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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$K\alpha$ 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.