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# The unanticipated oxidation of a tertiary amine in a tetracyclic glyoxal-cyclam condensate yielding zinc(II) coordinated to a sterically hindered amine oxide

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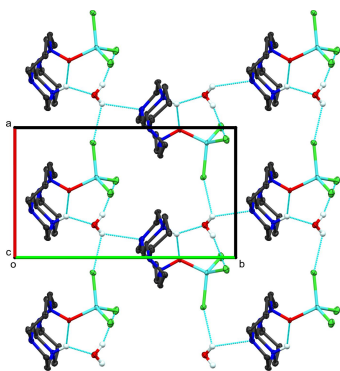
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The complex, trichlorido(1,4,11-triaza-8-azoniatetracyclo[6.6.2.0<sup>4,16</sup>.0<sup>11,15</sup>]-hexadecane 1-oxide- $\kappa O$ )zinc(II) monohydrate,  $[\text{ZnCl}_3(\text{C}_{12}\text{H}_{23}\text{N}_4\text{O})]\cdot\text{H}_2\text{O}$  (**1**), has monoclinic symmetry (space group  $P2_1/n$ ) at 120 K. The zinc(II) center adopts a slightly distorted tetrahedral coordination geometry and is coordinated by three chlorine atoms and the oxygen atom of the oxidized tertiary amine of the tetracycle. The amine nitrogen atom, inside the ligand cleft, is protonated and forms a hydrogen bond to the oxygen of the amine oxide. Additional hydrogen-bonding interactions involve the protonated amine, the water solvate oxygen atom, and one of the chloro ligands.

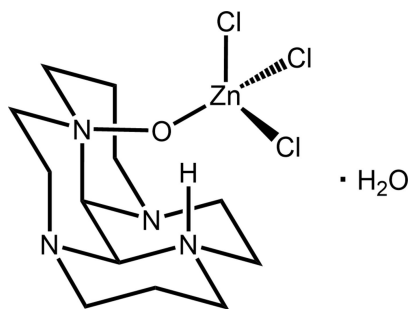
## 1. Chemical context

Tetracyclic tetraamines formed by the condensation of dialdehyde glyoxal and tetraazamacrocycles, such as cyclen and cyclam, have been known since the 1980s (Alcock *et al.*, 1980; Weisman *et al.*, 1980). They can act as rigid, sterically hindered, bidentate chelates to form coordination complexes, but have not been exploited fully for this purpose (Hubin, McCormick, Busch & Alcock 1998; Hubin *et al.*, 1999, 2002; May *et al.*, 2004; Won *et al.*, 2015). Instead, their greatest utility has been as crucial starting materials for the synthesis of ethylene cross-bridged tetraazamacrocycles (Weisman *et al.*, 1990, 1996; Wong *et al.*, 2000; Hubin, 2003; Matz *et al.*, 2015). Their folded structures generally lead to dialkylation of only two non-adjacent nitrogens, which can then be reduced to ethylene cross-bridged ligands whose rigid and topologically complex transition-metal complexes exhibit astounding kinetic stability under harsh conditions (Hubin, McCormick, Collinson, *et al.*, 1998; Hubin *et al.*, 2000, 2003; Sun *et al.*, 2002; Boswell *et al.*, 2004; Woodin *et al.*, 2005; Odendaal *et al.*, 2011; Matz *et al.*, 2015; Jones *et al.*, 2015).

Tertiary amines, like those found in glyoxal-tetraazamacrocycle condensates, are known to oxidize to amine oxides under oxidizing conditions, usually in the presence of hydrogen peroxide or 3-chloroperbenzoic acid (O'Neal *et al.*, 2001; Bernier *et al.*, 2009). These amine oxides can be reduced back to amines in the presence of reducing agents (Hayashi *et al.*, 1959); zinc metal is often involved in the reduction reaction (Emerson & Rees, 1962; Kagami & Motoki, 1978; Jousseume & Chanson, 1987; Balicki, 1989). In the present case, the tertiary amine was oxidized to the amine oxide in the presence of air, methanol, and zinc(II) chloride. Molecular oxygen is



