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$K_2B_{12}F_{12}$: A rare A_2X structure for an ionic compound at ambient conditions[☆]

Dmitry V. Peryshkov, Steven H. Strauss *

Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA

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ABSTRACT

The anhydrous salt $K_2B_{12}F_{12}$ crystallized from aqueous solution and its structure was determined by single crystal X-ray diffraction. The Ni_2In-type structure it exhibits is rare for an A_2X ionic compound at 25 °C and 1 atm., consisting of an expanded hexagonal close-packed array of $B_{12}F_{12}^{2-}$ centroids (cent···cent distances: 7.204–8.236 Å) with half of the K^+ ions filling all of the O_h holes and half of the K^+ ions filling all of the D_{3h} trigonal holes in the close-packed layers that are midway between two "empty" T_d holes. The structure is also unusual in that the bond-valence sum for the K^+ ions in O_h holes is less than or equal to 0.73 (the bond-valence sum for the other type of K^+ ion is 1.16). A variation of the Ni_2In structure is exhibited by the previously published monohydrate $Cs_2(H_2O)B_{12}F_{12}$, for which an improved structure is also reported here. For $K_2B_{12}F_{12}$: monoclinic, $C2/c$, $a = 8.2072(8)$, $b = 14.2818(7)$, $c = 11.3441(9)$ Å, $\beta = 92.832(5)^\circ$, $Z = 4$, $T = 120(2)$ K. For $Cs_2(H_2O)B_{12}F_{12}$: orthorhombic, $P2_12_12_1$, $a = 9.7475(4)$, $b = 10.2579(4)$, $c = 15.0549(5)$ Å, $Z = 4$, $T = 110(1)$ K.

1. Introduction

Binary compounds with 99+% ionic character are generally limited to alkali metal halides and oxides [1], but the interactions between alkali metal cations and high-symmetry fluoroanions such as BF_4^-, AsF_6^-, BeF_4^{2-}, SiF_6^{2-}, and MnF_6^{2-} (among many others) are also predominantly ionic in nature. The packing of anions and cations under normal conditions in KF and K_2O are easily described as the sodium chloride and antifluorite structures, respectively. A wider variety of structure types are exhibited when the aforementioned fluoroanions are paired with a given alkali metal ion to form AX or A_2X salts. For example, there are at least two polymorphs of K_2MnF_6. One has the antifluorite structure [2] (in this paper we equate the packing arrangement of EF_n^{m-} anions to the packing arrangement of their central atoms, not their fluorine atoms) and one has a Cs_2S-type structure [3] (approximate HCP packing of anions with K^+ ions near the centers of all Mn_6 O_h holes and near the centers of half of the Mn_4 T_d holes) [4]. Similarly, K_2SiF_6 and K_2GeF_6 each exhibit two polymorphs. For K_2SiF_6, the situation is similar to K_2MnF_6: one polymorph has the antifluorite structure [5] and the other, which is a naturally occurring mineral recently found in the La Fossa crater on Volcano Island near Sicily, has a Cs_2S-type structure [6]. However, one polymorph of K_2GeF_6 has a Cs_2S-type structure [7] and the other has an unusual hexagonal structure consisting of superimposed close-packed layers of anions with K^+ ions significantly off-center in half of the trigonal-prismatic holes [8].

We recently reported the efficient, sub-ambient-temperature, and large-scale synthesis of $K_2B_{12}F_{12}$ [9] and are now exploring the structural chemistry of the icosahedral $B_{12}F_{12}^{2-}$ fluoroanion. It is significantly larger than tetrahedral and octahedral EF_n^{m-} fluoroanions, and also differs from them in having multiple fivefold symmetry axes in addition to multiple threefold and twofold axes. For these reasons, it seemed likely that unusual structure types might be exhibited by $B_{12}F_{12}^{2-}$ salts, even for predominantly ionic compounds with simple stoichiometries. We wish to report that the structure of crystalline $K_2B_{12}F_{12}$ is almost without precedent for solvent-free A_2X ionic compounds at atmospheric pressure. The Ni_2In-like structure it exhibits was reported in 2003 for Cs_2Pt at ambient temperature and pressure [10]. In addition, the Ni_2In-like structure of $K_2B_{12}F_{12}$ is related to the structures of $Cs_2(H_2O)B_{12}F_{12}$ and $Cs_2(H_2O)B_{12}H_5F_7$, both of which were reported in 1992 [11], although in the original report the Ni_2In-like packing of anions and cations was not discussed in detail. We also report an improved structure of $Cs_2(H_2O)B_{12}F_{12}$.

