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Bis(9-allyl-6-carboxy-9*H*-carbazole-3-carboxylato-$\kappa^2O^3,O^{3'}$)diaquazinc

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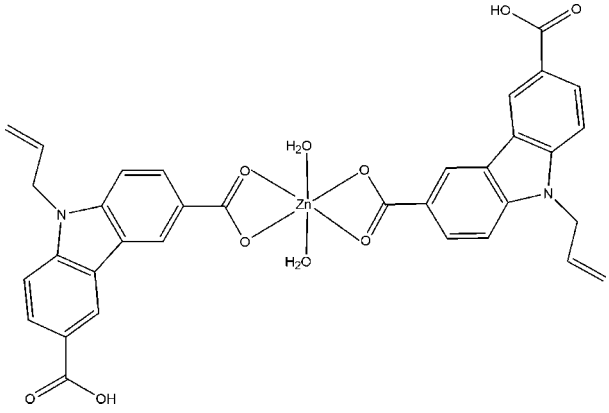
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.004 Å; R factor = 0.036; wR factor = 0.100; data-to-parameter ratio = 13.8.

In the title compound, $[Zn(C_{17}H_{12}NO_4)_2(H_2O)_2]$, the Zn^{II} atom is located on a twofold rotation axis and is six-coordinated by four carboxylate O atoms from two chelating 9-allyl-6-carboxy-9*H*-carbazole-3-carboxylate ligands and two O atoms from two water molecules. In the crystal, O—H···O hydrogen bonds link the molecules into a layer structure parallel to $(\bar{1}01)$.

Related literature

For the design and properties of complexes with supramolecular metal-organic framework structures, see: Li *et al.* (2011); Yang *et al.* (2007). For related structures, see: Wang *et al.* (2010).



Experimental

Crystal data

$[Zn(C_{17}H_{12}NO_4)_2(H_2O)_2]$
M_r = 689.95
Monoclinic, $C2/c$
a = 30.8562 (18) Å
b = 5.0491 (3) Å
c = 21.8915 (13) Å
β = 119.403 (1)°
V = 2971.3 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.89 mm^{-1}
T = 173 K
0.22 × 0.16 × 0.14 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.828, T_{max} = 0.885
7758 measured reflections
2942 independent reflections
2390 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.100
S = 1.02
2942 reflections
213 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected bond lengths (Å).

Zn1—O1	2.4040 (15)	Zn1—O1*W*	1.9824 (16)
Zn1—O2	2.0392 (15)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*A*···O4^{i}	0.84	1.81	2.654 (2)	177
O1*W*—H1*B*···O2^{ii}	0.85	1.88	2.728 (2)	170
O3—H3*A*···O1^{i}	0.87	1.77	2.634 (2)	173

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{5}{2}, -z+1$; (ii) $-x+1, y+1, -z+\frac{3}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL* and *Mercury* (Macrae *et al.*, 2006); 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: VN2058).

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supporting information

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Bis(9-allyl-6-carboxy-9*H*-carbazole-3-carboxylato-$\kappa^2O^3,O^{3'}$)diaquazinc

Dailin Li

S1. Comment

Crystal engineering based on metal-organic frameworks (MOFs) continues to attract considerable interest not only because of their intriguing variety of architectures but also for their potential functional properties, such as magnetism, nonlinear optics, hydrogen storage and catalysis (Li *et al.*, 2011; Yang *et al.*, 2007). Multifunctional ligands can link metal ions into one-, two- or three-dimensional structures. In order to extend the investigations in this field, we designed and synthesized the title zinc(II) compound and report here its structure.

The asymmetric unit of the title complex (Fig. 1) contains a Zn^{II} atom, one 9-allyl-9*H*-carbazole-6-carboxy-3-carboxylate ligand and one coordinated water molecule. The Zn^{II} atom, lying on a twofold rotation axis, is six-coordinated by four O atoms from two carboxylate ligands and two water molecules in an irregular geometry. The bond distances (Table 1) and angles are normal (Wang *et al.*, 2010). In the crystal structure, O—H···O hydrogen bonds (Table 2) link the complex molecules into a layer structure parellel to (-1 0 1) (Fig. 2).

S2. Experimental

The synthesis was performed under hydrothermal conditions. A mixture of 9-allyl-9*H*-carbazole-3,6-dicarboxylic acid (0.2 mmol, 0.062 g), $Zn(NO_3)_2.6H_2O$ (0.1 mmol, 0.030 g) and H_2O (15 ml) in a 25 ml stainless steel reactor with a Teflon liner was heated from 293 to 433 K in 2 h and maintained at 433 K for 72 h. Hereafter the mixture was cooled to 298 K, and colorless crystals of the title compound were obtained (yield: 59%).

