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Journal of Fluorine Chemistry

# Anion packing, hole filling, and HF solvation in $A_2(HF)_n B_{12}F_{12}$ and $K_2(HF)TiF_6$ (A = K, Cs)

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#### ARTICLE INFO

Article history: Received 4 October 2012 Received in revised form 11 October 2012 Accepted 17 October 2012 Available online 29 October 2012

*Keywords:* Fluoroanion Hydrogen fluoride complex Potassium Polyhedral borane

## ABSTRACT

The crystal structures of three new HF solvates of fluoroanion salts of alkali metal ions are reported,  $K_2(HF)TiF_6$ ,  $K_2(HF)_{3}B_{12}F_{12}$ , and  $Cs_2(HF)B_{12}F_{12}$ . The anion packing in  $K_2(HF)TiF_6$  ( $P2_1/m$ ) is distorted cubic close-packed with Ti  $\cdots$  Ti distances that range from 5.717(1) to 7.394(1) Å (average 6.18 Å). Half of the K<sup>+</sup> ions are in  $T_d$  holes and half are in  $O_h$  holes (i.e., this is a distorted version of the  $Cs_2S$  structure). Each HF molecule is bonded to a K<sup>+</sup> ion in the  $O_h$  holes (K–F(H) = 2.679(5) Å) and also weakly interacts with two other K<sup>+</sup> ions in adjacent  $O_h$  holes (K $\cdots$ F(H) = 3.238(2) Å). The anion packing in  $K_2(HF)_{3}B_{12}F_{12}$  ( $Fm\bar{3}m$ ) is simple cubic. The (B<sub>12</sub> centroid)  $\cdots$  (B<sub>12</sub> centroid) distance ( $\odot \cdots \odot$  distance) is 7.242 Å, and disordered  $K_2(\mu-HF)_3^{2+}$  cations occupy each cube. The anion packing in  $Cs_2(HF)B_{12}F_{12}$  ( $P2_1/c$ ) is distorted hexagonal close-packed with  $\odot \cdots \odot$  distances that range from 7.217 to 9.408 Å (average 8.304 Å). The HF molecule bridges  $Cs^+$  ions in adjacent  $O_h$  holes, forming infinite  $Cs^+ - (\mu-HF) - Cs^+ - (\mu-HF) - chains. The other half of the <math>Cs^+$  ions are in  $T_d$  holes, displaced nearly 1 Å from the center of those holes. This structure is similar to the distorted Ni<sub>2</sub>In structure exhibited by  $Cs_2(H_2O)B_{12}F_{12}$ . The new results are used to compare and contrast the strength of M-F(H) interactions with M-F interactions involving F atoms from fluoroanions as well as the solid-state packing of icosahedral  $B_{12}F_{12}^{2-}$  anions and octahedral  $MF_6^{2-}$  anions in alkalimetal salts, both with and without the inclusion of weakly-basic HF solvent molecules.

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## 1. Introduction

The packing of regular convex polyhedra in three-dimensional space is a longstanding problem in mathematics, physics, and chemistry [1–3]. Although chemical species with  $T_d$ ,  $O_h$ , or  $I_h$  symmetry abound, only rarely are such species congruent with a tetrahedron (i.e., a species having just four atoms (vertexes) joined by six bonds (edges), as in  $P_4$ ), an octahedron (a species having just six atoms joined by 12 bonds, as in the Ga<sub>6</sub> clusters in Ba<sub>5</sub>Ga<sub>6</sub> [4] or the B<sub>6</sub><sup>2–</sup> clusters in CaB<sub>6</sub> [5] and BaB<sub>6</sub> [6]), a cube (8 atoms, 12 bonds), a dodecahedron (20 atoms, 30 bonds, as in the hypothetical phosphorus allotrope  $P_{20}$  [7–9]), an icosahedron (12 atoms, 20 bonds, as in the B<sub>12</sub> units in several allotropes of boron [10] or an icosahedral species that also has a 13th atom at the center, as in the Ag<sub>13</sub> cluster in Ag<sub>13</sub>OsO<sub>6</sub> [11] or the Zn<sub>13</sub> cluster in NaZn<sub>13</sub> [12,13]),

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or a truncated icosahedron such as C<sub>60</sub>. More commonly, *T*<sub>d</sub>, *O*<sub>h</sub>, or *I*<sub>h</sub> species have bonds that radiate from a central atom (e.g., CH<sub>4</sub>, BF<sub>4</sub><sup>-</sup>, Zn(CN)<sub>4</sub><sup>2-</sup>, SF<sub>6</sub>, AsF<sub>6</sub><sup>-</sup>, CrF<sub>6</sub><sup>2-</sup> [14], Mo(CO)<sub>6</sub>, Fe(CN)<sub>6</sub><sup>3-/4-</sup>) or from the vertexes of a tetrahedral, octahedral, cubic, dodecahedral, or icosahedral core (e.g., B<sub>4</sub>Cl<sub>4</sub> [15], B<sub>6</sub>H<sub>6</sub><sup>2-</sup> [16], C<sub>8</sub>H<sub>8</sub> [17], C<sub>20</sub>H<sub>20</sub> [18], or B<sub>12</sub>H<sub>12</sub><sup>2-</sup> [19], respectively). When the polyhedral species is an anion, the three-dimensional packing includes countercations. These can be as simple as atomic metal cations but can also include cationic polynuclear metal clusters, metal cations with a complement of ligands, or non-metal cations.

