

Synthesis and Properties of the Tetrakis(trifluoromethyl)borate Anion, $[\text{B}(\text{CF}_3)_4]^-$: Structure Determination of $\text{Cs}[\text{B}(\text{CF}_3)_4]$ by Single-Crystal X-ray Diffraction

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Abstract: Salts of the tetrakis(trifluoromethyl)borate anion, $\text{M}[\text{B}(\text{CF}_3)_4]$, $\text{M} = \text{Li}, \text{K}, \text{Cs}, \text{Ag}$, have been prepared by two different routes for the first time. The colorless compounds are thermally stable up to 425 °C (Cs salt) and soluble in anhydrous HF, water, and most organic solvents. Single crystals of $\text{Cs}[\text{B}(\text{CF}_3)_4]$ were grown from diethyl ether by diffusion of CH_2Cl_2 vapor into the solution. The molecular structure was obtained by single-crystal X-ray diffraction. Crystal data: rhombohedral space group $R\bar{3}m$ (no. 160); $a = 7.883(1)$, $c = 13.847(4)$ Å; $V = 748.2$ Å³; $Z = 3$; $T = 150$ K; $R1 = 0.0118$, $wR2 = 0.0290$. The internal bond parameters of the $[\text{B}(\text{CF}_3)_4]^-$ ion were compared to those

of the $\text{C}(\text{CF}_3)_4$ molecule. Due to a disorder of the anions in the cesium salt, it is not possible to distinguish between T and T_d symmetry by X-ray diffraction experiments alone. However, a comprehensive IR and Raman study demonstrated that in the potassium and cesium salt as well as in aqueous solution, the anion exhibits T symmetry with all CF_3 groups rotated off the staggered position required for T_d symmetry. The vibrational study is supported by DFT calculations, which provide, in addition to the

equilibrium structure and vibrational wavenumbers, estimates of IR and Raman band intensities. The anion is resistant against strong oxidizing (e.g., F_2) as well as reducing agents (e.g., Na) and is not affected by nucleophiles like $\text{C}_2\text{H}_5\text{O}^-$ or electrophiles such as H_3O^+ . It is very weakly coordinating, as demonstrated by the low-equilibrium CO pressure over the $[\text{Ag}(\text{CO})_x][\text{B}(\text{CF}_3)_4]$ ($x = 1, 2$) co-adducts and the formation of $[\text{Ag}(\text{CO})_x][\text{B}(\text{CF}_3)_4]$ ($x = 3, 4$) at higher CO pressure. The ¹¹B, ¹³C, and ¹⁹F NMR data as well as the structural parameters of the anion are compared with those for other borates containing F, CN, and CF_3 ligands.

Keywords: ab initio calculations • borates • structure elucidation • weakly coordinating anions

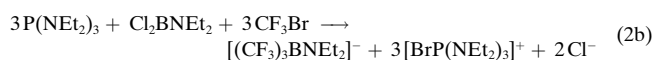
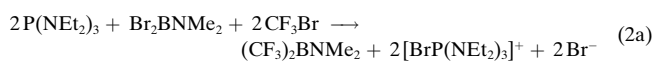
Introduction

The chemistry of boron compounds with trifluoromethyl substituents has suffered in the past from the fact that species with tricoordinated boron are rather unstable and will decompose easily with elimination of difluorocarbene. On the other hand it is well established that species with tetracoordinated boron containing perfluoroalkyl groups are stable and inert. The first trifluoromethylborate was reported

by Chambers et al. in 1960. It is formed by reaction of Me_3SnCF_3 and BF_3 in CCl_4 solution^[1] according to Equation (1).



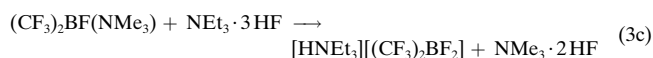
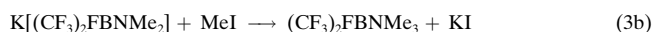
Subsequently, the potassium salt $\text{K}[\text{CF}_3\text{BF}_3]$ was obtained by using $\text{KF}/\text{H}_2\text{O}$.^[1] Its structure was determined by X-ray diffraction.^[2] When a large excess of Me_3SnCF_3 is treated with BX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$), salts with the $[(\text{CF}_3)_2\text{BF}_2]^-$ ion can also be isolated under appropriate conditions.^[2] The transfer of two or three CF_3 groups to boron is accomplished by using the reagent combination $\text{P}(\text{NET}_2)_3/\text{CF}_3\text{Br}$, developed by Ruppert et al.^[3] according to Equations (2a) and (2b):



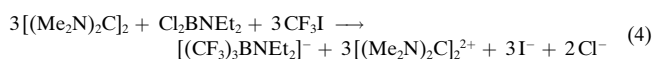
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Thus, starting from $(\text{CF}_3)_2\text{BNMe}_2$, different salts of the $[(\text{CF}_3)_2\text{BF}_2]^-$ anion are formed in quantitative yield in a three step process according to Equations (3a)–(3c).^[4]



Instead of the reagents $\text{P}(\text{NEt}_2)_3/\text{CF}_3\text{Br}$, $[(\text{Me}_2\text{N})_2\text{C}]_2/\text{CF}_3\text{I}$ can be used alternatively to transfer three CF_3 groups [Eq. (4)].



$[(\text{CF}_3)_3\text{BNEt}_2]^-$ is converted into the ammine adduct $(\text{CF}_3)_3\text{BNH}_3$ on treatment with hypobromite (Br_2/KOH) and dehalogenation of the intermediate *N,N*-dibromoborate using sulfite in sulfuric acid [Eq. (5)].



By deprotonation, different $[(\text{CF}_3)_3\text{BNH}_2]^-$ salts become accessible in high yields.^[2, 5] Aminotris(trifluoromethyl)borate is a useful starting material for the preparation of other borates. By halogenation, *N,N*-dihaloamino- and halotris(trifluoromethyl)borates $[(\text{CF}_3)_3\text{BNX}_2]^-$ and $[(\text{CF}_3)_3\text{BX}]^-$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) have been recently prepared and fully characterized.^[6] The preparation of additional tris(trifluoromethyl)borates $[(\text{CF}_3)_3\text{BY}]^-$, $\text{Y} = \text{N}_2\text{R}_F$ ($\text{R}_F = \text{CF}_3, \text{C}_2\text{F}_5$), OH, NO_2 , as well as the general aspects of perfluoroalkylborates have been recently reviewed.^[7]

With increasing trifluoromethylation the central boron atom becomes more and more protected by a sphere of fluorine atoms. Hence thermal elimination of difluorocarbene, oxidative B–C bond cleavage, and attack by electrophilic reagents become increasingly kinetically hindered. In this respect these borates differ strongly in their properties from their non-fluorinated alkylborate congeners.^[8]

Protection of the B–C bonds is expected to be even more efficient in the tetrakis(trifluoromethyl)borate anion, $[\text{B}(\text{CF}_3)_4]^-$. In this species the BC_4 skeleton would be symmetrically surrounded by a sphere of 12 fluorine atoms, and the negative charge delocalized over four ligands. Due to their bulkiness, the poor polarizability of the fluorine sphere, and the strength of the C–F bonds, species such as these would constitute the perfect weakly coordinating anion.^[9–13] Weakly coordinating anions attract interest in pure chemistry for the stabilization of unusual cations that are inaccessible in traditional superacidic media.^[14–17]

In summary, all attempts made over the last 40 years to synthesize salts with the $[\text{B}(\text{CF}_3)_4]^-$ ion by using CF_3 transfer reagents have failed, and direct fluorination of $[\text{B}(\text{CH}_3)_4]^-$ salts is impractical because the tetramethylborate anion undergoes fast oxidative B–C bond cleavage. However, the homologous species $[\text{M}(\text{CF}_3)_4]^-$ ($\text{M} = \text{Ga}, \text{In}, \text{Tl}$) have been described in the literature.^[18] In this publication we report the

synthesis of the previously unknown tetrakis(trifluoromethyl)borate anion, $[\text{B}(\text{CF}_3)_4]^-$, and describe its chemical, spectroscopic, and structural properties, with reference to those of isoelectronic perfluoroneopentane, $\text{C}(\text{CF}_3)_4$, which has been known since 1955.^[19–22]

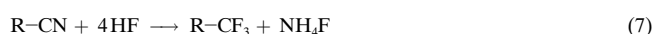
Results and Discussion

Synthesis: Two different routes were developed to yield salts with the $[\text{B}(\text{CF}_3)_4]^-$ ion. Starting from commercially available chemicals, salts containing the $[\text{B}(\text{CF}_3)_4]^-$ ion can be synthesized in high yields in a two-step reaction. In the first step the tetracyanoborates, $\text{M}[\text{B}(\text{CN})_4]$ ($\text{M} = \text{Li}, \text{K}, \text{NH}_4, \text{Cs}, \text{Ag}$ etc.) are prepared.^[23] The second step involves the fluorination of the tetracyanoborates in anhydrous HF solution with an excess of ClF_3 or ClF . The reaction is started at -78°C for 1 h and then continued at room temperature for 24 h. From $\text{M}[\text{B}(\text{CN})_4]$ (1 mol), gaseous N_2 (1.9 mol), NF_3 (0.2 mol), and Cl_2 (1.5 mol) are formed according to the mass balance given in Equation (6).



