

Crystal structure of 3,14-diethyl-2,13-diaza-6,17-diazoniatricyclo[16.4.0.0^{7,12}]docosane dinitrate dihydrate from synchrotron X-ray data

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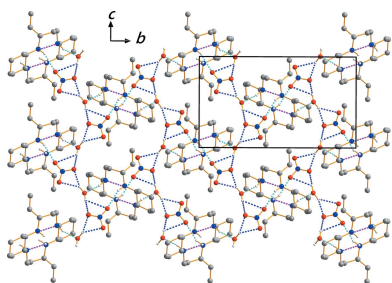
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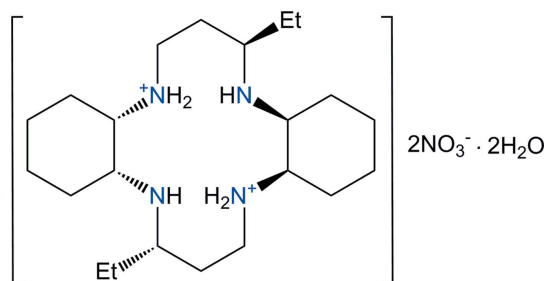
Keywords: crystal structure; protonated macrocycle; nitrate; hydrate; hydrogen bonds; synchrotron radiation.**CCDC reference:** 1918729**Supporting information:** this article has supporting information at journals.iucr.org/e

The crystal structure of title salt, $C_{22}H_{46}N_4^{2+} \cdot 2NO_3^- \cdot 2H_2O$, has been determined using synchrotron radiation at 220 K. The structure determination reveals that protonation has occurred at diagonally opposite amine N atoms. The asymmetric unit contains half a centrosymmetric dication, one nitrate anion and one water molecule. The molecular dication, $C_{22}H_{46}N_4^{2+}$, together with the nitrate anion and hydrate water molecule are involved in an extensive range of hydrogen bonds. The molecule is stabilized, as is the conformation of the dication, by forming intermolecular $N-H \cdots O$, $O-H \cdots O$, together with intramolecular $N-H \cdots N$ hydrogen bonds.

1. Chemical context

The 3,14-diethyl-2,6,13,17-tetraazatricyclo(16.4.0.0^{7,12})docosane macrocycle ($C_{22}H_{44}N_4$, *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 structure. The macrocyclic ligand *L* is a strongly basic amine capable of forming the dication, $[C_{22}H_{46}N_4]^{2+}$ or the tetracation $[C_{22}H_{48}N_4]^{4+}$ in which all of the N–H bonds are generally available for hydrogen-bond formation. These di- or tetra-ammonium cations may be suitable for the removal of toxic heavy metal ions from water. The crystal structures of $[Cu(L)](ClO_4)_2$ (Lim *et al.*, 2006), $[Cu(L)](NO_3)_2$, $[Cu(L)(H_2O)_2](SCN)_2$ (Choi *et al.*, 2012), $[Ni(L)(NO_3)_2]$ (Subhan & Choi, 2014), $[Ni(L)(N_3)_2]$ (Lim *et al.*, 2015) and $[Ni(L)(NCS)_2]$ (Lim & Choi, 2017) have been reported. In these complexes, Cu^{II} or Ni^{II} cations have tetragonally distorted octahedral environments with the four N atoms of the macrocyclic ligand in equatorial positions and the O/N atoms of anions or water molecules in the axial positions, while $[Ni(L)](ClO_4)_2 \cdot 2H_2O$ (Subhan & Choi, 2014) has a square-planar geometry around the Ni^{II} atom that binds to the four nitrogen atoms of the macrocyclic ligand. The macrocyclic ligands in the Cu^{II} and Ni^{II} complexes adopt the most stable *trans*-III conformation. Recently, we also reported the crystal structures of $[C_{22}H_{46}N_4](ClO_4)_2$ (Aree *et al.*, 2018), $[C_{22}H_{46}N_4]Cl_2 \cdot 4H_2O$ (Moon *et al.*, 2013) and $(C_{22}H_{44}N_4)_2 \cdot 2NaClO_4$ (Aree *et al.*, 2018). To further investigate the hydrogen-bonding behavior, we report here on the synthesis of a new hydrated nitrate salt, $[C_{22}H_{46}N_4](NO_3)_2 \cdot 2H_2O$, (I), and its structural characterization by synchrotron single-crystal X-ray diffraction.





