

# {2,2'-[(1,2-Dicyanoethene-1,2-diyl)bis-(nitrilomethanylylidene)]diphenolato- $\kappa^4O,N,N',O'$ }(methanol- $\kappa O$ )zinc

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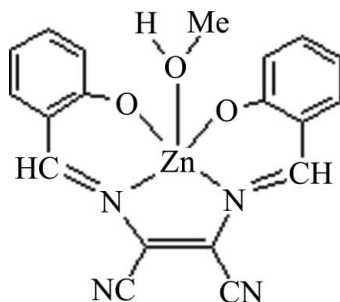
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 Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(C-C) = 0.005$  Å; disorder in main residue;  $R$  factor = 0.036;  $wR$  factor = 0.104; data-to-parameter ratio = 12.1.

In the title complex,  $[Zn(C_{18}H_{10}N_4O_2)(CH_4O)]$ , the  $Zn^{2+}$  cation is located on a mirror plane and is coordinated by a tetradentate Schiff base ligand anion ( $L^{2-}$ ) and a methanol molecule. The  $Zn^{2+}$  cation is surrounded by two N atoms and two O atoms from  $L^{2-}$ , in a nearly planar configuration, and one methanol O atom, forming a slightly distorted square-pyramidal geometry. The methanol molecule is disordered over two sets of sites in a 0.5:0.5 ratio. In the crystal, O—H...O hydrogen bonds link the molecules into chains parallel to [001].

## Related literature

For background to tetradentate Schiff-base complexes of transition metal ions, see: Bottcher *et al.* (1997); Mukherjee *et al.* (2008).



## Experimental

### Crystal data

$[Zn(C_{18}H_{10}N_4O_2)(CH_4O)]$	$V = 1805.2 (4) \text{ \AA}^3$
$M_r = 411.71$	$Z = 4$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 18.052 (2) \text{ \AA}$	$\mu = 1.39 \text{ mm}^{-1}$
$b = 19.846 (2) \text{ \AA}$	$T = 293 \text{ K}$
$c = 5.0388 (6) \text{ \AA}$	$0.20 \times 0.15 \times 0.10 \text{ mm}$

### Data collection

Bruker APEXII diffractometer	5185 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 1999)	1608 independent reflections
$T_{\min} = 0.769$ , $T_{\max} = 0.874$	1090 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.044$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	12 restraints
$wR(F^2) = 0.104$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{\max} = 0.39 \text{ e \AA}^{-3}$
1608 reflections	$\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$
133 parameters	

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O2-H2\cdots O1^i$	0.93	1.85	2.776 (5)	178

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: publCIF (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JJ2167).

## References

- Bottcher, A., Takeuchi, T., Hardcastle, K. I., Meade, T. J., Gray, H. B., Cwikel, D. & Kapon, M. (1997). *Inorg. Chem.* **36**, 2498–2504.
- Bruker (1999). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2009). SAINT and APEX2. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Mukherjee, P., Drew, M. G. B., Estrader, M., Diaz, C. & Ghosh, A. (2008). *Inorg. Chim. Acta*, **361**, 161–172.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

## supporting information

*Acta Cryst.* (2013). E69, m419 [https://doi.org/10.1107/S1600536813016863]

**{2,2'-[(1,2-Dicyanoethene-1,2-diyl)bis(nitrilomethanylylidene)]diphenolato- $\kappa^4$ O,N,N',O'}(methanol- $\kappa$ O)zinc**

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### S1. Comment

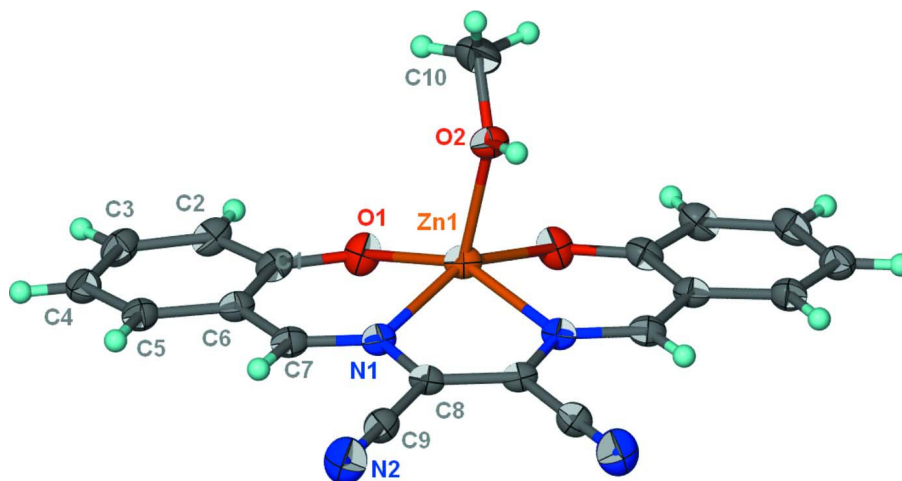
The title complex is an example of a tetradentate Schiff-base group coordinated to a transition metal ion (Bottcher *et al.*, 1997; Mukherjee *et al.*, 2008). It consists of a Zn<sup>2+</sup> ion, coordinated to a Schiff-base ligand ion ( $L^{2-}$ ), and a CH<sub>3</sub>OH molecule (Fig. 1). The zinc ion, located on an inversion center is surrounded by two nitrogen atoms and two oxygen atoms from  $L^{2-}$ , and one oxygen atom from CH<sub>3</sub>OH molecule which upon symmetry expansion forms a slightly distorted quadrangular pyramid configuration. In the crystal, O—H $\cdots$ O hydrogen bonds (Table 1) link the molecules into one-dimensional chains (Fig. 2).

