

# Crystal structure of 3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0<sup>7,12</sup>]docosane tetrachloride tetrahydrate from synchrotron X-ray data

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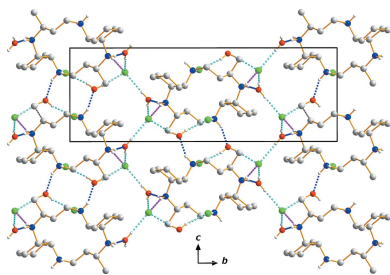
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The crystal structure of the title salt,  $C_{20}H_{44}N_4^{4+} \cdot 4Cl^- \cdot 4H_2O$ , has been determined using synchrotron radiation at 220 K. The structure determination reveals that protonation has occurred at all four amine N atoms. The asymmetric unit contains one half-cation (completed by crystallographic inversion symmetry), two chloride anions and two water molecules. There are two molecules in the unit cell. The  $Cl^-$  anions and hydrate molecules are involved in hydrogen bonding. The crystal structure is stabilized by intermolecular hydrogen bonds involving the macrocycle N—H groups and water O—H groups as donors and the O atoms of the water molecules and the  $Cl^-$  anions as acceptors, giving rise to a three-dimensional network.

## 1. Chemical context

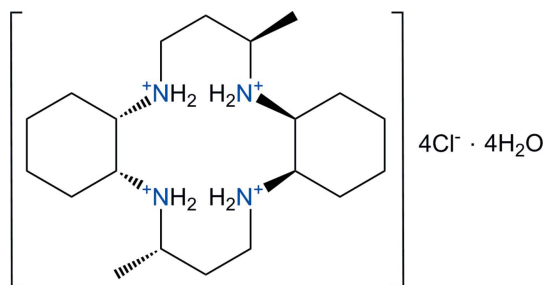
The macrocycle 3,14-dimethyl-2,6,13,17-tetraazatricyclo-(16.4.0.0<sup>7,12</sup>)docosane ( $C_{20}H_{40}N_4$ , *L*) is a strongly basic amine capable of forming the  $[C_{20}H_{42}N_4]^{2+}$  dication or the  $[C_{20}H_{44}N_4]^{4+}$  tetracation in which all of the N—H bonds are generally available for hydrogen-bond formation. These di- or tetraammonium cations may be suitable for the removal of toxic heavy metal ions from water. The macrocycle *L* contains a cyclam backbone with two cyclohexane subunits. Methyl groups are attached to the 3 and 14 carbon atoms of the propyl chains that bridge opposite pairs of N atoms in the structure. Previously, we have reported the crystal structures of  $[Cu(L)](NO_3)_2 \cdot 3H_2O$ ,  $[Cu(L)](NO_3)_2$ ,  $[Cu(L)](ClO_4)_2$  and  $[Cu(L)(H_2O)_2](BF_4)_2 \cdot 2H_2O$  together with  $[Zn(L)(OCOCH_3)_2]$ . In these structures, the copper(II) or zinc(II) cations have tetragonally distorted octahedral environments with the four N atoms of the macrocyclic ligand in equatorial positions and O atoms of counter-anions, water molecules or acetate ligands in axial positions (Choi *et al.*, 2006, 2007, 2012*a,b*; Ross *et al.*, 2012). In these  $Cu^{II}$  and  $Zn^{II}$  complexes, the macrocyclic ligands adopt their most stable *trans*-III configurations. The crystal structures of the di-cations  $C_{20}H_{40}N_4 \cdot 2C_{11}H_{10}O$  (Choi *et al.*, 2012*c*) and  $[C_{20}H_{42}N_4](SO_4) \cdot 2MeOH$  (White *et al.*, 2015) have also been reported. As part of our research program in this area, we report here the preparation of the new tetracationic compound,  $[C_{20}H_{44}N_4]Cl_4 \cdot 4H_2O$ , (I), as the hydrated chloride salt and its structural characterization by synchrotron single-crystal X-ray diffraction.



