Electrochemical and Ozone Oxidation of $(CF_3)_3B \cdot NH_3$: Formation and Characterization of Products with Nondegradated $(CF_3)_3B$ Groups

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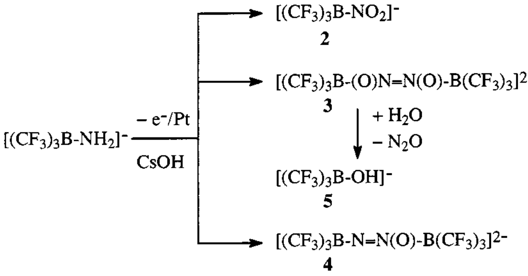
$(CF_3)_3B \cdot NH_3$ (**1**) has been oxidized in aqueous solution using a platinum anode. At pH = 8–9 in $CsOH/Cs_2CO_3$ solution $Cs[(CF_3)_3B–NO_2]$ (**2**), $Cs_2[(CF_3)_3B–N(O){=}N(O)–B(CF_3)_3]$ (**3**) and $Cs_2[(CF_3)_3B–N{=}N(O)–B(CF_3)_3]$ (**4**) are formed. Compound **3** slowly hydrolyses to yield the hydroxyborate $Cs[(CF_3)_3B–OH]$ (**5**). Compound **2** and traces of **3** and **5** were also formed by oxidation of **1** or $(CF_3)_3B \cdot NHEt_2$ with ozone. The constitution of the novel borates has been deduced from multinuclear NMR, IR and mass spectra. The structures of **2**–**5** have been investigated by single-crystal X-ray diffraction.

Introduction

Homoleptic, donor-free (perfluoroalkyl)boranes, e. g. $(R_f)_3B$ (R_f = CF_3, C_2F_5, ...), are still unknown in spite of considerable efforts made in the past towards their synthesis.[1] The simplest species tris(trifluoromethyl)borane, $(CF_3)_3B$, is expected to readily decompose under elimination of difluorocarbene and formation of BF_3. However, various amine adducts of $(CF_3)_3B$ are accessible, and they have been shown to be amazingly stable.[2a−2d] As a result of the presumed high Lewis acidity of the $(CF_3)_3B$ moiety and despite its relative bulkiness, the B−N bond in amine −tris(trifluoromethyl)boranes is thermodynamically extraordinarily strong. Attempts to selectively cleave this bond have failed so far. Such amine−boranes withstand e. g. concentrated hydrochloric acid as well as concentrated solutions of KOH. SbF_5 or superacids like $HSbF_6/HF$ react at 10°C with e. g. $(CF_3)_3B \cdot NHEt_2$ with cleavage of the B−N bond and formation of BF_3, perfluoropropene or HCF_3. Since the isolation of the donor-free tris(trifluoromethyl)borane remains a challenge, we have focused our continuing interest on the synthesis of alternative promising precursor molecules. We decided to start from ammine−tris(trifluoromethyl)borane, $(CF_3)_3B \cdot NH_3$ (**1**), the synthesis of which has been improved.[3] We hoped that oxidation of its nitrogen atom might favor low-temperature B−N cleavage reactions.

Results

Ammine−tris(trifluoromethyl)borane (**1**) is a hygroscopic compound which forms a crystalline tetrahydrate when exposed to moist air. Dissolved in water it is a weak acid with a $pK_a = 5$ and behaves like an ammonium cation. Attempts to electrochemically oxidize the nitrogen atom on platinum anodes in acidic solution failed, only H_2 and O_2 being evolved. On raising the pH to 8−9, the nitrogen atom in **1** is deprotonated to form the aminotris(trifluoromethyl)borate anion $[(CF_3)_3B{-}NH_2]^-$. In view of planned X-ray crystal studies a $CsOH/Cs_2CO_3$ mixture was used to adjust the pH to 8.5 because cesium salts of the oxidation products were expected to crystallize well. Under these alkaline conditions the nitrogen atom was found to be readily oxidized at a 4.5 V potential difference between electrodes. The progress of the oxidation was monitored by measurement of ^{19}F-NMR spectra of the solution. The electrolysis was interrupted every two hours in order to isolate the insoluble, colorless material which accumulated on the anode and at the bottom of the cell. Work-up of the precipitated material revealed that it consisted mainly of a mixture of cesium azodioxybis[tris(trifluoromethyl)borate] $Cs_2[(CF_3)_3B{-}N(O){=}N(O){-}B(CF_3)_3]$ (**3**) and cesium azoxybis[tris(trifluoromethyl)borate] $Cs_2[(CF_3)_3B{-}N{=}N(O){-}B(CF_3)_3]$ (**4**) (Equation 1).



(1)

The main product of the anodic oxidation, however, was the nitroborate $Cs[(CF_3)_3B{-}NO_2]$ (**2**) which precipitated when the concentrated solution was cooled to 4°C. Concentration of the solution to dryness gave a residue which contained substantial quantities of $Cs[(CF_3)_3B{-}OH]$ (**5**). Besides these main products, which according to ^{19}F-NMR spectra account for 95% of all formed from **1**, several other (trifluoromethyl)borates were detected. These include compounds with either three or two CF_3 groups attached to the boron atom. However, separation and characterization of these species failed.

