13652). The X-ray diffractometer system was purchased with funds from the National Science Foundation (Grant MPS 75-05911).

Registry No. $[Cu_2(tren)_2(BZD)](NO_3)_4$, 65776-91-2.

Supplementary Material Available: Stereoscopic views of the two binuclear cations, Tables V (least-squares planes), VI (Cu–Cu distances within the asymmetric unit), VII (O–Cu distances less than 4.4 Å), VIII (network of nitrates between binuclear cations), and IX (possible hydrogen-bond distances and angles), final values of F_o and F_c for $[Cu_2(tren)_2(BZD)](NO_3)_4$ with unobserved reflections marked with asterisks (44 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Camille and Henry Dreyfus Teacher–Scholar Fellow, 1972–1977; A. P. Sloan Foundation Fellow, 1976–1978. Author to whom correspondence should be addressed at the University of Illinois.

(2) R. Micu-Semeniuc and L. Silaghi-Dumitrescu, *Stud. Univ. Babes-Bolyai, Ser. Chem.*, **19**, 112 (1974), and references therein.

(3) N. Sadasivan and C. G. Kumbhar, *Indian J. Chem., Sect. A*, **14**, 357 (1976).

(4) R. Micu-Semeniuc, L. Silaghi-Dumitrescu, and I. Haiduc, *Inorg. Chim. Acta*, **17**, 5 (1976).

(5) Y. Mathey, C. Mazieres, and R. Setton, *Inorg. Nucl. Chem. Lett.*, **13**, 1 (1977).

(6) R. Micu-Semeniuc, S. Gh. Macarovici, and M. Bossanyi, *Rev. Chim. (Bucharest)*, **19**, 1157 (1974), and references therein.

(7) S. M. F. Rahman, N. Ahmad, and V. Kumar, *Indian J. Chem.*, **13**, 86 (1975).

(8) Dimeric complexes have been proposed; for example, see R. Constantinescu and R. Micu-Semeniuc, *Synth. React. Inorg. Met.-Org. Chem.*, **7**, 399 (1977).

(9) K. Rieder, U. Hauser, J. Siegenthaler, E. Schmidt, and A. Ludi, *Inorg. Chem.*, **14**, 1902 (1975).

(10) L. Broman, B. G. Malmström, R. Aasa, and T. Vänngard, *Biochim. Biophys. Acta*, **75**, 365 (1963).

(11) J. Peisach and W. G. Levine, *Biochim. Biophys. Acta*, **77**, 615 (1963).

(12) E. Frieden and H. S. Hsieh, *Adv. Enzymol.*, **44**, 187 (1976), and references therein.

(13) T. R. Felthouse and D. N. Hendrickson, *Inorg. Chem.*, **17**, 2636 (1978).

(14) T. R. Felthouse, E. N. Duesler, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **100**, 618 (1978).

(15) All crystallographic calculations were carried out with the Syntex EXTL X-ray crystallographic package, based on the Data General ECLIPSE computer. Due to the number of variable parameters (937), only Gauss–Siedel block refinements were used to refine the structure.

(16) A simple absorption correction was attempted on the Cu Kα reflection data; however, no improvement resulted from this effort. All results using the Cu Kα data were based on the original reflection data not corrected for absorption.

(17) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).

(18) Sixteen reflections were observed to be suffering severely from absorption ($\Delta/\sigma(F) \geq 20.0$) and these were not included in the last stages of the refinement of the Cu Kα data.

(19) "International Tables for X-ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., Kynoch Press, Birmingham, England, 1974: (a) pp 99–102; (b) pp 148, 150.

(20) Supplementary material.

(21) The weighted mean was calculated using a weight of $1/\sigma^2$, where σ is the estimated standard deviation from the refinement. The standard deviations for mean values are calculated from the formula $[\sum_m(l_m - \bar{l})^2/m(m-1)]^{1/2}$, see G. H. Stout and L. H. Jensen, "X-ray Structure Determination, A Practical Guide", Macmillan, New York, N.Y., 1968, p 423.

(22) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **13**, 1911 (1974).

(23) E. J. Laskowski, D. M. Duggan, and D. N. Hendrickson, *Inorg. Chem.*, **14**, 2449 (1975).

(24) P. C. Jain and E. C. Lingafelter, *J. Am. Chem. Soc.*, **89**, 6131 (1967).

(25) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, Table 7-6, p 229.

(26) C. H. Koo, H. S. Shin, and M. H. Kang, *Taehan Hwahak Hoechi*, **14**, 123 (1970); *Chem. Abstr.*, **73**, 114003 (1970).

(27) I. Ikemoto, K. Chikaishi, K. Yakushi, and H. Kuroda, *Acta Crystallogr., Sect. B*, **28**, 3502 (1972).

(28) K. Yakushi, I. Ikemoto, and H. Kuroda, *Acta Crystallogr., Sect. B*, **30**, 835 (1974).

(29) K. Yakushi, I. Ikemoto, and H. Kuroda, *Acta Crystallogr., Sect. B*, **30**, 1738 (1974).

(30) N. Tachikawa, K. Yakushi, and H. Kuroda, *Acta Crystallogr., Sect. B*, **30**, 2770 (1974).

(31) K. Yakushi, N. Tachikawa, I. Ikemoto, and H. Kuroda, *Acta Crystallogr., Sect. B*, **31**, 738 (1975).

(32) S. A. Chawdhury, A. Hargreaves, and R. A. L. Sullivan, *Acta Crystallogr., Sect. B*, **24**, 1222 (1968).

(33) S. A. Chawdhury, A. Hargreaves, and S. H. Rizvi, *Acta Crystallogr., Sect. B*, **24**, 1633 (1968).

(34) H. Tsuchiya, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 659 (1973), and references therein.

