control of the geometry, and sulfur–sulfur bonding interactions may dominate the structure.

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14-Coordinate Uranium(IV). The Structure of Uranium Borohydride by Single-Crystal Neutron Diffraction[1]

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The structure of $U(BH_4)_4$ has been refined by a single-crystal neutron diffraction study. The X-ray structure (tetragonal, $P4_32_12$ ($P4_12_12$), $a = 7.49$ (1) Å, $c = 13.24$ (1) Å, $Z = 4$, $\rho_{calcd} = 2.66$ g/cm^3) has been confirmed and, in addition, all hydrogen atoms have been located to a precision of 0.04 Å. Four of the six BH_4^- ions surrounding each uranium atom are attached to it by two hydrogen atoms, and use their remaining two hydrogen atoms to bridge neighboring uranium atoms in a helical polymeric structure. Two additional tetrahydroborate groups in a cis configuration are bonded to the uranium atom by three hydrogen atoms, resulting in an overall coordination number of 14. The mean U–H bond length is 2.38 (2) Å. The BH_4^- ions are approximately tetrahedral with a mean B–H distance (corrected for thermal motion) of 1.29 (4) Å. A capped hexagonal antiprism is considered to be a useful reference coordination polyhedron, and distortions from this idealized geometry are described. The difference between the solid-state structures of $Zr(BH_4)_4$ and $U(BH_4)_4$ are discussed in terms of sphere packing and molecular orbital considerations. The results have also been used in conjunction with diffraction data on other metal tetrahydroborate compounds and with tabulated ionic radii to develop a single and consistent picture in which the metal–boron distance is shown to correlate with the geometry of the metal borohydride attachment.

Introduction

Knowledge of the molecular geometry of metal tetrahydroborate complexes is required for the interpretation of their physical and chemical properties. Of special interest is the mode of attachment of the BH_4^- group to the central metal ion, in particular, whether there are one, two, or three hydrogen atoms in the bridge bonds. To date, X-ray diffraction studies have established a two-point attachment for bis(tetrahydroborato)beryllium(II),[4] tetrahydroboratobis(triphenylphosphine)copper(I),[5] tris(tetrahydroborato)trimethylaminealuminum(III),[6] and tetrahydroboratobis(h^5-cyclopentadienyl)titanium(III),[7] while electron diffraction results imply a similar bonding mode for tris(tetrahydroborato)aluminum(III).[8] Only tetrakis(tetrahydroborato)zirconium(IV) has been reported as having three hydrogen bridge bonds between the central transition metal atom and boron. This geometry has been suggested both by single-crystal X-ray diffraction[9] and gas-phase electron diffraction[10] studies.

The investigation of the crystal structure of uranium borohydride by X-ray[11] and neutron diffraction techniques was motivated by two basic considerations. First, knowledge of the geometry of the U–BH_4 attachment was desired in conjunction with the analysis of the spectroscopic properties of $M(BH_4)_4$ compounds, M = Zr, Hf, U, Th.[12] The need for sound structural data, in which the positions of all atoms are unambiguously located, is underscored by past difficulties with vibrational analyses of $M(BH_4)_4$ molecules.[13] For example, $Zr(BH_4)_4$ (12-coordinate, T_d symmetry, four BH_4^- groups having a three-point attachment)[9,10] and $U(BH_4)_4$ (14-coordinate, C_2 symmetry, four BH_4^- groups having a two-point and two BH_4^- groups having a three-point attachment, *vide infra*)[11] have been assumed on the basis of infrared data to be isostructural.[13,14] Thus, when dealing with such systems as $M(BH_4)_4$, knowledge of the molecular geometry is especially useful, perhaps even necessary, for the interpretation of vibrational data. Second, optical and electron paramagnetic resonance spectroscopic results on $U(BH_4)_4$ are now available[15] and their analysis depends in part on exact structural details.

A report of the single-crystal X-ray diffraction study of $U(BH_4)_4$ has already appeared.[11,16] The crystal

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structure was determined to be tetragonal, space group $P4_32_12$ ($P4_12_12$), $a = 7.49$ (1) Å, $c = 13.24$ (1) Å, $Z = 4$, $\rho_{calcd} = 2.66$ g/cm³, uranium site symmetry 2. A surprising feature of the structure revealed by the X-ray diffraction study is that each uranium atom is surrounded by six boron atoms, two of which (in a cis configuration) are 2.53 Å from a single uranium atom and four of which are approximately equidistant from two uranium atoms with an average U–B distance of 2.87 Å. These latter bridging tetrahydroborate groups serve to link the uranium atoms in a polymeric structure, with individual members of the interlocking helical chains related by a fourfold screw axis. While no hydrogen atoms could be located, it was guessed that the bridging BH_4^- were symmetrically bonded to two uranium atoms by two-point attachments, as in $Be(BH_4)_2$,[4] and that the terminal groups were also bonded through two hydrogen atoms. As described in the present report, a neutron diffraction investigation confirms the geometry proposed for the bridging tetrahydroborate ligands, but shows the terminal BH_4^- groups to be coordinated by three-point attachment.

Experimental Section

Uranium borohydride was prepared according to the method of Schlesinger and Brown[17] from uranium tetrafluoride (Research Inorganic) and aluminum borohydride, previously prepared from aluminum chloride (Rocky Mountain Research) vacuum sublimed onto lithium borohydride (Alfa) following Schlesinger, *et al.*[18] All preparations and purifications (by fractional sublimation) were done in a grease-free vacuum system. Products were stored under vacuum and resublimed before use.

Dark green crystals having well developed faces were grown from the vapor. A polycrystalline mass in one end of an evacuated Pyrex tube was warmed to ~35°, and single crystals of various sizes were deposited at the other, room temperature, end of the tube. Crystal size and shape were found to be dependent on growth rate and temperature gradient, many attempts being necessary to obtain good quality crystals of proper size for the neutron diffraction study. The tabular crystal used for data collection was bounded by faces of the form {001}, {110}, and {101} giving the appearance of a truncated octahedron; the maximum dimensions were approximately 2 × 2 × 1 mm. Accurate microscopic measurement of the faces gave a calculated volume of 1.82 mm³.

In a nitrogen-purged glove bag, the crystal was mounted on an aluminum pin using Varian Torr Seal epoxy resin. (Torr Seal was chosen for its solventless hardening process and its apparent lack of reactivity toward $U(BH_4)_4$.) The crystal was mounted with the [110] direction parallel to the diffractometer φ axis and was then covered with a thin walled quartz cap to prevent decomposition due to atmospheric water and oxygen. Inspection after termination of data collection (a period of about 3 weeks) revealed no visible crystal decomposition or discoloration.

