

Bis(μ -3-carboxy-2-hydroxypropane-1,2-dicarboxylato)bis(diaquazinc)–1,2-bis(pyridin-4-yl)ethene–water (1/1/2)

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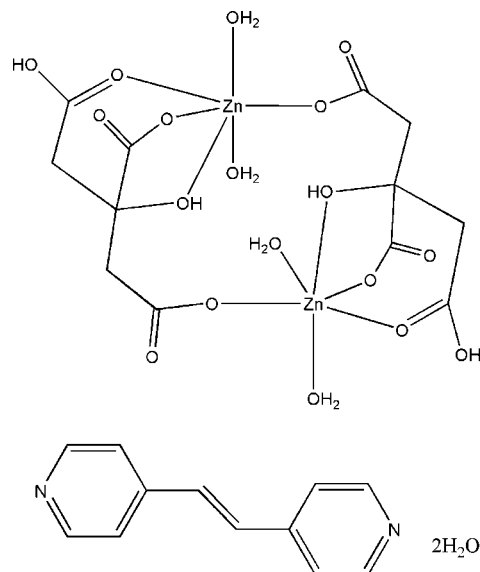
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Key indicators: single-crystal X-ray study; $T = 170$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.051; wR factor = 0.140; data-to-parameter ratio = 12.2.

The asymmetric unit of the title compound, $[\text{Zn}_2(\text{C}_6\text{H}_6\text{O}_7)_2(\text{H}_2\text{O})_4] \cdot \text{C}_{12}\text{H}_{10}\text{N}_2 \cdot 2\text{H}_2\text{O}$, comprises half of a centrosymmetric complex dimer, half of a 1,2-bis(pyridin-4-yl)ethene molecule, which lies across an inversion centre, and one lattice water molecule. Carboxylate groups of two dianionic citrate ligands bridge two Zn^{II} ions to give the cyclic dimer, with each Zn^{II} ion coordinated by four O atoms from the chelating citrate ligand (one hydroxy and three carboxylate, with one bridging) and two water O atoms, forming a distorted octahedral environment [$\text{Zn}-\text{O} = 2.040$ (3)– 2.244 (3) Å]. In the crystal, $\text{O}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds involving hydroxy groups and both coordinating and lattice water molecules link the dimers to give a three-dimensional framework structure.

Related literature

For interactions of metal ions with biologically active molecules, see: Daniele *et al.* (2008); Parkin (2004); Tshuva & Lippard (2004); Stoumpos *et al.* (2009). For a manganese citrate complex, see: Hwang *et al.* (2012). For related complexes, see: Shin *et al.* (2009); Yu *et al.* (2009); Kim *et al.* (2011).



Experimental

Crystal data

$[\text{Zn}_2(\text{C}_6\text{H}_6\text{O}_7)_2(\text{H}_2\text{O})_4] \cdot \text{C}_{12}\text{H}_{10}\text{N}_2 \cdot 2\text{H}_2\text{O}$
 $M_r = 801.31$
Triclinic, $P\bar{1}$
 $a = 9.4360$ (19) Å
 $b = 9.4540$ (19) Å
 $c = 10.098$ (2) Å
 $\alpha = 66.87$ (3)°

$\beta = 70.19$ (3)°
 $\gamma = 75.91$ (3)°
 $V = 773.0$ (3) Å³
 $Z = 1$
Mo $K\alpha$ radiation
 $\mu = 1.64$ mm⁻¹
 $T = 170$ K
 $0.30 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 1997)
 $T_{\text{min}} = 0.638$, $T_{\text{max}} = 0.853$

4216 measured reflections
2924 independent reflections
2382 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.140$
 $S = 1.09$
2924 reflections
239 parameters
7 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.77$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.36$ e Å⁻³

