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Structures of Metallocarboranes. II.
Crystal and Molecular Structure of the Metallocarborane Complex Cesium 3-η-Cyclopentadienyloctahydro-4-carba-3-cobalta-*closo*-nonaborate(1−), $Cs^+[(C_5H_5)Co(CB_7H_8)]^-$

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The crystal and molecular structure of $Cs^+[(C_5H_5)Co(CB_7H_8)]^-$ has been determined by a complete three-dimensional X-ray diffraction study. The compound crystallizes in the monoclinic centrosymmetric space group $C2/c$ ($C_{2h}{}^6$; No. 15) with $a = 12.643$ (2) Å, $b = 11.815$ (2) Å, $c = 16.376$ (2) Å, $\beta = 90.34$ (1)°, and $Z = 8$. Observed and calculated densities are 1.92 (2) and 1.916 g cm^{-3}, respectively. Diffraction data to $2\theta_{max} = 50°$ (Mo Kα radiation) were collected on a Syntex $P\bar{1}$ automated diffractometer and the structure was solved by conventional Patterson, Fourier, and full-matrix least-squares refinement techniques. The final discrepancy index is $R = 4.0\%$ for the 1521 independent nonzero reflections. All atoms except three hydrogen atoms were located. The molecule consists of a cobalt(III) atom sandwiched between $C_5H_5{}^-$ and $CB_7H_8{}^{3-}$ moieties, with cesium ions in general positions. The $CoCB_7$ skeleton approximates the shape of a tricapped trigonal prism in which two boron atoms and the carbon atom are in the low-coordinate "cap" positions. The cobalt atom is bonded to five boron atoms with an average bond distance of 2.09 Å.

Introduction

The reactions of carboranes and metallocarboranes with base have been widely investigated in the past several years.[1] Alcoholic potassium hydroxide was found to effect formal removal of a boron atom from 1,2-$C_2B_{10}H_{12}$ to produce the 1,2-$C_2B_9H_{12}{}^-$ ion;[2] when the reaction was performed in the presence of $CoCl_2$ and C_5H_6, the cobalt atom inserted into the vacant polyhedral position and a good yield of (η-C_5H_5)Co(η-$C_2B_9H_{11}$) was achieved.[3]

Similar reactions may be performed on metallocarboranes. Base degradation followed by two-electron oxidation of certain metallocarboranes produced the next lower metallocarborane homolog (eq 1) and was termed the "polyhedral contraction" reaction.[4] Bimetallocarboranes were formed from monometallocarboranes when an appropriate metal salt was added to the degradation mixture.[5]

$$(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}C_2B_nH_{n+2}) \xrightarrow[2.\ -2e^-\ (n = 8, 9)]{1.\ -BH^{2+}} (\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}C_2B_{n-1}H_{n+1}) \quad (1)$$

An attempt to effect polyhedral contraction upon the orange, 13-vertex metallocarborane (η-C_5H_5)Co^{III}(η-6,7-$C_2B_{10}H_{12}$)[6,7] surprisingly resulted in the isolation of an anionic product $[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}CB_7H_8)]^-$ in which the removal of four vertices from the starting material, three BH and one CH, had occurred.[8] The extent of degradation of the starting complex and the removal of a polyhedral CH unit are unprecedented in metallocarborane chemistry.

Analysis of the 80.5-MHz ^{11}B nmr spectrum of the tetramethylammonium salt $[(CH_3)_4N][(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}CB_7H_8)]$ led to the suggestion that the structure of the anion was based on a nine-vertex, tricapped trigonal prism similar to the geometries found for $B_9H_9{}^{2-}$,[9] $C_2B_7H_7(CH_3)_2$,[10] and $[(\eta\text{-}C_2B_6H_8)Mn(CO)_3]^-$.[11] The unique carbon atom is required to reside on a mirror plane of the tricapped trigonal prism; however spectroscopic data could not establish which of the possible polyhedral positions was occupied by the carbon atom.

We have carried out a full three-dimensional X-ray crystallographic study of the cesium salt $Cs[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}CB_7H_8)]$ in order to confirm the proposed geometry of the anion and determine the position of the polyhedral carbon atom. The structure of this complex is also of interest due to its recent use as the starting material in the synthesis of several isomeric heterobimetallocarboranes of the formula $(C_5H_5)_2CoNiCB_7H_8$.[12]

Unit Cell and Space Group

A sample of the complex was furnished by Dr. Donald F. Dustin. It is air stable and does not decompose upon exposure to X-rays.

