Hexaaquazinc(II) dinitrate bis[5-(pyridinium-3-yl)-tetrazol-1-ide]
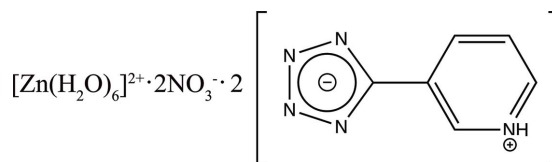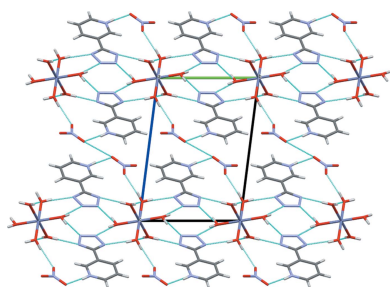
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Hexaaquazinc(II) dinitrate 5-(pyridinium-3-yl)tetrazol-1-ide, $[Zn(H_2O)_6](NO_3)_2 \cdot 2C_6H_5N_5$, crystallizes in the space group $P\bar{1}$. The asymmetric unit contains one zwitterionic 5-(pyridinium-3-yl)tetrazol-1-ide molecule, one NO_3^- anion and one half of a $[Zn(H_2O)_6]^{2+}$ cation ($\bar{1}$ symmetry). The pyridinium and tetrazolide rings in the zwitterion are nearly coplanar, with a dihedral angle of 5.4 (2)°. Several O—H···N and N—H···O hydrogen-bonding interactions exist between the $[Zn(H_2O)_6]^{2+}$ cation and the N atoms of the tetrazolide ring, and between the nitrate anions and the N—H groups of the pyridinium ring, respectively, giving rise to a three-dimensional network. The 5-(pyridinium-3-yl)tetrazol-1-ide molecules show parallel-displaced $\pi-\pi$ stacking interactions; the centroid–centroid distance between adjacent tetrazolide rings is 3.6298 (6) Å and that between the pyridinium and tetrazolide rings is 3.6120 (5) Å.

1. Chemical context

Tetrazole functional groups have attracted increased attention in recent years due to their use in drug design and their employment as isosteric subtitutents of carboxylic acids (Herr, 2002), as well as their ability to produce a large variety of metal–organic frameworks (MOFs) (Zhao *et al.*, 2008; Chi-Duran *et al.*, 2018). Push–pull tetrazole complexes with both electron-donor and electron-acceptor substituents have shown efficient second-order nonlinear optical activity in powdered samples (Masahiko *et al.*, 1994), ferroelectric behaviour (Liu *et al.*, 2015) and strong photoluminescence (Zhang *et al.*, 2014). The *in-situ* synthesis of tetrazole compounds can be realized by the Demko–Sharpless method, in which zinc salts catalyze the cycloaddition reaction between sodium azide and nitrile compounds to form the tetrazole ring (Demko & Sharpless, 2001). In this work, pyridyltetrazole, synthesized at low pH using the Demko–Sharpless method, is cocrystallized in the presence of $[Zn(H_2O)_6]^{2+}$ and NO_3^- ions, to obtain the title compound (Fig. 1).

$$[Zn(H_2O)_6]^{2+} \cdot 2NO_3^- \cdot 2$$

2. Structural commentary

The asymmetric unit of the title compound is composed of one 5-(pyridinium-3-yl)tetrazol-1-ide zwitterion, one NO_3^- anion and one half of a $[Zn(H_2O)_6]^{2+}$ cation. The hexaaquazinc(II)

Table 1
Selected geometric parameters (Å, °).

