

# Dichlorido[2-hydroxyimino-*N'*-[1-(2-pyridyl)ethylidene]propanohydrazide- $\kappa^3N,N',O$ ]zinc(II) hemihydrate

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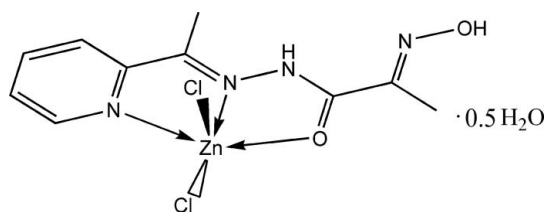
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.037;  $wR$  factor = 0.070; data-to-parameter ratio = 17.7.

The title compound,  $[\text{ZnCl}_2(\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_2)] \cdot 0.5\text{H}_2\text{O}$ , was readily prepared by the reaction between  $\text{ZnCl}_2$  and 2-hydroxyimino-*N'*-[1-(2-pyridyl)ethylidene]propanohydrazide. The Zn atom has a distorted trigonal-bipyramidal geometry with two Cl atoms and one azomethine N atom in the equatorial plane and one pyridine N atom and one amide O atom in the axial positions. In the crystal structure, complex molecules are connected in pairs by  $\text{N}-\text{H} \cdots \text{Cl}$  hydrogen bonds, formed between the amide NH of one molecule and the Cl atom of a neighboring one. Molecular pairs are connected by hydrogen bonds involving the uncoordinated water molecule, which lies on a twofold axis.

## Related literature

For details of the structure and biological activity of zinc(II) complexes, see: Canary *et al.* (1998); Comba *et al.* (2002); Kasuga *et al.* (2003); Panosyan *et al.* (2003); Rodriuez-Argüelles *et al.* (1995); Sousa *et al.* (2003). For the preparation of 2-(oximato)propanehydrazide, see: Fritsky *et al.* (1998).



## Experimental

### Crystal data

$[\text{ZnCl}_2(\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_2)] \cdot 0.5\text{H}_2\text{O}$   $a = 14.5666$  (8) Å  
 $M_r = 365.51$   $b = 12.9898$  (8) Å  
Monoclinic,  $C2/c$   $c = 15.8671$  (8) Å

$\beta = 109.873$  (5)°  
 $V = 2823.5$  (3) Å<sup>3</sup>  
 $Z = 8$   
Mo  $K\alpha$  radiation

$\mu = 2.13$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
 $0.5 \times 0.1 \times 0.05$  mm

### Data collection

Kuma KM-4 CCD area-detector diffractometer  
Absorption correction: multi-scan (PLATON; Spek, 2003)  
 $T_{\min} = 0.774$ ,  $T_{\max} = 0.891$

17382 measured reflections  
3373 independent reflections  
3069 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.043$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.070$   
 $S = 1.21$   
3373 reflections  
191 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.45$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.37$  e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

|           |             |           |            |
|-----------|-------------|-----------|------------|
| Zn1—N1    | 2.1409 (19) | Zn1—Cl2   | 2.2513 (6) |
| Zn1—N2    | 2.1142 (18) | Zn1—Cl3   | 2.2195 (6) |
| Zn1—O1    | 2.2348 (16) |           |            |
| N2—Zn1—N1 | 74.71 (7)   | N2—Zn1—O1 | 72.57 (6)  |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$                     | $D-H$    | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|------------------------------------|----------|--------------|--------------|----------------|
| N3—H2 $\cdots$ Cl3 <sup>i</sup>    | 0.80 (3) | 2.59 (3)     | 3.310 (2)    | 150 (3)        |
| O1W—H1W $\cdots$ Cl2 <sup>ii</sup> | 0.81 (3) | 2.44 (3)     | 3.182 (2)    | 153 (3)        |
| O2—H1 $\cdots$ O1W <sup>iii</sup>  | 0.88 (3) | 1.89 (4)     | 2.7015 (19)  | 153 (3)        |

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

Data collection: *KM-4 CCD Software* (Kuma, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2108).

