Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Diaquabis(5-bromo-2-hydroxybenzoato)-bis(*N*-methylnicotinamide)zinc(II)

Zuzana Bujdošová,* Juraj Kuchár and Katarína Györyová

Department of Inorganic Chemistry, Institute of Chemistry, P. J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovakia
Correspondence e-mail: zuzana.bujdosova@upjs.sk

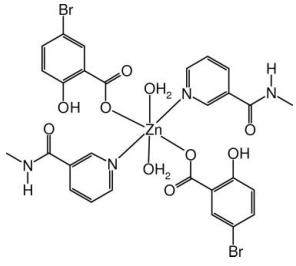
Received 26 February 2010; accepted 8 March 2010

Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.003 Å; R factor = 0.022; wR factor = 0.064; data-to-parameter ratio = 16.2.

The title mononuclear complex molecule, $[Zn(C_7H_4BrO_3)_2(C_7H_8N_2O)_2(H_2O)_2]$, has a crystallographically imposed centre of symmetry. The zinc(II) atom is coordinated by two N atoms from two *N*-methylnicotinamide ligands, two O atoms from two 5-bromosalicylate anions and two aqua O atoms in a slightly distorted octahedral geometry. Intramolecular O—H···O hydrogen-bonding interactions are present. In the crystal structure, molecules are linked by intermolecular O—H···O and N—H···O hydrogen bonds, forming a two-dimensional network perpendicular to [100].

Related literature

For general background to the properties of carboxylic acid–metal complexes, see: Nagar (1990); Cavagiolio *et al.* (2000). For the synthesis and properties of zinc(II) carboxylates reported by our group, see: Györyová *et al.* (2005, 2006); Bujdošová *et al.* (2009); Gebicki *et al.* (2003). For related structures, see: Necefoglu *et al.* (2001*a*,*b*); Hökelek *et al.* (2007, 2009*a*,*b*); Öztürk *et al.* (2008); Sarı *et al.* (2007); Liu *et al.* (2004).



Experimental

Crystal data

$[Zn(C_7H_4BrO_3)_2(C_7H_8N_2O)_2(H_2O)_2]$
M_r = 805.73
Triclinic, $P\overline{1}$
a = 8.1600 (2) Å
b = 10.1122 (3) Å
c = 10.4291 (3) Å
α = 66.800 (3)°
β = 74.334 (2)°
γ = 80.743 (2)°
V = 760.15 (4) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 3.50 mm^{-1}
T = 290 K
0.57 × 0.30 × 0.26 mm

Data collection

Oxford Diffraction Xcalibur Sapphire2 diffractometer
Absorption correction: numerical [Clark & Reid (1995) in *CrysAlis PRO* (Oxford Diffraction, 2009)]
T_{min} = 0.289, T_{max} = 0.484
32240 measured reflections
3153 independent reflections
2686 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.064
S = 1.15
3153 reflections
195 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1*O3*···O2	0.82	1.81	2.540 (2)	147
N2—H1*N2*···O3^{i}	0.86	2.55	3.1109 (19)	123
O5—H2*O5*···O2^{ii}	0.82	1.88	2.6694 (18)	162
O5—H1*O5*···O4^{iii}	0.82	1.94	2.7568 (13)	179

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); 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: *DIAMOND* (Crystal Impact, 2007); software used to prepare material for publication: *SHELXL97*.

Financial support by the Slovak Ministry of Education (VEGA project No. 1/0122/08) is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2423).

