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# Monoclinic polymorph of poly[[di- $\mu$ -aqua-triaquadi- $\mu$ -oxalato-barium(II)-copper(II)] monohydrate]

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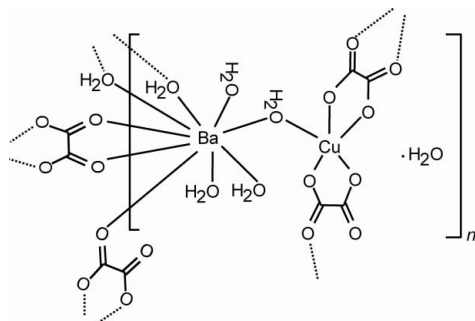
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.020;  $wR$  factor = 0.050; data-to-parameter ratio = 14.1.

A monoclinic polymorph of the title compound,  $\{[\text{BaCu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_5]\cdot\text{H}_2\text{O}\}_n$ , is reported. The structure is best described as a coordination polymer where the  $\text{Cu}^{\text{II}}$  and  $\text{Ba}^{\text{II}}$  centers are coordinated by five and nine O atoms, respectively, in capped quadratic antiprismatic and tetragonal pyramidal geometries. The polymerization arises due to the presence of bridging mono- and bidentate oxalate ligands as well as bridging water molecules. The crystal structure is consolidated by a three-dimensional network of hydrogen bonding.

## Related literature

For related literature, see: B elomb e *et al.* (2003, 2006); Belombe, Nenwa, Bebga *et al.* (2007); B elomb e, Nenwa, Mbiangu e *et al.* (2007); Bouayad *et al.* (1995); Nenwa (2004). For synthesis, see: Kirschner (1960).



## Experimental

### Crystal data

$[\text{BaCu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_5]\cdot\text{H}_2\text{O}$   
 $M_r = 485.02$

Monoclinic,  $C2/c$   
 $a = 15.744$  (2) Å

$b = 10.7565$  (15) Å  
 $c = 15.345$  (2) Å  
 $\beta = 97.331$  (2)°  
 $V = 2577.5$  (6) Å<sup>3</sup>  
 $Z = 8$

Mo  $K\alpha$  radiation  
 $\mu = 4.76$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 $0.28 \times 0.14 \times 0.10$  mm

### Data collection

Bruker APEX CCD area detector diffractometer  
Absorption correction: multi-scan (SADABS; Bruker, 2001)  
 $T_{\text{min}} = 0.462$ ,  $T_{\text{max}} = 0.631$

17321 measured reflections  
3213 independent reflections  
3180 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$   
 $wR(F^2) = 0.050$   
 $S = 1.32$   
3213 reflections  
228 parameters

12 restraints  
All H-atom parameters refined  
 $\Delta\rho_{\text{max}} = 0.49$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.00$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Ba—O11	2.751 (2)	Ba—O15 <sup>i</sup>	2.8765 (19)
Ba—O13	2.770 (2)	Ba—O10	2.9140 (18)
Ba—O7	2.7888 (17)	Cu—O3	1.9252 (16)
Ba—O12	2.800 (2)	Cu—O2	1.9326 (16)
Ba—O8	2.8066 (17)	Cu—O4	1.9393 (17)
Ba—O6	2.8393 (17)	Cu—O1	1.9440 (16)
Ba—O15	2.846 (2)	Cu—O10	2.451 (3)
O3—Cu—O2	174.10 (8)	O2—Cu—O1	84.69 (7)
O3—Cu—O4	85.44 (7)	O4—Cu—O1	165.84 (8)
O2—Cu—O4	93.52 (7)	O4—Cu—O10	96.48 (7)
O3—Cu—O1	94.90 (7)		

