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$Ca_5Zr_3F_{22}$

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Key indicators: single-crystal X-ray study; T = 296 K; mean σ(Zr–F) = 0.002 Å; R factor = 0.036; wR factor = 0.058; data-to-parameter ratio = 24.9.

Single crystals of $Ca_5Zr_3F_{22}$, pentacalcium trizirconium docosafluoride, were obtained unexpectedly by solid-state reaction between CaF_2 and ZrF_4 in the presence of AgF. The structure of the title compound is isotypic with that of $Sr_5Zr_3F_{22}$ and can be described as being composed of layers with composition $[Zr_3F_{20}]^{8-}$ made up from two different $[ZrF_8]^{4-}$ square antiprisms (one with site symmetry 2) by corner-sharing. The layers extending parallel to the (001) plane are further linked by Ca^{2+} cations, forming a three-dimensional network. Amongst the four crystallographically different Ca^{2+} ions, three are located on twofold rotation axes. The Ca^{2+} ions exhibit coordination numbers ranging from 8 to 12, depending on the cut off, with very distorted fluorine environments. Two of the Ca^{2+} ions occupy interstices between the layers whereas the other two are located in void spaces of the $[Zr_3F_{20}]^{8-}$ layer and alternate with the two Zr atoms along [010]. The crystal under investigation was an inversion twin.

Related literature

For the isotypic Sr analogue, see: Le Bail (1996). The crystal chemistry of fluorides has been reviewed by Babel & Tressaud (1985). For phase relationships in the CaF_2–ZrF_4 system, see: L'Helgoualch *et al.* (1971); Kotsar *et al.* (1973); Ratnikov *et al.* (1977); Laval *et al.* (1987). For bond-valence analysis, see: Brese & O'Keeffe (1991).

Experimental

Crystal data

$Ca_5Zr_3F_{22}$
M_r = 892.06
Orthorhombic, $P2_12_12$
a = 9.9844 (3) Å
b = 7.4059 (2) Å
c = 9.9046 (3) Å
V = 732.38 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 4.09 mm^{-1}
T = 296 K
0.19 × 0.06 × 0.03 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.587, T_{max} = 0.747
7993 measured reflections
3466 independent reflections
2909 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.058
S = 0.99
3466 reflections
139 parameters
$\Delta\rho_{max}$ = 0.88 e Å^{-3}
$\Delta\rho_{min}$ = −0.77 e Å^{-3}
Absolute structure: Flack (1983), 1462 Friedel pairs
Flack parameter: 0.0 (4)

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: *CaRine* (Boudias & Monceau, 1998) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2595).

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supplementary materials

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Comment

Despite several reports related to investigations of the pseudo-binary system CaF_2–ZrF_4 (L′Helgoualch *et al.* 1971; Kotsar *et al.* 1973; Ratnikov *et al.* 1977; Babel & Tressaud, 1985; Laval *et al.* 1987) the title compound has never been mentioned previously. Therefore the determination of its crystal structure was of prime importance to complete a thorough examination of the phase diagram of this system.

The orthorhombic structure of the title compound is isotypic with that of $Sr_5Zr_3F_{22}$ reported by Le Bail (1996). As with this latter, the structure of $Ca_5Zr_3F_{22}$ has also been determined from an inversion twinned crystal although the crystals were grown in very different ways. Figure 1 displays the polyhedral string in $Ca_5Zr_3F_{22}$. Both Zr1 and Zr2 cations are 8-coordinated by the fluoride ions, in distorted square antiprismatic environments. The square antiprism surrounding Zr2 (site symmetry 2) with Zr—F distances ranging from 2.0771 (19) Å to 2.148 (2) Å is less distorted than that surrounding Zr1 (site symmetry 1) where Zr—F distances range from 2.062 (2) to 2.2154 (19) Å. Each Zr2 square antiprism is connected by sharing corners to four Zr1 square antiprisms as shown in Fig. 2. The crystal structure is built up from layers of corner-sharing $[ZrF_8]^{4-}$ square antiprisms. The layers extending parallel to (001) are further held together by Ca^{2+} cations to form the three-dimensional network (Fig. 3). The calcium ions are divided into four crystallographically different atoms exhibiting coordination numbers from 8 to 12, depending on the cut off, with very distorted fluorine environments. The bond-valence analysis of the title structure carried out using Brese & O′Keeffe's R_{ij} parameters for solids (Brese & O′Keeffe, 1991) is displayed in Figure 4. Large deviations from the ideal value 2 have been obtained for both Ca1 and Ca2. For this latter the value of 1.730 valence units (v.u.) is obtained with Ca—F distances up to 2.661 Å considered as relevant for the first coordination sphere whereas the value of 1.843 v.u. is reached with four additional interactions involving distances up to 3.109 Å. Despite these four additional contributions the formal charge for Ca2 still shows a deficit. For comparison, bond-valence calculations have also been performed for the homologuous $Sr_5Zr_3F_{22}$ from bond lengths reported by Le Bail (1996). Significant deviations (see Fig. 4) are also observed for the alkaline earth cations but the formal charges are in excess in this case. This may be most likely related to the size difference of the ionic radii of Ca^{2+} and Sr^{2+}. Ca2 and Ca4 occupy interstices between the layers whereas Ca3 and Ca1 are located in void spaces of the $[Zr_3F_{20}]^{8-}$ layer and alternate with Zr2 and Zr1, respectively, along [010]. Thus Ca3 and Ca4 also appear as being located in channels parallel to [001].

