rules. Molecular orbital treatments[29] strongly suggest that localized Co–Co and Ni–Ni bonding plays an important role in these systems. In the family of cobaltaboranes under consideration here, in which the general formula is $[(C_5R_5)Co]_{10-n}B_nH_{n+4}$, only the members for which $n = 8$, 9, or 10 are presently known. Stable species with quite high metal content may well exist, but major structural deviation from the $B_{10}H_{14}$ geometry can be expected.

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Registry No. 6-$[C_5Me_5]CoB_9H_{13}$, 80145-64-8; 6,9-$[C_5Me_5]_2Co_2B_8H_{12}$, 80160-31-2; 5,7-$[C_5Me_5]_2Co_2B_8H_{12}$, 80145-65-9; 6-Cl-5,7-$[C_5Me_5]_2CoB_8H_{11}$, 80145-66-0.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic thermal parameters, C–C distances in $C_5(CH_3)_5$ rings, and selected mean planes (60 pages). Ordering information is given on any current masthead page.

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[29] Cox, D. N.; Mingos, D. M. P.; Hoffmann, R. *J. Chem. Soc., Dalton Trans.* **1981**, 788.

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Crystal and Molecular Structure of $[\eta^5\text{-}C_5(CH_3)_5]_3Co_3B_4H_4$, an Electron-Hyperdeficient Cluster with Severe Intramolecular Ligand–Ligand Crowding[1]

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An X-ray diffraction study of the title compound confirmed its structure as a *closo*-Co_3B_3 octahedron whose tricobalt face is capped by BH, analogous to the previously described complex $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$. The three $C_5(CH_3)_5$ ligands are η^5-coordinated to cobalt and are in close proximity to each other, with interligand C_{methyl}–C_{methyl} contacts as short as 3.33 Å. This molecule is the first structurally characterized complex in which three mutually bonded metal atoms are each η^5-coordinated to a $C_5(CH_3)_5$ ligand. The methyl groups are bent out of the C_5 ring planes by 0.08–0.19 Å (average deflection 0.14 Å), and the three Co–Co bond distances are increased to a mean value of 2.497 (5) Å compared to 2.441 (1) Å for the $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$ analogue; both effects are ascribed to relief of steric crowding of the $C_5(CH_3)_5$ ligands. The observed structure is in conformity with the ^1H and ^{11}B NMR data and with the electron-counting rules for polyhedral cluster systems. Crystal data: mol wt 630; space group $P\bar{1}$; $Z = 2$; $a = 8.480$ (9), $b = 10.747$ (8), $c = 17.585$ (15) Å; $\alpha = 89.55$ (7), $\beta = 85.76$ (6), $\gamma = 71.59$ (8)°; $V = 1516$ Å^3; $R = 0.069$ for 2699 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

Introduction

In the two accompanying articles we describe the synthesis[2] of a series of (pentamethylcyclopentadienyl)cobaltaboranes from the $B_5H_8^-$ ion, $CoCl_2$, and $C_5(CH_3)_5^-$ ion in THF solution and the structural characterization[3] of several 10-vertex complexes containing CoB_9 or Co_2B_8 nido cage systems. These 10-vertex species, which are structural and electronic analogues of $B_{10}H_{14}$, have been shown[2] to originate from the $B_9H_{14}^-$ ion, which under certain conditions is formed in large concentration during the deprotonation of B_5H_9 with NaH. However, under other conditions the predominant borane species is $B_5H_8^-$, and its reaction with $CoCl_2$ and $C_5(CH_3)_5^-$ ion generates primarily *small* cobaltaboranes having 5- to 7-vertex cages.[2] Several of these products are counterparts of cyclopentadienylcobaltaboranes obtained previously[4] from $B_5H_8^-$, $CoCl_2$, and $C_5H_5^-$. One such complex, formulated as $[C_5(CH_3)_5]_3Co_3B_4H_4$, appeared to be analogous to the known species $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$, which was earlier shown from NMR[4] and X-ray[5] studies to have a capped-octahedral cage geometry in which a BH unit is coordinated to a Co_3 face of a *closo*-Co_3B_3 polyhedron.

The apparent analogy between these $(C_5R_5)_3Co_3B_4H_4$ complexes was reinforced by the ^1H and ^{11}B FT NMR data,[2,4] which are closely similar and support a C_{3v} capped-octahedral geometry for $[C_5(CH_3)_5]_3Co_3B_4H_4$. This structure, however, requires a triangular, bonded Co_3 array with each cobalt η^5-coordinated to a $C_5(CH_3)_5$ ligand; a priori, such an arrangement seemed incompatible with the large steric requirements of the bulky pentamethylcyclopentadienyl groups. Hence an X-ray crystallographic study was undertaken to establish the solid-state geometry.

