IUCrData

ISSN 2414-3146

(4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane-κ^8N_2,O_6)rubidium 4,4′-bipyridinidyl

Kerstin Mayer, Wilhelm Klein and Thomas F. Fässler*

Technische Universität München, Department of Chemistry, Lichtenbergstrasse 4, 85747 Garching, Germany. *Correspondence e-mail: thomas.faessler@lrz.tu-muenchen.de

Received 9 March 2016
Accepted 24 March 2016

Edited by M. Weil, Vienna University of Technology, Austria

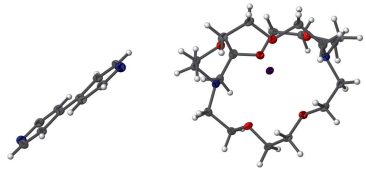
Keywords: crystal structure; bipyridine; organic radicals.

CCDC reference: 1470480

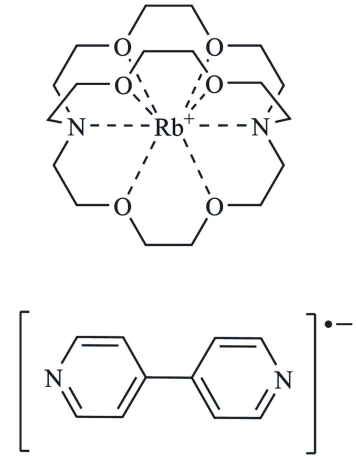
Structural data: full structural data are available from iucrdata.iucr.org

The crystal structure of the title salt, $[Rb(C_{18}H_{36}N_2O_6)](C_{10}H_8N_2)$, consists of Rb^+ cations sequestered by a [2.2.2]cryptand molecule and 4,4′-bipyridinidyl radical monoanions. Both entities are centred by special positions: the Rb^+ cation is located on a twofold rotation axis and the 4,4′-bipyridinidyl anion is located about an inversion centre, so half of each moiety form the asymmetric unit. The planar 4,4′-bipyridinidyl molecules and the complexed cations are arranged in the sense of a distorted rock salt type of structure.

3D view



Chemical scheme



Structure description

From the reaction of pyridine with alkali metals, it is known that pyridine undergoes a coupling reaction to 4,4′-bipyridine which leads to the corresponding radical monoanion (Ward, 1961; Schmulbach *et al.*, 1968). Recently, we have investigated the same species after reaction of the Zintl phase $K_{12}Si_{17}$ with pyridine (Benda & Fässler, 2014). During our recent experiments with pyridine, we found $Rb_{12}Si_{17}$ also works as a reducing agent, leading to 4,4′-bipyridinidyl radical monoanions. Due to inversion symmetry, the bipyridinidyl molecule in the title compound is planar (Fig. 1). The C—C distances range between 1.368 (3) and 1.431 (3) Å and the C—N distances are 1.353 (3) and 1.354 (3) Å, which agree well with those of previously reported compounds (Benda & Fässler, 2014; Denning *et al.*, 2008). In the crystal, the molecular entities are arranged in a rock salt type of structure (Figs. 2 and 3).

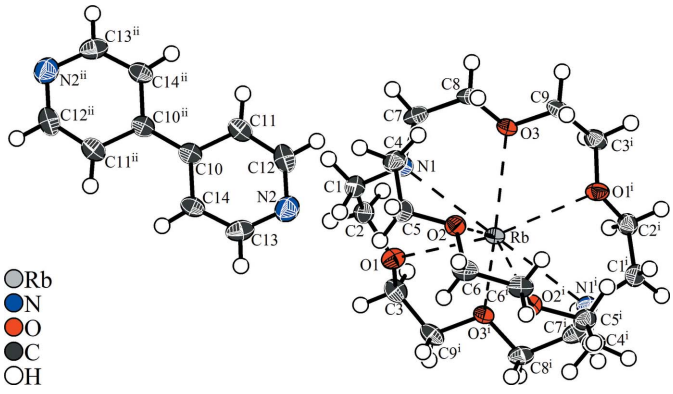


Figure 1
Molecular entities of the title compound. Anisotropic displacement ellipsoids are drawn at the 70% probability level. [Symmetry codes: (i) $-x+\frac{3}{2}, y, -z+\frac{1}{2}$; (ii) $-x, -y+1, -z$.]

