Nature of mercury inclusion in intermediate 6-valence electron [M@Au8Hgx(PPh3)8]n+ (M = Au, Pd, Pt; x = 0-2) protected gold superatoms: Insights from relativistic density functional theory calculations

Quintana C.G.

Ocayo F.

Guajardo Maturana R.

Hurtado J.J.

Muñoz-Castro A.

Superatomic clusters offer useful templates displaying distinctive physical and chemical characteristics. Here, we explore the [M@Au8(PPh3)8]n+ (M = Au, n = 3; Pd, Pt, n = 2) robust framework to gain an understanding of the nature of the inclusion of mercury atoms at Au4 faces, leading to [M@Au8Hgx(PPh3)8]n+ (x = 1, 2). Our results show a weak interaction of about 25 kcal mol?1 per Hg atom, which is mainly of electrostatic character, followed by orbital and London dispersion-type interactions. This weak interaction can be understood as the formation of host-guest species, for which the inherent electronic and optical properties of the [M@Au8(PPh3)8] cluster along the series do not vary to a large extent. This demonstrates that, in [M@Au8Hgx(PPh3)8], each Hg can be considered an inclusion atom rather than a dopant element, where the parent cluster is able to act as a Lewis acid host. Furthermore, the viable formation of such species can serve as useful examples to stimulate future experimental characterization of inclusion complexes involving related superatomic structures with available open faces. © 2019 Wiley Periodicals, Inc.

clusters

gold clusters

Lewis-acid

mercury

Atoms

Gold

Mercury (metal)

Optical properties

clusters

Electronic and optical properties

Experimental characterization

Gold clusters

Lewis Acid

Physical and chemical characteristics

Relativistic density functional theory

Weak interactions

Density functional theory