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Synthesis and mutual transformations of nitronium tetrakis(nitrooxy)- and tetrakis(2,2,2-trifluoroacetoxy)borates†

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Nitronium borates of $NO_2[B(OX)_4]$ type with X = CF_3CO and NO_2 as ligands were synthesized, and their structures were determined by powder X-ray diffraction. Crystalline $NO_2[B(ONO_2)_4]$ is relatively stable at room temperature and undergoes transformation to B_2O_3 upon heating. The $[B(CF_3COO)_4]^-$ anion was obtained for the first time and characterized as a structural fragment of a solid compound. The possibility of reversible modification of the complex anion by replacement of the nitrate or trifluoroacetate ligand was demonstrated for the first time by the mutual transformations of $NO_2[B(ONO_2)_4]$ and $NO_2[B(CF_3COO)_4]$.

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1. Introduction

Nitrate and trifluoroacetate moieties are used in the synthesis of various complex compounds. Nitronium salts available at the moment include a large number of metal–nitrate structures, such as $[Fe(NO_3)_4]^-$,[1,2] $[Zr(NO_3)_5]^-$,[2] $[Al(NO_3)_4]^-$,[3–5] $[Au(NO_3)_4]^-$,[6,7] $[Ga(NO_3)_4]^-$,[8,9] $[Hf(NO_3)_5]^-$,[10] $[Th(NO_3)_6]^{2-}$,[11,12] $[UO_2(NO_3)_3]^-$,[13] and $[In(NO_3)_4]^-$.[12] However, only one nitronium salt is known, which has the trifluoroacetate ligands at the central metal atom in the coordination sphere of the anion, namely, $[NO_2]_2[Sn(CF_3COO)_6]$.[14,15] Nitronium salts containing $[B(NO_3)_4]^-$ and $[B(CF_3COO)_4]^-$ anions are unknown. Since nitronium tetranitroborate $NO_2[B(NO_3)_4]$ (**1**) contains a large excess of oxygen, it seems to be potentially interesting as a rocket propellant oxidizer. The main advantage of compound **1** over the known tetraperchloratoborate $NO_2[B(ClO_4)_4]$[16] is that it is halogen-free and thus quite attractive from the standpoint of green applications. Related tetranitroborates with alkylammonium or alkali metal cations $M^+[B(NO_3)_4]^-$ were synthesized from the corresponding tetrachloroborates and N_2O_4 (Scheme 1.1).[17–20] However, alkali metal tetranitratoborates[19,20] appeared to be very unstable in contrast to alkylammonium salts[17,18] and complexes of $B(NO_3)_3$ with amines.[21]

Among the borates of $M^+[B(OX)_4]^-$ type, tetraperchloratoborates (X = ClO_3) have also been synthesized previously.[16,20,22] For example, the nitronium salt $NO_2[B(ClO_4)_4]$ was obtained from BCl_3 and NO_2ClO_4 in carbonyl dichloride at −78 °C (Scheme 1.2).[16] This compound is of interest from the standpoint of its practical application as a propellant oxidizer. The addition of the corresponding (alkyl)ammonium chloride to the reaction mass made it possible to obtain tetraperchloratoborates containing (alkyl)ammonium cations (Scheme 1.3). Various tetraperchloratoborates $M^+[B(ClO_4)_4]^-$ were synthesized using a modified method from BCl_3 and metal,[23] ammonium, or nitronium[24] perchlorates in anhydrous $HClO_4$ (Scheme 1.4). In addition, alkali metal tetraperchloratoborates

$$M[BCl_4] + 4N_2O_4 \longrightarrow M[B(NO_3)_4] + 4NOCl \quad (M = K, Cs, Me_4N) \quad (1.1)$$

$$BCl_3 + 4NO_2ClO_4 \longrightarrow NO_2[B(ClO_4)_4] + 3NO_2Cl \quad (1.2)$$

$$BCl_3 + 5NO_2ClO_4 + R_4NCl \longrightarrow NR_4[B(ClO_4)_4] + 3NO_2Cl \quad (R = H, Alk) \quad (1.3)$$

$$BCl_3 + 3HClO_4 + MClO_4 \longrightarrow M[B(ClO_4)_4] + 3HCl \quad (M = NH_4, NO_2, K, Rb, Cs) \quad (1.4)$$

$$M[BCl_4] + 4HClO_4 \longrightarrow M[B(ClO_4)_4] + 4HCl \quad (M = K, Rb, Cs) \quad (1.5)$$

Scheme 1 Known methods for the synthesis of compounds of $M^+[B(OX)_4]^-$ type (X = ClO_3, NO_2).

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† Electronic supplementary information (ESI) available: The spectral data, crystallographic data and refinement parameters. CCDC 1980143 and 1985253. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0nj02835e

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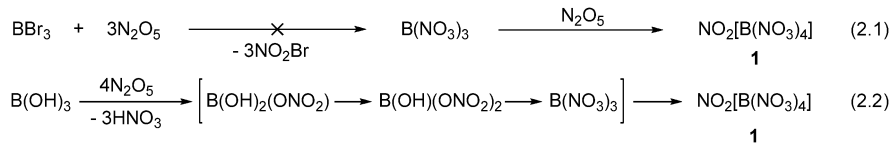

Scheme 2 Synthesis of $NO_2[B(NO_3)_4]$ (**1**).

were synthesized *via* the reaction of $M[BCl_4]$ with anhydrous $HClO_4$ (Scheme 1.5).[23]

It should be noted that the $[B(CF_3COO)_4]^-$ anion was never obtained as a structural fragment of an individual crystalline compound, although it was detected by mass spectrometry.[25] The aim of this work was to develop methods for the synthesis of previously unknown nitronium borates $NO_2^+[B(NO_3)_4]^-$ (**1**) and $NO_2^+[B(CF_3COO)_4]^-$ (**2**) and to study their properties.