(35) Z. P. Povet'eva and Z. V. Zvonkova, *Kristallografiya*, **20**, 69 (1975); *Sov. Phys.—Crystallogr. (Engl. Transl.)*, **20**, 37 (1975).

(36) R. Chandrasekaran, *Acta Crystallogr., Sect. B*, **25**, 369 (1969).

(37) This is the sum of the van der Waals radii for N and O, as taken from the "Handbook of Chemistry and Physics", 53rd ed., R. C. Weast, Ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1972, p D146.

(38) A. F. Wells, "Structural Inorganic Chemistry", 4th ed., Clarendon Press, Oxford, 1975, p 304.

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Crystal Structure of a Closo Six-Vertex Metalloboron Cluster, 1,2-$(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$, with Hydrogen Atoms Bridging Co_2B Triangular Faces

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Received June 21, 1978

A single-crystal X-ray diffraction investigation of the title compound established the structure as an octahedral Co_2B_4 cage with the metal atoms occupying adjacent vertices and each cobalt coordinated to an η^5-cyclopentadienyl ring, in agreement with the geometry originally proposed from ^{11}B and ^1H NMR data. Two crystallographically equivalent hydrogen atoms occupy face-bridging positions approximately over the centers of the two Co_2B triangular faces, in a manner very similar to face bridging of trimetallic faces in metal-cluster compounds. This structure represents the first instance in which face-bridging hydrogen atoms on an M_2N face (where M and N are metal and nonmetal atoms, respectively) have been located and refined and is the second example of a face-bridging hydrogen on a closo polyhedral boron cage (after CB_5H_7) to be precisely located. The Co–Co bond distance is 2.557 (1) Å, the longest such distance thus far known in a cobalt–boron cage compound; the unusual length is attributed to the presence of bridging hydrogen atoms on both sides of the Co–Co vector, which are thought to produce a lowering of the Co–Co bond order. The implications of these findings with respect to other closo metalloboranes and metallocarboranes containing "extra" hydrogen atoms are discussed. Crystal data: $M_r = 297.4$; space group $P2_1/m$; $a = 7.601$ (5), $b = 9.060$ (4), $c = 9.793$ (5) Å; $\beta = 108.07$ (5)°; $V = 641$ (1) Å^3; μ(Mo Kα) $= 26.5$ cm^{-1}; ρ(calcd) $= 1.544$ g cm^{-3} for $Z = 2$. The structure was refined by full-matrix least-squares methods to a final R value of 0.039 for the 994 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

Introduction

An extensive series of air-stable, crystalline cobaltaboranes, several of which are structurally unique, is formed in the reaction of $CoCl_2$, $B_5H_8^-$, and $C_5H_5^-$ in cold tetrahydrofuran (THF). The isolation and characterization of a number of these compounds have been described elsewhere,[1] and X-ray structure determinations on 2-$(\eta^5\text{-}C_5H_5)CoB_4H_8$,[2] $(\eta^5\text{-}C_5H_5)CoB_9H_{13}$,[3] $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$,[4] $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$,[4]

0020-1669/79/1318-0252$01.00/0

μ-C_3H_4-(η^5-C_5H_5)$_2Co_2C_2B_3H_3$,[5] and (η^5-C_5H_5)$_4Co_4B_4H_4$[6] have been conducted. The present article reports a crystallographic study on the violet six-vertex complex 1,2-(η^5-C_5H_5)$_2Co_2B_4H_6$, which completes the detailed structural characterization of the seven parent cluster species obtained in the original reaction (in addition, several derivatives have been isolated and spectroscopically identified[1]).

Four of the cobaltaborane products are closed polyhedral (closo) species, and two of these—the Co_2B_4 and Co_3B_3 complexes—contain cage hydrogen atoms in excess of one per boron. The presence of "extra" hydrogens on a *closo framework* is a relatively new phenomenon in boron chemistry and is virtually restricted to metal-containing species (metalloboranes and metallocarboranes). There are, for example, no binary boron hydrides containing this feature, and thus far the only carborane in this category is CB_5H_7, an octahedral cage whose unique hydrogen tautomerizes through equivalent positions on the four B_3 triangular faces.[7] The location of the face-bridging hydrogen atom on CB_5H_7, originally suggested from NMR spectra, was indirectly shown in a microwave analysis[8] and has been definitively established from an electron diffraction study.[9]

Several metallocarboranes we have reported[10] (e.g., (η^5-C_5H_5)$FeHC_2B_4H_6$) are presumed to have face-bridging hydrogens on closo frameworks, but in no case has any of these hydrogen atoms been precisely located. An X-ray study[4] of the octahedral metalloborane 1,2,3-(η^5-C_5H_5)$_3Co_3B_3H_5$ revealed electron density corresponding to bridging hydrogen atoms in the vicinity of the three Co–Co edges, in agreement with proton NMR spectra,[1a,c] but these peaks could not be successfully refined.

In the closely related complex 1,2-(η^5-C_5H_5)$_2Co_2B_4H_6$, ^{11}B and ^1H NMR evidence[1a,c] again pointed to a closo six-vertex cage with two bridging hydrogens closely associated with the cobalt atoms, and an X-ray diffraction study was undertaken with the objective of locating and refining these hydrogen atoms. Two other considerations added significance to this effort. First, there have been very few instances in which hydrogen atoms bridging trimetallic (M_3) faces in metal clusters have been crystallographically established,[11] and apparently none involving a hydrogen-bridged M_2N face (where N is a nonmetal atom). Second, 1,2-(η^5-C_5H_5)$_2Co_2B_4H_6$ and (η^5-C_5H_5)$_3Co_3B_3H_5$ represent direct electronic and structural links, or "hybrids", between the boranes (e.g., $B_6H_6^{2-}$) and the large family of six-vertex metal clusters. Detailed structural information on six-vertex metalloboron cages, particularly those containing metal–metal bonding interactions, is vital to the further development of theoretical ideas[17] which seek to relate these different classes of cluster systems.