### S2. Experimental

To a solution, containing 2,3-bis(2-hydroxybenzylideneimino)-2,3-butenedinitrile (H<sub>2</sub>L)(0.948 g, 3 mmol) and triethylamine (0.600 g, 6 mmol) in methanol (30 ml), Zn(CH<sub>3</sub>CO<sub>2</sub>) $\cdot$ 2H<sub>2</sub>O(0.659 g, 3 mmol) was added and the mixture was stirred for 15 min. The solution was allowed to slowly evaporate, affording brown crystals, which were collected and dried *in vacuo* (0.786 g, 68%). Calcd for C<sub>19</sub>H<sub>14</sub>ZnN<sub>4</sub>O<sub>3</sub>: C, 55.38; H, 3.40; N, 13.60. Found: C, 56.19; H, 3.55; N, 13.81.

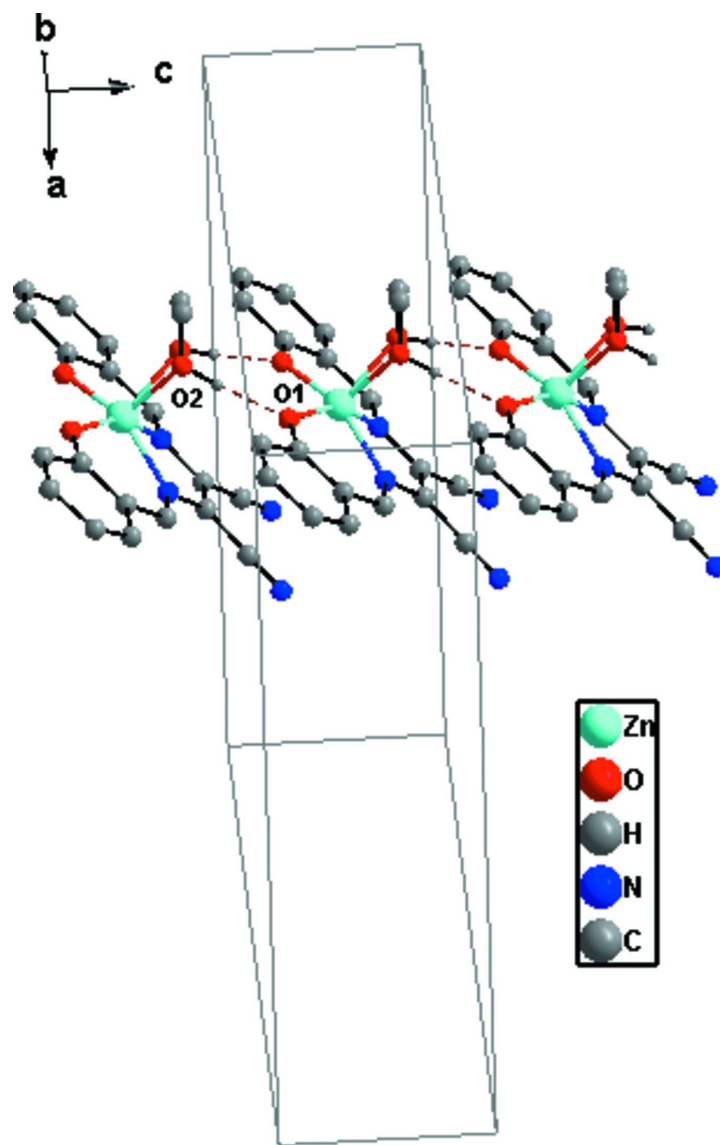
### S3. Refinement

H atoms were positioned geometrically and refined using a riding model, with C-H = 0.93-0.97 Å and with  $U_{\text{iso}}(\text{H}) = 1.2$  (1.5 for methyl groups) times  $U_{\text{eq}}(\text{C})$ . The C and O atoms of methano (C10, O2) are disordered over two positions (0.50:0.50). The geometric parameters of two disordered components in each group were restrained by using SADI restraints and ISOR constraints. The bond lengths of the disordered atoms were restrained by using DFIX. All non-hydrogen atoms were treated anisotropically.



