where $\beta$, the coefficient of vibronic mixing, assuming for simplicity that no quanta of vibration are present in the fundamental state, takes the form

$$\beta = \left(\frac{\hbar}{2\nu}\right)^{1/2} \frac{\langle xy\,|q_{xy}\,|z^2\rangle}{\Delta_2} = \left(\frac{\hbar}{2\nu}\right)^{1/2} \frac{\langle x^2 - y^2|q_{x^2-y^2}|z^2\rangle}{\Delta_2}$$

In this expression $\Delta_2$ is the energy difference between $^2A_2'$ and $^2E'$. Expressions 5 and 6 for $g_\parallel$ and $g_\perp$ have been obtained by means of standard methods of calculation,[23] neglecting terms in $\zeta^2/\Delta_2^2$ and $\beta^2$.

**Registry No.** CuBr(Me$_6$tren)Br, 14405-54-0; CuI(Me$_6$tren)I, 59172-14-4; Cu(NH$_3$)$_2$Ag(SCN)$_3$, 12075-57-9; NiCl(np$_3$), 54423-06-2; NiBr(np$_3$), 54382-82-0; NiI(np$_3$), 54353-75-2.

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### Synthesis of μ-Disulfido-bis(undecahydro-*closo*-dodecaborate)(4–) and of a Derived Free Radical


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We report the isolation and some properties of tetracesium μ-disulfido-bis(undecahydro-*closo*-dodecaborate)(4–) hemihydrate, $Cs_4B_{12}H_{11}SSB_{12}H_{11}\cdot0.5H_2O$, following the oxidation of $B_{12}H_{11}SH^{2-}$ with iodosobenzoate.

$B_{12}H_{11}SSB_{12}H_{11}^{4-}$ is of particular interest in the neutron-capture therapy of gliomas[2a] as it may possess favorable biological properties.[2b,3]

Prior to the synthesis of this compound, the oxidative coupling of two polyhedral borane anions has been accomplished chemically only for $B_{10}H_{10}^{2-}$ and $B_{10}H_9(\text{ligand})^-$.[4] Oxidation of $B_{10}H_{10}^{2-}$ with Fe(III) or Ce(IV) in aqueous solution produces $B_{20}H_{18}^{2-}$ in which the two $B_{10}$ polyhedra are connected by three center B–B–B bonds.[5,6] Subsequent reduction of $B_{20}H_{18}^{2-}$ yields $B_{20}H_{18}^{4-}$ in which a single B–B bond links both cages.[6,7] Another type of bond linking two $B_{10}$ polyhedra is produced by the ultraviolet irradiation of $B_{20}H_{18}^{2-}$.[8] This product, an isomer of $B_{20}H_{18}^{2-}$, has two B–H–B three-center bonds joining the cages. Oxidation of $B_{10}H_{10}^{2-}$ may also be accomplished by $NO_2$ to produce $B_{20}H_{18}NO^{3-}$,[9,10] in which a bridging NO group links the cages. The $B_{12}H_{12}^{2-}$ anion and several polyhedral heteroborane anions have also been coupled, though only via electrochemical oxidation.[11,12]

Although the product described here, $B_{12}H_{11}SSB_{12}H_{11}^{4-}$, is the first example of two borane anions being linked by a disulfide bridge, several other disulfides are known in polyhedral borane chemistry and include the neutral disulfides of mercapto-*o*-carboranes, $RCB_{10}H_{10}CSH$, and the disulfide of the metallocarborane $(1,2\text{-}B_9C_2H_{10})Co(SH)_2^-$.[13,14] The latter disulfide is interesting in that two carbollide ligands are linked via a disulfide bond. The disulfide described in this report is, however, distinguished by its large negative charge, a probable reflection of which is the formation of an exceptionally stable free radical. Some properties of this free radical are also described.

## Experimental Section

**Spectra.** $^{11}B$ NMR were obtained at 32.1 MHz using a Varian XL-100 with Fourier transform and a pulsed deuterium lock. Samples of the sodium salts, obtained by ion exchange of the cesium salts using Bio-Rad AG 50W-X8 $Na^+$ resin, were dissolved in a 50% solution of $D_2O$ in water to give a final concentration of approximately 0.1 M. The samples were run in 12-mm tubes and referenced relative to external $Et_2O\cdot BF_3$ by sample interchange. Both normal and hydrogen-decoupled spectra were taken and each of these was run with and without line-narrowing techniques.[15] From the latter the $^{11}B$ chemical shifts and hydrogen coupling constants were obtained. Chemical shifts are estimated to be to an accuracy of ±0.1 ppm and coupling constants to ±6 Hz.

