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3,3′-(Dodecane-1,12-diyl)bis(1-methylimidazolium) 5,5′-azotetrazolate heptahydrate

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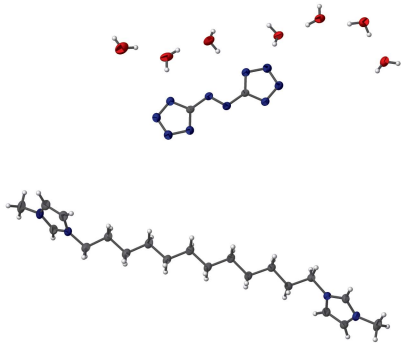
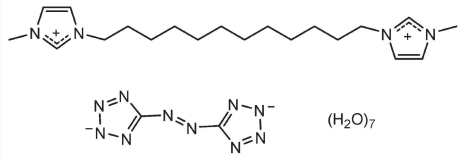
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{20}H_{36}N_4\cdot C_2N_{10}\cdot 7H_2O$, was obtained by reaction of 1-methylimidazole with 1,12-dibromododecane, followed by repeated ion metathesis (bromide → sulfate → azotetrazolate). An intricate network of hydrogen bonds is formed between anions and water molecules, leading to a layered arrangement parallel to (101).

3D view



Chemical scheme



Structure description

Two heterocyclic cations joined by hydrocarbon linkage chains and paired with different anions constitute a new class of ionic liquids. Dicationic imidazolium-based ionic liquids exhibit superior thermal stabilities compared to those of traditional ionic liquids (Anderson *et al.*, 2005). Coincidentally, heterocyclic dianions are of interest as components for nitrogen-rich salts (Laus *et al.*, 2016) or potential explosives (Singh *et al.*, 2006). A combination of these dications and dianions was presumed to furnish products with interesting structural attributes. Repeated ion metathesis (bromide → sulfate → azotetrazolate) was successfully employed for the synthesis of the desired salts, the crystal structure of one of which is reported here.

In the crystal structure of the title hydrated salt, an intricate network of O—H···O and O—H···N hydrogen-bonded anions and water molecules is observed (Table 1) which can be adequately described by graph-set symbols (Etter, 1990; Etter *et al.*, 1990). One azotetrazolate dianion is surrounded by various water molecules enclosing pairs of $R_4^4(10)$, $R_3^3(11)$ and $R_7^7(16)$ ring motifs each, as well as one $R_4^4(9)$ and one $R_7^7(15)$ ring motif (Fig. 1). The planar dianion [the maximum deviation from the least-squares plane is 0.027 (2) Å for N9] and seven water molecules are located near the (101) plane, whereas the bar-shaped dications are found above and beneath this layer (Fig. 2). The dihedral angle between the two 1-methylimidazolium moieties in the dication is 8.57 (15)°.

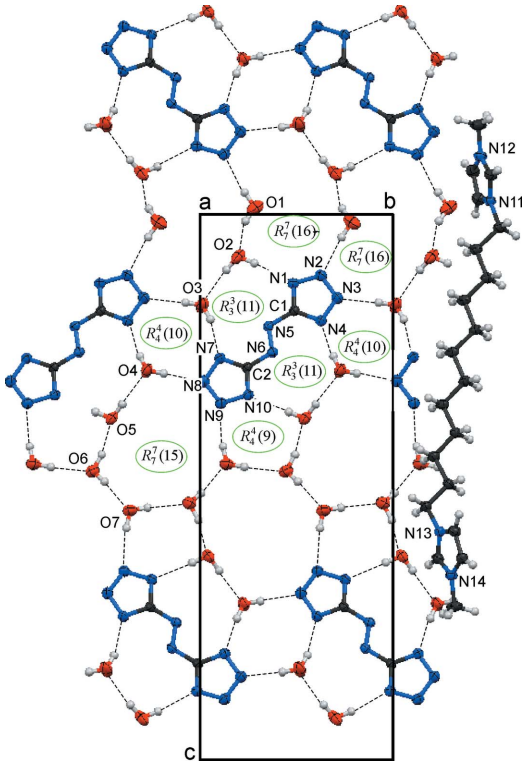


Figure 1
The arrangement of molecular entities in the crystal structure of the title compound, showing selected atom labels and displacement ellipsoids at the 50% probability level for non-H atoms. Hydrogen bonds are shown as dashed lines. Graph-set symbols indicate the hydrogen-bond patterns.

