

Acknowledgments. This work was supported by the National Science Foundation (Grant MPS 75-03056) and the National Institute of General Medical Sciences, U.S. Public Health Service (Grants GM 22432, 10224, and 11072), to whom grateful acknowledgment is made. We wish to thank Dr. Craig Bradley of Bruker Scientific, Inc., and Ms. Valerie Hu for their assistance in measuring the ^{15}N and ^1H NMR spectra.

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Tetracarbon Metallocarboranes. 4.¹ Structure of the Nido System $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_6\text{OC}_2\text{H}_5$. The Problem of the Structural Diversity of Electronically Analogous Cage Systems

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Abstract: The crystal structure of 12-($\text{C}_2\text{H}_5\text{O}$)-1,2,3,7,8-($\eta^5\text{-C}_5\text{H}_5$) $\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_6$, a red, air-stable metallocarborane, has been determined from a single-crystal x-ray diffraction study. The molecule has a novel structure resembling a severely distorted icosahedron whose two halves have been partially separated, creating a huge opening on one side. The structure can be viewed as a derivative of $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ in which an apex BH unit has been replaced by $(\eta^5\text{-C}_5\text{H}_5)\text{Co}$, and the central C-C bond in the cage has been severed. The title compound is the fifth example of a 12-vertex, 28-electron cage system to have been structurally characterized, the others being the $\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{11}^-$ ion ($\text{R} = \text{C}_6\text{H}_5$ or CH_3), $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_8$, and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_4\text{B}_6\text{H}_{10}$. The fact that four distinctly different cage geometries are represented in this group of five compounds, despite their cage-isoelectronic relationship, is discussed in relation to the skeletal electron-count theory for cluster compounds, and some limitations of the theory are examined. Crystal data follow: space group $P2_1/n$; $a = 8.322$ (3), $b = 14.284$ (5), $c = 16.810$ (8) Å; $\beta = 102.94$ (3)°; $\rho_{\text{calcd}} = 1.230$ g cm⁻³ for $Z = 4$. The structure was refined by full-matrix least-squares methods to a final R value of 0.065 and R_w of 0.083 for the 1808 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

The success of the polyhedral skeletal electron-count theory² in rationalizing the geometries of a wide array of cage and cluster compounds and in providing a reliable means of predicting the structures of new species is well documented.^{2,3} The theory is particularly useful in dealing with cluster systems which are not readily amenable to detailed molecular orbital calculations, such as those having low symmetry or containing several types of framework atoms. While full awareness of these ideas among chemists has not yet arrived, inorganic textbooks have begun to incorporate them, and in time the art of skeletal electron counting may be as familiar in chemical education as is, for example, the valence shell electron pair repulsion (VSEPR) model.⁴

Like the VSEPR and other qualitative approaches to chemical bonding, it is inevitable that limits to the utility of the skeletal electron-count theory will be found; situations will be discovered in which the theory can be applied only with modification, and others in which it fails altogether. It is obviously important to the further development of cluster chemistry to probe these limiting cases and to try to identify the factors which cause deviation from the predicted structures. It can be hoped that in time this will lead to a more sophisticated version of the theory which will increase its usefulness still further.

In our work we have encountered several situations in which the electron-counting rules are violated, a recent example being the 14-vertex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ isomers which are discussed elsewhere.⁵ In the present article we describe the crystallographic structure determination of a recently prepared⁶ metallocarborane, $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_6\text{OC}_2\text{H}_5$, which is one of five structurally established examples of a 12-vertex, 28-electron cage system. Of these five compounds, we are amazed to find that no fewer than four markedly different polyhedral geometries are represented, and hence a detailed comparison of their structures seems warranted.

Experimental Section

Red crystals of 12-($\text{C}_2\text{H}_5\text{O}$)-1,2,3,7,8-($\eta^5\text{-C}_5\text{H}_5$) $\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_6$, prepared⁶ by the treatment of $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2$ with CoCl_2 and C_5H_6 in ethanolic KOH at 70 °C, were grown by the vapor diffusion of pentane into a methylene chloride solution of the compound. One crystal was mounted on a glass fiber in an arbitrary orientation and examined by preliminary precession photographs which indicated acceptable crystal quality. The chosen crystal was a rectangular parallelepiped with one edge truncated, creating a seventh face. Approximate maximum dimensions were 0.21 × 0.23 × 0.48 mm. Crystal data follow: $\text{CoOC}_{15}\text{B}_7\text{H}_{28}$; mol wt 359.00; space group

