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Crystal structure and Hirshfeld surface analysis of the orthorhombic polymorph of a Zn^{II} complex with 3,5-dinitrobenzoic acid and ethylenediamine

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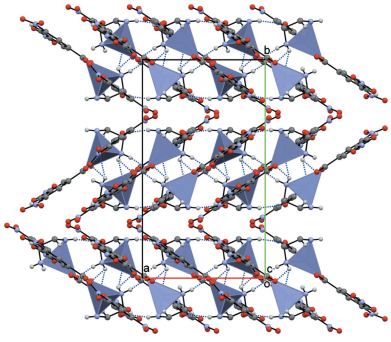
During systematic investigations of the biological action enhancement of well known compounds, a new metal complex, namely, bis(3,5-dinitrobenzoato)-(ethane-1,2-diamine)zinc(II), $[Zn(C_7H_3N_2O_6)_2(C_2H_8N_2)]$, was synthesized and the structure of its orthorhombic form has determined. The synthesis and crystal structure of the monoclinic polymorph has previously been reported [Ibragimov *et al.* (2020). *Rep. Uzb. Acad. Sci.* **1**, 45–50]. The zinc ion has a distorted tetrahedral environment formed by two monodentate 3,5-dinitrobenzoato anions and chelating ethylenediamine molecule. In the crystal, the complex molecules are linked by N—H···O and C—H···O hydrogen bonds into a two-dimensional network parallel to the *ac* plane. The Hirshfeld surface analysis indicates that the most important contributions to the crystal packing are from H···O/O···H (43.4%) and O···C/C···O (17.7%) interactions.

1. Chemical context

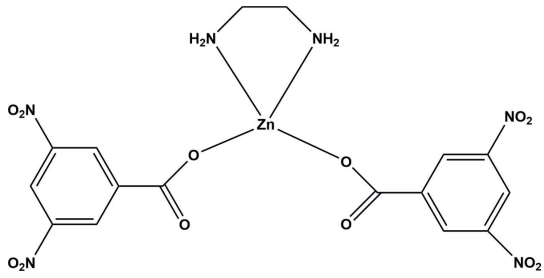
The benzoic acid derivative 3,5-dinitrobenzoic acid (DNBA) is an important corrosion inhibitor that is also applied in photography (Elks & Ganellin, 1990). This aromatic compound is used by chemists in the fluorometric analysis of creatinine (Lewinska *et al.*, 2018; Chandrasekaran *et al.*, 2013). It demonstrates a weak antimicrobial activity against bacteria and yeasts with a minimum inhibitory concentration (MIC) of 3 mmol L^{-1}, but shows moderate biological action with respect to the filamentous fungi *M. gypseum* with IC50 = 2.1 mmol L^{-1} (Vaskova *et al.*, 2009).

Ethylenediamine (En) is widely used in the chemical industry. It is a well-known bidentate chelating ligand that donates lone pairs of electrons of two nitrogen atoms (Matsushita & Taira, 1999). En is not itself biologically active against different strains of microoraganisms, but its Co^{III} complex demonstrates a strong antifungal action relative to a broad spectrum of *Candida* species (Turecka *et al.*, 2018).

DNBA is poorly water soluble; its solubility is only 1.35 g L^{-1} at 25°C. In order to enhance its water solubility and antimicrobial activity, we tested some of the presently known approaches (Jain *et al.*, 2015). More promising is a preparation of organic salts of DNBA and En as well as mixed-ligand complexes based on them. Such an approach has been applied for the biopharmaceutical optimization of 4-nitrobenzoic acid (Ibragimov *et al.*, 2017) and 4-aminobenzoic acid (Ibragimov *et al.*, 2016) yielding impressive results.



However, an analysis of the Cambridge Structural Database (CSD Version 5.41, update of November 2019; Groom *et al.*, 2016) attests that organic salts based on DNBA and En have already been obtained as ethylendiammonium bis(3,5-dinitrobenzoate) (refcode VUJXIH; Nethaji *et al.*, 1992) and ethylendiammonium bis(3,5-dinitrobenzoate) bis(3,5-dinitrobenzoic acid) (FONCER; Jones *et al.*, 2005). Therefore, we synthesized two polymorphic forms of the zinc mixed-ligand complex. The synthesis and crystal structure of the monoclinic polymorph has been published recently (Ibragimov *et al.*, 2020), and the present paper is devoted to an orthorhombic polymorph that crystallizes in space group *Pbca*.



