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Poly[[tetradecakis(μ-propionato)heptabarium] propionic acid monosolvate tetrahydrate]

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The title compound, $\{[Ba_7(C_3H_5O_2)_{14}]\cdot 0.946C_3H_6O_2\cdot 4H_2O\}_n$, is represented by a metal–organic framework structure that is held together by Ba—O—Ba bonds, as well as by O—H···O hydrogen bonds of moderate strength. The structure comprises of four independent Ba^{2+} cations (one of which is situated on a twofold rotation axis), seven independent propionate and two independent water molecules. The bond-valence sums of all the cations indicate a slight overbonding. There is also an occupationally, as well as a positionally disordered propionic acid molecule present in the structure. Its occupation is slightly lower than the full occupation while the disordered molecules occupy two positions related by a rotation about a twofold rotation axis. In addition, the methyl group in the symmetry-independent propionic acid molecule is also disordered, and occupies two positions. Each propionic acid molecule coordinates to just one cation from a pair of symmetry-equivalent Ba^{2+} sites and is simultaneously bonded by an $O—H\cdots O_{propionate}$ hydrogen bond. This means that on a microscopic scale, the coordination number of the corresponding Ba^{2+} site is either 9 or 10. The methyl as well as hydroxy hydrogen atoms of the disordered propionic acid molecule were not determined.

1. Chemical context

A relatively low number of structurally determined metal propionates with divalent cations are known so far, as manifested by comparison of the numbers of propionates, acetates and formates with alkaline-earth cations which were retrieved from the Cambridge Structural Database (Groom *et al.*, 2016; version 5.40 from November 2018). Their numbers are 8, 60 and 70, respectively. One of the reasons for such a low number of determined structures might be associated with the tendency for difficult crystallization in case of some propionates. As an example of a difficult crystallization of a propionate salt from aqueous solution, Ca(propionate)$_2$ and Cd(propionate)$_2$ in a 2:1 molar ratio (Fábry, 2020) can be given.

Among the propionate salts, the most studied compounds are the isostructural salts Ca_2Pb(propionate)$_6$ and Ca_2Sr(propionate)$_6$. In the latter compounds, ferroelectric phases occur (see a short review by Nakamura & Deguchi, 1992). Structurally related Ca_2Ba(propionate)$_6$ shows interesting structural properties such as positional disorder of propionate chains in the room-temperature phase with symmetry $Fd\bar{3}m$ (Stadnicka & Glazer, 1980). This disorder is a reason for diffuse streaks in the diffraction pattern, indicating correlated occurrence of the disordered propionate molecules. The latter compound undergoes low-temperature phase transitions to phases with suggested orthorhombic symmetry (Gesi, 1993).

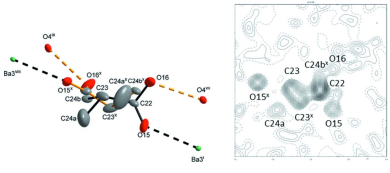
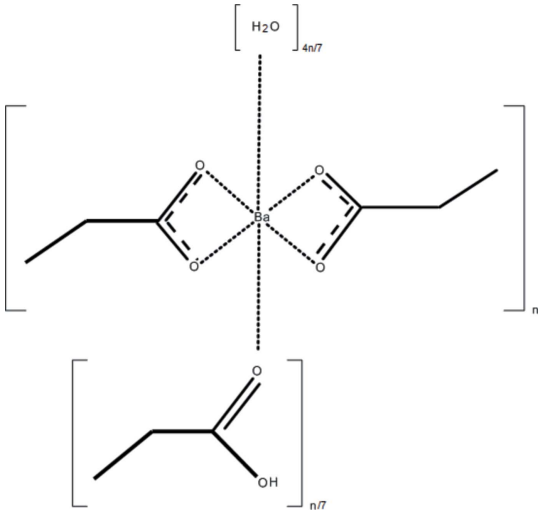


Table 1
Bonding properties of Ba^{2+} cations[a] in the title structure.

Atom	Coordination number	d_{min}(Ba—O) (Å)	d_{max}(Ba—O) (Å)	Bond valence sum (v.u.)[a]
Ba1	9	2.666 (2)	2.923 (2)	2.191 (5)
Ba2	9	2.685 (2)	2.940 (2)	2.286 (5)
Ba3[b]	9.473	2.673 (2)	3.084 (2)	2.248 (5)
Ba3[c]	9.500	2.673 (2)	3.084 (2)	2.255 (5)
Ba3[d]	9	2.673 (2)	3.084 (2)	2.138 (5)
Ba3[e]	10	2.673 (2)	3.084 (2)	2.372 (6)
Ba4	8	2.670 (2)	2.868 (2)	2.204 (5)

Notes: (*a*) Calculation with the parameters of Brese & O'Keeffe (1991); (*b*) consideration of a disordered propionic acid molecule with refined occupancy = 0.473 (4); (*c*) consideration of a disordered propionic acid molecule with 0.5 occupancy; (*d*) excluding the disordered propionic acid molecule; (*e*) local full occupation.



The title compound was prepared serendipitously. A few crystals of it were isolated from a batch of seemingly cubic crystals (they showed no extinction under polarized light) that grew from aqueous solutions of propionic acid (molar proportion > 30) with the amounts of $BaCO_3$ and $4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$ in a molar ratio of 5:2; the pH of the solution was about 6. The motivation for the synthesis was a planned preparation of an analogue of $Ca_2Ba(propionate)_6$ where Ca^{2+} and Ba^{2+} are overbonded and slightly underbonded (Brese & O'Keeffe, 1991), respectively. For example, in the above-mentioned room-temperature phase of $Ca_2Ba(propionate)_6$, the bond-valence sums (Brese & O'Keeffe, 1991) of Ca^{2+} and Ba^{2+} amount to 2.78 (1) and 1.93 (1) valence units, respectively [see the refinement/model 'A' given in the article by Stadnicka & Glazer (1980) who discussed strong bonding of Ca^{2+} in this structure]. It was therefore hoped that a hypothetical structure '$Ba_2Mg(propionate)_6$' might be isostructural to $Ca_2Ba(propionate)_6$ or related to it despite an expected lowering of the bond-valence sum by smaller Mg^{2+} cations. Indeed, alongside a few crystals of the title compound, cubic crystals were obtained, the structure determination of which is ongoing at present.

2. Structural commentary

A view of the crystal structure is given in Fig. 1. There are four independent Ba^{2+} cations that are all coordinated by oxygen atoms stemming either from the carboxylate or carboxylic groups or from water molecules. The latter molecules coordinate exclusively to $Ba2^{2+}$. $Ba3^{2+}$ is coordinated by the carboxylic group of an occupationally and positionally disordered propionic acid molecule. $Ba4^{2+}$ is situated on a twofold

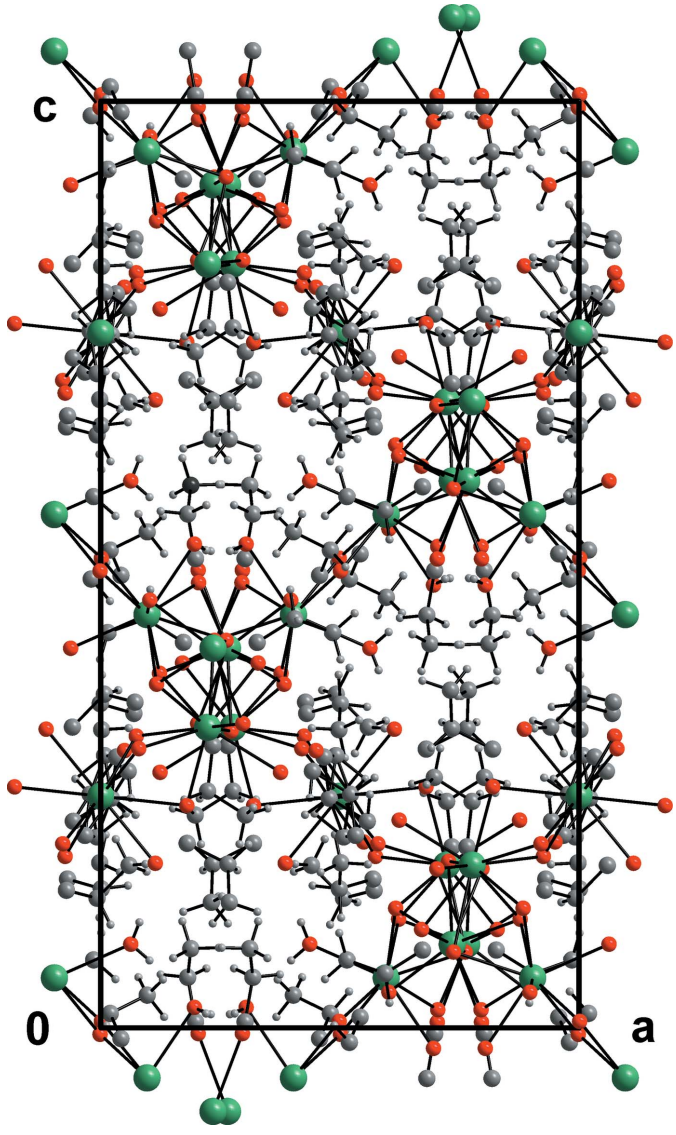


Figure 1
A view of the crystal structure along the *b* axis. Ba, O, C and water H atoms are shown as green, red, dark gray and tiny gray spheres, respectively.

