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Synthesis and Chemistry of Mercaptoundecahydro-*closo*-dodecaborate(2–)

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In these studies, various synthetic routes toward the mercaptoborane $B_{12}H_{11}SH^{2-}$ were investigated as was the chemistry of this anion. The most favorable synthesis involved nucleophilic attack of *N*-methylbenzothiazole-2-thione on $B_{12}H_{12}^{2-}$ followed by basic hydrolysis. Other routes invariably resulted in considerable by-products, some of which were $B_{12}H_{10}(SH)_2^{2-}$, $B_{12}H_{11}OH^{2-}$, and polymeric boranes. Various oxidative reactions of $B_{12}H_{11}SH^{2-}$ were observed, and new products isolated include the mixed disulfides $B_{12}H_{11}SSR^{2-}$ (R is an organic function) and the disulfide monoxide $B_{12}H_{11}SOSB_{12}H_{11}^{4-}$.

Introduction

As part of a program designed to investigate the feasibility of boron neutron capture therapy for the treatment of malignant brain tumors,[2,3] we have synthesized mercaptoundecahydro-*closo*-dodecaborate(2–) ($B_{12}H_{11}SH^{2-}$) and a number of its derivatives. Some animal studies with these anions have been published.[3,4]

The synthesis of $B_{12}H_{11}SH^{2-}$ by the reaction between the partially hydrated acid form of dodecahydro-*closo*-dodecaborate(2–) ($B_{12}H_{12}^{2-}$) and hydrogen sulfide was originally described by Knoth et al. as part of the extensive research into the chemistry of polyhedral boron anions undertaken by the du Pont chemists;[5] but in carrying out this reaction we initially experienced considerable difficulty in isolating the thiol as a pure crystalline salt. Although we eventually were successful in this respect, the low yield of $B_{12}H_{11}SH^{2-}$, the somewhat protracted work-up procedure involved, and the inconvenience of a high-pressure reaction prompted us to seek alternative synthetic routes. Nevertheless, because some of our initial preparations of $B_{12}H_{11}SH^{2-}$, which were contaminated with small amounts of other boranes, demonstrated more favorable biological properties than the pure thiol, we investigated this reaction in greater detail.

Subsequent to the completion of the work described here, Nakagawa and Nagai[21] reported the synthesis of $B_{12}H_{11}SH^{2-}$ by a route analogous to the one explored by us. We feel, however, that our route offers the advantage of utilizing commercially available reagents.

In addition to the synthesis of the mercaptan, we also report on some of the chemistry of this borane anion.

Results and Discussion

The Reaction of $(H_3O)_2B_{12}H_{12}\cdot nH_2O$ and Hydrogen Sulfide. Under the conditions of partial hydration employed in the reaction of the acidic form of $B_{12}H_{12}^{2-}$ with hydrogen sulfide to form $B_{12}H_{11}SH^{2-}$,[5] the boron polyhedron presumably exists to some extent in the protonated form $B_{12}H_{13}^{-}$.[6] Protonation of the related decahydro-*closo*-decaborate(2–) anion ($B_{10}H_{10}^{2-}$) has been observed by Wegner et al.[7] Although the position of the additional proton is not known, strong evidence for the involvement of a triangular face has been given in the case of the carborane CB_5H_7,[8–11] and $B_{12}H_{12}^{2-}$ may behave similarly, though the formation of a B–H–B bridge (incorporation into an edge) would seem to be possible. These two alternatives may be described, according to Williams,[12] as 7,7′,7″ and 7,7′, respectively. In either case the high coordination sites formed would be expected to render the molecule more reactive thereby permitting subsequent attack by a Lewis base to take place at elevated temperatures, with the evolution of hydrogen, to form the substituted-borane anion. A possible mechanism which takes into account the reductive properties of boranes and is in accord with their known stereochemical behavior is depicted in Scheme I. Attack by the Lewis base effectively adds two electrons to the skeletal framework of the cage converting the closo form of the 12-membered polyhedron to the nido form (I).[12–15] The nido structure may be considered as being derived from an idealized 13-atom polyhedron by removing one vertex; similar structures have been seen in 13-membered metallocarboranes.[16] Such a structure obeys the coordination pattern recognition theory of Williams[12] in having the bridge hydrogens in favorable 6,6′ sites on an open face and in having the Lewis base bound to a boron atom in a low coordination site. Other structures possessing 7,6′ bridge hydrogens or endo hydrogens may be possible, though less likely, according to Williams' theory. Finally, loss of hydrogen removes a pair of electrons and the nido structure reconverts to the closo form whence further protonation and substitution may follow.

Multisubstitution was observed to take place more readily for more anhydrous reaction mixtures. This is understandable, however, if the first substituents on the polyhedron are sufficiently strong bases to add to the competition between the borane and the water of hydration for the limited number of protons present. Such reasoning implies that trisubstitution, or higher, possibly leading to the eventual breakdown of the borane polyhedron will not readily occur. Indeed, this was our impression, though this point was not investigated in detail.

On the basis of the arguments presented so far, the products depicted in Scheme I might be expected to be synthesized. The oxygen- or sulfur-linked polymeric structures (IX) would be formed by hydroxy- and mercapto-substituted boranes acting as Lewis bases. There is also the possibility (not shown) that a boron polyhedron may itself donate a pair of electrons to form directly coupled cage structures. Such coupling has been reported by Bechtold and Kaczmarczyk,[17] but evidence presented here suggests that the mercapto and hydroxy groups are stronger bases than a borane polyhedron under neutral and slightly acidic conditions. If such behavior were exhibited under the strongly acidic conditions employed in this reaction, then the oxygen- and sulfur-linked polymers would predominate over the directly coupled cage polymers. Of the various products formed during the reaction of hydrated $H_2B_{12}H_{12}$ with hydrogen sulfide we only attempted to isolate the mono- and dimercaptans. Evidence is presented, however, which suggests that the other monomeric products shown in Scheme I were formed together with a substantial amount of higher molecular weight multicharged materials which are not inconsistent with the proposed structures.

Mercapto Derivatives. Analysis by anion-exchange thin-layer chromatography (TLC)[18] of the products of the reaction between hydrated $H_2B_{12}H_{12}$ and hydrogen sulfide showed the presence of eight or more components, the number and relative intensities of which varied according to the degree of hydration of the borane acid; the greater the number of products formed, the lower was the degree of hydration. The monomercaptan $B_{12}H_{11}SH^{2-}$ (II) was isolated as the tetrapropylammonium salt from *N*,*N*-dimethylformamide–water solutions and was characterized as the cesium salt by elemental analysis and Raman spectroscopy (ν_{S-H} 2579 cm^{-1})[4] and as the sodium salt by ^{11}B NMR (Table I) spectroscopy. However, an identical work-up procedure of material obtained from a rather more dehydrated reaction mixture gave rise to somewhat smaller