2. Structural commentary

Two DNBA anions coordinate the Zn^{II} ion in a monodentate mode *via* the oxygen atoms of the carboxylate groups. As is usual, the En molecule acts as a chelating ligand through the two nitrogen atoms (Fig. 1). The coordination tetrahedron is distorted because of the Zn1···O2 and Zn1···O2′ interactions, the angles N3—Zn1—N4 [87.09 (7)°] and O1—Zn1—O1′ [101.82 (5)°] being less than the idealized tetrahedral values. The least-squares planes through the nitro groups are almost parallel to the planes of the aromatic rings. The nitro group N2′O5′O6′ subtends the largest dihedral angle to the attached aromatic ring [16.65 (11)°]. The conformation of the complex molecule is fixed due to the intramolecular N4—H4*A*···O2 hydrogen bond, which closes a six-membered ring with graph-set notation *S*(6) (Etter, 1990).

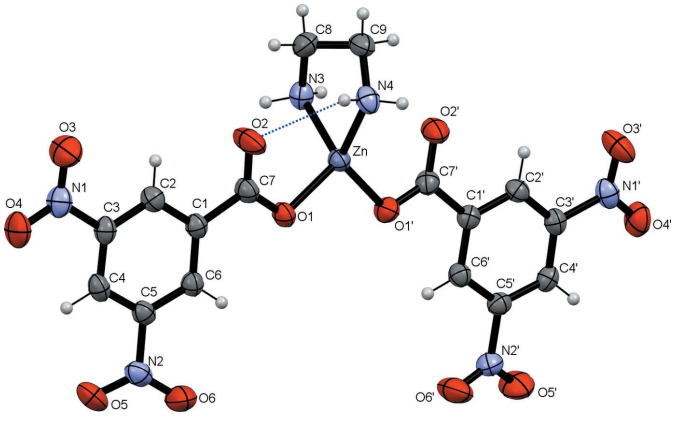


Figure 1
Molecular structure of $[Zn(DNBA)_2(En)]$ with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4′—H4′···O6^{i}	0.93	2.63	3.539 (2)	167
C8—H8*A*···O3^{ii}	0.97	2.51	3.353 (3)	145
N3—H3*A*···O2′^{iii}	0.89 (1)	2.19 (1)	3.055 (2)	165 (2)
N4—H4*A*···O2	0.89 (1)	2.42 (2)	3.010 (2)	124 (2)
N4—H4*A*···O5′^{iv}	0.89 (1)	2.58 (2)	3.273 (3)	136 (2)
N4—H4*B*···O1^{v}	0.88 (1)	2.18 (1)	3.021 (2)	159 (2)

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

3. Supramolecular features

In the crystal, complex molecules are linked by three relatively weak hydrogen bonds of the N—H···O type and two bonds of C—H···O type (Table 1). The N3—H3*A*···O2′, N4—H4*A*···O5′ and N4—H4*B*···O1 hydrogen bonds link the complex molecules into a two-dimensional network parallel to the *ac* plane. Weak C6′—H6′···O6′ and C8—H8*B*···O3 hydrogen bonds strengthen the association of the complex molecules into this network (Fig. 2). Thus, only the H3*B* hydrogen on the N3 atom is without an acceptor and five oxygen atoms O1′, O3′, O4′, O4 and O5 do not participate in hydrogen bonding.

4. Hirshfeld surface analysis

In order to visualize the intermolecular interactions in the crystals of the title compound, a Hirshfeld surface analysis was carried out using *Crystal Explorer 17.5* (Turner *et al.*, 2017). The Hirshfeld surface mapped over d_{norm} (Fig. 3) shows the expected bright-red spots near atoms O1, O2, O2, O3, O5′, O6, H3*A*, H4*A*, H4′, H4*B* and H8*A* involved in the N—H···O and

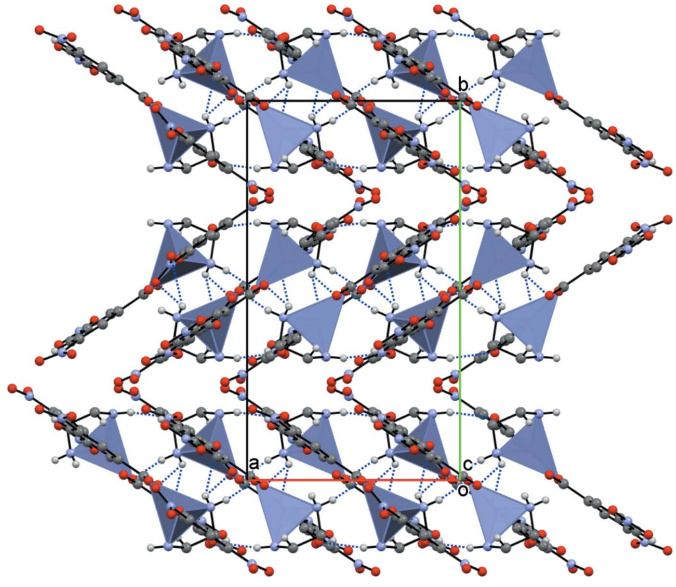


Figure 2
A packing diagram for $[Zn(DNBA)_2(En)]$ showing the two-dimensional networks parallel to (010). For clarity, H atoms not involved in hydrogen bonding are omitted.