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## supporting information

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## Dichlorido{2-hydroxyimino-*N'*-[1-(2-pyridyl)ethylidene]propanohydrazide- $\kappa^3N,N',O$ }zinc(II) hemihydrate

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### S1. Comment

In the past few decades mononuclear zinc(II) complexes attract a lot of attention because of their biological and catalytical activity (Kasuga *et al.*, 2003; Panosyan *et al.*, 2003; Rodriuez-Argüelles *et al.*, 1995; Sousa *et al.*, 2003). On the other hand, many zinc mononuclear complexes containing additional vacant donor sets and chelate centers are taken as ligands for building of homo- and heteropolynuclear systems, which are widely used in bioinorganic modeling and catalysis. The properties of the obtained compounds are closely connected with their structure, so the best results one could obtain using well designed ligand systems. We report here the synthesis and structure of a zinc complex,  $[ZnCl_2(C_{10}H_{12}N_4O_2)] \cdot 0.5H_2O$ , based on a novel polynucleative ligand 2-(oximato)-*N'*-(1-(pyridin-2-yl)ethylidene)propanehydrazide (*L*).

The title compound consists of neutral complex molecules and solvated water molecules (Fig. 1). The Zn atom has a distorted trigonal-bipyramidal geometry, defined by two Cl atoms and one azomethine N atom at the equatorial plane and a pyridine N atom and an amide O atom at the axial positions. The Zn—N, Zn—O and Zn—Cl bond lengths are comparable to previously reported zinc complexes with thiosemicarbasone and semicarbasone derivatives (Kasuga *et al.*, 2003) and with pyridine complexed to the metal ion (Canary *et al.*, 1998; Comba *et al.*, 2002) (Table 1). The bite angles around the central atom deviate from an ideal square-planar configuration [*e.g.* N2—Zn1—O1 = 72.57 (6)°, N2—Zn1—N1 = 74.71 (7)°], that is a consequence of the formation of two almost flat five-membered chelate rings. In the crystal packing, the molecules are connected in pairs by N—H⋯Cl hydrogen bonds (Fig. 2), where the protonated amide group from one molecule acts as a donor and the Cl atom from the neighboring molecule as an acceptor (Table 2). The weak  $\pi$ -stacking interaction is observed between the pyridine ring and oximic group. The molecular pairs are connected to each other by hydrogen bonds involving the solvated water molecules, resulting in an extensive three-dimensional system (Fig. 3).

