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**NH₄[BAsO₄F] - a new layer fluoro-boroarsenate with a
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NH₄[BAsO₄F]

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a new layer fluoro-boroarsenate with a silicate related topologyAlexandra Lieb^{a,b}, Mark T. Weller^{a,*}

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Abstract

The fluoro-boroarsenate NH₄[BAsO₄F] has been obtained by the melt reaction of NH₄H₂AsO₄, B(OH)₃ and LiBF₄. The dry reaction mixture, in a 3 : 3 : 2 ratio, was treated at 240 °C for 14 days. After cooling to room temperature and washing with hot water the product was isolated as colourless crystals and powder. The crystal structure was determined by single-crystal X-ray diffraction: monoclinic, space group *Cc* (no. 9), *Z* = 4, *a* = 4.4307(5) Å, *b* = 8.0991(9) Å, *c* = 12.674(2) Å, *β* = 90.230(6)°, *V* = 454.81(9) Å³, *R*1 = 0.0456, *wR*2 = 0.0900, *Flack* parameter = 0.13(3). The structure consists of [BAsO₄F]⁻ layers, separated by ammonium ions, having a unique orientations of the tetrahedra forming the constituent six-membered rings. The topology of the fluoro-boroarsenate layer is related to those of the silicate δ-Na₂Si₂O₅ and the borophosphate Mg(H₂O)₂[B₂P₂O₈(OH)₂]·H₂O. NH₄[BAsO₄F] was further characterised by powder X-ray diffraction, IR spectroscopy and EDX analyses.

Keywords: boroarsenate; ammonium; single crystal X-ray structure; silicate; borophosphate

1. Introduction

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3 Oxotetrahedral frameworks are the most prevalent structures among framework
4 materials, as exemplified by the large number of known zeolites, aluminophosphates
5 and zincophosphates. The quest for structural diversity in framework materials has
6 lead to the use of more uncommon units, e.g. borate BO_4 , together with other oxo-
7 species, for example phosphate PO_4 , to produce a range of new structures [1].
8 Borate groups in a 1:1 combination with group 15 oxotetrahedra, such as PO_4 ,
9 produce building-blocks isoelectronic with silicates and lead to analogous structures,
10 such as the quartz heterotype BPO_4 [2], chain structures and three-dimensional
11 frameworks [3,4]. This compositional equivalence also holds for the combination of
12 borate groups with arsenate groups, where detailed investigations have only recently
13 started [5]. Additionally, substitution of O with F gives rise to fluoro-boroarsenates
14 generating further possibilities for variations of properties and structures of
15 boroarsenate frameworks.
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18 As BPO_4 and BAsO_4 are III/V-heterotype variants of quartz SiO_2 [2] the potential
19 for structural similarities among the borophosphates, boroarsenates and classical
20 tectosilicates exists. Where F substitutes, or partially substitutes, for oxygen or
21 hydroxide in the silicates equivalent formulae to families such as the sorosilicates
22 and inosilicates may be derived. In this paper we describe the synthesis of a new
23 fluoro-boroarsenate, produced in a boric acid melt, with a layer structure showing a
24 comparable but still different anionic layer to its related borophosphate and silicate
25 structures; this demonstrates further the structural versatility of such compounds
26 formed from linked tetrahedra. All the three structures show 6^3 network layers made
27 up from six membered tetrahedra rings but with different up/down *directedness*
28 patterns of the tetrahedra.
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49 2. Experimental

50 2.1 Syntheses

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55 LiBF_4 (0.469 g / 5 mmol, Sigma Aldrich, 98%), $\text{NH}_4\text{H}_2\text{AsO}_4$ (1.192 g / 7.5 mmol,
56 ABCR, 98%) and $\text{B}(\text{OH})_3$ (0.460 g / 7.5 mmol, Sigma Aldrich, 99+%) were thoroughly
57 mixed with a pestle and mortar in a molar ratio of 2:3:3. The dry mixture was
58 transferred into a 23 ml *Parr* autoclave and treated at 240 °C for 14 days. After
59
60

washing the resulting product mixture with hot water $\text{NH}_4[\text{BAsO}_4\text{F}]$ was isolated as a colourless polycrystalline powder.

2.2 Crystal-Structure Analysis

2.2.1 Single-Crystal X-Ray Analysis

X-ray diffraction data of $\text{NH}_4[\text{BAsO}_4\text{F}]$ were collected on a Bruker-Nonius FR591 rotating anode diffractometer equipped with 10 cm confocal mirrors and a Bruker-Nonius APEX II CCD camera on a κ -goniostat using Mo-K_α radiation. According to the observed reflection conditions of the monoclinic lattice, the space group *Cc* (no. 9) was determined. The crystal structure of $\text{NH}_4[\text{BAsO}_4\text{F}]$ was solved by direct methods using SHELXTL [6] and refined with anisotropic thermal displacement parameters for all atoms, except the boron atom B1 and the oxygen atom O1. Relevant crystallographic data and details of the X-ray data collection are shown in Table 1.

Table 1: Crystallographic data and details of the single crystal X-ray data collection for $\text{NH}_4[\text{BAsO}_4\text{F}]$.

diffractometer	Bruker-Nonius FR591 rotating anode
monochromator	10 cm confocal mirrors
radiation	MoK_α ($\lambda = 0.71073 \text{ \AA}$)
temperature / K	120(2)
space group	<i>Cc</i> (no. 9), monoclinic
lattice parameter, $a / \text{Å}$	4.4307(5)
$b / \text{Å}$	8.0991(9)
$c / \text{Å}$	12.674(2)
$\beta / ^\circ$	90.230(6)
cell volume, $V / \text{Å}^3$	454.81(9)
formula units	$Z = 4$
crystal size / mm^3	0.04 x 0.04 x 0.02
crystal color	colourless
calculated density / g cm^{-3}	2.728
diffraction range / $^\circ$	$5.8 < 2\theta < 55$
measured reflections	2092
independent reflections	957

observed reflections	914
ref. parameters / restraints	64 / 2
R_{int}	0.0458
$F(000)$	360.0
absorption correction	multi-scan, sadabs 2007/2
absorption coefficient / mm^{-1}	7.414
min. / max. transmission	0.751 / 0.862
<i>Flack</i> parameter	0.13(3)
min. / max. residual electron density / $\text{e} / \text{\AA}^3$	-0.949 / 0.911
GooF	1.134
$R_1 [I > 2\sigma(I)]$	0.0456 [0.0420]
$wR_2 [I > 2\sigma(I)]$	0.0900 [0.0877]

Some selected distances and angles within the single crystal structure are shown in Table 2.

