

**Andrei V. Churakov,<sup>a\*</sup>**  
**Lyudmila G. Kuz'mina,<sup>a</sup>**  
**Petr V. Prikhodchenko<sup>a</sup> and**  
**Judith A. K. Howard<sup>b</sup>**

<sup>a</sup>N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Science, 31 Leninskii prospect, Moscow 119991, Russian Federation, and <sup>b</sup>Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham DH1 3LE, England

Correspondence e-mail: churakov@igic.ras.ru

#### Key indicators

Single-crystal X-ray study  
 $T = 120\text{ K}$   
 Mean  $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$   
 $R$  factor = 0.037  
 $wR$  factor = 0.090  
 Data-to-parameter ratio = 12.7

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

# The first molecular structure containing four hydroperoxy groups: piperazine-2,3,5,6-tetrayl tetrahydroperoxide pyrazine disolvate dihydrate

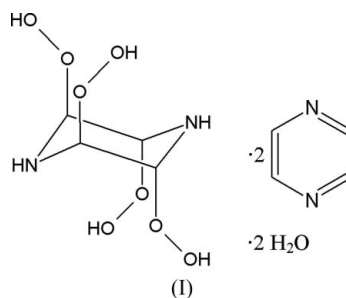
The reaction of pyrazine with hydrogen peroxide resulted in piperazine-2,3,5,6-tetrayl tetrahydroperoxide, crystallizing as its pyrazine disolvate dihydrate,  $\text{C}_4\text{H}_{10}\text{N}_2\text{O}_8 \cdot 2\text{C}_4\text{H}_4\text{N}_2 \cdot 2\text{H}_2\text{O}$ . In the crystal structure, the tetrahydroperoxy molecules, which possess a crystallographically imposed centre of symmetry, are linked into a three-dimensional network by hydrogen-bonding interactions involving the pyrazine and water molecules.

Received 21 April 2006

Accepted 4 May 2006

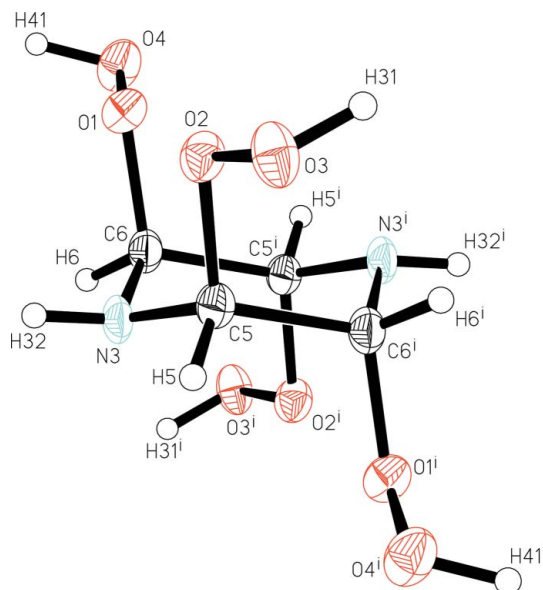
## Comment

Peroxo derivatives of organic compounds attract particular interest as environmentally friendly bleaching compounds and oxidation agents in organic synthesis (Marwah *et al.*, 2004). As part of our study of organic hydrogen peroxide solvates (Churakov *et al.*, 2004, 2005), we tried to investigate the behaviour of small organic donor molecules, such as pyrazine or pyrimidine, in concentrated  $\text{H}_2\text{O}_2$  solutions. The unexpected title compound, (I), was formed upon freezing of a pyrazine solution in 50% hydrogen peroxide. The nature of this process remains unclear. The centrosymmetric molecule of (I) (Fig. 1) contains four hydroperoxy substituents. The piperazine ring adopts a chair conformation and all hydroperoxy groups occupy axial positions. Atom N3 is slightly flattened, the sum of valence angles around it being  $346.0^\circ$ . The O—O bond lengths [1.470 (1) and 1.471 (1) Å] are somewhat longer than the mean value of 1.462 Å found for related compounds (85 entries, 106 fragments) in the Cambridge Structural Database (CSD, Version 5.27 of January 2006; Allen, 2002).

