

Poly[[$(\mu_2$ -but-2-ynedioato)[μ_2 -1,2-(pyridin-4-yl)-ethylene]zinc(II)] dihydrate]

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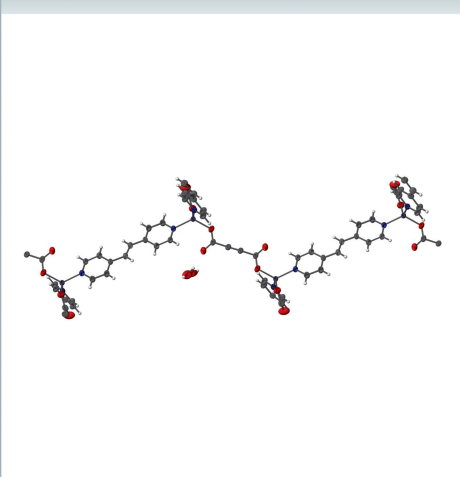
Keywords: crystal structure; Zn-MOF; 2-butyndioate; 1,2-(pyridin-4-yl)ethylene.

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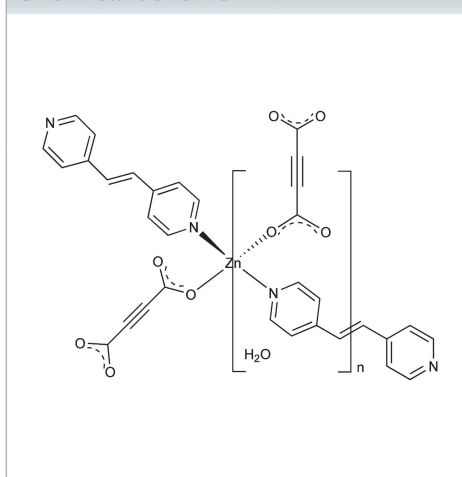
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, poly[[$(\mu_2$ -oxalato)[μ_2 -1,2-(pyridin-4-yl)ethylene]-zinc(II)] dihydrate], $\{[\text{Zn}(\mu_2\text{-C}_4\text{O}_4)(\mu_2\text{-C}_{12}\text{H}_{10}\text{N}_2)]\cdot 2\text{H}_2\text{O}\}_n$, 2-butyndioate and 1,2-bis(pyridin-4-yl)ethylene ligands bridge Zn^{II} ions to form a three-dimensional network. The three-dimensional networks are fivefold interpenetrated, and each network features a 4-connected unimodal net with a Schläfli symbol of 6^6 (**dia**) with the Zn^{II} ions as the nodes. Twofold rotation axes are located at the Zn^{II} ions and the midpoints of the $\text{C}\equiv\text{C}$ bond of 2-butyndioate and the $\text{C}=\text{C}$ bond of 1,2-bis(pyridin-4-yl)ethylene. The coordination geometry around the Zn^{II} ions is tetrahedral constructed from two O atoms from 2-butyndioate and two N atoms from 1,2-bis(pyridin-4-yl)ethylene. Solvate water molecules are connected with each other *via* hydrogen bonds to create chains running parallel to [010] that are captured in infinite channels of the three-dimensional framework through hydrogen bonds to the non-coordinating carboxylate O atoms of the 2-butyndioate units. The water molecules are disordered, with two alternative positions that are distinguished by the direction of the chains, but that share the H atom hydrogen bonded to the carboxylate O atom.

3D view



Chemical scheme



Structure description

Rigid aromatic dicarboxylates have been used for the synthesis of MOFs (metal–organic frameworks), providing high surface areas and large pore volumes suitable for various advanced applications. Flexible dicarboxylates as well as rigid aromatic dicarboxylates have been paid attention in the design of new MOFs. Recently, various MOFs containing flexible α,ω -alkane (or alkene)-dicarboxylates have been reported: three-dimensional Zn^{II} frameworks containing malonates and various bipyridyl pillars [4,4-bipyridine, 1,2-bis(pyridin-4-yl)ethane, 1,2-bis(pyridin-4-yl)ethylene, and 1,3-bis(pyridin-4-yl)propane]