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Scheme I

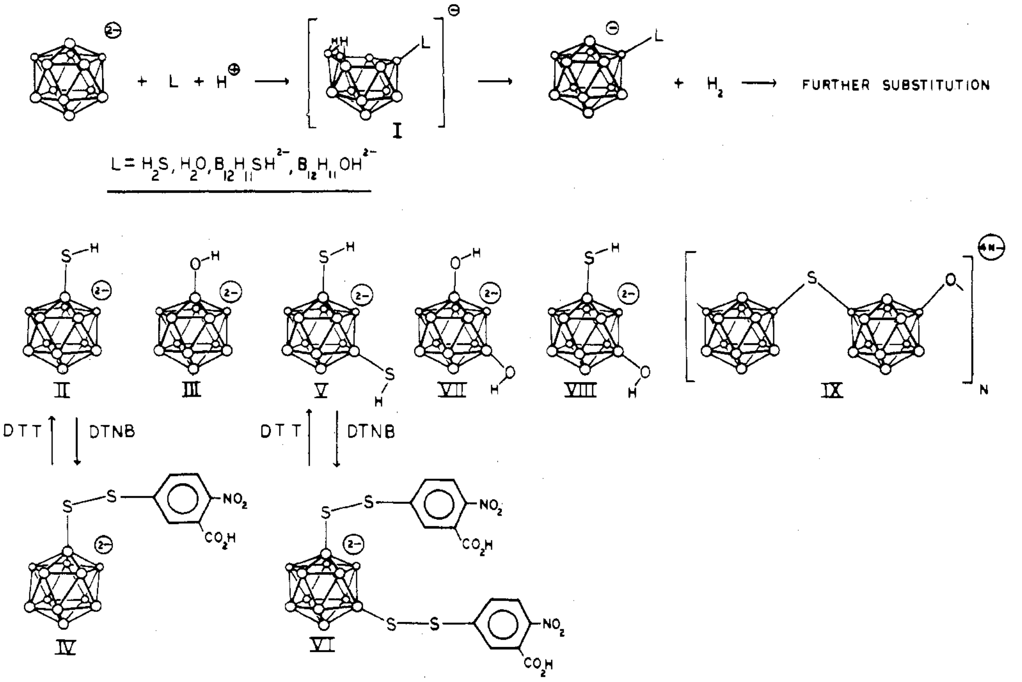


Table I. ^{11}B NMR Data of $B_{12}H_{11}SH^{2-}$ and Its Derivatives

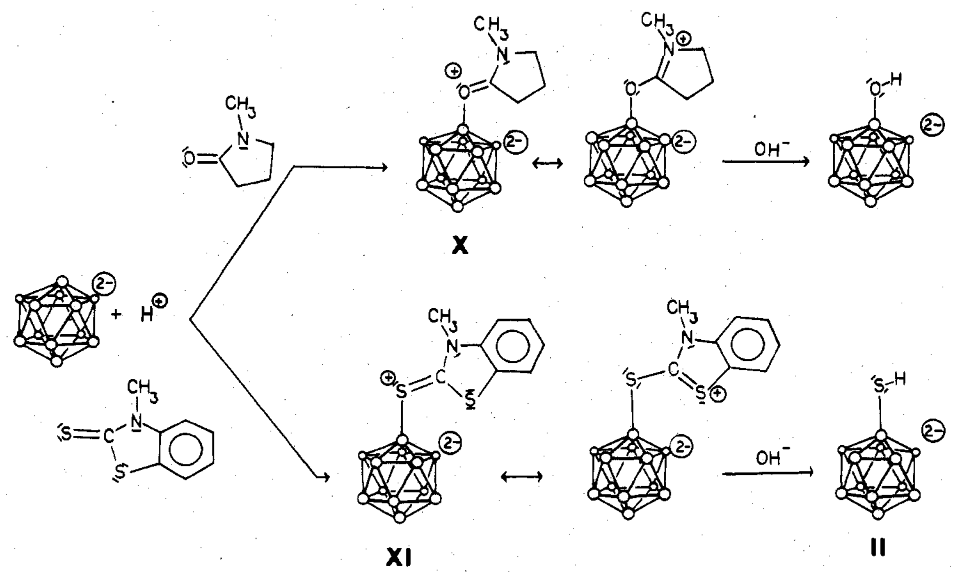
compound	chemical shifts, ppm[a] B–S	chemical shifts, ppm[a] B–H (J_{B-H}, Hz)	rel intens
$B_{12}H_{11}SOSB_{12}H_{11}{}^{2-}$	−5.0, −8.1	−16.9 (131)	1:1:22
$B_{12}H_{11}SSB_{12}H_{11}{}^{4-}$	−6.7	−15.6 (138), −17.2 (131), −20.3 (139)	2:10:10:2
$B_{12}H_{10}[SSC_6H_3(NO_2)CO_2H]^{2-}$	−6.9	−15.8 (120)[b]	2:10
$B_{12}H_{11}SSCH_2CH_2OH^{2-}$	−7.1	−16.6 (125)[b]	1:11
$B_{12}H_{11}SSCH_2CO_2H^{2-}$	−7.2	−16.6 (119)[b]	1:11
$B_{12}H_{11}SSC_6H_3(NO_2)(CO_2H)^{2-}$	−7.2	−16.6 (120)[b]	1:11
$B_{12}H_{11}SC_6H_3(NO_2)_2{}^{2-}$	−9.5	−16.6 (122)[b]	1:11
$B_{12}H_{11}SH^{2-}$	−10.4	−14.8 (125), −17.0 (112), −20.5 (135)	1:5:5:1
$B_{12}H_{11}SSO_2C_6H_4CH_3{}^{2-}$	−11.0	−16.8 (131)[b]	1:11
$B_{12}H_{11}SCTh^{-}$ [c]		−14.3 (129)	1
$B_{12}H_{10}(SH)_2{}^{2-}$ [d]	−10.9	−14.5, −17.5, −20.9	

[a] Chemical shift relative to $Et_2O \cdot BF_3$; see ref 19. [b] Hydrogen-decoupled peak asymmetric, with shoulder on high-field side. This appears to be due to the unresolved boron resonance para to the sulfur-bonded atom. [c] SCTh = *N*-methylbenzothiazole-2-thione. [d] Hydrogen decoupled spectra. All peaks were broad and overlapping.

cesium salt crystals which contained a higher sulfur content. TLC showed only a single spot of R_f equal to that for $B_{12}H_{11}SH^{2-}$. Reaction with excess 5,5′-dithiobis(2-nitrobenzoate) gave rise to two borane products according to TLC (R_f 0.35 and 0.16). These compounds were subsequently separated by ether extraction, and the higher R_f product was identified as the mixed disulfide, $B_{12}H_{11}SSC_6H_3(NO_2)CO_2H^{2-}$ (IV), of the monomercaptan, a discussion of which will be presented in a later section. The lower R_f product was characterized as the mixed disulfide, $B_{12}H_{10}[SSC_6H_3(NO_2)CO_2H]_2{}^{2-}$ (VI), of the dimercaptan $B_{12}H_{10}(SH)_2{}^{2-}$ (V). The extinction coefficient in water of VI at pH 12.5 (λ_{max} 370 nm, ϵ 3.75×10^{-4} M^{-1} cm^{-1}) is approximately twice that of IV. The ^{11}B NMR of VI has a singlet at −6.9 ppm[19] and an asymmetrical doublet at −15.8 ppm (J_{B-H} = 120 Hz) in the area of 2:10. Line narrowing of the hydrogen-decoupled resonance at −15.8 ppm reduced the half-width from 165 to 65 Hz but did not resolve this peak into components. Crystalline salts of this anion could not be produced and we conclude that this derivative is a mixture of isomers. Reduction of the mixed disulfide to the dimercaptan could be achieved using excess dithiothreitol and it gave a pink product, as did the monomercaptan, with alkaline nitroprusside. The dimercaptan exhibited a marked tendency to undergo autoxidation, and the ^{11}B NMR was obtained in the presence of dithiothreitol. This spectrum is consistent with the existence of isomers of $B_{12}H_{10}(SH)_2{}^{2-}$. As with the mixed sulfide derivative, salts of the dimercaptan could not be crystallized and, partly as a consequence of this, we were unable to obtain an analytically pure sample. The presence of the dimercaptan could be detected by TLC as the mixed disulfide, after reaction with 5,5′-dithiobis(2-nitrobenzoate) in all runs of the $H_2B_{12}H_{12}$–hydrogen sulfide reaction.

