

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

Diaquabis(pyridine-2-carboxylato- $\kappa^2N,O$ )zinc dimethylformamide hemisolvateLilia Croitor,<sup>a\*</sup> Diana Chisca,<sup>b</sup> Eduard B. Coropceanu<sup>b</sup> and Marina S. Fonari<sup>a</sup>

<sup>a</sup>Institute of Applied Physics, Academy of Sciences of R. Moldova, Academy str. 5, MD2028 Chisinau, Republic of Moldova, and <sup>b</sup>Institute of Chemistry, Academy of Sciences of R. Moldova, Academy str. 3, MD2028 Chisinau, Republic of Moldova  
Correspondence e-mail: croitor.lilia@gmail.com

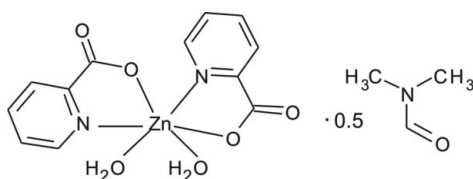
Received 28 June 2013; accepted 9 July 2013

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(C-C) = 0.009$  Å; disorder in solvent or counterion;  $R$  factor = 0.062;  $wR$  factor = 0.114; data-to-parameter ratio = 11.7.

In the title compound,  $[Zn(C_6H_4NO_2)_2(H_2O)_2] \cdot 0.5C_3H_7NO$ , the  $Zn^{II}$  ion is coordinated in a distorted octahedral  $N_2O_4$  environment by two  $N,O$ -chelating pyridine-2-carboxylate ligands and two *cis* water molecules. The chelating pyridine-2-carboxylate ligands create two five-membered  $Zn/N/C/C/O$  rings, which form a dihedral angle of  $86.4(2)^\circ$ . In the crystal,  $O-H \cdots O$  hydrogen bonds link the complex molecules into a two-dimensional network parallel to (100). The dimethylformamide solvent molecule is disordered about a twofold rotation axis.

## Related literature

For background to polydentate ligands, see: Udvardy *et al.* (2013); Groni *et al.* (2008); Golenya *et al.* (2011); Ma *et al.* (2009). For related structures, see: Chen & Hu (2011); Li *et al.* (2008); Lumme *et al.* (1969); Takenaka *et al.* (1970); Uggla *et al.* (1969). For hydrogen-bond graph-set motifs, see: Bernstein *et al.* (1995).



## Experimental

## Crystal data

 $[Zn(C_6H_4NO_2)_2(H_2O)_2] \cdot 0.5C_3H_7NO$ 
 $M_r = 382.16$   
Monoclinic,  $C2/c$ 
 $a = 25.777(3)$  Å  
 $b = 8.6754(4)$  Å  
 $c = 16.7916(17)$  Å  
 $\beta = 125.228(15)^\circ$   
 $V = 3067.4(5)$  Å<sup>3</sup>
 $Z = 8$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.64$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.18 \times 0.12 \times 0.02$  mm

## Data collection

 Agilent Xcalibur Eos diffractometer  
 Absorption correction: multi-scan  
 (*CrysAlis PRO*; Agilent, 2011)  
 $T_{min} = 0.906$ ,  $T_{max} = 1.000$ 

 4865 measured reflections  
 2844 independent reflections  
 1772 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.055$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.062$   
 $wR(F^2) = 0.114$   
 $S = 1.00$   
 2844 reflections  
 244 parameters  
 162 restraints

 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{max} = 0.47$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.44$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1W-H1W1 \cdots O4^i$	0.86 (2)	1.86 (2)	2.715 (6)	174 (5)
$O1W-H2W1 \cdots O2^{ii}$	0.86 (2)	1.89 (2)	2.723 (5)	163 (5)
$O2W-H1W2 \cdots O2^{iii}$	0.86 (2)	1.98 (3)	2.768 (5)	152 (4)
$O2W-H2W2 \cdots O3^i$	0.87 (2)	1.85 (2)	2.704 (5)	170 (4)

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

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; 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: LH5630).

