Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

catena-Poly[[(diaquazinc)-μ-3-carboxypyrazine-2-carboxylato-$\kappa^4N^1,O^2;N^4,O^3$] nitrate]

Wojciech Starosta and Janusz Leciejewicz*

Institute of Nuclear Chemistry and Technology, ul. Dorodna 16, 03-195 Warszawa, Poland
Correspondence e-mail: j.leciejewicz@ichtj.waw.pl

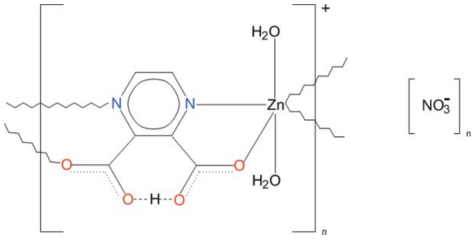
Received 7 December 2011; accepted 15 December 2011

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.032; wR factor = 0.097; data-to-parameter ratio = 16.2.

The crystal structure of the title compound, $\{[Zn(C_6H_3N_2O_4)(H_2O)_2]NO_3\}_n$, is built of zigzag cationic chains propagating in [010] with nitrate anions located in the space between the chains. The Zn^{II} ion is coordinated by N and O atoms of two symmetry-related ligands in equatorial sites, and by two water O atoms at the axial sites of a distorted octahedron. One carboxylate group of the ligand remains protonated, serving as a donor in a short intramolecular O—H···O hydrogen bond. The coordinated water molecules are donors and the nitrate O atoms act as acceptors in a network of O—H···O hydrogen bonds.

Related literature

For the crystal structures of Zn^{II} complexes with pyrazine-2,3-dicarboxylato and aqua ligands, see: Richard *et al.* (1974); Ptasiewicz-Bąk & Leciejewicz (1999); Gryz *et al.* (2005).



Experimental

Crystal data

$[Zn(C_6H_3N_2O_4)(H_2O)_2]NO_3$
M_r = 330.52
Monoclinic, $P2_1/n$
a = 8.7431 (17) Å
b = 10.867 (2) Å
c = 11.412 (2) Å
β = 100.48 (3)°
V = 1066.2 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.36 mm^{-1}
T = 293 K
0.20 × 0.19 × 0.15 mm

Data collection

Kuma KM-4 four-circle diffractometer
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2008)
T_{min} = 0.636, T_{max} = 0.747
3232 measured reflections
3101 independent reflections
2397 reflections with $I > 2\sigma(I)$
R_{int} = 0.012
3 standard reflections every 200 reflections
intensity decay: 1.6%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.097
S = 1.03
3101 reflections
192 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Selected bond lengths (Å).

Zn1—O6	2.052 (2)	Zn1—O1	2.0816 (17)
Zn1—O5	2.069 (2)	Zn1—N1	2.1663 (18)
Zn1—O4^{i}	2.0769 (18)	Zn1—N2^{i}	2.1946 (19)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H61···O13^{ii}	0.84 (4)	1.90 (4)	2.732 (3)	176 (3)
O5—H52···O12^{iii}	0.83 (4)	1.88 (4)	2.696 (3)	169 (4)
O6—H62···O11^{iii}	0.72 (5)	2.04 (5)	2.758 (3)	175 (5)
O5—H51···O3^{ii}	0.73 (6)	2.37 (5)	2.983 (3)	142 (5)
O5—H51···O11^{i}	0.73 (6)	2.63 (6)	3.094 (4)	123 (5)
O2—H3···O3	1.20 (5)	1.22 (5)	2.404 (2)	170 (4)

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

Data collection: *KM-4 Software* (Kuma, 1996); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Kuma, 2001); 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: KP2377).

References

Gryz, M., Starosta, W. & Leciejewicz, J. (2005). *J. Coord. Chem.* **58**, 931–935.
Kuma (1996). *KM-4 Software*. Kuma Diffraction Ltd, Wrocław, Poland.
Kuma (2001). *DATAPROC*. Kuma Diffraction Ltd, Wrocław, Poland.
Oxford Diffraction (2008). *CrysAlis RED*. Oxford Diffraction Ltd, Yarnton, England.
Ptasiewicz-Bąk, H. & Leciejewicz, J. (1999). *Pol. J. Chem.* **73**, 1887–1893.
Richard, P., Tranqui, D. & Bertaut, E. F. (1974). *Acta Cryst.* B**30**, 628–633.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2012). E**68**, m75 [doi:10.1107/S1600536811054031]

catena-Poly[[(diaquazinc)-μ-3-carboxypyrazine-2-carboxylato-$\kappa^4N^1,O^2;N^4,O^3$] nitrate]