Some Cl_2 was dissolved in the liquid HF/ ClF_3 mixture used in the synthesis. When the reaction is performed with an excess of tetracyanoborates the mixed species $\text{M}[\text{B}(\text{CF}_3)_n(\text{CN})_{4-n}]$ ($n = 1, 2, 3$) are observed, but no intermediates that contain, for example, $\text{CF}_2\text{-NX}_2$ ($\text{X} = \text{Cl}, \text{F}$) groups are found. There are a few precedents known in the literature for the conversion of CN into CF_3 groups. It is reported that BrF_3 mixed with HF reacts with organic nitriles of lower molecular weight to give the respective trifluoromethyl compounds.^[24] Recently Baker et al. used BrF_3 for the conversion of $\text{NCCH}_2\text{CH}_2\text{CN}$ into $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ at 60°C in good yields.^[25] However, in the literature it is described, that ClF in general converts RCN into RCF_2NCl_2 .^[26]

In principle, it is of interest to elucidate the mechanism of this reaction. A cyano group could undergo a solvolytic reaction in liquid HF to yield a trifluoromethyl group [Eq. (7)].



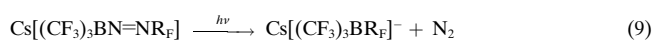
However, this reaction is kinetically hindered, because salts of the tetracyanoborates can be recrystallized from anhydrous HF without any decomposition. Moreover, this reaction may also be thermodynamically unfavorable, because the elimination of HF from CF_3NH_2 to yield FCN is a reaction that occurs readily.^[27] The ease of oxidative fluorination found in this study is surprising. The reaction is presumably initiated by an addition of ClF across the CN bond. This should lead to species with an $\text{R-CF}_2\text{-NCl}_2$ group. *N*-Chloro compounds, which are usually prepared under alkaline conditions, are less stable in an acidic medium like HF. Cleavage of the C–N bond by HF would lead to R-CF_3 and HNCl_2 , which further decomposes to form HCl, N_2 , and Cl_2 . The formation of N_2 may occur either inter- or intra-molecularly. This could be checked by fluorination of a 1:1 mixture of $[\text{B}(\text{C}^{15}\text{N})_4]^-$ and

$[\text{B}(\text{CN})_4]^-$ in HF solution and analysis of the resulting N_2 isotopomers by mass spectrometry. Such experiments are beyond the scope of this study.

The second synthesis uses $\text{Cs}[(\text{CF}_3)_3\text{BNH}_2]$ as the starting material, prepared as outlined in Equations (3) and (5). $\text{Cs}[(\text{CF}_3)_3\text{BNH}_2]$ is treated with R_FNO ($\text{R}_F = \text{CF}_3$ or C_2F_5) in the presence of Cs_2CO_3 in THF solution to form orange-yellow fluoroalkyldiazenidotris(trifluoromethyl)borates $\text{Cs}[(\text{CF}_3)_3\text{BN}=\text{NR}_F]$ in high yields according to Equation (8):



By analogy to $\text{CF}_3\text{N}=\text{NCF}_3$, for example, which forms perfluoroethane when irradiated with the 254 nm line of a mercury lamp,^[28] the diazenidoborates $[(\text{CF}_3)_3\text{BN}=\text{NR}_F]^-$ undergo elimination of N_2 to form the anions $[(\text{CF}_3)_3\text{BR}_F]^-$ ($\text{R}_F = \text{CF}_3, \text{C}_2\text{F}_5$) [Eq. (9)].



However, solvents in which the cesium salts are soluble (acetone, acetonitrile, diethyl ether, ...) take part in the photolysis reaction to give a variety of largely unknown products. Therefore, the photolysis reaction is carried out in the solid state. By evaporating a solution of the cesium salt in acetone a thin film is deposited on the walls of the photolysis reactor. The film is further cooled in an ice bath to avoid thermal decomposition which is known to produce $[(\text{CF}_3)_3\text{BF}]^-$ above 150°C ^[29] [Eq. (10)].



However, under the chosen reaction conditions localized overheating of the film cannot be completely avoided. This results in the formation of a 1:1 mixture of $[(\text{CF}_3)_3\text{BR}_F]^-$ and $[(\text{CF}_3)_3\text{BF}]^-$. Though this method principally allows the synthesis of tetrakis(perfluoroalkyl)borates with perfluoroalkyl groups other than CF_3 , the difficulties encountered in the photolysis reaction and the rather exotic starting materials (R_FNO) prevented us from developing this synthetic route further.

Properties: All the $\text{M}[\text{B}(\text{CF}_3)_4]$ salts ($\text{M} = \text{Li}, \text{K}, \text{Cs}, \text{Ag}$) are colorless solids that are soluble in HF, water, diethyl ether, tetrahydrofuran, acetonitrile, and acetone. The Li, K, and Cs salts are insoluble in methylene chloride, chloroform, and hexane. An aqueous solution of $\text{K}[\text{B}(\text{CF}_3)_4]$ is optically transparent in the visible and UV regions. A very weak absorption starting at 250 nm with increasing intensity towards 200 nm is observed (extinction coefficient of $\varepsilon_{200\text{nm}} = 7 \text{ L mol}^{-1} \text{ cm}^{-1}$); however, this may be due to an organic impurity. The cation in the lithium salt is a good Lewis acid with a high charge density, and it is difficult to isolate the solvent-free salt. Single crystals of the solvent-free potassium and cesium salts, several millimeters in diameter, are easily grown by diffusion of CH_2Cl_2 vapor into a saturated solution in diethyl ether. The crystals appear remarkably hard and brittle and are electrostatically charged while grinding.

The thermal behavior and stability of the $\text{M}[\text{B}(\text{CF}_3)_4]$ salts ($\text{M} = \text{Li}, \text{K}, \text{Cs}, \text{Ag}$) have been investigated by differential scanning calorimetry (DSC) and the results are presented in Table 1. Between -100 and $+100^\circ\text{C}$ the potassium and cesium salt reveal reversible endothermic phase transitions

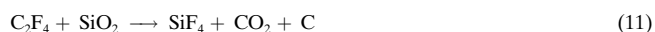
Table 1. Thermal data of some $[\text{B}(\text{CF}_3)_4]^-$ salts, determined by DSC measurements.

	Phase transitions				Decomposition	
	$T^{[a]}$	$\Delta H^{[b]}$	$T^{[a]}$	$\Delta H^{[b]}$	$T^{[a]}$	$\Delta H^{[b]}$
$\text{Li}[\text{B}(\text{CF}_3)_4]$					185	-140
$\text{Ag}[\text{B}(\text{CF}_3)_4]$					260	-90
$\text{K}[\text{B}(\text{CF}_3)_4]$	-65	4.5	-50	8	320	-90
$\text{Cs}[\text{B}(\text{CF}_3)_4]$			50	25	425	-45

[a] Onset temperature [$^\circ\text{C}$]. [b] Enthalpy [J g^{-1}].

whose onset temperatures and enthalpies increase with increasing mass of the cation. These phase transitions will be investigated in detail by vibrational spectroscopy and X-ray diffraction in a forthcoming study. At higher temperatures all salts decompose exothermically, and the stability of the salts increases strongly with decreasing acidity of the counter cation. It is also noted that in high vacuum ($< 10^{-5}$ mbar) the potassium and cesium salt can be sublimed at about 300°C , while the lithium and silver salt decompose under gas evolution above 200°C . Due to the exothermic decomposition of these salts, they can in principle be explosive. However, a small sample of $\text{K}[\text{B}(\text{CF}_3)_4]$ struck with a hammer on an anvil is not found to be shock sensitive. This is a great advantage over the promising, but explosive "inert" anion $[\text{CB}_{11}(\text{CF}_3)_{12}]^-$.^[11]

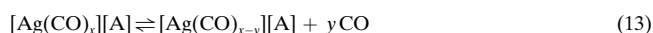
To identify the products of the thermal decomposition, two small crystals of $\text{K}[\text{B}(\text{CF}_3)_4]$ (0.11 mmol) were heated at 500°C in a small quartz vessel connected to an evacuated IR gas cell of 300 mL volume. After 30 minutes the evolution of 0.21 mmol of gaseous products (followed by the increase of the pressure) was complete and a black residue in the quartz vessel was observed. Analysis of the gaseous products by IR spectroscopy resulted in the following composition: C_2F_4 (0.055 mmol), CF_3CFCF_2 (0.023 mmol), SiF_4 (0.048 mmol), CO_2 (0.060 mmol), and BF_3 (0.024 mmol). The olefins C_2F_4 and CF_3CFCF_2 are formed from the initial decomposition product difluorocarbene (CF_2). The products SiF_4 and CO_2 are formed at the rather high temperature in reactions between C_2F_4 and the surface of the quartz vessel according to Equation (11). Taking the loss of C_2F_4 in account, the main thermal decay proceeds as shown in Equation (12). Gaseous BF_3 may be formed by the thermal decomposition of $\text{K}[\text{BF}_4]$.



