Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

A dimeric zinc(II) complex: bis[μ-1,2-bis(1,2,4-triazol-4-yl)ethane-$\kappa^2N^1:N^{1'}$]-bis[dinitritozinc(II)]

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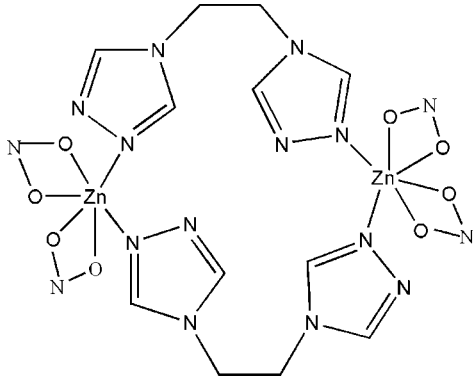
Received 12 July 2010; accepted 25 August 2010

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.040; wR factor = 0.104; data-to-parameter ratio = 12.5.

The coordination geometry of the Zn^{II} atom in the title complex, $[Zn_2(NO_2)_4(C_6H_8N_6)_2]$, is distorted octahedral, in which the Zn^{II} atom is coordinated by two N atoms from the triazole rings of two symmetry-related 1,2-bis(1,2,4-triazol-4-yl)ethane ligands and four O atoms from two nitrite ligands. Two Zn^{II} atoms are bridged by two organic ligands, forming a centrosymmetric dimer. Weak C—H···N and C—H···O hydrogen bonds play an important role in the intermolecular packing.

Related literature

For background to 1,2,4-triazole and its derivatives, see: Haasnoot (2000). For a related structure, see: Habit *et al.* (2009). For hydrogen bonding, see: Mascal (1998).



Experimental

Crystal data

$[Zn_2(NO_2)_4(C_6H_8N_6)_2]$ M_r = 643.15
Monoclinic, $C2/c$
a = 20.491 (4) Å
b = 6.7087 (13) Å
c = 17.289 (4) Å
β = 97.125 (5)°
V = 2358.3 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.11 mm^{-1}
T = 293 K
0.60 × 0.20 × 0.20 mm

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: multi-scan (Blessing, 1995, 1997)
T_{min} = 0.364, T_{max} = 0.678
10892 measured reflections
2144 independent reflections
1945 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.104
S = 1.06
2144 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}

Table 1
Selected bond lengths (Å).

Zn1—N4^{i}	2.002 (3)	Zn1—O3	2.046 (3)
Zn1—O1	2.031 (3)	Zn1—O2	2.477 (3)
Zn1—N1	2.036 (3)	Zn1—O4	2.488 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1B···O2^{ii}	0.97	2.53	3.396 (5)	149
C2—H2A···O1^{iii}	0.97	2.49	3.417 (4)	160
C3—H3A···O2^{ii}	0.93	2.66	3.412 (5)	139
C6—H6A···N2^{iv}	0.93	2.39	3.314 (4)	176

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

Data collection: *CrystalClear* (Rigaku, 2000); 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); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BV2153).

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supporting information

Acta Cryst. (2010). E**66**, m1208 [doi:10.1107/S1600536810034203]

A dimeric zinc(II) complex: bis[μ-1,2-bis(1,2,4-triazol-4-yl)ethane-$\kappa^2N^1:N^{1'}$]bis-[dinitritozinc(II)]

Rongxian Zhang, Qiuyun Chen, Jing Gao and Xiangyang Wu

S1. Comment

1,2,4-Triazole and its derivatives are very interesting ligands, because they combine the coordination geometry of both pyrazole and imidazole with regard to the arrangement of their three heteroatoms. A large number of mononuclear, oligonuclear and polynuclear transition metal complexes of 1,2,4-triazole derivatives have been synthesized and characterized because of their magnetic properties and novel topologies (Haasnoot, 2000).

In the present work, we report here the preparation and crystal structure of a dimeric zinc^{II} complex, namely, $[Zn(btre)NO_2)_2]_2$ (I) (btre = 1,2-bis(1,2,4-triazol-4-yl)ethane.

