at 100, 32.1, 94.4, and 40.4 MHz, respectively. Chemical shifts were obtained by tube interchange.

The infrared spectrum was determined with a Beckman IR-12 in a 75-mm gas cell equipped with CsI windows.

Material.—PF_2H was prepared by the reaction of PF_2I, PH_3, and Hg.[6] B_4H_{10} and B_2H_6 were kindly supplied by Callery Chemical Co. B_4H_8CO was prepared by the reaction of B_5H_{11} and CO. $(CH_3)_2NPF_2 \cdot B_4H_8$ was prepared by the reaction of B_4H_8CO and $(CH_3)_2NPF_2$[2] and also by the reaction of $(CH_3)_2NPF_2$ with B_5H_{11}.

Preparation of $PF_2HB_4H_8$.—In a typical reaction, 0.981 mmol of PF_2H and 0.919 mmol of B_4H_8CO were placed in a 100-ml reaction vessel. The reactants were warmed to 25°, were allowed to stand for 15 min, and then were frozen with liquid nitrogen. The trap was opened to the Toepler system through two −196° traps. The material stopping in the −196° traps was recondensed into the reaction vessel after all of the CO had been removed. This procedure was continued until, upon freezing at −196°, no noncondensable gas was recovered from the reactants. The products were then passed through traps cooled to −63, −85, and −196°. A 0.608-mmol sample of $PF_2HB_4H_8$ was found in the trap at −63°. The −85° trap contained 0.148 mmol of B_4H_8CO; the −196° trap contained 0.410 mmol of mostly PF_2H. The amount of CO released was found to be 0.652 mmol. The distillation should not be carried over too long a period of time, because $PF_2HB_4H_8$ will pass slowly through −63° to a colder trap. The vapor density molecular weight was found to be 123 g/mol (calculated for $HF_2PB_4H_8$: 121.4) at 23° (20 mm). The mass spectrum gave a parent peak at 121 and a fragmentation pattern expected for a B_4 species. The identification of $PF_2HB_4H_8$ was established unequivocally by the ^1H, ^{19}F, ^{11}B, and ^{31}P nmr spectra (see above). Although no elemental analysis was run, the identification and analysis by nmr were unequivocal.

Reaction of B_5H_{11} with $(CH_3)_2NPF_2$.—A 0.551-mmol sample of B_5H_{11} and a 1.10-mmol sample of $(CH_3)_2NPF_2$ were condensed in a 20-ml reaction bulb at −196°. The mixture was allowed to warm to room temperature and then was cooled to 0° and was allowed to set for 4 hr. The products were then distilled through traps cooled to −25, −35, and −196°. The −25° trap contained a trace of unidentified solid, and pure $(CH_3)_2NPF_2B_4H_8$ was found at −35°, while $(CH_3)_2NPF_2BH_3$ and $(CH_3)_2NPF_2$ were found at −196°. The product weighed 81.8 mg (0.50 mmol of $(CH_3)_2NPF_2 . B_4H_8$) for 91% yield.

Properties of $F_2HPB_4H_8$.—The vapor pressure data for $F_2HPB_4H_8$ are: −54.6° (1.0 mm), −24.8° (5.5 mm), −0.1° (23.1 mm), 11.1° (40.0 mm), 22.7° (67.5 mm); extrapolated bp 90.2°; mp −80.4 to −79.3° in a sealed tube; Trouton's constant 20.98 cal/deg mol. The vapor pressure data can be summarized by the equation

$$\log P(\text{mm}) = -\frac{1667}{T} + 7.463$$

The infrared spectrum is similar to that for other B_4H_8 species.[7] Assignments for $F_2HPB_4H_8$ are based on the assignments given earlier for these molecules. Absorptions and assignments are as follows: 2592 (m) [ν_{as}(B–H)]; 2559 (s) [ν_s(B–H)]; 2530 (w); 2505 (w); 2432 (s) [ν_s(P–H)]; 2332 (w); 1920 (m), 1612 (m), 1504 (s) (H bridge modes); 1169 (m); 1082 (s) [δ_s(P–H)]; 1031 (w); 983 (m); 898 (s) [ν_s, ν_{as}(PF)$_2$]; 822 (m); 757 (w); 565 (s) [ν(PB)]; 412 (m); 324 (s) [δ_s(PF$_2$)]. (The symbols used above are defined as: ν, stretch; δ, deformation; s, strong; m, moderate; w, weak; v, very. All values are in cm^{-1}.)

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[6] R. W. Rudolph and H. W. Schiller, *J. Am. Chem. Soc.*, **90**, 3581 (1968).

[7] G. L. TerHaar, Doctoral Dissertation, University of Michigan, 1962.

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Electrochemical Preparation and Halogenation of 1,1′-μ-Hydro-bis(undecahydro-*closo*-dodecaborate)(3−), $B_{24}H_{23}^{3-}$[1]

BY R. J. WIERSEMA AND R. L. MIDDAUGH[2]

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The product of the one-electron electrochemical oxidation of $B_{12}H_{12}^{2-}$ in acetonitrile is $B_{24}H_{23}^{3-}$. Halogenation reactions of $B_{24}H_{23}^{3-}$ yield compounds of the type $B_{24}X_nH_{23-n}^{3-}$ (X = I, n = 2; X = Br, n = 7, 10, 11) and $B_{24}X_nH_{22-n}^{4-}$ (X = Br, n = 11, 14, 18; X = Cl, n = 18). Sodium in liquid ammonia cleaves the $B_{24}H_{23}^{3-}$ ion and regenerates $B_{12}H_{12}^{2-}$. Under basic conditions, there is no H–D exchange; however, acidic deuteration gives almost complete H–D exchange in the $B_{24}H_{23}^{3-}$ ion. The proposed structure of the $B_{24}H_{23}^{3-}$ ion is two B_{12} units linked by a hydrogen-bridge bond, analogous to that of $B_{20}H_{19}^{3-}$ ion.