S3. Refinement

All H atoms on C atoms were positioned geometrically and refined as riding atoms, with C—H = 0.95 and 0.99 Å and with U_{iso}(H) = 1.2U_{eq}(C). H atoms bonded to O atoms were located in a difference Fourier map and refined as riding, with U_{iso}(H) = 1.5U_{eq}(O). Reflection (2 0 0) was affected by the beamstop shadow and excluded from the refinement by an *OMIT* instruction.

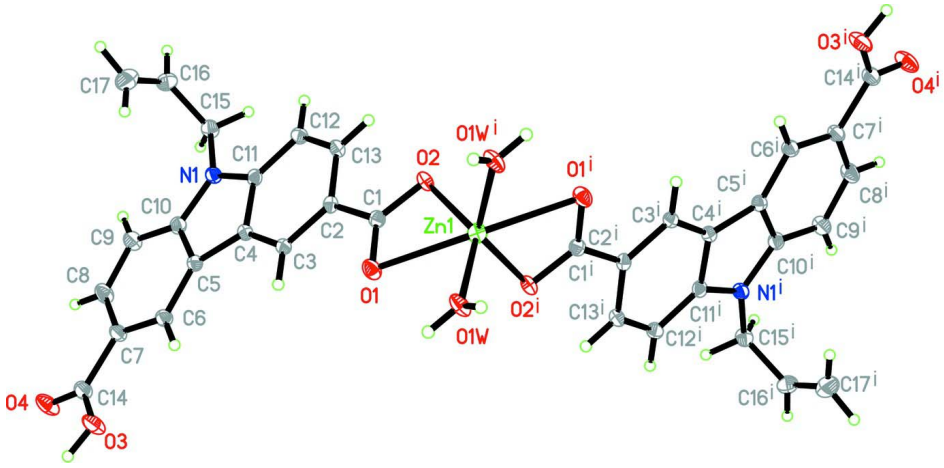

Figure 1

Molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) 1 - *x*, *y*, 3/2 - *z*.]

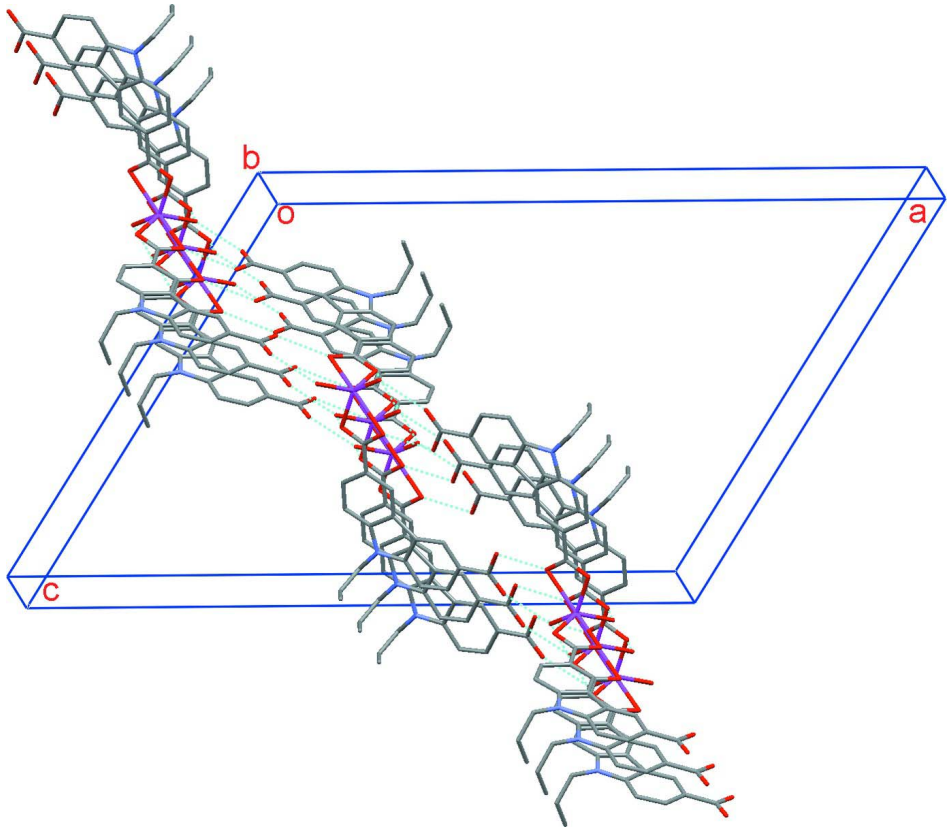

Figure 2

View of the layer structure in the title compound, built by hydrogen bonds (dashed lines).

