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Crystal structure of $Rb_6[B_{12}O_{18}(OH)_6]\cdot 2H_2O$

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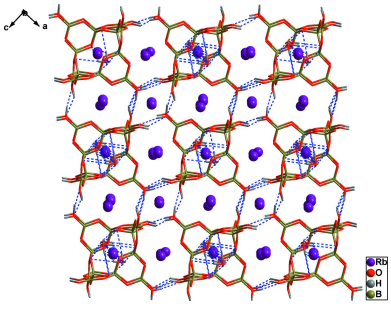
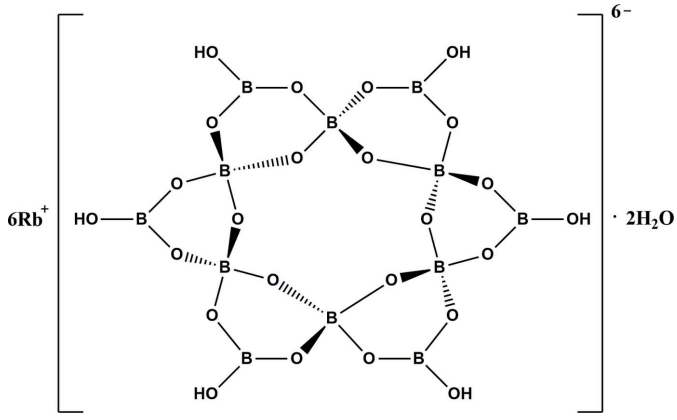
The solvothermal reaction of H_3BO_3, sodium *tert*-butoxide, Rb_2CO_3 and pyridine led to a new alkaline metal borate hexarubidium hexahydroxydodecaborate dihydrate, $Rb_6[B_{12}O_{18}(OH)_6]\cdot 2H_2O$. Its structure contains a large cyclic dodecaoxoboron cluster, $[B_{12}O_{18}(OH)_6]^{6-}$, formed by six $\{B_3O_3\}$ rings. In the crystal, O—H···O hydrogen bonds between the components lead to the formation of a three-dimensional supramolecular framework.

1. Chemical context

In recent years, borates have made excellent contributions to the development of nonlinear optical (NLO) materials and so they are the focus of material chemists (Bashir *et al.*, 2018; Qiu *et al.*, 2021*a*; Wei *et al.*, 2016). Scientists have found that alkali- and alkaline-earth–metal borates often exhibit a short ultraviolet cut-off edge due to no *d*–*d* and *f*–*f* electron transition in the ultraviolet region with wide transparency ranges (Shi *et al.*, 2019; Tang *et al.*, 2019). Generally, boron has two kinds of coordination modes: either BO_3 trigonal or BO_4 tetrahedral, and they further bond to each other through common O atoms forming different oxoboron clusters, which can further polymerize into isolated clusters, one-dimensional chains, two-dimensional layers or three-dimensional frameworks. Here, single crystals of $Rb_6[B_{12}O_{18}(OH)_6]\cdot 2H_2O$ with alkali metal atoms and isolated oxoboron clusters have been obtained under solvothermal conditions.





2. Structural commentary

There are 13.5 independent atoms in the asymmetric unit of the title compound, including 3 B, 9/2 O, 3/2 OH, 3/2 Rb, and 1/

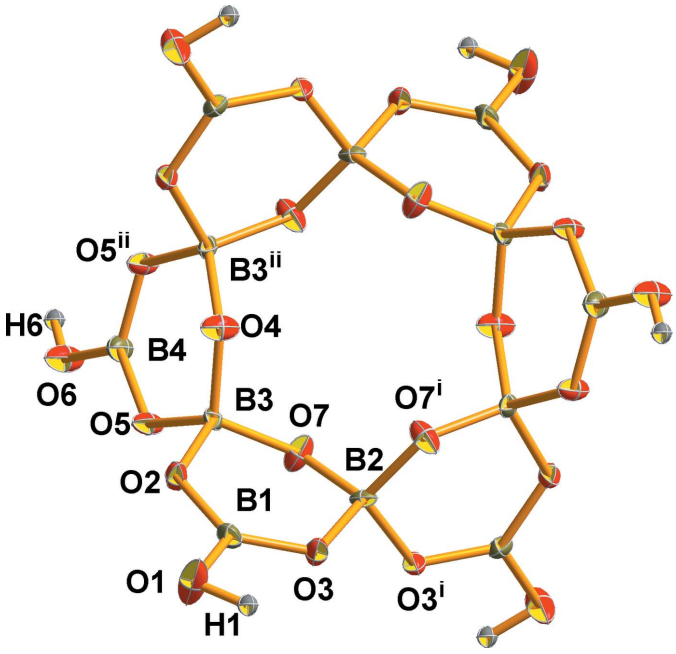


Figure 1
The asymmetric unit of the oxoboron cluster of $[B_{12}O_{18}(OH)_6]^{6-}$ [symmetry codes: (i) $2-x, 2-y, z$; (ii) $x, y, 2-z$]. Displacement ellipsoids are drawn at the 50% probability level.

2 H_2O. It should be noted that the Rb1, Rb2, B2, B4, O4, O6 and O8 atoms are located on special positions with occupancy of 0.25 or 0.5, while the remaining Rb, B and O atoms are located at general positions with an occupancy of 1. Bond-valence-sum calculations show that Rb and B are consistent with the expected oxidation states (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991). Six trigonal $BO_2(OH)$ units [B—O(av.) = 1.360 Å] and six tetrahedral BO_4 units [B—O(av.) = 1.474 Å] are linked by vertex sharing. Each BO_4 unit provides two terminal oxygen atoms to connect with two neighboring

