

## Thiolate-Induced Structural Reconstruction of Gold Clusters Probed by $^{197}\text{Au}$ Mössbauer Spectroscopy

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Small (<100 atoms) gold clusters protected by organic ligands have aroused interest as prototypical systems for fundamental studies on quantum size effects and as a building block of nanoscale devices.<sup>1</sup> Conventionally, phosphines have been used to stabilize gold clusters. The geometric structures of PPh<sub>3</sub>-stabilized Au<sub>*n*</sub> clusters with *n* = 11, 13, 20, 39, and 55 have been determined by X-ray crystallography as well as by theoretical calculations.<sup>2</sup> The stability has been explained in terms of electronic shell closing of the Au cores.<sup>3</sup> Thiolates (RS) are another class of ligands that have been used extensively since the first report by Schiffrin.<sup>4</sup> Several research groups have recently synthesized Au:SR clusters with well-defined chemical compositions, such as Au<sub>25</sub>(SR)<sub>18</sub>, Au<sub>38</sub>(SR)<sub>24</sub>, and Au<sub>55</sub>(SR)<sub>32</sub>, using size-separation techniques in combination with mass spectrometry.<sup>5,6</sup> Nevertheless, geometric structures of Au:SR have not been determined experimentally mainly owing to the unavailability of single crystals of these compounds. The lack of structural information for small Au:SR clusters hinders a full understanding of the origin of their stability and novel properties (e.g., photoluminescence,<sup>5</sup> magnetism,<sup>7</sup> and optical activity<sup>5a,8</sup>).

In the present study, we investigated the structures of a series of glutathionate-protected gold (Au:SG) clusters using  $^{197}\text{Au}$  Mössbauer spectroscopy, which has been applied to probe the local environment of the Au sites of Au<sub>9</sub>(PPh<sub>3</sub>)<sub>8</sub>(NO<sub>3</sub>)<sub>3</sub> and Au<sub>55</sub>(PPh<sub>3</sub>)<sub>12</sub>Cl<sub>6</sub> via isomer shift (IS) and quadrupole splitting (QS).<sup>9</sup> Spectral analysis, with the help of recent theoretical results on methanethiolated gold clusters,<sup>10</sup> revealed that thiolate ligation heavily modifies the electronic and geometric structures of the underlying gold clusters. Specifically, a core-in-cage structure theoretically predicted for [Au<sub>25</sub>(SCH<sub>3</sub>)<sub>18</sub>]<sup>+</sup> (ref 10d) explains the Mössbauer spectrum of Au<sub>25</sub>(SG)<sub>18</sub>, and thereby explains the high stability against core-etching reactions by free GSH.<sup>6</sup>

Details of the sample preparation were given in ref 5c. Briefly, Au<sub>*n*</sub>(SG)<sub>*m*</sub> samples with (*n*, *m*) = (10, 10), (15, 13), (18, 14), (22, 16), (22, 17), (25, 18), (29, 20), (33, 22), (39, 24) and (45, 28) were fractionated from nearly monodisperse Au:SG clusters (*d*<sub>av</sub> ≈ 1 nm) using polyacrylamide gel electrophoresis (PAGE). The typical yield of each Au<sub>*n*</sub>(SG)<sub>*m*</sub> sample was only a few to submilligrams by PAGE using a gel with a dimension of 3 mm × 160 mm × 160 mm. To obtain Mössbauer spectra with sufficient *S/N* ratios, each cluster was synthesized with a mass in the range 50–100 mg by repeating the elaborative PAGE procedure using two sets of slab gel electrophoresis units, which employs six gels.  $^{197}\text{Au}$  Mössbauer measurements were conducted using a constant-acceleration spectrometer with an NaI scintillation counter installed at the Research Reactor Institute of Kyoto University. The  $^{197}\text{Au}$  γ-ray source (77.3 keV) was obtained by the β<sup>-</sup>-decay (half-life =

18.3 h) of  $^{197}\text{Pt}$  generated by the neutron irradiation for 98%-enriched  $^{196}\text{Pt}$  metal foil. The γ-ray source and samples were cooled to 16 K, and the spectra were recorded in a transmission geometry. The IS value of a gold foil was referenced as 0 mm/s. The spectra were deconvoluted into the least possible set of Lorentzian curves of an identical width.<sup>11</sup>