Related structures of geminal dications with traditional anions (Anderson *et al.*, 2005) as well as related azotetrazolate salts with traditional cations (Laus *et al.*, 2012) have been reported.

Synthesis and crystallization

Silver sulfate (156 mg, 0.50 mmol) was added to a solution of 3,3′-(dodecane-1,12-diyl)bis(1-methylimidazolium) bromide (246 mg, 0.50 mmol; Tadesse *et al.*, 2012) in water (5 ml). The mixture was stirred at 323 K for 10 min and ultrasonicated for 5 min. Subsequently, the precipitate was removed by centrifugation. Barium 5,5′-azotetrazolate pentahydrate (196 mg, 0.50 mmol; Hammerl *et al.*, 2002) was added to the supernatant, and the mixture was again stirred at 323 K for 10 min and ultrasonicated for 5 min. After centrifugation, the supernatant solution was filtered (0.45 µm) and taken to dryness in a rotary evaporator under reduced pressure, the temperature not exceeding 323 K. The yellow residue was recrystallized from hot water, collected by filtration and vacuum-dried to

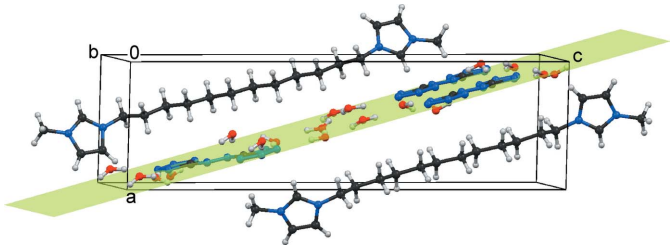


Figure 2
Arrangement of cations above and beneath the plane of anions and water molecules in the unit cell of the title compound.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H11*O*···N2^{i}	0.87 (3)	2.02 (3)	2.884 (3)	174 (3)
O1—H12*O*···O2	0.89 (5)	2.00 (4)	2.850 (3)	159 (4)
O2—H22*O*···O3	0.84 (4)	2.00 (4)	2.819 (3)	162 (4)
O2—H21*O*···N1	0.82 (3)	2.06 (3)	2.875 (3)	174 (3)
O3—H32*O*···N3^{ii}	0.85 (4)	2.00 (4)	2.853 (3)	172 (4)
O3—H31*O*···N7	0.84 (4)	2.14 (3)	2.959 (3)	165 (4)
O4—H42*O*···N4^{ii}	0.86 (3)	2.06 (3)	2.914 (3)	175 (3)
O4—H41*O*···N8	0.87 (3)	1.99 (3)	2.853 (3)	171 (3)
O5—H52*O*···N10^{ii}	0.82 (3)	2.06 (3)	2.879 (3)	179 (3)
O5—H51*O*···O4	0.87 (3)	1.94 (3)	2.790 (3)	166 (4)
O6—H61*O*···O5	0.90 (3)	1.89 (3)	2.755 (3)	161 (3)
O6—H62*O*···O7	0.84 (4)	1.93 (3)	2.753 (3)	169 (3)
O7—H71*O*···O6^{iii}	0.86 (3)	1.96 (3)	2.807 (4)	169 (4)
O7—H72*O*···N9^{iv}	0.84 (3)	2.10 (3)	2.931 (3)	170 (3)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{36}N_4{\cdot}C_2N_{10}{\cdot}7H_2O$
M_r	622.76
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	183
a, b, c (Å)	7.2847 (3), 8.9932 (4), 25.3962 (11)
β (°)	91.062 (1)
V (Å^3)	1663.49 (12)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.17 × 0.12 × 0.08
Data collection	
Diffractometer	Bruker D8 QUEST PHOTON 100
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.848, 0.888
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	29637, 6171, 5428
R_{int}	0.032
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.606
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.081, 1.04
No. of reflections	6171
No. of parameters	447
No. of restraints	15
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, −0.15
Absolute structure	Flack x determined using 2270 quotients [$(I^+)-(I^-)$]/[$(I^+)+(I^-)$] (Parsons *et al.*, 2013).
Absolute structure parameter	−0.2 (4)

