The Crystal Structure of Ca(BF₄)₂

By T. H. Jordan,* B. Dickens,† L. W. Schroeder† & W. E. Brown‡

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, U.S.A.

Ca(BF₄)₂ crystallizes in the orthorhombic space group *Pbca* with $Z = 8$. The unit-cell parameters are $a = 9\cdot2792$ (6), $b = 8\cdot9103$ (10) and $c = 13\cdot3719$ (10) Å. The structure was refined by full-matrix least-squares calculations to $R_w(F) = 0\cdot025$, $R = 0\cdot024$, using 2896 measurable X-ray data collected by a counter method and corrected for absorption. The refinement allowed for anisotropic thermal motion, isotropic secondary extinction and anomalous dispersion. The structure consists of columns of BF_4^- ions and columns of alternating Ca^{2+} and BF_4^- ions, all parallel to [010]. There are twice as many $[Ca^{2+}, BF_4^-]$ columns as $[BF_4^-, BF_4^-]$ columns. All columns are linked together through $Ca \cdots F$ bonds. The Ca^{2+} ion is coordinated by a square antiprism of fluorine atoms, each from a different BF_4^- ion. Each fluorine atom is bonded to one Ca^{2+} ion, and the four Ca^{2+} ions bonded to a BF_4^- ion are arranged approximately tetrahedrally about the BF_4^- ion. Although neither of the two crystallographically discrete BF_4^- ions occupies a site of special symmetry, each is essentially tetrahedral in configuration.

Introduction

We have begun a study of the general properties of the BF_4^- ion and its hydrolysis products. Various salts of the end members of this series, BF_4^- and $B(OH)_4^-$, have been reported (Pawlenko, 1962; Marezio, 1969). Many of these salts have several degrees of hydration. The intermediate members of the series have received little attention in the literature. Some work has been done on $BF_3(OH)^-$ (Pawlenko, 1962a, b) and $BF(OH)_3^-$ (Sengupta & Mukerjee, 1967), but very little is known about $BF_2(OH)_2^-$. Our initial approach is to characterize the series by determining the crystal structures of several of its members. Here we report the crystal structure of Ca(BF₄)₂.

Data collection and structure refinement

A sample of Ca(BF₄)₂ was prepared by mixing CaCO₃ and HBF₄ in a 1:2 molar ratio, storing the solution overnight in a desiccator containing concentrated H_2SO_4 as a desiccant, and filtering the solution the following day to remove CaF₂. The filtrate was stored in a desiccator with P_2O_5 and kept at 40°C until Ca(BF₄)₂ crystals formed (Wilke-Dorfurt & Balz, 1926). Several crystals of this compound were ground into spheres and sealed in glass capillaries to prevent hydrolysis. Since Ca(BF₄)₂ is hygroscopic, the procedure of grinding and sealing the crystals was carried out in a glove box with a dry nitrogen atmosphere. A

sphere with radius 0·152 (6) mm was chosen for data collection.

Crystal data

Ca(BF₄)₂, cell orthorhombic at 25°C; $a = 9\cdot2792$ (6), $b = 8\cdot9103$ (10), $c = 13\cdot3719$ (10) Å; $V = 1105\cdot6$ Å³. Space group *Pbca*; $Z = 8$. Reciprocal lattice extinctions: $h = 2n + 1$ for $hk0$; $k = 2n + 1$ for $0kl$; $l = 2n + 1$ for $h0l$. $d_{calc} = 2\cdot567$, $d_{obs} = 2\cdot560$ (3) g cm⁻³ (De Pape & Ravez, 1962); $\mu(Mo) = 11\cdot25$ cm⁻¹.

The cell dimensions were determined from 30 2θ values obtained by automatically centering reflections on a four-circle Picker§ diffractometer equipped with a highly oriented graphite monochromator. The wavelength $Mo(K\alpha_1) = 0\cdot7093$ Å was assumed. The standard deviations, given in parentheses, were determined from least-squares refinements. The diffractometer-controlling program was written by Lenhert (1970).