Experimental

Single crystals of $Ca_5Zr_3F_{22}$ were unexpectedly obtained from an equimolar mixture of AgF, CaF_2 and ZrF_4 heated at 873 K in a sealed platinum tube during the study of the phase diagram of the ternary system AgF–CaF_2–ZrF_4. After heating at this temperature for 24 h, the sample was cooled to room temperature at the rate of 5 $K{\cdot}h^{-1}$ for the first 24 h and then by switching the power off. Small platelet like crystals of $Ca_5Zr_3F_{22}$ could have been extracted from the batch.

Both AgF and CaF_2 were commercial products whereas ZrF_4 was prepared by direct fluorination of ZrO_2 under pure fluorine gas flow at 873 K with intermediate grindings. CaF_2 was also heated at 873 K overnight under fluorine gas flow prior to use.

Refinement

The highest residual peak in the final difference Fourier map was located 0.04 Å from atom Zr2 and the deepest hole was located 1.05 Å from atom F9.

Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CaRine* (Boudias & Monceau, 1998) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

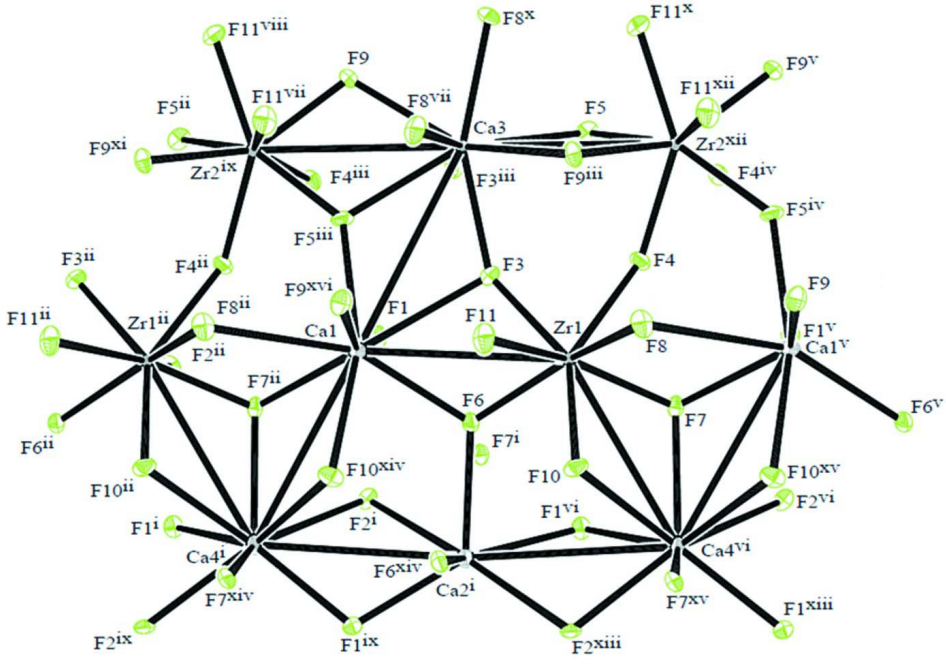

Figure 1

View of the polyhedral linkage in $Ca_5Zr_3F_{22}$. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) 3/2 - *x*, -1/2 + *y*, 2 - *z*; (ii) *x*, -1 + *y*, *z*; (iii) 2 - *x*, -*y*, *z*; (iv) 2 - *x*, 1 - *y*, *z*; (v) *x*, 1 + *y*, *z*; (vi) 3/2 - *x*, 1/2 + *y*, 2 - *z*; (vii) 3/2 - *x*, -1/2 + *y*, 1 - *z*; (viii) 1/2 + *x*, -1/2 - *y*, 1 - *z*; (ix) -1/2 + *x*, -1/2 - *y*, 2 - *z*; (*x*) 1/2 + *x*, 1/2 - *y*, 1 - *z*; (xi) 2 - *x*, -1 - *y*, *z*; (xii) 3/2 - *x*, 1/2 + *y*, 1 - *z*; (xiii) -1/2 + *x*, 1/2 - *y*, 2 - *z*; (xiv) 1 - *x*, -*y*, *z*; (xv) 1 - *x*, 1 - *y*, *z*; (xvi) -1/2 + *x*, -1/2 - *y*, 1 - *z*;