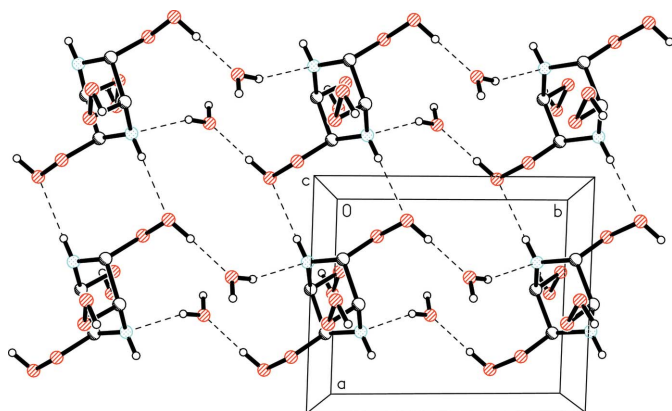


The hydroperoxy atom O3 acts as both donor (for symmetry-related) molecules and acceptor (for water molecules) of hydrogen bonds, forming layers perpendicular to the  $c$  axis (Fig. 2). Pyrazine molecules accept hydrogen bonds from the peroxo O4 and water O5 atoms, cross-linking the layers of the main molecules into a three-dimensional network (Fig. 3).

To date, the CSD contains structures of compounds with no more than two hydroperoxy groups. The title compound is the



**Figure 1**  
The molecular structure of the tetraperoxo molecule of (I), showing 50% probability displacement ellipsoids [symmetry code: (i)  $1 - y, 2 - x, 2 - z$ ].

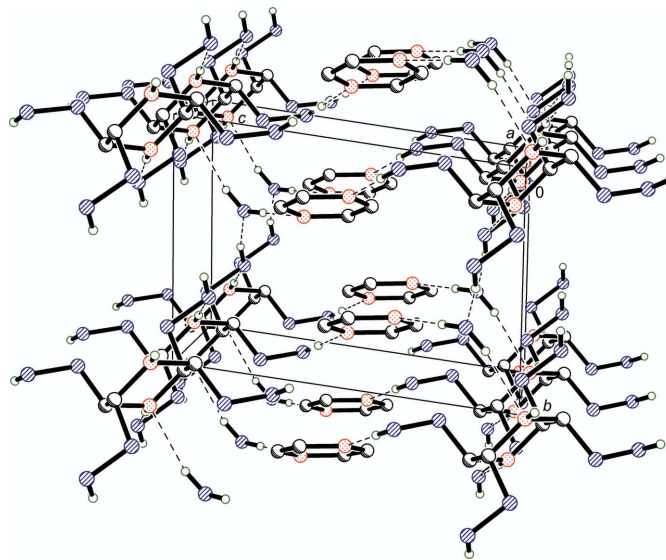


**Figure 2**  
The hydrogen-bonded (dashed lines) layer in (I) perpendicular to the *c* axis. H atoms not involved in hydrogen bonds have been omitted for clarity.

first example of a molecular structure containing four OOH substituents. To the best of our knowledge, (I) is one of the most rich in oxygen organic molecules.

## Experimental

Pyrazine (99%) and 50% hydrogen peroxide were purchased from Aldrich. Pyrazine (0.03 g) was dissolved in approximately 1 ml of 50%  $H_2O_2$ . This solution was stored in a freezer at 255 K. After six months, several tiny crystals were found on the wall of a sample bottle. The amount of crystalline material was not enough to investigate it with usual spectroscopic methods. In order to analyse the mother liquor by NMR, it was evaporated in vacuum and the residual oil was dissolved in  $D_2O$ . Unfortunately, the recorded  $^1H$  and  $^{13}C$  spectra of this complex mixture were non-interpretable.



**Figure 3**  
The crystal packing of (I), viewed approximately along the *a* axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonds have been omitted for clarity.

