

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

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hydrogen bonding; synchrotron radiation.

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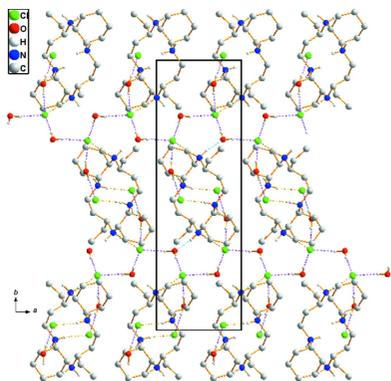
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The crystal structure of the hydrated title salt,  $C_{22}H_{48}N_4^{4+} \cdot 4Cl^- \cdot 4H_2O$  ( $C_{22}H_{48}N_4 = H_4L = 3,14$ -diethyl-2,6,13,17-tetraazoniatricyclo[16.4.0.0<sup>7,12</sup>]docosane), has been determined using synchrotron radiation at 220 K. The structure determination reveals that protonation has occurred at all four amine N atoms. The asymmetric unit comprises one half of the macrocyclic cation (completed by crystallographic inversion symmetry), two chloride anions and two water molecules. The macrocyclic ring of the tetracation adopts an exodentate (3,4,3,4)-*D* conformation. 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 chloride anions as acceptors, giving rise to a three-dimensional network.

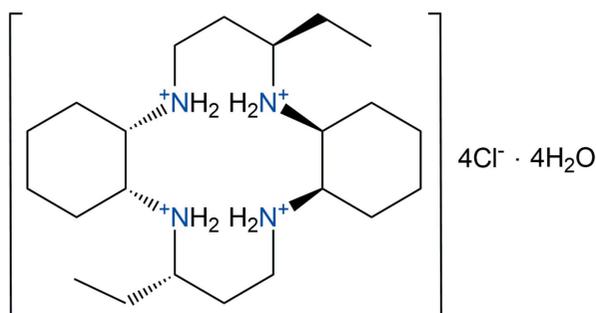
## 1. Chemical context

In recent years, derivatives of 1,4,8,11-tetraazacyclotetradecane (cyclam) have been found to exhibit anti-HIV effects (Ronconi & Sadler, 2007; Ross *et al.*, 2012) and to stimulate the activity of stem cells from bone marrow (De Clercq, 2010). The conformation of the macrocyclic ligand, the orientations of the N—H bonds and crystal packing forces in respective metal complexes are very important factors for CXCR4 chemokine receptor recognition. Therefore, knowledge of the conformations and crystal-packing features of complexes containing cyclam derivatives has become important in the development of new highly effective anti-HIV drugs that specifically target alternative events in the HIV replicative cycle. The macrocycle 3,14-diethyl-2,6,13,17-tetraazoniatricyclo-(16.4.0.0<sup>7,12</sup>)docosane ( $C_{22}H_{44}N_4$ , *L*) contains a cyclam backbone with two cyclohexane subunits. Ethyl groups are also attached to the 3 and 14 carbon atoms of the propyl chains that bridge opposite pairs of N atoms in the molecule. The macrocycle *L* is a strongly basic amine capable of forming the dication  $C_{22}H_{46}N_4^{2+}$  or even the tetracation  $C_{22}H_{48}N_4^{4+}$  in which all of the N—H bonds are generally available for hydrogen-bond formation. It is known that the neutral macrocycle and its dication adopt an endodentate conformation along the centre of the macrocyclic cavity. The stabilization of such an endo conformation can be attributed to strong intramolecular N—H...N hydrogen bonds. Unlike the free macrocycle and its dication, the tetracation adopts an exodentate conformation. Furthermore, the 14-membered cyclam moiety of the tetracation can adopt four exodentate