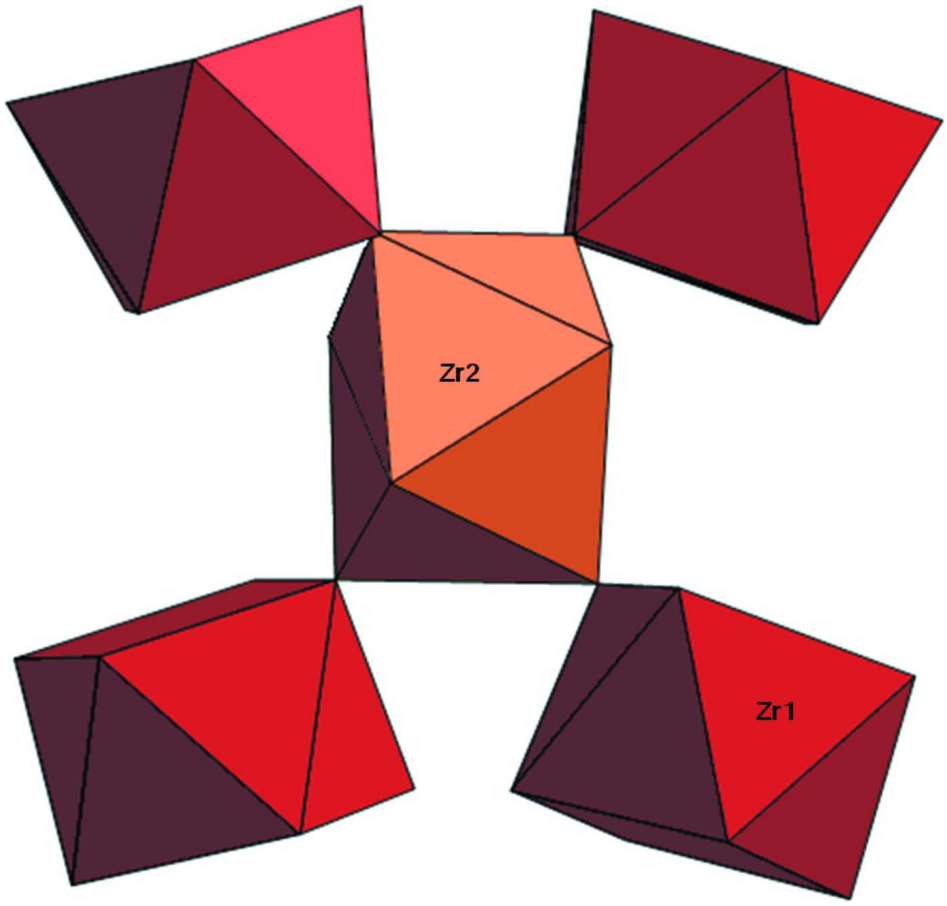

Figure 2

Details of the connection between Zr2 and Zr1 square antiprisms in $Ca_5Zr_3F_{22}$.

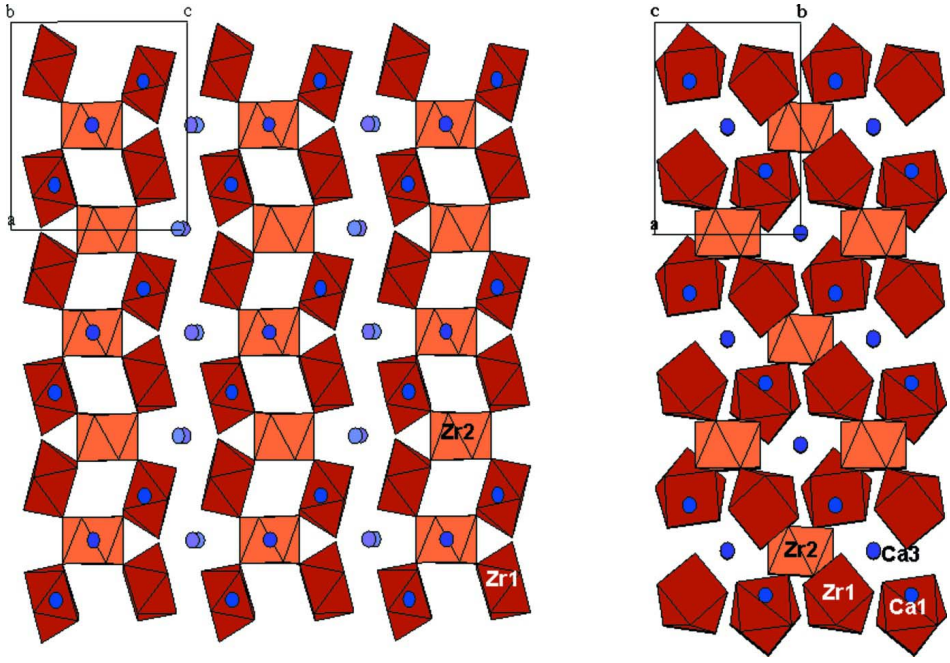

Figure 3

Projection of the structure of $Ca_5Zr_3F_{22}$ along [010] showing the $[Zr_3F_{20}]^{8-}$ layers held together by Ca^{2+} ions.

$Ca_5Zr_3F_{22}$	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11	Σv_{ij}
Fluoride ions environments	Ca1 + Ca2 + Ca4	Zr1 + Ca2 + Ca4	Zr1 + Ca1 + Ca3 + Ca4	Zr1 + Zr2 + Ca2	Zr2 + Ca1 + Ca3	Zr1 + Ca1 + Ca2	Zr1 + Ca1 + Ca2 + Ca4	Zr1 + Ca1 + Ca3	Zr2 + Ca1 + Ca3	Zr1 + Ca1 + Ca2 + Ca4	Zr1 + Zr2 + Ca1	
Zr1 bonds		2.0701	2.098	2.2154		2.079	2.062	2.073		2.0937	2.148	
v_{ij}		0.558	0.517	0.377		0.544	0.570	0.553		0.523	0.452	4.094
Zr2 bonds				2.148 x2	2.0771 x2				2.039 x2		2.117 x2	
v_{ij}				0.452	0.547				0.607		0.491	4.193
Ca1 bonds	2.2514		2.661		2.3214	2.331	2.344	2.769	2.412	2.3651	2.848	
v_{ij}	0.331		0.109		0.274	0.267	0.257	0.082	0.214	0.243	0.066	1.843
Ca2 bonds	2.283 x2	2.429 x2		2.645 x2		2.366 x2	3.1091 x2			3.040 x2		
v_{ij}	0.304	0.205		0.114		0.243	0.033			0.039		1.874
Ca3 bonds			2.295 x2		2.4327 x2			2.292 x2	2.4055 x2			
v_{ij}			0.294		0.203			0.296	0.218			2.022
Ca4 bonds	2.264 x2	2.367 x2	3.085 x2				2.418 x2			2.5067 x2		
v_{ij}	0.320	0.242	0.035				0.211			0.166		1.946
Σv_{ij}	0.954	1.004	0.955	0.942	1.024	1.054	1.071	0.931	1.034	0.972	1.009	

