

# Dibenzoato- $\kappa$ O; $\kappa^2$ O, $O'$ -(6,6'-dimethyl-2,2'-bipyridine- $\kappa^2$ N, $N'$ )zinc(II)–benzoic acid (1/1)

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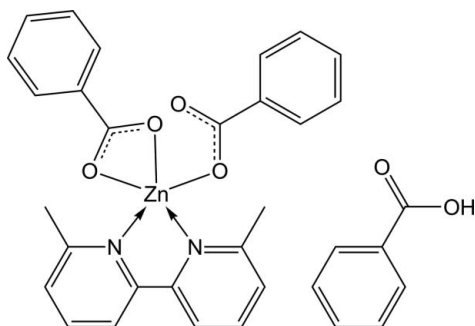
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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}–\text{C}) = 0.009$  Å; R factor = 0.065; wR factor = 0.136; data-to-parameter ratio = 14.3.

In the crystal structure of the title compound,  $[\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_{12}\text{H}_{12}\text{N}_2)] \cdot \text{C}_6\text{H}_5\text{COOH}$ , the Zn atom is pentacoordinated in distorted square-pyramidal geometry by two O atoms of a benzoate anion and two N atoms of a 6,6'-dimethyl-2,2'-bipyridine ligand occupying the basal plane and an O atom of another benzoate anion located at the apical site. In the crystal structure, intermolecular O–H...O and C–H...O hydrogen bonds and C–H... $\pi$  interactions are present.

## Related literature

For related structures, see: Alizadeh *et al.* (2009); Cui *et al.* (2005); Hökelek *et al.* (2009a,b); Klausmeyer *et al.* (2007); Phatchimkun *et al.* (2009); Zhang *et al.* (2009).



## Experimental

### Crystal data

$[\text{Zn}(\text{C}_6\text{H}_5\text{O}_2)_2(\text{C}_{12}\text{H}_{12}\text{N}_2)] \cdot \text{C}_7\text{H}_6\text{O}_2$   
 $M_r = 613.96$   
 Triclinic,  $P\bar{1}$   
 $a = 9.974$  (6) Å  
 $b = 12.546$  (7) Å  
 $c = 12.798$  (8) Å  
 $\alpha = 96.631$  (11)°  
 $\beta = 97.016$  (12)°  
 $\gamma = 105.060$  (12)°  
 $V = 1516.7$  (16) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.86$  mm<sup>-1</sup>  
 $T = 296$  K  
 $0.16 \times 0.14 \times 0.12$  mm

### Data collection

Bruker APEXII CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 2005)  
 $T_{\min} = 0.875$ ,  $T_{\max} = 0.904$   
 8123 measured reflections  
 5295 independent reflections  
 2785 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.046$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$   
 $wR(F^2) = 0.136$   
 $S = 1.04$   
 5295 reflections  
 370 parameters  
 14 restraints  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.64$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.64$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D–H \cdots A$                                  | $D–H$ | $H \cdots A$ | $D \cdots A$ | $D–H \cdots A$ |
|---|-------|--------------|--------------|----------------|
| $\text{C24}–\text{H24} \cdots \text{O5}^i$      | 0.93  | 2.44         | 3.340 (8)    | 162            |
| $\text{C33}–\text{H33C} \cdots \text{O1}$       | 0.96  | 2.52         | 3.199 (8)    | 128            |
| $\text{C22}–\text{H22A} \cdots \text{O2}$       | 0.96  | 2.57         | 3.289 (7)    | 132            |
| $\text{O6}–\text{H6} \cdots \text{O4}^{ii}$     | 0.82  | 1.85         | 2.655 (5)    | 166            |
| $\text{C31}–\text{H31} \cdots \text{Cg1}^{iii}$ | 0.93  | 2.79         | 3.708 (7)    | 170            |

Symmetry codes: (i)  $-x, -y, -z + 1$ ; (ii)  $x, y, z + 1$ ; (iii)  $-x + 1, -y + 1, -z$ . Cg1 is the centroid of the C9–C14 ring.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; 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.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2173).

## References

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**supplementary materials**

*Acta Cryst.* (2009). E65, m1408 [ doi:10.1107/S1600536809042093 ]

## Dibenzoato- $\kappa O$ ; $\kappa^2 O, O'$ -(6,6'-dimethyl-2,2'-bipyridine- $\kappa^2 N, N'$ )zinc(II)-benzoic acid (1/1)

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### Comment

As a contribution to structural characterization of 6,6'-dimethyl-2,2'-bipyridine complexes [Alizadeh *et al.*, (2009); Cui *et al.*, (2005); Hökelek *et al.*, (2009a,b); Klausmeyer *et al.*, (2007); Phatchimkun *et al.* (2009); Zhang *et al.*, (2009)], we present here the molecular structure of the title complex,  $ZnL(C_6H_5COO)_2C_6H_5COOH$ , where  $L$  is 6,6'-dimethyl-2,2'-bipyridine.

The title compound, contains two benzoate anions, one 6,6'-dimethyl-2,2'-bipyridine ligand and one benzoic acid molecules. One of the benzoate anions acts as a bidentate ligand, while the other is monodentate.

