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Diethyl 4-(4-chloro-2-propyl-1*H*-imidazol-5-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate monohydrate

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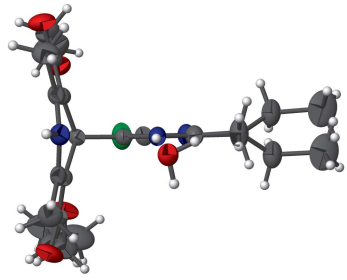
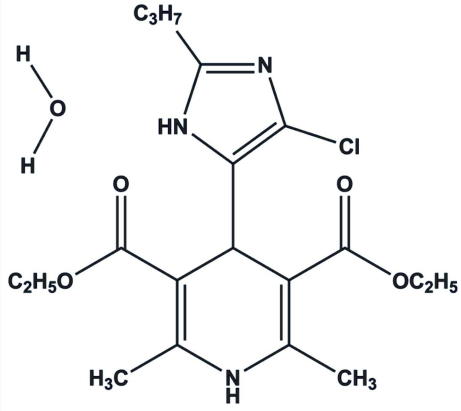
Structural data: full structural data are available from iucrdata.iucr.org

In the title hydrate, $C_{19}H_{26}ClN_3O_4\cdot H_2O$, the imidazole ring is nearly perpendicular [dihedral angle = 89.5 (1)°] to the dihydropyridine moiety. The propyl and one of the ethyl groups are disordered over two resolved sets of sites [occupancy factors 0.524 (8):0.476 (8) and 0.640 (16):0.360 (16), respectively]. In the crystal, a three-dimensional network is constructed by O—H···O, N—H···O and N—H···N hydrogen bonds involving both the main molecule and the water molecule of crystallization, as well as C—H···π(ring) interactions.

3D view



Chemical scheme



Structure description

Hantzsch 1,4-dihydropyridine derivatives are important components of several commonly used drugs (Sharma & Singh, 2017). The broad bioactivities shown by imidazole derivatives may result from the fact that they are electron-rich due to the presence of two nitrogen atoms (Zhang *et al.*, 2014). The crystal structures of several 1,4-dihydropyridine derivatives have been reported (Jasinski *et al.*, 2013). As part of our studies in this area, a new imidazole-dihydropyridine derivative has been synthesized and its crystal structure is reported here, Fig. 1.

A Cremer–Pople puckering analysis of the conformation of the dihydropyridine ring yielded the parameters Q = 0.274 (4) Å, θ = 103.4 (8)° and φ = 359.1 (9)°. The ring adopts a shallow boat conformation with N1 and C3 deviating by 0.155 (5) and 0.315 (6) Å, respectively, from the C1/C2/C4/C5 plane towards the imidazole group. The imidazole and dihydropyridine rings are almost perpendicular to one another, as indicated by the

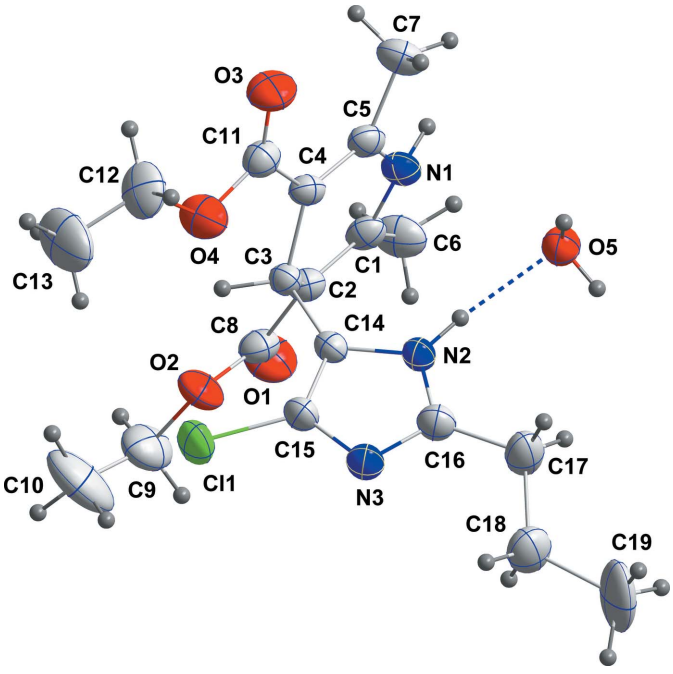


Figure 1
The asymmetric unit with the atom-labelling scheme and 50% probability ellipsoids. Only the major disorder components are shown. The N—H···O hydrogen bond to the water molecule of crystallization (Table 1) is shown as a dashed line.