The X-ray data were collected using θ–2θ scans at a rate of 2° min⁻¹ for 2θ. Each background was counted for 10 s. In this manner 7887 reflections in the $hk \pm l$ quadrant were measured. After absorption corrections for a spherical crystal had been applied, the data were merged into a unique set of 3450 reflections of which 2914 were of observable intensity and 536 were 'unobserved', *i.e.* had intensity less than $2\sigma(I)$ above background. Equivalent reflections agreed within 3·1% on average. Several weak reflections which violated the space-group extinctions for *Pbca* were observed during the data collection. However, we found that the peak heights of these anomalous reflections varied by as much as 90% on rotation about the scattering vector, while checks on a few reflections allowed by the space

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* Permanent address: Cornell College, Mt. Vernon, Iowa 52314, U.S.A.

† Research Associate of the American Dental Association Health Foundation at the National Bureau of Standards, Washington, D.C. 20234, U.S.A.

‡ Director, American Dental Association Health Foundation Research Unit at the National Bureau of Standards, Washington, D.C. 20234, U.S.A.

group revealed a maximum variation of about 10%. Thus we concluded that the violations of the space-group symmetry were due to multiple diffraction.

The positions of the Ca^{2+} ion and one of the BF$_4^-$ groups in the asymmetric unit were determined from a sharpened Patterson map. The location of the second BF$_4^-$ group was then readily obtained from an electron-density synthesis. Four cycles of full-matrix least-squares refinement of these atoms with isotropic temperature factors led to an R_w value of 0·121 and R of 0·107. R_w is defined as $[\sum w(|F_o|-|F_c|)^2/w(|F_o|^2)]^{1/2}$ and R as $\sum||F_o|-|F_c||/\sum|F_o|$. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$. Weights were derived according to criteria developed in the program *DMERGE* (Schroeder & Dickens, 1974). In general these weights are based on counting statistics or the unbiased estimate as obtained from equivalent reflections. In rare instances these weights were increased because of significant disagreement between equivalent reflections. Scattering factors were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). The unpublished full-matrix least-squares program *RFINE*, written by L. W. Finger of the Carnegie Institute of Washington, was used for all refinements. Two cycles of refinement with

anisotropic temperature factors for all atoms reduced R_w to 0·062 and R to 0·052. At this stage it was obvious that the data were significantly affected by secondary extinction. A domain size factor was therefore introduced into the refinement at this stage and four more cycles led to the final structure with an R_w of 0·025 and R of 0·024. The domain size refined to a value larger than is justified by the approximations used in calculating the secondary extinction correction by the Zachariasen (1967) equation. Thus the domain radius was not varied in the last cycle, but was held fixed at 2 μm. For 18 reflections, the extinction factor was less than the lower threshold ~0·70, the limit of the validity of the Zachariasen approximation as estimated from the work of Cooper & Rouse (1970). These reflections were therefore omitted from the final stage of refinement.

The two highest peaks in a difference electron-density synthesis calculated after the final cycle were about 0·5 e as judged by comparison of their electron density with that of a fluorine atom. These and other peaks ~0·3 e in height are attributed to the background. The highest correlation coefficient in the final cycle was ~0·51 between the scale factor and U_{11} of Ca.

