

REACTIONS OF $B_{10}H_{10}^{-2}$ ION

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Recent studies have extended the chemical principles¹ of boron hydrides to include boron-boron bonds between polyhedra or polyhedral fragments² and rearrangements^{3, 4} of boron frameworks. We report here results, suggesting new areas of research, including a condensation reaction to form $B_{20}H_{18}^{-2}$ from $B_{10}H_{10}^{-2}$, a substitution reaction on $B_{10}H_{10}^{-2}$ to form $B_{10}H_9OH^{-2}$, a suggestion of polyhedral isomerization, the presence of essentially covalent metal bonds to B in $B_{10}H_{10}^{-2}$, and a new type of free radical.

The $B_{20}H_{18}^{-2}$ Ion.—Reaction of dilute aqueous $B_{10}H_{10}(HNEt_3)_2$ solutions with $FeCl_3$ yields nearly white crystals of $B_{20}H_{18}(HNEt_3)_2$, insoluble in cold water but soluble in several polar organic solvents, melting with decomposition at 175–174°C, and having a density of 0.941 gm cm⁻³. The rough molecular weight of 420 from the vapor pressure depression of CH_3OH solutions allowed the number of molecules per unit cell of the crystal to be fixed at two and led to the crystallographically determined molecular weight of 437 ± 2 in agreement with the expected value of 439. Moreover, the ion is centrosymmetric, since the space group is $P2_1/a$. The B^{11} nuclear magnetic resonance (NMR) spectrum (Fig. 1) is related to that² of $B_{10}H_{10}^{-2}$ in a way which suggests that one apex¹ B atom and one equatorial B atom of each B_{10} unit are involved in the formation of $B_{20}H_{18}^{-2}$. The only structure¹ consistent with the present valence theory is now being tested by X-ray diffraction methods in this laboratory. The ultraviolet spectrum has intense bands at 293 and 230 m μ , neither of which is present in the $B_{10}H_{10}^{-2}$ spectrum in noticeable intensity. The chemical reaction



goes to 95 per cent yield in aqueous solution with slight excess of Fe^{+3} . Analytical results for the $HNEt_3^+$ salt and the NMe_4^+ salt (mp > 300°C) are shown in Table 1.

The $B_{10}H_9OH^{-2}$ Ion.—A quantitative reaction of $B_{20}H_{18}(HNEt_3)_2$ with aqueous base,



establishes a substituted $B_{10}H_{10}^{-2}$ ion. The salt $K_2B_{10}H_9OH \cdot 2H_2O$ loses water at room temperature to form a stable monohydrate (Table 1) but is stable as high as 300°C except for further loss of H_2O . The $B_{10}H_9OH^{-2}$ ion may be the same as that prepared by quite different methods by Knoth *et al.*,⁵ whose research we became aware of after completion of our own.

Polyhedral Isomerization.—Upon initial deuteration in strong acid, $B_{10}H_{10}^{-2}$ is apex⁵ substituted. Also, when freshly prepared, $B_{10}H_9OH^{-2}$ is apex substituted. The large high field doublet, initially like⁷ that in $B_{10}H_{10}^{-2}$, of the B^{11} NMR spectrum becomes unsymmetrical after a few hours at room temperature, thus suggesting an apparent partial migration of the substituent. A probable transformation process is shown in Figure 2. If this process is more general, it may occur in $B_{12}H_{10}X_2^{-2}$, where two X atoms on adjacent B atoms may wander to nonadjacent

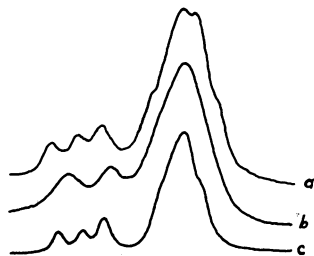


FIG. 1.—The B^{11} N.M.R. spectra of $B_{20}H_{18}(HNEt_3)_2$. (a) The pure compound in perdeuteroacetone. (b) The compound in the presence of Fe^{+++} in a methanol-acetone mixture. (c) The extensively deuterated sample in acetone. The free apex B-H remains undeuterated, contrary to the behavior in $B_{10}H_{10}^{-2}$.

