DOI: 10.1002/ejic.200800068

Salts with the Triborate Anion $[B_3O_3F_2(OH)_2]^-$: A Combined Experimental and Theoretical Study

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Keywords: Boron / Triborates / Fluoroborates / Structure elucidation / DFT calculations

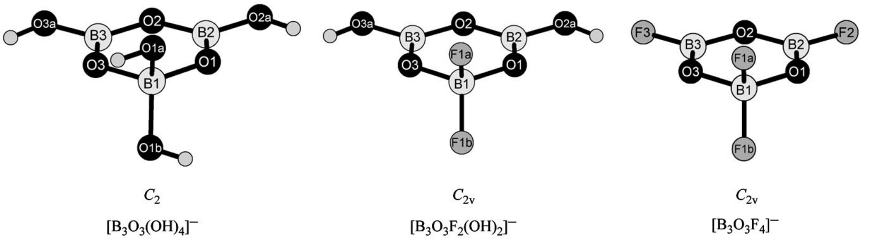
Reactions of $[3\text{-NC-}B_{11}F_{10}]^{2-}$ with aqueous bases resulted in a cluster degradation. From the reaction mixtures, salts of the $[B_3O_3F_2(OH)_2]^-$ anion (1) with $[Ph_4P]^+$ or $[Ph_3MeP]^+$ as countercations were isolated. Both salts were investitgated by single-crystal X-ray diffraction. In the solid state the triborate anions form infinite hydrogen-bonded chains. In the $[Ph_4P]^+$ salt the anions and the chains are coplanar, whereas in the $[Ph_3MeP]^+$ salt the planes of the anions are twisted against each other. The bonding parameters of the anion are compared to values of the related $[B_3O_3(OH)_4]^-$ anion (2) and to values derived from density functional calculations. In addition, the triborate anion **1** was characterized by ^{11}B and ^{19}F NMR spectroscopy as well as by MALDI mass spectrometry. The experimental chemical shifts are compared to calculated values (DFT-GIAO).

Introduction

In the course of our continuing study on *closo*-borate and -carborate anions, we are investigating the reactions, stability limits, and decomposition pathways of the cyano-*closo*-undecaborate dianion $[3\text{-NC-}closo\text{-}B_{11}F_{10}]^{2-}$.[1] It is obtained from the fluorinated monocarba-*closo*-dodecaborate anion $[1\text{-}H_2N\text{-}closo\text{-}CB_{11}F_{11}]^{-}$[2] by an unusual carbon extrusion/cluster contraction reaction.[1] Major degradation products of $K_2[3\text{-NC-}closo\text{-}B_{11}F_{10}]$ are salts of the difluorodihydroxytriborate anion $[B_3O_3F_2(OH)_2]^-$ (**1**) (Figure 1).

To the best of our knowledge, anion **1** is unknown and only a small number of other partially fluorinated borates with boron oxygen rings have been reported so far: $[Ph_3PH]_2[B_4F_{10}O_2]$ ($\{[Ph_3PH]^+\}_2$**4**),[3] $[(iPr_3PAu)_6C][B_3O_3F_4]_2{\cdot}3CH_2Cl_2$ ($[(iPr_3PAu)_6C]^+$**3**$\cdot 3CH_2Cl_2$),[4] and $M_2[B_2O_2F_2(OH)_2]{\cdot}2H_2O$ (M = K, NH_4).[5] In the case of $[(iPr_3PAu)_6C]^+$**3**$\cdot 3CH_2Cl_2$ the degree of fluorination of the triborate anion is not fully proven.[4] Both anions **1** and **3** are closely related to the anion $[B_3O_3(OH)_4]^-$ (**2**) (Figure 1), which was found in the mineral ameghinite Na^+**2**,[6] and later the potassium salt K^+**2**$\cdot H_2O$ was synthesized.[7,8] In general, B_3O_3 boroxyl rings, as are present in the anions **1**–**3**, are common structural motifs in borate minerals[9] and important building blocks in synthetic borates.[10,11]

In this contribution we report on the isolation of $[Ph_4P][B_3O_3F_2(OH)_2]$ and $[Ph_3MeP][B_3O_3F_2(OH)_2]$ and their solid-state structures. The anion **1** is furthermore characterized by ^{11}B as well as by ^{19}F NMR spectroscopy and MALDI mass spectrometry. In addition, the experimental structural and NMR spectroscopic data of **1** are supported by values derived from DFT calculations.



