Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# Bis(4-amino-3,5-di-2-pyridyl-1,2,4-triazole-$\kappa^2N^1,N^5$)diaquazinc(II) dinitrate

**Jia Hua,* Lu Gao and Baiyan Li**

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China
Correspondence e-mail: huajia@jlu.edu.cn

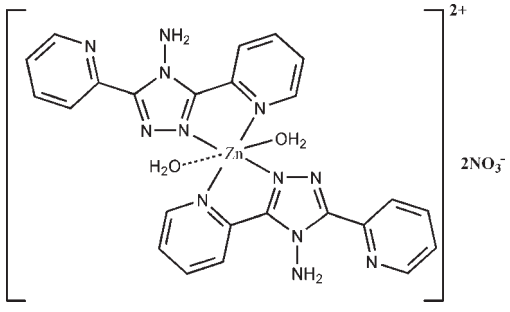
Received 17 July 2009; accepted 13 August 2009

Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.045; $wR$ factor = 0.101; data-to-parameter ratio = 14.1.

The asymmetric unit of the title compound, $[Zn(C_{12}H_{10}N_6)_2(H_2O)_2](NO_3)_2$, contains one-half of the complex molecule and one $NO_3^-$ anion. The $Zn^{II}$ ion displays a distorted tetragonal-pyramidal geometry with four N atoms from two chelating 4-amino-3,5-di-2-pyridyl-1,2,4-triazole (2-bpt) ligands in the basal plane and one water molecule occupying the apical site. Another water molecule at the opposite of the apical site has a weak interaction with the $Zn^{II}$ ion [Zn—O = 2.852 (5) Å]. The $Zn^{II}$ ion and the two water molecules lie on a twofold rotation axis. An extensive system of hydrogen bonds involving the $NH_2$ groups of the 2-bpt ligands, water molecules and nitrate anions links all residues into a three-dimensional network.

## Related literature

For transition metal complexes of 4-amino-3,5-di-2-pyridyl-1,2,4-triazole (2-bpt), see: Shao & Geng (2009); Hartmann & Vahrenkamp (1995); Keij *et al.* (1984); Kitchen *et al.* (2008); Koningsbruggen *et al.* (1998); Tong *et al.* (2007). For rare earth metal complexes of 2-bpt, see: Garcia *et al.* (1986); Rheingold *et al.* (1993). For hydrogen-bonding interactions involving 2-bpt in organic compounds, see: Mernari *et al.* (1998).




## Experimental

### Crystal data

$[Zn(C_{12}H_{10}N_6)_2(H_2O)_2](NO_3)_2$
$M_r$ = 701.94
Monoclinic, $C2/c$
$a$ = 14.856 (3) Å
$b$ = 9.4185 (19) Å
$c$ = 20.230 (4) Å
$\beta$ = 91.99 (3)°
$V$ = 2829 (1) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.95 mm$^{-1}$
$T$ = 298 K
0.25 × 0.20 × 0.20 mm

### Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.797, $T_{max}$ = 0.828
13550 measured reflections
3210 independent reflections
2424 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.067

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.101
$S$ = 1.03
3210 reflections
228 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.32 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.64 e Å$^{-3}$

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Zn1—O1*W* | 2.008 (3) | Zn1—N1 | 2.078 (2) |
| Zn1—O2*W* | 2.852 (5) | Zn1—N5 | 2.141 (2) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N4—H4*A*···O2$^{i}$ | 0.94 (4) | 2.25 (4) | 3.100 (3) | 149 (3) |
| N4—H4*A*···O2 | 0.94 (4) | 2.55 (4) | 3.192 (4) | 126 (3) |
| N4—H4*B*···N6 | 0.89 (4) | 2.13 (4) | 2.875 (3) | 141 (3) |
| N4—H4*B*···O3 | 0.89 (4) | 2.43 (4) | 3.005 (3) | 122 (3) |
| O1*W*—H1*W*···O3$^{ii}$ | 0.79 (3) | 1.93 (3) | 2.714 (3) | 170 (3) |
| O2*W*—H2*W*···O1$^{iii}$ | 0.92 (5) | 2.02 (5) | 2.900 (4) | 161 (5) |

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999) and *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

We thank the National Natural Science Foundation of China for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2215).

