Crystal structure of $\text{Rb}_6[\text{B}_{12}\text{O}_{18}(\text{OH})_6]\cdot2\text{H}_2\text{O}$

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The solvothermal reaction of $\text{H}_3\text{BO}_3$, sodium tert-butoxide, $\text{Rb}_2\text{CO}_3$ and pyridine led to a new alkaline metal borate hexarubidium hexahydroxydodecaborate dihydrate, $\text{Rb}_6[\text{B}_{12}\text{O}_{18}(\text{OH})_6]\cdot2\text{H}_2\text{O}$. Its structure contains a large cyclic dodecaoxoboron cluster, $[\text{B}_{12}\text{O}_{18}(\text{OH})_6]^{6-}$, formed by six $[\text{B}_3\text{O}_3]$ rings. In the crystal, $\text{O}—\text{H}\cdots\text{O}$ 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., 2021a; 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 $\text{Rb}_6[\text{B}_{12}\text{O}_{18}(\text{OH})_6]\cdot2\text{H}_2\text{O}$ 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/
2 H₂O. 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 BO₂(OH) units [B—O(avg.) = 1.360 Å] and six tetrahedral BO₄ units [B—O(avg.) = 1.474 Å] are linked by vertex sharing. Each BO₄ unit provides two terminal oxygen atoms to connect with two neighboring BO₄ units and shares the other two corners with the BO₂(OH) unit to form a [B₁₂O₁₈(OH)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 [B₁₂O₁₈(OH)₆]⁻ cluster is connected to other clusters by O1—H1—O6 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 K₂[(BO₃)Mn[B₁₂O₁₈(OH)₆]]·H₂O (Zhang et al., 2004), and Na₂Cs₂Ba₂[B₁₂O₂⁻(OH)₆]·4OH (Zhang et al., 2016). Both compounds crystallize in the non-centrosymmetric Pmn2₁ 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 [B₁₂O₂₄] ring gave eight hits. In the crystals of Li₆Na₂KRb₂B₁₂O₂₄, Li₇Na₂₂K₁₀S₀₇B₁₂O₂₄, Li₆Na₆K₁₂Cs₁₈B₁₅O₁₈, and Li₇Na₂₂Rb₂Ba₂B₁₂O₂₄ (refcodes: JOGBIT, JOGBOZ, JOFNEA, JOFNIE, trigonal, R3 space group; Baiheti et al., 2019), the terminal oxygens of this type of the [B₁₂O₂₄] ring can be completely deprotonated [B₁₂O₂₄]⁻ and fail to extend to high-dimensional structures through covalent bonds and hydrogen bonds. In the crystal of Na₅[B₁₂O₂₀(OH)₄] (refcode: ETIJAU, monoclinic, P2₁/c space group; Menchetti et al., 1979), the partially protonated [B₁₂O₂₀(OH)₄]⁺⁻ unit also fails to extend to a higher dimensional structure through O—B—O bonds. While KN₄[Li@B₁₂O₁₈(OH)₆](CO₃)₂ (refcode: EBUCAJ, trigonal, R3 space group; Qiu et al., 2021b) is a borate carbonate with the isolated [Li@B₁₂O₁₈(OH)₆]⁻ cluster and interesting layers formed by Na⁺ and CO₃²⁻ ions, thus forming a two-dimensional supramolecular structure. After changing the synthetic conditions, the isolated [Li@B₁₂O₁₈(OH)₆]⁻ cluster was successfully extended to a layered structure via B—O—B...
bonds in Cs[Li@B12O20(OH)2]·3H2O (refcode: EBUCIR, monoclinic, Pbc a space group; Qiu et al., 2021b), by condensation reactions with the elimination of water molecules between oxoboron clusters.