**Figure 1**

Ortep view of the title compound, at the 30% probability level.



**Figure 2**

Packing diagram of the title compound viewed along the *b* axis. Dashed lines indicate O2—H2...O1 hydrogen bonds.

$\{2,2'-[(1,2\text{-Dicyanoethene-1,2-diyl})\text{bis}(\text{nitrilomethanylylidene})]\text{diphenolato-}\kappa^4\text{O},\text{N},\text{N}',\text{O}'\}(\text{methanol-}\kappa\text{O})\text{zinc}$

*Crystal data*

$[\text{Zn}(\text{C}_{18}\text{H}_{10}\text{N}_4\text{O}_2)(\text{CH}_4\text{O})]$

$M_r = 411.71$

Orthorhombic, *Pnma*

Hall symbol:  $-P\ 2ac\ 2n$

$a = 18.052\ (2)\ \text{\AA}$

$b = 19.846\ (2)\ \text{\AA}$

$c = 5.0388\ (6)\ \text{\AA}$

$V = 1805.2\ (4)\ \text{\AA}^3$

$Z = 4$

$F(000) = 840$

$D_x = 1.515\ \text{Mg m}^{-3}$

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

Cell parameters from 5185 reflections

$\theta = 2.1\text{--}25^\circ$

$\mu = 1.39\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, orange

$0.2 \times 0.15 \times 0.1\ \text{mm}$

Data collection

Bruker APEXII diffractometer	5185 measured reflections
Radiation source: fine-focus sealed tube	1608 independent reflections
Graphite monochromator	1090 reflections with $I > 2\sigma(I)$
Detector resolution: 0.8409 pixels mm <sup>-1</sup>	$R_{\text{int}} = 0.044$
$\omega$ scan	$\theta_{\text{max}} = 25.0^\circ$ , $\theta_{\text{min}} = 2.1^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$h = -19 \rightarrow 21$
$T_{\text{min}} = 0.769$ , $T_{\text{max}} = 0.874$	$k = -20 \rightarrow 23$
	$l = -3 \rightarrow 5$

Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.036$	H-atom parameters constrained
$wR(F^2) = 0.104$	$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
1608 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
133 parameters	$\Delta\rho_{\text{max}} = 0.39 \text{ e } \text{Å}^{-3}$
12 restraints	$\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{Å}^{-3}$
Primary atom site location: structure-invariant direct methods	

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 ( $\text{Å}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Zn1	0.36935 (3)	0.7500	0.52857 (11)	0.0500 (2)	
O1	0.34404 (15)	0.67853 (13)	0.2792 (5)	0.0617 (7)	
O2	0.2889 (2)	0.7701 (2)	0.8065 (9)	0.0519 (16)	0.50
H2	0.3085	0.7877	0.9624	0.062*	0.50
N1	0.44377 (14)	0.68348 (14)	0.7145 (5)	0.0450 (7)	
N2	0.5754 (2)	0.64994 (18)	1.2118 (8)	0.0825 (11)	
C1	0.3527 (2)	0.61308 (19)	0.3065 (7)	0.0520 (9)	
C2	0.3159 (2)	0.5695 (2)	0.1276 (8)	0.0611 (11)	
H2A	0.2857	0.5879	-0.0032	0.073*	
C3	0.3233 (2)	0.5009 (2)	0.1413 (8)	0.0634 (11)	
H3	0.2987	0.4739	0.0188	0.076*	
C4	0.3672 (2)	0.4708 (2)	0.3366 (8)	0.0603 (10)	
H4	0.3712	0.4242	0.3466	0.072*	
C5	0.4036 (2)	0.51024 (18)	0.5092 (8)	0.0552 (9)	
H5	0.4330	0.4901	0.6382	0.066*	
C6	0.39885 (19)	0.58166 (19)	0.5023 (7)	0.0489 (9)	

