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Structural evolution of glutathionate-protected gold clusters studied by means of ^{197}Au Mössbauer spectroscopy

Norimichi Kojima · Yasuhiro Kobayashi · Yuichi Negishi · Makoto Seto · Tatsuya Tsukuda

Abstract ^{197}Au Mössbauer spectra of a series of glutathionate-protected gold clusters, $Au_n(SG)_m$, with $n = 10 - {\sim}55$, were re-analyzed to understand the structure evolution behavior. The numbers of gold atoms coordinated by different numbers (0, 1, and 2) of the GS ligands were successfully determined by assuming individual isomer shifts and quadrupole splittings for the three sites in $Au_{25}(SG)_{18}$ (Tsukuda et al., Chem Lett 40:1292, 2011). The analysis revealed the drastic structural evolution of $Au_n(SG)_m$ in the range of $n = 10 - {\sim}55$. In $Au_{10}(SG)_{10}$, all the gold atoms are bonded to GS ligands, indicating –Au–S(G)– cyclic structures. A catenane structure was proposed for $Au_{10}(SG)_{10}$. At $n = 25$, a single Au atom without the GS ligation appeared, consistent with the formation of an icosahedral Au_{13} core protected by six staples, –S(G)–[Au–S(G)–]$_2$. At $n = 39$, it is considered that $Au_{39}(SG)_{24}$ has a similar structure to that of $Au_{38}(SC_2H_4Ph)_{24}$ with face-fused bi-icosahedral Au_{23} core.

Keywords Gold cluster · ^{197}Au Mössbauer spectroscopy · Nanomaterial

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N. Kojima (✉)
Graduate School of Arts and Sciences, The University of Tokyo, Tokyo 153-8902, Japan
e-mail: cnori@mail.ecc.u-tokyo.ac.jp

Y. Kobayashi · M. Seto
Research Reactor Institute, Kyoto University, Osaka 590-0949, Japan

Y. Negishi
Department of Applied Chemistry, Faculty of Science,
Tokyo University of Science, Tokyo 162-8601, Japan

T. Tsukuda
Department of Chemistry, Graduate School of Science,
The University of Tokyo, Tokyo 113-0033, Japan
e-mail: tsukuda@chem.s.u-tokyo.ac.jp

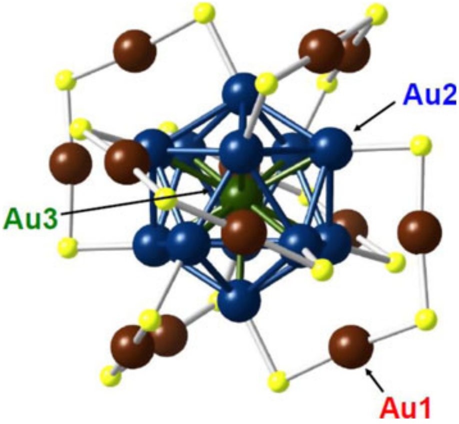

Fig. 1 Structural framework of $Au_{25}(SR)_{18}$ [10–12]. Large and small balls represent Au and S atoms, respectively. The R group is omitted for simplicity

1 Introduction

In the last few decades, thiolate (RS)-protected small Au clusters composed of less than 100 atoms have attracted much attention as a prototypical system for fundamental studies on quantum size effect and as a building block of nanoscale devices [1–3]. Among thiolate-protected Au clusters, the $Au_{25}(SR)_{18}$ cluster has been studied most extensively as a prototype system of stable $Au_n(SR)_m$ clusters [4–7]. In 2007, the present authors proposed the structure of $Au_{25}(SG)_{18}$ by ^{197}Au Mössbauer spectroscopy [8], based on the "core-in-cage" model theoretically predicted by Iwasa and Nobusada; the planar Au_7 core is sandwiched between two $–[Au–S(R)–]_3$ cyclic oligomers and surrounded by one $–[Au–S(R)–]_{12}$ cyclic oligomer [9]. Then, the geometrical structure of $Au_{25}(SC_2H_4Ph)_{18}$ was determined by single-crystal X-ray diffraction [10, 11] and by theoretical calculation [12]; $Au_{25}(SR)_{18}$ was found to be composed of an icosahedral Au_{13} core whose surface atoms are completely protected by six staples, $–S(R)–[Au–S(R)–]_2$ (Fig. 1). Close inspection of Fig. 1 shows that the Au atoms in $Au_{25}(SR)_{18}$ are classified into three in terms of chemical environment: twelve Au atoms on the outermost layer, which are bound by two thiolates (**Au1**, red ball); twelve Au atoms at the core surface, each of which are bound by a single thiolate (**Au2**, blue ball); and a single central Au atom at the core (**Au3**, green ball). The ^{197}Au Mössbauer spectrum of $Au_{25}(SG)_{18}$ was reanalyzed by assuming the contribution of the above three components [13]. Importantly, the analysis quantitatively gave the numbers of Au atoms in each category, suggesting that ^{197}Au Mössbauer spectroscopy is a powerful tool for structural characterization of $Au_n(SR)_m$. In the present work, we studied the structure evolution of $Au_n(SG)_m$ ($n = 10 - \sim 55$) by extending the above idea.

