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The Crystal Structure of Tetraamminezinc Octahydrooctaborate(−2), $Zn(NH_3)_4B_8H_8$

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The molecular and crystal structures of tetraamminezinc octahydrooctaborate(−2), $Zn(NH_3)_4B_8H_8$, have been determined from three-dimensional X-ray counter data. This compound crystallizes in the tetragonal space group $P4_2/nmc$ with two molecules in a cell of dimensions $a = 7.503 \pm 0.005$ and $c = 10.784 \pm 0.008$ Å. The structure was refined by least-squares procedures to a conventional R of 0.078. The structure contains $Zn(NH_3)_4^{2+}$ cations and $B_8H_8^{2-}$ anions. The $B_8H_8^{2-}$ polyhedron is a distorted dodecahedron of D_{2d} ($\bar{4}2m$) point symmetry similar to that observed in the B_8Cl_8 and $B_6H_6C_2(CH_3)_2$ structures. Molecular orbital calculations indicate that the five-coordinate boron atoms are the more negative of the two sets of five- and six-coordinate boron atoms.

Introduction

Until recently the molecular geometries of the eight-atom boron polyhedra of the boranes and the analogous carboranes were unknown. Recently the syntheses of $B_8H_8^{2-}$ and $B_8H_8^-$ were reported together with some preliminary X-ray results on the $B_8H_8^{2-}$ anion and a discussion of the bonding possibilities for six different B_8 symmetry polyhedra.[1] Earlier proposed geometries for the eight-atom boranes and carboranes included an Archimedian antiprism of D_{4d} symmetry, a dodecahedron of D_{2d} symmetry, and an intermediate structure of C_{2v} symmetry.[2–5] The D_{4d} antiprism and D_{2d} dodecahedron differ very little from a geometrical and bonding point of view.[1,5] The crystal structure of $Zn(NH_3)_4B_8H_8$ reported here and that of $B_6H_6C_2(CH_3)_2$ recently reported by Hart and Lipscomb[6] establish the D_{2d} dodecahedral geometry for the polyhedral B_8 boranes and B_6C_2 carboranes. This geometry is very similar to that found for the neutral B_8Cl_8 molecule.[7]

Crystal Data and Structure Determination

Crystals of $Zn(NH_3)_4B_8H_8$ are tetragonal with cell parameters of $a = 7.503 \pm 0.005$ and $c = 10.784 \pm 0.008$ Å. These values result from an averaging of values measured on the diffractometer (axial reflections with λ(Mo Kα) 0.7093 Å) and on Weissenberg and precession camera photographs. The calculated density on the basis of two molecules per cell is 1.25 g/cm^3. The experimental density was not measured because the available sample consisted of only a few crystals. Crystals gave the characteristic uniaxial interference figure with convergent light viewed in the direction of the optic axis. The systematic absences observed on Weissenberg and precession films are $\{hk0\}$, $h + k = 2n + 1$, and $\{hhl\}$, $l = 2n + 1$. These absences are uniquely characteristic of the space group $P4_2/nmc$.[8] The $B_8H_8^{2-}$ polyhedral cage must have D_{2d} ($\bar{4}2m$) symmetry in the absence of disorder. The origin of the cell was taken at the center of symmetry and atoms were placed in the special positions 8g except for the zinc atoms which were placed in 2h, the only other positions in the cell with precise $\bar{4}2m$ symmetry.

The crystal chosen for data collection was 0.07 × 0.07 × 0.15 mm with faces of the $\{110\}$ and $\{001\}$ forms and the long dimension parallel to c. The crystal was mounted on a Picker four-circle automatic diffractometer equipped with a scintillation counter and a pulse-height discriminator with the $1\bar{1}0$ axis coincident with the φ axis of the diffractometer. The data were measured using Zr-filtered Mo Kα radiation and the θ–2θ scan technique with a symmetric scan range of 1.5° plus the angular separation for Kα_1 and Kα_2 for each reflection. A scan speed of 0.5°/min was used and individual backgrounds of 40 sec were measured before and after each scan. Only the unique data according to the D_{4h} Laue symmetry were measured giving a total of 363 reflections out to 2θ of 50°; this group included the $\{hhl\}$, $l = 2n + 1$, space-group-forbidden reflections which were unobserved and not included in the structure factor calculations. Higher angle data were not measured because of very limited observed diffraction beyond a 2θ value of 50°.