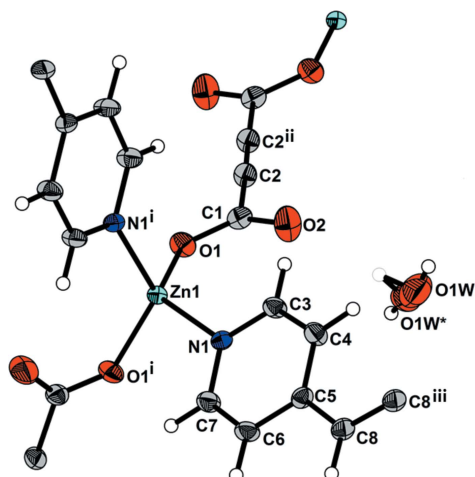


Figure 1
A fragment of the three-dimensional network of the title compound showing displacement ellipsoids at the 50% probability level. The disordered water solvate molecules are shown, and one of the H atoms is set to be exactly shared between the two water molecules. [Symmetry codes: (i) $-x, y, \frac{3}{2} - z$; (ii) $-x, -y, 1 - z$; (iii) $\frac{1}{2} - x, \frac{5}{2} - y, 2 - z$.]

have been prepared and their structures determined (Hyun *et al.* 2013). Zn-MOFs containing five flexible α,ω -alkane- (or alkene-)dicarboxylates and bipyridyl ligands have also been synthesized and their structures determined (Hwang *et al.*, 2013; Kim *et al.*, 2017). Bifunctional three-dimensional Cu-MOFs containing glutarates and bipyridyl ligands possess a very similar pore shape with different pore dimensions, and both MOFs showed good CO₂ selectivity over N₂ and H₂

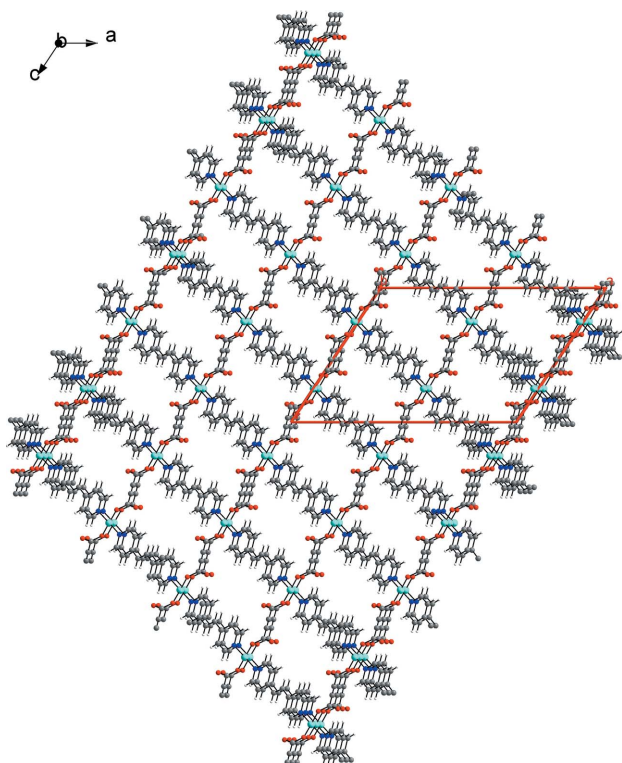


Figure 2
Three-dimensional network viewed along the *b* axis. Water solvate molecules are omitted for clarity.

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C3—H3···O2	0.95	2.52	3.208 (2)	129
O1W—H1B···O1W ⁱ	0.87 (2)	2.28 (4)	2.984 (4)	138 (6)
O1W*—H1B*···O1W* ⁱⁱ	0.83 (2)	2.39 (9)	3.041 (16)	136 (11)
O1W—H1A···O2	0.84 (2)	2.08 (2)	2.880 (7)	160 (4)
O1W*—H1A*···O2	0.81 (2)	2.08 (2)	2.81 (2)	150 (4)

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

(Hwang *et al.*, 2012). Cd^{II}-MOFs containing succinate and bipyridyl ligands have been prepared and their structures determined (Lee *et al.*, 2014). We report here the structure of $\{[\text{Zn}(\mu_2\text{-C}_4\text{O}_4)(\mu_2\text{-C}_{12}\text{H}_{10}\text{N}_2)] \cdot 2\text{H}_2\text{O}\}_n$ containing a rigid non-aromatic 2-butyndioate ligand.

