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# Crystal structure of the coordination polymer *catena*-poly[[bis[hydroxy(phenyl)acetato-$\kappa^2O^1,O^2$]-zinc(II)]-$\mu_2$-1,2-bis(pyridin-4-yl)ethane-$\kappa^2N:N'$]

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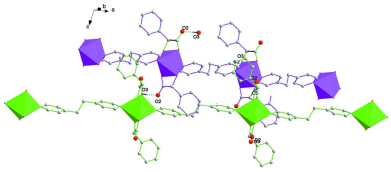
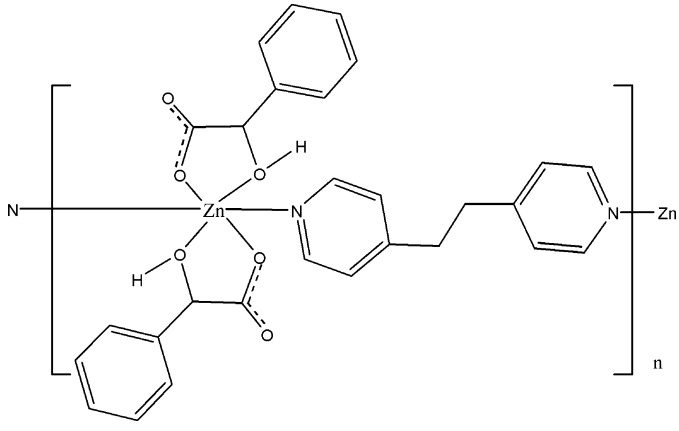
In the title polymeric $Zn^{II}$ compound, $[Zn(C_8H_7O_3)_2(C_{12}H_{12}N_2)]_n$, the Zn cation is coordinated by two N atoms from 1,2-bis(pyridin-4-yl)ethane unit and four O atoms from two mandelate [or hydroxy(phenyl)acetate] anions in a slightly distorted octahedral coordination geometry. The 1,2-bis(pyridin-4-yl)ethane unit bridges two $Zn^{II}$ cations, related by an inversion centre, to form a polymeric chain along [110]. The crystal structure features extensive O—H···O and weak C—H ···O hydrogen bonds, with C—H ··· $\pi$ interactions and $\pi$–$\pi$ interactions also being present. The centroid–centroid distance between the phenyl ring of the mandelate group and the 1,2-bis(pyridine-4-yl)ethane moiety is 4.951 (2) Å. The 1,2-bis(pyridin-4-yl)ethane ligand is disordered over two positions, with a refined occupancy of 0.578 (14) for the major component.

## 1. Chemical context

$\alpha$-Hydroxycarboxylic acids play an important role in many biological processes and in coordination chemistry (Miyamoto *et al.*, 1989). The deprotonated anion of one example, mandelic acid (2-hydroxy-2-phenylacetic acid), can behave as a multifunctional ligand and can act as a bridging ligand in metal complexes by involving the oxygen atoms of the carboxylate and hydroxy groups (Zechel *et al.*, 2019; Smatanová *et al.*, 2000; Bromant *et al.*, 2005). We report the preparation and structural characterization of a new coordination polymer in which the $Zn^{II}$ cations are coordinated to two mandelate anions, behaving as bidentate ligands, and linked together *via* 1,2-bis(4-pyridyl)ethane molecules. 1,2-Bis(4-pyridyl)ethane is a versatile building block for the purposes of crystal engineering as the pyridyl N atoms can connect to adjacent metals to form a chain (Lee & Kim, 2015).



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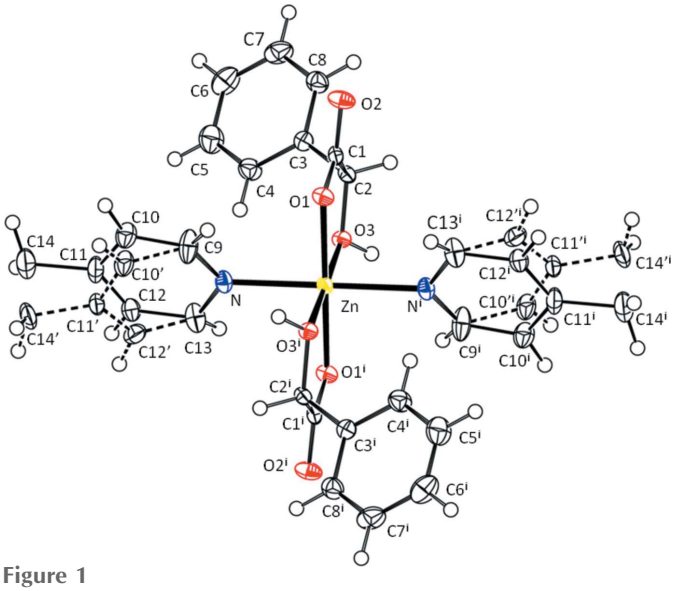


**Figure 1**
View of the title compound with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level [symmetry code: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$]. The major disorder component of the pyridine unit is drawn using solid lines and the minor disorder component is drawn using dashed lines.