ESR spectra were obtained using an Alfa Scientific Laboratories Al-X-10 spectrometer operating at 9.26 GHz. Field strength was determined by reference to perylene in 98% sulfuric acid. Raman spectra were determined using a Spex Ramalog instrument with a Coherent Radiation Model 52 G argon ion laser (4880-Å excitation). The sample was run as a solid using techniques described elsewhere.[16] Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer using KBr pellets. Absorbances in the visible region were observed using a Cary Model 14 spectrophotometer to determine $\lambda_{max}$.

**Chromatography.** Thin-layer chromatography (TLC) was carried out as described elsewhere using Baker-Flex DEAE cellulose thin-layer chromatography sheets.[17] A solvent system of 1:1 v/v 3 M $NH_4NO_3$–$CH_3CN$ was employed. Visualization was achieved using both palladium chloride and sodium nitroprusside. For the latter technique the TLC sheets, after development, were dipped into a 10% aqueous sodium nitroprusside solution. After excess solution was drained off, the sheets were placed in a jar containing filter paper saturated with concentrated ammonium hydroxide. Under these conditions thiol-containing components visualized as pink spots.

**Materials.** *o*-Iodosobenzoic acid obtained from K & K Laboratories, Inc., was dissolved in a minimum of aqueous sodium hydroxide and diluted to give a 0.1 M solution at pH 9.5. Trifluoroacetic acid and dithiothreitol were from Aldrich. *N,N*-Dimethylformamide, 99 mol % pure from Fisher, was used without further purification. All other solvents were of reagent grade.

**Synthesis of $Cs_4B_{12}H_{11}SSB_{12}H_{11}\cdot0.5H_2O$.** To 2.29 g (5 mmol) of $Cs_2B_{12}H_{11}SH\cdot H_2O$[18] in 30 mL of water was slowly added 25 mL of 0.1 M aqueous sodium iodosobenzoate at pH 9.5. A white precipitate formed immediately. Water was evaporated to give a final volume of approximately 10 mL; the flask was cooled in ice and the mixture filtered to yield 1.90 g of product. This salt was dissolved in 100 mL

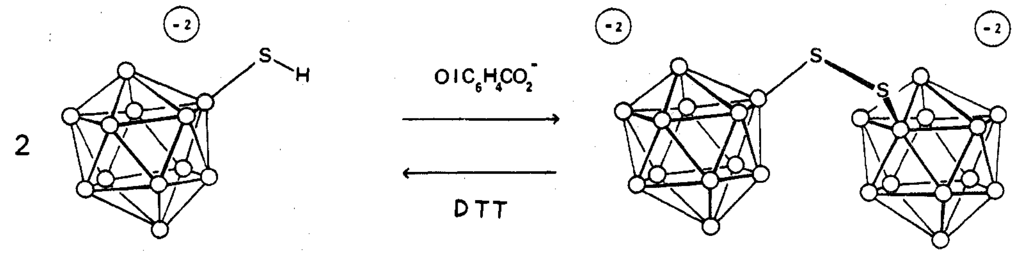


**Figure 1.** Oxidation of the thiol $B_{12}H_{11}SH^{2-}$ by iodosobenzoate to the disulfide $B_{12}H_{11}SSB_{12}H_{11}^{4-}$ which can then be reduced by dithiothreitol (DTT). The circles in the polyhedra represent boron atoms with hydrogen atoms attached except where sulfur is a substituent.

of water at 60 °C and cooled slowly to yield 1.43 g (65%) of whitish gray disulfide crystals, $R_f$ 0.33.

Other oxidizing agents such as hydrogen peroxide or ferric chloride failed to give the disulfide as the major product under similar conditions as evidenced by thin-layer chromatography and infrared spectra.