References

Bujdošová, Z., Györyová, K., Kovářová, J., Hudecová, D. & Halás, L. (2009). *J. Therm. Anal. Calorim.* **98**, 151–159.
Cavagiolio, G., Benedetto, L., Boccaleri, E., Colangelo, D., Viano, I. & Osella, D. (2000). *Inorg. Chim. Acta*, **305**, 61–68.
Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.
Crystal Impact (2007). *DIAMOND*. Crystal Impact, Bonn, Germany.
Gebicki, J., Sysa-Jedrzejowska, A. & Adamus, J. (2003). *Pol. J. Pharmacol.* **55**, 109–112.
Györyová, K., Chomič, J. & Kovářová, J. (2005). *J. Therm. Anal. Calorim.* **80**, 375–380.
Györyová, K., Chomič, J., Szunyogová, E., Piknová, L., Zeleňák, V. & Vargová, Z. (2006). *J. Therm. Anal. Calorim.* **84**, 727–732.
Hökelek, T., Çaylak, N. & Necefoğlu, H. (2007). *Acta Cryst.* E**63**, m2561–m2562.
Hökelek, T., Dal, H., Tercan, B., Özbek, F. E. & Necefoğlu, H. (2009*a*). *Acta Cryst.* E**65**, m607–m608.
Hökelek, T., Dal, H., Tercan, B., Özbek, F. E. & Necefoğlu, H. (2009*b*). *Acta Cryst.* E**65**, m481–m482.
Liu, Z.-D., Qu, Y., Tan, M.-Y. & Zhu, H.-L. (2004). *Acta Cryst.* E**60**, o1310–o1311.
Nagar, R. (1990). *J. Inorg. Biochem.* **40**, 349–356.
Necefoglu, H., Clegg, W. & Scott, A. J. (2001*a*). *Acta Cryst.* E**57**, m462–m464.
Necefoglu, H., Clegg, W. & Scott, A. J. (2001*b*). *Acta Cryst.* E**57**, m465–m466.

Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.
Öztürk, A., Hökelek, T., Özbek, F. E. & Necefoğlu, H. (2008). *Acta Cryst.* E**64**, m1218–m1219.
Sarı, M., Gökçe, G., Gökçe, S., Şahin, E. & Necefoğlu, H. (2007). *Acta Cryst.* E**63**, m2191.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2010). E**66**, m394–m395 [doi:10.1107/S1600536810008834]

Diaquabis(5-bromo-2-hydroxybenzoato)bis(*N*-methylnicotinamide)zinc(II)

Zuzana Bujdošová, Juraj Kuchár and Katarína Györyová

S1. Comment

The complexes of carboxylic acids with metals, e.g. zinc, are interesting due to different coordination modes of a carboxylate group bound to a metal ion. It is well documented that heterocyclic compounds, especially N-donor ligand systems, play a significant role in many biological systems, being a component of several vitamins and drugs (Nagar, 1990; Cavagiolio *et al.*, 2000). As a part of our ongoing studies of zinc(II) carboxylates (Györyová *et al.*, 2005; Györyová *et al.*, 2006; Bujdošová *et al.*, 2009) we have been exploring the synthesis and crystal structure of zinc(II) 5-bromo-salicylate containing *N*-methylnicotinamide, shown at in vitro study to be a potent anti-inflammatory agent (Gebicki *et al.*, 2003).

In the title monomeric complex $[Zn(C_7H_4BrO_3)_2(C_7H_8N_2O)_2(H_2O)_2]$ (Fig. 1), the zinc(II) atom, which lies on an inversion centre, exhibits a slightly distorted octahedral coordination geometry. The coordination sphere consists of three pairs of *trans*-arranged monodentate ligands. The two *N*-methylnicotinamide ligands are coordinated to the zinc atom through nitrogen atoms of the pyridine rings. The 5-bromosalicylate anion is coordinated through one oxygen atom of the carboxylate group. The similar distances O1—C1 (1.256 (2) Å) and O2—C1 (1.262 (2) Å) in the carboxylate group indicate a delocalized bonding arrangement and may be compared with the corresponding distances found in $[Zn(C_7H_4ClO_2)_2(C_{10}H_{14}N_2O)_2(H_2O)_2]$ (Sarı *et al.*, 2007). The plane of the carboxylate group is approximately coplanar with the plane of the benzene ring; the dihedral angle between these planes is 5.5 (3)°. Such behaviour is not unusual; a similar arrangement was observed in other compounds (e.g. diaquabis(*N*,*N*-diethylnicotinamide-*N*)bis(4-fluorobenzoato-O)zinc(II) (Hökelek *et al.*, 2007)). All other geometric parameters of the coordinated anion are similar to that found in free 5-bromosalicylic acid (Liu *et al.*, 2004). The distorted octahedral coordination is completed by two pyridine nitrogen atoms of two *N*-methylnicotinamide ligands in the axial positions. The Zn—N distance (2.1583 (9) Å) is in good agreement with the values reported for other octahedrally coordinated zinc(II) complexes [viz., Diaquabis(4-chloro-benzoato)bis(*N*,*N*-diethylnicotinamide)zinc(II), Zn—N: 2.157 (3) Å; Sarı *et al.*, 2007]. The coordination environment of the zinc(II) atom is completed by water molecules, forming with carboxylate oxygen atoms the basal plane of the distorted octahedron. The Zn—O distance (2.1396 (8) Å) is comparable with those found in similar compounds [viz. di-aquabis(2-bromobenzoato)bis(*N*,*N*-diethylnicotinamide)zinc(II), Zn—O: 2.1269 (12) Å; Hökelek *et al.*, 2009b]. Intramolecular hydrogen bonding interactions involving the hydroxyl groups and carboxylate oxygen atoms (O3—H1O3···O2) and the equatorially coordinated water molecule and carboxylate oxygen atom (O5—H2O5···O2) stabilize the molecular structure (Fig. 2). Intramolecular hydrogen bonds also influences the orientation and delocalized character of carboxylate group. The molecules of the title compound are linked into a two-dimensional network perpendicular to [100] by intermolecular O5—H1O5···O4 and N2—H1N2···O3 hydrogen bonds (Fig. 3).