### 1.1. Structural commentary

The asymmetric unit of the title compound comprises one $Zn^{II}$ cation, one mandelate anion and one half of a 1,2-bis(4-pyridin-4-yl)ethane molecule. There is an inversion centre located at the mid-point of the ethane C—C bond in the 1,2-bis(4-pyridin-4-yl)ethane molecule. Each $Zn^{II}$ cation is coordinated by two N atoms from two 1,2-bis(4-pyridin-4-yl)ethane molecules in a *trans* arrangement and four O atoms from two mandelate anions in a slightly distorted octahedral coordination geometry, as shown in Table 1 and Fig. 1. The mandelate anions are coordinated to the central $Zn^{2+}$ cation

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Zn—O1 | 2.0290 (14) | O2—C1 | 1.250 (3) |
| Zn—O3 | 2.1013 (15) | O3—C2 | 1.424 (2) |
| Zn—N | 2.2217 (19) | N—C13 | 1.334 (3) |
| O1—C1 | 1.260 (2) | N—C9 | 1.339 (3) |
| | | | |
| O1—Zn—O3 | 80.02 (6) | C9—N—C13 | 117.3 (2) |
| O1—Zn—N | 90.25 (7) | O2—C1—C2 | 116.10 (17) |
| O1—Zn—O3$^{i}$ | 99.98 (6) | O1—C1—O2 | 124.67 (19) |
| O1—Zn—N$^{i}$ | 89.75 (7) | O1—C1—C2 | 119.21 (18) |
| O3—Zn—N | 88.73 (6) | O3—C2—C3 | 110.90 (18) |
| O3—Zn—N$^{i}$ | 91.27 (6) | O3—C2—C1 | 110.17 (16) |
| Zn—O1—C1 | 116.96 (13) | N—C9—C10 | 118.8 (4) |
| Zn—O3—C2 | 113.41 (12) | N—C9—C10′ | 127.1 (6) |
| Zn—N—C13 | 120.03 (16) | N—C13—C12′ | 116.3 (4) |
| Zn—N—C9 | 122.45 (16) | N—C13—C12 | 126.5 (3) |

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

form five-membered chelate rings *via* an oxygen atom of the OH group [Zn—O3 = 2.1013 (15) Å] and an oxygen atom of the carboxyl group [Zn—O1= 2.0290 (14) Å]. The $Zn^{II}$ cations are linked together *via* 1,2-bis(4-pyridin-4-yl)ethane bridges, forming a polymeric chain along [110].

## 2. Supramolecular features

The crystal structure features extensive O—H···O hydrogen bonding [O3···O2$^{ii}$ =2.572 (2) Å] (Fig. 2), establishing a three-dimensional network that is consolidated by further C—H···O hydrogen-bonding interactions. The C2—H2*A*···O1$^{ii}$, C8—H8*A*···O2$^{iii}$ and C13—H13*A*···O2$^{ii}$ distances are 3.193 (2), 3.378 (3), and 3.064 (3) Å, respectively (Table 2). In addition, C—H $\cdots\pi$ interactions [C9—H9*A*···*Cg*5$^{iv}$ = 3.781 (2) Å and C12′–H12*B*···*Cg*5$^{ii}$ = 3.649 (8) Å, Table 2] and $\pi$–$\pi$ stacking are present in the crystal structure. The distance *Cg*5···*Cg*3$^{iv}$ between the centroids of the phenyl ring (C3–C8) of the mandelate group and of the 1,2-bis(pyridine-4-

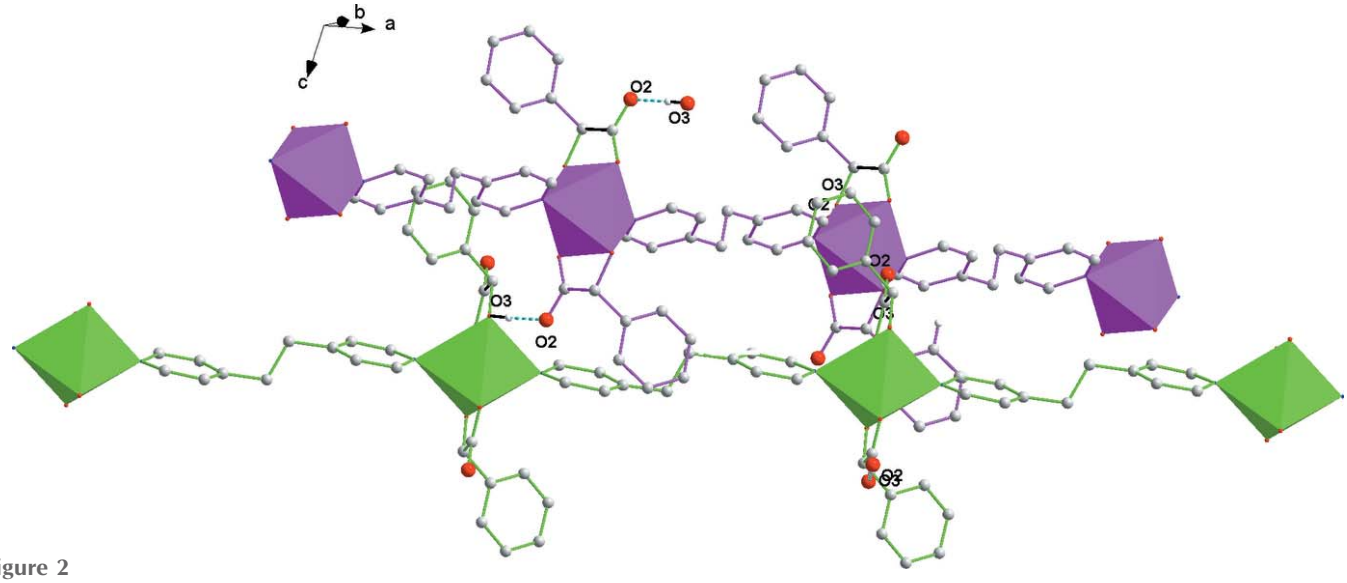


**Figure 2**
The molecular packing of the title compound. Hydrogen bonds are shown as dashed lines. The minor occupancy components of the disordered pyridine carbon atoms have been omitted for clarity.