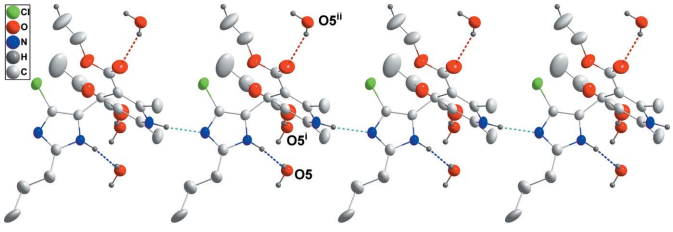


Figure 2
Detail of the chain formed by N—H···N hydrogen bonds (light-blue dashed lines) and the surrounding sets of O—H···O bonded (red dashed lines) water molecules [Symmetry codes: (i) x, $1+y$, z; (ii) $1+y$, $1-x$, $\frac{1}{4}+z$] viewed towards ($0\bar{1}1$) (the a axis extends horizontally to the right).

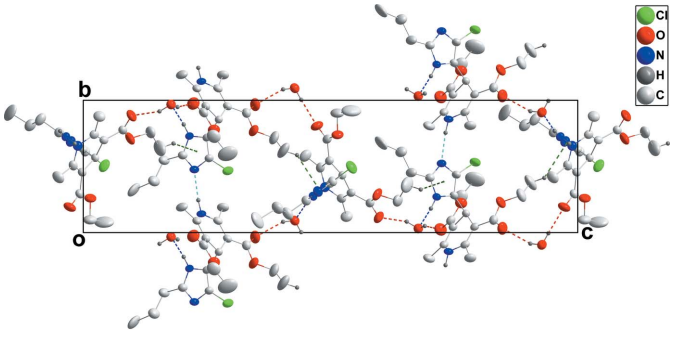


Figure 3
Packing viewed along the a-axis direction. O—H···O hydrogen bonds are shown as red dashed lines while the N—H···O and N—H···N hydrogen bonds are depicted by dark- and light-blue dashed lines, respectively. The C—H···π(ring) interactions are depicted by green dashed lines.

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the N2/N3/C14–C16 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N3^{i}	0.91	2.00	2.906 (4)	173
N2—H2···O5	0.91	1.94	2.827 (4)	165
O5—H5A···O3^{ii}	0.87	2.07	2.853 (4)	149
O5—H5B···O1^{iii}	0.87	1.98	2.823 (5)	163
C13—H13B···Cg1^{iv}	0.98	2.78	3.518 (14)	133

Symmetry codes: (i) $x+1, y, z$; (ii) $-y+1, x-1, z-\frac{1}{4}$; (iii) $x, y-1, z$; (iv) $y, -x+1, z+\frac{1}{4}$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{26}ClN_3O_4\cdot H_2O$
M_r	413.89
Crystal system, space group	Tetragonal, $P4_3$
Temperature (K)	200
a, c (Å)	8.5308 (11), 31.893 (4)
V (Å^3)	2321.0 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.20
Crystal size (mm)	0.34 × 0.29 × 0.20
Data collection	
Diffractometer	Bruker *SMART APEX* CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.48, 0.96
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21675, 5536, 4641
R_{int}	0.069
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.660
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.065, 0.182, 1.06
No. of reflections	5536
No. of parameters	277
No. of restraints	43
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.82, −0.22
Absolute structure	Flack x determined using 1897 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.01 (4)

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012 and *SHELXTL* (Sheldrick, 2008).

dihedral angle of 89.5 (1)° between the C1/C2/C4/C5 and C14/C15/N3/C16/N2 planes. The propyl group (C17–C19) and the C12/C13 ethyl group are disordered over two resolved sets of sites with occupancy factors 0.524 (8):0.476 (8) and 0.640 (16):0.360 (16), respectively.