Wojciech Starosta and Janusz Leciejewicz

S1. Comment

The structures of three Zn^{II} coordination compounds with pyrazine-2,3-dicarboxylate ligand (2,3-PZDC), each with a different molecular pattern were reported. In the triclinic structure of $Zn(2,3\text{-PZDC})(H_2O)_2.H_2O$ (Richard *et al.*, 1974) molecular ribbons are observed while the monoclinic $Zn(2,3\text{-PZDC})(H_2O)_3.H_2O$ (Ptasiewicz-Bąk & Leciejewicz, 1999) shows a zigzag catenated molecular pattern. The monoclinic structure of $(H_3O)^+_2$ $[Zn(2,3\text{-PZDC})^{2-}$ is built of catenated doubly layered polyanions with hydronium cations in the interstitials (Gryz *et al.* 2005). The structure of the title compound is composed of zigzag molecular chains propagating along the crystal *b* axis in which Zn^{II} ions are coordinated by *N*,*O* chelating groups of two singly deprotonated ligand molecules; their planes make a dihedral angle of 82.1 (1)° each to the other (Fig. 1). Two water O atoms complete the coordination of the Zn^{II} ion to six, located at the apices of a distorted octahedron. O1, N1, $O4^i$ and O5 atoms form its basal plane with r.m.s. of 0.1408 (2) Å. Zn—O and Zn—N bond lengths are close to those observed in the structures of other Zn complexes with the title ligand (Richard, *et al.*, 1974; Ptasiewicz-Bąk & Leciejewicz, 1999; Gryz, *et al.*, 2005). A pyrazine ring is planar [r.m.s. 0.0146 (2) Å, the carboxylate groups C7/O1/O2 and C8/O3/O4 make with it dihedral angles of 4.8 (1)° and 171.9 (1)°, respectively. One of the carboxylate groups remains protonated and participates in a short, intra-molecular hydrogen bond of 2.404 (2) Å. Consequently, each building unit of the chain shows a singly positive charge which is compensated by a nitrate anion located in the space between chains (Fig. 2). Hydrogen bonds are observed between coordinated water molecules which act as donors and nitrate O atoms as acceptors (Table 2).

S2. Experimental

Single crystals of the title compound were found incidently in the course of an attempt to obtain dinuclear magnesium-zinc complex with the pyrazine-2,3-dicarboxylate ligand. A solution containing 2 mmols of pyrazine-2,3-dicarboxylic acid dihydrate, 1 mmol of magnesium nitrate dihydrate and a small excess over 1 mmol of zinc nitrate hexahydrate in 100 mL of doubly distilled water was boiled under reflux with stirring for 10 h. After cooling to room temperature, two drops of 95% hydrazine were added to the solution which was left to crystallise. Colourless single-crystal blocks of the title compound and crystals of $Zn(H_2O)_6(NO_3)_2$ were found in an unidentified polycrystalline material after evaporation to dryness. The crystals of the title complex were extracted, washed with ethanol and dried in air.

S3. Refinement

Water hydrogen atoms were located in a difference map and refined isotropically while H atoms attached to pyrazine-ring C atoms were located at calculated positions and treated as riding on the parent atoms with C—H=0.93 Å and $U_{iso}(H)=1.2U_{eq}(C)$.

