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Crystal structure of bis(1,3-diaminopropane-κ^2N,N')bis[2-(4-nitrophenyl)acetato-κO]zinc(II)

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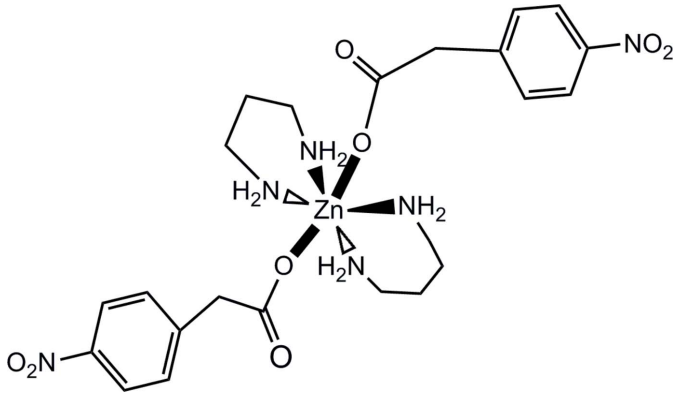
In the structure of the title compound, $[Zn(C_8H_6NO_4)_2(C_3H_{10}N_2)_2]$, the Zn^{II} atom is located on a center of symmetry with one independent Zn—O distance of 2.199 (2) Å, and two Zn—N distances of 2.157 (2) and 2.144 (2) Å. The overall coordination geometry around the Zn^{II} atom is octahedral. Several types of hydrogen-bonding interactions are evident. Both intramolecular [2.959 (3) Å] and intermolecular [3.118 (3) and 3.124 (3) Å interactions occur between the O atoms of the acetate group and the amino N atoms, and weak intermolecular C—H—O interactions involving the nitro groups, leading to an extended chain of the molecules aligned along the *ac* plane.

Keywords: crystal structure; zinc complex; coordination.

CCDC reference: 1438434

1. Related literature

For related polymeric Zn^{II} tetrahedral structural studies, see: Sheng *et al.* (2014).



2. Experimental

2.1. Crystal data

$[Zn(C_8H_6NO_4)_2(C_3H_{10}N_2)_2]$
M_r = 573.91
Monoclinic, $P2_1/c$
a = 14.3933 (18) Å
b = 11.0261 (14) Å
c = 8.2453 (11) Å
β = 105.119 (13)°
V = 1263.3 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.03 mm^{-1}
T = 180 K
0.24 × 0.21 × 0.08 mm

2.2. Data collection

Agilent Xcalibur, Eos diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min} = 0.952, T_{max} = 1.000
5782 measured reflections
2243 independent reflections
1858 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.075
S = 1.06
2243 reflections
169 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···O2	0.90	2.14	2.959 (3)	150
N1—H1A···O2^{i}	0.90	2.26	3.118 (3)	158
N2—H2D···O2^{ii}	0.90	2.25	3.124 (3)	165
C10—H10A···O4^{iii}	0.97	2.70	3.634 (3)	161
C7—H7···O3^{iv}	0.93	2.46	3.209 (3)	138

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

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *Olex2.solve* (Bourhis *et al.*, 2015); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

Acknowledgements

The Innovation Venture grant provided by the College of Arts and Sciences for curriculum development at NCAT is kindly acknowledged (ZA). The authors also acknowledge support from the National Science Foundation, CHE-0959406 (ZA) and CHE-0846680 (RES).

Supporting information for this paper is available from the IUCr electronic archives (Reference: HG5460).

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supporting information

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T. J. Roberts, T. F. Mehari, Z. Assefa, T. Hamby and R. E. Sykora

S1. Chemical context

The structure shows a weak N—H···O intramolecular H-bonding interaction involving a N atom of the diaminopropane ligand and an O atom of the nitrophenylacetic acid ligand. Additional intermolecular N—H···O H-bonding interactions involving these same ligands are also present. Several weak intermolecular H-bonding interactions of the C—H—O type also exist involving the nitro groups and neigbouring phenyl protons. The asymmetric unit consist of half of the molecule as the Zn atom is located at center of symmetry.

S2. Structural commentary

The structure shows a weak H-bond intramolecular N—H···O interaction involving the N atoms of the diaminopropane ligand and the O atoms of nitrophenylacetic acid ligand. Several weak intermolecular H-bonding interactions of the C—H—O type also exist involving the nitro groups and neigbouring C—H protons. The asymmetric unit consist of half of the molecule as the Zn atom is located at center of symmetry.