The crystal was mounted on a computer-controlled four-circle diffractometer[19] at the Brookhaven National Laboratory high-flux beam reactor. Initial scans of Bragg reflections indicated that the mosaic spread of the crystal was rather large (full width at half maximum about 2°)—too large for our usual θ–2θ scans to provide reliable integrated intensities. A detector aperture was chosen which allowed integration over the wavelength spread and divergence of the incident beam, and data were collected using ω scans with a fixed detector. The length of the scan was 4° and the diffracted intensity was measured at steps of 0.1° in ω. Examination of the profiles indicated that this procedure was adequate for all data and that a proper evaluation of the background could be obtained by averaging the five points at each end of the scan and assigning the 31 central points to the peak. The neutron wavelength was 1.014 (1) Å monochromatized by reflection from the (220) plane of a germanium single crystal. The neutron flux at the $U(BH_4)_4$ crystal was approximately 5×10^6 cm^{-2} sec^{-1}. A total of 543 scans of Bragg reflections were made out to a scattering angle of $2\theta = 90°$ ($(\sin\theta)/\lambda = 0.7$). Reflections were not scanned if a preliminary check indicated that the net intensity at the peak position was less than the estimated standard deviation based on counting statistics for a count of 20 sec. Background counting rates were about 400 cpm.

All observable reflections with h, k, and l all positive, as well as a small number with h negative, were scanned. In the absence of anomalous scattering, $|F(hkl)| = |F(khl)|$ for point group 422; but due to the anomalous scattering of boron, this condition does not obtain for this compound. The 543 reflections included 19 measurements of (402) and (32$\bar{2}$) made at regular intervals. These measurements showed there was no systematic intensity change with time. The agreement among replicated measurements was consistent with Poisson counting statistics. The data were corrected for absorption using a Gaussian grid integration procedure and a linear absorption coefficient of 12.54 cm^{-1} (based on a cross section for pure absorption of 428×10^{-24} cm^2 for natural boron[20] and 40×10^{-24} cm^2 for incoherent scattering of hydrogen). Transmission coefficients ranged from 0.21 to 0.43. Equivalent reflections were averaged to produce 403 independent reflections, 80 of which had been observed more than once. The agreement among these reflections was such that $\Sigma|F_1^2 - F_2^2|/\Sigma^1/_2(F_1^2 + F_2^2) = 0.153$ and $[\Sigma w(F_1^2 - F_2^2)^2/(^1/_2)\Sigma w(F_1^2 + F_2^2)^2]^{1/2} = 0.081$ with weights w based on counting statistics. These values are larger than typical for high-quality neutron diffraction work but are indicative of the low intensities for this crystal. Space group extinct reflections were scanned, and there were no violations of the space group as determined by X-rays.

A structure factor calculation for 172 observed reflections with $|F_o| > 0$ and $(\sin\theta)/\lambda < 0.5$ using the uranium and boron coordinates from the X-ray study, followed by one cycle of scale factor refinement, led to a value of $R(F) = 0.44$. The phases from this structure factor calculation were used with the observed structure amplitudes to calculate both a ρ_{obsd} map and a ($\rho_{obsd} - \rho_{calcd}$) map. The maximum positive scattering density in the $\Delta\rho$ map was 1.5 fm Å^{-3}. There were 11 negative peaks of greater amplitude (maximum 2.6 fm Å^{-3}). Of these, eight corresponded to reasonable hydrogen positions. The other three were in chemically unreasonable positions.

A series of full-matrix least-squares refinements was carried out on the full data set of observed reflections (313 after elimination of space-group extinctions and reflections with observed net intensity less than zero). The weights were calculated as $w = 1/\sigma^2(F)$, $\sigma(F) = \sigma(F^2)/2F$, with $\sigma(F^2)$ being the larger of $[\sigma^2_{count} + (0.05F^2)^2]^{1/2}$ or the standard deviation based on the agreement among equivalent reflections (σ^2_{count} is the variance based on Poisson counting statistics). Position and general anisotropic thermal parameters for all atoms, together with a single scale factor, were refined. There was no evidence for extinction. Scattering lengths used were U, 8.5 fm; H, −3.72 fm; and B, 5.34 + 0.2 i fm.[21] An attempt was made to vary the real part of the B scattering length for the two atoms independently. The refined values were 4.9 (3) and 6.1 (4), not significantly different from the assumed value. To verify further some apparently anomalous B–H bond lengths, an idealized BH_4^- tetrahedron with B–H bond lengths of 1.25 Å was used as a starting point for another refinement. This refinement converged to a structure identical with that reported below.

In view of the boron anomalous scattering, it would in principle be possible to determine which enantiomorph was studied. The R factors for refinement in space groups $P4_32_12$ and $P4_12_12$ were not significantly different. An examination of 43 pairs (hkl) and (khl) for strong reflections indicated better agreement for $P4_12_12$, although a χ^2 test indicated satisfactory agreement between the observed and calculated differences, $F(hkl) - F(khl)$, for both assignments. The largest anomalous difference is (in space group $P4_12_12$) F_{calcd} (122) = 3.47, F_{obsd} (122) = 3.58 (15) and F_{calcd} (212) = 3.73, F_{obsd} (212) = 3.74 (15). Clearly the data are not

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Table I

Position and Thermal Parameters ($\times 10^4$ Å^2) for $U(BH_4)_4$[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	−0.0711 (11)	x	0	375 (36)	U_{11}	245 (53)	−110 (55)	−14 (35)	$-U_{13}$
	−0.06953 (8)	x	0	167 (2)	U_{11}	126 (4)	−17 (3)	−8 (4)	$-U_{13}$
B(T)	0.2108 (16)	−0.0798 (26)	−0.1039 (11)	255 (72)	578 (105)	577 (95)	−160 (71)	97 (67)	−115 (99)
	0.2128 (37)	−0.0771 (39)	−0.1063 (22)	Isotropic U = 329 (51)					
B(B)	−0.2038 (16)	−0.3445 (20)	−0.1257 (12)	233 (62)	398 (77)	628 (105)	−179 (62)	−94 (87)	40 (80)
	−0.2103 (38)	−0.3497 (32)	−0.1267 (21)	Isotropic U = 393 (51)					
H(1)	0.3751 (29)	0.3490 (41)	0.3816 (24)	249 (102)	1514 (265)	1405 (234)	−144 (125)	−429 (156)	383 (227)
H(2)	0.1460 (29)	0.4469 (33)	0.3149 (14)	572 (137)	802 (157)	364 (99)	62 (138)	−19 (91)	372 (115)
H(3)	0.1479 (34)	0.3686 (29)	0.4586 (21)	970 (206)	462 (132)	939 (179)	−171 (114)	349 (161)	−53 (141)
H(4)	0.1764 (33)	0.1782 (25)	0.3432 (20)	1589 (227)	315 (125)	647 (155)	−116 (147)	−61 (152)	−47 (110)
H(5)	0.0101 (36)	0.0894 (37)	0.1464 (16)	1450 (280)	863 (183)	723 (150)	222 (192)	−517 (165)	29 (166)
H(6)	0.2874 (36)	0.3437 (34)	0.1587 (17)	415 (126)	1005 (218)	517 (126)	−287 (149)	−507 (264)	164 (120)
H(7)	0.4986 (35)	0.2694 (28)	0.2362 (19)	1073 (277)	828 (186)	710 (159)	304 (137)	−459 (152)	−681 (150)
H(8)	0.4214 (36)	0.1468 (30)	0.0981 (19)	790 (152)	699 (162)	985 (194)	−440 (130)	551 (148)	−612 (138)

