Heteroatom Chemistry
Volume 17, Number 2, 2006

Tetrabutylammonium Salt of the $B_{24}F_{22}^{4-}$ Anion. Two $B_{12}F_{11}^{2-}$ Icosahedra Linked by a 2c–2e B–B Bond and Surrounded by a Sheath of CH···FB Hydrogen Bonds

Yoshihiro Kobayashi,[1] Sergei V. Ivanov,[1] Alexey A. Popov,[2] Susie M. Miller,[1] Oren P. Anderson,[1] Konstantin A. Solntsev,[3] and Steven H. Strauss[1]

[1] *Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA*

[2] *Chemistry Department, Moscow State University, Moscow 119992, Russia*

[3] *Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow 117907, Russia*

Received 21 July 2005; revised 22 September 2005

ABSTRACT: *The $B_{24}F_{22}^{4-}$ anion, which was formed as a minor by-product when the $B_{12}H_{12}^{2-}$ anion was treated with F_2 in liquid HF, has been isolated as its $N(n\text{-}Bu)_4^+$ salt and characterized by ^{10}B, ^{11}B, and ^{19}F NMR spectroscopy, electrospray mass spectrometry, cyclic voltammetry, single-crystal X-ray diffraction, and calculations at the DFT level of theory. The $B_{24}F_{22}^{4-}$ anion has idealized D_5 symmetry and consists of two $B_{12}F_{11}^{2-}$ icosahedra linked by a 2c–2e boron–boron single bond with a B—B distance of 1.725(4) Å. In the solid state, the anion interacts with eight $N(n\text{-}Bu)_4^+$ cations via a network of 34 CH···FB hydrogen bonds with H···F distances that range from 2.26 to 2.55 Å. These hydrogen bonds were successfully modeled by DFT calculations, which showed that the hydrogen bonds probably have a measurable, albeit subtle, effect on the structure of the $B_{24}F_{22}^{4-}$.*

Heteroatom Chem 17:181–187, 2006;

DOI 10.1002/hc.20220

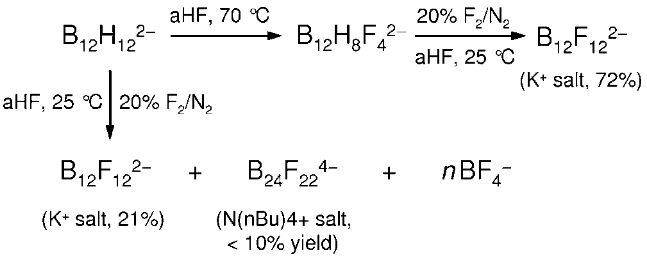
INTRODUCTION

We have been interested in poly- and per-B-fluorinated borane and carborane cluster anions for the past decade [1], largely because of their potential use as superweak anions for a variety of applications [2–6]. The icosahedral anions we have isolated and studied include 12-$CB_{11}H_{11}F^-$ [1], 1-R—$CB_{11}F_{11}^-$ (R = H, Me, Et, Bn) [7–9], $Me_3NB_{12}F_{11}^-$ [10], and $B_{12}F_{12}^{2-}$ [11]. Although it has a 2− charge, the $B_{12}F_{12}^{2-}$ anion in crystalline $[CPh_3]_2[B_{12}F_{12}]$ [11] exhibits longer, presumably weaker BF···CAr_3 contacts (2@3.087(2) Å) than were observed in crystalline $[CPh_2(p\text{-}OMe\text{—}C_6H_4)][BF_4]$ (2.68 Å) and $[CPh(p\text{-}OMe\text{—}C_6H_4)_2][BF_4]$ (2.68 Å) [12,13] (the sum of van der Waals radii for carbon and fluorine atoms is 3.17 Å [14]). In the course of the synthesis

---

Correspondence to: Steven H. Strauss; e-mail: steven.strauss@colostate.edu.

Contract grant sponsor: National Science Foundation.
Contract grant number: CHE-9905482.
Contract grant sponsor: Research Computing Center of Moscow State University.



SCHEME 1

of salts of the $B_{12}F_{12}^{2-}$ anion, we noted that under certain conditions one or more B_{24}-containing species were formed [11], as shown in Scheme 1 (aHF = liquid anhydrous HF). We now report that the principal B_{24} species that was formed is the double-icosahedron $B_{24}F_{22}^{4-}$, which has been isolated as $[N(n\text{-Bu})_4]_4[B_{24}F_{22}]$ and characterized by NMR spectroscopy and mass spectrometry, cyclic voltammetry, single-crystal X-ray diffraction, and quantum mechanical calculations at the DFT level of theory.