C_2 $[B_3O_3(OH)_4]^-$ C_{2v} $[B_3O_3F_2(OH)_2]^-$ C_{2v} $[B_3O_3F_4]^-$

Figure 1. Representations of the calculated structures of $[B_3O_3(OH)_4]^-$ (**2**), $[B_3O_3F_2(OH)_2]^-$ (**1**), and $[B_3O_3F_4]^-$ (**3**) at the B3LYP/6-311++G(d,p) level of theory.

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Results and Discussion

The [3-NC-*closo*-$B_{11}F_{10}$]$^{2–}$ anion[1] is indefinitely stable in THF solution and no degradation was observed in aqueous solutions under neutral conditions. In contrast, under basic conditions the cyano-*closo*-undecaborate dianion decomposes to yield a mixture of so far unidentified boron clusters and borate anions as deduced from ^{11}B and ^{19}F NMR spectra of the reaction mixtures. The borate anions are easily separated by the precipitation of salts with large organic cations, e.g. [Ph_4P]$^+$ or [Ph_3MeP]$^+$, from aqueous solutions. Recrystallization of these mixtures of salts from dichloromethane resulted in colorless crystals of [Ph_4P]$^+$**1** and [Ph_3MeP]$^+$**1**, respectively. MALDI mass spectra recorded in the negative ion mode showed the signal corresponding to the molar mass of **1**, with the expected isotopic pattern due to ^{10}B and ^{11}B.

The formation of the [$B_3O_3F_2(OH)_2$]$^–$ anion (**1**) is unprecedented because the triborate anion contains a BF_2 unit; in contrast, in the [3-NC-*closo*-$B_{11}F_{10}$]$^{2–}$ dianion no BF_2 group is present. Probably, one reason for its formation is the relatively low concentration of water during the decomposition of the cyano-*closo*-undecaborate dianion, which prevents the exchange of $F^–$ by $OH^–$. However, up to now the decomposition pathway of [3-NC-*closo*-$B_{11}F_{10}$]$^{2–}$ and the mechanism for the formation of **1** remain mostly unclear.

The triborate anion **1** was characterized by ^{11}B and ^{19}F NMR spectroscopy solely in CD_3CN. The ^{11}B NMR spectrum of **1** shows two signals with a relative intensity distribution of 1:2. The signal at 0.7 ppm is assigned to the tetrahedral BO_2F_2 fragment and the second signal with a chemical shift of 19.4 ppm to both equivalent $BO_2(OH)$ units (Table 1). These ^{11}B NMR chemical shifts are similar to values measured for the related anion [$B_3O_3(OH)_4$]$^–$ (**2**) in solid triborate-pillared hydrotalcites $M_4Al_2(OH)_{12}$-[$B_3O_3(OH)_4$]$_2$·$x$$H_2O$ (M = Mg, Zn) with the MAS technique (Table 1).[11] A smaller line width (17 Hz) is observed for the signal of the ^{11}B nucleus of the BO_2F_2 group, whereas the signal corresponding to the $BO_2(OH)$ fragments is broader (105 Hz): this finding displays the different surroundings of the boron atoms, resulting in different electric field gradients at the quadrupolar ^{11}B nuclei.[12] As a consequence of the relatively broad signals coupling to the ^{19}F nuclei is not resolved.