## References


Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Bruker (2007). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Garcia, M. P., Manero, J. A., Oro, L. A., Apreda, M. C., Cano, F. H., Foces, C. F., Haasnot, J. G., Prins, R. & Reedijk, J. (1986). *Inorg. Chim. Acta*, **122**, 235–241.

Hartmann, U. & Vahrenkamp, H. (1995). *Inorg. Chim. Acta*, **239**, 13–17.

Keij, F. S., Graaff, R. A. G., Haasnoot, J. G. & Reedijk, J. (1984). *J. Chem. Soc. Dalton Trans.* pp. 2093–2097.

Kitchen, J. A., Noble, A., Brandt, C. D., Moubaraki, B., Murray, K. S. & Brooker, S. (2008). *Inorg. Chem.* **47**, 9450–9458.

Koningsbruggen, P. J., Goubitz, K., Haasnoot, J. G. & Reedijk, J. (1998). *Inorg. Chim. Acta*, **268**, 37–42.

Mernari, B., El Azhar, M., El Attari, H., Lagrenée, M. & Pierrot, M. (1998). *Acta Cryst.* C**54**, 1983–1986.

Rheingold, A. L., Saisuwan, P. & Thomas, N. C. (1993). *Inorg. Chim. Acta*, **214**, 41–45.

Shao, C.-F. & Geng, L.-C. (2009). *Acta Cryst.* E**65**, m511–m512.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Tong, M. L., Hong, C. G., Zheng, L. L., Peng, M. X., Gaita-Arino, A. & Juan, J. M. C. (2007). *Eur. J. Inorg. Chem.* pp. 3710–3717.

# supporting information

*Acta Cryst.* (2009). E**65**, m1106–m1107 [doi:10.1107/S1600536809032103]

## Bis(4-amino-3,5-di-2-pyridyl-1,2,4-triazole-$\kappa^2N^1,N^5$)diaquazinc(II) dinitrate

**Jia Hua, Lu Gao and Baiyan Li**

### S1. Comment

Recently, 4-amino-3,5-di-2-pyridyl-1,2,4-triazole (2-bpt) has been used as ligand because it has potential ability of multi-coordination modes, generating hydrogen-bonding and/or aromatic stacking interactions. The zinc(II) complex of 2-bpt has been reported previously. Hartmann & Vahrenkamp (1995) prepared the complexes based on 2-bpt with $Zn(ClO_4)_2$, $ZnCl_2$, $Zn(NO_3)_2$ and $Zn(BF_4)_2$. But they just obtained the single-crystal structure of $Zn(ClO_4)_2$ complex, in which $Zn^{II}$ atom adopts octahedral geometry. Herein, we reported the crystal structure of the title compound obtained by reacting 2-bpt with $Zn(NO_3)_2$, in which 2-bpt acts as a chelating ligand and hydrogen-bonding interactions play an important role in stabilizing the solid-state structure.

The structure analysis reveals that the asymmetric unit of the title compund contains half a $Zn^{II}$ atom, one 2-bpt molecule, two half water molecules and one $NO_3^-$ anion. As depicted in Fig. 1, the distorted tetragonal pyramidal $Zn^{II}$ atom is located on an inversion center. The basal plane is defined by four N atoms from two 2-bpt ligands with a chelating mode, and the apical site is occupied by one water molecule (O1W) with a Zn—O distance of 2.008 (3)Å (Table 1). Another water molecule (O2W) has a weak interaction with the Zn atom [Zn1—O2W = 2.852 (5) Å], which makes the crystal structure differ from the recently reported nickel complex (Shao & Geng, 2009) because of Jahn-Teller effect. The 2-bpt molecule exhibits *trans*-conformation. The two 2-bpt molecules are not coplanar, with a dihedral angle of 48.54 (5)°. N—H···O, N—H···N and O—H···O hydrogen bonds are observed in the crystal structure (Table 2; Fig. 2).

### S2. Experimental

To an ethanol solution (20 ml) of 2-bpt (0.012 g, 0.05 mmol) was added an aqueous solution (5 ml) of $Zn(NO_3)_2.6H_2O$ (0.018 g, 0.05 mmol) with stirring. After vigorous stirring for *ca* 40 min, the resultant solution was filtered and left to stand at room temperature. Colorless block crystals suitable for X-ray analysis were produced by slow evaporation of the solvent for two weeks.