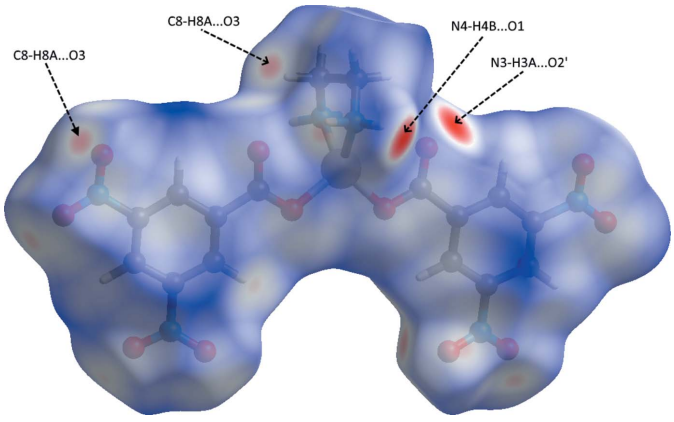


Figure 3
View of the three-dimensional Hirshfeld surface of the title compound plotted over d_{norm} in the range −0.4180 to 1.3344 a.u.

C—H···O hydrogen-bonding interactions described above. Fingerprint plots (Fig. 4) reveal that while H···O/O···H interactions make the greatest contributions to the surface contacts, as would be expected for a molecule with such a predominance of oxygen atoms, O···C/C···O, H···H and O···O contacts are also substantial (Table 2), while H···C/C···H, O···N/N···O, H···N/N···H, C···C, N···C/C···N and N···N contacts are less significant.

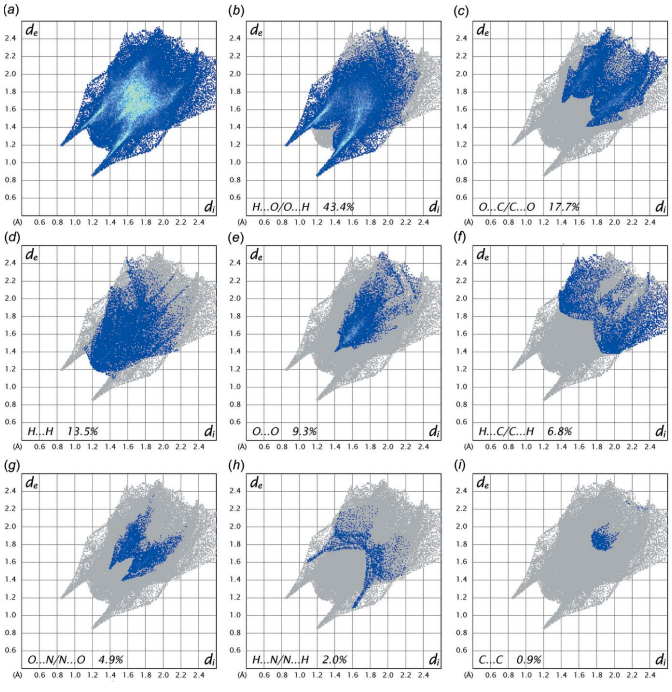


Figure 4
Full two-dimensional fingerprint plots for the title compound, showing all interactions (*a*), and delineated into (*b*) H···O/O···H, (*c*) O···C/C···O, (*d*) H···H, (*e*) O···O, (*f*) H···C/C···H, (*g*) O···N/N···O, (*h*) H···N/N···H and (*i*) C···C interactions. The d_i and d_e values are the closest internal and external distances (in Å) from a given point on the Hirshfeld surface.

Table 2
Percentage contributions to the Hirshfeld surface for $[Zn(DNBA)_2(En)]$.

