other B_nH_n cations employing only two- and three-center bonding. Since $3(n - 1) < 3n$, there are not enough electrons. Four- and higher-center bonds are required in order to use all available orbitals.

We may view the stability of the 2− ions as arising from a compromise between the destabilization caused by charge separation (which probably rules out 4− and 6− ions) and the added stabilization offered by the greater number of allowed valence structures. While the number of allowed valence structures mut be determined for each species by testing all possible structures for compliance with the topological rules, it seems likely that a greater number of *possible* structures will give rise to more *allowed* structures. For polyhedra in which each boron has three neighbors (*e.g.*, tetrahedron, trigonal bipyramid, octahedron) one can show that there are $3n - 6$ possible two-center and $3n - 8$ possible central three-center bonds. Thus B_nH_n will have $(3n - 8)!/[n!(2n - 8)!]$ possible structures arising from the different ways of choosing n objects from $3n - 8$. $B_nH_n^{2-}$ will have $[(3n - 8)!(3n - 6)!]/[(n - 2)!(2n - 6)!(3n - 9)!3!]$ where the additional terms arise from the possibility of choosing the two-center bonds in different ways. The ratio of the number of possible valence structures for $B_nH_n^{2-}$ to that for B_nH_n is thus $[(3n - 8)(3n - 7)(3n - 6)(n)\cdot(n - 1)]/[6(2n - 7)(2n - 6)]$, which increases from a minimum value of 120 at $n = 4$ and approaches $9n^3/8$ as n approaches infinity. Thus the 2− ions offer many more possible valence structures and, presumably, more allowable ones. Similar arguments may be given for polyhedra in which boron atoms have other numbers of nearest neighbors. Of course, the problem of symmetry degeneracy can spoil a resonance argument, and it does for tetrahedral B_4H_4, just as in organic chemistry it does for cyclobutadiene.

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The Crystal Structure and Molecular Geometry of a Bridged Bis-Dicarbollide Complex of Cobalt, $[(B_9C_2H_{10})_2S_2CH]Co^{III}$

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The novel substitution product $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ has previously been prepared by Francis and Hawthorne from the reaction of $K^+[(B_9C_2H_{11})_2Co^{III}]^-$ with carbon disulfide in the presence of $AlCl_3$; it crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ (D_2^4, no. 19) with $a = 10.923 (10)$, $b = 13.173 (10)$, and $c = 12.869 (10)$ Å; $\rho_{obsd} = 1.421 (6)$ and $\rho_{calcd} = 1.431$ g cm^{-3} for $Z = 4$. X-Ray diffraction data to $\sin\theta = 0.42$ (Mo Kα radiation) were collected by counter methods, the structure being solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms (including hydrogen) have been located, the final discrepancy index being $R_F = 7.88\%$ for the 1558 independent nonzero reflections. The crystal consists of molecular units of $[(B_9C_2H_{10})_2S_2CH]Co^{III}$, separated by normal van der Waals distances. The cobalt atom is "sandwiched" between two mutually staggered 1,2-dicarbollide ligands and is linked symmetrically to the five atoms of each basal pentagonal face (Co–B = 2.017–2.128 Å, Co–C = 2.037–2.056 Å). The two icosahedra which share the cobalt(III) atom as a common apex are further linked *via* a S–CH–S bridge which spans B(8) and B(8′), the central boron atoms of the two metal-bonded B_3C_2 pentagonal faces.

Introduction

The substitution chemistry of bis-(1,2-dicarbollide) metal complexes is a newly developing field in which little structural work has been done.[3,4] Francis and Hawthorne[5] have prepared $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ by the reaction of $K^+[(B_9C_2H_{11})_2Co^{III}]^-$ with carbon disulfide in the presence of aluminum trichloride. Since this new product was believed to possess some unique structural features, it has been subjected to an X-ray diffraction study. Preliminary results have been reported previously;[6] complete details are given below.

Unit Cell and Space Group

Crystals of $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ were supplied by Professor M. F. Hawthorne of the University of California, Los Angeles, Calif. They crystallize as bright orange parallelepipeds which are extended in the b direction. Optical examination and preliminary X-ray diffraction photographs indicated that the crystals were orthorhombic. A study of $hk0$, $h0l$ Weissenberg and 0–$1kl$, $hk0$–1, $h0l$ precession photographs revealed the systematic absences $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$; these are consistent only with the noncentrosymmetric orthorhombic space group $P2_12_12_1$ (D_2^4, no. 19).

Unit cell parameters, obtained from calibrated ($a_{NaCl} = 5.640$ Å) precession photographs taken with Mo Kα radiation (λ 0.7107 Å) at 24 ± 2°, are $a = 10.923$ (10), $b = 13.173$ (10), and $c = 12.869$ (10) Å. The unit cell volume is 1851.7 Å^3. The observed density of 1.421 (6) g cm^{-3}, by flotation in aqueous zinc iodide, is in excellent agreement with the value of 1.431 g cm^{-3} calculated for $M = 399.06$ and $Z = 4$.

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[3] B. G. deBoer, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **7**, 2289 (1968).

[4] M. R. Churchill and K. Gold, *J. Amer. Chem. Soc.*, **92**, 1180 (1970).

[5] J. N. Francis and M. F. Hawthorne, personal communication.

[6] M. R. Churchill, K. Gold, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 1222 (1969).

No restrictions are imposed upon the molecular geometry by crystallographic elements of symmetry.

