

Endohedral clusters: a playground for computational chemistry.

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Endohedral clusters, structures where one or more transition metal is encapsulated inside a shell of main-group atoms, present a perhaps uniquely diverse platform for exploring the nature of the chemical bond. Whilst the interactions between the metal and the cage can be, and indeed very often are, strong, radial bonding is not essential to the integrity of the structure. This point is illustrated most elegantly by the endohedral fullerenes such as Ne@C₆₀, where stability is due to the kinetic barrier associated with the endohedral atom passing through the wall of the cluster rather than any strong Ne-C bonding. The fact that strong bonding is not essential allows a wide range of bond types to emerge within a series of structurally related clusters, from strong covalent through to weak magnetic coupling. Here, I will focus on a relatively small but rapidly expanding group of endohedral clusters where the transition metal (or metals) have an open-shell configuration, and show how the complex interplay of single-site exchange, metal-metal and metal-cage bonding leads to remarkable structural chemistry and spectroscopy. For example, the characteristic properties of the series [Ni₂Bi₁₂]⁴⁺, [Fe₂Sn₄Bi₈]³⁻ and [Cr₂Sb₁₂]³⁻ mirrors precisely the trends seen in analogues with a single metal center such as [NiPb₁₂]²⁻, [MnPb₁₂]³⁻ and [RuGe₁₂]³⁻. By identifying these patterns and their underlying causes, we can begin to understand the complex landscape presented by this remarkable family of compounds.

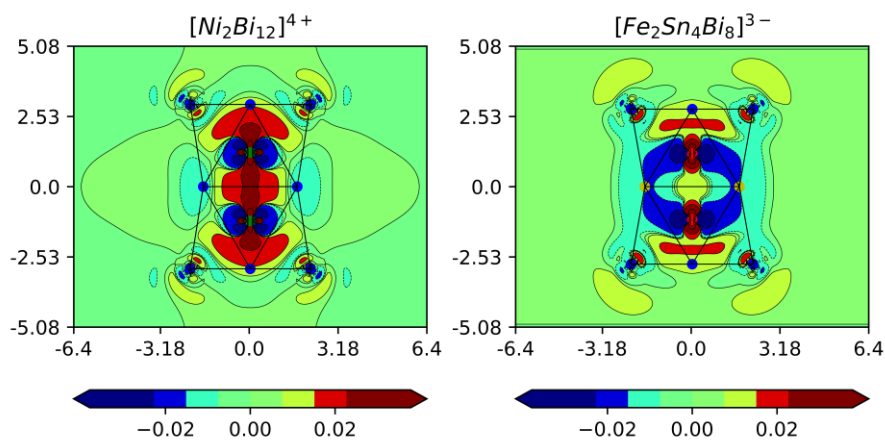


Figure 1 Difference densities in the formation of [Ni₂Bi₁₂]⁴⁺ and [Fe₂Sn₄Bi₈]³⁻.