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The Low Temperature Crystal and Molecular Structure of Beryllium Bis(octahydrotriborate), $Be(B_3H_8)_2$

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Abstract: The solid state structure of beryllium bis(octahydrotriborate), $Be(B_3H_8)_2$, consists of two bidentate $B_3H_8^-$ ligands bound to a central beryllium atom by two Be–H–B bridge hydrogen bonds from adjacent boron atoms in each $B_3H_8^-$ unit. Crystals of $Be(B_3H_8)_2$ form in the monoclinic space group $P2_1/n$ with unit cell parameters a = 10.503 (8) Å, b = 7.641 (3) Å, c = 11.399 (9) Å, β = 118.49 (6)°, V = 804 (1) Å^3, and Z = 4. The x-ray crystal structure was solved by direct methods and refined to R_1 = 0.050 and R_2 = 0.061 for 944 independent observed reflections. The molecule has molecular C_2 symmetry with an approximately tetrahedral beryllium atom and $B_3H_8^-$ ligands essentially undistorted from free $B_3H_8^-$ in their internal bonding. $Be(B_3H_8)_2$ is the first reported metal complex having two octahydrotriborate ligands bound to a metal.

Beryllium bis(octahydrotriborate), $Be(B_3H_8)_2$, is a colorless liquid prepared by gently heating an intimate mixture of TlB_3H_8 and $BeCl_2$ in vacuo.[2] Preliminary variable-temperature ^{11}B and ^1H NMR studies indicated three basic molecular forms. The two higher temperature forms correspond to partially and completely fluxional molecules, while the low temperature form (observed below −10°) appeared to be static and have C_2 molecular symmetry. In order to confirm the NMR analysis we initiated a low-temperature single-crystal x-ray determination of the static configuration of $Be(B_3H_8)_2$.

Structure Determination

Single-Crystal X-Ray Data. The $Be(B_3H_8)_2$ used was prepared and purified as previously described.[2] Due to the compound's extreme air sensitivity, it was necessary to load and seal the Pyrex x-ray capillaries on the vacuum line.[3] A capillary containing liquid $Be(B_3H_8)_2$ (mp −51°) was placed on a Syntex P$\bar{1}$ four-circle computer-controlled diffractometer equipped with low-temperature accessories, and an irregularly shaped single-crystal was grown at −77 ± 3°. The low crystal-growing temperature was necessary because of the tendency of $Be(B_3H_8)_2$ to supercool. The crystal was subsequently cooled to −175 ± 5° and 15 diffraction maxima were automatically centered

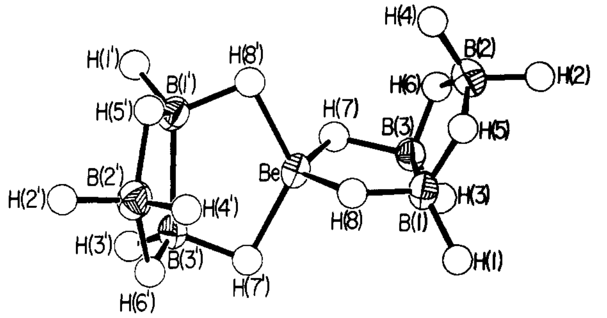

Figure 1. The static molecular structure of $Be(B_3H_8)_2$ showing the numbering system used in this paper. In this ORTEP diagram, 50% probability contours were plotted for the atomic vibration ellipsoids. The hydrogen atoms are represented by spheres of 0.14 Å radius.

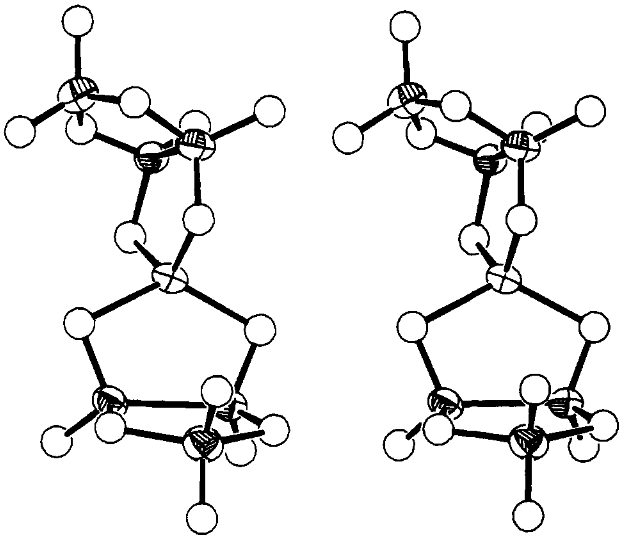

Figure 2. A stereoscopic view of $Be(B_3H_8)_2$.

