y, z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $1 - x, 1 - y, -z$.]

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O3-H3 \cdots O1$	0.872 (17)	1.819 (17)	2.6463 (10)	157.8 (15)
$O4-H4 \cdots O2^i$	0.866 (18)	1.889 (18)	2.7490 (10)	172.2 (15)
$O6-H6 \cdots O1$	0.881 (16)	1.760 (16)	2.6412 (10)	177.4 (14)
$O5-H5 \cdots O6^{ii}$	0.883 (17)	1.898 (18)	2.7777 (12)	174.4 (15)
$N1-H1 \cdots O3^{iii}$	0.912 (15)	1.961 (15)	2.8336 (11)	159.6 (13)
$N1-H2 \cdots O4^{iv}$	0.875 (15)	2.112 (15)	2.9459 (11)	159.1 (12)

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

Stapleton & Tiekink, 2001) and pipicolinic acid tetrahydrate [(III); Bhattacharjee & Chacko, 1979; Lyssenko *et al.*, 2006]. As observed for (II) and (III), the pipicolinic acid molecule in (I) adopts a chair conformation with the carboxylate group occupying the equatorial position. It is of interest to note in all three structures (I), (II), and (III), the core amino acid fragments N—C—CO₂ are almost planar, with N—C—C—O torsion angles of less than 22°. This is obviously caused by electrostatic interactions between the oppositely charged amino and carboxylic groups.

3. Supramolecular features

In the crystal, the organic molecule acts as a donor of two $N^+ - H \cdots OHOH$, and as an acceptor of three $COO^- \cdots HOOH$ hydrogen bonds (Table 1, Fig. 2). The O—O bond lengths [1.4600 (9) and 1.4646 (11) Å] are typical for amino acid peroxosolvates (mean value of 1.465 Å according to the latest, March 2020 version of the CSD; Groom *et al.*, 2016). Both crystallographically independent peroxide molecules occupy general positions and adopt skew conformations with H—O—O—H torsion angles of 102.5 (15) and -105.1 (15)°. It is well known that peroxide molecules always form at least two donor hydrogen bonds in the structures of organic peroxosolvates (Chernyshov *et al.*, 2017) and

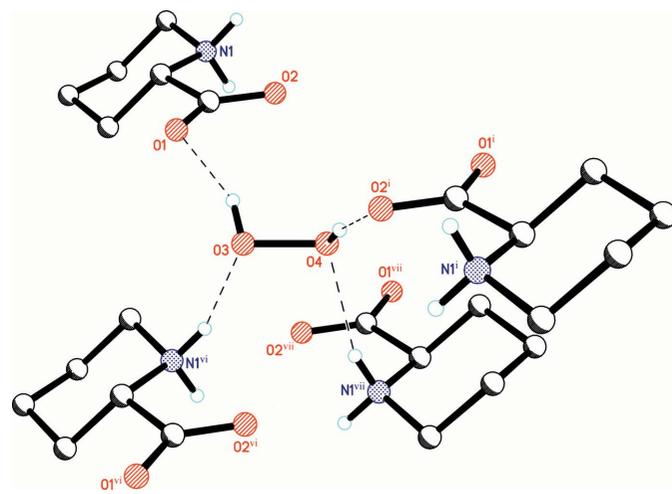


Figure 3
Hydrogen bonds formed by the peroxide molecule H3—O3—O4—H4. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $1 - x, 1 - y, -z$; (vi) $1 + x, y, z$; (vii) $1 - x, 1 - y, 1 - z$.]

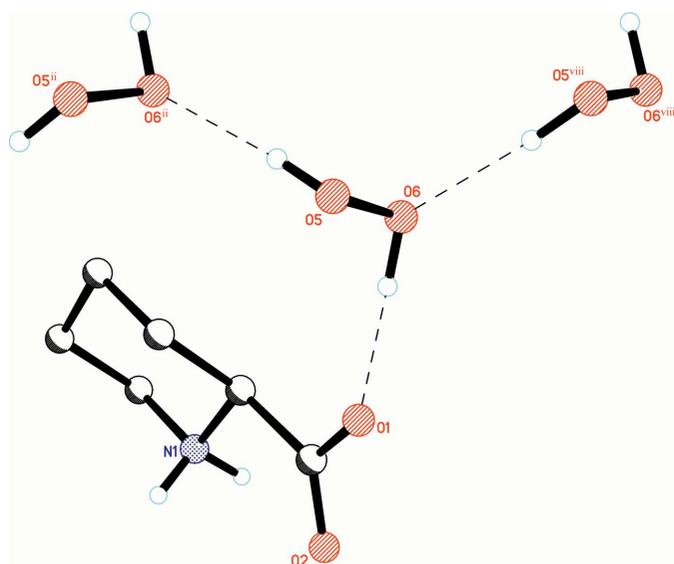


Figure 4
Hydrogen bonds formed by peroxide molecule H5—O5—O6—H6. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (ii) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (viii) $x, \frac{3}{2} - y, -\frac{1}{2} + z$.]