Hydroxlyated Derivatives. The presence of the mono- and dihydroxyborane derivatives $B_{12}H_{11}OH^{2-}$ (III) and $B_{12}H_{10}(OH)_2{}^{2-}$ (VII) in the reaction products was inferred by comparing the TLC behavior of the mixture with authentic samples of these hydroxylated boranes. In addition, the component identified as $B_{12}H_{11}OH^{2-}$ by TLC was obtained as a cocrystal with $B_{12}H_{11}SH^{2-}$ as the cesium salt. An infrared spectrum of this material confirmed the presence of $B_{12}H_{11}OH^{2-}$. A third component in the product mixture with a chromatographic mobility between that of $B_{12}H_{11}OH^{2-}$ and $B_{12}H_{11}SH^{2-}$, and which stained pink with alkaline nitroprusside, is posulated to be the disubstituted borane $B_{12}H_{10}(OH)SH^{2-}$ (VIII). This structure is consistent with its chromatographic behavior[18] and is in keeping with the other mono- and disubstituted derivatives produced in this reaction.

Scheme II



Polymeric Products. Invariably present in the product mixture were a number of components which, despite their good aqueous solubility with cations such as H^+ or Na^+, exhibited very low to zero mobilities during anion-exchange chromatography. This behavior is presumed to be indicative of the presence of multiply charged sites on these anions as would be expected in polymeric materials such as IX in Scheme I. The relatively low R_f values of $B_{24}H_{23}^{3-}$, $B_{24}H_{22}S_2^{4-}$, or $B_{24}H_{22}SSO^{4-}$, as compared to $B_{12}H_{12}^{2-}$ or other monomeric dodecaborate anions, suggest a trend in which their ionic mobilities, under conditions of anion-exchange chromatography, are inversely related to the number and charge of the coupled polyhedra. In addition, these same components were very slow to pass through a dialysis membrane, dialysis still being incomplete after more than 1 week in some cases, whereas the monomeric ions under the same conditions would dialyze within a few days. The limitations of our analytical systems prevented us from isolating any of these components and we were unable to obtain any in crystalline form.

Alternative Routes to the Synthesis of $B_{12}H_{11}SH^{2-}$. Reaction of $B_{12}H_{12}^{2-}$ with Thiones. An interesting synthesis of $B_{12}H_{11}OH^{2-}$ reported by Muetterties, Knoth, and co-workers[5] involves the basic hydrolysis of $B_{12}H_{11}O\underline{C(CH_2)_3N}CH_3^-$, a complex which has the carbonyl oxygen of *N*-methylpyrrolidinone bonded to a boron atom on $B_{12}H_{12}^{2-}$. The attack by hydroxide ion on the complex probably takes place at the carbonyl function (C2) although direct attack on the boron polyhedron is also possible. The facile hydrolysis of this complex to form the monohydroxyl derivative suggested that an analogous route to the mercaptan of $B_{12}H_{12}^{2-}$ using an analogous thione might be feasible, and indeed this was accomplished. The synthesis of the mercaptan by this route indicates that in the aforementioned amide complex hydroxide attack does take place at the carbonyl function.

Initially, a number of thione-containing compounds, including ethylene trithiocarbonate, diphenylthiourea, tetramethylthiourea, and *N*-methylbenzothiazole-2-thione, were heated with $Na_2B_{12}H_{12}\cdot 2H_2O$ in the presence of concentrated aqueous hydrochloric acid. Of these materials, only the latter two gave relatively clean reactions producing intermediates which could be hydrolyzed with aqueous base to $B_{12}H_{11}SH^{2-}$ as identified by TLC. In the case of tetramethylthiourea an additional product which was resistant to hydrolysis was also formed. This presumably arose from the reaction of the borane with the thiourea nitrogen. Analogous behavior was reported in the reaction of $B_{10}H_{10}^{2-}$ with *N*,*N*-dimethylformamide.[5]

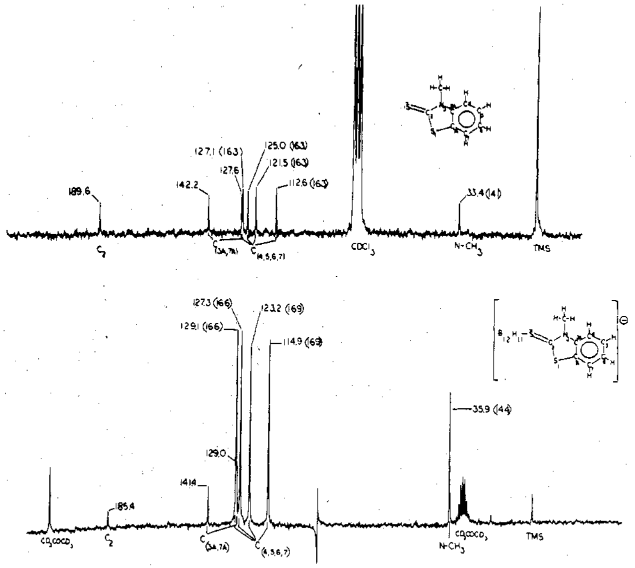


Figure 1. Hydrogen gated decoupled ^{13}C spectra of *N*-methylbenzothiazole-2-thione (SCTh) and its complex, $B_{12}H_{11}SCTh^-$. Chemical shifts relative to Me_4Si are given above the peaks and coupling constants in Hertz are in parentheses. The solvent used with SCTh was $CDCl_3$ having 0.1 M $Cr(acac)_3$. With the complex, CD_3COCD_3–D_2O (3:1) was the solvent mixture used. (The derivative-shaped peak in the center of the complex ($B_{12}H_{11}SCTh^-$) spectrum is an artifact resulting from the instrumentation.)

The product resulting from the reaction of $B_{12}H_{12}^{2-}$ with *N*-methylbenzothiazole-2-thione was isolated and was characterized as being the required adduct, $B_{12}H_{11}\underline{SCSC_6H_4N}CH_3^-$ (XI), similar to the oxygen-bonded *N*-methylpyrrolidinone adduct $B_{12}H_{11}O\underline{C(CH_2)_3N}CH_3^-$ (X).[5] In each of these molecules several different valence structures may be considered possible. The hydrogen-decoupled ^{13}C NMR spectra of *N*-methylbenzothiazole-2-thione and its $B_{12}H_{12}^{2-}$ complex are shown in Figure 1. A solvent of deuterated chloroform containing 0.1 M $Cr(acac)_3$ was used with the thione, while deuterated acetone–water (3:1) was employed for the borane. The similarity of these two spectra indicate that the electronic nature of the thione is basically unchanged in the adduct. Because $Cr(acac)_3$ was added to the thione in deuterated chloroform to decrease the T_1's of C2, C3A, and C7A, the significance of the direction of the

