metal-organic compounds

Tetraaqua(pyridine-2,5-dicarboxylato-κ^2N,O^2)nickel(II) monohydrate

Hossein Aghabozorg,[a]* Zohreh Derikvand,[a] Andya Nemati[a] and Mohammad Ghadermazi[b]

[a]Faculty of Chemistry, Teacher Training University, 49 Mofateh Avenue, 15614 Tehran, Iran, and [b]Department of Chemistry, University of Kurdistan, Sanandaj, Iran
Correspondence e-mail: haghabozorg@yahoo.com

The title compound, $[\mathrm{Ni(C_7H_3NO_4)(H_2O)_4}]\cdot\mathrm{H_2O}$, synthesized by reaction of nickel(II) nitrate hexahydrate with pyridine-2,5-dicarboxylic acid and piperazine in water. It has essentially the same structure with the analogous nickel(II) dihydrate complex [Shiu, Chen, Liao & Wang (2003). *Acta Cryst*. E**59**, m1072–m1074]. The compound contains a six-coordinate $\mathrm{Ni^{II}}$ ion, which is bonded to the N and an O atom of the carboxylate group in the 2-position of the pyridine-2,5-dicarboxylate ligand, and four water O atoms. The $\mathrm{Ni^{II}}$ atom has a distorted octahedral coordination environment. Intermolecular hydrogen-bonding interactions are present, linking the nickel(II) complex and water molecules in the crystal structure.

Related literature

For related literature, see: Aghabozorg, Ghadermazi & Attar Gharamaleki (2006); Aghabozorg, Ghasemikhah *et al*. (2006); Aghabozorg, Nakhjavan *et al*. (2006); Aghabozorg, Attar Gharamaleki *et al* (2007); Aghabozorg, Ghadermazi *et al* (2007); Aghabozorg, Ghasemikhah *et al* (2007); Sheshmani *et al*. (2007).
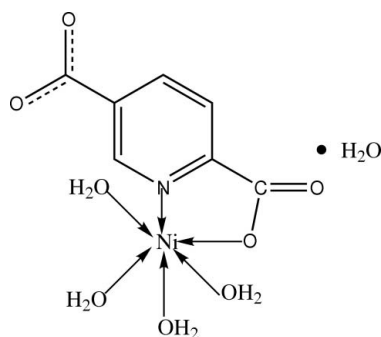
Experimental

Crystal data

$[\mathrm{Ni(C_7H_3NO_4)(H_2O)_4}]\cdot\mathrm{H_2O}$	$\gamma = 67.6991\,(8)^\circ$
$M_r = 313.89$	$V = 553.81\,(4)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 6.6633\,(3)$ Å	Mo $K\alpha$ radiation
$b = 8.3996\,(3)$ Å	$\mu = 1.80$ mm^{-1}
$c = 10.7882\,(4)$ Å	$T = 100\,(2)$ K
$\alpha = 84.7541\,(9)^\circ$	$0.25 \times 0.20 \times 0.10$ mm
$\beta = 83.3010\,(8)^\circ$	

Data collection

Bruker APEX2 CCD area-detector diffractometer	9105 measured reflections
Absorption correction: multi-scan (*APEX2*; Bruker, 2005)	2950 independent reflections
	2710 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.662$, $T_{\max} = 0.841$	$R_{\mathrm{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	163 parameters
$wR(F^2) = 0.067$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\max} = 0.58$ e Å^{-3}
2950 reflections	$\Delta\rho_{\min} = -0.48$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1WB$\cdots$O3$^{\mathrm{i}}$	0.85	1.87	2.7235 (15)	179
O1W—H1WA$\cdots$O3W$^{\mathrm{ii}}$	0.85	1.98	2.8233 (15)	175
O2W—H2WA$\cdots$O2$^{\mathrm{iii}}$	0.85	1.90	2.7484 (16)	173
O2W—H2WB$\cdots$O4$^{\mathrm{iv}}$	0.85	1.82	2.6658 (17)	170
O3W—H3WA$\cdots$O2$^{\mathrm{v}}$	0.85	1.86	2.7005 (16)	169
O3W—H3WB$\cdots$O5W$^{\mathrm{vi}}$	0.85	1.96	2.7909 (17)	164
O4W—H4WA$\cdots$O1$^{\mathrm{vii}}$	0.85	1.89	2.7366 (16)	174
O4W—H4WB$\cdots$O3$^{\mathrm{viii}}$	0.85	1.86	2.6732 (15)	161
O5W—H5WB$\cdots$O2W	0.85	2.23	3.0541 (19)	164
O5W—H5WA$\cdots$O4$^{\mathrm{ix}}$	0.85	1.98	2.7619 (18)	152
C3—H3A$\cdots$O5W$^{\mathrm{x}}$	0.95	2.44	3.3182 (19)	154