The molecular structure of the title complex is shown on Fig. 1. In the crystal structure, the face-to-face separation of 3.783 (4)Å suggests no  $\pi \cdots \pi$  stacking between parallel bipyridine ring systems, intermolecular O—H $\cdots$ O and C—H $\cdots$ O hydrogen bonds (Table 1) link the molecules into a one dimensional structure, in which they may be effective in the stabilization of the structure. One weak C—H $\cdots$  $\pi$  interactions (Table 1) are also found. Cg1 is the centroid of the C9<sup>iii</sup>-C14<sup>iii</sup> ring. Symmetry code: (iii) 1-x, 1-y, -z.

### Experimental

The title compound was synthesized hydrothermally in a teflon-lined autoclave (25 ml) by heating a mixture of 6,6'-dimethyl-2,2'-bipyridine (0.2 mmol), benzoic acid (0.4 mmol) and  $ZnSO_4 \cdot H_2O$  (0.2 mmol) in water (10 ml) at 393 K for 3 d. Crystals suitable for X-ray analysis were obtained.

### Refinement

The carboxy H atom was located in a difference Fourier map and refined with a O—H distance of 0.82Å [ $U_{iso}(H) = 1.5U_{eq}(O)$ ]. H atoms bonded to C atoms were positioned geometrically and refined using a riding model with C—H = 0.93Å and 0.96Å for aromatic and methyl H atoms, respectively, and  $U_{iso}(H)$  values were calculated at 1.5 $U_{eq}(C)$  for methyl groups and 1.2 $U_{eq}(C)$  for aromatic.

### Figures

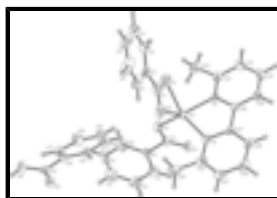


Fig. 1. The molecular structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are presented as small spheres of arbitrary radius.

## Dibenzoato- $\kappa O; \kappa^2 O, O'$ -(6,6'-dimethyl-2,2'-bipyridine- $\kappa^2 N, N'$ )zinc(II)-benzoic acid (1/1)

### Crystal data

|  |   |
|--|---|
| $[\text{Zn}(\text{C}_7\text{H}_5\text{O}_2)_2(\text{C}_{12}\text{H}_{12}\text{N}_2)] \cdot \text{C}_7\text{H}_6\text{O}_2$ | $Z = 2$   |
| $M_r = 613.96$   | $F_{000} = 636$   |
| Triclinic, $P\bar{1}$  | $D_x = 1.344 \text{ Mg m}^{-3}$                         |
| Hall symbol: -P 1  | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $a = 9.974 (6) \text{ \AA}$  | Cell parameters from 1683 reflections                   |
| $b = 12.546 (7) \text{ \AA}$   | $\theta = 2.5\text{--}27.8^\circ$                       |
| $c = 12.798 (8) \text{ \AA}$   | $\mu = 0.86 \text{ mm}^{-1}$                            |
| $\alpha = 96.631 (11)^\circ$   | $T = 296 \text{ K}$                                     |
| $\beta = 97.016 (12)^\circ$  | Block, colourless                                       |
| $\gamma = 105.060 (12)^\circ$  | $0.16 \times 0.14 \times 0.12 \text{ mm}$               |
| $V = 1516.7 (16) \text{ \AA}^3$  |   |

### Data collection

|  |  |
|--|--|
| Bruker APEXII CCD area-detector diffractometer           | 5295 independent reflections           |
| Radiation source: fine-focus sealed tube                 | 2785 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite                                  | $R_{\text{int}} = 0.046$               |
| $T = 296 \text{ K}$                                      | $\theta_{\text{max}} = 25.0^\circ$     |
| $\varphi$ - and $\omega$ -scans                          | $\theta_{\text{min}} = 1.6^\circ$      |
| Absorption correction: multi-scan (SADABS; Bruker, 2005) | $h = -10 \rightarrow 11$               |
| $T_{\text{min}} = 0.875$ , $T_{\text{max}} = 0.904$      | $k = -14 \rightarrow 13$               |
| 8123 measured reflections                                | $l = -15 \rightarrow 15$               |

### Refinement

|  |  |
|--|--|
| Refinement on $F^2$  | Secondary atom site location: difference Fourier map     |
| Least-squares matrix: full                                     | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.065$                                | H-atom parameters constrained                            |
| $wR(F^2) = 0.136$  | $w = 1/[\sigma^2(F_o^2) + (0.0455P)^2]$                  |
| $S = 1.04$   | where $P = (F_o^2 + 2F_c^2)/3$                           |
| 5295 reflections   | $(\Delta/\sigma)_{\text{max}} < 0.001$                   |
| 370 parameters   | $\Delta\rho_{\text{max}} = 0.64 \text{ e \AA}^{-3}$      |
| 14 restraints  | $\Delta\rho_{\text{min}} = -0.64 \text{ e \AA}^{-3}$     |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none                              |