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations^a

Atom	X	Y	Z	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Co	0.2486 (1)	0.154 00 (7)	0.089 45 (6)	0.0147 (1)	0.006 07 (5)	0.003 93 (3)	0.0020 (2)	0.0042 (1)	-0.001 82 (9)
O	-0.1543 (6)	0.1361 (4)	0.3308 (3)	0.0227 (9)	0.0074 (3)	0.0060 (2)	-0.001 (1)	0.0114 (7)	-0.0007 (5)
C(2)	0.1359 (8)	0.2599 (5)	0.1354 (4)	0.017 (1)	0.0053 (4)	0.0036 (3)	0.003 (1)	0.0035 (10)	-0.0011 (6)
C(3)	0.2928 (8)	0.2334 (5)	0.1873 (4)	0.012 (1)	0.0060 (4)	0.0044 (3)	0.001 (1)	0.0044 (9)	-0.0015 (6)
C(7)	0.0468 (9)	0.2558 (5)	0.2799 (4)	0.017 (1)	0.0048 (4)	0.0048 (3)	-0.002 (1)	0.0070 (10)	-0.0008 (6)
C(8)	0.1531 (9)	0.1849 (5)	0.3120 (4)	0.017 (1)	0.0062 (4)	0.0034 (3)	-0.006 (1)	0.0021 (10)	-0.0010 (6)
CM(2)	0.1059 (11)	0.3571 (5)	0.0960 (5)	0.029 (2)	0.0051 (4)	0.0054 (3)	0.006 (2)	0.0059 (13)	0.0039 (7)
CM(3)	0.4345 (10)	0.3056 (6)	0.2121 (5)	0.017 (1)	0.0077 (5)	0.0068 (4)	-0.012 (1)	0.0028 (13)	-0.0034 (8)
CM(7)	0.0300 (12)	0.3496 (6)	0.3241 (5)	0.037 (2)	0.0059 (5)	0.0069 (4)	-0.004 (2)	0.0169 (12)	-0.0059 (7)
CM(8)	0.2653 (12)	0.1856 (8)	0.3991 (5)	0.027 (2)	0.0135 (8)	0.0034 (3)	-0.008 (2)	-0.0044 (14)	0.0002 (9)
CE(1)	-0.2284 (10)	0.0416 (6)	0.3313 (6)	0.021 (2)	0.0078 (5)	0.0083 (5)	-0.011 (2)	0.0064 (14)	0.0015 (9)
CE(2)	-0.2084 (21)	0.0113 (9)	0.4133 (7)	0.103 (5)	0.0126 (8)	0.0077 (6)	-0.040 (3)	0.0186 (27)	0.0003 (12)
CP(1)	0.4635 (10)	0.1559 (8)	0.0506 (5)	0.023 (1)	0.0149 (9)	0.0064 (4)	0.000 (2)	0.0162 (10)	-0.0020 (10)
CP(2)	0.4103 (12)	0.0675 (7)	0.0530 (5)	0.054 (2)	0.0079 (6)	0.0106 (4)	0.019 (2)	0.0385 (11)	0.0040 (8)
CP(3)	0.2586 (11)	0.0603 (8)	0.0004 (5)	0.030 (2)	0.0229 (9)	0.0109 (4)	-0.024 (2)	0.0233 (13)	-0.0255 (9)
CP(4)	0.2133 (13)	0.1429 (10)	-0.0348 (6)	0.040 (2)	0.0300 (14)	0.0039 (3)	0.040 (3)	0.0095 (14)	0.0007 (13)
CP(5)	0.3436 (14)	0.2073 (7)	-0.0046 (5)	0.075 (2)	0.0085 (6)	0.0089 (4)	0.009 (2)	0.0428 (12)	0.0027 (9)
B(4)	0.299 (1)	0.1341 (6)	0.2173 (5)	0.011 (1)	0.0062 (5)	0.0039 (3)	0.003 (1)	0.000 (1)	0.0002 (7)
B(5)	0.128 (1)	0.0715 (6)	0.1582 (5)	0.018 (2)	0.0054 (5)	0.0040 (3)	-0.002 (2)	0.003 (1)	-0.0021 (7)
B(6)	0.012 (1)	0.1721 (6)	0.1070 (5)	0.012 (1)	0.0062 (6)	0.0034 (3)	0.000 (1)	-0.000 (1)	-0.0014 (7)
B(9)	0.125 (1)	0.0873 (6)	0.2629 (5)	0.015 (1)	0.0055 (5)	0.0043 (4)	0.003 (2)	0.003 (1)	0.0004 (7)
B(10)	-0.058 (1)	0.1099 (6)	0.1835 (5)	0.013 (1)	0.0058 (5)	0.0043 (4)	-0.001 (2)	0.001 (1)	-0.0017 (8)
B(11)	-0.051 (1)	0.2339 (6)	0.1905 (5)	0.014 (1)	0.0060 (5)	0.0045 (4)	0.005 (2)	0.003 (1)	0.0009 (8)
B(12)	-0.052 (1)	0.1551 (6)	0.2781 (5)	0.016 (1)	0.0054 (5)	0.0043 (3)	0.000 (2)	0.003 (1)	-0.0006 (8)
HB(4)	0.417 (7)	0.102 (4)	0.250 (3)	3. (1)					
HB(5)	0.146 (8)	0.001 (4)	0.137 (4)	5. (2)					
HB(6)	-0.084 (7)	0.173 (4)	0.055 (3)	4. (1)					
HB(9)	0.148 (7)	0.022 (4)	0.303 (3)	4. (1)					
HB(10)	-0.169 (7)	0.065 (4)	0.165 (3)	5. (2)					
HB(11)	-0.148 (7)	0.267 (4)	0.164 (3)	5. (1)					

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

Table II. Bond Distances (Å)