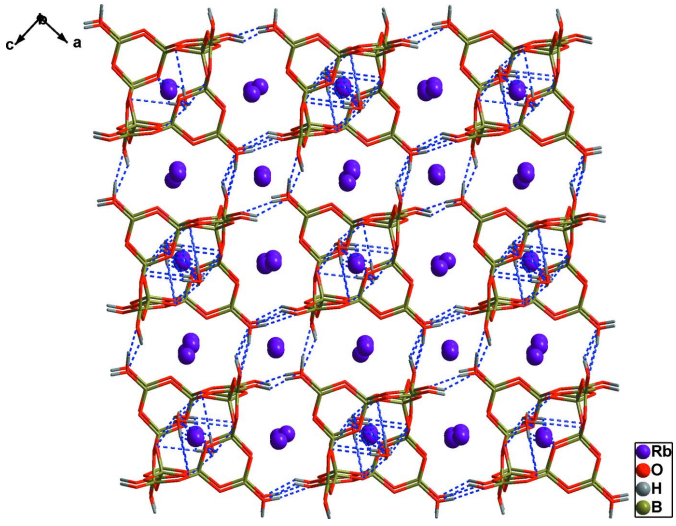


Figure 2
View of the three-dimensional supramolecular framework along the [010] direction. All of the Rb—O bonds are omitted for clarity and blue dashed lines represent O—H···O hydrogen bonds.

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

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8B···O7^{i}	0.85	2.25	3.046 (6)	155
O8—H8B···O4^{i}	0.85	1.68	2.224 (7)	119
O8—H8A···O7^{ii}	0.85	1.70	2.231 (5)	118
O8—H8A···O4^{ii}	0.85	2.17	2.958 (7)	155
O6—H6···O1^{iii}	0.82	1.86	2.670 (5)	167
O1—H1···O6^{iv}	0.94	1.91	2.670 (5)	136

Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+\frac{3}{2}$; (iv) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$.

BO_4 units and shares the other two corners with the $BO_2(OH)$ unit to form a $[B_{12}O_{18}(OH)_6]^{6-}$ cluster (Fig. 1). Each Rb atom is six-coordinate, with Rb—O distances in the range of 2.793 (5)-3.359 (5) Å.

3. Supramolecular features

In the title compound, each $[B_{12}O_{18}(OH)_6]^{6-}$ cluster is connected to other clusters by O1—H1···O6, and O6—H6···O1 hydrogen bonds, resulting in a three-dimensional supramolecular framework (Fig. 2, Table 1). Water molecules are also attached to supramolecular structure *via* O—H···O hydrogen bonds. The title structure is different from those of previously reported analogues $K_7\{(BO_3)Mn[B_{12}O_{18}(OH)_6]\}\cdot H_2O$ (Zhang *et al.*, 2004), and $Na_2Cs_4Ba_2[B_{12}O_{18}(OH)_6]\cdot 4OH$ (Zhang *et al.*, 2016). Both compounds crystallize in the non-centrosymmetric $Pmn2_1$ space group and their supramolecular structures are different from that of the title compound. Therefore, the use of different alkali metals as templates may affect the crystallization of the oxoboron supramolecular structure.

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.43, update June 2022; Groom *et al.*, 2016) for the cyclic dodeca-oxoboron unit $\{B_{12}O_{24}\}$ ring gave eight hits. In the crystals of $Li_7Na_2KRb_2B_{12}O_{24}$, $Li_{7.35}Na_{2.36}K_{1.50}Cs_{0.78}B_{12}O_{24}$, $Li_{6.97}Na_{2.63}K_{1.24}Cs_{1.15}B_{12}O_{24}$, and $Li_{7.27}Na_{2.67}Rb_{2.06}B_{12}O_{24}$ (refcodes: JOGBIT, JOGBOZ, JOFNEA, JOFNIE, trigonal, $R\overline{3}$ space group; Baiheti *et al.*, 2019), the terminal oxygens of this type of the $\{B_{12}O_{24}\}$ ring can be completely deprotonated $[B_{12}O_{24}]^{12-}$ and fail to extend to high-dimensional structures through covalent bonds and hydrogen bonds. In the crystal of $Na_8[B_{12}O_{20}(OH)_4]$ (refcode: ETIJAU, monoclinic, $P2_1/c$ space group; Menchetti *et al.*, 1979), the partially protonated $[B_{12}O_{20}(OH)_4]^{8-}$ unit also fails to extend to a higher dimensional structure through O—B—O bonds. While $KNa_8[Li@B_{12}O_{18}(OH)_6](CO_3)_2$ (refcode: EBUCAJ, trigonal, $R\overline{3}$ space group; Qiu *et al.*, 2021*b*) is a borate carbonate with the isolated $[Li@B_{12}O_{18}(OH)_6]^{5-}$ cluster and interesting layers formed by Na^+ and CO_3^{2-} ions, thus forming a two-dimensional supramolecular structure. After changing the synthetic conditions, the isolated $[Li@B_{12}O_{18}(OH)_6]^{5-}$ cluster was successfully extended to a layered structure *via* B—O—B

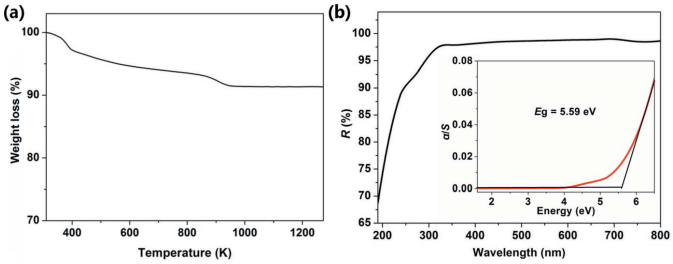


Figure 3
(*a*) Thermogravimetric curve and (*b*) ultraviolet visible diffuse reflectance spectrum of the title compound. Inset: plots of α/S *versus* E.

bonds in $Cs_5[Li@B_{12}O_{20}(OH)_2]\cdot 3H_2O$ (refcode: EBUCIR, monoclinic, *Pc* space group; Qiu *et al.*, 2021*b*), by condensation reactions with the elimination of water molecules between oxoboron clusters.

