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**Bonding Properties of FCC-like Au₄₄(SR)₂₈ Clusters from X-ray Absorption
Spectroscopy**

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Abstract: Thiolate-protected gold clusters with precisely controlled atomic composition have recently emerged as promising candidates for a variety of applications because of their unique optical, electronic and catalytic properties. The recent discovery of the $\text{Au}_{44}(\text{SR})_{28}$ total structure is considered as an interesting finding in terms of the face-centered cubic (FCC)-like core structure in small gold–thiolate clusters. Herein, the unique bonding properties of $\text{Au}_{44}(\text{SR})_{28}$ is analyzed using temperature-dependent X-ray absorption spectroscopy (XAS) measurements at the Au L_3 -edge, and compared with other FCC-like clusters such as $\text{Au}_{36}(\text{SR})_{24}$ and $\text{Au}_{28}(\text{SR})_{20}$. A negative thermal expansion was detected for the Au-Au bonds of the metal core (the first Au-Au shell), and was interpreted based on the unique Au core structure consisting of the Au_4 units. EXAFS fitting results from $\text{Au}_{28}(\text{SR})_{20}$, $\text{Au}_{36}(\text{SR})_{24}$ and $\text{Au}_{44}(\text{SR})_{28}$ show a size dependent negative thermal expansion behavior in the first Au-Au shell, further highlighting the importance of the Au_4 units in determining the Au core bonding properties, and shedding lights on the growth mechanism of these FCC-like Au clusters.

Keywords: thiolate-protected gold clusters, face-centered cubic (FCC)-like, X-ray absorption spectroscopy (XAS), negative thermal expansion

1 Introduction

Thiolate-stabilized Au clusters are one of the most widely studied Au clusters due to their high stability and functional surface environment.^{1–4} The development of precisely

size-controlled synthesis of these Au clusters allows for a variety of size-specific studies^{5–15} such as the bonding and electronic properties^{3,16–20}. Recent studies on the thiolate stabilized Au clusters indicated their varied core structures such as the icosahedral Au core^{7,12,21} the face-centered-cubic (FCC)-like Au core^{8–11} and others^{6,14}. Among these clusters, FCC-like Au clusters attract significant amount of interest because these ultrasmall particles exhibit unexpected core structure of FCC geometry, similar to that of bulk gold.^{16,17,22–24} The reported $\text{Au}_{44}(\text{SR})_{28}$ is one of the thiolate protected Au clusters with a FCC-like core structure in the FCC-like series including the well-studied $\text{Au}_{28}(\text{SR})_{20}$ and $\text{Au}_{36}(\text{SR})_{24}$.^{8,10,11} In the research of Au clusters, XAS has been found useful to probe the bonding properties of these Au clusters.³ For instance, the unique structural and electronic properties were found in $\text{Au}_{28}(\text{SR})_{20}$ and $\text{Au}_{36}(\text{SR})_{24}$ clusters by comparing with icosahedral Au clusters, where the small tetrahedral Au_4 units within the gold cores play a very important role in controlling their bonding and electronic properties.^{16,17} Furthermore, based on the results from temperature-dependent X-ray absorption spectroscopy (XAS) experiments, it is interesting to note that a negative thermal expansion was found in the first Au-Au shell in $\text{Au}_{36}(\text{SR})_{24}$, but not in $\text{Au}_{28}(\text{SR})_{20}$ clusters.^{16,17} However, such studies only focus on individual sizes of Au clusters by comparing the FCC with the icosahedral counterpart. The overall trend of size-dependent bonding in FCC-like “magic series” from the XAS perspective is still unavailable with only two Au clusters ($\text{Au}_{28}(\text{SR})_{20}$ and $\text{Au}_{36}(\text{SR})_{24}$).

In this work, we have compared the recently discovered $\text{Au}_{44}(\text{SR})_{28}$ with the other two Au clusters ($\text{Au}_{28}(\text{SR})_{20}$ and $\text{Au}_{36}(\text{SR})_{24}$). Based on a multi-shell EXAFS fitting analysis and temperature-dependent XAS measurements, the size-dependent bonding behavior of these

clusters is discussed herein. This work, together with our previous studies, highlights the bonding trend in the FCC-like magic series.

