Crystal structure of 9,20-dimethyl-1,8,12,19-tetra-azatetracyclo[17.3.1.0^{2,7}.0^{13,18}]tricosane dihydrate from synchrotron X-ray data

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The structure of the title compound, $C_{21}H_{40}N_4 \cdot 2H_2O$, has been determined from synchrotron X-ray radiation data. The asymmetric unit comprises one 12-membered macropolycycle and two lattice water molecules. The macropolycycle contains two cyclohexane rings and one 1,3-diazacyclohexane ring, all in chair conformations. The C—N and C—C bond lengths are in the ranges 1.4526 (16)–1.4786 (17) and 1.517 (2)–1.5414 (17) Å, respectively. One intramolecular N—H···N hydrogen bond helps to stabilize the molecular conformation while medium-strength intermolecular N—H···O, O—H···N and O—H···O hydrogen bonds involving the lattice water molecules connect the components into a three-dimensional network.

1. Chemical context

Macrocyclic ligands and their complexes are involved in diverse application fields such as catalysis, enzyme mimics, chemical sensors, purification of waste water, selective metal-ion recovery and antitumor agents and therapy (Meyer *et al.*, 1998). The family of macrocyclic amines with fourteen-membered inner rings has received attention due to their anti-HIV activity (Liang & Sadler, 2004; Ronconi & Sadler, 2007; Ross *et al.*, 2012). There has also been considerable interest in *C*- or *N*-functionalized macrocyclic compounds and their metal complexes because the structural and chemical properties are often quite different from those of the corresponding non-functionalized compounds (Barefield, 2010; Choi *et al.*, 2010). Structural modifications of the macrocycles based on methylene bridging of adjacent nitrogen atoms have been achieved using various methods (Royal *et al.*, 1998; Tripier *et al.*, 2001; Hubin, 2003; Kang *et al.*, 2008).
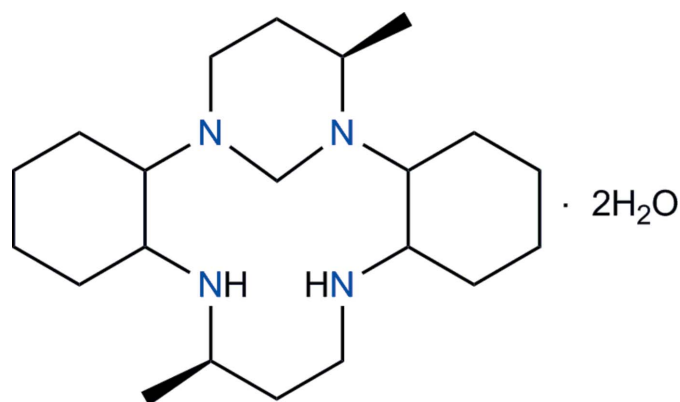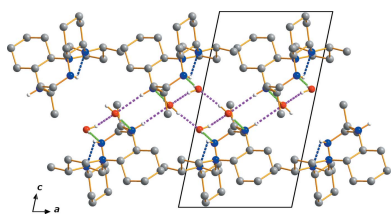
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Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1N1⋯O1W^{i}	0.914 (15)	2.395 (15)	3.2763 (19)	162.0 (13)
N4—H1N4⋯N3	0.882 (16)	2.287 (15)	2.8304 (16)	119.8 (12)
O1W—H1O1⋯N1	0.85 (1)	2.06 (1)	2.9077 (18)	178 (2)
O1W—H2O1⋯O2W^{ii}	0.83 (1)	1.99 (1)	2.816 (2)	175 (2)
O2W—H1O2⋯N4	0.84 (1)	2.10 (1)	2.9190 (18)	168 (2)
O2W—H2O2⋯O1W^{iii}	0.83 (1)	1.98 (1)	2.7975 (17)	166 (2)

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

The synthesis of the 9,20-dimethyl-1,8,12,19-tetraazatetra-cyclo[17.3.1.0^{2,7}.0^{13,18}]tricosane (L^{2}) monohydrated compound, L^{2}·H$_2$O has been described previously (Kang *et al.*, 2008), but we could not obtain a suitable single crystal of this compound for structure determination using X-ray diffraction. Formaldehyde has been utilized for the synthesis of such polyaza macrocyclic and macropolycyclic compounds containing five- or six-membered rings. We recently described the preparation, spectroscopic properties and the molecular and crystal structure of 3,14-dimethyl-2,6,13,17-tetraaza-pentacyclo(16.4.1^{2,17}.1^{6,13}.0.0^{7,12})tetracosane containing two 1,3-diazacyclopentane rings, which was the major product from the reaction of 3,14-dimethyl-2,6,13,17-tetraazatri-cyclo(16.4.0^{1,18}.0^{7,12})docosane (L^{1}) with two equivalents of formaldehyde (Moon *et al.*, 2016).

