R = Me), to determine the minimum size of substituents in the blocking positions on the borazine ring for prevention of free rotation of tolyl groups.

Acknowledgement. The authors wish to express appreciation to Dr. B. L. Therrell and Professor G. R. Dobson for helpful discussions.

Registry No. *o*-Tolylmagnesium bromide, 932-31-0; *B*-trichloro-*N*-triethylborazine, 2608-99-3; *B*-tri-*o*-tolyl-*N*-triethylborazine, 52176-10-0; ethylmagnesium bromide, 925-90-6; *B*-trichloro-*N*-tri-*o*-tolylborazine, 5775-58-6; *B*-triethyl-*N*-tri-*o*-tolylborazine, 52176-11-1.

Contribution No. 3237 from the Department of Chemistry,
University of California, Los Angeles, California 90024

Observations Regarding Cu-H-B Interactions in $Cu^I{}_2B_{10}H_{10}$

Timm E. Paxson,[1] M. Frederick Hawthorne,*[2] Leo D. Brown,[3]
and William N. Lipscomb*[4]

Received May 16, 1974 AIC40312P

In 1962 Dobrott and Lipscomb[5,6] confirmed the D_{4d} symmetry of the $B_{10}H_{10}{}^{2-}$ anion by an X-ray diffraction study of $Cu^I{}_2B_{10}H_{10}$ (shown in Figure 1), and the nature of the covalent interactions of the copper atoms with the borane aggregate was discussed in detail.[5] The authors postulated either an sp hybridized Cu^I forming three-center bonds with B-B edges or a tetrahedrally hybridized Cu^I interacting with the four nearest B atoms. The latter interpretation was discounted since the B-Cu-B angles were acute (44.6-46.9°, uncorrected for rigid-body motion). A third interpretation of the covalent bonding, not mentioned by Dobrott and Lipscomb, is the possible involvement of the borane terminal hydrogen atoms with sp^3 hybridized copper orbitals, thus forming three-center Cu-H-B bridge bonds.

We have recently found that enough Cu-H-B interaction exists in $Cu^I{}_2B_{10}H_{10}$ to affect its ir spectrum substantially. In addition to the four terminal B-H stretching bands observed at 2510, 2535, 2560, and 2570 cm^{-1} (Nujol mull), there is a broad absorption at 2100-2300 cm^{-1}. Muetterties[7] made note of this broad band and also observed that the bands characteristic of $B_{10}H_{10}{}^{2-}$ at 1015 and 1070 cm^{-1} had vanished. Lippard and Ucko[8] reported bridging Cu-H-B stretching frequencies of 2045 (broad) and 2100 cm^{-1} (broad, Nujol mull) for $(PPh_3)_2Cu^IB_3H_8$; the ir band at 2300-2100 cm^{-1} of $Cu^I{}_2B_{10}H_{10}$ is comparable.

The perdeuterated complex $Cu^I{}_2B_{10}D_{10}$ was synthesized and examined for alterations of the ir spectrum in the 1800-2500-cm^{-1} region. Analysis revealed that the B-D stretching bands were located at 1885, 1905, 1925, and 1935 cm^{-1}, and a broad absorption was centered at 1655 cm^{-1} (Nujol mull).

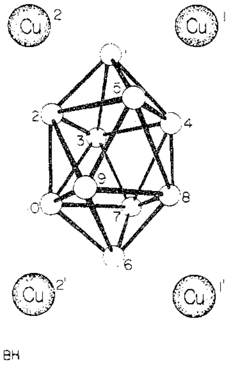

Figure 1. Structure of $Cu^I{}_2B_{10}H_{10}$ using the numbering system of ref 5. The structure only depicts the relative positions of the atoms and is not drawn to crystallographic scale.

The ratio of $\nu(BH)/\nu(BD)$ was determined as 1.33 (calcd 1.35) for all five ir bands; these data are consistent with Cu-H-B bonding interactions. Also synthesized was $(PPh_3)_2Cu^I B_{10}H_{10}Cu^I(PPh_3)_2$ from an alcoholic solution of triphenylphosphine and $Cu^I{}_2B_{10}H_{10}$. The ir spectrum (Nujol mull) contained two broad bands at 2230 and 2325 cm^{-1} consistent for Cu-H-B stretching modes.