Table 1. Experimental and calculated[a] ^{11}B and ^{19}F NMR chemical shifts of [$B_3O_3F_2(OH)_2$]$^–$ (**1**), [$B_3O_3(OH)_4$]$^–$ (**2**), and [$B_3O_3F_4$]$^–$ (**3**).[b]

Anion	δ(^{11}B) [ppm]				δ(^{19}F) [ppm]			
	B1		B2/B3		F1a/F1b		F2/F3	
	exp.	calcd.	exp.	calcd.	exp.	calcd.	exp.	calcd.
1[c]	0.7[d]	0.1	19.4[d]	18.6	–140.1[e]	–181.3	–	–
2[f]	2.9	1.1	19.6	18.5	–	–	–	–
3	n.o.[g]	0.5	n.o.	16.4	n.o.	–166.4	n.o.	–180.3

[a] Calculated by the GIAO method at the B3LYP/6-311++G(2d,p) level of theory using geometries at the B3LYP/6-311++G(d,p) level. [b] Labeling of the atoms according to Figure 1. [c] Solvent: CD_3CN. [d] Measured line width, B1: σ = 17 Hz, B2/B3: σ = 105 Hz. [e] ^1J(^{11}B,^{19}F) = 9.0 Hz; measured line width: σ = 4 Hz. [f] ^{11}B MAS NMR spectroscopic data of $M_4Al_2(OH)_{12}$[B_3O_3-$(OH)_4$]$_2$·$x$$H_2O$ (M = Mg, Zn).[11] [g] n.o. = not observed.

The ^{19}F NMR signal of the triborate anion **1** is found at δ = –140.1 ppm. Only little broadening of this signal due to the interaction with the ^{11}B nucleus (σ = 4 Hz) is observed; hence, the signal shows the expected splitting into a quartet with lines of equal intensity due to the coupling to the ^{11}B nucleus [^1J(^{11}B,^{19}F) = 9.0 Hz].

In Table 1 the experimental ^{11}B and ^{19}F chemical shifts of both triborate anions **1** and **2** are compared to values derived from DFT calculations with the GIAO method. In addition, theoretical data for [$B_3O_3F_4$]$^–$ (**3**) are listed. The agreement between experimental and calculated data for δ(^{11}B) is very good, whereas δ(^{19}F) for [$B_3O_3F_2(OH)_2$]$^–$ (**1**) deviates by about –40 ppm. As expected, the deviation between experimental and calculated chemical shifts is larger for δ(^{19}F) than for δ(^{11}B).[2]

Structural Aspects

The tetraphenylphosphonium triborate [Ph_4P][$B_3O_3F_2$-$(OH)_2$] ([Ph_4P]$^+$**1**) crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with four formula units in the unit cell (Figure 2). Replacement of the fluorine atoms by hydroxy groups resulted in a significant increase of the R values of the final structure refinement; hence, this is an additional proof for the structure of **1** with two fluorine atoms bonded to the tetrahedral boron atom, in agreement with the NMR spectroscopic and mass spectrometric data. The shortest distances between the weakly coordinating organic phosphonium cation [Ph_4P]$^+$ and the borate anion **1** are in the typical range of weak interionic interactions.[13] The anion **1** also gave crystals with the [Ph_3MeP]$^+$ cation. A detailed discussion of the geometrical parameters of this structure is not possible, because of the low quality of the data. However, it is quite clear that this structure includes anion **1** with a topology nearly identical to that in [Ph_4P]$^+$**1**.

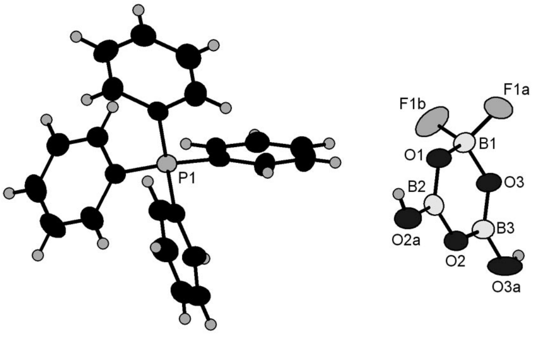


Figure 2. One formula unit of [Ph_4P]$^+$(**1**) in the crystal structure (displacement ellipsoids at the 50% probability level).

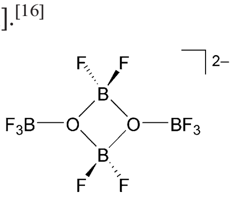
Selected experimental and calculated bonding parameters of **1** are collected in Table 2 and they are compared to the respective values of the [$B_3O_3(OH)_4$]$^–$ anion (**2**) as well as to theoretical values of [$B_3O_3F_4$]$^–$ (**3**). Experimental and calculated values are in good agreement. In the solid-state structures of the triborate anion **1** with [Ph_4P]$^+$ and

Table 2. Selected experimental and calculated[a] bond lengths and angles of $[B_3O_3F_2(OH)_2]^-$ (**1**), $[B_3O_3(OH)_4]^-$ (**2**), and $[B_3O_3F_4]^-$ (**3**).

