Potential to stabilize 16-vertex tetrahedral coinage-metal cluster architectures related to Au20

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DFT calculations were carried out on a series of tetrahedral 16-atom superatomic clusters having 20 or 18 jellium electrons (je) and structurally related to Au20, namely, [M16]4-/2- (M = Cu, Ag, and Au) and [M4?M12??]0/2+ (M? = Zn, Cd, Hg; M?? = Cu, Ag, Au). While the bare homonuclear 20-je species required further stabilization to be isolated, their 18-je counterparts exhibited better stability. Lowering the electron count led to structural modification from a compact structure (20-je) to a hollow sphere (18-je). Such a change could be potentially controlled by tuning redox properties. Among the 20-je heteronuclear [M4?M12??] neutral series, [Zn4Au12] appeared to meet the best stability criteria, but their 18-je relatives [M4?M12??]+, in particular [Zn4Cu12]2+ and [Cd4Au12]2+, offered better opportunities for obtaining stable species. Such species exhibit the smallest models for the M(111) surface of fcc metals, which expose designing rules towards novel high-dopant-ratio clusters as building blocks of nanostructured materials.