metal-organic compounds

Diaquabis(2-hydroxy-5-methoxy-benzoato-κO^1)zinc

Tao Li,[a]* Li-Rong Tang,[b] Lin Yang[a] and Biao Huang[b]

[a]School of Life Sciences, Fujian Agriculture and Forestry University, Fuzhou, Fujian 350002, People's Republic of China, and [b]Material Engineering College, Fujian Agriculture and Forestry University, Fuzhou, Fujian 350002, People's Republic of China

Correspondence e-mail: ltdl@sina.com

The title compound, [Zn(C$_8$H$_7$O$_4$)$_2$(H$_2$O)$_2$], has been synthesized by hydrothermal methods. The Zn^{II} atom, whose symmetry element is a twofold axis, is four coordinated by two O atoms from 5-methoxysalicylate anions and two aqua O atoms in a distorted tetrahedral geometry. In the crystal, molecules are linked into a layer by O—H···O hydrogen bonds, which stabilize the packing.

Related literature

For coordination polymers constructed by hydrogen bonds, see: Li *et al.* (2006); Jiang *et al.* (2011). For the structure of the complex with 5-methoxysalicylate ligands and its analogues, see: Púčeková-Repická *et al.* (2007); Valigura *et al.* (2006).
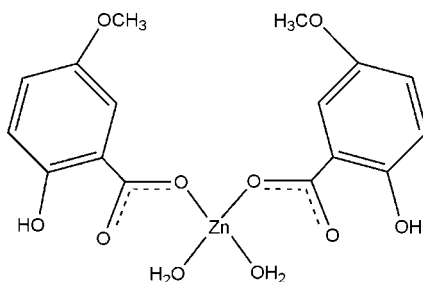
Experimental

Crystal data

[Zn(C$_8$H$_7$O$_4$)$_2$(H$_2$O)$_2$]
M_r = 435.67
Monoclinic, $C2/c$
a = 25.113 (4) Å
b = 5.5065 (6) Å
c = 12.648 (3) Å
β = 97.845 (12)°
V = 1732.7 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.47 mm^{-1}
T = 173 K
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku Mercury CCD/AFC diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2007)
T_{min} = 0.745, T_{max} = 0.752
6403 measured reflections
1986 independent reflections
1837 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.082
S = 1.08
1986 reflections
136 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1···O1	0.87 (3)	1.76 (3)	2.5771 (19)	155 (2)
O4—H4A···O2^i	0.73 (3)	1.93 (3)	2.643 (2)	169 (3)
O4—H4B···O5^{ii}	0.84 (3)	1.97 (3)	2.790 (2)	167 (3)

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

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

References

Brandenburg, K. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Jiang, Y. M., Yin, Z., He, K. H., Zeng, M. H. & Kurmoo, M. (2011). *Inorg. Chem.* **50**, 2329–2333.
Li, T., Hu, S. M., Li, Z. H. & Du, S. W. (2006). *Chin. J. Struct. Chem.* **25**, 85–89.
Púčeková-Repická, Z., Moncol, J., Valigura, D., Lis, T., Korabik, M., Melník, M., Mroziński, J. & Mazúr, M. (2007). *J. Coord. Chem.* **60**, 2449–2460.
Rigaku (2007). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Valigura, D., Moncol, J., Korabik, M., Púčeková, Z., Lis, T., Mroziński, J. & Melník, M. (2006). *Eur. J. Inorg. Chem.* pp. 3813–3817.

supporting information

Diaquabis(2-hydroxy-5-methoxybenzoato-*κO*[1])zinc

Tao Li, Li-Rong Tang, Lin Yang and Biao Huang

S1. Comment

Generally, the self-assembly of inorganic metal species and organic ligands can be achieved by the use of noncovalent contacts. Among the noncovalent contacts, hydrogen bonds have the great influence in determining the geometry of the obtained metal complexes (Li *et al.* 2006; Jiang *et al.* 2011). In the other hand, the reactions of transition metal ions with 5-MeOSal ligands and its analogues are relatively rare (Valigura *et al.*, 2006; Púčeková-Repická *et al.*,2007). In this paper we present results of hydrothermal reactions of $ZnCl_2$ and 5-MeOSal ligand. Title Compound was isolated as molecular complex and the intermolecular O—H—O hydrogen bonds in (I) together with intramolecular O—H—O hydrogen bonds promote the molecules into two-dimensional structure.