*Special details*

**Geometry.** All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )*

|     | x           | y           | z           | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|-------------|----------------------------------|
| Zn1 | 0.41555 (6) | 0.22239 (5) | 0.15235 (4) | 0.0561 (2)                       |
| N1  | 0.2722 (4)  | 0.0734 (3)  | 0.0835 (3)  | 0.0509 (10)                      |
| N2  | 0.4792 (4)  | 0.2028 (3)  | 0.0057 (3)  | 0.0461 (10)                      |
| O1  | 0.6236 (4)  | 0.2621 (4)  | 0.2360 (3)  | 0.1060 (12)                      |
| O2  | 0.4751 (4)  | 0.1472 (3)  | 0.2994 (3)  | 0.0945 (13)                      |
| O3  | 0.3506 (4)  | 0.3454 (3)  | 0.2070 (3)  | 0.0708 (10)                      |
| O4  | 0.2026 (4)  | 0.3185 (3)  | 0.0566 (2)  | 0.0672 (10)                      |
| O5  | 0.1962 (4)  | 0.1688 (3)  | 0.8042 (3)  | 0.0760 (11)                      |
| O6  | 0.2806 (4)  | 0.3497 (3)  | 0.8688 (3)  | 0.0717 (10)                      |
| H6  | 0.2520      | 0.3287      | 0.9225      | 0.108*                           |
| C1  | 0.5999 (8)  | 0.1987 (7)  | 0.3044 (5)  | 0.1025 (12)                      |
| C2  | 0.7122 (5)  | 0.1859 (4)  | 0.3773 (3)  | 0.0997 (13)                      |
| C3  | 0.8523 (6)  | 0.2392 (4)  | 0.3750 (4)  | 0.128 (3)                        |
| H3  | 0.8755      | 0.2882      | 0.3265      | 0.153*                           |
| C4  | 0.9579 (4)  | 0.2192 (5)  | 0.4450 (5)  | 0.164 (4)                        |
| H4  | 1.0517      | 0.2549      | 0.4434      | 0.196*                           |
| C5  | 0.9232 (6)  | 0.1460 (5)  | 0.5174 (4)  | 0.172 (5)                        |
| H5  | 0.9938      | 0.1326      | 0.5642      | 0.206*                           |
| C6  | 0.7831 (7)  | 0.0926 (4)  | 0.5197 (4)  | 0.153 (4)                        |
| H6A | 0.7599      | 0.0436      | 0.5681      | 0.183*                           |
| C7  | 0.6775 (5)  | 0.1126 (4)  | 0.4497 (4)  | 0.111 (3)                        |
| H7  | 0.5837      | 0.0769      | 0.4513      | 0.134*                           |
| C8  | 0.2506 (6)  | 0.3676 (4)  | 0.1480 (4)  | 0.0535 (13)                      |
| C9  | 0.1893 (5)  | 0.4536 (4)  | 0.1966 (4)  | 0.0537 (13)                      |
| C10 | 0.2524 (7)  | 0.5206 (5)  | 0.2920 (4)  | 0.0894 (19)                      |
| H10 | 0.3346      | 0.5114      | 0.3277      | 0.107*                           |
| C11 | 0.1952 (9)  | 0.6015 (6)  | 0.3357 (5)  | 0.116 (2)                        |
| H11 | 0.2383      | 0.6463      | 0.4003      | 0.139*                           |
| C12 | 0.0740 (9)  | 0.6148 (6)  | 0.2822 (7)  | 0.125 (3)                        |
| H12 | 0.0324      | 0.6668      | 0.3120      | 0.150*                           |
| C13 | 0.0151 (7)  | 0.5522 (6)  | 0.1864 (7)  | 0.117 (3)                        |
| H13 | -0.0654     | 0.5631      | 0.1496      | 0.140*                           |
| C14 | 0.0726 (6)  | 0.4730 (4)  | 0.1430 (5)  | 0.0780 (17)                      |