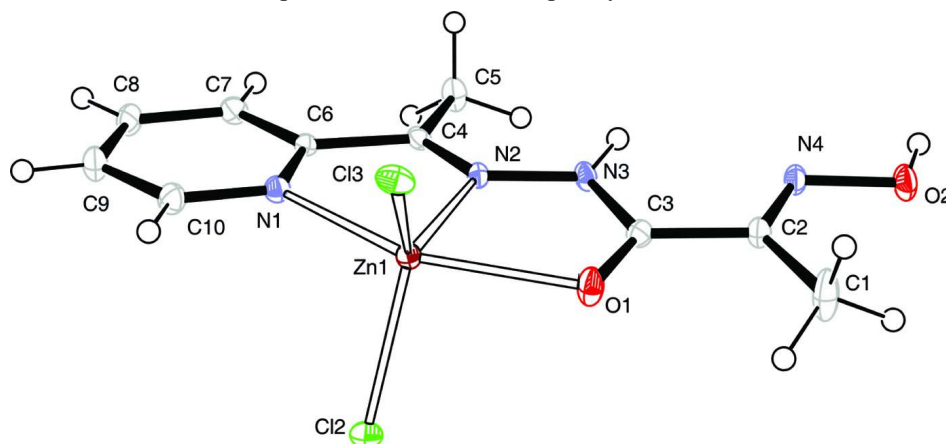
### S2. Experimental

2-(Oximato)-*N'*-(1-(pyridin-2-yl)ethylidene)propanehydrazide (*L*) was prepared according to early reported method (Fritsky *et al.*, 1998). 2-Acetylpyridine (1.2 ml, 0.0107 mol) was added to a stirred warm ethanol/water solution (20 ml) of 2-(oximato)propanehydrazide (1.17 g, 0.01 mol). After stirring at 333 K for 6 h, the solution was cooled and a white precipitate was formed immediately. It was filtered off, washed with water and acetone and dried under vacuum (yield 72%, 1.59 g). <sup>1</sup>H NMR, 400.13 MHz, (DMSO-*d*<sub>6</sub>): 12.118 (s, 1H, N—OH), 10.242 (s, 1H, NH), 8.608 (dt, 1H, py-6, J<sub>6,5</sub> = 4.8 Hz, J<sub>6,4</sub> = 1.8 Hz), 8.066 (d, 1H, py-3, J<sub>3,4</sub> = 7.8 Hz), 7.861 (td, 1H, py-4, J<sub>4,5,3</sub> = 7.8 Hz, J<sub>4,6</sub> = 1.8 Hz), 7.415 (ddd, 1H, py-5, J<sub>5,6</sub> = 4.8 Hz, J<sub>5,4</sub> = 7.8 Hz, J = 1.2 Hz), 2.376 (s, 3H, CH<sub>3</sub>(py)), 1.985 (s, 3H, CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 1660 (CO<sub>amid</sub>), 1030 (NO<sub>oxim</sub>), 3340 (NH<sub>as</sub>). Analysis calculated for C<sub>10</sub>H<sub>12</sub>N<sub>4</sub>O<sub>2</sub>: C 54.54, H 5.49, N 25.44%; found: C 54.41, H 5.62, N 25.42%.

Zinc(II) chloride (0.014 g, 0.1 mmol) in H<sub>2</sub>O (5 ml) was added to 10 ml of hot methanol solution of *L* (0.022 g, 0.1 mmol). The solution was left for slow evaporation at room temperature. After 5 days cubic crystals of the title compound suitable for X-ray analysis were obtained.

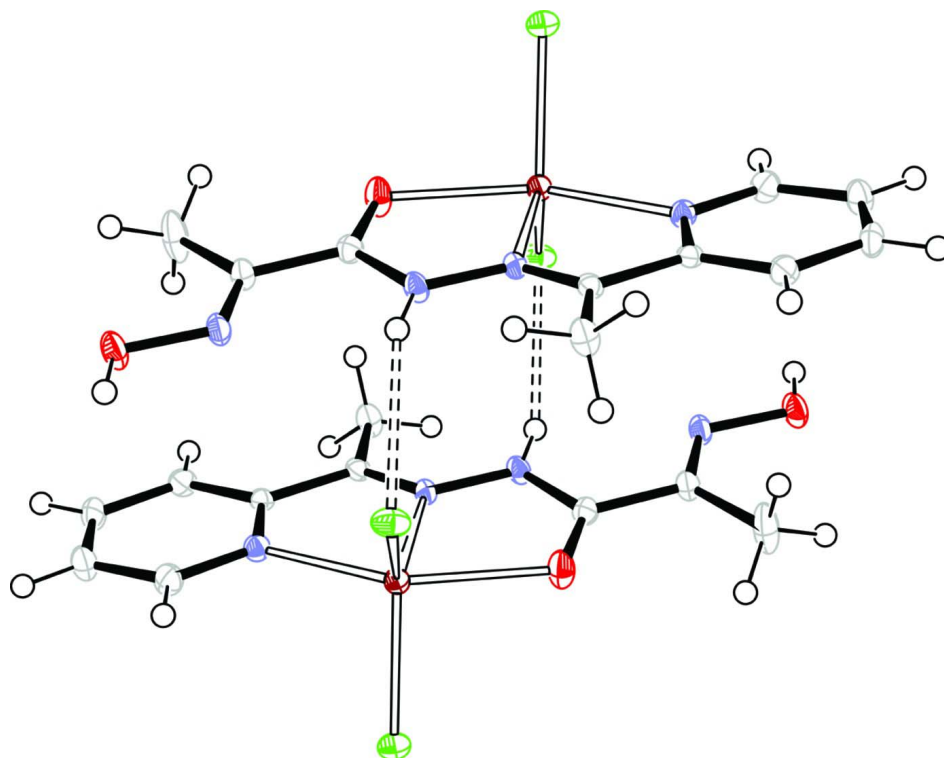
### S3. Refinement

H atoms on C atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å (CH) and 0.96 Å (CH<sub>3</sub>), and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl group. H atoms on N and O atoms were located from a difference Fourier map and were refined isotropically.

