

Nature of hydride and halide encapsulation in Ag_8 cages: insights from the structure and interaction energy of $[\text{Ag}_8(\text{X})\{\text{S}_2\text{P}(\text{O}^i\text{Pr})_2\}_6]^+$ ($\text{X} = \text{H}^-$, F^- , Cl^- , Br^- , I^-) from relativistic DFT calculations

- Guajardo Maturana R.^a,
- Ortolan A.O.^b,
- Rodríguez-Kessler P.L.^c,
- Caramori G.F.^b
- Parreira R.L.T.^d
- Muñoz-Castro A.^c

Abstract

Unraveling the different contributing terms to an efficient anion encapsulation is a relevant issue for further understanding of the underlying factors governing the formation of endohedral species. Herein, we explore the favorable encapsulation of hydride and halide anions in the $[\text{Ag}_8(\text{X})\{\text{S}_2\text{P}(\text{OPr})_2\}_6]^+$ ($\text{X}^- = \text{H}, 1, \text{F}, 2, \text{Cl}, 3, \text{Br}, 4$, and $\text{I}, 5$) series on the basis of relativistic DFT-D level of theory. The resulting $\text{Ag}_8\text{-X}$ interaction is sizable, which decreases along the series: -232.2 (1) > -192.1 (2) > -165.5 (3) > -158.0 (4) > -144.2 kcal mol⁻¹(5), denoting a more favorable inclusion of hydride and fluoride anions within the silver cage. Such interaction is mainly stabilized by the high contribution from electrostatic type interactions (80.9 av%), with a lesser contribution from charge-transfer (17.4 av%) and London type interactions (1.7 av%). Moreover, the ionic character of the electrostatic contributions decreases from 90.7% for hydride to 68.6% for the iodide counterpart, in line with the decrease in hardness according to the Pearson's acid-base concept (HSAB) owing to the major role of higher electrostatic interaction terms related to the softer (Lewis) bases. Lastly, the $[\text{Ag}_8\{\text{S}_2\text{P}(\text{OPr})_2\}_6]^{2+}$ cluster is able to adapt its geometry in order to maximize the interaction towards respective monoatomic anion, exhibiting structural flexibility. Such insights shed light on the physical reasoning necessary for a better understanding of the different stabilizing and destabilizing contributions related to metal-based cavities towards favorable incorporation of different monoatomic anions. © the Owner Societies 2021.