in the *c* direction and with large vibrations perpendicular to the *c* direction. Possible explanations for this are systematic errors in the data, fractional occupancy of these layers, partial occupancy of adjacent sites in these layers, and disorder in the form of stacking faults. We can make some comments as to our evaluation of the various alternatives. The fact that both atoms in these layers exhibit the same effect suggests that it is more than just errors in the data. There is no way we can rule out fractional occupancy of these layers. Noteworthy here, however, is the fact that even with partial occupancy of these layers the over-all composition could correspond to ThI_2. The chemical analysis was good with an average $I/Th = 2.01$.[3] We did not refine population parameters for the atoms in the antiprismatic layers because we did not feel justified in assuming temperature factors for these atoms in such a refinement. The electron density difference map seems to discount the possibility of partial occupancy of adjacent sites in these layers. Finally, we feel the presence of stacking faults is probably the best explanation of the effect observed. A layer structure with weak interactions between layers can be easily two-dimensionally disordered. The disorder could appear in our model as large thermal motion perpendicular to *c*. This same disorder could contribute to the diffuse scattering observed.

The Th–I distances found here appear to be equivalent to those found in ThI_4 where they range from 3.13 to 3.29 Å with a mean of 3.20 Å.[14] This indicates the presence of Th^{4+} cores in ThI_2 and supports the Clark and Corbett formulation[3] of thorium diiodide as $Th^{4+}(I^-)_2(e^-)_2$. The extra electrons are presumably extensively delocalized within the layers. The Th–Th distance in thorium metal is 3.60 Å[15] so that the 3.97 Å distance here might be short enough for some Th–Th overlap, but this overlap would be very small. The implication is that the iodine atoms must play a role in accounting for the metallike conduction.[16] Our data are not good enough, especially in the low $(\sin\theta)/\lambda$ range, to differentiate between Th^{2+} and Th^{4+} cores on the basis of atom form factor differences.

In view of the diffuse scattering observed, some static lattice defects have not been explicitly accounted for, but we do not believe these would alter the essential structure features described here. Furthermore, we would expect that different polytypes might be obtained under different reaction conditions or different sample treatment. Scaife and Wylie's α-ThI_2 might be a different polytype in view of the obvious similarities in the powder patterns for their α and β phases. However it is difficult to rationalize their 7.13 Å powder line on the basis of a layered structure with an *a* cell edge similar to that of the β phase.

Acknowledgment.—The authors wish to thank Professor J. D. Corbett for helpful discussions.

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[14] A. Zalkin, J. D. Forrester, and D. H. Templeton, *Inorg. Chem.*, **3**, 639 (1964).

[15] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, p s11.

[16] For further discussion of this possibility see J. D. Corbett, R. A. Sallach, and D. A. Lokken in "Lanthanide–Actinide Chemistry," Advances in Chemistry Series, No. 71, American Chemical Society, Washington, D. C., 1968, p 61.

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The Chemistry of Boranes. XXXIII.[1] The Crystal Structure of $Rb_2B_9H_9$

BY L. J. GUGGENBERGER

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The crystal structure of $Rb_2B_9H_9$ has been determined from three-dimensional X-ray data collected on a four-circle diffractometer at room temperature. The material crystallizes in the tetragonal space group P4/nmm with two molecules in a cell of dimensions $a = 6.33$ and $c = 11.50$ Å. The structure was refined by least-squares methods to a conventional *R* factor of 0.063. The $B_9H_9^{2-}$ ions consist of discrete triangulated polyhedral units. The individual units lack the complete symmetry of the space group and are disordered so that C_{2v} point symmetry is imposed on the units. The resulting symmetry of the anion cage is idealized D_{3h}. The Rb ion interactions with the polyhedral cage are ionic in nature. Extended Hückel calculations are presented and discussed for the two most plausible $B_9H_9^{2-}$ symmetries (D_{3h} and C_{4v}).

Introduction

The structures of the binary boron hydrides can be characterized as triangulated polyhedra.[2] A characteristic of the highly symmetrical polyhedral borane anions is that individual anion point symmetries change readily with only slight changes in atom positions. For the $B_9H_9^{2-}$ ion the B^{11} nmr spectrum indicated an anion cage with D_{3h} point symmetry,[2] but the X-ray diffraction symmetry of single crystals of $Rb_2B_9H_9$ showed D_{4h} point symmetry suggesting a different structure for the solid state. The crystal structure of $Rb_2B_9H_9$ was determined to establish the solid-state structure of the $B_9H_9^{2-}$ unit and its relationship with the solution structure.

