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Poly[[aqua(μ_2-oxalato)(μ_2-2-oxidopyridinium-3-carboxylato)holmium(III)] monohydrate]

Hui-Lan Zhu,[a] Hui-Ling Lai,[a] Lu Han,[a] Yi-Fan Luo[a]* and Rong-Hua Zeng[a,b]

[a]School of Chemistry and Environment, South China Normal University, Guangzhou 510006, People's Republic of China, and [b]Key Laboratory of Technology on Electrochemical Energy Storage and Power Generation in Guangdong Universities, South China Normal University, Guangzhou 510006, People's Republic of China
Correspondence e-mail: luoyf2004@yahoo.com.cn

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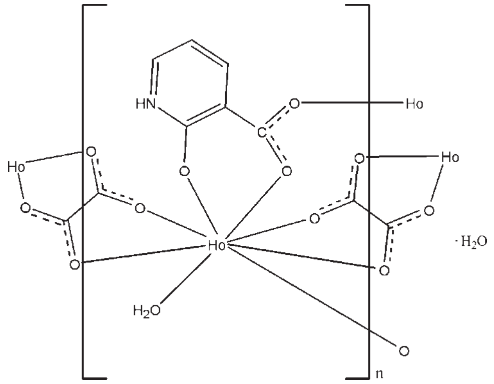
Key indicators: single-crystal X-ray study; *T* = 296 K; mean σ(C–C) = 0.011 Å; *R* factor = 0.034; *wR* factor = 0.090; data-to-parameter ratio = 10.8.

In the title complex, $\{[\mathrm{Ho}(\mathrm{C_2O_4})(\mathrm{C_6H_4NO_3})(\mathrm{H_2O})]\cdot(\mathrm{H_2O})\}_n$, the $\mathrm{Ho^{III}}$ ion is coordinated by three O atoms from two 2-oxidopyridinium-3-carboxylate ligands, four O atoms from two oxalate ligands and one water molecule in a distorted bicapped trigonal-prismatic geometry. The 2-oxidopyridinium-3-carboxylate and oxalate ligands link the $\mathrm{Ho^{III}}$ ions into a layer in (100). These layers are further connected by intermolecular O—H⋯O hydrogen bonds involving the coordinated water molecules to assemble a three-dimensional supramolecular network. The uncoordinated water molecule is involved in N—H⋯O and O—H⋯O hydrogen bonds within the layer.

Related literature

For general background to molecular self-assembly of supramolecular architectures, see: Deng *et al.* (2008); Zeng *et al.* (2007). For 2-oxidopyridinium-3-carboxylic acid and oxalic acid as building blocks, see: Huang *et al.* (2009).



Experimental

Crystal data

$[\mathrm{Ho}(\mathrm{C_2O_4})(\mathrm{C_6H_4NO_3})(\mathrm{H_2O})]\cdot\mathrm{H_2O}$
$M_r = 427.08$
Triclinic, $P\overline{1}$
$a = 6.5391$ (11) Å
$b = 9.5305$ (16) Å
$c = 9.7391$ (16) Å
$\alpha = 71.810$ (2)°
$\beta = 78.862$ (2)°
$\gamma = 80.359$ (2)°
$V = 562.01$ (16) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 7.09$ mm^{-1}
$T = 296$ K
0.20 × 0.18 × 0.17 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.332$, $T_{\max} = 0.379$
2884 measured reflections
1983 independent reflections
1862 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.090$
$S = 1.06$
1983 reflections
184 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 2.75$ e Å^{-3}
$\Delta\rho_{\min} = -2.19$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Ho1—O1	2.354 (5)	Ho1—O5$^{\mathrm{ii}}$	2.364 (5)
Ho1—O2$^{\mathrm{i}}$	2.348 (5)	Ho1—O6	2.394 (5)
Ho1—O3	2.279 (5)	Ho1—O7$^{\mathrm{iii}}$	2.392 (5)
Ho1—O4	2.406 (4)	Ho1—O1*W*	2.348 (5)

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x, -y+1, -z$; (iii) $-x, -y+1, -z+1$.

