faces on $C_6B_6H_{12}$ could then be closed by insertion of two zero-electron donors such as $Cr(CO)_3$ or $(\eta^5-C_5H_5)Mn$ to create a closo 14-vertex cage analogous to $(\eta^5-C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$.

Acknowledgment. We thank Professor Ekk Sinn for assistance during data collection and Dr. Richard Weiss for supplying the crystal. This work was supported by National Science Foundation Grant No. CHE 76-04491.

Registry No. 1,14,2,5,9,12-$(C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$ (isomer VIII), 64201-89-4.

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

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Crystal Structure of a Novel Triple-Decked Sandwich Metallocarborane, $\mu(2,3)$-1,3-C_3H_4-1,7,2,3-$(\eta^5-C_5H_5)_2Co_2C_2B_3H_3$, a Complex Containing a Bicyclic Planar Carborane Ligand Related to Pentalene. Partial Incorporation of a Cyclopentadienyl Ring into a Polyhedral Borane Cage

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Received July 13, 1977

The structure of the title compound was determined from a single-crystal x-ray diffraction study and was found to consist of a seven-vertex $Co_2C_2B_3$ pentagonal bipyramid with the two cage carbon atoms bridged by an exo-polyhedral propenylene group. The exo-polyhedral ring together with the equatorial ring of the polyhedron forms a planar bicyclic $C_5B_3H_7^{4-}$ ligand which is isoelectronic with the pentalenide monoanion $C_8H_7^-$. This complex consists of a metalloborane polyhedron into which a cyclopentadienyl group has been partially inserted and represents the first example of such insertion. The molecule is also a *C,C′*-1,3-propenylene-substituted derivative of the known triple-decked complex 1,7,2,3-$(\eta^5-C_5H_5)_2Co_2C_2B_3H_5$ but has a slightly longer cage C–C bond than the latter species. Crystal data: mol wt 347.60; space group $P2_1/n$; a = 8.672 (2), b = 16.441 (4), c = 10.873 (3) Å; β = 108.95 (2)°; V = 1466.3 (9) Å^3; d_{calcd} = 1.58 g cm^{-3} for Z = 4. The structure was refined by full-matrix least-squares methods to a final R value of 5.9% for the 2012 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The reaction between $Na^+B_5H_8^-$, $CoCl_2$, and $Na^+C_5H_5^-$ in tetrahydrofuran (THF) yields a family of structurally varied cobaltaboranes which can be isolated as air-stable crystalline solids.[1] These molecules consist of open and closed polyhedral cages containing one to four $(\eta^5-C_5H_5)Co$ groups, whose structures were deduced from NMR spectra and supported in several cases by x-ray structural studies [2-$(C_5H_5)CoB_4H_8$,[2] $(C_5H_5)CoB_9H_{13}$,[3a] $(C_5H_5)_3Co_3B_3H_5$,[3a] $(C_5H_5)_3Co_3B_4H_4$,[3a] and $(C_5H_5)_4Co_4B_4H_4$[3b]].

One product, obtained in very low yield,[1c] was characterized tentatively as σ-$C_5H_5(\eta^5-C_5H_5)_2Co_2B_3H_2$, i.e., a σ-cyclopentadienyl-, B-substituted cobaltaborane whose (unknown) parent species would be trigonal-bipyramidal $(\eta^5-C_5H_5)_2Co_2B_3H_3$. In one respect this formulation seemed reasonable, since several σ-C_5H_9- and σ-C_5H_7-substituted cobaltaboranes had been isolated from the same reaction;[1] it was clear that the $C_5H_5^-$ ion can function as an attacking reagent and is not restricted merely to the role of a capping ligand for cobalt. However, we were uncomfortable with the postulated Co_2B_3 cage which would have only 10 skeletal valence electrons instead of the 12 expected[4] for a five-vertex closo polyhedron. Accordingly, an x-ray investigation was undertaken and disclosed the altogether surprising result that the extra cyclopentadienyl ring is fused into the polyhedral cage, which thereby becomes not a five-vertex Co_2B_3 cobaltaborane, but a seven-vertex $Co_2C_2B_3$ cobaltacarborane having triple-decked sandwich geometry. This finding has been briefly described in an earlier paper,[1c] and we present here the details of the structural investigation.