Symmetry code: (i)  $-x, y, -z + \frac{1}{2}$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O10—H10A $\cdots$ O7 <sup>ii</sup>	0.82 (2)	1.93 (2)	2.740 (2)	168 (3)
O10—H10B $\cdots$ O5 <sup>iii</sup>	0.80 (2)	2.02 (3)	2.801 (2)	163 (4)
O10—H10B $\cdots$ O8 <sup>ii</sup>	0.80 (2)	2.59 (3)	3.114 (2)	125 (3)
O11—H11A $\cdots$ O2	0.80 (2)	2.13 (3)	2.903 (3)	161 (4)
O11—H11B $\cdots$ O6 <sup>iv</sup>	0.84 (3)	2.00 (3)	2.835 (3)	172 (4)
O11—H11B $\cdots$ O2 <sup>v</sup>	0.84 (3)	2.63 (4)	3.127 (3)	119 (3)
O12—H12A $\cdots$ O1 <sup>vi</sup>	0.80 (2)	1.98 (3)	2.768 (3)	165 (4)
O13—H13A $\cdots$ O5 <sup>vii</sup>	0.82 (3)	2.02 (3)	2.832 (3)	168 (6)
O13—H13B $\cdots$ O14 <sup>i</sup>	0.81 (3)	2.41 (3)	3.180 (4)	159 (6)
O14—H14A $\cdots$ O11 <sup>viii</sup>	0.80 (3)	2.25 (3)	3.041 (3)	171 (5)
O14—H14B $\cdots$ O4 <sup>vii</sup>	0.83 (3)	2.21 (3)	3.007 (3)	163 (5)
O15—H15A $\cdots$ O3 <sup>iv</sup>	0.81 (2)	2.05 (3)	2.845 (3)	165 (4)
O12—H12B $\cdots$ O14	0.78 (2)	2.14 (3)	2.918 (3)	173 (4)
O15—H15B $\cdots$ O14 <sup>i</sup>	0.76 (3)	2.24 (3)	2.952 (3)	156 (5)

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

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2219).

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**supplementary materials**

*Acta Cryst.* (2008). E64, m116-m117 [ doi:10.1107/S1600536807064525 ]

## Monoclinic polymorph of poly[[di- $\mu$ -aqua-triaquadi- $\mu$ -oxalato-barium(II)copper(II)] monohydrate]

J. Nenwa, M. M. Belombe, B. P. T. Fokwa and R. Dronskowski

### Comment

Bouayad *et al.* (1995) reported the structure of the title compound, (I), in the triclinic space group  $P-1$ . Herein, a new polymorph of (I) is reported which crystallizes in the monoclinic space group  $C2/c$ . It was obtained unintentionally from aqueous solution during an on-going study of oxalate-based multifunctional materials (Bélombé *et al.*, 2003, 2006; Belombe, Nenwa, Bebga *et al.*, 2007; Bélombé, Nenwa, Mbiangué *et al.*, 2007; Nenwa, 2004), and is formulated as  $\{[\text{Ba}(\text{H}_2\text{O})_4][\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ . The two polymorphs structurally differ with respect to their crystal systems as well as in their coordination modes around the metal centers and in the formation of their lattice networks in the bulk.

The lattice network reported by Bouayad *et al.* (1995) was shown to be a coordination polymer where each oxalate ion acts as a bidentate ligand, coordinating the metal centers in three different modes: first with the "internal", then with the "external" O atoms linked, respectively to  $\text{Cu}^{\text{II}}$  and  $\text{Ba}^{\text{II}}$  centers (thus generating pentacyclic rings) and, finally, with one "internal" and one "external" oxalato-O atoms bound to a neighboring Ba atom (thus forming a tetracyclic ring). In that structure, each  $\text{Cu}^{\text{II}}$  ion is hexa-coordinated by six O atoms that define a highly distorted octahedral geometry. By contrast, in the monoclinic polymorph, the  $\text{Cu}^{\text{II}}$  atom is penta-coordinated in an approximately square pyramidal geometry defined by five O atoms, with the Cu site slightly displaced from the least-squares plane through the O1–O4 atoms towards the axial water-O10 atom (Fig. 1). Therein, the coordination sphere around each  $\text{Ba}^{\text{II}}$  center which assumes coordination number nine, as opposed to coordination number eleven in the triclinic polymorph, is emphasized. In the monoclinic form, the Ba site is located approximately at the center of a capped tetragonal antiprism, reminiscent of the geometry around the  $\text{K}^+$  site in the salt  $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$  (Bélombé *et al.*, 2006). Selected geometric parameters for the monoclinic polymorph are listed in Table 1 and compare very well with the published data for the triclinic polymorph (Bouayad *et al.*, 1995).

