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THE CRYSTAL STRUCTURE OF A BROMINATED CARBORANE–METAL SANDWICH COMPOUND—$N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$

Barry G. DeBoer, Allan Zalkin, and David H. Templeton

April 1968

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April 1968

Contribution from the Department of Chemistry and Lawrence Radiation Laboratory, University of California, Berkeley, California 94720

The Crystal Structure of a Brominated Carborane - Metal Sandwich Compound — $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$.[1]

by Barry G. DeBoer,[2] Allan Zalkin, and David H. Templeton

Received

Abstract

The crystal structure of the tetramethylammonium salt of bis-π-(5,9,10-tribromo-(1)-2,3-dicarbollyl)cobalt(III), $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$, has been determined by an X-ray diffraction study of a single crystal specimen. The monoclinic unit cell, space group $P2_1/c$, with $\underline{a}$ = 19.893 A, $\underline{b}$ = 19.487 A, $\underline{c}$ = 15.058 A, and $\beta = 93.15^{\circ}$ contains eight formula units and four crystallographically independent anions. The calculated density is 1.967 g/cc, in agreement with the measured 1.98 g/cc. The structure was solved by centrosymmetric statistical methods and refined by a least-squares procedure to a conventional $\underline{R}$ 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).

Introduction

Hawthorne and co-workers[3-8] have recently synthesized a number of π-dicarbollyl metal compounds analogous to the π-cyclopentadienyl "sandwich" compounds. They found[8,9] 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[9] to be the first example of a substitution upon the intact bis-dicarbollyl-metal "sandwich" compound.

This determination 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.

Experimental

Crystals of $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$ were sent to us by Professor 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} (μ^{-1} = .065 mm). We estimate that the absorption effect on intensities may vary by a factor of the order of 1.5 between the most extreme cases. Both crystals were glued to the ends of Pyrex glass fibers with the plate perpendicular to the fiber, the instrument ϕ axis, and the $\underline{b}$ axis. 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 2 θ (θ is the Bragg angle) values of the $\underline{h}00$, $0\underline{k}0$, and $00\underline{\ell}$ reflections. The alpha doublet was resolved ($\lambda(MoK_{\alpha 1})$ = 0.70926 A). The β angle was obtained directly from the angle on the ϕ circle between the $\underline{h}00$ and $00\underline{\ell}$ 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). 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 $(-h,k,-\ell)$ 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 $|\ell| \leq 6$) also had their equivalent $(-h,k,-\ell)$ reflections measured. These figures do not include the space group extinctions which were also measured and found to confirm the extinction rules ($0k0$, $k \neq 2n$ and $h0\ell$, $\ell \neq 2n$) obtained from preliminary Weissenberg photographs.

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

$$I = C - (t_C/2t_B)(B_1 + B_2) \quad \text{and:}$$

$$\sigma^2(I) = C + (t_C/2t_B)^2(B_1 + B_2) + (0.06 \times I)^2$$

where C is the number of counts accumulated in scanning through the reflection in time t_C, and B_1 and B_2 are the background counts, each obtained in time t_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: $(\Sigma_i \sigma_i^2/n^2)^{1/2}$ or $(\Sigma_i \Delta_i^2/n^2)^{1/2}$, where σ_i and Δ_i are the standard deviation and deviation from the average of the ith measurement and 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 $0.06 \times I$ included in $\sigma(I)$, but this was approximately corrected when the two data sets were combined as described below. A scaling function between the two data sets was sought, but found to differ from 1.00 by only small amounts (~ 5% in F).

The combined data set was generated by averaging (without scaling) those F_o values[10] which the two sets had in common and setting:

$$\sigma^2(F_{ave}) = 0.5[\sigma^2(F_1) - (0.03F_1)^2] + 0.5[\sigma^2(F_2) - (0.03F_2)^2] + (0.03F_{ave})^2,$$

where the terms in square brackets were set to zero if they were negative. If it gave a larger number, $\sigma^2(F_{ave}) = 0.5(F_1 - F_2)^2$ was used and 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 I). A plot of the resulting $\sigma(F_o)$ versus F_o revealed that the great majority of points fall on or near a smooth curve. We have found no simple description of this curve, but it starts near 10 electrons for small F_o, stays near 3 electrons for F_o = 40 to 100 electrons, and follows the 3% of F_o line thereafter. Forty-five percent of the data have $F_o \geq$ 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[11] which were used in Long's sign-determining program[12] as described below. Our unpublished version of the Ganzel-Sparks-Trueblood least-squares program 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.

