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Syntheses, crystal structures and Raman spectra of $Ba(BF_4)(PF_6)$, $Ba(BF_4)(AsF_6)$ and $Ba_2(BF_4)_2(AsF_6)(H_3F_4)$; the first examples of metal salts containing simultaneously tetrahedral BF_4^- and octahedral AF_6^- anions

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ABSTRACT

In the system $BaF_2/BF_3/PF_5$/anhydrous hydrogen fluoride (aHF) a compound $Ba(BF_4)(PF_6)$ was isolated and characterized by Raman spectroscopy and X-ray diffraction on the single crystal. $Ba(BF_4)(PF_6)$ crystallizes in a hexagonal $P\overline{6}2m$ space group with $a = 10.2251(4)$ Å, $c = 6.1535(4)$ Å, $V = 557.17(5)$ Å^3 at 200 K, and $Z = 3$. Both crystallographically independent Ba atoms possess coordination polyhedra in the shape of tri-capped trigonal prisms, which include F atoms from BF_4^- and PF_6^- anions. In the analogous system with AsF_5 instead of PF_5 the compound $Ba(BF_4)(AsF_6)$ was isolated and characterized. It crystallizes in an orthorhombic *Pnma* space group with $a = 10.415(2)$ Å, $b = 6.325(3)$ Å, $c = 11.8297(17)$ Å, $V = 779.3(4)$ Å^3 at 200 K, and $Z = 4$. The coordination around Ba atom is in the shape of slightly distorted tri-capped trigonal prism which includes five F atoms from AsF_6^- and four F atoms from BF_4^- anions. When the system $BaF_2/BF_3/AsF_5$/aHF is made basic with an extra addition of BaF_2, the compound $Ba_2(BF_4)_2(AsF_6)(H_3F_4)$ was obtained. It crystallizes in a hexagonal $P6_3/mmc$ space group with $a = 6.8709(9)$ Å, $c = 17.327(8)$ Å, $V = 708.4(4)$ Å^3 at 200 K, and $Z = 2$. The barium environment in the shape of tetra-capped distorted trigonal prism involves 10 F atoms from four BF_4^-, three AsF_6^- and three $H_3F_4^-$ anions. All F atoms, except the central atom in H_3F_4 moiety, act as μ_2-bridges yielding a complex 3-D structural network.

1. Introduction

The crystallisation of the compounds of the type $M^n(AF_6)_n$ (M is a metal in an oxidation state n and A is P, As, Sb, Bi, Nb, Ta, etc.) from anhydrous HF (aHF) solutions frequently yields coordination compounds in which neutral HF molecule(s) are coordinated to the metal center. In the cases when F^- anions are also present in aHF solution they could react with HF molecules yielding different (poly)hydrogen-fuoride anions, such as HF_2^-, $H_2F_3^-$ and $H_3F_4^-$, e.g. $M_2(H_2F_3)(HF_2)_2(AF_6)$ ($M = Ca$, $A = As$; $M = Sr$, $A = As$, P) [1] and $Ba(H_3F_4)_2$ [2]. Recently we have reported on the synthesis and X-ray crystal structure investigations of mixed-anion compounds of the type $Ba_4F_4(HF_2)(PF_6)_3$ and $Pb_2F_2(HF_2)(PF_6)$ [3] where (poly)-hydrogen-fluoride anions and F^- anions are found besides octahedral anions. Nevertheless, there were no examples of compounds containing simultaneously tetrahedral and octahedral perfluorinated anions, i.e. perfluorinated analogues of the natural alumosilicates.

In this paper we are describing the isolation and characterization of the compounds $Ba(BF_4)(PF_6)$, $Ba(BF_4)(AsF_6)$ and $Ba_2(BF_4)_2(AsF_6)(H_3F_4)$ which contain BF_4^- and AF_6^- ($A = P$ and As, respectively) anions, while the third compound has an additional $H_3F_4^-$ anion. To our knowledge, these are the first examples of the metal salts containing simultaneously tetrahedral BF_4^- and octahedral AF_6^- anions.

2. Experimental

Caution: Anhydrous hydrogen fluoride, BF_3, AsF_5 and PF_5 must be handled in a well-ventilated hood and protective clothing must be worn at all times! The experimentalist must become familiar with these reagents and the hazards associated with them. Fresh tubes of calcium gluconate gel should always be on hand for the fast treatment of skin exposed to these reagents. For treatment of HF injuries see Ref. [4].

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2.1. General experimental procedures

A nickel vacuum line and Teflon vacuum system were used as previously described [5]. Volatile materials, such as anhydrous HF, PF_5, AsF_5, BF_3, were manipulated in an all-Teflon vacuum line equipped with Teflon valves. Non-volatile materials, sensitive to traces of moisture, were handled in a dry box with maximum content of 0.1 ppm of water vapor (Mbraun, Garching, Germany). A FEP reaction vessel equipped with a Teflon valve and a Teflon-covered mixing bar was used for the syntheses. A T-shaped FEP reaction vessel constructed from one large FEP tube (16 mm i.d.) and a smaller FEP tube (4 mm i.d.) joint at a right angle and equipped with Teflon valve was used for crystallization.

2.2. Reagents

BaF_2 (Alfa Aesar, 99.99%), BF_3 (Union Carbide, 99.5%) and fluorine (Solvay, 99.98%) were used as purchased. PF_5 was prepared by fluorination of P_2O_5 powder under high-pressure of fluorine as previously described [6]. AsF_5 was synthesized by fluorination of As_2O_3 by elemental fluorine in a closed system [7]. Its purity was checked by IR spectroscopy. Anhydrous HF (Fluka, purum) was treated by K_2NiF_6 (Ozark-Mahoning, 99%) for several days prior to use.