S3. Supramolecular features

H-atoms were placed in calculated positions and allowed to ride during subsequent refinement, with U_{iso}(H) = 1.2U_{eq}(C) and C—H distances of 0.93 Å for aromatic hydrogens, U_{iso}(H) = 1.2U_{eq}(C) and C—H distances of 0.97 Å for secondary methyl hydrogens, and U_{iso}(H) = 1.2U_{eq}(N) and N—H distances of 0.90 Å for amino hydrogens.

S4. Synthesis and crystallization

Undergraduate student participants enrolled in an open inquiry laboratory (OIL) course conducted the synthesis and charcterization procedures. 0.2 mmol (27.2 mg) of anhydrous $ZnCl_2$, 0.4 mmol (29.7 mg) of 1,3-diaminopropane, and 0.4 mmol (72.5 mg) of 4- nitrophenylacetic acid were weighed and added into a 25-mL round-bottom flask containing 10 mL of 1:1 CH_3CN/H_2O mixture. The flask was connected to a condenser and placed on a sand bath and refluxed for 1 hr. The flask was then removed from the sandbath and cooled to room temperature. After filtering the solution, the clear supernatant was collected, and covered with a parafilm for slow evaporation. Single crystals suitable for X-ray measurement were found after several days.

S5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

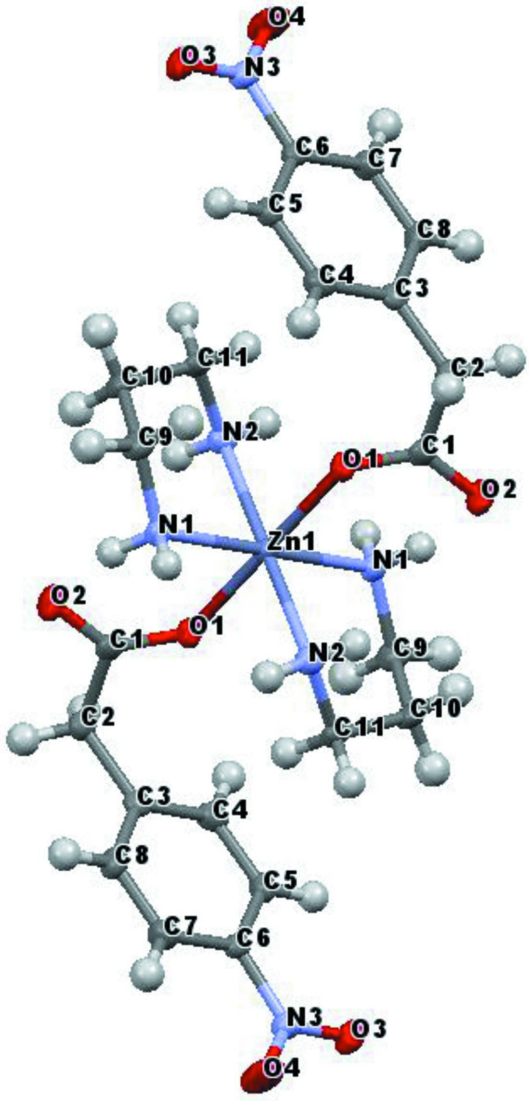

Figure 1

A thermal ellipsoid diagram of the title compound.

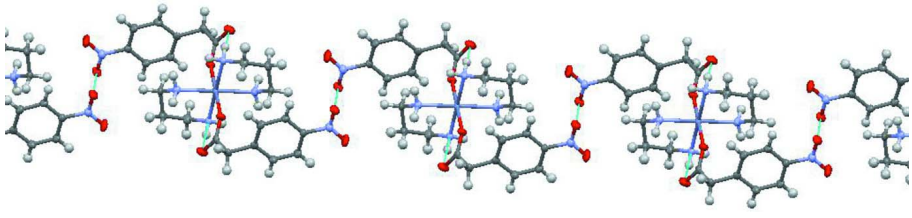

Figure 2

A packing diagram of the title compound.

