

# Poly[ $\mu$ -aqua-aqua- $\mu_4$ -naphthalene-1,8-dicarboxylato-barium]: a layer structure

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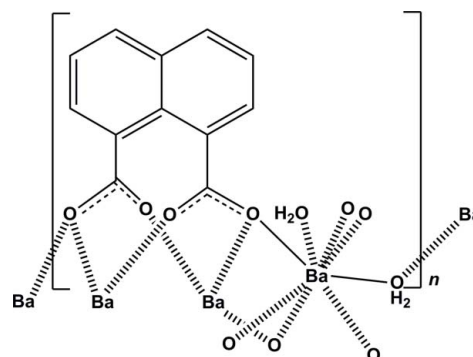
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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(C-C) = 0.004$  Å;  $R$  factor = 0.019;  $wR$  factor = 0.043; data-to-parameter ratio = 17.8.

The title compound,  $[Ba(C_{12}H_6O_4)(H_2O)_2]_n$ , is represented by a layer-like structure built of  $BaO_8$  polyhedra. The asymmetric unit contains a  $Ba^{2+}$  ion, half a coordinating water molecule and half a  $\mu_4$ -bridging naphthalene-1,8-dicarboxylate (1,8-nap) ligand, the whole structure being generated by twofold rotational symmetry. The carboxylate groups of the 1,8-nap ligands act as bridges linking four  $Ba^{2+}$  ions, while each  $Ba^{2+}$  ion is eight-coordinated by O atoms from four 1,8-nap ligands and two coordinating water molecules. In the crystal, there are  $O-H \cdots O$  hydrogen bonds involving the water molecules and carboxylate O atoms in the  $BaO_8$  polyhedra. Each  $BaO_8$  polyhedron is connected *via* corner-sharing water O atoms or edge-sharing ligand O atoms, forming a sheet parallel to the  $bc$  plane. These sheets stack along the  $a$ -axis direction and are connected *via* van der Waals forces only. The naphthalene groups protrude above and below the layers of the  $BaO_8$  polyhedra and there are voids of *ca*  $208$  Å<sup>3</sup> bounded by these groups. No residual electron density was found in this region. The crystal studied was twinned by pseudo-merohedry, with a refined twin component ratio of 0.5261 (1):0.4739 (1).

## Related literature

For other compounds based on 1,8-nap ligands, see: Wen *et al.* (2007, 2008); Zhang *et al.* (2008); Fu *et al.* (2011).



## Experimental

### Crystal data

$[Ba(C_{12}H_6O_4)(H_2O)_2]$   
 $M_r = 369.52$   
 Orthorhombic,  $Ibca$   
 $a = 8.9643$  (11) Å  
 $b = 30.539$  (6) Å  
 $c = 8.9625$  (12) Å

$V = 2453.6$  (7) Å<sup>3</sup>  
 $Z = 8$   
 Mo  $K\alpha$  radiation  
 $\mu = 3.25$  mm<sup>-1</sup>  
 $T = 296$  K  
 $0.20 \times 0.05 \times 0.05$  mm

### Data collection

Bruker APEXII CCD area-detector diffractometer  
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)  
 $T_{min} = 0.563$ ,  $T_{max} = 0.855$

7968 measured reflections  
 1511 independent reflections  
 1344 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.035$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$   
 $wR(F^2) = 0.043$   
 $S = 1.05$   
 1511 reflections

85 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{max} = 0.54$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.57$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$      | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---------------------|-------|--------------|--------------|----------------|
| $O3-H3 \cdots O2^i$ | 0.86  | 2.07         | 2.777 (2)    | 140            |

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2556).