in 2θ, χ, and ω. Graphite monochromated Mo Kα (λ 0.7107 Å) radiation was used throughout the alignment and data collection procedures. The Syntex routines[4] indicated a monoclinic lattice with dimensions of $a = 10.503$ (8) Å, $b = 7.641$ (3) Å, $c = 11.399$ (9) Å, $\beta = 118.49$ (6)°, and unit cell volume = 804 (1) Å^3. Systematic absences for $0k0$ with k = odd and $h0l$ with $h + l$ = odd indicated that the space group was $P2_1/n$ (nonstandard setting of $P2_1/c$ ($C_{2h}{}^5$, No. 14)). The equivalent positions for this space group are $x, y, z; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; and $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. The monoclinic symmetry and associated lattice constants were verified by partial rotation photographic projections along each of the three reciprocal axes. Because of the low melting point of $Be(B_3H_8)_2$, a density could not be conveniently determined. The calculated density of $Be(B_3H_8)_2$ is 0.743 g/cm^3 (at −175°) with $Z = 4$. This is a typical density for a compound of this type; e.g., the reported density of $Be(BH_4)_2$ is 0.609 g/cm^3.[5]

Intensity data were collected using the θ-2θ scan technique with variable scan speeds (from 2 to 24°/min) with each background count lasting two-thirds of the time used for the scan count. Two standard reflections (020 and 002) were monitored every 50 reflections during the entire data collection procedure and showed no significant deviation in intensity. All data were collected with the crystal temperature held at −175 ± 5°. A total of 1638 reflections were collected over the range $3.0° \leq 2\theta < 50.0°$. The data were reduced in the usual manner, with the standard deviation of each corrected intensity estimated from the formula $\sigma(I) = T_R[S + (B_1 + B_2)/B_R{}^2 + q(I)^2]^{1/2}$, where T_R is the 2θ scan rate in degrees per minute, S is the total integrated scan count, B_1 and B_2 are the background counts, B_R is the ratio of the background to scan count times, and q is set equal to 0.003. The merged data yielded 1138 independent reflections, of which 944 were observed ($I > 2.0\sigma(I)$) and were used in the solution and refinement of the structure.

Solution and Refinement of the Structure. Solution of the structure was accomplished using direct methods.[6] From the first E-Fourier synthesis the six most intense peaks corresponded to boron atoms and the seventh highest intensity peak to the beryllium atom. Five hydrogen atoms were also located from this map. The positions of the remaining hydrogen atoms were determined from the usual Fourier, least-squares, and difference electron density sequence.[7] Isotropic least-squares refinement for all atoms converged to $R_1 = 0.065$[8a] and $R_2 = 0.078$[8b]. Least-squares refinement converged to a final R_1 =

Table I. Final Atom Positional Parameters (×10^4) and Thermal Parameters[a] (Å^2)

Atom	x	y	z	B
B(1)	662 (3)	2412 (3)	2262 (2)	
B(2)	2528 (2)	2207 (3)	3618 (2)	
B(3)	968 (2)	2339 (3)	3925 (2)	
B(1′)	−346 (2)	−2195 (3)	2695 (2)	
B(2′)	−1764 (3)	−2333 (3)	950 (2)	
B(3′)	−1945 (2)	−962 (3)	2184 (2)	
Be	−141 (3)	372 (3)	2748 (3)	
H(1)	14 (24)	3585 (32)	1660 (22)	3.9 (5)
H(2)	3131 (25)	3358 (31)	3799 (24)	3.9 (5)
H(3)	606 (19)	3453 (26)	4235 (18)	1.9 (4)
H(4)	3006 (22)	980 (30)	3683 (21)	3.0 (5)
H(5)	1840 (21)	2303 (26)	2327 (20)	2.5 (4)
H(6)	2091 (22)	2144 (26)	4587 (20)	2.5 (4)
H(7)	573 (18)	1032 (25)	4172 (17)	1.7 (4)
H(8)	71 (19)	1136 (26)	1639 (17)	1.9 (4)
H(1′)	−41 (23)	−3082 (29)	3590 (22)	3.5 (5)
H(2′)	−2337 (22)	−3530 (28)	707 (21)	3.1 (5)
H(3′)	−2524 (20)	−1264 (25)	2725 (18)	1.9 (4)
H(4′)	−1438 (20)	−1657 (25)	282 (20)	2.5 (4)
H(5′)	−453 (23)	−2927 (29)	1751 (22)	3.4 (5)
H(6′)	−2631 (23)	−1175 (30)	1160 (23)	3.5 (5)
H(7′)	−1727 (18)	509 (25)	2170 (16)	1.8 (4)
H(8′)	697 (20)	−1333 (25)	2949 (18)	2.4 (4)