Co-C(2)	2.022 (4)	B(10)-B(11)	1.774 (8)
Co-C(3)	1.963 (4)	B(10)-B(12)	1.707 (7)
Co-B(4)	2.115 (5)	B(11)-B(12)	1.854 (7)
Co-B(5)	2.059 (5)	C(2)-CM(2)	1.535 (6)
Co-B(6)	2.070 (5)	C(3)-CM(3)	1.552 (6)
Co-CP(1)	2.037 (5)	C(7)-CM(7)	1.555 (6)
Co-CP(2)	2.021 (5)	C(8)-CM(8)	1.550 (6)
Co-CP(3)	2.024 (6)	CP(1)-CP(2)	1.342 (9)
Co-CP(4)	2.048 (7)	CP(2)-CP(3)	1.37 (1)
Co-CP(5)	2.064 (6)	CP(3)-CP(4)	1.34 (1)
C(2)-C(3)	1.448 (5)	CP(4)-CP(5)	1.42 (1)
C(7)-C(8)	1.374 (6)	CP(5)-CP(1)	1.41 (1)
C(2)-B(6)	1.625 (6)	B(12)-O	1.383 (6)
C(2)-B(11)	2.019 (7)	O-CE(1)	1.484 (6)
C(3)-B(4)	1.502 (6)	CE(1)-CE(2)	1.419 (8)
C(7)-B(11)	1.572 (6)	B(4)-HB(4)	1.11 (3)
C(7)-B(12)	1.655 (6)	B(5)-HB(5)	1.08 (4)
C(8)-B(4)	2.326 (7)	B(6)-HB(6)	1.04 (3)
C(8)-B(9)	1.610 (6)	B(9)-HB(9)	1.14 (3)
C(8)-B(12)	1.731 (6)	B(10)-HB(10)	1.11 (4)
B(4)-B(5)	1.783 (7)	B(11)-HB(11)	0.95 (4)
B(4)-B(9)	1.908 (7)		
B(5)-B(6)	1.835 (7)		
B(5)-B(9)	1.781 (7)		
B(5)-B(10)	1.787 (8)		
B(6)-B(10)	1.767 (7)		
B(6)-B(11)	1.834 (7)		
B(9)-B(10)	1.817 (7)		
B(9)-B(12)	1.831 (7)		

$P2_1/n$, $Z = 4$; $a = 8.322 (3)$, $b = 14.284 (5)$, $c = 16.810 (8)$ Å; $\beta = 102.94 (3)^\circ$; $V = 1947 (2)$ Å³; $\mu(\text{Mo K}\alpha) = 9.183 \text{ cm}^{-1}$; $\rho(\text{calcd}) = 1.230 \text{ g/cm}^3$; $F(000) = 752$. For this crystal the Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and to provide approximate cell dimensions. Refined cell dimensions and their estimated standard deviations were

obtained from 28 accurately centered reflections using the Enraf-Nonius program UNICELL. The mosaicity of the crystal was examined by the ω scan technique and found acceptable. Systematic absences of $k = 2n + 1$ for $0k0$ and of $h + l = 2n + 1$ for $h0l$ uniquely determined the space group as $P2_1/n$. For $Z = 4$ this is consistent with the molecular formula assuming 20.3 Å³ per nonhydrogen atom. $P2_1/n$ is a nonstandard setting of $P2_1/c$ (no. 14) and can be converted to $P2_1/c$ by the transformation $a' = a$, $b' = b$, and $c' = -a + c$.

Collection and Reduction of the Data. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo K α radiation from a highly oriented graphite crystal monochromator. The θ - 2θ scan technique was used to record the intensities for all reflections for which $1^\circ \leq 2\theta \leq 48^\circ$. Scan widths were calculated from the formula $SW = A + B \tan \theta$ where A is estimated from the mosaicity of the crystal and B compensates for the increase in the width of the peak due to $K\alpha_1$ and $K\alpha_2$ splitting. The values of A and B were 0.60 and 0.30°, respectively. This calculated scan angle was extended at each side by 25% for background determination (BG1 and BG2). The net count (NC) was then calculated as $NC = \text{TOT} - 2(\text{BG1} + \text{BG2})$ where TOT is the estimated peak intensity. Reflection data were considered insignificant for intensities registering less than ten counts above background on a rapid prescan, and these reflections were rejected automatically by the computer. The intensities of three standard reflections were monitored at intervals of 100 reflections and showed no systematic trends. Raw intensity data were corrected for Lorentz-polarization effects which resulted in a total of 1984 intensities of which 1808 had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics using an ignorance factor of 0.03.⁷ These latter reflections were used in the final refinement of the structural parameters.

Solution and Refinement of the Structure. The coordinates of the cobalt atom were determined by inspection from a three-dimensional Patterson map. An electron density map phased on these coordinates after refinement yielded the remaining 23 nonhydrogen atoms. Least-squares refinement of the coordinates of all nonhydrogen atoms, first with isotropic and later with anisotropic thermal parameters, plus an absorption correction (maximum transmission factor = 0.88, minimum = 0.86), reduced R to 0.071 and R_w to 0.094. R and R_w are

Table III. Selected Bond Angles (deg)