	$[B_3O_3F_2(OH)_2]^-$ (**1**)		$[B_3O_3(OH)_4]^-$ (**2**)		$[B_3O_3F_4]^-$ (**3**)
	$[Ph_4P]^+$ salt[b]	calcd.[a]	K^+ salt[8]	calcd.[a]	calcd.[a]
Bond lengths [Å]					
B1–O1/B1–O3	1.463(4)[c]	1.479	1.482(2)[c]	1.498	1.487
B2–O1/B3–O3	1.361(4)[c]	1.343	1.352(3)[c]	1.340	1.324
B2–O2/B3–O2	1.380(4)[c]	1.386	1.392(3)[c]	1.387	1.386
B1–F1a/B1–F1b/B1–O1a/B1–O1b	1.390(3)[c]	1.415	1.457(3)[c]	1.466	1.406
B2–O2a/B2–F2a/B3–O3a/B3–F3a	1.343(4)[c]	1.390	1.352(2)[c]	1.394	1.359
Bond angles [°]					
O1–B1–O3	111.4(2)	110.7	110.5(1)	110.0	110.4
B1–O1–B2/B1–O3–B3	123.4(2)[c]	123.1	123.9(2)[c]	123.0	122.9
O1–B2–O2/O2–B3–O3	119.9(2)[c]	123.1	121.4(2)[c]	123.5	124.0
O2–B2–O3	119.9(2)	116.9	118.9(2)	116.9	116.0
O1a–B1–O1b/F1a–B1–F1b	108.0(2)[c]	109.1	110.1(2)[c]	112.7	110.1
O1a–B1–O1/F1a–B1–O1/...[d]	109.3(2)[c]	109.2	109.1(2)[c]	106.1	109.1

[a] B3LYP/6-311++G(d,p). [b] This work. [c] Averaged values. [d] O1a–B1–O1/F1a–B1–O1/O1a–B1–O2/F1a–B1–O2/O1b–B1–O1/F1b–B1–O1/O1b–B1–O2/F1b–B1–O2.

$[Ph_3MeP]^+$ as countercations the BF_2 moieties are slightly bent out of the plane of the six-membered BO rings (ca. 6°). In contrast, DFT calculations predict a flat boroxyl ring. However, the difference in energy for a bent structure with a tilt angle of 6° is calculated to be only 5 kJ mol^{-1}. Hence, bending of the anion **1** in its solid-state structures with $[Ph_4P]^+$ and $[Ph_3MeP]^+$ is rationalized by packing effects. The B–O/B–F bond lengths of the three related triborate anions **1**–**3** in the $BO_2(OH)/BO_2F$ units are shorter than the values found for the tetrahedral $BO_2F_2/BO_2(OH)_2$ fragments, thus displaying the different bonding situations. The B–O distances between the O atoms bonded to the tetrahedral boron atom and the respective trigonal boron atoms are slightly shorter than *d*(B–O) measured between these boron atoms and the oxygen atom opposite to the tetrahedral boron atom. In general, the B–F bond lengths are shorter than the respective B–O bond lengths. The X–B–X (X = O, F) angles for the different groups are in agreement with the tetrahedral and trigonal geometries, respectively. The bonding parameters in the BO_2F_2 group in the triborate anion **1** are comparable to those of the BO_2F_2 units in the cyclic dianion $[B_4F_{10}O_2]^{2-}$ (**4**) found in the solid-state structure of $\{[Ph_3PH]^+\}_2$**4**,[3] to bonding parameters of the $[BF_2(OMe)_2]^-$ anion in the structure of $[CuL][BF_2(OMe)_2][BF_4]$ [L = 1,2-bis(amidino-*O*-ethylurea)ethane],[14] as well as to bond lengths and angles of BO_2F_2 groups in a variety of ligands in transition metal complexes,[15,16] e.g. $[MeCo(dmgBF_2)_2L]$ [$dmgBF_2$ = (difluoroboryl)dimethyloximato; L = pyridine, PEt_3].[16]