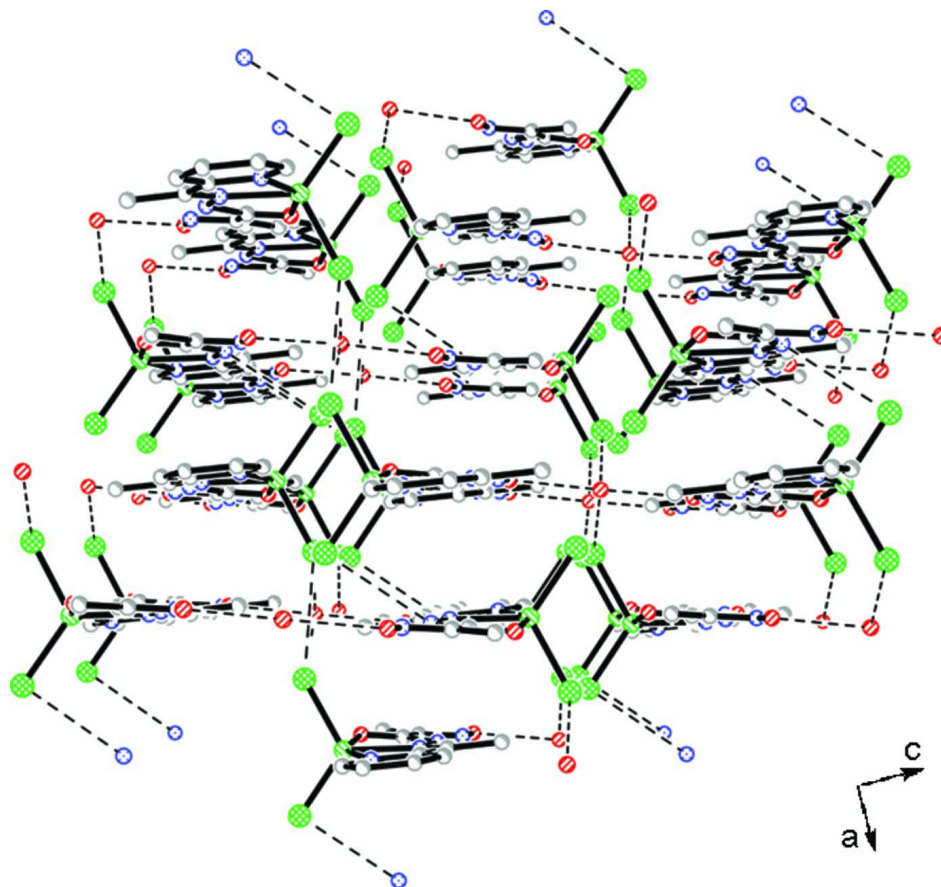


**Figure 1**

The molecular structure of the title compound. Displacement ellipsoids are shown at the 40% probability level. Water molecule is not shown.

**Figure 2**

A view of a pair of the complex molecules. Displacement ellipsoids are shown at the 40% probability level. Hydrogen bonds are indicated by dashed lines.

**Figure 3**

A packing diagram of the title compound along the *b*-axis direction. Hydrogen bonds are indicated by dashed lines. H atoms have been omitted for clarity.

**Dichlorido[2-hydroxyimino-*N'*-[1-(2-pyridyl)ethylidene]propanohydrazide- $\kappa^3N,N',O$ ]zinc(II) monohydrate**

*Crystal data*

$[\text{ZnCl}_2(\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_2)] \cdot 0.5\text{H}_2\text{O}$

$M_r = 365.51$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 14.5666\ (8)\ \text{\AA}$

$b = 12.9898\ (8)\ \text{\AA}$

$c = 15.8671\ (8)\ \text{\AA}$

$\beta = 109.873\ (5)^\circ$

$V = 2823.5\ (3)\ \text{\AA}^3$

$Z = 8$

$F(000) = 1480$

$D_x = 1.720\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3373 reflections

$\theta = 3.1\text{--}28.5^\circ$

$\mu = 2.13\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Cubic, yellow

$0.5 \times 0.1 \times 0.05\ \text{mm}$

*Data collection*

Kum KM4 CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(*PLATON*; Spek, 2003)