EXPERIMENTAL

Isolation of (N(n-Bu)$_4$)$_4$B$_{24}$F$_{22}$

Colorless crystals of this compound were isolated as follows from the reaction shown at the bottom of Scheme 1 [11]. After removal of anhydrous HF, the solid mixture of products was dissolved in water. The aqueous solution contained the $B_{12}F_{12}^{2-}$, $B_{24}F_{22}^{4-}$, and BF_4^- anions and the K^+ and H_3O^+ cations. Addition of $NHEt_3Cl$ caused the precipitation of white, microcrystalline $[NHEt_3]_2[B_{12}F_{12}]$, which was isolated by filtration. The filtrate was treated with $N(n\text{-Bu})_4Cl$, which caused the precipitation of relatively pure, white, microcrystalline $[N(n\text{-Bu})_4]_4[B_{24}F_{22}]$ (i.e., both $[NHEt_3][BF_4]$ and $[N(n\text{-Bu})_4][BF_4]$ are soluble to some extent in water). It was purified by successive recrystallizations from acetone/toluene. The final yield was less than 10% based on the $K_2B_{12}H_{12}$ starting material.

Spectroscopic and Electrochemical Measurements

Samples for ^{10}B, ^{11}B, and ^{19}F NMR spectroscopy were acetonitrile-d_3 solutions in 5-mm glass tubes and were recorded on a Varian Inova-300 spectrometer. Chemical shifts (δ scale) are relative to external $BF_3(OEt_2)$ (^{10}B and ^{11}B) and internal $CFCl_3$ (^{19}F). Samples for negative-ion electrospray mass spectrometry were solutions in acetonitrile and were recorded on a Finnigan LCQ DUO mass spectrometer. The cyclic voltammogram of $[N(n\text{-Bu})_4]_4[B_{24}F_{22}]$ in acetonitrile containing 0.1 M $N(n\text{-Bu})_4ClO_4$ was recorded with a PAR 173 potentiostat using a standard three-electrode cell (0.25-mm diameter platinum working electrode, platinum wire counter electrode, and SCE reference electrode).

TABLE 1 Crystallographic Data for $[N(n\text{-Bu})_4]_4[B_{24}F_{22}]^a$

Empirical formula = $C_{32}H_{72}B_{12}F_{11}N_2$	*Empirical formula weight =* *823.64*
$a = 14.6217(12)$ Å	Space group = *Pbcn*
$b = 34.858(3)$ Å	$T = 100(1)$ K
$c = 17.5935(14)$ Å	$\lambda = 0.71073$ Å
$D_{\text{calcd}} = 1.222$ g cm^{-3}	$\mu = 0.098$ mm^{-1}
$V = 8967.0(13)$ Å^3	$R_1 = 0.0514$
$Z = 8$	$wR_2 = 0.1224$

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Single-Crystal X-ray Analysis

An X-ray diffraction dataset from a single crystal of $[N(n\text{-Bu})_4]_4[B_{24}F_{22}]$ was recorded on a Bruker Nonius SMART CCD diffractometer employing Mo Kα radiation (graphite monochromator). Selected crystallographic details are listed in Table 1. Unit cell parameters were obtained from a least-squares fit to the angular coordinates of all reflections, and intensities were integrated from a series of frames covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied by using SADABS [15]. The structure was solved by using direct methods and refined (on F^2, using all data) by a full-matrix, weighted least-squares process. All non-hydrogen atoms were refined by using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined by using a riding model. Standard Bruker Nonius control (SMART) and integration (SAINT) software was employed, and Bruker Nonius SHELXTL [16] software was used for structure solution, refinement, and graphics.

DFT Calculations

The DFT-optimized structure of $B_{24}F_{22}^{4-}$ and the $[N(n\text{-Bu})_4]_4[B_{24}F_{22}]$ formula unit were determined with the PRIRODA package [17] using the PBE functional of Perdew et al. [18] and the TZ2P {6,1,1,1,1,1/4,1,1/1,1} basis set.

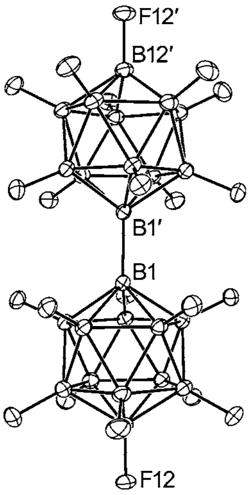


FIGURE 1 Drawing of the $B_{24}F_{22}^{4-}$ anion (50% probability ellipsoids). Selected bond distances (Å): B1—B1′, 1.725(4); other B—B, 1.771(3)–1.808(3); B—F, 1.385(2)–1.393(2).

RESULTS AND DISCUSSION

Molecular Structure of $B_{24}F_{22}^{4-}$

The C_2-symmetric $B_{24}F_{22}^{4-}$ anion, shown in Fig. 1, consists of two $B_{12}F_{11}^{2-}$ icosahedra with a B—B single bond connecting their respective B1 atoms. Selected interatomic distances and angles are listed in Table 2, which also lists the corresponding DFT values for the isolated $B_{24}F_{22}^{4-}$ anion. There is good agreement between the X-ray and DFT bond distances except for the 2c–2e B1—B1′ bond distance, which is 0.05 Å shorter than predicted. The 1.725(4) Å B1—B1′ distance can be compared with the 2c–2e B—B distances linking B_{12} icosahedra in rhombohedral α-boron (1.71(1) Å [19]), in $Al_{2.1}C_8B_{51}$ (1.774(3) Å [20]), in $NaAlB_{14}$ (1.756(3) and 1.773(2) Å [21]), and in $MgAlB_{14}$ (1.75 Å [22]). As would be expected, the B1—B1′ bond is considerably longer than the 1.576(5) Å B—N bond in $Me_3NB_{12}F_{11}^-$ [10].