In the complex (I), the coordination geometry of the zinc^{II} atom in the title complex, $[Zn(C_6H_8N_6)(NO_2)_2]_2$ or $[Zn(btre)(NO_2)_2]_2$, where btre is μ-[1,2-bis(1,2,4-triazol-4-yl)ethane], is a distorted octahedron, in which the Zn^{II} atom is coordinated by two N atoms from the triazole rings of two symmetry-related btre ligands and four O atoms from two NO_2^- ligands. Two Zn^{II} atoms are bridged by two organic ligands to form a dimer. Each NO_2^- anion acts as a chelating coordination mode.

The crystal structure of (I) is built up from a neutral dimeric metallocycle. The dimer is centrosymmetric. As shown in Fig.1, in each dimer, two zinc^{II} centres are connected by two btre ligands resulting in a discrete $Zn_2(btre)_2$ 18-membered binuclear metallocycle.

Each zinc^{II} centre is six-coordinated by two N atoms of btre ligands and four O atoms from two NO_2^- ligands (Table 1), forming a distorted octahedral geometry. Each btre exhibits a *gauche* conformation in (I). The N3—C1—C2—N6 torsion angle is 64.9 (4)°. The dihedral angle between the two triazole ring is 40.1 (2)°. The Zn···Zn separation *via* the bridging btre ligand is 7.809 (2)Å in (I), compared with the corresponding values 7.8750 (2)Å in $[Zn(btre)Cl_2]_2$ and 7.7980 (5)Å in $[Zn(btre)I_2]_2$ (Habit *et al.*, 2009).

Weak hydrogen bonds play an important role in the formation of the crystal structure. The intermolecular packing is organized by C—H···N and C—H···O hydrogen bonds (Table 2 and Figure 2; Mascal 1998).

S2. Experimental

A 10 ml aqueous solution of $Zn(NO_2)_2$ (1 mmol) was added to a tube, and a 10 ml MeOH solution of 1,2-bis(1,2,4-triazol-4-yl)ethane (btre) (1.0 mmol) was carefully added above the aqueous solution. Colourless crystal were obtained after about two weeks. Anal. Calcd. for $C_{12}H_{16}N_{16}O_8Zn_2$: C, 22.41; H, 2.51; N, 34.85%. Found: C, 22.36; H, 2.44; N, 34.69%.

S3. Refinement

H atom were placed in idealized positions and refined as riding, with C—H distances of 0.93 (triazole) and 0.97Å (ethane), and with $U_{iso}(H) = 1.2U_{eq}(C)$.

