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Letter

Tetrafluoroborate-Monofluorophosphate $(NH_4)_3[PO_3F][BF_4]$: First Member of Oxyfluoride with B−F and P−F Bonds

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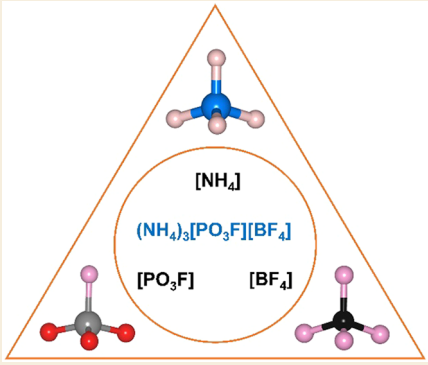
ABSTRACT: Inspired by the strategy of fluorine introduction in borates and phosphates, the inorganic oxyfluoride $(NH_4)_3[PO_3F][BF_4]$ with B−F and P−F bonds has been characterized as the first fluoroborate-fluorophosphate. The International Union of Pure and Applied Chemistry (IUPAC) name for $(NH_4)_3[PO_3F][BF_4]$ should be ammonium tetrafluoroborate-monofluorophosphate according to the structure characteristics. The existence and coordination of fluorine in $(NH_4)_3[PO_3F][BF_4]$ were confirmed by several approaches, including single-crystal structure analysis; bond valence analysis; and X-ray energy dispersive, infrared spectrum, and also nuclear magnetic resonance spectroscopy. This work is of great significance to enrich the solid-state chemistry of borates and phosphates and also open a new branch of mixed anion compound with fluoroborate-fluorophosphates.



KEYWORDS: *Oxyfluoride, fluoroborate-fluorophosphate, mixed anions, borates, phosphates*

Within the past decade, there has been an increasing interest in solids with mixed anions that can improve the finding of new novel structures and materials.[1−4] The multiple or mixed anion compound is a phase that contains more than one type of anion, which shows better performance and rich structural chemistry when compared with its homoanionic compounds.[1]

Oxyfluoride (or oxide-fluoride) is an important branch of mixed anion compounds, and therefore, considerable efforts have been made to find new oxyfluorides and also to understand the crucial roles of multiple anions on property modification.[1,2,5] In recent years, oxyfluorides with different types of fluorinated $[MO_{m-n}F_n]$ (M = B, P, S, Si; m = 4, 6; n = 1−3, etc.) units have been designed using the strategy of fluorine introduction in oxides, which has expanded the solid-state chemistry with newly developed branches and systems like fluorooxoborates,[6−16] fluorophosphates,[17,18] fluorooxosilicates,[19,20] and fluorooxosulfates.[21,22] The fluorinated units in these oxyfluorides have an indispensable role for the improved symmetry, enlarged energy gap, and enhanced polarizability anisotropy, which can be regarded as new optical-active units for regulating the microstructures and optical properties. Fluorooxoborates tend to form layered configurations, which can be verified by the increased proportion of fluorooxoborates in two-dimensional layered structures (53.33%) when compared with borates (10.26%) without fluorinated $[BO_{4-n}F_n]$ (n = 1−3) units.[3] Also, unlike $[PO_4]$ units in phosphates that can produce a high degree of polymerization,[23−25] fluorinated $[PO_3F]$ and $[PO_2F_2]$ units are generally in isolated form (a few $[PO_3F]$ units can form $[P_2O_5F_2]$ dimers),[17,18] reducing the dimension of fluorophosphates to zero dimensional structure.

The combination of different anion groups is also a common design strategy for synthesizing new mixed anion compounds. With respect to the combination of borates and phosphates, there are two types of compounds with B−O and P−O bonds according to the classification proposed by Kniep et al:[26] (i) borophosphates and (ii) borate-phosphates, in which the B−O units link with P−O units for the former branch, whereas the two different anion groups are in isolated configuration in the latter. The number of borate-phosphates is extremely limited when compared with borophosphates.[26] In principle, the introduction of fluorine in above two systems can form more oxyfluorides, like fluoroborophosphates, borofluorophosphates, fluorooxoborate-fluorophosphates, and fluoroborate-fluorophosphates. But there are only a few cases for fluoroborophosphates and borofluorophosphates,[27−29] and no related inorganic compounds are reported in fluorooxoborate-fluorophosphates and fluoroborate-fluorophosphates (with both B−F and P−F bonds). Herein, by combining fluoroborates and fluorophosphates, $(NH_4)_3[PO_3F][BF_4]$, the first inorganic oxyfluoride with both B−F and P−F bonds has

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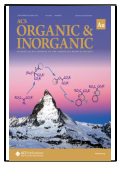

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been synthesized, which is the first case in fluoroborate-fluorophosphate system.