The mean B—F distance in $B_{24}F_{22}^{4-}$, 1.387(2) Å, is marginally longer than the mean fluorocarborane anion B—F distance of 1.365(3) Å in $[Cu(CO)_4][1\text{-}Et\text{—}CB_{11}F_{11}]$ and the same as the mean B—F distances of 1.386(5) and 1.384(5) Å in the $B_{12}F_{12}^{2-}$ [11] and $Me_3NB_{12}F_{11}^-$ [10] anions, respectively (in all cases the number in parentheses is one estimated standard deviation for the individual B—F distances).

The pseudo-C_5 axes of the symmetry-related $B_{12}F_{11}^{2-}$ moieties in $B_{24}F_{22}^{4-}$ are nearly co-linear (the F12—B12···B1 and B12···B1—B1′ angles are 179.7° and 177.7°, respectively). Therefore, the $B_{24}F_{22}^{4-}$ anion has idealized D_5 symmetry. The three unique $F_n\cdots B1\text{—}B1'\cdots F'_n$ torsion angles are $26.5° \pm 0.3°$ ($n = 2$–6). The DFT-predicted symmetry for the isolated $B_{24}F_{22}^{4-}$ anion, which was not intentionally fixed, is D_{5d}, with all $F_n\cdots B1\text{—}B1'\cdots F'_n$ torsion angles equal to exactly 36°. The B_{12} cores in the X-ray and DFT $B_{24}F_{22}^{4-}$ anions are both distorted from idealized icosahedral symmetry by elongation of the B1···B12 vector, as shown in Fig. 2. The B1···B12 distance in $B_{24}F_{22}^{4-}$, 3.463(3) Å, is significantly longer than the other five antipodal B···B distances, 3.390(3)–3.409(3) Å. Figure 2 also shows that a similar axial distortion was observed for the $Me_3NB_{12}F_{11}^-$ anion and, as expected, was not observed for the $B_{12}F_{12}^{2-}$, $B_{12}H_{12}^{2-}$, and $B_{12}Me_{12}^{2-}$

TABLE 2 Selected Interatomic Distances (Å) and Angles (°) for the $B_{24}F_{22}^{4-}$ Anion[a]

Parameter	*X-ray*[b]	*DFT $B_{24}F_{22}^{4-}$*	*DFT $[N(n\text{-}Bu)_4]_4[B_{24}F_{22}]$*
Interatomic distance (Å)			
B1—B1′	1.725	1.792	1.745
B1—B_{ub}	1.796–1.808	1.836	1.816
B_{ub}—B_{ub}	1.771–1.784	1.800	1.787
B_{ub}—B_{lb}	1.795–1.807	1.817	1.802
B_{lb}—B_{lb}	1.796–1.808	1.795	1.783
B_{lb}—B12	1.788–1.794	1.799	1.787
B_{ub}—F	1.378–1.389	1.403	1.405–1.409
B_{lb}—F	1.386–1.393	1.419	1.397–1.403
B12—F12	1.392	1.423	1.388
Interatomic angle (°)			
B12···B1—B1′	177.7	180	178.7
F12—B12···B1	179.7	180	179.5
$F_n\cdots B1\text{—}B1'\cdots F'_n$	26.2–26.8	36	29.5–29.7

[a] All values are from this work; B_{ub}: upper-belt boron atoms connected to B1 (i.e., B2—B6); B_{lb}: lower-belt boron atoms connected to B12 (i.e., B7—B11); $n = 2$–6.

[b] The estimated standard deviations are 0.004 Å for B1—B1′, 0.003 Å for other B—B bonds, 0.002 Å for all B—F bonds, and 0.1° for the bond angles.