## supplementary materials

|      |            |             |             |             |
|------|------------|-------------|-------------|-------------|
| H14  | 0.0320     | 0.4318      | 0.0763      | 0.094*      |
| C15  | 0.2525 (5) | 0.2627 (5)  | 0.7920 (4)  | 0.0529 (13) |
| C16  | 0.2973 (5) | 0.2925 (5)  | 0.6902 (4)  | 0.0538 (13) |
| C17  | 0.3171 (6) | 0.3999 (5)  | 0.6671 (4)  | 0.0758 (16) |
| H17  | 0.3070     | 0.4564      | 0.7167      | 0.091*      |
| C18  | 0.3528 (7) | 0.4224 (6)  | 0.5677 (5)  | 0.097 (2)   |
| H18  | 0.3660     | 0.4941      | 0.5508      | 0.116*      |
| C19  | 0.3684 (7) | 0.3383 (7)  | 0.4953 (5)  | 0.098 (2)   |
| H19  | 0.3910     | 0.3533      | 0.4291      | 0.118*      |
| C20  | 0.3510 (6) | 0.2331 (6)  | 0.5199 (5)  | 0.0866 (19) |
| H20  | 0.3653     | 0.1771      | 0.4720      | 0.104*      |
| C21  | 0.3122 (5) | 0.2107 (5)  | 0.6159 (4)  | 0.0689 (15) |
| H21  | 0.2955     | 0.1380      | 0.6308      | 0.083*      |
| C22  | 0.1317 (6) | 0.0689 (5)  | 0.2271 (4)  | 0.0847 (18) |
| H22A | 0.2067     | 0.0747      | 0.2840      | 0.127*      |
| H22B | 0.0452     | 0.0241      | 0.2431      | 0.127*      |
| H22C | 0.1232     | 0.1421      | 0.2192      | 0.127*      |
| C23  | 0.1631 (6) | 0.0156 (5)  | 0.1256 (4)  | 0.0633 (15) |
| C24  | 0.0820 (6) | -0.0880 (5) | 0.0732 (6)  | 0.0798 (18) |
| H24  | 0.0049     | -0.1267     | 0.1009      | 0.096*      |
| C25  | 0.1145 (7) | -0.1335 (5) | -0.0189 (6) | 0.087 (2)   |
| H25  | 0.0622     | -0.2045     | -0.0524     | 0.105*      |
| C26  | 0.2243 (6) | -0.0747 (4) | -0.0621 (4) | 0.0719 (16) |
| H26  | 0.2461     | -0.1040     | -0.1259     | 0.086*      |
| C27  | 0.3021 (5) | 0.0296 (4)  | -0.0087 (4) | 0.0482 (12) |
| C28  | 0.4195 (5) | 0.1021 (4)  | -0.0519 (4) | 0.0471 (12) |
| C29  | 0.4627 (6) | 0.0693 (5)  | -0.1451 (4) | 0.0648 (15) |
| H29  | 0.4218     | -0.0020     | -0.1832     | 0.078*      |
| C30  | 0.5682 (7) | 0.1441 (6)  | -0.1813 (4) | 0.0785 (17) |
| H30  | 0.5997     | 0.1236      | -0.2440     | 0.094*      |
| C31  | 0.6250 (6) | 0.2471 (5)  | -0.1248 (5) | 0.0753 (16) |
| H31  | 0.6951     | 0.2982      | -0.1492     | 0.090*      |
| C32  | 0.5798 (6) | 0.2774 (4)  | -0.0311 (4) | 0.0601 (14) |
| C33  | 0.6386 (6) | 0.3902 (4)  | 0.0338 (5)  | 0.095 (2)   |
| H33A | 0.5630     | 0.4200      | 0.0507      | 0.142*      |
| H33B | 0.6962     | 0.4388      | -0.0060     | 0.142*      |
| H33C | 0.6944     | 0.3846      | 0.0985      | 0.142*      |

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

|     | $U^{11}$    | $U^{22}$   | $U^{33}$   | $U^{12}$    | $U^{13}$     | $U^{23}$     |
|-----|-------------|------------|------------|-------------|--------------|--------------|
| Zn1 | 0.0556 (4)  | 0.0578 (4) | 0.0511 (4) | 0.0185 (3)  | -0.0002 (3)  | -0.0035 (3)  |
| N1  | 0.040 (2)   | 0.057 (3)  | 0.053 (3)  | 0.013 (2)   | -0.002 (2)   | 0.013 (2)    |
| N2  | 0.038 (2)   | 0.046 (3)  | 0.054 (2)  | 0.016 (2)   | 0.005 (2)    | 0.002 (2)    |
| O1  | 0.0884 (18) | 0.162 (3)  | 0.069 (2)  | 0.063 (2)   | -0.0244 (18) | -0.003 (2)   |
| O2  | 0.093 (3)   | 0.124 (3)  | 0.066 (2)  | 0.061 (3)   | -0.034 (2)   | -0.0054 (18) |
| O3  | 0.081 (3)   | 0.074 (2)  | 0.056 (2)  | 0.037 (2)   | -0.008 (2)   | -0.0079 (18) |
| O4  | 0.078 (3)   | 0.075 (2)  | 0.044 (2)  | 0.0216 (19) | 0.0045 (19)  | -0.0047 (18) |