C7	0.44203 (19)	0.61794 (19)	0.6914 (7)	0.0509 (9)	
H7	0.4712	0.5930	0.8074	0.061*	
C8	0.49009 (18)	0.71569 (16)	0.8927 (6)	0.0439 (8)	
C9	0.5382 (2)	0.67901 (18)	1.0708 (8)	0.0528 (9)	
C10	0.2165 (4)	0.7640 (8)	0.8168 (19)	0.090 (4)	0.50
H10A	0.2010	0.7610	0.9987	0.135*	0.50
H10B	0.2017	0.7240	0.7239	0.135*	0.50
H10C	0.1939	0.8026	0.7354	0.135*	0.50

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.0500 (4)	0.0662 (4)	0.0338 (3)	0.000	-0.0057 (3)	0.000
O1	0.0808 (18)	0.0637 (17)	0.0407 (15)	-0.0081 (13)	-0.0153 (13)	0.0054 (13)
O2	0.047 (2)	0.069 (5)	0.040 (2)	-0.006 (2)	-0.003 (2)	-0.005 (2)
N1	0.0451 (16)	0.0554 (18)	0.0346 (16)	-0.0042 (13)	-0.0033 (13)	-0.0055 (14)
N2	0.086 (3)	0.081 (2)	0.080 (3)	0.000 (2)	-0.034 (2)	0.016 (2)
C1	0.053 (2)	0.066 (2)	0.037 (2)	-0.0128 (17)	0.0024 (17)	-0.0018 (19)
C2	0.066 (3)	0.072 (3)	0.045 (2)	-0.016 (2)	-0.005 (2)	0.000 (2)
C3	0.068 (3)	0.071 (3)	0.052 (2)	-0.022 (2)	0.001 (2)	-0.010 (2)
C4	0.056 (2)	0.060 (2)	0.064 (3)	-0.005 (2)	0.005 (2)	-0.009 (2)
C5	0.0480 (19)	0.062 (2)	0.056 (2)	-0.0038 (17)	-0.0036 (19)	-0.002 (2)
C6	0.0430 (17)	0.062 (2)	0.042 (2)	-0.0059 (16)	0.0011 (17)	-0.0050 (19)
C7	0.045 (2)	0.065 (2)	0.043 (2)	-0.0025 (17)	0.0014 (18)	0.0003 (19)
C8	0.0398 (18)	0.0580 (18)	0.0338 (18)	0.0036 (15)	-0.0024 (16)	-0.0016 (16)
C9	0.053 (2)	0.058 (2)	0.048 (2)	-0.0058 (18)	-0.0068 (19)	-0.0028 (19)
C10	0.064 (4)	0.095 (10)	0.111 (6)	0.017 (5)	0.001 (4)	-0.004 (6)

*Geometric parameters (Å, °)*

Zn1—O1	1.949 (2)	C2—H2A	0.9300
Zn1—O1 <sup>i</sup>	1.949 (2)	C3—C4	1.398 (5)
Zn1—O2	2.057 (4)	C3—H3	0.9300
Zn1—O2 <sup>i</sup>	2.057 (4)	C4—C5	1.341 (5)
Zn1—N1 <sup>i</sup>	2.104 (3)	C4—H4	0.9300
Zn1—N1	2.104 (3)	C5—C6	1.420 (5)
O1—C1	1.315 (4)	C5—H5	0.9300
O2—C10	1.313 (8)	C6—C7	1.426 (5)
O2—H2	0.9300	C7—H7	0.9300
N1—C7	1.306 (4)	C8—C8 <sup>i</sup>	1.362 (6)
N1—C8	1.383 (4)	C8—C9	1.445 (5)
N2—C9	1.135 (5)	C10—H10A	0.9600
C1—C2	1.416 (5)	C10—H10B	0.9600
C1—C6	1.434 (5)	C10—H10C	0.9600
C2—C3	1.369 (5)		
O1—Zn1—O1 <sup>i</sup>	93.38 (15)	C1—C2—H2A	119.0
O1—Zn1—O2	114.48 (14)	C2—C3—C4	121.1 (4)

