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THE CRYSTAL AND MOLECULAR STRUCTURES OF THREE BORON COMPOUNDS

Barry Goodwin DeBoer

(Ph.D. Thesis)

August 1968

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Barry Goodwin DeBoer
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The Crystal and Molecular Structures of Three Boron Compounds

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The Crystal and Molecular Structures of Three Boron Compounds

Barry Goodwin DeBoer

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August, 1968

Abstract

The crystal and molecular structures of three boron-containing compounds have been determined by X-ray diffraction studies of single crystal specimens. They are: the rubidium salt of an octadecahydro-eicosaborate(2-) photoisomer, $Rb_2B_{20}H_{18}$; the tetramethylammonium salt of a brominated carborane-metal "sandwich" ion, $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$; and tris-difluorobora-borane — phosphorus trifluoride, $B_4F_6PF_3$.

Crystals of $Rb_2B_{20}H_{18}$ are orthorhombic, space group $Pn2_1a$, with a = 12.344 ± .007 A, b = 19.014 ± .010 A, c = 7.260 ± .005 A, and contain four formula units per unit cell. The calculated density is 1.58 g/cc (by flotation, 1.57 g/cc). The structure was determined by Patterson and Fourier techniques and refined by a full-matrix least-squares procedure to a conventional R of 0.127 for 1175 scintillation-counter data (0.073 for the 935 non-zero data). The non-centric nature of the space group was demonstrated by the measurement of anomalous dispersion effects. The

anion consists of two capped-square-antiprismatic B_{10} polyhedra joined by a pair of hydrogen bridges, one between each pair of equatorial four-rings, such that the result has an approximate 2/m (C_{2h}) point symmetry. A list of thirteen possible isomers covering reasonable choices of bridge positions is presented together with their point symmetries.

Crystals of $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$ are monoclinic, space group $P2_1/c$, with a = 19.893 ± .010 A, b = 19.487 ± .010 A, c = 15.058 ± .010 A, $\beta = 93.15^\circ \pm .05^\circ$, and contain eight formula units and four crystallographically independent anions per unit cell. The calculated density is 1.967 g/cc, in agreement with the measured value of 1.98 ± .01 g/cc. The structure was solved by statistical methods and refined by a least-squares procedure to a conventional R of 8.7% on 3002 data collected by counter methods. All four independent anions have the same shape to within the accuracy of this determination. The anion, the product of a bromination during which the bis-dicarbollyl cobalt "sandwich" is believed to remain intact, consists of two substituted icosahedra with the cobalt as their common vertex. In each icosahedron, the carbons are adjacent to each other and to the cobalt, while the three borons bonded to bromine form the corners of a triangular face. Two corners of this face are as far as possible from the carbons, and the third is adjacent to the cobalt. These bromination sites are consistent with a charge distribution in the reactant which is analogous to that in o-$B_{10}C_2H_{12}$, but modified slightly by the presence of the Co(III).

Crystals of $B_4F_6PF_3$ are orthorhombic, space group Pnma, with a = 13.893 ± .005 A, b = 10.578 ± .005 A, c = 6.075 ± .005 A, and contain

four formula units per unit cell. The calculated density is 1.82 g/cc. The structure was solved by statistical methods and refined by full-matrix least-squares to a conventional R of 9.3% for 703 data collected by counter methods (6.7% for the 603 non-zero data). The molecule consists of a central boron atom, tetrahedrally bonded to three BF_2 groups and the PF_3 group in such a way that the molecule has approximately 3m (C_{3v}) point symmetry, one mirror of which is required by the crystal symmetry. Distances found (uncorrected for thermal motion) are: B–F, 1.305 A; B–B, 1.68 A; B–P, 1.825 A; and P–F, 1.51 A (all ± .015 A).

I. Introduction

Determinations of molecular structure form a large and important part of chemistry and the study of matter in general. A knowledge of the three-dimensional atomic arrangements in the molecules of substances is a prerequisite to an understanding of many of the physical and chemical properties of those substances. One of the most powerful methods of determining such atomic arrangements is the examination of the diffraction of X-rays by single crystals. The method is powerful because it is applicable to a wide range of compounds and is able to handle molecules composed of many more atoms than those amenable to study by, for instance, spectroscopic methods. Crystal structure studies such as those described here may be thought of as a form of inverted spectroscopy, in which an unknown diffraction grating is examined by the use of a known radiation source, rather than vice versa. Since our crystal "diffraction grating" is composed of units which are arranged with three-dimensional periodicity, the three-dimensional locations of the atoms within the repeated unit may be deduced from the diffraction intensities. These locations provide the desired image of the molecule(s), with the information it carries as to composition, conformation, substitution sites, etc. These locations may also be used to calculate interatomic distances and angles from which inferences may be drawn concerning bonding, electronic structure, non-bonded forces, and other detailed properties of the molecules.

The principle parts of this thesis describe the application of the single-crystal X-ray diffraction technique to three compounds drawn from the rapidly expanding field of boron chemistry. They are, in order, a

borohydride anion, a metallo-carborane, and a novel boron fluoride compound. Each of these compounds was chosen for study because each is the product of a type of reaction which has not previously been observed in the chemistry of boron, and the compounds themselves are likewise unique. They represent opportunities to observe previously unseen facets of boron chemistry and so increase our knowledge of this element. However, since these compounds are not very closely related otherwise, and because the determination of the structure of one crystal is well separated from that of another, the work on each compound is presented separately. Each presentation has its own introduction, descriptions of the experimental procedure and method of solution, and discussions of the results and their implications.

II. The Crystal Structure of the Rubidium Salt of an Octadecahydroeicosaborate(2-) Photoisomer

A. Introduction

In the last few years, there has been considerable interest in the reactions of the $B_{20}H_{18}^{2-}$ ion, and proposals have been made for the probable structures of the products.[1-9*] The structure of the parent ion has been established[5,6] as a pair of capped-square-antiprismatic B_{10} polyhedra connected by a pair of three-center bonds which join the 1-2 edge of one polyhedron to the 2' position of the other and the 1'-2' edge of the second to the 2 position of the first.[10]

Recently, Hawthorne and Pilling[2] observed the isomerization of $B_{20}H_{18}^{2-}$ in acetonitrile solution when exposed to light from a mercury lamp. They predicted that the photoisomer was one of the two possible structures which result when two B_{10} polyhedra are joined by a pair of B-H-B bridges, one between each pair of equatorial four-rings.

This work was undertaken to determine the geometry of the photoisomerization product. The results prove that the geometry is the centrosymmetric (2/m or C_{2h}) alternative of the pair suggested by Hawthorne and Pilling.

B. Experimental

Crystals of the rubidium salt were received from Professor M. F. Hawthorne of the University of California, Riverside. Part of this material was recrystallized from water by slow evaporation. Two sets of intensity

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* References and Footnotes for part II are to be found on page 26.

data were recorded from different crystals, one from the original sample and the other from the recrystallized portion.

A small, colorless crystal fragment from the original sample was glued to the end of a Pyrex glass fiber, with its long direction parallel to the fiber, the instrument φ axis, and the $\underline{a}$ axis of the crystal. Preliminary oscillation and Weissenberg photographs were taken with Cu$\underline{K}\alpha$ radiation to find the Laue group, extinction rules, and cell dimensions. More accurate cell dimensions were derived from Bragg angles of the $\underline{h}00$, $0\underline{k}0$, and $00\underline{\ell}$ reflections measured with a manual General Electric XRD-5 apparatus using molybdenum radiation and a Zr filter at the receiving slit. The components of the alpha doublet ($\lambda(\underline{K}\alpha_1) = 0.70926$ A) were resolved. The same apparatus was used to measure intensities of 1153 independent (in the sense of Laue group) reflections, including 283 recorded as zero, but not including space group absences. Each reflection was counted for 10 seconds with crystal and counter stationary and a large ($\sim 3.5^{\circ}$) take-off angle from the X-ray tube anode. Coincidence losses were negligible. For each reflection which was seriously affected by streaking from other orders, individual backgrounds were measured by seeking a minimum on the low-2θ side of the peak; otherwise, the background was taken from a plot of background as a function of 2θ for various values of phi and chi. The measurements included reflections to $2\theta = 45^{\circ}$, or $\sin\theta/\lambda = 0.540$. Repeated measurements of several arbitrarily chosen reflections showed systematic trends in which one reflection actually became slightly stronger and others decreased by various ratios, in one case a factor of two. It is suspected that these changes were caused by a bending or cracking of the crystal induced at least in part by radiation

damage. In spite of these inauspicious circumstances, this data was used in the early stages of the analysis. When it became evident that the quality of the data was unacceptable, a second crystal about 0.11 x 0.06 x 0.05 mm in size and of much better appearance than the first was selected from the recrystallized material. Cell dimensions and reflection intensities were measured with the same technique as before except that a shutter excluded the X-rays from the crystal except during the actual counting time. The measurements included 1158 Laue-independent reflections, including 240 recorded as zero. The intensities of several reflections which were measured at frequent intervals showed only random fluctuations of the size expected for counting statistics.

Calculations with the partly refined structure permitted identification of reflections which were most likely to show violations of Friedel's rule. Eleven of these and six others of simple indices were selected. Each member of the sets $\pm\underline{h}$, $\underline{k}$, $\pm\underline{\ell}$, and $\pm\underline{h}$, $-\underline{k}$, $\pm\underline{\ell}$ which was observable with the quarter-circle goniometer in this setting ($\underline{a}$ axis) was counted at least twice for 100 seconds. These data gave a total of 1175 intensities (independent in the sense of the point group, but including 17 Friedel pairs). Standard deviations of five percent of the intensity or one count per second, which ever was greater, were assigned to all the raw intensities, except for the anomalous dispersion data, for which standard deviations were estimated from the scatter between measurements made within the sets $\underline{k} > 0$ and $\underline{k} < 0$. Weighting factors were derived from these standard deviations as one over the square of the resulting

standard deviations of the observed structure factors. The calculated absorption coefficient, μ, of 60 cm^{-1}, and the dimensions of this crystal indicate that μs is limited between 0.3 and 0.5, where s is the maximum path length of an X-ray within the crystal. It is estimated that the variation in intensities due to absorption is not more than twenty percent and is distributed in such a way as to be largely absorbed by temperature factors.

Both data sets were corrected for Lorentz and polarization effects, but no corrections were made for absorption or extinction.

Pyroelectricity was indicated by attraction of a crystal to the side of the glass dewar after the crystal was quickly dipped into liquid nitrogen.

Computations were performed on an IBM 7044 with a 32K memory except for final refinements, which were done on a CDC 6600. Fourier syntheses and distance-and-angle calculations were done by Zalkin's (unpublished) FORDAP and DISTAN programs. The unpublished version of the Ganzel-Sparks-Trueblood least-squares program which was used, minimizes the function $\Sigma w(|kF_o| - |F_c|)^2/\Sigma w|kF_o|^2$, where F_o and F_c are the observed and calculated structure factors, respectively, w is the weighting factor, and k is the scale factor. This least-squares program has been modified to handle anomalous dispersion and these effects were included in the later refinements. The atomic scattering factors[11] for Rb^+ were corrected by $\Delta f' = -0.9$ electrons and $\Delta f'' = +3.1$ electrons as the real and imaginary parts of the anomalous dispersion. Scattering factors for boron and hydrogen were also taken from standard tables.[11] The anisotropic

temperature factors used have the form: $\exp(-0.25\Sigma_i\Sigma_j h_i h_j b_i b_j B_{ij})$, $i,j = 1, 2, 3$, where b_i is the ith reciprocal axis.

C. Results

Four formula units of $Rb_2B_{20}H_{18}$ are contained in the orthorhombic unit cell with dimensions $a = 12.344 \pm .007$ A, $b = 19.014 \pm .010$ A, $c = 7.260 \pm .005$ A. The calculated density of 1.58 g/cc agrees with the value (1.57 ± .01 g/cc) obtained by flotation in a mixture of carbon tetrachloride and dibromoethane. These measurements apply to room temperature (~ 23°C) and their standard deviations are estimates. The Laue symmetry and observed extinction rules of $0k\ell$, $k+\ell \neq 2n$ and $hk0$, $h \neq 2n$ correspond to both the centric Pnma and the non-centric $Pn2_1a$. The positive test for pyroelectricity and the violations of Friedel's rule (presented below) indicate the non-centric $Pn2_1a$, and this choice leads to a successful structure with each atom in the general set of positions: $(x, y, z;\ \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z;\ -x, \frac{1}{2} + y, -z;\ \frac{1}{2} + x, y, \frac{1}{2} - z)$.

1. Determination of Structure

The Patterson function calculated from the first data set was consistent with either one rubidium ion in the eight-fold Pnma or a pair of nearly-centric rubidium ions in the four-fold $Pn2_1a$. The latter was chosen because of the observed pyroelectric effect and the broadening of the Patterson peaks in the a and c directions. Four cycles of least-squares on two slightly non-centric rubidium ions with isotropic temperature factors reduced the R factor for 811 low-angle data of the

first set to 0.323 where $\underline{R} = \Sigma||\underline{kF_o}| - |\underline{F_c}|| / \Sigma|\underline{kF_o}|$. The zero coordinate of the $\underline{y}$ axis in the polar space group $Pn2_1a$ was defined by requiring the two rubidium ions to have equal and opposite $\underline{y}$ coordinates in this and all subsequent refinements. A Fourier synthesis phased on the rubidiums was calculated and various choices of peaks refined as boron atoms on a cut-and-try basis. In these trials, the appearance of a large temperature factor was taken as an indication of a poor choice of atomic position. After several trials, a difference Fourier was calculated on the basis of the two rubidium ions and 16 borons which had been "found" ($\underline{R}$ = 0.297, all data). This difference Fourier indicated that the rubidium ions were rather badly anisotropic. The same 16 borons plus four more selected from the difference Fourier were refined with the rubidium ions allowed anisotropic temperature factors. $\underline{R}$ dropped to 0.233 with two of the new borons going to large temperature factors. It was suddenly seen that sixteen of the eighteen "good" borons were arranged in pairs about a pseudo-center (local, non-crystallographic inversion center) and that the addition of two more borons in positions pseudo-centric to the remaining pair produced two capped square anti-prisms which had a pair of short equatorial-equatorial distances between them. Two anisotropic rubidium atoms and these twenty borons refined to $\underline{R}$ = 0.218 on all 1153 data of the first set.

An empirical correction for absorption and for degradation of the crystal was attempted, but $\underline{R}$ was not significantly reduced. The possibilities of disorder in the orientation of the boron structure, of being in the wrong space group, and of having the rubidium atoms "trapped" in

the wrong places by false minima were all investigated without improving the agreement.

It was at this time that the second data set was taken and the first set discarded. The structure found from the first data set immediately refined to R = 0.158 on the 1158 data of the second set. An inspection of the observed and calculated structure factors revealed a systematic error in the second data set caused by the scattering of the irradiating X-ray beam off a telescope into the counter near a particular value of theta. When the affected data were removed by deleting all data with $\sin\theta/\lambda \geqq .50$, R dropped to 0.114 on 925 data.

All the data in the neighborhood of the systematic error (40 to 45 degrees 2θ) were retaken with a lead sheet shielding the counter from the spurious X-rays, and other data showing large disagreements were remeasured to check for errors such as mis-set angles and mis-punched cards. At this time, the seventeen reflections were selected and examined for anomalous dispersion effects. These data showed that the wrong alternative had been chosen for the polarity. When the structure was inverted as required, a refinement of two anisotropic rubidium ions and twenty borons, including anomalous dispersion, gave an R of 0.136 on the 1175 data of the corrected second set. Another difference Fourier showed peaks ranging from 0.78 to 0.46 electrons/A^3 in reasonable positions for all eighteen hydrogens. Only eight non-hydrogen peaks larger than 0.46 electrons/A^3 were not explainable by such things as pile-up of errors near the rubidium ions or ill-fitting borons (e.g. a peak midway between two boron positions). Many attempts at refining the hydrogen positions

under various restrictions produced various degrees of agreement, various unacceptable temperature factors and boron-hydrogen distances, and much frustration. The structure was finally refined in two ways: with no hydrogen included, and with each hydrogen in a calculated position 1.2 A from its boron (~ 1.3 A in the case of the two bridging hydrogens) and constrained to "ride"[12] on its boron. All hydrogens were also required to have the same temperature factor. Both refinements were done with the weighting scheme described.

In the no-hydrogen case the final $\underline{R}$ was 0.133 on all 1175 data and 0.079 on the 935 non-zero data. In the last cycle, no parameter shifted by more than 0.04 of the standard deviation calculated for it from the least-squares matrix.

In the case which included hydrogens, the final $\underline{R}$ was 0.127 on all 1175 data and 0.073 on the 935 non-zero data. In the last cycle, no parameter shifted by more than 0.03 of its standard deviation. The standard deviation of an observation of unit weight, defined as $[\Sigma \underline{w}(|\underline{kF_o}| - |\underline{F_c}|)^2/(\underline{u}-\underline{v})]^{\frac{1}{2}}$ where $\underline{u}$ is the number of data and $\underline{v}$ is the number of independent parameters refined, was 1.73. The root-mean-square difference in boron positions between the two refinements is 0.05 A, and the greatest difference is 0.11 A.

The results of the refinement which included hydrogen are believed to be more accurate on the basis of better agreement and smaller scatter in both the boron temperature factors and in boron-boron distances. All results presented hereinafter refer to the refinement on the corrected second data set which included hydrogens. The final positional and thermal

parameters are presented in Table I, while Table II lists the observed and calculated structure factors. Observed and calculated values of the function

$$\frac{|\underline{F}(+)| - |\underline{F}(-)|}{0.5(|\underline{F}(+)| + |\underline{F}(-)|}$$

where $\underline{F}(+)$ and $\underline{F}(-)$ are structure factors for $\underline{k} > 0$ and $\underline{k} < 0$, are tabulated in Table III for the seventeen anomalous dispersion data. The agreement of magnitudes and signs clearly establishes the non-centric space group and is strong evidence of the correctness of the structure.

2. Discussion

The structure of the photoisomeric $B_{20}H_{18}^{2-}$ anion found in this study is shown in Figure 1. This structure is the more symmetric one of the two possibilities postulated by Hawthorne and Pilling.[2] The anion has an approximate $2/\underline{m}(\underline{C}_{2\underline{h}})$ point symmetry. A calculation of the anion's deviations from perfect $2/\underline{m}$ symmetry gave a root-mean-square deviation of 0.07 A (excluding B5', see below). It is felt that this is nearly, if not entirely, within the accuracy of the determination. Thus the non-centric nature of the space group is a result of an unsymmetrical arrangement (Figure 2) of symmetric pieces. No significance is assigned to the handedness found for the particular sample from which the data were obtained, and another crystal would be expected to have an equal chance of having either handedness.

An examination of the boron-boron distances given in Table IV shows that B5' is apparently mis-located in a position too far from the apex and too close to the opposite equatorial ring. The author does not

Table I. Final Positional and Thermal Parameters in $Rb_2B_{20}H_{18}$

Atom	x	y	z	B[a]
Rb(1)	-.3714(2)[b]	-.0801(1)	.3225(4)	(c)
Rb(2)	.3688(2)	.0801(1)	-.3299(4)	(c)
B(1)	.039(2)	.176(1)	.566(4)	4.4(6)
B(2)	.052(1)	.219(1)	.369(3)	1.1(4)
B(3)	.158(2)	.167(1)	.457(3)	2.7(5)
B(4)	.069(2)	.092(1)	.499(3)	3.0(5)
B(5)	-.044(1)	.146(1)	.407(2)	0.8(3)
B(6)	.140(2)	.181(1)	.218(3)	1.8(4)
B(7)	.162(2)	.091(1)	.315(4)	3.2(5)
B(8)	.022(2)	.075(2)	.275(4)	4.8(7)
B(9)	.000(2)	.160(1)	.174(3)	2.3(4)
B(10)	.096(2)	.111(1)	.110(4)	3.0(5)
B(1')	.138(2)	.389(1)	.400(3)	2.9(4)
B(2')	.095(2)	.316(1)	.293(3)	2.8(5)
B(3')	.077(2)	.405(1)	.195(3)	2.3(5)
B(4')	.229(1)	.421(1)	.239(2)	0.9(4)
B(5')	.241(2)	.329(1)	.312(3)	2.4(4)
B(6')	.081(2)	.330(1)	.048(3)	2.8(5)
B(7')	.172(2)	.403(1)	.005(4)	3.1(5)
B(8')	.287(2)	.350(1)	.104(3)	3.1(5)
B(9')	.188(2)	.284(1)	.153(3)	4.0(5)
B(10')	.204(2)	.318(1)	-.062(3)	3.2(5)

Table I, continued

H(1)[d]	.019	.197	.717	1.2
H(3)	.229	.187	.556	1.2
H(4)	.064	.054	.631	1.2
H(5)	-.136	.150	.463	1.2
H(7)	.238	.053	.286	1.2
H(8)	-.017	.022	.214	1.2
H(9)	-.051	.177	.040	1.2
H(10)	.116	.089	-.041	1.2
H(1')	.117	.412	.550	1.2
H(3')	.003	.445	.217	1.2
H(4')	.267	.475	.295	1.2
H(5')	.297	.309	.437	1.2
H(6')	.008	.309	-.047	1.2
H(7')	.173	.440	-.128	1.2
H(8')	.378	.344	.046	1.2
H(10')	.225	.295	-.212	1.2
H(2-2')	.027	.285	.403	1.2
H(6-9')	.210	.215	.114	1.2

(a) The units are A^2.

(b) The number in parentheses is the standard deviation in the least significant digit as derived from the least-squares matrix.

Table I, continued

(c) The anisotropic temperature factors for Rb(1) are: ($\underline{B}_{11}$, 4.1(2); $\underline{B}_{22}$, 2.5(2); $\underline{B}_{33}$, 5.6(2); $\underline{B}_{12}$, 0.7(1); $\underline{B}_{13}$, 1.4(1); $\underline{B}_{23}$, 0.3(1)) and for Rb(2): ($\underline{B}_{11}$, 4.3(2); $\underline{B}_{22}$, 3.1(2); $\underline{B}_{33}$, 3.8(2); $\underline{B}_{12}$, -0.7(1); $\underline{B}_{13}$, -1.1(1); $\underline{B}_{23}$, 1.1(1)), where the units are $Å^2$.

