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Piperazine-1,4-dium bis(2-carboxy-1H-pyrazole-4-carboxylate) tetrahydrate

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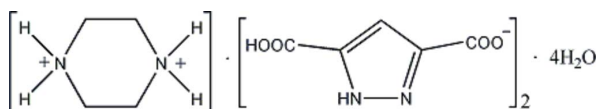
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Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.059; wR factor = 0.147; data-to-parameter ratio = 11.5.

The asymmetric unit of the title compound, $\text{C}_4\text{H}_{12}\text{N}_2^{2+} \cdot 2\text{C}_5\text{H}_3\text{N}_2\text{O}_4^- \cdot 4\text{H}_2\text{O}$, comprises one-half of a piperazine-1,4-dium cation, which lies on an inversion centre, a 2-carboxy-1H-pyrazole-4-carboxylate anion and two water molecules. An extensive network of intermolecular $\text{O}-\text{H} \cdots \text{O}$, $\text{N}-\text{H} \cdots \text{O}$, $\text{N}-\text{H} \cdots \text{N}$ and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds between the cations, anions and water molecules leads to a three-dimensional supramolecular framework.

Related literature

For 3,5-pyrazoledicarboxylic acid, see: King *et al.* (2003); Pan *et al.* (2001). For reference structural data, see: Li & Su (2007); Reviriego *et al.* (2006).



Experimental

Crystal data

 $\text{C}_4\text{H}_{12}\text{N}_2 \cdot 2\text{C}_5\text{H}_3\text{N}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ $M_r = 470.41$ Monoclinic, $P2_1/c$ $a = 8.3363$ (13) Å $b = 16.246$ (3) Å $c = 7.3930$ (11) Å $\beta = 90.812$ (3)° $V = 1001.2$ (3) Å³ $Z = 2$ Mo $K\alpha$ radiation $\mu = 0.14$ mm⁻¹ $T = 291$ K

0.15 × 0.14 × 0.12 mm

Data collection

Bruker SMART APEX CCD diffractometer

Absorption correction: multi-scan (SADABS; Bruker, 2000)

 $T_{\min} = 0.980$, $T_{\max} = 0.984$

5265 measured reflections

1946 independent reflections

1524 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.051$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.059$ $wR(F^2) = 0.147$ $S = 1.10$

1946 reflections

169 parameters

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.41$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1} \cdots \text{O5}^{\text{i}}$	0.84 (3)	1.93 (3)	2.746 (3)	167 (3)
$\text{O2}-\text{H2} \cdots \text{O4}^{\text{ii}}$	0.87 (3)	1.65 (3)	2.520 (2)	175 (3)
$\text{N3}-\text{H3A} \cdots \text{O4}$	0.88 (3)	2.36 (3)	2.918 (3)	121 (2)
$\text{N3}-\text{H3A} \cdots \text{N2}$	0.88 (3)	2.01 (3)	2.865 (3)	162 (3)
$\text{N3}-\text{H3B} \cdots \text{O3}^{\text{iii}}$	0.88 (3)	2.20 (3)	2.999 (3)	150 (3)
$\text{O5}-\text{H5B} \cdots \text{O6}$	0.85 (4)	2.00 (4)	2.831 (3)	166 (3)
$\text{O5}-\text{H5A} \cdots \text{O6}^{\text{iv}}$	0.92 (4)	1.96 (4)	2.833 (3)	157 (3)
$\text{O6}-\text{H6C} \cdots \text{O3}^{\text{v}}$	0.93 (3)	1.85 (3)	2.779 (3)	173 (3)
$\text{O6}-\text{H6D} \cdots \text{O3}^{\text{vi}}$	0.76 (3)	2.14 (3)	2.858 (3)	158 (4)
$\text{C6}-\text{H6B} \cdots \text{O5}^{\text{vii}}$	0.97	2.53	3.348 (4)	142
$\text{C7}-\text{H7A} \cdots \text{O1}^{\text{viii}}$	0.97	2.53	3.091 (3)	117

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

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: DIAMOND (Brandenburg, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2361).