2 Experimental Methods

$\text{Au}_{28}(\text{SR})_{20}$ NCs were prepared from the reaction between excess thiol ligands and $\text{Au}_{25}(\text{SR})_{18}$ -precursor at 80 °C for 2 hours.¹⁰ Using a similar method, the $\text{Au}_{36}(\text{SR})_{24}$ NCs were prepared from the reaction between excess thiol ligands and $\text{Au}_{38}(\text{SR})_{24}$ precursor at 80 °C for more than 12 hours.¹¹ Unlike the above FCC-like Au NCs, the $\text{Au}_{44}(\text{SR})_{28}$ NCs were synthesized using both routes via a two-step “size focusing” process. In the first step, size-mixed $\text{Au}_x(\text{SR})_y$ NCs were formed from HAuCl_4 precursor (i.e. atoms to clusters). In the second step, the size-mixed NCs were dissolved in toluene and etchant thiol ligands. After reacting at 60 °C for 24 hours, $\text{Au}_{44}(\text{SR})_{28}$ NCs were produced in high field.⁸ All the syntheses produced Au NCs in high purity which is supported by Mass Spec data. The Au L_3 -edge XAS measurements were then carried out in transmission mode at the Sector20-BM beamline of the Advanced Photon Source (Argonne National Laboratory, IL, U.S.A.). $\text{Au}_{44}(\text{SR})_{28}$ powder samples were packed into Kapton film pouches, sealed and folded to ensure high quality EXAFS signals are collected. The samples were measured in transmission mode which is represented using $\log(I_0/I_1)$.²⁵ Here, I_0 is the intensity of the incident beam and I_1 is intensity of the transmitted beam. A Au foil reference was placed in between the I_1 detector and another detector I_2 to simultaneously collect the XAFS data for calibration of the energy of Au L_3 absorption edge.

$$\chi(k) = \sum_j \frac{S_0^2 N_j e^{-2k^2 \sigma_j^2} e^{-2R_j/\lambda(k)} f_j(k)}{k R_j^2} \sin[2k R_j + \delta_j(k)]$$

The data measured from Au foil can then be used to determine the amplitude reduction factor ($S_0^2 = 0.9$) as shown in the EXAFS equation, where N is the coordination number, σ^2 is the Debye-Waller factor, $\lambda(k)$ is the photoelectron mean-free path and R is the scattering distance. Scattering amplitude functions ($f(k)$) and phase-shift functions ($\lambda(k)$) in the EXAFS equation can be used to simulate specific scattering route by theoretical calculations. Here, the XAS data were collected at both low temperature (LT: 90K) using a helium-cooled cryostat chamber and room temperature (RT: 300K) under ambient conditions.

The XAS data processing and fitting were performed using the WinXAS 3.1 software package²⁵ and FEFF8.2 computer code²⁶. In the refinement process, the amplitude reduction factor (S_0^2) of 0.9 was obtained by fitting the Au foil EXAFS and fixed for the EXAFS fitting of Au clusters. For multishell EXAFS fitting, coordination numbers (CN) of Au-S and Au-Au shells are fixed based on the published $\text{Au}_{44}(\text{SR})_{28}$ total structure.⁸ A k -range of 3-14 $\text{\AA}^{-1}$ was used for fitting the EXAFS of $\text{Au}_{44}(\text{SR})_{28}$ and a shorter k -range (3-11.25 $\text{\AA}^{-1}$) was used for qualitatively comparing the EXAFS of the three clusters in order to make their k -range consistent for the comparison. All the E_0 shift values were correlated to reduce the number of free running parameters, allowing for the incorporation of up to three scattering shells.

3 Results and discussion

3.1 Qualitative XAS comparison

The Au L₃-edge XANES of Au₂₈(SR)₂₀, Au₃₆(SR)₂₄ and Au₄₄(SR)₂₈ is first compared in Figure 1. Interestingly, when the XANES is closely compared in the overlapped plot in Figure, identical features are observed for the three clusters in the whole XANES region, including the white line (the first feature following the absorption edge) intensity. These observations imply that their electronic properties are identical and independent of the cluster size. A more detailed discussion on this finding will be presented together with the EXAFS fitting results in the later section.

Figure 1. Overlapped XANES of Au₂₈(SR)₂₀, Au₃₆(SR)₂₄ and Au₄₄(SR)₂₈.