TABLE 1
ANALYTICAL RESULTS

$B_{20}H_{18}(HNEt_3)_2$	B	H	N	C
Obs. (1)	49.3	11.6	6.8	33.4
Obs. (2)	51.0	11.0	6.5	29.7
Calc.	49.2	11.5	6.4	32.9
$B_{20}H_{18}(NMe_3)_2$				
Obs.	43.0*	11.7	7.4	24.7
Calc.	56.5	11.1	7.3	25.1
$K_2B_{10}H_9OH \cdot 2H_2O$	B	H	K	O
Obs.	42.2	4.8†	31.8	(21.2)‡
Calc.	43.5	5.7	31.5	19.3
$K_2B_{10}H_9OH \cdot H_2O$				
Obs.	46.8	5.1	34.0	(14.1)‡
Calc.	46.9	5.2	33.9	13.9
$Cu_2B_{10}H_{10}$	B	H	Cu	
Obs.	43.4	4.1	53.0	
Calc.	44.2	4.1	51.7	

* The low B analysis is due to incomplete hydrolysis.

† This sample loses water at room temperature.

‡ By difference.

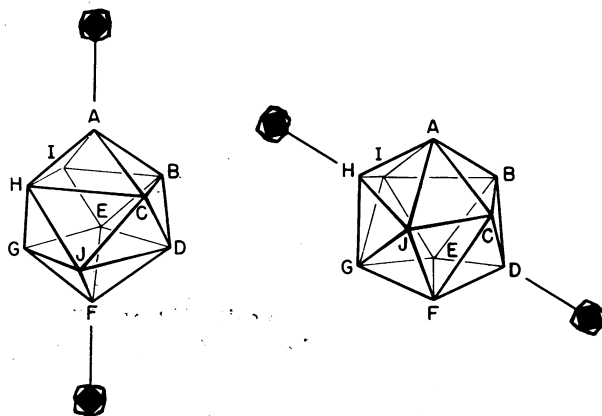


FIG. 2.—A plausible explanation of rearrangement of apex $B_{10}H_9X^{-2}$ to equatorial $-B_{10}H_9X^{-2}$ in which the B-X bond remains unbroken and in which no atom moves more than $1/2$ of an Angstrom. A four-coordinated apex atom may move toward five-coordination in order to start the rearrangement.

positions by transformation from the icosahedral structure through a structure like the cube-octahedral one to another icosahedral structure in which the B atoms are effectively relabeled.

Single Crystal X-Ray Study of $Cu_2B_{10}H_{10}$.—The water-insoluble compound (Table 1) was prepared by reaction of $(H_3O^+)_2B_{10}H_{10}^{-2}$, a very strong acid prepared from

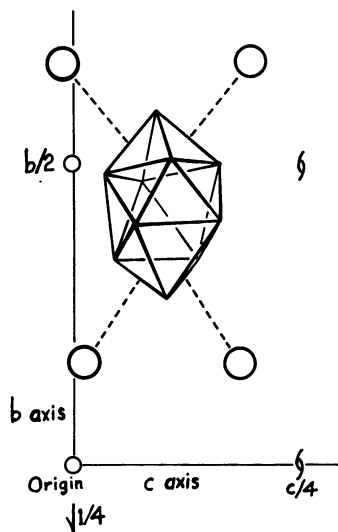


FIG. 3.—One-eighth of the unit cell of $\text{Cu}_2\text{B}_{10}\text{H}_{10}$, showing Cu — — polyhedral edge interactions as dashed lines. Relations of atomic positions to centers of symmetry (small circles) and twofold screw axes of Pcab are indicated.