5. Synthesis and crystallization

A mixture of H_3BO_3 (0.618 g, 10 mmol), sodium *tert*-butoxide (0.096 g, 1 mmol) and Rb_2CO_3 (0.231 g, 1 mmol) was added into pyridine (3.0 mL). After stirring for 15 min, the resulting mixture was sealed in a 25 mL Teflon-lined stainless steel autoclave, heated at 483 K for 7 days, and then slowly cooled to room temperature. Colorless block-shaped crystals of $Rb_6[B_{12}O_{18}(OH)_6]\cdot 2H_2O$ were obtained (yield 51% based on H_3BO_3). Infrared (KBr pallet, cm^{-1}): 3445*vs*, 1639*m*, 1427*s*, 1320*m*, 1003*m*, 939*w*, 873*m*, 721*m*, 622*w*, 542*m*. The thermogravimetric curve of the title compound is shown in Fig. 3*a*. The weight loss of 8.6% (cal. 8.4%) in the temperature range 350–950 K for the compound is attributed to the loss of the water molecules and the removal of dehydration of the hydroxyl groups. The compound has almost no weight loss after 950 K. The ultraviolet visible diffuse reflectance spectrum of the title compound is shown in Fig. 3*b*. The band gap obtained by extrapolating the linear part of the rising curve to zero for the compound is 5.59 eV.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen-atom coordinates were refined without any constraints or restraints. Their U_{iso} values were set to $1.2U_{eq}$ of the parent atoms.

Table 2
Experimental details.

Crystal data	
Chemical formula	$Rb_6[B_{12}O_{18}(OH)_6]\cdot 2H_2O$
M_r	1068.62
Crystal system, space group	Orthorhombic, *Pnnm*
Temperature (K)	296
a, *b*, *c* (Å)	13.395 (4), 9.251 (2), 12.368 (4)
V (Å^3)	1532.7 (7)
Z	2
Radiation type	Mo *Kα*
μ (mm^{-1})	9.60
Crystal size (mm)	0.08 × 0.07 × 0.07
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.452, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17510, 1980, 1523
R_{int}	0.057
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.061, 0.173, 1.07
No. of reflections	1980
No. of parameters	110
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.57, −1.16

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT2018/3* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

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Crystal structure of $Rb_6[B_{12}O_{18}(OH)_6]\cdot 2H_2O$

Qi-Ming Qiu, Li Yan and Jian-Biao Song

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXT2018/3* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015*b*); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

hexarubidium hexahydroxydodecaborate dihydrate, $Rb_6[B_{12}O_{18}(OH)_6]\cdot 2H_2O$

Crystal data

$Rb_6[B_{12}O_{18}(OH)_6]\cdot 2H_2O$
M_r = 1068.62
Orthorhombic, *Pnnm*
a = 13.395 (4) Å
b = 9.251 (2) Å
c = 12.368 (4) Å
V = 1532.7 (7) Å^3
Z = 2
F(000) = 1000
D_x = 2.316 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 3469 reflections
θ = 2.7–26.1°
μ = 9.60 mm^{-1}
T = 296 K
Block, colorless
0.08 × 0.07 × 0.07 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube, Bruker (Mo) X-ray Source
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.452, T_{max} = 0.746
17510 measured reflections
1980 independent reflections
1523 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 28.3°, θ_{min} = 2.2°
h = −17→17
k = −12→12
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.173
S = 1.07
1980 reflections
110 parameters
0 restraints
Hydrogen site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0825P)^2 + 9.4675P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.57 e Å^{-3}
$\Delta\rho_{min}$ = −1.16 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)
Rb1	1.000000	1.000000	0.500000	0.0418 (4)	
Rb2	1.000000	0.500000	1.000000	0.0529 (5)	
Rb3	0.74535 (5)	1.03106 (9)	0.73060 (7)	0.0489 (3)	
O1	1.0385 (4)	0.6325 (4)	0.6768 (4)	0.0397 (12)	
H1	1.089080	0.687977	0.643718	0.048*	
O2	0.9347 (3)	0.7048 (4)	0.8193 (3)	0.0191 (8)	
O3	1.0311 (3)	0.8776 (4)	0.7204 (3)	0.0203 (8)	
O4	0.9428 (4)	0.7903 (6)	1.000000	0.0204 (11)	
O5	0.7857 (3)	0.7944 (4)	0.9032 (3)	0.0194 (8)	
O6	0.6357 (4)	0.7801 (7)	1.000000	0.0270 (13)	
H6	0.599457	0.797673	0.948224	0.032*	0.5
O7	0.9137 (3)	0.9603 (4)	0.8563 (3)	0.0224 (8)	
O8	0.4074 (4)	0.3941 (5)	0.500000	0.0144 (9)	
H8A	0.401585	0.483846	0.486660	0.017*	0.5
H8B	0.456785	0.383526	0.542470	0.017*	0.5
B1	0.9999 (4)	0.7413 (6)	0.7399 (4)	0.0193 (11)	
B2	1.000000	1.000000	0.7919 (6)	0.0127 (14)	
B3	0.8956 (4)	0.8163 (6)	0.8960 (4)	0.0114 (10)	
B4	0.7386 (6)	0.7897 (9)	1.000000	0.0176 (15)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rb1	0.0586 (9)	0.0472 (8)	0.0196 (6)	0.0159 (6)	0.000	0.000
Rb2	0.0971 (13)	0.0268 (6)	0.0348 (7)	0.0271 (7)	0.000	0.000
Rb3	0.0324 (4)	0.0516 (5)	0.0628 (5)	0.0101 (3)	−0.0090 (3)	0.0248 (4)
O1	0.059 (3)	0.0192 (19)	0.041 (3)	−0.011 (2)	0.036 (2)	−0.0119 (18)
O2	0.0257 (18)	0.0140 (16)	0.0175 (18)	−0.0067 (14)	0.0084 (15)	−0.0047 (13)
O3	0.0296 (18)	0.0153 (16)	0.0158 (17)	−0.0080 (15)	0.0094 (15)	−0.0048 (14)
O4	0.010 (2)	0.036 (3)	0.015 (2)	0.007 (2)	0.000	0.000
O5	0.0110 (15)	0.036 (2)	0.0117 (16)	−0.0044 (15)	−0.0006 (13)	−0.0003 (14)
O6	0.013 (2)	0.052 (4)	0.016 (2)	−0.004 (2)	0.000	0.000
O7	0.0223 (19)	0.0154 (17)	0.029 (2)	0.0031 (14)	0.0108 (16)	0.0055 (15)
O8	0.017 (2)	0.012 (2)	0.013 (2)	0.0099 (18)	0.000	0.000
B1	0.025 (3)	0.018 (3)	0.014 (2)	−0.007 (2)	0.004 (2)	−0.007 (2)
B2	0.016 (3)	0.015 (3)	0.006 (3)	0.002 (3)	0.000	0.000
B3	0.008 (2)	0.014 (2)	0.012 (2)	−0.0031 (18)	−0.0010 (18)	−0.0018 (19)
B4	0.013 (4)	0.024 (4)	0.016 (4)	−0.004 (3)	0.000	0.000