### S3. Refinement

C-bound H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93 Å and with $U_{iso}$(H) = 1.2$U_{eq}$(C). H atoms attached to N atom were found in a difference Fourier map. Their coordinates were refined and $U_{iso}$ factors were fixed. H atoms of water molecules were found in a difference Fourier map and refined isotropically.

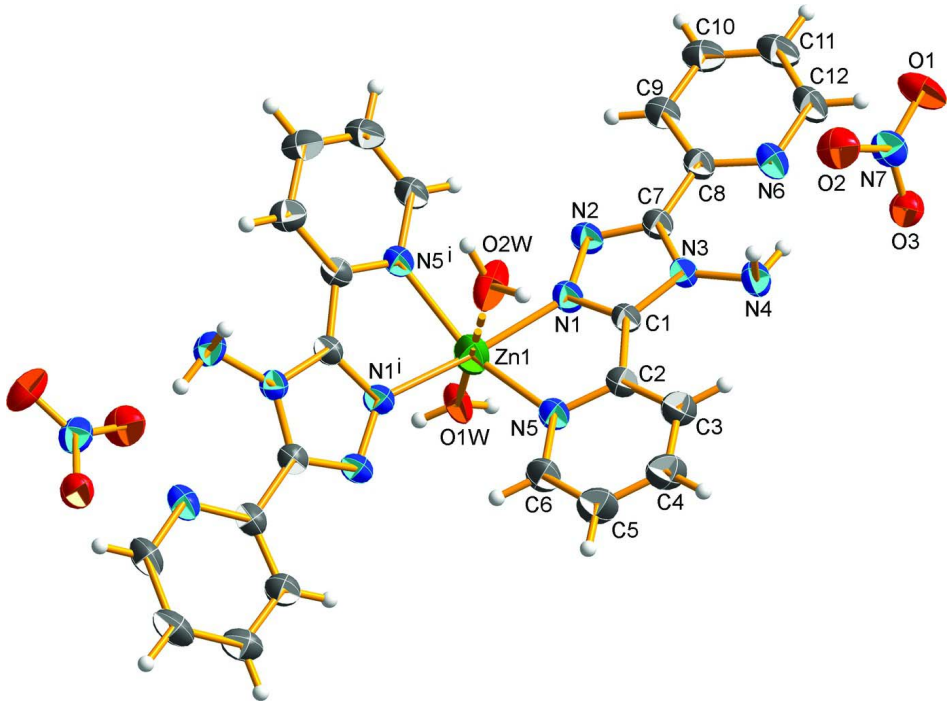



**Figure 1**

Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) -*x*, *y*, 3/2 - *z*.]