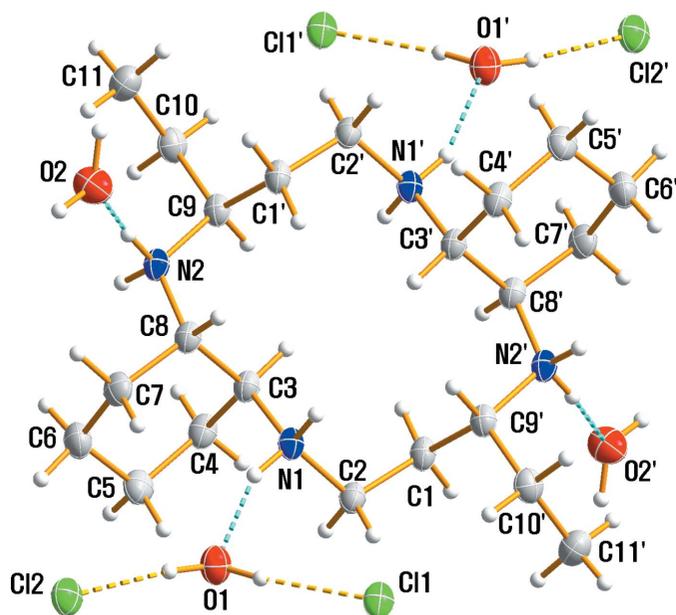
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(3,4,3,4)-(A-D) conformations (Meyer *et al.*, 1998; Nowicka *et al.*, 2012). Previously, the syntheses and crystal structures of the related compounds  $(C_{22}H_{44}N_4) \cdot NaClO_4$  (Aree *et al.*, 2018),  $[C_{22}H_{46}N_4](ClO_4)_2$  (Aree *et al.*, 2018),  $[C_{22}H_{46}N_4]Cl_2 \cdot 4H_2O$  (Moon *et al.*, 2013) and  $[C_{22}H_{46}N_4](NO_3)_2 \cdot 2H_2O$  (Moon *et al.*, 2019) have been reported. However, there is no report of a compound with the 3,14-diethyl-2,6,13,17-tetraazoniatri-cyclo(16.4.0.0<sup>7,12</sup>)docosane cation and any counter-anions. As another contribution to our research on this macrocyclic compound family, we report here the preparation of a new tetracationic compound  $[C_{22}H_{48}N_4]Cl_4 \cdot 4H_2O$ , (I), as the hydrated tetrachloride salt and its structural characterization by synchrotron single-crystal X-ray diffraction.



## 2. Structural commentary

The molecular structure of (I) is shown in Fig. 1 along with the atom-numbering scheme. The organic cation lies across a crystallographic inversion centre and hence the asymmetric



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

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1-H1O1 \cdots Cl2$	0.92 (1)	2.25 (1)	3.1616 (11)	172 (1)
$O1-H2O1 \cdots Cl1$	0.92 (1)	2.17 (1)	3.0746 (11)	169 (1)
$O2-H1O2 \cdots Cl2^i$	0.92 (1)	2.34 (1)	3.2518 (15)	172 (2)
$O2-H2O2 \cdots Cl2^{ii}$	0.91 (1)	2.26 (1)	3.1622 (12)	173 (2)
$N1-H1A \cdots Cl1^{iii}$	0.90	2.22	3.1072 (12)	169
$N1-H1B \cdots O1$	0.90	1.92	2.7740 (15)	157
$N2-H2A \cdots O2$	0.90	1.91	2.7716 (14)	161
$N2-H2B \cdots Cl2^{iv}$	0.90	2.45	3.3357 (12)	167

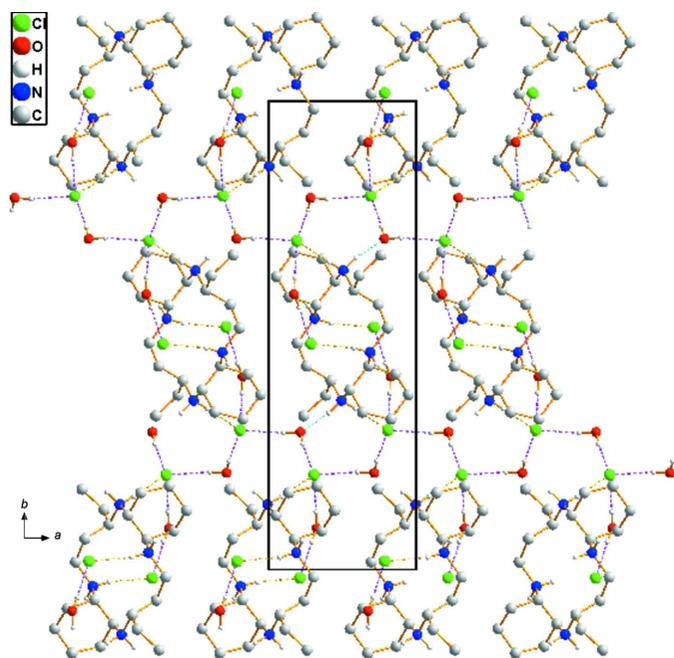
Symmetry codes: (i)  $x - 1, y, z - 1$ ; (ii)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $-x + 1, -y + 1, -z + 2$ ; (iv)  $x, y, z - 1$ .