Microanalysis of a sample of powdered crystals dried for 24 h in vacuo was carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Anal. Calcd for $Cs_4B_{24}H_{22}S_2 \cdot 0.5H_2O$: Cs, 59.98; B, 29.27; H, 2.62; S, 7.24; $H_2O$, 1.02. Found: Cs, 59.41; B, 28.77; H, 2.86; S, 7.29; $H_2O$, 1.19. Water content was estimated by weight loss at 110 °C in a stream of nitrogen. No further weight loss was observed under similar conditions at 165 °C.

Raman bands of the cesium salt were observed at 2508 (s), 2476 (s), 976 (w), 964 (w), 940 (sh), 846 (w), 820 (w), 744 (s), 721 (m), 620 (w), 576 (m), 496 (m), 366 (w) cm$^{-1}$; infrared bands of the cesium salt were observed at 3584 (m, br), 2500 (s), 2370 (sh), 1603 (w), 1058 (s), 978 (m), 953 (w, sh), 845 (s), 824 (w), 723 (m) cm$^{-1}$ (abbreviations: s, strong; m, medium; w, weak; sh, shoulder; br, broad).

**Free-Radical Formation.** On addition of the sodium salt of the disulfide to a solution of trifluoroacetic acid ($5 \times 10^{-3}$ M) in DMF at 25 °C, the solution rapidly turned blue giving rise to a maximum absorbance of $0.465 \times 10^4[S]_0$ ($\lambda_{max}$ 630 nm) where $[S]_0$ is the initial disulfide concentration ($10^{-4}$ to $2 \times 10^{-3}$ M). A similar blue color was formed in formic acid and in solutions of trifluoroacetic acid in either acetone, acetonitrile, or ethanol. Aqueous solutions of the disulfide (0.01 M) at pH 2 were observed to be yellow at 25 °C but changed reversibly to blue at 90 °C. An ESR spectrum of the blue DMF solution showed a resonance with a $g$ factor of 2.019, similar to literature values for sulfur radicals,[19] and $w_{1/2}$ of 19.3 G. No fine structure was observed. The ESR and blue color disappeared when excess sodium ethoxide was added to the acidified DMF–disulfide solution but returned on addition of further trifluoroacetic acid. The blue solutions were observed to fade slowly ($t_{1/2}$ approximately 8 days) on standing at 25 °C. Free-radical formation was not observed when $B_{12}H_{11}SH^{2-}$ was dissolved in organic solvents containing trifluoroacetic acid.

**Kinetic Experiments.** These studies were carried out by adding appropriate volumes of 0.1 M aqueous $Na_4B_{12}H_{11}SSB_{12}H_{11}$ to solutions of trifluoroacetic acid in DMF. The absorbance at 630 nm was followed using 0.1-, 0.5-, 1.0-, and 5.0-cm path length cells in a Bausch and Lomb Spectronic 70. Low-temperature runs were performed in a thermostated cold room with the temperature of the sample being maintained to within ±0.5 °C. Oxygen was not usually excluded; when it was, the DMF was degassed under reduced pressure and then equilibrated under an atmosphere of nitrogen. The cuvettes were filled while nitrogen was bubbling through; they were then capped with tightly fitting Teflon stoppers. Absorbance readings were taken within 1 min after the addition of the disulfide to the acidified DMF.

With the hydrogen ion concentration being maintained at $5 \times 10^{-3}$ M, the initial disulfide concentration, $[S]_0$, was varied from $2.0 \times 10^{-4}$ to $2.0 \times 10^{-3}$ M, meanwhile adjusting the cell path length, $b$, so that $b[S]_0$ was $2 \times 10^{-4}$ M cm. Under these conditions identical curves of absorbance vs. time were obtained. This observation, together with the assumptions that the blue color ($\lambda_{max}$ 630 nm) was due to a single free-radical species and that the disulfide concentration [S] may be expressed as $[S] = [S]_0(1 - (A/A_{max}))$, where $A$ is absorbance, suggests a first-order rate dependence on the disulfide concentration. This behavior was observed at 265.7, 276.2, and 298.2 K.[20]

A dependence of the reaction rate on the hydrogen ion concentration was observed when the initial trifluoroacetic acid concentration was varied while maintaining the initial disulfide concentration at $1.8 \times 10^{-4}$ M. Under these conditions the initial half-life of the reaction decreased nonlinearly from >3600 to 343 s as the initial trifluoroacetic acid concentration was varied from $2 \times 10^{-4}$ to $5 \times 10^{-3}$ M, respectively. (Note: trifluoroacetic acid is completely dissociated in DMF.[21]) Finally, reducing the oxygen concentration as described above decreased the rate of reaction by over an order of magnitude.