Contacts	Included surface area %
H···O/O···H	43.4
O···C/C···O	17.7
H···H	13.5
H···C/C···H	6.8
O···N/N···O	4.9
H···N/N···H	2.0
C···C	0.9
N···C/C···N	0.4
N···N	0.1

5. Database survey

A search of the Cambridge Structural Database (CSD Version 5.41, update of November 2019; Groom *et al.*, 2016) found 277 metal complexes involving DNBA. Among them, 29 hits are zinc complexes, of which 14 have the coordination number four. In all of these complexes, two DNBA anions are coordinated in a monodentate fashion and only in structures JOHYEN (Torres *et al.*, 2019) and VIQFAE (Dey *et al.*, 2013) is the coordination of Zn^{II} accomplished by chelating ligands: 1,1′-methylenebis(3,5-dimethyl-1*H*-pyrazole and 2,2′-bipyridyl for JOHYEN and VIQFAE, respectively.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Zn(C_7H_3N_2O_6)_2(C_2H_8N_2)]$
M_r	547.70
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	293
a, *b*, *c* (Å)	10.26799 (6), 18.26557 (10), 21.67365 (12)
V (Å^3)	4064.91 (4)
Z	8
Radiation type	Cu *Kα*
μ (mm^{-1})	2.45
Crystal size (mm)	0.42 × 0.3 × 0.18
Data collection	
Diffractometer	Rigaku Oxford Diffraction Xcalibur, Ruby
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.613, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26085, 4214, 4070
R_{int}	0.024
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.629
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.032, 0.091, 1.09
No. of reflections	4214
No. of parameters	333
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, −0.52

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

6. Synthesis and crystallization

To an aqueous solution (2.5 ml) of $ZnCl_2$ (0,068 g, 0.5 mmol) was slowly added a mixture of ethanol (4 ml), En (60 µL) and DNBA (0.212 g, 1 mmol) under constant stirring. A white crystalline product was obtained at room temperature by slow solvent evaporation after 5 d, yield: 70%. Elemental analysis for $C_{16}H_{14}N_6O_{12}Zn$ (547.70): calculated C: 35.09, H: 2.58, N:15.34%; found: C: 35.12, H: 2.62, N: 15.41%.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C-bound hydrogen atoms were placed in calculated positions and refined using the riding-model approximation with $U_{iso}(H) = 1.2U_{eq}(C)$, C—H = 0.93 and 0.97 Å for aromatic and methylene hydrogen atoms, respectively. N-bound H atoms were located in a difference-Fourier map and refined with bond-length restraints of 0.89 (1) Å.

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Crystal structure and Hirshfeld surface analysis of the orthorhombic polymorph of a Zn^{II} complex with 3,5-dinitrobenzoic acid and ethylenediamine

Avazbek Ibragimov, Jamshid Ashurov, Aziz Dusmatov and Aziz Ibragimov

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Bis(3,5-dinitrobenzoato)(ethane-1,2-diamine)zinc(II)

Crystal data

$[Zn(C_7H_3N_2O_6)_2(C_2H_8N_2)]$
M_r = 547.70
Orthorhombic, *Pbca*
a = 10.26799 (6) Å
b = 18.26557 (10) Å
c = 21.67365 (12) Å
V = 4064.91 (4) Å^3
Z = 8
$F(000)$ = 2224
D_x = 1.790 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 19707 reflections
θ = 4.3–76.0°
μ = 2.44 mm^{-1}
T = 293 K
Block, white
0.42 × 0.3 × 0.18 mm

Data collection

Rigaku Oxford Diffraction Xcalibur, Ruby diffractometer
Radiation source: Enhance (Cu) X-ray Source
Graphite monochromator
Detector resolution: 10.2576 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2015)
T_{min} = 0.613, T_{max} = 1.000
26085 measured reflections
4214 independent reflections
4070 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 76.0°, θ_{min} = 4.1°
h = −12→12
k = −20→22
l = −20→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.091
S = 1.09
4214 reflections
333 parameters
4 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 1.5574P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

Extinction correction: SHELXL-2018/3 (Sheldrick 2018), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00077 (6)

