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Poly[[tetramethanolbis[4-oxo-3-(pyridin-4-yl)-1-(2,4,6-trichlorophenyl)-4,5-dihydro-1*H*-pyrazolo-[3,4-*d*]pyrimidin-6-olato]disodium]–diethyl ether–methanol (1/1/2)]

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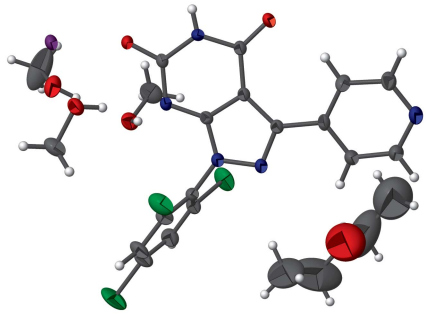
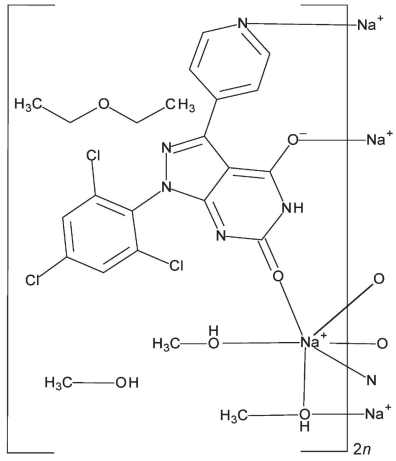
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $[Na_2(C_{16}H_7Cl_3N_5O_2)_2(CH_3OH)_4]\cdot C_4H_{10}O\cdot 2CH_3OH$, the central pyrazolo[3,4-*d*]pyrimidine system makes dihedral angles of 82.98 (7)° with the trichlorophenyl ring and 13.11 (15)° with the pyridine ring. The sodium ion has an octahedral environment, being coordinated by four methanol molecules and one O and one N atom of two different heterocyclic ring systems.

3D view



Chemical scheme



Structure description

In the framework of investigating the efficiency of 4-(4-fluorophenyl)-3-(pyridin-4-yl)-1-(aryl)-1*H*-pyrazol-5-amines as inhibitors for kinases relevant to cancer, many derivatives of this compound have been synthesized (Abu Thaher, Arnsmann *et al.*, 2012). Recently, we have reported the crystal structures of several amino pyrazoles (Abu Thaher, Koch *et al.*, 2012*a*,*b*,*c*,*d*,*e*). Finally, in our approach of synthesizing new derivatives, we managed to prepare crystals of the title compound (Fig. 1). It crystallizes with three methanol molecules which have quite different functions in the crystal structure – only two coordinate to the sodium cation and the third one does not. However, all three are involved hydrogen bonds to the pyrazolo[3,4-*d*]pyrimidine system (see Table 1). The sodium cation is surrounded by by four methanol O atoms and one O and one N atom of two different heterocyclic ring systems. The position of the negative charge could not be determined, and we assum that it is delocalized over the pyrazolo[3,4-*d*]pyrimidine system. The dihedral angle between the pyrazolo[3,4-*d*]pyrimidine ring system and the pyridine ring is 13.11 (15)°, smaller than that subtended to the trichlorophenyl plane

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···O14^{i}	0.81 (3)	1.99 (3)	2.771 (3)	160 (3)
C21—H21···O15	0.95	2.29	3.096 (3)	142
O1L—H1L···N2	0.86 (4)	2.21 (4)	3.062 (3)	172 (3)
O2L—H2L···N2	0.78 (4)	2.06 (4)	2.815 (3)	163 (4)
O3L—H3L···O2L	0.84 (4)	1.94 (4)	2.783 (3)	176 (4)

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

[82.98 (7)°]. One diethyl ether solvent molecule is disordered about the twofold rotation axis and fills a channel parallel to the b axis.