$T_{\min} = 0.774$ ,  $T_{\max} = 0.891$

17382 measured reflections

3373 independent reflections

3069 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.043$   
 $\theta_{\text{max}} = 28.5^\circ$ ,  $\theta_{\text{min}} = 3.1^\circ$   
 $h = -19 \rightarrow 19$

$k = -16 \rightarrow 16$   
 $l = -20 \rightarrow 21$

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.070$   
 $S = 1.21$   
 3373 reflections  
 191 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 3.185P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.002$   
 $\Delta\rho_{\text{max}} = 0.45 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.37 \text{ e } \text{\AA}^{-3}$

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

|     | <i>x</i>      | <i>y</i>      | <i>z</i>      | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|---------------|---------------|----------------------------------|
| C1  | 0.8446 (2)    | 0.45584 (19)  | 0.90460 (16)  | 0.0300 (6)                       |
| H1A | 0.8849        | 0.3958        | 0.9225        | 0.045*                           |
| H1B | 0.8500        | 0.4827        | 0.8501        | 0.045*                           |
| H1C | 0.7778        | 0.4378        | 0.8949        | 0.045*                           |
| C2  | 0.87720 (17)  | 0.53560 (17)  | 0.97658 (14)  | 0.0155 (4)                       |
| C3  | 0.86291 (17)  | 0.64543 (17)  | 0.95017 (14)  | 0.0149 (4)                       |
| C4  | 0.89866 (16)  | 0.89516 (17)  | 1.03894 (14)  | 0.0127 (4)                       |
| C5  | 0.96032 (18)  | 0.89213 (18)  | 1.13564 (14)  | 0.0187 (5)                       |
| H5A | 0.9937        | 0.8272        | 1.1490        | 0.028*                           |
| H5B | 0.9197        | 0.9003        | 1.1718        | 0.028*                           |
| H5C | 1.0073        | 0.9469        | 1.1483        | 0.028*                           |
| C6  | 0.86661 (16)  | 0.99579 (17)  | 0.99301 (14)  | 0.0124 (4)                       |
| C7  | 0.89136 (17)  | 1.08943 (18)  | 1.03628 (15)  | 0.0163 (5)                       |
| H7  | 0.9293        | 1.0921        | 1.0967        | 0.020*                           |
| C8  | 0.85855 (19)  | 1.17985 (18)  | 0.98807 (16)  | 0.0194 (5)                       |
| H8  | 0.8745        | 1.2437        | 1.0157        | 0.023*                           |
| C9  | 0.80194 (19)  | 1.17314 (18)  | 0.89857 (16)  | 0.0203 (5)                       |
| H9  | 0.7788        | 1.2323        | 0.8650        | 0.024*                           |
| C10 | 0.78027 (17)  | 1.07659 (18)  | 0.85973 (15)  | 0.0181 (5)                       |
| H10 | 0.7424        | 1.0722        | 0.7994        | 0.022*                           |
| N1  | 0.81153 (14)  | 0.98950 (15)  | 0.90538 (12)  | 0.0140 (4)                       |
| N2  | 0.86837 (14)  | 0.81687 (14)  | 0.98712 (12)  | 0.0127 (4)                       |
| N3  | 0.88998 (14)  | 0.71758 (14)  | 1.01651 (13)  | 0.0144 (4)                       |
| N4  | 0.91703 (14)  | 0.51964 (14)  | 1.06044 (12)  | 0.0161 (4)                       |
| O1  | 0.82753 (14)  | 0.67055 (12)  | 0.87067 (10)  | 0.0213 (4)                       |
| O2  | 0.92836 (13)  | 0.41557 (13)  | 1.08008 (11)  | 0.0211 (4)                       |
| Cl2 | 0.88241 (4)   | 0.85938 (4)   | 0.75864 (3)   | 0.01726 (13)                     |
| Cl3 | 0.63307 (4)   | 0.81753 (5)   | 0.78506 (4)   | 0.01874 (13)                     |
| Zn1 | 0.793127 (19) | 0.838156 (19) | 0.848619 (16) | 0.01239 (8)                      |
| H1  | 0.954 (3)     | 0.413 (3)     | 1.139 (2)     | 0.048 (10)*                      |

|     |           |              |           |             |
|-----|-----------|--------------|-----------|-------------|
| O1W | 0.0000    | 0.34448 (19) | 0.2500    | 0.0206 (5)  |
| H1W | 0.045 (2) | 0.308 (3)    | 0.250 (2) | 0.048 (11)* |
| H2  | 0.905 (2) | 0.699 (2)    | 1.068 (2) | 0.024 (8)*  |