Bis(9-allyl-6-carboxy-9*H*-carbazole-3-carboxylato- $\kappa^2O^3,O^{3'}$)diaquazinc

Crystal data

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Hall symbol: -C 2yc
$a = 30.8562$ (18) Å
$b = 5.0491$ (3) Å
$c = 21.8915$ (13) Å
$\beta = 119.403$ (1)°
$V = 2971.3$ (3) Å^3
$Z = 4$
$F(000) = 1424$
$D_x = 1.542$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3306 reflections
$\theta = 2.7$–$26.1°$
$\mu = 0.89$ mm^{-1}
$T = 173$ K
Block, colourless
0.22 × 0.16 × 0.14 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.828$, $T_{max} = 0.885$
7758 measured reflections
2942 independent reflections
2390 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 26.1°$, $\theta_{min} = 1.9°$
$h = -38 \rightarrow 37$
$k = -4 \rightarrow 6$
$l = -27 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.100$
$S = 1.02$
2942 reflections
213 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.5000	1.62460 (7)	0.7500	0.02411 (14)
C1	0.45216 (8)	1.3295 (4)	0.64103 (11)	0.0209 (5)
C2	0.43305 (8)	1.1274 (4)	0.58455 (11)	0.0208 (5)
C3	0.38251 (8)	1.0739 (4)	0.54621 (11)	0.0216 (5)

H3	0.3596	1.1705	0.5547	0.026*
C4	0.36580 (8)	0.8774 (4)	0.49528 (11)	0.0214 (5)
C5	0.31714 (8)	0.7713 (5)	0.44657 (11)	0.0225 (5)
C6	0.26914 (9)	0.8305 (5)	0.43223 (12)	0.0254 (5)
H6	0.2633	0.9672	0.4571	0.030*
C7	0.22985 (8)	0.6862 (5)	0.38084 (12)	0.0266 (5)
C8	0.23887 (9)	0.4838 (5)	0.34407 (13)	0.0330 (6)
H8	0.2115	0.3861	0.3095	0.040*
C9	0.28585 (9)	0.4234 (5)	0.35656 (13)	0.0316 (6)
H9	0.2915	0.2885	0.3310	0.038*
C10	0.32518 (9)	0.5698 (5)	0.40878 (11)	0.0251 (5)
C11	0.40064 (8)	0.7341 (5)	0.48402 (11)	0.0218 (5)
C12	0.45129 (8)	0.7873 (5)	0.52155 (11)	0.0255 (5)
H12	0.4743	0.6911	0.5132	0.031*
C13	0.46686 (8)	0.9849 (5)	0.57137 (11)	0.0245 (5)
H13	0.5013	1.0260	0.5975	0.029*
C14	0.17785 (9)	0.7384 (5)	0.36266 (12)	0.0297 (6)
C15	0.39846 (9)	0.3622 (5)	0.40603 (12)	0.0281 (5)
H15A	0.3796	0.1938	0.3946	0.034*
H15B	0.4327	0.3252	0.4441	0.034*
C16	0.40095 (10)	0.4511 (6)	0.34362 (13)	0.0386 (7)
H16	0.4190	0.3423	0.3285	0.046*
C17	0.38062 (11)	0.6661 (7)	0.30711 (15)	0.0517 (8)
H17A	0.3622	0.7812	0.3202	0.062*
H17B	0.3843	0.7069	0.2675	0.062*
N1	0.37548 (7)	0.5493 (4)	0.43157 (9)	0.0238 (4)
O1	0.42355 (6)	1.4699 (3)	0.65268 (8)	0.0284 (4)
O2	0.49925 (5)	1.3547 (3)	0.68019 (8)	0.0235 (4)
O3	0.17182 (6)	0.9470 (4)	0.39349 (9)	0.0400 (5)
H3A	0.1397	0.9621	0.3761	0.060*
O4	0.14358 (6)	0.6002 (4)	0.32174 (10)	0.0418 (5)
O1W	0.45497 (6)	1.8957 (3)	0.75397 (8)	0.0285 (4)
H1A	0.4237	1.9018	0.7291	0.043*
H1B	0.4664	2.0419	0.7755	0.043*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0264 (2)	0.0185 (2)	0.0267 (2)	0.000	0.01250 (18)	0.000
C1	0.0207 (12)	0.0198 (12)	0.0214 (11)	0.0020 (9)	0.0097 (9)	0.0046 (9)
C2	0.0213 (12)	0.0211 (12)	0.0170 (10)	0.0001 (9)	0.0072 (9)	0.0013 (9)
C3	0.0182 (11)	0.0258 (13)	0.0203 (11)	0.0023 (9)	0.0091 (9)	−0.0006 (9)
C4	0.0192 (11)	0.0231 (12)	0.0203 (11)	0.0007 (10)	0.0085 (9)	0.0003 (9)
C5	0.0199 (12)	0.0260 (13)	0.0200 (11)	−0.0011 (10)	0.0085 (9)	−0.0025 (10)
C6	0.0234 (12)	0.0278 (13)	0.0249 (12)	0.0009 (10)	0.0118 (10)	−0.0037 (10)
C7	0.0193 (12)	0.0304 (14)	0.0275 (12)	0.0006 (10)	0.0095 (10)	−0.0024 (10)
C8	0.0241 (13)	0.0347 (15)	0.0333 (13)	−0.0041 (12)	0.0087 (11)	−0.0099 (12)
C9	0.0267 (13)	0.0325 (15)	0.0316 (13)	0.0008 (11)	0.0112 (11)	−0.0095 (11)

