A Neutron Diffraction Study of $[N(PPh_3)_2]^+[B_2H_7]^-\cdot CH_2Cl_2$† at 80 K

Saeed I. Khan, Michael Y. Chiang, and Robert Bau *
Department of Chemistry, University of Southern California, Los Angeles, CA 90089, U.S.A.
Thomas F. Koetzle
Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, U.S.A.
Sheldon G. Shore and Steven H. Lawrence
Department of Chemistry, Ohio State University, Columbus, Ohio 43210, U.S.A.

The structure of the $[B_2H_7]^-$ anion, reported by us earlier in an *X*-ray structure determination, has been analysed more accurately by neutron diffraction. Data were collected at 80 K on a sample of $[N(PPh_3)_2]^+[B_2H_7]^-\cdot CH_2Cl_2$ using the Brookhaven High Flux Beam Reactor. The essential results of the *X*-ray analysis are confirmed, with more accurate molecular parameters. The $[B_2H_7]^-$ anion has a non-crystallographic C_s symmetry, with a bent geometry [B–H–B 127(2)°] and staggered terminal B–H bonds. Average terminal and bridging B–H bond lengths are 1.18(2) and 1.27(6) Å respectively, and the B $\cdots$ B distance is 2.27(1) Å. There is a slight asymmetry of the B–H–B bridge [B(1)–H 1.32(2), B(2)–H 1.21(2) Å], which is on the borderline of being significant. $[N(PPh_3)_2]^+[B_2H_7]^-\cdot CH_2Cl_2$ crystallizes in the triclinic space group $P\bar{1}$, with a = 9.633(1), b = 10.513(1), c = 16.938(1) Å, α = 90.599(7), β = 93.142(8), γ = 93.744(8)°, and Z = 2 at 80 K. The final R factor is 0.096 for the 1 479 reflections with $F_o^2 > 3\sigma(F_o^2)$.

In an earlier communication[1] we reported the results of an *X*-ray structural analysis on the $[B_2H_7]^-$ anion, which showed a bent, singly-bridged B–H–B bond with some asymmetry in the B–H distances of the bridging H atom [1.00(5) and 1.27(5) Å]. However, due to the relatively low precision in hydrogen atom positions, as is usual in *X*-ray studies, more definitive conclusions regarding the nature of the B–H–B bridge could not be made. We now report the results of a more accurate structural determination on the $[B_2H_7]^-$ anion using neutron diffraction.

Table 1. Summary of crystal data and refinement results for $[N(PPh_3)_2]^+[B_2H_7]^-\cdot CH_2Cl_2$ at 80 K

Space group	$P\bar{1}$
M	652.2
a/Å	9.633(1)
b/Å	10.513(1)
c/Å	16.938(1)
α/°	90.599(7)
β/°	93.142(8)
γ/°	93.744(8)
Z	2
U/Å^3	1 709(8)
D_c/g cm^{-3}	1.267
μ/cm^{-1}	3.156
Crystal dimensions (mm)	2.0 × 0.7 × 1.7
Crystal volume (mm^3)	2.38
Crystal boundary faces	(010), (001), ($\bar{1}$00), (101)
Neutron wavelength (Å)	1.160 38(4)
(sinθ)/λ limit (Å^{-1})	0.494 (2θ = 70°)
Total number of reflections measured	3 277
Number of unique reflections	2 907
Number of reflections used in analysis (n_o)	1 479
Number of variable parameters (n_v)	171
Final agreement factors	
$R(F^2) = \Sigma\|F_o^2 - k^2F_c^2\|/\Sigma F_o^2$	0.096
$R'(F^2) = [\Sigma w\|F_o^2 - k^2F_c^2\|^2/\Sigma wF_o^4$	0.102
$S = \Sigma w\|F_o^2 - k^2F_c^2\|^2/(n_o - n_v)$	1.563