Experimental Section

From a very large red single crystal,[5] grown by the vapor diffusion of pentane into a dichloromethane solution of the title compound, a cone-shaped fragment of maximum dimensions 0.65 × 0.4 mm was cut and mounted on a glass fiber. After preliminary precession photographs indicated good crystal quality, this crystal was used for data collection. Crystal data: $Co_2C_{15}B_3H_{17}$; mol wt 347.60; space group $P2_1/n$; Z = 4; a = 8.672 (2), b = 16.441 (4), c = 10.873 (3) Å; β = 108.95 (2)°; V = 1466.3 (9) Å^3; μ(Mo Kα) = 23.4 cm^{-1}; d_{calcd} = 1.58 g cm^{-3}; $F(000)$ = 704. For this crystal, the Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then employed in the program INDEX to obtain an orientation matrix for data collection and also to provide approximate cell constants. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately

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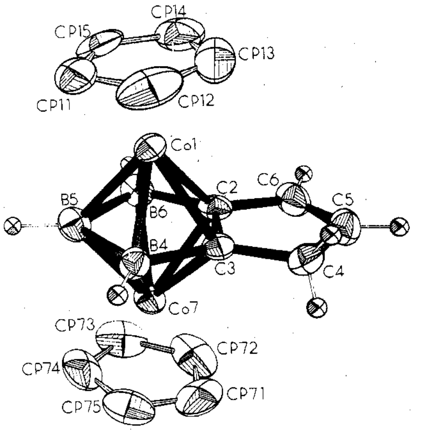


Figure 1. ORTEP drawing of the molecular structure with nonhydrogen atoms represented as 50% probability thermal ellipsoids and hydrogen atoms as spheres of fixed radius.

centered reflections. The mosaicity of the crystal was examined by the ω-scan technique and found to be marginally acceptable. Systematic absences for $k = 2n + 1$ on $0k0$ and $h + l = 2n + 1$ on $h0l$ uniquely determine the space group to be $P2_1/n$. This is a nonstandard setting of $P2_1/c$ (No. 14) but can be converted to it by the transformation $a' = a$, $b' = b$, and $c' = -a + c$, where a, b, and c are axes in $P2_1/n$ and a', b', and c' are the axes in $P2_1/c$. All data collection and refinement were conducted in the $P2_1/n$ setting.

Collection and Reduction of the Data. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo $K\alpha$ radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the unique intensities for all reflections for which $1° < 2\theta < 48.00°$. Scan widths (SW) were calculated from the formula $SW = A + B \tan \theta$ where A is estimated from the mosaicity of the crystal and B allows for the increase in the width of each peak due to $K\alpha_1$ and $K\alpha_2$ splitting. The values of A and B respectively were 1.3 and 0.4°. 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 if the intensities registered less than ten counts above background on a rapid prescan, such reflections being rejected automatically by the computer. The intensities of three standard reflections were monitored at 100-reflection intervals and showed no systematic trends. The raw intensity data were corrected for Lorentz–polarization effects and their standard deviations were calculated in the usual manner from counting statistics ($\rho = 0.03$).[6] This resulted in 2197 reflections of which 2012 had $F_o^2 > 3\sigma(F_o^2)$. Only those reflections for which $F_o^2 > 3\sigma(F_o^2)$ were used in the solution and refinement of the structural parameters. Due to the highly irregular shape of the crystal, no absorption correction was made.

Solution and Refinement of the Structure. A three-dimensional Patterson map was used to locate the positions of the two cobalt atoms. Refinement of their coordinates and isotropic thermal parameters reduced R to 28.1% where R is defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$. An electron-density map was then phased with the two cobalt atoms and yielded the positions of the remaining 18 nonhydrogen atoms. Isotropic refinement followed by full-matrix anisotropic refinement of all atoms reduced R to 6.8%. Another electron density map clearly indicated the positions of six of the seven noncyclopentadienyl hydrogen atoms. The position of the seventh hydrogen (H5) had to be calculated. Further refinement including these hydrogen atoms with isotropic thermal parameters plus the cyclopentadienyl hydrogens at fixed positions (0.95 Å from carbon, $B = 5.0$ Å^2) reduced R to its final value of 5.9%. The cyclopentadienyl hydrogen positions were then recalculated and refinement was continued for several more cycles, but this did not reduce the residual. In the final cycle of refinement the largest parameter shift was 0.04 times its estimated standard deviation. The weighted R factor, defined as $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, was 7.2%. The estimated standard deviation of an observation of unit weight was 3.8. A final difference electron density map was featureless.

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 $2F_o/\sigma(F_o^2)$ 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.[8] The effects of anomalous dispersion were included in F_c using Cromer and Ibers'[9] values for $\Delta f'$ and $\Delta f''$. The computing system and programs used are described elsewhere.[10] After the final cycle of refinement, a structure factor calculation including those reflections for which $F_o^2 < 3\sigma(F_o^2)$ gave an R of 6.4% indicating that the structure determination would not be improved by accurately recollecting these reflections. A table of structure factors is available (see paragraph on supplementary material at the end of the paper).

