Nitrosonium tetrafluoridoborate, NOBF₄

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The crystal structure of oxidonitrogen(1+) tetrafluoridoborate (nitrosonium tetrafluoridoborate), NO⁺BF₄⁻, 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 fluorido 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 (NOBF₄), 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 Å, b = 8.911 Å, c = 5.675 Å, space group Pbnm; Evans et al., 1964). Nitrosonium tetrafluoridoborate crystallizes in the baryte (BaSO₄) 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 NOBF₄ 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 BF₄⁻ anion has a slightly distorted tetrahedral shape, with F—B—F bond angles ranging from 108.42 (6) to 111.11 (7)° and B—F bond lengths of 1.3863 (10), 1.3872 (10) and 1.4042 (6) Å involving atoms F1, F2, and F3, respectively. Similar values were observed in NO₂BF₄ (Krossing et al., 2007) and other BF₄⁻ salts (Radan et al., 2011; Lozinšek et al., 2009) or complexes (Tučar & Žemva, 2005). The NO⁺ cation is disordered across a crystallographic mirror plane, with atoms N1 and O1 sharing...
the same site. It is noteworthy that the orientational cationic disorder in the salt NOBF₄ 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 NOBF₄ is similar to the values reported for other nitrosonium fluoride salts, for instance: 1.052 (6) Å in NOUF₆ at 100 K (Scheibe et al., 2016) and 1.012 (6) Å in NOSbF₆ at 150 K (Mazej & Goreshnik, 2021), with both salts also exhibiting disordered 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 NO⁺ cations are oriented parallel to the b axis (Fig. 2).

Synthesis and crystallization

A sample of NOBF₄ 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, H₂O < 0.5 ppm). A suitable colorless crystal was 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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Table 1

| Crystal data | NO⁺BF₄⁻ |
|--------------|--------|
| 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 (Å³) | 341.25 (2) |
| Z | 4 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 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 (CrysAlis PRO; Rigaku OD, 2021) |
T_min, T_max | 0.948, 0.975 |
No. of reflections | 16165, 976, 824 |
R(int) | 0.054 |
(sin θ/λ)max (Å⁻¹) | 0.864 |
R[F² > 2σ(F²)], wR(F²), S | 0.025, 0.081, 1.10 |
No. of reflections | 976 |
No. of parameters | 37 |
Δρ_max, Δρ_min (e Å⁻³) | 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).

Figure 1

Expanded asymmetric unit of NOBF₄ with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) x, −y + 1/2, z.]

Figure 2

View of the packing in the unit cell of the NOBF₄ crystal structure.
data reports

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Oxidonitrogen(1+) tetrafluoridoborate

Crystal data
NO⁺·BF₄⁻  
Mr = 116.82
Orthorhombic, Pnma
a = 8.8588 (3) Å
b = 5.6268 (2) Å
c = 6.8460 (2) Å
V = 341.25 (2) Å³
Z = 4
F(000) = 224

Data collection
New Gemini, Dual, Cu at home/near, Atlas diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 10.6426 pixels mm⁻¹
ω scans
Absorption correction: analytical
(CrysAlisPro; Rigaku OD, 2021)

Refinement
Refinement on F²
Least-squares matrix: full
R(F² > 2σ(F²)) = 0.025
wR(F²) = 0.081
S = 1.10
976 reflections
37 parameters
0 restraints
Primary atom site location: iterative

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|   | x     | y     | z     | Ueq1/2 (Å²) | Occ. (<1) |
|---|-------|-------|-------|-------------|-----------|
| F1| 0.34796 (7) | 0.250000 | 0.97160 (7) | 0.02402 (13) |           |
\begin{tabular}{lcccc}
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) \\
N1 & 0.31375 (5) & 0.34078 (9) & 0.35238 (7) & 0.02274 (12) \\
\end{tabular}

\textit{Atomic displacement parameters (Å$^2$)}

\begin{tabular}{lcccccc}
 & $U_{11}$ & $U_{22}$ & $U_{33}$ & $U_{12}$ & $U_{13}$ & $U_{23}$ \\
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) \\
\end{tabular}

\textit{Geometric parameters (Å, º)}

\begin{tabular}{lcccc}
F1—B1 & 1.3863 (10) & F3—B1 & 1.4042 (6) \\
F2—B1 & 1.3872 (10) & O1—N1$^i$ & 1.0216 (10) \\
F1—B1—F2 & 111.11 (7) & F2—B1—F3$^i$ & 109.32 (4) \\
F1—B1—F3$^i$ & 109.32 (4) & F2—B1—F3 & 109.32 (4) \\
F1—B1—F3 & 109.31 (4) & F3$^i$—B1—F3 & 108.42 (6) \\
\end{tabular}

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

\textit{IUCrData (2021). 6, x211215 data-2}