2. Results and discussion

2.1 Nitronium tetrakis(nitrooxy)borate: synthesis and properties

Complexation between Lewis acids (LAs) including metal nitrates and N_2O_5 results in the formation of $[NO_2^+]_n[M(NO_3)_m]^-$ species (see the Introduction and ref. 26). We believe that the addition of N_2O_5 to $B(NO_3)_3$ treated as an LA is the simplest and most convenient method for the synthesis of compound **1**. However, $B(NO_3)_3$ is very unstable under normal conditions. Attempts to synthesize this compound by the reaction of BCl_3 with N_2O_5 (resulting in B_2O_3)[27] or by the reaction of BCl_3 with NO_3Cl[28] were unsuccessful. We also failed to synthesize boron trinitrate or nitronium salt **1** by the reaction of BBr_3 with an excess of N_2O_5 (Scheme 2.1). Even at −70 °C, the reaction proceeded very vigorously with the elimination of NO_2Br. It seems that the monomolecular elimination of NO_2Hal from the intermediate $B(NO_3)_2Hal$ leads to the formation of $O{=}BONO_2$,[28] and then B_2O_3 is formed.

We developed a "one-pot" method for the synthesis of compound **1** from boric acid and N_2O_5 (Scheme 2.2). Gradual nitration of hydroxyl groups was followed by liquefaction of the solid mixture. The nitro ester moieties of the intermediate dinitrate $B(OH)(ONO_2)_2$ as electron-withdrawing groups strongly deactivate the unreacted hydroxyl substituent. To increase the electrophilicity of the reactant, nitric acid was preliminarily added to the reaction mixture in order to transform covalent dinitrogen pentoxide into the ionic form $[NO_2]^+[NO_3]^-$[29–31] and thus facilitate nitration. Since the interaction of boric acid with N_2O_5 produces HNO_3, no additional nitric acid may be needed, but in this case the reaction proceeds slower and with a lower yield. Boron trinitrate reacts with N_2O_5 and successfully transforms into the crystalline salt $NO_2^+[B(NO_3)_4]^-$ (**1**) (Scheme 2.2).

Since the structure of compound **1** was previously unknown, we carried out B3LYP/6-311++g(d,p) calculations,[32] but a stable gas-phase configuration of molecule **1** was not determined. The calculations unambiguously led to the decay of compound **1** with elimination of either N_2O_5, or N_2O_4 and O_2. Therefore, we believe that an isolated molecule of $NO_2[B(NO_3)_4]$ cannot be stable.

In the Raman spectrum of solid compound **1**, symmetric vibrations $\nu^s_{NO_2}$ of linear nitronium cations appear as a strong line at 1400 cm^{-1} (Fig. S1, ESI†). The IR spectrum of solid **1** also exhibits the corresponding bands of the NO_2^+ ion, *viz.*, $\nu^{comb}_{NO_2}$ at 3748 cm^{-1} and $\nu^{as}_{NO_2}$ at 2296–2388 cm^{-1} (Fig. S2, ESI†). It may be emphasized that asymmetric vibrations of the nitro ester moieties appear in the vibrational spectra of the $[B(NO_3)_4]^-$ anion of compound **1** as four $\nu^{as}_{NO_2}$ bands in the range of 1599–1653 cm^{-1} (Raman spectrum, see ref. 26 and 33) and in the range of 1610–1675 cm^{-1} (IR spectrum). Symmetric vibrations $\nu^s_{NO_2}$ of nitro ester groups appear in the Raman spectrum of compound **1** as two strong broad bands at 1311 and 1325 cm^{-1}, the latter being more intense (Fig. S1, ESI†). As for the IR spectrum, the $\nu^s_{NO_2}$ vibrations appear as bands in the range of 1240–1320 cm^{-1} (Fig. S2, ESI†).

The ^{14}N NMR spectra of solutions of nitronium tetranitratoborate **1** demonstrate an interesting feature. The signals δ(N) at −45 ± 2 ppm are typical of nitrate groups, but the shift from −90 ppm (in a sulfolane solution) to −63 ppm ($MeNO_2$) is far from the shifts characteristic of nitronium salts (−130 ± 3 ppm),[26,34,35] and are close to the shifts of covalent nitro esters (N_2O_5, CF_3COONO_2 and $C_2F_5COONO_2$).[36–38] We suppose that dissolved nitronium tetranitroborate **1** can reversibly decompose into covalent N_2O_5 and boron trinitrate. Both NMR data and the results of calculations (see above) confirm that the isolated molecule of $NO_2[B(NO_3)_4]$ is unstable similar to the isolated N_2O_5 molecule.[39–41]