### Crystal data

$C_4H_{10}N_2O_8 \cdot 2C_4H_4N_2 \cdot 2H_2O$   
 $M_r = 410.36$   
 Triclinic,  $P\bar{1}$   
 $a = 6.1538$  (6) Å  
 $b = 7.3047$  (8) Å  
 $c = 10.3364$  (12) Å  
 $\alpha = 97.729$  (3)°  
 $\beta = 95.974$  (4)°  
 $\gamma = 91.417$  (3)°

$V = 457.56$  (9) Å<sup>3</sup>  
 $Z = 1$   
 $D_x = 1.489$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 0.13$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 Needle, colourless  
 $0.25 \times 0.04 \times 0.03$  mm

### Data collection

Bruker SMART 6K diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 1997)  
 $T_{min} = 0.968, T_{max} = 0.996$

2645 measured reflections  
 2162 independent reflections  
 1710 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.012$   
 $\theta_{max} = 28.0^\circ$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.090$   
 $S = 0.99$   
 2162 reflections  
 170 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0248P)^2 + 0.2345P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.31$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.23$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O4-H41 \cdots N1^i$	0.88 (2)	1.88 (2)	2.7573 (18)	176.2 (18)
$O3-H31 \cdots O5^{ii}$	0.88 (2)	1.74 (2)	2.6068 (16)	168.2 (19)
$N3-H32 \cdots O3^{iii}$	0.83 (2)	2.17 (2)	2.9985 (16)	178.1 (17)
$O5-H51 \cdots N2$	0.88 (3)	1.97 (3)	2.8483 (19)	177 (2)
$O5-H52 \cdots N3^{iv}$	0.86 (3)	2.14 (3)	2.9648 (18)	160 (2)

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

All H atoms were located in a difference Fourier map and refined isotropically.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Bruker, 2000); software used to prepare material for publication: *SHELXTL-Plus*.

AVC is grateful to the Russian Science Support Foundation.

## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bruker (2000). *SHELXTL-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2001). *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Churakov, A. V., Prikhodchenko, P. V. & Howard, J. A. K. (2005). *CrystEngComm*, **7**, 664–669.
- Churakov, A. V., Prikhodchenko, P. V., Kuz'mina, L. G. & Howard, J. A. K. (2004). *Chem. Listy*, **98**, s43–s44.
- Marwah, P., Marwah, A. & Lardy, H. A. (2004). *Green Chem.* **6**, 570–577.
- Sheldrick, G. M. (1997). *SADABS*, *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

## supporting information

*Acta Cryst.* (2006). E62, o2265–o2267 [https://doi.org/10.1107/S1600536806016485]

**The first molecular structure containing four hydroperoxo groups:  
piperazine-2,3,5,6-tetraol tetrahydroperoxide pyrazine disolvate dihydrate**

**Andrei V. Churakov, Lyudmila G. Kuz'mina, Petr V. Prikhodchenko and Judith A. K. Howard**

piperazine-2,3,5,6-tetraol tetrahydroperoxide pyrazine disolvate dihydrate

*Crystal data*

$C_4H_{10}N_2O_8 \cdot 2C_4H_4N_2 \cdot 2H_2O$

$M_r = 410.36$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 6.1538$  (6) Å

$b = 7.3047$  (8) Å

$c = 10.3364$  (12) Å

$\alpha = 97.729$  (3)°

$\beta = 95.974$  (4)°

$\gamma = 91.417$  (3)°

$V = 457.56$  (9) Å<sup>3</sup>

$Z = 1$

$F(000) = 216$

$D_x = 1.489$  Mg m<sup>-3</sup>

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

Cell parameters from 1131 reflections

$\theta = 2.8$ – $30.5$ °

$\mu = 0.13$  mm<sup>-1</sup>

$T = 120$  K

Needle, colourless

$0.25 \times 0.04 \times 0.03$  mm

*Data collection*

Bruker SMART 6K  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan  
(SADABS; Sheldrick, 1997)

$T_{\min} = 0.968$ ,  $T_{\max} = 0.996$

2645 measured reflections

2162 independent reflections

1710 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.012$

$\theta_{\max} = 28.0$ °,  $\theta_{\min} = 2.0$ °

$h = -8 \rightarrow 7$

$k = -9 \rightarrow 9$

$l = -13 \rightarrow 11$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.090$

$S = 0.99$

2162 reflections

170 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

$w = 1/[\sigma^2(F_o^2) + (0.0248P)^2 + 0.2345P]$

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

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

$\Delta\rho_{\max} = 0.31$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.23$  e Å<sup>-3</sup>