2.3. Synthesis

2.3.1. Synthesis of $Ba(BF_4)(PF_6)$

At first, the reaction was performed with equimolar mixture of BaF_2, BF_3 and PF_5 in aHF as a solvent. After crystallization only already known compounds $Ba(H_3F_4)_2$ [2] and $Ba(BF_4)_2$ [8] were found.

The successful synthetic procedure yielding $Ba(BF_4)(PF_6)$ was performed in the following way. At first $Ba(BF_4)_2$ was prepared. BaF_2 (0.261 g, 1.49 mmol) was weighed into the reaction vessel inside the dry box. The reaction vessel was cooled with liquid nitrogen, and aHF was added at −196 °C. Then the reaction vessel was warmed up to room temperature and weighed. The vessel was cooled again to −196 °C and an excess of BF_3 (1.84 g, 27.13 mmol) was added. The reaction vessel was kept at room temperature for 24 h and the reaction mixture was continuously stirred. Anhydrous HF and excess of BF_3 were pumped off at room temperature. The yield of the product $Ba(BF_4)_2$ was 0.473 g (1.52 mmol).

For the further reaction the crystallization vessel was modified so that both parts of the vessel (A and B) were separated by a Teflon valve. Inside the dry box the previously synthesized product, $Ba(BF_4)_2$ (0.132 g, 0.42 mmol) was weighed into the vessel A and BaF_2 (0.075 g, 0.43 mmol) into the vessel B. Then the vessels A and B were cooled with liquid nitrogen and aHF was added at −196 °C to both of them. The valve between A and B was closed. In the vessel B an excess of PF_5 (0.339 g, 2.69 mmol) was added. The reaction vessel B was warmed up to the room temperature and the solution of $Ba(PF_6)_2$ in aHF, still under the pressure of an excess of PF_5, was decanted into the vessel A and stirred for one day. The crystals of $Ba(BF_4)(PF_6)$ were isolated by pumping off aHF and an excess of PF_5 at room temperature. Inside the dry box, the crystals were put in perfluorinated oil (ABCR, FO5960). Than outside the dry box crystals, immersed in perfluorinated oil, were selected under a microscope, and quickly transferred into a cold nitrogen stream of the CryoSystem installed on the X-ray diffractometer.

2.3.2. Synthesis of $Ba(BF_4)(AsF_6)$

The compound $Ba(BF_4)(AsF_6)$ was prepared by the reaction between equimolar quantities of $Ba(BF_4)_2$ and $Ba(AsF_6)_2$. The latter compound was prepared as follows. BaF_2 (0.180 g, 1.03 mmol) was weighed into the reaction vessel inside the dry box. The reaction vessel was cooled with liquid nitrogen, and aHF was added at −196 °C. Then the reaction vessel was warmed up to room temperature and weighed. The vessel was cooled again to −196 °C, and an excess of AsF_5 (1.76 g, 10.36 mmol) was added. The vessel was kept at room temperature for at least 24 h, and the reaction mixture was stirred continuously. Anhydrous HF and excess of AsF_5 were pumped off at room temperature. The weight of the product $Ba(AsF_6)_2$ was 0.543 g (1.05 mmol). $Ba(BF_4)_2$ (0.033 g, 0.106 mmol) and $Ba(AsF_6)_2$ (0.052 g, 0.100 mmol) were weighed into the wider part of the crystallization vessel inside the dry box. The wider part of the crystallization vessel was cooled with liquid nitrogen, and aHF was added at −196 °C. Then the crystallization vessel was warmed up to room temperature. The solution was decanted into the narrower part of the reaction vessel, which was left at room temperature while the wider part was slightly cooled to generate a small temperature gradient. The obtained crystals were isolated by pumping off aHF at room temperature. Further procedure was performed as described in Section 2.3.1.

2.3.3. Synthesis of $Ba_2(BF_4)_2(AsF_6)(H_3F_4)$

$Ba(BF_4)_2$ (0.124 g, 0.40 mmol), $Ba(AsF_6)_2$ (0.104 g, 0.20 mmol) and BaF_2 (0.037 g, 0.21 mmol) were weighed into the wider part of the crystallization vessel inside the dry box and aHF was added at −196 °C. Then the crystallization vessel was warmed up to room temperature and the obtained solution was decanted into the narrower part of the reaction vessel, which was left at room temperature while the wider part was slightly cooled to generate a small temperature gradient. Further procedure with the crystals was the same as described in Section 2.3.1.

2.4. Crystal structure determination

For all three compounds the data were collected on Rigaku AFC7R diffractometer equipped with Mercury CCD area detector using graphite monochromated Mo*K*α radiation at 200 K. The $Ba(BF_4)(AsF_6)$ compound has been first measured on Nonius Kappa CCD diffractometer at 150 K. For more accurate comparison of interatomic distances with previously measured at 200 K another two described in this article compounds another crystal of $Ba(BF_4)(AsF_6)$ has been later measured on Rigaku AFC7R machine at 200 K. The data were corrected for Lorentz and polarization effects. A multi-scan absorption correction was applied to all data sets. All structures were solved by direct methods using SIR-92 [9] program implemented in program package TeXsan [10] and refined with SHELXL-97 [11] software (program packages TeXsan and WinGX [12]). The figures were prepared using DIAMOND 3.1 software [13]. The crystal data and the details of the structure refinement for all three compounds are given in Table 1, selected distances and bond lengths in Tables 2–4, respectively.

2.5. Raman spectroscopy

Raman spectra of the powdered samples in sealed quartz capillaries and crystals covered by perfluorinated oil were taken on a Renishaw Raman imaging microscope system 1000 with the exciting line at 632.8 nm of a He–Ne laser. Geometry for all the Raman experiments was 180° back scattering with laser power 25 mW.

