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Boron Clusters

closo-$[B_{21}H_{18}]^-$: A Face-Fused Diicosahedral Borate Ion**

Eduard Bernhardt, David J. Brauer, Maik Finze, and Helge Willner**

Dedicated to Professor Hans Bürger on the occasion of his 70th birthday

The first *closo*-borate ion $[B_{10}H_{10}]^{2-}$[1] was synthesized in 1959, and all further members of the series $[B_nH_n]^{2-}$ ($n = 6$–12)[2–8] were discovered in the following eight years. In addition, a few coupled *closo*-borate ions were obtained in which two *closo* fragments were usually linked by a 2c–2e bond between two boron atoms as in $[(B_6H_5)_2]^{4-}$[6] and $[(B_{10}H_9)_2]^{4-}$.[9] To the best of our knowledge, no coupled *closo*-borate ion has previously been described which contains either shared corners, edges, or faces. However, a *closo*-borane with the formula $B_{20}H_{16}$ is known in which two B_{12} icosahedra share four borane atoms.[10,11]

The synthesis of new weakly coordinating anions is of general interest not only for basic research but also for technical applications.[12–23] The most promising class of such anions is halogenated *closo*-carborane ions, for example, $[RCB_{11}Hal_{11}]^-$ (Hal = F, Cl, Br,).[14,16,17,20,23] Halogenated *closo*-dodecaborate dianions have also been described as weakly coordinating anions, but they have a distinct disadvantage in possessing a doubly negative charge. The *closo*-$[B_{21}H_{18}]^-$ ion, which contains two face-shared B_{12} icosahedra, has only been the subject of theoretical calculations[24] and aroused our interest as a synthetic target because of the low charge density of this anion. Herein we report on a three-step synthesis of salts containing the *closo*-$[B_{21}H_{18}]^-$ ion starting from commercially available *closo*-$[B_{10}H_{10}]^{2-}$ salts [Eq. (1)].

$$\textit{closo}\text{-}[B_{10}H_{10}]^{2-}\xrightarrow{\text{oxidation}}\textit{trans}\text{-}[B_{20}H_{18}]^{2-}\xrightarrow{\text{isomerization}}\textit{fac}\text{-}[B_{20}H_{18}]^{2-}\xrightarrow{\text{Aufbau}}\textit{closo}\text{-}[B_{21}H_{18}]^- \qquad (1)$$

In the first step two *closo*-$[B_{10}H_{10}]^{2-}$ ions are oxidatively coupled to the *trans*-$[B_{20}H_{18}]^{2-}$ ion by a known method.[9] Besides the *trans* isomer, two less stable isomers were described, the structures of which are shown in Figure 1.[9] Now we have found that *trans*-$M_2[B_{20}H_{18}]$ (M = $[Et_3NH]$ or $[Et_4N]$) rearranges upon protonation in anhydrous HF to the face-shared $[B_{20}H_{19}]^-$ ion, which is designated as *fac*-$[B_{20}H_{19}]^-$ in the following discussion. It is known that under acidic conditions the *closo*-$[B_{10}H_{10}]^{2-}$ ion reacts to form *nido*-$B_{10}H_{13}X$,[25,26] *nido*-$B_{10}H_{12}X_2$,[27,28] or $BF_3/[BF_4]^-$.[29–31] In view of these reactions, the rearrangement of *trans*-$[B_{20}H_{18}]^{2-}$ (Figure 1) might be initiated by protonation of one of its two $\{B_{10}\}$ fragments with subsequent incorporation of the second $\{B_{10}\}$ fragment. Further rearrangements lead to formation of *fac*-$[B_{20}H_{19}]^-$, and deprotonation yields the new *fac*-$[B_{20}H_{18}]^{2-}$ ion. Density functional calculations show that this borate ion is the most stabile isomer with the formula $[B_{20}H_{18}]^{2-}$ (Figure 1).[32]