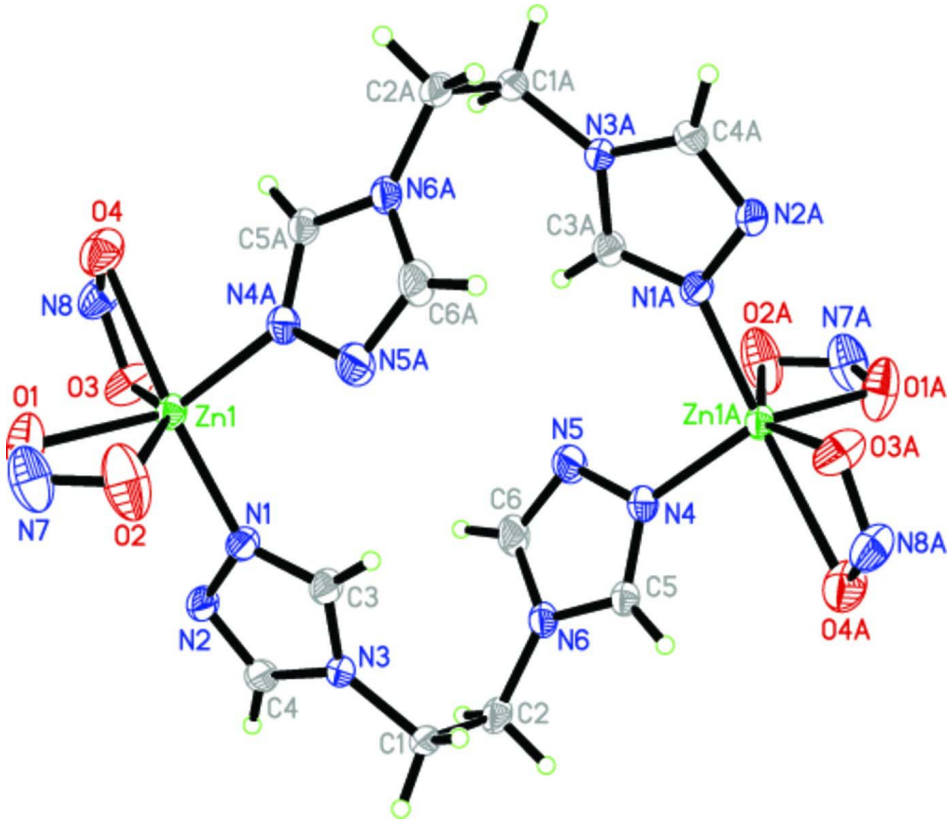

Figure 1

A dimeric structure of (I), with displacement ellipsoids drawn at the 30% probability level. [Symmetry code: A -*x* + 1/2, -*y* - 1/2, -z21.]

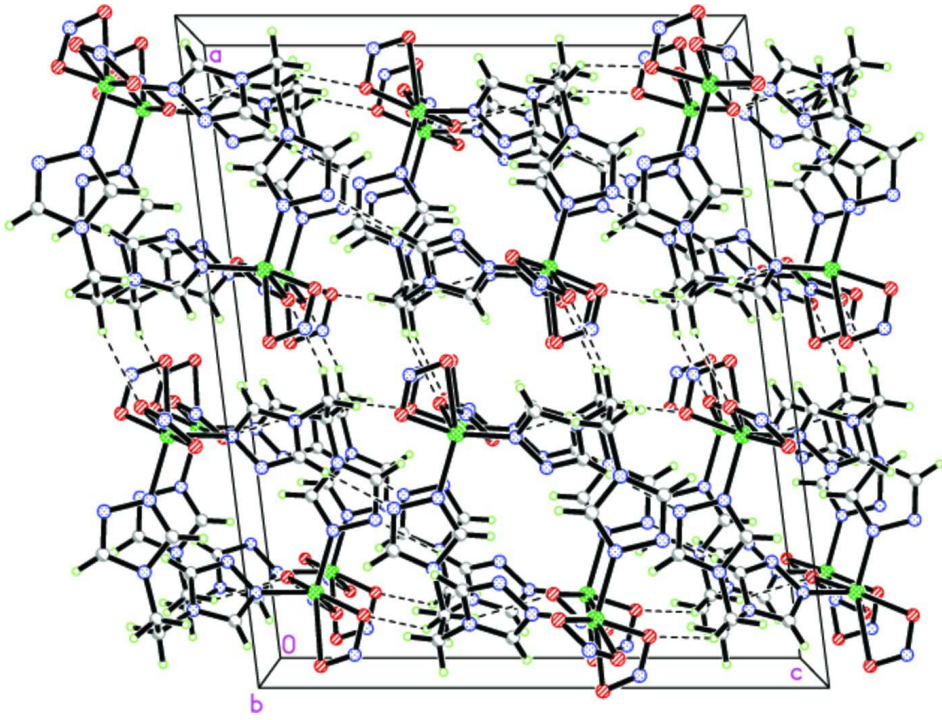

Figure 2

The cell packing of (I) along [010] direction.

bis[μ-1,2-bis(1,2,4-triazol-4-yl)ethane- $\kappa^2N^1:N^{1'}$]bis[dinitritozinc(II)]

Crystal data

$[Zn_2(NO_2)_4(C_6H_8N_6)_2]$
$M_r = 643.15$
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Hall symbol: -c 2yc
$a = 20.491$ (4) Å
$b = 6.7087$ (13) Å
$c = 17.289$ (4) Å
$\beta = 97.125$ (5)°
$V = 2358.3$ (8) Å^3
$Z = 4$
$F(000) = 1296$
$D_x = 1.811$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71070$ Å
Cell parameters from 4261 reflections
$\theta = 3.2$–$25.4°$
$\mu = 2.11$ mm^{-1}
$T = 293$ K
Block, colorless
0.60 × 0.20 × 0.20 mm

