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$Ca(BF_4)_2 \cdot xH_2O$ redefined from powder diffraction as hydrogen-bonded $Ca(H_2O)_4(BF_4)_2$ ribbons

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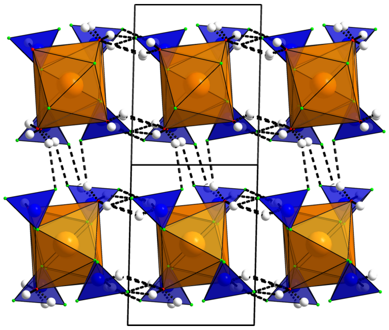
The crystal structure of the calcium bis(tetrafluoroborate) hydrate $Ca(BF_4)_2 \cdot xH_2O$ has been determined from laboratory powder diffraction data. The water molecules all belong to $[CaO_4F_4]$ square antiprisms sharing F corners with $[BF_4]$ tetrahedra, forming a mono-dimensional structure of infinite ribbons interconnected by $H \cdots F$ and $H \cdots O$ hydrogen bonds. No place is found for interstitial water molecules, so that the compound has to be reformulated as $Ca(H_2O)_4(BF_4)_2$, which is isostructural with calcium perchlorate tetrahydrate, $Ca(ClO_4)_2 \cdot 4H_2O$.



1. Introduction

Calcium-based rechargeable batteries were thought to be impossible until the demonstration of the feasibility of calcium plating at moderate temperatures (Ponrouch *et al.*, 2016). It was observed that optimal Ca metal deposition occurred using electrolytes containing $Ca(BF_4)_2$ in a mixture of ethylene carbonate and propylene carbonate at $T > 75$ °C. There was then a need for dry and contaminant-free $Ca(BF_4)_2$. Different synthetic routes were explored as alternatives to the drying of the commercial hydrated salt $Ca(BF_4)_2 \cdot xH_2O$ which proved to be not trivial by Forero-Saboya *et al.* (2020), who proposed a value for x of 4.6, estimated by Karl–Fisher coulometer titration. However, this would correspond to 28 wt%, and a two-step decomposition is observed during thermogravimetric analysis (TGA), at 158 and 240 °C, with losses of 14.3 and 52.5 wt%, respectively. Close to two water molecules would escape first and it is believed that the remaining water persists in the solid and participates in the anion hydrolysis at temperatures above 170 °C. An older estimation for x (= 5) can be found in the PDF card 00-022-0523, dated 1969 (Kabekkodu *et al.*, 2024). The present work aims at providing a definitive value for x, if any, by a successful attempt to determine the structure using the powder diffraction route since no single crystal is available.

2. Experimental

2.1. Powder diffraction

Two powder diffraction patterns of the commercial calcium bis(tetrafluoroborate) hydrate [$Ca(BF_4)_2 \cdot xH_2O$, Alfa Aesar] were measured using a D501 Siemens Bragg–Brentano diffractometer, the sample being either pressed or dusted on the horizontal holder, showing strong differences due to preferred orientation (see Fig. S1 in the supporting information).

Table 1
Experimental details.

Crystal data	
Chemical formula	$Ca(BF_4)_2.4H_2O$
M_r	285.76
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
a, b, c (Å)	5.5192 (3), 7.6756 (3), 11.6518 (5)
α, β, γ (°)	77.439 (3), 89.579 (3), 88.625 (2)
V (Å^3)	481.65 (4)
Z	2
Radiation type	Cu $K\alpha$, λ = 1.540560 Å
Specimen shape, size (mm)	Flat sheet, 25 × 10
Data collection	
Diffractometer	Siemens D501
Specimen mounting	Plate sample holder
Data collection mode	Reflection
Scan method	Step
2θ values (°)	$2\theta_{min}$ = 4.817, $2\theta_{max}$ = 109.817, $2\theta_{step}$ = 0.020
Refinement	
R factors and goodness of fit	R_p = 6.213, R_{wp} = 8.419, R_{exp} = 1.973, R_{Bragg} = 3.78, χ^2 = 18.207
No. of parameters	115
No. of restraints	56

Computer programs: *McMaille* (Le Bail, 2004), *ESPOIR* (Le Bail, 2001, *FULLPROF* (Rodríguez-Carvajal, 1993), *DIAMOND* (Brandenburg, 1999) and *publCIF* (Westrip, 2010).

