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Bis(2-amino-6-methylpyridinium) tris(pyridine-2,6-dicarboxylato)-zirconate(IV) dihydrate

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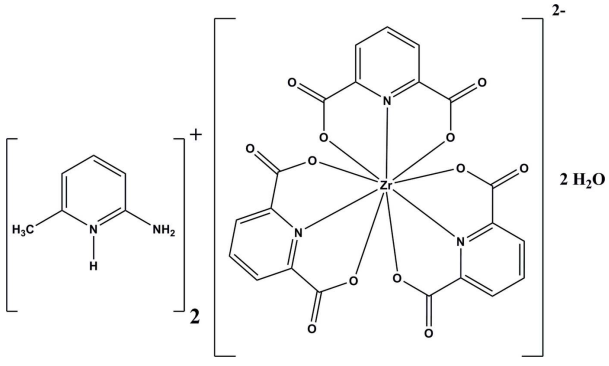
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.002 Å; R factor = 0.023; wR factor = 0.060; data-to-parameter ratio = 17.4.

In the title compound, $(C_6H_9N_2)_2[Zr(C_7H_3NO_4)_3]\cdot 2H_2O$, the Zr^{IV} atom is nine-coordinated by three pyridine-2,6-dicarboxylate ligands in a distorted tricapped trigonal–prismatic ZrN_3O_6 environment. The crystal packing is stabilized by intermolecular N—H···O and O—H···O hydrogen bonds.

Related literature

For background to proton-transfer compounds, see: Aghabozorg *et al.* (2008). For related structures, see: Aghabozorg *et al.* (2005); Daneshvar *et al.* (2008); Willey *et al.* (1998); Pasdar *et al.* (2010, 2011).



Experimental

Crystal data

$(C_6H_9N_2)_2[Zr(C_7H_3NO_4)_3]\cdot 2H_2O$
M_r = 840.87
Monoclinic, $C2/c$
a = 18.719 (4) Å
b = 10.536 (2) Å
c = 18.781 (4) Å
β = 108.58 (3)°
V = 3511.0 (14) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.39 mm^{-1}
T = 298 K
0.35 × 0.30 × 0.25 mm

Data collection

Stoe IPDS II diffractometer
Absorption correction: numerical [shape of crystal determined optically (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2005)]
T_{min} = 0.870, T_{max} = 0.903
12273 measured reflections
4705 independent reflections
4284 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.060
S = 1.03
4705 reflections
271 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7B···O3	0.87 (4)	2.09 (4)	2.938 (2)	164 (3)
O7—H7A···O6^{i}	0.82 (3)	2.14 (3)	2.9568 (19)	173 (3)
N4—H4B···O1^{ii}	0.86 (2)	2.57 (2)	3.1755 (18)	127.6 (17)
N4—H4B···O7	0.86 (2)	2.28 (2)	3.027 (3)	144.1 (18)
N4—H4A···O4^{iii}	0.82 (2)	2.05 (2)	2.861 (2)	168 (2)
N3—H3A···O2^{ii}	0.91 (2)	1.91 (2)	2.8194 (18)	175.1 (18)

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

Data collection: *X-AREA* (Stoe & Cie, 2005); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5467).

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supporting information

Acta Cryst. (2011). E**67**, m294 [doi:10.1107/S1600536811003072]

Bis(2-amino-6-methylpyridinium) tris(pyridine-2,6-dicarboxylato)zirconate(IV) dihydrate

Hoda Pasdar, Ali Ebdam, Hossein Aghabozorg and Behrouz Notash

S1. Comment

Pyridine-2,6-dicarboxylic acid ($pydcH_2$) was commonly used as an acid in proton transfer systems (Aghabozorg *et al.*, 2008). Continuing the path to synthesize proton transfer compounds, our group has focused on forming ion pairs between 2,6-$pydcH_2$ and various organic bases (Pasdar *et al.*, 2010; Pasdar *et al.*, 2011). The structures of two proton transfer compounds containing $[Zr^{IV}(2,6\text{-}pydc)_3]^{2-}$ moiety were reported with the counter cationic part of 2,6-pyridinediamine (Aghabozorg *et al.*, 2005) and 2,4,6-triamino-1,3,5-triazine (Daneshvar *et al.*, 2008), respectively. The structure of $K_4[Zr^{IV}(2,6\text{-}pydc)_3]_2$ has been reported by Willey *et al.* (1998).

