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Geometry and Charge State of Mixed-Ligand Au₁₃ Nanoclusters

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Abstract. The integration of synthetic, experimental and theoretical tools into a self-consistent data analysis methodology allowed us to develop unique new levels of detail in nanoparticle characterization. We describe our methods using an example of Au₁₃ monolayer-protected clusters (MPCs), synthesized by ligand exchange methods. The combination of atom counting methods of scanning transmission electron microscopy and Au L3-edge EXAFS allowed us to characterize these clusters as icosahedral, with surface strain reduced from 5% (as in ideal, regular icosahedra) to 3%, due to the interaction with ligands. Charge transfer from Au to the thiol and phosphine ligands was evidenced by S and P K-edge XANES. A comparison of total energies of bare clusters of different geometries was performed by equivalent crystal theory calculations.

Keywords: nanoclusters, electron microscopy, total energy calculations, EXAFS, XANES

PACS: 61.46.Df; 61.50.Ah, 07.79.Cz, 61.10.Ht

INTRODUCTION

Although multiple-scattering (MS) EXAFS allows determination of the bonding geometry in the nanoscale, it provides *ensemble-average* information. On the other hand, transmission electron microscopy (TEM) probes the structure and chemistry of *individual* nanoparticles. Using high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) or “Z-contrast” imaging, we correlated the absolute image intensity to the scattering cross-section, so that the number of atoms can be

directly counted (Fig.1). Furthermore, high resolution (HR) TEM provides direct visualization of nanoparticle shape and structure. Finally, our synthesis ensures narrow size distribution of the nanoparticles – a prerequisite for the integrated MS EXAFS, [1,2] Z-contrast STEM and HRTEM methods, as well as charge transfer studies by XANES. We tested this integrated approach by applying it to mixed-ligand gold nanoclusters (Au₁₃[PPh₃]₄[S(CH₂)₁₁CH₃]₂Cl₂ and Au₁₃[PPh₃]₄[S(CH₂)₁₁CH₃]₄) that were characterized by narrow size distribution as evidenced by the atom counting HAADF-STEM.[3,4]

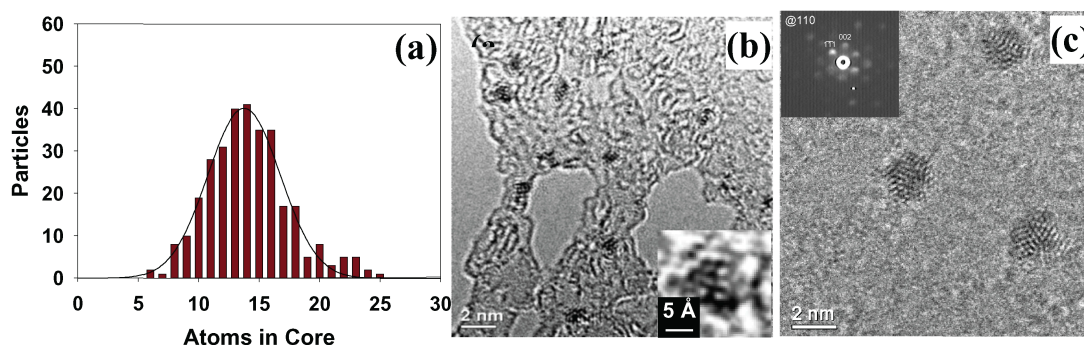


FIGURE 1. (a) Histogram of quantitative STEM results of Au₁₃ clusters. N=313. (b) High-resolution electron micrograph of Au₁₃[PPh₃]₄[S(CH₂)₁₁CH₃]₄. The inset shows a filtered image of a single cluster. (c) Larger thiolate-protected MPCs with cubic packing. The inset shows an indexed μ -diffraction image taken from a single particle with a 2-nm diameter.

EXAFS ANALYSIS

For the mixed-ligand clusters, we obtained that they were characterized by quasi-spherical Au₁₃ cores. The standard deviation in cluster core atom counts in Fig. 1a is ± 3.4 atoms. The uncertainty estimated for the HAADF-STEM experimental technique was ± 3 atoms suggesting an actual deviation in the core stoichiometry of ± 1 Au atom. This monodispersity provides rigorous constraints on the interpretation of the EXAFS data. The coordination numbers of the first three Au-Au coordination shells, as well as those of multiple scatterings contributions, were obtained from the best MS fits to the EXAFS data (Fig. 2).