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supporting information

Acta Cryst. (2010). E66, o2578 [doi:10.1107/S160053681003655X]

Piperazine-1,4-dium bis(2-carboxy-1*H*-pyrazole-4-carboxylate) tetrahydrate

Xin-Hui Zhou

S1. Comment

Hydrogen bonding, as the strongest and most directional intermolecular force, has been intensively investigated in organic crystalline solids. The ligand, 3,5-pyrazoledicarboxylic acid, known both as a multiple proton donor and acceptor, has six potential hydrogen-bond sites involving both the nitrogen atoms of the pyrazole ring and all of the carboxylate O atoms. and it can form mono-, di- and trianionic ligand species through deprotonation (King *et al.* 2003; Pan *et al.* 2001).

We report here the synthesis and structure of piperazine-1,4-dium bis(2-carboxy-1*H*-pyrazole-4-carboxylate) tetrahydrate, as shown in Fig.1, which was obtained from a solution of 3,5-pyrazoledicarboxylic acid, Cd(NO₃)₂·4H₂O and piperazine. Bond distances and angles are normal (Li & Su, 2007; Reviriego *et al.* 2006). The asymmetric unit of the title compound comprises one half of the piperazine-1,4-dium cation, which lies about an inversion centre, a 2-carboxy-1*H*-pyrazole-4-carboxylate anion and two water molecules. In the crystal structure molecules are interlinked by hydrogen bonds (Table 1 and Fig. 2). The 2-carboxy-1*H*-pyrazole-4-carboxylate anions are interconnected with each other through the O2—H2···O4ⁱⁱⁱ hydrogen bonds. The 2-carboxy-1*H*-pyrazole-4-carboxylate anions are connected with the piperazine-1,4-dium cations through the N3—H3A···O4, N3—H3A···N2, N3—H3B···O3^{iv} and C7—H7A···O1^{viii} hydrogen bonds to form the three-dimensional supramolecular framework.

S2. Experimental

A mixture of 3,5-pyrazoledicarboxylic acid (0.2 mmol, 34.8 mg), Cd(NO₃)₂·4H₂O (0.1 mmol, 30.8 mg), piperazine (0.2 mmol, 17.2 mg) and H₂O (8 ml) was sealed in a 15 ml Teflon-lined bomb and heated at 150°C for 5 days. The reaction mixture was slowly cooled to room temperature to obtain the colorless block crystals of (I) suitable for X-ray diffraction analysis.

S3. Refinement

Hydrogen atoms bonded to the carbon atoms were placed in calculated positions and refined as riding mode, with C—H = 0.93 Å for aromatic H atom, 0.97 Å for methylene H atoms, respectively, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms on the O and N atoms were located in difference Fourier map with their bond lengths freely refined and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O or N})$.

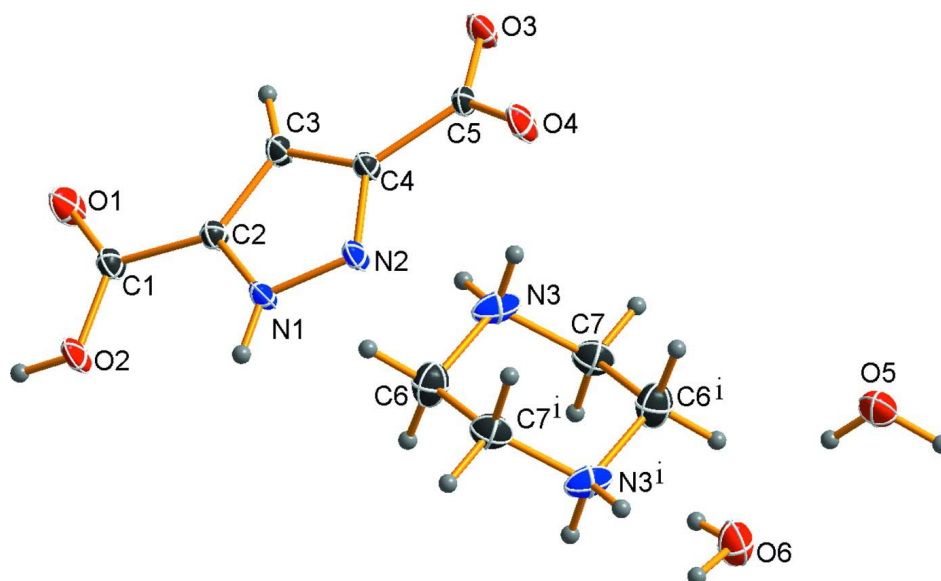


Figure 1

The molecular structure of the title compound with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. [Symmetry code; (i) $1 - x, 1 - y, -z$.]