The data were corrected for the Lorentz and polarization effects in the usual way and for absorption using Prewitt's program ACACA.[9] For Mo Kα radiation the linear absorption coefficient is 20.3 cm^{-1}. The crystal was defined by six plane faces for the absorption correction. The minimum and maximum calculated transmission factors were 0.74 and 0.87, respectively. The standard deviations of the structure factors were

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

[2] F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 609 (1966).

[3] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

[4] R. E. Williams and F. J. Gerhart, *J. Am. Chem. Soc.*, **87**, 3513 (1965).

[5] W. N. Lipscomb, *Science*, **153**, 373 (1966).

[6] H. Hart and W. N. Lipscomb, *Inorg. Chem.*, **7**, 1070 (1968).

[7] (a) G. S. Pawley, *Acta Cryst.*, **20**, 631 (1966); (b) R. A. Jacobson and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 605 (1959); (c) R. A. Jacobson and W. N. Lipscomb, *J. Am. Chem. Soc.*, **80**, 5571 (1958).

[8] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, p 238.

[9] C. T. Prewitt, local unpublished computer program, 1968. Other programs used in this work included Prewitt's least-squares program SFLS5, the Busing–Levy error function program ORFFE, and the Fourier program FOUR written originally by C. J. Fritchie, Jr.

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR $Zn(NH_3)_4B_8H_8$

Atom	x	y	z	$\beta_{11}{}^a$ or B	β_{22}	β_{33}	β_{23}
Zn	$^1/_4$	$^3/_4$	$^3/_4$	0.0144 (5)	β_{11}	0.0077 (3)	0
N	$^1/_4$	0.9747 (16)	0.8585 (9)	0.0202 (30)	0.0147 (29)	0.0066 (11)	−0.0011 (16)
B_1	$^1/_4$	0.5813 (23)	0.2170 (12)	0.0206 (40)	0.0109 (36)	0.0044 (18)	0.0004 (19)
B_2	$^1/_4$	0.6461 (23)	0.3697 (16)	0.0195 (40)	0.0131 (38)	0.0088 (17)	−0.0000 (22)
H_1	$^1/_4$	0.415 (21)	0.207 (12)	4.0			
H_2	$^1/_4$	0.548 (22)	0.446 (14)	4.0			

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{23}kl)]$. The β_{12} and β_{13} terms are zero for all atoms.

assigned according to a scheme reported earlier[10] except for the following change. When the total count was less than the total background count plus twice the estimated background error, the intensity was set equal to the estimated background error and this reflection was considered unobserved.

The structure solution was initiated by placing zinc atoms at $\pm(^1/_4, {}^3/_4, {}^3/_4)$, surrounded by the expected tetrahedron of nitrogen atoms. The agreement factor, R $(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$, was 0.259 after varying the scale factor, nitrogen positional parameters, and zinc and nitrogen isotropic thermal parameters in two least-squares cycles. An electron density map disclosed the boron atom positions and after three cycles of refinement the R was 0.128. At this point 75 reflections were remeasured on the diffractometer. These were either strong reflections with high backgrounds or weak reflections where the chart was now used to check the rejection criterion. The weak reflections were averaged with the old data and the few strong reflections remeasured were used in place of the old data. The eight hydrogen atoms of the B_8 polyhedral cage were placed in positions corresponding to the largest peaks in an electron density difference map with phases determined from the model containing all the nonhydrogen atoms. The hydrogen atom positional parameters were varied in subsequent refinement cycles, but not the thermal parameters which were set equal to 4.0 Å². The hydrogen atoms of the ammine groups could not be located on an electron density difference map and hence were not included in the refinement. The refinement converged after five more cycles of least squares with a final R and weighted R $([\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with $w = 1/\sigma^2(F_o))$ of 0.078 and 0.076, respectively. The minimum and maximum peaks in an electron density difference map calculated at the end of the refinement were −0.7 and 0.7 e⁻/Å³ both in the region of the ammine hydrogen atoms. These small peaks could not be unambiguously interpreted in terms of thermal effects or hydrogen atom positions.