## References

- Agilent (2011). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.  
 Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed.* **34**, 1555–1573.  
 Chen, W.-T. & Hu, L. (2011). *Acta Chim. Slov.* **58**, 167–170.  
 Golenya, I. A., Boyko, A. N., Kalibabchuk, V. A., Haukka, M. & Tomy, S. V. (2011). *Acta Cryst.* **E67**, m1558–m1559.  
 Groni, S., Dorlet, P., Blain, G., Bourcier, S., Guillot, R. & Anxolabehere-Mallart, E. (2008). *Inorg. Chem.* **47**, 3166–3172.  
 Li, X.-B., Shang, R.-L. & Sun, B.-W. (2008). *Acta Cryst.* **E64**, m131.  
 Lumme, P., Lundgren, G. & Mark, W. (1969). *Acta Chem. Scand.* **23**, 3011–3022.  
 Ma, K., Shi, Q., Hu, M., Cai, X. & Huang, S. (2009). *Inorg. Chim. Acta*, **362**, 4926–4930.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Takenaka, A., Utsumi, H., Ishihara, N., Furusaki, A. & Nitta, I. (1970). *J. Chem. Soc. Jpn Pure Chem.* **91**, 921–928.  
 Udvardy, A., Bényei, A. C., Juhász, P., Joó, F. & Kathó, Á. (2013). *Polyhedron*, **60**, 1–9.  
 Uggla, R., Lundell, S. & Patrikka, J. (1969). *Suom. Kemistil. B*, **42**, 270.

## supporting information

*Acta Cryst.* (2013). E69, m454 [doi:10.1107/S1600536813018941]

**Diaquabis(pyridine-2-carboxylato- $\kappa^2N,O$ )zinc dimethylformamide hemisolvate**

Lilia Croitor, Diana Chisca, Eduard B. Coropceanu and Marina S. Fonari

**S1. Comment**

Polydentate ligands such as pyridine-2-carboxylic acid (Hpic=picolinic acid) play important role in coordination chemistry and homogeneous catalysis. The combination of pyridyl and carboxyl groups in a single *bridge*-type ligand results in highly interconnected networks and gives limitless possibilities for increased network stability (Udvardy *et al.*, 2013; Groni *et al.*, 2008; Golenya *et al.* 2011). The COO<sup>-</sup> group and the nitrogen atom in Hpic have strong coordination abilities and multiple coordination modes (Ma *et al.*, 2009). Herein, we report the crystal structure of the title compound.

The molecular structure of the title complex is shown in Fig. 1. The Zn<sup>II</sup> ion is coordinated in a distorted octahedral N<sub>2</sub>O<sub>4</sub> environment by two pyridine N-atoms, two carboxylate O atoms and two O atoms of two *cis*-coordinated water molecules. Each of two coordinated pic residues results in the formation of a five-membered chelate ring. The dihedral angle between two chelate rings is 86.4 (2)°. In some similar pyridine-2-carboxylato Zn(II) complexes (Chen & Hu, 2011; Li *et al.*, 2008; Lumme *et al.*, 1969; Takenaka *et al.*, 1970; Ugglä *et al.*, 1969) the two pic ligands lie in the equatorial plane, and the water molecules are in a *trans*-arrangement.

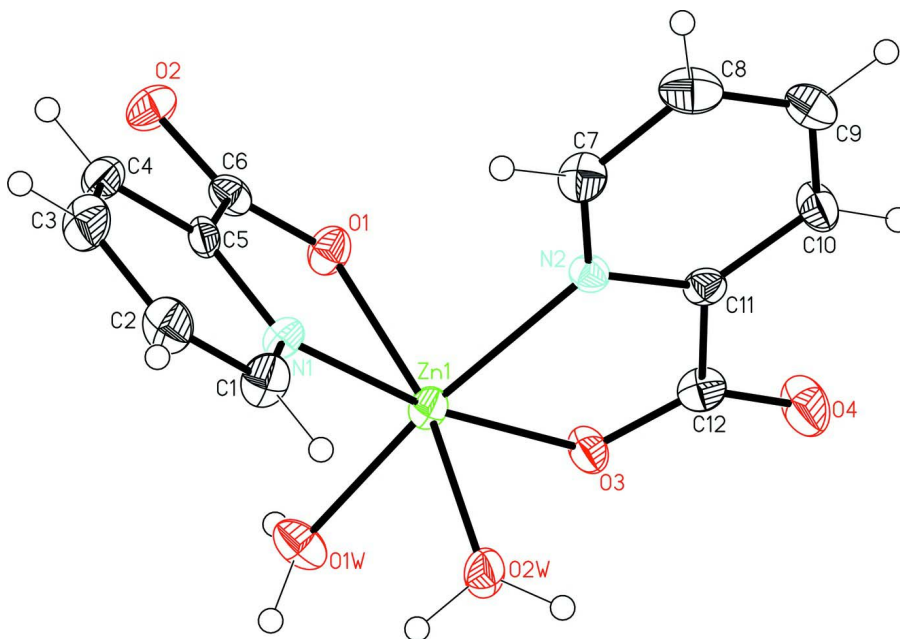
The crystal packing is directed by hydrogen bond interactions with the participation of water H-donor atoms and carboxylic group O atoms acting as acceptors. Complex molecules are combined into ladder-like tapes *via* alternation of two similar  $R_2^2(8)$  (Bernstein *et al.*, 1995) graph-set motifs (Table 1, Figs. 2 and 3). The overall hydrogen bond motif is a two-dimensional layer parallel to (100). The title compound is isotypic with [Mn(C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].0.5C<sub>2</sub>H<sub>3</sub>N (Groni *et al.*, 2008), where the dimethylformamide solvent in the title compound is substituted by the acetonitrile.