C(2)-Co-C(3)	42.6 (2)	B(10)-B(9)-B(12)	55.8 (3)
C(3)-Co-B(4)	43.0 (2)	B(5)-B(10)-B(6)	62.2 (3)
B(4)-Co-B(5)	50.6 (2)	B(5)-B(10)-B(9)	59.2 (3)
B(5)-Co-B(6)	52.8 (2)	B(6)-B(10)-B(11)	62.4 (3)
B(6)-Co-C(2)	46.8 (2)	B(9)-B(10)-B(12)	62.5 (3)
Co-C(2)-C(3)	66.5 (2)	B(11)-B(10)-B(12)	64.3 (3)
Co-C(2)-B(6)	68.2 (2)	C(2)-B(11)-B(6)	49.6 (2)
B(6)-C(2)-B(11)	59.3 (3)	B(6)-B(11)-B(10)	58.6 (3)
Co-C(3)-C(2)	70.9 (2)	C(7)-B(11)-B(12)	57.1 (3)
Co-C(3)-B(4)	73.9 (2)	B(10)-B(11)-B(12)	56.1 (3)
Co-B(4)-C(3)	63.1 (2)	C(7)-B(12)-C(8)	47.8 (2)
Co-B(4)-B(5)	63.1 (2)	C(8)-B(12)-B(9)	53.6 (3)
B(5)-B(4)-B(9)	57.6 (3)	B(9)-B(12)-B(10)	61.7 (3)
Co-B(5)-B(4)	66.4 (2)	B(10)-B(12)-B(11)	59.6 (3)
Co-B(5)-B(6)	63.9 (2)	C(7)-B(12)-B(11)	52.9 (3)
B(4)-B(5)-B(9)	64.7 (3)	C(3)-C(2)-B(11)	111.1 (3)
B(6)-B(5)-B(10)	58.4 (3)	C(2)-C(3)-B(4)	114.2 (4)
B(9)-B(5)-B(10)	61.2 (3)	C(3)-B(4)-B(9)	119.5 (4)
Co-B(6)-C(2)	65.0 (2)	B(4)-B(9)-C(8)	82.3 (3)
Co-B(6)-B(5)	63.3 (2)	C(7)-C(8)-B(9)	115.4 (4)
C(2)-B(6)-B(11)	71.1 (3)	C(8)-C(7)-B(11)	112.4 (4)
B(5)-B(6)-B(10)	59.5 (3)	C(2)-B(11)-C(7)	96.4 (3)
B(10)-B(6)-B(11)	59.0 (3)	Co-C(2)-CM(2)	123.8 (3)
C(8)-C(7)-B(12)	69.0 (3)	C(3)-C(2)-CM(2)	122.3 (4)
B(11)-C(7)-B(12)	70.1 (3)	B(6)-C(2)-CM(2)	122.7 (4)
C(7)-C(8)-B(12)	63.2 (3)	B(11)-C(2)-CM(2)	107.3 (3)
B(9)-C(8)-B(12)	66.4 (3)	Co-C(3)-CM(3)	126.7 (3)
B(4)-B(9)-B(5)	57.7 (3)	C(2)-C(3)-CM(3)	121.1 (4)
B(5)-B(9)-B(10)	59.6 (3)	B(4)-C(3)-CM(3)	124.6 (4)
C(8)-B(9)-B(12)	60.0 (3)	C(8)-C(7)-CM(7)	124.5 (4)
		B(11)-C(7)-CM(7)	123.0 (4)
		B(12)-C(7)-CM(7)	131.3 (4)
		C(7)-C(8)-CM(8)	124.4 (4)
		B(9)-C(8)-CM(8)	118.6 (4)
		B(12)-C(8)-CM(8)	130.9 (4)
		C(7)-B(12)-O	122.3 (4)
		C(8)-B(12)-O	122.7 (4)
		B(9)-B(12)-O	128.0 (4)
		B(10)-B(12)-O	129.0 (4)
		B(11)-B(12)-O	137.7 (4)
		B(12)-O-CE(1)	119.8 (4)
		O-CE(1)-CE(2)	108.9 (5)
		CP(2)-CP(1)-CP(5)	108.7 (7)
		CP(1)-CP(2)-CP(3)	108.2 (7)
		CP(2)-CP(3)-CP(4)	110.3 (9)
		CP(3)-CP(4)-CP(5)	107.2 (8)
		CP(4)-CP(5)-CP(1)	105.6 (7)

defined as $\Sigma|F_o| - |F_c|/\Sigma|F_o|$ and $(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, respectively. A new electron density map phased with these refined nonhydrogen atoms yielded the six hydrogens bonded to boron atoms. Further careful examination of the map gave no indication of any disorder associated with the ethoxy group. Continued least-squares refinement including the BH hydrogen atoms with the latter assigned isotropic thermal parameters reduced the residuals to their final values of $R = 0.065$ and $R_w = 0.083$. During the final cycle of refinement no parameter shifted more than 0.12 times its estimated standard deviation. The estimated standard deviation of an observation of unit weight is 3.376 and the final data to parameter ratio is 7.50. An analysis of $w(F_o - F_c)^2$ as a function of F_o , setting angles, and Miller indexes revealed no unusual trends and suggested that the weighting scheme was reasonable. The value of R including unobserved reflections is 0.071, indicating that nothing would be gained by careful recollection of these data.

Full-matrix least-squares refinement was based on F , and the function minimized was $w(|F_o| - |F_c|)^2$. The weights w were taken as $[2F_o/\sigma(F_o^2)]^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber⁸ and those for hydrogen from Stewart.⁹ The effects of anomalous dispersion were included in F_c using Cromer and Ibers¹⁰ values of $\Delta f'$ and $\Delta f''$. The computing system and programs are described elsewhere.¹¹ A table of the observed and calculated structure factors is available.¹²