Zn1—O3	2.0353 (11)	Zn1—O2^i	2.1011 (12)
Zn1—O3^i	2.0354 (11)	Zn1—O1^i	2.1841 (11)
Zn1—O2	2.1011 (12)	Zn1—O1	2.1841 (11)
O3—Zn1—O2	90.01 (5)	O2—Zn1—O1^i	92.10 (5)
O3—Zn1—O2^i	89.99 (5)	O3—Zn1—O1	89.47 (4)
O3—Zn1—O1^i	90.53 (4)	O2—Zn1—O1	87.90 (5)

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

complex exhibits regular octahedral geometry (Table 1), and the tetrazolide and pyridinium rings of the zwitterion are close to being coplanar, with a dihedral angle of 5.4 (2)° (Fig. 2). The geometric parameters of the tetrazolide ring are comparable to those in other reported tetrazole compounds (Mu *et al.*, 2010; Dai & Chen, 2011*a*,*b*). The H atom attached to the N atom of the pyridine ring could not be located in the Fourier density map. Therefore, the H atom was placed in accordance with similar reported structures containing $[Mg(H_2O)_6]X_2$ ($X = Cl^-$, Br^-) cocrystallized with 5-(pyridinium-3-yl)tetrazol-1-ide (Dai & Chen, 2011*a*,*b*).

3. Supramolecular features

A three-dimensional network of hydrogen bonds involving the pyridinium–tetrazolide zwitterions, hexaaquazinc(II) complex cations and nitrate ions serves to hold the structure together (Table 2 and Fig. 3). The N atoms of the tetrazole ring interact
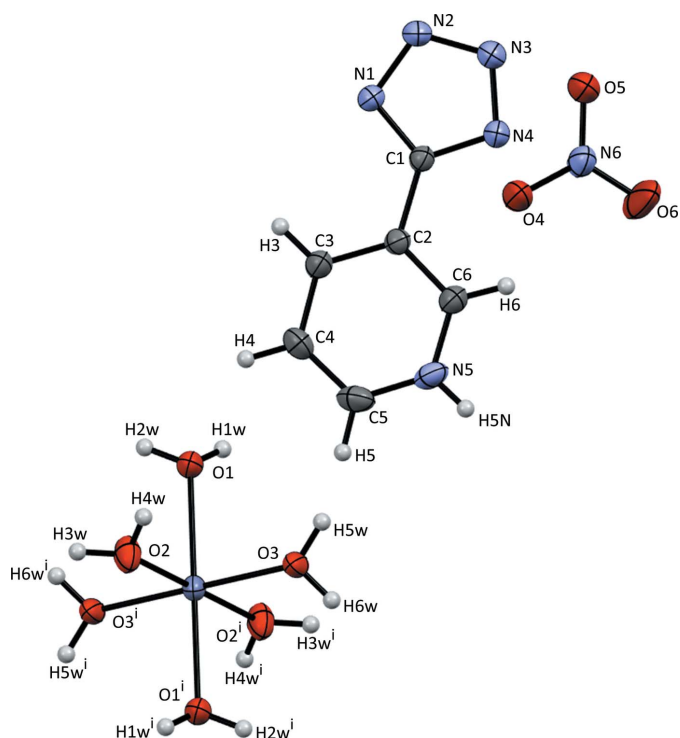
Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$W\cdots$O5^{ii}	0.85	1.96	2.8067 (17)	172
O1—H2$W\cdots$N1^{iii}	0.85	1.96	2.8029 (17)	173
O2—H3$W\cdots$N4^{iv}	0.85	2.02	2.8589 (17)	170
O2—H4$W\cdots$O1^{v}	0.85	2.08	2.9228 (17)	171
O3—H5$W\cdots$N3^{ii}	0.85	1.91	2.7446 (17)	168
O3—H6$W\cdots$N1^{vi}	0.85	2.72	3.4294 (17)	142
O3—H6$W\cdots$N2^{vi}	0.85	1.97	2.8076 (17)	169
N5—H5$N\cdots$N6^{vii}	0.82	2.61	3.344 (2)	149
N5—H5$N\cdots$O4^{vii}	0.82	1.92	2.7384 (18)	173
N5—H5$N\cdots$O5^{vii}	0.82	2.62	3.1347 (19)	123
C4—H4$\cdots$O5^{viii}	0.93	2.65	3.452 (2)	145
C5—H5$\cdots$O4^{ix}	0.93	2.52	3.292 (2)	141
C5—H5$\cdots$O6^{ix}	0.93	2.52	3.422 (3)	165
C6—H6$\cdots$O5^{vii}	0.93	2.41	3.047 (2)	126