## 2. Structural commentary

The title compound contains a positively charged macrocyclic cation, 4 $Cl^-$  anions and four solvent water molecules and was

characterized during studies of the macrocyclic ligand and its copper(II) complexes. An ellipsoid plot of the molecular components in (I) with the atom-numbering scheme is shown in Fig. 1. The asymmetric unit consists of one half of the macrocycle, which lies about a center of inversion, two chloride anions and two solvent water molecules. The four N atoms are coplanar, and the two methyl substituents are *anti* with respect to the macrocyclic plane as a result of the molecular inversion symmetry. The six-membered cyclohexane ring is in a stable chair conformation. Within the centrosymmetric tetra-protonated amine unit  $[C_{20}H_{44}N_4]^{4+}$ , the C–C and N–C bond lengths vary from 1.522 (2) to 1.542 (2) Å and from 1.506 (2) to 1.522 (2) Å, respectively. The ranges of N–C–C and C–N–C angles are 106.85 (10) to 114.32 (11)° and 116.70 (10) to 118.89 (10)°, respectively. The bond lengths and angles within the  $[C_{20}H_{44}N_4]^{4+}$  tetra-cation are comparable to those found in the free ligand or the di-cation in  $C_{20}H_{40}N_4 \cdot 2C_{11}H_{10}O$  (Choi *et al.*, 2012c),  $[C_{20}H_{42}N_4](SO_4) \cdot 2MeOH$  (White *et al.*, 2015) and  $[C_{20}H_{42}N_4][Fe\{HB(pz)_3\}(CN)_3\}_2 \cdot 2H_2O \cdot 2MeOH$  (Kim *et al.*, 2004).



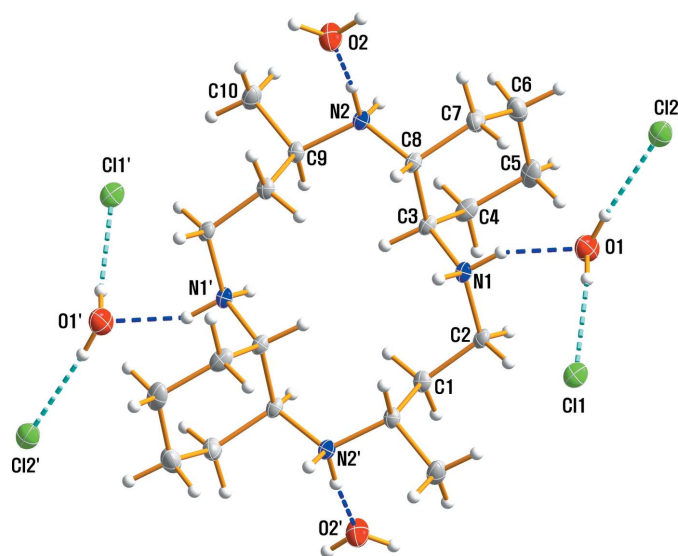
### 3. Supramolecular features

Extensive O–H···Cl, N–H···Cl and N–H···O hydrogen-bonding interactions occur in the crystal structure (Table 1). All of the Cl<sup>−</sup> anions and the O atoms of the water molecules serve as hydrogen-bond acceptors. O–H···Cl hydrogen bonds link the water molecules to the neighboring Cl<sup>−</sup> anions, while N–H···Cl and N–H···O hydrogen bonds interconnect the  $[C_{20}H_{44}N_4]^{4+}$  cations with both anions and water molecules (Figs. 1 and 2). The hydrogen atoms on N1 and N2 both form bifurcated hydrogen bonds with O and Cl atoms. The extensive array of these contacts generates a three-dimensional

**Table 1**  
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>
O1–H1O1···Cl1	0.84 (1)	2.26 (1)	3.0837 (13)	167 (2)
O1–H2O1···Cl2	0.84 (1)	2.30 (1)	3.1329 (13)	173 (2)
O2–H1O2···Cl2 <sup>i</sup>	0.83 (1)	2.32 (1)	3.1403 (14)	172 (2)
O2–H2O2···Cl2 <sup>ii</sup>	0.83 (1)	2.35 (1)	3.1839 (16)	174 (2)
N1–H1AN···Cl1 <sup>iii</sup>	0.90	2.20	3.0939 (12)	171
N1–H1B···O1	0.90	1.90	2.7484 (17)	156
N2–H2AN···Cl2 <sup>iv</sup>	0.90	2.41	3.2819 (13)	164
N2–H2B···O2	0.90	1.85	2.7245 (16)	163