Table IV. Selected Intramolecular Planes^a

Atom	Deviation	Atom	Deviation
Plane 1: C(2), C(3), B(4), B(5), B(6)			
$-0.6212x + 0.1724y + 0.7645z = 1.9242$			
C(2)	-0.026	B(5)	0.061
C(3)	0.080	B(6)	-0.027
B(4)	-0.088	* Co	1.500
Plane 2: C(7), C(8), B(9), B(10), B(11)			
$-0.8228x - 0.2091y + 0.5284z = 2.0733$			
C(7)	-0.132	B(10)	-0.154
C(8)	0.006	B(11)	0.180
B(9)	0.100	* B(12)	-1.092
Plane 3: Cyclopentadienyl Ring			
$0.6202x - 0.2440y - 0.7456z = 1.114$			
CP(1)	-0.001	CP(4)	-0.005
CP(2)	-0.003	CP(5)	0.004
CP(3)	0.005	* Co	-1.669
Plane 4: O, CE(1), CE(2)			
$-0.9084x + 0.4164y + 0.0382z = 3.3142$			
Plane 5: C(2), B(4), B(9), B(11)			
$0.1909x + 0.6080y + 0.7706z = 4.1547$			
C(2)	0.069	B(9)	0.068
B(4)	-0.073	B(11)	-0.064
Planes	Angle, deg	Planes	Angle, deg
1,2	28.5	2,4	47.1
1,3	4.2	2,5	82.9
1,4	48.3	3,4	46.1
1,5	54.9	3,5	52.8
2,3	31.4	4,5	83.7

^a Atoms marked with an asterisk are not included in the calculated plane.

Table V. Intermolecular Contacts (<3.8 Å)

Atom 1	Atom 2	Distance Å	Relationship
CP(2)	CP(2)	3.212 (11)	$1 - x, -y, -z$
O	CP(5)	3.562 (9)	$-1/2 + x, 1/2 - y, 1/2 + z$
CP(2)	CP(3)	3.583 (13)	$1 - x, -y, -z$
CM(7)	CP(5)	3.655 (8)	$-1/2 + x, 1/2 - y, 1/2 + z$
CM(7)	CP(2)	3.706 (8)	$1/2 - x, 1/2 + y, 1/2 - z$

Results and Discussion

Final positional and thermal parameters are given in Table I while Tables II and III contain intramolecular distances and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figure quoted and were derived from the inverse matrix of the last cycle of least-squares refinement calculations. Tables IV and V list selected mean planes and intermolecular contacts, respectively. Figure 1 is a stereoscopic view of the molecule.

Description of the Structure. The CoC₄B₇ cage resembles an opened, elongated clamshell, the two halves of which are a CoC₂B₃ and a C₂B₄ unit. The structure reflects, in a gross sense, its synthesis⁶ from [2,3-(CH₃)₂C₂B₄H₄]₂FeH₂; in the latter complex,¹³ two C₂B₄ units are sandwiched around the metal atom such that the CH₃C-CCH₃ groups in the two ligands are in close proximity.¹⁴ The formation of the cobalt species constitutes a new example of "ligand fusion" related to the preparation¹³ of (CH₃)₄C₄B₈H₈ from [2,3-(CH₃)₂-C₂B₄H₄]₂FeH₂, in which two pyramidal carborane ligands become fused into a single cage framework.

The alignment of the two "half-clamshell" CoC₂B₃ and C₂B₄ sections is reminiscent of (CH₃)₄C₄B₈H₈,¹⁵ in the sense that the CH₃C-CCH₃ groups have an approximately cis orientation with respect to each other. One can, in fact, view the present structure as a grossly modified (CH₃)₄C₄B₈H₈ cage (II in Figure 2) in which an apex BH group has been replaced

