Research paper

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A comparative DFT study of interactions of Au and small gold clusters Au_n (n=2−4) with CH_3S and CH_2 radicals

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Abstract

We compare DFT binding energies (BEs) of Au and small gold clusters interacting with CH_3S and CH_2 ligands (Au_n−L complexes, n=1−4). The spin state and the binding mechanism in Au_n−L varies with the participation of singly occupied non−bonding orbitals or doubly occupied lone-pair orbitals of a ligand and on the number of atoms (even or odd) of Au_n. The highest BE, 354 kJ/mol, exhibits the Au_3−CH_2 complex with the covalent bond in which participate two singly occupied orbitals of the triplet state of CH_2. With CH_3S the highest BE (277 kJ/mol) is calculated for Au_3−SCH_3.with the single Au−S bond.

Keywords: gold clusters, methylene, methylthiolate, binding energy, open shell complexes, thermochemistry, DFT, CCSD(T)

1. INTRODUCTION

The methylthio radical CH_3S interacting with a metallic atom is the smallest species which may serve as a model for understanding the binding characteristics in the important class of species, Self-Assembled Monolayers (SAMs), created most frequently on the gold surfaces. Most important SAMs, based on the family of thiolate containing ligands[1–4] are considered in material science, catalysis and nanotechnologies. Since both CH_3S and the Au atom are doublets in their ground state (X^2E and ^2S, respectively), their interaction leads to either closed shell singlet or to the triplet state product[5]. The structure and stability of the closed shell Au−SCH_3 complex ($^1A'$, assuming simplified C_{3v} structure of CH_3S) is determined by quite strong Au−S covalent bond