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Crystal structure of 2,3,5,6-tetrakis(pyridin-2-yl)pyrazine hydrogen peroxide 4.75-solvate

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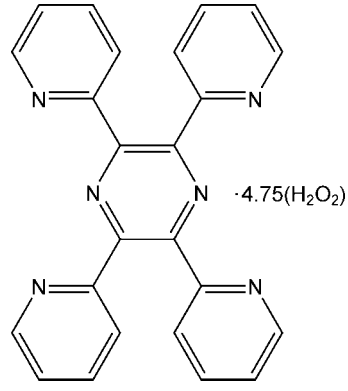
The structure of the title co-crystal, $C_{24}H_{16}N_6\cdot4.75H_2O_2$, consists of a 2,3,5,6-tetrakis(pyridin-2-yl)pyrazine coformer and hydrogen peroxide solvent molecules in an overall ratio of 1:4.75. Three of the six H_2O_2 molecules modelled in the structure were found to be cross-orientationally disordered over two positions with occupancy ratios 0.846 (9):0.154 (9), 0.75 (2):0.25 (2), and 0.891 (9):0.109 (9). In the crystal, all of the peroxide molecules are linked into hydrogen-bonded chains that propagate parallel to the *a* axis. These chains are further linked by O—H···N hydrogen bonds to the pyridine groups of the main molecule.

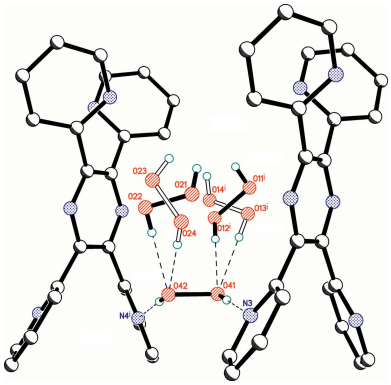
1. Chemical context

Peroxosolvates are solids that contain H_2O_2 molecules in a manner analogous to the water in crystalline hydrates. Nowadays, some peroxosolvates find widespread use as environmentally friendly decontaminating and bleaching compounds (Jakob *et al.*, 2012), and as oxidizing agents in organic synthesis (Ahn *et al.*, 2015). Hydrogen bonding in peroxosolvates is of particular interest because it may be used for modelling of hydrogen peroxide behaviour in various significant biochemical processes, especially oxidative stress and transport through cellular membranes (Kapustin *et al.*, 2014).



2. Structural commentary

The title structure consists of a 2,3,5,6-tetrakis(pyridin-2-yl)pyrazine coformer and six crystallographically independent peroxide molecules (Fig. 1), namely Per1 (major occupancy component H11/O11/O12/H12, minor component H13/O13/O14/H14); Per2 (major occupancy component H21/O21/O22/



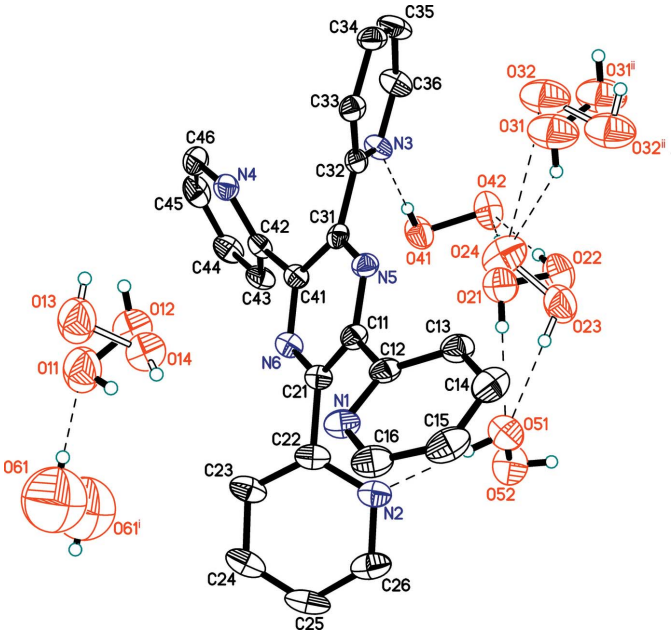


Figure 1
Labelling scheme for organic coformer and six crystallographically independent peroxide molecules. Displacement ellipsoids are shown at the 50% probability level. Hydrogen bonds are drawn as dashed lines. [Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $-x, 2-y, 1-z$.]

H22, minor component H23/O23/O24/H24); Per3 (major occupancy component H31/O31/O31/H31, minor component H32/O32/O32/H32); Per4 (H41/O41/O42/H42); Per5 (H51/O51/O52/H52); Per6 (H61/O61/O61/H61). Molecules Per1, Per2, Per4, Per5 occupy general positions and thus exhibit a skew geometry. Molecules Per3 and Per6 lie on inversion centres. Three of the six H_2O_2 molecules are cross-orientationally disordered over two positions (Fig. 2). This type of disorder was previously reported for several inorganic peroxosolvates (Adams & Pritchard, 1977; Carrondo *et al.*, 1977; Pritchard & Islam, 2003; Medvedev *et al.*, 2012).