$Sr_5Zr_3F_{22}$	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11	Σv_{ij}
Fluoride ions environments	Zr1 + Sr2 + Sr4	Zr1 + Sr1 + Sr2	Zr1 + Sr1 + Sr4	Zr1 + Sr1 + Sr2	Zr1 + Sr1 + Sr3	Zr1 + Zr2 + Sr4	Zr1 + Sr1 + Sr3	Zr1 + Zr2	Zr2 + Sr1 + Sr3	Sr1 + Sr2 + Sr4	Zr2 + Sr1 + Sr3	
Zr1 bonds	2.074	2.069	2.083	2.103	2.085	2.297	2.070	2.212				
v_{ij}	0.552	0.559	0.539	0.510	0.536	0.302	0.558	0.380				3.935
Zr2 bonds						2.181 x2		2.172 x2	2.061 x2		2.072 x2	
v_{ij}						0.413		0.423	0.572		0.555	3.926
Sr1 bonds		2.484	2.468	2.488	2.745		2.838		2.473	2.351	2.485	
v_{ij}		0.285	0.297	0.282	0.141		0.109		0.293	0.408	0.284	2.098
Sr2 bonds	2.489 x2	2.579 x2		2.576 x2						2.353 x2		
v_{ij}	0.281	0.220		0.222						0.405		2.257
Sr3 bonds					2.424 x2		2.430 x2		2.555 x2		2.555 x2	
v_{ij}					0.335		0.329		0.235		0.235	2.267
Sr4 bonds	2.550 x2		2.517 x2			2.737 x2				2.379 x2		
v_{ij}	0.238		0.260			0.144				0.378		2.040
Σv_{ij}	1.071	1.064	1.096	1.014	1.011	0.859	0.996	0.803	1.100	1.191	1.073	

Figure 4

Bond-valence analysis of the structures of $Ca_5Zr_3F_{22}$ (top) and $Sr_5Zr_3F_{22}$ (bottom) using parameters for solids ($R_{Zr—F}$ = 1.854, $R_{Ca—F}$ = 1.842, $R_{Sr—F}$ = 2.019) from Brese & O′Keeffe (1991). It should be noted that the atom labelling in the two isotypic structures is different.

pentacalcium trizirconium docosafluoride

Crystal data

$Ca_5Zr_3F_{22}$
M_r = 892.06
Orthorhombic, $P2_12_12$
Hall symbol: P 2 2ab
a = 9.9844 (3) Å
b = 7.4059 (2) Å
c = 9.9046 (3) Å
V = 732.38 (4) Å^3
Z = 2
$F(000)$ = 836
D_x = 4.045 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1507 reflections
θ = 4.0–35.8°
μ = 4.09 mm^{-1}
T = 296 K
Platelet, colourless
0.19 × 0.06 × 0.03 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
ω and φ–scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.587, T_{max} = 0.747
7993 measured reflections
3466 independent reflections
2909 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 36.0°, θ_{min} = 3.4°
h = −16→16
k = −12→6
l = −16→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.058
S = 0.99
3466 reflections
139 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0112P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.88 e Å^{-3}
$\Delta\rho_{min}$ = −0.77 e Å^{-3}
Absolute structure: Flack (1983), 1462 Friedel pairs
Flack parameter: 0.0 (4)

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^2)

	x	y	z	U_{iso}*/U_{eq}
Zr1	0.71210 (3)	0.25190 (5)	0.77653 (3)	0.00516 (5)
Zr2	0.5000	0.0000	0.46134 (5)	0.00610 (9)
Ca1	0.71132 (6)	−0.23978 (10)	0.75189 (6)	0.00980 (11)
Ca2	1.0000	0.5000	0.94489 (11)	0.01098 (18)
Ca3	1.0000	0.0000	0.53761 (10)	0.00549 (16)