Taken individually, the  $[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^{2-}$  complex anions are virtually the same but are connected differently in the triclinic and monoclinic polymorphs. In the monoclinic polymorph, these ions are interconnected into layers parallel to the (101) plane *via* O–H $\cdots$ O bridges which involve the uncoordinated water molecules (Fig. 2). The 3-D polymerization arises from the linkage of "external" oxalato-O atoms to neighboring Ba centers *via* mono- or bi-dentate coordination modes, and by single and double water bridges across the O10 and O15/O15<sup>i</sup> atoms, respectively (Table 2). The latter double bridge interconnects the next two neighboring Ba atoms, related by a center of inversion, with a Ba $\cdots$ Ba separation of 4.788 (2) Å.

In conclusion, the present study reveals that the unit cell symmetry in both structural polymorphs is basically dictated by the differing spatial orientations of the common anionic complexes,  $[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^{2-}$ , and variable coordination modes of the  $\text{Ba}^{\text{II}}$  centers.

## Experimental

Compound (**I**) was obtained by mixing Ba(NO<sub>3</sub>)<sub>2</sub> (0.31 g, 1.2 mmol, Riedel-de Haën, pure) and K<sub>2</sub>[Cu(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>].2H<sub>2</sub>O (0.18 g, 0.51 mmol), freshly prepared according to the method of Kirschner (1960), in warm water (60 °C; 100 ml). A solid precipitated immediately. The mixture was stirred for about 1 h at the same temperature and left to stand undisturbed over three days at ambient temperature. The blue prismatic crystals that formed were isolated by filtration, dried in air and one of these was used in the X-ray diffraction analysis.

## Refinement

All water-bound H atoms were first located in a difference Fourier map and then refined with distance restraints of O–H = 0.83 (3) Å with all  $U_{\text{iso}}(\text{H})$  freely refined. The highest peak and deepest hole in the final difference Fourier map are, respectively, 0.49 Å from atom H13B and 1.00 Å from Cu.

## Figures

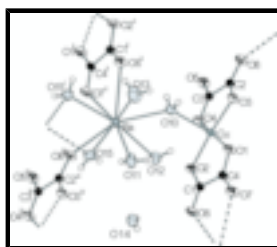


Fig. 1. A view of the molecular structure of (**I**), expanded to show the coordination geometry around the Ba<sup>II</sup> center, showing atom-numbering scheme and 50% probability displacement ellipsoids. Symmetry codes: (i)  $-x, y, -z + 1/2$ ; (ii)  $x, -y + 1, z + 1/2$ ; (iii)  $x - 1/2, y - 1/2, z$ ; (iv)  $x, -y + 1, z - 1/2$ ; (v)  $x + 1/2, y + 1/2, z$ .

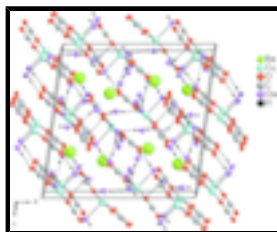


Fig. 2. A view of the crystal packing in (**I**) projected down the  $b$  axis. Hydrogen bonds are drawn as dashed lines and coordinate bonds to the Ba centers are omitted for clarity.

## poly[[di- $\mu$ -aqua-triaquadi- $\mu$ -oxalato-barium(II)copper(II)] monohydrate]

### Crystal data

[BaCu(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>5</sub>].H<sub>2</sub>O

$M_r = 485.02$

Monoclinic,  $C2/c$

Hall symbol:  $-C 2yc$

$a = 15.744$  (2) Å

$b = 10.7565$  (15) Å

$c = 15.345$  (2) Å

$\beta = 97.331$  (2)°

$V = 2577.5$  (6) Å<sup>3</sup>

$F_{000} = 1864$

$D_x = 2.500$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 3213 reflections

