Structural Consequences of Electron 'Deficiencies' in Metallaheteroboranes; Hyperpolyhedral Metal–Metal Bonding

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Summary *closo*-Metallaheteroboranes which appear to have fewer than (n + 1) skeletal electron pairs to hold their n skeletal atoms together may have incompletely filled metal d-orbitals or hyperpolyhedral metal–metal bonding.

CONVENTIONAL electron counting schemes[1] for boranes, carbaboranes, and their metalla-derivatives associate a *closo*-structure with n skeletal atoms and (n + 1) skeletal electron pairs. The metal carbonyl and metallaborane clusters such as $[Rh_7(CO)_{16}]^{3-}$,[2] $[Os_6(CO)_{18}]$,[3] or $[\eta\text{-}C_5H_5)_3\text{-}Co_3B_4H_4]$[4] suggest that capped *closo*-structures may be expected for systems with fewer skeletal electron pairs. However, metallacarbaboranes of the early transition metals, such as $[(C_2B_9H_{11})_2Cr^{III}]^-$ or $[(C_2B_{10}H_{12})_2Ti^{II}]^{2-}$, which are apparently[1] several electrons (three and four, respectively, in these cases) short of the number appropriate for a *closo*-structure nevertheless adopt *closo*- (not capped *closo*-) structures.[5] This is because metallaheteroboranes with apparently fewer than $(n + 1)$ skeletal electron pairs to hold n cluster atoms together may actually possess precisely $(n + 1)$ such pairs, and adopt *closo*- (rather than capped *closo*-) structures because their metal atoms either have incompletely filled (nonbonding) *d*-orbitals[6] or relieve their electron 'deficiency' by extra metal–metal bonding. In some cases, this extra or 'hyperpolyhedral' metal–metal bonding may distort the geometry predicted by skeletal electron pair theory. The first example of hyperpolyhedral metal–metal bonding in metallaborane chemistry is now described.

Previously, the ten-vertex diferracarbaborane $[(\eta\text{-}C_5H_5)_2Fe_2C_2B_6H_8]$ was incorrectly deduced to contain 10 $(=n)$ skeletal electron pairs.[1,4,7] On the basis of this count, an idealised geometry of a capped tricapped trigonal prism (CTTP) would be predicted.[3,4,8] Nevertheless, this was not confirmed by an *X*-ray structural analysis of the diamagnetic isomer[7a] and as a result, the unusual arrangement† of the atoms in this isomer has been subjectively or incorrectly described in no less than five different ways.[4,7,9] However, the magnetic data for the paramagnetic isomer[7a] (μ_{eff} 3·05 B.M.) dictate that the iron atoms must be described as nominal 17-electron d^5-Fe^{III} atoms, each iron vertex then being the source of two (rather than one[1,7a,9]) skeletal electrons. Thus, $[(\eta\text{-}C_5H_5)_2Fe_2C_2B_6H_8]$ contains precisely 11 $(= n + 1)$ skeletal electron pairs and the structure of the paramagnetic isomer may be predicted to be an idealised bicapped Archimedean antiprism (BAA). The diamagnetism and the Fe–Fe distance of 2·571(7) Å in the second isomer[7a] is direct evidence of a hyperpolyhedral metal–metal bond. The singular arrangement of the cluster atoms in the diamagnetic species might now be attributed to a distortion of a BAA concomitant with the hyperpolyhedral metal–metal bond formation and can be objectively described as a convex ten-vertex hexadecahedron of C_s symmetry (if all atoms were the same) which is isogonal[10] to and a permutation of a BAA. Contrary to previous claims,[4,7] this arrangement is not a CTTP, CTTP's being isogonal *concave* hexadecahedrons of either C_s or C_{3v} symmetry. Hence, the diamagnetic isomer is in a *closo*-structural classification in accord with skeletal electron pair theory.

Hyperpolyhedral metal–metal bonding should not have a singular existence and it is predicted that this phenomenon will occur in other bi- and poly-metallic metallaheteroboranes containing transition metals to the left of the cobalt triad.

Added in proof: Recently, electron 'deficient' ferracobalta- and diferra-carbaboranes were shown or tentatively proposed to exhibit regular idealised *closo*-structures in the absence of direct hyperpolyhedral metal–metal bonding.[11]

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† See ref. 7(a) for a drawing of, and the structural data for this isomer.

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