C10	0.0254 (13)	0.0258 (13)	0.0231 (12)	0.0021 (10)	0.0111 (10)	−0.0015 (9)
C11	0.0224 (12)	0.0214 (12)	0.0199 (11)	0.0032 (10)	0.0092 (9)	0.0031 (9)
C12	0.0224 (12)	0.0303 (13)	0.0240 (11)	0.0052 (10)	0.0115 (10)	−0.0001 (10)
C13	0.0175 (11)	0.0293 (13)	0.0233 (11)	0.0010 (10)	0.0072 (9)	0.0016 (10)
C14	0.0243 (13)	0.0325 (14)	0.0298 (13)	0.0010 (11)	0.0115 (11)	−0.0028 (11)
C15	0.0287 (13)	0.0251 (13)	0.0299 (12)	0.0058 (11)	0.0140 (11)	−0.0020 (10)
C16	0.0380 (16)	0.0498 (18)	0.0353 (14)	0.0066 (14)	0.0236 (13)	−0.0029 (13)
C17	0.053 (2)	0.063 (2)	0.0472 (17)	0.0068 (16)	0.0314 (16)	0.0143 (16)
N1	0.0209 (10)	0.0261 (11)	0.0233 (10)	0.0026 (8)	0.0100 (8)	−0.0044 (8)
O1	0.0211 (9)	0.0290 (9)	0.0296 (9)	0.0026 (7)	0.0083 (7)	−0.0079 (7)
O2	0.0150 (8)	0.0241 (9)	0.0250 (8)	−0.0015 (7)	0.0047 (7)	−0.0010 (7)
O3	0.0206 (9)	0.0479 (12)	0.0461 (11)	0.0008 (8)	0.0122 (8)	−0.0178 (9)
O4	0.0200 (9)	0.0454 (12)	0.0514 (11)	−0.0048 (8)	0.0109 (8)	−0.0197 (9)
O1W	0.0164 (8)	0.0239 (9)	0.0367 (9)	−0.0017 (7)	0.0065 (7)	−0.0062 (7)

Geometric parameters (Å, º)

Zn1—O1	2.4040 (15)	C9—H9	0.9500
Zn1—O2	2.0392 (15)	C10—N1	1.381 (3)
Zn1—O1W	1.9824 (16)	C11—N1	1.385 (3)
C1—O1	1.252 (3)	C11—C12	1.389 (3)
C1—O2	1.281 (3)	C12—C13	1.379 (3)
C1—C2	1.484 (3)	C12—H12	0.9500
C2—C3	1.387 (3)	C13—H13	0.9500
C2—C13	1.409 (3)	C14—O4	1.216 (3)
C3—C4	1.389 (3)	C14—O3	1.313 (3)
C3—H3	0.9500	C15—N1	1.448 (3)
C4—C11	1.414 (3)	C15—C16	1.475 (3)
C4—C5	1.452 (3)	C15—H15A	0.9900
C5—C6	1.387 (3)	C15—H15B	0.9900
C5—C10	1.408 (3)	C16—C17	1.311 (4)
C6—C7	1.388 (3)	C16—H16	0.9500
C6—H6	0.9500	C17—H17A	0.9500
C7—C8	1.410 (3)	C17—H17B	0.9500
C7—C14	1.475 (3)	O3—H3A	0.8721
C8—C9	1.371 (3)	O1W—H1A	0.8438
C8—H8	0.9500	O1W—H1B	0.8534
C9—C10	1.401 (3)		