Experimental Section

Yellow crystals of the title compound, prepared as described elsewhere,[2] were grown by slow evaporation of a pentane solution at 0 °C. A small platelet was selected for data collection after preliminary precession photographs indicated satisfactory crystal quality. Crystal data: $Co_3C_{30}B_4H_{49}$, mol wt 630; space group $P\bar{1}$; $Z = 2$; $a = 8.480$ (9), $b = 10.747$ (8), $c = 17.585$ (15) Å; $\alpha = 89.55$ (7), $\beta = 85.76$ (6), $\gamma = 71.59$ (8)°; $V = 1516$ Å^3; $\rho_{calcd} = 1.34$ g cm^{-3}; μ(Mo Kα) = 17.0 cm^{-1}; crystal dimensions (distances in mm of faces from centroid) (100) 0.21, ($\bar{1}$00) 0.21, (010) 0.11, (0$\bar{1}$0) 0.11, (001) 0.09, (00$\bar{1}$) 0.09; maximum and minimum transmission coefficients 0.88 and 0.79.

The Enraf-Nonius program SEARCH was used to obtain 25 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of the crystal was examined by the ω-scan technique and judged to be satisfactory.

Collection and Reduction of the Data. Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, with Mo Kα radiation from a highly oriented graphite-crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 46°$. Scan widths (SW) were calculated from SW = $(A + B \tan\theta)°$, where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to Kα_1–Kα_2 splitting. The values of A and B were 0.6 and 0.35,

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[1] Taken in part from the Ph.D. dissertation of T.L.V., University of Virginia, 1982.

[2] Venable, T. L.; Grimes, R. N. *Inorg. Chem.*, first of two preceding papers in this issue.

[3] Venable, T. L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.*, immediately preceding paper in this issue.

[4] Miller, V. R.; Weiss, R.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 5646.

[5] Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 3255.

0020-1669/82/1321-0904$01.25/0

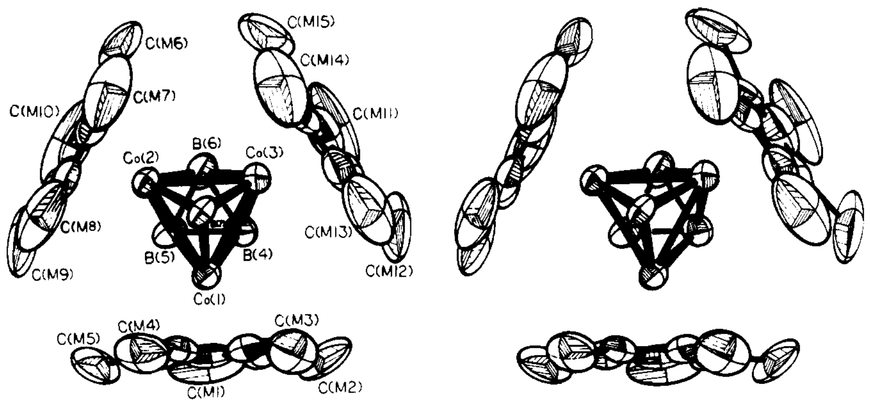

Figure 1. Stereoview directed approximately along the idealized C_3 axis.

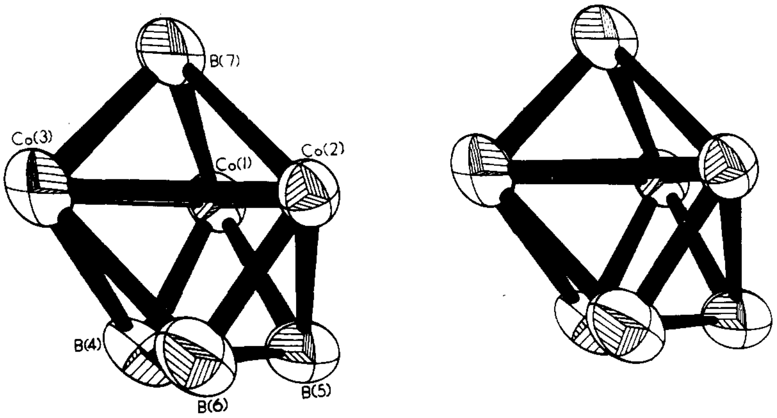

Figure 2. View of the Co_3B_4 polyhedron.