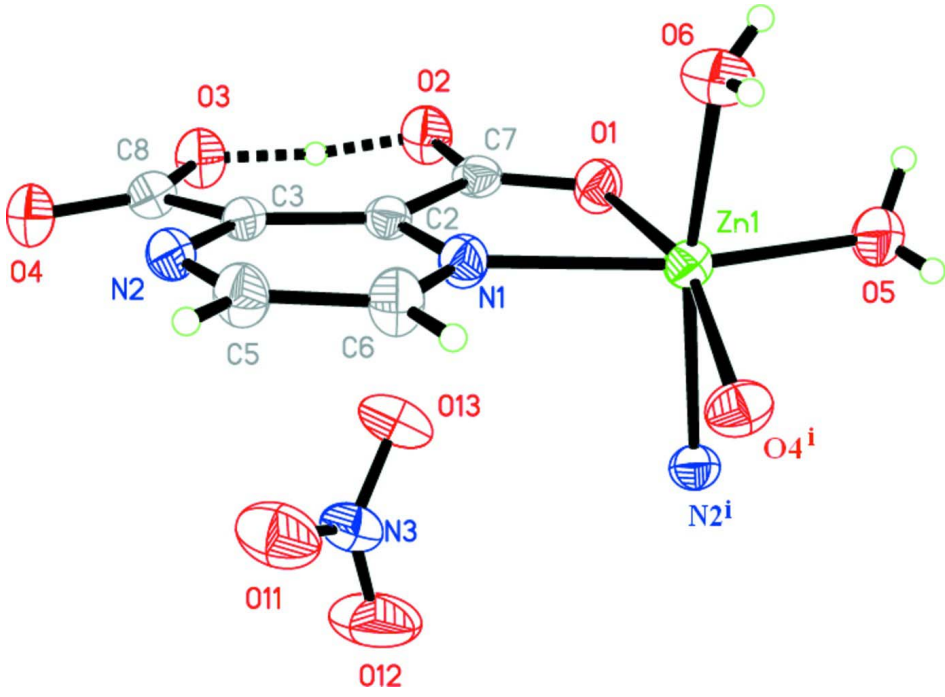


Figure 1

A structural unit of the title compound with atom labelling scheme and 50% probability displacement ellipsoids. Symmetry code: (i) -*x* + 1/2, *y* + 1/2,-*z* + 1/2. An intramolecuular hydrogen bond is shown by dashed lines.

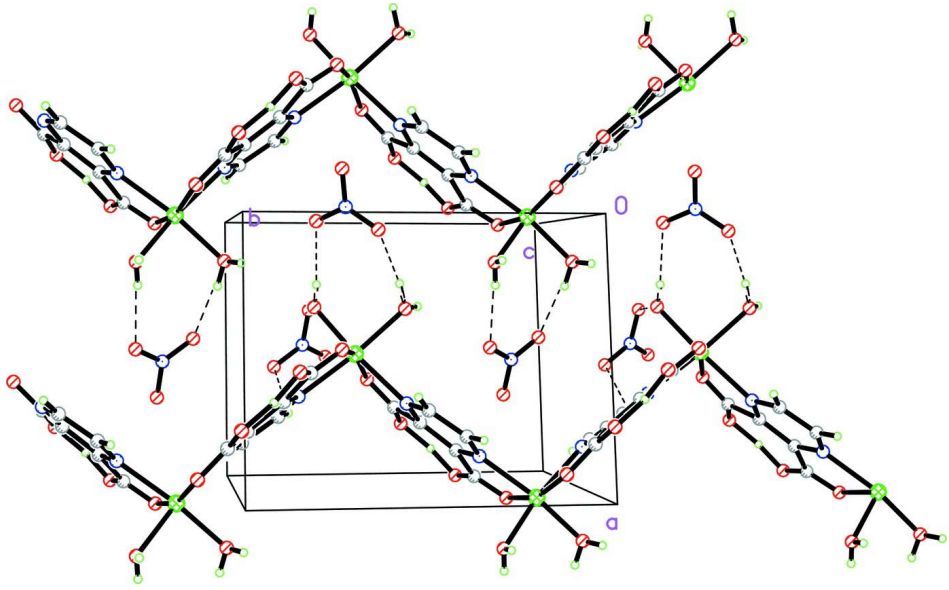


Figure 2

Packing diagram of the structure viewed along the *c* axis.

catena-Poly[[(diaquazinc)-μ-3-carboxypyrazine-2-carboxylato- $\kappa^4N^1,O^2;N^4,O^3$] nitrate]

Crystal data

$[Zn(C_6H_3N_2O_4)(H_2O)_2]NO_3$
M_r = 330.52
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 8.7431 (17) Å
b = 10.867 (2) Å
c = 11.412 (2) Å
β = 100.48 (3)°
V = 1066.2 (4) Å^3
Z = 4
$F(000)$ = 664
D_x = 2.059 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 6–15°
μ = 2.36 mm^{-1}
T = 293 K
Blocks, colourless
0.20 × 0.19 × 0.15 mm

Data collection

Kuma KM-4 four-circle diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
profile data from $\omega/2\theta$ scans
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2008)
T_{min} = 0.636, T_{max} = 0.747
3232 measured reflections
3101 independent reflections
2397 reflections with $I > 2\sigma(I)$
R_{int} = 0.012
θ_{max} = 30.1°, θ_{min} = 2.6°
h = −10→12
k = −15→0
l = −16→0
3 standard reflections every 200 reflections
intensity decay: 1.6%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.097
S = 1.03
3101 reflections
192 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
$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2 + 0.8069P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 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	−0.00406 (3)	0.82559 (2)	0.26307 (2)	0.02503 (9)
C7	0.0503 (2)	0.68275 (19)	0.06020 (18)	0.0235 (4)
C2	0.1549 (2)	0.61605 (18)	0.16261 (17)	0.0212 (4)