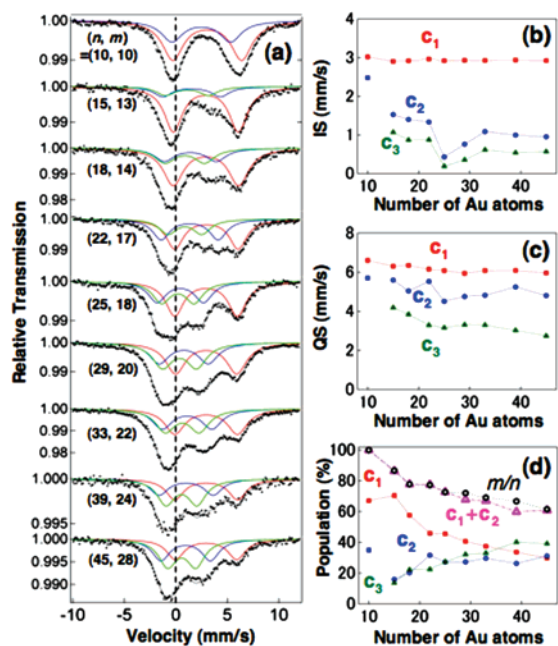
The  $^{197}\text{Au}$  Mössbauer spectra of Au<sub>*n*</sub>(SG)<sub>*m*</sub> evolve drastically as a function of the core size, *n*, as shown in Figure 1a. The asymmetric doublet profile of the Au<sub>10</sub>(SG)<sub>10</sub> spectrum could be fitted by a superposition of two sets of doublets. The IS and QS values obtained are 3.04 and 6.67 mm/s, respectively, for the major component and 2.46 and 5.70 mm/s, respectively, for the minor component.<sup>11</sup> According to the correlation between the IS and QS values established for various kinds of Au<sup>I</sup> and Au<sup>III</sup> compounds,<sup>12</sup> these components are assigned to Au<sup>I</sup> sites directly bound to GS ligands. Recently, two structural isomers have been predicted for Au<sub>10</sub>(SCH<sub>3</sub>)<sub>10</sub>; a monocyclic oligomer having an Au–S repeating unit and a cartenane in which two Au<sub>5</sub>(SCH<sub>3</sub>)<sub>5</sub> rings are interlocked.<sup>10c</sup> The cartenane isomer was calculated to be more stable than the monocyclic one<sup>10c</sup> and has been synthesized for (AuSC<sub>6</sub>H<sub>4</sub>-*p*-CMe<sub>3</sub>)<sub>10</sub>.<sup>13</sup> However, comparison of the optical spectra calculated for these isomers with the experimental data for Au<sub>10</sub>(SG)<sub>10</sub> (ref 5c) implies that the major component arises from the monocyclic oligomer. The minor component may be due to the cartenane or Au<sub>*n*</sub>(SG)<sub>*m*</sub> (*n* = 11, 12) impurities contained in the Au<sub>10</sub>(SG)<sub>10</sub> sample.<sup>5c</sup>

The spectra of larger (*n* ≥ 15) clusters were successfully fitted by three sets of doublets as shown in Figure 1a.<sup>11</sup> The IS, QS, and population of each component are plotted in Figure 1 panels b, c, and d, respectively, as a function of the core size. Two components, **c**<sub>1</sub> and **c**<sub>2</sub>, are assigned to Au<sup>I</sup> sites directly bound to the GS ligands since the IS and QS values are similar to those of Au<sub>10</sub>(SG)<sub>10</sub>. Component **c**<sub>3</sub>, having the smallest IS and QS values, is assigned to Au sites which are not directly bound to GS ligands. These assignments for **c**<sub>1</sub>–**c**<sub>3</sub> are supported by the optimized structure of [Au<sub>25</sub>(SCH<sub>3</sub>)<sub>18</sub>]<sup>+</sup> (ref 10d) which reproduces the optical spectrum and X-ray diffraction pattern of Au<sub>25</sub>(SG)<sub>18</sub>. The structure of [Au<sub>25</sub>(SCH<sub>3</sub>)<sub>18</sub>]<sup>+</sup> shown in Figure 2 illustrates that there are three types of Au sites: 12 atoms in the (Au–SCH<sub>3</sub>)<sub>12</sub> ring, 6 atoms in the two (Au–SCH<sub>3</sub>)<sub>3</sub> rings, and 7 atoms at the core, which are colored red, blue, and green, respectively. In contrast, the numbers of Au atoms for components **c**<sub>1</sub>–**c**<sub>3</sub> of Au<sub>25</sub>(SG)<sub>18</sub> are estimated to be 11, 7, and 7, respectively (Figure 1d). These comparisons lead us to conclude that **c**<sub>1</sub> and **c**<sub>2</sub> correspond to the Au<sup>I</sup> sites in the (Au–SCH<sub>3</sub>)<sub>12</sub> and (Au–SCH<sub>3</sub>)<sub>3</sub> rings, respectively, whereas **c**<sub>3</sub> are due to Au atoms at the core. The following population analysis confirms that other-sized Au<sub>*n*</sub>(SG)<sub>*m*</sub> clusters also have a similar structural motif, in which an Au core is surrounded by Au–SG oligomers. In Figure 1d, we plot the *m/n* ratios for Au<sub>*n*</sub>(SG)<sub>*m*</sub> and