Scattering factors[13] 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[13]. 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.

Results

The monoclinic unit cell, space group $P2_1/c$, $a = 19.893 \pm .010$ A, $b = 19.487 \pm .010$ A, $c = 15.058 \pm .010$ A, $\beta = 93.15 \pm .05^\circ$, 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 $\pm(x,y,z;\ x,1/2-y,1/2+z)$.

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[11], E_h, were calculated and used in Long's sign-determining program[12] 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 working out enough of the signs by hand to discover a good

set of "starting reflections" for input, a run of Long's program on 379 $\underline{E}$'s ≥ 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: $\Sigma_{\underline{h}}\Sigma_{\underline{k}}\underline{E}_{\underline{h}}\underline{E}_{\underline{k}}\underline{E}_{\underline{h}-\underline{k}} / \Sigma_{\underline{h}}\Sigma_{\underline{k}}\left|\underline{E}_{\underline{h}}\underline{E}_{\underline{k}}\underline{E}_{\underline{h}-\underline{k}}\right|$. A Fourier synthesis using the signed $\underline{E}$'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 $\underline{R} = 0.26$ where $\underline{R} = \Sigma \left|\left|\underline{kF}_{\underline{o}}\right| - \left|\underline{F}_{\underline{c}}\right|\right| / \Sigma\left|\underline{kF}_{\underline{o}}\right|$. A difference Fourier phased by these sixteen atoms showed all fifty-four of the non-hydrogen light atoms. The asymmetric unit contains four half-anions plus two tetramethylammoniums. 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 $[\Sigma \underline{w}(|\underline{kF_o}| - |\underline{F_c}|)^2/(\underline{u}-\underline{v})]^{1/2}$, 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 all within ten or twenty per cent of those obtained from one cycle of full-matrix refinement which included all parameters[14]. 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.

Discussion. — Figure 1 illustrates the structure of the $Co(B_9C_2H_{11}Br_3)_2^{-1}$ anion which was found 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. The same atomic arrangement was found for all four crystallographically unrelated anions. The anions are also all the same shape, within the accuracy of this determination. 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[15-20] for similar compounds. The Br-B-B angles are all (with one exception) within 5° of their 121° average

Table I

Final Positional and Thermal Parameters[a] in $(CH_3)_4N[(B_9C_2H_8Br_3)_2Co]$

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)
2 B(6)	.541(1)	.436(1)	.101(2)	2.9(6)
2 B(7)	.578(2)	.357(2)	-.050(2)	6.7(8)
2 B(8)	.488(1)	.342(2)	-.079(2)	6.4(8)

atom	x	y	z	B
3 C(2)	.068(1)	.463(1)	.038(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)
4 B(6)	.445(1)	-.085(1)	.046(2)	3.7(6)
4 B(7)	.372(2)	.030(2)	.128(2)	6.7(8)
4 B(8)	.346(1)	.060(1)	.018(2)	4.5(7)

Table I, continued

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 $(CH_3)_4N\left[(B_9C_2H_8Br_3)_2Co\right]$

Table III

Distances[a] in $(CH_3)_4N[(B_9C_2H_8Br_3)_2Co]$

ion no.:	1	2	3	4
atoms	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 are 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, $[\Sigma\Delta^2/(\underline{n}-1)]^{1/2}$, for the preceeding set of distances. These are given for comparison with the standard deviations calculated from the standard deviations of coordinates.

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° with a root-mean-square deviation of $\pm 1.7^{\circ}$ 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 $58\ 1/2^{\circ}$ while the four C-B-C and eight B-C-C angles average 57° and $61\ 1/2^{\circ}$. All four of these sets of angles show $2\ 1/2^{\circ}$ root-mean-square deviations from these averages. The root-mean-square deviations are believed to be better measurements of the accuracy of these angles than the $\sim 1.6^{\circ}$ 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 tetramethylammoniums is very similar to that of KHF_2[21] as indicated in Figure 2. The higher symmetry (tetragonal, I4/mcm) of the KHF_2 structure[21] 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 $\sim 3^{\circ}$

and ~ .07 A, respectively. This is interpreted as the effect of the Br(5) of one 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 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)[22]. A similar steric effect of about the same size, but in the opposite direction (carbons farther from metal than the borons) was found[23] in $B_9C_2H_9(CH_3)_2PdC_4(C_6H_5)_4$ in which the methyl groups are on the dicarbollyl carbons.