3. Results

3.1. Description of the crystal structure of Ba(BF$_4$)(PF$_6$)

The structure of Ba(BF$_4$)(PF$_6$) contains two crystallographically independent barium atoms. The coordination sphere of the atom Ba1 (Fig. 1) consists of nine F atoms, belonging to six BF$_4^-$ and three PF$_6^-$ anions. Six F atoms from six BF$_4$ moieties are located on the corners of a trigonal prism. Three F atoms from three PF$_6^-$ anions complete metal surrounding in the shape of tri-capped trigonal prism. Ba1–F$_B$ distances of 2.636(6) Å are shorter than Ba–F$_P$ distances of 2.900(9) Å. The coordination polyhedron of Ba2 is also tri-capped trigonal prism with six F atoms from six PF$_6^-$ anions located on the corners of a trigonal prism while the three F atoms which are capping the trigonal prism are belonging to three BF$_4$ units. Distances Ba2–F$_B$ are 2.588(8) Å, and Ba2–F$_P$ bond lengths are 2.748(5) Å. PF$_6^-$ anions have five bridging F atoms which are bonded to five metal centers while one F atom is terminal. P–F distance for the terminal F atom (1.51(1) Å) is much shorter as for the bridging F atoms (1.591(5)–1.605(9) Å). All F atoms in BF$_4$ units act as μ_2-bridges which results in a very similar B–F distances of 1.348(11)–1.350(9) Å. The shape of fluorine atoms thermal ellipsoids indicates weak rotational disordering of PF$_6$ moiety with an axe of rotation Ba1–F12–P1–F11 (Fig. 1). Interesting, that the F12 atom appears to be markedly removed from the metal atom (Ba1–F12 distance of 2.900(9) Å is noticeably longer than Ba1–F13 ones 2.748(5) Å). The P1–F12–Ba1 angle is 180°, whereas P1–F13–Ba1 ones are equal to 166°. Basing on rather large U values for F21 and F22 atoms one may assume also frequently observed disordering of BF4$^-$ unit.

The chemical formula of Ba1 surrounding is $Ba(BF_4)_{6/4}(PF_6)_{3/5}$. The environment of Ba2 can be described as $Ba(BF_4)_{3/4}(PF_6)_{6/5}$. Because the molar ratio between Ba1 and Ba2 in the unit cell is 1:2 the overall formula appears to be $Ba_3(BF_4)_{12/4}(PF_6)_{15/5}$, i.e. simply Ba(BF$_4$)(PF$_6$). Owing to the bridging function of the cations and both anions a complex 3-D network appears in the structure (Fig. 2).

Table 1
Crystal data and structure refinement for Ba(BF$_4$)(PF$_6$), Ba(AsF$_6$)(BF$_4$) and Ba$_2$(AsF$_6$)(BF$_4$)$_2$(H$_3$F$_4$) compounds.

Empirical formula	Ba B F$_{10}$ P	As B2 Ba2 F18 H3	As B Ba F$_{10}$
Fw	369.11	716.22	413.07
T (K)	200	200	*200* *150*
Space group	$P\overline{6}2m$ (no.189)	$P63/mmc$ (no.194)	$Pnma$ (no. 62)
a (Å)	10.2251(4)	6.8709(9)	10.415(2) *10.3638*(3)
b (Å)			6.325(3) *6.3305*(2)
c (Å)	6.1535(4)	17.327(8)	11.8297(17) *11.7736*(3)
Volume (Å^3)	557.17(5)	708.4(4)	779.3(4) *772.44*(4)
Z value	3	2	4
$D_{\mathrm{calculated}}$ (g cm^{-3})	3.3	3.358	3.521 *3.552*
λ (Å)	0.71069	0.71069	0.71069
μ (mm^{-1})	5.698	8.036	9.44 *9.524*
$R1$[a]; w$R2$	0.0334; 0.0718	0.0435; 0.0969	0.061; 0.147 *0.0356*; 0.0967
GOF	1.167	1.155	1.15 *1.391*

[a] $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, w$R2=[w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$, GOF $=[\Sigma w(F_o^2-F_c^2)^2)/N_o-N_p)]^{1/2}$, where N_o = no. of reflns and N_p = no. of refined parameters.

3.2. Description of crystal structure of Ba(BF$_4$)(AsF$_6$)

The coordination sphere of Ba atom (Fig. 3) consists of nine F atoms, belonging to four BF$_4^-$ and five AsF$_6^-$ anions. Four F atoms from four AsF$_6^-$ moieties and two F atoms from two BF$_4^-$ moieties

Table 3
Interatomic distances (Å) in Ba(BF$_4$)(AsF$_6$) at 200 K (regular font) and 150 K (italic).

Ba1—F1^{i}, Ba1—F1^{ii}	*2.603(7)* *2.593*(5)	As2—F8	1.678(9) *1.685*(7)
Ba1—F4^{iii}	*2.618(9)* *2.591*(8)	As2—F7, As2—F7^{viii}	1.713(6) *1.713*(5)
Ba1—F3	*2.624(8)* *2.605*(8)	As2—F9, As2—F9^{viii}	*1.716(7)* *1.718*(5)
Ba1—F5^{iv}	*2.749(8)* *2.745*(7)	As2—F5	*1.725(8)* *1.717*(7)
Ba1—F9, Ba1—F9^{v}	*2.773(6)* *2.765*(5)	B12—F1, B12—F1^{v}	*1.366(12)* *1.367*(8)
Ba1—F7^{vi}, Ba1—F7^{vii}	2.810(6) *2.799*(5)	B12—F3	*1.352(17)* *1.335*(13)
		B12—F4	*1.35(2)* *1.383*(14)

Symmetry codes: (i) $-x+3, y+1/2, -z+1$; (ii) $-x+3, -y-1, -z+1$; (iii) $x-1/2, -y-1/2, -z+1/2$; (iv) $-x+2, -y, -z+1$; (v) $x, -y-1/2, z$; (vi) $x+1/2, y-1, -z+1/2$; (vii) $x+1/2, -y+1/2, -z+1/2$; (viii) $x, -y+1/2, z$; (ix) $x+1/2, -y-1/2, -z+1/2$; (x) $x-1/2, -y+1/2, -z+1/2$.