We report herein the synthesis and crystal structure of $(2a6mpH)_2[Zr(2,6\text{-}pydc)_3].2H_2O$ by the reaction of $ZrCl_4$, 2-amino-6-methylpyridine and 2,6-pyridinedicarboxylic acid in aqueous media. The molecular structure of the title compound is shown in Fig.1. The zirconium(IV) ion is coordinated by three $pydc^{2-}$ ligands in a distorted tricapped trigonal prismatic geometry. The geometry around the zirconium(IV) centre in the title compound is shown in Fig. 2. The Zr—N and Zr—O bond lengths and angles are comprable with those previously reported (Aghabozorg *et al.*, 2005; Daneshvar *et al.*, 2008). The crystal packing diagram of $(2a6mpH)_2[Zr(2,6\text{-}pydc)_3].2H_2O$ is presented in Fig. 3. There are several intermolecular N—H···O, O—H···O hydrogen bonds which stabilize crystal structure of the compound (Table 1 and Fig. 3).

S2. Experimental

A solution of $ZrCl_4$ (0.114 mg,0.5 mmol) in water (15 ml) was added to an aqueous solution of 2-amino-6-methylpyridine (0.114,1 mmol) and 2,6-pyridinedicarboxylic acid (0.504 mg, 3 mmol) in water (15 ml). Crystals of the title compound suitable for X-ray characterization were obtained after a few weeks at room temperature (m.p: 145 °C).

S3. Refinement

The hydrogen atoms bonded to N and O were found in difference Fourier map and refined isotropically without restraint. The C—H protons were positioned geometrically and refined as riding atoms with C—H = 0.93 Å and *U*iso(H) = 1.2 *U*eq(C) for aromatic C—H and C—H = 0.96 Å and *U*iso(H) = 1.5 *Ueq*(C) for methyl groups.

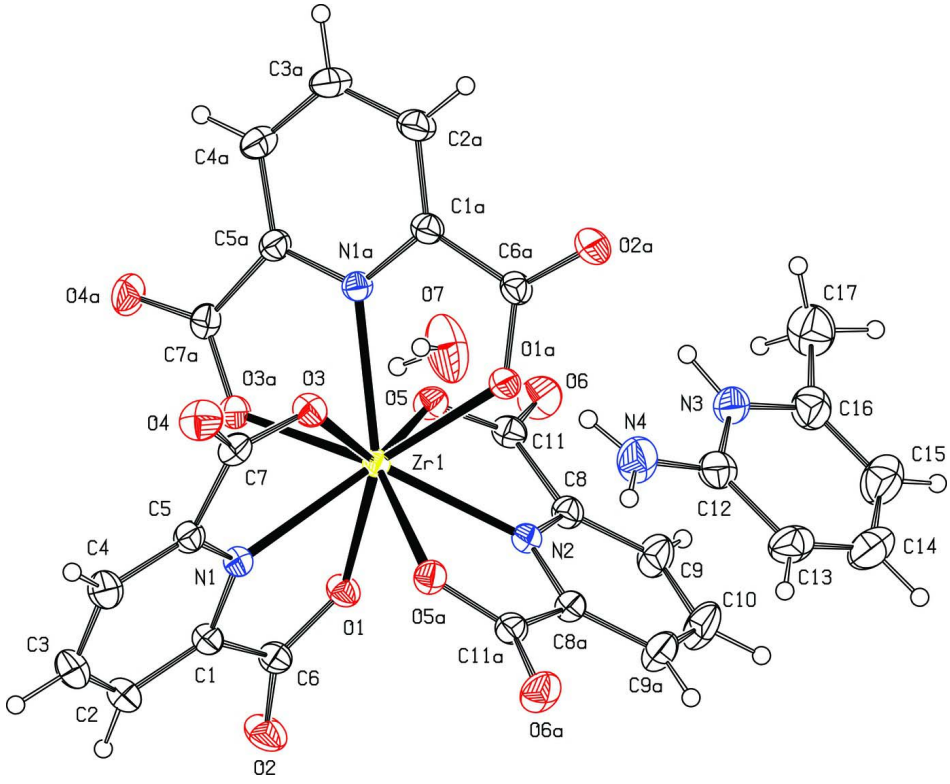

Figure 1

The molecular structure of $(2a6mpH)_2[Zr(2,6\text{-}pydc)_3].2H_2O$ with displacement ellipsoids drawn at 30% probability level.Symmetry code: (*a*) -*x* + 1, *y*, -*z* + 3/2.

