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Crystal Structure of a Tetracobalt Tetraboron Cluster, $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$. Structural Patterns in Eight-Vertex Polyhedra

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The structure of the title compound was determined by single-crystal X-ray diffraction and found to consist of an eight-vertex Co_4B_4 closo polyhedron with symmetry very close to idealized D_{2d}. The cobalt atoms occupy contiguous positions at the 5-coordinate vertices on the polyhedron while the boron atoms are located at the four 4-coordinate vertices, as orginally proposed from boron-11 and proton NMR data. The compound crystallizes in the monoclinic $C2/c$ space group. Of the 12 molecules in the unit cell, eight are in general positions while the remaining four are bisected by crystallographic twofold axes. The molecule in a general position was found to have a 0.20-weight chlorine atom bonded to one of the borons, evidently as a consequence of repeated recrystallization from chlorinated hydrocarbon solvents. The violation of Wade's electron-counting rules by the Co_4B_4 cluster, which has only 16 skeletal electrons in comparison with 18 normally expected for an eight-vertex closo polyhedron, is discussed in light of the established structures of other eight-vertex cluster compounds. Crystal data: $M_r = 543.4$; space group $C2/c$; $a = 23.70$ (2), $b = 17.974$ (7), $c = 18.562$ (10) Å; $\beta = 129.14$ (5)°; $V = 6134$ (7) Å^3; $\mu(\text{Mo K}\alpha) = 33.4$ cm^{-1}; $\rho_{\text{calcd}}(\text{for } Z = 12) = 1.780$ g cm^{-3}. The structure was refined by full-matrix least-squares methods to a final R value of 0.042 for the 1912 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The tetrametallic cluster $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$, a green air-stable solid whose preparation has been described elsewhere,[1] is the first metalloboron cage compound having four metal atoms in the same polyhedron (very recently, two additional examples, $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$ and $(\eta^5\text{-}C_5H_5)_4Ni_4B_5H_5$, were isolated and characterized in our laboratory[2]). These metal-rich boron clusters are members of a rapidly burgeoning family of metalloboron "hybrid" systems which bridges the gap between the metal cluster and borane classes and which also includes such complexes as $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$,[1,3] $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$,[1,3] $(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$,[1] $(\eta^5\text{-}C_5H_5)_3Ni_3CB_5H_6$,[4] and $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_4FeB_3H_3$.[5]

The structural characterization of $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ presented an intriguing problem. Although the ^{11}B and ^1H NMR spectra[1] revealed single $Co(C_5H_5)$ and BH environments, consistent with a highly symmetric (D_{2d}) dodecahedral structure analogous to the $B_8H_8^{2-}$ ion,[6] the tetracobalt species has only 16 framework valence electrons, two fewer than a "normal" closo eight-vertex polyhedron (such as $B_8H_8^{2-}$) would have according to theory.[7] Electron-poor ("electron-hyperdeficient"[8]) cage systems usually adopt capped polyhedral structures, e.g., $Os_6(CO)_{18}$,[9] a capped trigonal bipyramid, and $Os_7(CO)_{21}$[9,10] and $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$,[1,3] both capped octahedra; hence $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ might have been expected to adopt the shape of a capped pentagonal bipyramid. Such geometry would not be consistent with the NMR data unless fluxional behavior was occurring, a possibility that was judged unlikely but could not be ruled out.[1]

In order to resolve the structural questions, and to provide definitive characterization of this prototype M_4B_4 cluster (which also happens to be the first eight-vertex metalloboron cage compound to be crystallographically characterized), we

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have conducted an X-ray investigation on $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ and report herein the results.

Experimental Section

After many unsuccessful attempts using a variety of solvent systems, a crystal of $(C_5H_5)_4Co_4B_4H_4$ suitable for X-ray data collection was grown by the vapor diffusion of pentane into a methylene chloride solution. The small irregularly shaped crystal, with seven well-defined faces and maximum dimensions of 0.04 × 0.30 × 0.13 mm, was mounted in an arbitrary orientation on a glass fiber. After preliminary precession photographs indicated acceptable quality, this crystal was employed for data collection. Crystal data: $Co_4C_{20}B_4H_{24}$; $M_r = 543.4$; space group $C2/c$ (No. 15); $Z = 12$; $a = 23.70$ (2), $b = 17.974$ (7), $c = 18.562$ (10) Å; $\beta = 129.14$ (5)°; $V = 6134$ (7) Å^3; μ(Mo Kα) = 33.4 cm^{-1}; ρ_{calcd}(assuming 0.86% Cl present, vide infra) = 1.780 g/cm^3; $F(000) = 3289.6$. 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 $h + k = 2n + 1$ for hkl and of $l = 2n + 1$ for $h0l$ indicated the space group to be either Cc (No. 9) or $C2/c$ (No. 14). With $Z = 12$ (assuming 18.3 Å^3 per nonhydrogen atom), Cc would require three independent molecules in the asymmetric unit whereas $C2/c$ would require only 1.5. $C2/c$ was initially assumed as the correct space group, a choice which was subsequently proven correct by the successful solution and refinement of the structure. With 1.5 molecules in the asymmetric unit and $Z = 12$, eight molecules per unit cell are required to occupy general positions while four others are bisected by the twofold axes.

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 Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all reflections for which $1° \leq 2\theta \leq 46°$. 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 Kα_1 and Kα_2 splitting. The values of A and B were 0.6 and 0.3°, 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 = TOT − 2(BG1 + 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 and polarization effects which resulted in a total of 2447 intensities of which 1912 had $F_o^2 \geq 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics using an ignorance factor of 0.03.[11] These latter reflections were used in the final refinement of the structural parameters.