S2. Experimental

Analytical reagent grade chemicals were used for the preparation of the title compound. The synthesis was carried out by reaction of aqueous solutions (20 ml) of $ZnCl_2$ (0.14 g, 1 mmol) and $NaHCO_3$ (0.17 g, 2 mmol). After complete removal of chloride anions, an acetone solution (10 ml) of 5-bromosalicylic acid (0.44 g, 2 mmol) was added. The resulting solution of $(5\text{-}BrC_6H_3\text{-}2\text{-}(OH)COO)_2Zn$ (0.50 g, 1 mmol) was mixed with an aqueous solution (10 ml) of *N*-methylnicotinamide (0.27 g, 2 mmol). The reaction mixture was stirred for 2 h and left aside for crystallization at room temperature. After two days, a small amount of colourless bright crystals appeared. The resulting crystals were isolated by filtration.

S3. Refinement

The hydrogen atoms of the water molecule were located in difference Fourier map and refined with the O—H distances constrained to 0.82 Å and with $U_{iso}(H) = 1.5U_{eq}(O)$. The H atom bound to N2 was located in a difference Fourier map and refined $U_{iso}(H) = 1.2U_{eq}(N)$. All other H atoms were positioned geometrically and constrained to ride on their parent atoms, with O—H = 0.82 Å, C—H = 0.93–0.96 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C, O)$ for methyl and hydroxyl H atoms.

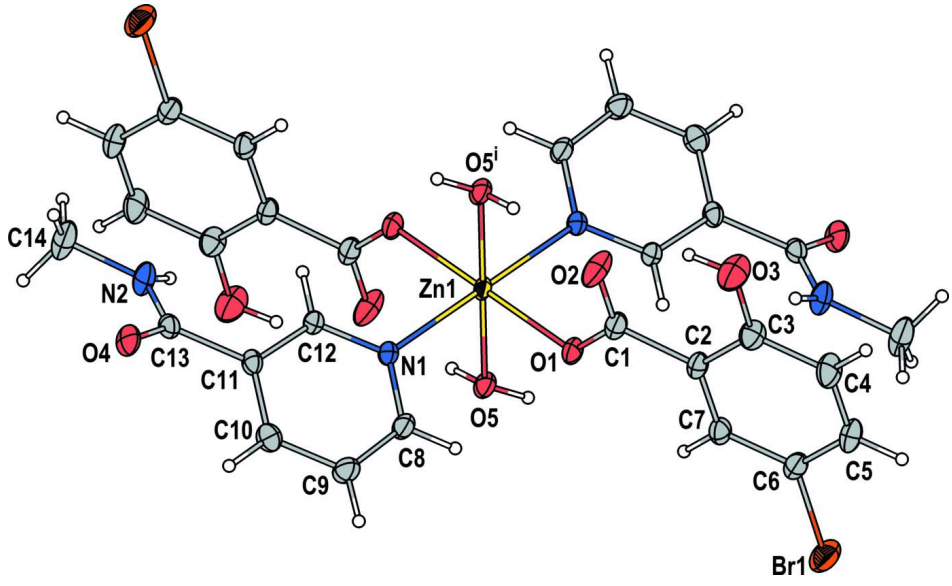


Figure 1

The molecular structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: (i) 1-x, -y, -z.