Experimental

The title compound was prepared according to a published procedure.[2] Crystals for neutron diffraction studies were obtained as follows. An unweighed quantity of $[N(PPh_3)_2]^+$-$[B_2H_7]^-\cdot CH_2Cl_2$ (20—50 mg) was placed into a round-bottomed tube sealed to a 9-mm Solv-Seal joint. This was attached to a stopcock adapter and the assembly was evacuated, followed by addition of enough CH_2Cl_2 completely to dissolve the solid. After all the solid dissolved, the solution was cooled to −78 °C and a diethyl ether–dichloromethane mixture (5:1 v/v) was *very slowly* condensed onto the CH_2Cl_2 solution so as to avoid premature mixing. The assembly was allowed to stand at room temperature. Crystals large enough for neutron diffraction studies were obtained in 4—7 d.

As reported earlier,[1] crystals of $[N(PPh_3)_2]^+[B_2H_7]^-\cdot CH_2Cl_2$ show a pronounced tendency to lose molecules of crystallization (CH_2Cl_2) in a dry atmosphere. Thus the crystal was mounted under a nitrogen atmosphere in a glove-box saturated with CH_2Cl_2. Two of the best three samples were coated with a thin film of Styrofoam (*i.e.* quickly dipped in a solution of Styrofoam dissolved in CH_2Cl_2), and the other one coated with epoxy glue. Each of the crystals was then mounted on an aluminium pin and sealed in an aluminium can, together with a piece of glass wool, soaked in CH_2Cl_2 and placed at the bottom of the can. After initial screening, the selected sample (one of the Styrofoam-coated crystals), with the [$\bar{1}$00] axis approximately parallel to the Al pin, was placed in a closed-cycle helium refrigerator (Air Products DISPLEX CS-202) mounted on a four-circle diffractometer[3] at the Brookhaven High Flux Beam Reactor. A germanium (220) single-crystal monochromator was employed to obtain a neutron beam of wavelength 1.160 38(4) Å [based on KBr (a = 6.6000 Å at 295 K)]. Diffraction data were collected at 80.0(5) K with the

---

† Bis(triphenylphosphine)iminium heptahydrodiborate–dichloromethane (1/1).

Supplementary data available (No. SUP 56561, 6 pp.): $[B_2H_7]^-$ least-squares plane and torsion angles, Ph group atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

temperature monitored by a Pt resistor which was calibrated against the magnetic phase transition at 78.38(1) K of an FeF_2 crystal.[4] The unit-cell parameters at 80 K were determined by least-squares procedures based on the ($\sin^2\theta$) values of 32 reflections ($50 < 2\theta < 60°$), and are listed in Table 1.

Intensity measurements were carried out with an ω step-scan technique. The scan width was $\Delta\omega = 4.0°$ with 100 steps per scan. Counts were accumulated at each step for approximately 3.5 s, the exact time interval being determined by monitoring the incident beam intensity. The intensities of three monitor reflections [(3,$\bar{3}$,11), (5,0,0), (1,4,3)] were measured at 100-reflection intervals and showed no significant variation during the course of data collection.

Integrated intensities were calculated by taking seven points on either end of each scan as a measure of the background. Observed intensities were then corrected for absorption by numerical integration over a Gaussian grid of points[5] and converted to squared structure factors, $F_o^2 = I\sin 2\theta$. The minimum and maximum transmission coefficients were 0.626 and 0.810 respectively. Altogether, 3 277 reflections were measured, which were then averaged for multiple observations to give 2 907 independent values of F_o^2.