[a] Neutron parameters for U and B on first line, X-ray parameters on second. The anisotropic temperature factor is expressed as $\exp[-\Sigma_{ij} 2\pi^2 a_i^* a_j^* h_i h_j U_{ij}]$.

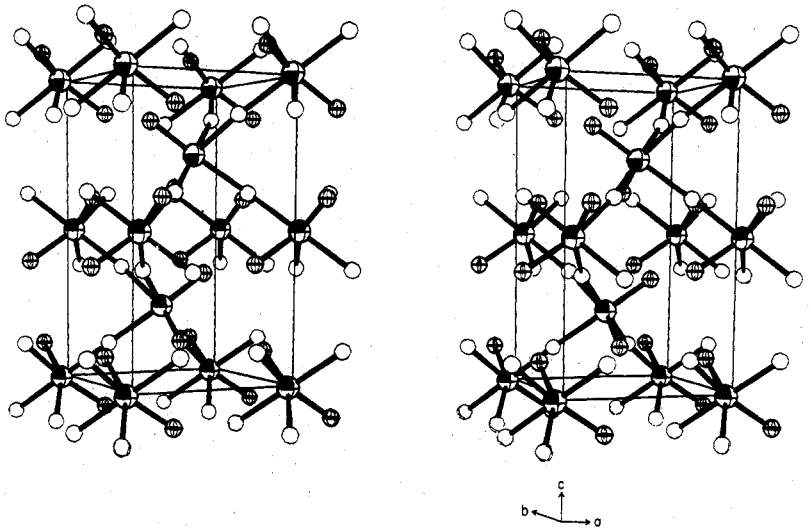

Figure 1.—Stereoscopic unit cell packing diagram for $U(BH_4)_4$. Fourfold screw axes parallel to c intersect the ab plane at ($1/2$, 0) and (0, $1/2$). Lines connecting the uranium (large spheres) and boron atoms are drawn to illustrate the U–BH_4 connectivity and are not meant to imply direct U–B bonding. Hydrogen atoms are not shown.

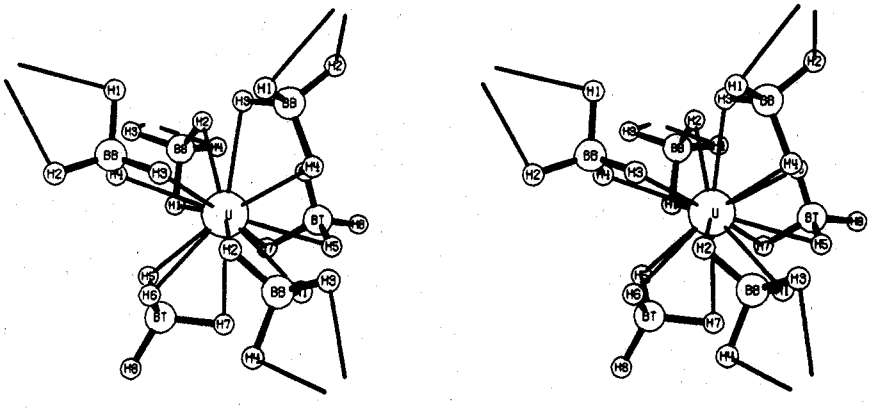

Figure 2.—Stereoscopic drawing of the $U(BH_4)_4$ site geometry. Hydrogen atoms bound to another uranium site are indicated by "dangling" bonds.

precise enough to discriminate between the two enantiomorphs, and in the ensuing discussion the structure is presented in space group $P4_32_12$ so that the results may be more easily compared with the reported X-ray structure. (Crystals of both chiralities undoubtedly exist.)

The statistical measures of fit are

$$R = \frac{\sum||F_o| - |F_c||}{\sum|F_o|} = 0.139$$

$$wR = \left[\frac{\sum w||F_o| - |F_c||^2}{\sum w|F_o|^2}\right]^{1/2} = 0.069$$

$$S = \left[\frac{\sum w||F_o| - |F_c||^2}{313 - 96}\right]^{1/2} = 1.01$$

in satisfactory agreement with the values expected on the basis of the agreement among equivalent reflections.

The refinement converged with shifts in the last least-squares

cycle being less than 0.1σ for all parameters. A final difference map showed no positive or negative peaks with amplitudes greater than 0.65 fm Å^{-3}. The estimated $\sigma(\rho)$ is 0.5 fm Å^{-3}. The average peak heights on a final observed scattering density map were 19.8, 11.9, −5.1 fm Å^{-3} for U, B, and H, respectively. The observed and calculated structure factors appear in the microfilm edition of this journal.[22a,22b]

Results and Discussion

The refined uranium and boron positions (Table I) do not differ significantly from the X-ray study (Figure 1), which is thus confirmed. The uranium parameters are less precise and the boron parameters more so than in the X-ray study. The omission of hydrogen atoms from the X-ray refinement did not bias the positions of the boron atoms.

14-Coordination.—The most striking result of the present investigation is that the uranium atoms are tetradecacoordinated (Figure 2). The four bridging BH_4^- groups provide two hydrogen atoms each to the coordination polyhedron of the uranium atom. There are two terminal BH_4^- groups, each of which forms three B–H···U bridge bonds. The remaining hydrogen atom on each terminal borohydride group does not participate in the bonding of the borohydride group to the uranium atoms. That the terminal BH_4^- ions are bonded to uranium very nearly along their threefold axes is indicated by the H(8)–B(T)–U angle of 177.0 (1.9). Because of the C_2 site symmetry at the uranium atom, all distances and angles occur in pairs, and the more interesting values are included in Table II.

