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Diaqua[*N*-(5-nitro-2-oxidobenzylidene)-glycinato]copper(II) dihydrate

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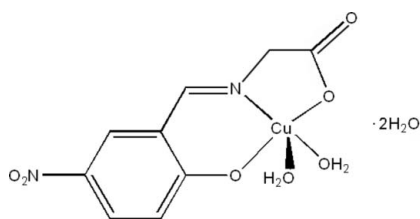
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.045; wR factor = 0.074; data-to-parameter ratio = 11.1.

In the title complex, $[\text{Cu}(\text{C}_9\text{H}_6\text{N}_2\text{O}_5)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, the Cu^{II} atom has a square-pyramidal coordination environment with a tridentate *N*-(5-nitro-2-oxidobenzylidene)glycinate Schiff base ligand and a water molecule in the basal plane. The apical site is occupied by an O atom from another coordinated water molecule. The crystal structure is stabilized by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, building a two-dimensional network parallel to (100).

Related literature

For general background to metabolic reactions requiring pyridoxal-5'-phosphate as a cofactor, see: Bkouche-Waksman *et al.* (1988); Wetmore *et al.* (2001); Zabinski & Toney (2001). For related Schiff base complexes, see: Ganguly *et al.* (2008); Jammi *et al.* (2008). For a related structure, see: Ueki *et al.* (1967).



Experimental

Crystal data

$[\text{Cu}(\text{C}_9\text{H}_6\text{N}_2\text{O}_5)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$
 $M_r = 357.76$
 Monoclinic, $P2_1/c$
 $a = 17.306$ (4) Å
 $b = 10.837$ (2) Å
 $c = 7.185$ (2) Å
 $\beta = 91.63$ (1)°

$V = 1347.0$ (5) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.67$ mm⁻¹
 $T = 293$ K
 $0.25 \times 0.20 \times 0.15$ mm

Data collection

Bruker SMART 1000 CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.68$, $T_{\text{max}} = 0.78$

6554 measured reflections
 2369 independent reflections
 1107 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.122$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.074$
 $S = 0.62$
 2369 reflections
 214 parameters
 8 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.53$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.41$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O6}-\text{H6A} \cdots \text{O7}$	0.80 (4)	1.90 (4)	2.666 (5)	162 (5)
$\text{O6}-\text{H6B} \cdots \text{O9}^{\text{i}}$	0.80 (3)	1.96 (3)	2.726 (5)	162 (5)
$\text{O7}-\text{H7A} \cdots \text{O3}^{\text{ii}}$	0.85 (3)	1.90 (3)	2.749 (4)	178 (4)
$\text{O7}-\text{H7B} \cdots \text{O9}^{\text{iii}}$	0.85 (3)	2.03 (4)	2.814 (5)	154 (4)
$\text{O8}-\text{H8D} \cdots \text{O1}^{\text{iv}}$	0.82 (3)	2.05 (3)	2.860 (4)	167 (5)
$\text{O8}-\text{H8E} \cdots \text{O7}$	0.85 (4)	1.96 (4)	2.792 (5)	166 (4)
$\text{O9}-\text{H9B} \cdots \text{O8}^{\text{v}}$	0.84 (3)	2.04 (2)	2.827 (5)	156 (5)
$\text{O9}-\text{H9D} \cdots \text{O2}^{\text{iv}}$	0.78 (3)	1.99 (3)	2.764 (5)	173 (5)

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

Data collection: SMART (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and DIAMOND (Brandenburg, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2290).

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supporting information

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Diaqua[*N*-(5-nitro-2-oxidobenzylidene)glycinato]copper(II) dihydrate

Yang Zou, Yin-Zhi Jiang and Wei-Zu Wang

S1. Comment

Metal Schiff-base complexes derived from amino acids (or peptides) play an important role as key compounds for modeling more complicated PLP-amino acid Schiff bases (PLP = pyridoxal-5'-phosphate), as these are key intermediates in a variety of metabolic reactions involving amino acids, such as decarboxylation, transamination, racemization and C—C bond cleavage, which are catalyzed by enzymes that require PLP as a cofactor (Bkouche-Waksman *et al.*, 1988; Wetmore *et al.*, 2001; Zabinski & Toney, 2001). Considerable effort has been devoted to the preparation, structural characterization, appropriate spectroscopy and magnetic studies of Schiff-base complexes derived from salicylaldehyde and amino acids and reduced salicylidene amino acid (Ganguly *et al.*, 2008), but little attention has been given to Schiff bases derived from nitro-substituted salicylaldehyde, and few structurally characterized complexes have been reported (Jammi *et al.*, 2008). Herein, we report the synthesis and structural study of a copper(II) complex with the Schiff base derived from glycine and 5-nitrosalicylaldehyde.