unit consists of one half of the cationic macrocycle, of two chloride anions and two solvent water molecules. Within the centrosymmetric tetraprotonated amine unit  $C_{22}H_{48}N_4^{4+}$ , the C—C and N—C bond lengths range from 1.5208 (19) to 1.5431 (16)  $\text{\AA}$  and from 1.5076 (15) to 1.5247 (15)  $\text{\AA}$ , respectively; the range of N—C—C and C—N—C angles is 107.08 (9) to 111.72 (10) $^\circ$  and 116.40 (9) to 117.87 (9) $^\circ$ , respectively.

The four N atoms of the macrocycle are coplanar, and the two ethyl substituents are *anti* with respect to the macrocyclic plane as a result of the molecular inversion symmetry. The six-membered cyclohexane ring is in its stable chair conformation. The cyclam moiety of the tetracation adopts an exodentate rectangular (3,4,3,4)-D conformation, which differs from the endodentate conformation of the free macrocycle or the dication (Aree *et al.*, 2018; Moon *et al.*, 2013). Only two of the four nitrogen atoms, N2 and N2' [symmetry code: (')  $-x + 1, -y + 1, -z + 1$ ] are located at the corners of the macrocyclic square. The other two corner positions are occupied by carbon atoms C2 and C2'. Thus, the remaining two nitrogen atoms, N1 and N1' are components of the hydrocarbon side chain. Interestingly, the *exo*-[3,4,3,4]-D conformation of (I) also differs from the *exo*-[3,4,3,4]-B conformation of  $[H_4TMC](CrO_3Cl)_2Cl_2$  (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; Moon & Choi, 2020a), and the *exo*-[3,4,3,4]-C conformation of  $[H_4TMC](ClO_4)_2Cl_2$  (Moon & Choi, 2020b) or  $(H_4cyclam)[Cr_2O_7]_2 \cdot H_2O$  (Moon & Choi, 2017). The detailed understanding and insight into the crystal packing and conformation may be helpful in the development of new anti-HIV drugs.

## 3. Supramolecular features

Extensive O—H $\cdots$ Cl, N—H $\cdots$ Cl and N—H $\cdots$ O hydrogen-bonding interactions occur in the crystal structure (Table 1). All of the chloride anions and the O atoms of the water molecules serve as hydrogen-bond acceptors. The organic  $C_{22}H_{48}N_4^{4+}$  cation is linked to four water molecules *via* N—H $\cdots$ O hydrogen bonds whereas the O—H $\cdots$ Cl hydrogen bonds link the chloride anions to neighbouring water molecules. In addition, neighbouring organic cations are interconnected to chloride anions *via* several N—H $\cdots$ Cl hydrogen bonds. An extensive array of these contacts generates a three-



**Figure 2**  
The crystal packing in (I), viewed perpendicular to the  $ab$  plane. Dashed lines represent O—H...Cl (pink), N—H...O (cyan), and N—H...Cl (yellow) hydrogen-bonding interactions, respectively. For clarity, C-bound H atoms have been omitted.

dimensional network of molecules. The crystal packing of (I) viewed perpendicular to the  $ab$  plane is shown in Fig. 2.

#### 4. Database survey

A search of the Cambridge Structural Database (CSD; version 5.42, November 2020; Groom *et al.*, 2016) revealed five matches for organic compounds containing the macrocycles ( $C_{22}H_{44}N_4$ ),  $C_{22}H_{46}N_4^{2+}$  or  $C_{22}H_{48}N_4^{4+}$ . The crystal structures of  $(C_{22}H_{44}N_4) \cdot NaClO_4$  (Aree *et al.*, 2018),  $[C_{22}H_{46}N_4](ClO_4)_2$  (Aree *et al.*, 2018),  $[C_{22}H_{46}N_4]Cl_2 \cdot 4H_2O$  (Moon *et al.*, 2013) and  $[C_{22}H_{46}N_4](NO_3)_2 \cdot 2H_2O$  (Moon *et al.*, 2019) have been reported previously. All bond lengths and angles within the tetracation  $C_{22}H_{48}N_4^{4+}$  in (I) are similar to those found in the database structures.

