metal-organic compounds

catena-Poly[[lithium-μ_2-(dihydrogen pyrazine-2,3,5,6-tetracarboxylato)-$\kappa^6O^2,N^1,O^6;O^3,N^4,O^5$-lithium-di-$\mu$-aqua-$\kappa^4O:O$] 2.5-hydrate]

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The title coordination polymer, $\{[Li_2(C_8H_2N_2O_8)(H_2O)_2]\cdot 2.5H_2O\}_n$, is built up from molecular ribbons propagating in the c-axis direction of the orthorhombic unit cell; the ligand bridges two Li⁺ ions using both its N,O,O'-bonding sites and adjacent Li⁺ ions are bridged by pairs of water molecules. The coordination geometry of the metal ion is distorted trigonal bipyramidal, with the ligand O atoms in the axial sites. Two of the carboxylate groups of the ligand remain protonated and form short symmetric O—H···O hydrogen bonds. In the crystal, the ribbons interact *via* a network of O—H···O hydrogen bonds in which coordinating water molecules act as donors and carboxylate O atoms within adjacent ribbons act as acceptors, giving rise to a three-dimensional framework. O—H···N interactions are also observed. The asymmetric unit contains quarter of the ligand and the complete ligand has $2/m$ symmetry; the Li⁺ ion lies on a special position with $m..$ site symmetry. Both bridging water molecules have $m2m$ site symmetry and both lattice water molecules have $m..$ site symmetry; one of the latter was modelled with a site occupancy of 0.25.

Related literature

For the structures of related lithium complexes with pyrazine-2,3,5,6-tetracarboxylate and water ligands, see: Starosta & Leciejewicz (2010, 2014).
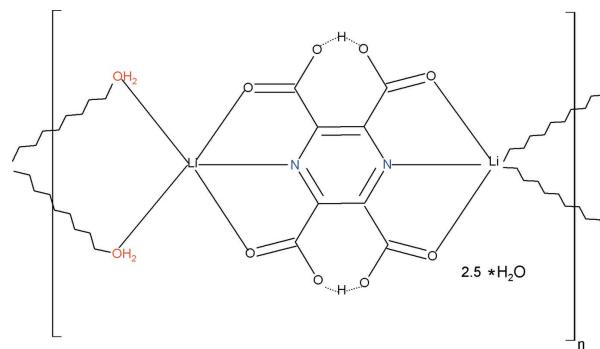
Experimental

Crystal data

$[Li_2(C_8H_2N_2O_8)(H_2O)_2]\cdot 2.5H_2O$	$V = 1489.80$ (6) Å³
$M_r = 174.53$	$Z = 8$
Orthorhombic, $Cmcm$	Mo $K\alpha$ radiation
$a = 12.0554$ (3) Å	$\mu = 0.15$ mm⁻¹
$b = 6.39040$ (17) Å	$T = 567$ K
$c = 19.3383$ (4) Å	$0.24 \times 0.20 \times 0.05$ mm

Data collection

Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer	7496 measured reflections
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)	1151 independent reflections
	997 reflections with $I > 2\sigma(I)$
$T_{min} = 0.701$, $T_{max} = 1.000$	$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.122$	
$S = 1.07$	
1151 reflections	$\Delta\rho_{max} = 0.25$ e Å⁻³
85 parameters	$\Delta\rho_{min} = -0.29$ e Å⁻³
3 restraints	

Table 1
Selected bond lengths (Å).

Li1—O1	2.1538 (13)	Li1—O4	1.976 (4)
Li1—O3	1.982 (4)	Li1—N1	2.116 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O6—H62···N1	0.87 (2)	2.28 (11)	2.886 (12)	127 (12)
O5—H5···O1ⁱ	0.85 (2)	1.95 (2)	2.7711 (13)	163 (2)
O3—H3···O5ⁱⁱ	0.82 (4)	1.92 (4)	2.730 (2)	173 (4)
O4—H4···O5ⁱⁱⁱ	0.90 (3)	1.83 (3)	2.726 (2)	179 (3)
O2—H2···O2ⁱᵛ	1.21 (1)	1.21 (1)	2.409 (3)	175 (1)

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

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7224).