Preliminary X-ray diffraction photographs of the black, brick-shaped crystals indicated monoclinic symmetry. Upper layer Weissenberg photographs (taken with Cu Kα radiation) revealed the systematic absences hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, indicating space groups Cc or $C2/c$ ($C_s{}^4$, No. 9, and $C_{2h}{}^6$, No. 15, respectively);[13] successful solution was accomplished in the latter, centrosymmetric, space group.

Unit cell parameters and their standard deviations, obtained from a least-squares refinement of the positions of 15 accurately centered reflections, are $a = 12.643$ (2) Å, $b = 11.815$ (2) Å, $c = 16.376$ (2) Å, and $\beta = 90.34$ (2)°. The unit cell volume is 2446.3 (5) Å^3. The observed density ($\rho_{obsd} = 1.92 \pm 0.02$ g cm^{-3}, by flotation in hexane-bromoform) is in good agreement with the value calculated for mol wt 352.69 and $Z = 8$ ($\rho_{calcd} = 1.916$ g cm^{-3}).

Collection and Reduction of the Diffraction Data

Intensity data were collected on a Syntex $P\bar{1}$ automatic diffractom-

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eter. Monochromatic molybdenum Kα radiation (λ 0.71069 Å) was achieved by use of a graphite crystal monochromator. The crystal chosen for the data collection was a parallelepiped bounded by $\{110\}$, $\{1\bar{1}0\}$, and $\{10\bar{3}\}$ and their centrosymmetrically related faces. Crystal dimensions normal to these faces were 0.125, 0.095, and 0.44 mm, respectively.

A scan rate of 2.4°/min from 1.5° below the Kα_1 reflection to 1.0° above Kα_2 was employed with a θ-2θ scan technique. The ratio of time spent in counting background to the time spent in counting the reflection was 0.8. The scintillation counter was 18.5 cm from the crystal and equipped with a 1-mm collimator. A takeoff angle of 4° was employed.

A total of 2653 unique reflections were collected to the limit $2\theta_{\max} = 50.0°$. $I(hkl)$, the intensity of the reflection hkl, and $\sigma[I(hkl)]$, its estimated standard deviation, were calculated according to the equations $I = \mathrm{CT} - (t_c/t_b)(B_1 + B_2)/2$ and $\sigma(I) = [\sigma_s^2 + (0.04I)^2]^{1/2}$ where I is the net integrated intensity, CT is the total integrated count, t_c and t_b are times employed for counting the scan and background, respectively, B_1 and B_2 are the background counts on the low and high sides of the peak, and σ_s is the standard deviation of the intensity due to counting statistics. Reflections having an intensity less than 3 times their standard deviations were defined as unobserved and not included in subsequent calculations.

Three standard reflections were measured after every 97 reflections to monitor changes in tube intensity or crystal deterioration. No significant changes in intensities were observed over the period of data collection. All data were adjusted for Lorentz and polarization effects and edited to remove unobserved reflections.[14]

Solution and Refinement of the Structure

A Patterson map calculated using the 1523 observed reflections was solved with some difficulty to afford coordinates of the cesium and cobalt atoms. The near-identical values of y and z for the two heavy atoms and the proximity of y's to $^1/_8$ made assignment of the Cs-Cs, Cs-Co, and Co-Co vectors ambiguous. Several trial solutions for the cesium and cobalt atom positions were found, and a least-squares cycle was run on one of them in which positional parameters and the scale factor were refined. A three-dimensional Fourier synthesis, phased on the refined parameters ($R = 22.9\%$ and $R_w = 27.2\%$[15]) showed the positions of all other nonhydrogen atoms. Three cycles of full-matrix least-squares refinement of the coordinates and isotropic temperature factors of all 15 atoms (all cage atoms treated as boron atoms) reduced R to 10.3% and R_w to 13.3%.

Two more least-squares cycles, with anisotropic temperature factors assigned to the cesium and cobalt atoms and anomalous scattering corrections, gave $R = 7.4\%$ and $R_w = 9.7\%$. Inspection of the observed and calculated structure factors at this point revealed that several reflections with small values of l showed a significant difference, $F_o < F_c$. An absorption correction was made at this time ($\mu = 43.96$ for Mo Kα radiation), with transmission factors ranging from 0.819 for (002) to 0.396 for (110). Three cycles of least-squares refinement on the corrected data gave $R = 5.1\%$ and $R_w = 6.0\%$. A difference Fourier synthesis calculated at this time showed the positions of three of the cyclopentadienyl hydrogen atoms and six of the cage hydrogen atoms. These atomic positions were included in all subsequent calculations, but these parameters were not refined. Inspection of bond distances in the cage at this stage uniquely established the location of the carbon atom at position 5 (Figure 1); distances to the atom in this position ranged from 1.60 to 1.64 Å, while distances between other cage atoms were 1.70–2.03 Å. Subsequent refinement treated this atom as a carbon.