The origin of **5** became apparent from a study of the hydrolysis of **3**. This compound slowly reacts with water at

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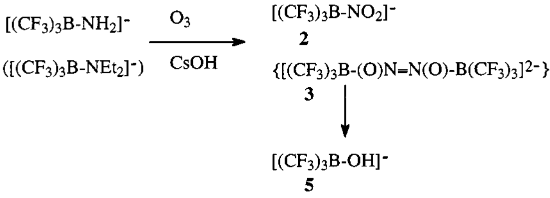
room temperature – the elimination of N_2O, which was confirmed by IR spectroscopy, and formation of **5** being completed within one week. We are sure that this pathway accounts for all of **5** produced.

Besides the electrochemical oxidation, attempts were also undertaken to oxidize compound **1** chemically. The results of such oxidation reactions will be reported later, but one case is mentioned here. Ozone reacts readily with **1** in cesium hydroxide solution to form **2** and **5** in a ratio of 7:2. Moreover, we found that $(CF_3)_3B \cdot NHEt_2$, the precursor molecule for **1**, is also directly converted into similar quantities of **2** and **5** (Equation 2). The fate of the *N*-ethyl groups has not yet been elucidated.



$$[(CF_3)_3B\text{-}NH_2]^- \; ([(CF_3)_3B\text{-}NEt_2]^-) \xrightarrow[\text{CsOH}]{O_3} \underset{\mathbf{2}}{[(CF_3)_3B\text{-}NO_2]^-} \; \underset{\mathbf{3}}{\{[(CF_3)_3B\text{-}(O)N{=}N(O)\text{-}B(CF_3)_3]^{2-}\}} \rightarrow \underset{\mathbf{5}}{[(CF_3)_3B\text{-}OH]^-} \quad (2)$$

Spectra and Properties

The NMR chemical shifts and coupling constants of **2**−**5** are set out in Table 1 and are consistent with the proposed structures. For **3** and one of the $B(CF_3)_3$ groups of **4** the resonances of the CF_3 groups were not found in the ^{13}C-NMR spectra due to quadrupolar broadening by the boron nucleus.

Table 1. NMR-spectral data for **2**−**5**

Compound	**2**	**3**	**4**	**5**
^1H NMR				
δ(OH)				2.1
^{19}F NMR				
δ(CF_3)	−64.8	−59.6	−60.7	−68.0
^2J(BF)	28.5		25.9	26.8
δ(CF_3)			−63.0	
^{11}B NMR				
δ(B)	−9.8	−10.3	−13.0	−10.6
^2J(BF)	28.5		25.9	26.7
δ(B)			−10.8	
^{13}C NMR				
δ(C)	130.1		134.1	134.7
^1J(BC)	82.0		75.7	75.8
^1J(CF)	301.6		309.2	311.4
^3J(CF)				ca. 2.7
δ(C)			131.2	
^{14}N NMR				
δ(N)	42			

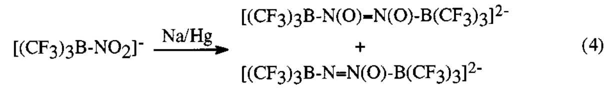
Infrared and Raman spectra of **2**−**5** were recorded. All of these novel borates contain a $(CF_3)_3B{-}X$ (X = N, O) moiety, the vibrational frequencies of which fall into well-defined ranges. First the bands in the range of 1300−1280 cm^{-1} and 1140−1060 cm^{-1} are assigned to $\nu(CF_3)$ vibrations which are associated with very strong infrared absorptions but medium to weak Raman lines. Then, the $\delta_s(CF_3)$ mode is found at ca. 720 and 690 cm^{-1} where the former mode appears as a strong Raman line and the latter as a medium to strong infrared band. Near 500 cm^{-1} $\delta_{as}(CF_3)$ features with medium infrared and weak Raman intensity occur while $\rho(CF_3)$ is associated with weak infrared bands and medium to strong Raman lines at 350−280 cm^{-1}. The BC_3 and B−X stretching vibrations are strongly coupled and may be assigned to several infrared bands between 950 and 860 cm^{-1} showing $^{10/11}B$ isotopic patterns. Compound **2** has an NO_2 group, which exhibits characteristic frequencies. Thus, the infrared bands/Raman lines [cm^{-1}] were assigned as follows: 1471 vs/1484 m (ν_{as} NO_2), 1400 w/1400 vs (ν_s NO_2), 795 s/797 s (δ_s NO_2), 595 m/− (δ_{op} BNO_2). Compound **3** has *trans* configuration with C_i symmetry in the crystal. Consequently, backbone vibrations which occur in characteristic ranges obey the mutual exclusion principle of the infrared and Raman frequencies. These vibrations were assigned to infrared bands/Raman lines [cm^{-1}] at: −/1415 vs (ν NN), −/1125 m (ν NO i.p.), 685 −/m (δ NNO), ca. 1100 s/− (ν NO o.p.), 620 s/− (δ NNO). Compound **4** has strongly coupled N−N and N−O stretching vibrations which were assigned to infrared bands/Raman lines [cm^{-1}] at 1511 m/1514 m (ν NN) and 1258 vs/1265 m (ν NO). The N−N−O bending mode is associated with features in the IR and Raman spectrum at 800 m/805 w cm^{-1}. The O−H stretching and B−O−H bending vibrations of **5** were unambiguously assigned to IR bands at 3650 and 1520 cm^{-1}.

