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Aqua(4-nitrophthalato)bis[2-(1*H*-pyrazol-3-yl)pyridine]zinc(II) hemihydrate

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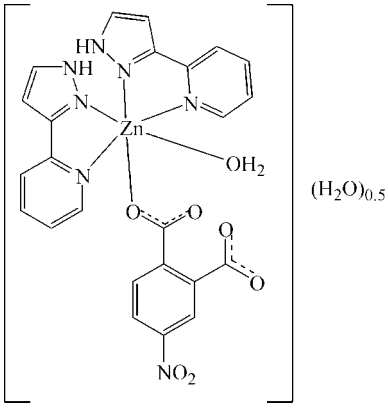
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.005 Å; H-atom completeness 96%; R factor = 0.035; wR factor = 0.104; data-to-parameter ratio = 11.7.

In the title compound, $[Zn(C_8H_3NO_6)(C_8H_7N_3)_2(H_2O)]\cdot 0.5H_2O$, the Zn^{II} atom shows a distorted octahedral ZnN_4O_2 coordination environment and is bonded to two 3-(2-pyridyl)-1*H*-pyrazole ligands *via* the N atoms, one monodentate 4-nitrophthalate ligand and one associated water molecule. Additionally, one water of crystallization, with a site-occupation factor of 0.5, is present. The two 3-(2-pyridyl)-1*H*-pyrazole ligands are planar [r.m.s. deviations = 0.03 (1) and 0.35 (1) Å] and the dihedral angle between the two planar 3-(2-pyridyl)-1*H*-pyrazole ligands is 67.31 (4)°. Intermolecular π–π stacking interactions between 3-(2-pyridyl)-1*H*-pyrazole ligands with a face-to-face separation of 3.64 (1) Å are observed. Moreover, the crystal structure is stabilized by O—H···O and N—H···O hydrogen bonds between the water of crystallization, the associated water molecule and the 3-(2-pyridyl)-1*H*-pyrazole ligands.

Related literature

For background to metal-organic frameworks, see: Hagrman *et al.* (1999); Kitagawa *et al.* (2004).



Experimental

Crystal data

$[Zn(C_8H_3NO_6)(C_8H_7N_3)_2(H_2O)]\cdot 0.5H_2O$
M_r = 591.84
Triclinic, $P\overline{1}$
a = 10.4284 (6) Å
b = 11.1844 (7) Å
c = 11.9656 (8) Å
α = 96.508 (3)°
β = 112.091 (3)°
γ = 96.366 (3)°
V = 1266.84 (14) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.03 mm^{-1}
T = 294 K
0.12 × 0.10 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.886, T_{max} = 0.922
9062 measured reflections
4258 independent reflections
3825 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.104
S = 1.00
4258 reflections
364 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H2*W*···O5^{i}	0.82 (3)	1.81 (3)	2.627 (3)	174 (3)
N5—H5*A*···O4^{i}	0.86	1.95	2.788 (3)	166
N2—H2*A*···O2	0.86	1.82	2.606 (4)	150

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2226).

References

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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

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Acta Cryst. (2011). E**67**, m105 [https://doi.org/10.1107/S1600536810051949]

Aqua(4-nitrophthalato)bis[2-(1*H*-pyrazol-3-yl)pyridine]zinc(II) hemihydrate

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S1. Comment

The synthesis of entangled metal-organic frameworks (MOFs) has attracted continuous research interest not only because of their appealing structural and topological novelty, but also due to their unusual optical, electronic, magnetic, and catalytic properties, as well as their potential medical application (Hagrman *et al.* (1999); Kitagawa *et al.* (2004)). Here, we describe the synthesis and structural characterization of the title compound resulting from an attempted MOF synthesis in which Zn and Gd complex building blocks were expected to be the constituents.