compound (I) is no exception. However, the symmetry-independent peroxide molecules in (I) form a different total number of hydrogen bonds: two donor HOOH \cdots O₂C and two acceptor N⁺—H \cdots OHOH for H3—O3—O4—H4 ([2,2]

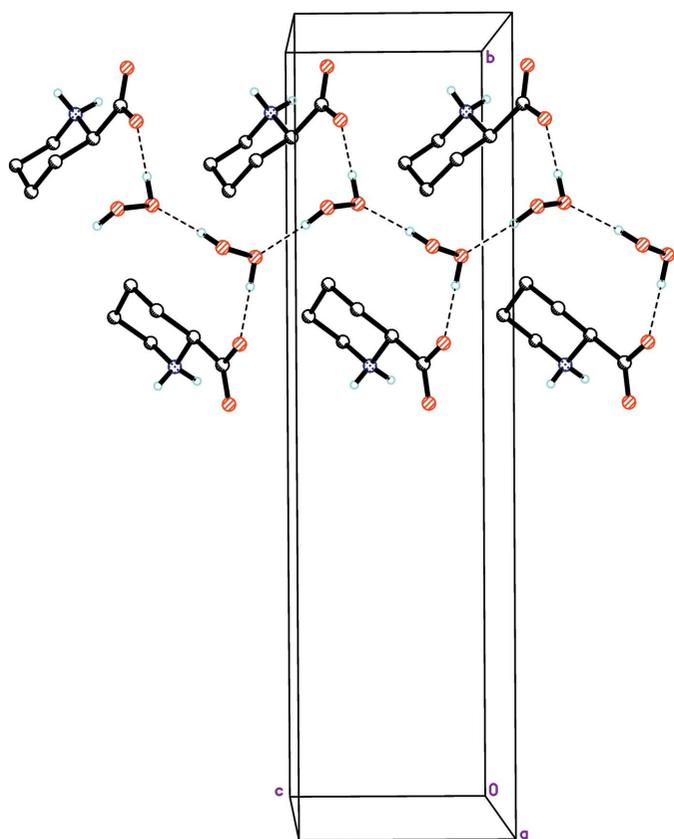


Figure 5
Peroxide hydrogen-bonded chains parallel to the *c* axis. Hydrogen bonds are shown as dashed lines.

mode; Table 1, Fig. 3) and two donor HOOH \cdots O₂C and HOOH \cdots OHOH together with one acceptor for H5—O5—O6—H6 ([2,1] mode; Table 1, Fig. 4). The occurrence of interperoxide hydrogen-bonds results in the formation of simple infinite hydrogen-bonded ‘hydroperoxo’-linked chains (Grishanov *et al.*, 2017), running along the *c*-axis direction (Fig. 5). It is significant that such chains and HOOH \cdots OHOH hydrogen bonds were not observed previously in the structures of aliphatic α -amino acid peroxosolvates. The reason for this is that charge-assisted HOOH \cdots O₂C bonds are energetically preferable to HOOH \cdots OHOH interactions (Jesus & Redinha, 2011; Zick & Geiger, 2018). For example, in (I) the only interperoxide hydrogen-bond O5—H5 \cdots O6 is noticeably longer [2.778 (1) Å] than the three HOOH \cdots O₂C bonds [2.641 (1)–2.749 (1) Å].

4. Database survey

Aliphatic α -amino acids contain side chains without heteroatoms suitable for hydrogen-bonding. Up to date, six structures of their peroxosolvates are known: monoperoxosolvates of *N,N*-dimethylglycine (C₄H₉NO₂; Kapustin *et al.*, 2014), *N*-methylglycine (sarcosine) (C₃H₇NO₂; Navasardyan *et al.*, 2017), isoleucine (C₆H₁₃NO₂; Prikhodchenko *et al.*, 2011); sesquiperioxosolvates of glycine (C₂H₅NO₂), *DL*-2-aminobutyric acid (C₄H₉NO₂) and *L*-phenylalanine (C₉H₁₁NO₂; Prikhodchenko *et al.*, 2011). In all of these structures, the organic molecules exist as zwitterions and all peroxide hydrogen atoms are involved in charge-assisted hydrogen-bonds with the carboxylate groups. All peroxide molecules adopt skew conformations with H—O—O—H torsion angles varying between 88.6 and 166.3°.