This is the first case, to our knowledge, of tetradecacoordination in a complex molecular crystal, although 14-coordination is common in metallic phases.[23] One of the idealized polyhedra for 14-coordination is the capped hexagonal antiprism (Figure 3a). The coordination in our compound (Figure 3b and 3c) could be regarded as a distorted version of this figure. We regard the two H(6) atoms as forming the poles of the figure and the two H(1)–H(2)–H(3)–H(4)–H(5)–H(7) boat-like hexagonal rings as forming the hexagonal faces of the antiprism. The principal distortion is a bending up of part of the hexagonal ring [H(2)] toward the apical hydrogens. In addition the H(6)–U–H(6) angle is 157.8 (1.5) rather than 180°. A comparison of idealized and real angles and distances is given in Table II. The one factor which makes the connectivity inconsistent with the idealized figure is that in the quadrilateral H(2)–H(3)–H(3)–H(4), the idealized geometry would require the short contact to be the diagonal H(2)–H(3) = 3.53 Å, whereas in actuality the short contact is H(4)–H(3) = 3.00 Å. In our figure atoms H(6) and H(4) each have six hydrogen neighbors, H(2) has four and all others have five. In the idealized figure H(2) and H(4) each has five. Despite these distortions, we have found the description as a capped hexagonal antiprism to be useful.

That it is possible to obtain 14 atoms surrounding U and not around Zr or Hf may be due to the larger

(22) (a) Structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-3009. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche. (b) The computer programs used in this analysis have been described by E. O. Schlemper, W. C. Hamilton, and S. J. La Placa, *J. Chem. Phys.*, **54**, 3990 (1971).

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TABLE II

INTERATOMIC DISTANCES IN Å AND ANGLES (DEG) IN $U(BH_4)_4$[a]

A. Coordination of Borohydride Groups to Uranium[b]

1. Distances and Angles Involving Terminal BH_4^- Group

U–B(T)	2.52 (1)	B–H(5)–U	82 (1)
U–H(5)	2.36 (2)	B–H(6)–U	86 (1)
U–H(6)	2.34 (2)	B–H(7)–U	82 (1)
U–H(7)	2.33 (2)	B(T)–U–B(T)	110

2. Distances and Angles Involving Bridging BH_4^- Group

U–B(B)	2.90 (1)	B–H(1)–U	97 (2)
U–H(1)	2.44 (3)	B–H(2)–U	99 (1)
U–H(2)	2.46 (2)	B–H(3)–U	99 (1)
U–B(B)	2.82 (2)	B–H(4)–U	96 (2)
U–H(3)	2.36 (2)	B(B)–U–B(B)	81, 180,
U–H(4)	2.36 (2)		two at 83, two at 97

3. B(T)–U–B(B) Angles: two each at 87, 157, 79, 101

4. U–B(B)–U 165

B. H–H Distances and Angles Compared with Ideal Values for the Capped Hexagonal Antiprism with U–H Distance R[c]

1. Distances and Angles Involving the Apical Atom H(6)

H(6)–H(1)	3.02	H(1)–H(6)–H(2)	47
H(6)–H(2)	2.45	H(2)–H(6)–H(3)	48
H(6)–H(3)	2.64	H(3)–H(6)–H(4)	47
H(6)–H(4)	2.65	H(4)–H(6)–H(5)	63
H(6)–H(5)	1.89	H(5)–H(6)–H(7)	64
H(6)–H(7)	1.97	H(7)–H(6)–H(1)	48
Mean	2.44		53
Ideal	1.10R		49

2. Distances and Angles Around Hexagonal Prism Face

H(1)–H(2)	2.07	H(1)–H(2)–H(3)	126
H(2)–H(3)	2.06	H(2)–H(3)–H(4)	122
H(3)–H(4)	2.10	H(3)–H(4)–H(5)	106
H(4)–H(5)	2.45	H(4)–H(5)–H(7)	116
H(5)–H(7)	2.05	H(5)–H(7)–H(1)	128
H(7)–H(1)	2.23	H(6)–H(1)–H(2)	94
Mean	2.16		116
Ideal	0.92R		120

3. Hexagon-to-Hexagon Distances

H(3)–H(3)	2.57	H(1)–H(5)	1.94
H(3)–H(2)	3.53[d]	H(5)–H(7)	2.77
H(2)–H(4)	2.49	H(7)–H(7)	2.48
H(4)–H(1)	2.49	Mean[e]	2.61
		Ideal	0.92R

C. Geometry of the BH_4^- Groups[f] (see Figure 4)

	Apparent distance	Dist cor for thermal motion	Angles	
		1. Terminal (BH_4) Groups		
B(T)–H(5)	1.26 (3)	1.33 (4)	H(1)–B(B)–H(2)	113
B(T)–H(6)	1.09 (4)	1.10 (4)	H(1)–B(B)–H(3)	106
B(T)–H(7)	1.34 (3)	1.38 (4)	H(1)–B(B)–H(4)	102
B(T)–H(8)	1.24 (3)	1.28 (3)	H(2)–B(B)–H(3)	113
			H(3)–B(B)–H(4)	110
			H(3)–B(B)–H(4)	112
Mean	1.23 (5)	1.27 (6)		109.4
		2. Bridging (BH_4) Groups		
B(B)–H(1)	1.29 (3)	1.36 (3)	H(8)–B(T)–H(5)	113
B(B)–H(2)	1.18 (3)	1.22 (3)	H(8)–B(T)–H(6)	114
B(B)–H(3)	1.21 (3)	1.24 (4)	H(8)–B(T)–H(7)	111
B(B)–H(4)	1.33 (3)	1.38 (3)	H(5)–B(T)–H(6)	107
			H(5)–B(T)–H(7)	104
			H(6)–B(T)–H(7)	108
Mean	1.25 (4)	1.30 (4)		109.6

[a] Estimated standard deviations in last significant figure are in parentheses unless otherwise indicated. [b] See Figures 2 and 4 for numbering. [c] Esd are 0.04 for distance and 2° for angles (see Figure 3). [d] This is the long diagonal of a rhombic face. The short diagonal is H(3)–H(4) 3.00. Use of the long diagonal makes the connectivity identical with that of the idealized figure. [e] These figures imply a stretching of the antiprism along the $\bar{1}2$ axis. [f] Esd in angles is 2°.