The structure of $NO_2[B(NO_3)_4]$ (**1**) was determined by powder X-ray diffraction analysis (Fig. 1). The space group is $I\bar{4}$, and the

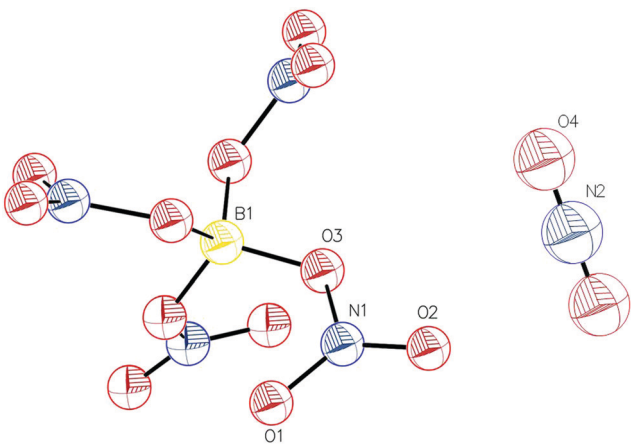

Fig. 1 General view of compound **1** in a crystal. Isotropic displacement parameters for atoms are drawn at 50% probability.

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$$2\ NO_2[B(NO_3)_4] \xrightarrow[-\ N_2O_5,\ -\ N_2O_4,\ -\ O_2]{>\ 170\ ^\circ C} B_2O_3$$
1

Scheme 3 Thermolysis of $NO_2[B(NO_3)_4]$ (**1**).

lattice constants are $a = 9.10760(9)$ Å and $c = 5.86902(8)$ Å. In the crystal, all NO_3 groups of the tetranitratoborate anion are symmetrically equivalent. The NO_2^+ cation forms four short contacts N···O (N···O distance 2.697 Å) with the oxygen atoms of the anion.

It is known that at room temperature, symmetric sulfate $(NO_2)_2SO_4$ undergoes very fast dimerization to the relatively stable disulfate $(NO_2)_2S_2O_7$ with the elimination of N_2O_5.[26] Unlike the unstable dinitronium sulfate[26] and alkali metal tetranitratoborates,[19] thermal decomposition of solid nitratoborate **1** occurs at higher temperatures with the formation of nitrogen oxides (Scheme 3 and Fig. 2). Thermolysis of borate **1** features a one-step mass loss ($\Delta m = -82\%$, extrapolated onset temperature $T_{eo} = 83$ °C). The process is accompanied by an endothermic heat effect of -530 J g^{-1}. After heating to 300 °C (Fig. 2), complete conversion of compound **1** to B_2O_3 occurs (Scheme 3).

In Table 1, the characteristics of nitronium borate **1** are compared with those of known oxidizing agents and related structures.

Table 1 Characteristics of compound **1** and other oxidizers

Compound	Gross formula	[O][a] (%)	α	T_{dec} (°C)
$NO_2[B(ClO_4)_4]$[b]	$B_1Cl_4N_1O_{18}$	65.1	13.3	—[c]
$NO_2[B(NO_3)_4]$	$B_1N_5O_{14}$	65.6	9.3	~83
NH_4ClO_4[b]	$ClH_4N_1O_4$	34	2.7	~150
$NH_4N(NO_2)_2$	$H_4N_4O_4$	25.8	2.0	~150[42]
NH_4NO_3	$H_4N_2O_3$	20	1.5	~170
$(CH_3)_4N[B(NO_3)_4]$	$B_1C_4H_{12}N_5O_{12}$	−16.8	0.77	~75[18]
$(CH_3)_3N\ B(NO_3)_3$[21]	$B_1C_3H_9N_4O_9$	−18.8	0.58	—[c]

[a] [O] is the oxygen balance, α is the oxidizer excess ratio and T_{dec} is the temperature of the onset of intense decomposition. [b] The oxidizer isn't "green". [c] No data are available.

2.2 Nitronium tetrakis(trifluoroacetato)borate

Nitronium borate $NO_2[B(CF_3COO)_4]$ (**2**) was synthesized by the reaction of boron tris(trifluoroacetate) **3** with TFAN (Scheme 4A and B) and from boric acid (Scheme 4C). In the former case, mixing N_2O_5 and trifluoroacetic acid anhydride led to the gradual formation of trifluoroacetyl nitrate[36] that added to LA **3**, and crystals of the nitronium salt **2** precipitated. Preliminary addition of trifluoroacetic acid to $B(CF_3COO)_3$ (**3**) (see Scheme 4A) catalyzed the formation of compound **2** probably due to the formation of intermediate **4**. The yield of compound **2** was 72–91% (Scheme 4C). We believe that the synthesis of salt **2** from boric acid (Scheme 4C) involves nitration of hydroxyl groups followed by replacement of nitro groups by trifluoroacetyl ones. Nitronium cation is the most electrophilic particle; therefore, it is obvious that $B(NO_3)_3$ and/or compound **1** were formed as intermediates. Besides, we established that the interaction of hydroxyl groups of boric acid with excess of TFAA leads to dehydration of the acid to give B_2O_3 rather than $B(CF_3COO)_3$ (**3**).