Single crystal X-ray diffraction analyses revealed that the asymmetric unit of the title compound, $[(Zn(C_8H_7N_3)_2(C_8NH_3O_6)(H_2O)].(H_2O)_{0.5}$, consists of one Zn^{2+} ion, two 3-(2-pyridyl)-1*H*-pyrazole ligands, one 4-Nitrophthalato ligand, one associated water molecule, and half water of crystallization. As shown in Figure 1, the Zn^{2+} ion is hexacoordinated by four N atoms from 3-(2-pyridyl)-1*H*-pyrazole ligands and two oxygen atoms from 4-Nitrophthalato ligand and one associated water molecule, exhibiting a distorted octahedral arrangement of ZnN_4O_2. Moreover, the Rms deviations of the two 3-(2-pyridyl)-1*H*-pyrazole groups from planarity are 0.03 (1) and 0.35 (1) Å, respectively. The dihedral angle between the two 3-(2-pyridyl)-1*H*-pyrazole planars is 67.31 (4) Å. Interestingly, between the molecules, there is π-π stacking interactions with the face-to-face separation (*ca* 3.64 (1) Å) between the 3-(2-pyridyl)-1*H*-pyrazole planars. Meantime, there are extensive hydrogen bonds between water of crystallization, associated water molecule, and 3-(2-pyridyl)-1*H*-pyrazole, and leads to a consolidation of the structure (Figure 2).

S2. Experimental

A mixture of zinc oxalate dihydrate (0.26 mmol, 0.050 g), 3-(2-pyridyl)-1*H*-pyrazole (0.32 mmoL, 0.05 g), 4-nitrophthalic acid (0.24 mmoL, 0.05 g), gadolinium(III) nitrate pentahydrate (0.12 mmoL, 0.05 g), and 14 ml H_2O was sealed in a 25 ml Teflon-lined stainless steel autoclave at 433 K for three days. Pink crystals suitable for the X-ray experiment were obtained. The yield is 60% based on the zinc salt. Anal. Calc. for $C_{48}H_{40}N_{14}O_{15}Zn_2$: C 48.65, H 3.38, N 16.55%; Found: C 48.32, H 3.15, N 16.39%.

S3. Refinement

All hydrogen atoms bound to carbon were refined using a riding model with distance C—H = 0.93 Å, U_{iso} = 1.2U_{eq} (C) for aromatic atoms. The H atoms of the coordinated water molecule were located from difference density maps and were refined with d(O—H) = 0.83 (2) Å, and with a fixed U_{iso} of 0.80 Å^2. H atoms at the solvent water molecule could not be derived from the Fourier map. Due to the site occupation factor of 0.5 for O1W these positions wer excluded from the final refinement.

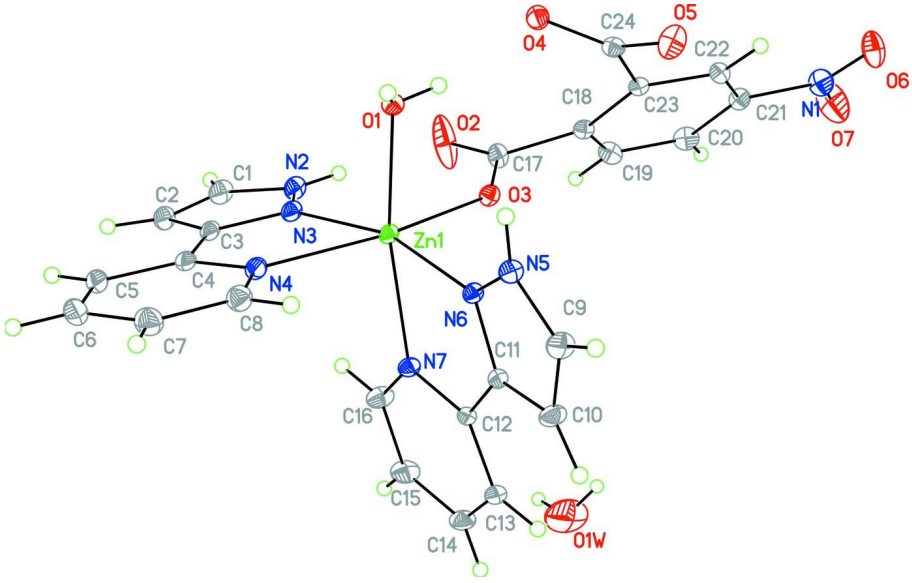

Figure 1

Molecular structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level; H atoms are given as spheres of arbitrary radius.