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

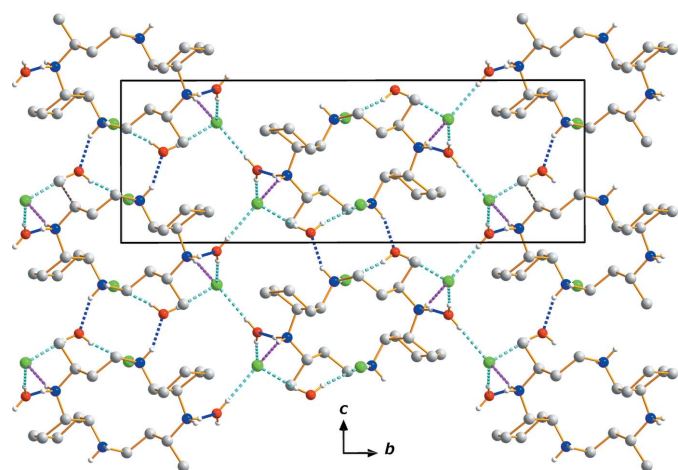


**Figure 1**  
The molecular structure of compound (I), drawn with displacement ellipsoids at the 50% probability level. Dashed lines represent hydrogen-bonding interactions and primed atoms are related by the symmetry code (1 − *x*, 1 − *y*, 1 − *z*).

network structure (Fig. 2), and these hydrogen-bonding interactions help to stabilize the crystal structure.

### 4. Database survey

A search of the Cambridge Structural Database (Version 5.38, May 2017 with three updates; Groom *et al.*, 2016) gave just three hits for compounds containing the macrocycles  $[C_{20}H_{44}N_4]^{4+}$ ,  $[C_{20}H_{42}N_4]^{2+}$  or  $(C_{20}H_{40}N_4)$ . The crystal structures of  $C_{20}H_{40}N_4 \cdot 2C_{11}H_{10}O$  (Choi *et al.*, 2012c),  $[C_{20}H_{42}N_4](SO_4) \cdot 2MeOH$  (White *et al.*, 2015) and  $[C_{20}H_{42}N_4][Fe\{HB(pz)_3\}(CN)_3\}_2 \cdot 2H_2O \cdot 2MeOH$  (Kim *et al.*, 2004) were



**Figure 2**  
The crystal packing in compound (I), viewed perpendicular to the *bc* plane. Dashed lines represent N–H···O (blue), N–H···Cl (pink) and O–H···Cl (cyan) hydrogen-bonding interactions, respectively. C-bound H atoms have been omitted.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{44}N_4^{4+} \cdot 4Cl^- \cdot 4H_2O$
$M_r$	554.45
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	220
$a, b, c$ (Å)	7.5450 (15), 23.190 (5), 8.3370 (17)
$\beta$ (°)	103.32 (3)
$V$ (Å <sup>3</sup> )	1419.5 (5)
$Z$	2
Radiation type	Synchrotron, $\lambda = 0.630$ Å
$\mu$ (mm <sup>-1</sup> )	0.32
Crystal size (mm)	0.08 × 0.06 × 0.06
Data collection	
Diffractometer	Rayonix MX225HS CCD area detector
Absorption correction	Empirical (using intensity measurements) ( <i>HKL3000sm SCALEPACK</i> ; Otwinowski & Minor, 1997)
$T_{min}, T_{max}$	0.919, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	13816, 3797, 3504
$R_{int}$	0.061
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.683
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.046, 0.141, 1.14
No. of reflections	3797
No. of parameters	158
No. of restraints	6
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> )	0.80, -0.33

Computer programs: *PAL BL2D-SMDC* (Shin *et al.*, 2016), *HKL3000sm* (Otwinowski & Minor, 1997), *SHELXT2015* (Sheldrick, 2015a), *SHELXL2015* (Sheldrick, 2015b), *DIAMOND* (Putz & Brandenburg, 2014) and *pubCIF* (Westrip, 2010).

reported previously. However, to our knowledge no crystal structure of any compound with  $[C_{20}H_{44}N_4]^{4+}$  has been reported.