In the organic molecule, all four pyridin-2-yl substituents are significantly inclined with respect to the central pyrazine ring (Fig. 3), such that the N—C—C—N torsion angles range between 130.8 (6) and 140.0 (4)°. Similar conformations have been observed for all three known polymorphs of the pure coformer (Bock *et al.*, 1992; Behrens & Rehder, 2009; Malecki,

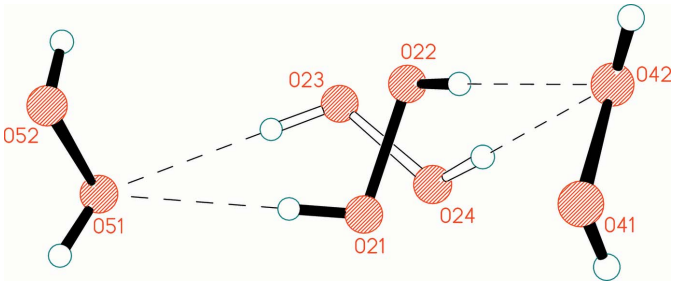


Figure 2
Molecule Per2 cross-orientationally disordered over two positions, showing hydrogen bonds (drawn as dashed lines) to molecules Per4 and Per5. The minor component of disorder is depicted with open bonds.

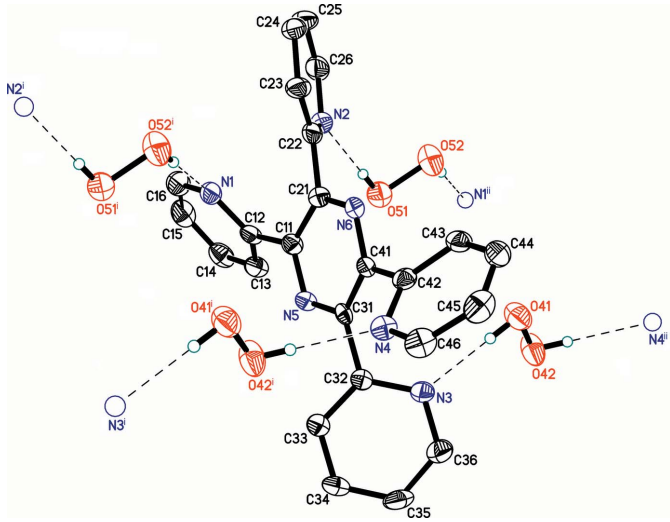


Figure 3
Organic coformer with hydrogen-bonded peroxide molecules. Displacement ellipsoids are shown at the 50% probability level. Hydrogen bonds are drawn as dashed lines. [Symmetry codes: (i) $x, -1+y, z$; (ii) $x, 1+y, z$.]

2010). Of structural significance, the pairs of pyridinyl nitrogen atoms N1, N4 and N2, N3 are located at opposite sides of the central pyrazine ring. This arrangement clearly facilitates the organization of hydrogen-bonded chains in the structure (see below). All four pyridinyl nitrogen atoms are involved as hydrogen-bond acceptors, but neither of the pyrazine N atoms participate in hydrogen bonding, presumably because of steric hindrance.

In the peroxide molecules, the O—O distances range between 1.44 (4) and 1.485 (5) Å. The mean value of 1.465 Å

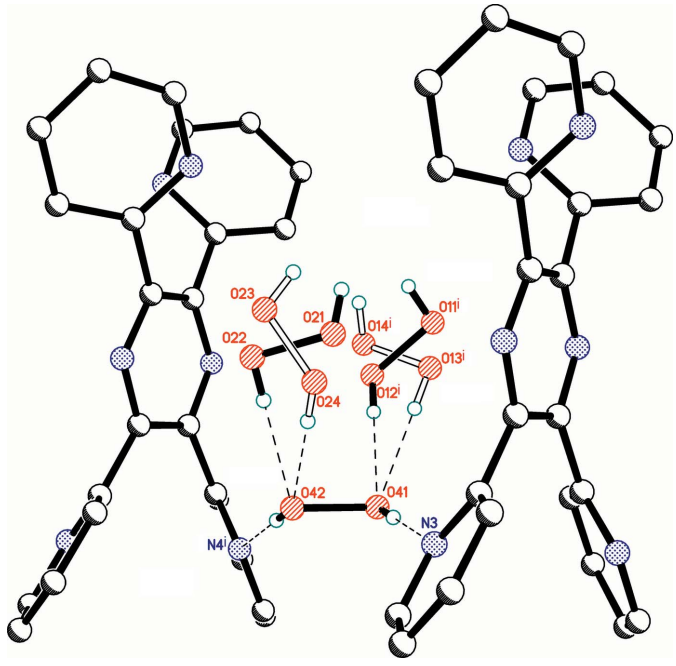


Figure 4
Hydrogen bonds formed by molecule Per4. Minor components of disorder are drawn with open bonds. Hydrogen bonds are drawn as dashed lines. [Symmetry code: (i) $x, 1+y, z$.]