## Discussion

**Characterization of the Disulfide.** The formation of a disulfide-linked tetravalent anion $B_{12}H_{11}SSB_{12}H_{11}^{4-}$ by the oxidation of $B_{12}H_{11}SH^{2-}$ with iodosobenzoate is supported by both chemical and spectral evidence.

The stoichiometry of the reaction (which is essentially quantitative by TLC) is in agreement with the disulfide being the product. Elemental analysis of the cesium salt indicates a boron:sulfur ratio of 12 and a boron:cesium ratio of 6 consistent with the tetravalent disulfide structure. Furthermore the product is reduced by the action of excess dithiothreitol, at pH 11 or higher, over a period of several days to give a single product. Base alone had no effect. This reduced borane is indistinguishable by TLC from $B_{12}H_{11}SH^{2-}$. Had the reduced product been a tri- or tetravalent ion, it is unlikely that it would have the same $R_f$ as $B_{12}H_{11}SH^{2-}$ as it has been observed that a higher anionic charge corresponds to a lower $R_f$ in this TLC system.

No evidence for a B–H–B bridge was observed in the infrared spectrum (BHB stretch reported at 1800 cm$^{-1}$ [11]). The Raman spectrum showed features similar to those reported for $B_{12}H_{12}^{2-}$ [22] with an additional peak at 495 cm$^{-1}$ which is assigned to the S–S stretch. This peak was absent in the Raman spectrum of $Cs_2B_{12}H_{11}SH \cdot H_2O$. Conversely the S–H stretch at 2579 cm$^{-1}$ in the Raman spectrum of the sulfhydryl compound was absent in the disulfide.

The NMR (see Figure 2) showed a singlet (6.7 ppm) of area 1 corresponding to the sulfur-bound boron, two doublets of area 5 (15.6 ppm, $J_{B-H} = 138$ Hz; 17.2 ppm, $J_{B-H} = 132$ Hz), and a doublet of area 1 (20.3 ppm, $J_{B-H} = 139$ Hz), all of which appeared as singlets on hydrogen decoupling. These observations tend to rule out the possibility of an additional B–B two-center bond serving to couple the borane cages together. This spectrum compares with that obtained for $B_{12}H_{11}SH^{2-}$ which gave a singlet of area 1 (10.7 ppm), two doublets of area 5 (14.8 ppm, $J_{B-H} = 125$ Hz; 17.0 ppm, $J_{B-H} = 130$ Hz), and a doublet of area 1 (20.5 ppm, $J_{B-H} = 135$ Hz).

**Characterization of the Free Radical.** The rapid appearance of a free radical upon adding the disulfide, $Na_4B_{12}H_{11}SSB_{12}H_{11}$, but not the thiol, $Na_2B_{12}H_{11}SH$, to acidified solvents clearly indicates that the free-radical formation is dependent on the presence of the disulfide linkage. Short-lived thiyl radicals, RS·, are postulated as being formed in a number of reactions involving organic disulfides, and may be produced by a homolytic fissioning mechanism or by a displacment on the disulfide by organic radicals such as $(CH_3)_2\dot{C}CN$. Analogously this suggests that either a thiyl radical, $B_{12}H_{11}\dot{S}^{2-}$, or a thiol radical, $B_{12}H_{11}\dot{S}H^-$, is formed from the disulfide $B_{12}H_{11}SSB_{12}H_{11}^{4-}$ in acidified organic solvents. The ESR data suggest that the unpaired electron is localized on one or more sulfur atoms and indicate, furthermore, that in the case of a thiol radical fast proton exchange in the acidic solution av-