References

Agilent (2011). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Starosta, W. & Leciejewicz, J. (2010). *Acta Cryst.* E**66**, m1561–m1562.
Starosta, W. & Leciejewicz, J. (2014). *Acta Cryst.* E**70**, m172.

supporting information

catena-Poly[[lithium-μ_2-(dihydrogen pyrazine-2,3,5,6-tetracarboxylato)-$\kappa^6O^2,N^1,O^6;O^3,N^4,O^5$-lithium-di-$\mu$-aqua-$\kappa^4O:O$] 2.5-hydrate]

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S1. Comment

The structure of the title compound is composed of molecular ribbons propagating in the crystal [001] direction. The structural unit of a ribbon is built of a centro-symmetric ligand molecule which bridges two Li ions using its both *N,O,O* bonding sites. Two water molecules chelated simultaneously to Li ions belonging to adjacent structural units, bridge them into a molecular ribbon [Fig.1]. The coordination environment of a Li ion is distorted trigonal bipyramidal. Its equatorial plane is composed of coplanar Li1, N1,O3,O4 atoms; O1 and O1^i are at the apices. The Li—O and Li—N bond distances are usual (Table 2). Within a ligand two carboxylate groups remain protonated to maintain charge balance and form short, intramolecular symmetric hydrogen bonds of 2.409 (1) Å (Table 3). The ligand ring is almost planar (r.m.s. is 0.0003 (1) Å; the carboxylate C17/O1/O12 group makes with it a dihedral angle of 2.6 (1)°. Bond distances and bond angles within the hetero-ring do not differ from those reported in the structures of two other Li complexes with the title ligand (Starosta & Leciejewicz, 2010, 2014). The Fourier map shows two solvation water molecules (O5 and O6), both at special positions. The refinemt reveals a disorder of the O6 aqua molecule with 0.25 positional occupancy *i.e.* two molecules at random in a unit cell. This molecule locates coplanarly with the N1, O3, O4 and Li1 atoms at a distance of 2.538 (2) Å from the latter. The ribbons are held together by a system of hydrogen bonds in which coordinated and solvation water molecules act as donors and carboxylate O atoms as acceptors giving rise to a three-dimensional framework. The structures of two other Li complexes with the title ligand have been recently reported. The structural unit of the title polymer is closely related to that one observed in the structure of the first compound which cosists of discrete dimeric molecules built of two aqua-coordinated Li ions bridged by the ligand molecule *via* both its N,O,O bonding sites (Starosta & Leciejewicz, 2014). The structure of the second complex is built of anions each consisting of an aqua coordinated Li ion cheleted to a doubly deprotonated ligand molecule and of aqua coordinated Li cations (Starosta & Leciejewicz, 2010).

S2. Experimental

An aqueous solution containing 2 mmol of lithium nitrate and a small excess over 1 mmol of pyrazine-2,3,5,6-tetracarboxylic acid dihydrate was heated under reflux with stirring at *ca* 330 K for 10 h. After cooling to room temperature the solution was left to evaporate. Three days later well formed colorless blocks of the title compound were found, which were washed with cold methanol and dried in the air.

S3. Refinement

Water and carcoxylate H atoms were found in the Fourier map and refined isotropically.
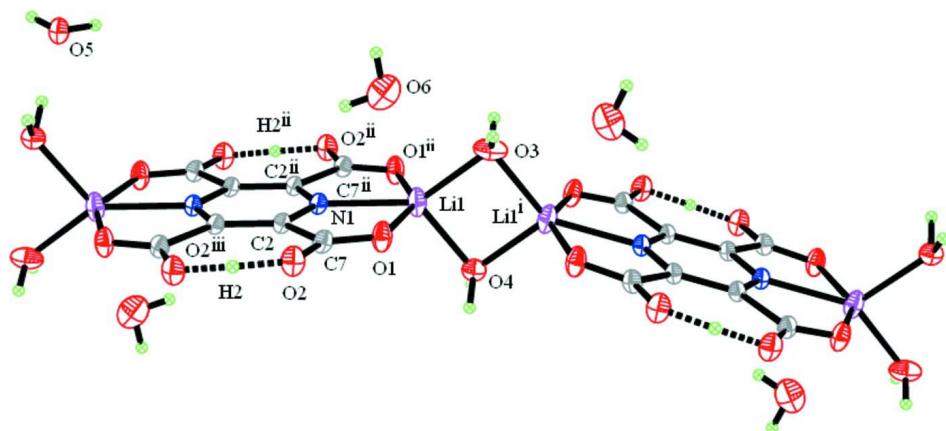
Figure 1