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

D—H···A	D—H	H···A	D···A	D—H···A
O11—H11···O52^{i}	0.80	1.99	2.793 (7)	179
O12—H12···O41^{i}	0.80	1.99	2.789 (7)	180
O13—H13···O41^{i}	0.80	1.89	2.69 (4)	180
O14—H14···O52^{i}	0.80	2.05	2.85 (3)	179
O21—H21···O51	0.80	2.02	2.820 (9)	180
O22—H22···O42	0.80	2.07	2.866 (11)	180
O23—H23···O51	0.80	1.96	2.77 (3)	180
O24—H24···O42	0.80	1.84	2.64 (3)	180
O31—H31···O22	0.80	2.15	2.947 (9)	176
O32—H32···O24	0.80	2.34	3.14 (5)	173
O41—H41···N3	0.80	1.93	2.729 (5)	180
O42—H42···N4^{ii}	0.80	1.97	2.770 (5)	180
O51—H51···N2	0.80	1.94	2.737 (5)	180
O52—H52···N1^{ii}	0.80	1.94	2.740 (5)	180
O61—H61···O11	0.80	1.64	2.440 (17)	178

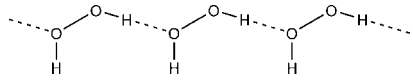
Symmetry codes: (i) $x, y-1, z$; (ii) $x, y+1, z$.

is close to those previously observed in the accurately determined structures of crystalline hydrogen peroxide [1.461 (3) Å; Savariault & Lehmann, 1980] and urea perhydrate [1.4573 (8) Å; Fritchie & McMullan, 1981].

The ordered molecules Per4 and Per5 form four hydrogen bonds (two as donor and two as acceptor) in [2,2] mode (Fig. 4). This coordination environment of the peroxide molecules is the most common arrangement in organic peroxosolvates (Prikhodchenko *et al.*, 2011). In contrast, the disordered or partially occupied molecules Per1, Per2, Per3, and Per6 are involved in just two or three hydrogen bonds with adjacent peroxide molecules, but not with the organic coformer. It should be noted that the maximum number of hydrogen bonds possible for H_2O_2 is six (two as donor and four as acceptor), but such cases are quite rare (Chernyshov *et al.*, 2017).

3. Supramolecular features

In the crystal, all six peroxide molecules are linked into hydrogen-bonded chains that propagate parallel to the *a*-axis (Table 1, Fig. 5). To the best of our knowledge, this is only the second example of hydrogen-bonded chains formed exclusively from peroxide molecules. Recently we reported the structure of thymine peroxosolvate obtained from 98% hydrogen peroxide (Chernyshov *et al.*, 2017). However, in the latter compound, the peroxide chains are very simple (see Scheme below), belonging to the C1 type according to the Infantes–Motherwell notation of water clusters (Infantes & Motherwell, 2002). In the title structure, the chains represent the more complicated *T*4(0)*A*1 motif (Fig. 5).



The peroxide chains are interconnected *via* the organic molecules by moderate HOO—H···N hydrogen bonds. Despite the aromatic nature of organic coformer, no π–π stacking or T-shaped C—H···π intermolecular interactions are observed in the structure. Thus, hydrogen bonding plays the predominant role in the crystal packing.

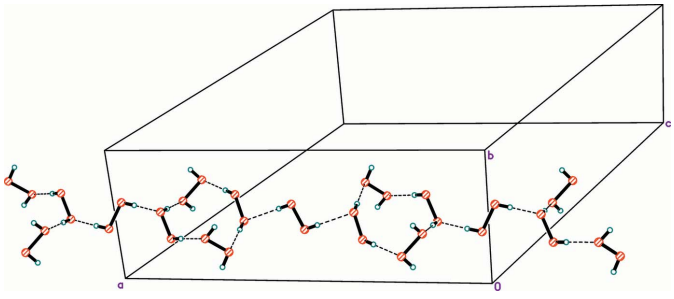


Figure 5
Peroxide hydrogen-bonded chains parallel to the *a*-axis. Minor components of disorder are not shown for clarity. Hydrogen bonds are drawn as dashed lines.

4. Database survey

The Cambridge Structural Database (Version 5.38: Groom *et al.*, 2016) contains data for 72 individual 'true' peroxosolvates (78 refcodes), in which the peroxide molecules do not form direct bonds to metal atoms. A few of these represent examples of mixed halogen–peroxide chains of general formula $\cdots Hal^{-}\cdots(H_2O_2)_n\cdots Hal^{-}\cdots(H_2O_2)_k\cdots$ ($n, k = 1, 2$; Hal = Cl, Br; CAZHAN, CAZHER, CAZHIV, CAZHOB, CAZHUH, CAZJAP: Churakov *et al.*, 2005), mixed carbonate–peroxide chains (WUXSIT: Medvedev *et al.*, 2012) and disordered mixed peroxide–water chains (WINSAO: Churakov & Howard, 2007; QOHXUH: Laus *et al.*, 2008).

5. Synthesis and crystallization

98% 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 2,3,5,6-tetrakis(pyridin-2-yl)pyrazine (Aldrich) in 96% hydrogen peroxide to 255 K.

Several crystals were examined. All of them exhibited poor crystallinity, presumably as a result of the rather extensive disorder of the peroxide molecules.

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. Three of the six H_2O_2 molecules were found to be cross-orientationally disordered over two positions with occupancy ratios 0.846 (9):0.154 (9), 0.75 (2):0.25 (2), and 0.891 (9):0.109 (9), and were refined with restrained O—O distances.

The centrosymmetric peroxide molecule modelled as H61/O61/O61^{i}/H61^{i} [symmetry code: (i) $1-x, -y, 1-z$] was

found to be partially occupied. Simultaneous refinement of occupancy and thermal parameters for atom O61 was not stable and resulted in oscillating occupancies between 0.46 and 0.53 for consecutive cycles of refinement. It was therefore fixed at 0.5 for the final refinement.