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

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O1}-\text{H1O} \cdots \text{O6}$	0.93 (1)	1.80 (2)	2.626 (4)	146 (4)
$\text{O5}-\text{H5} \cdots \text{N11}^{\text{i}}$	0.84	1.81	2.633 (5)	168
$\text{O8}-\text{H8B} \cdots \text{O5}^{\text{i}}$	0.86 (1)	1.88 (1)	2.733 (5)	173 (5)
$\text{O8}-\text{H8A} \cdots \text{O7}^{\text{ii}}$	0.86 (1)	2.04 (2)	2.866 (4)	161 (5)
$\text{O9}-\text{H9B} \cdots \text{O1W}^{\text{ii}}$	0.86 (1)	1.87 (1)	2.725 (5)	179 (5)
$\text{O9}-\text{H9A} \cdots \text{O3}^{\text{iii}}$	0.86 (1)	2.57 (4)	3.145 (5)	125 (4)
$\text{O9}-\text{H9A} \cdots \text{O2}^{\text{iii}}$	0.86 (1)	2.01 (1)	2.860 (5)	168 (5)
$\text{O1W}-\text{H1WA} \cdots \text{O3}$	0.96 (1)	1.88 (1)	2.838 (5)	172 (5)
$\text{O1W}-\text{H1WB} \cdots \text{O7}^{\text{iv}}$	0.96 (1)	2.04 (3)	2.880 (5)	145 (4)

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2234).

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supporting information

Acta Cryst. (2012). E68, m1305–m1306 [https://doi.org/10.1107/S1600536812039761]

Bis(μ -3-carboxy-2-hydroxypropane-1,2-dicarboxylato)bis(diaquazinc)–1,2-bis-(pyridin-4-yl)ethene–water (1/1/2)

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S1. Comment

Citric acid has often been used as a model ligand to examine the interaction between transition metal ions with biologically active molecules (Daniele *et al.*, 2008; Parkin, 2004; Tshuva & Lippard, 2004; Stoumpos *et al.*, 2009). Recently, our group has also reported a novel compound from the reaction of manganese(II) nitrate as a building block and citric acid as a ligand (Hwang *et al.*, 2012). In order to study the effects of secondary metal ions on the interaction between transition metal ions and citric acid (Shin *et al.*, 2009; Yu *et al.*, 2009; Kim *et al.*, 2011), we have employed zinc as a metal ion source. We report here the structure of $[\text{Zn}_2(\text{H}_2\text{O})_4(\text{C}_6\text{H}_8\text{O}_7)_2] \cdot \text{C}_{12}\text{H}_{10}\text{N}_2 \cdot 2\text{H}_2\text{O}$.

In the structure of the title compound (Fig. 1) the asymmetric unit contains half of a centrosymmetric complex dimer, half of a 1,2-bis(pyridin-4-yl)ethene molecule which lies across an inversion centre and one water molecule. Carboxylate groups of two dianionic citrate ligands bridge two Zn^{II} ions giving the cyclic dimer, with each ZnO_6 centre coordinated by four O atoms from the ligand (one hydroxyl and three carboxyl) and two water O atoms, forming a distorted octahedral environment [$\text{Zn}—\text{O}$, 2.040 (3)–2.244 (3) Å]. In the crystal, $\text{O}—\text{H}—\text{O}$ and $\text{O}—\text{H} \cdots \text{N}$ hydrogen bonds involving hydroxyl groups and both coordinated and solvent water molecules (Table 1) link the dimers giving a three-dimensional framework structure. The crystal structure is further stabilized by weak intermolecular π – π interactions involving the 1,2-bis(pyridin-4-yl)ethene molecule [centroid = C11–C15/N11; ring centroid separation = 3.97 (7) Å; symmetry code: $-x, -y + 1, -z + 2$].

S2. Experimental

Citric acid (19.4 mg, 0.1 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (30.4 mg, 0.1 mmol) were dissolved in 4 ml of H_2O and carefully layered by 4 ml of an acetonitrile solution of 1,2-bis(4-pyridyl)ethylene (37.6 mg, 0.2 mmol). Suitable crystals of the title compound were obtained in a month.

