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## Bis[ $\mu$ -2-[(2-oxidobenzylidene)aminomethyl]phenolato- $\kappa^3$ O,N,O']-bis[(pyridine- $\kappa$ N)zinc(II)]

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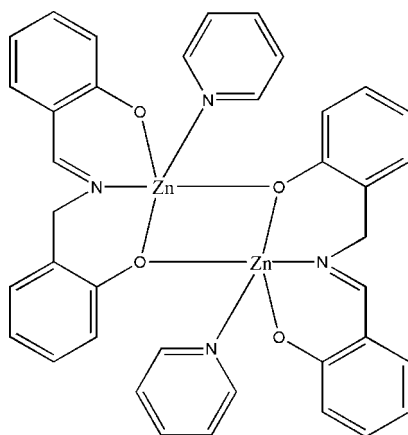
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Key indicators: single-crystal X-ray study;  $T = 294$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.037;  $wR$  factor = 0.084; data-to-parameter ratio = 16.4.

In the title centrosymmetric zinc(II) complex,  $[\text{Zn}_2(\text{C}_4\text{H}_{13}\text{NO}_2)_2(\text{C}_6\text{H}_5\text{N})_2]$ , each  $\text{Zn}^{\text{II}}$  atom is coordinated by two 2-[(2-oxidobenzylidene)aminomethyl]phenolate ( $L$ ) ligands and one pyridine (py) molecule in a distorted trigonal-bipyramidal geometry. Each  $L$  ligand behaves as a tridentate ligand and provides a phenolate oxygen bridge which links the two  $\text{Zn}^{\text{II}}$  atoms. The  $\text{Zn}L(\text{py})$  units are linked by  $\pi$ - $\pi$  interactions between adjacent pyridine molecules, with a centroid-centroid distance of 3.724 Å, resulting in a two-dimensional structure.

### Related literature

For the biochemical and catalytic activity of zinc(II) complexes, see: Marco *et al.* (2004); Kim *et al.* (2000).  $\text{Zn}^{\text{II}}$  ions in phenoxide-bridged dinuclear complexes provide flexible coordination numbers, see: Atakol *et al.* (1999); Huang *et al.* (2006). For the preparation of  $\text{H}_2L$ , see: Moustafa (2003).



### Experimental

#### Crystal data

$[\text{Zn}_2(\text{C}_{14}\text{H}_{13}\text{NO}_2)_2(\text{C}_5\text{H}_5\text{N})_2]$   
 $M_r = 739.42$   
 Monoclinic,  $P2_1/c$   
 $a = 10.145$  (6) Å  
 $b = 13.806$  (8) Å  
 $c = 12.671$  (8) Å  
 $\beta = 102.063$  (10)°

$V = 1735.5$  (18) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.43$  mm<sup>-1</sup>  
 $T = 294$  (2) K  
 $0.20 \times 0.18 \times 0.12$  mm

#### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\text{min}} = 0.693$ ,  $T_{\text{max}} = 1.000$   
 (expected range = 0.584–0.843)

9656 measured reflections  
 3561 independent reflections  
 2440 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.056$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.084$   
 $S = 1.00$   
 3561 reflections

217 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.40$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.32$  e Å<sup>-3</sup>

Data collection: SMART-NT (Bruker, 1998); cell refinement: SAINT-NT (Bruker, 1998); data reduction: SAINT-NT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL-NT (Sheldrick, 2008); software used to prepare material for publication: SHELXTL-NT.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2532).