Salts of icosahedral  $B_{12}X_{12}^{2-}$  anions have exhibited, and no doubt will continue to exhibit, unanticipated as well as unprecedented structures from the standpoint of anion packing and cation hole filling (X = H, Cl, F). For example,  $K_2B_{12}H_{12}$  and  $Li_2B_{12}H_{12}$  both have CCP arrays of  $B_{12}H_{12}^{2-}$  anions (in this paper we equate the packing arrangement of  $B_{12}X_{12}^{2-}$  and  $MF_6^{2-}$  anions with the packing arrangement of their  $B_{12}$  centroids (abbreviated  $\odot$ ) or central M atoms, respectively, not with the arrays of X or F atoms). However, the cations in  $K_2B_{12}H_{12}$  are in tetrahedral holes (the antifluorite structure)[20] while the cations in  $Li_2B_{12}H_{12}$  are nearly centered in trigonal holes in the close-packed layers (they are 0.44 Å out of the plane of the trigonal hole and 2.32 Å from the

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center of an O<sub>h</sub> hole (i.e., *pairs* of Li<sup>+</sup> cations share the O<sub>h</sub> holes in this structure)) [21]. In another example, we recently reported the unusual Ni<sub>2</sub>In structure of  $K_2B_{12}F_{12}$ , a structure that is not exhibited by any other alkali-metal  $MF_6^{2-}$  salt despite the fact that K<sub>2</sub>MF<sub>6</sub> salts do exhibit a wide variety of structure types [22]. We also recently reported the syntheses and structures of the ternary salts K<sub>3</sub>(AsF<sub>6</sub>)B<sub>12</sub>F<sub>12</sub> and Cs<sub>3</sub>(AsF<sub>6</sub>)B<sub>12</sub>F<sub>12</sub> in Ref. [23]. It was found that the formula-unit volumes of these salts are slightly larger than the sum of the formula-unit volumes of the corresponding MAsF<sub>6</sub> and M<sub>2</sub>B<sub>12</sub>F<sub>12</sub> salts (by 5% and 2%, respectively), showing that, at least in these cases, ternary salts with fluoroanions of different shapes and charges do not pack as efficiently as the component binary salts. At the other end of the spectrum of cations, a series of  $B_{12}H_{12}^{2-}$  and  $B_{12}F_{12}^{2-}$  salts of heterocyclic cations such as imidazolium(1+) and triazolium(1+) have been reported, in which weak  $(N)H \cdots H(B)$  and  $(N)H \cdots F(B)$ hydrogen bonding was observed [24-26]. Finally, it has recently been shown that  $B_{12}F_{12}^{2-}$  is the least basic of the four anions  $B_{12}X_{12}^{2-}$  (X = F, Cl, Br, I) [27]; it is almost certainly less basic than  $B_{12}H_{12}^{2-}$ , and DFT calculations predicted that the fluoroanion is significantly less polarizable than  $B_{12}H_{12}^{2-}$  [28]. For these reasons, we expect that diffraction-quality single crystals of solvent-free salts of  $B_{12}F_{12}^{2-}$  will be rare, and to date the only example is K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> [22].

In this work, we report the structures of three new HF solvates,  $K_2(HF)TiF_6$ ,  $K_2(HF)_3B_{12}F_{12}$ , and  $Cs_2(HF)B_{12}F_{12}$ . The new results are used to compare and contrast the strength of M–F(H) interactions with M–F interactions involving F atoms from fluoroanions as well as the solid-state packing of icosahedral  $B_{12}F_{12}^{2-}$  anions and octahedral  $MF_6^{2-}$  anions in alkali-metal salts, both with and without the inclusion of weakly-basic HF solvent molecules. The results also reveal the reasons that the transformations  $K_2(HF)TiF_6(s) \Leftrightarrow K_2TiF_6(s) + HF(g)$  and  $K_2(HF)TiF_6(s) \Leftrightarrow K_2B_{12}F_{12}(s) + 3$  HF(g) can be rapid at 25 °C even though the cation/anion packing in  $K_2(HF)TiF_6$  and  $K_2TiF_6$ , or in  $K_2(HF)_3B_{12}F_{12}$  and  $K_2B_{12}F_{12}$ , are not the same (i.e., even though solvation and desolvation by gaseous HF requires lattice reconstruction).

# 2. Results and discussion

## 2.1. General Information

There are a growing number of structurally-characterized compounds with HF molecules coordinated to metal ions from all regions of the periodic table [14,29,30] (these are distinctly different from compounds with  $HF_2^-$  anions coordinated to metal ions [31], which we will not discuss in this paper). The 29 compounds that have been structurally characterized by single-crystal X-ray diffraction, including the three new compounds reported here, are listed in supplementary data Table S-1. In the remainder of this paper, frequent reference will be made to individual K–F and Cs–F bond valence (BV) and sums of bond valence ( $\sum BV$ ) values for the title compounds and related compounds. The bond-valence parameters and bond-valence equation used in this work are standard [32] and are listed in the supplementary data along with tables of K–F and Cs–F bond valences for the compounds discussed below (Tables S-2–S-8).