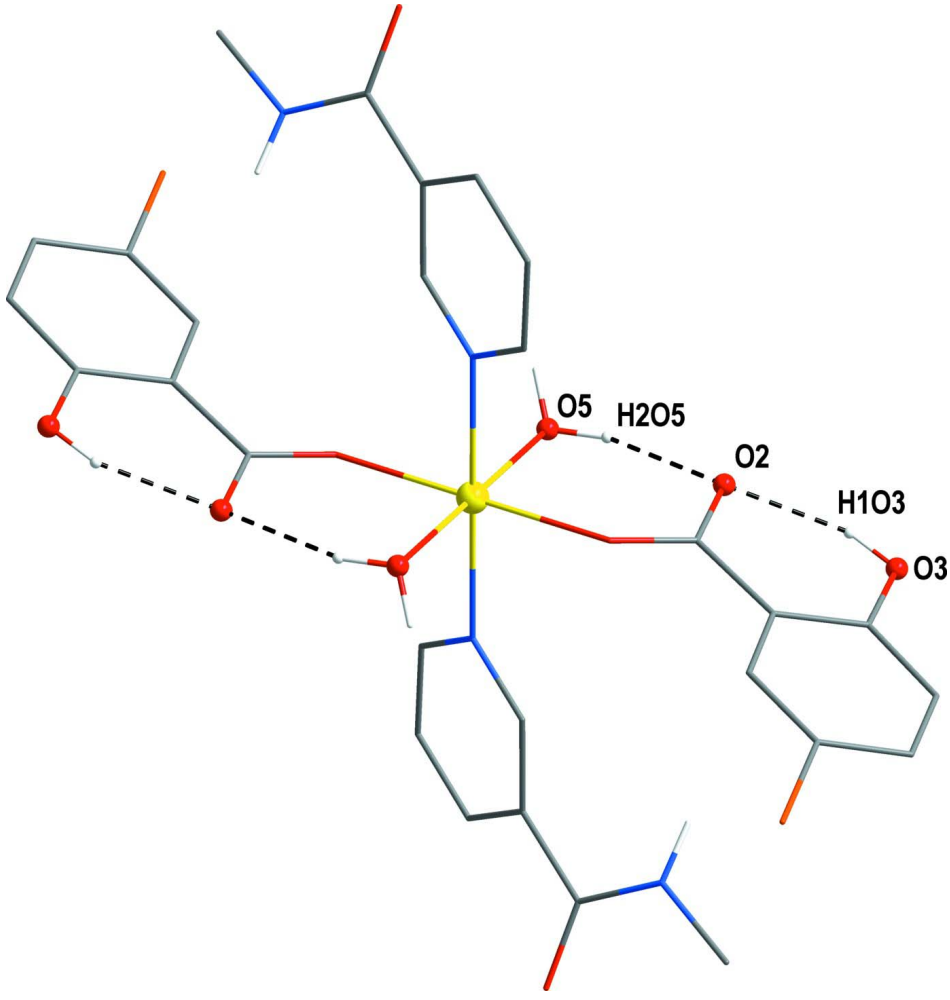


Figure 2

View of the intramolecular hydrogen bonds (dashed lines) of the title compound. Hydrogen atoms of aromatic rings and methyl groups are omitted for clarity.