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	0.67282 (2)	0.42317 (2)	0.24573 (2)	0.03229 (10)
O1	0.53739 (12)	0.49815 (7)	0.23272 (6)	0.0371 (3)
O1′	0.68069 (13)	0.41811 (7)	0.33561 (6)	0.0414 (3)
O4′	1.02982 (15)	0.26641 (9)	0.58578 (7)	0.0576 (4)
O2′	0.83739 (14)	0.33654 (10)	0.31937 (6)	0.0544 (4)
O5	0.02506 (14)	0.68636 (8)	0.22153 (8)	0.0551 (4)
N3	0.62989 (16)	0.32537 (8)	0.20461 (7)	0.0396 (3)
N1′	1.02277 (14)	0.27851 (8)	0.53038 (8)	0.0410 (3)
N4	0.82786 (14)	0.42902 (9)	0.18869 (8)	0.0389 (3)
O3	0.28325 (19)	0.57939 (10)	−0.01964 (7)	0.0670 (5)
O6′	0.57039 (17)	0.47877 (10)	0.55318 (8)	0.0695 (5)
N2′	0.64170 (16)	0.43071 (9)	0.57126 (7)	0.0419 (4)
O4	0.11575 (17)	0.64392 (10)	0.00591 (7)	0.0634 (4)
O2	0.57988 (17)	0.48659 (12)	0.13270 (7)	0.0750 (6)
N1	0.21307 (17)	0.60866 (9)	0.01838 (7)	0.0459 (4)
N2	0.13183 (16)	0.66326 (8)	0.23606 (8)	0.0425 (4)
C1	0.39543 (16)	0.55533 (9)	0.16039 (8)	0.0324 (3)
C2′	0.89150 (16)	0.32663 (9)	0.44488 (8)	0.0336 (3)
H2′	0.947315	0.302924	0.417622	0.040*
C5′	0.72941 (16)	0.39536 (9)	0.52664 (7)	0.0333 (3)
C6′	0.70569 (16)	0.40357 (9)	0.46427 (8)	0.0326 (3)
H6′	0.636643	0.432089	0.450362	0.039*
C1′	0.78781 (15)	0.36807 (9)	0.42272 (7)	0.0314 (3)
C5	0.21151 (16)	0.62756 (9)	0.18838 (8)	0.0345 (3)
C3′	0.91054 (16)	0.32112 (9)	0.50751 (8)	0.0333 (3)
C2	0.35964 (17)	0.56172 (9)	0.09885 (8)	0.0350 (3)
H2	0.409358	0.539865	0.068072	0.042*
C4	0.17179 (16)	0.63447 (9)	0.12799 (9)	0.0372 (4)
H4	0.096968	0.660232	0.117358	0.045*
C7	0.51413 (17)	0.50986 (10)	0.17523 (8)	0.0377 (4)
C3	0.24905 (17)	0.60106 (9)	0.08403 (8)	0.0354 (3)
C6	0.32130 (15)	0.58895 (9)	0.20600 (8)	0.0336 (3)
H6	0.344937	0.585566	0.247323	0.040*
C4′	0.83052 (15)	0.35433 (9)	0.55020 (8)	0.0335 (3)
H4′	0.843953	0.349357	0.592423	0.040*