2. Results and discussion

Only two other structures containing $B_{12}F_{12}^{2-}$ anions have been previously published, $Cs_2(H_2O)B_{12}F_{12}$ [11] and $(CPh_3)_2B_{12}F_{12}$ [12] (in addition, two mixed-anion salts, $K_3(AsF_6)B_{12}F_{12}$ and

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[☆] We dedicate this paper to a rare and very special teacher–scholar, Professor Russell P. Hughes, in honor is his receiving the 2010 ACS Award for Creative Work in Fluorine Chemistry.

* Corresponding author. Tel.: +1 970 491 5104; fax: +1 970 491 1801.
E-mail address: steven.strauss@colostate.edu (S.H. Strauss).

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Table 1
Crystallographic data collection and refinement parameters.

Compound	$K_2B_{12}F_{12}$	$Cs_2(H_2O)B_{12}F_{12}$
Empirical formula	$B_{12}F_{12}K_2$	$B_{12}Cs_2F_{12}H_2O$
Formula weight ($g\,mol^{-1}$)	435.92	641.56
Habit, color	Prism, colorless	Prism, colorless
Space group	$C2/c$	$P2_12_12_1$
a (Å)	8.2072(8)	9.7475(4)
b (Å)	14.2818(17)	10.2579(4)
c (Å)	11.3441(9)	15.0549(5)
α (°)	90	90
β (°)	92.832(5)	90
γ (°)	90	90
V (Å^3)	1328.1(2)	1505.3(1)
Z	4	4
T (K)	120(2)	110(1)
ρ_{calc} ($g\,cm^{-3}$)	2.180(1)	2.831(1)
$R(F)$ ($I > 2\sigma(I)$)[a]	0.0493	0.0123
$wR(F^2)$ [all data][a]	0.1084	0.0328
min., max. e^- dens. (e Å^{-3})	−0.36, 0.39	−0.56, 0.95

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$.

$Cs_3(AsF_6)B_{12}F_{12}$, are being published in the same issue of this journal [13]). In this work, the structure of $K_2B_{12}F_{12}$ and an improved structure of $Cs_2(H_2O)B_{12}F_{12}$ were determined by single-crystal X-ray diffraction at 120(2) and 110(1) K, respectively. Selected data collection and refinement parameters for both structures are listed in Table 1 and relevant interatomic distances are listed in Table 2. The $B_{12}F_{12}^{2-}$ anions in both structures are, as expected, essentially icosahedral and are otherwise unremarkable. It is the packing of ions in the stoichiometrically simple A_2X compound $K_2B_{12}F_{12}$ that is unusual and therefore of interest.

Several drawings of the structure of $K_2B_{12}F_{12}$, using the same relative orientation, are shown in Figs. 1–4. A labeled thermal ellipsoid plot of the $B_{12}F_{12}^{2-}$ anion is shown in Fig. S-1 in supplementary data. The positions of the B_{12} centroids form an idealized hexagonal close-packed (HCP) array, as shown in Figs. 1 and 2, not unlike the HCP arrays of Si, Ge, or Mn atoms in the hexagonal polymorphs of K_2SiF_6 [6], K_2GeF_6 [7], and K_2MnF_6 [14], all of which have a Cs_2S-like structure. However, unlike those structures, which have half of the K^+ ions filling every interstitial O_h hole and half filling every other T_d hole, half of the K^+ ions in $K_2B_{12}F_{12}$ fill every O_h hole and half fill every D_{3h} trigonal hole *within* the close-packed layers, holes that are midway between two T_d holes. This type of hole filling in an HCP lattice is known as the Ni_2In structure and is exhibited by a variety of intermetallic compounds [15,16] and, more recently, as the high-pressure (GPa) structure of ionic compounds including BaF_2, SrH_2, and K_2S [17–19]. As mentioned above, $Cs_2(H_2O)B_{12}F_{12}$ and $Cs_2(H_2O)B_{12}H_5F_7$ were the first examples of the Ni_2In-type structure for ionic compounds at 25 °C and 1 atm. [11], and Cs_2Pt was the first example of a rigorous Ni_2In structure for an ionic compound at ambient conditions [10].