S3. Refinement

H atoms bonded to carbon were placed in calculated positions with $\text{C}—\text{H} = 0.95$ Å (aromatic C) and 0.99 Å (methylene C) and were included in the refinement in a riding-motion approximation with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atom bonded to the carboxylate O was placed in a calculated position with $\text{O}—\text{H} = 0.84$ Å and was also included in the refinement in the riding-motion approximation with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The position of hydroxyl H atom was refined with $\text{O}—\text{H} = 0.93$ Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The positions of $\text{O}—\text{H}$ atoms of the coordinated water ligands were refined with $\text{O}—\text{H} = 0.86$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. The positions of $\text{O}—\text{H}$ atoms of the free water molecule were refined with $\text{O}—\text{H} = 0.96$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

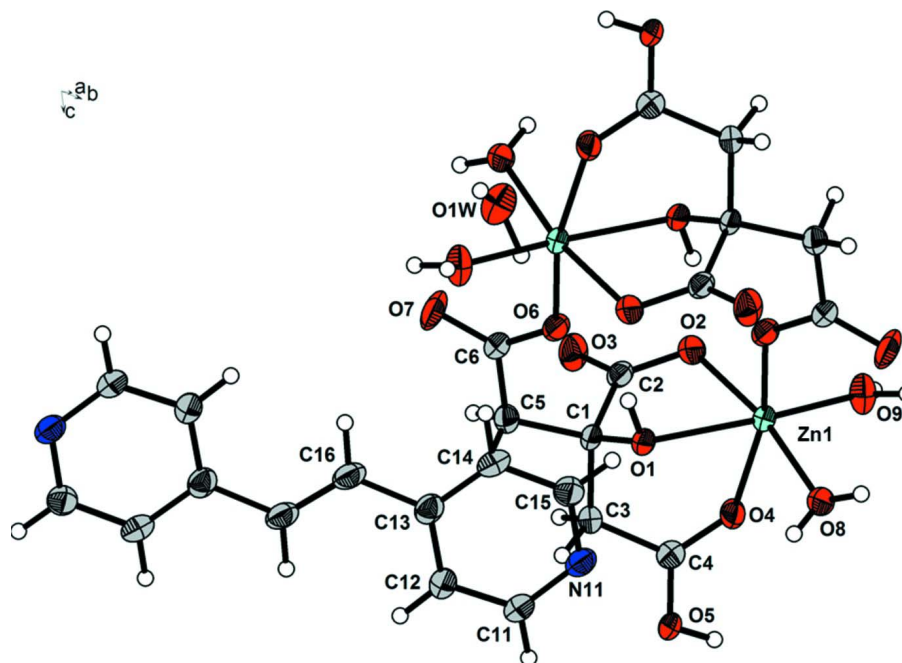


Figure 1

The structure of the title compound showing the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level. The labelled atoms are related with unlabelled atoms by symmetry code: $-x + 1, -y + 1, -z + 1$ for the diaquabis(citrato)dizinc fragment and $-x, -y, -z + 2$ for the 1,2-bis(pyridin-4-yl)ethene molecule.

Bis(μ -3-carboxy-2-hydroxypropane-1,2-dicarboxylato)bis(diaquazinc)– 1,2-bis(pyridin-4-yl)ethene–water (1/1/2)

Crystal data

$[\text{Zn}_2(\text{C}_6\text{H}_6\text{O}_7)_2(\text{H}_2\text{O})_4] \cdot \text{C}_{12}\text{H}_{10}\text{N}_2 \cdot 2\text{H}_2\text{O}$

$M_r = 801.31$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 9.4360(19)\ \text{\AA}$

$b = 9.4540(19)\ \text{\AA}$

$c = 10.098(2)\ \text{\AA}$

$\alpha = 66.87(3)^\circ$

$\beta = 70.19(3)^\circ$

$\gamma = 75.91(3)^\circ$

$V = 773.0(3)\ \text{\AA}^3$

$Z = 1$

$F(000) = 412$

$D_x = 1.721\ \text{Mg m}^{-3}$

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

Cell parameters from 11909 reflections

$\theta = 2.7\text{--}27.6^\circ$

$\mu = 1.64\ \text{mm}^{-1}$

$T = 170\ \text{K}$

Block, colourless

$0.30 \times 0.10 \times 0.10\ \text{mm}$

Data collection

Bruker SMART CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 1997)

$T_{\min} = 0.638, T_{\max} = 0.853$

4216 measured reflections

2924 independent reflections

2382 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 26.0^\circ, \theta_{\min} = 2.3^\circ$