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014/7* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

yield 280 mg (90%) of the title compound. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.29 (*s*, 2H), 7.81 (*s*, 2H), 7.73 (*s*, 2H), 4.18 (*t*, J = 7.2 Hz, 4H), 3.88 (*s*, 6H), 1.74 (*m*, 4H), 1.17 (*m*, 16H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 173.5, 136.7, 123.6, 122.3, 48.8, 35.8, 29.4, 28.8, 28.7, 28.3, 25.4. IR (neat): ν 3351 *s*, 2919 *m*, 2855 *m*, 1651 *w*, 1588 *m*, 1473 *m*, 1394 *m*, 1163 *s*, 732 *m* cm^{-1}.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms bound to water molecules were found from difference maps and were included in the refinement with distance restraints of d(O—H) = 0.82 Å. Three reflections, (101), (202) and (505), were omitted because of poor agreement between calculated and observed intensities.

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full crystallographic data

IUCrData (2017). **2**, x171255 [https://doi.org/10.1107/S241431461701255X]

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Crystal data

$C_{20}H_{36}N_4{\cdot}C_2N_{10}{\cdot}7H_2O$
M_r = 622.76
Monoclinic, $P2_1$
a = 7.2847 (3) Å
b = 8.9932 (4) Å
c = 25.3962 (11) Å
β = 91.062 (1)°
V = 1663.49 (12) Å^3
Z = 2
$F(000)$ = 672
D_x = 1.243 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9972 reflections
θ = 2.4–25.6°
μ = 0.10 mm^{-1}
T = 183 K
Prism, colourless
0.17 × 0.12 × 0.08 mm

Data collection

Bruker D8 QUEST PHOTON 100 diffractometer
Radiation source: Incoatec Microfocus
Multi layered optics monochromator
Detector resolution: 10.4 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
T_{min} = 0.848, T_{max} = 0.888
29637 measured reflections
6171 independent reflections
5428 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 25.5°, θ_{min} = 2.4°
h = −8→8
k = −10→10
l = −30→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.081
S = 1.04
6171 reflections
447 parameters
15 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.1318P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Extinction correction: SHELXL-2014/7 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.026 (2)
Absolute structure: Flack x determined using 2270 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013).
Absolute structure parameter: −0.2 (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.

Refinement. Hydrogens at water molecules O1–O7 were found and refined with bond restraints (d=83 (2)pm).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.8692 (3)	0.4847 (2)	0.12571 (8)	0.0307 (5)
N2	0.8791 (3)	0.6275 (2)	0.11135 (8)	0.0373 (5)
N3	0.8434 (3)	0.7122 (2)	0.15240 (8)	0.0400 (5)
N4	0.8089 (3)	0.6279 (2)	0.19435 (8)	0.0340 (5)
N5	0.8068 (3)	0.3557 (2)	0.20434 (8)	0.0261 (4)
N6	0.7696 (3)	0.3769 (2)	0.25202 (7)	0.0263 (4)
N7	0.7674 (3)	0.1051 (2)	0.26322 (8)	0.0329 (5)
N8	0.7297 (3)	0.0225 (2)	0.30551 (8)	0.0378 (5)
N9	0.6900 (3)	0.1093 (2)	0.34584 (8)	0.0336 (5)
N10	0.7021 (3)	0.2510 (2)	0.33069 (7)	0.0292 (5)
N11	0.5418 (3)	1.5010 (2)	−0.02519 (7)	0.0305 (5)
N12	0.5847 (3)	1.4521 (2)	−0.10701 (8)	0.0348 (5)
N13	−0.1024 (3)	1.2390 (2)	0.58176 (7)	0.0290 (5)
N14	−0.1585 (3)	1.3001 (2)	0.66194 (7)	0.0307 (5)
C1	0.8260 (3)	0.4893 (3)	0.17634 (8)	0.0251 (5)
C2	0.7486 (3)	0.2445 (3)	0.28024 (8)	0.0241 (5)
C3	0.4658 (3)	1.5052 (3)	−0.07287 (9)	0.0349 (6)
H3	0.3458	1.5405	−0.0813	0.042*
C4	0.7151 (3)	1.4425 (3)	−0.02907 (10)	0.0353 (6)
H4	0.8004	1.4263	−0.0009	0.042*
C5	0.7411 (3)	1.4128 (3)	−0.07982 (10)	0.0380 (6)
H5	0.8490	1.3717	−0.0945	0.046*
C6	0.5567 (4)	1.4409 (4)	−0.16425 (10)	0.0505 (8)
H6A	0.4453	1.4954	−0.1747	0.076*
H6B	0.5433	1.3362	−0.1742	0.076*
H6C	0.6626	1.4837	−0.1820	0.076*
C7	0.4564 (4)	1.5521 (3)	0.02358 (10)	0.0381 (6)
H7A	0.3320	1.5906	0.0152	0.046*
H7B	0.5299	1.6347	0.0387	0.046*
C8	0.4423 (3)	1.4289 (3)	0.06399 (9)	0.0320 (6)
H8A	0.5644	1.3825	0.0694	0.038*
H8B	0.3569	1.3515	0.0506	0.038*
C9	0.3744 (3)	1.4871 (3)	0.11621 (9)	0.0338 (6)
H9A	0.4631	1.5613	0.1301	0.041*
H9B	0.2556	1.5384	0.1102	0.041*
C10	0.3493 (4)	1.3665 (3)	0.15710 (9)	0.0319 (6)
H10A	0.4637	1.3074	0.1600	0.038*
H10B	0.2498	1.2990	0.1450	0.038*