2.2. Refinement

Indexing was realized using the *McMaille* software (Le Bail, 2004), leading to a triclinic cell. It was then confirmed and the intensities were extracted using the Le Bail method (Le Bail, 2005) implemented in the *FULLPROF* software (Rodríguez-Carvajal, 1993). The orthorhombic crystal structure of anhydrous $Ca(BF_4)_2$ (Jordan *et al.*, 1975) has a volume close to 1100 Å^3 for Z = 8; one would expect Z = 2 for the hydrated phase having $V \sim 500$ Å^3. The direct-space *ESPOIR* software (Le Bail, 2001) provided a starting solution when using the $[CaF_8]$ square antiprism taken from the anhydrous phase, moved randomly in the triclinic cell together with two B and five O atoms. In the resulting model, $[BF_2O_2]$ tetrahedra were formed interconnecting $[CaF_8]$ antiprisms in isolated infinite ribbons. After Rietveld (1969) refinements from this initial model, still using *FULLPROF*, it was concluded that $x = 4$; the initial $[CaF_8]$ block sharing four of its F corners with $[BF_4]$ tetrahedra should be redefined as a $[CaO_4F_4]$ square antiprism. The hydrogen-bonding scheme was then guessed observing the shortest distances between the O atoms and the terminal F atoms of the $[BF_4]$ tetrahedra not in common with the calcium; six O—H···F and two O—H···O hydrogen bonds were disclosed. During the final refinement, soft constraints were applied on the bonding scheme and on the $[BF_4]$ tetrahedra. Scattering factors for B^{3+} cations were taken from Olukayode *et al.* (2023). The Rietveld plot is shown in Fig. 1. Crystal data, data collection and structure refinement details are summarized in Table 1.

3. Results and discussion

Given that all four water molecules are part of the $[CaO_4F_4]$ square antiprisms, the compound chemistry can be reformulated as $Ca(H_2O)_4(BF_4)_2$ instead of the previous $Ca(BF_4)_2\cdot(x = 4)H_2O$. Indeed, there is no place to acccomodate any additional water molecule. Projections of the structure along the *a* and *b* axes are shown, respectively, in Figs. 2 and 3, disclosing the complex hydrogen-bonding scheme inter-