The carboxylate anions possess four *sp*²-hybridized lone electron pairs suitable for hydrogen-bond formation (Fig. 6)

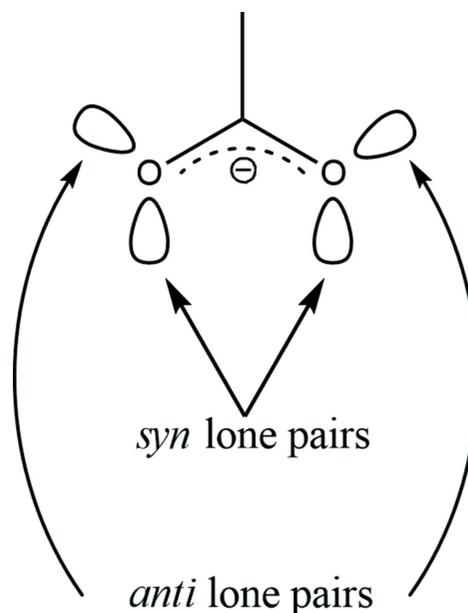


Figure 6
The mutual arrangement of *syn* and *anti* lone electron pairs of the carboxylate anion.

(Mills & Dean, 1996). It is well known that *syn* and *anti* lone pairs exhibit noticeably different basicity (Gandour, 1981; Pal *et al.*, 2018) and hydrogen-bonding properties as a result of electronic and steric effects (Gorbitz & Etter, 1992; Pranata, 1993). Nine hydrogen-bonded linkage modes are theoretically possible in the structures of amino acid peroxosolvates, taking into account that bifurcated $\text{HOOH} \cdots \text{O}$ bonds are not known (Fig. 7). The two simplest modes [0;S] and [0;A] have not been observed in peroxosolvates of α -amino acids, since the peroxide/acid molar ratio is greater than or equal to 1 in each reported structure. The [S;S] linkage was observed in sarcosine monoperoxosolvate. The [S;A] mode was found for the *N,N*-dimethylglycine and isoleucine monosolvates. Examples of neither the [0;SA] nor the [A;A] case are currently known. As for three hydrogen bonds, both [S;SA] and [SA;A] linkages were found in the sesquiperioxosolvate structures of glycine, DL-2-aminobutyric acid and L-phenylalanine. Following the same logic, we expected to find [SA;SA] in the structure of the title diperoxosolvate (I). However, the triple hydrogen-bonded case [S;SA] occurred, with the fourth donor hydrogen bond $\text{HOOH} \cdots \text{O}$ engaged in forming hydrogen-bonded peroxide chains. It has been shown that the ability of carboxylic *anti*-orbitals to form hydrogen bonds is strongly affected by steric hindrance caused by β -substituents in the side chains of carboxylic acids (Gorbitz & Etter, 1992). It is clear that in (I) the unfeasibility of the fourth carboxylic