Collection of X-Ray Data

Intensity data were collected with a 0.01°-incrementing Supper-Pace "Buerger Automated Diffractometer" using Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å). The diffractometer was programmed to collect all data in a given Weissenberg zone using a "stationary-background, ω-scan, stationary-background" counting sequence and equiinclination Weissenberg geometry. A description of the apparatus and experimental technique has appeared previously.[7] The following details are specific to the present analysis. (i) The angle scanned was chosen as $\omega = [1.5 + (1.0/L)]°$, where $1/L$ is the Lorentz factor. The count associated with this scan is C. (ii) Initial and final backgrounds, B_1 and B_2, were each measured for one-fourth the time of the ω scan. (iii) Within each zone, the stability of the entire system was monitored by remeasuring a carefully preselected strong check reflection after each batch of 20 reflections had been collected. [No deviations $\geqslant 2\%$ from the mean were observed.] (iv) The integrated intensity (I) of a reflection was calculated as $I = C - 2(B_1 + B_2)$. (v) As a result of previous experience using the ω-scan technique and Zr-filtered molybdenum radiation, the following weights were applied to reflections: $I \geqslant 4900$, $\sigma(I) = 0.1I$; $I \leqslant 4900$, $\sigma(I) = 3.5I^{1/2}$. (vi) Reflections were omitted from subsequent consideration on two bases: (a) B_1/B_2 or $B_2/B_1 \geqslant 3.0$ (symptomatic of possible overlap between adjacent reflections); (b) $I < 3[C + 4B_1 + 4B_2]^{1/2}$ (*i.e.*, reflection not significantly different from zero at the 3σ level).

Two crystals were used in the X-ray analysis. Crystal A (0.29 × 0.47 × 0.33 mm) was mounted on its extended b axis and was used to collect data to $\sin\theta = 0.42$ from the levels h0–15l. Crystal B (0.12 × 0.28 × 0.10 mm) was mounted on its c axis and used in collecting correlation data for the levels hk0–6.

All data were corrected for Lorentz and polarization effects, and absorption corrections were applied.[8] With $\mu = 10.56\ \text{cm}^{-1}$, transmission factors range from 0.790 to 0.815 for crystal A and 0.792 to 0.945 for crystal B. The 23 zones of data were merged to a common scale using a least-squares procedure which minimized a sum of residuals linear in the logarithms of the individual scale factors.[9] The resulting 1558 independent nonzero reflections were used in a Wilson plot,[10] from which the (approximate) absolute scale factor was determined.

Solution and Refinement of the Structure

All crystallographic computations were, unless otherwise stated, carried out using the CRYRM system[11] on the Harvard University IBM 7094 computer. Scattering factors for neutral cobalt, sulfur, carbon, boron, and hydrogen were taken from the compilation of Ibers.[12] The values for cobalt and sulfur were corrected for the real, but not the imaginary,[13] component of dispersion [$\Delta f'(\text{Co}) = +0.4$, $\Delta f''(\text{Co}) = +1.1$, $\Delta f'(\text{S}) = +0.1$, $\Delta f''(\text{S}) = +0.2\ \text{e}^-$].

Discrepancy indices used are $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$, where $w(hkl) = [\sigma(F^2(hkl))]^{-2}$ and $\sigma(F^2(hkl))$ is derived from $\sigma(I(hkl))$ by appropriate adjustment for Lorentz polarization, absorption, and scale factors.

The positions of the cobalt and two sulfur atoms were found from a three-dimensional Patterson synthesis whose origin peak had been removed and which had been sharpened such that the average intensity was no longer θ dependent. A subsequent Fourier synthesis, phased by three atoms ($R_F = 0.39$, $R_{wF^2} = 0.47$), quickly revealed the location of all nonhydrogen atoms. Three cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters for all 26 nonhydrogen atoms (assuming all cage atoms to be boron) led to convergence at $R_F = 0.120$, $R_{wF^2} = 0.099$. Examination of isotropic thermal parameters of the cage atoms showed four to be significantly smaller than the rest. A Fourier synthesis also showed these same four atoms to have the highest electron density of all atoms within the icosahedral cages; they were therefore redefined as carbon atoms for subsequent crystallographic processes. A further three cycles of refinement of positional and isotropic thermal parameter refinement converged to $R_F = 0.115$ and $R_{wF^2} = 0.092$. Further refinement, now using anisotropic thermal parameters for cobalt and sulfur atoms, reduced the discrepancy indices to $R_F = 0.097$ and $R_{wF^2} = 0.067$. A difference Fourier synthesis now revealed evidence of anisotropic thermal motion for most carbon and boron atoms and also indicated the positions of all 21 hydrogen atoms with peak heights ranging from 0.40 to 0.81 e$^-$ Å^{-3}. A subsequent structure factor calculation, including all 47 atoms, yielded reduced discrepancy indices of $R_F = 0.092$ and $R_{wF^2} = 0.063$. A further six cycles of least-squares refinement of positional and anisotropic thermal parameters for nonhydrogen atoms led to final convergence [$(\Delta/\sigma)_{\max} < 0.1$] at $R_F = 0.0788$ and $R_{wF^2} = 0.045$. [Hydrogen atoms were fixed in calculated positions, with C–H = 1.08 Å and B–H = 1.00 Å, and an isotropic thermal parameter of 1.5 Å^2. These positions were continuously updated with respect to the refined carbon and boron positions.]