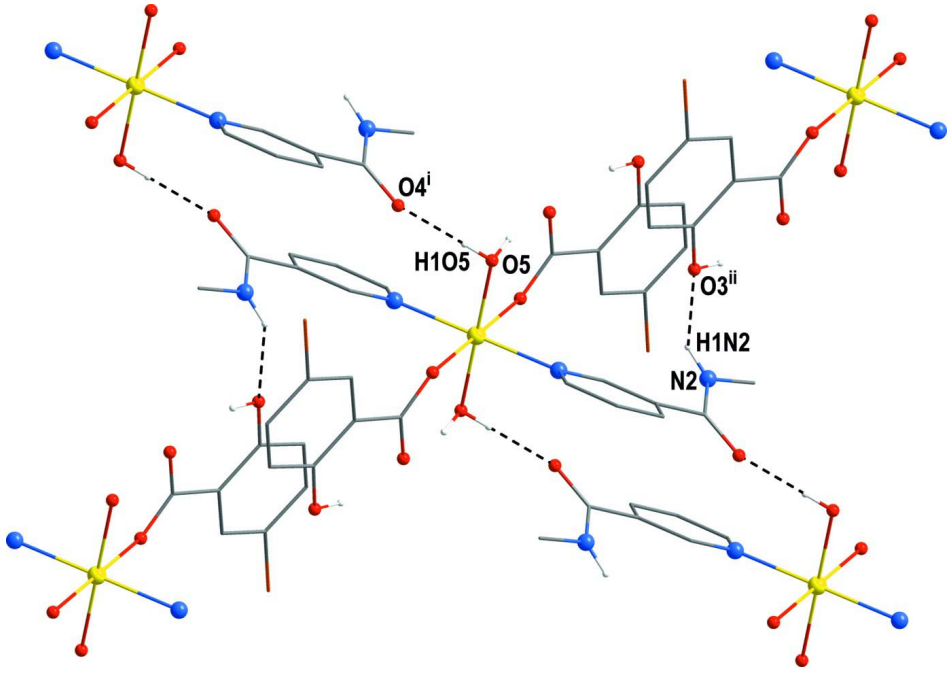


Figure 3

View of the intermolecular hydrogen bonds (dashed lines) of the title compound. Hydrogen atoms of aromatic rings and methyl groups are omitted for clarity. Symmetry codes: (i) x, -1+y, z; (ii) x, y, 1+z

Diaquabis(5-bromo-2-hydroxybenzoato)bis(*N*-methylnicotinamide)zinc(II)

Crystal data

$[Zn(C_7H_4BrO_3)_2(C_7H_8N_2O)_2(H_2O)_2]$
M_r = 805.73
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.1600 (2) Å
b = 10.1122 (3) Å
c = 10.4291 (3) Å
α = 66.800 (3)°
β = 74.334 (2)°
γ = 80.743 (2)°
V = 760.15 (4) Å^3
Z = 1
$F(000)$ = 404
D_x = 1.760 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 19248 reflections
θ = 3.0–29.6°
μ = 3.50 mm^{-1}
T = 290 K
Prism, colourless
0.57 × 0.30 × 0.26 mm

Data collection

Oxford Diffraction Xcalibur Sapphire2 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 8.3438 pixels mm^{-1}
ω scans
Absorption correction: numerical [Clark & Reid (1995) in *CrysAlis PRO* (Oxford Diffraction, 2009)]
T_{min} = 0.289, T_{max} = 0.484
32240 measured reflections
3153 independent reflections
2686 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 26.5°, θ_{min} = 3.0°
h = −10→10
k = −12→12
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.064$
$S = 1.15$
3153 reflections
195 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
$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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	0.0000	0.0000	0.02312 (9)
O1	0.67676 (14)	−0.02707 (13)	−0.17587 (12)	0.0305 (3)
O2	0.5864 (2)	0.14251 (15)	−0.36177 (15)	0.0493 (4)
O3	0.6562 (2)	0.11216 (16)	−0.60156 (15)	0.0550 (4)
H1O3	0.6075	0.1466	−0.5409	0.083*
C1	0.6699 (2)	0.02704 (19)	−0.30545 (19)	0.0299 (4)
C2	0.7659 (2)	−0.05359 (18)	−0.40050 (18)	0.0270 (4)
C3	0.7497 (2)	−0.00760 (19)	−0.54230 (19)	0.0348 (4)
C4	0.8343 (3)	−0.0873 (2)	−0.6265 (2)	0.0425 (5)
H4	0.8233	−0.0574	−0.7204	0.051*
C5	0.9340 (3)	−0.2099 (2)	−0.5713 (2)	0.0403 (5)
H5	0.9899	−0.2629	−0.6276	0.048*
C6	0.9505 (2)	−0.25379 (19)	−0.43114 (19)	0.0319 (4)
C7	0.8667 (2)	−0.17721 (18)	−0.34631 (18)	0.0295 (4)
H7	0.8777	−0.2085	−0.2522	0.035*
Br1	1.08861 (3)	−0.42202 (2)	−0.35493 (2)	0.05222 (9)
N1	0.66055 (11)	0.14385 (9)	0.01039 (9)	0.0245 (3)
N2	0.48397 (11)	0.41145 (9)	0.24800 (9)	0.0384 (4)
H1N2	0.4560	0.3237	0.2876	0.046*
C8	0.82847 (11)	0.13682 (9)	−0.04349 (9)	0.0302 (4)
H8	0.8741	0.0682	−0.0843	0.036*
C9	0.9368 (2)	0.2262 (2)	−0.0414 (2)	0.0373 (4)
H9	1.0533	0.2178	−0.0794	0.045*
C10	0.8694 (2)	0.32926 (19)	0.0186 (2)	0.0352 (4)
H10	0.9399	0.3919	0.0205	0.042*