Anisotropic refinement of cyclopentadienyl carbon atoms and cage boron atoms whose terminal hydrogen atoms had been located reduced R to 4.4% and R_w to 5.0%. At this point two reflections which showed evidence of being affected by extinction, (202) and $(20\bar{2})$, were removed from further calculations and a second difference Fourier map was calculated. This map revealed the position of one additional cage hydrogen atom. Positions for the three remaining hydrogen atoms were calculated and included in subsequent calculations, but not refined. Three further least-squares cycles, with anisotropic temperature factors assigned to all heavy atoms, resulted in convergence $[(\Delta/\sigma)_{\max} < 0.2]$ at $R = 4.0\%$ and $R_w = 4.6\%$. The standard deviation of an observation of unit weight was 1.47.

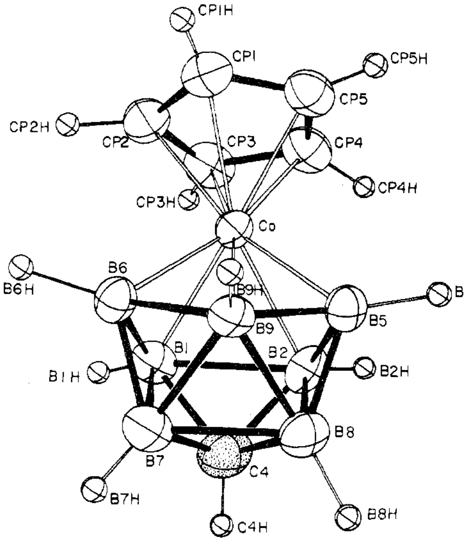

Figure 1. Structure and numbering of the $[C_5H_5CoCB_7H_8]^-$ anion. The hydrogen atoms have been given an arbitrary radius of 0.1 Å.

Scattering factors for neutral cobalt, carbon, and boron and unipositive cesium were taken from ref 16; hydrogen scattering factors were obtained from Stewart, Davidson, and Simpson;[17] and the real and imaginary corrections for anomalous scattering of cesium and cobalt were taken from Cromer.[18] The function $\Sigma w||F_o| - |F_c||^2$ was minimized during least-squares refinement.

The final observed atomic fractional coordinates are collected in Table I. Anisotropic thermal parameters are listed in Table II.

The Molecular Structure

Intramolecular distances and their estimated standard deviations (esd's) are listed in Table IIIa. Average bond distances, with their root-mean-square deviations, are collected in Table IIIb. The individual bond angles and their associated esd's are presented in Table IV. The structure of the $[(C_5H_5)Co(CB_7H_8)]^-$ anion is shown in Figure 1, which illustrates the numbering system employed.[19]

In the original reports of the preparation of the $[(C_5H_5)Co(CB_7H_8)]^-$ anion,[8] a structure similar to that shown in Figure 1 but with the positions of C4 and B9 interconverted was proposed, although the alternate structure which we have found in this work was not ruled out at that time. Our results agree with the observation that carbon atoms in carboranes and metallocarboranes generally occupy low-coordinate positions.[20,21]

The $[(C_5H_5)Co(CB_7H_8)]^-$ anion consists formally of a d^6 cobalt(III) atom sandwiched between a planar (Table V) cyclopentadienide ring and a five-boron-atom face of the $CB_7H_8^{3-}$ ligand. If the cobalt atom is considered to be a vertex, the CoCB$_7$ group has the shape of a distorted tricapped trigonal prism in which the caps are C4, B5, and B6, and the trigonal faces consist of Co, B1, B2 and B7, B8, B9 (Figure 1). This group has an almost perfect noncrystallographic mirror plane through the atoms Co, B9, and C4;

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(14) The programs used in this work included locally written data reduction programs; JBPATT, JBFOUR, and PEAKLIST, modified versions of Fourier programs written by J. Blount; local versions of ORFLS (Busing, Martin, and Levy), structure factor calculations and full-matrix least-squares refinement; ORTEP (C. K. Johnson), figure plotting; ABSN (Coppens), absorption correction; MGTL (Gantzel and Trueblood), least-squares planes; and ORFFE (Busing, Martin, and Levy), distance, angle, and error computations. All calculations were carried out on an IBM 360-91KK computer operated by the UCLA Campus Computing Nework.