In the present work, we attempted the reaction of L^{1} with one equivalent of formaldehyde and synthesized the title compound, C$_{21}$H$_{40}$N$_4$·2H$_2$O, (I). Interestingly, the title compound, containing a six-membered 1,3-diazacyclohexane ring, was the main product of the synthesis, while the compound containing a five-membered 1,3-diazacyclopentane ring did not crystallize. In order to determine the molecular and crystal structure of the title compound, single-crystal X-ray structural determination was performed by using synchrotron data.
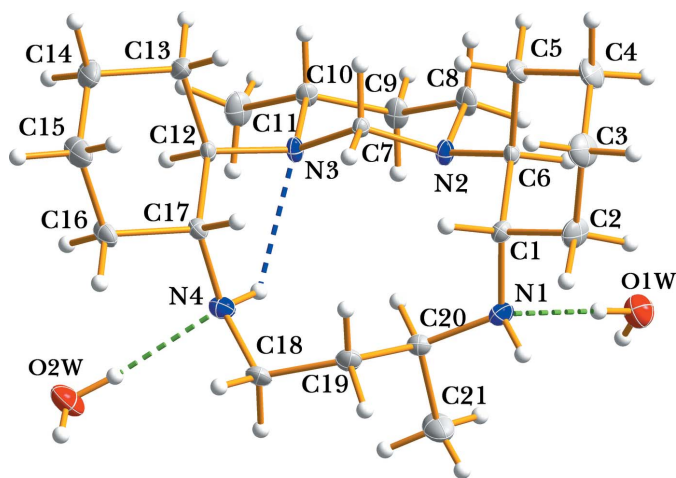
2. Structural commentary

Fig. 1 shows an ellipsoid plot of the molecular components of compound (I). The asymmetric unit comprises a macrocyclic C$_{21}$H$_{40}$N$_4$ molecule and two lattice water molecules. The two methyl substituents of the C10 and C20 atoms are on the same side with respect to the macrocyclic plane of the four N atoms (Fig. 1). The cyclohexane rings, together with the 1,3-diaza-cyclohexane ring and the 1,3- diamino-1-methylpropane moiety, are fused to the 12-membered macrocycle. All six-membered rings exist in a slightly distorted chair conformation. The N1—C1—C6—N2 and N3—C12—C17—N4 torsion angle displays a *gauche* conformation. The bond lengths are in the ranges 1.4526 (16)–1.4786 (17) Å and 1.517 (2)–1.5414 (17) Å for the C—N and C—C bonds, respectively. The N1—C20 distance is the longest C—N distance, presumably as a consequence of the methyl group on the C20 atom and the N⋯H—O hydrogen bond involving N1. The bond angles within the six-membered 1,3-diazacyclohexane ring, N2—C7—N3, C7—N2—C8, and C7—N3—C10, are 109.89 (10), 109.60 (10), and 108.08 (9)°, respectively. All other C—N, C—C, and C—H bond lengths and corresponding angles are in the normal range for such compounds (Royal *et al.*, 1998; Tripier *et al.*, 2001). The intramolecular hydrogen bond between the amine group N4—H1N4 and the tertiary N3 atom lends some rigidity to the 12-membered macropolycycle L^{2} ring (Fig. 1).

3. Supramolecular features

In the crystal, the macropolycycle and the two water molecules are held together by N—H⋯O, and O—H⋯O hydrogen bonds (Table 1); O—H⋯O hydrogen bonds between the water molecules are also observed. All intermolecular hydrogen-bonding interactions are of medium strength and lead to the formation of a three-dimensional network between the components. The packing along the *b* axis is shown in Fig. 2.

Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Non-H atoms are shown as displacement ellipsoids at the 50% probability level. Hydrogen-bonding interactions are indicated by dashed lines.
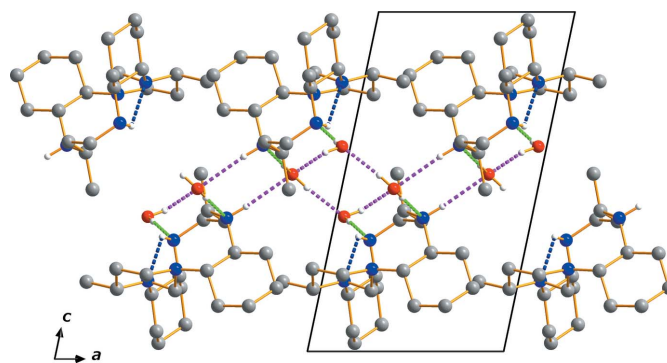

Figure 2
Crystal packing diagram of (I), viewed perpendicular to the *ac* plane. H atoms not involved in hydrogen bonds have been omitted. The dashed lines represent N—H⋯N (blue), O—H⋯O (pink) and O—H⋯N (green) hydrogen bonds, respectively.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{21}H_{40}N_4 \cdot 2H_2O$
M_r	384.60
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	173
a, b, c (Å)	8.3870 (17), 10.275 (2), 14.115 (3)
α, β, γ (°)	87.20 (3), 77.83 (3), 72.31 (3)
V (Å³)	1132.8 (5)
Z	2
Radiation type	Synchrotron, $\lambda = 0.610$ Å
μ (mm⁻¹)	0.06
Crystal size (mm)	$0.08 \times 0.07 \times 0.05$
Data collection	
Diffractometer	ADSC Q210 CCD area detector
Absorption correction	Empirical (using intensity measurements) (*HKL3000sm SCALEPACK*; Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.878, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11640, 5950, 3853
R_{int}	0.045
$(\sin\theta/\lambda)_{max}$ (Å⁻¹)	0.719
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.123, 0.92
No. of reflections	5950
No. of parameters	265
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⁻³)	0.37, −0.27

Computer programs: *PAL BL2D-SMDC* (Shin *et al.*, 2016), *HKL3000sm* (Otwinowski & Minor, 1997), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND 4* (Putz & Brandenburg, 2014) and *publCIF* (Westrip, 2010).

4. Database survey

A search of the Cambridge Structural Database (Version 5.37, May 2016 with three updates; Groom *et al.* 2016) gave just one hit for a 9,20-dimethyl-1,8,12,19-tetraazatetracyclo-[17.3.1.0²,⁷.0¹³,¹⁸]tricosane (L^2) unit, *viz.* the crystal structure of $[Cr(L^2)(H_2O)](ClO_4)_2 \cdot 3H_2O$ (Kang *et al.*, 2008). However, no structure of any other compound with L^2 has been deposited.

5. Synthesis and crystallization

Commercially available (Sigma–Aldrich) 1,2-cyclohexanediamine was used as provided. All other chemicals were reagent grade and used without further purification. The starting material, 3,14-dimethyl-2,6,13,17-tetraazatricyclo-(16.4.0¹,¹⁸.0⁷,¹²)docosane (L^1) was synthesized according to a literature protocol (Kang & Jeong, 2003). To a solution of L^1 (0.5 g, 1.5 mmol) in H_2O (40 mL) was rapidly added 37% formaldehyde (0.11 mL, 1.5 mmol) at room temperature. The reaction mixture was refluxed for 3 h. After cooling, the resultant white solid was filtered, washed with water, and

dried. The crude product of $L^2 \cdot 2H_2O$, (I), was recrystallized from a hot THF/H_2O (1:2 *v*/*v*) solution to give colourless crystals suitable for X-ray analysis.

6. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 2. All C-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 0.98–1.00 Å with $U_{iso}(H)$ values of 1.5 and 1.2 U_{eq} of the parent atoms, respectively. N- and O-bound H atoms were assigned based on a difference Fourier map, and were refined with distance restraints of 0.91 (4) and 0.88 (2) Å (using DFIX and DANG commands), respectively, and with $U_{iso}(H)$ values of $1.2U_{eq}$ of the parent atoms.

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supporting information

Crystal structure of 9,20-dimethyl-1,8,12,19-tetraazatetracyclo-[17.3.1.0²,⁷.0¹³,¹⁸]tricosane dihydrate from synchrotron X-ray data

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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: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *DIAMOND 4* (Putz & Brandenburg, 2014); software used to prepare material for publication: *publCIF* (Westrip, 2010).