N1	0.1442 (2)	0.66517 (17)	0.26888 (16)	0.0255 (4)
C3	0.2546 (2)	0.51569 (19)	0.15702 (18)	0.0214 (4)
C8	0.3008 (3)	0.45650 (19)	0.04721 (19)	0.0247 (4)
C6	0.2221 (3)	0.6151 (2)	0.36834 (19)	0.0303 (5)
H6	0.2153	0.6495	0.4418	0.036*
O5	−0.1653 (2)	0.96368 (18)	0.2120 (2)	0.0403 (4)
N2	0.3300 (2)	0.46525 (17)	0.25858 (16)	0.0246 (3)
O3	0.2334 (2)	0.48857 (16)	−0.05626 (14)	0.0314 (3)
O4	0.4046 (2)	0.37756 (16)	0.06479 (15)	0.0313 (3)
O2	0.0421 (2)	0.64513 (17)	−0.04597 (14)	0.0323 (4)
O1	−0.02615 (19)	0.77131 (15)	0.08585 (14)	0.0295 (3)
O6	−0.1700 (2)	0.71769 (19)	0.3183 (2)	0.0373 (4)
C5	0.3133 (3)	0.5120 (2)	0.36293 (19)	0.0294 (4)
H5	0.3634	0.4752	0.4330	0.035*
O11	0.5234 (3)	0.7166 (3)	0.2043 (2)	0.0568 (6)
O12	0.5562 (3)	0.8786 (3)	0.1012 (3)	0.0758 (9)
O13	0.3449 (2)	0.7771 (2)	0.05949 (19)	0.0463 (5)
N3	0.4762 (2)	0.7915 (2)	0.1237 (2)	0.0366 (5)
H61	−0.166 (4)	0.723 (3)	0.392 (3)	0.035 (8)*
H52	−0.256 (5)	0.946 (4)	0.181 (4)	0.056 (11)*
H62	−0.251 (6)	0.722 (4)	0.289 (4)	0.081 (16)*
H51	−0.165 (6)	1.002 (5)	0.265 (5)	0.095 (19)*
H3	0.143 (5)	0.574 (4)	−0.056 (4)	0.088 (15)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02357 (14)	0.02086 (13)	0.02998 (14)	−0.00042 (9)	0.00303 (9)	−0.00081 (9)
C7	0.0212 (9)	0.0232 (9)	0.0241 (9)	−0.0025 (7)	−0.0014 (7)	0.0015 (7)
C2	0.0199 (8)	0.0202 (8)	0.0224 (9)	−0.0013 (7)	0.0010 (7)	0.0010 (7)
N1	0.0253 (8)	0.0249 (9)	0.0249 (8)	0.0031 (7)	0.0006 (7)	−0.0020 (6)
C3	0.0205 (9)	0.0197 (8)	0.0234 (8)	−0.0014 (7)	0.0022 (7)	−0.0003 (7)
C8	0.0260 (10)	0.0236 (9)	0.0246 (9)	−0.0015 (7)	0.0047 (7)	−0.0003 (7)
C6	0.0353 (11)	0.0328 (11)	0.0214 (9)	0.0080 (9)	0.0016 (8)	−0.0015 (8)
O5	0.0317 (10)	0.0276 (9)	0.0589 (13)	0.0062 (7)	0.0010 (9)	−0.0050 (8)
N2	0.0231 (8)	0.0236 (8)	0.0260 (8)	0.0020 (6)	0.0013 (6)	0.0012 (6)
O3	0.0360 (9)	0.0348 (9)	0.0231 (7)	0.0068 (7)	0.0041 (6)	0.0002 (6)
O4	0.0353 (9)	0.0296 (8)	0.0297 (8)	0.0079 (7)	0.0075 (7)	0.0003 (6)
O2	0.0345 (9)	0.0363 (9)	0.0233 (7)	0.0070 (7)	−0.0022 (6)	−0.0015 (6)
O1	0.0291 (8)	0.0264 (8)	0.0295 (8)	0.0060 (6)	−0.0035 (6)	−0.0009 (6)
O6	0.0315 (10)	0.0400 (10)	0.0393 (11)	−0.0078 (8)	0.0041 (8)	0.0034 (8)
C5	0.0318 (11)	0.0309 (11)	0.0236 (9)	0.0057 (9)	−0.0004 (8)	0.0014 (8)
O11	0.0473 (12)	0.0708 (16)	0.0467 (12)	−0.0080 (11)	−0.0060 (9)	0.0132 (11)
O12	0.0526 (15)	0.0659 (17)	0.100 (2)	−0.0293 (13)	−0.0098 (14)	0.0186 (16)
O13	0.0259 (9)	0.0682 (14)	0.0428 (10)	−0.0089 (9)	0.0006 (8)	0.0042 (10)
N3	0.0265 (10)	0.0452 (12)	0.0379 (11)	−0.0069 (9)	0.0052 (8)	−0.0012 (9)

