

What Is the Maximum Coordination Number in a Planar Structure?

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Thinking about molecules that do not yet exist on Earth is an amazing mental experiment.^[1] Using the established rules of chemistry, we are able to find and—in many cases—to understand what is the most favorable structure of a set of atoms. Exceptions to these rules are occasionally found, in particular if small numbers of atoms are concerned, and they can cause strong conceptual troubles. Paraphrasing Benson, these exceptions drive us to go deeper and push the limits.^[2] So, studying new exotic molecules is more than curiosity, it is to prove the limits, to learn, and eventually to understand important concepts in chemistry such as the chemical bond or aromaticity.

Molecules containing planar tetracoordinate carbon (ptC) atoms are good examples.^[3] In fact, each new ptC structure that is realized experimentally contradicts the classical structural theory of organic chemistry. Furthermore, it gives confidence in predictive theory as a discipline to establish the limits of such seemingly outlandish structures. Recently, viable planar pentacoordinate carbon (ppC) atoms were predicted in silico.^[4] In 2000, Exner and Schleyer suggested CB_6^{2-} as the first anionic molecule with a planar hexacoordinate carbon atom.^[5] However, experimental evidence shows that carbon avoids such type of arrangements. The most stable form of CB_6^{2-} is also planar, but the carbon atom is dicoordinate.^[6] So, it would appear that the maximum coordination number of carbon in planar molecules is five.

Chemistry can be interpreted in terms of perturbation theory: substituting a single atom in a molecule can induce a strong change in its structure and properties. When the

carbon nucleus in CB_6^{2-} is substituted by boron, and two electrons are removed, the result is a quasiplanar B_7^- structure with a hexacoordinate boron atom.^[7] The addition of one boron atom to the periphery generates a ring within which the central boron atom is accommodated comfortably.^[8]

As a consequence of its electron-deficient character and propensity for deltahedral bonding, boron is intrinsically suitable for designing ring systems containing one or more hypercoordinate elements, including boron itself. Several boron rings enclosing planar hypercoordinate main group elements have been proposed in silico.^[9] However, none of them has yet been detected experimentally, except those composed exclusively of boron.^[10]

In 2008, Luo as well as Ito et al. explored if it was viable to theoretically design boron wheels containing transition metals.^[11] Three years later, Romanescu et al. detected boron rings in the gas phase with a central transition metal atom.^[12] These doped boron clusters were produced in a laser-vaporization supersonic molecular beam, and the structures were probed and confirmed by photoelectron spectroscopy. Thus, they evidently exist in the gas phase, but we cannot expect them to be produced in macroscopic quantities in the near future. The reported clusters (Co@B_8^- , Ru@B_9^- , Rh@B_9^- , and Ir@B_9^-) are extraordinary in chemistry because of their perfectly planar structures with coordination numbers of 8 and 9 (Figure 1). In addition to the strong and localized

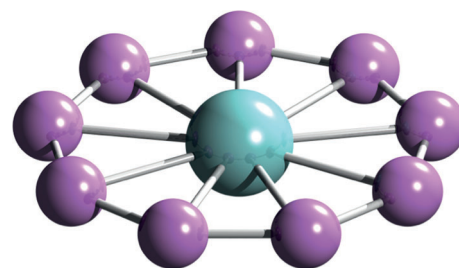


Figure 1. Structure of M@B_9^- ($\text{M} = \text{Ru}, \text{Rh}, \text{Ir}$).

bonding between the ring atoms, there are two types of delocalized bonding—the in-plane σ and the out-of-plane π bonding, each of which follows the $(4n+2)$ Hückel rule for aromaticity.

As we have learned from theoretical chemistry, the stability of these boron wheels is determined by the perfect

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combination of ring cavity and electronegativity, electronic configuration, and volume of the central atom. However, one could also predict that an increase in the covalent radius of the central transition-metal atom would necessitate a higher coordination number to stabilize a planar form. The problem is to select the correct piece (atom) of the puzzle.

This masterpiece has now been achieved by the research groups of Wang and Boldyrev, who combined theoretical and experimental techniques to predict, produce, and detect the systems with the highest coordination number in planar clusters so far known: namely, TaB_{10}^- and NbB_{10}^- (Figure 2).^[13] The bonding analysis of the two clusters revealed ten two-center–two-electron (2c-2e) peripheral σ bonds, five

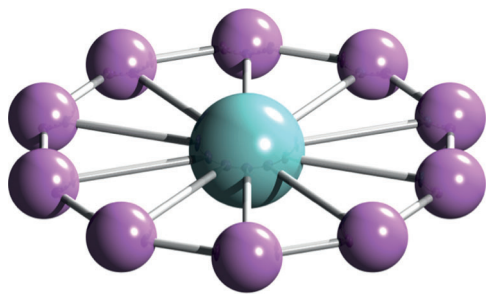


Figure 2. Structure of M@B_{10}^- ($\text{M} = \text{Nb}, \text{Ta}$).

delocalized σ bonds, and three delocalized π bonds. Thus, the systems are doubly (σ and π) aromatic. The availability of the d orbitals of Nb and Ta to participate in the σ -delocalized bonding with the peripheral boron atoms is essential to stabilize these doubly aromatic structures.

Are TaB_{10}^- and NbB_{10}^- the planar systems with the highest coordination number? We don't know. However, both clusters prove the limits of structural chemistry and of course we will learn so much from them.

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