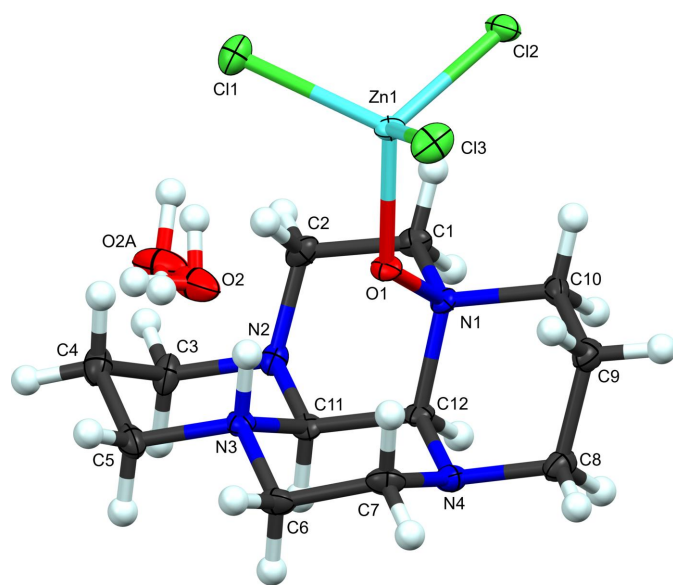
able to oxidize tertiary amines (Bernier *et al.*, 2009), although it is generally inefficient and often is improved by the presence of transition metal ions, which may form metal-oxo catalysts *in situ*, although unlikely in the present case with zinc(II) (Jain & Sain, 2002; Wang *et al.*, 1999; Imada *et al.*, 2003). Under development in our labs are more efficient ways to make the mono- and diamine oxides of glyoxal-tetraazamacrocyclic condensates – at present both hydrogen peroxide and 3-chloroperbenzoic acid have shown increased activity over molecular oxygen – and will be reported in due course.



Here, we present the first example of a glyoxal-tetraazamacrocyclic condensate that serendipitously oxidized to a mono-amine-oxide during a complexation reaction with zinc(II) chloride. The resulting sterically demanding amine oxide coordinates in a monodentate fashion to a zinc(II) ion concomitantly coordinated to three additional chloro ligands.

## 2. Structural commentary

We pioneered the use of glyoxal-tetraazamacrocyclic condensates as rigid, bulky, bidentate ligands for transition metal ions (Hubin, McCormick, Busch & Alcock 1998), and have



**Figure 1**  
The molecular structure of (I). Atomic displacement ellipsoids shown at 50% probability with hydrogen atoms shown as spheres of arbitrary radius.

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

Zn1—O1	1.9856 (11)	Zn1—Cl1	2.2616 (5)
Zn1—Cl3	2.2345 (5)	Zn1—Cl2	2.2856 (5)
O1—Zn1—Cl3	107.03 (4)	Cl3—Zn1—Cl2	111.244 (19)
O1—Zn1—Cl1	109.33 (4)	Cl1—Zn1—Cl2	106.531 (18)
Cl3—Zn1—Cl1	111.812 (19)	N1—O1—Zn1	124.84 (9)
O1—Zn1—Cl2	110.93 (3)		

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

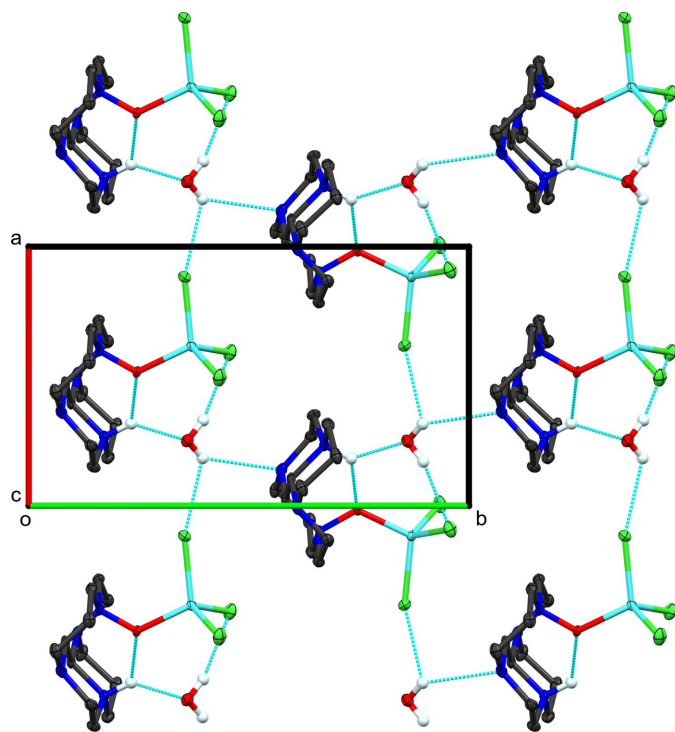
D—H...A	D—H	H...A	D...A	D—H...A
N3—H3...O1	1.00	2.15	2.8297 (18)	123
N3—H3...O2	1.00	1.94	2.763 (6)	138
N3—H3...O2A	1.00	1.98	2.786 (7)	136
O2—H2C...Cl2 <sup>i</sup>	0.87 (4)	2.61 (8)	3.154 (6)	121 (7)
O2—H2C...N4 <sup>ii</sup>	0.87 (4)	2.61 (8)	3.262 (6)	133 (8)
O2—H2D...Cl1	0.87 (4)	2.39 (4)	3.227 (6)	162 (6)
O2A—H2E...Cl2 <sup>i</sup>	0.87 (4)	2.69 (8)	3.295 (6)	128 (9)
O2A—H2E...N4 <sup>ii</sup>	0.87 (4)	2.84 (9)	3.202 (6)	107 (7)
O2A—H2F...Cl1	0.98 (6)	2.04 (7)	2.996 (6)	163 (5)