9,20-Dimethyl-1,8,12,19-tetraazatetracyclo[17.3.1.0²,⁷.0¹³,¹⁸]tricosane dihydrate

Crystal data

$C_{21}H_{40}N_4 \cdot 2H_2O$	$Z = 2$
$M_r = 384.60$	$F(000) = 428$
Triclinic, $P\bar{1}$	$D_x = 1.128$ Mg m^{-3}
$a = 8.3870$ (17) Å	Synchrotron radiation, $\lambda = 0.610$ Å
$b = 10.275$ (2) Å	Cell parameters from 63772 reflections
$c = 14.115$ (3) Å	$\theta = 0.4$–33.6°
$\alpha = 87.20$ (3)°	$\mu = 0.06$ mm^{-1}
$\beta = 77.83$ (3)°	$T = 173$ K
$\gamma = 72.31$ (3)°	Block, colorless
$V = 1132.8$ (5) Å^3	$0.08 \times 0.07 \times 0.05$ mm

Data collection

ADSC Q210 CCD area detector diffractometer	11640 measured reflections
Radiation source: PLSII 2D bending magnet	5950 independent reflections
ω scan	3853 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (using intensity measurements) (*HKL3000sm SCALEPACK*; Otwinowski & Minor, 1997)	$R_{int} = 0.045$
	$\theta_{max} = 26.0°$, $\theta_{min} = 1.3°$
	$h = -11 \rightarrow 11$
	$k = -14 \rightarrow 14$
	$l = -18 \rightarrow 18$
$T_{min} = 0.878$, $T_{max} = 1.000$	

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.047$	
$wR(F^2) = 0.123$	$w = 1/[\sigma^2(F_o^2) + (0.0685P)^2]$
$S = 0.92$	where $P = (F_o^2 + 2F_c^2)/3$
5950 reflections	$(\Delta/\sigma)_{max} < 0.001$
265 parameters	$\Delta\rho_{max} = 0.37$ e Å^{-3}
6 restraints	$\Delta\rho_{min} = -0.27$ e Å^{-3}

Extinction correction: SHELXL2014
(Sheldrick, 2015*b*),
$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.042 (4)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.44588 (14)	0.16840 (11)	0.39264 (8)	0.0138 (2)
H1N1	0.532 (2)	0.1462 (15)	0.4261 (11)	0.017*
N2	0.24153 (13)	0.20083 (10)	0.24205 (8)	0.0101 (2)
N3	0.11157 (13)	0.43397 (10)	0.20720 (8)	0.0094 (2)
N4	0.19952 (14)	0.60232 (11)	0.32752 (8)	0.0129 (2)
H1N4	0.138 (2)	0.5454 (16)	0.3368 (11)	0.015*
C1	0.52453 (16)	0.12714 (13)	0.29073 (9)	0.0118 (3)
H1	0.5594	0.2047	0.2563	0.014*
C2	0.68449 (18)	0.00477 (14)	0.28851 (11)	0.0200 (3)
H2A	0.7651	0.0318	0.3197	0.024*
H2B	0.6516	−0.0698	0.3268	0.024*
C3	0.77460 (18)	−0.04848 (15)	0.18675 (11)	0.0241 (3)
H3A	0.8724	−0.1306	0.1902	0.029*
H3B	0.8199	0.0219	0.1503	0.029*
C4	0.65341 (19)	−0.08452 (14)	0.13344 (11)	0.0222 (3)
H4C	0.6182	−0.1622	0.1654	0.027*
H4D	0.7124	−0.1123	0.0658	0.027*
C5	0.49601 (18)	0.03878 (13)	0.13402 (10)	0.0165 (3)
H5A	0.4168	0.0139	0.1004	0.020*
H5B	0.5314	0.1139	0.0980	0.020*
C6	0.40204 (16)	0.08885 (12)	0.23757 (9)	0.0109 (2)
H6	0.3714	0.0099	0.2724	0.013*
C7	0.26051 (15)	0.31402 (12)	0.17952 (9)	0.0097 (2)
H7A	0.2718	0.2882	0.1112	0.012*
H7B	0.3654	0.3357	0.1852	0.012*
C8	0.09840 (17)	0.15840 (13)	0.22515 (10)	0.0159 (3)
H8A	0.0817	0.0839	0.2696	0.019*
H8B	0.1225	0.1242	0.1577	0.019*
C9	−0.06214 (17)	0.28106 (14)	0.24294 (11)	0.0176 (3)
H9A	−0.0941	0.3061	0.3127	0.021*
H9B	−0.1574	0.2555	0.2258	0.021*
C10	−0.03765 (16)	0.40486 (13)	0.18391 (10)	0.0132 (3)
H10	−0.0115	0.3802	0.1135	0.016*
C11	−0.19966 (17)	0.52625 (15)	0.20482 (11)	0.0222 (3)
H11A	−0.2158	0.5617	0.2705	0.033*

