# Mono- and Biligand Silver Clusters with Cholesterol and Thiocholesterol: the DFT study.

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Hybrid nanosystems based on stabilised silver nanoparticles attract the attention of researchers due to their unique physicochemical properties and a wide range of practical applications including biomedicine. Atoms and small clusters obtained as a beam using thermal evaporation of bulk metal under high vacuum conditions and followed by condensation on cooled support surfaces of different preparative cryostats possess a high chemical reactivity as compared to that of bulk metals. Silver nanoparticles with size of 2-3 nm can interact with cholesteric molecules forming hybrid linear aggregates (10 μ) which possess plasmonic collective absorbtion in the visible range of wavelengths [1]. In recent years stabilised silver nanoparticles have been actively used as drug carriers for transport delivery. Cholesterol and it's derivatives are natural biocompatible biomolecules with good cell penetration. So the practical interest to these systems stimulates the need for theoretical modeling developing primarily with modern quantum-chemical calculations.

This work is devoted to experimental studies and DFT calculations of the silver cluster ($Ag_{13}$) and it's complexes with O-containing cholesterol ligand (Ch) and S-containing thiocholesterol (TCh) ligand. TEM experimental data for Ag-Ch and Ag-TCh systems showed the formation of silver nanoclusters with sizes of (5.5±0.5)nm and (2.7±0.5)nm [1]. Supramolecular organisation of the systems due to donor-acceptor or electrostatic interactions with cholesteric ligands led to the formation of elongated helix aggregates with plasmonic absorbtion in visible and near-IR spectral regions (450 nm and 470 nm accordingly). Using the DFT/B3LYP5 method the structures of biligand complexes of $Ag_{13}$ silver cluster with cholesteric ligands were modeled and compared with the structure of monoligand complexes. Thus the energies of the model reactions of monoligand complex formation were -19.9 kcal/mol ($Ag_{13}$-TCh) and -3.5 kcal/mol ($Ag_{13}$-Ch) [2]. The formation energies of the bigand complexes were -21.1 kcal/mol ($Ag_{13}$-$(TCh)_2$) and -6.9 kcal/mol ($Ag_{13}$-$(Ch)_2$) [3]. O- and S-containing ligands were coordinated by vertices on different sides of the $Ag_{13}$ icosahedron. So a tendency of the $Ag_{13}$ metal cluster to attach more ligands was found out. It can be assumed that the system retains the tendency of further aggregation with the attaching of the additional ligand molecules [3].

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