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

continued our efforts (Hubin *et al.*, 1999, 2002; May *et al.*, 2004, Won *et al.*, 2015) in coordinating various metal-containing species, in this case  $\text{ZnCl}_2$ , to these bidentate amines of the glyoxal-cyclam condensate. During the course of the current work, air oxidation of one amine occurred, which produced an amine oxide moiety that subsequently resulted in coordination of  $[\text{ZnCl}_3]^-$  in a monodentate fashion. In the majority of the unoxidized amine examples, where two non-adjacent amine nitrogen atoms point into the cleft of the folded ligand, the metal ion coordinates in a bidentate fashion [palladium(II) and copper(II) examples: Hubin, McCormick, Alcock, *et al.*, 1998; Hubin *et al.*, 2002; May *et al.*, 2004; Won *et al.*, 2015]. However, in the present case (Fig. 1), the oxygen atom, O1, extends the reach of the amine oxide and renders bidentate coordination unfavorable. Furthermore, the oxygen of the amine oxide moiety is situated in the center of the tetracycle cavity by virtue of the distorted tetrahedral geometry about the atoms participating in the intramolecular  $\text{N3}\cdots\text{O1}$  hydrogen-bonding interaction. In addition, the oxygen atom fills most of this cavity created by the tetracycle, thus the larger than expected  $\text{N1—O1—Zn1}$  bond angle [124.84 (9)°, Table 1] is instrumental in minimizing the steric hindrance caused by the bulk of the trichloro zinc unit. An interesting comparison can be drawn to our copper(I) glyoxal-cyclam condensate structure (Hubin *et al.*, 1999). In that case, the low coordination number preferred by copper(I), along with the steric bulk of the ligand, resulted in a copper(I) complex with two cyclam-glyoxal ligands coordinated in a linear fashion to the metal.

## 3. Supramolecular features

Within the asymmetric unit, the ring nitrogen atom, N1, forms a bifurcated hydrogen bond with both the water, O2, and *N*-oxide oxygen, O1, atoms (see Fig. 2, Table 2 for details). One water hydrogen forms a hydrogen bond to one chlorine, Cl1,



**Figure 2**  
Packing diagram of (I) viewed along the *c*-axis. Hydrogen atoms, except those involved in hydrogen bonding, and one component of the disordered water of crystallization are omitted for clarity. Light-blue dashed lines represent hydrogen-bonding interactions. One layer of molecules is shown for clarity.

of the standard molecule resulting in an  $R_2^2(10)$  ring (Etter *et al.*, 1990). The remaining water hydrogen atom forms a bifurcated hydrogen bond to a neighboring chlorine, Cl2, related by translation along the *a*-axis and to a tetracycle nitrogen atom related by the screw-axis parallel to the *b*-axis. This is true for both components of the disordered water molecule (see below). The overall motif is a di-periodic network (Nespolo, 2019) of hydrogen-bonded molecules parallel to the *ab* plane. The remaining interactions within the structure (primarily C—H...Cl) are van der Waals contacts that direct the packing.

#### 4. Database survey

We have found only two structural analogues of this zinc(II) coordination sphere – tertiary amine oxide and three chlorides coordinated to tetrahedral zinc(II) (Jasiewicz *et al.*, 2011; refcodes: EWOZOG, EWOZUM). The Jasiewicz complexes utilize a spartein backbone ligand, which naturally form a folded structure with the amine lone pair of electrons pointed either concave or convex to the remainder of the structure. Analogous to our tetraazamacrocyclic-glyoxal condensate, this generates either a concave or convex metal binding site. The most direct comparison to our own compound would be the concave isomer [(-)-spartein-16-ium *N*-1-oxide]trichloro-zinc(II). In both this complex and our own, an important non-