Symmetry codes: (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 2, -z + 1$; (iv) $x, y + 1, z + 1$; (v) $-x + 1, -y + 2, -z + 2$; (vi) $x - 1, y, z + 1$; (vii) $x - 1, y, z$; (viii) $x - 1, y + 1, z$; (ix) $-x, -y + 1, -z + 1$.

with the octahedral complex, $[Zn(H_2O)_6]^{2+}$, through O—H$\cdots$N hydrogen bonds, exhibiting $D\cdots A$ distances in the range 2.7446 (17)–2.8589 (17) Å. Additionally, the pyridinium ring is involved in N—H$\cdots$O hydrogen bonding to nitrate atom O4, with an N$\cdots$O distance of 2.7384 (18) Å. These interactions are shown in the crystal packing diagram (Fig. 3). The structure also shows parallel-displaced π–π stacking interactions, which arise from partial overlap between the

Figure 1
The molecular structure of the asymmetric unit (plus the three water molecules of the hexaaquazinc cation generated by symmetry), showing the atom labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x, 2 - y, 2 - z$.]

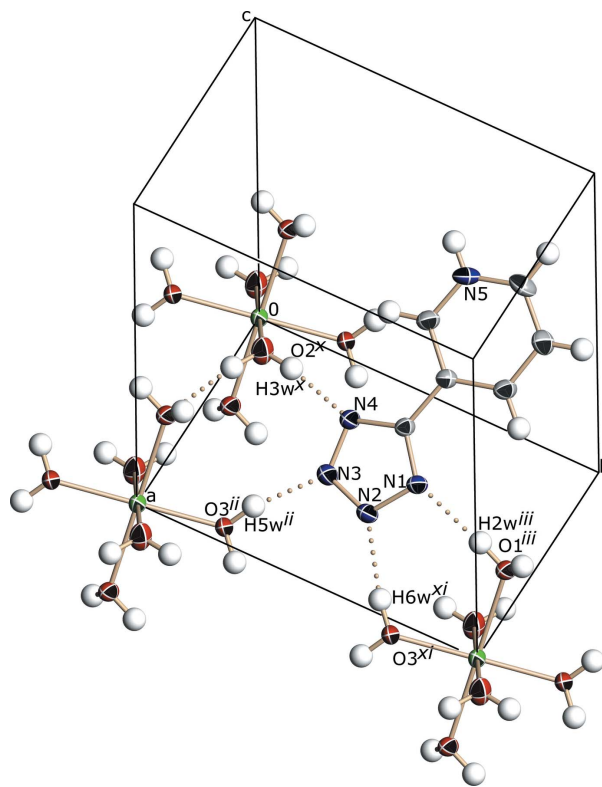**Figure 2**
Partial crystal packing of the title compound, showing the hydrogen-bonding interactions between $[Zn(H_2O)_6]^{2+}$ and the tetrazolide ring. [Symmetry codes: (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 2, -z + 1$; (x) $x, y - 1, z - 1$; (xi) $x + 1, y, z - 1$.]

Table 3
π–π stacking interaction lengths (Å).

*Cg*1 and *Cg*2 are the centroids of the C1/N1/N2/N3/N4 and C2–C6/N5 rings, respectively.