(d) H(1) is on B(1) and similarly. H(2-2') and H(6-9') are the two bridging hydrogens. No standard deviations are given for the positional parameters since these are assumed positions.

Table II. Observed and Calculated Structure Factors for $Rb_2B_{20}H_{18}$

H,L= 0, 0

K	FOB	FCA
2	70	65
-2	66	65
4	243	232
6	197	204
8	185	186
10	55	84
12	181	184
14	74	75
-14	76	71
16	40	42
18	70	70
-18	68	68
20	64	60

H,L= 0, 1

K	FOB	FCA
1	28	33
-1	36	32
3	171	166
-3	171	165
5	139	136
7	71	72
9	129	131
11	80	80
13	0	18
15	76	78
17	77	65
19	12	14

H,L= 0, 2

K	FOB	FCA
0	133	138
2	88	85
-2	88	86
4	24	24
6	136	130
8	77	75
10	28	28
12	78	75
14	46	50
16	0	16
18	54	45

H,L= 0, 3

K	FOB	FCA
1	22	15
3	21	14
5	15	18
7	33	34
9	27	23
11	0	6
13	0	7
15	29	23
17	17	15

H,L= 0, 4

K	FOB	FCA
0	42	43
2	12	22
4	9	18
6	33	33
8	23	18
10	10	11
12	15	7
14	35	37
16	0	12

H,L= 0, 5

K	FOB	FCA
1	34	32
3	68	90
5	43	44
7	18	18
9	69	60
11	54	54
13	0	12
15	37	38

H,L= 0, 6

K	FOB	FCA
0	71	67
2	41	42
4	28	25
6	75	74
8	44	41
10	17	28
12	54	45

H,L= 0, 7

K	FOB	FCA
1	20	26
3	52	55
5	56	56
7	32	30
9	37	38

H,L= 1, 0

K	FOB	FCA
0	67	60
1	31	33
2	16	19
3	47	49
4	37	44
5	29	37
6	33	33
7	0	12
8	27	26
9	42	45
-9	38	39
10	15	9
11	27	29
12	32	30
13	12	15
14	0	20
15	32	30

H,L= 1, 1

K	FOB	FCA
0	41	43
1	42	39
2	48	44
3	62	62
4	7	9
5	58	57
6	17	17
7	45	48
8	11	13
9	84	83
10	0	4
11	48	47
12	13	18
13	26	29
14	0	4
15	44	53
16	0	4
17	16	23
18	0	9
19	0	9

H,L= 1, 2

K	FOB	FCA
0	129	135
1	40	45
2	68	68
3	212	114
4	54	55
5	71	73
6	115	113
7	45	45
8	51	55
9	77	82
10	17	18
11	53	52
12	71	72
13	22	18
14	58	59
15	59	61
16	18	17
17	45	42
18	35	43
19	0	7

H,L= 1, 3

K	FOB	FCA
0	124	129
1	63	65
2	75	77
-2	71	73
3	132	135
-3	138	140
4	65	65
5	66	65
6	105	104
7	38	41
8	57	58
9	65	101
10	31	28
11	57	57
12	78	81
13	31	29
14	37	41
15	48	53
16	20	19
17	42	42
-17	38	38
18	30	40

H,L= 1, 4

K	FOB	FCA
0	88	92
1	37	37
2	44	47
3	81	82
4	40	40
5	58	59
6	87	88
7	31	31
8	51	49
9	79	82
10	32	32
11	31	37
12	55	55
13	22	20
14	30	35
15	37	36
16	12	12
17	32	32

H,L= 1, 5

K	FOB	FCA
0	67	60
1	31	33
2	16	19
3	47	49
4	37	44
5	29	37
6	33	33
7	0	12
8	27	26
9	42	45
-9	38	39
10	15	9
11	27	29
12	32	30
13	12	15
14	0	20
15	32	30

H,L= 1, 6

K	FOB	FCA
0	11	6
1	0	3
2	11	11
3	0	15
4	21	24
5	11	19
6	15	21
7	16	13
8	0	4
9	11	14
10	12	13
11	0	5
12	0	11
13	0	10

H,L= 1, 7

K	FOB	FCA
0	12	8
1	12	9
2	0	10
3	0	10
4	0	13
5	12	6
6	0	5
7	0	8
8	12	7
9	18	9

H,L= 2, 0

K	FOB	FCA
1	29	31
2	15	11
3	55	54
4	26	22
5	15	21
6	0	2
7	0	9
8	0	13
9	15	43
10	42	46
11	40	42
12	0	10
13	16	15
14	0	2
15	16	24
16	0	6
17	25	26

H,L= 2, 2

K	FOB	FCA
0	110	120
1	53	51
2	51	55
3	74	78
-3	76	87
4	30	31
5	59	61
6	103	104
7	21	24
8	68	68
9	71	71
10	23	23
11	43	45
12	66	65
13	0	2
14	58	56
15	51	51
16	12	8
17	34	35
18	41	39

H,L= 2, 3

K	FOB	FCA
0	55	53
1	0	8
2	23	24
3	0	9
4	24	25
5	0	6
6	34	38
7	0	2
8	28	28

H,L= 2, 4

K	FOB	FCA
0	96	99
1	44	47
2	34	35
3	56	59
4	16	18
5	51	51
6	87	95
7	28	26
8	44	47
9	41	58
10	30	30
11	24	27
12	36	37
13	0	9
14	32	32
15	33	33
16	0	5
17	20	19
18	23	28
19	0	1

H,L= 2, 5

K	FOB	FCA
1	75	73
2	64	66
3	144	146
4	65	63
5	39	45
6	74	79
7	23	27
8	58	56
9	89	89
10	20	20
11	64	67
12	67	69
13	33	33
14	21	25
15	43	48
16	0	5
17	35	36
18	32	33
19	0	4

H,L= 2, 6

K	FOB	FCA
C	C	4
0	69	69
1	36	37
2	45	48
3	94	98
5	36	36
6	11	5
7	22	19
8	0	1
9	59	54
10	0	4
11	36	35
12	0	3

H,L= 2, 7

K	FOB	FCA
0	55	53
1	0	8
2	23	24
3	0	9
4	24	25
5	0	6
6	34	38
7	0	2
8	28	28

H,L= 3, 1

K	FOB	FCA
0	96	99
1	44	47
2	34	35
3	56	59
4	16	18
5	51	51
6	87	95
7	28	26
8	44	47
9	41	58
10	30	30
11	24	27
12	36	37
13	0	9
14	32	32
15	33	33
16	0	5
17	20	19
18	23	28
19	0	1

H,L= 3, 2

K	FOB	FCA
0	119	122
1	75	73
2	64	66
3	144	146
4	65	63
5	39	45
6	74	79
7	23	27
8	58	56
9	89	89
10	20	20
11	64	67
12	67	69
13	33	33
14	21	25
15	43	48
16	0	5
17	35	36
18	32	33
19	0	4

H,L= 3, 3

K	FOB	FCA
0	110	120
1	53	51
2	51	55
3	74	78
-3	76	87
4	30	31
5	59	61
6	103	104
7	21	24
8	68	68
9	71	71
10	23	23
11	43	45
12	66	65
13	0	2
14	58	56
15	51	51
16	12	8
17	34	35
18	41	39

H,L= 3, 4

K	FOB	FCA
0	65	67
1	36	39
2	41	42
3	21	20
4	30	30
5	15	21
6	69	66
7	0	4
8	50	47
9	13	11
10	36	33
11	0	12
12	59	52
13	21	17
14	28	29
15	11	5
16	0	9
17	0	5
18	47	40

H,L= 3, 5

K	FOB	FCA
0	24	22
1	11	17
2	19	20
3	0	12
4	0	14
5	0	7
6	11	7
7	11	9
8	0	6
9	0	14
10	14	13
11	0	9
12	0	11
13	15	19
14	0	2
15	0	11
16	0	2
17	12	1

H,L= 3, 6

K	FOB	FCA
0	17	9
1	17	17
2	17	8
3	0	9
4	12	6
5	12	7
6	21	19
7	12	15

H,L= 4, 0

K	FOB	FCA
0	198	204
1	21	21
2	127	120
3	26	29
4	112	105
5	27	25
6	195	197
7	43	42
8	83	87
9	47	42
10	69	69
11	13	12
12	111	113
13	20	8
14	50	51
15	15	12
16	11	13
17	0	4
18	69	61
19	0	4

H,L= 4, 1

K	FOB	FCA
0	16	19
1	85	86
2	45	47
3	194	187
4	12	12
5	108	106
6	17	21
7	40	51
8	14	13
9	121	119
10	25	19
11	98	98
12	27	24
13	10	18
14	0	16
15	100	78
16	0	2
17	53	51
18	0	13
19	0	15

H,L= 4, 2

K	FOB	FCA
0	79	79
1	10	9
2	39	38
3	7	12
4	33	33
5	14	4
6	78	78
7	0	6
8	50	47
9	13	11
10	36	33
11	0	12
12	59	52
13	21	17
14	28	29
15	11	5
16	0	9
17	0	5
18	47	40

H,L= 4, 3

K	FOB	FCA
0	24	22
1	11	17
2	19	20
3	0	12
4	0	14
5	0	7
6	11	7
7	11	9
8	0	6
9	0	14
10	14	13
11	0	9
12	0	11
13	15	19
14	0	2
15	0	11
16	0	2
17	12	1

H,L= 4, 4

K	FOB	FCA
0	44	38
1	29	33
2	37	39
3	0	8
4	23	21
5	31	27
6	53	56
7	0	3
8	32	24
9	0	10
10	0	12
11	0	9
12	25	21
13	11	14
14	29	23
15	0	7
16	12	9

H,L= 4, 5

K	FOB	FCA
0	79	79
1	17	20
2	12	12
3	45	40
4	0	6
5	19	21
6	0	4

H,L= 4, 6

K	FOB	FCA
0	41	43
1	25	30
2	34	35
3	70	74
4	30	29
5	21	20
6	33	34
7	20	24
8	26	25
9	32	34
10	0	1
11	40	38
12	36	33
13	0	7
14	19	21
15	29	30
16	0	4
17	20	25
18	12	14

H,L= 5, 0

K	FOB	FCA
0	87	94
1	29	32
2	46	45
3	58	60
4	16	16
5	50	50
6	93	95
7	21	21
8	65	67
9	60	59
-9	62	67
10	27	29
11	36	34
12	58	57
13	0	10
14	46	46
15	39	39
16	0	7
17	24	25
18	33	31

H,L= 5, 1

K	FOB	FCA
0	41	43
1	25	30
2	34	35
3	70	74
4	30	29
5	21	20
6	33	34
7	20	24
8	26	25
9	32	34
10	0	1
11	40	38
12	36	33
13	0	7
14	19	21
15	29	30
16	0	4
17	20	25
18	12	14

H,L= 5, 2

K	FOB	FCA
0	87	94
1	29	32
2	46	45
3	58	60
4	16	16
5	50	50
6	93	95
7	21	21
8	65	67
9	60	59
-9	62	67
10	27	29
11	36	34
12	58	57
13	0	10
14	46	46
15	39	39
16	0	7
17	24	25
18	33	31

H,L= 5, 3

K	FOB	FCA
0	80	82
1	44	47
2	55	55
3	129	133
4	45	45
5	64	63
6	87	87
7	63	61
8	32	37
9	86	87
10	25	29
11	44	44
12	56	52
13	23	23
14	29	29
15	55	58
16	12	9
17	35	38

H,L= 5, 4

K	FOB	FCA
0	100	106
1	44	45
2	30	32
3	47	44
4	42	41
5	19	23
6	52	47
7	14	16
8	51	49
9	47	45
10	19	12
11	35	33
12	41	37
13	16	12
14	27	29
15	27	30

H,L= 5, 5

K	FOB	FCA
0	25	21
1	0	11
2	15	22
3	39	37
4	10	16
5	32	36
6	34	36
7	29	22
8	22	19
9	41	41
10	16	14
11	12	17
12	24	21
13	12	9

H,L= 5, 6

K	FOB	FCA
0	32	36
1	11	10
2	11	9
3	0	4
4	16	20
5	0	2
6	14	19
7	0	4
8	14	7
9	19	13
10	0	16
11	0	1
12	0	12
13	11	8
14	0	1
15	0	2
16	0	10

H,L= 5, 7

K	FOB	FCA
0	19	27
1	19	20
2	42	40
3	146	144
4	26	29
5	114	115
6	29	23
7	59	49
8	25	18
9	149	144
10	42	39
11	68	79
12	23	20
13	24	23
14	31	31
15	83	83
16	12	5
17	49	49
18	0	6

H,L= 6, 1

K	FOB	FCA
0	142	149
1	27	29
2	66	67
3	29	30
-3	32	34
4	72	71
5	8	14
6	93	95
7	0	8
8	79	68
9	33	40
10	31	29
11	14	17
12	84	86
13	0	12
14	33	39
15	0	7
16	0	17
18	50	50

H,L= 6, 2

K	FOB	FCA
0	10	10
1	41	40
2	48	47
3	85	90
4	19	23
5	47	50
6	14	14
7	45	42
8	34	33
9	58	57
10	14	20
11	40	41
12	24	21
13	0	11
14	19	20
15	49	52
16	0	7
17	21	23

H,L= 6, 3

K	FOB	FCA
0	13	10
1	0	4
2	0	4
3	0	4
4	16	20
5	0	6
6	14	19
7	0	4
8	14	7
9	19	13
10	0	16
11	0	1
12	0	12
13	11	8
14	0	1
15	0	2
16	0	10

H,L= 6, 4

K	FOB	FCA
0	0	9
1	22	19
2	32	30
3	11	10
4	0	4
5	27	28
6	10	13
7	10	15
8	11	13
9	29	28
10	11	9
11	12	10
12	12	10
13	0	10
14	0	8
15	18	11

H,L= 6, 5

K	FOB	FCA
0	49	44
1	0	2
2	43	45
3	15	15
4	29	29
5	15	11
6	69	61
7	0	4
8	30	29
9	12	7
10	12	10
11	12	5
12	39	39

H,L= 6, 6

K	FOB	FCA
0	20	17
1	49	49
2	0	8
3	56	53
4	0	10
5	24	33
6	17	15
7	24	22
8	0	8
9	35	33
10	0	1
11	0	5
12	11	11

H,L= 7, 0

K	FOB	FCA
1	33	36
2	28	22
3	41	47
4	24	21
5	58	56
6	60	63
7	47	44
8	28	31
9	33	33
10	21	21
11	34	34
12	29	33
13	16	18
14	20	21
15	40	36
16	0	5

H,L= 7, 1

K	FOB	FCA
0	67	65
1	27	32
2	29	31
3	48	42
4	32	34
5	22	22
6	45	48
7	0	5
8	59	57
9	37	38
10	0	7
11	35	34
12	60	59
13	0	5
14	36	37
15	21	24

H,L= 7, 2

K	FOB	FCA
0	105	107
1	20	16
2	48	70
3	33	32
4	60	53
5	34	33
6	53	52
7	24	21
8	65	65
9	31	35
10	18	17
11	26	15
12	83	79
13	11	7
14	44	41
15	12	12
16	0	10

H,L= 7, 3

K	FOB	FCA
0	67	65
1	27	32
2	29	31
3	48	42
4	32	34
5	22	22
6	45	48
7	0	5
8	59	57
9	37	38
10	0	7
11	35	34
12	60	59
13	0	5
14	36	37
15	21	24

H,L= 7, 4

K	FOB	FCA
0	18	22
1	0	12
2	11	4
3	C	2
4	11	14
5	16	9
6	12	5
7	C	4
8	12	13
9	C	5
10	C	11
11	12	5
12	24	24

H,L= 8, 0

K	FOB	FCA
0	43	42
1	22	24
2	16	20
3	11	17
4	19	20
5	C	15
6	32	30
7	0	5
8	17	22
9	17	26
10	21	15
11	12	11

H,L= 8, 1

K	FOB	FCA
0	33	36
1	37	39
2	31	31
3	41	40
4	C	12
5	10	15
6	21	17
7	C	8
8	15	14
9	41	37
10	0	5
11	12	16
12	45	49
13	0	2
14	12	16

H,L= 8, 2

K	FOB	FCA
0	76	84
1	16	15
2	21	29
3	0	16
4	31	35
5	C	7
6	47	44
7	C	9
8	42	42
9	C	13
10	11	17
11	11	4
12	54	52
13	C	7
14	C	15
15	C	8

H,L= 8, 3

K	FOB	FCA
0	52	49
1	11	16
2	27	27
3	26	25
4	23	22
5	16	15
6	48	44
7	17	16
8	34	30
9	21	21
10	12	14

H,L= 8, 4

K	FOB	FCA
0	49	49
1	16	12
2	27	27
3	28	22
4	23	22
5	16	15
6	48	44
7	17	16
8	34	30
9	21	21
10	12	14

H,L= 8, 5

K	FOB	FCA
0	11	5
1	C	10
2	C	17
3	25	31
4	12	10
5	21	27
6	47	50
7	19	7
8	46	41
9	35	31
10	11	8
11	41	43
12	14	32

H,L= 9, 0

K	FOB	FCA
1	46	46
2	21	27
3	86	93
4	26	25
5	44	40
6	26	25
7	31	33
8	25	14
9	59	60
10	41	37
11	33	37
12	17	20
13	21	17

H,L= 9, 1

K	FOB	FCA
0	63	67
1	37	39
2	41	42
3	31	20
4	30	30
5	15	21
6	69	66
7	21	17
8	45	43
9	16	14
10	20	15
11	12	16
12	45	49
13	0	2

H,L= 9, 2

K	FOB	FCA
0	20	22
1	41	45
2	23	25
3	86	89
4	C	11
5	61	63
6	24	22
7	47	46
8	20	26
9	24	15
10	11	23
11	39	37
12	19	19
13	11	7
14	24	27
15	55	60
16	0	4

H,L= 9, 3

K	FOB	FCA
0	42	42
-3	40	43
4	16	12
5	47	50
6	17	7
7	46	41
8	35	31
9	8	8
10	11	8
11	41	43
12	32	32
13	C	11
14	30	32

H,L= 9, 4

K	FOB	FCA
0	52	49
1	11	16
2	27	27
3	28	25
4	23

Table III. Values of $\frac{|\underline{F}(+)| - |\underline{F}(-)|}{0.5(|\underline{F}(+)| + |\underline{F}(-)|)}$ for $Rb_2B_{20}H_{18}$[a]

h	k	ℓ	Obs.	Calc.
1	1	1	-0.13	-0.15
9	3	2	-0.13	-0.14
1	17	3	0.11	0.10
1	9	5	0.10	0.14
6	3	1	-0.10	-0.12
8	3	0	-0.10	-0.11
1	3	1	0.06	0.07
5	9	2	-0.05	-0.07
1	2	3	0.05	0.05
0	1	1	0.05	0.03
1	3	3	-0.04	-0.03
0	14	0	0.04	0.03
3	3	3	-0.03	-0.04
0	18	0	0.03	0.03
0	2	0	0.01	0.01
0	2	2	0.	-0.01
0	3	1	0.	0.01

(a) Where $\underline{F}(+)$ and $\underline{F}(-)$ are the structure factors for ($\underline{h}$, $\underline{k}$, $\underline{\ell}$) and ($\underline{h}$, $-\underline{k}$, $\underline{\ell}$), respectively.