Synthesis and crystallization

2 mmol of *N*-(2,4,6-trichlorophenyl)-4-pyridinecarbohydrazonoyl chloride and 1.5 equiv. of ethyl (2-cyanoacetyl)carbamate were dissolved in 20 ml dry ethanol and cooled to 273 K in an ice bath. 2.0 equiv. of sodium ethoxide solution (21% ethanol) was added dropwise and the reaction was stirred overnight. The precipitate was filtered from the reaction mixture, washed with water and then with diethyl ether. Yield: 30%. Suitable crystals for X-ray analysis were obtained by slow evaporation of a methanol/diethyl ether solution.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. One molecule of ether is disordered about the twofold rotation axis. Consequently, the site occupation factors of all ether atoms were set to 0.5 and the displacement parameters were fixed to an isotropic behaviour.

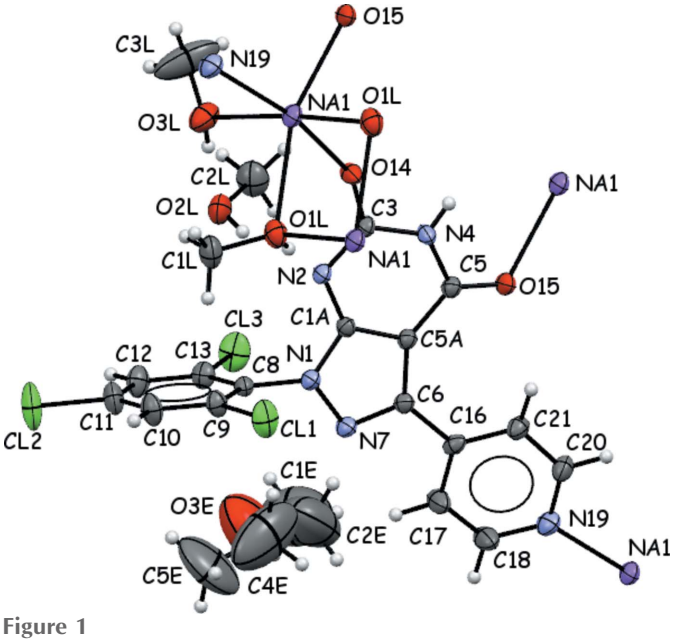


Figure 1
The molecular structure of the title compound, with the atom labelling and displacement ellipsoids drawn at the 50% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Na_2(C_{16}H_7Cl_3N_5O_2)_2(CH_4O)_4]\cdot C_4H_{10}O\cdot 2CH_4O$
M_r	1127.58
Crystal system, space group	Monoclinic, $P2/n$
Temperature (K)	173
a, b, c (Å)	11.1721 (7), 8.1249 (5), 28.8799 (18)
β (°)	100.213 (1)
V (Å^3)	2580.0 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.42
Crystal size (mm)	0.56 × 0.32 × 0.19
Data collection	
Diffractometer	Bruker SMART APEXII
Absorption correction	Multi-scan (*SADABS*; Bruker, 2000)
T_{min}, T_{max}	0.659, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27638, 6097, 5149
R_{int}	0.032
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.657
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.055, 0.131, 1.15
No. of reflections	6097
No. of parameters	357
No. of restraints	34
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.43, −0.40

Computer programs: *APEX2* and *SAINT* (Bruker, 2005), *SIR97* (Altomare *et al.*, 1995), *SHELXL2014* (Sheldrick, 2015).

The C—C distances in the ether molecule were restrained to 1.54 (2) Å, the C—O distances to 1.46 (2) Å.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161081 [https://doi.org/10.1107/S2414314616010816]

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Crystal data

$[Na_2(C_{16}H_7Cl_3N_5O_2)_2(CH_4O)_4]\cdot C_4H_{10}O\cdot 2CH_4O$
M_r = 1127.58
Monoclinic, $P2/n$
a = 11.1721 (7) Å
b = 8.1249 (5) Å
c = 28.8799 (18) Å
β = 100.213 (1)°
V = 2580.0 (3) Å^3
Z = 2
$F(000)$ = 1164
D_x = 1.451 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7933 reflections
θ = 2.5–27.3°
μ = 0.42 mm^{-1}
T = 173 K
Plate, colourless
0.56 × 0.32 × 0.19 mm

Data collection

Bruker SMART APEXII diffractometer
Radiation source: sealed Tube
Graphite monochromator
CCD scan
Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.659, T_{max} = 0.746
27638 measured reflections
6097 independent reflections
5149 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 27.8°, θ_{min} = 1.9°
h = −14→14
k = −10→10
l = −37→36