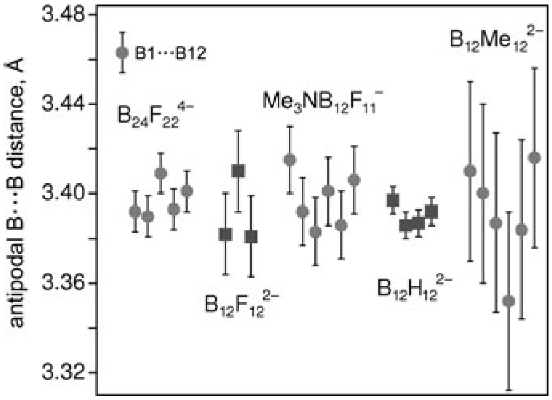


FIGURE 2 Comparison of the antipodal B. . .B distances in $B_{24}F_{22}^{4-}$ (this work), $B_{12}F_{12}^{2-}$ ([11]), $Me_3NB_{12}F_{11}^{-}$ ([10]), the $B_{12}H_{12}^{2-}$ anion in $[NMe_4]_2[B_{12}H_{12}]\cdot CH_3CN$ ([23]), and the $B_{12}Me_{12}^{2-}$ anion in $[(C_5H_5N)_2CH_2][B_{12}Me_{12}]$ ([24]).

anions [10,11,23,24]. In addition, Fig. 2 reveals that the size of the icosahedral B_{12} core in $B_{12}F_{12}^{2-}$ was not affected by the substitution of the 12 hydrogen atoms for fluorine atoms.

Given the current interest in intermolecular/interionic CH· · ·X hydrogen bonding (X = O, N, halogen) [25–32], a relevant aspect of the structure of $[N(n\text{-}Bu)_4]_4[B_{24}F_{22}]$ is the nature of the cation–anion interactions. Figure 3 shows two views of the solid-state packing around one $B_{24}F_{22}^{4-}$ anion, one with eight $N(n\text{-}Bu)_4^{+}$ nearest neighbors that form 34 CH· · ·F hydrogen bonds ranging in distance from 2.26 to 2.55 Å and one, for clarity, with only four nearest-neighbor cations that form 2 CH· · ·F hydrogen bonds. The cations form a sheath of C—H bonds in which the anion is suspended. For each $B_{12}F_{11}^{2-}$ fragment, only two of the fluorine atoms do not form a CH· · ·F hydrogen bond shorter than 2.6 Å. The C—H· · ·F angles range from 168.4° (H· · ·F = 2.26 Å) to 112.8° (H· · ·F = 2.54 Å). These distances and angles are similar to those observed or calculated for CH· · ·F(B,P) interactions involving the fluoroanions BF_4^{-} and PF_6^{-} [33,34]. Figure 4 shows the packing of anions and cations, revealing the layering of cations and anions and the extended one-dimensional channels formed by the cations in which the anions are stuffed.

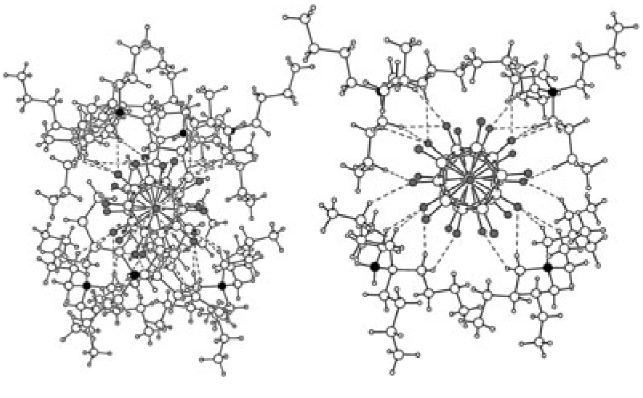


FIGURE 3 Two drawings of the network of CH· · ·FB hydrogen bonds shorter than 2.55 Å between the $B_{24}F_{22}^{4-}$ anion and its nearest-neighbor $N(n\text{-}Bu)_4^{+}$ cations in the structure of $[N(n\text{-}Bu)_4]_4[B_{24}F_{22}]$. The gray atoms and black atoms are fluorine atoms and nitrogen atoms, respectively. In the drawing on the left, all 34 H· · ·F hydrogen bonds from the eight nearest-neighbor $N(n\text{-}Bu)_4^{+}$ cations are shown (the H· · ·F distances range from 2.259 to 2.548 Å). In the drawing on the right, only four $N(n\text{-}Bu)_4^{+}$ cations and 22 H· · ·F hydrogen bonds are shown for clarity.

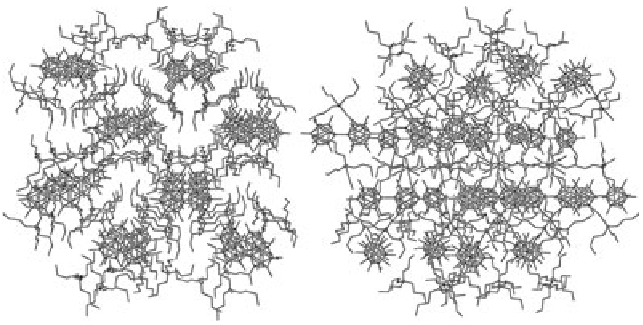


FIGURE 4 Two perpendicular views of the layers of cations and anions in the structure of $[N(n\text{-}Bu)_4]_4[B_{24}F_{22}]$. Only the nitrogen atoms are shown as spheres (arbitrary radius). Hydrogen atoms have been omitted for clarity. The figure on the left reveals the one-dimensional channels in which the prolate $B_{24}F_{22}^{4-}$ anions are stuffed.