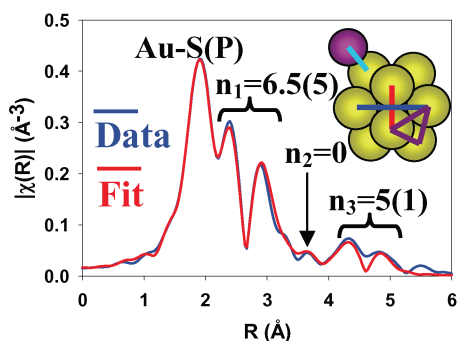


FIGURE 2. Data and FEFF6 fit of Au₁₃ mixed ligand cluster. The arrow indicates the location of a second nearest neighbor in a closed packed (fcc) structure. The inset shows the photoelectron paths used in the fits.

The results for the Au₁₃ clusters unambiguously confirmed an icosahedral model. Fig. 3 shows that this model is preferred to the alternative closed packed regular 13 atom cluster (cuboctahedral), given the agreement of the 1NN, 2NN, and 3NN experimental coordination numbers with the former model.

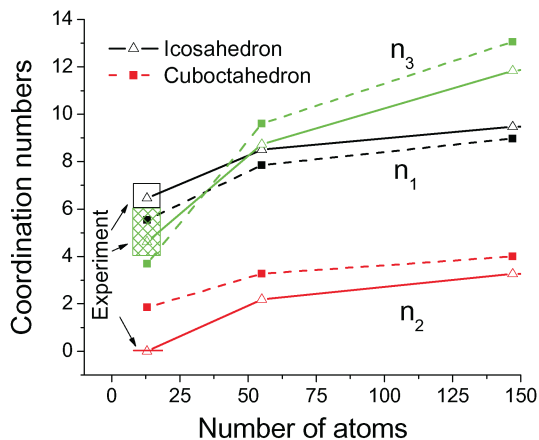


FIGURE 3. Model calculations of the 1NN, 2NN and 3NN coordination numbers for the icosahedral and cuboctahedral clusters.

These results were independently supported by our HRTEM and electron microdiffraction measurements (Fig. 1 b,c) which provided the same structural motifs, albeit with less accurate structural detail. In icosahedral Au₁₃ clusters, the concurrent refinement of the single scattering (SS) and MS contributions allowed us to measure local strain (due to the 1NN bonds within the shell being longer than the 1NN bonds between the layers), and compare it with that of an ideal icosahedron (5%). We obtained that the actual strain is ca. 3%. Such strain relaxation can be correlated with the presence of the ligands on the cluster surface.

The combination of HRTEM, HAADF-STEM, and MS-EXAFS which included Au-S contributions, allowed us to obtain the coordination number (0.72 ± 0.05) of ligands in mixed ligand clusters and deduce their binding geometries (Fig. 4). For the Au₁₃[PPh₃]₄[S(CH₂)₁₁CH₃]₄ cluster, it is consistent with a model where two thiolates are bound at on-top sites, two thiolates at bridge sites, and four phosphines at on-top sites. Such a bonding motif is strikingly different from that in the two-dimensional Au(111) thiol self-assembled monolayers where the thiols are thought to be bound at the 3-fold sites.

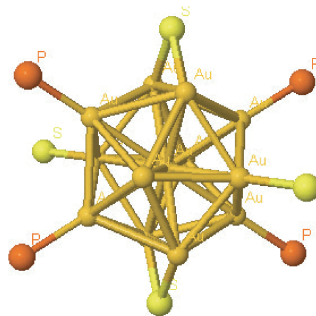


FIGURE 4. One possible ligand arrangement (yellow: thiols, orange: phosphines) in Au₁₃[PPh₃]₄[S(CH₂)₁₁CH₃]₄ clusters, as suggested by our multi-technique analysis results.