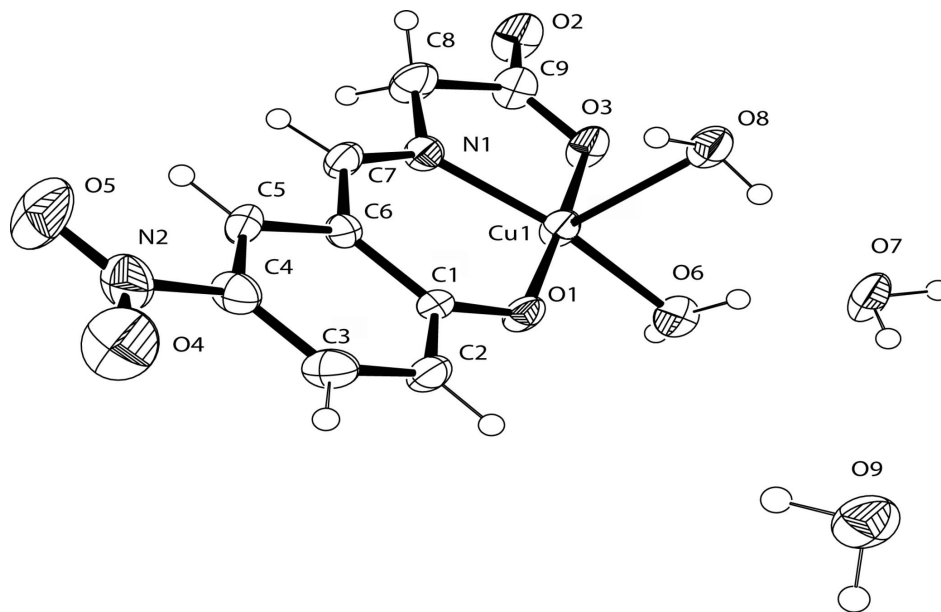
The title complex is characterized by a square-pyramidal Cu^{II} coordination with a deprotonated tridentate Schiff base, 5-nitrosalicylidene-glycinato, and a water molecule in the basal plane (Fig. 1). The Cu—N bond distance is 1.897 (4) Å. The two Cu—O bonds are 1.916 (3) and 1.930 (3) Å. The apical Cu1—O8 bond length is 2.447 (4) Å, which is little longer than that in the parent compound of this structure type, aqua(*N*-salicylidene-glycinato)copper(II) hemihydrate [2.334 (6) Å] (Ueki *et al.*, 1967). The phenyl ring (C1—C6) and the C1, C6, C7, N1, O1, Cu1 chelating ring are almost coplanar, with a small dihedral angle of 4.3 (4)°. Hydrogen bonds between the coordinated water molecules and the phenol O atoms of symmetry-related complex molecules lead to the formation of zigzag chains along the *c* axis (Table 1). Hydrogen bonds between the uncoordinated water molecules and carbonylate O atoms link the chains into a two-dimensional layer (Fig. 2).

S2. Experimental

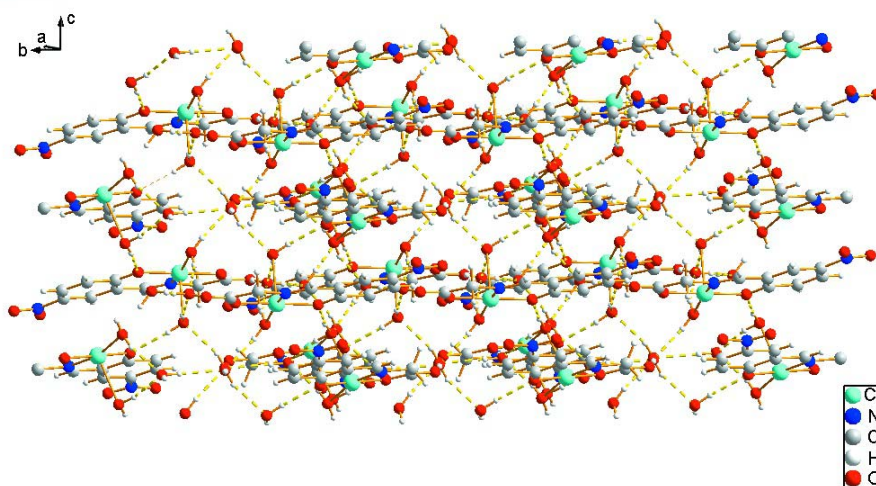
The title compound was prepared as follows: Glycine (10 mmol), 5-nitrosalicylaldehyde (10 mmol) and LiOH (20 mmol) were dissolved and refluxed in MeOH/H₂O (v/v 1:1). CuCl₂·2H₂O (10 mmol) was then added to the solution and the resulting solution was adjusted to pH = 9–11. The mixture was stirred at room temperature for 24 h. Violet-blue precipitate that formed was filtered. The filtrate was allowed to evaporate slowly at room temperature. After several days, blue crystals suitable for X-ray diffraction were obtained.