The B_{12} centroids (cent's) in $K_2B_{12}F_{12}$ do not form a perfect HCP array, but, with one exception, the deviations are minor. The cent···cent distances within the rigorously planar close-packed-like layers are 8.207 and 8.236 Å, and the acute cent···cent···cent angles within the close-packed-like layers are 60.0° ± 0.2°. The cent···K1···cent angles are within ±2.7° of the ideal angles of 60°, 90°, 120°, and 180°, and the cent···K2···cent angles are within ±7.6° of the ideal angle of 90° (the *trans* angles are rigorously 180°). The exception is that the cent···cent distances between the layers, 7.204, 7.471, and 7.517 Å, are ca. 10% shorter than within the layers. This is undoubtedly due to the absence of cations in the T_d holes, which has allowed the perpendicular distance between the layers to decrease. (Even highly symmetric structures like hexagonal ZnS (wurtzite) do not have rigorous HCP lattices with 12 equal S···S distances for each S^{2-} ion: the S···S distances between the close-packed layers are 1.2% longer than the S···S distances within the layers, in this case *because* half of the T_d holes are filled, and for this reason there are also two different Zn···S distances [20].)

There are two previously published structures of hydrates that have a distorted version of the $K_2B_{12}F_{12}$ structure, $Cs_2(H_2O)B_{12}F_{12}$ and $Cs_2(H_2O)B_{12}H_5F_7$ [11]. The $B_{12}H_5F_7^{2-}$ anion in the latter structure is disordered, and this structure will not be discussed further. The standard errors for individual B–B bonds in the original report for $Cs_2(H_2O)B_{12}F_{12}$ were ±0.01 Å [11]. For this reason, we decided to redetermine this structure (see Tables 1 and 2; $R(F) = 0.012$, B–B = 1.779(3)–1.808(3) Å). A drawing of the hole filling in this structure is shown in Fig. 5. The B_{12} centroids form a pseudo expanded-HCP lattice, although the cent···cent distances span a much wider range (7.166–10.162 Å) than in $K_2B_{12}F_{12}$ (7.204–8.236 Å) and are not rigorously coplanar within the pseudo close-packed planes. Half of the Cs^+ cations occupy the O_h holes (displaced from the centers due to the presence of the H_2O molecules, which bridge Cs2 ions) and half occupy D_{3h}-like holes, with Cs1···cent distances of 5.029, 5.150, and 6.006 Å.

Table 2
Selected interatomic distances (Å) and angles (°)[a].

Parameter	$K_2B_{12}F_{12}$[b]	$Cs_2(H_2O)B_{12}F_{12}$[c]
Approximate positions of B_{12} cent's	HCP	Distorted HCP
Cent···cent (within close-packed layers)	8.207 × 2, 8.236 × 4	8.076, 9.747, 10.162, all × 2
Cent···cent (between close-packed layers)	7.204, 7.471, 7.517, all × 2	7.166, 7.368, 8.038, all × 2
M1···F(B) (within close-packed layers)	2.651(2), 2.734(2), 2.880(2), 3.405(2), all × 2	3.109(1)–3.387(1) (7 values)
M1···F(B) (between close-packed layers)	2.664(2) × 2	3.049(1)–3.259(1) (4 values)
M2···F(B)	2.615(2), 2.819(2), 3.147(2), 3.324(2), all × 2	3.069(1)–3.470(1) (7 values)
Σ(M1–F bond-valences)	1.16	1.08
Σ(M2–F bond-valences)	0.70 (0.73; see text)	0.71
Σ(Cs2–O bond-valences)[d]	–	0.23
M1···cent (within close-packed layers)	4.719 × 2, 4.810	5.029, 5.150, 6.006
M1···cent (between close-packed layers)	5.672 × 2	5.225, 5.253
M2···cent	5.445, 5.497, 5.652, all × 2	5.162, 5.603, 5.652, 5.786, 5.931
shortest M1···M1	7.239(1)	6.584(1)
shortest M2···M2	5.672(1)	5.493(1)
shortest M1···M2	5.421(1)	4.928(1)
B–F	1.378(3)–1.392(3)	1.378(2)–1.389(2)
B–B	1.767(4)–1.805(5)	1.779(3)–1.808(3)

[a] Cent = B_{12} centroid; all data from this work.
[b] M = K.
[c] M = Cs.
[d] The two Cs–O distances are 3.1480(16) and 3.3044(16) Å.