C11	0.6960 (2)	0.33753 (16)	0.07550 (17)	0.0250 (3)
C12	0.5966 (2)	0.24263 (16)	0.06900 (17)	0.0241 (3)
H12	0.4799	0.2479	0.1072	0.029*
C13	0.6211 (2)	0.44766 (17)	0.14122 (19)	0.0282 (4)
C14	0.39754 (10)	0.50534 (8)	0.32554 (9)	0.0531 (6)
H14C	0.2890	0.4692	0.3828	0.080*
H14A	0.3809	0.6011	0.2583	0.080*
H14B	0.4660	0.5074	0.3864	0.080*
O4	0.68500 (13)	0.56491 (9)	0.09551 (11)	0.0373 (3)
O5	0.63493 (12)	−0.17592 (8)	0.13428 (10)	0.0300 (3)
H2O5	0.5760	−0.1834	0.2138	0.045*
H1O5	0.6509	−0.2531	0.1229	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02369 (15)	0.02253 (14)	0.02842 (16)	−0.00151 (10)	−0.00284 (11)	−0.01690 (11)
O1	0.0301 (6)	0.0377 (7)	0.0285 (7)	−0.0004 (5)	−0.0009 (5)	−0.0214 (6)
O2	0.0659 (10)	0.0349 (7)	0.0386 (8)	0.0174 (7)	−0.0051 (7)	−0.0168 (6)
O3	0.0737 (11)	0.0479 (9)	0.0376 (9)	0.0209 (8)	−0.0187 (8)	−0.0152 (7)
C1	0.0294 (9)	0.0296 (9)	0.0322 (10)	−0.0047 (7)	0.0013 (7)	−0.0175 (8)
C2	0.0290 (9)	0.0285 (9)	0.0242 (9)	−0.0033 (7)	0.0008 (7)	−0.0143 (7)
C3	0.0416 (11)	0.0330 (10)	0.0272 (9)	−0.0004 (8)	−0.0060 (8)	−0.0102 (8)
C4	0.0580 (13)	0.0465 (12)	0.0239 (10)	0.0003 (10)	−0.0069 (9)	−0.0170 (9)
C5	0.0489 (12)	0.0433 (11)	0.0322 (10)	−0.0008 (9)	0.0002 (9)	−0.0246 (9)
C6	0.0315 (10)	0.0310 (9)	0.0344 (10)	0.0009 (7)	−0.0031 (8)	−0.0172 (8)
C7	0.0321 (9)	0.0342 (9)	0.0247 (9)	−0.0028 (7)	−0.0033 (7)	−0.0152 (7)
Br1	0.05614 (16)	0.04580 (14)	0.05557 (16)	0.01938 (10)	−0.01506 (11)	−0.02663 (11)
N1	0.0260 (7)	0.0214 (7)	0.0303 (8)	−0.0008 (5)	−0.0066 (6)	−0.0140 (6)
N2	0.0486 (10)	0.0283 (8)	0.0416 (10)	−0.0049 (7)	−0.0014 (8)	−0.0213 (7)
C8	0.0287 (9)	0.0277 (9)	0.0376 (10)	0.0011 (7)	−0.0036 (7)	−0.0192 (8)
C9	0.0248 (9)	0.0371 (10)	0.0539 (12)	−0.0040 (8)	−0.0013 (8)	−0.0249 (9)
C10	0.0346 (10)	0.0300 (9)	0.0462 (11)	−0.0087 (7)	−0.0085 (8)	−0.0173 (8)
C11	0.0327 (9)	0.0181 (8)	0.0272 (9)	−0.0012 (6)	−0.0100 (7)	−0.0097 (7)
C12	0.0262 (8)	0.0215 (8)	0.0273 (9)	0.0006 (6)	−0.0069 (7)	−0.0122 (7)
C13	0.0331 (9)	0.0229 (8)	0.0359 (10)	0.0034 (7)	−0.0163 (7)	−0.0151 (7)
C14	0.0612 (15)	0.0488 (13)	0.0547 (14)	−0.0050 (11)	0.0057 (11)	−0.0365 (11)
O4	0.0450 (8)	0.0217 (6)	0.0504 (8)	−0.0032 (5)	−0.0097 (6)	−0.0191 (6)
O5	0.0316 (7)	0.0239 (6)	0.0381 (7)	0.0014 (5)	−0.0059 (5)	−0.0175 (5)