H11B	−0.2983	0.4969	0.1996	0.033*
H11C	−0.1889	0.5981	0.1578	0.033*
C12	0.14475 (16)	0.56142 (12)	0.16863 (9)	0.0106 (2)
H12	0.0332	0.6355	0.1839	0.013*
C13	0.20962 (19)	0.56205 (14)	0.05870 (10)	0.0177 (3)
H13A	0.3206	0.4899	0.0406	0.021*
H13B	0.1274	0.5408	0.0255	0.021*
C14	0.2320 (2)	0.70002 (15)	0.02457 (11)	0.0253 (3)
H14A	0.2810	0.6949	−0.0459	0.030*
H14B	0.1191	0.7708	0.0359	0.030*
C15	0.3498 (2)	0.73944 (16)	0.07885 (11)	0.0266 (4)
H15A	0.4663	0.6744	0.0613	0.032*
H15B	0.3565	0.8318	0.0592	0.032*
C16	0.28572 (19)	0.73863 (14)	0.18812 (10)	0.0178 (3)
H16A	0.1736	0.8094	0.2063	0.021*
H16B	0.3669	0.7616	0.2212	0.021*
C17	0.26717 (16)	0.59943 (12)	0.22211 (9)	0.0111 (2)
H17	0.3818	0.5290	0.2067	0.013*
C18	0.33000 (18)	0.56602 (13)	0.38753 (10)	0.0174 (3)
H18A	0.2716	0.5898	0.4558	0.021*
H18B	0.4065	0.6238	0.3681	0.021*
C19	0.44121 (17)	0.41627 (14)	0.38303 (10)	0.0158 (3)
H19A	0.5250	0.4061	0.4250	0.019*
H19B	0.5064	0.3938	0.3157	0.019*
C20	0.34221 (17)	0.31229 (13)	0.41426 (9)	0.0138 (3)
H20	0.2452	0.3333	0.3795	0.017*
C21	0.2677 (2)	0.32446 (16)	0.52319 (11)	0.0285 (4)
H21A	0.1971	0.2630	0.5408	0.043*
H21B	0.1973	0.4188	0.5399	0.043*
H21C	0.3611	0.2993	0.5587	0.043*
O1W	0.26626 (14)	−0.02391 (11)	0.47877 (8)	0.0248 (3)
H1O1	0.3177 (19)	0.0321 (15)	0.4526 (11)	0.030*
H2O1	0.1784 (15)	0.0183 (16)	0.5179 (10)	0.030*
O2W	0.04284 (15)	0.88477 (11)	0.39664 (9)	0.0291 (3)
H1O2	0.075 (2)	0.8012 (10)	0.3828 (13)	0.035*
H2O2	0.1220 (18)	0.9029 (17)	0.4144 (13)	0.035*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0154 (6)	0.0140 (5)	0.0119 (6)	−0.0022 (4)	−0.0064 (4)	0.0016 (4)
N2	0.0090 (5)	0.0082 (5)	0.0147 (6)	−0.0034 (4)	−0.0053 (4)	0.0028 (4)
N3	0.0078 (5)	0.0066 (5)	0.0147 (6)	−0.0021 (4)	−0.0045 (4)	0.0016 (4)
N4	0.0142 (5)	0.0141 (5)	0.0116 (6)	−0.0064 (4)	−0.0020 (4)	−0.0014 (4)
C1	0.0113 (6)	0.0118 (6)	0.0119 (6)	−0.0028 (5)	−0.0032 (5)	0.0016 (4)
C2	0.0135 (6)	0.0198 (7)	0.0239 (8)	0.0017 (5)	−0.0082 (5)	0.0023 (5)
C3	0.0152 (7)	0.0209 (7)	0.0294 (9)	0.0037 (6)	−0.0026 (6)	−0.0031 (6)
C4	0.0217 (7)	0.0134 (7)	0.0253 (8)	0.0028 (6)	−0.0019 (6)	−0.0053 (5)