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

*Cg*5 is the centroid of the C3–C8 ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H3*A*···O2$^{ii}$ | 0.86 (3) | 1.72 (3) | 2.572 (2) | 177.3 (15) |
| C2—H2*A*···O1$^{ii}$ | 1.00 | 2.46 | 3.193 (2) | 129 |
| C8—H8*A*···O2$^{iii}$ | 0.95 | 2.44 | 3.378 (3) | 168 |
| C13—H13*A*···O2$^{ii}$ | 0.96 | 2.43 | 3.064 (3) | 124 |
| C9—H9*A*···*Cg*5$^{iv}$ | 0.96 | 2.88 | 3.781 (2) | 157 |
| C12′—H12*B*···*Cg*5$^{ii}$ | 0.95 | 2.75 | 3.649 (8) | 159 |

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

yl)ethane moiety (C9–C13) [symmetry code: (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$] is 4.951 (2) Å and the dihedral angle between the two rings is 62.6 (2)°.

## 3. Database survey

Other examples of complexes containing the mandelate anion and the 1,2-bis(pyridine-4-yl)ethane moiety were found in the Cambridge Structural Database (CSD, version 5.40, update of August 2019; Groom *et al.*, 2016). These include *catena*-[[$\mu$-oxido(phenyl)acetato]($\mu$-4,4′-ethane-1,2-diyldipyridine)-zinc(II) perchlorate monohydrate] (CSD refcode QEBFUB; Guo *et al.*, 2015), which has a $ClO_4^-$ counter-ion. An Ni complex, *catena*-[bis[(hydroxy)(phenyl)acetato]{$\mu$-4-[2-(pyridin-4-yl)ethyl]pyridine}nickel(II)], isostructural with the title compound, has also been reported (QEBFAH; Guo *et al.*, 2015). A complex with the same molecular formula but different coordination environment of the Zn atom, *catena*-[[$\mu_2$-1,2-bis(4-pyridyl)ethane]bis(2-hydroxy-2-phenylacetato)-zinc(II)] (MUBZEP; Yu *et al.*, 2009) has also been characterized. In this case, the 1,2-bis(pyridine-4-yl)ethane and mandelate units are *cis* to each other.

## 4. Synthesis and crystallization

$Zn(NO_3)_2$ (91.4 mg, 0.50 mmol), 1,2-bi(4-pyridyl)ethane (92.1 mg, 0.50 mmol) and mandelic acid (76.0 mg, 0.50 mmol) were mixed in deionized water. The mixture was placed in a 25 mL Teflon linear reactor and heated at 423 K in an autoclave for 24 h. The resulting solution was slowly cooled to room temperature. Yellow transparent single crystals of the title compound were obtained in 75% yield (based on Zn).

## 5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. Atoms C10, C11, C12, C14 of the pyridine ring are disordered over two sets of sites with an occupancy of 0.578 (14) for the major moiety. C-bound H atoms were included in calculated positions and treated as riding: C—H = 0.95 Å with $U_{iso}$(H) = 1.5$U_{eq}$(C-methyl) and 1.2$U_{eq}$(C) for other H atoms·The hydroxy H atoms, which could not be located in a difference-Fourier map, were included in idealized calculated positions that gave the most sensible geometry.

**Table 3**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $[Zn(C_8H_7O_3)_2(C_{12}H_{12}N_2)]$ |
| $M_r$ | 551.90 |
| Crystal system, space group | Monoclinic, *C*2/*c* |
| Temperature (K) | 150 |
| *a*, *b*, *c* (Å) | 25.6754 (19), 9.8838 (5), 10.6208 (7) |
| $\beta$ (°) | 108.234 (7) |
| *V* (Å$^3$) | 2559.9 (3) |
| *Z* | 4 |
| Radiation type | Mo *K*$\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.01 |
| Crystal size (mm) | 0.35 × 0.32 × 0.26 |
| | |
| Data collection | |
| Diffractometer | Oxford Diffraction Gemini-S CCD detector |
| Absorption correction | Multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009) |
| $T_{min}$, $T_{max}$ | 0.936, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 5016, 2270, 1970 |
| $R_{int}$ | 0.027 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.031, 0.082, 1.04 |
| No. of reflections | 2270 |
| No. of parameters | 210 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.43, −0.41 |

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2009), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *DIAMOND* (Brandenburg & Putz, 1999) and *PLATON* (Spek, 2020).

## Funding information

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# supporting information

*Acta Cryst.* (2020). E**76**, 1868-1870 [https://doi.org/10.1107/S2056989020014322]

# Crystal structure of the coordination polymer *catena*-poly[[bis[hydroxy(phenyl)-acetato-$\kappa^2O^1,O^2$]zinc(II)]-$\mu_2$-1,2-bis(pyridin-4-yl)ethane-$\kappa^2N:N'$]

**Shen Fwu Ming and Lush Shie Fu**

## Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 1999); software used to prepare material for publication: *PLATON* (Spek, 2020).