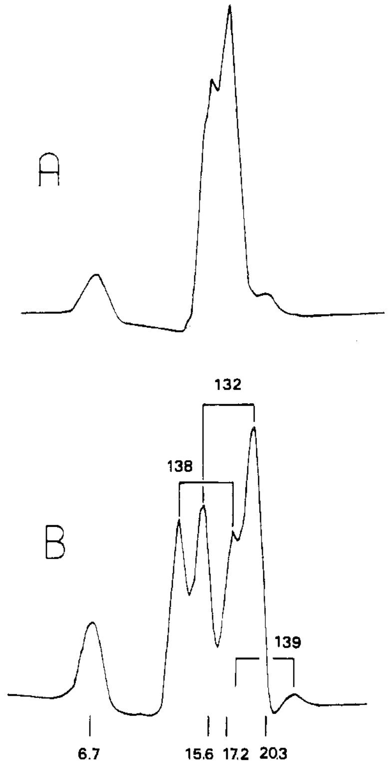


**Figure 2.** The $^{11}B$ NMR of $Na_4B_{12}H_{11}SSB_{12}H_{11}$: (A) hydrogen decoupled; (B) coupled. Chemical shifts in ppm relative to $Et_2O{\cdot}BF_3$ are given below the peaks. Coupling constants in Hz are shown above.

erages out the hyperfine splitting by the thiol proton.

If the free radical is of the thiyl or thiol type, homolytic fissioning of the disulfide must be discounted since such a mechanism would give rise to a first-order rate dependence on the disulfide concentration and a zeroth order dependence on the oxygen concentration. However, our kinetic runs showed that the reaction rate is strongly dependent on the oxygen concentration. They also indicated a rate dependence on both the hydrogen ion and disulfide concentrations.

Another means by which a free radical could be formed under our experimental conditions involves a one-electron autoxidation mechanism. A multielectron oxidation mechanism seems unlikely as the first oxidized derivative of the disulfide, $B_{12}H_{11}SOSB_{12}H_{11}^{4-}$, does not readily produce free radicals in acidic media, and this species is surprisingly reluctant to undergo further oxidation.[23]

The surprisingly long lifetime of these anionic radicals may be explained by postulating that their electrostatic repulsion in solvents other than water inhibits their recombination.

Finally, preliminary biological testing of the disulfide in tumor-bearing rats has been carried out and will be reported elsewhere.[24] Whether the derived radical is produced in vivo has not been resolved.

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**Registry No.** $Cs_4B_{12}H_{11}SSB_{12}H_{11}$, 62962-07-6; $Cs_2B_{12}H_{11}SH$, 12448-23-6; $Na_4B_{12}H_{11}SSB_{12}H_{11}$, 62962-06-5.

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(20) The nature of our experimental conditions did not allow the absorbance to be measured for $t < t_{0.05}$. A plot of log ([S]/[S]$_0$) vs. time was linear for $t < t_{0.66}$ but did not pass through the origin as expected. A better fit can be obtained if we assume that there is an initial leap of absorbance to $0.05A_{max}$ followed by a first-order reaction. Strictly for the purpose of reporting our data we will assume this model. Now the disulfide concentration can be expressed as $[S] = [S]_0(1 - (A - 0.05A_{max})/0.95A_{max})$. A least-mean-squares fit of ln [S] vs. $t$ for the integrated expression at several temperatures gave good correlations ($r^2 = 0.99$) with the following first-order rate constants: $8.2 \times 10^{-4}$, 265.7 K; $1.8 \times 10^{-3}$, 276.2 K; $7.1 \times 10^{-3}$, 298.2 K.
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## Kinetics and Mechanism of the Nitrogen(IV) Oxidation of Molybdenum(V)

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As a continuation of our earlier studies[1,2] concerning the oxidation of $MoOCl_3(OPPh_3)_2$ by nitrate and nitrite ions, we here report the oxidation of this complex by nitrogen(IV) oxide. This study is also of interest since no information concerning the kinetics and mechanism of nitrogen(IV) oxidations of transition metal centers appears to have been reported.

### Experimental Section

All manipulations were performed under an atmosphere of purified nitrogen. Dichloromethane (normal commercial grade) was purified by distillation from $CaH_2$ and equilibrium mixtures of $NO_2/N_2O_4$ in this solvent were prepared by the appropriate dilution of liquid $N_2O_4$ (BDH Chemicals, s.g. 1.49, 99.5%). $MoOCl_3(OPPh_3)_2$ was prepared as described previously[3] and $Ph_3PO$ (BDH Chemicals), was used without further purification. Infrared and UV/vis spectra were recorded, respectively, on Perkin-Elmer 257 and Unicam SP800 spectrophotometers.

$CH_2Cl_2$ solutions of the reactants were prepared immediately prior to the study and transferred using syringe techniques to the storage