S3. Refinement

H atoms of water molecules were located in a difference Fourier map and refined with distance restraints of O—H = 0.85 (1) Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. Other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 (CH) and 0.97 (CH₂) Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.


Figure 1

Molecular structure of the title complex. Displacement ellipsoids are drawn at the 40% probability level.


Figure 2

A view of the hydrogen-bonded (dashed lines) two-dimensional network.

Diaqua[*N*-(5-nitro-2-oxidobenzylidene)glycinato]copper(II) dihydrate

Crystal data

$[\text{Cu}(\text{C}_9\text{H}_6\text{N}_2\text{O}_5)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

$M_r = 357.76$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1ybc$

$a = 17.306\ (4)\ \text{\AA}$

$b = 10.837\ (2)\ \text{\AA}$

$c = 7.185\ (2)\ \text{\AA}$

$\beta = 91.63\ (1)^\circ$

$V = 1347.0\ (5)\ \text{\AA}^3$

$Z = 4$

$F(000) = 732$

$D_x = 1.764\ \text{Mg m}^{-3}$

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

Cell parameters from 1107 reflections

$\theta = 2.2\text{--}25.0^\circ$
 $\mu = 1.67\text{ mm}^{-1}$
 $T = 293\text{ K}$

Block, blue
 $0.25 \times 0.2 \times 0.15\text{ mm}$

Data collection

Bruker SMART 1000 CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.68, T_{\max} = 0.78$

6554 measured reflections
 2369 independent reflections
 1107 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.122$
 $\theta_{\max} = 25.0^\circ, \theta_{\min} = 2.2^\circ$
 $h = -20 \rightarrow 20$
 $k = -8 \rightarrow 12$
 $l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.074$
 $S = 0.62$
 2369 reflections
 214 parameters
 8 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
 $w = 1/[\sigma^2(F_o^2)]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.53\text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.41\text{ e \AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.68418 (3)	0.93382 (5)	1.05603 (9)	0.0332 (2)
N1	0.7825 (2)	0.9810 (4)	0.9699 (6)	0.0313 (11)
N2	0.9642 (3)	0.5241 (5)	0.7898 (7)	0.0533 (15)
C1	0.7707 (3)	0.7116 (5)	1.0012 (7)	0.0262 (13)
C2	0.7740 (3)	0.5812 (4)	0.9948 (7)	0.0342 (14)
H2	0.7324	0.5352	1.0357	0.041*
C3	0.8371 (3)	0.5222 (5)	0.9296 (7)	0.0384 (15)
H3	0.8381	0.4364	0.9284	0.046*
C4	0.8991 (3)	0.5861 (5)	0.8659 (7)	0.0362 (14)
C5	0.8984 (3)	0.7134 (5)	0.8696 (7)	0.0326 (14)
H5	0.9409	0.7572	0.8285	0.039*
C6	0.8343 (2)	0.7767 (4)	0.9347 (7)	0.0241 (12)
C7	0.8375 (2)	0.9109 (4)	0.9286 (6)	0.0319 (14)
H7	0.8832	0.9473	0.8917	0.038*
C8	0.7918 (3)	1.1165 (4)	0.9543 (8)	0.0452 (16)
H8A	0.8051	1.1380	0.8281	0.054*
H8B	0.8334	1.1440	1.0377	0.054*
C9	0.7174 (3)	1.1797 (5)	1.0040 (8)	0.0404 (15)
O1	0.70921 (17)	0.7616 (3)	1.0634 (5)	0.0314 (9)
O2	0.71569 (18)	1.2917 (3)	0.9976 (5)	0.0533 (12)
O3	0.66318 (17)	1.1087 (3)	1.0507 (5)	0.0405 (10)