[a] Standard deviations of the last significant figure are given in parentheses in this and in all following tables.

Table II. Anisotropic Thermal Parameters[a] (×10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
B(1)	71 (3)	75 (4)	47 (2)	−16 (3)	26 (2)	0 (3)
B(2)	64 (3)	105 (5)	62 (2)	−12 (3)	33 (2)	−10 (3)
B(3)	51 (3)	69 (4)	50 (2)	−7 (3)	24 (2)	−5 (3)
B(1′)	66 (3)	62 (4)	51 (2)	−1 (3)	25 (2)	−2 (2)
B(2′)	80 (3)	84 (4)	52 (2)	−10 (3)	22 (2)	−10 (3)
B(3′)	54 (3)	65 (4)	58 (3)	−9 (3)	24 (2)	−6 (3)
Be	63 (3)	58 (4)	50 (3)	−6 (3)	28 (2)	−0 (3)

[a] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Interatomic Distances (Å) for $Be(B_3H_8)_2$

B(1)–B(2)	1.834 (4)	B(1′)–B(2′)	1.833 (4)
B(1)–B(3)	1.766 (3)	B(1′)–B(3′)	1.765 (3)
B(2)–B(3)	1.834 (3)	B(2′)–B(3′)	1.835 (4)
B(1)–Be	1.973 (3)	B(1′)–Be	1.971 (3)
B(2)–Be	2.855 (4)	B(2′)–Be	2.837 (4)
B(3)–Be	1.981 (3)	B(3′)–Be	1.971 (4)
B(1)–H(1)	1.136 (23)	B(1′)–H(1′)	1.137 (22)
B(2)–H(2)	1.045 (24)	B(2′)–H(2′)	1.056 (21)
B(3)–H(3)	1.059 (19)	B(3′)–H(3′)	1.078 (19)
B(2)–H(4)	1.050 (22)	B(2′)–H(4′)	1.101 (20)
B(1)–H(5)	1.207 (19)	B(1′)–H(5′)	1.169 (22)
B(2)–H(5)	1.295 (20)	B(2′)–H(5′)	1.317 (22)
B(2)–H(6)	1.384 (20)	B(2′)–H(6′)	1.371 (22)
B(3)–H(6)	1.065 (20)	B(3′)–H(6′)	1.051 (23)
B(3)–H(7)	1.167 (19)	B(3′)–H(7′)	1.149 (19)
Be–H(7)	1.514 (18)	Be–H(7′)	1.474 (16)
B(1)–H(8)	1.191 (19)	B(1′)–H(8′)	1.190 (19)
Be–H(8)	1.502 (18)	Be–H(8′)	1.527 (19)