The function minimized in the least-squares calculation was $\Sigma w(|F_o| - |F_c|)^2$. The atomic scattering factors used were those calculated for neutral atoms.[11] The anomalous dispersion effect for Zn was included in the calculated structure factors using values reported by Templeton.[12]

The final atomic 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.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10) FOR $Zn(NH_3)_4B_8H_8$

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H,K= 0, 0    8 108 104   11  56  50*   4  49  13*   2 204 204    6 177 167    1 110  95
 2 997 984    9 112 100   H,K= 3, 3    5 177 181    3  96 105    7  96  18*   2  54  25*
 4  45 101*  10  53   1*   0  51  74*   6  53  46*   4 204 211    8  87  62    3 167 155
 6 221 233   11 112 102    2 205 212    7 183 177    5  53  15*   9  62  42*   4  89  19
 8 369 387   12  56  13*   4 301 309    8  88  44    6 160 144   H,K= 6, 3    5 150 155
10 220 206   H,K= 2, 2    6 211 216    9 150 129    7  54  10*   1 159 154    6  54   8*
12  58  14*   0  75  40    8 115 111   10  61   2*   8 123  87    2  59  44*   7 110  79
H,K= 1, 0     2 282 285   10 142 102   H,K= 4, 4    9  59  39*   3 145 145   H,K= 7, 3
 1 343 293    4 451 466   H,K= 4, 0    0 194 223   H,K= 5, 4    4  60  50*   0  89  70
 2 241 178    6 325 338    0 606 611    2 210 202    1 294 284    5 159 137    1  56   7*
 3 359 384    8 170 143    1  46  59*   4 175 158    2  54  21*   6  57  36*   2 127 111
 4  40  12*  10 105  88    2 368 399    6 106 115    3  90 107    7 139 110    3  79   0
 5 266 260   12 121 108    3  80  14    8 111 100    4  54  28*   8  57  36*   4 143 147
 6 125 126   H,K= 3, 0    4 157 167   H,K= 5, 0    5  95  52   H,K= 6, 4    6 117 103
 7 213 231    1 429 429    5 111 113    1 286 304    6  55  22*   0 141 132   H,K= 7, 4
 8  84  77    2 299 267    6 188 164    2  75  99    7 124 132    1  55  20*   1 128 119
 9 211 216    3 382 375    7 121 108    3 145 142    8  58  20*   2 167 157    2  57  35*
10  52   4*   4  85  45    8 204 207    4  50   4*  H,K= 5, 5    3  56  15*   3 109  92
11 193 178    5 281 285    9  55  29*   5 102  78    0 204 184    4 174 167    4  57  24*
12  56  15*   6 232 255   10 146 147    6 110  79    2 183 179    5  56  40*   5  65  77*
H,K= 1, 1     7 206 216   11  57   6*   7 153 160    4 157 155    6 118 109   H,K= 7, 5
010301032    8 158 156   H,K= 4, 1    8  53  27*   6 119 100    7  58  61*   0 104  85
 2 637 630    9 172 162    1 425 441    9 168 172   H,K= 6, 0   H,K= 6, 5    1  83  29