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## supporting information

*Acta Cryst.* (2013). E69, m219–m220 [doi:10.1107/S1600536813006259]

## Poly[ $\mu$ -aqua-aqua- $\mu_4$ -naphthalene-1,8-dicarboxylato-barium]: a layer structure

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### S1. Comment

In recent years, supramolecular assemblies based on polyoxometalates (POMs) have been intensively investigated in many field such as catalysis, electrical conductivity, and biological chemistry. The ligand naphthalene-1,8-dicarboxylic (1,8-nap) has been used extensively to construct a number of metal organic complexes (Wen *et al.*, 2007,2008; Zhang *et al.*, 2008), including the related barium compound Ba(C<sub>12</sub>H<sub>6</sub>O<sub>4</sub>) [Fu *et al.*, 2011]. To prepare a new barium complex incorporating 1,8-nap ligand, we have synthesized the title compound and report herein on its crystal structure.

The title compound is a non-interpenetrating two-dimensional layer-like structure consisting of BaO<sub>8</sub> clusters, which are similar to the reported compound Ba(C<sub>12</sub>H<sub>6</sub>O<sub>4</sub>) [Fu *et al.*, 2011]. As shown in Fig. 1 the asymmetric unit of the title complex contains one crystallographically independent Ba atom, one coordination water molecule and a half 1,8-nap ligand. Each barium atom is eight-coordinated by O atoms in a square antiprismatic geometry, in which six oxygen atoms come from four 1,8-nap ligands (two of them adopt a chelate connection) and two oxygen atoms come from two coordinated water molecules. The Ba–O bond distances range from 2.723 (2) to 2.8806 (14) Å, in which the Ba1–O3 water bond gives the longest bond distance.

The 1,8-nap ligands are not planar, with the carboxylate groups and the naphthalene ring dihedral angles being 49.0 (3)° and 52.4 (3)°, respectively. The carboxylate groups of the 1,8-nap ligand act as  $\mu_2$ -bridges to link four Ba atoms. Furthermore, each BaO<sub>8</sub> polyhedra is connected *via* corner-sharing H<sub>2</sub>O oxygen atoms or edge-sharing ligand oxygen atoms to form a two-dimensional sheet parallel to the *bc* plane. All Ba atoms in the two-dimensional layer are coplanar, with adjacent Ba···Ba distance of 4.4821 (6), 4.9292 (6) and 5.0972 (6) Å.

By considering the Ba atoms as the nodes, this two-dimensional layered structure can be topologically represented as a 6-connected (3,6) net.

In the crystal, there are O–H···O hydrogen bonds involving the water molecules and the carboxylate O atoms in the BaO<sub>8</sub> clusters (Fig. 2 and Table 1). There are no  $\pi$ - $\pi$  stacking interactions, only van der Waals forces are present between the layers that stack along the *a* direction. The naphthalene groups protrude above and below the layers of the BaO<sub>8</sub> clusters and there are voids of ca. 208 Å<sup>3</sup> bounded by these groups. No residual electron density was found in this region.