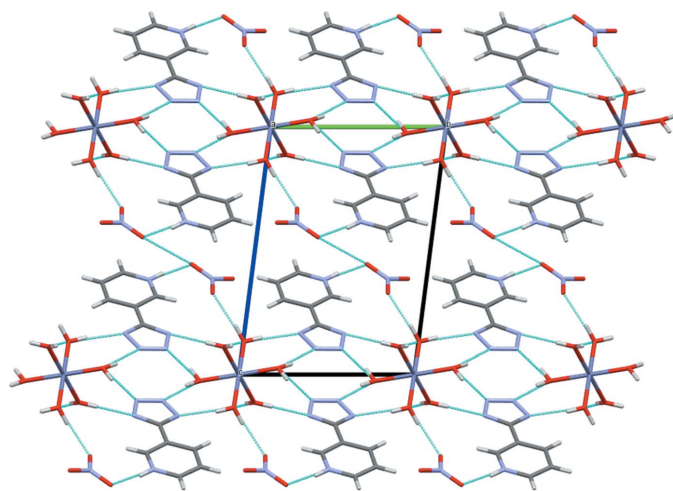| Centroid–centroid	Distance	Tetrazolide interplane distance
$Cg1$–$Cg1^{ii}$	3.6298 (6)	3.23 (1)
$Cg1$–$Cg2^{vii}$	3.6120 (5)	3.10 (3)

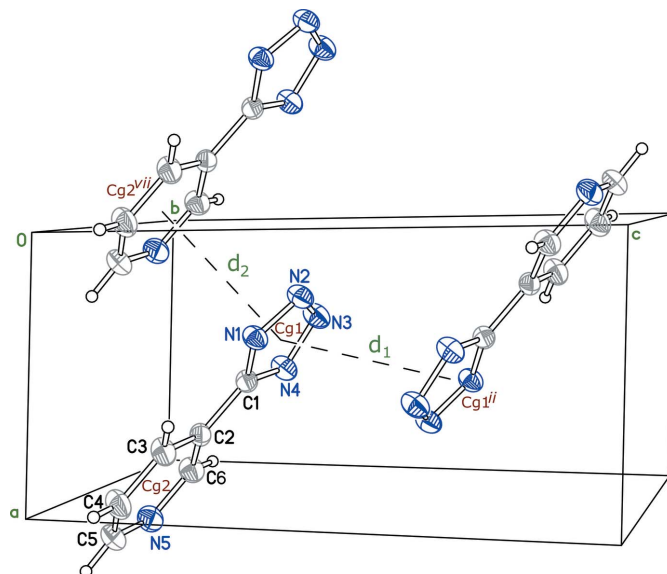Symmetry codes: (ii) $-x + 1, -y + 1, -1 + z$; (vii) $x - 1, y, z$.

tetrazolide and pyridinium rings in adjacent zwitterions, and extend along the *a* axis parallel to the (010) plane. These parallel-displaced π–π interactions lead to interplanar distances of 3.21 (1) and 3.10 (3) Å, and two centroid–centroid distances (Table 3). The centroid–centroid distance between the tetrazolide groups is 3.6298 (6) Å and between the pyridinium and tetrazolide rings is 3.6120 (5) Å (Table 3 and Fig. 4).

4. Database survey

We found two previously reported structures that are closely related to the title compound. They both involve a hexa-aquamagnesium(II) cation with a halide counter-ion [chloride (Dai & Chen, 2011*b*) or bromide (Dai & Chen, 2011*a*)] cocrystallized in the presence of 5-(pyridinium-3-yl)tetrazol-1-ide zwitterions (Dai & Chen, 2011*a,b*). There are more hydrogen-bonding interactions in our compound than in the $[Mg(H_2O)_6]X_2\cdot2C_6H_5N_5$ structures, as more hexaaquazinc(II) complexes can interact with the N atoms of the tetrazole units. Parallel-displaced π–π stacking interactions occur in the title compound and in $[Mg(H_2O)_6]X_2\cdot2C_6H_5N_5$. In $[Mg(H_2O)_6]Cl_2\cdot2C_6H_5N_5$, the pyridinium–tetrazolide zwitterions have alternating orientations in the supramolecular arrangement, whereas in the title compound, the zwitterions are oriented in the same direction, allowing a possible coupling transition

Figure 4
Partial crystal packing, showing π–π interactions between tetrazole and pyridinium rings, with d_1 = 3.6298 (6) Å and d_2 = 3.6120 (5) Å. [Symmetry codes: (ii) $-x + 1, -y + 1, -1 + z$; (vii) $x - 1, y, z$.]

between dipole moments similar to J-aggregates (Spano, 2010).