 4 288 293   10  53   5*   2  47  11*  10  63  24*   0 322 320    1 124 114    2 107 101
 6 316 307   11  89 108    3 261 273   H,K= 5, 1    1  54   3*   2  54  33*   3  59  36*
 8 295 293   12  62   7*   4  48  51*   0 364 381    2 271 279    3  56  59*  H,K= 8, 0
10 162 152   H,K= 3, 1    5 180 177    1  80  88    3  55  15*   4  96  20    0 183 173
12  56  39*   0 358 360    6  92  71    2 300 311    4 220 213    5  67  52*   1  59  11*
H,K= 2, 0     1  44   4*   7 193 192    3 115 103    5  54   5*   6  61   6*   2 128 117
 0 751 768    2 350 361    8  53  24*   4 219 218    6 154 157   H,K= 6, 6    3  55  26*
 1 268 198    3  68  63    9 170 165    5  51  40*   7  56  25*   0 127  86    4  58  49*
 2 544 546    4 309 320   10  56   4*   6 169 170    8 123 105    2 158 119    5  89  23
 3 401 363    5  74  88   11 108  90    7  98  50    9  61  27*  H,K= 7, 0   H,K= 8, 1
 4 322 324    6 263 257   H,K= 4, 2    8 154 138   H,K= 6, 1    1 115 101    1 115 111
 5  68  81    7  75  64    0 209 206    9  55  20*   1 153 130    2  79  90    2  62  13*
 6 297 298    8 176 186    1 149 141   10 103  89    2  90 104    3 127 120    3 133 119
 7  72  39    9  57  40*   2 238 247   H,K= 5, 2    3 154 150    4  59  17*   4  57  21*
 8 255 255   10 128 123    3 163 177    1 264 268    4  59  42*   5 119 118    5 121  96
 9  53  42*  11  55  33*   4 246 261    2  51  31*   5 133 146    6  62  65*  H,K= 8, 2
10 137 140   H,K= 3, 2    5  72  53    3 199 207    6  62  33*   7  62  80*   0  88  89
11  85  83    1 365 368    6 198 195    4  52   9*   7 137 117   H,K= 7, 1    1  57   9*
12  61  56*   2  45  17*   7 116 112    5 171 170    8  56   3*   0 174 163    2  63  80*
H,K= 2, 1     3 464 477    8 120 130    6  75  53    9  96  85    1  59   8*   3  57  12*
 1 292 306    4  80  30    9  54   2*   7 161 154   H,K= 6, 2    2 154 167    4  90  69
 2 262 222    5 411 432   10 109 105    8  67  61*   0 149 131    3  54  15*  H,K= 8, 3
 3 553 555    6  54  21*  11 106  50    9 139 110    1  53  42*   4 170 158    1 114 117
 4  43   9*   7 211 206   H,K= 4, 3   10  62  20*   2 181 195    5  57   2*   2  58  30*
 5 460 491    8  51   5*   1 389 415   H,K= 5, 3    3  54  67*   6 147 121    3 137 111
 6 153 164    9  60  74*   2  81  64    0 178 177    4 232 246    7  56  17*
 7 215 220   10  55   7*   3 250 259    1  81  69    5  53  29*  H,K= 7, 2
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Description of the Structure