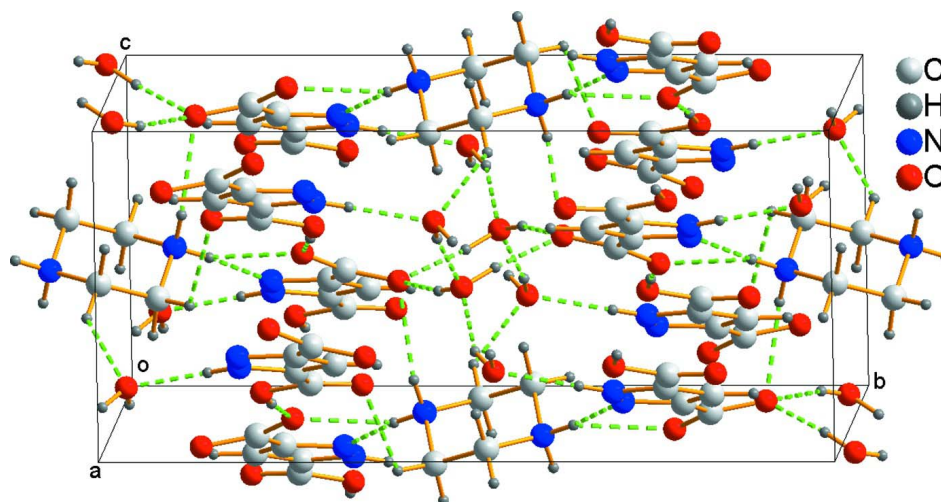


Figure 2

A view of the crystal packing. Hydrogen bonds are indicated by green dashed lines.

Piperazine-1,4-dium bis(2-carboxy-1*H*-pyrazole-4-carboxylate) tetrahydrate

Crystal data

$C_4H_{12}N_2 \cdot 2C_3H_3N_2O_4 \cdot 4H_2O$

$M_r = 470.41$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1/c$

$a = 8.3363 (13) \text{ \AA}$

$b = 16.246 (3) \text{ \AA}$

$c = 7.3930 (11) \text{ \AA}$

$\beta = 90.812 (3)^\circ$

$V = 1001.2 (3) \text{ \AA}^3$

$Z = 2$

$F(000) = 496$

$D_x = 1.560 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1373 reflections

$\theta = 2.7\text{--}24.0^\circ$

$\mu = 0.14 \text{ mm}^{-1}$

$T = 291$ K $0.15 \times 0.14 \times 0.12$ mm
 Block, white

Data collection

Bruker SMART APEX CCD diffractometer Radiation source: fine-focus sealed tube Graphite monochromator phi and ω scans Absorption correction: multi-scan (SADABS; Bruker, 2000) $T_{\min} = 0.980$, $T_{\max} = 0.984$	5265 measured reflections 1946 independent reflections 1524 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.051$ $\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 2.4^\circ$ $h = -10 \rightarrow 10$ $k = -13 \rightarrow 19$ $l = -8 \rightarrow 9$
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Refinement

Refinement on F^2 Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.059$ $wR(F^2) = 0.147$ $S = 1.10$ 1946 reflections 169 parameters 0 restraints Primary atom site location: structure-invariant direct methods	Secondary atom site location: difference Fourier map Hydrogen site location: inferred from neighbouring sites H atoms treated by a mixture of independent and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0729P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.41 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{\AA}^{-3}$
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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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	1.1506 (3)	0.78226 (15)	0.2962 (3)	0.0267 (6)
C2	0.9861 (3)	0.77149 (14)	0.2216 (3)	0.0233 (6)
C3	0.8727 (3)	0.82885 (15)	0.1741 (3)	0.0256 (6)
H3	0.8827	0.8858	0.1785	0.031*
C4	0.7391 (3)	0.78344 (14)	0.1178 (3)	0.0226 (5)
C5	0.5785 (3)	0.81182 (15)	0.0528 (3)	0.0246 (6)
C6	0.6653 (4)	0.51108 (17)	-0.0379 (5)	0.0455 (8)
H6A	0.7149	0.4999	0.0790	0.055*
H6B	0.7496	0.5242	-0.1223	0.055*
C7	0.4237 (3)	0.56416 (16)	0.1024 (4)	0.0380 (7)
H7A	0.3509	0.6107	0.1070	0.046*
H7B	0.4666	0.5548	0.2233	0.046*
N1	0.9196 (2)	0.69726 (13)	0.1933 (3)	0.0266 (5)

