Gold-Thiolate Clusters: A Relativistic Density Functional Study of the Model Species $Au_{13}(SR)_n$, R = H, CH_3, n = 4, 6, 8

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The binding of sulfanyl and alkylsulfanyl model ligands to gold clusters was studied for the case of $Au_{13}(SR)_n$ with R = H, CH_3 and $n = 4, 6, 8$. Accurate all-electron electronic structure calculations and geometry optimizations of these gold-thiolate clusters have been performed with a scalar relativistic Kohn-Sham procedure as implemented in the density functional program PARAGAUSS. In all structures obtained, bridge coordination was preferred for both types of ligands; no higher coordinated sites where occupied. While in many cases ligand decoration did not change the overall structure of the Au_{13} core, also more open structures with Au-Au distances elongated beyond the bulk value have been obtained. The effects due to increasing ligand decoration were small: a small decrease of the binding energy per ligand does not exclude higher ligand coverages. The differences between the model ligands SH and SCH_3 were consistent in all cases considered: SCH_3 exhibits weaker binding and a slightly smaller charge separation between cluster core and ligand shell, which amounts up to about 1.5 *e* for 8 ligands. Overall, the Au_{13} core of the clusters was found to be quite flexible. This can be rationalized by the fact that the calculated binding energy per ligand is comparable or even exceeds the binding energy per atom in Au_{13}.

Key words: Gold Clusters, Gold-Thiolate Bonding, Relativistic Density Functional Calculations