Results and Discussion

Tables I–III contain positional and thermal parameters, interatomic distances, and selected bond angles, respectively. The numbers in parentheses are the estimated standard deviations of the last digits quoted. Table IV lists selected molecular planes while Table V contains the short intermolecular distances (<3.7 Å). Figures 1 and 2 present, respectively, the molecular structure and numbering system and a diagram of the unit cell contents.

The molecule consists of a seven-vertex $Co_2C_2B_3$ polyhedron with η^5-C_5H_5 ligands on the metal atoms and a terminal hydrogen on each boron atom. The cage carbon atoms are attached to an exo-polyhedral 1,3-propenylene group which completes a five-membered C_5H_4 ring system, fused on one edge to the equatorial ring of the polyhedron. The μ-C_3H_4-1,7,2,3-$(\eta^5$-$C_5H_5)_2Co_2C_2B_3H_3$ system is actually a C,C'-1,3-propenylene derivative of the known triple-decked

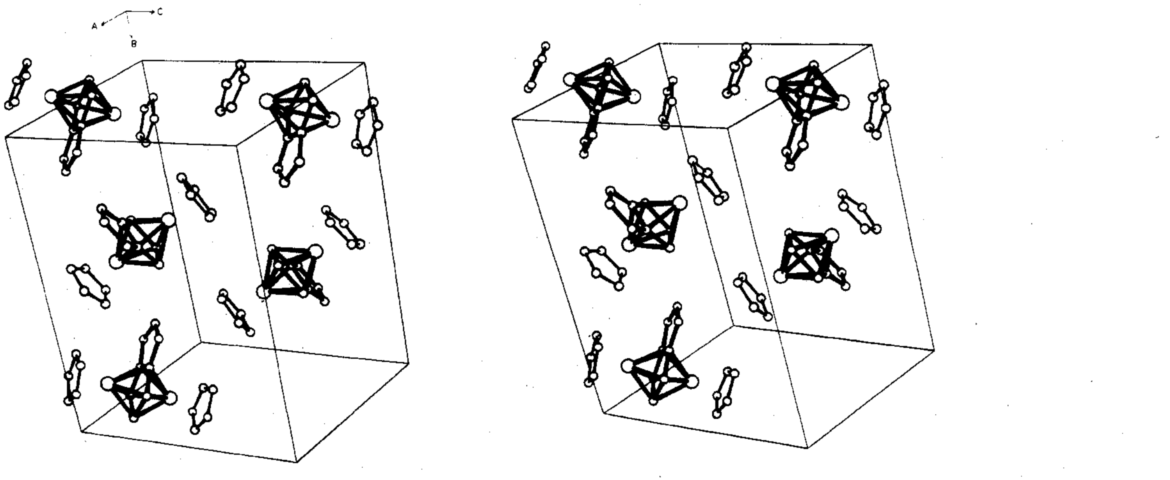


Figure 2. Packing diagram showing the contents of one unit cell plus an additional molecule (upper left) which is related by translation along the c axis to the molecule at upper right.

