Poster Presentation

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Strategies for distinguishing between B and C atoms in metallacarborane cages

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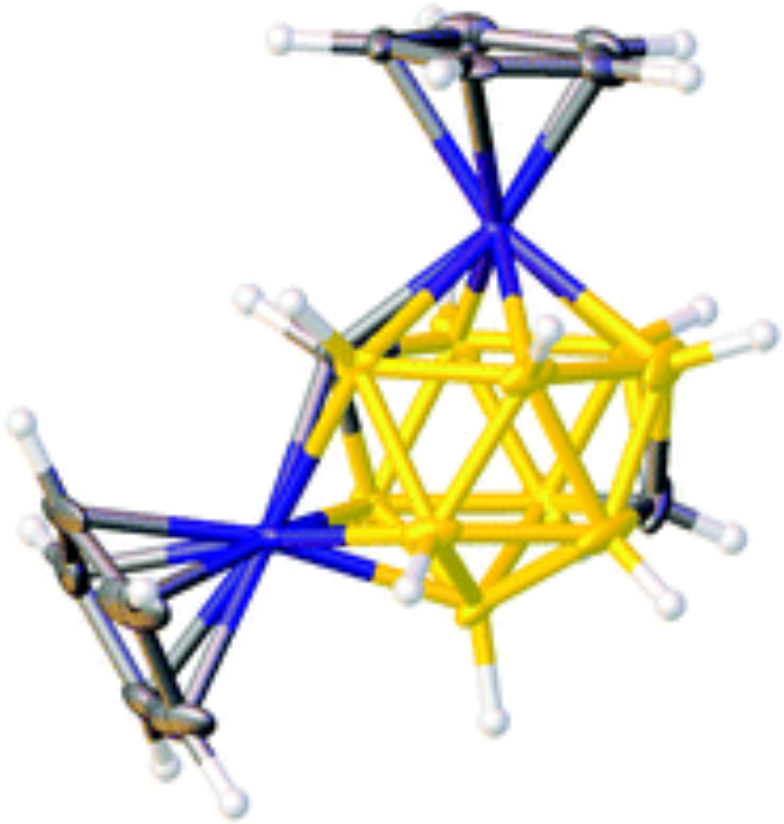
Carboranes and metallacarboranes demonstrate diverse geometric structures. Carborane cages are comprised of a mixture of carbon and boron vertices whereas metallacarboranes contain one or more metal atoms in addition to C and B atoms. The most common structure is the 12 vertex icosahedron but sub-icosahedral and supraicosahedral (13 vertex and even 14 and 15 vertex) cages are known. A common problem in structural studies of such species is how to distinguish between C and B given their very similar X-ray scattering powers. Usually in crystallography, displacement parameters and the Hirshfeld test are used as tools to check whether elemental assignment is correct. Although these are very useful in many circumstances, there are occasions when the displacement parameters are less well-defined and the Hirshfeld results consequently unreliable. Since correct element assignment is crucial in understanding the chemistries of carboranes and metallacarboranes we have developed new techniques to distinguish the C atom positions from the B atom positions in these cages. At Heriot-Watt University we have recently reported the Vertex-to-Centroid Distance (VCD) method [1] and a complementary approach, the Boron–H Distance (BHD) method [2], which was first communicated in 2002 [3]. The VCD and BHD methods have been used to distinguish between cage B and cage C atoms in a wide range of crystallographically-determined structures, both leading to the same clear conclusions and thus allowing the identities of these species to be established unambiguously. The methods are particularly useful when traditional approaches, e.g. using displacement parameters, fail, as demonstrated for asymmetric 14-vertex metallacarboranes [2] (Figure).

[1] *A. McAnaw, G. Scott, L. Elrick, et al., Dalton Trans., 2013, 42, 645-664,* ***[2]*** *A. McAnaw, D. Ellis, M.E. Lopez, et al., Dalton Trans., 2014, 43, 5095-5105,* ***[3]*** *A. Burke, R. McIntosh, D. Ellis, et al., Collect. Czech. Chem. Commun., 2002, 67, 991-1006.*



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