Table 4
Experimental details.

Crystal data	
Chemical formula	$[Zn(H_2O)_6](NO_3)_2\cdot2C_6H_5N_5$
M_r	591.81
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
a, b, c (Å)	5.6582 (11), 8.4632 (16), 12.046 (2)
α, β, γ (°)	97.209 (2), 91.123 (2), 93.949 (2)
V (Å^3)	570.67 (19)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.16
Crystal size (mm)	$0.49 \times 0.21 \times 0.09$
Data collection	
Diffractometer	Bruker SMART CCD area detector
Absorption correction	Numerical (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.742, 0.903
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	4429, 2217, 2132
R_{int}	0.013
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.022, 0.054, 1.08
No. of reflections	2217
No. of parameters	198
No. of restraints	13
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.37, −0.35

Computer programs: *SMART* and *SAINT* (Bruker, 2008), *SHELXTL* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

Figure 3
The crystal packing of the title compound, viewed along the [100] direction, showing O—H···N and N—H···O interactions (cyan lines).

5. Synthesis and crystallization

All the reactants and chemicals were purchased from Sigma Aldrich and utilized without further purification. A mixture of 3-cyanopyridine (4 mmol), NaN_3 (6 mmol) and $ZnCl_2$ (2 mmol) were dissolved in 6 ml of distilled water. This mixture was transferred to a glass bottle and then heated at 378 K for 24 h. The pH was adjusted using a HNO_3 (66%) solution immediately after mixing the reactants, and was monitored with a pH meter (pH2700 Oakton) until reaching a pH of 2.0. The reaction mixture was then cooled to 318 K and kept at this temperature for 16 h. The colourless block-shaped crystals obtained were washed with ethanol to give 353 mg (yield 30%) of the title compound.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All H atoms bonded to C atoms were positioned geometrically and treated as riding atoms, using C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Moreover, all H atoms in the hexaaquazinc(II) complex were refined with a distance restraint of O—H = 0.85 Å and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Funding information

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supporting information

Hexaaquazinc(II) dinitrate bis[5-(pyridinium-3-yl)tetrazol-1-ide]

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Computing details

Data collection: *SMART* (Bruker, 2008); cell refinement: *SMART* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Hexaaquazinc(II) dinitrate bis[5-(pyridinium-3-yl)tetrazol-1-ide]

Crystal data

$[Zn(H_2O)_6](NO_3)_2 \cdot 2C_6H_5N_5$	$Z = 1$
$M_r = 591.81$	$F(000) = 304$
Triclinic, $P\bar{1}$	$D_x = 1.722$ Mg m^{-3}
$a = 5.6582$ (11) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 8.4632$ (16) Å	Cell parameters from 7831 reflections
$c = 12.046$ (2) Å	$\theta = 2.8$–29.5°
$\alpha = 97.209$ (2)°	$\mu = 1.16$ mm^{-1}
$\beta = 91.123$ (2)°	$T = 293$ K
$\gamma = 93.949$ (2)°	Block, colorless
$V = 570.67$ (19) Å^3	$0.49 \times 0.21 \times 0.09$ mm

Data collection

Bruker SMART CCD area detector diffractometer	2217 independent reflections
	2132 reflections with $I > 2\sigma(I)$
Radiation source: sealed tube	$R_{int} = 0.013$
phi and ω scans	$\theta_{max} = 26.0°$, $\theta_{min} = 2.4°$
Absorption correction: numerical (SADABS; Bruker, 2008)	$h = -6 \rightarrow 6$
	$k = -10 \rightarrow 10$
$T_{min} = 0.742$, $T_{max} = 0.903$	$l = -14 \rightarrow 14$
4429 measured reflections	

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.022$	$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2 + 0.1986P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.054$	
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
2217 reflections	$\Delta\rho_{max} = 0.37$ e Å^{-3}
198 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-3}
13 restraints	Extinction correction: SHELXL2014 (Sheldrick, 2015), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Hydrogen site location: mixed	Extinction coefficient: 0.009 (2)

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.