2 Experimental

The $Au_n(SG)_m$ samples with $(n, m) = (10, 10), (15, 13), (18, 14), (22, 16), (22, 17), (25, 18), (29, 20), (33, 22), (39, 24), (45, 28)$, and $(\sim 55, m)$ [14] were fractionated from nearly monodisperse Au:SG clusters ($d_{av} \sim 1$ nm), using polyacrylamide gel electrophoresis (PAGE) [4, 15]. In order to obtain the ^{197}Au Mössbauer spectra

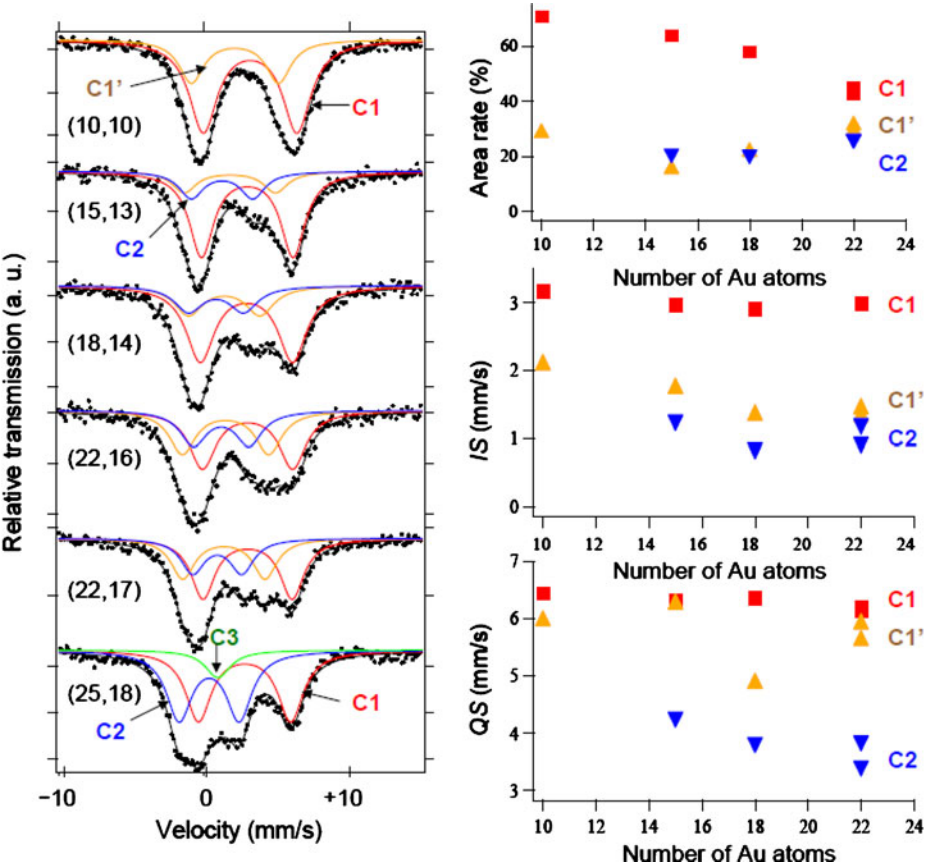

Fig. 2 ^{197}Au Mössbauer spectra and the corresponding Mössbauer parameters (*IS*, *QS*, area) of $\mathrm{Au}_n(\mathrm{SG})_m$ $(n = 10 - 25)$

with sufficient S/N ratio, each cluster sample was accumulated up to 50–100 mg by repeating the elaborative PAGE procedure [8].