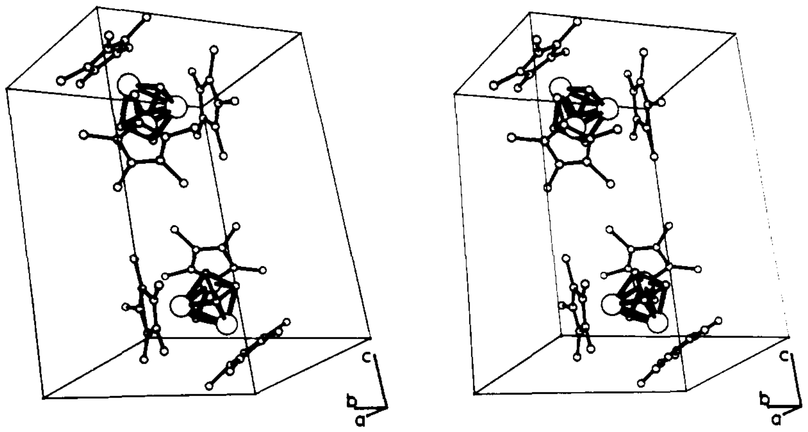

Figure 3. Stereoview of the contents of a unit cell.

respectively. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as NC = TOT − 2(BG1 + BG2), where TOT is the integrated peak intensity.

The intensities of four standard reflections, monitored at periodic intervals, showed no greater fluctuations during data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects (including the polarization effect of the crystal monochromator) and then for absorption. After equivalent reflections were averaged, the data were reduced to 4101 independent intensities, of which 2699 had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics ($p = 0.03$).[6] These data were used in the final refinement of the structural parameters.

Solution and Refinement of the Structure. 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 then 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[7] and those for hydrogen from Stewart et al.[8] The effects of anomalous dispersion for all nonhydrogen atoms were included in F_c with use of the values of Cromer and Ibers[9] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

The positions of the three cobalt atoms were determined from a three-dimensional Patterson function calculated from all intensity data. The data were phased sufficiently well by these positional coordinates to permit location of the remaining nonhydrogen atoms from Fourier difference functions. Anisotropic temperature factors were introduced for all nonhydrogen atoms. The four hydrogen atoms were placed at calculated positions and refined with constant temperature factors. The model converged with $R = 0.069$ and $R_w = 0.081$.

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(6) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

(7) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(8) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(9) Cromer, D. T.; Ibers, J. A. Reference 7.

Table I. Positional Parameters and Their Estimated Standard Deviations for $(C_5Me_5)_3Co_3B_4H_4$

atom	x	y	z	atom	x	y	z
Co(1)	0.7904 (1)	0.4122 (1)	0.24325 (7)	C(M9)	0.684 (3)	0.2892 (20)	0.0217 (9)
Co(2)	0.8079 (1)	0.1920 (1)	0.19110 (7)	C(M10)	0.521 (2)	0.1115 (18)	0.1141 (10)
Co(3)	0.8405 (2)	0.2203 (1)	0.32930 (7)	C(11)	0.776 (1)	0.1618 (14)	0.4364 (7)
C(1)	0.656 (1)	0.6094 (9)	0.2336 (8)	C(12)	0.861 (2)	0.2508 (13)	0.4448 (6)
C(2)	0.770 (1)	0.5964 (9)	0.2926 (6)	C(13)	1.016 (1)	0.2068 (11)	0.4115 (6)
C(3)	0.931 (1)	0.5409 (8)	0.2592 (6)	C(14)	1.040 (2)	0.0845 (11)	0.3803 (6)
C(4)	0.924 (1)	0.5232 (8)	0.1807 (6)	C(15)	0.895 (2)	0.0542 (9)	0.3960 (6)
C(5)	0.758 (1)	0.5655 (9)	0.1652 (7)	C(M11)	0.607 (2)	0.1682 (23)	0.4723 (10)
C(M1)	0.471 (2)	0.6723 (13)	0.2428 (14)	C(M12)	0.789 (3)	0.3818 (17)	0.4933 (8)
C(M2)	0.715 (2)	0.6427 (11)	0.3746 (8)	C(M13)	1.157 (2)	0.2713 (17)	0.4142 (9)
C(M3)	1.096 (1)	0.5235 (11)	0.2967 (8)	C(M14)	1.204 (2)	−0.0013 (20)	0.3425 (10)
C(M4)	1.077 (2)	0.4812 (11)	0.1249 (8)	C(M15)	0.864 (3)	−0.0782 (15)	0.3823 (11)
C(M5)	0.692 (2)	0.5789 (13)	0.0846 (8)	B(4)	0.621 (1)	0.3629 (11)	0.3155 (7)
C(6)	0.833 (2)	0.0038 (9)	0.1502 (6)	B(5)	0.600 (1)	0.3437 (10)	0.2217 (7)
C(7)	0.982 (1)	0.0309 (10)	0.1294 (6)	B(6)	0.635 (1)	0.2145 (12)	0.2807 (7)
C(8)	0.943 (1)	0.1349 (10)	0.0837 (6)	B(7)	0.975 (1)	0.2489 (9)	0.2390 (6)
C(9)	0.775 (2)	0.1771 (11)	0.0747 (6)	H(4)	0.552 (10)	0.412 (8)	0.367 (5)
C(10)	0.700 (1)	0.0983 (11)	0.1177 (7)	H(5)	0.522 (9)	0.380 (8)	0.174 (5)
C(M6)	0.799 (3)	−0.1107 (12)	0.1961 (10)	H(6)	0.608 (10)	0.147 (7)	0.282 (5)
C(M7)	1.158 (2)	−0.0476 (17)	0.1448 (9)	H(7)	1.100 (10)	0.236 (8)	0.225 (5)
C(M8)	1.074 (2)	0.1841 (15)	0.0396 (9)				