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The anions in $[Ph_4P]^+$**1** form infinite chains along the *b* axis by means of hydrogen bonds resulting in hydrogen-bonded motifs of the $R^2_2(8)$ type[17] (Figure 3). Within the experimental error these chains are flat: the planes of the six-membered BO rings are parallel to the plane of the respective chain. In the crystal structure of $[Ph_3MeP]^+$**1** analogous chains of the anions are found as depicted in Figure 3. However, in contrast to the structure of $[Ph_4P]^+$**1**, these chains are twisted with dihedral angles of approximately 50° between the planes of neighboring anions. Most probably, the different chains are a result of packing effects of the different countercations. Similar chains with $R^2_2(8)$ type[17] hydrogen-bonded motifs have previously been reported for a variety of other compounds.[18]

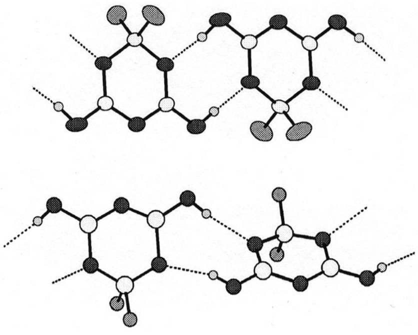

Figure 3. Parts of chains formed by the anions **1** through hydrogen bonds in the crystal structures of $[Ph_4P]^+$**1** (top, displacement ellipsoids at the 40% probability level) and $[Ph_3MeP]^+$**1** (bottom, ball and stick representation). Selected interatomic distances (Å) and angles (°) of $[Ph_4P]^+$**1**: O1···O5, 2.711(3); O5–H5, 0.84(3); O1–H5, 1.88(3); O3···O4, 2.700(3); O4–H4, 0.82(3); O3–H4, 1.88(3).

Conclusions

A first, although limited, report on the reactions of the novel cyano-*closo*-undecaborate dianion $[3\text{-NC-}closo\text{-}B_{11}F_{10}]^{2-}$[1] resulting in the formation of the partially fluorinated triborate anion $[B_2O_3F_2(OH)_2]^-$ (**1**) is presented. The structural and NMR spectroscopic characterization of **1** provides a detailed insight into a partially fluorinated triborate anion. The hydrogen bonded chain structure, especially, is of interest because related borates with anions containing boroxyl rings and organic countercations such as diamines are the subject of intensive investigations as a result of their potential application in material sciences, e.g. as precursors for porous materials.[10,11] Currently, detailed studies concerning the reactions of [3-NC-*closo*-$B_{11}F_{10}]^{2-}$ with hydroxide and alkoxide anions are in progress and we hope to gain a deeper insight into the degradation reactions of this unusual *closo*-undecaborate anion.

Experimental Section

General Remarks: $K_2[3\text{-NC-}B_{11}F_{10}]$ was synthesized from K[1-H_2N–$CB_{11}F_{11}$][2] according to a published procedure.[1] All other chemicals were obtained from commercial sources. ^{11}B and ^{19}F NMR spectra were recorded at room temperature in CD_3CN with a Bruker Avance DRX-500 spectrometer operating at 470.59 or 160.46 MHz for ^{19}F and ^{11}B nuclei, respectively. NMR signals were referenced to $CFCl_3$ (^{19}F) and $BF_3{\cdot}OEt_2$ in CD_3CN (^{11}B) as external standards. Matrix-assisted laser desorption/ionization (MALDI) mass spectra in the negative-ion mode were recorded with a Bruker Ultraflex TOF spectrometer.