Solution and Refinement of the Structure. The coordinates of the six unique cobalt atoms were located from a three-dimensional Patterson map, assuming the space group to be $C2/c$. The map strongly implied the centric space group $C2/c$ instead of the acentric Cc from the presence of many peaks corresponding to Harker sections, which would be unacceptable in Cc. Least-squares refinement of the six cobalt atoms with isotropic temperature factors reduced the conventional residual to 0.21. An electron density difference map phased on these refined cobalts clearly located 35 of the remaining 36 nonhydrogen atoms. Isotropic refinement of these atoms as well as the cobalts reduced R to 0.097. The remaining nonhydrogen atom was then located on a second map. At this point the data were corrected for absorption (maximum transmission factor = 0.907, minimum = 0.702), and all atoms were refined anisotropically. Several cycles of refinement reduced R to 0.047 and R_w to 0.052. The residuals are defined as follows: $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Another difference map was now calculated in an attempt to locate hydrogen atoms. To our surprise this map had one peak whose height was approximately three times greater than any others in the map, located 1.72 Å from B(7) (on the molecule in a general position) and in the correct orientation for a terminal atom bonded to B(7). In order to measure its intensity, another map was calculated in which one cyclopentadienyl carbon atom was deliberately omitted; this map established that the height of the mysterious peak was about two-thirds that of a carbon atom, suggesting perhaps a half-weight OH group. In any case, the eight molecules in the unit cell general positions were seen to be clearly different from the four molecules that are bisected by twofold axes. There was no indication of any corresponding peak associated with either of the unique borons in the molecule having rigorous twofold symmetry. Refinement of the new peak as either a full-weight boron or a half-weight oxygen lowered R to 0.043 and R_w to 0.046. Application of Hamilton's significance test[12] indicated that the improvement was real at the 0.005 significance level. Furthermore, average Co–B(7) distances fell from 2.087 to 2.025 Å when a full-weight boron was employed (2.029 Å with a half-weight oxygen), making it much more consistent with the other Co–B distances; also, B(7)–B(8) fell from 1.92 to 1.88 Å. This shortening of bond lengths strongly implied that the refinement process had been trying to compensate for the lack of density near B(7) by moving B(7) away from the cage in the direction of the missing atom.

At this point a mass spectrum taken on the same sample that produced the crystal employed in this study clearly indicated the presence of a small amount of $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_3Cl$ (reexamination of the original mass spectra of this compound[1] revealed no trace of the chlorinated species). Partial chlorination of the present sample evidently occurred to a slight extent during the many crystallization attempts using halogenated solvents. The chlorine occupancy corresponds to 0.20 at B(7) in the molecule in a general position, or $^2/_3 \times 0.20 = 0.13$ occupancy for all molecules in the unit cell; thus, approximately one molecule in each 7.5 is halogenated, with chlorination occurring only at B(7). The occupancy factor at B(7) was estimated by refinement of the chlorine isotropically with weights varying between 0.15 and 0.25. In all cases R fell to 0.042, but the behavior of the temperature factor (4.4 Å^2) and the Co–B(7) distances both appeared most reasonable when a weight of 0.20 was employed, as compared to refinements using higher and lower values. The final R and R_w were 0.042 and 0.045, respectively.

The estimated standard deviation of an observation of unit weight is 1.565. A final electron density map gave no indication of residual density near the Cl atom. Several possible hydrogen atom peaks were located, but no attempt was made to refine them; otherwise the map was featureless. Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. 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 Waber[13] and those for hydrogen from Stewart.[14] The effects of anomalous dispersion were included in F_c using Cromer and Ibers'[15] values of $\Delta f'$ and $\Delta f''$. The computing system and programs are described elsewhere.[16]

Tables of observed and calculated structure factors and of intermolecular distances are available as supplementary material. There are no unusually close intermolecular contacts, the nearest being Cl–C(35′) (3.246 Å) and C(52′)–C(53′) (3.483 Å).

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 in the course of least-squares refinement calculations. Table IV lists selected mean planes. Figures 1 and 2 are stereoscopic views of the molecule with Figure 1 showing the atom numbering scheme. A diagram of the unit cell packing is given in Figure 3.

Description of the Molecular Structure. The presence of two crystallographically distinct $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ molecules in the crystal, one in a general and the other a special position, affords an unusually good opportunity to compare chemically equivalent bond distances and angles; thus, there are ten independent Co–Co distances (seven bonded and three nonbonded), 18 independent Co–B bonds, and three independent B–B interactions, as summarized in Table II. There is no

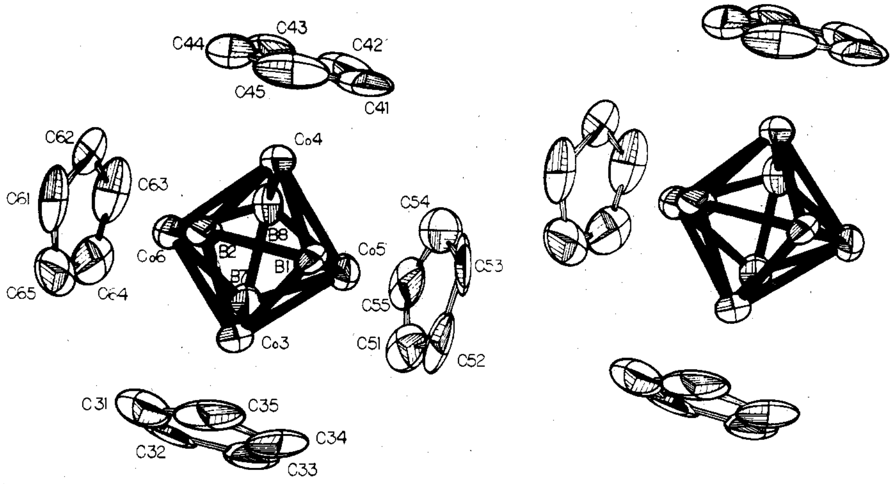

Figure 1. Stereoview of the molecule occupying a general position in the unit cell, indicating the numbering scheme. Nonhydrogen atoms are shown as 50% thermal ellipsoids (the one-fifth-weight chlorine atom attached to B(7) is omitted in this and other figures). View is down the pseudo-twofold axis.

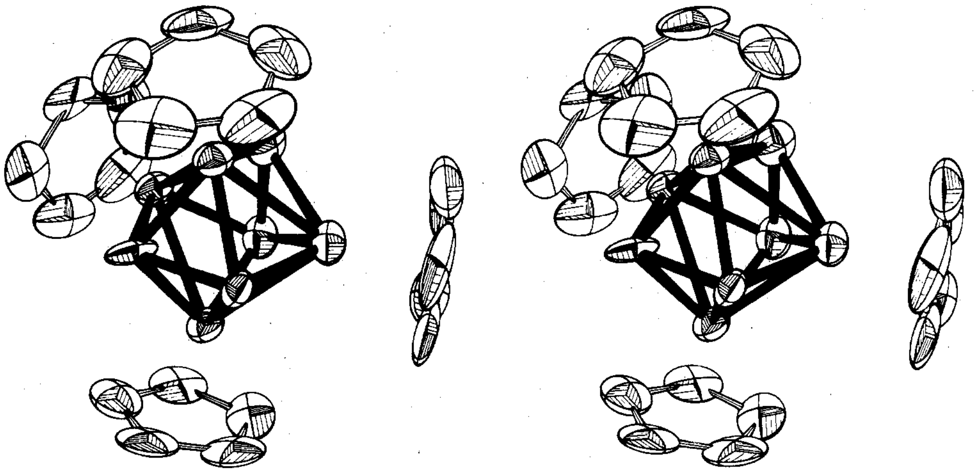

Figure 2. Alternate view of the molecule from an oblique angle.

