LBL-10855 c.2
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BONDING IN METAL-BOROHYDRIDE COMPLEXES

Norman Edelstein

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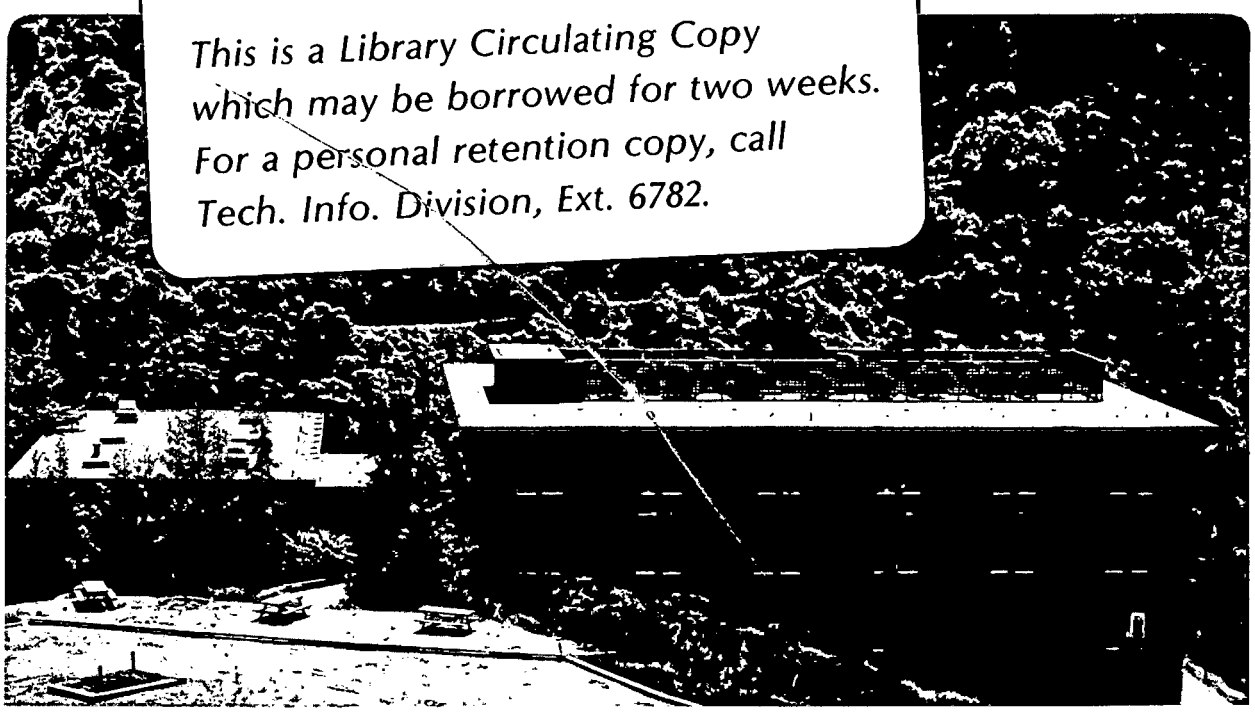

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

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LBL 10855

Bonding in Metal-Borohydride Complexes

Norman Edelstein

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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The borohydride ligand has been shown in various structural studies to bond to a wide variety of metal ions via bidentate,[1-23] tridendate,[10,16,21-31] and (in one instance) monodentate hydrogen bridges.[32] Vibrational spectroscopy also provides data which can be used to determine the metal-borohydride coordination geometry in a large number of compounds.[33,34] Bernstein et al.,[21] in their discussion of the neutron diffraction structure of $U(BH_4)_4$, which has both double and triple-hydrogen-bridged metal boron bonds, proposed using the metal-boron bond length as a criterion for determining whether the metal ion is bonded by two or three bridging hydrogen atoms to the boron atom. This idea implies one can assign an ionic radius to the borohydride ion. Bernstein et al. determined the values ∿1.3Å and ∿1.6Å for the ionic radii of triple hydrogen bridge and a double hydrogen bridge BH_4^- groups, respectively.

Raymond and coworkers[35,36] have recently systematized the structural criteria for ionic bonding in $(C_5H_5)^-$, $(C_8H_8)^=$ and $N[Si(CH_3)_3]_2^-$ metal complexes and have followed Pauling's approach[37] to calculate corrections for differences in coordination number for a particular ion. Following Raymond's criteria we have correlated the structural data for doubly and

triply hydrogen bridged metal-boron bonds with ionic radii for the metal ions obtained from Shannon's table.[38]

Table 1 and Table 2 list the available data for the compounds structurally characterized. The ionic radii as given in Tables 1 and 2 were obtained from Shannon's table for the particular oxidation state of the metal ion with the coordination number closest to that found in the metal-borohydride complex. Corrections for coordination number were made as described by Raymond.[35] Plots of ionic radius vs. metal-boron distance are shown in Figures 1 and 2.

