Structural Investigation of the Ligand Exchange Reaction with Rigid Dithiol on Doped (Pt, Pd) Au_{25} Clusters

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ABSTRACT: The ligand exchange reaction between heteroatom doped (Pd, Pt) Au_{25}(2-PET)_{18} (2-PET = 2-phenylethylthiolate) clusters and enantiopure 1,1′-binaphthyl-2,2′-dithiol (BINAS) was monitored in situ using chiral high-performance liquid chromatography (HPLC). During the ligand exchange reactions, replacement of two protecting thiols (2-PET) with one new entering BINAS ligand on the cluster surface occurs. The rigid dithiol BINAS adsorbs in a specific mode that bridges the apex and one core site of two adjacent S(R)−Au−S(R)−Au−S(R) units. This is the most favorable binding mode and theoretically preserves the original structure. A kinetic investigation on these in situ ligand exchange reactions revealed a decrease in reactivity after multiple exchange. A comparison of relative rate constants demonstrates a similar exchange rate toward BINAS for both (Pd, Pt) systems. The possible structural deformation after incorporation of BinAS was investigated by X-ray absorption spectroscopy (XAS) at the S K-edge and Au L3-edge. First, a thorough assignment of all sulfur contributions to the XANES spectrum was performed, distinguishing for the unaltered Au_{25} structure, except for some slight influence on the Au−S bonds. Additionally, an intact staple motif was confirmed after incorporation of rigid dithiol BINAS by both XANES and EXAFS. This finding agrees with a BINAS interstaple binding mode predicted by calculation, which does not perturb the cluster structure.

INTRODUCTION

Thiolate protected gold nanoclusters are a promising group of atomically precise metal nanostructures featuring unique size-dependent physical, chemical, and optical properties. Their structure is characterized by a gold core stabilized by a ligand shell. In the case of thiolated ligands, a peculiar binding mode, SR−(Au−SR)_{n} (n = 1, 2), called the staple motif, is observed in many clusters. Highly stable clusters are formed when particular combinations of Au atoms and thiolates are achieved like in the case of Au_{25}(SR)_{18}, Au_{38}(SR)_{24}, Au_{40}(SR)_{24}, and Au_{40}(SR)_{30}. Further functionalization can be easily performed both on the metallic core, influencing physical properties of the cluster, and on the organic protecting ligand shell, modulating the (bio)chemical properties.

Heteroatom doping of the metal core is used for modifying the cluster properties. Metals such as Pd, Pt, Ag, or Cu have been demonstrated to influence the stability, catalytic activity, and electronic and physical properties of the clusters. Many examples of heteroatom doping were reported for Au_{25}(SR)_{18}. Incorporation of the different metal atoms can be achieved by two-metal direct synthesis or by mixing the already formed cluster with a heterometal complex/cluster. These doping methods often produce a multidoped product, due to the difficulty to control the amount of doping agents. Exceptions of this trend are found in Pt and Pd doping, where only one heterometal substitutes the central gold in the Au_{25} cluster. A similar situation was found for Au_{38} and Pd doping, where Pd_{2}Au_{36} and Pd_{2}Au_{37} doped clusters were reported. Doping Au_{25} with Pd and Pt atoms has resulted in an increased catalytic activity toward alcohol and styrene oxidation.

Engineering the ligand shell through postsynthetic ligand exchange represents an easy way to introduce functionalities onto clusters and tune their chemical behavior. The ligand exchange reaction involves the replacement on the Au_{25}(SR)_{m} cluster surface of one of the protecting thiols (ligand) with a new entering ligand SR. Therefore, the ligand-exchange
reaction is an extremely useful method of precise functionalization that enables the design of unique properties.