***catena*-Poly[[bis[hydroxy(phenyl)acetato-$\kappa^2O^1,O^2$]zinc(II)]-$\mu_2$-1,2-bis(pyridin-4-yl)ethane-$\kappa^2N:N'$]**

*Crystal data*

$[Zn(C_8H_7O_3)_2(C_{12}H_{12}N_2)]$
$M_r$ = 551.90
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
*a* = 25.6754 (19) Å
*b* = 9.8838 (5) Å
*c* = 10.6208 (7) Å
*β* = 108.234 (7)°
*V* = 2559.9 (3) Å$^3$
*Z* = 4
*F*(000) = 1144
$D_x$ = 1.432 Mg m$^{-3}$
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 1818 reflections
*θ* = 2.8–29.2°
*μ* = 1.00 mm$^{-1}$
*T* = 150 K
Parallelepiped, yellow
0.35 × 0.32 × 0.26 mm

*Data collection*

Oxford Diffraction Gemini-S CCD detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
*ω* scans
Absorption correction: multi-scan (CrysAlisPro; Oxford Diffraction, 2009)
$T_{min}$ = 0.936, $T_{max}$ = 1.000
5016 measured reflections
2270 independent reflections
1970 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.027
$\theta_{max}$ = 25.0°, $\theta_{min}$ = 2.8°
*h* = −23→30
*k* = −7→11
*l* = −12→11

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.082
*S* = 1.04
2270 reflections
210 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

$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 2.1396P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.43$ e Å$^{-3}$
$\Delta\rho_{min} = -0.40$ e Å$^{-3}$

*Special details*

**Geometry**. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Zn | 0.25000 | 0.25000 | 0.50000 | 0.0138 (1) | |
| O1 | 0.25093 (6) | 0.37191 (14) | 0.65439 (14) | 0.0171 (5) | |
| O2 | 0.26248 (7) | 0.37664 (14) | 0.87065 (15) | 0.0229 (5) | |
| O3 | 0.28062 (6) | 0.11415 (15) | 0.65814 (14) | 0.0151 (5) | |
| N | 0.16575 (7) | 0.18198 (19) | 0.48454 (18) | 0.0189 (6) | |
| C1 | 0.26431 (9) | 0.3184 (2) | 0.7677 (2) | 0.0146 (6) | |
| C2 | 0.28282 (9) | 0.1695 (2) | 0.7835 (2) | 0.0154 (7) | |
| C3 | 0.33972 (9) | 0.1537 (2) | 0.8826 (2) | 0.0164 (6) | |
| C4 | 0.38568 (10) | 0.1438 (2) | 0.8401 (2) | 0.0249 (7) | |
| C5 | 0.43745 (11) | 0.1262 (3) | 0.9311 (3) | 0.0349 (9) | |
| C6 | 0.44387 (11) | 0.1178 (3) | 1.0644 (3) | 0.0352 (9) | |
| C7 | 0.39842 (11) | 0.1278 (2) | 1.1077 (2) | 0.0319 (8) | |
| C8 | 0.34670 (10) | 0.1461 (2) | 1.0174 (2) | 0.0235 (7) | |
| C9 | 0.13113 (11) | 0.2581 (2) | 0.5259 (3) | 0.0279 (8) | |
| C10 | 0.0768 (3) | 0.2104 (9) | 0.5048 (9) | 0.0261 (19) | 0.578 (14) |
| C11 | 0.0594 (2) | 0.0835 (5) | 0.4523 (9) | 0.026 (2) | 0.578 (14) |
| C12 | 0.0972 (3) | 0.0046 (6) | 0.4172 (10) | 0.0260 (18) | 0.578 (14) |
| C13 | 0.14957 (10) | 0.0569 (2) | 0.4432 (3) | 0.0310 (8) | |
| C14 | 0.0017 (3) | 0.0308 (7) | 0.4359 (5) | 0.0341 (17) | 0.578 (14) |
| C12′ | 0.1046 (4) | 0.0024 (8) | 0.4827 (13) | 0.025 (3) | 0.422 (14) |
| C14′ | 0.0228 (4) | 0.0209 (9) | 0.5626 (7) | 0.028 (3) | 0.422 (14) |
| C10′ | 0.0870 (5) | 0.2148 (13) | 0.5599 (12) | 0.026 (3) | 0.422 (14) |
| C11′ | 0.0722 (3) | 0.0805 (6) | 0.5343 (12) | 0.021 (2) | 0.422 (14) |
| H4A | 0.38160 | 0.14900 | 0.74820 | 0.0300* | |
| H7A | 0.40270 | 0.12210 | 1.19970 | 0.0380* | |
| H5A | 0.46860 | 0.12000 | 0.90120 | 0.0420* | |
| H6A | 0.47930 | 0.10510 | 1.12650 | 0.0420* | |
| H10A | 0.05140 | 0.26770 | 0.52760 | 0.0320* | 0.578 (14) |
| H12A | 0.08770 | −0.08160 | 0.37700 | 0.0310* | 0.578 (14) |
| H13A | 0.17770 | −0.00500 | 0.43840 | 0.0370* | |
| H14A | −0.02490 | 0.10630 | 0.40920 | 0.0410* | 0.578 (14) |
| H14B | −0.00830 | −0.03820 | 0.36490 | 0.0410* | 0.578 (14) |
| H8A | 0.31580 | 0.15360 | 1.04800 | 0.0280* | |
| H9A | 0.13500 | 0.35420 | 0.51880 | 0.0330* | |
| H2A | 0.25660 | 0.11780 | 0.81760 | 0.0180* | |
| H3A | 0.2653 (11) | 0.036 (3) | 0.647 (3) | 0.039 (8)* | |