$\theta = 2.3$ – $28.3$ °

$\mu = 4.76$  mm<sup>-1</sup>

$T = 293$  (2) K

Prism, blue

$0.28 \times 0.14 \times 0.10$  mm

$Z = 8$

*Data collection*

Bruker APEX CCD area detector diffractometer	3213 independent reflections
Radiation source: fine-focus sealed tube	3180 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.022$
$T = 293(2)$ K	$\theta_{\text{max}} = 28.3^\circ$
$\omega$ & $\varphi$ scans	$\theta_{\text{min}} = 2.3^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$h = -20 \rightarrow 20$
$T_{\text{min}} = 0.462$ , $T_{\text{max}} = 0.631$	$k = -14 \rightarrow 14$
17321 measured reflections	$l = -20 \rightarrow 20$

*Refinement*

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.020$	All H-atom parameters refined
$wR(F^2) = 0.050$	$w = 1/[\sigma^2(F_o^2) + (0.0219P)^2 + 2.8035P]$
$S = 1.32$	where $P = (F_o^2 + 2F_c^2)/3$
3213 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
228 parameters	$\Delta\rho_{\text{max}} = 0.49 \text{ e } \text{\AA}^{-3}$
12 restraints	$\Delta\rho_{\text{min}} = -1.00 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

*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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Ba	0.141583 (8)	0.466998 (11)	0.208698 (8)	0.01861 (5)
Cu	0.392694 (18)	0.57358 (3)	0.044543 (18)	0.02206 (7)
O1	0.32532 (11)	0.68548 (15)	-0.03636 (11)	0.0259 (3)

## supplementary materials

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O2	0.32797 (11)	0.44372 (15)	-0.02082 (11)	0.0246 (3)
O3	0.46519 (11)	0.70211 (15)	0.10073 (11)	0.0253 (3)
O4	0.47712 (11)	0.45898 (14)	0.10183 (12)	0.0265 (4)
O5	0.59239 (11)	0.46396 (15)	0.20210 (12)	0.0269 (4)
O6	0.23179 (11)	0.57822 (15)	0.36098 (11)	0.0266 (3)
O7	0.23098 (12)	0.32494 (15)	0.34220 (12)	0.0297 (4)
O8	0.08384 (11)	0.22003 (16)	0.19560 (12)	0.0286 (4)
C1	0.27787 (14)	0.4853 (2)	-0.08588 (15)	0.0191 (4)
C2	0.52919 (14)	0.6586 (2)	0.15113 (14)	0.0201 (4)
C3	0.53447 (14)	0.5145 (2)	0.15330 (15)	0.0195 (4)
C4	0.27694 (14)	0.6281 (2)	-0.09552 (15)	0.0201 (4)
