Rerefinement of the crystal structure of BiF$_5$

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The crystal structure of bismuth pentafluoride, BiF$_5$, was rerefined from single-crystal data. BiF$_5$ crystallizes in the $\alpha$-UF$_5$ structure type in the form of colorless needles. In comparison with the previously reported crystal-structure model [Hebecker (1971). Z. Anorg. Allg. Chem. 384, 111–114], the lattice parameters and fractional atomic coordinates were determined to much higher precision and all atoms were refined anisotropically, leading to a significantly improved structure model. The Bi atom (site symmetry $4/m..$) is surrounded by six F atoms in a distorted octahedral coordination environment. The [BiF$_6$] octahedra are corner-linked to form infinite straight chains extending parallel to [001]. Density functional theory (DFT) calculations at the PBE0/TZVP level of theory were performed on the crystal structure of BiF$_5$ to calculate its IR and Raman spectra. These are compared with experimental data.

1. Chemical context

Bismuth(V) fluoride was first synthesized in the year 1940 (von Wartenberg et al., 1940). Hebecker first determined its crystal structure in 1971 (Hebecker, 1971). During our studies of the chemistry of BiF$_5$, we rerefined its crystal structure on basis of single-crystal data and recorded its IR and Raman spectra.

2. Structural commentary

Bismuth(V) fluoride crystallizes in the tetragonal space group $I4/m$, Pearson symbol tI12 and Wyckoff sequence 87.hba. BiF$_5$ adopts the $\alpha$-UF$_5$ structure type and exhibits Bi–F bond lengths of 1.941 (4) (4x) and 2.1130 (5) Å (2x). The structure consists of chains of trans-corner-sharing [BiF$_6$] octahedra (point group symmetry $4/m..$; Fig. 1) running parallel to the c axis. The chains can be described by the Niggli formula $\bar{c}[BiF_{4/1}F_{2/2}]$. The F1 atom bridges adjacent Bi atoms in the straight chain. As expected, the axial Bi–F1 bond lengths are longer than the four equatorial Bi–F2 bond lengths to the terminal ligands. Sections of the crystal structure showing the chains are shown in Fig. 2.

van der Waals contacts exist between neighbouring chains with interatomic distances of 2.944 (5) Å (F2•••F2$'$) and 2.952 (5) Å (F1•••F2$'$) [symmetry code: (v) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$]. Compared with the distances reported previously (Hebecker, 1971), these are 0.12 Å shorter for $d$(F2•••F2) and 0.05 Å longer for $d$(F1•••F2).

Regarding the crystal packing, a Bi atom is surrounded by 14 other Bi atoms in the shape of a distorted rhombic dodecahedron, which would correspond to the arrangement of the atoms in the W structure type. However, the rhombic dodecahedron is compressed due to the shorter intrachain and the longer interchain Bi•••Bi distances. The F1 atoms reside in...
the octahedral voids of the (idealized) body-centered cubic packing, while the F2 atoms are strongly displaced from these as the octahedra are rotated around the c axis (Fig. 2).

3. Vibrational spectra

IR and Raman spectra were recorded on a polycrystalline sample of BiF₅ at 293 K. Quantum-chemical calculations at the DFT-PBE0/TZVP level of theory (Dovesi et al., 2018; Zicovich-Wilson et al., 2004; Pascale et al., 2004; Maschio et al., 2013) were performed on basis of the crystal structure of BiF₅ to obtain the theoretical IR and Raman spectra. The recorded and calculated spectra are in good agreement, as shown in Figs. 3 and 4. A comparison of the observed and calculated bands is given in Table 1.

![Figure 1](image1.png)

**Figure 1**
The coordination sphere of the Bi atom in the crystal structure of BiF₅. Displacement ellipsoids are drawn at the 70% probability level. [Symmetry codes: (i) x, y, z − 1; (ii) y, −x, z; (iii) −y, x, z; (iv) −x, −y, z.]

the octahedral voids of the (idealized) body-centered cubic packing, while the F2 atoms are strongly displaced from these as the octahedra are rotated around the c axis (Fig. 2).

![Figure 2](image2.png)

**Figure 2**
Crystal structure of BiF₅ viewed along the b axis (left) and the c axis (right). The [BiF₆] octahedra are shown in grey.