The title compounds were crystallized either by cooling or by evaporating anhydrous HF solutions of  $K_2TiF_6$  [33],  $K_2B_{12}F_{12}$  [28], and  $Cs_2B_{12}F_{12}$  [28], (see Section 3). The lability of the HF ligands and the corrosive nature of HF precluded characterization of the title compounds by elemental analysis or spectroscopic methods. It is possible that phases of  $K_2(HF)_nTiF_6$ ,  $K_2(HF)_nB_{12}F_{12}$ , and  $Cs_2(HF)_nB_{12}F_{12}$  with *n* values other than those observed for the title compounds could be isolated using different conditions (e.g.,

Fable 1
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Crystallographic and data-collection parameters.<sup>a</sup>

Compound	K <sub>2</sub> (HF)TiF <sub>6</sub>	$K_2(HF)_3B_{12}F_{12}$	Cs <sub>2</sub> (HF)B <sub>12</sub> F <sub>12</sub>
Empirical formula	HF7KTi	$H_3B_{12}F_{15}K_2$	$HB_{12}Cs_2F_{13} \\$
Formula weight	260.06	495.93	643.55
Habit, color	Plate, colorless	Prism, light-yellow	Prism, colorless
Crystal system	Monoclinic	Cubic	Monoclinic
Space group	$P2_1/m$	Fm3c	$P2_1/c$
a (Å)	6.187(3)	14.4841(17)	8.3463(8)
<i>b</i> (Å)	5.986(2)	14.4841(17)	16.1160(17)
c (Å)	8.895(4)	14.4841(17)	11.5031(9)
β (°)	99.330(4)	-	98.059(7)
$V(Å^3)$	325.1(2)	3038.6(6)	1532.0(3)
Ζ	2	8	4
<i>T</i> (K)	200(2)	133(2)	133(2)
$ ho_{ m calc}~( m gcm^{-3})$	2.657	2.168	2.790
$R(F) (I > 2\sigma(I))^{a}$	0.0582	0.0283	0.0204
$wR(F^2)$ [all data] <sup>a</sup>	0.1468	0.0760	0.0495
Min., max. $\Delta ho$ (e Å $^{-3}$ )	-0.89, 0.97	-0.17, 0.23	-0.57, 0.75

<sup>a</sup>  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$ ;  $wR2 = [\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]]^{1/2}$ .

both  $K_2(HF)CrF_6$  [34] and  $K_2(HF)_2CrF_6$  [14] are known), but there is no evidence for this at the present time. Crystallographic and datacollection parameters are listed in Table 1, and selected interatomic distances and angles are listed in Table 2.

## 2.2. Structure of $K_2(HF)TiF_6$

Drawings of the structure that emphasize the packing of anions and cations and the corrugated ribbons of edge-sharing  $[K_2(HF)_2]^{2+}$ rhombs are shown in Figs. 1–4. The structure consists of an idealized cubic close-packed array of TiF<sub>6</sub><sup>2-</sup> anions with half of the K<sup>+</sup> cations in idealized  $T_d$  holes (K1) and half in idealized  $O_h$  holes (K2), as shown in Figs. 1–3. The Ti–F distances and F–Ti–F angles are normal [35,36]. The Ti $\cdots$ Ti distances range from 5.717(1) to 7.394(1) Å. The K1 cations are nearly centered in the  $T_d$  holes, with four K1 $\cdots$ Ti distances that range from 3.561(1) to 3.633(1) Å. In contrast, the six K2 $\cdots$ Ti distances span a wider range, from 4.242(1) to 4.777(1) Å.

The distribution of K1 cations in half of the  $T_d$  holes in the CCP lattice of TiF<sub>6</sub><sup>2–</sup> anions is such that they form nearly-square-planar arrays, with K1···K1 distances of 4.235(1) and 4.377(1) Å. There are also four K2 nearest neighbors for each K1 cation, at 4.125(1) (×2), 4.259(1), and 4.277(1) Å. The K2 cations are linked by triply-bridging HF ligands, with K2–F(H) distances of 2.679(5) (BV = 0.156) and 3.238(2) Å (×2; BV = 0.035). The K2 cations form rigorously-planar rectangular arrays, with K2···K2 distances of 5.986(1) and 6.187(1) Å, that are parallel to the K1 arrays. However, the shortest K2···K2 distance is 4.575(1) Å. The K1 nearly-planar and K2 planar arrays are tilted ca. 49° from the idealized close-packed Ti planes.

The K1 and K2 cations form bonds, albeit with significant electrostatic contributions, with 12 and 9 F atoms, respectively, as

Table 2		
Selected	distances (Å) and angles	(°).

Parameter	K <sub>2</sub> (HF)TiF <sub>6</sub> <sup>a</sup>	$K_2(HF)_3B_{12}F_{12}{}^a$	Cs <sub>2</sub> (HF)B <sub>12</sub> F <sub>12</sub> <sup>b</sup>
$M{\cdots}F(Ti)$ or $M{\cdots}F(B)$ range	2.784(3)-3.317(4) (K1); 2.666(3)-2.932(4) (K2)	2.710(1)×4	2.981(2)-3.706(2)
$M{\cdots}FTi$ or $M{\cdots}FB$ range		134.71(5)	99.5(2)-164.2(2)
$M{\cdots}F(H)$	2.679(5), 3.238(2) × 2	2.62(1), 2.68(1), 2.76(1)	3.05(1), 3.44(1)
$M{\cdots}F(H){\cdots}M$		100.3(3)×2, 100.8(3)	130.0(3)
$MF_n$ coordination sphere	K(1)F <sub>12</sub> ; K(2)F <sub>9</sub>	KF <sub>7</sub>	Cs(1)F <sub>12</sub> ; Cs(2)F <sub>10</sub>
$\sum$ (bond valences to F(Ti)) $\sum$ (bond valences to F(B))	1.07 (K1); 0.85 (K2)	0.58	0.96 (Cs1); 0.99 (Cs2)
$\sum$ (all bond valences)	1.07 (K1); 1.07 (K2)	1.04	0.96 (Cs1); 1.18 (Cs2)
$M{\cdots}M$	4.235(1), 4.377(1) (K1···K1); 5.986(1), 6.187(1) (K2···K2); 4.125 (K1···K2)	4.129(1)	5.787(3) (Cs1…Cs1); 5.155(3), 5.616(3) (Cs1…Cs2); 5.890(3) (Cs2…Cs2)
$M{\cdots}Ti \text{ or } M{\cdots}{\odot}^c$	3.561(1)-3.633(1) (K1); 4.242(1)-4.777(1) (K2)	5.352 × 4	5.122–6.073 (Cs1); 5.249–6.012 (Cs2)
$Ti{\cdots}Ti \ or \ \odot{\cdots}{\odot}^c$	5.714(1)-6.187(1)	$7.242 \times 6$	7.217-9.408
Ti-F or B-F range	1.842(3)-1.884(4)	1.387(2)×12	1.371(4)-1.392(4)
B–B range		1.794(2)-1.796(2)	1.772(4)-1.804(5)

