

# Nitrosonium tetrafluoridoborate, $\text{NOBF}_4$

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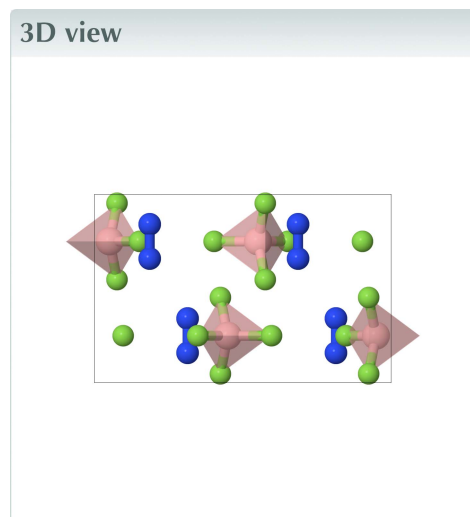
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Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

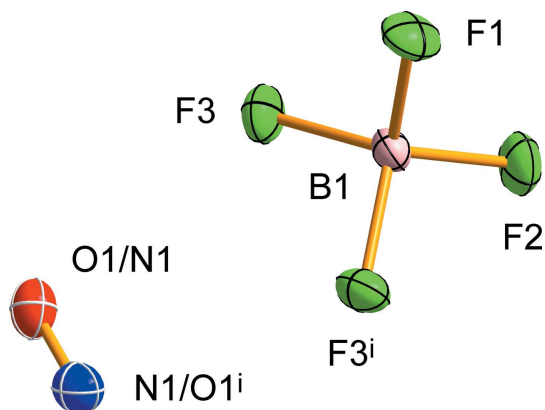
The crystal structure of oxidonitrogen(1+) tetrafluoridoborate (nitrosonium tetrafluoridoborate),  $\text{NO}^+\text{BF}_4^-$ , was refined on the basis of single-crystal X-ray diffraction data at 150 K. The compound crystallizes in the baryte structure type with orthorhombic  $Pnma$  symmetry. The crystal structure exhibits cationic disorder with equal occupation of N and O atoms at the same site.



## Structure description

Numerous nitrosonium fluoro salts are known (*e.g.*, Sunder *et al.*, 1979; Mazej *et al.*, 2009) and several of them have been structurally characterized (*e.g.*, Adam *et al.*, 1996). Nonetheless, for nitrosonium tetrafluoridoborate ( $\text{NOBF}_4$ ), which is an efficient one-electron oxidant, nitrosating and diazotizing agent (Olah *et al.*, 2004), only the unit-cell parameters derived from X-ray powder diffraction data have been reported previously ( $a = 6.983 \text{ \AA}$ ,  $b = 8.911 \text{ \AA}$ ,  $c = 5.675 \text{ \AA}$ , space group  $Pbnm$ ; Evans *et al.*, 1964). Nitrosonium tetrafluoridoborate crystallizes in the baryte ( $\text{BaSO}_4$ ) structure type and is isotypic with ammonium, alkali metal (K, Rb, Cs) (Clark & Lynton, 1969) and dioxygen(1+) tetrafluoridoborates (Wilson *et al.*, 1971). The current unit cell (Table 1) refined from single-crystal X-ray data at 150 K is in good agreement with the aforementioned previously published values.

The asymmetric unit of the  $\text{NOBF}_4$  crystal structure is composed of atoms B1, F1, and F2, which coincide with the crystallographic mirror plane (Wyckoff position 4c; site symmetry  $m.$ ), whereas atoms F3 and disordered N1/O1, are located on general positions (Wyckoff position 8d) (Fig. 1). The  $\text{BF}_4^-$  anion has a slightly distorted tetrahedral shape, with F–B–F bond angles ranging from  $108.42(6)$  to  $111.11(7)^\circ$  and B–F bond lengths of  $1.3863(10)$ ,  $1.3872(10)$  and  $1.4042(6) \text{ \AA}$  involving atoms F1, F2, and F3, respectively. Similar values were observed in  $\text{NO}_2\text{BF}_4$  (Krossing *et al.*, 2007) and other  $\text{BF}_4^-$  salts (Radan *et al.*, 2011; Lozinšek *et al.*, 2009) or complexes (Tavčar & Žemva, 2005). The  $\text{NO}^+$  cation is disordered across a crystallographic mirror plane, with atoms N1 and O1 sharing

