Tangential Ligand-Induced Strain in Icosahedral Au$_{13}$

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Metal nanoclusters[1] (and gold nanoclusters in particular[2]) can exhibit structures that differ significantly from that corresponding to the bulk, ones that depend strongly on cluster size. Detailed knowledge of these structures is crucial for understanding and predicting nanocluster properties, including chemical, electrical, magnetic, and optical ones. The experimental determination of atomistic structural information is a very difficult task: analyses by imaging or scattering methods are presently limited by insufficient spatial resolution or by the coherent scattering size of these techniques. As a result, most structural determinations proceed indirectly by comparing experimentally accessible properties (e.g., ion mobility, photoemission spectra, polarizability, optical absorption, etc.) with those computed theoretically for candidate structures.

A more direct approach to the determination of nanocluster structure is afforded by the extended X-ray absorption fine structure (EXAFS) technique.[3,4] By careful analysis of oscillations on the high photon energy side of the X-ray absorption edge in sufficiently monodisperse clusters, one can extract accurate information as to the identity, average distance, and coordination of the neighbors to the X-ray absorbing atom. Even so, EXAFS only yields ensemble-averaged information. If applied to size-controlled nanoclusters, however, it yields a more detailed understanding of the structure, size, and shape of the nanoclusters because it drastically reduces the number of candidate structures that are a priori potentially consistent with it. A recent combination of EXAFS and atom counting methods of transmission electron microscopy (TEM) on such specially synthesized nanoclusters (Au$_{13}$[PPh$_3$]$_4$[S(CH$_2$)$_{11}$-CH$_3$]$_4$) has found them to be highly monodisperse, with their overall structure possessing, on average, 13 gold atoms, with Au—Au coordination number of 6.7 ± 0.7, an average a Au—Au bond length of 2.85 ± 0.02 Å, and an average Au—ligand distance of 2.324 ± 0.007 Å.[5] The presence of eight ligands per cluster was deduced from X-ray photoelectron spectroscopy data.[6]

While the combination of the experimental results points toward an icosahedral shape of the Au$_{13}$ core, theoretical verification and a detailed interpretation of such a model was lacking. In particular, two central questions—ligand placement and anomalously high Au—Au bond length disorder—were left unanswered by the experimental results. First, EXAFS is not capable of discriminating between Au—S and Au—P neighbors, treating them cumulatively as Au—L (L = S/P) pairs and obtaining the *overall* Au—L coordination number as the total number of Au—S and Au—P bonds divided by the total number of Au atoms. However, the phosphines and the thiolates may have distinctly different bonding motifs: on-top for phosphines[7] and bridge sites for thiolates.[8] Thus, the preferred ligand placement remains ambiguous. Second, the experimental distribution of Au—Au bond lengths was $\sigma^2 = 0.017 \pm 0.005$ Å^2, which

is much larger than that in bulk gold (0.008 Å^2) at the same temperature (300 K).[5] Such enhanced σ^2 must be configurational in nature because the temperature-dependent, dynamic component in nanoparticles has previously exhibited only weak, if any, size dependence.[4] However, neither EXAFS nor TEM provide enough information to uncover its origin.

The gaps left in our understanding of the three-dimensional structure of ligand-stabilized gold nanoparticles are filled here using first principles calculations based on density functional theory (DFT)[9] that provide a consistent interpretation of the experiments. In this Communication, we use the EXAFS and TEM results as a starting point for a theoretical analysis of the mixed-ligand Au$_{13}$ nanocluster, Au$_{13}$[PPh$_3$]$_4$[S(CH$_2$)$_{11}$CH$_3$]$_4$.

All calculations were performed using the GAUSSIAN03 code[10] using the local density approximation for the exchange correlation. The LANL2DZ basis set was used for Au, and the 6-31G(d,p) basis set was used for all other elements. The robustness of the results was ascertained via comparison of select results to those obtained with a hybrid functional and with larger basis sets. As a further test, for the Au dimer, we found a bond length of 2.48 Å, in good agreement with previous theoretical studies[11,12] and with experiment (2.47 Å).[13]

For bare Au$_{13}$ nanoclusters, many structures, including icosahedral,[14] cuboctahedral,[15] biplanar,[16] and amorphous[17] ones, have been predicted theoretically as comprising the lowest energy configuration. Both ordered and disordered structures were predicted theoretically for ligated Au$_{38}$ structures,[18−20] and experimental verification was limited to scattering methods (e.g., X-ray diffraction) which are less than ideal for clusters of this size. This may reflect the existence of several energetically close isomers.[20] Nevertheless, the high order determined from the EXAFS data allowed us to focus on high-symmetry metal cores. We hypothesized that all four phosphine ligands and two of the thiolates are bonded on-top a Au atom and that the two other thiolates bridge two Au atoms, leaving two Au atoms uncapped. This model is supported by the experimentally observed Au—L coordination number, $N_{Au-L} = 0.76 \pm 0.05$. This coordination number is consistent with 9−10 of the surface atoms being bonded to a ligand.[5] However, it is inconsistent with alternative models where all eight ligands are bound to on-top sites ($N_{Au-L} = 0.615$) or all four thiolates are bound to bridge sites ($N_{Au-L} = 0.92$). In the calculations, the long-chain thiolates were replaced with methyl—thiol groups and the triphenylphosphines were replaced by phosphine groups for numerical expediency.