### References

- Atakol, O., Tatar, L., Akay, M. A. & Ülkü, D. (1999). *Anal. Sci.* **15**, 199–200.  
 Bruker, (1998). SMART-NT and SAINT-NT. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Huang, W., Zhu, H. B. & Gou, S. H. (2006). *Coord. Chem. Rev.* **250**, 414–423.  
 Kim, H. S., Kim, J. J. & Lee, B. G. (2000). *Angew. Chem. Int. Ed.* **39**, 4096–4098.  
 Marco, V. B. D., Tapparo, A., Dolmella, A. & Bombi, G. G. (2004). *Inorg. Chim. Acta*, **357**, 135–142.  
 Moustafa, M. E. (2003). *Synth. React. Inorg. Met.-Org. Chem.* **33**, 453–468.  
 Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

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**supplementary materials**

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## Bis{ $\mu$ -2-[(2-oxidobenzylidene)aminomethyl]phenolato- $\kappa^3 O,N,O'$ }bis[(pyridine- $\kappa N$ )zinc(II)]

C. Yang, O.-Y. Yan, Q.-L. Wang and D.-Z. Liao

### Comment

The schiff base ligand,  $N,N'$ -bis-salicylidene-1,3-diaminopropane give a phenoxide-bridged homodinuclear complex with  $ZnCl_2$ . In the crystal structure, one  $Zn^{II}$  center has a distorted square pyramid geometry, the other one has a distorted tetrahedral geometry (Atakol *et al.*, 1999). In the tetra-imine macrocyclic cavity of dinuclear zinc(II) complexes, both of the two  $Zn^{II}$  ions take a distorted square pyramid geometry with an apical position occupied by a water molecule (Huang *et al.*, 2006).

The title complex  $[Zn_2(py)_2(L)_2]$ , (I), is the first dinuclear zinc(II) complex containing 2-hydroxybenzylamine-2'-hydroxybenzylidene( $H_2L$ ) and pyridine(py). In (I), there are two phenoxide bridges between two  $Zn^{II}$  atoms (Fig. 1). As can be seen from Table 1, in this complex the Zn—N(pyridine type) distance (2.129 Å) is similar to the average value of the reported structures, which is 2.132 Å (Marco *et al.*, 2004). The Zn—O bond lengths of 2.155(Zn1—O1A), 1.988(Zn1—O2A) and 1.9814 (Zn1—O1) Å in the title complex are comparable to those found in previously reported cadmium and zinc phenoxide complexes (1.864–2.170 Å) (Kim *et al.*, 2000). The bond lengths and angles show that the five coordinations around  $Zn^{II}$  atoms are not ideal square pyramid or trigonal bipyramid. The evaluation between the two geometries can be quantified using the  $\tau$  parameter (Atakol *et al.*, 1999), the  $\tau$  value is calculated as 0.81, indicating a distorted trigonal bipyramid geometry. The Zn—O—Zn—O ring is planar (360°). Calculation indicates that Zn···Zn distance is 3.3 Å. The packing diagram of complex (I) is shown in Fig.2. The distance between adjacent pyridines is 3.724 Å. The  $[Zn_2(py)_2(L)_2]$  units are thus linked by  $\pi\cdots\pi$  interaction between pyridine molecules, resulting in the formation of a two-dimensional structure.

### Experimental

The schiff base ligand  $H_2L$  was prepared by a published procedure (Moustafa, 2003).  $H_2L$  (0.1135 g, 0.5 mmol) was dissolved in methanol (20 ml). After a hot solution of zinc(II) acetate dihydrate (0.1097 g, 0.5 mmol) in water (10 ml) was added dropwise to the solution with continuous stirring, yellow precipitation came into being. When py (5 ml) was added to the turbid solution, the yellow precipitation was dissolved quickly and completely. After stirring further for 1 h with heating, the resulting solution was cooled and filtered. After about 1 week, single crystals of (I), suitable for X-ray structure determination, were obtained by slow evaporation of the solution at room temperature. Analysis calculated for  $C_{38}H_{32}N_4O_4Zn_2$ : C 61.73, N 7.58, H 4.36%. Found: C 62.39, N 7.59, H 4.30%.

### Refinement

All H atoms were positioned geometrically, with C—H = 0.93 and 0.97 Å for methylene and methyl H, and constrained to ride on their parent atoms, with  $U_{iso}(H) = 1.2U_{eq}(C)$ .