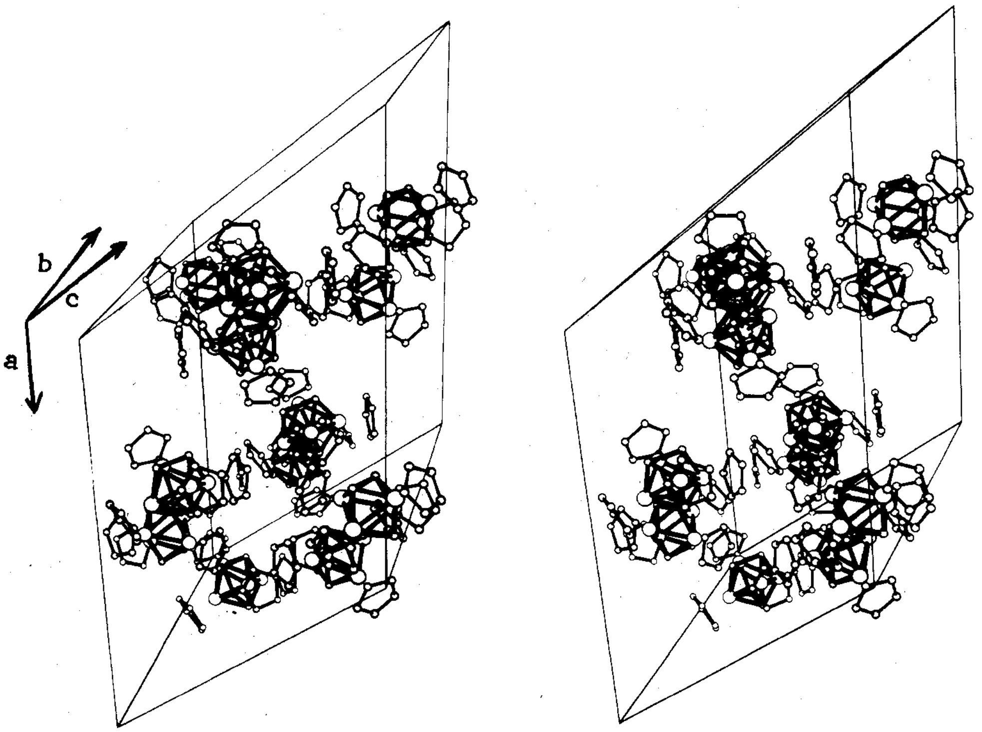

Figure 3. Stereoview of the unit cell contents.