The FT-EXAFS of Au₂₈(SR)₂₀, Au₃₆(SR)₂₄ and Au₄₄(SR)₂₈, collected at room and low temperatures (RT and LT), are next plotted in Figure 2. The most intense peak around 1.9 Å in each spectrum is caused by the Au-S scattering. The intensity of these peaks decreases when their size increases in both RT and LT series. To understand this trend, we calculated the CN

of the Au-S coordination when the cluster size increases. The Au-S CN gives a value of 1.43 for $\text{Au}_{28}(\text{SR})_{20}$, 1.33 for $\text{Au}_{36}(\text{SR})_{24}$ and 1.27 for $\text{Au}_{44}(\text{SR})_{28}$. From these calculated CN values, we can understand that the observed trend for these EXAFS peaks is caused by the decrease

Figure 2. FT-EXAFS of $\text{Au}_{28}(\text{SR})_{20}$, $\text{Au}_{36}(\text{SR})_{24}$ and $\text{Au}_{44}(\text{SR})_{28}$ at RT and LT. In the comparison, the k-range of $3\text{--}11.25\text{ \AA}^{-1}$ was used for all the Au clusters.

of Au-S CNs when the cluster size increases. Furthermore, the small peaks between $2.5\text{ \AA}$ and $3.5\text{ \AA}$ correspond to Au-Au scattering. The similar patterns of the FT-EXAFS of the three Au clusters at RT and LT indicate a similar local structure for these FCC-like Au clusters. In addition, spectra with lower peak intensity in the Au-Au scattering region are found at RT comparing with the LT data. This is because thermal vibrations at higher temperature lead to a higher degree of thermal disorder, which reduces the EXAFS scattering intensity. Quantitative information of these scattering shells will be obtained by the refinement of FT-EXAFS in the next section.

3.2 EXAFS fitting analysis of $\text{Au}_{44}(\text{SR})_{28}$

In order to perform a reliable EXAFS analysis, the bond distance distribution of $\text{Au}_{44}(\text{SR})_{28}$ was first studied based on the reported total structure.⁸ Three scattering shells were found,

Figure 3. Bond distance distribution for $\text{Au}_{44}(\text{SR})_{28}$ and representative EXAFS scattering shells.

The bonds in each shell are represented by red sticks.

which are displayed in Figure 3. The first shell with the shortest distance corresponds to the Au-S bonds in the clusters. The other two longer distance shells are caused by the Au-Au interactions. The shorter Au-Au shell (Au-Au_1) in the region of 2.707-2.849 Å accounts for the Au-Au bonding within the Au_4 unit of the cluster core. The longer Au-Au shell (Au-Au_2) in the region of 2.877-3.104 Å corresponds to the long distance Au-Au interactions between surface, bridge and center Au atoms.

The theoretical CN was calculated from the bond distance distribution (Figure 3). For the Au-S scattering shell, the average CN is found to be 1.27 ((56 Au-S bonds)/44 Au atoms). The

average CN for Au-Au₁ and Au-Au₂ scattering shells are 1.82 ((40 Au-Au bonds) * 2 / 44 Au atoms) and 2.68 ((59 Au-Au bonds) * 2 / 44 Au atoms), respectively. The calculated CNs of the Au-S and two Au-Au scattering shells can then be used in the EXAFS fit, and were fixed in the EXAFS refinement process.

Figure 4. Experimental FT-EXAFS (k -range: 3-14 $\text{\AA}^{-1}$) and the best fits for $\text{Au}_{44}(\text{SR})_{28}$ at (a) RT and (b) LT.

To verify the reliability of the assignment of these three shells, a three shell Au L₃-edge EXAFS (Au-S, Au-Au₁, Au-Au₂) fit was performed for $\text{Au}_{44}(\text{SR})_{28}$ at LT since the total structure was also previously obtained at LT.⁸ Figure 4a) shows the best fit of $\text{Au}_{44}(\text{SR})_{28}$ at 90 K and the fitting results are recorded in Table 1. From Table 1, it can be seen that the bond distances of Au-S (2.33 $\text{\AA}$), Au-Au₁ (2.74 $\text{\AA}$) and Au-Au₂ (2.93 $\text{\AA}$) shells determined from the EXAFS refinement are very consistent with the calculated bond lengths from the total structure (i.e. Au-S: 2.33 $\text{\AA}$, Au-Au₁: 2.77 $\text{\AA}$, Au-Au₂: 2.97 $\text{\AA}$). This verifies the reliability of the three shell fitting method used in this work.