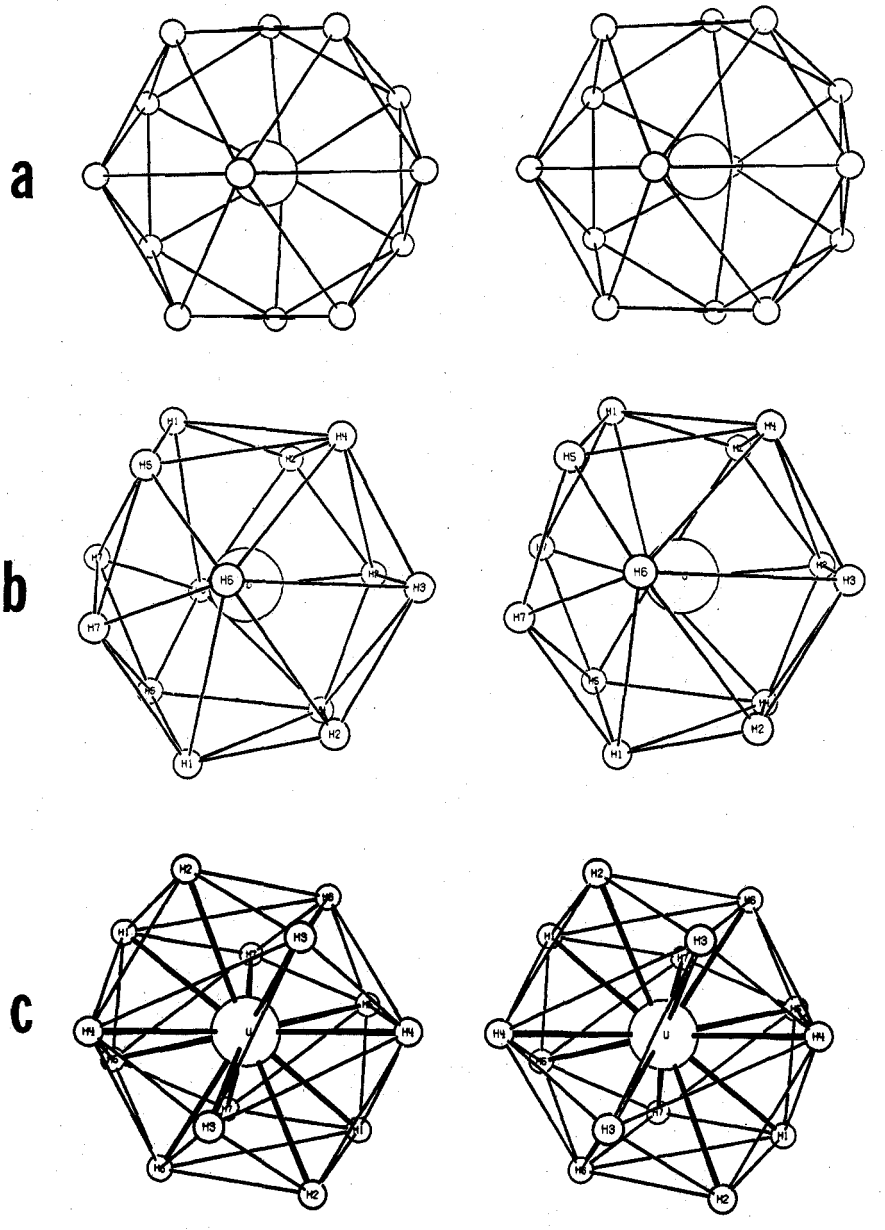

Figure 3.—(a) Stereoscopic drawing of the idealized tetradecacoordination polyhedron, as viewed along its S_{12} axis. This figure is a bicapped hexagonal antiprism. (b) Stereoscopic drawing of the hydrogen coordination polyhedron about the uranium atom in $U(BH_4)_4$. It is viewed in an orientation similar to that of the idealized polyhedron (Figure 3a). (c) Stereoscopic drawings of the hydrogen coordination polyhedron about the uranium atom in $U(BH_4)_4$ viewed down the C_2 axis. The U–H attachments are shown.

radius of uranium, the coordination geometry in this view being simply limited by the packing of spheres (and of course any restraints imposed by the tetrahedrality of the BH_4^- ion). If we take the radii (for eight-coordination) of Zr^{4+} and Hf^{4+} as 0.98 Å and U^{4+} as 1.14 Å,[24] the ratio of the surface areas of the spheres would be 1.35, large enough so that U^{4+} could accommodate 16 rather than 14 H atoms if Zr^{4+} and Hf^{4+} can accommodate 12. The lack of correlation of the U–H distances with coordination type and the agreement of the mean 2.38 (2) Å with the U–H distance of 2.32 Å in uranium hydride[25] suggests that the U–H bond distances are determined largely by U and H radii as discussed in more detail below.

Geometry of the BH_4—Ions.—The bond distances and angles in the BH_4^- ions are presented in Table IIC. These include corrections for thermal motion in the riding model[26] which would seem to be a reasonable approximation here. Although there are some apparent distortions, particularly in the bond lengths, we hesitate to say that these are real. The unusually short B–H bond is not the terminal bond; the B(T)–H(8) distance is indistinguishable from the mean of the others. If we are conservative and multiply our estimated standard deviations by 1.5, a χ^2 test would indicate that we cannot reject at the 1% significance level the hypothesis that all the B–H distances are equal. The mean value is in good agreement with the value of 1.26 (2) Å found in alkali borohydrides[27] and with the average values of 1.31 (5) Å in bis(triphenylphosphine)-

(24) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).
(25) R. E. Rundle, *J. Amer. Chem. Soc.*, **73**, 4172 (1951).
(26) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).
(27) P. T. Ford and R. E. Richards, *Discuss. Faraday Soc.*, **19**, 230 (1955).