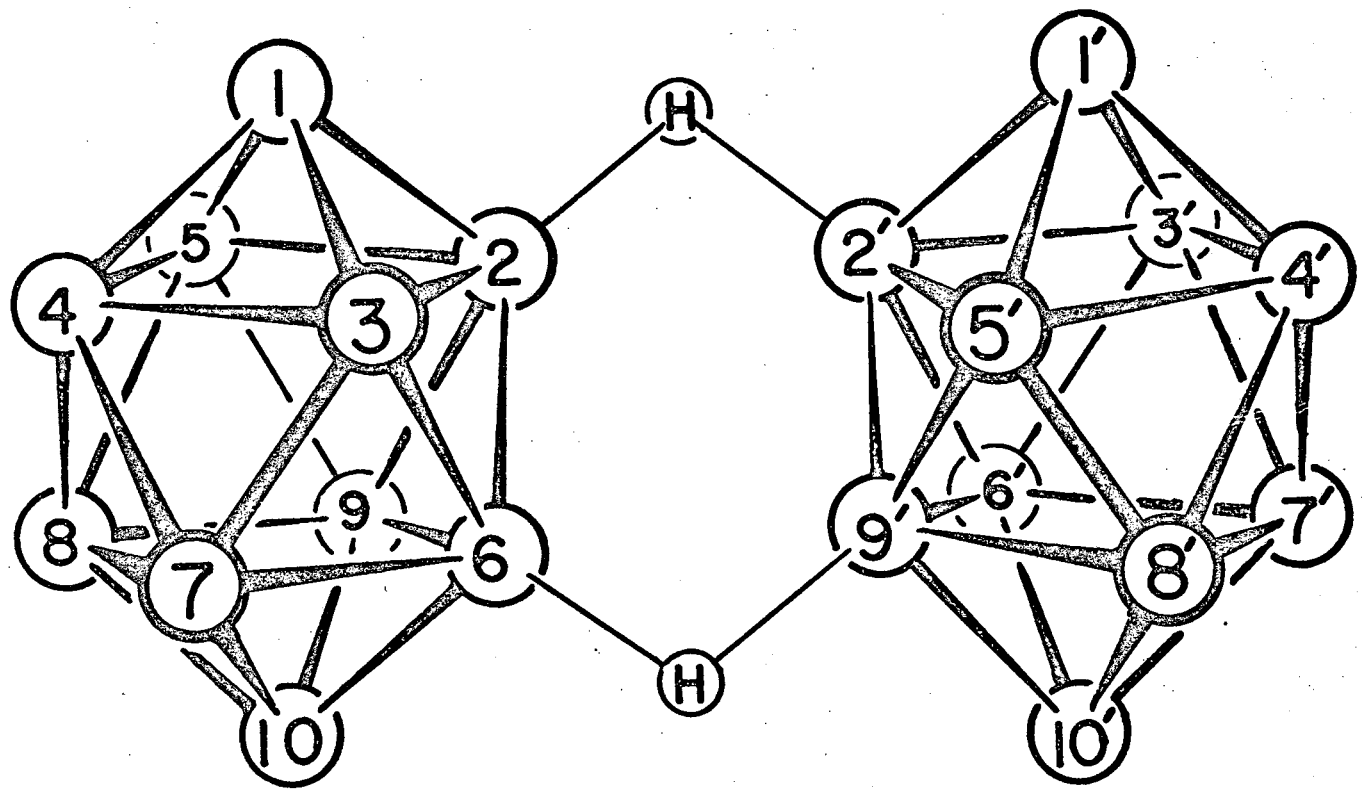

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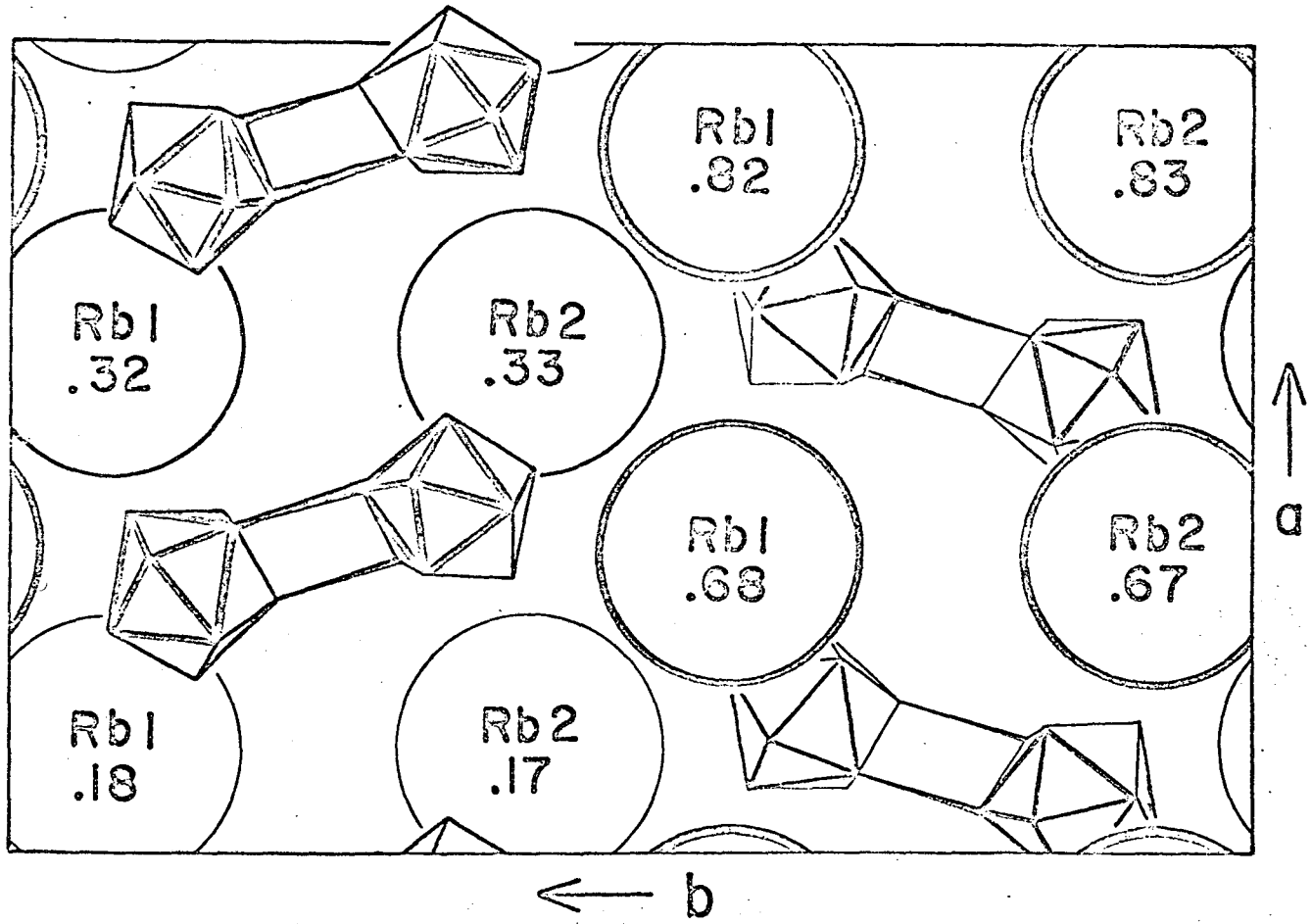
Figure 1. - $B_{20}H_{18}^{2-}$ photoisomer (terminal hydrogens omitted for clarity).



XBL 678-4462

Figure 2. - One unit cell of $Rb_2B_{20}H_{18}$ seen down c axis (hydrogens omitted). Numbers on Rb ions are z coordinates as decimal fractions of c; the centers of the B_{20} units are approximately at $z = \frac{1}{4}$ and $z = \frac{3}{4}$.

Table IV. Distances[a] in $Rb_2B_{20}H_{18}$

apex-ring	A	intra-ring	A	inter-ring	A
B(1)-B(2)	1.66(3)	B(2)-B(3)	1.77(3)	B(2)-B(6)[c]	1.72(3)
-B(3)	1.67(3)	B(3)-B(4)	1.82(3)	B(6)-B(3)	1.78(3)
-B(4)	1.70(3)	B(4)-B(5)	1.87(3)	B(3)-B(7)	1.77(3)
-B(5)	1.64(3)	B(5)-B(2)	1.85(3)	B(7)-B(4)	1.76(3)
B(10)-B(6)	1.64(3)	B(6)-B(7)	1.86(3)	B(4)-B(8)	1.76(4)
-B(7)	1.73(4)	B(7)-B(8)	1.78(3)	B(8)-B(5)	1.85(4)
-B(8)	1.65(4)	B(8)-B(9)	1.80(4)	B(5)-B(9)	1.80(3)
-B(9)	1.58(3)	B(9)-B(6)	1.80(3)	B(9)-B(2)	1.91(3)
B(1')-B(2')	1.68(3)	B(2')-B(3')	1.86(3)	B(2')-B(6')	1.80(3)
-B(3')	1.70(3)	B(3')-B(4')	1.93(3)	B(6')-B(3')	1.79(3)
-B(4')	1.73(3)	B(4')-B(5')	1.83(3)	B(3')-B(7')	1.82(3)
-B(5')[b]	1.82(3)	B(5')-B(2')	1.83(3)	B(7')-B(4')	1.88(3)
B(10')-B(6')	1.73(3)	B(6')-B(7')	1.82(3)	B(4')-B(8')	1.82(3)
-B(7')	1.73(3)	B(7')-B(8')	1.88(3)	B(8')-B(5')[b]	1.66(3)
-B(8')	1.70(3)	B(8')-B(9')	1.79(3)	B(5')-B(9')[b]	1.58(3)
-B(9')	1.70(4)	B(9')-B(6')	1.76(3)	B(9')-B(2')[c]	1.65(3)
		across bridges			
		B(2)-B(2')	1.98(3)		
		B(6)-B(9')	2.10(3)		

Table IV, continued

(a) These distances are not corrected for thermal motion. The terminal digits in parentheses are the standard deviations as estimated from the least-squares matrix in units of .01 A. However, the author feels that the root-mean-square deviations from the averages given in the text of ~.05 A are a better measure of the accuracy of these distances.

(b) Evidence that B(5') is displaced from its "true" position.

(c) Pairs of borons in the same B_{10} unit which are involved in hydrogen bridges.

Table V. Angles[a] in $Rb_2B_{20}H_{18}$

Angle, B-B-B Numbers	degrees, unprimed	degrees, primed	Angle, B-B-B Numbers	degrees, unprimed	degrees, primed
2 1 3	64	67	6 2 9	59	61
3 1 4	65	68	6 3 7	63	61
4 1 5	68	62	7 4 8	61	61
5 1 2	68	63	8 5 9	59	67
6 10 7	67	63	2 6 3	61	62
7 10 8	63	66	3 7 4	62	63
8 10 9	68	63	4 8 5	62	63
9 10 6	68	62	2 9 5	60	69
e-a-e ave. = $66^{\circ} \pm 2^{\circ}$			e-e'-e ave. = $61^{\circ} \pm 2^{\circ}$		
1 2 3	58	57	3 2 6	61	59
1 2 5	55	62	5 2 9	57	54
1 3 2	58	56	2 3 6	58	59
1 3 4	58	57	4 3 7	59	60
1 4 3	57	55	3 4 7	59	57
1 4 5	55	61	5 4 8	61	54
1 5 2	56	55	2 5 9	63	57
1 5 4	58	57	4 5 8	57	63
10 6 7	59	58	2 6 9	66	55
10 6 9	55	58	3 6 7	58	60
10 7 6	54	58	3 7 6	58	59
10 7 8	56	56	4 7 8	60	58
10 8 7	60	57	4 8 7	60	61

Table V, continued

10	8	9	54	58	5	8	9	59	55
10	9	6	57	60	2	9	6	55	64
10	9	8	58	58	5	9	8	62	59
a-e-e ave. = $57^{\circ} \pm 2^{\circ}$					e-e-e' ave. = $59^{\circ} \pm 3^{\circ}$				
2	1	4	102	101	3	2	2'	115	
3	1	5	101	97	9	6	9'	116	
6	10	8	100	99	2	2'	5'	112	
7	10	9	103	94	6	9'	6'	110	
ave. = $100^{\circ} \pm 3^{\circ}$					ave. = $113^{\circ} \pm 3^{\circ}$				
2	3	4	93	88	5	2	2'	155	
3	4	5	88	89	7	6	9'	154	
4	5	2	89	92	2	2'	3'	157	
5	2	3	90	91	6	9'	8'	153	
6	7	8	88	89	ave. = $155^{\circ} \pm 2^{\circ}$				
7	8	9	93	86	6	2	2'	93	
8	9	6	89	95	2	6	9'	86	
9	6	7	90	89	2	2'	9'	91	
					6	9'	2'	91	
ave. = $90^{\circ} \pm 2^{\circ}$					ave. = $90^{\circ} \pm 3^{\circ}$				

(a) Standard deviations for these angles as calculated from the least-squares matrix are ~ 1.5°, but the author feels that the given root-mean-square deviations from the average show that ~ 2.5° would be nearer the truth.

understand how this effect arises but did exclude B5' from the calculation of the deviations of the anion from 2/m symmetry and from the calculations of average boron-boron distances.

The average of 15 apical-equatorial distances (excluding B1'-B5') is 1.68 ± .04 A and the average of 28 equatorial-equatorial distances (excluding B5'-B8', B5'-B9', and the inter-bridging-boron distances) is 1.82 ± .05 A. The shortened inter-bridging-boron distances average 1.68_5 ± .05 A and the B-B distances across the B-H-B bridges average 2.04 ± .09 A. The errors quoted are root-mean-square deviations. The increase in calculated bond distances due to thermal motion is estimated to be ~.02 A, or about half a standard deviation. These averages may be compared with those found[13] for the cuprous salt of $B_{10}H_{10}^{2-}$ which are 1.73 ± .02 A for apical-equatorial distances, 1.86 ± .03 A for distances within the equatorial rings, and 1.81_5 ± $.01_5$ A for distances between equatorial rings.

The two rubidium ions are nearly centrically located, as can be seen from the table of atomic coordinates. The distance between one rubidium ion and the invert ($\bar{1}$) of the other's position is 0.062 ± .008 A. The rubidium-hydrogen distances are normal for van derWaals contacts. The average of the eight shortest Rb-H distances (four on each rubidium) is 2.8 A, and the shortest single distance is 2.6 A. The minimum boron-rubidium distance is 3.3 A.

The $B_{20}H_{18}^{2-}$ ion described above is not the only one which might be constructed by joining two B_{10} polyhedra with two B-H-B bridges involving adjacent borons in each B_{10} unit. There are thirteen isomers which may

be so constructed, five of which are symmetric and the remaining eight of which form four enantiomorphic pairs. Other isomers involving bridging to non-adjacent atoms were not considered because of the drastic crowding of the pair of B-H groups which lie between any such non-adjacent pair. The thirteen isomers are listed in Table VI, together with the point groups to which they belong and an indication of which pairs of atoms in each polyhedron are involved in the hydrogen bridges. The isomer found in this investigation is the fifth listed in Table VI, while number 1 was proposed[9] for the structure of the parent $B_{20}H_{18}^{2-}$ ion before it was shown[5,6] to be linked by a pair of B-B-B three-center bonds rather than hydrogen bridges. Hawthorne and Pilling mention[2] "the formation of unidentified metastable intermediates" in the thermal reversion of the photoisomer studied here to the parent ion. Thus it may be that some or all of the isomers discussed here also exist.

Table VI. Possible $(B_{10}H_8)\langle^{H}_{H}\rangle(B_{10}H_8)^{2-}$ Isomers

no.[a]	bridge locations[b]	pairs linked[c]	point group[d]
1	(1-2', 2-1')	A-A	$2/\underline{m} = \underline{C}_{2\underline{h}}$
2	(1-1', 2-2')	A-A	$\underline{mm}2 = \underline{C}_{2\underline{v}}$
3	(2-3', 3-2')	E-E	$\underline{mm}2 = \underline{C}_{2\underline{v}}$
4	(2-2', 3-3')	E-E	$2/\underline{m} = \underline{C}_{2\underline{h}}$
5	(2-2', 6-9')	E'-E'	$2/\underline{m} = \underline{C}_{2\underline{h}}$
6a	(2-2', 6-6')	E'-E'	$222 = \underline{D}_2$
6b	(2-2', 9-9')		
7a	(1-2', 2-3')	A-E	$1 = \underline{C}_1$
7b	(1-3', 2-2')		
8a	(1-2', 2-6')	A-E'	$1 = \underline{C}_1$
8b	(1-2', 2-9')		
9a	(2-2', 3-6')	E-E'	$1 = \underline{C}_1$
9b	(2-2', 3-9')		

(a) The a-b pairs are enantiomers.

(b) Reference 10.

(c) A denotes an apex-equatorial pair, E denotes a pair in the same equatorial ring, and E' denotes a pair which has one member in each ring.

(d) In Hermann-Mauguin and Schoenflies notations, respectively.

References and Footnotes

(1) A description of this work has been published by B. G. DeBoer, A. Zalkin, and D. H. Templeton, Inorg. Chem., 7, 1085 (1968).

(2) M. F. Hawthorne and R. L. Pilling, J. Am. Chem. Soc., 88, 3873 (1966).

(3) M. F. Hawthorne, R. L. Pilling, and P. M. Garrett, ibid., 87, 4740 (1965).

(4) M. F. Hawthorne, R. L. Pilling, and P. F. Stokely, ibid., 87, 1892 (1965).

(5) R. L. Pilling, M. F. Hawthorne, and E. A. Pier, ibid., 86 3568 (1964).

(6) B. L. Chamberland and E. L. Muetterties, Inorg. Chem., 3, 1450 (1964).

(7) M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garret, J. Am. Chem. Soc., 85, 3704 (1963).

(8) A. R. Pitochelli, W. N. Lipscomb, and M. F. Hawthorne, ibid., 84, 3026 (1962).

(9) A. Kaczmarczyk, R. Bobrott, and W. N. Lipscomb, Proc. Nat'l. Acad. Sci. U. S., 48, 729 (1962).

(10) Numbering according to: R. Adams, Inorg. Chem., 2, 1087 (1963); See Figure 1.

(11) "International Tables for X-ray Crystallography", Vol III, The Kynoch Press, Birmingham, England, 1962, pp. 202, 206, 216.

(12) Each B-H unit was refined as a rigid, non-rotating body.

(13) R. Dobrott and W. N. Lipscomb, J. Chem. Phys., 37, 1779 (1962).

III. The Crystal Structure of a Brominated Carborane - Metal Sandwich Compound — $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$

A. Introduction

Hawthorne and co-workers[1-6*] have recently synthesized a number of π-dicarbollyl metal compounds analogous to the π-cyclopentadienyl "sandwich" compounds. They found[6,7] that one of these substances, $Co(B_9C_2H_{11})_2^{-1}$, could be electrophilically brominated by treatment with neat bromine or bromine in glacial acetic acid to give $Co(B_9C_2H_8Br_3)_2^{-1}$. This is thought[7] to be the first example of a substitution upon the intact bis-dicarbollyl metal "sandwich" compound.

This determination[8] of the crystal structure of the tetramethylammonium salt of the product ion once again establishes the bis-dicarbollyl metal structure as two icosahedra with the metal atom as their common vertex. This work was undertaken in order to ascertain the positions of bromine substitution upon these icosahedra. It was found that the bromines are bonded to three borons in each icosahedron which form a triangular face, one corner of which is adjacent to the cobalt atom. The other two corners of the brominated face are as far as possible from the two carbon atoms, which are adjacent to each other and to the cobalt.

B. Experimental

Crystals of $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$ were received from Professor

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* References and Footnotes for part III are to be found on page 49.

M. F. Hawthorne of the University of California, Riverside. Intensity data were collected from two of these orange-brown crystals, both of which were approximately 0.1 mm square and 0.05 mm thick. The calculated linear absorption coefficient, μ, was 153 cm^{-1} (for CuKα). It is estimated that the absorption effect on intensities may vary by a factor of the order of 1.5 between the extreme cases. Both crystals were mounted by being glued to the ends of Pyrex glass fibers in such a way that the fiber, the instrument φ axis, and the b axis were all perpendicular to the plate. A General Electric XRD-5 X-ray diffractometer equipped with a molybdenum X-ray tube, a manual quarter-circle Eulerian-cradle goniostat, and a Zr filter at the receiving slit was used to measure cell dimensions. They were obtained from carefully measured 2θ (θ is the Bragg angle) values of the h00, 0k0, and 00ℓ reflections. The alpha doublet ($\lambda(MoK\alpha_1)$ = 0.70926 A) was resolved. The β angle was obtained directly from the angle on the φ circle between the h00 and 00ℓ sets of reflections. A card-controlled version of the same apparatus, using a copper X-ray tube and a Ni filter between crystal and counter, measured intensities by scanning 2θ at the rate of 1°/min., beginning 0.7° below the α_1 peak and ending 0.7° above the α_2 peak ($\lambda(CuK\alpha_1,K\alpha_2)$ = 1.5405, 1.5443 A). The take-off angle at the X-ray tube anode was approximately 4°. Coincidence losses were negligible. Ten-second stationary background counts were taken at each end of the scan. Three reflections which were measured at frequent intervals showed no systematic trends over the course of taking either data set. The maximum 2θ was 75° ($\sin\theta/\lambda$ = 0.395).

The first crystal yielded 1598 independent intensities before it

was accidentally destroyed. Of these, ~ 23% were measured once, ~ 64% either two or three times, and the remainder up to six times. These multiple measurements include remeasurements of the same reflection and measurements of equivalent $(-\underline{h},\underline{k},-\underline{\ell})$ reflections in an irregular pattern caused by the fact that these measurements were made during an initial exploration of the use of the newly-acquired diffractometer. The second crystal gave a complete set of 3002 independent intensities. Approximately 75% of these (those with $|\underline{\ell}| \leq 6$) also had their equivalent $(-\underline{h},\underline{k},-\underline{\ell})$ reflections measured. These figures do not include the space group extinctions which were also measured and found to confirm the extinction rules ($0\underline{k}0$, $\underline{k} \neq 2\underline{n}$ and $\underline{h}0\underline{\ell}$, $\underline{\ell} \neq 2\underline{n}$) obtained from preliminary Weissenberg photographs.

The intensity, $\underline{I}$, and standard deviation, $\sigma(\underline{I})$, for each measurement was calculated by:

$$\underline{I} = \underline{C} - (\underline{t}_{\underline{C}}/2\underline{t}_{\underline{B}})(\underline{B}_1 + \underline{B}_2) \qquad \text{and:}$$

$$\sigma^2(\underline{I}) = \underline{C} + (\underline{t}_{\underline{C}}/2\underline{t}_{\underline{B}})^2(\underline{B}_1 + \underline{B}_2) + (0.06 \times \underline{I})^2$$

where $\underline{C}$ is the number of counts accumulated in scanning through the reflection in time $\underline{t}_{\underline{C}}$, and $\underline{B}_1$ and $\underline{B}_2$ are the background counts, each obtained in time $\underline{t}_{\underline{B}}$. Within each data set, multiple measurements (including measurements of equivalent reflections) were averaged and the averages assigned standard deviations equal to the greater of: $(\Sigma_{\underline{i}}\sigma_{\underline{i}}^2/\underline{n}^2)^{\frac{1}{2}}$ or $(\Sigma_{\underline{i}}\Delta_{\underline{i}}^2/\underline{n}^2)^{\frac{1}{2}}$, where $\sigma_{\underline{i}}$ and $\Delta_{\underline{i}}$ are the standard deviation and deviation from the average of the $\underline{i}$th measurement and $\underline{n}$ is the number of measurements averaged. The latter expression did give the greater value in 10% of the

cases in the first set and 15% in the second set. Later, it was realized that this procedure tends to "average out" the 0.06 x $\underline{I}$ included in $\sigma(\underline{I})$, but this was approximately corrected when the two data sets were combined as described below. Observed structure factors for reflections which were included in both data sets were larger in the first set about as often as in the second, and corresponding values were typically in disagreement by 5%. There was no statistically valid deviation from equal scaling, and the combined data set was generated by averaging (without scaling) those $\underline{F}_o$ values[9] which the two sets had in common and setting:

$$\sigma^2(\underline{F}_{ave}) = 0.5[\sigma^2(\underline{F}_1) - (0.03\underline{F}_1)^2] + 0.5[\sigma^2(\underline{F}_2) - (0.03\underline{F}_2)^2] + (0.03\underline{F}_{ave})^2,$$

where the terms in square brackets were set to zero if they were negative. If the expression: $\sigma^2(\underline{F}_{ave}) = 0.5(\underline{F}_1 - \underline{F}_2)^2$ gave a larger number, it was used instead. In no case was any reflection of the combined set allowed to have a standard deviation less than 3% of itself (corresponding to 6% of $\underline{I}$). A plot of the resulting $\sigma(\underline{F}_o)$ versus $\underline{F}_o$ revealed that the great majority of points fall on or near a smooth curve. This curve starts near 10 electrons for small $\underline{F}_o$, stays near 3 electrons for $\underline{F}_o$ = 40 to 100 electrons, and follows the 3% of $\underline{F}_o$ line thereafter. Forty-five percent of the data have $\underline{F}_o \geqq 70$ electrons, and of these, only about 8% have standard deviations more than three electrons above the curve described, with the 002 reflection by far the worst at 441 ± 66 electrons. These large deviations were, of course, caused by disagreements between the two data sets obtained from the two different crystals. All data were corrected for Lorentz and polarization effects, but no corrections beyond the averaging just described were made for absorption or extinction.