Table 1. *Atomic parameters in* Ca(BF$_4$)$_2$

Positional parameters are $\times 10^5$. Thermal parameters have the form exp $[-2\pi\sum U_{ij}h_ih_ja_i^*a_j^*]$; they have been multiplied by 10^4. The figures in parentheses are standard deviations in the last digit.

|	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	3428 (1)	21860 (1)	10383 (1)	101 (1)	108 (1)	109 (1)	4 (1)	6 (1)	−2 (1)
B(1)	27892 (8)	−363 (9)	−5722 (6)	110 (3)	115 (3)	145 (3)	−4 (2)	10 (2)	7 (2)
B(2)	39709 (9)	32339 (9)	15854 (6)	120 (3)	172 (3)	105 (3)	−17 (3)	−12 (2)	20 (3)
F(1)	18698 (6)	9316 (6)	−633 (4)	274 (2)	251 (3)	307 (3)	95 (2)	114 (2)	−36 (2)
F(2)	−12742 (6)	41997 (6)	11614 (4)	209 (2)	213 (2)	177 (2)	98 (2)	−31 (2)	21 (2)
F(3)	−19615 (6)	9856 (6)	11627 (4)	239 (2)	287 (3)	245 (3)	−144 (2)	−8 (2)	−40 (2)
F(4)	14244 (6)	41450 (6)	1180 (4)	207 (2)	241 (3)	322 (3)	−21 (2)	57 (2)	127 (2)
F(5)	41408 (7)	47767 (6)	16925 (5)	423 (3)	161 (2)	262 (3)	−66 (2)	−20 (2)	38 (2)
F(6)	43040 (6)	28270 (7)	6064 (4)	228 (2)	367 (3)	114 (2)	13 (2)	20 (2)	−12 (2)
F(7)	25514 (5)	28338 (7)	17892 (4)	136 (2)	393 (3)	196 (2)	−78 (2)	2 (2)	21 (2)
F(8)	48783 (6)	24995 (6)	22496 (4)	217 (2)	304 (3)	152 (2)	80 (2)	−48 (2)	33 (2)
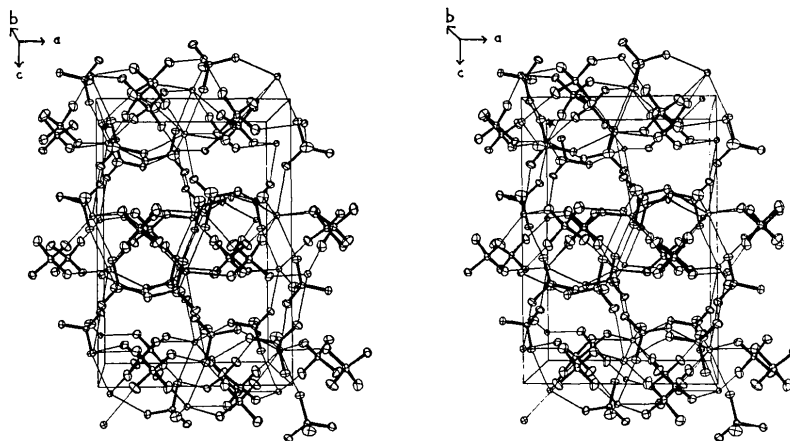
Fig. 1. A stereoscopic view down [010] of the Ca(BF$_4$)$_2$ structure. The origin of the crystallographic coordinate system is the upper left corner. No atoms are labeled, but the BF$_4$ groups are obvious because of their thicker bonds which denote covalent B–F bonds. The light lines denote ionic bonds between Ca and F.

The atomic parameters obtained from the final cycle of least-squares calculations are given in Table 1, and the observed and calculated structure factors are given in Table 2.* The average shift/error in the last cycle was 0·08. The standard deviation of an observation of unit weight, $S=[\sum w(|F_o|-|F_c|)^2/(2896-100)]^{1/2}$, was 1·67 and is included in the standard deviations quoted in the tables.

Description of the structure

The structure (Fig. 1) contains as its asymmetric unit one Ca^{2+} ion and two BF_4^- ions. There are columns of $B(1)F_4^-$ ions and columns of $[Ca^{2+},B(2)F_4^-]$ ions parallel to [010] with twice as many $[Ca^{2+},B(2)F_4^-]$ columns as $[B(1)F_4^-]$ columns. Each Ca^{2+} is bonded to only one of the two neighboring $B(2)F_4^-$ ions in each $[Ca^{2+},B(2)F_{4\underline{s}}^-]$ column. This bond is $Ca^{2+}\cdots F(5)$.