|     |            |            |           |            |              |             |
|-----|------------|------------|-----------|------------|--------------|-------------|
| O5  | 0.092 (3)  | 0.073 (3)  | 0.065 (2) | 0.021 (2)  | 0.019 (2)    | 0.014 (2)   |
| O6  | 0.100 (3)  | 0.068 (2)  | 0.051 (2) | 0.030 (2)  | 0.016 (2)    | 0.0073 (19) |
| C1  | 0.086 (2)  | 0.158 (3)  | 0.066 (2) | 0.065 (2)  | -0.0219 (19) | -0.006 (2)  |
| C2  | 0.084 (2)  | 0.155 (4)  | 0.064 (2) | 0.066 (2)  | -0.021 (2)   | -0.007 (2)  |
| C3  | 0.075 (5)  | 0.201 (8)  | 0.097 (5) | 0.050 (5)  | 0.003 (4)    | -0.027 (5)  |
| C4  | 0.096 (6)  | 0.256 (12) | 0.121 (7) | 0.078 (7)  | -0.032 (6)   | -0.055 (7)  |
| C5  | 0.135 (9)  | 0.205 (11) | 0.155 (9) | 0.101 (8)  | -0.086 (7)   | -0.069 (8)  |
| C6  | 0.211 (10) | 0.094 (6)  | 0.134 (7) | 0.068 (6)  | -0.083 (7)   | -0.003 (5)  |
| C7  | 0.117 (6)  | 0.095 (5)  | 0.100 (5) | 0.043 (4)  | -0.057 (5)   | -0.030 (4)  |
| C8  | 0.068 (4)  | 0.049 (3)  | 0.042 (3) | 0.014 (3)  | 0.014 (3)    | 0.003 (3)   |
| C9  | 0.059 (3)  | 0.053 (3)  | 0.047 (3) | 0.019 (3)  | 0.006 (3)    | -0.002 (3)  |
| C10 | 0.120 (5)  | 0.095 (5)  | 0.063 (4) | 0.058 (4)  | 0.004 (4)    | -0.005 (3)  |
| C11 | 0.160 (8)  | 0.120 (6)  | 0.075 (5) | 0.071 (6)  | 0.012 (5)    | -0.024 (4)  |
| C12 | 0.114 (7)  | 0.120 (6)  | 0.147 (7) | 0.064 (5)  | 0.025 (6)    | -0.030 (6)  |
| C13 | 0.071 (5)  | 0.101 (6)  | 0.166 (8) | 0.039 (4)  | -0.012 (5)   | -0.033 (5)  |
| C14 | 0.060 (4)  | 0.068 (4)  | 0.096 (4) | 0.021 (3)  | -0.003 (4)   | -0.016 (3)  |
| C15 | 0.048 (3)  | 0.059 (4)  | 0.055 (3) | 0.022 (3)  | 0.005 (3)    | 0.011 (3)   |
| C16 | 0.049 (3)  | 0.066 (4)  | 0.045 (3) | 0.016 (3)  | 0.002 (3)    | 0.009 (3)   |
| C17 | 0.075 (4)  | 0.082 (5)  | 0.065 (4) | 0.012 (3)  | 0.011 (3)    | 0.013 (3)   |
| C18 | 0.103 (5)  | 0.101 (5)  | 0.074 (4) | -0.001 (4) | 0.018 (4)    | 0.028 (4)   |
| C19 | 0.090 (5)  | 0.141 (7)  | 0.055 (4) | 0.014 (5)  | 0.017 (4)    | 0.018 (5)   |
| C20 | 0.084 (5)  | 0.117 (6)  | 0.060 (4) | 0.031 (4)  | 0.015 (3)    | 0.002 (4)   |
| C21 | 0.072 (4)  | 0.082 (4)  | 0.054 (3) | 0.026 (3)  | 0.009 (3)    | 0.006 (3)   |
| C22 | 0.063 (4)  | 0.116 (5)  | 0.078 (4) | 0.021 (4)  | 0.014 (3)    | 0.026 (4)   |
| C23 | 0.052 (4)  | 0.069 (4)  | 0.069 (4) | 0.018 (3)  | -0.006 (3)   | 0.025 (3)   |
| C24 | 0.058 (4)  | 0.065 (5)  | 0.110 (5) | 0.003 (3)  | 0.001 (4)    | 0.034 (4)   |
| C25 | 0.075 (5)  | 0.056 (4)  | 0.114 (6) | 0.004 (4)  | -0.017 (4)   | 0.008 (4)   |
| C26 | 0.069 (4)  | 0.054 (4)  | 0.079 (4) | 0.011 (3)  | -0.012 (3)   | -0.004 (3)  |
| C27 | 0.046 (3)  | 0.043 (3)  | 0.051 (3) | 0.015 (3)  | -0.012 (3)   | 0.002 (3)   |
| C28 | 0.047 (3)  | 0.046 (3)  | 0.051 (3) | 0.025 (3)  | -0.003 (3)   | 0.000 (3)   |
| C29 | 0.076 (4)  | 0.061 (4)  | 0.060 (4) | 0.032 (3)  | 0.005 (3)    | -0.008 (3)  |
| C30 | 0.096 (5)  | 0.104 (5)  | 0.055 (4) | 0.053 (4)  | 0.030 (4)    | 0.016 (4)   |
| C31 | 0.073 (4)  | 0.086 (5)  | 0.074 (4) | 0.030 (4)  | 0.019 (3)    | 0.017 (4)   |
| C32 | 0.060 (4)  | 0.056 (4)  | 0.064 (4) | 0.019 (3)  | 0.005 (3)    | 0.009 (3)   |
| C33 | 0.099 (5)  | 0.066 (4)  | 0.099 (4) | -0.012 (3) | 0.023 (4)    | 0.005 (4)   |

*Geometric parameters (Å, °)*

|        |           |         |           |
|--------|-----------|---------|-----------|
| Zn1—O3 | 1.917 (3) | C13—H13 | 0.9300    |
| Zn1—N1 | 2.059 (4) | C14—H14 | 0.9300    |
| Zn1—N2 | 2.062 (4) | C15—C16 | 1.484 (7) |
| Zn1—O1 | 2.120 (4) | C16—C21 | 1.368 (6) |
| Zn1—O2 | 2.283 (4) | C16—C17 | 1.381 (7) |
| N1—C27 | 1.344 (6) | C17—C18 | 1.402 (7) |
| N1—C23 | 1.350 (6) | C17—H17 | 0.9300    |
| N2—C28 | 1.335 (5) | C18—C19 | 1.375 (8) |
| N2—C32 | 1.353 (6) | C18—H18 | 0.9300    |
| O1—C1  | 1.252 (8) | C19—C20 | 1.365 (8) |
| O2—C1  | 1.235 (8) | C19—H19 | 0.9300    |