The aqueous chemical oxidation of $B_{10}H_{10}^{2-}$ produces $B_{20}H_{18}^{2-}$, the result of a two-electron oxidation per B_{10} unit.[3-7] Under milder conditions, it is also possible to isolate good yields of $B_{20}H_{19}^{3-}$, the result of a one-electron oxidation of $B_{10}H_{10}^{2-}$.[3,6,7] The electrochemical oxidation of $B_{10}H_{10}^{2-}$ has been characterized as an initial one-electron transfer, followed by a homogeneous chemical reaction, to yield $B_{20}H_{19}^{3-}$. The $B_{20}H_{19}^{3-}$ ion can undergo a further two-electron oxidation to give $B_{20}H_{18}^{2-}$.[8]

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[2] Author to whom inquiries should be addressed.

[3] M. F. Hawthorne, R. L. Pilling, and P. F. Stokely, *J. Am. Chem. Soc.*, **87**, 1893 (1965).

[4] A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Nat'l. Acad. Sci. U. S.*, **48**, 729 (1962).

[5] A. R. Pitochelli, W. N. Lipscomb, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 3026 (1962).

[6] M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, *ibid.*, **85**, 3705 (1963).

[7] B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, **3**, 1450 (1964).

[8] R. L. Middaugh and F. Farha, Jr., *J. Am. Chem. Soc.*, **88**, 4147 (1966).

Attempts to oxidize $B_{12}H_{12}^{2-}$ in aqueous solution have been unsuccessful or have yielded only borates as products.[9,10] We have reported that the electrochemical oxidation $B_{12}H_{12}^{2-}$ in acetonitrile yields the $B_{24}H_{23}^{3-}$ ion.[11] Subsequently, various reactions have been used to characterize the chemical behavior and probable structure of this compound.

Results and Discussion

Voltammetry of $[(C_2H_5)_4N]_2B_{12}H_{12}$ at a rotating platinum electrode in acetonitrile (0.1 *M* tetraethylammonium perchlorate as supporting electrolyte) shows an anodic oxidation wave with $E_{1/2} = +1.50$ V (*vs.* sce). At a stationary platinum button electrode, an anodic peak is observed at +1.50 V, with a shoulder at +1.85 V on a large anodic wave.

Preliminary bulk electrolysis experiments using a rotating platinum gauze electrode and tetraethylammonium perchlorate as supporting electrolyte indicated that the oxidation process caused severe filming problems on the platinum electrode. An additional problem was encountered in the separation of the product from the supporting electrolyte. The use of a graphite cloth electrode without supporting electrolyte gave good yields of the desired product with a minimum of experimental difficulties.

Typically, 30 mmol of $Na_2B_{12}H_{12}$ in 150 ml of acetonitrile was exhaustively electrolyzed. The current was monitored, and the oxidation process corresponded to a one-electron oxidation per B_{12} unit (eq 1). On this basis, the $B_{24}H_{23}^{3-}$ ion should be related to the $B_{20}H_{19}^{3-}$ ion, the one-electron oxidation product of $B_{10}H_{10}^{2-}$.

$$2B_{12}H_{12}^{2-} \longrightarrow B_{24}H_{23}^{3-} + H^+ + 2e^- \qquad (1)$$

The tetraethylammonium salt of the oxidation product in acetonitrile (0.1 *M* tetraethylammonium perchlorate as supporting electrolyte) exhibited only the oxidation wave at +1.85 V, which had been observed in the cyclic voltammetry of $B_{12}H_{12}^{2-}$. No reduction wave was observed to −2.8 V. The elemental analyses and equivalent weight data support the formulation as $[(C_2H_5)_4N]_3B_{24}H_{23}$. The infrared spectrum of this compound in KBr included absorptions at 2250 and 940 cm^{-1}, in addition to the normal absorptions of $B_{12}H_{12}^{2-}$ at 2500, 1050, and 710 cm^{-1}. This compound exhibited no absorptions in the ultraviolet region above 210 nm.

The ^{11}B nmr spectrum of aqueous $Na_3B_{24}H_{23}$ consisted of an unsymmetrical doublet at +33.8 ppm, with $J = 130$ Hz. The 100-MHz ^{1}H nmr spectrum irradiated at 32.0 MHz consisted of two peaks of approximately equal intensities. The optimum decoupling frequencies for the two peaks differed by about 30 Hz, which implies that the ^{11}B unsymmetrical doublet includes two doublets separated by less than 1 ppm. The low-field ^{1}H peak was considerably broader under optimum decoupling conditions than was the high-field peak. The appearance of two peaks in the ^{1}H nmr spectrum is typical of a monosubstituted $B_{12}H_{12}^{2-}$ ion.

Yields of the coupled product were typically 80–85% of crude material. A less than quantitative yield is to be expected, because of diffusion losses resulting from bulk electrolysis without supporting electrolyte. In addition, small yields of $B_{12}H_{11}NHCOCH_3^{2-}$ were also obtained, especially when the electrolysis was performed on more concentrated solutions. This side product can be formed by an acid-catalyzed reaction of $B_{12}H_{12}^{2-}$ with acetonitrile to give $B_{12}H_{11}NCCH_3^-$, which hydrolyzes to the amide in the work-up (eq 2, 3).

$$B_{12}H_{12}^{2-} + CH_3CN + H^+ \longrightarrow B_{12}H_{11}NCCH_3^- + H_2 \qquad (2)$$

$$B_{12}H_{11}NCCH_3^- + H_2O \longrightarrow B_{12}H_{11}NHCOCH_3^{2-} + H^+ \qquad (3)$$

The $B_{20}H_{19}^{3-}$ ion has been shown to consist of two B_{10} units linked by a bridging hydrogen.[6] The bridging hydrogen in $B_{20}H_{19}^{3-}$ gives rise to an absorption at 1850 cm^{-1} in the infrared spectrum. The $B_{24}H_{23}^{3-}$ ion exhibits an absorption at 2250 cm^{-1} which we assign to a bridging hydrogen in this compound. The $B_{20}H_{19}^{3-}$ ion can be converted to $B_{20}H_{18}^{4-}$ by aqueous base, with a corresponding loss of the ir band at 1850 cm^{-1}. The $B_{20}H_{19}^{3-}$ ion is regenerated when the $B_{20}H_{18}^{4-}$ ion is treated with acid. Treatment of $B_{24}H_{23}^{4-}$ with 1 *M* aqueous acid or base has no effect on the compound, which can be recovered unchanged. This result is in qualitative agreement with the higher frequency absorption of the bridging hydrogen; *i.e.*, it is more hydridic in $B_{24}H_{23}^{3-}$ than in $B_{20}H_{19}^{3-}$.