XANES ANALYSIS

Formation of Au-S and Au-P bonds was separately established by S and P K-edge XANES, respectively, at the X15B beamline at the NSLS. Transition states “1” and “3” of P in pure PPh₃ and “2” of sulfur in pure dodecanethiol (Fig. 4) are modified in their complexes with Au nanoparticles. In agreement with previous studies of Au-thiol complexes,^[5] we attribute the peak “2” in S XANES of pure thiols to the S 1s \rightarrow S-C transitions. Similarly, we interpret the peak “3” in S XANES of Au₁₃[PPh₃]₄[S(CH₂)₁₁CH₃]₂Cl₂ nanoparticles as due to the same transition but shifted

by 1.0 eV to higher energy due to the formation of the Au-S bond (peak “1”) and the concomitant charge transfer from Au to S. Charge transfer between Au and P in two different mixed ligand clusters: $\text{Au}_{13}[\text{PPh}_3]_4[\text{S}(\text{CH}_2)_{11}\text{CH}_3]_2\text{Cl}_2$ and $\text{Au}_{13}[\text{PPh}_3]_4[\text{S}(\text{CH}_2)_{11}\text{CH}_3]_4$ is similar, as probed by P K-edge XANES. However, the XANES in the two clusters

differ from that of pure PPh_3 : the transition energy of P $1s \rightarrow \text{P-C}$ molecular orbitals in the nanoclusters shifts by 0.7 eV to higher energy relative to the PPh_3 reference. Such a shift is consistent with phosphines acting as acceptors of d-electrons from Au into P-C and P 3d orbitals.

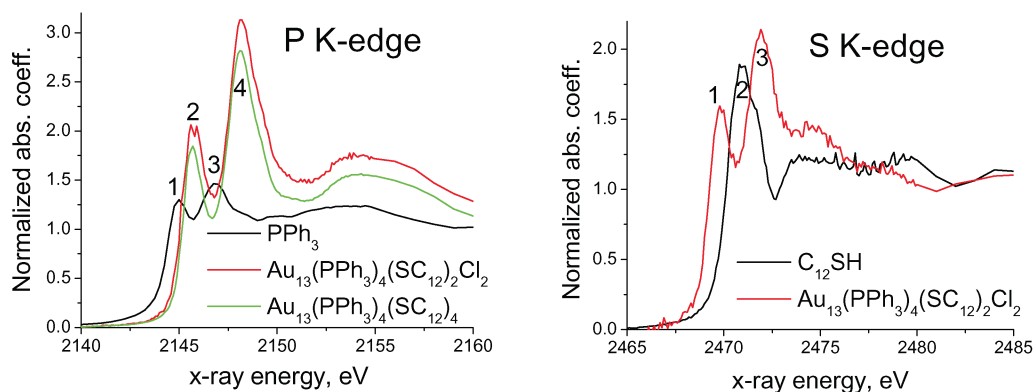


FIGURE 5. (a) P K-edge and (b) S K-edge XANES data in mixed ligand Au_{13} clusters and standard compounds.

CLUSTER ENERGY CALCULATIONS

To study the energetics of bare and ligand-stabilized clusters, we adapted an Equivalent Crystal Theory (ECT) method, previously used to study bulk defects and surface properties.^[6] Surface energy and vacancy formation energy in bulk Au were calculated by the ECT as a test of its accuracy, and discrepancy from the DFT calculations was obtained to be less than 15% (Table 1). The total energy of the Au clusters was calculated by ECT by treating each atom as embedded in the nanoparticle and calculating the lattice parameter of an “equivalent crystal” – a perfect crystal that has the same electron density as the cluster. Utilizing a universal equation that relates cohesive energy of most crystals to its lattice parameter, we calculated the total cohesive energy and, therefore, the total energy of the nanoclusters. Such calculations are fast (a few seconds per cluster) and can be done for large sizes, larger than 50 atoms, i.e., at those sizes which cannot be accessed by ab initio calculations.

In summary, our integrated approach allowed us to achieve new levels of detail about the 3D structure of ligand-stabilized nanoparticles.

TABLE 1. Total energy calculations (in eV) for 13-atom cuboctahedral Au clusters: perfect (P) and with atoms removed from center (C) and surface (S)

Cluster	DFT	ECT	Error (%)
Au_{13} (P)	-23.4	-26.1	12
Au_{12} (C)	-20.6	-19.3	-7
Au_{12} (S)	-21.4	-20.1	-6

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