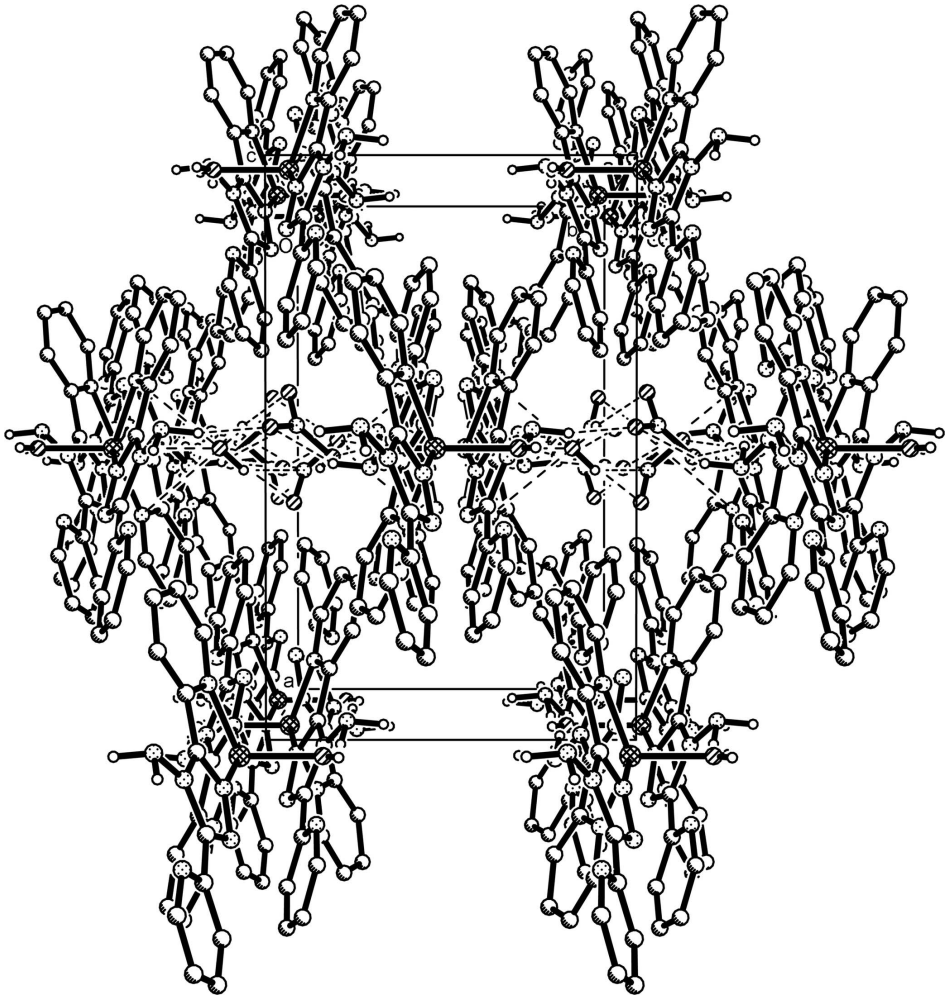


**Figure 2**

The crystal packing of the title compound. Dashed lines denote hydrogen bonds.

**Bis(4-amino-3,5-di-2-pyridyl-1,2,4-triazole- $\kappa^2N^1,N^5$)diaquazinc(II) dinitrate**

*Crystal data*

$[Zn(C_{12}H_{10}N_6)_2(H_2O)_2](NO_3)_2$
$M_r = 701.94$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 14.856$ (3) Å
$b = 9.4185$ (19) Å
$c = 20.230$ (4) Å
$\beta = 91.99$ (3)°
$V = 2829$ (1) Å$^3$
$Z = 4$
$F(000) = 1440$
$D_x = 1.648$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3210 reflections
$\theta = 3.2$–27.4°
$\mu = 0.95$ mm$^{-1}$
$T = 298$ K
Block, colorless
0.25 × 0.20 × 0.20 mm

*Data collection*

Bruker SMART 1000 CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.797$, $T_{max} = 0.828$

13550 measured reflections
3210 independent reflections
2424 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 27.4°$, $\theta_{min} = 3.2°$
$h = -19 \rightarrow 19$
$k = -12 \rightarrow 12$
$l = -22 \rightarrow 26$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.101$
$S = 1.03$
3210 reflections
228 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 4.1918P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å$^{-3}$
$\Delta\rho_{min} = -0.64$ e Å$^{-3}$