In the crystal, N1—H1···N3 hydrogen bonds (Table 1) form chains, extending alternately along the a- and b-axis directions. Each chain is surrounded by three rows of water molecules of crystallization anchored by N3—H3A···O5, O5—H5A···O1 and O5—H5B···O3 hydrogen bonds (Table 2 and Fig. 2). The water molecules form O—H···O bridges between adjacent chains and bind them together into a three-dimensional

network, which is further reinforced by C13—H13*B*···*Cg*1 interactions (Table 1 and Fig. 3).

Synthesis and crystallization

A mixture of 4-chloro-2-propyl-1*H*-imidazole-5-carbaldehyde (1.72 g, 0.01 mol), ethyl acetoacetate (0.02 mol) and ammonium acetate (5 g) was refluxed for 8 h in 30 ml of ethanol. The reaction mixture was cooled to room temperature and the solid product obtained was filtered and recrystallized by slow evaporation from ethanol solution in 78% yield (m.p. 498 K).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. One of the ethyl ester groups and the *n*-propyl group are disordered over two resolved orientations. The occupancies for the C12 and C13 atoms of the ethyl group refined to 0.640 (16) and 0.360 (16), while those for the C17–C19 propyl group are 0.524 (8) and 0.476 (8). In each case, two disorder components were refined with restraints so that their geometries are comparable.

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full crystallographic data

IUCrData (2018). **3**, x181470 [https://doi.org/10.1107/S2414314618014700]

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Crystal data

$C_{19}H_{26}ClN_3O_4·H_2O$
M_r = 413.89
Tetragonal, $P4_3$
a = 8.5308 (11) Å
c = 31.893 (4) Å
V = 2321.0 (7) Å^3
Z = 4
F(000) = 880
D_x = 1.184 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7831 reflections
θ = 2.4–25.3°
μ = 0.20 mm^{-1}
T = 200 K
Block, colourless
0.34 × 0.29 × 0.20 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.48, T_{max} = 0.96
21675 measured reflections
5536 independent reflections
4641 reflections with $I > 2\sigma(I)$
R_{int} = 0.069
θ_{max} = 28.0°, θ_{min} = 2.4°
h = −11→11
k = −11→11
l = −41→41

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.182
S = 1.06
5536 reflections
277 parameters
43 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1247P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.82 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Absolute structure: Flack x determined using 1897 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.01 (4)

Special details

Experimental. The diffraction data were collected in three sets of 363 frames (0.5° width in ω) at φ = 0, 120 and 240°. A scan time of 40 sec/frame was used.

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.99 Å) while those attached to nitrogen and oxygen were placed in locations derived from a difference map and their coordinates adjusted to give N—H = 0.91 %A and O—H = 0.87 Å. All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms. The propyl substituent and the ethyl group of one of the ester substituents are each disordered over two sites. The components of the disorder were refined with restraints that the geometries be comparable.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	0.46749 (12)	0.49418 (16)	0.54263 (4)	0.0528 (3)	
O1	0.9755 (5)	0.8067 (4)	0.47266 (13)	0.0582 (9)	
O2	0.7765 (4)	0.7394 (4)	0.51427 (12)	0.0486 (8)	
O3	0.9671 (5)	0.1161 (4)	0.59772 (11)	0.0586 (10)	
O4	0.7708 (4)	0.2888 (4)	0.59462 (11)	0.0540 (9)	
N1	1.1423 (4)	0.3440 (4)	0.48885 (11)	0.0357 (7)	
H1	1.245197	0.327894	0.482713	0.033 (11)*	
N2	0.7297 (4)	0.2751 (4)	0.46475 (10)	0.0305 (6)	
H2	0.817274	0.232166	0.453195	0.041 (13)*	
N3	0.4772 (4)	0.3110 (4)	0.47461 (11)	0.0386 (7)	
C1	1.0894 (4)	0.4920 (5)	0.47960 (12)	0.0350 (8)	
C2	0.9557 (4)	0.5435 (4)	0.49772 (12)	0.0320 (7)	
C3	0.8546 (4)	0.4339 (4)	0.52409 (11)	0.0286 (7)	
H3	0.812065	0.495378	0.548243	0.034*	
C4	0.9551 (4)	0.3013 (4)	0.54169 (12)	0.0306 (7)	
C5	1.0896 (4)	0.2586 (5)	0.52216 (13)	0.0336 (8)	
C6	1.1934 (6)	0.5810 (7)	0.44948 (18)	0.0532 (12)	
H6A	1.262391	0.507243	0.434815	0.080*	
H6B	1.257065	0.656739	0.465094	0.080*	
H6C	1.128277	0.636602	0.429009	0.080*	
C7	1.1910 (5)	0.1220 (6)	0.53262 (17)	0.0494 (11)	
H7A	1.270799	0.108950	0.510796	0.074*	
H7B	1.126603	0.027033	0.534251	0.074*	
H7C	1.242248	0.140061	0.559687	0.074*	
C8	0.9068 (5)	0.7067 (5)	0.49327 (13)	0.0380 (8)	
C9	0.7276 (8)	0.9030 (6)	0.5138 (2)	0.0655 (15)	
H9A	0.815436	0.971131	0.522711	0.079*	
H9B	0.696083	0.933900	0.485068	0.079*	
C10	0.5964 (10)	0.9206 (9)	0.5423 (4)	0.108 (3)	