Table 4
Interatomic distances (Å) in Ba$_2$(BF$_4$)$_2$(AsF$_6$)(H$_3$F$_4$).

Ba1—F22	2.640(11)
Ba1—F21^{i}, Ba1—F21^{ii}, Ba1—F21	2.682(6)
Ba1—F1, Ba1—F1^{i}, Ba1—F1^{ii}	2.738(4)
Ba1—F11^{iii}, Ba1—F11^{iv}, Ba1—F11^{v}	2.825(6)
As1—F11, As1—F11^{vi}, As1—F11^{iii}	1.700(6)
As1—F11^{vii}, As1—F11^{x}, As1—F11i^{x}	
B2—F21^{x}, B2—F21^{xi}, B2—F21^{xii}	1.355(8)
B2—F22	1.44(2)

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

Table 2
Interatomic distances (Å) in Ba(BF$_4$)(PF$_6$).

Ba1—F21^{i}, Ba1—F21^{ii}, Ba1—F21^{iii}, Ba1—F21^{iv}, Ba1—F21, Ba1—F21^{v}			2.636(6)
Ba2—F13^{x}, Ba2—F13^{ix}, Ba2—F13, Ba2—F13^{xi}, Ba2—F13^{xii}, Ba2—F13^{vi}			2.748(5)
Ba1—F12^{vi}, Ba1—F12^{vii}, Ba1—F12^{viii}			2.900(9)
Ba2—F22, Ba2—F22^{vi}, Ba2—F22^{ix}			2.588(8)
P1—F13, P1—F13^{iii}, P1—F13^{xiii}, P1—F13^{xiv}			1.591(5)
P1—F11	1.511(10)	P1—F12	1.605(9)
B2—F21, B2—F21^{x}	1.350(9)	B2—F22^{vi}, B2—F22^{xvi}	1.348(11)

Symmetry codes: (i) $-x+y, -x, z$; (ii) $-y, x-y, -z+1$; (iii) $x, y, -z+1$; (iv) $-x+y, -x, -z+1$; (v) $-y, x-y, z$; (vi) $-x+y+1, -x+1, z$; (vii) $-y, x-y-1, z$; (viii) $x-1, y, z$; (ix) $-y+1, x-y, z$; (x) $x, y, -z$; (xi) $-y+1, x-y, -z$; (xii) $-x+y+1, -x+1, -z$; (xiii) $x-y, -y, z$; (xiv) $x-y, -y, -z+1$; (xv) $x+1, y, z$; (xvi) $y, x-1, z$.

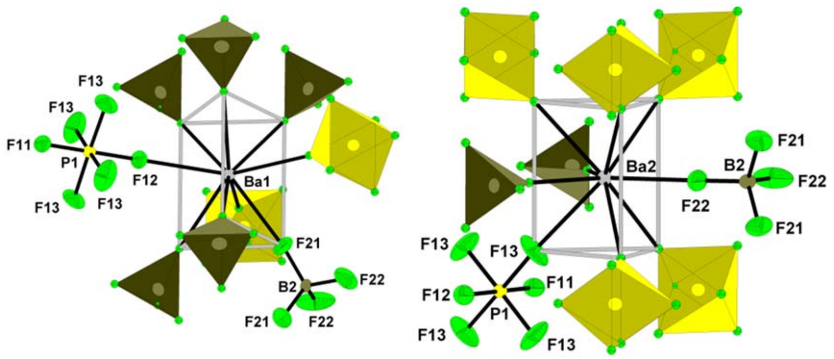

Fig. 1. Coordination environment of crystallographically independent Ba1 and Ba2 atoms in the structure of Ba(BF_4)(PF_6). The thermal ellipsoids are drawn at 40% probability.

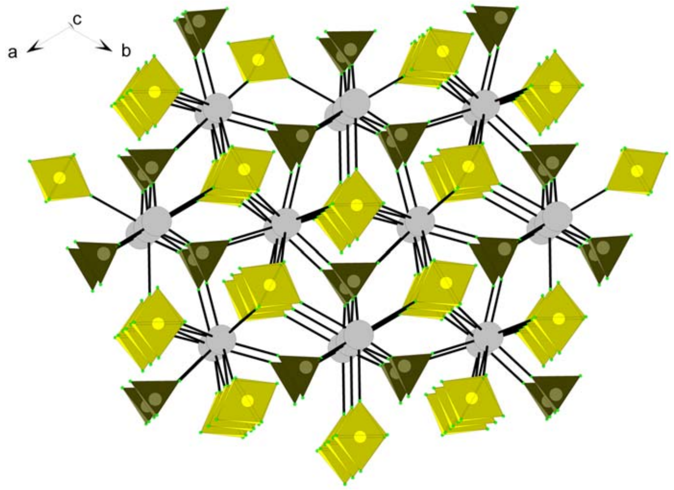

Fig. 2. Packing diagram of Ba(BF_4)(PF_6).