Single crystals of $(NH_4)_3[PO_3F][BF_4]$ were grown via liquid phase neutralization at room temperature. A mixture of Na_2PO_3F, $(NH_4)HF_2$ and H_3BO_3 with the molar ratio of 1:3:1 was dissolved in 50 mL deionized water and stirred to make it completely clear. Then, colorless $(NH_4)_3[PO_3F][BF_4]$ crystals were obtained at the bottom of beaker after several days with the yield of about 70%. Single-crystal X-ray diffraction analysis and Rietveld refinement were used to determine the crystal structure and confirm the purity of as-prepared polycrystalline samples. The fitted profile matches well with the experimental powder X-ray diffraction patterns, having the acceptable R values of R_P = 0.0606 and R_{wP} = 0.0848 (Figures S1 and S2 in the Supporting Information (SI)). According to the structure characteristics of $(NH_4)_3[PO_3F][BF_4]$ ($[PO_3F]$ and $[BF_4]$ are in isolated configuration), the International Union of Pure and Applied Chemistry (IUPAC) name[30] for $(NH_4)_3[PO_3F][BF_4]$ should be ammonium tetrafluoroborate-monofluorophosphate. $(NH_4)_3[PO_3F][BF_4]$ crystallizes in the monoclinic crystal system with the space group $P2_1/m$ (see Table S1 in the SI for details). As shown in Figure 1, the structure of $(NH_4)_3[PO_3F][BF_4]$ is composed of three isolated units, that is, $[NH_4]$, $[PO_3F]$, and $[BF_4]$ units. In an asymmetric unit, there are three crystallographically independent $[NH_4]$ ammonium cations, one $[PO_3F]$ monofluorophosphate anion, and one $[BF_4]$ perfluorinated anion (Tables S1−S7 in the SI). It should be noted that all the $[PO_3F]$ and $[BF_4]$ units are in an isolated configuration without any connection and thus

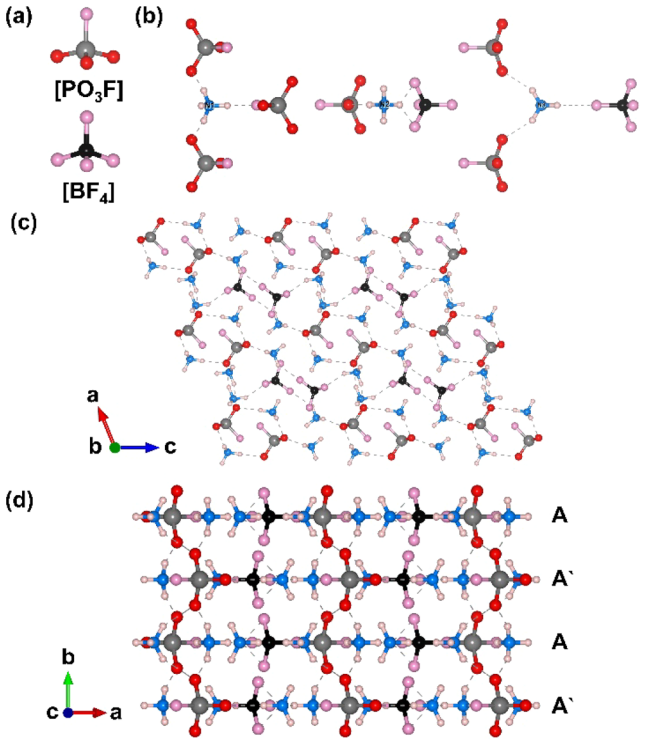

Figure 1. (a) Two types of anionic units in $(NH_4)_3[PO_3F][BF_4]$. (b) Coordination environment of three crystallographically independent $[NH_4]$ units. (c, d) Crystal structure of $(NH_4)_3[PO_3F][BF_4]$ along b and c axes, respectively. Atomic models: N (blue balls), P (gray balls), B (black balls), H (baby pink balls), O (red balls), and F (pink balls).