## supplementary materials

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|            |             |              |           |
|------------|-------------|--------------|-----------|
| O3—C8      | 1.285 (5)   | C20—C21      | 1.369 (7) |
| O4—C8      | 1.233 (5)   | C20—H20      | 0.9300    |
| O5—C15     | 1.204 (5)   | C21—H21      | 0.9300    |
| O6—C15     | 1.327 (5)   | C22—C23      | 1.496 (7) |
| O6—H6      | 0.8200      | C22—H22A     | 0.9600    |
| C1—C2      | 1.423 (7)   | C22—H22B     | 0.9600    |
| C2—C3      | 1.3900      | C22—H22C     | 0.9600    |
| C2—C7      | 1.3900      | C23—C24      | 1.384 (7) |
| C3—C4      | 1.3900      | C24—C25      | 1.362 (8) |
| C3—H3      | 0.9300      | C24—H24      | 0.9300    |
| C4—C5      | 1.3900      | C25—C26      | 1.368 (8) |
| C4—H4      | 0.9300      | C25—H25      | 0.9300    |
| C5—C6      | 1.3900      | C26—C27      | 1.384 (6) |
| C5—H5      | 0.9300      | C26—H26      | 0.9300    |
| C6—C7      | 1.3900      | C27—C28      | 1.492 (6) |
| C6—H6A     | 0.9300      | C28—C29      | 1.372 (6) |
| C7—H7      | 0.9300      | C29—C30      | 1.382 (7) |
| C8—C9      | 1.485 (7)   | C29—H29      | 0.9300    |
| C9—C14     | 1.369 (6)   | C30—C31      | 1.349 (7) |
| C9—C10     | 1.377 (6)   | C30—H30      | 0.9300    |
| C10—C11    | 1.384 (8)   | C31—C32      | 1.379 (7) |
| C10—H10    | 0.9300      | C31—H31      | 0.9300    |
| C11—C12    | 1.374 (9)   | C32—C33      | 1.488 (7) |
| C11—H11    | 0.9300      | C33—H33A     | 0.9600    |
| C12—C13    | 1.352 (8)   | C33—H33B     | 0.9600    |
| C12—H12    | 0.9300      | C33—H33C     | 0.9600    |
| C13—C14    | 1.369 (8)   |              |           |
| O3—Zn1—N1  | 119.74 (16) | O5—C15—C16   | 123.5 (5) |
| O3—Zn1—N2  | 124.65 (15) | O6—C15—C16   | 113.6 (5) |
| N1—Zn1—N2  | 80.07 (17)  | C21—C16—C17  | 119.5 (5) |
| O3—Zn1—O1  | 102.78 (16) | C21—C16—C15  | 119.1 (5) |
| N1—Zn1—O1  | 132.61 (16) | C17—C16—C15  | 121.3 (5) |
| N2—Zn1—O1  | 93.04 (16)  | C16—C17—C18  | 119.0 (6) |
| O3—Zn1—O2  | 104.33 (15) | C16—C17—H17  | 120.5     |
| N1—Zn1—O2  | 91.25 (15)  | C18—C17—H17  | 120.5     |
| N2—Zn1—O2  | 127.89 (14) | C19—C18—C17  | 120.0 (6) |
| O1—Zn1—O2  | 56.64 (17)  | C19—C18—H18  | 120.0     |
| C27—N1—C23 | 119.8 (4)   | C17—C18—H18  | 120.0     |
| C27—N1—Zn1 | 113.4 (3)   | C20—C19—C18  | 120.4 (6) |
| C23—N1—Zn1 | 126.6 (4)   | C20—C19—H19  | 119.8     |
| C28—N2—C32 | 119.6 (4)   | C18—C19—H19  | 119.8     |
| C28—N2—Zn1 | 113.8 (3)   | C19—C20—C21  | 119.4 (6) |
| C32—N2—Zn1 | 126.4 (3)   | C19—C20—H20  | 120.3     |
| C1—O1—Zn1  | 98.0 (4)    | C21—C20—H20  | 120.3     |
| C1—O2—Zn1  | 90.6 (4)    | C20—C21—C16  | 121.6 (6) |
| C8—O3—Zn1  | 117.4 (3)   | C20—C21—H21  | 119.2     |
| C15—O6—H6  | 109.5       | C16—C21—H21  | 119.2     |
| O2—C1—O1   | 114.7 (6)   | C23—C22—H22A | 109.5     |
| O2—C1—C2   | 124.5 (7)   | C23—C22—H22B | 109.5     |