C5	0.0195 (7)	0.0122 (6)	0.0161 (7)	−0.0014 (5)	−0.0041 (5)	−0.0025 (5)
C6	0.0122 (6)	0.0068 (5)	0.0131 (6)	−0.0016 (5)	−0.0035 (5)	0.0014 (4)
C7	0.0095 (6)	0.0082 (5)	0.0111 (6)	−0.0016 (4)	−0.0032 (4)	0.0013 (4)
C8	0.0145 (6)	0.0126 (6)	0.0253 (8)	−0.0085 (5)	−0.0082 (5)	0.0037 (5)
C9	0.0119 (6)	0.0171 (7)	0.0273 (8)	−0.0080 (5)	−0.0073 (5)	0.0045 (5)
C10	0.0105 (6)	0.0126 (6)	0.0184 (7)	−0.0034 (5)	−0.0075 (5)	0.0010 (5)
C11	0.0119 (7)	0.0200 (7)	0.0338 (9)	−0.0015 (5)	−0.0084 (6)	0.0027 (6)
C12	0.0118 (6)	0.0065 (6)	0.0133 (6)	−0.0019 (5)	−0.0038 (5)	0.0009 (4)
C13	0.0286 (8)	0.0143 (6)	0.0123 (7)	−0.0080 (6)	−0.0071 (5)	0.0028 (5)
C14	0.0424 (9)	0.0170 (7)	0.0160 (7)	−0.0114 (7)	−0.0022 (6)	0.0048 (5)
C15	0.0417 (9)	0.0217 (8)	0.0187 (8)	−0.0203 (7)	0.0049 (7)	−0.0003 (6)
C16	0.0246 (7)	0.0137 (6)	0.0169 (7)	−0.0113 (6)	0.0006 (5)	−0.0017 (5)
C17	0.0117 (6)	0.0099 (6)	0.0113 (6)	−0.0037 (5)	−0.0004 (5)	−0.0012 (4)
C18	0.0241 (7)	0.0160 (7)	0.0154 (7)	−0.0077 (6)	−0.0080 (5)	−0.0029 (5)
C19	0.0167 (7)	0.0173 (7)	0.0167 (7)	−0.0072 (5)	−0.0077 (5)	0.0002 (5)
C20	0.0146 (6)	0.0150 (6)	0.0123 (7)	−0.0048 (5)	−0.0032 (5)	−0.0008 (5)
C21	0.0408 (10)	0.0258 (8)	0.0164 (8)	−0.0129 (7)	0.0047 (7)	−0.0028 (6)
O1W	0.0230 (6)	0.0241 (6)	0.0268 (6)	−0.0091 (5)	−0.0009 (5)	0.0011 (4)
O2W	0.0286 (6)	0.0219 (6)	0.0355 (7)	−0.0030 (5)	−0.0075 (5)	−0.0120 (5)

Geometric parameters (Å, º)

N1—C1	1.4744 (17)	C10—C11	1.5253 (19)
N1—C20	1.4786 (17)	C10—H10	1.0000
N1—H1N1	0.914 (15)	C11—H11A	0.9800
N2—C7	1.4526 (16)	C11—H11B	0.9800
N2—C8	1.4618 (16)	C11—H11C	0.9800
N2—C6	1.4731 (16)	C12—C13	1.5327 (19)
N3—C7	1.4621 (16)	C12—C17	1.5414 (17)
N3—C10	1.4745 (16)	C12—H12	1.0000
N3—C12	1.4754 (16)	C13—C14	1.5278 (19)
N4—C18	1.4718 (17)	C13—H13A	0.9900
N4—C17	1.4747 (17)	C13—H13B	0.9900
N4—H1N4	0.882 (16)	C14—C15	1.523 (2)
C1—C2	1.5307 (18)	C14—H14A	0.9900
C1—C6	1.5403 (17)	C14—H14B	0.9900
C1—H1	1.0000	C15—C16	1.523 (2)
C2—C3	1.517 (2)	C15—H15A	0.9900
C2—H2A	0.9900	C15—H15B	0.9900
C2—H2B	0.9900	C16—C17	1.5287 (18)
C3—C4	1.521 (2)	C16—H16A	0.9900
C3—H3A	0.9900	C16—H16B	0.9900
C3—H3B	0.9900	C17—H17	1.0000
C4—C5	1.5258 (19)	C18—C19	1.5344 (19)
C4—H4C	0.9900	C18—H18A	0.9900
C4—H4D	0.9900	C18—H18B	0.9900
C5—C6	1.5375 (19)	C19—C20	1.5375 (19)
C5—H5A	0.9900	C19—H19A	0.9900