| | | | | | |
|---|---|---|---|---|---|
| H10B | 0.06730 | 0.27390 | 0.59920 | 0.0310* | 0.422 (14) |
| H12B | 0.09720 | −0.09190 | 0.47220 | 0.0300* | 0.422 (14) |
| H14C | 0.00800 | 0.08830 | 0.61150 | 0.0340* | 0.422 (14) |
| H14D | 0.03450 | −0.05930 | 0.62030 | 0.0340* | 0.422 (14) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn | 0.0156 (2) | 0.0132 (2) | 0.0143 (2) | −0.0016 (2) | 0.0070 (2) | −0.0005 (1) |
| O1 | 0.0242 (9) | 0.0122 (7) | 0.0164 (8) | 0.0026 (7) | 0.0086 (6) | 0.0012 (6) |
| O2 | 0.0352 (10) | 0.0182 (8) | 0.0176 (8) | 0.0074 (7) | 0.0115 (7) | −0.0001 (6) |
| O3 | 0.0222 (9) | 0.0085 (7) | 0.0157 (8) | −0.0012 (7) | 0.0075 (6) | −0.0007 (6) |
| N | 0.0166 (10) | 0.0191 (10) | 0.0217 (10) | −0.0016 (9) | 0.0072 (8) | 0.0046 (8) |
| C1 | 0.0134 (11) | 0.0133 (11) | 0.0193 (11) | −0.0012 (9) | 0.0084 (9) | −0.0006 (9) |
| C2 | 0.0208 (12) | 0.0109 (11) | 0.0183 (11) | −0.0013 (10) | 0.0115 (9) | −0.0014 (8) |
| C3 | 0.0214 (12) | 0.0088 (10) | 0.0196 (11) | 0.0000 (9) | 0.0074 (9) | 0.0015 (8) |
| C4 | 0.0221 (13) | 0.0303 (13) | 0.0227 (12) | 0.0043 (11) | 0.0075 (10) | 0.0005 (10) |
| C5 | 0.0222 (14) | 0.0431 (16) | 0.0388 (16) | 0.0047 (13) | 0.0089 (12) | 0.0005 (12) |
| C6 | 0.0274 (15) | 0.0358 (15) | 0.0324 (15) | 0.0032 (12) | −0.0049 (12) | 0.0040 (12) |
| C7 | 0.0412 (17) | 0.0305 (14) | 0.0187 (12) | −0.0026 (13) | 0.0016 (11) | 0.0041 (10) |
| C8 | 0.0298 (14) | 0.0198 (12) | 0.0234 (12) | −0.0020 (11) | 0.0118 (10) | 0.0015 (10) |
| C9 | 0.0229 (14) | 0.0229 (13) | 0.0414 (15) | 0.0022 (11) | 0.0151 (12) | 0.0065 (11) |
| C10 | 0.014 (3) | 0.038 (3) | 0.028 (4) | −0.001 (3) | 0.009 (3) | −0.005 (4) |
| C11 | 0.016 (2) | 0.032 (3) | 0.030 (5) | −0.007 (2) | 0.007 (3) | 0.005 (2) |
| C12 | 0.024 (3) | 0.020 (2) | 0.034 (4) | −0.003 (2) | 0.009 (3) | −0.001 (3) |
| C13 | 0.0174 (13) | 0.0188 (13) | 0.0563 (17) | 0.0011 (11) | 0.0110 (12) | 0.0067 (12) |
| C14 | 0.022 (3) | 0.042 (3) | 0.040 (3) | −0.006 (3) | 0.012 (2) | 0.007 (3) |
| C12′ | 0.024 (4) | 0.016 (3) | 0.036 (6) | −0.005 (3) | 0.011 (4) | −0.002 (4) |
| C14′ | 0.026 (5) | 0.031 (4) | 0.035 (4) | −0.008 (4) | 0.020 (3) | 0.002 (3) |
| C10′ | 0.022 (5) | 0.029 (4) | 0.025 (6) | −0.004 (3) | 0.006 (5) | −0.011 (5) |
| C11′ | 0.014 (3) | 0.028 (3) | 0.021 (6) | −0.005 (3) | 0.007 (3) | 0.001 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zn—O1 | 2.0290 (14) | C11—C12 | 1.384 (10) |
| Zn—O3 | 2.1013 (15) | C11—C14 | 1.528 (10) |
| Zn—N | 2.2217 (19) | C11′—C14′ | 1.512 (13) |
| Zn—O1$^{i}$ | 2.0290 (14) | C11′—C12′ | 1.369 (14) |
| Zn—O3$^{i}$ | 2.1013 (15) | C12—C13 | 1.385 (9) |
| Zn—N$^{i}$ | 2.2217 (19) | C12′—C13 | 1.450 (11) |
| O1—C1 | 1.260 (2) | C14—C14$^{ii}$ | 1.519 (8) |
| O2—C1 | 1.250 (3) | C14′—C14′$^{ii}$ | 1.528 (12) |
| O3—C2 | 1.424 (2) | C2—H2A | 1.0000 |
| O3—H3A | 0.86 (3) | C4—H4A | 0.9500 |
| N—C13 | 1.334 (3) | C5—H5A | 0.9500 |
| N—C9 | 1.339 (3) | C6—H6A | 0.9500 |
| C1—C2 | 1.540 (3) | C7—H7A | 0.9500 |
| C2—C3 | 1.518 (3) | C8—H8A | 0.9500 |