**S2. Experimental**

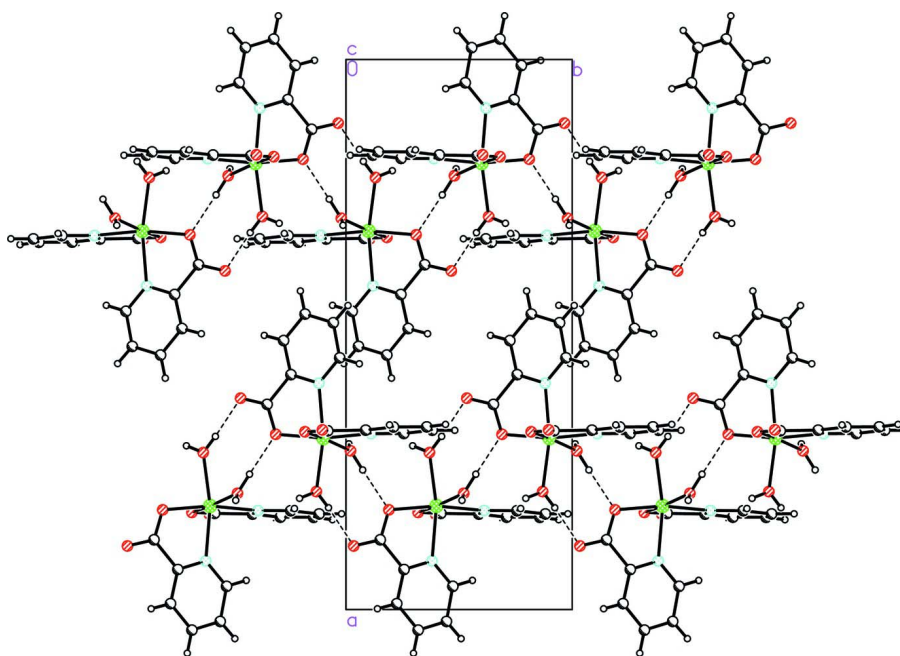
To Zn(BF<sub>4</sub>)<sub>2</sub>(240 mg, 1 mmol) dissolved in 15 ml of water was added Hpic(246 mg, 2 mmol) dissolved in 15 ml of mixture methanol/dimethylformamide 1:1 (v/v). The reaction mixture was refluxed for ~ 15 min, and upon cooling to room temperature prism-shape colorless crystals precipitated (yield: 52%).