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.131
S = 1.15
6097 reflections
357 parameters
34 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 4.0979P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	0.45803 (8)	1.01629 (9)	0.10052 (3)	0.0431 (2)	
Cl2	0.40976 (11)	1.11088 (12)	0.27980 (3)	0.0642 (3)	
Cl3	0.37696 (9)	0.50085 (9)	0.20830 (3)	0.0475 (2)	
Na1	−0.11263 (9)	0.89845 (12)	0.03200 (3)	0.0254 (2)	
N1	0.42042 (17)	0.6597 (2)	0.11953 (7)	0.0220 (4)	
C1A	0.3251 (2)	0.6160 (3)	0.08581 (8)	0.0191 (4)	
N2	0.21387 (17)	0.6884 (2)	0.08078 (7)	0.0206 (4)	
C3	0.1322 (2)	0.6233 (3)	0.04576 (8)	0.0216 (5)	
N4	0.16419 (18)	0.4928 (3)	0.01943 (7)	0.0238 (4)	
H4	0.109 (3)	0.463 (4)	−0.0010 (11)	0.029*	
C5	0.2751 (2)	0.4123 (3)	0.02483 (8)	0.0206 (5)	
C5A	0.3650 (2)	0.4882 (3)	0.06008 (8)	0.0193 (4)	
C6	0.4902 (2)	0.4656 (3)	0.08111 (8)	0.0203 (5)	
N7	0.52267 (18)	0.5672 (2)	0.11695 (7)	0.0230 (4)	
C8	0.4183 (2)	0.7679 (3)	0.15784 (8)	0.0204 (5)	
C9	0.4335 (2)	0.9364 (3)	0.15336 (8)	0.0261 (5)	
C10	0.4302 (3)	1.0434 (3)	0.19022 (10)	0.0347 (6)	
H10	0.4397	1.1585	0.1865	0.042*	
C11	0.4126 (3)	0.9778 (4)	0.23280 (10)	0.0372 (7)	
C12	0.3975 (3)	0.8119 (4)	0.23925 (9)	0.0347 (6)	
H12	0.3860	0.7694	0.2688	0.042*	
C13	0.3998 (2)	0.7089 (3)	0.20122 (9)	0.0271 (5)	
O14	0.02442 (15)	0.6747 (2)	0.03630 (7)	0.0294 (4)	
O15	0.28421 (15)	0.2879 (2)	0.00110 (6)	0.0275 (4)	
C16	0.5838 (2)	0.3550 (3)	0.06783 (9)	0.0221 (5)	
C17	0.6945 (2)	0.3344 (4)	0.09772 (11)	0.0374 (7)	
H17	0.7116	0.3935	0.1265	0.045*	
C18	0.7793 (3)	0.2279 (4)	0.08534 (12)	0.0415 (7)	
H18	0.8541	0.2149	0.1066	0.050*	
N19	0.7630 (2)	0.1411 (3)	0.04513 (8)	0.0315 (5)	
C20	0.6562 (2)	0.1618 (3)	0.01668 (9)	0.0293 (6)	
H20	0.6415	0.1018	−0.0120	0.035*	
C21	0.5649 (2)	0.2660 (3)	0.02643 (9)	0.0259 (5)	
H21	0.4905	0.2757	0.0048	0.031*	
O1L	0.10188 (18)	1.0229 (2)	0.04918 (7)	0.0316 (4)	
H1L	0.140 (3)	0.933 (5)	0.0582 (12)	0.047*	
C1L	0.1214 (3)	1.1374 (4)	0.08720 (10)	0.0411 (7)	
H1L1	0.2081	1.1643	0.0950	0.062*	
H1L2	0.0947	1.0887	0.1147	0.062*	