$h = -11 \rightarrow 6$

$k = -11 \rightarrow 11$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.140$
 $S = 1.09$
 2924 reflections
 239 parameters
 7 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
 $w = 1/[\sigma^2(F_o^2) + (0.0822P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.77 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.36 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.68767 (6)	0.59099 (5)	0.60957 (5)	0.02122 (19)
O1	0.5132 (3)	0.4257 (3)	0.7203 (3)	0.0209 (6)
H1O	0.466 (4)	0.431 (5)	0.651 (4)	0.031*
O2	0.8003 (4)	0.3981 (3)	0.5435 (3)	0.0260 (7)
O3	0.8228 (4)	0.1376 (3)	0.6320 (4)	0.0341 (8)
O4	0.7490 (4)	0.4656 (3)	0.8125 (3)	0.0282 (7)
O5	0.6894 (4)	0.3353 (3)	1.0577 (3)	0.0310 (7)
H5	0.7402	0.3981	1.0558	0.046*
O6	0.4181 (4)	0.3256 (3)	0.5605 (3)	0.0262 (7)
O7	0.4259 (5)	0.0698 (3)	0.6153 (4)	0.0427 (9)
O8	0.5622 (4)	0.7538 (3)	0.7112 (3)	0.0287 (7)
H8A	0.542 (6)	0.8518 (11)	0.668 (5)	0.034*
H8B	0.480 (3)	0.733 (5)	0.782 (4)	0.034*
O9	0.8800 (4)	0.7008 (3)	0.5133 (4)	0.0333 (7)
H9A	0.9753 (13)	0.675 (6)	0.507 (6)	0.040*
H9B	0.866 (6)	0.8005 (4)	0.482 (5)	0.040*
C1	0.5996 (5)	0.2711 (4)	0.7563 (4)	0.0192 (8)
C2	0.7522 (5)	0.2671 (4)	0.6340 (4)	0.0222 (9)
C3	0.6235 (5)	0.2336 (4)	0.9105 (4)	0.0249 (9)
H3A	0.5242	0.2187	0.9867	0.030*
H3B	0.6906	0.1340	0.9338	0.030*
C4	0.6919 (5)	0.3555 (4)	0.9255 (4)	0.0238 (9)
C5	0.5058 (5)	0.1490 (4)	0.7724 (4)	0.0235 (9)
H5A	0.5694	0.0469	0.7911	0.028*