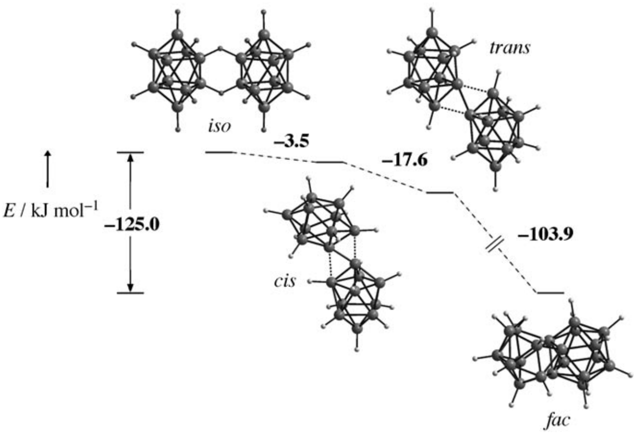

Figure 1. Relative energies of the known isomers of $[B_{20}H_{18}]^{2-}$ ions and the new *fac* species (B3LYP/6-311++G(d,p)).[43]

Boranes and borates with the face-shared $\{B_{20}\}$ framework have been obtained by reaction of $B_{20}H_{16}$ with Lewis bases,[10,11,33] and the crystal structures of $B_{20}H_{16}(NCMe)_2\cdot NCMe$[34] and $[(PMe_2Ph)_3HReB_{20}H_{15}Ph(PHMe_2)]$[33] have been described. The synthesis of salts of the *fac*-$[B_{20}H_{18}]^{2-}$ ion would also seem to be possible starting from poorly accessible $B_{20}H_{16}$.[33,35–37]

The crystal structure of $K_2[B_{20}H_{18}]\cdot 4\,MeCN$ was determined,[38] and a view of the anion is shown in Figure 2. The anion consists of a *nido*-$\{B_{11}\}$ and a *closo*-$\{B_{12}\}$ fragment which share the B41, B42, and B43 atoms. Compared to the *closo* fragment, the B31 and H31 atoms are missing in the *nido* fragment. Instead, the *nido* fragment has a disordered H atom that bridges either the B11–B22 bond (Figure 2) or the B11–B23 bond. In the structure 72 % of the anions have the *closo* fragment positioned as in Figure 2; reflection through the B41-B42-B43 plane generates the other 28 %. This disorder is only obvious for the B31, H31, and bridging H atoms. Atomic coordinates of the anion, as obtained from DFT calculations,[32] confirm the approximate mirror symmetry for the above-mentioned plane. All H atoms of the borate ion were

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[*] Dr. E. Bernhardt, Prof. Dr. D. J. Brauer, Prof. Dr. H. Willner
Fachbereich C—Anorganische Chemie
Bergische Universität Wuppertal
Gaussstrasse 20, 42097 Wuppertal (Germany)
Fax: (+49) 202-439-3052
E-mail: edbern@uni-wuppertal.de
willner@uni-wuppertal.de
Dr. M. Finze
Institut für Anorganische Chemie und Strukturchemie II
Heinrich-Heine-Universität Düsseldorf
Universitätsstrasse 1, 40225 Düsseldorf (Germany)

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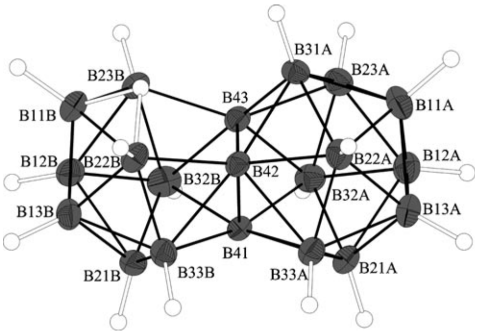

Figure 2. Structure of the *fac*-$[B_{20}H_{18}]^{2-}$ ion in $K_2[B_{20}H_{18}]\cdot 4\,MeCN$ with 25 % probability thermal ellipsoids for the B atoms.