The $[\text{B}(\text{CF}_3)_4]^-$ anion is chemically rather inert as indicated by selected experiments. We have been unable to oxidize the anion at room temperature with fluorine in anhydrous HF. No reaction occurs with sodium dissolved in liquid ammonia. After evaporation of ammonia and removal of the sodium metal by reaction with ethanol, it is possible to recover

Na[B(CF₃)₄] unchanged. Furthermore, salts of [B(CF₃)₄][−] can be treated in dilute mineral acids without any decomposition of the anion. Hence the anion is resistant towards strong oxidizing as well as reducing agents, and is not affected by normal nucleophiles (C₂H₅O[−]) or electrophiles (Li⁺, H₃O⁺).

The coordinating ability of the [B(CF₃)₄][−] ion has been examined by using CO as a ligand on the silver cation in the solvent-free Ag[B(CF₃)₄] salt. The solvent-free silver salt was prepared from anhydrous HF. Because HF has a very weak coordinating ability it was possible to remove all of the HF molecules in vacuo. Depending on the CO equilibrium pressure over Ag[B(CF₃)₄], the formation of several different species [Ag(CO)_x][B(CF₃)₄] (x = 1–4) was observed at 25 °C in the Raman spectrum. The equilibrium CO pressures of the different carbonyls are compared with the literature data of [Ag(CO)_x] adducts of other weakly coordinating anions in Table 2.^[30–35] The existence of silver carbonyl cations [Ag(CO)_x]⁺ (x = 1–3) in salts with weakly coordinating anions has been studied in detail by Strauss and co-workers for many years^[31–33, 36] and has been the subject of several theoretical calculations.^[34, 37] In all of these cases the mono-carbonyl adducts are more thermally stable than the poly-carbonyls and, hence, more data are available for the monocarbonyls. Even at room temperature or below, the counterion [A][−] competes with the CO ligand in the coordination sphere of the [Ag(CO)_x]⁺ ion according to Equation (13).



The equilibrium pressure of CO over solid [Ag(CO)_x] adducts depends strongly on the nature of the counterion and the temperature. Even though the data presented in Table 2 are somewhat imprecise, due to the uncertainty of the temperature, of the pressure measurement, the stated purity of the salts, and sample preparation, the [B(CF₃)₄][−] ion ranks in this group as an “at least” coordinating anion. At first glance it may be difficult to imagine that the [B(CF₃)₄][−] ion is more weakly coordinating than the [Nb(OTeF₅)₆][−] ion, because the latter carries more fluorine atoms in the periphery. However, quantum-chemical calculations demonstrate that the atomic charges of the fluorine atoms in the –OTeF₅ group are higher than in the –CF₃ group (e.g., CF₄

–0.27 e; TeF₆ –0.38 e) and, therefore, –CF₃ should be less coordinating than –OTeF₅.

Furthermore, it is interesting to note that ν(CO) of the monocarbonyls increases with increasing thermal stability of the salts, but this measurement is much less sensitive to the nature of the counterion than the equilibrium CO pressure is.

The proficiency of this method for ranking anion coordination ability arises from the relatively low Ag–CO bond energy in gaseous [(OC)_xAg–CO]⁺ (x = 0, 1, 2, 3; D_e = ca. 95, 115, 55, 50 kJ mol^{−1}, respectively)^[37] to the M–CO bond energies of thermally stable metal carbonyl cations (e.g. [(OC)Au–CO]⁺; D_e = ca 220 kJ mol^{−1}).^[37] Therefore, salts of the [Ag(CO)_x]⁺ ions are on the border between thermally stable homoleptic metal carbonyl cations^[16, 17] and nonisolable cationic metal–carbonyl adducts.

NMR spectra: The tetrakis(trifluoromethyl)borate anion contains four different NMR active nuclei: ¹¹B (I = 3/2, 80.42 %), ¹⁰B (I = 3, 19.58 %), ¹³C (I = 1/2, 1.108 %), and ¹⁹F (I = 1/2, 100 %); these provide the basis for a comprehensive NMR study. Due to the high symmetry of the anion in solution, the quadrupole moments of ¹¹B and ¹⁰B do not influence the spectra and the signals are very sharp (half-width at half signal height < 1 Hz), as demonstrated by the NMR spectra depicted in Figures 1–3. The 13-line pattern shown in Figure 1 is caused by the ²J(¹¹B, ¹⁹F) coupling of the 12 equivalent ¹⁹F nuclei, and the intensity ratio between the outer and the central signal is close to the calculated value of 1:9:24. The ¹⁹F and ¹³C NMR spectra are shown in Figures 2

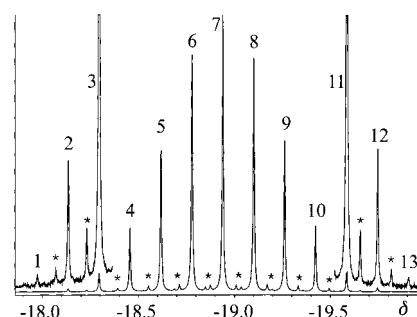


Figure 1. ¹¹B NMR spectrum of K[B(CF₃)₄] dissolved in CD₃CN. The pattern is due to coupling with the 12 equivalent F atoms and the intensity ratio between the outer lines (1, 13) and the inner line (7) is 1:9:24. * indicate ¹³C satellites.

Table 2. Equilibrium pressure of CO [bar = 10⁵ Pa] over different [Ag(CO)_x][A] (x = 1–4) salts at approximately 25 °C and their ν(CO) wavenumbers [cm^{−1}].

Anion	[Ag(CO) ₄] ⁺		[Ag(CO) ₃] ⁺		[Ag(CO) ₂] ⁺		[Ag(CO)] ⁺		Ref.
	p	ν(CO) Raman	p	ν _s (CO) Raman ν _{as} (CO) IR, Raman	p	ν _s (CO) Raman ν _{as} (CO) IR	p	ν(CO) IR, Raman	
gas (calcd)				2165 2166		2180 2180		2177	[34]
[B(CF ₃) ₄] [−]	9	2204	3	2197 n.o. ^[e]	0.0045	2216 ^[a] n.o.	0.0013	2205	this work
[Nb(OTeF ₅) ₄] [−]	–	–	< 13	n.o.	0.011	2220 2196	< 0.010	2204–2208	[32]
[B(OTeF ₅) ₄] [−]	–	–	–	–	0.241	n.o. 2198	< 0.015 ^[b,c]	2204	[31, 32]
[Sb ₂ F ₁₁] [−]	–	–	–	–	–	–	0.053	2198–2202	[30]
[OTeF ₅] [−]	–	–	–	–	–	–	0.421 ^[e]	2189	[31, 32]
[SO ₃ F] [−]	–	–	–	–	19	n.o. 2190	1 ^[c,d]	2190	[32, 35]
[SbF ₆] [−]	–	–	–	–	–	–	> 1	2185	[32, 33]

[a] Additional weak cation band at 230 cm^{−1}. [b] Decomposes into AgOTeF₅ and B(OTeF₅)₃. [c] O atom on Ag⁺ coordinated. [d] Measured at 10 °C. [e] n.o. = not observed.