Structure Analysis.—The structure analysis was carried out with data having $F_o^2 > 3\sigma(F_o^2)$ (1 479 reflections). Initial refinement was carried out using differential synthesis[6] with the starting model defined by the non-hydrogen atoms from the *X*-ray analysis.[1] All hydrogen atoms, including those of the anion, were located from subsequent difference scattering-density maps and positions were refined to convergence. In order to reduce the parameter-to-data ratio, the final least-squares refinement cycles were carried out using rigid-body methods.* The rigid-group parameters for the six phenyl groups of the cation were calculated using an idealized geometry (C–H 1.80 Å, C–C 1.396 Å). The 11 atoms of each phenyl group were assigned individual isotropic thermal parameters. Least-squares refinement was carried out minimizing the value $\Sigma w(F_o^2 - k^2F_o^2)^2$ with weights defined as $w = 1/\sigma^2$, where $\sigma^2 = [\sigma^2_{\text{count}} + (0.02\ F_o^2)^2]$. A total of 171 parameters (a scale factor, positional and isotropic thermal parameters of 17 non-group atoms, and 102 group parameters) were refined to final agreement factors of $R(F^2) = 0.096$ and $R'(F^2) = 0.102$. A difference synthesis computed at this stage was essentially featureless. The neutron scattering lengths[7] used were (in units of 10^{-12} cm): $b_B = 0.535$, $b_C = 0.665$, $b_H = -0.374$, $b_N = 0.930$, and $b_P = 0.519$.

Results and Discussion

The final atomic parameters (excluding the phenyl rings) are given in Table 2. Selected bond lengths and angles are listed in Table 3; the group parameters are given in Table 4.

The molecular structure of the $[B_2H_7]^-$ anion, with the numbering scheme, is illustrated in Figure 1. The geometry around each boron atom is a distorted tetrahedron with the six terminal hydrogen atoms arranged in a staggered conformation. The displacements through a least-squares plane passing through the atoms H(1), B(1), H, B(2), and H(4) are listed in SUP 56561 as are the torsion angles describing the $[B_2H_7]^-$ conformation. The cation, $[N(PPh_3)_2]^+$, as usual, has a bent structure with a P–N–P angle of 136.7(6)°. The overall geometry of the anion as determined by neutron diffraction at 80 K is essentially the same as that derived from the *X*-ray analysis at 177 K.[1]

Table 2. Final positional (× 10^4) parameters for the non-group atoms of $[N(PPh_3)_2]^+[B_2H_7]^-\cdot CH_2Cl_2$

Atom	*x*	*y*	*z*
N	8 789(6)	4 867(5)	7 523(3)
P(1)	8 050(10)	3 455(9)	7 465(5)
P(2)	10 255(10)	5 543(9)	7 316(6)
B(1)	−4 918(13)	2 893(11)	2 962(7)
B(2)	−4 630(13)	769(10)	2 843(6)
H	−4 227(25)	1 850(23)	3 045(14)
H(1)	−3 963(27)	3 609(24)	3 122(14)
H(2)	−5 668(27)	2 855(23)	3 503(15)
H(3)	−5 429(26)	3 011(23)	2 341(15)
H(4)	−5 821(21)	488(17)	2 765(10)
H(5)	−4 021(22)	565(20)	2 266(13)
H(6)	−4 088(24)	247(21)	3 436(13)
C	2 704(10)	1 225(8)	1 257(5)
H(s1)	2 142(22)	480(20)	1 592(12)
H(s2)	3 526(21)	1 670(18)	1 640(11)
Cl(1)	3 382(7)	464(6)	446(4)
Cl(2)	1 524(7)	2 367(6)	961(4)

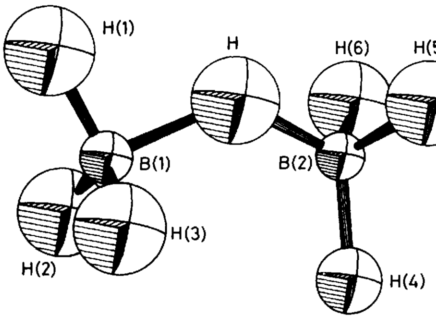

Figure 1. Molecular plot of the $[B_2H_7]^-$ anion. The atoms are displayed as 50% probability spheres