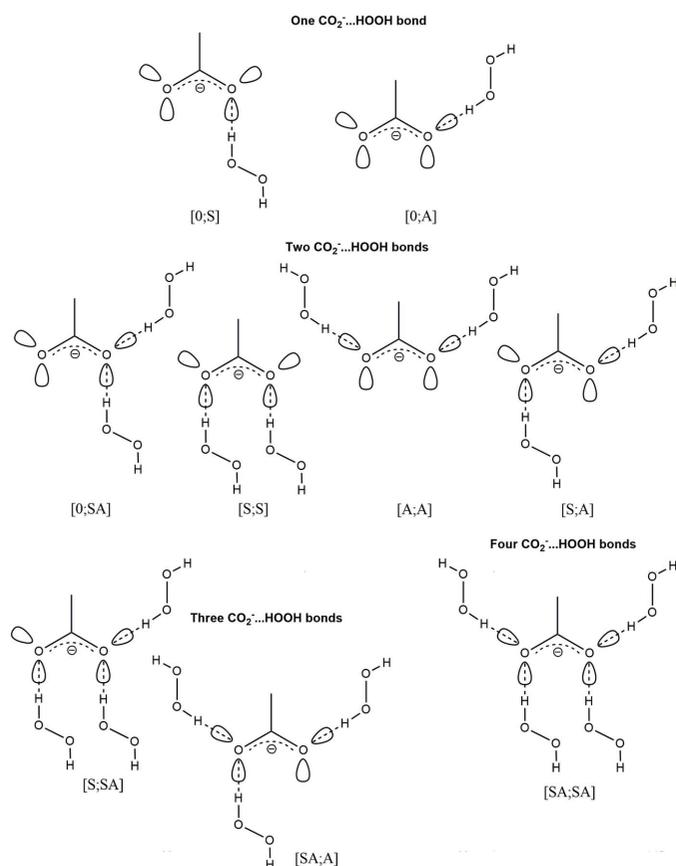


Figure 7
Possible hydrogen-bonded motifs in the structures of amino acid peroxosolvates.

Table 2
Experimental details.

Crystal data	
Chemical formula	$\text{C}_6\text{H}_{11}\text{NO}_2 \cdot 2\text{H}_2\text{O}_2$
M_r	197.19
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	6.5739 (4), 22.9278 (15), 6.0647 (4)
β (°)	93.770 (1)
V (Å ³)	912.12 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.13
Crystal size (mm)	0.50 × 0.50 × 0.50
Data collection	
Diffractometer	Bruker SMART APEXII
Absorption correction	Multi-scan (SADABS; Bruker, 2008)
T_{\min} , T_{\max}	0.659, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9809, 2418, 2170
R_{int}	0.018
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.682
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.084, 1.08
No. of reflections	2418
No. of parameters	178
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.44, -0.19

Computer programs: APEX2 and SAINT (Bruker, 2008), SHELXL2018/3 (Sheldrick, 2015) and XP in SHELXTL (Sheldrick, 2008).

hydrogen bond is the result of steric effects caused by the peroxide molecules hydrogen bonded with the ammonium group (Fig. 2). It should be noted that the spatial arrangement of the endocyclic amino group in (I) is predefined by the aforementioned planarity of the $\text{N}-\text{C}-\text{CO}_2$ amino acid fragment.

5. Synthesis and crystallization

96% Hydrogen peroxide was prepared by an extraction method from serine peroxosolvate (Wolanov *et al.*, 2010). Colourless prismatic crystals of the title compound were obtained by cooling a saturated solution (r.t.) of pipercolinic acid (Aldrich) in 96% hydrogen peroxide to 255 K. Handling procedures for concentrated hydrogen peroxide have been described in detail (danger of explosion!) by Schumb *et al.* (1955).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were found in difference-Fourier maps and were refined with independent positional and isotropic displacement parameters.

Acknowledgements

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supporting information

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DL-Piperidinium-2-carboxylate bis(hydrogen peroxide): unusual hydrogen-bonded peroxide chains

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Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SAINTE* (Bruker, 2008); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008).

DL-Piperidinium-2-carboxylate bis(hydrogen peroxide)

Crystal data

$C_6H_{11}NO_2 \cdot 2H_2O_2$

$M_r = 197.19$

Monoclinic, $P2_1/c$

$a = 6.5739$ (4) Å

$b = 22.9278$ (15) Å

$c = 6.0647$ (4) Å

$\beta = 93.770$ (1)°

$V = 912.12$ (10) Å³

$Z = 4$

$F(000) = 424$

$D_x = 1.436$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5232 reflections

$\theta = 3.1$ – 30.6 °

$\mu = 0.13$ mm⁻¹

$T = 150$ K

Nugget, colourless

$0.50 \times 0.50 \times 0.50$ mm

Data collection

Bruker SMART APEXII
diffractometer

ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2008)

$T_{\min} = 0.659$, $T_{\max} = 0.746$

9809 measured reflections

2418 independent reflections

2170 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$

$\theta_{\max} = 29.0$ °, $\theta_{\min} = 3.1$ °

$h = -8 \rightarrow 8$

$k = -30 \rightarrow 31$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.084$

$S = 1.08$

2418 reflections

178 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.218P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.44$ e Å⁻³