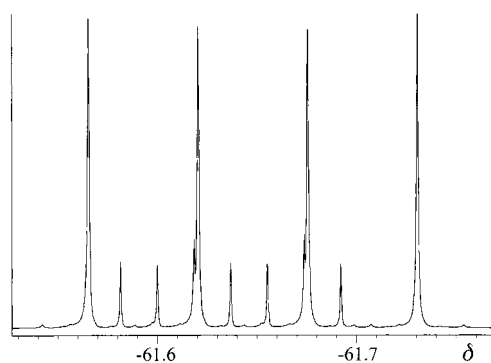


Figure 2. ^{19}F NMR spectrum of $\text{K}[\text{B}(\text{CF}_3)_4]$ dissolved in CD_3CN . The quartet and septet are due to coupling with ^{11}B and ^{10}B , respectively.

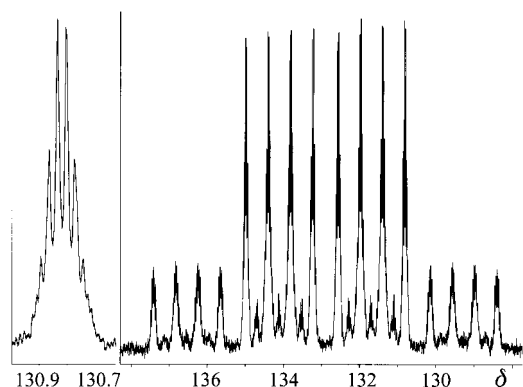


Figure 3. ^{13}C NMR spectrum of $\text{K}[\text{B}(\text{CF}_3)_4]$ dissolved in CD_3CN . Large quartet (1:2:2:1): $^1J(^{13}\text{C},^{19}\text{F})$; small quartet (1:1:1:1): $^1J(^{13}\text{C},^{11}\text{B})$; septet of $^1J(^{13}\text{C},^{10}\text{B})$ partially obscured; expanded section $^3J(^{13}\text{C},^{19}\text{F})$ pattern.

and 3, respectively, in which the $^2J(^{11}\text{B},^{19}\text{F})$, $^2J(^{10}\text{B},^{19}\text{F})$ and $^1J(^{13}\text{C},^{19}\text{F})$, $^1J(^{13}\text{C},^{11}\text{B})$, $^1J(^{13}\text{C},^{10}\text{B})$, $^3J(^{13}\text{C},^{19}\text{F})$ coupling can be recognized. All NMR data of the $[\text{B}(\text{CF}_3)_4]^-$ ion are compared in Table 3^[7, 23] with those of related compounds, except the coupling constants $^3J(^{13}\text{C},^{19}\text{F}) = 3.9$ Hz and $^4J(^{19}\text{F},^{19}\text{F}) = 5.8$ Hz, for which no comparative data are available. The coupling constants involving the ^{10}B nucleus are not listed in Table 3 because they are identical to the values calculated from the respective ^{11}B coupling constants by using the

gyromagnetic ratio $\gamma(^{11}\text{B})/\gamma(^{10}\text{B}) = 2.9858$. Furthermore, the following isotopic shifts^[38] have been observed; these reflect the vibrational motions of the $[\text{B}(\text{CF}_3)_4]^-$ anion and their amplitudes: $^1\Delta^{11}\text{B}(^{12/13}\text{C}) = 0.0030$ ppm, $^1\Delta^{13}\text{C}(^{10/11}\text{B}) = 0.0029$ ppm, $^1\Delta^{19}\text{F}(^{12/13}\text{C}) = 0.1315$ ppm, $^2\Delta^{19}\text{F}(^{10/11}\text{B}) = 0.0111$ ppm, and $^3\Delta^{19}\text{F}(^{12/13}\text{C}) = 0.0010$ ppm.

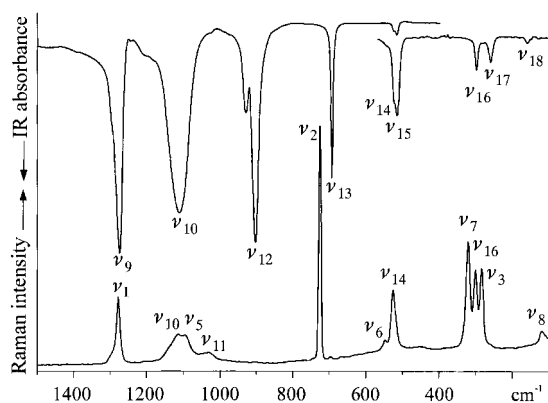
NMR data of borate anions that contain F, CN, and CF_3 ligands are given in Table 3. Most of these species are new and are formed during the synthesis of $\text{M}[\text{B}(\text{CN})_4]$ salts or as by-products in the fluorination of the tetracyanoborates. The ^{11}B chemical shift is significantly affected by the nature of the ligand, with the lowest resonance frequency observed for $[\text{B}(\text{CN})_4]^-$ and the highest for $[\text{BF}_4]^-$. This is expected, due to a dominant influence of the electronegativity of the ligand on the diamagnetic term of the chemical shift. The ^{13}C and ^{19}F chemical shifts of the CF_3 groups in the different anions vary very little. However, the ^{19}F chemical shifts and $^1J(^{11}\text{B},^{19}\text{F})$ coupling constants of the BF group are strongly dependent on the other ligands. There is a jump in the $^1J(^{11}\text{B},^{19}\text{F})$ coupling constant on replacement of one fluorine atom in the $[\text{BF}_4]^-$ ion by another ligand. In the $[\text{BF}_4]^-$ ion itself this coupling constant is too small to be observed, but it appears in the NMR spectrum of the $\text{Li}[\text{BF}_4]$ salt, dissolved in CD_3CN , ($\delta^{11}\text{B} = -1.4$; $\delta^{19}\text{F} = -151.7$; $^1J(^{11}\text{B},^{19}\text{F}) = 3.5$ Hz). The reason is that the Li^+ ion coordinates in solution to the $[\text{BF}_4]^-$ ion and, therefore, the data measured on Li^+ salts should be considered with care (see Table 3). A further significant probe for the electronic situation in borate anions that contain ligands with carbon atoms is the $^1J(^{11}\text{B},^{13}\text{C})$ coupling constant.

Vibrational spectra: The IR and Raman spectra of $\text{K}[\text{B}(\text{CF}_3)_4]$ are depicted in Figure 4, and all vibrational band positions and intensities of the potassium and cesium salt are compared with the data of the isoelectronic $\text{C}(\text{CF}_3)_4$ molecule in Table 4;^[20] vibrational data are predicted from DFT calculations (vide infra). According to the DFT calculations, the free $[\text{B}(\text{CF}_3)_4]^-$ ion and the $\text{C}(\text{CF}_3)_4$ molecule possesses T symmetry with the CF_3 groups rotated from the staggered position that corresponds to T_d symmetry. Such a conforma-

Table 3. NMR data of the $[\text{B}(\text{CF}_3)_4]^-$ ion and related species.

	$\delta^{11}\text{B}$	$\delta^{13}\text{C}$	$\delta^{19}\text{F}$ (CF_3)	$\delta^{19}\text{F}$ (BF)	$^1J(^{11}\text{B},^{13}\text{C})$ [Hz]	$^1J(^{13}\text{C},^{19}\text{F})$ (CF_3) [Hz]	$^2J(^{13}\text{C},^{19}\text{F})$ (BF) [Hz]	$^2J(^{11}\text{B},^{19}\text{F})$ (CF_3) [Hz]	$^1J(^{11}\text{B},^{19}\text{F})$ (BF) [Hz]	$^3J(^{19}\text{F},^{19}\text{F})$ (BF/ CF_3) [Hz]	Ref.
$[\text{BF}_4]^-$	-1.1	-	-	-150.1	-	-	-	-	< 0.5	-	[7], this work
$[\text{BF}_3\text{CF}_3]^-$	-1.3	131.9	-75.0	-155.4	109.9	312	66.6	32.5	39.3	2.4	[7], this work
$[\text{BF}_3\text{CN}]^-$	-3.6	n.o. ^[a]	-	-136.3	89.3	-	n.o.	-	26.6	-	this work
$[\text{BF}_2(\text{CF}_3)_2]^-$	-2.0	132.0	-73.9	-181.0	91.0	309.4	42.0	30.5	57.2	< 5	[7], this work
$[\text{BF}_2(\text{CF}_3)\text{CN}]^-$	-3.8	n.o.	-76.6	-167.9	n.o.	n.o.	n.o.	34.6	48.6	< 5	this work
$[\text{BF}_2(\text{CN})_2]^-$	-7.3	129.1 ^[b]	-	-152.9	80.7	-	50.6 ^[b]	-	40.6	-	this work
$[\text{BF}(\text{CF}_3)_3]^-$	-7.1	132.6	-68.8	-230.4	80.0	309.4	30.5	28.3	59.4	5.5	[7], this work
$[\text{BF}(\text{CF}_3)_2\text{CN}]^-$	-9.2	n.o.	-70.8	-225.3	n.o.	n.o.	n.o.	31.6	54.1	7.5	this work
$[\text{BF}(\text{CF}_3)(\text{CN})_2]^-$	-12.8	n.o.	-73.0	-218.6	n.o.	n.o.	n.o.	35.7	48.8	8.9	this work
$[\text{BF}(\text{CN})_3]^-$	-17.8	128.0 ^[b]	-	-210.6	77.9	-	37.4 ^[b]	-	44.0	-	this work
$[\text{B}(\text{CF}_3)_4]^-$	-18.9	132.9	-61.6	-	73.4	304.3	-	25.9	-	-	this work
$[\text{B}(\text{CF}_3)_3\text{CN}]^-$	-22.2	n.o.	-62.2	-	n.o.	n.o.	-	28.9	-	-	this work
$[\text{B}(\text{CF}_3)_2(\text{CN})_2]^-$	-26.5	n.o.	-63.6	-	n.o.	n.o.	-	32.5	-	-	this work
$[\text{B}(\text{CF}_3)(\text{CN})_3]^-$	-32.0	n.o.	-65.2	-	69.5 ^[c]	301.8	-	36.4	-	-	this work
$[\text{B}(\text{CN})_4]^-$	-38.5	122.3	-	-	71.3	-	-	-	-	-	[23]