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

	x	y	z	$U_{iso}*/U_{eq}$
Zn1	0.0000	1.0000	1.0000	0.02186 (9)
O1	0.25606 (19)	1.00502 (12)	0.86692 (9)	0.0269 (2)
H1W	0.226 (4)	0.9463 (19)	0.8050 (8)	0.044 (6)*
H2W	0.303 (3)	1.0972 (10)	0.8515 (16)	0.041 (5)*
O2	0.2699 (2)	1.10732 (13)	1.11255 (11)	0.0345 (3)
H3W	0.307 (4)	1.2067 (5)	1.1282 (17)	0.048 (6)*
H4W	0.401 (2)	1.065 (3)	1.116 (2)	0.065 (7)*
O3	0.0981 (2)	0.78032 (12)	1.02590 (10)	0.0293 (2)
H5W	0.187 (3)	0.725 (2)	0.9825 (14)	0.051 (6)*
H6W	−0.008 (3)	0.7116 (19)	1.0423 (19)	0.059 (7)*
N1	0.5987 (2)	0.68143 (14)	0.16630 (10)	0.0246 (3)
N2	0.7365 (2)	0.58336 (15)	0.10516 (11)	0.0270 (3)
N3	0.6508 (2)	0.43523 (15)	0.10431 (11)	0.0296 (3)
N4	0.4544 (2)	0.43180 (14)	0.16488 (11)	0.0269 (3)
N5	−0.0918 (2)	0.58146 (17)	0.38266 (11)	0.0315 (3)
H5N	−0.180 (3)	0.5136 (17)	0.4067 (15)	0.042 (5)*
C1	0.4273 (2)	0.58463 (16)	0.20195 (12)	0.0212 (3)
C2	0.2376 (2)	0.64009 (17)	0.27458 (11)	0.0218 (3)
C3	0.2065 (3)	0.80168 (18)	0.30257 (13)	0.0284 (3)
H3A	0.3075	0.8778	0.2748	0.034*
C4	0.0250 (3)	0.8491 (2)	0.37189 (14)	0.0334 (4)
H4	0.0048	0.9570	0.3914	0.040*
C5	−0.1243 (3)	0.7363 (2)	0.41142 (14)	0.0345 (4)
H5	−0.2470	0.7668	0.4578	0.041*
C6	0.0827 (3)	0.53073 (19)	0.31686 (13)	0.0279 (3)
H6	0.0997	0.4219	0.2996	0.033*
N6	0.6295 (3)	0.22071 (16)	0.38657 (12)	0.0353 (3)
O4	0.5953 (2)	0.34960 (14)	0.44531 (11)	0.0442 (3)
O5	0.8117 (2)	0.21012 (15)	0.33009 (11)	0.0431 (3)
O6	0.4892 (4)	0.1062 (2)	0.38679 (19)	0.1001 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02070 (14)	0.01556 (13)	0.02905 (15)	0.00093 (8)	0.00394 (9)	0.00145 (9)
O1	0.0295 (6)	0.0203 (5)	0.0304 (6)	−0.0002 (4)	0.0092 (4)	0.0015 (4)
O2	0.0292 (6)	0.0230 (6)	0.0485 (7)	−0.0009 (5)	−0.0073 (5)	−0.0031 (5)
O3	0.0283 (6)	0.0193 (5)	0.0419 (6)	0.0056 (4)	0.0149 (5)	0.0063 (5)
N1	0.0232 (6)	0.0217 (6)	0.0282 (6)	−0.0018 (5)	0.0064 (5)	0.0013 (5)

