Perfectly planar CoB_{18}^- as a motif for metallo-borophenes

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Received: 18 May 2016; Accepted: 18 May 2016

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Over the past decade, extensive collaborative experimental and theoretical researches have systematically elucidated the structures and chemical bonding of boron clusters as a function of size and have revealed an intriguing set of structures, ranging from planar hydrocarbon-analogs to nanotubular and fullerene-like structures (borospherenes) [1–7]. Small boron clusters have the propensity for planarity with delocalized σ and π electrons over the whole molecular plane, giving rise to the concept of multiple aromaticity. Particularly, the discovery of the planar B_{36} with a central hexagonal vacancy [8] has been a major landmark in the study of boron clusters, because it can be viewed as the basis for the formation of monolayer two-dimensional (2D) boron materials and provided the first indirect evidence for the viability of 2D borons with hexagonal holes [9, 10]. This momentous finding prompted the proposal of a new name “borophene” for the new 2D boron [8], in analogy with graphene, by Jun Li and Lai-Sheng Wang.

The reason that the name borophene was coined, rather than borene, was because the later had already been used in chemistry to represent R-B=B-R types of organoboron molecules. Very recently, borophenes have been successfully synthesized by atomic deposition on a silver surface [11, 12]. These rapid progresses in experimental syntheses and theoretical studies have paved the way for possible applications of borophenes

in nanoscience and nanotechnology.

Now, a team led by Prof. Jun Li from Tsinghua University and Prof. Lai-Sheng Wang from Brown University reported the first perfectly planar transition-metal doped boron cluster (CoB_{18}^- , Fig. 1) implying a promising future for “hetero-borophenes” [13]. The CoB_{18}^- cluster was studied thoroughly by both photoelectron spectroscopy and quantum chemistry, and it was found to consist of a seven-membered ring of boron atoms with a central Co atom that has rather strong covalent interactions with the boron surrounding. The Co atom at the center holds the highly flexible boron structure so that a perfect plane can be formed without any defect in the boron framework. The B–B lengths on the periphery of the cluster are shorter than the internal ones due to dangling bonds in the periphery. The team performed chemical bonding analyses, which indicate that Co interacts with the surrounding B_7 ring via six four-centered, two-electron ($4c-2e$) σ bonding orbitals. The inner B_7 ring bonds with the outer B_{11} ring via both σ and π type bonding, thus ensuring electronic stability of the framework. There are ten π electrons delocalized over the whole plane, suggesting unique π aromaticity (Fig. 2) for the planar CoB_{18}^- cluster.

They also showed that the central Co atom has a rare oxidation state of +1 with d^8 electron configuration due to the strong covalent interactions between Co and

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Figure 1 The global minimum of CoB_{18}^- . Reproduced with permission from Ref. [13], ©John Wiley and Sons 2016.

Figure 2 Chemical bonding analyses of CoB_{18}^- using AdNDP at the PBE0/Def2-TZVP level. Reproduced with permission from Ref. [13], ©John Wiley and Sons 2016.

the B_{18} frame, which enriches the low-oxidation-state chemistry of transition metals. Such a planar cluster can be viewed as a basis for extended 2D metal-doped boron sheets and points to a promising class of metallo-borophenes that may have potential applications as novel catalytical, optical, and magnetic materials.

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