A single-crystal X-ray diffraction study of (I) reveals a discrete coordination complex that crystallizes in the space group *C*2/*c*. Coordination of the Zn atoms in (I) is a slightly distorted tetrahedral geometry with each Zn atom bonding to four oxygen atoms, in which two from the monodentate 5-MeOSal ligands and two from the waters (Fig.1). Further inspection into the structure reveals that there are O—H—O intramolecular and intermolecular hydrogen bonds. (Table 1). As described in Figure 2, the intramolecular hydrogen bonds from hydroxyl hydrogen atom of the 5-MeOSal anions to the coordinated carboxylate oxygen atoms O3—H—O1 with the distance of 2.577 (1) Å, then create six-memberedrings(O_2C_3H), and stabilize the structure. The mean deviation from the planes C(2)—C(3)—C(4)—C(5)—C(6)-(7), and O(1)—H(13)—O(3)—C(3)—C(2)—C(1)are 0.0032 and 0.0229 Å,respectively. Furthermore the dihedral angles between planes is 0.9°, indicating a planar structure for this ligand. Furthermore the uncoordinated oxygen atoms of the carboxyl group and methoxy group of the 5-MeOSal anions(O2, O5) are hydrogen bonded with the hydrogen atoms of coordinated water with the distances of 2.643 (2) and 2.790 (2) Å, respectively. As a result every coordinated water molecule is connected by two oxygen atoms through hydrogen bonds and the isolated units are to be form a 2-D layer. A prospective view of the structure packing from *a* direction is presented in Fig. 3.

S2. Experimental

The title compound was hydrothermally synthesized under autogenous pressure. A mixture of $ZnCl_2$ (68 mg, 0.5 mmol), 5-MeOSal (84 mg, 0.5 mmol), and H_2O (6 ml) was sealed in a stainless reactor with Teflon liner, which was heated to 358 K for two days. After slow cooling to room temperature, prism pale yellow crystals were obtained as a major phase by filtration, which were washed with distilled water, and finally dried in air(65% yield).Anal. calc. for $C_{16}H_{18}O_{10}Zn$: C, 44.11; H, 4.16; O, 36.72%; Found: C, 44.32; H, 4.15; O, 36.23%. IR (KBr pellet):3448(*w*), 3290(*w*), 2839(*w*), 2615(*w*), 1661(*s*), 1616(*s*), 1486(*s*), 1428(*s*), 1223(*s*), 1188(*s*), 1033(*m*), 824(*m*), 788(*m*), 761(*m*), 678(*m*), 555(*m*), 464(*w*).

S3. Refinement

All the hydrogen atoms were discernible in the difference electron density maps. However, the H atoms were situated into idealized positions and constrained by the riding model approximation: O—H$_{hydroxyl}$ = 0.869, C$_{aryl}$—H$_{aryl}$ = 0.95, C$_{methyl}$—