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

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(3')[b]	0.44456 (8)	0.19309 (9)	0.16772 (9)	0.0441 (7)	0.0293 (9)	0.0270 (5)	0.0074 (7)	0.0202 (4)	0.0034 (7)
Co(5')	0.49367 (8)	0.06861 (9)	0.17835 (10)	0.0377 (7)	0.0358 (10)	0.0393 (7)	0.0038 (8)	0.0151 (5)	−0.0126 (7)
Co(3)	0.27643 (8)	0.35325 (9)	0.32247 (9)	0.0438 (7)	0.0322 (9)	0.0327 (6)	0.0026 (7)	0.0240 (4)	−0.0043 (7)
Co(4)	0.32696 (7)	0.41996 (9)	0.51348 (9)	0.0427 (6)	0.0315 (9)	0.0318 (5)	−0.0016 (7)	0.0246 (4)	−0.0038 (7)
Co(5)	0.38082 (8)	0.31831 (9)	0.48411 (9)	0.0440 (7)	0.0391 (10)	0.0387 (6)	0.0116 (7)	0.0266 (4)	0.0088 (7)
Co(6)	0.32517 (8)	0.47815 (9)	0.39085 (9)	0.0460 (7)	0.0288 (9)	0.0384 (5)	−0.0032 (7)	0.0283 (4)	−0.0004 (7)
Cl[c,d]	0.428 (1)	0.391 (1)	0.362 (1)	0.096 (8)					
C(31')	0.4044 (8)	0.2993 (7)	0.1444 (8)	0.129 (10)	0.050 (8)	0.040 (6)	0.058 (8)	0.031 (5)	0.027 (6)
C(32')	0.3445 (7)	0.2490 (8)	0.0959 (8)	0.081 (8)	0.094 (11)	0.037 (6)	0.057 (7)	0.022 (5)	0.031 (7)
C(33')	0.3495 (6)	0.2110 (7)	0.0333 (7)	0.088 (7)	0.060 (8)	0.022 (5)	0.045 (7)	0.023 (4)	0.026 (6)
C(34')	0.4060 (6)	0.2385 (8)	0.0376 (7)	0.081 (7)	0.073 (10)	0.060 (5)	0.013 (7)	0.048 (4)	0.037 (6)
C(35')	0.4437 (8)	0.2930 (8)	0.1090 (9)	0.099 (11)	0.055 (9)	0.051 (7)	−0.011 (9)	0.006 (7)	0.030 (7)
C(51')	0.5214 (8)	−0.0357 (8)	0.1627 (10)	0.118 (11)	0.074 (9)	0.083 (9)	0.061 (7)	−0.003 (7)	−0.056 (7)
C(52')	0.5460 (7)	0.0167 (10)	0.1351 (9)	0.077 (7)	0.159 (13)	0.125 (7)	−0.001 (8)	0.058 (5)	−0.101 (7)
C(53')	0.4779 (7)	0.0532 (9)	0.0576 (8)	0.090 (7)	0.111 (12)	0.091 (6)	0.001 (8)	0.063 (4)	−0.046 (7)
C(54')	0.4186 (7)	0.0224 (7)	0.0434 (7)	0.097 (8)	0.043 (8)	0.048 (6)	−0.011 (7)	0.031 (5)	−0.033 (6)
C(55')	0.4448 (9)	−0.0334 (8)	0.1121 (9)	0.147 (13)	0.037 (8)	0.065 (8)	−0.013 (9)	0.030 (7)	−0.034 (7)
C(31)	0.1928 (6)	0.3725 (8)	0.1840 (7)	0.057 (7)	0.082 (11)	0.032 (5)	−0.007 (7)	0.020 (4)	−0.016 (6)
C(32)	0.2578 (6)	0.3540 (8)	0.1969 (6)	0.095 (7)	0.084 (10)	0.020 (4)	−0.018 (8)	0.035 (3)	−0.020 (6)
C(33)	0.2781 (6)	0.2801 (8)	0.2354 (7)	0.091 (7)	0.083 (10)	0.043 (5)	0.020 (7)	0.040 (4)	−0.021 (6)
C(34)	0.2249 (7)	0.2566 (8)	0.2440 (8)	0.104 (10)	0.066 (10)	0.050 (6)	−0.025 (8)	0.031 (5)	−0.045 (6)
C(35)	0.1726 (7)	0.3122 (8)	0.2111 (8)	0.061 (7)	0.090 (10)	0.046 (6)	−0.024 (8)	0.018 (4)	−0.051 (7)
C(41)	0.3239 (6)	0.3847 (8)	0.6193 (7)	0.150 (7)	0.074 (11)	0.077 (5)	−0.002 (7)	0.097 (3)	−0.018 (6)
C(42)	0.3891 (7)	0.4235 (10)	0.6581 (7)	0.076 (7)	0.126 (13)	0.032 (5)	0.017 (9)	0.030 (4)	−0.008 (7)
C(43)	0.3716 (7)	0.4971 (8)	0.6229 (7)	0.125 (8)	0.062 (9)	0.049 (5)	−0.020 (8)	0.055 (4)	−0.030 (6)
C(44)	0.2960 (6)	0.5042 (8)	0.5596 (7)	0.122 (7)	0.067 (10)	0.069 (5)	0.023 (7)	0.077 (3)	0.003 (6)
C(45)	0.2655 (6)	0.4343 (9)	0.5584 (7)	0.089 (5)	0.129 (14)	0.093 (5)	−0.015 (7)	0.085 (3)	−0.036 (7)
C(51)	0.4355 (6)	0.2311 (8)	0.4813 (8)	0.075 (6)	0.060 (9)	0.087 (6)	0.032 (6)	0.057 (4)	0.016 (7)
C(52)	0.3828 (7)	0.2016 (7)	0.4812 (9)	0.090 (8)	0.033 (8)	0.105 (8)	0.037 (7)	0.051 (5)	0.036 (7)
C(53)	0.3965 (7)	0.2250 (8)	0.5657 (8)	0.167 (8)	0.052 (8)	0.121 (6)	0.066 (7)	0.117 (4)	0.071 (6)
C(54)	0.4609 (7)	0.2714 (8)	0.6154 (8)	0.107 (9)	0.080 (10)	0.052 (7)	0.061 (8)	0.032 (6)	0.024 (7)
C(55)	0.4857 (7)	0.2744 (8)	0.5617 (8)	0.061 (7)	0.058 (9)	0.078 (8)	0.042 (7)	0.027 (5)	0.029 (7)
C(61)	0.2565 (7)	0.5733 (7)	0.3229 (8)	0.077 (7)	0.032 (7)	0.106 (7)	0.003 (6)	0.051 (5)	0.041 (6)
C(62)	0.3229 (7)	0.5921 (6)	0.4116 (8)	0.118 (9)	0.007 (7)	0.084 (7)	−0.009 (6)	0.061 (5)	0.007 (6)
C(63)	0.3830 (6)	0.5749 (8)	0.4157 (9)	0.056 (7)	0.042 (8)	0.134 (9)	−0.011 (6)	0.050 (5)	0.027 (7)
C(64)	0.3536 (7)	0.5451 (8)	0.3294 (8)	0.167 (7)	0.049 (9)	0.123 (6)	0.010 (7)	0.125 (4)	0.026 (6)
C(65)	0.2780 (8)	0.5443 (7)	0.2697 (8)	0.145 (10)	0.041 (9)	0.062 (6)	−0.017 (8)	0.060 (5)	0.010 (6)
B(1')	0.4184 (6)	0.0941 (8)	0.1912 (8)	0.033 (6)	0.046 (9)	0.045 (6)	0.007 (6)	0.024 (4)	0.020 (6)
B(2')	0.4539 (7)	0.1663 (9)	0.2810 (8)	0.036 (7)	0.067 (11)	0.027 (5)	0.013 (7)	0.013 (4)	0.019 (7)
B(1)	0.2762 (6)	0.3307 (7)	0.4285 (7)	0.043 (6)	0.027 (8)	0.033 (5)	0.012 (6)	0.021 (4)	−0.000 (5)
B(2)	0.2456 (7)	0.4240 (7)	0.3774 (7)	0.066 (7)	0.020 (7)	0.035 (5)	−0.021 (6)	0.033 (4)	−0.012 (5)
B(7)	0.3815 (7)	0.3881 (8)	0.3988 (8)	0.051 (7)	0.045 (9)	0.046 (6)	0.011 (7)	0.032 (4)	0.010 (6)
B(8)	0.4103 (7)	0.4285 (9)	0.5113 (8)	0.068 (7)	0.038 (9)	0.054 (6)	0.003 (7)	0.040 (4)	0.013 (7)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2(a^*)^2 + U_{22}k^2(b^*)^2 + U_{33}l^2(c^*)^2 + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] Atoms marked with primes are in the molecule which is located in a special position (twofold axis). [c] Chlorine atom multiplicity is 0.20. [d] The chlorine atom was refined isotropically. The form of the isotropic thermal parameter is $\exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$.

significant variation in bond lengths corresponding to chemically equivalent interactions; the range of bonded Co–Co distances throughout the structure is 2.471 (2)–2.482 (2) Å, and the ranges of Co–B and B–B lengths are similarly narrow. The Co–Co and Co–B distances are typical for polyhedral clusters; the mean Co–Co length of 2.478 (1) Å, for example, can be compared with mean values of 2.483 (1) Å in $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$,[3] 2.441 (1) Å in $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$,[3] 2.557 (1) Å in $(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$,[17] 2.47 Å in $(CO)_9Co_3CR$ clusters,[18] 2.50 Å in $[Co_6(CO)_{14}]^{4-}$,[19] 2.50 Å in $[Co_4Ni_2(CO)_{14}]^{2-}$,[20] and 2.46 Å in $Co_4(CO)_{10}C_2(C_2H_5)_2$.[21] However, the bonded boron–boron interactions in the Co_4B_4 cage (mean value 1.86 (1) Å) are long in comparison with the corresponding distances (i.e., between low-coordinate borons) in other eight-vertex polyhedra: for $B_8H_8^{2-}$,[6] $(CH_3)_2C_2B_6H_6$ (B–C bond),[22] and B_8Cl_8[23] the mean values are 1.56 (2), 1.50 (1), and 1.78 (4) Å. There may be significance in the fact that the longest of these three distances is found in B_8Cl_8, which like $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ is a 16-electron polyhedron; the other two species are 18-electron systems.