The crystal structure of $Zn(NH_3)_4B_8H_8$ contains tetraamminezinc cations and discrete $B_8H_8{}^{2-}$ anions. The B_8H_8 polyhedron is depicted in Figure 1; the resultant molecular configuration may be described as a slightly distorted trigonal dodecahedron. The numbering system used is such that atoms with the same principal subscript are related by the S_4 $(\bar{4})$ axis which passes through the midpoints of the B_{2a}–B_{2b} and B_{2c}–B_{2d} bonds. Each cage is required to possess D_{2d} $(\bar{4}2m)$ symmetry exactly. A selected set of interatomic distances and angles is given in Table III. The errors in the distances and angles are relatively large due in part to the fact that the crystal was small and most intensities were weak, giving poor counting statistics.

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(10) L. J. Guggenberger, *Inorg. Chem.*, **7**, 2260 (1968).

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

(12) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215.

TABLE III

SELECTED INTERATOMIC DISTANCES AND ANGLES FOR $Zn(NH_3)_4B_8H_8$[a]

Atoms	Dist, Å	Atoms	Angle, deg
Zn–N	2.05 (1)	B_{2a}–B_{1a}–B_{2b}	52.7 (9)
B_{1a}–B_{1b}	1.93 (2)	B_{2a}–B_{1a}–B_{1d}	55.4 (8)
B_{1a}–B_{2a}	1.76 (2)	B_{1d}–B_{1a}–B_{2d}	57.3 (7)
B_{1a}–B_{2d}	1.72 (2)	B_{2a}–B_{1a}–H_{1a}	132 (5)
B_{1a}–B_{1c}	2.53 (3)	B_{1d}–B_{1a}–H_{1a}	133 (3)
B_{1a}–B_{2c}	2.63 (2)	B_{2d}–B_{1a}–H_{1a}	111 (6)
B_{1a}–H_{1a}	1.25 (14)	B_{2a}–B_{1a}–B_{2d}	107.9 (9)
B_{2a}–B_{2b}	1.56 (3)	B_{1a}–B_{2a}–B_{2b}	63.6 (5)
B_{2a}–B_{2c}	2.81 (3)	B_{1a}–B_{2a}–B_{1d}	67.3 (8)
B_{2a}–H_{2a}	1.11 (14)	B_{1d}–B_{2a}–B_{2b}	106.5 (8)
		B_{1a}–B_{2a}–B_{1c}	92.2 (9)
		B_{1a}–B_{2a}–H_{2a}	134 (1)
		B_{2b}–B_{2a}–H_{2a}	132 (8)
		B_{1d}–B_{2a}–H_{2a}	122 (8)

[a] The standard deviations of the least significant digits are given in parentheses. Distances and angles not given are related to those given by the molecular symmetry.

The B_8 polyhedron observed here is similar to that found in B_8Cl_8[7] and $B_6H_6C_2(CH_3)_2$,[6] assuming equal atoms in the polyhedron for the carborane. The distances observed are compared in Table IV. The 1.56 (3) Å distance for B_{2a}–B_{2b} is one of the shortest polyhedral B–B distances observed. The boron atoms of one chemically and crystallographically equivalent set (B_{1a}, B_{1b}, B_{1c}, B_{1d}) are six-coordinate while those of the other set (B_{2a}, B_{2b}, B_{2c}, B_{2d}) are five-coordinate. The distribution of B–B distances for B_8 polyhedra (Table IV) can be correlated with the coordination numbers of the borons involved, *i.e.*, the shortest bond is between two five-coordinate boron atoms, the intermediate lengths are between five- and six-coordinate boron atoms, and the longest length is between two six-coordinate boron atoms. The dihedral angles between planes observed in the $Zn(NH_3)_4B_8H_8$ structure are 72.9° for the angle between the planes (B_{1a}, B_{2a}, B_{2b}) and (B_{1c}, B_{2a}, B_{2b}), 77.3° between the planes (B_{1b}, B_{1c}, B_{2c}) and (B_{1c}, B_{2c}, B_{1d}), and 56.7° between the planes (B_{1b}, B_{1c}, B_{2b}) and (B_{1c}, B_{2a}, B_{2b}).

TABLE IV

B–B DISTANCES (Å) IN B_8 POLYHEDRA[a]

Bond type	$B_8H_8^{2-}$	$B_6H_6C_2(CH_3)_2$[b]	B_8Cl_8[d]
B_{2a}–B_{2b}	1.56 (2)	1.50 (1)[c]	1.68 (1)
B_{1a}–B_{2d}	1.72 (2)	1.70 (1)	1.81 (2)
B_{1a}–B_{2a}	1.76 (2)	1.79 (2)	1.75 (1)
B_{1a}–B_{1d}	1.93 (2)	1.88 (2)	2.00 (3)

[a] The distances in the carborane and B_8Cl_8 structures were averaged and the estimated errors were calculated according to $(\Sigma(d_i - \bar{d})^2)^{1/2}/(n - 1)$, where d_i and $\bar{d}$ are the distances and mean distance, respectively. [b] See ref 6. [c] The 1.50-Å distance is for a B–C distance. [d] See ref 7a.