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

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co1	0.11586 (8)	0.14914 (5)	−0.11051 (6)	0.00927 (9)	0.00248 (3)	0.00618 (6)	−0.00024 (9)	0.0099 (1)	−0.00022 (7)
Co7	0.28824 (9)	0.05243 (4)	−0.27766 (6)	0.01196 (10)	0.00221 (3)	0.00514 (5)	−0.00029 (9)	0.0088 (1)	−0.00104 (7)
C2	0.2518 (6)	0.1724 (3)	−0.2351 (5)	0.0108 (7)	0.0023 (2)	0.0062 (4)	0.0018 (7)	0.0091 (8)	−0.0003 (5)
C3	0.3510 (6)	0.1288 (3)	−0.1161 (5)	0.0092 (6)	0.0022 (2)	0.0061 (4)	0.0002 (6)	0.0093 (8)	−0.0013 (5)
C4	0.5006 (6)	0.1778 (4)	−0.0562 (5)	0.0084 (7)	0.0032 (2)	0.0101 (5)	−0.0003 (7)	0.0085 (10)	−0.0027 (6)
C5	0.4868 (7)	0.2469 (4)	−0.1440 (6)	0.0130 (8)	0.0029 (2)	0.0125 (6)	−0.0045 (8)	0.0159 (10)	−0.0035 (7)
C6	0.3472 (7)	0.2450 (4)	−0.2454 (5)	0.0159 (8)	0.0023 (2)	0.0104 (5)	−0.0015 (8)	0.0157 (10)	0.0001 (6)
CP11	−0.0422 (7)	0.1316 (4)	−0.0114 (6)	0.0194 (8)	0.0033 (3)	0.0142 (5)	−0.0003 (9)	0.0266 (9)	0.0004 (7)
CP12	0.1072 (9)	0.1640 (5)	0.0740 (6)	0.0190 (10)	0.0083 (4)	0.0080 (5)	0.0065 (12)	0.0153 (11)	−0.0011 (8)
CP13	0.1284 (8)	0.2400 (5)	0.0238 (7)	0.0241 (10)	0.0059 (3)	0.0191 (6)	−0.0112 (10)	0.0341 (11)	−0.0136 (8)
CP14	−0.0051 (8)	0.2541 (4)	−0.0897 (7)	0.0248 (10)	0.0036 (3)	0.0189 (7)	0.0033 (10)	0.0347 (11)	0.0019 (8)
CP15	−0.1062 (7)	0.1872 (4)	−0.1104 (6)	0.0106 (7)	0.0052 (3)	0.0133 (6)	0.0043 (9)	0.0165 (10)	0.0000 (8)
CP71	0.5049 (8)	0.0181 (5)	−0.3016 (6)	0.0143 (9)	0.0068 (4)	0.0135 (6)	0.0011 (10)	0.0157 (11)	−0.0099 (8)
CP72	0.4075 (9)	0.0554 (4)	−0.4137 (6)	0.0380 (11)	0.0038 (3)	0.0152 (5)	−0.0021 (11)	0.0419 (10)	−0.0029 (7)
CP73	0.2591 (10)	0.0098 (5)	−0.4588 (5)	0.0248 (13)	0.0059 (3)	0.0056 (5)	0.0060 (12)	0.0063 (13)	−0.0040 (7)
CP74	0.2748 (9)	−0.0532 (4)	−0.3717 (7)	0.0255 (12)	0.0034 (3)	0.0133 (7)	−0.0029 (10)	0.0197 (14)	−0.0068 (7)
CP75	0.4256 (9)	−0.0479 (4)	−0.2755 (6)	0.0244 (12)	0.0040 (3)	0.0101 (6)	0.0066 (10)	0.0146 (13)	−0.0008 (7)
B4	0.2729 (7)	0.0493 (4)	−0.0888 (6)	0.0090 (8)	0.0024 (2)	0.0064 (5)	−0.0009 (8)	0.006 (1)	0.0001 (6)
B5	0.0864 (8)	0.0436 (4)	−0.2180 (6)	0.0128 (9)	0.0025 (2)	0.0057 (5)	−0.0010 (9)	0.006 (1)	−0.0008 (6)
B6	0.0884 (8)	0.1314 (4)	−0.3083 (6)	0.0132 (10)	0.0027 (3)	0.0056 (5)	0.0003 (9)	0.006 (1)	0.0007 (6)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
HB4	0.323 (5)	0.008 (3)	−0.005 (4)	2 (1)	HC13	0.218 (0)	0.276 (0)	0.060 (0)	5 (0)
HB5	−0.003 (7)	−0.006 (4)	−0.236 (5)	4 (1)	HC14	−0.022 (0)	0.301 (0)	−0.143 (0)	5 (0)
HB6	−0.001 (6)	0.156 (3)	−0.392 (4)	2 (1)	HC15	−0.204 (0)	0.180 (0)	−0.181 (0)	5 (0)
HC41	0.587 (7)	0.148 (3)	−0.034 (5)	4 (1)	HC71	0.611 (0)	0.035 (0)	−0.251 (0)	5 (0)
HC42	0.522 (8)	0.196 (4)	0.044 (6)	5 (1)	HC72	0.434 (0)	0.103 (0)	−0.453 (0)	5 (0)
HC5	0.566 (7)	0.287 (4)	−0.124 (6)	4 (1)	HC73	0.168 (0)	0.621 (0)	−0.534 (0)	5 (0)
HC6	0.307 (6)	0.285 (3)	−0.302 (4)	2 (1)	HC74	0.195 (0)	−0.094 (0)	−0.377 (0)	5 (0)
HC11	−0.089 (0)	0.081 (0)	−0.002 (0)	5 (0)	HC75	0.466 (0)	−0.084 (0)	−0.204 (0)	5 (0)
HC12	0.178 (0)	0.139 (0)	0.150 (0)	5 (0)					

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

Table II. Interatomic Distances (Å)