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	[ZnCl <sub>3</sub> (C <sub>12</sub> H <sub>23</sub> N <sub>4</sub> O)]·H <sub>2</sub> O
<i>M<sub>r</sub></i>	429.08
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.7253 (8), 14.3482 (14), 14.0718 (13)
$\beta$ (°)	104.760 (2)
<i>V</i> (Å <sup>3</sup> )	1703.5 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.92
Crystal size (mm)	0.21 × 0.12 × 0.09
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Numerical ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.699, 0.793
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	32386, 4237, 3572
<i>R</i> <sub>int</sub>	0.044
( $\sin \theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , <i>S</i>	0.024, 0.056, 1.01
No. of reflections	4237
No. of parameters	220
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.42, -0.33

Computer programs: *APEX4* and *SAINT* (Bruker, 2021), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2019/2* (Sheldrick, 2015b), *OLEX2 1.5* (Dolomanov *et al.*, 2009), *Mercury* (Macrae *et al.*, 2020), and *publCIF* (Westrip, 2010).

covalent interaction is the hydrogen bond formed by the oxygen of the amine oxide and the proton located on the non-adjacent nitrogen. The folded nature of the amine oxide functionalized concave backbones allow the zinc atom to fit tightly inside the ligand. Notably, the sparteine compound shows similar average C—N—O bond angles (111.0° *cf* 110.68°) and a larger N—O—Zn bond angle than our compound [127.4 (5) and 124.84 (9)°, respectively]. These two angles work in conjunction to determine how far into the cavity the metal atom can approach. The smaller N—O—Zn angle of our tetraazamacrocyclic ligand allows the zinc to sit further into and, ideally, interact more strongly with atoms forming the cavity.

#### 5. Synthesis and crystallization

The cyclam-glyoxal condensate was prepared according to a literature procedure (Le Baccon *et al.*, 2001): 0.24 g (1 mmol) of cyclam-glyoxal and 0.14 g (1 mmol) of ZnCl<sub>2</sub> were stirred for three days in methanol (20 mL) in the presence of air. A white solid product precipitated and was filtered from the solution on a fine glass frit, and washed with a minimal amount of methanol before being dried under vacuum. X-ray quality colorless block crystals were obtained by ether diffusion into a 2-butanone solution.

## 6. Refinement

The structure was solved by dual-space methods (*SHELXT*; Sheldrick, 2015a) and refinement was routine (*SHELXL*; Sheldrick, 2015b; Table 3). All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. The water of crystallization exhibited mild positional disorder that was modeled over two equal occupancy sites. Hydrogen atoms on the water and protonated amine nitrogen were initially located in a difference-Fourier map. The amine hydrogen atom was ultimately refined using a riding model. The coordinates of the water hydrogen atoms were allowed to refine, with similarity restraints applied to all four O–H distances. Atomic displacement parameters of these hydrogen atoms were tied to that of the N or O to which they are bonded. All other hydrogen atoms were positioned at geometrically calculated positions with C–H = 0.99 or 1.00 Å for methylene and methine carbon atoms respectively;  $U_{\text{iso}}(\text{H}) = 1.5 \times U_{\text{eq}}(\text{O})$  or  $1.2 \times U_{\text{eq}}(\text{N/C})$ .

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## supporting information

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## The unanticipated oxidation of a tertiary amine in a tetracyclic glyoxal-cyclam condensate yielding zinc(II) coordinated to a sterically hindered amine oxide

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### Computing details

Trichlorido(1,4,11-triaza-8-azoniatetracyclo[6.6.2.0<sup>4,16</sup>.0<sup>11,15</sup>]hexadecane 1-oxide- $\kappa$ O)zinc(II) monohydrate

#### Crystal data

[ZnCl<sub>3</sub>(C<sub>12</sub>H<sub>23</sub>N<sub>4</sub>O)]·H<sub>2</sub>O

$M_r = 429.08$

Monoclinic,  $P2_1/n$

$a = 8.7253$  (8) Å

$b = 14.3482$  (14) Å

$c = 14.0718$  (13) Å

$\beta = 104.760$  (2)°

$V = 1703.5$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 888$

$D_x = 1.673$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 8725 reflections

$\theta = 2.5$ – $28.1$ °

$\mu = 1.92$  mm<sup>-1</sup>

$T = 120$  K

Block, colorless

$0.21 \times 0.12 \times 0.09$  mm

#### Data collection

Bruker APEXII CCD

diffractometer

Radiation source: X-ray

Detector resolution: 8.33 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans

Absorption correction: numerical

(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.699$ ,  $T_{\max} = 0.793$

32386 measured reflections

4237 independent reflections

3572 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.044$

$\theta_{\max} = 28.3$ °,  $\theta_{\min} = 2.1$ °

$h = -11 \rightarrow 11$

$k = -19 \rightarrow 19$

$l = -18 \rightarrow 18$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.056$