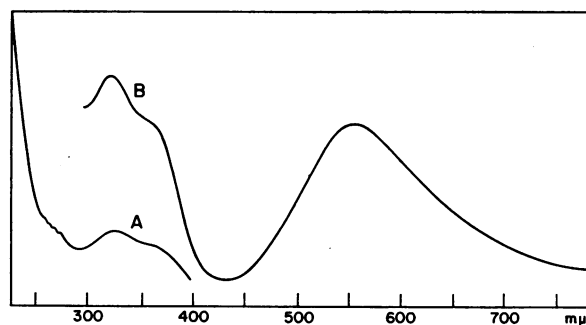


FIG. 4.—Visible (curve B) and ultraviolet (curve A) spectra of radical produced by reaction of CuCl_2 with $\text{K}_2\text{B}_{10}\text{H}_{10}$ in diethyl ether. The two curves are not relatively correlated in amount of absorption, plotted along the vertical axis.

aqueous $\text{K}_2\text{B}_{10}\text{H}_{10}$ by ion exchange, with aqueous $\text{Cu}(\text{ClO}_4)_2$ at 100°C . A single crystal was shown to have unit cell dimensions $a = 10.36$, $b = 11.38$, and $c = 14.53$ Å, the space group Pcab , and $8\text{Cu}_2\text{B}_{10}\text{H}_{10}$ per unit cell. The B^{11} NMR spectrum of an acetonitrile solution showed the characteristic $\text{B}_{10}\text{H}_{10}^{-2}$ spectrum,⁷ but the centers of B^{11} resonances were less widely separated than in $\text{K}_2\text{B}_{10}\text{H}_{10}$.

The structure, which has now been solved ($\sum|F_0^2 - F_c^2|/\sum F_0^4 = 0.19$ for the 1,184 observed reflections), indicates the correctness of the $\text{B}_{10}\text{H}_{10}^{-2}$ structure proposed earlier,⁶ and most interestingly indicates the occurrence of eight distinct Cu-B interactions in the range of 2.1 to 2.3 Å, which are to be compared with the sum of covalent radii $0.84 + 1.18 = 2.02$ Å for B and Cu.⁸ The essentially covalent nature of these bonds is supported also by the solubility properties of $\text{Cu}_2\text{B}_{10}\text{H}_{10}$. The geometry and covalent nature of this interaction is a possible model for other systems, such as the insoluble $\text{Ag}_2\text{B}_{10}\text{H}_{10}$, the Fe^{+3} complexes⁷ or H^+ complexes with $\text{B}_{10}\text{H}_{10}^{-2}$, and the free radical described below. The Cu interacts with $\text{B}_{10}\text{H}_{10}^{-2}$ at the apex-equatorial edges, each Cu interacting with two polyhedra, and hence each polyhedron interacting with four Cu (Fig. 3).

A Free Radical.—Some related preliminary observations are here reported on an unusual free radical produced by reaction of $\text{CuCl}_2(\text{s})$ with $\text{K}_2\text{B}_{10}\text{H}_{10}(\text{s})$ to produce a soluble free radical in the presence of certain solvents such as diethyl ether, acetic acid, ethyl acetate, tetrahydrofuran, or nitrobenzene. Other reactions, including production of H^+ , but not H_2 , and reduction of some Cu^{II} to Cu^{I} also occur. The purple color is due to the absorption band near $550 \text{ m}\mu$ (Fig. 4), which resembles that of certain Cu^{II} complexes, and the electron spin resonance spectrum (left side of Fig. 5) yields the interesting value of $g = 2.018$, which is small for Cu^{II} but large

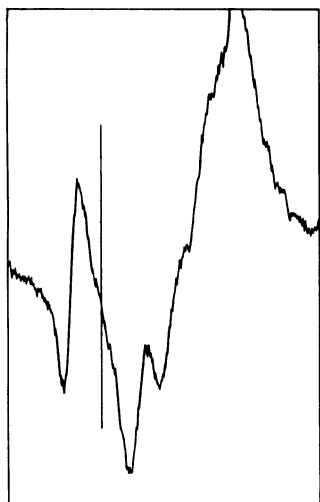


FIG. 5.—Electron spin resonance of radical produced by reaction of CuCl_2 with $\text{K}_2\text{B}_{10}\text{H}_{10}$ in tetrahydrofuran. The signal to the left of the vertical line is due to the new radical, while that to the right is due to the usual Cu^{II} complexes with Cl^- .