Co1–Co2	3.135 (1)	Co7–CP71	2.058 (4)
Co1–C2	2.100 (3)	Co7–CP72	2.063 (4)
Co1–C3	2.086 (3)	Co7–CP73	2.028 (3)
Co1–B4	2.096 (3)	Co7–CP74	2.000 (3)
Co1–B5	2.062 (3)	Co7–CP75	2.030 (4)
Co1–B6	2.106 (4)	CP11–CP12	1.430 (6)
Co7–C2	2.074 (3)	CP12–CP13	1.398 (6)
Co7–C3	2.082 (3)	CP13–CP14	1.411 (7)
Co7–B4	2.101 (3)	CP14–CP15	1.378 (6)
Co7–B5	2.059 (4)	CP15–CP11	1.384 (5)
Co7–B6	2.104 (4)	CP71–CP72	1.381 (6)
C2–C3	1.485 (4)	CP72–CP73	1.432 (6)
C3–B4	1.544 (4)	CP73–CP74	1.380 (6)
B4–B5	1.767 (5)	CP74–CP75	1.387 (6)
B5–B6	1.750 (5)	CP75–CP71	1.363 (6)
B6–C2	1.537 (5)	B4–HB4	1.11 (3)
C3–C4	1.486 (4)	B5–HB5	1.10 (3)
C4–C5	1.464 (5)	B6–HB6	1.06 (3)
C5–C6	1.347 (5)	C4–HC41	0.86 (3)
C6–C2	1.477 (4)	C4–HC42	1.09 (4)
Co1–CP11	2.020 (3)	C5–HC5	0.92 (4)
Co1–CP12	2.046 (4)	C6–HC6	0.90 (3)
Co1–CP13	2.067 (4)	⟨B–H⟩	1.09
Co1–CP14	2.069 (4)	⟨C–H⟩	0.94
Co1–CP15	2.025 (3)		

Table III. Selected Bond Angles (deg)

C2–Co1–C3	41.6 (1)	B4–C3–C4	138.5 (3)
C3–Co1–B4	43.3 (1)	C6–C2–C3	106.0 (3)
B4–Co1–B5	50.3 (1)	C2–C3–C4	107.2 (3)
B5–Co1–B6	49.6 (1)	C3–C4–C5	105.1 (3)
B6–Co1–C2	42.9 (1)	C4–C5–C6	112.1 (3)
C2–Co7–C3	41.9 (1)	C5–C6–C2	109.5 (3)
C3–Co7–B4	43.3 (1)	CP11–Co1–CP12	41.2 (2)
B4–Co7–B5	50.3 (1)	CP12–Co1–CP13	39.8 (2)
B5–Co7–B6	49.7 (1)	CP13–Co1–CP14	39.9 (2)
B6–Co7–C2	43.2 (1)	CP14–Co1–CP15	39.3 (2)
Co1–C2–C3	68.7 (2)	CP15–Co1–CP11	40.0 (2)
Co1–C3–C2	69.7 (2)	CP71–Co7–CP72	39.2 (2)
Co1–C3–B4	68.7 (2)	CP72–Co7–CP73	41.0 (2)
Co1–B4–C3	68.0 (2)	CP73–Co7–CP74	40.1 (2)
Co1–B4–B5	63.8 (2)	CP74–Co7–CP75	40.3 (2)
Co1–B5–B4	65.8 (2)	CP75–Co7–CP71	38.9 (2)
Co1–B5–B6	66.5 (2)	CP15–CP11–CP12	108.0 (3)
Co1–B6–B5	63.9 (2)	CP11–CP12–CP13	106.6 (4)
Co1–B6–C2	68.4 (2)	CP12–CP13–CP14	108.3 (4)
Co1–C2–B6	68.8 (2)	CP13–CP14–CP15	108.0 (4)
Co7–C2–C3	69.4 (2)	CP14–CP15–CP11	109.1 (4)
Co7–C3–C2	68.8 (2)	CP75–CP71–CP72	109.4 (4)
Co7–C3–B4	69.0 (2)	CP71–CP72–CP73	107.0 (4)
Co7–B4–C3	67.7 (2)	CP72–CP73–CP74	106.4 (4)
Co7–B4–B5	63.6 (2)	CP73–CP74–CP75	109.2 (4)
Co7–B5–B4	66.1 (2)	CP74–CP75–CP71	108.0 (4)
Co7–B5–B6	66.5 (2)	C3–B4–HB4	127 (1)
Co7–B6–B5	63.8 (2)	B5–B4–HB4	129 (1)
Co7–B6–C2	67.4 (2)	B4–B5–HB5	126 (2)
Co7–C2–B6	69.5 (2)	B6–B5–HB5	131 (2)
B6–C2–C3	114.5 (3)	B5–B6–HB6	131 (1)
C2–C3–B4	114.2 (2)	C2–B6–HB6	125 (2)
C3–B4–B5	103.8 (2)	C3–C4–HC41	111 (2)
B4–B5–B6	103.2 (2)	C5–C4–HC41	120 (2)
B5–B6–C2	104.3 (3)	C3–C4–HC42	115 (2)
Co1–C2–C6	129.9 (2)	C5–C4–HC42	113 (2)
Co7–C2–C6	128.4 (2)	C4–C5–HC5	120 (2)
C3–C2–C6	106.0 (3)	C6–C5–HC5	128 (2)
B6–C2–C6	139.5 (3)	C5–C6–HC6	126 (2)
Co1–C3–C4	128.5 (2)	C2–C6–HC6	123 (2)
Co7–C3–C4	130.4 (2)	HC41–C4–HC42	92 (3)
C2–C3–C4	107.2 (3)		