Treatment of $K_2[3\text{-NC-}B_{11}F_{10}]$ with Aqueous Potassium Hydroxide: A sample of $K_2[3\text{-NC-}B_{11}F_{10}]$ (150 mg, 0.4 mmol) was dissolved in THF (10 mL) and subsequently treated with an aqueous KOH solution (1 M, 1 mL). The reaction mixture was stirred for 15 min and then water (20 mL) was added. After removing the THF, a solution of $[Ph_4P]Br$ (400 mg, 1.2 mmol) in water (200 mL) was added. Immediately a white solid precipitated, which was isolated by filtration. Yield 210 mg. According to the ^{11}B NMR spectra the precipitate contains a mixture of the triborate anion **1** and unidentified boron clusters. Assuming that the boron clusters are 11- and 10-vertex species, the relative intensities of the sum of their ^{11}B NMR signals versus the intensities of the two signals corresponding to the triborate anion **1** indicate a composition of 1:1 of anion **1** versus boron clusters.

The white solid was recrystallized from dichloromethane by the slow uptake of diethyl ether vapor. A few colorless crystals of $[Ph_4P]^+$**1** were isolated from the oily residue. MALDI-MS: *m*/*z* (isotopic abundance) for $[B_3O_3F_2(OH)_2]^-$: calcd. 151(18), 152(74), 153(100); found 151(14), 152(71), 153(100).

Crystals of $[Ph_3MeP]^+$**1** were obtained in a similar manner.

Crystal Structure Determination: A colorless crystal of $[Ph_4P][B_3O_3F_2(OH)_2]$ ($[Ph_4P]^+$**1**) suitable for X-ray diffraction was investigated with an image plate diffraction system (Stoe & Cie GmbH) using Mo-K_α radiation (λ = 0.71073 Å) at 150 K. The triborate crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with Z = 4 and unit cell parameters of a = 13.854(2), b = 11.486(1), c = 15.226(3) Å, β = 95.47(2)°, and V = 2411.8(6) Å^3; $\rho_{\text{calcd.}}$ = 1.354 Mg m^{-3}, μ(Mo-K_α) = 0.163 mm^{-1}, F(000) = 1016. A total of 30467 reflections were collected ($5.1 < \theta_{\max} < 25.0°$). The structure was solved by direct methods[19] and refinement based on full-matrix least-squares calculations on F^2 with 4212 independent reflections [1689 independent reflections with $I > 2\sigma(I)$] and 324 variables.[20] The positions of all H atoms were located from ΔF-synthesis. For CH idealized bond lengths and angles were used. The isotropic displacement parameters of the aromatic H atoms were kept equal to 130% of the equivalent isotropic displacement parameters of the respective parent C atom. The hydrogen atoms of both hydroxy groups were refined without using any restraints. All non-hydrogen atoms were refined anisotropically. The final refinement resulted in $R_1[F_o^2 > 2\sigma(F_o^2)]$ = 0.034, wR_2 = 0.051 (all data), $w = 1/[\sigma^2(F_o^2)]$, $\Delta\rho_{\max}/\Delta\rho_{\min}$ = +0.18 and –0.22 e Å^{-3}.

CCDC-675108 contains the supplementary crystallographic data for $[Ph_4P]^+$**1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum Chemical Calculations: DFT calculations[21] were carried out using Becke's three-parameter hybrid functional and the Lee–Yang–Parr correlation functional (B3LYP)[22] with the Gaussian 03 program suite.[23] Geometries were optimized and energies were calculated with the 6-311++G(d,p) basis set. All structures represent true minima on the respective hypersurface; no imaginary frequency. Diffuse functions were incorporated because improved energies are obtained for anions.[24] DFT-GIAO[25] NMR shielding constants $\sigma(^{11}B)$, $\sigma(^{13}C)$, and $\sigma(^{19}F)$ were calculated at the B3LYP/6-311++G(2d,p) level of theory. The ^{11}B and ^{19}F NMR shielding constants were calibrated to the respective chemical shift scale $\delta(^{11}B)$ and $\delta(^{19}F)$ using predictions on diborane(6) and $CFCl_3$ with chemical shifts of –16.6 ppm for B_2H_6[26] and 0 ppm for $CFCl_3$.[27]

Acknowledgments

Financial support by the Fonds der Chemischen Industrie (FCI) is gratefully acknowledged. The authors thank Professor W. Frank for generous support, and Mrs. E. Hammes as well as Dr. P. Tommes for technical support.

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Received: January 15, 2008