O10	0.29911 (11)	0.57403 (16)	0.16050 (12)	0.0251 (3)
O11	0.21699 (14)	0.32422 (18)	0.09118 (15)	0.0383 (5)
O12	0.09995 (15)	0.58277 (19)	0.04541 (13)	0.0363 (4)
O13	0.09098 (17)	0.7070 (2)	0.24223 (18)	0.0485 (6)
O14	-0.06779 (16)	0.6935 (2)	0.05515 (17)	0.0482 (5)
O15	0.03947 (12)	0.45626 (19)	0.34874 (13)	0.0290 (4)
H10A	0.287 (2)	0.648 (2)	0.166 (2)	0.041 (9)*
H10B	0.332 (2)	0.557 (3)	0.2032 (19)	0.042 (10)*
H11A	0.257 (2)	0.351 (4)	0.069 (2)	0.053 (11)*
H11B	0.237 (2)	0.254 (3)	0.106 (3)	0.061 (12)*
H12A	0.129 (2)	0.643 (3)	0.040 (2)	0.046 (10)*
H12B	0.0539 (18)	0.611 (4)	0.043 (3)	0.056 (12)*
H13A	0.097 (4)	0.779 (3)	0.226 (4)	0.104 (14)*
H13B	0.078 (3)	0.721 (5)	0.291 (2)	0.104 (14)*
H14A	-0.106 (2)	0.697 (4)	0.016 (2)	0.069 (14)*
H14B	-0.047 (3)	0.764 (3)	0.061 (3)	0.091 (17)*
H15A	0.047 (2)	0.386 (3)	0.368 (2)	0.051 (11)*
H15B	0.059 (3)	0.506 (4)	0.381 (3)	0.066 (14)*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ba	0.01904 (8)	0.01779 (7)	0.01834 (8)	-0.00038 (4)	-0.00019 (5)	0.00062 (4)
Cu	0.02429 (14)	0.01650 (13)	0.02248 (14)	-0.00159 (10)	-0.00821 (10)	-0.00040 (10)
O1	0.0300 (8)	0.0164 (7)	0.0279 (8)	-0.0009 (6)	-0.0089 (7)	-0.0011 (6)
O2	0.0303 (9)	0.0172 (7)	0.0234 (8)	-0.0024 (6)	-0.0086 (7)	0.0024 (6)
O3	0.0263 (8)	0.0181 (7)	0.0286 (8)	-0.0022 (6)	-0.0071 (6)	-0.0001 (6)
O4	0.0285 (9)	0.0182 (7)	0.0294 (9)	0.0000 (6)	-0.0090 (7)	-0.0023 (6)
O5	0.0244 (8)	0.0235 (8)	0.0302 (9)	0.0007 (6)	-0.0059 (7)	0.0022 (6)
O6	0.0294 (8)	0.0197 (8)	0.0275 (8)	0.0049 (6)	-0.0090 (7)	0.0004 (6)
O7	0.0349 (9)	0.0191 (8)	0.0307 (9)	-0.0022 (7)	-0.0132 (7)	-0.0014 (7)
O8	0.0256 (8)	0.0252 (8)	0.0328 (9)	-0.0071 (7)	-0.0053 (7)	-0.0035 (7)
C1	0.0189 (9)	0.0173 (9)	0.0208 (10)	-0.0010 (7)	0.0009 (8)	0.0002 (8)
C2	0.0215 (10)	0.0193 (10)	0.0194 (10)	-0.0025 (8)	0.0023 (8)	-0.0002 (8)
C3	0.0206 (10)	0.0189 (10)	0.0190 (10)	-0.0006 (8)	0.0026 (8)	0.0001 (8)
C4	0.0204 (10)	0.0162 (9)	0.0228 (10)	0.0003 (7)	-0.0003 (8)	0.0008 (8)
O10	0.0253 (8)	0.0215 (8)	0.0266 (8)	0.0002 (7)	-0.0044 (7)	-0.0004 (7)

