The Crystal Structure of NH$_4$BiF$_4$
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The investigation of NH$_4$BiF$_4$ is a part of a general study of the coordination of bismuth in different bismuth oxide salts containing fluorine.

Single crystals of NH$_4$BiF$_4$ were investigated by X-ray single crystal methods (Buerger precession camera). The intensity data were made up of 1314 independent reflections. The intensities were corrected for absorption. The unit-cell dimensions were determined from X-ray Guinier diffractionograms. The following data are derived for the compound:

Space group: $P2_1/c$ (No. 14).

4 Bi, 4 N, 4 F, 4 F in 4(e): $\pm (x,y,z; x,1/2-y,1/2+z)$.

Unit-cell dimensions: $a = 8.317$, $b = 7.597$, $c = 6.486$, $\alpha = 93.5\,$.$\,$°.

Cell content: 4 formula units NH$_4$BiF$_4$.

Final coordinates, isotropic temperature factors and standard deviations from the least-squares refinement, $R = 16.5\,$.$\,$%, absent reflections included. (Table 1).

The bismuth atoms in the structure are coordinated by nine fluorine atoms with the distances Bi-F ranging from 2.19 ± 0.03 Å to 2.86 ± 0.03 Å. The coordination polyhedra are linked by sharing edges and faces to infinite layers of the composition Bi$_2$F$_4$. The shortest distances bismuth-bismuth and fluorine-fluorine in the structure are 3.905 ± 0.003 Å and 2.45 ± 0.03 Å, respectively. A drawing of the resulting endless two-dimensional network is given in Fig. 1. The coordination of bismuth in this structure is very similar to the coordination Y·F$^-$ in YF$_3$ and Bi·F$^-$ in BiF$_3$ (o-rh).$^*$

The nitrogen atoms are arranged in layers parallel to the $yz$ plane around $x = 1/4$, in between the layers Bi$_2$F$_4$-$^*$. They are irregularly coordinated by eight fluorine atoms. Two groups of distances nitrogen to fluorine occur in the coordination polyhedron, viz. the short distances ranging from 2.73 ± 0.05 Å to 2.93 ± 0.05 Å, and the long distances, from 3.10 ± 0.05 Å to 3.39 ± 0.05 Å. If the formation of groups is ascribed to bonds N-H-F as in the structure of NH$_4$HF$_4$,$^5$ it seems probable from electrostatical reasons that the N-H-F bonds are directed as shown in Fig. 2, where a projection of the structure is drawn on the $ac$ plane. The values of the angles F-N-F found in the structure, do not support this assumption, however. Efforts to ascertain the positions of

*Fig. 1. The four equivalent positions in the point position 4(e) in $P2_1/c$ (No. 14) have been numbered in the following way:
Atom, e.g. F$_{4a}$:

$F_{4a}$: $x,y,z; F_{4b}$: $x,1/2-y,1/2+z$; $F_{4c}$: $x,y,1/2+z$.

The repeat units of the two chains

---Bi$_{11}$---Bi$_{13}$---Bi$_{13}$---Bi$_{11}$---

and

---Bi$_{11}$---Bi$_{13}$---Bi$_{13}$---Bi$_{11}$---

in the structure of NH$_4$BiF are shown in the figure. Together these chains and their associated fluorine atoms form an infinite two-dimensional network of linked polyhedra.

To make the arrangement of the two chains more obvious they have been separated in the $y$ direction in the drawing. Fluorine atoms which coincide in the twodimensional repeat units are marked by black circles, other fluorine atoms are marked by open circles and bismuth atoms by open squares. The $x$, $y$, $z$ axes are parallel to the crystallographic ones. * denotes an atom in an adjacent unit cell.

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The Crystal Structure of $\text{Bi}_2\text{GeO}_4$

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The investigation of the crystal structures of $\text{Bi}_2\text{GeO}_4$ and $\text{Bi}_2\text{SiO}_4$ is a part of the more general study of the coordination of bismuth in compounds containing tetrahedral anions.

The compounds were synthesized by heating a mixture of the corresponding oxides in the molecular proportions 1:1 in platinum crucibles, immersed in a series of porcelain crucibles in an electrical furnace. The temperature was slowly increased to $\sim1000^\circ\text{C}$. After 2 or 3 h at that temperature, the samples were cooled down very slowly. This mode of preparation explains why previous investigators of the systems $\text{Bi}_2\text{O}_3\cdot\text{GeO}_2$ and $\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ have not reported these phases.

Single crystals of $\text{Bi}_2\text{GeO}_4$ were investigated by X-ray single crystal diffraction methods. The intensity material was made up of 272 independent reflections. The intensities were corrected for absorption. The unit-cell dimensions of the compounds were determined from X-ray Guinier diagrams.

The following data were derived for the compounds:

Space group: $\text{Cmc}2_1$ (No. 36).
8 Bi, 8 O, and 8 O, in $8(b)$:
$(0,0,0; 0,0,0) + x,y,z; x,y,z; x,y,z + z; x,y,z + z$.
4 Ge (Si) and 4 O, in $4(a)$:
$(0,0,0; 0,0,0) + 0,y,z; 0,y,z + z$.