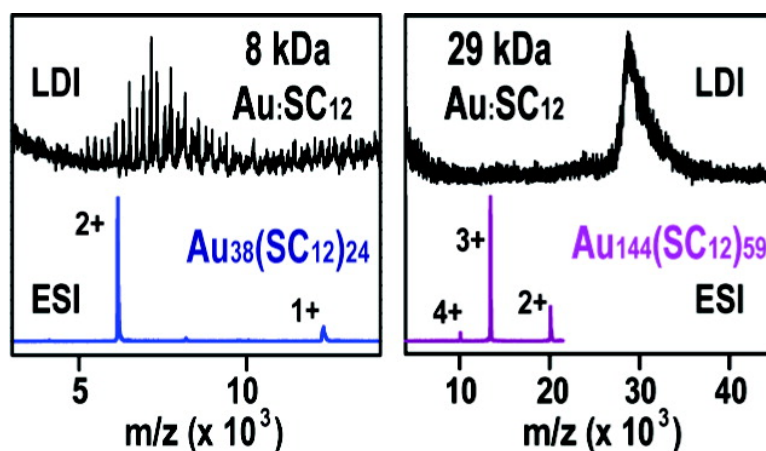


## Ubiquitous 8 and 29 kDa Gold:Alkanethiolate Cluster Compounds: Mass-Spectrometric Determination of Molecular Formulas and Structural Implications

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## Ubiquitous 8 and 29 kDa Gold:Alkanethiolate Cluster Compounds: Mass-Spectrometric Determination of Molecular Formulas and Structural Implications

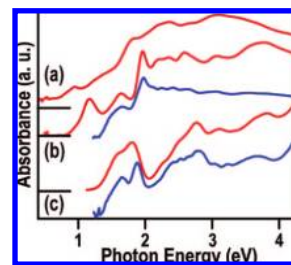
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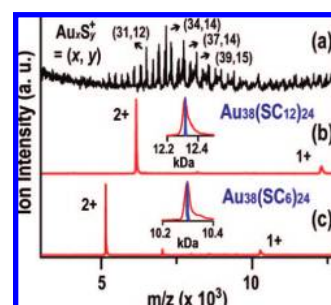
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Since the first report of chemical preparation of thiolate-protected gold (Au:SR) clusters by Brust et al.,<sup>1</sup> the synthesis has reached a stage where  $Au_n(SR)_m$  can be isolated with a well-defined formula. Elucidation of the structures of a series of stable  $Au_n(SR)_m$  is of fundamental importance to understand both the aufbau principle and the origin of the unique physicochemical properties of these compounds. Alkanethiolate-protected gold (Au:SC<sub>n</sub>) clusters are ideal systems to address these challenges because the sequence of preferred core sizes has been established and their stabilities are mostly governed by those of the Au–S core moieties. Whetten and others have shown that Au:SC<sub>n</sub> clusters, with core masses of ca. 5, 8, 14, 22, and 29 kDa, can be isolated as stable compounds on the basis of the mass distributions of Au<sub>n</sub>S<sub>y</sub><sup>+</sup> fragment ions in the laser-desorption ionization (LDI) mass spectra.<sup>2–6</sup> Of these, only the 5, 8, and 29 kDa clusters can survive the harsh conditions of etching by free thiols, whereas the others are degraded by core etching.<sup>2f,6b,7</sup> This indicates that the former three clusters are thermodynamically and chemically stable, whereas the others correspond to metastable species trapped by kinetic stabilization.<sup>8</sup> The smallest Au:SC<sub>6</sub> (5 kDa) clusters, originally believed to have a Au<sub>28</sub>-based core,<sup>2g,9</sup> have recently been reassigned to [Au<sub>25</sub>(SC<sub>6</sub>)<sub>18</sub>]<sup>z</sup> (z = 1–, 0, 1+) using nondestructive electrospray ionization mass spectrometry (ESI-MS).<sup>10</sup> The ubiquitous nature of Au<sub>25</sub>(SR)<sub>18</sub> has been evidenced by the fact that Au<sub>25</sub>(SG)<sub>18</sub><sup>11</sup> and Au<sub>25</sub>(SC<sub>2</sub>Ph)<sub>18</sub><sup>12</sup> were identified by ESI-MS (where GS and PhC<sub>2</sub>S represent glutathionate and phenylethanthiolate, respectively). The characteristic absorption spectra (Figure 1c) can be used as a fingerprint of Au<sub>25</sub>(SR)<sub>18</sub>.<sup>13</sup> Initial density functional theory studies have predicted that [Au<sub>25</sub>(SC<sub>1</sub>)<sub>18</sub>]<sup>z</sup> has a nearly planar Au<sub>7</sub><sup>z</sup> core, surrounded by a cage consisting of one [–Au–SC<sub>1</sub>–]<sub>12</sub> and two [–Au–SC<sub>1</sub>–]<sub>3</sub> cyclic oligomers.<sup>14</sup> However, recent single-crystal X-ray diffraction (XRD) studies on [Au<sub>25</sub>(SC<sub>2</sub>Ph)<sub>18</sub>]<sup>–</sup> and theoretical studies on [Au<sub>25</sub>(SC<sub>1</sub>)<sub>18</sub>]<sup>–</sup> revealed that icosahedral Au<sub>13</sub> is completely protected by six [–SR–Au–SR–Au–SR–] oligomers.<sup>15–17</sup> This fully protected structure explains the magic stability of [Au<sub>25</sub>(SG)<sub>18</sub>]<sup>z</sup> against core etching and redox reactions.<sup>7,10</sup> It is also suggested that the stability of the negative charge state of [Au<sub>25</sub>(SC<sub>2</sub>Ph)<sub>18</sub>]<sup>–</sup> is ascribed to the closing of an electronic shell with eight electrons.<sup>16</sup>