## Figures

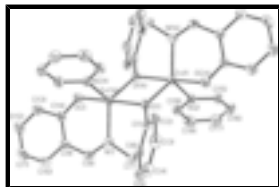


Fig. 1. The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.



Fig. 2. A view of the crystal packing along the *b* axis.

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### Crystal data

[Zn<sub>2</sub>(C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>]

$M_r = 739.42$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 10.145$  (6) Å

$b = 13.806$  (8) Å

$c = 12.671$  (8) Å

$\beta = 102.063$  (10)°

$V = 1735.5$  (18) Å<sup>3</sup>

$Z = 2$

$F_{000} = 760$

$D_x = 1.415$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 2807 reflections

$\theta = 2.5$ – $24.3$ °

$\mu = 1.43$  mm<sup>-1</sup>

$T = 294$  (2) K

Block, yellow

$0.20 \times 0.18 \times 0.12$  mm

### Data collection

Bruker SMART APEX CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 294$ (2) K

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.693$ ,  $T_{\max} = 1.000$

9656 measured reflections

3561 independent reflections

2440 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.056$

$\theta_{\text{max}} = 26.5$ °

$\theta_{\text{min}} = 2.1$ °

$h = -12 \rightarrow 12$

$k = -17 \rightarrow 14$

$l = -15 \rightarrow 14$

### Refinement

Refinement on  $F^2$

Secondary atom site location: difference Fourier map

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.036$$

$$wR(F^2) = 0.084$$

$$S = 1.00$$

3561 reflections

217 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

### 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 ( $\text{\AA}^2$ )

|     | <i>x</i>     | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| Zn1 | 0.60866 (3)  | 1.08479 (2)  | 0.49115 (2)  | 0.03166 (11)                     |
| O1  | 0.46079 (18) | 1.05680 (13) | 0.56701 (14) | 0.0360 (5)                       |
| O2  | 0.3413 (2)   | 0.78111 (13) | 0.45886 (14) | 0.0444 (5)                       |
| N1  | 0.4099 (2)   | 0.87742 (16) | 0.66733 (16) | 0.0326 (5)                       |
| N2  | 0.7965 (2)   | 1.02458 (17) | 0.57069 (17) | 0.0356 (6)                       |
| C1  | 0.4150 (3)   | 1.09767 (19) | 0.6492 (2)   | 0.0330 (6)                       |
| C2  | 0.3621 (3)   | 1.1911 (2)   | 0.6419 (2)   | 0.0422 (7)                       |
| H2  | 0.3611       | 1.2278       | 0.5802       | 0.051*                           |
| C3  | 0.3106 (3)   | 1.2300 (2)   | 0.7263 (3)   | 0.0531 (9)                       |
| H3  | 0.2740       | 1.2920       | 0.7201       | 0.064*                           |
| C4  | 0.3136 (3)   | 1.1771 (2)   | 0.8189 (3)   | 0.0550 (9)                       |
| H4  | 0.2799       | 1.2035       | 0.8754       | 0.066*                           |
| C5  | 0.3670 (3)   | 1.0849 (2)   | 0.8273 (2)   | 0.0492 (8)                       |
| H5  | 0.3695       | 1.0497       | 0.8903       | 0.059*                           |
| C6  | 0.4171 (3)   | 1.0433 (2)   | 0.7438 (2)   | 0.0351 (7)                       |
| C7  | 0.4791 (3)   | 0.9441 (2)   | 0.7531 (2)   | 0.0429 (7)                       |
| H7A | 0.5732       | 0.9494       | 0.7489       | 0.051*                           |
| H7B | 0.4753       | 0.9170       | 0.8230       | 0.051*                           |
| C8  | 0.3665 (3)   | 0.7963 (2)   | 0.6971 (2)   | 0.0351 (7)                       |
| H8  | 0.3792       | 0.7859       | 0.7710       | 0.042*                           |
| C9  | 0.3000 (3)   | 0.7197 (2)   | 0.6279 (2)   | 0.0340 (6)                       |
| C10 | 0.2446 (3)   | 0.6435 (2)   | 0.6794 (2)   | 0.0503 (8)                       |