Unfortunately, the H positions in $Cu^I{}_2B_{10}H_{10}$ are not directly determined from the X-ray work[5] and probably would not be reliable within ~0.1 Å even if they were. Clearly a neutron diffraction study of the $Cu^I{}_2B_{10}H_{10}$ structure is desirable. However, some observations can be made on the basis of the Cu and B positions.

The Cu-B distances range from 2.06 to 2.33 Å (average 2.20 Å), uncorrected for rigid-body motion. Assuming a single-bond boron radius[9] of 0.88 Å and a Cu^I sp radius[10] of 1.17 Å, we must lengthen the Cu-B single bond by about 0.15 Å to reproduce the observed average distance. The result, 2.20 Å, would be consistent with a three-center bond in which Cu is bonded to two B-B edges of the boron polyhedra. The bond order here is ~0.5 from Pauling's relation[11]

$$D(n) = D(l) - 0.60A \log (n)$$

where n is the bond order. Appreciable covalent Cu-B bonding would probably still remain even at the 2.33-Å distance.

In an alternative view, we might assume a Cu^I sp^3 radius[12] of 1.35 Å. We would then have almost a full (although bent) Cu-B bond of 2.23 Å if we add the B covalent radius of 0.88 Å. Large amounts of covalent Cu-B bonding would still be likely at 2.33 Å.

If the H atoms of the boron polyhedron are not grossly distorted from the local D_{4d} symmetry, we may utilize this symmetry and information from X-ray structure determinations[13,14] of analogous compounds to estimate the H positions from the B positions. Using the numbering system from ref 5, we find four H atoms approximately 1.6-2.2 Å distant from Cu_1 and four H atoms approximately 1.7-2.1 Å distant from Cu_2 (average 1.9 Å). One of these H atoms is between two Cu atoms, at 2.1 Å from each if it is equidistant as the orientation of the B_{10} cage suggests. This distance

---

[1] National Science Foundation Trainee, 1972-1973.

[2] Department of Chemistry, University of California, Los Angeles, Calif. 90024.

[3] National Science Foundation Fellow.

[4] Department of Chemistry, Harvard University, Cambridge, Mass. 02138.

[5] R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.,* 37, 1779 (1962).

[6] A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.,* 48, 729 (1962).

[7] E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.,* 3, 444 (1964).

[8] S. J. Lippard and D. A. Ucko, *Inorg. Chem.,* 7, 1050 (1968).

[9] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.

[10] Reference 9, p 256.

[11] Reference 9, p 255.

[12] Reference 9, p 246.

[13] F. E. Scarbrough and W. N. Lipscomb, *Inorg. Chem.,* 11, 369 (1972).

[14] C. H. Schwalbe and W. N. Lipscomb, *Inorg. Chem.,* 10, 160 (1971).

of 2.1 Å, probably accurate to within ±0.02 Å, and the less accurate range of 1.6–2.2 Å can be used as indicators of the strength of the Cu-H interaction. The Cu-H distances are somewhat longer than the summed covalent radii, indicating bond orders of less than 1. Of course, an sp hybridized Cu would be inconsistent with the geometry positions and with the Cu-H bond distances in these boron compounds. However, addition of the Cu sp radius of 1.17 Å and an H radius[15] of 0.31 Å would give 1.48 Å, consistent with the Cu-H distance of 1.46 Å in diatomic Cu-H.[16] Nevertheless, this distance is considerably less than the Cu-H distances in $Cu^{I}_{2}B_{10}H_{10}$. Alternatively, an sp^3 hybridized Cu radius of 1.35 Å added to an H radius of 0.31 Å would give a Cu-H bond length of 1.66 Å, consistent with the shortest of the calculated Cu-H distances, but 0.44 Å short of the most reliable distance. The necessity of adding 0.24 and 0.54 Å to reach the average and longest Cu-H distances, respectively, would indicate a considerable reduction of bond order, more than that expected from reduction from a single bond to a three-center bond. Probably the bond order is reduced to 0.2 in the case of the 2.1-Å Cu-H distance. In contrast, the difference between the bridge and terminal B-H distances in B_2H_6 is only 0.14 Å.[17]