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

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$      | $U^{13}$     | $U^{23}$     |
|-----|--------------|--------------|--------------|---------------|--------------|--------------|
| C1  | 0.0471 (17)  | 0.0123 (12)  | 0.0180 (12)  | −0.0014 (11)  | −0.0052 (11) | −0.0005 (9)  |
| C2  | 0.0178 (11)  | 0.0114 (11)  | 0.0162 (11)  | −0.0004 (9)   | 0.0045 (9)   | 0.0004 (8)   |
| C3  | 0.0163 (11)  | 0.0135 (11)  | 0.0150 (10)  | −0.0008 (9)   | 0.0054 (9)   | −0.0011 (8)  |
| C4  | 0.0134 (11)  | 0.0124 (11)  | 0.0129 (10)  | −0.0022 (8)   | 0.0054 (8)   | −0.0001 (8)  |
| C5  | 0.0235 (13)  | 0.0145 (12)  | 0.0138 (10)  | −0.0020 (9)   | 0.0005 (9)   | 0.0002 (9)   |
| C6  | 0.0122 (10)  | 0.0130 (11)  | 0.0135 (10)  | 0.0006 (8)    | 0.0063 (8)   | 0.0016 (8)   |
| C7  | 0.0181 (12)  | 0.0163 (11)  | 0.0141 (10)  | −0.0019 (9)   | 0.0050 (9)   | −0.0016 (8)  |
| C8  | 0.0256 (13)  | 0.0108 (11)  | 0.0220 (12)  | −0.0017 (9)   | 0.0086 (10)  | −0.0027 (9)  |
| C9  | 0.0243 (13)  | 0.0140 (12)  | 0.0211 (12)  | 0.0019 (9)    | 0.0058 (10)  | 0.0033 (9)   |
| C10 | 0.0196 (12)  | 0.0179 (12)  | 0.0152 (11)  | 0.0031 (9)    | 0.0039 (9)   | 0.0019 (9)   |
| N1  | 0.0153 (9)   | 0.0132 (9)   | 0.0130 (9)   | −0.0003 (7)   | 0.0042 (7)   | −0.0008 (7)  |
| N2  | 0.0150 (9)   | 0.0103 (9)   | 0.0130 (9)   | 0.0011 (7)    | 0.0051 (7)   | 0.0016 (7)   |
| N3  | 0.0202 (10)  | 0.0115 (9)   | 0.0097 (9)   | −0.0001 (8)   | 0.0028 (8)   | 0.0021 (7)   |
| N4  | 0.0208 (10)  | 0.0103 (9)   | 0.0169 (9)   | 0.0011 (8)    | 0.0062 (8)   | 0.0019 (7)   |
| O1  | 0.0333 (10)  | 0.0136 (8)   | 0.0122 (7)   | 0.0026 (7)    | 0.0015 (7)   | 0.0002 (6)   |
| O2  | 0.0322 (10)  | 0.0126 (8)   | 0.0164 (8)   | 0.0014 (7)    | 0.0054 (7)   | 0.0043 (6)   |
| Cl2 | 0.0152 (3)   | 0.0210 (3)   | 0.0172 (3)   | −0.0004 (2)   | 0.0076 (2)   | −0.0007 (2)  |
| Cl3 | 0.0154 (3)   | 0.0255 (3)   | 0.0158 (3)   | −0.0057 (2)   | 0.0059 (2)   | −0.0026 (2)  |
| Zn1 | 0.01436 (14) | 0.01195 (13) | 0.01015 (12) | −0.00066 (10) | 0.00323 (9)  | −0.00064 (9) |
| O1W | 0.0272 (14)  | 0.0137 (12)  | 0.0202 (12)  | 0.000         | 0.0070 (11)  | 0.000        |