H10A	0.572799	1.032164	0.545959	0.162*	
H10B	0.623239	0.874375	0.569507	0.162*	
H10C	0.504424	0.867017	0.530726	0.162*	
C11	0.9040 (5)	0.2247 (5)	0.57994 (12)	0.0365 (8)	
C12	0.7170 (16)	0.2420 (14)	0.6360 (3)	0.061 (3)	0.640 (16)
H12A	0.655582	0.143916	0.633696	0.073*	0.640 (16)
H12B	0.808779	0.220946	0.654162	0.073*	0.640 (16)
C13	0.6218 (18)	0.3615 (18)	0.6548 (4)	0.093 (4)	0.640 (16)
H13A	0.683452	0.457725	0.657961	0.139*	0.640 (16)
H13B	0.586070	0.326148	0.682471	0.139*	0.640 (16)
H13C	0.530725	0.382297	0.636939	0.139*	0.640 (16)
C12A	0.705 (3)	0.201 (3)	0.6295 (6)	0.061 (3)	0.360 (16)
H12C	0.694499	0.088692	0.621944	0.073*	0.360 (16)
H12D	0.774495	0.208879	0.654368	0.073*	0.360 (16)
C13A	0.555 (3)	0.268 (4)	0.6382 (7)	0.093 (4)	0.360 (16)
H13D	0.568732	0.370181	0.651812	0.139*	0.360 (16)
H13E	0.496011	0.198304	0.656902	0.139*	0.360 (16)
H13F	0.496892	0.281704	0.611956	0.139*	0.360 (16)
C14	0.7186 (4)	0.3699 (4)	0.49976 (11)	0.0290 (7)	
C15	0.5620 (4)	0.3880 (5)	0.50448 (12)	0.0343 (8)	
C16	0.5849 (5)	0.2426 (5)	0.45107 (13)	0.0376 (8)	
C17	0.5464 (12)	0.144 (5)	0.4135 (9)	0.0525 (14)	0.524 (8)
H17A	0.542924	0.032752	0.422055	0.063*	0.524 (8)
H17B	0.631123	0.155890	0.392517	0.063*	0.524 (8)
C18	0.3896 (12)	0.1877 (13)	0.3930 (3)	0.0576 (18)	0.524 (8)
H18A	0.396508	0.299632	0.384965	0.069*	0.524 (8)
H18B	0.308351	0.180172	0.415038	0.069*	0.524 (8)
C19	0.3234 (14)	0.0935 (19)	0.3523 (4)	0.088 (3)	0.524 (8)
H19A	0.222441	0.138200	0.343833	0.132*	0.524 (8)
H19B	0.398360	0.103007	0.329169	0.132*	0.524 (8)
H19C	0.309558	−0.017327	0.359461	0.132*	0.524 (8)
C17A	0.5500 (13)	0.149 (6)	0.4125 (10)	0.0525 (14)	0.476 (8)
H17C	0.636510	0.073361	0.407746	0.063*	0.476 (8)
H17D	0.545851	0.220029	0.388049	0.063*	0.476 (8)
C18A	0.3948 (12)	0.0580 (14)	0.4153 (3)	0.0576 (18)	0.476 (8)
H18C	0.312568	0.134258	0.423352	0.069*	0.476 (8)
H18D	0.404806	−0.016940	0.438878	0.069*	0.476 (8)
C19A	0.3291 (16)	−0.040 (2)	0.3751 (4)	0.088 (3)	0.476 (8)
H19D	0.229519	−0.089897	0.382512	0.132*	0.476 (8)
H19E	0.312735	0.032066	0.351558	0.132*	0.476 (8)
H19F	0.405573	−0.120117	0.367186	0.132*	0.476 (8)
O5	0.9682 (3)	0.0915 (4)	0.42764 (10)	0.0414 (7)	
H5A	0.916316	0.082739	0.404279	0.062*	
H5B	0.949174	0.004180	0.440755	0.062*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0337 (5)	0.0708 (8)	0.0539 (6)	0.0073 (5)	0.0067 (5)	−0.0214 (5)