Three additional considerations in describing the Cu-H-B interaction should be mentioned. First, the use of bent bonds from sp^3 Cu to B would approximate the geometry of the Cu-H-B bonds and relieve the angular constraints that argued against simple sp^3 Cu-B bonds. Such bent bonds would be consistent with a slight shortening of the Cu-B distance. The H positions are consistent with such a distorted tetrahedral geometry. Second, the back-bonding of the hydrogens of the anion toward Cu^I would enhance the direct Cu-B bonding. Third, theoretical studies of diborane[18] and beryllium borohydride[19,20] have shown that B-B (and Be-B) overlap populations can be comparable to B-H (Be-H) overlap populations. Specifically, in B_2H_6 the B-B overlap population is 0.29 while the $B\text{-}H_{bridge}$ overlap population is 0.39. In beryllium borohydride the B-Be overlap population is 0.26, while the $Be\text{-}H_b$ overlap population is 0.31, and the $B\text{-}H_b$ overlap population is 0.52. These overlap populations suggest that caution should be exercised in estimating the relative importance of the metal-H interaction and the metal-B interaction in a metal-H-B bond. Arguments from summed covalent radii are particularly difficult for Be because of the variable nature of its radius. Frequently, therefore, both types of bonding are present.

A number of compounds have been studied[21] which have metal-H-B bonds, including two Cu^I compounds having analogous structures $(PPh_3)_2Cu^IB_3H_8$[22] and $(PPh_3)_2Cu^IBH_4$.[23] In the former the Cu-B distance is 2.30 Å with Cu-H distances of 1.84 and 1.85 Å. In the latter, the Cu-B distance is 2.18 Å with a Cu-H distance of 2.02 Å. These distances are comparable to those in $Cu^{I}_{2}B_{10}H_{10}$, suggesting similar problems in interpreting the bonding. Some chemical evidence that Cu-H interactions are less than fully bridged in $(PPh_3)_2Cu^IBH_4$ is the failure of cleavage reactions in which a number of ligand molecules were tested.[24]

In summary, one may say qualitatively that there are both Cu-B and Cu-H-B interactions in the complexes of Cu^I with the boron hydride anions BH_4^-, $B_3H_8^-$, and $B_{10}H_{10}^-$. The Cu-H distances of 1.8–2.1 Å probably indicate less than full bridge bonds, even though the bonding they do show modifies their infrared spectra as compared with that of terminal B-H units.

Experimental Section

Reagents. Triphenylphosphine was recrystallized three times from ethanol before use. The $K_2B_{10}H_{10}$ was prepared as described in the literature.[25] Copper(II) acetate was used as supplied except for the preparation of $Cu^{I}_{2}B_{10}D_{10}$ in which case it was dried at 100° under high vacuum for 2 days before use. Deuterium oxide (Thompson Packard), trifluoroacetic acid, and trifluoroacetic anhydride were used as supplied as were all other solvents and reagents.

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrometer and a Perkin-Elmer Model 421 grating spectrophotometer. Combustion analysis of $[(PPh_3)_2Cu]_2B_{10}H_{10}$ was obtained from Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Preparation of $Cu^{I}_{2}B_{10}H_{10}$. In a 250-ml erlenmeyer flask were placed $K_2B_{10}H_{10}$ (1.0 g, 5.1 mmol), $Cu^{II}(C_2H_3O_2)_2\cdot H_2O$ (5.1 g, 25.5 mmol), and 100 ml of water. Trifluoroacetic acid (10 ml) was added to the flask, and the resulting intense blue solution was heated on a steam bath with occasional stirring. After approximately 5 min a white precipitate formed. (If formation of $Cu^{I}_{2}B_{10}H_{10}$ had not occurred at this point, trifluoroacetic acid was added dropwise until reaction commenced.) The solution was heated an additional 15 min and then filtered; the solid was washed with copious amounts of water and allowed to air-dry.