C11	0.3028 (3)	1.4261 (3)	0.21137 (9)	0.0311 (6)
H11A	0.1935	1.4910	0.2079	0.037*
H11B	0.4063	1.4883	0.2243	0.037*
C12	0.2647 (3)	1.3067 (3)	0.25226 (9)	0.0309 (5)
H12A	0.1618	1.2437	0.2394	0.037*
H12B	0.3744	1.2424	0.2563	0.037*
C13	0.2169 (3)	1.3705 (3)	0.30569 (9)	0.0313 (6)
H13A	0.3160	1.4393	0.3171	0.038*
H13B	0.1026	1.4294	0.3018	0.038*
C14	0.1903 (3)	1.2553 (3)	0.34859 (9)	0.0300 (5)
H14A	0.3072	1.2013	0.3546	0.036*
H14B	0.0971	1.1822	0.3365	0.036*
C15	0.1296 (3)	1.3233 (3)	0.40039 (9)	0.0303 (6)
H15A	0.2243	1.3950	0.4126	0.036*
H15B	0.0145	1.3795	0.3939	0.036*
C16	0.0977 (4)	1.2114 (3)	0.44382 (9)	0.0314 (6)
H16A	0.2131	1.1564	0.4511	0.038*
H16B	0.0039	1.1387	0.4318	0.038*
C17	0.0341 (3)	1.2848 (3)	0.49451 (9)	0.0311 (6)
H17A	0.1332	1.3493	0.5087	0.037*
H17B	−0.0740	1.3483	0.4866	0.037*
C18	−0.0161 (4)	1.1707 (3)	0.53555 (9)	0.0332 (6)
H18A	−0.1018	1.0974	0.5196	0.040*
H18B	0.0961	1.1169	0.5472	0.040*
C19	−0.0403 (3)	1.2306 (3)	0.63118 (9)	0.0319 (6)
H19	0.0699	1.1829	0.6426	0.038*
C20	−0.2646 (3)	1.3162 (3)	0.58112 (9)	0.0349 (6)
H20	−0.3385	1.3386	0.5509	0.042*
C21	−0.2997 (3)	1.3544 (3)	0.63103 (9)	0.0336 (6)
H21	−0.4030	1.4088	0.6428	0.040*
C22	−0.1416 (4)	1.3157 (4)	0.71928 (9)	0.0455 (7)
H22A	−0.0381	1.2557	0.7323	0.068*
H22B	−0.2549	1.2815	0.7356	0.068*
H22C	−0.1204	1.4204	0.7283	0.068*
O1	1.1165 (3)	0.2885 (3)	−0.01317 (9)	0.0604 (6)
H11O	1.119 (5)	0.234 (4)	−0.0413 (12)	0.081 (13)*
H12O	1.057 (6)	0.238 (6)	0.0114 (16)	0.13 (2)*
O2	0.9157 (3)	0.1993 (3)	0.07677 (9)	0.0511 (6)
H21O	0.900 (4)	0.283 (3)	0.0887 (12)	0.053 (10)*
H22O	0.950 (6)	0.140 (5)	0.1007 (15)	0.114 (19)*
O3	0.9542 (3)	0.0143 (2)	0.16588 (9)	0.0564 (6)
H31O	0.904 (5)	0.056 (5)	0.1916 (12)	0.090 (14)*
H32O	0.911 (6)	−0.073 (4)	0.1609 (18)	0.112 (17)*
O4	0.6059 (3)	−0.2736 (2)	0.28580 (8)	0.0447 (5)
H41O	0.656 (4)	−0.187 (3)	0.2911 (13)	0.060 (10)*
H42O	0.664 (4)	−0.308 (4)	0.2595 (10)	0.060 (10)*
O5	0.6601 (3)	−0.4551 (2)	0.37380 (8)	0.0422 (5)
H51O	0.624 (6)	−0.400 (4)	0.3475 (13)	0.095 (15)*