Table 2: Selected interatomic distances (\AA) and angles ($^\circ$) in the structure of $\text{NH}_4[\text{BAsO}_4\text{F}]$ determined by single-crystal X-ray diffraction with standard deviations in parentheses. Constrained values are marked with an asterisk.

As1 – O1	1.645(5)	B1 – O1	1.45(1)	N1 – H1A	0.8391 *
As1 – O2	1.699(5)	B1 – O2	1.49(1)	N1 – H1B	0.8432 *
As1 – O3	1.695(6)	B1 – O3	1.47(1)	N1 – H1C	0.8507 *
As1 – O4	1.703(5)	B1 – F1	1.42(1)	N1 – H1D	0.8437 *
O1 – As1 – O2	104.2(3)	O1 – B1 – O2	107.4(6)	H1A – N1 – H1B	109.9 *
O1 – As1 – O3	111.1(3)	O1 – B1 – O3	115.1(6)	H1A – N1 – H1C	109.8 *
O1 – As1 – O4	106.0(3)	O2 – B1 – O3	107.5(7)	H1B – N1 – H1C	108.2 *
O2 – As1 – O3	102.8(3)	O1 – B1 – F1	111.9(7)	H1A – N1 – H1D	109.7 *
O2 – As1 – O4	116.3(3)	O2 – B1 – F1	109.7(6)	H1B – N1 – H1D	110.4 *
O3 – As1 – O4	115.9(3)	O3 – B1 – F1	105.2(6)	H1C – N1 – H1D	108.7 *
B1 – O1 – As1	128.2(5)	B1 – O2 – As1	124.4(5)	B1 – O3 – As1	124.3(5)

Details of the single crystal structures of $\text{NH}_4[\text{BAsO}_4\text{F}]$ may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, e-mail crysdata@FIZ-karlsruhe.de, by quoting the depository number CSD-420517.

2.2.2 X-Ray Powder Diffraction

An X-ray powder diffraction pattern was obtained from a sample of $\text{NH}_4[\text{BAsO}_4\text{F}]$ using a PANalytical X'Pert PRO MPD diffractometer in transmission geometry. The compound was measured in a flat sample holder. The detected reflections of $\text{NH}_4[\text{BAsO}_4\text{F}]$ have been indexed and a *Rietveld* refinement was performed (using GSAS [7]). BAsO_4 was also included as a very minor second phase contributing to the X-ray powder pattern. Some very weak additional reflections were detected deriving from an unknown by-product. The structural model of $\text{NH}_4[\text{BAsO}_4\text{F}]$ from single crystal was employed and the isotropic thermal displacement parameters of B and O within BAsO_4 had to be fixed to reasonable values. Relevant crystallographic data and details of the powder X-ray data collection are shown in Table 2.

Table 2: Crystallographic data and details of the powder X-ray diffraction data collection and the *Rietveld* refinement of $\text{NH}_4[\text{BAsO}_4\text{F}]$ (including 9.5% of BAsO_4)

diffractometer	PANalytical X'Pert PRO MPD
monochromator	none
detector	PSD, PIXcel (scanning mode)
temperature / K	293(2)
lattice parameter, $a / \text{\AA}$	4.43873(7)
$b / \text{\AA}$	8.0986(2)
$c / \text{\AA}$	12.7502(3)
$\beta / ^\circ$	90.242(2)
cell volume, $V / \text{\AA}^3$	458.34(2)
observed reflections (total)	340
ref. Parameters	59
GooF (all data)	3.67
R_{wp} / R_p	0.1302 / 0.0788
R_{F^2} of $\text{NH}_4[\text{BAsO}_4\text{F}] / \text{BAsO}_4$	0.0295 / 0.0594
red. χ^2	13.14

2.3 Vibrational spectroscopy

Mid-IR spectra were recorded on an ATI Matheson Genesis in the spectral range $4000\text{-}400\text{ cm}^{-1}$. The sample was thoroughly ground together with dried KBr (~1 mg sample / 150 mg KBr) and a pellet was prepared for the measurement.

2.4 EDX analysis

Qualitative chemical analyses on the microscale by energy dispersive X-ray spectroscopy (EDX) were carried out with a Jeol JSM-5910 scanning electron microscope equipped with an energy dispersive X-ray (EDX) analyzer using an accelerating voltage of 15 kV and INCA software.

3. Results and Discussion

3.1 Crystal Structure

The structure of $\text{NH}_4[\text{BAsO}_4\text{F}]$ represents a new layer structure type in the family of boroarsenate compounds. It consists of anionic tetrahedra layers and NH_4^+ cations (Figure 1).

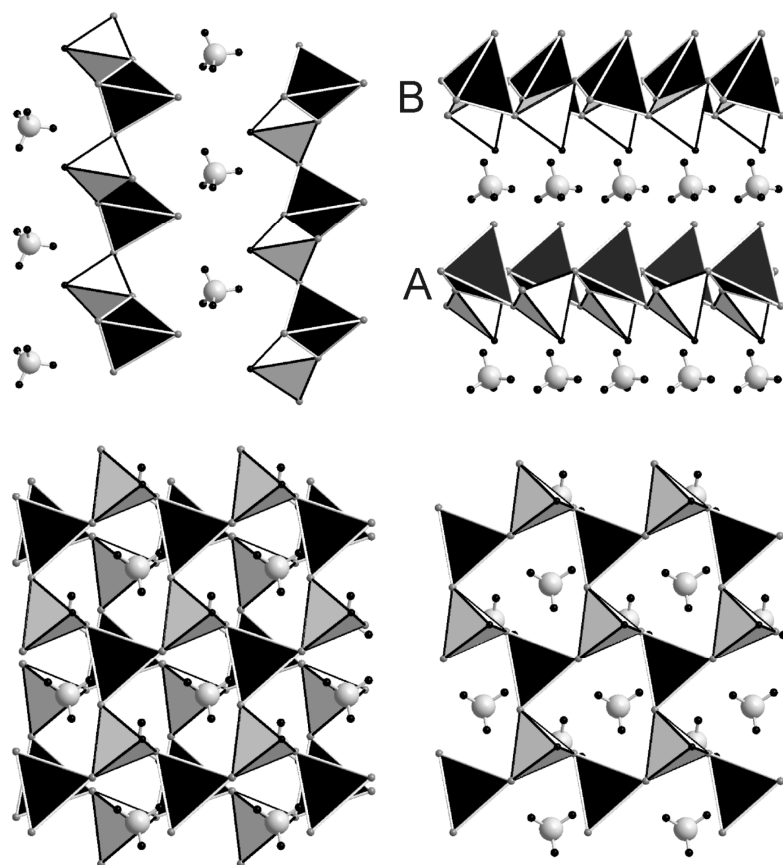


Figure 1: Structural overview of $\text{NH}_4[\text{BAsO}_4\text{F}]$, view along a (top left), view along b (top right) showing the stacking of the layers in an ABAB manner, view along c (bottom left) of two layers of the structure demonstrating the staggered arrangement