Data collection

Rigaku Mercury CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (Blessing, 1995, 1997)
$T_{min} = 0.364$, $T_{max} = 0.678$
10892 measured reflections
2144 independent reflections
1945 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 25.3°$, $\theta_{min} = 3.2°$
$h = -24\rightarrow24$
$k = -7\rightarrow8$
$l = -20\rightarrow20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.104$
$S = 1.06$
2144 reflections
172 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
$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 2.1848P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.61$ 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	0.377036 (17)	0.06273 (5)	0.900523 (19)	0.03325 (17)
O1	0.42015 (16)	0.3236 (5)	0.8755 (2)	0.0767 (10)
O2	0.3646 (2)	0.3909 (5)	0.96266 (18)	0.0876 (12)
O3	0.40736 (13)	−0.1027 (4)	0.81217 (16)	0.0581 (7)
O4	0.48542 (14)	−0.1050 (5)	0.90120 (16)	0.0662 (8)
N1	0.28080 (13)	0.0744 (4)	0.85410 (15)	0.0353 (6)
N2	0.26438 (14)	0.0921 (4)	0.77408 (15)	0.0401 (7)
N3	0.17452 (13)	0.0807 (4)	0.83012 (15)	0.0325 (6)
N4	0.12627 (14)	−0.4368 (4)	0.99508 (15)	0.0353 (6)
N5	0.17231 (16)	−0.4949 (5)	0.94714 (18)	0.0499 (8)
N6	0.10563 (13)	−0.2736 (4)	0.88654 (14)	0.0355 (6)
N7	0.4027 (2)	0.4550 (5)	0.9200 (2)	0.0712 (11)
N8	0.46565 (16)	−0.1617 (6)	0.83561 (19)	0.0568 (8)
C1	0.10463 (16)	0.0757 (5)	0.8402 (2)	0.0413 (8)
H1A	0.0807	0.1668	0.8034	0.050*
H1B	0.0992	0.1202	0.8924	0.050*
C2	0.07634 (16)	−0.1309 (6)	0.82762 (19)	0.0448 (8)
H2A	0.0292	−0.1254	0.8292	0.054*
H2B	0.0837	−0.1775	0.7763	0.054*
C3	0.22636 (17)	0.0689 (5)	0.88560 (19)	0.0360 (7)
H3A	0.2237	0.0584	0.9388	0.043*
C4	0.20115 (17)	0.0957 (5)	0.76274 (18)	0.0392 (8)
H4A	0.1767	0.1072	0.7139	0.047*
C5	0.08740 (15)	−0.3056 (5)	0.95728 (17)	0.0330 (7)
H5A	0.0522	−0.2435	0.9766	0.040*

C6	0.15788 (19)	−0.3936 (6)	0.8829 (2)	0.0468 (9)
H6A	0.1808	−0.4031	0.8399	0.056*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0323 (3)	0.0385 (3)	0.0298 (2)	−0.00378 (14)	0.00707 (16)	0.00015 (14)
O1	0.080 (2)	0.0613 (18)	0.098 (2)	−0.0275 (16)	0.0486 (19)	−0.0208 (18)
O2	0.142 (4)	0.071 (2)	0.0574 (19)	−0.033 (2)	0.041 (2)	−0.0132 (16)
O3	0.0422 (16)	0.0766 (18)	0.0542 (16)	0.0062 (13)	0.0013 (12)	−0.0270 (14)
O4	0.0506 (18)	0.098 (2)	0.0485 (16)	−0.0159 (16)	0.0018 (13)	−0.0053 (15)
N1	0.0298 (15)	0.0439 (16)	0.0322 (14)	−0.0011 (11)	0.0038 (11)	0.0003 (11)
N2	0.0341 (16)	0.0556 (17)	0.0321 (14)	0.0014 (13)	0.0100 (12)	0.0078 (12)
N3	0.0279 (14)	0.0353 (14)	0.0354 (14)	0.0019 (10)	0.0083 (11)	0.0064 (11)
N4	0.0377 (15)	0.0387 (15)	0.0309 (14)	−0.0026 (11)	0.0097 (12)	−0.0004 (11)
N5	0.052 (2)	0.0539 (17)	0.0480 (18)	0.0126 (15)	0.0243 (15)	0.0090 (15)
N6	0.0336 (14)	0.0440 (15)	0.0293 (13)	−0.0075 (12)	0.0056 (11)	0.0035 (11)
N7	0.110 (3)	0.0459 (19)	0.062 (2)	−0.022 (2)	0.028 (2)	−0.0096 (17)
N8	0.0402 (18)	0.078 (2)	0.0531 (19)	0.0002 (17)	0.0121 (15)	−0.0140 (17)
C1	0.0286 (17)	0.056 (2)	0.0415 (18)	0.0098 (14)	0.0106 (14)	0.0181 (15)
C2	0.0274 (17)	0.074 (2)	0.0320 (17)	−0.0075 (17)	−0.0009 (13)	0.0115 (17)
C3	0.0348 (18)	0.0455 (19)	0.0287 (15)	0.0005 (14)	0.0082 (13)	−0.0004 (13)
C4	0.0374 (19)	0.0522 (19)	0.0285 (16)	0.0049 (15)	0.0060 (14)	0.0088 (14)
C5	0.0317 (17)	0.0392 (16)	0.0290 (15)	−0.0046 (14)	0.0072 (12)	−0.0003 (13)
C6	0.053 (2)	0.053 (2)	0.0378 (18)	0.0008 (17)	0.0219 (16)	0.0017 (16)