$H_{methyl} = 0.98$ and $U_{iso}H_{aryl} = 1.2U_{eq}(C)$, $U_{iso}H_{methyl} = 1.5U_{eq}(C)$. The highest electron-density peak is situated 1.2 Å from Zn1 and the deepest hole 0.78 Å from Zn1.
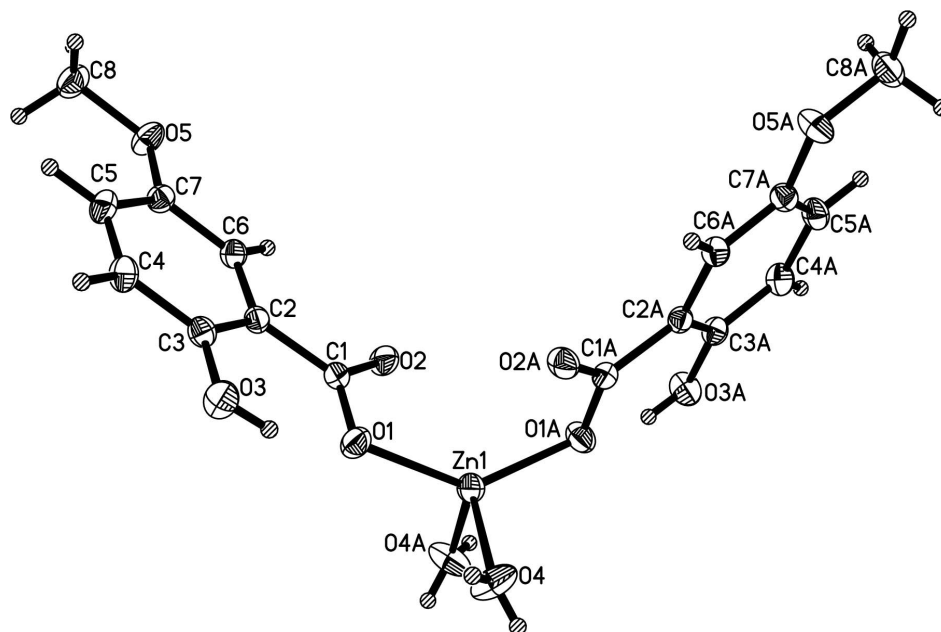