<sup>a</sup> M = K.

<sup>b</sup> M=Cs.

<sup>c</sup>  $\odot = B_{12}$  centroid.

shown in Fig. 4. The  $\sum$ BV values are 1.07 for both K1 and K2. The KF<sub>12</sub> coordination sphere for K1 is an idealized CCP array of F atoms. The KF<sub>9</sub> coordination sphere for K2 is a tri-capped trigonal prism. The three bonds between K2 and the HF molecules, which represent one-third of the nine F–K2 interactions, account for only 21% of the  $\sum$ BV value for K2. Nevertheless, the shortest K2–F(H) distance, at 2.679 Å, is shorter than all but two of the six K2–F(Ti) distances (see Table S-3). Another structural feature relevant to the discussion below is that five of the six F atoms of the TiF<sub>6</sub><sup>2–</sup> anions

bridge three or four  $K^+$  ions: F1 and F4 atoms, which account for four of the six F atoms, bridge three cations each, F3 bridges four cations, and F2 is bonded to only one  $K^+$  cation).

Crystals of  $K_2$ (HF)TiF<sub>6</sub> rapidly lost HF in an air-free environment at 25 °C. Powder X-ray diffraction demonstrated that the trigonal



**Fig. 1.** The packing of K<sup>+</sup> cations and Ti atoms in  $K_2(HF)TiF_6$  (F and H atoms omitted for clarity. The CCP arrangement of  $TiF_6^{2-}$  anions is indicated by the Ti...Ti vectors. The nearly-planar layers of K1 cations and the rigorously-planar layers of K2 cations are both tilted ca. 49° from the idealized close-packed planes of Ti atoms.



**Fig. 2.** The disposition of the K1 cations in  $T_d$  holes of the idealized CCP lattice of  $\text{TiF}_6^{2-}$  anions in the structure of  $K_2(\text{HF})\text{TiF}_6$  (50% probability ellipsoids). The 12 K1– F distances range from 2.784(3) to 3.317(4) Å.



**Fig. 3.** Left. The disposition of the K2 cations in  $O_h$  holes of the idealized CCP lattice  $TiF_6^{2-}$  anions in the structure of  $K_2(HF)TiF_6$  (50% probability ellipsoids except for the three H atoms, which are shown as spheres of arbitrary size). The three F5 atoms, from the HF ligands, are highlighted for clarity. The 12 K2–F distances range from 2.666(3) to 3.328(2) Å. Right. Fragment of the corrugated infinite ribbon of edge-sharing  $[K_2(HF)_2]^{2+}$  rhombs involving the K2 cations and triply-bridging HF ligands in  $K_2(HF)TiF_6$ . Each rhomb shares K–F(H) = 2.679(5) Å edges with two nearest-neighbor rhombs.

polymorph of  $K_2TiF_6$  (which exhibits the  $K_2GeF_6$  structure) was formed [35,36]. In this structure, the stacking of  $TiF_6^{2-}$  anions is  $AAA \cdots$  and the K<sup>+</sup> ions are in trigonal-prismatic holes defined by the Ti atoms and are each bonded to 12 F atoms (see Figure S-1; interestingly, the F atoms form an idealized CCP array around K1 in K<sub>2</sub>(HF)TiF<sub>6</sub> and form an idealized HCP array around the K atoms in trigonal K<sub>2</sub>TiF<sub>6</sub>). Fig. 5 depicts the transformations of the idealized CCP lattice and the actual CCP-like lattice of K<sub>2</sub>(HF)TiF<sub>6</sub> to solventfree trigonal  $K_2 TiF_6$  (only two layers of Ti atoms are shown; the idealized lattice was constructed by moving one layer of Ti atoms so that they were centered over trigonal holes in the adjacent layer). For the two  $K^+$  ions depicted in these drawings, the  $K \cdots K$ distance is 7.40 Å in  $K_2(HF)TiF_6$  and 6.86 Å in trigonal  $TiF_6$  $(\Delta(K \cdots K) = 0.54 \text{ Å}; \text{ note that these are not the closest } K \cdots K$ distances in these structures). There is a ca. 3.3 Å shift of one closepacked array of Ti atoms on going from the CCP-like packing in  $K_2(HF)TiF_6$  to the AAA... packing in trigonal  $K_2TiF_6$ . Nevertheless, the desolvation can apparently occur with little change in  $\sum$ BV during the transformation, and hence can occur relatively rapidly (this is depicted in more detail in Figure S-2). The  $\sum$ BV values are 1.07 for K1 and K2 in  $K_2(HF)TiF_6$  and 1.02 in trigonal  $K_2TiF_6$ . Finally, the perpendicular distances between planes of Ti atoms are virtually the same, 4.69 Å in  $K_2(HF)TiF_6$  and 4.66 Å in trigonal  $K_2TiF_6$ .