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[1] Paper XXXII: W. H. Knoth, N. E. Miller, and W. R. Hertler, *Inorg. Chem.*, **6**, 1977 (1967).

[2] F. Klanberg and E. L. Muetterties, *ibid.*, **5**, 1955 (1966).

Experimental Section

Crystal Data.—Crystals of $Rb_2B_9H_9$ and the isomorphous $Cs_2B_9H_9$ were supplied by Dr. F. Klanberg of this laboratory. The $Rb_2B_9H_9$ compound was chosen for this structural study. Crystals of $Rb_2B_9H_9$ are tetragonal with cell dimensions of $a = 6.33 \pm 0.01$ and $c = 11.50 \pm 0.01$ Å. The density observed by flotation is 1.99 g/cm^3 and the calculated density using $Z = 2$ is 2.00 g/cm^3. Weissenberg and precession films showed that the diffraction symmetry is D_{4h} with the only systematic absence being $hk0$, $h + k = 2n + 1$. This establishes the space group as P4/nmm.

Intensities.—A crystal of dimensions $0.15 \times 0.15 \times 0.07$ mm was used for the intensity measurements. The crystal was mounted with the a axis coincident with the φ axis of a Picker automatic diffractometer equipped with a molybdenum tube (λ 0.7107 Å), a scintillation counter, and a pulse-height discriminator. The θ–2θ scan technique was used with a scan speed of 1°/min. Individual backgrounds of 20 sec were measured before and after each scan. The scan length was 2° plus the angular separation for $K\alpha_1$ and $K\alpha_2$ for each reflection. Two sets of data were collected on the same crystal. Initially 458 reflections were measured in half of one octant of the reciprocal lattice. Later 791 reflections were measured in one complete octant of the reciprocal lattice. The data collection and data reduction were the same for both sets of data.

The intensities were corrected for Lorentz-polarization effects in the usual way and for absorption using Prewitt's program ACACA.[3] For the absorption correction the crystal was defined by 14 plane faces; the calculated transmission factors varied from 0.24 to 0.52. The linear absorption coefficient for Mo $K\alpha$ radiation is 111.1 cm^{-1}.

The errors in the intensities were estimated by

$$\sigma(I) = (\mathrm{CN} + (t_c/2t_b)^2(\mathrm{BG}_1 + \mathrm{BG}_2) + (0.03I)^2)^{1/}$$

where CN is the total count measured in time t_c, BG_1 and BG_2 are the background counts each measured in time t_b, and I is the integrated intensity after subtracting out the background. The $\sigma(F)$ was obtained from $\sigma(I)$ after the method of Williams[4] by

$$\sigma(F) = (\mathrm{Lp}T)^{-1/2}[(I + \sigma(I))^{1/2} - I^{1/2}]$$

where Lp is the Lorentz-polarization factor and T is the transmission factor. This method of calculating $\sigma(F)$ from $\sigma(I)$ is equivalent to using

$$\sigma(F) = (\mathrm{Lp}T)^{-1/2}(\sigma(I)/2F)$$

for all but the very small F's where the latter formula gives unrealistic values for $\sigma(F)$. The $\sigma(F)$'s for F's large enough to be called observed are generally the same using both methods of calculating $\sigma(F)$ from $\sigma(I)$, but the former equation gives more realistic values of $\sigma(F)$ for small F's usually considered unobserved. Structure factors for which F was less than $\sigma(F)$ were called unobserved. The function minimized in least squares was $\Sigma w(|F_o| - |F_c|)^2$. The atomic scattering factors used were for neutral B and H atoms[5] and for the Rb^+ ion. The anomalous dispersion effect for Rb was included in the calculated structure factors using $\Delta f' = -0.90$ and $\Delta f'' = 3.10$.[6] Unless specified, local programs were used with the least-squares program being written by Prewitt.[3]

Determination of Structure

The first set of data was used to establish and partly refine all of the nonhydrogen positions. One set of Rb atoms was placed in special positions with all of the positional parameters fixed; the z parameter for the other set of Rb atoms was determined from a Patterson synthesis. These atom positions were then used to calculate an electron density map from which all of the boron atoms were located. Atoms were placed in the space group P4/nmm in the following way: Rb's in b, ($^1/_4$, $^3/_4$, $^1/_2$); Rb's, B's, and H's in c ($^1/_4$, $^1/_4$, z); B's and H's in j (x, x, z); and B's and H's in i ($^1/_4$, x, z).[7]