H1L3	0.0748	1.2380	0.0780	0.062*	
O2L	0.08388 (19)	0.6785 (3)	0.15581 (7)	0.0356 (5)	
H2L	0.127 (3)	0.697 (5)	0.1379 (14)	0.053*	
C2L	0.0432 (4)	0.5118 (4)	0.15216 (13)	0.0524 (8)	
H2L1	0.1136	0.4382	0.1550	0.079*	
H2L2	−0.0095	0.4948	0.1216	0.079*	
H2L3	−0.0024	0.4880	0.1774	0.079*	
O3L	−0.1123 (2)	0.8688 (3)	0.11335 (8)	0.0422 (5)	
H3L	−0.051 (4)	0.815 (5)	0.1263 (14)	0.063*	
C3L	−0.2187 (4)	0.8095 (8)	0.1267 (2)	0.113 (2)	
H3L1	−0.2072	0.8028	0.1611	0.170*	
H3L2	−0.2862	0.8842	0.1151	0.170*	
H3L3	−0.2371	0.6998	0.1132	0.170*	
C1E	0.758 (3)	0.042 (3)	0.2224 (9)	0.216 (12)	0.5
H1E1	0.7528	−0.0644	0.2377	0.324*	0.5
H1E2	0.6874	0.0568	0.1973	0.324*	0.5
H1E3	0.8327	0.0470	0.2090	0.324*	0.5
C2E	0.760 (4)	0.180 (3)	0.2586 (10)	0.205 (14)	0.5
H2E1	0.6850	0.1772	0.2724	0.246*	0.5
H2E2	0.8311	0.1674	0.2843	0.246*	0.5
O3E	0.768 (2)	0.331 (2)	0.2334 (5)	0.185 (8)	0.5
C4E	0.762 (3)	0.459 (3)	0.2683 (7)	0.198 (13)	0.5
H4E1	0.7028	0.4289	0.2888	0.238*	0.5
H4E2	0.8426	0.4763	0.2882	0.238*	0.5
C5E	0.723 (2)	0.603 (2)	0.2411 (7)	0.159 (9)	0.5
H5E1	0.7165	0.6952	0.2623	0.239*	0.5
H5E2	0.7820	0.6289	0.2209	0.239*	0.5
H5E3	0.6432	0.5819	0.2216	0.239*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0704 (5)	0.0314 (4)	0.0307 (4)	−0.0097 (3)	0.0179 (3)	0.0028 (3)
Cl2	0.1083 (8)	0.0513 (5)	0.0354 (4)	0.0011 (5)	0.0191 (5)	−0.0229 (4)
Cl3	0.0732 (6)	0.0238 (3)	0.0498 (5)	0.0001 (3)	0.0227 (4)	0.0082 (3)
Na1	0.0244 (5)	0.0230 (5)	0.0289 (5)	0.0052 (4)	0.0045 (4)	−0.0061 (4)
N1	0.0189 (9)	0.0217 (10)	0.0251 (10)	0.0020 (8)	0.0034 (8)	−0.0043 (8)
C1A	0.0202 (11)	0.0167 (10)	0.0208 (11)	−0.0012 (8)	0.0047 (9)	−0.0015 (9)
N2	0.0189 (9)	0.0202 (9)	0.0223 (10)	0.0037 (8)	0.0026 (8)	−0.0045 (8)
C3	0.0219 (11)	0.0190 (11)	0.0236 (12)	0.0037 (9)	0.0033 (9)	−0.0032 (9)
N4	0.0196 (10)	0.0241 (10)	0.0254 (10)	0.0034 (8)	−0.0025 (8)	−0.0099 (9)
C5	0.0206 (11)	0.0180 (11)	0.0235 (11)	0.0018 (9)	0.0044 (9)	−0.0010 (9)
C5A	0.0186 (10)	0.0170 (10)	0.0226 (11)	0.0011 (8)	0.0045 (8)	−0.0014 (9)
C6	0.0193 (11)	0.0180 (11)	0.0236 (11)	0.0002 (9)	0.0042 (9)	−0.0011 (9)
N7	0.0186 (9)	0.0211 (10)	0.0289 (11)	0.0027 (8)	0.0032 (8)	−0.0048 (8)
C8	0.0187 (11)	0.0216 (11)	0.0204 (11)	0.0010 (9)	0.0023 (9)	−0.0036 (9)
C9	0.0342 (14)	0.0253 (12)	0.0191 (12)	−0.0028 (10)	0.0057 (10)	0.0002 (10)
C10	0.0518 (17)	0.0200 (12)	0.0325 (14)	−0.0027 (12)	0.0081 (13)	−0.0063 (11)