Experimental Section

Small crystals of the title compound[1a,c] grown by the vapor diffusion of pentane into a dichloromethane solution were mounted (in arbitrary orientations) on glass fibers and examined by preliminary precession photographs. Since very high crystal quality was indicated, a data set was collected on one crystal having at least 10 faces and maximum dimensions of 0.13 × 0.20 × 0.30 mm. Crystal data: $Co_2C_{10}B_4H_{16}$; M_r = 297.35; space group $P2_1/m$ (No. 11); Z = 2; a = 7.601 (5), b = 9.060 (4), c = 9.793 (5) Å; β = 108.07 (5)°; V = 641 (1) Å^3; μ(Mo Kα) = 26.5 cm^{-1}; ρ(calcd) = 1.544 g/cm^3; F(000) = 300. For this crystal the Enraf-Nonius program SEARCH was used to obtain 25 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 these 25 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 $2n + 1$ for $0k0$ indicated that the space group is either $P2_1$ or $P2_1/m$; the latter was shown to be correct by the successful solution and refinement of the structure. An assumption of $Z = 2$ requires that the molecule be bisected by a crystallographic mirror plane and is consistent with the molecular formula assuming 20.0 Å^3 per nonhydrogen atom.

Collection and Reduction of the Data. Two data sets were collected (vide infra) of which only the second was employed for final refinement of the structure. Both sets 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. In the second data collection, the θ–2θ scan technique was used to record the intensities for all reflections for which 1° $\le 2\theta \le$ 50°. 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 0.60 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 = 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 1198 intensities of which 994 had $F_o^2 \ge 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics using an ignorance factor of 0.03.[18] These latter reflections were used in the final refinement of the structural parameters. No absorption correction was made due to the difficulty of accurately measuring the many faces (at least 10) on this crystal. Given the small crystal size and the low absorption coefficient of the compound, the error introduced from this source is assumed to be negligible.

Solution and Refinement of the Structure. A Patterson map synthesized from the initial data set gave the coordinates of two cobalt atoms, assuming the space group to be $P2_1/m$. The map strongly implied that the space group was $P2_1/m$ rather than $P2_1$; thus, the Co(1)–Co(2) vector appeared at x = 0.04, y = 0, z = 0.27, consistent with a location of the two cobalt atoms on the mirror plane at y = 0.25 in $P2_1/m$. (The space group could not be $P2_1$ unless the two cobalts happened to lie on the same y coordinate, a possible but less likely occurrence.) A series of electron density difference maps revealed the locations of several nonhydrogen atoms as well as the probable positions of several hydrogens associated with the cage. However, least-squares refinement of all 11 unique nonhydrogen atoms converged to a rather unsatisfactorily high value of 0.075 for the conventional residual R, where $R = \sum||F_o| - |F_c||/\sum|F_o|$. Also, several bond distances and angles seemed questionable in comparison with other metalloborane structures. Further electron density difference maps clearly ruled out any disorder or missing atoms. Comparison of observed and calculated structure factors strongly suggested that instrumental problems had seriously affected the quality of the data set, and a second data set was collected on the same crystal. Refinement of all nonhydrogen atoms with these data reduced R to 0.046, and an examination of F_o vs. F_c disclosed no systematic trends; there were no reflections for which $(|F_o| - |F_c|)/\sigma(F_o)$ was unacceptably large. A difference map at this stage clearly revealed the locations of all three unique terminal hydrogen atoms bonded to boron, as well as the position of the unique bridging hydrogen H(123). The latter atom was located over the Co(1)–Co(2)–B(3) face (see Figure 1 for the atom numbering system). Further refinement including all cage hydrogen atoms reduced R to 0.040. The hydrogens appeared to refine except that the terminal B–H distances became either fairly short (0.93 Å) or quite long (1.25 and 1.47 Å). However, the angles of the B–H vectors relative to other cluster atoms were very reasonable, as were the hydrogen thermal parameters. Therefore, the terminal hydrogen atoms were reset to locations 1.05 Å from their refined B–H vectors and in the final cycles of refinement were held fixed at these positions; their thermal parameters were also held fixed at the previously refined values. The positional coordinates and isotropic thermal parameter of the bridging hydrogen H(123) were, however, allowed to vary. Further refinement reduced R to its final value of 0.039 and R_w to 0.056 where $R_w = (w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. The largest parameter shift in the final cycle of refinement was 0.01 times its estimated error, and the estimated standard deviation of an observation of unit weight was 2.56. A structure factor calculation including reflections with $F_o^2 < 3\sigma(F_o^2)$ gave R = 0.053. A final

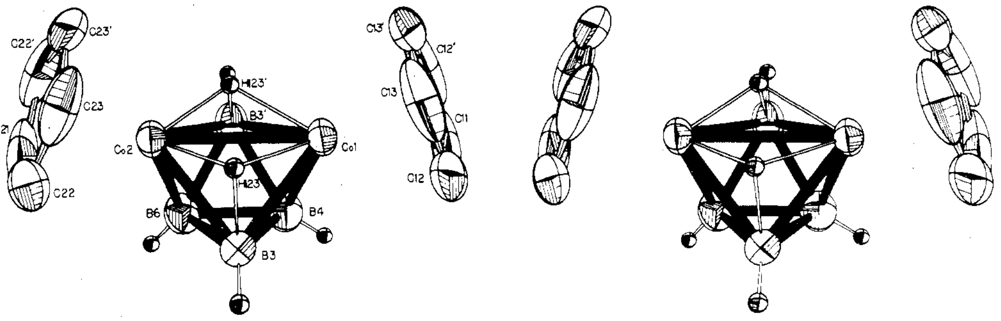

Figure 1. Stereoview of the molecular structure and numbering system. Primed atoms are related to the corresponding unprimed atoms by a crystallographic mirror plane through Co(1), Co(2), B(4), and B(6).