Some of us have studied ligand exchange reactions using the chiral dithiol BINAS ([1,1'-binaphthalene]-2,2'-dithiol, see Figure 1).\(^{30,31}\) When the BINAS molecule binds to Au\(_{38}\)(SR)\(_{24}\) racemization between the two enantiomeric forms of Au\(_{38}\) becomes less favorable.\(^{32,33}\) Exchange on Au\(_{38}\)(SR)\(_{18}\) instead induced chirality on the cluster, allowing the separation of the different exchange products by chiral HPLC.\(^{34}\) Due to its conformation and two thiolate functionalities, BINAS is able to strongly bind to clusters like Au\(_{38}\), Au\(_{40}\), and Au\(_{42}\).\(^{31}\) Calculations point toward an interstaple binding mode, which preserves both the structure of BINAS as well as the Au\(_{38}\) cluster.\(^{35}\) However, no experimental structural analysis was yet performed on the incorporation of bulky ligands in the thiolate protecting shell. X-ray absorption spectroscopy (XAS) has been a very useful technique over the last years for obtaining detailed information on the local structure (coordination number, oxidation state, bond distances) at the molecular level. Many studies have been reported in the literature on gold clusters of different sizes,\(^{36,37}\) in different states (solid or liquid),\(^{38}\) during different stages of catalysis,\(^{39}\) and at different temperatures.\(^{40}\) XAS also played a huge role in the analysis of the doped Au-cluster by revealing the exact location of dopant atoms.\(^{30,32}\) On the contrary, only few XAS studies focus on understanding the protecting ligand shell of Au clusters. For example, Negishi et al. reported the EXAFS characterization of selenite-protected Au\(_{38}\) and telluriate-protected Au\(_{38}\).\(^{41-43}\) Also, for sulfur edge XAS, only a few examples are reported in the literature focusing mainly on either the variation of ligand length or the variation of cluster size.\(^{44,45}\) However, no investigation has been performed on the mixed ligand shell of a gold cluster by this technique.

In this study, we present an investigation on the ligand exchange with BINAS on Au\(_{25}\) and doped (Pd, Pt) Au\(_{25}\). The kinetics can be well described by a consecutive pseudo-first-order model. The influence of the BINAS and the doping on the structure was studied by Au-EXAFS and S-XANES. This analysis represents the first example of a S K-edge XANES and Au L3-edge EXAFS study on thiolate protected gold nano-clusters that focuses on ligand exchange reaction at a molecular level.

### Experimental Section

**Synthesis of Au\(_{25}\)(2-PET)\(_{18}\), PdAu\(_{24}\)(2-PET)\(_{18}\), and PtAu\(_{24}\)(2-PET)\(_{18}\).** All chemicals were used as received without further purification. Nanopure water (18.2 M\(\Omega\)) was used in all experiments that involve water. BINAS was synthesized from BINOL as reported earlier.\(^{46}\) Synthesis of the clusters was performed as previously reported.\(^{45,47}\)

**In Situ Ligand Exchange Reactions.** Ligand exchange reactions were performed and followed in situ similar as described in previous work.\(^{46}\) A solution of cluster (0.5 mg/mL, toluene) with a 100-fold molar excess of R-BINAS was prepared and injected (7 \(\mu\)L) in the HPLC system, using a chiral CHIRALPAKIA column, every 3 h. Similar to the separation method proposed by Negishi et al.,\(^{30}\) a step-gradient mobile phase composition was applied. This step-gradient method allows the clusters to first adsorb onto the stationary phase, due to precipitation from MeOH. After substitution of the solvent to a mixture MeOH/THF, the clusters sequentially elute into the mobile phase. MALDI analysis was taken after 72 h to confirm the ligand exchange reaction occurred (Figure S1).

**X-ray Absorption Spectroscopy.** XAFS measurements were conducted at the XAS beamline at Elettra-Sincrotrone Trieste (Italy).\(^{48}\) EXAFS and XANES were performed at different energies (S K-edge, 2.4720 keV; Au L3-edge, 11.919 keV) on three groups of metal cluster samples: monometallic Au\(_{25}\)(2-PET)\(_{18}\), bimetallic PdAu\(_{24}\)(2-PET)\(_{18}\), and PtAu\(_{24}\)(2-PET)\(_{18}\) clusters. A Si(111) double-crystal monochromator was used to monochromatize the white beam. The photon flux was about 10\(^9\) photons/s. Experiments were performed in both fluorescence and transmission mode using a silicon drift detector and ionization chambers as detectors (Oxford Instruments), respectively. In order to achieve the best signal-to-noise ratio, a high concentrated dichloromethane solution of clusters was drop-cast onto sulfur-free polyimide (Kapton) tape. S K-edge measurements were performed in a special cell for fluorescence measurements under high vacuum. On the other hand, measurements at the Au L3-edge were done for the full range of EXAFS in transmission mode, using another cell (beamline) that allowed us to work at low temperatures (80 K) by a liquid nitrogen cooling system and also under a vacuum.

