are consistently high, the measured density is high, the magnetic susceptibility is high, and the electrical resistivity indicates metallic behavior instead of the expected semiconducting behavior which is found for monoclinic (D type) Dy_2S_3. Of course, this does not preclude the possibility that more stoichiometric cubic Dy_2S_3 might be prepared under other conditions.

The unit cell dimensions of the Th_3P_4 type rare earth sulfides[2] are nearly invariant over the composition range $R_{2.677}S_4$ (R_2S_3) to R_3S_4 for R = La, Ce, Pr, and Nd. This means that the average cation-to-sulfur distance is nearly invariant over this range because the *average* distance changes very little with changes in the one positional parameter. The average cation size might be expected to increase since formally some cations are being reduced from R^{3+} to R^{2+}. The filling of some cation vacancies would not be expected to compensate for such an increase; consequently, the best rationalization appears to be that the cations do not increase in size when they are formally reduced because the additional electrons are not localized at the cations. The expected increase in unit cell dimensions does occur on going from Sm_2S_3 to Sm_3S_4 indicating that Sm^{2+} is really present and the additional electron has not been delocalized. This conclusion is supported by magnetic and electrical data[24] in that CeS is metallic with a magnetic moment corresponding to Ce^{3+}, whereas SmS is a semiconductor with a magnetic moment corresponding to Sm^{2+}. Of course, Sm^{2+} is well known in other compounds, whereas Ce^{2+} is not.

At this time it is not possible to state with certainty whether or not the Th_3P_4 phase can exist at *exactly* the sesquisulfide stoichiometry for the rare earth sulfides. It is possible that this C-type structure is a valid high-temperature form, but it is likewise possible that in the high-temperature preparations of this form at least some sulfur is always lost. Clarification of this point will have to await more sophisticated preparative or analytical techniques.

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

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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 $a = 19.893 \pm 0.010$ Å, $b = 19.487 \pm 0.010$ Å, $c = 15.058 \pm 0.010$ Å, and $\beta = 93.15 \pm 0.05°$, contains eight formula units and four crystallographically independent anions. The calculated density is 1.967 g/cm³, in agreement with the measured value of 1.98 ± 0.01 g/cm³. 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).

Introduction

Hawthorne and coworkers[3-8] have recently synthesized a number of π-dicarbollylmetal compounds analogous to the π-cyclopentadienyl "sandwich" compounds. They found[8,9] that one of these substances, $Co(B_9C_2H_{11})_2^-$, could be electrophilically brominated by treatment with neat bromine or bromine in glacial acetic acid to give $Co(B_9C_2H_8Br_3)_2^-$. 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 ascer-

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

(2) National Science Foundation graduate fellow.

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(9) M. F. Hawthorne, private communication.

tain 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 Section

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, Calif. 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 Cu Kα). 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 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 α doublet was resolved (λ(Mo Kα_1) 0.70926 Å). 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 (λ(Cu Kα_1, Kα_2) 1.5405, 1.5443 Å). The takeoff angle at the X-ray tube anode was approximately 2°. 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° ($\lambda^{-1} \sin\theta = 0.395$).

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 ($\bar{h}k\bar{l}$) 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 $|l| \leq 6$) also had their equivalent ($\bar{h}k\bar{l}$) 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 $h0l$, $l \neq 2n$) obtained from preliminary Weissenberg photographs.

