Survey of short and long cuprophilic d10-d10 contacts for tetranuclear copper clusters. Understanding of bonding and ligand role from a planar superatom perspective

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Polynuclear copper(i) complexes involving d10-d10 interactions have been studied to a lesser extent in comparison to their gold counterparts. Here, we attempt to gain a deeper understanding of ligand-protected d10 copper clusters based on density functional theory calculations, based on the evaluation of several tetranuclear copper arrays offering different cuprophilic interactions, showing short- and long-contact d10-d10 situations. Our results show that the protecting ligands display a fundamental role in the stabilization of the closed-shell central core since there is a direct relationship between ligand charge donation to the ns combinations of multinuclear metallic center and the collateral increasing of the copper-copper stabilizing interactions. Further, quantification of the incoming population of ns shell levels through a selective analysis of coefficients of its corresponding wave functions depicts a useful and novel methodology toward the characterization of the copper-metallophilic phenomena that appears in these closed-shell systems. Thereby, here we use the planar superatom approach to describe the ns valence population in terms of superatomic two-dimensional shell set levels, namely, 1s, 1px, 1py, and 1dxy. Thus, the tetranuclear clusters can be viewed as formally 8-valence electron systems, which gives a better understanding of the stable core structures. The formation of different types of cuprophilic interaction in d10-d10 Cu-Cu structures can be used to generate strongly bound closed-shell interactions in lighter counterparts from the coinage metal group, similarly to gold-gold compounds. We expect that this analysis can be extended to linear and polymeric d10-d10 Cu-Cu arrays in order to gain a deeper understanding of the closed-shell bonding situation.

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