The solid was dissolved in acetonitrile, stored in a refrigerator, and allowed to recrystallize slowly. The resulting white crystals were collected and dried under high vacuum until no bands attributable to acetonitrile were evident in the infrared spectrum; yield 0.61 g, 53%.

Preparation of $Cu^{I}_{2}B_{10}D_{10}$. The $K_2B_{10}D_{10}$ was prepared from $(Et_3NH)_2B_{10}D_{10}$[26] in D_2O by the addition of a stoichiometric amount of potassium hydroxide and subsequent removal of the D_2O by evaporation under high vacuum. Anhydrous copper(II) acetate (4.6 g, 32.7 mmol) and $K_2B_{10}D_{10}$ (1.0 g, 4.8 mmol) were charged into a 250-ml Schlenk flask in a nitrogen-filled drybox. The flask was removed and connected to a nitrogen bubbler. While flushing the flask with nitrogen, 100 ml of D_2O was added and the solution was heated on a steam bath. Trifluoroacetic anhydride was cautiously added *via* syringe until reaction commenced (*ca.* 12 ml). The solution was heated an additional 15 min and filtered using Schlenk apparatus. The product was washed with 25 ml of D_2O and finally washed with copious amounts of water and air-dried. The yield was 0.58 g (47%) of a colorless microcrystalline solid.

Preparation of $[(PPh_3)_2Cu^I]_2B_{10}H_{10}$. Triphenylphosphine (4.82 g, 16.3 mmol) was dissolved in 100 ml of absolute ethanol in a 250-ml erlenmeyer flask placed on a steam bath. A slurry of $Cu^{I}_{2}B_{10}H_{10}$ (1.0 g, 4.08 mmol) and 100 ml of ethanol was heated to *ca.* 65° on a steam bath and the triphenylphosphine solution was added in small aliquots with stirring and heating of the $Cu^{I}_{2}B_{10}H_{10}$ slurry between additions. After addition was complete (*ca.* 15–20 min) the solution was heated an additional 15 min and the solid collected by filtration.

---

(15) Reference 9, pp 226–227. A value of 0.31 Å was chosen with consideration of the electronegativities of H, B, and Cu.

(16) *Chem. Soc., Spec. Publ.*, No. 11, M8 (1958).

(17) L. S. Bartell and B. L. Carroll, *J. Chem. Phys.*, 42, 1135 (1965).

(18) W. E. Palke and W. N. Lipscomb, *J. Chem. Phys.*, 45, 3948 (1966).

(19) D. S. Marynick and W. N. Lipscomb, *Inorg. Chem.*, 11, 820 (1972).

(20) D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 95, 7244 (1973).

(21) (a) B. A. Frenz and J. A. Ibers, "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, pp 66–69, and references therein; (b) F. A. Cotton, M. Jeremic, and A. Shaver, *Inorg. Chim. Acta*, 6, 543 (1972), and references therein; (c) K. M. Melmed, D. Coucouvanis, and S. J. Lippard, *Inorg. Chem.*, 12, 232 (1973); (d) K. M. Melmed, T. Li, J. J. Mayerle, and S. J. Lippard, *J. Amer. Chem. Soc.*, 96, 69 (1974).

(22) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 8, 2755 (1969).

(23) (a) S. J. Lippard and K. M. Melmed, *J. Amer. Chem. Soc.*, 89, 3929 (1967); (b) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 6, 2223 (1967).

(24) B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *Inorg. Chem.*, 6, 1979 (1967).

(25) M. F. Hawthorne and R. L. Pilling, *Inorg. Syn.*, 9, 16 (1967).

(26) M. F. Hawthorne, R. L. Pilling, and P. F. Stokely, *J. Amer. Chem. Soc.*, 87, 1893 (1965).