H1	0.962 (3)	0.6522 (18)	0.220 (4)	0.032*
N2	0.7696 (2)	0.70254 (12)	0.1296 (3)	0.0262 (5)
N3	0.5556 (3)	0.58226 (14)	-0.0224 (3)	0.0399 (7)
H3A	0.604 (4)	0.6268 (19)	0.020 (4)	0.048*
H3B	0.514 (4)	0.5944 (18)	-0.130 (4)	0.048*
O1	1.2097 (2)	0.85001 (11)	0.3144 (3)	0.0454 (6)
O2	1.2193 (2)	0.71272 (11)	0.3390 (3)	0.0360 (5)
H2	1.311 (4)	0.7215 (17)	0.394 (4)	0.043*
O3	0.5431 (2)	0.88609 (10)	0.0779 (3)	0.0360 (5)
O4	0.4901 (2)	0.75870 (11)	-0.0188 (3)	0.0358 (5)
O5	0.0107 (3)	0.53912 (14)	0.2765 (4)	0.0528 (7)
H5A	-0.077 (5)	0.510 (2)	0.316 (5)	0.063*
H5B	0.093 (5)	0.539 (2)	0.346 (5)	0.063*
O6	0.2621 (2)	0.51492 (13)	0.5325 (3)	0.0476 (6)
H6C	0.323 (4)	0.472 (2)	0.486 (5)	0.057*
H6D	0.320 (4)	0.549 (2)	0.556 (5)	0.057*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0215 (13)	0.0285 (14)	0.0299 (15)	0.0002 (11)	-0.0059 (11)	0.0006 (11)
C2	0.0199 (12)	0.0226 (13)	0.0272 (14)	-0.0006 (10)	-0.0039 (10)	0.0002 (10)
C3	0.0205 (13)	0.0193 (12)	0.0369 (15)	-0.0020 (9)	-0.0056 (10)	-0.0016 (10)
C4	0.0189 (12)	0.0203 (12)	0.0286 (14)	0.0011 (10)	-0.0045 (10)	-0.0004 (10)
C5	0.0159 (12)	0.0228 (13)	0.0351 (15)	-0.0025 (10)	-0.0040 (10)	0.0030 (11)
C6	0.0399 (17)	0.0443 (18)	0.052 (2)	-0.0078 (14)	0.0024 (14)	-0.0050 (15)
C7	0.0455 (17)	0.0286 (15)	0.0398 (17)	0.0027 (12)	-0.0021 (14)	-0.0035 (12)
N1	0.0191 (11)	0.0186 (11)	0.0417 (14)	0.0025 (9)	-0.0092 (9)	0.0022 (9)
N2	0.0169 (10)	0.0215 (11)	0.0398 (13)	-0.0001 (8)	-0.0103 (9)	0.0011 (9)
N3	0.0616 (17)	0.0210 (12)	0.0370 (15)	-0.0144 (11)	-0.0069 (12)	-0.0007 (10)
O1	0.0326 (11)	0.0284 (11)	0.0745 (16)	-0.0083 (8)	-0.0248 (10)	0.0010 (10)
O2	0.0195 (9)	0.0284 (10)	0.0597 (14)	-0.0004 (8)	-0.0183 (9)	0.0030 (9)
O3	0.0239 (10)	0.0218 (10)	0.0622 (14)	0.0044 (8)	-0.0093 (9)	-0.0002 (9)
O4	0.0221 (9)	0.0282 (10)	0.0566 (13)	-0.0002 (8)	-0.0167 (9)	-0.0048 (9)
O5	0.0395 (12)	0.0361 (12)	0.0826 (19)	0.0042 (10)	-0.0040 (12)	0.0144 (11)
O6	0.0345 (12)	0.0334 (12)	0.0748 (17)	-0.0035 (9)	-0.0015 (11)	-0.0107 (11)