C11	0.0507 (17)	0.0351 (15)	0.0253 (13)	0.0015 (13)	0.0057 (12)	−0.0113 (12)
C12	0.0465 (16)	0.0362 (15)	0.0220 (13)	0.0052 (13)	0.0078 (12)	0.0017 (11)
C13	0.0333 (13)	0.0202 (11)	0.0281 (13)	0.0025 (10)	0.0065 (10)	0.0022 (10)
O14	0.0208 (8)	0.0265 (9)	0.0372 (10)	0.0083 (7)	−0.0047 (7)	−0.0123 (8)
O15	0.0225 (8)	0.0242 (9)	0.0352 (10)	0.0034 (7)	0.0035 (7)	−0.0120 (8)
C16	0.0192 (11)	0.0164 (10)	0.0320 (13)	0.0017 (9)	0.0084 (9)	0.0003 (9)
C17	0.0273 (13)	0.0352 (15)	0.0457 (17)	0.0082 (12)	−0.0044 (12)	−0.0184 (13)
C18	0.0261 (13)	0.0410 (16)	0.0532 (19)	0.0092 (12)	−0.0049 (13)	−0.0205 (15)
N19	0.0251 (11)	0.0292 (11)	0.0404 (13)	0.0061 (9)	0.0065 (10)	−0.0066 (10)
C20	0.0319 (13)	0.0331 (14)	0.0243 (12)	0.0083 (11)	0.0089 (10)	−0.0017 (11)
C21	0.0246 (12)	0.0322 (13)	0.0214 (12)	0.0055 (10)	0.0049 (9)	0.0019 (10)
O1L	0.0381 (11)	0.0242 (9)	0.0316 (10)	0.0037 (8)	0.0043 (8)	−0.0045 (8)
C1L	0.0551 (19)	0.0356 (16)	0.0342 (15)	−0.0047 (14)	0.0124 (14)	−0.0105 (13)
O2L	0.0424 (12)	0.0380 (11)	0.0276 (10)	0.0035 (9)	0.0094 (8)	−0.0040 (9)
C2L	0.064 (2)	0.0436 (19)	0.052 (2)	−0.0085 (17)	0.0164 (17)	−0.0005 (16)
O3L	0.0369 (11)	0.0505 (13)	0.0408 (12)	0.0119 (10)	0.0113 (9)	0.0069 (10)
C3L	0.063 (3)	0.145 (5)	0.145 (5)	0.033 (3)	0.055 (3)	0.088 (5)
C1E	0.17 (2)	0.22 (3)	0.26 (3)	0.01 (2)	0.03 (2)	−0.01 (2)
C2E	0.15 (2)	0.31 (3)	0.15 (3)	0.10 (3)	0.03 (2)	0.05 (3)
O3E	0.231 (19)	0.198 (14)	0.110 (12)	0.043 (14)	−0.016 (13)	0.000 (11)
C4E	0.19 (2)	0.29 (3)	0.136 (18)	−0.09 (2)	0.087 (19)	−0.09 (2)
C5E	0.18 (2)	0.178 (17)	0.086 (15)	0.044 (16)	−0.062 (11)	−0.011 (12)

Geometric parameters (Å, º)

Cl1—C9	1.724 (3)	C18—N19	1.343 (4)
Cl2—C11	1.740 (3)	C18—H18	0.9500
Cl3—C13	1.727 (3)	N19—C20	1.334 (3)
Na1—O3L	2.361 (2)	N19—Na1^{iv}	2.479 (2)
Na1—O14	2.3660 (19)	C20—C21	1.392 (3)
Na1—O1L^{i}	2.453 (2)	C20—H20	0.9500
Na1—N19^{ii}	2.479 (2)	C21—H21	0.9500
Na1—O15^{iii}	2.496 (2)	O1L—C1L	1.426 (3)
Na1—O1L	2.567 (2)	O1L—Na1^{i}	2.453 (2)
Na1—Na1^{i}	3.758 (2)	O1L—H1L	0.86 (4)
N1—C1A	1.357 (3)	C1L—H1L1	0.9800
N1—N7	1.380 (3)	C1L—H1L2	0.9800
N1—C8	1.417 (3)	C1L—H1L3	0.9800
C1A—N2	1.359 (3)	O2L—C2L	1.426 (4)
C1A—C5A	1.396 (3)	O2L—H2L	0.78 (4)
N2—C3	1.345 (3)	C2L—H2L1	0.9800
C3—O14	1.258 (3)	C2L—H2L2	0.9800
C3—N4	1.387 (3)	C2L—H2L3	0.9800
N4—C5	1.386 (3)	O3L—C3L	1.398 (5)
N4—H4	0.81 (3)	O3L—H3L	0.84 (4)
C5—O15	1.236 (3)	C3L—H3L1	0.9800
C5—C5A	1.436 (3)	C3L—H3L2	0.9800
C5A—C6	1.434 (3)	C3L—H3L3	0.9800