$S = 1.01$

4237 reflections

220 parameters

3 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0244P)^2 + 0.8924P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.42$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.33$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*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	0.38352 (2)	0.63073 (2)	0.74182 (2)	0.01361 (6)	
Cl1	0.40927 (6)	0.54285 (3)	0.61336 (3)	0.02305 (10)	
Cl2	0.11765 (5)	0.64610 (3)	0.72669 (3)	0.02054 (9)	
Cl3	0.50553 (6)	0.56614 (3)	0.88570 (3)	0.02517 (10)	
O1	0.48379 (13)	0.75415 (7)	0.73622 (8)	0.0143 (2)	
N1	0.40264 (16)	0.83922 (9)	0.72215 (10)	0.0128 (3)	
N2	0.49127 (17)	0.88977 (9)	0.54778 (10)	0.0158 (3)	
N3	0.73297 (16)	0.82844 (9)	0.66434 (10)	0.0150 (3)	
H3	0.682588	0.767367	0.672505	0.018*	
N4	0.63893 (17)	0.92560 (10)	0.81784 (10)	0.0168 (3)	
C1	0.2840 (2)	0.84123 (12)	0.62400 (12)	0.0168 (3)	
H1A	0.200438	0.794152	0.622381	0.020*	
H1B	0.233240	0.903358	0.612818	0.020*	
C2	0.3667 (2)	0.82071 (12)	0.54517 (12)	0.0187 (4)	
H2A	0.413817	0.757581	0.555104	0.022*	
H2B	0.289180	0.822203	0.480114	0.022*	
C3	0.5688 (2)	0.87961 (12)	0.46713 (13)	0.0211 (4)	
H3A	0.620783	0.939150	0.458245	0.025*	
H3B	0.487426	0.866169	0.405469	0.025*	
C4	0.6919 (2)	0.80197 (13)	0.48621 (13)	0.0221 (4)	
H4A	0.639472	0.741237	0.489173	0.027*	
H4B	0.745027	0.799462	0.431914	0.027*	
C5	0.8131 (2)	0.81999 (13)	0.58233 (13)	0.0210 (4)	
H5A	0.890506	0.768148	0.596338	0.025*	
H5B	0.871458	0.878211	0.577319	0.025*	
C6	0.8502 (2)	0.85260 (12)	0.75866 (13)	0.0200 (4)	
H6A	0.900038	0.913375	0.751790	0.024*	
H6B	0.934682	0.804743	0.773996	0.024*	
C7	0.7694 (2)	0.85777 (12)	0.84095 (13)	0.0203 (4)	
H7A	0.727310	0.795572	0.851407	0.024*	
H7B	0.847102	0.876364	0.902397	0.024*	
C8	0.5621 (2)	0.93873 (12)	0.89888 (12)	0.0206 (4)	
H8A	0.507952	0.999931	0.891293	0.025*	
H8B	0.644199	0.939192	0.962106	0.025*	
C9	0.4420 (2)	0.86239 (12)	0.90143 (12)	0.0198 (4)	
H9A	0.496925	0.801698	0.916110	0.024*	
H9B	0.388001	0.875842	0.953828	0.024*	
C10	0.3211 (2)	0.85768 (11)	0.80278 (12)	0.0171 (3)	
H10A	0.244040	0.807317	0.803837	0.020*	

H10B	0.262410	0.917304	0.789926	0.020*	
C11	0.6037 (2)	0.90373 (11)	0.63997 (12)	0.0145 (3)	
H11	0.659039	0.963672	0.634126	0.017*	
C12	0.5264 (2)	0.91649 (11)	0.72469 (12)	0.0142 (3)	
H12	0.466658	0.976619	0.712488	0.017*	
O2	0.7488 (7)	0.6396 (4)	0.7042 (5)	0.0387 (13)	0.5
H2C	0.816 (8)	0.605 (6)	0.684 (5)	0.058*	0.5
H2D	0.670 (6)	0.604 (4)	0.677 (5)	0.058*	0.5
O2A	0.7280 (7)	0.6345 (4)	0.6550 (4)	0.0399 (14)	0.5
H2E	0.806 (8)	0.618 (7)	0.704 (5)	0.060*	0.5
H2F	0.631 (8)	0.598 (4)	0.631 (4)	0.060*	0.5