Aromatic H atoms were placed in calculated positions with C—H = 0.95 Å and refined as riding atoms with relative isotropic displacement parameters U_{iso}(H) = 1.2U_{eq}(C). Peroxide hydrogen atoms were placed on the lines connecting hydrogen-bonded atoms at a distance of 0.80 Å from the corresponding O atoms. They were refined as riding atoms with relative isotropic displacement parameters U_{iso}(H) = 1.5U_{eq}(O).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{24}H_{16}N_6{\cdot}4.75H_2O_2$
M_r	550.00
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	19.000 (7), 7.382 (3), 20.212 (7)
β (°)	114.271 (5)
V (Å^3)	2584.3 (16)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.11
Crystal size (mm)	0.40 × 0.40 × 0.30
Data collection	
Diffractometer	Bruker SMART APEXII
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.957, 0.967
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16397, 4563, 3870
R_{int}	0.035
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.596
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.090, 0.191, 1.17
No. of reflections	4563
No. of parameters	388
No. of restraints	3
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.39, −0.36

Computer programs: *APEX2* and *SAINT* (Bruker, 2008) and *SHELXTL* (Sheldrick, 2008).

Acknowledgements

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Funding information

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supporting information

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Crystal structure of 2,3,5,6-tetrakis(pyridin-2-yl)pyrazine hydrogen peroxide 4.75-solvate

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Computing details

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

2,3,5,6-Tetrakis(pyridin-2-yl)pyrazine hydrogen peroxide 4.75-solvate

Crystal data

$C_{24}H_{16}N_6 \cdot 4.75H_2O_2$
$M_r = 550.00$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 19.000$ (7) Å
$b = 7.382$ (3) Å
$c = 20.212$ (7) Å
$\beta = 114.271$ (5)°
$V = 2584.3$ (16) Å^3
$Z = 4$
$F(000) = 1150$
$D_x = 1.414$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5939 reflections
$\theta = 2.2$–$30.1°$
$\mu = 0.11$ mm^{-1}
$T = 150$ K
Prism, colourless
0.40 × 0.40 × 0.30 mm

Data collection

Bruker SMART APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2008)
$T_{min} = 0.957$, $T_{max} = 0.967$
16397 measured reflections
4563 independent reflections
3870 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 25.1°$, $\theta_{min} = 1.2°$
$h = -22 \rightarrow 22$
$k = -8 \rightarrow 8$
$l = -24 \rightarrow 23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.090$
$wR(F^2) = 0.191$
$S = 1.17$
4563 reflections
388 parameters
3 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

$w = 1/[\sigma^2(F_o^2) + (0.010P)^2 + 10.P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
Extinction correction: SHELXTL (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0017 (4)

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.

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O11	0.3518 (4)	−0.0660 (7)	0.4736 (3)	0.0662 (16)	0.846 (9)
H11	0.3640	−0.0353	0.5148	0.099*	0.846 (9)
O12	0.3037 (3)	0.0865 (7)	0.4355 (3)	0.0500 (13)	0.846 (9)
H12	0.2602	0.0537	0.4129	0.075*	0.846 (9)
O13	0.302 (2)	−0.084 (3)	0.4427 (16)	0.0662 (16)	0.154 (9)
H13	0.2574	−0.0674	0.4170	0.099*	0.154 (9)
O14	0.325 (2)	0.101 (4)	0.4650 (18)	0.0500 (13)	0.154 (9)
H14	0.3448	0.0846	0.5079	0.075*	0.154 (9)
O21	0.1982 (4)	0.8976 (8)	0.5494 (5)	0.046 (2)	0.75 (2)
H21	0.2428	0.9008	0.5768	0.068*	0.75 (2)
O22	0.1750 (5)	1.0887 (9)	0.5388 (5)	0.045 (2)	0.75 (2)
H22	0.1578	1.0953	0.4955	0.068*	0.75 (2)
O23	0.2088 (15)	1.053 (3)	0.5761 (17)	0.054 (6)	0.25 (2)
H23	0.2513	1.0114	0.5961	0.081*	0.25 (2)
O24	0.1651 (17)	0.951 (3)	0.5117 (15)	0.056 (7)	0.25 (2)
H24	0.1496	0.9992	0.4729	0.084*	0.25 (2)
O31	0.0252 (3)	0.9210 (7)	0.5133 (3)	0.0661 (17)	0.891 (9)
H31	0.0661	0.9677	0.5224	0.099*	0.891 (9)
O32	−0.014 (2)	0.952 (6)	0.4653 (14)	0.0661 (17)	0.109 (9)
H32	0.0309	0.9595	0.4745	0.099*	0.109 (9)
O41	0.15205 (18)	0.9727 (4)	0.35656 (18)	0.0412 (8)	
H41	0.1267	0.8912	0.3612	0.062*	
O42	0.1137 (2)	1.1114 (4)	0.38369 (18)	0.0440 (9)	
H42	0.1200	1.1955	0.3618	0.066*	
O51	0.35556 (18)	0.9097 (5)	0.64562 (18)	0.0438 (8)	
H51	0.3802	0.8260	0.6415	0.066*	
O52	0.3959 (2)	1.0412 (5)	0.61765 (18)	0.0496 (9)	
H52	0.3851	1.1264	0.6362	0.074*	
O61	0.4922 (9)	−0.0768 (15)	0.5192 (8)	0.149 (6)*	0.50
H61	0.4462	−0.0750	0.5046	0.224*	0.50
N1	0.35882 (19)	0.3326 (5)	0.68106 (18)	0.0299 (8)	