Computations were performed on an IBM 7044 and a CDC 6600. Zalkin's FORDAP and DISTAN programs (unpublished) were used for Fourier syntheses and distance-and-angle calculations. An unpublished Wilson-plot program by Maddox and Maddox gave normalized structure factor magnitudes[10] which were used in Long's sign-determination program[11] as described below. The unpublished version of the Ganzel-Sparks-Trueblood least-squares program which was used, minimizes the function $\Sigma \underline{w}(|\underline{kF_o}| - |\underline{F_c}|)^2/\Sigma \underline{w}|\underline{kF_o}|^2$, where $\underline{F_o}$ and $\underline{F_c}$ are the observed and calculated structure factors, $\underline{k}$ is the scale factor, and $\underline{w}$ is the weighting factor. Scattering factors[12] for Co^{+3} and neutral Br were corrected for the real part of anomalous dispersion by -2.2 and -0.9 electrons, respectively. The imaginary part of anomalous dispersion was neglected. Scattering factors for neutral nitrogen, carbon, and boron were also taken from standard tables[12]. The anisotropic temperature factors used have the form:

$$\exp(-0.25\ \Sigma_{\underline{i}}\Sigma_{\underline{j}}\underline{h_i}\underline{h_j}\underline{b_i}\underline{b_j}\underline{B_{ij}}),$$

$\underline{i},\underline{j}$ = 1,2,3, where $\underline{b_i}$ is the $\underline{i}$th reciprocal cell length.

C. Results

The monoclinic unit cell, space group $P2_1/c$, $\underline{a}$ = 19.893 ± .010 A, $\underline{b}$ = 19.487 ± .010 A, $\underline{c}$ = 15.058 ± .010 A, β = 93.15 ± .05°, contains eight formula units of $N(CH_3)_4[Co(B_9C_2H_8Br_3)_2]$. The calculated density of 1.967 g/cc agrees with the value (1.98 ± .01 g/cc) found by flotation in a mixture of bromoform and ethylene dichloride. These measurements apply to room temperature (~ 23° C) and the error figures given are estimates. The observed extinctions correspond to space group $P2_1/c$. All four of

the two-fold sets of special positions are occupied by cobalt atoms and all other atoms are in general four-fold positions $\pm(x,y,z;\ x,\frac{1}{2}-y,\frac{1}{2}+z)$.

1. Determination of Structure

Attempts to interpret the Patterson function calculated from the second (complete) data set failed because of an error in communication which resulted in the mistaken idea that there were four, rather than eight, molecules per unit cell. Normalized structure factor magnitudes,[10] E_h, were calculated and used in Long's sign-determining program[11] which iteratively applies the relation; $sE_h \sim s\Sigma_k E_k E_{h-k}$, where s is to be read "the sign of". After enough of the signs were worked out by hand to yield a good set of "starting reflections" for input, a run of Long's program on 379 E's $\geqq 1.5$ gave one set of signs which was better than any other as judged by the smaller number of passes necessary to reach it and by its high consistency index (0.82 as against the second-best 0.65). The consistency index is defined as: $\Sigma_h \Sigma_k E_h E_k E_{h-k} / \Sigma_h \Sigma_k |E_h E_k E_{h-k}|$. A Fourier synthesis using the signed E's as coefficients showed sixteen largest peaks ranging in relative size from 1.00 to 0.57 with a definite break down to the seventeenth at 0.28. Isotropic bromines at these sixteen positions, four of which were the two-fold special positions, quickly refined to $R = 0.26$ where $R = \Sigma\,||kF_o| - |F_c||\,/\,\Sigma|kF_o|$. A difference Fourier synthesis phased by these sixteen atoms showed all fifty-four of the non-hydrogen light atoms. Their locations showed that the asymmetric unit contains four half-anions plus two tetramethylammonium ions and that the cobalt atoms are those in the four two-fold sets of

special positions. The refinement beyond this point was routine except that, because of the large number of parameters involved, it was done in a block diagonal fashion. The heavy atoms (four anisotropic cobalts fixed at the special positions plus twelve anisotropic bromines) were refined full-matrix while the light atoms were held fixed, alternately with full-matrix refinements of the fifty-four isotropic light atoms with the heavy atoms fixed. The two carbons in each of the four icosahedral fragments were identified by their low temperature factors when refined as borons and the shorter distance between them. The partial data set from the first crystal was averaged in as described above when the refinement halted at $\underline{R}$ = 0.11 and it was found that the large disagreements were concentrated at low angle (where most of the partial data set had been obtained). Continued refinement using this composite data set changed the structure only slightly, but $\underline{R}$ fell to nearly its final value and the distribution of large disagreements became more uniform. Six cycles of diagonal-matrix least-squares (all parameters) finished the refinement and gave the final $\underline{R}$ value of 0.087. The standard deviation of an observation of unit weight, defined as $[\Sigma \underline{w}(|\underline{kF}_o| - |\underline{F}_c|)^2/(\underline{u}-\underline{v})]^{\frac{1}{2}}$, where $\underline{u}$ is the number of data and $\underline{v}$ is the number of independent parameters refined, was 2.28. Standard deviations derived from the final diagonal matrix were typically 10% less than those obtained from one cycle of full-matrix refinement which included all parameters, and ranged from approximately 5% larger to approximately 25% smaller.[13] In the last cycle, no parameter shifted more than 4% of the standard deviation calculated for it, except for the tetramethylammonium ions, where a few parameters shifted by as much as 11%

of their calculated standard deviations. The six largest peaks in a final difference Fourier (1.9, 1.8, 1.8, 1.3, 1.1, and 0.9 electrons/A^3) were all judged to be due to errors in the data, since their positions (far from any atom) made no chemical sense. This result made a search for hydrogens unjustified. The final atomic coordinates and thermal parameters are listed in Table I and the values of $|\underline{F}_o|$ and $\underline{F}_c$ are given in Table II.

2. Discussion

All four crystallographically unrelated anions were found to have the same atomic arrangement with corresponding dimensions equal to within the experimental accuracy. Figure 1 illustrates the structure of the $Co(B_9C_2H_8Br_3)_2^{-1}$ anion and the numbering system used in this study. The top and bottom halves of the anion are related by a crystallographic inversion center located at the cobalt. Interatomic distances are presented in Table III and averages thereof in Table IV. The average B-B, B-C, C-C, B-Br, and Br-Br distances are in agreement with those found[14-19] for similar compounds. The Br-B-B angles are all (with one exception) within 5° of their 121° average and show no significant deviations from this value which are systematic over the four anions. The Br(5)-B(5)-Co angles are slightly smaller (116° to 119°) as expected from the protrusion of the icosahedron's cobalt vertex. This protrusion is also shown by the smaller angles (49.4^o with a root-mean-square deviation of $\pm$ 1.7^o about this value) at cobalt. The 120 B-B-B angles necessarily average to exactly 60° and have a root-mean-square deviation of 2°. The sixteen B-C-B and thirty-two C-B-B angles average 63° and $58\ \frac{1}{2}^o$ while the four C-B-C and

Table I. Final Positional and Thermal Parameters[a] in $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
1 Co	0.	0.	0.	3.1(2)	2.1(2)	3.0(2)	0.7(2)	0.1(2)	0.0(2)
1 Br(5)	.0939(1)[b]	.0812(1)	-.1619(2)	6.1(1)	5.8(2)	5.0(2)	-0.1(1)	0.9(1)	0.6(1)
1 Br(9)	.1640(2)	.1975(2)	.0155(2)	7.9(2)	6.9(2)	8.3(2)	-2.5(1)	-1.2(2)	0.2(2)
1 Br(10)	-.0010(1)	.2408(1)	-.1278(2)	7.6(2)	3.4(1)	8.4(2)	-0.1(1)	-1.5(2)	2.2(1)
2 Co	0.5	0.5	0.	2.2(2)	2.2(2)	2.2(2)	-0.1(2)	0.4(2)	-0.2(2)
2 Br(5)	.3829(1)	.4459(1)	.1533(2)	4.9(1)	4.7(1)	5.4(2)	-0.8(1)	2.5(1)	0.4(1)
2 Br(9)	.3712(2)	.2769(2)	.0308(2)	12.7(2)	8.2(2)	6.5(2)	-7.7(1)	1.4(2)	-1.0(2)
2 Br(10)	.5025(1)	.3069(1)	.2262(2)	8.3(2)	5.0(1)	4.8(2)	-1.0(1)	0.2(1)	2.0(1)
3 Co	0.	0.5	0.	2.1(2)	2.1(2)	3.1(3)	0.3(2)	0.3(2)	0.0(2)
3 Br(5)	.0684(1)	.6171(1)	-.1475(2)	5.1(1)	5.9(1)	8.4(2)	0.1(1)	1.8(1)	4.2(1)
3 Br(9)	.1905(1)	.4844(2)	-.2110(2)	6.2(1)	7.8(2)	6.9(2)	-1.3(1)	3.5(1)	-2.1(1)
3 Br(10)	.2332(1)	.6034(2)	-.0147(2)	4.3(1)	8.4(2)	8.6(2)	-3.1(1)	1.3(1)	-2.1(2)
4 Co	0.5	0.	0.	2.6(2)	2.5(2)	2.9(3)	0.9(2)	0.4(2)	0.2(2)
4 Br(5)	.4304(1)	-.1082(1)	-.1688(2)	5.8(1)	4.2(1)	3.3(1)	-0.5(1)	0.4(1)	-0.6(1)
4 Br(9)	.2666(1)	-.0179(2)	-.1510(2)	4.8(1)	7.5(2)	6.9(2)	0.1(1)	-2.0(1)	1.8(2)
4 Br(10)	.3133(1)	-.1774(1)	-.0066(2)	6.4(1)	4.7(1)	5.0(2)	-1.7(1)	0.6(1)	0.0(1)

Table I, continued

atom	x	y	z	B
1 C(2)	-.060(1)	.070(1)	.057(1)	3.5(5)
1 C(3)	.012(1)	.050(1)	.115(2)	4.7(6)
1 B(4)	.079(1)	.058(1)	.058(2)	3.8(6)
1 B(5)	.044(1)	.091(1)	-.055(2)	3.4(6)
1 B(6)	-.040(1)	.092(1)	-.042(2)	3.1(6)
1 B(7)	-.034(2)	.124(2)	.141(2)	7.5(9)
1 B(8)	.060(1)	.124(1)	.136(2)	4.3(7)
1 B(9)	.079(1)	.150(2)	.029(2)	6.2(8)
1 B(10)	.005(1)	.169(1)	-.036(2)	3.8(6)
1 B(11)	-.068(2)	.151(2)	.033(2)	7.4(9)
1 B(12)	.011(2)	.192(2)	.073(2)	7.7(9)
2 C(2)	.580(1)	.435(1)	-.001(1)	4.3(6)
2 C(3)	.522(1)	.422(1)	-.082(1)	4.1(5)
2 B(4)	.443(1)	.413(1)	-.048(2)	3.9(6)
2 B(5)	.455(1)	.418(1)	.073(2)	1.8(5)

atom	x	y	z	B
3 C(2)	.068(1)	.463(1)	.088(2)	4.8(6)
3 C(3)	.053(1)	.413(1)	.004(1)	4.4(5)
3 B(4)	.056(1)	.451(1)	-.099(2)	3.9(6)
3 B(5)	.085(1)	.540(1)	-.067(2)	2.2(5)
3 B(6)	.090(1)	.546(1)	.052(2)	3.9(6)
3 B(7)	.131(2)	.398(2)	.056(2)	7.0(9)
3 B(8)	.122(1)	.399(2)	-.053(2)	5.7(8)
3 B(9)	.147(1)	.477(1)	-.096(2)	3.3(6)
3 B(10)	.164(1)	.532(1)	-.009(2)	3.5(6)
3 B(11)	.159(2)	.483(2)	.091(2)	6.2(8)
3 B(12)	.185(1)	.445(2)	-.007(2)	5.6(8)
4 C(2)	.447(1)	-.009(1)	.113(1)	3.4(5)
4 C(3)	.425(1)	.060(1)	.053(1)	3.7(5)
4 B(4)	.407(1)	.037(1)	-.064(2)	3.9(6)
4 B(5)	.416(1)	-.055(1)	-.063(2)	4.5(7)

Table I, continued

2 B(6)	.541(1)	.436(1)	.101(2)	2.9(6)	4 B(6)	.445(1)	-.085(1)	.046(2)	3.7(6)
2 B(7)	.578(2)	.357(2)	-.050(2)	6.7(8)	4 B(7)	.372(2)	.030(2)	.128(2)	6.7(8)
2 B(8)	.488(1)	.342(2)	-.079(2)	6.4(8)	4 B(8)	.346(1)	.060(1)	.018(2)	4.5(7)
2 B(9)	.447(1)	.340(2)	.023(2)	5.7(8)	4 B(9)	.336(1)	-.017(1)	-.052(2)	3.4(6)
2 B(10)	.509(1)	.352(2)	.109(2)	5.4(7)	4 B(10)	.357(1)	-.088(1)	.014(2)	2.9(6)
2 B(11)	.589(1)	.361(1)	.064(2)	4.7(7)	4 B(11)	.378(1)	-.060(1)	.124(2)	4.7(7)
2 B(12)	.527(2)	.301(2)	.019(2)	6.3(8)	4 B(12)	.311(1)	-.020(1)	.060(2)	5.0(7)
1 N	.773(1)	.255(1)	.265(1)	4.9(4)	2 N	.269(1)	.259(1)	.272(1)	6.3(5)
1 Me(1)	.796(2)	.214(2)	.345(3)	14.8(13)	2 Me(1)	.237(2)	.301(3)	.196(3)	17.4(16)
1 Me(2)	.701(2)	.245(2)	.250(2)	11.1(10)	2 Me(2)	.240(3)	.216(3)	.337(5)	24.5(24)
1 Me(3)	.812(1)	.235(1)	.187(2)	8.1(8)	2 Me(3)	.312(2)	.209(2)	.233(3)	17.3(16)
1 Me(4)	.791(2)	.329(2)	.300(3)	12.6(11)	2 Me(4)	.301(2)	.317(2)	.328(3)	14.0(13)

(a) The units are A^2.

(b) The numbers in parentheses are the standard deviations in the least significant digit as calculated from the final diagonal least-squares matrix. They are not significantly different from those obtained from the complete matrix (see text and footnote 13).

Table II. Observed and Calculated Structure Factors for $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$

H,K* 0, 0		
L	FOB	FCA
2	441	521
4	224	263
6	578	615
8	248	254
10	32	-31

H,K* 0, 1		
L	FOB	FCA
1	7	-4
2	128	-156
3	65	-92
4	47	-61
5	34	-35
6	217	-235
7	110	136
8	148	-150
9	159	-164
10	94	-91
11	34	20

H,K* 0, 2		
L	FOB	FCA
0	244	303
1	149	192
2	165	114
3	11	-3
4	198	-212
5	52	-62
6	175	160
7	13	-16
8	79	-62
9	112	104
10	11	6
11	41	-22

H,K* 0, 3		
L	FOB	FCA
1	55	-73
2	256	-308
3	97	-115
4	159	143
5	182	-151
6	235	260
7	53	-51
8	89	-91
9	64	-62
10	51	40
11	128	-128

H,K* 0, 4		
L	FOB	FCA
0	269	265
1	70	-71
2	58	-33
3	132	147
4	113	143
5	139	-150
6	52	-54
7	87	86
8	155	154
9	52	54
10	118	121
11	58	-43

H,K* 0, 5		
L	FOB	FCA
1	200	222
2	79	88
3	265	214
4	73	-76
5	61	-51
6	45	-43
7	249	256
8	59	-55
9	68	59
10	63	69
11	50	40

H,K* 0, 6		
L	FOB	FCA
0	70	-64
1	68	76
2	99	112
3	77	-10
4	318	321
5	43	-37
6	23	-4
7	16	-3
8	156	157
9	10	-5
10	190	186

H,K* 0, 7		
L	FOB	FCA
1	20	14
2	71	-79
3	42	43
4	60	-62
5	18	17
6	43	52
7	33	33
8	17	18
9	19	6
10	99	-95

H,K* 0, 8		
L	FOB	FCA
0	72	69
1	143	-155
2	43	-47
3	39	-38
4	115	-116
5	5	-17
6	68	70
7	80	-14
8	84	75
9	79	-84
10	33	18

H,K* 0, 9		
L	FOB	FCA
1	83	-98
2	46	-33
3	259	-269
4	15	6
5	124	-131
6	135	125
7	42	42
8	149	-142
9	90	-87

H,K* 0, 10		
L	FOB	FCA
0	246	268
1	123	-139
2	84	100
3	145	141
4	279	290
5	112	118
6	226	222
7	0	-18
8	63	64
9	60	49

H,K* 0, 11		
L	FOB	FCA
1	145	147
2	193	-215
3	9	22
4	90	93
5	39	44
6	29	31
7	131	132
8	117	-115

H,K* 0, 12		
L	FOB	FCA
0	132	127
1	116	-121
2	110	110
3	42	-49
4	113	116
5	147	154
6	53	59
7	63	-67

H,K* 0, 13		
L	FOB	FCA
2	111	111
3	139	-140
4	20	21
5	27	-23
6	14	2

H,K* 0, 14		
L	FOB	FCA
0	44	-54
1	70	-72
2	79	85
3	89	89
4	60	65

H,K* 0, 15		
L	FOB	FCA
1	15	-3
2	94	97

H,K* 1, 0		
L	FOB	FCA
1	429	432
2	157	-143
3	25	30
4	80	77
5	57	76
6	6	0
7	37	-30
8	100	-101
9	61	-57
10	84	81

H,K* 1, 1		
L	FOB	FCA
0	10	-10
2	216	238
4	451	-481
6	35	40
8	71	71
10	20	-41

H,K* 1, 2		
L	FOB	FCA
0	86	-86
1	106	98
2	59	-75
3	67	50
4	67	52
5	91	-53
6	23	18
7	83	-89
8	33	-29
9	28	16
10	62	49

H,K* 1, 3		
L	FOB	FCA
1	43	33
2	61	70
3	56	-63
4	219	-247
5	260	293
6	256	215
7	33	-28
8	133	-151
9	149	-148
10	24	6
11	77	73
12	44	-40
13	36	-30
14	27	-22
15	43	-40
16	24	4
17	39	-54
18	42	32
19	11	11
20	0	22

H,K* 1, 4		
L	FOB	FCA
1	47	47
2	102	102
3	95	102
4	53	59
5	195	-208
6	85	85
7	97	97
8	24	10
9	24	-21
10	76	73
11	90	-72

H,K* 1, 5		
L	FOB	FCA
1	97	-88
2	112	107
3	11	-20
4	17	-20
5	143	-152
6	87	104
7	165	169
8	112	124
9	13	-14
10	152	-145
11	6	2

H,K* 1, 6		
L	FOB	FCA
1	114	-124
2	110	110
3	42	-49
4	113	116
5	147	154
6	53	59
7	63	-67

H,K* 1, 13		
L	FOB	FCA
1	6	16
2	111	111
3	139	-140
4	20	21
5	27	-23
6	14	2

H,K* 1, 6		
L	FOB	FCA
0	147	147
1	151	151
2	147	151
3	27	-35
4	39	44
5	23	-15
6	86	95

H,K* 1, 14		
L	FOB	FCA
0	147	147
1	257	-264
2	266	289
3	101	-105
4	35	-12
5	328	-366
6	162	159
7	159	-169
8	76	69
9	69	-64
10	23	-31
11	60	-73

H,K* 1, 15		
L	FOB	FCA
2	13	5
4	75	50
0	55	-59
1	24	23
2	34	-26

H,K* 2, 0		
L	FOB	FCA
5	55	-64
6	49	-44
7	20	-24
8	72	-68
9	72	-92
10	79	-92
11	72	-68
12	13	13
13	50	50
14	65	49
15	14	9
16	19	-99
17	123	-125
18	120	120
19	65	65
20	124	-125
21	65	49
22	57	-137
23	10	14
24	99	-91
25	131	-138
26	380	350
27	133	-122
28	39	-39
29	58	-71
30	116	116
31	11	13

H,K* 2, 1		
L	FOB	FCA
0	58	-71
1	116	116
2	106	-106
3	47	52
4	47	-52
5	65	-67
6	59	57
7	65	64

H,K* 1, 13		
L	FOB	FCA
-6	155	155
-5	46	-34
-4	127	156
-3	114	-121
-2	32	41
-1	120	117
0	147	147
1	151	151
2	147	151
3	27	-35
4	39	44
5	23	-15
6	86	95

H,K* 1, 14		
L	FOB	FCA
10	23	-31
11	60	-73

H,K* 2, 6		
L	FOB	FCA
2	100	101
3	19	-15
4	50	62
5	66	-72
6	138	-136

H,K* 2, 14		
L	FOB	FCA
4	170	172
-3	116	-119
-2	193	193
-1	19	-16
0	76	75
1	59	63
2	147	210
3	110	110
4	121	138

H,K* 2, 15		
L	FOB	FCA
0	19	19
-1	59	-51
0	190	-165
1	69	-59
2	22	-26
3	37	46
4	235	221
5	133	-134
6	131	136
7	94	105
8	116	-121
9	77	66
10	72	67

H,K* 3, 7		
L	FOB	FCA
-10	153	148
-6	74	68
-6	105	99
-4	124	130
-2	217	-203
0	311	264
2	54	56
4	193	179
6	112	-132
8	331	344
10	137	153

H,K* 4, 1		
L	FOB	FCA
-11	148	-139
-10	23	16
-9	75	-79
-8	25	-6
-7	38	44
-6	66	82
-5	255	-235
-4	12	7
-3	135	-117
-2	67	62
-1	73	-78
0	25	33
1	66	64
2	320	348
3	230	-210
4	207	204
5	16	6
6	0	12
7	76	81
8	202	212
9	49	-57
10	75	70
11	23	19

