

η -Aromaticity-Induced Stabilization of Heterometallic Supertetrahedral Clusters [Zn₆Ge₁₆]⁴⁺ and [Cd₆Ge₁₆]⁴⁺

Xu H.-L.

Popov I.A.

Tkachenko N.V.

Wang Z.-C.

Muñoz-Castro A.

Boldyrev A.I.

Sun Z.-M.

In this work, the largest heterometallic supertetrahedral clusters, [Zn₆Ge₁₆]⁴⁺ and [Cd₆Ge₁₆]⁴⁺, were directly self-assembled through highly-charged [Ge₄]⁴⁺ units and transition metal cations, in which 3-center- η -2-electron η bonding in Ge₂Zn or Ge₂Cd triangles plays a vital role in the stabilization of the whole structure. The cluster structures have an open framework with a large central cavity of diameter 4.6 Å for Zn and 5.0 Å for Cd, respectively. Time-dependent HRESI-MS spectra show that the larger clusters grow from smaller components with a single [Ge₄]⁴⁺ and ZnMes₂ units. Calculations performed at the DFT level indicate a very large HOMO-LUMO energy gap in [M₆Ge₁₆]⁴⁺ (2.22 eV), suggesting high kinetic stability that may offer opportunities in materials science. These observations offer a new strategy for the assembly of heterometallic clusters with high symmetry. © 2020 Wiley-VCH GmbH

planar tetracoordinate Zn/Cd

supertetrahedron

T_d symmetry

Zintl clusters

η -aromaticity

Cadmium compounds

Stabilization

Transition metals

Zinc compounds

Cluster structure

Heterometallic clusters

Heterometallics

Kinetic stability

Open frameworks

Sigma aromaticity

Time dependent

Transition metal cations

Germanium compounds