^{197}Au Mössbauer measurements were carried out at the Research Reactor Institute of Kyoto University. The γ-ray source (77.3 keV), ^{197}Pt, was generated by neutron irradiation to a 98 %-enriched ^{196}Pt metal foil. The γ-ray source and samples were cooled down to 16 K. The isomer shift (*IS*) of Au foil was referenced to 0 mm/s. The spectra were calibrated and referenced by using the six lines of a body-centered cubic iron foil (α-Fe). Mössbauer spectra were fitted with a MossWinn 3.0 program [16].

3 Results

Figures 2 and 3 show the ^{197}Au Mössbauer spectra of $\mathrm{Au}_n(\mathrm{SG})_m$ with $n = 10 - 25$ and $25 - {\sim}55$, respectively. The ^{197}Au Mössbauer spectra of a series of $\mathrm{Au}_n(\mathrm{SG})_m$

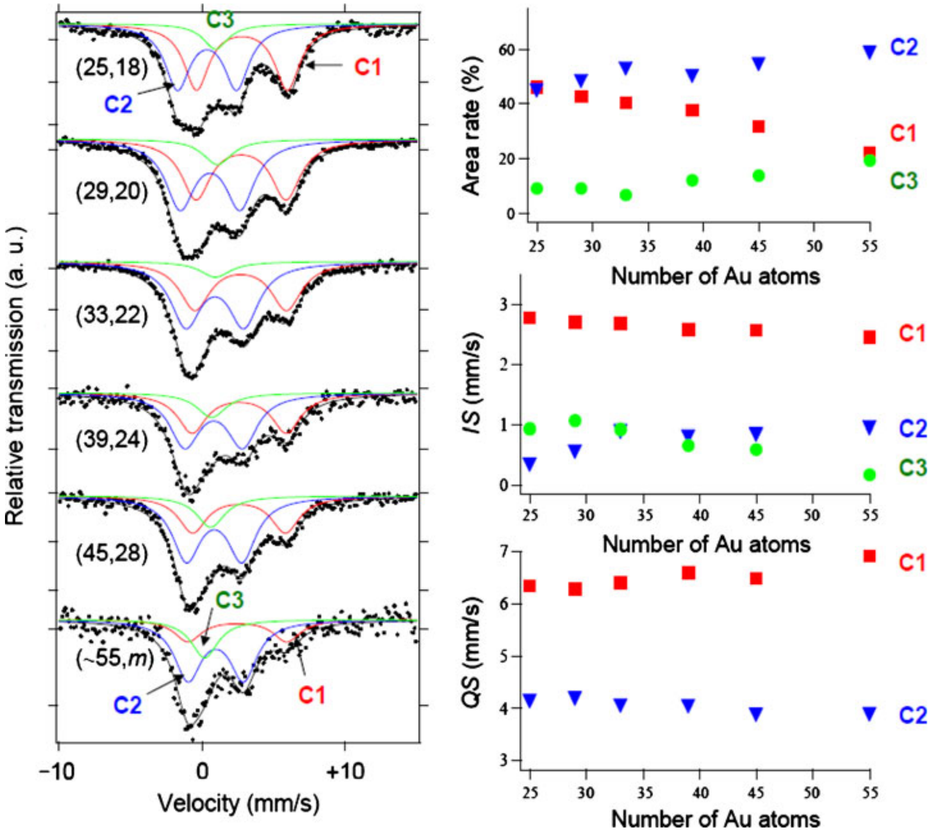

Fig. 3 ^{197}Au Mössbauer spectra and the corresponding Mössbauer parameters (*IS*, *QS*, area) of $\mathrm{Au}_n(\mathrm{SG})_m$ ($n = 25- \sim 55$)

evolve appreciably as a function of the core size. These spectra were analyzed on the basis of the following assumptions:

(1) The $\mathrm{Au}_n(\mathrm{SG})_m$ clusters are composed of three types of Au atoms, depending on the number of coordinated thiolates (2, 1, and 0) for **Au1**, **Au2**, and **Au3**, respectively (Fig. 1). That is, **Au1**, **Au2**, and **Au3** correspond to the Au atoms in the –S(G)–Au– oligomers, at the surface of the Au core, and within the Au core, respectively.