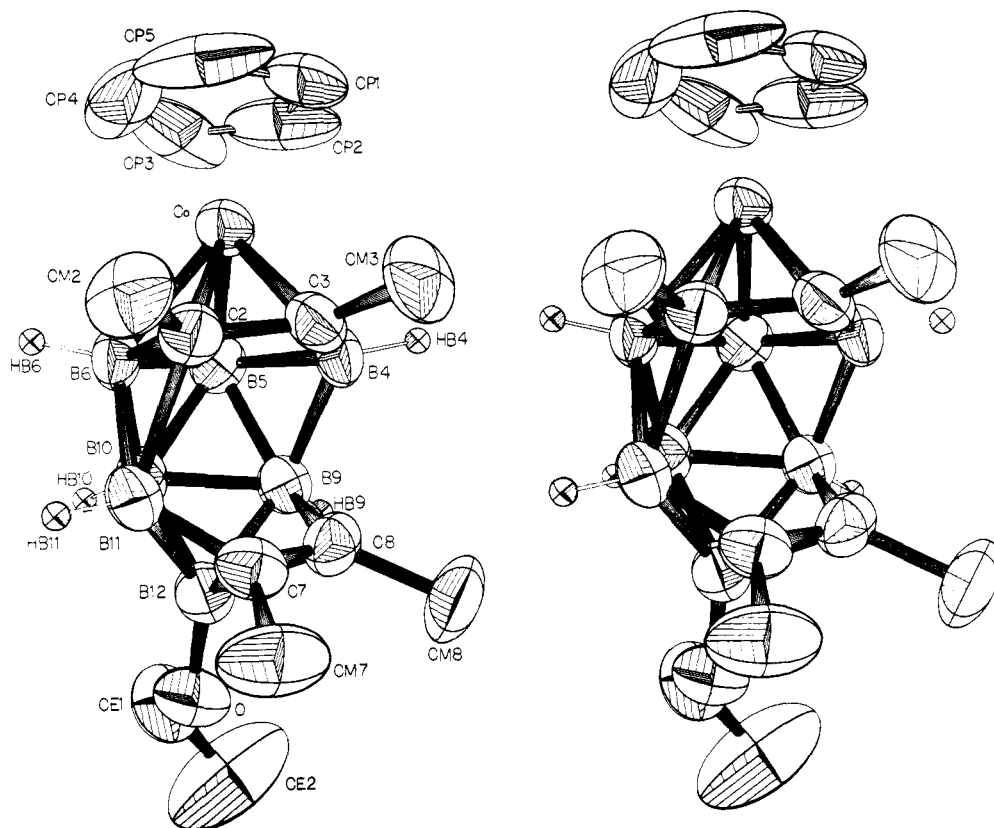


Figure 1. Stereoview of the molecule with nonhydrogen atoms represented as 50% probability thermal ellipsoids and B-H hydrogen atoms as spheres of arbitrary fixed radius.

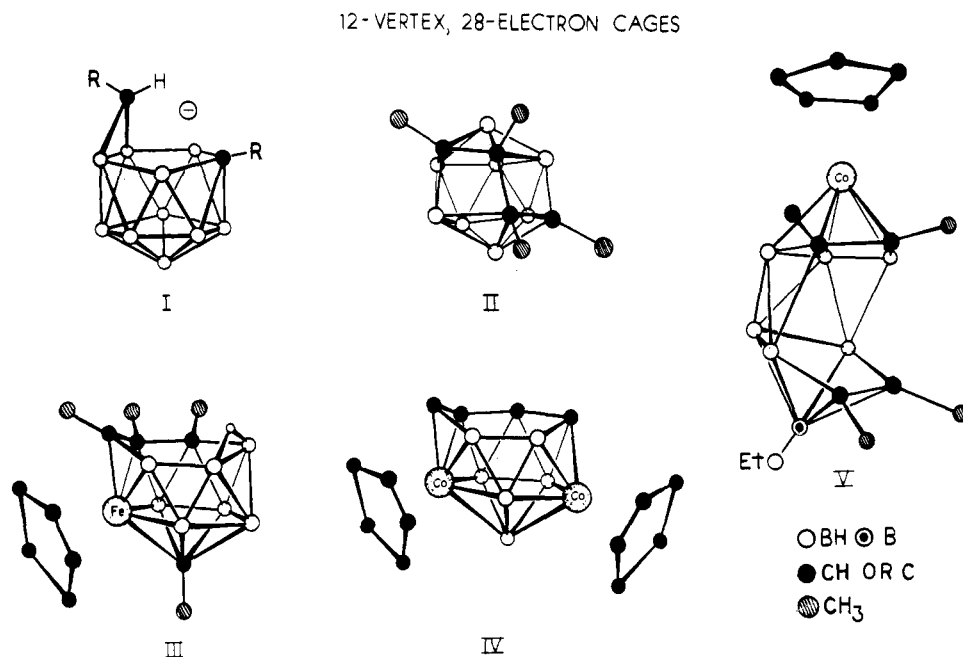


Figure 2. Structures of the five crystallographically studied 12-vertex, 28-electron cage systems: $R_2C_2B_{10}H_{11}^-$ (I) ($R = C_6H_5^{21a}$ or CH_3^{21b}), $(CH_3)_4C_4B_8H_8^{15}$ (II), $(\eta^5-C_5H_5)Fe(CH_3)_4C_4B_7H_8^{5a}$ (III), $(\eta^5-C_5H_5)_2Co_2C_4B_6H_{10}^{22}$ (IV), and the title compound (V). Each molecule occurs in the crystal in two enantiomeric forms, and the choices of enantiomer here are arbitrary.²⁷

by $Co(\eta^5-C_5H_5)$ and the central C-C bond in the cage has been severed. The extent of this stretch-distortion can be appreciated from the distances involved: C(2)-C(7), 2.694 (6); C(3)-C(7), 2.854 (6); C(3)-C(8), 2.705 (6); and B(4)-C(8), 2.326 (7) Å, all clearly nonbonding (the 2.019 (7) Å link between C(2) and B(11) is unusually long but is regarded as a bonding interaction). Another measure of the extent to which

the "clamshell" has been opened is the 28.5° dihedral angle between the planes C(2)-C(3)-B(4)-B(5)-B(6) and C(7)-C(8)-B(9)-B(10)-B(11); in a regular icosahedron the corresponding planes would, of course, be parallel.

The remaining distances and angles within the molecule are for the most part normal, although we note that the C(7)-C(8) bond is particularly short at 1.374 (6) Å, a distance which can

be compared with 1.448 (5) Å for C(2)–C(3). The latter figure is typical¹⁶ of C–C bond lengths involving low-coordinate carbon atoms (those linked to four or fewer atoms in the cage framework); thus, the C(7)–C(8) link, which is apparently the shortest carbon–carbon bond yet found in a boron cage, denotes a significantly greater than normal bond order between these particular carbons. This can be at least partially attributed to the fact that both C(7) and C(8) are three-coordinate with respect to the cage, in contrast to C(2) which is four-coordinate. There is a clear positive correlation between coordination number and bond lengths associated with carbon atoms in carboranes, as reflected, for example, in the long C–C distances in icosahedral carboranes¹⁹ and in other systems having six-coordinate carbons.

Like all η^5 -cyclopentadienyl transition metal metalloboron compounds, this molecule can also be viewed as a sandwich complex; thus, the C₅H₅ and C(2)–C(3)–B(4)–B(5)–B(6) planes are nearly parallel with an angle of only 4.2° and are located 1.67 and 1.50 Å, respectively, from the cobalt atom.