Table IV. Intramolecular Bond Angles (deg) for $Be(B_3H_8)_2$

B(2)-B(1)-B(3)	61.2 (1)	B(2′)-B(1′)-B(3′)	61.3 (1)
B(2)-B(1)-Be	97.1 (2)	B(2′)-B(1′)-Be	96.4 (2)
B(3)-B(1)-Be	63.7 (1)	B(3′)-B(1′)-Be	63.4 (1)
B(3)-B(1)-H(1)	115.0 (11)	B(3′)-B(1′)-H(1′)	115.5 (11)
B(3)-B(1)-H(5)	106.0 (10)	B(3′)-B(1′)-H(5′)	107.0 (11)
B(3)-B(1)-H(8)	113.0 (9)	B(3′)-B(1′)-H(8′)	113.9 (9)
H(1)-B(1)-H(5)	113.1 (14)	H(1′)-B(1′)-H(5′)	113.8 (15)
H(1)-B(1)-H(8)	107.1 (14)	H(1′)-B(1′)-H(8′)	106.2 (14)
H(5)-B(1)-H(8)	101.9 (13)	H(5′)-B(1′)-H(8′)	99.3 (14)
B(1)-B(2)-B(3)	57.5 (1)	B(1′)-B(2′)-B(3′)	57.5 (1)
H(2)-B(2)-H(4)	120.9 (16)	H(2′)-B(2′)-H(4′)	123.4 (15)
H(2)-B(2)-H(5)	97.7 (15)	H(2′)-B(2′)-H(5′)	99.2 (15)
H(2)-B(2)-H(6)	105.8 (15)	H(2′)-B(2′)-H(6′)	105.2 (15)
H(4)-B(2)-H(5)	96.9 (14)	H(4′)-B(2′)-H(5′)	94.3 (13)
H(4)-B(2)-H(6)	104.0 (14)	H(4′)-B(2′)-H(6′)	105.7 (13)
H(5)-B(2)-H(6)	133.7 (12)	H(5′)-B(2′)-H(6′)	131.5 (14)
B(1)-B(3)-B(2)	61.2 (1)	B(1′)-B(3′)-B(2′)	61.2 (1)
B(1)-B(3)-Be	63.2 (1)	B(1′)-B(3′)-Be	63.4 (1)
B(1)-B(3)-H(3)	115.0 (10)	B(1′)-B(3′)-H(3′)	113.9 (10)
B(1)-B(3)-H(6)	109.7 (11)	B(1′)-B(3′)-H(6′)	108.9 (12)
B(1)-B(3)-H(7)	112.5 (9)	B(1′)-B(3′)-H(7′)	111.2 (9)
B(2)-B(3)-Be	96.8 (2)	B(2′)-B(3′)-Be	96.3 (2)
H(3)-B(3)-H(6)	109.2 (14)	H(3′)-B(3′)-H(6′)	109.1 (16)
H(3)-B(3)-H(7)	112.4 (13)	H(3′)-B(3′)-H(7′)	112.8 (14)
H(6)-B(3)-H(7)	96.3 (13)	H(6′)-B(3′)-H(7′)	99.9 (15)
B(1)-H(5)-B(2)	94.2 (14)	B(1′)-H(5′)-B(2′)	94.8 (15)
B(2)-H(6)-B(3)	96.1 (14)	B(1′)-H(6′)-B(3′)	97.7 (16)
B(3)-H(7)-Be	94.4 (12)	B(3′)-H(7′)-Be	96.6 (12)
B(1)-H(8)-Be	93.5 (11)	B(1′)-H(8′)-Be	92.2 (11)
B(1)-Be-B(3)	53.1 (1)	B(1′)-Be-B(3′)	53.2 (1)
B(1)-Be-B(3′)	142.2 (2)	B(1′)-Be-B(3)	142.8 (2)
H(7)-Be-H(8)	125.2 (10)	H(7′)-Be-H(8′)	125.1 (11)
H(7)-Be-H(8′)	99.7 (10)	H(7′)-Be-H(8)	100.7 (9)
B(1)-Be-B(1′)	146.4 (2)		
B(3)-Be-B(3′)	141.0 (2)		
H(7)-Be-H(7′)	109.3 (9)		
H(8)-Be-H(8′)	98.7 (10)		

Table V. Deviation of Atoms from Selected Planes

Plane	Atom	Deviation of atom from plane (Å)[a]
B(1)B(2)B(3)	H(5)	0.0009[b]
	H(6)	0.0581[b]
B(1′)B(2′)B(3′)	H(5′)	0.0305[b]
	H(6′)	0.0143[b]
B(1)B(3)Be	H(7)	−0.1138[c]
	H(8)	−0.0868[c]
	B(2′)	0.0531
	H(2′)	0.0489
	H(4′)	−0.0876
B(1′)B(3′)Be	H(7′)	0.0850[c]
	H(8′)	0.0812[c]
	B(2)	−0.0388
	H(2)	−0.0343
	H(4)	0.0644

[a] All atoms closer than ±0.2 Å to the defined plane are listed. [b] In $(Ph_3P)_2CuB_3H_8$ these bridge hydrogens are +0.2 and −0.8 Å out of the plane defined by the boron atoms. S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **8**, 2755 (1969). [c] In $(Ph_3P)_2CuB_3H_8$ these bridge hydrogens are 0.38 and 0.40 Å above the CuB(1)B(3) plane.