(2) These three sites should exhibit different isomer shift (*IS*) and quadrupole splitting (*QS*), due to the difference in the density of s-electrons at the nucleus and the symmetry of charge distribution around the nucleus, respectively. The analysis of $\mathrm{Au}_{25}(\mathrm{SG})_{18}$ gave the following Mössbauer parameters: $IS = 2.78$ mm/s and $QS = 6.35$ mm/s for **Au1**; $IS = 0.34$ mm/s and $QS = 4.14$ mm/s for **Au2**; and $IS = 0.94$ mm/s and $QS = 0.00$ mm/s for **Au3** [13]. These Mössbauer parameters for **Au1** are similar to those of Au(I) coordinated by two sulfur atoms [17].

Table 1 ^{197}Au Mössbauer parameters of $\mathrm{Au}_n(\mathrm{SG})_m$ at 16 K

(n, m)	Component **C1**			Component **C1'**			Component **C2**			Component **C3**		
	IS^a	*QS*^{a}	Area^b	*IS*^{a}	*QS*^{a}	Area^b	*IS*^{a}	*QS*^{a}	Area^b	*IS*^{a}	*QS*^{a}	Area^b
(10, 10)	3.16	6.45	70.8	2.12	6.00	29.2						
(15, 13)	2.96	6.31	63.9	1.77	6.29	16.1	1.23	4.23	20.1			
(18, 14)	2.91	6.36	57.8	1.38	4.91	22.4	0.82	3.79	19.7			
(22, 16)	2.99	6.21	42.7	1.47	5.95	32.0	1.17	3.82	25.4			
(22, 17)	2.99	6.14	44.7	1.36	5.66	29.9	0.90	3.38	25.4			
(25, 18)	2.78	6.36	46.1				0.34	4.14	44.8	0.94	0.0	9.1
(29, 20)	2.72	6.29	42.7				0.55	4.18	48.2	1.07	0.0	9.1
(33, 22)	2.69	6.40	40.0				0.89	4.05	52.8	0.92	0.0	6.7
(39, 24)	2.59	6.60	37.8				0.80	4.04	50.1	0.66	0.0	12.1
(45, 28)	2.58	6.49	31.8				0.84	3.88	54.4	0.59	0.0	13.8
(∼55, *m*)	2.46	6.91	22.1				0.95	3.89	58.6	0.17	0.0	19.3

^{a}in mm/s. ^{b}in %

Table 2 Estimated numbers of Au atoms for the **Au1**, **Au2**, and **Au3** sites in $\mathrm{Au}_n(\mathrm{SG})_m$ ($n = 10 - {\sim}55$)

(n, m)	Number of Au atoms		
	N(**Au1**)	*N*(**Au2**)	*N*(**Au3**)
(10, 10)	10	0	0
(15, 13)	12	3	0
(18, 14)	14	4	0
(22, 16)	17	5	0
(22, 17)	17	5	0
(25, 18)	12	12	1
(29, 20)	13	15	1
(33, 22)	14	18	1
(39, 24)	16	21	2
(45, 28)	15	27	3
(∼55, *m*)	∼13	∼37	5

In this manner, the line profile of ^{197}Au Mössbauer spectra for $\mathrm{Au}_{25}(\mathrm{SG})_{18}$ can be reproduced well by the superposition of a singlet corresponding to the **Au3** site and two doublets corresponding to the **Au1** and **Au2** sites.

In the case of $\mathrm{Au}_{10}(\mathrm{SG})_{10}$, the asymmetric doublet profile could be fitted by a superposition of two sets of doublets. The *IS* and *QS* values obtained are 3.06 and 6.68 mm/s, respectively, for the major component (**C1**), whereas those for the minor component (**C1'**) are 2.48 and 5.71 mm/s, respectively. According to the correlation between the *IS* and *QS* values established for various kinds of Au(I) and Au(III) compounds, both components fall into a category of **Au1** directly coordinated by two SG ligands [17].

The spectra of $\mathrm{Au}_n(\mathrm{SG})_m$ ($15 \leq n \leq 22$) were fitted by three sets of doublets. Two components, **C1** and **C1'**, were assigned to **Au1**, as the *IS* and *QS* values correlate smoothly with those of $\mathrm{Au}_{10}(\mathrm{SG})_{10}$. The third component, **C2**, having the smallest *IS* and *QS* values, was assigned to **Au2**, which correlates smoothly with the **C2** in $\mathrm{Au}_{25}(\mathrm{SG})_{18}$.