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zn1 | 0.0000 | 0.04107 (5) | 0.7500 | 0.03188 (15) |
| O1W | 0.0000 | −0.1721 (3) | 0.7500 | 0.0441 (8) |
| O2W | 0.0000 | 0.3439 (5) | 0.7500 | 0.1050 (19) |
| O1 | 0.09893 (16) | 0.4526 (3) | 1.17312 (12) | 0.0646 (7) |
| O2 | 0.03688 (16) | 0.4946 (2) | 1.07668 (12) | 0.0586 (6) |
| O3 | −0.01516 (15) | 0.3294 (2) | 1.13778 (10) | 0.0511 (6) |
| N1 | 0.03975 (14) | 0.0690 (2) | 0.84865 (10) | 0.0298 (5) |
| N2 | 0.11637 (14) | 0.0466 (2) | 0.88711 (10) | 0.0304 (5) |
| N3 | 0.01446 (13) | 0.1534 (2) | 0.94627 (9) | 0.0250 (4) |
| N4 | −0.03229 (16) | 0.2187 (3) | 0.99862 (11) | 0.0345 (5) |
| N5 | −0.12105 (14) | 0.1149 (2) | 0.79303 (10) | 0.0305 (5) |
| N6 | 0.13761 (15) | 0.1407 (2) | 1.06063 (10) | 0.0335 (5) |
| N7 | 0.04037 (16) | 0.4274 (2) | 1.12933 (12) | 0.0371 (5) |
| C1 | −0.02138 (16) | 0.1310 (3) | 0.88464 (11) | 0.0251 (5) |
| C2 | −0.11171 (16) | 0.1616 (3) | 0.85638 (12) | 0.0267 (5) |
| C3 | −0.18075 (18) | 0.2271 (3) | 0.88886 (14) | 0.0349 (6) |
| H3 | −0.1720 | 0.2599 | 0.9320 | 0.080* |
| C4 | −0.26341 (18) | 0.2426 (3) | 0.85559 (15) | 0.0409 (7) |
| H4 | −0.3112 | 0.2859 | 0.8762 | 0.080* |
| C5 | −0.27402 (18) | 0.1930 (3) | 0.79131 (15) | 0.0428 (7) |
| H5 | −0.3291 | 0.2014 | 0.7684 | 0.080* |
| C6 | −0.20152 (18) | 0.1311 (3) | 0.76189 (13) | 0.0378 (7) |
| H6 | −0.2087 | 0.0990 | 0.7185 | 0.080* |
| C7 | 0.10017 (17) | 0.0992 (3) | 0.94616 (12) | 0.0268 (5) |
| C8 | 0.16653 (17) | 0.0977 (3) | 1.00174 (12) | 0.0282 (5) |
| C9 | 0.25491 (18) | 0.0556 (3) | 0.99173 (13) | 0.0331 (6) |
| H9 | 0.2726 | 0.0256 | 0.9503 | 0.080* |
| C10 | 0.31574 (18) | 0.0597 (3) | 1.04516 (15) | 0.0393 (7) |
| H10 | 0.3750 | 0.0306 | 1.0404 | 0.080* |