It should be noted that limitations in the storage capacity of the IBM 7094 computer necessitated the "blocking" of variables into three submatrices. Matrix I contained the scale factor plus positional and thermal parameters for Co, S(1), S(2), and C(13); matrix II contained parameters for C(1), C(2), and B(4)–B(12); matrix III contained parameters for C(1′), C(2′), and B(4′)–B(12′). We believe, based on previous experience, that this will result in estimated standard deviations in atomic parameters being underestimated systematically by less than 20%.

A final difference-Fourier map showed no peaks greater than 0.5 e$^-$ Å^{-3} thus confirming that the structure was both correct and complete.

A table of observed and calculated structure factors

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[7] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 1123 (1968).

[8] Using a local version of the IBM 7094 program GNABS; see C. W. Burnham, *Amer. Mineral.*, **51**, 159 (1966).

[9] A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965).

[10] A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

[11] CRYRM is an integrated package of crystallographic routines written for the IBM 7094 under the direction of Dr. R. E. Marsh at the California Institute of Technology.

[12] "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, pp 202–203, 211.

[13] Reference 12, p 216.

TABLE I
FINAL ATOMIC COORDINATES FOR $[(B_9C_2H_{10})_2S_2CH]Co^{III}$, WITH ESTIMATED STANDARD DEVIATIONS

Atom	*x*	*y*	*z*
Co	0.27338 (13)	0.16837 (9)	0.25987 (11)
S(1)	0.2910 (3)	0.4215 (2)	0.1705 (3)
S(2)	0.1975 (4)	0.2663 (3)	0.0131 (3)
C(1)	0.3760 (12)	0.1638 (9)	0.3925 (10)
C(2)	0.4490 (11)	0.1233 (9)	0.2918 (11)
B(4)	0.3055 (15)	0.2776 (10)	0.3733 (12)
B(5)	0.4442 (17)	0.2621 (12)	0.4508 (12)
B(6)	0.5340 (16)	0.1619 (10)	0.3991 (12)
B(7)	0.4396 (14)	0.2061 (10)	0.1938 (10)
B(8)	0.3516 (12)	0.3113 (8)	0.2438 (12)
B(9)	0.4313 (14)	0.3600 (9)	0.3549 (14)
B(10)	0.5733 (13)	0.2887 (11)	0.3723 (13)
B(11)	0.5752 (12)	0.1948 (9)	0.2707 (11)
B(12)	0.5175 (13)	0.3179 (9)	0.2479 (13)
C(1′)	0.1938 (10)	0.0271 (7)	0.2679 (10)
C(2′)	0.1136 (11)	0.1174 (8)	0.3226 (10)
B(4′)	0.2384 (14)	0.0590 (10)	0.1418 (12)
B(5′)	0.1202 (15)	−0.0318 (11)	0.1675 (15)
B(6′)	0.0434 (14)	0.0020 (12)	0.2839 (15)
B(7′)	0.0911 (10)	0.2174 (9)	0.2413 (11)
B(8′)	0.1720 (12)	0.1793 (12)	0.1293 (12)
B(9′)	0.0979 (17)	0.0643 (10)	0.0722 (13)
B(10′)	−0.0239 (16)	0.0339 (14)	0.1617 (17)
B(11′)	−0.0260 (12)	0.1252 (11)	0.2651 (16)
B(12′)	0.0079 (14)	0.1597 (12)	0.1364 (11)
C(13)	0.2362 (15)	0.3777 (10)	0.0546 (12)
H(1)	0.3317	0.1137	0.4385
H(2)	0.4552	0.0490	0.2722
H(4)	0.2183	0.3040	0.4073
H(5)	0.4451	0.2803	0.5340
H(6)	0.5911	0.1140	0.4477
H(7)	0.4381	0.1875	0.1101
H(9)	0.4248	0.4410	0.3761
H(10)	0.6577	0.3217	0.4029
H(11)	0.6625	0.1678	0.2367
H(12)	0.5659	0.3716	0.1970
H(1′)	0.2539	−0.0153	0.3089
H(2′)	0.1188	0.1337	0.3990
H(4′)	0.3239	0.3696	0.1012
H(5′)	0.1300	−0.1117	0.1423
H(6′)	0.0019	−0.0555	0.3351
H(7′)	0.0823	0.2971	0.2650
H(9′)	0.0926	0.0462	−0.0116
H(10′)	−0.1080	−0.0036	0.1337
H(11′)	−0.1113	0.1466	0.3059
H(12′)	−0.0568	0.2055	0.0912
H(13)	0.2236	0.4358	0.0049

has been deposited.[14] Final atomic fractional coordinates are collected in Table I. Anisotropic thermal parameters are shown in Table IIa; their associated atomic vibration ellipsoids are listed in Table IIb and are shown pictorially in Figure 1.[15]

The Molecular Structure

Individual bond lengths are given in Table IIIa; mean values are shown in Table IIIb. Average bond angles, with their deviations from the mean, are collected in Table IV. [In view of the fact that the bis icosahedral $(B_9C_2)_2Co$ framework *alone* defines 240 angles, it was thought inappropriate to report individual angles.] Important intramolecular planes, with individual atomic deviations, are collected in Table V.

