

On Heteronuclear Isoelectronic Alternatives to $[\text{Au}_{13}(\text{dppe})_5\text{Cl}_2]^{3+}$: Electronic and Optical Properties of the 18-Electron $\text{Os}@[\text{Au}_{12}(\text{dppe})_5\text{Cl}_2]$ Cluster from Relativistic Density Functional Theory Computations

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Abstract

The development of well-defined atomically precise heteronuclear nanoclusters passivated by protecting ligands is presently a booming area, owing to the fact that doping well-known homonuclear nanostructures allows fine-tuning of their properties. Here, we explore by means of density functional theory calculations the possibility of doping the central gold atom in the classical $[\text{Au}_{13}(\text{dppe})_5\text{Cl}_2]^{3+}$ cluster (1) by Os. Although both $[\text{Au}_{13}(\text{dppe})_5\text{Cl}_2]^{3+}$ and $[\text{Os}@[\text{Au}_{12}(\text{dppe})_5\text{Cl}_2]]$ have the same total number of electrons, we show that they are not isoelectronic within the formalism of the superatom model, being respectively an 8- and an 18-electron species. It results that they exhibit similar structures but present significantly different optical behaviors (ultraviolet/visible and circular dichroism). Similar results are obtained for the Ru and Fe relatives. Emission properties indicate some redshift of the $T_1 \rightarrow S_1$ decay with respect to $[\text{Au}_{13}(\text{dppe})_5\text{Cl}_2]^{3+}$, involving an equatorial distortion of the $\text{Au}_{12}\text{Cl}_2$ core in the T_1 state, rather than the axial distortion afforded by 1. The sizable highest occupied molecular orbital-lowest unoccupied molecular orbital gaps found for the three doped species suggest that further experimental exploration of different stable doped species derived from the ligand-protected $\text{Au}_{12}\text{Cl}_2$ core should be encouraged.

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