N2	0.43995 (19)	0.6236 (5)	0.63149 (18)	0.0310 (8)
N3	0.06552 (18)	0.6947 (5)	0.37238 (18)	0.0276 (8)
N4	0.13565 (19)	0.4025 (5)	0.30774 (17)	0.0270 (8)
N5	0.19869 (18)	0.5011 (5)	0.53122 (17)	0.0232 (7)
N6	0.29935 (18)	0.5095 (5)	0.46312 (17)	0.0243 (7)
C11	0.2751 (2)	0.4834 (6)	0.5698 (2)	0.0242 (9)
C12	0.3013 (2)	0.4523 (6)	0.6494 (2)	0.0255 (9)
C13	0.2670 (2)	0.5469 (6)	0.6880 (2)	0.0307 (10)
H13A	0.2254	0.6277	0.6639	0.037*
C14	0.2949 (3)	0.5205 (7)	0.7624 (2)	0.0374 (11)
H14A	0.2723	0.5826	0.7900	0.045*
C15	0.3561 (3)	0.4026 (7)	0.7959 (2)	0.0414 (12)
H15A	0.3772	0.3847	0.8470	0.050*
C16	0.3856 (3)	0.3116 (7)	0.7531 (2)	0.0375 (11)
H16A	0.4271	0.2296	0.7761	0.045*
C21	0.3263 (2)	0.4994 (6)	0.5354 (2)	0.0248 (9)
C22	0.4120 (2)	0.5050 (6)	0.5756 (2)	0.0287 (9)
C23	0.4586 (2)	0.3985 (7)	0.5539 (2)	0.0329 (10)
H23A	0.4367	0.3177	0.5140	0.039*
C24	0.5380 (2)	0.4123 (7)	0.5916 (2)	0.0380 (11)
H24A	0.5716	0.3398	0.5784	0.046*
C25	0.5674 (2)	0.5328 (8)	0.6485 (3)	0.0444 (13)
H25A	0.6217	0.5459	0.6747	0.053*
C26	0.5169 (2)	0.6350 (7)	0.6671 (3)	0.0396 (11)
H26A	0.5378	0.7166	0.7068	0.048*
C31	0.1721 (2)	0.5232 (5)	0.45945 (19)	0.0199 (8)
C32	0.0876 (2)	0.5562 (5)	0.42050 (19)	0.0215 (8)
C33	0.0354 (2)	0.4529 (6)	0.4356 (2)	0.0240 (9)
H33A	0.0530	0.3572	0.4700	0.029*
C34	−0.0424 (2)	0.4894 (6)	0.4006 (2)	0.0283 (9)
H34A	−0.0791	0.4196	0.4102	0.034*
C35	−0.0658 (2)	0.6309 (7)	0.3507 (2)	0.0371 (11)
H35A	−0.1190	0.6598	0.3256	0.045*
C36	−0.0101 (2)	0.7290 (7)	0.3384 (2)	0.0356 (11)
H36A	−0.0265	0.8252	0.3042	0.043*
C41	0.2231 (2)	0.5160 (5)	0.4245 (2)	0.0217 (8)
C42	0.1960 (2)	0.5127 (6)	0.3444 (2)	0.0249 (9)
C43	0.2327 (2)	0.6153 (6)	0.3100 (2)	0.0294 (9)
H43A	0.2757	0.6893	0.3376	0.035*
C44	0.2056 (2)	0.6080 (7)	0.2353 (2)	0.0334 (10)
H44A	0.2299	0.6763	0.2107	0.040*
C45	0.1427 (3)	0.4993 (7)	0.1970 (2)	0.0372 (11)
H45A	0.1225	0.4932	0.1456	0.045*
C46	0.1094 (3)	0.3989 (6)	0.2350 (2)	0.0329 (10)
H46A	0.0662	0.3245	0.2083	0.039*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O11	0.075 (4)	0.052 (3)	0.057 (3)	0.014 (3)	0.013 (3)	−0.001 (2)
O12	0.053 (3)	0.051 (3)	0.046 (3)	−0.002 (2)	0.020 (3)	0.005 (3)
O13	0.075 (4)	0.052 (3)	0.057 (3)	0.014 (3)	0.013 (3)	−0.001 (2)
O14	0.053 (3)	0.051 (3)	0.046 (3)	−0.002 (2)	0.020 (3)	0.005 (3)
O21	0.045 (3)	0.022 (3)	0.062 (5)	0.006 (2)	0.015 (3)	0.009 (3)
O22	0.054 (5)	0.034 (4)	0.051 (4)	0.011 (3)	0.026 (4)	0.008 (3)
O23	0.053 (12)	0.050 (12)	0.054 (14)	0.018 (9)	0.017 (11)	−0.002 (10)
O24	0.067 (15)	0.039 (12)	0.054 (12)	−0.013 (10)	0.015 (12)	0.015 (10)