taken from difference Fourier syntheses. The terminal B–H bond lengths range from 1.06(3) to 1.17(3) Å. Relatively short H···H contacts (2.10(4) and 2.22(4) Å) arise between H atoms that are adjacent to the bridging face, and the resulting repulsions lead to a lengthening of the corresponding B–B bonds. Thus, the largest B–B bond lengths are observed for the B32–B41 and B33–B41 bonds (1.894(5) and 1.950(5) Å, respectively). This strain also affects the B32–B43 (1.836(5) Å) and B33–B42 bonds (1.892(5) Å). All other B–B bond lengths (1.688(6)–1.834(5) Å) resemble those of the parent ion $[B_{12}H_{12}]^{2-}$ (1.78 Å).[39]

Both the *fac*-$[B_{20}H_{18}]^{2-}$ and *fac*-$[B_{20}H_{19}]^{-}$ ions were also characterized by NMR spectroscopy, and the assignment of all signals was facilitated by $^{11}B,^{11}B$ and $^{11}B,^{1}H$ correlation experiments (Tables 1 and 2) and supported by DFT GIAO calculations.[32] Figure 3 displays the $^{11}B\{^1H\},^{11}B\{^1H\}$ COSY NMR spectrum of the *fac*-$[B_{20}H_{18}]^{2-}$ ion. The *fac*-$[B_{20}H_{19}]^{-}$ ion has C_s symmetry in contrast to the C_1 symmetry of the *fac*-$[B_{20}H_{18}]^{2-}$ ion (Figure 2). However, the latter anion exhibits C_s symmetry on the NMR time scale probably because of rapid exchange of the bridging H atom.

Table 1: NMR data of the *fac*-$[B_{20}H_{18}]^{2-}$ ion in CD_3CN at room temperature.

Assignment[a]	No. of B atoms	$\delta(^{11}B)$ [ppm]	$\sigma(^{11}B)$ [Hz]	$^1J(^1H,^{11}B)$ [Hz]	$\delta(^1H)$ [ppm]	$\sigma(^1H)$ [Hz]
31A	1	2.3	81	141	2.81	12
32B, 33B	2	−2.1	130	152	3.20	15
12A, 13A	2	−4.1	58	135	1.94	16
32A, 33A	2	−6.3	91	147	2.02	14
11A	1	−8.4	63	135	1.70	15
12B, 13B	2	−11.3	61	135	1.56	16
22B, 23B	2	−14.7	70	135	1.53	14
42, 43	2	−15.1	70	–	–	–
22A, 23A	2	−16.8	79	136	0.97	16
11B	1	−18.0	60	138	0.97	16
21A	1	−18.1	60	138	1.19	13
41	1	−20.9	63	–	–	–
21B	1	−35.8	71	138	0.46	13
μ-H	(1 H)	–	–	–	−1.89	21

[a] The B atoms are labelled according to the Scheme shown in Figure 2.

Table 2: NMR data of the *fac*-$[B_{20}H_{19}]^{-}$ ion in CD_2Cl_2 at room temperature.

Assignment[a]	No. of B atoms	$\delta(^{11}B)$ [ppm]	$\sigma(^{11}B)$ [Hz]	$^1J(^1H,^{11}B)$ [Hz]	$\delta(^1H)$ [ppm]	$\sigma(^1H)$ [Hz]
32B, 33B	2	9.9	118	164	4.26	18
31A	1	−1.9	90	150	2.46	14
11A	1	−4.5	62	141	2.17	14
11B	1	−4.5	62	141	2.74	17
12A, 13A	2	−4.5	62	141	2.42	14
12B, 13B	2	−6.4	60	150	2.44	14
32A, 33A	2	−6.6	100	157	2.71	16
42, 43	2	−8.8	62	–	–	–
22A, 23A	2	−14.0	67	167	1.57	13
21A	1	−18.6	70	143	0.95	14
41	1	−23.1	52	–	–	–
21B	1	−24.5	69	146	1.44	11
22B, 23B	2	−31.0	72	141	1.06	16
μ-H	(2 H)	–	–	–	−1.34	20

[a] The B atoms are labelled according to the scheme shown in Figure 2 for *fac*-$[B_{20}H_{18}]^{2-}$.