The data analysis was performed according to standard procedures.\(^{49}\) XAS spectra were normalized, after background subtraction, to the averaged absorption coefficient at high energy. The EXAFS signals were extracted from the spectra by using the Athena software,\(^{50}\) removing the background and normalizing the magnitude of the oscillations to the edge jump. The corresponding pseudoradial distribution function around the photoabsorbing atom has been obtained by performing the Fourier transform (FT) of the EXAFS signals (filtered in the interval 2.5 Å\(^{-1}\) \(\leq k \leq 11.5\) Å\(^{-1}\)). The fitting to the experimental data was carried out in both R-space and q-space, by using the program Artemis, also within the IFEFFIT package.\(^{50}\)

**Characterization.** HPLC separation was performed on a JASCO 20XX HPLC system equipped with a Daicel CHIRALPAKIA column (5 μm, 250 mm \(\times\) 4.6 mm), and the eluting analytes were detected with a JASCO 207þ plus UV detector (420 nm). The analytes were dissolved in toluene and eluted with MeOH/tetrahydrofuran (100:0; 70:30) at a flow rate of 0.5 mL min\(^{-1}\). Mass spectra were recorded on a Bruker...
Autoflex mass spectrometer equipped with a nitrogen laser at near-threshold laser intensity in positive linear mode using DCTB as the matrix.

## RESULTS AND DISCUSSION

### Ligand Exchange Reaction Kinetics

The Au$_{25}$(SR)$_{18}$ is a highly symmetric cluster; it is characterized by an icosahedral Au$_{13}$ core surrounded by six $S_{\text{core}}$(R)$\equiv$Au$\equiv$S$_{\text{spec}}$(R)$\equiv$Au$\equiv$S$_{\text{core}}$(R) motifs (also known as long staples). Figure 1 shows the two unique thiolate binding sites on the long staples; for simplicity, they will be called $S_{\text{core}}$ and $S_{\text{spec}}$. The differentiation of these binding sites arises from the symmetry of the cluster and as observed by several techniques (e.g., NMR). When the central gold atom is replaced with a Pd or Pt (vide supra), no significant changes are observed in the structure compared to Au$_{25}$(SR)$_{18}$. A BINAS ligand exchange was performed on all three clusters (Au$_{25}$(SR)$_{18}$, PdAu$_{24}$(SR)$_{18}$, PtAu$_{24}$(SR)$_{18}$) at different reaction times to allow the formation of similar exchanged products. The reaction outputs where then injected in chiral HPLC (Figure 2A); the chromatogram shows that for the doped clusters a better separation of the different exchanged products was achieved. For this reason, in this study, we focused our attention on the Pd and Pt doped Au$_{25}$ clusters and their relative BINAS exchange products. Figure 2B shows the HPLC chromatogram with the different peaks related to the exchange reaction where two 2-PET ligands are replaced by one BINAS ligand. From the chromatogram, the consumption of the starting cluster (PdAu$_{24}$(2-PET)$_{18}$) and the formation of the exchange products can be observed.

Table 1. First-Order Rate Constants (in h$^{-1}$) and Ratio of Pd/Pt Doped Au$_{25}$ Exchange$^a$

<table>
<thead>
<tr>
<th>PdAu$_{24}$</th>
<th>ratio</th>
<th>PtAu$_{24}$</th>
<th>ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>0.1662 ± 0.010</td>
<td>$k_1$</td>
<td>0.0805 ± 0.003</td>
</tr>
<tr>
<td>$k_2$</td>
<td>0.0669 ± 0.004</td>
<td>$k_2$</td>
<td>0.0430 ± 0.002</td>
</tr>
<tr>
<td>$k_3$</td>
<td>0.0390 ± 0.002</td>
<td>$k_3$</td>
<td>0.0122 ± 0.001</td>
</tr>
<tr>
<td>$k_4$</td>
<td>0.0196 ± 0.003</td>
<td>$k_4$</td>
<td>0.0147 ± 0.007</td>
</tr>
</tbody>
</table>

$^a$Errors correspond to 95% confidence intervals emerging from the least squares fit.