0.050 and R_2 = 0.061 when the nonhydrogen atoms were allowed anisotropic thermal motion. The final data to parameter ratio was 7.4. The standard deviation in an observation of unit weight was 1.46.[8c] Refinement of the hydrogen atoms anisotropically is not warranted by the data to parameter ratio.[9] The scattering factors of Hanson et al.[10] were used for the nonhydrogen atoms and those of Stewart et al.[11] for the hydrogen atoms. All least-squares refinements were based on the minimization of $\Sigma w_i(|F_o| - |F_c|)^2$, with the weights w_i set equal to $1/\sigma(F_o)^2$. The estimated standard deviations given in the tables in this paper were calculated from the full variance-covariance matrix obtained from the last least-squares refinement cycle.

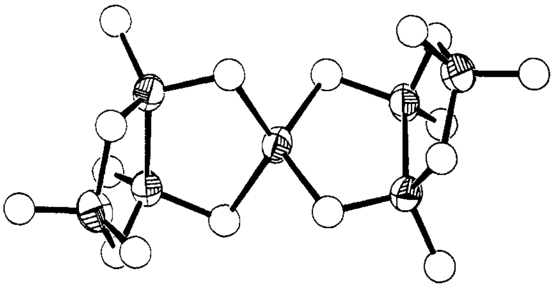

Figure 3. A view of the $Be(B_3H_8)_2$ molecule looking down the C_2 axis.

Description of the Structure

The static molecular structure of the $Be(B_3H_8)_2$ molecule and the numbering system used in this study are shown in Figure 1. The stereoscopic projection is shown in Figure 2. The atomic coordinates and isotropic thermal parameters of the hydrogen atoms in $Be(B_3H_8)_2$ are listed in Table I, and the anisotropic temperature factors for the nonhydrogen atoms are listed in Table II. Interatomic distances and intramolecular angles are listed in Tables III and IV, respectively, and Table V lists the deviations of several atoms from their idealized plane positions. Observed and calculated structure factors are also given; see paragraph at end of paper regarding supplementary material. Although the space group $P2_1/n$ does not require any molecular symmetry (none was used in the structural refinement), the $Be(B_3H_8)_2$ molecule possesses C_2 symmetry, verified by the close agreement observed for the symmetry-related bond lengths and angles (see Tables III and IV). A view of $Be(B_3H_8)_2$ looking down the C_2 axis is shown in Figure 3. Beryllium bis(octahydrotriborate) exists as discrete molecules with normal van der Waals packing. All contacts between molecules were examined. The shortest nonhydrogen contact is 3.838 Å between B(1′) and B(2′) ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$). The closest intermolecular nonbonding distance between a hydrogen and a nonhydrogen atom is 3.217 Å between B(2′) and H(1′) ($-\frac{1}{2} + x$, $-\frac{1}{2} - y$, $-\frac{1}{2} + z$). The shortest contact between hydrogen atoms is the 2.608 Å separation between H(3′) and H(7′) ($-\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$).

The $B_3H_8^-$ group functions as a bidentate ligand in $Be(B_3H_8)_2$ and except for $(CO)_3MnB_3H_8$,[12] this is the only mode of attachment known for this ligand. Beryllium bis(octahydrotriborate) is the first example of a metal complex having two $B_3H_8^-$ ligands.[13]

The bonding in $Be(B_3H_8)_2$ is electron deficient in nature, as illustrated by the four Be-H-B three-center two-electron bonds to beryllium. Each of these Be-H-B localized bonds can be considered to be comprised of one sp^3 orbital from the beryllium atom, one sp^3 orbital from the boron atom, and the hydrogen s orbital. The average Be-H-B angle of 94.2° in $Be(B_3H_8)_2$ is probably a result of electronic rather than stereochemical effects, since the s orbital of the hydrogen atom has a spherical distribution and can thus bond equally well regardless of the Be-H-B angle. The average Be-Hμ bond length of 1.504 Å in $Be(B_3H_8)_2$ is longer than the average B-Hμ bond length of 1.174 Å—too long to be explained by the greater tetrahedral covalent radius of beryllium vs. that of boron (1.06 vs. 0.88 Å, respectively).[14] This Be-Hμ vs. B-Hμ bond length difference may result from the greater positive charge on the beryllium atom compared to that on the boron atom. The dihedral angle between the planes H(7)-Be-H(8) and H(7′)-Be-H(8′) is 91.6 (8)°, within 2σ of the ideal 90° dihedral angle for a tetrahedral atom. Note, however, that the six H-Be-H angles range from 98.7 to 125.2°, quite different from the ideal 109.5°. The average Be-B distance in