*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>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	1.1231 (2)	0.79178 (18)	0.50775 (13)	0.0261 (3)
N2	0.7499 (2)	0.63944 (18)	0.35086 (14)	0.0290 (3)
C1	0.9426 (3)	0.7464 (2)	0.55999 (16)	0.0281 (3)
C2	0.7583 (3)	0.6716 (2)	0.48149 (18)	0.0299 (4)
C3	1.1158 (3)	0.7607 (2)	0.37735 (15)	0.0256 (3)
C4	0.9304 (3)	0.6850 (2)	0.29966 (16)	0.0272 (3)
N3	0.32175 (19)	0.87876 (16)	0.97556 (12)	0.0182 (3)
C5	0.3104 (2)	1.03857 (19)	1.07043 (14)	0.0176 (3)
C6	0.4605 (2)	0.88510 (19)	0.87366 (14)	0.0182 (3)
O1	0.36537 (16)	1.00211 (14)	0.78281 (10)	0.0218 (2)
O2	0.19076 (15)	1.17748 (13)	1.00797 (10)	0.0200 (2)
O3	0.11802 (16)	1.30694 (14)	1.11516 (11)	0.0228 (2)
O4	0.47963 (18)	0.96406 (16)	0.66468 (11)	0.0265 (3)
O5	0.4042 (2)	0.58225 (17)	0.14218 (13)	0.0325 (3)
H1	0.940 (3)	0.768 (3)	0.651 (2)	0.033 (5)*
H2	0.628 (3)	0.643 (3)	0.519 (2)	0.040 (5)*
H3	1.240 (3)	0.794 (2)	0.3417 (18)	0.027 (5)*
H4	0.929 (3)	0.668 (2)	0.2075 (19)	0.029 (5)*
H51	0.508 (4)	0.600 (4)	0.209 (3)	0.068 (8)*
H52	0.412 (4)	0.661 (4)	0.088 (3)	0.061 (7)*
H5	0.230 (3)	1.008 (2)	1.1425 (16)	0.017 (4)*
H6	0.469 (2)	0.764 (2)	0.8258 (15)	0.012 (4)*
H32	0.202 (3)	0.826 (3)	0.9490 (18)	0.026 (5)*
H31	0.211 (3)	1.400 (3)	1.1126 (19)	0.034 (5)*
H41	0.369 (3)	0.907 (3)	0.612 (2)	0.034*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0255 (7)	0.0265 (7)	0.0251 (7)	0.0008 (5)	-0.0012 (5)	0.0022 (5)
N2	0.0236 (7)	0.0254 (7)	0.0367 (8)	0.0001 (5)	-0.0034 (6)	0.0042 (6)
C1	0.0340 (9)	0.0272 (8)	0.0236 (8)	0.0036 (6)	0.0055 (6)	0.0028 (6)
C2	0.0250 (8)	0.0265 (8)	0.0399 (9)	0.0009 (6)	0.0086 (7)	0.0064 (7)
C3	0.0248 (8)	0.0268 (8)	0.0255 (8)	-0.0005 (6)	0.0023 (6)	0.0050 (6)
C4	0.0304 (8)	0.0271 (8)	0.0234 (8)	0.0025 (6)	-0.0017 (6)	0.0043 (6)
N3	0.0118 (5)	0.0184 (6)	0.0227 (6)	-0.0051 (4)	-0.0016 (4)	0.0009 (5)

C5	0.0131 (6)	0.0187 (6)	0.0204 (7)	-0.0018 (5)	-0.0004 (5)	0.0030 (5)
C6	0.0150 (6)	0.0171 (6)	0.0211 (7)	-0.0023 (5)	-0.0014 (5)	0.0008 (5)
O1	0.0198 (5)	0.0249 (5)	0.0203 (5)	0.0018 (4)	-0.0001 (4)	0.0034 (4)
O2	0.0163 (5)	0.0197 (5)	0.0228 (5)	0.0014 (4)	-0.0007 (4)	0.0007 (4)
O3	0.0166 (5)	0.0204 (5)	0.0303 (6)	-0.0018 (4)	0.0050 (4)	-0.0025 (4)
O4	0.0209 (5)	0.0369 (6)	0.0208 (5)	-0.0035 (5)	0.0015 (4)	0.0024 (4)
O5	0.0359 (7)	0.0268 (6)	0.0327 (7)	-0.0132 (5)	-0.0085 (5)	0.0082 (5)