Deuteration Studies.—The rate of H–D exchange of $B_{10}H_{10}^{2-}$ has been found to be pH dependent, promoted by acid and inhibited by base.[12]

When $B_{24}H_{23}^{3-}$ was refluxed with D_2O containing K_2CO_3 for 24 hr no exchange was noted; *i.e.*, the ir bands at 2500 and 2250 cm^{-1} did not diminish. Under acidic conditions using D_2O and DCl, it was possible to obtain an almost completely deuterated product. The infrared spectrum of the deuterated compound exhibited absorptions at 1870 cm^{-1} (B–D; B–H at 2500 cm^{-1}) and 1660 cm^{-1} (bridging B–D–B; B–H–B at 2250 cm^{-1}).

These results indicate that the bridging hydrogen is not appreciably acidic. In addition, the infrared spectra of partially deuterated species indicate no preferential site of deuteration.

Sodium Reduction of Coupled Products.—When $B_{24}H_{23}^{3-}$ was treated with sodium in liquid ammonia, the product was $B_{12}H_{12}^{2-}$ (eq 4). Under similar conditions, the $B_{20}H_{18}^{2-}$ and $B_{20}H_{19}^{3-}$ ions yield known isomers of $B_{20}H_{18}^{4-}$, with no cleavage of the linked boron cages.

$$B_{24}H_{23}^{3-} + NH_3 + 2e^- \longrightarrow 2B_{12}H_{12}^{2-} + NH_2^- \qquad (4)$$

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[9] D. Kaczmarczyk, G. B. Kolski, and W. P. Townsend, *J. Am. Chem. Soc.*, **87**, 1413 (1965).

[10] M. F. Hawthorne, "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, Chapter 5.

[11] R. L. Middaugh and R. J. Wiersema, *J. Am. Chem. Soc.*, **89**, 5078 (1967).

[12] E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

Halogenation Reactions.—Under mild conditions, the various coupled B_{20} species can be partially halogenated. However, under more drastic conditions halogenation results in cleavage to yield $B_{10}X_{10}^{2-}$ and boric acid.[7]

The $B_{24}H_{23}^{3-}$ ion reacted with iodine at room temperature to yield $B_{24}H_{21}I_2^{3-}$ (eq 5). The ^1H nmr

$$B_{24}H_{23}^{3-} + 2I_2 \longrightarrow B_{24}H_{21}I_2^{3-} + 2HI \qquad (5)$$

spectrum of $B_{24}H_{21}I_2^{3-}$ has been found to be consistent with a 1,1′-μ-hydro-bis(7-iododecahydro-*closo*-dodecaborate)(3 −) structure by comparison with the reported ^1H spectrum of 1,7-$B_{12}H_{10}I_2^{2-}$.[13] The proton magnetic resonance spectrum, with boron decoupled, consists of three types of hydrogens in the ratio of 1:3:1, consistent with a *meta*-substituted linked cage species.

Single crystals of $[(CH_3)_3NC_6H_5]_4B_{24}H_{20}I_2 \cdot [(CH_3)_3NC_6H_5]I$ were obtained by ion exchange of the tetraethylammonium salt and addition of trimethylphenylammonium iodide. A single-crystal structure determination is in progress.

Various brominated derivatives of $B_{24}H_{23}^{3-}$ were obtained, depending on the mole ratio of the reactants and the temperature of the reaction. Owing to the initial rapid reaction of $B_{24}H_{23}^{3-}$ and bromine, it is to be expected that the products may be mixtures of a number of brominated species. The empirical formulas for the products of the reactions reflect only the average composition of the solid material. No attempt was made to obtain isomerically pure compounds. The products obtained in this series were $B_{24}Br_7H_{16}^{3-}$, $B_{24}Br_{10}H_{13}^{3-}$, $B_{24}Br_{11}H_{12}^{3-}$, $B_{24}Br_{11}H_{11}^{4-}$, $B_{24}Br_{14}H_8^{4-}$, and, under drastic conditions, $B_{24}Br_{18}H_4^{4-}$. No evidence for decomposition (*i.e.*, borate formation) was noted in any of these reactions.

The existence of compounds with varying degrees of bromination from a given reaction was indicated by the presence of additional small waves in the cyclic voltammetry of the reaction products. The variation in isomerism or composition was greatest for compounds with less bromine substitution.

The analytical data for $[(C_2H_5)_4N]B_{24}Br_{11}H_{12}$ are clearly inconsistent with a formulation as a substituted B_{12} monomeric ion or as a substituted B_{24} ion with either a 2− or 4− charge. The much lower potential for oxidation of the substituted B_{24} ions compared to that of $B_{12}Br_6H_6^{2-}$ (Table I) is another indication that no cleavage has occurred. Finally, the conditions which led to the formation of $B_{24}Br_{18}H_4^{4-}$ have been shown to result in complete bromination of $B_{12}H_{12}^{2-}$.[13]