H,K* 4, 2		
L	FOB	FCA
-11	47	-39
-10	202	197
-9	167	184
-8	26	22
-7	33	18
-6	317	348
-5	161	-161
-4	288	268
-3	565	572
-2	399	394
-1	108	94
0	107	-74
1	22	12
2	429	415
3	382	394
4	265	253
5	231	244
6	80	70
7	22	-17
8	113	120
9	178	183
10	39	39
11	102	97

H,K* 4, 3		
L	FOB	FCA
-11	20	12
-10	52	50
-9	15	-11
-8	45	51
-7	9	-1
-6	105	-137
-5	14	-6
-4	119	-123
-3	18	35
-2	178	194
-1	15	8
0	55	-64
1	18	21
2	237	-246
3	55	-54
4	159	160
5	56	42
6	49	39
7	51	-54
8	38	-28
9	80	-74
10	34	-34
11	22	20

H,K* 3, 4		
L	FOB	FCA
-11	59	47
-10	131	-136
-9	81	80
-8	154	154
-7	18	08
-6	80	-62
-5	13	1
-4	365	-384
-3	232	252
-2	413	-451
-1	90	-79
0	100	89

H,K* 2, 12		
L	FOB	FCA
-7	32	-42
-6	33	26
-5	122	-127
-4	60	59
-3	113	7
-2	164	155
-1	101	-109
0	94	78
1	19	17
2	162	159
3	108	-105
4	44	40
5	18	12
6	101	98
7	76	-68

H,K* 2, 13		
L	FOB	FCA
-6	26	-27
-5	67	-63
-4	128	135
-3	251	-251
-2	86	92
-1	159	146
0	269	-273
1	131	-149
2	45	49
3	269	-312
4	236	220
5	215	220
6	186	-209
7	137	-139
8	19	-25
9	28	24
10	128	124

H,K* 3, 6		
L	FOB	FCA
-10	79	-67
-9	52	-36
-8	0	5
-7	61	-55
-6	24	26
-5	124	-112
-4	154	-177
-3	161	-156
-2	296	300
-1	59	-51
0	190	-165
1	69	-59
2	22	-26
3	37	46
4	235	221
5	133	-134
6	131	136
7	94	105
8	116	-121
9	77	66
10	72	67

H,K* 3, 7		
L	FOB	FCA
-10	50	51
-9	63	55
-8	44	49
-7	99	98
-6	174	-184
-5	65	-65
-4	152	169
-3	145	156
-2	269	274
-1	265	252
0	140	-119
1	40	-34
2	70	51
3	38	-31
4	235	244
5	223	241
6	104	100
7	25	-5
8	19	-20
9	90	-97
10	75	75

H,K* 3, 8		
L	FOB	FCA
-10	24	-6
-9	34	33
-8	21	-21
-7	54	43
-6	7	1
-5	104	-107
-4	136	110
-3	7	-14
-2	86	-96
-1	182	-167
0	53	56
1	190	-171
2	20	10
3	211	-225
4	79	-77
5	90	-89
6	111	-116
7	54	-56
8	93	86
9	89	-84

H,K* 3, 9		
L	FOB	FCA
-11	72	59
-10	51	-43
-9	31	-41
-8	31	-41
-7	96	-94
-6	52	-66
-5	143	147
-4	103	-119
-3	55	60
-2	33	41
-1	60	47
0	116	-105
1	45	41
2	104	-167
3	199	232
4	124	109
5	8	-3
6	89	92
7	69	77
8	16	-13
9	18	8
10	85	-86
11	10	16

H,K* 3, 3		
L	FOB	FCA
-11	128	-119
-10	18	21
-9	174	-170
-8	78	76
-7	0	-2
-6	16	4
-5	32	34
-4	129	120
-3	95	94
-2	149	-151
-1	103	-97
0	247	-241
1	119	121
2	152	163
3	50	52
4	115	-120
5	76	74
6	35	-21
7	11	15
8	15	30

H,K* 3, 11		
L	FOB	FCA
-8	47	56
-7	111	-113
-6	165	158
-5	321	-343
0	114	115
1	114	106
2	166	-165
3	41	40
4	66	-49
5	55	48
6	155	159
7	54	-50

H,K* 3, 12		
L	FOB	FCA
-6	22	22
-5	122	-127
-4	96	89
-3	31	45
-2	79	78
-1	36	-31
0	270	224
1	148	139
2	25	8
3	129	-137
4	153	144
5	122	126
6	153	167
7	46	37
8	82	91
9	70	-66
10	22	8

H,K* 4, 7		
L	FOB	FCA
-10	96	89
-9	93	99
-8	87	-87
-7	42	32
-6	142	136
-5	32	32
-4	103	106
-3	22	32
-2	148	152
-1	9	1
0	259	266
1	62	52
2	6	-19
3	125	-127
4	177	172
5	70	65
6	177	190
7	54	-51
8	70	59
9	29	-25

H,K* 4, 8		
L	FOB	FCA
-9	115	-112
-8	181	166
-7	51	59
-6	352	358
-5	64	62
-4	95	-79
-3	138	-133
-2	224	208
-1	130	128
0	302	296
1	34	-41
2	130	125
3	111	-114
4	30	25
5	67	60
6	142	146
7	63	65
8	123	116
9	127	-117

H,K* 4, 9		
L	FOB	FCA
-8	51	-56
-7	35	20
-6	139	-165
-5	89	99
-4	170	-11
-3	90	80
-2	223	228
-1	95	90
0	210	199
1	140	138
2	51	49
3	42	36
4	51	-62

H,K* 4, 13		
L	FOB	FCA
-5	149	148
-4	58	53
-3	30	36
-2	38	67
-1	44	-52
0	61	60
1	164	156
2	20	14
3	39	34
4	78	77
5	44	-49

H,K* 4, 14		
L	FOB	FCA
-4	69	61
-3	75	-69
-2	18	20
-1	13	-16
0	39	-20
1	35	-31
2	95	97
3	15	15

H,K* 5, 0		
L	FOB	FCA
-10	16	9
-9	0	8
-8	31	-20
-7	270	263
-6	220	224
-5	72	-60
-4	37	30
-3	81	90
-2	42	58
-1	204	201
0	278	247
1	148	139
2	25	8
3	129	-137
4	153	144
5	122	126
6	153	167
7	46	37
8	82	91
9	70	-66
10	22	8

H,K* 5, 1		
L	FOB	FCA
-11	24	25
-10	155	-156
-9	59	50
-8	142	145
-7	132	-134
-6	144	173
-5	171	-164
-4	93	83
-3	127	140
-2	79	84
-1	213	-165
0	341	322
1	52	-39
2	149	163
3	42	34
4	12	16
5	246	-230
6	67	77
7	76	-68
8	65	-63
9	16	-11
10	67	68
11	27	-46

H,K* 5, 2		
L	FOB	FCA
-11	23	-19
-10	134	140
-9	39	-76
-8	49	-35
-7	70	-77
-6	114	106
-5	109	-121
-4	352	352
-3	137	-140
-2	274	-262
-1	47	53
0	127	126
1	317	-302
2	50	-49
3	42	38
4	65	67
5	109	106
6	139	-165
7	51	-56
8	74	72
9	30	-23
10	11	14

H,K* 5, 3		
L	FOB	FCA
-7	116	115
-6	54	60

H,K* 5, 10		
L	FOB	FCA
-6	40	63
-5	52	52
-4	11	20
-3	13	22
-2	74	74
-1	72	-62
0	95	78
1	11	16
2	11	3
3	51	49
4	33	36
5	43	-42
6	23	2
7	28	-26
8	59	60
9	106	105
10	19	-3

H,K* 5, 6		
L	FOB	FCA
-10	12	-4
-9	48	-40
-8	97	-86
-7	0	6
-6	28	-6
-5	171	163
-4	52	-58
-3	88	-80
-2	69	-70
-1	17	8
0	240	-197
1	92	82
2	190	-193
3	155	129
4	32	21
5	193	-194
6	115	-111
7	114	113
8	161	-159
9	101	103
10	0	-3

H,K* 5, 7		
L	FOB	FCA
-9	137	-123
-8	34	34
-7	111	-113
-6	165	161
-5	13	-5
-4	63	47
-3	58	-46
-2	31	-39
-1	39	39
0	221	187
1	59	60
2	79	60
3	106	115
4	74	86
5	14	-0
6	63	-72
7	124	129
8	25	-16
9	61	-64
10	79	93

H,K* 6, 0		
L	FOB	FCA
-10	37	-34
-9	41	21
-8	65	-61
-7	40	-45
-6	195	191
-5	99	96
-4	304	304
-3	76	-74
-2	127	95
-1	146	142
0	451	439
1	246	226
2	223	205
3	62	-54
4	278	271
5	61	81
6	233	232
7	29	-12
8	64	60
9	30	24

H,K* 6, 1		
L	FOB	FCA
-10	269	264
-9	407	422
-8	165	-159
-7	334	-336
-6	373	367
-5	64	56
-4	88	94
-3	48	40
-2	373	367
-1	240	-197
0	92	82
1	190	-193
2	155	129
3	102	96
4	250	247

H,K* 6, 2		
L	FOB	FCA
-10	55	-37
-9	0	8
-8	31	-20
-7	270	263
-6	220	224
-5	72	-60
-4	37	30
-3	81	90
-2	42	58
-1	204	201
0	278	247
1	148	139
2	25	8
3	129	-137
4	153	144
5	122	126
6	153	167
7	46	37
8	82	91
9	70	-66
10	22	8

H,K* 6, 3		
L	FOB	FCA
-9	137	-123
-8	34	34
-7	111	-113
-6	165	161
-5	13	-5
-4	63	47
-3	58	-46
-2	31	-39
-1	39	39
0	221	187
1	59	60
2	79	60
3	106	115
4	74	86
5	14	-0
6	63	-72
7	124	129
8	25	-16
9	61	-64
10	79	93

H,K* 6, 4		
L	FOB	FCA
-10	37	-34
-9	41	21
-8	65	-61
-7	40	-45
-6	195	191
-5	99	96
-4	304	304
-3	76	-74
-2	127	95
-1	146	142
0	451	439
1	246	226
2	223	205
3	62	-54
4	278	271
5	61	81
6	233	232
7	29	-12
8	64	60
9	30	24

H,K* 6, 5		
L	FOB	FCA
-10	269	264
-9	407	422
-8	165	-159
-7	334	-336
-6	373	367
-5	64	56
-4	88	94
-3	48	40
-2	373	367
-1	240	-197
0	92	82
1	190	-193
2	155	129
3	102	96
4	250	247

H,K* 6, 6		
L	FOB	FCA
-9	137	-123
-8	34	34
-7	111	-113
-6	165	161
-5	13	-5
-4	63	47
-3	58	-46
-2	31	-39
-1	39	39
0	221	187
1	59	60
2	79	60
3	106	115
4	74	86
5	14	-0
6	63	-72
7	124	129
8	25	-16
9	61	-64
10	79	93

H,K* 6, 7		
L	FOB	FCA
-8	0	0
-7	229	-231
-6	99	-103
-5	36	-42
-4	96	-82
-3	102	97
-2	67	-96
-1	71	-70
0	107	103
1	116	110
2	142	-155
3	75	76
4	67	-67
5	61	61
6	60	50
7	42	36
8	22	-22

H,K* 7, 0		
L	FOB	FCA
-10	154	-156
-9	31	23
-8	0	9
-7	130	126
-6	64	34
-5	69	-59
-4	65	-64
-3	193	-197
-2	142	-155
-1	486	466
0	116	110
1	42	-56
2	144	-155
3	157	-155
4	15	-10
5	221	231
6	41	36
7	17	25
8	30	-16
9	54	-59
10	98	99

H,K* 7, 1		
L	FOB	FCA
-10	154	-156
-9	31	23
-8	0	9
-7	130	126
-6	64	34
-5	69	-59
-4	65	-64
-3	193	-197
-2	142	-155
-1	486	466
0	116	110
1	42	-56
2	144	-155
3

Table II, continued

H,K= 8, 2
L FOB FCA
-10 3 27
-9 118-109
-8 146 153
-7 23 -4
-6 247 265
-5 25 -25
-4 27 -24
-3 104-113
-2 182 191
-1 35 -34
0 34 -19
1 220 206
2 217 204
3 172-166
4 110 117
5 87 72
6 219 232
7 153 160
8 148 147
9 16 -5

H,K= 8, 3
L FOB FCA
-10 26 19
-9 110 113
-8 45 -48
-7 69 -63
-6 12 -4
-5 240 239
-4 18 -11
-3 [illegible]
-2 95 -77
-1 147 141
0 67 60
1 218 203
2 74 -90
3 46 62
4 10 -2
5 158 164
6 146 144
7 24 35
8 23 -16
9 112 113

H,K= 8, 4
L FOB FCA
-10 70 -64
-9 24 -25
-8 86 88
-7 56 57
-6 282 293
-5 202 195
-4 59 -43
-3 63 -62
-2 67 55
-1 235 220
0 364 364
1 161 171
2 181 184
3 21 -18
4 109-100
5 17 -15
6 208 202
7 113 114
8 157 169
9 93 -91

H,K= 8, 5
L FOB FCA
-9 33 -31
-8 133 137
-7 27 15
-6 87 93
-5 59 66
-4 77 -79
-3 88 -61
-2 82 74
-1 68 -68
0 17 5
1 41 33

2 119-111
3 176-169
4 42 37
5 133-130
6 16 35
7 44 -45
8 101-100
9 112-121

H,K= 6, 6
L FOB FCA
-9 126-114
-8 122-112
-7 60 -71
-6 79 76
-5 111-112
-4 88 79
-3 62 -88
-2 124-113
-1 232-234
0 32 -31
1 21 32
2 69 72
3 150-137

H,K= 8, 11
L FOB FCA
4 52 -48
5 57 -56
6 22 -10
7 52 -48
8 55 50

H,K= 6, 7
L FOB FCA
-9 36 -35
-8 14 44
-7 59 -63
-6 80 -83
-5 145 149
-4 193-196
-3 107-101
-2 263 264
-1 40 29
0 11 2
1 163 169
2 207-216
3 6 15
4 279 282
5 48 42
6 109 114
7 41 34
8 33 20

H,K= 6, 8
L FOB FCA
-8 93 81
-7 21 6
-6 120 122
-5 47 -44
-4 269 265
-3 86 93
-2 291 284
-1 32 30
0 71 61
1 67 -63
2 392 386
3 2 -7
4 76 71
5 16 -12
6 58 54
7 35 -33

H,K= 8, 9
L FOB FCA
-7 45 48
-6 46 55
-5 23 28
-4 26 34
-3 97 -99
-2 41 27
-1 24 -19
0 25 13
1 58 55
2 64 65

3 96 -93
4 70 65
5 42 -37
6 15 1
7 63 63

H,K= 6, 10
L FOB FCA
-7 11 -31
-6 42 30
-5 56 -43
-4 243 240
-3 39 39
-2 141 140
-1 0 6
0 30 -12
1 19 11
2 176 167
3 0 -10
4 168 174
5 12 6
6 58 -53

H,K= 8, 11
L FOB FCA
-6 47 58
-5 46 -37
-4 20 -6
-3 29 -34
-2 60 -63
-1 39 -34
0 42 -42
1 116-101

H,K= 9, 3
L FOB FCA
-9 17 23
-8 42 -42
-7 36 -39
-6 120 120
-5 20 10
-4 190 190
-3 191 179
-2 55 59
-1 67 -73
0 83 90
1 126 124
2 69 66
3 101 99
4 19 6
5 13 -6
6 8 -14
7 22 39
8 55 67
9 19 26

H,K= 9, 4
L FOB FCA
-9 22 6
-8 47 -48
-7 150 147
-6 10 6
-5 52 -53
-4 72 -68
-3 45 51
-2 127-124
-1 52 46
0 129-130
1 77 75
2 43 41
3 95 -89
4 170-173
5 71 73
6 179-179
7 0 6
8 111 107

H,K= 9, 5
L FOB FCA
-8 16 16
-7 59 67
-6 60 -50
-5 16 5
-4 22 8
-3 143-156
-2 226-234
-1 15 -21
0 151-135

1 102 94
2 81 83
3 190-191
4 70 -75
5 4 9
6 67 -69
7 16 -20
8 12 22
9 12 -5

H,K= 9, 2
L FOB FCA
-9 74 -74
-8 103 -96
-7 16 4
-6 28 -30
-5 179-176
-4 64 56
-3 148-156
-2 108 105
-1 132 110
0 75 -71
1 91-101
2 33 32
3 55 -57
4 289 290
5 16 -9
6 60 -60
7 16 16
8 24 11
9 47 -57

H,K= 9, 7
L FOB FCA
-8 97 -93
-7 62 -65
-6 72 -71
-5 26 21
-4 24 -13
-3 142 138
-2 157-153
-1 136-134
0 16 15
1 74 74
2 129-137
3 91 85
4 136-130
5 84 -87
6 62 65
7 44 -44

H,K= 9, 8
L FOB FCA
-7 15 -22
-6 23 18
-5 46 -48
-4 28 -32
-3 33 28
-2 17 -27
-1 [illegible] -41
0 [illegible] 86
1 7 12
2 24 -17
3 48 -44
4 49 52
5 15 -40
6 7 -18
7 8 29

H,K= 9, 9
L FOB FCA
-7 23 -23
-6 83 67
-5 37 -48
-4 0 14
-3 72 -75
-2 73 -75
-1 58 -56
0 17 -3
1 11 -4

-4 70 55
-3 177 165
-2 142-147
-1 114-108
0 105 106
1 119 107
2 125 126
3 111 111
4 51 -55
5 38 -39
6 30 23
7 36 -38
8 97 100

H,K= 9, 6
L FOB FCA
-8 129-130
-7 31 20
-6 60 57
-5 79 88
-4 88 77
-3 44 -36
-2 43 -45
-1 13 8
0 161-155
1 30 36
2 161 163
3 25 30
4 11 5
5 92 -91
6 76 -72
7 47 48
8 21 30

H,K= 9, 12
L FOB FCA
-3 64 -67
-2 22 -16
-1 49 -38
0 107 113
1 92 -98
2 11 13

H,K= 10, 0
L FOB FCA
-8 63 -57
-6 37 27
-4 26 [illegible]
-2 102 -85
0 220 214
2 85 -85
4 168 179
6 120 118
8 154 145

H,K= 10, 1
L FOB FCA
-9 33 30
-8 50 -52
-7 88 82
-6 160 174
-5 64 -69
-4 144 137
-3 145 141
-2 18 14
-1 26 21
0 204 193
1 26 23
2 229 232
3 25 15
4 124 122
5 16 6
6 43 47
7 22 20
8 121 119

H,K= 10, 2
L FOB FCA
-9 49 -50
-8 25 26
-7 35 33
-6 185 191

2 73 67
3 38 -39
4 67 51
5 14 2
6 70 -72

H,K= 9, 10
L FOB FCA
-6 93 104
-5 31 -19
-4 66 -59
-3 115 117
-2 87 88
-1 65 58
0 24 14
1 87 83
2 23 16
3 54 47
4 23 13
5 31 -34

H,K= 9, 11
L FOB FCA
-5 15 10
-4 70 72
-3 16 26
-2 16 14
-1 40 -38
0 22 -25
1 100 -96
2 46 -42
3 33 -34
4 39 39

H,K= 9, 12
L FOB FCA

H,K= 10, 4
L FOB FCA
-9 121-107
-8 22 39
-7 168-164
-6 158 160
-5 21 26
-4 47 38
-3 116-107
-2 93 102
-1 125-107
0 230 223
1 112-116
2 39 30
3 22 -10
4 170 165
5 172-180
6 61 57
7 41 -48
8 68 55

H,K= 10, 5
L FOB FCA
-8 27 36
-7 29 32
-6 12 4
-5 213-227
-4 39 -35
-3 113 113
-2 110-108
-1 34 28
0 47 44
1 117-109
2 12 6
3 54 54
4 61 -48
5 69 77
6 34 -23
7 0 -8

H,K= 10, 6
L FOB FCA
-8 74 81
-7 58 -70
-6 61 64
-5 62 48

-5 99 102
-4 154 152
-3 65 -61
-2 88 88
-1 43 -49
0 23 19
1 142 136
2 62 63
3 118-129
4 140 142
5 44 -45
6 75 79
7 39 42
8 58 -55

H,K= 10, 3
L FOB FCA
-7 43 -38
-6 76 -79
-5 31 20
-4 72 -69
-3 53 52
-2 104 93
-1 114-108
0 23 -17
1 22 25
2 63 -54
3 84 96
4 50 50
5 25 24
6 61 57

H,K= 10, 8
L FOB FCA
-7 0 -4
-6 17 -25
-5 44 -49
-4 72 69
-3 142 143
-2 242 234
-1 50 38
0 44 29
1 49 -50
2 100 93
3 214 214
4 127 133
5 38 39
6 58 69

H,K= 10, 9
L FOB FCA
-6 119-106
-5 101 102
-4 39 36
-3 30 17
-2 96 -86
-1 108-111
0 64 -61
1 75 72
2 31 -15
3 55 -61
4 46 -37
5 126-138

H,K= 10, 10
L FOB FCA
-5 81 -84
-4 50 50
-3 143-150
-2 23 -9
-1 14 -21
0 62 -54
1 95-104
2 77 -67
3 4 -14
4 126 136

H,K= 10, 11
L FOB FCA
-6 44 46
-5 68 65
-4 96 100
-3 27 -21
-2 29 -23
-1 76 -75

-4 266 261
-3 214 218
-2 227 222
-1 102-101
0 122 130
1 15 17
2 87 79
3 216 225
4 293 296
5 10 12
6 37 44
7 50 -52

H,K= 10, 7
L FOB FCA
-6 48 -50
-4 291-290
-2 55 59
0 119 109
2 264-257
4 117-116
6 139 153
8 93 -91

H,K= 11, 1
L FOB FCA
-8 52 42
-7 89 95
-6 49 -58
-5 46 48
-4 161 151
-3 113-102
-2 0 -20
-1 59 60
0 44 -51
1 48 60
2 137 128
3 25 -17
4 33 38
5 0 -4
6 55 -49
7 103 105

H,K= 11, 2
L FOB FCA
-8 69 88
-7 55 64
-6 32 -19
-5 114 116
-4 18 -8
-3 8 -13
-2 63 -66
-1 84 74
0 116 117
1 97 91
2 196-200
3 82 83
4 30 25
5 40 -39
6 62 59
7 76 75