(15) $R = [\Sigma ||F_o| - |F_c||/\Sigma |F_o|]$; $R_w = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/(\sigma_F)^2$.

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Table I. Final Atomic Positions[a]

Atom	x	y	z	Atom	x	y	z
			I. Heavy Atoms				
Cs	0.10159 (5)	0.12223 (5)	0.38920 (4)	B2	0.7738 (9)	0.5159 (9)	0.2220 (6)
Co	0.82683 (8)	0.60107 (9)	0.11133 (6)	C4	0.7559 (7)	0.3876 (8)	0.1968 (5)
Cp1	0.8772 (8)	0.7243 (7)	0.0295 (5)	B5	0.6876 (8)	0.5992 (8)	0.1664 (5)
Cp2	0.9600 (7)	0.6472 (7)	0.0451 (5)	B6	0.7934 (8)	0.4659 (8)	0.0445 (5)
Cp3	0.9820 (7)	0.6489 (7)	0.1303 (6)	B7	0.7213 (8)	0.3749 (8)	0.1014 (6)
Cp4	0.9117 (8)	0.7293 (7)	0.1671 (5)	B8	0.6520 (8)	0.4645 (9)	0.1834 (6)
Cp5	0.8492 (8)	0.7751 (7)	0.1034 (6)	B9	0.6775 (8)	0.5251 (8)	0.0783 (6)
B1	0.8475 (9)	0.4235 (8)	0.1352 (6)				
			II. Hydrogen Atoms[b]				
Cp1H	0.8467	0.7509	−0.0287	C4H[c]	0.7650	0.3133	0.2425
Cp2H	0.9875	0.5898	−0.0002	B5H	0.6351	0.6678	0.1981
Cp3H[c]	1.0374	0.6004	0.1604	B6H	0.8293	0.4375	−0.0227
Cp4H	0.9081	0.7364	0.2371	B7H	0.6875	0.2979	0.0755
Cp5H[c]	0.7929	0.8354	0.1102	B8H	0.5772	0.4228	0.2166
B1H	0.9292	0.3694	0.1382	B9H	0.6214	0.5625	0.0250
B2H	0.7928	0.5554	0.2846				

[a] Estimated standard deviations, shown in parentheses, refer to the last digit of the preceding number. [b] Coordinates found on difference Fourier map, included but not refined in final least-squares cycles. [c] Calculated positions, assuming a C–H distance of 1.0 Å; included but not refined in final least-squares cycles.

Table II. Anisotropic Thermal Parameters[a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Cs	45.6 (5)	77.7 (5)	36.5 (3)	−5.5 (4)	−2.1 (2)	12.3 (3)
Co	24.6 (8)	41.3 (8)	23.0 (4)	−1.1 (6)	−0.4 (4)	−0.8 (5)
Cp1	53 (8)	61 (7)	28 (4)	−16 (6)	0 (4)	8 (4)
Cp2	37 (6)	65 (7)	40 (4)	−17 (6)	17 (4)	−2 (4)
Cp3	17 (6)	62 (8)	59 (5)	−1 (5)	−6 (4)	5 (5)
Cp4	45 (7)	54 (7)	40 (4)	−16 (6)	−13 (4)	−9 (4)
Cp5	39 (7)	42 (6)	47 (5)	−10 (5)	−3 (4)	−1 (4)
B1	26 (7)	43 (7)	45 (5)	−3 (6)	−4 (5)	4 (5)
B2	44 (8)	85 (10)	19 (3)	7 (7)	6 (4)	−3 (5)
C4	45 (7)	70 (8)	38 (4)	1 (7)	7 (4)	14 (5)
B5	33 (7)	54 (8)	28 (4)	1 (6)	3 (4)	−4 (4)
B6	32 (7)	54 (8)	23 (4)	−6 (6)	5 (4)	−6 (4)
B7	33 (7)	52 (8)	43 (4)	3 (7)	4 (4)	−1 (5)
B8	27 (7)	65 (9)	37 (5)	−1 (6)	11 (5)	14 (5)
B9	28 (7)	45 (7)	29 (4)	−4 (6)	−2 (4)	3 (4)

[a] See footnote *a* of Table I. The anisotropic temperature factor T is defined as $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Thermal ellipsoids are depicted in Figure 1.