The anion model in these early stages of refinement had C_{4v} point symmetry. The R factor $(\Sigma(||F_o| - |F_c||)/\Sigma|F_o|)$ was 0.12 after four cycles of least-squares using isotropic thermal parameters. It was observed here that the temperature factors of the atoms in the open square face were twice those in the capped square face for this C_{4v} model. On varying the atom thermal parameters anisotropically, R went to 0.095. An electron density map at this point showed that the boron atoms on the open square face were disordered. The nature of the disorder is shown in Figure 1. The average structure refined is the C_{4v} model shown in b, but, in fact, this model is a superposition of models a and c in Figure 1. This was clearly evident in the Fourier synthesis since the boron peaks in the open face were very elongated. They were elongated in a special way with a considerable amount of broadening in the z direction which is necessary since closing the open square face gives two sets of boron atoms that are separated by 0.32 Å in the c direction. At this point the second set of data was measured. The octant chosen here did not include the half-octant measured in the first data set. This was done purposely to examine a greater volume of reciprocal space. The two equivalent members of the $\{hkl\}$ form measured in the second data set were averaged leaving a total of 435 independent pieces of data, 374 of which were considered observed. The σ values for the averaged structure factors were obtained according to $\sigma(\mathrm{av}) = {}^1/_2(\sigma(F_1)^2 + \sigma(F_2)^2)^{1/2}$. The agreement between symmetry-equivalent reflections was very good with a maximum difference between the symmetry-equivalent structure factors of 1.5σ.

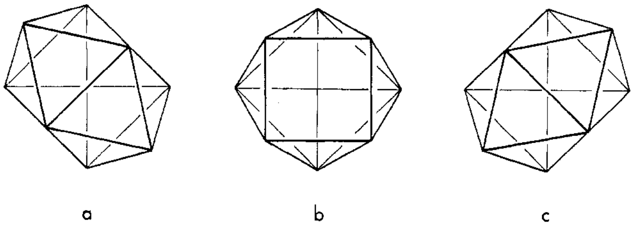

Figure 1.—The C_{4v} symmetry for the $B_9H_9^{2-}$ cage results from a superposition of the D_{3h} forms a and c. The threefold axis in a and c is in the plane of the paper and in the direction of the bond closing the square face in b.

The refinement was continued using as starting parameters the refined parameters obtained from the first set of data. The hydrogen atoms were placed in positions indicated by the electron density difference map. The hydrogen atom positional parameters were varied but not the isotropic temperature factors which

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(3) C. T. Prewitt, local unpublished computer programs, 1967.

(4) D. E. Williams and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 1660 (1964).

(5) H. P. Hansen, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, **17**, 1040 (1964).

(6) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 206, 215.

(7) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, p 224.

Table I

Positional and Thermal Parameters for $Rb_2B_9H_9$

Atom	x	y	z	$\beta_{11}{}^a$ or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rb_1	0.25	0.75	0.50	0.01326 (20)	0.01326 (20)	0.00376 (9)	0.0	0.0	0.0
Rb_2	0.25	0.25	0.12802 (12)	0.02474 (30)	0.02474 (30)	0.00370 (11)	0.0	0.0	0.0
B_1	0.25	0.25	0.6125 (15)	0.0141 (24)	0.0141 (24)	0.0057 (14)	0.0	0.0	0.0
B_2	0.1038 (8)	0.1038 (8)	0.7043 (6)	0.0159 (12)	0.0159 (12)	0.0033 (5)	−0.0039 (15)	−0.0001 (6)	−0.0001 (6)
B_3	0.25	0.0260 (28)	0.8241 (16)	2.81 (31)					
B_4	0.1070 (24)	0.25	0.8519 (13)	2.18 (26)					
H_1	0.25	0.25	0.5023 (136)	1.00					
H_2	−0.0069 (86)	−0.0069 (86)	0.6686 (63)	1.00					
H_3	0.25	−0.1318 (174)	0.8645 (104)	1.00					
H_4	0.0163 (171)	0.25	0.9671 (112)	1.00					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II