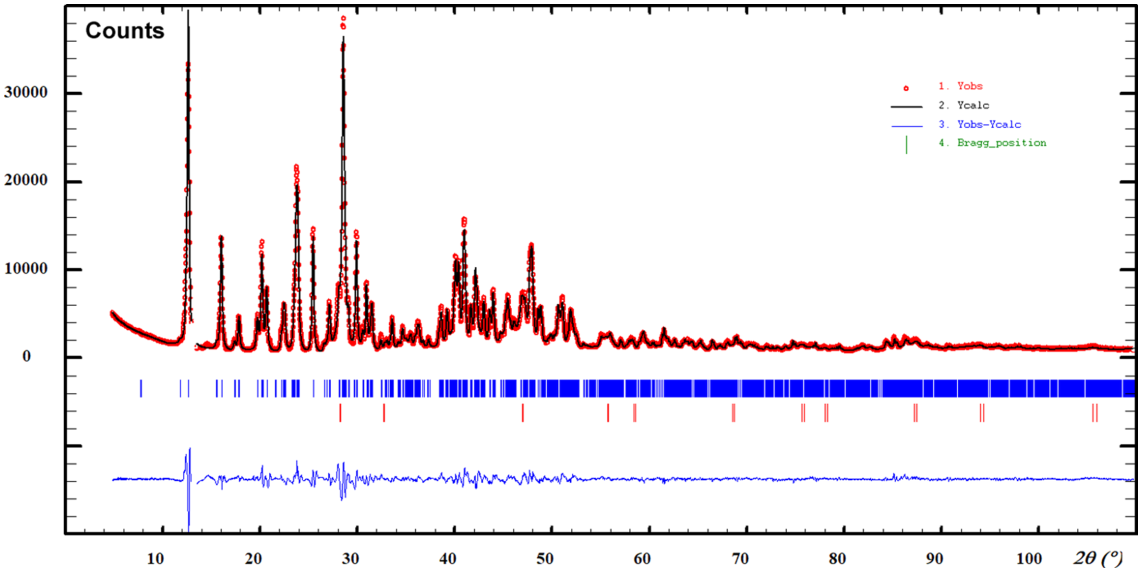


Figure 1
Refined diffraction pattern from laboratory data for $Ca(H_2O)_4(BF_4)_2$. Red dots represent the observed data and the black line represents the calculated pattern. Bragg ticks are the peak positions (main phase at the top and the CaF_2 impurity below). The bottom blue curve shows the difference between the observed and calculated patterns. A peak close to 13° (2θ) which may correspond to the (002) reflection from one tiny single crystal of the anhydrous phase in diffraction position was removed by an excluded zone (see also Fig. S1 in the supporting information, showing another pattern where there is no such peak).

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H11$\cdots$O3$^{\rm i}$	0.84 (4)	2.19 (4)	2.859 (14)	138 (4)
O1—H12$\cdots$F2$^{\rm ii}$	0.83 (7)	2.17 (6)	2.925 (14)	151 (5)
O2—H21$\cdots$O4$^{\rm iii}$	0.86 (3)	2.23 (5)	3.015 (13)	152 (6)
O2—H22$\cdots$F2$^{\rm iv}$	0.88 (2)	2.18 (3)	3.041 (12)	170 (7)
O3—H31$\cdots$F5$^{\rm v}$	0.83 (5)	2.20 (4)	2.847 (12)	136 (4)
O3—H32$\cdots$F6$^{\rm vi}$	0.82 (5)	2.07 (5)	2.845 (13)	156 (6)
O4—H41$\cdots$F1	0.85 (4)	2.16 (4)	2.848 (13)	139 (4)
O4—H42$\cdots$F6	0.86 (6)	2.05 (7)	2.873 (13)	161 (6)

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

connecting ribbons built from the calcium in square antiprisms sharing their F corners with [BF$_4$] tetrahedra (Table 2). A view in the direction of the ribbons (Fig. 4) shows how they are efficiently stacked. Six of the eight hydrogen bonds are H$\cdots$F pointing towards the terminal F atoms of the two BF$_4^-$ anions (F1, F2, F5 and F6, not shared with Ca), the remaining two hydrogen bonds are H$\cdots$O bonds involving atoms O3 and O4. There is no intra-ribbon hydrogen bond in the structure. Each ribbon is interconnected by hydrogen bonding to four adjacent ribbons (Fig. 4), completing the structure cohesion to three dimensions. It should be noticed that this bonding scheme is an hypothesis proposed from powder diffraction data, *i.e.* the H atoms do not come from a Fourier difference map. Then subtleties like bifurcated bonds are hardly seen; however, bond valence calculations in the supporting material are satisfying. Trying to explain the first step in the thermogravimetric analysis (TGA) corresponding closely to the departure of two water molecules would be hazardous. Which two O atoms would first escape at 158 °C? A thermodiffractometry study would possibly reveal the existence of a dihydrate which could be formulated Ca(H$_2$O)$_2$(BF$_4$)$_2$. So the final model presented here would require either the production of large-enough single crystals or a neutron powder diffraction approach for complete confirmation, but the new Ca(H$_2$O)$_4$(BF$_4$)$_2$ formula looks likely. At least we definitely have a cell and the positions of the non-H atoms.