A fragment of a [001] chain in the title compound with 50% probability displacement ellipsoids. Symmetry code: [i] $x, y, -z + 1$; [ii] $-x + 1, y, z$; [iii] $x, -y, -z + 1$.
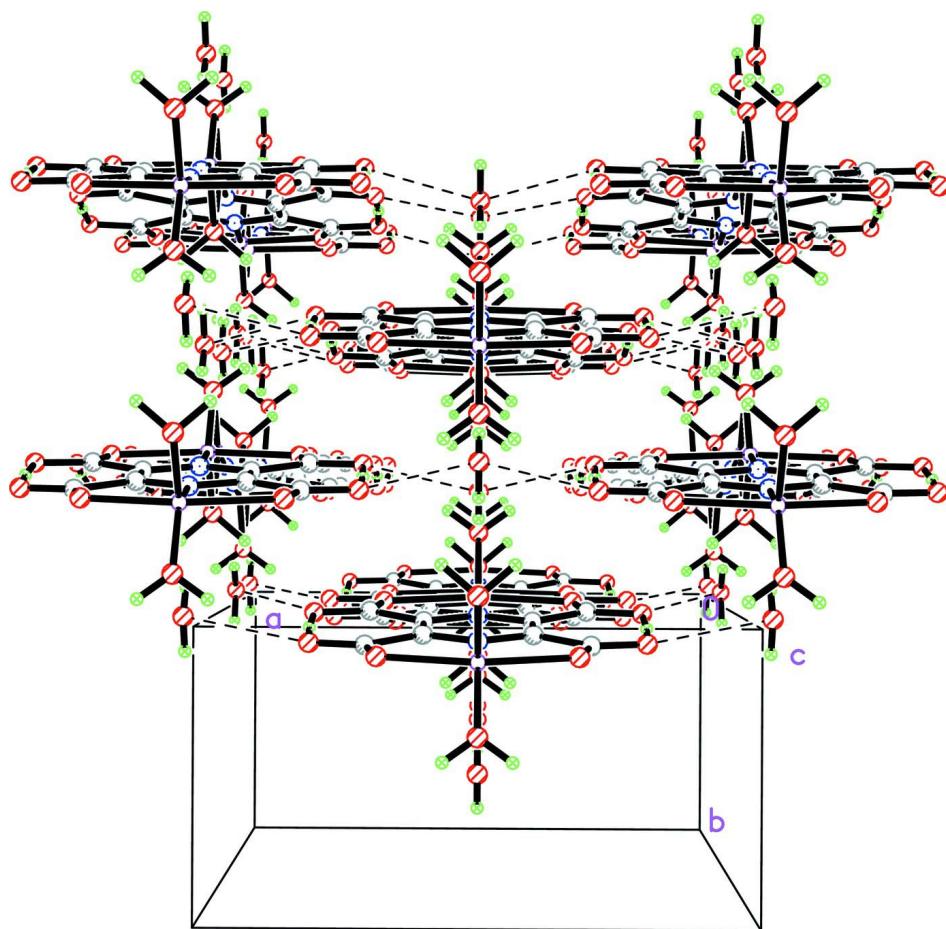
Figure 2

The alignment of the ribbons viewed along the crystal *a* direction.

catena-Poly[[lithium-*μ*₂-(dihydrogen pyrazine-2,3,5,6-tetracarboxylato)-*κ*⁶O^2,N^1,O^6;O^3,N^4,O^5-lithium-di-*μ*-aqua-*κ*⁴O:O] 2.5-hydrate]

Crystal data

[Li($C_8H_2N_2O_8$)(H_2O)$_2$]·2.5H_2O	$F(000) = 716$
$M_r = 349.06$	$D_x = 1.556$ Mg m⁻³
Orthorhombic, *Cmcm*	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2c 2	Cell parameters from 3296 reflections
$a = 12.0554$ (3) Å	$\theta = 3.8–31.9°$
$b = 6.39040$ (17) Å	$\mu = 0.15$ mm⁻¹
$c = 19.3383$ (4) Å	$T = 293$ K
$V = 1489.80$ (6) Å³	Block, colourless
$Z = 4$	0.24 × 0.20 × 0.05 mm