## supplementary materials

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|     |            |            |            |             |
|-----|------------|------------|------------|-------------|
| H10 | 0.2511     | 0.6465     | 0.7536     | 0.060*      |
| C11 | 0.1821 (4) | 0.5660 (2) | 0.6240 (3) | 0.0643 (10) |
| H11 | 0.1460     | 0.5170     | 0.6597     | 0.077*      |
| C12 | 0.1733 (4) | 0.5613 (2) | 0.5133 (3) | 0.0640 (10) |
| H12 | 0.1308     | 0.5087     | 0.4745     | 0.077*      |
| C13 | 0.2264 (3) | 0.6333 (2) | 0.4608 (2) | 0.0552 (9)  |
| H13 | 0.2191     | 0.6281     | 0.3866     | 0.066*      |
| C14 | 0.2920 (3) | 0.7152 (2) | 0.5145 (2) | 0.0365 (7)  |
| C15 | 0.9071 (3) | 1.0806 (2) | 0.5933 (2) | 0.0446 (7)  |
| H15 | 0.8991     | 1.1462     | 0.5762     | 0.054*      |
| C16 | 1.0325 (3) | 1.0443 (3) | 0.6410 (2) | 0.0561 (9)  |
| H16 | 1.1073     | 1.0849     | 0.6558     | 0.067*      |
| C17 | 1.0448 (3) | 0.9487 (3) | 0.6659 (3) | 0.0607 (10) |
| H17 | 1.1287     | 0.9229     | 0.6970     | 0.073*      |
| C18 | 0.9335 (3) | 0.8906 (3) | 0.6452 (3) | 0.0603 (9)  |
| H18 | 0.9401     | 0.8251     | 0.6630     | 0.072*      |
| C19 | 0.8101 (3) | 0.9309 (2) | 0.5970 (2) | 0.0461 (8)  |
| H19 | 0.7343     | 0.8913     | 0.5826     | 0.055*      |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$      | $U^{13}$     | $U^{23}$      |
|-----|--------------|--------------|--------------|---------------|--------------|---------------|
| Zn1 | 0.02991 (19) | 0.03587 (19) | 0.03086 (18) | -0.00479 (15) | 0.01014 (13) | -0.00201 (15) |
| O1  | 0.0333 (11)  | 0.0390 (11)  | 0.0407 (11)  | -0.0073 (8)   | 0.0192 (9)   | -0.0102 (9)   |
| O2  | 0.0649 (14)  | 0.0390 (12)  | 0.0338 (10)  | -0.0139 (10)  | 0.0206 (10)  | -0.0039 (9)   |
| N1  | 0.0330 (13)  | 0.0348 (13)  | 0.0293 (12)  | 0.0030 (10)   | 0.0044 (10)  | -0.0020 (10)  |
| N2  | 0.0286 (13)  | 0.0446 (15)  | 0.0342 (13)  | -0.0056 (11)  | 0.0076 (10)  | -0.0026 (11)  |
