in which detailed electron density projections are employed do show that the atoms in the anions of phosphates and other similar oxyacids share electrons, occasional reports[22] purporting to demonstrate the existence of such highly charged ions as P^{+5} occasionally appear in the crystallographic literature. Publication of such results is to be deplored unless it is definitely demonstrated that a covalent picture cannot explain the data[23] or unless it is stated that ionic structure factors are used for convenience and do not necessarily indicate that the real structure is ionic.

It is believed that the detailed electron density projections[21] along with the indirect spin–spin splitting and other nuclear magnetic resonance data reported here and in Paper II of this series demonstrate that an ionic representation[24] of phosphorus in its compounds must be considered absurd unless one is equally ready to represent carbon in organic compounds as being ionized, *e.g.*, C^{+4} in CCl_4 or C^{-4} in CH_4.

Acknowledgment.—The authors wish to thank Dr. Bruno Blaser of Henkel und Cie. for donation of the samples of disodium pyrophosphite, tetrasodium isohypophosphate tetrahydrate and trisodium diphosphite; and B. M. Zeffert, Norbert Muller and H. Finegold of the Chemical Warfare Laboratories, Army Chemical Center, for the spectra of sodium tripolyphosphate, disodium pyrophosphite and trisodium diphosphite at the higher field. The assistance of R. C. Jones of Varian in obtaining the data and of J. R. Parks of Monsanto in interpreting it is greatly appreciated.

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[22] *E.g.*, see R. Brill and A. P. de Bretteville, *Acta Cryst.*, **8**, 567 (1955). In recent private communication, Dr. R. Brill made the following statement concerning this reference: "The results primarily indicate only that the scattering powers of Al and P are equal at the third order of the basis reflections. This would be expected for the ions Al^{+3} and P^{+5}. However, this would also be the case if Al and P contain the same number of electrons and the distribution of electrons around both atoms would not differ too much."

[23] We believe this to be impossible for the phosphates, at least.

[24] For recent extreme ionic views, see W. A. Weyl, "The Screening of Cations as a Basic Principle of Inorganic Chemistry," Office of Naval Research, Technical Report No. 52, Contract No. N6onr 269 Task Order 8, Pennsylvania State College, July, 1952.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Molecular Structure of $B_{10}H_{12}I_2$[1]

BY RILEY SCHAEFFER

RECEIVED FEBRUARY 4, 1957

The structure of $B_{10}H_{12}I_2$, obtained from $B_{10}H_{14}$ by treatment with I_2, has been determined by X-ray diffraction techniques. The unique space group D_{2h}^{10}Pccn and the presence of four molecules per unit cell requires the molecule to possess a twofold axis and makes possible the unambiguous determination of the intramolecular iodine–iodine distance. This observed distance is in agreement with that expected if substitution has occurred at the apices of the two pentagonal pyramids which share a common edge in the $B_{10}H_{14}$ structure.

Introduction

Although substituted diboranes ($B_2H_2R_4$) and borines (HBR_2) have been known for many years and present few structural problems, only two substitution derivatives of higher boranes have been described. Both $B_{10}H_{12}I_2$ and $B_{10}H_{12}Br_2$ were prepared by Stock by direct action of the halogen on $B_{10}H_{14}$.[2] Although many isomeric dihalides of decaborane are possible, the nature of the products obtained by Stock indicates that a single isomer was obtained at least in large part. Apparently, effects are operative in determining the mechanism of substitution which have not as yet been adequately assessed and it was consequently of considerable interest to determine which of the isomers was formed.

Experimental

A sample of $B_{10}H_{12}I_2$ crystallized from benzene as flat plates was available. Several crystals were selected, mounted, coated with Krylon and examined by X-ray diffraction. The crystals were not well formed but one showed only a small amount of extraneous scattering, which did not interfere with indexing, and was used for further study. Weissenberg and rotation photographs taken with filtered Cu radiation and precession photographs taken with filtered Mo radiation showed orthorhombic symmetry and gave the following unit cell dimensions: $a = 13.13$, $b = 7.26$, $c = 12.00$ Å.

Comparison of the unit cell dimensions with those of the disordered unit of $B_{10}H_{14}$ strongly suggested that only four molecules were present per unit cell. Indexing of the reflections on the basis of this unit cell led to the criteria for systematic extinction

$$hkl \text{ present in all orders} \qquad (1)$$

$$0kl \text{ present only for } l = 2n \qquad (2)$$

$$hk0 \text{ present only for } h + k = 2n \qquad (3)$$

$$h0l \text{ present only for } l = 2n \qquad (4)$$

The space group was thus uniquely established as D_{2h}^{10}-Pccn.