| | | | | |
|---|---|---|---|---|
| C11 | 0.2877 (2) | 0.1073 (3) | 1.10541 (15) | 0.0416 (7) |
| H11 | 0.3279 | 0.1131 | 1.1415 | 0.080* |
| C12 | 0.1988 (2) | 0.1460 (3) | 1.11125 (13) | 0.0381 (6) |
| H12 | 0.1802 | 0.1774 | 1.1522 | 0.080* |
| H4A | −0.026 (3) | 0.317 (4) | 0.9919 (19) | 0.080* |
| H4B | 0.004 (3) | 0.204 (4) | 1.034 (2) | 0.080* |
| H1W | 0.001 (2) | −0.214 (3) | 0.7165 (14) | 0.046 (10)* |
| H2W | 0.040 (3) | 0.410 (5) | 0.734 (3) | 0.13 (2)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn1 | 0.0277 (2) | 0.0478 (3) | 0.0200 (2) | 0.000 | −0.00160 (16) | 0.000 |
| O1W | 0.066 (2) | 0.0431 (18) | 0.0229 (16) | 0.000 | −0.0029 (15) | 0.000 |
| O2W | 0.151 (5) | 0.057 (3) | 0.111 (4) | 0.000 | 0.071 (4) | 0.000 |
| O1 | 0.0634 (15) | 0.0664 (16) | 0.0616 (16) | −0.0025 (13) | −0.0322 (13) | −0.0026 (13) |
| O2 | 0.0622 (15) | 0.0615 (15) | 0.0514 (14) | −0.0047 (12) | −0.0083 (12) | 0.0277 (12) |
| O3 | 0.0537 (13) | 0.0614 (15) | 0.0383 (12) | −0.0128 (12) | 0.0016 (10) | 0.0083 (10) |
| N1 | 0.0270 (11) | 0.0368 (13) | 0.0253 (11) | 0.0028 (9) | −0.0030 (9) | −0.0018 (9) |
| N2 | 0.0271 (11) | 0.0375 (12) | 0.0261 (11) | 0.0024 (10) | −0.0054 (9) | −0.0002 (10) |
| N3 | 0.0267 (10) | 0.0266 (11) | 0.0215 (10) | 0.0003 (9) | −0.0009 (8) | −0.0023 (8) |
| N4 | 0.0344 (12) | 0.0418 (13) | 0.0273 (12) | 0.0038 (11) | 0.0018 (10) | −0.0097 (10) |
| N5 | 0.0278 (11) | 0.0394 (13) | 0.0242 (11) | 0.0010 (10) | −0.0028 (9) | 0.0017 (9) |
| N6 | 0.0422 (13) | 0.0328 (12) | 0.0250 (11) | 0.0006 (10) | −0.0047 (10) | 0.0003 (9) |
| N7 | 0.0366 (13) | 0.0393 (14) | 0.0350 (13) | 0.0044 (11) | −0.0049 (10) | 0.0015 (11) |
| C1 | 0.0262 (12) | 0.0264 (12) | 0.0225 (12) | −0.0008 (10) | −0.0026 (10) | 0.0001 (10) |
| C2 | 0.0278 (12) | 0.0245 (12) | 0.0275 (13) | 0.0000 (10) | −0.0022 (10) | 0.0012 (10) |
| C3 | 0.0326 (14) | 0.0338 (14) | 0.0380 (15) | 0.0030 (12) | −0.0006 (12) | −0.0029 (12) |
| C4 | 0.0293 (14) | 0.0428 (16) | 0.0505 (18) | 0.0073 (12) | −0.0015 (13) | −0.0043 (14) |
| C5 | 0.0302 (14) | 0.0546 (19) | 0.0430 (17) | 0.0058 (13) | −0.0079 (13) | 0.0075 (14) |
| C6 | 0.0300 (14) | 0.0540 (18) | 0.0288 (14) | 0.0012 (13) | −0.0068 (11) | 0.0038 (13) |
| C7 | 0.0278 (12) | 0.0265 (12) | 0.0261 (13) | 0.0003 (10) | −0.0014 (10) | 0.0010 (10) |
| C8 | 0.0328 (13) | 0.0265 (13) | 0.0252 (12) | −0.0028 (11) | −0.0027 (11) | 0.0017 (10) |
| C9 | 0.0317 (13) | 0.0338 (14) | 0.0334 (14) | −0.0006 (12) | −0.0040 (11) | −0.0006 (12) |
| C10 | 0.0320 (14) | 0.0390 (16) | 0.0463 (17) | −0.0017 (12) | −0.0092 (13) | 0.0050 (13) |
| C11 | 0.0438 (17) | 0.0413 (16) | 0.0384 (16) | −0.0059 (13) | −0.0173 (13) | 0.0066 (13) |
| C12 | 0.0479 (17) | 0.0404 (16) | 0.0251 (13) | −0.0030 (13) | −0.0097 (12) | 0.0019 (12) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zn1—O1W | 2.008 (3) | N6—C12 | 1.346 (3) |
| Zn1—O2W | 2.852 (5) | C1—C2 | 1.469 (3) |
| Zn1—N1 | 2.078 (2) | C2—C3 | 1.382 (4) |
| Zn1—N5 | 2.141 (2) | C3—C4 | 1.387 (4) |
| O1W—H1W | 0.79 (3) | C3—H3 | 0.9300 |
| O2W—H2W | 0.92 (5) | C4—C5 | 1.386 (4) |
| O1—N7 | 1.243 (3) | C4—H4 | 0.9300 |
| O2—N7 | 1.238 (3) | C5—C6 | 1.378 (4) |

| | | | |
|---|---|---|---|
| O3—N7 | 1.253 (3) | C5—H5 | 0.9300 |
| N1—C1 | 1.319 (3) | C6—H6 | 0.9300 |
| N1—N2 | 1.373 (3) | C7—C8 | 1.469 (3) |
| N2—C7 | 1.323 (3) | C8—C9 | 1.393 (4) |
| N3—C1 | 1.355 (3) | C9—C10 | 1.385 (4) |
| N3—C7 | 1.372 (3) | C9—H9 | 0.9300 |
| N3—N4 | 1.426 (3) | C10—C11 | 1.377 (4) |
| N4—H4A | 0.94 (4) | C10—H10 | 0.9300 |
| N4—H4B | 0.89 (4) | C11—C12 | 1.379 (4) |
| N5—C6 | 1.340 (3) | C11—H11 | 0.9300 |
| N5—C2 | 1.358 (3) | C12—H12 | 0.9300 |
| N6—C8 | 1.343 (3) | | |