Table II. Bond Distances (Å) in $[\eta^5\text{-}C_5(CH_3)_5]_3Co_3B_4H_4$

	Cage Framework		
Co(1)–Co(2)	2.501 (9)	Co(2)–B(5)	2.030 (7)
Co(1)–Co(3)	2.493 (9)	Co(2)–B(6)	2.030 (7)
Co(2)–Co(3)	2.498 (9)	Co(3)–B(4)	2.032 (7)
Co(1)–B(7)	1.944 (6)	Co(3)–B(6)	2.012 (7)
Co(2)–B(7)	1.954 (5)	B(4)–B(5)	1.693 (10)
Co(3)–B(7)	1.964 (6)	B(4)–B(6)	1.678 (9)
Co(1)–B(4)	2.039 (7)	B(5)–B(6)	1.689 (10)
Co(1)–B(5)	2.036 (6)	⟨B–H⟩	1.011 (4)
	$C_5(CH_3)_5$ Ligands		
Co(1)–C(1)	2.078 (5)	C(10)–C(6)	1.411 (12)
Co(1)–C(2)	2.118 (5)	C(6)–C(M6)	1.555 (11)
Co(1)–C(3)	2.122 (5)	C(7)–C(M7)	1.503 (10)
Co(1)–C(4)	2.135 (6)	C(8)–C(M8)	1.530 (10)
Co(1)–C(5)	2.100 (6)	C(9)–C(M9)	1.554 (12)
C(1)–C(2)	1.443 (9)	C(10)–C(M10)	1.487 (11)
C(2)–C(3)	1.393 (9)	Co(3)–C(11)	2.071 (8)
C(3)–C(4)	1.402 (8)	Co(3)–C(12)	2.088 (6)
C(4)–C(5)	1.378 (8)	Co(3)–C(13)	2.123 (6)
C(5)–C(1)	1.421 (10)	Co(3)–C(14)	2.105 (6)
C(1)–C(M1)	1.500 (9)	Co(3)–C(15)	2.074 (7)
C(2)–C(M2)	1.520 (9)	C(11)–C(12)	1.382 (11)
C(3)–C(M3)	1.550 (9)	C(12)–C(13)	1.340 (10)
C(4)–C(M4)	1.516 (9)	C(13)–C(14)	1.378 (10)
C(5)–C(M5)	1.551 (10)	C(14)–C(15)	1.376 (13)
Co(2)–C(6)	2.094 (6)	C(15)–C(11)	1.425 (13)
Co(2)–C(7)	2.130 (6)	C(11)–C(M11)	1.502 (12)
Co(2)–C(8)	2.124 (6)	C(12)–C(M12)	1.576 (11)
Co(2)–C(9)	2.101 (6)	C(13)–C(M13)	1.561 (10)
Co(2)–C(10)	2.074 (6)	C(14)–C(M14)	1.518 (12)
C(6)–C(7)	1.413 (11)	C(15)–C(M15)	1.549 (11)
C(7)–C(8)	1.341 (10)	⟨Co–C⟩	2.102 (2)
C(8)–C(9)	1.378 (10)	$\langle C_{ring}\text{–}C_{ring}\rangle$	1.392 (3)
C(9)–C(10)	1.397 (12)	$\langle C_{ring}\text{–}C_{methyl}\rangle$	1.531 (3)

Table III. Selected Bond Angles (Deg) in $[\eta^5\text{-}C_5(CH_3)_5]_3Co_3B_4H_4$