**S3. Refinement**

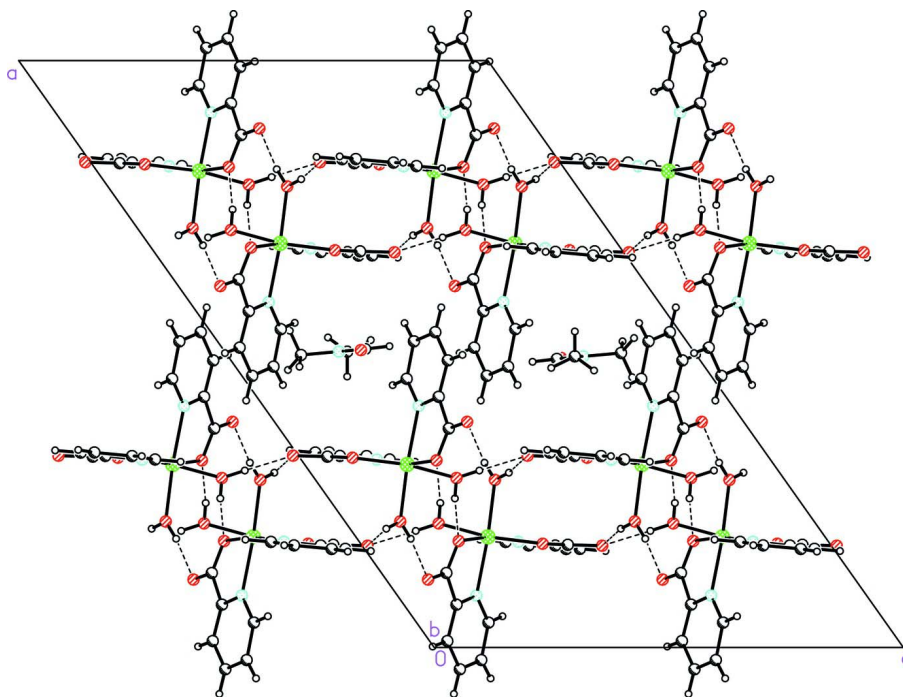
The C-bound hydrogen atoms were placed in calculated positions with C—H = 0.93 Å and were treated using a riding-model approximation with  $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$  or C—H = 0.96 Å and  $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{C})$  for methyl H atoms. Water O—H hydrogen atoms were located from a difference Fourier map at intermediate stage of the refinement and the O—H and H···H distances were restrained to be 0.86 (1) and 1.46 (1) Å. These hydrogen atoms were refined with isotropic displacement parameter  $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{O})$ . The dimethylformamide molecule is disordered about crystallographic twofold rotation axis.

**Figure 1**

The molecular structure of  $[\text{Zn}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2]$ . Displacement ellipsoids are shown at the 30% probability level. H atoms are presented as small spheres of arbitrary radius.

**Figure 2**

View along the crystallographic  $c$  axis. Solvent molecules are not shown. Hydrogen bonds are shown as dashed lines.

**Figure 3**

Part of the crystal structure showing incorporation of DMF molecules in the crystal. The view is along the crystallographic *b* axis. Hydrogen bonds are shown as dashed lines.

### Diaquabis(pyridine-2-carboxylato- $\kappa^2N,O$ )zinc dimethylformamide hemisolvate

#### Crystal data

$[\text{Zn}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 0.5\text{C}_3\text{H}_7\text{NO}$

$M_r = 382.16$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 25.777\ (3)\ \text{\AA}$

$b = 8.6754\ (4)\ \text{\AA}$

$c = 16.7916\ (17)\ \text{\AA}$

$\beta = 125.228\ (15)^\circ$

$V = 3067.4\ (5)\ \text{\AA}^3$

$Z = 8$

$F(000) = 1568$

$D_x = 1.655\ \text{Mg m}^{-3}$

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

Cell parameters from 957 reflections

$\theta = 3.0\text{--}28.9^\circ$

$\mu = 1.64\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Prism, colourless

$0.18 \times 0.12 \times 0.02\ \text{mm}$

#### Data collection

Agilent Xcalibur Eos  
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution:  $15.9914\ \text{pixels mm}^{-1}$

$\omega$  scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Agilent, 2011)

$T_{\min} = 0.906$ ,  $T_{\max} = 1.000$

4865 measured reflections

2844 independent reflections

1772 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$

$\theta_{\max} = 25.5^\circ$ ,  $\theta_{\min} = 3.0^\circ$

$h = -31 \rightarrow 25$

$k = -10 \rightarrow 5$

$l = -9 \rightarrow 20$

Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.062$   
 $wR(F^2) = 0.114$   
 $S = 1.00$   
 2844 reflections  
 244 parameters  
 162 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  
 $w = 1/[\sigma^2(F_o^2) + (0.025P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.47 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.44 \text{ e } \text{Å}^{-3}$