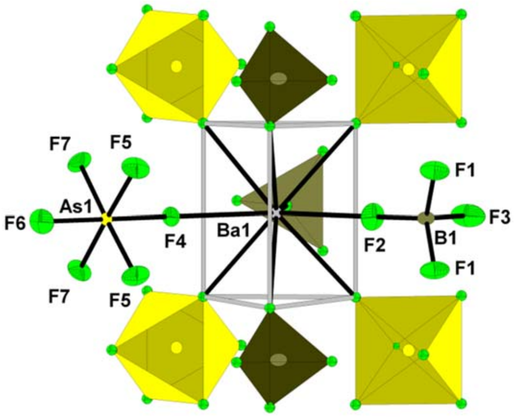

Fig. 3. Coordination environment of Ba atom in the structure of Ba(BF_4)(AsF_6). The thermal ellipsoids are drawn at 40% probability.

are located on the corners of a slightly distorted trigonal prism. Two F atoms from two BF_4^- anions and one F atom from AsF_6^- anion complete metal surrounding in the shape of tri-capped trigonal prism. Ba–F_B distances from 2.603(7)–2.624(8) Å are shorter than Ba–F_P (2.749(8)–2.810(6) Å) distances (these values relate to the data collected at 200 K for correct comparison with the other two structures).

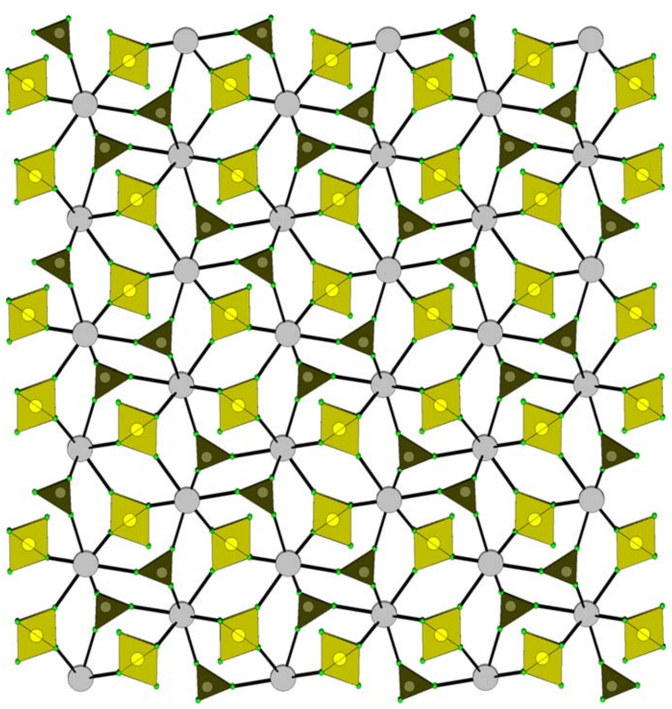

Fig. 4. Packing diagram in the structure of Ba(BF_4)(AsF_6).

AsF_6^- anions, similarly to PF_6^- in Ba(BF_4)(PF_6), have five bridging F atoms which are bonded to five metal centers while one F atom is terminal. As–F distance for the terminal F atom 1.678(9) Å is shorter as the distances for the bridging F atoms (1.713(6)–1.725(8) Å). All F atoms in BF_4^- anions are bridging with a very similar B–F distances of 1.35(2)–1.37(1) Å thus forming a complex 3-D network (Fig. 4). The AF_6^- anion, similarly as in Ba(BF_4)(PF_6), demonstrate weak rotational disordering. Also enlarged (especially in the case of F3 atom) the displacement ellipsoids may indicate small disordering of BF_4 moiety.

3.3. *Description of crystal structure of* $Ba_2(BF_4)_2(AsF_6)(H_3F_4)$

The metal atom, located at 4*f* Wyckoff position with local 3*m* symmetry, is surrounded by 10 F atoms. Three pairs of F atoms, belonging to two BF_4^-, two AsF_6^- and two $H_3F_4{}^-$ anions respectively, form distorted trigonal prism. Two rectangular planes are capped by F atoms belonging to H_3F_4 and BF_4 moieties while the third rectangular plane is bi-capped by F(BF_4) and F(AsF_6) species (Fig. 5). The Ba–F bond lengths clearly depend on the anion's

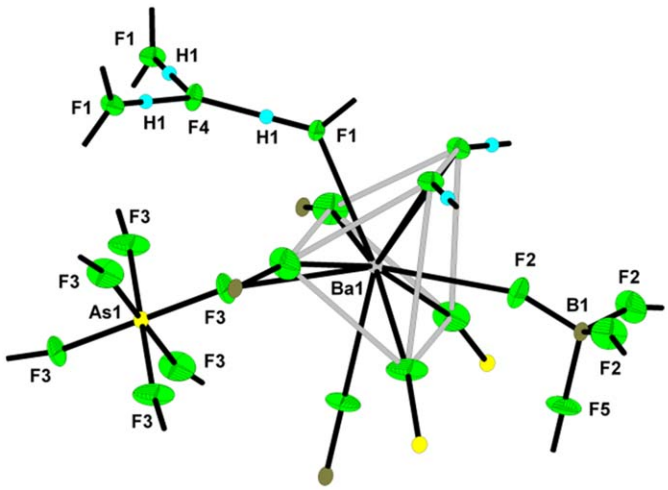

Fig. 5. Coordination environment of Ba atom in the structure of $Ba_2(AsF_6)(BF_4)_2(H_3F_4)$. The thermal ellipsoids are drawn at 40% probability. Some fluorine atoms are omitted for clarity.