In this work, we present a kinetic study of BINAS exchange on PdAu$_{24}$(2-PET)$_{18}$ and PtAu$_{24}$(2-PET)$_{18}$ using chiral HPLC.
Ligand exchange reactions take place at the S atoms located at the staple (\(-S-Au-S\)) of the cluster structure. Therefore, the main bonds affected during this process are S–C and S–Au. In order to study the possible electronic and structure changes during the ligand exchange reactions, XAFS analysis at two main energy edges was performed: S K-edge and Au L3-edge XAS.

In the case of S K-edge, only the XANES region has been studied due to the presence of Au M1-edge (2.7430 keV) and Au M2-edge (2.2911 keV) absorption energies close to the S K-edge (2.4720 keV). The spectrum can overlap or affect the pre-edge region and also the post-edge oscillations, which limits the k-space (EXAFS region) spectrum until 6 Å⁻¹.

Figure 4 shows the S K-edge spectrum of the \(\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}\) cluster, which agrees with previous studies reported in the literature.\(^{44,45,56,57}\) The pre-edge feature at 2.471 keV is assigned to the Au–S bond involving both the s and p character of S. A shoulder at 2.4715 keV at the white line just after the pre-edge feature is also observed. This shoulder by deconvolution is formed by two signals that could be related to two different sulfur environments (core and apex sulfur) present in the staple motif \(S_{\text{core}}(R)-Au-S_{\text{apo}}(R)-Au-S_{\text{core}}(R)\), in agreement with previous calculations of Zhang et al.\(^{55}\) The ratio 1:2 of these two signals also suggests their assignment to \(S_{\text{apo}}\) and \(S_{\text{core}}\). The main feature at 2.474 keV corresponds to the bonding of S–C related with the thiol ligands.

The pre-edge feature for the S K-edge has been shown to be dependent on the size of the Au core. Zhang et al.\(^{55}\) showed S–Au XANES pre-edge features change depending on the cluster size \((\text{Au}_{125}, \text{Au}_{38}, \text{and} \text{Au}_{144})\). A red-shift in peak position was observed as the size increases (2.4711 keV for \(\text{Au}_{125}\), 2.4707 keV for \(\text{Au}_{38}\) and 2.4705 keV for \(\text{Au}_{144}\)) as well as an increase of the fitted S–Au relative peak intensity (0.064 for \(\text{Au}_{125}\), 0.122 for \(\text{Au}_{38}\), and 0.207 for \(\text{Au}_{144}\)). This was ascribed to the differences in size but could also be related to the electronic structure changes of the cluster.

Heteroatom doping has been shown to modify the electronic structure of the cluster structure. In the case of \(\text{Au}_{125}\), Pd or Pt doped atoms are localized on the center core; therefore, only an effect on the electronic configuration is expected to be observed.
in the Au–S bond. S K-edge spectra of the three clusters are shown in Figure 5A. The doped clusters show a clear shift to higher energies of the pre-edge features, related to the Au–S bond in comparison to the undoped Au25. This confirms the different electronic structure of the three clusters, which was demonstrated in previous theoretical (DFT calculations) and experimental work (XPS and voltammetry) by Lee et al.58 It was shown that incorporation of heteroatoms with a lower electronegativity (Pd, Pt) than gold induces an internal charge transfer. This transfer changes the electronic structure of its neighboring Au atoms and therefore influences the surrounding Au–S bonds.