# 2.3. Structure of $K_2(HF)_3B_{12}F_{12}$

Drawings of the structure are shown in Figs. 6–9. The distances and angles in the  $B_{12}F_{12}^{2-}$  anions are normal [22,37]. The  $B_{12}$ centroids form a rigorous cubic array with a  $\odot \cdots \odot$  edge length of 7.242(2) Å, as shown in Fig. 6. The anions are oriented 90° relative to each other, as shown in Fig. 7. The high symmetry of the unit cell requires that (i) there is only one unique B–F moiety in the asymmetric unit and (ii) the K<sup>+</sup> ions are disordered over six positions, with the three K···K vectors coincident with the C<sub>4</sub> axes of the cube. In this model, the three HF ligands, two of which are symmetry-related, are disordered over 21 positions. The best model, after analysis of K–F(B), K–F(H), and (H)F···F(B) contacts, is that K<sub>2</sub>(HF)<sub>3</sub><sup>2+</sup> units, with idealized trigonal-bipyramidal K<sub>2</sub>F<sub>3</sub> cores having axial K<sup>+</sup> ions, are centered in each B<sub>12</sub>-centroid cube,



**Fig. 4.** The idealized CCP array of F atoms around K1 (left) and the tri-capped trigonal prismatic array of F atoms around K2 in K<sub>2</sub>(HF)TiF<sub>6</sub> (right; 50% probability ellipsoids except for the three H atoms, which are shown as spheres of arbitrary size). The three F5 atoms, from the HF ligands, are highlighted for clarity. The separation of the cations is not to scale.



**Fig. 5.** Depictions of the transformation of  $K_2(HF)TiF_6$  to solvent-free trigonal  $K_2TiF_6$  (F and H atoms omitted for clarity). The red and light blue spheres are central Ti atoms of  $TiF_6^{2-}$  anions in two adjacent close-packed or pseudo-close-packed layers. The short arrows depict the approximate directions (but not the distances) of the motions of the Ti atoms in the upper layer during the desolvation process. The two labeled Ti atoms are the same before and after desolvation.

as shown in Figs. 6 and 8. The choice of the two  $K^+$  positions was straightforward. If one  $K^+$  ion is arbitrarily selected, then the second one can only be in the opposite "octahedral" position in *Fm*3*c* (the other four possible  $K^+$  positions are only 2.2 Å away). The



**Fig. 6.** The  $K_2(HF)_3^{2+}$  unit and one of the eight equivalent  $B_{12}F_{12}^{2-}$  anions that surround it at the corners of a cube with  $\odot \cdots \odot$  distances of 7.242 Å (50% probability ellipsoids;  $\odot = B_{12}$  centroid). Four F1 atoms from four corners coordinate to each K<sup>+</sup> cation. The F2 and F3 atoms belong to the HF molecules. The H atoms were not located.

choice of the F(H) atom positions was similarly straightforward. All F atom positions less than 2.2 Å from the chosen pair of K<sup>+</sup> ions and/ or less than 2.4 Å from other F atoms were excluded (cf. the 2.66 Å K–F distance in KF).

In addition to the three HF molecules, the K<sup>+</sup> ions are coordinated to four F(B) atoms, one from each of four  $B_{12}F_{12}^{2-}$  anions that form one face of the cube. Each K<sup>+</sup> ion is located inside the  $B_{12}$ -centroid cube, 1.554 Å along a perpendicular from the center of the closest face of cube (this face is coplanar with the four F1 atoms coordinated to K<sup>+</sup> and the four B1 atoms to which these F1 atoms are attached). Even though the disorder of the HF molecules made it impossible to locate the H atoms with any precision, it is clear that there is significant hydrogen bonding between the HF molecules and F(B) atoms. The (H)F2 $\cdots$ F(B) distance is 2.58(2) Å, similar to the (H)F $\cdots$ F(H) distances of 2.51–2.53 Å observed in crystalline HF (DF) and gas-phase DF oligomers [38,39]. Two (H)F3 $\cdots$ F(B) contacts of 2.72(1) Å suggests that this HF molecule is involved in a bifurcated pair of hydrogen bonds.

Only seven (7) F atoms are coordinated to each  $K^+$  ion in  $K_2(HF)_3B_{12}F_{12}$ , as shown in Fig. 9, fewer than in  $K_2B_{12}F_{12}$  (8 and 10 for the two different  $K^+$  ions), fewer than in  $K_2(HF)TiF_6$  (9 and 12 for the two different  $K^+$  ions), and far fewer than in any  $K_2MF_6$  or  $K_2MF_4$  salt (e.g., 12 for trigonal  $K_2TiF_6$  [35,36]). The K–F distances, and hence the corresponding BV values, are essentially the same for the K–F(B) and K–F(H) bonds. The four BV values for the equivalent K–F(B) bonds are 0.144, and the three BV values for the K–F(H) bonds are 0.183, 0.156, and 0.125 (average 0.155). The K–F(H) BV values account for 45% of the  $\sum BV$ , which is 1.04 (note that 3/7 is equivalent to 43%). It appears that the  $B_{12}F_{12}^{2-}$  anion is