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1*W*—H1*W*⋯O2$^{\mathrm{iv}}$	0.84 (6)	2.02 (6)	2.737 (7)	142 (8)
O1*W*—H2*W*⋯O4$^{\mathrm{v}}$	0.85 (7)	1.96 (4)	2.749 (7)	154 (8)
O2*W*—H3*W*⋯O6	0.84 (7)	2.36 (11)	2.882 (10)	121 (8)
O2*W*—H4*W*⋯O1	0.86 (7)	2.27 (3)	3.082 (8)	157 (9)
N1—H1⋯O2*W*$^{\mathrm{vi}}$	0.86	1.99	2.781 (10)	154

Symmetry codes: (iv) $-x+1, -y, -z+1$; (v) $x+1, y, z$; (vi) $x, y, z-1$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2226).

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m1218 Zhu *et al.* • $[Ho(C_2O_4)(C_6H_4NO_3)(H_2O)]\cdot H_2O$ *Acta Cryst.* (2009). E**65**, m1217–m1218

supporting information

Acta Cryst. (2009). E**65**, m1217–m1218 [doi:10.1107/S1600536809036344]

Poly[[aqua(μ_2-oxalato)(μ_2-2-oxidopyridinium-3-carboxylato)holmium(III)] monohydrate]

Hui-Lan Zhu, Hui-Ling Lai, Lu Han, Yi-Fan Luo and Rong-Hua Zeng

S1. Comment

Molecular self-assembly of supramolecular architectures has received much attention during recent decades (Deng *et al.*, 2008; Zeng *et al.*, 2007). The structures and properties of such systems depend on the coordination and geometric preferences of both the central metal ions and the bridging building blocks, as well as the influence of weaker non-covalent interactions, such as hydrogen bonds and π–π stacking interactions. As a building block, 2-oxynicotinic acid and oxalic acid are good ligands with multifunctional coordination sites providing a high likelihood for the generation of structures with high dimensions (Huang *et al.*, 2009). Recently, we obtained the title coordination polymer, which was synthesized under hydrothermal conditions.

In the title compound (Fig. 1), the Ho^{III} centre is eight-coordinated by seven O atoms from two 2-oxynicotinate ligands and two oxalate ligands, and by one water molecule in a distorted bicapped trigonal prismatic geometry, with Ho—O distances and O—Ho—O angles ranging from 2.279 (5) to 2.406 (4) Å and 67.30 (17) to 148.26 (17)°, respectively (Table 1). The carboxylate groups of the 2-oxynicotinates and oxalates act as bridging ligands, linking the Ho centres into a layer parallel to the (100) plane (Fig. 2). The layers are further connected by intermolecular O—H···O hydrogen bonds involving the coordinated water molecules into a three-dimensional supramolecular network (Table 2). The uncoordinated water molecule is involved in N—H···O and O—H···O hydrogen bonds within the layer (Table 2).

S2. Experimental

A mixture of Ho_2O_3 (0.375 g, 1 mmol), 2-oxynicotinic acid (0.127 g, 1 mmol), oxalic acid (0.09 g, 1 mmol), water (10 ml) in the presence of HNO_3 (0.024 g, 0.385 mmol) was stirred vigorously for 20 min and then sealed in a Teflon-lined stainless-steel autoclave (20 ml capacity). The autoclave was heated and maintained at 446 K for 2 d, and then cooled to room temperature at 5 K h^{-1}, giving colourless block crystals.

S3. Refinement

Water H atoms were tentatively located in difference Fourier maps and refined with distance restraints of O—H = 0.84 (1) and H···H = 1.35 (1) Å, and with a fixed U_{iso}(H) = 0.064 Å^2. H atoms attached to C and N atoms were placed at calculated positions and treated as riding on their parent atoms, with C—H = 0.93 and N—H= 0.86 Å and with U_{iso}(H) = 1.2U_{eq}(C,N). The highest residual electron density was found 0.94 Å from Ho1 and the deepest hole 0.91 Å from Ho1.