Observed and Calculated Structure Factors (×10) for $Rb_2B_9H_9$

```
 H,K= 0, 0  15 106  77  12  56  20  11 379 386  11  89  46  11  82  57  12 107  38   H,K= 4, 4   3 101 107   7 267 275   2 182 180  10 100 104   H,K= 6, 6   5  37  58*  3 208 181
 1 188 187  16  64  50  13 230 241  12  48   7* 12 309 300  12 322 321  13 145 124   0 500 516   4 497 498   8  39  58*  3 327 333  11 194 160   0 181 194   6  74  83   4   0  45*
 2 232 232   H,K= 1, 1  14 169 172  13 203 219  13  80  68  13  49  87  14  43  78*  1 184 178   5 157 164   9 197 204   4  77  53   H,K= 6, 3   1 100  89   7  33  16*  5 179 157
 310991052   0 294 287  15  66   5  14 166 170  14 137 121  14  67  77   H,K= 4, 2   2 188 200   6 210 204  10 141 129   5 330 318   1 124 126   2 120 102   8  65  13   6 121 137
 4  69 101   1 9771005   H,K= 2, 1  15  33  11* 15 229 219   H,K= 4, 0   0 614 629   3 308 309   7 345 349  11 106  59   6 230 229   2 135 126   3 152 135   9  85  28   7  73  38
 5 942 941   2 714 712   1 398 399   H,K= 3, 0   H,K= 3, 2   0 717 716   1 192 202   4 106 100   8  30  45* 12 186 189   7   0  29*  3  36  40*  4  23  49*  H,K= 7, 3   H,K= 8, 1
 6 691 679   3 163 165   2 566 555   1 404 392   1 283 281   1 163 134   2 323 327   5 323 336   9 237 234   H,K= 5, 4   8 250 263   4  33  15*  H,K= 7, 0   0 107 116   1  30  16*
 7 146 106   410741074   3 261 250   2 360 345   2 463 468   2 442 422   3 458 465   6 229 228  10 202 183   1  92  80   9 162 135   5  85  81   1   0  19*  1 203 202   2 117  61
 8 639 633   5 161 158   4  38  14   3 139 139   3 220 222   3 695 675   4  78  83   7 103  79  11  95  56   2 141 148  10 146 135   6 145 135   2 144 116   2 127 108   3  34  33*
 9 249 266   6 340 338   5 311 298   4 119 114   4 104  89   4  47  21   5 426 438   8 252 254  12 212 214   3  75  82  11 233 192   7  66  21   3  72  77   3  36  76*  4  20   1*
10 278 282   7 732 741   6 402 397   5 232 221   5 275 274   5 375 358   6 261 261   9 125 127  13 115  73   4  55   4   H,K= 6, 1   8  60  35   4  66  33   4 237 234   5  31  26*
11 435 455   8  21  11*  7 169 151   6 448 441   6 282 273   6 341 349   7 100  98  10 202 186   H,K= 5, 2   5  70  90   1  76  56   9  26  38*  5  67  44   5 138 125   6  36  45*
12  22  48*  9 403 409   8  74  49   7 113 128   7 107 103   7 178 160   8 395 402  11 179 180   1 133 130   6 147 136   2 184 169  10  27  59*  6  82  36   6 150 135   H,K= 8, 2
13 211 212  10 279 293   9 187 191   8  87  82   8  55  45   8 475 482   9 151 126  12  34  13*  2 229 233   7  75  64   3 109  94   H,K= 6, 4   7  73  62   7 135 130   0 187 182
14 234 227  11   0  28* 10 233 228   9 143 123   9 184 188   9 135 118  10 209 197   H,K= 5, 0   3 121 116   8  28  11*  4  91  26   0 245 242   8   0  44*  8  97  18   1  99  89
15  72  63  12 405 421  11 128 114  10 213 202  10 187 178  10 114 120  11 263 260   1 128 109   4  52  24   9  88  86   5 119  84   1 122 107   9  75  67   H,K= 7, 4   2 148 132
16 215 208  13 113 122  12  35  22* 11 156 155  11  45  44* 11 279 283  12  30   9*  2 194 187   5 138 134  10 112  93   6  82  96   2 209 197   H,K= 7, 1   1  81  70   3 161 162
 H,K= 1, 0  14  89  95  13 100 136  12   0  46* 12   0  24* 12 105  81  13 184 169   3 117 115   6 175 169  11  35  25*  7  60  67   3 263 250   0  29  21*  2  49  55   4  66  49