Synthesis and crystallization

All manipulations were carried out under an argon atmosphere using standard Schlenk and glove-box techniques. Cryptand [2.2.2] was dried *in vacuo*. Anhydrous pyridine (VWR) was stored over a molecular sieve in an argon-filled glove box. Toluene was dried over a molecular sieve (4 Å) in a solvent purificater (MBraun, MB-SPS). Liquid ammonia was stored over elemental Na for one day and freshly distilled before use. $Rb_{12}Si_{17}$ was prepared from a stoichiometric mixtures of 557 mg (6.52 mmol) Rb and 259 mg (9.23 mmol) Si sealed in a tantalum container, which was encapsulated in an evacuated fused silica tube and heated to 1073 K (2 K min^{-1}) for 15 h and slowly cooled to room temperature at a rate of 0.5 K min^{-1}.

$Rb_{12}Si_{17}$ (90.2 mg; 60 µmol) and cryptand [2.2.2] (127 mg; 337 µmol) were weighed into a Schlenk tube. 2 ml of liquid ammonia were condensed to the reactants, leading to a deep-red solution. The mixture was stirred for 4 h at 195 K, after that time the liquid ammonia was evaporated. The residue was dissolved in 3 ml of anhydrous pyridine and stirred overnight at room temperature. The resulting deep-purple solution was filtered and layered with 4 ml toluene. The title compound

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Rb(C_{18}H_{36}N_2O_6)](C_{10}H_8N_2)$
M_r	618.14
Crystal system, space group	Monoclinic, *P*2/*n*
Temperature (K)	100
a, *b*, *c* (Å)	11.2326 (4), 8.0250 (3), 16.3653 (7)
β (°)	91.950 (3)
V (Å^3)	1474.34 (10)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	1.73
Crystal size (mm)	0.25 × 0.20 × 0.15
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2001).
T_{min}, T_{max}	0.617, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12998, 2895, 2530
R_{int}	0.040
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.029, 0.065, 1.04
No. of reflections	2895
No. of parameters	265
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.54, −0.33

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *DIAMOND* (Brandenburg & Putz, 2012).

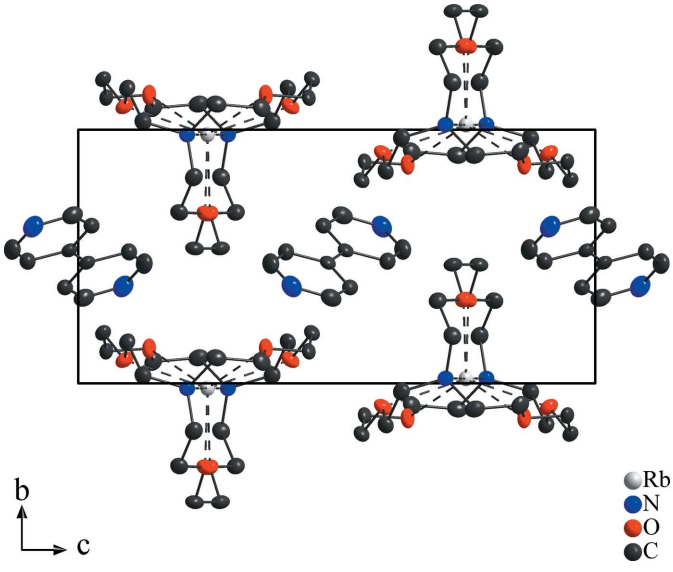


Figure 2
Part of the crystal structure in a view along [100]. Anisotropic displacement ellipsoids are drawn at the 70% probability level, H atoms are omitted for clarity.

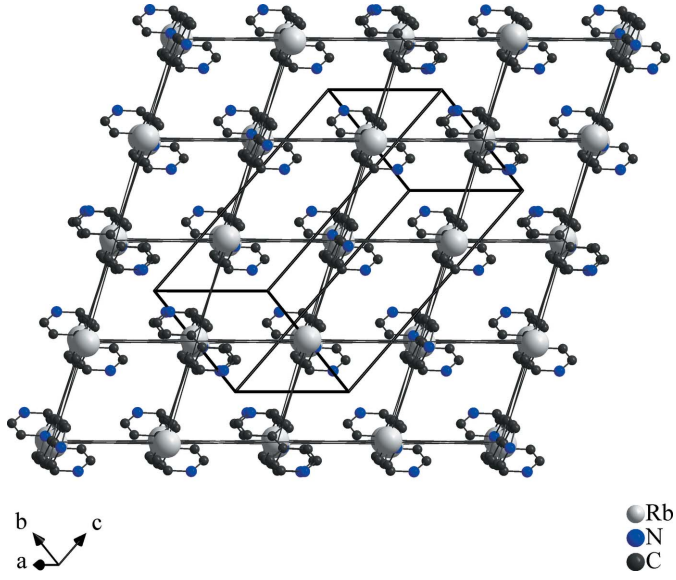


Figure 3
Distorted rock salt type packing of the entities in the title compound. H atoms and cryptand molecules are omitted for clarity.

crystallized as deep purple/black plates and was isolated after 7 months.