Data collection

Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer	$T_{min} = 0.701$, $T_{max} = 1.000$
	7496 measured reflections
Radiation source: SuperNova (Mo) X-ray Source	1151 independent reflections
	997 reflections with $I > 2\sigma(I)$
Mirror monochromator	$R_{int} = 0.029$
Detector resolution: 16.0131 pixels mm⁻¹	$\theta_{max} = 30.0°$, $\theta_{min} = 3.4°$
ω scans	$h = -16 \rightarrow 16$
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)	$k = -8 \rightarrow 8$
	$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.042$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.122$	
$S = 1.07$	H atoms treated by a mixture of independent and constrained refinement
1151 reflections	
85 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0592P)^2 + 0.9014P]$
3 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.25$ e Å⁻³
	$\Delta\rho_{min} = -0.29$ e Å⁻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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.67161 (8)	0.07053 (19)	0.35355 (5)	0.0435 (3)	
O4	0.5000	−0.1345 (3)	0.2500	0.0388 (4)	

O2	0.79263 (8)	0.04117 (18)	0.43921 (5)	0.0413 (3)	
O5	0.33035 (11)	0.4166 (2)	0.7500	0.0379 (3)	
O3	0.5000	0.3004 (4)	0.2500	0.0533 (6)	
N1	0.5000	0.0321 (2)	0.43101 (7)	0.0270 (3)	
C2	0.59630 (8)	0.01679 (18)	0.46407 (6)	0.0259 (3)	
C7	0.69421 (10)	0.0441 (2)	0.41465 (6)	0.0310 (3)	
Li1	0.5000	0.0823 (7)	0.32284 (17)	0.0463 (8)	
H4	0.555 (2)	−0.229 (5)	0.2500	0.070 (9)*	
H3	0.445 (3)	0.377 (7)	0.2500	0.097 (13)*	
H5	0.2920 (19)	0.432 (3)	0.7135 (10)	0.068 (7)*	
H2	0.797 (3)	0.0000	0.5000	0.097 (12)*	
O6	0.5000	0.4486 (17)	0.3733 (5)	0.077 (2)	0.25
H61	0.5000	0.578 (7)	0.386 (7)	0.115*	0.25
H62	0.5000	0.39 (2)	0.413 (4)	0.115*	0.25

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0302 (5)	0.0732 (8)	0.0270 (5)	−0.0022 (4)	0.0051 (3)	0.0037 (4)
O4	0.0299 (9)	0.0406 (10)	0.0459 (11)	0.000	0.000	0.000
O2	0.0207 (4)	0.0659 (7)	0.0374 (5)	−0.0024 (4)	0.0029 (3)	0.0018 (4)
O5	0.0240 (6)	0.0562 (9)	0.0334 (7)	0.0024 (6)	0.000	0.000
O3	0.0336 (11)	0.0356 (11)	0.0908 (18)	0.000	0.000	0.000
N1	0.0207 (6)	0.0370 (7)	0.0232 (6)	0.000	0.000	−0.0010 (5)
C2	0.0198 (5)	0.0335 (6)	0.0244 (5)	−0.0005 (4)	0.0010 (4)	−0.0025 (4)
C7	0.0226 (5)	0.0410 (7)	0.0295 (6)	−0.0015 (4)	0.0048 (4)	−0.0021 (5)
Li1	0.0421 (18)	0.070 (2)	0.0271 (15)	0.000	0.000	0.0075 (15)
O6	0.049 (4)	0.101 (7)	0.081 (5)	0.000	0.000	−0.020 (5)

Geometric parameters (Å, º)

O1—C7	1.2242 (16)	O3—Li1^{ii}	1.982 (4)
Li1—O1	2.1538 (13)	O3—H3	0.82 (4)
Li1—O1^i	2.1538 (13)	N1—C2	1.3289 (12)
Li1—O3	1.982 (4)	N1—C2^i	1.3289 (12)
Li1—O4	1.976 (4)	C2—C2^{iii}	1.406 (2)
Li1—N1	2.116 (3)	C2—C7	1.5287 (15)
O4—Li1^{ii}	1.976 (4)	Li1—O6	2.536 (11)
O4—H4	0.90 (3)	Li1—Li1^{ii}	2.817 (7)
O2—C7	1.2780 (15)	O6—H61	0.86 (2)
O2—H2	1.2057 (19)	O6—H62	0.87 (2)
O5—H5	0.85 (2)		
C7—O1—Li1	119.00 (12)	O3—Li1—O1	102.74 (10)
Li1^{ii}—O4—Li1	91.0 (2)	N1—Li1—O1	73.87 (9)
Li1^{ii}—O4—H4	118.2 (11)	O4—Li1—O1^i	99.91 (12)
Li1—O4—H4	118.2 (11)	O3—Li1—O1^i	102.74 (10)
C7—O2—H2	113.8 (18)	N1—Li1—O1^i	73.87 (9)