The intensity, I, and standard deviation, $\sigma(I)$, for each measurement were calculated by: $I = C - (t_C/2t_B)(B_1 + B_2)$ and $\sigma^2(I) = C + (t_C/2t_B)^2(B_1 + B_2) + (0.06I)^2$, 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 were 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 $0.06I$ included in $\sigma(I)$, 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 F_o values[10] which the two sets had in common and setting

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

where the terms in brackets were set equal to zero if they were negative. If the expression $\sigma^2(F_{av}) = 0.5(F_1 - F_2)^2$ 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 I). A plot of the resulting $\sigma(F_o)$ *vs.* F_o revealed that the great majority of points fall on or near a smooth curve. This curve starts near 10 electrons for small F_o, stays near 3 electrons for F_o = 40–100 electrons, and follows the 3% of F_o line thereafter. Forty-five per cent 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 Gantzel–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 ± 0.010 Å, b = 19.487 ± 0.010 Å, c = 15.058 ± 0.010 Å, β = 93.15 ± 0.05°, contains eight formula units of $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$. The calculated density of 1.967 g/cm^3 agrees with the value (1.98 ± 0.01 g/cm^3) found by flotation in a mixture of bromoform and ethylene dichloride. These measurements apply to room temperature (~23°) and the error figures given are estimates. The observed extinctions correspond to space group $P2_1/c$. All four of the twofold sets of special positions are occupied by cobalt atoms and all other atoms are in general fourfold 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 mis-

(10) 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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Table I

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

Atoms	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)	0.0939 (1)[b]	0.0812 (1)	−0.1619 (2)	6.1 (1)	5.8 (2)	5.0 (2)	−0.1 (1)	0.9 (1)	0.6 (1)
1 Br(9)	0.1640 (2)	0.1975 (2)	0.0155 (2)	7.9 (2)	6.9 (2)	8.3 (2)	−2.5 (1)	−1.2 (2)	0.2 (2)
1 Br (10)	−0.0010 (1)	0.2408 (1)	−0.1278 (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)	0.3829 (1)	0.4459 (1)	0.1533 (2)	4.9 (1)	4.7 (1)	5.4 (2)	−0.8 (1)	2.5 (1)	0.4 (1)
2 Br(9)	0.3712 (2)	0.2769 (2)	0.0308 (2)	12.7 (2)	8.2 (2)	6.5 (2)	−7.7 (1)	1.4 (2)	−1.0 (2)
2 Br(10)	0.5025 (1)	0.3069 (1)	0.2262 (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)	0.0684 (1)	0.6171 (1)	−0.1475 (2)	5.1 (1)	5.9 (1)	8.4 (2)	0.1 (1)	1.8 (1)	4.2 (1)
3 Br(9)	0.1905 (1)	0.4844 (2)	−0.2110 (2)	6.2 (1)	7.8 (2)	6.9 (2)	−1.3 (1)	3.5 (1)	−2.1 (1)
3 Br(10)	0.2332 (1)	0.6034 (2)	−0.0147 (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)	0.4304 (1)	−0.1082 (1)	−0.1688 (2)	5.8 (1)	4.2 (1)	3.3 (1)	−0.5 (1)	0.4 (1)	−0.6 (1)
4 Br(9)	0.2666 (1)	−0.0179 (2)	−0.1510 (2)	4.8 (1)	7.5 (2)	6.9 (2)	0.1 (1)	−2.0 (1)	1.8 (2)
4 Br(10)	0.3133 (1)	−0.1774 (1)	−0.0066 (2)	6.4 (1)	4.7 (1)	5.0 (2)	−1.7 (1)	0.6 (1)	0.0 (1)