Geometric parameters (Å, º)

Zn1—O1^{i}	2.0879 (11)	N1—C8	1.3352 (13)
Zn1—O1	2.0879 (11)	N1—C12	1.3359 (17)
Zn1—O5	2.1396 (9)	N2—C13	1.328 (2)
Zn1—O5^{i}	2.1396 (9)	N2—C14	1.4609 (13)
Zn1—N1^{i}	2.1583 (9)	N2—H1N2	0.8578
Zn1—N1	2.1583 (9)	C8—C9	1.372 (2)

O1—C1	1.256 (2)	C8—H8	0.9300
O2—C1	1.262 (2)	C9—C10	1.387 (2)
O3—C3	1.341 (2)	C9—H9	0.9300
O3—H1O3	0.8200	C10—C11	1.382 (2)
C1—C2	1.508 (2)	C10—H10	0.9300
C2—C7	1.386 (2)	C11—C12	1.384 (2)
C2—C3	1.402 (3)	C11—C13	1.497 (2)
C3—C4	1.396 (2)	C12—H12	0.9300
C4—C5	1.377 (3)	C13—O4	1.235 (2)
C4—H4	0.9300	C14—H14C	0.9600
C5—C6	1.389 (3)	C14—H14A	0.9600
C5—H5	0.9300	C14—H14B	0.9600
C6—C7	1.376 (2)	O5—H2O5	0.8196
C6—Br1	1.8968 (18)	O5—H1O5	0.8197
C7—H7	0.9300		

O1^{i}—Zn1—O1	180.00 (8)	C6—C7—H7	119.9
O1^{i}—Zn1—O5	92.30 (4)	C2—C7—H7	119.9
O1—Zn1—O5	87.70 (4)	C8—N1—C12	117.96 (11)
O1^{i}—Zn1—O5^{i}	87.70 (4)	C8—N1—Zn1	120.28 (7)
O1—Zn1—O5^{i}	92.30 (4)	C12—N1—Zn1	121.77 (9)
O5—Zn1—O5^{i}	180.00 (10)	C13—N2—C14	122.98 (11)
O1^{i}—Zn1—N1^{i}	91.23 (4)	C13—N2—H1N2	120.1
O1—Zn1—N1^{i}	88.77 (4)	C14—N2—H1N2	115.5
O5—Zn1—N1^{i}	91.78 (3)	N1—C8—C9	122.98 (11)
O5^{i}—Zn1—N1^{i}	88.22 (3)	N1—C8—H8	118.5
O1^{i}—Zn1—N1	88.77 (4)	C9—C8—H8	118.5
O1—Zn1—N1	91.23 (4)	C8—C9—C10	118.76 (15)
O5—Zn1—N1	88.22 (4)	C8—C9—H9	120.6
O5^{i}—Zn1—N1	91.78 (3)	C10—C9—H9	120.6
N1^{i}—Zn1—N1	180.00 (4)	C11—C10—C9	118.99 (16)
C1—O1—Zn1	128.42 (11)	C11—C10—H10	120.5
C3—O3—H1O3	109.5	C9—C10—H10	120.5
O1—C1—O2	125.03 (16)	C10—C11—C12	118.22 (15)
O1—C1—C2	117.54 (15)	C10—C11—C13	119.77 (15)
O2—C1—C2	117.42 (16)	C12—C11—C13	122.01 (15)
C7—C2—C3	119.42 (15)	N1—C12—C11	123.07 (14)
C7—C2—C1	119.96 (15)	N1—C12—H12	118.5
C3—C2—C1	120.57 (16)	C11—C12—H12	118.5
O3—C3—C4	118.17 (17)	O4—C13—N2	123.41 (16)
O3—C3—C2	122.26 (16)	O4—C13—C11	120.51 (15)
C4—C3—C2	119.57 (17)	N2—C13—C11	116.08 (15)
C5—C4—C3	120.41 (18)	N2—C14—H14C	109.5
C5—C4—H4	119.8	N2—C14—H14A	109.5
C3—C4—H4	119.8	H14C—C14—H14A	109.5
C4—C5—C6	119.57 (17)	N2—C14—H14B	109.5
C4—C5—H5	120.2	H14C—C14—H14B	109.5
C6—C5—H5	120.2	H14A—C14—H14B	109.5