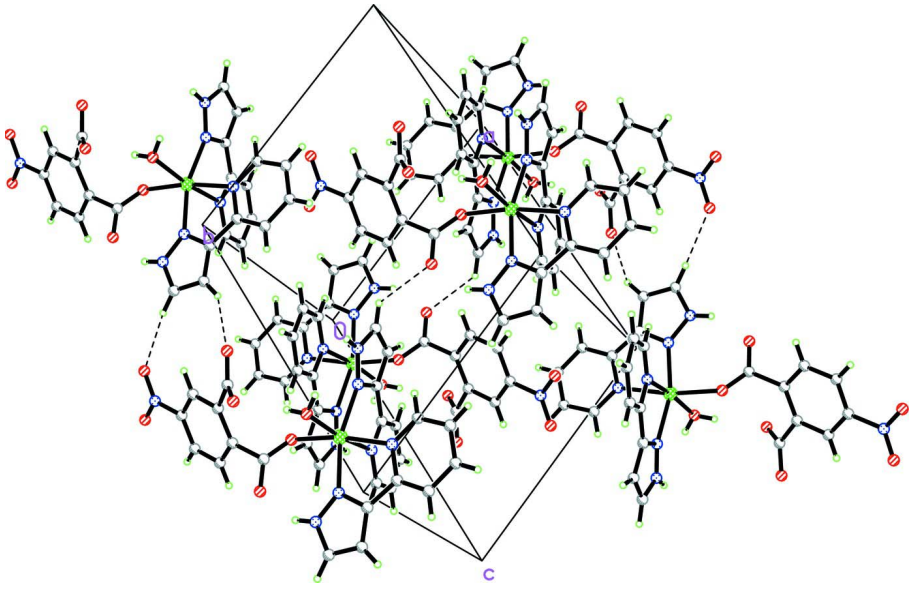

Figure 2

Crystal packing of the title compound, displayed with hydrogen bonds as dashed lines.

Aqua(4-nitrophthalato)bis[2-(1*H*-pyrazol-3-yl)pyridine]zinc(II) hemihydrate

Crystal data

$[Zn(C_8H_3NO_6)(C_8H_7N_3)_2(H_2O)]\cdot 0.5H_2O$
$M_r = 591.84$
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Hall symbol: -P 1
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$c = 11.9656\ (8)$ Å
$\alpha = 96.508\ (3)°$
$\beta = 112.091\ (3)°$
$\gamma = 96.366\ (3)°$

V = 1266.84 (14) Å^3
Z = 2
F(000) = 604
D_x = 1.552 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4528 reflections
θ = 2.4–27.3°
μ = 1.03 mm^{-1}
T = 294 K
Block, colorless
0.12 × 0.10 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.886, T_{max} = 0.922
9062 measured reflections
4258 independent reflections
3825 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 25.0°, θ_{min} = 1.9°
h = −12→12
k = −13→13
l = −14→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.104
S = 1.00
4258 reflections
364 parameters
3 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
$w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 0.7068P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 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}
C1	0.7155 (4)	0.7772 (3)	0.9195 (3)	0.0652 (9)
H1	0.6311	0.7613	0.9291	0.078*
C2	0.8440 (4)	0.8158 (3)	1.0110 (3)	0.0618 (9)
H2	0.8654	0.8318	1.0946	0.074*
C3	0.9371 (3)	0.8262 (2)	0.9526 (3)	0.0471 (7)
C4	1.0889 (3)	0.8628 (2)	0.9968 (3)	0.0476 (7)
C5	1.1747 (4)	0.9022 (3)	1.1197 (3)	0.0610 (8)
H5	1.1367	0.9060	1.1788	0.073*
C6	1.3160 (4)	0.9354 (3)	1.1522 (3)	0.0719 (10)
H6	1.3755	0.9618	1.2339	0.086*