Atoms	x	y	z	B	Atoms	x	y	z	B
1 C(2)	−0.060 (1)	0.070 (1)	0.057 (1)	3.5 (5)	3 C(2)	0.068 (1)	0.463 (1)	0.088 (2)	4.8 (6)
1 C(3)	0.012 (1)	0.050 (1)	0.115 (2)	4.7 (6)	3 C(3)	0.053 (1)	0.413 (1)	0.004 (1)	4.4 (5)
1 B(4)	0.079 (1)	0.058 (1)	0.058 (2)	3.8 (6)	3 B(4)	0.056 (1)	0.451 (1)	−0.099 (2)	3.9 (6)
1 B(5)	0.044 (1)	0.091 (1)	−0.055 (2)	3.4 (6)	3 B(5)	0.085 (1)	0.540 (1)	−0.067 (2)	2.2 (5)
1 B(6)	−0.040 (1)	0.092 (1)	−0.042 (2)	3.1 (6)	3 B(6)	0.090 (1)	0.546 (1)	0.052 (2)	3.9 (6)
1 B(7)	−0.034 (2)	0.124 (2)	0.141 (2)	7.5 (9)	3 B(7)	0.131 (2)	0.398 (2)	0.056 (2)	7.0 (9)
1 B(8)	0.060 (1)	0.124 (1)	0.136 (2)	4.3 (7)	3 B(8)	0.122 (1)	0.399 (2)	−0.053 (2)	5.7 (8)
1 B(9)	0.079 (1)	0.150 (2)	0.029 (2)	6.2 (8)	3 B(9)	0.147 (1)	0.477 (1)	−0.096 (2)	3.3 (6)
1 B(10)	0.005 (1)	0.169 (1)	−0.036 (2)	3.8 (6)	3 B(10)	0.164 (1)	0.532 (1)	−0.009 (2)	3.5 (6)
1 B(11)	−0.068 (2)	0.151 (2)	0.033 (2)	7.4 (9)	3 B(11)	0.159 (2)	0.483 (2)	0.091 (2)	6.2 (8)
1 B(12)	0.011 (2)	0.192 (2)	0.073 (2)	7.7 (9)	3 B(12)	0.185 (1)	0.445 (2)	−0.007 (2)	5.6 (8)
2 C(2)	0.580 (1)	0.435 (1)	−0.001 (1)	4.3 (6)	4 C(2)	0.447 (1)	−0.009 (1)	0.113 (1)	3.4 (5)
2 C(3)	0.522 (1)	0.422 (1)	−0.082 (1)	4.1 (5)	4 C(3)	0.425 (1)	0.060 (1)	0.053 (1)	3.7 (5)
2 B(4)	0.443 (1)	0.413 (1)	−0.048 (2)	3.9 (6)	4 B(4)	0.407 (1)	0.037 (1)	−0.064 (2)	3.9 (6)
2 B(5)	0.455 (1)	0.418 (1)	0.073 (2)	1.8 (5)	4 B(5)	0.416 (1)	−0.055 (1)	−0.063 (2)	4.5 (7)
2 B(6)	0.541 (1)	0.436 (1)	0.101 (2)	2.9 (6)	4 B(6)	0.445 (1)	−0.085 (1)	0.046 (2)	3.7 (6)
2 B(7)	0.578 (2)	0.357 (2)	−0.050 (2)	6.7 (8)	4 B(7)	0.372 (2)	0.030 (2)	0.128 (2)	6.7 (8)
2 B(8)	0.488 (1)	0.342 (2)	−0.079 (2)	6.4 (8)	4 B(8)	0.346 (1)	0.060 (1)	0.018 (2)	4.5 (7)
2 B(9)	0.447 (1)	0.340 (2)	0.023 (2)	5.7 (8)	4 B(9)	0.336 (1)	−0.017 (1)	−0.052 (2)	3.4 (6)
2 B(10)	0.509 (1)	0.352 (2)	0.109 (2)	5.4 (7)	4 B(10)	0.357 (1)	−0.088 (1)	0.014 (2)	2.9 (6)
2 B(11)	0.589 (1)	0.361 (1)	0.064 (2)	4.7 (7)	4 B(11)	0.378 (1)	−0.060 (1)	0.124 (2)	4.7 (7)
2 B(12)	0.527 (2)	0.301 (2)	0.019 (2)	6.3 (8)	4 B(12)	0.311 (1)	−0.020 (1)	0.060 (2)	5.0 (7)
1 N	0.773 (1)	0.255 (1)	0.265 (1)	4.9 (4)	2 N	0.269 (1)	0.259 (1)	0.272 (1)	6.3 (5)
1 CH_3(1)	0.796 (2)	0.214 (2)	0.345 (3)	14.8 (13)	2 CH_3 (1)	0.237 (2)	0.301 (3)	0.196 (3)	17.4 (16)
1 CH_3(2)	0.701 (2)	0.245 (2)	0.250 (2)	11.1 (10)	2 CH_3(2)	0.240 (3)	0.216 (3)	0.337 (5)	24.5 (24)
1 CH_3(3)	0.812 (1)	0.235 (1)	0.187 (2)	8.1 (8)	2 CH_3(3)	0.312 (2)	0.209 (2)	0.233 (3)	17.3 (16)
1 CH_3(4)	0.791 (2)	0.329 (2)	0.300 (3)	12.6 (11)	2 CH_3(4)	0.301 (2)	0.317 (2)	0.328 (3)	14.0 (13)