C5—H5B	0.9900	C19—H19B	0.9900
C6—H6	1.0000	C20—C21	1.5285 (19)
C7—H7A	0.9900	C20—H20	1.0000
C7—H7B	0.9900	C21—H21A	0.9800
C8—C9	1.5238 (19)	C21—H21B	0.9800
C8—H8A	0.9900	C21—H21C	0.9800
C8—H8B	0.9900	O1W—H1O1	0.847 (9)
C9—C10	1.5290 (18)	O1W—H2O1	0.833 (9)
C9—H9A	0.9900	O2W—H1O2	0.837 (9)
C9—H9B	0.9900	O2W—H2O2	0.830 (9)
C1—N1—C20	118.35 (10)	C11—C10—H10	108.6
C1—N1—H1N1	106.9 (10)	C9—C10—H10	108.6
C20—N1—H1N1	109.3 (10)	C10—C11—H11A	109.5
C7—N2—C8	109.60 (10)	C10—C11—H11B	109.5
C7—N2—C6	113.54 (10)	H11A—C11—H11B	109.5
C8—N2—C6	114.55 (10)	C10—C11—H11C	109.5
C7—N3—C10	108.08 (9)	H11A—C11—H11C	109.5
C7—N3—C12	112.33 (10)	H11B—C11—H11C	109.5
C10—N3—C12	116.57 (10)	N3—C12—C13	115.37 (10)
C18—N4—C17	115.03 (11)	N3—C12—C17	110.39 (10)
C18—N4—H1N4	111.0 (9)	C13—C12—C17	110.37 (11)
C17—N4—H1N4	105.5 (10)	N3—C12—H12	106.7
N1—C1—C2	108.50 (11)	C13—C12—H12	106.7
N1—C1—C6	112.59 (10)	C17—C12—H12	106.7
C2—C1—C6	109.49 (11)	C14—C13—C12	111.80 (11)
N1—C1—H1	108.7	C14—C13—H13A	109.3
C2—C1—H1	108.7	C12—C13—H13A	109.3
C6—C1—H1	108.7	C14—C13—H13B	109.3
C3—C2—C1	113.15 (12)	C12—C13—H13B	109.3
C3—C2—H2A	108.9	H13A—C13—H13B	107.9
C1—C2—H2A	108.9	C15—C14—C13	110.44 (12)
C3—C2—H2B	108.9	C15—C14—H14A	109.6
C1—C2—H2B	108.9	C13—C14—H14A	109.6
H2A—C2—H2B	107.8	C15—C14—H14B	109.6
C2—C3—C4	111.16 (12)	C13—C14—H14B	109.6
C2—C3—H3A	109.4	H14A—C14—H14B	108.1
C4—C3—H3A	109.4	C16—C15—C14	111.33 (12)
C2—C3—H3B	109.4	C16—C15—H15A	109.4
C4—C3—H3B	109.4	C14—C15—H15A	109.4
H3A—C3—H3B	108.0	C16—C15—H15B	109.4
C3—C4—C5	109.76 (12)	C14—C15—H15B	109.4
C3—C4—H4C	109.7	H15A—C15—H15B	108.0
C5—C4—H4C	109.7	C15—C16—C17	111.59 (11)
C3—C4—H4D	109.7	C15—C16—H16A	109.3
C5—C4—H4D	109.7	C17—C16—H16A	109.3
H4C—C4—H4D	108.2	C15—C16—H16B	109.3
C4—C5—C6	111.95 (12)	C17—C16—H16B	109.3