Geometric parameters (Å, º)

Zn1—N4^{i}	2.002 (3)	N4—C5	1.307 (4)
Zn1—O1	2.031 (3)	N4—N5	1.386 (4)
Zn1—N1	2.036 (3)	N4—Zn1^{i}	2.002 (3)
Zn1—O3	2.046 (3)	N5—C6	1.304 (5)
Zn1—O2	2.477 (3)	N6—C5	1.340 (4)
Zn1—O4	2.488 (3)	N6—C6	1.347 (5)
O1—N7	1.251 (4)	N6—C2	1.471 (4)
O2—N7	1.218 (5)	C1—C2	1.508 (5)
O3—N8	1.276 (4)	C1—H1A	0.9700
O4—N8	1.217 (4)	C1—H1B	0.9700
N1—C3	1.301 (4)	C2—H2A	0.9700
N1—N2	1.388 (4)	C2—H2B	0.9700
N2—C4	1.286 (4)	C3—H3A	0.9300
N3—C3	1.342 (4)	C4—H4A	0.9300
N3—C4	1.350 (4)	C5—H5A	0.9300
N3—C1	1.464 (4)	C6—H6A	0.9300
N4^{i}—Zn1—O1	128.32 (12)	C5—N6—C6	105.1 (3)
N4^{i}—Zn1—N1	103.43 (11)	C5—N6—C2	126.9 (3)
O1—Zn1—N1	107.96 (13)	C6—N6—C2	128.0 (3)

N4^{i}—Zn1—O3	119.46 (12)	O2—N7—O1	112.2 (3)
O1—Zn1—O3	97.34 (12)	O4—N8—O3	112.9 (3)
N1—Zn1—O3	95.48 (11)	N3—C1—C2	111.6 (3)
N4^{i}—Zn1—O2	88.11 (11)	N3—C1—H1A	109.3
O1—Zn1—O2	52.96 (11)	C2—C1—H1A	109.3
N1—Zn1—O2	89.42 (13)	N3—C1—H1B	109.3
O3—Zn1—O2	149.67 (12)	C2—C1—H1B	109.3
N4^{i}—Zn1—O4	86.27 (10)	H1A—C1—H1B	108.0
O1—Zn1—O4	88.80 (12)	N6—C2—C1	112.5 (3)
N1—Zn1—O4	147.07 (10)	N6—C2—H2A	109.1
O3—Zn1—O4	53.47 (10)	C1—C2—H2A	109.1
O2—Zn1—O4	122.68 (12)	N6—C2—H2B	109.1
N7—O1—Zn1	108.1 (2)	C1—C2—H2B	109.1
N7—O2—Zn1	86.7 (2)	H2A—C2—H2B	107.8
N8—O3—Zn1	106.9 (2)	N1—C3—N3	110.1 (3)
N8—O4—Zn1	86.7 (2)	N1—C3—H3A	125.0
C3—N1—N2	107.8 (3)	N3—C3—H3A	125.0
C3—N1—Zn1	132.3 (2)	N2—C4—N3	112.0 (3)
N2—N1—Zn1	120.0 (2)	N2—C4—H4A	124.0
C4—N2—N1	105.6 (3)	N3—C4—H4A	124.0
C3—N3—C4	104.6 (3)	N4—C5—N6	110.0 (3)
C3—N3—C1	127.8 (3)	N4—C5—H5A	125.0
C4—N3—C1	127.6 (3)	N6—C5—H5A	125.0
C5—N4—N5	107.9 (3)	N5—C6—N6	111.6 (3)
C5—N4—Zn1^{i}	130.4 (2)	N5—C6—H6A	124.2
N5—N4—Zn1^{i}	121.5 (2)	N6—C6—H6A	124.2
C6—N5—N4	105.3 (3)		