The product was washed with 50 ml of acetonitrile, two 100-ml aliquots of ethanol, and finally 100 ml of diethyl ether.

The compound was recrystallized from methylene chloride–hexane solution to yield small colorless blocks (yield 4.30 g, 81%; mp 220–222°, sealed tube, uncorrected). *Anal.* Calcd for $C_{72}H_{70}B_{10}Cu_2P_4$: C, 66.80; H, 5.47; B, 8.35; Cu, 9.82; P, 9.57. Found: C, 66.47; H, 5.56; B, 8.22; Cu, 9.51; P, 9.18. Infrared spectrum (cm^{-1}, Nujol mull): 3090 (m), 2500 (s), 2490 (s), 2480 (s), 2410 (m), 2325 (br), 2230 (br), 1480 (s), 1430 (s), 1320 (w), 1180 (m), 1160 (m), 1100 (s), 1070 (w), 1035 (m), 1010 (m), 925 (w), 850 (w), 750 (vs), 695 (vs). The 80.5-MHz ^{11}B nmr spectrum (in CH_2Cl_2) displayed a doublet at +1.19 ppm (130 ± 20, 1)[27] and a broad singlet at +25.8 ppm (4).[27]

Acknowledgment. The authors wish to thank the Office of Naval Research for its generous support of this research. The award of an NSF traineeship (to T. E. P.) and an NSF fellowship (to L. D. B.) is gratefully acknowledged.

Registry No. $Cu^I{}_2B_{10}H_{10}$, 52322-30-2; $Cu^I{}_2B_{10}D_{10}$, 52322-31-3; PPh_3, 603-35-0; $[(PPh_3)_2Cu^I]_2B_{10}H_{10}$, 52306-14-6.

[27] The first number in parentheses lists the magnitude of J_{B-H} in Hz; the single integer specifies relative area. The chemical shift given is relative to external $BF_3 \cdot OEt_2$.

Contribution from the Chemistry Division,
Argonne National Laboratory, Argonne, Illinois 60439,
and the Department of Chemistry, Rosary College,
River Forest, Illinois 60305

Kinetic Study of the Reduction of Americium(VI) by Neptunium(V)[1]

Mary Woods[2a] and James C. Sullivan*[2b]

Received May 17, 1974 AIC40318E

The empirical form of the rate law for the reduction of Am(VI) by Np(V) in aqueous perchlorate media at 25°, $I = 1.0$ *M*, and $0.10\ M < [H^+] < 1.0\ M$, is $-d[Am(VI)]/dt = k'[Am(VI)][Np(V)]$ where $k' = 2.45 \pm 0.04 \times 10^4\ M^{-1}\ sec^{-1}$. The variation of k' with ionic strength and temperature is presented and values calculated for $\Delta H^* = 6.66 \pm 0.08$ kcal/mol and $\Delta S^* = -16.22 \pm 0.27$ eu. The dynamic parameters are compared with those previously reported for the Np(VI)–(V) electron transfer reaction.

There is a variety of evidence consistent with the formulation that the oxo cations of the 5f transition series are isostructural.[3] In particular, the +5 and +6 oxidation states of Am and Np exist as the aquo $O\text{-}M\text{-}O^{+,2+}$ ions in aqueous perchloric acid solutions. The formal potentials of these VI–V couples vary significantly from 1.6 V for Am to 1.14 V for Np.[4]

This note presents the results obtained in a kinetic study of the reaction

$$Am(VI) + Np(V) = Am(V) + Np(VI) \qquad (1)$$

Two of the considerations that prompted this investigation are (a) to determine the effect on the kinetic parameters for reactions of the type noted above when there is a marked difference in the ΔF° values for the respective reactions and (b) to increase the limited knowledge of the reactivity pattern of the oxidant,[5] Am(VI).

