

Crystal and Molecular Structure of a Novel Bimetallocarborane Anion

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Summary The bimetallocarborane, $[\text{Et}_4\text{N}][(\eta\text{-C}_5\text{H}_5)\text{-Co-C}_2\text{B}_8\text{H}_{10}\text{-Co-C}_2\text{B}_8\text{H}_{10}]$, which was prepared by the polyhedral expansion of $1,6\text{-C}_2\text{B}_8\text{H}_{10}$ at -80° , was studied by single-crystal diffraction techniques; the anion was found to contain a bimetallic $\text{Co}_2\text{C}_2\text{B}_8\text{H}_{10}$ unit in which one cobalt atom was shared with a terminal $\text{C}_2\text{B}_8\text{H}_{10}$ group.

THE polyhedral expansion of $1,6\text{-C}_2\text{B}_8\text{H}_{10}$ at room temperature produced $1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-1-Co-2,3-C}_2\text{B}_8\text{H}_{10}$.¹ When the reaction was carried out at -80° , the yield of this monometallic carborane was markedly reduced, and three new bimetallic species were isolated. Two of these were isomers of $(\eta\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_8\text{H}_{10}$.² The third, the structure of which is reported here, was a bimetallocarborane anion containing two different carborane units.

The anionic complex was isolated as the tetraethylammonium salt and the elemental analysis established the formula to be $[\text{Et}_4\text{N}][(\text{C}_5\text{H}_5)\text{Co}_2(\text{C}_2\text{B}_8\text{H}_{10})_2]$. The anion appeared to contain a bimetallic $\text{Co}_2\text{C}_2\text{B}_8\text{H}_{10}$ unit in which one cobalt atom was terminally bonded to a cyclopentadienyl ring and the other to a $\text{C}_2\text{B}_8\text{H}_{10}^{2-}$ unit. The

$100\text{ MHz }^1\text{H}$ n.m.r. spectrum in CD_3CN consisted of a sharp singlet of area 5 at τ 4.7 and three broad singlets of area ratios 2:1:1 at τ 4.3, 6.1, and 7.4. These were assigned to the cyclopentadienyl protons and to three types of carborane C-H units, respectively. Resonances due to the tetraethylammonium protons were also observed.

The $80.5\text{ MHz }^{11}\text{B}$ n.m.r. spectrum, complicated owing to the presence of two different types of carborane units, appeared to be the 2:4:2 pattern of a terminal $\text{CoC}_2\text{B}_8\text{H}_{10}$ unit found for $1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-1-Co-2,3-C}_2\text{B}_8\text{H}_{10}$ superimposed upon a pattern of eight non-equivalent boron resonances due to the $\text{Co}_2\text{C}_2\text{B}_8\text{H}_{10}$ portion of the complex. The structure originally proposed² for the anion is shown in the Figure. This structure was subsequently confirmed by an X-ray diffraction study.

Crystal data: $\text{C}_{16}\text{H}_{45}\text{B}_{16}\text{Co}_2\text{N}$, monoclinic, space group $P2_1/c$; $a = 13.070(7)$, $b = 12.442(5)$, $c = 18.183(13)$ Å, $\beta = 99.34(4)^\circ$; $U = 2917.99$ Å³, $D_m = 1.25$, $D_c = 1.26$ g cm⁻³, $Z = 4$, $M = 554.38$.

Three-dimensional data consisting of 2895 reflections were collected with a Picker 4-circle diffractometer equipped with a graphite monochromator using Mo-K_α radiation

($\lambda = 0.71069 \text{ \AA}$) and controlled by the Brookhaven multiple spectrometer system. The structure was solved by direct methods (Multan) for the heavy atoms (Co) and some of the

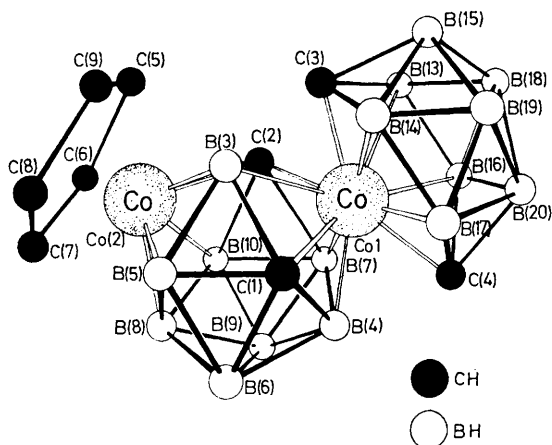


FIGURE. The molecular geometry of the $[\eta\text{-C}_6\text{H}_5)_2\text{-Co-C}_2\text{B}_8\text{H}_{10}\text{-Co-C}_2\text{B}_8\text{H}_{10}]^-$ anion.

light ones. The remaining light atoms were located by standard Fourier syntheses. The atomic parameters were refined by the full matrix least-squares method to $R_1(F) = 0.054$ and $R_2(F) = 0.075$. A set of average values of the B-B, B-C, B-Co, and Co-Co, bonds are given in the Table.

Although the C_{2v} octadecahedral structure found in $\text{C}_2\text{B}_9\text{H}_{11}$ ³ and proposed for $\text{B}_{11}\text{H}_{11}$ ²⁻⁴ has previously been proposed for 11-vertex metallocarboranes, these results represent the first crystallographic confirmation of this

TABLE. Average interatomic distances (in \AA)

Co(1)-Co(2)	3.174
Co(1)-C	(terminal cage)	1.978
Co(1)-C	(bridging cage)	2.094
Co(1)-B	(" cage)	2.090
Co(2)-C	(" cage)	2.010
Co(2)-B	(" cage)	2.048
Co(2)-C	(of C_6H_5 ring)	2.064
C-B	(bridging cage)	1.702
C-B	(terminal cage)	1.595
B-B	(bridging cage)	1.797
B-B	(terminal cage)	1.812

geometry for a metal-containing species. Furthermore, the structure of this red-brown species constitutes another example of a bimetallocarborane containing non-adjacent cobalt atoms which does not exhibit electronic spectral absorptions at wavelengths greater than 540 nm .^{5†}

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† λ_{max} (MeCN) ($\log \epsilon$): 248 (4.91), 292 (4.70), 348 (4.53), and 448 (3.50) nm.

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