C7′	0.76869 (16)	0.37360 (10)	0.35383 (7)	0.0354 (3)
C8	0.7149 (2)	0.32148 (11)	0.14984 (9)	0.0461 (4)
H8A	0.675173	0.348006	0.115951	0.055*
H8B	0.725379	0.270824	0.137340	0.055*
C9	0.84714 (18)	0.35432 (11)	0.16435 (9)	0.0434 (4)
H9A	0.891841	0.324435	0.194691	0.052*
H9B	0.899990	0.356017	0.127285	0.052*
O5′	0.64367 (18)	0.40972 (11)	0.62426 (7)	0.0680 (5)
O6	0.17650 (17)	0.66780 (11)	0.28763 (8)	0.0723 (5)
O3′	1.10353 (16)	0.25867 (9)	0.49322 (7)	0.0613 (4)
H3A	0.5474 (12)	0.3214 (13)	0.1932 (11)	0.053 (6)*
H3B	0.647 (2)	0.2916 (10)	0.2324 (9)	0.052 (6)*
H4A	0.804 (2)	0.4583 (12)	0.1581 (9)	0.058 (7)*
H4B	0.9014 (15)	0.4475 (13)	0.2027 (11)	0.060 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.03023 (15)	0.03616 (16)	0.03048 (15)	0.00523 (8)	−0.00034 (8)	0.00139 (8)
O1	0.0346 (6)	0.0406 (6)	0.0359 (6)	0.0097 (5)	−0.0028 (5)	0.0036 (5)
O1′	0.0477 (7)	0.0479 (7)	0.0286 (6)	0.0089 (5)	−0.0025 (5)	0.0032 (5)
O4′	0.0614 (9)	0.0618 (9)	0.0495 (8)	0.0088 (7)	−0.0174 (7)	0.0118 (7)
O2′	0.0478 (8)	0.0838 (11)	0.0315 (7)	0.0216 (7)	0.0036 (5)	−0.0027 (7)
O5	0.0417 (7)	0.0530 (8)	0.0707 (10)	0.0174 (6)	0.0058 (7)	0.0022 (7)
N3	0.0381 (8)	0.0375 (8)	0.0432 (8)	−0.0031 (6)	−0.0070 (6)	0.0030 (6)
N1′	0.0356 (7)	0.0349 (7)	0.0524 (9)	−0.0006 (6)	−0.0056 (7)	0.0090 (6)
N4	0.0312 (8)	0.0455 (9)	0.0402 (9)	−0.0006 (6)	0.0017 (6)	0.0066 (6)
O3	0.0748 (11)	0.0892 (13)	0.0370 (8)	0.0189 (9)	0.0014 (8)	0.0096 (7)
O6′	0.0760 (11)	0.0794 (11)	0.0530 (9)	0.0400 (9)	0.0073 (8)	−0.0040 (8)
N2′	0.0421 (8)	0.0484 (9)	0.0351 (8)	0.0024 (7)	0.0012 (6)	−0.0068 (6)
O4	0.0625 (9)	0.0736 (10)	0.0542 (9)	0.0172 (8)	−0.0210 (7)	0.0129 (8)
O2	0.0726 (11)	0.1122 (15)	0.0401 (8)	0.0598 (11)	0.0008 (7)	0.0021 (8)
N1	0.0489 (9)	0.0474 (9)	0.0414 (8)	−0.0008 (7)	−0.0080 (7)	0.0114 (7)
N2	0.0415 (8)	0.0343 (7)	0.0518 (9)	0.0064 (7)	0.0014 (7)	−0.0021 (6)
C1	0.0305 (8)	0.0299 (7)	0.0368 (8)	0.0014 (6)	−0.0025 (6)	0.0030 (6)
C2′	0.0315 (8)	0.0338 (8)	0.0355 (8)	0.0009 (6)	0.0033 (6)	0.0015 (6)
C5′	0.0347 (8)	0.0325 (7)	0.0326 (8)	−0.0031 (6)	0.0013 (6)	−0.0029 (6)
C6′	0.0324 (8)	0.0328 (7)	0.0327 (8)	0.0009 (6)	−0.0011 (6)	0.0019 (6)
C1′	0.0313 (7)	0.0321 (7)	0.0307 (8)	−0.0026 (6)	0.0004 (6)	0.0022 (6)
C5	0.0315 (8)	0.0299 (7)	0.0423 (9)	0.0013 (6)	−0.0002 (7)	−0.0001 (6)
C3′	0.0299 (8)	0.0310 (7)	0.0389 (8)	−0.0025 (6)	−0.0026 (6)	0.0052 (6)
C2	0.0352 (8)	0.0327 (8)	0.0371 (9)	0.0007 (7)	0.0002 (7)	0.0042 (6)
C4	0.0299 (8)	0.0332 (8)	0.0484 (10)	0.0031 (6)	−0.0064 (7)	0.0054 (7)
C7	0.0363 (8)	0.0390 (8)	0.0378 (9)	0.0093 (7)	−0.0025 (7)	0.0039 (7)
C3	0.0344 (8)	0.0350 (8)	0.0369 (8)	−0.0026 (7)	−0.0063 (7)	0.0072 (6)
C6	0.0324 (8)	0.0320 (8)	0.0364 (9)	0.0007 (6)	−0.0042 (6)	0.0014 (6)
C4′	0.0363 (8)	0.0353 (8)	0.0289 (8)	−0.0057 (6)	−0.0035 (6)	0.0020 (6)
C7′	0.0324 (8)	0.0435 (9)	0.0304 (8)	−0.0018 (7)	0.0012 (6)	0.0024 (6)

C8	0.0520 (11)	0.0485 (10)	0.0376 (9)	0.0067 (9)	−0.0072 (8)	−0.0096 (8)
C9	0.0383 (9)	0.0543 (11)	0.0376 (9)	0.0118 (8)	0.0030 (7)	−0.0031 (8)
O5′	0.0750 (11)	0.0951 (13)	0.0339 (8)	0.0224 (10)	0.0123 (7)	0.0028 (8)
O6	0.0726 (12)	0.0943 (13)	0.0500 (10)	0.0323 (9)	−0.0066 (8)	−0.0238 (9)
O3′	0.0454 (8)	0.0677 (10)	0.0709 (10)	0.0218 (7)	0.0111 (7)	0.0211 (8)

Geometric parameters (Å, º)