The very air- and moisture-sensitive crystals were transferred from the mother liquor into perfluoropolyalkyl ether oil inside a glove box. Single crystals were fixed on a glass capillary and positioned in a 100 K cold N_2 stream.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The highest and lowest remaining electron densities are located at 0.99 Å and at 0.80 Å from the Rb site, respectively.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) through the TUM International Graduate School of Science and Engineering (IGSSE) and the Technische Universität München within the funding programme Open Access Publishing.

References

Benda, C. & Fässler, T. F. (2014). *Z. Naturforsch. Teil B*, **69**, 1119–1123.
Brandenburg, K. & Putz, H. (2012). *DIAMOND* . Crystal Impact GbR, Bonn, Germany.
Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2012). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Denning, M. S., Irwin, M. & Goicoechea, J. M. (2008). *Inorg. Chem.* **47**, 6118–6120.
Schmulbach, C. D., Hinckley, C. C. & Wasmund, D. (1968). *J. Am. Chem. Soc.* **90**, 6600–6602.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Ward, R. L. (1961). *J. Am. Chem. Soc.* **83**, 3623–3626.

full crystallographic data

IUCrData (2016). **1**, x160505 [doi:10.1107/S2414314616005058]

(4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane-κ^8N_2,O_6)rubidium 4,4′-bipyridinidyl

Kerstin Mayer, Wilhelm Klein and Thomas F. Fässler

(4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane-κ^8N_2,O_6)rubidium 4,4′-bipyridinidyl