 1  29  49  15 226 223  14 127 128  13 184 168  13 125  91  13 220 209   H,K= 4, 3   4   0  43*  7  92  74   H,K= 5, 5   8  31  21*  4  68  50   1 236 237   3  30  12*  5 120 129
 2 627 597   H,K= 2, 0  15 106  54  14  86  86  14 126 105  14  72  98   1 107 106   5 123 106   8  23  16*  0  69  59   9 120  81   5 185 157   2 196 203   4  62  26   6 141 101
 3 420 402   011621160   H,K= 2, 2   H,K= 3, 1   H,K= 3, 3   H,K= 4, 1   2 314 323   6 220 205   9 127 108   1 247 244  10  94  92   6 152 137   3 151 114   5  51  35*  H,K= 8, 3
 4  41  43   1 175 172   0 899 921   0 127 119   0  12  17*  1 247 245   3 180 186   7  96 112  10 125 115   2 173 176   H,K= 6, 2   7 102 103   4 274 270   6  92  86   1  61  48
 5 281 273   2 620 606   1 296 301   1 710 715   1 465 472   2 299 287   4  96  89   8  59   9  11  31  36*  3 111  87   0 347 356   8 217 206   5 113  75   H,K= 7, 5   2  33  51*
 6 369 351   31043 996   2 489 491   2 361 367   2 399 408   3 146 141   5 188 185   9 111 105  12  33  15*  4 270 270   1 148 144   9  89  70   6 143 128   0  32  51*  3  16  14*
 7 301 292   4  90  53   3 629 641   3 117 113   3 268 277   4  73  51   6 169 162  10 162 146   H,K= 5, 3   5 141 128   2 229 227   H,K= 6, 5   7 241 231   1 140 141   4  33  11*
 8  55  77   5 660 634   4  37  27*  4 805 800   4 520 532   5 194 181   7 132 110  11  95  69   0  71  63   6 140 132   3 287 288   1  62  48   8  54  51*  2 137 108
 9 265 277   6 458 434   5 641 655   5 247 244   5  78  72   6 315 317   8  40   4* 12  66  18   1 326 336   7 192 183   4   0  54*  2  82  70   9 139 127   3  72  68
10 300 309   7 111  93   6 358 342   6 352 338   6 298 300   7 129 115   9 174 179  13 127  85   2 238 251   8  59  53   5 257 263   3  33  28*  H,K= 7, 2   4 155 159
11 113  93   8 693 684   7 116 114   7 452 466   7 448 448   8  27  45* 10 154 149   H,K= 5, 1   3 137 147   9 144 138   6 171 174   4   0  11*  1  98  81   H,K= 8, 0
12  55  10   9 173 152   8 581 601   8  30  24*  8  47  72*  9 129 127  11  37  13*  0  53  26   4 370 376   H,K= 6, 0   7  87  88   5  69  37   2 106 102   0 276 264
13 140 126  10 209 186   9  88 103   9 383 395   9 289 294  10 182 172  12  45  25*  1 432 447   5 136 129   0 519 503   8 287 271   6  48  72*  3  32  33*  1 110  87
14 181 190  11 407 413  10 220 213  10 289 286  10 127 133  11 118  97  13  71  58   2 306 303   6 203 199   1 141 133   9 100  82   7  44  24*  4  30   3*  2 139 105
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were set at 1.0. Three more cycles of least squares were run with the Rb's and ordered boron atoms having anisotropic thermal parameters and all other atoms having isotropic thermal parameters. The final R and wR, where wR is $(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$, are 0.063 and 0.039, respectively. For all reflections R = 0.075 and wR = 0.040. Throughout the refinement it was assumed that the crystal was composed of 50% of both models a and c in Figure 1. The disorder was accounted for in the refinement by using two sets of boron and hydrogen atoms in positions i of the space group with atom site populations of 0.5. At the end of the refinement the standard deviation of an observation of unit weight was 1.45 indicating that the σ values were too small. An analysis of the average values of $w||F_o| - |F_c||^2$ as a function of F_o suggested that the large structure factors should have had somewhat larger σ values; however, in view of the disorder no weighting scheme changes were made.