O1	0.068 (2)	0.0387 (17)	0.068 (2)	−0.0017 (15)	0.0072 (18)	0.0179 (16)
O2	0.0483 (17)	0.0336 (15)	0.064 (2)	0.0106 (13)	0.0019 (15)	0.0027 (14)
O3	0.073 (2)	0.059 (2)	0.0445 (18)	0.0164 (17)	−0.0028 (17)	0.0197 (16)
O4	0.0550 (19)	0.065 (2)	0.0417 (16)	0.0101 (16)	0.0175 (14)	0.0228 (16)
N1	0.0216 (14)	0.0432 (18)	0.0423 (17)	0.0004 (12)	0.0020 (13)	0.0006 (15)
N2	0.0245 (14)	0.0345 (15)	0.0323 (15)	0.0002 (11)	0.0020 (12)	−0.0032 (13)
N3	0.0256 (15)	0.0485 (19)	0.0416 (18)	0.0006 (13)	−0.0002 (13)	−0.0068 (15)
C1	0.0257 (17)	0.044 (2)	0.0350 (18)	−0.0058 (15)	−0.0033 (14)	0.0028 (16)
C2	0.0308 (17)	0.0326 (18)	0.0327 (18)	−0.0008 (13)	−0.0038 (14)	0.0028 (15)
C3	0.0265 (16)	0.0313 (17)	0.0280 (16)	0.0023 (13)	0.0010 (13)	0.0010 (14)
C4	0.0282 (16)	0.0288 (16)	0.0347 (17)	−0.0003 (13)	−0.0062 (15)	0.0010 (15)
C5	0.0279 (17)	0.0344 (18)	0.0385 (19)	−0.0011 (14)	−0.0072 (15)	−0.0025 (16)
C6	0.035 (2)	0.063 (3)	0.061 (3)	−0.002 (2)	0.011 (2)	0.018 (2)
C7	0.034 (2)	0.050 (3)	0.064 (3)	0.0100 (19)	−0.001 (2)	0.004 (2)
C8	0.0398 (19)	0.037 (2)	0.0373 (19)	0.0001 (15)	−0.0086 (16)	0.0053 (17)
C9	0.076 (4)	0.037 (2)	0.083 (4)	0.013 (2)	−0.009 (3)	0.001 (3)
C10	0.095 (5)	0.056 (4)	0.172 (10)	0.034 (4)	0.028 (6)	−0.004 (5)
C11	0.041 (2)	0.0343 (19)	0.0347 (18)	−0.0018 (15)	−0.0027 (16)	0.0016 (16)
C12	0.077 (4)	0.063 (6)	0.043 (4)	−0.004 (4)	0.023 (3)	0.008 (4)
C13	0.100 (7)	0.112 (8)	0.066 (6)	0.028 (6)	0.048 (6)	0.019 (5)
C12A	0.077 (4)	0.063 (6)	0.043 (4)	−0.004 (4)	0.023 (3)	0.008 (4)
C13A	0.100 (7)	0.112 (8)	0.066 (6)	0.028 (6)	0.048 (6)	0.019 (5)
C14	0.0274 (16)	0.0283 (16)	0.0312 (17)	0.0043 (12)	0.0029 (14)	0.0016 (14)
C15	0.0273 (17)	0.040 (2)	0.035 (2)	0.0045 (15)	0.0018 (14)	−0.0036 (16)
C16	0.0307 (18)	0.042 (2)	0.040 (2)	0.0000 (15)	0.0000 (16)	−0.0017 (17)
C17	0.037 (2)	0.067 (3)	0.054 (3)	−0.002 (2)	−0.003 (2)	−0.021 (2)
C18	0.048 (4)	0.065 (4)	0.060 (4)	−0.006 (3)	−0.007 (3)	−0.015 (3)
C19	0.078 (5)	0.117 (8)	0.069 (5)	−0.008 (6)	0.043 (5)	−0.042 (5)
C17A	0.037 (2)	0.067 (3)	0.054 (3)	−0.002 (2)	−0.003 (2)	−0.021 (2)
C18A	0.048 (4)	0.065 (4)	0.060 (4)	−0.006 (3)	−0.007 (3)	−0.015 (3)
C19A	0.078 (5)	0.117 (8)	0.069 (5)	−0.008 (6)	0.043 (5)	−0.042 (5)
O5	0.0416 (16)	0.0426 (16)	0.0400 (16)	0.0000 (12)	−0.0005 (12)	−0.0037 (12)