A fragment of the three-dimensional framework of the title compound is shown in Fig. 1. 2-Butyndioate and 1,2-bis-(pyridin-4-yl)ethylene ligands bridge Zn^{II} ions to form a three-dimensional network (Fig. 2). The networks are fivefold interpenetrated (Fig. 3), and each features a 4-connected unimodal net with a Schläfli symbol of 6⁶ (**dia**) with the Zn^{II} ions as nodes, based on a *ToposPro* analysis (Blatov *et al.*, 2014). Twofold rotation axes are located at the Zn^{II} ions and the midpoints of the C≡C bond of 2-butyndioate and the C=C bond of 1,2-bis(pyridin-4-yl)ethylene. The coordination geometry around the Zn^{II} ion is approximately tetrahedral constructed by two O atoms from 2-butyndioate and two N atoms from 1,2-bis(pyridin-4-yl)ethylene. The solvate water molecule was refined as disordered, with one of the H atoms, hydrogen-bonded to the oxygen atom of the 2-butyndioate units not coordinated to zinc, set to be shared exactly between the disordered water molecules. Hydrogen bonds between neighboring water solvate molecules lead to the formation of chains along [010] (Table 1). Each disordered water molecule forms one infinite chain, distinguished from the other by the

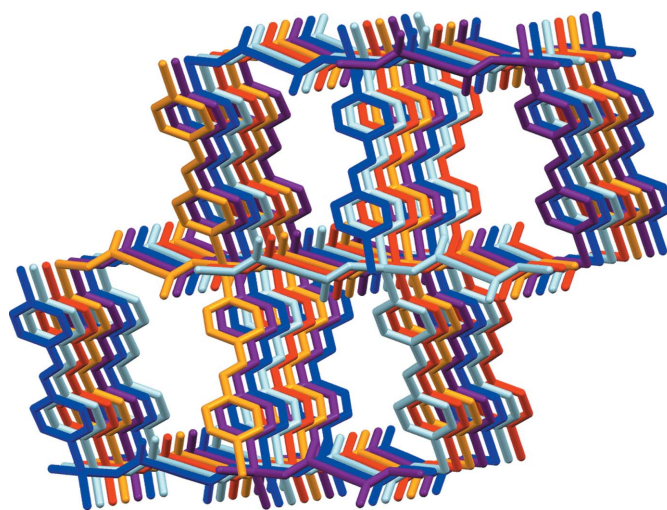


Figure 3
Fivefold interpenetrated three-dimensional networks of the title compound are shown in different colors. Water solvate molecules and all hydrogen atoms are omitted for clarity.

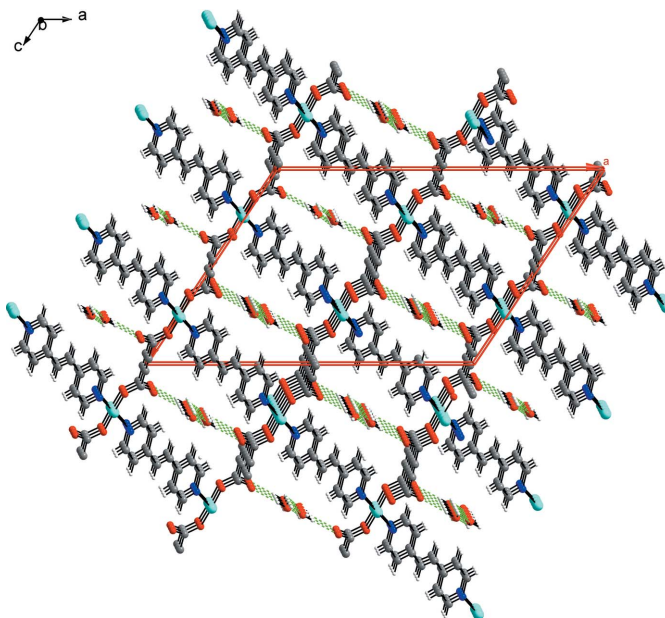


Figure 4
Hydrogen-bonding interactions (green dotted lines) between water solvate molecules forming chains and between these chains and non-coordinating carboxylate O atoms (Table 1). Only the chains formed from the major of the two disordered water molecules are shown.