Bis(1,3-diaminopropane-κ^2N,N')bis[2-(4-nitrophenyl)acetato-κO]zinc(II)

Crystal data

$[Zn(C_8H_6NO_4)_2(C_3H_{10}N_2)_2]$
$M_r = 573.91$
Monoclinic, $P2_1/c$
$a = 14.3933$ (18) Å
$b = 11.0261$ (14) Å
$c = 8.2453$ (11) Å
$\beta = 105.119$ (13)°
$V = 1263.3$ (3) Å^3
$Z = 2$
$F(000) = 600$
$D_x = 1.509$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2201 reflections
$\theta = 3.2$–$27.2°$
$\mu = 1.03$ mm^{-1}
$T = 180$ K
, colourless
0.24 × 0.21 × 0.08 mm

Data collection

Agilent Xcalibur, Eos diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.0514 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
$T_{min} = 0.952$, $T_{max} = 1.000$
5782 measured reflections
2243 independent reflections
1858 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 25.1°$, $\theta_{min} = 2.9°$
$h = -16\rightarrow17$
$k = -13\rightarrow12$
$l = -9\rightarrow9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.075$
$S = 1.06$
2243 reflections
169 parameters
0 restraints
Primary atom site location: iterative
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0245P)^2 + 0.7294P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ 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	0.5000	1.0000	0.01900 (13)
N3	1.03741 (14)	0.5615 (2)	1.3353 (2)	0.0256 (5)
O3	1.06699 (12)	0.46346 (16)	1.3979 (2)	0.0292 (4)
O2	0.57083 (13)	0.64366 (17)	0.6651 (2)	0.0351 (5)

C1	0.63039 (17)	0.5747 (2)	0.7576 (3)	0.0205 (6)
C4	0.84282 (17)	0.4574 (2)	0.9699 (3)	0.0240 (6)
H4	0.8148	0.3851	0.9235	0.029*
C3	0.81098 (16)	0.5666 (2)	0.8894 (3)	0.0197 (5)
O1	0.61567 (11)	0.50684 (15)	0.8709 (2)	0.0243 (4)
O4	1.07279 (15)	0.65867 (17)	1.3915 (2)	0.0482 (6)
C6	0.95606 (16)	0.5630 (2)	1.1840 (3)	0.0196 (5)
C8	0.85334 (17)	0.6733 (2)	0.9612 (3)	0.0244 (6)
H8	0.8323	0.7468	0.9094	0.029*
C2	0.73151 (16)	0.5702 (2)	0.7286 (3)	0.0240 (6)
H2A	0.7364	0.4989	0.6624	0.029*
H2B	0.7404	0.6409	0.6642	0.029*
C5	0.91535 (17)	0.4548 (2)	1.1176 (3)	0.0220 (6)
H5	0.9362	0.3817	1.1710	0.026*
C7	0.92621 (18)	0.6726 (2)	1.1082 (3)	0.0258 (6)
H7	0.9545	0.7447	1.1551	0.031*
N2	0.40460 (13)	0.42319 (18)	0.7777 (2)	0.0230 (5)
H2C	0.4313	0.4334	0.6913	0.028*
H2D	0.4002	0.3429	0.7937	0.028*
N1	0.45008 (13)	0.67537 (17)	0.9027 (2)	0.0210 (5)
H1A	0.4698	0.7295	0.9863	0.025*
H1B	0.4800	0.6941	0.8227	0.025*
C11	0.30623 (16)	0.4742 (2)	0.7291 (3)	0.0222 (6)
H11A	0.2767	0.4641	0.8214	0.027*
H11B	0.2679	0.4296	0.6334	0.027*
C9	0.34572 (17)	0.6935 (2)	0.8304 (3)	0.0273 (6)
H9A	0.3340	0.7765	0.7918	0.033*
H9B	0.3122	0.6800	0.9168	0.033*
C10	0.30620 (18)	0.6076 (2)	0.6844 (3)	0.0277 (6)
H10A	0.2406	0.6316	0.6301	0.033*
H10B	0.3437	0.6178	0.6032	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0173 (2)	0.0156 (2)	0.0208 (2)	−0.00001 (18)	−0.00090 (15)	0.00156 (17)
N3	0.0224 (11)	0.0271 (13)	0.0249 (12)	0.0014 (11)	0.0017 (9)	0.0007 (10)
O3	0.0300 (10)	0.0269 (10)	0.0277 (10)	0.0089 (9)	0.0020 (8)	0.0051 (8)
O2	0.0287 (10)	0.0400 (12)	0.0358 (11)	0.0111 (10)	0.0069 (8)	0.0188 (9)
C1	0.0219 (12)	0.0209 (14)	0.0165 (12)	−0.0026 (12)	0.0010 (10)	−0.0045 (11)
C4	0.0234 (13)	0.0198 (14)	0.0287 (14)	−0.0019 (12)	0.0068 (11)	−0.0044 (11)
C3	0.0165 (12)	0.0248 (14)	0.0204 (13)	0.0009 (11)	0.0094 (10)	0.0001 (11)
O1	0.0208 (9)	0.0283 (10)	0.0247 (9)	0.0035 (8)	0.0074 (7)	0.0097 (8)
O4	0.0500 (13)	0.0269 (11)	0.0486 (12)	−0.0097 (11)	−0.0210 (10)	−0.0022 (9)
C6	0.0162 (12)	0.0217 (14)	0.0204 (13)	0.0009 (11)	0.0038 (10)	0.0010 (11)
C8	0.0264 (13)	0.0195 (14)	0.0259 (14)	0.0061 (12)	0.0043 (11)	0.0046 (11)
C2	0.0225 (13)	0.0310 (15)	0.0190 (13)	−0.0002 (12)	0.0061 (10)	0.0012 (11)
C5	0.0223 (13)	0.0174 (13)	0.0263 (14)	0.0013 (11)	0.0064 (11)	0.0027 (11)