	Cage Framework		
Co(2)–Co(1)–Co(3)	60.0 (2)	Co(1)–B(4)–Co(3)	75.5 (2)
Co(2)–Co(1)–B(5)	51.9 (2)	Co(1)–B(4)–B(6)	101.1 (4)
Co(2)–Co(1)–B(7)	50.3 (2)	Co(3)–B(4)–B(5)	101.2 (4)
Co(3)–Co(1)–B(4)	52.1 (2)	B(5)–B(4)–B(6)	60.2 (4)
Co(3)–Co(1)–B(7)	50.7 (2)	Co(1)–B(5)–Co(2)	75.9 (2)
B(4)–Co(1)–B(5)	49.1 (3)	Co(1)–B(5)–B(6)	100.8 (4)
Co(1)–Co(2)–Co(3)	59.8 (2)	Cl(2)–B(5)–B(4)	101.7 (4)
Co(1)–Co(2)–B(5)	52.2 (2)	B(4)–B(5)–B(6)	59.5 (4)
Co(1)–Co(2)–B(7)	49.9 (2)	Co(2)–B(6)–Co(3)	76.3 (3)
Co(3)–Co(2)–B(6)	51.6 (2)	Co(2)–B(6)–B(4)	102.3 (4)
Co(3)–Co(2)–B(7)	50.6 (2)	Co(3)–B(6)–B(5)	102.1 (4)
B(5)–Co(2)–B(6)	49.2 (3)	B(4)–B(6)–B(5)	60.4 (4)
Co(1)–Co(3)–Co(2)	60.1 (2)	Co(1)–B(7)–H(7)	128.1 (5)
Co(1)–Co(3)–B(4)	52.4 (2)	Co(2)–B(7)–H(7)	133.2 (4)
Co(2)–Co(3)–B(7)	50.2 (2)	Co(3)–B(7)–H(7)	135.9 (5)
Co(2)–Co(3)–B(6)	52.2 (2)	Co(1)–B(7)–Co(2)	79.8 (2)
Co(2)–Co(3)–B(7)	50.2 (2)	Co(1)–B(7)–Co(3)	79.3 (2)
B(4)–Co(3)–B(6)	49.0 (3)	Co(2)–B(7)–Co(3)	79.2 (2)
	$C_5(CH_3)_5$ Ligands		
C(2)–C(1)–C(5)	105.6 (6)	C(M7)–C(7)–C(8)	124 (1)
C(1)–C(2)–C(3)	107.5 (6)	C(M8)–C(8)–C(7)	123 (1)
C(2)–C(3)–C(4)	109.3 (6)	C(M8)–C(8)–C(9)	126 (1)
C(3)–C(4)–C(5)	107.7 (6)	C(M9)–C(9)–C(8)	126 (1)
C(4)–C(5)–C(1)	109.9 (6)	C(M9)–C(9)–C(10)	125 (1)
C(M1)–C(1)–C(2)	125.9 (9)	C(M10)–C(10)–C(9)	122 (1)
C(M1)–C(1)–C(5)	128.1 (9)	C(M10)–C(10)–C(6)	133 (1)
C(M2)–C(2)–C(1)	123.8 (8)	C(12)–C(11)–C(15)	103.9 (8)
C(M2)–C(2)–C(3)	128.7 (8)	C(11)–C(12)–C(13)	111.6 (8)
C(M3)–C(3)–C(2)	126.9 (6)	C(12)–C(13)–C(14)	108.1 (7)
C(M3)–C(3)–C(4)	123.0 (7)	C(13)–C(14)–C(15)	107.6 (8)
C(M4)–C(4)–C(3)	123.5 (7)	C(14)–C(15)–C(11)	108.7 (6)
C(M4)–C(4)–C(5)	128.4 (6)	C(M11)–C(11)–C(12)	128 (1)
C(M5)–C(5)–C(4)	125.7 (8)	C(M11)–C(11)–C(15)	128 (1)
C(M5)–C(5)–C(1)	124.1 (8)	C(M12)–C(12)–C(11)	124 (1)
C(7)–C(6)–C(10)	109.1 (7)	C(M12)–C(12)–C(13)	124 (1)
C(6)–C(7)–C(8)	106.7 (7)	C(M13)–C(13)–C(12)	128 (1)
C(7)–C(8)–C(9)	110.3 (7)	C(M13)–C(13)–C(14)	124 (1)
C(8)–C(9)–C(10)	109.0 (7)	C(M14)–C(14)–C(13)	124 (1)
C(9)–C(10)–C(6)	104.8 (7)	C(M14)–C(14)–C(15)	129 (1)
C(M6)–C(6)–C(7)	131 (1)	C(M15)–C(14)–C(15)	128 (1)
C(M6)–C(6)–C(10)	120 (1)	C(M15)–C(15)–C(11)	123 (1)
C(M7)–C(7)–C(6)	129 (1)	⟨C(M)–C–C⟩	126