The molecular masses of **2** and **5** were determined by ESI/neg. spectra (CH_3CN + 10% H_2O). Compound **2** showed the peak of the anion $[(CF_3)_3B{-}NO_2]^-$, 100%, and the cluster peak $[Cs[(CF_3)_3B{-}NO_2]_2]^-$, 10%, whereas **5** gave only the anion peak $[(CF_3)_3B{-}OH]^-$, 100%.

The cesium borates **2**−**5** are colorless solids. Their approximate decomposition temperatures determined thermogravimetrically are 260°C (**2**), 80°C (**3**), 190°C (**4**), and 150°C (**5**). Because the decomposition of **3** is violent, reliable elemental analyses were difficult to obtain.

Compound **2** is stable towards acids like HCl, H_3PO_4, or H_2SO_4. Dissolved in neat CF_3SO_3H **2** reacts within 1 d under elimination of difluorocarbene. This subsequently inserts into the O−H bond to form the ester $CF_3SO_2OCF_2H$, which was identified by its NMR spectra. Reaction of **2** with ethereal HCl forms the sublimable ether adduct $(CF_3)_3B{-}NO_2H \times Et_2O$. The latter is hydrolyzed by moist air to form what appears to be a pentahydrate **2a** $(CF_3)_3B{-}NO_2H \times 5\ H_2O$. Titration of **2a** revealed a pK_a of ca. 1.9 and a molecular mass of 359 g/mol which is in line with a pentahydrate (355.93 g/mol), while elemental analyses were in agreement both with a penta- or a hexahydrate. Compound **2a** is stable at room temperature and decomposes according to thermogravimetric experiments at 75°C without leaving any residue. Compound **2** reacts with zinc in aqueous KOH to form **1** (Equation 3) and it is reduced by sodium amalgam in ether to form, according to NMR spectra, a mixture of **3** and **4** (Equation 4).

$$[(CF_3)_3B\text{-}NO_2]^- \xrightarrow{Zn/NaOH/H_2O} [(CF_3)_3B\text{-}NH_2]^- \qquad (3)$$



$$[(CF_3)_3B\text{-}NO_2]^- \xrightarrow{Na/Hg} \begin{array}{c}[(CF_3)_3B\text{-}N(O)\text{=}N(O)\text{-}B(CF_3)_3]^{2-}\\ +\\ [(CF_3)_3B\text{-}N\text{=}N(O)\text{-}B(CF_3)_3]^{2-}\end{array} \qquad (4)$$

We were unable to isolate **3** and **4** from this reduction because the ethereal solutions decomposed violently upon concentration. This might be ascribed to precipitation of the salts $Na_2[(CF_3)_3B-N(O)=N(O)-B(CF_3)_3]$ and $Na_2[(CF_3)_3B-N=N(O)-B(CF_3)_3]$ from this sodium-rich system. Such salts might be thermally less stable than their cesium counterparts; that is, small cations are stronger Lewis acids than Cs^+ and tend to abstract fluoride from the CF_3 groups. This is underscored by the rather low decomposition temperature of $Li[(CF_3)_3B-NO_2]$, 70°C, compared with that of $Cs[(CF_3)_3B-NO_2]$, 260°C.

Only little information on the chemical properties of **3** and **4** has been gathered. We have no evidence for an equilibrium $[(CF_3)_3B-N(O)=N(O)-B(CF_3)_3]^{2-} \rightleftarrows 2\ [(CF_3)_3B-N=O]^-$ which is known to exist for aliphatic nitroso compounds. Since monomers of the latter compounds are intensely colored whereas solutions of **3** are colorless, any such equilibrium for **3** must be shifted far to the left. The protonation of **5** has been investigated in more detail. Upon treatment with ethereal HCl, protonation and formation of a sublimable ether adduct $(CF_3)_3B-OH_2 \times Et_2O$, which is analogous to compound **2**, was observed. The ether is readily replaced by water on contact with moist air to form an oily product which, according to thermogravimetric analysis, is a pentahydrate **5a**. This behaves as an acid, with a pK_a of 1.6, and is thermally stable up to 70°C.

Discussion

Hydroxyborate anions of the general formula $[R_3BOH]^-$ with R = F,[4] H,[5] CH_3,[6] C_6H_5[7] are well known, and compound **5** might be regarded as a further homologue with R = CF_3. Unlike **5**, such anions for R = alkyl or aryl are only stable under alkaline conditions, and species with R = F or H are of limited thermal and kinetic stability which decompose upon protonation. Compounds **2**, **3** and **4** have, to our knowledge, no real counterparts in boron chemistry. The formation of the $[F_3BNO_2]^-$ anion in solution has been reported.[8] This anion, only characterized by ^{19}F-NMR spectra, was found prone to disproportionation into $[BF_4]^-$ and $[F_2B(NO_2)_2]^-$. The stability of **2** towards dissociation gives an impression of the Lewis acid strength of illusive free $(CF_3)_3B$.