N2	0.0232 (6)	0.0257 (7)	0.0315 (7)	0.0011 (5)	0.0082 (5)	0.0013 (5)
N3	0.0282 (7)	0.0241 (6)	0.0360 (7)	0.0024 (5)	0.0095 (6)	0.0006 (5)
N4	0.0268 (7)	0.0199 (6)	0.0333 (7)	−0.0005 (5)	0.0086 (5)	0.0006 (5)
N5	0.0275 (7)	0.0374 (8)	0.0295 (7)	−0.0062 (6)	0.0086 (6)	0.0067 (6)
C1	0.0217 (7)	0.0197 (7)	0.0214 (7)	−0.0017 (5)	0.0015 (5)	0.0014 (5)
C2	0.0218 (7)	0.0228 (7)	0.0199 (7)	−0.0015 (5)	0.0018 (5)	0.0002 (5)
C3	0.0311 (8)	0.0239 (7)	0.0285 (8)	−0.0041 (6)	0.0076 (6)	−0.0004 (6)
C4	0.0373 (9)	0.0279 (8)	0.0332 (8)	0.0044 (7)	0.0079 (7)	−0.0049 (6)
C5	0.0283 (8)	0.0457 (10)	0.0284 (8)	0.0044 (7)	0.0092 (6)	−0.0015 (7)
C6	0.0279 (8)	0.0255 (8)	0.0297 (8)	−0.0030 (6)	0.0055 (6)	0.0033 (6)
N6	0.0398 (8)	0.0279 (7)	0.0346 (8)	−0.0094 (6)	0.0107 (6)	−0.0048 (6)
O4	0.0508 (8)	0.0301 (6)	0.0480 (7)	−0.0067 (5)	0.0237 (6)	−0.0080 (5)
O5	0.0428 (7)	0.0333 (6)	0.0502 (8)	−0.0024 (5)	0.0194 (6)	−0.0063 (6)
O6	0.0959 (14)	0.0607 (11)	0.1238 (16)	−0.0531 (10)	0.0672 (13)	−0.0446 (11)

Geometric parameters (Å, º)

Zn1—O3	2.0353 (11)	N4—C1	1.3345 (19)
Zn1—O3ⁱ	2.0354 (11)	N5—C6	1.339 (2)
Zn1—O2	2.1011 (12)	N5—C5	1.339 (2)
Zn1—O2ⁱ	2.1011 (12)	N5—H5N	0.8201 (11)
Zn1—O1ⁱ	2.1841 (11)	C1—C2	1.463 (2)
Zn1—O1	2.1841 (11)	C2—C6	1.381 (2)
O1—H1W	0.8500	C2—C3	1.391 (2)
O1—H2W	0.8499	C3—C4	1.385 (2)
O2—H3W	0.8499	C3—H3A	0.9300
O2—H4W	0.8499	C4—C5	1.367 (2)
O3—H5W	0.8499	C4—H4	0.9300
O3—H6W	0.8501	C5—H5	0.9300
N1—C1	1.3384 (18)	C6—H6	0.9300
N1—N2	1.3405 (18)	N6—O6	1.210 (2)
N2—N3	1.3113 (18)	N6—O5	1.2485 (18)
N3—N4	1.3421 (18)	N6—O4	1.2525 (18)
O3—Zn1—O3ⁱ	180.0	N2—N3—N4	109.65 (12)
O3—Zn1—O2	90.01 (5)	C1—N4—N3	104.64 (12)
O3ⁱ—Zn1—O2	89.99 (5)	C6—N5—C5	122.90 (14)
O3—Zn1—O2ⁱ	89.99 (5)	C6—N5—H5N	117.6 (14)
O3ⁱ—Zn1—O2ⁱ	90.01 (5)	C5—N5—H5N	119.5 (14)
O2—Zn1—O2ⁱ	180.0	N4—C1—N1	111.53 (13)
O3—Zn1—O1ⁱ	90.53 (4)	N4—C1—C2	124.52 (13)
O3ⁱ—Zn1—O1ⁱ	89.47 (4)	N1—C1—C2	123.93 (13)
O2—Zn1—O1ⁱ	92.10 (5)	C6—C2—C3	118.26 (14)
O2ⁱ—Zn1—O1ⁱ	87.90 (5)	C6—C2—C1	119.94 (13)
O3—Zn1—O1	89.47 (4)	C3—C2—C1	121.80 (13)
O3ⁱ—Zn1—O1	90.53 (4)	C4—C3—C2	119.93 (14)
O2—Zn1—O1	87.90 (5)	C4—C3—H3A	120.0
O2ⁱ—Zn1—O1	92.10 (5)	C2—C3—H3A	120.0