The final parameters are given in Table I. The observed and calculated structure factors are given in Table II where an asterisk is used to denote an unobserved reflection.

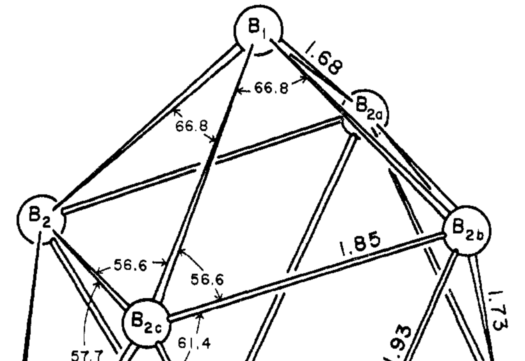

Figure 2.—Molecular configuration of the $B_9H_9{}^{2-}$ ion showing bond distances and angles. The estimated errors in the bond lengths are 0.015 Å.

Description of the Structure

The structure of the $B_9H_9{}^{2-}$ ion is a discrete triangulated polyhedral cage (Figure 2). The cage can be described as a tricapped trigonal prism where the triangular prism faces contain atoms B_2–B_{2a}–B_4 and B_{2c}–B_{2b}–B_{4a} and the centroids of these faces are coincident with the idealized C_3 axis. Each cage is required to have C_{2v} symmetry exactly; however, each cage has idealized D_{3h} symmetry.

In the solid state the crystal structure is disordered in space (not time) such that the other equivalent cage with B_3 and B_{3a} bonded instead of B_4 and B_{4a} is equally favored and the two cages occur at random in equivalent sites throughout the crystal. This immediately establishes the relationship between the solid-state and solution structures of the B_9H_9 dianion and so fulfills the goal of this structural study. In fact, then, the molecular configuration of $B_9H_9^{2-}$ is the same in the solid state as it is in solution.

The unique nonhydrogen-bond distances and angles are shown in Figure 2. The numbering is such that atoms with the same principal subscript are related by symmetry, *i.e.*, B_2, B_{2a}, B_{2b}, and B_{2c} are related by the C_4 axis of the space group. The estimated standard deviations in the bond lengths are 0.015 Å for B–B bonds and 0.15 Å for B–H bonds; for the angles not fixed by symmetry involving only boron atoms, σ = 0.6°. All distances and angles not specifically shown in Figure 2 are related to one of those shown by one of the vertical mirror planes.

A terminal hydrogen atom is attached to each boron atom. The unique B–H distances are 1.27 Å for B_1–H_1, 1.07 Å for B_2–H_2, 1.10 Å for B_6–H_6, and 1.44 Å for B_9–H_9. The first three values are in the range expected for B–H bonds of this type while the last distance is a little long, but the refinement of H_9 is not expected to be good because of its vicinity to boron in the disordered model. The reasonableness of the B–H distances is the justification for including their positional parameters in the refinement.

The intramolecular bond distances and bond angles are in the range usually found in the boranes.[8] The average B–B distance is 1.78 Å. The molecular symmetry is very nearly D_{3h}, and, in view of the disorder, it is felt that any slight deviations from this symmetry are not significant. The dihedral angle between the triangular faces of the trigonal prism, B_2–B_{2a}–B_4 and B_{2c}–B_{2b}–B_{4a}, is 2.5°.