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 ( $\text{Å}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Zn1	0.18837 (3)	0.40000 (7)	0.78138 (4)	0.0278 (2)	
N1	0.18028 (19)	0.6106 (5)	0.8391 (3)	0.0273 (11)	
N2	0.08845 (19)	0.3806 (5)	0.6684 (3)	0.0253 (10)	
O1	0.17673 (17)	0.3193 (4)	0.8877 (2)	0.0338 (10)	
O2	0.17327 (17)	0.3959 (4)	1.0115 (2)	0.0367 (10)	
O3	0.18125 (17)	0.1902 (4)	0.7129 (3)	0.0335 (10)	
O4	0.11570 (19)	0.0343 (5)	0.5895 (3)	0.0555 (13)	
C1	0.1798 (3)	0.7558 (6)	0.8114 (4)	0.0396 (16)	
H1	0.1837	0.7722	0.7603	0.048*	
C2	0.1738 (3)	0.8813 (6)	0.8553 (4)	0.0433 (16)	
H2	0.1739	0.9808	0.8347	0.052*	
C3	0.1677 (3)	0.8573 (7)	0.9300 (4)	0.0441 (17)	
H3	0.1633	0.9405	0.9606	0.053*	
C4	0.1681 (2)	0.7106 (6)	0.9593 (4)	0.0336 (14)	
H4	0.1646	0.6931	1.0107	0.040*	
C5	0.1738 (2)	0.5873 (6)	0.9120 (3)	0.0256 (13)	
C6	0.1751 (2)	0.4195 (6)	0.9396 (4)	0.0279 (13)	
C7	0.0422 (3)	0.4729 (6)	0.6531 (4)	0.0364 (15)	
H7	0.0529	0.5598	0.6921	0.044*	
C8	-0.0215 (3)	0.4441 (7)	0.5811 (4)	0.0461 (17)	
H8	-0.0529	0.5086	0.5735	0.055*	
C9	-0.0372 (3)	0.3196 (7)	0.5217 (4)	0.0428 (16)	
H9	-0.0794	0.2990	0.4717	0.051*	
C10	0.0109 (3)	0.2248 (7)	0.5376 (4)	0.0376 (15)	

H10	0.0014	0.1393	0.4980	0.045*	
C11	0.0729 (3)	0.2570 (6)	0.6122 (4)	0.0268 (13)	
C12	0.1270 (3)	0.1516 (6)	0.6384 (4)	0.0326 (14)	
O1W	0.28549 (18)	0.3692 (5)	0.8823 (3)	0.0389 (10)	
H1W1	0.3148 (18)	0.425 (5)	0.888 (4)	0.05 (2)*	
H2W1	0.298 (2)	0.296 (4)	0.924 (3)	0.042 (19)*	
O2W	0.2112 (2)	0.5202 (5)	0.6968 (3)	0.0413 (11)	
H1W2	0.199 (2)	0.512 (5)	0.6369 (16)	0.031 (16)*	
H2W2	0.2454 (17)	0.575 (6)	0.732 (3)	0.05 (2)*	
O1X	0.9935 (9)	0.7274 (12)	0.7077 (8)	0.142 (8)	0.50
N1X	0.9961 (14)	0.9688 (8)	0.7567 (15)	0.065 (4)	0.50
C1X	0.9916 (9)	0.8645 (13)	0.6968 (9)	0.093 (8)	0.50
H1X	0.9865	0.8999	0.6404	0.112*	0.50
C2X	1.0023 (11)	0.9255 (17)	0.8428 (12)	0.090 (7)	0.50
H2XA	0.9611	0.9229	0.8307	0.135*	0.50
H2XB	1.0286	0.9990	0.8933	0.135*	0.50
H2XC	1.0214	0.8252	0.8629	0.135*	0.50
C3X	0.996 (3)	1.1310 (9)	0.739 (3)	0.194 (10)	0.50
H3XA	1.0385	1.1673	0.7715	0.292*	0.50
H3XB	0.9750	1.1854	0.7631	0.292*	0.50
H3XC	0.9731	1.1486	0.6700	0.292*	0.50