and (bottom right) view of only one layer displaying the 6^3 network structure. Light grey tetrahedra: BO_3F , black spheres: fluorine atoms, black tetrahedra: AsO_4 , grey spheres: oxygen atoms, large light grey spheres: nitrogen atoms, small black spheres: hydrogen atoms.

The anionic layers $[\text{BAsO}_4\text{F}]^-$ are topologically related to the $[\text{Si}_2\text{O}_5]^{2-}$ layers of the silicate $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ [8] and the $[\text{BPO}_4(\text{OH})]^-$ layers of the borophosphate $\text{Mg}(\text{H}_2\text{O})_2[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2]\cdot\text{H}_2\text{O}$ [9].

The fluoro-boroarsenate layers consist solely of Q^3 tetrahedra, which is typical for unbranched single layer structures. The terminal ligand atoms are oxygen atoms from AsO_4 tetrahedra and fluorine atoms from BO_3F tetrahedra. The basic building unit (BBU) of the layer is a fluoro-boroarsenate dimer $[\text{BAsO}_6\text{F}]$ and three of these form the fundamental building unit (FBU) of the structure, which is a six membered tetrahedra ring $[\text{B}_3\text{As}_3\text{O}_{15}\text{F}_3]$. These six membered rings form 6^3 networks which can be found quite frequently in silicate layer structures. Following *Burns* [10] the building units of $\text{NH}_4[\text{BAsO}_4\text{F}]$ are characterised with the symbols $2\Box:2\Box$ (dimeric unit) and $6\Box:<6\Box>$ (six membered ring). According to *Liebau* [11] the layer is classified as an unbranched *zweier* single layer, also referring to a tetrahedra dimer as the repeating unit of the structure (Figure 2).

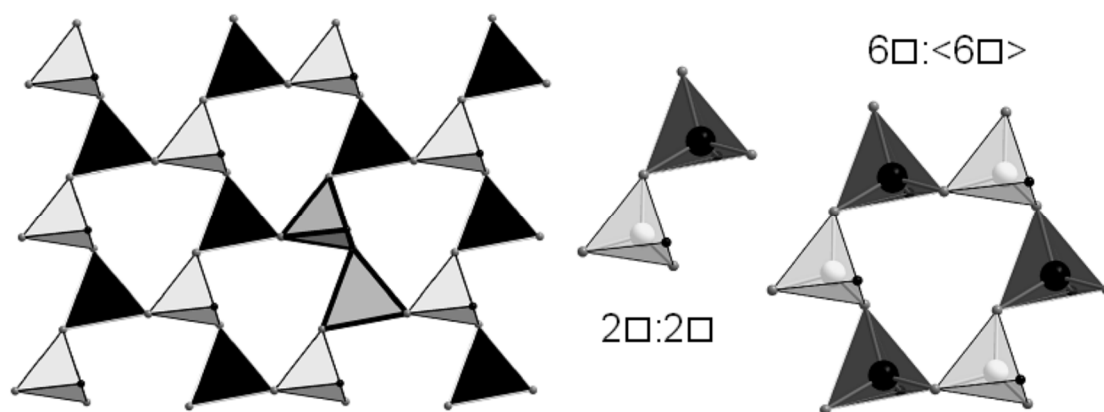


Figure 2: Classification of the anionic layer in $\text{NH}_4[\text{BAsO}_4\text{F}]$ (view along c). On the left side the classification according to *Liebau* is displayed, the layer is called an unbranched *zweier* single layer, the repeating unit is emphasised as grey tetrahedra with thick black edges. On the right side the basic building unit (BBU), a fluoro-boroarsenate dimer and the fundamental building unit (FBU) a six membered ring are

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3 shown. The symbols follow the nomenclature suggested by *Burns*. White tetrahedra:
4 BO_3F , black tetrahedra: AsO_4 , small grey spheres: oxygen atoms, small black
5 spheres: fluorine atoms, large white spheres: boron atoms, large black spheres:
6 arsenic atoms.
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12 Comparing $\text{NH}_4[\text{BAsO}_4\text{F}]$ with the structures of the silicate $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ and the
13 borophosphate $\text{Mg}(\text{H}_2\text{O})_2[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2]\cdot\text{H}_2\text{O}$, which contains layer of the same
14 connectivity i.e. $[\text{Si}_2\text{O}_5]^{2-}$ and $[\text{BPO}_4(\text{OH})]^-$ also forming 6^3 networks, some important
15 differences can be observed. Most importantly the corrugation of the three layers is
16 different, increasing from $\text{NH}_4[\text{BAsO}_4\text{F}]$ via $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ to
17 $\text{Mg}(\text{H}_2\text{O})_2[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2]\cdot\text{H}_2\text{O}$ (Figure 3), which shows a tuning of the layer element of
18 these structures in response to the different cations contained within them, i.e. NH_4^+ ,
19 Na^+ , Mg^{2+} .
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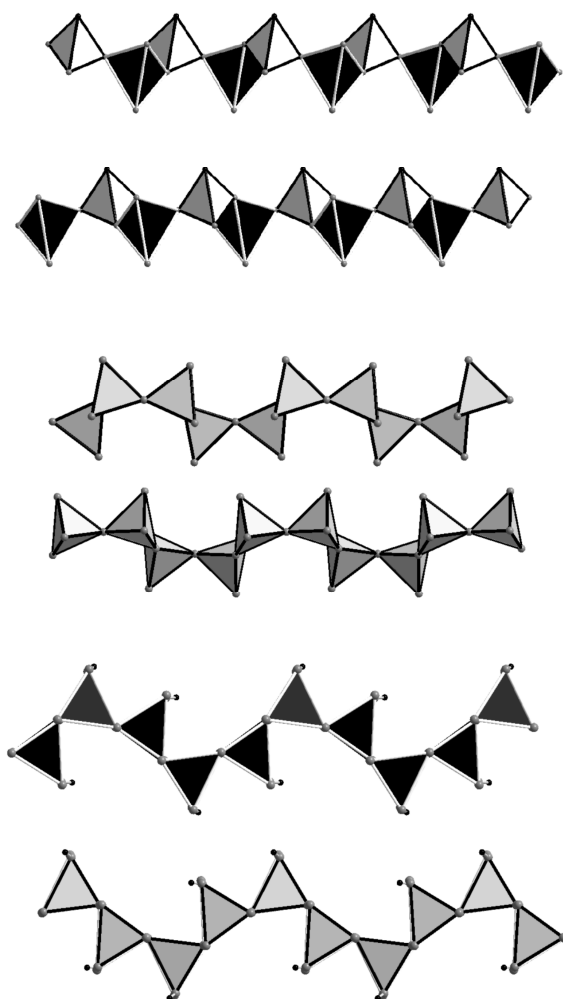


