

Understanding planar ligand-supported MAu5 and MAu6 cores. theoretical survey of [MAu5(Mes)5] and [MAu6(Mes)6] (M = Cu, Ag, Au; Mes = 2,4,6-Me3C6H2) under the planar superatom model

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The planar superatom model has been applied to the case of planar ligand-supported MAu5 and MAu6 cores, where M = Cu(I), Ag(I), and Au(I), in order to increase the understanding of the electronic structure and bonding properties of planar golden clusters. The study of [Au5(Mes)5], [Au6(Mes)6], [MAu5(Mes)5], and [MAu6(Mes)6] has been carried out by using relativistic DFT calculations, which describe the short d10-d10 contacts due to the bonding stabilization within the Aun core in addition to the respective aurophilic phenomena. The results under the planar superatom approach allow us to characterize the electronic structure in all the systems as formally 10 valence electron cores, depicting an overall $1s^2 1p_x^1 1p_y^1 1d_{xy}^1 1d_{x^2-y^2}^2$ configuration as a result of the ligand-metal interaction. The inclusion of the respective M(I) closed shell center increases the number of superatomic shells as $1s^1 1p^1 1d^2 \rightarrow 1s^1 1p^1 1d^2 s^1$, denoting the interaction between each concentric section. Our results suggest that the MAun cores could be conveniently viewed as the combination of concentric structures denoted by [M@Aun]. In addition, the role of the inclusion of the spin-orbit term into the planar superatom model is discussed. © 2014 American Chemical Society.