H,K= 11, 3
L FOB FCA
-8 86 -85
-7 119 122
-6 224-240
-5 29 -27
-4 58 59
-3 30 29
-2 71 67
-1 43 36
0 229-226
1 7 -17
2 37 30
3 13 -21
4 44 34
5 30 -25
6 63 -65
7 105 109

H,K= 11, 4
L FOB FCA
-8 44 38
-7 64 63
-6 44 46
-5 55 54
-4 96 100
-3 27 -21
-2 29 -23
-1 76 -75

2 62 66
3 26 27

H,K= 11, 0
L FOB FCA
-8 105 100
-6 48 -50
-4 291-290
-2 55 59
0 119 109
2 264-257
4 117-116
6 139 153
8 93 -91

H,K= 11, 1
L FOB FCA
-6 76 -79
-5 31 20
-4 72 -69
-3 53 52
-2 104 93
-1 114-108
0 23 -17
1 22 25
2 63 -54
3 84 96
4 50 50
5 25 24
6 61 57

H,K= 11, 6
L FOB FCA
-7 36 -12
-6 48 -54
-5 76 72
-4 82 77
-3 87 -78
-2 76 -80
-1 74 74
0 47 -44
1 20 -9
2 60 60
3 69 96
4 27 29
5 105 106
6 40 41

H,K= 11, 7
L FOB FCA
-6 7 -3
-5 65 -64
-4 40 44
-3 96 95
-2 176 169
-1 71 73
0 106 104
1 31 -28
2 35 -37
3 34 34
4 41 32
5 54 -57
6 130 134

H,K= 11, 8
L FOB FCA
-6 0 -4
-5 18 -21
-4 30 35
-3 58 -55
-2 37 -35
-1 66 62
0 57 54
1 96 -96
2 109-107
3 66 -71
4 19 -7
5 85 84

H,K= 11, 9
L FOB FCA
-5 19 -33
-4 75 -76
-3 27 -4
-2 20 14
-1 114 109

0 218 218
1 33 37
2 94 85
3 100 -69
4 76 -89
5 29 -15
6 70 71
7 36 -39

H,K= 11, 10
L FCB FCA
-3 13 -12
-2 30 -24
-1 49 43
0 53 -55
1 30 -38
2 16 -14
3 5 -10

H,K= 12, 0
L FOB FCA
-8 105 102
-6 115 113
-4 280 304
-2 22 20
0 283 283
2 207 199
4 70 -76
6 103 104

H,K= 12, 1
L FOB FCA
-8 101 -98
-7 8 -13
-6 21 20
-5 126 136
-4 103-103
-3 146-147
-2 83 -69
-1 24 -3
0 126-109
1 118 117
2 48 -50
3 47 -38
4 71 -68
5 94 -97
6 87 -90
7 91 85

H,K= 12, 2
L FOB FCA
-7 60 65
-6 62 67
-5 51 52
-4 203 218
-3 20 15
-2 36 39
-1 33 49
0 50 34
1 77 77
2 241 234
3 82 -86
4 29 23
5 22 13
6 61 73

H,K= 12, 3
L FOB FCA
-7 22 -12
-6 22 -5
-5 16 -3
-4 49 41
-3 140-135
-2 28 -22
-1 59 55
0 41 -39
1 92-103
2 103-101
3 85 -94
4 59 -72
5 49 -50
6 14 -9

H,K= 12, 4
L FOB FCA

0 65 -69
1 18 12
2 60 -54
3 26 27
4 25 36

H,K= 12, 5
L FOB FCA
-7 39 -34
-6 36 -30
-5 45 43
-4 102 102
-3 53 50
-2 64 54
-1 99 98
0 81 77
1 26 -30
2 188 181
3 67 57
4 58 58
5 71 73
6 53 58

H,K= 12, 6
L FOB FCA
-4 10 24
-3 69 70
-2 32 -19
-1 150 148
0 54 68
1 8 -8
2 153 148
3 120 120
4 53 -59
5 64 63
6 0 2

H,K= 12, 7
L FOB FCA
-5 65 62
-4 55 -54
-3 46 -47
-2 15 -4
-1 98 -94
0 29 14
1 67 -67
2 62 -57
3 87 84
4 85 -91

H,K= 12, 8
L FOB FCA
-5 99-112
-4 77 -70
-3 97-100
-2 39 38
-1 63 -63
0 58 70
1 124-123
2 35 38
3 74 -76
4 75 -71

H,K= 12, 9
L FOB FCA
-3 33 -19
-2 53 42
-1 65 -77
0 82 74
1 84 91
2 65 60

H,K= 13, 0
L FOB FCA
-6 59 63
-4 49 -35
-2 149 165
0 103 111
2 207 213
4 14 -5
6 53 59

H,K= 13, 1
L FOB FCA
-7 122-134
-6 17 -3
-5 89 86
-4 98 113
-3 46 46
-2 36 46
-1 150-145
0 29 -21
1 59 -63
2 50 56
3 116 110
4 44 -34
5 26 -31
6 76 -74

H,K= 13, 2
L FOB FCA
-7 61 -70
-6 28 -26
-5 71 75
-4 30 -31
-3 54 -66
-2 56 -59
-1 192-192
0 88 -99
1 15 11
2 20 -2
3 36 35
4 32 -30
5 132-134

H,K= 13, 3
L FOB FCA
-6 97 -94
-5 24 -23
-4 27 35
-3 68 -67
-2 128 134
-1 99 -97
0 51 -57
1 66 -70
2 24 -19
3 13 10
4 31 37
5 20 6

H,K= 13, 4
L FOB FCA
-6 43 -51
-5 39 29
-4 37 -30
-3 43 37
-2 24 -26
-1 185-185
0 46 -45
1 91 85
2 62 61
3 43 36
4 66 -62
5 16 -8

H,K= 13, 5
L FOB FCA
-5 122 126
-4 34 -32
-3 30 15
-2 40 30
-1 171 174
0 49 43
1 80 85

2 44 41
3 26 18
4 19 13

H,K= 13, 6
L FOB FCA
-5 31 39
-4 38 36
-3 32 -23
-2 75 69
-1 62 -72
0 117-113
1 40 -46
2 69 74
3 21 3
4 59 65

H,K= 13, 7
L FOB FCA
-4 102 -96
-3 21 -12
-2 62 51
-1 18 9
0 70 65
1 25 -13
2 69 -63
3 38 44

H,K= 13, 8
L FOB FCA
-3 31 34
-2 48 56
-1 43 42
0 27 -29
1 74 74

H,K= 14, 0
L FOB FCA
-4 8 -9
-2 135 150
0 151 153
2 80 -77
4 25 23

H,K= 14, 1
L FOB FCA
-5 83 92
-4 5 5
-3 43 36
-2 33 38
-1 62 -52
0 32 -33
1 23 34
2 14 -12
3 74 -81
4 63 61

H,K= 14, 2
L FOB FCA
-5 76 -71
-4 47 44
-3 14 -17
-2 211 217
-1 41 -34
0 28 4
1 65 -48
2 64 66
3 45 -49
4 127 144

H,K= 14, 3
L FOB FCA
-4 76 96
-3 57 54
-2 190 195
-1 63 67
0 23 8
1 44 33
2 19 9
3 0 -29
4 119 125

H,K= 14, 4
L FOB FCA
-4 41 48
-3 19 6
-2 203 214
-1 33 37
0 22 20
1 126-129
2 15 9
3 10 -16

H,K= 14, 5
L FOB FCA
-4 84 77
-3 22 -19
-2 72 -82
-1 26 -15
0 58 -63
1 89 -87
2 62 51
3 73 -68

H,K= 14, 6
L FOB FCA
-3 75 79
-2 116 125
-1 6 -15
0 23 35
1 10 2
2 23 13

H,K= 15, 0
L FOB FCA
-4 90-100
-2 141-136
0 47 -44
2 0 -12

H,K= 15, 1
L FOB FCA
-4 30 -32
-3 113 120
-2 52 -45
-1 22 -17
0 19 13
1 8 14
2 26 -8

H,K= 15, 2
L FOB FCA
-3 24 -21
-2 54 -59
-1 107-104
0 56 52
1 81 -85
2 26 14

H,K= 15, 3
L FOB FCA
-3 22 -16
-2 85 84
-1 14 11
0 40 48
1 67 60
2 64 -63

H,K= 15, 4
L FOB FCA
-2 26 16
-1 21 -10
0 96 104
1 29 -31

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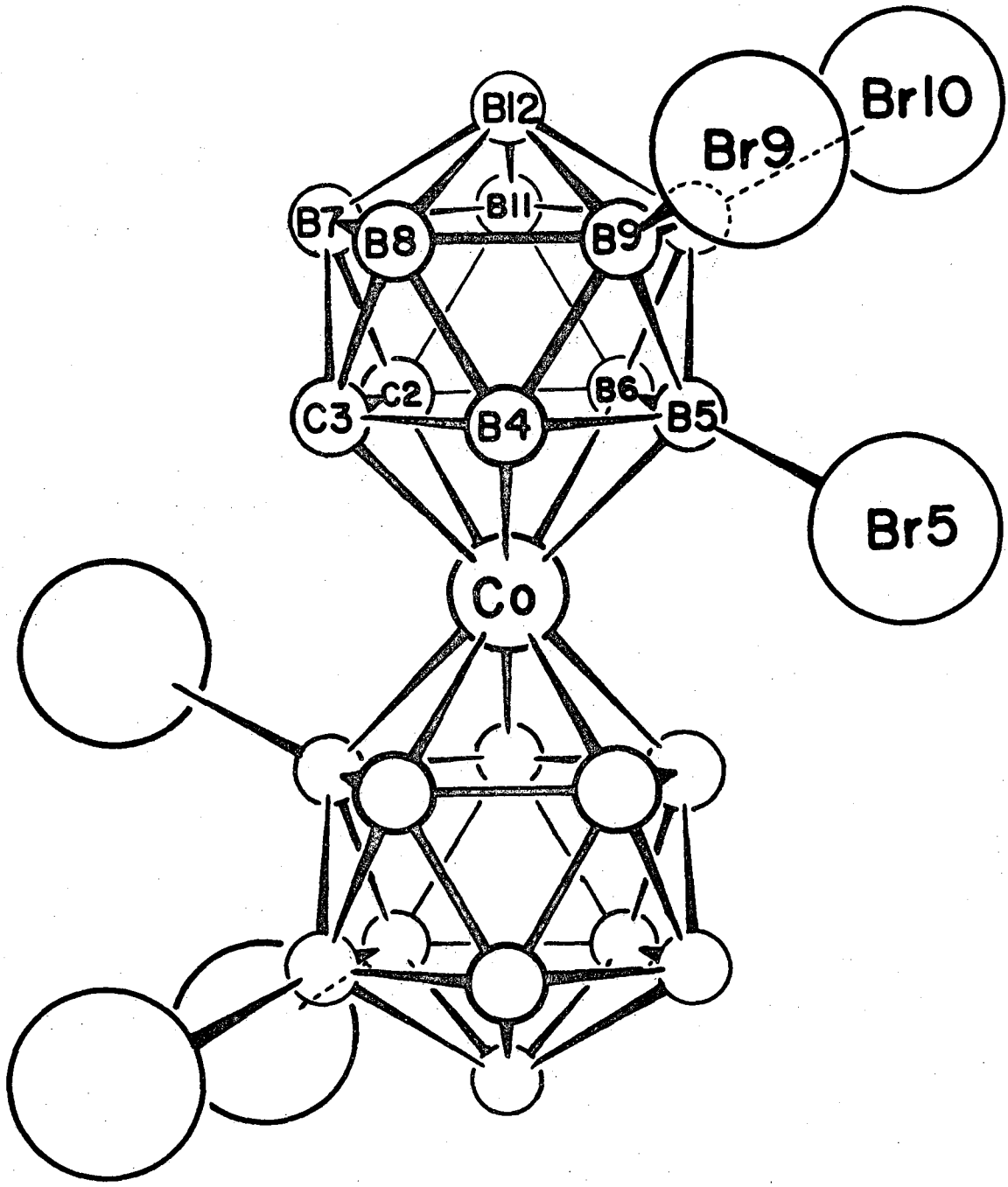

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Figure 1. - $(B_9C_2H_8Br_3)_2Co^-$ (hydrogens omitted).

Table III. Distances[a] in $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$

ion no.:	1	2	3	4
atom	distances, Angstroms			
Co-C(2)	2.04(2)[b]	2.03(2)	1.98(2)	2.05(2)
Co-C(3)	1.99(2)	2.02(2)	2.00(2)	2.09(2)
	r.m.s. scatter[c] = .034			
Co-B(4)	2.09(3)	2.13(3)	2.14(3)	2.17(3)
Co-B(6)	2.05(2)	2.10(2)	2.12(3)	2.12(3)
	r.m.s. scatter = .037			
Co-B(5)	2.17(3)	2.17(2)	2.15(2)	2.16(3)
	r.m.s. scatter = .007			
Co-Br(5)	3.527(3)	3.530(3)	3.511(3)	3.527(3)
	r.m.s. scatter = .009			
Br(5)-Br(9)	3.716(5)	3.775(4)	3.709(4)	3.725(4)
Br(5)-Br(10)	3.689(4)	3.730(4)	3.756(4)	3.719(4)
	r.m.s. scatter = .027			
Br(9)-Br(10)	3.921(5)	3.869(5)	3.816(5)	3.876(4)
	r.m.s. scatter = .043			
B(5)-Br(5)	1.95(3)	2.00(2)	1.96(2)	1.94(3)
B(9)-Br(9)	1.96(3)	1.95(3)	1.98(3)	1.97(3)
B(10)-Br(10)	1.96(3)	1.98(3)	1.96(3)	1.96(2)
	r.m.s. scatter = .017			

Table III, continued

C(2)-C(3)	1.68(3)	1.65(3)	1.63(3)	1.66(3)
	r.m.s. scatter = .023			
C(2)-B(6)	1.63(3)	1.75(3)	1.77(4)	1.78(3)
C(3)-B(4)	1.64(3)	1.68(3)	1.72(3)	1.84(3)
C(2)-B(11)	1.63(4)	1.75(4)	1.84(4)	1.72(3)
C(3)-B(8)	1.75(3)	1.69(4)	1.68(4)	1.64(3)
C(2)-B(7)	1.71(4)	1.71(4)	1.86(4)	1.71(4)
C(3)-B(7)	1.76(4)	1.73(4)	1.73(4)	1.69(4)
	r.m.s. scatter = .064			
B(4)-B(5)	1.91(4)	1.82(4)	1.88(3)	1.81(4)
B(4)-B(8)	1.79(4)	1.73(4)	1.76(4)	1.82(4)
B(4)-B(9)	1.84(4)	1.79(4)	1.88(3)	1.77(4)
B(5)-B(6)	1.69(3)	1.78(3)	1.80(4)	1.81(4)
B(5)-B(9)	1.81(4)	1.70(4)	1.82(3)	1.77(4)
B(5)-B(10)	1.74(4)	1.74(4)	1.77(3)	1.81(4)
B(6)-B(10)	1.74(4)	1.75(4)	1.81(4)	1.79(3)
B(6)-B(11)	1.74(4)	1.84(4)	1.90(4)	1.88(4)
B(7)-B(8)	1.88(4)	1.83(4)	1.63(5)	1.81(4)
B(7)-B(11)	1.79(5)	1.73(4)	1.82(5)	1.77(4)
B(7)-B(12)	1.91(5)	1.84(5)	1.74(4)	1.83(4)
B(8)-B(9)	1.75(4)	1.79(4)	1.74(4)	1.83(4)
B(8)-B(12)	1.89(4)	1.82(5)	1.67(4)	1.84(4)
B(9)-B(10)	1.76(4)	1.76(4)	1.71(4)	1.75(4)
B(9)-B(12)	1.75(5)	1.77(4)	1.62(4)	1.79(4)

Table III, continued

B(10)-B(11)	1.86(4)	1.76(4)	1.79(4)	1.76(4)
B(10)-B(12)	1.71(4)	1.74(4)	1.74(4)	1.78(4)
B(11)-B(12)	1.82(5)	1.79(4)	1.76(4)	1.79(4)
	r.m.s. scatter = .060			
N-Me(1)	1.49(5)	1.52(6)		
N-Me(2)	1.46(4)	1.43(7)		
N-Me(3)	1.49(3)	1.44(5)		
N-Me(4)	1.57(4)	1.53(5)		
	r.m.s. scatter = .048			

(a) None of these distances is corrected for thermal motion.

(b) The numbers in parentheses are the standard deviations in the least significant digit as calculated from the standard deviations of coordinates (Table I).

(c) Each of the "r.m.s. scatter" values given is the root-mean-square deviation from the average, $[\Sigma\Delta^2/(\underline{n}-1)]^{\frac{1}{2}}$, for the preceeding set of distances. These are given for comparison with the standard deviations calculated from the standard deviations of coordinates.

Table IV. Average Distances[a] in $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$

number averaged	atoms	distance, A
4	C-C	1.654 ± .017[b]
24	C-B	1.725 ± .013
72	B-B	1.786 ± .007
12	B-Br	1.963 ± .008
8	Co-C(2,3)	2.024 ± .013
8	Co-B(4,6)	2.115 ± .014
4	Co-B(5)	2.162 ± .014
4	Co-Br(5)	3.524 ± .005
8	Br(5)-Br(9,10)	3.727 ± .010
4	Br(9)-Br(10)	3.870 ± .025
8	N-Me	1.491 ± .018

(a) None of these distances is corrected for thermal motion.

(b) The error figures are the author's best estimate of the precision of these averages. They have been pessimistically chosen as the greater of $[(\Sigma\Delta^2)^{\frac{1}{2}}/(\underline{n}-1)]$ or $[(\Sigma\sigma^2)^{\frac{1}{2}}/\underline{n}]$, where Δ is the deviation from the average, σ is the standard deviation of a single distance as calculated

Table IV, continued

from the standard deviations of coordinates, and n is the number of distances averaged. The latter expression was the larger for the C-C, B-Br, and Co-B(5) distances.

eight B-C-C angles average 57° and $61\frac{1}{2}^{\circ}$. All four of these sets of angles show $2\frac{1}{2}^{\circ}$ root-mean-square deviations from the averages. The root-mean-square deviations are believed to be better measurements of the accuracy of these angles than the ~ 1.6° values derived from the standard deviations of coordinates. The temperature factors in the dicarbollyl portion of the anions seem to indicate some rigid-body motion, but a rigid-body analysis was not done because of the absorption errors known to be in the data and because of the excessive effort it would require.

The packing of the approximately dumbbell-shaped anions and the tetramethylammonium ions is very similar to that of KHF_2[20] as indicated in Figure 2. The higher symmetry (tetragonal, I4/mcm) of the KHF_2 structure[20] is broken down to its $P2_1/c$ subgroup (on the doubled cell) by the anion's lack of cylindrical symmetry and the up and down (in z) distribution of the bromine substituents. If we consider only the arrangement of plus and minus charges, this is approximately a CsCl-type structure.

The pentagonal rings adjacent to cobalt are all planar to within the accuracy of this determination, but are tilted or slid over in such a way as to decrease the cobalt-carbon distance and increase the cobalt-boron distances (Table IV). The tilt and slide descriptions are equivalent and amount to ~ 3° and ~ .07 A, respectively. This is interpreted as the effect of the Br(5) of each dicarbollyl being crowded up against the hydrogens on the carbons of the other. This interpretation is supported by the short Br(5)-Br(9) and Br(5)-Br(10) distances (Table IV). If we assume that each hydrogen is 1.10 A from its carbon and in line with the carbon and the opposite icosahedral vertex, the bromine-hydrogen distance

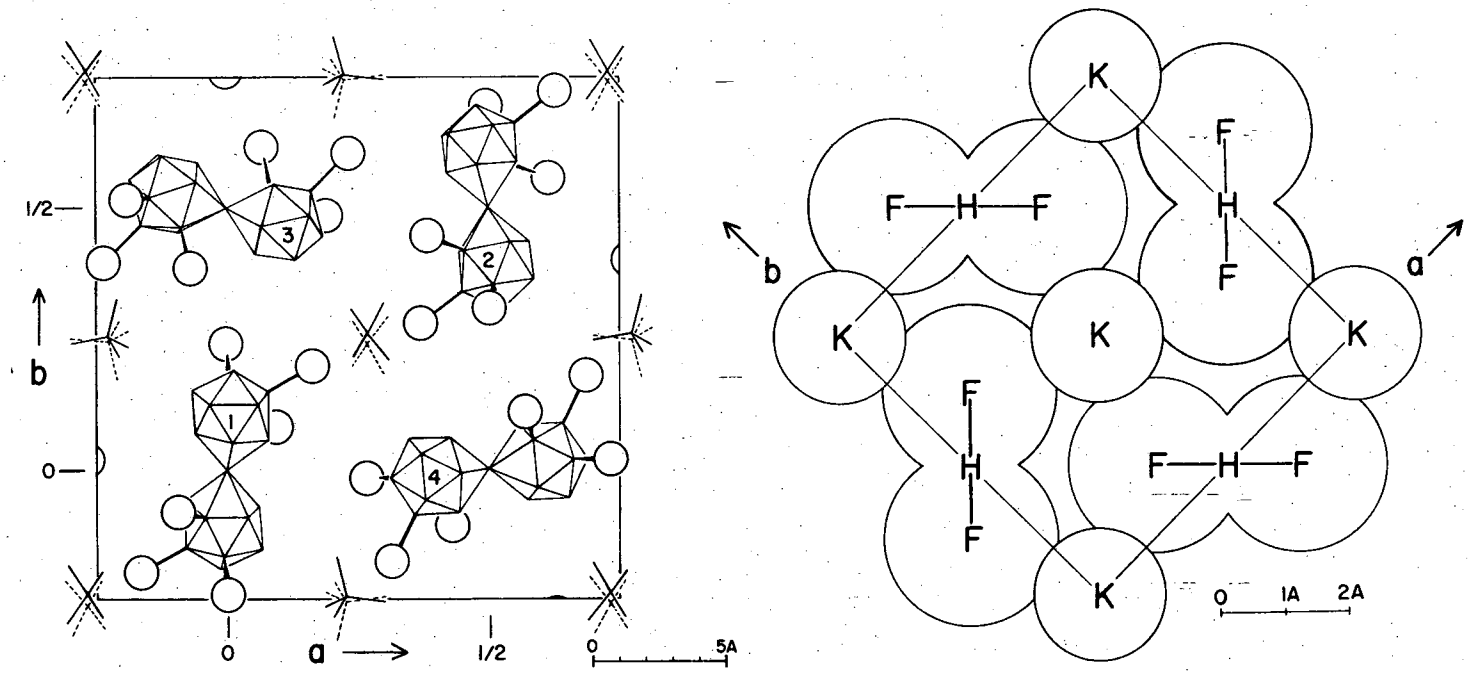

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Figure 2. - The crystal structure of $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$ compared with that of KHF_2. In both drwaings, the cations are at $\underline{z} = \pm \frac{1}{4}$ and the anions at $\underline{z} = 0$. The anions at $\underline{z} = \frac{1}{2}$ (not shown) are related to those shown by the $\underline{c}$ glide which runs horizontally across the center of each drawing.

is only 2.75 A, which is 0.40 A less than the sum of their van der Waals radii (1.95 ± 1.2 = 3.15 A).[21] A similar steric effect of about the same size, but in the opposite direction (carbons farther from metal than the borons) was found[22] in $B_9C_2H_9(CH_3)_2PdC_4(C_6H_5)_4$ in which the methyl groups are on the dicarbollyl carbons. These steric effects are not to be confused with the larger shift (about 0.6 A) observed by Wing[23] in the $Cu(B_9C_2H_{11})_2^{2-}$ anion where bonding effects are believed to be involved.