Table IIIa. Interatomic Distances[a]

Atoms	Dist, Å	Atoms	Dist, Å
	I. Distances around Cobalt		
Co–Cp1	2.081 (8)	Co–B1	2.150 (9)
Co–Cp2	2.080 (8)	Co–B2	2.183 (10)
Co–Cp3	2.063 (9)	Co–B5	1.983 (10)
Co–Cp4	2.066 (8)	Co–B6	1.980 (9)
Co–Cp5	2.080 (8)	Co–B9	2.157 (10)
	II. Distances in the Cyclopentadienyl Ring		
Cp1–Cp2	1.409 (13)	Cp3–Cp4	1.436 (13)
Cp1–Cp5	1.398 (12)	Cp4–Cp5	1.413 (12)
Cp2–Cp3	1.421 (13)		
	III. Boron–Boron Distances in the $CB_7H_8^{3-}$ Cage		
B1–B2	2.025 (14)	B5–B8	1.678 (14)
B1–B6	1.706 (14)	B6–B7	1.693 (13)
B1–B7	1.781 (14)	B6–B9	1.719 (14)
B2–B5	1.724 (14)	B7–B8	1.925 (14)
B2–B8	1.768 (15)	B9–B7	1.897 (13)
B5–B9	1.692 (13)	B9–B8	1.894 (13)
	IV. Carbon–Boron Distances in the $CB_7H_8^{3-}$ Cage		
C4–B1	1.598 (14)	C4–B7	1.626 (14)
C4–B2	1.587 (14)	C4–B8	1.611 (13)

[a] See footnote *a*, Table I.

Table IIIb. Average Bond Lengths

Atoms	No.	Range,[a] Å	Av,[b] Å
Co–C	5	2.080 (8)–2.063 (9)	2.07 (1)
Co–B	5	1.980 (10)–2.183 (10)	2.09 (10)
B–B	12	1.678 (14)–2.025 (14)	1.79 (12)
C–B	4	1.587 (14)–1.626 (14)	1.61 (2)
C–C	5	1.398 (12)–1.436 (12)	1.42 (1)

[a] See footnote *a*, Table I. [b] Esd's for average bond lengths were calculated using the equation $\sigma^2 = \Sigma_{i=1}^{i=N}(\chi_i - \bar{\chi})^2]/(N-1)$ where χ_i is the *i*th bond length and $\bar{\chi}$ is the mean of the N equivalent bond lengths.

variations from mirror symmetry are within three standard deviations of the bond distances and angles except for Co-B1-B2 and its related angle Co-B2-B1.

The cobalt atom is bonded unequally to the five boron atoms of the carborane ligand; three of the Co–B distances are in the range 2.15-2.18 Å, and the remaining two, which are to the low-coordinate capping atoms B4 and B6, are 1.97 and 1.98 Å. Similar bond length inequalities are observed in $B_9H_9^{2-}$ [9] and may reflect the ability of the lower coordinate caps to form stronger bonds.

The five carbon atoms of the cyclopentadienyl ring are equidistant from the cobalt atom within experimental error. The cyclopentadienyl ring is rotated such that the mirror plane of the tricapped trigonal prism does not pass through it, thereby presumably minimizing intra- and intermolecular repulsions. The ring itself is strictly planar (Table V) and exhibits the variations in the carbon–carbon bond distances common in π-cyclopentadienyl metal complexes. The empirical correlation[22] that carbon atoms forming the short-

(22) M. E. Gress and R. A. Jacobson, *Inorg. Chem.*, 12, 1746 (1973), and references therein.