Borate ions with $N_2O_2{}^{2-}$ or N_2O^{2-} as coordinating ligands as revealed in **3** and **4** are unknown whereas a Lewis acid/base complex with SO_3, $[O-N=N(O)-SO_3]^{2-}$, has been characterized. The latter anion is formed when NO is introduced into an alkaline $SO_3{}^{2-}$ solution,[9] and the structure of the ammonium salt has been determined.[10] This salt hydrolyses slowly in water to form $SO_4{}^{2-}$ and N_2O, and experiments with ^{15}N-labeled material proved that the hyponitrite anion is an intermediate.[11] Therefore the slow hydrolysis of **3** with elimination of N_2O and formation of **5** is in line with the behavior of $[O\text{-}N=N(O)\text{-}SO_3]^{2-}$.

The stability of the $(CF_3)_3BN$ skeleton towards oxidation is remarkable. This results in part from the steric bulk of three CF_3 groups, which efficiently shield the boron atom, the boron−carbon bonds as well as the boron−nitrogen bond in **1**, **2**, and **4**. In the course of the oxidation reactions, the nitrogen atom changes its oxidation state in alkaline solution from −3 in **1** over "average" ±0 in **4** to +1 in **3** and finally to +3 in **2**. One of the oxidizing reagents that is able to accomplish this oxidation is ozone. Its oxidation strength in alkaline solution is clearly larger than is that of hydrogen peroxide; for example, the standard reduction potential for the half reaction $O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$, +1.24 V, is much larger than for $HO_2{}^- + H_2O + 2e^- \rightarrow 3OH^-$, +0.87 V. Whereas O_3 readily oxidizes **1** to **2**, concentrated H_2O_2 in alkaline solution is unable to perform an oxidation. Apparently, the lower limit for oxidation of **1** in alkaline solution must lie between +0.87 V and +1.24 V; so in the absence of kinetic hindrance, any other reagent with standard reduction potentials higher than +1.24 V should be able to convert **1** into **2**. Similar to ozone, fluorine reacts in alkaline solution readily with **1** to form **2** whereas in acidic solution only water is oxidized. The oxidation of $Cs[(CF_3)_3B-NH_2]$ in acetonitrile has been studied by cyclic voltammetry. The anion is irreversibly oxidized at a potential against an Ag reference electrode of ca. 1.82 V which is close to the limit dictated by the acetonitrile solvent. This high potential might explain why XeF_2 failed to react with $Cs[(CF_3)_3B-NH_2]$ in acetonitrile.

The oxidation of **1**, which leads ultimately to the formation of a nitro group, resembles the oxidation of aniline to nitrobenzene which also can be performed with ozone[12] or electrochemically.[13] Diazene bis(oxides) $R-N(O)=N(O)-R$ (azodioxy compounds) or diazene *N*-oxides $R-N=N(O)-R$ (azoxy compounds) with R = alkyl, aryl are also formed both by oxidation or reduction of precursor molecules. For example *cyclo*-$C_6H_{11}-(O)N=N(O)-$*cyclo*-C_6H_{11} is formed from *cyclo*-$C_6H_{11}NH_2$ using peracetic acid[14] while $C_6H_5-N=N(O)-C_6H_5$ is obtained by reduction of nitrobenzene with Zn[15] or Pb.[16] On the other hand azoxybenzene is prepared more conveniently by oxidation of aniline with a mixture of hydrogen peroxide and acetonitrile.[17] In this respect compound **1** behaves like an ammonium cation which is deprotonated in alkaline solution to form an "amine" before it is oxidized. Consequently, compounds **2**, **3** and **4** correspond to a nitroalkane, a diazene bis(oxide) and a diazene *N*-oxide, respectively, bearing overall negative charges.

Crystal Structures

In the anion of **2** (Figure 1) the nitro group is coplanar with the boron atom to within 0.002 Å. Despite the sp^2 hybridization of the nitrogen atom, the B−N bond length [1.606(4) Å] is more typical for a linkage of a $B(CF_3)_3$ group to an sp^3-hybridized nitrogen atom such as in $(CF_3)_3B \cdot NH_3$, 1.595(8) Å,[2d] than to an sp^2-hybridized nitrogen atom such as in $(CF_3)_3B \cdot NHCHNMe_2$, 1.541(4) Å.[2d] Similarly, an average distance between a nitro group and a quaternary carbon atom is given as 1.533(13) Å,[18] which compares well with the C−N distance reported for the *tert*-butylammonium cation, 1.506(3) Å.[19] The average value of the B−C bond length in **2**, 1.618(10) Å, is normal, as are the respective averages of the C−B−C and N−B−C bond angles, 111.5(8) and 107.4(14)°. The small but significant spread in these angles [1.5(4) and 2.7(4)°, respectively] results in part from the mismatch in the symmetries of the $B(CF_3)_3$ (C_{3v}) and BNO_2 (C_{2v}) groups. Thus, the symmetry of the anion can not exceed C_s, and the magnitude of the O(2)−N−B−C(2) torsion angle, 19.6(5)°, shows that the structure is even less symmetric.