We also optimized the geometry of the $[N(n\text{-}Bu)_4]_4[B_{24}F_{22}]$ formula unit at the DFT level of theory. Interestingly, the predicted B1–B1′ bond distance decreased from 1.792 Å in the isolated $B_{24}F_{22}^{4-}$ anion to 1.745 Å in the $[N(n\text{-}Bu)_4]_4[B_{24}F_{22}]$ formula unit, as shown in Table 2. In fact, all of the distances and angles listed in Table 2 for the X-ray determined structure of the $B_{24}F_{22}^{4-}$ anion in $[N(n\text{-}Bu)_4]_4[B_{24}F_{22}]$ are better matched by the formula unit DFT structure than by the isolated $B_{24}F_{22}^{4-}$ anion DFT structure except for the upper-belt B–F bonds. Furthermore, the network of 22 CH· · ·FB hydrogen bonds in the formula unit DFT structure (not shown) is virtually indistinguishable from the right-hand portion of Fig. 3. Therefore, it appears that aliphatic hydrocarbon chains on countercations can effectively and significantly interact with polyhedral fluoroborane and carborane anions via multiple CH· · ·FB hydrogen bonds, a cumulative type of interaction that may be important in determining the structures of ion-pairs in solution. This is currently under investigation in our laboratory.

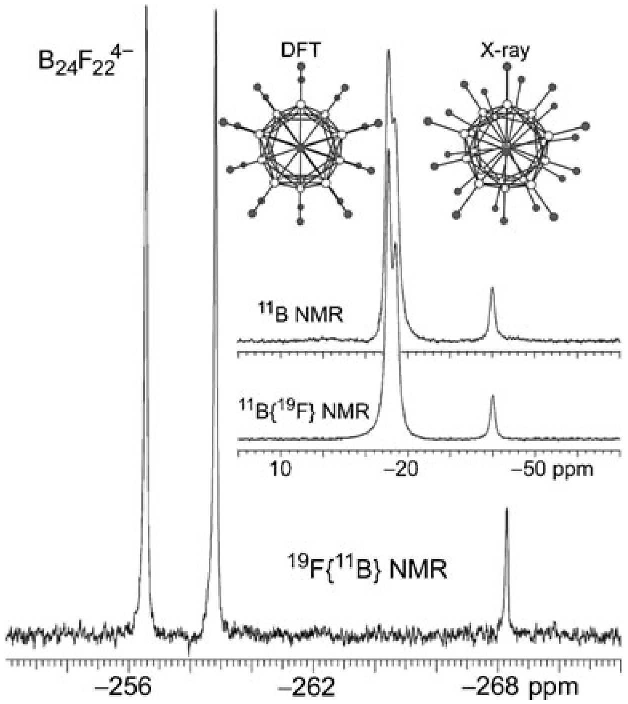


FIGURE 5 96.3 MHz ^{11}B and ^{11}B{^{19}F} and 282.3 MHz ^{19}F{^{11}B} NMR spectra of $[N(n\text{-}Bu)_4]_4[B_{24}F_{22}]$ (acetonitrile-d_3, 24°C, external BF_3OEt_2 ($\delta(^{11}B) = 0$) or internal $CFCl_3$ ($\delta(^{19}F) = 0$). The molecular drawings are end-on views of the DFT optimized and X-ray structure of the $B_{24}F_{22}{}^{4-}$ anion.

Spectroscopic and Electrochemical Characterization of $B_{24}F_{22}{}^{4-}$

A negative-ion electrospray mass spectrum of $[N(n\text{-}Bu)_4]_4[B_{24}F_{22}]$ in acetonitrile (not shown) exhibited a group of peaks for the $[N(n\text{-}Bu)_4]_3[B_{24}F_{22}]^-$ monoanion with the expected isotope pattern (the most intense peak was at *m/z* 1404.9 (calcd 1404.8)). Also present were less intense groups of isotopomers assigned to the $[N(n\text{-}Bu)_4]_2[B_{24}F_{22}]^{2-}$ dianion (*m/z* 581.5, $\Delta m/z = \pm 0.5$ (calcd *m/z* 581.2)) and the $[N(n\text{-}Bu)_4][B_{24}F_{22}]^{3-}$ trianion (*m/z* 303.3, $\Delta m/z < \pm 0.33$ (i.e., unresolved; calcd 303.6)). Notably absent from the mass spectrum were peaks due to fragmentation of the $B_{24}F_{22}{}^{4-}$ molecular ion into two $B_{12}F_{11}{}^{2-}$ dianions. Although the $[N(n\text{-}Bu)_4][B_{12}F_{11}]^-$ anion would also have its peaks centered at *m/z* 581.2, it would exhibit an isotope pattern with $\Delta m/z = \pm 1$, and this was not observed.