Until now, no crystal structure of a compound with the tetracation  $C_{22}H_{48}N_4^{4+}$  and any counter-anion has been deposited.

#### 5. Synthesis and crystallization

Ethyl vinyl ketone (97%), *trans*-1,2-cyclohexanediamine (99%) and copper(II) chloride dihydrate (99%) were purchased from Sigma–Aldrich and were used as received. All other chemicals were of analytical reagent grade. The solvents were of reagent grade and purified by usual methods. As a starting material, the 3,14-diethyl-2,6,13,17-tetraazatricyclo-(16.4.0.0<sup>7,12</sup>)docosane macrocycle *L* was prepared according to a published procedure (Lim *et al.*, 2006). A solution of *L* (0.091 g, 0.25 mmol) in water (10 mL) was added dropwise to a

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{48}N_4^{4+} \cdot 4Cl^- \cdot 4H_2O$
$M_r$	582.50
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	220
$a, b, c$ (Å)	7.6550 (15), 23.533 (5), 8.3130 (17)
$\beta$ (°)	102.45 (3)
$V$ (Å <sup>3</sup> )	1462.3 (5)
$Z$	2
Radiation type	Synchrotron, $\lambda = 0.610$ Å
$\mu$ (mm <sup>-1</sup> )	0.29
Crystal size (mm)	0.08 × 0.07 × 0.04
Data collection	
Diffractometer	Rayonix MX225HS CCD area detector
Absorption correction	Empirical (using intensity measurements) ( <i>HKL3000sm SCALEPACK</i> ; Otwinowski <i>et al.</i> , 2003)
$T_{min}, T_{max}$	0.868, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	14961, 4016, 3517
$R_{int}$	0.038
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.693
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.105, 1.09
No. of reflections	4016
No. of parameters	167
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> )	0.41, -0.22

Computer programs: *PAL BL2D-SMDC* (Shin *et al.*, 2016), *HKL3000sm* (Otwinowski *et al.*, 2003), *SHELXT2018* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *DIAMOND* (Putz & Brandenburg, 2014) and *pubCIF* (Westrip, 2010).

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 373 K. After cooling to 298 K, the pH was adjusted to 3.0 by 1.0 M HCl. The solution was filtered and left at room temperature. A mixture of colourless, red and violet crystals formed from the solution over the next few days. The product mixture was added to a 30 ml MeOH–acetone (1:2 v:v) solution under stirring, and the stirring was continued for 30 min at 298 K. The red and violet compounds were manually removed, and block-like colorless single crystals of (I) suitable for X-ray analysis were obtained by filtration.

#### 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, and with an N—H distance of 0.90 Å with  $U_{iso}(H)$  values of 1.2 and 1.5  $U_{eq}$  of the parent atoms, respectively. 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 (0.94 and 1.55 Å, respectively).

### Acknowledgements

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## supporting information

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

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### Computing details

Data collection: *PAL BL2D-SMDC* (Shin *et al.*, 2016); cell refinement: *HKL3000sm* (Otwinowski *et al.*, 2003); data reduction: *HKL3000sm* (Otwinowski *et al.*, 2003); program(s) used to solve structure: *SHELXT2018* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Putz & Brandenburg, 2014); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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

#### Crystal data

$C_{22}H_{48}N_4^{4+} \cdot 4Cl^- \cdot 4H_2O$

$M_r = 582.50$

Monoclinic,  $P2_1/n$

$a = 7.6550$  (15) Å

$b = 23.533$  (5) Å

$c = 8.3130$  (17) Å

$\beta = 102.45$  (3)°

$V = 1462.3$  (5) Å<sup>3</sup>

$Z = 2$

$F(000) = 632$

$D_x = 1.323$  Mg m<sup>-3</sup>

Synchrotron radiation,  $\lambda = 0.610$  Å

Cell parameters from 50732 reflections

$\theta = 0.4$ – $33.7$ °

$\mu = 0.28$  mm<sup>-1</sup>

$T = 220$  K

Block, colorless

$0.08 \times 0.07 \times 0.04$  mm

#### Data collection

Rayonix MX225HS CCD area detector  
diffractometer

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

Absorption correction: empirical (using  
intensity measurements)

(*HKL3000sm Scalepack*; Otwinowski *et al.*,  
2003)