Crystal data

$[Rb(C_{18}H_{36}N_2O_6)](C_{10}H_8N_2)$
M_r = 618.14
Monoclinic, *P*2/*n*
Hall symbol: -P 2yac
a = 11.2326 (4) Å
b = 8.0250 (3) Å
c = 16.3653 (7) Å
β = 91.950 (3)°
V = 1474.34 (10) Å^3
Z = 2
F(000) = 650
D_x = 1.392 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 3923 reflections
θ = 3.1–31.1°
μ = 1.73 mm^{-1}
T = 100 K
Block, violet
0.25 × 0.20 × 0.15 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 16 pixels mm^{-1}
φ– and ω–rotation scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001).
T_{min} = 0.617, T_{max} = 0.746
12998 measured reflections
2895 independent reflections
2530 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 26.0°, θ_{min} = 2.8°
h = −13→13
k = −9→7
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.065
S = 1.04
2895 reflections
265 parameters
0 restraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 0.2598P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Rb	0.7500	0.98082 (3)	0.2500	0.01492 (9)
N1	0.48347 (14)	0.98021 (19)	0.21052 (10)	0.0173 (4)
O1	0.65700 (11)	1.09295 (17)	0.08964 (8)	0.0197 (3)
O2	0.62010 (11)	0.66979 (16)	0.24532 (8)	0.0184 (3)
O3	0.59695 (11)	1.13750 (17)	0.36291 (8)	0.0191 (3)
C1	0.45767 (18)	1.0318 (3)	0.12513 (13)	0.0198 (4)
H1A	0.4648 (16)	0.933 (2)	0.0903 (12)	0.012 (5)*
H1B	0.3742 (19)	1.070 (3)	0.1178 (13)	0.020 (5)*
C2	0.54038 (18)	1.1634 (3)	0.09462 (13)	0.0190 (4)
H2A	0.5114 (16)	1.200 (2)	0.0410 (14)	0.018 (5)*
H2B	0.5454 (17)	1.260 (3)	0.1307 (13)	0.018 (5)*
C3	0.73661 (18)	1.1993 (3)	0.04795 (13)	0.0198 (4)
H3A	0.7116 (18)	1.210 (3)	−0.0112 (14)	0.026 (6)*
H3B	0.7376 (15)	1.309 (2)	0.0703 (11)	0.007 (5)*
C4	0.43388 (18)	0.8127 (3)	0.22370 (14)	0.0201 (5)
H4A	0.4206 (18)	0.798 (3)	0.2818 (14)	0.023 (6)*
H4B	0.3556 (18)	0.801 (2)	0.1961 (13)	0.019 (5)*
C5	0.51306 (18)	0.6740 (3)	0.19518 (13)	0.0201 (5)
H5A	0.4743 (18)	0.573 (3)	0.1981 (13)	0.018 (5)*
H5B	0.5364 (17)	0.690 (2)	0.1353 (14)	0.020 (5)*
C6	0.69328 (18)	0.5319 (3)	0.22490 (14)	0.0203 (4)
H6A	0.6518 (18)	0.433 (3)	0.2362 (13)	0.018 (5)*
H6B	0.7109 (18)	0.532 (2)	0.1699 (14)	0.020 (6)*
C7	0.43213 (19)	1.1010 (3)	0.26717 (13)	0.0203 (5)
H7A	0.4509 (18)	1.213 (3)	0.2512 (14)	0.028 (6)*
H7B	0.3478 (19)	1.093 (3)	0.2669 (13)	0.020 (5)*
C8	0.47558 (18)	1.0854 (3)	0.35481 (13)	0.0206 (5)
H8A	0.4293 (18)	1.156 (3)	0.3860 (14)	0.023 (6)*
H8B	0.4711 (17)	0.967 (3)	0.3760 (13)	0.015 (5)*
C9	0.64053 (19)	1.1263 (3)	0.44585 (12)	0.0196 (5)
H9A	0.5880 (17)	1.191 (3)	0.4829 (13)	0.019 (5)*
H9B	0.6428 (16)	1.008 (2)	0.4627 (12)	0.013 (5)*
C10	0.05631 (17)	0.4756 (2)	0.01722 (12)	0.0175 (4)
C11	0.09578 (19)	0.5182 (3)	0.09816 (13)	0.0224 (5)
H11	0.0443 (19)	0.578 (3)	0.1335 (14)	0.023 (6)*
C12	0.2064 (2)	0.4722 (3)	0.12761 (14)	0.0272 (5)
H12	0.230 (2)	0.509 (3)	0.1814 (16)	0.033 (6)*
N2	0.28739 (16)	0.3822 (2)	0.08709 (12)	0.0287 (4)
C13	0.24848 (19)	0.3376 (3)	0.01101 (14)	0.0244 (5)
H13	0.3029 (18)	0.271 (3)	−0.0177 (13)	0.019 (5)*
C14	0.14073 (18)	0.3783 (3)	−0.02572 (13)	0.0194 (4)
H14	0.1230 (17)	0.341 (2)	−0.0796 (13)	0.016 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rb	0.01480 (14)	0.01598 (16)	0.01421 (14)	0.000	0.00399 (10)	0.000
N1	0.0178 (8)	0.0164 (9)	0.0177 (9)	−0.0012 (7)	0.0017 (7)	−0.0001 (7)
O1	0.0187 (7)	0.0181 (8)	0.0226 (8)	−0.0006 (6)	0.0048 (6)	0.0061 (6)
O2	0.0186 (7)	0.0166 (8)	0.0198 (8)	0.0002 (6)	0.0006 (6)	−0.0025 (6)
O3	0.0169 (7)	0.0275 (8)	0.0133 (7)	0.0004 (6)	0.0042 (6)	−0.0010 (6)
C1	0.0176 (10)	0.0222 (12)	0.0196 (11)	0.0004 (9)	−0.0017 (8)	−0.0010 (9)
C2	0.0194 (11)	0.0197 (12)	0.0178 (11)	0.0022 (9)	−0.0004 (9)	0.0020 (9)
C3	0.0255 (11)	0.0168 (12)	0.0174 (11)	−0.0039 (9)	0.0024 (9)	0.0030 (9)
C4	0.0166 (11)	0.0222 (12)	0.0219 (12)	−0.0027 (9)	0.0035 (9)	0.0017 (9)
C5	0.0196 (11)	0.0187 (12)	0.0220 (12)	−0.0038 (9)	0.0012 (9)	−0.0012 (9)
C6	0.0239 (11)	0.0131 (11)	0.0242 (12)	−0.0005 (9)	0.0056 (9)	−0.0017 (9)
C7	0.0138 (11)	0.0197 (12)	0.0279 (12)	0.0019 (9)	0.0051 (9)	−0.0026 (9)
C8	0.0179 (11)	0.0227 (12)	0.0219 (12)	0.0011 (9)	0.0087 (9)	−0.0040 (9)
C9	0.0274 (12)	0.0187 (12)	0.0131 (10)	0.0048 (9)	0.0054 (9)	−0.0013 (8)
C10	0.0218 (10)	0.0133 (10)	0.0175 (10)	−0.0023 (8)	0.0038 (8)	0.0030 (8)
C11	0.0291 (11)	0.0203 (12)	0.0178 (10)	−0.0007 (10)	0.0028 (9)	−0.0004 (9)
C12	0.0323 (12)	0.0294 (13)	0.0196 (11)	−0.0032 (10)	−0.0052 (10)	0.0007 (9)
N2	0.0248 (10)	0.0325 (12)	0.0286 (11)	0.0019 (8)	−0.0004 (8)	0.0055 (8)
C13	0.0222 (12)	0.0222 (12)	0.0293 (13)	0.0021 (9)	0.0090 (10)	0.0044 (9)
C14	0.0240 (11)	0.0170 (11)	0.0175 (11)	−0.0014 (9)	0.0052 (9)	0.0003 (8)