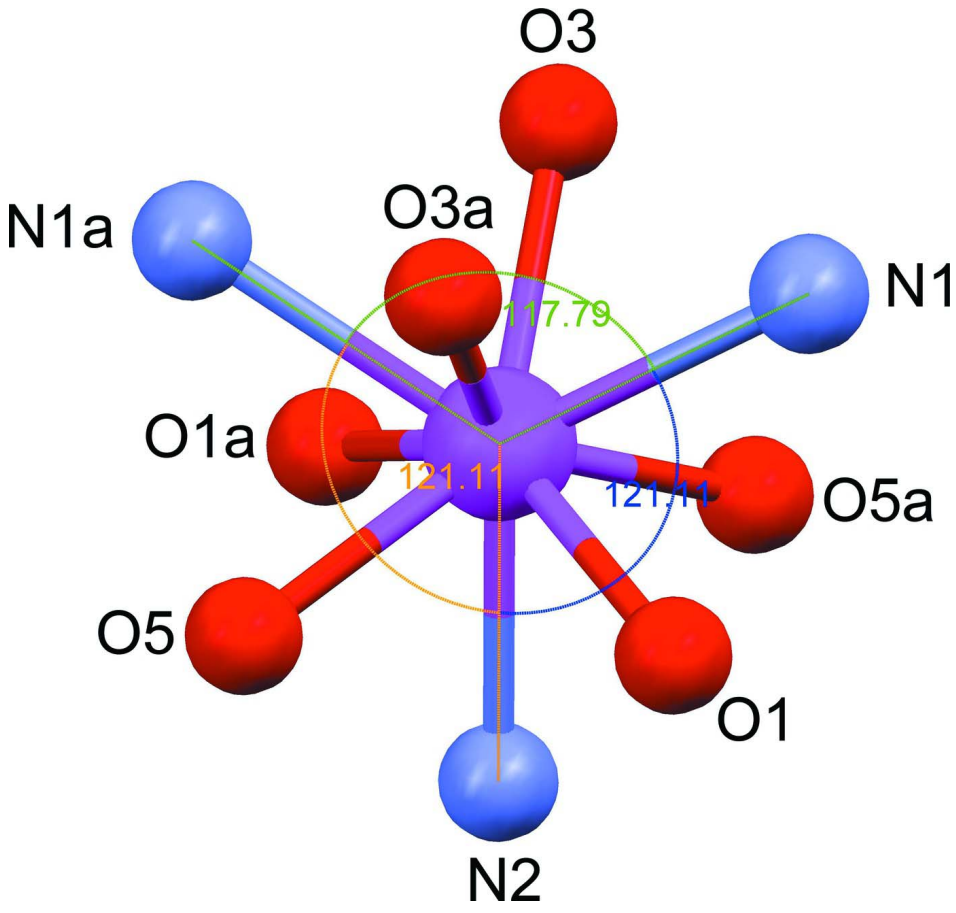

Figure 2

The coordination environment around Zr^{IV} ion in the title compound. Symmetry code: (*a*) -*x* + 1, *y*, -*z* + 3/2.

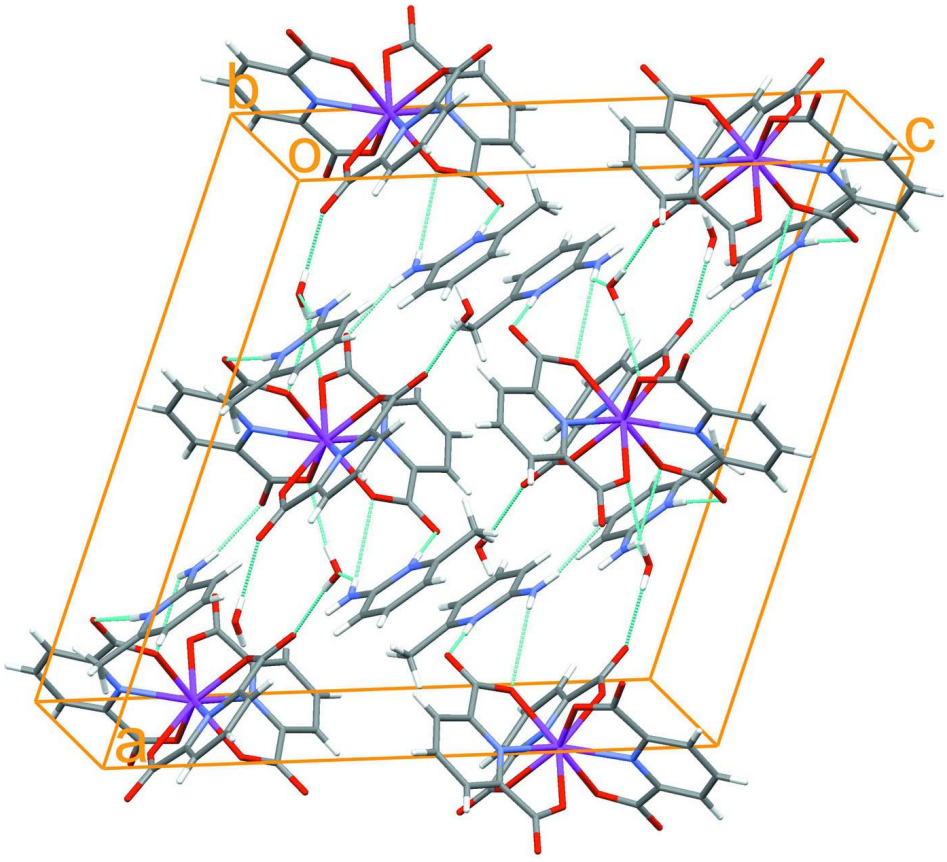

Figure 3

The packing diagram of $(2a6mpH)_2[Zr(2,6\text{-}pydc)_3].2H_2O$. The intermolecular N—H···O, O—H···O hydrogen bonds are shown as blue dashed lines.