Ca4	1.0000	0.0000	0.97774 (11)	0.01109 (19)
F1	0.88717 (17)	−0.2405 (3)	0.89417 (19)	0.0127 (4)
F2	0.85135 (16)	0.2410 (3)	0.93117 (18)	0.0108 (3)
F3	0.8514 (2)	0.0603 (2)	0.7085 (3)	0.0170 (5)
F4	0.88835 (19)	0.4117 (2)	0.7118 (3)	0.0126 (4)
F5	1.10993 (18)	0.2790 (3)	0.6049 (2)	0.0128 (4)
F6	0.65761 (18)	0.0167 (3)	0.8771 (2)	0.0113 (4)
F7	0.69569 (18)	0.4936 (3)	0.87846 (19)	0.0114 (4)
F8	0.6504 (2)	0.4338 (3)	0.6301 (2)	0.0156 (5)
F9	1.10631 (18)	−0.2758 (3)	0.4672 (2)	0.0131 (4)
F10	0.51040 (18)	0.2795 (2)	0.83055 (19)	0.0139 (4)
F11	0.6171 (2)	0.0833 (3)	0.6283 (3)	0.0177 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr1	0.00491 (11)	0.00437 (10)	0.00621 (12)	0.00005 (14)	−0.00025 (10)	0.00010 (14)
Zr2	0.0070 (2)	0.00559 (19)	0.0057 (2)	−0.0005 (2)	0.000	0.000
Ca1	0.0079 (2)	0.0118 (3)	0.0097 (3)	−0.0004 (3)	0.0000 (2)	0.0002 (3)
Ca2	0.0104 (4)	0.0085 (4)	0.0139 (5)	0.0006 (4)	0.000	0.000
Ca3	0.0047 (4)	0.0059 (4)	0.0059 (4)	0.0005 (5)	0.000	0.000
Ca4	0.0097 (4)	0.0065 (4)	0.0170 (5)	−0.0010 (4)	0.000	0.000
F1	0.0108 (8)	0.0113 (8)	0.0161 (9)	−0.0008 (9)	−0.0033 (7)	−0.0009 (10)
F2	0.0100 (8)	0.0125 (8)	0.0098 (8)	−0.0027 (10)	−0.0044 (6)	0.0024 (10)
F3	0.0194 (11)	0.0113 (9)	0.0203 (13)	0.0026 (8)	0.0086 (10)	−0.0019 (9)
F4	0.0118 (10)	0.0128 (9)	0.0133 (11)	−0.0041 (7)	0.0021 (9)	0.0004 (8)
F5	0.0103 (8)	0.0159 (11)	0.0122 (10)	0.0038 (7)	−0.0044 (7)	−0.0006 (8)
F6	0.0129 (9)	0.0090 (9)	0.0120 (10)	−0.0019 (8)	0.0002 (7)	−0.0007 (8)
F7	0.0129 (9)	0.0084 (8)	0.0130 (10)	−0.0016 (9)	−0.0016 (8)	−0.0023 (9)
F8	0.0202 (12)	0.0145 (10)	0.0120 (12)	0.0008 (8)	−0.0061 (9)	0.0047 (8)
F9	0.0135 (9)	0.0108 (10)	0.0151 (10)	−0.0034 (8)	0.0041 (7)	0.0002 (8)
F10	0.0077 (8)	0.0177 (10)	0.0161 (10)	0.0009 (8)	0.0012 (8)	−0.0044 (7)
F11	0.0233 (12)	0.0146 (10)	0.0151 (13)	−0.0028 (9)	−0.0065 (10)	−0.0028 (9)

Geometric parameters (Å, º)

Zr1—F7	2.062 (2)	Ca2—F6^{x}	2.366 (2)
Zr1—F2	2.0701 (16)	Ca2—F2^{xi}	2.429 (2)
Zr1—F8	2.073 (2)	Ca2—F2	2.429 (2)
Zr1—F6	2.079 (2)	Ca2—F4	2.645 (3)
Zr1—F10	2.0937 (18)	Ca2—F4^{xi}	2.645 (3)
Zr1—F3	2.098 (2)	Ca2—F10^{x}	3.040 (2)
Zr1—F11	2.148 (2)	Ca2—F10^{ix}	3.040 (2)
Zr1—F4	2.2154 (19)	Ca2—F7	3.1091 (18)
Zr2—F5^{i}	2.0771 (19)	Ca2—F7^{xi}	3.1091 (18)
Zr2—F5^{ii}	2.0771 (19)	Ca3—F8^{i}	2.292 (2)
Zr2—F9^{iii}	2.0939 (18)	Ca3—F8^{xii}	2.292 (2)
Zr2—F9^{iv}	2.0939 (18)	Ca3—F3^{vi}	2.295 (2)
Zr2—F11	2.117 (2)	Ca3—F3	2.295 (2)
Zr2—F11^{v}	2.117 (2)	Ca3—F9	2.4055 (19)

Zr2—F4^{ii}	2.148 (2)	Ca3—F9^{vi}	2.4055 (19)
Zr2—F4^{i}	2.148 (2)	Ca3—F5	2.4327 (19)
Ca1—F1	2.2514 (18)	Ca3—F5^{vi}	2.4327 (19)
Ca1—F5^{vi}	2.3214 (19)	Ca4—F1	2.264 (2)
Ca1—F6	2.331 (2)	Ca4—F1^{vi}	2.264 (2)
Ca1—F7^{vii}	2.344 (2)	Ca4—F2^{vi}	2.367 (2)
Ca1—F10^{v}	2.3651 (19)	Ca4—F2	2.367 (2)
Ca1—F9^{iv}	2.412 (2)	Ca4—F7^{ix}	2.418 (2)
Ca1—F3	2.661 (2)	Ca4—F7^{xiii}	2.418 (2)
Ca1—F8^{vii}	2.769 (2)	Ca4—F10^{ix}	2.5067 (19)
Ca1—F11	2.848 (2)	Ca4—F10^{xiii}	2.5067 (19)
Ca2—F1^{viii}	2.283 (2)	Ca4—F3	3.085 (3)
Ca2—F1^{vi}	2.283 (2)	Ca4—F3^{vi}	3.085 (3)
Ca2—F6^{ix}	2.366 (2)		