<table>
<thead>
<tr>
<th>Band positions (cm⁻¹) and band assignment of the IR and Raman spectra of solid BiF₅ based on the calculated spectrum.</th>
</tr>
</thead>
<tbody>
<tr>
<td>v stretching vibration, δ bending vibration, s symmetric, as asymmetric, – not observed.</td>
</tr>
<tr>
<td>IR</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>630</td>
</tr>
<tr>
<td>–</td>
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<td>–</td>
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<td>–</td>
</tr>
</tbody>
</table>

4. Synthesis and crystallization

Bismuth(III) fluoride (1.05 g, 3.95 mmol) was loaded in a corundum boat and placed inside a tube furnace. By passing diluted fluorine (F₂/Ar, 10:90 v/v, Solvay) over the submitted sample, the reaction mixture was heated to 500 °C and maintained for 2 hours. After cooling to room temperature, the crystals were filtered, washed with ethanol, and dried in vacuo.

![Figure 3](image3.png)

**Figure 3**
Recorded IR spectrum of crystalline BiF₅ in black and calculated IR absorbance spectrum of solid BiF₅ at the DFT-PBE0/TZVP level of theory in red. No bands were observed in the region from 1000 to 4000 cm⁻¹.

![Figure 4](image4.png)

**Figure 4**
Recorded Raman spectrum (532 nm laser) of crystalline BiF₅ in black, calculated Raman spectrum of solid BiF₅ at the DFT-PBE0/TZVP level of theory in red. No bands were observed in the region from 1000 to 4000 cm⁻¹.
material, bismuth(V) fluoride was synthesized at 723 K, using a heating rate of 4 K min\(^{-1}\) from room temperature to 723 K and a holding time of 10 h while diluted fluorine was passed with a flow rate of 5 standard cubic centimeters per minute. After cooling down to room temperature, colorless needles of bismuth(V) fluoride (601 mg, 1.98 mmol, 57\%) were isolated.

5. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements
We thank the X-ray facilities of Dr Sergei I. Ivlev for their great service. We thank Solvay for the kind donation of fluorine. We thank Dr Tambornino for drawing our attention to BiF\(_5\).

References

Table 2: Experimental details.

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>BiF(_5)</th>
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<tbody>
<tr>
<td>Chemical formula</td>
<td>Mr = 303.98</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Tetragonal, I(4/m)</td>
</tr>
<tr>
<td>Temperature (K)</td>
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</tr>
<tr>
<td>(a, c) (Å)</td>
<td>6.4439 (9), 4.2260 (9)</td>
</tr>
<tr>
<td>(V) (Å(^3))</td>
<td>175.48 (6)</td>
</tr>
<tr>
<td>(Z)</td>
<td>2</td>
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<tr>
<td>Radiation type</td>
<td>Mo Kα</td>
</tr>
<tr>
<td>(\mu) (mm(^{-1}))</td>
<td>49.84</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.31 × 0.13 × 0.11</td>
</tr>
</tbody>
</table>

Data collection
Diffractometer | Stoe IPDS 2T |
Absorption correction | Multi-scan (LANA; Koziskova et al., 2016) |
\(T_{\text{min}}, T_{\text{max}}\) | 0.006, 0.078 |
No. of measured, independent and observed \([I > 2\sigma(I)]\) reflections | 1134, 174, 174 |
\(R_{\text{int}}, wR(F^2), S\) | 0.027, 0.042, 1.12 |
No. of reflections | 174 |
No. of parameters | 12 |
\(\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}}\) (e Å\(^{-3}\)) | 0.90, −1.38 |


Stoe (2020). X-AREA. Stoe & Cie, Darmstadt, Germany.
Rerefinement of the crystal structure of BiF₅

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Computing details

Bismuth pentafluoride

Crystal data

BiF₅

$M_r = 303.98$

Tetragonal, $I4/m$

$a = 6.4439 (9)$ Å

$c = 4.2260 (9)$ Å

$V = 175.48 (6)$ Å³

$Z = 2$

$F(000) = 256$

$D_r = 5.753$ Mg m⁻³

Mo Kα radiation, $λ = 0.71073$ Å

Cell parameters from 5333 reflections

$θ = 8.8–60.0°$

$μ = 49.84$ mm⁻¹

$T = 100$ K

Needle, colorless

$0.31 × 0.13 × 0.11$ mm

Data collection

Stoe IPDS 2T
diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4 mm long-focus

Detector resolution: 6.67 pixels mm⁻¹

rotation method, $ω$ scans

Absorption correction: multi-scan

(LANA; Koziskova et al., 2016)