No evidence of significant distortion from regular closo dodecahedral geometry is evident in either of the crystallographically independent Co_4B_4 polyhedra, and the solid-state structure is consistent with that deduced from NMR studies as mentioned above.

Correlation of Molecular Shape with Electron Population. With the structure of $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ now firmly established in the solid state, we turn to the question of why this cage system, with only 16 skeletal valence electrons,[24] adopts the same polyhedral geometry as the 18-electron systems $B_8H_8^{2-}$, $C_2B_6H_8$, and $(CH_3)_2C_2B_6H_6$. The fundamental thesis of the skeletal electron-counting theory for polyhedral molecules ("Wade's rules")[7] is that addition or removal of electrons to or from a closo $(2n + 2)$-electron cage dictates a change in gross polyhedral shape; clearly this is not the case in the Co_4B_4 cluster. In fact, this molecule represents one of the first, if not the first, unequivocal violations of Wade's rules among small metalloboron species. Although nonconforming cage geometry can be produced by the presence of heavy metals such as Pt or Pd in the framework,[25] and also occurs in certain large (e.g., 14-vertex) cages for which the thermodynamically favored structure is kinetically inaccessible except at high temperatures,[26] the Co_4B_4 system presents an altogether different situation.

It is clear that $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ reflects a broader problem which is centered on the structures of eight-vertex cages in general. For example, an X-ray crystallographic study[27] of the previously mentioned nickel counterpart $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$[2] has revealed it to have a closo D_{2d} structure also but with the metal atoms in *low-* rather than high-co-

Table II. Selected Intramolecular Distances (A)[a]

Co(3′)-Co(5′)	2.472 (2)	Co(3)-C(35)	2.11 (1)
Co(3′)-Co(3′)*	2.471 (3)	Co(4)-C(41)	2.11 (1)
Co(5′)-Co(5′)*	2.482 (3)	Co(4)-C(42)	2.10 (1)
Co(3′)-Co(5′)*	3.167 (2)	Co(4)-C(43)	2.11 (1)
Co(3)-Co(5)	2.479 (2)	Co(4)-C(44)	2.09 (1)
Co(3)-Co(6)	2.477 (2)	Co(4)-C(45)	2.10 (1)
Co(4)-Co(5)	2.479 (2)	Co(5)-C(51)	2.06 (1)
Co(4)-Co(6)	2.481 (2)	Co(5)-C(52)	2.10 (1)
Co(3)-Co(4)	3.175 (2)	Co(5)-C(53)	2.13 (1)
Co(5)-Co(6)	3.179 (2)	Co(5)-C(54)	2.10 (1)
Co(3′)-B(1′)	2.02 (1)	Co(5)-C(55)	2.09 (1)
Co(3′)-B(2′)	2.03 (1)	Co(6)-C(61)	2.14 (1)
Co(3′)-B(2′)*	2.01 (1)	Co(6)-C(62)	2.09 (1)
Co(5′)-B(1′)	2.00 (1)	Co(6)-C(63)	2.08 (1)
Co(5′)-B(1′)*	2.01 (1)	Co(6)-C(64)	2.04 (1)
Co(5′)-B(2′)*	2.00 (1)	Co(6)-C(65)	2.13 (1)
Co(3)-B(1)	2.01 (1)	C(31′)-C(32′)	1.43 (2)
Co(3)-B(2)	2.03 (1)	C(32′)-C(33′)	1.42 (2)
Co(3)-B(7)	2.04 (1)	C(33′)-C(34′)	1.38 (2)
Co(4)-B(1)	2.03 (1)	C(34′)-C(35′)	1.42 (2)
Co(4)-B(2)	1.99 (1)	C(35′)-C(31′)	1.44 (2)
Co(4)-B(8)	2.01 (2)	C(51′)-C(52′)	1.37 (3)
Co(5)-B(1)	2.01 (1)	C(52′)-C(53′)	1.47 (3)
Co(5)-B(7)	2.03 (1)	C(53′)-C(54′)	1.37 (2)
Co(5)-B(8)	2.05 (1)	C(54′)-C(55′)	1.42 (2)
Co(6)-B(2)	1.99 (1)	C(55′)-C(51′)	1.42 (3)
Co(6)-B(7)	2.04 (1)	C(31)-C(32)	1.44 (2)
Co(6)-B(8)	2.04 (1)	C(32)-C(33)	1.44 (2)
B(1′)-B(2′)	1.84 (2)	C(33)-C(34)	1.43 (2)
B(1)-B(2)	1.84 (2)	C(34)-C(35)	1.40 (2)
B(7)-B(8)	1.89 (2)	C(35)-C(31)	1.40 (2)
B(7)-Cl	1.63 (2)	C(41)-C(42)	1.41 (2)
Co(3′)-C(31′)	2.05 (1)	C(42)-C(43)	1.42 (2)
Co(3′)-C(32′)	2.10 (1)	C(43)-C(44)	1.40 (2)
Co(3′)-C(33′)	2.08 (1)	C(44)-C(45)	1.44 (2)
Co(3′)-C(34′)	2.13 (1)	C(45)-C(41)	1.42 (2)
Co(3′)-C(35′)	2.10 (1)	C(51)-C(52)	1.36 (2)
Co(5′)-C(51′)	2.07 (2)	C(52)-C(53)	1.45 (2)
Co(5′)-C(52′)	2.08 (2)	C(53)-C(54)	1.45 (2)
Co(5′)-C(53′)	2.05 (2)	C(54)-C(55)	1.44 (2)
Co(5′)-C(54′)	2.12 (1)	C(55)-C(51)	1.42 (2)
Co(5′)-C(55′)	2.10 (1)	C(61)-C(62)	1.42 (2)
Co(3)-C(31)	2.06 (1)	C(62)-C(63)	1.41 (2)
Co(3)-C(32)	2.08 (1)	C(63)-C(64)	1.39 (2)
Co(3)-C(33)	2.10 (1)	C(64)-C(65)	1.39 (2)
Co(3)-C(34)	2.10 (1)	C(65)-C(61)	1.46 (2)

[a] Atoms marked with an asterisk are related to their unmarked counterparts by a crystallographic twofold axis. Atoms marked with primes are in the molecule occupying a special position (twofold axis); all others are in the molecule in a general position.

