Geometry of the ($B_8C_2H_{10}{\cdot}C_5H_5N^{2-}$) Anion from an *X*-Ray Structural Analysis of $[Et_4N^+][(B_9C_2H_{11})Co(B_8C_2H_{10}{\cdot}C_5H_5N)^-]$

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Summary The crystal structure of $[Et_4N^+][(B_9C_2H_{11})Co(B_8C_2H_{10}{\cdot}C_5H_5N)^-]$ has been elucidated; the d^6 cobalt(III) ion is "sandwiched" between mutually-staggered ($B_9C_2H_{11}^{2-}$) and ($B_8C_2H_{10}{\cdot}C_5H_5N^{2-}$) ions, the latter of these having a unique B_8C_2 skeleton which defines an icosahedron from which two adjacent apices have been removed; it is linked to cobalt *via* an open 4-atom (C–B–B–B) bonding face.

HAWTHORNE and his co-workers have examined the base degradation of $[\{\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}\}_2Co^{III-}]$ and have evidence for the π-monodentate ($B_8C_2H_{10}^{2-}$) ion and its derivatives.[1] We report the results of a single-crystal *X*-ray structural analysis of $[Et_4N^+][(B_9C_2H_{11})Co(B_8C_2H_{10}{\cdot}C_5H_5N)^-]$ which shows unambiguously the geometry of the boron–carbon–nitrogen skeleton of the ($B_8C_2H_{10}{\cdot}C_5H_5N^{2-}$) ion.

The bright red crystals are centrosymmetric monoclinic, space group $P2_1/c$ (C_{2h}^5; No. 14); $a = 16{\cdot}903(15)$, $b = 10{\cdot}771(10)$, $c = 15{\cdot}990(14)$ Å, $\beta = 99{\cdot}28(5)°$, $D_m = 1{\cdot}20(2)$ g cm^{-3}, $D_c = 1{\cdot}205$ g cm^{-3} for M 521·47 and $Z = 4$.

X-Ray diffraction data, $\sin\theta_{max} = 0{\cdot}77$ (Cu-K_α), were collected for levels $h(0$—$11)\ l$ and $(0$—$9)\ kl$ using a Supper-Pace diffractometer and equi-inclination Weissenberg geometry. Data were corrected for absorption (μ 46 cm^{-1}) and were merged to a common scale. The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques, to a final R value of 6·7% for 2058 independent non-zero reflections. All hydrogen atoms of the Et_4N^+, $B_9C_2H_{11}^{2-}$, and C_5H_5N moieties were located, as were the nine *terminal* hydrogen atoms of the $B_8C_2H_{10}$ residue; attempts to locate the tenth hydrogen of the last fragment were not successful.

The Figure shows the geometry of a $[(B_9C_2H_{11})Co(B_8C_2H_{10}{\cdot}C_5H_5N)^-]$ anion. The anion is optically active; the crystal consists of an ordered racemic mixture of the two enantiomers.

The $(B_8C_2H_{10}{\cdot}C_5H_5N^{2-})$ ligand has a decaborane structure, with the B_8C_2 framework defining an icosahedron from which two (mutually *ortho*) apices have been removed; the open six-atom face is defined by C(7′), B(2′), B(6′), B(10′), B(9′), C(8′), the pyridine substituent being N-bonded to B(9′) with Py(N)–B(9′) = 1·592(11) Å.

The $(B_8C_2H_{10}{\cdot}C_5H_5N^{2-})$ ion donates six electrons to the central Co(III) atom; co-ordination occurs *via* the four atom plane C(7′)–B(2′)–B(6′)–B(10′). Individual cobalt–(ligand atom) bonding distances vary appreciably, with Co–C(7′) = 2·014(8), Co–B(2′) = 2·082(10), Co–B(6′) = 2·126(9), and Co–B(10′) = 2·191(10) Å. The dihedral angle between this plane (root-mean-square atomic deviation 0·003 Å) and the bonding pentagonal face of the 1,2-dicarbollide ligand is 4°22′.

This structural analysis has failed to locate the site of the 'extra' hydrogen atom in the $(B_8C_2H_{10}{\cdot}C_5H_5N^{2-})$ ligand. It does not occupy a terminal position, for the nine terminal hydrogen atoms have been located in correctly apical positions. The pyridine substituent on B(9′) is also in an apical position, angles about B(9′) being Py(N)–B(9′)–C(8′) = 129.8(7), Py(N)–B(9′)–B(10′) = 122·3(7), Py(N)–B(9′)–B(4′) = 114·2(7), and Py(N)–B(9′)–B(5′) = 120·5(7)°. Geometrically possible locations for a bridging hydride ligand include B(9′)–H–B(10′), B(9′)–H–C(8′), or C(8′)–H–C(7′). In the absence of any known examples of B–H–C or C–H–C bridges, we presume that the 'missing' ligand lies between B(9′) and B(10′). However, an unambiguous assignment must come from spectroscopic or magnetic resonance studies.†

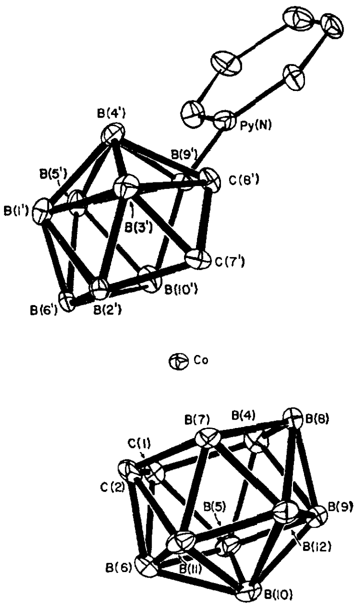

FIGURE. *Geometry of a* $[(B_9C_2H_{11})Co(B_8C_2H_{10}{\cdot}C_5H_5N)^{2-}]$ *anion, with hydrogen atoms omitted.* (*The conventional nomenclature* (cf. *ref.* 1) *leads to the depicted* B_8C_2 *ion having a rather different numbering scheme to its enantiomer* viz., $[\pi\text{-}(11)\text{-}7,8\text{-}B_8C_2H_{10}\text{-}9\text{-}C_5H_5N^{2-}]$ vs. $[\pi\text{-}(9)\text{-}7,8\text{-}B_8C_2H_{10}\text{-}11\text{-}C_5H_5N^{2-}]$).

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† We may note that a ^1H n.m.r. spectrum contains a very broad resonance at +9·2 p.p.m. from tetramethylsilane. This peak is attributed[1] to a B–H–B bridge hydrogen.

[1] C. J. Jones, J. N. Francis, and M. F. Hawthorne, preceding communication.