While an icosahedral metallic core is potentially consistent with the experimental data, we also tested the possibility of a cuboctahedral core. Starting from a ligand configuration as explained above, upon relaxation, all S atoms reverted to a bridging configuration, increasing the Au—L coordination number to 0.92, in contrast with the EXAFS experiment. In addition, the average Au—Au bond

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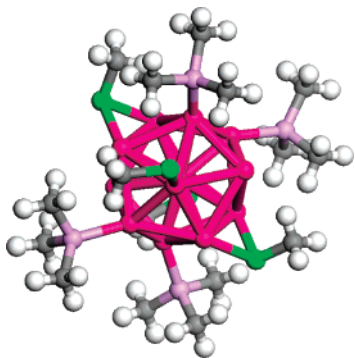
Figure 1. Optimized structure of the icosahedral Au_{13} cluster: red = Au; green = S; purple = P; gray = C; white = H.

length (2.92 Å, in agreement with previous work[21,22]) and its standard deviation (0.06 Å^2) were both significantly larger than in experiment. Thus, we focus on the icosahedral core.

Calculations of different ligand structures relaxed from an initial I_h Au core geometry establish that the symmetric bonded-ligand configuration, shown in Figure 1, is energetically preferable. Here, the results of the calculations were found to be in good *quantitative* agreement with the EXAFS data: The mixed on-top and bridge thiol geometry was maintained, the average Au−Au bond length was 2.88 Å with a standard deviation of $\sigma^2 = 0.018$ Å^2, the coordination number, N_{Au-L}, was 0.77, and the average Au−ligand distance was 2.35 Å, that is, in good agreement with all experimental results.[5,23]

In the relaxed, bare icosahedron, $R(Au-Au)_{rad} = 2.73$ Å and $R(Au-Au)_{tan} = 2.87$ Å with (as in the ideal regular icosahedron) $\sigma^2_{rad} = \sigma^2_{tan} = 0$, yielding an overall $\sigma^2 = 0.004$ Å^2. For the ligated cluster, variation in the radial distances from the central atom to the other Au atoms is very small: $R(Au-Au)_{rad} = 2.78$ Å with $\sigma^2_{rad} = 0.005$ Å^2. However, the in-shell tangential Au−Au bond lengths exhibit a much greater dispersion: $R(Au-Au)_{tan} = 2.92$ Å with $\sigma^2_{tan} = 0.017$ Å^2, with the smallest distance found between two thiol-ligated Au atoms and the largest between one thiol-ligated and one free Au atom. This is consistent with the strong covalent interaction expected between the S and Au atoms.[24,25]

The above results clearly reveal that the tangential strain induced by the ligands is much larger than the radial one. Both radial and tangential bond lengths in the ligated cluster are larger by ∼1.8% with respect to the bare one, but the induced dispersion in tangential bond lengths is much larger than in the radial ones. These findings can be interpreted via a combination of the asymmetry of the effective pair potential and the non-close-packed structure of the icosahedron. The ligands do not disorder the relatively stiff radial bonds, but do disorder atoms within the shell. This interpretation is supported by additional experiments:[5] clusters stabilized by four phosphines, two thiols, and two chlorines are structurally very similar to those simulated in this work (i.e., icosahedral), with similar disorder parameters. This can be understood within the framework of both the strong radial stability of these clusters, where replacement of two thiols by two chlorines should mostly affect the tangential rearrangement, and their icosahedral framework, where in-shell bonds are longer and weaker than radial bonds. Our results suggest that it is the weakness of the in-shell Au−Au bonds, and thus lower energy penalty compared to the strong radial Au−

Au bonds, that relieves otherwise strong stresses due to the asymmetry in the nature and bonding sites of thiolate and phosphine ligands. On the basis of these arguments, we expect distorted, tangentially strained cluster shapes (as opposed to idealized, regular polyhedral ones) to be generally typical of nanoscale, ligand-protected clusters.

In conclusion, a quantitative comparison of first principles calculations and EXAFS/TEM measurements provides strong evidence that the Au_{13} nanocrystals are stabilized in a slightly distorted icosahedral structure by on-top phosphine ligands and a combination of on-top and bridging thiol ligands. Importantly, the ligands change the icosahedral strain (i.e., the radial−tangential bond length ratio) significantly, with the tangential bonds within the Au core exhibiting much more disorder than the radial ones.

Supporting Information Available: Complete ref 10. This material is available free of charge via the Internet at http://pubs.acs.org.

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