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.0328 (4)	0.0260 (4)	0.0265 (4)	-0.0006 (3)	0.0182 (3)	-0.0013 (3)
N1	0.034 (3)	0.026 (2)	0.026 (2)	0.001 (2)	0.020 (2)	0.002 (2)
N2	0.024 (3)	0.024 (3)	0.028 (3)	0.001 (2)	0.015 (2)	0.000 (2)
O1	0.045 (3)	0.027 (2)	0.032 (2)	-0.002 (2)	0.024 (2)	-0.0019 (18)
O2	0.046 (3)	0.041 (2)	0.032 (2)	0.005 (2)	0.027 (2)	0.0093 (19)
O3	0.024 (2)	0.033 (2)	0.034 (2)	0.0005 (19)	0.011 (2)	-0.0076 (19)
O4	0.039 (3)	0.047 (3)	0.065 (3)	0.000 (2)	0.022 (3)	-0.030 (2)
C1	0.057 (5)	0.029 (3)	0.038 (4)	-0.006 (3)	0.030 (4)	0.004 (3)
C2	0.053 (4)	0.022 (3)	0.053 (4)	-0.008 (3)	0.030 (4)	-0.006 (3)
C3	0.053 (5)	0.032 (4)	0.049 (4)	0.003 (3)	0.030 (4)	-0.011 (3)
C4	0.039 (4)	0.037 (4)	0.031 (3)	-0.002 (3)	0.024 (3)	-0.003 (3)
C5	0.019 (3)	0.029 (3)	0.020 (3)	-0.001 (3)	0.006 (3)	-0.006 (3)
C6	0.021 (3)	0.030 (3)	0.027 (3)	0.000 (3)	0.010 (3)	0.005 (3)
C7	0.039 (4)	0.028 (3)	0.041 (4)	0.008 (3)	0.023 (3)	-0.001 (3)
C8	0.036 (4)	0.045 (4)	0.062 (5)	0.019 (3)	0.031 (4)	0.013 (3)
C9	0.026 (4)	0.050 (4)	0.046 (4)	0.001 (3)	0.017 (3)	0.001 (4)
C10	0.029 (4)	0.036 (4)	0.038 (4)	-0.005 (3)	0.013 (3)	-0.010 (3)
C11	0.032 (3)	0.024 (3)	0.031 (3)	-0.002 (3)	0.021 (3)	0.001 (3)
C12	0.037 (4)	0.025 (3)	0.040 (4)	0.005 (3)	0.025 (3)	0.003 (3)
O1W	0.030 (3)	0.032 (3)	0.041 (3)	-0.005 (2)	0.013 (2)	0.012 (2)
O2W	0.049 (3)	0.049 (3)	0.026 (2)	-0.020 (2)	0.022 (2)	-0.005 (2)
O1X	0.117 (11)	0.095 (9)	0.19 (2)	0.029 (11)	0.074 (17)	-0.078 (9)
N1X	0.123 (11)	0.043 (6)	0.074 (8)	0.023 (15)	0.082 (8)	0.005 (13)

C1X	0.072 (14)	0.13 (2)	0.071 (16)	0.034 (17)	0.040 (14)	-0.035 (15)
C2X	0.132 (18)	0.084 (15)	0.072 (14)	0.015 (12)	0.069 (14)	0.015 (10)
C3X	0.45 (3)	0.055 (9)	0.26 (2)	0.02 (5)	0.31 (3)	0.03 (3)