$(NH_4)_3[PO_3F][BF_4]$ can be classified as fluoroborate-fluorophosphates, which is the first case in this family. The P−O, P−F, and B−F bond lengths are in the region of 1.471−1.478, 1.590, and 1.385−1.396 Å, respectively, which show a good match with other reported fluorooxoborates and fluorophosphates.[6−18] The reasonable bond lengths also give the acceptable bond valence sum calculations and oxidation states of related atoms (Table S2 in the SI). The hydrogen bonds from $[NH_4]$ units in $(NH_4)_3[PO_3F][BF_4]$ link the whole structure, that is N−H···O bonds for $[PO_3F]$ and N−H···F bonds for $[BF_4]$ units, respectively. For three ammonium cations with different crystallographic positions (Figure 1b), $[N(1)H_4]$, $[N(2)H_4]$, and $[N(3)H_4]$ link with three $[PO_3F]$ units, one $[PO_3F]$ and one $[BF_4]$ unit, and two $[PO_3F]$ and one $[BF_4]$ units with N−H···O and N−H···F bonds, respectively. Along the c axis (Figure 1d), two alternate pseudolayers composed of $[NH_4]$, $[PO_3F]$, and $[BF_4]$ units further stack in the − AA′AA′− sequence, of which the interlayer force only comes from N−H···O bonds, whereas the intramural force originates from N−H···O and N−H···F bonds.[31]

The existence and coordination of fluorine in $(NH_4)_3[PO_3F][BF_4]$ were confirmed by several approaches: **(1) Single-crystal structure analysis and bond valence model.** Based on the single-crystal structure analysis, the final solved structure reveals that the related bond lengths and bond angles in $[PO_3F]$ and $[BF_4]$ of $(NH_4)_3[PO_3F][BF_4]$ are consistent with those of reported monofluorophosphates and tetrafluoroborates,[6−18] giving preliminary confirmation of well-ordered O/F anions in $(NH_4)_3[PO_3F][BF_4]$. According to the results of bond valence calculations (BVS) (Table S1 in the SI), the valences of P (5.31), B (3.00), O (1.81−1.82), and F (0.73−0.87) are also reasonable, which verifies that the assignment of O and F atoms. **(2) X-ray energy dispersive and infrared spectrum.** According to the results of EDS (Figure S3 in the SI), the existence of P, B, and F was confirmed. In addition, as shown in Figure S4 in the SI, the IR spectrum of $(NH_4)_3[PO_3F][BF_4]$ shows that the characteristic vibrations at 2919−3363 cm^{-1} can be assigned to the stretching of $[NH_4]$.[9,32] The asymmetrical, symmetrical stretching and scissoring vibrations of P−O bonds are observed at 1069−1124, 1022, 539 cm^{-1}, respectively. Particularly, the P−F stretching vibrations are observed at 760 cm^{-1}.[17] Whereas, the peaks at 995 and 521 cm^{-1} are assigned to the stretching and scissoring vibrations of $[BF_4]$, respectively.[33−35] All the assignments marked in Figure S4 are all based on the infrared spectra of related fluorophosphates, tetrafluoroborates and on other related literature data. **(3) Nuclear magnetic resonance spectroscopy.** The ^{19}F and $^{11}B/^{31}P$ magic-angle spinning (MAS) NMR spectra of $(NH_4)_3[PO_3F][BF_4]$ are visualized in Figure 2, in which the spinning sidebands are marked by asterisks. From the ^{19}F MAS NMR spectrum (Figure 2c), the signals at −71.43 and −73.24 ppm are assigned to F in $[PO_3F]$ units, whereas the signals at −140.26 and −146.49 ppm are assigned to F in $[BF_4]$ units, which are consistent with previous reports.[34,36] For the ^{31}P MAS NMR spectrum (Figure 2a), two signals at −2.43 and 1.79 ppm of ^{31}P NMR are close to the chemical shifts in $NaNH_4PO_3F{\cdot}H_2O$ with similar $[PO_3F]$ tetrahedra.[32] The $^{11}B\{^{19}F\}$ and $^{31}P\{^{19}F\}$ REDOR tests were carried out to establish the B−F and P−F bonds for tetrahedral $[BF_4]$ and $[PO_3F]$ units and the obtained different spectra are shown in Figurs 2d and e, indicating that there are tetrahedral