In contrast, molecular formulas of the ubiquitous 8 and 29 kDa clusters have not been determined unambiguously but have been suggested to be Au<sub>38</sub>(SC<sub>n</sub>)<sub>24</sub> and Au<sub>140–146</sub>(SC<sub>n</sub>)<sub>50–60</sub>, respectively, based on LDI mass spectra and elemental analyses.<sup>2,4</sup> Several fundamental questions remain unanswered: Are these clusters composed of single species or mixtures of clusters with size distribution? What are the precise molecular formulas? What is the preferential



**Figure 1.** Optical absorption spectra of as-prepared Au:SC<sub>12</sub> clusters with a core mass of (a) 29 and (b) 8 kDa, and (c) [Au<sub>25</sub>(SC<sub>12</sub>)<sub>18</sub>]<sup>0</sup>. The superimposed blue curves are the spectra of films at 25 K.



**Figure 2.** (a) LDI mass spectrum of as-prepared Au:SC<sub>12</sub> (8 kDa). (b) ESI mass spectra of oxidized Au:SC<sub>12</sub> (8 kDa) and (c) Au:SC<sub>6</sub> (8 kDa). Insets of panels b and c show expanded views of the molecular weights derived from the 2+ peaks and the isotopomer distributions of Au<sub>38</sub>(SC<sub>12</sub>)<sub>24</sub> and Au<sub>38</sub>(SC<sub>6</sub>)<sub>24</sub>, respectively.