Table I. Rate Parameters for the Reaction Am(VI) + Np(V)[a]

$10^4[Am(VI)]_0, M$	$10^3[Np(V)]_0, M$	No. of expts	$10^{-4}k',^b\ M^{-1}\ sec^{-1}$
6.00	1.41	8	2.679 ± 0.069
9.82	1.41	6	2.486 ± 0.119
5.81	3.108	11	2.626 ± 0.014
8.74	2.059	10	2.281 ± 0.043
14.23	0.723	10	2.309 ± 0.068
7.86	1.554	10	2.384 ± 0.040[c]

[a] Temperature 25.0 ± 0.05°, ionic strength 1.0 *M*, and $[H^+] = 0.98\ M$. [b] Uncertainties calculated for 95% confidence level. [c] $[H^+] = 0.10\ M$.

Table II. Temperature Dependence of k'^a

Temp (±0.05°), °C	$10^{-4}k',^b\ M^{-1}\ sec^{-1}$	No. of expts
2.27	0.853 ± 0.0083	30
14.1	1.355 ± 0.023	32
25.0	2.454 ± 0.040	55[c]
36.2	4.012 ± 0.043	15

[a] $[H^+] = 0.98\ M$ and ionic strength 1.0 *M*. [b] Initial concentrations of Am(VI) and Np(V) covered same range as in Table I. [c] Includes experiments at $[H^+] = 0.10\ M$.

Table III. Ionic Strength Dependence of k'^a

I, M	$10^4[Am(VI)]_0, M$	$10^3[Np(V)]_0, M$	$[H^+], M$	No. of expts	$10^{-4}k,\ M^{-1}\ sec^{-1}$
0.10	8.38	1.483	0.08	10	0.964 ± 0.011
0.65	4.74	2.35	0.63	8	2.081 ± 0.056
1.00	5.81–14.23	0.723–3.11	0.98	55	2.454 ± 0.040
1.5	7.10	1.483	0.08	11	2.895 ± 0.059
2.0	7.31	1.483	0.08	5	3.865 ± 0.097

[a] Temperature 25.0°; ionic strength varied with $LiClO_4$.

Experimental Section

Reagents. The neptunium(V), americium(VI), and lithium perchlorate and perchloric acid solutions were prepared and standardized as described previously.[5,6]

Kinetic Procedures. A Durrum stopped-flow spectrophotometer was used for the dynamic investigations by monitoring the change in absorbance at 350 nm due to the disappearance of Am(VI). The output from the Durrum instrument was stored in a Biomation 802 transient recorder which was interfaced with a Xerox Sigma V digital computer and the data analysis was carried out as previously described.[5]

Results and Discussion

The formal potentials of the relevant couples provide necessary evidence that reaction 1 will go to completion as written. To demonstrate that unwanted side reactions are not occurring under the experimental conditions used, the value of 0.0097 was obtained for $\{\Delta[Np(V)]_{calcd} - \Delta[Np(V)]_{obsd}\}/\Delta[Np(V)]_{calcd}$ at 25°, 0.96 *M* $HClO_4$, and initial $[Am(VI)] = 5.58 \times 10^{-4}\ M$ and $[Np(V)] = 8.082 \times 10^{-4}\ M$.

The data presented in Table I provide the basis for the empirical form of the rate law

$$-d[Am(VI)]/dt = k'[Am(VI)][Np(V)] \qquad (2)$$

It should be noted that the data presented provide no evidence for a kinetic path dependent upon hydrogen ion concentration.

In Table II the variation of the rate parameter as a func-

---

[1] Investigation conducted under the auspices of the U. S. Atomic Energy Commission.

[2] (a) Rosary College. (b) Argonne National Laboratory.

[3] C. Keller, "The Chemistry of the Transuranium Elements," G. E. Spandel, Nuremberg, 1971.

[4] G. Charlot, A. Collumeau, and M. J. Marchon, "Selected Constants and Oxidation-Reduction Potentials of Inorganic Substances in Aqueous Solution," Butterworths, London, 1971.

[5] M. Woods and J. C. Sullivan, *J. Inorg. Nucl. Chem.*, **36**, in press.

[6] R. C. Thompson and J. C. Sullivan, *J. Amer. Chem. Soc.*, **89**, 1096 (1967).