Table 2
Hydrogen-bond geometry (Å, °).

The hydrogen bond O16···O4^{vii} is missing from this table because of the undetermined position of the bridging hydrogen atom.

D—H···A	D—H	H···A	D···A	D—H···A
O1w—H1$O1w$···O1^{iv}	0.82 (3)	2.25 (3)	2.957 (3)	145 (4)
O1w—H2$O1w$···O2^{iii}	0.82 (3)	2.00 (3)	2.813 (3)	171 (3)
O2w—H1$O2w$···O1w^{iii}	0.82 (3)	2.15 (3)	2.963 (4)	172 (4)
O2w—H2$O2w$···O14^{vi}	0.81 (3)	2.01 (3)	2.807 (3)	164 (4)
C17—H1c17···O16^{viii}	0.99	2.43	2.989 (15)	115.22

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

rotation axis, *i.e.* on the Wyckoff position *c*. An overview of the coordination environments around each of the Ba^{2+} cations is given in Table 1 with corresponding illustrations shown in Fig. 2*a*–*d*. All Ba^{2+} cations are slightly overbonded (Table 1). Fig. 3*a*–*g* shows all seven independent propionate molecules coordinating the Ba^{2+} cations.

It can readily be seen from Fig. 1 that the cohesion within the crystal structure is mostly provided by a three-dimensional network of Ba—O—Ba bonds. This network is shown in more detail in Fig. 4, which also includes O—H···O hydrogen bonds of moderate strength (Gilli & Gilli, 2009). The corresponding donor groups are water molecules while the acceptors are carboxylate oxygen atoms. Numerical details of hydrogen-bonding interactions are provided in Table 2, excluding the $O_{propionic\ acid}$—H···$O_{propionate}$ hydrogen bond along O16···O4^{vii} [2.706 (13) Å; symmetry code: (vii) $-x+1, -y, -z+1$] that is donated by the free propionic acid molecule. This molecule is disordered over two positions related by $(-x+1, y, -z+\frac{1}{2})$ about a twofold rotation axis (Wyckoff position *c*). The low occupancy is probably the reason why the bridging hydrogen atom of the O16···O4^{vii} hydrogen bond could not be located in the difference electron density map. However, the angle C22—O16···O4^{vii}, which measures 110.8 (8)°, is close to the tetrahedral angle and is in agreement with the assumed presence of a hydrogen bond. The longer C22—O16 bond [1.303 (18) Å] in comparison with the C22—O15 bond [1.187 (12) Å)] indicates that the bridging hydrogen atom is attached to O16. Table 2 also lists a weak C—H···O interaction between a methyl group and the carboxylic O atom of the propionic acid molecule. The numerical parameters conform to the criteria for a weak hydrogen bond (Desiraju & Steiner, 1999).

Fig. 5*a* shows a detailed view of the disordered propionic acid molecule over two positions associated with the above-mentioned twofold rotation. The refined occupation of the molecule of propionic acid converged to 0.473 (4) (full occupation of the site corresponds to 0.5). *SQUEEZE*, a func-

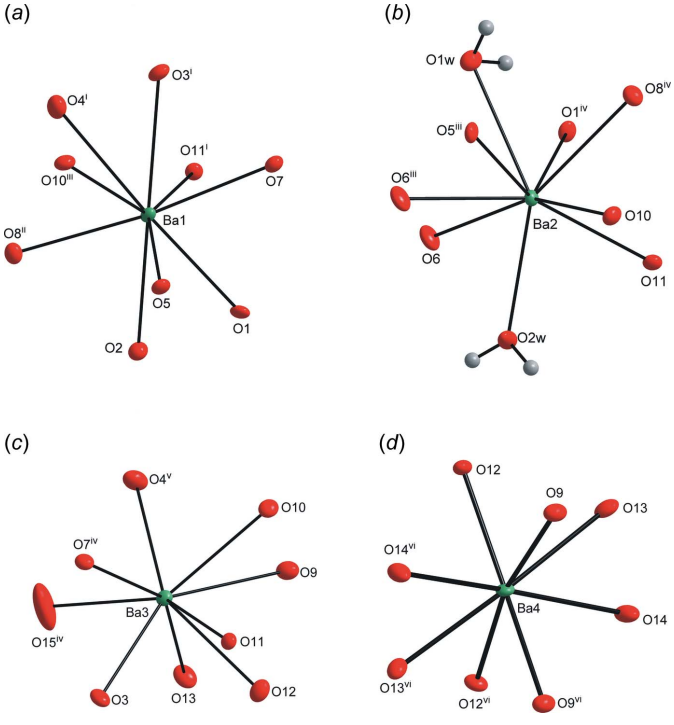


Figure 2
A view of the oxygen coordination around the cations, with displacement ellipsoids shown at the 50% probability level. (*a*) $Ba1^{2+}$, (*b*) $Ba2^{2+}$, (*c*) $Ba3^{2+}$ and (*d*) $Ba4^{2+}$ [Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (v) $x+\frac{3}{2}, y+\frac{1}{2}, z$; (vi) $-x+1, y, -z+\frac{3}{2}$].

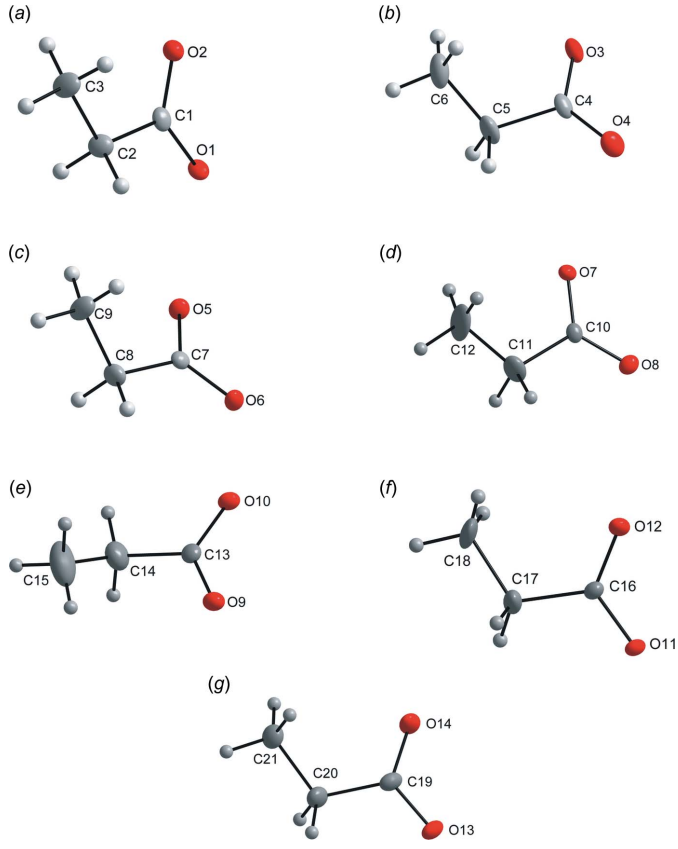


Figure 3
Molecular structures of the propionate molecules, with displacement ellipsoids shown at the 50% probability level. (*a*) molecules with the carboxylate atom C1, (*b*) molecules with the carboxylate atom C4, (*c*) molecules with the carboxylate atom C7, (*d*) molecules with the carboxylate atom C10, (*e*) molecules with the carboxylate atom C13, (*f*) molecules with the carboxylate atom C16 and (*g*) molecules with the carboxylate atom C19.