Figure 3: Comparison of the different corrugation of the layers of $\text{NH}_4[\text{BAsO}_4\text{F}]$ (top, light grey tetrahedra: BO_3F , black tetrahedra: AsO_4), $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ (middle, medium grey tetrahedra: SiO_4) and $\text{Mg}(\text{H}_2\text{O})_2[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2]\cdot\text{H}_2\text{O}$ (bottom, light grey tetrahedra: BO_4H , black tetrahedra: PO_4).

Also the *directedness* of the tetrahedra, meaning the orientation of the tetrahedra, pointing either up (U) or down (D), within the layers is different in each of these structures. This can be easily realised by considering the patterns of the six membered rings which is UDUDUD for $\text{NH}_4[\text{BAsO}_4\text{F}]$, UUDUUD or DDUDDU for adjacent layers in $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ and UUDDDD or DDUUUU in neighbouring layers $\text{Mg}(\text{H}_2\text{O})_2[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2]\cdot\text{H}_2\text{O}$ (Figure 4).

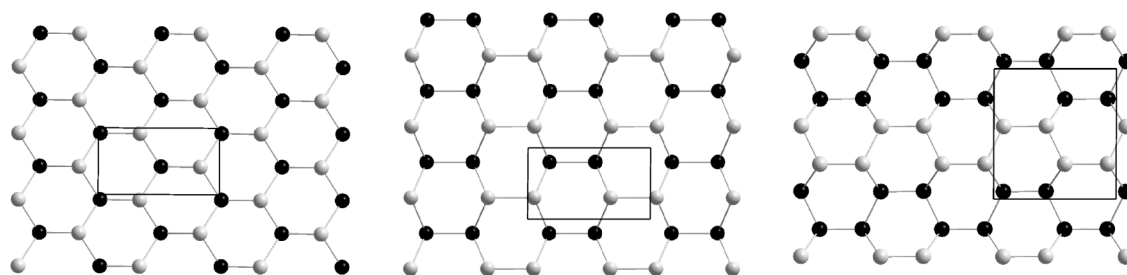


Figure 4: Comparison of the *directedness* patterns of the layers of $\text{NH}_4[\text{BAsO}_4\text{F}]$ (left), $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ (middle) and $\text{Mg}(\text{H}_2\text{O})_2[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2]\cdot\text{H}_2\text{O}$ (right). White spheres symbolise tetrahedra pointing up (U), black spheres symbolise tetrahedra pointing down (D). The grey lines symbolise the topological connection of the tetrahedra and visualise the 6^3 networks of the structures.

The NH_4^+ cations in $\text{NH}_4[\text{BAsO}_4\text{F}]$ are located in a strongly distorted (4+2) six-fold co-ordination sphere forming three strong single and one trifurcated hydrogen bonds to terminal oxygen and fluorine atoms of the layers (Figure 5, Table 4). This hydrogen-bonded arrangement helps explain the relative orientation of adjacent $[\text{BAsO}_4\text{F}]^-$ layers giving rise to the non-centrosymmetric space group Cc .

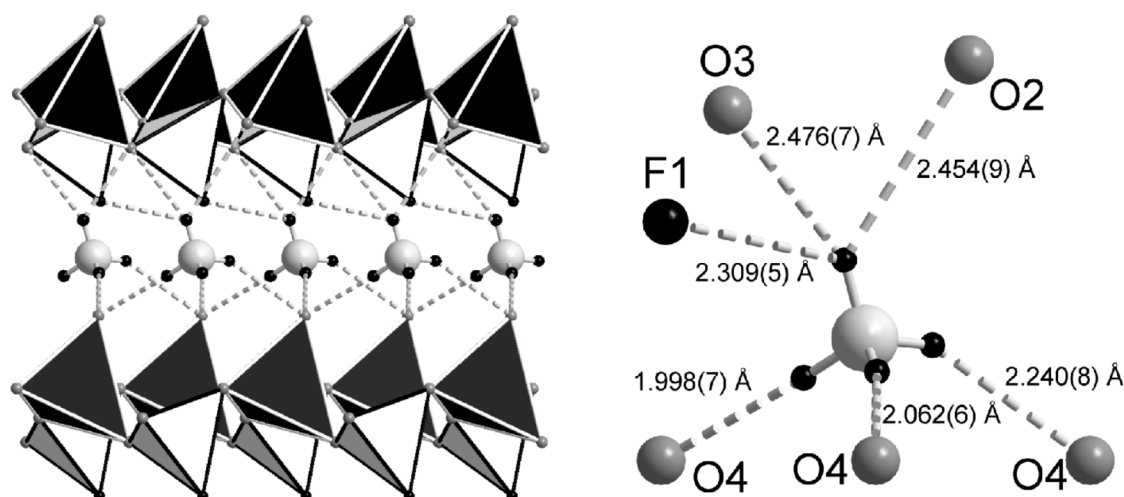


Figure 5: Surrounding of the NH_4^+ cations in $\text{NH}_4[\text{BAsO}_4\text{F}]$ showing the interactions of the hydrogen atom with the nearest oxygen and fluorine atoms (right side). On the left side the NH_4^+ cations are shown between the fluoro-boroarsenate layers, hydrogen bonds are displayed as dashed lines (view along b). Large light grey spheres: nitrogen atoms, small black spheres: hydrogen atoms, medium size black spheres: fluorine atoms, medium size grey spheres: oxygen atoms.

