

# $\eta$ -Aromaticity-Induced Stabilization of Heterometallic Supertetrahedral Clusters [Zn<sub>6</sub>Ge<sub>16</sub>]<sup>4-</sup> and [Cd<sub>6</sub>Ge<sub>16</sub>]<sup>4-</sup>

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In this work, the largest heterometallic supertetrahedral clusters, [Zn<sub>6</sub>Ge<sub>16</sub>]<sup>4-</sup> and [Cd<sub>6</sub>Ge<sub>16</sub>]<sup>4-</sup>, were directly self-assembled through highly-charged [Ge<sub>4</sub>]<sup>4-</sup> units and transition metal cations, in which 3-center-2-electron  $\eta$  bonding in Ge<sub>2</sub>Zn or Ge<sub>2</sub>Cd 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 [Ge<sub>4</sub>]<sup>4-</sup> and ZnMes<sub>2</sub> units. Calculations performed at the DFT level indicate a very large HOMO-LUMO energy gap in [M<sub>6</sub>Ge<sub>16</sub>]<sup>4-</sup> (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<sub>d</sub> symmetry

Zintl clusters

$\eta$ -aromaticity