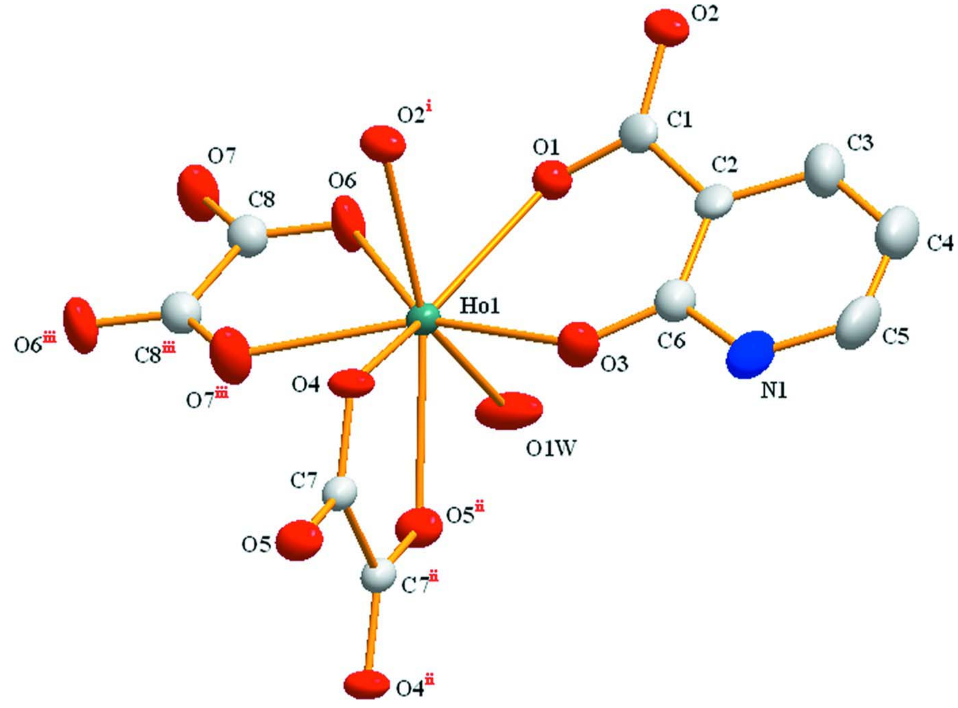

Figure 1

The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) -x, -y, 1 - z; (ii) -x, 1 - y, -z; (iii) -x, 1 - y, 1 - z.]

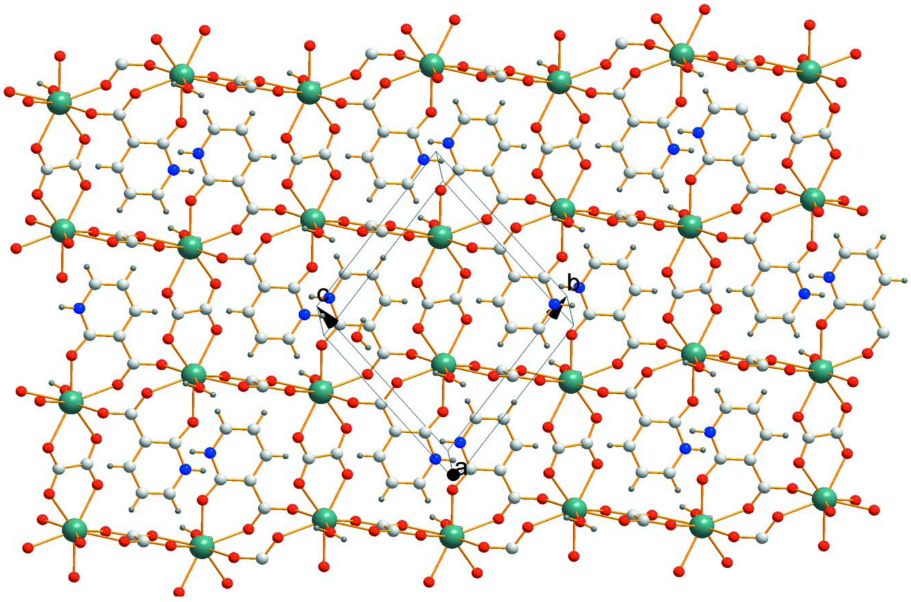

Figure 2

View of a layered network of the title compound.