The trifluoroacetyl moiety can replace the nitrate anion of inorganic nitrates, the covalent nitro ester group and even one of two nitronium cations in dinitronium sulfates.[14,26,37,43,44] Therefore, replacement of the nitrate moieties of $B(NO_3)_3$ and $[B(NO_3)_4]^-$ by the trifluoroacetyl group is real, and we proved it *via* the direct synthesis of borate **2** from borate **1** (Scheme 4E). It should be noted that the reverse reaction, namely, substitution of trifluoroacetate groups in the coordination sphere of the central boron atom of compound **2** by nitrate groups also successfully led to the formation of compound **1** (Scheme 4D).

The Raman (Fig. S3, ESI†) and IR spectra (Fig. S4, ESI†) of crystalline compound **2** exhibit clearly seen bands in the range from 1757 to 1792 cm^{-1} corresponding to carbonyl groups. Quantum chemical calculations demonstrated that the experimental (Fig. S3, ESI†) and calculated (Fig. S5, ESI†) Raman frequencies of the $[B(CF_3COO)_4]^-$ ion are close. In the Raman

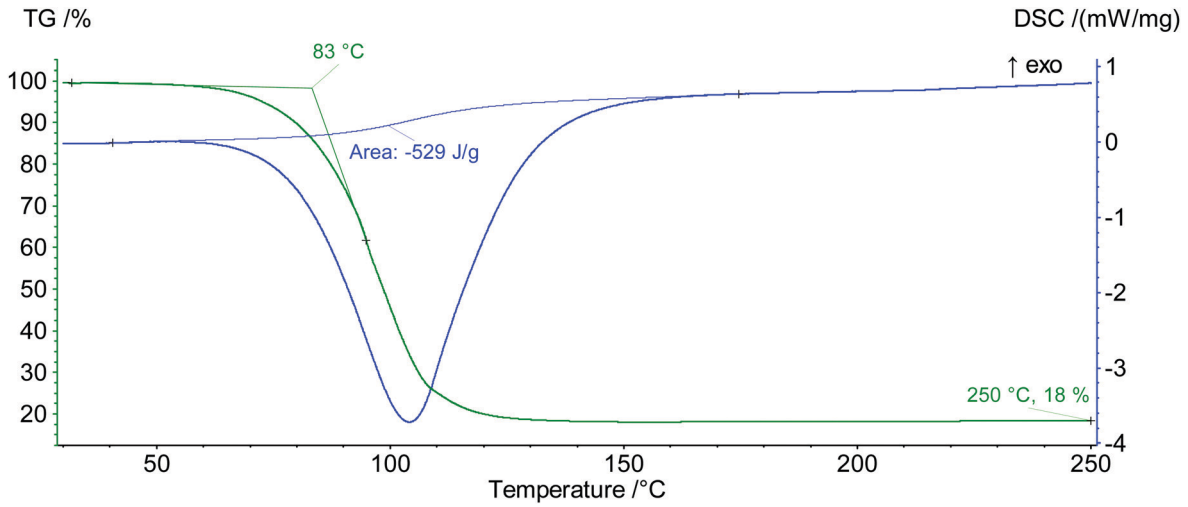

Fig. 2 Thermogravimetry (TG, green curve) and differential scanning calorimetry (DSC, blue curve) traces for sample **1** (conditions: linear heating at 10 K min^{-1} in argon flow).

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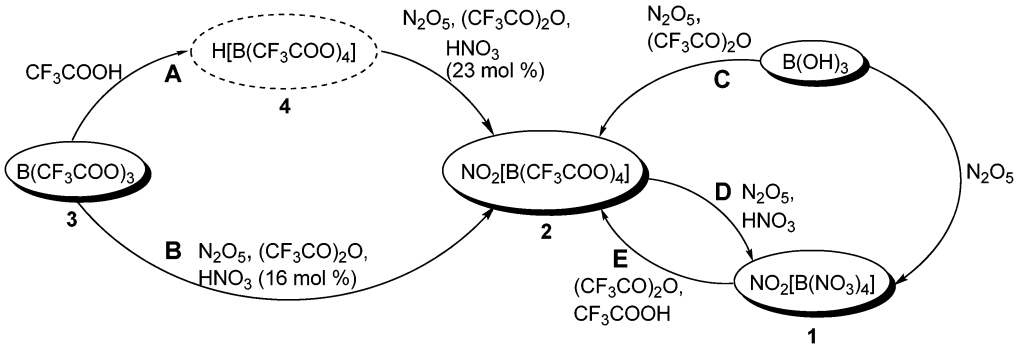


Scheme 4 Methods of synthesis of $NO_2[B(NO_3)_4]$ (**1**) and $NO_2[B(CF_3COO)_4]$ (**2**).