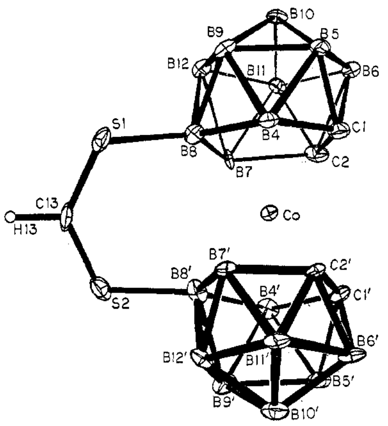

Figure 1.—The $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ molecule, projected onto the S(1)–C(13)–S(2) plane (OTLIPS diagram[15]).

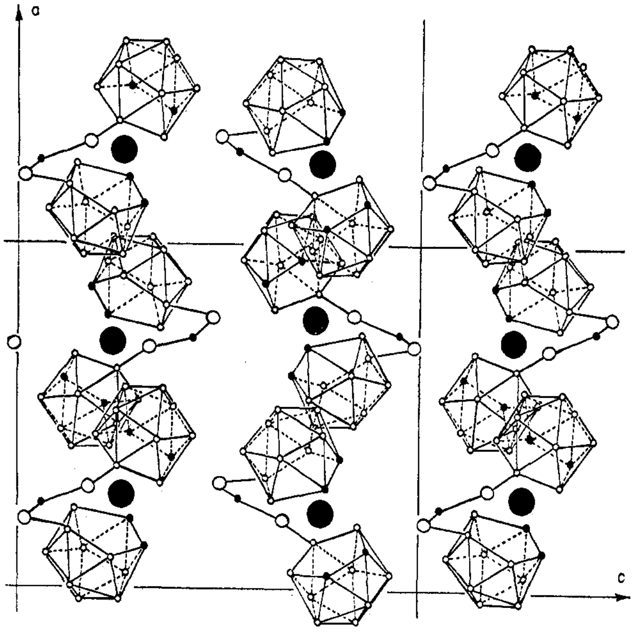

Figure 2.—Packing of $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ molecules, viewed down *b*.

The labeling of nonhydrogen atoms is depicted in Figure 1. [Hydrogen atoms are numbered similarly to the boron or carbon atoms to which they are bonded.]

The completed crystallographic analysis shows the central metal atom to be "sandwiched" between two icosahedral 1,2-dicarbollide ligands. Individual cobalt–carbon bond distances range from 2.037 to 2.056, averaging 2.047 (8) Å, while cobalt–boron distances range from 2.017 to 2.128, averaging 2.079 (35) Å. The central d^6 Co(III) ion thus attains the noble gas configuration (*i.e.*, that of krypton) appropriate with the diamagnetism of the complex, by the donation of six electrons from each of the 1,2-dicarbollide ligands.

The two B_9C_2 icosahedral skeletons are further linked *via* an S–CH–S bridge which spans B(8) and B(8′)—*i.e.*, the center of the three boron atoms in each of the open (basal) pentagonal faces (hereafter referred to as the α and α′ planes[16]).

Whereas an apical substituent bonded to an atom (X)

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[14] A compilation of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this journal. Single copies may be obtained from the Reprint Office, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

[15] This figure was prepared using OTLIPS, an IBM 1620/CALCOMP program written by Dr. P. H. Bird.

[16] As shown in Table V, the pentagonal rings of the B_9C_2 icosahedral fragments are labeled as planes α, α′, β, β′—the α faces being directly bonded to the central Co(III) ion.

TABLE IIa

ANISOTROPIC THERMAL PARAMETERS (WITH ESD'S) FOR $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ [a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Co	38.2 (1.1)	22.9 (0.6)	29.9 (0.8)	−5.1 (1.4)	0.4 (1.7)	−5.5 (1.3)
S(1)	69 (3)	28 (1)	89 (3)	7 (4)	−5 (5)	40 (4)
S(2)	78 (4)	87 (3)	39 (2)	−21 (6)	−17 (4)	37 (4)
C(1)	67 (12)	34 (6)	53 (9)	−11 (16)	−23 (17)	−20 (14)
C(2)	32 (9)	47 (7)	63 (10)	12 (14)	−31 (15)	−19 (14)
B(4)	61 (15)	37 (7)	48 (10)	−21 (18)	−19 (19)	−13 (16)
B(5)	98 (17)	54 (8)	30 (10)	−59 (22)	−18 (21)	−1 (16)
B(6)	96 (17)	28 (6)	48 (10)	−32 (19)	−51 (21)	1 (15)
B(7)	61 (14)	37 (7)	25 (8)	2 (16)	−24 (16)	40 (13)
B(8)	61 (12)	29 (6)	46 (9)	18 (14)	8 (20)	−12 (14)
B(9)	62 (13)	27 (7)	60 (12)	−31 (16)	17 (21)	−11 (15)
B(10)	38 (12)	47 (8)	52 (11)	−30 (17)	−36 (19)	7 (17)
B(11)	51 (12)	31 (6)	26 (8)	−1 (13)	−18 (18)	−5 (12)
B(12)	56 (12)	30 (6)	49 (9)	−18 (14)	7 (20)	6 (16)
C(1′)	56 (11)	18 (4)	47 (9)	−3 (11)	11 (16)	−21 (12)
C(2′)	54 (10)	26 (5)	36 (8)	−29 (14)	11 (15)	−26 (11)
B(4′)	52 (12)	40 (7)	44 (10)	23 (16)	4 (19)	−19 (14)
B(5′)	69 (14)	42 (7)	63 (12)	−23 (19)	−48 (23)	−17 (17)
B(6′)	36 (12)	51 (9)	75 (15)	−32 (19)	−6 (21)	−41 (19)
B(7′)	27 (9)	38 (6)	32 (8)	−22 (13)	18 (16)	−14 (14)
B(8′)	18 (10)	69 (9)	50 (10)	25 (17)	7 (16)	31 (19)
B(9′)	113 (19)	33 (6)	45 (11)	−10 (20)	20 (24)	−46 (16)
B(10′)	69 (16)	64 (11)	77 (14)	−31 (23)	−39 (26)	−27 (22)
B(11′)	28 (11)	59 (8)	77 (14)	−24 (17)	−15 (22)	−21 (21)
B(12′)	46 (12)	68 (9)	35 (9)	2 (20)	−20 (17)	0 (18)
C(13)	94 (15)	50 (8)	80 (11)	−9 (20)	−11 (23)	98 (17)