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(1)	0.2745 (1)	0.2500 (0)	0.31591 (8)	0.0360 (4)	0.0453 (5)	0.0282 (3)	0.0000 (0)	0.0126 (3)	0.0000 (0)
Co(2)	0.2443 (1)	0.2500 (0)	0.04848 (8)	0.0464 (4)	0.0359 (4)	0.0285 (4)	0.0000 (0)	0.0144 (3)	0.0000 (0)
C(11)	0.3362 (12)	0.2500 (0)	0.5256 (8)	0.078 (5)	0.275 (17)	0.027 (3)	0.000 (0)	0.025 (3)	0.000 (0)
C(12)	0.2356 (9)	0.1283 (9)	0.4786 (6)	0.205 (4)	0.103 (5)	0.122 (3)	0.073 (4)	0.139 (2)	0.066 (3)
C(13)	0.0673 (7)	0.1734 (8)	0.3942 (5)	0.087 (2)	0.137 (5)	0.068 (2)	−0.058 (3)	0.059 (2)	−0.042 (3)
C(21)	0.2722 (15)	0.2500 (0)	−0.1475 (8)	0.119 (7)	0.201 (15)	0.029 (4)	0.000 (0)	0.027 (4)	0.000 (0)
C(22)	0.1775 (10)	0.1286 (8)	−0.1362 (6)	0.136 (5)	0.088 (4)	0.042 (3)	0.037 (4)	−0.010 (3)	−0.030 (3)
C(23)	0.0123 (8)	0.1704 (7)	−0.1095 (5)	0.090 (4)	0.098 (4)	0.034 (2)	−0.045 (3)	−0.014 (3)	0.008 (3)
B(3)	0.4153 (7)	0.1102 (7)	0.2097 (5)	0.057 (3)	0.047 (3)	0.039 (2)	0.013 (3)	0.015 (2)	0.006 (2)
B(4)	0.5394 (10)	0.2500 (0)	0.3197 (9)	0.038 (3)	0.071 (6)	0.049 (4)	0.000 (0)	0.013 (3)	0.000 (0)
B(6)	0.5219 (10)	0.2500 (0)	0.1430 (8)	0.042 (3)	0.071 (6)	0.050 (4)	0.000 (0)	0.020 (3)	0.000 (0)

atom	x	y	z	B_{iso}, Å^2	atom	x	y	z	B_{iso}, Å^2
H(3)	0.400	−0.005	0.204	6	H(6)	0.640	0.250	0.108	6
H(4)	0.652	0.250	0.416	5	H(123)	0.216 (6)	0.159 (7)	0.166 (4)	6 (1)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2(a^*)^2 + U_{22}k^2(b^*)^2 + U_{33}l^2(c^*)^2 + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{22}\cdot klb^*c^*)]$.

electron density difference synthesis contained no significant features.

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[19] and those for hydrogen from Stewart.[20] The effects of anomalous dispersion were included in F_c using Cromer and Ibers'[21] values of $\Delta f'$ and $\Delta f''$. The computing system and programs are described elsewhere.[22]

Results and Discussion

Table I contains the final positional and thermal parameters, and Tables II and III list intramolecular distances and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Tables IV and V list selected mean planes and the nearest intermolecular contacts, respectively. A stereoview of the structure is presented in Figure 1.

The Polyhedral Cage. The molecule contains a *closo*-Co_2B_4 framework with the cobalt atoms occupying adjacent vertices, in agreement with the original structural assignment[1a,c] based on ^{11}B and ^1H NMR data. The closo geometry is also in accord with the presence of 14 skeletal valence electrons (two from each $Co(C_5H_5)$ and BH unit and two from the bridging hydrogen atoms) as expected[17] for a $(2n + 2)$-electron system where n is the number of vertices in the polyhedron. The average B–B bond length is 1.729 (3) Å, which is similar to the corresponding distances in the closely related octahedral cages, $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$ [1.721 (3) Å][4] and $B_6H_6^{2-}$ [1.69 (1) Å],[23] and the capped-octahedral complex $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_4$ [1.706 (3) Å];[4] these values are all significantly shorter than typical B–B distances in larger cages such as 5-$(\eta^5\text{-}C_5H_5)CoB_9H_{13}$ [mean value 1.769 (2) Å].[3] The

Table II. Bond Distances (Å)[a]

Co(1)–Co(2)	2.557 (1)	B(6)–H(6)	1.05[b]
Co(1)–B(3)	2.126 (4)	Co(1)–C(11)	1.959 (6)
Co(1)–B(4)	2.001 (5)	Co(1)–C(12)	2.033 (4)
Co(2)–B(3)	2.125 (3)	Co(1)–C(13)	2.074 (3)
Co(2)–B(6)	2.024 (5)	Co(2)–C(21)	1.995 (6)
Co(1)–H(123)	1.62 (3)	Co(2)–C(22)	2.042 (4)
Co(2)–H(123)	1.48 (3)	Co(2)–C(23)	2.081 (3)
B(3)–H(123)	1.51 (3)	C(11)–C(12)	1.339 (8)
B(3)–B(4)	1.739 (5)	C(12)–C(13)	1.353 (7)
B(3)–B(6)	1.737 (5)	C(13)–C(13′)	1.38 (1)
B(3)–H(3)	1.05[b]	C(21)–C(22)	1.337 (7)
B(4)–B(6)	1.694 (7)	C(22)–C(23)	1.411 (7)
B(4)–H(4)	1.05[b]	C(23)–C(23′)	1.443 (9)

[a] Primed atoms are related to their unprimed counterparts by the mirror plane at $y = 0.25$. [b] B-terminal H distances were held fixed during final refinement cycles.