$T_{\min} = 0.868$ ,  $T_{\max} = 1.000$

14961 measured reflections

4016 independent reflections

3517 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 25.0$ °,  $\theta_{\min} = 1.5$ °

$h = -10 \rightarrow 10$

$k = -32 \rightarrow 32$

$l = -11 \rightarrow 11$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.105$

$S = 1.09$

4016 reflections

167 parameters

6 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 0.2081P]$

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

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.41$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.22$  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	0.71371 (4)	0.51779 (2)	1.23367 (4)	0.02947 (10)
C12	0.80805 (4)	0.29797 (2)	1.26093 (4)	0.03510 (10)
O1	0.82713 (14)	0.41203 (4)	1.06447 (12)	0.0341 (2)
H1O1	0.822 (2)	0.3768 (4)	1.1119 (19)	0.041*
H2O1	0.792 (2)	0.4405 (5)	1.1271 (18)	0.041*
O2	0.21622 (14)	0.29355 (5)	0.47672 (14)	0.0405 (2)
H1O2	0.1034 (16)	0.2916 (8)	0.4106 (19)	0.049*
H2O2	0.233 (2)	0.2681 (6)	0.5609 (16)	0.049*
N1	0.68792 (13)	0.46398 (4)	0.76471 (12)	0.0234 (2)
H1A	0.576535	0.473733	0.773054	0.028*
H1B	0.728900	0.438497	0.844668	0.028*
N2	0.49393 (13)	0.36101 (4)	0.42080 (12)	0.0239 (2)
H2A	0.409339	0.334408	0.420241	0.029*
H2B	0.588974	0.343395	0.395724	0.029*
C1	0.74209 (15)	0.56567 (5)	0.68089 (15)	0.0247 (2)
H1C	0.713036	0.551403	0.567493	0.030*
H1D	0.840569	0.592881	0.689320	0.030*
C2	0.80442 (16)	0.51617 (5)	0.79715 (16)	0.0255 (2)
H2C	0.926151	0.505782	0.788904	0.031*
H2D	0.809475	0.528837	0.910366	0.031*
C3	0.67631 (15)	0.43519 (5)	0.60043 (14)	0.0232 (2)
H3	0.622610	0.462009	0.511758	0.028*
C4	0.86023 (16)	0.41738 (5)	0.57551 (15)	0.0270 (2)
H4A	0.848164	0.401294	0.464927	0.032*
H4B	0.937435	0.450940	0.583476	0.032*
C5	0.94712 (16)	0.37373 (6)	0.70283 (17)	0.0307 (3)
H5A	0.968765	0.390841	0.812822	0.037*
H5B	1.062841	0.362317	0.680786	0.037*
C6	0.82840 (18)	0.32133 (6)	0.69882 (17)	0.0325 (3)
H6A	0.881223	0.296219	0.790489	0.039*
H6B	0.825026	0.300529	0.596063	0.039*
C7	0.63628 (17)	0.33618 (5)	0.71111 (16)	0.0288 (3)
H7A	0.562168	0.301986	0.687145	0.035*
H7B	0.636910	0.347551	0.824645	0.035*
C8	0.55016 (15)	0.38374 (5)	0.59487 (14)	0.0237 (2)
H8	0.441439	0.396678	0.630583	0.028*
C9	0.42198 (15)	0.40325 (5)	0.28341 (14)	0.0240 (2)
H9	0.516285	0.431990	0.282803	0.029*
C10	0.38798 (17)	0.37228 (5)	0.11758 (15)	0.0285 (2)