C7	1.3695 (4)	0.9292 (3)	1.0618 (3)	0.0708 (10)
H7	1.4651	0.9517	1.0817	0.085*
C8	1.2775 (4)	0.8889 (3)	0.9417 (3)	0.0589 (8)
H8	1.3136	0.8841	0.8814	0.071*
C9	1.2913 (3)	0.7454 (3)	0.5661 (3)	0.0594 (8)
H9	1.3580	0.7702	0.5356	0.071*
C10	1.2595 (3)	0.6312 (3)	0.5882 (3)	0.0576 (8)
H10	1.2987	0.5629	0.5755	0.069*
C11	1.1556 (3)	0.6392 (2)	0.6339 (2)	0.0381 (5)
C12	1.0801 (3)	0.5491 (2)	0.6763 (2)	0.0369 (5)
C13	1.0886 (3)	0.4254 (2)	0.6620 (3)	0.0493 (7)
H13	1.1427	0.3953	0.6223	0.059*
C14	1.0159 (4)	0.3486 (3)	0.7075 (3)	0.0621 (9)
H14	1.0200	0.2656	0.6988	0.075*
C15	0.9378 (4)	0.3948 (3)	0.7654 (4)	0.0680 (9)
H15	0.8888	0.3442	0.7977	0.082*
C16	0.9322 (4)	0.5181 (3)	0.7755 (3)	0.0606 (8)
H16	0.8783	0.5491	0.8150	0.073*
C17	0.6685 (3)	0.7186 (3)	0.5137 (3)	0.0499 (7)
C18	0.5894 (3)	0.6933 (2)	0.3769 (2)	0.0403 (6)
C19	0.4792 (3)	0.5955 (3)	0.3277 (3)	0.0539 (7)
H19	0.4518	0.5534	0.3799	0.065*
C20	0.4097 (3)	0.5596 (3)	0.2034 (3)	0.0586 (8)
H20	0.3366	0.4936	0.1711	0.070*
C21	0.4512 (3)	0.6235 (3)	0.1282 (3)	0.0496 (7)
C22	0.5606 (3)	0.7203 (2)	0.1733 (2)	0.0431 (6)
H22	0.5887	0.7600	0.1200	0.052*
C23	0.6285 (2)	0.7579 (2)	0.2984 (2)	0.0371 (5)
C24	0.7389 (3)	0.8724 (2)	0.3428 (3)	0.0442 (6)
Zn1	0.97417 (3)	0.78410 (2)	0.71551 (3)	0.03624 (12)
N1	0.3763 (3)	0.5867 (3)	−0.0053 (3)	0.0720 (8)
N2	0.7314 (3)	0.7660 (2)	0.8127 (2)	0.0519 (6)
H2A	0.6641	0.7428	0.7420	0.062*
N3	0.8669 (3)	0.7961 (2)	0.8318 (2)	0.0452 (5)
N4	1.1400 (3)	0.8564 (2)	0.9082 (2)	0.0477 (6)
N5	1.2091 (2)	0.8153 (2)	0.5964 (2)	0.0442 (5)
H5A	1.2100	0.8911	0.5895	0.053*
N6	1.1256 (2)	0.75232 (18)	0.63868 (19)	0.0374 (5)
N7	1.0006 (2)	0.59453 (19)	0.7312 (2)	0.0423 (5)
O1	0.95913 (19)	0.95872 (16)	0.67148 (17)	0.0420 (4)
O2	0.5984 (3)	0.7250 (6)	0.5755 (3)	0.165 (2)
O3	0.79649 (18)	0.72281 (17)	0.55259 (17)	0.0433 (4)
O4	0.7478 (3)	0.94256 (18)	0.43546 (19)	0.0594 (6)
O5	0.8072 (3)	0.8910 (2)	0.2798 (3)	0.0751 (7)
O6	0.4156 (3)	0.6389 (3)	−0.0729 (2)	0.0957 (10)
O7	0.2773 (4)	0.5050 (4)	−0.0427 (3)	0.1448 (18)
O1W	0.5000	0.0000	0.5000	0.198 (4)
H1W	0.901 (2)	0.943 (3)	0.6007 (10)	0.080*