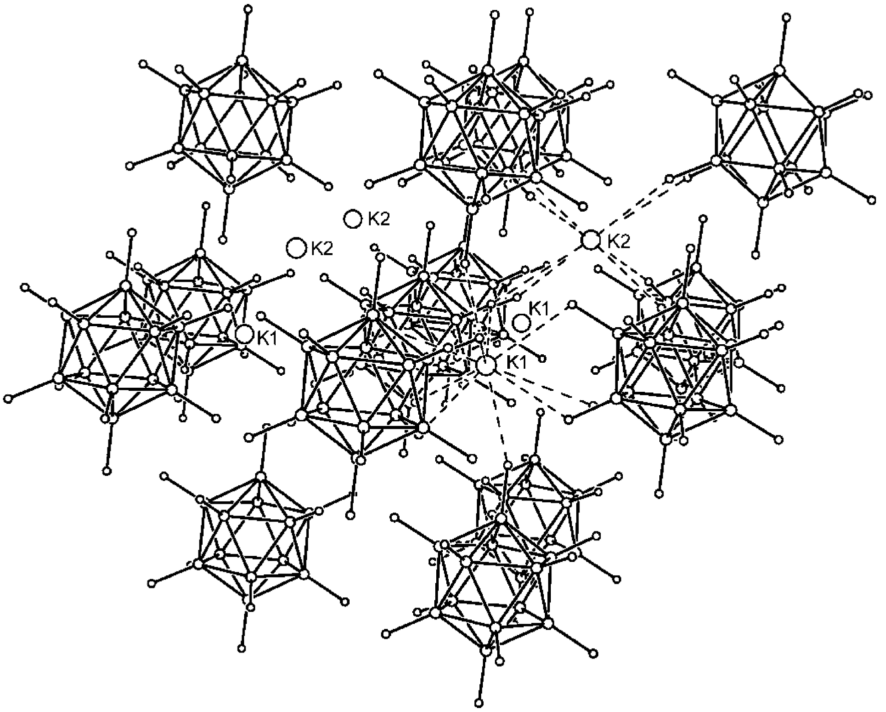

Fig. 1. The structure of $K_2B_{12}F_{12}$. For clarity, only those $K1^+$ ions in the D_{3h} holes (common to two T_d holes) in the middle layer of expanded close-packed $B_{12}F_{12}^{2-}$ anions (i.e., the expanded close-packed layer of their B_{12} centroids) are shown, and only those $K2^+$ ions in O_h holes between the top and the middle layers of close-packed-like $B_{12}F_{12}^{2-}$ anions are shown. The $K1^+$ ions are rigorously coplanar with the B_{12} centroids in the middle layer, and the $K2^+$ ions are equidistant from the top and middle planes of B_{12} centroids.

The $(K1)F_{10}$ and $(K2)F_8$ coordination spheres in $K_2B_{12}F_{12}$ resemble a bicapped square antiprism and an idealized cubic prism, respectively, as shown in Figs. 3 and 4 (see also Fig. S-2 in supplementary data). Note that K1 is bonded to F1 atoms belonging to dodecafluoroborate(2−) anions above and below the close-packed-like plane containing K1. These are not weak or secondary interactions: the two K1···F1 distances are 2.664(2) Å, which are only slightly longer than the shortest K1···F5 distances of 2.651(2) Å in the $(K1)F_{10}$ coordination sphere. In this sense it can be said that the K1 ions are in trigonal bipyramidal holes, not just trigonal holes, although the distance from K1 to the "apical" B_{12} centroids, 5.672 Å, is ca. 20% longer than the distances to the "equatorial" centroids, 4.719 and 4.810 Å.