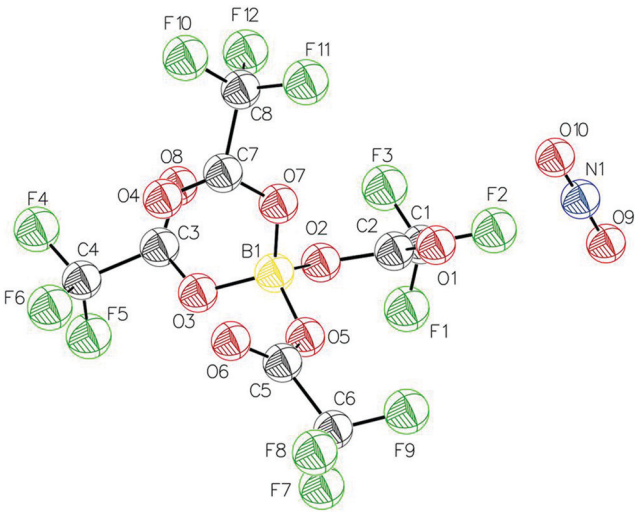
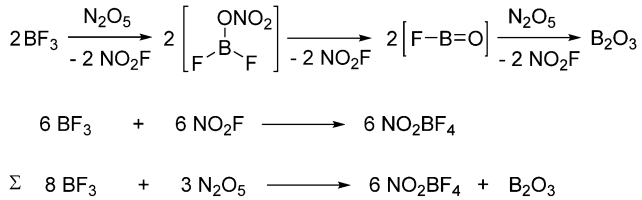


Fig. 3 General view of $NO_2[B(CF_3COO)_4]$ (**2**) in a crystal. Isotropic displacement parameters for atoms are drawn at 50% probability. The disordered fluorine atoms were omitted for clarity.

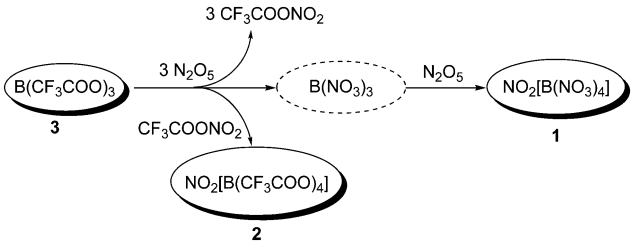
spectrum of compound **2** the characteristic frequency of symmetric vibrations $\nu^{s}_{NO_2}$ of the nitronium cation (~1408 cm^{-1}) is somewhat higher than that of NO_2BF_4 (1405 cm^{-1}), but the $\nu^{comb}_{NO_2}$ frequencies in the IR spectra of $NO_2[B(CF_3COO)_4]$ (**2**) and NO_2BF_4[35] are very close (3769 and 3767 cm^{-1}, respectively). Unlike borate **1**, the δ(N) shifts in the ^{14}N NMR spectra of borate **2** are ~−132 ppm (sulfolane, CF_3COOD), which is typical of nitronium salts.

The structure of $NO_2[B(CF_3COO)]_4$ (**2**) was determined by powder X-ray diffraction analysis (Fig. 3).

The space group is *Pbca*, the lattice constants are a = 15.28529(13) Å, b = 14.44923(11) Å, and c = 15.48814(17) Å. In



Scheme 5 Reaction of BF_3 with N_2O_5 (see ref. 45).



Scheme 6 Reaction of $B(CF_3COO)_3$ (**3**) with N_2O_5.

the crystal, all CF_3COO groups adopt a staggered conformation relative to the B–O bond, thus indicating a large contribution from the repulsion between carboxyl groups. The NO_2^+ cation forms four short contacts N···O (average distance N···O 2.675 Å) with C═O groups of the tetrakis(2,2,2-trifluoroacetoxy)borate anion.

It was previously shown that anions of the $[BCl_3X]^-$ type (X = ONO_2, $C(NO_2)_3$) readily decomposed due to disproportionation.[20] Reaction of BF_3 with N_2O_5 resulted in the formation of $NO_2[BF_4]$[45] instead of complex $BF_3{\cdot}N_2O_5$ ($NO_2^+[BF_3(NO_3)]^-$).[46,47] This transformation occurred due to the elimination of NO_2F and its subsequent interaction with other BF_3 molecules (Scheme 5). Hence, anions with heterotypic ligands in the coordination sphere of the central boron atom are probably unstable. The reaction of LA $B(CF_3COO)_3$ (**3**) with N_2O_5 confirmed this assumption (Scheme 6). According to the spectral data, the interaction led to a mixture of salts **1** and **2** rather than the expected nitronium

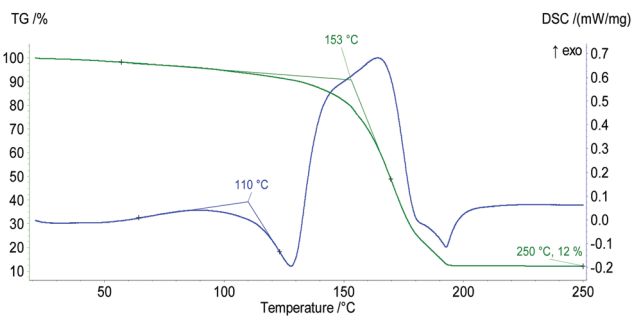


Fig. 4 Thermogravimetry (TG, green curve) and differential scanning calorimetry (DSC, blue curve) traces for sample **2** (conditions: linear heating at 10 K min^{-1} in argon flow).

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borate $NO_2[B(CF_3COO)_3(NO_3)]$. The Raman spectrum of the mixture obtained represents a superposition of the spectra of compounds **1** and **2** including the characteristic lines of nitronium cations at 1400 and 1408 cm^{-1} (Fig. S6, ESI†).