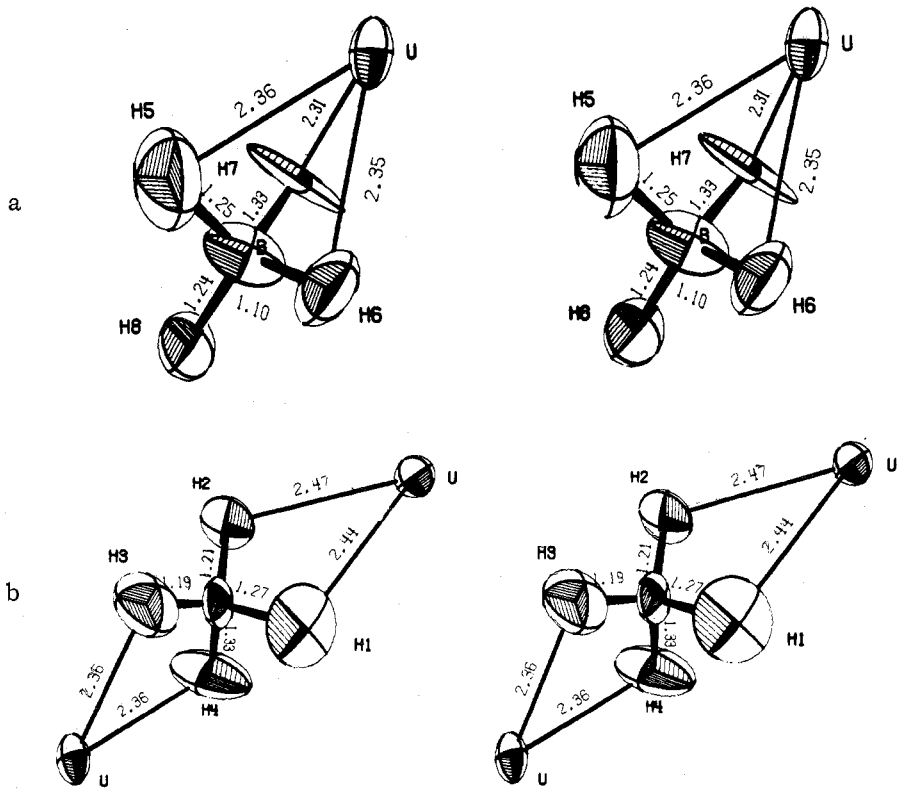

Figure 4.—(a) Stereoscopic view of the B(T) site with 50% probability thermal ellipsoids. Bond distances in Å are given over the bonds. (b) Stereoscopic view of the B(B) site with 50% probability thermal ellipsoids. Bond distances in Å are given over the bonds.

copper borohydride[5] and of 1.32 (10) Å in tetrahydroboratobis(h^5-cyclopentadienyl)titanium(III).[7] The angles again do not deviate greatly from tetrahedral. Those for the terminal BH_4^- group suggest a bending in of the umbrella toward the U, but this is not statistically significant. Drawings of the two groups appear in Figures 4a and 4b. The errors on the thermal motion components are large, but generally there are large amplitudes perpendicular to the B–H bonds and smaller components along the bonds, indicating a large amplitude librational motion of the BH_4^- ion in the lattice (see Table III). The root-mean-square librational

TABLE III

RMS COMPONENTS × 10^2 Å OF THERMAL MOTION ALONG PRINCIPAL AXES AND FOR HYDROGEN ATOMS THE ANGLES THAT THESE MAKE WITH THE B–H BOND

Atom	$U_1^{1/2}$	$U_2^{1/2}$	$U_3^{1/2}$	∠1	∠2	∠3
U	12 (2)	16 (2)	24 (2)			
B(T)	15 (2)	22 (2)	28 (2)			
B(B)	11 (3)	22 (2)	26 (2)			
H(1)	10 (5)	33 (4)	44 (4)	170 (6)	80 (7)	99 (5)
H(2)	12 (4)	24 (3)	32 (3)	160 (11)	73 (12)	78 (8)
H(3)	20 (3)	25 (4)	37 (3)	97 (26)	160 (15)	70 (13)
H(4)	17 (3)	26 (3)	40 (3)	170 (18)	80 (18)	93 (7)
H(5)	20 (3)	29 (3)	42 (4)	146 (17)	57 (17)	83 (9)
H(6)	17 (4)	22 (3)	34 (3)	133 (10)	78 (21)	134 (8)
H(7)	08 (6)	27 (3)	43 (3)	47 (9)	130 (11)	71 (9)
H(8)	15 (4)	19 (3)	44 (3)	173 (15)	88 (40)	83 (5)

amplitude is 16° for each of two degrees of freedom.

Molecular Orbital Description of Bonding in Transition Metal Borohydrides.—While accurate molecular orbital descriptions of transition metal borohydrides are surely outside the scope of current qualitative theory, it is perhaps possible to explain or understand bonding in $U(BH_4)_4$ or $Th(BH_4)_4$ (assumed isostructural) in *comparison* with $Zr(BH_4)_4$ or $Hf(BH_4)_4$ on the level of a molecular orbital scheme.[15] Arguments leading to a 14-coordinate U^{4+} and a 12-coordinate Zr^{4+} and Hf^{4+} structure are involved and of a highly approximate nature. The main thrust of this reasoning, however, is simply stated; there are σ-bonding ligand (BH_4^-) molecular orbitals of appropriate symmetry to overlap and mix with all available empty metal orbitals. Zr^{4+} and Hf^{4+}, with no energetically reasonable empty f orbitals, can only accept 12 electrons, while U^{4+}, with available and empty 5f orbitals, can accept more than 12 electrons. In this picture the BH_4^- ligand donates one electron per hydrogen bridge bond to the metal ion and U^{4+} is equated to Hf^{4+} plus low lying 5f orbitals.

Metal–Boron Distance Implications.—The Zr–B distances reported for $Zr(BH_4)_4$[9,10] are ~0.2 Å less than the U–B(T) distance. The difference in Zr^{4+} and U^{4+} radii is also ~0.2 Å,[24] Zr^{4+} being the smaller ion. However, the difference between the Zr–B separation and the U–B(B) separation is ~0.5 Å, 0.3 Å greater than the radii difference. Thus it seems plausible that the bonding in $Zr(BH_4)_4$ is similar to the bonding between U and B(T) in $U(BH_4)_4$, namely tridentate. Although the X-ray structure[9] of $Zr(BH_4)_4$ is suggestive of such bonding, a definitive test of this hypothesis must await further neutron diffraction studies.[12]

It is felt that metal–boron distances themselves should generally be indicative of whether a BH_4^- group utilizes two or three bridging hydrogens to bind to the metal. A needed piece of evidence is provided by a comparison of $U(BH_4)_4$ and $Be(BH_4)_2$,[4] since $Be(BH_4)_2$ has only two-point attachment for both terminal and bridging BH_4^- groups. Of course, from charge considerations, BH_4^- groups bridging two metal sites will

TABLE IV

COMPARISON OF KNOWN METAL–BORON DISTANCES WITH IONIC AND ATOMIC RADII[a]

