TABLE I

	a, Å.	b, Å.	c, Å.	β, deg.
$Ga(OH_2)YH$	8.347 ± 0.005	8.840 ± 0.005	17.565 ± 0.010	99.86 ± 0.05
$Fe(OH_2)YH$	8.364 ± .005	8.942 ± .005	17.83 ± .010	99.46 ± .05
$Cr(OH_2)YH$	8.40 ± .01	8.82 ± .01	17.64 ± .02	99.9 ± .1

The first[5] and the third listed formulations are not presently in question. What we have to report, in full agreement on both points with Lambert, Godsey, and Seitz,[2] is that the Fe(III) acid in solutions of low pH behaves usually as a moderately strong acid (pK about[2] 2.2) and that crystalline $Fe(OH_2)YH$, with an infrared absorption spectrum indicative of a free $\cdot CH_2COOH$ arm, is the usual polymorph, readily preparable despite its excessively large solubility in water.

Crystals of $M(OH_2)YH$, M = Cr, Fe, Ga, are monoclinic, with four molecules of no required symmetry in the unit cell. The space group is $P2_1/c$, and the lattice constants are given in Table I.

Using all three-dimensional data recordable with Mo $K\alpha$ radiation by the counter technique, but from a crystal having less than 10% of the optimum volume, structure determination for $Fe(OH_2)YH$ was readily achieved. Subsequent determination of structure for $Ga(OH_2)YH$ utilized bigger and better crystals. The molecular configuration, as predicted[3] for $Cr(OH_2)YH$, is a dimensionally modified version of the quinquedentate octahedral configuration with *one* uncomplexed arm established[6] for $Ni(OH_2)YH$. Averaged bond distances, Fe–N = 2.22, Fe–O = 2.00 Å. in $Fe(OH_2)YH$ are to be compared with Fe–N = 2.325, Fe–O = 2.057 Å. in the seven-coordinate $Fe(OH_2)Y^-$ anion. A large difference between M–N and M–O bond lengths occurs also in $Ga(OH_2)YH$: Ga–N = 2.12, Ga–O = 1.95 Å. In $Cr(OH_2)YH$, however, one may expect Cr–N to exceed Cr–O by no more than 0.04 Å. (the difference of the covalent radii for N and O) as is observed[7] for the sexadentate octahedral CoY^- and for the bonds in the "square" girdle[6] of $Ni(OH_2)YH_2$.

Given inconsequential contributions from nitrogen atoms, the advantage to any Fe(III) complex of having five tightly held oxygen atoms becomes the more evident. We suggest that, in solution, a quinquedentate seven-coordinate bisaquo $Fe(OH_2)_2YH$ with free arm is the preferred form of the complex acid, but that a water molecule is lost from each complex during crystallization. The $Fe(OH_2)YH$ structural type is characterized by a high packing density (as EDTA complexes go), and the solubility of this phase, with allowance for ionization, seems excessively high unless the dissolving $Fe(OH_2)YH$ molecules are largely transformed into other (neutral) species. Alternative or simultaneous crystallization of various salts at surprisingly low pH and cationic concentration, and some disproportionation of $Fe(OH_2)YH$ during recrystallization, are usual. The distinctive color pattern—amber to deep brown depending upon concentration or crystal size—which characterizes the solutions (pH 1–7) and all crystalline complexes except the bright yellow $Fe(OH_2)YH$ seems attributable to the seven-coordinate species.

Schwarzenbach and Heller[8] assigned $pK < 1.5$ to the Fe(III) acid by titrating the potassium salt with hydrochloric acid and noting that at low pH the curve was identical with that of KCl–HCl mixtures at the same formal concentrations. The sluggish kinetics of opening a chelate ring thus displayed encourages efforts to prepare crystals of an amber-brown complex acid crystallographically related to the ammonium salt—*i.e.*, the acid seemingly obtained[3] in small amount 5 years past.

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[5] Expanded evidence for an $Fe(OH_2)Y^-$ anion of the specified character is developed elsewhere: M. D. Lind and J. L. Hoard, *Inorg. Chem.*, in press, and M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, in press.

[6] G. S. Smith and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 556 (1959); *cf.* Fig. 1 and 4. One protonated arm $\cdot CH_2COOH$ is chelated to Ni.

[7] H. A. Weakliem and J. L. Hoard, *ibid.*, **81**, 549 (1959).

[8] G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 576 (1951).