| | | | |
|---|---|---|---|
| O1W—Zn1—N1 | 97.28 (6) | N5—C2—C3 | 122.7 (2) |
| O1W—Zn1—N1$^{i}$ | 97.28 (6) | N5—C2—C1 | 111.5 (2) |
| N1—Zn1—N1$^{i}$ | 165.44 (12) | C3—C2—C1 | 125.9 (2) |
| O1W—Zn1—N5$^{i}$ | 108.96 (6) | C2—C3—C4 | 118.4 (3) |
| N1—Zn1—N5$^{i}$ | 97.73 (8) | C2—C3—H3 | 120.8 |
| N1$^{i}$—Zn1—N5$^{i}$ | 77.47 (8) | C4—C3—H3 | 120.8 |
| O1W—Zn1—N5 | 108.96 (6) | C5—C4—C3 | 119.3 (3) |
| N1—Zn1—N5 | 77.47 (8) | C5—C4—H4 | 120.3 |
| N1$^{i}$—Zn1—N5 | 97.73 (8) | C3—C4—H4 | 120.3 |
| N5$^{i}$—Zn1—N5 | 142.09 (12) | C6—C5—C4 | 118.9 (3) |
| O2W—Zn1—N1 | 82.73 (5) | C6—C5—H5 | 120.6 |
| O2W—Zn1—N5 | 71.05 (5) | C4—C5—H5 | 120.6 |
| Zn1—O1W—H1W | 120 (2) | N5—C6—C5 | 122.9 (3) |
| C1—N1—N2 | 109.2 (2) | N5—C6—H6 | 118.6 |
| C1—N1—Zn1 | 114.07 (16) | C5—C6—H6 | 118.6 |
| N2—N1—Zn1 | 136.65 (16) | N2—C7—N3 | 109.8 (2) |
| C7—N2—N1 | 106.3 (2) | N2—C7—C8 | 123.3 (2) |
| C1—N3—C7 | 106.0 (2) | N3—C7—C8 | 126.9 (2) |
| C1—N3—N4 | 124.4 (2) | N6—C8—C9 | 123.1 (2) |
| C7—N3—N4 | 129.6 (2) | N6—C8—C7 | 116.7 (2) |
| N3—N4—H4A | 105 (2) | C9—C8—C7 | 120.2 (2) |
| N3—N4—H4B | 104 (2) | C10—C9—C8 | 118.1 (3) |
| H4A—N4—H4B | 102 (3) | C10—C9—H9 | 120.9 |
| C6—N5—C2 | 117.9 (2) | C8—C9—H9 | 120.9 |
| C6—N5—Zn1 | 126.42 (18) | C11—C10—C9 | 119.4 (3) |
| C2—N5—Zn1 | 115.42 (16) | C11—C10—H10 | 120.3 |
| C8—N6—C12 | 117.3 (2) | C9—C10—H10 | 120.3 |
| O2—N7—O1 | 121.5 (3) | C10—C11—C12 | 118.8 (3) |
| O2—N7—O3 | 119.0 (2) | C10—C11—H11 | 120.6 |
| O1—N7—O3 | 119.4 (2) | C12—C11—H11 | 120.6 |
| N1—C1—N3 | 108.7 (2) | N6—C12—C11 | 123.2 (3) |
| N1—C1—C2 | 120.6 (2) | N6—C12—H12 | 118.4 |
| N3—C1—C2 | 130.7 (2) | C11—C12—H12 | 118.4 |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N4—H4*A*···O2$^{ii}$ | 0.94 (4) | 2.25 (4) | 3.100 (3) | 149 (3) |
| N4—H4*A*···O2 | 0.94 (4) | 2.55 (4) | 3.192 (4) | 126 (3) |
| N4—H4*B*···N6 | 0.89 (4) | 2.13 (4) | 2.875 (3) | 141 (3) |
| N4—H4*B*···O3 | 0.89 (4) | 2.43 (4) | 3.005 (3) | 122 (3) |
| O1*W*—H1*W*···O3$^{iii}$ | 0.79 (3) | 1.93 (3) | 2.714 (3) | 170 (3) |
| O2*W*—H2*W*···O1$^{iv}$ | 0.92 (5) | 2.02 (5) | 2.900 (4) | 161 (5) |

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