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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 α-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.

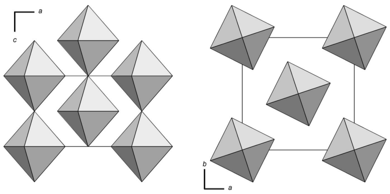
1. Chemical context

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 α-UF_5 structure type and exhibits Bi—F bond lengths of 1.941 (4) (4×) and 2.1130 (5) Å (2×). 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 $^{1}_{\infty}[BiF_{4/1}F_{2/2}]$. 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 ($F2\cdots F2^{v}$) and 2.952 (5) Å ($F1\cdots F2^{v}$) [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 $d(F2\cdots F2)$ and 0.05 Å longer for $d(F1\cdots F2)$.



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 $Bi\cdots Bi$ distances. The F1 atoms reside in

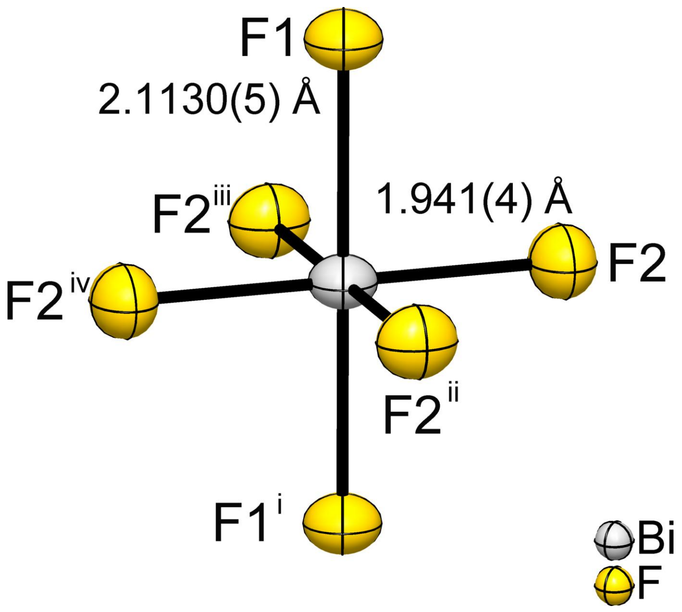


Figure 1
The coordination sphere of the Bi atom in the crystal structure of BiF_5. Displacement ellipsoids are drawn at the 70% probability level. [Symmetry codes: (i) $x, y, z - 1$; (ii) $y, -x, z$; (iii) $-y, x, z$; (iv) $-x, -y, z$.]

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).

3. Vibrational spectra

IR and Raman spectra were recorded on a polycrystalline sample of BiF_5 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 BiF_5 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.

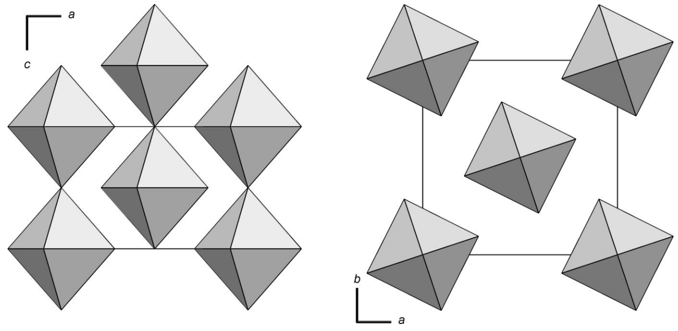


Figure 2
Crystal structure of BiF_5 viewed along the *b* axis (left) and the *c* axis (right). The [BiF_6] octahedra are shown in grey.

Table 1
Band positions (cm^{-1}) and band assignment of the IR and Raman spectra of solid BiF_5 based on the calculated spectrum.

ν = stretching vibration, δ = bending vibration, *s* = symmetric, *as* = asymmetric, – = not observed.

IR		Raman		Assignment
ν_{calc}	ν_{obs}	ν_{calc}	ν_{obs}	
630	618	–	–	ν_{as}(Bi—F2) + δ(Bi—F1—Bi)
–	–	607	596, 593	ν_s(Bi—F2)
–	–	578	571, 567	ν_{as}(Bi—F2)
453	441	–	–	ν_{as}(Bi—F_μ)
–	–	256	254	δ(F2—Bi—F2)
202	–	–	–	δ(F—Bi—F)
168	–	–	–	δ(F—Bi—F)
–	–	177	164	δ(F2—Bi—F1)
125	–	–	–	δ(F2—Bi—F1) + ν_{as}(Bi—F1)

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 (F_2/Ar, 10:90 *v*/*v*, Solvay) over the submitted

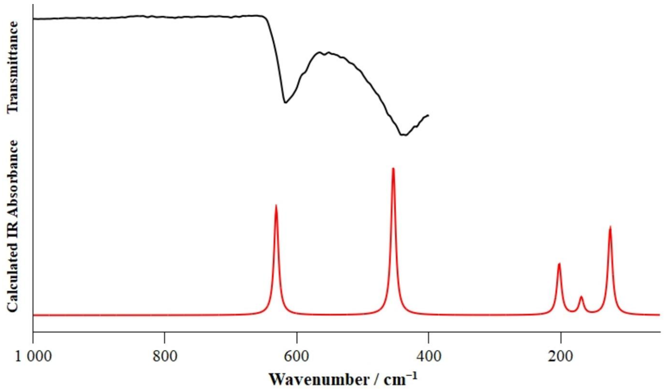


Figure 3
Recorded IR spectrum of crystalline BiF_5 in black and calculated IR absorbance spectrum of solid BiF_5 at the DFT-PBE0/TZVP level of theory in red. No bands were observed in the region from 1000 to 4000 cm^{-1}.