sandwich compound[11] 1,7,2,3-(η^5-C_5H_5)$_2$$Co_2C_2B_3H_5$, notwithstanding the fact that the method of preparation of the present species is totally different from the routes employed for the parent compound and other triple-decked sandwich complexes[11] (the earlier syntheses involved metal insertion into carborane substrates). The central polyhedral cage can be compared with several boron cage compounds of similar type (pentagonal pyramids or pentagonal bipyramids) for which x-ray data are available, as shown in Table VI. The metal–central ring vectors are virtually identical for the four cobalt species, while those of the iron, manganese, and gallium complexes are somewhat longer. This can be correlated with the fact that the metal atoms in the Fe, Mn, and Ga species

Table IV

Selected Molecular Planes

Atom	Dev, Å	Atom	Dev, Å
Plane 1: C2, C3, B4, B5, B6, C4, C5, C6 $0.6656x - 0.5163y - 0.5389z = 1.8454$			
C2	0.000	C4	−0.022
C3	0.004	C5	0.005
B4	0.012	C6	0.016
B5	0.004	Co1	−1.571
B6	−0.018	Co7	1.564
Plane 2: Co1, Co7, B5, C5 $-0.3099x + 0.4806y - 0.8203z = 1.6927$			
Co1	−0.014	B5	0.020
Co2	−0.014	C5	0.008
Plane 3: CP11, CP12, CP13, CP14, CP15 $-0.7190x + 0.4316y + 0.5448z = 1.0987$			
CP11	−0.005	CP14	−0.006
CP12	0.001	CP15	0.007
CP13	0.003	Co1	1.662
Plane 4: CP71, CP72, CP73, CP74, CP75 $0.6098x - 0.5749y - 0.5456z = 4.8413$			
CP71	−0.001	CP74	0.001
CP72	0.002	CP75	0.000
CP73	−0.002	Co7	−1.657

Dihedral Angles between Planes

Planes	Angle, deg	Plane	Angle, deg
1,2	90.71	2,3	89.05
1,3	5.75	2,4	91.02
1,4	4.66	3,4	10.34

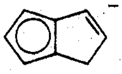
Table V. Intermolecular Contacts (<3.7 Å)

Atoms	Distance, Å	Relation
CP72–CP72	3.37	$1 - x, -y, -1 - z$
C5–CP15	3.57	$1 + x, y, z$
CP71–CP72	3.63	$1 - x, -y, -1 - z$
C4–CP15	3.65	$1 + x, y, z$

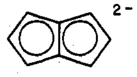
are present in lower formal oxidation states (2+, 1+) than in the cobalt systems (3+).

The equatorial (C2–C3) carbon–carbon bond length is larger in the propenylene-bridged complex than in any of the other species, possibly excepting $CH_3GaC_2B_4H_6$. In particular, the difference in the C–C distances found in the μ-propenylene and methyl derivatives of 1,7,2,3-$(C_5H_5)_2Co_2C_2B_3H_5$ appears significant (especially in view of the fact that geometric constraints imposed by the cage structure would tend to inhibit any large variation in this parameter) and suggests that the equatorial C–C interaction has a lower bond order in the propenylene-bridged species than is the case in other closely related systems. Some time ago Lipscomb[19] proposed multiple-bond character for the carbon–carbon bond in 2,3-$C_2B_4H_8$, and NMR observations in our laboratory[11d] suggest that the same is true in 1,7,2,3-$(C_5H_5)_2Co_2C_2B_3H_5$. In the μ-propenylene derivative of this system, the presence of a double bond between C5 and C6 (vide infra) creates what could be regarded as a conjugated C3–C2–C6–C5 chain; partial electron delocalization in this region may well lower the electron density between C2 and C3 relative to the parent and alkyl-substituted species, thereby producing an increase in the C2–C3 bond distance.