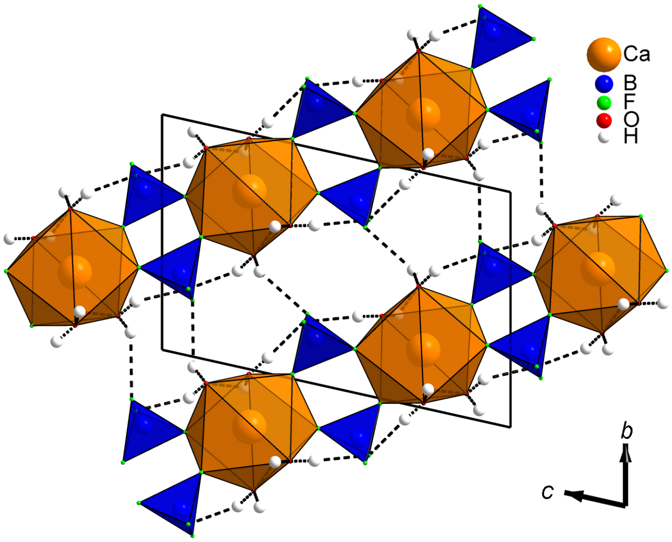


Figure 2
Unit-cell projection of the Ca(H$_2$O)$_4$(BF$_4$)$_2$ structure along the *a* axis, showing the [BF$_4$] tetrahedra in blue forming infinite ribbons extending along [011] by sharing half of their F corners with the [CaO$_4$F$_4$] square antiprisms. This view shows mainly the O—H$\cdots$F inter-ribbon bonding involving the terminal F atoms of the [BF$_4$] tetrahedra (not shared with Ca).

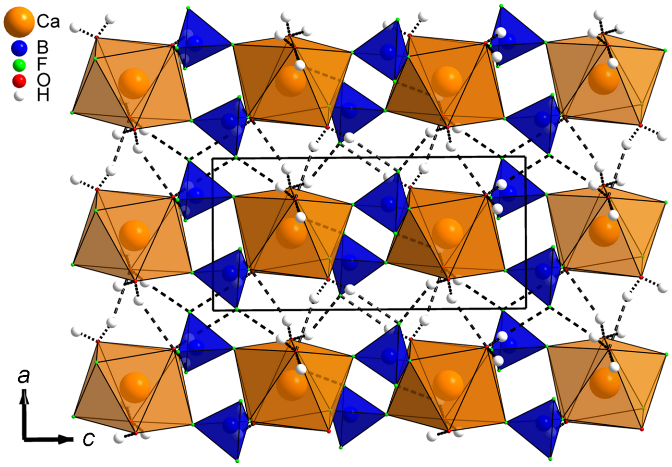


Figure 3
Unit-cell projection of the Ca(H$_2$O)$_4$(BF$_4$)$_2$ structure along the *b* axis, showing the intricate hydrogen-bonding scheme, with both O—H$\cdots$F and O—H$\cdots$O hydrogen bonds maintaining in 3D the 1D ribbons built from [CaO$_4$F$_4$] square antiprisms sharing F corners with [BF$_4$] tetrahedra.

Searching ultimately for related materials, the title compound was finally found to be isostructural with calcium perchlorate tetrahydrate, Ca(ClO$_4$)$_2$·4H$_2$O (Hennings *et al.*, 2014*a*), which is not unexpected. A search was made using the ‘tetrahydrate’ keyword in all *Acta Crystallographica* articles, the calcium perchlorate tetrahydrate appeared 49th in a list of 1313 papers. The unit-cell parameters of these two compounds

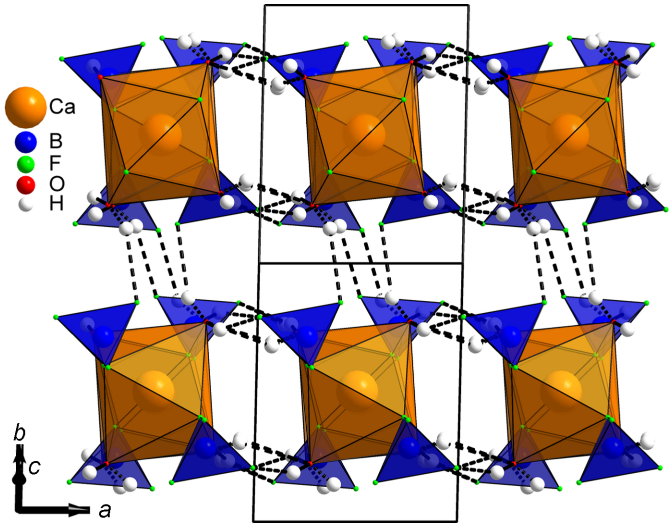


Figure 4
Unit-cell projection of the Ca(H$_2$O)$_4$(BF$_4$)$_2$ structure along the [0$\bar{1}$1] axis, showing the space between the 1D ribbons and how they are interconnected by hydrogen bonding.