H5B	0.4176	0.1417	0.8617	0.028*
C6	0.4474 (5)	0.1808 (4)	0.6386 (4)	0.0228 (9)
N11	0.1862 (4)	0.4370 (4)	0.9552 (4)	0.0282 (8)
C11	0.1610 (6)	0.3080 (5)	1.0802 (5)	0.0300 (10)
H11	0.1826	0.3029	1.1674	0.036*
C12	0.1051 (5)	0.1855 (5)	1.0827 (5)	0.0290 (10)
H12	0.0875	0.0967	1.1705	0.035*
C13	0.0741 (5)	0.1939 (5)	0.9522 (5)	0.0271 (9)
C14	0.0990 (5)	0.3284 (5)	0.8255 (5)	0.0280 (10)
H14	0.0771	0.3372	0.7372	0.034*
C15	0.1555 (5)	0.4480 (5)	0.8300 (5)	0.0285 (10)
H15	0.1729	0.5388	0.7441	0.034*
C16	0.0212 (5)	0.0643 (5)	0.9421 (4)	0.0297 (10)
H16	0.0168	0.0727	0.8467	0.036*
O1W	0.8324 (4)	0.0166 (4)	0.4122 (4)	0.0430 (9)
H1WA	0.819 (6)	0.057 (6)	0.490 (4)	0.052*
H1WB	0.736 (3)	0.034 (6)	0.391 (6)	0.052*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0271 (3)	0.0171 (3)	0.0208 (3)	−0.00588 (19)	−0.0053 (2)	−0.00706 (19)
O1	0.0261 (16)	0.0154 (12)	0.0223 (14)	−0.0028 (12)	−0.0067 (13)	−0.0072 (11)
O2	0.0314 (17)	0.0210 (14)	0.0240 (14)	−0.0041 (13)	−0.0066 (13)	−0.0064 (12)
O3	0.0333 (19)	0.0196 (14)	0.0436 (18)	0.0001 (13)	−0.0025 (15)	−0.0135 (13)
O4	0.0400 (19)	0.0243 (15)	0.0248 (15)	−0.0135 (14)	−0.0144 (14)	−0.0028 (12)
O5	0.047 (2)	0.0309 (15)	0.0236 (14)	−0.0232 (15)	−0.0075 (15)	−0.0089 (13)
O6	0.0399 (19)	0.0193 (13)	0.0234 (14)	−0.0032 (13)	−0.0146 (14)	−0.0066 (11)
O7	0.076 (3)	0.0190 (15)	0.0502 (19)	−0.0098 (16)	−0.037 (2)	−0.0102 (14)
O8	0.040 (2)	0.0188 (14)	0.0242 (15)	−0.0045 (14)	−0.0040 (14)	−0.0081 (12)
O9	0.0251 (17)	0.0230 (15)	0.0490 (19)	−0.0057 (14)	−0.0071 (16)	−0.0103 (14)
C1	0.025 (2)	0.0144 (17)	0.0204 (19)	−0.0048 (16)	−0.0068 (17)	−0.0062 (15)
C2	0.025 (2)	0.0218 (19)	0.023 (2)	−0.0038 (18)	−0.0084 (18)	−0.0098 (16)
C3	0.032 (3)	0.0210 (19)	0.022 (2)	−0.0100 (18)	−0.0042 (19)	−0.0062 (16)
C4	0.024 (2)	0.024 (2)	0.025 (2)	−0.0020 (18)	−0.0075 (18)	−0.0095 (17)
C5	0.028 (2)	0.0186 (18)	0.024 (2)	−0.0050 (17)	−0.0079 (18)	−0.0052 (16)
C6	0.027 (2)	0.0221 (19)	0.0231 (19)	−0.0049 (17)	−0.0074 (18)	−0.0098 (16)
N11	0.031 (2)	0.0290 (18)	0.0293 (18)	−0.0035 (17)	−0.0072 (17)	−0.0162 (16)
C11	0.039 (3)	0.029 (2)	0.028 (2)	−0.006 (2)	−0.009 (2)	−0.0143 (18)
C12	0.036 (3)	0.025 (2)	0.029 (2)	−0.0079 (19)	−0.010 (2)	−0.0094 (18)
C13	0.026 (2)	0.026 (2)	0.031 (2)	−0.0023 (19)	−0.0034 (19)	−0.0156 (18)
C14	0.031 (3)	0.031 (2)	0.028 (2)	−0.0002 (19)	−0.011 (2)	−0.0169 (18)
C15	0.028 (3)	0.030 (2)	0.028 (2)	−0.0052 (19)	−0.0042 (19)	−0.0118 (18)
C16	0.037 (3)	0.029 (2)	0.027 (2)	0.000 (2)	−0.009 (2)	−0.0172 (18)
O1W	0.042 (2)	0.0371 (18)	0.057 (2)	−0.0027 (17)	−0.0159 (19)	−0.0224 (17)

Geometric parameters (Å, °)