Geometric parameters (Å, º)

Rb1—O3	2.980 (4)	Rb3—O5	3.105 (4)
Rb1—O3^{i}	2.980 (4)	Rb3—O3^{ii}	3.114 (4)
Rb1—O3^{ii}	2.980 (4)	Rb3—O1^{xi}	3.359 (5)
Rb1—O3^{iii}	2.980 (4)	Rb3—B3	3.491 (5)
Rb1—O6^{iv}	3.166 (6)	Rb3—B2	3.5061 (19)
Rb1—O6^{v}	3.166 (6)	Rb3—B3^{v}	3.603 (5)
Rb1—B2^{iii}	3.610 (7)	Rb3—B4^{v}	3.729 (5)
Rb1—B2	3.610 (7)	O1—B1	1.374 (7)
Rb1—Rb3	4.4556 (12)	O1—H1	0.9433
Rb1—Rb3^{i}	4.4556 (12)	O2—B1	1.357 (6)
Rb1—Rb3^{ii}	4.4556 (12)	O2—B3	1.495 (6)
Rb1—Rb3^{iii}	4.4556 (12)	O3—B1	1.350 (7)
Rb2—O4^{vi}	2.793 (5)	O3—B2	1.496 (5)
Rb2—O4	2.793 (5)	O4—B3^{vii}	1.453 (5)
Rb2—O2^{vii}	3.058 (4)	O4—B3	1.453 (5)
Rb2—O2^{viii}	3.058 (4)	O5—B4	1.354 (5)
Rb2—O2^{vi}	3.058 (4)	O5—B3	1.490 (6)
Rb2—O2	3.058 (4)	O6—B4	1.381 (9)
Rb2—B3	3.488 (5)	O6—H6	0.8200
Rb2—B3^{vii}	3.488 (5)	O6—H6^{vii}	0.8200
Rb2—B3^{viii}	3.488 (5)	O7—B3	1.441 (6)
Rb2—B3^{vi}	3.488 (5)	O7—B2	1.452 (5)
Rb2—Rb3^{ix}	4.3609 (11)	O8—H8A	0.8500
Rb2—Rb3^{x}	4.3609 (11)	O8—H8B	0.8500
Rb3—O7	2.816 (4)	O8—H8A^{i}	0.8500
Rb3—O2^{v}	2.963 (4)	O8—H8B^{i}	0.8500
Rb3—O5^{v}	2.974 (4)		

O3—Rb1—O3^{i}	132.24 (13)	O3^{ii}—Rb3—O1^{xi}	158.35 (10)
O3—Rb1—O3^{ii}	47.76 (13)	O7—Rb3—B3	23.42 (11)
O3^{i}—Rb1—O3^{ii}	180.00 (5)	O2^{v}—Rb3—B3	154.19 (11)
O3—Rb1—O3^{iii}	180.0	O5^{v}—Rb3—B3	150.79 (11)
O3^{i}—Rb1—O3^{iii}	47.76 (13)	O5—Rb3—B3	25.25 (10)
O3^{ii}—Rb1—O3^{iii}	132.24 (13)	O3^{ii}—Rb3—B3	67.90 (10)
O3—Rb1—O6^{iv}	66.97 (7)	O1^{xi}—Rb3—B3	91.11 (11)
O3^{i}—Rb1—O6^{iv}	66.97 (7)	O7—Rb3—B2	23.45 (12)
O3^{ii}—Rb1—O6^{iv}	113.03 (7)	O2^{v}—Rb3—B2	151.80 (8)
O3^{iii}—Rb1—O6^{iv}	113.03 (7)	O5^{v}—Rb3—B2	108.86 (9)
O3—Rb1—O6^{v}	113.03 (7)	O5—Rb3—B2	67.94 (10)
O3^{i}—Rb1—O6^{v}	113.03 (7)	O3^{ii}—Rb3—B2	25.24 (9)
O3^{ii}—Rb1—O6^{v}	66.97 (7)	O1^{xi}—Rb3—B2	133.79 (11)
O3^{iii}—Rb1—O6^{v}	66.97 (7)	B3—Rb3—B2	42.74 (11)
O6^{iv}—Rb1—O6^{v}	180.0	O7—Rb3—B3^{v}	146.09 (12)
O3—Rb1—B2^{iii}	156.12 (7)	O2^{v}—Rb3—B3^{v}	23.88 (10)
O3^{i}—Rb1—B2^{iii}	23.88 (7)	O5^{v}—Rb3—B3^{v}	23.81 (10)
O3^{ii}—Rb1—B2^{iii}	156.12 (7)	O5—Rb3—B3^{v}	155.00 (10)