Table 4: Hydrogen bonds of the NH_4^+ cations to the fluoro-boroarsenate layers in $\text{NH}_4[\text{BAsO}_4\text{F}]$

donor-H-acceptor	$d(\text{D-H}) / \text{\AA}$	$d(\text{H}\dots\text{A}) / \text{\AA}$	angle DHA / $^\circ$	$d(\text{D}\dots\text{A}) / \text{\AA}$
N1-H1A...O4 [$x+1/2, y-1/2, z$]	0.839(6)	2.062(6)	170.9(5)	2.894(9)
N1-H1B...O4 [$x+1, y-1, z$]	0.843(6)	2.240(8)	152.8(5)	3.02(1)
N1-H1C...O4 [$x, y-1, z$]	0.851(7)	1.998(7)	175.8(5)	2.85(1)
N1-H1D...F1 [$x-1/2, -y+1/2, z-1/2$]	0.844(6)	2.309(5)	115.5(5)	2.78(1)
N1-H1D...O2 [$x, -y+1, z-1/2$]	0.844(6)	2.454(9)	133.5(5)	3.10(2)
N1-H1D...O3 [$x, -y, z-1/2$]	0.844(6)	2.476(7)	131.5(5)	3.10(1)

Additionally a Rietveld refinement of the X-ray powder data of $\text{NH}_4[\text{BAsO}_4\text{F}]$ was performed to confirm the structure model and the final profile fit plot obtained is shown in Figure 6. BAsO_4 was refined as an additional phase and the phase fraction was found to be 9.5%. The hydrogen positions of the structure model of $\text{NH}_4[\text{BAsO}_4\text{F}]$ were included in the structure model but not refined.

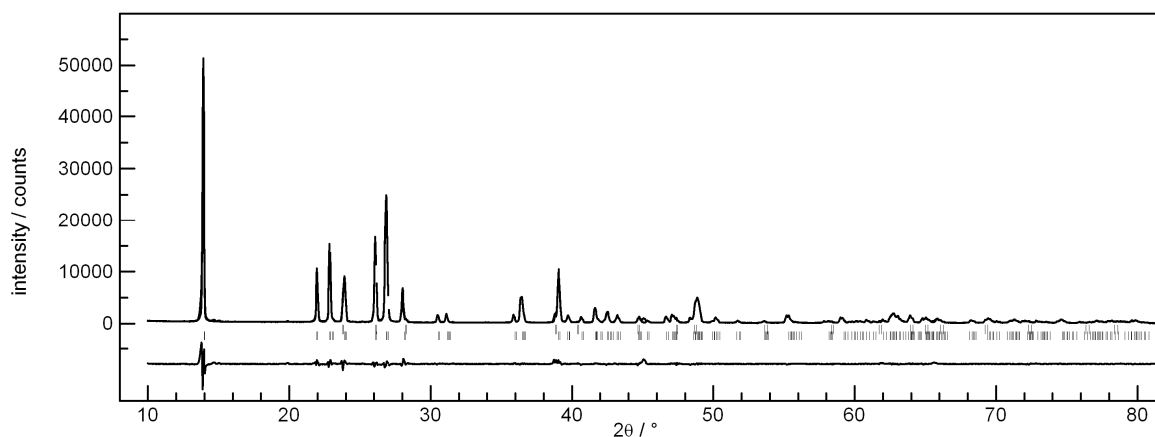


Figure 6: Rietveld profile fit of the powder X-ray data at ambient temperature of $\text{NH}_4[\text{BAsO}_4\text{F}]$. Observed (crosses) and calculated (line) powder diffractograms as well as difference profile (lower line). The two rows of vertical lines indicate the possible reflection positions of the refined phases, the upper row shows BAsO_4 , the lower row shows $\text{NH}_4[\text{BAsO}_4\text{F}]$. The small peaks in the difference curve around 14.5° and $45^\circ 2\theta$ indicate the presence of an additional unknown phase.

3.2 Further characterisation of $\text{NH}_4[\text{BAsO}_4\text{F}]$ by spectroscopy and EDX

The presence of ammonium ions and its hydrogen bonding could be confirmed by IR spectroscopy (Figure 7).