Thermolysis of borate **2** features a multistep mass loss (overall $\Delta m = -88\%$, extrapolated onset temperature $T_{eo} = 153$ °C). The process is accompanied by an exothermic heat effect with two overlapping endothermic effects (Fig. 4).

3. Conclusions

We developed different synthetic routes to nitronium borates $NO_2[B(NO_3)_4]$ (**1**) and $NO_2[B(CF_3COO)_4]$ (**2**) and prepared stable solid compounds. Nitronium borates **1** and **2** as well as the $[B(CF_3COO)_4]^-$ anion were obtained for the first time and characterized using spectral methods. Thermographic studies showed that compounds **1** and **2** are relatively stable, and $NO_2[B(NO_3)_4]$ can be considered as a potential rocket propellant oxidizer. Thermolysis of borate **1** leads to B_2O_3. The possibility of reversible substitution of acid ligands in the coordination sphere of boron was demonstrated for the first time by the mutual transformations of compounds **1** and **2**. It was confirmed that anions with heterotypic acid ligands in the coordination sphere of the central boron atom are unstable.

4. Experimental section

$B(CF_3COO)_3$ was synthesized following a known procedure.[48] All manipulations of reagents were performed in an argon atmosphere. Nitrogen pentoxide was prepared using a known method[49] modified by us (see below).

The ^{11}B (96.29 MHz), ^{13}C (75.47 MHz), ^{14}N (21.69 MHz) and ^{19}F (282.40 MHz) NMR spectra were recorded on a Bruker AM300 spectrometer. Capillaries with acetone-d_6 as a lock solvent were used for recording spectra of solutions in non-deuterated solvents. The ^{14}N NMR spectra were recorded with CH_3NO_2 (10–15 mg) as the internal standard (high-field chemical shifts have negative values), and the ^{13}C and the ^{19}F NMR spectra were recorded with TMS and with $CFCl_3$ as the external standard, respectively.

The IR spectra (Fig. S2 and S4, ESI†) were recorded on a Bruker Vertex 70V FTIR spectrometer equipped with a Platinum ATR accessory in the range of 400–4000 cm^{-1} (resolution 2 cm^{-1}) in a nitrogen atmosphere. The spectrum in Fig. S7 (ESI†) was recorded on a Bruker ALPHA-T spectrometer with CaF_2 optics (Nujol mull).

The technique for performing X-ray powder diffractometry was as follows. Samples of compounds **1** and **2** were sandwiched between Kapton films and the space between the Kapton films was evacuated. Then the samples were mounted on a Bruker AXS D8 Advance Xray powder diffractometer equipped with a primary Ge^{111} monochromator (Cu $K_{\alpha 1}$, $\lambda = 1.54056$ Å) and a LynxEye 1D position sensitive detector. Data were collected at room temperature in the range 10–90° 2θ for **1** 9–90° 2θ for **2** and with a 0.01° 2θ step size in transmission mode.

The diffraction patterns of compounds **1** and **2** were indexed using the SVD (singular value decomposition) index algorithm[50] as implemented in Bruker TOPAS 5.0,[51] and the space group determination were carried out using systematic absences analysis. Parallel tempering, as implemented in FOX,[52] was used to solve the crystal structures in direct space. The structure of compound **1** contains only 13 positional parameters and allows for unrestrained Rietveld refinement. The restrained Rietveld refinement for compound **2** (with Bruker TOPAS 5.0) was carried out using the methodology described elsewhere.[53] Agreement between the Rietveld refined structures and the PW-DFT-D optimized ones was good.[54]

PW-DFT-D calculations were performed using VASP 5.4.4[55–58] using the PBE functional[59] corrected by Grimme D3 van der Waals correction[60] with Becke-Jonson damping.[61] A planewave basis set with 'normal' projector augmented wave (PAW) pseudopotentials[62,63] as supplied by VASP was used. Optimizations with both fixed and optimized unitcell parameters were performed using an energy cutoff of 600 eV.

CCDC 1985253 contains all the information about the structure of compound **1** and the Rietveld refinement along with the raw powder pattern. CCDC 1980143 contains all the information about the structure of compound **2** and the Rietveld refinement along with the raw powder pattern.

The Raman spectra of solid samples were recorded in the range of 100–2500 cm^{-1} on an Acton Research spectrometer with a focus distance of 500 mm on a 1200 lines per mm grid. A Princeton Instruments CCD cooled with liquid nitrogen was used as the light-sensitive detector of the optical signal. The spectra were measured using the 641.7 nm line of a krypton laser (radiation power up to 4 mW) in the Raman backscattering configuration. The spectral resolution was 1.5 cm^{-1}. The optical path of the instrument was designed by the confocal microscope scheme with a spatial resolution of 2 μm.

The thermal behavior of compounds was studied using a Netzsch STA449 F3 thermal analyzer under linear heating at a rate of 10 K min^{-1}. A weighed sample (0.7 mg) was placed in alumina pans and covered with pierced lids. Measurements were performed in argon stream (70 mL min^{-1}) in the temperature range from room temperature to 600 °C.

The boron content in the sample was determined using the gravimetric method based on the mass of boric acid. The nitronium salts were completely decomposed by boiling water for 5 minutes; after evaporation of H_2O and volatile components under reduced pressure, subsequent drying of the residue in air at room temperature to a constant weight gives the mass of $B(OH)_3$.