The ethoxy group is unremarkable except for the unusually short carbon–carbon distance of 1.419 (8) Å, which is attributed primarily to the large thermal motion of CE(2). The root mean square displacements of this atom along the principal axes of the ellipse are 0.2569, 0.3312, and 0.6303 Å. Since the true length of the C–C bond in this substituent group has no particular significance with respect to the metallocarborane cage, no attempt was made to correct for rotary oscillation. There are no evident crystallographic problems in this region of the molecule and the relevant angles [CE(2)–CE(1)–O = 108.9 (5)°, CE(1)–O–B(12) = 119.8(4)°] are reasonable, as is the B(12)–O distance of 1.383 (6) Å. The location of the ethoxy group on B(12), the boron atom furthest from cobalt in the cage framework, does not, unfortunately, provide any reliable guide to charge distribution in the parent cobaltacarborane system. Since the parent species ($\eta^5\text{-C}_5\text{H}_5$)Co(CH₃)₄C₄B₇H₇ was not found as a coproduct during the synthesis of the ethoxy derivative,⁶ but at the same time the diethoxycarborane (CH₃)₄C₄B₈H₆(OC₂H₅)₂ was found, it is quite possible that the title compound was in fact derived from the diethoxy species by replacement of a B(OC₂H₅) group with Co($\eta^5\text{-C}_5\text{H}_5$). In that event, it is probable that the ethoxy substituents in (CH₃)₄C₄B₈H₆(OC₂H₅)₂ are located at the apex (1,12) boron positions, an assignment which is in full agreement with the previously reported⁶ ¹¹B and ¹H NMR spectra for that compound.

Comparison with Electronically Analogous Systems. The 12-vertex CoC₄B₇ cage is a 28-electron (2*n* + 4) system based on a contribution of two electrons from each cobalt and boron atom and three from each carbon, to the bonding orbitals in the skeletal framework.² The geometry predicted for (2*n* + 4)-electron cages is nido, defined² as a closo polyhedron with one vertex removed; for *n* = 12 the anticipated nido structure would correspond to a 13-vertex polyhedron with a vacant vertex, as found in the metallocarboranes III and IV in Figure 2. Clearly, the observed structure of the title compound (V) is markedly different from those of III and IV, and bears no simple relationship to the established geometry of 13-vertex *closo*-metallocarboranes.²⁰ Moreover, V is also strikingly different from the cage-isoelectronic carboranes I and II.

The molecules I–V depicted in Figure 2 are the only structurally established examples of 12-vertex, 28-electron cage systems.²⁷ The (C₆H₅)₂C₂B₁₀H₁₁^{−21a} and (CH₃)₂C₂B₁₀H₁₁^{−21b} ions (C, C′-disubstituted derivatives of C₂B₁₀H₁₃[−]) each consist of an 11-vertex nido CB₁₀ cage with a methylenic RCH group bridging a B–B edge on the open face. The tetracarbon carborane¹⁵ (CH₃)₄C₄B₈H₈ (II) is a slightly distorted icosahedron in which two C–C edges have been stretched to nonbonding distances, thereby creating the novel situation of two four-sided open faces. A third structural

class is represented by the tetracarbon metallocarboranes III^{5a} and IV,²² which as mentioned above have the molecular shape one would anticipate a priori for a 12-vertex nido system. Finally, the geometry of ($\eta^5\text{-C}_5\text{H}_5$)Co(CH₃)₄C₄B₇H₆OC₂H₅ (V) is related to that of (CH₃)₄C₄B₈H₈ as discussed earlier, but is sufficiently different from it to constitute still another structural class.

That the five 12-vertex nido systems²⁷ whose structures are known should turn out to have four different cage geometries is remarkable and presents an engrossing theoretical challenge. The electron-count theory for polyhedra is successful in these systems only to the limited extent that it correctly predicts non-closo structures. This in itself is significant, since the regular closo geometry for 12-vertex cages is the ubiquitous icosahedron, and the absence of icosahedral geometry in any of these 28-electron structures is conspicuous. Beyond this, however, the theory in its simplest form cannot readily account for the diversity of nido geometries which are observed in this group of molecules. Other considerations, such as the preferences of carbon for low-coordinate vertexes and of bridging hydrogen atoms for locations on an open face,²³ also resist straightforward application here. Although most of the carbon atoms are low coordinate, the carbon locations in the group as a whole do not fit an obvious pattern, and of the two molecules containing “extra” hydrogens (I and III), only one has a B–H–B bridge. Moreover, structures III and IV share a common cage geometry despite the fact that one has a hydrogen bridge and the other does not; thus it is difficult to argue that the B–H–B group in the iron compound exerts any large influence on its shape.

We believe at the present time that the number of structures in hand is insufficient to support broad conclusions with any confidence. Nevertheless, we venture some observations. Most of the known violations of the electron-count rules occur either in cage systems containing metals of the third transition series²⁴ or in very large polyhedra (12 or more vertices).^{5b} Distortions caused by the inequality of d-orbital contributions in heavy atoms such as platinum have been dealt with theoretically elsewhere²⁵ and do not seem relevant to the molecules considered here. Cage size, on the other hand, is emerging as an important factor influencing the shapes of nido systems. The 14-vertex system ($\eta^5\text{-C}_5\text{H}_5$)₂Fe₂(CH₃)₄C₄B₈H₈ has eight known isomers which fall into at least three structural classes;^{5b} the prevalence of isomers is evidently a kinetic effect associated with unwieldy size, which prevents the nido species from rearranging to the thermodynamically favored, highly symmetrical closo isomer except at high temperature.