Table II. ^{1}H Chemical Shifts in ppm Relative to Me_4Si^a

	compound	chemical shift	rel area
1	SCTh[b]	6.9 (c), 3.58 (s)	4:3
2	$NaB_{12}H_{11}SCTh^c$	7.3 (c), 3.76 (s)	4:3
3	NMP[c]	3.46 (7.0, t), 2.8 (s), 2.3–1.9 (c)	2:3:4
4	$NaB_{12}H_{11}NMP^c$	3.78 (7.5, t), 3.24 (7.5, t), 3.03 (s), 2.4–1.9 (c)	2:2:3:2
5	$[(CH_3)_4N]_4B_{12}H_{11}SC_6H_3(NO_2)_2{}^c$	9.12 (9.1, d), 8.50 (s),[d] 8.06 (9.3, d),[d] 3.34 (s)	1:1:1:24
6	$[(CH_3)_4N]_2B_{12}H_{11}SSC_6H_3(NO_2)CO_2H^c$	7.9–8.0 (c),[e] 3.34 (s)	3:24
7	$[(CH_3)_4N]_2B_{12}H_{11}(SSC_6H_3(NO_2)CO_2H)_2{}^c$	7.9–8.0 (c),[e] 3.34 (s)	6:24
8	$H_2B_{12}H_{11}SSCH_2CH_2OH^f$	3.67 (12, t), 2.68 (12, t)	1:1
9	$H_2B_{12}H_{11}SSCH_2CO_2H^f$	2.46 (s)	
10	$H_2B_{12}H_{11}SSO_2C_6H_4CH_3{}^f$	7.92 (8.4, t), 7.46 (8.4, d), 2.41 (s)	2:2:3

[a] Coupling constants (J_{H-H}), given in hertz, are enclosed in parentheses as are the types of splitting patterns using the following notation: s, singlet; d, doublet; t, triplet, c, complex pattern. [b] SCTh = *N*-methylbenzothiazole-2-thione. Solvent used was $CDCl_3$. [c] Solvent used was CD_3COCD_3–D_2O (3:1). [d] Fine structure: $J_{H-C-C-C-H}$ = 2.6 Hz. [e] When the solvent is 0.01 N NaOH in D_2O, this part of spectrum simplifies to two singlets of relative areas 2:1 at 7.85 and 7.51 ppm. [f] Salts were passed down an H^+ exchange resin before spectra were taken.

chemical shifts from the adduct to the thione is not clear. In the ^{13}C NMR spectrum of *N*-methylbenzothiazole-2-thione, the resonances of the unsubstituted carbon atoms are assigned, by comparison with 2-methylbenzothiazole,[20] as follows: C2, 189.6; C3A, 142.2; C7A, 127.6 ppm. Carbon atoms C4, C5, C6, and C7 are associated with the resonances of 127.1, 125.0, 121.5, and 112.6 ppm. The proton NMR data are listed in Table II. The four hydrogens on the aryl ring of the complex form a multiplet centered at 7.3 ppm while the *N*-methyl hydrogen resonances are observed at 3.76 ppm, these values being shifted downfield 0.4 and 0.18 ppm, respectively, from those found in the thione. To what extent these downfield shifts observed in the complex are due to a reduction in electron density and to what extent they are solvent effects is not clear. The ^{11}B NMR spectrum of the complex showed only a doublet (J_{B-H} = 129 Hz) which hydrogen decoupled to an apparently symmetrical peak indicating coincidental resonances at this resolution. Using line-narrowing techniques, the half-width of the decoupled resonance was reduced to 78 Hz, but this still failed to show any of the expected fine structure or even any significant asymmetry.

Upon reaction with aqueous sodium hydroxide the complex cleaved to give the monomercaptan which could be isolated in 40% overall yield making this a useful route to its synthesis.

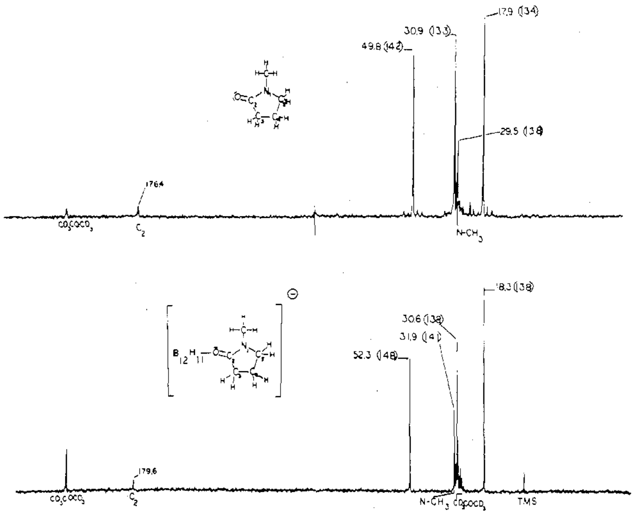
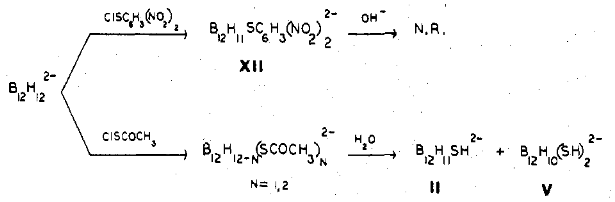


Figure 2. Hydrogen-decoupled ^{13}C spectra of NMP and $B_{12}H_{11}NMP^-$ in deuterated acetone–water (3:1). Chemical shifts relative to Me_4Si are given above the peaks and coupling constants in hertz are in parentheses. C3, C4, and C5 in NMP are assigned to the respective resonances 30.9, 17.9, and 49.8 ppm.[19a]

It is interesting to compare the somewhat analogous borane complexes $B_{12}H_{11}O\underline{C(CH_2)_3N}CH_3^-$ and $B_{12}H_{11}SC\underline{S\text{-}C_6H_4N}CH_3^-$. As with the thione complex, confirmation that the *N*-methylpyrrolidinone structure remains basically intact in the former borane is obtained from the previously unreported ^{13}C (Figure 2) and ^{1}H (Table II) NMR spectra taken in deuterated acetone and water (3:1). The ^{13}C resonances obtained are consistent with the assignments given for *N*-ethylpyrrolidinone.[20] They are as follows: C2, 176.4; C3, 30.9; C4, 17.9; C5, 49.8; CN, 29.5 ppm. As in the case of the sulfur compound a slight general downfield shift is observed for the *N*-methylpyrrolidinone complex as compared to *N*-methylpyrrolidinone (see Figure 2), which correlates with the increased positive charge on the ligand. The relative sizes of these shifts is consistent with the positive charge being spread principally over O, C2, and N. (As the ^{13}C spectra of both *N*-methylpyrrolidinone and the borane derivative X were taken in identical solvent mixtures, all differences in chemical shifts should reflect internal electronic differences.) There is also a small increase in the coupling constants of C3 and C5 in the complex indicating a decrease in the p character of the C–H bonds. In the hydrogen NMR spectra of the two molecules, the change in the chemical shifts is more dramatic due to the closeness in the absolute shifts, all the hydrogens being shifted downfield in the complex between 0.2 and 0.6 ppm except for H3 and H3′ which are shifted by over 1 ppm. The large increases in the chemical shifts of H3 and H3′ may not be due entirely to a decrease in the electron density on these atoms; there may be also a paramagnetic component of these shifts from the borane cage. If some CO double-bond character is maintained in the complex, then two isomers might be possible, one with the methyl group nearest the borane polyhedron and the other with the C3 hydrogens nearest. However, molecular models indicate that the former possibility is not favored due to steric interactions between the methyl group with the borane cage. Even if the double bond is shifted to CN, and some amount of such bonding in the complex $B_{10}H_9OCHN(CH_3)_2^-$ has been indicated by proton NMR studies which show that the methyl groups are nonequivalent,[5] free rotation around the CO bond is still prevented by *N*-methyl–borane steric interference.