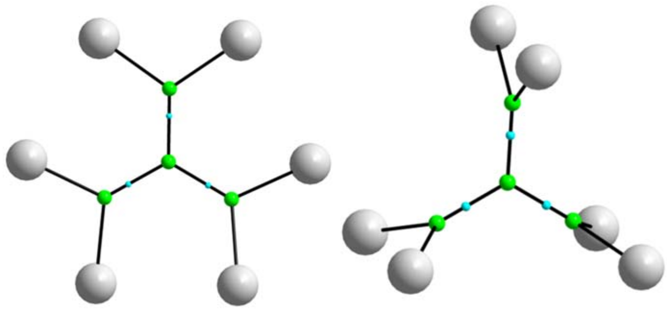

Fig. 6. Coordination behavior of $H_3F_4^-$ anion in $Ba(H_3F_4)_2$ (left) and in the structure of $Ba_2(AsF_6)(BF_4)_2(H_3F_4)$ (right).

nature: the distances Ba–F(BF_4) of 2.640(11)–2.682(6) Å appear to be the shortest, medium values were found for Ba–F(H_3F_4) contacts of 2.738(4) Å, and Ba–F(AsF_6) bonds are the longest (2.825(6) Å). Such differences are in an agreement with the effective negative charge on the F atoms in these species. All F atoms in BF_4^- and AsF_6^- anions act as μ_2-bridges—i.e. each BF_4 unit is bound to four and each AsF_6 moiety—to six metal atoms. The (poly)-hydrogen-fluoride anion $H_3F_4^-$ demonstrates a more complex bridging role. Each terminal F atom connects a pair of Ba atoms, similarly as observed in $Ba(H_3F_4)_2$ compound [2]. In the structure of $Ba(H_3F_4)_2$ the Ba atoms connected to one H_3F_4 anion lie in a common plane and form nearly regular hexagon while in this structure six Ba atoms form trigonal prism (Fig. 6). The double layer, containing Ba atoms, BF_4^- and AsF_6^- anions, is shown in Fig. 7. In this double layer each BF_4^- anion is connected to the three Ba atoms in "the lower part" and to the forth one in "the upper part" of the same double layer, whereas AsF_6^- moiety is linked to the three metal centers in "the upper part" and to the three Ba atoms in "the lower part" of the same double layer. $H_3F_4^-$ anions, located between mentioned double layers, are bonded to the three barium atoms in "the upper double layer" and to the three Ba atoms in "the lower double layer" what results in a complicated 3-D network (Fig. 8). Similarly to that in $Ba(H_3F_4)_2$, each pair of Ba atoms from the closest double layers is bound via three F bridges belonging to three $H_3F_4^-$ anions.

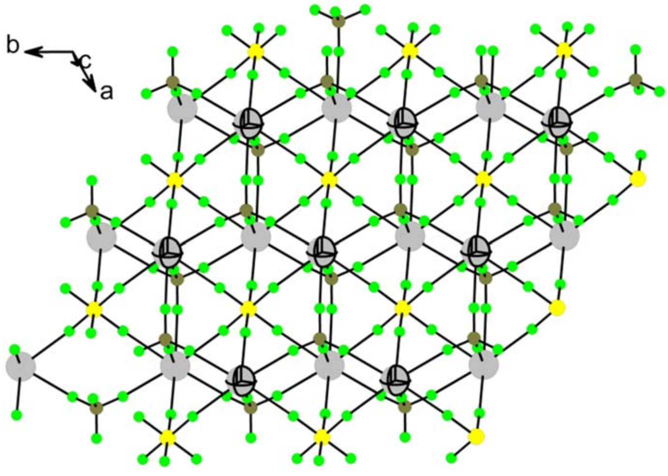

Fig. 7. $\{[Ba_2(AsF_6)(BF_4)_2]_n\}^{n+}$ double layer in $Ba_2(AsF_6)(BF_4)_2(H_3F_4)$. Ba atoms in the upper layer are shown as "octants" and Ba atoms in the lower layer are represented as "solid".

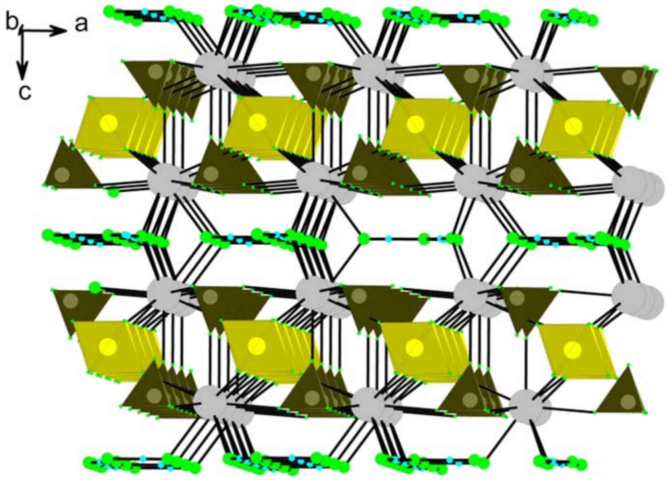

Fig. 8. Connection of two double layers with $H_3F_4^-$ anions in $Ba_2(AsF_6)(BF_4)_2(H_3F_4)$.

In $Ba_2(BF_4)_2(AsF_6)$ (H_3F_4) the shape of thermal ellipsoids of F atoms in H_3F_4 anions agrees well with their trigonal surrounding. In the case of terminal F1 the longest axe is oriented perpendicularly to the plane formed by two Ba and one H atoms. The thermal ellipsoid of central F4 atom is elongated in direction perpendicularly to the plane of whole H_3F_4 unit. Flattening of fluorine thermal ellipsoids roughly corresponds to the bridging role of F atoms in AsF_6 anion, i.e. the principal axe of ellipsoid oriented along As–F–Ba directions appears to be the shortest. Similar flattening is also observed for F atoms of BF_4^- anion.