**Fig. 7.** One face of the cube of  $B_{12}F_{12}^{2-}$  anions in the structure of  $K_2(HF)_3B_{12}F_{12}$ . The  $\odot \cdots \odot$  distances are 7.242 Å. The anions are oriented 90° relative to their nearest neighbors to minimize  $F \cdots F$  repulsions. The closest  $F \cdots F$  contacts are 3.066(1) Å.

so weakly coordinating that a neutral HF molecule can compete with it for coordination to K<sup>+</sup>: two of the three K–F(H) BV values are larger than the K–F(B) BV values. This was also the case for K<sub>2</sub>(HF)TiF<sub>6</sub> (see Table S-3). However, a significant difference between the structures of K<sub>2</sub>(HF)<sub>3</sub>B<sub>12</sub>F<sub>12</sub> and K<sub>2</sub>(HF)TiF<sub>6</sub> is that none of the F atoms in the former structure bridge K<sup>+</sup> ions and five of the six F atoms in the latter structure bridge either three or four K<sup>+</sup> ions. In fact, no B<sub>12</sub>F<sub>12</sub><sup>2-</sup> salt reported to date has an F atom that bridges more than two metal ions.

Crystals of  $K_2(HF)_3B_{12}F_{12}$  also rapidly lost HF in an air-free environment at 25 °C, forming solvent-free  $K_2B_{12}F_{12}$  [22]. Fig. 10



**Fig. 8.** Part of the structure of  $K_2(HF)_3B_{12}F_{12}$  (50% probability ellipsoids). The F2 and F3 atoms belong to the three HF molecules. The H atoms were not located, but are probably positioned between their respective F2 or F3 atoms and the F1 atoms to which they are closest: F2…F1, 2.58(1); F3…F1, 2.72(1)Å.

depicts the transformations of the idealized simple-cubic lattice of  $K_2(HF)_3B_{12}F_{12}$  and the pseudo-HCP lattice of  $K_2(HF)_3B_{12}F_{12}$ . Even though these are entirely different lattices, the transformations caused by desolvation/resolvation can occur with only small changes in the relative positions of the cations and anions (as was the case with the transformation of  $K_2(HF)TF_6$  to solvent-free trigonal  $K_2TF_6$ ). The  $\odot \cdots \odot \cdots \odot$  angles change from 90° in  $K_2(HF)_3B_{12}F_{12}$  to ca. 60° in  $K_2B_{12}F_{12}$  (54.3°, 56.4°, and 60.1°), the  $\odot \cdots \odot$  distances change from 7.242 Å in  $K_2(HF)_3B_{12}F_{12}$  to 7.517, 8.207, and 8.236 Å in  $K_2B_{12}F_{12}$  to 4.719 (×2) and 4.810 Å for K1 and 5.445 (×2), 5.445 (×2), and 5.445 Å (×2) for K2 in  $K_2B_{12}F_{12}$ . The  $K \cdots K$  distance changes from 4.129(1) Å in  $K_2(HF)_3B_{12}F_{12}$  to 5.629(1) Å in  $K_2B_{12}F_{12}$  (the latter is the



**Fig. 9.** The KF<sub>7</sub> coordination sphere in the structure of  $K_2(HF)_3B_{12}F_{12}$  (50% probability ellipsoids). The F2 and F3 atoms belong to the three HF molecules that bridge two K<sup>+</sup> ions. The H atoms belonging to these HF molecules were not located. Selected interatomic distances (Å) and angles (°): K–F1, 2.710(1); K–F2, 2.76(1); K–F2', 2.62(1); K–F3, 2.68(1); F1…F1', 3.136(2); F2…F2', 3.40(2); F2…F3, 2.84(2).



Fig. 10. The transformation of the simple-cubic array of B<sub>12</sub> centroids in K<sub>2</sub>(HF)<sub>3</sub>B<sub>12</sub>F<sub>12</sub> (left) to the HCP array of B<sub>12</sub> centroids in solvent-free K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> (right).

distance between K1 and K2 in Fig. 10; the shortest K1···K2 distance in  $K_2B_{12}F_{12}$  is actually 5.421(1)Å). Finally, Fig. 11 shows the change from four  $K-B_{12}F_{12}^{2-}$  interactions with a total of four K-F bonds in  $K_2(HF)_3B_{12}F_{12}$  to three  $K-B_{12}F_{12}^{2-}$  interactions in  $K_2B_{12}F_{12}$  with the same set of anions but with a total of eight K-F bonds.

The structure of  $K_2(HF)_3B_{12}F_{12}$  more closely resembles the structure of  $K_2(HF)_2CrF_6$  [14] as shown in Fig. 12, than it does the structure of  $K_2(HF)_1CF_6$ . There is an elongated pseudo-cubic array of  $CrF_6^{2-}$  anions with  $K_2(HF)_2^{2+}$  moieties inside; each  $K^+$  ion is also engaged in K–F(H)–F bridging to another  $K^+$  ion in a neighboring cube. The result is that each  $K^+$  ion is bonded to three HF molecules, as in  $K_2(HF)_3B_{12}F_{12}$ . The K···K distance inside each cube is 4.773(1) Å(cf. 4.129(1) Å in  $K_2(HF)_3B_{12}F_{12})$ . However, the shorter Cr···Cr distances in  $K_2(HF)_2CrF_6$ , 5.235(1) and 5.837 (×2) Å, relative to the  $\odot \cdots \odot$  distances of 7.242 Å in  $K_2(HF)_3B_{12}F_{12}$ , allow  $K^+$  ions in neighboring cubes in  $K_2(HF)_2CrF_6$  to engage in HF-bridge bonding; the K···K distances between cubes in  $K_2(HF)_2CrF_6$  are 4.136(1) and 4.353(1) Å, whereas the K···K distances between cubes in  $K_2(HF)_3B_{12}F_{12}$  are 5.574 Å, too long for HF-bridging.