2. Structural commentary

The title compound has a positively charged macrocyclic dication, two nitrate anions and two solvent water molecules and was prepared during a study of the macrocyclic ligand and its silver(II) complex. An ellipsoid plot of the molecular components in compound (I) is shown in Fig. 1 along with the atom-numbering scheme. The asymmetric unit consists of one half of the macrocycle, which lies about a center of inversion, one nitrate anion and one solvent water molecule. The four N atoms 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 a stable chair conformation. Within the centrosymmetric diprotonated amine unit $[C_{22}H_{46}N_4]^{2+}$, the C–C and N–C bond lengths vary from 1.517 (2) to 1.533 (2) Å and from 1.485 (2) to 1.501 (2) Å, respectively. The macrocycle is protonated at the N2 atom, which is similar to the situation found for $[C_{22}H_{46}N_4](ClO_4)_2$ (Aree *et al.*, 2018), but differs from the protonation of the N1 atom in $[C_{22}H_{46}N_4]Cl_2 \cdot 4H_2O$ (Moon *et al.*, 2013). The protonation on the N atom might

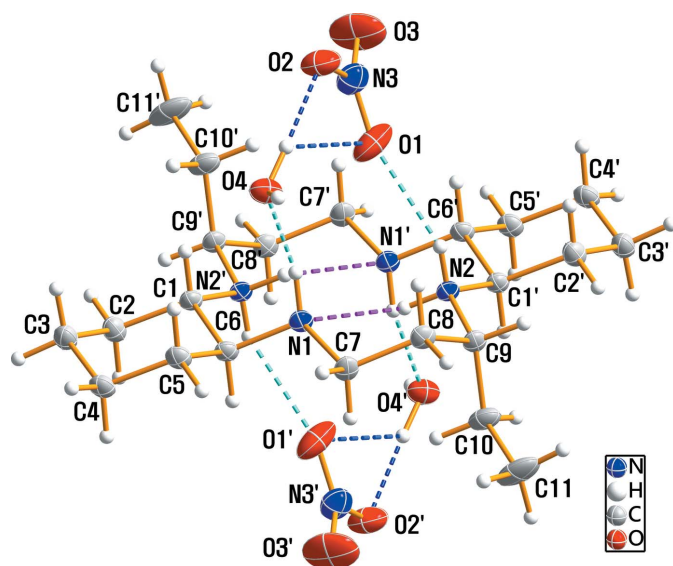


Figure 1
The molecular structure of (I), drawn with displacement ellipsoids at the 30% probability level. Primed atoms are related by the symmetry code $(1 - x, 1 - y, 1 - z)$. Dashed lines represent N–H···O (cyan), N–H···N (pink) and O–H···O (blue) hydrogen-bonding interactions, respectively.

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>
N2–H2AN···N1	0.90	2.40	2.9703 (18)	121
N2–H2AN···N1 ⁱ	0.90	2.41	2.8141 (17)	107
N1–H1N···O4	0.94	1.84	2.7493 (19)	163
N2–H2AN···N1	0.90	2.40	2.9703 (18)	121
N2–H2BN···O1	0.90	2.27	3.031 (2)	142
O4–H1O···O1	0.94 (1)	2.57 (2)	3.169 (3)	122 (2)
O4–H1O···O2	0.94 (1)	1.84 (1)	2.768 (2)	174 (2)
O4–H2O···O2 ⁱⁱ	0.94 (1)	2.04 (1)	2.914 (2)	155 (2)
O4–H2O···O3 ⁱⁱ	0.94 (1)	2.31 (2)	3.120 (4)	144 (2)

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

depend on the location of the acceptor atoms of the counter-anion involved in hydrogen bonding. The ranges of N–C–C and C–N–C angles are 108.07 (11) to 111.14 (12)° and 115.09 (11) to 115.19 (10)°, respectively. The bond lengths and angles within the $[C_{22}H_{46}N_4]^{2+}$ dication are comparable to those found in $[C_{22}H_{46}N_4](ClO_4)_2$ (Aree *et al.*, 2018) and $[C_{22}H_{46}N_4]Cl_2 \cdot 4H_2O$ (Moon *et al.*, 2013). The nitrate counter-anion has a distorted trigonal-planar geometry as a result of the influence of hydrogen bonding on the N–O bond lengths and the O–N–O angles. The N–O bond distances range from 1.204 (3) to 1.214 (2) Å and the O–N–O angles from 117.4 (2) to 123.1 (3)°.