5. Synthesis and crystallization

A mixture of H3BO3 (0.618 g, 10 mmol), sodium tert-butoxide (0.096 g, 1 mmol) and Rb2CO3 (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 Rb6[B12O18(OH)6]·2H2O were obtained (yield 51% based on H3BO3). Infrared (KBr pallet, cm−1): 3445vs, 1639m, 1427s, 1320m, 1003m, 939w, 873m, 721m, 622w, 542m. The thermogravimetric curve of the title compound is shown in Fig. 3a. 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. 3b. 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 Uiso values were set to 1.2U eq of the parent atoms.

Table 2

| Experimental details |
|----------------------|
| Chemical formula     | Rb6[B12O18(OH)6]·2H2O |
| M r                  | 1068.62               |
| Crystal system, space group | Orthorhombic, Pnam |
| Temperature (K)      | 296                   |
| a, b, c (Å)          | 13.395 (4), 9.251 (2), 12.368 (4) |
| Z                    | 2                     |
| Radiation type       | Mo Kα                 |
| μ (mm⁻¹)             | 9.60                  |
| Crystal size (mm)    | 0.08 × 0.07 × 0.07    |

Data collection

Diffractometer Bruker APEX2
Absorption correction Multi-scan (SADABS; Krause et al., 2015)

No. of measured, independent and observed | 1980 | 1523 |
| ∣ wR2 | 0.061, 0.173, 1.07 |
| No. of reflections | 1980 |
| No. of parameters | 110 |
| H-atom treatment | H-atom parameters constrained |
| δFmax, δFmin (e Å⁻³) | 1.57, −1.16 |

Computer programs: APEX2 and SADINT (Bruker, 2014), SHELXTL2018/3 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b) and SHELXTL (Sheldrick, 2008).

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Crystal structure of Rb₆[B₁₂O₁₈(OH)₆]·2H₂O

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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, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

hexarubidium hexahydroxydodecaborate dihydrate, Rb₆[B₁₂O₁₈(OH)₆]·2H₂O

Crystal data

| Parameter               | Value                          |
|-------------------------|--------------------------------|
| Chemical formula        | Rb₆[B₁₂O₁₈(OH)₆]·2H₂O          |
| Mr                      | 1068.62                        |
| Crystal system          | Orthorhombic                    |
| Space group             | Pnnm                           |
| a (Å)                   | 13.395 (4)                     |
| b (Å)                   | 9.251 (2)                      |
| c (Å)                   | 12.368 (4)                     |
| V (Å³)                  | 1532.7 (7)                     |
| Z                        | 2                              |
| F(000)                  | 1000                           |

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)

Tmin = 0.452, Tmax = 0.746

17510 measured reflections
1980 independent reflections
1523 reflections with I > 2σ(I)

Refinement

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.061

wr( F²) = 0.173

S = 1.07

1980 reflections
110 parameters
0 restraints

Hydrogen site location: difference Fourier map

H-atom parameters constrained

w = 1/[σ²(Fo²) + (0.0825P)² + 9.4675P]

where P = (Fo² + 2Fc²)/3

(Δσ)max < 0.001

Δρmax = 1.57 e Å⁻³

Δρmin = -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(eq)  |
|-----|-------|-------|-------|--------|
| 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* |
| 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) |
| 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)**

|     | U¹¹ | U¹² | U¹³ | U²² | U²³ | U³³ |
|-----|-----|-----|-----|-----|-----|-----|
| 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, °)