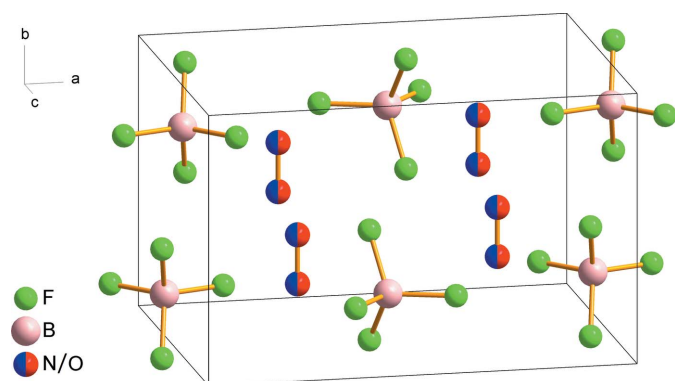


**Figure 1**  
Expanded asymmetric unit of  $\text{NOBF}_4$  with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i)  $x, -y + \frac{1}{2}, z$ .]

the same site. It is noteworthy that the orientational cationic disorder in the salt  $\text{NOBF}_4$  was studied previously by heat capacity measurements from 10 to 304 K (Callanan *et al.*, 1981). The N–O bond length of 1.0216 (10) Å in  $\text{NOBF}_4$  is similar to the values reported for other nitrosonium fluoride salts, for instance: 1.052 (6) Å in  $\text{NOUF}_6$  at 100 K (Scheibe *et al.*, 2016) and 1.012 (6) Å in  $\text{NOSbF}_6$  at 150 K (Mazej & Goreshnik, 2021), with both salts also exhibiting disordered  $\text{NO}^+$  groups. Each anion is surrounded by seven cations and *vice versa*, with fourteen (N/O)··F contacts shorter than 3.0 Å; the shortest contacts [2.6211 (6), 2.6222 (6), and 2.6560 (6) Å] involve atom F3. In the crystal structure, the  $\text{NO}^+$  cations are oriented parallel to the *b* axis (Fig. 2).

### Synthesis and crystallization

A sample of  $\text{NOBF}_4$  suitable for single-crystal X-ray diffraction was obtained from a commercial source (Alfa Aesar, 98%). Crystals were placed onto a watch glass and covered with a protective layer of perfluorodecalin (ABCR, AB102850, 98%, *cis* and *trans*) inside an argon-filled glovebox (MBraun,  $\text{H}_2\text{O} < 0.5$  ppm). A suitable colorless crystal was



**Figure 2**  
View of the packing in the unit cell of the  $\text{NOBF}_4$  crystal structure.

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	$\text{NO}^+\text{BF}_4^-$
$M_r$	116.82
Crystal system, space group	Orthorhombic, $Pnma$
Temperature (K)	150
$a, b, c$ (Å)	8.8588 (3), 5.6268 (2), 6.8460 (2)
$V$ (Å <sup>3</sup> )	341.25 (2)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.31
Crystal size (mm)	0.24 × 0.19 × 0.12
Data collection	
Diffractometer	New Gemini, Dual, Cu at home/near, Atlas
Absorption correction	Analytical ( <i>CrysAlis PRO</i> ; Rigaku OD, 2021)
$T_{\min}, T_{\max}$	0.948, 0.975
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	16165, 976, 824
$R_{\text{int}}$	0.054
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.864
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.025, 0.081, 1.10
No. of reflections	976
No. of parameters	37
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.22, -0.28

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SUPERFLIP* (Palatinus & Chapuis, 2007; Palatinus & van der Lee, 2008; Palatinus *et al.*, 2012), *SHELXL* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009), *DIAMOND* (Brandenburg, 2005) and *publCIF* (Westrip, 2010).

selected under a polarizing microscope outside the glovebox, mounted on a MiTeGen Dual Thickness MicroLoop with the aid of Baysilone-Paste, and quickly transferred into a cold nitrogen stream of the X-ray diffractometer.

### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The coordinates and anisotropic displacement parameters of the disordered atoms O1 and N1 sharing the same site were constrained to be equal (EXYZ, EADP) and their site occupancy factor set to 0.5.