The greatest parameter shift in the final least-squares cycle was less than 0.01 times its standard deviation, and the esd of an observation of unit weight was 3.39. A final Fourier difference function was essentially featureless. Tables of the observed and calculated structure factors are available. (See paragraph at end of paper regarding supplementary material.) The principal programs used are described elsewhere.[10]

Results and Discussion

Table I lists the final positional parameters while Tables II and III contain intramolecular distances and angles. Tables of thermal parameters and selected mean planes are available as supplementary data. The molecular structure as viewed down the pseudothreefold axis is shown in Figure 1, while Figure 2 depicts an oblique view of the Co_3B_4 polyhedral cage. Figure 3 shows the packing arrangement in the unit cell.

Consistent with the NMR evidence,[2] the molecule does in fact contain a Co_3B_3 cluster whose tricobalt face is capped by BH, analogous to the previously established geometry[5] of

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[10] Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447.

Table IV. Comparison of Bond Distances in $(\eta^5\text{-}C_5R_5)_3Co_3B_4H_4$ Complexes

	length (mean value), Å	
bond	R = CH_3	R = H
Co–Co	2.497 (5)	2.441 (1)
Co–B_{basal}	2.030 (3)	2.027 (2)
Co–B_{apical}	1.954 (3)	1.952 (3)
B–B	1.687 (6)	1.706 (3)
Co–C	2.102 (2)	2.08 (1)
C–C (ring)	1.392 (3)	1.42 (1)

$(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$. While there is no imposed crystallographic symmetry, there is a virtual C_3 axis through the apex boron atom [B(7)] and the center of the Co_3 triangle; the $C_5(CH_3)_5$ ligands are well-ordered and also conform roughly to the pseudothreefold symmetry. The three independent Co–Co bond lengths are virtually identical, as are the six Co–B_{basal} and the three Co–B_{apical} distances (Table II).

This geometry is in agreement with the skeletal electron-count scheme for clusters,[11] which predicts capped-closo geometry for *n*-vertex polyhedra having 2*n* skeletal electrons;[12] the $(\eta^5\text{-}C_5R_5)_3Co_3B_4H_4$ complexes, on the basis of the usual assignment[11] of two skeletal electrons for each $Co(C_5R_5)$ and BH unit, are 7-vertex, 14-electron systems. Further discussion of the "capping principle" as applied to polyhedral boranes is given elsewhere.[5]

Comparison with $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$. The Co_3B_4 polyhedra in the $C_5(CH_3)_5$- and C_5H_5-containing species are, as noted, closely similar, but there is at least one notable difference: the Co–Co bond distances in the pentamethylcyclopentadienyl complex [mean value 2.497 (5) Å] are significantly longer than those in the cyclopentadienyl compound [2.441 (1) Å], the increase corresponding to about 10 standard deviations. The relatively long Co–Co interactions in $[\eta^5\text{-}C_5(CH_3)_5]_3Co_3B_4H_4$ can be explained in terms of relief of interligand repulsion involving methyl groups on adjacent $C_5(CH_3)_5$ ligands. That the effect is primarily steric rather than electronic in origin is suggested by the fact that *no other* corresponding framework bond lengths in the two clusters are significantly different at the 3σ level, as shown in Table IV.

Further evidence of strong repulsive steric interaction between the ligands is given by the fact that the methyl groups are displaced out of their respective C_5 ring planes by an average of 0.14 Å, in a direction away from the neighboring cobalt atom. Although methyl displacements are invariably observed in other pentamethylcyclopentadienyl complexes[13] even when ligand–ligand contacts are absent, the magnitude in such cases is usually substantially smaller; for example, in the four structures reported in the preceding paper, i.e., for 6-$[\eta^5\text{-}C_5(CH_3)_5]CoB_9H_{13}$, 6,9-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{12}$, 5,7-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{12}$, and 6-Cl-5,7-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{11}$, the average out-of-plane deflections of the methyl groups are respectively 0.048, 0.047, 0.061, and 0.115 Å (in the last case cited, the methyl displacements are increased due to interactions with the chlorine substituent located between the $C_5(CH_3)_5$ ligands).[3] Similarly, the $C_5(CH_3)_5$ methyl groups in μ-$[(\eta^5\text{-}C_5(CH_3)_5)Co(CH_3)_2C_2B_3H_4]HgCl$[14] and $[\eta^5\text{-}C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$[15] are bent out of the C_5 plane by an average of 0.080 and 0.049 Å, respectively. Thus, the deformation of the $C_5(CH_3)_5$ groups in $[\eta^5\text{-}C_5(CH_3)_5]_3Co_3B_4H_4$ is significantly larger than in any other structurally characterized boron cluster containing that ligand.[16] Moreover, the largest individual methyl deflections in the present case (0.19 Å) involve those CH_3 groups that are in closest proximity to neighboring $C_5(CH_3)_5$ units.

