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# Aqua(iminodiacetato- $\kappa^3O,N,O'$ )(1,10-phenanthroline- $\kappa^2N,N'$ )zinc(II) sesquihydrate

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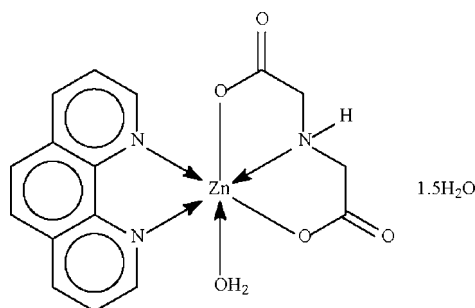
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 Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(C-C) = 0.007$  Å; disorder in solvent or counterion;  $R$  factor = 0.048;  $wR$  factor = 0.146; data-to-parameter ratio = 15.6.

The iminodiacetate dianion in the title compound,  $[Zn(C_4H_5NO_4)(C_{12}H_8N_2)(H_2O)] \cdot 1.5H_2O$ , chelates to the  $Zn^{II}$  center with its N and two O atoms. The metal atom is also chelated by the  $N$ -heterocycle and coordinated by one water molecule, leading to a distorted octahedral environment. The dianion, and coordinated and uncoordinated water molecules interact through  $O-H \cdots O$  hydrogen bonds, generating a three-dimensional network. One of the two uncoordinated water molecules has half-site occupancy. The crystal studied was a non-merohedral twin with a 15% twin component.

## Related literature

For the structure of zinc bis[iminodiacetate(1-)] tetrahydrate, see: Sinkha *et al.* (1975). For the dihydrated adenine adduct of zinc iminodiacetate, see: Morel *et al.* (2003). For the use of *PLATON* to separate twin fractions from diffraction data, see: Spek (2003).



## Experimental

## Crystal data

|  |   |
|--|---|
| $[Zn(C_4H_5NO_4)(C_{12}H_8N_2)(H_2O)] \cdot 1.5H_2O$ | $\beta = 91.845 (1)^\circ$                |
| $M_r = 421.70$                                       | $\gamma = 92.190 (1)^\circ$               |
| Triclinic, $P\bar{1}$                                | $V = 806.56 (2) \text{ \AA}^3$            |
| $a = 6.5989 (1) \text{ \AA}$                         | $Z = 2$                                   |
| $b = 10.6440 (1) \text{ \AA}$                        | Mo $K\alpha$ radiation                    |
| $c = 11.5456 (2) \text{ \AA}$                        | $\mu = 1.57 \text{ mm}^{-1}$              |
| $\alpha = 95.156 (1)^\circ$                          | $T = 100 (2) \text{ K}$                   |
|  | $0.35 \times 0.25 \times 0.15 \text{ mm}$ |

## Data collection

|  |  |
|--|--|
| Bruker SMART APEX diffractometer                                     | 7242 measured reflections              |
| Absorption correction: multi-scan ( <i>SADABS</i> ; Sheldrick, 1996) | 3640 independent reflections           |
| $T_{\min} = 0.610$ , $T_{\max} = 0.799$                              | 3455 reflections with $I > 2\sigma(I)$ |
|  | $R_{\text{int}} = 0.025$               |

## Refinement

|                                 |  |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.048$ | 72 restraints  |
| $wR(F^2) = 0.146$               | H-atom parameters constrained                        |
| $S = 1.22$                      | $\Delta\rho_{\text{max}} = 1.02 \text{ e \AA}^{-3}$  |
| 3640 reflections                | $\Delta\rho_{\text{min}} = -0.88 \text{ e \AA}^{-3}$ |
| 233 parameters                  |  |

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$            | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---------------------------|-------|--------------|--------------|----------------|
| $O1w-H11 \cdots O1^i$     | 0.84  | 2.17         | 2.801 (4)    | 132            |
| $O1w-H12 \cdots O3^{ii}$  | 0.84  | 1.92         | 2.757 (4)    | 172            |
| $O2w-H21 \cdots O2^j$     | 0.84  | 1.98         | 2.815 (5)    | 177            |
| $O2w-H22 \cdots O4^{iii}$ | 0.84  | 1.92         | 2.756 (5)    | 177            |
| $O3w-H31 \cdots O2w$      | 0.84  | 1.94         | 2.780 (9)    | 174            |

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2009).