O3^{iii}—Rb1—B2^{iii}	23.88 (7)	O3^{ii}—Rb3—B3^{v}	106.72 (10)
O6^{iv}—Rb1—B2^{iii}	90.0	O1^{xi}—Rb3—B3^{v}	92.62 (11)
O6^{v}—Rb1—B2^{iii}	90.0	B3—Rb3—B3^{v}	166.87 (12)
O3—Rb1—B2	23.88 (7)	B2—Rb3—B3^{v}	131.60 (10)
O3^{i}—Rb1—B2	156.12 (7)	O7—Rb3—B4^{v}	121.68 (14)
O3^{ii}—Rb1—B2	23.88 (7)	O2^{v}—Rb3—B4^{v}	62.59 (13)
O3^{iii}—Rb1—B2	156.12 (7)	O5^{v}—Rb3—B4^{v}	19.43 (12)
O6^{iv}—Rb1—B2	90.0	O5—Rb3—B4^{v}	165.50 (14)
O6^{v}—Rb1—B2	90.0	O3^{ii}—Rb3—B4^{v}	74.88 (13)
B2^{iii}—Rb1—B2	180.0	O1^{xi}—Rb3—B4^{v}	126.70 (14)
O3—Rb1—Rb3	63.01 (7)	B3—Rb3—B4^{v}	141.27 (14)
O3^{i}—Rb1—Rb3	135.79 (7)	B2—Rb3—B4^{v}	99.31 (15)
O3^{ii}—Rb1—Rb3	44.21 (7)	B3^{v}—Rb3—B4^{v}	39.47 (14)
O3^{iii}—Rb1—Rb3	116.99 (7)	O7—Rb3—Rb2^{v}	161.66 (8)
O6^{iv}—Rb1—Rb3	119.50 (7)	O2^{v}—Rb3—Rb2^{v}	44.45 (7)
O6^{v}—Rb1—Rb3	60.50 (7)	O5^{v}—Rb3—Rb2^{v}	65.47 (7)
B2^{iii}—Rb1—Rb3	129.799 (15)	O5—Rb3—Rb2^{v}	122.29 (7)
B2—Rb1—Rb3	50.201 (15)	O3^{ii}—Rb3—Rb2^{v}	135.72 (7)
O3—Rb1—Rb3^{i}	135.79 (7)	O1^{xi}—Rb3—Rb2^{v}	64.64 (7)
O3^{i}—Rb1—Rb3^{i}	63.01 (7)	B3—Rb3—Rb2^{v}	141.29 (9)
O3^{ii}—Rb1—Rb3^{i}	116.99 (7)	B2—Rb3—Rb2^{v}	150.36 (11)
O3^{iii}—Rb1—Rb3^{i}	44.21 (7)	B3^{v}—Rb3—Rb2^{v}	50.87 (8)
O6^{iv}—Rb1—Rb3^{i}	119.50 (7)	B4^{v}—Rb3—Rb2^{v}	65.52 (11)
O6^{v}—Rb1—Rb3^{i}	60.50 (7)	O7—Rb3—Rb1	74.06 (8)
B2^{iii}—Rb1—Rb3^{i}	50.202 (15)	O2^{v}—Rb3—Rb1	121.65 (7)
B2—Rb1—Rb3^{i}	129.798 (15)	O5^{v}—Rb3—Rb1	78.67 (7)
Rb3—Rb1—Rb3^{i}	79.60 (3)	O5—Rb3—Rb1	105.16 (7)
O3—Rb1—Rb3^{ii}	44.21 (7)	O3^{ii}—Rb3—Rb1	41.86 (7)
O3^{i}—Rb1—Rb3^{ii}	116.99 (7)	O1^{xi}—Rb3—Rb1	145.17 (7)
O3^{ii}—Rb1—Rb3^{ii}	63.01 (7)	B3—Rb3—Rb1	84.08 (9)
O3^{iii}—Rb1—Rb3^{ii}	135.79 (7)	B2—Rb3—Rb1	52.28 (12)
O6^{iv}—Rb1—Rb3^{ii}	60.50 (7)	B3^{v}—Rb3—Rb1	99.81 (8)
O6^{v}—Rb1—Rb3^{ii}	119.50 (7)	B4^{v}—Rb3—Rb1	60.50 (11)
B2^{iii}—Rb1—Rb3^{ii}	129.798 (14)	Rb2^{v}—Rb3—Rb1	98.86 (3)
B2—Rb1—Rb3^{ii}	50.202 (14)	B1—O1—Rb3^{xii}	116.5 (4)
Rb3—Rb1—Rb3^{ii}	100.40 (3)	B1—O1—H1	96.8
Rb3^{i}—Rb1—Rb3^{ii}	180.0	Rb3^{xii}—O1—H1	78.5
O3—Rb1—Rb3^{iii}	116.99 (7)	B1—O2—B3	120.9 (4)
O3^{i}—Rb1—Rb3^{iii}	44.21 (7)	B1—O2—Rb3^{x}	120.5 (3)
O3^{ii}—Rb1—Rb3^{iii}	135.79 (7)	B3—O2—Rb3^{x}	102.8 (2)
O3^{iii}—Rb1—Rb3^{iii}	63.01 (7)	B1—O2—Rb2	119.9 (3)
O6^{iv}—Rb1—Rb3^{iii}	60.50 (7)	B3—O2—Rb2	93.7 (3)
O6^{v}—Rb1—Rb3^{iii}	119.50 (7)	Rb3^{x}—O2—Rb2	92.81 (9)
B2^{iii}—Rb1—Rb3^{iii}	50.202 (14)	B1—O3—B2	121.0 (4)
B2—Rb1—Rb3^{iii}	129.798 (14)	B1—O3—Rb1	118.4 (3)
Rb3—Rb1—Rb3^{iii}	180.0	B2—O3—Rb1	102.4 (3)
Rb3^{i}—Rb1—Rb3^{iii}	100.40 (3)	B1—O3—Rb3^{ii}	122.9 (3)
Rb3^{ii}—Rb1—Rb3^{iii}	79.60 (3)	B2—O3—Rb3^{ii}	92.20 (15)