F7—Zr1—F2	74.04 (8)	F1^{viii}—Ca2—F7	58.94 (6)
F7—Zr1—F8	75.80 (8)	F1^{vi}—Ca2—F7	115.01 (6)
F2—Zr1—F8	137.96 (9)	F6^{ix}—Ca2—F7	143.78 (7)
F7—Zr1—F6	118.16 (7)	F6^{x}—Ca2—F7	60.56 (6)
F2—Zr1—F6	77.79 (8)	F2^{xi}—Ca2—F7	126.67 (6)
F8—Zr1—F6	143.31 (8)	F2—Ca2—F7	51.62 (6)
F7—Zr1—F10	73.37 (7)	F4—Ca2—F7	53.12 (6)
F2—Zr1—F10	117.44 (7)	F4^{xi}—Ca2—F7	103.35 (6)
F8—Zr1—F10	80.18 (8)	F10^{x}—Ca2—F7	97.57 (5)
F6—Zr1—F10	73.00 (7)	F10^{ix}—Ca2—F7	100.25 (5)
F7—Zr1—F3	142.87 (8)	F1^{viii}—Ca2—F7^{xi}	115.01 (6)
F2—Zr1—F3	76.47 (9)	F1^{vi}—Ca2—F7^{xi}	58.94 (6)
F8—Zr1—F3	114.32 (10)	F6^{ix}—Ca2—F7^{xi}	60.56 (6)
F6—Zr1—F3	76.16 (8)	F6^{x}—Ca2—F7^{xi}	143.78 (7)
F10—Zr1—F3	141.78 (8)	F2^{xi}—Ca2—F7^{xi}	51.62 (6)
F7—Zr1—F11	143.54 (8)	F2—Ca2—F7^{xi}	126.67 (6)
F2—Zr1—F11	141.23 (9)	F4—Ca2—F7^{xi}	103.35 (6)
F8—Zr1—F11	76.60 (8)	F4^{xi}—Ca2—F7^{xi}	53.12 (6)
F6—Zr1—F11	74.05 (8)	F10^{x}—Ca2—F7^{xi}	100.25 (5)
F10—Zr1—F11	78.86 (8)	F10^{ix}—Ca2—F7^{xi}	97.57 (5)
F3—Zr1—F11	71.33 (9)	F7—Ca2—F7^{xi}	155.57 (8)
F7—Zr1—F4	74.98 (8)	F8^{i}—Ca3—F8^{xii}	87.10 (12)
F2—Zr1—F4	72.62 (8)	F8^{i}—Ca3—F3^{vi}	156.41 (7)
F8—Zr1—F4	71.74 (8)	F8^{xii}—Ca3—F3^{vi}	98.78 (8)
F6—Zr1—F4	142.56 (8)	F8^{i}—Ca3—F3	98.78 (8)
F10—Zr1—F4	141.80 (7)	F8^{xii}—Ca3—F3	156.41 (7)
F3—Zr1—F4	75.04 (7)	F3^{vi}—Ca3—F3	84.96 (13)
F11—Zr1—F4	117.61 (9)	F8^{i}—Ca3—F9	84.10 (7)
F5^{i}—Zr2—F5^{ii}	143.17 (11)	F8^{xii}—Ca3—F9	71.48 (7)
F5^{i}—Zr2—F9^{iii}	117.63 (7)	F3^{vi}—Ca3—F9	76.31 (7)
F5^{ii}—Zr2—F9^{iii}	75.52 (7)	F3—Ca3—F9	131.65 (7)
F5^{i}—Zr2—F9^{iv}	75.52 (7)	F8^{i}—Ca3—F9^{vi}	71.48 (7)
F5^{ii}—Zr2—F9^{iv}	117.63 (7)	F8^{xii}—Ca3—F9^{vi}	84.10 (7)
F9^{iii}—Zr2—F9^{iv}	140.46 (11)	F3^{vi}—Ca3—F9^{vi}	131.65 (7)