[a] The units are Å^2. [b] The numbers in parentheses are the standard deviations in the least significance digits 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 15).

taken 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 Sayre relation: $sE_h \sim s\Sigma_k E_k E_{h-k}$, where s is to be read "the sign of." After enough signs were worked out by hand to yield a good set of "starting reflections" for input,[14] 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 for the signed E's is defined as: $\Sigma_h\Sigma_k|E_hE_kE_{h-k}|/\Sigma_h\Sigma_k|E_hE_kE_{h-k}|$. A Fourier synthesis using the signed E's as coefficients showed 16 largest peaks ranging in relative size from 1.00 to 0.57 with a definite breakdown to the 17th at 0.28. Isotropic bromines at these 16 positions, 4 of which were the twofold 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 16 atoms showed all 54 of the nonhydrogen light atoms. Their locations showed that the asymmetric unit contains 4 half-anions plus 2 tetramethylammonium ions and that the cobalt atoms are those in the 4 twofold 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 (4 anisotropic cobalts fixed at the special positions plus 12 an-

(14) The origin was defined by assigning positive phases to $42\bar{3}$, $71\bar{1}$, and 874. All combinations of positive and negative phases were assigned to 441, 640, and $78\bar{7}$ to generate the successive sets of signs.

isotropic bromines) were refined by a full matrix while the light atoms were held fixed, alternately with full-matrix refinements of the 54 isotropic light atoms with the heavy atoms fixed. The 2 carbons in each of the 4 icosahedral fragments were identified by their low thermal parameters 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 $R = 0.11$ 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 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 R value of 0.087. The standard deviation of an observation of unit weight, defined as $[\Sigma w(|kF_o| - |F_c|)^2/(u - v)]^{1/2}$, where u is the number of data and 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.[15] 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 $e^-/Å^3$) were all judged to be due to error 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 $|kF_o|$ and F_c are given in Table II.

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-$(B_9C_2H_8Br_3)_2^-$ 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 are presented in Table IV. The average B–B, B–C, C–C, B–Br, and Br–Br distances are in agreement with those found[16–21]

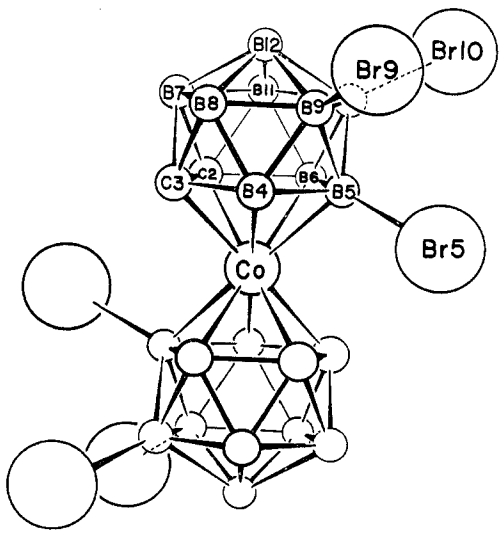

Figure 1.—Structure of $(B_9C_2H_8Br_3)_2Co^-$ (hydrogens omitted).