Sets of precession pictures of varying intensity were obtained by timed exposures of the *h0l* and *hk0* zones and the intensities of individual spots estimated visually with the aid of a standard scale prepared from the same crystal. Values of F_{hkl}^2 (on an arbitrary scale) were calculated from the observed intensities by application of the Lorentz and polarization factors.

Iodine positions were located readily by analytical interpretation of the Patterson function. Since the general positions of the space group are eightfold and only four molecules are present, the molecules must possess a center of symmetry or lie on a twofold axis. If the molecule is structurally derived from $B_{10}H_{14}$ it cannot possess a center of symmetry and must consequently have iodines substituted in one of the five sets of positions equivalent under twofold rotation (see Fig. 1). The intramolecular iodine–iodine distance could then be determined readily from the *hk0* projection of the iodine

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[1] Presented at the American Chemical Society Meeting in Cincinnati, Ohio, in April, 1955. This work was supported in part by a Summer Research Grant to Iowa State College in 1954 by E. I. du Pont de Nemours and Company which is gratefully acknowledged.

[2] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, pp. 120–122.

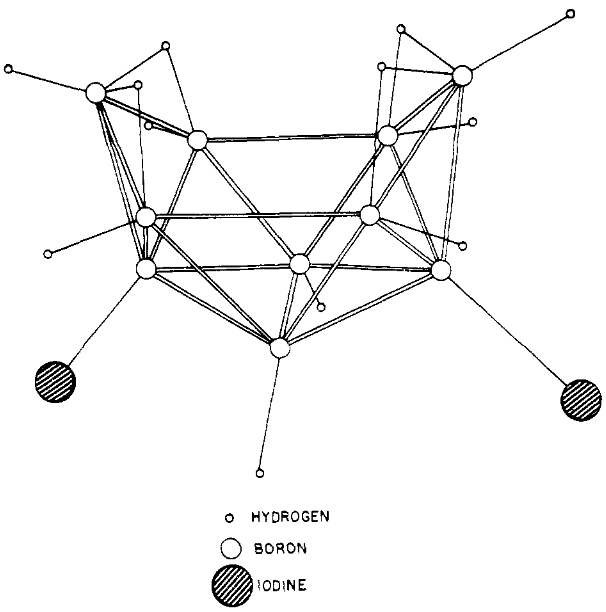

Fig. 1.—The molecular structure of $B_{10}H_{12}I_2$.

positions since they were required by the space group to lie in a plane perpendicular to the C-axis; this distance was found to be 6.25 Å. Using 2.20 Å. as a close approximation to the expected B–I bond distance (the sum of the covalent radii of the atoms), the iodine–iodine distance was calculated for each of the pairs of positions related by the twofold axis by an analytical extension of the B–H bond in the decaborane unit cell using the coördinates of Kasper, Lucht and Harker.[3] It was immediately apparent that position 5 need not be considered since the sum of the bond distances is only 6.12 Å. and the B–H angle is about 120°. It was also necessary to consider only one of the sets 1 and 4 since they would lead to identical I–I distances. Iodine–iodine distances calculated for substitution on positions 1, 2 and 3 were 7.28, 5.92 and 7.56 Å., respectively.[4] In view of the fact that Kasper, *et al.*, were not able to determine the hydrogen positions with high precision, agreement between the observed value (6.25 Å.) and that calculated for position 2 (5.92 Å.) may be considered good. A further refinement of the $B_{10}H_{14}$ structure by Moore and Lipscomb leads to the following somewhat different parameters of interest[5]

	x	$y - {}^1/_4$	z
B_1	0.034	0.080	0.000
B_2	.100	.023	.168
B_3	.116	.028	− .131
H_1	.041	.138	.000
H_2	.164	.026	.320
H_3	.195	.042	− .220

Recalculation of the expected I–I distances for substitution on position 1, 2 and 3 leads to values of 7.88, 6.21 and 7.60, respectively. The agreement between the calculated distance for position 2 and the observed is now better than one has any right to expect when one considers the accuracy with which the hydrogen positions in $B_{10}H_{14}$ are known and possible variation in the B–I bond distance from that assumed.

Structure factors calculated for the crystal based on the assumption that only iodine was present in the cell were in moderately good agreement with the observed values; the usual index of reliability $R = ||F_{\mathrm{obsd}}| - |F_{\mathrm{calcd}}{}^1|/F_{\mathrm{obsd}}|$ was 0.18 for the $hk0$ zone and 0.20 for the $h0l$ zone after application of a temperature factor correction of the usual form with $B = 4.42$ and adjustment of the scale of F_{obsd} to provide the best fit to F_{calcd}. Fourier syntheses were calculated for both $hk0$ and $h0l$ zones using the largest observed structure factors and assigning to them the signs calculated from the iodine positions. No direct indication of molecular shape was present in the $hk0$ projection since two molecules overlap. However the $h0l$ projection shown in Fig. 2 distinctly suggests a cup shaped boron arrangement with the iodine near the closed surface and thus bonded to either position 2 or 5. As noted above, the latter position is not suitable on the basis of I–I distance.