O31	0.046 (3)	0.066 (4)	0.084 (4)	−0.006 (2)	0.023 (3)	0.019 (3)
O32	0.046 (3)	0.066 (4)	0.084 (4)	−0.006 (2)	0.023 (3)	0.019 (3)
O41	0.0441 (19)	0.0314 (18)	0.060 (2)	−0.0005 (15)	0.0332 (17)	0.0008 (16)
O42	0.062 (2)	0.0319 (19)	0.055 (2)	0.0017 (16)	0.0406 (18)	0.0050 (16)
O51	0.0428 (19)	0.040 (2)	0.053 (2)	0.0024 (16)	0.0236 (16)	0.0053 (16)
O52	0.062 (2)	0.044 (2)	0.050 (2)	−0.0047 (18)	0.0307 (18)	0.0026 (17)
N1	0.0267 (18)	0.034 (2)	0.0260 (18)	−0.0024 (16)	0.0076 (14)	0.0065 (15)
N2	0.0246 (18)	0.033 (2)	0.0324 (19)	−0.0004 (15)	0.0087 (15)	0.0069 (16)
N3	0.0224 (17)	0.032 (2)	0.0316 (18)	0.0030 (15)	0.0143 (14)	0.0028 (15)
N4	0.0268 (18)	0.031 (2)	0.0245 (17)	0.0013 (15)	0.0114 (14)	−0.0026 (15)
N5	0.0201 (16)	0.0252 (18)	0.0246 (17)	−0.0034 (14)	0.0096 (13)	−0.0016 (14)
N6	0.0235 (17)	0.0241 (18)	0.0271 (17)	0.0006 (14)	0.0123 (14)	0.0058 (14)
C11	0.0234 (19)	0.024 (2)	0.0248 (19)	−0.0030 (16)	0.0097 (16)	−0.0010 (16)
C12	0.0208 (19)	0.031 (2)	0.025 (2)	−0.0072 (17)	0.0096 (16)	−0.0005 (17)
C13	0.026 (2)	0.039 (3)	0.027 (2)	−0.0044 (19)	0.0112 (17)	−0.0007 (18)
C14	0.039 (2)	0.046 (3)	0.031 (2)	−0.012 (2)	0.017 (2)	−0.003 (2)
C15	0.043 (3)	0.050 (3)	0.024 (2)	−0.013 (2)	0.007 (2)	0.004 (2)
C16	0.033 (2)	0.045 (3)	0.029 (2)	−0.003 (2)	0.0070 (19)	0.008 (2)
C21	0.0216 (19)	0.026 (2)	0.025 (2)	0.0003 (17)	0.0082 (16)	0.0015 (17)
C22	0.023 (2)	0.037 (3)	0.024 (2)	−0.0014 (18)	0.0079 (16)	0.0115 (19)
C23	0.024 (2)	0.051 (3)	0.026 (2)	0.006 (2)	0.0129 (17)	0.011 (2)
C24	0.026 (2)	0.051 (3)	0.040 (2)	0.010 (2)	0.017 (2)	0.020 (2)
C25	0.019 (2)	0.063 (4)	0.047 (3)	0.004 (2)	0.009 (2)	0.019 (3)
C26	0.028 (2)	0.041 (3)	0.039 (2)	−0.009 (2)	0.0039 (19)	0.008 (2)
C31	0.0243 (19)	0.0136 (19)	0.0240 (19)	−0.0047 (15)	0.0121 (16)	−0.0011 (15)
C32	0.0224 (19)	0.024 (2)	0.0203 (18)	−0.0004 (16)	0.0112 (15)	−0.0025 (16)
C33	0.025 (2)	0.029 (2)	0.0189 (18)	−0.0030 (17)	0.0103 (16)	−0.0022 (16)
C34	0.0204 (19)	0.040 (3)	0.026 (2)	−0.0063 (18)	0.0105 (16)	−0.0057 (19)
C35	0.018 (2)	0.054 (3)	0.036 (2)	0.006 (2)	0.0076 (18)	0.002 (2)
C36	0.027 (2)	0.041 (3)	0.039 (2)	0.007 (2)	0.0141 (19)	0.008 (2)
C41	0.0215 (19)	0.019 (2)	0.027 (2)	−0.0008 (16)	0.0120 (16)	0.0035 (16)
C42	0.0221 (19)	0.028 (2)	0.027 (2)	0.0058 (17)	0.0122 (16)	0.0016 (17)
C43	0.022 (2)	0.040 (3)	0.030 (2)	0.0027 (18)	0.0144 (17)	0.0044 (19)
C44	0.033 (2)	0.044 (3)	0.031 (2)	0.006 (2)	0.0208 (19)	0.009 (2)
C45	0.044 (3)	0.049 (3)	0.023 (2)	0.012 (2)	0.0183 (19)	0.001 (2)
C46	0.035 (2)	0.038 (3)	0.024 (2)	0.001 (2)	0.0107 (18)	−0.0081 (19)