O4	0.9629 (2)	0.4122 (3)	0.7780 (6)	0.0807 (16)
O5	1.0193 (2)	0.5843 (4)	0.7388 (6)	0.0828 (16)
O6	0.59324 (19)	0.9035 (4)	1.2066 (5)	0.0389 (10)
H6A	0.559 (3)	0.890 (5)	1.134 (5)	0.053*
H6B	0.583 (3)	0.942 (4)	1.297 (5)	0.047*
O7	0.48642 (17)	0.8064 (3)	0.9756 (6)	0.0466 (11)
H7A	0.4407 (11)	0.834 (3)	0.966 (7)	0.053*
H7B	0.481 (2)	0.729 (3)	0.982 (7)	0.053*
O8	0.6090 (2)	0.8942 (3)	0.7687 (6)	0.0403 (10)
H8E	0.5724 (19)	0.857 (3)	0.821 (6)	0.053*
H8D	0.631 (2)	0.844 (4)	0.703 (6)	0.048*
O9	0.58080 (19)	0.0716 (3)	0.4864 (5)	0.0438 (10)
H9D	0.621 (2)	0.105 (4)	0.486 (7)	0.053*
H9B	0.576 (2)	0.026 (4)	0.580 (4)	0.053*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0270 (3)	0.0226 (3)	0.0505 (4)	0.0012 (3)	0.0084 (3)	0.0002 (4)
N1	0.028 (2)	0.023 (3)	0.044 (3)	0.006 (2)	0.005 (2)	0.004 (2)
N2	0.039 (3)	0.058 (4)	0.064 (4)	0.024 (3)	0.009 (3)	0.000 (3)
C1	0.022 (3)	0.029 (3)	0.028 (3)	-0.001 (3)	0.003 (3)	0.006 (3)
C2	0.027 (3)	0.027 (3)	0.049 (4)	-0.001 (3)	0.011 (3)	0.007 (3)
C3	0.045 (4)	0.035 (3)	0.036 (4)	0.004 (3)	0.008 (3)	0.003 (3)
C4	0.038 (3)	0.033 (4)	0.038 (4)	0.015 (3)	0.005 (3)	0.000 (3)
C5	0.021 (3)	0.038 (4)	0.039 (4)	-0.004 (3)	0.004 (3)	0.001 (3)
C6	0.023 (3)	0.022 (3)	0.027 (3)	0.001 (2)	0.000 (3)	-0.002 (3)
C7	0.025 (3)	0.029 (3)	0.041 (4)	-0.005 (3)	0.005 (3)	0.001 (3)
C8	0.043 (4)	0.026 (3)	0.067 (5)	-0.003 (3)	0.011 (3)	0.005 (3)
C9	0.038 (4)	0.033 (4)	0.051 (4)	0.000 (3)	0.005 (3)	-0.010 (3)
O1	0.026 (2)	0.020 (2)	0.048 (3)	-0.0014 (15)	0.0092 (19)	0.0026 (17)
O2	0.049 (3)	0.016 (2)	0.096 (3)	-0.0022 (19)	0.011 (2)	-0.005 (2)
O3	0.031 (2)	0.018 (2)	0.073 (3)	-0.0009 (16)	0.010 (2)	-0.0023 (19)
O4	0.077 (3)	0.037 (3)	0.130 (4)	0.025 (2)	0.026 (3)	-0.013 (3)
O5	0.048 (3)	0.068 (3)	0.135 (4)	0.022 (3)	0.047 (3)	-0.003 (3)
O6	0.037 (2)	0.036 (3)	0.044 (3)	0.0001 (19)	0.007 (2)	-0.008 (2)
O7	0.027 (2)	0.035 (2)	0.079 (3)	-0.0045 (19)	0.008 (2)	-0.001 (2)
O8	0.039 (2)	0.029 (2)	0.053 (3)	0.0002 (17)	0.008 (2)	0.000 (2)
O9	0.045 (2)	0.032 (2)	0.056 (3)	-0.004 (2)	0.010 (2)	0.001 (2)

Geometric parameters (Å, °)

Cu1—N1	1.897 (4)	C5—C6	1.396 (6)
Cu1—O1	1.916 (3)	C5—H5	0.9300
Cu1—O3	1.930 (3)	C6—C7	1.456 (6)
Cu1—O6	1.963 (4)	C7—H7	0.9300
Cu1—O8	2.447 (4)	C8—C9	1.511 (6)
N1—C7	1.260 (5)	C8—H8A	0.9700