We thank Universiti Tunku Abdul Rahman and the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2469).

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**supplementary materials**

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## Aqua(iminodiacetato- $\kappa^3O,N,O'$ )(1,10-phenanthroline- $\kappa^2N,N'$ )zinc(II) sesquihydrate

H. L. Ng, C. H. Ng and S. W. Ng

### Comment

(type here to add)

### Experimental

An methanol solution of zinc(II) nitrate hexahydrate (0.30 g, 1 mmol) and 1,10-phenanthroline (0.20 g, 1 mmol) was mixed with an aqueous solution of iminodiacetic acid (0.14 g, 1 mmol) and sodium hydroxide (0.08 g, 2 mmol). The mixture was briefly heated. The cool solution yielded a white solid. This was recrystallized from a water-methanol mixture to give colorless crystals.

### Refinement

Carbon- and nitrogen-bound hydrogen atoms were placed at calculated positions (C–H 0.95–0.98 Å, N–H 0.88 Å) and were treated as riding on their parent atoms, with  $U(H)$  set to 1.2 times  $U_{eq}(C \text{ or } N)$ . The water H-atoms were placed in chemically-sensible positions on the basis of hydrogen bonding, but were not refined; their temperature factors were tied by a factor of 1.5.

For the three phenanthroline groups, the central six-membered ring was refined as a rigid hexagon of 1.39 Å sides. The temperature factors of the carbon atoms of this fused-ring system were restrained to be nearly isotropic.

The O3w atom gave a large temperature factor when allowed to refined at full occupancy. The occupancy could be refined, and this refined to nearly 0.5. As such, the occupancy was then fixed as exactly 0.5. This water molecule was within hydrogen bonding distance of only one other acceptor atom.

The structure is a non-merohedral twin. *PLATON* (Spek, 2003) was used to de-twin the structure. The twin component refined to 15%; the inclusion of the twin law lowered the  $R$  index from 6.4%. More importantly, it improved the weighting scheme. The final difference Fourier map was now diffuse, with the largest peak of slightly over  $1 e \text{ \AA}^{-3}$  in the vicinity of C12.

### Figures

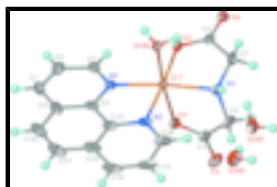


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of  $Zn(H_2O)(C_4H_5NO_4)(C_{12}H_8N_2) \cdot 1.5H_2O$  at the 70% probability level. Hydrogen atoms are drawn as spheres of arbitrary radius. The O3w water molecule, which lies on a general position, has 0.5 occupancy.

# supplementary materials

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## Aqua(iminodiacetato- $\kappa^3O,N,O'$ )(1,10-phenanthroline- $\kappa^2N,N'$ )zinc(II) sesquihydrate

### Crystal data

|   |   |
|---|---|
| $[\text{Zn}(\text{C}_4\text{H}_5\text{NO}_4)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})] \cdot 1.5\text{H}_2\text{O}$ | $Z = 2$                                   |
| $M_r = 421.70$  | $F_{000} = 434$                           |
| Triclinic, $P\bar{1}$   | $D_x = 1.736 \text{ Mg m}^{-3}$           |
| Hall symbol: -P 1   | Mo $K\alpha$ radiation                    |
| $a = 6.5989 (1) \text{ \AA}$  | $\lambda = 0.71073 \text{ \AA}$           |
| $b = 10.6440 (1) \text{ \AA}$   | Cell parameters from 6223 reflections     |
| $c = 11.5456 (2) \text{ \AA}$   | $\theta = 2.5\text{--}28.3^\circ$         |
| $\alpha = 95.156 (1)^\circ$   | $\mu = 1.57 \text{ mm}^{-1}$              |
| $\beta = 91.845 (1)^\circ$  | $T = 100 (2) \text{ K}$                   |
| $\gamma = 92.190 (1)^\circ$   | Block, colorless                          |
| $V = 806.56 (2) \text{ \AA}^3$  | $0.35 \times 0.25 \times 0.15 \text{ mm}$ |