$T_{min} = 0.006, T_{max} = 0.078$

1134 measured reflections

174 independent reflections

174 reflections with $I > 2σ(I)$

$R_{int} = 0.027$

$θ_{max} = 31.8°, θ_{min} = 4.5°$

$h = −9→9$

$k = −9→9$

$l = −5→6$

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R(F^2 > 2σ(F^2)) = 0.016$

$wR(F^2) = 0.042$

$S = 1.12$

174 reflections

12 parameters

0 restraints

Primary atom site location: dual

$w = 1/[σ^2(F_o^2) + (0.0237P)^2 + 2.0256P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(Δ/σ)_{max} < 0.001$

$Δρ_{max} = 0.90$ e Å⁻³

$Δρ_{min} = −1.38$ e Å⁻³

Extinction correction: SHELXL2018/3 (Sheldrick 2015b),

$Fc^r = kFc[1+0.001xFc^2/λ^2sin(2θ)]^{1/4}$

Extinction coefficient: 0.0080 (17)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\(\text{Å}^2\))

<table>
<thead>
<tr>
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<th>(z)</th>
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Atomic displacement parameters (\(\text{Å}^2\))

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</table>

Geometric parameters (\(\text{Å}, \text{°}\))

|          | \(\text{Bi}--\text{F}_2^{i}\) | \(\text{Bi}--\text{F}_2^{ii}\) | \(\text{Bi}--\text{F}_2^{iii}\) | \(\text{F}_2^{i}--\text{Bi}--\text{F}_2^{ii}\) | \(\text{F}_2^{i}--\text{Bi}--\text{F}_2^{iii}\) | \(\text{F}_2^{i}--\text{Bi}--\text{F}_1\) | \(\text{F}_2^{ii}--\text{Bi}--\text{F}_2\) | \(\text{F}_2^{iii}--\text{Bi}--\text{F}_2\) | \(\text{F}_2^{ii}--\text{Bi}--\text{F}_1\) | \(\text{F}_2^{ii}--\text{Bi}--\text{F}_1\) | \(\text{F}_2^{iii}--\text{Bi}--\text{F}_1\) | \(\text{F}_2^{i}--\text{Bi}--\text{F}_1\) |
|----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| \(\text{Bi}--\text{F}_2^{i}\) | 1.941 (4) | 1.941 (4) | 1.941 (4) |
| \(\text{Bi}--\text{F}_2^{ii}\) | 1.941 (4) | 1.941 (4) | 2.1130 (5) |
| \(\text{Bi}--\text{F}_2^{iii}\) | 1.941 (4) | 1.941 (4) | 2.1130 (5) |
| \(\text{F}_2^{i}--\text{Bi}--\text{F}_2^{ii}\) | 90.0 | F2\(\text{iii}--\text{Bi}--\text{F}_1\) | 90.0 |
| \(\text{F}_2^{i}--\text{Bi}--\text{F}_2^{iii}\) | 90.0 | F2\(\text{iii}--\text{Bi}--\text{F}_1\) | 90.0 |
| \(\text{F}_2^{i}--\text{Bi}--\text{F}_2\) | 90.0 | F2\(\text{iii}--\text{Bi}--\text{F}_1\) | 90.0 |
| \(\text{F}_2^{ii}--\text{Bi}--\text{F}_2\) | 180.0 (3) | F2\(\text{ii}--\text{Bi}--\text{F}_1\) | 90.0 |
| \(\text{F}_2^{ii}--\text{Bi}--\text{F}_2\) | 180.0 (3) | F2\(\text{ii}--\text{Bi}--\text{F}_1\) | 90.0 |
| \(\text{F}_2^{ii}--\text{Bi}--\text{F}_1\) | 90.0 | F2\(\text{ii}--\text{Bi}--\text{F}_1\) | 180.0 |
| \(\text{F}_2^{iii}--\text{Bi}--\text{F}_1\) | 90.0 | F2\(\text{iii}--\text{Bi}--\text{F}_1\) | 180.0 |
| \(\text{F}_2^{iii}--\text{Bi}--\text{F}_1\) | 90.0 | F2\(\text{iii}--\text{Bi}--\text{F}_1\) | 180.0 |
| \(\text{F}_2^{iii}--\text{Bi}--\text{F}_1\) | 90.0 | F2\(\text{iii}--\text{Bi}--\text{F}_1\) | 180.0 |

Symmetry codes: (i) \(x, -y, -z\); (ii) \(y, -x, -z\); (iii) \(-y, x, z\); (iv) \(x, y, z+1\); (v) \(x, y, z+1\).

Fractional atomic coordinates and isotropic displacement parameters (\(\text{Å}^2\)).

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<td>0.0275 (8)</td>
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</table>

*supporting information*