Table I

Anodic Oxidation Behavior of Selected Polyhedral Borane Ions

Compound[a]	$E_{p/2}$, V *vs.* sce[b]	Compound[a]	$E_{p/2}$, V *vs.* sce[b]
$B_{12}H_{12}^{2-}$	+1.43	$B_{24}Br_7H_{16}^{3-}$	+0.78
$B_{12}H_{11}I^{2-}$	+1.88	$B_{24}Br_{10}H_{13}^{3-}$	+0.98
$B_{12}Br_6H_6^{2-}$	+2.00	$B_{24}Br_{11}H_{12}^{3-}$	+1.14
$B_{12}Br_{12}^{2-}$	>+2.20	$B_{24}Br_{14}H_8^{4-}$	+1.30
$B_{12}Cl_{10}H_2^{2-}$	>+2.20	$B_{24}Br_{18}H_4^{4-}$	+1.30
$B_{24}H_{23}^{3-}$	+1.74	$B_{24}Cl_{18}H_4^{4-}$	+1.76
$B_{24}H_{21}I_2^{3-}$	+1.19		

[a] Compounds examined as tetraethylammonium salts in acetonitrile containing 0.1 *M* tetraethylammonium perchlorate. Pt button electrode; scan rate 4 V/min. [b] No reduction wave associated with the oxidation wave was observed in the cyclic voltammetry in the range from zero to the potential at which oxidation occurs.

Although the various brominated derivatives were probably not isomerically pure, these compounds exhibited some interesting chemical properties. As the degree of bromination increases, the ir absorption of the bridging hydrogen is shifted toward lower frequency. The $B_{24}Br_{11}H_{12}^{3-}$ ion exhibits an ir band at 2100 cm^{-1}, as compared to 2250 cm^{-1} in the unbrominated product. When $[(C_2H_5)_4N]_3B_{24}Br_{11}H_{12}$ was passed through an acid ion-exchange column, titration of the effluent with standardized sodium hydroxide yielded only one break in the titration curve, corresponding to three protons per $B_{24}Br_{11}H_{12}^{3-}$ unit. However, when the alkaline solution was evaporated to a small volume on a hot plate, the only product obtained was $B_{24}Br_{11}H_{11}^{4-}$. Treatment of this 4− ion with a strong acid did not yield the 3− ion which would have been expected on the basis of simple acid–base equilibrium. Attempted deuteration of $B_{24}Br_{11}H_{12}^{3-}$ in D_2O containing K_2CO_3 produced no exchange but instead led to formation of $B_{24}Br_{11}H_{11}^{4-}$ by an acid–base reaction. None of the 4− ions exhibited any absorptions attributable to a bridging hydrogen.

Exhaustive chlorination of $B_{24}H_{23}^{3-}$ in H_2O gave $B_{24}Cl_{18}H_4^{4-}$, with no evidence of decomposition. Under comparable conditions, $B_{12}H_{12}^{2-}$ yields the approximate formulation $B_{12}Cl_{10}H_2^{2-}$.[13] The molar conductivity of the cesium salt is 685 ohm $^{-1}$ cm^{-1}, calculated for a $B_{24}Cl_{18}H_4^{4-}$ salt, and would be 342 ohm^{-1} cm^{-1} for a monomeric $B_{12}Cl_9H_3^{3-}$ salt. Yoo cites the values 520–660 ohm^{-1} cm^{-1} for 4:1 electrolytes and 250–310 ohm^{-1} cm^{-1} for 2:1 electrolytes. Additional support for the dimeric B_{24} ion formulation is taken from the potential for oxidation (Table I), which is consistent with those of the brominated dimeric ions. The "$B_{12}Cl_{10}H_2^{2-}$" ion prepared by chlorination of $B_{12}H_{12}^{2-}$ was not oxidized at potentials up to +2.20 V.

The acid–base behavior of the various substituted compounds can be explained on the basis of an increased acidity of the bridging hydrogen upon halogen substitution, which allows the proton to be removed by aqueous base. The shift of the ir absorption of the bridging hydrogen toward lower frequency with increasing bromine substitution also suggests that the substitution causes an increase in the acidity of the hydrogen bridge. The irreversibility of the proton transfer could be explained on the basis of a molecular rearrangement of the halogenated species following proton transfer and/or the solubility properties of one form of the compound. The $B_{20}H_{19}^{3-}$ ion has been shown to exhibit time-dependent rearrangement in

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[13] W. H. Knoth, H. C. Miller, J. C. Sauer, J. A. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964).

acid–base equilibria, in addition to preferential precipitation of one form of the compound.[3,14]

The half-wave potentials for the oxidation of various polyhedral borane ions are listed in Table I. Iodine, bromine, and chlorine substitutions on the $B_{12}H_{12}{}^{2-}$ ion cause an increase in the potential for the oxidation process. Iodination of $B_{24}H_{23}{}^{3-}$ causes a decrease in the half-wave potential for the oxidation. Bromination of the coupled product causes an increase in the oxidation half-wave potential, after an initial decrease with only minor substitution. While a quantitative discussion of the effects of substitution upon the half-wave potential for oxidation processes of the various B_{24} species is impossible until a more complete study of the products is performed, the observed potentials have proved helpful in verifying that halogenation does not yield substituted monomeric products. The halogenated B_{12} species all exhibit an increase in the half-wave potential for the oxidation, while the B_{24} species exhibit a decrease in the half-wave potential, followed by an increase upon further halogenation.

Summary

The product of the one-electron electrochemical oxidation of $B_{12}H_{12}{}^{2-}$ is $B_{24}H_{23}{}^{3-}$. Its structure consists of two boron cages linked by a hydrogen-bridge bond, similar to that of the $B_{20}H_{19}{}^{3-}$ ion. The variance in the chemical reactivity of the two species is primarily a reflection of the greater stability of the $B_{12}H_{12}{}^{2-}$ ion than of the $B_{10}H_{10}{}^{2-}$ ion toward various halogenation reactions and not necessarily a reflection of the strength of the cage–cage linkage. The B_{20} system has been shown to be unstable with respect to cleavage under polyhalogenating conditions but stable to cleavage under basic reducing conditions. The B_{24} system can be polyhalogenated with no evidence for cleavage or decomposition; however, the cage–cage linkage is cleaved under basic reducing conditions.