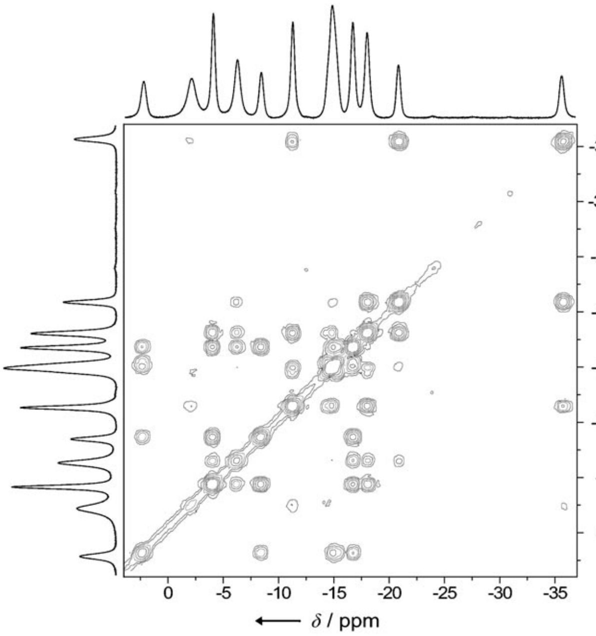

Figure 3. $^{11}B\{^1H\},^{11}B\{^1H\}$ COSY NMR spectrum of *fac*-$[B_{20}H_{18}]^{2-}$.

When dissolved in $BH_3\cdot NEt_2$, *fac*-$[Et_3NH]_2[B_{20}H_{18}]$ reacts at 150 °C to form the *closo*-$[B_{21}H_{18}]^{-}$ ion [Eq. (2)].

$$\textit{fac}\text{-}[Et_3NH]_2[B_{20}H_{18}] + BH_3\cdot NEt_3 \xrightarrow[150\,^\circ C,\ 5\,h]{BH_3\cdot NEt_3} [Et_4N][B_{21}H_{18}]^{+} + 2\,Et_3N + 2\,H_2 \qquad (2)$$

Side reactions lead to the formation of cations such as $[BH_2(NEt_3)_2]^{+}$, which have been characterized crystallographically and by NMR spectroscopy.[32] The analogous reaction of the quaternary ammonium salt *fac*-$[Et_4N]_2[B_{20}H_{18}]$ with $BH_3\cdot NEt_3$ proceeds markedly slower, and starting material can still be detected by NMR spectroscopy even after several days. The slower reaction rate is probably due to both the lower solubility of this salt and the high stability of the $[Et_4N]^+$ cation. In fact, the $[B_{12}H_{12}]^{2-}$ ion is also formed during the reaction [Eq. (3)].

$$\begin{aligned} &3\,fac\text{-}[Et_4N]_2[B_{20}H_{18}] + 6\,BH_3\cdot NEt_3 \xrightarrow[150\,^{\circ}C,\ 2.5\,h]{BH_3\cdot NEt_3} \\ &\quad 2\,[Et_4N][B_{21}H_{18}] + 2\,[Et_4N]_2[B_{12}H_{12}] + 6\,Et_3N + 6\,H_2 \end{aligned} \tag{3}$$