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

TABLE IIb

DIRECTION COSINES[a-c] FOR ATOMIC VIBRATION ELLIPSOIDS IN $[(B_9C_2H_{10})_2S_2CH]Co^{III}$

Atom	$B_{\max}$ (dc's, maj axis)	B_{med} (dc's, med axis)	$B_{\min}$ (dc's, minor axis)
Co	2.07 (282, −417, 864)	1.86 (−892, 217, 396)	1.46 (353, 882, 311)
S(1)	6.33 (−23, −297, 955)	3.33 (−992, −123, 14)	1.50 (122, −947, 298)
S(2)	6.64 (−242, 918, 315)	3.57 (−953, −287, 102)	2.10 (184, −275, 944)
C(1)	4.06 (−515, −225, 827)	3.14 (759, −568, 318)	1.81 (398, 792, 464)
C(2)	4.77 (−275, −440, 855)	2.95 (−51, 893, 444)	1.24 (960, −78, 268)
B(4)	3.62 (−597, −13, 802)	3.27 (557, −726, 403)	1.78 (577, 687, 441)
B(5)	5.99 (−796, 599, 92)	2.60 (−505, −739, 446)	1.78 (334, 308, 891)
B(6)	5.66 (−845, 213, 491)	2.53 (352, −470, 809)	1.52 (403, 856, 322)
B(7)	3.70 (−449, 668, 593)	2.89 (861, 501, 89)	0.52 (237, −550, 800)
B(8)	3.23 (519, −50, 853)	3.11 (−754, −497, 430)	1.60 (−403, 866, 296)
B(9)	4.37 (479, −300, 825)	3.05 (−731, 384, 564)	1.39 (486, 873, 35)
B(10)	4.31 (−469, 543, 697)	3.10 (32, −778, 628)	1.09 (883, 316, 347)
B(11)	2.70 (−882, −72, 466)	2.16 (165, −973, 162)	1.45 (441, 220, 870)
B(12)	3.29 (285, 48, 957)	2.96 (−817, 534, 216)	1.72 (−501, −844, 192)
C(1′)	3.48 (372, −299, 879)	2.55 (−928, −131, 348)	1.01 (−11, 945, 326)
C(2′)	3.62 (622, −556, 552)	2.16 (−707, −95, 701)	1.00 (337, 826, 453)
B(4′)	3.66 (−349, −720, 600)	2.83 (686, 240, 687)	1.71 (−638, 651, 410)
B(5′)	5.17 (−574, −48, 817)	3.55 (496, −815, 301)	1.69 (651, 578, 492)
B(6′)	5.82 (88, −541, 837)	3.20 (−500, 702, 506)	1.19 (861, 463, 209)
B(7′)	3.26 (380, −779, 499)	1.88 (94, 570, 817)	0.97 (−920, −263, 289)
B(8′)	5.46 (158, 882, 445)	2.75 (−70, −439, 896)	0.75 (−985, 175, 7)
B(9′)	5.64 (920, −226, 321)	3.96 (−392, −591, 705)	1.02 (−30, 774, 632)
B(10′)	5.81 (−228, −426, 875)	4.86 (−598, 771, 220)	2.13 (769, 473, 430)
B(11′)	5.48 (−14, −449, 893)	3.98 (−292, 856, 426)	1.06 (956, 255, 143)
B(12′)	4.72 (−20, −1000, 4)	2.83 (−662, 16, 749)	1.71 (750, −12, 662)
C(13)	7.89 (−114, 602, 791)	4.43 (994, 63, 95)	0.94 (−7, 796, 605)

[a] Direction cosines have been multiplied by 10^3. [b] The major, median, and minor axes of the atomic vibration ellipsoids are defined in terms of $\underline{B}$ (the normal isotropic thermal parameter, having units of Å^2). The transformation to root-mean-square displacement, $(\overline{U^2})^{1/2}$, is $(\overline{U^2})^{1/2} = [B/8\pi^2]^{1/2}$. [c] The atomic vibration ellipsoids are illustrated in Figure 1.

in a regular icosahedral cage will ideally make angles of 121° 43′ with all five cage atoms adjacent to X, the sulfur atoms in the present structure are seen to deviate significantly from this geometry. As may be seen from the angles[17] S–B(8)–B(4) = 124.1 (1.0)°, S–B(8)–B(7) = 125.3 (0.9)°, S–B(8)–B(9) = 105.7 (0.9)°, and S–B(8)–B(12) = 107.6 (0.9)°, the sulfur atoms are displaced away from the idealized substituent geometry and toward the planes β [S(1)] and β' [S(2)]. This distortion presumably results from the rigidity of the S–CH–S bridge, in which the relative position of the two sulfur atoms is dictated by the angle S(1)–C(13)–S(2) = 133.4 (1.0)°. Other angles within this bridging group are B(8)–S(1)–C(13) = 107.8 (0.7)° and B(8′)–S(2)–C(13) = 109.0 (0.7)°. Individual bond lengths within this system are B(8)–S(1) = 1.853 (13), S(1)–C(13) = 1.707 (15), C(13)–S(2) = 1.618 (15), and S(2)–B(8′) = 1.904 (15) Å. Neither the S(1)–C(13) nor S(2)–C(13) bond length deviates by as much as 3σ from the mean distance of 1.663 Å, a value in keeping with

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[17] The values given are the average of S(1)–B(n)–B(m) and S(2)–B(n')–B(m').