for any free radical formed from first-row atoms not including NO groups. Care to remove O_2 and peroxides from the system increases the yield of the radical. The B^{11} NMR spectrum is like a very smeared $\text{B}_{10}\text{H}_{10}^{-2}$ spectrum, thus suggesting that the mild conditions of preparation have not destroyed the B_{10} units. Its solubility characteristics and g value lead to a tentative suggestion of a Cu^{II} complex with a monomeric or polymeric (by H bridging) $(\text{B}_{10}\text{H}_x)_n^{-2}$ species in which the free electron is mostly in the boron framework, but is at least partly on the associated Cu^{II} or $\text{Cu}^{\text{II}}\text{Cl}$.

Note added in proof: An oxazahydroborate salt resulting from reaction of $\text{B}_{10}\text{H}_{10}(\text{NHEt}_3)_2$ with NO_2 and assigned the formula $\text{B}_{14}\text{H}_{12}\text{NO}(\text{NEt}_3)_2$ by Wiesboeck, Pitochelli, and Hawthorne, *J. Am. Chem. Soc.*, **83**, 4108 (1961) seems to us to be a $\text{B}_{20}\text{H}_x\text{NO}(\text{NHEt}_3)_3$ salt, where the $\text{B}_{20}\text{H}_x\text{NO}^{-3}$ ion may be related to the proposed¹ $\text{B}_{20}\text{H}_{19}^{-3}$ ion by formal replacement of H by NO. This conclusion is based upon an X-ray formula weight of 576 ± 3 (or twice this value) determined in cooperation with R. Lewin of this laboratory.

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- ³ Grimes, R., and W. N. Lipscomb, these PROCEEDINGS, **48**, 496 (1962).
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⁵ Knoth, W. H., H. C. Miller, D. C. England, G. W. Parshall, J. C. Sauer, and E. L. Muettterties, *J. Am. Chem. Soc.*, in press (private communication, 1962).
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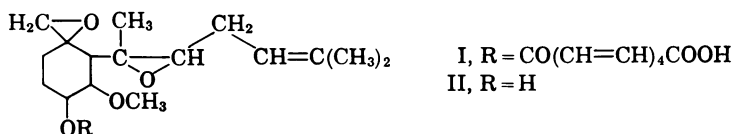
THE STEREOCHEMISTRY OF FUMAGILLIN*

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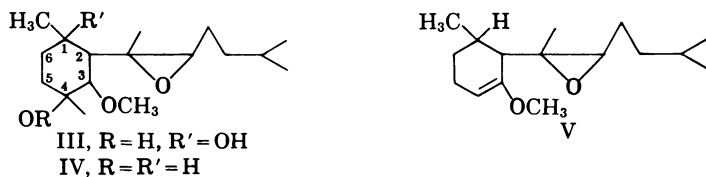
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Extensive degradative and synthetic studies^{1, 2} have allowed the assignment of structures I and II to the antibiotic fumagillin and its saponification product alcohol-I. These structures have been confirmed by X-ray analysis.³ Consideration of published information² and of some additional results allows assignment of configurations to the asymmetric centers in the cyclohexane ring, in agreement with those from the X-ray work;³ in addition, optical rotatory dispersion measurements allow an assignment of absolute configurations. The arguments follow.



Reduction of II yields the tetrahydro compound III, and dehydration of the latter (III, R = COCH₃) gives two isomeric unsaturated compounds, with an exocyclic methylene and a 1,6-double bond, respectively.² Oxidation of the 1,6-isomer gives the 1,6-epoxide, and this is converted to the tetrahydroalcohol III by hydride reduction.² The epoxide ring opening is certainly diaxial;⁴ hence, the C-O bond at C-1 in III is axial, and the corresponding bond in the spiroepoxide in I is axial. The large side chain at C-2 must be equatorial.⁵ The hydroxyl at C-4 and



the hydrogen at C-3 are both axial, because dehydration of desoxytetrahydroalcohol IV gives V, by a diaxial elimination. The methoxyl group is therefore equatorial. The structure of V is based on analysis and on the presence of a single vinyl proton (τ 5.36) in the n.m.r. spectrum.