Table V. Interligand C–C Contact Distances in $[\eta^5\text{-}C_5(CH_3)_5]_3Co_3B_4H_4$[a]

atoms	distance, Å	atoms	distance, Å
C(M2)–C(M12)	3.407	C(M6)–C(M15)	3.390
C(M3)–C(M13)	3.331	C(M7)–C(M14)	3.588
C(M4)–C(M8)	3.543	⟨C(M)–C(M)⟩	3.433
C(M5)–C(M9)	3.338		

[a] Closest inter*molecular* contact is 3.61 Å between C(M2) and C(M6), symmetry operation *x*, 1 + *y*, *z*.

Table VI. Comparative Data in Capped Tricobalt Cluster Systems

	mean value			
	$[C_5(CH_3)_5]_3$-$Co_3B_4H_4$[a]	$(C_5H_5)_3$-$Co_3B_4H_4$[b]	μ-CO-$(C_5H_5)_3$-$Co_3B_3H_3$[c]	$(CO)_9$-Co_3CR[d]
Co–Co, Å	2.497 (5)	2.441 (1)	2.444 (1)	2.47
Co–B(C),[e] Å	1.954 (3)	1.953 (5)	1.945 (8)	1.92
Co–B(C)–Co, deg[e]	79.4 (1)	77.4 (2)	77.8 (9)	81
Co–B–H, deg[e]	132 (1)	134 (1)	....	...
Co–C–R, deg[e]			133.5 (4)	131
^1H NMR $\delta_{H(apex)}$	12.98	14.45[f]		12.08[g]

[a] This work. [b] Reference 5. [c] Gromek, J. M.; Donohue, J. *Cryst. Struct. Commun.* 1981, *10*, 849. [d] Penfold, B. R.; Robinson, B. H. *Acc. Chem. Res.* 1973, *6*, 73. [e] Apical boron or carbon atom only. [f] Reference 4. [g] R = H (see ref 18).

The severity of the interligand crowding can be measured by the nonbonded C–C distances between methyl carbon atoms, as listed in Table V. These interactions average 3.43 Å, and the shortest of them [C(M3)···C(M13) and C(M5)···C(M9)] are less than 3.35 Å, nearly $^2/_3$ Å less than the "normal" expected[17] van der Waals methyl–methyl separation of 4.0 Å. Unfortunately, the data did not permit location and refinement of the methyl hydrogen atoms, so that a more detailed picture of the interactions of the CH_3 groups is not presently available.

In summary, it appears that the mutual repulsions of adjacent $C_5(CH_3)_5$ ligands are mitigated somewhat by lengthening of the cobalt–cobalt vectors and bending of the methyl groups out of the C_5 ring planes. Curiously, the $C_5(CH_3)_5$ rings are not staggered with respect to each other as might have been expected; a possible explanation may be that the methyl hydrogen atoms are oriented in an interlocking manner that serves to stabilize the observed arrangement of the $C_5(CH_3)_5$ rings, but as noted above, these hydrogen positions were not determined.

Comparison with Other Related Clusters. Table VI presents corresponding data for several tricobalt complexes whose common structural feature is a triangular array of cobalt atoms which is face-coordinated to a BH, CO, or CR unit. The general similarity is apparent, and the unusually deshielded ^1H NMR signals of the apex protons in the two $(C_5R_5)_3Co_3B_4H_4$ species[2,4] and $(CO)_9Co_3CH$[18] suggest that the analogy is not only geometric but may be, to a degree at least, electronic as well.

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(11) See ref 26 of the preceding paper in this issue.

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(16) Larger out-of-plane methyl displacements (up to 0.28 Å) have, however, been reported for $Th[\eta^5\text{-}C_5(CH_3)_5]_2[\eta^2\text{-}CON(C_2H_5)_2)]Cl$ and $U[\eta^5\text{-}C_5(CH_3)_5]_2[\eta^2\text{-}CON(CH_3)_2]_2$. See: Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206. In these complexes the carbamoyl ligand(s) between the $C_5(CH_3)_5$ rings force the latter to bend close together, with interligand contacts as short as 3.39 Å.

(17) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; p 261.