*Geometric parameters (Å, °)*

N1—C3	1.332 (2)	C5—O2	1.4502 (16)
N1—C1	1.338 (2)	C5—C6 <sup>i</sup>	1.5286 (19)
N2—C4	1.333 (2)	C5—H5	0.984 (16)
N2—C2	1.334 (2)	C6—O1	1.4427 (17)
C1—C2	1.379 (2)	C6—C5 <sup>i</sup>	1.5286 (19)
C1—H1	0.932 (19)	C6—H6	0.958 (16)
C2—H2	0.95 (2)	O1—O4	1.4695 (14)
C3—C4	1.382 (2)	O2—O3	1.4713 (14)
C3—H3	0.924 (18)	O3—H31	0.88 (2)
C4—H4	0.943 (19)	O4—H41	0.88 (2)
N3—C5	1.4281 (18)	O5—H51	0.88 (3)
N3—C6	1.4279 (18)	O5—H52	0.86 (3)
N3—H32	0.83 (2)		
C3—N1—C1	116.91 (14)	N3—C5—O2	108.69 (11)
C4—N2—C2	116.13 (14)	N3—C5—C6 <sup>i</sup>	110.81 (11)
N1—C1—C2	121.06 (15)	O2—C5—C6 <sup>i</sup>	110.11 (11)
N1—C1—H1	119.6 (12)	N3—C5—H5	110.3 (10)
C2—C1—H1	119.4 (12)	O2—C5—H5	107.5 (9)
N2—C2—C1	122.40 (15)	C6 <sup>i</sup> —C5—H5	109.3 (10)
N2—C2—H2	116.8 (13)	N3—C6—O1	108.62 (11)
C1—C2—H2	120.8 (13)	N3—C6—C5 <sup>i</sup>	111.10 (12)
N1—C3—C4	121.54 (15)	O1—C6—C5 <sup>i</sup>	109.50 (11)
N1—C3—H3	116.6 (12)	N3—C6—H6	110.2 (9)
C4—C3—H3	121.9 (12)	O1—C6—H6	107.5 (9)
N2—C4—C3	121.95 (15)	C5 <sup>i</sup> —C6—H6	109.8 (9)
N2—C4—H4	118.5 (11)	C6—O1—O4	105.82 (9)
C3—C4—H4	119.5 (11)	C5—O2—O3	106.00 (9)
C5—N3—C6	119.31 (11)	O2—O3—H31	98.2 (12)
C5—N3—H32	113.8 (12)	O1—O4—H41	97.7 (12)
C6—N3—H32	112.9 (12)	H51—O5—H52	113 (2)
C3—N1—C1—C2	-0.2 (2)	C6—N3—C5—C6 <sup>i</sup>	-49.07 (18)
C4—N2—C2—C1	-0.5 (2)	C5—N3—C6—O1	-71.31 (15)
N1—C1—C2—N2	0.5 (3)	C5—N3—C6—C5 <sup>i</sup>	49.20 (18)
C1—N1—C3—C4	0.0 (2)	N3—C6—O1—O4	-165.20 (10)
C2—N2—C4—C3	0.2 (2)	C5 <sup>i</sup> —C6—O1—O4	73.31 (12)

N1—C3—C4—N2	0.0 (2)	N3—C5—O2—O3	160.69 (10)
C6—N3—C5—O2	72.06 (15)	C6 <sup>i</sup> —C5—O2—O3	-77.76 (12)

Symmetry code: (i)  $-x+1, -y+2, -z+2$ .

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O4—H41...N1 <sup>ii</sup>	0.88 (2)	1.88 (2)	2.7573 (18)	176.2 (18)
O3—H31...O5 <sup>iii</sup>	0.88 (2)	1.74 (2)	2.6068 (16)	168.2 (19)
N3—H32...O3 <sup>iv</sup>	0.83 (2)	2.17 (2)	2.9985 (16)	178.1 (17)
O5—H51...N2	0.88 (3)	1.97 (3)	2.8483 (19)	177 (2)
O5—H52...N3 <sup>v</sup>	0.86 (3)	2.14 (3)	2.9648 (18)	160 (2)

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