| Bond          | Length (Å) | Bond          | Length (Å) |
|---------------|------------|---------------|------------|
| Rb1—O3       | 2.980 (4)  | Rb3—O5       | 3.105 (4)  |
| Rb1—O3i      | 2.980 (4)  | Rb3—O3ii     | 3.114 (4)  |
| Rb1—O3ii     | 2.980 (4)  | Rb3—O1vi     | 3.359 (5)  |
| Rb1—O3iii    | 2.980 (4)  | Rb3—B3       | 3.491 (5)  |
| Rb1—O6iv     | 3.166 (6)  | Rb3—B2       | 3.5061 (19)|
| Rb1—O6v      | 3.166 (6)  | Rb3—B3'      | 3.603 (5)  |
| Rb1—B2iii    | 3.610 (7)  | Rb3—B4'      | 3.729 (5)  |
| Rb1—B2       | 3.610 (7)  | O1—B1        | 1.374 (7)  |
| Rb1—Rb3      | 4.4556 (12)| O1—H1        | 0.9433     |
| Rb1—Rb3'     | 4.4556 (12)| O2—B1        | 1.357 (6)  |
| Rb1—Rb3''    | 4.4556 (12)| O2—B3        | 1.495 (6)  |
| Rb1—Rb3iii   | 4.4556 (12)| O3—B1        | 1.350 (7)  |
| Rb2—O4vi     | 2.793 (5)  | O3—B2        | 1.496 (5)  |
| Rb2—O4       | 2.793 (5)  | O4—B3''      | 1.453 (5)  |
| Rb2—O2vii    | 3.058 (4)  | O4—B3''      | 1.453 (5)  |
| Rb2—O2viii   | 3.058 (4)  | O5—B4        | 1.354 (5)  |
| Rb2—O2ix     | 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—B3v      | 3.488 (5)  | O6—H6''      | 0.8200     |
| Rb2—B3vi     | 3.488 (5)  | O7—B3        | 1.441 (6)  |
| Rb2—Rb3v     | 4.3609 (11)| O7—B2        | 1.452 (5)  |
| Rb2—Rb3''    | 4.3609 (11)| O8—H8A       | 0.8500     |
| Rb3—O7       | 2.816 (4)  | O8—H8B       | 0.8500     |
| Rb3—O2v      | 2.963 (4)  | O8—H8B'      | 0.8500     |
| Rb3—O5v      | 2.974 (4)  |                |            |
| O3—Rb1—O3i   | 132.24 (13)| O3''—Rb3—O1vi| 158.35 (10)|
| O3—Rb1—O3ii  | 47.76 (13) | O7—Rb3—B3    | 23.42 (11) |
| O3''—Rb1—O3a | 180.00 (5) | O2''—Rb3—B3  | 154.19 (11)|
| O3—Rb1—O3iii | 180.0       | O5''—Rb3—B3  | 150.79 (11)|
| O3''—Rb1—O3ii| 47.76 (13) | O5—Rb3—B3    | 25.25 (10) |
| O3''—Rb1—O3a | 132.24 (13)| O3''—Rb3—B3  | 67.90 (10) |
| O3—Rb1—O6v   | 66.97 (7)  | O1''—Rb3—B3  | 91.11 (11) |
| O3''—Rb1—O6a | 66.97 (7)  | O7—Rb3—B2    | 23.45 (12) |
| O3''—Rb1—O6a | 113.03 (7) | O2''—Rb3—B2  | 151.80 (8) |
| O3''—Rb1—O6v | 113.03 (7) | O5''—Rb3—B2  | 108.86 (9) |
| O3—Rb1—O6a   | 113.03 (7) | O5—Rb3—B2    | 67.94 (10) |
| O3''—Rb1—O6v | 113.03 (7) | O3''—Rb3—B2  | 25.24 (9)  |
| O3—Rb1—O6v   | 66.97 (7)  | O1''—Rb3—B2  | 133.79 (11)|
| O3''—Rb1—O6v | 66.97 (7)  | B3—Rb3—B2    | 42.74 (11) |
