Stabilizing heteroatom-centered 16-vertex group 11 tetrahedral architectures: Bonding and structural considerations toward versatile endohedral species

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Density functional theory (DFT) calculations were carried out on a series of clusters made of a centered tetrahedral 16-atom superatomic cage having 20 or 18 jellium electrons (je) and structurally related to [Au20], namely [X@M16] (M = group 11; X = group 2, 4, 12, 14 element). Such species provide further information of how two different electron counts offer a more preferred endohedral situation for specific group elements. Calculations show that the encapsulated atom provides supplementary orbitals to stabilize the bonding M16 MO's. Different favored electron counts are found depending on the nature of the encapsulated atom, as observed by the formation of 20-je species when encapsulating a group 14 element and 18-je species when encapsulating a group 2 element. In addition, the capabilities to enable reactive sites along the cage structure are found via the formation of ? holes at the coinage-metal edges, as shown by their electrostatic potential surface. Such naked species, which constitute an interesting addition to libraries of examples as small models for doped M(111) surfaces of fcc metals, reveal that different superatomic electronic configurations can favor the encapsulation of certain group elements. These results can guide further design of endohedral species. © 2019 Wiley Periodicals, Inc.

DFT

heteroatom doping

superatoms

tetrahedral structure

Chemical bonds

Design for testability

Digital libraries

Cage structures

Coinage metals

Electronic configuration

Electrostatic potential surface

Group 14 element

Heteroatoms

Superatoms

Tetrahedral structures

Density functional theory