(*a*) B–H *Distances*.—The most significant result of the present analysis is that the existence of the bent, singly-bridged B–H–B bond is confirmed. The bridging hydrogen atom occupies a position which is best described as marginally asymmetric (at the 5.5σ level), the two bridging distances being 1.32(2) [B(1)–H] and 1.21(2) Å [B(2)–H]. The only other neutron diffraction study reported for a boron hydride is on $B_{10}H_{14}$,[8] and interestingly in that analysis the bridging hydrogen atoms were also asymmetric, with average bond lengths of 1.298(5) and 1.347(7) Å. (However, it should be pointed out that in $B_{10}H_{14}$ the boron atoms of the B–H–B bridges are chemically inequivalent.) A compound with a singly-bridged BH_4 group, $[Cu(PPh_2Me)_3(BH_4)]$, has also been investigated[9] with neutron diffraction, but has a B–H bridging distance of 1.170(5) Å, somewhat shorter than those found here. As has been pointed out earlier,[1] if we accept the asymmetry of the B–H–B bridge in $[B_2H_7]^-$ to be significant, a chemically intuitive explanation could be a donor–acceptor interaction between the two halves of the anion: *i.e.* $[BH_4]^- \rightarrow BH_3$.

The mean terminal B–H distance of the anion is in good agreement with the other boron hydrides and metal borate complexes for which accurate B–H distances are available from neutron diffraction and other spectroscopic methods (see Table 5). However, one of the terminal B–H distances in the $[B_2H_7]^-$

---

* The program used for the rigid-body refinement was UCIGLS, a version of ORFLS (W. R. Busing and H. A. Levy), modified by J. A. Ibers and R. J. Doedens. See R. J. Doedens, in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, p. 198. Phenyl group positions were defined by (*a*) three angles which correspond to rotations about the central axes, and (*b*) the co-ordinates of the group centroid, giving six refined positional parameters for each phenyl ring.

Table 3. Selected bond distances (Å) and angles (°) in $[N(PPh_3)_2]^+$-$[B_2H_7]^- \cdot CH_2Cl_2$

B(1)–B(2)	2.27(1)	B(2)–H(6)	1.25(2)
B(1)–H	1.32(2)	P(1)–N	1.60(1)
B(1)–H(1)	1.16(2)	P(2)–N	1.59(1)
B(1)–H(2)	1.19(2)	Cl(1)–C	1.76(1)
B(1)–H(3)	1.14(2)	Cl(2)–C	1.76(1)
B(2)–H	1.21(2)	H(s1)–C	1.10(2)
B(2)–H(4)	1.16(2)	H(s2)–C	1.07(2)
B(2)–H(5)	1.19(2)		

B(1)–H–B(2)	127.2(20)	H–B(2)–H(4)	119.9(17)
H(1)–B(1)–H(2)	108.8(18)	H–B(2)–H(5)	104.6(17)
H(1)–B(1)–H(3)	114.6(19)	H–B(2)–H(6)	95.4(16)
H(2)–B(1)–H(3)	117.0(20)	P(1)–N–P(2)	136.7(6)
H–B(1)–H(1)	95.8(18)	Cl(1)–C–Cl(2)	112.3(5)
H–B(1)–H(2)	103.7(17)	Cl(1)–C–H(s1)	107.0(12)
H–B(1)–H(3)	114.1(18)	Cl(1)–C–H(s2)	111.0(12)
H(4)–B(2)–H(5)	113.1(15)	Cl(2)–C–H(s1)	108.4(13)
H(4)–B(2)–H(6)	111.3(16)	Cl(2)–C–H(s2)	109.5(12)
H(5)–B(2)–H(6)	110.9(17)	H(s1)–C–H(s2)	108.3(16)

anion is significantly longer [1.25(2) Å] than the other five [average 1.17(1) Å]. A similar observation has been reported[9] for the neutron structure of $[Cu(PPh_2Me)_3(BH_4)]$, where one of the B–H bonds is significantly longer [1.330(6) Å] than the other three [average 1.179(5) Å]. The thermal parameters of H(1), H(2), and H(3) are somewhat larger than those for H(4), H(5), and H(6), and this may imply some sort of minor disorder in the packing of the molecules. Attempts to resolve any disorder with the present data set were not successful.