The difference in acidic properties of the two ions is reflected in the infrared absorption of the bridging hydrogen, which occurs at higher frequency in the B_{24} unit. This result can be interpreted as the bridging hydrogen being more hydridic in $B_{24}H_{23}{}^{3-}$ than in $B_{20}H_{19}{}^{3-}$.

At present there is very little basis for comparison of the amount of interaction between the two cages in the linked species, but it is hoped that the results of the X-ray structure determination, currently under investigation, will give more information about the bonding between the coupled boron cages.

Experimental Section

Physical Measurements.—Infrared spectra were obtained using a Perkin-Elmer 421 infrared spectrophotometer. The ^1H and ^{11}B nmr spectra were obtained using a Varian Associates HA-100 spectrometer, at 100 and 32.0 MHz, respectively. Heteronuclear decoupling experiments were performed using an NMR Specialties HD-60A decoupler. The ^{11}B nmr chemical shifts are referenced to an external capillary of methyl borate.

Cyclic voltammetry experiments were carried out using an instrument based on the design of Alden, Chambers, and Adams[15] and modified by Hawley.[16] Potentials are reported relative to the saturated aqueous calomel electrode. The rotating platinum electrode was a platinum wire sealed in glass. The stationary electrode was a Beckman Model 39273 platinum inlay electrode with a surface area of about 0.22 cm². The bulk electrolyses were performed using a Kepco, Inc., Model OPS 40–0.5 power supply. The electrolysis cell consisted of a 250-ml wide-mouth sample jar, with the top drilled to accommodate the graphite cloth working electrode, saturated calomel electrode, nitrogen bubbler, and a Coors unglazed porcelain cup (25-mm o.d.). The auxiliary graphite cloth electrode was placed in the porcelain cup containing a 20% aqueous acetonitrile solution, and the cup was placed in the sample jar. The potential of the working electrode was monitored with VTVM. The current was monitored by measuring the potential across a 10-ohm precision resistor in series with the working electrode. The potential was measured with a Moseley Model 7101A strip chart recorder.

Reagents.—Acetonitrile and tetraethylammonium perchlorate were purified as previously reported.[8] Decaborane and triethylamine–borane were obtained from Callery Chemical Co. The decaborane was used as received; triethylamine–borane was distilled at reduced pressure prior to use. All other reagents were the highest quality available and used as received. $B_{12}H_{12}{}^{2-}$, $B_{12}H_{11}I^{2-}$, $B_{12}Br_6H_6{}^{2-}$, $B_{12}Br_{12}{}^{2-}$, and $B_{12}Cl_{10}H_2{}^{2-}$ were prepared according to the procedures described in the literature.[13,17]

Analytical Methods.—Equivalent weights were determined by dissolving the compound in an acetonitrile–water mixture and passing the solution through an acid ion-exchange column (Amberlite IR-120). The effluent was titrated with standardized sodium hydroxide. Each of the compounds exhibited only one break in the titration curve, typical of a strong acid.

Boron was determined by a Kjeldahl-type digestion, using a selenium catalyst, followed by titration of the resulting boric acid as the mannitol complex.[18,19] Halogens were determined by sodium fusion, followed by potentiometric titration of the halides with $AgNO_3$.[20]

Conductance Measurements.—An Industrial Instruments, Inc., conductivity bridge, Model RC-16B2, was used to measure the conductance of 0.001 *M* aqueous solutions of selected compounds. The conductivity cell had a cell constant of approximately 0.1 cm⁻¹, which was recalibrated for each set of experiments.

$B_{24}H_{23}{}^{3-}$.—In a typical experiment, 30 mmol of $Na_2B_{12}H_{12}$ in 150 ml of acetonitrile was exhaustively electrolyzed under nitrogen at +1.45 V, using a graphite cloth anode, with no supporting electrolyte. The current was monitored using a strip chart recorder; the value $n = 0.96$ equiv/mol of $Na_2B_{12}H_{12}$ was found. The electrolysis solution was diluted with 75 ml of H_2O, and the acetonitrile was evaporated at room temperature. The pale yellow solution was filtered through Celite, and the filtrate was neutralized with NaOH. Addition of CsF to the aqueous solution precipitated crystals of $Cs_3B_{24}H_{23}$, which were recrystallized from an acetonitrile–water mixture.

Anal. Calcd for $Cs_3B_{24}H_{23}\cdot 3H_2O$: B, 35.29. Found: B, 35.11. The infrared spectrum of $Cs_3B_{24}H_{23}$ includes absorptions at 2500 (s), 2250 (sh), 1050 (m), and 940 (m) cm⁻¹ and multiple absorptions from 750 to 710 cm⁻¹.

The conductivity of $Cs_3B_{24}H_{23}\cdot 3H_2O$ in H_2O gave $\Lambda_m = 462$ ohm⁻¹ cm⁻¹, typical of a 3:1 electrolyte.[21]

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[14] A. Kaczmarczyk, *Inorg. Chem.*, **7**, 164 (1968).

[15] J. R. Alden, J. Q. Chambers, and R. N. Adams, *J. Electroanal. Chem.*, **5**, 152 (1963).

[16] M. D. Hawley, private communication.

[17] H. C. Miller and E. L. Muetterties, *Inorg. Syn.*, **10**, 88 (1967).

[18] G. Ingram, "Organic Elemental Microanalysis," Reinhold Publishing Corp., New York, N. Y., 1962, Chapter 3.

[19] R. D. Strahm in "Treatise on Analytical Chemistry," Vol. 12, Part II, I. M. Kolthoff and P. J. Elving, Ed., John Wiley & Sons, Inc., New York, N. Y., 1965, p 169.

[20] G. W. Armstrong, H. H. Gill, and R. F. Rolf in "Treatise on Analytical Chemistry," Vol. 7, Part II, I. M. Kolthoff and P. J. Elving, Ed., John Wiley & Sons, Inc., New York, N. Y., 1961, p 335.