H52O	0.672 (4)	−0.539 (3)	0.3618 (13)	0.054 (10)*
O6	0.5478 (3)	−0.5538 (3)	0.47071 (8)	0.0532 (6)
H61O	0.564 (5)	−0.507 (4)	0.4400 (11)	0.075 (11)*
H62O	0.492 (5)	−0.493 (4)	0.4895 (13)	0.069 (11)*
O7	0.4008 (3)	−0.3607 (3)	0.54270 (8)	0.0468 (5)
H71O	0.431 (6)	−0.270 (3)	0.5374 (16)	0.091 (15)*
H72O	0.383 (5)	−0.379 (4)	0.5748 (10)	0.071 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0356 (11)	0.0304 (11)	0.0264 (10)	0.0008 (9)	0.0036 (8)	0.0002 (9)
N2	0.0483 (14)	0.0328 (13)	0.0310 (12)	0.0018 (10)	0.0074 (10)	0.0034 (10)
N3	0.0570 (14)	0.0296 (12)	0.0337 (12)	−0.0005 (10)	0.0102 (10)	0.0017 (10)
N4	0.0458 (13)	0.0280 (12)	0.0285 (11)	0.0005 (10)	0.0061 (9)	0.0009 (9)
N5	0.0272 (11)	0.0263 (11)	0.0249 (11)	0.0000 (8)	0.0023 (8)	−0.0034 (8)
N6	0.0249 (10)	0.0282 (10)	0.0258 (11)	0.0016 (8)	0.0012 (8)	−0.0014 (9)
N7	0.0431 (13)	0.0273 (11)	0.0284 (11)	−0.0015 (9)	0.0082 (9)	−0.0021 (9)
N8	0.0508 (13)	0.0284 (12)	0.0346 (12)	−0.0033 (10)	0.0087 (10)	−0.0013 (10)
N9	0.0404 (13)	0.0298 (12)	0.0308 (11)	−0.0021 (10)	0.0087 (9)	−0.0015 (9)
N10	0.0330 (11)	0.0275 (11)	0.0274 (10)	−0.0006 (9)	0.0048 (8)	−0.0024 (9)
N11	0.0325 (11)	0.0330 (12)	0.0261 (10)	0.0009 (9)	0.0051 (8)	0.0020 (9)
N12	0.0386 (12)	0.0405 (13)	0.0257 (10)	−0.0052 (10)	0.0059 (9)	0.0022 (10)
N13	0.0368 (11)	0.0258 (10)	0.0245 (10)	0.0034 (9)	0.0052 (8)	0.0009 (9)
N14	0.0346 (11)	0.0345 (11)	0.0231 (10)	−0.0019 (10)	0.0049 (8)	−0.0005 (9)
C1	0.0243 (12)	0.0254 (12)	0.0257 (12)	0.0012 (10)	0.0016 (9)	−0.0028 (10)
C2	0.0241 (12)	0.0244 (12)	0.0240 (11)	0.0008 (10)	0.0022 (9)	−0.0028 (10)
C3	0.0347 (14)	0.0412 (15)	0.0290 (13)	0.0039 (12)	0.0013 (11)	0.0046 (12)
C4	0.0285 (13)	0.0418 (15)	0.0357 (13)	−0.0005 (11)	0.0028 (10)	0.0046 (12)
C5	0.0319 (14)	0.0433 (15)	0.0393 (14)	−0.0016 (12)	0.0118 (11)	0.0033 (12)
C6	0.065 (2)	0.062 (2)	0.0253 (13)	−0.0115 (16)	0.0055 (13)	−0.0008 (13)
C7	0.0430 (15)	0.0424 (15)	0.0290 (14)	0.0076 (13)	0.0060 (11)	−0.0012 (12)
C8	0.0321 (14)	0.0374 (14)	0.0268 (12)	−0.0042 (11)	0.0024 (10)	−0.0016 (11)
C9	0.0314 (13)	0.0431 (15)	0.0269 (12)	0.0022 (12)	0.0026 (10)	−0.0026 (12)
C10	0.0294 (13)	0.0412 (15)	0.0251 (12)	−0.0046 (11)	0.0012 (10)	−0.0030 (11)
C11	0.0275 (12)	0.0411 (14)	0.0246 (12)	−0.0004 (11)	0.0022 (10)	−0.0036 (11)
C12	0.0272 (13)	0.0393 (14)	0.0265 (12)	−0.0009 (11)	0.0025 (9)	−0.0022 (11)
C13	0.0308 (13)	0.0380 (14)	0.0253 (12)	−0.0026 (11)	0.0041 (10)	−0.0032 (11)
C14	0.0263 (12)	0.0378 (14)	0.0260 (12)	0.0021 (10)	0.0030 (9)	0.0001 (11)
C15	0.0310 (13)	0.0354 (14)	0.0245 (12)	0.0024 (11)	0.0037 (10)	0.0003 (10)
C16	0.0340 (14)	0.0326 (14)	0.0277 (13)	0.0054 (11)	0.0061 (10)	0.0002 (11)
C17	0.0375 (14)	0.0283 (12)	0.0279 (12)	0.0033 (11)	0.0050 (10)	0.0029 (11)
C18	0.0447 (15)	0.0281 (13)	0.0270 (13)	0.0069 (11)	0.0078 (11)	0.0012 (11)
C19	0.0357 (14)	0.0333 (13)	0.0270 (13)	0.0020 (11)	0.0036 (10)	0.0047 (11)
C20	0.0359 (14)	0.0392 (14)	0.0296 (13)	0.0070 (12)	0.0008 (10)	0.0052 (11)
C21	0.0343 (14)	0.0346 (13)	0.0322 (13)	0.0050 (11)	0.0074 (10)	0.0010 (11)
C22	0.0520 (17)	0.0611 (19)	0.0234 (13)	−0.0051 (15)	0.0041 (11)	−0.0045 (13)
O1	0.0662 (15)	0.0664 (15)	0.0485 (13)	−0.0007 (13)	−0.0049 (11)	−0.0205 (13)