[a] n.o. = not observed. [b] Li salt. [c] B-CN.

Figure 4. IR and Raman spectrum of K[B(CF₃)₄].

tion is also found in the molecular structure of C(CF₃)₄,^[22] determined in the gas phase by electron diffraction.

In addition, vibrational spectroscopy allows us to distinguish between T_d and T symmetry by means of vibrational selection rules given in Equations (14) and (15), respectively.

$$T_d: \Gamma_{\text{vib}} = 3A_1(\text{Ra,p}) + 1A_2(-) + 4E(\text{Ra,dp}) + 4F_1(-) + 7F_2(\text{IR;Ra,dp}) \quad (14)$$

$$T: \Gamma_{\text{vib}} = 4A(\text{Ra,p}) + 4E(\text{Ra,dp}) + 11F(\text{IR;Ra,dp}) \quad (15)$$

By lowering the symmetry from T_d to T , the inactive modes A_2 and F_1 become active. Consequently, there are, in principle, four extra active fundamentals in the IR spectrum and five in the Raman spectrum. The vibrational spectra of the potassium and cesium salts are very similar (except for the relative band intensities below 300 cm⁻¹ in the IR spectrum), and from the

number of observed vibrations, a symmetry lower than T_d can be deduced for the [B(CF₃)₄]⁻ ion. This distortion from T_d symmetry in the solid state is not caused by the lattice sites, because the crystal structures of both [B(CF₃)₄]⁻ salts are different. Indeed, the structure of the [B(CF₃)₄]⁻ ion seems to depend very little on the environment, as the Raman spectra of the solid Li⁺ and Ag⁺ salts as well as those of their aqueous solutions (see Experimental Section) are nearly identical to the Raman data presented in Table 4. From the possible 19 fundamentals of the [B(CF₃)₄]⁻ ion, the wavenumbers of 17 fundamentals are obtained experimentally. The unobserved CF₃ torsional modes are outside the range of our spectrometer, and according to calculations are too weak for detection (vide infra). The same is true for the C(CF₃)₄ molecule, based on the reported experimental data.^[20] However, Bürger et al. have assigned the bands under T_d symmetry and have attributed some observed fundamental bands to combination modes. The assignment of the bands presented in Table 4 is supported by a comparison of calculated and observed band positions and IR band intensities. The agreement between observed and calculated Raman band intensities is not satisfactory, and only slightly useful for assignment purposes. All calculated wavenumbers for the stretching modes are higher than the observed band positions, but the band sequence generally corresponds to that of the observations. The bands ν_9 and ν_1 are an exception, but in these cases the selection rules enables an unambiguous assignment. The spectra of the isoelectronic species [B(CF₃)₄]⁻ and C(CF₃)₄ are very similar, except for the band intensities of the ν_9/ν_{10} vibrations. For C(CF₃)₄ all bands are blue-shifted; this implies that all bonds in the C(CF₃)₄ molecule are significantly stronger than those in the [B(CF₃)₄]⁻ ion.

Table 4. Experimental and calculated vibrational data for the [B(CF₃)₄]⁻ ion and those of the isoelectronic C(CF₃)₄ molecule.

M[B(CF ₃) ₄]		[B(CF ₃) ₄] ⁻ (calcd) ^[d]			C(CF ₃) ₄ ^[h]			C(CF ₃) ₄ (calcd) ^[d]		Assignment ^[l]				
IR M = Cs	IR M = K	Raman M = Cs	Raman M = K	IR int. ^[b]	Raman active ^[c]	Band position	IR int. ^[e]	Raman active ^[f]	IR gas	Raman solid	Raman active	Band position	IR int. ^[i]	
1293	1298	1294	1296	10/7	9/6	1305	17	2 ^[g]						ν_9 , T, ν_2 (CF ₃) ¹⁰ B
1273	1276	1276 ^[a]	1279 ^[a]	35/53	– ^[a]	1288	71	8	1301 (vvs)	–	–	1331	100	ν_9 , T, ν_3 (CF ₃) ¹¹ B
–	–	1276	1279	–	52/51	1294	0	132	–	1292	8	1309	0	ν_1 , A, ν_3 (CF ₃)
–	–	1104 ^[a]	1095	–	– ^[a] /26	1139	0	10	–	1248 ^[i]	0.5	1274	0	ν_5 , E, ν_{as} (CF ₃)
1098	1112	1104	1111	100	68/37	1151	100	38	1203 (s)	–	–	1213	1.4	ν_{10} , T, ν_{as} (CF ₃)
–	–	1030	1026	–	7/7	1059	0.00	6	–	1160	1	1176	0.01	ν_{11} , T, ν_{as} (CF ₃)
930	931	–	–	9/13	–	947	13	0.2 ^[g]	–	–	–	–	–	ν_{12} , T, ν_{as} (BC ₄) ¹⁰ B
902	904	901	900	43/49	0.9/0.6	921	42	0.6	995 (vs)	–	–	1006	17	ν_{12} , T, ν_{as} (BC ₄) ¹¹ B
–	–	725	726	–	100	717	0	100	–	771	100	764	0	ν_2 , A, δ_s (CF ₃)
698	694	695	696	12/15	0.8/0.8	689	8	0.6	737 (vs)	–	–	727	4.8	ν_{13} , T, δ_s (CF ₃)
–	–	546	547	–	7/7	541	0	5	–	584	2	577	0	ν_6 , E, δ_{as} (CF ₃)
523 ^[a]	525	526	527	– ^[a] /0.5	50/46	513	0.09	9	–	550.5	8	539	0.09	ν_{14} , T, δ_{as} (CF ₃)
523	518	526 ^[a]	518 (sh)	1.5/13	– ^[a]	508	1.3	11	539 (vs)	538	4	528	0.9	ν_{15} , T, δ_{as} (CF ₃)
319	–	320	321	0.03/–	90/69	317	0	26	–	351	23	345	0	ν_7 , E, ρ (CF ₃)
297	299	298	301	0.7/0.4	51/43	292	0.16	10	326 (w)	326	22	329	0.02	ν_{16} , T, ρ (CF ₃)
280	–	281	284	0.04/–	62/54	270	0	26	–	317	60	319	0	ν_3 , A, ν_3 (BC ₄)
253	260	–	–	0.01/0.4	–	252	0.02	0.2	298 (w)	295	4	298	0.01	ν_{17} , T, ρ (CF ₃)
156	160	–	–	0.5/0.05	–	130	0.07	0.01	–	200 ^[i]	1	199	0.13	ν_{18} , T, δ (CBC)
–	–	117	118	–	12/6	96	0	0.2	–	150	3	147	0	ν_8 , E, δ (CBC)
–	–	–	–	–	–	53	0.00	0.00	–	–	–	90	0.01	ν_{19} , T, τ (CF ₃)
–	–	–	–	–	–	47	0	0.00	–	–	–	81	0	ν_4 , A, τ CF ₃

[a] Obscured by the next strong band. [b] Relative integrated IR absorbance of the Cs/K salts, $\nu_{11} \equiv 100$. [c] Relative integrated Raman intensity of the Cs/K salts, $\nu_2 \equiv 100$. [d] B3LYP/6-31G*. [e] Relative IR oscillator strength (ν_{10} 334 km mol⁻¹), all values, except for ν_9 and ν_{12} are averaged from the calculated values for ¹¹B(80%) and ¹⁰B(20%), 0 \equiv inactive, 0.00 \equiv int. < 0.01. [f] Relative Raman scattering (ν_2 8.2 Å⁴ AMU⁻¹) for ¹¹B. [g] Calculated from the ¹⁰B/¹¹B isotopic mass ratio. [h] Ref. [20]. [i] Derived from combinations several fundamentals and the Figure 1 in ref. [20]. [j] Relative IR oscillator strength ($\nu_9 = 768$ km mol⁻¹). [l] Assignment according to T symmetry approximate description of modes.