Another unusual feature of the structure of $K_2B_{12}F_{12}$ is the disparity in the bond-valence sums [21] for K1 and K2. The bond-valence sum for the ten K1···F "bonds" from 2.651(2) to 3.405(2) is 1.16 (the ideal value for K^+ is 1.00 [21]; the next closest F atom to K1 is more than 4 Å away). However, the bond-valence sum for the eight K2···F bonds from 2.615(2) to 3.324(2) is only 0.70, an exceptionally low value (the next closest F atom to K2 is 3.8 Å

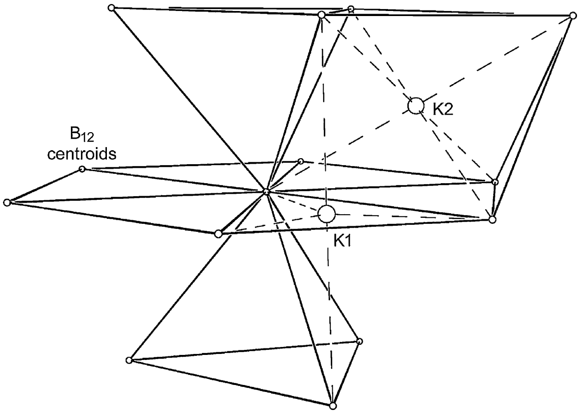

Fig. 2. The expanded HCP-like geometry of B_{12} centroids (cent; small spheres) and K^+ ions (large spheres) in the structure of $K_2B_{12}F_{12}$. For clarity, only one $K1^+$ ion and one $K2^+$ ion are shown. The acute cent···cent···cent angles within the close-packed-like planes of centroids are 60.0° ± 0.2°. The cent···cent distances are 8.207 and 8.236 Å within the close-packed-like planes of centroids and are 7.204, 7.471, and 7.517 Å between the planes of centroids. The K1···cent distances are 4.719 and 4.810 Å within the middle close-packed-like plane of centroids and are 5.672 Å between two adjacent planes of centroids. The K2···cent distances are 5.445, 5.497, and 5.652 Å.

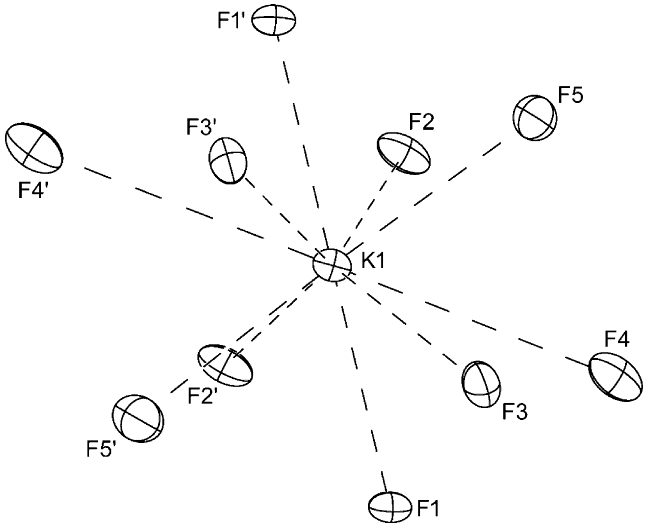

Fig. 3. The ten K1···F contacts in the structure of $K_2B_{12}F_{12}$ (50% probability ellipsoids; the $K1^+$ ions are in D_{3h} holes in the close-packed-like layers of B_{12} centroids). The K1···F1 distances, which involve the $B_{12}F_{12}^{2-}$ anions above and below the $K1^+$ ions, are 2.664(1) Å. The other K1·F distances range from 2.651(1) to 3.405(1) Å. The KF_{10} coordination sphere is a distorted bicapped square antiprism (the F1 atoms are the capping atoms; see supplementary data).

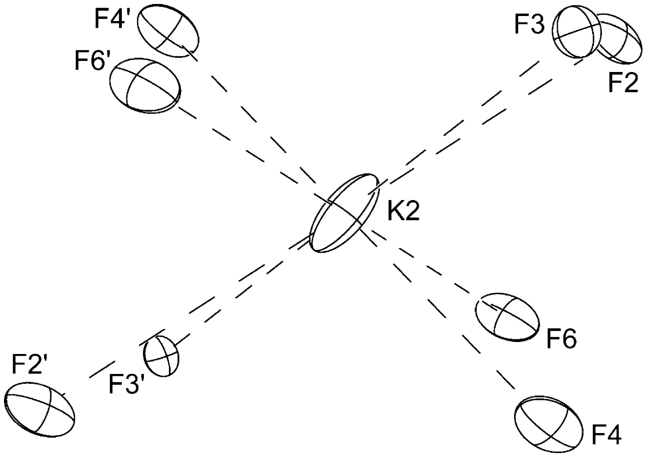

Fig. 4. The eight K2·F contacts in the structure of $K_2B_{12}F_{12}$ (50% probability ellipsoids; the $K2^+$ ions are in O_h holes between close-packed-like layers of B_{12} centroids). The K2·F distances range from 2.615(1) to 3.324(1) Å. The KF_8 coordination sphere is an idealized cubic prism.