| O6v—Rb1—O6v  | 180.0      | O7—Rb3—B3v   | 146.09 (12)|
| O3—Rb1—B2iii | 156.12 (7) | O2v—Rb3—B3v  | 23.88 (10) |
| O3—Rb1—B2''  | 23.88 (7)  | O5—Rb3—B3v   | 23.81 (10) |
| O3''—Rb1—B2''| 156.12 (7) | O5—Rb3—B3v   | 155.00 (10)|
| Bond                      | Distance (Å) | Bond                      | Distance (Å) |
|---------------------------|--------------|---------------------------|--------------|
| O3̅i—Rb1—B2̅ii            | 23.88 (7)    | O3̅—Rb3—B3̅              | 106.72 (10)  |
| O6̅i—Rb1—B2̅ii            | 90.0         | O1̅i—Rb3—B3̅              | 92.62 (11)   |
| O6̅—Rb1—B2̅ii             | 90.0         | B3—Rb3—B3̅               | 166.87 (12)  |
| O3̅—Rb1—B2                | 23.88 (7)    | B2—Rb3—B3̅               | 131.60 (10)  |
| O3̅i—Rb1—B2̅              | 156.12 (7)   | O7—Rb3—B4̅               | 121.68 (14)  |
| O3̅—Rb1—B2                | 23.88 (7)    | O2̅—Rb3—B4̅               | 62.59 (13)   |
| O6̅—Rb1—B2                | 156.12 (7)   | O5̅—Rb3—B4̅               | 19.43 (12)   |
| O6̅—Rb1—B2                | 90.0         | O5—Rb3—B4̅               | 165.50 (14)  |
| O6̅—Rb1—B2                | 90.0         | O3̅—Rb3—B4̅               | 74.88 (13)   |
| B2̅ii—Rb1—B2              | 180.0        | O1̅i—Rb3—B4̅              | 126.70 (14)  |
| O3̅—Rb1—Rb3               | 63.01 (7)    | B3—Rb3—B4̅               | 141.27 (14)  |
| O3̅i—Rb1—Rb3              | 135.79 (7)   | B2—Rb3—B4̅               | 99.31 (15)   |
| O3̅—Rb1—Rb3               | 44.21 (7)    | B3—Rb3—B4̅               | 39.47 (14)   |
| O3̅—Rb1—Rb3               | 116.99 (7)   | O3̅—Rb3—B4̅               | 135.72 (7)  |
| O6̅—Rb1—Rb3               | 119.50 (7)   | O2̅—Rb3—B4̅               | 44.45 (7)    |
| O6̅—Rb1—Rb3               | 60.50 (7)    | O5̅—Rb3—B4̅               | 65.47 (7)    |
| B2̅ii—Rb1—Rb3              | 129.79 (15)  | O5—Rb3—B4̅               | 122.29 (7)  |
| B2—Rb1—Rb3                | 50.20 (15)   | O3̅—Rb3—B4̅               | 135.72 (7)  |
| O3—Rb1—Rb3i               | 135.79 (7)   | O1i—Rb3—Rb2               | 64.64 (7)    |
| O3̅—Rb1—Rb3i              | 63.01 (7)    | B3—Rb3—Rb2               | 141.29 (9)   |
| O3̅i—Rb1—Rb3i              | 116.99 (7)  | B2—Rb3—Rb2               | 150.36 (11)  |
| O3̅ii—Rb1—Rb3i             | 44.21 (7)   | B3—Rb3—Rb2               | 50.87 (8)    |