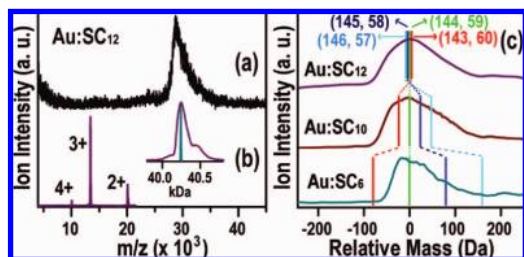
charge state of the core? In order to address these issues, the 8 and 29 kDa clusters have been characterized using ESI-MS. These clusters were determined to be composed of single species, formulated as [Au<sub>38</sub>(SC<sub>n</sub>)<sub>24</sub>]<sup>z</sup> and [Au<sub>144</sub>(SC<sub>n</sub>)<sub>59</sub>]<sup>z</sup>, respectively, with charge states of z ≥ 0. Possible geometric structures for Au<sub>38</sub>(SC<sub>n</sub>)<sub>24</sub> and Au<sub>144</sub>(SC<sub>n</sub>)<sub>59</sub> are proposed, based on experimentally and theoretically determined structures of the relevant systems, [Au<sub>25</sub>(SR)<sub>18</sub>]<sup>–</sup><sup>15–17</sup> and Au<sub>102</sub>(p-MBA)<sub>44</sub> (p-MBA = p-mercaptobenzoic acid),<sup>18,19</sup> in which the Au cores are protected by monomers [–SR–Au–SR–] and/or dimers [–SR–Au–SR–Au–SR–]. The origin of the magic stability and the structural correlation with other related systems are discussed.

A crude mixture of Au:SC<sub>n</sub> clusters (n = 6, 10, 12) was prepared using the Brust method<sup>1</sup> with a slight modification. The clusters were then incubated in a solution of neat thiols at 353 K in order to enhance the populations of stable clusters by etching.<sup>2f,6,7,10</sup> The stable clusters in the mixture were fractionated by extraction using various ratios of toluene/acetone at different stages of the preparation. The core sizes of the clusters in the fractions were probed using LDI-MS, and the fractions that contained the 8 and 29 kDa clusters (Figures 2a and 3a) were further characterized by optical absorption spectroscopy and

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**Figure 3.** (a) LDI mass spectrum of as-prepared Au:SC<sub>12</sub> (29 kDa) and (b) ESI mass spectrum of oxidized Au:SC<sub>12</sub> (29 kDa). The inset of panel b shows an expanded view of the molecular weight derived from the 3+ peak and the isotopomer distribution of Au<sub>144</sub>(SC<sub>12</sub>)<sub>59</sub>. (c) Molecular weights determined from the ESI mass spectra of Au:SC<sub>6</sub>, Au:SC<sub>10</sub>, and Au:SC<sub>12</sub> and those calculated for possible formulas.

voltammetry. Figure 1 shows the optical spectra of isolated Au:SC<sub>12</sub> clusters with a core mass of 29 and 8 kDa, along with that of [Au<sub>25</sub>(SC<sub>12</sub>)<sub>18</sub>]<sup>0</sup> for comparison.<sup>10</sup> The spectral features indicate that the quantization of the electronic states and the onset of absorption are in good agreement with those previously reported for the 8 and 29 kDa clusters.<sup>2b,c,h,5,6b</sup> The peaks become prominent in the spectra of the cluster films measured at 25 K, as shown by the blue curves in Figure 1. Voltammograms (Figure S1) also reproduced previously reported results, thereby confirming our assignment.