TABLE IIIa

DISTANCES WITHIN THE $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ MOLECULE[a]

Atoms	Distance, Å	Atoms	Distance, Å
I. Distances from Cobalt Atom			
Co···S(1)	3.532 (3)	Co···S(2)	3.525 (4)
Co---C(1)	2.043 (12)	Co---C(1′)	2.056 (11)
Co---C(2)	2.050 (12)	Co---C(2′)	2.037 (11)
Co---B(4)	2.079 (15)	Co---B(4′)	2.128 (14)
Co---B(7)	2.066 (13)	Co---B(7′)	2.107 (12)
Co---B(8)	2.078 (13)	Co---B(8′)	2.017 (14)
Co···B(5)	3.323 (16)	Co···B(5′)	3.342 (16)
Co···B(6)	3.364 (15)	Co···B(6′)	3.348 (16)
Co···B(9)	3.293 (15)	Co···B(9′)	3.374 (16)
Co···B(11)	3.318 (13)	Co···B(11′)	3.320 (16)
Co···B(12)	3.319 (14)	Co···B(12′)	3.309 (15)
II. Distances within –S–CH–S System			
S(1)–C(13)	1.707 (15)	S(2)–C(13)	1.618 (15)
S(1)–B(8)	1.853 (13)	S(2)–B(8′)	1.904 (15)
III. Carbon–Carbon Bond Lengths			
C(1)–C(2)	1.613 (17)	C(1′)–C(2′)	1.636 (16)
IV. Carbon–Boron Bond Lengths			
C(1)–B(4)	1.703 (19)	C(1′)–B(4′)	1.745 (18)
C(1)–B(5)	1.672 (20)	C(1′)–B(5′)	1.708 (20)
C(1)–B(6)	1.728 (20)	C(1′)–B(6′)	1.689 (20)
C(2)–B(6)	1.739 (19)	C(2′)–B(6′)	1.775 (20)
C(2)–B(7)	1.670 (18)	C(2′)–B(7′)	1.701 (16)
C(2)–B(11)	1.691 (18)	C(2′)–B(11′)	1.698 (19)
V. Boron–Boron Bond Lengths			
B(4)–B(5)	1.826 (22)	B(4′)–B(5′)	1.791 (22)
B(4)–B(8)	1.797 (20)	B(4′)–B(8′)	1.750 (29)
B(4)–B(9)	1.767 (21)	B(4′)–B(9′)	1.767 (21)
B(5)–B(6)	1.773 (22)	B(5′)–B(6′)	1.774 (23)
B(5)–B(9)	1.791 (22)	B(5′)–B(9′)	1.780 (23)
B(5)–B(10)	1.769 (22)	B(5′)–B(10′)	1.799 (25)
B(6)–B(10)	1.759 (21)	B(6′)–B(10′)	1.786 (25)
B(6)–B(11)	1.766 (20)	B(6′)–B(11′)	1.807 (23)
B(7)–B(8)	1.805 (19)	B(7′)–B(8′)	1.764 (19)
B(7)–B(11)	1.788 (18)	B(7′)–B(11′)	1.790 (20)
B(7)–B(12)	1.838 (19)	B(7′)–B(12′)	1.796 (19)
B(8)–B(9)	1.792 (20)	B(8′)–B(9′)	1.868 (22)
B(8)–B(12)	1.815 (19)	B(8′)–B(12′)	1.814 (21)
B(9)–B(10)	1.827 (21)	B(9′)–B(10′)	1.805 (25)
B(9)–B(12)	1.757 (20)	B(9′)–B(12′)	1.798 (22)
B(10)–B(11)	1.801 (19)	B(10′)–B(11′)	1.793 (26)
B(10)–B(12)	1.756 (20)	B(10′)–B(12′)	1.724 (24)
B(11)–B(12)	1.765 (19)	B(11′)–B(12′)	1.757 (22)
VI. Interannular Contacts			
C(1)···C(1′)	3.126	B(4)···B(7′)	3.000
C(1)···C(2′)	3.065	B(7)···B(4′)	3.005
C(2)···C(1′)	3.077	B(7)···B(8′)	3.059
C(2)···B(4′)	3.120	B(8)···B(7′)	3.103
B(4)···C(2′)	3.045	B(8)···B(8′)	3.007

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit of the previous number.