Bis(2-amino-6-methylpyridinium) tris(pyridine-2,6-dicarboxylato)zirconate(IV) dihydrate

Crystal data

$(C_6H_9N_2)_2[Zr(C_7H_3NO_4)_3]\cdot 2H_2O$
$M_r = 840.87$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 18.719\ (4)$ Å
$b = 10.536\ (2)$ Å
$c = 18.781\ (4)$ Å
$\beta = 108.58\ (3)°$
$V = 3511.0\ (14)$ Å^3
$Z = 4$
$F(000) = 1720$
$D_x = 1.591$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4705 reflections
$\theta = 2.3–29.2°$
$\mu = 0.39$ mm^{-1}
$T = 298$ K
Prism, colorless
0.35 × 0.3 × 0.25 mm

Data collection

Stoe IPDS II diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 0.15 mm pixels mm^{-1}
rotation method scans
Absorption correction: numerical [shape of crystal determined optically (*X-SHAPE* and *X-RED32*; Stoe& Cie, 2005)]
$T_{min} = 0.870$, $T_{max} = 0.903$
12273 measured reflections
4705 independent reflections
4284 reflections with $I > 2\sigma(I)$

R_{int} = 0.025
θ_{max} = 29.2°, θ_{min} = 2.3°
h = −25→25
k = −12→14
l = −25→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.060
S = 1.03
4705 reflections
271 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
$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 1.0948P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 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}
C17	0.61732 (13)	0.9817 (2)	0.98635 (13)	0.0731 (5)
H17A	0.6130	1.0629	1.0079	0.110*
H17B	0.6397	0.9220	1.0258	0.110*
H17C	0.5681	0.9524	0.9571	0.110*
Zr1	0.5000	0.572850 (14)	0.7500	0.02355 (5)
N1	0.48851 (5)	0.45657 (9)	0.63879 (6)	0.02849 (19)
C5	0.53457 (7)	0.35957 (11)	0.64083 (7)	0.0320 (2)
C1	0.43464 (7)	0.48587 (12)	0.57517 (7)	0.0322 (2)
C2	0.42369 (9)	0.41586 (14)	0.51009 (8)	0.0426 (3)
H2	0.3856	0.4369	0.4661	0.051*
C4	0.52766 (9)	0.28548 (14)	0.57799 (8)	0.0449 (3)
H4	0.5604	0.2182	0.5800	0.054*
C3	0.47076 (10)	0.31419 (15)	0.51223 (9)	0.0502 (4)
H3	0.4643	0.2650	0.4695	0.060*
N3	0.68745 (7)	0.88262 (13)	0.91339 (7)	0.0443 (3)
N4	0.74780 (9)	0.76062 (17)	0.84880 (10)	0.0600 (4)
C12	0.73020 (8)	0.87419 (17)	0.86785 (9)	0.0468 (3)
C16	0.66558 (9)	0.99384 (17)	0.93708 (10)	0.0539 (4)
C13	0.75373 (9)	0.98893 (19)	0.84391 (10)	0.0580 (4)
H13	0.7833	0.9879	0.8124	0.070*
C15	0.68835 (12)	1.10440 (19)	0.91395 (13)	0.0694 (5)