### Data collection

|   |  |
|---|--|
| Bruker SMART APEX diffractometer                            | 3640 independent reflections           |
| Radiation source: fine-focus sealed tube                    | 3455 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite                                     | $R_{\text{int}} = 0.025$               |
| $T = 100(2) \text{ K}$                                      | $\theta_{\text{max}} = 27.5^\circ$     |
| $\omega$ scans  | $\theta_{\text{min}} = 1.8^\circ$      |
| Absorption correction: Multi-scan (SADABS; Sheldrick, 1996) | $h = -8 \rightarrow 8$                 |
| $T_{\text{min}} = 0.610$ , $T_{\text{max}} = 0.799$         | $k = -13 \rightarrow 13$               |
| 7242 measured reflections                                   | $l = -14 \rightarrow 14$               |

### Refinement

|  |  |
|--|--|
| Refinement on $F^2$  | Secondary atom site location: difference Fourier map     |
| Least-squares matrix: full                                     | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.048$                                | H-atom parameters constrained                            |
| $wR(F^2) = 0.146$  | $w = 1/[\sigma^2(F_o^2) + (0.0241P)^2 + 4.8628P]$        |
| $S = 1.22$   | where $P = (F_o^2 + 2F_c^2)/3$                           |
| 3640 reflections   | $(\Delta/\sigma)_{\text{max}} = 0.001$                   |
| 233 parameters   | $\Delta\rho_{\text{max}} = 1.02 \text{ e \AA}^{-3}$      |
| 72 restraints  | $\Delta\rho_{\text{min}} = -0.88 \text{ e \AA}^{-3}$     |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none                              |