The spectral profile abruptly changes on going from $\mathrm{Au}_{22}(\mathrm{SG})_{16}$ to $\mathrm{Au}_{25}(\mathrm{SG})_{18}$, which is attributed to the appearance of a **Au3** site without the GS ligation. The ^{197}Au Mössbauer spectra from $\mathrm{Au}_{25}(\mathrm{SG})_{18}$ to $\mathrm{Au}_{\sim55}(\mathrm{SG})_m$ were fitted by two sets of doublets and a singlet. The ^{197}Au Mössbauer parameters of $Au_n(SG)_m$ ($n = 10 - {\sim}55$) are listed in Table 1.

In order to estimate the number of Au atoms in the **Au1**, **Au2**, and **Au3** sites for $Au_n(SG)_m$, the relative ratio of recoil-free fractions was determined from the analysis of the $Au_{25}(SG)_{18}$ spectrum. The ratio of the recoil-free fractions was determined to be f(**Au1**): f(**Au2**): f(**Au3**) = 1.03: 1.00: 2.44 by dividing the spectral areas of **C1**, **C2**, and **C3** (46.1 %, 44.8 %, 9.1 %) with the numbers of Au atoms (12, 12, 1) for the **Au1**, **Au2**, and **Au3** sites determined by the X-ray structural analysis [10, 11]. The numbers of Au atoms for the **Au1**, **Au2**, and **Au3** sites for other $Au_n(SG)_m$ were estimated on the basis of these recoil-free fractions; they are summarized in Table 2.

4 Discussion

In the following, we discuss the structural evolution of $Au_n(SG)_m$ with increase in n, on the basis of Table 2.

***n* = 10** The absence of **Au2** and **Au3** in $Au_{10}(SG)_{10}$ clearly indicates that it has a cyclic –Au–SG– structure. The presence of two types of **Au1** (**C1** and **C1'**) suggests that there are two different environments for Au atoms bonded by two thiolates. There are two possible scenarios to explain this observation, based on the density functional theory calculation for $Au_{10}(SCH_3)_{10}$ [18]. The first scenario is the formation of a catenane structure consisting of two interlocked pentamers. In the case of two interlocked pentamers, $2[Au_5(SCH_3)_5]$, there are two Au–S distances: 2.40 Å for the Au atom at the center of the ring and 2.35 Å for the others [18]. In the case of ^{197}Au Mössbauer spectrum, *IS* shifts to the lower velocity side, and *QS* decreases with increasing Au–S distance [17]. Therefore, **C1'** and **C1** should be attributed to the center Au site of the ring and the others, respectively, where the numbers of Au atoms for **C1'** and **C1** are estimated to be 2.92 and 7.08, respectively, on condition that the recoil-free fractions for the center Au site of the ring and the others are the same. These numbers are almost consistent with the numbers of the center Au site of the ring and the others (2 and 8). The second and less probable scenario is a contribution from cyclic oligomers with different lengths as minor fractions, such as $Au_{11}(SG)_{11}$ and $Au_{12}(SG)_{12}$ [4].

***n* = 15 − 22** The first appearance of **Au2** at $Au_{15}(SG)_{13}$ indicates that the formation of small Au aggregates starts at this critical size. There are two notable features in Table 2. First, the numbers of **Au2** for $Au_{15}(SG)_{13}$, $Au_{22}(SG)_{16}$, and $Au_{22}(SG)_{17}$ are not even, but odd. This indicates that at least one of the –SR–Au oligomers attached to the Au core has an open structure. The second feature is that the numbers of the **Au1** and thiolates are nearly equivalent: (N (**Au1**), m) = (12, 13), (14, 14), (17, 16), and (17, 17) for $Au_{15}(SG)_{13}$, $Au_{18}(SG)_{14}$, $Au_{22}(SG)_{16}$, and $Au_{22}(SG)_{17}$, respectively. This result excludes the possibility that Au cores are protected by –S(G)–(Au–S(G)–)$_{1,2,3}$ oligomers in a bidentate fashion, but indicates the attachment of –SR–Au oligomers to the Au end. Instability of $Au_n(SG)_m$ with $n = 15 - 22$ against etching by GSH [5] is probably associated with such structures. Garzón predicted that the most stable structure of $Au_{18}(SMe)_{14}$ consists of a prolate Au_8 core covered with two dimer (–S(R)–Au–S(R)–Au–S(R)–) and two trimer (–S(R)–Au–S(R)–Au–S(R)–Au–S(R)–) motifs [19]. This calculation indicates that 10 and 8

Au atoms belong to **Au1** and **Au2**, respectively. Although this model explains a high stability, it is not consistent with our Mössbauer results (Table 2).