As far as B–H–B and M–H–B angles are concerned, the data from Table 5 clearly indicate that singly-bridged linkages produce angles substantially larger than those of the other molecules listed.

(*b*) *The Three-centre Two-electron Bond in* $[B_2H_7]^-$.—For the past several years, neutron diffraction analyses[10] carried out by our group and others on molecules containing unsupported* three-centre two-electron (3c-2e) bonds have suggested that the nature of such interactions is 'closed'.† Thus, systems containing M–H–M {*e.g.*, $[W_2H(CO)_9(NO)]$, $[W_2H(CO)_{10}]$, *etc.*}[10] and M–H–B linkages {*e.g.*, $[Cu(PPh_2Me)_3(BH_4)]$}[9] have invariably shown that the bridging hydride is not only bent but also off-axis (see below). In this respect the B–H–B bond in $[B_2H_7]^-$ offers the simplest and perhaps the best example for probing the details of 3c-2e bonds. The present result, as expected, shows that the B–H–B linkage in $[B_2H_7]^-$ is again bent (B–H–B 127.2°) and 'closed', *i.e.* the bridging hydride is significantly displaced (average 18°) off the pseudo-three-fold axis defined by each terminal BH_3 group (see Figure 2). This can also be seen from the fact that, although the H_t–B–H_t angles (t = terminal) are reasonably close to being tetrahedral [range 108.8(18)—117.0(20)°], the H_b–B–H_t angles (b = bridging) show considerable scatter [range 95.4(16)—119.9(17)°]. The same phenomenon was pointed out earlier in $[Cu(PPh_2Me)_3(BH_4)]$.[9] This observation implies the existence of a significant amount of B–B interaction in the title compound.

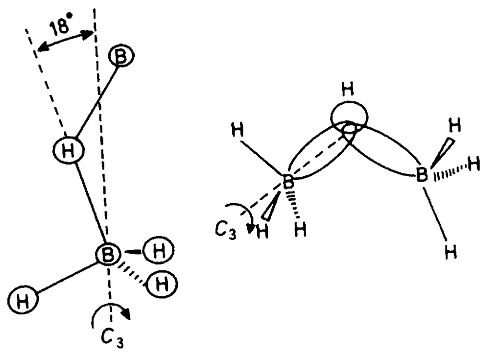

Figure 2. Schematic diagrams showing that the B–H–B bridge is not only bent but also 'off-axis' (see text). The displacement of the bridging H atom off the local C_3 axis of each BH_3 fragment averages to *ca.* 18°. This is interpreted as evidence that the B–H–B bond is of the 'closed' type

(*c*) *Theoretical Studies on the* $[B_2H_7]^-$ *Anion.*—In the past, the $[B_2H_7]^-$ anion has been a target of several theoretical investigations probing the details of the 3c-2e bond. Earlier *ab initio* calculations had suggested that the central B–H–B linkage would be linear.[11] In contrast, a more sophisticated theoretical calculation of the isoelectronic $[C_2H_7]^+$ cation predicted a bent central C–H–C backbone.[12] The results from our *X*-ray diffraction analysis[1] on $[B_2H_7]^-$ showed a considerably bent B–H–B bond [B–H–B 136(4)°], consistent with the results for $[C_2H_7]^+$. The apparent inconsistency between the experimental and theoretical results for $[B_2H_7]^-$ led Raghavachari *et al.*[13] to reinvestigate the $[B_2H_7]^-$ system with a higher level of optimization than employed for previous calculations. The results of this most recent analysis showed the central B–H–B bond to be bent with a B–H–B angle of 126.4°, a value which compares very well with the present neutron diffraction result [B–H–B 127.2(20)°]. Finally, another recent *ab initio* calculation by Sapse and Osorio[14] has also concluded that the central B–H–B backbone is bent, but with an angle of 149.9°.