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[18-20], and dipole moments[24] found for $B_{10}C_2H_{12}$ derivatives and molecular orbital calculations[18,19] 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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Table IV

Average Distances[a] in $(CH_3)_4N[(B_9C_2H_8Br_3)_2Co]$

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 are corrected for thermal motion.

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

Table IV, continued

calculated 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.

References and Footnotes

(1) Work done under the auspices of the U. S. Atomic Energy Commission.

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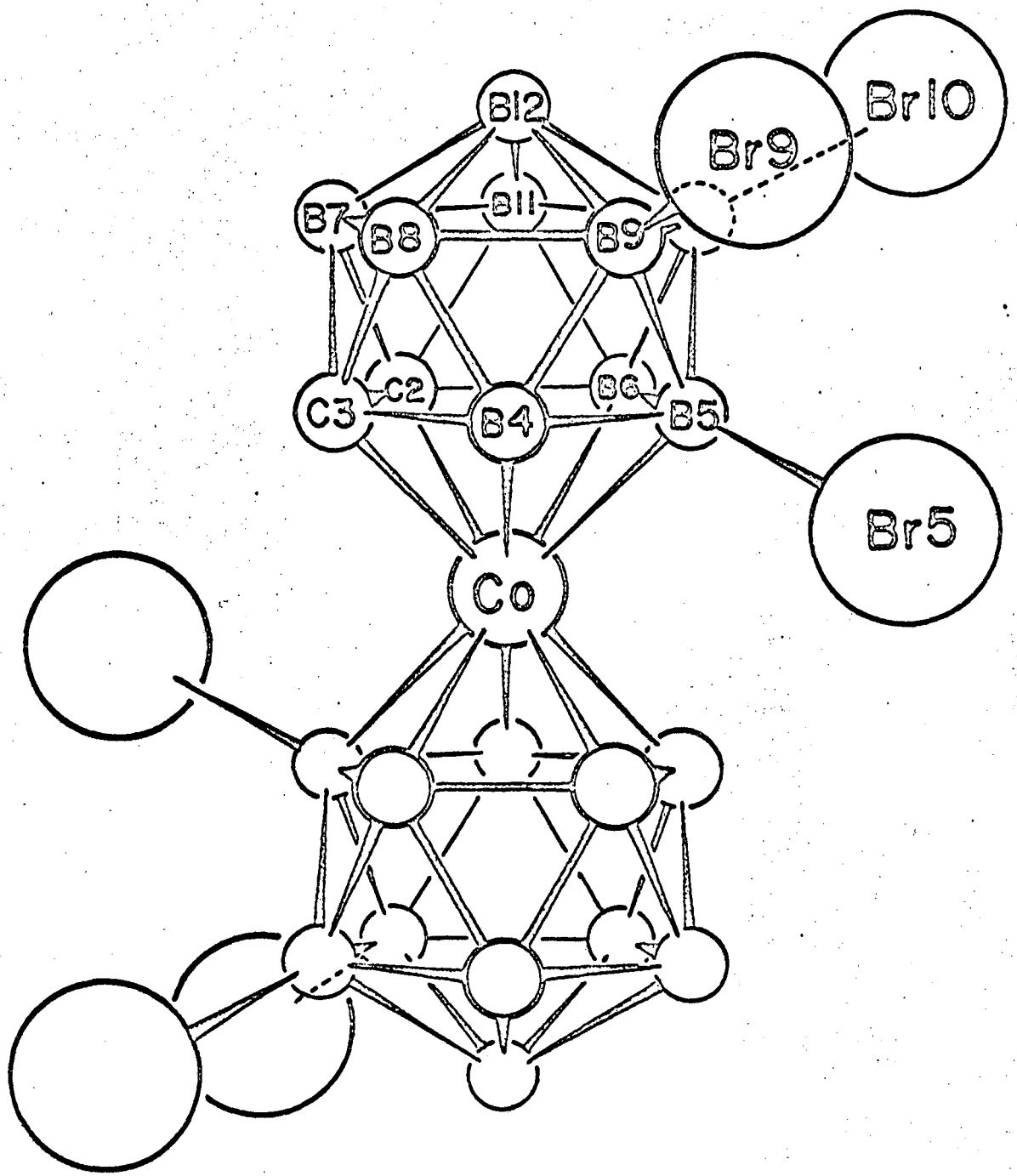
Figure Captions