Table IV. Interatomic Angles[a]

Atoms 1-2-3	Angle, deg	Atoms 1-2-3	Angle, deg
I. Angles around Cobalt			
A. C_5H_5-Co-C_5H_5			
Cp1-Co-Cp2	39.6 (4)	Cp1-Co-Cp3	67.1 (4)
Cp1-Co-Cp5	39.3 (4)	Cp1-Co-Cp4	67.2 (4)
Cp2-Co-Cp3	40.1 (4)	Cp2-Co-Cp4	67.6 (4)
Cp3-Co-Cp4	40.5 (4)	Cp2-Co-Cp5	66.2 (4)
Cp4-Co-Cp5	40.7 (4)	Cp3-Co-Cp5	67.0 (4)
B. $CB_7H_8^{3-}$-Co-$CB_7H_8^{3-}$			
B1-Co-B2	55.7 (4)	B1-Co-B9	75.3 (4)
B1-Co-B6	48.6 (4)	B2-Co-B9	75.1 (4)
B6-Co-B9	48.9 (4)	B1-Co-B5	90.8 (4)
B5-Co-B9	48.0 (4)	B2-Co-B6	91.2 (4)
B2-Co-B5	48.6 (4)	B5-Co-B6	93.2 (4)
C. $C_5H_5^-$-Co-$CB_7H_8^{3-}$			
Cp1-Co-B1	139.7 (4)	Cp3-Co-B5	141.3 (4)
Cp1-Co-B2	162.5 (6)	Cp3-Co-B9	169.1 (4)
Cp1-Co-B5	125.2 (4)	Cp4-Co-B1	124.9 (4)
Cp1-Co-B6	105.9 (4)	Cp4-Co-B2	97.6 (4)
Cp1-Co-B9	113.6 (4)	Cp4-Co-B6	160.8 (4)
Cp2-Co-B1	104.6 (4)	Cp4-Co-B5	105.5 (4)
Cp2-Co-B2	143.9 (4)	Cp4-Co-B9	150.2 (4)
Cp2-Co-B5	164.4 (4)	Cp5-Co-B1	163.7 (4)
Cp2-Co-B6	95.4 (4)	Cp5-Co-B2	123.4 (4)
Cp2-Co-B9	133.5 (4)	Cp5-Co-B6	142.3 (4)
Cp3-Co-B1	97.2 (4)	Cp5-Co-B5	99.3 (4)
Cp3-Co-B2	107.3 (4)	Cp5-Co-B9	121.0 (4)
Cp3-Co-B6	120.2 (4)		
II. Cyclopentadienyl Ring Angles			
A. C-C-C Angles			
Cp1-Cp2-Cp3	108.1 (8)	Cp4-Cp5-Cp1	109.3 (9)
Cp2-Cp3-Cp4	107.6 (7)	Cp5-Cp1-Cp2	108.2 (8)
Cp3-Cp4-Cp5	106.8 (8)		
B. C-C-Co Angles			
Cp1-Cp2-Co	70.3 (5)	Cp3-Cp4-Co	69.5 (5)
Cp1-Cp5-Co	70.4 (5)	Cp4-Cp3-Co	69.7 (5)
Cp2-Cp1-Co	70.2 (5)	Cp4-Cp5-Co	69.5 (5)
Cp2-Cp3-Co	70.6 (5)	Cp5-Cp4-Co	70.6 (5)
Cp3-Cp2-Co	69.3 (5)	Cp5-Cp1-Co	70.3 (5)

Atoms 1-2-3	Angle, deg	Atoms 1-2-3	Angle, deg
III. $CB_7H_8^{3-}$ Cage Angles			
A. B-B-B Angles			
B2-B1-B6	105.6 (7)	B6-B7-B8	106.5 (7)
B2-B1-B7	88.6 (7)	B6-B7-B9	56.9 (5)
B6-B1-B7	58.0 (6)	B8-B7-B9	59.4 (5)
B1-B2-B5	103.2 (6)	B2-B8-B7	92.3 (6)
B1-B2-B8	88.1 (6)	B2-B8-B9	92.5 (6)
B5-B2-B8	57.4 (6)	B5-B8-B7	106.4 (6)
B2-B5-B8	62.6 (6)	B5-B8-B9	56.2 (5)
B2-B5-B9	101.5 (7)	B7-B8-B9	59.6 (5)
B8-B5-B9	68.4 (6)	B5-B9-B6	115.1 (7)
B1-B6-B7	63.2 (6)	B5-B9-B7	107.0 (7)
B1-B6-B9	100.3 (7)	B5-B9-B8	55.4 (5)
B7-B6-B9	67.6 (6)	B6-B9-B7	55.6 (5)
B1-B7-B6	58.8 (6)	B6-B9-B8	106.8 (6)
B1-B7-B8	91.0 (7)	B7-B9-B8	61.0 (5)
B1-B7-B9	91.2 (6)		
B. C-B-B Angles			
B2-B1-C4	50.3 (5)	C4-B7-B6	109.1 (7)
C4-B1-B6	109.8 (8)	C4-B7-B8	53.2 (5)
C4-B1-B7	57.2 (6)	C4-B7-B9	100.5 (6)
B1-B2-C4	50.8 (5)	B2-B8-C4	55.8 (6)
C4-B2-B5	108.6 (8)	C4-B8-B5	109.8 (7)
C4-B2-B8	57.1 (6)	C4-B8-B7	53.9 (5)
B1-B7-C4	55.7 (6)	C4-B8-B9	101.2 (6)
C. B-C-B Angles			
B1-C4-B2	78.9 (6)	B2-C4-B7	112.0 (7)
B1-C4-B7	67.1 (6)	B2-C4-B8	67.1 (6)
B1-C4-B8	111.0 (7)	B7-C4-B8	73.0 (6)
D. B-B-Co Angles			
B2-B1-Co	62.9 (4)	B9-B5-Co	71.4 (5)
B6-B1-Co	60.5 (4)	B1-B6-Co	70.9 (5)
B7-B1-Co	98.6 (6)	B7-B6-Co	108.8 (6)
B1-B2-Co	61.3 (4)	B9-B6-Co	70.9 (5)
B5-B2-Co	59.6 (4)	B5-B9-Co	60.6 (4)
B8-B2-Co	97.6 (5)	B6-B9-Co	60.2 (4)
B2-B5-Co	71.8 (5)	B7-B9-Co	94.9 (5)
B8-B5-Co	109.0 (6)	B8-B9-Co	94.7 (5)
E. C-B-Co Angles			
C4-B1-Co	106.6 (6)	C4-B2-Co	105.6 (5)