| | | | |
|---|---|---|---|
| C3—C8 | 1.388 (3) | C9—H9A | 0.9600 |
| C3—C4 | 1.393 (4) | C10—H10A | 0.9500 |
| C4—C5 | 1.388 (4) | C10′—H10B | 0.9500 |
| C5—C6 | 1.376 (4) | C12—H12A | 0.9500 |
| C6—C7 | 1.385 (4) | C12′—H12B | 0.9500 |
| C7—C8 | 1.385 (3) | C13—H13A | 0.9600 |
| C9—C10 | 1.422 (9) | C14—H14B | 0.9900 |
| C9—C10′ | 1.361 (14) | C14—H14A | 0.9900 |
| C10—C11 | 1.388 (11) | C14′—H14C | 0.9900 |
| C10′—C11′ | 1.384 (14) | C14′—H14D | 0.9900 |

| | | | |
|---|---|---|---|
| O1···O3 | 2.656 (2) | C9···H4A$^{i}$ | 2.9700 |
| O1···N | 3.015 (2) | C10···H14B$^{ii}$ | 3.0700 |
| O1···C2 | 2.419 (2) | C10′···H7A$^{iv}$ | 2.9600 |
| O1···C9 | 3.156 (3) | C12′···H14C$^{ii}$ | 2.8900 |
| O1···C13$^{i}$ | 3.123 (3) | C13···H3A | 3.09 (3) |
| O1···C2$^{iii}$ | 3.193 (2) | C14′···H12B$^{ii}$ | 3.0700 |
| O1···N$^{i}$ | 3.002 (2) | H2A···O1$^{v}$ | 2.4600 |
| O1···O3$^{i}$ | 3.164 (2) | H2A···C1$^{v}$ | 3.0900 |
| O2···C8$^{iv}$ | 3.378 (3) | H2A···H8A | 2.4700 |
| O2···O3$^{iii}$ | 2.572 (2) | H3A···O1$^{v}$ | 2.79 (3) |
| O2···C2$^{iii}$ | 3.350 (2) | H3A···C13 | 3.09 (3) |
| O2···C8 | 3.192 (3) | H3A···O2$^{v}$ | 1.72 (3) |
| O2···C13$^{iii}$ | 3.064 (3) | H3A···C1$^{v}$ | 2.54 (3) |
| O3···O1$^{i}$ | 3.164 (2) | H4A···O3 | 2.4900 |
| O3···N | 3.024 (2) | H4A···N$^{i}$ | 2.9200 |
| O3···C1 | 2.431 (3) | H4A···C9$^{i}$ | 2.9700 |
| O3···O2$^{v}$ | 2.572 (2) | H5A···H10A$^{vi}$ | 2.4000 |
| O3···C1$^{v}$ | 3.326 (3) | H6A···H6A$^{vii}$ | 2.5000 |
| O3···O1 | 2.656 (2) | H7A···C10′$^{iv}$ | 2.9600 |
| O3···N$^{i}$ | 3.092 (2) | H7A···H10B$^{iv}$ | 2.2800 |
| O1···H13A$^{i}$ | 2.6800 | H8A···H2A | 2.4700 |
| O1···H3A$^{iii}$ | 2.79 (3) | H8A···O2$^{iv}$ | 2.4400 |
| O1···H9A | 2.8800 | H9A···C8$^{iii}$ | 2.9700 |
| O1···H2A$^{iii}$ | 2.4600 | H9A···C7$^{iii}$ | 3.0200 |
| O2···H8A$^{iv}$ | 2.4400 | H9A···O1 | 2.8800 |
| O2···H3A$^{iii}$ | 1.72 (3) | H10A···H14A | 2.5300 |
| O2···H13A$^{iii}$ | 2.4300 | H10A···C5$^{viii}$ | 2.9700 |
| O3···H4A | 2.4900 | H10A···H5A$^{viii}$ | 2.4000 |
| N···O1 | 3.015 (2) | H10B···H14C | 2.4100 |
| N···O3 | 3.024 (2) | H10B···H7A$^{iv}$ | 2.2800 |
| N···O1$^{i}$ | 3.002 (2) | H12A···H14B | 2.4700 |
| N···O3$^{i}$ | 3.092 (2) | H12A···C7$^{v}$ | 2.8900 |
| N···H4A$^{i}$ | 2.9200 | H12B···H14D | 2.6000 |
| C1···O3$^{iii}$ | 3.326 (3) | H12B···C14′$^{ii}$ | 3.0700 |
| C2···O2$^{v}$ | 3.350 (2) | H12B···C7$^{v}$ | 2.9100 |
| C2···O1$^{v}$ | 3.193 (2) | H12B···C8$^{v}$ | 2.9500 |
| C8···O2 | 3.192 (3) | H12B···H14C$^{ii}$ | 2.5700 |