H15	0.6743	1.1819	0.9292	0.083*
C14	0.73318 (11)	1.10031 (19)	0.86693 (12)	0.0675 (5)
H14	0.7491	1.1759	0.8513	0.081*
O1	0.40841 (5)	0.64343 (9)	0.65095 (5)	0.03362 (18)
O2	0.34539 (6)	0.65095 (11)	0.52861 (6)	0.0505 (3)
C6	0.39137 (7)	0.60152 (12)	0.58346 (7)	0.0333 (2)
N2	0.5000	0.79516 (13)	0.7500	0.0288 (3)
O5	0.42116 (5)	0.65285 (9)	0.80434 (5)	0.03414 (18)
C8	0.45374 (7)	0.85771 (12)	0.77872 (7)	0.0326 (2)
C11	0.40782 (7)	0.77095 (12)	0.81082 (7)	0.0332 (2)
O6	0.36459 (7)	0.81504 (11)	0.84149 (7)	0.0520 (3)
C9	0.45124 (9)	0.98904 (14)	0.77885 (10)	0.0483 (3)
H9	0.4178	1.0321	0.7977	0.058*
C10	0.5000	1.0542 (2)	0.7500	0.0603 (7)
H10	0.5000	1.1425	0.7500	0.072*
O4	0.64121 (6)	0.25978 (10)	0.72642 (6)	0.0482 (2)
C7	0.59251 (7)	0.34202 (12)	0.71639 (7)	0.0324 (2)
O3	0.58564 (5)	0.41882 (9)	0.76672 (5)	0.03380 (18)
O7	0.74136 (9)	0.47442 (18)	0.85925 (12)	0.0865 (6)
H3A	0.6742 (11)	0.810 (2)	0.9320 (12)	0.064 (6)*
H4B	0.7294 (12)	0.690 (2)	0.8587 (12)	0.066 (6)*
H4A	0.7747 (12)	0.755 (2)	0.8218 (12)	0.068 (6)*
H7A	0.7728 (18)	0.425 (3)	0.8528 (17)	0.105 (10)*
H7B	0.6993 (19)	0.445 (3)	0.8293 (19)	0.121 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C17	0.0748 (13)	0.0714 (13)	0.0801 (14)	0.0028 (11)	0.0344 (11)	−0.0088 (11)
Zr1	0.02282 (7)	0.02414 (7)	0.02305 (8)	0.000	0.00640 (5)	0.000
N1	0.0303 (4)	0.0279 (4)	0.0274 (5)	−0.0010 (3)	0.0094 (4)	−0.0011 (4)
C5	0.0370 (6)	0.0285 (5)	0.0338 (6)	0.0001 (4)	0.0158 (5)	−0.0007 (5)
C1	0.0338 (5)	0.0335 (6)	0.0279 (6)	−0.0029 (5)	0.0080 (4)	−0.0008 (5)
C2	0.0499 (7)	0.0455 (7)	0.0289 (6)	−0.0053 (6)	0.0077 (5)	−0.0046 (6)
C4	0.0597 (8)	0.0364 (7)	0.0426 (7)	0.0051 (6)	0.0222 (7)	−0.0067 (6)
C3	0.0703 (10)	0.0455 (8)	0.0366 (7)	−0.0022 (7)	0.0196 (7)	−0.0127 (6)
N3	0.0399 (6)	0.0458 (6)	0.0432 (7)	−0.0095 (5)	0.0077 (5)	0.0018 (5)
N4	0.0627 (9)	0.0603 (9)	0.0665 (10)	−0.0172 (7)	0.0342 (8)	−0.0101 (8)
C12	0.0372 (6)	0.0571 (9)	0.0406 (7)	−0.0126 (6)	0.0048 (6)	0.0019 (7)
C16	0.0480 (8)	0.0519 (9)	0.0550 (9)	−0.0017 (7)	0.0069 (7)	−0.0012 (8)
C13	0.0472 (8)	0.0668 (11)	0.0538 (10)	−0.0144 (8)	0.0073 (7)	0.0165 (8)
C15	0.0661 (11)	0.0478 (9)	0.0845 (14)	0.0016 (8)	0.0102 (10)	0.0063 (9)
C14	0.0571 (10)	0.0577 (11)	0.0746 (13)	−0.0119 (8)	0.0026 (9)	0.0254 (9)
O1	0.0330 (4)	0.0357 (4)	0.0283 (4)	0.0059 (3)	0.0044 (3)	−0.0009 (3)
O2	0.0530 (6)	0.0550 (6)	0.0322 (5)	0.0155 (5)	−0.0024 (4)	0.0022 (5)
C6	0.0307 (5)	0.0356 (6)	0.0296 (6)	0.0004 (4)	0.0041 (4)	0.0018 (5)
N2	0.0306 (6)	0.0285 (6)	0.0260 (6)	0.000	0.0072 (5)	0.000
O5	0.0361 (4)	0.0330 (4)	0.0374 (5)	0.0024 (3)	0.0174 (4)	0.0019 (4)

C8	0.0353 (6)	0.0304 (6)	0.0308 (6)	0.0035 (5)	0.0089 (5)	−0.0012 (5)
C11	0.0331 (5)	0.0368 (6)	0.0306 (6)	0.0051 (5)	0.0112 (5)	0.0002 (5)
O6	0.0572 (6)	0.0494 (6)	0.0625 (7)	0.0113 (5)	0.0375 (6)	−0.0011 (5)
C9	0.0575 (8)	0.0322 (6)	0.0612 (10)	0.0056 (6)	0.0273 (8)	−0.0039 (6)
C10	0.0776 (16)	0.0267 (9)	0.0865 (19)	0.000	0.0399 (15)	0.000
O4	0.0482 (5)	0.0431 (5)	0.0556 (6)	0.0190 (4)	0.0197 (5)	0.0058 (5)
C7	0.0320 (5)	0.0292 (5)	0.0389 (6)	0.0022 (4)	0.0154 (5)	0.0037 (5)
O3	0.0314 (4)	0.0355 (4)	0.0324 (4)	0.0060 (3)	0.0072 (3)	0.0000 (4)
O7	0.0527 (8)	0.0816 (11)	0.1081 (13)	0.0094 (8)	0.0016 (8)	−0.0399 (10)