Table III. Selected Bond Angles (deg)[a]

Co(3′)*-Co(3′)-Co(5′)	79.71 (6)	Co(4)-B(1)-B(2)	61.7 (5)
Co(3′)-Co(5′)-Co(5′)*	79.50 (6)	Co(3)-B(2)-Co(6)	75.9 (5)
Co(5)-Co(3)-Co(6)	79.81 (6)	Co(4)-B(2)-Co(6)	77.1 (5)
Co(5)-Co(4)-Co(6)	79.74 (6)	Co(3)-B(2)-B(1)	62.4 (6)
Co(3)-Co(5)-Co(4)	79.65 (6)	Co(4)-B(2)-B(1)	63.9 (5)
Co(3)-Co(6)-Co(4)	79.66 (6)	Co(3)-B(7)-Co(5)	75.2 (5)
Co(5′)-Co(3′)-B(1′)	51.6 (4)	Co(3)-B(7)-Co(6)	74.7 (5)
Co(5′)-Co(3′)-B(2′)*	51.9 (4)	Co(5)-B(7)-B(8)	63.2 (6)
Co(3′)*-Co(3′)-B(2′)	52.0 (4)	Co(6)-B(7)-B(8)	62.5 (6)
Co(3′)*-Co(3′)-B(2′)*	52.6 (3)	Co(3)-B(7)-Cl	125 (1)
B(1′)-Co(3′)-B(2′)	54.2 (5)	Co(5)-B(7)-Cl	133 (1)
Co(3′)-Co(5′)-B(1′)	52.4 (4)	Co(6)-B(7)-Cl	122 (1)
Co(3′)-Co(5′)-B(2′)	52.1 (4)	B(8)-B(7)-Cl	126 (1)
Co(5′)*-Co(5′)-B(1′)	52.0 (4)	Co(4)-B(8)-Co(5)	75.2 (5)
Co(5′)*-Co(5′)-B(1′)*	51.5 (4)	Co(4)-B(8)-Co(6)	75.6 (5)
B(1′)*-Co(5′)-B(2′)*	54.7 (5)	Co(5)-B(8)-B(7)	61.8 (6)
Co(3′)-B(1′)-Co(5′)	76.0 (4)	Co(6)-B(8)-B(7)	62.6 (6)
Co(5′)-B(1′)-Co(5′)*	76.5 (5)	C(35′)-C(31′)-C(32′)	109 (1)
Co(3′)-B(1′)-B(2′)	63.2 (6)	C(31′)-C(32′)-C(33′)	105 (2)
Co(5′)*-B(1′)-B(2′)	62.4 (6)	C(32′)-C(33′)-C(34′)	111 (1)
Co(3′)-B(2′)-Co(3′)*	75.4 (5)	C(33′)-C(34′)-C(35′)	108 (1)
Co(3′)*-B(2′)-Co(5′)*	76.0 (5)	C(34′)-C(35′)-C(31′)	106 (2)
Co(3′)-B(2′)-B(1′)	62.6 (6)	C(55′)-C(51′)-C(52′)	114 (2)
Co(5′)*-B(2′)-B(1′)	62.9 (6)	C(51′)-C(52′)-C(53′)	102 (2)
Co(5)-Co(3)-B(1)	51.8 (4)	C(52′)-C(53′)-C(54′)	112 (2)
Co(5)-Co(3)-B(7)	52.3 (4)	C(53′)-C(54′)-C(55′)	107 (2)
Co(6)-Co(3)-B(2)	51.3 (3)	C(54′)-C(55′)-C(51′)	106 (2)
Co(6)-Co(3)-B(7)	52.8 (4)	C(35)-C(31)-C(32)	110 (1)
B(1)-Co(3)-B(2)	54.0 (4)	C(31)-C(32)-C(33)	106 (1)
Co(5)-Co(4)-B(1)	51.7 (4)	C(32)-C(33)-C(34)	106 (1)
Co(5)-Co(4)-B(8)	53.3 (4)	C(33)-C(34)-C(35)	110 (2)
Co(6)-Co(4)-B(2)	51.5 (4)	C(34)-C(35)-C(31)	108 (2)
Co(6)-Co(4)-B(8)	52.9 (4)	C(45)-C(41)-C(42)	108 (2)
B(1)-Co(4)-B(2)	54.4 (4)	C(41)-C(42)-C(43)	109 (1)
Co(3)-Co(5)-B(1)	52.0 (3)	C(42)-C(43)-C(44)	109 (1)
Co(3)-Co(5)-B(7)	52.6 (4)	C(43)-C(44)-C(45)	107 (1)
Co(4)-Co(5)-B(1)	52.5 (3)	C(44)-C(45)-C(41)	108 (1)
Co(4)-Co(5)-B(8)	51.5 (4)	C(55)-C(51)-C(52)	112 (1)
B(7)-Co(5)-B(8)	55.0 (5)	C(51)-C(52)-C(53)	108 (2)
Co(3)-Co(6)-B(2)	52.8 (4)	C(52)-C(53)-C(54)	106 (2)
Co(3)-Co(6)-B(7)	52.5 (4)	C(53)-C(54)-C(55)	108 (1)
Co(4)-Co(6)-B(2)	51.4 (3)	C(54)-C(55)-C(51)	106 (1)
Co(4)-Co(6)-B(8)	51.6 (4)	C(65)-C(61)-C(62)	105 (1)
B(7)-Co(6)-B(8)	55.0 (5)	C(61)-C(62)-C(63)	111 (1)
Co(3)-B(1)-Co(5)	76.1 (5)	C(62)-C(63)-C(64)	106 (2)
Co(4)-B(1)-Co(5)	75.8 (4)	C(63)-C(64)-C(65)	112 (2)
Co(3)-B(1)-B(2)	63.6 (5)	C(64)-C(65)-C(61)	106 (1)