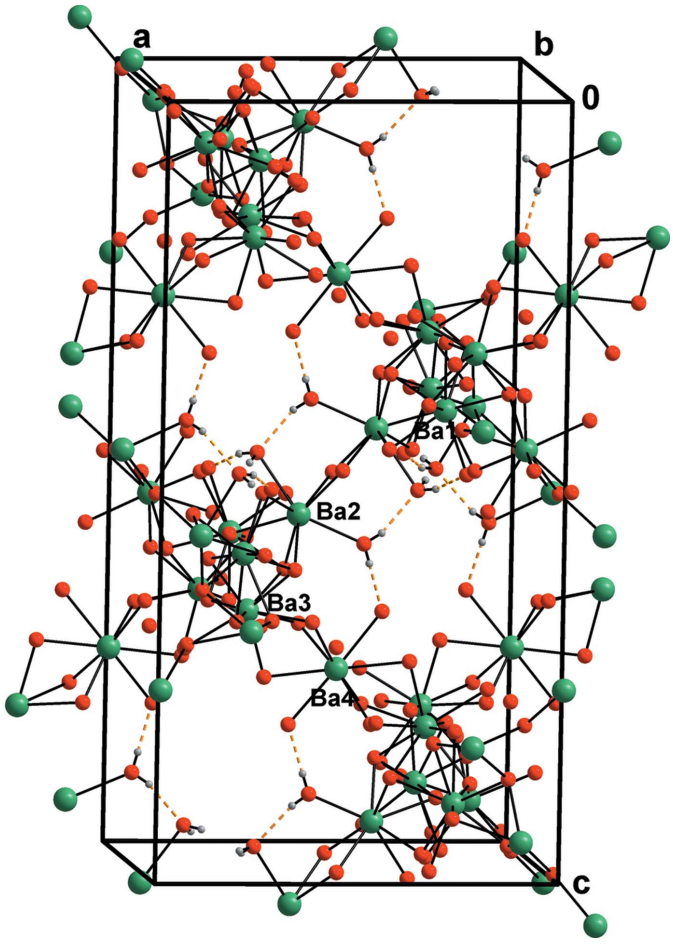


Figure 4
A view of the crystal structure excluding the propionate methylene and methyl groups as well as the disordered propionic acid molecule. Ba—O—Ba bonds and O—H···O bonds [except for O16···O4^{vii} ($-x+1, -y, -z+1$) where the bridging hydrogen atom was not found] are displayed. For colour codes, see caption for Fig. 1.

tionality included in *PLATON* (Spek, 2015), yielded a value of 0.431. This means that the occupation of the disordered molecule is not full; however, analysis of the bond-valence sum for $Ba3^{2+}$ still points to a slight overbonding (Table 1) even without the presence of propionic acid. On a microscopic scale, the propionic acid molecule is only bonded to one of the $Ba3^{2+}$ cations from the pair of symmetry-equivalent cations ($Ba3^{i}$ and $Ba3^{viii}$; see Fig. 5 and the symmetry codes given therein) by the bond (O15—$Ba3^{i}$, $O15^{x}$—$Ba3^{viii}$). At the same time, it forms the above mentioned O—H···O hydrogen bonds along O16···O4^{vii} and $O16^{x}$···O4^{ix} [2.706 (13) Å]. In addition to the occupational disorder of the propionic acid molecule, its methyl group was found to be disordered over two positions. One of these positions (the methyl C24b^{x} atom) is very close to atom C22 (Fig. 5*b*). The occupational parameters of the disordered methyl groups split into C24*a* and C24*b* converged to 0.30 (2) and 0.17 (1); methyl hydrogen atoms were not found. The displacement parameters of the methyl group C24*a* (Fig. 5*a*) are quite large and indicate an intense libration. The displacement parameter of C24*b* was constrained to that of C22 (Fig. 5*a*).

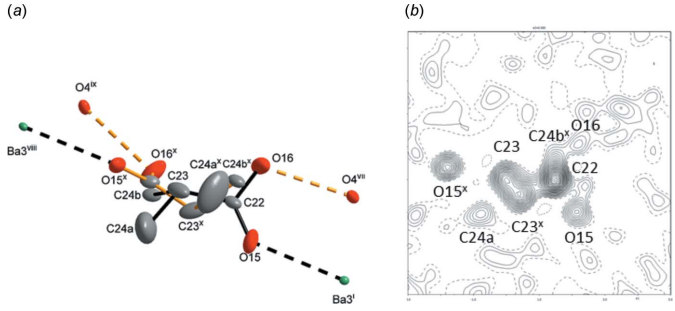


Figure 5
(*a*) A view of a disordered propionic acid molecule with displacement ellipsoids shown at the 30% probability level. (*b*) Section of the difference electron density map (Petříček *et al.*, 2014) through the atoms C22, C23 and C24b^{x}. This section shows the region of the disordered propionic acid molecule in part. Increments of positive and negative contours are 0.01 and 0.05 e Å^{-3}. [Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (vii) $-x+1, -y, -z+1$; (viii) $-x+\frac{3}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (ix) $x, -y, z-\frac{1}{2}$]. The disordered atoms are related by a symmetry operation (Wyckoff position *c*) (x) $-x+1, y, -z+1/29$. For colours, see caption for Fig. 1.

Reported structures comprising propionate anions and/or propionic acid molecules were retrieved from the Cambridge Structural Database (Groom *et al.*, 2016; version 5.40 from November 2018). Fig. 6 shows a scattergram of the shorter C—O (or C═O) and longer C—O (or C—OH) distances in the carboxylate or carboxylic group, respectively. Corresponding distances in the title structure are normal although those pertinent to the carboxylates are on the verge of the region where both C—O distances are about the same. Interestingly, there is no large difference between these parameters in the carboxylate (black squares) and the carboxylic groups (red circles) in the propionate or propionic acid molecules, respectively. There seem to be a clustering of points at about 1.21 and 1.35 Å, which manifest different bonding types in these molecules.

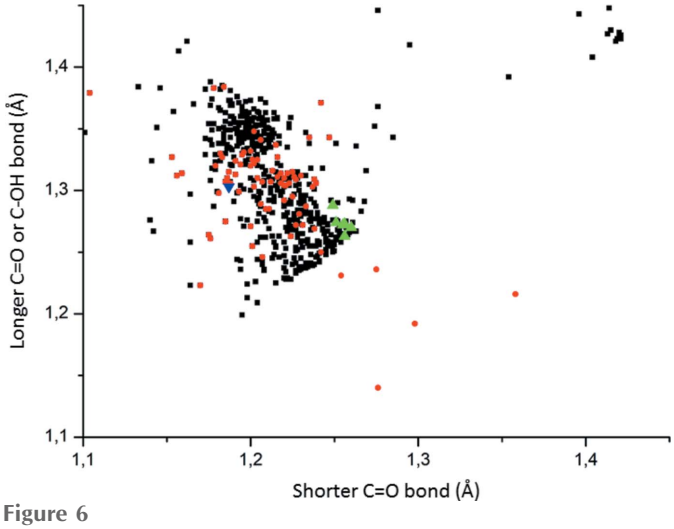


Figure 6
Scattergram of the distances for the shorter and the longer C═O bonds in the carboxylate groups in propionates (black squares) as well as of C═O bonds and C—OH bonds in propionic acid molecules (red circles). The corresponding values for the propionates and the propionic acid molecule present in the title structure are shown as green and blue triangles, respectively.

3. Synthesis and crystallization

1 g of $BaCO_3$ and 0.95 g of basic magnesium carbonate [Aldrich, product number 13118, the powder diagram of which corresponded best to that of the powder diffraction file 01-070-0361 of PDF-4 (International Centre for Diffraction Data, 2019)], *i.e.* $4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$], were dissolved in an aqueous solution of 2.28 g of propionic acid. These masses correspond to molar ratios of 5:2:30. The majority of the solid dissolved in the acid solution and a few ml of propionic acid (100%) were added to the solution, maintaining its pH between 6 and 7. The solution was then filtered through a sintered disk. The filtrate was concentrated by evaporation at 323 K until colourless crystals appeared. A prevalent majority of the crystals were of cubic form with a typical size of 1 mm. Under a polarizating microscope, these crystals did not show extinction, *i.e.* they were optically isotropic. However, among these crystals a few crystals that showed extinction were found. They were isolated and one of them was chosen for single crystal X-ray structure determination.