TABLE IIIb

AVERAGE BOND LENGTHS WITHIN THE $[(B_9C_2H_{10})_2S_2CH]CO^{III}$ MOLECULE

Bond type	No.	Range[a]	Av[b]
Co—C	4	2.037–2.056	2.047 (8)
Co—B	6	2.017–2.128	2.079 (35)
C—C	2	1.613–1.636	1.625 (16)
C—B	12	1.670–1.775	1.710 (31)
B—B	36	1.724–1.868	1.788 (25)
	60		
Co···S	2	3.525–3.532	3.529 (5)
Co···B(β)	10	3.293–3.374	3.331 (26)
S—C	2	1.618–1.707	1.663 (63)
S—B	2	1.853–1.904	1.879 (36)

[a] Esd's for individual values appear in Table IIIa. [b] Esd's for "equivalent" bond lengths were calculated from the equation

$$\sigma = \left\{\left[\sum_{i=1}^{i=N} (\chi_i - \bar{\chi})^2\right] \Big/ (N - 1)\right\}^{1/2}$$

where χ_i is the *i*th bond length and $\bar{\chi}$ is the mean of the N equivalent bond length.

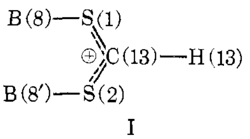
TABLE IV

AVERAGE BOND ANGLES WITHIN THE $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ MOLECULE

Angle type	No.	Range	Av[a]
I. Angles Involved in the –S–CH–S– Bridge.			
B–S–C	2	107.8–109.0	108.4 (0.8)
S–C–S	1	...	133.4 (1.0)[b]
S–B–B	8	104.0–127.6	115.7 (10.0)
II. Angles around All Triangular Faces			
C–Co–C	2	46.4–47.1	46.8 (0.6)
C–Co–B	4	47.9–49.3	48.6 (0.6)
B–Co–B	4	49.8–51.6	50.8 (0.7)
Co–C–C	4	65.8–67.1	66.6 (0.6)
Co–C–B	4	66.6–67.9	67.2 (0.6)
Co–B–C	4	63.2–65.6	64.1 (1.1)
Co–B–B	8	61.8–68.4	64.6 (2.4)
C–C–B	4	59.2–64.5	62.1 (2.2)
C–B–C	2	55.4–56.3	55.9 (0.6)
B–C–B	8	61.9–65.5	63.3 (1.2)
C–B–B	16	56.4–60.7	58.4 (1.3)
B–B–B	60	57.2–63.9	60.0 (1.4)
	120		
III. Angles around All Pentagonal Rings			
C–Co–B	8	82.5–84.6	83.6 (0.8)
B–Co–B	2	87.5–88.5	88.0 (0.7)
Co–C–B	8	122.8–126.6	125.2 (1.2)
Co–B–B	12	115.7–120.5	117.5 (1.5)
C–C–B	8	109.7–113.8	111.6 (1.6)
B–C–B	4	115.3–118.1	116.3 (1.3)
C–B–B	24	100.8–105.8	103.4 (1.3)
B–B–B	54	104.3–113.0	108.2 (1.9)
	120		

[a] Esd's for average angles were calculated by the method outlined in footnote *b* to Table IIIb. [b] This value comes from standard deviations in the positions of the three atoms involved.

that expected for a $C\overset{\cdots}{-}S$ linkage of bond order 1.5.[18] It is suggested, therefore, that the S(1)–C(13)–S(2) system is delocalized as shown in I. This is consistent



I

with the conventional assignment of electronic charge within the remainder of the molecule, *viz.* 3+ for the cobalt ion {as expected for a nonredox product from $[(B_9C_2H_{11})_2Co^{III}]^-$} and 2− for each of the icosahedral 1,2-dicarbollide ligands. The molecule may more simply be considered as a zwitterion with the S_2CH fragment bearing a net positive charge and the $(B_9C_2H_{10})_2$-Co^{III} fragment having a net negative charge. The packing of molecules within the unit cell (see Figure 2) is consistent with this latter description, since the "negative end" of one molecule is adjacent to the "positive end" of its nearest neighbor. That is, the packing is such that (within the framework of the zwitterion description) repulsive electrostatic interactions are minimized.

The $(B_9C_2H_{10})_2Co$ portion of the molecule has structural characteristics similar to those of the parent

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(18) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 276.

TABLE V

IMPORTANT PLANES WITHIN THE $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ MOLECULE[a]

Atom	Dev, Å	Atom	Dev, Å
α Plane: C(1), C(2), B(4), B(7), B(8) $0.8268X + 0.4501Y + 0.3371Z = 6.0520$			
C(1)	+0.018 (13)	Co	−1.457
C(2)	+0.001 (13)	B(5)	+1.470
B(4)	−0.027 (15)	B(6)	+1.462
B(7)	−0.018 (14)	B(9)	+1.518
B(8)	+0.027 (14)	B(11)	+1.473
		B(12)	+1.583
β Plane: B(5), B(6), B(9), B(11), B(12) $0.8301X + 0.4229Y + 0.3633Z = 7.5940$			
B(5)	+0.002 (17)	C(1)	−1.437
B(6)	+0.015 (15)	C(2)	−1.471
B(9)	−0.019 (15)	B(4)	−1.532
B(11)	−0.027 (13)	B(7)	−1.553
B(12)	+0.029 (14)	B(8)	−1.532
		B(10)	+0.954
α′ Plane: C(1′), C(2′), B(4′), B(7′), B(8′) $0.8347X + 0.4214Y + 0.3543Z = 3.1475$			
C(1′)	−0.008 (11)	Co	+1.465
C(2′)	+0.011 (12)	B(5′)	−1.464
B(4′)	+0.008 (14)	B(6′)	−1.446
B(7′)	−0.010 (12)	B(9′)	−1.569
B(8′)	+0.006 (15)	B(11′)	−1.481
		B(12′)	−1.567
β′ Plane: B(5′), B(6′), B(9′), B(11′), B(12′) $0.8348X + 0.4306Y + 0.3161Z = 1.5757$			
B(5′)	+0.013 (17)	C(1′)	+1.443
B(6′)	−0.014 (17)	C(2′)	+1.470
B(9′)	−0.007 (17)	B(4′)	+1.526
B(11′)	+0.009 (16)	B(7′)	+1.527
B(12′)	−0.001 (15)	B(8′)	+1.583
		B(10′)	−0.935
μ Plane: Co, B(8), S(1), C(13), S(2), B(8′) $-0.8598X + 0.2813Y + 0.4261Z = -0.5204$			
Co	+0.002 (01)	C(13)	+0.002 (15)
S(1)	+0.284 (04)	B(8)	−0.291 (4)
S(2)	−0.276 (04)	B(8′)	+0.278 (15)
μ′ Plane: S(1), C(13), S(2) $-0.9360X + 0.1544Y + 0.3162Z = -1.4241$			
S(1)	0.000	Co	0.029
C(13)	0.000	B(8)	−0.545
S(2)	0.000	B(8′)	+0.556
μ″ Plane: Co, B(8), B(8′) $-0.7499X + 0.3983Y + 0.5281Z = 0.4102$			
Co	0.000	S(1)	+0.576
B(8)	0.000	S(2)	−0.542
B(8′)	0.000	C(13)	+0.008