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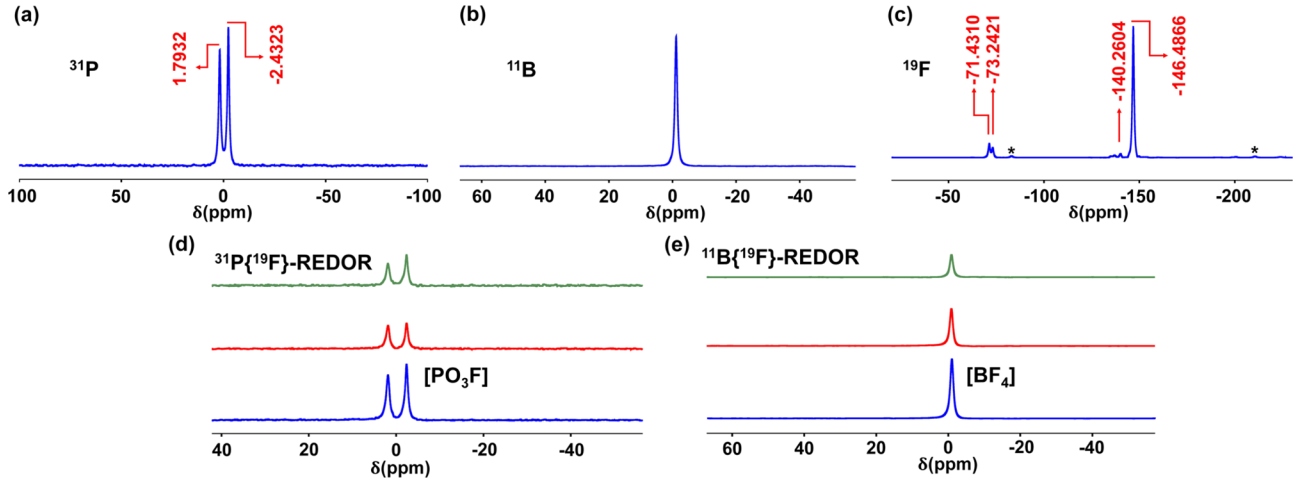

Figure 2. (a) ^{31}P, (b) ^{11}B, (c) ^{19}F, (d) ^{31}P{^{19}F} REDOR MAS, and (e) ^{11}B{^{19}F} REDOR MAS NMR of $(NH_4)_3[PO_3F][BF_4]$.

coordinated B and P nuclei with B−F and P−F bonds in the structure of $(NH_4)_3[PO_3F][BF_4]$. The ^{31}P{^{19}F} REDOR NMR experiment (Figure 2d) shows that two sharp peaks are typical for monofluorophosphates and provides powerful evidence for the existence of $[PO_3F]$ units in title compound.[37,38] For the ^{11}B MAS NMR spectrum (Figure 2b), tetrahedral coordinated B atoms with high local electronic symmetry can be determined by the single signal near 0 ppm. In addition, the existence of B−F bonds is also confirmed by the ^{11}B{^{19}F} REDOR NMR experiment (Figure 2e), illustrating that $(NH_4)_3[PO_3F][BF_4]$ possesses tetrahedral $[BF_4]$ units with the chemical shift close to 0 ppm.[36] Based on the above analysis, the existences of $[PO_3F]$ and $[BF_4]$ tetrahedra are further confirmed.

In order to study the thermal stability of $(NH_4)_3[PO_3F][BF_4]$, thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were performed. As shown in Figure S5 in the SI, $(NH_4)_3[PO_3F][BF_4]$ releases three NH_3, one HF, and one BF_3 gas molecule at about 195, 208, and 304 °C, respectively, as indicated on the DSC curve. The mass loss (26.84%) of the first stage comes from NH_3 and HF, whereas the mass loss (28.19%) of the latter curve is from BF_3, which is consistent with the theoretical values of 29.75 and 28.38%, respectively. The UV−vis−NIR diffuse reflectance spectrum (Figure S6 in the SI) indicates that the cutoff edge of $(NH_4)_3[PO_3F][BF_4]$ is below 190 nm, proving that $(NH_4)_3[PO_3F][BF_4]$ crystal possesses a high potential of deep-UV optical crystal. Even at 190 nm, its reflectance rate is nearly 74%, which is comparable or shorter to most of alkali and alkaline earth metal fluorooxoborates and fluorophosphates.[6−18] The short cutoff edge of $(NH_4)_3[PO_3F][BF_4]$ can be explained by the following structural aspects: (1) The constituents in $(NH_4)_3[PO_3F][BF_4]$, that is, N, P, B, O, F, and H atoms, effectively inhibit the unfavorable *d*−*d* and *f*−*f* electronic transitions and broaden the transparency window into deep-UV spectral region. (2) The anionic framework of $(NH_4)_3[PO_3F][BF_4]$ is exclusively constructed by non-π-conjugated tetrahedra, $[BF_4]$ and $[PO_3F]$ units, which is beneficial for a wider band gap and shorter cutoff edge. Furthermore, the electronic structures of $(NH_4)_3[PO_3F][BF_4]$ based on density functional theory (DFT) were calculated and analyzed. As shown in Figure 3a, $(NH_4)_3[PO_3F][BF_4]$ is an indirect band gap compound with the value of 5.02 eV (GGA). In order to analyze the determinant of the band gap, the total