4. Structure determination and refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

The structure can be divided into a non-disordered part composed of the Ba^{2+} cations, propionate anions and water molecules, and the disordered molecule of propionic acid. The refinement of the non-disordered structure part was straightforward, with methylene hydrogen atoms calculated and their parameters constrained to C—H = 0.99 Å and U_{iso}(H) = 1.2U_{eq}(C). The methyl hydrogen atoms of the propionate molecules were discernible in the difference electron density map. They were constrained with C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C). The water hydrogen atoms were also discernible in the difference electron density map. Their positional parameters were restrained in such a way that O—H distances were set to 0.82 (1) Å, with U_{iso}(H) = 1.5U_{eq}(O). The residual maxima in the difference electron density map after the refinement of the non-disordered part of the structure conformed to the expected shape of the non-hydrogen atoms of a propionic acid molecule (see Fig. 5*a*,*b*). The functionality of *SQUEEZE* included in *PLATON* (Spek, 2015) indicated 138 electrons corresponding to the symmetry-related regions with the disordered molecule present in the unit cell. Since a propionic acid molecule has 40 electrons, the expected occupational parameter for the disordered molecule is 138/160 = 0.8625 or 0.4313 for the occupancy considering the special position (twofold rotation axis) in its vicinity. The value of the expected occupancy is in fair agreement with the refined value of 0.473 (4) for the molecule of propionic acid where four hydrogen atoms remained undetermined (the methyl as well as the hydroxy hydrogen atoms). This disorder results in a statistical distribution of the molecule about the twofold rotation axis, indicating that vacancies without the molecule of propionic acid are likely to be present in the crystal structure.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Ba_7(C_3H_5O_2)_{14}]{\cdot}0.946C_3H_6O_2{\cdot}4H_2O$
M_r	2126.4
Crystal system, space group	Orthorhombic, *Pbcn*
Temperature (K)	95
a, *b*, *c* (Å)	15.7831 (2), 14.0136 (2), 30.5583 (3)
V (Å^3)	6758.83 (15)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	4.10
Crystal size (mm)	0.22 × 0.12 × 0.10
Data collection	
Diffractometer	Rigaku Oxford Diffraction SuperNova, Dual, Cu at home/near, AtlasS2
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2019)
T_{min}, T_{max}	0.568, 0.656
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	112254, 8981, 8215
R_{int}	0.043
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.696
Refinement	
$R[I > 3\sigma(I)]$, $wR(F)$, S	0.028, 0.071, 1.92
No. of reflections	8981
No. of parameters	428
No. of restraints	7
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.14, −0.72

Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *SHELXT* (Sheldrick, 2015*a*), *JANA2006* (Petříček *et al.*, 2014), *DIAMOND* (Brandenburg, 2015), *Origin* (Origin, 2000) and *JANA2006* (Petříček *et al.*, 2014).

Reliability factors of a trial refinement with assumed full occupation of the disordered molecule converged with negligibly worse values and are collated in the refine_special_details section of the CIF. The respective electron densities of the peaks that were assigned to the atoms O15, O16, C22, C23 and C24*a* are 1.22, 0.97, 0.96, 0.82 and 0.31 e$^-$ Å^{-3}. The independently refined occupational parameters of the atoms of the disordered molecule converged to the following values: O15: 0.410 (7); O16: 0.362 (7); C22: 0.571 (11); C23: 0.391 (9); C24: 0.184 (12), pointing to another type of occupational disorder, in particular regarding the distribution of the methyl group, which may partly overlap with atom C22 (Fig. 5*b*). Treatment of these atoms after localization of all non-hydrogen atoms of the disordered propionic acid molecule is described in detail in the refine_special_details section of the CIF.

43 reflections were discarded from the refinement because $|I_{obs} - I_{calc}|/\sigma(I_{obs}) > 10$. They are listed in the refine_special_details section of the CIF, together with the results of an alternative refinement with *SHELXL* (Sheldrick, 2015*b*) where the contributions of the disordered propionic acid molecule were removed using the *SQUEEZE* option in *PLATON* (Spek, 2015).

Acknowledgements

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supporting information

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Poly[[tetradecakis(μ-propionato)heptabarium] propionic acid monosolvate tetrahydrate]

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2019); cell refinement: *CrysAlis PRO* (Rigaku OD, 2019); data reduction: *CrysAlis PRO* (Rigaku OD, 2019); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015); program(s) used to refine structure: *JANA*2006 (Petříček *et al.*, 2014); molecular graphics: *DIAMOND* (Brandenburg, 2015) and *Origin* (Origin, 2000); software used to prepare material for publication: *JANA2006* (Petříček *et al.*, 2014).

Poly[[tetradecakis(μ-propionato)heptabarium] propionic acid monosolvate tetrahydrate]

Crystal data

$[Ba_7(C_3H_5O_2)_{14}]\cdot 0.946C_3H_6O_2\cdot 4H_2O$
M_r = 2126.4
Orthorhombic, *Pbcn*
Hall symbol: -P 2n 2ab
a = 15.7831 (2) Å
b = 14.0136 (2) Å
c = 30.5583 (3) Å
V = 6758.83 (15) Å^3
Z = 4
F(000) = 4063.4
D_x = 2.090 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 70680 reflections
θ = 2.8–29.6°
μ = 4.10 mm^{-1}
T = 95 K
Prism, colourless
0.22 × 0.12 × 0.10 mm

Data collection

Rigaku Oxford Diffraction SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer
Radiation source: X-ray tube
Mirror monochromator
Detector resolution: 5.2027 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2019)
T_{min} = 0.568, T_{max} = 0.656
112254 measured reflections
8981 independent reflections
8215 reflections with $I > 3\sigma(I)$
R_{int} = 0.043
θ_{max} = 29.6°, θ_{min} = 2.4°
h = −19→21
k = −18→18
l = −40→41

Refinement

Refinement on F^2
$R[F > 3\sigma(F)]$ = 0.028for R[I>3σ (I)]
$wR(F)$ = 0.071
S = 1.92
8981 reflections
428 parameters
7 restraints
196 constraints
H atoms treated by a mixture of independent and constrained refinement
Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(I) + 0.0004I^2)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.72 e Å^{-3}