	Appropriate radii and differences[b]										
			Shannon and Prewitt[c]			Slater (atomic)[d]		Pauling (ionic)[e]			
Metal hydroborates (two-H bridge)	M–B_2	|UB(B) − MB_2|	r_M(F)	r_M(O)	|r_U − r_M|$_{SP}$	r_M	|r_U − r_M|$_S$	r_M	|r_U − r_M|$_P$	BH_4^- "ionic" radii(2)[f]	[|UB(B) − MB_2| − |r_U − r_M|]
$U^{IV}(BH_4)_4$[g]	2.86[g]		1.19	1.05		1.75		0.97		1.67	
$(Cp)_2Ti^{III}(BH_4)$[h]	2.37	0.49	0.81	0.67	0.38	1.40	0.35	0.76	0.21	1.57	0.11
$(CH_3)_3N{\cdot}Al^{III}(BH_3)_3$[i]	2.25	0.61	0.67	0.53	0.52	1.25	0.50	0.50	0.47	1.58	0.09
$Al(BH_4)_3$[j]	2.14	0.72	0.67	0.53	0.52	1.25	0.50	0.50	0.47	1.47	0.20
$(P(C_6H_5)_3)_2Cu^I(BH_4)$[k]	2.18	0.67	0.60	0.46	0.59	1.35	0.40	0.96	0.01	1.58	0.08
$Be^{II}(BH_4)_2$[l]	1.96	0.90	0.41	0.27	0.78	1.05	0.70	0.31	0.66	1.54	0.12
$B_2^{III}H_6$[m]	1.77	1.09	0.26	0.12	0.93	0.85	0.90	0.20	0.77	1.51	0.16
	M–B_3	|UB(T) − MB_3|								BH_4^- "ionic" radii(3)[f]	[|UB(T) − MB_3| − |r_U − r_M|]
$U^{IV}(BH_4)_4$[n]	2.52[f]		1.19	1.05		1.75		0.97		1.33	
$Zr^{IV}(BH_4)_4$[o]	2.34	0.18	0.98	0.84	0.21	1.55	0.20	0.80	0.17	1.36	0.03

[a] Consistent trends can be found from comparison of columns 3, 6, 8, and 10; differences listed were obtained by subtracting appropriate values for the metal hydroborate from those of $U(BH_4)_4$ (see text). A measure of consistancy is indicated in column 12 as the difference between \|UB_b − MB_2\| and the Shannon and Prewitt \|r_U − r_M\| values. (B_2 indicates two hydrogen bridges; B_3 indicates three. All values are in Å.) [b] Ionic radii were chosen for appropriate ions of the same valence and similar coordination numbers. [c] Reference 24. Note that \|r_U(O) − r_M(O)\| = \|r_U(F) − r_M(F)\|, where r_M(O) is determined from oxides and r_M(F) from fluorides. [d] Reference 28. [e] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960. [f] See text for explanation. [g] Present work, average of the two observed U–B(B) distances. [h] Reference 7. [i] Reference 6. [j] Reference 8. [k] Reference 5. [l] Reference 4—the three Be–B values are given here as the average. [m] W. N. Lipscomb and H. W. Smith, *J. Chem. Phys.*, **43**, 1060 (1965). [n] Present work, U–B(T) distance. [o] Reference 9.

have slightly larger metal–boron separations than nonsite bridging BH_4^- groups having like attachment. But the $U(BH_4)_4$ and $Be(BH_4)_2$ results, taken together, clearly indicate that the double *vs.* triple hydrogen bridge bond effect has an even more profound influence on the metal–boron distances than the terminal *vs.* site bridging (polymeric) effect. Specifically, the difference in the U–B(B) and U–B(T) distances is ~0.3 Å, while the difference between the Be–B(B) and the Be–B(T) distance is only ~0.1 Å. The significantly greater shortening observed in $U(BH_4)_4$ is primarily due to a difference in hydrogen bridge bonding, not to a polymeric or site bridging effect. Thus if the structure has at least two different types of boron sites it is possible to interpret a metal borohydride crystal structure for which only the metal and boron positions are known, in terms of its probable boron–hydrogen–metal attachments from consideration of the *relative* metal–boron separations. For example, if a boron is located equidistant between two metal sites, it is probably doubly hydrogen bridge bonded to each site. Other borons in the structure having M–B distances similar (±0.1 Å) to those of the two-site boron would also be expected to be doubly hydrogen bridge bonded. Borons with much shorter M–B distances would then be expected to be triply hydrogen bridge bonded.

A detailed comparison of known metal–boron distances reveals that such qualitative arguments are probably applicable to metal borohydrides generally. As previously implied for $Zr(BH_4)_4$, ionic radii arguments can be of use in understanding such compounds. The $U(BH_4)_4$ structure (with both double and triple hydrogen bridge bonding occurring on the same metal center) serves as an excellent reference upon which to base this thesis. To illustrate such an approach, it is helpful to prepare a table of known metal–boron distances, ionic radii,[24] atomic radii,[28] and the differences between those values and the values for $U(BH_4)_4$. From Table IV it is obvious that trends in ionic and atomic radii parallel trends in metal–boron distances for the doubly hydrogen bridged complexes.[29] Since there are only two known triply hydrogen bridged structures, trends are hard to verify; but as shown above the Zr–B and U–B(T) distances also differ by approximately the same amount as do the ionic and atomic radii.

The import of this tabulation is that, in the absence of ability to determine hydrogen positions, a diffraction determined M–B distance yielding a \|UB(B) − MB\| difference approximately the same as the appropriate \|r_U − r_M\| difference is likely to be due to a double hydrogen bridged BH_4^- group.[30] Similarly, a M–B distance giving a \|UB(B) − MB\| difference much greater (*e.g.*, ~0.3 Å) than the appropriate \|r_U − r_M\| difference is likely to be due to a triple hydrogen bridged BH_4^- group. The latter case implies similarity of the \|UB(T) − MB\| difference and \|r_U − r_M\| differences.

Consistent with the above considerations, one might assign an "ionic radius" of about 1.3 to a triply bridged BH_4^- group and an "ionic radius" of about 1.6 to a doubly bridged BH_4^- group (column 11, Table IV).[31] Such BH_4^- "ionic radii" are certainly subject to an error of at least ±0.1 Å, and are probably limited to metals of high valence; yet present published results remain consistent within these limits. Only more structural data can determine further generality of these values.

One hypothesis which may explain the metal–boron distances in the complex borohydrides is that the metal–hydrogen interaction is dominant. This implies that the metal–hydrogen distance is given by the sum of the

(28) J. C. Slater, *J. Chem. Phys.*, **41**, 3199 (1964).

(29) Both Slater atomic and Pauling ionic radii for Cu fail to fit the scheme due to insufficient compensation for the low valence of Cu(I) which is corrected for by Shannon and Prewitt's coordination sensitive ionic radii.

(30) We note that for the doubly hydrogen bridged BH_4^- groups, the differences in the UB(B) and MB distances, \|UB(B) − MB\|, are consistently slightly larger (~0.1 Å) than the differences in the U^{4+} and M^{n+} ionic radii, \|r_U − r_N\|$_{SP}$. This relatively long U–B distance could be due to polymeric effects or to the high coordination of $U(BH_4)_4$, but this does not affect the trends in M–B distances.