| O6̅—Rb1—Rb3i              | 119.50 (7)   | B4—Rb3—Rb2               | 65.52 (11)   |
| O6—Rb1—Rb3i               | 60.50 (7)    | O7—Rb3—Rb1               | 74.06 (8)    |
| B2̅ii—Rb1—Rb3i             | 50.20 (15)   | O2̅—Rb3—Rb1               | 121.65 (7)   |
| B2—Rb1—Rb3i               | 129.79 (15)  | O5̅—Rb3—Rb1               | 78.67 (7)    |
| Rb3—Rb1—Rb3i              | 79.60 (3)    | O5—Rb3—Rb1               | 105.16 (7)   |
| O3—Rb1—Rb3i               | 44.21 (7)    | O3̅—Rb3—Rb1               | 41.86 (7)    |
| O3̅—Rb1—Rb3i              | 116.99 (7)   | O1i—Rb3—Rb1               | 145.17 (7)   |
| O3̅ii—Rb1—Rb3i             | 63.01 (7)   | B3—Rb3—Rb1               | 84.08 (9)    |
| O6̅—Rb1—Rb3i              | 135.79 (7)   | B2—Rb3—Rb1               | 52.28 (12)   |
| O6—Rb1—Rb3i               | 60.50 (7)    | B3—Rb3—Rb1               | 99.81 (8)    |
| B2̅ii—Rb1—Rb3i             | 119.50 (7)   | B4—Rb3—Rb1               | 60.50 (11)   |
| B2—Rb1—Rb3i               | 129.79 (14)  | Rb2—Rb3—Rb1               | 98.86 (3)    |
| Rb3—Rb1—Rb3i              | 50.20 (14)   | B1—O1—Rb3i               | 116.5 (4)    |
| Rb3—Rb1—Rb3i              | 100.40 (3)   | B1—O1—H1                 | 96.8         |
| Rb3—Rb1—Rb3i              | 180.0        | Rb3i—O1—H1               | 78.5         |
| O3—Rb1—Rb3ii              | 116.99 (7)   | B1—O2—B3                 | 120.9 (4)    |
| O3̅—Rb1—Rb3ii             | 44.21 (7)    | B1—O2—Rb3i               | 120.5 (3)    |
| O3̅—Rb1—Rb3ii             | 135.79 (7)   | B3—O2—Rb3i               | 102.8 (2)    |
| O6̅—Rb1—Rb3ii             | 63.01 (7)    | B1—O2—Rb2                | 119.9 (3)    |
| O6—Rb1—Rb3ii              | 60.50 (7)    | B3—O2—Rb2                | 93.7 (3)     |
| O6—Rb1—Rb3ii              | 119.50 (7)   | Rb3—O2—Rb2               | 92.81 (9)    |
| B2̅—Rb1—Rb3ii              | 50.20 (14)   | B1—O3—B2                 | 121.0 (4)    |
| B2—Rb1—Rb3ii              | 129.79 (14)  | B1—O3—Rb1                | 118.4 (3)    |
| Rb3—Rb1—Rb3ii             | 180.0        | B2—O3—Rb1                | 102.4 (3)    |
| Rb3—Rb1—Rb3iii            | 100.40 (3)   | B1—O3—Rb3i               | 122.9 (3)    |
| Rb3—Rb1—Rb3iii            | 79.60 (3)    | B2—O3—Rb3i               | 92.20 (15)   |