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The Structure of Neocarborane

Sir:

Hoffmann and Lipscomb[1] recently discussed the potential existence of three geometrical isomers for the icosahedral carborane system. In these structures (Fig. 1) the two carbon atoms are either adjacent (*ortho*), intermediate (*meta*), or opposite (*para*) to each other. To date two parent isomers of this class of compounds have been found which are called carborane[2,3] and neocarborane.[4] Efforts to establish their structures based on chemical and spectral evidence especially by n.m.r. studies have been conducted in this laboratory.

The theoretical ^{11}B n.m.r. spectra of the geometrical isomers can be qualitatively deduced from the environments of the individual boron atoms in their respective icosahedral configurations. All boron atoms of the *para* isomer (1,12) are geometrically equal in that each is adjacent to one of the carbon atoms. Therefore the spectrum should consist of only one doublet. The *meta* isomer (1,7), on the other hand, has three kinds of geometrically different boron atoms. Two of them (2,3) are affiliated with both carbons, six of them with only one carbon, and the remaining two (9,10) have no

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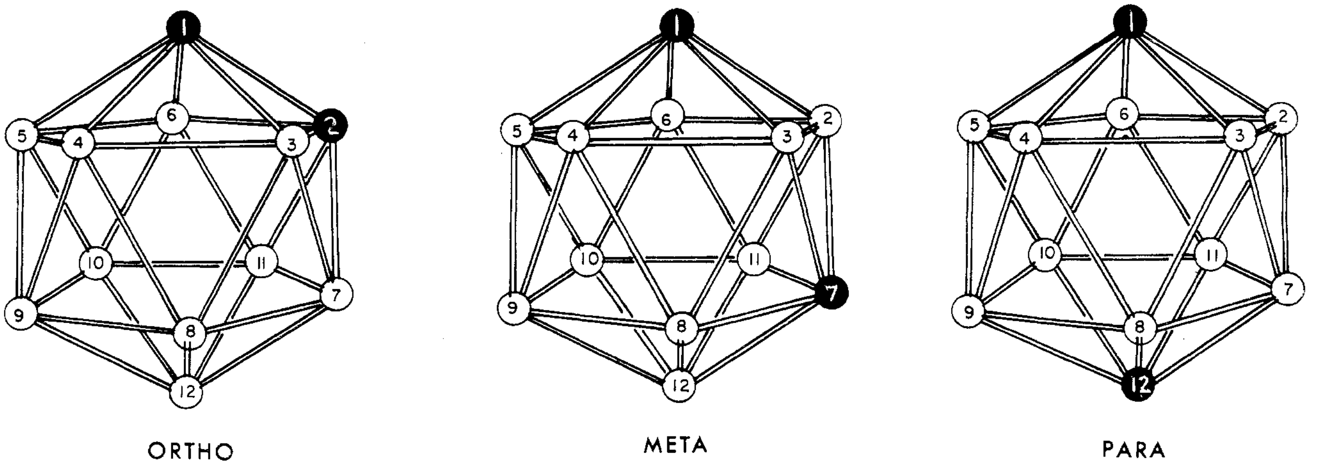
[1] R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 213 (1963).

[2] T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *ibid.*, **2**, 1089 (1963).

[3] M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1111 (1963).

[4] D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).



ORTHO META PARA

Fig. 1.—Icosahedral carborane configurations.

carbon in their immediate environment. Based upon these assumptions, the spectrum should display three doublets with an intensity ratio of 2:6:2.

In the case of the *ortho* isomer (1,2) we have, in contrast to the other structures, two adjacent carbon atoms. Again two of the boron atoms (3,6) are distinguished by their affiliation with both carbon atoms. Of the remaining eight boron atoms, four are adjacent to one or the other carbon and four have only boron atoms in their environment. This rationalization should be reflected in a three-doublet spectrum. However, the presence of the unique carbon–carbon bond in this isomer might easily result in a spectrum in which these eight borons appear equal.

As reported recently,[5] we examined the ^{11}B n.m.r. spectra (Fig. 2) of carborane and decachlorocarborane. The former compound displayed two doublets with an area ratio of 2:8. Exchange of all boron-bound protons by chlorine atoms in $B_{10}Cl_{10}C_2H_2$ produced a spectrum of two singlets with an intensity ratio of 2:8. Since these spectra were consistent only with the requirements of the *ortho* configuration, we assigned this structure to carborane.