O11	0.0501 (12)	0.0192 (8)	0.0503 (12)	-0.0010 (8)	0.0250 (10)	-0.0001 (8)
O12	0.0451 (12)	0.0278 (10)	0.0344 (10)	-0.0054 (9)	-0.0014 (9)	0.0072 (8)
O13	0.0605 (15)	0.0242 (10)	0.0625 (15)	0.0077 (10)	0.0139 (12)	0.0060 (10)
O14	0.0460 (13)	0.0465 (13)	0.0501 (14)	-0.0039 (11)	-0.0018 (11)	0.0160 (11)
O15	0.0263 (9)	0.0353 (10)	0.0245 (9)	-0.0004 (7)	-0.0005 (7)	0.0006 (8)

*Geometric parameters (Å, °)*

Ba—O11	2.751 (2)	O7—C4 <sup>ii</sup>	1.231 (3)
Ba—O13	2.770 (2)	O8—C2 <sup>iii</sup>	1.222 (3)
Ba—O7	2.7888 (17)	C1—O6 <sup>iv</sup>	1.228 (3)
Ba—O12	2.800 (2)	C1—C4	1.542 (3)
Ba—O8	2.8066 (17)	C2—O8 <sup>v</sup>	1.222 (3)
Ba—O6	2.8393 (17)	C2—C3	1.552 (3)
Ba—O15	2.846 (2)	C4—O7 <sup>iv</sup>	1.231 (3)
Ba—O15 <sup>i</sup>	2.8765 (19)	O10—H10A	0.82 (2)
Ba—O10	2.9140 (18)	O10—H10B	0.80 (2)
Ba—Ba <sup>i</sup>	4.7880 (7)	O11—H11A	0.80 (2)
Cu—O3	1.9252 (16)	O11—H11B	0.84 (3)
Cu—O2	1.9326 (16)	O12—H12A	0.80 (2)
Cu—O4	1.9393 (17)	O12—H12B	0.78 (2)
Cu—O1	1.9440 (16)	O13—H13A	0.82 (3)
Cu—O10	2.451 (3)	O13—H13B	0.81 (3)
O1—C4	1.269 (3)	O14—H14A	0.80 (3)
O2—C1	1.272 (3)	O14—H14B	0.83 (3)
O3—C2	1.278 (3)	O15—Ba <sup>i</sup>	2.8765 (19)
O4—C3	1.270 (3)	O15—H15A	0.81 (2)
O5—C3	1.230 (3)	O15—H15B	0.76 (3)
O6—C1 <sup>ii</sup>	1.228 (3)		
O11—Ba—O13	143.20 (7)	O3—Cu—O2	174.10 (8)
O11—Ba—O7	87.48 (6)	O3—Cu—O4	85.44 (7)
O13—Ba—O7	120.30 (7)	O2—Cu—O4	93.52 (7)
O11—Ba—O12	74.52 (7)	O3—Cu—O1	94.90 (7)
O13—Ba—O12	73.24 (7)	O2—Cu—O1	84.69 (7)
O7—Ba—O12	160.00 (6)	O4—Cu—O1	165.84 (8)
O11—Ba—O8	65.64 (6)	O4—Cu—O10	96.48 (7)
O13—Ba—O8	142.89 (7)	C4—O1—Cu	112.60 (14)
O7—Ba—O8	70.27 (5)	C1—O2—Cu	112.70 (14)
O12—Ba—O8	108.68 (6)	C2—O3—Cu	112.62 (14)
O11—Ba—O6	124.22 (6)	C3—O4—Cu	112.01 (14)
O13—Ba—O6	65.15 (7)	C1 <sup>ii</sup> —O6—Ba	120.20 (14)
O7—Ba—O6	58.25 (5)	C4 <sup>ii</sup> —O7—Ba	122.45 (14)
O12—Ba—O6	125.77 (6)	C2 <sup>iii</sup> —O8—Ba	138.63 (15)
O8—Ba—O6	125.53 (5)	O6 <sup>iv</sup> —C1—O2	125.4 (2)
O11—Ba—O15	143.62 (6)	O6 <sup>iv</sup> —C1—C4	119.5 (2)
O13—Ba—O15	72.18 (7)	O2—C1—C4	115.03 (19)