## 5. Synthesis and crystallization

Commercially available *trans*-1,2-cyclohexanediamine and methyl vinyl ketone (Sigma–Aldrich) were used as provided. All chemicals were reagent grade and used without further purification. As a starting material, the macrocycle 3,14-dimethyl-2,6,13,17-tetraazatricyclo(16.4.0.0<sup>7,12</sup>)docosane was prepared according to a published procedure (Kang *et al.*, 1991). A solution of the macrocyclic ligand (0.084 g, 0.25 mmol) in water (10 mL) was added dropwise to a stirred solution of  $CuCl_2 \cdot 2H_2O$  (0.085 g, 0.5 mmol) in water (15 mL). The solution was heated for 1 h at 338 K. After cooling to 298 K, the pH was adjusted to 3.0 with 1.0 M HCl. The solution was filtered and left at room temperature. Colourless crystals

suitable for X-ray analysis were obtained unexpectedly from the solution over a period of a few days.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All C and N-bound H atoms in the complex were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H distances of 0.97–0.99 Å, an N–H distance of 0.9 Å and with  $U_{iso}(H)$  values of  $1.2U_{eq}(C, N)$  and  $1.5U_{eq}(C\text{-methyl})$ . O-bound H atoms of the water molecules were located in a difference-Fourier map, and the O–H distances and the H–O–H angles were restrained using DFIX and DANG constraints (0.84 and 1.36 Å).

## Funding information

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## supporting information

*Acta Cryst.* (2018). E74, 1039-1041 [https://doi.org/10.1107/S2056989018009337]

## Crystal structure of 3,14-dimethyl-2,6,13,17-tetraazoniatricyclo[16.4.0.0<sup>7,12</sup>]docosane tetrachloride tetrahydrate from synchrotron X-ray data

**Dohyun Moon and Jong-Ha Choi**

### Computing details

Data collection: *PAL BL2D-SMDC* (Shin *et al.*, 2016); cell refinement: *HKL3000sm* (Otwinowski & Minor, 1997); data reduction: *HKL3000sm* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXT2015* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2015* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Putz & Brandenburg, 2014); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

### 3,14-Dimethyl-2,6,13,17-tetraazoniatricyclo[16.4.0.0<sup>7,12</sup>]docosane tetrachloride tetrahydrate

#### Crystal data

C<sub>20</sub>H<sub>44</sub>N<sub>4</sub><sup>4+</sup>·4Cl<sup>-</sup>·4H<sub>2</sub>O

*M<sub>r</sub>* = 554.45

Monoclinic, *P2<sub>1</sub>/n*

*a* = 7.5450 (15) Å

*b* = 23.190 (5) Å

*c* = 8.3370 (17) Å

$\beta$  = 103.32 (3)°

*V* = 1419.5 (5) Å<sup>3</sup>

*Z* = 2

*F*(000) = 600

*D<sub>x</sub>* = 1.297 Mg m<sup>-3</sup>

Synchrotron radiation,  $\lambda$  = 0.630 Å

Cell parameters from 44298 reflections

$\theta$  = 0.4–33.6°

$\mu$  = 0.32 mm<sup>-1</sup>

*T* = 220 K

Block, colourless

0.08 × 0.06 × 0.06 mm

#### Data collection

Rayonix MX225HS CCD area detector  
diffractometer

Radiation source: PLSII 2D bending magnet  
 $\omega$  scans

Absorption correction: empirical (using  
intensity measurements)

(*HKL3000sm SCALEPACK*; Otwinowski &  
Minor, 1997)