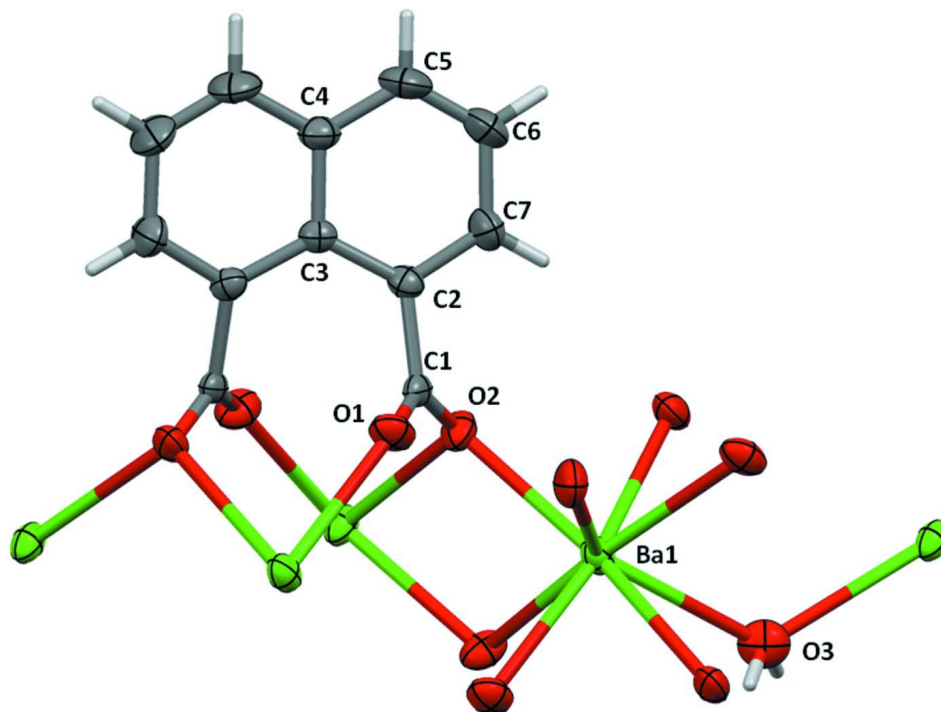
### S2. Experimental

A mixture of naphthalene-1,8-dicarboxylic (0.2 g), BaCO<sub>3</sub> (0.05 g) and H<sub>2</sub>O (15 ml) was heated at 443 K for 3 d in a sealed 25 ml Teflon-lined stainless steel vessel under autogenous pressure. After cooling to room temperature at a rate of 20°C h<sup>-1</sup>, colourless prismatic crystals suitable for single-crystal X-ray diffraction analysis were obtained in low yield.

### S3. Refinement

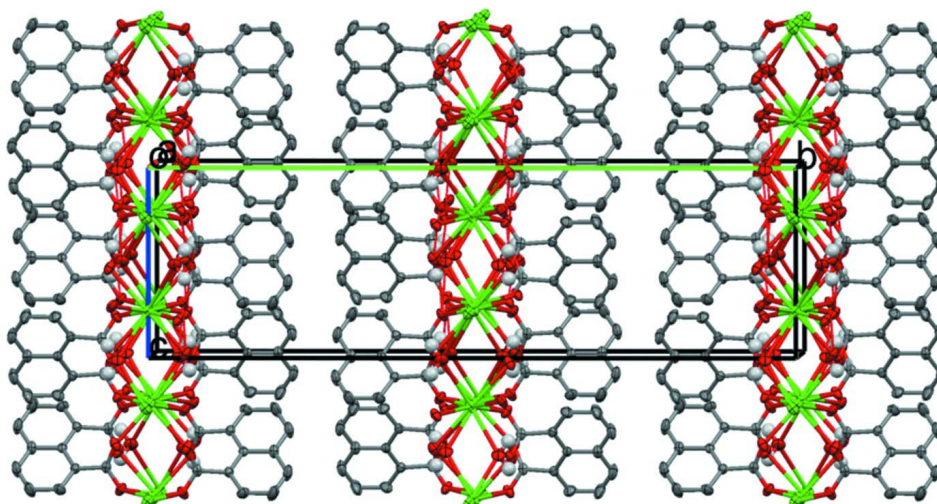
The crystal is a pseudo-merohedral twin, with twin law (00-1, 0-10, -100) giving an ca. 1:1 ratio of twin moieties [refined BASF value = 0.5261 (1)]. The C-bound H atoms were positioned geometrically and refined with a riding model: C—H

= 0.93 Å with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The water H atoms were located in difference Fourier maps and refined initially with distance restraints: O–H = 0.86 Å, then as riding atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ .



**Figure 1**

The molecular structure of the title compound showing the coordination environment of the Ba atom. Displacement ellipsoids are drawn at the 50% probability level



**Figure 2**

A view along the a axis of the crystal packing of the title compound. The O–H...O hydrogen bonds are shown as red dashed lines (see Table 1 for details).