Figure 5 shows ^{11}B and ^{19}F NMR spectra of $[N(n\text{-}Bu)_4]_4[B_{24}F_{22}]$ in acetonitrile-d_3 solution. The expected 5:5:1 ^{19}F{^{11}B} pattern at δ −256.6, −258.8, and −268.3 (F12), respectively, was observed. It is interesting to note that the resonance for F12 is shielded with respect to the resonances for the upper- and lower-belt fluorine atoms. The F12 resonances for the 1-H—$CB_{11}F_{11}{}^-$, $H_3NB_{12}F_{11}{}^-$, and $Me_3NB_{12}F_{11}{}^-$ monoanions are *deshielded* relative to the F2—F11 resonances, but the F12 resonances are *shielded* relative to the F2–F11 resonances in the deprotonated $CB_{11}F_{11}{}^{2-}$ [7] and $H_2NB_{12}F_{11}{}^{2-}$ dianions [10], suggesting that there may be a correlation between the F12 chemical shift and the negative charge density on F12 [35].

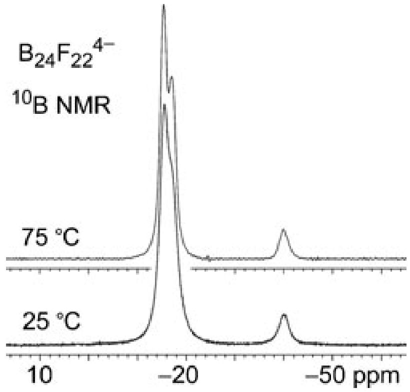


FIGURE 6 32.2 MHz ^{10}B NMR spectra of $[N(n\text{-}Bu)_4]_4[B_{24}F_{22}]$ at 25 and 75°C (acetonitrile-d_3, external BF_3OEt_2 ($\delta(^{11}B) = 0$)).

The ^{11}B and ^{10}B NMR spectra shown in Figs. 5 and 6, respectively, show the B1 resonance at δ −40.0, the B12 resonance at δ −15.5, and the upper- and lower-belt boron resonances at δ −15.5 and −17.0 (these two peaks cannot be definitively assigned at this time). In favorable cases, it has been possible to measure $^1J(^{11}B^{11}B)$ coupling constants for symmetry-related boron atoms in a 2c–2e bond by recording the ^{10}B NMR spectrum and observing the $^1J(^{10}B^{11}B)$ splitting [36]. However, as shown in Fig. 6, this was not possible in the present case, even at elevated temperature (i.e., no splittings were observed) [37]. Although it is possible that the nuclear spin–spin coupling between B1 and B1′ is very small, many $^1J(^{11}B^{11}B)$ values for the boron atoms in 2c–2e B—B bonds are greater than 100 Hz [38–40]. Therefore, it is more likely that the spin–lattice relaxation time of a ^{10}B atom at the B1 position in $B_{24}F_{22}{}^{4-}$ is sufficiently short (i.e., in the range where $2\pi J(^{10}B^{11}B)T_1$ is ca. 0.3) that a single, featureless resonance would be expected [36].

A cyclic voltammogram of $[N(n\text{-}Bu)_4]_4[B_{24}F_{22}]$ taken with a small diameter platinum disc electrode at a scan rate of 4 V s^{-1} is shown in Fig. 7 (acetonitrile, 0.1 M $N(n\text{-}Bu)_4ClO_4$). Two quasi-reversible one-electron oxidations are evident at $E_{1/2}$ values of 1.35 V versus SCE ($\Delta E_p = 86$ mV) and 1.66 V versus SCE ($\Delta E_p = 76$ mV). For comparison, the second oxidation occurs at only 10–20 mV less positive than the first oxidation of $B_{12}F_{12}{}^{2-}$ in a mixture of ethylene

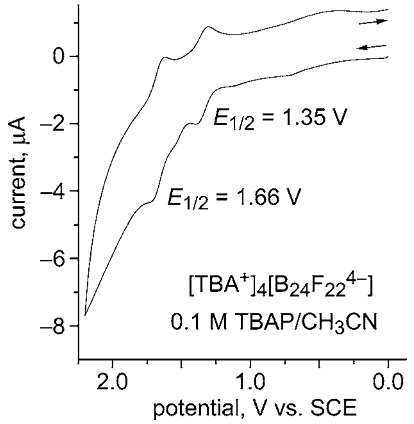


FIGURE 7 Cyclic voltammogram of [N(n-Bu)$_4$]$_4$[$B_{24}F_{22}$] at 25°C (acetonitrile, 0.1 M N(n-Bu)$_4$ClO$_4$, 4 V s^{-1} scan speed). The background current is relatively large because the concentration of [N(n-Bu)$_4$]$_4$[$B_{24}F_{22}$] was very low.

carbonate and dimethyl carbonate [11].