Figure 1

Displacement ellipsoids are drawn at the 30% probability level. ($-x$, y, $-z + 1/2$)
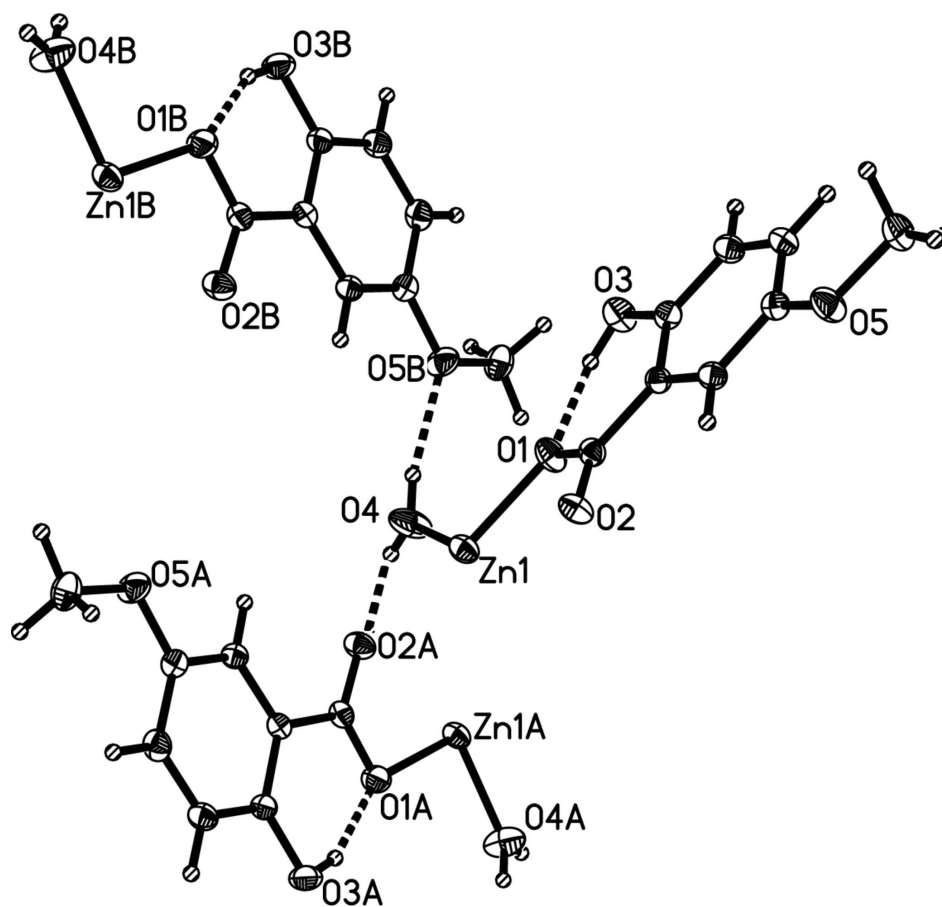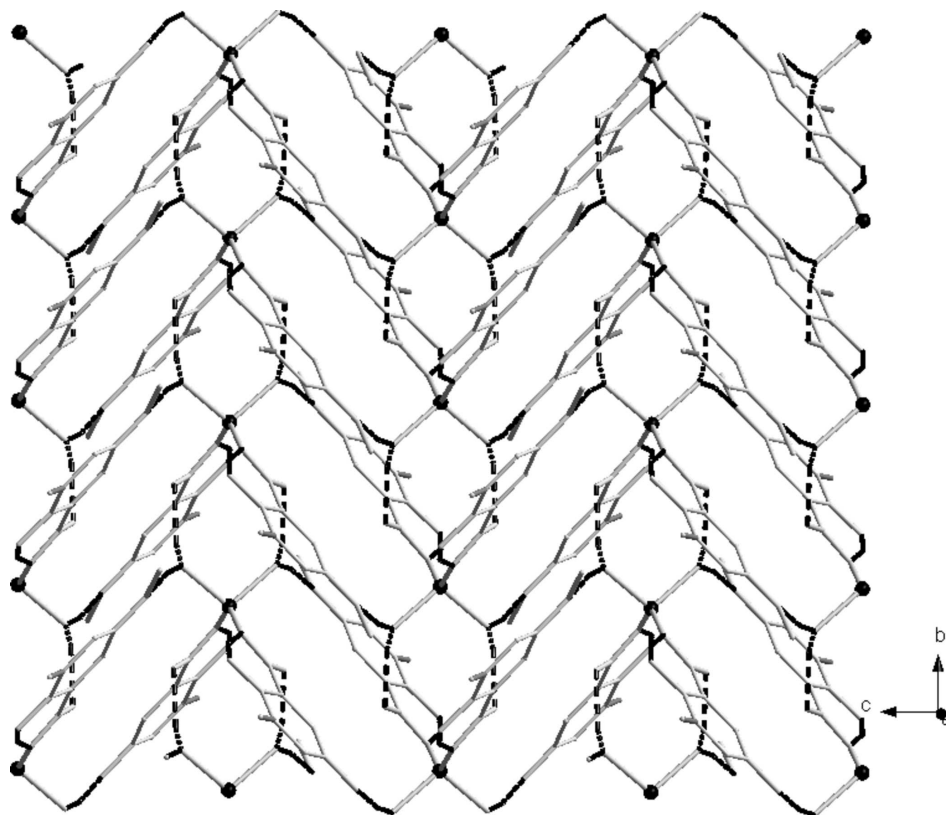
Figure 2

The intramolecular and intermoleclar hydrogen bonds (the dashed lines) in title compound. Symmetry codes: (A)x, $-y + 2$, $z + 1/2$; (B)x, $-y + 1$, $z + 1/2$.

Figure 3

The 2-D layer of title compound by O—H—O interactions (black dash lines) viewed from *a* direction.

Diaquabis(2-hydroxy-5-methoxybenzoato-*κO*¹)zinc(II)

Crystal data

$[Zn(C_8H_7O_4)_2(H_2O)_2]$	$F(000) = 896$
$M_r = 435.67$	$D_x = 1.670$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 2689 reflections
$a = 25.113$ (4) Å	$\theta = 2.1–27.5°$
$b = 5.5065$ (6) Å	$\mu = 1.47$ mm^{-1}
$c = 12.648$ (3) Å	$T = 173$ K
$\beta = 97.845$ (12)°	Prism, pale yellow
$V = 1732.7$ (5) Å^3	$0.20 \times 0.20 \times 0.20$ mm
$Z = 4$	