3. Supramolecular features

Extensive N–H···O, O–H···O and N–H···N hydrogen-bonding interactions occur in the crystal structure (Table 1).

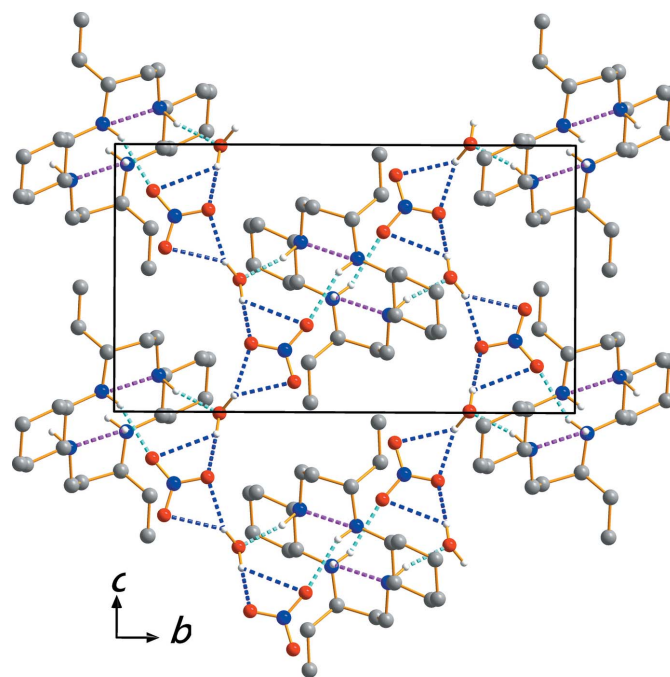


Figure 2
The crystal packing in (I), viewed perpendicular to the *bc* plane. Dashed lines represent N–H···O (cyan), N–H···N (pink) and O–H···O (blue) hydrogen bonding interactions, respectively. H atoms bound to C have been omitted.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{46}N_4^{2+} \cdot 2NO_3^- \cdot 2H_2O$
M_r	526.68
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	220
a, b, c (Å)	8.6420 (17), 16.687 (3), 9.7340 (19)
β (°)	96.46 (3)
V (Å ³)	1394.8 (5)
Z	2
Radiation type	Synchrotron, $\lambda = 0.610$ Å
μ (mm ⁻¹)	0.07
Crystal size (mm)	0.13 × 0.09 × 0.05
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	14284, 3736, 2968
R_{int}	0.027
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.693
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.062, 0.211, 1.10
No. of reflections	3736
No. of parameters	170
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.73, -0.56

Computer programs: *PAL BL2D-SMDC Program* (Shin *et al.*, 2016), *HKL3000sm* (Otwinowski & Minor, 1997), *SHELXT2018* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *DIAMOND 4* (Putz & Brandenburg, 2014) and *pubCIF* (Westrip, 2010).

The crystal packing viewed along the a axis is shown in Fig. 2. The O—H...O hydrogen bonds link the water molecules to neighboring nitrate anions, while N—H...O hydrogen bonds interconnect the $[C_{22}H_{46}N_4]^{2+}$ cations with both the nitrate anions and the water molecules. The crystal structure is stabilized by molecular hydrogen bonds involving the macrocycle N—H groups and water O—H groups as donors, and the O atoms of the water molecules and nitrate anions as acceptors, giving rise to a three-dimensional framework (Figs. 1 and 2).