The stacking of the anions in the cell is illustrated in Figure 3 where only one of the limiting configurations of D_{3h} symmetry is depicted. The Rb atom interactions are considered to be of the normal ionic type. For Rb_1 the nearest interactions are in a tetrahedral fashion to four triangular faces with the shortest Rb–B distance being 3.37 Å. For Rb_2 the nearest interactions are to five cage edges with four Rb–B distances of 3.66 Å and one of 3.30 Å.

The configuration of the polyhedral cage observed here is similar to that reported recently for the structure of the $B_7H_7C_2(CH_3)_2$ carborane.[9] In the latter structure the B_3 and B_{3a} positions in Figure 2 are occupied by C atoms each containing a terminal methyl group. Average bond distances observed in the $B_7H_7C_2(CH_3)_2$ structure agree reasonably well with the distances found here except that the B_2–B_{2a} and B_2–B_{2c} distances in the carborane are not equivalent by cell symmetry and form two nonequivalent sets at 2.00 and 1.78 Å, respectively. Other bond distances in the carborane structure are 1.72 Å for B_1–B_{2a}, 1.97 Å for B_{2b}–B_{4a}, and 1.77 Å for B_4–B_{4a}.

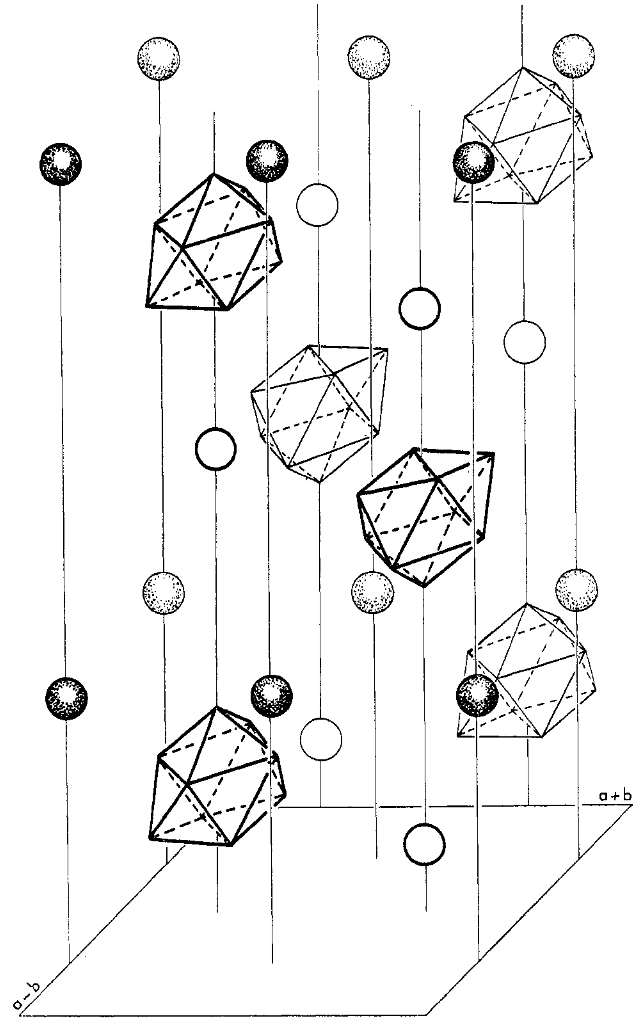

Figure 3.—Crystal packing of $Rb_2B_9H_9$. Only one of the disordered anion forms is shown. The height in this view corresponds to $^3/_2c$.

Extended Hückel Calculations on $B_9H_9^{2-}$

Calculations of the LCAO–MO extended Hückel variety similar to those reported earlier[10] on B_8H_8 geometries were performed on several B_9H_9 geometries to see whether they might elucidate the ground-state geometry of this system. Similar calculations were reported for the $B_7H_7C_2(CH_3)_2$ carborane.[9] The Hoffman–Lipscomb procedure[11] was used assuming regular geometries with B–B and B–H distances of 1.80 and 1.19 Å, respectively. The basis set consisted of 9 hydrogen Slater orbitals, exponent 1.0, and 9 boron 2s and 27 boron 2p Slater orbitals, exponent 1.3. The H_{ii} terms were chosen as H_{ii}(H1s) = −13.60, H_{ii} (B2s) = −14.91, and H_{ii}(B2p) = −8.42 eV. The off-diagonal matrix elements were evaluated using the relationship

$$H_{ij} = (k/2)(H_{ii} + H_{jj})S_{ij} \qquad (k = 1.75)$$

The geometries examined are depicted in Figure 4. The total energies and the gap energies between the highest occupied and lowest unoccupied levels are given

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[8] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1966.

[9] T. F. Koetzle, F. E. Scarbrough, and W. N. Lipscomb, *Inorg. Chem.*, **7**, 1076 (1968).

[10] F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *ibid.*, **6**, 1271 (1967).

[11] R. Hoffman and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962).

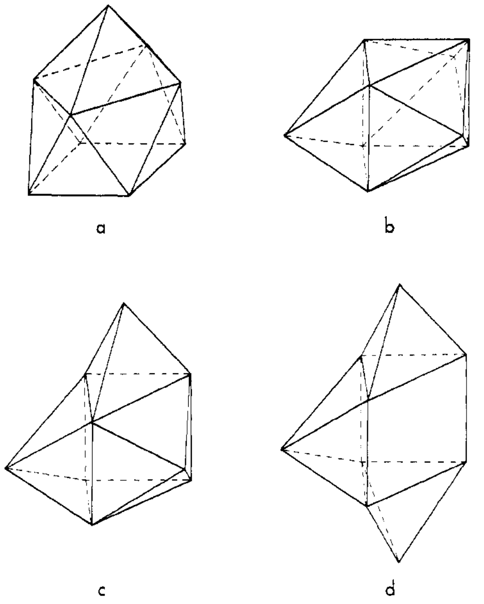

Figure 4.—Models used for the MO calculations. Configurations a and b have C_{4v} and D_{3h} point symmetry, respectively. Configurations c and d are lower symmetry, higher energy configurations.

below. The two most plausible geometries are the C_{4v} and D_{3h} models, a and b in Figure 4. Models c and d were included to test the usefulness of the calculations since they should predict these two models to be undesirable configurations if the calculations are at all meaningful. We are guided here by our past experiences and the empirical rule that triangular faces prevail in closed boron polyhedral structures. The calculations confirmed our initial predictions exactly with regard to models c and d, showing that these models have unfavorable total energies and poor gap energies in comparison to model b. Model d is the least plausible from these calculations as we had predicted.

