

Electronic and Geometric Structure of the Cluster Compound $\text{Au}_{55}[\text{P}(\text{C}_6\text{H}_5)_3]_{12}\text{Cl}_6$. A Computational Study

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Z. Naturforsch. **2009**, *64b*, 1246–1258; received September 13, 2009

Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

Relativistic density functional calculations have been carried out on the model cluster $\text{Au}_{55}(\text{PH}_3)_{12}\text{Cl}_6$ assuming a cuboctahedral or an icosahedral Au_{55} metal core to model the experimentally suggested cluster compound assigned as $\text{Au}_{55}[\text{P}(\text{C}_6\text{H}_5)_3]_{12}\text{Cl}_6$. Besides the overall shape of the metal core, the study focused on the unresolved issue at which sites the chlorine ligands are attached. The calculations reproduce characteristic interatomic distances within ~ 2 pm, with the exception of the Au–Cl bonds. Chlorine ligands were calculated to prefer higher coordinated sites whereas the previously postulated on-top coordination at the center of the Au (100) facets of a cuboctahedron was found to be unstable. In fact, the present model results suggest an ensemble of several higher coordinated sites. The often assumed cuboctahedral shape of the metal cluster core was determined to be slightly less stable than an approximately icosahedral shape. The calculations allow a rationalization of the difficulties faced in experiments that attempted to discriminate cluster isomers.

Key words: DFT Calculations, Au_{55} , Cluster Compound, Metal Ligand Interaction