4. Database survey

A search of the Cambridge Structural (Version 5.40, Feb 2019 with 1 update; Groom *et al.*, 2016) gave just three hits for organic compounds containing the macrocycles $[C_{22}H_{48}N_4]^{4+}$, $[C_{22}H_{46}N_4]^{2+}$ or $(C_{22}H_{44}N_4)$. The crystal structures of $[C_{22}H_{46}N_4](ClO_4)_2$ (Aree *et al.*, 2018), $[C_{22}H_{46}N_4]Cl_2 \cdot 4H_2O$ (Moon *et al.*, 2013) and $(C_{22}H_{44}N_4)_2 \cdot 2NaClO_4$ (Aree *et al.*, 2018) were reported by us previously. Until now, no crystal structures of any $[C_{22}H_{46}N_4]^{2+}$ or $[C_{22}H_{48}N_4]^{4+}$ compounds with a nitrate anion have been deposited.

5. Synthesis and crystallization

Commercially available *trans*-1,2-cyclohexanediamine, ethyl vinyl ketone and silver nitrate (Sigma–Aldrich) were used as provided. All other chemicals were reagent grade and used without further purification. As a starting material, 3,14-diethyl-2,6,13,17-tetraazatricyclo(16.4.0.0^{7,12})docosane, L was prepared according to a published procedure (Lim *et al.*, 2006). A solution of the macrocyclic ligand, L (0.33 g, 1.0 mmol) in methanol 10 mL was added dropwise to a stirred solution of $AgNO_3$ (0.34 g, 2.0 mmol) in water 10 mL. The solution turned an orange color and the metallic silver that formed was filtered off. The orange filtrate was kept in an open beaker, protected from light, at room temperature. Block-like colorless crystals of suitable for X-ray analysis were obtained unexpectedly from the solution over a period of a few weeks.

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 $U_{\text{iso}}(\text{H})$ values of 1.2 and 1.5 times the U_{eq} of the parent atoms, respectively. The N-bound H atoms of the $[C_{22}H_{46}N_4]^{2+}$ cation and the O-bound H atoms of the water molecules were located in a difference-Fourier map and refined isotropically, with the N—H distance restrained using DFIX [0.9 (2) Å] and the O—H distances and H—O—H angles restrained using DFIX and DANG constraints [0.94 (2) and 1.55 (2) Å], respectively.

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supporting information

Acta Cryst. (2019). E75, 921-924 [https://doi.org/10.1107/S2056989019007655]

Crystal structure of 3,14-diethyl-2,13-diaza-6,17-diazoniatricyclo-[16.4.0.0^{7,12}]docosane dinitrate dihydrate from synchrotron X-ray data

Dohyun Moon, Sunghwan Jeon, Keon Sang Ryo and Jong-Ha Choi

Computing details

Data collection: *PAL BL2D-SMDC Program* (Shin *et al.*, 2016); cell refinement: *HKL3000sm* (Otwinowski & Minor, 1997); data reduction: *HKL3000sm* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXT2018* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *DIAMOND 4* (Putz & Brandenburg, 2014); software used to prepare material for publication: *publCIF* (Westrip, 2010).

3,14-Diethyl-2,13-diaza-6,17-diazoniatricyclo[16.4.0.0^{7,12}]docosane dinitrate dihydrate

Crystal data

C₂₂H₄₆N₄²⁺·2NO₃⁻·2H₂O

M_r = 526.68

Monoclinic, *P2₁/c*

a = 8.6420 (17) Å

b = 16.687 (3) Å

c = 9.7340 (19) Å

β = 96.46 (3)°

V = 1394.8 (5) Å³

Z = 2

F(000) = 576

D_x = 1.254 Mg m⁻³

Synchrotron radiation, λ = 0.610 Å

Cell parameters from 46866 reflections

θ = 0.4–33.7°

μ = 0.07 mm⁻¹

T = 220 K

Block, colorless

0.13 × 0.09 × 0.05 mm

Data collection

Rayonix MX225HS CCD area detector
diffractometer

Radiation source: PLSII 2D bending magnet
ω scan

Absorption correction: empirical (using
intensity measurements)

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

T_{min} = 0.919, *T_{max}* = 1.000

14284 measured reflections

3736 independent reflections

2968 reflections with *I* > 2σ(*I*)

R_{int} = 0.027

θ_{max} = 25.0°, θ_{min} = 2.0°

h = -11→11

k = -21→21

l = -13→13

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.062

wR(*F*²) = 0.211

S = 1.10

3736 reflections

170 parameters

4 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

w = 1/[σ²(*F_o*²) + (0.1295*P*)² + 0.2454*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.73 e Å⁻³