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|---|---|---|---|
| C8···O2$^{iv}$ | 3.378 (3) | H12B···C6$^{v}$ | 3.0400 |
| C13···O2$^{v}$ | 3.064 (3) | H13A···O1$^{i}$ | 2.6800 |
| C1···H3A$^{iii}$ | 2.54 (3) | H13A···O2$^{v}$ | 2.4300 |
| C1···H2A$^{iii}$ | 3.0900 | H14A···C5$^{viii}$ | 2.8500 |
| C5···H10A$^{vi}$ | 2.9700 | H14A···H10A | 2.5300 |
| C5···H14A$^{vi}$ | 2.8500 | H14B···H12A | 2.4700 |
| C6···H12B$^{iii}$ | 3.0400 | H14B···C10$^{ii}$ | 3.0700 |
| C7···H12B$^{iii}$ | 2.9100 | H14C···H10B | 2.4100 |
| C7···H12A$^{iii}$ | 2.8900 | H14C···C12′$^{ii}$ | 2.8900 |
| C7···H9A$^{v}$ | 3.0200 | H14C···H12B$^{ii}$ | 2.5700 |
| C8···H12B$^{iii}$ | 2.9500 | H14D···H12B | 2.6000 |
| C8···H9A$^{v}$ | 2.9700 | | |

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|---|---|---|---|
| O1—Zn—O3 | 80.02 (6) | C10′—C11′—C14′ | 122.1 (9) |
| O1—Zn—N | 90.25 (7) | C11—C12—C13 | 117.1 (6) |
| O1—Zn—O1$^{i}$ | 180.00 | C11′—C12′—C13 | 123.0 (7) |
| O1—Zn—O3$^{i}$ | 99.98 (6) | N—C13—C12′ | 116.3 (4) |
| O1—Zn—N$^{i}$ | 89.75 (7) | N—C13—C12 | 126.5 (3) |
| O3—Zn—N | 88.73 (6) | C11—C14—C14$^{ii}$ | 111.1 (6) |
| O1$^{i}$—Zn—O3 | 99.98 (6) | C11′—C14′—C14′$^{ii}$ | 113.2 (7) |
| O3—Zn—O3$^{i}$ | 180.00 | O3—C2—H2A | 108.00 |
| O3—Zn—N$^{i}$ | 91.27 (6) | C1—C2—H2A | 108.00 |
| O1$^{i}$—Zn—N | 89.75 (7) | C3—C2—H2A | 108.00 |
| O3$^{i}$—Zn—N | 91.27 (6) | C3—C4—H4A | 120.00 |
| N—Zn—N$^{i}$ | 180.00 | C5—C4—H4A | 120.00 |
| O1$^{i}$—Zn—O3$^{i}$ | 80.02 (6) | C4—C5—H5A | 120.00 |
| O1$^{i}$—Zn—N$^{i}$ | 90.25 (7) | C6—C5—H5A | 120.00 |
| O3$^{i}$—Zn—N$^{i}$ | 88.73 (6) | C5—C6—H6A | 120.00 |
| Zn—O1—C1 | 116.96 (13) | C7—C6—H6A | 120.00 |
| Zn—O3—C2 | 113.41 (12) | C6—C7—H7A | 120.00 |
| C2—O3—H3A | 111 (2) | C8—C7—H7A | 120.00 |
| Zn—O3—H3A | 115 (2) | C3—C8—H8A | 120.00 |
| Zn—N—C13 | 120.03 (16) | C7—C8—H8A | 120.00 |
| Zn—N—C9 | 122.45 (16) | N—C9—H9A | 116.00 |
| C9—N—C13 | 117.3 (2) | C10—C9—H9A | 116.00 |
| O2—C1—C2 | 116.10 (17) | C10′—C9—H9A | 117.00 |
| O1—C1—O2 | 124.67 (19) | C9—C10—H10A | 119.00 |
| O1—C1—C2 | 119.21 (18) | C11—C10—H10A | 119.00 |
| O3—C2—C3 | 110.90 (18) | C9—C10′—H10B | 122.00 |
| O3—C2—C1 | 110.17 (16) | C11′—C10′—H10B | 122.00 |
| C1—C2—C3 | 111.79 (17) | C11—C12—H12A | 122.00 |
| C2—C3—C8 | 120.4 (2) | C13—C12—H12A | 121.00 |
| C2—C3—C4 | 120.78 (18) | C13—C12′—H12B | 119.00 |
| C4—C3—C8 | 118.8 (2) | C11′—C12′—H12B | 118.00 |
| C3—C4—C5 | 120.5 (2) | N—C13—H13A | 116.00 |
| C4—C5—C6 | 120.3 (3) | C12—C13—H13A | 117.00 |
| C5—C6—C7 | 119.7 (3) | C12′—C13—H13A | 117.00 |
| C6—C7—C8 | 120.3 (2) | C14$^{ii}$—C14—H14B | 109.00 |