We have previously shown that molecular formulas can be determined using ESI-MS, even for neutral Au:SC<sub>n</sub>, such as [Au<sub>25</sub>(SC<sub>12</sub>)<sub>18</sub>]<sup>0</sup>, via oxidation or reduction of the core by Ce(SO<sub>4</sub>)<sub>2</sub> or NaBH<sub>4</sub>, respectively.<sup>10</sup> Thus, ESI mass analysis of the 8 and 29 kDa clusters was performed after they were oxidized by Ce(SO<sub>4</sub>)<sub>2</sub>,<sup>20</sup> so as not to miss the clusters in the neutral charge state. Figure 2b represents the ESI mass spectrum of the Au:SC<sub>12</sub> (8 kDa) clusters thus oxidized. The ESI mass spectrum is composed of two sharp peaks, attributed to intact clusters with charge states of 2+ and 1+, whereas the LDI mass spectrum exhibits a broad distribution of fragment ions Au<sub>x</sub>S<sub>y</sub><sup>+</sup> in the range of 5–10 kDa (Figure 2a). As shown in the inset of Figure 2b, the isotopomer distribution of Au<sub>38</sub>(SC<sub>12</sub>)<sub>24</sub> explains the experimentally determined molecular weight. The molecular formula is further confirmed by comparing the spectra with the mass spectrum of Au:SC<sub>6</sub> (8 kDa) (Figure 2c). The molecular weight derived from the 2+ peak can be explained by the isotopomer distribution of Au<sub>38</sub>(SC<sub>6</sub>)<sub>24</sub>. To the best of our knowledge, this is the first direct demonstration that the Au:SC<sub>n</sub> (8 kDa) clusters are composed of a single species with a formula of Au<sub>38</sub>(SC<sub>n</sub>)<sub>24</sub>. It is worth noting that the as-prepared Au:SC<sub>n</sub> (8 kDa) are also composed of cations with the same formula, [Au<sub>38</sub>(SC<sub>n</sub>)<sub>24</sub>]<sup>z</sup>, with z ≥ 0 (Figure S2). Oxidation by Ce(SO<sub>4</sub>)<sub>2</sub> resulted in little change of the optical spectrum and a small increase in the relative population of the z = 2+ state (Figure S2). Thus, the reaction with Ce(SO<sub>4</sub>)<sub>2</sub> mostly contributed to the increase in the count rate of the ion signals. It is a formidable task to quantitatively evaluate the charge distribution of [Au<sub>38</sub>(SC<sub>n</sub>)<sub>24</sub>]<sup>z</sup>, because the relative intensities of the mass peaks of different charge states (Figures 2b,c, and S2) are dependent on the conditions of preparation and storage and the ion optics of the mass spectrometer.

The Au:SC<sub>12</sub> (29 kDa) clusters were also analyzed by ESI-MS after oxidation with Ce(SO<sub>4</sub>)<sub>2</sub> (Figure 3b). A series of sharp peaks due to the charge states from 2+ to 4+ can be seen in Figure 3b, from which the molecular weight of the intact form is calculated to be 40250 ± 50 Da. It is not trivial to assign the molecular weight to a certain molecular formula(s) out of many possibilities, mainly due to limitation of the resolution of our mass spectrometer. In an effort to facilitate assignment, the mass spectrum was compared to those of Au:SC<sub>n</sub> (29 kDa) with n = 6 and 10. Figure 3c compares the molecular weights derived from the 3+ mass spectral peaks of Au:SC<sub>6</sub>, Au:SC<sub>10</sub>, and Au:SC<sub>12</sub> clusters along with the molecular weights calculated for

**Table 1.** Structural Models of Au:SR Compounds Determined Previously and Proposed in This Work

formula	1's <sup>c</sup>	2's <sup>d</sup>	S anchors <sup>e</sup>	Au cores
25–18 <sup>a</sup>	<b>0</b>	<b>6</b>	<b>12</b>	<b>13</b>
38–24	0	8	16	22
	3	6	18	23
	6	4	20	24
	<b>9</b>	<b>2</b>	<b>22</b>	<b>25</b>
	12	0	24	26
102–44 <sup>b</sup>	<b>19</b>	<b>2</b>	<b>42</b>	<b>79</b>
144–59	1	19	40	105
	4	17	42	106
	7	15	44	107
	10	13	46	108
	13	11	48	109
	16	9	50	110
	19	7	52	111
	22	5	54	112
25	3	56	113	
	<b>28</b>	<b>1</b>	<b>58</b>	<b>114</b>

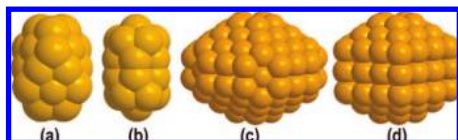
<sup>a</sup> References 15–17. <sup>b</sup> References 18, 19. <sup>c</sup> Numbers of [–SR–Au–SR–]. <sup>d</sup> Numbers of [–SR–Au–SR–Au–SR–]. <sup>e</sup> Total numbers of sulfur atoms in the oligomers.

several possible formulas. The molecular weights can be explained using the Au<sub>144</sub>(SC<sub>n</sub>)<sub>59</sub> formula. The [Au<sub>144</sub>(SC<sub>12</sub>)<sub>59</sub>]<sup>z</sup> ions with z = 2+ and 3+ were detected in the ESI mass spectra with intensities comparable to those of the as-prepared Au:SC<sub>12</sub> (29 kDa) clusters (Figure S3), whereas no anions were detected in the negative mode. This indicates that [Au<sub>144</sub>(SC<sub>12</sub>)<sub>59</sub>]<sup>z</sup> takes the charge state z ≥ 0 and that there is no distinctive preference in the charge state.