Model (Figure 4)	Total energy, eV	Gap energy, eV
a	−548.78	0.00
b	−545.46	2.80
c	−544.12	1.09
d	−543.20	0.15

The one-electron Hückel energies and orbital symmetries for the C_{4v} and D_{3h} models are given in Table III. Significantly, the C_{4v} model with 38 electrons does not correspond to a closed-shell configuration as the last two electrons must be placed in a degenerate set of orbitals. This electronic configuration is symmetry imposed. On the other hand, the D_{3h} model gives a closed-shell configuration with a respectable gap energy. Thus these calculations support a D_{3h} structure for the B_9H_9 dianion in solution and in the solid state since a closed-shell configuration is to be expected for this diamagnetic species. The argument here is extended to include the solid state since packing forces do not seem to be important in determining the structural configuration of the polyhedral cage.[12]

TABLE III

ONE-ELECTRON ENERGIES FOR D_{3h} AND C_{4v} MODELS OF $B_9H_9^{2-}$

C_{4v}		D_{3h}	
Level	Energy, eV	Level	Energy, eV
b_2	57.945	e''	59.488
b_1	57.944	a_1'	50.835
a_1	45.394	a_2''	49.717
e	42.787	e'	41.672
a_1	38.267	e'	31.490
e	35.178	e''	25.558
b_1	23.398	a_1'	23.598
b_2	23.396	e'	20.268
a_1	21.987	e'	15.088
e	21.612	a_1'	7.925
a_1	12.558	a_2'	7.444
a_1	11.278	e''	4.996
e	8.522	a_2''	4.504
a_2	7.243	a_1''	0.492
e	5.969	e''	−0.958
b_2	−0.057	e'	−2.914
b_1	−0.058	a_2''	−6.553
a_2	−0.390	a_2'	−9.355
e	−2.630	e'	−9.724
e	−8.682	e''	−10.545
e	−10.386	a_1'	−11.224
b_2	−10.920	a_2''	−12.059
b_1	−10.920	e'	−12.450
a_1	−11.136	a_1'	−13.928
e	−12.058	e''	−15.680
a_1	−12.437	a_1'	−15.843
a_1	−14.063	e'	−16.385
a_1	−15.913	a_2''	−18.327
b_2	−15.956	e'	−19.721
b_1	−15.957	a_1'	−22.987
e	−16.298		
e	−19.271		
a_1	−19.475		
a_1	−22.904		

The net atom charges for the D_{3h} model are −0.030 and −0.066 for borons and −0.179 and −0.181 for hydrogens for the symmetry-equivalent sets of six and three atoms, respectively; otherwise, the details of the calculations are rather uninteresting. The calculations suggest that the C_{4v} ground state could prevail on a two-electron oxidation or reduction of the cage. The reduction especially would lead to a nice energy level scheme with a gap energy of 6.05 eV; however, it would be difficult to effect this reduction chemically.

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(12) It is noteworthy that the solid-state infrared and Raman spectra of $Rb_2B_9H_9$ also seem to be consistent with the D_{3h} model as evidenced by the numbers of B–H vibrations observed. There are five sharp peaks of approximately equal intensity in the Raman spectrum at 2546, 2490, 2460, 2427, and 2410 cm^{-1}. In the ir spectrum (Nujol mull and KBr disk) there are three principal bands at 2540, 2480, and 2418 cm^{-1} and a shoulder at 2450 cm^{-1}. For a cage of D_{3h} symmetry there should be five Raman bands ($2A_1'$, $2E'$, E'') and three ir bands (A_2'', $2E'$). For a cage of C_{4v} symmetry there should be seven Raman bands (B_1, B_2, $3A_1$, $2E$) and five ir bands ($3A_1$, $2E$).