Geometric parameters (Å, °)

C1—O1	1.213 (3)	C6—H6B	0.9700
C1—O2	1.304 (3)	C7—N3	1.476 (4)
C1—C2	1.481 (3)	C7—C6 ⁱ	1.504 (4)
C2—N1	1.342 (3)	C7—H7A	0.9700
C2—C3	1.369 (3)	C7—H7B	0.9700
C3—C4	1.395 (3)	N1—N2	1.333 (3)
C3—H3	0.9300	N1—H1	0.84 (3)
C4—N2	1.341 (3)	N3—H3A	0.88 (3)
C4—C5	1.489 (3)	N3—H3B	0.88 (3)

C5—O4	1.248 (3)	O2—H2	0.87 (3)
C5—O3	1.256 (3)	O5—H5A	0.92 (4)
C6—N3	1.480 (4)	O5—H5B	0.85 (4)
C6—C7 ⁱ	1.504 (4)	O6—H6C	0.93 (3)
C6—H6A	0.9700	O6—H6D	0.76 (3)
O1—C1—O2	125.7 (2)	H6A—C6—H6B	108.0
O1—C1—C2	121.4 (2)	N3—C7—C6 ⁱ	109.4 (2)
O2—C1—C2	112.9 (2)	N3—C7—H7A	109.8
N1—C2—C3	106.9 (2)	C6 ⁱ —C7—H7A	109.8
N1—C2—C1	122.8 (2)	N3—C7—H7B	109.8
C3—C2—C1	130.3 (2)	C6 ⁱ —C7—H7B	109.8
C2—C3—C4	105.2 (2)	H7A—C7—H7B	108.2
C2—C3—H3	127.4	N2—N1—C2	112.3 (2)
C4—C3—H3	127.4	N2—N1—H1	122.4 (18)
N2—C4—C3	110.4 (2)	C2—N1—H1	125.1 (19)
N2—C4—C5	119.6 (2)	N1—N2—C4	105.21 (19)
C3—C4—C5	130.0 (2)	C7—N3—C6	111.1 (2)
O4—C5—O3	126.1 (2)	C7—N3—H3A	106 (2)
O4—C5—C4	116.5 (2)	C6—N3—H3A	113 (2)
O3—C5—C4	117.5 (2)	C7—N3—H3B	108 (2)
N3—C6—C7 ⁱ	111.0 (2)	C6—N3—H3B	110 (2)
N3—C6—H6A	109.4	H3A—N3—H3B	108 (3)
C7 ⁱ —C6—H6A	109.4	C1—O2—H2	110.5 (18)
N3—C6—H6B	109.4	H5A—O5—H5B	117 (3)
C7 ⁱ —C6—H6B	109.4	H6C—O6—H6D	107 (3)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O5 ⁱⁱ	0.84 (3)	1.93 (3)	2.746 (3)	167 (3)
O2—H2 \cdots O4 ⁱⁱⁱ	0.87 (3)	1.65 (3)	2.520 (2)	175 (3)
N3—H3A \cdots O4	0.88 (3)	2.36 (3)	2.918 (3)	121 (2)
N3—H3A \cdots N2	0.88 (3)	2.01 (3)	2.865 (3)	162 (3)
N3—H3B \cdots O3 ^{iv}	0.88 (3)	2.20 (3)	2.999 (3)	150 (3)
O5—H5B \cdots O6	0.85 (4)	2.00 (4)	2.831 (3)	166 (3)
O5—H5A \cdots O6 ^v	0.92 (4)	1.96 (4)	2.833 (3)	157 (3)
O6—H6C \cdots O3 ^{vi}	0.93 (3)	1.85 (3)	2.779 (3)	173 (3)
O6—H6D \cdots O3 ^{vii}	0.76 (3)	2.14 (3)	2.858 (3)	158 (4)
C6—H6B \cdots O5 ⁱ	0.97	2.53	3.348 (4)	142
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