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 (116–119°) as expected from the protrusion of the cobalt vertex of the icosahedron. This protrusion is also shown by the smaller angles (49.4° with a root-mean-square deviation of ±1.7° 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 16 B–C–B and 32 C–B–B angles average 63 and 58.5° while the 4 C–B–C and 8 B–C–C angles average 57 and 61.5°. All four of these sets of angles show 2.5° 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 ~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 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[22] as indicated in Figure 2. The higher symmetry (tetragonal, I4/mcm) of the KHF_2 structure[22] is broken down to its $P2_1/c$ subgroup (on the doubled cell) by the lack of cylindrical symmetry of the anion 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

(15) 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 min on a CDC 6600. These figures may be compared with the requirements for the final diagonal-matrix refinements of 28K storage and 2.24 min/cycle.

(16) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *J. Am. Chem. Soc.*, **87**, 3988 (1965).

(17) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *Inorg. Chem.*, **5**, 1189 (1966).

(18) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *ibid.*, **6**, 1911 (1967).

(19) H. Beall and W. N. Lipscomb, *ibid.*, **6**, 874 (1967), and references therein.

(20) J. A. Potenza and W. N. Lipscomb, *ibid.*, **5**, 1471, 1478, 1483 (1966), and references therein.

(21) J. A. Potenza and W. N. Lipscomb, *ibid.*, **3**, 1673 (1964).

(22) R. W. G. Wyckoff, "Crystal Structures," Vol. 2, Interscience Publishers, New York, N. Y., 1964, p 277 ff.

Table II

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

TABLE II (*Continued*)

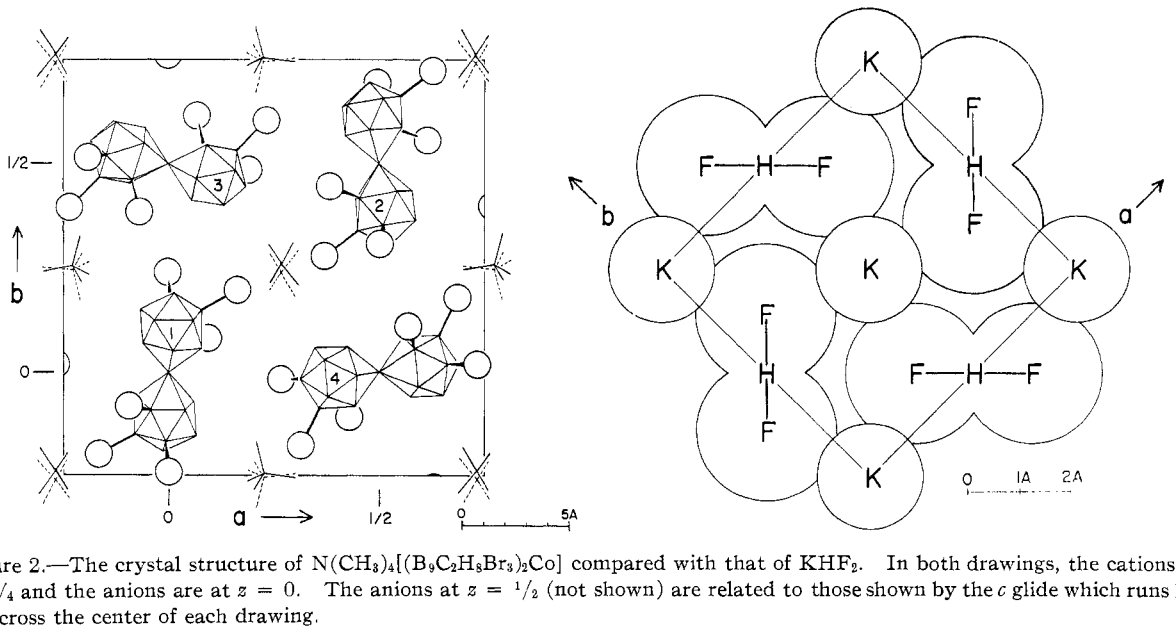

Figure 2.—The crystal structure of $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$ compared with that of KHF_2. In both drawings, the cations are at $z = \pm 1/4$ and the anions are at $z = 0$. The anions at $z = 1/2$ (not shown) are related to those shown by the c glide which runs horizontally across the center of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