The equatorial C_2B_3 ring together with the exo-polyhedral carbon atoms from a bicyclic C_5B_3 ring system which is completely planar within experimental error (Table IV). The entire molecule can therefore be described as two (η^5-C_5H_5)Co^{2+} groups sandwiched around a central $C_5B_3H_7^{4-}$ ligand which is an isoelectronic analogue of the bicyclic anion $C_8H_7^-$ (**1**); this latter ion is formally derived from the pentaleneide dianion[20] $C_8H_6^{2-}$ (**2**) by addition of a proton. The suggested analogy of the carboranyl ligand to **1** is fully supported by the crystallographic findings. In addition to the planarity of the C_5B_3 system, the presence of a CH_2 group at C4 and of a double bond between C5 and C6 [1.347 (5) Å] is clearly established. These structural features are also evident in the 100-MHz Fourier-transform NMR spectrum,[1c] which is first-order and exhibits an H5–H6 coupling constant of 5.2 Hz, typical of an olefinic group (J_{HH} for the interaction of the methylenic protons with H5 and H6 is approximately 2 Hz).



1



2

The cyclopentadienyl rings are planar and are nonparallel with the plane of the central ligand, being tilted away from the propenylene group at an average angle of 5.21°. A similar effect has been noted in 2-CH_3-1,7,2,3-(η^5-C_5H_5)$_2Co_2C_2B_3H_4$[11a] and in 2,3-$(CH_3)_2$-1,2,3-(η^5-C_5H_5)-$CoC_2B_4H_4$,[16] in which the C_5H_5 rings are inclined to the equatorial (or basal) ring at average angles of 5.0 and 7.5°, respectively, away from the *C*-methyl substituents in both cases. (In 2-CH_3-1,7,2,4-(η^5-C_5H_5)$_2Co_2C_2B_3H_4$ there is unaccountably an approximate 3° tilt of the C_5H_5 planes *toward* the methyl group,[12] but the disorder of boron and carbon atoms in the central ring makes this observation somewhat ambiguous.) These ring-tilting effects probably originate in the electronic structure of the molecules, since in

Table VI. Bond Distances (Å) in Triple-Decked Sandwich Metalloboron Compounds and Related Species

Compd	Metal–equatorial ring[a]	Metal–C_5H_5 ring[a]	Equatorial mean distances C–C	B–B	B–C	Ref
Triple-Decked Complexes						
μ-C_3H_4-1,7,2,3-$(C_5H_5)_2Co_2C_2B_3H_3$	1.568 (1)	1.660 (1)	1.485 (4)	1.759 (4)	1.541 (4)	This work
2-CH_3-1,7,2,3-$(C_5H_5)_2Co_2C_2B_3H_4$	1.570 (1)	1.655 (2)	1.441 (7)	1.726 (6)	1.548 (6)	11a
2-CH_3-1,7,2,4-$(C_5H_5)_2Co_2C_2B_3H_4$	1.569 (3)	1.66 (1)		1.65 (3)[b]	1.60 (3)[c]	12
$[(CO)_3Mn]_2(C_6H_5)BC_4H_3C_2H_5$	*d*		1.44		1.58	13
$[(CO)_3Mn]_2(C_2H_5)_2C_2SB(CH_3)_2$	1.753 (1)		*d*		*d*	14
$(C_5H_5)_2Fe_2(C_2H_5)_2C_2SB(CH_3)_2$	1.618 (1)	*d*	*d*		*d*	15
Other Seven-Vertex Closo Structures						
2,3-$(CH_3)_2$-1,2,3-$(C_5H_5)CoC_2B_4H_4$	1.566 (1)	1.647 (1)	1.461 (2)	1.686 (1)	1.556 (2)	16
1-CH_3-1,2,3-$GaC_2B_4H_6$	1.76 (1)		1.47 (4)	1.70 (3)	1.57 (4)	17
Nido Structures						
1,2,3-$(CO)_3FeC_2B_3H_7$	1.617 (1)		1.410 (4)	1.852 (3)[e]	1.520 (3)	18
2,3-$C_2B_4H_8$			1.418 (6)	1.783 (6)[e]	1.509 (6)	19
2,3-$(CH_3)_2C_2B_4H_6$			1.431 (6)	1.778 (6)[e]	1.521 (6)	19

[a] Mean distance along a vector normal to the ring plane. [b] B–BC distance (BC = disordered boron/carbon atoms). [c] BC–BC distance is 1.52 (4) Å. [d] Not calculable from published data. [e] B–H–B bridged bond.

none of these species are there any close intermolecular contacts which would suggest packing effects. In the present structure the shortest such distance (Table V) is 3.37 Å.