Δρ_{min} = -0.56 e Å⁻³

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.51219 (14)	0.59626 (8)	0.36407 (11)	0.0308 (3)
H1N	0.473300	0.634200	0.422800	0.037*
N2	0.28123 (13)	0.47313 (7)	0.42499 (11)	0.0278 (3)
H2AN	0.385711	0.476834	0.431710	0.033*
H2BN	0.246719	0.513235	0.475356	0.033*
C1	0.76020 (15)	0.60393 (9)	0.51374 (13)	0.0286 (3)
H1	0.716885	0.647557	0.566781	0.034*
C2	0.93544 (17)	0.61843 (10)	0.51640 (16)	0.0365 (3)
H2A	0.983763	0.617356	0.612413	0.044*
H2B	0.981148	0.575002	0.466503	0.044*
C3	0.97155 (18)	0.69835 (10)	0.45121 (17)	0.0386 (4)
H3A	0.936038	0.742285	0.506664	0.046*
H3B	1.084368	0.703693	0.450342	0.046*
C4	0.89135 (18)	0.70410 (10)	0.30389 (15)	0.0373 (3)
H4A	0.935358	0.663904	0.245983	0.045*
H4B	0.910323	0.757161	0.266013	0.045*
C5	0.71640 (17)	0.69051 (9)	0.30041 (15)	0.0342 (3)
H5A	0.667680	0.692382	0.204553	0.041*
H5B	0.670830	0.733224	0.352056	0.041*
C6	0.68403 (16)	0.60924 (9)	0.36398 (13)	0.0296 (3)
H6	0.726833	0.566354	0.308993	0.035*
C7	0.42136 (18)	0.59147 (10)	0.22379 (14)	0.0353 (3)
H7A	0.467359	0.550519	0.168718	0.042*
H7B	0.427202	0.643030	0.176434	0.042*
C8	0.25211 (17)	0.57083 (9)	0.23440 (14)	0.0337 (3)
H8A	0.192762	0.580870	0.144215	0.040*
H8B	0.212715	0.607652	0.300777	0.040*
C9	0.21823 (17)	0.48504 (9)	0.27811 (13)	0.0314 (3)
H9	0.103745	0.478672	0.271539	0.038*
C10	0.2802 (3)	0.42191 (11)	0.18588 (16)	0.0471 (4)
H10A	0.393272	0.428242	0.189202	0.056*
H10B	0.259978	0.368749	0.222744	0.056*
C11	0.2090 (4)	0.42595 (16)	0.0363 (2)	0.0792 (8)
H11A	0.096417	0.427628	0.032597	0.119*
H11B	0.239639	0.378996	-0.012820	0.119*
H11C	0.245453	0.473817	-0.006600	0.119*
N3	0.2912 (2)	0.63006 (12)	0.76865 (18)	0.0581 (5)
O1	0.3086 (2)	0.58294 (10)	0.6746 (2)	0.0812 (6)
O2	0.2872 (2)	0.70307 (10)	0.74420 (17)	0.0696 (5)