direction of the hydrogen-bonding interactions. The hydrogen-bonded water solvate chains are captured in infinite channels of the three-dimensional network through hydrogen-bonding interactions to the non-coordinating carboxylate O atoms (Fig. 4 and Table 1). The solvent-free Zn^{II} three-dimensional framework has a 19.1% void volume based on a *PLATON* analysis (Spek, 2009).

Synthesis and crystallization

2-Butyndioic acid (0.1 mmol, 11.4 mg) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol, 30.4 mg) were dissolved in 4 ml water, and 1.5 ml 25% ammonia water was added. This solution was carefully layered with an 4 ml acetonitrile solution of 1,2-bis(pyridin-4-yl)ethylene (0.2 mmol, 36.4 mg). Suitable crystals of the title compound were obtained in a few weeks, yield 58 mg (14.6%). The pale-yellow block-shaped crystals retain crystallinity upon desolvation.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms hydrogen bonded to the 2-butyndioate O atom were constrained to be exactly shared between the two disordered units. The disorder ratio of the water molecules refined to 0.76 (3) to 0.24 (3).

Funding information

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Table 2
Experimental details.

Crystal data	
Chemical formula	$[\text{Zn}(\text{C}_4\text{O}_4)(\text{C}_{12}\text{H}_{10}\text{N}_2)] \cdot 2\text{H}_2\text{O}$
M_r	395.66
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	170
a, b, c (Å)	22.771 (5), 5.5777 (11), 16.306 (3)
β (°)	123.679 (3)
V (Å ³)	1723.4 (6)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	1.46
Crystal size (mm)	0.15 × 0.10 × 0.08
Data collection	
Diffractometer	Bruker <i>SMART</i> CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2003)
$T_{\text{min}}, T_{\text{max}}$	0.830, 0.891
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5404, 2071, 1980
R_{int}	0.015
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.669
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.028, 0.076, 1.17
No. of reflections	2071
No. of parameters	134
No. of restraints	25
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.36, -0.34

Computer programs: *SMART* and *SAINT* (Bruker, 2003), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2015* (Sheldrick, 2015) and *DIAMOND* (Brandenburg & Berndt, 1998).

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full crystallographic data

IUCrData (2017). 2, x171642 [https://doi.org/10.1107/S241431461701642X]

Poly[[$(\mu_2$ -but-2-ynedioato)[μ_2 -1,2-(pyridin-4-yl)ethylene]zinc(II)] dihydrate]

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Poly[[$(\mu_2$ -but-2-ynedioato)[μ_2 -1,2-(pyridin-4-yl)ethylene]zinc(II)] dihydrate]*Crystal data*

[Zn(C₄O₄)(C₁₂H₁₀N₂)]·2H₂O

$M_r = 395.66$

Monoclinic, $C2/c$

$a = 22.771$ (5) Å

$b = 5.5777$ (11) Å

$c = 16.306$ (3) Å

$\beta = 123.679$ (3)°

$V = 1723.4$ (6) Å³

$Z = 4$

$F(000) = 808$

$D_x = 1.525$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3432 reflections

$\theta = 2.5$ – 27.9 °

$\mu = 1.46$ mm⁻¹

$T = 170$ K

Block, pale yellow

$0.15 \times 0.10 \times 0.08$ mm

Data collection

Bruker SMART CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2003)

$T_{\min} = 0.830$, $T_{\max} = 0.891$

5404 measured reflections

2071 independent reflections

1980 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\max} = 28.4$ °, $\theta_{\min} = 3.0$ °

$h = -30 \rightarrow 29$

$k = -7 \rightarrow 5$

$l = -18 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.076$

$S = 1.17$

2071 reflections

134 parameters

25 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.9936P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.36$ e Å⁻³