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Aghabozorg, H., Attar Gharamaleki, J., Ghasemikhah, P., Ghadermazi, M. & Soleimannejad, J. (2007). *Acta Cryst.* E**63**, m1710–m1711.
Aghabozorg, H., Ghadermazi, M. & Attar Gharamaleki, J. (2006). *Acta Cryst.* E**62**, o3174–o3176.
Aghabozorg, H., Ghadermazi, M., Soleimannejad, J. & Sheshmani, S. (2007). *Acta Cryst.* E**63**, m1917–m1918.
Aghabozorg, H., Ghasemikhah, P., Ghadermazi, M. & Sheshmani, S. (2006). *Acta Cryst.* E**62**, m2835–m2837.
Aghabozorg, H., Ghasemikhah, P., Ghadermazi, M., Soleimannejad, J. & Adams, H. (2007). *Acta Cryst.* E**63**, m1487–m1489.

metal-organic compounds

Aghabozorg, H., Nakhjavan, B., Ghadermazi, M. & Ramezanipour, F. (2006). *Acta Cryst.*, **E62,** m1527-m1529.

Bruker (2005). *APEX2*. Bruker AXS Inc., Madison, WI 5317.

Sheldrick, G. M. (1998). *SHELXTL*. Version 5.10. Bruker AXS, Madison, Wisconsin, USA.

Sheshmani, S., Aghabozorg, H. & Ghadermazi, M. (2007). *Acta Cryst.* E**63**, o2869.

Shiu, K.-B., Chen, Z.-W., Liao, F.-L. & Wang, S.-L. (2003). *Acta Cryst.* E**59**, m1072–m1074.

supplementary materials

Tetraaqua(pyridine-2,5-dicarboxylato-$\kappa^2 N,O^2$)nickel(II) monohydrate

H. Aghabozorg, Z. Derikvand, A. Nemati and M. Ghadermazi

Comment

The data collection temperature in our work was 100 (2) K, whereas, the previous work was conducted at the room temperature.

The N1 and O1 atoms of the (py-2,5-dc)$^{2-}$ group, O1W and O2W occupy the equatorial positions, while O3W and O4W atoms accupy axial positions. The O3W—Ni1—O4W, O1—Ni1—O2W and N1- Ni1—O1W angles which equal to 174.15 (4)°, 172.73 (4)° and 171.48 (5)°, respectively, deviate from linearity. Bond distances and bond angles show the coordination around Ni^{II} is distorted octahedral. There are a large number of O—H···O and C—H···O hydrogen bonds with distances ranging from 2.6658 (17) Å to 2.8233 (15) Å between [Ni(py-2,5-dc)(H$_2$O)$_4$] and water molecules Considerable π–π staking 3.76 Å (1 − x, 2 − y, 2 − z) and C—H···π 3.247 Å interactions between two aromatic rings of py-2,5-dc are observed. Hydrogen bonds and π–π stacking and van der Waals forces result in the formation of a supramolecular structure.

Experimental

The proton transfer compound [(pipzH$_2$)(py-2,5-dc)]·2H$_2$O, was prepared by the reaction of pyridine-2,5-dicarboxylic acid, py-2,5-dcH$_2$, with piperazine, (pipz). The reaction between Ni(NO$_3$)$_2$·6H$_2$O (145 mg, 0.5 mmol) in water (25 ml) and the proton transfer compound, (pipzH$_2$)(py-2,5-dc) (253 mg, 1.0 mmol) in water (25 ml), in a 1:2 molar ratio was carried by the slow evaporation of the solvent at room temperature.

Refinement

The hydrogen atoms of OH2 molecules were found in difference Fourier synthesis. The H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model with the U_{iso}(H) parameters equal to 1.2 U_{eq}(Ci), where U(Ci) the equivalent thermal parameters of the carbon atoms to which corresponding H atoms are bonded.