We now have examined the ^{11}B spectrum of neocarborane (Fig. 2). It consists of three doublets which can be decoupled into singlets by irradiating with a saturating 60 Mc. field. Since the overlapping of the doublets did not permit the area measurement required for the structure determination, the novel decachloroneocarborane was synthesized by direct chlorination of neocarborane in refluxing carbon tetrachloride in 90% yield, m.p. 235°. *Anal.* Calcd. for $C_2H_2B_{10}Cl_{10}$ (488.8): C, 4.91; H, 0.41; B, 22.14; Cl, 72.54. Found: C, 4.95; H, 0.50; B, 22.15; Cl, 72.65; mol. wt., 492.0. Neo-$B_{10}Cl_{10}C_2H_2$ exhibited the expected three singlets (Fig. 2) with an area ratio of 2:6:2. Since these findings were consistent with the requirements described above for the *meta* configuration, we propose to assign this structure to neocarborane.

This conclusion, which is based upon nuclear magnetic resonance spectroscopy, reconciles theoretical

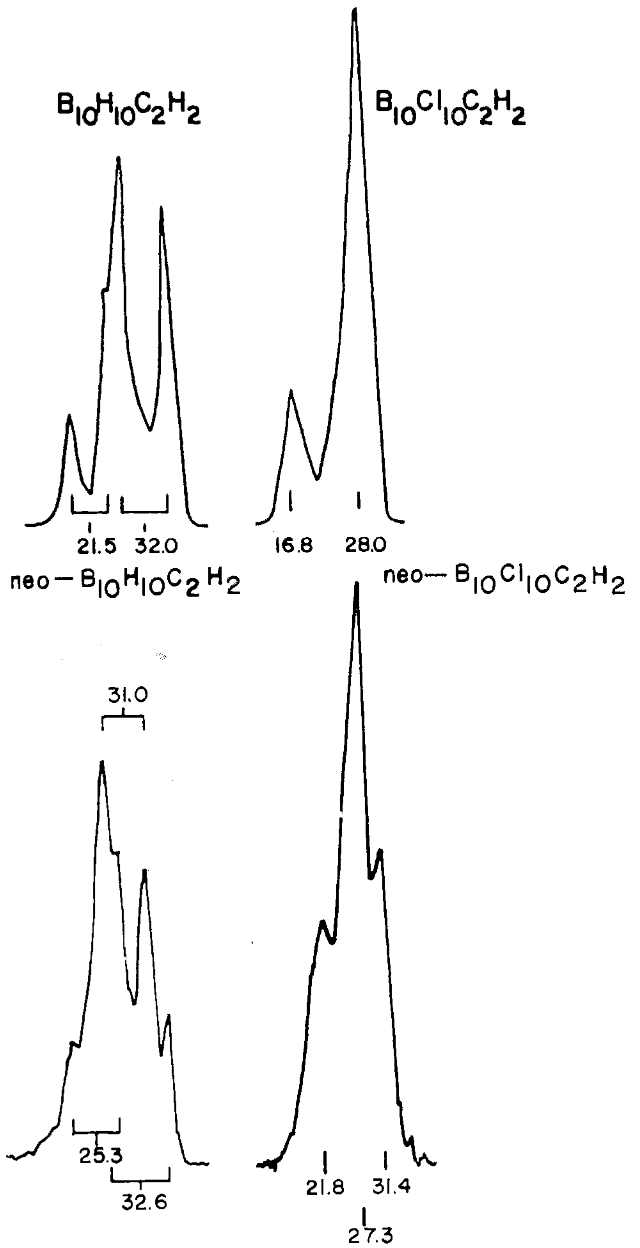


Fig. 2.—^{11}B n.m.r. spectra of two carboranes and two neocarboranes in acetonitrile in displacement (in p.p.m.) from methyl borate. The chemical shifts of the boron resonance doublets were obtained from the decoupled spectra.

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[5] H. Schroeder, T. L. Heying, and J. R. Reiner, *Inorg. Chem.*, **2**, 1092 (1963).

considerations with the chemistry reported. It was proposed from bonding principles[6] and molecular orbital energies[7] that the *meta* isomer should be more stable than the *ortho* isomer. Thus the preparation of neocarborane,[4] which was obtained from carborane at approximately 470°, is in accord with this assumption. As opposed to the participation of carborane in five-membered exocyclic rings,[2,3] similar reactions of neocarborane[4] led only to noncyclic derivatives. Also, comparison of neocarborane derivatives with the analogous carborane derivatives has shown that the former are almost invariably lower melting; this would indicate that the former are of a more unsymmetrical conformation than the latter. From additional work in progress in this laboratory, we have not encountered any evidence which would contradict this assignment.