*T<sub>min</sub>* = 0.919, *T<sub>max</sub>* = 1.000

13816 measured reflections

3797 independent reflections

3504 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.061

$\theta_{\max}$  = 25.5°,  $\theta_{\min}$  = 1.6°

*h* = -10→10

*k* = -31→31

*l* = -11→11

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.046

*wR*(*F*<sup>2</sup>) = 0.141

*S* = 1.14

3797 reflections

158 parameters

6 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0863*P*)<sup>2</sup> + 0.2986*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.001

Δρ<sub>max</sub> = 0.80 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.28649 (4)	0.48361 (2)	-0.23231 (4)	0.02152 (13)
C12	0.23041 (5)	0.70611 (2)	-0.24081 (5)	0.02724 (13)
O1	0.17644 (18)	0.59115 (5)	-0.06048 (14)	0.0292 (3)
H1O1	0.211 (3)	0.5659 (7)	-0.118 (2)	0.044*
H2O1	0.190 (3)	0.6234 (5)	-0.101 (3)	0.044*
O2	0.81871 (15)	0.70598 (5)	0.55335 (16)	0.0285 (3)
H1O2	0.807 (3)	0.7293 (8)	0.476 (2)	0.043*
H2O2	0.9243 (18)	0.7082 (9)	0.612 (2)	0.043*
N1	0.31217 (15)	0.54018 (5)	0.24038 (13)	0.0135 (2)
H1AN	0.424887	0.529030	0.234909	0.016*
H1B	0.273908	0.566098	0.159468	0.016*
N2	0.52610 (14)	0.64198 (5)	0.58563 (14)	0.0145 (2)
H2AN	0.431936	0.660340	0.612559	0.017*
H2B	0.612982	0.668566	0.585565	0.017*
C1	0.24830 (16)	0.43768 (5)	0.32273 (16)	0.0151 (2)
H1A	0.142456	0.413129	0.322216	0.018*
H1AB	0.292168	0.452568	0.434890	0.018*
C2	0.18858 (17)	0.48834 (5)	0.20562 (17)	0.0151 (3)
H2A	0.182324	0.475365	0.092579	0.018*
H2AB	0.065641	0.500024	0.212226	0.018*
C3	0.32531 (16)	0.57005 (5)	0.40305 (15)	0.0139 (2)
H3	0.374735	0.542524	0.493008	0.017*
C4	0.13998 (17)	0.59125 (6)	0.42271 (17)	0.0190 (3)
H4A	0.055377	0.558611	0.409763	0.023*
H4AB	0.152601	0.606815	0.534063	0.023*
C5	0.06125 (19)	0.63767 (7)	0.29694 (19)	0.0240 (3)
H5A	-0.055674	0.650884	0.315737	0.029*
H5AB	0.039283	0.621385	0.185629	0.029*
C6	0.1913 (2)	0.68874 (7)	0.31020 (19)	0.0257 (3)
H6A	0.199462	0.708191	0.416010	0.031*
H6AB	0.142341	0.716389	0.222244	0.031*
C7	0.38260 (19)	0.67021 (6)	0.29703 (18)	0.0205 (3)
H7A	0.378106	0.658961	0.182857	0.025*
H7AB	0.464730	0.703370	0.323138	0.025*
C8	0.46174 (16)	0.62004 (5)	0.41108 (15)	0.0141 (2)
H8	0.569077	0.605031	0.374969	0.017*
C9	0.60141 (16)	0.59907 (5)	0.72246 (16)	0.0144 (2)
H9	0.501674	0.573469	0.737922	0.017*
C10	0.6708 (2)	0.63373 (6)	0.87937 (17)	0.0233 (3)