|               |            |                 |            |
|---------------|------------|-----------------|------------|
| O1—C1—C2      | 120.8 (7)  | H22A—C22—H22B   | 109.5      |
| C3—C2—C7      | 120.0      | C23—C22—H22C    | 109.5      |
| C3—C2—C1      | 122.6 (5)  | H22A—C22—H22C   | 109.5      |
| C7—C2—C1      | 117.3 (5)  | H22B—C22—H22C   | 109.5      |
| C4—C3—C2      | 120.0      | N1—C23—C24      | 119.8 (5)  |
| C4—C3—H3      | 120.0      | N1—C23—C22      | 117.9 (5)  |
| C2—C3—H3      | 120.0      | C24—C23—C22     | 122.2 (6)  |
| C3—C4—C5      | 120.0      | C25—C24—C23     | 120.2 (6)  |
| C3—C4—H4      | 120.0      | C25—C24—H24     | 119.9      |
| C5—C4—H4      | 120.0      | C23—C24—H24     | 119.9      |
| C4—C5—C6      | 120.0      | C24—C25—C26     | 120.0 (6)  |
| C4—C5—H5      | 120.0      | C24—C25—H25     | 120.0      |
| C6—C5—H5      | 120.0      | C26—C25—H25     | 120.0      |
| C7—C6—C5      | 120.0      | C25—C26—C27     | 118.4 (6)  |
| C7—C6—H6A     | 120.0      | C25—C26—H26     | 120.8      |
| C5—C6—H6A     | 120.0      | C27—C26—H26     | 120.8      |
| C6—C7—C2      | 120.0      | N1—C27—C26      | 121.7 (5)  |
| C6—C7—H7      | 120.0      | N1—C27—C28      | 115.9 (4)  |
| C2—C7—H7      | 120.0      | C26—C27—C28     | 122.4 (5)  |
| O4—C8—O3      | 123.0 (5)  | N2—C28—C29      | 121.7 (5)  |
| O4—C8—C9      | 120.3 (5)  | N2—C28—C27      | 115.4 (4)  |
| O3—C8—C9      | 116.7 (4)  | C29—C28—C27     | 122.9 (5)  |
| C14—C9—C10    | 118.3 (5)  | C28—C29—C30     | 118.8 (5)  |
| C14—C9—C8     | 120.0 (5)  | C28—C29—H29     | 120.6      |
| C10—C9—C8     | 121.6 (5)  | C30—C29—H29     | 120.6      |
| C9—C10—C11    | 121.0 (6)  | C31—C30—C29     | 119.3 (5)  |
| C9—C10—H10    | 119.5      | C31—C30—H30     | 120.4      |
| C11—C10—H10   | 119.5      | C29—C30—H30     | 120.4      |
| C12—C11—C10   | 119.1 (6)  | C30—C31—C32     | 120.5 (6)  |
| C12—C11—H11   | 120.5      | C30—C31—H31     | 119.7      |
| C10—C11—H11   | 120.5      | C32—C31—H31     | 119.7      |
| C13—C12—C11   | 120.0 (7)  | N2—C32—C31      | 120.0 (5)  |
| C13—C12—H12   | 120.0      | N2—C32—C33      | 117.5 (5)  |
| C11—C12—H12   | 120.0      | C31—C32—C33     | 122.5 (5)  |
| C12—C13—C14   | 120.8 (7)  | C32—C33—H33A    | 109.5      |
| C12—C13—H13   | 119.6      | C32—C33—H33B    | 109.5      |
| C14—C13—H13   | 119.6      | H33A—C33—H33B   | 109.5      |
| C9—C14—C13    | 120.8 (6)  | C32—C33—H33C    | 109.5      |
| C9—C14—H14    | 119.6      | H33A—C33—H33C   | 109.5      |
| C13—C14—H14   | 119.6      | H33B—C33—H33C   | 109.5      |
| O5—C15—O6     | 122.9 (5)  |                 |            |
| O3—Zn1—N1—C27 | 134.4 (3)  | C8—C9—C10—C11   | 179.1 (6)  |
| N2—Zn1—N1—C27 | 10.0 (3)   | C9—C10—C11—C12  | -0.2 (11)  |
| O1—Zn1—N1—C27 | -74.9 (4)  | C10—C11—C12—C13 | -2.5 (13)  |
| O2—Zn1—N1—C27 | -118.3 (3) | C11—C12—C13—C14 | 1.9 (13)   |
| O3—Zn1—N1—C23 | -50.8 (4)  | C10—C9—C14—C13  | -4.0 (9)   |
| N2—Zn1—N1—C23 | -175.2 (4) | C8—C9—C14—C13   | -179.8 (6) |
| O1—Zn1—N1—C23 | 99.9 (4)   | C12—C13—C14—C9  | 1.4 (11)   |
| O2—Zn1—N1—C23 | 56.5 (4)   | O5—C15—C16—C21  | -18.5 (7)  |