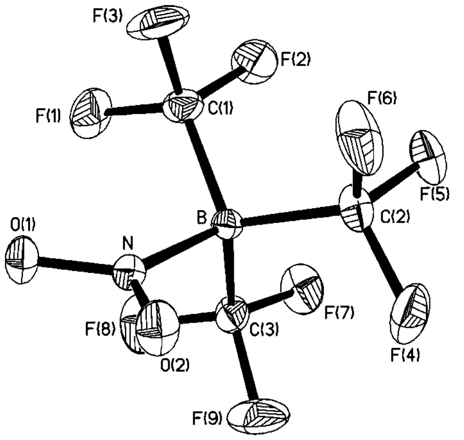


Figure 1. A perspective drawing of the $[(CF_3)_3BNO_2]^-$ anion with 20% probability thermal ellipsoids

While all atoms of **3** occupy general positions in the crystal, the midpoint of the N−N bond of the anion (Figure 2) lies on an inversion center. The $B_2N_2O_2$ fragment is planar to within 0.004 Å, and the N−N′ and N−O bond lengths of 1.30(2) and 1.30(1) Å, respectively, indicate delocalized π bonding in the azodioxy anion. These atom distances agree to within experimental error with the corresponding values for the azodioxysulfonate $[O{-}N{=}N(O){-}SO_3]^{2-}$.[10] In **3** the B−N bond length is 1.59(2) Å, and the B−N−N′ angle [123(1)°] is significantly larger than the B−N−O angle [117(1)°].

In crystals of **4**, the two crystallographically unique Cs cations as well as the B(1), B(2), C(2), C(4), F(5) and F(10) atoms of the anion (Figure 3) lie on a crystallographic mirror plane. Since the azoxy group is oriented perpendicular to this plane, the positions of its atoms are disordered. A further consequence of this disorder is that the locations found for the $B(CF_3)_3$ groups are superpositions of two distinct orientations; for example, the C_3 axis of the $B(CF_3)_3$ group of the B(1) atom will either lie along the B(1)−N(2) or B(1)−N(2′) directions − the angle between these C_3 axes being 33.7(9)°. Therefore the atom distances and angles in this structure should not be taken too seriously although the agreement factors (Table 2) are acceptable. The N(1)−N(2) bond length [1.25(1) Å] should not be prejudiced by the disorder, and this value does not differ significantly from that of the analogous linkage in *p*-azoxyanisole, 1.218(5) Å.[20]

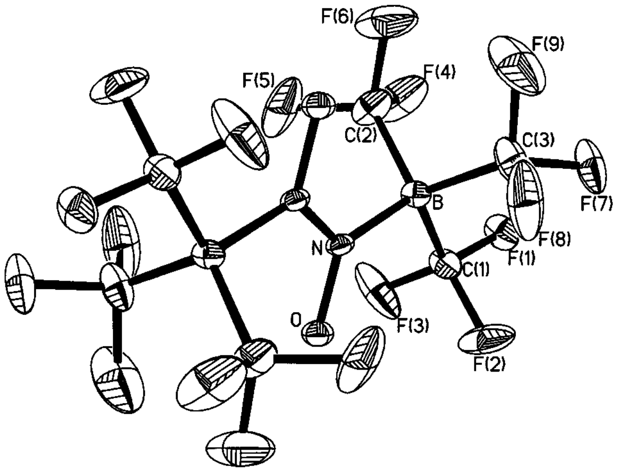


Figure 2. A perspective drawing of the $[(CF_3)_3B{-}N(O){=}N(O){-}B(CF_3)_3]^{2-}$ anion with 20% probability thermal ellipsoids

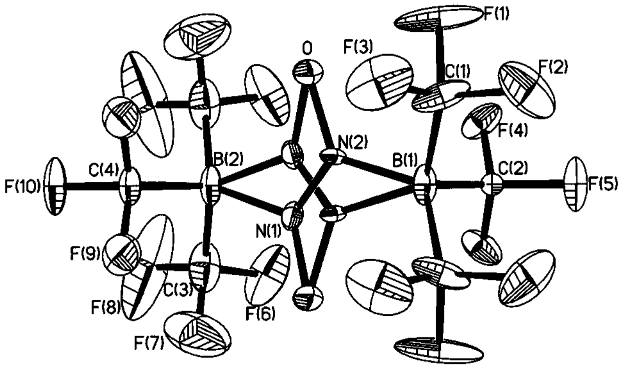


Figure 3. A perspective drawing of the $[(CF_3)_3B{-}N{=}N(O){-}B(CF_3)_3]^{2-}$ anion with 20% probability thermal ellipsoids showing the disorder of the azoxy group

Crystals of **5** contain the cations Cs(1) and Cs(2) in C_3 and S_6 symmetry sites, respectively, while the H, O, B, C(2) and F(4) atoms of the anion (Figure 4) lie on a mirror plane. The B−O bond length of 1.447(7) Å falls in the range, 1.432(3)−1.465(3) Å, found for hydroxyborates bearing two boron-bonded trifluoromethyl substituents.[21] In **5** the average B−C bond length, 1.617(6) Å, is in excellent agreement with that found in **2**. While the length determined for the O−H bond, 0.76(7) Å, is obviously too short, the B−O−H angle albeit imprecise seems to be acceptable, 109(5)°. No interionic hydrogen bonding is present since no oxygen or fluorine atom in a neighboring ion lies within 2.50 Å of the hydrogen atom even after extension of the O−H bond to 0.973 Å. The hydrogen atom lies in the plane which bisects the C(1)−B−C(1′) angle. The latter angle, 111.7(6)°, is larger than its C(1)−B−C(2) counterpart, 108.0(3)°. Furthermore, the O−B−C(1) angle, 111.4(3)°, is markedly larger than O−B−C(2), 106.1(4)°. Thus, significant deviations from C_{3v} symmetry are apparent at the boron atom, and although they correlate with the orientation of the hydroxy group, they may well have resulted from packing forces.