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|---|---|---|---|
| C3—C8—C7 | 120.5 (2) | H14A—C14—H14B | 108.00 |
| N—C9—C10 | 118.8 (4) | C14$^{ii}$—C14—H14A | 109.00 |
| N—C9—C10′ | 127.1 (6) | C11—C14—H14A | 109.00 |
| C9—C10—C11 | 122.6 (7) | C11—C14—H14B | 109.00 |
| C9—C10′—C11′ | 116.7 (10) | C11′—C14′—H14C | 109.00 |
| C12—C11—C14 | 120.9 (6) | C11′—C14′—H14D | 109.00 |
| C10—C11—C14 | 122.2 (6) | H14C—C14′—H14D | 108.00 |
| C10—C11—C12 | 116.9 (6) | C14′$^{ii}$—C14′—H14C | 109.00 |
| C12′—C11′—C14′ | 120.9 (7) | C14′$^{ii}$—C14′—H14D | 109.00 |
| C10′—C11′—C12′ | 117.1 (9) | | |

| | | | |
|---|---|---|---|
| O3—Zn—O1—C1 | −4.48 (16) | O1—C1—C2—C3 | 122.9 (2) |
| N—Zn—O1—C1 | 84.19 (17) | O2—C1—C2—O3 | 177.3 (2) |
| O3$^{i}$—Zn—O1—C1 | 175.52 (16) | O2—C1—C2—C3 | −58.9 (3) |
| N$^{i}$—Zn—O1—C1 | −95.81 (17) | O3—C2—C3—C4 | 25.8 (3) |
| O1—Zn—O3—C2 | 3.79 (14) | O3—C2—C3—C8 | −152.94 (18) |
| N—Zn—O3—C2 | −86.69 (14) | C1—C2—C3—C4 | −97.6 (2) |
| O1$^{i}$—Zn—O3—C2 | −176.21 (14) | C1—C2—C3—C8 | 83.7 (2) |
| N$^{i}$—Zn—O3—C2 | 93.31 (14) | C2—C3—C4—C5 | −178.5 (2) |
| O1—Zn—N—C9 | 25.77 (19) | C8—C3—C4—C5 | 0.2 (3) |
| O1—Zn—N—C13 | −148.46 (19) | C2—C3—C8—C7 | 178.15 (18) |
| O3—Zn—N—C9 | 105.78 (19) | C4—C3—C8—C7 | −0.6 (3) |
| O3—Zn—N—C13 | −68.45 (19) | C3—C4—C5—C6 | 0.3 (4) |
| O1$^{i}$—Zn—N—C9 | −154.23 (19) | C4—C5—C6—C7 | −0.4 (4) |
| O1$^{i}$—Zn—N—C13 | 31.54 (19) | C5—C6—C7—C8 | 0.0 (4) |
| O3$^{i}$—Zn—N—C9 | −74.22 (19) | C6—C7—C8—C3 | 0.5 (3) |
| O3$^{i}$—Zn—N—C13 | 111.55 (19) | N—C9—C10—C11 | 5.1 (10) |
| Zn—O1—C1—O2 | −173.77 (19) | C9—C10—C11—C12 | −1.7 (13) |
| Zn—O1—C1—C2 | 4.3 (3) | C9—C10—C11—C14 | 177.2 (6) |
| Zn—O3—C2—C1 | −2.7 (2) | C10—C11—C12—C13 | 2.9 (12) |
| Zn—O3—C2—C3 | −127.04 (14) | C14—C11—C12—C13 | −176.0 (6) |
| Zn—N—C9—C10 | 176.2 (4) | C10—C11—C14—C14$^{ii}$ | −83.6 (9) |
| C13—N—C9—C10 | −9.5 (5) | C12—C11—C14—C14$^{ii}$ | 95.2 (9) |
| Zn—N—C13—C12 | −173.7 (5) | C11—C12—C13—N | −8.3 (11) |
| C9—N—C13—C12 | 11.8 (6) | C11—C14—C14$^{ii}$—C11$^{ii}$ | 180.0 (5) |
| O1—C1—C2—O3 | −0.9 (3) | | |

Symmetry codes: (i) −*x*+1/2, −*y*+1/2, −*z*+1; (ii) −*x*, −*y*, −*z*+1; (iii) −*x*+1/2, *y*+1/2, −*z*+3/2; (iv) −*x*+1/2, −*y*+1/2, −*z*+2; (v) −*x*+1/2, *y*−1/2, −*z*+3/2; (vi) *x*+1/2, −*y*+1/2, *z*+1/2; (vii) −*x*+1, *y*, −*z*+5/2; (viii) *x*−1/2, −*y*+1/2, *z*−1/2.

*Hydrogen-bond geometry (Å, º)*

*Cg*5 is the centroid of the C3–C8 ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H3*A*···O2$^{v}$ | 0.86 (3) | 1.72 (3) | 2.572 (2) | 177.3 (15) |
| C2—H2*A*···O1$^{v}$ | 1.00 | 2.46 | 3.193 (2) | 129 |
| C8—H8*A*···O2$^{iv}$ | 0.95 | 2.44 | 3.378 (3) | 168 |
| C13—H13*A*···O2$^{v}$ | 0.96 | 2.43 | 3.064 (3) | 124 |

| | | | | |
|---|---|---|---|---|
| C9—H9*A*···*Cg*5$^{iii}$ | 0.96 | 2.88 | 3.781 (2) | 157 |
| C12′—H12*B*···*Cg*5$^{v}$ | 0.95 | 2.75 | 3.649 (8) | 159 |

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