F5^{i}—Zr2—F11	140.20 (8)	F3—Ca3—F9^{vi}	76.31 (7)
F5^{ii}—Zr2—F11	74.04 (8)	F9—Ca3—F9^{vi}	146.27 (10)
F9^{iii}—Zr2—F11	77.57 (8)	F8^{i}—Ca3—F5	132.51 (7)
F9^{iv}—Zr2—F11	71.76 (8)	F8^{xii}—Ca3—F5	73.82 (7)
F5^{i}—Zr2—F11^{v}	74.04 (8)	F3^{vi}—Ca3—F5	70.82 (6)
F5^{ii}—Zr2—F11^{v}	140.20 (8)	F3—Ca3—F5	85.66 (7)
F9^{iii}—Zr2—F11^{v}	71.76 (8)	F9—Ca3—F5	126.99 (6)
F9^{iv}—Zr2—F11^{v}	77.57 (8)	F9^{vi}—Ca3—F5	63.72 (6)
F11—Zr2—F11^{v}	77.30 (13)	F8^{i}—Ca3—F5^{vi}	73.82 (7)
F5^{i}—Zr2—F4^{ii}	73.35 (7)	F8^{xii}—Ca3—F5^{vi}	132.51 (7)
F5^{ii}—Zr2—F4^{ii}	77.41 (8)	F3^{vi}—Ca3—F5^{vi}	85.66 (7)
F9^{iii}—Zr2—F4^{ii}	76.44 (8)	F3—Ca3—F5^{vi}	70.82 (6)
F9^{iv}—Zr2—F4^{ii}	140.78 (7)	F9—Ca3—F5^{vi}	63.72 (6)
F11—Zr2—F4^{ii}	145.25 (7)	F9^{vi}—Ca3—F5^{vi}	126.99 (6)
F11^{v}—Zr2—F4^{ii}	115.20 (9)	F5—Ca3—F5^{vi}	148.20 (10)
F5^{i}—Zr2—F4^{i}	77.41 (8)	F1—Ca4—F1^{vi}	137.12 (11)
F5^{ii}—Zr2—F4^{i}	73.35 (7)	F1—Ca4—F2^{vi}	69.36 (7)
F9^{iii}—Zr2—F4^{i}	140.78 (7)	F1^{vi}—Ca4—F2^{vi}	102.12 (7)
F9^{iv}—Zr2—F4^{i}	76.44 (8)	F1—Ca4—F2	102.12 (7)
F11—Zr2—F4^{i}	115.20 (9)	F1^{vi}—Ca4—F2	69.36 (7)
F11^{v}—Zr2—F4^{i}	145.25 (7)	F2^{vi}—Ca4—F2	157.52 (10)
F4^{ii}—Zr2—F4^{i}	73.99 (11)	F1—Ca4—F7^{ix}	129.24 (8)
F1—Ca1—F5^{vi}	78.04 (7)	F1^{vi}—Ca4—F7^{ix}	78.34 (7)
F1—Ca1—F6	81.27 (8)	F2^{vi}—Ca4—F7^{ix}	67.84 (6)
F5^{vi}—Ca1—F6	127.77 (7)	F2—Ca4—F7^{ix}	127.36 (7)
F1—Ca1—F7^{vii}	73.44 (8)	F1—Ca4—F7^{xiii}	78.34 (7)
F5^{vi}—Ca1—F7^{vii}	106.33 (7)	F1^{vi}—Ca4—F7^{xiii}	129.24 (8)
F6—Ca1—F7^{vii}	112.73 (7)	F2^{vi}—Ca4—F7^{xiii}	127.36 (7)
F1—Ca1—F10^{v}	121.56 (7)	F2—Ca4—F7^{xiii}	67.84 (6)
F5^{vi}—Ca1—F10^{v}	155.59 (7)	F7^{ix}—Ca4—F7^{xiii}	107.84 (10)
F6—Ca1—F10^{v}	73.18 (7)	F1—Ca4—F10^{ix}	144.10 (7)
F7^{vii}—Ca1—F10^{v}	69.93 (7)	F1^{vi}—Ca4—F10^{ix}	75.15 (7)
F1—Ca1—F9^{iv}	154.42 (7)	F2^{vi}—Ca4—F10^{ix}	127.81 (7)
F5^{vi}—Ca1—F9^{iv}	77.06 (7)	F2—Ca4—F10^{ix}	71.47 (6)
F6—Ca1—F9^{iv}	109.85 (7)	F7^{ix}—Ca4—F10^{ix}	60.51 (6)
F7^{vii}—Ca1—F9^{iv}	119.50 (7)	F7^{xiii}—Ca4—F10^{ix}	66.43 (7)
F10^{v}—Ca1—F9^{iv}	84.00 (7)	F1—Ca4—F10^{xiii}	75.15 (7)
F1—Ca1—F3	72.14 (9)	F1^{vi}—Ca4—F10^{xiii}	144.10 (7)
F5^{vi}—Ca1—F3	66.37 (7)	F2^{vi}—Ca4—F10^{xiii}	71.47 (6)
F6—Ca1—F3	61.73 (7)	F2—Ca4—F10^{xiii}	127.81 (7)
F7^{vii}—Ca1—F3	145.59 (7)	F7^{ix}—Ca4—F10^{xiii}	66.43 (7)
F10^{v}—Ca1—F3	130.46 (7)	F7^{xiii}—Ca4—F10^{xiii}	60.51 (6)
F9^{iv}—Ca1—F3	92.47 (8)	F10^{ix}—Ca4—F10^{xiii}	81.52 (9)
F1—Ca1—F8^{vii}	116.23 (8)	F1—Ca4—F3	63.80 (7)
F5^{vi}—Ca1—F8^{vii}	77.68 (7)	F1^{vi}—Ca4—F3	79.01 (6)
F6—Ca1—F8^{vii}	153.18 (7)	F2^{vi}—Ca4—F3	104.03 (7)
F7^{vii}—Ca1—F8^{vii}	58.87 (7)	F2—Ca4—F3	54.59 (6)
F10^{v}—Ca1—F8^{vii}	80.17 (7)	F7^{ix}—Ca4—F3	153.52 (7)
F9^{iv}—Ca1—F8^{vii}	63.55 (6)	F7^{xiii}—Ca4—F3	97.08 (6)