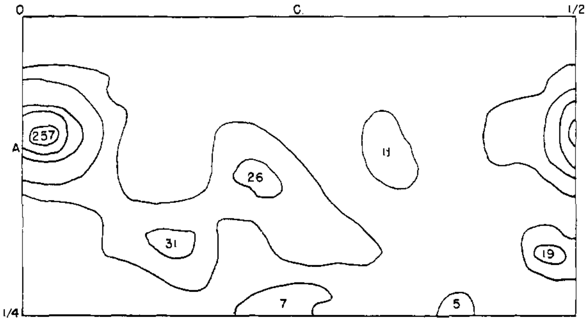

Fig. 2.—$h0l$ Fourier projection of $B_{10}H_{12}I_2$.

Both the $hk0$ and $h0l$ projections suggested parameters for two of the borons (well defined election density maxima) and corrections of structure factors were made for these. A difference synthesis for each zone suggested positions for the remaining boron atoms and second difference syntheses, which included contributions of these borons in F_{calcd}, suggested only slight shifts in parameters for all atoms in the cell. On the basis of the final positions located by the difference synthesis, R values of 0.103 were calculated for both the $hk0$ and $h0l$ zones. The low R values obtained make it apparent that further refinement will be difficult since agreement already is nearly as good as expected experimental error in estimating intensities will permit. Although the R values for each zone are surprisingly sensitive to the boron locations, values of the parameters common to both zones differ by as much as 0.020. Furthermore, attempts to obtain boron positions in the $0kl$ projection (where only data obtained with Cu radiation were available) were unsuccessful. Since the isomer problem had already been adequately resolved, further refinement with the diiodide seemed unprofitable. The partial refinement that was possible with the iodine compound makes it seem quite likely that accurate boron positions could be obtained for $B_{10}H_{12}Br_2$ and study of this compound has been initiated.

Discussion

The dipole moment of $B_{10}H_{14}$ is 3.52 ± 0.02 debye units according to Laubengayer and Bottei.[6] Calculations of Eberhardt, Crawford and Lipscomb[7] show that considerable negative charge should be located on the borons at positions 2. The fact that these atoms are the site of the iodines in $B_{10}H_{12}I_2$ strongly suggests that the mechanism of iodination of the borane is similar to that of an aromatic hydrocarbon in which attack of a positive halogen species occurs at the site of localized negative charge within the substrate molecule. Experiments carried out in this Laboratory by Mr. Gerald Brennan using ICl and N-bromosuccinimide tend to support this mechanism for halogenation and will

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(3) J. S. Kasper, C. M. Lucht and D. Harker, *Acta Cryst.*, **3**, 436 (1950). The numbering system used in this paper has been adopted for the present work.

(4) Recalculation of the B–H bond distances using the data of Kasper, Lucht and Harker leads to values somewhat different from those reported by them. The recalculated bond lengths were used in calculating the expected I–I distances.

(5) E. B. Moore, Jr., and W. N. Lipscomb, unpublished results. The author wishes to thank Professor Lipscomb for permission to quote a portion of his results.

(6) A. W. Laubengayer and R. Bottei, THIS JOURNAL, **24**, 1618 (1952).

(7) W. H. Eberhardt, B. L. Crawford and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

be reported in detail at a later date. Other substitution reactions which might proceed by similar mechanisms will warrant investigation.

Acknowledgments.—The author is greatly indebted to Professor R. E. Rundle and members of his research group for many helpful discussions during the course of this work. The facilities of the Institute for Atomic Research of Iowa State College were used during this investigation.

AMES, IOWA

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Kinetics of 1,10-Phenanthroline Chelation. II. Effect of Hydroxide Ion on the Dissociation Rate of Tris-(1,10-phenanthroline)-iron(II)[1,2]

BY D. W. MARGERUM

RECEIVED DECEMBER 10, 1956

Hydroxide ion greatly increases the rate of dissociation of tris-(1,10-phenanthroline)-iron(II) despite the fact that there are no acidic protons in the complex. The value of k_0, first-order dissociation rate constant with respect to the complex, is dependent on the hydroxide ion concentration: $k_0 = k_d + k_1[OH^-] + k_2[OH^-]^2 + k_3[OH^-]^3$. The kinetics may be explained by an SN2 mechanism with nucleophilic attack by water or hydroxide ion to form reaction intermediates, which are in turn attacked by water or hydroxide ion, or by an SN1 mechanism with similar intermediates.