Geometric parameters (Å, º)

Cl1—C15	1.718 (4)	C10—H10C	0.9800
O1—C8	1.226 (5)	C12—C13	1.436 (12)
O2—C8	1.328 (5)	C12—H12A	0.9900
O2—C9	1.456 (6)	C12—H12B	0.9900
O3—C11	1.212 (5)	C13—H13A	0.9800
O4—C11	1.346 (6)	C13—H13B	0.9800
O4—C12	1.453 (6)	C13—H13C	0.9800
O4—C12A	1.453 (7)	C12A—C13A	1.435 (12)
N1—C5	1.364 (5)	C12A—H12C	0.9900

N1—C1	1.373 (5)	C12A—H12D	0.9900
N1—H1	0.9100	C13A—H13D	0.9800
N2—C16	1.339 (5)	C13A—H13E	0.9800
N2—C14	1.382 (5)	C13A—H13F	0.9800
N2—H2	0.9100	C14—C15	1.354 (5)
N3—C16	1.323 (5)	C16—C17A	1.498 (7)
N3—C15	1.364 (5)	C16—C17	1.499 (7)
C1—C2	1.352 (5)	C17—C18	1.53 (2)
C1—C6	1.512 (6)	C17—H17A	0.9900
C2—C8	1.460 (5)	C17—H17B	0.9900
C2—C3	1.525 (5)	C18—C19	1.626 (13)
C3—C14	1.498 (5)	C18—H18A	0.9900
C3—C4	1.527 (5)	C18—H18B	0.9900
C3—H3	1.0000	C19—H19A	0.9800
C4—C5	1.356 (5)	C19—H19B	0.9800
C4—C11	1.451 (5)	C19—H19C	0.9800
C5—C7	1.489 (6)	C17A—C18A	1.54 (2)
C6—H6A	0.9800	C17A—H17C	0.9900
C6—H6B	0.9800	C17A—H17D	0.9900
C6—H6C	0.9800	C18A—C19A	1.629 (13)
C7—H7A	0.9800	C18A—H18C	0.9900
C7—H7B	0.9800	C18A—H18D	0.9900
C7—H7C	0.9800	C19A—H19D	0.9800
C9—C10	1.451 (12)	C19A—H19E	0.9800
C9—H9A	0.9900	C19A—H19F	0.9800
C9—H9B	0.9900	O5—H5A	0.8699
C10—H10A	0.9800	O5—H5B	0.8699
C10—H10B	0.9800		