O2	0.0565 (13)	0.0432 (13)	0.0536 (14)	0.0068 (11)	−0.0016 (11)	−0.0204 (12)
O3	0.0778 (15)	0.0367 (12)	0.0560 (13)	−0.0055 (11)	0.0364 (12)	−0.0107 (11)
O4	0.0577 (13)	0.0309 (11)	0.0463 (12)	−0.0036 (10)	0.0217 (10)	−0.0080 (9)
O5	0.0539 (12)	0.0330 (11)	0.0397 (11)	−0.0008 (10)	0.0039 (9)	−0.0105 (10)
O6	0.0789 (16)	0.0460 (13)	0.0349 (11)	0.0130 (11)	0.0050 (10)	−0.0038 (10)
O7	0.0619 (13)	0.0476 (13)	0.0312 (11)	0.0055 (10)	0.0102 (9)	−0.0005 (10)

Geometric parameters (Å, º)

N1—C1	1.330 (3)	C11—C12	1.523 (3)
N1—N2	1.337 (3)	C11—H11A	0.9900
N2—N3	1.321 (3)	C11—H11B	0.9900
N3—N4	1.335 (3)	C12—C13	1.520 (3)
N4—C1	1.334 (3)	C12—H12A	0.9900
N5—N6	1.260 (3)	C12—H12B	0.9900
N5—C1	1.405 (3)	C13—C14	1.518 (3)
N6—C2	1.399 (3)	C13—H13A	0.9900
N7—C2	1.335 (3)	C13—H13B	0.9900
N7—N8	1.338 (3)	C14—C15	1.524 (3)
N8—N9	1.324 (3)	C14—H14A	0.9900
N9—N10	1.335 (3)	C14—H14B	0.9900
N10—C2	1.333 (3)	C15—C16	1.514 (3)
N11—C3	1.323 (3)	C15—H15A	0.9900
N11—C4	1.373 (3)	C15—H15B	0.9900
N11—C7	1.470 (3)	C16—C17	1.526 (3)
N12—C3	1.326 (3)	C16—H16A	0.9900
N12—C5	1.368 (3)	C16—H16B	0.9900
N12—C6	1.468 (3)	C17—C18	1.512 (3)
N13—C19	1.329 (3)	C17—H17A	0.9900
N13—C20	1.370 (3)	C17—H17B	0.9900
N13—C18	1.475 (3)	C18—H18A	0.9900
N14—C19	1.330 (3)	C18—H18B	0.9900
N14—C21	1.372 (3)	C19—H19	0.9500
N14—C22	1.466 (3)	C20—C21	1.342 (3)
C3—H3	0.9500	C20—H20	0.9500
C4—C5	1.333 (3)	C21—H21	0.9500
C4—H4	0.9500	C22—H22A	0.9800
C5—H5	0.9500	C22—H22B	0.9800
C6—H6A	0.9800	C22—H22C	0.9800
C6—H6B	0.9800	O1—H11O	0.87 (2)
C6—H6C	0.9800	O1—H12O	0.89 (3)
C7—C8	1.515 (4)	O2—H21O	0.82 (2)
C7—H7A	0.9900	O2—H22O	0.84 (3)
C7—H7B	0.9900	O3—H31O	0.84 (2)
C8—C9	1.517 (3)	O3—H32O	0.85 (3)
C8—H8A	0.9900	O4—H41O	0.87 (2)
C8—H8B	0.9900	O4—H42O	0.85 (2)
C9—C10	1.515 (4)	O5—H51O	0.87 (2)

C9—H9A	0.9900	O5—H52O	0.82 (2)