N4^{i}—Zn1—O1—N7	−48.4 (4)	O4—Zn1—N1—N2	−55.0 (3)
N1—Zn1—O1—N7	76.1 (3)	C3—N1—N2—C4	−0.1 (4)
O3—Zn1—O1—N7	174.4 (3)	Zn1—N1—N2—C4	−180.0 (2)
O2—Zn1—O1—N7	1.1 (3)	C5—N4—N5—C6	0.0 (4)
O4—Zn1—O1—N7	−132.7 (3)	Zn1^{i}—N4—N5—C6	176.0 (2)
N4^{i}—Zn1—O2—N7	142.3 (3)	Zn1—O2—N7—O1	1.5 (4)
O1—Zn1—O2—N7	−1.1 (3)	Zn1—O1—N7—O2	−1.9 (5)
N1—Zn1—O2—N7	−114.3 (3)	Zn1—O4—N8—O3	−0.1 (3)
O3—Zn1—O2—N7	−14.4 (5)	Zn1—O3—N8—O4	0.1 (4)
O4—Zn1—O2—N7	57.9 (3)	C3—N3—C1—C2	−96.2 (4)
N4^{i}—Zn1—O3—N8	−59.3 (3)	C4—N3—C1—C2	82.9 (4)
O1—Zn1—O3—N8	82.9 (3)	C5—N6—C2—C1	84.7 (4)
N1—Zn1—O3—N8	−168.1 (3)	C6—N6—C2—C1	−92.2 (4)
O2—Zn1—O3—N8	93.6 (3)	N3—C1—C2—N6	64.9 (4)
O4—Zn1—O3—N8	−0.1 (2)	N2—N1—C3—N3	0.4 (3)
N4^{i}—Zn1—O4—N8	131.5 (2)	Zn1—N1—C3—N3	−179.7 (2)
O1—Zn1—O4—N8	−100.0 (3)	C4—N3—C3—N1	−0.6 (3)
N1—Zn1—O4—N8	22.4 (3)	C1—N3—C3—N1	178.7 (3)
O3—Zn1—O4—N8	0.1 (2)	N1—N2—C4—N3	−0.2 (4)
O2—Zn1—O4—N8	−143.1 (2)	C3—N3—C4—N2	0.5 (4)

N4^{i}—Zn1—N1—C3	21.0 (3)	C1—N3—C4—N2	−178.7 (3)
O1—Zn1—N1—C3	−117.4 (3)	N5—N4—C5—N6	−0.1 (4)
O3—Zn1—N1—C3	143.0 (3)	Zn1^{i}—N4—C5—N6	−175.7 (2)
O2—Zn1—N1—C3	−67.0 (3)	C6—N6—C5—N4	0.3 (4)
O4—Zn1—N1—C3	125.2 (3)	C2—N6—C5—N4	−177.2 (3)
N4^{i}—Zn1—N1—N2	−159.2 (2)	N4—N5—C6—N6	0.2 (4)
O1—Zn1—N1—N2	62.4 (2)	C5—N6—C6—N5	−0.3 (4)
O3—Zn1—N1—N2	−37.2 (2)	C2—N6—C6—N5	177.1 (3)
O2—Zn1—N1—N2	112.8 (2)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···O2^{ii}	0.97	2.53	3.396 (5)	149
C2—H2*A*···O1^{iii}	0.97	2.49	3.417 (4)	160
C3—H3*A*···O2^{ii}	0.93	2.66	3.412 (5)	139
C6—H6*A*···N2^{iv}	0.93	2.39	3.314 (4)	176

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