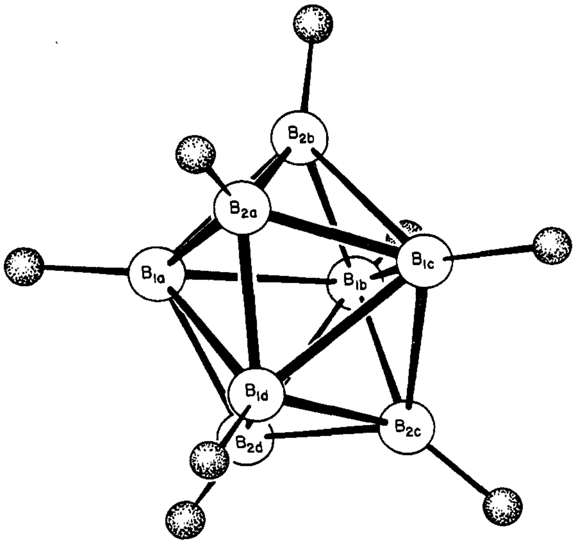

Figure 1.—The molecular configuration of $B_8H_8^{2-}$.

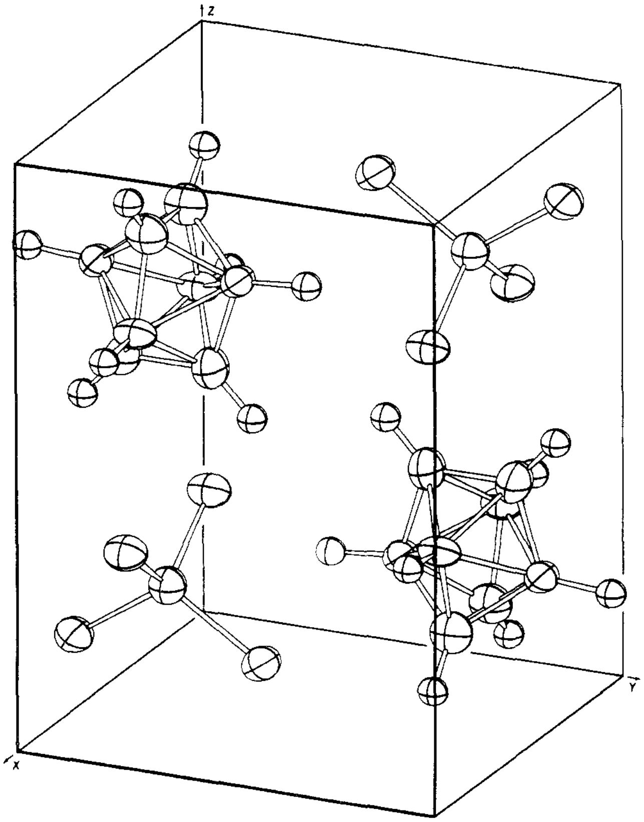

Figure 2.—One unit cell of the $Zn(NH_3)_4B_8H_8$ structure.

The inclusion of the hydrogen atoms in the refinement did not improve the *R* values significantly.[13] However, the hydrogen atom positions were clearly defined on the electron density difference map and the resultant B–H distances are reasonable for this type of geometry.[5,10] The Zn–N distance of 2.05 (1) Å may be compared with the value of 2.01 Å for the sum of the tetrahedral covalent radii.[14] The tetrahedral angles subtended at Zn are 110.5 ± 0.6 and 109.0 ± 0.3° for angles involving nitrogen atoms on the same mirror plane and on different mirrors planes, respectively.