In the series depicted in Figure 2 the problem is somewhat different since we are not dealing with isomers, but there is a similarity with the 14-vertex diiron system in the sense that large cage size again plays a significant role. Each of the five molecules has two electrons in excess of the 26 allowed for a closo (icosahedral) structure; distortion from icosahedral geometry is therefore dictated, but the precise nature of this distortion is controlled in each case by local bonding conditions in various parts of the molecule. In (CH₃)₄C₄B₈H₈ (II) and in R₂C₂B₁₀H₁₁[−] (I), with cages composed exclusively of boron and carbon, the distortion is relatively mild (even in the latter case the “bridging” carbon is within 0.8 Å of closing the icosahedron),²⁶ but in the remaining structures, all containing transition metal atoms, the variance from icosahedral geometry is more severe. In these latter molecules, the tendency of the metal atoms to impose “normal” sandwich coordination geometry on the carborane ligand (e.g., a planar bonding face approximately parallel to the C₅H₅ ring) produces sharp constraints on the overall cage geometry.

The presence of carbon atoms in adjacent locations in the framework introduces the possibility of localized C–C multiple bonding, which is yet another factor influencing molecular

shape. In the tetracarbon species (structures II–V), this may become particularly important (we have already pointed out the extremely short bond between C(7) and C(8) in V).

Obviously, the method of synthesis also plays a major role in determining the cage geometry, as is clearly evident in the structure described in this paper. It will be interesting to see how the interplay of these various factors develops as additional metalboron nido cage structures are determined.

Acknowledgments. This work was supported by National Science Foundation Grant CHE 76-04491.

Supplementary Material Available: A listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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- (27) NOTE ADDED IN PROOF. A recent crystallographic study of another 12-vertex, 28-electron system, (η⁵-C₅H₅)₂Co₂(CH₃)₄C₄B₆H₈, revealed it to have a geometry like that of V, with the cobalt atoms occupying the 1, 12 vertices: J. R. Pipal and R. N. Grimes, in preparation.

Electronic and Resonance Raman Spectra of the [Mo₂Br₈]⁴⁻ Ion

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Abstract: The electronic and resonance Raman spectra of [Mo₂Br₈]⁴⁻ ion have been recorded at room temperature and at ca. 80 K. The strong band at ca. 18 000 cm⁻¹ is assigned to the ¹A_{2u}←¹A_{1g}, δ*(b_{1u})←δ(b_{2g}) transition; its wavenumber is in accord with that expected from the relation between the MoMo bond length, *r*(MM), and the δ*←δ wavenumber for [M₂X₈]ⁿ⁻ ions. The 18 000-cm⁻¹ band displays a ten-membered progression at ca. 80 K in ν₁(MoMo)a_{1g} (320 cm⁻¹). Resonance Raman spectra, excited by use of radiation with a wavenumber corresponding to that of the δ*←δ transition, consists of an intense progression in ν₁(MoMo)a_{1g} reaching to 6 ν₁ at room temperature and 11 ν₁ at ca. 80 K, together with a much weaker progression ν₂(MoBr)a_{1g} + ν₁ν₁. The spectroscopic constants ω₁ and x₁₁ are calculated to be 336.9 and -0.48 cm⁻¹ respectively. The MM bond dissociation energies of the [Mo₂X₈]⁴⁻ and [Re₂X₈]²⁻ ions (X = Cl or Br) are estimated to be ca. 500 kJ mol⁻¹.

Recent studies of the Raman spectra of metal-metal (MM) bonded species, particularly those for which the metal-metal bond is multiple, have shown that under resonance conditions very large enhancements take place to the ν (MM) band and its overtones.¹ Particularly spectacular in this respect have been the studies on species which belong, or to a first approximation belong, to the D_{4h} point group, viz., the [Mo₂Cl₈]⁴⁻,^{2,3} [Re₂Cl₈]²⁻,⁴ and [Re₂Br₈]²⁻ ions,⁴ the carboxylate-bridged species Ru₂(O₂CR)₄Cl (R = CH₃ or *n*-C₄H₉),⁵ the oxygen-bridged species [Ru₂OCl₁₀]⁴⁻, and other structurally identical ions.⁶ The recent synthesis of the [Mo₂Br₈]⁴⁻ ion⁷ opens the way to the possible study of its electronic and resonance Raman (rR) spectra, and thus to

detailed comparisons of its spectroscopic properties with those of other structurally related [M₂X₈]ⁿ⁻ ions. The results of this study allow the relation between the MM bond length and the ¹A_{2u}←¹A_{1g} (δ*←δ) transition energy to be delineated for [M₂X₈]ⁿ⁻ ions, and also permit approximate MM bond dissociation energies to be calculated.

Experimental Section

The [Mo₂Br₈]⁴⁻ ion was prepared according to the method of Brenčič et al.⁷ Anal. Calcd for (NH₄)₄[Mo₂Br₈]: N, 6.20; Br, 70.77. Found: N, 6.16; Br, 70.5.

Raman spectra were recorded using a Spex 1401 double spectrometer in conjunction with Coherent Radiation Models 12 and 52