C8—O2—C9	115.8 (4)	C12—C13—H13B	109.5
C11—O4—C12	118.1 (5)	H13A—C13—H13B	109.5
C11—O4—C12A	112.3 (8)	C12—C13—H13C	109.5
C5—N1—C1	123.4 (3)	H13A—C13—H13C	109.5
C5—N1—H1	113.9	H13B—C13—H13C	109.5
C1—N1—H1	114.2	C13A—C12A—O4	106.5 (13)
C16—N2—C14	108.7 (3)	C13A—C12A—H12C	110.4
C16—N2—H2	122.8	O4—C12A—H12C	110.4
C14—N2—H2	128.2	C13A—C12A—H12D	110.4
C16—N3—C15	103.9 (3)	O4—C12A—H12D	110.4
C2—C1—N1	118.9 (3)	H12C—C12A—H12D	108.6
C2—C1—C6	127.1 (4)	C12A—C13A—H13D	109.5
N1—C1—C6	113.9 (4)	C12A—C13A—H13E	109.5
C1—C2—C8	120.6 (4)	H13D—C13A—H13E	109.5
C1—C2—C3	120.9 (3)	C12A—C13A—H13F	109.5
C8—C2—C3	118.5 (3)	H13D—C13A—H13F	109.5
C14—C3—C2	112.1 (3)	H13E—C13A—H13F	109.5
C14—C3—C4	110.8 (3)	C15—C14—N2	102.9 (3)
C2—C3—C4	109.8 (3)	C15—C14—C3	131.7 (3)

C14—C3—H3	108.0	N2—C14—C3	125.3 (3)
C2—C3—H3	108.0	C14—C15—N3	113.0 (3)
C4—C3—H3	108.0	C14—C15—Cl1	127.0 (3)
C5—C4—C11	121.3 (3)	N3—C15—Cl1	120.0 (3)
C5—C4—C3	120.3 (3)	N3—C16—N2	111.4 (4)
C11—C4—C3	118.3 (3)	N3—C16—C17A	124.3 (6)
C4—C5—N1	119.6 (3)	N2—C16—C17A	124.2 (5)
C4—C5—C7	126.8 (4)	N3—C16—C17	123.2 (5)
N1—C5—C7	113.6 (4)	N2—C16—C17	125.3 (5)
C1—C6—H6A	109.5	C16—C17—C18	113.4 (15)
C1—C6—H6B	109.5	C16—C17—H17A	108.9
H6A—C6—H6B	109.5	C18—C17—H17A	108.9
C1—C6—H6C	109.5	C16—C17—H17B	108.9
H6A—C6—H6C	109.5	C18—C17—H17B	108.9
H6B—C6—H6C	109.5	H17A—C17—H17B	107.7
C5—C7—H7A	109.5	C17—C18—C19	121.6 (9)
C5—C7—H7B	109.5	C17—C18—H18A	106.9
H7A—C7—H7B	109.5	C19—C18—H18A	106.9
C5—C7—H7C	109.5	C17—C18—H18B	106.9
H7A—C7—H7C	109.5	C19—C18—H18B	106.9
H7B—C7—H7C	109.5	H18A—C18—H18B	106.7
O1—C8—O2	121.6 (4)	C18—C19—H19A	109.5
O1—C8—C2	125.4 (4)	C18—C19—H19B	109.5
O2—C8—C2	113.0 (3)	H19A—C19—H19B	109.5
C10—C9—O2	108.2 (5)	C18—C19—H19C	109.5
C10—C9—H9A	110.1	H19A—C19—H19C	109.5
O2—C9—H9A	110.1	H19B—C19—H19C	109.5
C10—C9—H9B	110.1	C16—C17A—C18A	113.1 (16)
O2—C9—H9B	110.1	C16—C17A—H17C	109.0
H9A—C9—H9B	108.4	C18A—C17A—H17C	109.0
C9—C10—H10A	109.5	C16—C17A—H17D	109.0
C9—C10—H10B	109.5	C18A—C17A—H17D	109.0
H10A—C10—H10B	109.5	H17C—C17A—H17D	107.8
C9—C10—H10C	109.5	C17A—C18A—C19A	120.5 (9)
H10A—C10—H10C	109.5	C17A—C18A—H18C	107.2
H10B—C10—H10C	109.5	C19A—C18A—H18C	107.2
O3—C11—O4	121.5 (4)	C17A—C18A—H18D	107.2
O3—C11—C4	127.2 (4)	C19A—C18A—H18D	107.2
O4—C11—C4	111.3 (3)	H18C—C18A—H18D	106.8
C13—C12—O4	111.3 (8)	C18A—C19A—H19D	109.5
C13—C12—H12A	109.4	C18A—C19A—H19E	109.5
O4—C12—H12A	109.4	H19D—C19A—H19E	109.5
C13—C12—H12B	109.4	C18A—C19A—H19F	109.5
O4—C12—H12B	109.4	H19D—C19A—H19F	109.5
H12A—C12—H12B	108.0	H19E—C19A—H19F	109.5
C12—C13—H13A	109.5	H5A—O5—H5B	104.1