The lines in Figures 1 and 2 represent a linear least squares fit to the data which were all assigned equal weight. For bidentate coordination the slope was equal to .97 with a correlation coefficient of .98. Note that both types of bidentate coordination (polymeric type and with terminal H atoms) were included in Figure 1 and Table 1. For tridentate coordination (Figure 2, not including the Th point), the slope was equal to 1.02 with a correlation coefficient of .94.

Considering the uncertainties in the metal ion-boron bond lengths, the different methods, temperatures, and phases for which structures were determined, the large range of coordination number and of the periodic table covered, plus the variety of other ligands attached to the metal atom, the correlation between ionic radius and the metal-boron bond length is remarkably good. For most molecules the metal-boron bond distance can be calculated with reasonable accuracy using the ionic bonding model. Clearly, it is not possible to draw conclusions about covalent bonding between the metal atom and the borohydride group solely from structural considerations based on the metal-boron distance.

The one compound which does not fit this correlation is $[((CH_3)_3Si)_2N]_3ThBH_4$.[28] The Th ion is formally six coordinate in this molecule, and the ionic radius obtained for the triple-hydrogen bridged BH_4^- group (unambiguously assigned from the infra-red spectrum)[28] is much too large (Figure 2). The bistrimethylsilylamide group is an extremely bulky ligand which is known to form low coordination number complexes with metal ions of large ionic radii such as the lanthanides.[39] Although this ligand acts in a monodentate manner, it appears to have a much larger effective coordination number due to its steric bulk. From Figure 2 one can extrapolate an effective coordination number $\geqslant 12$ for the Th ion in $[((CH_3)_3Si)_2N]_3ThBH_4$.

From the present tabulation it appears that an ionic radius of $\sim 1.6 \pm .1$Å can be assigned to the borohydride ligand when it forms a bidentate bridge to the metal atom, and $\sim 1.36 \pm .06$Å when it forms a tridentate bridge to the metal atom. The difference in energy between the various possible modes of bonding is small and the coordination number of the metal ion and the steric hindrance by other ligands appear to determine which mode of attachment will prevail for the borohydride ligand.

I would like to thank D.H. Templeton, S.J. Simpson, R.A. Andersen, A. Zalkin, and K.N. Raymond for helpful discussions.

This work was supported by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. W-7405-Eng-48.

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TABLE 1

Compounds with Metal-Boron Bidentate Hydrogen Bridges

Compound	M^{Z+} Coord. No.	M^{Z+} IR(Å)[a]	M-B(Å)	$(BH_4)^-$ IR(Å)[b]	Ref.	Comments[c]
$Be(BH_4)_2$	6	.45	1.918(4)	1.47	1	RT,X-ray,crys.
$Be(BH_4)_2$	6	.45	2.001(4)(db)[d]	1.55	1	RT,X-ray,crys.
$[(CH_3)_3CO]Be_3(BH_4)_2$	4	.27	1.93(1)	1.66	2	RT,X-ray,crys.
B_2H_6	4	.11	1.775(3)	1.67	3	25°C,ED,gas
B_2H_6	4	.11	1.776(10)	1.67	4	-190°C,X-ray,crys.
$Al(BH_4)_3$	6	.535	2.143(3)	1.61	5	20°C,ED,gas
$Al(BH_4)_3 \cdot NH_3$	7	.58	2.229(8)	1.65	6	RT,X-ray,crys.
$Al(BH_4)_3N(CH_3)_3$	7	.58	2.24(1)	1.66	7	-160°C,X-ray,crys.
$Al(BH_4)_3N(CH_3)_3$	7	.58	2.19(2)	1.61	7	25°C,X-ray,crys.
$[Al(BH_4)_2N(CH_2)_2]_2$	6	.535	2.19(1)	1.66	8	RT,X-ray,crys.
$Al(BH_4)(CH_3)_2$	4	.39	2.128(8)	1.74	9	RT,ED,gas
$Sc(BH_4)_3(OC_4H_8)_2$	10	.95	2.551(5)	1.60	10	RT,X-ray,crys.
$(C_5H_5)_2Ti(BH_4)$	8	.76	2.37(1)	1.61	11	23°C,X-ray,crys.
$(C_5H_5)_2Ti(BH_4)$	8	.76	2.31(4)	1.55	12	RT,ED,gas
$Co(p_3)(BH_4)$[e]	5	f	2.21(3)		13	22°C,X-ray,crys. Co^+,high spin d^8
$[CoH(BH_4)\{P(C_6H_{11})_3\}_2]$	5	.59	2.13(1)	1.54	14	RT,X-ray,crys. Co^{2+},low spin d^7
$[(C_6H_5)_3P]_2Cu(BH_4)$	4	.64	2.184(9)	1.54	15	RT,X-ray,crys.