To the best of our knowledge, no sulfur XAS studies have been performed on heteroatom doped thiolate protected gold clusters. Therefore, two heterodoped (Pd, Pt) Au25 clusters were analyzed and compared to monometallic Au25. Figure 5 presents the three XANES spectra. The features of the two doped systems correspond well to the reference Au25. A very clear shift toward higher energy of the prepeak, correlating to the Au–S_{pre} interaction (marked with dots) can be observed for the doped systems. Additionally, deconvolution of the XANES spectra (Figure 5B) clarified an increased intensity of the Au–S_{pre} contribution of the doped clusters. A similar shift toward higher energy is observed for the Au–S_{core} bond (Figure 5C) (marked with circles); however, in this case, a decrease of deconvoluted contribution is seen. The inset shows a small broadening of the edge of the Pt doped cluster.

The samples from the kinetics studies discussed above were collected after different times for structural XAFS analysis, in order to get insights on the structure and electronic structure changes during the ligand exchange reactions with BINAS. Figure 6 shows the spectrum at the S K-edge of the collected samples of Au25(2-PET)_{18} (Figure 6A) and PdAu24(2-PET)_{18} (Figure 6B) clusters. In both figures, the spectra of both free ligands, 2-PET and BINAS, are also shown. In the case of Au25, the peak (2.4747 keV) related with the S–C bond is shifted to lower energies (2.4745 keV) and decreased in intensity upon ligand exchange reaction after 24 h. A contrary effect is observed in the case of the doped PdAu24 samples, with a slight shift to higher energies and increase in intensity. Comparing to the reference ligand spectrum, an increasing amount of BINAS ligands in comparison with 2-PET is expected to induced a shift to higher energies as well as a broadening of the peak. These two effects are observed in both cases.

The pre-edge features of Au25 between 2.471 and 2.473 keV related to the Au–S bonds are less pronounced after 24 h of reaction, whereas no differences are observed with the doped samples under reaction.
Table 2. R-Space Analysis from EXAFS and Theoretical Fitting at the Au L3-Edge: Comparison to the Fresh PdAu24 Sample Adn after Different Times of Ligand Exchange Reaction with BINAS.

<table>
<thead>
<tr>
<th>CN (theoretical)</th>
<th>PdAu24</th>
<th>PdAu24-A</th>
<th>PdAu24-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>R (Au−M)</td>
<td>1</td>
<td>2.72 ± 0.09</td>
<td>2.72 ± 0.02</td>
</tr>
<tr>
<td>R (Au−Au)</td>
<td>1</td>
<td>3.07 ± 0.04</td>
<td>2.81 ± 0.02</td>
</tr>
<tr>
<td>R1 (Au−S)</td>
<td>1</td>
<td>2.30 ± 0.05</td>
<td>2.35 ± 0.02</td>
</tr>
<tr>
<td>R2 (Au−S)</td>
<td>2</td>
<td>2.28 ± 0.09</td>
<td>2.29 ± 0.03</td>
</tr>
<tr>
<td>R_factor</td>
<td>0.011</td>
<td>0.010</td>
<td>0.008</td>
</tr>
</tbody>
</table>

“The experimental CN (Au−Au) of samples A and B is 4.8 and 4.2, respectively; the experimental CN (Au−Pd) is 0.8.”

Variation in the S K-edge XANES spectra related to the ligand exchange reactions and cluster doping was observed for the first time by the XAFS technique. Future XAFS studies on different types of clusters will be carried out focusing on systems with different staples and different types of ligands (e.g., P−, Se−, etc.). This will bring new complementary structural information helpful to understand the ligand exchange reactions.

**Au L3-Edge EXAFS Studies.** A previous XRD study has shown how the Au25 structure remained unaltered after exchange with simple monothiols. However, rigid dithiolate ligands such as BINAS could affect strongly the staple motifs and consequently the complete Au25 structure. It has been assumed and confirmed by theoretical calculations34,35 that the structure of the cluster remains unaffected during this exchange reaction; however, experimental confirmation is still missing. Therefore, a complementary Au L3 edge EXAFS study of the ligand exchange reactions and their influence on the Au−S bond was performed.