[21] J. S. Yoo, Ph.D. Thesis, University of Kansas, Lawrence, Kansas, 1964.

In a similar experiment, tetraethylammonium bromide was added to the aqueous solution, giving the corresponding tetraethylammonium salt of $B_{24}H_{23}^{3-}$. White crystals of this material were obtained after several recrystallizations from an acetonitrile–water mixture; the yield was 85%.

Anal. Calcd for $[(C_2H_5)_4]_3B_{24}H_{23}$: C, 42.82; H, 12.42; N, 6.24; B, 38.52; equiv wt, 224.5. Found: C, 42.93; H, 12.72; N, 6.18; B, 38.66; equiv wt, 227.

The ^{11}B nmr spectrum of a solution of $Na_3B_{24}H_{23}$ in H_2O consisted of an unsymmetrical doublet at +33.8 ppm, with J = 130 Hz. The ^1H spectrum, irradiated at 32.0 MHz, consisted of two peaks of approximately equal intensities at +3.02 and +3.21 ppm from H_2O.

$[(C_2H_5)_4N]_3B_{24}H_{21}I_2$.—Iodine (0.381 g, 1.5 mmol) was added to 100 ml of an acetonitrile–methanol solution containing $[(C_2H_5)_3N]_3B_{24}H_{23}$ (0.469 g, 0.7 mmol). The solution was stirred overnight at room temperature. Water was added and the excess iodine was removed by reaction with sodium bisulfite. The solution was evaporated at room temperature and then neutralized with NaOH. The precipitate which had formed during evaporation was filtered and washed with water. This reaction gave 0.469 g of compound; the yield was 76%.

Anal. Calcd for $[(C_2H_5)_4N]_3B_{24}H_{21}I_2$: B, 28.03; I, 27.43; equiv wt, 308.4. Found: B, 28.1; I, 26.1; equiv wt, 323.

The infrared spectrum of this compound included absorptions at 2500 and 2240 cm^{-1}.

The ^{11}B nmr spectrum of $[(C_2H_5)_4N]_3B_{24}H_{21}I_2$ in acetonitrile consisted of a poorly resolved doublet at +32.0 ppm, with a definite shoulder at +42.7 ppm. The ^1H spectrum of an aqueous solution of $Na_3B_{24}H_{21}I_2$, irradiated at 32.0 MHz, consisted of three peaks at +2.57, +2.84, and +3.28 ppm from H_2O, in the ratio of 1:3:1, respectively.

$[(CH_3)_3NC_6H_5]_4B_{24}H_{20}I_2 \cdot (CH_3)_3NC_6H_5I$.—$[(C_2H_5)_4N]_3B_{24}H_{21}I_2$ (0.469 g, 0.51 mmol) was dissolved in an acetonitrile–water mixture and passed through an acid ion-exchange column. The effluent was neutralized with 0.05 M NaOH and evaporated to a volume of 10 ml. Trimethylphenylammonium iodide (0.8 g, 3 mmol) was added to the aqueous solution. The resulting precipitate was collected and recrystallized repeatedly from an acetonitrile–water mixture. Single crystals of $[(CH_3)_3NC_6H_5]_4B_{24}H_{20}I_2 \cdot (CH_3)_3NC_6H_5I$ were obtained by slow evaporation of an acetonitrile–water mixture.

Anal. Calcd for $[(CH_3)_3NC_6H_5]_4B_{24}H_{20}I_2 \cdot (CH_3)_3NC_6H_5I$: B, 20.06. Found: B, 20.6.

The infrared spectrum of this compound lacked the absorption at 2240 cm^{-1}, which was present in the 3− anion above.

A single crystal of this compound was examined by X-ray diffraction (Zr-filtered Mo radiation) using a Buerger precession camera. The crystal exhibited the symmetry of the monoclinic space group, $P2_1/c$. The unit cell dimensions are a = 10.97 Å, b = 17.06 Å, and c = 15.98 Å, with β = 94° 30′. Density (by flotation) is 1.47 ± 0.01 g/cm^3; density calculated for $Z = 2$ is 1.44 g/cm^3.

$[(C_2H_5)_4N]_3B_{24}Br_7H_{16}$.—$[(C_2H_5)_4N]_3B_{24}H_{23}$ (300 mg, 0.44 mmol) was dissolved in 50 ml of an acetonitrile–water mixture and cooled to −15°, with a methanol–ice bath. Bromine (1 ml, 19 mmol) was diluted to 10 ml with acetonitrile and added dropwise to the cooled solution containing $B_{24}H_{23}^{3-}$, until the bromine color persisted for a few minutes. This required 2 ml, 3.8 mmol, of bromine. The excess bromine was destroyed with $NaHSO_3$, and the solution was neutralized with NaOH. The solution was evaporated to dryness at room temperature, and the residue was recrystallized from an acetonitrile–methanol mixture. A solid having an average empirical formula of $[(C_2H_5)_4N]_3B_{24}Br_7H_{16}$ (200 mg, 0.16 mmol) was obtained; the yield was 37%.

Anal. Calcd for $[(C_2H_5)_4N]_3B_{24}Br_7H_{16}$: B, 21.17; equiv wt, 408.6. Found: B, 21.3; equiv wt, 392.

The infrared spectrum included absorptions at 2530 and 2200 cm^{-1}. The ^{11}B nmr spectrum of this compound in acetonitrile consisted of a broad singlet at +31.8 ppm.

$[(C_2H_5)_4N]_3B_{24}Br_{10}H_{13}$.—The above reaction was repeated, using $[(C_2H_5)_4N]_3B_{24}H_{23}$ (153 mg, 0.23 mmol) and bromine (2.8 mmol), at 0°. The product, which was precipitated by addition of H_2O, had an average empirical formula of $[(C_2H_5)_4N]_3B_{24}Br_{10}H_{13}$ (270 mg, 0.20 mmol); the yield was 85%.

Anal. Calcd for $[(C_2H_5)_4N]_3B_{24}Br_{10}H_{13}$: B, 17.74; equiv wt, 487.4. Found: B, 17.2; equiv wt, 448.