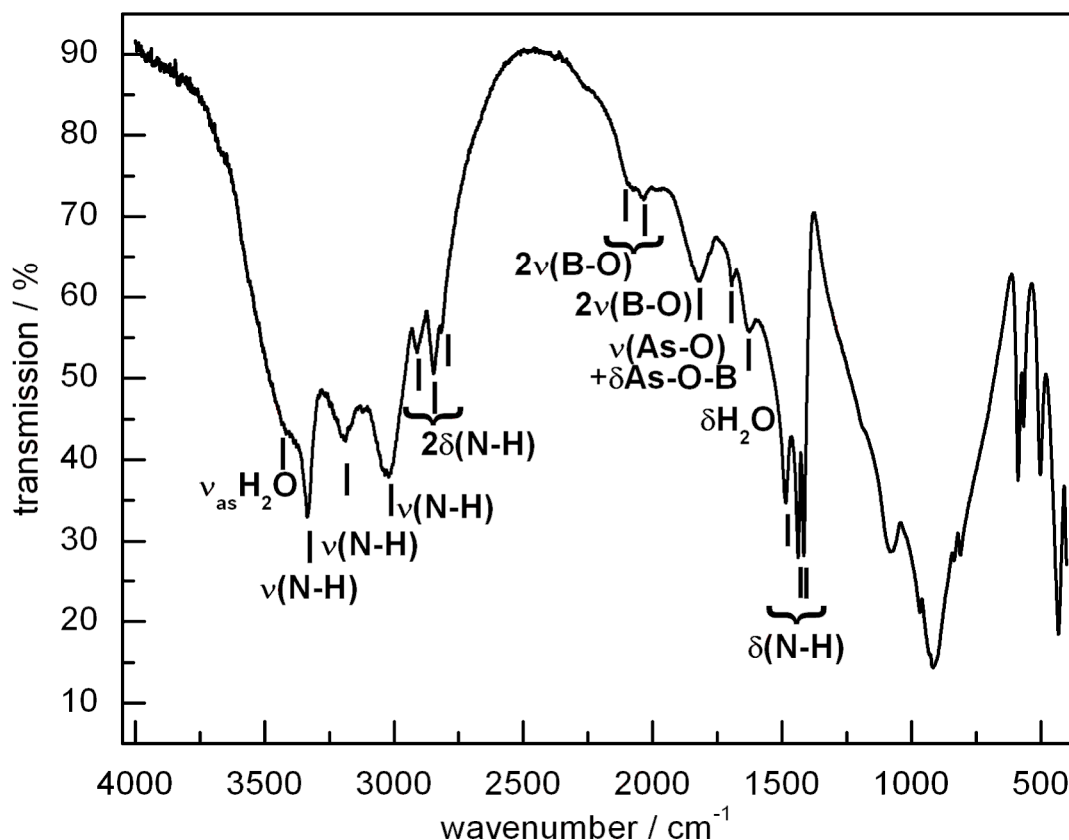


Figure 7: Mid-IR spectrum of $\text{NH}_4[\text{BAsO}_4\text{F}]$.

The bands could be assigned as following: $\nu(\text{H}_2\text{O})$ as broad band around 3420 cm^{-1} , $\nu(\text{N-H})$: 3334 cm^{-1} , 3195 cm^{-1} , 3024 cm^{-1} , $2\delta(\text{N-H})$: 2910 cm^{-1} , 2847 cm^{-1} , 2817 cm^{-1} , $2\delta(\text{B-O})$: 2090 cm^{-1} , 2037 cm^{-1} , $2\nu(\text{B-O})$: 1822 cm^{-1} , $\nu(\text{As-O}) + \delta(\text{As-O-B})$: 1695 cm^{-1} , $\delta(\text{H}_2\text{O})$: 1630 cm^{-1} , $\delta(\text{N-H})$: 1486 cm^{-1} , 1438 cm^{-1} , 1416 cm^{-1} . The lower bands derive from different combinations of framework vibrations.

Using EDX, a powder sample of $\text{NH}_4[\text{BAsO}_4\text{F}]$ was investigated. The measurement shows the presence of fluorine, oxygen, nitrogen and arsenic in the sample. Due to the low atom number of fluorine, oxygen and nitrogen a quantification was not possible. Boron could not be detected because its low atomic weight which is below the detectable value of the apparatus.

Conclusions

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3 A new member of the boroarsenate family, the fluoro-boroarsenate $\text{NH}_4[\text{BAsO}_4\text{F}]$,
4 has been synthesised and characterised. This material is formed under "dry"
5 synthesis conditions with boric acid as the reaction medium but also a reactant. The
6 investigation of its structure and the relationship to the structures of the silicate
7 $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ and the borophosphate $\text{Mg}(\text{H}_2\text{O})_2[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2]\cdot\text{H}_2\text{O}$ shows the
8 interesting differences of these tetrahedra framework compounds related by
9 substitution of the tetrahedra centre atoms.
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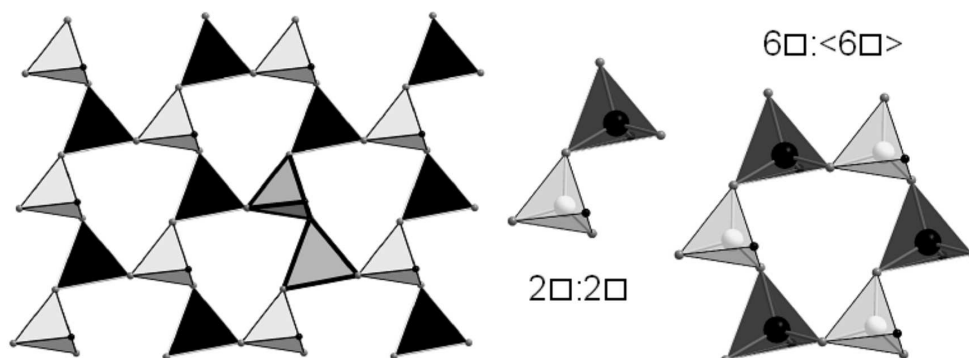


Figure 2: Classification of the anionic layer in $\text{NH}_4[\text{BAsO}_4\text{F}]$ (view along c). On the left side the classification according to Liebau is displayed, the layer is called an unbranched zweier single layer, the repeating unit is emphasised as grey tetrahedra with thick black edges. On the right side the basic building unit (BBU), a fluoro-boroarsenate dimer and the fundamental building unit (FBU) a six membered ring are shown. The symbols follow the nomenclature suggested by Burns. White tetrahedra: BO_3F , black tetrahedra: AsO_4 , small grey spheres: oxygen atoms, small black spheres: fluorine atoms, large white spheres: boron atoms, large black spheres: arsenic atoms.