## supplementary materials

|                |            |                 |            |
|----------------|------------|-----------------|------------|
| O3—Zn1—N2—C28  | -130.2 (3) | O6—C15—C16—C21  | 161.4 (4)  |
| N1—Zn1—N2—C28  | -10.8 (3)  | O5—C15—C16—C17  | 158.1 (5)  |
| O1—Zn1—N2—C28  | 122.0 (3)  | O6—C15—C16—C17  | -22.0 (6)  |
| O2—Zn1—N2—C28  | 73.0 (3)   | C21—C16—C17—C18 | -0.3 (8)   |
| O3—Zn1—N2—C32  | 55.2 (4)   | C15—C16—C17—C18 | -176.9 (5) |
| N1—Zn1—N2—C32  | 174.6 (4)  | C16—C17—C18—C19 | -0.4 (9)   |
| O1—Zn1—N2—C32  | -52.6 (4)  | C17—C18—C19—C20 | -0.8 (10)  |
| O2—Zn1—N2—C32  | -101.6 (4) | C18—C19—C20—C21 | 2.6 (10)   |
| O3—Zn1—O1—C1   | 100.7 (4)  | C19—C20—C21—C16 | -3.4 (9)   |
| N1—Zn1—O1—C1   | -53.5 (5)  | C17—C16—C21—C20 | 2.2 (8)    |
| N2—Zn1—O1—C1   | -132.8 (4) | C15—C16—C21—C20 | 178.9 (5)  |
| O2—Zn1—O1—C1   | 1.8 (4)    | C27—N1—C23—C24  | -0.5 (7)   |
| O3—Zn1—O2—C1   | -97.8 (4)  | Zn1—N1—C23—C24  | -175.0 (4) |
| N1—Zn1—O2—C1   | 141.0 (4)  | C27—N1—C23—C22  | -178.6 (4) |
| N2—Zn1—O2—C1   | 62.6 (4)   | Zn1—N1—C23—C22  | 6.9 (6)    |
| O1—Zn1—O2—C1   | -1.8 (4)   | N1—C23—C24—C25  | 2.1 (8)    |
| N1—Zn1—O3—C8   | -45.9 (4)  | C22—C23—C24—C25 | -179.9 (5) |
| N2—Zn1—O3—C8   | 52.9 (4)   | C23—C24—C25—C26 | -2.7 (9)   |
| O1—Zn1—O3—C8   | 155.8 (3)  | C24—C25—C26—C27 | 1.6 (8)    |
| O2—Zn1—O3—C8   | -145.8 (3) | C23—N1—C27—C26  | -0.6 (6)   |
| Zn1—O2—C1—O1   | 2.8 (6)    | Zn1—N1—C27—C26  | 174.6 (3)  |
| Zn1—O2—C1—C2   | -174.3 (6) | C23—N1—C27—C28  | 176.8 (4)  |
| Zn1—O1—C1—O2   | -3.0 (7)   | Zn1—N1—C27—C28  | -7.9 (5)   |
| Zn1—O1—C1—C2   | 174.2 (5)  | C25—C26—C27—N1  | 0.1 (7)    |
| O2—C1—C2—C3    | 175.0 (5)  | C25—C26—C27—C28 | -177.2 (5) |
| O1—C1—C2—C3    | -1.9 (8)   | C32—N2—C28—C29  | 3.7 (6)    |
| O2—C1—C2—C7    | -2.0 (8)   | Zn1—N2—C28—C29  | -171.4 (3) |
| O1—C1—C2—C7    | -178.9 (5) | C32—N2—C28—C27  | -175.3 (4) |
| C7—C2—C3—C4    | 0.0        | Zn1—N2—C28—C27  | 9.7 (4)    |
| C1—C2—C3—C4    | -176.9 (5) | N1—C27—C28—N2   | -1.2 (5)   |
| C2—C3—C4—C5    | 0.0        | C26—C27—C28—N2  | 176.3 (4)  |
| C3—C4—C5—C6    | 0.0        | N1—C27—C28—C29  | 179.9 (4)  |
| C4—C5—C6—C7    | 0.0        | C26—C27—C28—C29 | -2.7 (7)   |
| C5—C6—C7—C2    | 0.0        | N2—C28—C29—C30  | -1.8 (7)   |
| C3—C2—C7—C6    | 0.0        | C27—C28—C29—C30 | 177.1 (4)  |
| C1—C2—C7—C6    | 177.1 (4)  | C28—C29—C30—C31 | -0.5 (8)   |
| Zn1—O3—C8—O4   | -5.0 (6)   | C29—C30—C31—C32 | 0.8 (8)    |
| Zn1—O3—C8—C9   | 172.6 (3)  | C28—N2—C32—C31  | -3.3 (7)   |
| O4—C8—C9—C14   | 4.8 (7)    | Zn1—N2—C32—C31  | 171.1 (3)  |
| O3—C8—C9—C14   | -172.9 (5) | C28—N2—C32—C33  | 177.4 (4)  |
| O4—C8—C9—C10   | -170.8 (5) | Zn1—N2—C32—C33  | -8.2 (6)   |
| O3—C8—C9—C10   | 11.5 (7)   | C30—C31—C32—N2  | 1.0 (8)    |
| C14—C9—C10—C11 | 3.4 (9)    | C30—C31—C32—C33 | -179.7 (5) |

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

| <i>D</i> —H $\cdots$ <i>A</i>    | <i>D</i> —H | H $\cdots$ <i>A</i> | <i>D</i> $\cdots$ <i>A</i> | <i>D</i> —H $\cdots$ <i>A</i> |
|----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| C24—H24 $\cdots$ O5 <sup>i</sup> | 0.93        | 2.44                | 3.340 (8)                  | 162                           |
| C33—H33C $\cdots$ O1             | 0.96        | 2.52                | 3.199 (8)                  | 128                           |

|                              |      |      |           |     |
|------------------------------|------|------|-----------|-----|
| C22—H22A···O2                | 0.96 | 2.57 | 3.289 (7) | 132 |
| O6—H6···O4 <sup>ii</sup>     | 0.82 | 1.85 | 2.655 (5) | 166 |
| C31—H31···Cg1 <sup>iii</sup> | 0.93 | 2.79 | 3.708 (7) | 170 |

Symmetry codes: (i)  $-x, -y, -z+1$ ; (ii)  $x, y, z+1$ ; (iii)  $-x+1, -y+1, -z$ .

Fig. 1