C6—N7	1.323 (3)	C1E—C2E	1.525 (18)
C6—C16	1.480 (3)	C1E—H1E1	0.9800
C8—C9	1.388 (3)	C1E—H1E2	0.9800
C8—C13	1.391 (3)	C1E—H1E3	0.9800
C9—C10	1.380 (4)	C2E—O3E	1.437 (18)
C10—C11	1.386 (4)	C2E—H2E1	0.9900
C10—H10	0.9500	C2E—H2E2	0.9900
C11—C12	1.375 (4)	O3E—C4E	1.458 (15)
C12—C13	1.384 (4)	C4E—C5E	1.433 (17)
C12—H12	0.9500	C4E—H4E1	0.9900
O15—Na1^{iii}	2.496 (2)	C4E—H4E2	0.9900
C16—C21	1.381 (3)	C5E—H5E1	0.9800
C16—C17	1.387 (4)	C5E—H5E2	0.9800
C17—C18	1.377 (4)	C5E—H5E3	0.9800
C17—H17	0.9500		

O3L—Na1—O14	89.01 (8)	C18—C17—H17	120.2
O3L—Na1—O1L^{i}	170.31 (9)	C16—C17—H17	120.2
O14—Na1—O1L^{i}	96.29 (7)	N19—C18—C17	124.1 (3)
O3L—Na1—N19^{ii}	80.25 (8)	N19—C18—H18	118.0
O14—Na1—N19^{ii}	167.94 (8)	C17—C18—H18	118.0
O1L^{i}—Na1—N19^{ii}	93.60 (8)	C20—N19—C18	115.8 (2)
O3L—Na1—O15^{iii}	100.64 (8)	C20—N19—Na1^{iv}	118.07 (17)
O14—Na1—O15^{iii}	89.99 (7)	C18—N19—Na1^{iv}	123.76 (18)
O1L^{i}—Na1—O15^{iii}	87.50 (7)	N19—C20—C21	124.0 (2)
N19^{ii}—Na1—O15^{iii}	97.33 (7)	N19—C20—H20	118.0
O3L—Na1—O1L	90.65 (8)	C21—C20—H20	118.0
O14—Na1—O1L	73.70 (7)	C16—C21—C20	119.2 (2)
O1L^{i}—Na1—O1L	83.11 (7)	C16—C21—H21	120.4
N19^{ii}—Na1—O1L	100.76 (8)	C20—C21—H21	120.4
O15^{iii}—Na1—O1L	160.08 (7)	C1L—O1L—Na1^{i}	122.62 (17)
O3L—Na1—Na1^{i}	130.64 (7)	C1L—O1L—Na1	114.57 (17)
O14—Na1—Na1^{i}	83.09 (6)	Na1^{i}—O1L—Na1	96.90 (7)
O1L^{i}—Na1—Na1^{i}	42.70 (5)	C1L—O1L—H1L	109 (2)
N19^{ii}—Na1—Na1^{i}	99.70 (7)	Na1^{i}—O1L—H1L	114 (2)
O15^{iii}—Na1—Na1^{i}	127.87 (6)	Na1—O1L—H1L	97 (2)
O1L—Na1—Na1^{i}	40.40 (5)	O1L—C1L—H1L1	109.5
C1A—N1—N7	111.75 (19)	O1L—C1L—H1L2	109.5
C1A—N1—C8	127.10 (19)	H1L1—C1L—H1L2	109.5
N7—N1—C8	120.57 (19)	O1L—C1L—H1L3	109.5
N1—C1A—N2	123.3 (2)	H1L1—C1L—H1L3	109.5
N1—C1A—C5A	107.0 (2)	H1L2—C1L—H1L3	109.5
N2—C1A—C5A	129.6 (2)	C2L—O2L—H2L	111 (3)
C3—N2—C1A	113.27 (19)	O2L—C2L—H2L1	109.5
O14—C3—N2	121.9 (2)	O2L—C2L—H2L2	109.5
O14—C3—N4	117.6 (2)	H2L1—C2L—H2L2	109.5
N2—C3—N4	120.5 (2)	O2L—C2L—H2L3	109.5
C5—N4—C3	127.6 (2)	H2L1—C2L—H2L3	109.5