Table 1. EXAFS multi-shell fitting results of $\text{Au}_{44}(\text{SR})_{28}$ at both LT and RT.

Temperature(K)	Shells	CN ^a	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)
90 (LT)	Au-S	1.27	2.327 (9)	0.0048 (6)	1.60 (2)
	Au-Au ₁	1.82	2.744 (9)	0.0038 (4)	1.60 (0)
	Au-Au ₂	2.68	2.930 (12)	0.008 (1)	1.60 (0)
300 (RT)	Au-S	1.27	2.321 (10)	0.0061 (6)	-0.10 (17)
	Au-Au ₁	1.82	2.724 (17)	0.0080 (9)	-0.10 (0)
	Au-Au ₂	2.68	2.907 (24)	0.012 (3)	-0.10 (0)

^a CN values are fixed to the values calculated from total structure (No errors for fixed CN values). Difference in the uncertainty values is associated with both the data quality and the relative intensity of each EXAFS shell.

Next, we performed fits on the RT EXAFS to study the temperature dependent properties of $\text{Au}_{44}(\text{SR})_{28}$. The Au-S bond distance is essentially unchanged when the temperature is varied. However, the distances of both the Au-Au₁ and Au-Au₂ shells are found to be sensitive to the change in temperature. When the temperature increases from 90 K to 300 K, the bond distances of the Au-Au₁ shell display a negative thermal expansion (NTE) behavior, that is, a decrease from 2.744 Å to 2.724 Å (decrement = 0.020 Å). The Au-Au₂ shell also shows a NTE from 2.930 Å to 2.907 Å (decrement = 0.023 Å). It has been known that the tetrahedral Au_4 units within the gold core of other FCC-like clusters such as $\text{Au}_{28}(\text{SR})_{20}$ and $\text{Au}_{36}(\text{SR})_{24}$ play an

important role in controlling their electronic properties.^{16,17} Therefore, we next focus on a close comparison of the temperature-dependent behavior of the Au-Au₁ shells for these three FCC-like clusters.

3.3 The size-dependent trend

In previous studies, the Au-Au shell in Au₂₈(SR)₂₀ appears to be invariant to the temperature change, remaining at around 2.73(2) Å at both LT and RT.¹⁷ Unlike Au₂₈(SR)₂₀, the Au-Au₁ shell in Au₃₆(SR)₂₄ displays a NTE, that is, the Au-Au distance decreases from

Figure 5. Bond distances of Au-Au₁ in Au₂₈(SR)₂₀, Au₃₆(SR)₂₄ and Au₄₄(SR)₂₈ clusters at LT (blue) and RT (red).

2.746(3) Å to 2.732(4) Å as the temperature increases.¹⁶ Comparing with Au₃₆(SR)₂₄, Au₄₄(SR)₂₈ shows an even more pronounced NTE in the Au-Au₁ shell. These results are summarized in Figure 5. Therefore, the change of bond distances in the Au-Au₁ shells shows

an interesting size-dependent trend for the three Au clusters, that is, the NTE becomes stronger when the size of the Au clusters increases.

Figure 6. The kernels (first Au-Au shell) of (a) $\text{Au}_{28}(\text{SR})_{20}$, (b) $\text{Au}_{36}(\text{SR})_{24}$ and (c) $\text{Au}_{44}(\text{SR})_{28}$. (Red dash lines: missing Au-Au bonds. Green dash lines: extra Au-Au bonds.)

To understand this phenomenon, their core structures, produced from X-ray crystallography data, are plotted in Figure 6 for a close comparison. As is shown in the figure, $\text{Au}_{28}(\text{SR})_{20}$ has two sets of Au_4 units in the core, each set consisting of two Au_4 units connected by sharing one corner Au atom (Figure 6a). In the core of $\text{Au}_{36}(\text{SR})_{24}$, two sets of Au_4 units were also observed. Each set consists of three Au_4 units connected by sharing two corner Au atoms (Figure 6b). The core of $\text{Au}_{44}(\text{SR})_{28}$ also has two sets of Au_4 units, each set consisting of four

