

# Heavy element metallacycles: Insights into the nature of host-guest interactions involving dihalide mercuramacrocyclic complexes

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Host-guest chemistry is a relevant issue in materials science, which encompasses the study of highly structured molecular frameworks composed of at least two complementary entities associated through noncovalent interactions, where structures involving several metallic centers, namely, metallacycles, acting as host species, offer significant advantages over organic systems due to the high versatility of their binding sites in terms of ion recognition. In this context, we study via relativistic density functional calculations the host-guest formation of systems involving a heavy element metallacycle,  $[\text{HgC}(\text{CF}_3)_2]_5$ , which binds to several halide anions to give  $[(\text{HgC}(\text{CF}_3)_2)_5 2\text{X}]_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ). Our results reveal an interesting case where the expected soft acid-soft base pair is not the more stable situation. Instead, a surprising hard-soft pair arises as the preferred species, with stronger forces toward  $\text{Cl}^-$  than those corresponding to  $\text{I}^-$  by about 24 kcal/mol. To understand such a situation, the use of a detailed analysis of the energy decomposition analysis (EDA) terms suggests the electrostatic character of the host-guest pair, which is ruled by the ion-dipole term by about 97%, favoring the inclusion of the hard base, namely,  $\text{Cl}^-$ , instead of the softer counterpart,  $\text{I}^-$ . The current approach allows determining the role of certain Coulombic terms in the electrostatic nature of the interaction, leading to a clear rationalization of the soft-soft or hard-soft preferences into the formation of host-guest pairs, which can be extended to the study of the behavior of several organic or inorganic systems. © 2014 American Chemical Society.