Poly[[aqua(μ_2-oxalato)(μ_2-2-oxidopyridinium-3-carboxylato)holmium(III)] monohydrate]

Crystal data

$[Ho(C_2O_4)(C_6H_4NO_3)(H_2O)]\cdot H_2O$
$M_r = 427.08$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 6.5391$ (11) Å
$b = 9.5305$ (16) Å
$c = 9.7391$ (16) Å
$\alpha = 71.810$ (2)°
$\beta = 78.862$ (2)°
$\gamma = 80.359$ (2)°
$V = 562.01$ (16) Å^3
$Z = 2$
$F(000) = 404$
$D_x = 2.524$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2285 reflections
$\theta = 2.2$–28.1°
$\mu = 7.09$ mm^{-1}
$T = 296$ K
Block, colourless
0.20 × 0.18 × 0.17 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.332$, $T_{max} = 0.379$
2884 measured reflections
1983 independent reflections
1862 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 25.2°$, $\theta_{min} = 2.2°$
$h = -7 \rightarrow 6$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.090$
$S = 1.06$
1983 reflections
184 parameters
6 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
$w = 1/[\sigma^2(F_o^2) + (0.0695P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.75$ e Å^{-3}
$\Delta\rho_{min} = -2.19$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Ho1	0.09083 (4)	0.29059 (3)	0.30045 (3)	0.01784 (15)
O4	−0.1655 (7)	0.3863 (5)	0.1370 (5)	0.0219 (10)
O3	0.1549 (8)	0.1295 (6)	0.1626 (5)	0.0311 (11)
O6	0.1351 (9)	0.3228 (5)	0.5267 (6)	0.0338 (12)
O1	0.2127 (8)	0.0581 (5)	0.4520 (5)	0.0251 (10)
O5	−0.2292 (7)	0.5458 (5)	−0.0767 (5)	0.0258 (10)
N1	0.2729 (11)	−0.0557 (8)	0.0581 (7)	0.0366 (15)
H1	0.2407	0.0054	−0.0227	0.044*
C6	0.2307 (12)	−0.0067 (8)	0.1802 (8)	0.0266 (15)
C8	0.0606 (11)	0.4422 (8)	0.5578 (8)	0.0261 (15)
C5	0.3624 (14)	−0.1948 (10)	0.0574 (10)	0.044 (2)
H5	0.3862	−0.2213	−0.0290	0.052*