O4^{vi}—Rb2—O4	180.0	Rb1—O3—Rb3^{ii}	93.93 (9)
O4^{vi}—Rb2—O2^{vii}	132.41 (6)	B3^{vii}—O4—B3	124.6 (5)
O4—Rb2—O2^{vii}	47.59 (6)	B3^{vii}—O4—Rb2	106.2 (3)
O4^{vi}—Rb2—O2^{viii}	47.59 (6)	B3—O4—Rb2	106.2 (3)
O4—Rb2—O2^{viii}	132.41 (6)	B4—O5—B3	121.2 (4)
O2^{vii}—Rb2—O2^{viii}	180.0	B4—O5—Rb3^{x}	113.6 (4)
O4^{vi}—Rb2—O2^{vi}	47.59 (6)	B3—O5—Rb3^{x}	102.5 (3)
O4—Rb2—O2^{vi}	132.41 (6)	B4—O5—Rb3	123.3 (4)
O2^{vii}—Rb2—O2^{vi}	86.08 (13)	B3—O5—Rb3	92.0 (3)
O2^{viii}—Rb2—O2^{vi}	93.92 (13)	Rb3^{x}—O5—Rb3	99.83 (10)
O4^{vi}—Rb2—O2	132.41 (6)	B4—O6—Rb1^{x}	128.7 (5)
O4—Rb2—O2	47.59 (6)	B4—O6—H6	125.4
O2^{vii}—Rb2—O2	93.92 (13)	Rb1^{x}—O6—H6	79.7
O2^{viii}—Rb2—O2	86.08 (13)	B4—O6—H6^{vii}	125.35 (13)
O2^{vi}—Rb2—O2	180.0	Rb1^{x}—O6—H6^{vii}	79.74 (6)
O4^{vi}—Rb2—B3	156.42 (9)	H6—O6—H6^{vii}	102.7
O4—Rb2—B3	23.58 (9)	B3—O7—B2	123.7 (3)
O2^{vii}—Rb2—B3	68.60 (11)	B3—O7—Rb3	105.6 (3)
O2^{viii}—Rb2—B3	111.40 (11)	B2—O7—Rb3	106.0 (3)
O2^{vi}—Rb2—B3	154.67 (10)	H8A—O8—H8B	107.7
O2—Rb2—B3	25.33 (10)	H8A—O8—H8A^{i}	22.4
O4^{vi}—Rb2—B3^{vii}	156.42 (9)	H8B—O8—H8A^{i}	93.7
O4—Rb2—B3^{vii}	23.58 (9)	H8A—O8—H8B^{i}	93.7
O2^{vii}—Rb2—B3^{vii}	25.33 (10)	H8B—O8—H8B^{i}	76.3
O2^{viii}—Rb2—B3^{vii}	154.67 (10)	H8A^{i}—O8—H8B^{i}	107.7
O2^{vi}—Rb2—B3^{vii}	111.40 (11)	O3—B1—O2	124.1 (5)
O2—Rb2—B3^{vii}	68.60 (11)	O3—B1—O1	117.8 (5)
B3—Rb2—B3^{vii}	43.27 (17)	O2—B1—O1	118.1 (5)
O4^{vi}—Rb2—B3^{viii}	23.58 (9)	O7^{ii}—B2—O7	113.4 (6)
O4—Rb2—B3^{viii}	156.42 (9)	O7^{ii}—B2—O3^{ii}	110.79 (19)
O2^{vii}—Rb2—B3^{viii}	154.67 (10)	O7—B2—O3^{ii}	107.1 (2)
O2^{viii}—Rb2—B3^{viii}	25.33 (10)	O7^{ii}—B2—O3	107.1 (2)
O2^{vi}—Rb2—B3^{viii}	68.60 (11)	O7—B2—O3	110.79 (19)
O2—Rb2—B3^{viii}	111.40 (11)	O3^{ii}—B2—O3	107.5 (5)
B3—Rb2—B3^{viii}	136.73 (17)	O7^{ii}—B2—Rb3	150.8 (3)
B3^{vii}—Rb2—B3^{viii}	180.0	O7—B2—Rb3	50.53 (19)
O4^{vi}—Rb2—B3^{vi}	23.58 (9)	O3^{ii}—B2—Rb3	62.57 (15)
O4—Rb2—B3^{vi}	156.42 (9)	O3—B2—Rb3	101.8 (2)
O2^{vii}—Rb2—B3^{vi}	111.40 (11)	O7^{ii}—B2—Rb3^{ii}	50.52 (19)
O2^{viii}—Rb2—B3^{vi}	68.60 (11)	O7—B2—Rb3^{ii}	150.8 (3)
O2^{vi}—Rb2—B3^{vi}	25.33 (10)	O3^{ii}—B2—Rb3^{ii}	101.8 (2)
O2—Rb2—B3^{vi}	154.67 (10)	O3—B2—Rb3^{ii}	62.57 (15)
B3—Rb2—B3^{vi}	180.00 (9)	Rb3—B2—Rb3^{ii}	155.0 (2)
B3^{vii}—Rb2—B3^{vi}	136.73 (17)	O7^{ii}—B2—Rb1	123.3 (3)
B3^{viii}—Rb2—B3^{vi}	43.27 (17)	O7—B2—Rb1	123.3 (3)
O4^{vi}—Rb2—Rb3^{ix}	74.33 (8)	O3^{ii}—B2—Rb1	53.8 (3)
O4—Rb2—Rb3^{ix}	105.67 (8)	O3—B2—Rb1	53.8 (3)
O2^{vii}—Rb2—Rb3^{ix}	77.20 (7)	Rb3—B2—Rb1	77.52 (12)

