Tiara-like Complexes acting as Iodine Encapsulating Agents: The Role of M?I Interactions in [M(?-SCH2CO2Me)2]8?I2 (M = Ni, Pd, Pt) Inclusion Compounds

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A proposed series of tiara-like complexes [M(?-SCH2CO2Me)2]8 (where M = Ni, Pd, Pt) are here studied through DFT methodologies prompted by the synthesis of the palladium parent and their potential application in iodine encapsulation from spent nuclear fuel. Their hollow structure with a suitable cavity size, and the presence of several transition-metal centers capable to directly interact with an I2 molecule through noncovalent forces, make them attractive inclusion agents. Herein, an energy decomposition analysis reveals that forces responsible for keeping the guest molecule in the inner cavity are mainly electrostatic; a remarkable feature given, in principle, the neutral nature of both the host and guest species, offering us an interesting study case where the electronic cloud distortion of the binding sites and iodine atoms can be estimated and related to the intensity of the host-guest interactions. Our results shed light into the application of the nickel tiara-like host as an alternative to the reported [Pd(?-SCH2CO2Me)2]8 system. This research can be useful for further evaluation of nickel-based iodine sequestering agents prior to engaging in explorative synthesis efforts.