O1 <sup>i</sup> —Zn1—O2	97.60 (14)	C2—C3—H3	119.5
O1—Zn1—O2 <sup>i</sup>	97.60 (14)	C4—C3—H3	119.5
O1 <sup>i</sup> —Zn1—O2 <sup>i</sup>	114.48 (14)	C5—C4—C3	119.0 (4)
O2—Zn1—O2 <sup>i</sup>	22.4 (2)	C5—C4—H4	120.5
O1—Zn1—N1 <sup>i</sup>	153.31 (12)	C3—C4—H4	120.5
O1 <sup>i</sup> —Zn1—N1 <sup>i</sup>	88.86 (10)	C4—C5—C6	122.5 (4)
O2—Zn1—N1 <sup>i</sup>	91.51 (14)	C4—C5—H5	118.8
O2 <sup>i</sup> —Zn1—N1 <sup>i</sup>	105.64 (14)	C6—C5—H5	118.8
O1—Zn1—N1	88.86 (10)	C5—C6—C7	117.0 (3)
O1 <sup>i</sup> —Zn1—N1	153.31 (12)	C5—C6—C1	119.1 (3)
O2—Zn1—N1	105.64 (14)	C7—C6—C1	123.9 (3)
O2 <sup>i</sup> —Zn1—N1	91.51 (14)	N1—C7—C6	125.1 (3)
N1 <sup>i</sup> —Zn1—N1	77.74 (15)	N1—C7—H7	117.4
C1—O1—Zn1	128.6 (2)	C6—C7—H7	117.4
C10—O2—Zn1	135.4 (6)	C8 <sup>i</sup> —C8—N1	117.52 (18)
C10—O2—H2	112.3	C8 <sup>i</sup> —C8—C9	120.23 (18)
Zn1—O2—H2	112.3	N1—C8—C9	122.2 (3)
C7—N1—C8	122.2 (3)	N2—C9—C8	179.3 (4)
C7—N1—Zn1	124.7 (2)	O2—C10—H10A	109.5
C8—N1—Zn1	112.6 (2)	O2—C10—H10B	109.5
O1—C1—C2	118.8 (3)	H10A—C10—H10B	109.5
O1—C1—C6	124.8 (3)	O2—C10—H10C	109.5
C2—C1—C6	116.4 (4)	H10A—C10—H10C	109.5
C3—C2—C1	122.0 (4)	H10B—C10—H10C	109.5
C3—C2—H2A	119.0		
O1 <sup>i</sup> —Zn1—O1—C1	174.4 (2)	O1—C1—C2—C3	178.9 (4)
O2—Zn1—O1—C1	-85.6 (3)	C6—C1—C2—C3	0.5 (6)
O2 <sup>i</sup> —Zn1—O1—C1	-70.3 (3)	C1—C2—C3—C4	0.9 (6)
N1 <sup>i</sup> —Zn1—O1—C1	80.2 (4)	C2—C3—C4—C5	-1.3 (6)
N1—Zn1—O1—C1	21.1 (3)	C3—C4—C5—C6	0.3 (6)
O1—Zn1—O2—C10	-27.0 (11)	C4—C5—C6—C7	-178.1 (3)
O1 <sup>i</sup> —Zn1—O2—C10	70.3 (10)	C4—C5—C6—C1	1.0 (5)
O2 <sup>i</sup> —Zn1—O2—C10	-70.5 (10)	O1—C1—C6—C5	-179.7 (3)
N1 <sup>i</sup> —Zn1—O2—C10	159.3 (10)	C2—C1—C6—C5	-1.4 (5)
N1—Zn1—O2—C10	-123.0 (10)	O1—C1—C6—C7	-0.7 (6)
O1—Zn1—N1—C7	-19.1 (3)	C2—C1—C6—C7	177.6 (3)
O1 <sup>i</sup> —Zn1—N1—C7	-114.4 (3)	C8—N1—C7—C6	-176.3 (3)
O2—Zn1—N1—C7	96.0 (3)	Zn1—N1—C7—C6	11.9 (5)
O2 <sup>i</sup> —Zn1—N1—C7	78.5 (3)	C5—C6—C7—N1	-179.3 (3)
N1 <sup>i</sup> —Zn1—N1—C7	-175.9 (2)	C1—C6—C7—N1	1.7 (5)
O1—Zn1—N1—C8	168.4 (2)	C7—N1—C8—C8 <sup>i</sup>	177.1 (2)
O1 <sup>i</sup> —Zn1—N1—C8	73.1 (3)	Zn1—N1—C8—C8 <sup>i</sup>	-10.2 (2)
O2—Zn1—N1—C8	-76.4 (2)	C7—N1—C8—C9	-1.8 (5)
O2 <sup>i</sup> —Zn1—N1—C8	-94.0 (2)	Zn1—N1—C8—C9	170.9 (3)
N1 <sup>i</sup> —Zn1—N1—C8	11.7 (2)	C8 <sup>i</sup> —C8—C9—N2	119 (38)

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Zn1—O1—C1—C2	166.1 (3)	N1—C8—C9—N2	-62 (38)
Zn1—O1—C1—C6	-15.6 (5)		

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

*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

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$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 $\cdots$ O1 <sup>ii</sup>	0.93	1.85	2.776 (5)	178

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