PLANAR CoB_{18}^- CLUSTER: A NEW MOTIF FOR HETERO- AND METALLO-BOROPHENES

TENG-TENG CHEN, TIAN JIAN, GARY LOPEZ, *Department of Chemistry, Brown University, Providence, RI, USA*; WAN-LU LI, XIN CHEN, JUN LI, *Department of Chemistry, Tsinghua University, Beijing, China*; LAI-SHENG WANG, *Department of Chemistry, Brown University, Providence, RI, USA*.

Combined Photoelectron Spectroscopy (PES) and theoretical calculations have found that anion boron clusters (B_n^-) are planar and quasi-planar up to B_{25}^-. Recent works show that anion pure boron clusters continued to be planar at B_{27}^-,B_{30}^-,B_{35}^- and B_{36}^-. B_{35}^- and B_{36}^- provide the first experimental evidence for the viability of the two-dimensional (2D) boron sheets (Borophene). The 2D to three-dimensional (3D) transitions are shown to happen at B_{40}^-,B_{39}^- and B_{28}^-, which possess cage-like structures. These fullerene-like boron cage clusters are named as Borospherene. Recently, borophenes or similar structures are claimed to be synthesized by several groups.

Following an electronic design principle, a series of transition-metal-doped boron clusters ($M©B_n^-$, n=8-10) are found to possess the monocyclic wheel structures. Meanwhile, CoB_{12}^- and RhB_{12}^- are revealed to adopt half-sandwich-type structures with the quasi-planar B_{12} moiety similar to the B_{12}^- cluster. Very lately, we show that the CoB_{16}^- cluster possesses a highly symmetric Cobalt-centered drum-like structure, with a new record of coordination number at 16.

Here we report the CoB_{18}^- cluster to possess a unique planar structure, in which the Co atom is doped into the network of a planar boron cluster. PES reveals that the CoB_{18}^- cluster is a highly stable electronic system with the first adiabatic detachment energy (ADE) at 4.0 eV. Global minimum searches along with high-level quantum calculations show the global minimum for CoB_{18}^- is perfectly planar and closed shell ($^1A_1$) with C_{2v} symmetry. The Co atom is bonded with 7 boron atoms in the closest coordination shell and the other 11 boron atoms in the outer coordination shell. The calculated vertical detachment energy (VDE) values match quite well with our experimental results. Chemical bonding analysis by the Adaptive Natural Density Partitioning (AdNDP) method shows the CoB_{18}^- cluster is π-aromatic with four 4-centered-2-electron (4c-2e) π bonds and one 19-centered-2-electron (19c-2e) π bond, 10 π electrons in total. This perfectly planar structure reveals the viability of creating a new class of hetero-borophenes and metallo-borophenes by doping metal atoms into the plane of monolayer boron atoms. This gives a new approach to design perspective hetero-borophenes and metallo-borophenes materials with tunable chemical, magnetic and optical properties.