Figures
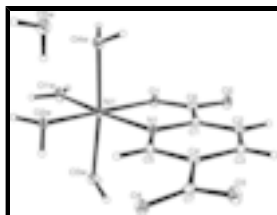
The structure of (**I**), showing the atom-numbering scheme and displacement. Ellipsoids are at the 50% probability level.
Unit cell packing of the title compound, (**I**). Hydrogen bonds are shown as dashed lines.

supplementary materials

Tetraaqua(pyridine-2,5-dicarboxylato-$\kappa^2 N,O^2$)nickel(II) monohydrate

Crystal data

[Ni($C_7H_3NO_4$)(H_2O)$_4$]·H_2O	$Z = 2$
$M_r = 313.89$	$F_{000} = 324$
Triclinic, $P\overline{1}$	$D_x = 1.882$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 6.6633$ (3) Å	Cell parameters from 5275 reflections
$b = 8.3996$ (3) Å	$\theta = 2.6–34.8º$
$c = 10.7882$ (4) Å	$\mu = 1.80$ mm^{-1}
$\alpha = 84.7541$ (9)º	$T = 100$ (2) K
$\beta = 83.0010$ (8)º	Prism, blue
$\gamma = 67.6991$ (8)º	0.25 × 0.20 × 0.10 mm
$V = 553.81$ (4) Å^3	

Data collection

Bruker APEX2 CCD area-detector diffractometer	2950 independent reflections
Radiation source: fine-focus sealed tube	2710 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.024$
$T = 100(2)$ K	$\theta_{max} = 29.0º$
φ and ω scans	$\theta_{min} = 1.9º$
Absorption correction: multi-scan (APEX2; Bruker, 2005)	$h = -9 \rightarrow 9$
$T_{min} = 0.662$, $T_{max} = 0.841$	$k = -11 \rightarrow 11$
9105 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.024$	H-atom parameters constrained
$wR(F^2) = 0.067$	$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.1995P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
2950 reflections	$\Delta\rho_{max} = 0.58$ e Å^{-3}
163 parameters	$\Delta\rho_{min} = -0.48$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.77628 (3)	0.75902 (2)	0.630569 (16)	0.00700 (7)
O1W	0.77995 (19)	0.68571 (14)	0.45564 (10)	0.0126 (2)
H1WB	0.7787	0.7443	0.3870	0.015*
H1WA	0.8033	0.5842	0.4356	0.015*
O2W	0.78206 (18)	0.52659 (13)	0.72019 (10)	0.0098 (2)
H2WA	0.7725	0.4447	0.6835	0.012*
H2WB	0.8982	0.4780	0.7563	0.012*
O3W	1.11699 (17)	0.65681 (13)	0.60822 (10)	0.0103 (2)
H3WA	1.1717	0.6918	0.5411	0.012*
H3WB	1.1825	0.6608	0.6700	0.012*
O4W	0.44345 (18)	0.83688 (14)	0.64479 (10)	0.0105 (2)
H4WA	0.3886	0.8822	0.5770	0.013*
H4WB	0.3777	0.9136	0.6975	0.013*
O1	0.75524 (18)	1.00066 (13)	0.56414 (10)	0.0098 (2)
O2	0.73095 (19)	1.25596 (13)	0.62085 (10)	0.0117 (2)
N1	0.7735 (2)	0.86760 (16)	0.79577 (11)	0.0081 (2)
O3	0.78193 (19)	0.87359 (14)	1.23625 (10)	0.0132 (2)
O4	0.88292 (18)	0.62574 (14)	1.14249 (10)	0.0116 (2)
C1	0.7470 (2)	1.03522 (18)	0.77991 (13)	0.0082 (3)
C2	0.7297 (2)	1.13475 (18)	0.87916 (13)	0.0088 (3)
H2A	0.7081	1.2532	0.8654	0.011*
C3	0.7443 (2)	1.05790 (19)	0.99975 (14)	0.0092 (3)
H3A	0.7299	1.1236	1.0698	0.011*
C4	0.7805 (2)	0.88336 (18)	1.01541 (13)	0.0075 (3)
C5	0.7925 (2)	0.79291 (18)	0.91115 (13)	0.0082 (3)
H5A	0.8149	0.6741	0.9222	0.010*
C6	0.7433 (2)	1.10494 (19)	0.64500 (14)	0.0089 (3)
C7	0.8158 (2)	0.78780 (19)	1.14149 (13)	0.0086 (3)
O5W	0.3102 (2)	0.61554 (15)	0.83049 (11)	0.0174 (2)
H5WB	0.4476	0.5843	0.8153	0.021*
H5WA	0.2859	0.5247	0.8543	0.021*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.00988 (11)	0.00577 (10)	0.00542 (10)	−0.00289 (7)	−0.00096 (7)	−0.00040 (6)
O1W	0.0224 (6)	0.0090 (5)	0.0065 (5)	−0.0058 (4)	−0.0019 (4)	−0.0007 (4)
O2W	0.0135 (5)	0.0069 (5)	0.0098 (5)	−0.0041 (4)	−0.0031 (4)	0.0007 (4)
O3W	0.0119 (5)	0.0114 (5)	0.0081 (5)	−0.0052 (4)	−0.0008 (4)	0.0004 (4)
O4W	0.0117 (5)	0.0104 (5)	0.0083 (5)	−0.0026 (4)	−0.0014 (4)	−0.0012 (4)
O1	0.0151 (5)	0.0085 (5)	0.0069 (5)	−0.0054 (4)	−0.0020 (4)	−0.0006 (4)
O2	0.0186 (6)	0.0090 (5)	0.0089 (5)	−0.0068 (4)	−0.0019 (4)	0.0004 (4)
N1	0.0095 (6)	0.0078 (5)	0.0074 (5)	−0.0036 (5)	−0.0007 (4)	−0.0006 (4)
O3	0.0201 (6)	0.0107 (5)	0.0067 (5)	−0.0031 (4)	−0.0015 (4)	−0.0014 (4)
O4	0.0161 (5)	0.0086 (5)	0.0104 (5)	−0.0045 (4)	−0.0034 (4)	0.0012 (4)
C1	0.0085 (6)	0.0088 (6)	0.0074 (6)	−0.0035 (5)	−0.0013 (5)	0.0010 (5)
C2	0.0096 (7)	0.0072 (6)	0.0096 (6)	−0.0030 (5)	−0.0014 (5)	−0.0004 (5)
C3	0.0089 (6)	0.0108 (7)	0.0084 (6)	−0.0040 (5)	−0.0006 (5)	−0.0020 (5)
C4	0.0062 (6)	0.0091 (6)	0.0064 (6)	−0.0018 (5)	−0.0006 (5)	0.0000 (5)
C5	0.0093 (6)	0.0076 (6)	0.0076 (6)	−0.0031 (5)	−0.0011 (5)	0.0001 (5)
C6	0.0092 (7)	0.0094 (6)	0.0081 (6)	−0.0035 (5)	−0.0018 (5)	0.0012 (5)
C7	0.0070 (6)	0.0106 (6)	0.0080 (6)	−0.0034 (5)	−0.0003 (5)	0.0002 (5)
O5W	0.0168 (6)	0.0141 (5)	0.0223 (6)	−0.0078 (5)	0.0001 (5)	−0.0007 (5)