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

|        |           |         |             |
|--------|-----------|---------|-------------|
| C1—C2  | 1.495 (3) | C7—H7   | 0.9300      |
| C1—H1A | 0.9600    | C8—C9   | 1.381 (3)   |
| C1—H1B | 0.9600    | C8—H8   | 0.9300      |
| C1—H1C | 0.9600    | C9—C10  | 1.386 (3)   |
| C2—N4  | 1.275 (3) | C9—H9   | 0.9300      |
| C2—C3  | 1.482 (3) | C10—N1  | 1.337 (3)   |
| C3—O1  | 1.233 (3) | C10—H10 | 0.9300      |
| C3—N3  | 1.364 (3) | Zn1—N1  | 2.1409 (19) |
| C4—N2  | 1.288 (3) | N2—N3   | 1.371 (3)   |
| C4—C5  | 1.492 (3) | Zn1—N2  | 2.1142 (18) |
| C4—C6  | 1.492 (3) | N3—H2   | 0.80 (3)    |
| C5—H5A | 0.9600    | N4—O2   | 1.384 (2)   |
| C5—H5B | 0.9600    | Zn1—O1  | 2.2348 (16) |
| C5—H5C | 0.9600    | O2—H1   | 0.88 (3)    |
| C6—N1  | 1.351 (3) | Zn1—Cl2 | 2.2513 (6)  |
| C6—C7  | 1.383 (3) | Zn1—Cl3 | 2.2195 (6)  |
| C7—C8  | 1.394 (3) | O1W—H1W | 0.81 (3)    |

|               |              |                |              |
|---------------|--------------|----------------|--------------|
| C2—C1—H1A     | 109.5        | C7—C8—H8       | 120.5        |
| C2—C1—H1B     | 109.5        | C8—C9—C10      | 118.7 (2)    |
| H1A—C1—H1B    | 109.5        | C8—C9—H9       | 120.6        |
| C2—C1—H1C     | 109.5        | C10—C9—H9      | 120.6        |
| H1A—C1—H1C    | 109.5        | N1—C10—C9      | 122.7 (2)    |
| H1B—C1—H1C    | 109.5        | N1—C10—H10     | 118.6        |
| N4—C2—C3      | 115.0 (2)    | C9—C10—H10     | 118.6        |
| N4—C2—C1      | 126.8 (2)    | C10—N1—C6      | 118.69 (19)  |
| C3—C2—C1      | 118.27 (19)  | C10—N1—Zn1     | 125.33 (15)  |
| O1—C3—N3      | 121.2 (2)    | C6—N1—Zn1      | 115.73 (15)  |
| O1—C3—C2      | 120.9 (2)    | C4—N2—N3       | 122.44 (18)  |
| N3—C3—C2      | 117.88 (19)  | C4—N2—Zn1      | 120.30 (15)  |
| N2—C4—C5      | 126.3 (2)    | N3—N2—Zn1      | 117.03 (13)  |
| N2—C4—C6      | 113.42 (18)  | C3—N3—N2       | 114.28 (18)  |
| C5—C4—C6      | 120.29 (19)  | C3—N3—H2       | 119 (2)      |
| C4—C5—H5A     | 109.5        | N2—N3—H2       | 125 (2)      |
| C4—C5—H5B     | 109.5        | C2—N4—O2       | 111.77 (18)  |
| H5A—C5—H5B    | 109.5        | C3—O1—Zn1      | 114.29 (14)  |
| C4—C5—H5C     | 109.5        | N4—O2—H1       | 104 (2)      |
| H5A—C5—H5C    | 109.5        | N2—Zn1—N1      | 74.71 (7)    |
| H5B—C5—H5C    | 109.5        | N2—Zn1—Cl3     | 123.36 (5)   |
| N1—C6—C7      | 121.8 (2)    | N1—Zn1—Cl3     | 105.30 (5)   |
| N1—C6—C4      | 115.30 (19)  | N2—Zn1—O1      | 72.57 (6)    |
| C7—C6—C4      | 122.86 (19)  | N1—Zn1—O1      | 147.07 (6)   |
| C6—C7—C8      | 119.1 (2)    | Cl3—Zn1—O1     | 95.66 (5)    |
| C6—C7—H7      | 120.5        | N2—Zn1—Cl2     | 117.91 (5)   |
| C8—C7—H7      | 120.5        | N1—Zn1—Cl2     | 97.91 (5)    |
| C9—C8—C7      | 119.0 (2)    | Cl3—Zn1—Cl2    | 118.08 (2)   |
| C9—C8—H8      | 120.5        | O1—Zn1—Cl2     | 94.10 (5)    |
|               |              |                |              |
| N4—C2—C3—O1   | 178.0 (2)    | Zn1—N2—N3—C3   | 2.7 (2)      |
| C1—C2—C3—O1   | −2.0 (4)     | C3—C2—N4—O2    | −179.79 (19) |
| N4—C2—C3—N3   | −2.1 (3)     | C1—C2—N4—O2    | 0.2 (4)      |
| C1—C2—C3—N3   | 177.9 (2)    | N3—C3—O1—Zn1   | −8.3 (3)     |
| N2—C4—C6—N1   | 0.0 (3)      | C2—C3—O1—Zn1   | 171.56 (16)  |
| C5—C4—C6—N1   | 179.6 (2)    | C4—N2—Zn1—N1   | −6.55 (17)   |
| N2—C4—C6—C7   | −179.8 (2)   | N3—N2—Zn1—N1   | 178.85 (17)  |
| C5—C4—C6—C7   | −0.1 (3)     | C4—N2—Zn1—Cl3  | −105.03 (17) |
| N1—C6—C7—C8   | 0.0 (3)      | N3—N2—Zn1—Cl3  | 80.36 (16)   |
| C4—C6—C7—C8   | 179.7 (2)    | C4—N2—Zn1—O1   | 169.73 (19)  |
| C6—C7—C8—C9   | 0.3 (4)      | N3—N2—Zn1—O1   | −4.88 (15)   |
| C7—C8—C9—C10  | −0.4 (4)     | C4—N2—Zn1—Cl2  | 84.41 (17)   |
| C8—C9—C10—N1  | 0.3 (4)      | N3—N2—Zn1—Cl2  | −90.20 (15)  |
| C9—C10—N1—C6  | −0.1 (3)     | C10—N1—Zn1—N2  | −179.8 (2)   |
| C9—C10—N1—Zn1 | −173.99 (18) | C6—N1—Zn1—N2   | 6.09 (15)    |
| C7—C6—N1—C10  | −0.1 (3)     | C10—N1—Zn1—Cl3 | −58.74 (19)  |
| C4—C6—N1—C10  | −179.9 (2)   | C6—N1—Zn1—Cl3  | 127.17 (14)  |
| C7—C6—N1—Zn1  | 174.42 (17)  | C10—N1—Zn1—O1  | 173.63 (16)  |