Introduction

It is known that the brightly colored complex, tris-(1,10-phenanthroline)-iron(II), is stable in aqueous solution in the *p*H range 2–9.[3] Outside this *p*H range there is noticeable dissociation of the complex. Although the rate of dissociation of tris-(1,10-phenanthroline)-iron(II) (hereafter abbreviated $FePh_3^{++}$) has been studied by a number of workers,[4–6] all of these studies have been performed in acidic solutions. Under the conditions of these studies, the rate of dissociation of the complex is first order with respect to the concentration of $FePh_3^{++}$ and independent of acidity. The acidities examined were from 0.005 to 0.50 *M* H_2SO_4. The kinetics of the over-all iron(II)-1,10-phenanthroline system are summarized as follows,[4] omitting the coördinated water molecules

$$\left.\begin{array}{l} Fe^{++} + Ph \rightleftarrows FePh^{++} \\ FePh^{++} + Ph \rightleftarrows FePh_2^{++} \end{array}\right\} \text{Fast}$$

$$FePh_2^{++} + Ph \underset{k_d}{\rightleftarrows} FePh_3^{++} \quad \text{Slow}$$

where $k_d = 0.0045$ min.$^{-1}$. Only the addition or removal of the third 1,10-phenanthroline molecule to iron(II) proceeds at a measurable rate. Because of the stability of the mono and tris complexes, the bis-(1,10-phenanthroline)-iron(II) ion, $FePh_2^{++}$, does not exist in any appreciable concentration in solutions of varying iron(II) and 1,10-phenanthroline concentration.[7]

Tris-(1,10-phenanthroline)-iron(II) has been resolved into its optical isomers and the rate of its racemization has been studied.[6] The racemization rate is also independent of acidity (from 0.1 to 1.0 *M* HCl), but is greater than the dissociation rate. It has been suggested that racemization of $FePh_3^{++}$ proceeds both by a dissociation mechanism and by an intramolecular racemization mechanism.

Much more work has been done on the mechanism of substitution reactions with cobalt(III) complexes than with other coördination compounds. When weak nucleophilic groups react with cobalt(III) complexes, the reactions proceed by SN1 kinetics. More powerful nucleophilic substitutions may be interpreted as SN2[8] or SN1CB[9,10] reactions. The SN1CB reaction is one where the conjugate base of the complex is formed prior to a slow first-order step in the reaction mechanism. In support of the SN1CB kinetics it has been pointed out that "complexes containing no acidic protons release their replaceable ligands at a rate independent of the *p*H of the solution."[10] This generalization may be applicable to the cobalt(III) complexes but it does not fit all complexes. Tris-(1,10-phenanthroline)-iron(II) contains no acidic protons but its dissociation rate in basic solution is highly dependent upon the *p*H of the solution. This paper is concerned with the nature and significance of the hydroxide ion effect on the rate of dissociation of $FePh_3^{++}$.

Experimental

A stock solution of $FePh_3^{++}$ was prepared using a slight excess of 1,10-phenanthroline so that the concentration of $FePh_3^{++}$ was 4.87×10^{-4} *M* and the excess 1,10-phenanthroline was 2.55×10^{-4} *M*. Ten-ml. aliquots of this solution were diluted to 100 ml. volumes in solutions containing KCl, NaOH and slight amounts of ethylenediaminetetraacetic acid. The latter was added to help displace the equilibrium by reacting with Fe(II) and to prevent the precipitation of iron hydroxides. The KCl was used to maintain constant ionic strength. The dissociation rates were followed at 510 mμ with a thermostated (25.0°) Beckman DU spectrophotometer. All measurements were started 1 to 3 minutes after mixing the reagents and readings were taken every 30 or 60 seconds for 10 to 20 minutes.

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(1) Presented at the Atlantic City Meeting of the American Chemical Society, September, 1956.

(2) For paper I in this series see THIS JOURNAL, **78**, 4211 (1956).

(3) W. B. Fortune and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **10**, 60 (1938).

(4) T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 3596 (1948).

(5) W. W. Brandt and D. K. Gullstrom, *ibid.*, **74**, 3532 (1952).

(6) F. Basolo, J. C. Hayes and H. M. Neuman, *ibid.*, **76**, 3807 (1954).

(7) I. M. Kolthoff, D. L. Leussing and T. S. Lee, *ibid.*, **72**, 2173 (1950).

(8) D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2678 (1953).

(9) J. S. Anderson, H. V. A. Briscoe and N. F. Spoor, *ibid.*, 361 (1943).

(10) R. G. Pearson, R. E. Meeker and F. Basolo, THIS JOURNAL, **78**, 709 (1956).