| C1  | 0.0239 (14)  | 0.0372 (16)  | 0.0392 (16)  | -0.0080 (12)  | 0.0096 (12)  | -0.0133 (13)  |
| C2  | 0.0455 (19)  | 0.0363 (17)  | 0.0480 (18)  | -0.0079 (14)  | 0.0171 (14)  | -0.0074 (14)  |
| C3  | 0.051 (2)    | 0.0375 (18)  | 0.073 (2)    | 0.0010 (15)   | 0.0197 (18)  | -0.0152 (17)  |
| C4  | 0.060 (2)    | 0.055 (2)    | 0.059 (2)    | -0.0088 (17)  | 0.0321 (18)  | -0.0267 (18)  |
| C5  | 0.056 (2)    | 0.056 (2)    | 0.0395 (17)  | -0.0135 (17)  | 0.0188 (15)  | -0.0146 (16)  |
| C6  | 0.0332 (16)  | 0.0377 (16)  | 0.0336 (15)  | -0.0057 (13)  | 0.0050 (12)  | -0.0114 (13)  |
| C7  | 0.0418 (18)  | 0.0504 (18)  | 0.0330 (15)  | 0.0001 (14)   | 0.0000 (13)  | -0.0070 (14)  |
| C8  | 0.0325 (16)  | 0.0437 (18)  | 0.0291 (14)  | 0.0082 (13)   | 0.0064 (12)  | 0.0048 (13)   |
| C9  | 0.0332 (16)  | 0.0392 (16)  | 0.0306 (14)  | 0.0015 (13)   | 0.0086 (12)  | 0.0030 (13)   |
| C10 | 0.057 (2)    | 0.056 (2)    | 0.0392 (17)  | -0.0067 (17)  | 0.0138 (15)  | 0.0105 (16)   |
| C11 | 0.073 (3)    | 0.060 (2)    | 0.064 (2)    | -0.0266 (19)  | 0.026 (2)    | 0.0044 (19)   |
| C12 | 0.079 (3)    | 0.054 (2)    | 0.064 (2)    | -0.0310 (19)  | 0.025 (2)    | -0.0107 (18)  |
| C13 | 0.075 (2)    | 0.053 (2)    | 0.0420 (18)  | -0.0196 (18)  | 0.0224 (17)  | -0.0087 (16)  |
| C14 | 0.0387 (17)  | 0.0359 (16)  | 0.0376 (16)  | -0.0031 (13)  | 0.0142 (13)  | -0.0022 (13)  |
| C15 | 0.0351 (17)  | 0.054 (2)    | 0.0463 (17)  | -0.0098 (15)  | 0.0123 (14)  | -0.0063 (15)  |
| C16 | 0.0306 (18)  | 0.086 (3)    | 0.050 (2)    | -0.0117 (17)  | 0.0054 (15)  | -0.008 (2)    |
| C17 | 0.0317 (19)  | 0.098 (3)    | 0.051 (2)    | 0.0096 (19)   | 0.0062 (15)  | 0.012 (2)     |
| C18 | 0.052 (2)    | 0.067 (2)    | 0.062 (2)    | 0.0123 (18)   | 0.0121 (17)  | 0.0219 (18)   |
| C19 | 0.0376 (18)  | 0.053 (2)    | 0.0483 (18)  | -0.0027 (15)  | 0.0095 (14)  | 0.0083 (15)   |