Recent single crystal XRD and theoretical studies of [Au<sub>25</sub>(SR)<sub>18</sub>]<sup>–</sup> and Au<sub>102</sub>(SR)<sub>44</sub> revealed that the Au cores are protected by [–SR–Au–SR–] (**1**) and/or [–SR–Au–SR–Au–SR–] (**2**) with “staple” motifs.<sup>15–19</sup> In [Au<sub>25</sub>(SR)<sub>18</sub>]<sup>–</sup>, 6 **2**'s are anchored to an icosahedral Au<sub>13</sub> core.<sup>15–17</sup> In Au<sub>102</sub>(SR)<sub>44</sub>, 19 **1**'s and 2 **2**'s are anchored to a D<sub>5h</sub>-symmetric Au<sub>79</sub> core (Table 1).<sup>19</sup> These results imply that the following three principles are operative in passivation of the core by oligomers **1** and **2**. First, the Au cores form highly symmetric and stable geometric structures. Second, the relative population of **2** is higher for smaller clusters, probably because smaller Au cores with larger curvature prefer protection by **2**, which has a bent structure. Third, all the surface atoms on the Au core are bound by thiolates at both ends of **1** and **2**. In [Au<sub>25</sub>(SR)<sub>18</sub>]<sup>–</sup>, 12 surface atoms of the Au<sub>13</sub> core are anchored by 12 sulfurs of the oligomers.<sup>15–17</sup> In Au<sub>102</sub>(SR)<sub>44</sub>, 42 sulfurs of the oligomers are anchored to 40 atoms of the Au<sub>79</sub> core, with some duplication (Table 1).<sup>19</sup>

In the following, we consider the geometrical structures of Au<sub>38</sub>(SC<sub>n</sub>)<sub>24</sub> and Au<sub>144</sub>(SC<sub>n</sub>)<sub>59</sub> according to the above criteria. The molecular formula of Au<sub>38</sub>(SC<sub>n</sub>)<sub>24</sub> corresponds with that predicted by Landman, based on a truncated octahedral Au<sub>38</sub> core.<sup>21</sup> Later, Garzón et al. pointed out that the Au<sub>38</sub> core is considerably deformed by thiolate ligation,<sup>22</sup> and recently Häkkinen et al. proposed a structural motif for Au<sub>38</sub>(SC<sub>12</sub>)<sub>24</sub>, in which the Au<sub>14</sub> core is fully protected by six [–Au–SC<sub>1</sub>–]<sub>4</sub> cyclic tetramers.<sup>23</sup> Motivated by the experimental results of Jadzinski et al.,<sup>18</sup> Jiang obtained a more stable form in which the Au core is protected by 6 **1**'s and 4 **2**'s.<sup>24</sup> Other combinations of **1** and **2** also give the formula Au<sub>38</sub>(SC<sub>n</sub>)<sub>24</sub> (see Table 1). Among these possibilities, we propose a structure in which 9 **1**'s and 2 **2**'s protect a closed-shell Au<sub>25</sub> core with face-centered-cubic (Figure 4a), bi-icosahedral (Figure 4b), or bicapped icosahedral (not shown) motifs, as indicated by boldface in Table 1. According to the above principle, the icosahedral-based core is more plausible since the number of surface atoms of these Au<sub>25</sub> cores is 22, whereas that of the fcc Au<sub>25</sub> core is 24.