C4	0.4170 (14)	−0.2947 (9)	0.1807 (10)	0.048 (3)
H4	0.4851	−0.3882	0.1795	0.057*
C3	0.3695 (13)	−0.2550 (9)	0.3094 (10)	0.0396 (19)
H3	0.3999	−0.3250	0.3960	0.048*
C2	0.2776 (10)	−0.1133 (7)	0.3126 (7)	0.0251 (15)
C1	0.2306 (10)	−0.0747 (7)	0.4529 (7)	0.0236 (14)
C7	−0.1147 (10)	0.4807 (7)	0.0161 (7)	0.0190 (13)
O2W	0.2278 (13)	0.0635 (9)	0.7646 (8)	0.0621 (19)
O2	0.2125 (7)	−0.1813 (5)	0.5703 (5)	0.0262 (10)
O7	0.0730 (9)	0.4748 (6)	0.6691 (5)	0.0358 (13)
O1W	0.4526 (8)	0.2970 (7)	0.2822 (6)	0.0427 (15)
H3W	0.164 (16)	0.149 (7)	0.758 (10)	0.064*
H4W	0.203 (16)	0.041 (10)	0.691 (6)	0.064*
H1W	0.508 (12)	0.263 (11)	0.359 (5)	0.064*
H2W	0.549 (10)	0.332 (11)	0.215 (6)	0.064*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ho1	0.0166 (2)	0.0197 (2)	0.0158 (2)	−0.00221 (12)	−0.00168 (12)	−0.00363 (13)
O4	0.018 (2)	0.027 (2)	0.017 (2)	−0.0088 (18)	−0.0019 (18)	0.0028 (19)
O3	0.039 (3)	0.031 (3)	0.020 (2)	0.002 (2)	−0.005 (2)	−0.007 (2)
O6	0.046 (3)	0.023 (3)	0.034 (3)	0.010 (2)	−0.013 (2)	−0.013 (2)
O1	0.027 (3)	0.024 (2)	0.022 (2)	−0.0029 (19)	−0.0024 (19)	−0.0050 (19)
O5	0.016 (2)	0.035 (3)	0.023 (2)	−0.0035 (19)	−0.0071 (19)	−0.001 (2)
N1	0.040 (4)	0.043 (4)	0.028 (3)	−0.009 (3)	0.003 (3)	−0.016 (3)
C6	0.025 (4)	0.027 (4)	0.029 (4)	−0.007 (3)	−0.001 (3)	−0.010 (3)
C8	0.024 (4)	0.026 (4)	0.028 (4)	−0.005 (3)	−0.003 (3)	−0.007 (3)
C5	0.048 (5)	0.046 (5)	0.042 (5)	−0.011 (4)	0.014 (4)	−0.028 (4)
C4	0.055 (6)	0.036 (5)	0.050 (6)	−0.008 (4)	0.013 (5)	−0.021 (5)
C3	0.038 (5)	0.032 (4)	0.047 (5)	0.000 (3)	0.001 (4)	−0.015 (4)
C2	0.018 (3)	0.025 (3)	0.029 (4)	−0.008 (3)	0.007 (3)	−0.006 (3)
C1	0.012 (3)	0.026 (3)	0.028 (4)	0.000 (3)	−0.003 (3)	−0.003 (3)
C7	0.018 (3)	0.020 (3)	0.020 (3)	−0.006 (2)	0.001 (3)	−0.007 (3)
O2W	0.069 (5)	0.078 (5)	0.041 (4)	−0.022 (4)	−0.020 (4)	−0.005 (4)
O2	0.019 (2)	0.027 (3)	0.027 (3)	−0.0043 (19)	−0.0037 (19)	0.002 (2)
O7	0.056 (4)	0.031 (3)	0.024 (3)	0.008 (2)	−0.018 (2)	−0.013 (2)
O1W	0.021 (3)	0.062 (4)	0.029 (3)	−0.012 (3)	−0.008 (2)	0.015 (3)

Geometric parameters (Å, º)

Ho1—O1	2.354 (5)	C6—C2	1.421 (10)
Ho1—O2^{i}	2.348 (5)	C8—O7	1.237 (9)
Ho1—O3	2.279 (5)	C8—C8^{iii}	1.546 (15)
Ho1—O4	2.406 (4)	C5—C4	1.347 (13)
Ho1—O5^{ii}	2.364 (5)	C5—H5	0.9300
Ho1—O6	2.394 (5)	C4—C3	1.384 (11)
Ho1—O7^{iii}	2.392 (5)	C4—H4	0.9300

Ho1—O1W	2.348 (5)
O4—C7	1.262 (8)
O3—C6	1.279 (9)
O6—C8	1.263 (9)
O1—C1	1.249 (8)
O5—C7	1.232 (8)
O5—Ho1^{ii}	2.364 (4)
N1—C5	1.358 (11)
N1—C6	1.373 (10)
N1—H1	0.8600
C3—C2	1.390 (10)
C3—H3	0.9300
C2—C1	1.487 (10)
C1—O2	1.271 (8)
C7—C7^{ii}	1.554 (12)
O2W—H3W	0.84 (7)
O2W—H4W	0.86 (7)
O1W—H1W	0.84 (6)
O1W—H2W	0.85 (7)