Geometric parameters (Å, °)

Ni1—O1W	2.0325 (11)	N1—C5	1.3395 (18)
Ni1—O1	2.0483 (10)	N1—C1	1.3481 (18)
Ni1—O4W	2.0505 (11)	O3—C7	1.2532 (18)
Ni1—N1	2.0700 (12)	O4—C7	1.2608 (18)
Ni1—O2W	2.0867 (10)	C1—C2	1.385 (2)
Ni1—O3W	2.0915 (11)	C1—C6	1.518 (2)
O1W—H1WB	0.8501	C2—C3	1.396 (2)
O1W—H1WA	0.8500	C2—H2A	0.9500
O2W—H2WA	0.8500	C3—C4	1.390 (2)
O2W—H2WB	0.8500	C3—H3A	0.9500
O3W—H3WA	0.8500	C4—C5	1.3917 (19)
O3W—H3WB	0.8500	C4—C7	1.5116 (19)
O4W—H4WA	0.8500	C5—H5A	0.9500
O4W—H4WB	0.8500	O5W—H5WB	0.8500
O1—C6	1.2668 (18)	O5W—H5WA	0.8501
O2—C6	1.2446 (18)		
O1W—Ni1—O1	91.77 (4)	C6—O1—Ni1	116.37 (9)
O1W—Ni1—O4W	87.70 (4)	C5—N1—C1	118.74 (12)
O1—Ni1—O4W	90.52 (4)	C5—N1—Ni1	128.30 (10)
O1W—Ni1—N1	171.48 (5)	C1—N1—Ni1	112.96 (9)
O1—Ni1—N1	79.73 (4)	N1—C1—C2	122.40 (13)
O4W—Ni1—N1	93.03 (5)	N1—C1—C6	114.88 (12)
O1W—Ni1—O2W	95.03 (4)	C2—C1—C6	122.70 (13)