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(13) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

(14) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

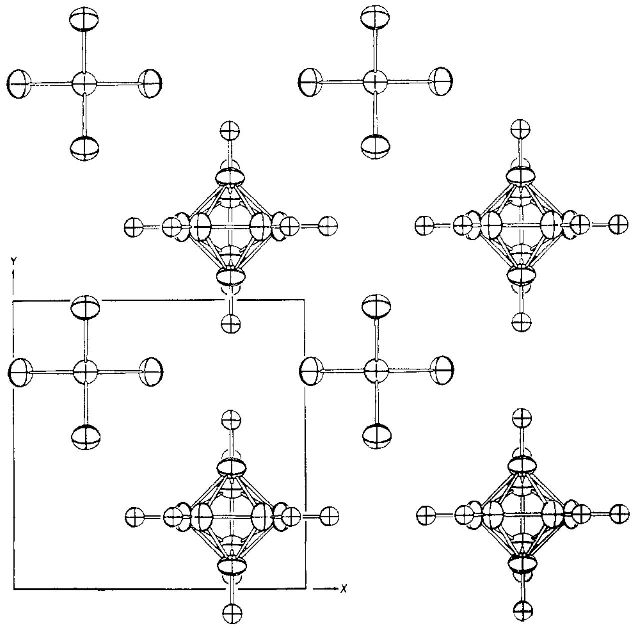

Figure 3.—The (001) projection of the $z = {}^3/_4$ layer of the $Zn(NH_3)_4B_8H_8$ structure. The area of one unit cell in this projection is outlined.

The contents of one unit cell are shown in Figure 2. The (001) projection of the layer of anions and cations centered about $z = {}^3/_4$ is shown in Figure 3. In these figures the atoms are represented by their thermal ellipsoids[15] plotted at the 50% probability level; the H (spheres) were drawn for $B = 2.0$ Å^2 for emphasis. No unusually short intermolecular contacts were found. The shortest intermolecular distances are 2.48 Å between H_1 atoms on neighboring anions and 2.91 Å between H_1 and adjacent N atoms. No nonhydrogen contacts less than 3.47 Å were observed.

Extended Hückel LCAO–MO calculations[3,16] were done for the $B_8H_8^{2-}$ polyhedron using the structural parameters obtained here. Slater orbitals (H1s, B2s, B2p) with exponents of 1.0 for H and 1.3 for B were used. The diagonal matrix elements were chosen as the negatives of the valence-state ionization potentials (−13.60 eV for H1s, −14.91 eV for B2s, and −8.42 eV for B2p); the off-diagonal matrix elements were evaluated using the Wolfsberg–Helmholz approximation[17] with $K = 1.75$. This approximation led to the closed-shell ground-state configuration $(1a_1)^2(1b_2)^2(1e)^4(2b_2)^2(2a_1)^2(2e)^4(3a_1)^2(3b_2)^2(3e)^4(1b_1)^2(4a_1)^2(4e)^4(4b_2)^2$, in order of increasing energy, with a gap energy of 2.92 eV between the highest occupied and lowest unoccupied molecular orbitals. Further details of the computational procedure are given in ref 1. The same molecular orbitals are used in bonding with the regular dodecahedral geometry except that the ordering of the $2b_2$ and 2e molecular orbitals is reversed as is the ordering of the $1b_1$ and $4a_1$ molecular orbitals. The results of these calculations are consistent with those of Hart and Lipscomb[6] on the carborane $B_6H_6C_2(CH_3)_2$ with regard to preferred sites for electrophilic and nucleophilic substitution. The B_1 set of boron atoms is the most positive; the net atom charges for B_1 and B_2 are 0.054 and −0.164, respectively. No charge iteration was done in this calculation. This type of charge distribution can be rationalized in terms of boron coordination number differences. Qualitatively, the six-coordinate boron atom (B_1) uses more electron density than the five-coordinate boron atom (B_2) in overlap populations (bonding) with neighboring atoms and hence has a larger positive charge. This effect is much greater when there are one or more carbon atoms in the polyhedral cage because of the larger valence-state ionization potentials of the carbon atomic orbitals.

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(15) C. K. Johnson, Report No. 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(16) R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963).

(17) M. Wolfsberg and L. Helmholz, *ibid.*, **20**, 837 (1952).