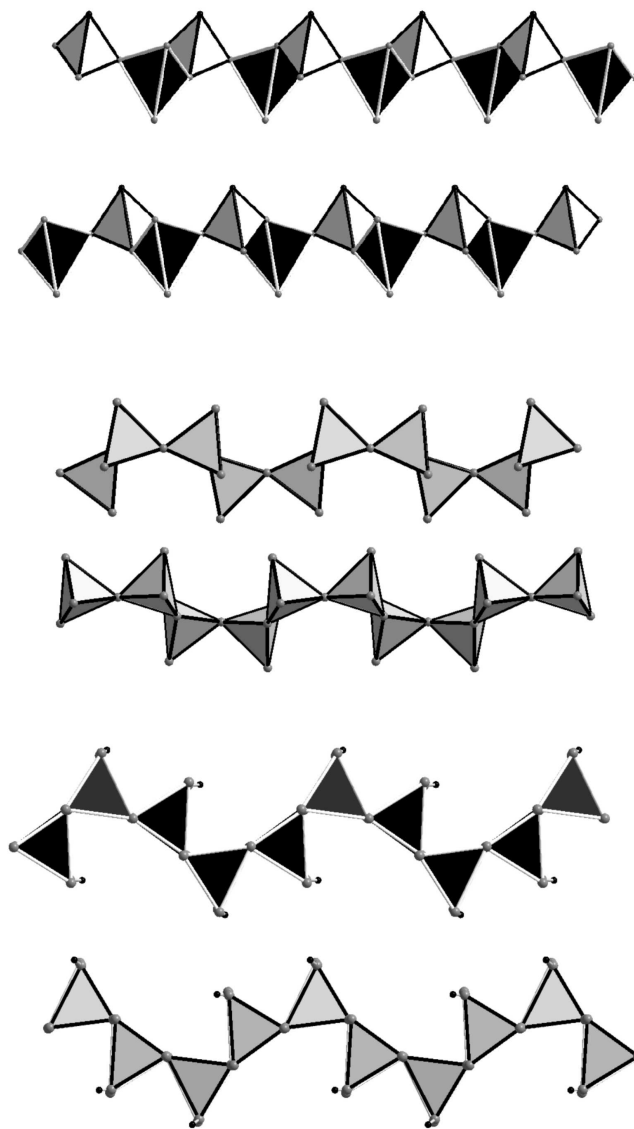


Figure 3: Comparison of the different corrugation of the layers of $\text{NH}_4[\text{BAsO}_4\text{F}]$ (top, light grey tetrahedra: BO_3F , black tetrahedra: AsO_4), $\delta \text{Na}_2\text{Si}_2\text{O}_5$ (middle, medium grey tetrahedra: SiO_4) and $\text{Mg}(\text{H}_2\text{O})_2[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2] \cdot \text{H}_2\text{O}$ (bottom, light grey tetrahedra: BO_4H , black tetrahedra: PO_4).

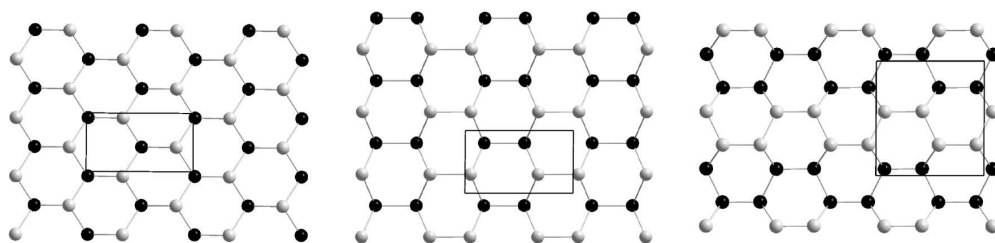


Figure 4: Comparison of the directedness patterns of the layers of $\text{NH}_4[\text{BAsO}_4\text{F}]$ (left), $\delta \text{Na}_2\text{Si}_2\text{O}_5$ (middle) and $\text{Mg}(\text{H}_2\text{O})_2[\text{B}_2\text{P}_2\text{O}_8(\text{OH})_2] \cdot \text{H}_2\text{O}$ (right). White spheres symbolise tetrahedra pointing up (U), black spheres symbolise tetrahedra pointing down (D). The grey lines symbolise the topological connection of the tetrahedra and visualise the 63 networks of the structures.

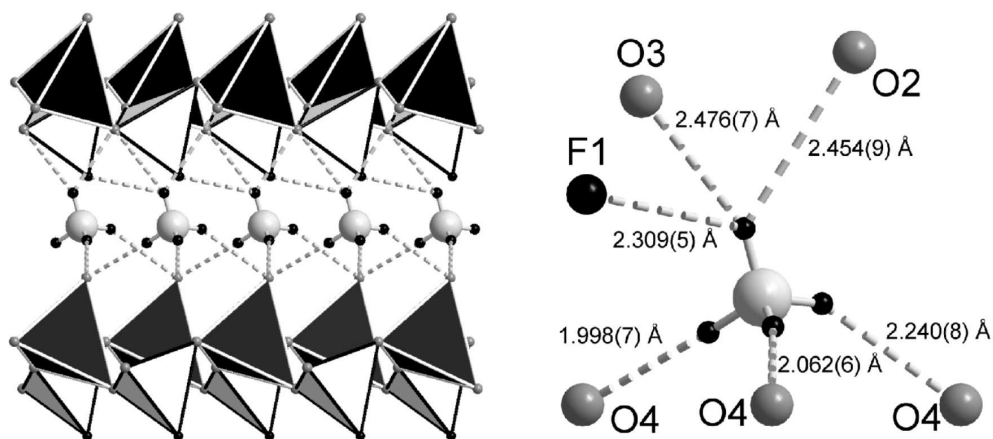


Figure 5: Surrounding of the NH₄⁺ cations in NH₄[BAsO₄F] showing the interactions of the hydrogen atom with the nearest oxygen and fluorine atoms (right side). On the left side the NH₄⁺ cations are shown between the fluoro-boroarsenate layers, hydrogen bonds are displayed as dashed lines (view along b). Large light grey spheres: nitrogen atoms, small black spheres: hydrogen atoms, medium size black spheres: fluorine atoms, medium size grey spheres: oxygen atoms.

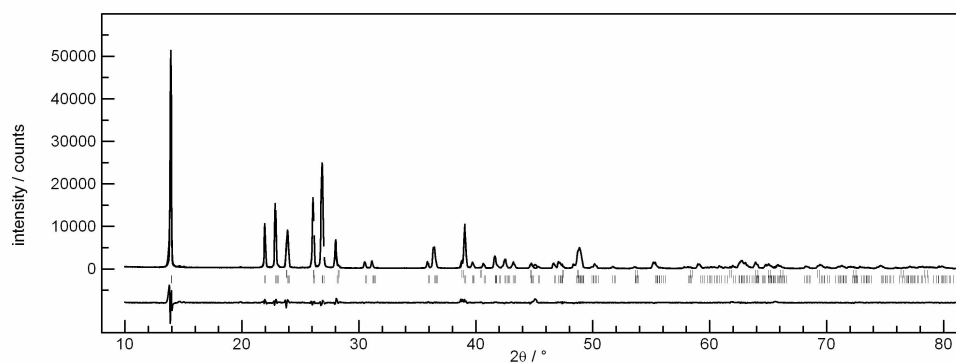
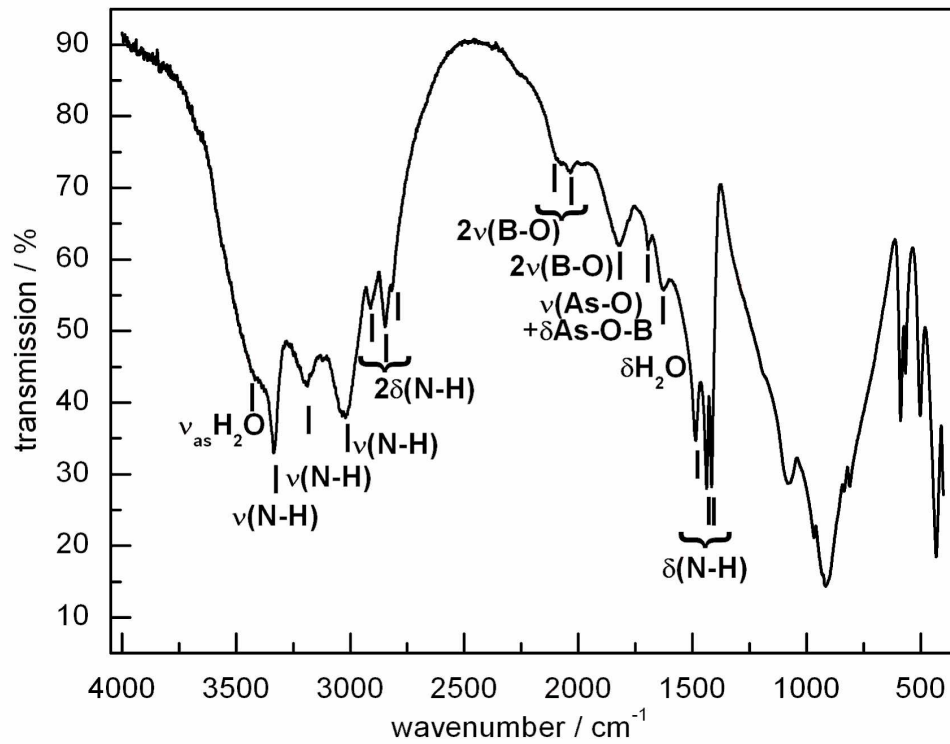