C5—N4—H4	120 (2)	H2L2—C2L—H2L3	109.5
C3—N4—H4	113 (2)	C3L—O3L—Na1	117.3 (3)
O15—C5—N4	118.9 (2)	C3L—O3L—H3L	111 (3)
O15—C5—C5A	128.9 (2)	Na1—O3L—H3L	111 (3)
N4—C5—C5A	112.1 (2)	O3L—C3L—H3L1	109.5
C1A—C5A—C6	104.4 (2)	O3L—C3L—H3L2	109.5
C1A—C5A—C5	116.6 (2)	H3L1—C3L—H3L2	109.5
C6—C5A—C5	138.8 (2)	O3L—C3L—H3L3	109.5
N7—C6—C5A	111.3 (2)	H3L1—C3L—H3L3	109.5
N7—C6—C16	118.3 (2)	H3L2—C3L—H3L3	109.5
C5A—C6—C16	130.4 (2)	C2E—C1E—H1E1	109.5
C6—N7—N1	105.50 (18)	C2E—C1E—H1E2	109.5
C9—C8—C13	117.6 (2)	H1E1—C1E—H1E2	109.5
C9—C8—N1	121.3 (2)	C2E—C1E—H1E3	109.5
C13—C8—N1	121.0 (2)	H1E1—C1E—H1E3	109.5
C10—C9—C8	121.9 (2)	H1E2—C1E—H1E3	109.5
C10—C9—Cl1	118.4 (2)	O3E—C2E—C1E	106 (2)
C8—C9—Cl1	119.67 (19)	O3E—C2E—H2E1	110.6
C9—C10—C11	118.0 (2)	C1E—C2E—H2E1	110.6
C9—C10—H10	121.0	O3E—C2E—H2E2	110.6
C11—C10—H10	121.0	C1E—C2E—H2E2	110.6
C12—C11—C10	122.5 (3)	H2E1—C2E—H2E2	108.7
C12—C11—Cl2	118.9 (2)	C2E—O3E—C4E	104.2 (16)
C10—C11—Cl2	118.6 (2)	C5E—C4E—O3E	104.5 (15)
C11—C12—C13	117.7 (3)	C5E—C4E—H4E1	110.9
C11—C12—H12	121.1	O3E—C4E—H4E1	110.9
C13—C12—H12	121.1	C5E—C4E—H4E2	110.9
C12—C13—C8	122.2 (2)	O3E—C4E—H4E2	110.9
C12—C13—Cl3	118.3 (2)	H4E1—C4E—H4E2	108.9
C8—C13—Cl3	119.51 (19)	C4E—C5E—H5E1	109.5
C3—O14—Na1	148.44 (16)	C4E—C5E—H5E2	109.5
C5—O15—Na1^{iii}	125.15 (15)	H5E1—C5E—H5E2	109.5
C21—C16—C17	117.3 (2)	C4E—C5E—H5E3	109.5
C21—C16—C6	122.4 (2)	H5E1—C5E—H5E3	109.5
C17—C16—C6	120.3 (2)	H5E2—C5E—H5E3	109.5
C18—C17—C16	119.5 (3)		