H10A	0.706638	0.607639	0.972125	0.035*
H10B	0.574944	0.659033	0.897628	0.035*
H10C	0.774932	0.656615	0.868372	0.035*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.01190 (19)	0.0294 (2)	0.0260 (2)	-0.00148 (11)	0.01001 (14)	-0.00336 (13)
Cl2	0.0223 (2)	0.0314 (2)	0.0275 (2)	0.00606 (13)	0.00466 (16)	-0.00617 (14)
O1	0.0377 (6)	0.0317 (6)	0.0187 (5)	0.0038 (5)	0.0078 (5)	-0.0001 (4)
O2	0.0175 (5)	0.0358 (6)	0.0316 (6)	-0.0066 (4)	0.0043 (5)	0.0089 (5)
N1	0.0089 (4)	0.0188 (5)	0.0133 (5)	0.0003 (4)	0.0036 (4)	-0.0002 (4)
N2	0.0105 (5)	0.0176 (5)	0.0151 (5)	-0.0007 (4)	0.0024 (4)	-0.0005 (4)
C1	0.0102 (5)	0.0195 (5)	0.0163 (6)	0.0012 (4)	0.0045 (4)	0.0007 (5)
C2	0.0093 (5)	0.0183 (5)	0.0162 (6)	-0.0006 (4)	-0.0001 (4)	-0.0021 (5)
C3	0.0106 (5)	0.0192 (5)	0.0124 (5)	-0.0028 (4)	0.0036 (4)	-0.0016 (4)
C4	0.0121 (6)	0.0275 (6)	0.0198 (6)	-0.0038 (5)	0.0083 (5)	-0.0062 (5)
C5	0.0130 (6)	0.0349 (7)	0.0236 (7)	0.0061 (5)	0.0035 (5)	-0.0039 (6)
C6	0.0254 (7)	0.0249 (6)	0.0250 (7)	0.0071 (6)	0.0024 (6)	0.0034 (6)
C7	0.0188 (6)	0.0223 (6)	0.0189 (6)	-0.0018 (5)	0.0012 (5)	0.0054 (5)
C8	0.0104 (5)	0.0192 (5)	0.0127 (5)	-0.0026 (4)	0.0024 (4)	-0.0004 (5)
C9	0.0106 (5)	0.0190 (5)	0.0137 (6)	0.0008 (4)	0.0028 (4)	0.0009 (4)
C10	0.0242 (7)	0.0278 (7)	0.0159 (6)	0.0051 (6)	0.0004 (5)	-0.0054 (5)

*Geometric parameters (Å, °)*

O1—H1O1	0.837 (9)	C3—H3	0.9900
O1—H2O1	0.837 (9)	C4—C5	1.524 (2)
O2—H1O2	0.833 (9)	C4—H4A	0.9800
O2—H2O2	0.834 (9)	C4—H4AB	0.9800
N1—C3	1.5056 (16)	C5—C6	1.526 (2)
N1—C2	1.5080 (16)	C5—H5A	0.9800
N1—H1AN	0.9000	C5—H5AB	0.9800
N1—H1B	0.9000	C6—C7	1.534 (2)
N2—C8	1.5122 (17)	C6—H6A	0.9800
N2—C9	1.5217 (16)	C6—H6AB	0.9800
N2—H2AN	0.9000	C7—C8	1.5338 (18)
N2—H2B	0.9000	C7—H7A	0.9800
C1—C2	1.5277 (18)	C7—H7AB	0.9800
C1—C9 <sup>i</sup>	1.5333 (17)	C8—H8	0.9900
C1—H1A	0.9800	C9—C10	1.5217 (19)
C1—H1AB	0.9800	C9—H9	0.9900
C2—H2A	0.9800	C10—H10A	0.9700
C2—H2AB	0.9800	C10—H10B	0.9700
C3—C4	1.5263 (17)	C10—H10C	0.9700
C3—C8	1.5416 (17)		
H1O1—O1—H2O1	108.0 (17)	H4A—C4—H4AB	107.9