[a] Atom symbols are explained in Table II.

ordinate vertices! Although the number of skeletal bonding electrons[24] is 20 in the Ni_4B_4 system, 16 in $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ and B_8Cl_8, and 18 in $B_8H_8^{2-}$ and $C_2B_6H_8$, all of these systems, remarkably, adopt the same (D_{2d}) polyhedral geometry.[28] Other eight-vertex boron cages are known, but with the exception of B_8H_{12}[30] their structures have not been established (Table V). It seems significant that, in the five structurally characterized boron species in which bridge hydrogens are absent, the cage geometry is D_{2d} dodecahedral regardless of the number of framework electrons. Where B–H–B bridges are present, open-cage structures are likely,[31] as found in B_8H_{12} and postulated for several other boranes and carboranes listed in Table V. An open structure has also been proposed for $(CH_3)_4C_4B_4H_4$,[38] which evidently lacks bridging hydrogens; if correct, this geometry would contrast sharply with the electronically analogous molecule $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$, a D_{2d} closo system.[2,27]

When consideration of eight-vertex clusters is extended to species other than boron-containing ones, a greater variety in polyhedral shape is encountered, as summarized in Table V for a few selected cases. Most of these are 24-electron ($2n + 8$) systems which adopt highly opened structures such as the cube and chair; this is basically in accord with expectation from theory,[7] as is the observation[40] that $(\eta^5\text{-}C_5H_5)_4Fe_4S_4$, with 20 electrons, is somewhat closer to a closed (i.e., triangulated) cage structure than are the 24-electron clusters. Also significant is the shortening of two Fe–Fe distances in the $(\eta^5\text{-}C_5H_5)_4Fe_4S_4^+$ monocation relative to the neutral molecule, a result entirely consistent with removal of an antibonding electron.[48] It is clear, however, that eight-vertex systems as a group are relatively pliable cages whose geometries are unusually sensitive to subtle electronic and steric influences. In contrast, most classes of polyhedra having other than eight vertices tend to follow predictable patterns based on simple electron-counting arguments;[7,49,50] in other words, it appears that eight-vertex polyhedra constitute something of a special case. Indeed, this is the implication of recent extended Hückel MO calculations[51] on polyhedral $B_nH_n^{2-}$ ions for n = 6–9, which disclosed that while $B_6H_6^{2-}$, $B_7H_7^{2-}$, and $B_9H_9^{2-}$ each have a thermodynamically preferred structure (O_h, D_{5h}, and D_{3h}, respectively), $B_8H_8^{2-}$ is stereochemically nonrigid and has several easily accessible geometries, i.e., D_{2d}, D_{4d}, and C_{2v}. This conclusion[51,52] is in accord with NMR studies of these ions.[53]

For the boron clusters without bridge hydrogens, several factors probably favor the D_{2d} structure: high symmetry, relatively close approach to spherical shape (as compared to other alternatives), absence of an open face, and high average coordination number for vertex atoms. Moreover, pathways

Table IV

Selected Mean Planes[a]

atom	dev, Å	atom	dev, Å
Plane 1: B(1), B(2), Co(5), Co(6)			
$-0.3222x + 0.3749y + 0.8693z = 7.1142$			
B(1)	−0.009	Co(3)	1.592
B(2)	0.009	Co(4)	−1.583
Co(5)	0.015	B(7)	0.916
Co(6)	−0.015	B(8)	−0.969
Plane 2: Co(3), Co(4), B(7), B(8)			
$-0.0700x + 0.9032y - 0.4234z = 3.5706$			
Co(3)	0.004	B(1)	−0.921
Co(4)	−0.004	B(2)	0.915
B(7)	−0.007	Co(5)	−1.589
B(8)	0.007	Co(6)	1.590
Plane 3: Co(3′)*, Co(5′), B(1′), B(2′)			
$0.0989x + 0.7086y - 0.6987z = 0.0316$			
Co(3′)*	0.002	Co(3′)	1.588
B(1′)	0.003	Co(5′)*	−1.580
B(2′)	−0.003	B(1′)*	−0.935
Co(5′)	−0.002	B(2′)*	+0.910
Plane 4: Co(3′), Co(5′)*, B(1′)*, B(2′)			
$-0.0989x + 0.7086y + 0.6987z = 3.2971$			
Co(3′)	−0.002	Co(3′)*	1.588
Co(5′)*	0.002	Co(5′)	1.580
B(1′)*	−0.003	B(1′)	0.935
B(2′)*	0.003	B(2′)	−0.910
Plane 5: C(31′), C(32′), C(34′), C(35′)			
$-0.2044x + 0.7006y - 0.6837z = 0.7368$			
C(31′)	−0.004	C(34′)	0.019
C(33′)	0.015	C(35′)	−0.009
C(33′)	−0.021	Co(3′)	−1.709
Plane 6: C(51′), C(52′), C(53′), C(54′), C(55′)			
$0.3867x - 0.6667y - 0.6372z = 2.9600$			
C(51′)	0.016	C(54′)	0.015
C(52′)	−0.007	C(55′)	−0.019
C(53′)	−0.005	Co(5′)	−1.701
Plane 7: C(31), C(32), C(33), C(34), C(35)			
$-0.0422x + 0.3823y + 0.9231z = 4.8930$			
C(31)	−0.009	C(34)	−0.008
C(32)	0.004	C(35)	0.011
C(33)	0.002	Co(3)	−1.703
Plane 8: C(41), C(42), C(43), C(44), C(45)			
$-0.5874x + 0.3039y + 0.7501z = 8.5407$			
C(44)	0.000	C(44)	0.014
C(42)	0.009	C(45)	−0.009
C(43)	−0.014	Co(4)	1.720
Plane 9: C(51), C(52), C(53), C(54), C(55)			
$0.3446x - 0.8098y + 0.4748z = 1.5417$			
C(51)	0.001	C(54)	0.005
C(52)	0.002	C(55)	−0.004
C(53)	−0.004	Co(5)	1.710
Plane 10: C(61), C(62), C(63), C(64), C(65)			
$0.2217x + 0.9191y - 0.3257z = 8.4757$			
C(61)	−0.009	C(64)	−0.012
C(62)	0.003	C(65)	0.013
C(63)	0.005	Co(6)	−1.716

Selected Angles between Planes

planes	angle, deg	planes	angle, deg
1, 2	89.60	2, 8	89.9
3, 4	90.24	2, 9	16.9
1, 7	16.4	2, 10	17.7
1, 8	17.2	3, 5	17.5
1, 9	90.1	3, 6	90.4
1, 10	89.4	4, 5	92.2
2, 7	87.6	4, 6	17.1

[a] Atom symbols are explained in Table II.