3.4. Raman spectra

The Raman spectra of the investigated compounds, recorded on the powdered samples in quartz capillaries, were not very illustrative. The Raman spectrum of the compound $Ba(BF_4)(PF_6)$ is showing only two peaks at 743 and 770 cm^{-1}. To record the Raman spectra of the compounds $Ba(BF_4)(AsF_6)$ and $Ba_2(BF_4)_2(AsF_6)(H_3F_4)$ a new technique was used. The spectra were obtained directly on the corresponding crystal, which was protected against the moisture in the air by covering it

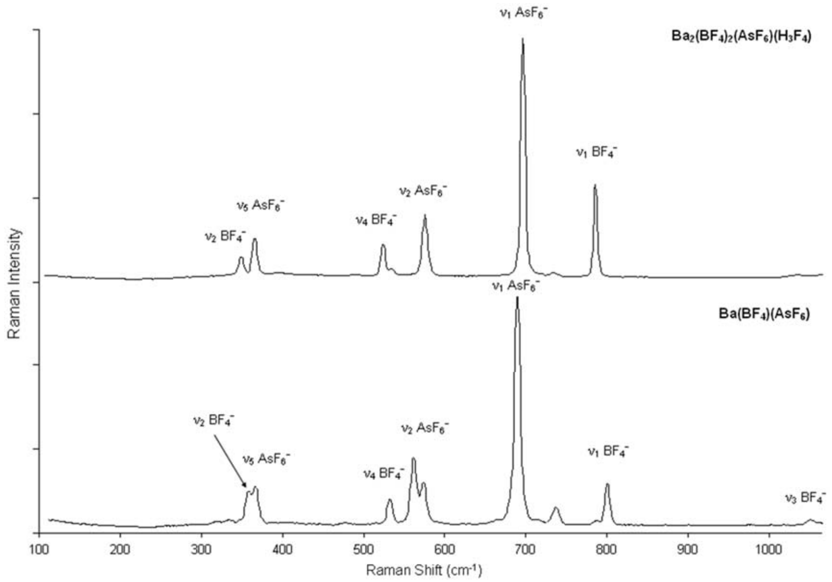

Fig. 9. Raman spectrum of $Ba(BF_4)(AsF_6)$.

Table 5
Raman frequencies, intensities and tentative assignments for $Ba(BF_4)(AsF_6)$ and $Ba_2(BF_4)_2(AsF_6)(H_3F_4)$.

$Ba(BF_4)(AsF_6)$		$Ba_2(BF_4)_2(AsF_6)(H_3F_4)$	
Raman frequencies	Assignments	Raman frequencies	Assignments
1050(6)	ν_3 BF_4^-		
800(21)	ν_1 BF_4^-	786(40)	ν_1 BF_4^-
737(11)		733(4)	
689(100)	ν_1 AsF_6^-	696(100)	ν_1 AsF_6^-
574(22)	ν_2 AsF_6^-	576(28)	ν_2 AsF_6^-
562(32)			
532(15)	ν_4 BF_4^-	534(5)	ν_4 BF_4^-
		523(15)	
365(20)	ν_5 AsF_6^-	366(18)	ν_5 AsF_6^-
359(18)	ν_2 BF_4^-	349(10)	ν_2 BF_4^-

with perfluorinated oil. The Raman spectra of the compounds $Ba(BF_4)(AsF_6)$ and $Ba_2(BF_4)_2(AsF_6)(H_3F_4)$ recorded in this way are shown in Fig. 9. The frequencies, intensities and tentative assignments are presented in Table 5.

4. Discussion

4.1. Syntheses

The fluoride ion affinities of the Lewis acids AsF_5, PF_5 and BF_3 are 105.9, 94.9 and 83.1 kcal mol^{-1}, respectively [14]. Although PF_5 has higher fluoride ion affinity as BF_3 and in principle it should replace BF_3 in the fluoroborates, the reaction between equimolar mixtures of BaF_2, BF_3 and PF_5 in a solvent aHF did not proceed in the desired direction. BF_3 and PF_5 interacted with BaF_2 yielding stable $Ba(BF_4)_2$ and unstable $Ba(PF_6)_2$. The formation and the stability of the latter compound require an overpressure of PF_5. Besides, BaF_2 dissolved in aHF yielded F^- anions which further reacted with solvated $[Ba^{2+}(HF)_x]$ cations yielding the compound $Ba(H_3F_4)_2$. Therefore the products obtained in this system were only $Ba(BF_4)_2$ and $Ba(H_3F_4)_2$.

The best synthetic route for the preparation of the compound $Ba(BF_4)(PF_6)$ is to pour together the solutions of $Ba(BF_4)_2$ and $Ba(PF_6)_2$ in aHF in the mole ratio 1:1. The compound $Ba(PF_6)_2$ should be all the time maintained under pressure of PF_5 in order to prevent its decomposition to BaF_2 and PF_5. The formation of $Ba(BF_4)(PF_6)$ is favored by its low solubility in aHF.

The synthesis of the analogous compound $Ba(BF_4)(AsF_6)$ is simple because both starting compounds are stable in aHF at room temperature. $Ba(BF_4)_2$ and $Ba(AsF_6)_2$ were dissolved in aHF and left to react in the mole ratio 1:1.

The compound $Ba_2(BF_4)_2(AsF_6)(H_3F_4)$ is the best prepared from the mixture of the compounds $Ba(BF_4)_2$, $Ba(AsF_6)_2$ and BaF_2 in the mole ratio 2:1:1 in aHF. BaF_2 is providing F^- anions which are making the solution basic and forming $H_3F_4^-$ anions. Stable anions BF_4^-, AsF_6^- and $H_3F_4^-$ present in the right mole ratio in the solution combine with Ba^{2+} cations yielding the final product $Ba_2(BF_4)_2(AsF_6)(H_3F_4)$. Its low solubility is again essential for the synthesis of this compound.

4.2. Crystal structures

In all studied structures the bond distances Ba–F(BF_4) are much shorter than the bond distances Ba–F(PF_6) or Ba–F(AsF_6). There are at least two main reasons for this. First, the volume of the tetrahedral BF_4^- anion is much smaller than the volumes of the octahedral AF_6^- anions ($PF_6^-:BF_4^- = 1.49$; $AF_6^-:BF_4^- = 1.51$) [15]. Second, it appears that on the average the charge on the F ligand in the BF_4^- anion is larger than the average charge on the AF_6^- anion ligands ($A = $ P, As). Of course, the lower ligand number in the BF_4^- anion is a major contributor to this.