The ^{11}B nmr spectrum of this compound in acetonitrile consisted of a broad singlet at +29.9 ppm, with a high-field shoulder at +34.8 ppm. The infrared spectrum included absorptions at 2540 and 2170 cm^{-1}.

$[(C_2H_5)_4N]_3B_{24}Br_{11}H_{12}$.—$[(C_2H_5)_4N]_3B_{24}H_{23}$ (256 mg, 0.375 mmol) in an acetonitrile–water mixture was passed through an acid ion-exchange column. The effluent was neutralized, evaporated to a volume of 25 ml, and diluted with an equal volume of methanol. Bromine (0.24 ml, 4.5 mmol) was added dropwise to the solution which was then stirred at room temperature for 6 hr. The excess bromine was removed with $NaHSO_3$, and excess tetraethylammonium bromide was added to the neutralized solution. The resulting precipitate, having the average empirical formula of $[(C_2H_5)_4N]_3B_{24}Br_{11}H_{12}$ (502 mg, 0.325 mmol), was washed with water; the yield was 87%.

In a similar experiment using $[(C_2H_5)_4N]_3B_{24}H_{23}$ in an acetonitrile–methanol mixture, the same product was obtained.

Anal. Calcd for $[(C_2H_5)_4N]_3B_{24}Br_{11}H_{12}$: B, 16.83; Br, 57.03; equiv wt, 513.8. Found: B, 16.3; Br, 53.9; equiv wt, 508.

The infrared spectrum included absorptions at 2550 and 2100 cm^{-1}.

$[(C_2H_5)_4N]_4B_{24}Br_{11}H_{11}$.—$[(C_2H_5)_4N]_3B_{24}Br_{11}H_{12}$ (340 mg, 0.22 mmol) was dissolved in an acetonitrile–water mixture and passed through an acid ion-exchange column; the effluent was titrated with NaOH to a pH of 10 and evaporated to a volume of 25 ml. Addition of excess tetraethylammonium bromide precipitated $[(C_2H_5)_4N]_4B_{24}Br_{11}H_{11}$.

Anal. Calcd for $[(C_2H_5)_4N]_4B_{24}Br_{11}H_{11}$: B, 15.53; equiv wt, 417.6. Found: B, 15.4; equiv wt, 459.

The infrared spectrum of this compound did not exhibit the band at 2100 cm^{-1} which was present in the starting material.

The 4− compound was heated with 1 M H_2SO_4 for a period of several hours in an attempt to convert it to the original 3− product. However, the only product obtained was the 4− compound, with no conversion to the 3− compound.

$[(C_2H_5)_4N]_4B_{24}Br_{14}H_8$.—$[(C_2H_5)_4N]_3B_{24}H_{23}$ (1.5 g, 2.24 mmol) was dissolved in 50 ml of an acetonitrile–water mixture. Bromine (2.5 ml, 47.5 mmol) was added, and the solution was stirred at room temperature for 24 hr. The excess bromine was removed with $NaHSO_3$, and the solution was neutralized and evaporated to dryness at room temperature. The residue was dissolved in 50 ml of H_2O, and $[(C_2H_5)_4N]_4B_{24}Br_{14}H_8$ was precipitated by addition of tetraethylammonium bromide. The product was dissolved in acetonitrile, filtered, and precipitated by dilution with H_2O.

Anal. Calcd for $[(C_2H_5)_4N]_4B_{24}Br_{14}H_8$: B, 13.60; equiv wt, 476.8. Found: B, 13.6; equiv wt, 477.

The infrared spectrum included an absorption at 2530 cm^{-1}. The ^{11}B nmr spectrum of this compound in acetonitrile consisted of a broad singlet at +29.6 ppm, with a high-field shoulder at +36.0 ppm.

$[(C_2H_5)_4N]_4B_{24}Br_{18}H_4$.—$[(C_2H_5)_4N]_3B_{24}H_{23}$ (1.35 g, 2 mmol) was dissolved in 50 ml of an acetonitrile–water mixture. Bromine was added dropwise until the color persisted; then an additional 2 ml, 38 mmol, was added. Chlorine gas was bubbled through the solution for 0.5 hr.[22] The solution was evaporated to a thick syrup at room temperature, diluted with H_2O, and neutralized with NH_4OH. The insoluble material was filtered and recrystallized twice from an acetonitrile–methanol mixture. $[(C_2H_5)_4N]_4B_{24}Br_{18}H_4$ (1.13 g, 0.5 mmol) was obtained; the yield was 25%.

Anal. Calcd for $[(C_2H_5)_4N]_4B_{24}Br_{18}H_4$: equiv wt, 555.7; Br, 64.71. Found: equiv wt, 560; Br, 62.9.

The infrared spectrum included a weak absorption at 2580 cm^{-1}. The ^{11}B nmr spectrum of this compound in acetonitrile exhibited a broad singlet at +30.4 ppm.

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[22] See ref 13, footnote 5.

$B_{24}Cl_{18}H_4^{4-}$.—$[(C_2H_5)_4N]_3B_{24}H_{23}$ (386 mg, 0.58 mmol) was dissolved in an acetonitrile–water mixture and passed through an acid ion-exchange column. The effluent was neutralized with NaOH and evaporated to a volume of about 50 ml. Chlorine was rapidly bubbled through the solution for 2 hr at room temperature. Nitrogen was then bubbled through the solution to remove the excess chlorine. The aqueous solution was neutralized with 0.5 *M* NaOH. Addition of excess tetraethylammonium bromide precipitated $[(C_2H_5)_4N]_4B_{24}Cl_{18}H_4$ (691 mg, 0.52 mmol); the yield was 89%. The precipitate was filtered and washed with water.

Anal. Calcd for $[(C_2H_5)_4N]_4B_{24}Cl_{18}H_4$: equiv wt, 355.7; Cl, 44.86. Found: equiv wt, 349; Cl, 43.9.