N7—N1—C1A—N2	180.0 (2)	C13—C8—C9—Cl1	179.50 (19)
C8—N1—C1A—N2	8.7 (4)	N1—C8—C9—Cl1	−1.1 (3)
N7—N1—C1A—C5A	0.6 (3)	C8—C9—C10—C11	0.8 (4)
C8—N1—C1A—C5A	−170.6 (2)	Cl1—C9—C10—C11	−178.9 (2)
N1—C1A—N2—C3	−178.6 (2)	C9—C10—C11—C12	−0.5 (5)
C5A—C1A—N2—C3	0.6 (4)	C9—C10—C11—Cl2	179.3 (2)
C1A—N2—C3—O14	179.6 (2)	C10—C11—C12—C13	−0.4 (5)
C1A—N2—C3—N4	1.2 (3)	Cl2—C11—C12—C13	179.8 (2)
O14—C3—N4—C5	−177.1 (2)	C11—C12—C13—C8	1.0 (4)
N2—C3—N4—C5	1.3 (4)	C11—C12—C13—Cl3	−178.3 (2)
C3—N4—C5—O15	173.1 (2)	C9—C8—C13—C12	−0.7 (4)

C3—N4—C5—C5A	−5.1 (4)	N1—C8—C13—C12	179.9 (2)
N1—C1A—C5A—C6	−1.2 (2)	C9—C8—C13—Cl3	178.6 (2)
N2—C1A—C5A—C6	179.5 (2)	N1—C8—C13—Cl3	−0.9 (3)
N1—C1A—C5A—C5	174.7 (2)	N2—C3—O14—Na1	34.4 (5)
N2—C1A—C5A—C5	−4.6 (4)	N4—C3—O14—Na1	−147.2 (2)
O15—C5—C5A—C1A	−171.8 (2)	N4—C5—O15—Na1^{iii}	−25.5 (3)
N4—C5—C5A—C1A	6.1 (3)	C5A—C5—O15—Na1^{iii}	152.3 (2)
O15—C5—C5A—C6	2.1 (5)	N7—C6—C16—C21	−168.5 (2)
N4—C5—C5A—C6	−180.0 (3)	C5A—C6—C16—C21	9.0 (4)
C1A—C5A—C6—N7	1.4 (3)	N7—C6—C16—C17	12.9 (4)
C5—C5A—C6—N7	−173.0 (3)	C5A—C6—C16—C17	−169.6 (3)
C1A—C5A—C6—C16	−176.2 (2)	C21—C16—C17—C18	−0.3 (4)
C5—C5A—C6—C16	9.4 (5)	C6—C16—C17—C18	178.4 (3)
C5A—C6—N7—N1	−1.0 (3)	C16—C17—C18—N19	0.7 (5)
C16—C6—N7—N1	176.9 (2)	C17—C18—N19—C20	−0.7 (5)
C1A—N1—N7—C6	0.2 (3)	C17—C18—N19—Na1^{iv}	−163.0 (3)
C8—N1—N7—C6	172.1 (2)	C18—N19—C20—C21	0.3 (4)
C1A—N1—C8—C9	−87.6 (3)	Na1^{iv}—N19—C20—C21	163.6 (2)
N7—N1—C8—C9	101.9 (3)	C17—C16—C21—C20	−0.1 (4)
C1A—N1—C8—C13	91.8 (3)	C6—C16—C21—C20	−178.8 (2)
N7—N1—C8—C13	−78.7 (3)	N19—C20—C21—C16	0.1 (4)
C13—C8—C9—C10	−0.2 (4)	C1E—C2E—O3E—C4E	177 (2)
N1—C8—C9—C10	179.2 (2)	C2E—O3E—C4E—C5E	−159 (3)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···O14^{iii}	0.81 (3)	1.99 (3)	2.771 (3)	160 (3)
C21—H21···O15	0.95	2.29	3.096 (3)	142
O1*L*—H1*L*···N2	0.86 (4)	2.21 (4)	3.062 (3)	172 (3)
O2*L*—H2*L*···N2	0.78 (4)	2.06 (4)	2.815 (3)	163 (4)
O3*L*—H3*L*···O2*L*	0.84 (4)	1.94 (4)	2.783 (3)	176 (4)

Symmetry code: (iii) −*x*, −*y*+1, −*z*.