Significant differences, however, still remain between the experimental and theoretical results. The observed B–B and B–H distances are all shorter than their calculated values. Perhaps more importantly, all theoretical calculations predict a symmetric B–H–B bond. Indeed, experimental results on $[Me_3Al\text{-}H\text{-}AlMe_3]^-$[15] and theoretical calculations on $[H_3Al\text{-}H\text{-}AlH_3]^-$[16] both show a symmetric and linear Al–H–Al bond. In the $[B_2H_7]^-$ case, although the experimental results reported here show the B–H–B bond to be much less asymmetrical than was the case in the earlier *X*-ray work[1] [B–H_b 1.27(5), 1.00(5) Å], the current neutron values still show asymmetry [B–H_b 1.32(2), 1.21(2) Å; difference 5.5σ]. One can interpret this as being due to a partial contribution from a 'donor–acceptor' type of interaction in the B–H–B bridge (see above). Alternatively, one might argue that the asymmetry we observe is an artifact arising from disorder or crystal-packing effects (*i.e.* non-equivalent environments around two ends of the $[B_2H_7]^-$ anion in the crystal lattice), but there are no unusually short non-bonded contacts to support this latter contention (minimum H • • • H 2.02 Å). We intend to continue studying this problem by structurally investigating other salts of $[B_2H_7]^-$ and its derivatives (such as $[Ph_3B\text{-}H\text{-}BPh_3]^-$).

Acknowledgements

Research at Brookhaven National Laboratory was carried out

---

* We define a molecule having an unsupported 3c-2e bond as one in which the two halves of the molecule are held together solely by one 3c-2e bond, without other bridging groups. Thus, molecules such as B_2H_6 or $[Re_2H_2(CO)_8]$, which have two X–H–X bridges, are not included by this definition.

† A 'closed' 3c-2e bond is one in which all three orbitals overlap in a common region of space; in the case of the B–H–B bond this would mean that there is a significant amount of B–B bonding as well as B–H bonding.

Table 4. Refined group parameters* of the phenyl rings

	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6
10^4x	6 720(3)	5 416(3)	10 094(3)	11 940(3)	11 968(3)	9 704(3)
10^4y	2 716(2)	3 436(2)	1 397(2)	6 384(2)	3 736(2)	8 055(2)
10^4z	5 745(1)	8 541(1)	8 132(1)	8 939(1)	6 264(1)	6 344(1)
φ/°	−0.8(1)	−9.8(1)	−115.1(3)	149.5(1)	−103.1(1)	89.1(1)
θ/°	166.3(1)	−170.4(1)	111.0(1)	−151.43(6)	−134.0(1)	−159.9(1)
ρ/°	64.7(1)	−37.4(1)	−109.5(3)	−72.2(1)	121.9(1)	148.0(1)

* The definitions of the orientation angles, φ, θ, and ρ, are given by R. J. Doedens, in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, pp. 198—200.

Table 5. A Comparison of B–B and B–H distances in various boron-containing molecules for which accurate measurements are available