Reaction of $B_{12}H_{12}^{2-}$ with Sulfenyl Chlorides. The reactions of *N*-methylpyrrolidinone and *N*-methylbenzothiazole-2-thione with dodecahydro-*closo*-dodecaborate(2−) under acidic conditions are typical of those reactions of this borane which may be classified as acid-catalyzed nucleophilic substitutions. The many examples of electrophilic substitution on borane polyhedral anions, however, suggested that the mercaptan function may also be introduced via an electrophile. One class of reagents which appeared to be potentially useful in this regard was that of the sulfenyl chlorides. Several of these have been used to prepare mercapto derivatives of organic molecules possessing π bonds. For instance, Kharasch and Swidler[22] showed that 2,4-dinitrobenzenesulfenyl chloride in the presence

Scheme III



of a Friedel–Crafts catalyst could be added to aromatic systems and the product cleaved by base to yield the aromatic thiol. The analogous 2,4-dinitrobenzene sulfide derivative of $B_{12}H_{12}^{2-}$, $B_{12}H_{11}SC_6H_3(NO_2)_2^{2-}$ (XII), was readily prepared by mixing the sulfenyl chloride and the borane. This yellow monosubstituted product has an absorption maxima in the visible region at 383 nm with an extinction coefficient of 9.44 × 10^{-3} M^{-1} cm^{-1}. ^{11}B and ^1H NMR (Tables I and II) spectra are consistent with single substitution involving a B–S bond. In contrast to the organic analogue, the sodium salt of this sulfide does not hydrolyze in base or acid, possibly because of an increased electron density on the ring carbon to sulfur from the dinegatively charged borane moiety. Acetylsulfenyl chloride, $ClSCOCH_3$,[23-25] also reacted rapidly with $B_{12}H_{12}^{2-}$, but in the relatively nonaqueous solvent system employed in order to solvate the sodium salt of the borane, the mono- and dimercaptans $B_{12}H_{11}SH^{2-}$ and $B_{12}H_{10}(SH)_2^{2-}$ were detected without any evidence of the anticipated thioester intermediates, $B_{12}H_{11}SCOCH_3^{2-}$ and $B_{12}H_{10}(SCOCH_3)_2^{2-}$. Similar results were obtained using other nonaqueous solvents when water or alcohols were present during work up indicating that this type of thioester borane is very susceptible to hydrolysis. The principal products of this reaction, the mono- and dimercaptans, were isolated as their derivatives in 36 and 16% yields, respectively. Reduction to the mercaptans could be carried out using mercaptoethanol, but initial attempts to obtain these in crystalline form failed, and this was not pursued as the yield of the monomercaptan was already below that obtainable by the *N*-methylbenzothiazole-2-thione routes.

Chemical Reactions of $B_{12}H_{11}SH^{2-}$. The general reactions exhibited by the mercaptan described in Scheme IV are typical of this functional group. Reaction with excess 2-hydroxylethyl disulfide $(SCH_2CH_2OH)_2$, dithioglycolic acid $(SCH_2CO_2H)_2$, or, as discussed earlier, dithiobis(2-nitrobenzoic acid) $[SC_6H_3(NO_2)CO_2H]_2$ produced in high yield the respective mixed disulfides, $B_{12}H_{11}SSR^{2-}$ (R is an organic function) (XV, XIV, IV). The ^{11}B spectra of these (Table I) are typical of monosubstituted $B_{12}H_{12}^{2-}$, and ^1H NMR supports the integrity of the organic substituents in the mixed disulfides. In all three derivatives the chemical shift of the substituted boron is −7.2 ppm, within experimental error, making this a characteristic chemical shift of mixed organic disulfides of $B_{12}H_{11}SH^{2-}$. Oxidation of the monomercaptan with 1 equiv of iodosobenzoate or molecular oxygen yields the disulfide $B_{12}H_{11}SSB_{12}H_{11}^{4-}$ (XVI) reported earlier. The chemical shifts of the two similar boron atoms attached to the disulfide group (i.e., BSSB) are −6.2 ppm. Contrasting this chemical shift with the corresponding one in the mixed organic disulfides makes it clear that the γ atom in a disulfide substituent of $B_{12}H_{12}^{2-}$ (i.e., $B_{12}H_{11}S_\alpha S_\beta X_\gamma \cdots)^{2-}$ significantly influences the resonance of the substituted boron atom.

The addition of 1 mol of hydrogen peroxide to aqueous solutions of either the disulfide $B_{12}H_{11}SSB_{12}H_{11}^{4-}$ or the monomercaptan $B_{12}H_{11}SH^{2-}$ gives the disulfide monoxide $B_{12}H_{11}SOSB_{12}H_{11}^{4-}$ (XVIII) which has a TLC R_f value identical with that of the disulfide. The two substituted boron atoms which are chemically different in this structure produce resonances in the ^{11}B NMR spectrum at −5.0 and −8.1 ppm (Figure 3). Assuming Lorentzian shapes for these resonances, the areas of the substituted boron atoms relative to the unsubstituted ones at −16.9 ppm are found to be 2:22 as expected.

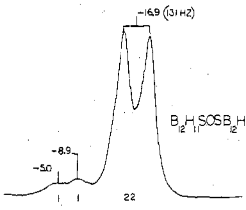


Figure 3. The ^{11}B spectrum of $B_{12}H_{11}SOSB_{12}H_{11}^{4-}$ taken at 28.9 MHz. Chemical shifts in ppm are given above resonances and the coupling constant, in parentheses, is given in hertz. Relative areas, given below peaks, were calculated assuming Lorentzian shapes for the resonances. Broad-band irradiation of the hydrogens does not collapse the peaks at −5.0 and −8.9 ppm which are assigned to the substituted boron atoms. Chemical shifts are relative to an external sample of $Et_2O{\cdot}BF_3$.

An interesting property of the bis(borane) disulfide (XVI) is its rapid conversion at room temperature in acidified organic solvents containing dissolved oxygen to an intensely blue (λ_{max} 630 nm) stable free radical.[4] In the case of either the mixed disulfides or the disulfide monoxide (XVIII), vigorous heating under these conditions is needed to produce a much less intense blue coloration. It appears, therefore, that the ready production of an intensely blue color under the conditions described is indicative of the presence of the BSSB group. If less than 1 mol of hydrogen peroxide is added to $B_{12}H_{11}SH^{2-}$, no blue color is seen when the product is exposed to conditions which would produce the free radical from the disulfide. This indicates the absence of the disulfide and implies that oxidation of the disulfide to the disulfide monoxide by hydrogen peroxide takes place much more rapidly than the oxidation of the mercaptan to the disulfide. Excess hydrogen peroxide, at neutral pH, was not observed to oxidize the disulfide monoxide further, a somewhat surprising result in light of the reactivity of analogous organic disulfide monoxides.

Under a nitrogen atmosphere and aqueous conditions both *p*-toluenesulfinyl chloride, $CH_3C_6H_4SOCl$, and *p*-toluenesulfonyl chloride, $CH_3C_6H_4SO_2Cl$, reacted with $B_{12}H_{11}SH^{2-}$ to give the same product, $B_{12}H_{11}SSO_2C_6H_4CH_3^{2-}$ (XIX). No evidence of the mixed disulfide monoxide was observed. Both the ^{11}B and ^1H NMR spectrum are consistent with the assignment of this structure.