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

|      | <i>x</i>    | <i>y</i>    | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|-------------|-------------|--------------|----------------------------------|-----------|
| Zn1  | 0.30260 (7) | 0.63033 (5) | 0.84683 (4)  | 0.01073 (15)                     |           |
| O1   | -0.0016 (5) | 0.7036 (3)  | 0.8533 (3)   | 0.0154 (6)                       |           |
| O2   | -0.1646 (5) | 0.8841 (3)  | 0.8519 (4)   | 0.0242 (8)                       |           |
| O3   | 0.3125 (5)  | 0.6228 (3)  | 1.0256 (3)   | 0.0137 (6)                       |           |
| O4   | 0.3975 (5)  | 0.7409 (3)  | 1.1911 (3)   | 0.0168 (7)                       |           |
| O1W  | 0.6167 (5)  | 0.5782 (3)  | 0.8460 (3)   | 0.0137 (6)                       |           |
| H11  | 0.6902      | 0.6376      | 0.8795       | 0.021*                           |           |
| H12  | 0.6294      | 0.5131      | 0.8812       | 0.021*                           |           |
| O2W  | 0.5864 (6)  | 1.0151 (3)  | 0.7055 (3)   | 0.0270 (8)                       |           |
| H21  | 0.6601      | 0.9737      | 0.7475       | 0.040*                           |           |
| H22  | 0.5886      | 1.0902      | 0.7349       | 0.040*                           |           |
| O3W  | 0.7199 (12) | 1.0113 (7)  | 0.4793 (7)   | 0.0287 (16)                      | 0.50      |
| H31  | 0.6705      | 1.0115      | 0.5455       | 0.043*                           | 0.50      |
| H32  | 0.7870      | 1.0790      | 0.4740       | 0.043*                           | 0.50      |
| N1   | 0.3717 (6)  | 0.8255 (3)  | 0.8921 (3)   | 0.0155 (8)                       |           |
| H1   | 0.4735      | 0.8496      | 0.8507       | 0.019*                           |           |
| N2   | 0.1966 (5)  | 0.4443 (4)  | 0.7994 (3)   | 0.0142 (7)                       |           |
| N3   | 0.3044 (5)  | 0.6254 (4)  | 0.6611 (3)   | 0.0157 (7)                       |           |
| C1   | -0.0062 (7) | 0.8228 (4)  | 0.8568 (4)   | 0.0153 (8)                       |           |
| C2   | 0.1934 (7)  | 0.8985 (4)  | 0.8650 (5)   | 0.0207 (10)                      |           |
| H2A  | 0.2137      | 0.9349      | 0.7901       | 0.025*                           |           |
| H2B  | 0.1849      | 0.9696      | 0.9259       | 0.025*                           |           |
| C3   | 0.4372 (7)  | 0.8367 (4)  | 1.0155 (4)   | 0.0178 (9)                       |           |
| H3A  | 0.3811      | 0.9141      | 1.0538       | 0.021*                           |           |
| H3B  | 0.5869      | 0.8478      | 1.0206       | 0.021*                           |           |
| C4   | 0.3754 (6)  | 0.7252 (4)  | 1.0842 (4)   | 0.0127 (8)                       |           |
| C5   | 0.1390 (6)  | 0.3577 (4)  | 0.8671 (4)   | 0.0149 (8)                       |           |
| H5   | 0.1355      | 0.3802      | 0.9485       | 0.018*                           |           |
| C6   | 0.0828 (7)  | 0.2336 (5)  | 0.8242 (5)   | 0.0200 (9)                       |           |
| H6   | 0.0424      | 0.1735      | 0.8760       | 0.024*                           |           |
| C7   | 0.0864 (7)  | 0.1993 (5)  | 0.7068 (4)   | 0.0198 (9)                       |           |
| H7   | 0.0504      | 0.1151      | 0.6768       | 0.024*                           |           |
| C9   | 0.1991 (4)  | 0.4127 (3)  | 0.67929 (18) | 0.0146 (8)                       |           |
| C8   | 0.1450 (5)  | 0.2916 (2)  | 0.6299 (2)   | 0.0186 (9)                       |           |
| C10  | 0.1399 (5)  | 0.2654 (2)  | 0.5097 (3)   | 0.0265 (11)                      |           |
| H10  | 0.1029      | 0.1827      | 0.4759       | 0.032*                           |           |
| C11  | 0.1889 (5)  | 0.3603 (3)  | 0.43886 (18) | 0.0271 (11)                      |           |
| H11A | 0.1854      | 0.3423      | 0.3567       | 0.032*                           |           |
| C12  | 0.2430 (5)  | 0.4813 (3)  | 0.4883 (2)   | 0.0213 (10)                      |           |
| C13  | 0.2481 (4)  | 0.5075 (2)  | 0.6085 (2)   | 0.0168 (9)                       |           |
| C14  | 0.2936 (7)  | 0.5828 (6)  | 0.4185 (4)   | 0.0254 (11)                      |           |
| H14  | 0.2912      | 0.5683      | 0.3360       | 0.030*                           |           |
| C15  | 0.3446 (7)  | 0.6986 (5)  | 0.4710 (4)   | 0.0220 (10)                      |           |
| H15  | 0.3765      | 0.7668      | 0.4262       | 0.026*                           |           |
| C16  | 0.3497 (7)  | 0.7169 (5)  | 0.5941 (4)   | 0.0209 (10)                      |           |