Geometric parameters (Å, º)

O11—H11	0.8000	C12—C13	1.392 (6)
O12—H12	0.8001	C13—C14	1.387 (6)
O13—H13	0.8000	C13—H13A	0.9500
O14—H14	0.7999	C14—C15	1.386 (7)
O21—O22	1.467 (12)	C14—H14A	0.9500
O21—H21	0.8000	C15—C16	1.383 (7)
O22—H22	0.8002	C15—H15A	0.9500
O23—O24	1.44 (4)	C16—H16A	0.9500
O23—H23	0.8001	C21—C22	1.491 (5)
O24—H24	0.7998	C22—C23	1.384 (6)
O31—O31^{i}	1.465 (9)	C23—C24	1.386 (6)
O31—H31	0.7999	C23—H23A	0.9500
O31—H32	0.8813	C24—C25	1.378 (7)
O32—O32^{i}	1.463 (13)	C24—H24A	0.9500
O32—H32	0.7999	C25—C26	1.389 (7)
O41—O42	1.486 (4)	C25—H25A	0.9500
O41—H41	0.7997	C26—H26A	0.9500
O42—H42	0.8001	C31—C41	1.415 (5)
O51—O52	1.485 (5)	C31—C32	1.489 (5)
O51—H51	0.8002	C32—C33	1.382 (5)
O52—H52	0.8001	C33—C34	1.377 (5)
O61—O61^{ii}	1.471 (10)	C33—H33A	0.9500
O61—H61	0.7999	C34—C35	1.391 (6)
N1—C16	1.340 (5)	C34—H34A	0.9500
N1—C12	1.345 (5)	C35—C36	1.387 (6)
N2—C26	1.340 (5)	C35—H35A	0.9500
N2—C22	1.354 (6)	C36—H36A	0.9500
N3—C36	1.338 (5)	C41—C42	1.483 (5)
N3—C32	1.353 (5)	C42—C43	1.394 (6)
N4—C46	1.345 (5)	C43—C44	1.381 (6)
N4—C42	1.352 (5)	C43—H43A	0.9500
N5—C31	1.336 (5)	C44—C45	1.383 (6)
N5—C11	1.342 (5)	C44—H44A	0.9500
N6—C41	1.335 (5)	C45—C46	1.391 (6)
N6—C21	1.337 (5)	C45—H45A	0.9500
C11—C21	1.416 (5)	C46—H46A	0.9500
C11—C12	1.493 (5)		

O12—O11—H11	100.6	C22—C23—C24	118.6 (4)
O11—O12—H12	110.1	C22—C23—H23A	120.7
H12—O12—H14	128.2	C24—C23—H23A	120.7
H13—O12—H14	107.7	C25—C24—C23	118.8 (4)
O14—O13—H13	99.5	C25—C24—H24A	120.6
H11—O14—H12	115.4	C23—C24—H24A	120.6
O13—O14—H14	97.8	C24—C25—C26	119.2 (4)
O22—O21—H21	104.0	C24—C25—H25A	120.4

O21—O22—H22	100.4	C26—C25—H25A	120.4
O24—O23—H23	110.2	N2—C26—C25	122.9 (5)
O23—O24—H24	119.8	N2—C26—H26A	118.5
O31^{i}—O31—H31	99.7	C25—C26—H26A	118.5
O32^{i}—O32—H32	78.8	N5—C31—C41	120.5 (3)
O42—O41—H41	93.7	N5—C31—C32	116.0 (3)
O41—O42—H42	97.0	C41—C31—C32	123.5 (3)
O52—O51—H51	92.9	N3—C32—C33	122.5 (4)
O51—O52—H52	93.7	N3—C32—C31	116.9 (3)
O61^{ii}—O61—H61	102.7	C33—C32—C31	120.6 (3)
C16—N1—C12	117.7 (4)	C34—C33—C32	119.6 (4)
C26—N2—C22	117.1 (4)	C34—C33—H33A	120.2
C36—N3—C32	117.5 (4)	C32—C33—H33A	120.2
C46—N4—C42	117.5 (4)	C33—C34—C35	118.4 (4)
C31—N5—C11	118.6 (3)	C33—C34—H34A	120.8
C41—N6—C21	118.5 (3)	C35—C34—H34A	120.8
N5—C11—C21	120.2 (3)	C36—C35—C34	118.8 (4)
N5—C11—C12	116.4 (3)	C36—C35—H35A	120.6
C21—C11—C12	123.4 (3)	C34—C35—H35A	120.6
N1—C12—C13	122.6 (4)	N3—C36—C35	123.2 (4)
N1—C12—C11	117.4 (4)	N3—C36—H36A	118.4
C13—C12—C11	120.0 (4)	C35—C36—H36A	118.4
C14—C13—C12	118.6 (4)	N6—C41—C31	120.7 (3)
C14—C13—H13A	120.7	N6—C41—C42	116.3 (3)
C12—C13—H13A	120.7	C31—C41—C42	122.9 (3)
C15—C14—C13	119.2 (4)	N4—C42—C43	122.6 (4)
C15—C14—H14A	120.4	N4—C42—C41	116.4 (3)
C13—C14—H14A	120.4	C43—C42—C41	121.0 (4)
C16—C15—C14	118.3 (4)	C44—C43—C42	119.1 (4)
C16—C15—H15A	120.9	C44—C43—H43A	120.5
C14—C15—H15A	120.9	C42—C43—H43A	120.5
N1—C16—C15	123.6 (4)	C43—C44—C45	118.8 (4)
N1—C16—H16A	118.2	C43—C44—H44A	120.6
C15—C16—H16A	118.2	C45—C44—H44A	120.6
N6—C21—C11	120.6 (3)	C44—C45—C46	119.0 (4)
N6—C21—C22	115.8 (3)	C44—C45—H45A	120.5
C11—C21—C22	123.5 (3)	C46—C45—H45A	120.5
N2—C22—C23	123.3 (4)	N4—C46—C45	123.0 (4)
N2—C22—C21	116.0 (4)	N4—C46—H46A	118.5
C23—C22—C21	120.6 (4)	C45—C46—H46A	118.5