H10A	0.361097	0.400848	0.029936	0.034*
H10B	0.499099	0.353289	0.107674	0.034*
C11	0.2386 (2)	0.32840 (6)	0.08671 (18)	0.0371 (3)
H11A	0.259808	0.300603	0.174946	0.056*
H11B	0.235881	0.309471	-0.017459	0.056*
H11C	0.124952	0.347133	0.082958	0.056*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.02435 (15)	0.02771 (17)	0.04097 (18)	-0.00112 (10)	0.01724 (12)	-0.00061 (11)
C12	0.03364 (17)	0.03180 (18)	0.04254 (19)	0.00500 (12)	0.01410 (14)	-0.00293 (12)
O1	0.0398 (5)	0.0299 (5)	0.0361 (5)	0.0030 (4)	0.0156 (4)	0.0005 (4)
O2	0.0314 (5)	0.0430 (6)	0.0482 (6)	-0.0074 (4)	0.0111 (4)	0.0115 (5)
N1	0.0220 (4)	0.0202 (5)	0.0305 (5)	0.0007 (3)	0.0112 (4)	0.0001 (4)
N2	0.0223 (4)	0.0193 (4)	0.0322 (5)	-0.0009 (3)	0.0107 (4)	-0.0002 (4)
C1	0.0242 (5)	0.0191 (5)	0.0339 (6)	-0.0003 (4)	0.0134 (4)	-0.0003 (4)
C2	0.0227 (5)	0.0204 (5)	0.0343 (6)	-0.0008 (4)	0.0083 (4)	-0.0021 (4)
C3	0.0229 (5)	0.0199 (5)	0.0290 (5)	-0.0017 (4)	0.0106 (4)	-0.0011 (4)
C4	0.0250 (5)	0.0241 (5)	0.0361 (6)	-0.0028 (4)	0.0161 (5)	-0.0031 (5)
C5	0.0240 (5)	0.0294 (6)	0.0410 (6)	0.0034 (5)	0.0123 (5)	-0.0023 (5)
C6	0.0343 (6)	0.0239 (6)	0.0400 (7)	0.0035 (5)	0.0097 (5)	0.0025 (5)
C7	0.0299 (6)	0.0224 (6)	0.0352 (6)	-0.0038 (4)	0.0096 (5)	0.0036 (5)
C8	0.0224 (5)	0.0210 (5)	0.0304 (5)	-0.0019 (4)	0.0114 (4)	-0.0011 (4)
C9	0.0229 (5)	0.0203 (5)	0.0312 (5)	-0.0006 (4)	0.0114 (4)	0.0017 (4)
C10	0.0292 (6)	0.0284 (6)	0.0310 (6)	0.0044 (5)	0.0133 (5)	-0.0006 (5)
C11	0.0415 (7)	0.0312 (7)	0.0381 (7)	-0.0035 (6)	0.0077 (6)	-0.0063 (6)

*Geometric parameters (Å, °)*

O1—H1O1	0.924 (9)	C4—C5	1.5213 (18)
O1—H2O1	0.922 (9)	C4—H4A	0.9800
O2—H1O2	0.919 (9)	C4—H4B	0.9800
O2—H2O2	0.910 (9)	C5—C6	1.5279 (19)
N1—C2	1.5076 (15)	C5—H5A	0.9800
N1—C3	1.5099 (15)	C5—H5B	0.9800
N1—H1A	0.9000	C6—C7	1.5364 (18)
N1—H1B	0.9000	C6—H6A	0.9800
N2—C8	1.5155 (16)	C6—H6B	0.9800
N2—C9	1.5247 (15)	C7—C8	1.5318 (17)
N2—H2A	0.9000	C7—H7A	0.9800
N2—H2B	0.9000	C7—H7B	0.9800
C1—C2	1.5231 (17)	C8—H8	0.9900
C1—C9 <sup>i</sup>	1.5366 (16)	C9—C10	1.5312 (17)
C1—H1C	0.9800	C9—H9	0.9900
C1—H1D	0.9800	C10—C11	1.5208 (19)
C2—H2C	0.9800	C10—H10A	0.9800
C2—H2D	0.9800	C10—H10B	0.9800