Special details

Refinement. 1) Reliability factors considering full occupation of the disordered propionic acid molecule: _refine_ls_R_factor_gt (0.0277), _refine_ls_wR_factor_gt (0.0698), _refine_ls_R_factor_all (0.0324), _refine_ls_wR_factor_ref (0.0712), _refine_ls_goodness_of_fit_ref (1.93), _refine_ls_goodness_of_fit_gt (1.98).
2) Details of the disorder in the proprionic acid molecule: The overall occupational parameter of the disordered propionic acid molecule was determined by refinement of the molecular part comprising of the atoms O15, O16 and C23 which seemed to be the ones least-affected by disorder or overlapping. This refined value has then been used as a value to which the sum of partial occupational parameters of the methyl atoms C24a and C24b should equal while refining the occupational parameter of C24b. The displacement parameter of C24b due to its proximity was supposed to be equal to that of C22 which was refined.
The positions of the methylene hydrogen atoms of C23a and C23b H1C23a, H2C23a; H1C23b, H2C23b) were calculated, with occupational parameters constrained to be equal to the occupational parameters of C24a and C24b, respectively, and with C—H = 0.99Å, U_{iso}(H) = 1.2U_{eq}(C). The distance C22—C23 was restrained to 1.52 (1) Å while the distances C23—C24a and C23—C24b were restrained to 1.50 (1) Å.
3) 43 diffractions with (Iobs-Icalc)/sigma(w)>10 were discarded from the refinement:
0 8 0; 6 4 1; 7 7 2; 1 8 2; 5 8 2; 6 8 2; 7 8 2; 2 10 2; 7 4 3; 8 1 4; 4 10 4; 3 4 5; 7 4 5; 6 6 6; 1 10 6; 5 10 6; 6 3 7; 3 4 7; 6 8 8; 0 10 8; 6 2 9; 1 3 9; 3 4 9; 6 6 9; 7 10 10; 5 1 11; 7 1 2; 3 3 12; 1 1 13; 5 1 13; 3 4 13; 4 5 13; 1 2 15; 1 6 15; 4 1 16; 0 2 17; 0 6 17; 1 1 19; 1 2 19; 3 4 21; 1 4 22; 1 1 25; 0 2 25.
4) An alternative refinement of the structure with the disordered propionic acid molecule being removed was carried out with SHELXL (Sheldrick, 2015*b*) using the *SQUEEZE* option in *PLATON* (Spek, 2015). The refinement converged with the folowing reliability factors: _refine_ls_R_factor_all = 0.0308, _refine_ls_R_factor_gt = 0.0280, _refine_ls_wR_factor_ref = 0.0584, _refine_ls_wR_factor_gt = 0.0577, 385 parameters, 9024 diffractions, 4 restraints, condition for the observed diffractions $I_{obs}>2\sigma(I_{obs})$.
These values are slightly better than those obtained from the refinement with *JANA*2006 (Petříček *et al.*, 2014) with the same conditions for the observed diffractions $I_{obs}>2\sigma(I_{obs})$: _refine_ls_R_factor_all = 0.0324, _refine_ls_R_factor_gt = 0.0291, _refine_ls_wR_factor_ref = 0.0710, _refine_ls_wR_factor_gt = 0.0703, 428 parameters, 8981 diffractions, 7 restraints, 196 constraints. However, the refinement with *JANA*2006 did not include 4 × 4 × 0.946 electrons per unit cell into the calculation because the positions of the hydroxy as well as of the methyl hydrogen atoms of propionic acid were not determined.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ba1	0.265102 (12)	0.276842 (14)	0.409817 (6)	0.01040 (6)	
O1	0.20473 (14)	0.15684 (17)	0.48047 (7)	0.0141 (7)	
O2	0.20378 (14)	0.31250 (17)	0.49391 (7)	0.0160 (7)	
C1	0.19826 (19)	0.2274 (3)	0.50646 (10)	0.0139 (10)	
C2	0.1819 (2)	0.2043 (3)	0.55457 (10)	0.0194 (11)	
H1c2	0.125429	0.174223	0.557629	0.0233*	
H2c2	0.221038	0.153268	0.564196	0.0233*	
C3	0.1884 (3)	0.2883 (3)	0.58557 (11)	0.0265 (12)	
H1c3	0.170755	0.268526	0.614948	0.0397*	
H2c3	0.247161	0.310864	0.586517	0.0397*	
H3c3	0.151542	0.339958	0.575311	0.0397*	
O3	0.77274 (14)	0.27521 (18)	0.67975 (7)	0.0165 (7)	
O4	0.70280 (16)	0.13907 (18)	0.67159 (8)	0.0216 (8)	
C4	0.7343 (2)	0.2046 (3)	0.69537 (10)	0.0161 (10)	
C5	0.7235 (3)	0.1981 (3)	0.74443 (11)	0.0272 (13)	
H1c5	0.706908	0.132246	0.752502	0.0327*	
H2c5	0.675065	0.238198	0.753611	0.0327*	
C6	0.8025 (3)	0.2269 (3)	0.77026 (11)	0.0310 (13)	

H1c6	0.79028	0.223693	0.801666	0.0465*
H2c6	0.849043	0.183217	0.763236	0.0465*
H3c6	0.818705	0.29217	0.762411	0.0465*
Ba2	0.596864 (11)	0.480169 (14)	0.553971 (6)	0.00925 (6)
O5	0.39730 (13)	0.31291 (17)	0.46155 (7)	0.0149 (7)
O6	0.50137 (14)	0.39354 (17)	0.49305 (7)	0.0170 (7)
C7	0.45768 (19)	0.3181 (2)	0.48840 (9)	0.0124 (9)
C8	0.4801 (2)	0.2324 (3)	0.51561 (11)	0.0221 (11)
H1c8	0.519283	0.251628	0.539298	0.0266*
H2c8	0.511697	0.185977	0.497441	0.0266*
C9	0.4028 (2)	0.1839 (3)	0.53535 (12)	0.0265 (12)
H1c9	0.421114	0.132078	0.554706	0.0397*
H2c9	0.369982	0.230539	0.55218	0.0397*
H3c9	0.367423	0.15771	0.511864	0.0397*
O1w	0.69585 (16)	0.53342 (18)	0.47792 (8)	0.0176 (8)
H1o1w	0.720 (2)	0.4835 (17)	0.4845 (14)	0.0264*
H2o1w	0.730 (2)	0.575 (2)	0.4853 (13)	0.0264*
O2w	0.43714 (16)	0.4553 (2)	0.59034 (8)	0.0263 (9)
H1o2w	0.398 (2)	0.454 (3)	0.5728 (12)	0.0395*
H2o2w	0.419 (3)	0.472 (3)	0.6140 (8)	0.0395*
Ba3	0.723298 (12)	0.460242 (14)	0.675708 (6)	0.01063 (6)
O7	0.32899 (14)	0.09999 (17)	0.39377 (7)	0.0146 (7)
O8	0.26230 (14)	−0.02799 (17)	0.41819 (8)	0.0147 (7)
C10	0.3271 (2)	0.0247 (2)	0.41603 (10)	0.0124 (9)
C11	0.4054 (2)	−0.0038 (3)	0.44141 (13)	0.0280 (13)
H1c11	0.396235	0.00861	0.472953	0.0336*
H2c11	0.413213	−0.07378	0.439522	0.0336*
C12	0.4852 (2)	0.0456 (3)	0.42663 (16)	0.0426 (17)
H1c12	0.501238	0.022104	0.397576	0.0639*
H2c12	0.475349	0.114565	0.425252	0.0639*
H3c12	0.530935	0.03221	0.447435	0.0639*
O9	0.57946 (15)	0.58185 (18)	0.69864 (7)	0.0184 (7)
O10	0.61677 (15)	0.58789 (17)	0.62908 (7)	0.0152 (7)
C13	0.5694 (2)	0.6136 (2)	0.66061 (11)	0.0159 (10)
C14	0.4989 (2)	0.6848 (3)	0.65013 (13)	0.0311 (13)
H1c14	0.502517	0.70361	0.618957	0.0373*
H2c14	0.443144	0.653296	0.653563	0.0373*
C15	0.5020 (3)	0.7718 (4)	0.67817 (18)	0.0504 (19)
H1c15	0.459821	0.817969	0.667909	0.0756*
H2c15	0.489699	0.754313	0.708558	0.0756*
H3c15	0.558621	0.800339	0.676466	0.0756*
O11	0.62289 (13)	0.33741 (17)	0.61727 (7)	0.0127 (7)
O12	0.57444 (14)	0.35474 (18)	0.68509 (7)	0.0177 (7)
C16	0.5717 (2)	0.3152 (2)	0.64849 (10)	0.0147 (10)
C17	0.5076 (3)	0.2391 (3)	0.63987 (13)	0.0366 (14)
H1c17	0.536797	0.177233	0.635543	0.0439*
H2c17	0.479622	0.251292	0.611423	0.0439*
C18	0.4407 (4)	0.2285 (4)	0.67540 (16)	0.069 (2)