Poly[ $\mu$ -aqua-aqua- $\mu_4$ -naphthalene-1,8-dicarboxylato-barium]

## Crystal data

[Ba(C<sub>12</sub>H<sub>6</sub>O<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>] $M_r = 369.52$ Orthorhombic, *Ibca*

Hall symbol: -I 2b 2c

 $a = 8.9643$  (11) Å $b = 30.539$  (6) Å $c = 8.9625$  (12) Å $V = 2453.6$  (7) Å<sup>3</sup> $Z = 8$  $F(000) = 1408$  $D_x = 2.001$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2836 reflections

 $\theta = 2.7$ – $27.1^\circ$  $\mu = 3.25$  mm<sup>-1</sup> $T = 296$  K

Prism, colourless

 $0.20 \times 0.05 \times 0.05$  mm

## Data collection

Bruker APEXII CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 83.33 pixels mm<sup>-1</sup> $\omega$  scansAbsorption correction: multi-scan  
(*SADABS*; Sheldrick, 1996) $T_{\min} = 0.563$ ,  $T_{\max} = 0.855$ 

7968 measured reflections

1511 independent reflections

1344 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.035$  $\theta_{\max} = 28.4^\circ$ ,  $\theta_{\min} = 1.3^\circ$  $h = -11 \rightarrow 5$  $k = -40 \rightarrow 38$  $l = -11 \rightarrow 10$ 

## Refinement

Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.019$  $wR(F^2) = 0.043$  $S = 1.05$ 

1511 reflections

85 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
mapHydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0197P)^2 + 0.1976P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 0.54$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.57$  e Å<sup>-3</sup>

## 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.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

|     | <i>x</i>    | <i>y</i>    | <i>z</i>   | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|------------|----------------------------------|
| Ba1 | 0.61452 (2) | 0.0000      | 0.2500     | 0.02892 (7)                      |
| O1  | 0.4190 (2)  | 0.05878 (6) | 0.5240 (3) | 0.0360 (5)                       |
| C1  | 0.3754 (3)  | 0.07360 (9) | 0.4035 (4) | 0.0236 (6)                       |
| O2  | 0.3671 (2)  | 0.05119 (7) | 0.2858 (2) | 0.0341 (5)                       |

|    |            |              |            |             |
|----|------------|--------------|------------|-------------|
| C2 | 0.3410 (3) | 0.12190 (9)  | 0.3935 (3) | 0.0253 (6)  |
| O3 | 0.7500     | -0.04396 (9) | 0.0000     | 0.0418 (8)  |
| H3 | 0.7197     | -0.0594      | -0.0742    | 0.050*      |
| C3 | 0.2500     | 0.14342 (12) | 0.5000     | 0.0239 (8)  |
| C4 | 0.2500     | 0.19041 (12) | 0.5000     | 0.0324 (10) |
| C5 | 0.3323 (4) | 0.21277 (11) | 0.3902 (5) | 0.0486 (10) |
| H5 | 0.3325     | 0.2432       | 0.3899     | 0.058*      |
| C6 | 0.4105 (4) | 0.19121 (11) | 0.2860 (4) | 0.0527 (10) |
| H6 | 0.4610     | 0.2067       | 0.2123     | 0.063*      |
| C7 | 0.4163 (4) | 0.14507 (10) | 0.2877 (3) | 0.0386 (8)  |
| H7 | 0.4720     | 0.1303       | 0.2160     | 0.046*      |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| Ba1 | 0.01894 (11) | 0.03182 (12) | 0.03599 (14) | 0.000        | 0.000        | 0.00999 (13) |
| O1  | 0.0321 (12)  | 0.0315 (11)  | 0.0445 (13)  | 0.0027 (9)   | -0.0065 (10) | 0.0124 (10)  |
| C1  | 0.0140 (12)  | 0.0213 (14)  | 0.0356 (16)  | -0.0012 (10) | 0.0042 (11)  | -0.0009 (12) |
| O2  | 0.0330 (11)  | 0.0314 (11)  | 0.0380 (14)  | -0.0029 (8)  | 0.0096 (8)   | -0.0132 (9)  |
| C2  | 0.0279 (15)  | 0.0225 (15)  | 0.0255 (15)  | -0.0033 (12) | -0.0016 (11) | -0.0004 (12) |
| O3  | 0.0412 (19)  | 0.0472 (18)  | 0.037 (2)    | 0.000        | -0.0162 (15) | 0.000        |
| C3  | 0.025 (2)    | 0.0220 (19)  | 0.025 (2)    | 0.000        | -0.0046 (16) | 0.000        |
| C4  | 0.034 (2)    | 0.022 (2)    | 0.041 (3)    | 0.000        | -0.0010 (19) | 0.000        |
| C5  | 0.061 (2)    | 0.0203 (17)  | 0.065 (3)    | -0.0016 (16) | 0.0042 (19)  | 0.0087 (16)  |
| C6  | 0.067 (2)    | 0.0326 (18)  | 0.058 (3)    | -0.0034 (16) | 0.0213 (19)  | 0.0164 (15)  |
| C7  | 0.0463 (18)  | 0.0366 (17)  | 0.033 (2)    | -0.0007 (14) | 0.0128 (13)  | 0.0060 (13)  |