# supplementary materials

H16                    0.3874                    0.7985                    0.6304                    0.025\*

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

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Zn1 | 0.0119 (2)  | 0.0110 (2)  | 0.0096 (2)  | 0.00101 (17) | 0.00101 (17) | 0.00212 (17) |
| O1  | 0.0118 (14) | 0.0139 (14) | 0.0205 (16) | -0.0007 (11) | 0.0005 (12)  | 0.0029 (12)  |
| O2  | 0.0160 (16) | 0.0179 (16) | 0.040 (2)   | 0.0051 (13)  | 0.0028 (15)  | 0.0070 (15)  |
| O3  | 0.0180 (15) | 0.0111 (14) | 0.0121 (15) | 0.0005 (12)  | 0.0027 (12)  | 0.0010 (11)  |
| O4  | 0.0199 (16) | 0.0168 (15) | 0.0137 (15) | 0.0026 (12)  | -0.0020 (12) | 0.0013 (12)  |
| O1W | 0.0139 (14) | 0.0114 (14) | 0.0162 (15) | -0.0003 (11) | -0.0003 (12) | 0.0035 (12)  |
| O2W | 0.036 (2)   | 0.0172 (17) | 0.0267 (19) | 0.0008 (15)  | -0.0018 (16) | -0.0029 (14) |
| O3W | 0.038 (4)   | 0.023 (4)   | 0.026 (4)   | 0.005 (3)    | 0.006 (3)    | 0.003 (3)    |
| N1  | 0.0130 (18) | 0.0134 (17) | 0.021 (2)   | 0.0021 (14)  | 0.0008 (14)  | 0.0051 (14)  |
| N2  | 0.0089 (16) | 0.0159 (18) | 0.0175 (19) | 0.0032 (13)  | -0.0017 (14) | -0.0013 (14) |
| N3  | 0.0078 (16) | 0.027 (2)   | 0.0135 (18) | 0.0044 (14)  | 0.0017 (13)  | 0.0069 (15)  |
| C1  | 0.014 (2)   | 0.017 (2)   | 0.016 (2)   | 0.0014 (16)  | 0.0028 (16)  | 0.0052 (17)  |
| C2  | 0.013 (2)   | 0.014 (2)   | 0.037 (3)   | 0.0018 (16)  | 0.0014 (19)  | 0.0100 (19)  |
| C3  | 0.023 (2)   | 0.0123 (19) | 0.018 (2)   | -0.0015 (17) | 0.0011 (18)  | -0.0002 (16) |
| C4  | 0.0091 (18) | 0.0126 (19) | 0.017 (2)   | 0.0027 (15)  | 0.0023 (15)  | 0.0016 (16)  |
| C5  | 0.0088 (18) | 0.019 (2)   | 0.016 (2)   | 0.0008 (15)  | -0.0006 (15) | -0.0006 (16) |
| C6  | 0.016 (2)   | 0.018 (2)   | 0.027 (2)   | 0.0023 (17)  | 0.0023 (18)  | 0.0038 (18)  |
| C7  | 0.014 (2)   | 0.019 (2)   | 0.025 (2)   | 0.0023 (17)  | -0.0019 (18) | -0.0068 (18) |
| C9  | 0.0073 (18) | 0.024 (2)   | 0.013 (2)   | 0.0044 (16)  | 0.0002 (15)  | 0.0001 (17)  |
| C8  | 0.0083 (19) | 0.024 (2)   | 0.023 (2)   | 0.0015 (16)  | 0.0000 (16)  | -0.0039 (18) |
| C10 | 0.011 (2)   | 0.042 (3)   | 0.024 (2)   | 0.004 (2)    | -0.0026 (18) | -0.012 (2)   |
| C11 | 0.013 (2)   | 0.050 (3)   | 0.016 (2)   | 0.005 (2)    | -0.0006 (17) | -0.006 (2)   |
| C12 | 0.0075 (18) | 0.041 (3)   | 0.016 (2)   | 0.0062 (18)  | 0.0046 (16)  | 0.0011 (19)  |
| C13 | 0.0101 (19) | 0.026 (2)   | 0.015 (2)   | 0.0059 (17)  | 0.0009 (15)  | 0.0034 (17)  |
| C14 | 0.014 (2)   | 0.053 (3)   | 0.010 (2)   | 0.010 (2)    | 0.0018 (17)  | 0.008 (2)    |
| C15 | 0.012 (2)   | 0.042 (3)   | 0.016 (2)   | 0.0095 (19)  | 0.0052 (16)  | 0.015 (2)    |
| C16 | 0.013 (2)   | 0.033 (3)   | 0.018 (2)   | 0.0052 (18)  | 0.0019 (17)  | 0.0109 (19)  |

