## **Report: My Favorite Element**

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## **Boron, My Favorite Element**

#### by M. Frederick Hawthorne

Success in a profession can often be traced to being at the right place at the right time. Such was the case when I became involved with boron hydrides (boranes, carboranes, etc.) as the leader of a new exploratory research group for the Rohm and Haas Company at the Army's Redstone Arsenal, near Huntsville, AL. This was during the 1950s and my mission was the exploration of borane chemistry, which could be applied to Cold War rocket motors having very energetic performance provided by borane fuels. The job was especially challenging since very little was actually known about borane synthesis, reactions, bonding, or structures at the time; furthermore, the powerful analytical instruments and theoretical structural methods were just being invented.

My Ph.D. at UCLA and postdoc at Iowa State were in the field of physical organic chemistry and the only boron compound I had used was BF<sub>3</sub>! I made the assumption that the rare, unstable, and under-studied borane chemistry would turn out to resemble organic chemistry. Boron and carbon were neighbors on the periodic table and these were the two elements that formed compounds by combining with themselves (catenation) and with each other. Carbon gave us organic chemistry and boron had, at that point, given us fascinating electron-deficient structures such as B<sub>2</sub>H<sub>6</sub>, B<sub>5</sub>H<sub>9</sub>, B<sub>10</sub>H<sub>14</sub>, about 30 in all. Decaborane, B<sub>10</sub>H<sub>14</sub>, was available from a contemporary jet engine fuel program (Air Force/Navy projects HEF and ZIP). Making this more mystical was the classified nature of the research. I simply took B<sub>10</sub>H<sub>14</sub> (air-stable solid) and explored its characteristics in well-known organic reactions. Patterns of similarity soon appeared and serendipity coupled with experimental care soon proved that only a minute portion of possible borane chemistry was known and that borane chemistry was represented by previously unknown compounds analogous to aliphatic, aromatic,

heterocyclic, and organometallic organic compounds. The first boranes had been discovered in Germany by Alfred Stock in the early 1900s (B<sub>2</sub>H<sub>6</sub>, B<sub>4</sub>H<sub>10</sub>, B<sub>5</sub>H<sub>9</sub>, etc.) and these relatively unstable species corresponded to the aliphatic hydrocarbons.

Exploratory work revealed the borane analogs of aromatic hydrocarbons, which proved to be a complete family of  $B_nH_n^{2-}$  dianions with  $\underline{n}=6$  to 12 inclusive and having closed polyhedral structures. Like the aromatic hydrocarbons, these species were very stable and the icosahedral  $B_{12}H_{12}^{2-}$  ion is probably the most

Figure 1. Starting with  $B_{12}(OH)_{12}^{2-}$  as a core, the Hawthorne group creates nanoparticles capable of carrying various payload molecules—an imaging contrast agent, a biomolecule for tumor or organ targeting, or a drug—for potential all-in-one life-saving therapy, as shown schematically. In one example, they have created a potential anticancer agent by attaching 12 copies of doxorubicin to the  $B_{12}$  core via enzymatically cleavable peptides. Courtesy of Fred Hawthorne.

thermally stable metal hydride structure known (600 °C). In these polyhedral structures, one may replace one or more boron vertices by atoms such as N, S, P, C, etc. The  $C_2B_{10}H_{12}$  structures are possible as three isomers depending on the C-atom positions. Another huge class of derivatives is based upon the addition of all types of metals as boron substitutes. These are the analogs of organometallic compounds. One cannot fail to love borane chemistry since it recaptures the early days of organic chemistry and the attendant sense of rewarding exploration.

Another feature of boron is its two isotopes, <sup>10</sup>B and <sup>11</sup>B that differ by an extra neutron in the <sup>11</sup>B nucleus. Cancer therapy may benefit from the chemistry of boron coupled to the reaction of the <sup>10</sup>B nucleus with a neutron

$$^{10}$$
B +  $^{1}$ n  $\rightarrow$   $^{7}$ Li +  $^{4}$ He +  $\gamma$  + 2.4 MeV

If this boron neutron capture reaction can be targeted to cancer cells, the Li and He products will kill the cell without damage to the healthy neighboring cells. This highly specific reaction is unique among the light elements and provides an additional attractive feature for boron, another reason boron is my favorite element.

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