$\Delta\rho_{\min} = -0.34$ e Å⁻³

Extinction correction: SHELXL2015

(Sheldrick, 2015),

$F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0073 (8)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. H atoms bonded to C atoms of pyridylaromatic rings were placed in calculated positions with C—H distances of 0.95 Å. They were included in the refinement in riding-motion approximation with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms bonded to O atoms of the water solvate molecule were refined with O—H distances restrained to 0.84 (2) Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The H atoms hydrogen bonded to the 2-butynedioate O atom were constrained to be exactly shared between the two disordered units. H···H distances within the water solvate molecules were restrained to 1.36 (2) Å, and the H1A···O2 distance was restrained to 2.10 (2)

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Zn1	0.0000	0.42032 (4)	0.7500	0.02426 (12)	
O1	−0.00608 (7)	0.2056 (2)	0.65262 (10)	0.0404 (3)	
O2	0.07226 (10)	0.3913 (3)	0.63460 (15)	0.0639 (5)	
N1	0.08162 (7)	0.6435 (3)	0.83668 (10)	0.0275 (3)	
C1	0.02781 (9)	0.2373 (3)	0.61313 (13)	0.0349 (4)	
C2	0.00843 (10)	0.0689 (3)	0.53244 (15)	0.0354 (4)	
C3	0.10795 (10)	0.7876 (3)	0.79870 (12)	0.0345 (4)	
H3	0.0911	0.7699	0.7311	0.041*	
C4	0.15811 (11)	0.9591 (4)	0.85292 (14)	0.0384 (4)	
H4	0.1754	1.0568	0.8230	0.046*	
C5	0.18358 (9)	0.9893 (3)	0.95234 (12)	0.0315 (3)	
C6	0.15629 (10)	0.8391 (4)	0.99139 (13)	0.0386 (4)	
H6	0.1723	0.8526	1.0588	0.046*	
C7	0.10609 (10)	0.6709 (4)	0.93236 (13)	0.0369 (4)	
H7	0.0880	0.5702	0.9604	0.044*	
C8	0.23647 (9)	1.1699 (3)	1.01505 (13)	0.0360 (4)	
H8	0.2527	1.1723	1.0827	0.043*	
O1W	0.2227 (3)	0.450 (3)	0.7360 (5)	0.093 (2)	0.76 (3)
H1A	0.1820 (7)	0.395 (7)	0.708 (3)	0.139*	0.76 (3)
H1B	0.219 (3)	0.592 (7)	0.713 (5)	0.139*	0.76 (3)
O1W*	0.2192 (10)	0.326 (7)	0.7361 (13)	0.079 (4)	0.24 (3)
H1A*	0.1820 (7)	0.395 (7)	0.708 (3)	0.118*	0.24 (3)
H1B*	0.216 (4)	0.182 (9)	0.746 (13)	0.118*	0.24 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02654 (16)	0.02265 (16)	0.02250 (15)	0.000	0.01291 (12)	0.000
O1	0.0499 (7)	0.0386 (7)	0.0373 (7)	−0.0020 (6)	0.0271 (6)	−0.0106 (5)
O2	0.0668 (11)	0.0659 (11)	0.0721 (12)	−0.0311 (9)	0.0466 (10)	−0.0396 (9)
N1	0.0272 (6)	0.0269 (6)	0.0237 (6)	−0.0003 (5)	0.0112 (5)	−0.0017 (5)
C1	0.0362 (8)	0.0322 (8)	0.0322 (8)	0.0043 (7)	0.0164 (7)	−0.0065 (7)
C2	0.0368 (9)	0.0343 (9)	0.0376 (9)	−0.0001 (7)	0.0223 (8)	−0.0068 (6)
C3	0.0404 (9)	0.0361 (9)	0.0260 (8)	−0.0088 (7)	0.0178 (7)	−0.0063 (6)
C4	0.0443 (10)	0.0419 (10)	0.0320 (9)	−0.0153 (8)	0.0231 (8)	−0.0088 (7)
C5	0.0281 (8)	0.0337 (8)	0.0281 (8)	−0.0041 (7)	0.0127 (7)	−0.0068 (7)
C6	0.0427 (9)	0.0455 (10)	0.0237 (8)	−0.0104 (8)	0.0159 (7)	−0.0056 (7)
C7	0.0407 (9)	0.0398 (9)	0.0279 (8)	−0.0089 (8)	0.0177 (7)	−0.0019 (7)