[a] See footnote *a*, Table I.

Table V. Important Planes in the Molecule[a]

Atom	Dev, Å	Atom	Dev, Å
Cyclopentadienyl Ring: Cp1, Cp2, Cp3, Cp4, Cp5			
$-0.6768X - 0.7219Y + 0.1440Z = -13.621$			
Cp1	−0.001	Cp4	−0.008
Cp2	−0.004	Cp5	+0.005
Cp3	+0.008		
Tetragonal-Prismatic Face: B7, B8, B1, B2			
$0.0511X - 0.7716Y + 0.6340Z = -1.905$			
B7	+0.005	B1	−0.005
B8	−0.006	B2	+0.005
Tetragonal-Prismatic Face: B9, B8, B2, Co			
$-0.4660X + 0.8404Y + 0.2766Z = +1.595$			
B9	−0.013	B2	−0.014
B8	+0.016	Co	+0.012
Tetragonal-Prismatic Face: B9, B7, B1, Co			
$-0.3404X + 0.1153Y + 0.9332Z = -1.019$			
B9	+0.018	B1	+0.019
B7	−0.021	Co	−0.016
Trigonal-Prismatic Face: B7, B8, B9			
$0.8858X + 0.3422Y + 0.3133Z = +10.106$			
Trigonal-Prismatic Face: Co, B1, B2			
$0.8795X + 0.1901Y + 0.4363Z = +11.330$			

[a] Planes are defined as $C_1X + C_2Y + C_3Z = d$, where X, Y, Z are orthogonal coordinates (in angstroms) and the axes parallel *a*, *b*, *c**.

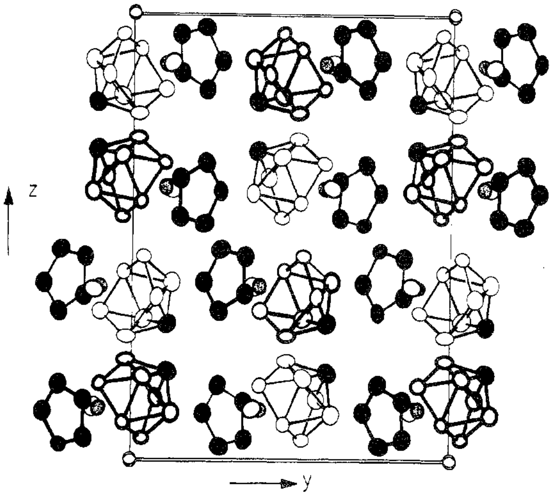

Figure 2. The packing of ions within the unit cell. Hydrogen atoms have been omitted for clarity.

est metal–carbon bonds have the longest C–C bonds holds true in this complex.

The presence of the cobalt atom in a trigonal plane of the tricapped trigonal prism results in more severe distortion from the idealized geometry than observed in $B_9H_9^{2-}$ or $(CH_3)_2C_2B_7H_7$. The extent of this distortion is evidenced by the dihedral angle between the two triangular faces of 11.2° and is due to the longer bonds to the cobalt atom.