Au₄ units which are connected by sharing three corner Au atoms. To more clearly see these Au₄ units within Au₄₄(SR)₂₈, the two sets of Au₄ units are plotted separately in Figure 6c). Note that for all these structures, the Au-Au bonds are identified based on a specific bond distance (2.880 Å from bulk Au) which is the commonly used metallic Au-Au bond distance. When the Au-Au distances within the tetrahedral unit are longer than 2.880 Å, these Au-Au bonds are considered as non-metallic bonds (i.e. metallic bonds missing), and are shown with red dashed lines (Figure 6). In Au₂₈(SR)₂₀, all the metallic bonds are well maintained in the Au₄ units. As the size of the Au clusters increases, the Au₄ tetrahedrons begin to lose Au-Au metallic bonds. Specifically, two metallic bonds are missing in Au₃₆(SR)₂₄ and ten are missing in Au₄₄(SR)₂₈. (Figure 6. a-c)

The missing metallic bonds shown in the Figure 6, indicate larger clusters have more defective Au₄ units within their core structures. Table 2 summarizes our quantitative analysis of the Au-Au metallic bonds for the Au₄ units in each cluster, including the ratio of observed metallic bonds to ideal metallic bonds (for a perfect Au₄ tetrahedron) within the Au₄ units. As the size of the clusters increases, the ratio decreases from 100% for Au₂₈(SR)₂₀ to 94% for

Table 2. Number of Au-Au bonds in first Au-Au scattering shells (a), number of Au-Au bonds in the ideal first Au-Au scattering shells (b), and the ratio of a to b.

Au clusters	# of Au-Au ₁ bonds (a)	Ideal # of Au-Au ₁ bonds (b)	a/b (%)
Au₂₈(SR)₂₀	24	24	100
Au₃₆(SR)₂₄	34	36	94
Au₄₄(SR)₂₈	38	48	83

$\text{Au}_{36}(\text{SR})_{24}$ and then to 83% for $\text{Au}_{44}(\text{SR})_{28}$ (Table 2). In other words, when the cluster size increases, the Au core exhibits more pronounced defective Au_4 units.

Based on the information in Figure 6 and Table 2, we proceed to discuss the origin of the observed size-dependent NTE. For the smallest clusters, $\text{Au}_{28}(\text{SR})_{20}$, the core structure has a perfect Au_4 based structure (i.e. no defect) and thus is the most rigid. Such a rigid core structure will exhibit the least amount of change in bond distance when temperature is varied. In contrast, the cores of larger clusters with a less perfect Au_4 bonding motif, will be less rigid, and thus, more sensitive to temperature change. As a result, larger clusters will exhibit more pronounced temperature-dependent NTE. In this comparative study, $\text{Au}_{44}(\text{SR})_{28}$ was found to have the least rigid core structure, and thus, it exhibits the most pronounced NTE.

The size-dependent NTE trend we observed in FCC-like Au cores is an important finding which may help develop a better understanding of the growth mechanism of Au clusters. In these FCC-like Au clusters, the Au cores grow by the addition of Au_4 units to the two base sets which follow a “double helix” structure.⁸ During the growth process, the bonding motif of Au_4 units within the core is not perfectly maintained and becomes more defective when the cluster size increases. This makes the Au core less rigid, and thus, more susceptible to change upon varied conditions (i.e. temperature).

4 Conclusions

In conclusion, the bonding properties of $\text{Au}_{44}(\text{SR})_{28}$ was studied and compared with two

other FCC-like Au clusters, $\text{Au}_{28}(\text{SR})_{20}$ and $\text{Au}_{36}(\text{SR})_{24}$. A multi-shell EXAFS fitting analysis was first established to reliably probe the site-specific bonding properties of the $\text{Au}_{44}(\text{SR})_{28}$. Temperature-dependent EXAFS measurements indicate the existence of a negative thermal expansion behavior for the Au-Au interactions of the $\text{Au}_{44}(\text{SR})_{28}$. Comparison of the bonding behavior of $\text{Au}_{44}(\text{SR})_{28}$ with that of $\text{Au}_{28}(\text{SR})_{20}$ and $\text{Au}_{36}(\text{SR})_{24}$ shows an interesting size-dependent trend for the negative thermal expansion behavior of the first-shell Au-Au bonds. Specifically, the Au clusters with larger size exhibit more pronounced negative thermal expansion than the smaller ones. This observation can be understood as an effect related to the significant role of the bonding motif of Au_4 units within the Au cores. The bonding motif of the Au_4 units within the “double helix” structures of these clusters are observed to be less perfectly maintained when the size of FCC-like Au clusters increases. Our findings demonstrate the unique bonding properties of the FCC-like Au clusters, and may be further the understanding of the growth mechanism of these Au clusters.

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