$\Delta\rho_{\min} = -0.19$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	−0.02450 (12)	0.57964 (3)	0.57611 (13)	0.01528 (16)
H1	−0.093 (2)	0.5604 (6)	0.463 (2)	0.029 (3)*
H2	0.039 (2)	0.5538 (6)	0.661 (2)	0.025 (3)*
O1	0.40875 (11)	0.60608 (3)	0.25095 (12)	0.02266 (17)
O2	0.21298 (11)	0.52860 (3)	0.30218 (11)	0.02005 (16)
C1	−0.17311 (14)	0.61336 (4)	0.70359 (15)	0.01777 (18)
H11	−0.2642 (19)	0.5851 (6)	0.759 (2)	0.021 (3)*
H12	−0.2449 (19)	0.6384 (6)	0.597 (2)	0.024 (3)*
C2	−0.05768 (15)	0.64708 (4)	0.88702 (15)	0.01993 (19)
H21	−0.157 (2)	0.6679 (6)	0.968 (2)	0.029 (3)*
H22	0.010 (2)	0.6192 (6)	0.988 (2)	0.029 (3)*
C3	0.10082 (16)	0.68727 (4)	0.79508 (17)	0.0218 (2)
H32	0.033 (2)	0.7172 (6)	0.703 (2)	0.027 (3)*
H31	0.179 (2)	0.7082 (6)	0.916 (2)	0.030 (3)*
C4	0.24769 (14)	0.65223 (4)	0.66075 (16)	0.01923 (19)
H41	0.343 (2)	0.6784 (6)	0.590 (2)	0.027 (3)*
H42	0.326 (2)	0.6256 (6)	0.759 (2)	0.027 (3)*
C5	0.13006 (13)	0.61800 (4)	0.47837 (14)	0.01483 (17)
H52	0.0520 (18)	0.6451 (5)	0.377 (2)	0.019 (3)*
C6	0.26188 (13)	0.58042 (4)	0.33422 (14)	0.01570 (18)
O3	0.74598 (11)	0.54761 (3)	0.18291 (11)	0.01986 (16)
O4	0.72361 (11)	0.48529 (3)	0.13828 (12)	0.02162 (16)
H4	0.737 (2)	0.4839 (7)	−0.003 (3)	0.040 (4)*
H3	0.620 (3)	0.5583 (7)	0.194 (3)	0.040 (4)*
O5	0.67290 (12)	0.72538 (4)	0.33260 (14)	0.02787 (18)
O6	0.49801 (12)	0.71623 (3)	0.17405 (13)	0.02507 (17)
H5	0.613 (2)	0.7454 (7)	0.434 (3)	0.041 (4)*
H6	0.472 (2)	0.6792 (7)	0.199 (2)	0.034 (4)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0163 (3)	0.0143 (4)	0.0153 (3)	−0.0005 (3)	0.0025 (3)	−0.0015 (3)
O1	0.0229 (4)	0.0170 (3)	0.0293 (4)	−0.0015 (3)	0.0110 (3)	−0.0023 (3)
O2	0.0237 (3)	0.0149 (3)	0.0221 (3)	−0.0016 (2)	0.0060 (3)	−0.0044 (2)
C1	0.0169 (4)	0.0183 (4)	0.0185 (4)	0.0023 (3)	0.0044 (3)	−0.0002 (3)
C2	0.0237 (5)	0.0202 (4)	0.0163 (4)	0.0037 (4)	0.0042 (3)	−0.0023 (3)
C3	0.0251 (5)	0.0179 (4)	0.0225 (5)	−0.0009 (4)	0.0036 (4)	−0.0074 (4)
C4	0.0186 (4)	0.0182 (4)	0.0211 (4)	−0.0024 (3)	0.0023 (3)	−0.0057 (3)

C5	0.0165 (4)	0.0132 (4)	0.0150 (4)	-0.0002 (3)	0.0028 (3)	-0.0004 (3)
C6	0.0170 (4)	0.0162 (4)	0.0140 (4)	0.0019 (3)	0.0018 (3)	-0.0012 (3)
O3	0.0193 (3)	0.0172 (3)	0.0229 (3)	0.0006 (3)	0.0008 (3)	-0.0044 (2)
O4	0.0301 (4)	0.0158 (3)	0.0187 (3)	0.0029 (3)	0.0003 (3)	-0.0012 (2)
O5	0.0261 (4)	0.0308 (4)	0.0265 (4)	-0.0044 (3)	0.0001 (3)	-0.0053 (3)
O6	0.0308 (4)	0.0200 (4)	0.0237 (4)	-0.0027 (3)	-0.0029 (3)	0.0024 (3)

Geometric parameters (Å, °)

