Structural, electronic and magnetic properties of copper(I) cubic clusters

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Abstract
We report the molecular and electronic structure, and the calculated electronic excitation energies, using the time dependent density functional methodologies (TD-DFT), and the induced magnetic field (B_i) of a series of Cu(I) dithiolato and diselenolato species of formula $[Cu_8(L)_6]$. They are composed by eight copper atoms forming a Cu_8 cube and six bidentate ligands (L), where twelve chalcogen atoms (Q) bridging the edges of the copper cube, in such a way that chalcogen atoms describe an icosahedron, enclosing a cubic $[Cu8(\mu-Q_{12})]^{4-}$ core of T_h symmetry. The Q...Q bite distance is similar in all clusters, without being influenced by the Cu-Cu distance, suggesting the existence of metallophilic interactions that stabilize the cluster structure. Despite of the structural similarities, the electronic structure of these clusters present some differences which are magnified on their optical properties. Excitation energies and their composition depend on the nature of each different ligand in these clusters, according to $CT_{\lambda(M)}$ index to determine the ligand to metal (LM) or metal to ligand charge transfer (MLCT) character of each calculated electronic transition. The magnetic properties calculations show the importance to separate the magnetic response into their individual components (B_i with i = x, y, z, iso), and diamagnetic and paramagnetic contributions to understand the differences according to the type of ligand on the cluster structure.

Author keywords
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