Table 5. Selected bond lengths [\AA] and angles [$^\circ$] for $\text{Cs}[\text{B}(\text{CF}_3)_4]$, $\text{C}(\text{CF}_3)_4$, and related compounds.

Parameter ^[a]	$\text{K}[\text{BF}_3(\text{CF}_3)]$	$\text{Cs}[\text{BF}_2(\text{CF}_3)_2]$	$\text{Cs}[\text{BCl}(\text{CF}_3)_3]$	$\text{Cs}[\text{B}(\text{CF}_3)_4]$		$\text{C}(\text{CF}_3)_4$	
	exptl ^[b]	exptl ^[c]	exptl ^[d]	exptl	calcd ^[e]	exptl ^[f]	calcd ^[e]
M–C	1.625(6)	1.617(9)	1.627(4)	1.625(3)	1.633	1.562(2)	1.563
B–X	1.391(5)	1.391(4)	1.861(6)	–	–	–	–
C–F	1.343(5)	1.353(10)	1.340(5)	1.355(3)	1.369	1.325(2)	1.341
C–M–C	–	113.6(5)	110.8(2)	109.5(3)	109.47	109.47	109.47
C–B–X	109.1(3)	108.7(4)	108.1(2)	–	–	–	–
X–B–X	109.9(3)	108.1(4)	–	–	–	–	–
B–C–F	113.7(3)	114.0(7)	113.8(3)	113.6(2)	113.4	110.8	110.8
F–C–F	104.9(3)	104.0(8)	104.8(3)	105.0(2)	105.2	108.1(2)	108.1
F–C–M–C	51.7	60, 0	53.9	52.7(8)	45.8	41.7(5)	43.6
τ ^[g]	8.3	0, 60	6.1	7.3(8)	14.2	18.3(5)	16.4
pointgroup	$C_1 \sim C_3$	C_s	C_3	$C_3 \sim T$	T	T	T

[a] M = B or C; X = F or Cl. [b] Ref. [39]. [c] Ref. [40]. [d] Ref. [6]. [e] B3LYP/6-31G*. [f] Ref. [22]. [g] Torsional angle from the staggered orientation of the CF_3 group.

Quantum-chemical calculations: The geometries of the $[\text{B}(\text{CF}_3)_4]^-$ anion and the $\text{C}(\text{CF}_3)_4$ molecule were fully optimized with the B3LYP approximation, by using the 6-31G* basis set. For both species the energy minimum is predicted for T symmetry with the CF_3 groups rotated off the eclipsed position by 14.2° and 16.4° , respectively. The energy difference between the T_d form and the energy minimum amounts to 2.69 kJ mol^{-1} for the $[\text{B}(\text{CF}_3)_4]^-$ ion. Interestingly, the total charge on the boron atom was calculated to be nearly zero, while the charges for carbon and fluorine are about 0.68 and $-0.31 e^-$, respectively. In the $\text{C}(\text{CF}_3)_4$ molecule the calculated charges are C(central): -0.53 , C(terminal): 0.87, and F: $-0.25 e^-$.

Calculated bond parameters and vibrational frequencies as well as IR and Raman band intensities are compared to the corresponding experimental values in Tables 4 and 5.^[6, 22, 39, 40]

All quantum chemical calculations were performed with the Gaussian98 program suite.^[41]

The crystal and molecular structure of $\text{Cs}[\text{B}(\text{CF}_3)_4]$: A large fraction of the isolated crystals consisted of two interpenetrated tetrahedra that could be shown to represent inversion twins (see Table 6). The amount of individual tetrahedra within the crop was below 1%. They represent single crystals as well as those obtained by splitting the bi-tetrahedral species. For the data set used to derive the final structural model, an isolated tetrahedral crystal with extremely narrow intensity profiles (mean width at half height less than 0.6° in omega) was chosen for data collection with a scan range adjusted to 0.8° .

$\text{Cs}[\text{B}(\text{CF}_3)_4]$ crystallizes in a distorted NaCl-type lattice with $[\text{B}(\text{CF}_3)_4]^-$ ions defining the cubic closest packing. The

Table 6. Crystallographic data for the structure determination of four different crystals of $\text{Cs}[\text{B}(\text{CF}_3)_4]$ at 150 K.

	tetrahedron	Crystal form		
		cleaved crystal ^[a]	two interpenetrated tetrahedra (twin) ^[b]	plate (103) (twin)
chemical formula		$\text{C}_4\text{BCsF}_{12}$		
formula weight		419.76		
crystal system, space group		rhombohedral, $R\bar{3}m$, (No. 160)		
a [\AA]	7.883(1)	7.883(1)	7.880(1)	7.878(1)
c [\AA]	13.847(4)	13.830(3)	13.849(3)	13.870(4)
V [\AA^3]; $Z = 3$	745.2	744.3	744.7	745.5
ρ_{calcd} [Mg m^{-3}]	2.806	2.810	2.808	2.805
μ [mm]	3.885	3.890	3.888	3.884
extinction coefficient	0.0055(4)	0.0067(7)	0.021(1)	0.0166(8)
absolute structure parameter			0.29(4)	0.61(2)
θ range [$^\circ$]	3.33–29.95	3.33–29.97	3.33–29.96	3.33–29.97
index range	$-11 < h < 0$ $-9 < k < 11$ $-19 < l < 19$	$-11 < h < 0$ $-9 < k < 11$ $-19 < l < 19$	$0 < h < 11$ $-11 < k < 0$ $-19 < l < 19$	$-11 < h < 0$ $-9 < k < 11$ $-19 < l < 19$
reflections collected/unique	1555/589	1555/589	857/448	1555/589
reflection observed [$I > 2\sigma(I)$]	589	589	448	589
R (int)	0.0241	0.0453	0.0185	0.0488
R (sigma)	0.0226	0.0365	0.0115	0.0393
data/restraints/parameters	589/5/55	589/5/55	448/5/56	589/5/56
$R1$ (all data) ^[c]	0.0118	0.0173	0.0173	0.0159
$wR2$ (all data) ^[d]	0.0290	0.0349	0.0417	0.0306
goodness-of-fit on F^2	1.063	1.059	1.080	1.050
largest diff. peak/hole [$e \text{\AA}^{-3}$]	0.29/–0.18	1.47/–0.54	0.80/–0.69	0.37/–1.29
refined diff. density rms [$e \text{\AA}^{-3}$]	0.044	0.084	0.083	0.074

[a] Obtained from cleavage of two interpenetrated tetrahedra. [b] For $l < 0$ not all reflections are measured. [c] $R1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$. [d] $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^{1/2}$.

Cs atoms are surrounded by twelve fluorine atoms at distances ranging from 3.194 to 3.466 Å.

In the initial structural model, the $[\text{B}(\text{CF}_3)_4]^-$ ions appeared to have ideal T_d symmetry. However, from spectroscopic data and quantum chemical calculations (vide supra) a less symmetric architecture has to be taken into account. This prediction could finally be verified by the X-ray data, which also support a structure of symmetry T . This structure was derived from the initial model by rotating the CF_3 groups around their B–C vectors from T_d symmetry by approximately 7° . These torsion angles are smaller than the theoretical predicted angles (14.2°) based on DFT calculations (vide supra).

The final structural model is the result of a superposition of two spatial orientations in a 1:1 ratio that are related by a mirror plane. An ordered structure can be excluded due to a lack of superstructure reflections. Geometrical data of the $[\text{B}(\text{CF}_3)_4]^-$ ion are given in Table 5 together with relevant bond lengths and valence angles of $\text{C}(\text{CF}_3)_4$ and related compounds containing tetrahedral $[\text{B}(\text{CF}_3)_n\text{X}_{4-n}]^-$ ($\text{X} = \text{F}, \text{Cl}$) units. The molecular structure is shown in Figure 5. It is interesting to note that the B–C and C–F bond lengths in the anionic species are all the same within the error limits. They are systematically longer than in the $\text{C}(\text{CF}_3)_4$ molecule in agreement with the lower vibrational frequencies of the $[\text{B}(\text{CF}_3)_4]^-$ ion.