*Geometric parameters (Å, °)*

|                                      |             |             |           |
|--------------------------------------|-------------|-------------|-----------|
| Zn1—O1                               | 1.9814 (19) | C6—C7       | 1.501 (4) |
| Zn1—O2 <sup>i</sup>                  | 1.988 (2)   | C7—H7A      | 0.9700    |
| Zn1—N1 <sup>i</sup>                  | 2.045 (2)   | C7—H7B      | 0.9700    |
| Zn1—N2                               | 2.129 (2)   | C8—C9       | 1.448 (4) |
| Zn1—O1 <sup>i</sup>                  | 2.155 (2)   | C8—H8       | 0.9300    |
| O1—C1                                | 1.349 (3)   | C9—C10      | 1.415 (4) |
| O1—Zn1 <sup>i</sup>                  | 2.155 (2)   | C9—C14      | 1.423 (4) |
| O2—C14                               | 1.313 (3)   | C10—C11     | 1.362 (4) |
| O2—Zn1 <sup>i</sup>                  | 1.988 (2)   | C10—H10     | 0.9300    |
| N1—C8                                | 1.288 (3)   | C11—C12     | 1.389 (4) |
| N1—C7                                | 1.484 (3)   | C11—H11     | 0.9300    |
| N1—Zn1 <sup>i</sup>                  | 2.045 (2)   | C12—C13     | 1.368 (4) |
| N2—C19                               | 1.335 (3)   | C12—H12     | 0.9300    |
| N2—C15                               | 1.344 (3)   | C13—C14     | 1.413 (4) |
| C1—C2                                | 1.394 (4)   | C13—H13     | 0.9300    |
| C1—C6                                | 1.411 (4)   | C15—C16     | 1.383 (4) |
| C2—C3                                | 1.392 (4)   | C15—H15     | 0.9300    |
| C2—H2                                | 0.9300      | C16—C17     | 1.357 (5) |
| C3—C4                                | 1.376 (4)   | C16—H16     | 0.9300    |
| C3—H3                                | 0.9300      | C17—C18     | 1.366 (5) |
| C4—C5                                | 1.379 (4)   | C17—H17     | 0.9300    |
| C4—H4                                | 0.9300      | C18—C19     | 1.390 (4) |
| C5—C6                                | 1.389 (4)   | C18—H18     | 0.9300    |
| C5—H5                                | 0.9300      | C19—H19     | 0.9300    |
| O1—Zn1—O2 <sup>i</sup>               | 101.29 (8)  | C6—C7—H7A   | 109.1     |
| O1—Zn1—N1 <sup>i</sup>               | 127.04 (8)  | N1—C7—H7B   | 109.1     |
| O2 <sup>i</sup> —Zn1—N1 <sup>i</sup> | 92.31 (8)   | C6—C7—H7B   | 109.1     |
| O1—Zn1—N2                            | 112.80 (9)  | H7A—C7—H7B  | 107.8     |
| O2 <sup>i</sup> —Zn1—N2              | 93.97 (9)   | N1—C8—C9    | 127.0 (3) |
| N1 <sup>i</sup> —Zn1—N2              | 117.01 (8)  | N1—C8—H8    | 116.5     |
| O1—Zn1—O1 <sup>i</sup>               | 76.26 (8)   | C9—C8—H8    | 116.5     |
| O2 <sup>i</sup> —Zn1—O1 <sup>i</sup> | 175.72 (8)  | C10—C9—C14  | 119.2 (3) |
| N1 <sup>i</sup> —Zn1—O1 <sup>i</sup> | 86.51 (8)   | C10—C9—C8   | 116.3 (2) |
| N2—Zn1—O1 <sup>i</sup>               | 90.23 (8)   | C14—C9—C8   | 124.4 (2) |
| C1—O1—Zn1                            | 135.25 (16) | C11—C10—C9  | 122.3 (3) |
| C1—O1—Zn1 <sup>i</sup>               | 120.19 (15) | C11—C10—H10 | 118.9     |
| Zn1—O1—Zn1 <sup>i</sup>              | 103.74 (8)  | C9—C10—H10  | 118.9     |
| C14—O2—Zn1 <sup>i</sup>              | 125.11 (17) | C10—C11—C12 | 118.8 (3) |
| C8—N1—C7                             | 117.6 (2)   | C10—C11—H11 | 120.6     |
| C8—N1—Zn1 <sup>i</sup>               | 122.84 (19) | C12—C11—H11 | 120.6     |
| C7—N1—Zn1 <sup>i</sup>               | 119.56 (18) | C13—C12—C11 | 120.6 (3) |
| C19—N2—C15                           | 117.8 (3)   | C13—C12—H12 | 119.7     |