**Figure 4.** Models for the Au cores of  $\text{Au}_{38}(\text{SR})_{24}$  and  $\text{Au}_{144}(\text{SR})_{59}$ : (a) fcc  $\text{Au}_{25}$ ; (b) bi-icosahedral  $\text{Au}_{25}$ ; (c) m-Dh  $\text{Au}_{144}$ ; (d) I-Dh  $\text{Au}_{114}$ .

It has been suggested, from LDI-MS and elemental analysis, that the compositions of the 29 kDa clusters lie within the range of  $\text{Au}_{140-146}(\text{SC}_n)_{50-60}$ .<sup>2h,4</sup> Powder XRD analysis, high-resolution transmission electron microscopy, and theoretical simulation have suggested the formation of a Marks-decahedral (m-Dh)  $\text{Au}_{146}$  core.<sup>2h,21a,b</sup> In this model, thiolates are assumed to be adsorbed on 10 (111) and 5 (100) crystalline facets of the m-Dh  $\text{Au}_{146}$  core, according to the conventional adsorption model of thiolates on extended Au surfaces.<sup>25</sup> The core size,  $\text{Au}_{144}$ , determined here may suggest that the two Au atoms located at the apex sites of the m-Dh  $\text{Au}_{146}$  are removed (Figure 4c). However, we propose another structure in the framework of the oligomer-protected model. As for  $\text{Au}_{144}(\text{SC}_n)_{59}$ , there are 10 possible combinations of **1** and **2**, as shown in Table 1. Among these possibilities, the structure in which the  $\text{Au}_{114}$  core is protected by 28 **1**'s and 1 **2** is most probable (indicated by boldface in Table 1). This is because the stable  $\text{Au}_{114}$  core can be constructed by removing two atoms from the apex sites of an Ico-decahedral (i-Dh)  $\text{Au}_{116}$  (Figure 4d). Interestingly, i-Dh  $\text{Au}_{114}$  is comprised as a partial structure in m-Dh  $\text{Au}_{144}$  (Figure 4c). Thus, this core also explains the previous experimental results; the XRD pattern of the 29 kDa clusters is reproduced by that of i-Dh  $\text{Au}_{116}$  theoretically simulated.<sup>21a</sup> While the relative population of **1** in  $\text{Au}_{144}(\text{SC}_n)_{59}$  is higher than that in  $\text{Au}_{102}(\text{SR})_{44}$  as expected, 58 sulfur atoms anchor to 75 surface atoms of i-Dh  $\text{Au}_{116}$ .

In summary, we have demonstrated that a mass spectrometric approach, which employs nondestructive ESI, is highly effective for determining the molecular formula and charge states of hydrophobic  $\text{Au}:\text{SC}_n$  clusters. The 8 and 29 kDa clusters have been determined as being composed of  $[\text{Au}_{38}(\text{SC}_n)_{24}]^z$  and  $[\text{Au}_{144}(\text{SC}_n)_{59}]^z$ , with charge states  $z \geq 0$ , respectively. Structural models are proposed, in which highly symmetrical, stable cores are fully protected by staple oligomers **1** and **2**.<sup>26</sup> The preferential formation of the 8 and 29 kDa clusters may be associated with high stability due to geometrical factors. Structures similar to these interface structures can be found in Au(I)-thiolate oligomers<sup>27</sup> and thiolate monolayers on a Au(111) surface; recent experimental and theoretical studies have shown the existence of AuSR monomers and  $-\text{SR}-\text{Au}-\text{RS}-$  monomers on a Au(111) surface.<sup>28</sup> These suggest that the Au-thiolate interface takes on common motifs, regardless of the size of the underlying Au core.

**Note Added in Proof.** We have recently become aware that a face-fused bi-icosahedral  $\text{Au}_{23}$  core has been theoretically predicted for  $\text{Au}_{38}(\text{SR})_{24}$  by Y. Pei et al. (*J. Am. Chem. Soc.* **2008**, *130*, 7830–7832).

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**Supporting Information Available:** Experimental procedures and characterization results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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