H2W	1.031 (2)	1.004 (3)	0.681 (3)	0.080*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.086 (3)	0.066 (2)	0.074 (2)	0.0190 (18)	0.061 (2)	0.0210 (17)
C2	0.092 (3)	0.0636 (19)	0.0523 (18)	0.0227 (18)	0.0484 (19)	0.0194 (15)
C3	0.0754 (19)	0.0368 (13)	0.0434 (15)	0.0165 (13)	0.0361 (14)	0.0114 (11)
C4	0.0715 (19)	0.0345 (13)	0.0434 (15)	0.0159 (13)	0.0270 (14)	0.0103 (11)
C5	0.091 (3)	0.0509 (17)	0.0440 (16)	0.0205 (17)	0.0269 (17)	0.0116 (13)
C6	0.088 (3)	0.062 (2)	0.0500 (19)	0.0151 (18)	0.0103 (18)	0.0082 (15)
C7	0.066 (2)	0.065 (2)	0.069 (2)	0.0092 (17)	0.0149 (18)	0.0103 (17)
C8	0.0617 (19)	0.0566 (18)	0.0591 (19)	0.0092 (15)	0.0251 (16)	0.0092 (15)
C9	0.0543 (18)	0.072 (2)	0.075 (2)	0.0182 (15)	0.0457 (17)	0.0238 (17)
C10	0.0617 (18)	0.0580 (18)	0.075 (2)	0.0287 (15)	0.0436 (17)	0.0208 (16)
C11	0.0386 (13)	0.0403 (13)	0.0372 (13)	0.0119 (10)	0.0157 (11)	0.0063 (10)
C12	0.0373 (12)	0.0372 (12)	0.0346 (12)	0.0100 (10)	0.0112 (10)	0.0072 (10)
C13	0.0568 (16)	0.0407 (14)	0.0500 (16)	0.0176 (13)	0.0181 (13)	0.0071 (12)
C14	0.073 (2)	0.0354 (14)	0.074 (2)	0.0138 (14)	0.0228 (18)	0.0132 (14)
C15	0.078 (2)	0.0462 (17)	0.097 (3)	0.0088 (16)	0.049 (2)	0.0330 (17)
C16	0.067 (2)	0.0456 (16)	0.090 (2)	0.0122 (14)	0.0504 (19)	0.0229 (16)
C17	0.0393 (15)	0.0692 (19)	0.0479 (15)	0.0069 (13)	0.0247 (13)	0.0119 (14)
C18	0.0305 (12)	0.0452 (14)	0.0499 (15)	0.0083 (10)	0.0196 (11)	0.0111 (11)
C19	0.0434 (15)	0.0562 (17)	0.0664 (19)	−0.0021 (13)	0.0262 (14)	0.0210 (15)
C20	0.0389 (15)	0.0493 (16)	0.077 (2)	−0.0103 (12)	0.0170 (15)	0.0051 (15)
C21	0.0367 (13)	0.0525 (16)	0.0486 (16)	0.0028 (12)	0.0087 (12)	−0.0012 (13)
C22	0.0384 (13)	0.0467 (14)	0.0441 (14)	0.0028 (11)	0.0165 (12)	0.0102 (12)
C23	0.0314 (12)	0.0347 (12)	0.0455 (14)	0.0047 (10)	0.0160 (11)	0.0061 (10)
C24	0.0407 (14)	0.0352 (13)	0.0491 (15)	0.0008 (11)	0.0104 (12)	0.0079 (12)
Zn1	0.04219 (19)	0.03371 (17)	0.04103 (19)	0.00763 (12)	0.02487 (14)	0.00712 (12)
N1	0.0539 (16)	0.077 (2)	0.0604 (18)	−0.0016 (15)	0.0026 (14)	−0.0046 (15)
N2	0.0599 (15)	0.0532 (14)	0.0574 (15)	0.0075 (12)	0.0395 (13)	0.0110 (11)
N3	0.0587 (14)	0.0411 (12)	0.0493 (13)	0.0113 (10)	0.0346 (11)	0.0102 (10)
N4	0.0606 (15)	0.0407 (12)	0.0460 (13)	0.0110 (11)	0.0254 (11)	0.0056 (10)
N5	0.0450 (12)	0.0422 (12)	0.0544 (13)	0.0050 (10)	0.0288 (11)	0.0124 (10)
N6	0.0392 (11)	0.0351 (10)	0.0414 (11)	0.0058 (9)	0.0202 (9)	0.0059 (9)
N7	0.0463 (12)	0.0344 (11)	0.0526 (13)	0.0084 (9)	0.0252 (11)	0.0104 (9)
O1	0.0434 (10)	0.0361 (9)	0.0475 (10)	0.0010 (7)	0.0204 (8)	0.0079 (8)
O2	0.0457 (15)	0.393 (7)	0.0555 (17)	0.021 (3)	0.0304 (13)	0.017 (3)
O3	0.0376 (10)	0.0464 (10)	0.0458 (10)	0.0068 (8)	0.0176 (8)	0.0030 (8)
O4	0.0814 (15)	0.0387 (10)	0.0495 (12)	−0.0046 (10)	0.0213 (11)	0.0036 (9)
O5	0.0723 (15)	0.0643 (14)	0.0923 (18)	−0.0264 (12)	0.0529 (15)	−0.0085 (13)
O6	0.0778 (18)	0.140 (3)	0.0511 (14)	−0.0108 (18)	0.0169 (14)	0.0024 (16)
O7	0.124 (3)	0.145 (3)	0.082 (2)	−0.076 (3)	−0.021 (2)	0.003 (2)
O1W	0.196 (7)	0.229 (8)	0.280 (10)	0.104 (7)	0.185 (8)	0.091 (8)