Zn1—O9	2.060 (3)	C1—C2	1.551 (6)
Zn1—O6 ⁱ	2.069 (3)	C3—C4	1.527 (5)
Zn1—O8	2.086 (3)	C3—H3A	0.9900
Zn1—O2	2.105 (3)	C3—H3B	0.9900
Zn1—O4	2.122 (3)	C5—C6	1.525 (5)
Zn1—O1	2.244 (3)	C5—H5A	0.9900
O1—C1	1.461 (4)	C5—H5B	0.9900
O1—H1O	0.930 (2)	N11—C15	1.351 (5)
O2—C2	1.296 (5)	N11—C11	1.366 (5)
O3—C2	1.248 (5)	C11—C12	1.374 (6)
O4—C4	1.264 (5)	C11—H11	0.9500
O5—C4	1.265 (5)	C12—C13	1.412 (6)
O5—H5	0.8400	C12—H12	0.9500
O6—C6	1.299 (5)	C13—C14	1.404 (6)
O6—Zn1 ⁱ	2.069 (3)	C13—C16	1.481 (6)
O7—C6	1.236 (5)	C14—C15	1.384 (6)
O8—H8A	0.860 (2)	C14—H14	0.9500
O8—H8B	0.860 (2)	C15—H15	0.9500
O9—H9A	0.860 (2)	C16—C16 ⁱⁱ	1.345 (8)
O9—H9B	0.860 (2)	C16—H16	0.9500
C1—C3	1.539 (5)	O1W—H1WA	0.960 (2)
C1—C5	1.547 (5)	O1W—H1WB	0.960 (2)
O9—Zn1—O6 ⁱ	102.94 (13)	C4—C3—H3A	108.4
O9—Zn1—O8	94.22 (13)	C1—C3—H3A	108.4
O6 ⁱ —Zn1—O8	94.62 (12)	C4—C3—H3B	108.4
O9—Zn1—O2	92.48 (13)	C1—C3—H3B	108.4
O6 ⁱ —Zn1—O2	90.97 (11)	H3A—C3—H3B	107.4
O8—Zn1—O2	170.11 (11)	O4—C4—O5	123.4 (4)
O9—Zn1—O4	92.53 (13)	O4—C4—C3	121.6 (3)
O6 ⁱ —Zn1—O4	164.39 (12)	O5—C4—C3	114.9 (3)
O8—Zn1—O4	86.23 (12)	C6—C5—C1	115.6 (3)
O2—Zn1—O4	86.21 (11)	C6—C5—H5A	108.4
O9—Zn1—O1	167.91 (11)	C1—C5—H5A	108.4
O6 ⁱ —Zn1—O1	83.38 (11)	C6—C5—H5B	108.4
O8—Zn1—O1	95.54 (12)	C1—C5—H5B	108.4
O2—Zn1—O1	76.98 (11)	H5A—C5—H5B	107.5
O4—Zn1—O1	81.02 (11)	O7—C6—O6	124.9 (4)
C1—O1—Zn1	105.3 (2)	O7—C6—C5	118.7 (3)
C1—O1—H1O	106 (3)	O6—C6—C5	116.3 (3)
Zn1—O1—H1O	109 (3)	C15—N11—C11	120.6 (4)
C2—O2—Zn1	114.9 (2)	N11—C11—C12	121.5 (4)
C4—O4—Zn1	130.7 (3)	N11—C11—H11	119.3
C4—O5—H5	109.5	C12—C11—H11	119.3
C6—O6—Zn1 ⁱ	126.1 (3)	C11—C12—C13	118.8 (4)
Zn1—O8—H8A	127 (3)	C11—C12—H12	120.6