$n = 25 - {\sim}55$ At $Au_{25}(SG)_{18}$, two notable transitions are observed: a **Au3** atom appears for the first time, and the ratio of N (**Au1**) with respect to m decreases significantly from ~1. As already established by X-ray crystallography [10, 11], these changes are related to the formation of a 3-dimensional Au_{13} icosahedral core and its protection by –S(G)–[Au–S(G)–$]_2$ in a bidentate fashion. For $Au_{29}(SG)_{20}$ and $Au_{33}(SG)_{22}$, bidentate oligomers are probably bonded on the Au_{16} and Au_{19} core, respectively, because the ratios of N (**Au1**) with respect to m for $Au_{29}(SG)_{20}$ and $Au_{33}(SG)_{22}$ are similar to that of $Au_{25}(SG)_{18}$. However, at least one surface atom of the Au_{16} core for $Au_{29}(SG)_{20}$ is bonded by a linear oligomer in a monodentate fashion, as the N (**Au2**) value is odd. For $Au_{33}(SG)_{22}$, we cannot construct a satisfactory model in which all the core surface atoms are completely protected by bidentate –S(G)–(Au–S(G)–$)_{1,2,3}$ oligomers. The imperfectness of these structures is the origin of the chemical instability of $Au_{29}(SG)_{20}$ and $Au_{33}(SG)_{22}$ against etching by an excess amount of GSH [5].

At $Au_{39}(SG)_{24}$, the number of **Au3** increases from 1 to 2, suggesting that a structural transition occurs at this size. The estimated numbers (16, 21, 2) of Au atoms for the **Au1**, **Au2**, and **Au3** sites for $Au_{39}(SG)_{24}$ are almost consistent with those for $Au_{38}(SC_2H_4Ph)_{24}$, whose structure was determined by the single-crystal X-ray diffraction [20]. The geometrical structure of $Au_{38}(SC_2H_4Ph)_{24}$ is based on a face-fused bi-icosahedral Au_{23} core, which is protected by three monomeric staples (–S(R)–Au–S(R)–) and six dimeric staples (–S(R)–[Au–S(R)–$]_2$). In this geometrical structure, the numbers of Au atoms for the **Au1**, **Au2**, and **Au3** sites are 15, 21, and 2, respectively. Consequently, $Au_{39}(SG)_{24}$ and $Au_{38}(SG)_{24}$ present in the sample [14] would have similar and identical structures to that of $Au_{38}(SC_2H_4Ph)_{24}$ [20].

5 Conclusion

The evolution of the geometrical structures of glutathionate-protected gold clusters, $Au_n(SG)_m$, in a $n = 10 - {\sim}55$ size range, was studied by using ^{197}Au Mössbauer spectroscopy. Successful analysis of the $Au_{25}(SG)_{18}$ spectrum, based on the crystallographically determined structure [13], enabled us to estimate quantitatively the numbers of gold atoms coordinated by different numbers (0, 1, and 2) of GS ligands for other $Au_n(SG)_m$ clusters. In $Au_{10}(SG)_{10}$, all the gold atoms are bonded to GS ligands, indicating –Au–S(G)– cyclic structures. A catenane structure was proposed for $Au_{10}(SG)_{10}$. At $n = 15$, gold atoms bonded to a single GS ligand appeared, suggesting the formation of small clusters. At $n = 25$, a single Au atom without the GS ligation appeared, consistent with the formation of an icosahedral Au_{13} core protected by six staples, –S(G)–[Au–S(G)–$]_2$. At $n = 39$, the number of Au atoms increased from one to two. This change suggests that $Au_{39}(SG)_{24}$ has a similar structure to that of $Au_{38}(SC_2H_4Ph)_{24}$ with face-fused bi-icosahedral Au_{23} core. These results demonstrate that ^{197}Au Mössbauer spectroscopy will provide detailed information on the structures of thiolated Au clusters whose single crystals are difficult to make.

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