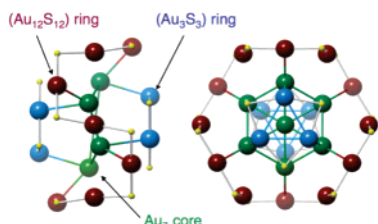
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**Figure 1.** (a)  $^{197}\text{Au}$  Mössbauer spectra of  $\text{Au}_n(\text{SG})_m$ . (b) Isomer shifts, (c) quadrupole splittings, and (d) populations of deconvoluted components ( $c_1$ – $c_3$ ). The total populations of  $c_1$  and  $c_2$  and the  $m/n$  ratios of  $\text{Au}_n(\text{SG})_m$  are also plotted in panel d.



**Figure 2.** Side (left) and front (right) views of structural model of  $[\text{Au}_{25}(\text{SCH}_3)_{18}]^+$  (ref 10d). The large and small yellow balls represent gold and sulfur, respectively. The methyl groups are omitted for clarity.

the populations of Au sites directly bound to the GS ligands estimated from the total populations of  $c_1$  and  $c_2$ . The quantitative agreement between the two plots suggests that the  $\text{Au}_n(\text{SG})_m$  cluster is composed of an  $\text{Au}_{n-m}$  core and  $(\text{Au}-\text{SG})_m$  cages, comprising two distinct cyclic rings. The structural motif proposed here qualitatively agrees with theoretical results on  $\text{Au}_{38}(\text{SCH}_3)_{24}$  (ref 14a) and Raman studies on  $[\text{Au}_{140}(\text{SPh})_{78}]^{3-}$ .<sup>14b</sup> These results offer a microscopic model for the interface structure of a thiolate monolayer on an extended Au(111) surface, which is still a matter of active debate.<sup>15</sup>

Nonzero values of IS and QS for unthiolated Au sites ( $c_3$ ) indicate that their electronic structures are very different from those of bulk gold (IS = QS = 0 mm/s) and of the  $\text{Au}_{13}$  core of  $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$  (IS  $\approx$  -0.1 mm/s, QS = 0 mm/s).<sup>9a</sup> Although it appears that the spectral profile of  $\text{Au}_n(\text{SG})_m$  smoothly converges to that of  $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$  (ref 9a), the origin of the nonzero IS values for core atoms is different between  $\text{Au}_n(\text{SG})_m$  and  $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ . The slightly negative IS value for  $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$  has been attributed to the elongation of the Au–Au bond in the  $\text{Au}_{13}$  core.<sup>9a</sup> In contrast, the positive IS and QS values for  $c_3$  are explained such that the unthiolated Au sites do not form a closed-packed geometry and/or interact electronically with the Au sites of the adjacent Au–SG rings. The profile abruptly changes from  $\text{Au}_{22}(\text{SG})_{16}$  to  $\text{Au}_{25}(\text{SG})_{18}$  as shown in Figure 1a. Figure 1b clearly shows that this transition is associated with an abrupt decrease in the IS values for components  $c_2$  and  $c_3$ . Within the framework of the structural model

shown in Figure 2, the transition implies that an  $\text{Au}_7$  core with more bulklike features is generated within a cage of the Au–SCH<sub>3</sub> rings.

In summary,  $^{197}\text{Au}$  Mössbauer spectroscopy of size-selected  $\text{Au}_n(\text{SG})_m$  in the range of  $n = 10$ –45 provided evidence for the formation of Au–SG rings around the Au core. The high stability of  $\text{Au}_{25}(\text{SG})_{18}$  against thiol-mediated core etching<sup>6</sup> is ascribed to the completion of a cage structure around the core. The positive values of IS and QS for the Au core of  $\text{Au}_n(\text{SG})_m$  suggest a nontrivial effect of thiolate ligation on the electronic structure of the underlying gold clusters.

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**Supporting Information Available:** Details of spectral analysis and a list of the Mössbauer parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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