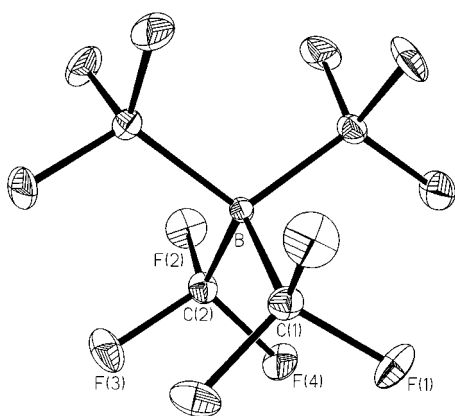


Figure 5. The isolated $[\text{B}(\text{CF}_3)_4]^-$ anion in $\text{Cs}[\text{B}(\text{CF}_3)_4]$.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 164428. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Conclusion

Two different routes lead to several salts of the previously unknown tetrakis(trifluoromethyl)borate anion. According to the NMR spectra the twelve fluorine atoms are equivalent and all possible chemical shifts and coupling constants have

been observed. The four CF_3 groups protect the central boron atom completely and they are oriented in a framework of T symmetry, as deduced from vibrational spectroscopy of the anion in different environments, and from X-ray diffraction of $\text{Cs}[\text{B}(\text{CF}_3)_4]$. This result and all observed vibrational and structural data are in agreement with the results of quantum-chemical calculations. The anion is surprisingly kinetically and thermally stable and very weakly coordinating like the tetrakis(perfluoroalkoxy)aluminate $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ anion.^[12, 13] Its coordination ability is ranked by the measured equilibrium CO pressure over different $[\text{Ag}(\text{CO})_x]^+$ salts ($x = 1-4$), and the $[\text{Ag}(\text{CO})_4]^+$ ion is observed for the first time. Due to these excellent properties, we intend to try and use the $[\text{B}(\text{CF}_3)_4]^-$ ion as a counterion for the stabilization of hitherto unknown highly electrophilic species in all areas of chemistry, especially for carbonyl cations like $[\text{Co}(\text{CO})_5]^+$, $[\text{Ni}(\text{CO})_4]^{2+}$, $[\text{CICO}]^+$, and so forth.

To our knowledge the fluorination of a complex cyano anion in anhydrous HF with ClF or ClF_3 to give the corresponding trifluoromethyl complex is new, and we intend to adapt this methodology to the fluorination of further cyano complexes, such as $[\text{Pt}(\text{CN})_6]^{2-}$ and $[\text{Au}(\text{CN})_4]^-$, that are stable in anhydrous HF.

Experimental Section

Apparatus: Volatile materials were manipulated in stainless steel or glass vacuum lines of known volume equipped with capacitance pressure gauges (type 280E Setra Instruments, Acton MA, or type 221 AHS-1000 MKS Baratron, Burlington, MA). The stainless steel line was fitted with bellow valves (type BPV 25004 Balzers and type SS4BG Nupro) as well as with Gyrolok™ and Cajon™ fittings, while the glass vacuum line was fitted with PTFE stem valves (Young, London) and NS 14.5 standard tapers. The glass vacuum line was equipped with three U-traps and connected to an IR cell (optical path length 200 mm, Si windows 0.5 mm thick) contained in the sample compartment of the FTIR instrument. Anhydrous HF was stored in a PFA tube (12 mm o.d., 300 mm long), heat sealed at the bottom, and connected at the top to a stainless steel needle valve (3762 H46Y Hoke, Cresskill, NJ). For synthetic reactions in HF a reactor was used that consisted of a 250 mL PFA bulb with a NS29 socket standard taper (Bohlander, Lauda, Germany) in connection with a PFA NS29 cone standard taper and a PFA needle valve (type 204-30 Galtek, fluoroware™, Chaska, Minnesota). The parts were held together with a metal compression flange and the reactor was leakproof ($< 10^{-5}$ mbar L s^{-1}) without using grease. Hygroscopic $\text{Li}[\text{B}(\text{CF}_3)_4]$ was manipulated inside an inert atmosphere box (Braun, München, Germany) flushed with argon, with a residual moisture content of less than 0.1 ppm.

Chemicals: Anhydrous HF (Solvay AG, Hannover, Germany), ClF_3 , ClF (ABCR GmbH, Karlsruhe, Germany) as well as all standard chemicals and solvents were obtained from commercial sources. $\text{CF}_3\text{NO}(\text{C}_2\text{F}_5\text{NO})$ was prepared from $\text{CF}_3\text{I}(\text{C}_2\text{F}_5\text{I})$ and NO , as reported.^[42, 43] The salts $\text{M}[\text{B}(\text{CN})_4]$ ($\text{M} = \text{Li}^+, \text{Ag}^+, \text{NH}_4^+$) were synthesized as described previously.^[23]

Vibrational spectroscopy: Infrared spectra were recorded at room temperature on an IFS-66v FT spectrometer (Bruker, Karlsruhe, Germany). Two different DTGS detectors together with a Ge/KBr or a 6 μm Mylar beam splitter operating in the region 4000–400 or 550–80 cm^{-1} , respectively, were used. For each spectrum 128 scans were co-added with an apodized resolution of 2 or 4 cm^{-1} . Solid $\text{K}[\text{B}(\text{CF}_3)_4]$ or $\text{Cs}[\text{B}(\text{CF}_3)_4]$ samples were measured as KBr or CsBr discs, respectively, in the region 4000–400 cm^{-1} , and as Nujol mulls between polyethylene discs in the region 550–80 cm^{-1} . Raman spectra were recorded at room temperature with a Bruker RFS 100/S FT Raman spectrometer using the 1064 nm exciting line (≈ 500 mW) of a Nd/YAG laser. Crystalline samples contained in large melting point capillaries (2 mm o.d.) were used for recording spectra in the

region 3500–50 cm⁻¹ with a resolution of 2 cm⁻¹. For each spectrum 256 scans were co-added, and the Raman intensities were corrected by calibration of the spectrometer with a tungsten halogen lamp.

Raman spectra of [Ag(CO)_x][B(CF₃)₄] (*x* = 0–4) were obtained from a small sample (ca. 0.1 mmol) placed in a small Raman cell (*V* = 1 mL) connected with a rotational symmetrical valve (Young, London).^[44] Equilibrium pressures of CO (below 100 mbar) over the sample were measured directly at a vacuum line of 50 mL internal volume with a capacity manometer (type 221 AHS-100 MKS Baratron, Burlington, MA). Higher equilibrium pressures were estimated by PVT measurements after expansion of the CO from the Raman cell into the vacuum line. Achievement of the gas/solid equilibrium needed about one hour in our experimental setup. For 40 different Ag:CO ratios the respective Raman spectra were recorded and evaluated.

NMR spectroscopy: NMR spectra were obtained at room temperature on a Bruker Avance DRX-500 spectrometer operating at 125.758, 160.461, or 470.593 MHz for ¹³C, ¹¹B, or ¹⁹F nuclei, respectively. All samples (K⁺, NH₄⁺, or Cs⁺ salts; the NMR data of Li[BF₄] and some other Li⁺ salts were significantly different) were dissolved in CD₃CN (*c* = 0.1 to 1 mol L⁻¹), which also served as a lock, and transferred into 5 mm o.d. NMR tubes. The NMR signals were referenced with respect to TMS and CFC₃ as internal standards and BF₃·Et₂O/CD₃CN as external standard and recorded with the following typical acquisition parameters: ¹³C spectral width 32680 Hz/260 ppm, 4.3 μs (45°) pulse, 8 s relaxation delay, 0.5 Hz per data point, 400 scans. ¹¹B spectral width 7310 Hz/46 ppm, 2 μs (20°) pulse, 4.5 s relaxation delay, 0.5 Hz per data point, 32 scans.

Differential scanning calorimetry: Thermo-analytical measurements were made with a Netzsch DSC204 instrument. Temperature and sensitivity calibrations in the temperature range of 20–500 °C were carried out with naphthalene, benzoic acid, KNO₃, AgNO₃, LiNO₃, and CsCl. About 25–40 mg of the solid samples were weighed and contained in sealed aluminium crucibles. They were studied in the temperature range –100–+450 °C with a heating rate of 10 K min⁻¹; throughout this process the furnace was flushed with dry nitrogen. For the evaluation of the output, the Netzsch Protens4.0 software was employed.