Tsukuda et al.40 showed the importance of working at lower temperatures (for XAFS measurements), as this significantly reduces the thermal vibration of the cluster. Additionally, a reduced temperature plays an important role on the disorder of the system. This disorder or mean squared displacement (\(\sigma^2\)) can be attributed both to the distribution of bond lengths within the cluster (static disorder) and to the low coordinate bonding environment (dynamic disorder). The liquid helium temperatures (8 K) are required to be able to fit the cluster structure core related with the Au−Au bonds which are proved to be influenced by temperature. Au−S bonds are more rigid than the Au−Au bonds, and liquid nitrogen temperature (80 K) is sufficient for the measurements. We can state that the staples are significantly less responsive to the temperature change than the Au11 core, making the staples essential for the robustness of clusters. In order to increase sensitivity and observe any subtle structural changes after ligand exchange, these experiments were performed at liquid N₂ temperature and under vacuum conditions, as previously reported.35,36

EXAFS refinement of the 2-PET protected reference structures Au25(2-PET)\(_{18}\), PdAu24(2-PET)\(_{18}\), and PtAu24(2-PET)\(_{18}\) reveals average bond lengths which agree with the previously reported structures31,32,34,36 (Figure S4, Table S2). Although light distortions of the structures have been reported upon doping,38,46 the overall structures of Pd/Pt doped Au25 are very similar. Contrary to regular fittings, two different Au−S interactions in the staple motif, corresponding to apex (CN = 2) and core (CN = 1) sulfur, were distinguished.

The reference fitted structure of the 2-PET protected (Pd, Pt) Au25 cluster represents the starting material of the ligand exchange. We then proceed in investigating Au L3-edge EXAFS of BINAS-substituted PdAu24 samples collected after different reaction times. Hereby, we aim to follow any structural changes upon incorporation of bulky dithiol ligands. During the fitting, a general increase of the Debye−Waller factor is observed on samples containing mixed ligand shells. This increased disorder can be related to the temperature-independent structural disorder, which is induced after integration of foreign ligands, generating multiple exchanged species.

The experimentally fitted parameters of the ligand exchanged samples (taken after 18 and 30 h, identical as in the XANES analysis) were obtained after FT-manipulations, resulting in the R-space fitting (Figure S5). More interesting for this study is the lower R-range as the Au−S bonds are positioned there. The bond distances of PdAu24(2-PET)\(_{18−24}\)(BINAS)\(_x\) (\(x\) varies from 0 to 3) are summarized in Table 2. Overall, these values are in good agreement with the reported distances. The Pd−Au bonds measured with EXAFS22,40 and XRD,60 respectively, are 2.750 ± 0.005 and 2.769 ± 0.020 Å. Identical for the Au−Au bonds on the surface of the Au13 core, which have been reported previously in the literature: 2.912 ± 0.166 Å (XRD) and 2.936 ± 0.006 Å (EXAFS of Au25); and for Au−S bonds: 2.319 ± 0.004 Å (EXAFS of Au25).

After ligand exchange reaction, a slight compression of the inner Au13 core is observed without perturbation of the main structure. From the results obtained, ligand exchange with the rigid dithiol BINAS leaves a practically intact doped Au25 cluster. It should be noted that the Pd−Au distance of PdAu24(2-PET)\(_{18}\) is affected by a considerable error, so its value might be misleading.

### CONCLUSION

It was shown before that the incorporation of BINAS into Au38 increases the stability of this chiral cluster against racemization.35 Additionally, our previous work61 revealed a drastic influence of the BINAS on the Au−S vibrations. However, from the present work, it can be concluded that attachment of BINAS does not disturb the Au−S framework of the cluster, which is in agreement with the theoretical calculations.35 This supports the interstaple motif binding of BINAS, connecting one S\(_{core}\) and one S\(_{spec}\) of two adjacent staples, because the corresponding S−S distances fit perfectly.34 Furthermore, doping (Pt, Pd) does not affect the gold environment of the Au25 cluster. Changes in S-interaction are induced by the doping, although the heteroatom is not directly bound to the staple.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b12066.
Synthesis of Pd, Pt doped and monometallic Au$_{25}$(SR)$_{18}$ clusters; additional MALDI and HPLC of PdAu$_{24}$(2-PET)$_{18}$-2$_{2}$-BINAS$_{3}$ ligand exchange samples; and the program code of the Matlab routine and K-range, FT-EXAFS, and fitted parameters of all measured samples (PDF)

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