All the derivatives discussed can be reduced by dithiothreitol under basic conditions to yield the parent mercaptan $B_{12}H_{11}SH^{2-}$, as detected by TLC. The bis(borane) derivatives, however, are much less labile in this respect and after 1 week are incompletely reduced under conditions whereby the organic borane mixed disulfides and disulfide dioxide are completely reduced in 1 day. Of the bis(boranes) the disulfide monoxide is reduced most slowly.

Experimental Section

Spectra and Analyses. ^{11}B, ^{13}C, and ^1H NMR spectra were obtained at 28.9, 22.6, and 90.0 MHz, respectively, using a Bruker WH-90-DX spectrometer with Fourier transform and a deuterium lock. ^{11}B resonances were referenced relative to external $BF_3{\cdot}Et_2O$ while ^{13}C and ^1H resonances were referenced relative to Me_4Si.

Infrared spectra were recorded on Perkin-Elmer 137 and 237 spectrometers. Samples were run as KBr pellets. The following symbolic descriptions are used: s, strong; m, medium; w, weak; sh, shoulder; br, broad. Visible and ultraviolet spectra were taken with a Cary Model 14 spectrophotometer.

Chemical analyses were performed by Schwarzkopf Microanalytical Laboratory of Woodside, N.Y.

Chromatography. Thin-layer chromatography (TLC) was carried out as described elsewhere[5] using Baker-Flex DEAE cellulose thin-layer chromatography sheets. Unless stated otherwise a solvent system composed of 2:1 v/v 3 M aqueous ammonium nitrate–acetonitrile was used. Visualization was achieved using both palladium chloride and sodium nitroprusside.[5]

Materials. Chemicals and solvents were of reagent quality, being further purified only when indicated. Sodium dodecahydro-*closo*-dodecaborate dihydrate was purchased from du Pont. It gave a single spot by TLC and was used without further purification.

Synthesis of Dicesium Mercaptoundecahydro-*closo*-dodecaborate(2–) Dihydrate, $Cs_2B_{12}H_{11}SH\cdot 2H_2O$ (II). A. From $B_{12}H_{12}^{2-}$ and Hydrogen Sulfide. $Na_2B_{12}H_{12}\cdot 2H_2O$ (300 g, 1.36 mol) was converted to its acid form by passage down a 4-equiv H^+ column of Bio-Rad AG 50W-X8, 20–50 mesh. After rotary evaporation at room temperature, the solidified acid was stored in vacuo over phosphorus pentoxide at 0 °C until it could be powdered using a pestle and mortar. The degree of hydration was monitored by titration and the drying was continued until $(H_3O)_2B_{12}H_{12}\cdot 4.6H_2O$ was obtained (1.13 mol). The white powder was then placed in a Teflon-lined cylindrical pressure reaction vessel (volume 1800 mL); the air was evacuated and the vessel was cooled in dry ice to permit the addition of H_2S (370 g, 11 mol). The temperature was increased to 100 °C where it was maintained for 4 h during which time the pressure rose to 1300 psi. After being cooled, the contents were taken into aqueous solution. Nitrogen was bubbled through to remove excess hydrogen sulfide and the solution was filtered. TLC showed the presence of a major spot corresponding to $B_{12}H_{11}SH^{2-}$ and several minor spots. The reaction solution was made up to 10 L with water and stirred under an atmosphere of nitrogen while 3.2 L of 10% aqueous tetrapropylammonium hydroxide was slowly added. The resulting precipitate was filtered and dried; the total weight was 789.6 g. This tetrapropylammonium salt was taken up in a minimum of *N,N*-dimethylformamide (DMF) (790 mL) and 10% by volume of water was added. Again a minimum of DMF was added to give complete solution and then water, amounting to one-third the total volume of DMF was added. The resulting precipitate was filtered and dried (210 g). This precipitate was again subjected to a similar DMF–water treatment giving a material which was essentially pure $(Pr_4N)_2B_{12}H_{11}SH$ by TLC. The filtrates were reworked in a similar fashion to obtain purified $(Pr_4N)_2B_{12}H_{11}SH$; the combined salts weighed 178 g. Conversion to the acid form was achieved by stirring with a 10-fold excess of H^+ Bio-Rad 50 W resin followed by passage down a 100-mL resin column of the same resin. After partial rotary evaporation, the acid solution was titrated to pH 7 using cesium hydroxide and then was crystallized from water taking care not to allow the temperature to exceed 40 °C. Three crops of crystals of $Cs_2B_{12}H_{11}SH\cdot H_2O$ were obtained totaling 85.56 g (0.187 mol) for a yield of 14%.

B. From $B_{12}H_{12}^{2-}$ and *N*-Methylbenzothiazole-2-thione. *N*-Methylbenzothiazole-2-thione (14.3 g, 80 mmol), recrystallized from toluene prior to use, was melted at 95 °C and $Na_2B_{12}H_{12}\cdot 2H_2O$ (2.24 g, 10 mmol) added. With good stirring, concentrated hydrochloric acid (5 mL, 60 mmol HCl) was added dropwise over a 10-min period and the temperature elevated to 105 °C. A vigorous gas evolution occurred, but after about 6 h this had greatly diminished in intensity. Water (20 mL) was added to the hot reaction mixture and stirred for a few minutes. After being cooled, the aqueous layer was discarded. The organic mixture was remelted and a further 30 mL of water was added and stirred again for several minutes. This mixture was allowed to stand overnight at 4 °C. The thick aqueous suspension was decanted and washed twice with 25 mL of toluene to remove unreacted thione. Two drops of concentrated hydrochloric acid was added to the aqueous solution and this was washed twice with 30 mL each of ethyl acetate. Another drop of acid was added and the solution was washed once more with 30 mL of ethyl acetate. The ethyl acetate solutions were combined and were washed three times with 15 mL each of 2 M aqueous potassium acetate. The ethyl acetate solution was evaporated to dryness, 35 mL of 1 M sodium hydroxide was added, and the solution was heated to 55 °C for 20 min during which time a precipitate formed. After organic precipitate was allowed to settle, the aqueous solution was passed down a 50-mequiv H^+ resin column (Bio-Rad 50W-X8) and the acid solution was washed twice with 60 mL each of ethyl acetate. The aqueous solution was rotary evaporated to about half its volume and titrated with cesium hydroxide to neutrality. After further evaporation to saturation, the solution was filtered and the cesium salt crystallized by standing at 4 °C. In most preparations the crystals were a very pale yellow. This color could readily be removed by swirling the aqueous solution with a small quantity of activated charcoal prior to filtering and crystallizing; yield 1.83 g, 41%. A sample was powdered and dried over P_2O_5 in vacuo. Anal. Calcd for $Cs_2B_{12}H_{11}SH\cdot {}^1/_4H_2O$: Cs, 59.84; B, 29.21; H, 2.84; S, 7.22; H_2O, 1.01. Found: Cs, 57.78; B, 30.01; H, 2.91; S, 7.00; H_2O, 0.89.