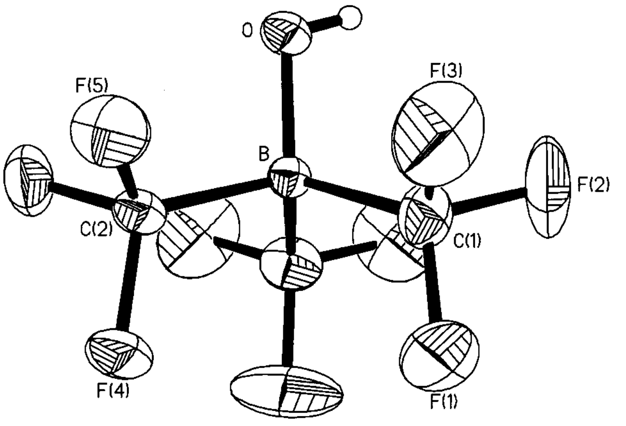


Figure 4. A perspective drawing of the $[(CF_3)_3BOH]^-$ anion with 20% probability thermal ellipsoids for the nonhydrogen atoms

The coordination polyhedra of the cesium cations in **2**−**5** are mostly irregular. The shortest Cs−O and Cs−F contacts are 3.054(9) and 3.049(5) Å, respectively, and most cations form between four and eight contacts shorter than 3.25 Å. If all contacts with oxygen and fluorine atoms which are less than 3.80 Å are counted, then the cation coordination numbers are 12 in **3** and **5** (both cases) and 14 in **2** and **4** (both cases). High coordination numbers imply low bonding strength for the cations,[22] and these weakly acidic centers are apparently well matched to the weakly basic CF_3 donors. The condensation of the coordination polyhedra in **5** is particularly fascinating. First, coordination spheres of the Cs(1) cations are bridged across their O_3 faces to dimers which possess crystallographic C_{3h} symmetry (Figure 5). This bridging gives rise to a Cs−Cs distance [4.616(2) Å], which is shorter than the 5.25 Å value found in the metal. Second, the symmetry of the complexation of the Cs(2) cation is higher (S_6); that is, it is surrounded by two interpenetrating trigonal antiprisms of fluorine atoms. These polyhedra are fused along F_3 faces to form infinite chains of C_3 symmetry parallel to the *c* axis (Figure 6). However, the interactions which bridge the Cs(2) cations [Cs(2)−F(4), 3.518(2) Å] are much longer and weaker than those which link the Cs(1) cations to dimers [Cs(1)−O, 3.182(3) Å]; as a result, the Cs(2)−Cs(2) separations along the chain are much longer, 6.180(2) Å, than the Cs(1)−Cs(1) contacts in the dimers. In addition to the long bridging distances, the other contacts involving the second cation [Cs(2)−F(1), 3.546(6) Å] are also relatively long. Indeed the cavity enclosed by the Cs(2) coordination polyhedron is large enough to allow marked rattling of the cation. Thus, the equivalent isotropic temperature factor of the Cs(2) cation, 0.0881(3) Å^2, is much larger than is that of Cs(1), 0.0559 Å^2, and is in fact the largest of all cations studied.

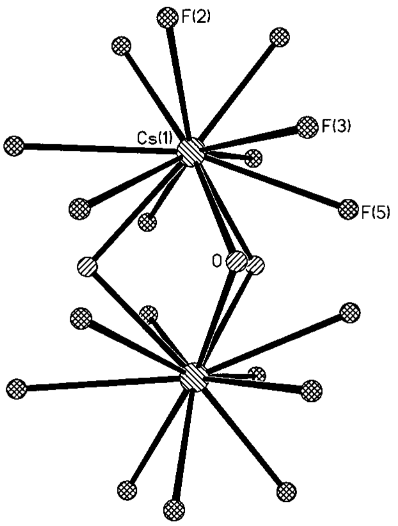


Figure 5. A perspective drawing of a Cs(1) dimer in **5** with atoms not bonded to Cs(1) omitted; selected bond lengths in [Å]: Cs(1)−O 3.182(3), Cs(1)−F(2) 3.131(4), Cs(1)−F(3) 3.599(6), Cs(1)−F(5) 3.440(4)

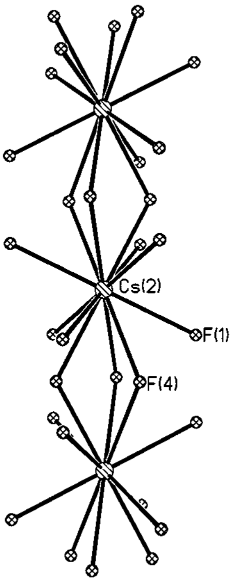


Figure 6. A perspective view of a segment of the infinite Cs(2) chain in **5** with atoms not bonded to Cs(2) omitted; selected distances in [Å]: Cs(2)−F(1) 3.546(6), Cs(2)−F(4) 3.518(2)

Experimental Section

General: NMR: Bruker ARX 400 (400 MHz, 100.6 MHz and 376.5 MHz, for ^1H, ^{13}C and ^{19}F, respectively), Bruker AC 250 (79.8 MHz for ^{11}B). [D$_3$]acetonitrile as solvent and internal standard ^1H: δ_H = 1.95, ^{13}C: δ_C = 1.30, ^{19}F: external standard $CFCl_3$, ^{11}B: external standard $BF_3\cdot OEt_2$. − IR: Bruker IFS 25. − Raman: Cary 82 Kr$^+$ 647.1 nm. − MS: Varian MAT 311 (70 eV). − Thermogravimetry: Mettler TA4000. − Ozone Generator: Fischer 501.