Geometric parameters (Å, º)

C1—N2	1.343 (4)	C16—N7	1.333 (4)
C1—C2	1.357 (5)	C16—H16	0.9300
C1—H1	0.9300	C17—O2	1.221 (4)
C2—C3	1.396 (4)	C17—O3	1.231 (3)
C2—H2	0.9300	C17—C18	1.506 (4)
C3—N3	1.334 (4)	C18—C19	1.390 (4)
C3—C4	1.460 (4)	C18—C23	1.396 (4)
C4—N4	1.352 (4)	C19—C20	1.374 (5)
C4—C5	1.390 (4)	C19—H19	0.9300
C5—C6	1.369 (5)	C20—C21	1.371 (5)
C5—H5	0.9300	C20—H20	0.9300
C6—C7	1.390 (6)	C21—C22	1.376 (4)
C6—H6	0.9300	C21—N1	1.474 (4)
C7—C8	1.382 (5)	C22—C23	1.383 (4)
C7—H7	0.9300	C22—H22	0.9300
C8—N4	1.330 (4)	C23—C24	1.518 (3)
C8—H8	0.9300	C24—O5	1.235 (4)
C9—N5	1.341 (4)	C24—O4	1.250 (4)
C9—C10	1.363 (5)	Zn1—O1	2.0871 (18)
C9—H9	0.9300	Zn1—N3	2.089 (2)
C10—C11	1.393 (4)	Zn1—O3	2.0981 (18)
C10—H10	0.9300	Zn1—N6	2.147 (2)
C11—N6	1.336 (3)	Zn1—N7	2.188 (2)
C11—C12	1.460 (4)	Zn1—N4	2.287 (2)
C12—N7	1.342 (3)	N1—O7	1.204 (4)
C12—C13	1.391 (4)	N1—O6	1.211 (4)
C13—C14	1.371 (5)	N2—N3	1.341 (3)
C13—H13	0.9300	N2—H2A	0.8600
C14—C15	1.359 (5)	N5—N6	1.337 (3)
C14—H14	0.9300	N5—H5A	0.8600
C15—C16	1.379 (4)	O1—H1W	0.820 (13)
C15—H15	0.9300	O1—H2W	0.82 (3)
N2—C1—C2	108.1 (3)	C18—C19—H19	119.3
N2—C1—H1	126.0	C21—C20—C19	118.3 (3)
C2—C1—H1	126.0	C21—C20—H20	120.9
C1—C2—C3	105.1 (3)	C19—C20—H20	120.9
C1—C2—H2	127.4	C20—C21—C22	122.1 (3)
C3—C2—H2	127.4	C20—C21—N1	118.7 (3)
N3—C3—C2	109.9 (3)	C22—C21—N1	119.2 (3)
N3—C3—C4	116.7 (2)	C21—C22—C23	119.5 (3)
C2—C3—C4	133.4 (3)	C21—C22—H22	120.2
N4—C4—C5	122.4 (3)	C23—C22—H22	120.2
N4—C4—C3	114.5 (2)	C22—C23—C18	119.3 (2)
C5—C4—C3	123.1 (3)	C22—C23—C24	117.3 (2)
C6—C5—C4	118.8 (3)	C18—C23—C24	123.3 (2)