The ionic environment

The Ca ions

The environment of the Ca ion is shown in Fig. 2. The Ca ion is coordinated by a square antiprism of fluorine atoms; one square face consists of F(1), F(3), F(5) and F(6); the other consists of F(2), F(4), F(7) and F(8). Each F atom is from a different BF_4^- ion. The $Ca\cdots F$ distances (Table 3) lie in an unusually small range (2·330 to 2·401 Å). A similar coordination and small range of distances was found for the Ca ion coordinated by water molecules in $CaKAsO_4.8H_2O$ (Dickens & Brown, 1972) and the Ca environment in $CaCO_3.6H_2O$ (Dickens & Brown, 1970). As can be seen from Table 1 and Fig. 2, the apparent thermal motion parameters of Ca_2^+ in $Ca(BF_4)^2$ are essentially isotropic.

The BF_4^- ions

The details of the geometry of the BF_4^- ions and their

environments are given in Table 3 and shown in Fig. 2. The individual B–F bond distances average 1·389 Å, and 1·403 Å (range 1·398 to 1·408 Å) when riding-body corrections (Busing & Levy, 1964) based on the

Table 3. Atomic details in $Ca(BF_4)_2$

Ca environment

		∠ Ca-F-B
Ca-F(1)	2·330 (2) Å	168·5 (2)°
Ca-F(2)	2·345 (1)	140·4 (1)
Ca-F(8)	2·347 (1)	136·6 (1)
Ca-F(7)	2·354 (2)	164·1 (2)
Ca-F(4)	2·360 (2)	151·8 (2)
Ca-F(5)	2·367 (2)	162·0 (2)
Ca-F(3)	2·396 (2)	143·5 (1)
Ca-F(6)	2·401 (2)	142·4 (1)

BF_4 groups

i	j	k	d_{ij}	d_{jk}	d_{ik}	$\angle ijk$
F(1)	B(1)	F(2)	1·390 (3)Å 1·408*	1·390 (3)Å 1·398*	2·266 (2)Å	109·2 (2)°
F(1)	B(1)	F(3)		1·389 (3) 1·403*	2·254 (2)	108·4 (2)
F(1)	B(1)	F(4)		1·384 (3) 1·399*	2·258 (2)	108·9 (2)
F(2)	B(1)	F(3)			2·283 (2)	110·5 (2)
F(2)	B(1)	F(4)			2·263 (2)	109·3 (2)
F(3)	B(1)	F(4)			2·278 (2)	110·5 (2)
F(5)	B(2)	F(6)	1·390 (3) 1·408*	1·393 (3) 1·404*	2·268 (2)	109·2 (2)
F(5)	B(2)	F(7)		1·392 (3) 1·403*	2·278 (2)	109·9 (2)
F(5)	B(2)	F(8)		1·387 (3) 1·398*	2·267 (2)	109·4 (2)
F(6)	B(2)	F(7)			2·268 (2)	109·1 (2)
F(6)	B(2)	F(8)			2·279 (2)	110·2 (2)
F(7)	B(2)	F(8)			2·265 (2)	109·2 (2)

Environments†

F(1)···F(5)	2·729 (2) Å	F(5)···F(1)	2·729 (2) Å
F(1)···F(6)	2·724 (2)	F(5)···F(7)	2·917 (2)
F(2)···F(8)	2·820 (2)	F(6)···F(1)	2·724 (2)
F(2)···F(4)	2·867 (2)	F(6)···F(4)	2·810 (2)
F(3)···F(6)	2·845 (2)	F(7)···F(4)	2·730 (2)
F(3)···F(5)	2·917 (2)	F(7)···F(8)	2·810 (2)
F(4)···F(7)	2·730 (2)	F(8)···F(2)	2·820 (2)
F(4)···F(6)	2·810 (2)	F(8)···F(7)	2·810 (2)

* Riding-body correction as given by Busing & Levy (1964).