Dihedral Angles

α–β	2° 26′	β–α	1° 08′	μ′–μ″	21° 30′
α–β′	2° 18′	β–β′	3° 14′		
α–β′	1° 37′	α′–β′	2° 55′		

[a] Equations for planes are in Cartesian coordinates, *i.e.*, $X = xa$, $Y = yb$, $Z = zc$.

$[(B_9C_2H_{11})_2Co^{III}]^-$ anion, save that the S–CH–S bridge now eliminates the possibility of disorder (found in the anion[19]). As with the parent compound, the icosahedral 1,2-dicarbollide ligands in $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ take up a mutually staggered conformation. This is illustrated by angles through the central cobalt atom from atoms of plane α to those of plane α′, *i.e.*, C(1)–Co–B(8′) = 177.6(0.5)°, C(2)–Co–B(7′) = 174.9 (0.5)°, B(7)–Co–C(2′) = 174.7 (0.6)°, B(8)–Co–C(1′) = 177.1 (0.5)°, and B(4)–Co–B(4′) = 178.7 (0.5)° [average 176.6 ± 1.7°].

The geometry of the molecule approximates to point group C_2, with carbon atoms of the icosahedra occupying positions in the closest proximity allowed by a staggered configuration.

Distances of the cobalt atom from boron atoms in the β or β′ planes range from 3.292 to 3.374, averaging 3.331 (26) Å; the sulfur atoms are similarly equidistant from the central cobalt atom, individual distances being Co···S(1) = 3.532(3) and Co···S(2) = 3.525 (3) Å.

Lateral pentagons defined by the icosahedra have root-mean-square deviations from planarity of 0.021 (α), 0.009 (α′), 0.021 (β), and 0.010 Å (β) (see Table V).

The carborane ligands are essentially parallel, the dihedral angle defined by planes α and α′ being only 2° 18′. Thus the S–CH–S bridge does not destroy the essential "symmetrical sandwich" characteristics of the bis(1,2-dicarbollide)metal molecular framework. It should be noted, however, that the bridging group does not lie perpendicular to the two B_3C_2 bonding faces (α and α′) of the molecule; rather, the S–C–S plane makes angles of 126° 42′ with the α plane and 127° 10′ with the α′ plane. Finally we may observe that, while the cobalt atom lies essentially in the S–C–S plane (deviation +0.029 Å), the boron atoms B(8) and B(8′) are displaced symmetrically to either side of this plane, *i.e.*, by −0.545 and +0.556 Å, respectively.

All bond angles found within the $(B_9C_2H_{10})_2Co$ portion of the $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ molecule are in good agreement with the corresponding values found from studies on such species as $Cs^+[(B_9C_2H_{11})_2Co^{III}]^-$,[19] $(Cs^+)_2[(B_9C_2H_{11})Co(B_8C_2H_{10})Co(B_9C_2H_{11})^{2-}]\cdot H_2O$,[20] $[(C_2H_5)_4N^+]_3[(B_9C_2H_{11})Co(B_8C_2H_{10})Co(B_8C_2H_{10})Co(B_9C_2H_{11})^{3-}]$,[21] (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$,[2] and $(B_9C_2H_{11})Al(C_2H_5)$.[22] The S–CH–S bridging group thus causes no discernible distortions within the icosahedral framework.

Average distances within the icosahedra are B–B = 1.788 (25), B–C = 1.710 (31), and C–C = 1.625 (16) Å; angles around trigonal faces and pentagonal planes approximate to the ideal values of 60 and 108°, respectively, with due allowance being made for the slight variation in covalent radius of boron and carbon and with the exception of all angles involving the cobalt atom (see Table IV).

Crystal Packing

Figure 2 shows the packing of $[(B_9C_2H_{10})_2S_2CH]Co^{III}$ molecules within the unit cell as viewed down *b*. The individual molecules are separated by normal van der Waals distances. Closest intermolecular contacts (of each principal type) are S···H = 3.02, C···H = 2.93, B···H = 2.89, and H···H = 2.35 Å.

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