## supplementary materials

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|  |             |                              |            |
|--|-------------|------------------------------|------------|
| C19—N2—Zn1                               | 122.13 (19) | C11—C12—H12                  | 119.7      |
| C15—N2—Zn1                               | 120.0 (2)   | C12—C13—C14                  | 122.7 (3)  |
| O1—C1—C2                                 | 121.8 (2)   | C12—C13—H13                  | 118.6      |
| O1—C1—C6                                 | 119.1 (2)   | C14—C13—H13                  | 118.6      |
| C2—C1—C6                                 | 119.1 (2)   | O2—C14—C13                   | 119.3 (2)  |
| C3—C2—C1                                 | 120.5 (3)   | O2—C14—C9                    | 124.3 (2)  |
| C3—C2—H2                                 | 119.8       | C13—C14—C9                   | 116.4 (3)  |
| C1—C2—H2                                 | 119.8       | N2—C15—C16                   | 122.3 (3)  |
| C4—C3—C2                                 | 120.4 (3)   | N2—C15—H15                   | 118.8      |
| C4—C3—H3                                 | 119.8       | C16—C15—H15                  | 118.8      |
| C2—C3—H3                                 | 119.8       | C17—C16—C15                  | 119.1 (3)  |
| C3—C4—C5                                 | 119.6 (3)   | C17—C16—H16                  | 120.5      |
| C3—C4—H4                                 | 120.2       | C15—C16—H16                  | 120.5      |
| C5—C4—H4                                 | 120.2       | C16—C17—C18                  | 119.6 (3)  |
| C4—C5—C6                                 | 121.5 (3)   | C16—C17—H17                  | 120.2      |
| C4—C5—H5                                 | 119.2       | C18—C17—H17                  | 120.2      |
| C6—C5—H5                                 | 119.2       | C17—C18—C19                  | 118.8 (3)  |
| C5—C6—C1                                 | 119.0 (3)   | C17—C18—H18                  | 120.6      |
| C5—C6—C7                                 | 122.1 (3)   | C19—C18—H18                  | 120.6      |
| C1—C6—C7                                 | 118.9 (2)   | N2—C19—C18                   | 122.3 (3)  |
| N1—C7—C6                                 | 112.5 (2)   | N2—C19—H19                   | 118.8      |
| N1—C7—H7A                                | 109.1       | C18—C19—H19                  | 118.8      |
| O2 <sup>i</sup> —Zn1—O1—C1               | -14.5 (3)   | C2—C1—C6—C7                  | -177.7 (2) |
| N1 <sup>i</sup> —Zn1—O1—C1               | -116.1 (2)  | C8—N1—C7—C6                  | -125.5 (3) |
| N2—Zn1—O1—C1                             | 84.8 (3)    | Zn1 <sup>i</sup> —N1—C7—C6   | 56.0 (3)   |
| O1 <sup>i</sup> —Zn1—O1—C1               | 169.1 (3)   | C5—C6—C7—N1                  | 122.3 (3)  |
| O2 <sup>i</sup> —Zn1—O1—Zn1 <sup>i</sup> | 176.41 (8)  | C1—C6—C7—N1                  | -60.5 (3)  |
| N1 <sup>i</sup> —Zn1—O1—Zn1 <sup>i</sup> | 74.75 (12)  | C7—N1—C8—C9                  | -178.2 (2) |
| N2—Zn1—O1—Zn1 <sup>i</sup>               | -84.36 (10) | Zn1 <sup>i</sup> —N1—C8—C9   | 0.3 (4)    |
| O1 <sup>i</sup> —Zn1—O1—Zn1 <sup>i</sup> | 0.0         | N1—C8—C9—C10                 | -171.4 (3) |
| O1—Zn1—N2—C19                            | 53.3 (2)    | N1—C8—C9—C14                 | 11.1 (4)   |
| O2 <sup>i</sup> —Zn1—N2—C19              | 157.3 (2)   | C14—C9—C10—C11               | -0.8 (5)   |
| N1 <sup>i</sup> —Zn1—N2—C19              | -108.1 (2)  | C8—C9—C10—C11                | -178.5 (3) |
| O1 <sup>i</sup> —Zn1—N2—C19              | -21.9 (2)   | C9—C10—C11—C12               | 0.4 (5)    |
| O1—Zn1—N2—C15                            | -128.6 (2)  | C10—C11—C12—C13              | 0.0 (6)    |
| O2 <sup>i</sup> —Zn1—N2—C15              | -24.6 (2)   | C11—C12—C13—C14              | -0.1 (6)   |
| N1 <sup>i</sup> —Zn1—N2—C15              | 70.0 (2)    | Zn1 <sup>i</sup> —O2—C14—C13 | 162.6 (2)  |
| O1 <sup>i</sup> —Zn1—N2—C15              | 156.2 (2)   | Zn1 <sup>i</sup> —O2—C14—C9  | -17.7 (4)  |
| Zn1—O1—C1—C2                             | 63.6 (4)    | C12—C13—C14—O2               | 179.6 (3)  |
| Zn1 <sup>i</sup> —O1—C1—C2               | -128.6 (2)  | C12—C13—C14—C9               | -0.2 (5)   |
| Zn1—O1—C1—C6                             | -118.3 (2)  | C10—C9—C14—O2                | -179.1 (3) |
| Zn1 <sup>i</sup> —O1—C1—C6               | 49.4 (3)    | C8—C9—C14—O2                 | -1.6 (4)   |
| O1—C1—C2—C3                              | 177.4 (3)   | C10—C9—C14—C13               | 0.6 (4)    |
| C6—C1—C2—C3                              | -0.6 (4)    | C8—C9—C14—C13                | 178.1 (3)  |
| C1—C2—C3—C4                              | 1.1 (5)     | C19—N2—C15—C16               | 0.8 (4)    |