## 2.4. Structure of $Cs_2(HF)B_{12}F_{12}$

Drawings of the structure are shown in Figs. 13 and 14. The distances and angles in the  $B_{12}F_{12}^{2-}$  anions are normal [22,37]. The  $B_{12}$  centroids form a distorted HCP array  $\odot \cdots \odot$  distances that range from 7.217 to 9.408 Å (average 8.305 Å), as shown in Fig. 12. This is essentially the same structure as the monosolvate  $Cs_2(H_2O)B_{12}F_{12}$  [22] and these two structures are shown together for comparison in Figure S-4. It is also the same structure type as exhibited by  $K_2B_{12}F_{12}$ , viz. the Ni<sub>2</sub>In structure. The shortest F...F contact between anions in  $Cs_2(HF)B_{12}F_{12}$  is 2.776(2) Å. The HF molecule is disordered over two sites (see Section 3); only the maior F atom will be used in the discussion that follows.

The Cs<sup>+</sup> ions close to the trigonal holes in the close-packed layers of anions (Cs1) are bonded to 12 F atoms. The Cs1–F distances range from 3.105(2) (BV = 0.123) to 3.520(2) (BV = 0.038), with a  $\sum$ BV value of 0.96. The Cs<sup>+</sup> ions in  $O_h$  holes (Cs2) are bonded to 10 F atoms. The Cs2–F distances range from 3.021(2) (BV = 0.154) to 3.443(2) (BV = 0.049), with a  $\sum$ BV value of 1.18. The corresponding CsF<sub>12</sub> and CsF<sub>10</sub> coordination spheres are shown in Fig. 13. The H atom of the HF molecule is hydrogen bonded to an anion F atom, with (H)F···F(B) and F–H···F(B) values of 2.67(1)° and 157(2)°, respectively.



**Fig. 11.** Perpendicular views of the transformation of  $K_2(HF)_3B_{12}F_{12}$  (left; HF ligands omitted) to solvent-free  $K_2B_{12}F_{12}$  (right; the K<sup>+</sup> ion shown is K1). The K<sup>+</sup> ions move from being 1.554 A below the plane of the  $B_{12}$  centroids in  $K_2B_{12}F_{12}$  to being co-planar with the  $B_{12}$  centroids. In  $K_2(HF)_3B_{12}F_{12}$ , the three HF ligands complete the KF<sub>7</sub> coordination sphere; in  $K_2(HF)_3B_{12}F_{12}$ , two  $B_{12}F_{12}^{-2}$  anions above and below the plane (not shown) each donate one F atom to complete the KF<sub>10</sub> coordination sphere.



Fig. 12. The structure of K<sub>2</sub>(HF)<sub>2</sub>CrF<sub>6</sub>. See text for relevant interatomic distances.

The compound  $Cs_2B_{12}F_{12}$  crystallizes from anhydrous HF or from H<sub>2</sub>O with only one HF or H<sub>2</sub>O ligand, respectively, while  $K_2B_{12}F_{12}$  crystallizes from these solvents with three HF ligands and either two or four H<sub>2</sub>O ligands [40]. Note that this is similar to the situation observed when the alkali-metal salts of  $B_{12}Cl_{12}^{2-}$  were crystallized from SO<sub>2</sub>: the K<sup>+</sup> salt crystallized with eight SO<sub>2</sub> molecules per formula unit, with the formation of six K–O bonds, while the Cs<sup>+</sup> salt crystallized with only one SO<sub>2</sub> molecule per formula unit, and with only one, very weak, Cs–O bond [27].

The compound  $Cs_2(HF)_4CrF_6$  has an entirely different structure than  $Cs_2(HF)B_{12}F_{12}$  [14] and it is not fruitful to compare its structure to  $Cs_2(HF)B_{12}F_{12}$ . Each  $Cs^+$  ion is bonded to six HF molecules, each of which bridges three  $Cs^+$  ions. Two drawings of this structure are shown in Figures S-5 and S-6.

# 2.5. Comments on the crystal packing of $B_{12}F_{12}^{2-}$ anions

A crude estimation of the radius of the icosahedral  $B_{12}F_{12}^{2-}$ anion, if it is considered to be spherical, is half of the apical  $F \cdots F$ distance, ca. 3.08 Å, plus the van der Waals radius of fluorine, 1.47 Å, the sum of which is 4.55 Å. However,  $\odot \cdots \odot$  distances in  $B_{12}F_{12}^{2-}$  lattices are considerably shorter than 9.10 Å (i.e.,  $2 \times 4.55$  Å), even when solvent molecules are present (e.g., 7.242 Å in  $K_2(HF)_3B_{12}F_{12}$ , 7.276–7.295 Å in  $K_2(H_2O)_2B_{12}F_{12}$  [40], 6.915–8.598 Å in  $K_2(H_2O)_4B_{12}F_{12}$  [40], and 7.204–8.236 Å in solvent-free  $K_2B_{12}F_{12}$  [22]. Therefore, the effective radius of  $B_{12}F_{12}^{2-}$ , due to the dovetail-like interpenetration of adjacent anions shown in Fig. 7, is ca. 3.5–3.6 Å.