Figure 6: Rietveld profile fit of the powder X-ray data at ambient temperature of $\text{NH}_4[\text{BAsO}_4\text{F}]$. Observed (crosses) and calculated (line) powder diffractograms as well as difference profile (lower line). The two rows of vertical lines indicate the possible reflection positions of the refined phases, the upper row shows BAsO_4 , the lower row shows $\text{NH}_4[\text{BAsO}_4\text{F}]$. The small peaks in the difference curve around 14.5° and 45° 2θ indicate the presence of an additional unknown phase.

Figure 7: Mid-IR spectrum of $\text{NH}_4[\text{BAsO}_4\text{F}]$.

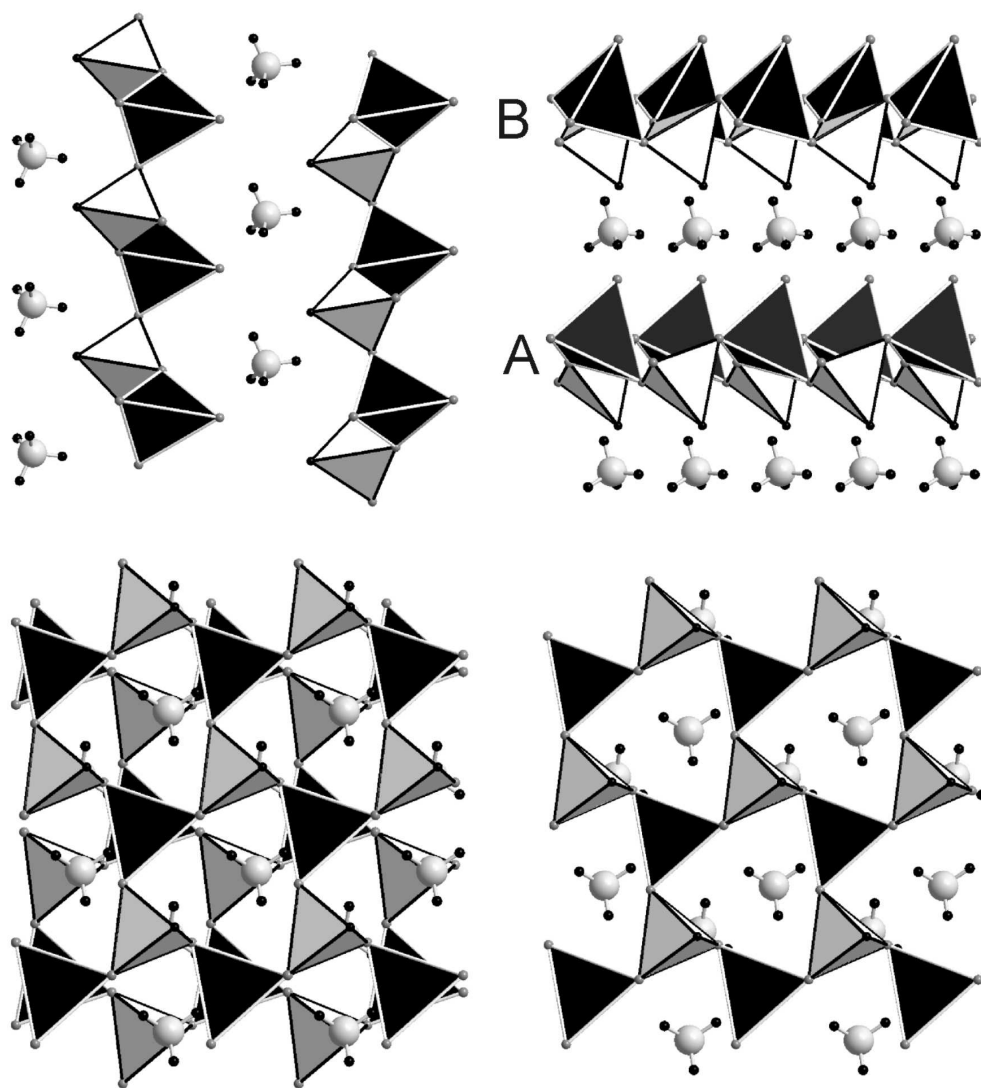


Figure 1: Structural overview of $\text{NH}_4[\text{BAsO}_4\text{F}]$, view along a (top left), view along b (top right) showing the stacking of the layers in an ABAB manner, view along c (bottom left) of two layers of the structure demonstrating the staggered arrangement and (bottom right) view of only one layer displaying the 63 network structure. Light grey tetrahedra: BO_3F , black spheres: fluorine atoms, black tetrahedra: AsO_4 , grey spheres: oxygen atoms, large light grey spheres: nitrogen atoms, small black spheres: hydrogen atoms.