*Geometric parameters (Å, °)*

|   |             |   |              |
|---|-------------|---|--------------|
| Ba1—O1 <sup>i</sup>                     | 2.723 (2)   | C2—C7                                     | 1.362 (4)    |
| Ba1—O1 <sup>ii</sup>                    | 2.723 (2)   | C2—C3                                     | 1.417 (3)    |
| Ba1—O2 <sup>iii</sup>                   | 2.7324 (19) | O3—Ba1 <sup>viii</sup>                    | 2.8806 (14)  |
| Ba1—O2                                  | 2.7324 (19) | O3—H3                                     | 0.8587       |
| Ba1—O2 <sup>iv</sup>                    | 2.7703 (19) | C3—C2 <sup>ix</sup>                       | 1.417 (3)    |
| Ba1—O2 <sup>v</sup>                     | 2.7703 (19) | C3—C4                                     | 1.435 (5)    |
| Ba1—O3 <sup>vi</sup>                    | 2.8806 (14) | C4—C5 <sup>ix</sup>                       | 1.407 (4)    |
| Ba1—O3                                  | 2.8806 (14) | C4—C5                                     | 1.407 (4)    |
| O1—C1                                   | 1.234 (4)   | C5—C6                                     | 1.341 (5)    |
| O1—Ba1 <sup>ii</sup>                    | 2.723 (2)   | C5—H5                                     | 0.9300       |
| C1—O2                                   | 1.259 (4)   | C6—C7                                     | 1.410 (4)    |
| C1—C2                                   | 1.509 (4)   | C6—H6                                     | 0.9300       |
| O2—Ba1 <sup>vii</sup>                   | 2.7703 (19) | C7—H7                                     | 0.9300       |
| O1 <sup>i</sup> —Ba1—O1 <sup>ii</sup>   | 167.34 (9)  | O2 <sup>iv</sup> —Ba1—Ba1 <sup>vii</sup>  | 144.82 (4)   |
| O1 <sup>i</sup> —Ba1—O2 <sup>iii</sup>  | 101.55 (6)  | O2 <sup>v</sup> —Ba1—Ba1 <sup>vii</sup>   | 144.82 (4)   |
| O1 <sup>ii</sup> —Ba1—O2 <sup>iii</sup> | 67.71 (6)   | O3 <sup>vi</sup> —Ba1—Ba1 <sup>vii</sup>  | 114.937 (13) |
| O1 <sup>i</sup> —Ba1—O2                 | 67.71 (6)   | O3—Ba1—Ba1 <sup>vii</sup>                 | 114.937 (13) |
| O1 <sup>ii</sup> —Ba1—O2                | 101.55 (6)  | C1 <sup>iii</sup> —Ba1—Ba1 <sup>vii</sup> | 50.87 (4)    |