O2^{viii}—Rb2—Rb3^{ix}	102.80 (7)	Rb3^{ii}—B2—Rb1	77.52 (12)
O2^{vi}—Rb2—Rb3^{ix}	42.74 (7)	O7—B3—O4	112.5 (4)
O2—Rb2—Rb3^{ix}	137.26 (7)	O7—B3—O5	108.2 (4)
B3—Rb2—Rb3^{ix}	126.76 (8)	O4—B3—O5	110.8 (4)
B3^{vii}—Rb2—Rb3^{ix}	96.67 (8)	O7—B3—O2	111.3 (4)
B3^{viii}—Rb2—Rb3^{ix}	83.33 (8)	O4—B3—O2	107.2 (4)
B3^{vi}—Rb2—Rb3^{ix}	53.24 (8)	O5—B3—O2	106.9 (4)
O4^{vi}—Rb2—Rb3^{x}	105.67 (8)	O7—B3—Rb2	146.6 (3)
O4—Rb2—Rb3^{x}	74.33 (8)	O4—B3—Rb2	50.3 (3)
O2^{vii}—Rb2—Rb3^{x}	102.80 (7)	O5—B3—Rb2	105.1 (3)
O2^{viii}—Rb2—Rb3^{x}	77.20 (7)	O2—B3—Rb2	61.0 (2)
O2^{vi}—Rb2—Rb3^{x}	137.26 (7)	O7—B3—Rb3	51.0 (2)
O2—Rb2—Rb3^{x}	42.74 (7)	O4—B3—Rb3	149.7 (3)
B3—Rb2—Rb3^{x}	53.24 (8)	O5—B3—Rb3	62.7 (2)
B3^{vii}—Rb2—Rb3^{x}	83.33 (8)	O2—B3—Rb3	102.9 (3)
B3^{viii}—Rb2—Rb3^{x}	96.67 (8)	Rb2—B3—Rb3	157.61 (16)
B3^{vi}—Rb2—Rb3^{x}	126.76 (8)	O7—B3—Rb3^{x}	128.1 (3)
Rb3^{ix}—Rb2—Rb3^{x}	180.0	O4—B3—Rb3^{x}	119.4 (3)
O7—Rb3—O2^{v}	153.22 (11)	O5—B3—Rb3^{x}	53.7 (2)
O7—Rb3—O5^{v}	127.55 (10)	O2—B3—Rb3^{x}	53.3 (2)
O2^{v}—Rb3—O5^{v}	47.64 (10)	Rb2—B3—Rb3^{x}	75.88 (10)
O7—Rb3—O5	46.94 (10)	Rb3—B3—Rb3^{x}	81.95 (10)
O2^{v}—Rb3—O5	131.85 (10)	O5—B4—O5^{vii}	124.3 (6)
O5^{v}—Rb3—O5	169.84 (10)	O5—B4—O6	117.8 (3)
O7—Rb3—O3^{ii}	46.81 (9)	O5^{vii}—B4—O6	117.8 (3)
O2^{v}—Rb3—O3^{ii}	128.83 (9)	O5—B4—Rb3^{x}	47.0 (3)
O5^{v}—Rb3—O3^{ii}	83.65 (10)	O5^{vii}—B4—Rb3^{x}	132.1 (5)
O5—Rb3—O3^{ii}	92.98 (9)	O6—B4—Rb3^{x}	90.9 (3)
O7—Rb3—O1^{xi}	111.56 (10)	O5—B4—Rb3^{xiii}	132.1 (5)
O2^{v}—Rb3—O1^{xi}	69.14 (10)	O5^{vii}—B4—Rb3^{xiii}	47.0 (3)
O5^{v}—Rb3—O1^{xi}	116.34 (10)	O6—B4—Rb3^{xiii}	90.9 (3)
O5—Rb3—O1^{xi}	65.88 (10)	Rb3^{x}—B4—Rb3^{xiii}	99.8 (2)

B2—O3—B1—O2	4.2 (8)	Rb2—O4—B3—O5	92.7 (4)
Rb1—O3—B1—O2	−123.3 (5)	B3^{vii}—O4—B3—O2	−147.0 (4)
Rb3^{ii}—O3—B1—O2	120.5 (5)	Rb2—O4—B3—O2	−23.6 (4)
B2—O3—B1—O1	−174.3 (5)	B3^{vii}—O4—B3—Rb2	−123.5 (7)
Rb1—O3—B1—O1	58.2 (6)	B3^{vii}—O4—B3—Rb3	40.4 (11)
Rb3^{ii}—O3—B1—O1	−58.1 (6)	Rb2—O4—B3—Rb3	163.9 (5)
B3—O2—B1—O3	−3.0 (8)	B3^{vii}—O4—B3—Rb3^{x}	−89.9 (6)
Rb3^{x}—O2—B1—O3	127.7 (5)	Rb2—O4—B3—Rb3^{x}	33.5 (3)
Rb2—O2—B1—O3	−118.4 (5)	B4—O5—B3—O7	−107.7 (6)
B3—O2—B1—O1	175.6 (5)	Rb3^{x}—O5—B3—O7	124.4 (3)
Rb3^{x}—O2—B1—O1	−53.8 (6)	Rb3—O5—B3—O7	23.9 (3)
Rb2—O2—B1—O1	60.1 (6)	B4—O5—B3—O4	15.9 (7)
Rb3^{xii}—O1—B1—O3	91.4 (5)	Rb3^{x}—O5—B3—O4	−111.9 (4)
Rb3^{xii}—O1—B1—O2	−87.2 (5)	Rb3—O5—B3—O4	147.5 (4)
B3—O7—B2—O7^{ii}	−87.0 (4)	B4—O5—B3—O2	132.3 (5)