Table III. Selected Bond Angles (deg)

Co(2)–Co(1)–B(3)	53.0 (1)	B(3)–B(6)–B(4)	60.9 (2)
B(3)–Co(1)–B(4)	49.7 (1)	Co(2)–B(6)–H(6)	136.4 (4)
Co(1)–Co(2)–B(3)	53.0 (1)	B(3)–B(6)–H(6)	131.7 (2)
B(3)–Co(2)–B(6)	49.4 (1)	B(4)–B(6)–H(6)	121.6 (4)
Co(1)–B(3)–Co(2)	74.0 (1)	Co(1)–H(123)–Co(2)	111.1 (3)
Co(1)–B(3)–B(4)	61.4 (2)	Co(1)–H(123)–B(3)	85.4 (2)
Co(2)–B(3)–B(6)	62.3 (2)	Co(2)–H(123)–B(3)	90.6 (2)
B(4)–B(3)–B(6)	58.3 (3)	C(11)–Co(1)–C(12)	39.1 (2)
Co(1)–B(3)–H(3)	123.4 (3)	C(12)–Co(1)–C(13)	38.5 (2)
Co(2)–B(3)–H(3)	121.4 (3)	C(13)–Co(1)–C(13′)	39.1 (3)
B(4)–B(3)–H(3)	141.9 (3)	C(21)–Co(2)–C(22)	38.7 (2)
B(6)–B(3)–H(3)	139.9 (3)	C(22)–Co(2)–C(23)	40.0 (2)
Co(1)–B(4)–B(3)	68.9 (2)	C(23)–Co(2)–C(23′)	40.6 (3)
B(3)–B(4)–B(6)	60.8 (2)	C(12)–C(11)–C(12′)	110.8 (8)
Co(1)–B(4)–H(4)	123.1 (4)	C(11)–C(12)–C(13)	107.0 (6)
B(3)–B(4)–H(4)	133.2 (2)	C(12)–C(13)–C(13′)	107.6 (4)
B(6)–B(4)–H(4)	134.1 (4)	C(22)–C(21)–C(22′)	110.6 (8)
Co(2)–B(6)–B(3)	68.3 (2)	C(21)–C(22)–C(23)	109.1 (5)
		C(22)–C(23)–C(23′)	105.5 (3)

Table IV

Selected Mean Planes

atom	dev, Å	atom	dev, Å
Plane 1: Co(1), Co(2), B(3)			
$0.7266x + 0.6657y + 0.1701z = 2.8269$			
Co(1)	0.000	B(3)	0.000
Co(2)	0.000	H(123)	0.776
Plane 2: Co(1), Co(2), B(4), B(6)			
$y = 2.2650$			
Co(1)	0.000	B(4)	0.000
Co(2)	0.000	B(6)	0.000
Plane 3: Co(1), B(3), B(3′), B(6)			
$0.5585x + 0.8295z = 3.0500$			
Co(1)	−0.019	B(3′)	0.023
B(3)	0.023	B(6)	−0.028
Plane 4: Co(2), B(3), B(3′), B(4)			
$0.8727x - 0.4882z = 1.2598$			
Co(2)	0.012	B(3′)	−0.014
B(3)	−0.014	B(4)	0.017
Plane 5: C(11), C(12), C(13), C(13′), C(12′)			
$-0.6004x + 0.7997z = 3.3508$			
C(11)	0.013	C(13′)	0.004
C(12)	−0.010	C(12′)	−0.010
C(13)	0.004	Co(1)	1.675
Plane 6: C(21), C(22), C(23), C(23′), C(22′)			
$-0.1714x - 0.9852z = 0.9358$			
C(21)	−0.015	C(23′)	−0.004
C(22)	0.011	C(22′)	0.011
C(23)	−0.004	Co(2)	−1.674

Angles between Planes

planes	angle, deg	planes	angle, deg
1,2	49.3	2,6	90.0
1,3	56.8	3,4	85.3
1,4	56.6	3,5	70.8
1,5	72.5	3,6	24.1
1,6	73.0	4,5	23.9
2,3	90.0	4,6	70.6
2,4	90.0	5,6	46.8
2,5	90.0		

Table V. Intermolecular Contacts <3.8 Å

atoms	distance	relationship
C(11)-C(21)	3.384 (9)	$x, y, 1 + x$
C(12)-C(21)	3.751 (8)	$x, y, 1 + x$
C(13)-C(22)	3.797 (6)	$\bar{x}, \bar{y}, \bar{z}$
C(23)-C(23)	3.797 (8)	$\bar{x}, \bar{y}, \bar{z}$

difference is attributed to the lower coordination of the boron atoms in the octahedral cages as opposed to larger polyhedra (similar effects have been noted with respect to carbon atoms in carboranes[24] and metallocarboranes[25]).

A notable feature of the Co_2B_4 structure is the length of the Co–Co vector, 2.557 (1) Å. Although this value is not greatly out of line with those in octahedral cobalt clusters (e.g., 2.50 Å in $[Co_6(CO)_{14}]^{4-}$[26] and in $[Co_4Ni_2(CO)_{14}]^{2-}$[27]), it is substantially and significantly longer than the metal–metal distances in most other metalloboranes and metallocarboranes of first-row transition metals, as shown in Table VI. The only longer distance occurs in the irregular polyhedron $(\eta^5\text{-}C_5H_5)_2Fe_2C_2B_6H_8$, where the length of the Fe–Fe interaction appears to be a consequence of cage distortions induced by a "deficiency" of two electrons.[33] It is especially striking that the Co–Co distance in the Co_2B_4 cluster is about 0.1 Å (~10 standard deviations) longer than those in the closely related Co_3B_3 and Co_3B_4 complexes. This observation implies, and the data in Table VI verify, that there is no general correlation of metal–metal distance with metal atom coordination numbers in metalloboron systems. Indeed, if there were a "coordination number" effect for metals, we would expect $(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$ to exhibit a *short* Co–Co distance since the metal atoms occupy only four-coordinate vertices.