Acknowledgment.—The authors are indebted to Prof. W. N. Lipscomb and Dr. T. L. Heying for helpful discussions and wish to acknowledge the support of this work by the Office of Naval Research.

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[6] W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **47**, 1791 (1961).

[7] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962).

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The Hydrogen Diiodide Anion[1]

Sir:

Previous attempts to prepare the hydrogen diiodide anion have resulted in black oils[2] or other products.[3,4] An extension of our synthesis of tropenium hydrogen dihalides[5] to the hydrogen diiodide likewise failed since tropenium ion is reduced by hydrogen iodide. We wish now to report the synthesis of tetrabutylammonium hydrogen diiodide, the first salt of this anion to be characterized.

Passage of hydrogen iodide over a stirred solution of tetrabutylammonium iodide in methylene chloride gives a yellow solution; addition of cyclohexane (saturated with hydrogen iodide) precipitates an oil which on repeated treatment with the same reagent crystallizes to yield 99.3% tetrabutylammonium hydrogen diiodide as brilliant yellow microneedles.

Anal. Calcd. for $C_{16}H_{36}NI$: HI, 0.00; I, 34.36. Calcd. for $C_{16}H_{37}NI_2$: HI, 25.72; I, 51.04. Found: HI, 24.99; I, 50.73.

The hydrogen diiodide dissolves in oxygen-free water to give strongly acidic yellow solutions. The crystals lose hydrogen iodide on heating or washing with acetone to yield the iodide. The hydrogen diiodide decomposes rapidly in the presence of light, oxygen, or moisture, but is reasonably stable in their absence; all manipulations were carried out as an oxygen-free drybox under red light.

Since there does not appear to be an opportunity for cation–anion charge transfer in this salt the yellow color of the compound must be ascribed to the anion.

Under similar conditions N-ethyl- and N-butylpyridinium iodides and tetrapropylammonium iodide failed to yield hydrogen diiodides.

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[1] Supported by the Petroleum Research Fund and the National Science Foundation.

[2] F. Kaufler and E. Kuntz, *Ber.*, **42**, 2482 (1909).

[3] A. Hantzsch, *ibid.*, **64**, 667 (1931).

[4] G. J. Janz and S. S. Danyluk, *J. Am. Chem. Soc.*, **81**, 3850 (1959).

[5] K. M. Harmon and S. Davis, *ibid.*, **84**, 4359 (1962).

[6] Petroleum Research Fund—American Chemical Society Scholar, 1963.

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Book Review

Advances in Inorganic Chemistry and Radiochemistry. Volume 4. Edited by H. J. EMELÉUS and A. G. SHARPE, University Chemical Laboratory, Cambridge, England. Academic Press, Inc., 111 Fifth Ave., New York, N. Y., 1962. viii + 344 pp. 16 × 23.5 cm. Price, $11.00

This book consists of a set of six review papers, each of which might appropriately have been published in *Chemical Reviews*. Each article deals with a limited topic of considerable recent activity. The widely diverse areas treated emphasize the extent of modern inorganic chemistry. Five of the papers carry comprehensive outlines of contents, and probably the greatest value of the book resides in the extensive list of references for each chapter. The title, authors, and a brief statement of the content of each article are given below.

(1) "Condensed Phosphates and Arsenates" by Erich Thilo, 75 pages, 372 references. This chapter, dealing primarily with phosphates, describes the properties of many phases prepared in high temperature systems and discusses some structural bases for these various phases. (2) "Olefin, Acetylene, and π-Allylic Complexes of Transition Metals" by R. G. Guy and B. L. Shaw, 55 pages, 223 references. This is a catalog of the multitude of compounds prepared in recent years with transition metal atoms bonded to unsaturated hydrocarbon groups. The results of infrared spectroscopy, n.m.r., and X-ray diffraction are cited in discussing the nature of individual compounds. Complexes formed from cyclopentadiene and its derivatives, carbon monoxide, or aromatic compounds are not treated comprehensively in this review. (3) "Recent Advances in the Stereochemistry of Nickel, Palladium and Platinum" by J. R. Miller, 63 pages, 270 references. The stereochemistry of these elements, primarily in the 0, +1, and +2 oxidation states, is discussed with the consideration of recent X-ray diffraction results, spectroscopic studies, and recent developments in ligand field theory. (4) "The Chemistry of Polonium" by K. W. Bagnall, 33 pages, 137 references. This paper is the book's only real condescension to the "Radiochemistry" in its title since all nuclides of this element are radioactive and macroscopic studies invariably involve massive radiation effects. It does not deal primarily