Table V. Some Eight-Vertex Cages and Clusters

formula	skeletal electrons[a]	cage geometry[b]	ref
Boron Systems (No Bridging Hydrogens)			
$B_8H_8^{2-}$	18	D_{2d}, closo	6
$C_2B_6H_8$	18	D_{2d}, closo[c]	22
$(\eta^5\text{-}C_5H_5)CoC_2B_5H_7$	18	[D_{2d}, closo]	32
$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_4H_6$	18	[D_{2d}, closo]	32
$(CO)_3FeC_2B_5H_7$	18	[D_{2d}, closo]	33
$C_3B_5H_7$	18	[D_{2d}, closo]	34
$(\eta^5\text{-}C_5H_5)CoSn(CH_3)_2\text{-}C_2B_4H_4$	18	[D_{2d}, closo]	35
B_8Cl_8	16	D_{2d}, closo	23
$(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$	16	D_{2d}, closo[d]	this work
$(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$	20	D_{2d}, closo[e]	2, 27
$(CH_3)_4C_4B_4H_4$	20	[nido or arachno]	38
Boron Systems with B-H-B Bridges			
B_8H_{12}	20	icosahedral fragment, arachno	30
B_8H_{14}	22	[icosahedral fragment, arachno]	36
$C_2B_6H_{10}$	20	[nido or arachno]	37
B_8H_{16}	24	?	39
Nonboron Clusters			
$(\eta^5\text{-}C_5H_5)_4Fe_4S_4$	20	D_{2d} nido polyhedron	40
C_8H_8 (cubane)	24	cube	41
$[(C_6H_5)P]_6Ni_8(CO)_8$	24	cube	42
$[(C_6H_5)_3P]_4Cu_4Cl_4$	24	cube	43
$[(C_6H_5)_3P]_4Cu_4X_4$ (X = Cl, Br)	24	chair	44
$(CO)_{12}Os_4O_4$	24	cube	45
$[(C_6H_5)_3P]_4Ag_4I_4$	24	distorted cube; chair (2 isomers)	46
$[(C_6H_5)_3P]_4Ag_4Cl_4$	24	distorted cube	47

[a] For electron-counting rules see ref 7a. [b] Geometries not definitely established are enclosed in brackets. [c] Structure established from *C,C′*-dimethyl derivative. [d] All metal atoms occupy high-coordinate vertices. [e] All metal atoms occupy low-coordinate vertices.

for the conversion of other eight-vertex polyhedra to the D_{2d} cage are easy to visualize.[53] In the case of $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$, a possible structure we had considered[1a] prior to the X-ray work was the capped pentagonal bipyramid, which would be consistent with the presence of 16 ($2n$) skeletal electrons; as was described previously,[1] it can be readily converted to the observed D_{2d} structure via cleavage of one bond and formation of another. If the advantages of the D_{2d} arrangement outweigh framework electron count in determining the favored geometry, the inducement for such a rearrangement is apparent.

Finally, in considering the problem of $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ in an earlier paper[1b] it was suggested that the D_{2d} polyhedron might be stabilized by trans-cage bonding interactions between Co(3)–Co(4) and Co(5)–Co(6) (different numbering was used previously). The observed distances [mean value 3.174 (1) Å], while formally nonbonding, are sufficiently short that an electronic interaction is conceivable; indeed, in the triple-decked sandwich complexes $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$, which exhibited NMR evidence for trans-cage effects between $(C_5H_5)Co$ groups,[54] the mean Co–Co distance (3.138 (1) Å for three crystal structures)[55] is only 0.03 Å shorter. In $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$, to which we have referred previously, the nickel atoms occupy the low-coordinate vertices and are therefore in well-separated Ni_2 pairs on the "ends" of the dodecahedral cage, in contrast to the Co_4B_4 cluster, whose cobalts form a contiguous belt around the middle. Since the Ni_4B_4 cluster has four more skeletal electrons than the Co_4B_4 system, it may be that the observed Ni_4B_4 structure is adopted in order to *avoid* trans-cage metal–metal interactions. Further development of these ideas will depend on continuing synthetic and structural investigations in the metalloboron cluster field.

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Registry No. $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$, 59370-82-0.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes and short intermolecular distances (10 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of an Iron Dihydrogen Metallocarborane, $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$. Steric Aspects of the Oxidative Fusion Process

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A single-crystal X-ray diffraction investigation of the title compound established the structure as a sandwich composed of two pentagonal-pyramidal carborane ligands face bonded to iron, in accord with the geometry proposed earlier from NMR data. The "extra" hydrogen atoms were not directly located, but strong evidence that they occupy bridging locations on the FeB_2 polyhedral faces is given by the orientation of the C_2B_3 bonding faces on the ligands. The C_2B_3 planes are inclined at an angle of 7.80° such that the methyl groups are forced close together, an effect attributed to the presence of the FeH_2 hydrogens wedged between the polyhedra on the side of the complex opposite the methyl groups. The relationship of this structure to that of $(CH_3)_4C_4B_8H_8$, which is produced from the title compound by oxidative fusion of the $[(CH_3)_2C_2B_4H_4]^{2-}$ ligands, is discussed. Crystal data: space group *Aba*2; $a = 12.861$ (4) Å, $b = 10.144$ (4) Å, $c = 11.257$ (5) Å; $V = 1469$ (2) Å^3; $\mu(\text{Mo K}\alpha) = 10.2$ cm^{-1}; $\rho(\text{calcd}) = 1.178$ g cm^{-3} for $Z = 4$. The structure was refined by full-matrix least-squares methods to a final R value of 0.039 for the 662 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The bis(2,3-dimethyl-2,3-dicarbahexaboranyl)iron(II) dihydrogen complex $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$, a deep red solid, has played an important role in the recent development of some novel metallocarborane and carborane chemistry.[1] A number of singular kinds of reactions involving this compound and its cobalt monohydrogen analogue, $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2CoH$, have been described elsewhere;[2] particularly significant is the

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