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.01529 (10)	0.00965 (9)	0.01544 (10)	−0.00118 (7)	0.00307 (7)	0.00082 (7)
Cl1	0.0301 (2)	0.0209 (2)	0.0180 (2)	0.00448 (18)	0.00584 (17)	−0.00187 (16)
Cl2	0.0149 (2)	0.01714 (19)	0.0298 (2)	−0.00291 (15)	0.00600 (17)	−0.00108 (16)
Cl3	0.0342 (3)	0.0201 (2)	0.0177 (2)	0.00302 (18)	0.00018 (18)	0.00485 (16)
O1	0.0134 (6)	0.0079 (5)	0.0209 (6)	0.0019 (4)	0.0034 (5)	0.0021 (4)
N1	0.0146 (7)	0.0085 (6)	0.0155 (7)	0.0017 (5)	0.0040 (5)	0.0003 (5)
N2	0.0217 (8)	0.0133 (7)	0.0132 (7)	0.0028 (5)	0.0055 (6)	0.0009 (5)
N3	0.0149 (7)	0.0112 (6)	0.0193 (7)	−0.0003 (5)	0.0050 (6)	0.0010 (5)
N4	0.0191 (7)	0.0156 (7)	0.0148 (7)	−0.0036 (6)	0.0026 (6)	−0.0011 (5)
C1	0.0145 (8)	0.0153 (8)	0.0180 (8)	0.0013 (6)	−0.0004 (6)	0.0008 (6)
C2	0.0208 (9)	0.0169 (8)	0.0160 (8)	0.0017 (7)	0.0006 (7)	−0.0013 (6)
C3	0.0313 (10)	0.0180 (8)	0.0168 (8)	0.0072 (7)	0.0113 (7)	0.0018 (7)
C4	0.0293 (10)	0.0181 (8)	0.0219 (9)	0.0053 (7)	0.0117 (8)	0.0007 (7)
C5	0.0206 (9)	0.0182 (8)	0.0280 (9)	0.0021 (7)	0.0133 (8)	0.0011 (7)
C6	0.0140 (8)	0.0199 (8)	0.0244 (9)	−0.0035 (7)	0.0015 (7)	−0.0009 (7)
C7	0.0171 (9)	0.0206 (9)	0.0202 (8)	−0.0039 (7)	−0.0010 (7)	0.0009 (7)
C8	0.0297 (10)	0.0175 (8)	0.0149 (8)	−0.0040 (7)	0.0060 (7)	−0.0019 (7)
C9	0.0272 (10)	0.0172 (8)	0.0169 (8)	−0.0015 (7)	0.0089 (7)	−0.0001 (7)
C10	0.0186 (9)	0.0141 (8)	0.0217 (8)	0.0015 (7)	0.0110 (7)	−0.0011 (7)
C11	0.0181 (8)	0.0083 (7)	0.0176 (8)	0.0003 (6)	0.0052 (7)	0.0024 (6)
C12	0.0179 (8)	0.0080 (7)	0.0168 (8)	−0.0021 (6)	0.0048 (6)	0.0006 (6)
O2	0.020 (2)	0.0159 (18)	0.084 (4)	0.0026 (16)	0.019 (3)	0.000 (3)
O2A	0.018 (2)	0.0196 (19)	0.079 (4)	0.0014 (15)	0.007 (3)	0.003 (3)

*Geometric parameters (Å, °)*

Zn1—O1	1.9856 (11)	C4—C5	1.512 (3)
Zn1—Cl3	2.2345 (5)	C4—H4A	0.9900
Zn1—Cl1	2.2616 (5)	C4—H4B	0.9900
Zn1—Cl2	2.2856 (5)	C5—H5A	0.9900
O1—N1	1.3996 (16)	C5—H5B	0.9900
N1—C1	1.500 (2)	C6—C7	1.504 (3)
N1—C10	1.508 (2)	C6—H6A	0.9900