are not close enough for obtaining a match from the *QualX* search-match sofware (Altomare *et al.*, 2015). Both phases present a similar hydrogen-bonding scheme. In spite of $Sr(BF_4)_2$ being isostructural with $Ca(BF_4)_2$ (Goreshnik *et al.*, 2010), no strontium tetrafluoroborate tetrahydrate was found in the literature; a trihydrate was characterized recently (Charkin *et al.*, 2023) and is tetragonal. Finally, $Sr(ClO_4)_2·4H_2O$ (Hennings *et al.*, 2014*b*) is not isostructural with $Ca(ClO_4)_2·4H_2O$; there is no ribbon and each perchlorate anion coordinates to a dimeric unit of two Sr^{2+} cations.

Anisotropy-induced physical properties are expected from such hydrogen-bonded ribbons (Xia *et al.*, 2003), which is beyond the scope of the present article, but suggests it would be of interest to look more closely at the title compound and the perchlorate analog.

4. Related literature

The following references are cited in the supporting information for this article: Brese & O'Keeffe (1991); Brown & Altermatt (1985).

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supporting information

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$Ca(BF_4)_2 \cdot xH_2O$ redefined from powder diffraction as hydrogen-bonded $Ca(H_2O)_4(BF_4)_2$ ribbons

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Computing details

Calcium bis(tetrafluoroborate) tetrahydrate $Ca(BF_4)_2.xH_2O$

Crystal data

$Ca(BF_4)_2.4H_2O$
M_r = 285.76
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 5.5192 (3) Å
b = 7.6756 (3) Å
c = 11.6518 (5) Å
α = 77.439 (3)°
β = 89.579 (3)°
γ = 88.625 (2)°
V = 481.65 (4) Å^3
Z = 2
F(000) = 284
D_x = 1.970 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.540560 Å
T = 293 K
Particle morphology: fine powder
white
flat_sheet, 25 × 10 mm
Specimen preparation: Prepared at 293 K

Data collection

Siemens D501 diffractometer
Radiation source: X-ray tube
Graphite monochromator
Specimen mounting: plate sample holder
Data collection mode: reflection
Scan method: step
$2\theta_{min}$ = 4.817°, $2\theta_{max}$ = 109.817°, $2\theta_{step}$ = 0.020°

Refinement

R_p = 6.213
R_{wp} = 8.419
R_{exp} = 1.973
R_{Bragg} = 3.78
5251 data points
Excluded region(s): from 13.18 to 13.70 2-theta
Profile function: pseudo-Voigt
115 parameters
56 restraints
Background function: manual
Preferred orientation correction: (011) direction, p = 0.939(3)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Ca	0.5043 (6)	0.2451 (4)	0.2506 (4)	0.0201 (11)*
B1	0.691 (3)	0.191 (2)	0.5625 (13)	0.035 (6)*
B2	0.243 (3)	0.6607 (19)	0.0545 (13)	0.035 (6)*
F1	0.5011 (13)	0.7110 (10)	0.4168 (9)	0.0358 (13)*
F2	0.0935 (10)	0.7473 (10)	0.4062 (8)	0.0358 (13)*
F3	0.3373 (14)	−0.0207 (10)	0.3737 (6)	0.0358 (13)*
F4	0.6916 (14)	0.1862 (10)	0.4474 (6)	0.0358 (13)*