Boron hydrides and substituted boron hydrides

Compound	Method[a]	B–B (Å)	B–H$_t$/Å	B–H$_b$/Å	B–H–B/°	Ref.
B_2H_6	E	1.775(3)	1.196(8)	1.339(6)	83.0	*b*
$B_2H_5CH_3$	M	1.82(2)	1.195(9) 1.187(5) 1.20(1)	1.34(6)		*c*
$B_2H_5NH_2$	M	1.916(2)	1.193(1)	1.355(5)	90.0(6)	*d*
$B_2H_5NMe_2$	M	1.916(4)	1.191(3)	1.365(6)	89.1(9)	*e*
B_4H_{10}	M	1.854(2) 1.718(2)		1.42(2)		*f*
B_5H_9	M	1.803(2) 1.690(2)	1.185(2)	1.352(4)		*g*
B_6H_{10}	M	1.818(4), 1.77(1) 1.710(6), 1.762(4) 1.654(3), 1.783(1)				*h*
$B_{10}H_{14}$[i]	N	1.775(5)	1.180(4)	1.298(5)[j] 1.347(7)	84.3(4)	8
$[B_2H_7]^-$	N	2.27(1)	1.17(2)	1.21(2) 1.32(2)	127(2)	*k*

Metal borate complexes

Compound	Method[a]	B–H$_t$/Å	B–H$_b$/Å	M–H$_b$/Å	M–B/Å	M–H–B/°	Ref.
$[U(BH_4)_4]$[l]	N	1.24(3)	1.23(3)	2.34(2)	2.52(1)	83(1)	*m*
$[U(BH_4)_4]$[n]	N	1.24(3)	1.25(4)	2.41(2)	2.86(2)	98(1)	*m*
$[Hf(BH_4)_4]$[l]	N	1.15(2)	1.23(1)	2.13(1)	2.28(1)	80.6(6)	*o*
$[Hf(\eta\text{-}C_5H_4Me)_2(BH_4)_2]$[n]	N	1.19(1)	1.23(1)	2.09(1)	2.553(6)	96.8(5)	*p*
$[Co(terpy)(BH_4)]$[n,q]	N	1.22(1)	1.29(1)	1.72(2)	2.15(1)	90.0(8)	*r*
$[Cu(PPh_2Me)_3(BH_4)]$[s]	N	1.23(5)	1.170(5)	1.697(5)	2.518(3)	121.7(4)	9

[a] E = Electron diffraction, M = microwave spectroscopy, N = neutron diffraction. [b] L. S. Bartell and B. L. Carroll, *J. Chem. Phys.*, 1965, **42**, 1135. [c] C. W. Chiu, A. B. Burg, and R. A. Beaudet, *Inorg. Chem.*, 1982, **21**, 1204. [d] K. K. Lau, A. B. Burg, and R. A. Beaudet, *Inorg. Chem.*, 1974, **13**, 2787. [e] E. A. Cohen and R. A. Beaudet, *Inorg. Chem.*, 1973, **12**, 1570. [f] N. P. C. Simmons, A. B. Burg, and R. A. Beaudet, *Inorg. Chem.*, 1981, **20**, 533. [g] D. Schwoch, A. B. Burg, and R. A. Beaudet, *Inorg. Chem.*, 1977, **16**, 3219. [h] D. Schwoch, B. Don, A. B. Burg, and R. A. Beaudet, *J. Chem. Phys.*, 1979, **83**, 1465. [i] Measurement performed on a deuteriated sample ($B_{10}D_{14}$). [j] Asymmetrically-bridging hydrogen atoms. [k] This work. [l] Triply bridging BH_4 unit, *i.e.* $M(\mu\text{-}H)_3BH$. [m] E. R. Bernstein, W. C. Hamilton, T. A. Keiderling, S. J. La Placa, S. J. Lippard, and J. J. Mayerle, *Inorg. Chem.*, 1972, **11**, 3009. [n] Doubly bridging BH_4 unit, *i.e.* $M(\mu\text{-}H)_2BH_2$. [o] T. J. Marks and J. M. Williams, personal communication, 1978. [p] P. L. Johnson, S. A. Cohen, T. J. Marks, and J. M. Williams, *J. Am. Chem. Soc.*, 1978, **100**, 2709. [q] terpy = 2,2′:6′,2″-terpyridyl. [r] E. J. Corey, N. J. Cooper, W. M. Canning, W. H. Lipscomb, and T. F. Koetzle, *Inorg. Chem.*, 1982, **21**, 192. [s] Singly bridging BH_4 unit, *i.e.* $M(\mu\text{-}H)BH_3$.

under contract to the U.S. Department of Energy and also supported by N.S.F. (to R. B.) and U.S. Army Research Office grants (to S. G. S.). In addition, stimulating discussions with Professor Paul v. R. Schleyer of the University of Erlangen/Nürnberg and the technical assistance of Mr. Joseph Henriques during neutron data collection are gratefully acknowledged.