A plausible explanation of the long cobalt–cobalt bond is that the two face-bridging protons (discussed below) divert electron density away from the Co–Co edge, thereby lowering the metal–metal bond order. One would expect such an effect to be particularly evident when two such protons are associated with the same metal–metal bond, as is the case in $(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$. In the $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$ complex[4] there are again two "extra" hydrogens which are associated with the three Co–Co edges. However, in that molecule there is an average of only $^2/_3$ of a bridging hydrogen per metal–metal bond, compared to 2 in the Co_2B_4 cluster; hence the bond-lengthening effect would be greater in the Co_2B_4 system, consistent with observation. Further comparison is afforded by the tetrahedral cluster $(\eta^5\text{-}C_5H_5)_4Co_4H_4$, in which the hydrogens bridge tricobalt faces.[12] The range of Co–Co distances is 2.448 (2)–2.478 (2) Å, again shorter than in the Co_2B_4 system; this can be correlated with the fact that the ratio of bridging hydrogen atoms to Co–Co edges in $(\eta^5\text{-}C_5H_5)_4Co_4H_4$ is only 2/3.

The Face-Bridging Hydrogen Atom. The location of the unique hydrogen H(123) and its mirror-related atom, H(123′), was established to a high degree of confidence, as shown by (1) the successful least-squares refinement of this atom, (2) the failure to find significant extraneous electron density elsewhere on or near the polyhedral surface, and (3) the chemically reasonable bond distances and angles associated with the unique hydrogen. Thus, H(123) is roughly equidistant from Co(1), Co(2), and B(3) (mean value 1.54 (3) Å) but is slightly closer to the latter two atoms; the bridging hydrogen is 0.78 Å above the plane of the Co(1)–Co(2)–B(3) face. These parameters are similar to those determined in an X-ray

Table VI. Metal–Metal Distances in Metalloboron Cage Compounds of the First Transition Series

compound	polyhedral vertices	M–M interaction(s)	av dist, Å	range, Å	ref
$1,2\text{-}(C_5H_5)_2Co_2B_4H_6$	6	Co–Co	2.557 (1)		this work
$1,2,3\text{-}(C_5H_5)_3Co_3B_3H_5$	6	Co–Co	2.483 (1)	2.488 (1)–2.472 (1)	4
$(C_5H_5)_3Co_3B_4H_4$	7[a]	Co–Co	2.441 (1)	2.441 (1)–2.435 (1)	4
$(C_5H_5)_4Co_4B_4H_4$	8[b]	Co–Co	2.478 (1)	2.482 (2)–2.471 (2)	6
$(C_5H_5)_4Ni_4B_4H_4$	8[c]	Ni–Ni	2.354 (1)		28
$(C_5H_5)CoFe(CH_3)_4C_4B_8H_8$	8[d]	Co–Fe	2.480 (1)		29
$1,7,5,6\text{-}(C_5H_5)_2Co_2C_2B_5H_7$	9[e]	Co–Co	2.444 (3)		30
$(C_5H_5)_3Ni_3CB_5H_6$	9[f]	Ni–Ni	2.404 (1)		31
$2,6,1,10\text{-}(C_5H_5)_2Co_2C_2B_6H_8$	10[g]	Co–Co	2.489 (1)		32
$(C_5H_5)_2Fe_2C_2B_6H_8$	10[h]	Fe–Fe	2.571 (1)		33
$2,3,1,7\text{-}(C_5H_5)_2Co_2C_2B_8H_{10}$	12[i]	Co–Co	2.387 (2)		34

[a] Capped octahedron. [b] D_{2d} dodecahedron with Co atoms in high-coordinate vertices. [c] D_{2d} dodecahedron with Ni atoms in low-coordinate vertices. [d] Two eight-vertex (capped pentagonal bipyramid) cages fused on a common edge. [e] Closo tricapped trigonal prism. [f] Nido monocapped square antiprism. [g] Closo bicapped square antiprism. [h] Closo capped tricapped trigonal prism. [i] Icosahedron.

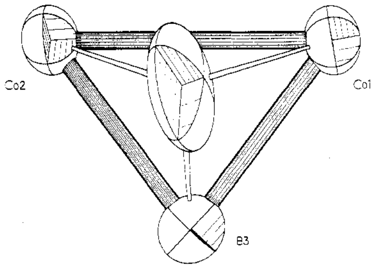

Figure 2. View of the Co(1)–Co(2)–Co(3) face showing the vibration ellipsoid of the bridging hydrogen atom H(123). The anisotropic thermal parameters of H(123) are $U_{11} = 0.077$, $U_{22} = 0.173$, $U_{33} = 0.047$, $U_{12} = 0.013$, $U_{13} = 0.048$, and $U_{23} = 0.006$. The root-mean-square amplitudes of vibration along the principal axes of the ellipsoid are 0.130, 0.293, and 0.418 Å. The anisotropic refinement of H(123) was conducted with positional and thermal parameters of all other atoms held fixed at their previously refined values and converged with the largest shift over error equal to 0.05.

study of the tetrahedral cluster HFeCo$_3$(CO)$_9$[P(OCH$_3$)$_3$]$_3$,[13a] which contains a hydrogen bridging a Co$_3$ triangular face; the mean Co–H distance is 1.63 (15) Å, and the hydrogen atom is 0.75 Å from the Co$_3$ plane.[35] In (η^5-C$_5$H$_5$)$_4$Co$_4$H$_4$ the corresponding values, established from X-ray data,[12] are 1.67 (7) and 0.80 Å, respectively. When one takes into account the intrinsic differences in the faces involved, i.e., nearly equilateral Co$_3$ triangles vs. a Co$_2$B isosceles triangle with one long Co–Co edge and two much shorter Co–B legs (Table II), there is a marked resemblance in the interactions of the bridging hydrogen atoms with the polyhedral faces in these various clusters.