Possible Mechanism of Formation of $B_{24}F_{22}^{4-}$

The $B_{24}F_{22}^{4-}$ anion is not the first structurally characterized [*closo*-$B_nX_{n-1}]_2^{4-}$ tetraanion. In 1992, Hawthorne and co-workers reported the structures of two isomers of $B_{20}H_{18}^{4-}$, each of which consisted of two $B_{10}H_9^{2-}$ moieties joined by a 2c–2e B—B bond (various hydrates of potassium salts of an equatorial–equatorial and an axial–axial isomer were studied by single-crystal X-ray diffraction) [41]. The protonated trianion $B_{20}H_{19}^{3-}$ [42] and different isomers of the two-electron oxidized dianion $B_{20}H_{18}^{2-}$ [43,44] have also been structurally characterized. This well-studied system stands in sharp contrast to the homologous $B_{24}H_{22}^{4-}$/$B_{24}H_{23}^{3-}$/$B_{24}H_{22}^{2-}$ system, about which much less is known. Electrochemical oxidation of $B_{12}H_{12}^{2-}$ in acetonitrile was reported to yield the $B_{24}H_{23}^{3-}$ trianion [45,46], but the structure of this species has never been unequivocally determined (i.e., even an unambiguous spectroscopic characterization of this species has not appeared in the last 30+ years). The same is true for the putative monohydroxy derivative, $B_{24}H_{22}OH^{3-}$ [47]. Similarly, a number of tetraanions with the formula $B_{24}H_{22-n}X_n^{4-}$ were reported in 1969 (X = Cl, Br, I), but neither their composition nor their isomeric purity were established (only elemental analysis, IR spectra, and ^{11}B NMR spectra consisting of one or two broad bands were reported) [46]. Finally, the dianion $B_{24}H_{20}I_2^{2-}$ has also been reported but, apparently, has never been characterized by modern spectroscopic techniques [48].

Therefore, the $B_{24}F_{22}^{4-}$ tetraanion represents the first well-characterized bis-B_{12} double-icosahedron molecular species, although related structures of icosahedral carboranes joined by a 2c–2e C—C or B—C bond have been structurally characterized [49,50]. We suggest that the $B_{24}F_{22}^{4-}$ anion may be formed in the early stages of the lower reaction in Scheme 1 by oxidation of $B_{12}H_{12}^{2-}$ by F_2 in anhydrous HF to the $B_{24}H_{23}^{3-}$ ion, which then undergoes fluorination to $B_{24}F_{22}^{4-}$. The reason that little or no $B_{24}F_{22}^{4-}$ anion is formed in the upper reaction sequence in Scheme 1 is probably because the partially fluorinated $B_{12}H_8F_4^{2-}$ anion [51] is more difficult to oxidize. Therefore, the partial fluorination of $B_{12}H_{12}^{2-}$ by HF at 70°C prevents the oxidative coupling reaction. In ongoing work, we are exploring the mechanism of formation and the chemistry of the $B_{24}F_{22}^{4-}$ anion and are reinvestigating the $B_{24}H_{22}^{4-}$/$B_{24}H_{23}^{3-}$/$B_{24}H_{22}^{2-}$ system.

Supplementary Material

CCDC 274277 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.

ACKNOWLEDGMENTS

We thank Dr. Olga V. Boltalina and Professor L. G. Sneddon for informative discussions concerning electrospray mass spectrometry and ^{10}B NMR spectroscopy, respectively.

REFERENCES

[1] Ivanov, S. V.; Lupinetti, A. J.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. Inorg Chem 1995, 34, 6419–6420.
[2] Lupinetti, A. J.; Strauss, S. H. Chemtracts 1998, 11, 565–595.
[3] Strauss, S. H. Chem Rev 1993, 93, 927–942.
[4] Hurlburt, P. K.; Van Seggen, D. M.; Rack, J. J.; Strauss, S. H. In Inorganic Fluorine Chemistry Toward the 21st Century (ACS Symposium Series 555); Thrasher, J. S.; Strauss, S. H. (Eds.); American Chemical Society: Washington, DC, 1994; pp. 338–349.
[5] Reed, C. A. Accounts Chem Res 1998, 31, 133–139.
[6] Krossing, I.; Raabe, I. Angew Chem 2004, 2066–2090.
[7] Ivanov, S. V.; Rockwell, J. J.; Polyakov, O. G.; Gaudinski, C. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. J Am Chem Soc 1998, 120, 4224–4225.
[8] Ivanova, S. M.; Ivanov, S. V.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. Inorg Chem 1999, 38, 3756–3757.
[9] Ivanov, S. V.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. Cryst Growth Design 2004, 4, 249–254.