There are two crystallographically different Ba atoms in the structure of the compound $Ba(BF_4)(PF_6)$. The bond distances Ba–F_B are not significantly different in both cases, being on the average a little shorter in the case of Ba2 because of only three BF_4 ligands in comparison with Ba1 with six BF_4 ligands. The main difference is in the case of PF_6^- ligands. The bond distance Ba1–F_P is significantly longer (3×2.901 Å) as the bond distance Ba2–F_P (6×2.748 Å) because the positive charge on Ba2 cation is higher as on the Ba1 cation as a consequence of lower number of BF_4 ligands on Ba2. Ba1–F_B distances of 2.636(6) Å and Ba2–F_B distances of 2.588(8) Å are shorter than in the $Ba(BF_4)_2$ compound (2.690–2.886 Å) [8], what is probably the consequence of higher coordination number of Ba (CN 14) in the latter case. The distance Ba–F in $Ba(BF_4)(PF_6)$ is even shorter than in BaF_2 (2.683 Å) [16] despite the lower coordination number of barium (CN 8) and the smaller volume of F^- anion in comparison with BF_4^- or PF_6^-. The compound $Ba(BF_4)(PF_6)$ represents the first example of the metal salt containing BF_4^- and PF_6^- anions simultaneously.

The analogous compound $Ba(BF_4)(AsF_6)$ has different crystal structure. Ba atom is crystalographically unique with the coordination number nine in the shape of tri-capped trigonal prism. Five F atoms are from five AsF_6^- anions and four F atoms are from four BF_4^- anions. The number of BF_4^- units is smaller as in the case of Ba1 and greater as in the case of Ba2 atoms in the compound $Ba(BF_4)(PF_6)$. The distance Ba–F_B is on the average insignificantly shorter as in the case of the atom Ba1 while it is on the average a little longer as in the case of the atom Ba2. The same is valid for the distances Ba–F_{As} which are shorter as in the case of the atom Ba1 and on the average a little longer as in the case of the atom Ba2. However, the fluoroarsenate anion is a significantly weaker F^- donor than the fluorophosphate anion [17], the gaseous ionization energies for the process $AF_6^- \rightarrow AF_5 + F^-$ being 4.08 ($A = P$) and 4.42 eV ($A = As$). This must be a consequence of greater effective nuclear charge at the As center than at the P atom. It is therefore to be expected that the F ligands of the AsF_6^- will bear less charge than those in the PF_6^- anion. The structural details of both compounds confirm that in the case of the compound $Ba(BF_4)(PF_6)$ the anion PF_6^- is able to compete with BF_4^- for the coordination of Ba atom while in the case of the compound $Ba(BF_4)(AsF_6)$ the anion AsF_6^- is less able to do so.

The $Ba_2(BF_4)_2(AsF_6)(H_3F_4)$ appears to be even more complex compound being composed from three different anions. The formation of $H_3F_4^-$ moieties could be explained by the reaction of F^- anions with the solvent molecules. It is interesting, that the local trigonal/hexagonal symmetry of BF_4, AF_6 and H_3F_4 moieties and a possibility of such symmetry for Ba surrounding results in the formation of the crystal structures in the hexagonal system.

4.3. Raman spectra

The Raman spectrum of the compound $Ba(BF_4)(PF_6)$, recorded on the powdered sample in the quartz capillary, was not very informative. Only two bands, at 743 and 770 cm^{-1}, were observed. The band ν_1 of O_h symmetry of the PF_6^- anion occurs at 756 cm^{-1} [18] therefore the band at 743 cm^{-1} could be related to the symmetric stretching mode of the PF_6^- anion. It can be seen from the crystal structure that PF_6^- anion is deformed and it has no longer O_h symmetry and therefore more bands are expected. In the case of T_d symmetry of BF_4^- anion ν_3 is found at 1070 cm^{-1}, ν_1 at 777 cm^{-1}, ν_4 at 533 cm^{-1} and ν_2 at 360 cm^{-1} [19]. Therefore the band at 770 cm^{-1} could be related to ν_1 of BF_4^-. All four F ligands in the anion BF_4^- are further connected to the Ba centers with practically the same length of the B–F bonds. In this way the anion BF_4^- is anchored between four Ba centers and therefore it could not freely vibrate. Again, more bands would be expected.

The Raman spectrum of the compound $Ba(BF_4)(AsF_6)$ was recorded on the crystal. All four Raman bands expected for the tetrahedral BF_4^- anion were observed. The same situation was in the case of the AsF_6^- anion where all Raman bands expected for O_h symmetry of the AsF_6^- anion (ν_1, ν_2 and ν_5) were observed [20] (see Table 5 and Fig. 9). Both anions are anchored between Ba atoms, each AsF_6^- anion between five Ba atoms and each BF_4^- anion between four Ba atoms. Therefore they do not possess O_h symmetry and are deformed.

The Raman spectrum of the compound $Ba_2(BF_4)_2(AsF_6)(H_3F_4)$ is showing the bands which could be expected for the anions BF_4^- and AsF_6^- (see Table 5 and Fig. 9). The vibrations of the $H_3F_4^-$ anion were not detected.

5. Supplementary material

Further details of the crystal structure investigation(s) can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: +49 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD-420597 for $Ba(BF_4)(PF_6)$, CSD-420598 for $Ba_2(BF_4)_2(AsF_6)(H_3F_4)$, CSD-420599 for $Ba(BF_4)(AsF_6)$ at 150 K, CSD-420600 for $Ba(BF_4)(AsF_6)$ at 200 K.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at 10.1016/j.jssc.2009.08.004.

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