|             |            |                 |            |
|-------------|------------|-----------------|------------|
| C2—C3—C4—C5 | -0.5 (5)   | Zn1—N2—C15—C16  | -177.4 (2) |
| C3—C4—C5—C6 | -0.6 (5)   | N2—C15—C16—C17  | 0.1 (5)    |
| C4—C5—C6—C1 | 1.0 (4)    | C15—C16—C17—C18 | -1.1 (5)   |
| C4—C5—C6—C7 | 178.2 (3)  | C16—C17—C18—C19 | 1.1 (5)    |
| O1—C1—C6—C5 | -178.5 (2) | C15—N2—C19—C18  | -0.7 (4)   |
| C2—C1—C6—C5 | -0.4 (4)   | Zn1—N2—C19—C18  | 177.5 (2)  |
| O1—C1—C6—C7 | 4.2 (4)    | C17—C18—C19—N2  | -0.3 (5)   |

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

Fig. 1

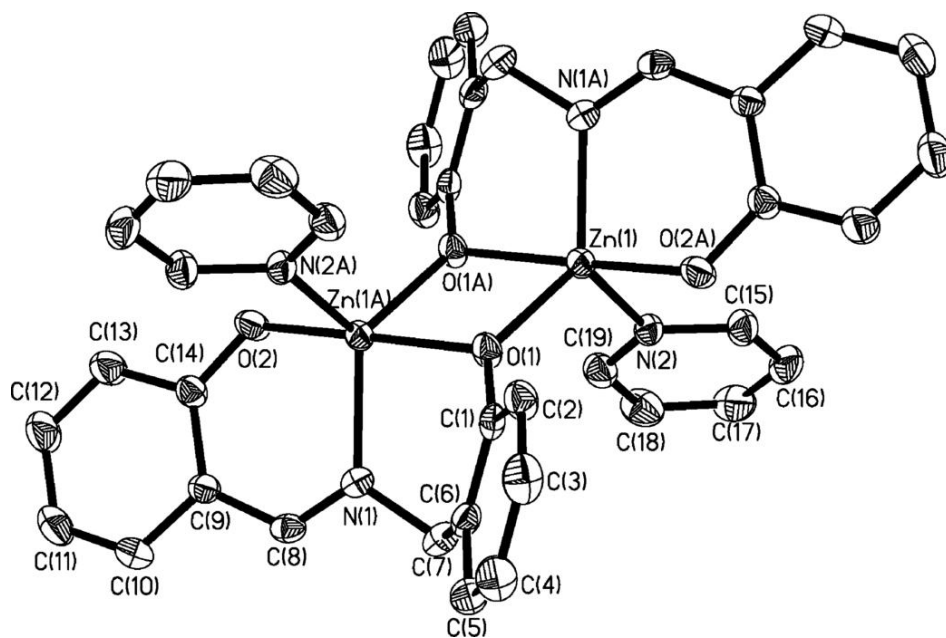


Fig. 2