Geometric parameters (Å, º)

C17—C16	1.491 (3)	N4—C12	1.320 (2)
C17—H17A	0.9600	N4—H4B	0.86 (2)
C17—H17B	0.9600	N4—H4A	0.82 (2)
C17—H17C	0.9600	C12—C13	1.409 (2)
Zr1—O5	2.2113 (9)	C16—C15	1.358 (3)
Zr1—O5^{i}	2.2113 (9)	C13—C14	1.348 (3)
Zr1—O1^{i}	2.2183 (11)	C13—H13	0.9300
Zr1—O1	2.2183 (11)	C15—C14	1.399 (3)
Zr1—O3^{i}	2.2320 (9)	C15—H15	0.9300
Zr1—O3	2.2320 (9)	C14—H14	0.9300
Zr1—N2	2.3422 (15)	O1—C6	1.2828 (15)
Zr1—N1	2.3713 (10)	O2—C6	1.2280 (16)
Zr1—N1^{i}	2.3713 (11)	N2—C8	1.3314 (14)
N1—C5	1.3297 (15)	N2—C8^{i}	1.3314 (14)
N1—C1	1.3313 (16)	O5—C11	1.2824 (16)
C5—C4	1.3863 (18)	C8—C9	1.3845 (19)
C5—C7	1.4979 (19)	C8—C11	1.5062 (18)
C1—C2	1.3857 (18)	C11—O6	1.2246 (15)
C1—C6	1.4986 (18)	C9—C10	1.3834 (19)
C2—C3	1.379 (2)	C9—H9	0.9300
C2—H2	0.9300	C10—C9^{i}	1.3834 (19)
C4—C3	1.383 (2)	C10—H10	0.9300
C4—H4	0.9300	O4—C7	1.2279 (15)
C3—H3	0.9300	C7—O3	1.2814 (15)
N3—C12	1.348 (2)	O7—H7A	0.82 (3)
N3—C16	1.362 (2)	O7—H7B	0.87 (4)
N3—H3A	0.91 (2)		
C16—C17—H17A	109.5	C1—C2—H2	120.9
C16—C17—H17B	109.5	C3—C4—C5	118.26 (13)
H17A—C17—H17B	109.5	C3—C4—H4	120.9
C16—C17—H17C	109.5	C5—C4—H4	120.9
H17A—C17—H17C	109.5	C2—C3—C4	119.92 (13)
H17B—C17—H17C	109.5	C2—C3—H3	120.0
O5—Zr1—O5^{i}	135.19 (5)	C4—C3—H3	120.0
O5—Zr1—O1^{i}	86.35 (4)	C12—N3—C16	124.41 (15)