Synthesis of $NO_2[B(NO_3)_4]$ (1)

From $B(OH)_3$. Crystalline N_2O_5 (4.13 g, 38.2 mmol) and boric acid (0.47 g, 7.64 mmol) were mixed under ice cooling, HNO_3 (0.24 g, 3.86 mmol) was added, and the reaction mixture was stirred for 4 h under ice cooling. Then CH_2Cl_2 (3 mL) was added and the mixture was stirred for 5 min. The solvent was decanted, CH_2Cl_2 (3 mL) was added again, and the precipitate was filtered off and washed with CH_2Cl_2 (3 × 2 mL). Nitronium

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tetranitratoborate $NO_2[B(NO_3)_4]$ (2.06 g, 88%) was obtained as a colorless crystalline compound. IR (selected bands), ν, cm^{-1}: 3748, 2388 (NO_2^+); 1609, 1308 (ONO_2). Raman (selected bands), ν, cm^{-1}: 1653, 1620, 1613, 1599, 1325, 1311 (ONO_2); 1400 (NO_2^+). ^{14}N NMR δ, (sulfolane): −45 ($\Delta\nu_{1/2}$ = 185 Hz, ONO_2); −92 ($\Delta\nu_{1/2}$ = 325 Hz); ($MeNO_2$): −45 ($\Delta\nu_{1/2}$ = 32 Hz, ONO_2); −63 ($\Delta\nu_{1/2}$ = 65 Hz); (CF_3COOD): −60 ($\Delta\nu_{1/2}$ = 105 Hz). ^{11}B NMR δ: 1.10 (sulfolane); 1.03 (CF_3COOD); 2.51 ($MeNO_2$). Found, %: B, 3.79. $B_1N_5O_{14}$. Calculated, %: B, 3.55.

From $NO_2[B(CF_3COO)_4]$. $NO_2[B(CF_3COO)_4]$ (1.097 g, 2.16 mmol), obtained from $B(CF_3COO)_3$, was mixed with N_2O_5 (2.65 g, 24.5 mmol) and HNO_3 (1 mL; 1.5 g, 25 mmol) at 0–5 °C. The mixture was stirred for 3 h at 0–5 °C and kept overnight in a refrigerator. The mixture was evacuated for 10 min, then ice-cold CH_2Cl_2 (2 mL) was added to the residue and white crystals were filtered off and washed with CH_2Cl_2 (2 mL). $NO_2[B(NO_3)_4]$ (**1**) (0.485 g, 74%) was obtained. The spectroscopic data corresponded to those of the authentic sample.

Synthesis of $NO_2[B(CF_3COO)_4]$ (2)

From $B(OH)_3$. (a) Crystalline N_2O_5 (1.73 g, 16 mmol) was mixed with $(CF_3CO)_2O$ (6.52 g, 31 mmol) and the mixture was kept in a refrigerator for 2 h. Then $B(OH)_3$ (0.51 g, 8.2 mmol) was added to the solution and the mixture was stirred for 8 h under ice cooling. The suspension thus obtained was allowed to stay overnight in a refrigerator. Then a CH_2Cl_2–MeCN (V = 4 : 1) mixture (10 mL) was added to the reaction mass under stirring and cooling in an ice–salt bath and the reaction vessel was kept overnight in a freezer. The precipitate was filtered off using a Schott funnel and washed with cold CH_2Cl_2 (3 mL). Crystalline $NO_2[B(CF_3COO)_4]$ (1.82 g) was obtained. As the solvent was removed from the mother liquor *in vacuo*, an additional 1.86 g of the reaction product was obtained as a white powder (a total of 3.72 g, 91%). IR (selected bands), ν, cm^{-1}: 3769, 2388 (NO_2^+); 1777 (C═O). Raman (selected bands), ν, cm^{-1}: 1793, 1784, 1769, 1758 (CO); 1408 (NO_2^+). ^{14}N NMR, δ (sulfolane): −132 ($\Delta\nu_{1/2}$ = 135 Hz, NO_2^+). ^{11}B NMR, δ (sulfolane): −0.5. ^{14}N NMR, δ (CF_3COOD): −131 ($\Delta\nu_{1/2}$ = 165 Hz, NO_2^+). ^{11}B NMR, δ (CF_3COOD): 6.7. ^{13}C NMR, δ (sulfolane): q, 154.7, J 40 Hz (C═O); q, 114.4, J 285 Hz (CF_3). ^{19}F NMR, δ (sulfolane): −78.09.

(b) To crystalline N_2O_5 (7.55 g, 70 mmol), $B(OH)_3$ (1.856 g, 30 mmol) was added, then nitric acid (0.3 mL, ∼17 mmol) was added at 0–5 °C, and the reaction mass was stirred for 4 h under ice cooling. The reaction mass became homogeneous and a precipitate formed later. Then, trifluoroacetic acid anhydride (16.6 mL, 118 mmol) was added dropwise to the suspension at 0–10 °C over a period of ∼1 h, and the mixture was stirred for 1 h. The reaction mass was allowed to stay overnight in a refrigerator (∼5 °C), then a cooled mixture of solvents (4 mL of CH_3CN and 12 mL of CH_2Cl_2) was added; the overall mixture was stirred at 0–5 °C for 1 h and then placed in a freezer for two days. Crystals thus formed were filtered off on a Schott funnel under an argon atmosphere. Nitronium borate $NO_2[B(CF_3COO)_4]$ (11.185 g, 72%) was obtained as colorless crystals of a regular shape. The spectroscopic data corresponded to those of the authentic sample.