H1c18	0.404027	0.174063	0.668575	0.1033*	
H2c18	0.468423	0.217922	0.703673	0.1033*	
H3c18	0.406464	0.286802	0.676826	0.1033*	
Ba4	0.5	0.45639 (2)	0.75	0.01352 (8)	
O13	0.68012 (16)	0.44722 (19)	0.76008 (7)	0.0211 (8)	
O14	0.61403 (16)	0.4787 (2)	0.82236 (8)	0.0269 (9)	
C19	0.6806 (2)	0.4662 (3)	0.80085 (11)	0.0192 (11)	
C20	0.7660 (2)	0.4712 (3)	0.82319 (11)	0.0248 (13)	
H1c20	0.808934	0.494763	0.802197	0.0298*	
H2c20	0.785871	0.405822	0.829933	0.0298*	
C21	0.7687 (2)	0.5316 (3)	0.86451 (12)	0.0225 (12)	
H1c21	0.82734	0.536988	0.874707	0.0338*	
H2c21	0.746258	0.595323	0.858178	0.0338*	
H3c21	0.734129	0.501355	0.887271	0.0338*	
C22	0.4426 (5)	−0.0002 (7)	0.2770 (3)	0.031 (4)	0.473 (4)
C24a	0.508 (2)	0.062 (4)	0.2061 (7)	0.16 (2)	0.304 (15)
C24b	0.533 (2)	−0.014 (2)	0.2077 (7)	0.031 (4)	0.169 (15)
H1c23a	0.552935	0.078307	0.268738	0.0718*	0.304 (15)
H2c23a	0.562725	−0.025336	0.251889	0.0718*	0.304 (15)
H1c23b	0.524842	0.099005	0.249815	0.0718*	0.169 (15)
H2c23b	0.572777	0.014063	0.270039	0.0718*	0.169 (15)
O15	0.3759 (5)	0.0388 (6)	0.2758 (2)	0.050 (3)	0.473 (4)
O16	0.4501 (8)	−0.0790 (10)	0.2993 (4)	0.071 (3)	0.473 (4)
C23	0.5222 (10)	0.0286 (11)	0.2521 (6)	0.060 (5)	0.473 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba1	0.01365 (10)	0.00916 (11)	0.00838 (10)	−0.00298 (7)	−0.00251 (6)	0.00078 (7)
O1	0.0172 (11)	0.0147 (13)	0.0103 (11)	−0.0051 (10)	−0.0004 (8)	−0.0024 (9)
O2	0.0184 (12)	0.0152 (13)	0.0143 (12)	−0.0012 (10)	0.0011 (9)	0.0008 (9)
C1	0.0091 (15)	0.0207 (19)	0.0118 (16)	−0.0031 (13)	−0.0017 (11)	−0.0001 (13)
C2	0.0243 (19)	0.020 (2)	0.0139 (17)	0.0002 (15)	−0.0026 (13)	0.0002 (13)
C3	0.043 (2)	0.023 (2)	0.0128 (17)	0.0025 (18)	0.0039 (15)	−0.0018 (14)
O3	0.0211 (13)	0.0181 (14)	0.0104 (12)	0.0062 (10)	0.0022 (9)	0.0031 (9)
O4	0.0291 (14)	0.0141 (14)	0.0216 (13)	0.0038 (11)	0.0049 (10)	0.0003 (10)
C4	0.0210 (18)	0.0154 (19)	0.0118 (16)	0.0085 (14)	0.0039 (12)	0.0006 (13)
C5	0.043 (2)	0.025 (2)	0.0132 (18)	−0.0031 (18)	0.0071 (15)	0.0051 (15)
C6	0.049 (3)	0.030 (2)	0.0146 (18)	0.007 (2)	−0.0027 (16)	0.0009 (16)
Ba2	0.00957 (10)	0.00981 (11)	0.00836 (10)	−0.00025 (7)	−0.00123 (6)	−0.00020 (7)
O5	0.0169 (12)	0.0160 (13)	0.0118 (11)	−0.0008 (10)	−0.0045 (8)	0.0012 (9)
O6	0.0163 (12)	0.0137 (13)	0.0211 (12)	−0.0008 (10)	−0.0078 (9)	−0.0027 (9)
C7	0.0123 (15)	0.0139 (17)	0.0110 (15)	0.0021 (13)	0.0009 (11)	−0.0033 (12)
C8	0.0190 (18)	0.018 (2)	0.030 (2)	0.0020 (15)	−0.0033 (14)	0.0085 (15)
C9	0.0220 (19)	0.024 (2)	0.034 (2)	−0.0054 (16)	−0.0079 (15)	0.0145 (17)
O1w	0.0204 (13)	0.0160 (14)	0.0162 (12)	−0.0027 (11)	−0.0002 (10)	−0.0005 (10)
O2w	0.0137 (13)	0.0527 (19)	0.0125 (13)	−0.0020 (12)	0.0019 (9)	0.0017 (12)
Ba3	0.01169 (10)	0.01076 (11)	0.00942 (10)	−0.00040 (7)	0.00187 (6)	−0.00148 (7)

O7	0.0172 (12)	0.0134 (12)	0.0132 (11)	−0.0022 (10)	−0.0025 (9)	0.0022 (9)
O8	0.0138 (12)	0.0120 (13)	0.0183 (12)	0.0010 (9)	0.0025 (9)	−0.0003 (9)
C10	0.0108 (15)	0.0144 (17)	0.0122 (16)	0.0017 (13)	−0.0001 (11)	−0.0040 (12)
C11	0.025 (2)	0.024 (2)	0.035 (2)	0.0055 (17)	−0.0136 (16)	0.0035 (17)
C12	0.014 (2)	0.039 (3)	0.075 (4)	−0.0002 (19)	−0.018 (2)	0.001 (2)
O9	0.0226 (13)	0.0167 (13)	0.0160 (12)	−0.0012 (11)	0.0052 (9)	0.0005 (10)
O10	0.0197 (12)	0.0160 (13)	0.0100 (11)	−0.0027 (10)	0.0002 (9)	−0.0001 (9)
C13	0.0175 (16)	0.0118 (17)	0.0184 (17)	−0.0030 (14)	0.0017 (13)	−0.0014 (13)
C14	0.024 (2)	0.031 (2)	0.038 (2)	0.0067 (18)	0.0017 (16)	−0.0008 (18)
C15	0.036 (3)	0.041 (3)	0.074 (4)	0.014 (2)	−0.008 (2)	−0.016 (3)
O11	0.0121 (11)	0.0153 (13)	0.0106 (11)	0.0013 (9)	0.0032 (8)	0.0008 (8)
O12	0.0168 (12)	0.0208 (14)	0.0154 (12)	−0.0028 (11)	0.0048 (9)	−0.0055 (9)
C16	0.0157 (16)	0.0146 (18)	0.0137 (16)	−0.0009 (14)	0.0046 (12)	−0.0008 (12)
C17	0.040 (2)	0.039 (3)	0.031 (2)	−0.026 (2)	0.0169 (18)	−0.0183 (19)
C18	0.073 (4)	0.071 (4)	0.062 (3)	−0.061 (4)	0.046 (3)	−0.035 (3)
Ba4	0.01414 (14)	0.01790 (16)	0.00851 (13)	0	0.00393 (9)	0
O13	0.0259 (14)	0.0265 (15)	0.0110 (12)	0.0051 (11)	−0.0003 (10)	−0.0023 (10)
O14	0.0211 (13)	0.048 (2)	0.0111 (13)	0.0057 (13)	0.0015 (10)	0.0005 (11)
C19	0.0256 (19)	0.0198 (19)	0.0123 (17)	0.0049 (15)	0.0013 (13)	0.0010 (13)
C20	0.023 (2)	0.037 (3)	0.0148 (19)	0.0069 (17)	−0.0013 (13)	−0.0007 (16)
C21	0.0209 (19)	0.025 (2)	0.0214 (19)	−0.0045 (16)	−0.0028 (14)	−0.0011 (15)
C22	0.037 (7)	0.028 (5)	0.029 (6)	−0.003 (5)	−0.014 (4)	0.006 (4)
C24a	0.12 (3)	0.23 (5)	0.14 (3)	0.01 (3)	0.05 (2)	0.09 (3)
C24b	0.037 (7)	0.028 (5)	0.029 (6)	0.003 (5)	−0.014 (4)	−0.006 (4)
O15	0.038 (4)	0.057 (5)	0.054 (5)	−0.020 (4)	0.014 (3)	−0.015 (4)
O16	0.037 (4)	0.059 (6)	0.116 (7)	0.000 (4)	0.002 (4)	0.046 (5)
C23	0.050 (11)	0.056 (8)	0.074 (9)	−0.014 (6)	−0.031 (9)	0.027 (7)

Geometric parameters (Å, º)

O1—C1	1.273 (4)	C18—H1c18	0.98
O2—C1	1.256 (4)	C18—H2c18	0.98
C1—C2	1.528 (4)	C18—H3c18	0.98
C2—H1c2	0.99	O13—C19	1.274 (4)
C2—H2c2	0.99	O14—C19	1.251 (4)
C2—C3	1.515 (5)	C19—C20	1.513 (5)
C3—H1c3	0.98	C20—H1c20	0.99
C3—H2c3	0.98	C20—H2c20	0.99
C3—H3c3	0.98	C20—C21	1.521 (5)
O3—C4	1.255 (4)	C21—H1c21	0.98
O4—C4	1.272 (4)	C21—H2c21	0.98
C4—C5	1.512 (5)	C21—H3c21	0.98
C5—H1c5	0.99	C22—O15	1.187 (12)
C5—H2c5	0.99	C22—O16	1.303 (18)
C5—C6	1.529 (6)	C22—C23	1.523 (18)
C6—H1c6	0.98	C24a—C23	1.50 (3)
C6—H2c6	0.98	C24b—C23	1.49 (3)
C6—H3c6	0.98	H1c23a—C23	0.99