O5^{i}—Zr1—O1^{i}	78.94 (4)	C12—N3—H3A	118.6 (13)
O5—Zr1—O1	78.94 (4)	C16—N3—H3A	116.9 (13)
O5^{i}—Zr1—O1	86.35 (4)	C12—N4—H4B	124.6 (14)
O1^{i}—Zr1—O1	140.83 (5)	C12—N4—H4A	118.8 (16)
O5—Zr1—O3^{i}	77.70 (4)	H4B—N4—H4A	116 (2)
O5^{i}—Zr1—O3^{i}	140.11 (3)	N4—C12—N3	118.80 (15)
O1^{i}—Zr1—O3^{i}	133.65 (3)	N4—C12—C13	124.11 (16)
O1—Zr1—O3^{i}	78.30 (4)	N3—C12—C13	117.09 (17)
O5—Zr1—O3	140.11 (3)	C15—C16—N3	118.41 (18)
O5^{i}—Zr1—O3	77.70 (4)	C15—C16—C17	125.88 (19)
O1^{i}—Zr1—O3	78.30 (4)	N3—C16—C17	115.71 (16)
O1—Zr1—O3	133.65 (3)	C14—C13—C12	119.64 (17)
O3^{i}—Zr1—O3	86.71 (5)	C14—C13—H13	120.2
O5—Zr1—N2	67.59 (2)	C12—C13—H13	120.2
O5^{i}—Zr1—N2	67.59 (2)	C16—C15—C14	119.2 (2)
O1^{i}—Zr1—N2	70.41 (3)	C16—C15—H15	120.4
O1—Zr1—N2	70.41 (3)	C14—C15—H15	120.4
O3^{i}—Zr1—N2	136.64 (2)	C13—C14—C15	121.26 (17)
O3—Zr1—N2	136.64 (2)	C13—C14—H14	119.4
O5—Zr1—N1	135.80 (4)	C15—C14—H14	119.4
O5^{i}—Zr1—N1	71.15 (4)	C6—O1—Zr1	126.56 (8)
O1^{i}—Zr1—N1	137.80 (3)	O2—C6—O1	124.76 (12)
O1—Zr1—N1	66.77 (4)	O2—C6—C1	121.01 (12)
O3^{i}—Zr1—N1	68.96 (4)	O1—C6—C1	114.21 (11)
O3—Zr1—N1	66.91 (4)	C8—N2—C8^{i}	120.65 (15)
N2—Zr1—N1	121.11 (2)	C8—N2—Zr1	119.67 (8)
O5—Zr1—N1^{i}	71.15 (4)	C8^{i}—N2—Zr1	119.67 (8)
O5^{i}—Zr1—N1^{i}	135.80 (4)	C11—O5—Zr1	126.32 (8)
O1^{i}—Zr1—N1^{i}	66.77 (4)	N2—C8—C9	121.48 (12)
O1—Zr1—N1^{i}	137.80 (3)	N2—C8—C11	112.92 (11)
O3^{i}—Zr1—N1^{i}	66.91 (4)	C9—C8—C11	125.59 (11)
O3—Zr1—N1^{i}	68.96 (4)	O6—C11—O5	126.19 (12)
N2—Zr1—N1^{i}	121.11 (3)	O6—C11—C8	120.34 (12)
N1—Zr1—N1^{i}	117.79 (5)	O5—C11—C8	113.43 (10)
C5—N1—C1	120.19 (11)	C10—C9—C8	117.95 (14)
C5—N1—Zr1	119.72 (8)	C10—C9—H9	121.0
C1—N1—Zr1	120.07 (8)	C8—C9—H9	121.0
N1—C5—C4	121.64 (13)	C9—C10—C9^{i}	120.45 (19)
N1—C5—C7	112.91 (10)	C9—C10—H10	119.8
C4—C5—C7	125.46 (12)	C9^{i}—C10—H10	119.8
N1—C1—C2	121.68 (12)	O4—C7—O3	125.20 (13)
N1—C1—C6	112.04 (10)	O4—C7—C5	120.70 (12)
C2—C1—C6	126.27 (12)	O3—C7—C5	114.10 (10)
C3—C2—C1	118.30 (14)	C7—O3—Zr1	126.28 (8)
C3—C2—H2	120.9	H7A—O7—H7B	103 (3)
O5—Zr1—N1—C5	−137.47 (8)	C2—C1—C6—O1	174.88 (12)
O5^{i}—Zr1—N1—C5	86.13 (9)	O5—Zr1—N2—C8	−2.02 (7)