C7—C6—C5	120.74 (17)	Zn1—O5—H2O5	100.9
C7—C6—Br1	119.51 (14)	Zn1—O5—H1O5	119.2
C5—C6—Br1	119.74 (14)	H2O5—O5—H1O5	111.8
C6—C7—C2	120.28 (16)		
O5—Zn1—O1—C1	167.76 (16)	O1—Zn1—N1—C8	−24.26 (8)
O5^{i}—Zn1—O1—C1	−12.24 (16)	O5—Zn1—N1—C8	63.39 (8)
N1^{i}—Zn1—O1—C1	75.93 (14)	O5^{i}—Zn1—N1—C8	−116.61 (8)
N1—Zn1—O1—C1	−104.07 (14)	O1^{i}—Zn1—N1—C12	−24.81 (11)
Zn1—O1—C1—O2	24.7 (3)	O1—Zn1—N1—C12	155.19 (11)
Zn1—O1—C1—C2	−153.98 (11)	O5—Zn1—N1—C12	−117.16 (10)
O1—C1—C2—C7	−4.4 (2)	O5^{i}—Zn1—N1—C12	62.84 (10)
O2—C1—C2—C7	176.77 (16)	C12—N1—C8—C9	−0.15 (17)
O1—C1—C2—C3	173.34 (16)	Zn1—N1—C8—C9	179.32 (11)
O2—C1—C2—C3	−5.5 (3)	N1—C8—C9—C10	−0.4 (2)
C7—C2—C3—O3	−178.98 (17)	C8—C9—C10—C11	0.7 (3)
C1—C2—C3—O3	3.3 (3)	C9—C10—C11—C12	−0.5 (3)
C7—C2—C3—C4	0.4 (3)	C9—C10—C11—C13	179.74 (17)
C1—C2—C3—C4	−177.40 (16)	C8—N1—C12—C11	0.3 (2)
O3—C3—C4—C5	179.01 (19)	Zn1—N1—C12—C11	−179.13 (12)
C2—C3—C4—C5	−0.4 (3)	C10—C11—C12—N1	0.0 (2)
C3—C4—C5—C6	−0.2 (3)	C13—C11—C12—N1	179.73 (14)
C4—C5—C6—C7	0.8 (3)	C14—N2—C13—O4	−2.0 (2)
C4—C5—C6—Br1	−179.66 (15)	C14—N2—C13—C11	178.73 (11)
C5—C6—C7—C2	−0.8 (3)	C10—C11—C13—O4	31.6 (2)
Br1—C6—C7—C2	179.66 (13)	C12—C11—C13—O4	−148.18 (17)
C3—C2—C7—C6	0.2 (3)	C10—C11—C13—N2	−149.10 (16)
C1—C2—C7—C6	178.00 (16)	C12—C11—C13—N2	31.1 (2)
O1^{i}—Zn1—N1—C8	155.74 (8)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1*O*3···O2	0.82	1.81	2.540 (2)	147
N2—H1*N*2···O3^{ii}	0.86	2.55	3.1109 (19)	123
O5—H2*O*5···O2^{i}	0.82	1.88	2.6694 (18)	162
O5—H1*O*5···O4^{iii}	0.82	1.94	2.7568 (13)	179

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