Zn1—O8—H8B	121 (3)	C13—C12—H12	120.6
H8A—O8—H8B	101 (5)	C14—C13—C12	118.9 (4)
Zn1—O9—H9A	137 (3)	C14—C13—C16	118.6 (4)
Zn1—O9—H9B	117 (4)	C12—C13—C16	122.5 (4)
H9A—O9—H9B	106 (5)	C15—C14—C13	119.6 (4)
O1—C1—C3	106.3 (3)	C15—C14—H14	120.2
O1—C1—C5	110.4 (3)	C13—C14—H14	120.2
C3—C1—C5	107.3 (3)	N11—C15—C14	120.7 (4)
O1—C1—C2	110.7 (3)	N11—C15—H15	119.7
C3—C1—C2	112.1 (3)	C14—C15—H15	119.7
C5—C1—C2	110.0 (3)	C16 ⁱⁱ —C16—C13	124.9 (5)
O3—C2—O2	124.3 (4)	C16 ⁱⁱ —C16—H16	117.5
O3—C2—C1	117.7 (3)	C13—C16—H16	117.5
O2—C2—C1	118.0 (3)	H1WA—O1W—H1WB	108 (5)
C4—C3—C1	115.6 (3)		
O9—Zn1—O1—C1	2.9 (6)	O1—C1—C3—C4	-52.5 (5)
O6 ⁱ —Zn1—O1—C1	125.2 (2)	C5—C1—C3—C4	-170.6 (3)
O8—Zn1—O1—C1	-140.8 (2)	C2—C1—C3—C4	68.5 (4)
O2—Zn1—O1—C1	32.6 (2)	Zn1—O4—C4—O5	-147.6 (3)
O4—Zn1—O1—C1	-55.5 (2)	Zn1—O4—C4—C3	33.9 (6)
O9—Zn1—O2—C2	148.1 (3)	C1—C3—C4—O4	-11.8 (6)
O6 ⁱ —Zn1—O2—C2	-108.9 (3)	C1—C3—C4—O5	169.6 (4)
O4—Zn1—O2—C2	55.8 (3)	O1—C1—C5—C6	55.0 (5)
O1—Zn1—O2—C2	-25.9 (3)	C3—C1—C5—C6	170.4 (4)
O9—Zn1—O4—C4	-170.7 (4)	C2—C1—C5—C6	-67.4 (4)
O6 ⁱ —Zn1—O4—C4	1.6 (7)	Zn1 ⁱ —O6—C6—O7	5.5 (7)
O8—Zn1—O4—C4	95.3 (4)	Zn1 ⁱ —O6—C6—C5	-171.6 (3)
O2—Zn1—O4—C4	-78.3 (4)	C1—C5—C6—O7	152.2 (4)
O1—Zn1—O4—C4	-0.9 (3)	C1—C5—C6—O6	-30.6 (5)
Zn1—O1—C1—C3	86.9 (3)	C15—N11—C11—C12	0.5 (7)
Zn1—O1—C1—C5	-157.0 (2)	N11—C11—C12—C13	0.4 (7)
Zn1—O1—C1—C2	-35.0 (3)	C11—C12—C13—C14	-1.2 (7)
Zn1—O2—C2—O3	-164.3 (3)	C11—C12—C13—C16	176.8 (4)
Zn1—O2—C2—C1	13.4 (4)	C12—C13—C14—C15	1.2 (7)
O1—C1—C2—O3	-165.1 (3)	C16—C13—C14—C15	-176.9 (4)
C3—C1—C2—O3	76.4 (4)	C11—N11—C15—C14	-0.5 (7)
C5—C1—C2—O3	-42.9 (5)	C13—C14—C15—N11	-0.4 (7)
O1—C1—C2—O2	17.0 (5)	C14—C13—C16—C16 ⁱⁱ	-173.2 (6)
C3—C1—C2—O2	-101.5 (4)	C12—C13—C16—C16 ⁱⁱ	8.8 (9)
C5—C1—C2—O2	139.2 (3)		

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y, -z+2$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O \cdots O6	0.93 (1)	1.80 (2)	2.626 (4)	146 (4)

O5—H5…N11 ⁱⁱⁱ	0.84	1.81	2.633 (5)	168
O8—H8B…O5 ⁱⁱⁱ	0.86 (1)	1.88 (1)	2.733 (5)	173 (5)
O8—H8A…O7 ⁱ	0.86 (1)	2.58 (4)	3.031 (4)	114 (4)
O8—H8A…O7 ^{iv}	0.86 (1)	2.04 (2)	2.866 (4)	161 (5)
O9—H9B…O1W ^{iv}	0.86 (1)	1.87 (1)	2.725 (5)	179 (5)
O9—H9A…O3 ^v	0.86 (1)	2.57 (4)	3.145 (5)	125 (4)
O9—H9A…O2 ^v	0.86 (1)	2.01 (1)	2.860 (5)	168 (5)
O1W—H1WA…O3	0.96 (1)	1.88 (1)	2.838 (5)	172 (5)
O1W—H1WB…O7 ^{vi}	0.96 (1)	2.04 (3)	2.880 (5)	145 (4)
C14—H14…O9 ⁱ	0.95	2.58	3.474 (5)	158
C12—H12…O3 ^{vii}	0.95	2.52	3.390 (5)	152
C11—H11…O4 ⁱⁱⁱ	0.95	2.52	3.132 (5)	122

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