X-ray Crystallographic Studies: Crystals were glued to glass fibers and transferred to a Siemens P3 diffractometer, which was equipped with a graphite monochromator. Intensities were determined from the profiles of the θ-2θ scans and corrected either by integration (**2**, **4** and **5**) or empirically (**3**) for absorption. The structures of **2**, **3** and **5** were solved by direct methods − the hydrogen atom of **5** being located with a difference Fourier synthesis and refined freely. In order to avoid unreasonable geometries for the CF_3 groups of **3**, C_3 restraints were applied to these groups with the C−F bond length and intra-group F···F contact being refined. The heavy-atom method was used to develop the structure of **4** −

Table 2. Crystal data for **2**−**5**

Compound	**2**	**3**	**4**	**5**
Formula	$C_3BCsF_9NO_2$	$C_6B_2Cs_2F_{18}N_2O_2$	$C_6B_2Cs_2F_{18}N_2O$	C_3HBCsF_9O
Mr	396.76	761.52	745.52	367.76
Crystal system	Triclinic	Monoclinic	Orthorhombic	Hexagonal
Space group	$P1$	$P2_1/n$	$Cmc2_1$	$P6_3/m$
a [Å]	6.4439(8)	7.3960(10)	7.556(2)	11.365(3)
b [Å]	7.8042(8)	15.241(2)	6.938(5)	11.365(3)
c [Å]	9.7989(13)	9.1755(14)	14.284(3)	12.360(5)
α [°]	91.594(10)	90	90	90
β [°]	97.469(10)	112.651(11)	90	90
γ [°]	91.665(9)	90	90	120
Z	2	2	4	6
D(calcd.) [g cm^{-3}]	2.699	2.650	2.709	2.650
T [K]	294(2)	295(2)	295(2)	294(2)
λ [Å]	0.71073	1.54184	0.71073	0.71073
θ range [°]	2.10−30.08	5.81−57.15	2.40−25.02	2.07−30.05
Index ranges	$-9 \le h \le 9$	$0 \le h \le 8$	$-8 \le h \le 8$	$0 \le h \le 16$
	$-10 \le k \le 10$	$0 \le k \le 16$	$0 \le k \le 20$	$-16 \le k \le 13$
	$0 \le l \le 13$	$-9 \le l \le 9$	$-17 \le l \le 17$	$-17 \le l \le 0$
Reflections collected	3008	1396	2958	4621
unique	2856	1284	1735	1417
R (int)	0.0248	0.0291	0.0303	0.0216
observed [$I > 2\sigma(I)$]	2568	1011	1684	1041
$\mu(\lambda)$ [mm^{-1}]	3.921	31.543	4.166	4.130
Crystal size [mm]	0.40 × 0.14 × 0.09	0.18 × 0.06 × 0.04	0.50 × 0.21 × 0.16	0.60 × 0.14 × 0.14
Transmission	0.5428−0.7363	0.1900−0.6331	0.4126−0.5624	0.5281−0.5904
Parameters	154	148	166	78
S on F^2	1.021	1.017	1.051	1.088
$R1$ (F, observed)	0.0290	0.0537	0.0350	0.0371
$wR2$ (F^2, all data)	0.0821	0.1420	0.0890	0.1117
Final ΔF [e Å^{-3}]	0.849 to −0.557	1.728 to −1.395	0.726 to −0.612	1.383 to −0.636

the NNO group being disordered over the mirror plane. Treatment of the structure as a pseudo-merohedral twin space group *Cc*, twinning plane (100)] gave comparable final residuals but poor convergence; thus, the disordered model in $Cmc2_1$ will be presented here. The absolute structure parameter for **4**, 0.02(5), implies that the polarity of the *c* axis has been chosen correctly. An extinction correction was only necessary for **3**. The structures were solved, refined and illustrated with the SHELXTL program package. Additional crystal data are given in Table 2. Further details of the crystal-structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-410079, -410078, -410077, and -410076 for **2**, **3**, **4** and **5**, respectively.

Preparation of Compounds: Cesium Tris(trifluoromethyl)nitroborate (2), Cesium Azodioxybis[tris(trifluoromethyl)borate] (3), Cesium Azoxybis[tris(trifluoromethyl)borate] (4), Cesium Tris(trifluoromethyl)hydroxyborate (5): $(CF_3)_3B \cdot NH_3 \times 4\ H_2O$ was prepared from $(CF_3)_3B \cdot NHEt_2$ according to ref.[3] 10 g ($33 \cdot 10^{-3}$ mol) of $(CF_3)_3B \cdot NH_3 \times 4\ H_2O$, 20 g ($61 \cdot 10^{-3}$ mol) of Cs_2CO_3 and 10 g ($60 \cdot 10^{-3}$ mol) of $CsOH \times H_2O$ were dissolved in 300 mL of water. This mixture was electrolyzed at 4.5 V/0.15 A for ca. 2 h using platinum net electrodes (DEGUSSA 303, diameter 35 mm, height 50 mm). Compounds **3** and **4**, which are poorly soluble in water, accumulated at the bottom of the reaction vessel as well as on the anode and were isolated and dried. The electrolysis was then continued until all starting material was consumed as indicated by ^{19}F-NMR spectroscopy. The solution was concentrated and upon cooling in an ice bath most of compound **2** precipitated (plates). After all of **2** had been isolated (ca. 50%), the mother liquor was concentrated in vacuo and the residue stirred with dry acetonitrile. The slurry was filtered, and the filtrate slowly concentrated until **5** crystallized (needles) (ca. 5%).