O5—C7	1.260 (4)	H2c23a—C23	0.99
O6—C7	1.270 (4)	H1c23b—C23	0.99
C7—C8	1.504 (5)	H2c23b—C23	0.99
C8—H1c8	0.99	Ba1—O1	2.898 (2)
C8—H2c8	0.99	Ba1—O2	2.791 (2)
C8—C9	1.521 (5)	Ba1—O3^{i}	2.835 (2)
C9—H1c9	0.98	Ba1—O4^{i}	2.923 (2)
C9—H2c9	0.98	Ba1—O5	2.666 (2)
C9—H3c9	0.98	Ba1—O7	2.720 (2)
O1w—H1o1w	0.82 (3)	Ba1—O8^{ii}	2.781 (2)
O1w—H2o1w	0.82 (3)	Ba1—O10^{iii}	2.913 (2)
O2w—H1o2w	0.82 (3)	Ba1—O11^{i}	2.879 (2)
O2w—H2o2w	0.81 (3)	Ba2—O1^{iv}	2.774 (2)
O7—C10	1.256 (4)	Ba2—O5^{iii}	2.940 (2)
O8—C10	1.263 (4)	Ba2—O6	2.685 (2)
C10—C11	1.513 (5)	Ba2—O6^{iii}	2.757 (2)
C11—H1c11	0.99	Ba2—O1w	2.898 (2)
C11—H2c11	0.99	Ba2—O2w	2.777 (3)
C11—C12	1.507 (6)	Ba2—O8^{iv}	2.827 (2)
C12—H1c12	0.98	Ba2—O10	2.765 (2)
C12—H2c12	0.98	Ba2—O11	2.813 (2)
C12—H3c12	0.98	Ba3—O3	2.711 (3)
O9—C13	1.255 (4)	Ba3—O4^{v}	2.767 (3)
O10—C13	1.272 (4)	Ba3—O7^{iv}	2.829 (2)
C13—C14	1.528 (5)	Ba3—O8^{iv}	3.084 (2)
C14—H1c14	0.99	Ba3—O9	2.924 (2)
C14—H2c14	0.99	Ba3—O10	2.838 (2)
C14—C15	1.491 (7)	Ba3—O11	2.943 (2)
C15—H1c15	0.98	Ba3—O12	2.791 (2)
C15—H2c15	0.98	Ba3—O13	2.673 (2)
C15—H3c15	0.98	Ba3—O15^{iv}	2.828 (7)
H1c15—H2c15	1.6003	Ba4—O9	2.670 (2)
H1c15—H3c15	1.6003	Ba4—O9^{vi}	2.670 (2)
H2c15—H3c15	1.6003	Ba4—O12	2.710 (2)
O11—C16	1.288 (4)	Ba4—O12^{vi}	2.710 (2)
O12—C16	1.249 (4)	Ba4—O13	2.862 (3)
C16—C17	1.494 (5)	Ba4—O13^{vi}	2.862 (3)
C17—H1c17	0.99	Ba4—O14	2.868 (2)
C17—H2c17	0.99	Ba4—O14^{vi}	2.868 (2)
C17—C18	1.522 (7)		

O1—C1—O2	122.8 (3)	O2—Ba1—O8^{ii}	71.65 (7)
O1—C1—C2	116.7 (3)	O2—Ba1—O10^{iii}	118.77 (6)
O2—C1—C2	120.5 (3)	O2—Ba1—O11^{i}	95.39 (6)
C1—C2—H1c2	109.47	O3^{i}—Ba1—O4^{i}	45.29 (7)
C1—C2—H2c2	109.47	O3^{i}—Ba1—O5	126.01 (6)
C1—C2—C3	115.2 (3)	O3^{i}—Ba1—O7	64.90 (7)
H1c2—C2—H2c2	103.07	O3^{i}—Ba1—O8^{ii}	110.40 (7)

H1c2—C2—C3	109.47	O3^{i}—Ba1—O10^{iii}	75.30 (6)
H2c2—C2—C3	109.47	O3^{i}—Ba1—O11^{i}	67.20 (6)
C2—C3—H1c3	109.47	O4^{i}—Ba1—O5	133.75 (7)
C2—C3—H2c3	109.47	O4^{i}—Ba1—O7	109.79 (7)
C2—C3—H3c3	109.47	O4^{i}—Ba1—O8^{ii}	68.25 (7)
H1c3—C3—H2c3	109.47	O4^{i}—Ba1—O10^{iii}	66.77 (7)
H1c3—C3—H3c3	109.47	O4^{i}—Ba1—O11^{i}	73.57 (7)
H2c3—C3—H3c3	109.47	O5—Ba1—O7	89.40 (7)
O3—C4—O4	122.7 (3)	O5—Ba1—O8^{ii}	83.15 (7)
O3—C4—C5	118.6 (3)	O5—Ba1—O10^{iii}	67.52 (6)
O4—C4—C5	118.6 (3)	O5—Ba1—O11^{i}	152.39 (7)
C4—C5—H1c5	109.47	O7—Ba1—O8^{ii}	166.01 (7)
C4—C5—H2c5	109.47	O7—Ba1—O10^{iii}	106.39 (7)
C4—C5—C6	113.8 (3)	O7—Ba1—O11^{i}	74.36 (6)
H1c5—C5—H2c5	104.72	O8^{ii}—Ba1—O10^{iii}	59.80 (7)
H1c5—C5—C6	109.47	O8^{ii}—Ba1—O11^{i}	116.89 (6)
H2c5—C5—C6	109.47	O10^{iii}—Ba1—O11^{i}	138.06 (6)
C5—C6—H1c6	109.47	O1^{iv}—Ba2—O5^{iii}	127.04 (6)
C5—C6—H2c6	109.47	O1^{iv}—Ba2—O6	76.61 (7)
C5—C6—H3c6	109.47	O1^{iv}—Ba2—O6^{iii}	126.29 (6)
H1c6—C6—H2c6	109.47	O1^{iv}—Ba2—O1w	62.81 (7)
H1c6—C6—H3c6	109.47	O1^{iv}—Ba2—O2w	128.49 (8)
H2c6—C6—H3c6	109.47	O1^{iv}—Ba2—O8^{iv}	73.22 (7)
O5—C7—O6	122.2 (3)	O1^{iv}—Ba2—O10	128.55 (7)
O5—C7—C8	119.4 (3)	O1^{iv}—Ba2—O11	71.28 (6)
O6—C7—C8	118.4 (3)	O5^{iii}—Ba2—O6	110.59 (7)
C7—C8—H1c8	109.47	O5^{iii}—Ba2—O6^{iii}	45.60 (6)
C7—C8—H2c8	109.47	O5^{iii}—Ba2—O1w	66.41 (7)
C7—C8—C9	112.8 (3)	O5^{iii}—Ba2—O2w	102.51 (8)
H1c8—C8—H2c8	105.89	O5^{iii}—Ba2—O8^{iv}	77.63 (6)
H1c8—C8—C9	109.47	O5^{iii}—Ba2—O10	65.91 (6)
H2c8—C8—C9	109.47	O5^{iii}—Ba2—O11	143.89 (6)
C8—C9—H1c9	109.47	O6—Ba2—O6^{iii}	67.25 (7)
C8—C9—H2c9	109.47	O6—Ba2—O1w	82.13 (7)
C8—C9—H3c9	109.47	O6—Ba2—O2w	73.22 (7)
H1c9—C9—H2c9	109.47	O6—Ba2—O8^{iv}	146.54 (7)
H1c9—C9—H3c9	109.47	O6—Ba2—O10	152.38 (7)
H2c9—C9—H3c9	109.47	O6—Ba2—O11	103.72 (7)
H1o1w—O1w—H2o1w	104 (3)	O6^{iii}—Ba2—O1w	73.74 (7)
H1o2w—O2w—H2o2w	109 (4)	O6^{iii}—Ba2—O2w	77.20 (7)
O7—C10—O8	122.6 (3)	O6^{iii}—Ba2—O8^{iv}	121.61 (7)
O7—C10—C11	118.7 (3)	O6^{iii}—Ba2—O10	98.40 (7)
O8—C10—C11	118.7 (3)	O6^{iii}—Ba2—O11	153.77 (6)
C10—C11—H1c11	109.47	O1w—Ba2—O2w	147.42 (7)
C10—C11—H2c11	109.47	O1w—Ba2—O8^{iv}	71.48 (7)
C10—C11—C12	114.1 (3)	O1w—Ba2—O10	117.64 (7)
H1c11—C11—H2c11	104.42	O1w—Ba2—O11	130.99 (7)
H1c11—C11—C12	109.47	O2w—Ba2—O8^{iv}	138.40 (7)