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## full crystallographic data

*IUCrData* (2021). 6, x211215 [https://doi.org/10.1107/S2414314621012153]

Nitrosonium tetrafluoridoborate, NOBF<sub>4</sub>

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## Oxidonitrogen(1+) tetrafluoridoborate

*Crystal data*

NO <sup>+</sup> ·BF <sub>4</sub> <sup>-</sup>	$D_x = 2.274 \text{ Mg m}^{-3}$
$M_r = 116.82$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Orthorhombic, <i>Pnma</i>	Cell parameters from 8015 reflections
$a = 8.8588 (3) \text{ \AA}$	$\theta = 3.8\text{--}37.6^\circ$
$b = 5.6268 (2) \text{ \AA}$	$\mu = 0.31 \text{ mm}^{-1}$
$c = 6.8460 (2) \text{ \AA}$	$T = 150 \text{ K}$
$V = 341.25 (2) \text{ \AA}^3$	Irregular, clear colourless
$Z = 4$	$0.24 \times 0.19 \times 0.12 \text{ mm}$
$F(000) = 224$	

*Data collection*

New Gemini, Dual, Cu at home/near, Atlas diffractometer	$T_{\min} = 0.948, T_{\max} = 0.975$
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source	16165 measured reflections
Graphite monochromator	976 independent reflections
Detector resolution: $10.6426 \text{ pixels mm}^{-1}$	824 reflections with $I > 2\sigma(I)$
$\omega$ scans	$R_{\text{int}} = 0.054$
Absorption correction: analytical (CrysAlisPro; Rigaku OD, 2021)	$\theta_{\max} = 37.9^\circ, \theta_{\min} = 3.8^\circ$
	$h = -15 \rightarrow 15$
	$k = -9 \rightarrow 9$
	$l = -11 \rightarrow 11$

*Refinement*

Refinement on $F^2$	0 restraints
Least-squares matrix: full	Primary atom site location: iterative
$R[F^2 > 2\sigma(F^2)] = 0.025$	$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.0254P]$
$wR(F^2) = 0.081$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{\max} < 0.001$
976 reflections	$\Delta\rho_{\max} = 0.22 \text{ e \AA}^{-3}$
37 parameters	$\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
F1	0.34796 (7)	0.250000	0.97160 (7)	0.02402 (13)	

F2	0.59689 (6)	0.250000	0.88293 (9)	0.02508 (13)	
F3	0.42423 (4)	0.45243 (7)	0.70118 (6)	0.02149 (11)	
B1	0.44886 (9)	0.250000	0.81682 (11)	0.01500 (14)	
O1	0.31375 (5)	0.34078 (9)	0.35238 (7)	0.02274 (12)	0.5
N1	0.31375 (5)	0.34078 (9)	0.35238 (7)	0.02274 (12)	0.5

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
F1	0.0301 (3)	0.0280 (3)	0.0140 (2)	0.000	0.00714 (18)	0.000
F2	0.0191 (2)	0.0290 (3)	0.0272 (3)	0.000	-0.01088 (19)	0.000
F3	0.02134 (18)	0.02461 (19)	0.01852 (18)	0.00146 (13)	-0.00060 (11)	0.00719 (12)
B1	0.0152 (3)	0.0187 (3)	0.0111 (3)	0.000	-0.0013 (2)	0.000
O1	0.0181 (2)	0.0266 (2)	0.0235 (2)	0.00024 (16)	-0.00237 (14)	0.00430 (17)
N1	0.0181 (2)	0.0266 (2)	0.0235 (2)	0.00024 (16)	-0.00237 (14)	0.00430 (17)

*Geometric parameters (Å, °)*

F1—B1	1.3863 (10)	F3—B1	1.4042 (6)
F2—B1	1.3872 (10)	O1—N1 <sup>i</sup>	1.0216 (10)
F1—B1—F2	111.11 (7)	F2—B1—F3 <sup>i</sup>	109.32 (4)
F1—B1—F3 <sup>i</sup>	109.32 (4)	F2—B1—F3	109.32 (4)
F1—B1—F3	109.31 (4)	F3 <sup>i</sup> —B1—F3	108.42 (6)

Symmetry code: (i)  $x, -y+1/2, z$ .