Geometric parameters (Å, º)

Zn1—O6	2.052 (2)	C6—C5	1.382 (3)
Zn1—O5	2.069 (2)	C6—H6	0.9300
Zn1—O4^{i}	2.0769 (18)	O5—H52	0.83 (4)
Zn1—O1	2.0816 (17)	O5—H51	0.73 (6)
Zn1—N1	2.1663 (18)	N2—C5	1.327 (3)
Zn1—N2^{i}	2.1946 (19)	N2—Zn1^{ii}	2.1947 (19)
C7—O1	1.237 (3)	O3—H3	1.22 (5)
C7—O2	1.268 (3)	O4—Zn1^{ii}	2.0769 (18)
C7—C2	1.529 (3)	O2—H3	1.20 (5)
C2—N1	1.344 (3)	O6—H61	0.84 (4)
C2—C3	1.405 (3)	O6—H62	0.72 (5)
N1—C6	1.330 (3)	C5—H5	0.9300
C3—N2	1.342 (3)	O11—N3	1.241 (3)
C3—C8	1.527 (3)	O12—N3	1.230 (3)
C8—O4	1.238 (3)	O13—N3	1.254 (3)
C8—O3	1.269 (3)		
O6—Zn1—O5	90.99 (9)	C2—C3—C8	128.54 (18)
O6—Zn1—O4^{i}	93.59 (8)	O4—C8—O3	122.9 (2)
O5—Zn1—O4^{i}	102.46 (9)	O4—C8—C3	117.00 (19)
O6—Zn1—O1	101.00 (8)	O3—C8—C3	120.06 (19)
O5—Zn1—O1	89.65 (9)	N1—C6—C5	120.2 (2)
O4^{i}—Zn1—O1	160.90 (7)	N1—C6—H6	119.9
O6—Zn1—N1	89.06 (8)	C5—C6—H6	119.9
O5—Zn1—N1	164.96 (9)	Zn1—O5—H52	120 (3)
O4^{i}—Zn1—N1	92.55 (7)	Zn1—O5—H51	107 (4)
O1—Zn1—N1	75.58 (7)	H52—O5—H51	110 (5)
O6—Zn1—N2^{i}	166.71 (8)	C5—N2—C3	120.11 (19)
O5—Zn1—N2^{i}	85.27 (8)	C5—N2—Zn1^{ii}	123.90 (15)
O4^{i}—Zn1—N2^{i}	74.86 (7)	C3—N2—Zn1^{ii}	115.27 (14)
O1—Zn1—N2^{i}	91.74 (7)	C8—O3—H3	114 (2)
N1—Zn1—N2^{i}	97.85 (7)	C8—O4—Zn1^{ii}	120.67 (15)
O1—C7—O2	122.53 (19)	C7—O2—H3	113 (2)
O1—C7—C2	117.50 (19)	C7—O1—Zn1	119.46 (14)
O2—C7—C2	119.96 (19)	Zn1—O6—H61	112 (2)
N1—C2—C3	119.66 (18)	Zn1—O6—H62	121 (4)
N1—C2—C7	111.79 (18)	H61—O6—H62	108 (4)
C3—C2—C7	128.54 (18)	N2—C5—C6	120.6 (2)
C6—N1—C2	119.93 (19)	N2—C5—H5	119.7
C6—N1—Zn1	124.51 (15)	C6—C5—H5	119.7
C2—N1—Zn1	115.56 (14)	O12—N3—O11	122.2 (2)
N2—C3—C2	119.29 (18)	O12—N3—O13	118.0 (3)
N2—C3—C8	112.05 (18)	O11—N3—O13	119.8 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H61···O13^{iii}	0.84 (4)	1.90 (4)	2.732 (3)	176 (3)
O5—H52···O12^{iv}	0.83 (4)	1.88 (4)	2.696 (3)	169 (4)
O6—H62···O11^{iv}	0.72 (5)	2.04 (5)	2.758 (3)	175 (5)
O5—H51···O3^{iii}	0.73 (6)	2.37 (5)	2.983 (3)	142 (5)
O5—H51···O11^{i}	0.73 (6)	2.63 (6)	3.094 (4)	123 (5)
O2—H3···O3	1.20 (5)	1.22 (5)	2.404 (2)	170 (4)

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