The electrophilic bromination sites found for this anion may be rationalized if we say that the charge distribution in the dicarbollyl portion is similar to that in 1,2 -dicarbaclovoduodecaborane ($B_{10}C_2H_{12}$), but modified by a polarization induced by the Co(III). Substitution sites[17-19] and dipole moments[24] found for $B_{10}C_2H_{12}$ derivatives and molecular orbital calculations[17,18] for the parent compound all lead to the conclusion that the borons farthest from carbon are the most susceptible to electrophilic attack and this susceptibility decreases as the carbons are approached. This analogy, considered alone, would indicate that our B(9) and B(10) are the most subject to electrophilic attack and B(5) and B(12) are second. Polarization by the cobalt would then determine the choice between B(5) and B(12), possibly causing B(5) to become more subject to electrophilic attack than the B(9)-B(10) pair.

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(8) A description of this work has been submitted to Inorganic Chemistry for publication.

(9) It may be argued that F^2 should be the quantity averaged, but the "error" incurred is only 5.4% even if $F_1 = 2F_2$ ($I_1 = 4I_2$).

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(12) "International Tables for X-ray Crystallography", vol. III, The Kynoch Press, Birmingham, England, 1962, pp. 204 - 207, 214.

(13) Late in the refinement, one cycle of full-matrix least-squares was run on all 361 parameters (12 fixed) and 3002 data to be sure that no errors were caused by the block-diagonal procedure. This one cycle required 74K storage and 43 minutes on a CDC 6600. These figures may be compared with the requirements for the final diagonal-matrix refinements of 28K storage and $2\frac{1}{4}$ minutes/cycle.

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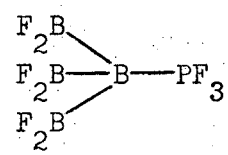
IV. The Crystal and Molecular Structure of Tris-difluorobora-borane — Phosphorus Trifluoride, $B_4F_6PF_3$

A. Introduction

Timms has recently reported[1*] the synthesis of a number of novel boron fluoride compounds by reactions of the high temperature species, boron monofluoride, on cold surfaces. Cocondensation of BF and PF_3 produces $B_4F_6PF_3$, a pyrophoric and water-sensitive substance which readily sublimes (m. p. 55°, b. p. 74°) to form well-developed, colorless crystals which are stable at room temperature. The present X-ray diffraction investigation[2] was undertaken to verify the proposed structure:



and to determine the bond distances and angles in this molecule.

B. Experimental

Samples of the compound, sealed into thin-walled glass capillaries, were provided by Professor Timms. Crystals formed quite readily as the compound was sublimed back and forth in the capillaries under the very mild heating provided by a beam from a low voltage lamp. Persistence seemed to be the only way to obtain a suitable crystal which did not have others nearby. Complete data sets were taken on two different crystals.

The first crystal was a plate about .16 x .51 x 2.2 mm, where the intermediate dimension is the inside diameter of its capillary. A crystal

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* References and Footnotes for part IV are to be found on page 69.

this large was accepted because there was no assurance of ever obtaining a better one, and because of the low absorption coefficient, μ, of 4.3 cm^{-1} (μ^{-1} = 2.3 mm) for MoKα radiation. The crystal was mounted with its long dimension, b axis, and capillary parallel to the instrument φ axis. Preliminary oscillation and Weissenberg photographs gave the extinction rules, Laue symmetry, and rough cell dimensions. More accurate cell dimensions were derived from the Bragg angles of the h00, 0k0, and 00ℓ reflections measured with a General Electric manual goniostat using molybdenum radiation and a Zr filter at the receiving slit. The components of the alpha doublet were resolved (λ(MoKα_1) = 0.70926 A) at the highest angles, but the peaks were broad and the positions of reflections at low chi angles could not be accounted for except by assuming a 2θ correction as a function of phi. It is suspected that these difficulties were caused by the large size of the crystal, which was certainly longer and probably wider than the beam diameter, and by strains in the crystal (see below). In spite of these troubles, a one-octant data set of 830 independent intensities, exclusive of space-group absences, was taken, using the same apparatus, by counting each reflection for 10 seconds with crystal and counter stationary and an approximately 3.5° take-off angle to the X-ray tube anode. Of these, 173 were recorded as zero. Measurements were also taken at all the locations in the region of the data set which correspond to space group absences. They were found to confirm the extinction rules of 0kℓ, $k + \ell \neq 2n$ and hk0, $h \neq 2n$. Individual backgrounds were measured for those reflections which were seriously affected by streaking from other orders; otherwise, backgrounds were taken from a plot of back-

ground as a function of 2θ at various values of phi and chi. Three standard reflections which were measured at frequent intervals during the course of data taking showed only small, random fluctuations. Measurements included reflections up to $2\theta = 50^{\circ}$ ($\sin\theta/\lambda = 0.595$). Standard deviations were assigned to the measurements of 5% of the intensity or a fixed minimum (8, 5, or 3 counts per second, for low, intermediate, and high 2θ), whichever was greater. The structure was initially solved using this data set, which was then definitely seen to be of unacceptable quality. A second set of samples was provided by Professor Timms, and a better crystal sought.

The second crystal had the shape of a cylinder ~.14 mm long and ~.15 mm in diameter (the inside diameter of its capillary). Nickel-filtered copper radiation was used in order to obtain as large a data set as possible from this smaller crystal. This crystal's smaller size made the larger absorption coefficient, μ, of 39 cm^{-1} (μ^{-1} = 0.26 mm) for CuKα radiation acceptable. The maximum variation in transmission factors is estimated to be less than 20%. The crystal was mounted with its cylinder axis, a axis, and capillary parallel to the instrument φ axis. The cell dimensions were determined as before, and found to correctly predict the positions of off-axis reflections, in contrast to the trouble experienced with the first crystal. When a narrow receiving slit was being used to obtain accurate cell dimensions, the peaks were sharp and well-formed and the alpha doublet ($\lambda(CuK\alpha_1)$ = 1.5405 A) was resolved in a majority of cases. After the slit was removed, the peaks at low chi angles showed a characteristic broad shape with an irregular top in both 2θ and omega scans. At high chi angles, a narrower, regular, peak shape

was maintained. This is again ascribed to distortions in the crystal, since the troubles with the two crystals (this and the previous one) seem to be correlated with the direction of the capillary axis and not with the directions of the crystallographic axes. The strains might have been the result of growth on a curved surface or of slight flexings of the thin-walled capillaries as they were handled. However, it was found that the calculated settings reproducibly gave the same part of the irregular peaks (and the tops of the regular ones) and that point counts taken at the calculated settings on a few peaks at chi = 0° and chi = 90° were in the same ratio as the integrated counts obtained by scanning through those peaks (in 2θ). A second data set of 703 intensities, including 100 recorded as zero, but not including space group absences, was taken in the same way as before. Backgrounds were likewise obtained as before, and again, frequently measured standard reflections showed no systematic variations. The maximum value of 2θ was 120° ($\sin\theta/\lambda = 0.562$). A standard deviation of 2.25 counts per second or 7.5% of the intensity, whichever was greater, was assigned to each measurement. Both data sets were corrected for Lorentz and polarization effects, but no corrections were made for absorption or extinction.

All computations were performed on a CDC 6600. Zalkin's unpublished FORDAP and DISTAN programs were used for Fourier syntheses and distance-and-angle calculations, while an unpublished Wilson-plot program by Maddox and Maddox gave normalized structure factor magnitudes[3] which were used in Long's sign-determining program[4] as described below. The unpublished version of the Ganzel-Sparks-Trueblood least-squares program which was used,

minimizes the function $\Sigma w(|kF_o| - |F_c|)^2/\Sigma w|kF_o|^2$, where F_o and F_c are the observed and calculated structure factors, k is the scale factor, and w is the weighting factor. For the early refinements, scattering factors for neutral phosphorus, fluorine, and boron were taken from standard tables.[5] The phosphorus scattering factors were corrected for the real part of anomalous dispersion by +0.1 electrons for the molybdenum data and +0.2 electrons for the copper data, and the imaginary part was neglected. The final refinements were performed using the scattering factors listed by Cromer and Waber[6] and both real and imaginary anomalous dispersion corrections given by Cromer.[7,8] The anisotropic temperature factors used have the form: $\exp(-0.25\ \Sigma_i \Sigma_j h_i h_j b_i b_j B_{ij})$, $i,j = 1,2,3$, where b_i is the ith reciprocal cell length.

C. Results

Four formula units of $(BF_2)_3BPF_3$ are contained in the orthorhombic unit cell, space group Pnma, with a = 13.893 ± .005 A, b = 10.578 ± .005 A, and c = 6.075 ± .005 A. The calculated density is 1.82 g/cc. No direct measurement of the density was attempted because of the highly reactive nature of the compound. The Laue symmetry and observed extinction rules correspond to space groups Pnma and $Pn2_1a$. Choosing the former space group leads to a successful solution with six atoms on the mirror plane in the fourfold special position set c: $\pm(x, \frac{1}{4}, z; \frac{1}{2} + x, \frac{1}{4}, \frac{1}{2} - z)$ and four more atoms in the general set of positions: $\pm(x, y, z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z; x, \frac{1}{2} - y, z; \frac{1}{2} + x, y, \frac{1}{2} - z)$.

1. Determination of Structure

The Patterson function calculated from the first (Mo) data set was discouragingly featureless, consisting primarily of two positive regions at $y = 0$ and $\frac{1}{2}$, with a negative region between (i.e. it was dominated by very strong $0,k,0$ reflections). Several attempts at refining various trial structures guessed at from this Patterson function met with no success whatever. The author reasoned that the strong $0,k,0$ reflections would arise only if some large fraction of the atoms were concentrated at or near the same y coordinate, as would be the case if the molecule were bisected by the mirror plane in Pnma. With this in mind, the Wilson-plot program was used to calculate normalized structure factor magnitudes,[3] E_h, for use in the statistical method of sign determination (centrosymmetric case). Long's program[4] which iteratively applies the relation: $sE_h \sim s\Sigma_k E_k E_{h-k}$, where s is to be read "the sign of" was employed for this purpose. After enough signs were worked out by hand to yield a good starting set (of E's) for input, a run of Long's program using 99 E's $\geqq 1.5$ gave one set of signs which was more consistent than any other and which was arrived at in the fewest passes. A Fourier synthesis using the signed E's as coefficients gave ten largest peaks, six of them in the mirror plane, which formed the expected molecule. Least-squares refinement of isotropic phosphorus, fluorine, and boron atoms in the appropriate positions quickly reduced the R factor to 0.29, where $R = \Sigma||kF_o| - |F_c||/\Sigma|kF_o|$. It was immediately evident that the $0k0$ reflections had given intensities which were systematically too large by factors between 3.6 and 5.2. A refinement in which the $0k0$ reflections were

given zero weight did not reduce $\underline{R}$, but when they were omitted from the calculation of $\underline{R}$, its value became 0.26. When all atoms were allowed anisotropic temperature factors, $\underline{R}$ fell to 0.180 on all data and 0.145 if the $0\underline{k}0$'s were omitted. These values could not be improved upon and a re-run of Long's program with the $0\underline{k}0$ reflections omitted gave the same structure a second time.

At this time the first (Mo) data set was discarded and the second crystal and second (Cu) data set were obtained as described above. The structure found from the first data set refined to $\underline{R}$ = 0.217 with isotropic temperature factors. When all atoms were allowed anisotropic temperature factors, the structure gave the final $\underline{R}$ value of 0.093 on all 703 data and this can be reduced to 0.067 by omitting the contributions from the 100 reflections which were recorded as having zero intensity. In the last cycle of the refinement, no parameter shifted by as much as 1% of the standard deviation calculated for it from the least-squares matrix. The standard deviation of an observation of unit weight, defined as $[\Sigma \underline{w}(|\underline{kF_o}| - |\underline{F_c}|)^2/(\underline{u} - \underline{v})]^{\frac{1}{2}}$, where $\underline{u}$ is the number of data and $\underline{v}$ is the number of independent parameters refined, was 1.33. Tests of slightly non-centric structures in the other space group ($Pn2_1a$) gave neither better agreement nor significant deviations from the higher symmetry. The magnitudes of the three largest peaks on a final difference Fourier were .50, .38, and .30 electrons/A^3. The final positional and thermal parameters are presented in Table I, while Table II lists $|\underline{F_o}|$ and $\underline{F_c}$.

Table I. Final Positional and Thermal Parameters in $B_4F_6PF_3$

atom	x	y	z	B_{11} [a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$[\overline{U^2}]^{\frac{1}{2}}$
P	.0998(1) [b]	$\frac{1}{4}$ [c]	.5699(4)	5.8(1)	6.0(1)	8.5(1)	0 [c]	0.0(1)	0	(.33,.27,.27) [d]
F1(P)	.0497(3)	$\frac{1}{4}$	.7931(10)	8.6(3)	15.8(5)	11.8(4)	0	4.8(3)	0	(.45,.44,.25)
F2(P)	.0524(2)	.1403(3)	.4588(7)	7.8(2)	9.2(2)	17.9(4)	-2.4(1)	-2.7(2)	-2.5(2)	(.49,.37,.25)
B(1)	.2311(5)	$\frac{1}{4}$	.5805(10)	4.9(3)	3.2(3)	3.7(3)	0	0.4(3)	0	(.26,.22,.21)
B(2)	.2788(7)	$\frac{1}{4}$	.3255(14)	7.3(5)	4.0(3)	5.3(5)	0	1.0(4)	0	(.31,.25,.23)
F1(2)	.2264(4)	$\frac{1}{4}$	.1424(7)	15.0(4)	8.9(3)	3.6(2)	0	-1.3(2)	0	(.44,.33,.20)
F2(2)	.3694(3)	$\frac{1}{4}$	.2902(8)	8.9(3)	9.7(3)	8.6(3)	0	4.2(2)	0	(.40,.35,.24)
B(3)	.2697(4)	.3788(5)	.7122(8)	7.8(3)	4.2(2)	4.4(2)	0.0(3)	-0.2(2)	0.3(2)	(.32,.24,.23)
F1(3)	.2131(2)	.4693(3)	.7870(5)	12.3(2)	4.9(1)	7.6(2)	1.4(1)	0.5(1)	-1.9(1)	(.40,.33,.21)
F2(3)	.3598(2)	.4004(3)	.7500(6)	9.3(2)	7.0(2)	11.3(2)	-1.8(2)	-3.1(2)	-1.7(2)	(.41,.34,.24)

(a) The units are A^2.

(b) The number in parentheses is the standard deviation in the least significant digit as derived from the least-squares matrix.

(c) Values expressed without the use of a decimal point are fixed by symmetry.

(d) These are the principal root-mean-square amplitudes of vibration, in order of magnitude. For orientations, see Figures 1 and 2.