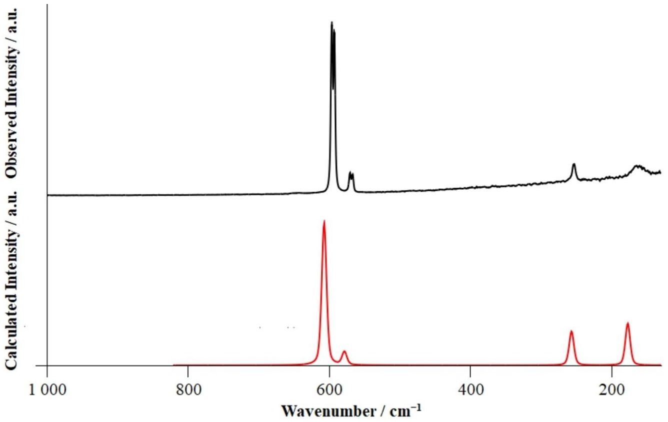


Figure 4
Recorded Raman spectrum (532 nm laser) of crystalline BiF_5 in black, calculated Raman spectrum of solid BiF_5 at the DFT-PBE0/TZVP level of theory in red. No bands were observed in the region from 1000 to 4000 cm^{-1}.

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.

Table 2
Experimental details.

Crystal data	
Chemical formula	BiF_5
M_r	303.98
Crystal system, space group	Tetragonal, *I*4/*m*
Temperature (K)	100
a, *c* (Å)	6.4439 (9), 4.2260 (9)
V ($Å^3$)	175.48 (6)
Z	2
Radiation type	Mo *Kα*
μ (mm^{-1})	49.84
Crystal size (mm)	0.31 × 0.13 × 0.11
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Multi-scan (*LANA*; Koziskova *et al.*, 2016)
$T_{\min}$, $T_{\max}$	0.006, 0.078
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	1134, 174, 174
R_{int}	0.027
$(\sin \theta/\lambda)_{\max}$ ($Å^{-1}$)	0.742
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.016, 0.042, 1.12
No. of reflections	174
No. of parameters	12
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e $Å^{-3}$)	0.90, −1.38

Computer programs: *X-AREA* (Stoe, 2020), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2022), *publCIF* (Westrip, 2010) and *ShelXle* (Hübschle *et al.*, 2011).

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Computing details

Bismuth pentafluoride

Crystal data

BiF_5
$M_r = 303.98$
Tetragonal, $I4/m$
$a = 6.4439$ (9) Å
$c = 4.2260$ (9) Å
$V = 175.48$ (6) Å^3
$Z = 2$
$F(000) = 256$

$D_x = 5.753$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5333 reflections
$\theta = 8.8$–$60.0°$
$\mu = 49.84$ 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-fine 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 $I > 2\sigma(I)$
$R_{\text{int}} = 0.027$
$\theta_{\max} = 31.8°$, $\theta_{\min} = 4.5°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -5 \rightarrow 6$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.042$
$S = 1.12$
174 reflections
12 parameters
0 restraints
Primary atom site location: dual

$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 2.0256P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.90$ e Å^{-3}
$\Delta\rho_{\min} = -1.38$ e Å^{-3}
Extinction correction: SHELXL2018/3 (Sheldrick 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
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 (Å²)

	x	y	z	$U_{\mathrm{iso}}*/U_{\mathrm{eq}}$
Bi	0.000000	0.000000	0.000000	0.0199 (2)
F1	0.000000	0.000000	0.500000	0.0255 (15)
F2	0.2859 (7)	0.0950 (7)	0.000000	0.0275 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Bi	0.0225 (2)	0.0225 (2)	0.0147 (2)	0.000	0.000	0.000
F1	0.029 (2)	0.029 (2)	0.018 (3)	0.000	0.000	0.000
F2	0.0232 (17)	0.0320 (19)	0.0274 (19)	−0.0031 (14)	0.000	0.000

Geometric parameters (Å, º)

Bi—F2$^{\mathrm{i}}$	1.941 (4)	Bi—F2	1.941 (4)
Bi—F2$^{\mathrm{ii}}$	1.941 (4)	Bi—F1	2.1130 (5)
Bi—F2$^{\mathrm{iii}}$	1.941 (4)	Bi—F1$^{\mathrm{iv}}$	2.1130 (5)
F2$^{\mathrm{i}}$—Bi—F2$^{\mathrm{ii}}$	90.0	F2$^{\mathrm{iii}}$—Bi—F1	90.0
F2$^{\mathrm{i}}$—Bi—F2$^{\mathrm{iii}}$	90.0	F2—Bi—F1	90.0
F2$^{\mathrm{ii}}$—Bi—F2$^{\mathrm{iii}}$	180.0 (3)	F2$^{\mathrm{i}}$—Bi—F1$^{\mathrm{iv}}$	90.0
F2$^{\mathrm{i}}$—Bi—F2	180.0	F2$^{\mathrm{ii}}$—Bi—F1$^{\mathrm{iv}}$	90.0
F2$^{\mathrm{ii}}$—Bi—F2	90.0	F2$^{\mathrm{iii}}$—Bi—F1$^{\mathrm{iv}}$	90.0
F2$^{\mathrm{iii}}$—Bi—F2	90.0	F2—Bi—F1$^{\mathrm{iv}}$	90.0
F2$^{\mathrm{i}}$—Bi—F1	90.0	F1—Bi—F1$^{\mathrm{iv}}$	180.0
F2$^{\mathrm{ii}}$—Bi—F1	90.0	Bi$^{\mathrm{v}}$—F1—Bi	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 (Å²).

	x	y	z	U_{iso}
Bi	0	0	0	0.0199 (2)
F1	0	0	1/2	0.0255 (15)
F2	0.2859 (7)	0.0950 (7)	0	0.0275 (8)