The only other structures in which a bridging hydrogen has been located on a triangular face of a cluster are the carborane complex CB$_5$H$_7$, mentioned earlier, and the rhenium complex H$_4$Re$_4$(CO)$_{12}$ (in this latter case the hydrogen atom peak was not refined).[14] Indirect crystallographic evidence for such hydrogen atoms has been obtained for (η^5-C$_5$H$_5$)$_3$Co$_3$B$_3$H$_5$[4] and [(CH$_3$)$_2$C$_2$B$_4$H$_4$]$_2$FeH$_2$,[36] to be discussed below. In addition there are a number of closo metal clusters[15,16,37] and metallocarboranes[10] in which the presence of bridging hydrogens associated with metal atoms has been postulated from spectroscopic data.

Although it involves a nido rather than a closo structure, a particularly interesting example of a face-bridging hydrogen occurs in the cobaltocenium-substituted carborane [(η^5-C$_5$H$_5$)Co(η^5-C$_5$H$_4$)]C$_2$B$_9$H$_{11}$, which contains an 11-vertex cage with an *open* five-membered C$_2$B$_3$ face. An X-ray crystallographic study[38] established that the "extra" hydrogen atom resides on this face, nominally bridging two boron atoms but displaced toward the center of the face sufficiently that there appear to be bonding interactions with the other three boron and carbon atoms as well. The conclusion that this hydrogen actually bridges the open face, as opposed to being disordered between edge-bridging (BHB) positions, was strengthened by anisotropic refinement of the bridging-hydrogen thermal parameters. The major axis of the vibration ellipsoid was found to be more consistent with a true face-bridging hydrogen than with a disordered or tautomerizing atom.

In our study, it seemed a potentially interesting exercise to conduct a similar anisotropic refinement of the unique hydrogen atom in (η^5-C$_5$H$_5$)$_2$Co$_2$B$_4$H$_6$, and an ORTEP drawing of the result is shown in Figure 2. Since the anisotropic refinement of this hydrogen atom is at best marginally justified, it would be inappropriate to attach a high level of chemical significance to this plot. However, it is of interest to note that the major thermal motion of the bridging hydrogen appears to be in or near the plane normal to the Co$_2$B face and bisecting the Co–Co edge. This type of behavior is consistent with an edge-bridging Co–H–Co hydrogen atom which experiences a weak, but real, bonding interaction with B(3). The relative weakness of the B–H bond is directly shown by the fact that the B–H and Co–H distances are comparable despite the much larger covalent radius of cobalt. The distance from B(3) to H(123) (1.51 (3) Å) is long for a boron–hydrogen interaction, whereas the Co–H(123) distances (1.48 (3) and 1.62 (3) Å) are typical; for example, the Co–H–B group on the open face of the 5-(η^5-C$_5$H$_5$)CoB$_9$H$_{13}$ nido cage has B–H and Co–H distances of 1.26 (1) and 1.49 (1) Å, respectively.[3] Such comparisons between four-center Co$_2$B–H and three-center Co–H–B interactions can, of course, be taken only in an approximate sense.

Conclusions

The results of this study, in addition to confirming the proposed structure of the Co$_2$B$_4$ polyhedron, validate the earlier judgement[1a,c] that the bridging-hydrogen atoms occupy face- or edge-bridging locations in the vicinity of the cobalt atoms. This assignment had been based on the extremely high-field ^{1}H NMR chemical shift (−12.58 ppm relative to (CH$_3$)$_4$Si) exhibited by the bridging protons. These findings have direct impact on the question of "extra" hydrogen locations in other closo metalloboron cage systems. In 1,2,3-(η^5-C$_5$H$_5$)$_3$Co$_3$B$_3$H$_5$, a similar ^{1}H NMR signal (−14.48 ppm) for the two nonterminal protons indicated tautomeric movement of these protons through three equivalent positions in association with the metal atoms,[1b,c] and crystallographic evidence[4] suggested that these hydrogens are disordered on or near the three Co–Co edges. The present work adds further support to that conclusion and leaves little doubt that the interactions of the bridging hydrogens with the cluster faces are basically the same in the two complexes.

A similar situation exists in the closo metallocarboranes containing extra hydrogen atoms,[10] all of which exhibit high-field proton NMR shifts (usually at least 10 ppm to high field of (CH$_3$)$_4$Si) indicative of metal–hydrogen binding. In several of these compounds, however, there is a structural feature not found in the cobaltaboranes; the metal atom links *two* polyhedral cages and is common to both, as in [(CH$_3$)$_2$C$_2$B$_4$H$_4$]$_2$FeH$_2$,[10b] [(CH$_3$)$_2$C$_2$B$_3$H$_5$]CoH[(CH$_3$)$_2$C$_2$B$_4$H$_4$],[10c] and a number of other complexes. If the extra hydrogen is in the vicinity of the metal (as it surely must be), there is a possibility of hydrogen face-bonding simultaneously to the two separate polyhedra. Double-face bonding of a BH unit has been demonstrated in (η^5-C$_5$H$_5$)CoFe(CH$_3$)$_4$C$_4$B$_8$H$_8$,[29] and the heavy-atom structure of [(CH$_3$)$_2$C$_2$B$_4$H$_4$]$_2$FeH$_2$[36] is certainly compatible with hydrogen atoms bridging two faces although these atoms were not directly observed. A point worth noting is that even if the bridging hydrogen can be precisely located, it may be difficult to distinguish between *apparent* double-face bridging (caused by geometric constraints on the hydrogen atom) and a true covalent interaction between the hydrogen and the two polyhedral faces. In single cages such as 1,2-(η^5-C$_5$H$_5$)$_2$Co$_2$B$_4$H$_6$, no such ambiguity exists.