Table 1 (continued)

Compound	M^{Z+} Coord. No.	M^{Z+}IR(Å)	M-B(Å)	$(BH_4)^-$IR(Å)	Ref.	Comments
$Ga(BH_4)(CH_3)_2$	4	.47	2.163(8)	1.69	9	RT,ED,gas
$Y(BH_3)_3(OC_4H_8)_3$	11	1.14	2.68(2)	1.54	16	23°C,X-ray,crys.
$(C_5H_5)_2Nb(BH_4)$	8	.81	2.26(6)	1.45	17	RT,X-ray,crys.
$\{[(C_6H_5)_3P]_2N\}\{Mo(CO)_4BH_4\}$	6	f	2.413(20)		18	RT,X-ray,crys.
$MoH(BH_4)(P(CH_3)_3)_4$	6	f	2.468(12)		19	RT,X-ray,crys.
$(CH_3C_5H_4)_2Hf(BH_4)_2$	10	.89	2.553(6)	1.66	20	RT,ND,crys.
$U(BH_4)_4$	14	1.22	2.86(4)(db)	1.64	21	RT,ND,crys.
$U(BH_4)_4 \cdot O(C_2H_5)_2$	14	1.22	2.89(1)	1.67	22	21°C,X-ray,crys.
$U(BH_4)_4 \cdot O(CH_3)_2$	14	1.22	2.89(1)	1.67	22	23°C,X-ray,crys.
$[U(BH_4)_4 \cdot O(n\text{-}C_3H_7)_2]_2$	13	1.20	2.90(4)(db)[g]	1.70	23	22°C,X-ray,crys.
$[U(BH_4)_4 \cdot O(n\text{-}C_3H_7)_2]_2$	14	1.22	2.84(5)(db)[g]	1.62	23	22°C,X-ray,crys.

a. From Shannon (Ref. 35) corrected for coordination no.; IR = ionic radius.

b. Obtained by subtraction of column 3 from column 4.

c. RT, room temperature; x-ray, x-ray diffraction; ND, neutron diffraction; ED, electron diffraction; crys, single crystal; gas, gaseous sample.

d. All metal bidentate hydrogen boron bridges have two terminal hydrogen atoms unless (db = double bridge) indicated.

e. p_3 = 1,1,1-tris (diphenylphosphinomethyl) ethane.

f. Ionic radius not available from Shannon.

g. Unsymmetrical dimer with one double bridge bidentate borohydride group between the U atoms.

TABLE 2

Compounds with Metal-Boron Tridentate Hydrogen Bridges

Compound	M^{Z+} Coord. No.	M^{Z+} IR(Å)[a]	M-B(Å)	$(BH_4)^-$ IR(Å)[b]	Ref.	Comments[c]
$Sc(BH_4)_3(OC_4H_8)_2$	10	.95	2.33(1)	1.38	10	RT.X-ray,crys.
$[C_5H_5TiCl(BH_4)]_2$	8	.76	2.17(1)	1.41	24	RT.X-ray,crys.
$Y(BH_4)_3(OC_4H_8)_3$	11	1.14	2.58(1)	1.44	16	23°C,X-ray,crys.
$Zr(BH_4)_4$	12	.98	2.308(10)	1.33	25	RT,ED,gas
$Zr(BH_4)_4$	12	.98	2.34(3)	1.36	26	-160°C,X-ray,crys.
$Hf(BH_4)_4$	12	.95	2.28(1)	1.33	27	ND,crys.
$U(BH_4)_4$	14	1.22	2.52(1)	1.30	21	RT,ND,crys.
$Th[N(Si(CH_3)_3)_2]_3BH_4$	6	.94	2.61(3)	1.67	28	22°C,X-ray,crys.
$(C_5H_5)_2U(BH_4)_2$	12	1.17	2.61(8)	1.44	29	RT,X-ray,crys.
$U(BH_4)_4(OC_4H_8)_2$	14	1.22	2.56(4)	1.34	30	23.5°C,X-ray,crys.
$U(BH_4)_4 \cdot O(C_2H_5)_2$	14	1.22	2.53(2)	1.31	22	21°C,X-ray,crys.
$U(BH_4)_4 \cdot O(CH_3)_2$	14	1.22	2.53(2)	1.31	22	23°C,X-ray,crys.
$[U(BH_4)_4 \cdot O(n\text{-}C_3H_7)_2]_2$[d]	13	1.20	2.51(5)	1.31	23	22°C,X-ray,crys.
$[U(BH_4)_4 \cdot O(n\text{-}C_3H_7)_2]_2$[d]	14	1.22	2.52(5)	1.30	23	22°C,X-ray,crys.
$Np(BH_4)_4$	12	1.10	2.46(3)	1.36	31	-143°C,X-ray,crys.