C9—H9B	0.9900	O6—H61O	0.90 (2)
C10—C11	1.522 (3)	O6—H62O	0.84 (2)
C10—H10A	0.9900	O7—H71O	0.86 (3)
C10—H10B	0.9900	O7—H72O	0.84 (2)

C1—N1—N2	104.39 (19)	C12—C11—H11A	108.6
N3—N2—N1	109.03 (19)	C10—C11—H11B	108.6
N2—N3—N4	110.2 (2)	C12—C11—H11B	108.6
C1—N4—N3	103.69 (19)	H11A—C11—H11B	107.6
N6—N5—C1	112.44 (18)	C13—C12—C11	113.0 (2)
N5—N6—C2	112.98 (18)	C13—C12—H12A	109.0
C2—N7—N8	103.75 (19)	C11—C12—H12A	109.0
N9—N8—N7	110.2 (2)	C13—C12—H12B	109.0
N8—N9—N10	108.86 (19)	C11—C12—H12B	109.0
C2—N10—N9	104.76 (18)	H12A—C12—H12B	107.8
C3—N11—C4	108.4 (2)	C14—C13—C12	114.7 (2)
C3—N11—C7	125.9 (2)	C14—C13—H13A	108.6
C4—N11—C7	125.75 (19)	C12—C13—H13A	108.6
C3—N12—C5	108.1 (2)	C14—C13—H13B	108.6
C3—N12—C6	126.3 (2)	C12—C13—H13B	108.6
C5—N12—C6	125.6 (2)	H13A—C13—H13B	107.6
C19—N13—C20	108.58 (19)	C13—C14—C15	112.9 (2)
C19—N13—C18	125.8 (2)	C13—C14—H14A	109.0
C20—N13—C18	125.6 (2)	C15—C14—H14A	109.0
C19—N14—C21	108.55 (19)	C13—C14—H14B	109.0
C19—N14—C22	125.8 (2)	C15—C14—H14B	109.0
C21—N14—C22	125.6 (2)	H14A—C14—H14B	107.8
N1—C1—N4	112.7 (2)	C16—C15—C14	114.4 (2)
N1—C1—N5	119.4 (2)	C16—C15—H15A	108.7
N4—C1—N5	127.95 (19)	C14—C15—H15A	108.7
N10—C2—N7	112.4 (2)	C16—C15—H15B	108.7
N10—C2—N6	119.17 (19)	C14—C15—H15B	108.7
N7—C2—N6	128.38 (19)	H15A—C15—H15B	107.6
N11—C3—N12	108.7 (2)	C15—C16—C17	112.3 (2)
N11—C3—H3	125.6	C15—C16—H16A	109.1
N12—C3—H3	125.6	C17—C16—H16A	109.1
C5—C4—N11	107.1 (2)	C15—C16—H16B	109.1
C5—C4—H4	126.5	C17—C16—H16B	109.1
N11—C4—H4	126.5	H16A—C16—H16B	107.9
C4—C5—N12	107.7 (2)	C18—C17—C16	111.7 (2)
C4—C5—H5	126.2	C18—C17—H17A	109.3
N12—C5—H5	126.2	C16—C17—H17A	109.3
N12—C6—H6A	109.5	C18—C17—H17B	109.3
N12—C6—H6B	109.5	C16—C17—H17B	109.3
H6A—C6—H6B	109.5	H17A—C17—H17B	107.9
N12—C6—H6C	109.5	N13—C18—C17	112.2 (2)
H6A—C6—H6C	109.5	N13—C18—H18A	109.2