|              |              |                |              |
|--------------|--------------|----------------|--------------|
| C4—C6—N1—Zn1 | −5.4 (2)     | C6—N1—Zn1—O1   | −0.5 (2)     |
| C5—C4—N2—N3  | 0.4 (3)      | C10—N1—Zn1—Cl2 | 63.31 (19)   |
| C6—C4—N2—N3  | 179.97 (19)  | C6—N1—Zn1—Cl2  | −110.78 (15) |
| C5—C4—N2—Zn1 | −173.95 (18) | C3—O1—Zn1—N2   | 6.96 (17)    |
| C6—C4—N2—Zn1 | 5.7 (3)      | C3—O1—Zn1—N1   | 13.6 (2)     |
| O1—C3—N3—N2  | 4.1 (3)      | C3—O1—Zn1—Cl3  | −116.27 (17) |
| C2—C3—N3—N2  | −175.80 (19) | C3—O1—Zn1—Cl2  | 124.96 (17)  |
| C4—N2—N3—C3  | −171.8 (2)   |                |              |

*Hydrogen-bond geometry (Å, °)*

| <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> |
|-----------------------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N3—H2 $\cdots$ Cl3 <sup>i</sup>                     | 0.80 (3)    | 2.59 (3)            | 3.310 (2)                  | 150 (3)                       |
| O1 <i>W</i> —H1 <i>W</i> $\cdots$ Cl2 <sup>ii</sup> | 0.81 (3)    | 2.44 (3)            | 3.182 (2)                  | 153 (3)                       |
| O2—H1 $\cdots$ O1 <i>W</i> <sup>iii</sup>           | 0.88 (3)    | 1.89 (4)            | 2.7015 (19)                | 153 (3)                       |

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