C. From $B_{12}H_{12}^{2-}$ and Acetylsulfenyl Chloride. To $Na_2B_{12}H_{12}\cdot 2H_2O$ (0.808 g, 3.58 mmol) in acetonitrile (40 mL + 1 mL water) was slowly added 1 mL of acetylsulfenyl chloride ($ClSCOCH_3$) in 20-μL increments. After 30 min the solvents were removed by rotary evaporation and the residue was taken up in 20 mL of 1 N NaOH. This solution was then acidified to pH 1 with concentrated hydrochloric acid and, after cooling in ice and filtering, 1.5 g of 5,5′-dithiobis(2-nitrobenzoic acid), $(SC_6H_3(NO_2)CO_2H)_2$, was added. The pH was adjusted to 11 with 6 N sodium hydroxide and the dark red solution was allowed to react for 24 h after which time the pH was again reduced to 1 and the unreacted 5,5′-dithiobis(2-nitrobenzoic acid) was removed by filtration. Removal of some by-product mercaptonitrobenzoic acid was effected by continuous ether extraction for 12 h maintaining the pH at 2.6. After the pH was adjusted to 1.6, continuous ether extraction selectively removed $H_2B_{12}H_{10}(SSC_6H_3NO_2CO_2H)_2$ as evidenced by TLC, R_f 0.16.

The aqueous layer was adjusted to pH 1.75 and extracted with one volume of ethyl acetate. The pH was then adjusted to 0.0 and the aqueous layer was extracted three times with ethyl acetate. These latter three washings were combined; one volume of petroleum ether was added and the solution extracted with water. The aqueous solution was reduced in volume to 5 mL and excess tetramethylammonium chloride was added. After being filtered and dried in vacuo, the yellow precipitate weighed 0.65 g; R_f 0.35. This borane salt was crystallized from water by adding just enough base to effect solution and then slowly cooling. Anal. Calcd for $[(CH_3)_4N]_2B_{12}H_{11}SSC_6H_3NO_2CO_2H\cdot {}^2/_3H_2O$: C, 33.91; H, 7.59; N, 7.91; B, 24.42; S, 12.05; H_2O, 2.26. Found: C, 34.08; H, 7.75; N, 8.20; B, 24.03; S, 12.73; H_2O, 2.45.

To a mixture of 1 mL of 1 N NaOH and 1 mL of ethanol was added 0.27 g (0.504 mmol) of $[(CH_3)_4N]_2B_{12}H_{11}SSC_6H_3NO_2CO_2H\cdot {}^2/_3H_2O$. The solution was passed down a column of Bio-Rad Na^+ AG50W-X8 resin, 0.27 mL of mercaptoethanol was added, and the mixture was allowed to react for 2 h under nitrogen. After this time the solution was acidified and extracted with ethyl acetate. Cesium chloride, 0.18 g (1.06 mmol), was added in aqueous solution and the mixture was cooled. The precipitate, which was identified as $Cs_2B_{12}H_{11}SH$ by TLC and by its reactions, was filtered off and dried, yielding 0.20 g of product.

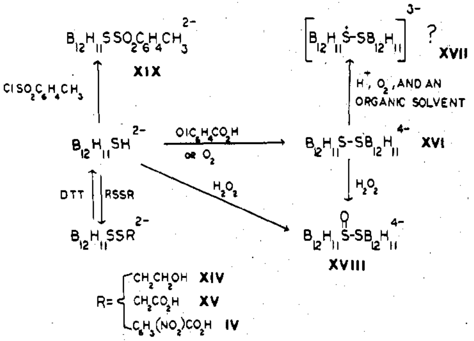
Bis(tetramethylammonium) Decahydrobis[3-nitro-4-(thiosulfeno)benzoato-*S*]-*closo*-dodecaborate(2–) (VI). The ethereal solution of $B_{12}H_{10}(SSC_6H_3NO_2CO_2H)_2^{2-}$ obtained in the previous reaction was washed once with one volume of 1 N hydrochloric acid. One volume of petroleum ether was added and the borane was extracted into water. This aqueous solution was reduced to 10 mL and excess tetramethylammonium chloride was added causing the precipitation of a yellow salt which, after filtering and drying in vacuo, weighed 0.50 g. Anal. Calcd for $[(CH_3)_4N]_2B_{12}H_{10}(SSC_6H_3NO_2CO_2H)_2$: C, 35.00; H, 5.56; N, 7.42; S, 16.96; B, 17.16. Found: C, 34.76; H, 6.09; N, 7.37; S, 17.19; B, 17.03.

***N*-Methylbenzothiazole-2-thiolatoundecahydro-*closo*-dodecaborate(2–) Acid Trihydrate (XI).** The reaction between *N*-methylthiazole-2-thione and $B_{12}H_{12}^{2-}$ was carried out as described earlier. After completion, the reaction mixture was washed once with water and then subjected to continuous water extraction while keeping the organic phase melted. After several hours the extract, which initially was pale yellow, became colorless though TLC still showed the presence of borane. On being cooled, this colorless extract gave rise to a white crystalline precipitate (XI) which hydrolyzed readily under basic conditions to give a product identified as $B_{12}H_{11}SH^{2-}$ by a single spot on TLC.

Infrared bands: 3704 (s), 3571 (s), 3279 (m), 2564 (s), 1618 (m), 1453 (m), 1422 (m), 1359 (s), 1304 (m), 1250 (m), 1116 (m), 1075 (m), 1031 (s), 939 (m, br) 830 (m), 797 (s), 741 (s), 708 (m), cm^{-1}. Anal. Calcd for $HB_{12}H_{11}S\underbrace{CSC_6H_4N}CH_3\cdot 3H_2O$: C, 25.48; H, 6.68; N, 3.71; S, 17.00; B, 34.40; H_2O, 14.33. Found: C, 22.45; H, 7.15; N, 3.79; S, 16.80; B, 34.55; H_2O, 15.12.

Triethylammonium (2,4-Dinitrobenzenethiolato)undecahydro-*closo*-dodecaborate(2–) (XII). To 2.0 g (9.93 mmol) of $Na_2B_{12}H_{12}\cdot 2H_2O$ in 75 mL of acetonitrile at 0 °C was added 2.05 g of 2,4-dinitrophenylsulfenyl chloride in 75 mL of acetonitrile. After 1 h, 4 mL of water was added and the mixture was rotary evaporated. To the residue was added 50 mL of water and, after stirring and filtering, excess aqueous triethylamine hydrochloride was added. After being cooled to 0 °C, the precipitate was filtered and dried to yield

Scheme IV



2.07 g (71%) of a yellow salt (XII). The sample was twice crystallized from ethanol plus several drops of water giving yellow crystals, mp 175–177 °C. Infrared bands: 3174 (w), 2506 (s), 1592 (m), 1515 (m), 1464 (m), 1374 (m), 1332 (s), 1086 (m), 1063 (w), 832 (m), 742 (w), 732 (w), 723 (sh, w), cm^{-1}. Anal. Calcd for $[(C_2H_5)_3NH]_2B_{12}H_{11}SC_6H_3(NO_2)_2$: C, 39.71; H, 8.52; N, 10.29; B, 23.83; S, 5.89. Found: C, 40.38, H, 8.81; N, 10.44; B, 23.71; S, 6.00.

Bis(tetramethylammonium) Undecahydro[3-nitro-4-(thiosulfeno)benzo-*S*]-*closo*-dodecaborate(2–)–$^2/_3$-Water (IV). This compound was isolated during the workup of the reaction between $B_{12}H_{12}^{2-}$ and acetylsulfenyl chloride. Its direct preparation from pure $B_{12}H_{11}SH^{2-}$ is described here.