H6B—C6—H6C	109.5	C17—C18—H18A	109.2
N11—C7—C8	112.2 (2)	N13—C18—H18B	109.2
N11—C7—H7A	109.2	C17—C18—H18B	109.2
C8—C7—H7A	109.2	H18A—C18—H18B	107.9
N11—C7—H7B	109.2	N13—C19—N14	108.4 (2)
C8—C7—H7B	109.2	N13—C19—H19	125.8
H7A—C7—H7B	107.9	N14—C19—H19	125.8
C7—C8—C9	111.5 (2)	C21—C20—N13	107.3 (2)
C7—C8—H8A	109.3	C21—C20—H20	126.3
C9—C8—H8A	109.3	N13—C20—H20	126.3
C7—C8—H8B	109.3	C20—C21—N14	107.2 (2)
C9—C8—H8B	109.3	C20—C21—H21	126.4
H8A—C8—H8B	108.0	N14—C21—H21	126.4
C10—C9—C8	113.4 (2)	N14—C22—H22A	109.5
C10—C9—H9A	108.9	N14—C22—H22B	109.5
C8—C9—H9A	108.9	H22A—C22—H22B	109.5
C10—C9—H9B	108.9	N14—C22—H22C	109.5
C8—C9—H9B	108.9	H22A—C22—H22C	109.5
H9A—C9—H9B	107.7	H22B—C22—H22C	109.5
C9—C10—C11	113.6 (2)	H11O—O1—H12O	108 (4)
C9—C10—H10A	108.8	H21O—O2—H22O	111 (4)
C11—C10—H10A	108.8	H31O—O3—H32O	111 (4)
C9—C10—H10B	108.8	H41O—O4—H42O	103 (3)
C11—C10—H10B	108.8	H51O—O5—H52O	106 (4)
H10A—C10—H10B	107.7	H61O—O6—H62O	105 (3)
C10—C11—C12	114.6 (2)	H71O—O7—H72O	113 (4)
C10—C11—H11A	108.6		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H11*O*···N2^{i}	0.87 (3)	2.02 (3)	2.884 (3)	174 (3)
O1—H12*O*···O2	0.89 (5)	2.00 (4)	2.850 (3)	159 (4)
O2—H22*O*···O3	0.84 (4)	2.00 (4)	2.819 (3)	162 (4)
O2—H21*O*···N1	0.82 (3)	2.06 (3)	2.875 (3)	174 (3)
O3—H32*O*···N3^{ii}	0.85 (4)	2.00 (4)	2.853 (3)	172 (4)
O3—H31*O*···N7	0.84 (4)	2.14 (3)	2.959 (3)	165 (4)
O4—H42*O*···N4^{ii}	0.86 (3)	2.06 (3)	2.914 (3)	175 (3)
O4—H41*O*···N8	0.87 (3)	1.99 (3)	2.853 (3)	171 (3)
O5—H52*O*···N10^{ii}	0.82 (3)	2.06 (3)	2.879 (3)	179 (3)
O5—H51*O*···O4	0.87 (3)	1.94 (3)	2.790 (3)	166 (4)
O6—H61*O*···O5	0.90 (3)	1.89 (3)	2.755 (3)	161 (3)
O6—H62*O*···O7	0.84 (4)	1.93 (3)	2.753 (3)	169 (3)
O7—H71*O*···O6^{iii}	0.86 (3)	1.96 (3)	2.807 (4)	169 (4)
O7—H72*O*···N9^{iv}	0.84 (3)	2.10 (3)	2.931 (3)	170 (3)

Symmetry codes: (i) −*x*+2, *y*−1/2, −*z*; (ii) *x*, *y*−1, *z*; (iii) −*x*+1, *y*+1/2, −*z*+1; (iv) −*x*+1, *y*−1/2, −*z*+1.