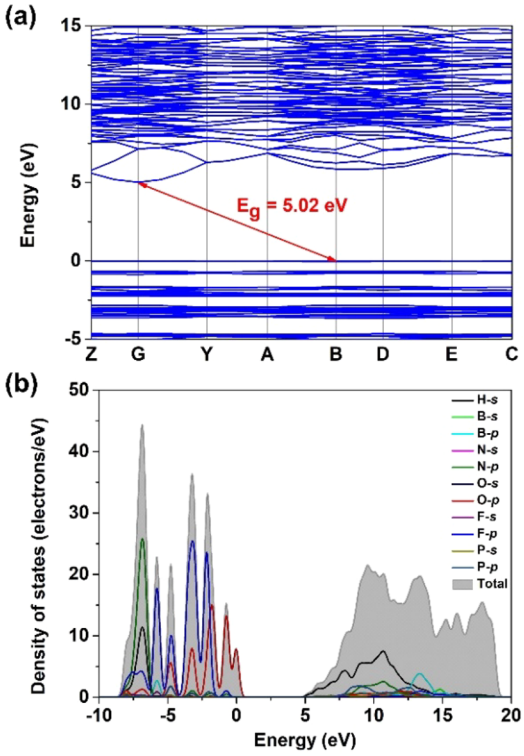

Figure 3. (a) Electron band structure of $(NH_4)_3[PO_3F][BF_4]$. (b) Calculated projected density of states in $(NH_4)_3[PO_3F][BF_4]$.

and partial densities of states (DOS and PDOS) of $(NH_4)_3[PO_3F][BF_4]$ are shown in Figure 3b. Obviously, near the Fermi level, the F 2*p*, O 2*p*, and N 2*p* orbitals play a decisive role on the top of the valence band. The bottom of the conduction band is mainly composed of P 3*s* and H 1*s* orbitals. Accordingly, the $[NH_4]$ and $[PO_3F]$ units have a major impact on the band gap. In addition, the calculated birefringence is 0.012@1064 nm by the first-principles calculations, and the birefringence dispersion curve is plotted in Figure S7 in the SI. Such a small birefringence can be accepted since the anionic framework of $(NH_4)_3[PO_3F][BF_4]$ is exclusively constructed by non-π-conjugated tetrahedra with relatively small optical anisotropy and they are also not in preferential arrangement.

In summary, a novel inorganic oxyfluoride $(NH_4)_3[PO_3F][BF_4]$ has been synthesized via liquid phase neutralization at

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room temperature. It is the first case that contains B−F and P−F bonds in oxyfluorides, and the anionic framework is exclusively constructed by two isolated tetrahedra, that is, $[PO_3F]$ and $[BF_4]$. Thus, $(NH_4)_3[PO_3F][BF_4]$ is also the first compound belonging to the classification of fluoroborate-fluorophosphates. The $^{11}B\{^{19}F\}$ and $^{31}P\{^{19}F\}$ REDOR tests confirm the existence of tetrahedral coordinated B and P nuclei with B−F and P−F bonds in the structure of $(NH_4)_3[PO_3F]$-$[BF_4]$.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsorginorgau.1c00018.

Experimental section, crystal data and structure refinement, atomic coordinates equivalent isotropic displacement parameters, bond valence sum, anisotropic displacement parameters, bond lengths, bond angles, hydrogen bonds, hydrogen atom coordinates, the experimental/calculated PXRD patterns, rietveld refinement of the powder XRD profile, the energy-dispersive X-ray spectroscopy, the IR spectrum, the TG-DSC curves, the UV−vis-NIR diffuse reflectance spectrum, and the birefringence curve for $(NH_4)_3[PO_3F][BF_4]$ (PDF)

Accession Codes

CCDC 2094843 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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