Geometric parameters (Å, º)

Rb—O3	2.8578 (13)	C4—H4A	0.97 (2)
Rb—O3^{i}	2.8578 (14)	C4—H4B	0.979 (19)
Rb—O2	2.8909 (13)	C5—H5A	0.93 (2)
Rb—O2^{i}	2.8909 (13)	C5—H5B	1.03 (2)
Rb—O1^{i}	2.9329 (13)	C6—C6^{i}	1.492 (4)
Rb—O1	2.9329 (13)	C6—H6A	0.94 (2)
Rb—N1^{i}	3.0411 (16)	C6—H6B	0.93 (2)
Rb—N1	3.0412 (16)	C7—C8	1.504 (3)
N1—C7	1.472 (3)	C7—H7A	0.96 (2)
N1—C4	1.474 (3)	C7—H7B	0.95 (2)
N1—C1	1.477 (3)	C8—H8A	0.93 (2)
O1—C3	1.426 (2)	C8—H8B	1.02 (2)
O1—C2	1.432 (2)	C9—H9A	1.00 (2)
O2—C6	1.425 (2)	C9—H9B	0.991 (19)
O2—C5	1.433 (2)	C10—C10^{ii}	1.422 (4)
O3—C8	1.428 (2)	C10—C11	1.424 (3)
O3—C9	1.430 (2)	C10—C14	1.431 (3)
C1—C2	1.503 (3)	C11—C12	1.368 (3)
C1—H1A	0.98 (2)	C11—H11	0.96 (2)
C1—H1B	0.99 (2)	C12—N2	1.353 (3)
C2—H2A	0.97 (2)	C12—H12	0.96 (2)
C2—H2B	0.97 (2)	N2—C13	1.354 (3)

C3—C9^{i}	1.499 (3)	C13—C14	1.372 (3)
C3—H3A	1.00 (2)	C13—H13	0.95 (2)
C3—H3B	0.956 (19)	C14—H14	0.95 (2)
C4—C5	1.509 (3)		