† Each F atom is bonded to Ca, as shown in the Ca ion environment. Here we list the two shortest F···F contacts between BF_4^- groups for each F atom.
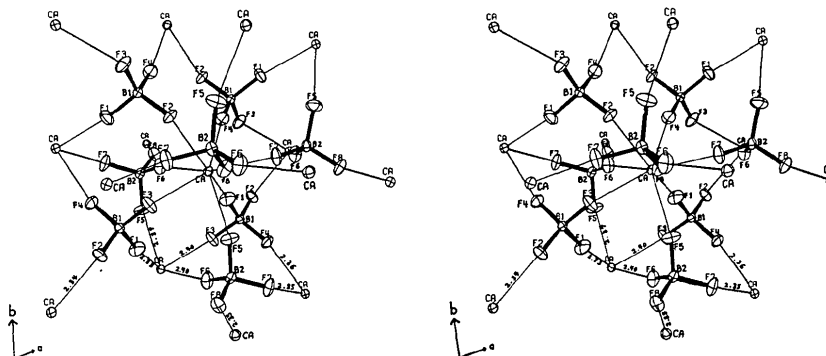
* Table 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30690 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 2. The Ca^{2+} and BF_4^- environments in $Ca(BF_4)_2$.

apparent thermal parameters have been applied. Each fluorine atom is coordinated to only one Ca^{2+} ion and therefore no BF_4^- edges are shared with Ca^{2+}. Because of this and because their environments are also approximately tetrahedral (see Fig. 2 and Table 3), both BF_4^- ions are essentially undistorted from tetrahedral geometry. Principal mean-square amplitudes of the fluorine atoms are appropriately perpendicular to the B–F covalent bonds and to the F···Ca ionic bonds, with the largest amplitude approximately perpendicular to the B–F···Ca plane (see Table 3 for B–F···Ca angles). The two closest approaches (2·724 and 2·729 Å) of F atoms in different BF_4^- ions are seen from Table 3 to involve F(1) and F(6) and F(1) and F(5), respectively. These interatomic distances are quite normal for fluorine, even though the cation–anion ratio in the compound necessitates appreciable anion–anion interaction.

Discussion of the structure

$Ca(BF_4)_2$ appears to provide a new structural type for calcium-containing compounds (see Dickens & Brown, 1972, for a listing with examples of five main structural types in calcium phosphates and related compounds). Certainly the stoichiometry, one small cation and two bulky XY_4 groups, i.e. 1:2, is not nearly as common as cation:XY_4 ratios of 1:1 or 2:1. The only other Ca compounds with this ratio that have been studied are $Ca(H_2PO_4)_2$ (Dickens, Prince, Schroeder & Brown, 1973) and $Ca(H_2AsO_4)_2$ (Ferraris, Jones & Yerkess, 1972). These structures do not crystallize in the $Ca(BF_4)_2$ structural type or in one of the five main structural types because anion···anion hydrogen bonding is available for $H_2AsO_4^-$ and $H_2PO_4^-$. Because the possibility of similar hydrogen bonding exists with $Ca(BF_3OH)_2$ and $Ca[BF_2(OH)_2]_2$, these compounds may form structures similar to that of $Ca(H_2PO_4)_2$.

The BF_4^- ions in $Ca(BF_4)_2$ are the most nearly tetrahedral BF_4^- ions found to date, even though their site symmetry is 1 and Ca is a powerful polarizing cation. Edge sharing of BF_4^- ions by cations is not present in $Ca(BF_4)_2$, but causes appreciable distortion from tetrahedral symmetry of the BF_4^- ions in the recently determined structures $NaBF_4$ (Brunton, 1968) and KBF_4 (Brunton, 1969).

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