Li1—O3—Li1ii	90.6 (3)	O1—Li1—O1i	147.72 (17)
Li1—O3—H3	114.8 (18)	O4—Li1—O6	157.2 (3)
Li1ii—O3—H3	114.8 (18)	O3—Li1—O6	67.9 (3)
C2—N1—C2i	121.76 (13)	N1—Li1—O6	76.1 (3)
C2—N1—Li1	119.12 (7)	O1—Li1—O6	85.76 (13)
C2i—N1—Li1	119.12 (7)	O1i—Li1—O6	85.76 (13)
N1—C2—C2iii	119.12 (7)	O4—Li1—Li1ii	44.52 (11)
N1—C2—C7	111.44 (10)	O3—Li1—Li1ii	44.70 (13)
C2iii—C2—C7	129.43 (6)	N1—Li1—Li1ii	171.28 (12)
O1—C7—O2	124.56 (11)	O1—Li1—Li1ii	106.01 (9)
O1—C7—C2	116.56 (11)	O1i—Li1—Li1ii	106.01 (9)
O2—C7—C2	118.87 (11)	O6—Li1—Li1ii	112.6 (3)
O4—Li1—O3	89.22 (15)	Li1—O6—H61	174 (10)
O4—Li1—N1	126.8 (2)	Li1—O6—H62	85 (10)
O3—Li1—N1	144.0 (2)	H61—O6—H62	101 (3)
O4—Li1—O1	99.91 (12)		
C2i—N1—C2—C2iii	0.1 (3)	Li1ii—O3—Li1—O6	180.000 (2)
Li1—N1—C2—C2iii	−179.94 (18)	C2—N1—Li1—O4	90.02 (13)
C2i—N1—C2—C7	−178.85 (10)	C2i—N1—Li1—O4	−90.02 (13)
Li1—N1—C2—C7	1.1 (2)	C2—N1—Li1—O3	−89.98 (13)
Li1—O1—C7—O2	−177.66 (16)	C2i—N1—Li1—O3	89.98 (13)
Li1—O1—C7—C2	1.3 (2)	C2—N1—Li1—O1	−0.42 (18)
N1—C2—C7—O1	−1.57 (17)	C2i—N1—Li1—O1	179.54 (12)
C2iii—C2—C7—O1	179.61 (16)	C2—N1—Li1—O1i	−179.55 (12)
N1—C2—C7—O2	177.46 (12)	C2i—N1—Li1—O1i	0.42 (18)
C2iii—C2—C7—O2	−1.4 (2)	C2—N1—Li1—O6	−89.98 (13)
Li1ii—O4—Li1—O3	0.0	C2i—N1—Li1—O6	89.98 (13)
Li1ii—O4—Li1—N1	180.0	C2—N1—Li1—Li1ii	90.02 (13)
Li1ii—O4—Li1—O1	−102.80 (12)	C2i—N1—Li1—Li1ii	−90.02 (13)
Li1ii—O4—Li1—O1i	102.80 (12)	C7—O1—Li1—O4	−126.14 (15)
Li1ii—O4—Li1—O6	0.000 (4)	C7—O1—Li1—O3	142.40 (14)
Li1ii—O3—Li1—O4	0.0	C7—O1—Li1—N1	−0.56 (19)
Li1ii—O3—Li1—N1	180.0	C7—O1—Li1—O1i	1.0 (5)
Li1ii—O3—Li1—O1	99.99 (14)	C7—O1—Li1—O6	76.2 (3)
Li1ii—O3—Li1—O1i	−99.99 (14)	C7—O1—Li1—Li1ii	−171.48 (10)

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

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O6—H62···N1	0.87 (2)	2.28 (11)	2.886 (12)	127 (12)
O5—H5···O1iv	0.85 (2)	1.95 (2)	2.7711 (13)	163 (2)
O3—H3···O5v	0.82 (4)	1.92 (4)	2.730 (2)	173 (4)
O4—H4···O5vi	0.90 (3)	1.83 (3)	2.726 (2)	179 (3)
O2—H2···O2iii	1.21 (1)	1.21 (1)	2.409 (3)	175 (1)

Symmetry codes: (iii) x, −y, −z+1; (iv) x−1/2, −y+1/2, −z+1; (v) x, −y+1, −z+1; (vi) −x+1, −y, −z+1.