away). Compare, for example, the following K^+ bond-valence sums, all of which are in the range 0.89–1.17: KF, 0.98 [22]; KBF_4, 1.03 [23]; $KAsF_6$, 0.92 [24]; K_2BeF_4, 0.89 and 1.17 [25]; K_2SiF_6, 1.03 [5]; K_2GeF_6, 1.04 and 1.13 [7]; and cubic K_2MnF_6, 1.01 [2].

Note that the thermal ellipsoid for K2, shown in Fig. 4, is elongated and might be the result of a slight disorder of two K2 positions along the long axis of the ellipsoid. This would result in a different set of K2···F distances. If K2 is artificially moved 0.255 Å in the direction of the long axis of its thermal ellipsoid (a reasonable movement given the size of the thermal ellipsoid), the eight new K2···F distances generate a bond-valence sum of 0.73 instead of 0.70. If it is moved 0.510 in this direction (an unreasonable movement), the bond-valence sum increases again to 0.75. As far as we are aware, a K^+ bond-valence sum ≤ 0.75 involving hard ligands in an isolable compound is unprecedented.

It is not possible, without additional structural evidence, to explain fully why the K^+ ions in $K_2B_{12}F_{12}$ are in the largest (O_h) and the smallest (D_{3h}) holes in an expanded HCP lattice of $B_{12}F_{12}^{2-}$ anions but not in the intermediate-size T_d holes, as they are in K_2BeF_4 [25] or K_2MnF_6 [14] (Cs_2S-like structures: half of the K^+ ions are in T_d holes) or in $K_2B_{12}H_{12}$ [26] (antifluorite structure; all of the K^+ ions in T_d holes). Similarly, $Cs_2B_{12}Cl_{12}$ has a Cs_2S-like structure [27], $Cs_2(H_2O)B_{12}F_{12}$ has a structure that resembles $K_2B_{12}F_{12}$ (this work), and $Cs_2B_{12}H_{12}$ has the antifluorite structure [28]. However, the answer is undoubtedly related to the different sizes and shapes of the high-symmetry fluoroanions BeF_4^{2-}, MnF_6^{2-}, and $B_{12}F_{12}^{2-}$, or the relative sizes and different polarizabilities of the dodecaborate anions $B_{12}H_{12}^{2-}$, $B_{12}F_{12}^{2-}$, and $B_{12}Cl_{12}^{2-}$ (i.e., the degree of covalency in K···(H, F, Cl) interactions; the polarizibilities of $B_{12}H_{12}^{2-}$ and $B_{12}F_{12}^{2-}$ in a dielectric-continuum model for acetonitrile have been predicted to be 36.5 and 26.4 Å^3, respectively [9]).

One-half of the F···F "diameter" of the $B_{12}F_{12}^{2-}$ anion in $K_2B_{12}F_{12}$ (i.e., the simplest measure of its radius, not including the van der Waals radius of an F atom) is 3.083(3) Å (the average of six distances). This can be compared with typical B–F, Be–F, Sb–F, Si–F, Ge–F, Mn–F, and Zr–F bond distances in BF_4^-, BeF_4^{2-}, SiF_6^{2-}, GeF_6^{2-}, SbF_6^-, MnF_6^{2-}, and ZrF_6^{2-}, which are 1.383(3) [29], 1.553(2) [30], 1.678(1) [31], 1.792 [7], 1.847(5) [32], 2.006 [2], and 2.002(2) Å [33], respectively. (The "radius" 3.083 Å can also be compared with one-half of the Cl···Cl diameter of the $B_{12}Cl_{12}^{2-}$ anion, ca. 3.5 Å [27].) The effective volume of $B_{12}F_{12}^{2-}$ can be estimated, using the procedure of Jenkins et al. [34], from the formula unit volume of $K_2B_{12}F_{12}$, 332.0(2) Å^3, by subtracting twice the volume of K^+, 19.7 Å^3 (2 × 9.86 Å^3) [34]. The result, 312 Å^3, can be compared with the effective volumes of BF_4^-, PF_6^-, AsF_6^-, and TiF_6^{2-} estimated from their alkali metal and alkaline earth metal salts, which are (73 ± 9), (109 ± 8), (110 ± 9), and (122 ± 8) Å^3, respectively [34]. Using the same procedure for $K_2B_{12}H_{12}$ [26], the effective volume of $B_{12}H_{12}^{2-}$ is 279 Å^3, ca. 12% smaller than for $B_{12}F_{12}^{2-}$ by this procedure.

