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

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
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.

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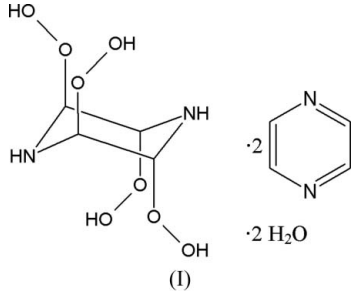
The reaction of pyrazine with hydrogen peroxide resulted in piperazine-2,3,5,6-tetrayl tetrahydroperoxide, crystallizing as its pyrazine disolvate dihydrate, $C_4H_{10}N_2O_8\cdot2C_4H_4N_2\cdot2H_2O$. In the crystal structure, the tetraperoxo molecules, which possess a crystallographically imposed centre of symmetry, are linked into a three-dimensional network by hydrogen-bonding interactions involving the pyrazine and water molecules.

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 H_2O_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 hydroperoxo substituents. The piperazine ring adopts a chair conformation and all hydroperoxo groups occupy axial positions. Atom N3 is slightly flattened, the sum of valence angles around it being 346.0°. 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).



(I)

The hydroperoxo 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 hydroperoxo groups. The title compound is the

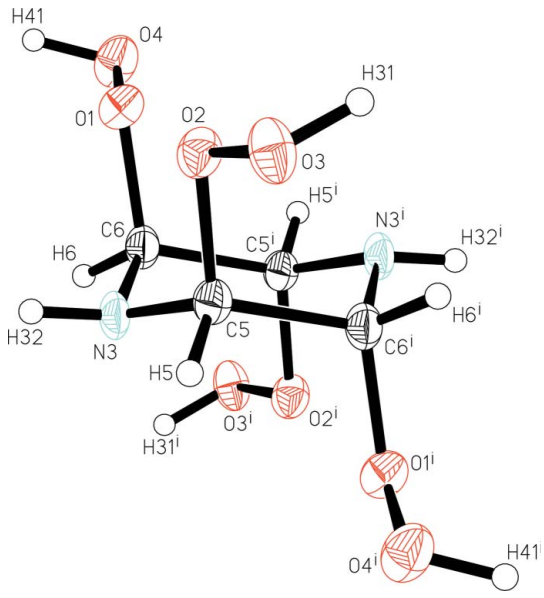


Figure 1
The molecular structure of the tetraperoxo molecule of (I), showing 50% probability displacement ellipsoids [symmetry code: (i) $1-y, 2-x, 2-z$].

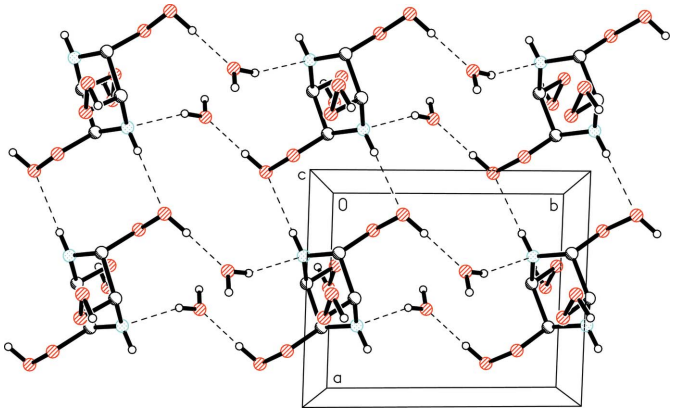


Figure 2
The hydrogen-bonded (dashed lines) layer in (I) perpendicular to the *c* axis. H atoms not involved in hydrogen bonds have been omitted for clarity.

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.

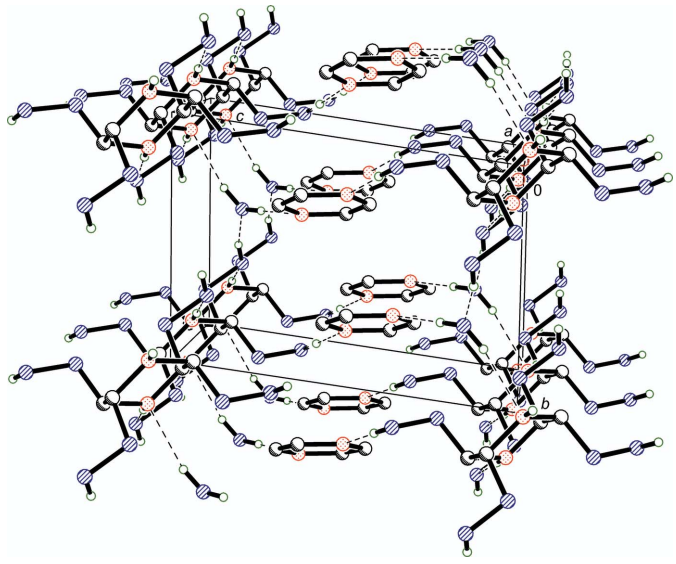


Figure 3
The crystal packing of (I), viewed approximately along the *a* axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonds have been omitted for clarity.

Crystal data

$C_4H_{10}N_2O_8\cdot2C_4H_4N_2\cdot2H_2O$
$M_r = 410.36$
Triclinic, $P\overline{1}$
$a = 6.1538$ (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^3
$Z = 1$
$D_x = 1.489$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.13$ mm^{-1}
$T = 120$ (2) K
Needle, colourless
0.25 × 0.04 × 0.03 mm

Data collection

Bruker SMART 6K diffractometer
ω 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 $I > 2\sigma(I)$
$R_{int} = 0.012$
$\theta_{max} = 28.0°$

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^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H41···N1^{i}	0.88 (2)	1.88 (2)	2.7573 (18)	176.2 (18)
O3—H31···O5^{ii}	0.88 (2)	1.74 (2)	2.6068 (16)	168.2 (19)
N3—H32···O3^{iii}	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^{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: *SAINT* (Bruker, 2001); data reduction: *SAINT*; 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*.

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