N1—C12	1.542 (2)	C6—H6B	0.9900
N2—C11	1.427 (2)	C7—H7A	0.9900
N2—C2	1.465 (2)	C7—H7B	0.9900
N2—C3	1.469 (2)	C8—C9	1.522 (2)
N3—C6	1.495 (2)	C8—H8A	0.9900
N3—C5	1.499 (2)	C8—H8B	0.9900
N3—C11	1.536 (2)	C9—C10	1.516 (2)
N3—H3	1.0000	C9—H9A	0.9900
N4—C12	1.429 (2)	C9—H9B	0.9900
N4—C7	1.470 (2)	C10—H10A	0.9900
N4—C8	1.475 (2)	C10—H10B	0.9900
C1—C2	1.498 (2)	C11—C12	1.523 (2)
C1—H1A	0.9900	C11—H11	1.0000
C1—H1B	0.9900	C12—H12	1.0000
C2—H2A	0.9900	O2—H2C	0.87 (4)
C2—H2B	0.9900	O2—H2D	0.87 (4)
C3—C4	1.523 (2)	O2A—H2E	0.87 (4)
C3—H3A	0.9900	O2A—H2F	0.98 (6)
C3—H3B	0.9900		
O1—Zn1—Cl3	107.03 (4)	N3—C5—H5A	109.6
O1—Zn1—Cl1	109.33 (4)	C4—C5—H5A	109.6
Cl3—Zn1—Cl1	111.812 (19)	N3—C5—H5B	109.6
O1—Zn1—Cl2	110.93 (3)	C4—C5—H5B	109.6
Cl3—Zn1—Cl2	111.244 (19)	H5A—C5—H5B	108.1
Cl1—Zn1—Cl2	106.531 (18)	N3—C6—C7	110.23 (14)
N1—O1—Zn1	124.84 (9)	N3—C6—H6A	109.6
O1—N1—C1	110.64 (12)	C7—C6—H6A	109.6
O1—N1—C10	111.42 (12)	N3—C6—H6B	109.6
C1—N1—C10	110.01 (13)	C7—C6—H6B	109.6
O1—N1—C12	107.32 (11)	H6A—C6—H6B	108.1
C1—N1—C12	108.81 (12)	N4—C7—C6	110.56 (14)
C10—N1—C12	108.55 (12)	N4—C7—H7A	109.5
C11—N2—C2	116.85 (13)	C6—C7—H7A	109.5
C11—N2—C3	111.79 (14)	N4—C7—H7B	109.5
C2—N2—C3	113.48 (14)	C6—C7—H7B	109.5
C6—N3—C5	110.74 (13)	H7A—C7—H7B	108.1
C6—N3—C11	109.42 (13)	N4—C8—C9	112.18 (14)
C5—N3—C11	110.19 (12)	N4—C8—H8A	109.2
C6—N3—H3	108.8	C9—C8—H8A	109.2
C5—N3—H3	108.8	N4—C8—H8B	109.2
C11—N3—H3	108.8	C9—C8—H8B	109.2
C12—N4—C7	117.04 (13)	H8A—C8—H8B	107.9
C12—N4—C8	112.30 (14)	C10—C9—C8	109.44 (14)
C7—N4—C8	113.11 (14)	C10—C9—H9A	109.8
C2—C1—N1	109.18 (13)	C8—C9—H9A	109.8
C2—C1—H1A	109.8	C10—C9—H9B	109.8
N1—C1—H1A	109.8	C8—C9—H9B	109.8