It appears that the symmetry of  $B_{12}F_{12}^{2-}$  allows it to pack more densely in a planar square array than in a planar close-packed hexagonal array, at least for the structures determined to date. The area per anion in square-planar arrays in  $K_2(HF)_3B_{12}F_{12}$  is 52.5 Å<sup>2</sup>, whereas the area per anion in the hexagonal arrays in  $K_2B_{12}F_{12}$ ( $\odot \cdots \odot = 8.207$  and  $8.236 (\times 2)$  Å within the close-packed planes of anions) is 58.4 Å<sup>2</sup>. If the structure of  $Li_2B_{12}F_{12}$  can be determined, and if it has the antifluorite structure, it is possible that the anions will pack more densely, in the close-packed planes, than in  $K_2(HF)_3B_{12}F_{12}$ .

# 3. Experimental

All manipulations were carried out under rigorously anhydrous conditions. Anhydrous HF (aHF; Linde) and F<sub>2</sub> (Solvay) were handled using a nickel–Teflon vacuum line; solids were handled in an argon-filled glovebox. The compounds KF and TiCl<sub>4</sub> (Sigma–Aldrich) were used as received. The compound TiF<sub>4</sub> was prepared by treating TiCl<sub>4</sub> with F<sub>2</sub> in a HF. Formation of TiF<sub>4</sub> was confirmed by Raman spectroscopy and chemical analysis. The compounds K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> and Cs<sub>2</sub>B<sub>12</sub>F<sub>12</sub> were prepared as previously described[28].

Single crystals of  $K_2(HF)TiF_6$  were prepared in an  $F_2$ -passivated T-shaped apparatus consisting of a 15.5 mm ID FEP tube and a 4 mm ID FEP tube, both equipped with Teflon valves. Anhydrous HF (5 mL) was condensed at 77 K in the wider FEP tube containing KF (0.82 mmol), TiF<sub>4</sub> (0.41 mmol), and a Teflon-coated stir bar. This mixture was warmed to 23(2) °C and, upon stirring, formed a clear, colorless solution, which was decanted into the 4 mm ID tube. Slow condensation of HF vapor in the 15.5 mm ID tube was accomplished by maintaining a ca. 10 °C temperature gradient between the two tubes, resulting in the formation of crystals of  $K_2(HF)TiF_6$  (and  $K_2TiF_6$ ). The crystals, immersed in perfluorodecalin (ABCR, 90%),



Fig. 13. The structure of  $Cs_2(HF)B_{12}F_{12}$ .



Fig. 14. The CsF<sub>12</sub> and CsF<sub>10</sub> coordination units of Cs1 and Cs2, respectively, in Cs<sub>2</sub>(HF)B<sub>12</sub>F<sub>12</sub> (50% probability ellipsoids except for the two H atoms, which are shown as spheres of arbitrary size).

were examined with a microscope in the glovebox and a suitable crystal was mounted on a glass fiber and attached to a goniometer in a stream of cold (-73 °C) N<sub>2</sub> gas. The crystals rapidly lost HF at room temperature in the glovebox. For this reason, it was not possible to obtain a "bulk" sample of pure K<sub>2</sub>(HF)TiF<sub>6</sub> for spectroscopic or compositional analysis. However, PXRD analysis of a bulk sample of crystals that had been crushed to a powder inside the glovebox showed that the dry powder was identical to a bonafide sample of K<sub>2</sub>TiF<sub>6</sub>.

Single-crystal diffraction data were collected using a Rigaku AFC7 diffractometer (graphite monochromatized MoK<sub> $\alpha$ </sub> radiation) equipped with a Mercury CCD area detector. The data were corrected for Lorentz, polarization, and absorption effects and were processed using Rigaku CrystalClear software [41]. The structure was solved by direct methods using the program SIR-92 [42] (teXan software from Molecular Structure Corporation [43]) and refined with SHELXL-97 software [44] implemented in the program package WinGX [45]. The coordinates and the isotropic thermal parameter ( $U_{iso}$ ) of the H atom were fixed before the final refinement ( $U_{iso}$ (H) was set at 1.2 times the equivalent isotropic thermal parameter of its F atom).

Suitable crystals of  $K_2(HF)_3B_{12}F_{12}$  and  $Cs_2(HF)B_{12}F_{12}$  were selected using a low-temperature stage of local design and mounted on the goniometer attached to a Bruker Smart CCD 1000 diffractometer (graphite monochromatized MoK $_{\alpha}$  radiation). The  $\Omega$  scan mode was used, and 1800 frames were measured at 20 s per frame. A semiempirical absorption correction (SADABS) was applied to the data, and the structure was solved and refined using SHELXTL software. [44] It was not possible to locate the H atoms in  $K_2(HF)_3B_{12}F_{12}$ . The F atom of the HF molecule in  $Cs_2(HF)B_{12}F_{12}$  was disordered between two unequally-populated positions (67% (F13) and 33% (F13a) 0.653 Å apart. The H atom was not disordered, and was refined using fixed H–F distances of 0.77 Å for both partial F atoms. The Cs2-F13, Cs2-F13a, Cs2'-F13, and Cs2'-F13a distances are 3.053(1), 2.981(1), 3.443(1), and 3.909(1)Å, respectively. Both partial F atoms are shown in Fig. 13. Only the major F13 atom was used in the Cs2 bond valence analysis and in preparing Fig. 14.

## Acknowledgments

This work was supported by ERC, Inc., the Slovenian Research Agency (ARRS grant P1-0045, Inorganic Chemistry and Technology), and the Colorado State University Foundation.

# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem. 2012.10.009.

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