Zn1—O1	1.9721 (12)	C1—C2	1.388 (2)
Zn1—O1′	1.9519 (13)	C1—C7	1.509 (2)
Zn1—N3	2.0445 (15)	C1—C6	1.391 (2)
Zn1—N4	2.0184 (15)	C2′—H2′	0.9300
O1—C7	1.287 (2)	C2′—C1′	1.392 (2)
O1′—C7′	1.278 (2)	C2′—C3′	1.375 (2)
O4′—N1′	1.223 (2)	C5′—C6′	1.382 (2)
O2′—C7′	1.230 (2)	C5′—C4′	1.378 (2)
O5—N2	1.216 (2)	C6′—H6′	0.9300
N3—C8	1.475 (3)	C6′—C1′	1.394 (2)
N3—H3A	0.885 (10)	C1′—C7′	1.509 (2)
N3—H3B	0.879 (10)	C5—C4	1.377 (2)
N1′—C3′	1.476 (2)	C5—C6	1.383 (2)
N1′—O3′	1.211 (2)	C3′—C4′	1.378 (2)
N4—C9	1.476 (3)	C2—H2	0.9300
N4—H4A	0.886 (10)	C2—C3	1.382 (2)
N4—H4B	0.881 (10)	C4—H4	0.9300
O3—N1	1.218 (2)	C4—C3	1.382 (3)
O6′—N2′	1.208 (2)	C6—H6	0.9300
N2′—C5′	1.471 (2)	C4′—H4′	0.9300
N2′—O5′	1.211 (2)	C8—H8A	0.9700
O4—N1	1.219 (2)	C8—H8B	0.9700
O2—C7	1.219 (2)	C8—C9	1.517 (3)
N1—C3	1.477 (2)	C9—H9A	0.9700
N2—C5	1.470 (2)	C9—H9B	0.9700
N2—O6	1.211 (2)		
O1—Zn1—N3	113.10 (6)	C1′—C6′—H6′	120.8
O1—Zn1—N4	115.58 (6)	C2′—C1′—C6′	119.53 (15)
O1′—Zn1—O1	101.82 (5)	C2′—C1′—C7′	118.50 (14)
O1′—Zn1—N3	113.74 (6)	C6′—C1′—C7′	121.97 (15)
O1′—Zn1—N4	125.53 (6)	C4—C5—N2	117.56 (15)
N4—Zn1—N3	87.09 (7)	C4—C5—C6	123.40 (16)
C7—O1—Zn1	112.64 (11)	C6—C5—N2	119.04 (16)
C7′—O1′—Zn1	111.57 (11)	C2′—C3′—N1′	118.75 (15)
Zn1—N3—H3A	113.6 (16)	C2′—C3′—C4′	123.08 (15)
Zn1—N3—H3B	105.8 (16)	C4′—C3′—N1′	118.17 (15)
C8—N3—Zn1	105.38 (11)	C1—C2—H2	120.5
C8—N3—H3A	109.7 (16)	C3—C2—C1	118.99 (16)
C8—N3—H3B	113.7 (16)	C3—C2—H2	120.5

H3A—N3—H3B	109 (2)	C5—C4—H4	121.8
O4′—N1′—C3′	118.10 (16)	C5—C4—C3	116.43 (15)
O3′—N1′—O4′	123.92 (16)	C3—C4—H4	121.8
O3′—N1′—C3′	117.96 (15)	O1—C7—C1	116.60 (15)
Zn1—N4—H4A	105.7 (16)	O2—C7—O1	124.85 (16)
Zn1—N4—H4B	119.1 (17)	O2—C7—C1	118.55 (16)
C9—N4—Zn1	106.00 (11)	C2—C3—N1	118.59 (16)
C9—N4—H4A	109.1 (17)	C2—C3—C4	122.76 (16)
C9—N4—H4B	111.2 (17)	C4—C3—N1	118.64 (15)
H4A—N4—H4B	105 (2)	C1—C6—H6	120.8
O6′—N2′—C5′	118.47 (16)	C5—C6—C1	118.36 (16)
O6′—N2′—O5′	123.21 (17)	C5—C6—H6	120.8
O5′—N2′—C5′	118.32 (16)	C5′—C4′—H4′	122.0
O3—N1—O4	124.53 (17)	C3′—C4′—C5′	116.09 (15)
O3—N1—C3	117.56 (16)	C3′—C4′—H4′	122.0
O4—N1—C3	117.92 (17)	O1′—C7′—C1′	116.11 (14)
O5—N2—C5	118.25 (16)	O2′—C7′—O1′	124.60 (16)
O6—N2—O5	123.82 (17)	O2′—C7′—C1′	119.29 (15)
O6—N2—C5	117.92 (16)	N3—C8—H8A	109.6
C2—C1—C7	117.68 (15)	N3—C8—H8B	109.6
C2—C1—C6	120.06 (15)	N3—C8—C9	110.10 (14)
C6—C1—C7	122.24 (15)	H8A—C8—H8B	108.2
C1′—C2′—H2′	120.4	C9—C8—H8A	109.6
C3′—C2′—H2′	120.4	C9—C8—H8B	109.6
C3′—C2′—C1′	119.28 (15)	N4—C9—C8	108.63 (14)
C6′—C5′—N2′	119.19 (15)	N4—C9—H9A	110.0
C4′—C5′—N2′	117.16 (15)	N4—C9—H9B	110.0
C4′—C5′—C6′	123.65 (15)	C8—C9—H9A	110.0
C5′—C6′—H6′	120.8	C8—C9—H9B	110.0
C5′—C6′—C1′	118.36 (15)	H9A—C9—H9B	108.3