O1—Ni1—O2W	172.73 (4)	C1—C2—C3	118.82 (13)
O4W—Ni1—O2W	87.21 (4)	C1—C2—H2A	120.6
N1—Ni1—O2W	93.48 (4)	C3—C2—H2A	120.6
O1W—Ni1—O3W	88.12 (4)	C4—C3—C2	118.71 (13)
O1—Ni1—O3W	93.70 (4)	C4—C3—H3A	120.6
O4W—Ni1—O3W	174.15 (4)	C2—C3—H3A	120.6
N1—Ni1—O3W	91.71 (5)	C3—C4—C5	118.96 (13)
O2W—Ni1—O3W	89.09 (4)	C3—C4—C7	121.86 (13)
Ni1—O1W—H1WB	127.7	C5—C4—C7	119.14 (12)
Ni1—O1W—H1WA	126.0	N1—C5—C4	122.29 (13)
H1WB—O1W—H1WA	105.7	N1—C5—H5A	118.9
Ni1—O2W—H2WA	124.1	C4—C5—H5A	118.9
Ni1—O2W—H2WB	110.2	O2—C6—O1	124.76 (13)
H2WA—O2W—H2WB	103.2	O2—C6—C1	119.37 (13)
Ni1—O3W—H3WA	114.0	O1—C6—C1	115.87 (12)
Ni1—O3W—H3WB	117.0	O3—C7—O4	124.86 (13)
H3WA—O3W—H3WB	110.6	O3—C7—C4	118.32 (13)
Ni1—O4W—H4WA	113.3	O4—C7—C4	116.80 (13)
Ni1—O4W—H4WB	114.0	H5WB—O5W—H5WA	106.3
H4WA—O4W—H4WB	103.8		
O1W—Ni1—O1—C6	178.63 (11)	C1—C2—C3—C4	1.4 (2)
O4W—Ni1—O1—C6	90.91 (11)	C2—C3—C4—C5	−2.4 (2)
N1—Ni1—O1—C6	−2.07 (10)	C2—C3—C4—C7	175.16 (13)
O3W—Ni1—O1—C6	−93.15 (11)	C1—N1—C5—C4	1.6 (2)
O1—Ni1—N1—C5	−176.85 (13)	Ni1—N1—C5—C4	−177.79 (10)
O4W—Ni1—N1—C5	93.17 (13)	C3—C4—C5—N1	1.0 (2)
O2W—Ni1—N1—C5	5.79 (13)	C7—C4—C5—N1	−176.67 (13)
O3W—Ni1—N1—C5	−83.40 (13)	Ni1—O1—C6—O2	179.57 (12)
O1—Ni1—N1—C1	3.74 (10)	Ni1—O1—C6—C1	0.15 (16)
O4W—Ni1—N1—C1	−86.23 (10)	N1—C1—C6—O2	−176.29 (13)
O2W—Ni1—N1—C1	−173.62 (10)	C2—C1—C6—O2	2.2 (2)
O3W—Ni1—N1—C1	97.19 (10)	N1—C1—C6—O1	3.17 (19)
C5—N1—C1—C2	−2.7 (2)	C2—C1—C6—O1	−178.29 (13)
Ni1—N1—C1—C2	176.73 (11)	C3—C4—C7—O3	9.8 (2)
C5—N1—C1—C6	175.80 (13)	C5—C4—C7—O3	−172.58 (14)
Ni1—N1—C1—C6	−4.73 (16)	C3—C4—C7—O4	−168.48 (14)
N1—C1—C2—C3	1.3 (2)	C5—C4—C7—O4	9.1 (2)
C6—C1—C2—C3	−177.16 (13)		

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WB···O3[i]	0.85	1.87	2.7235 (15)	179
O1W—H1WA···O3W[ii]	0.85	1.98	2.8233 (15)	175
O2W—H2WA···O2[iii]	0.85	1.90	2.7484 (16)	173
O2W—H2WB···O4[iv]	0.85	1.82	2.6658 (17)	170
O3W—H3WA···O2[v]	0.85	1.86	2.7005 (16)	169
O3W—H3WB···O5W[vi]	0.85	1.96	2.7909 (17)	164

O4W—H4WA···O1^{vii}	0.85	1.89	2.7366 (16)	174
O4W—H4WB···O3^{viii}	0.85	1.86	2.6732 (15)	161
O5W—H5WB···O2W	0.85	2.23	3.0541 (19)	164
O5W—H5WA···O4^{ix}	0.85	1.98	2.7619 (18)	152
C3—H3A···O5W^x	0.95	2.44	3.3182 (19)	154

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

Fig. 1