The cesium cations reside in general positions in the unit cell. The closest contact between cation and anion is Cs–Cp3H at 3.807 (1) Å; all other contacts are greater than 4 Å. The eight molecules in the unit cell are arranged as shown in Figure 2.

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Registry No. $Cs^+[(C_5H_5)Co(CB_7H_8)]^-$, 51248-07-8; $Cs^+[(C_5H_5)Co(CB_7H_8)]^-$ (ref 8), 38882-83-6.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1393.

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Structures of Metallocarboranes. III. Crystal and Molecular Structure of the Bimetallocarborane Complex 2,3-Di-η-cyclopentadienyl-1,7-dicarba-2,3-dicobaltadodecaborane(10), $(\eta\text{-}C_5H_5)_2Co_2C_2B_8H_{10}$

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The crystal and molecular structure of $2,3\text{-}(\eta\text{-}C_5H_5)_2\text{-}2,3\text{-}Co_2\text{-}1,7\text{-}C_2B_8H_{10}$ has been determined by a complete three-dimensional X-ray diffraction study. The compound crystallizes in the monoclinic centrosymmetric space group $P2_1/n$ with a = 14.940 (4) Å, b = 9.006 (2) Å, c = 11.503 (3) Å, β = 93.08 (2)°, and Z = 4. Observed and calculated densities are 1.56 (2) and 1.585 g cm^{-3}, respectively. Diffraction data to $2\theta_{max}$ = 50° (Mo Kα radiation) were collected on a Syntex $P\bar{1}$ automated diffractometer, and the structure was solved by conventional Patterson, Fourier, and full-matrix least-squares refinement techniques. The final discrepancy index is R = 6.7% for 1435 independent nonzero reflections. The molecule can be described as a distorted icosahedron comprised of two cobalt, two carbon, and eight boron vertices. The cobalt atoms occupy adjacent vertices with a metal–metal distance of 2.387 (2) Å and are further coordinated to π-bonded cyclopentadienyl rings with an average bond distance of 2.05 (2) Å.

Introduction

The "polyhedral expansion reaction" of carboranes and metallocarboranes[1] has proven to be an important new synthetic route to mono- and polymetallocarboranes. The treatment of $1,6\text{-}C_2B_8H_{10}$ with sodium naphthalide, sodium cyclopentadienide, and cobalt(II) chloride afforded the eleven-vertex polyhedral complex $1\text{-}(\eta\text{-}C_5H_5)\text{-}1\text{-}Co\text{-}2,3\text{-}C_2B_8H_{10}$.[2] Further polyhedral expansion of this metallocarborane afforded the bimetallic complex $(C_5H_5)_2Co_2C_2B_8H_{10}$,[3] which was also formed in the direct expansion of $1,6\text{-}C_2B_8H_{10}$ but in much lower yield.

The nmr spectral properties of this bimetallocarborane were consistent with an icosahedral arrangement of the $Co_2C_2B_8$ framework, but the relative positions of the cobalt atoms and carbon atoms could not be uniquely defined.[3] When it was established[4] that adjacent cobalt atoms were present in $(C_5H_5)_2Co_2C_2B_6H_8$, a product from the polyhedral expansion of $1,7\text{-}C_2B_6H_8$,[5] a structure for $(C_5H_5)_2Co_2C_2B_8H_{10}$ involving a similar metal-metal interaction was suggested.[6] This work reports an X-ray crystallographic investigation which provides detailed molecular parameters for this compound.

Unit Cell and Space Group

A sample of the compound was furnished by Dr. W. J. Evans. It is air stable and does not decompose upon exposure to X-rays.

Preliminary X-ray diffraction photographs of the green needle-shaped crystals indicated monoclinic symmetry with systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, indicative of space group $P2_1/n$, an alternate setting of $P2_1/c$ (C_{2h}^5, No. 14).[7] The density, measured by flotation in aqueous potassium iodide solution, was 1.56 (2) g cm^{-3}, in reasonable agreement with the calculated density of 1.585 g cm^{-3} for Z = 4.

Collection and Reduction of X-Ray Data

Intensity data were collected on a Syntex $P\bar{1}$ automated diffractometer equipped with scintillation counter and pulse height analyzer. A graphite crystal was employed to produce monochromatic Mo Kα

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