C4—C5—H5A	109.2	H16A—C16—H16B	108.0
C6—C5—H5A	109.2	N4—C17—C16	110.67 (10)
C4—C5—H5B	109.2	N4—C17—C12	109.40 (10)
C6—C5—H5B	109.2	C16—C17—C12	109.47 (11)
H5A—C5—H5B	107.9	N4—C17—H17	109.1
N2—C6—C5	113.91 (11)	C16—C17—H17	109.1
N2—C6—C1	111.74 (10)	C12—C17—H17	109.1
C5—C6—C1	109.61 (10)	N4—C18—C19	116.65 (11)
N2—C6—H6	107.1	N4—C18—H18A	108.1
C5—C6—H6	107.1	C19—C18—H18A	108.1
C1—C6—H6	107.1	N4—C18—H18B	108.1
N2—C7—N3	109.89 (10)	C19—C18—H18B	108.1
N2—C7—H7A	109.7	H18A—C18—H18B	107.3
N3—C7—H7A	109.7	C18—C19—C20	114.94 (11)
N2—C7—H7B	109.7	C18—C19—H19A	108.5
N3—C7—H7B	109.7	C20—C19—H19A	108.5
H7A—C7—H7B	108.2	C18—C19—H19B	108.5
N2—C8—C9	108.58 (10)	C20—C19—H19B	108.5
N2—C8—H8A	110.0	H19A—C19—H19B	107.5
C9—C8—H8A	110.0	N1—C20—C21	107.37 (11)
N2—C8—H8B	110.0	N1—C20—C19	114.21 (11)
C9—C8—H8B	110.0	C21—C20—C19	110.67 (12)
H8A—C8—H8B	108.4	N1—C20—H20	108.1
C8—C9—C10	112.39 (11)	C21—C20—H20	108.1
C8—C9—H9A	109.1	C19—C20—H20	108.1
C10—C9—H9A	109.1	C20—C21—H21A	109.5
C8—C9—H9B	109.1	C20—C21—H21B	109.5
C10—C9—H9B	109.1	H21A—C21—H21B	109.5
H9A—C9—H9B	107.9	C20—C21—H21C	109.5
N3—C10—C11	112.80 (11)	H21A—C21—H21C	109.5
N3—C10—C9	107.26 (10)	H21B—C21—H21C	109.5
C11—C10—C9	110.94 (12)	H1O1—O1W—H2O1	108.9 (15)
N3—C10—H10	108.6	H1O2—O2W—H2O2	107.8 (15)
C20—N1—C1—C2	153.36 (11)	C12—N3—C10—C9	−171.80 (10)
C20—N1—C1—C6	−85.30 (13)	C8—C9—C10—N3	−55.43 (14)
N1—C1—C2—C3	178.89 (12)	C8—C9—C10—C11	−179.03 (12)
C6—C1—C2—C3	55.66 (15)	C7—N3—C12—C13	54.74 (14)
C1—C2—C3—C4	−55.65 (16)	C10—N3—C12—C13	−70.74 (14)
C2—C3—C4—C5	55.09 (16)	C7—N3—C12—C17	−71.21 (12)
C3—C4—C5—C6	−57.78 (16)	C10—N3—C12—C17	163.31 (10)
C7—N2—C6—C5	−51.09 (14)	N3—C12—C13—C14	177.16 (11)
C8—N2—C6—C5	75.88 (14)	C17—C12—C13—C14	−56.88 (15)
C7—N2—C6—C1	73.80 (13)	C12—C13—C14—C15	55.58 (17)
C8—N2—C6—C1	−159.24 (11)	C13—C14—C15—C16	−55.15 (17)
C4—C5—C6—N2	−175.37 (11)	C14—C15—C16—C17	57.13 (17)
C4—C5—C6—C1	58.62 (14)	C18—N4—C17—C16	−89.72 (13)
N1—C1—C6—N2	56.17 (14)	C18—N4—C17—C12	149.58 (10)

C2—C1—C6—N2	176.96 (10)	C15—C16—C17—N4	−178.08 (11)
N1—C1—C6—C5	−176.58 (10)	C15—C16—C17—C12	−57.42 (15)
C2—C1—C6—C5	−55.80 (13)	N3—C12—C17—N4	−53.01 (13)
C8—N2—C7—N3	66.00 (13)	C13—C12—C17—N4	178.27 (10)
C6—N2—C7—N3	−164.48 (10)	N3—C12—C17—C16	−174.44 (10)
C10—N3—C7—N2	−67.79 (12)	C13—C12—C17—C16	56.85 (13)
C12—N3—C7—N2	162.22 (10)	C17—N4—C18—C19	−69.66 (15)
C7—N2—C8—C9	−57.21 (14)	N4—C18—C19—C20	−59.72 (16)
C6—N2—C8—C9	173.83 (11)	C1—N1—C20—C21	176.50 (12)
N2—C8—C9—C10	53.63 (15)	C1—N1—C20—C19	−60.40 (15)
C7—N3—C10—C11	−176.94 (11)	C18—C19—C20—N1	169.30 (11)
C12—N3—C10—C11	−49.35 (15)	C18—C19—C20—C21	−69.41 (15)
C7—N3—C10—C9	60.60 (13)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···O1*W*[i]	0.914 (15)	2.395 (15)	3.2763 (19)	162.0 (13)
N4—H1*N*4···N3	0.882 (16)	2.287 (15)	2.8304 (16)	119.8 (12)
O1*W*—H1*O*1···N1	0.85 (1)	2.06 (1)	2.9077 (18)	178 (2)
O1*W*—H2*O*1···O2*W*[ii]	0.83 (1)	1.99 (1)	2.816 (2)	175 (2)
O2*W*—H1*O*2···N4	0.84 (1)	2.10 (1)	2.9190 (18)	168 (2)
O2*W*—H2*O*2···O1*W*[iii]	0.83 (1)	1.98 (1)	2.7975 (17)	166 (2)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) −*x*, −*y*+1, −*z*+1; (iii) *x*, *y*+1, *z*.