O1W—Zn1—O1W^{i}	92.67 (10)	C5—C6—H6	120.6
O1W—Zn1—O2	138.07 (6)	C7—C6—H6	120.6
O1W^{i}—Zn1—O2	100.30 (6)	C6—C7—C8	120.3 (2)
O1W—Zn1—O2^{i}	100.30 (6)	C6—C7—C14	121.8 (2)
O1W^{i}—Zn1—O2^{i}	138.07 (6)	C8—C7—C14	117.9 (2)
O2—Zn1—O2^{i}	96.14 (9)	C9—C8—C7	122.2 (2)
O1W—Zn1—O1^{i}	126.12 (6)	C9—C8—H8	118.9
O1W^{i}—Zn1—O1^{i}	81.91 (6)	C7—C8—H8	118.9
O2—Zn1—O1^{i}	95.28 (6)	C8—C9—C10	116.9 (2)

O2^{i}—Zn1—O1^{i}	58.24 (6)	C8—C9—H9	121.5
O1W—Zn1—O1	81.91 (6)	C10—C9—H9	121.5
O1W^{i}—Zn1—O1	126.12 (6)	N1—C10—C9	128.6 (2)
O2—Zn1—O1	58.24 (6)	N1—C10—C5	109.44 (19)
O2^{i}—Zn1—O1	95.28 (6)	C9—C10—C5	121.9 (2)
O1^{i}—Zn1—O1	142.07 (8)	N1—C11—C12	129.1 (2)
O1W—Zn1—C1^{i}	117.02 (7)	N1—C11—C4	108.95 (19)
O1W^{i}—Zn1—C1^{i}	110.17 (7)	C12—C11—C4	121.9 (2)
O2—Zn1—C1^{i}	95.62 (6)	C13—C12—C11	117.5 (2)
O2^{i}—Zn1—C1^{i}	29.40 (6)	C13—C12—H12	121.3
O1^{i}—Zn1—C1^{i}	28.87 (6)	C11—C12—H12	121.3
O1—Zn1—C1^{i}	119.98 (7)	C12—C13—C2	121.7 (2)
O1W—Zn1—C1	110.17 (7)	C12—C13—H13	119.1
O1W^{i}—Zn1—C1	117.01 (7)	C2—C13—H13	119.1
O2—Zn1—C1	29.39 (6)	O4—C14—O3	123.2 (2)
O2^{i}—Zn1—C1	95.62 (7)	O4—C14—C7	122.3 (2)
O1^{i}—Zn1—C1	119.98 (6)	O3—C14—C7	114.5 (2)
O1—Zn1—C1	28.87 (6)	N1—C15—C16	114.6 (2)
C1^{i}—Zn1—C1	109.29 (10)	N1—C15—H15A	108.6
O1—C1—O2	119.3 (2)	C16—C15—H15A	108.6
O1—C1—C2	121.8 (2)	N1—C15—H15B	108.6
O2—C1—C2	118.8 (2)	C16—C15—H15B	108.6
O1—C1—Zn1	67.95 (12)	H15A—C15—H15B	107.6
O2—C1—Zn1	51.41 (10)	C17—C16—C15	126.1 (3)
C2—C1—Zn1	169.20 (16)	C17—C16—H16	116.9
C3—C2—C13	120.1 (2)	C15—C16—H16	116.9
C3—C2—C1	120.5 (2)	C16—C17—H17A	120.0
C13—C2—C1	119.4 (2)	C16—C17—H17B	120.0
C2—C3—C4	119.3 (2)	H17A—C17—H17B	120.0
C2—C3—H3	120.4	C10—N1—C11	108.79 (18)
C4—C3—H3	120.4	C10—N1—C15	125.86 (19)
C3—C4—C11	119.4 (2)	C11—N1—C15	125.34 (19)
C3—C4—C5	134.1 (2)	C1—O1—Zn1	83.19 (13)
C11—C4—C5	106.49 (19)	C1—O2—Zn1	99.20 (13)
C6—C5—C10	119.9 (2)	C14—O3—H3A	105.3
C6—C5—C4	133.7 (2)	Zn1—O1W—H1A	126.9
C10—C5—C4	106.33 (19)	Zn1—O1W—H1B	120.8
C5—C6—C7	118.7 (2)	H1A—O1W—H1B	110.9

Symmetry code: (i) $-x+1, y, -z+3/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*A*···O4^{ii}	0.84	1.81	2.654 (2)	177
O1*W*—H1*B*···O2^{iii}	0.85	1.88	2.728 (2)	170
O3—H3*A*···O1^{ii}	0.87	1.77	2.634 (2)	173

Symmetry codes: (ii) $-x+1/2, -y+5/2, -z+1$; (iii) $-x+1, y+1, -z+3/2$.