O3	0.2875 (5)	0.6094 (2)	0.8868 (3)	0.1636 (16)
O4	0.42576 (16)	0.72874 (9)	0.50503 (14)	0.0501 (3)
H1O	0.373 (3)	0.7221 (16)	0.5829 (17)	0.075*
H2O	0.366 (3)	0.7605 (14)	0.439 (2)	0.075*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0327 (6)	0.0418 (7)	0.0171 (5)	−0.0017 (5)	−0.0003 (4)	0.0035 (4)
N2	0.0303 (6)	0.0363 (6)	0.0163 (5)	−0.0001 (4)	−0.0003 (4)	0.0006 (4)
C1	0.0300 (6)	0.0370 (7)	0.0185 (6)	−0.0006 (5)	0.0012 (5)	0.0007 (5)
C2	0.0303 (7)	0.0486 (9)	0.0302 (7)	−0.0013 (6)	0.0012 (5)	0.0050 (6)
C3	0.0361 (7)	0.0496 (9)	0.0305 (7)	−0.0078 (6)	0.0055 (6)	0.0016 (6)
C4	0.0380 (7)	0.0482 (9)	0.0269 (7)	−0.0029 (6)	0.0090 (6)	0.0038 (6)
C5	0.0368 (7)	0.0423 (8)	0.0240 (6)	−0.0006 (5)	0.0048 (5)	0.0065 (5)
C6	0.0317 (6)	0.0389 (7)	0.0180 (6)	0.0007 (5)	0.0024 (5)	0.0015 (5)
C7	0.0393 (8)	0.0476 (8)	0.0176 (6)	−0.0062 (6)	−0.0027 (5)	0.0057 (5)
C8	0.0344 (7)	0.0437 (8)	0.0213 (6)	0.0024 (5)	−0.0040 (5)	0.0046 (5)
C9	0.0329 (7)	0.0430 (8)	0.0172 (6)	−0.0033 (5)	−0.0013 (5)	0.0010 (5)
C10	0.0721 (12)	0.0461 (10)	0.0240 (7)	−0.0041 (8)	0.0097 (7)	−0.0044 (6)
C11	0.141 (3)	0.0743 (15)	0.0214 (8)	−0.0135 (15)	0.0046 (11)	−0.0093 (9)
N3	0.0674 (11)	0.0633 (11)	0.0418 (9)	−0.0045 (8)	−0.0025 (8)	0.0016 (7)
O1	0.1056 (14)	0.0553 (10)	0.0739 (12)	0.0074 (8)	−0.0284 (10)	−0.0228 (8)
O2	0.1060 (14)	0.0545 (9)	0.0509 (9)	0.0048 (8)	0.0204 (9)	−0.0098 (6)
O3	0.285 (5)	0.140 (3)	0.0760 (18)	0.010 (3)	0.063 (2)	0.0501 (17)
O4	0.0555 (8)	0.0574 (8)	0.0384 (7)	0.0082 (6)	0.0088 (6)	−0.0009 (5)

Geometric parameters (Å, °)

N1—C7	1.4987 (17)	C5—H5B	0.9800
N1—C6	1.5009 (18)	C6—H6	0.9900
N1—H1N	0.94	C7—C8	1.517 (2)
N2—C1 ⁱ	1.4784 (18)	C7—H7A	0.9800
N2—C9	1.4850 (16)	C7—H7B	0.9800
N2—H2AN	0.9000	C8—C9	1.531 (2)
N2—H2BN	0.9000	C8—H8A	0.9800
C1—C2	1.5309 (19)	C8—H8B	0.9800
C1—C6	1.5330 (18)	C9—C10	1.520 (2)
C1—H1	0.9900	C9—H9	0.9900
C2—C3	1.524 (2)	C10—C11	1.517 (3)
C2—H2A	0.9800	C10—H10A	0.9800
C2—H2B	0.9800	C10—H10B	0.9800
C3—C4	1.524 (2)	C11—H11A	0.9700
C3—H3A	0.9800	C11—H11B	0.9700
C3—H3B	0.9800	C11—H11C	0.9700
C4—C5	1.525 (2)	N3—O3	1.204 (3)
C4—H4A	0.9800	N3—O1	1.229 (3)
C4—H4B	0.9800	N3—O2	1.241 (2)