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| Bond          | Bond Length (Å) | Bond Angle (°) |
|--------------|-----------------|----------------|
| O4vi—Rb2—O4  | 180.0           |                |
| O4vi—Rb2—O2vi | 132.41 (6)      |                |
| O4—Rb2—O2vi  | 47.59 (6)       |                |
| O4vi—Rb2—O2iii | 47.59 (6)      |                |
| O4—Rb2—O2     | 132.41 (6)      |                |
| O2vi—Rb2—O2iii | 180.0           |                |
| O4vi—Rb2—O2vi | 47.59 (6)       |                |
| O4—Rb2—O2     | 132.41 (6)      |                |
| O2vi—Rb2—O2   | 86.08 (13)      |                |
| O3—Rb1        | 93.93 (9)       |                |
| B3—O4—Rb2     | 106.2 (3)       |                |
| B3—O4—Rb2     | 124.6 (5)       |                |
| B3—O4—Rb2     | 113.6 (4)       |                |
| B3—O4—Rb2     | 102.5 (3)       |                |
| B3—O4—Rb2     | 123.3 (4)       |                |
| B3—O4—Rb2     | 92.0 (3)        |                |
| B3—O4—Rb2     | 98.83 (10)      |                |
| B3—O4—Rb2     | 128.7 (5)       |                |
| B3—O4—Rb2     | 125.4           |                |
| B3—O4—Rb2     | 79.7            |                |
| B3—O4—Rb2     | 125.35 (13)     |                |
| B3—O4—Rb2     | 79.74 (6)       |                |
| B3—O4—Rb2     | 102.7           |                |
| B3—O4—Rb2     | 123.7 (3)       |                |
| B3—O4—Rb2     | 105.6 (3)       |                |
| B3—O4—Rb2     | 106.0 (3)       |                |
| B3—O4—Rb2     | 107.7           |                |
| B3—O4—Rb2     | 97.83           |                |
| B3—O4—Rb2     | 101.8 (2)       |                |
| B3—O4—Rb2     | 62.57 (15)      |                |
| B3—O4—Rb2     | 101.8 (2)       |                |
| B3—O4—Rb2     | 50.52 (19)      |                |
| B3—O4—Rb2     | 150.8 (3)       |                |
| B3—O4—Rb2     | 101.8 (2)       |                |
| B3—O4—Rb2     | 62.57 (15)      |                |
| B3—O4—Rb2     | 155.0 (2)       |                |
| B3—O4—Rb2     | 123.3 (3)       |                |
| B3—O4—Rb2     | 123.3 (3)       |                |
| B3—O4—Rb2     | 53.8 (3)        |                |
| B3—O4—Rb2     | 53.8 (3)        |                |
| B3—O4—Rb2     | 77.52 (12)      |                |
| Bond/Angle | Value | Unit | Value | Unit |
|-----------|-------|------|-------|------|
| O2viii—Rb2—Rb3ix | 102.80 (7) |  | Rh3iii—B2—Rb1 | 77.52 (12) |
| O2vi—Rb2—Rb3ix | 42.74 (7) |  | O7—B3—O4 | 112.5 (4) |
| O2—Rb2—Rb3ix | 137.26 (7) |  | O7—B3—O5 | 108.2 (4) |
| B3—Rb2—Rb3ix | 126.76 (8) |  | O4—B3—O5 | 110.8 (4) |
| B3viii—Rb2—Rb3ix | 96.67 (8) |  | O7—B3—O2 | 111.3 (4) |
| B3vi—Rb2—Rb3x | 83.33 (8) |  | O4—B3—O2 | 107.2 (4) |
| O4v—Rb2—Rb3x | 53.24 (8) |  | O5—B3—O2 | 106.9 (4) |
| O4—Rb2—Rb3x | 105.67 (8) |  | O7—B3—Rb2 | 146.6 (3) |
| B3—Rb2—Rb3x | 74.33 (8) |  | O4—B3—Rb2 | 50.3 (3) |