equivalent and amount to ~3° and ~0.07° Å, 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 Å from its carbon and in line with the carbon and the opposite icosahedral vertex, the bromine–hydrogen distance is only 2.75 Å, which is 0.40 Å less than the sum of their van der Waals radii (1.95 + 1.2 = 3.15 Å).[23] A similar steric effect of about the same size, but in the opposite direction (carbons farther from

(23) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

Table III

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

Atoms	Ion no. 1	2	3	4
	Distance, Å			
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)
	Rms scatter[c] = 0.034			
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)
	Rms scatter = 0.037			
Co–B(5)	2.17 (3)	2.17 (2)	2.15 (2)	2.16 (3)
	Rms scatter = 0.007			
Co–Br(5)	3.527 (3)	3.530 (3)	3.511 (3)	3.527 (3)
	Rms scatter = 0.009			
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)
	Rms scatter = 0.027			
Br(9)–Br(10)	3.921 (5)	3.869 (5)	3.816 (5)	3.876 (4)
	Rms scatter = 0.043			
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)
	Rms scatter = 0.017			
C(2)–C(3)	1.68 (3)	1.65 (3)	1.63 (3)	1.66 (3)
	Rms scatter = 0.023			
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)
	Rms scatter = 0.064			
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)
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)
	Rms scatter = 0.060			
N–CH_3(1)	1.49 (5)	1.52 (6)		
N–CH_3(2)	1.46 (4)	1.43 (7)		
N–CH_3(3)	1.49 (3)	1.44 (5)		
N–CH_3(4)	1.57 (4)	1.53 (5)		
	Rms scatter = 0.048			

[a] None of these distances is corrected for thermal motion. [b] The numbers in parentheses are the standard deviations in the least significant digits as calculated from the standard deviations of coordinates (Table I). [c] Each of the "rms scatter" values given is the root-mean-square deviation from the average, $[\Sigma\Delta^2/(n-1)]^{1/2}$, for the preceding 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 $N(CH_3)_4[(B_9C_2H_8Br_3)_2Co]$

No. averaged	Atoms	Distances, Å
4	C–C	1.654 ± 0.017[b]
24	C–B	1.725 ± 0.013
72	B–B	1.786 ± 0.007
12	B–Br	1.963 ± 0.008
8	Co–C(2,3)	2.024 ± 0.013
8	Co–B(4,6)	2.115 ± 0.014
4	Co–B(5)	2.162 ± 0.014
4	Co–Br(5)	3.524 ± 0.005
8	Br(5)–Br(9,10)	3.727 ± 0.010
4	Br(9)–Br(10)	3.870 ± 0.025
8	N–CH_3	1.491 ± 0.018

[a] None of these distances is 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 $[(\Sigma\Delta^2)^{1/2}/(n-1)]$ or $[(\Sigma\sigma^2)^{1/2}/n]$, where Δ is the deviation from the average, σ is the standard deviation of a single distance as 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.

metal than the borons) was found[24] 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 Å) observed by Wing[25] 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-dicarbaclovododecaborane ($B_{10}C_2H_{12}$), but modified by a polarization induced by the Co(III). Substitution sites[19-21] and dipole moments[26] found for $B_{10}C_2H_{12}$ derivatives and molecular orbital calculations[19,20] 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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(25) R. M. Wing, *J. Am. Chem. Soc.*, **89**, 5599 (1967).

(26) R. Maruca, H. S. Schroeder, and A. W. Laubengayer, *Inorg. Chem.*, **6**, 572 (1967).