C2—C1—H1B	109.8	H9A—C9—H9B	108.2
N1—C1—H1B	109.8	N1—C10—C9	110.21 (14)
H1A—C1—H1B	108.3	N1—C10—H10A	109.6
N2—C2—C1	110.04 (14)	C9—C10—H10A	109.6
N2—C2—H2A	109.7	N1—C10—H10B	109.6
C1—C2—H2A	109.7	C9—C10—H10B	109.6
N2—C2—H2B	109.7	H10A—C10—H10B	108.1
C1—C2—H2B	109.7	N2—C11—C12	112.94 (14)
H2A—C2—H2B	108.2	N2—C11—N3	113.56 (13)
N2—C3—C4	112.29 (14)	C12—C11—N3	110.86 (13)
N2—C3—H3A	109.1	N2—C11—H11	106.3
C4—C3—H3A	109.1	C12—C11—H11	106.3
N2—C3—H3B	109.1	N3—C11—H11	106.3
C4—C3—H3B	109.1	N4—C12—C11	113.04 (14)
H3A—C3—H3B	107.9	N4—C12—N1	113.60 (13)
C5—C4—C3	109.50 (15)	C11—C12—N1	110.04 (13)
C5—C4—H4A	109.8	N4—C12—H12	106.5
C3—C4—H4A	109.8	C11—C12—H12	106.5
C5—C4—H4B	109.8	N1—C12—H12	106.5
C3—C4—H4B	109.8	H2C—O2—H2D	92 (7)
H4A—C4—H4B	108.2	H2E—O2A—H2F	124 (9)
N3—C5—C4	110.20 (14)		
Zn1—O1—N1—C1	-62.44 (15)	C12—N1—C10—C9	-57.12 (16)
Zn1—O1—N1—C10	60.28 (15)	C8—C9—C10—N1	58.25 (18)
Zn1—O1—N1—C12	178.98 (9)	C2—N2—C11—C12	-48.08 (19)
O1—N1—C1—C2	-55.24 (16)	C3—N2—C11—C12	178.82 (13)
C10—N1—C1—C2	-178.78 (13)	C2—N2—C11—N3	79.25 (17)
C12—N1—C1—C2	62.43 (16)	C3—N2—C11—N3	-53.85 (17)
C11—N2—C2—C1	52.82 (19)	C6—N3—C11—N2	176.31 (13)
C3—N2—C2—C1	-174.84 (14)	C5—N3—C11—N2	54.33 (18)
N1—C1—C2—N2	-59.05 (17)	C6—N3—C11—C12	-55.28 (17)
C11—N2—C3—C4	55.33 (19)	C5—N3—C11—C12	-177.27 (13)
C2—N2—C3—C4	-79.42 (19)	C7—N4—C12—C11	-47.23 (19)
N2—C3—C4—C5	-56.6 (2)	C8—N4—C12—C11	179.49 (13)
C6—N3—C5—C4	-176.21 (14)	C7—N4—C12—N1	79.08 (18)
C11—N3—C5—C4	-55.01 (17)	C8—N4—C12—N1	-54.20 (18)
C3—C4—C5—N3	56.74 (19)	N2—C11—C12—N4	176.91 (13)
C5—N3—C6—C7	-178.14 (14)	N3—C11—C12—N4	48.17 (18)
C11—N3—C6—C7	60.20 (17)	N2—C11—C12—N1	48.73 (17)
C12—N4—C7—C6	51.16 (19)	N3—C11—C12—N1	-80.01 (16)
C8—N4—C7—C6	-175.92 (14)	O1—N1—C12—N4	-64.71 (16)
N3—C6—C7—N4	-56.85 (18)	C1—N1—C12—N4	175.53 (13)
C12—N4—C8—C9	54.02 (19)	C10—N1—C12—N4	55.82 (17)
C7—N4—C8—C9	-81.15 (18)	O1—N1—C12—C11	63.16 (15)
N4—C8—C9—C10	-55.69 (19)	C1—N1—C12—C11	-56.59 (16)
O1—N1—C10—C9	60.84 (16)	C10—N1—C12—C11	-176.31 (13)
C1—N1—C10—C9	-176.07 (13)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3 $\cdots$ O1	1.00	2.15	2.8297 (18)	123
N3—H3 $\cdots$ O2	1.00	1.94	2.763 (6)	138
N3—H3 $\cdots$ O2 <i>A</i>	1.00	1.98	2.786 (7)	136
O2—H2 <i>C</i> $\cdots$ C12 <sup>i</sup>	0.87 (4)	2.61 (8)	3.154 (6)	121 (7)
O2—H2 <i>C</i> $\cdots$ N4 <sup>ii</sup>	0.87 (4)	2.61 (8)	3.262 (6)	133 (8)
O2—H2 <i>D</i> $\cdots$ C11	0.87 (4)	2.39 (4)	3.227 (6)	162 (6)
O2 <i>A</i> —H2 <i>E</i> $\cdots$ C12 <sup>i</sup>	0.87 (4)	2.69 (8)	3.295 (6)	128 (9)
O2 <i>A</i> —H2 <i>E</i> $\cdots$ N4 <sup>ii</sup>	0.87 (4)	2.84 (9)	3.202 (6)	107 (7)
O2 <i>A</i> —H2 <i>F</i> $\cdots$ C11	0.98 (6)	2.04 (7)	2.996 (6)	163 (5)
C1—H1 <i>A</i> $\cdots$ C12	0.99	2.78	3.6198 (18)	143
C2—H2 <i>B</i> $\cdots$ C13 <sup>iii</sup>	0.99	2.96	3.7412 (18)	136
C3—H3 <i>A</i> $\cdots$ N2 <sup>iv</sup>	0.99	2.64	3.348 (2)	129
C4—H4 <i>B</i> $\cdots$ C12 <sup>v</sup>	0.99	2.92	3.6201 (19)	128
C5—H5 <i>A</i> $\cdots$ C12 <sup>i</sup>	0.99	2.92	3.8290 (19)	154
C5—H5 <i>B</i> $\cdots$ C13 <sup>vi</sup>	0.99	2.90	3.8493 (19)	161
C6—H6 <i>A</i> $\cdots$ C11 <sup>vi</sup>	0.99	2.87	3.6295 (18)	135
C6—H6 <i>B</i> $\cdots$ C12 <sup>i</sup>	0.99	2.95	3.8679 (19)	154
C7—H7 <i>A</i> $\cdots$ O1	0.99	2.40	2.953 (2)	115
C8—H8 <i>A</i> $\cdots$ C12 <sup>vii</sup>	0.99	2.73	3.6088 (19)	149
C8—H8 <i>B</i> $\cdots$ C11 <sup>viii</sup>	0.99	2.73	3.7009 (19)	168
C10—H10 <i>A</i> $\cdots$ C12	0.99	2.67	3.5420 (17)	147
C10—H10 <i>B</i> $\cdots$ C11 <sup>vii</sup>	0.99	2.89	3.7018 (17)	139
C12—H12 $\cdots$ C12 <sup>vii</sup>	1.00	2.74	3.6524 (17)	152

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