Table II. Observed and Calculated Structure Factors (x 9.0) for $B_4F_6PF_3$

K	FOB	FCA
H,L=	0,	0
2	762	-952
4	484	484
6	545	-552
8	450	460
10	148	-147
H,L=	0,	1
1	383	411
3	764	858
5	190	177
7	0	-11
9	60	70
11	90	92
H,L=	0,	2
0	777	-866
2	351	-330
4	115	-118
6	89	93
8	0	-32
10	54	-64
H,L=	0,	3
1	78	-83
3	543	-528
5	152	156
7	98	-98
9	0	21
H,L=	0,	4
0	160	164
2	230	213
4	147	-129
6	46	51
8	24	20
H,L=	0,	5
1	164	183
3	78	-85
5	97	104
7	63	-80
H,L=	0,	6
0	30	-34
2	0	-4
4	16	-8
H,L=	1,	1
0	626	-639
1	405	390
2	305	286
3	194	-173
4	110	127
5	12	11
6	31	18
7	172	-171
8	129	-128
9	76	70
10	65	60
11	46	-49
H,L=	1,	2
0	121	-114
1	115	-105
2	379	370
3	292	277
4	99	-106
5	184	-182
6	151	153
7	107	123
8	99	-99
9	25	-44
10	17	9
11	15	25
H,L=	1,	3
0	367	-369
1	112	105
2	153	151
3	13	-9
4	76	-73
5	146	140
6	81	74
7	64	72
8	55	-42
9	34	30
10	23	26
H,L=	1,	4
0	194	-191
1	56	-65
2	43	52
3	54	51
4	217	-223
5	106	-95
6	80	71
7	30	29
8	17	-25
9	16	-19
H,L=	1,	5
0	93	96
1	0	19
2	64	-53
3	25	3
4	78	56
5	67	-65
6	38	-35
7	40	-48
8	0	14
H,L=	1,	6
0	42	37
1	0	-5
2	0	-11
3	0	22
4	62	73
5	0	-6
H,L=	2,	0
0	662	-653
1	356	-339
2	408	-406
3	475	489
4	430	-419
5	190	-194
6	161	137
7	103	-98
8	93	-87
9	186	-180
10	25	20
11	46	48
H,L=	2,	1
0	128	133
1	136	137
2	403	-416
3	779	-778
4	748	757
5	107	104
6	24	-15
7	175	-173
8	23	34
9	67	-59
10	83	-98
11	79	-79
H,L=	2,	2
0	747	751
1	564	-589
2	272	264
3	44	-50
4	66	-65
5	27	-16
6	33	44
7	302	283
8	104	103
9	30	-20
10	0	-14
11	26	26
H,L=	2,	3
0	151	136
1	37	27
2	74	-76
3	168	150
4	66	-64
5	86	77
6	169	-172
7	30	14
8	52	61
9	24	33
10	0	-2
H,L=	2,	4
0	21	10
1	122	120
2	183	-191
3	0	-1
4	52	57
5	24	19
6	70	-67
7	60	-70
8	0	-1
9	0	-11
H,L=	2,	5
0	0	39
1	114	-90
2	55	-65
3	39	30
4	84	98
5	35	-36
6	17	-14
7	28	31
H,L=	2,	6
0	0	-8
1	17	15
2	29	27
3	44	-34
4	16	-11
5	30	18
H,L=	3,	1
0	290	-275
1	585	579
2	42	-43
3	71	-74
4	143	136
5	103	98
6	74	-76
7	90	-85
8	0	17
9	97	86
10	0	10
11	16	-20
H,L=	3,	2
0	176	164
1	298	301
2	269	-243
3	283	-284
4	112	-113
5	40	47
6	43	41
7	105	-109
8	49	30
9	35	36
10	24	19
11	26	-30
H,L=	3,	3
0	156	163
1	26	35
2	19	-24
3	14	9
4	156	152
5	128	-134
6	76	-74
7	99	-85
8	0	5
9	0	13
10	31	-30
H,L=	3,	4
0	82	-77
1	15	-6
2	196	198
3	79	80
4	23	-34
5	17	19
6	65	62
7	30	33
8	50	-49
9	22	19
H,L=	3,	5
0	90	-90
1	67	-52
2	0	1
3	49	32
4	39	-34
5	0	34
6	17	22
7	50	48
H,L=	3,	6
0	0	-23
1	0	1
2	0	9
3	16	-26
4	54	-64
5	0	-5
H,L=	4,	0
0	30	20
1	783	-799
2	178	188
3	79	81
4	117	100
5	199	191
6	264	281
7	289	287
8	0	5
9	30	-17
10	17	-30
11	41	41
H,L=	4,	1
0	76	79
1	74	-75
2	373	-372
3	91	-74
4	87	-80
5	30	26
6	192	-199
7	145	147
8	30	38
9	80	71
10	34	41
11	41	45
H,L=	4,	2
0	19	-10
1	25	-33
2	37	-25
3	96	-95
4	258	-249
5	0	-13
6	47	-54
7	94	-99
8	65	-57
9	74	-82
10	23	29
H,L=	4,	3
0	0	22
1	187	-200
2	28	22
3	220	234
4	229	228
5	120	-120
6	0	-7
7	0	4
8	17	19
9	71	-70
10	15	-20
H,L=	4,	4
0	52	-65
1	86	-87
2	77	81
3	0	10
4	0	-18
5	17	5
6	82	80
7	55	57
8	0	2
9	15	16
H,L=	4,	5
0	30	-22
1	30	32
2	0	-2
3	55	-46
4	25	-26
5	0	18
6	23	-26
7	0	-8
H,L=	4,	6
0	33	28
1	17	20
2	33	-19
3	16	-6
4	15	7
H,L=	5,	1
0	324	332
1	233	210
2	170	-176
3	152	159
4	183	185
5	197	-193
6	141	-137
7	43	-48
8	96	90
9	39	48
10	55	-53
11	0	-13
H,L=	5,	2
0	17	14
1	58	62
2	101	94
3	23	-40
4	37	-35
5	110	103
6	76	84
7	17	18
8	30	-50
9	34	42
10	0	-3
H,L=	5,	3
0	85	-80
1	134	137
2	63	-64
3	67	-64
4	0	-16
5	79	77
6	38	-30
7	0	20
8	0	-2
9	16	12
H,L=	5,	4
0	16	10
1	71	66
2	0	-8
3	117	-126
4	118	-109
5	35	42
6	25	24
7	61	-65
8	16	11
H,L=	5,	5
0	17	16
1	17	-4
2	65	56
3	46	42
4	17	-12
5	51	-48
6	16	18
7	21	-21
H,L=	5,	6
0	16	4
1	28	40
2	0	-8
3	15	-6
4	33	39
H,L=	6,	0
0	543	-517
1	592	-574
2	401	377
3	216	-216
4	222	-234
5	54	-56
6	99	98
7	44	-50
8	193	-197
9	30	-40
10	70	72
H,L=	6,	1
0	263	261
1	52	-49
2	325	335
3	164	166
4	14	12
5	33	-36
6	27	-6
7	17	18
8	30	-18
9	52	-61
10	16	14
H,L=	6,	2
0	191	-194
1	197	205
2	87	99
3	73	-68
4	39	-40
5	260	260
6	142	139
7	24	-8
8	25	-13
9	29	16
10	27	22
H,L=	6,	3
0	274	-278
1	78	-76
2	0	-22
3	62	81
4	40	-46
5	123	-129
6	25	6
7	46	53
8	30	-21
9	16	-9
H,L=	6,	4
0	98	102
1	55	-51
2	81	-79
3	38	-39
4	67	62
5	17	-18
6	52	-55
7	0	0
8	0	1
H,L=	6,	5
0	17	26
1	58	-66
2	25	18
3	69	71
4	0	10
5	37	-35
6	0	5
H,L=	6,	6
0	16	6
1	16	-1
2	22	-13
3	0	5
4	38	-38
H,L=	7,	1
0	104	97
1	148	-139
2	60	-56
3	224	218
4	64	-59
5	232	-231
6	16	-23
7	127	126
8	43	42
9	38	-40
10	16	-14
H,L=	7,	2
0	245	255
1	0	-7
2	147	-159
3	148	-161
4	56	60
5	97	97
6	93	-90
7	60	-64
8	62	56
9	0	-1
10	21	-33
H,L=	7,	3
0	213	214
1	101	94
2	35	-38
3	59	58
4	34	35
5	34	-31
6	46	-39
7	17	-27
8	55	50
9	15	2
H,L=	7,	4
0	80	72
1	68	71
2	114	-113
3	0	-5
4	111	116
5	46	41
6	29	-34
7	0	-9
8	36	34
H,L=	7,	5
0	83	-76
1	0	-19
2	0	3
3	34	-27
4	17	-8
5	0	11
6	15	8
H,L=	7,	6
0	15	18
1	30	-30
2	0	6
3	52	-49
4	85	86
5	184	176
6	104	-105
7	88	-85
8	90	90
9	299	310
10	146	-134
11	63	-70
H,L=	8,	0
0	181	-184
1	14	9
2	117	-119
3	181	183
4	84	-97
5	129	-128
6	38	45
7	55	-58
8	0	-8
9	0	1
10	15	23
H,L=	8,	2
0	145	-153
1	47	58
2	15	-12
3	198	-199
4	169	159
5	56	45
6	17	11
7	99	-95
8	45	-48
9	31	30
H,L=	8,	3
0	104	-107
1	75	72
2	225	231
3	113	-102
4	83	-91
5	63	61
6	70	69
7	17	10
8	59	-57
H,L=	8,	4
0	17	18
1	46	-37
2	25	3
3	39	38
4	43	-41
5	17	15
6	0	-2
7	15	19
H,L=	8,	5
0	38	-38
1	38	37
2	17	11
3	0	-2
4	16	-28
5	0	-1
H,L=	9,	1
0	65	66
1	26	-28
2	110	111
3	57	58
4	182	-182
5	54	-52
6	85	80
7	0	48
8	24	-17
9	16	-15
H,L=	9,	2
0	16	-3
1	209	-211
2	48	-57
3	220	220
4	38	44
5	93	-91
6	17	-4
7	17	68
8	23	13
9	41	-48
H,L=	9,	3
0	104	-111
1	29	-27
2	24	25
3	0	7
4	49	-48
5	49	-48
6	48	47
7	23	11
8	30	-28
H,L=	9,	4
0	39	27
1	49	-47
2	0	3
3	39	-40
4	0	8
5	16	-5
6	16	-12
H,L=	9,	5
0	86	76
1	28	29
2	23	-14
3	0	-1
4	15	11
H,L=	10,	0
0	27	-102
1	95	83
2	42	-36
3	68	66
4	196	203
5	65	-51
6	43	-44
7	77	-80
8	0	11
H,L=	10,	1
0	28	34
1	16	-4
2	36	-30
3	60	-65
4	128	129
5	25	29
6	17	1
7	0	36
8	0	2
9	117	-119
H,L=	10,	2
0	90	93
1	96	-90
2	99	-99
3	24	6
4	65	65
5	17	17
6	91	-92
7	58	54
8	31	22
H,L=	10,	3
0	30	29
1	111	104
2	0	3
3	25	-23
4	63	-72
5	17	15
6	16	-20
7	48	-47
H,L=	10,	4
0	69	-55
1	24	22
2	30	25
3	0	12
4	0	10
5	0	-1
H,L=	10,	5
0	0	9
1	31	28
2	15	-14
H,L=	11,	1
0	38	-35
1	68	63
2	59	50
3	86	-85
4	97	-96
5	46	52
6	0	63
7	0	-23
8	15	-14
H,L=	11,	2
0	62	-58
1	46	-40
2	39	31
3	0	-7
4	17	15
5	0	-3
6	0	11
7	0	-6
H,L=	11,	3
0	78	83
1	30	-29
2	17	-16
3	0	7
4	17	-3
5	16	-5
6	0	-12
H,L=	11,	4
0	29	-29
1	33	-22
2	16	18
3	36	44
4	26	-22
H,L=	12,	0
0	105	-104
1	72	-75
2	25	11
3	43	32
4	25	18
5	60	-56
6	23	-21
7	51	51
H,L=	12,	1
0	70	69
1	0	9
2	17	6
3	50	-47
4	52	-61
5	0	10
6	0	-21
7	0	-11
H,L=	12,	2
0	58	55
1	17	25
2	25	-26
3	76	71
4	42	50
5	33	-25
6	31	-30
H,L=	12,	3
0	30	28
1	42	38
2	59	-51
3	17	-14
4	51	49
5	0	10
H,L=	12,	4
0	22	-29
1	27	-33
2	0	8
3	0	-2
H,L=	13,	1
0	17	21
1	46	37
2	17	-12
3	71	-71
4	0	-5
5	56	56
6	15	16
H,L=	13,	2
0	73	-80
1	0	1
2	63	63
3	0	5
4	42	-40
5	15	-5
H,L=	13,	3
0	16	11
1	0	4
2	0	-6
3	22	-13
4	15	-7
H,L=	14,	0
0	24	-7
1	24	-16
2	55	55
3	57	64
4	42	-36
5	47	-51
H,L=	14,	1
0	0	2
1	29	-25
2	0	-12
3	43	47
4	22	11
5	14	-14
H,L=	14,	2
0	53	-55
1	23	-22
2	22	17
3	22	26
H,L=	14,	3
0	48	50
H,L=	15,	1
0	43	48
1	15	-10
2	47	-50

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2. Discussion

The $B_4F_6PF_3$ molecule is shown in Figure 1. The duplicate atom labels are caused by the crystallographic mirror plane which bisects the molecule and contains F1(P), P, B(1), B(2), F1(2) and F2(2). The atoms F2(P), P, B(1), and B(3) all lie in another plane to within the accuracy of this determination; F1(3) and F2(3) deviate from it by only a small ($\sim 3^{\circ}$) rotation of the BF_2 group about the B-B bond. This second plane makes an angle of $120^{\circ} \pm 1^{\circ}$ with the mirror plane so that the molecule has approximately 3m (C_{3v}) point symmetry, only one mirror of which is required by crystal symmetry. The fluorines on phosphorus are in a staggered configuration with respect to the BF_2 groups on B(1), and the angles at B(1) are tetrahedral to within the experimental accuracy.

Distances and angles found in this structure are presented and compared with those found for related compounds in Table III. These interatomic distances must be corrected for the effect of thermal motion in order to arrive at quantities which are comparable to the results of studies by other methods (e.g., spectroscopic and electron-diffraction methods). This is particularly true in view of the large thermal parameters found here. Large thermal parameters are consistent with the observations that this is a low-melting, readily sublimable crystal. The accuracy of thermal corrections is poor, however, because of the ambiguity as to the correct model on which to base their calculation. The minimum and "riding-model" corrections[9] in Table III are included to indicate the approximate magnitude of the calculated corrections.

The author can find no chemical or molecular-packing-forces

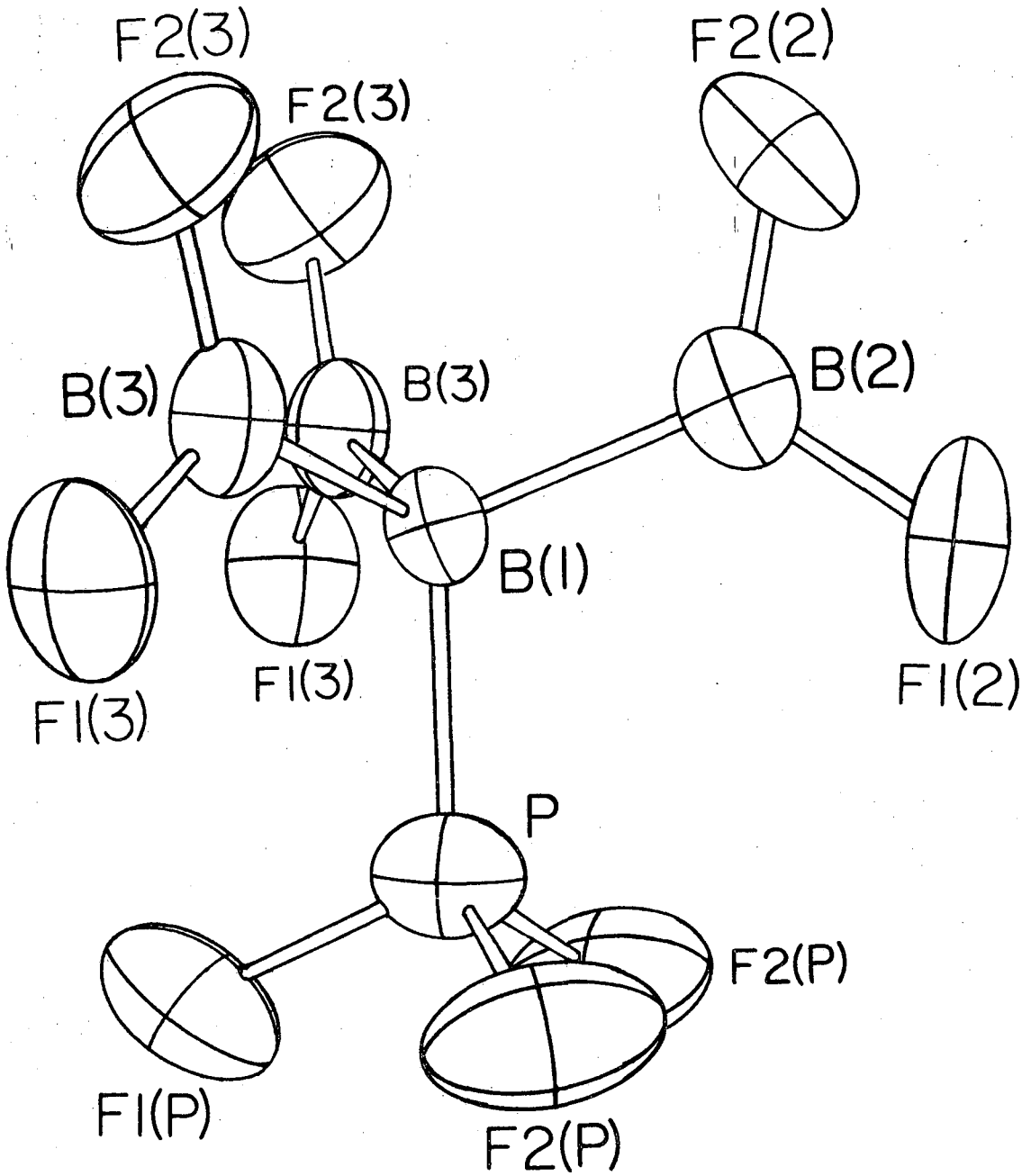

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Figure 1. - The $B_4F_6PF_3$ molecule. The molecule is bisected by a crystallographic mirror plane which contains F1(P), P, B(1), B(2), F1(2), and F2(2). The thermal elipsoids have been reduced to 30% probability contours for the sake of clarity.

Table III. Distances and Angles in $B_4F_6PF_3$ and Comparison Compounds

atoms	distance, A	comparison distance	comparison compound
B(2)-F1(2)	1.330(10)[a]		
B(2)-F2(2)	1.276(10)		
B(3)-F1(3)	1.319(6)		
B(3)-F2(3)	1.293(7)	1.30	BF_3[d]
average	1.305 ± .015[b]	1.32 ± .035	B_2F_4[e]
(thermal correction = .009, .051)[c]			
B(1)-B(2)	1.685(10)		
B(1)-B(3)	1.668(7)		
average	1.677 ± .015	1.67 ± .045	B_2F_4
(thermal correction = .001, .013)			
B(1)-P	1.825(7)		
	1.825 ± .015	1.836 ± .012	H_3BPF_3[f]
(thermal correction = .005, .026)			
P-F1(P)	1.525(6)		
P-F2(P)	1.496(4)	1.535 ± .02	PF_3[g]
average	1.511 ± .015	1.538 ± .008	H_3BPF_3
(thermal correction = .013, .066)			
	intra-molecular, non-bonded		
B(2)-B(3)	2.719(9)		

Table III, continued

B(3)-B(3)	2.725(11)		
F1(2)-F2(2)	2.180(7)		
F1(3)-F2(3)	2.176(4)	2.23 ± .024	B_2F_4
F1(P)-F2(P)	2.339(7)		
F2(P)-F2(P)	2.321(7)		
F2(2)-F2(3)	3.217(5)		
F2(3)-F2(3)	3.181(7)		
F1(2)-F2(P)	3.299(6)		
F1(3)-F1(P)	3.246(4)		
F1(3)-F2(P)	3.210(5)		
	inter-molecular F-F contacts		
F2(P)-F2(3)	3.088(5)	[3.09_5]	B_2F_4
F1(P)-F2(3)	3.092(5)	[3.11]	
F1(2)-F1(3)	3.174(4)	[3.12_5]	
F2(P)-F2(2)	3.178(6)	[3.22]	
F2(2)-F1(3)	3.183(3)	[3.27]	
F1(2)-F1(3)	3.209(4)	[3.28]	
F2(P)-F2(3)	3.236(5)	[3.28]	
F1(P)-F1(2)	3.244(7)	[3.30]	
F1(3)-F1(3)	3.271(2)	[3.34]	
F1(3)-F2(3)	3.292(5)	[3.37]	

Table III, continued

F2(P)-F2(P)	3.343(7)	[3.45]	
F1(2)-F2(3)	3.413(5)		
all others	> 3.5		
	bond angles		
F1(2)-B(2)-F2(2)	113.6(7)		
F1(3)-B(3)-F2(3)	112.8(5)		
average	$113.2^{\circ} \pm 1^{\circ}$	$[115^{\circ}]$	B_2F_4
B(1)-B(2)-F1(2)	123.6(7)		
B(1)-B(2)-F2(2)	122.8(7)		
B(1)-B(3)-F1(3)	124.5(5)		
B(1)-B(3)-F2(3)	122.7(5)		
average	$123.4^{\circ} \pm 1^{\circ}$	$[122.5^{\circ}]$	B_2F_4
B(2)-B(1)-B(3)	108.3(4)		
B(3)-B(1)-B(3)	109.5(5)		
B(2)-B(1)-P	111.1(5)		
B(3)-B(1)-P	109.8(3)		
average	$109.7^{\circ} \pm 1^{\circ}$	109.5°	(tetrahedral)
B(1)-P-F1(P)	115.2(3)		
B(1)-P-F2(P)	117.2(2)		
average	$116.2^{\circ} \pm 1^{\circ}$		

Table III, continued

F1(P)-P-F2(P)	101.5(2)		
F2(P)-P-F2(P)	101.8(3)	$100^{\circ} \pm 2^{\circ}$	PF_3
average	$101.7^{\circ} \pm 1^{\circ}$	$99.8^{\circ} \pm 1^{\circ}$	H_3BPF_3

(a) The number in parentheses is the standard deviation in the least significant digit as calculated from the standard deviations of coordinates.

(b) The standard deviations of .015 A and 1° listed for average values are based upon comparisons of distances expected to be the same and the author's past experience. They are believed to be better representations of the accuracy of these results than those calculated from the standard deviations of coordinates.

(c) The two corrections for thermal motion given are a minimum correction and a "riding-model" correction, respectively. Both are much less than the maximum possible correction. (see text and reference 9).

(d) "Tables of Interatomic Distances and Configuration in Molecules and Ions", Special Publication No.11, The Chemical Society, Burlington House, London, W.1, 1958, page M18.

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Table III, continued

(g) Q. Williams, J. Sheridan, and W. Gordy, ibid., 20 164 (1952). (microwave and electron diffraction study)

explanation for the apparent difference (~ .04 A) between the axially and equatorially directed B-F distances. Since this difference could have arisen from a small (~ .02 A $\leqq 2\sigma$) shift of the two borons, the author is not willing to assert that it is real in the absence of supporting evidence. The up-and-down orientations of the BF_2 groups was unexpected because the F-F distances between different groups would be greater if the BF_2 groups were in a propeller-like configuration. The observation that each fluorine has at least two inter-molecular F-F contacts shorter than any intra-molecular one (except between two fluorines bonded to the same atom) shows that the fluorine contacts within the molecule are not short enough to control the configuration. The BF_2 orientations are evidently governed by the meshing together of fluorines on adjacent molecules (see Figure 2). The existence of inter-molecular F-F contacts shorter than the intra-molecular ones also indicates that the B-P distance is not controlled by F-F interactions. This, and the fact that the B-P distance found here is not significantly different from that found for H_3BPF_3, indicates that BF_2 will not only formally replace hydrogen,[1] but is quite similar to hydrogen in its electronic effects on the rest of the molecule.

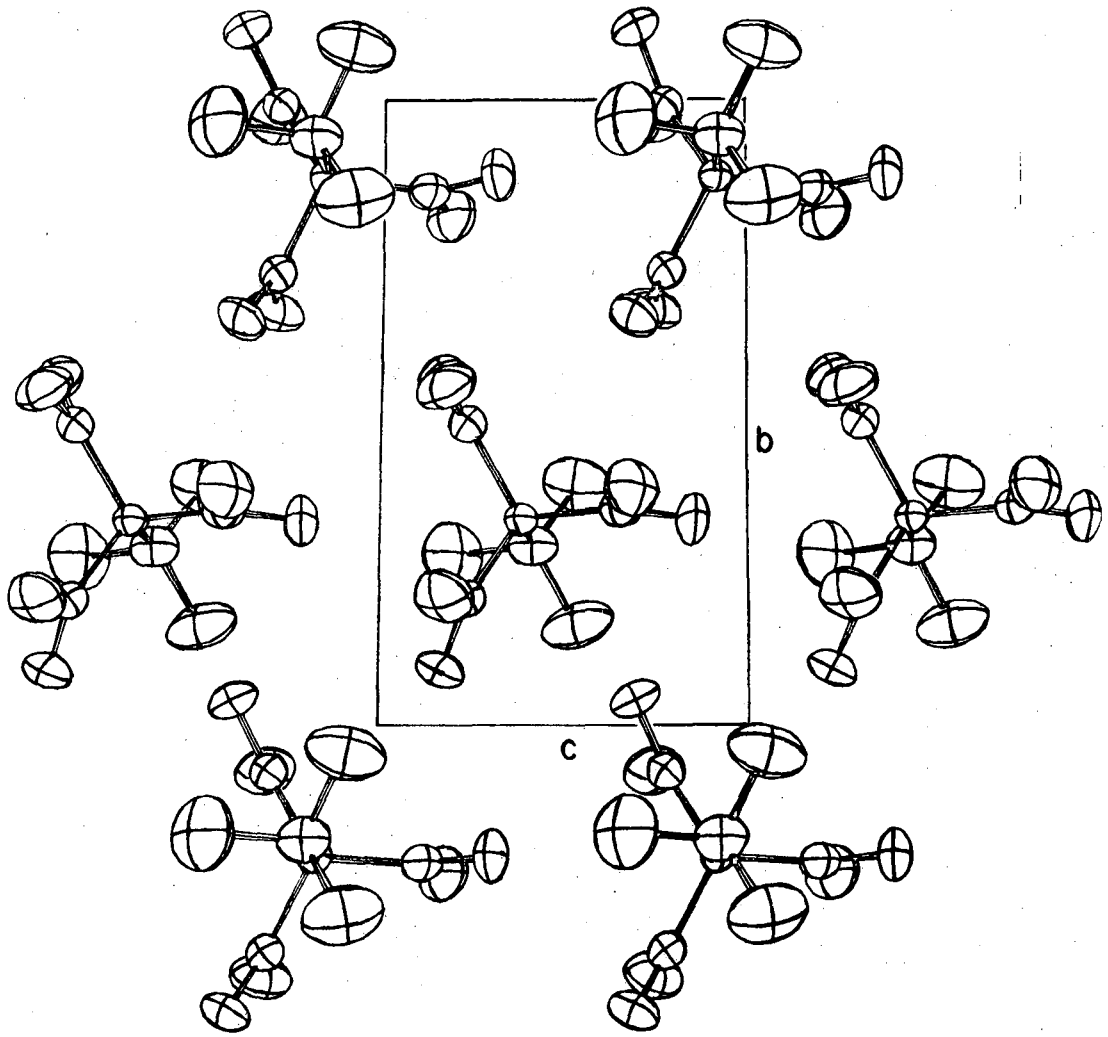

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Figure 2. - Molecular Packing in $B_4F_6PF_3$. This is one layer, approximately ½ a thick, seen in perspective. The other layers are related to the one shown by the a glide perpendicular to c.

References and Footnotes

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