## Geometric parameters ( $\text{\AA}$ , $^\circ$ )

|         |           |         |           |
|---------|-----------|---------|-----------|
| Zn1—O3  | 2.072 (3) | C2—H2B  | 0.9900    |
| Zn1—N2  | 2.093 (4) | C3—C4   | 1.535 (6) |
| Zn1—N1  | 2.124 (4) | C3—H3A  | 0.9900    |
| Zn1—N3  | 2.141 (4) | C3—H3B  | 0.9900    |
| Zn1—O1W | 2.166 (3) | C5—C6   | 1.401 (6) |
| Zn1—O1  | 2.182 (3) | C5—H5   | 0.9500    |
| O1—C1   | 1.267 (5) | C6—C7   | 1.373 (7) |
| O2—C1   | 1.255 (5) | C6—H6   | 0.9500    |
| O3—C4   | 1.278 (5) | C7—C8   | 1.433 (6) |
| O4—C4   | 1.233 (6) | C7—H7   | 0.9500    |
| O1W—H11 | 0.8399    | C9—C8   | 1.3900    |
| O1W—H12 | 0.8400    | C9—C13  | 1.3900    |
| O2W—H21 | 0.8400    | C8—C10  | 1.3900    |
| O2W—H22 | 0.8400    | C10—C11 | 1.3900    |

|             |             |              |           |
|-------------|-------------|--------------|-----------|
| O3W—H31     | 0.8401      | C10—H10      | 0.9500    |
| O3W—H32     | 0.8399      | C11—C12      | 1.3900    |
| N1—C3       | 1.469 (6)   | C11—H11A     | 0.9500    |
| N1—C2       | 1.475 (6)   | C12—C13      | 1.3900    |
| N1—H1       | 0.8800      | C12—C14      | 1.440 (6) |
| N2—C5       | 1.315 (6)   | C14—C15      | 1.350 (8) |
| N2—C9       | 1.398 (4)   | C14—H14      | 0.9500    |
| N3—C16      | 1.329 (6)   | C15—C16      | 1.415 (7) |
| N3—C13      | 1.376 (5)   | C15—H15      | 0.9500    |
| C1—C2       | 1.513 (6)   | C16—H16      | 0.9500    |
| C2—H2A      | 0.9900      |              |           |
| O3—Zn1—N2   | 98.01 (14)  | N1—C3—H3A    | 108.3     |
| O3—Zn1—N1   | 83.15 (14)  | C4—C3—H3A    | 108.3     |
| N2—Zn1—N1   | 172.78 (14) | N1—C3—H3B    | 108.3     |
| O3—Zn1—N3   | 175.75 (14) | C4—C3—H3B    | 108.3     |
| N2—Zn1—N3   | 79.24 (16)  | H3A—C3—H3B   | 107.4     |
| N1—Zn1—N3   | 99.99 (16)  | O4—C4—O3     | 125.7 (4) |
| O3—Zn1—O1W  | 88.31 (12)  | O4—C4—C3     | 117.1 (4) |
| N2—Zn1—O1W  | 92.50 (13)  | O3—C4—C3     | 117.2 (4) |
| N1—Zn1—O1W  | 94.66 (13)  | N2—C5—C6     | 122.7 (4) |
| N3—Zn1—O1W  | 88.57 (13)  | N2—C5—H5     | 118.6     |
| O3—Zn1—O1   | 90.74 (12)  | C6—C5—H5     | 118.6     |
| N2—Zn1—O1   | 93.69 (13)  | C7—C6—C5     | 119.5 (5) |
| N1—Zn1—O1   | 79.15 (13)  | C7—C6—H6     | 120.3     |
| N3—Zn1—O1   | 92.67 (13)  | C5—C6—H6     | 120.3     |
| O1W—Zn1—O1  | 173.81 (12) | C6—C7—C8     | 119.5 (4) |
| C1—O1—Zn1   | 114.4 (3)   | C6—C7—H7     | 120.3     |
| C4—O3—Zn1   | 114.8 (3)   | C8—C7—H7     | 120.3     |
| Zn1—O1W—H11 | 109.5       | C8—C9—C13    | 120.0     |
| Zn1—O1W—H12 | 109.4       | C8—C9—N2     | 121.7 (2) |
| H11—O1W—H12 | 109.5       | C13—C9—N2    | 118.2 (2) |
| H21—O2W—H22 | 108.3       | C10—C8—C9    | 120.0     |
| H31—O3W—H32 | 110.0       | C10—C8—C7    | 122.4 (3) |
| C3—N1—C2    | 114.7 (4)   | C9—C8—C7     | 117.5 (3) |
| C3—N1—Zn1   | 105.8 (3)   | C8—C10—C11   | 120.0     |
| C2—N1—Zn1   | 109.4 (3)   | C8—C10—H10   | 120.0     |
| C3—N1—H1    | 108.9       | C11—C10—H10  | 120.0     |
| C2—N1—H1    | 108.9       | C12—C11—C10  | 120.0     |
| Zn1—N1—H1   | 108.9       | C12—C11—H11A | 120.0     |
| C5—N2—C9    | 119.1 (4)   | C10—C11—H11A | 120.0     |
| C5—N2—Zn1   | 128.5 (3)   | C13—C12—C11  | 120.0     |
| C9—N2—Zn1   | 112.3 (3)   | C13—C12—C14  | 118.0 (3) |
| C16—N3—C13  | 118.5 (4)   | C11—C12—C14  | 122.0 (3) |
| C16—N3—Zn1  | 129.7 (4)   | N3—C13—C12   | 121.9 (2) |
| C13—N3—Zn1  | 111.8 (2)   | N3—C13—C9    | 118.1 (2) |
| O2—C1—O1    | 125.1 (4)   | C12—C13—C9   | 120.0     |
| O2—C1—C2    | 116.7 (4)   | C15—C14—C12  | 119.5 (4) |
| O1—C1—C2    | 118.3 (4)   | C15—C14—H14  | 120.2     |
| N1—C2—C1    | 114.4 (4)   | C12—C14—H14  | 120.2     |