C3—C4	1.5253 (16)	C11—H11A	0.9700
C3—C8	1.5431 (16)	C11—H11B	0.9700
C3—H3	0.9900	C11—H11C	0.9700
H1O1—O1—H2O1	111.5 (13)	C6—C5—H5A	109.4
H1O2—O2—H2O2	112.6 (15)	C4—C5—H5B	109.4
C2—N1—C3	116.40 (9)	C6—C5—H5B	109.4
C2—N1—H1A	108.2	H5A—C5—H5B	108.0
C3—N1—H1A	108.2	C5—C6—C7	112.85 (11)
C2—N1—H1B	108.2	C5—C6—H6A	109.0
C3—N1—H1B	108.2	C7—C6—H6A	109.0
H1A—N1—H1B	107.3	C5—C6—H6B	109.0
C8—N2—C9	117.87 (9)	C7—C6—H6B	109.0
C8—N2—H2A	107.8	H6A—C6—H6B	107.8
C9—N2—H2A	107.8	C8—C7—C6	114.35 (10)
C8—N2—H2B	107.8	C8—C7—H7A	108.7
C9—N2—H2B	107.8	C6—C7—H7A	108.7
H2A—N2—H2B	107.2	C8—C7—H7B	108.7
C2—C1—C9 <sup>i</sup>	113.50 (10)	C6—C7—H7B	108.7
C2—C1—H1C	108.9	H7A—C7—H7B	107.6
C9 <sup>i</sup> —C1—H1C	108.9	N2—C8—C7	109.85 (10)
C2—C1—H1D	108.9	N2—C8—C3	110.65 (9)
C9 <sup>i</sup> —C1—H1D	108.9	C7—C8—C3	111.90 (10)
H1C—C1—H1D	107.7	N2—C8—H8	108.1
N1—C2—C1	114.66 (10)	C7—C8—H8	108.1
N1—C2—H2C	108.6	C3—C8—H8	108.1
C1—C2—H2C	108.6	N2—C9—C10	109.14 (9)
N1—C2—H2D	108.6	N2—C9—C1 <sup>i</sup>	110.12 (9)
C1—C2—H2D	108.6	C10—C9—C1 <sup>i</sup>	114.39 (10)
H2C—C2—H2D	107.6	N2—C9—H9	107.6
N1—C3—C4	111.72 (10)	C10—C9—H9	107.6
N1—C3—C8	107.08 (9)	C1 <sup>i</sup> —C9—H9	107.6
C4—C3—C8	111.74 (10)	C11—C10—C9	116.80 (10)
N1—C3—H3	108.7	C11—C10—H10A	108.1
C4—C3—H3	108.7	C9—C10—H10A	108.1
C8—C3—H3	108.7	C11—C10—H10B	108.1
C5—C4—C3	111.65 (10)	C9—C10—H10B	108.1
C5—C4—H4A	109.3	H10A—C10—H10B	107.3
C3—C4—H4A	109.3	C10—C11—H11A	109.5
C5—C4—H4B	109.3	C10—C11—H11B	109.5
C3—C4—H4B	109.3	H11A—C11—H11B	109.5
H4A—C4—H4B	108.0	C10—C11—H11C	109.5
C4—C5—C6	111.17 (11)	H11A—C11—H11C	109.5
C4—C5—H5A	109.4	H11B—C11—H11C	109.5
C3—N1—C2—C1	63.32 (13)	C6—C7—C8—N2	76.17 (13)
C9 <sup>i</sup> —C1—C2—N1	74.65 (13)	C6—C7—C8—C3	-47.14 (14)
C2—N1—C3—C4	57.74 (13)	N1—C3—C8—N2	165.93 (9)

C2—N1—C3—C8	-179.62 (9)	C4—C3—C8—N2	-71.44 (12)
N1—C3—C4—C5	62.83 (13)	N1—C3—C8—C7	-71.22 (12)
C8—C3—C4—C5	-57.11 (13)	C4—C3—C8—C7	51.41 (13)
C3—C4—C5—C6	57.11 (13)	C8—N2—C9—C10	175.45 (9)
C4—C5—C6—C7	-52.02 (14)	C8—N2—C9—C1 <sup>i</sup>	-58.20 (12)
C5—C6—C7—C8	47.89 (15)	N2—C9—C10—C11	67.17 (13)
C9—N2—C8—C7	-174.08 (9)	C1 <sup>i</sup> —C9—C10—C11	-56.69 (15)
C9—N2—C8—C3	-50.04 (12)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O1 $\cdots$ Cl2	0.92 (1)	2.25 (1)	3.1616 (11)	172 (1)
O1—H2O1 $\cdots$ Cl1	0.92 (1)	2.17 (1)	3.0746 (11)	169 (1)
O2—H1O2 $\cdots$ Cl2 <sup>ii</sup>	0.92 (1)	2.34 (1)	3.2518 (15)	172 (2)
O2—H2O2 $\cdots$ Cl2 <sup>iii</sup>	0.91 (1)	2.26 (1)	3.1622 (12)	173 (2)
N1—H1A $\cdots$ Cl1 <sup>iv</sup>	0.90	2.22	3.1072 (12)	169
N1—H1B $\cdots$ O1	0.90	1.92	2.7740 (15)	157
N2—H2A $\cdots$ O2	0.90	1.91	2.7716 (14)	161
N2—H2B $\cdots$ Cl2 <sup>v</sup>	0.90	2.45	3.3357 (12)	167

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