Zn1—O1—C7—O2	−10.6 (3)	C5′—C6′—C1′—C7′	179.61 (15)
Zn1—O1—C7—C1	168.80 (11)	C6′—C5′—C4′—C3′	0.5 (2)
Zn1—O1′—C7′—O2′	−2.2 (2)	C6′—C1′—C7′—O1′	6.4 (2)
Zn1—O1′—C7′—C1′	177.15 (11)	C6′—C1′—C7′—O2′	−174.22 (17)
Zn1—N3—C8—C9	37.33 (17)	C1′—C2′—C3′—N1′	−178.51 (14)
Zn1—N4—C9—C8	40.97 (17)	C1′—C2′—C3′—C4′	0.7 (3)
O4′—N1′—C3′—C2′	−171.17 (16)	C5—C4—C3—N1	−178.17 (15)
O4′—N1′—C3′—C4′	9.6 (2)	C5—C4—C3—C2	0.9 (3)
O5—N2—C5—C4	11.9 (2)	C3′—C2′—C1′—C6′	0.4 (2)
O5—N2—C5—C6	−167.92 (17)	C3′—C2′—C1′—C7′	179.87 (15)
N3—C8—C9—N4	−54.1 (2)	C2—C1—C7—O1	−172.74 (16)
N1′—C3′—C4′—C5′	178.08 (14)	C2—C1—C7—O2	6.7 (3)
O3—N1—C3—C2	0.2 (3)	C2—C1—C6—C5	0.8 (2)
O3—N1—C3—C4	179.28 (18)	C4—C5—C6—C1	0.0 (3)
O6′—N2′—C5′—C6′	−16.6 (2)	C7—C1—C2—C3	177.96 (15)
O6′—N2′—C5′—C4′	164.53 (18)	C7—C1—C6—C5	−177.85 (15)
N2′—C5′—C6′—C1′	−178.32 (15)	C6—C1—C2—C3	−0.8 (2)

N2′—C5′—C4′—C3′	179.34 (14)	C6—C1—C7—O1	6.0 (2)
O4—N1—C3—C2	−179.51 (18)	C6—C1—C7—O2	−174.6 (2)
O4—N1—C3—C4	−0.4 (3)	C6—C5—C4—C3	−0.8 (3)
N2—C5—C4—C3	179.36 (15)	C4′—C5′—C6′—C1′	0.5 (2)
N2—C5—C6—C1	179.82 (15)	O5′—N2′—C5′—C6′	162.72 (18)
C1—C2—C3—N1	178.93 (15)	O5′—N2′—C5′—C4′	−16.1 (3)
C1—C2—C3—C4	−0.1 (3)	O6—N2—C5—C4	−168.19 (18)
C2′—C1′—C7′—O1′	−173.09 (15)	O6—N2—C5—C6	12.0 (3)
C2′—C1′—C7′—O2′	6.3 (2)	O3′—N1′—C3′—C2′	10.0 (2)
C2′—C3′—C4′—C5′	−1.1 (2)	O3′—N1′—C3′—C4′	−169.18 (17)
C5′—C6′—C1′—C2′	−0.9 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4′—H4′···O6^{i}	0.93	2.63	3.539 (2)	167
C8—H8*A*···O3^{ii}	0.97	2.51	3.353 (3)	145
N3—H3*A*···O2′^{iii}	0.89 (1)	2.19 (1)	3.055 (2)	165 (2)
N4—H4*A*···O2	0.89 (1)	2.42 (2)	3.010 (2)	124 (2)
N4—H4*A*···O5′^{iv}	0.89 (1)	2.58 (2)	3.273 (3)	136 (2)
N4—H4*B*···O1^{v}	0.88 (1)	2.18 (1)	3.021 (2)	159 (2)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*; (iii) *x*−1/2, *y*, −*z*+1/2; (iv) −*x*+3/2, −*y*+1, *z*−1/2; (v) *x*+1/2, *y*, −*z*+1/2.