From $B(CF_3COO)_3$. Crystalline N_2O_5 (0.17 g, 1.57 mmol) was mixed with $(CF_3CO)_2O$ (0.26 mL, 0.39 g, 1.85 mmol) and the mixture was kept in a refrigerator overnight. On the next day, the solution was added to a suspension of $B(CF_3COO)_3$ (0.78 g, 2.24 mmol) in CH_2Cl_2 (2 mL) under ice cooling and stirring. Nitric acid (0.02 g, 0.35 mmol) was added; the reaction mass was stirred for 10 h under ice cooling, and then kept in a refrigerator for three days. The residue was filtered off on a Schott funnel and washed with ice-cold CH_2Cl_2 (3 mL). Nitronium salt $NO_2[B(CF_3COO)_4]$ (0.85 g, 75%) was obtained as colorless crystals. The spectroscopic data corresponded to those of the authentic sample.

From BBr_3. To a solution of BBr_3 (0.82 g, 3.27 mmol) in CH_2Cl_2 (5 mL), a solution of CF_3COOH (1.51 g, 13.23 mmol) in CH_2Cl_2 (5 mL) was added gradually under ice cooling and stirring and the mixture was stirred in an ice bath for 2 h. The synthesis was accompanied by HBr evolution. The reaction mass was evaporated to dryness on a rotary evaporator and a colorless crystalline residue (1.25 g) was obtained. Crystalline N_2O_5 (0.82 g, 7.57 mmol) was mixed with $(CF_3CO)_2O$ (1.77 g, 8.41 mmol) in a separate vessel, the mixture was placed in a refrigerator for 3 h, and then the solution obtained was added to $B(CF_3COO)_3$ with stirring under ice cooling. After 30 min of stirring, a solution of HNO_3 (0.04 g, 0.63 mmol) in CH_2Cl_2 (1 mL) was added; the suspension was stirred for an additional 2 h and then placed in a refrigerator overnight. The residue was filtered off and washed with CH_2Cl_2 (2 × 3 mL). Nitronium borate $NO_2[B(CF_3COO_4)]$ (1.16 g, 84%) was obtained as colorless crystals. The spectroscopic data corresponded to those of the authentic sample.

From $NO_2[B(NO_3)_4]$. $NO_2[B(NO_3)_4]$ (0.37 g, 1.23 mmol), obtained from $B(OH)_3$, was mixed with CF_3COOH (0.28 g, 2.5 mmol) at room temperature, then $(CF_3CO)_2O$ (2 mL, 3.58 g, 20 mmol) was added, and the reaction mass was stirred for 4 h at 15–20 °C. The residue was filtered off and washed with ice-cold CH_2Cl_2 (2 mL). $NO_2[B(CF_3COO_4)]$ (0.48 g, 77%) was obtained as colorless crystals. The spectroscopic data corresponded to those of the authentic sample.

Reaction of $B(CF_3COO)_3$ with N_2O_5

To $B(CF_3COO)_3$ (0.47 g, 1.35 mmol), N_2O_5 (0.31 g, 2.8 mmol) was added under stirring in an ice bath, and the mixture was placed in a refrigerator to stay over a period of four days. Then, CH_2Cl_2 (2 mL) was added to the suspension under stirring and ice cooling, the reaction mass was stirred for an additional 5 h, and then the mixture was placed in a refrigerator overnight. The residue was filtered off and washed with CH_2Cl_2 (5 mL) to give a mixture of $NO_2[B(CF_3COO_4)]$ and $NO_2[B(NO_3)_4]$ (0.51 g) as colorless crystals in a ∼1 : 1 ratio (according to the Raman spectrum, see Fig. S7, ESI†).

Synthesis of N_2O_5

To white nitric acid (42 mL, 1 mol; d^{20} 1.5 g cm^{-3}), $(CF_3CO)_2O$ (69.5 mL, 0.49 mol) was added dropwise, the temperature was maintained at 2–10 °C (ice cooling). Immediately after addition, the solution was placed in a freezer to stay overnight, and then

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the crystals were filtered off and dried on a Schott funnel for 5 min in an argon stream (Fig. S8, ESI†). If cooling of the resulting solution was carried out with stirring, the crystal size was smaller, which made filtering and drying difficult. White crystals (Fig. S8, ESI†) of N_2O_5 (38.9 g, 72%) were used to synthesize the nitronium salt **2** without purification or were purified to prepare salt **1**. Purification of N_2O_5 was carried out by distillation over P_2O_5 with magnetic stirring, supplying a slow argon stream into a Schlenk flask containing the molten dinitrogen pentoxide at 40–50 °C. Dinitrogen pentoxide vapors (22–25 °C) were condensed in a receiving Schlenk flask cooled at ~−40 °C. To protect against air moisture, a tube with $CaCl_2$ was used. The Raman spectrum of N_2O_5 corresponded to those of the authentic sample,[35,36] and the admixture of N_2O_4 was absent.

Conflicts of interest

There are no conflicts to declare.

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