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The only capped-octahedral clusters other than the two $(\eta^5\text{-}C_5R_5)_3Co_3B_4H_4$ species for which X-ray diffraction studies have been reported are $Os_7(CO)_{21}$[19] and $Rh_7(CO)_{16}{}^{13-}$,[20] both of which are electronic analogues of the $(\eta^5\text{-}C_5R_5)_3Co_3B_4H_4$ systems and hence conform to the skeletal-electron paradigm alluded to earlier.

Conclusion. The $[\eta^5\text{-}C_5(CH_3)_5]_3Co_3B_4H_4$ molecule is, to our knowledge, the only structurally characterized species containing three mutually bonded $M[\eta^5\text{-}C_5(CH_3)_5]$ groups. As we note in the Introduction, prior to the crystal structure determination it was questionable whether such an arrangement would be viable, given the unavoidably severe interligand steric crowding. The fact that this structure is nonetheless adopted even at the expense of cobalt–cobalt bond lengthening and considerable bending of the methyl groups out of the C_5 ring planes implies strong thermodynamic preference for this particular cluster geometry as opposed to other, less sterically crowded arrangements. In principle, there exists a possibility that the observed structure is kinetically rather than thermodynamically dictated, but this is quite unlikely given (1) the high symmetry, (2) the fact that the same geometry is observed for both the C_5H_5- and the $C_5(CH_3)_5$-containing species, and (3) the failure to detect any other isomer. Indeed, it is probable that the formation of the $(\eta^5\text{-}C_5R_5)_3Co_3B_4H_4$ complexes from $B_5H_8^-$ involves rearrangement of other, less stable species that form in earlier stages of the reactions.

The present work indicates that the capped-*closo*-Co_3B_4 polyhedron is an electronic system of exceptional stability, which persists even in the face of strong steric inducement to adopt a different geometry. When quantitative molecular orbital treatments are conducted on this system, it will be surprising if they do not reveal a clear preference for the observed cage structure in relation to other conceivable alternatives.

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Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, thermal parameters, and selected mean planes (16 pages). Ordering information is given on any current masthead page.

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Investigations of the Coordination Chemistry of Molybdenum with Facultative Tetradentate Ligands Possessing N_2S_2 Donor Sets. 2.[1] Preparation, Chemical Characterization, and Electrochemical Study of the Molybdenum(IV)-, Molybdenum(V)-, and Molybdenum(VI)-Oxo Complexes

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The chemistry of the tetradentate N_2S_2 donor ligands *N,N′*-dimethyl-*N,N′*-bis(2-mercaptoethyl)ethylenediamine (LH_2) and *N,N′*-dimethyl-*N,N′*-bis(2-mercaptoethyl)-1,3-propanediamine ($L'H_2$) with molybdenum in the VI, V, and IV oxidation states is described. In methanol solution Mo(VI)–oxo reagents combine with LH_2 and $L'H_2$ to give $[MoO_2L]$ and $[MoO_2L']$. Reduction of these complexes with HSPh in methanol yields $[Mo_2O_3L_2]$ and $[H_2Mo_2O_4L'_2]$. The more common mono-oxo-bridged Mo(V) dimer $[Mo_2O_3L'_2]$ may be prepared by the reaction of $[MoO_2L']$ with PMe_2Ph in dry THF. The Mo(IV) species [MoOL] and [MoOL′] are obtained by treatment of the Mo(VI) species with excess PMe_2Ph in THF solution. The sulfido-bridged dimers $[Mo_2S_4L'_2]^{2-}$ and $[MoO_2S_2L'_2]^{2-}$ have also been prepared. The infrared, electronic, and proton magnetic resonance spectra of these complexes are noted. The electrochemical properties of the complexes are discussed in detail. The significant differences in the redox characteristics of $[MoO_2L]$ and $[MoO_2L']$ are reflected in the contrasting reactivity patterns with substituted hydrazines. Whereas $[MoO_2L]$ reacts with H_2NNR_2 and H_2NNHR species to give the common monosubstituted derivatives $[MoO(N_2R_2)L]$ and the disubstituted diazene complexes $[Mo(N_2R)_2L]$, $[MoO_2L']$ reacts only with benzoylhydrazides ($C_6H_5CONHNH_2$) to yield the potentially seven-coordinate species $[MoO(C_6H_5CONNH)L']$.

Introduction

There has been much recent interest in the synthesis and characterization of molybdenum–sulfur complexes.[3,4] This attention by coordination chemists stems largely from the recognition that molybdenum is a necessary cofactor for a number of redox-active enzymes.[5,6] On the basis of electron paramagnetic resonance studies[7–9] and, more recently, EXAFS investigations,[10–13] a number of these enzymes, other than nitrogenase, have been shown to possess molybdenum coordinated to both terminal oxo ligands and to sulfur groups, a

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