Separation of 3 and 4: When the mixture of **3** and **4**, dissolved in dry acetonitrile at 20°C, was cooled to −30°C, most of **3** crystallized (ca. 10%). After stripping off the acetonitrile, the residue **4** was recrystallized from methanol/acetone (yield ca. 24%).

Compounds **2** and **5** were formed by oxidation of $(CF_3)_3B \cdot NH_3 \times 4\ H_2O$ or $(CF_3)_3B \cdot NHEt_2$ in CsOH solution in a flow of ozone/oxygen in a ratio of 7:2. In a typical experiment $20 \cdot 10^{-3}$ mol of reactant was mixed with 50 mL 25% CsOH solution and a flow of ozone/oxygen (ca. 2 g O_3/h) was introduced into the stirred reaction mixture at 20°C through a Teflon PFA tube. The progress of the reaction was monitored by running ^{19}F-NMR spectra from the solution. In case of $(CF_3)_3B \cdot NHEt_2$, which is only slightly soluble in CsOH solution, the reaction was stopped when a clear solution was obtained. Work-up and separation as described above yielded ca. 65% of **2**. − **2:** $C_3BCsF_9NO_2$ (396.74): calcd. C 9.08, N 3.53; found C 9.0 N, 3.8. − **3:** $C_6B_2Cs_2F_{18}N_2O_2$ (761.48): calcd. C 9.46, N 3.68, F 44.91; found C 9.4, N 3.6, F 46.4. − **4:** $C_6B_2Cs_2F_{18}N_2O$ (745.48): calcd. C 9.67, N 3.76, F 45.87; found C 9.6, N 3.6, F 44.4. − **5:** C_3HBCsF_9O (367.74): calcd. C 9.80, H 0.27; found C 9.3, H 0.3.

Protonation of 2 and 5: To a stirred suspension of $12 \cdot 10^{-3}$ mol (4 g) of **2** in 20 mL of diethyl ether, 5 mL of 1 M ethereal HCl was added dropwise at 20°C. The reaction mixture was stirred for 20 min and the CsCl formed removed by filtration in air. Ether and HCl were removed in vacuo at 0.1 mbar/20°C and **2a** was purified by repeated sublimation at 60°C/10^{-2} mbar, yield 2.7 g (85%). Compound **5** was analogously protonated to yield 88% of **5a**. − MS (70 eV); *m/z*(%): **2a:** 99 (100) [CBF_4^+], 69 (78) [CF_3^+], 81 (36) [$C_2F_3^+$], 47 (13) [HNO_2^+], 246 (11) [$M^+ - F$]; **5a:** 66 (100) [F_2BOH^+], 46 (57) [FBO^+], 96 (20) [CF_3BO^+], 108 (16) [$C_2F_3BO^+$], 216 (16) [$M^+ - HF$]. − IR film: **2a**: $\tilde{\nu} = 3669$ cm^{-1} (OH), 1624

δ(NOH), 1479 (NO), 1397(NO), 1282 (CF), 1080−1150 (CF_3), 939, 917 (BC_3), 794 $\delta_s(NO_2)$, 718, 707, 700 $\delta_s(CF_3)$, 598 $\delta_{op}(BNO_2)$, 525 $\delta_{as}(CF_3)$; **5a**: $\tilde{\nu} = 3664\ cm^{-1}$ (OH), 1666, 1612 δ(BOH), 1273 (CF_3), 1105 (CF_3), 887 (BC_3), 682 $\delta_s(CF_3)$. − **2a:** ^{1}H NMR (CD_2Cl_2): $\delta = 7.8$. − ^{19}F NMR (CD_2Cl_2): $\delta = -66.4$. − **5a:** ^{1}H NMR ([D_3]acetonitrile): $\delta = 6.0$. − ^{19}F NMR ([D_3]acetonitrile): $\delta = -68.0$. − **2a:** $C_3H_{13}BF_9NO_8$ (372.93): calcd. C 9.66, H 3.51, N 3.76; $C_3H_{11}BF_9NO_7$ (354.92): calcd. C 10.15, H 3.12, N 3.95; found C 10.89, H 3.42, N 3.73. − **5a:** $C_3H_{12}BF_9O_6$ (325.92): calcd. C 11.06, H 3.71, found C 11.39, H 3.48.

Reduction of 2 to 1: To a stirred solution of $5 \cdot 10^{-3}$ mol (2 g) of **2** in 20 mL of water and 2 mL of 50% CsOH, 0.5 g of Zn powder was added at 60 °C. The reaction mixture was stirred for 2 h, filtered, the filtrate concentrated to dryness and **1** extracted with acetonitrile.

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