C6—C5—H5	120.6	O5—C24—O4	125.7 (3)
C4—C5—H5	120.6	O5—C24—C23	116.6 (2)
C5—C6—C7	119.3 (3)	O4—C24—C23	117.6 (3)
C5—C6—H6	120.4	O1—Zn1—N3	96.46 (8)
C7—C6—H6	120.4	O1—Zn1—O3	86.38 (7)
C8—C7—C6	118.5 (4)	N3—Zn1—O3	96.57 (9)
C8—C7—H7	120.8	O1—Zn1—N6	94.67 (8)
C6—C7—H7	120.8	N3—Zn1—N6	163.63 (9)
N4—C8—C7	123.2 (3)	O3—Zn1—N6	96.08 (7)
N4—C8—H8	118.4	O1—Zn1—N7	168.95 (8)
C7—C8—H8	118.4	N3—Zn1—N7	94.18 (9)
N5—C9—C10	107.6 (3)	O3—Zn1—N7	89.49 (8)
N5—C9—H9	126.2	N6—Zn1—N7	75.57 (8)
C10—C9—H9	126.2	O1—Zn1—N4	93.00 (8)
C9—C10—C11	105.1 (3)	N3—Zn1—N4	73.48 (9)
C9—C10—H10	127.5	O3—Zn1—N4	169.91 (8)
C11—C10—H10	127.5	N6—Zn1—N4	94.01 (8)
N6—C11—C10	110.3 (2)	N7—Zn1—N4	92.85 (8)
N6—C11—C12	118.0 (2)	O7—N1—O6	122.6 (3)
C10—C11—C12	131.8 (2)	O7—N1—C21	118.0 (4)
N7—C12—C13	121.8 (3)	O6—N1—C21	119.4 (3)
N7—C12—C11	114.8 (2)	N3—N2—C1	110.5 (3)
C13—C12—C11	123.4 (2)	N3—N2—H2A	124.7
C14—C13—C12	118.9 (3)	C1—N2—H2A	124.7
C14—C13—H13	120.6	C3—N3—N2	106.3 (2)
C12—C13—H13	120.6	C3—N3—Zn1	120.6 (2)
C15—C14—C13	119.5 (3)	N2—N3—Zn1	132.65 (19)
C15—C14—H14	120.3	C8—N4—C4	117.9 (3)
C13—C14—H14	120.3	C8—N4—Zn1	127.8 (2)
C14—C15—C16	119.0 (3)	C4—N4—Zn1	114.3 (2)
C14—C15—H15	120.5	N6—N5—C9	111.4 (2)
C16—C15—H15	120.5	N6—N5—H5A	124.3
N7—C16—C15	122.8 (3)	C9—N5—H5A	124.3
N7—C16—H16	118.6	C11—N6—N5	105.7 (2)
C15—C16—H16	118.6	C11—N6—Zn1	115.52 (17)
O2—C17—O3	126.1 (3)	N5—N6—Zn1	138.68 (16)
O2—C17—C18	116.8 (3)	C16—N7—C12	118.1 (2)
O3—C17—C18	117.0 (2)	C16—N7—Zn1	126.03 (19)
C19—C18—C23	119.3 (3)	C12—N7—Zn1	115.32 (17)
C19—C18—C17	117.7 (3)	Zn1—O1—H1W	101 (3)
C23—C18—C17	122.8 (2)	Zn1—O1—H2W	119 (3)
C20—C19—C18	121.4 (3)	H1W—O1—H2W	114 (3)
C20—C19—H19	119.3	C17—O3—Zn1	139.12 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H2*W*···O5^{i}	0.82 (3)	1.81 (3)	2.627 (3)	174 (3)

N5—H5*A*···O4^{i}	0.86	1.95	2.788 (3)	166
N2—H2*A*···O2	0.86	1.82	2.606 (4)	150

Symmetry code: (i) −*x*+2, −*y*+2, −*z*+1.