N1—C5	1.4955 (11)	C3—H32	0.974 (14)
N1—C1	1.4996 (11)	C3—H31	0.991 (14)
N1—H1	0.912 (15)	C4—C5	1.5247 (12)
N1—H2	0.875 (15)	C4—H41	0.986 (14)
O1—C6	1.2639 (11)	C4—H42	0.975 (14)
O2—C6	1.2429 (11)	C5—C6	1.5353 (12)
C1—C2	1.5166 (13)	C5—H52	0.991 (12)
C1—H11	0.958 (13)	O3—O4	1.4600 (9)
C1—H12	0.966 (13)	O3—H3	0.872 (17)
C2—C3	1.5239 (14)	O4—H4	0.866 (18)
C2—H21	0.968 (14)	O5—O6	1.4646 (11)
C2—H22	0.972 (14)	O5—H5	0.883 (17)
C3—C4	1.5313 (13)	O6—H6	0.881 (16)
C5—N1—C1	112.57 (7)	C4—C3—H31	109.3 (8)
C5—N1—H1	107.6 (9)	H32—C3—H31	106.3 (11)
C1—N1—H1	109.2 (9)	C5—C4—C3	110.40 (8)
C5—N1—H2	108.7 (9)	C5—C4—H41	107.7 (8)
C1—N1—H2	110.4 (9)	C3—C4—H41	110.7 (8)
H1—N1—H2	108.2 (12)	C5—C4—H42	110.0 (8)
N1—C1—C2	109.24 (7)	C3—C4—H42	109.4 (8)
N1—C1—H11	106.0 (8)	H41—C4—H42	108.6 (11)
C2—C1—H11	112.4 (8)	N1—C5—C4	109.91 (7)
N1—C1—H12	105.4 (8)	N1—C5—C6	108.62 (7)
C2—C1—H12	112.9 (8)	C4—C5—C6	115.06 (7)
H11—C1—H12	110.4 (11)	N1—C5—H52	106.0 (7)
C1—C2—C3	111.17 (8)	C4—C5—H52	110.1 (7)
C1—C2—H21	107.6 (8)	C6—C5—H52	106.7 (7)
C3—C2—H21	112.8 (8)	O2—C6—O1	125.38 (8)
C1—C2—H22	108.3 (8)	O2—C6—C5	118.40 (8)
C3—C2—H22	109.6 (8)	O1—C6—C5	116.16 (8)
H21—C2—H22	107.3 (11)	O4—O3—H3	101.8 (11)
C2—C3—C4	110.34 (8)	O3—O4—H4	101.7 (10)
C2—C3—H32	109.7 (8)	O6—O5—H5	99.6 (11)
C4—C3—H32	110.2 (8)	O5—O6—H6	100.4 (10)
C2—C3—H31	111.0 (8)		
C5—N1—C1—C2	-58.48 (10)	C3—C4—C5—C6	-179.22 (8)
N1—C1—C2—C3	56.95 (10)	N1—C5—C6—O2	6.85 (11)

C1—C2—C3—C4	-56.65 (11)	C4—C5—C6—O2	130.51 (9)
C2—C3—C4—C5	55.85 (11)	N1—C5—C6—O1	-175.64 (8)
C1—N1—C5—C4	58.51 (10)	C4—C5—C6—O1	-51.98 (11)
C1—N1—C5—C6	-174.80 (7)	H3—O3—O4—H4	102.5 (15)
C3—C4—C5—N1	-56.25 (10)	H5—O5—O6—H6	-105.1 (15)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O3—H3 \cdots O1	0.872 (17)	1.819 (17)	2.6463 (10)	157.8 (15)
O4—H4 \cdots O2 ⁱ	0.866 (18)	1.889 (18)	2.7490 (10)	172.2 (15)
O6—H6 \cdots O1	0.881 (16)	1.760 (16)	2.6412 (10)	177.4 (14)
O5—H5 \cdots O6 ⁱⁱ	0.883 (17)	1.898 (18)	2.7777 (12)	174.4 (15)
N1—H1 \cdots O3 ⁱⁱⁱ	0.912 (15)	1.961 (15)	2.8336 (11)	159.6 (13)
N1—H2 \cdots O4 ^{iv}	0.875 (15)	2.112 (15)	2.9459 (11)	159.1 (12)

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x, -y+3/2, z+1/2$; (iii) $x-1, y, z$; (iv) $-x+1, -y+1, -z+1$.