To 5.46 mmol of $Na_2B_{12}H_{11}SH$ in 50 mL of water was added 7.0 g (17.7 mmol) of 5,5′-dithiobis(2-nitrobenzoic acid) with stirring, and the pH was adjusted to 7 with 1 N sodium hydroxide. After 4 days the solution was acidified to pH 1; it was cooled, and the unreacted reagent which precipitated was filtered off. The addition of excess tetramethylammonium chloride caused the precipitation of a yellow product (λ_{max} 365 nm, ϵ 9.36 × 10^{-3}) which after filtering and drying over P_2O_5 weighed 4.37 g (82%). Crystallization from water was achieved as described earlier. Infrared bands: 3436 (br, w), 3049 (w), 2506 (s), 1727 (w), 1555 (w), 1511 (w), 1473 (m), 1325 (m), 1042 (m), 966 (m), 869 (w), 839 (w), 820 (w), 717 (w), cm^{-1}.

Dicesium Undecahydro(2-hydroxyethanethiosulfenato-*S*)-*closo*-dodecaborate(2–) (XIV). $Cs_2B_{12}H_{11}SH{\cdot}H_2O$, 2.4 g (5.46 mmol), was converted to its sodium form by ion exchange, and the aqueous solution was adjusted to a volume of 15 mL, 5 g (32.5 mmol) of 2-hydroxyethyl disulfide was added, and the pH was brought to 7.0 with 6 N sodium hydroxide. After being stirred at room temperature for 4 days, an aqueous solution at 3.4 g of cesium chloride was added and the solution was cooled. The resulting precipitate was filtered and dried over P_2O_5 to yield 2.34 g (83%) of product (XIV) which was crystallized from water at 50 °C by slow cooling. Infrared bands: 3650 (w), 2500 (s), 1370 (w), 1160 (w), 1048 (m), 969 (w), 927 (w), 840 (m), 717 (m) cm^{-1}. Anal. Calcd for $Cs_2B_{12}H_{11}S_2C_2H_4OH$: Cs, 51.53; B, 25.15; C, 4.66; H, 3.13; S, 12.43. Found: Cs, 51.43; B, 24.61; C, 5.20; H, 3.10; S, 12.30.

Dicesium Undecahydro[(thiosulfeno)acetato-*S*]-*closo*-dodecaborate(2–) (XV). The synthesis of XV was similar to that of XIV except that dithioglycolic acid was used instead of 2-hydroxyethyl disulfide and that the pH was adjusted to 2 prior to the addition of cesium chloride; yield 86%. Infrared bands: 4444 (sh, w), 3448 (m), 2475 (s), 1695 (m), 1385 (m), 1267 (m), 1188 (m), 1050 (m), 966 (w), 736 (br, s) cm^{-1}. Anal. Calcd for $Cs_2B_{12}H_{11}S_2CH_2CO_2H$: Cs, 50.17; B, 24.49; C, 4.53; H, 2.66; S, 12.10. Found: Cs, 44.13; B, 24.39; C, 4.66; H, 2.81; S, 12.44.

Tetrakis(tetramethylammonium) μ-Disulfido-bis(undecahydro-*closo*-dodecaborate)(4–) *S*-Oxide Monohydrate (XVIII). To a solution of $Cs_2B_{12}H_{11}SH{\cdot}H_2O$ (2.3 g, 5 mmol) in 40 mL of water was added 5.5 mmol of 30% hydrogen peroxide and the solution was stirred at room temperature for 48 h. After this time the reaction solution was converted to its acid form by ion exchange and it was then taken to pH 7 with tetramethylammonium hydroxide. The solution was concentrated to saturation by rotary evaporation at 25 °C and cooled slowly producing needle-like white crystals which were combined with a second crop. The total weight of air-dried crystals was 1.31 g. On further drying in vacuo over P_2O_5 the crystals became amorphous; final weight 1.2 g, 71% yield of XVIII. Infrared bands: 3704 (w), 3509 (w), 3077 (w), 2513 (s), 1626 (w), 1481 (s), 1445 (w), 1407 (w), 1282 (w), 1208 (w), 1044 (m), 948 (w), 837 (m), 816 (w), 717 (m) cm^{-1}. Anal. Calcd for $[(CH_3)_4N]_4B_{24}H_{22}S_2O{\cdot}H_2O$: C, 28.61; H, 10.73; O, 4.73; S, 9.68; N, 8.28; B, 38.68; H_2O, 2.66. Found: C, 28.23; H, 10.80; O, 4.97; S, 10.26; N, 8.85; B, 37.57; H_2O, 2.67.

Dicesium Undecahydro(*p*-toluenethiosulfonato-*S*)-*closo*-dodecaborate(2–) Monohydrate (XIX). To 5.46 mmol of $Na_2B_{12}H_{11}SH$ in 50 mL of water at 4 °C under nitrogen was added 13.5 g of sodium bicarbonate and 9.0 g (47 mmol) of *p*-toluenesulfonyl chloride. After being stirred for 4 days, the solution was allowed to warm-up to room temperature and 1.34 g (8 mmol) of cesium chloride in 6 mL of water was added. On slow cooling, large, light green crystals were produced which were filtered off and a further 0.673 g (4 mmol) of cesium chloride was added; the solution was again cooled to produce a second crop. After drying over P_2O_5, the total weight of crystals was 1.95 g (60%). Infrared bands: 3584 (w), 2500 (s), 1600 (w), 1258 (w), 1120 (m), 1070 (m), 1052 (sh, w), 1016 (w), 972 (w), 814 (m), 722 (w), 699 (w) cm^{-1}. Anal. Calcd for $Cs_2B_{12}H_{11}S_2O_2C_6H_4CH_3{\cdot}H_2O$: Cs, 43.44; C, 13.74; H, 3.30; B, 21.20; S, 10.68; H_2O, 2.94. Found: Cs 44.23; C, 13.86; H, 3.38; B, 21.09; S, 11.07; H_2O, 2.89.

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Registry No. Cs_2II, 64174-91-0; $[(CH_3)_4N]_2IV$, 67382-23-4; V, 67350-74-7; H_2VI, 67350-73-6; $[(CH_3)_4N]_2VI$, 67382-22-3; NaX, 67350-64-5; NaXI, 67350-72-5; HXI, 67350-71-4; $[(CH_3)_4N]_2XII$, 67382-24-5; $[(C_2H_5)_3NH]_2XII$, 67382-21-2; Cs_2XIV, 67350-68-9; H_2XIV, 67350-65-6; Cs_2XV, 67350-66-7; H_2XV, 67350-67-8; XVI, 67350-75-8; $[(CH_3)_4N]_4XVIII$, 67382-25-6; Cs_2XIX, 67350-69-0; H_2XIX, 67350-70-3; NMP, 872-50-4; $Na_2B_{12}H_{12}$, 12008-78-5; H_2S, 7783-06-4; SCTh, 29383-39-9; $(SC_6H_3(NO_2)CO_2H)_2$, 69-78-3; $ClSC_6H_3(NO_2)_2$, 528-76-7; $HO_2CCH_2SSCH_2CO_2H$, 505-73-7; $ClSO_2C_6H_4CH_3$, 26763-71-3; $Cl(SCOCH_3)$, 867-49-2; 2-hydroxyethyl disulfide, 1892-29-1.

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(19) According to the convention agreed upon at the Third International Meetng on Boron Chemistry, Munich and Ettal, West Germany, July 1976, all ^{11}B shifts upfield relative to $Et_2O{\cdot}BF_3$ are negative while those downfield are now positive.
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