The crystal structure of $K[B_{21}H_{18}]$ was investigated,[40] and a view of its anion is shown in Figure 4. While C_1 symmetry is required crystallographically, the symmetry of the anion deviates only slightly from D_{3h}. All H atoms were located in a difference Fourier map, and their coordinates and temperature factors were refined. The H–B bond lengths lie in the range 1.01(2)–1.16(2) Å. Similar to the *fac*-$[B_{20}H_{18}]^{2-}$ ion, short H···H contacts (2.10(2), 2.10(2), and 2.03(3) Å) arise in the *closo* anion across the shared face, and the concomitant repulsions lead to a lengthening of the 12 B_{ipso}–B_{ortho} bonds (average 1.901(9) Å). The lengths of the other B–B bonds vary from 1.753(3) to 1.823(3) Å and are thus similar to the B–B separations in the $[B_{12}H_{12}]^{2-}$ ion (1.78 Å).[39]

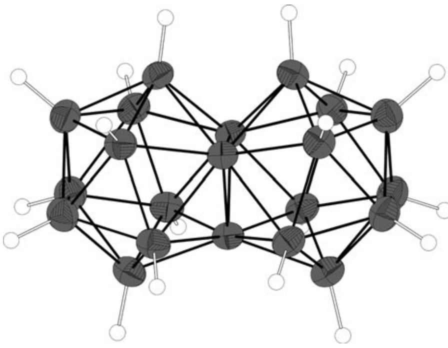

Figure 4. Structure of the *closo*-$[B_{21}H_{18}]^-$ ion in $K[B_{21}H_{18}]$ with 50% probability thermal ellipsoids for the B atoms.

In the ^{11}B NMR spectrum the 21 B atoms of the highly symmetrical anion give rise to four signals with an intensity ratio of 1:2:2:2 (Table 3). The signal of relative intensity one is not split by coupling to a H atom and can thus be assigned to the three *ipso* B atoms of the shared face. On the basis of the proton-decoupled ^{11}B,^{11}B COSY spectrum (Figure S1 in the Supporting Information), the resonance of the *para* B atoms was assigned as the signal exhibiting no coupling to the *ipso* B atoms. The other two resonances were assigned by comparison to the results of DFT calculations.[32] A ^{11}B,^{1}H 2D experiment was used to assign the signals of the ^{1}H NMR spectrum.

The $[B_{21}H_{18}]^-$ ion is the first example of a singly charged *closo*-borate species which contains two face-shared icosahedral entities. The simple synthesis of its salts starting from commercially available compounds makes it readily available for further studies. In particular the synthesis of the perfluorinated ion $[B_{21}F_{18}]^-$, which should be a very promising weakly coordinating anion, is an immediate goal.

Table 3: NMR data of the $[B_{21}H_{18}]^-$ ion in CD_3CN at room temperature.

Assignment	No. of B atoms	$\delta(^{11}B)$ [ppm]	$\sigma(^{11}B)$ [Hz]	$^1J(^1H,^{11}B)$ [Hz]	$\delta(^1H)$ [ppm]	$\sigma(^1H)$ [Hz]
ortho	6	4.7	85	169	3.92	18
para	6	1.9	43	146	2.88	16
meta	6	−18.4	59	147	1.07	13
ipso	3	−20.6	52	–	–	–

Experimental Section

fac-$[Et_3NH]_2[B_{20}H_{18}]$: HF (40 mL, 1 mol) was condensed into a 250-mL PFA flask containing *trans*-$[Et_3NH]_2[B_{20}H_{18}]$[9] (3.4 g, 7.7 mmol). The suspension was stirred at 25 °C for two days. Then all volatile material was removed in vacuum. The solid residue was extracted with Et_3N (20 mL) in acetonitrile (100 mL), filtered, and dried in vacuum. This solid was dissolved in acetonitrile (30 mL), water (400 mL) was added, and the suspension was stirred for one day. The light-yellow product was filtered off, washed with water, and dried in vacuum. Yield: 3.0 g, 6.9 mmol, 90 %; negative-ion MALDI-MS: *m/z* (%): 238.3 (4), 237.3 (39), 236.3 (57), 235.3 (100), 234.3 (100), 233.3 (68), 232.3 (50), 231.4 (21), 230.4 (7). Elemental analysis (%) calcd for $C_{12}H_{50}B_{20}N_2$: C 32.85, H 11.49, N 6.38; found: C 32.6, H 10.5, N 6.4.