References

1 S. G. Shore, S. H. Lawrence, M. I. Watkins, and R. Bau, *J. Am. Chem. Soc.*, 1982, **104**, 7669.
2 R. K. Hertz, H. D. Johnson, II, and S. G. Shore, *Inorg. Chem.*, 1973, **12**, 1875; 1977, **17**, 24.
3 R. K. McMullan, L. C. Andrews, T. F. Koetzle, F. Reidinger, R. Thomas, and G. J. B. Williams, NEXDAS, Neutron and *X*-Ray Data Acquisition System, unpublished work; D. G. Dimmler, N. Greenlaw, M. A. Kelley, D. W. Potter, S. Rankowitz, and F. W. Stubblefield, *IEEE Trans. Nucl. Sci.*, 1976, **23**, 398.
4 M. T. Hutchings, M. P. Schulhof, and H. J. Guggenheim, *Phys. Rev. B*, 1972, 150.
5 W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 1957, **10**, 180.
6 Program DIFSYN, R. K. McMullan, Brookhaven National Laboratory, New York, unpublished work.
7 L. Koester, H. Rauch, M. Herkens, and K. Schroder, Kernforschungsanlage Report, Jülich, 1981, 1755.
8 A. Tippe and W. C. Hamilton, *Inorg. Chem.*, 1969, **8**, 464.
9 F. Takusagawa, A. Fumagalli, T. F. Koetzle, S. G. Shore, T. Schmitkons, A. V. Fratini, K. W. Morse, C. Y. Wei, and R. Bau, *J. Am. Chem. Soc.*, 1981, **103**, 5165.
10 R. Bau and T. F. Koetzle, *Pure Appl. Chem.*, 1978, **50**, 55; R. Bau, R. G. Teller, S. W. Kirtley, and T. F. Koetzle, *Acc. Chem. Res.*, 1979, **12**, 176.
11 J. H. Hall, jun., D. S. Marynick, and W. N. Lipscomb, *Inorg. Chem.*,

1972, **11**, 3126; C. Hoheisel and W. Kutzelnigg, *J. Am. Chem. Soc.*, 1975, **97**, 6970; B. Bigot, R. M. Lequan, and A. Devaquet, *Nouv. J. Chim.*, 1978, **2**, 449; R. A. Whiteside, M. J. Frisch, J. S. Binkley, D. J. DeFrees, H. B. Schlegel, K. Raghavachari, and J. A. Pople, in 'Carnegie-Mellon Quantum Chemistry Archive,' 2nd edn., July 1981; J. S. Binkley, J. A. Pople, and W. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939.

12 K. Raghavachari, R. A. Whiteside, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1981, **103**, 5647.

13 K. Raghavachari, P. v. R. Schleyer, and G. W. Spitznagel, *J. Am. Chem. Soc.*, 1983, **105**, 5917.

14 A. M. Sapse and L. Osorio, *Inorg. Chem.*, 1984, **23**, 627.

15 J. L. Atwood, D. C. Hrncir, R. D. Rogers, and J. A. K. Howard, *J. Am. Chem. Soc.*, 1981, **103**, 6787.

16 J. M. Howell, A. M. Sapse, E. Singman, and G. Snyder, *J. Am. Chem. Soc.*, 1982, **104**, 4758.

Received 29th April 1985; *Paper* 5/698