C5—C6	1.529 (2)	O4—H1O	0.937 (10)
C5—H5A	0.9800	O4—H2O	0.941 (9)
C7—N1—C6	115.09 (11)	N1—C6—C1	108.07 (11)
C7—N1—H1N	114	C5—C6—C1	110.95 (12)
C6—N1—H1N	109	N1—C6—H6	109.0
C1 ⁱ —N2—C9	115.19 (10)	C5—C6—H6	109.0
C1 ⁱ —N2—H2AN	108.5	C1—C6—H6	109.0
C9—N2—H2AN	108.5	N1—C7—C8	111.11 (11)
C1 ⁱ —N2—H2BN	108.5	N1—C7—H7A	109.4
C9—N2—H2BN	108.5	C8—C7—H7A	109.4
H2AN—N2—H2BN	107.5	N1—C7—H7B	109.4
N2 ⁱ —C1—C2	114.50 (12)	C8—C7—H7B	109.4
N2 ⁱ —C1—C6	109.65 (11)	H7A—C7—H7B	108.0
C2—C1—C6	108.97 (11)	C7—C8—C9	116.55 (12)
N2 ⁱ —C1—H1	107.8	C7—C8—H8A	108.2
C2—C1—H1	107.8	C9—C8—H8A	108.2
C6—C1—H1	107.8	C7—C8—H8B	108.2
C3—C2—C1	112.32 (12)	C9—C8—H8B	108.2
C3—C2—H2A	109.1	H8A—C8—H8B	107.3
C1—C2—H2A	109.1	N2—C9—C10	111.14 (12)
C3—C2—H2B	109.1	N2—C9—C8	109.38 (11)
C1—C2—H2B	109.1	C10—C9—C8	113.13 (13)
H2A—C2—H2B	107.9	N2—C9—H9	107.7
C4—C3—C2	110.74 (13)	C10—C9—H9	107.7
C4—C3—H3A	109.5	C8—C9—H9	107.7
C2—C3—H3A	109.5	C11—C10—C9	113.86 (17)
C4—C3—H3B	109.5	C11—C10—H10A	108.8
C2—C3—H3B	109.5	C9—C10—H10A	108.8
H3A—C3—H3B	108.1	C11—C10—H10B	108.8
C3—C4—C5	110.87 (12)	C9—C10—H10B	108.8
C3—C4—H4A	109.5	H10A—C10—H10B	107.7
C5—C4—H4A	109.5	C10—C11—H11A	109.5
C3—C4—H4B	109.5	C10—C11—H11B	109.5
C5—C4—H4B	109.5	H11A—C11—H11B	109.5
H4A—C4—H4B	108.1	C10—C11—H11C	109.5
C4—C5—C6	110.41 (12)	H11A—C11—H11C	109.5
C4—C5—H5A	109.6	H11B—C11—H11C	109.5
C6—C5—H5A	109.6	O3—N3—O1	123.1 (3)
C4—C5—H5B	109.6	O3—N3—O2	117.4 (2)
C6—C5—H5B	109.6	O1—N3—O2	119.23 (19)
H5A—C5—H5B	108.1	H1O—O4—H2O	109.8 (18)
N1—C6—C5	110.75 (11)		
N2 ⁱ —C1—C2—C3	179.62 (12)	N2 ⁱ —C1—C6—C5	176.50 (11)
C6—C1—C2—C3	56.43 (16)	C2—C1—C6—C5	-57.46 (15)
C1—C2—C3—C4	-55.92 (17)	C6—N1—C7—C8	174.85 (12)
C2—C3—C4—C5	55.43 (18)	N1—C7—C8—C9	-71.31 (16)

C3—C4—C5—C6	-57.05 (17)	C1 ⁱ —N2—C9—C10	-61.66 (16)
C7—N1—C6—C5	64.03 (15)	C1 ⁱ —N2—C9—C8	172.72 (11)
C7—N1—C6—C1	-174.25 (12)	C7—C8—C9—N2	68.87 (16)
C4—C5—C6—N1	178.64 (11)	C7—C8—C9—C10	-55.60 (17)
C4—C5—C6—C1	58.63 (16)	N2—C9—C10—C11	174.71 (16)
N2 ⁱ —C1—C6—N1	54.91 (14)	C8—C9—C10—C11	-61.8 (2)
C2—C1—C6—N1	-179.05 (12)		

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

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

<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>
N2—H2AN \cdots N1	0.90	2.40	2.9703 (18)	121
N2—H2AN \cdots N1 ⁱ	0.90	2.41	2.8141 (17)	107
N1—H1N \cdots O4	0.94	1.84	2.7493 (19)	163
N2—H2AN \cdots N1	0.90	2.40	2.9703 (18)	121
N2—H2BN \cdots O1	0.90	2.27	3.031 (2)	142
O4—H1O \cdots O1	0.94 (1)	2.57 (2)	3.169 (3)	122 (2)
O4—H1O \cdots O2	0.94 (1)	1.84 (1)	2.768 (2)	174 (2)
O4—H2O \cdots O2 ⁱⁱ	0.94 (1)	2.04 (1)	2.914 (2)	155 (2)
O4—H2O \cdots O3 ⁱⁱ	0.94 (1)	2.31 (2)	3.120 (4)	144 (2)

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