$K[B_{21}H_{18}]$: A solution of *fac*-$[Et_3NH]_2[B_{20}H_{18}]$ (150 mg, 0.34 mmol) dissolved in $BH_3{\cdot}NEt_3$ (1.2 g, 10 mmol) was held at 150–160 °C until the yellow color of the $[B_{20}H_{18}]^{2-}$ ion vanished. After cooling, $BH_3{\cdot}NEt_3$ was removed by vacuum from the reaction mixture. The residue was treated with solutions of Na_2CO_3 (1 g, 0.01 mol) in water (20 mL) and $Na[BPh_4]$ (0.7 g, 2 mmol) in water (20 mL), as well as with CH_2Cl_2 (30 mL), and the mixture was stirred for 30 minutes. After precipitates (mainly $[BH_2Et_2][BPh_4]$) were filtered off, the aqueous phase was separated from CH_2Cl_2 and washed with CH_2Cl_2 (2 × 60 mL). Then K_2CO_3 (5 g, 36 mmol) was added to the aqueous phase, and the resulting suspension ($K[BPh_4]$) was filtered. The filtrate was washed with diethyl ether (3 × 40 mL), and the ether fractions were combined and dried with K_2CO_3. Removal of the diethyl ether yielded $K[B_{21}H_{18}]$ (70 mg, 0.25 mmol, 72 %) as a colorless salt. Negative-ion MALDI-MS: *m/z* (%): 249.3 (4), 248.3 (28), 247.3 (70), 246.3 (97), 245.4 (100), 244.4 (90), 243.4 (66), 242.4 (36), 241.4 (13), 240.4 (3), 239.4 (1).

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[38] Crystal structure of $K_2[B_{20}H_{18}]\cdot 4\,CH_3CN$: $C_8H_{30}B_{20}K_2N_4$, Bruker AXS P4-Smart 1 K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å),$T = 20$°C, monoclinic, space group $P2_1/n$ (Nr. 14), $a = 13.356(2)$, $b = 15.700(2)$, $c = 13.361(2)$ Å, $\beta = 100.265(3)$°, $V = 2756.8(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.149$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.35$ mm^{-1}, $F(000) = 976$, 13298 measured reflections ($1.99 < \theta < 23.29$°), structure solution by direct methods (SHELXS-97),[41] structure refinement on F^2 with 3966 independent relections (2557 of which having $I > 2\sigma(I)$), 389 parameters, 13 restraints (SHELXL-97),[42] $R1 = 0.0513$ ($F > 4\sigma(F)$), $wR2 = 0.1520$ (all reflections), $S = 0.846$. CCDC-622446 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[40] Crystal structure of $K[B_{21}H_{18}]$: $H_{18}B_{21}K$, Bruker AXS P4-Smart 1 K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 20$°C, monoclinic, space group $C2$ (Nr. 5), $a = 12.4860(8)$, $b = 7.1060(4)$, $c = 16.9436(11)$ Å, $\beta = 93.810(1)$°, $V = 1500.0(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.259$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.32$ mm^{-1}, $F(000) = 568$, 6144 measured reflections ($1.20 < \theta < 29.09$°), structure solution by direct methods (SHELXS-97),[41] structure refinement on F^2 with 2344 independent reflections (2080 of which having $I > 2\sigma(I)$), 272 parameters, 1 restraint (SHELXL-97),[42] $R1 = 0.0279$ ($F > 4\sigma(F)$),[42] $wR2 = 0.0706$ (all reflections), $S = 1.002$. CCDC-622447 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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