Cage structures based on Polyhedral Oligomeric Silsesquioxanes (POSS) with atomic and ionic impurities

FRANK HAGELBERG, SUNG SOO PARK, CHUANYUN XIAO, Computational Center for Molecular Structure and Interactions, Jackson State University, DELWAR HOSSAIN, CHARLES PITTMAN, SVEIN SAEBO, Department of Chemistry, Mississippi State University

— Endohedral and exohedral polyhedral cage molecules of the form \((\text{HAO}_{3/2})_8\) \((\text{A} = \text{C}, \text{Si}, \text{Ge})\) with double four-membered ring \(\text{D}_4\text{R}\) units complexed with the atomic or ionic species: \(\text{Li}^+, \text{Na}^+, \text{K}^+, \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{He}, \text{Ne}, \text{Ar}\) have been investigated using Density Functional Theory (DFT). Geometric, electronic and energetic properties were obtained. The symmetry of the endohedral complexes when \(X\) is a cation turned out to depend critically on the relative cation and cage sizes. The binding energies of the endohedral and exohedral complexes document a clear preference for the latter, except for halides, where the endohedral complexes are more stable. The formation of the endohedral complexes is discussed in terms of transition states that connect the exohedral and endohedral minima, as well as the activation barriers for insertion of the guest into the cage. Our studies predict that a fluoride anion can penetrate into the \((\text{HAO}_{3/2})_8\) cage without destroying it. For \(X = \text{Cl}^-, \) in contrast, the cage ruptures upon insertion of the impurity.

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