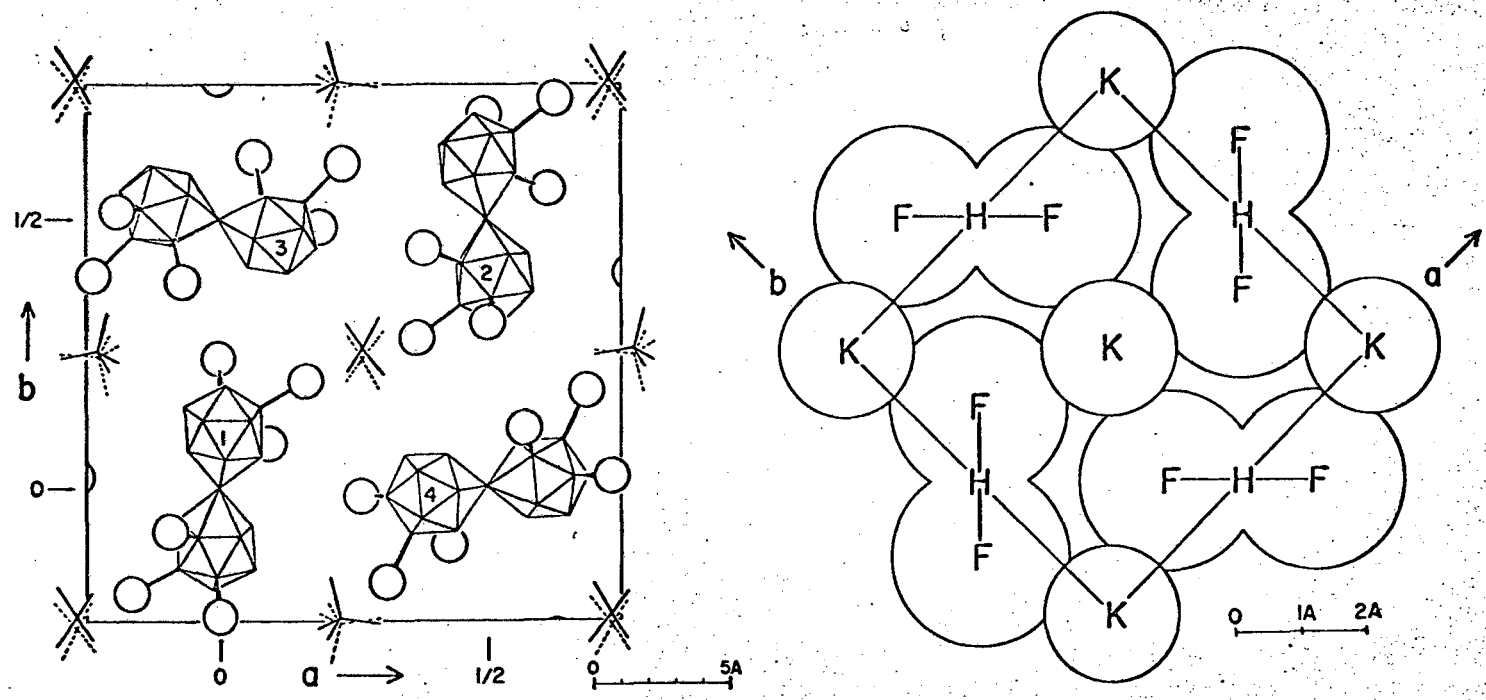
Figure 1. — $(B_9C_2H_8Br_3)_2Co^-$ (hydrogens omitted).

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



XBL 6711-6069

Fig. 1



XBL 6711-6068

Fig. 2

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