[10] Ivanov, S. V.; Davis, J. A.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. Inorg Chem 2003, 42, 4489–4491.
[11] Ivanov, S. V.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. J Am Chem Soc 2003, 125, 4694–4695.
[12] Bleasdale, C.; Clegg, W.; Ellwood, S. B.; Golding, B. T. Acta Cryst, Sect C (Cryst Struct Commum) 1991, 47, 550.
[13] Laube, T. Chem Rev 1998, 98, 1277.
[14] Bondi, A. J Phys Chem 1964, 68, 441.
[15] Sheldrick, G. M.; Bruker AXS; Madison, WI, 2000.
[16] Sheldrick, G. M.; Bruker AXS; Madison, WI, 2004.
[17] Laikov, D. N. Chem Phys Lett 1997, 281, 151–156.
[18] Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys Rev Lett 1996, 77, 3865–3868.
[19] Decker, B. F.; Kasper, J. S. Acta Crystallogr 1959, 12, 503–506.
[20] Perrota, A. J.; Townes, W. D.; Potenza, J. A. Acta Crystallogr, Sect B 1969, B25, 1223–1229.
[21] Okada, S.; Tanaka, T.; Sato, A.; Shishido, T.; Kudou, K.; Nakajima, K.; Lundstrom, T. J Alloys Compds 2005, 395, 231–235.
[22] Matkovic, V. I.; Economy, J. Acta Cryst, Sect B 1970, B26, 616–621.
[23] Hofmann, K.; Albert, B. Z Anorg Allg Chem 2001, 627, 1055–1058.
[24] Peymann, T.; Knobler, C. B.; Hawthorne, M. F. J Am Chem Soc 1999, 121, 5601–5602.
[25] Bryantsev, V. S.; Hay, B. P. J Am Chem Soc 2005, 127, 8282–8283.
[26] Diana, E.; Stanghellini, P. L. J Am Chem Soc 2004, 126, 7418–7419.
[27] Beckmann, J.; Dakternieks, D.; Duthie, A.; Tiekink, E. J Organomet Chem 2002, 648, 204–208.
[28] Zierbiewicz, W.; Jurecka, P.; Hobza, P. Chem Phys Chem 2005, 6, 609–617.
[29] Wojcik, J.; Kamienska-Trela, K.; Pecul, M.; Bartoszak-Adamska, E.; Vdovienko, S. I.; Gerus, I. I. Chem Phys Chem 2004, 5, 209–215.
[30] Alabugin, I. V.; Manoharan, M.; Peabody, S.; Weinhold, F. J Am Chem Soc 2003, 125, 5973–5987.
[31] Barnes, A. J. J Mol Struct 2004, 704, 3–9.
[32] Hermansson, K. J Phys Chem A 2002, 106, 4695–4702.
[33] Simpson, S. J. Acta Cryst, Sect C 1992, C48, 1137–1138.
[34] Katsyuba, S. A.; Dyson, P. J.; Vandyukova, E. E.; Chernova, A. V.; Vidis, A. Helv Chim Acta 2004, 87, 2556–2565.
[35] Hermanek, S. Chem Rev 1992, 92, 325–362.
[36] Anderson, J. A.; Astheimer, R. J.; Odom, J. D.; Sneddon, L. G. J Am Chem Soc 1984, 106, 2275–2283, and references therein.
[37] Marks, T. J.; Kolb, J. R. Chem Rev 1977, 77, 263–292.
[38] Boocock, S. K.; Cheek, Y. M.; Greenwood, N. N.; Hails, M. J.; Kennedy, J. D.; McDonald, W. S. J. D. J Chem Soc, Dalton Trans 1981, 1430–1437.
[39] Gaines, D. F.; Heppert, J. A.; Coons, D. E.; Jorgenson, M. W. Inorg Chem 1982, 21, 3662–3665.
[40] Astheimer, R. J.; Sneddon, L. G. Inorg Chem 1983, 22, 1928–1934.
[41] Ng, L.-L.; Ng, B. K.; Knobler, C. B.; Hawthorne, M. F. Inorg Chem 1992, 31, 3669–3671.
[42] Watson-Clark, R. A.; Knobler, C. B.; Hawthorne, M. F. Inorg Chem 1996, 35, 2963–2966.
[43] Schwalbe, C. H.; Lipscomb, W. H. Inorg Chem 1971, 10, 151–160.
[44] Li, F.; Shelly, K.; Knobler, C. B.; Hawthorne, M. F. Angew Chem Int Ed 1998, 37, 1868–1871.
[45] Wiersema, R. J.; Middaugh, R. L. J Am Chem Soc 1967, 89, 5078.
[46] Wiersema, R. J.; Middaugh, R. L. Inorg Chem 1969, 8, 2074–2079.
[47] Bechtold, R.; Kaczmarczyk, A. J Am Chem Soc 1974, 96, 5953–5954.
[48] Wiersema, R. J.; Middaugh, R. L. J Am Chem Soc 1970, 92, 223–224.
[49] Kirillova, N. I.; Klimova, A. I.; Struchkov, Y. T.; Stanko, V. I. Zh Struct Khim 1976, 17, 675.
[50] Yang, X.; Jiang, W.; Knobler, C. B.; Mortimer, M. D.; Hawthorne, M. F. Inorg Chim Acta 1995, 240, 371–378.
[51] Solntsev, K. A.; Mebel, A. M.; Votinova, N. A.; Kuznetsov, N. T.; Charkin, O. P. Koord Khim 1992, 18, 340.