Single-crystal X-ray diffraction, data collection, and structure solution and refinement: A crystal of the Cs[B(CF₃)₄] was mounted on top of a glass capillary with silicone grease and placed into the cold nitrogen stream of the cooling device of the goniometer. Intensity data were collected at 150 K with a Siemens P4RA four-circle diffractometer [MoK_α radiation (*λ* = 0.71073 Å), graphite monochromator, rotating anode generator, scintillation counter] under stable experimental conditions.^[45] These were subsequently corrected for Lorentz, polarization, and absorption effects. Lattice constants were obtained from a least-squares fit of the positions of 18 centered reflections of favorable spatial distribution in the 2θ range above 20°. The structure was solved by direct methods in the space group *R*3*m* (No. 160) and refined with anisotropic temperature factors.^[46, 47] A summary of experimental details is given in Table 6.

Synthetic reactions

Method A: The PFA reactor described above, containing a PTFE-coated magnetic stirring bar, was charged with NH₄[B(CN)₄] (105 mg, 0.79 mmol) and dried in vacuo. The ammonium salt was used as the starting material, because it is most soluble in anhydrous HF. By using the stainless steel vacuum line anhydrous HF (5 mL) and ClF₃ (11 mmol) or ClF (33 mmol, determined by PVT measurements) were admitted to the reactor at –196 °C. Cooling with an ethanol/dry ice bath, the content was stirred at –78 °C for one hour and then left at room temperature for one day. Subsequently, all volatile material was pumped off and the solid residue was treated with K₂CO₃ (300 mg, 2.17 mmol) dissolved in water (7 mL). The resulting solution was dried in vacuo (under these conditions the possible by-product NH₄HCO₃ evaporates) and the solid residue extracted with diethyl ether. After evaporation of the diethyl ether, pure K[B(CF₃)₄] (209 mg, 0.69 mmol) was obtained. Other M[B(CF₃)₄] salts (M = Li, Na, Rb, Cs) can be obtained analogously by using M₂CO₃ with M = Li, Na, Rb, Cs instead of K₂CO₃. However, some solvent (H₂O, diethyl ether) is strongly bonded in the isolated lithium and sodium salts.

The solvent-free silver or lithium salt were prepared by using M[B(CN)₄] (M = Ag, Li) as the starting material. The 250 mL PFA reactor, which contained a PTFE coated magnetic stirring bar, was charged with Ag[B(CN)₄] (180 mg, 0.8 mmol) or Li[B(CN)₄] (100 mg, 0.8 mmol) and

dried in vacuo. Anhydrous HF (5 mL) and ClF₃ (11 mmol) were transferred into the reactor at –196 °C. After stirring the contents at –78 °C for one hour the reactor was left for two days at room temperature. Subsequently all volatile material was pumped off until no pressure increase by evaporation of HF was observed. Both hygroscopic silver and lithium salts must be handled in a dry box.

Raman data for Li[B(CF₃)₄]: *ν* = 1289 (s), 1113 (m, br), 1055 (m, br), 728 (vs), 696 (w), 546 (w), 528 (s), 519 (s), 321 (s), 301 (m), 287 (s), 121 cm⁻¹ (w)

Raman data for Ag[B(CF₃)₄]: *ν* = 1297 (sh), 1277 (s), 1116 (m, br), 1069 (m, br), 1011 (m, br), 726 (vs), 696 (w), 546 (w), 528 (s), 518 (sh), 321 (s), 301 (s), 286 (s), 120 cm⁻¹ (w)

Raman data for [B(CF₃)₄]⁻ in aqueous solution: *ν* = 1297 (sh), 1277 (s), 1111 (m, br), 1064 (w, br), 1026 (w, br), 726 (vs), 698 (w), 547 (w), 526 (s), 319 (s), 298 (s), 279 (s), 116 cm⁻¹ (w)

For crystal growth a small test tube filled with a solution of K[B(CF₃)₄] or Cs[B(CF₃)₄] in diethyl ether was placed in a polyethylene bottle with the bottom covered with methylene chloride. In the closed container the solvents were allowed to diffuse in each other at room temperature and crystals of several millimeters diameter were formed within a few days. Crystal form: K[B(CF₃)₄], cubic; Cs[B(CF₃)₄], tetrahedra grown together.

Method B – Cesium pentafluoroethyldiazidenidetrifluoromethylborate Cs[(CF₃)₃BN=NC₂F₃]: C₂F₅NO (30 mmol) was condensed at –196 °C onto a mixture of Cs₂CO₃ (4 g, 12.3 mmol) and Cs[(CF₃)₃BNH₂] (3 g, 8.2 mmol) in THF (60 mL), and the resulting mixture was stirred for 48 h at –20 °C. Unreacted C₂F₅NO and THF were removed in vacuo, and the orange-yellow residue was extracted with acetone. The acetone was evaporated and the residue crystallized from water. Yield 3.4 g (78%); ¹⁹F NMR (470.461 MHz, [D₃]CH₃CN, 25 °C, CFC₃): *δ* = –64.7 (quartet, ²*J*(B,F) = 25.2 Hz, 9F; (CF₃)₃B), –83.8 (singlet, 3F; C–CF₃), –114.4 (singlet, 2F; –CF₂–N); ¹³C NMR (125.758 MHz, [D₃]CH₃CN, 25 °C, TMS): *δ* = 119.7 (quartet of triplets, ¹*J*(C,F) = 286.1 Hz, ²*J*(C,F) = 39.1 Hz, 1C; C–CF₃), 113.5 (triplet of quartets of quartets, ¹*J*(C,F) = 264.0 Hz, ³*J*(B,C) = 10.5 Hz, ²*J*(C,F) = 35.0 Hz, 1C; –CF₂–N), 133.1 (quartet of quartets, ¹*J*(C,F) = 306.4 Hz, ¹*J*(B,C) = 76.4 Hz, 3C; (CF₃)₃B); ¹¹B NMR (160.461 MHz, [D₃]CH₃CN, 25 °C, Et₂OBF₃): *δ* = –9.3 (decet, ²*J*(B,F) = 25.3 Hz, 1B); IR (film)/Raman: *ν* = 1575 cm⁻¹ (m) (N=N); UV/Vis (H₂O): *λ*_{max} (*ε*) = 442 nm (10 mol⁻¹ dm³ cm⁻¹).

Cesium trifluoromethyldiazenido-tris(trifluoromethyl)borate, Cs[(CF₃)₃BN=NCF₃] was prepared analogously from Cs[(CF₃)₃BNH₂] and C₂F₅NO in 80 % yield; spectroscopic data are given in ref [29].

Irradiation of Cs[(CF₃)₃BN=NR_F] (R_F = CF₃, C₂F₅): A solution of Cs[(CF₃)₃BN=NR_F] (2 g) in acetone (20 mL) was transferred into a cylindrical reactor (diameter 3.8 cm, length 20 cm). The acetone slowly evaporated as the reactor was rotated to obtain a thin film on the walls of the reaction vessel. The reactor was evacuated, cooled in an ice bath and irradiated with the 254 nm line of a mercury lamp (type TNN15/32, Heraeus Hanau) for 30 hours. ¹⁹F and ¹¹B NMR spectra were measured for the photolyzed material and showed that approximately 40 % of the starting material had not reacted. About 60 % of the material was found to be a 1:1 mixture of Cs[(CF₃)₃BF] and Cs[(CF₃)₃BR_F] (R_F = CF₃, C₂F₅). NMR spectral data of Cs[(CF₃)₃BC₂F₃]: ¹⁹F NMR (470.461 MHz, [D₃]CH₃CN, 25 °C, CFC₃): *δ* = –61.5 (quartet of sextets, ²*J*(B,F) = 25.9 Hz, ⁴*J*(F,F) ≈ ⁶*J*(F,F) ≈ 5.9 Hz, 9F; (CF₃)₃B), –83.4 (decet of triplet, ⁶*J*(F,F) = 5.6 Hz, ³*J*(F,F) = 0.9 Hz, 3F; CF₃–C); –122.4 (decet of quartets of quartets, ⁴*J*(F,F) = 5.9 Hz, ²*J*(B,F) = 17.9 Hz, ³*J*(F,F) = 0.9 Hz, 2F; CF₃B); ¹¹B NMR (160.461 MHz, [D₃]CH₃CN, 25 °C, Et₂OBF₃): *δ* = –18.7 (decet of triplets, ²*J*(B,F) = 25.8 Hz, ²*J*(B,F) = 17.7 Hz, 1B).

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