*Geometric parameters (Å, °)*

Zn1—O1W	2.078 (4)	C7—H7	0.9300
Zn1—O1	2.094 (3)	C8—C9	1.363 (7)
Zn1—O2W	2.101 (4)	C8—H8	0.9300
Zn1—O3	2.104 (3)	C9—C10	1.379 (7)
Zn1—N1	2.134 (4)	C9—H9	0.9300
Zn1—N2	2.150 (4)	C10—C11	1.375 (7)
N1—C1	1.341 (6)	C10—H10	0.9300
N1—C5	1.343 (6)	C11—C12	1.506 (7)
N2—C11	1.329 (6)	O1W—H1W1	0.857 (18)
N2—C7	1.333 (6)	O1W—H2W1	0.857 (18)
O1—C6	1.249 (6)	O2W—H1W2	0.863 (18)
O2—C6	1.251 (6)	O2W—H2W2	0.866 (19)
O3—C12	1.271 (6)	O1X—C1X	1.1999
O4—C12	1.233 (6)	N1X—C1X	1.3069
C1—C2	1.373 (7)	N1X—C2X	1.4118
C1—H1	0.9300	N1X—C3X	1.4373
C2—C3	1.368 (7)	C1X—H1X	0.9300
C2—H2	0.9300	C2X—H2XA	0.9600
C3—C4	1.362 (7)	C2X—H2XB	0.9600
C3—H3	0.9300	C2X—H2XC	0.9600
C4—C5	1.390 (7)	C3X—H3XA	0.9600
C4—H4	0.9300	C3X—H3XB	0.9600
C5—C6	1.523 (7)	C3X—H3XC	0.9600
C7—C8	1.389 (7)		
O1W—Zn1—O1	87.68 (16)	N1—C5—C6	115.4 (4)
O1W—Zn1—O2W	86.53 (18)	C4—C5—C6	123.6 (5)
O1—Zn1—O2W	167.39 (15)	O1—C6—O2	126.5 (5)
O1W—Zn1—O3	91.07 (15)	O1—C6—C5	117.2 (5)
O1—Zn1—O3	99.57 (14)	O2—C6—C5	116.3 (5)
O2W—Zn1—O3	91.74 (16)	N2—C7—C8	122.5 (5)
O1W—Zn1—N1	97.31 (16)	N2—C7—H7	118.8
O1—Zn1—N1	78.44 (15)	C8—C7—H7	118.8
O2W—Zn1—N1	91.19 (17)	C9—C8—C7	118.9 (5)
O3—Zn1—N1	171.28 (15)	C9—C8—H8	120.6
O1W—Zn1—N2	167.46 (16)	C7—C8—H8	120.6
O1—Zn1—N2	92.17 (15)	C8—C9—C10	118.4 (6)
O2W—Zn1—N2	95.90 (16)	C8—C9—H9	120.8
O3—Zn1—N2	76.58 (15)	C10—C9—H9	120.8
N1—Zn1—N2	94.94 (16)	C11—C10—C9	119.9 (5)
C1—N1—C5	118.5 (5)	C11—C10—H10	120.1
C1—N1—Zn1	129.1 (4)	C9—C10—H10	120.1

C5—N1—Zn1	112.4 (3)	N2—C11—C10	121.8 (5)
C11—N2—C7	118.5 (5)	N2—C11—C12	115.7 (5)
C11—N2—Zn1	114.0 (4)	C10—C11—C12	122.5 (5)
C7—N2—Zn1	127.4 (4)	O4—C12—O3	125.2 (5)
C6—O1—Zn1	116.2 (3)	O4—C12—C11	118.9 (5)
C12—O3—Zn1	117.7 (3)	O3—C12—C11	115.9 (5)
N1—C1—C2	122.7 (5)	Zn1—O1W—H1W1	126 (3)
N1—C1—H1	118.7	Zn1—O1W—H2W1	118 (3)
C2—C1—H1	118.7	H1W1—O1W—H2W1	116 (3)
C3—C2—C1	118.7 (5)	Zn1—O2W—H1W2	133 (3)
C3—C2—H2	120.6	Zn1—O2W—H2W2	113 (3)
C1—C2—H2	120.6	H1W2—O2W—H2W2	113 (3)
C4—C3—C2	119.5 (5)	C1X—N1X—C2X	120.7
C4—C3—H3	120.3	C1X—N1X—C3X	122.1
C2—C3—H3	120.3	C2X—N1X—C3X	117.2
C3—C4—C5	119.7 (5)	O1X—C1X—N1X	126.3
C3—C4—H4	120.2	O1X—C1X—H1X	116.9
C5—C4—H4	120.2	N1X—C1X—H1X	116.9
N1—C5—C4	121.0 (5)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1 <i>W</i> —H1 <i>W</i> 1 $\cdots$ O4 <sup>i</sup>	0.86 (2)	1.86 (2)	2.715 (6)	174 (5)
O1 <i>W</i> —H2 <i>W</i> 1 $\cdots$ O2 <sup>ii</sup>	0.86 (2)	1.89 (2)	2.723 (5)	163 (5)
O2 <i>W</i> —H1 <i>W</i> 2 $\cdots$ O2 <sup>iii</sup>	0.86 (2)	1.98 (3)	2.768 (5)	152 (4)
O2 <i>W</i> —H2 <i>W</i> 2 $\cdots$ O3 <sup>i</sup>	0.87 (2)	1.85 (2)	2.704 (5)	170 (4)

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