F5	0.5952 (10)	0.2388 (10)	0.9128 (8)	0.0358 (13)*
F6	1.0087 (12)	0.7163 (10)	0.0753 (8)	0.0358 (13)*
F7	0.2509 (14)	0.6727 (11)	0.9334 (6)	0.0358 (13)*
F8	0.2706 (13)	0.4841 (10)	0.1123 (7)	0.0358 (13)*
O1	0.8042 (15)	0.0218 (12)	0.2488 (12)	0.0490 (17)*
O2	0.2003 (15)	0.3521 (17)	0.3682 (8)	0.0490 (17)*
O3	0.2527 (18)	0.1006 (12)	0.1263 (9)	0.0490 (17)*
O4	0.7263 (16)	0.5128 (12)	0.2635 (10)	0.0490 (17)*
H11	0.929 (6)	0.083 (5)	0.237 (4)	0.05066*
H12	0.836 (8)	−0.066 (8)	0.303 (7)	0.05066*
H21	0.075 (6)	0.370 (11)	0.324 (2)	0.05066*
H22	0.131 (7)	0.327 (14)	0.4374 (14)	0.05066*
H31	0.344 (10)	0.044 (5)	0.090 (4)	0.05066*
H32	0.184 (14)	0.179 (8)	0.077 (3)	0.05066*
H41	0.609 (6)	0.576 (5)	0.280 (4)	0.05066*
H42	0.809 (10)	0.593 (5)	0.217 (7)	0.05066*

Geometric parameters (Å, º)

Ca—F3	2.422 (8)	F5—F8^{i}	2.227 (11)
Ca—F4	2.468 (8)	F6—F7^{viii}	2.195 (11)
Ca—F7^{i}	2.496 (8)	F6—F8^{ix}	2.237 (10)
Ca—F8	2.501 (8)	F7—F8^{x}	2.266 (10)
Ca—O1	2.357 (10)	O1—H11	0.84 (4)
Ca—O2	2.399 (11)	O1—H12	0.83 (6)
Ca—O3	2.461 (12)	O2—H21	0.86 (3)
Ca—O4	2.450 (10)	O2—H22	0.87 (2)
B1—F1^{i}	1.336 (18)	O3—H31	0.83 (5)
B1—F2^{i}	1.371 (18)	O3—H32	0.82 (5)
B1—F3^{ii}	1.368 (16)	O4—H41	0.85 (4)
B1—F4	1.350 (17)	O4—H42	0.86 (5)
B2—F5^{i}	1.305 (18)	H11—H12	1.34 (7)
B2—F6^{iii}	1.388 (18)	H21—H22	1.33 (3)
B2—F7^{iv}	1.394 (17)	H31—H32	1.33 (8)
B2—F8	1.382 (15)	H41—H42	1.31 (7)
F1—F2	2.261 (9)	F1—H41	2.15 (5)
F1—F3^{v}	2.186 (10)	F2—H12^{xi}	2.17 (6)
F1—F4^{i}	2.176 (13)	F2—H22^{xii}	2.17 (3)
F2—F3^{v}	2.222 (10)	F5—H31^{ii}	2.20 (4)
F2—F4^{i}	2.239 (12)	F6—H32^{xiii}	2.07 (5)
F3—F4^{ii}	2.199 (9)	F6—H42	2.04 (7)
F5—F6^{vi}	2.231 (9)	O3—H11^{iii}	2.19 (4)
F5—F7^{vii}	2.230 (12)	O4—H21^{ix}	2.23 (5)
F3—Ca—F4	69.9 (4)	O2—Ca—O4	85.8 (5)
F3—Ca—F7^{i}	138.3 (5)	O3—Ca—O4	146.0 (7)
F3—Ca—F8	126.0 (5)	F1^{i}—B1—F2^{i}	113.3 (13)
F3—Ca—O1	75.9 (5)	F1^{i}—B1—F3^{ii}	107.9 (12)