C5—N1—C1—C2	−15.6 (6)	C5—C4—C11—O3	−2.5 (6)

C5—N1—C1—C6	163.8 (4)	C3—C4—C11—O3	178.4 (4)
N1—C1—C2—C8	171.6 (3)	C5—C4—C11—O4	178.0 (4)
C6—C1—C2—C8	−7.7 (6)	C3—C4—C11—O4	−1.1 (5)
N1—C1—C2—C3	−6.9 (5)	C11—O4—C12—C13	154.4 (11)
C6—C1—C2—C3	173.8 (4)	C11—O4—C12A—C13A	−172.3 (18)
C1—C2—C3—C14	−98.7 (4)	C16—N2—C14—C15	−0.2 (4)
C8—C2—C3—C14	82.7 (4)	C16—N2—C14—C3	−179.2 (4)
C1—C2—C3—C4	24.9 (5)	C2—C3—C14—C15	−115.7 (4)
C8—C2—C3—C4	−153.6 (3)	C4—C3—C14—C15	121.2 (4)
C14—C3—C4—C5	100.0 (4)	C2—C3—C14—N2	63.0 (5)
C2—C3—C4—C5	−24.4 (5)	C4—C3—C14—N2	−60.1 (4)
C14—C3—C4—C11	−80.9 (4)	N2—C14—C15—N3	−0.2 (4)
C2—C3—C4—C11	154.7 (3)	C3—C14—C15—N3	178.7 (4)
C11—C4—C5—N1	−173.1 (3)	N2—C14—C15—Cl1	−180.0 (3)
C3—C4—C5—N1	5.9 (5)	C3—C14—C15—Cl1	−1.0 (6)
C11—C4—C5—C7	7.9 (6)	C16—N3—C15—C14	0.5 (5)
C3—C4—C5—C7	−173.0 (4)	C16—N3—C15—Cl1	−179.7 (3)
C1—N1—C5—C4	16.1 (6)	C15—N3—C16—N2	−0.6 (5)
C1—N1—C5—C7	−164.8 (4)	C15—N3—C16—C17A	−177 (3)
C9—O2—C8—O1	−4.4 (7)	C15—N3—C16—C17	−180 (2)
C9—O2—C8—C2	175.5 (4)	C14—N2—C16—N3	0.5 (5)
C1—C2—C8—O1	2.4 (6)	C14—N2—C16—C17A	177 (3)
C3—C2—C8—O1	−179.0 (4)	C14—N2—C16—C17	179 (2)
C1—C2—C8—O2	−177.6 (4)	N3—C16—C17—C18	26 (4)
C3—C2—C8—O2	1.0 (5)	N2—C16—C17—C18	−152.4 (14)
C8—O2—C9—C10	−172.8 (6)	C16—C17—C18—C19	−178.8 (18)
C12—O4—C11—O3	9.8 (9)	N3—C16—C17A—C18A	−34 (4)
C12A—O4—C11—O3	−7.5 (15)	N2—C16—C17A—C18A	150.1 (16)
C12—O4—C11—C4	−170.7 (7)	C16—C17A—C18A—C19A	175 (2)
C12A—O4—C11—C4	172.0 (14)		

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the N2/N3/C14–C16 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N3^{i}	0.91	2.00	2.906 (4)	173
N2—H2···O5	0.91	1.94	2.827 (4)	165
O5—H5*A*···O3^{ii}	0.87	2.07	2.853 (4)	149
O5—H5*B*···O1^{iii}	0.87	1.98	2.823 (5)	163
C13—H13*B*···*Cg*1^{iv}	0.98	2.78	3.518 (14)	133

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*y*+1, *x*−1, *z*−1/4; (iii) *x*, *y*−1, *z*; (iv) *y*, −*x*+1, *z*+1/4.