Table VI. Comparison of $Be(B_3H_8)_2$ to Related Molecules

	$Be(B_3H_8)_2$[b]	$[(CO)_4CrB_3H_8]^-$[c]	$(Ph_3P)_2CuB_3H_8$[d]	$B_3H_8^-$[e]	B_4H_{10}[f]
Bond (Å)[a]					
B(1)-B(2)	1.834	1.82	1.82	1.77	1.845
B(1)-B(3)	1.766	1.78	1.76	1.80	1.750
B(2)-B(3)	1.834	1.82	1.82	1.77	1.845
$B-H_{terminal}$	1.045-1.137	1.07-1.22	1.0-1.3	1.05-1.20	1.03-1.17
B(1)-H(5), B(3)-H(6)	1.188, 1.058	1.15	1.15	1.2	1.21
B(2)-H(5), B(2)-H(6)	1.306, 1.378	1.43	1.52	1.5	1.37
B(1)-H(8), B(3)-H(7)	1.190, 1.158	1.29	1.21	*k*	1.21
M-H(7), M-H(8)	1.494, 1.515[g]	1.78[h]	1.85[i]	*k*	1.37[j]
Angle (deg)					
B(1)B(2)B(3)	57.5	58.4	58.5	61.1	56.6
B(1)H(5)B(2), B(2)H(6)B(3)	94.5, 96.9	89	81	81.1	91.8
B(1)H(8)M, B(3)H(7)M	92.9, 95.5[g]	104[h]	99[i]	*k*	91.8[j]
H(5)B(1)H(8), H(6)B(3)H(7)	100.6, 98.1	89	100	*k*	95.6
H(2)B(2)H(4)	122.2	115	110	*k*	125.1
H(5)B(2)H(6)	132.6	134	144	145.3	134.7
H(7)MH(8)	125.2[g]	101[h]	103[i]	*k*	134.7[j]
Dihedral Angle between Planes (deg)					
B(1)B(2)B(3) to B(1)MB(3)	115.0[g]	118.5[h]	119.3[i]	*k*	118.1[j]

[a] The numbering systems in the various literature citations have been altered so that the bond and angle designations listed here are internally consistent. [b] These values are the averages of the symmetry related bonds and angles. [c] Reference 16. [d] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **8,** 2755 (1969). [e] C. R. Peters and C. E. Nordman, *J. Am. Chem. Soc.*, **82,** 5758 (1960). [f] C. E. Nordman and W. N. Lipscomb, *J. Chem. Phys.*, **21,** 1856 (1953). [g] M = Be. [h] M = Cr. [i] M = Cu. [j] M = B. [k] Unavailable or not symmetry related to $Be(B_3H_8)_2$.

$Be(B_3H_8)_2$ is 1.974 Å while in the polymeric $Be(BH_4)_2$ the average Be-B distances are 1.92 and 2.00 Å, with the beryllium atom six-coordinate and approximately trigonal prismatic.[5]

Molecular orbital calculations for $B_3H_8^-$ [15] and $(CO)_4CrB_3H_8^-$ [16] indicate that the unique boron atom, B(2), is more positive than B(1) and B(3). Thus, the observation that the relatively positively charged B-H-B bridge hydrogen atoms are closer to B(1) and B(3) in all known octahydrotriborate complexes comes as no surprise.

Table VI compares bond lengths and bond angles in $Be(B_3H_8)_2$ to the analogous bond lengths and bond angles in other octahydrotriborate species. Bonding around the metal-B(1)-B(3) region of the molecule, as expected, shows the largest variances when molecules are compared. Thus, $Be(B_3H_8)_2$ and $(Ph_3P)_2CuB_3H_8$ show better agreement in the metal-B(1)-B(3) region of the molecule than $Be(B_3H_8)_2$ and $(CO)_4CrB_3H_8^-$, since chromium has a higher coordination number. Note that the closest overall agreement in bond distances and angles occurs when $Be(B_3H_8)_2$ is compared to B_4H_{10}, an anticipated result based on the similar coordination, bonding, and size of beryllium and boron.

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Supplementary Material Available: Table of observed and calculated structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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(8) (a) $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. (b) $R_2 = [\Sigma w_i(|F_o| - |F_c|)^2/\Sigma w_i|F_o|^2]^{1/2}$. (c) The standard deviation of an observation of unit weight is defined as $[w_i(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where *m* is the number of observations and *n* is the number of parameters fitted to the data.
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