F3—Ca—O2	74.8 (5)	F1^{i}—B1—F4	108.2 (14)
F3—Ca—O3	71.9 (5)	F2^{i}—B1—F3^{ii}	108.5 (12)
F3—Ca—O4	141.2 (6)	F2^{i}—B1—F4	110.8 (13)
F4—Ca—F7^{i}	122.1 (5)	F3^{ii}—B1—F4	108.1 (12)
F4—Ca—F8	140.4 (5)	F5^{i}—B2—F6^{iii}	111.8 (12)
F4—Ca—O1	74.5 (5)	F5^{i}—B2—F7^{iv}	111.4 (14)
F4—Ca—O2	77.0 (5)	F5^{i}—B2—F8	111.9 (13)
F4—Ca—O3	140.9 (3)	F6^{iii}—B2—F7^{iv}	104.2 (13)
F4—Ca—O4	73.2 (4)	F6^{iii}—B2—F8	107.7 (12)
F7^{i}—Ca—F8	72.9 (4)	F7^{iv}—B2—F8	109.5 (11)
F7^{i}—Ca—O1	70.8 (4)	H11—O1—H12	107 (4)
F7^{i}—Ca—O2	143.9 (6)	H21—O2—H22	100 (4)
F7^{i}—Ca—O3	82.5 (5)	H31—O3—H32	107 (10)
F7^{i}—Ca—O4	73.3 (5)	H41—O4—H42	101 (4)
F8—Ca—O1	140.4 (6)	O1—H11—O3^{ix}	138 (3)
F8—Ca—O2	74.2 (5)	F2^{xiv}—H12—O1	151 (5)
F8—Ca—O3	72.0 (5)	O2—H21—O4^{iii}	152 (3)
F8—Ca—O4	78.1 (5)	F2^{xii}—H22—O2	170 (2)
O1—Ca—O2	144.6 (8)	F5^{ii}—H31—O3	135 (4)
O1—Ca—O3	88.3 (6)	F6^{xiii}—H32—O3	156 (4)
O1—Ca—O4	105.4 (6)	F1—H41—O4	139 (3)
O2—Ca—O3	101.1 (7)	F6—H42—O4	161 (4)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H11···O3^{ix}	0.84 (4)	2.19 (4)	2.859 (14)	138 (4)
O1—H12···F2^{xiv}	0.83 (7)	2.17 (6)	2.925 (14)	151 (5)
O2—H21···O4^{iii}	0.86 (3)	2.23 (5)	3.015 (13)	152 (6)
O2—H22···F2^{xii}	0.88 (2)	2.18 (3)	3.041 (12)	170 (7)
O3—H31···F5^{ii}	0.83 (5)	2.20 (4)	2.847 (12)	136 (4)
O3—H32···F6^{xiii}	0.82 (5)	2.07 (5)	2.845 (13)	156 (6)
O4—H41···F1	0.85 (4)	2.16 (4)	2.848 (13)	139 (4)
O4—H42···F6	0.86 (6)	2.05 (7)	2.873 (13)	161 (6)

Symmetry codes: (ii) −*x*+1, −*y*, −*z*+1; (iii) *x*−1, *y*, *z*; (ix) *x*+1, *y*, *z*; (xii) −*x*, −*y*+1, −*z*+1; (xiii) −*x*+1, −*y*+1, −*z*; (xiv) *x*+1, *y*−1, *z*.

Valence bond analysis according to the empirical expression from Brown & Altermatt (1985), using parameters for solids from Brese & O'Keefe (1991).

*References Brese, N. E. & O'Keefe, M. (1991). Acta Cryst. B**47**, 192–197. Brown, I. D. & Altermatt, D. (1985). Acta Cryst. B**41**, 244–247.*

	F1	F2	F3	F4	F5	F6	F7	F8	O1	O2	O3	O4	Σ	Σexpected
Ca			0.209	0.184			0.171	0.168	0.349	0.311	0.263	0.271	1.93	2
B1	0.862	0.784	0.790	0.830									3.27	3
B2					0.937	0.749	0.737	0.761					3.18	3

H11									0.8		0.2		1	1
H12		0.2							0.8				1	1
H21										0.8		0.2	1	1
H22		0.2								0.8			1	1
H31					0.2						0.8		1	1
H32						0.2					0.8		1	1
H41	0.2											0.8	1	1
H42						0.2						0.8	1	1
Σ	1.06	1.18	1.00	1.01	1.14	1.15	0.91	0.93	1.95	1.91	2.06	2.07		
Σexpected	1	1	1	1	1	1	1	1	2	2	2	2		