N1—C8	1.481 (5)	C8—H8B	0.9700
N2—O4	1.215 (5)	C9—O2	1.215 (5)
N2—O5	1.221 (5)	C9—O3	1.266 (5)
N2—C4	1.433 (6)	O6—H6B	0.80 (3)
C1—O1	1.286 (5)	O6—H6A	0.80 (4)
C1—C6	1.404 (6)	O7—H7A	0.85 (3)
C1—C2	1.415 (6)	O7—H7B	0.85 (3)
C2—C3	1.360 (6)	O8—H8D	0.82 (3)
C2—H2	0.9300	O8—H8E	0.85 (4)
C3—C4	1.367 (6)	O9—H9D	0.78 (3)
C3—H3	0.9300	O9—H9B	0.84 (3)
C4—C5	1.380 (6)		
N1—Cu1—O1	93.87 (15)	C5—C4—N2	118.9 (5)
N1—Cu1—O3	84.20 (15)	C4—C5—C6	120.3 (5)
O1—Cu1—O3	177.76 (14)	C4—C5—H5	119.8
N1—Cu1—O6	164.91 (16)	C6—C5—H5	119.8
O1—Cu1—O6	90.32 (15)	C5—C6—C1	120.4 (5)
O3—Cu1—O6	91.26 (15)	C5—C6—C7	116.8 (4)
N1—Cu1—O8	103.44 (14)	C1—C6—C7	122.9 (4)
O1—Cu1—O8	88.09 (13)	N1—C7—C6	124.5 (4)
O3—Cu1—O8	93.45 (13)	N1—C7—H7	117.7
O6—Cu1—O8	91.16 (14)	C6—C7—H7	117.7
C7—N1—C8	119.7 (4)	N1—C8—C9	109.6 (4)
C7—N1—Cu1	127.2 (3)	N1—C8—H8A	109.7
C8—N1—Cu1	113.1 (3)	C9—C8—H8A	109.7
O4—N2—O5	121.6 (5)	N1—C8—H8B	109.7
O4—N2—C4	118.8 (5)	C9—C8—H8B	109.7
O5—N2—C4	119.5 (5)	H8A—C8—H8B	108.2
O1—C1—C6	124.8 (5)	O2—C9—O3	126.9 (5)
O1—C1—C2	117.9 (4)	O2—C9—C8	117.6 (5)
C6—C1—C2	117.3 (5)	O3—C9—C8	115.5 (5)
C3—C2—C1	120.9 (5)	C1—O1—Cu1	126.1 (3)
C3—C2—H2	119.5	C9—O3—Cu1	117.5 (3)
C1—C2—H2	119.5	Cu1—O6—H6B	125 (4)
C2—C3—C4	121.5 (5)	Cu1—O6—H6A	106 (3)
C2—C3—H3	119.2	H6B—O6—H6A	116 (4)
C4—C3—H3	119.2	H7A—O7—H7B	105 (3)
C3—C4—C5	119.5 (5)	H8D—O8—H8E	108 (3)
C3—C4—N2	121.5 (5)	H9D—O9—H9B	112 (4)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6—H6A \cdots O7	0.80 (4)	1.90 (4)	2.666 (5)	162 (5)
O6—H6B \cdots O9 ⁱ	0.80 (3)	1.96 (3)	2.726 (5)	162 (5)
O7—H7A \cdots O3 ⁱⁱ	0.85 (3)	1.90 (3)	2.749 (4)	178 (4)
O7—H7B \cdots O9 ⁱⁱⁱ	0.85 (3)	2.03 (4)	2.814 (5)	154 (4)

O8—H8D···O1 ^{iv}	0.82 (3)	2.05 (3)	2.860 (4)	167 (5)
O8—H8E···O7	0.85 (4)	1.96 (4)	2.792 (5)	166 (4)
O9—H9B···O8 ^v	0.84 (3)	2.04 (2)	2.827 (5)	156 (5)
O9—H9D···O2 ^{iv}	0.78 (3)	1.99 (3)	2.764 (5)	173 (5)

Symmetry codes: (i) $x, y+1, z+1$; (ii) $-x+1, -y+2, -z+2$; (iii) $-x+1, y+1/2, -z+3/2$; (iv) $x, -y+3/2, z-1/2$; (v) $x, y-1, z$.