Acknowledgment. We thank the National Science Foundation, Grant No. CHE 76-04491, for support of this research and Professor Ekk Sinn for assistance during the data collection.

Registry No. 1,2-(η^5-C$_5$H$_5$)$_2$Co$_2$B$_4$H$_6$, 50924-50-0.

Supplementary Material Available: Listings of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 5078 (1973); (b) V. R. Miller and R. N. Grimes, *ibid.*, **98**, 1600 (1976); (c) V. R. Miller, R. Weiss, and R. N. Grimes, *ibid.*, **99**, 5646 (1977).
(2) L. G. Sneddon and D. Voet, *J. Chem. Soc., Chem. Commun.*, 118 (1976).
(3) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **16**, 3251 (1977).
(4) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **16**, 3255 (1977).
(5) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **17**, 10 (1978).

(6) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, following paper in this issue.
(7) (a) T. Onak, R. Drake, and G. B. Dunks, *J. Am. Chem. Soc.*, **87**, 2505 (1965); (b) T. Onak and J. B. Leach, *J. Chem. Soc., Chem. Commun.*, 76 (1971); (c) T. Onak and E. Wan, *J. Chem. Soc., Dalton Trans.*, 665 (1974).
(8) G. L. McKown, B. P. Don, R. A. Beaudet, P. J. Vergamini, and L. H. Jones, *J. Chem. Soc., Chem. Commun.*, 765 (1974); *J. Am. Chem. Soc.*, **98**, 6909 (1976).
(9) E. A. McNeill and F. R. Scholer, *Inorg. Chem.*, **14**, 1081 (1975).
(10) (a) L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 6623 (1973); (b) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *Inorg. Chem.*, **15**, 1343 (1976); (c) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 4818 (1976); (d) W. M. Maxwell, K.–S. Wong, and R. N. Grimes, *Inorg. Chem.*, **16**, 3094 (1977).
(11) Face-bridging hydrogen atoms have been located and refined in $(\eta^5\text{-}C_5H_5)_4Co_4H_4$[12] and in $HFeCo_3(CO)_9[P(OCH_3)_3]_3$.[13] Hydrogens of this type have been located, but not refined, in $H_4Re_4(CO)_{12}$[14] and indirectly located (positions inferred from metal–metal bond lengths) in $H_2Ru_6(CO)_{18}$[15] and $(\eta^5\text{-}C_5H_5)_4Ni_4H_3$.[16]
(12) G. Huttner and H. Lorenz, *Chem. Ber.*, **108**, 973 (1975).
(13) (a) B. T. Huie, C. B. Knobler, and H. D. Kaesz, *J. Am. Chem. Soc.*, **100**, 3059 (1978); (b) R. G. Teller, R. D. Wilson, R. K. McMullan, T. F. Koetzle, and R. Bau, *ibid.*, **100**, 3071 (1978).
(14) R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, **98**, 4687 (1976).
(15) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Commun.*, 458 (1970).
(16) G. Huttner and H. Lorenz, *Chem. Ber.*, **107**, 996 (1974).
(17) (a) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976); (b) R. W. Rudolph, *Acc. Chem. Res.*, **9**, 446 (1976); (c) D. M. P. Mingos, *Nature (London), Phys. Sci.*, **236**, 99 (1972); (d) R. N. Grimes, *Ann. N.Y. Acad. Sci.*, **239**, 180 (1974).
(18) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(19) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(20) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(21) D. T. Cromer and J. A. Ibers, ref 19.
(22) D. P. Freyberg, G. M. Mockler, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 447 (1976).
(23) R. Schaeffer, Q. Johnson, and G. S. Smith, *Inorg. Chem.*, **4**, 917 (1965).
(24) V. S. Mastryukov, L. V. Vilkov, and O. V. Dorofeeva, *J. Mol. Struct.*, **24**, 217 (1975).
(25) (a) J. R. Pipal and R. N. Grimes, *J. Am. Chem. Soc.*, **100**, 3083 (1978); (b) J. R. Pipal, W. M. Maxwell, and R. N. Grimes, *Inorg. Chem.*, **17**, 1447 (1978).
(26) V. Albano, P. L. Bellon, P. Chini, and V. Scatturin, *J. Organomet. Chem.*, **16**, 461 (1969).
(27) V. G. Albano, G. Ciani, and P. Chini, *J. Chem. Soc., Dalton Trans.*, 432 (1974).
(28) J. R. Bowser and R. N. Grimes, *J. Am. Chem. Soc.*, **100**, 4623 (1978).
(29) W. M. Maxwell, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 3490 (1976).
(30) R. N. Grimes, A. Zalkin, and W. T. Robinson, *Inorg. Chem.*, **15**, 2274 (1976).
(31) C. G. Salentine, C. E. Strouse, and M. F. Hawthorne, *Inorg. Chem.*, **15**, 1832 (1976).
(32) E. L. Hoel, C. E. Strouse, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1388 (1974).
(33) K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 296 (1975).
(34) K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1397 (1974).
(35) A neutron diffraction investigation of this molecule[13b] gave, as expected, larger values for the Co–H distances (mean 1.734 (4) Å) and for the distance of the bridging hydrogen from the Co_3 face (0.978 (3) Å).
(36) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, in press.
(37) C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 302 (1976).
(38) M. R. Churchill and B. G. DeBoer, *J. Am. Chem. Soc.*, **96**, 6310 (1974).

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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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Received June 21, 1978

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; μ(Mo Kα) = 33.4 cm^{-1}; ρ_{calcd}(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

0020-1669/79/1318-0257$01.00/0