C31—N5—C11—C21	3.9 (6)	C41—C31—C32—N3	−47.1 (5)
C31—N5—C11—C12	−177.8 (4)	N5—C31—C32—C33	−45.2 (5)
C16—N1—C12—C13	−3.0 (6)	C41—C31—C32—C33	135.2 (4)
C16—N1—C12—C11	176.3 (4)	N3—C32—C33—C34	0.4 (6)
N5—C11—C12—N1	140.0 (4)	C31—C32—C33—C34	178.0 (3)
C21—C11—C12—N1	−41.8 (6)	C32—C33—C34—C35	−0.1 (6)
N5—C11—C12—C13	−40.7 (6)	C33—C34—C35—C36	0.0 (6)

C21—C11—C12—C13	137.6 (4)	C32—N3—C36—C35	0.5 (7)
N1—C12—C13—C14	2.0 (6)	C34—C35—C36—N3	−0.2 (7)
C11—C12—C13—C14	−177.3 (4)	C21—N6—C41—C31	3.8 (6)
C12—C13—C14—C15	0.5 (7)	C21—N6—C41—C42	−175.4 (4)
C13—C14—C15—C16	−1.8 (7)	N5—C31—C41—N6	−8.3 (6)
C12—N1—C16—C15	1.6 (7)	C32—C31—C41—N6	171.2 (4)
C14—C15—C16—N1	0.7 (7)	N5—C31—C41—C42	170.9 (4)
C41—N6—C21—C11	4.3 (6)	C32—C31—C41—C42	−9.6 (6)
C41—N6—C21—C22	−176.0 (4)	C46—N4—C42—C43	−2.3 (6)
N5—C11—C21—N6	−8.4 (6)	C46—N4—C42—C41	179.2 (4)
C12—C11—C21—N6	173.4 (4)	N6—C41—C42—N4	135.6 (4)
N5—C11—C21—C22	171.9 (4)	C31—C41—C42—N4	−43.6 (5)
C12—C11—C21—C22	−6.2 (7)	N6—C41—C42—C43	−42.8 (6)
C26—N2—C22—C23	−0.4 (6)	C31—C41—C42—C43	137.9 (4)
C26—N2—C22—C21	−178.1 (4)	N4—C42—C43—C44	1.5 (6)
N6—C21—C22—N2	130.8 (4)	C41—C42—C43—C44	179.9 (4)
C11—C21—C22—N2	−49.6 (6)	C42—C43—C44—C45	0.2 (6)
N6—C21—C22—C23	−47.0 (6)	C43—C44—C45—C46	−1.0 (7)
C11—C21—C22—C23	132.7 (4)	C42—N4—C46—C45	1.6 (6)
N2—C22—C23—C24	0.6 (6)	C44—C45—C46—N4	0.1 (7)
C21—C22—C23—C24	178.1 (4)	H11—O11—O12—H12	−116.1
C22—C23—C24—C25	−0.8 (6)	H13—O13—O14—H14	127.8
C23—C24—C25—C26	0.9 (7)	H21—O21—O22—H22	125.3
C22—N2—C26—C25	0.5 (6)	H23—O23—O24—H24	−118.1
C24—C25—C26—N2	−0.8 (7)	H31—O31—O31^{i}—H31^{i}	180.0
C11—N5—C31—C41	4.1 (6)	H32—O32—O32^{i}—H32^{i}	180.0
C11—N5—C31—C32	−175.5 (4)	H41—O41—O42—H42	−152.1
C36—N3—C32—C33	−0.6 (6)	H51—O51—O52—H52	−158.2
C36—N3—C32—C31	−178.3 (4)	H61—O61—O61^{ii}—H61^{ii}	180.0
N5—C31—C32—N3	132.5 (4)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11—H11···O52^{iii}	0.80	1.99	2.793 (7)	179
O12—H12···O41^{iii}	0.80	1.99	2.789 (7)	180
O13—H13···O41^{iii}	0.80	1.89	2.69 (4)	180
O14—H14···O52^{iii}	0.80	2.05	2.85 (3)	179
O21—H21···O51	0.80	2.02	2.820 (9)	180
O22—H22···O42	0.80	2.07	2.866 (11)	180
O23—H23···O51	0.80	1.96	2.77 (3)	180
O24—H24···O42	0.80	1.84	2.64 (3)	180
O31—H31···O22	0.80	2.15	2.947 (9)	176
O32—H32···O24	0.80	2.34	3.14 (5)	173
O41—H41···N3	0.80	1.93	2.729 (5)	180
O42—H42···N4^{iv}	0.80	1.97	2.770 (5)	180

O51—H51···N2	0.80	1.94	2.737 (5)	180
O52—H52···N1^{iv}	0.80	1.94	2.740 (5)	180
O61—H61···O11	0.80	1.64	2.440 (17)	178

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