Acknowledgment. We are grateful to Professor Ekk Sinn for assistance during the data collection. This work was supported by National Science Foundation Grant No. CHE 76-04491.

Registry No. μ-C_3H_4-1,7,2,3-$(C_5H_5)_2Co_2C_2B_3H_3$, 64475-52-1.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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A Cobalt(III) Complex with a Six-Membered Chelate Ring Containing an Axial *C*–Methyl Group. Absolute Configuration and Circular Dichroism of $(-)_{546}$-β-Oxalato((4*R*,6*R*)-dimethyl-3,7-diazanonane-1,9-diamine)cobalt(III) Perchlorate, $(-)_{546}$-β-[Co(ox)(*R*,*R*-2,3″,2-tet)]ClO_4

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Received February 7, 1977

The structure of $(-)_{546}$-β-[Co(ox)(*R*,*R*-2,3″,2-tet)]ClO_4 has been determined from three-dimensional x-ray data collected by the diffractometer method. The compound forms orthorhombic crystals with $a = 9.116$ (1) Å, $b = 25.010$ (1) Å, $c = 7.657$ (2) Å, and $Z = 4$, in space group $P2_12_12_1$. The structure has been solved by the heavy-atom method and refined by least-squares methods with anisotropic temperature factors to give an R value of 0.038 for 1094 observed reflections. The calculated density of 1.654 g/cm^3 for four formula units in the unit cell agrees well with the observed density of 1.651 g/cm^3. The absolute configuration of the complex is Λ, the conformations of the two five-membered chelate rings are δ, and the central six-membered chelate ring adopts the chair conformation with one methyl group axial and the other equatorial. The absolute configurations about the two secondary nitrogen atoms are both *S*. The relationship between the absolute configuration around the central metal atom and the circular dichroism in the first absorption band is established.

Introduction

The stereospecific coordination of optically active tetramines to the octahedral metal complexes has been often observed. It is expected to give important information about the asymmetric synthesis in this system to clarify the factors by which stereoselectivity is induced. Therefore, it is an interesting subject to clarify the stereochemical behavior of the Co(III) complexes of the quadridentate tetramine (4*R*,6*R*)-dimethyl-3,7-diazanonane-1,9-diamine, hereafter *R*,*R*-2,3″,2-tet, which has the six-membered chelate ring with two methyl groups.

In our previous x-ray analysis study of $(+)_{546}$-[Co(ox)(*N*,*N*′-Me_2-*R*,*S*-2,3″,2-tet)]ClO_4 (I), where *N*,*N*′-Me_2-*R*,*S*-2,3″,2-tet is the tetradentate ligand (6*R*,8*S*)-6,8-dimethyl-2,5,9,12-tetraazatridecane, the central six-membered chelate ring adopts the chair conformation with both methyl groups equatorial.[1] On the other hand, Kobayashi et al.[2] reported that each 2,4-pentanediamine chelate ring in the [Co(*R*,*R*-2,4-pentanediamine)$_3$]$^{3+}$ ion took a skew boat conformation with both methyl groups equatorial. Thus, there are two possible conformations for the central 2,4-pentanediamine part of the tetramine in the [Co(ox)(*R*,*R*-2,3″,2-tet)]$^+$ ion known but similar product I oxalate dianion. Consequently, there are four possible isomers in this present complex as shown in Figure 1. Since the ^{1}H NMR spectrum of this complex indicated that the two *C*-methyl groups were nonequivalent to each other, the Λ-cis-α isomer is ruled out.[3] But, it is difficult to assign the geometry of this complex by absorption, CD, and ^{1}H NMR spectra. And the relationship between the absolute configuration of the optically active oxalate Co(III) complex with the 2,3,2-tet type ligand and CD spectrum has not been reported except for our previous x-ray study.[1] To elucidate the stereochemistry of this system, the crystal structure of $(-)_{546}$-[Co(ox)(*R*,*R*-2,3″,2-tet)]ClO_4 has been determined by x-ray structure analysis.

Experimental Section

A sample of $(-)_{546}$-β-[Co(ox)(*R*,*R*-2,3″,2-tet)]ClO_4 was generously supplied by Dr. F. Mizukami at the National Chemical Laboratory for Industry.

The specimens are red prismatic crystals elongated along the *b* axis. Weissenberg photographs of (0*kl*) and (*h*0*l*) nets indicated orthorhombic symmetry with the systematic absence of (*h*00) when *h* =

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