a. From Shannon (Ref. 35) corrected for coordination no.; IR = ionic radius.

b. Obtained by subtraction of column 3 from column 4.

c. RT, room temperature; x-ray, x-ray diffraction; ND, neutron diffraction; ED, electron diffraction; crys, single crystal; gas, gaseous sample.

d. Unsymmetrical dimer.

Figure Captions

Figure 1. Metal ionic radius vs. M-B bond length for compounds with metal-boron bidentate hydrogen bridges.

Figure 2. Metal ionic radius vs. M-B bond length for compounds with metal-boron tridentate hydrogen bridges.

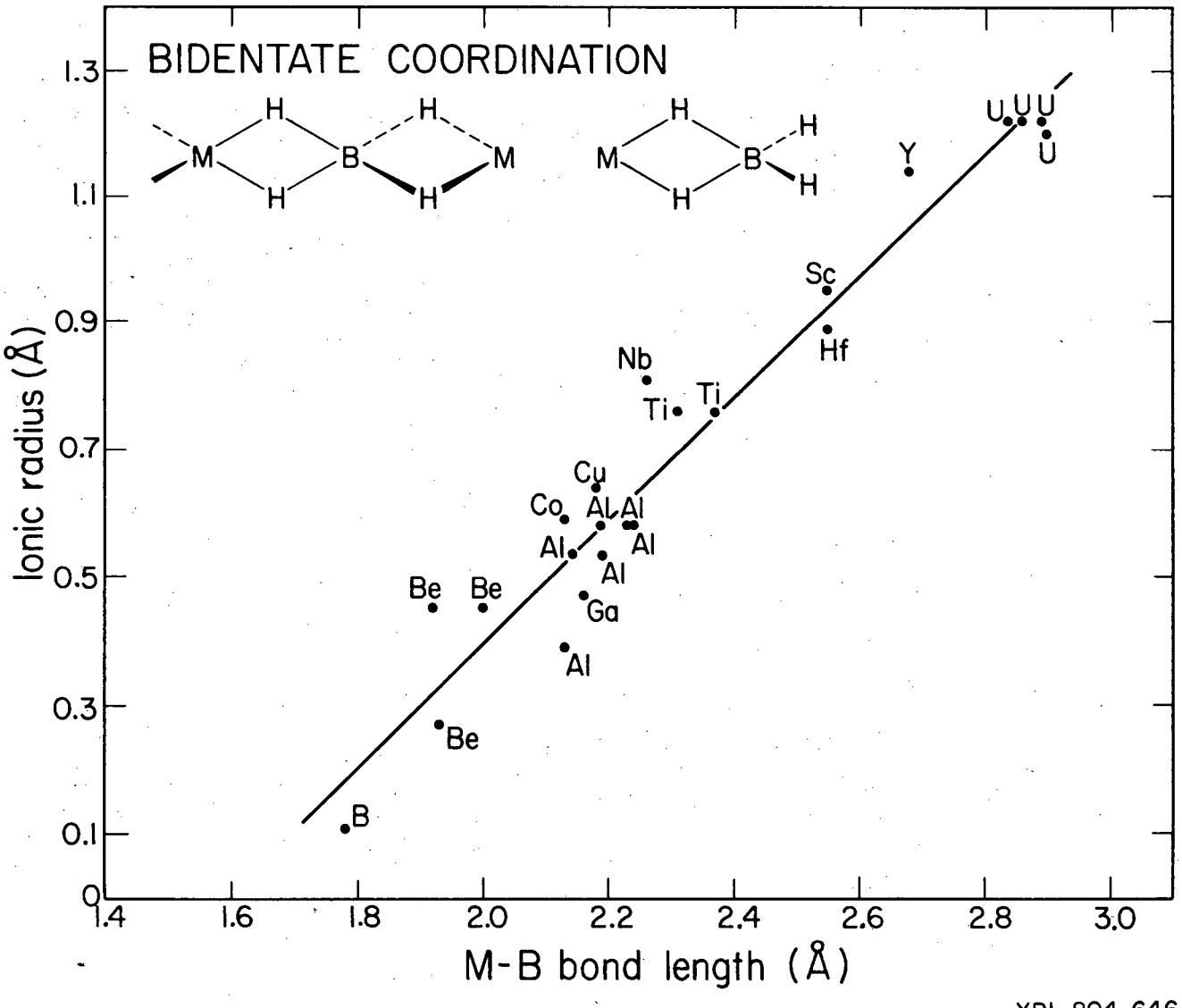

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Figure 1

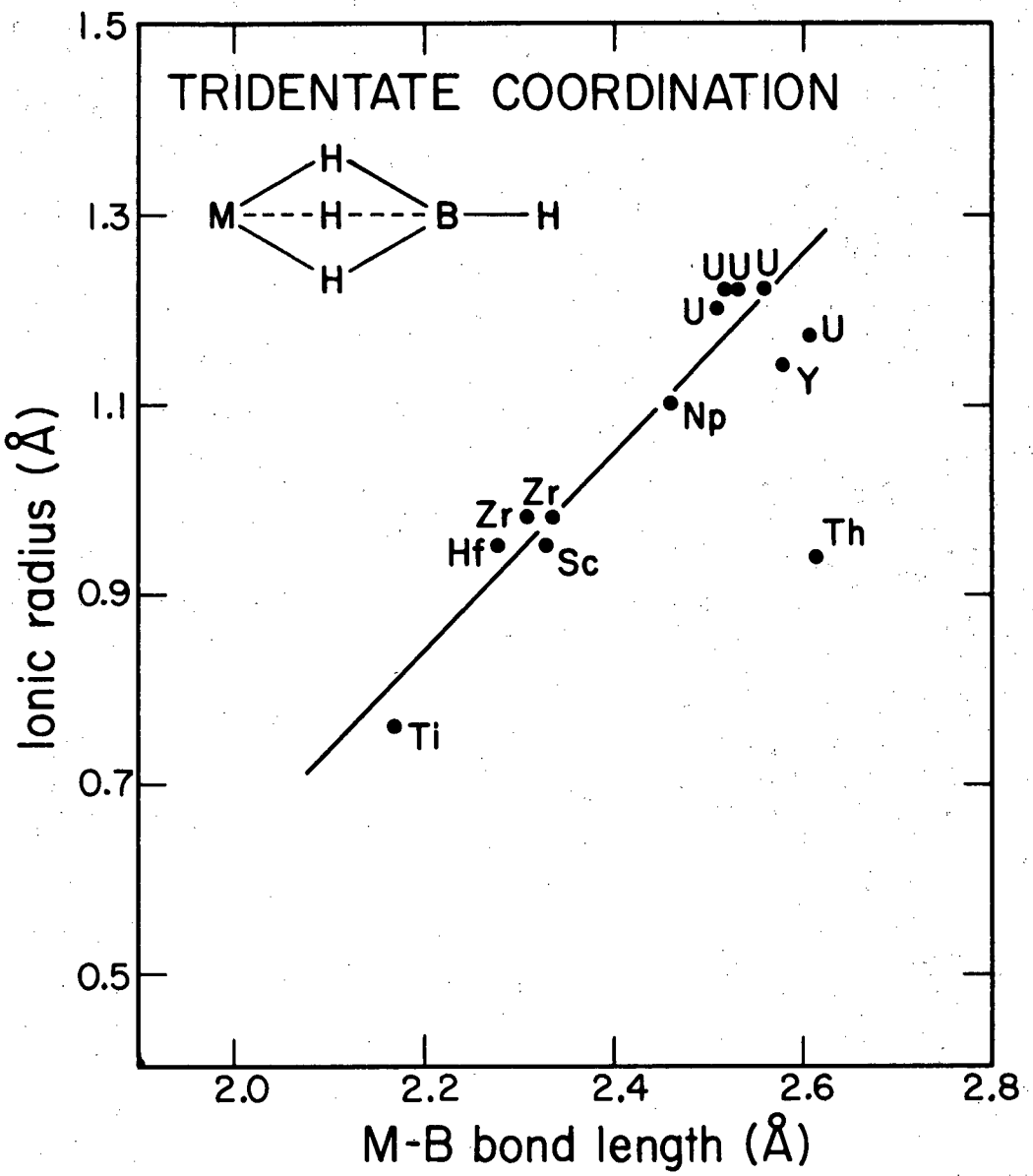

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Figure 2.

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