O3—Rb—O3^{i}	127.80 (6)	C9^{i}—C3—H3A	109.0 (12)
O3—Rb—O2	94.75 (4)	O1—C3—H3B	111.7 (11)
O3^{i}—Rb—O2	132.60 (4)	C9^{i}—C3—H3B	109.6 (10)
O3—Rb—O2^{i}	132.60 (4)	H3A—C3—H3B	106.7 (16)
O3^{i}—Rb—O2^{i}	94.75 (4)	N1—C4—C5	113.45 (17)
O2—Rb—O2^{i}	60.60 (5)	N1—C4—H4A	108.7 (13)
O3—Rb—O1^{i}	59.35 (4)	C5—C4—H4A	109.1 (13)
O3^{i}—Rb—O1^{i}	103.87 (4)	N1—C4—H4B	110.7 (12)
O2—Rb—O1^{i}	116.92 (4)	C5—C4—H4B	108.6 (12)
O2^{i}—Rb—O1^{i}	94.42 (4)	H4A—C4—H4B	106.0 (17)
O3—Rb—O1	103.87 (4)	O2—C5—C4	109.39 (16)
O3^{i}—Rb—O1	59.35 (4)	O2—C5—H5A	109.7 (12)
O2—Rb—O1	94.42 (4)	C4—C5—H5A	110.5 (13)
O2^{i}—Rb—O1	116.92 (4)	O2—C5—H5B	108.2 (11)
O1^{i}—Rb—O1	144.27 (5)	C4—C5—H5B	112.1 (11)
O3—Rb—N1^{i}	118.22 (4)	H5A—C5—H5B	107.0 (17)
O3^{i}—Rb—N1^{i}	61.87 (4)	O2—C6—C6^{i}	111.06 (15)
O2—Rb—N1^{i}	119.77 (4)	O2—C6—H6A	108.3 (13)
O2^{i}—Rb—N1^{i}	60.04 (4)	C6^{i}—C6—H6A	108.1 (12)
O1^{i}—Rb—N1^{i}	59.49 (4)	O2—C6—H6B	111.5 (13)
O1—Rb—N1^{i}	120.57 (4)	C6^{i}—C6—H6B	109.1 (13)
O3—Rb—N1	61.87 (4)	H6A—C6—H6B	108.6 (18)
O3^{i}—Rb—N1	118.22 (4)	N1—C7—C8	115.09 (17)
O2—Rb—N1	60.04 (4)	N1—C7—H7A	110.5 (14)
O2^{i}—Rb—N1	119.77 (4)	C8—C7—H7A	105.7 (13)
O1^{i}—Rb—N1	120.58 (4)	N1—C7—H7B	111.5 (13)
O1—Rb—N1	59.49 (4)	C8—C7—H7B	106.9 (13)
N1^{i}—Rb—N1	179.82 (6)	H7A—C7—H7B	106.7 (18)
C7—N1—C4	110.51 (17)	O3—C8—C7	109.98 (18)
C7—N1—C1	110.05 (16)	O3—C8—H8A	108.7 (13)
C4—N1—C1	109.33 (15)	C7—C8—H8A	107.6 (13)
C7—N1—Rb	105.61 (11)	O3—C8—H8B	107.5 (11)
C4—N1—Rb	110.15 (11)	C7—C8—H8B	112.7 (11)
C1—N1—Rb	111.14 (11)	H8A—C8—H8B	110.3 (19)
C3—O1—C2	112.38 (15)	O3—C9—C3^{i}	108.93 (17)
C3—O1—Rb	113.67 (11)	O3—C9—H9A	110.6 (11)
C2—O1—Rb	111.65 (11)	C3^{i}—C9—H9A	108.5 (11)
C6—O2—C5	111.30 (15)	O3—C9—H9B	109.2 (12)
C6—O2—Rb	112.47 (11)	C3^{i}—C9—H9B	109.9 (11)
C5—O2—Rb	114.08 (11)	H9A—C9—H9B	109.7 (17)
C8—O3—C9	111.38 (16)	C10^{ii}—C10—C11	123.2 (2)
C8—O3—Rb	113.86 (11)	C10^{ii}—C10—C14	123.4 (2)
C9—O3—Rb	113.09 (11)	C11—C10—C14	113.41 (18)

N1—C1—C2	114.05 (16)	C12—C11—C10	120.9 (2)
N1—C1—H1A	107.8 (11)	C12—C11—H11	118.7 (12)
C2—C1—H1A	108.1 (12)	C10—C11—H11	120.4 (12)
N1—C1—H1B	110.9 (12)	N2—C12—C11	126.1 (2)
C2—C1—H1B	109.4 (12)	N2—C12—H12	116.3 (14)
H1A—C1—H1B	106.2 (16)	C11—C12—H12	117.5 (14)
O1—C2—C1	108.57 (17)	C12—N2—C13	113.00 (18)
O1—C2—H2A	110.3 (12)	N2—C13—C14	126.3 (2)
C1—C2—H2A	108.7 (12)	N2—C13—H13	114.3 (12)
O1—C2—H2B	108.3 (11)	C14—C13—H13	119.4 (12)
C1—C2—H2B	112.3 (13)	C13—C14—C10	120.3 (2)
H2A—C2—H2B	108.6 (17)	C13—C14—H14	119.1 (12)
O1—C3—C9^{i}	108.96 (17)	C10—C14—H14	120.6 (12)
O1—C3—H3A	110.8 (12)		

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