Data collection

Rigaku Mercury CCD/AFC diffractometer	6403 measured reflections
Radiation source: fine-focus sealed tube	1986 independent reflections
Graphite monochromator	1837 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.027$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2007)	$\theta_{max} = 27.5°$, $\theta_{min} = 3.3°$
	$h = -31 \rightarrow 32$
	$k = -7 \rightarrow 7$
$T_{min} = 0.745$, $T_{max} = 0.752$	$l = -16 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier
Least-squares matrix: full	map
$R[F^2 > 2\sigma(F^2)] = 0.030$	Hydrogen site location: inferred from
$wR(F^2) = 0.082$	neighbouring sites
$S = 1.08$	H atoms treated by a mixture of independent
1986 reflections	and constrained refinement
136 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant	$(\Delta/\sigma)_{max} = 0.001$
direct methods	$\Delta\rho_{max} = 0.27$ e Å^{-3}
	$\Delta\rho_{min} = -0.69$ e Å^{-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 (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
Zn1	0.0000	0.94430 (5)	0.2500	0.03390 (13)
O1	0.07205 (5)	0.8141 (2)	0.23289 (10)	0.0398 (3)
O2	0.01520 (5)	0.6023 (2)	0.12225 (11)	0.0379 (3)
O3	0.17146 (5)	0.6892 (3)	0.27805 (10)	0.0433 (3)
O4	0.02830 (7)	1.1674 (3)	0.36768 (14)	0.0556 (4)
O5	0.12868 (6)	−0.0192 (3)	−0.03081 (11)	0.0432 (3)
C1	0.06216 (6)	0.6401 (3)	0.16527 (12)	0.0294 (3)
C2	0.10816 (6)	0.4881 (3)	0.14311 (13)	0.0269 (3)
C3	0.15997 (7)	0.5201 (3)	0.19989 (13)	0.0301 (3)
C4	0.20140 (7)	0.3720 (4)	0.17747 (14)	0.0358 (4)
H4	0.2364	0.3946	0.2153	0.043*
C5	0.19295 (7)	0.1916 (3)	0.10108 (14)	0.0355 (4)
H5	0.2219	0.0912	0.0866	0.043*
C6	0.09982 (6)	0.3065 (3)	0.06567 (12)	0.0297 (3)
H6	0.0651	0.2848	0.0266	0.036*
C7	0.14159 (7)	0.1582 (3)	0.04532 (12)	0.0307 (3)
C8	0.17070 (8)	−0.1737 (4)	−0.05639 (16)	0.0470 (5)
H8A	0.1989	−0.0751	−0.0818	0.070*
H8B	0.1562	−0.2881	−0.1123	0.070*
H8C	0.1859	−0.2639	0.0074	0.070*
H1	0.1412 (11)	0.767 (5)	0.275 (2)	0.065 (8)*
H4A	0.0164 (10)	1.283 (5)	0.378 (2)	0.052 (7)*
H4B	0.0570 (12)	1.135 (6)	0.407 (2)	0.081 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02475 (17)	0.03398 (19)	0.0432 (2)	0.000	0.00526 (12)	0.000
O1	0.0334 (6)	0.0375 (7)	0.0492 (7)	−0.0006 (5)	0.0087 (5)	−0.0142 (5)
O2	0.0256 (6)	0.0363 (6)	0.0511 (7)	0.0028 (5)	0.0025 (5)	−0.0042 (5)
O3	0.0319 (7)	0.0497 (8)	0.0462 (7)	−0.0039 (6)	−0.0015 (6)	−0.0164 (6)
O4	0.0486 (9)	0.0465 (9)	0.0660 (10)	0.0189 (8)	−0.0124 (8)	−0.0210 (8)
O5	0.0393 (7)	0.0429 (7)	0.0464 (8)	0.0083 (6)	0.0020 (6)	−0.0165 (6)
C1	0.0283 (8)	0.0280 (8)	0.0330 (8)	−0.0011 (7)	0.0081 (6)	0.0022 (6)
C2	0.0244 (8)	0.0279 (7)	0.0288 (8)	−0.0005 (7)	0.0051 (6)	0.0021 (6)
C3	0.0277 (8)	0.0338 (8)	0.0287 (8)	−0.0039 (7)	0.0027 (6)	−0.0002 (6)
C4	0.0237 (8)	0.0458 (9)	0.0366 (8)	0.0012 (8)	−0.0002 (7)	0.0002 (7)
C5	0.0279 (8)	0.0418 (9)	0.0372 (8)	0.0090 (7)	0.0053 (7)	0.0016 (7)
C6	0.0251 (7)	0.0330 (8)	0.0302 (7)	−0.0006 (6)	0.0015 (6)	−0.0004 (6)
C7	0.0321 (8)	0.0309 (8)	0.0291 (7)	0.0017 (7)	0.0045 (6)	−0.0003 (6)
C8	0.0519 (12)	0.0448 (11)	0.0466 (10)	0.0112 (9)	0.0155 (9)	−0.0063 (8)