## supplementary materials

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|                |            |                 |              |
|----------------|------------|-----------------|--------------|
| N1—C2—H2A      | 108.7      | C14—C15—C16     | 119.0 (5)    |
| C1—C2—H2A      | 108.7      | C14—C15—H15     | 120.5        |
| N1—C2—H2B      | 108.7      | C16—C15—H15     | 120.5        |
| C1—C2—H2B      | 108.7      | N3—C16—C15      | 123.0 (5)    |
| H2A—C2—H2B     | 107.6      | N3—C16—H16      | 118.5        |
| N1—C3—C4       | 115.9 (4)  | C15—C16—H16     | 118.5        |
| O3—Zn1—O1—C1   | 95.8 (3)   | Zn1—O3—C4—C3    | -1.0 (5)     |
| N2—Zn1—O1—C1   | -166.1 (3) | N1—C3—C4—O4     | -167.9 (4)   |
| N1—Zn1—O1—C1   | 12.9 (3)   | N1—C3—C4—O3     | 14.5 (6)     |
| N3—Zn1—O1—C1   | -86.8 (3)  | C9—N2—C5—C6     | 1.0 (6)      |
| N2—Zn1—O3—C4   | 179.4 (3)  | Zn1—N2—C5—C6    | -175.9 (3)   |
| N1—Zn1—O3—C4   | -7.8 (3)   | N2—C5—C6—C7     | -0.2 (7)     |
| O1W—Zn1—O3—C4  | 87.1 (3)   | C5—C6—C7—C8     | -0.9 (7)     |
| O1—Zn1—O3—C4   | -86.8 (3)  | C5—N2—C9—C8     | -0.8 (5)     |
| O3—Zn1—N1—C3   | 14.2 (3)   | Zn1—N2—C9—C8    | 176.55 (15)  |
| N3—Zn1—N1—C3   | -162.9 (3) | C5—N2—C9—C13    | 176.0 (3)    |
| O1W—Zn1—N1—C3  | -73.6 (3)  | Zn1—N2—C9—C13   | -6.6 (3)     |
| O1—Zn1—N1—C3   | 106.2 (3)  | C13—C9—C8—C10   | 0.0          |
| O3—Zn1—N1—C2   | -110.0 (3) | N2—C9—C8—C10    | 176.8 (3)    |
| N3—Zn1—N1—C2   | 72.9 (3)   | C13—C9—C8—C7    | -177.0 (3)   |
| O1W—Zn1—N1—C2  | 162.3 (3)  | N2—C9—C8—C7     | -0.2 (4)     |
| O1—Zn1—N1—C2   | -17.9 (3)  | C6—C7—C8—C10    | -175.9 (3)   |
| O3—Zn1—N2—C5   | 5.3 (4)    | C6—C7—C8—C9     | 1.0 (5)      |
| N3—Zn1—N2—C5   | -178.0 (4) | C9—C8—C10—C11   | 0.0          |
| O1W—Zn1—N2—C5  | 94.0 (4)   | C7—C8—C10—C11   | 176.9 (3)    |
| O1—Zn1—N2—C5   | -85.9 (4)  | C8—C10—C11—C12  | 0.0          |
| O3—Zn1—N2—C9   | -171.7 (2) | C10—C11—C12—C13 | 0.0          |
| N3—Zn1—N2—C9   | 5.0 (2)    | C10—C11—C12—C14 | -179.6 (3)   |