C7	0.0283 (14)	0.0186 (13)	0.0285 (14)	−0.0025 (12)	0.0039 (11)	−0.0022 (11)
N2	0.0236 (11)	0.0223 (12)	0.0224 (11)	−0.0005 (10)	0.0047 (9)	−0.0013 (9)
N1	0.0235 (11)	0.0194 (11)	0.0182 (10)	−0.0007 (10)	0.0020 (8)	0.0002 (9)
C11	0.0203 (12)	0.0263 (15)	0.0167 (12)	−0.0049 (11)	−0.0012 (10)	−0.0007 (10)
C9	0.0245 (14)	0.0204 (14)	0.0335 (15)	0.0062 (12)	0.0011 (11)	0.0008 (11)
C10	0.0217 (13)	0.0290 (15)	0.0262 (14)	0.0012 (12)	−0.0047 (11)	0.0050 (11)

Geometric parameters (Å, º)

Zn1—O1	2.1989 (16)	C8—C7	1.381 (3)
Zn1—O1^{i}	2.1989 (16)	C2—H2A	0.9700
Zn1—N2	2.1565 (18)	C2—H2B	0.9700
Zn1—N2^{i}	2.1565 (18)	C5—H5	0.9300
Zn1—N1^{i}	2.1444 (19)	C7—H7	0.9300
Zn1—N1	2.1444 (19)	N2—H2C	0.9000
N3—O3	1.226 (3)	N2—H2D	0.9000
N3—O4	1.224 (3)	N2—C11	1.478 (3)
N3—C6	1.472 (3)	N1—H1A	0.9000
O2—C1	1.246 (3)	N1—H1B	0.9000
C1—O1	1.257 (3)	N1—C9	1.478 (3)
C1—C2	1.536 (3)	C11—H11A	0.9700
C4—H4	0.9300	C11—H11B	0.9700
C4—C3	1.394 (3)	C11—C10	1.517 (3)
C4—C5	1.382 (3)	C9—H9A	0.9700
C3—C8	1.384 (3)	C9—H9B	0.9700
C3—C2	1.509 (3)	C9—C10	1.520 (3)
C6—C5	1.378 (3)	C10—H10A	0.9700
C6—C7	1.377 (3)	C10—H10B	0.9700
C8—H8	0.9300		
O1^{i}—Zn1—O1	180.00 (9)	C3—C2—H2B	108.9
N2—Zn1—O1^{i}	90.20 (7)	H2A—C2—H2B	107.7
N2^{i}—Zn1—O1	90.20 (7)	C4—C5—H5	120.8
N2—Zn1—O1	89.80 (7)	C6—C5—C4	118.5 (2)
N2^{i}—Zn1—O1^{i}	89.80 (7)	C6—C5—H5	120.8
N2^{i}—Zn1—N2	180.0	C6—C7—C8	118.6 (2)
N1^{i}—Zn1—O1	89.43 (7)	C6—C7—H7	120.7
N1—Zn1—O1	90.57 (7)	C8—C7—H7	120.7
N1—Zn1—O1^{i}	89.43 (7)	Zn1—N2—H2C	108.4
N1^{i}—Zn1—O1^{i}	90.57 (7)	Zn1—N2—H2D	108.4
N1—Zn1—N2	87.65 (7)	H2C—N2—H2D	107.4
N1^{i}—Zn1—N2^{i}	87.65 (7)	C11—N2—Zn1	115.69 (14)
N1^{i}—Zn1—N2	92.35 (7)	C11—N2—H2C	108.4
N1—Zn1—N2^{i}	92.35 (7)	C11—N2—H2D	108.4
N1^{i}—Zn1—N1	180.0	Zn1—N1—H1A	107.7
O3—N3—C6	118.6 (2)	Zn1—N1—H1B	107.7
O4—N3—O3	123.2 (2)	H1A—N1—H1B	107.1
O4—N3—C6	118.2 (2)	C9—N1—Zn1	118.60 (15)