F3—Ca1—F8^{vii}	140.74 (8)	F10^{ix}—Ca4—F3	125.49 (6)
F1—Ca1—F11	121.92 (8)	F10^{xiii}—Ca4—F3	136.83 (6)
F5^{vi}—Ca1—F11	95.13 (7)	F1—Ca4—F3^{vi}	79.01 (6)
F6—Ca1—F11	57.87 (7)	F1^{vi}—Ca4—F3^{vi}	63.80 (7)
F7^{vii}—Ca1—F11	156.31 (7)	F2^{vi}—Ca4—F3^{vi}	54.59 (6)
F10^{v}—Ca1—F11	86.38 (7)	F2—Ca4—F3^{vi}	104.03 (7)
F9^{iv}—Ca1—F11	55.22 (6)	F7^{ix}—Ca4—F3^{vi}	97.08 (6)
F3—Ca1—F11	53.29 (7)	F7^{xiii}—Ca4—F3^{vi}	153.52 (7)
F8^{vii}—Ca1—F11	118.27 (6)	F10^{ix}—Ca4—F3^{vi}	136.83 (6)
F1^{viii}—Ca2—F1^{vi}	154.59 (11)	F10^{xiii}—Ca4—F3^{vi}	125.49 (6)
F1^{viii}—Ca2—F6^{ix}	122.41 (8)	F3—Ca4—F3^{vi}	60.32 (8)
F1^{vi}—Ca2—F6^{ix}	77.99 (7)	Ca1—F1—Ca4	127.94 (11)
F1^{viii}—Ca2—F6^{x}	77.99 (7)	Ca1—F1—Ca2^{vii}	121.63 (10)
F1^{vi}—Ca2—F6^{x}	122.41 (8)	Ca4—F1—Ca2^{vii}	109.64 (7)
F6^{ix}—Ca2—F6^{x}	83.69 (10)	Zr1—F2—Ca4	126.50 (10)
F1^{viii}—Ca2—F2^{xi}	67.95 (7)	Zr1—F2—Ca2	114.89 (9)
F1^{vi}—Ca2—F2^{xi}	110.54 (6)	Ca4—F2—Ca2	101.62 (6)
F6^{ix}—Ca2—F2^{xi}	71.13 (7)	Zr1—F3—Ca3	142.87 (12)
F6^{x}—Ca2—F2^{xi}	114.00 (7)	Zr1—F3—Ca1	99.48 (8)
F1^{viii}—Ca2—F2	110.54 (6)	Ca3—F3—Ca1	107.24 (8)
F1^{vi}—Ca2—F2	67.95 (7)	Zr1—F3—Ca4	97.99 (9)
F6^{ix}—Ca2—F2	114.00 (7)	Ca3—F3—Ca4	107.36 (8)
F6^{x}—Ca2—F2	71.13 (7)	Ca1—F3—Ca4	89.55 (7)
F2^{xi}—Ca2—F2	173.59 (9)	Zr2^{iii}—F4—Zr1	143.70 (12)
F1^{viii}—Ca2—F4	78.94 (7)	Zr2^{iii}—F4—Ca2	113.76 (8)
F1^{vi}—Ca2—F4	78.93 (7)	Zr1—F4—Ca2	102.38 (9)
F6^{ix}—Ca2—F4	156.54 (6)	Zr2^{iii}—F5—Ca1^{vi}	134.66 (9)
F6^{x}—Ca2—F4	112.50 (7)	Zr2^{iii}—F5—Ca3	110.14 (8)
F2^{xi}—Ca2—F4	113.82 (7)	Ca1^{vi}—F5—Ca3	114.36 (8)
F2—Ca2—F4	59.90 (6)	Zr1—F6—Ca1	111.56 (9)
F1^{viii}—Ca2—F4^{xi}	78.93 (7)	Zr1—F6—Ca2^{xiii}	125.08 (9)
F1^{vi}—Ca2—F4^{xi}	78.94 (7)	Ca1—F6—Ca2^{xiii}	120.46 (8)
F6^{ix}—Ca2—F4^{xi}	112.50 (6)	Zr1—F7—Ca1^{viii}	117.66 (9)
F6^{x}—Ca2—F4^{xi}	156.54 (6)	Zr1—F7—Ca4^{x}	111.69 (8)
F2^{xi}—Ca2—F4^{xi}	59.90 (6)	Ca1^{viii}—F7—Ca4^{x}	110.63 (8)
F2—Ca2—F4^{xi}	113.82 (7)	Zr1—F7—Ca2	92.24 (7)
F4—Ca2—F4^{xi}	58.49 (9)	Ca1^{viii}—F7—Ca2	92.03 (6)
F1^{viii}—Ca2—F10^{x}	64.60 (6)	Ca4^{x}—F7—Ca2	131.65 (8)
F1^{vi}—Ca2—F10^{x}	138.65 (7)	Zr1—F8—Ca3^{iii}	147.21 (10)
F6^{ix}—Ca2—F10^{x}	60.87 (6)	Zr1—F8—Ca1^{viii}	101.38 (9)
F6^{x}—Ca2—F10^{x}	52.89 (6)	Ca3^{iii}—F8—Ca1^{viii}	105.84 (7)
F2^{xi}—Ca2—F10^{x}	61.59 (5)	Zr2^{i}—F9—Ca3	110.58 (8)
F2—Ca2—F10^{x}	123.90 (6)	Zr2^{i}—F9—Ca1^{xiv}	124.23 (9)
F4—Ca2—F10^{x}	142.40 (5)	Ca3—F9—Ca1^{xiv}	114.33 (8)
F4^{xi}—Ca2—F10^{x}	118.98 (5)	Zr1—F10—Ca1^{v}	143.51 (9)
F1^{viii}—Ca2—F10^{ix}	138.65 (7)	Zr1—F10—Ca4^{x}	107.27 (8)
F1^{vi}—Ca2—F10^{ix}	64.60 (6)	Ca1^{v}—F10—Ca4^{x}	106.96 (7)
F6^{ix}—Ca2—F10^{ix}	52.89 (6)	Zr1—F10—Ca2^{xiii}	98.83 (7)
F6^{x}—Ca2—F10^{ix}	60.87 (6)	Ca1^{v}—F10—Ca2^{xiii}	97.15 (6)

F2^{xi}—Ca2—F10^{ix}	123.90 (6)	Ca4^{x}—F10—Ca2^{xiii}	83.57 (6)
F2—Ca2—F10^{ix}	61.59 (5)	Zr2—F11—Zr1	161.30 (11)
F4—Ca2—F10^{ix}	118.98 (5)	Zr2—F11—Ca1	105.85 (7)
F4^{xi}—Ca2—F10^{ix}	142.40 (5)	Zr1—F11—Ca1	92.79 (8)
F10^{x}—Ca2—F10^{ix}	85.95 (7)		

Symmetry codes: (i) −*x*+3/2, *y*−1/2, −*z*+1; (ii) *x*−1/2, −*y*+1/2, −*z*+1; (iii) −*x*+3/2, *y*+1/2, −*z*+1; (iv) *x*−1/2, −*y*−1/2, −*z*+1; (v) −*x*+1, −*y*, *z*; (vi) −*x*+2, −*y*, *z*; (vii) *x*, *y*−1, *z*; (viii) *x*, *y*+1, *z*; (ix) *x*+1/2, −*y*+1/2, −*z*+2; (x) −*x*+3/2, *y*+1/2, −*z*+2; (xi) −*x*+2, −*y*+1, *z*; (xii) *x*+1/2, −*y*+1/2, −*z*+1; (xiii) −*x*+3/2, *y*−1/2, −*z*+2; (xiv) *x*+1/2, −*y*−1/2, −*z*+1.