| O1W—Zn1—N2—C9  | -83.1 (3)  | C16—N3—C13—C12  | 1.8 (5)      |
| O1—Zn1—N2—C9   | 97.0 (3)   | Zn1—N3—C13—C12  | -178.48 (15) |
| N2—Zn1—N3—C16  | 176.8 (4)  | C16—N3—C13—C9   | -179.4 (3)   |
| N1—Zn1—N3—C16  | 4.1 (4)    | Zn1—N3—C13—C9   | 0.3 (3)      |
| O1W—Zn1—N3—C16 | -90.4 (4)  | C11—C12—C13—N3  | 178.8 (3)    |
| O1—Zn1—N3—C16  | 83.5 (4)   | C14—C12—C13—N3  | -1.6 (4)     |
| N2—Zn1—N3—C13  | -2.9 (2)   | C11—C12—C13—C9  | 0.0          |
| N1—Zn1—N3—C13  | -175.6 (2) | C14—C12—C13—C9  | 179.6 (3)    |
| O1W—Zn1—N3—C13 | 89.9 (3)   | C8—C9—C13—N3    | -178.8 (3)   |
| O1—Zn1—N3—C13  | -96.2 (3)  | N2—C9—C13—N3    | 4.2 (3)      |
| Zn1—O1—C1—O2   | 174.2 (4)  | C8—C9—C13—C12   | 0.0          |
| Zn1—O1—C1—C2   | -4.4 (5)   | N2—C9—C13—C12   | -176.9 (3)   |
| C3—N1—C2—C1    | -97.2 (5)  | C13—C12—C14—C15 | 0.2 (5)      |
| Zn1—N1—C2—C1   | 21.6 (5)   | C11—C12—C14—C15 | 179.8 (3)    |
| O2—C1—C2—N1    | 169.4 (4)  | C12—C14—C15—C16 | 0.9 (7)      |
| O1—C1—C2—N1    | -11.9 (7)  | C13—N3—C16—C15  | -0.6 (6)     |
| C2—N1—C3—C4    | 101.9 (4)  | Zn1—N3—C16—C15  | 179.8 (3)    |
| Zn1—N1—C3—C4   | -18.9 (4)  | C14—C15—C16—N3  | -0.8 (7)     |
| Zn1—O3—C4—O4   | -178.3 (3) |                 |              |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i>     | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| N1—H1...O2w                 | 0.88        | 2.64          | 3.388 (5)             | 143                     |
| O1w—H11...O1 <sup>i</sup>   | 0.84        | 2.17          | 2.801 (4)             | 132                     |
| O1w—H12...O3 <sup>ii</sup>  | 0.84        | 1.92          | 2.757 (4)             | 172                     |
| O2w—H21...O2 <sup>i</sup>   | 0.84        | 1.98          | 2.815 (5)             | 177                     |
| O2w—H22...O4 <sup>iii</sup> | 0.84        | 1.92          | 2.756 (5)             | 177                     |
| O3w—H31...O2w               | 0.84        | 1.94          | 2.780 (9)             | 174                     |

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

Fig. 1