H1O2—O2—H2O2	108.9 (18)	C4—C5—C6	110.86 (12)
C3—N1—C2	116.70 (10)	C4—C5—H5A	109.5
C3—N1—H1AN	108.1	C6—C5—H5A	109.5
C2—N1—H1AN	108.1	C4—C5—H5AB	109.5
C3—N1—H1B	108.1	C6—C5—H5AB	109.5
C2—N1—H1B	108.1	H5A—C5—H5AB	108.1
H1AN—N1—H1B	107.3	C5—C6—C7	112.18 (12)
C8—N2—C9	118.89 (10)	C5—C6—H6A	109.2
C8—N2—H2AN	107.6	C7—C6—H6A	109.2
C9—N2—H2AN	107.6	C5—C6—H6AB	109.2
C8—N2—H2B	107.6	C7—C6—H6AB	109.2
C9—N2—H2B	107.6	H6A—C6—H6AB	107.9
H2AN—N2—H2B	107.0	C8—C7—C6	113.98 (11)
C2—C1—C9 <sup>i</sup>	113.35 (10)	C8—C7—H7A	108.8
C2—C1—H1A	108.9	C6—C7—H7A	108.8
C9 <sup>i</sup> —C1—H1A	108.9	C8—C7—H7AB	108.8
C2—C1—H1AB	108.9	C6—C7—H7AB	108.8
C9 <sup>i</sup> —C1—H1AB	108.9	H7A—C7—H7AB	107.7
H1A—C1—H1AB	107.7	N2—C8—C7	109.53 (10)
N1—C2—C1	114.32 (11)	N2—C8—C3	110.97 (10)
N1—C2—H2A	108.7	C7—C8—C3	112.51 (11)
C1—C2—H2A	108.7	N2—C8—H8	107.9
N1—C2—H2AB	108.7	C7—C8—H8	107.9
C1—C2—H2AB	108.7	C3—C8—H8	107.9
H2A—C2—H2AB	107.6	C10—C9—N2	107.10 (11)
N1—C3—C4	111.91 (10)	C10—C9—C1 <sup>i</sup>	112.18 (11)
N1—C3—C8	106.85 (10)	N2—C9—C1 <sup>i</sup>	110.41 (10)
C4—C3—C8	111.85 (11)	C10—C9—H9	109.0
N1—C3—H3	108.7	N2—C9—H9	109.0
C4—C3—H3	108.7	C1 <sup>i</sup> —C9—H9	109.0
C8—C3—H3	108.7	C9—C10—H10A	109.5
C5—C4—C3	112.03 (11)	C9—C10—H10B	109.5
C5—C4—H4A	109.2	H10A—C10—H10B	109.5
C3—C4—H4A	109.2	C9—C10—H10C	109.5
C5—C4—H4AB	109.2	H10A—C10—H10C	109.5
C3—C4—H4AB	109.2	H10B—C10—H10C	109.5
C3—N1—C2—C1	-64.11 (14)	C9—N2—C8—C3	52.13 (14)
C9 <sup>i</sup> —C1—C2—N1	-80.89 (14)	C6—C7—C8—N2	-76.56 (14)
C2—N1—C3—C4	-58.63 (14)	C6—C7—C8—C3	47.36 (16)
C2—N1—C3—C8	178.63 (10)	N1—C3—C8—N2	-163.70 (10)
N1—C3—C4—C5	-64.60 (14)	C4—C3—C8—N2	73.52 (13)
C8—C3—C4—C5	55.26 (15)	N1—C3—C8—C7	73.18 (13)
C3—C4—C5—C6	-57.49 (15)	C4—C3—C8—C7	-49.60 (15)
C4—C5—C6—C7	54.14 (16)	C8—N2—C9—C10	174.85 (11)

C5—C6—C7—C8	-49.87 (17)	C8—N2—C9—C1 <sup>i</sup>	52.43 (14)
C9—N2—C8—C7	176.95 (10)		

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

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1—H1O1...C11	0.84 (1)	2.26 (1)	3.0837 (13)	167 (2)
O1—H2O1...C12	0.84 (1)	2.30 (1)	3.1329 (13)	173 (2)
O2—H1O2...C12 <sup>ii</sup>	0.83 (1)	2.32 (1)	3.1403 (14)	172 (2)
O2—H2O2...C12 <sup>iii</sup>	0.83 (1)	2.35 (1)	3.1839 (16)	174 (2)
N1—H1AN...C11 <sup>iv</sup>	0.90	2.20	3.0939 (12)	171
N1—H1B...O1	0.90	1.90	2.7484 (17)	156
N2—H2AN...C12 <sup>v</sup>	0.90	2.41	3.2819 (13)	164
N2—H2B...O2	0.90	1.85	2.7245 (16)	163

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