The ^{11}B nmr spectrum of this compound in acetonitrile exhibited a broad singlet at +29.2 ppm, with a shoulder at +36.5 ppm. The infrared spectrum included an absorption at 2530 cm^{-1}.

The cesium salt of this compound was obtained by acid ion exchange of the tetraethylammonium salt and neutralization with CsOH. The infrared spectrum of $Cs_4B_{24}Cl_{18}H_4$ exhibited absorptions at 2540 (w), 1030 (b, s), 970, 850, and 700 cm^{-1}.

The molar conductivity of $Cs_4B_{24}Cl_{18}H_4$ in H_2O was $\Lambda_m = 685$ ohm^{-1} cm^{-1}, typical of a 4:1 electrolyte.[21]

$[(C_2H_5)_4N]_2B_{12}H_{11}NHCOCH_3$.—(A) The aqueous solution of the crude electrolysis solution containing the precipitate of $[(C_2H_5)_4N]_3B_{24}H_{23}$ was filtered, and the filtrate was evaporated to dryness on a steam bath. The residue was recrystallized from 2-propanol. The product was the tetraethylammonium salt of $B_{12}H_{11}NHCOCH_3^{2-}$, which was identified by comparison of its ir, nmr, and analytical data with those of the compound prepared by the acid-catalyzed reaction of $B_{12}H_{12}^{2-}$ and acetonitrile. The yield was approximately 5%, based on the amount of $B_{12}H_{12}^{2-}$ used in the electrolysis. The yield increased when the electrolysis was performed on more concentrated solutions (*i.e.*, 0.3 *M* $B_{12}H_{12}^{2-}$ in CH_3CN) due to the increased acid concentration in the electrolysis solution.

(B) The $B_{12}H_{11}NHCOCH_3^{2-}$ ion was prepared by hydrolysis of the product obtained from the acid-catalyzed reaction of $B_{12}H_{12}^{2-}$ and acetonitrile, using the method as outlined in the literature for the preparation of the analogously substituted $B_{10}H_{10}^{2-}$ ion.[23] $[(C_2H_5)_3NH]_2B_{12}H_{12}$ (3.5 g, 10 mmol) and *p*-toluenesulfonic acid (1.9 g, 10 mmol) in 70 ml of dry acetonitrile were refluxed for 24 hr. The ^{11}B nmr spectrum of the product in acetonitrile, assumed to be $B_{12}H_{11}NCCH_3^{-}$, exhibited a singlet at +25.5 ppm and a doublet at +34.3 ppm, in a relative ratio 1:11. The acetonitrile solution was evaporated at room temperature, and dilute NaOH was added to the residue. The aqueous solution was heated to remove the triethylamine, and an aqueous solution of tetraethylammonium bromide was added to precipitate $[(C_2H_5)_4N]_2B_{12}H_{11}NHCOCH_3$. Nearly quantitative yields were obtained by this procedure.

Anal. Calcd for $[(C_2H_5)_4N]_2B_{12}H_{11}NHCOCH_3$: equiv wt, 229.7. Found: equiv wt, 235.

The ^{11}B nmr spectrum of $[(C_2H_5)_4N]_2B_{12}H_{11}NHCOCH_3$ in H_2O exhibited a singlet at +24.6 ppm and a doublet at +34.4 ppm. The infrared spectrum of this compound included absorptions at 3220 (NH), 2470 (BH), and 1600 (C=O) cm^{-1}.

Deuteration Reactions.—The deuteration reactions were performed using the procedures outlined in the literature.[12]

Basic deuteration of $[(C_2H_5)_4N]_3B_{24}H_{23}$ (100 mg, 0.15 mmol) in 10 ml of D_2O containing a small amount of K_2CO_3 failed to accomplish any exchange after refluxing for 24 hr, as indicated by the infrared spectrum of the material.

Acidic deuteration of $[(C_2H_5)_4N]_3B_{24}H_{23}$ (200 mg, 0.30 mmol) in 10 ml of D_2O containing 0.6 *M* DCl accomplished essentially complete deuteration after repeated treatment with D_2O–DCl. The infrared spectrum of the deuterated compound included absorptions at 1870 and 1660 cm^{-1}, indicating that the $B_{24}H_{23}^{3-}$ had been converted to $B_{24}D_{23}^{3-}$.

The ^{11}B nmr of $B_{24}D_{23}^{3-}$ in an acetonitrile–D_2O mixture exhibited a single broad (width at half-height, 64 Hz) resonance at +34.6 ppm [$B(OCH_3)_3$ width at half-height, 34 Hz].

Chemical Reduction.—$[(C_2H_5)_4N]_3B_{24}H_{23}$ (100 mg, 0.15 mmol) was placed in a small test tube. Approximately 5 ml of anhydrous ammonia was condensed in the test tube, while it was suspended in a Dry Ice–acetone bath. Excess sodium metal was added, and the liquid ammonia solution remained blue for at least 0.5 hr. The test tube was removed from the cooling bath, and the ammonia was allowed to evaporate. The excess sodium was destroyed with methanol. Tetraethylammonium bromide in methanol was added to the reaction solution precipitating $[(C_2H_5)_4N]_2B_{12}H_{12}$, which was identified by comparison of its infrared spectrum, ^{11}B nmr, ^1H nmr, and electrochemical behavior to those of authentic $[(C_2H_5)_4N]_2B_{12}H_{12}$.

Under the same reaction conditions, $B_{20}H_{18}^{2-}$ and $B_{20}H_{19}^{3-}$ were found to yield $B_{20}H_{18}^{4-}$ (e^2 isomer) and $B_{20}H_{18}^{4-}$ (a^2 isomer), respectively. The isomers were identified by their ^{11}B nmr spectra, which have been previously reported.[3]

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(23) H. C. Miller, W. R. Hertler, E. L. Muetterties, W. H. Knoth, and N. E. Miller, *Inorg. Chem.*, **4**, 1216 (1965).