| O3vi—Rb2—Rb3x | 102.80 (7) |  | O5—B3—Rb2 | 105.1 (3) |
| O2viii—Rb2—Rb3x | 42.74 (7) |  | O5—B3—Rb3 | 62.7 (2) |
| O2vi—Rb2—Rb3x | 137.26 (7) |  | O2—B3—Rb3 | 109.2 (3) |
| B3—Rb2—Rb3x | 53.24 (8) |  | O7—B3—Rb3 | 128.1 (3) |
| O7—Rb3—O2v | 153.22 (11) |  | O4—B3—Rb3x | 119.4 (3) |
| O7—Rb3—O5v | 127.55 (10) |  | O5—B3—Rb3x | 53.7 (2) |
| O2—Rb3—O5v | 47.64 (10) |  | O2—B3—Rb3x | 53.3 (2) |
| O7—Rb3—O5 | 46.94 (10) |  | O7—B3—Rb3x | 81.95 (10) |
| O2—Rb3—O5 | 131.85 (10) |  | O2—B3—Rb3x | 124.3 (6) |
| O5—Rb3—O5 | 169.84 (10) |  | O5—B3—O6 | 117.8 (3) |
| O7—Rb3—O3ii | 46.81 (9) |  | O5—B4—O6 | 117.8 (3) |
| O2—Rb3—O3ii | 128.83 (9) |  | O5—B4—Rb3x | 47.0 (3) |
| O5—Rb3—O3ii | 83.65 (10) |  | O5iv—B4—Rb3x | 132.1 (5) |
| O5—Rb3—O3ii | 92.98 (9) |  | O5—B4—Rb3x | 90.9 (3) |
| O7—Rb3—O1xi | 111.56 (10) |  | O5—B4—Rb3xii | 132.1 (5) |
| O2—Rb3—O1xi | 69.14 (10) |  | O5iv—B4—Rb3xii | 47.0 (3) |
| O5—Rb3—O1xi | 116.34 (10) |  | O5—B4—Rb3xii | 90.9 (3) |
| O5—Rb3—O1xi | 65.88 (10) |  | Rh3x—B4—Rb3xii | 99.8 (2) |
| B2—O3—B1—O2 | 4.2 (8) |  | Rh2—O4—B3—O5 | 92.7 (4) |
| Rb1—O3—B1—O2 | −123.3 (5) |  | B3viii—O4—B3—O2 | −147.0 (4) |
| Rb3ix—O3—B1—O2 | 120.5 (5) |  | B2—O4—B3—O2 | −23.6 (4) |
| B2—O3—B1—O1 | −174.3 (5) |  | B3viii—O4—B3—Rb2 | −123.5 (7) |
| Rb1—O3—B1—O1 | 58.2 (6) |  | B2—O4—B3—Rb3 | 40.4 (11) |
| Rb3ix—O3—B1—O1 | −58.1 (6) |  | B2—O4—B3—Rb3x | 163.9 (5) |
| B3—O2—B1—O3 | −3.0 (8) |  | B3viii—O4—B3—Rb3x | −89.9 (6) |
| Rb3ix—O2—B1—O3 | 127.7 (5) |  | Rh2—O4—B3—Rb3x | 33.5 (3) |
| B2—O2—B1—O3 | −118.4 (5) |  | B4—O5—B3—O7 | −107.7 (6) |
| B3—O2—B1—O1 | 175.6 (5) |  | Rh3x—O5—B3—O7 | 124.4 (3) |
| Rb3ix—O2—B1—O1 | −53.8 (6) |  | Rb3—O5—B3—O7 | 23.9 (3) |
| B2—O2—B1—O1 | 60.1 (6) |  | Rb3—O5—B3—O4 | 15.9 (7) |
| Rb3ix—O1—B1—O3 | 91.4 (5) |  | Rh3x—O5—B3—O4 | −111.9 (4) |
| Rh3ix—O1—B1—O2 | −87.2 (5) |  | Rh3—O5—B3—O4 | 147.5 (4) |
| B3—O7—B2—O7 | −87.0 (4) |  | B4—O5—B3—O2 | 132.3 (5) |
### Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A | D···A   | D—H···A |
|-------------|------|-------|---------|---------|
| O8—H8B···O7x | 0.85 | 2.25  | 3.046 (6) | 155     |

Symmetry codes: (i) x, y, z; (ii) −x+1/2, −y−1/2, −z+1; (iii) −x+1/2, −y−1/2, −z+1; (iv) x+1/2, y+1/2, z; (v) −x+1, −y+1/2, −z+1; (vi) −x+1/2, y+1/2, −z+1; (vii) x−1, y+1, z; (viii) x+1, y+1, z; (ix) x+1, −y+1, z; (x) x+1, −y+1, z+1; (xi) x+1, −y+1, −z+1; (xii) x+1, −y+1, −z+1; (xiii) x+1, −y+1, −z+1.
| Bond                  | d (Å) | r (Å) | D (Å)  | Θ (°) |
|-----------------------|-------|-------|--------|-------|
| O8—H8B···O4\textsuperscript{x} | 0.85  | 1.68  | 2.224 (7) | 119   |
| O8—H8A···O7\textsuperscript{xiv} | 0.85  | 1.70  | 2.231 (5) | 118   |
| O8—H8A···O4\textsuperscript{xiv} | 0.85  | 2.17  | 2.958 (7) | 155   |
| O6—H6···O1\textsuperscript{xi} | 0.82  | 1.86  | 2.670 (5) | 167   |
| O1—H1···O6\textsuperscript{vi} | 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.