Geometric parameters (Å, º)

Zn1—O4	1.9852 (15)	C2—C6	1.395 (2)
Zn1—O4ⁱ	1.9852 (15)	C2—C3	1.409 (2)
Zn1—O1	1.9854 (13)	C3—C4	1.382 (2)
Zn1—O1ⁱ	1.9854 (13)	C4—C5	1.382 (3)
O1—C1	1.286 (2)	C4—H4	0.9500
O2—C1	1.247 (2)	C5—C7	1.395 (2)
O3—C3	1.360 (2)	C5—H5	0.9500
O3—H1	0.87 (3)	C6—C7	1.381 (2)
O4—H4A	0.73 (3)	C6—H6	0.9500
O4—H4B	0.84 (3)	C8—H8A	0.9800
O5—C7	1.379 (2)	C8—H8B	0.9800
O5—C8	1.427 (2)	C8—H8C	0.9800
C1—C2	1.484 (2)		
O4—Zn1—O4ⁱ	103.54 (11)	C4—C3—C2	119.37 (16)
O4—Zn1—O1	93.83 (6)	C3—C4—C5	121.33 (15)
O4ⁱ—Zn1—O1	112.34 (7)	C3—C4—H4	119.3
O4—Zn1—O1ⁱ	112.34 (7)	C5—C4—H4	119.3
O4ⁱ—Zn1—O1ⁱ	93.83 (6)	C4—C5—C7	119.43 (16)
O1—Zn1—O1ⁱ	137.66 (7)	C4—C5—H5	120.3
C1—O1—Zn1	104.20 (10)	C7—C5—H5	120.3
C3—O3—H1	102.2 (17)	C7—C6—C2	120.63 (14)
Zn1—O4—H4A	125 (2)	C7—C6—H6	119.7
Zn1—O4—H4B	120 (2)	C2—C6—H6	119.7
H4A—O4—H4B	115 (3)	O5—C7—C6	115.91 (14)
C7—O5—C8	118.04 (15)	O5—C7—C5	124.02 (15)
O2—C1—O1	120.00 (15)	C6—C7—C5	120.07 (15)
O2—C1—C2	122.53 (15)	O5—C8—H8A	109.5

O1—C1—C2	117.46 (14)	O5—C8—H8B	109.5
C6—C2—C3	119.16 (15)	H8A—C8—H8B	109.5
C6—C2—C1	119.38 (14)	O5—C8—H8C	109.5
C3—C2—C1	121.45 (15)	H8A—C8—H8C	109.5
O3—C3—C4	117.55 (15)	H8B—C8—H8C	109.5
O3—C3—C2	123.07 (16)		

Symmetry code: (i) −*x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1···O1	0.87 (3)	1.76 (3)	2.5771 (19)	155 (2)
O4—H4*A*···O2[ii]	0.73 (3)	1.93 (3)	2.643 (2)	169 (3)
O4—H4*B*···O5[iii]	0.84 (3)	1.97 (3)	2.790 (2)	167 (3)

Symmetry codes: (ii) −*x*, *y*+1, −*z*+1/2; (iii) *x*, −*y*+1, *z*+1/2.