We are continuing to explore the solid-state structural chemistry of the $B_{12}F_{12}^{2-}$ anion.

3. Experimental

The compounds $K_2B_{12}F_{12}$ and $Cs_2B_{12}F_{12}$ were prepared as previously described by bubbling 20%F_2/80%N_2 (APCI Inc.) through an acetonitrile solution of $K_2B_{12}H_{12}$ (Katchem) at 0 °C in the presence of a large excess of KF [9]. Distilled water was passed through a Barnstead Nanopure deionizer; the deionized distilled water had a resistivity of at least 18 MΩ. Colorless crystals of $K_2B_{12}F_{12}$ were formed during slow and complete evaporation of water from an aqueous solution at room temperature. Colorless crystals of $Cs_2(H_2O)B_{12}F_{12}$ were formed by cooling a hot aqueous solution to 0 °C.

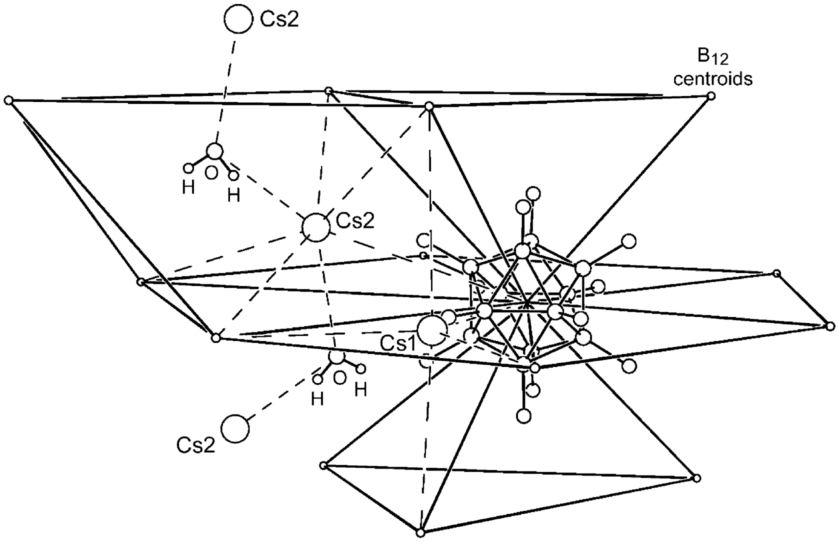

Fig. 5. The expanded HCP-like geometry of B_{12} centroids (small spheres) and some of the Cs^+ ions in the structure of $Cs_2(H_2O)B_{12}F_{12}$ (this work).

X-ray diffraction data from crystals of $K_2B_{12}F_{12}$ and $Cs_2(H_2O)B_{12}F_{12}$ were collected with a Bruker Kappa APEX II CCD diffractometer at 120(2) and 110(1) K, respectively, employing Mo Kα radiation (graphite monochromator). Unit cell parameters (see Table 1) were obtained from least-squares fits to the angular coordinates of all reflections, and intensities were integrated from a series of frames (ω and φ rotation) covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied using SADABS [35]. The structures were solved using direct methods and refined (on F^2, using all data) by a full-matrix, weighted least squares process. Standard Bruker control and integration software (APEX II) was employed [36], and Bruker SHELXTL software was used for structure solution, refinement, and molecular graphics [37]. All non-hydrogen atoms were refined using anisotropic atomic displacement parameters. The structure of $K_2B_{12}F_{12}$ was refined as a non-merohedral twin. The structure of $Cs_2(H_2O)B_{12}F_{12}$ was refined as a racemic twin. Hydrogen atoms of the H_2O molecule were restrained to have similar O–H distances and were constrained to have $U_{eq}(H) = 1.2\ U_{eq}(O)$.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2010.06.015.

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