O3—Ho1—O1W	90.4 (2)
O3—Ho1—O2^{i}	90.37 (18)
O1W—Ho1—O2^{i}	148.26 (17)
O3—Ho1—O1	73.45 (17)
O1W—Ho1—O1	75.15 (18)
O2^{i}—Ho1—O1	74.69 (16)
O3—Ho1—O5^{ii}	81.80 (17)
O1W—Ho1—O5^{ii}	67.83 (16)
O2^{i}—Ho1—O5^{ii}	143.49 (16)
O1—Ho1—O5^{ii}	134.91 (16)
O3—Ho1—O7^{iii}	148.06 (18)
O1W—Ho1—O7^{iii}	105.7 (2)
O2^{i}—Ho1—O7^{iii}	89.77 (18)
O1—Ho1—O7^{iii}	136.83 (16)
O5^{ii}—Ho1—O7^{iii}	79.25 (18)
O3—Ho1—O6	144.55 (17)
O1W—Ho1—O6	75.0 (2)
O2^{i}—Ho1—O6	86.35 (18)
O1—Ho1—O6	71.64 (16)
O5^{ii}—Ho1—O6	119.81 (18)
O7^{iii}—Ho1—O6	67.30 (17)
O3—Ho1—O4	77.17 (17)
O1W—Ho1—O4	135.57 (16)
O2^{i}—Ho1—O4	75.25 (15)
O1—Ho1—O4	137.32 (16)
O5^{ii}—Ho1—O4	68.24 (14)
O7^{iii}—Ho1—O4	72.00 (17)
O6—Ho1—O4	135.14 (16)
C7—O4—Ho1	118.2 (4)
C6—O3—Ho1	136.0 (5)
C8—O6—Ho1	120.3 (5)
C1—O1—Ho1	136.8 (4)
C7—O5—Ho1^{ii}	119.9 (4)
C5—N1—C6	123.9 (7)
C5—N1—H1	118.0
C6—N1—H1	118.0
O3—C6—N1	116.8 (7)
O3—C6—C2	127.2 (7)
N1—C6—C2	116.1 (7)
O7—C8—O6	127.4 (7)
O7—C8—C8^{iii}	117.7 (8)
O6—C8—C8^{iii}	114.9 (8)
C4—C5—N1	120.6 (8)
C4—C5—H5	119.7
N1—C5—H5	119.7
C5—C4—C3	118.5 (8)
C5—C4—H4	120.7
C3—C4—H4	120.7
C4—C3—C2	121.7 (8)
C4—C3—H3	119.1
C2—C3—H3	119.1
C3—C2—C6	119.1 (7)
C3—C2—C1	120.1 (7)
C6—C2—C1	120.8 (6)
O1—C1—O2	122.8 (6)
O1—C1—C2	119.9 (6)
O2—C1—C2	117.3 (6)
O5—C7—O4	126.5 (6)
O5—C7—C7^{ii}	117.4 (7)
O4—C7—C7^{ii}	116.0 (7)
H3W—O2W—H4W	105 (9)
C1—O2—Ho1^{i}	128.4 (4)
C8—O7—Ho1^{iii}	119.8 (5)
Ho1—O1W—H1W	119 (6)
Ho1—O1W—H2W	136 (6)
H1W—O1W—H2W	106 (3)

Symmetry codes: (i) $-x$, $-y$, $-z$+1; (ii) $-x$, $-y$+1, $-z$; (iii) $-x$, $-y$+1, $-z$+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O2^iv^	0.84 (6)	2.02 (6)	2.737 (7)	142 (8)
O1*W*—H2*W*···O4^v^	0.85 (7)	1.96 (4)	2.749 (7)	154 (8)
O2*W*—H3*W*···O6	0.84 (7)	2.36 (11)	2.882 (10)	121 (8)
O2*W*—H4*W*···O1	0.86 (7)	2.27 (3)	3.082 (8)	157 (9)
N1—H1···O2*W*^vi^	0.86	1.99	2.781 (10)	154

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