(31) These values were determined from averages of the differences in metal–boron distances and the appropriate crystal radii of ref 22 and hence are only applicable for use with metal ion radii from that list.

TABLE V

METAL–HYDROGEN AND METAL–BORON DISTANCES (IN Å) IN COMPLEX BOROHYDRIDES AS OBSERVED AND AS CALCULATED FROM A MODEL WHICH ASSUMES CONSTANT TETRAHEDRAL GEOMETRY OF THE BOROHYDRIDE ION

Metal	a $(M-H)_{exp}$[a]	b $(M-H)_{radii}$[b]	c $(M-H)_{calcd}$[c]	d R_H[d]	e R_H[e]	f $(M-B)_{obsd}$[f]	g $(M-B)_{calcd}$[g]
U(tri)	2.34 (2)	2.39	2.42	1.22	1.15	2.52	2.49
U(bi)	2.40 (3)	2.39	2.37	1.18	1.21	2.86*	2.87
Zr	2.21 (4)[h]	2.18	2.25	1.27	1.23	2.34	2.28
Ti	1.75 (8)	2.01	1.95	1.14	0.94	2.38	2.44
Al[i]	1.85 (6)*	1.87	1.84	1.17	1.18	2.25*	2.29
Al[j]	1.80 (1)	1.87	1.75	1.08	1.13	2.14	2.29
Cu	2.02 (5)	1.80	1.78	1.18	1.42	2.18	2.20
Be	1.59 (2)	1.61	1.61	1.20	1.18	1.96*	1.97

[a] Diffraction-determined metal–hydrogen distances. The estimated standard deviations are indicated. See Table IV footnotes for references. The experimental data are from the compounds listed in Table IV. * Averaged Data. [b] Sum of Shannon–Prewitt radius and a radius of 1.2 Å. [c] Calculated from assumption of regular tetrahedral BH_4^- ion and an assumed r(B–H) distance of 1.24 Å. [d] Hydrogen radius obtained by subtracting the Shannon–Prewitt metal radius from the values in column c. [e] Hydrogen radius obtained by subtracting the Shannon–Prewitt radii from the experimental value in column a. [f] Metal boron distances from the diffraction experiments. [g] Metal boron distances from assumption of tetrahedral geometry for BH_4^- and an H radius of 1.2 Å. [h] Reference 10. [i] Reference 6. [j] Reference 8.

metal ionic radius and a constant radius for hydrogen. An additional assumption which one may test for consistency is that the BH_4^- geometry is invariant, being for example a regular tetrahedron with a bond length of 1.24 Å.[32] For a regular BH_4^- tetrahedron in contact with a metal ion, let us define $R = r_{M-H}/r_{B-H}$ and $S = r_{M-B}/r_{B-H}$. Elementary geometrical considerations then allow us to derive for two-point attachment

$$S = \sqrt{3}/3 + (R^2 - 2/3)^{1/2} \quad (1)$$

for three-point attachment

$$S = 1/3 + (R^2 - 8/9)^{1/2} \quad (2)$$

It is then possible to construct a comparative table of calculated and observed bond lengths and covalent radii. In the three columns a–c of Table V we present (a) the experimental value of the M–H distance, (b) the value of the M–H distance calculated as a sum of the Shannon–Prewitt radius and a radius of 1.2 Å for hydrogen, and (c) the value calculated from eq 1 and 2 using the experimental values of the M–B distance. We note that the experimental values for M–H distances do not agree well with those calculated from the above simple models, the major discrepancies being for Ti and Cu. In column d of Table V is the hydrogen radius calculated from eq 1 and 2 under the assumption of the idealized BH_4^- geometry. The mean value is 1.18 (2) in good agreement with the 1.2 Å postulated above. The values for the hydrogen radius (e) calculated from the experimental M–H distance and the Shannon–Prewitt metal radius show considerable variability and would not appear to have good predictive value; the mean is 1.18 (5). The final two columns of the table give the observed M–B values (f) compared with the values calculated (g) from eq 1 and 2 and the assumption of a 1.2 Å hydrogen radius.

If this proposed model for borohydride geometry (1.2 Å van der Waals radius for hydrogen and a constant tetrahedral BH_4^-) is correct, columns b and c would be identical with column a and column d would be identical with column e in Table V. That this is not the case can be attributed to two factors. First, the model could simply be incorrect, that is, the BH_4^- does not assume a constant tetrahedral geometry throughout this series of compounds. Second, experimental determination of hydrogen atom positions by both X-ray and electron diffraction is not accurate enough, rendering this type of comparison inappropriate. At present it is not clear which of these reasons should be given the greater weight; however, we feel that the second one is most likely. The present neutron diffraction data on $U(BH_4)_4$ support this contention, and final resolution of this problem must await further neutron diffraction studies.

As with all qualitative trend arguments, care must be exercised when employing these approximate schemes to understanding metal borohydrides. In particular, one must always be aware of the dependence of observed ionic radii on metal valence *and* coordination. Of course, radii used must come from an internally consistent compilation such as that of Shannon and Prewitt.[24]

Conclusion and Summary

In this work the crystal structure and site geometry of $U(BH_4)_4$ have been determined. In an effort to explain these rather unexpected results (see Table II and Figures 1, 2, and 3) we have discussed some of the effects that could play important roles in transition metal borohydride bonding. Both packing of spheres around a central metal ion and availability of low lying molecular orbitals for BH_4^- ligand-donated electrons give a qualitative understanding of the bonding structures encountered. In addition, ligand availability in the gas as opposed to the crystal phase (*e.g.*, $U(BH_4)_4$ and $Be(BH_4)_4$) and steric interference of bulky nonborohydride ligands [*e.g.*, $[(C_6H_5)_3P]_2Cu(BH_4)$] undoubtedly are significant factors, in general, for the geometry of metal–borohydride coordination (number of hydrogen bridge bonds). Metal–hydrogen interaction may play a determining factor in the interatomic distance observed, but it is clear that more precise experimental data on hydrogen atom positions is necessary to confirm this. It is apparent that many effects can influence transition metal borohydride bonding geometry; and, from the available structural data, it is not at all obvious which is the dominant one. Whether or not two- or three-point hydrogen attachment is observed is probably governed by a number of competing interactions.

(32) The best evidence against this assumption is provided by the values of the B–H bond lengths in $Al(BH_4)_3$ with $B-H_t$ = 1.196 (12) Å and $B-H_b$ = 1.283 (12) Å. The H_b-B-H_b bond angle is 114.0 (2). The mean value is 1.24 Å, as in $U(BH_4)_4$, so that for semiquantitative arguments (predictive value within 0.1 Å), the idealized geometry may be adequate.