C8	0.0334 (8)	0.0406 (9)	0.0286 (8)	-0.0077 (7)	0.0138 (7)	-0.0100 (7)
O1W	0.0539 (18)	0.145 (7)	0.070 (2)	0.013 (3)	0.0282 (15)	-0.016 (3)
O1W*	0.062 (5)	0.137 (9)	0.047 (4)	0.020 (7)	0.037 (3)	0.009 (7)

Geometric parameters (Å, °)

Zn1—O1	1.9315 (13)	C4—H4	0.9500
Zn1—O1 ⁱ	1.9315 (13)	C5—C6	1.390 (3)
Zn1—N1 ⁱ	2.0219 (14)	C5—C8	1.464 (2)
Zn1—N1	2.0219 (14)	C6—C7	1.376 (3)
O1—C1	1.262 (2)	C6—H6	0.9500
O2—C1	1.221 (2)	C7—H7	0.9500
N1—C3	1.342 (2)	C8—C8 ⁱⁱⁱ	1.324 (4)
N1—C7	1.343 (2)	C8—H8	0.9500
C1—C2	1.471 (2)	O1W—H1A	0.831 (16)
C2—C2 ⁱⁱ	1.186 (4)	O1W—H1B	0.866 (19)
C3—C4	1.372 (2)	O1W*—H1A*	0.805 (18)
C3—H3	0.9500	O1W*—H1B*	0.83 (2)
C4—C5	1.397 (2)		
O1—Zn1—O1 ⁱ	103.37 (9)	C3—C4—C5	119.58 (17)
O1—Zn1—N1 ⁱ	100.84 (6)	C3—C4—H4	120.2
O1 ⁱ —Zn1—N1 ⁱ	125.13 (6)	C5—C4—H4	120.2
O1—Zn1—N1	125.13 (6)	C6—C5—C4	117.11 (16)
O1 ⁱ —Zn1—N1	100.84 (6)	C6—C5—C8	119.89 (16)
N1 ⁱ —Zn1—N1	104.00 (8)	C4—C5—C8	123.01 (17)
C1—O1—Zn1	123.18 (12)	C7—C6—C5	119.97 (16)
C3—N1—C7	117.66 (15)	C7—C6—H6	120.0
C3—N1—Zn1	121.26 (11)	C5—C6—H6	120.0
C7—N1—Zn1	120.69 (12)	N1—C7—C6	122.60 (17)
O2—C1—O1	126.62 (17)	N1—C7—H7	118.7
O2—C1—C2	119.67 (18)	C6—C7—H7	118.7
O1—C1—C2	113.70 (16)	C8 ⁱⁱⁱ —C8—C5	125.2 (2)
C2 ⁱⁱ —C2—C1	178.5 (3)	C8 ⁱⁱⁱ —C8—H8	117.4
N1—C3—C4	123.07 (16)	C5—C8—H8	117.4
N1—C3—H3	118.5	H1A—O1W—H1B	107 (3)
C4—C3—H3	118.5	H1A*—O1W*—H1B*	114 (4)

Symmetry codes: (i) $-x, y, -z+3/2$; (ii) $-x, -y, -z+1$; (iii) $-x+1/2, -y+5/2, -z+2$.*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C3—H3 \cdots O2	0.95	2.52	3.208 (2)	129
O1W—H1B \cdots O1W ^{iv}	0.87 (2)	2.28 (4)	2.984 (4)	138 (6)
O1W*—H1B* \cdots O1W* ^v	0.83 (2)	2.39 (9)	3.041 (16)	136 (11)

O1 <i>W</i> —H1A···O2	0.84 (2)	2.08 (2)	2.880 (7)	160 (4)
O1 <i>W</i> *—H1A*···O2	0.81 (2)	2.08 (2)	2.81 (2)	150 (4)

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