O2—C1—O1	126.5 (2)	C9—N1—H1A	107.7
O2—C1—C2	116.9 (2)	C9—N1—H1B	107.7
O1—C1—C2	116.5 (2)	N2—C11—H11A	109.2
C3—C4—H4	119.4	N2—C11—H11B	109.2
C5—C4—H4	119.4	N2—C11—C10	112.0 (2)
C5—C4—C3	121.1 (2)	H11A—C11—H11B	107.9
C4—C3—C2	121.4 (2)	C10—C11—H11A	109.2
C8—C3—C4	118.5 (2)	C10—C11—H11B	109.2
C8—C3—C2	120.1 (2)	N1—C9—H9A	109.3
C1—O1—Zn1	132.51 (15)	N1—C9—H9B	109.3
C5—C6—N3	119.3 (2)	N1—C9—C10	111.5 (2)
C7—C6—N3	118.6 (2)	H9A—C9—H9B	108.0
C7—C6—C5	122.0 (2)	C10—C9—H9A	109.3
C3—C8—H8	119.3	C10—C9—H9B	109.3
C7—C8—C3	121.3 (2)	C11—C10—C9	115.8 (2)
C7—C8—H8	119.3	C11—C10—H10A	108.3
C1—C2—H2A	108.9	C11—C10—H10B	108.3
C1—C2—H2B	108.9	C9—C10—H10A	108.3
C3—C2—C1	113.32 (19)	C9—C10—H10B	108.3
C3—C2—H2A	108.9	H10A—C10—H10B	107.4

Zn1—N2—C11—C10	63.2 (2)	O4—N3—C6—C7	2.9 (3)
Zn1—N1—C9—C10	−59.0 (2)	C8—C3—C2—C1	−92.6 (3)
N3—C6—C5—C4	−176.2 (2)	C2—C1—O1—Zn1	166.11 (15)
N3—C6—C7—C8	176.5 (2)	C2—C3—C8—C7	−180.0 (2)
O3—N3—C6—C5	0.2 (3)	C5—C4—C3—C8	−0.3 (4)
O3—N3—C6—C7	−176.5 (2)	C5—C4—C3—C2	−179.7 (2)
O2—C1—O1—Zn1	−15.1 (4)	C5—C6—C7—C8	−0.1 (4)
O2—C1—C2—C3	138.9 (2)	C7—C6—C5—C4	0.4 (4)
C4—C3—C8—C7	0.7 (4)	N2—Zn1—O1—C1	74.1 (2)
C4—C3—C2—C1	86.7 (3)	N2^{i}—Zn1—O1—C1	−105.9 (2)
C3—C4—C5—C6	−0.2 (4)	N2^{i}—Zn1—N1—C9	−135.43 (17)
C3—C8—C7—C6	−0.4 (4)	N2—Zn1—N1—C9	44.58 (17)
O1^{i}—Zn1—N2—C11	43.83 (16)	N2—C11—C10—C9	−70.8 (3)
O1—Zn1—N2—C11	−136.17 (16)	N1^{i}—Zn1—O1—C1	166.4 (2)
O1^{i}—Zn1—N1—C9	−45.65 (17)	N1—Zn1—O1—C1	−13.6 (2)
O1—Zn1—N1—C9	134.35 (17)	N1^{i}—Zn1—N2—C11	134.41 (16)
O1—C1—C2—C3	−42.2 (3)	N1—Zn1—N2—C11	−45.59 (16)
O4—N3—C6—C5	179.6 (2)	N1—C9—C10—C11	67.2 (3)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···O2	0.90	2.14	2.959 (3)	150
N1—H1*A*···O2^{ii}	0.90	2.26	3.118 (3)	158
N2—H2*D*···O2^{iii}	0.90	2.25	3.124 (3)	165

C10—H10*A*···O4^{iv}	0.97	2.70	3.634 (3)	161
C7—H7···O3^{v}	0.93	2.46	3.209 (3)	138

Symmetry codes: (ii) *x*, −*y*+3/2, *z*+1/2; (iii) −*x*+1, *y*−1/2, −*z*+3/2; (iv) *x*−1, *y*, *z*−1; (v) −*x*+2, *y*+1/2, −*z*+5/2.