O1ⁱ—Zn1—O1	180.0	C5—C4—C3	119.67 (15)
Zn1—O1—H1W	118.9 (14)	C5—C4—H4	120.2
Zn1—O1—H2W	115.7 (13)	C3—C4—H4	120.2
H1W—O1—H2W	107.0 (18)	N5—C5—C4	119.30 (15)
Zn1—O2—H3W	126.7 (15)	N5—C5—H5	120.3
Zn1—O2—H4W	120.1 (17)	C4—C5—H5	120.3
H3W—O2—H4W	104 (2)	N5—C6—C2	119.93 (15)
Zn1—O3—H5W	123.7 (14)	N5—C6—H6	120.0
Zn1—O3—H6W	118.5 (15)	C2—C6—H6	120.0
H5W—O3—H6W	103 (2)	O6—N6—O5	120.33 (15)
C1—N1—N2	104.70 (12)	O6—N6—O4	120.02 (15)
N3—N2—N1	109.48 (11)	O5—N6—O4	119.63 (13)
C1—N1—N2—N3	0.11 (16)	N1—C1—C2—C3	7.1 (2)
N1—N2—N3—N4	−0.01 (17)	C6—C2—C3—C4	0.5 (2)
N2—N3—N4—C1	−0.09 (17)	C1—C2—C3—C4	−179.80 (14)
N3—N4—C1—N1	0.17 (17)	C2—C3—C4—C5	−0.7 (3)
N3—N4—C1—C2	−178.53 (13)	C6—N5—C5—C4	0.5 (3)
N2—N1—C1—N4	−0.18 (16)	C3—C4—C5—N5	0.2 (3)
N2—N1—C1—C2	178.53 (13)	C5—N5—C6—C2	−0.7 (2)
N4—C1—C2—C6	5.4 (2)	C3—C2—C6—N5	0.2 (2)
N1—C1—C2—C6	−173.17 (14)	C1—C2—C6—N5	−179.53 (13)
N4—C1—C2—C3	−174.32 (15)		

Symmetry code: (i) −x, −y+2, −z+2.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*W*···O5ⁱⁱ	0.85	1.96	2.8067 (17)	172
O1—H2*W*···N1ⁱⁱⁱ	0.85	1.96	2.8029 (17)	173
O2—H3*W*···N4ⁱᵛ	0.85	2.02	2.8589 (17)	170
O2—H4*W*···O1ᵛ	0.85	2.08	2.9228 (17)	171
O3—H5*W*···N3ⁱⁱ	0.85	1.91	2.7446 (17)	168
O3—H6*W*···N1ᵛⁱ	0.85	2.72	3.4294 (17)	142
O3—H6*W*···N2ᵛⁱ	0.85	1.97	2.8076 (17)	169
N5—H5*N*···N6ᵛⁱⁱ	0.82	2.61	3.344 (2)	149
N5—H5*N*···O4ᵛⁱⁱ	0.82	1.92	2.7384 (18)	173
N5—H5*N*···O5ᵛⁱⁱ	0.82	2.62	3.1347 (19)	123
C4—H4···O5ᵛⁱⁱⁱ	0.93	2.65	3.452 (2)	145
C5—H5···O4ⁱˣ	0.93	2.52	3.292 (2)	141
C5—H5···O6ⁱˣ	0.93	2.52	3.422 (3)	165
C6—H6···O5ᵛⁱⁱ	0.93	2.41	3.047 (2)	126

Symmetry codes: (ii) −x+1, −y+1, −z+1; (iii) −x+1, −y+2, −z+1; (iv) x, y+1, z+1; (v) −x+1, −y+2, −z+2; (vi) x−1, y, z+1; (vii) x−1, y, z; (viii) x−1, y+1, z; (ix) −x, −y+1, −z+1.