## supplementary materials

O7—Ba—O15	72.77 (6)	O8 <sup>v</sup> —C2—O3	125.8 (2)
O12—Ba—O15	127.12 (6)	O8 <sup>v</sup> —C2—C3	119.7 (2)
O8—Ba—O15	78.85 (6)	O3—C2—C3	114.49 (18)
O6—Ba—O15	70.55 (6)	O5—C3—O4	125.7 (2)
O11—Ba—O15 <sup>i</sup>	105.69 (6)	O5—C3—C2	119.2 (2)
O13—Ba—O15 <sup>i</sup>	78.29 (7)	O4—C3—C2	115.09 (19)
O7—Ba—O15 <sup>i</sup>	126.20 (6)	O7 <sup>iv</sup> —C4—O1	126.5 (2)
O12—Ba—O15 <sup>i</sup>	68.53 (6)	O7 <sup>iv</sup> —C4—C1	118.73 (19)
O8—Ba—O15 <sup>i</sup>	68.95 (5)	O1—C4—C1	114.74 (19)
O6—Ba—O15 <sup>i</sup>	129.88 (5)	Ba—O10—H10A	98 (2)
O15—Ba—O15 <sup>i</sup>	66.20 (6)	Ba—O10—H10B	101 (3)
O11—Ba—O10	66.53 (6)	H10A—O10—H10B	105 (3)
O13—Ba—O10	87.32 (6)	Ba—O11—H11A	120 (3)
O7—Ba—O10	92.11 (5)	Ba—O11—H11B	120 (3)
O12—Ba—O10	72.95 (6)	H11A—O11—H11B	98 (4)
O8—Ba—O10	129.36 (5)	Ba—O12—H12A	113 (3)
O6—Ba—O10	71.93 (5)	Ba—O12—H12B	109 (3)
O15—Ba—O10	142.08 (5)	H12A—O12—H12B	103 (4)
O15 <sup>i</sup> —Ba—O10	141.29 (5)	Ba—O13—H13A	141 (4)
O11—Ba—Ba <sup>i</sup>	131.91 (5)	Ba—O13—H13B	117 (4)
O13—Ba—Ba <sup>i</sup>	69.58 (5)	H13A—O13—H13B	99 (5)
O7—Ba—Ba <sup>i</sup>	101.84 (4)	H14A—O14—H14B	106 (5)
O12—Ba—Ba <sup>i</sup>	96.74 (5)	Ba—O15—Ba <sup>i</sup>	113.60 (6)
O8—Ba—Ba <sup>i</sup>	73.44 (4)	Ba—O15—H15A	104 (3)
O6—Ba—Ba <sup>i</sup>	99.61 (4)	Ba <sup>i</sup> —O15—H15A	104 (3)
O15—Ba—Ba <sup>i</sup>	33.40 (4)	Ba—O15—H15B	104 (4)
O15 <sup>i</sup> —Ba—Ba <sup>i</sup>	33.00 (4)	Ba <sup>i</sup> —O15—H15B	118 (4)
O10—Ba—Ba <sup>i</sup>	156.72 (3)	H15A—O15—H15B	113 (4)

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

### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O10—H10A $\cdots$ O7 <sup>vi</sup>	0.82 (2)	1.93 (2)	2.740 (2)	168 (3)
O10—H10B $\cdots$ O5 <sup>vii</sup>	0.80 (2)	2.02 (3)	2.801 (2)	163 (4)
O10—H10B $\cdots$ O8 <sup>vi</sup>	0.80 (2)	2.59 (3)	3.114 (2)	125 (3)
O11—H11A $\cdots$ O2	0.80 (2)	2.13 (3)	2.903 (3)	161 (4)
O11—H11B $\cdots$ O6 <sup>viii</sup>	0.84 (3)	2.00 (3)	2.835 (3)	172 (4)
O11—H11B $\cdots$ O2 <sup>ix</sup>	0.84 (3)	2.63 (4)	3.127 (3)	119 (3)
O12—H12A $\cdots$ O1 <sup>x</sup>	0.80 (2)	1.98 (3)	2.768 (3)	165 (4)
O13—H13A $\cdots$ O5 <sup>xi</sup>	0.82 (3)	2.02 (3)	2.832 (3)	168 (6)
O13—H13B $\cdots$ O14 <sup>i</sup>	0.81 (3)	2.41 (3)	3.180 (4)	159 (6)
O14—H14A $\cdots$ O11 <sup>xii</sup>	0.80 (3)	2.25 (3)	3.041 (3)	171 (5)

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O14—H14B...O4 <sup>xi</sup>	0.83 (3)	2.21 (3)	3.007 (3)	163 (5)
O15—H15A...O3 <sup>viii</sup>	0.81 (2)	2.05 (3)	2.845 (3)	165 (4)
O12—H12B...O14	0.78 (2)	2.14 (3)	2.918 (3)	173 (4)
O15—H15B...O14 <sup>i</sup>	0.76 (3)	2.24 (3)	2.952 (3)	156 (5)

Symmetry codes: (vi)  $-x+1/2, y+1/2, -z+1/2$ ; (vii)  $-x+1, y, -z+1/2$ ; (viii)  $-x+1/2, y-1/2, -z+1/2$ ; (ix)  $-x+1/2, -y+1/2, -z$ ; (x)  $-x+1/2, -y+3/2, -z$ ; (xi)  $x-1/2, y+1/2, z$ ; (i)  $-x, y, -z+1/2$ ; (xii)  $-x, -y+1, -z$ .



Fig. 2