Rb3—O7—B2—O7^{ii}	151.1 (2)	Rb3^{x}—O5—B3—O2	4.5 (4)
B3—O7—B2—O3^{ii}	150.5 (4)	Rb3—O5—B3—O2	−96.0 (3)
Rb3—O7—B2—O3^{ii}	28.6 (4)	B4—O5—B3—Rb2	68.6 (6)
B3—O7—B2—O3	33.5 (6)	Rb3^{x}—O5—B3—Rb2	−59.2 (2)
Rb3—O7—B2—O3	−88.4 (3)	Rb3—O5—B3—Rb2	−159.77 (14)
B3—O7—B2—Rb3	121.9 (5)	B4—O5—B3—Rb3	−131.6 (6)
B3—O7—B2—Rb3^{ii}	−37.2 (9)	Rb3^{x}—O5—B3—Rb3	100.53 (14)
Rb3—O7—B2—Rb3^{ii}	−159.0 (5)	B4—O5—B3—Rb3^{x}	127.9 (6)
B3—O7—B2—Rb1	93.0 (4)	Rb3—O5—B3—Rb3^{x}	−100.53 (14)
Rb3—O7—B2—Rb1	−28.9 (2)	B1—O2—B3—O7	15.5 (6)
B1—O3—B2—O7^{ii}	106.5 (5)	Rb3^{x}—O2—B3—O7	−122.4 (3)
Rb1—O3—B2—O7^{ii}	−119.1 (3)	Rb2—O2—B3—O7	143.9 (3)
Rb3^{ii}—O3—B2—O7^{ii}	−24.6 (3)	B1—O2—B3—O4	−107.8 (5)
B1—O3—B2—O7	−17.7 (6)	Rb3^{x}—O2—B3—O4	114.3 (3)
Rb1—O3—B2—O7	116.7 (4)	Rb2—O2—B3—O4	20.6 (4)
Rb3^{ii}—O3—B2—O7	−148.8 (3)	B1—O2—B3—O5	133.4 (5)
B1—O3—B2—O3^{ii}	−134.4 (5)	Rb3^{x}—O2—B3—O5	−4.5 (4)
Rb1—O3—B2—O3^{ii}	0.000 (2)	Rb2—O2—B3—O5	−98.2 (3)
Rb3^{ii}—O3—B2—O3^{ii}	94.51 (12)	B1—O2—B3—Rb2	−128.3 (5)
B1—O3—B2—Rb3	−69.7 (5)	Rb3^{x}—O2—B3—Rb2	93.72 (13)
Rb1—O3—B2—Rb3	64.69 (18)	B1—O2—B3—Rb3	68.4 (5)
Rb3^{ii}—O3—B2—Rb3	159.20 (13)	Rb3^{x}—O2—B3—Rb3	−69.56 (19)
B1—O3—B2—Rb3^{ii}	131.1 (5)	Rb2—O2—B3—Rb3	−163.28 (12)
Rb1—O3—B2—Rb3^{ii}	−94.51 (12)	B1—O2—B3—Rb3^{x}	137.9 (5)
B1—O3—B2—Rb1	−134.4 (5)	Rb2—O2—B3—Rb3^{x}	−93.72 (13)
Rb3^{ii}—O3—B2—Rb1	94.51 (12)	B3—O5—B4—O5^{vii}	−4.5 (11)
B2—O7—B3—O4	87.7 (6)	Rb3^{x}—O5—B4—O5^{vii}	118.2 (7)
Rb3—O7—B3—O4	−150.2 (3)	Rb3—O5—B4—O5^{vii}	−121.1 (6)
B2—O7—B3—O5	−149.6 (4)	B3—O5—B4—O6	175.2 (6)
Rb3—O7—B3—O5	−27.6 (4)	Rb3^{x}—O5—B4—O6	−62.1 (8)
B2—O7—B3—O2	−32.5 (6)	Rb3—O5—B4—O6	58.6 (8)
Rb3—O7—B3—O2	89.5 (3)	B3—O5—B4—Rb3^{x}	−122.7 (6)
B2—O7—B3—Rb2	36.8 (8)	Rb3—O5—B4—Rb3^{x}	120.7 (4)
Rb3—O7—B3—Rb2	158.8 (4)	B3—O5—B4—Rb3^{xiii}	−64.7 (7)
B2—O7—B3—Rb3	−122.0 (5)	Rb3^{x}—O5—B4—Rb3^{xiii}	58.0 (5)
B2—O7—B3—Rb3^{x}	−91.9 (5)	Rb3—O5—B4—Rb3^{xiii}	178.7 (2)
Rb3—O7—B3—Rb3^{x}	30.1 (4)	Rb1^{x}—O6—B4—O5	90.1 (6)
B3^{vii}—O4—B3—O7	90.4 (7)	Rb1^{x}—O6—B4—O5^{vii}	−90.1 (6)
Rb2—O4—B3—O7	−146.2 (3)	Rb1^{x}—O6—B4—Rb3^{x}	49.90 (10)
B3^{vii}—O4—B3—O5	−30.8 (8)	Rb1^{x}—O6—B4—Rb3^{xiii}	−49.90 (10)

Symmetry codes: (i) *x*, *y*, −*z*+1; (ii) −*x*+2, −*y*+2, *z*; (iii) −*x*+2, −*y*+2, −*z*+1; (iv) *x*+1/2, −*y*+3/2, *z*−1/2; (v) −*x*+3/2, *y*+1/2, −*z*+3/2; (vi) −*x*+2, −*y*+1, −*z*+2; (vii) *x*, *y*, −*z*+2; (viii) −*x*+2, −*y*+1, *z*; (ix) *x*+1/2, −*y*+3/2, *z*+1/2; (x) −*x*+3/2, *y*−1/2, −*z*+3/2; (xi) *x*−1/2, −*y*+3/2, −*z*+3/2; (xii) *x*+1/2, −*y*+3/2, −*z*+3/2; (xiii) −*x*+3/2, *y*−1/2, *z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H8*B*···O7^{x}	0.85	2.25	3.046 (6)	155

O8—H8*B*···O4^{x}	0.85	1.68	2.224 (7)	119
O8—H8*A*···O7^{xiv}	0.85	1.70	2.231 (5)	118
O8—H8*A*···O4^{xiv}	0.85	2.17	2.958 (7)	155
O6—H6···O1^{xi}	0.82	1.86	2.670 (5)	167
O1—H1···O6^{iv}	0.94	1.91	2.670 (5)	136

Symmetry codes: (iv) $x+1/2, -y+3/2, z-1/2$; (x) $-x+3/2, y-1/2, -z+3/2$; (xi) $x-1/2, -y+3/2, -z+3/2$; (xiv) $x-1/2, -y+3/2, z-1/2$.