|   |            |   |             |
|---|------------|---|-------------|
| O2 <sup>iii</sup> —Ba1—O2                 | 71.48 (8)  | C1—Ba1—Ba1 <sup>vii</sup>                 | 50.87 (4)   |
| O1 <sup>i</sup> —Ba1—O2 <sup>iv</sup>     | 68.40 (6)  | O1 <sup>i</sup> —Ba1—Ba1 <sup>iv</sup>    | 96.33 (4)   |
| O1 <sup>ii</sup> —Ba1—O2 <sup>iv</sup>    | 123.25 (6) | O1 <sup>ii</sup> —Ba1—Ba1 <sup>iv</sup>   | 96.33 (4)   |
| O2 <sup>iii</sup> —Ba1—O2 <sup>iv</sup>   | 166.59 (9) | O2 <sup>iii</sup> —Ba1—Ba1 <sup>iv</sup>  | 144.26 (4)  |
| O2—Ba1—O2 <sup>iv</sup>                   | 110.74 (7) | O2—Ba1—Ba1 <sup>iv</sup>                  | 144.26 (4)  |
| O1 <sup>i</sup> —Ba1—O2 <sup>v</sup>      | 123.25 (6) | O2 <sup>iv</sup> —Ba1—Ba1 <sup>iv</sup>   | 35.18 (4)   |
| O1 <sup>ii</sup> —Ba1—O2 <sup>v</sup>     | 68.40 (6)  | O2 <sup>v</sup> —Ba1—Ba1 <sup>iv</sup>    | 35.18 (4)   |
| O2 <sup>iii</sup> —Ba1—O2 <sup>v</sup>    | 110.74 (7) | O3 <sup>vi</sup> —Ba1—Ba1 <sup>iv</sup>   | 65.063 (13) |
| O2—Ba1—O2 <sup>v</sup>                    | 166.59 (9) | O3—Ba1—Ba1 <sup>iv</sup>                  | 65.063 (13) |
| O2 <sup>iv</sup> —Ba1—O2 <sup>v</sup>     | 70.35 (8)  | C1 <sup>iii</sup> —Ba1—Ba1 <sup>iv</sup>  | 129.13 (4)  |
| O1 <sup>i</sup> —Ba1—O3 <sup>vi</sup>     | 108.54 (7) | C1—Ba1—Ba1 <sup>iv</sup>                  | 129.13 (4)  |
| O1 <sup>ii</sup> —Ba1—O3 <sup>vi</sup>    | 77.00 (7)  | Ba1 <sup>vii</sup> —Ba1—Ba1 <sup>iv</sup> | 180.0       |
| O2 <sup>iii</sup> —Ba1—O3 <sup>vi</sup>   | 134.45 (5) | C1—O1—Ba1 <sup>ii</sup>                   | 149.05 (19) |
| O2—Ba1—O3 <sup>vi</sup>                   | 89.09 (5)  | O1—C1—O2                                  | 123.5 (3)   |
| O2 <sup>iv</sup> —Ba1—O3 <sup>vi</sup>    | 58.83 (5)  | O1—C1—C2                                  | 118.3 (3)   |
| O2 <sup>v</sup> —Ba1—O3 <sup>vi</sup>     | 80.11 (6)  | O2—C1—C2                                  | 118.0 (3)   |
| O1 <sup>i</sup> —Ba1—O3                   | 77.00 (7)  | O1—C1—Ba1                                 | 84.93 (16)  |
| O1 <sup>ii</sup> —Ba1—O3                  | 108.54 (7) | O2—C1—Ba1                                 | 48.58 (13)  |
| O2 <sup>iii</sup> —Ba1—O3                 | 89.09 (5)  | C2—C1—Ba1                                 | 138.71 (18) |
| O2—Ba1—O3                                 | 134.45 (5) | C1—O2—Ba1                                 | 111.20 (16) |
| O2 <sup>iv</sup> —Ba1—O3                  | 80.11 (6)  | C1—O2—Ba1 <sup>vii</sup>                  | 116.85 (16) |
| O2 <sup>v</sup> —Ba1—O3                   | 58.83 (5)  | Ba1—O2—Ba1 <sup>vii</sup>                 | 109.08 (7)  |
| O3 <sup>vi</sup> —Ba1—O3                  | 130.13 (3) | C7—C2—C3                                  | 120.9 (3)   |
| O1 <sup>i</sup> —Ba1—C1 <sup>iii</sup>    | 93.75 (7)  | C7—C2—C1                                  | 116.6 (3)   |