H2c11—C11—C12	109.47	O2w—Ba2—O10	80.75 (7)
C11—C12—H1c12	109.47	O2w—Ba2—O11	76.60 (7)
C11—C12—H2c12	109.47	O8^{iv}—Ba2—O10	61.04 (7)
C11—C12—H3c12	109.47	O8^{iv}—Ba2—O11	80.03 (6)
H1c12—C12—H2c12	109.47	O10—Ba2—O11	78.51 (6)
H1c12—C12—H3c12	109.47	O3—Ba3—O4^{v}	138.34 (7)
H2c12—C12—H3c12	109.47	O3—Ba3—O7^{iv}	65.10 (7)
O9—C13—O10	121.8 (3)	O3—Ba3—O8^{iv}	106.22 (6)
O9—C13—C14	121.2 (3)	O3—Ba3—O9	140.37 (7)
O10—C13—C14	117.0 (3)	O3—Ba3—O10	142.77 (7)
C13—C14—H1c14	109.47	O3—Ba3—O11	67.87 (6)
C13—C14—H2c14	109.47	O3—Ba3—O12	74.39 (7)
C13—C14—C15	112.9 (3)	O3—Ba3—O13	87.95 (7)
H1c14—C14—H2c14	105.79	O3—Ba3—O15^{iv}	74.66 (16)
H1c14—C14—C15	109.47	O4^{v}—Ba3—O7^{iv}	89.29 (7)
H2c14—C14—C15	109.47	O4^{v}—Ba3—O8^{iv}	66.10 (6)
C14—C15—H1c15	109.47	O4^{v}—Ba3—O9	79.07 (7)
C14—C15—H2c15	109.47	O4^{v}—Ba3—O10	69.89 (7)
C14—C15—H3c15	109.47	O4^{v}—Ba3—O11	136.80 (6)
H1c15—C15—H2c15	109.47	O4^{v}—Ba3—O12	147.07 (7)
H1c15—C15—H3c15	109.47	O4^{v}—Ba3—O13	102.31 (7)
H2c15—C15—H3c15	109.47	O4^{v}—Ba3—O15^{iv}	70.16 (16)
O11—C16—O12	122.3 (3)	O7^{iv}—Ba3—O8^{iv}	43.61 (6)
O11—C16—C17	117.8 (3)	O7^{iv}—Ba3—O9	144.26 (6)
O12—C16—C17	119.9 (3)	O7^{iv}—Ba3—O10	99.24 (6)
C16—C17—H1c17	109.47	O7^{iv}—Ba3—O11	71.80 (6)
C16—C17—H2c17	109.47	O7^{iv}—Ba3—O12	114.55 (7)
C16—C17—C18	114.4 (4)	O7^{iv}—Ba3—O13	148.63 (7)
H1c17—C17—H2c17	104.01	O7^{iv}—Ba3—O15^{iv}	83.84 (15)
H1c17—C17—C18	109.47	O8^{iv}—Ba3—O9	101.45 (6)
H2c17—C17—C18	109.47	O8^{iv}—Ba3—O10	57.13 (6)
C17—C18—H1c18	109.47	O8^{iv}—Ba3—O11	73.92 (6)
C17—C18—H2c18	109.47	O8^{iv}—Ba3—O12	115.25 (6)
C17—C18—H3c18	109.47	O8^{iv}—Ba3—O13	165.74 (7)
H1c18—C18—H2c18	109.47	O8^{iv}—Ba3—O15^{iv}	108.43 (15)
H1c18—C18—H3c18	109.47	O9—Ba3—O10	45.02 (6)
H2c18—C18—H3c18	109.47	O9—Ba3—O11	93.91 (6)
O13—C19—O14	122.6 (3)	O9—Ba3—O12	68.32 (7)
O13—C19—C20	117.1 (3)	O9—Ba3—O13	67.09 (7)
O14—C19—C20	120.3 (3)	O9—Ba3—O15^{iv}	122.20 (16)
C19—C20—H1c20	109.47	O10—Ba3—O11	75.23 (6)
C19—C20—H2c20	109.47	O10—Ba3—O12	83.50 (7)
C19—C20—C21	115.2 (3)	O10—Ba3—O13	112.10 (7)
H1c20—C20—H2c20	103.1	O10—Ba3—O15^{iv}	139.87 (16)
H1c20—C20—C21	109.47	O11—Ba3—O12	45.51 (6)
H2c20—C20—C21	109.47	O11—Ba3—O13	114.08 (7)
C20—C21—H1c21	109.47	O11—Ba3—O15^{iv}	141.20 (16)
C20—C21—H2c21	109.47	O12—Ba3—O13	69.52 (7)

C20—C21—H3c21	109.47	O12—Ba3—O15^{iv}	131.73 (16)
H1c21—C21—H2c21	109.47	O13—Ba3—O15^{iv}	73.25 (16)
H1c21—C21—H3c21	109.47	O9—Ba4—O9^{vi}	97.61 (7)
H2c21—C21—H3c21	109.47	O9—Ba4—O12	73.28 (7)
O15—C22—O16	119.1 (10)	O9—Ba4—O12^{vi}	168.56 (7)
O15—C22—C23	126.5 (11)	O9—Ba4—O13	68.05 (7)
O16—C22—C23	114.3 (10)	O9—Ba4—O13^{vi}	115.65 (7)
C22—C23—C24a	115.3 (17)	O9—Ba4—O14	94.96 (7)
C22—C23—C24b	116.0 (17)	O9—Ba4—O14^{vi}	76.68 (7)
C22—C23—H1c23a	109.47	O9^{vi}—Ba4—O12	168.56 (7)
C22—C23—H2c23a	109.47	O9^{vi}—Ba4—O12^{vi}	73.28 (7)
C22—C23—H1c23b	109.47	O9^{vi}—Ba4—O13	115.65 (7)
C22—C23—H2c23b	109.47	O9^{vi}—Ba4—O13^{vi}	68.05 (7)
C24a—C23—H1c23a	109.47	O9^{vi}—Ba4—O14	76.68 (7)
C24a—C23—H2c23a	109.47	O9^{vi}—Ba4—O14^{vi}	94.96 (7)
C24b—C23—H1c23b	109.47	O12—Ba4—O12^{vi}	116.58 (7)
C24b—C23—H2c23b	109.47	O12—Ba4—O13	67.95 (7)
H1c23a—C23—H2c23a	102.92	O12—Ba4—O13^{vi}	109.16 (7)
H1c23b—C23—H2c23b	102.1	O12—Ba4—O14	110.46 (7)
O1—Ba1—O2	45.88 (7)	O12—Ba4—O14^{vi}	76.42 (7)
O1—Ba1—O3^{i}	125.73 (7)	O12^{vi}—Ba4—O13	109.16 (7)
O1—Ba1—O4^{i}	139.24 (7)	O12^{vi}—Ba4—O13^{vi}	67.95 (7)
O1—Ba1—O5	85.73 (6)	O12^{vi}—Ba4—O14	76.42 (7)
O1—Ba1—O7	74.18 (6)	O12^{vi}—Ba4—O14^{vi}	110.46 (7)
O1—Ba1—O8^{ii}	116.81 (7)	O13—Ba4—O13^{vi}	174.86 (7)
O1—Ba1—O10^{iii}	153.16 (6)	O13—Ba4—O14	45.47 (7)
O1—Ba1—O11^{i}	68.60 (6)	O13—Ba4—O14^{vi}	135.33 (7)
O2—Ba1—O3^{i}	161.74 (7)	O13^{vi}—Ba4—O14	135.33 (7)
O2—Ba1—O4^{i}	126.49 (7)	O13^{vi}—Ba4—O14^{vi}	45.47 (7)
O2—Ba1—O5	72.03 (6)	O14—Ba4—O14^{vi}	167.46 (9)
O2—Ba1—O7	117.23 (7)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*w*—H1*o*1*w*···O1^{iv}	0.82 (3)	2.25 (3)	2.957 (3)	145 (4)
O1*w*—H2*o*1*w*···O2^{iii}	0.82 (3)	2.00 (3)	2.813 (3)	171 (3)
O2*w*—H1*o*2*w*···O1*w*^{iii}	0.82 (3)	2.15 (3)	2.963 (3)	172 (4)
O2*w*—H2*o*2*w*···O14^{vi}	0.81 (3)	2.01 (3)	2.807 (3)	164 (4)
C17—H1*c*17···O16^{vii}	0.99	2.43	2.989 (15)	115.22

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