O1^{i}—Zr1—N1—C5	38.83 (11)	O5^{i}—Zr1—N2—C8	177.98 (7)
O1—Zr1—N1—C5	−179.67 (9)	O1^{i}—Zr1—N2—C8	−96.24 (7)
O3^{i}—Zr1—N1—C5	−93.76 (9)	O1—Zr1—N2—C8	83.76 (7)
O3—Zr1—N1—C5	1.82 (8)	O3^{i}—Zr1—N2—C8	37.42 (7)
N2—Zr1—N1—C5	133.57 (8)	O3—Zr1—N2—C8	−142.58 (7)
N1^{i}—Zr1—N1—C5	−46.43 (8)	N1—Zr1—N2—C8	129.04 (7)
O5—Zr1—N1—C1	40.43 (11)	N1^{i}—Zr1—N2—C8	−50.96 (7)
O5^{i}—Zr1—N1—C1	−95.97 (9)	O5—Zr1—N2—C8^{i}	177.98 (7)
O1^{i}—Zr1—N1—C1	−143.27 (8)	O5^{i}—Zr1—N2—C8^{i}	−2.02 (7)
O1—Zr1—N1—C1	−1.77 (8)	O1^{i}—Zr1—N2—C8^{i}	83.76 (7)
O3^{i}—Zr1—N1—C1	84.14 (9)	O1—Zr1—N2—C8^{i}	−96.24 (7)
O3—Zr1—N1—C1	179.72 (10)	O3^{i}—Zr1—N2—C8^{i}	−142.58 (7)
N2—Zr1—N1—C1	−48.53 (9)	O3—Zr1—N2—C8^{i}	37.42 (7)
N1^{i}—Zr1—N1—C1	131.47 (9)	N1—Zr1—N2—C8^{i}	−50.96 (7)
C1—N1—C5—C4	−0.84 (18)	N1^{i}—Zr1—N2—C8^{i}	129.04 (7)
Zr1—N1—C5—C4	177.05 (10)	O5^{i}—Zr1—O5—C11	1.94 (9)
C1—N1—C5—C7	178.88 (10)	O1^{i}—Zr1—O5—C11	72.24 (10)
Zr1—N1—C5—C7	−3.22 (13)	O1—Zr1—O5—C11	−71.27 (10)
C5—N1—C1—C2	1.35 (18)	O3^{i}—Zr1—O5—C11	−151.55 (11)
Zr1—N1—C1—C2	−176.54 (10)	O3—Zr1—O5—C11	139.09 (10)
C5—N1—C1—C6	−177.21 (10)	N2—Zr1—O5—C11	1.94 (9)
Zr1—N1—C1—C6	4.90 (13)	N1—Zr1—O5—C11	−110.25 (10)
N1—C1—C2—C3	−0.5 (2)	N1^{i}—Zr1—O5—C11	138.93 (11)
C6—C1—C2—C3	177.80 (13)	C8^{i}—N2—C8—C9	0.92 (11)
N1—C5—C4—C3	−0.4 (2)	Zr1—N2—C8—C9	−179.08 (11)
C7—C5—C4—C3	179.87 (13)	C8^{i}—N2—C8—C11	−178.02 (11)
C1—C2—C3—C4	−0.8 (2)	Zr1—N2—C8—C11	1.98 (11)
C5—C4—C3—C2	1.2 (2)	Zr1—O5—C11—O6	−179.35 (11)
C16—N3—C12—N4	179.94 (16)	Zr1—O5—C11—C8	−1.59 (15)
C16—N3—C12—C13	0.3 (2)	N2—C8—C11—O6	177.52 (11)
C12—N3—C16—C15	−0.3 (2)	C9—C8—C11—O6	−1.4 (2)
C12—N3—C16—C17	179.07 (16)	N2—C8—C11—O5	−0.38 (15)
N4—C12—C13—C14	−179.53 (18)	C9—C8—C11—O5	−179.28 (14)
N3—C12—C13—C14	0.1 (2)	N2—C8—C9—C10	−1.8 (2)
N3—C16—C15—C14	0.0 (3)	C11—C8—C9—C10	177.02 (11)
C17—C16—C15—C14	−179.37 (19)	C8—C9—C10—C9^{i}	0.86 (10)
C12—C13—C14—C15	−0.4 (3)	N1—C5—C7—O4	−176.83 (11)
C16—C15—C14—C13	0.4 (3)	C4—C5—C7—O4	2.9 (2)
O5—Zr1—O1—C6	−154.09 (10)	N1—C5—C7—O3	3.20 (15)
O5^{i}—Zr1—O1—C6	68.45 (10)	C4—C5—C7—O3	−177.09 (12)
O1^{i}—Zr1—O1—C6	135.95 (10)	O4—C7—O3—Zr1	178.19 (10)
O3^{i}—Zr1—O1—C6	−74.53 (10)	C5—C7—O3—Zr1	−1.84 (14)
O3—Zr1—O1—C6	−0.71 (12)	O5—Zr1—O3—C7	135.01 (9)
N2—Zr1—O1—C6	135.95 (10)	O5^{i}—Zr1—O3—C7	−74.37 (10)
N1—Zr1—O1—C6	−2.60 (9)	O1^{i}—Zr1—O3—C7	−155.43 (10)
N1^{i}—Zr1—O1—C6	−108.97 (10)	O1—Zr1—O3—C7	−1.71 (12)
Zr1—O1—C6—O2	−172.23 (10)	O3^{i}—Zr1—O3—C7	68.68 (9)
Zr1—O1—C6—C1	5.94 (15)	N2—Zr1—O3—C7	−111.32 (9)

N1—C1—C6—O2	171.61 (12)	N1—Zr1—O3—C7	0.18 (9)
C2—C1—C6—O2	−6.9 (2)	N1^{i}—Zr1—O3—C7	135.18 (10)
N1—C1—C6—O1	−6.64 (15)		

Symmetry code: (i) −*x*+1, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7*B*···O3	0.87 (4)	2.09 (4)	2.938 (2)	164 (3)
O7—H7*A*···O6^{ii}	0.82 (3)	2.14 (3)	2.9568 (19)	173 (3)
N4—H4*B*···O1^{i}	0.86 (2)	2.57 (2)	3.1755 (18)	127.6 (17)
N4—H4*B*···O7	0.86 (2)	2.28 (2)	3.027 (3)	144.1 (18)
N4—H4*A*···O4^{iii}	0.82 (2)	2.05 (2)	2.861 (2)	168 (2)
N3—H3*A*···O2^{i}	0.91 (2)	1.91 (2)	2.8194 (18)	175.1 (18)

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