| O1 <sup>ii</sup> —Ba1—C1 <sup>iii</sup>   | 78.20 (7)  | C3—C2—C1                                  | 122.1 (3)   |
| O2 <sup>iii</sup> —Ba1—C1 <sup>iii</sup>  | 20.22 (6)  | Ba1 <sup>viii</sup> —O3—Ba1               | 124.44 (10) |
| O2—Ba1—C1 <sup>iii</sup>                  | 85.06 (6)  | Ba1 <sup>viii</sup> —O3—H3                | 77.7        |
| O2 <sup>iv</sup> —Ba1—C1 <sup>iii</sup>   | 147.38 (7) | Ba1—O3—H3                                 | 136.4       |
| O2 <sup>v</sup> —Ba1—C1 <sup>iii</sup>    | 100.91 (6) | C2—C3—C2 <sup>ix</sup>                    | 124.8 (3)   |
| O3 <sup>vi</sup> —Ba1—C1 <sup>iii</sup>   | 152.80 (6) | C2—C3—C4                                  | 117.62 (17) |
| O3—Ba1—C1 <sup>iii</sup>                  | 69.07 (6)  | C2 <sup>ix</sup> —C3—C4                   | 117.62 (17) |
| O1 <sup>i</sup> —Ba1—C1                   | 78.20 (7)  | C5 <sup>ix</sup> —C4—C5                   | 121.9 (4)   |
| O1 <sup>ii</sup> —Ba1—C1                  | 93.75 (7)  | C5 <sup>ix</sup> —C4—C3                   | 119.0 (2)   |
| O2 <sup>iii</sup> —Ba1—C1                 | 85.06 (6)  | C5—C4—C3                                  | 119.0 (2)   |
| O2—Ba1—C1                                 | 20.22 (6)  | C6—C5—C4                                  | 121.6 (3)   |
| O2 <sup>iv</sup> —Ba1—C1                  | 100.91 (6) | C6—C5—H5                                  | 119.2       |
| O2 <sup>v</sup> —Ba1—C1                   | 147.38 (7) | C4—C5—H5                                  | 119.2       |
| O3 <sup>vi</sup> —Ba1—C1                  | 69.07 (6)  | C5—C6—C7                                  | 120.2 (3)   |
| O3—Ba1—C1                                 | 152.80 (6) | C5—C6—H6                                  | 119.9       |
| C1 <sup>iii</sup> —Ba1—C1                 | 101.74 (9) | C7—C6—H6                                  | 119.9       |
| O1 <sup>i</sup> —Ba1—Ba1 <sup>vii</sup>   | 83.67 (4)  | C2—C7—C6                                  | 120.5 (3)   |
| O1 <sup>ii</sup> —Ba1—Ba1 <sup>vii</sup>  | 83.67 (4)  | C2—C7—H7                                  | 119.7       |
| O2 <sup>iii</sup> —Ba1—Ba1 <sup>vii</sup> | 35.74 (4)  | C6—C7—H7                                  | 119.7       |
| O2—Ba1—Ba1 <sup>vii</sup>                 | 35.74 (4)  |   |             |

Symmetry codes: (i)  $-x+1, y, z-1/2$ ; (ii)  $-x+1, -y, -z+1$ ; (iii)  $x, -y, -z+1/2$ ; (iv)  $x+1/2, y, -z+1/2$ ; (v)  $x+1/2, -y, z$ ; (vi)  $-x+3/2, -y, z+1/2$ ; (vii)  $x-1/2, y, -z+1/2$ ; (viii)  $-x+3/2, -y, z-1/2$ ; (ix)  $-x+1/2, y, -z+1$ .

*Hydrogen-bond geometry (Å, °)*

| <i>D</i> —H··· <i>A</i> | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|-------------------------|-------------|---------------|-----------------------|-------------------------|
| O3—H3···O2 <sup>x</sup> | 0.86        | 2.07          | 2.777 (2)             | 140                     |

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