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^{197}Au Mössbauer Spectroscopy of $Au_{25}(SG)_{18}^{-}$ Revisited

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Reanalysis of the ^{197}Au Mössbauer spectrum of $Au_{25}(SG)_{18}^{-}$ (SG: glutathionate) based on the structure determined by single-crystal XRD analysis gave a reasonable fit, demonstrating that ^{197}Au Mössbauer spectroscopy is a powerful tool for predicting the structural motifs of thiolate-protected Au clusters.

A gold thiolate compound that consists of 25 gold atoms and 18 thiolates ($Au_{25}(SR)_{18}$) has been extensively studied as a prototype of stable $Au_n(SR)_m$ clusters. It was originally assigned as $Au_{28}(SR)_{16}$ by Whetten[1] and Tsukuda[2] and as $Au_{38}(SR)_{24}$ by Murray.[3] In 2005, Tsukuda corrected the assignment to $Au_{25}(SG)_{18}$ (SG: glutathionate) based on electrospray ionization mass spectrometric analysis[4] and demonstrated selective production on a sub-100 mg scale.[5] Selective synthesis of $Au_{25}(SR)_{18}$ is now well established by size-focused processing of larger $Au_n(SR)_m$ clusters.[6,7] In 2007, we studied the structures of $Au_{25}(SG)_{18}$ by ^{197}Au Mössbauer spectroscopy.[8] We analyzed the spectrum based on the "core-in-cage" model theoretically predicted by Nobusada in which the Au_7 core is enclosed by two $-[Au-S(R)-]_3$ cyclic oligomers and one $-[Au-S(R)-]_{12}$ cyclic oligomer.[9] In 2008, Murray[10] and Jin[11] determined the geometrical structure of $Au_{25}(SC_2H_4Ph)_{18}$ by single-crystal X-ray diffraction. Independently, the same structure was theoretically predicted by Häkkinen and Grönbeck.[12] These groundbreaking studies revealed that $Au_{25}(SR)_{18}$ consists of an icosahedral Au_{13} core and six oligomers $-S(R)-[Au-S(R)-]_2$ on the surface (Figure 1A). $Au_{25}(SR)_{18}$ was found to prefer the -1 charge state.[10–14] This preference was explained in terms of the closure of the electronic structures in which the eight Au 6s electrons occupy superatom orbitals with S and P characters ($1S^2 1P^6$).[12,15] This paper reports the results of reanalysis of the ^{197}Au Mössbauer spectrum of $Au_{25}(SG)_{18}^{-}$ based on the new structural model shown in Figure 1A.

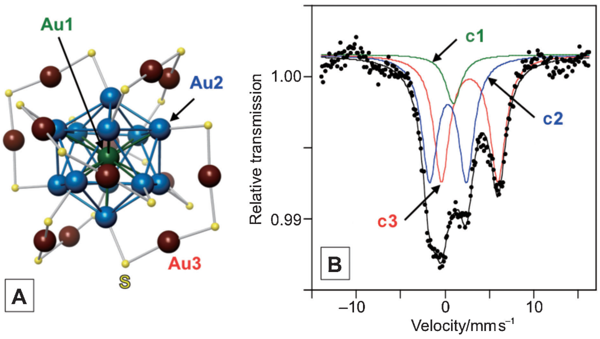

Figure 1. (A) Core structure of $Au_{25}(SR)_{18}^{-}$. Large and small spheres represent Au and S atoms, respectively. The R group is omitted for simplicity. (B) ^{197}Au Mössbauer spectrum of $Au_{25}(SG)_{18}^{-}$.

The $Au_{25}(SG)_{18}$ samples used in a previous ^{197}Au Mössbauer study[8] should be assigned to negatively charged clusters, $Au_{25}(SG)_{18}^{-}$, based on optical spectroscopy results.[14] Figure 1B shows a ^{197}Au Mössbauer spectrum of $Au_{25}(SG)_{18}^{-}$ obtained at 16 K.[8] The isomer shift (*IS*) of a gold foil was referenced as 0 mm s^{-1}. The Au atoms in $Au_{25}(SG)_{18}^{-}$ can be classified into three categories based on the number of thiolates they are directly bonded to: a single central Au atom of the core, which is not bound to any thiolates (**Au1**; green ball in Figure 1A); 12 Au atoms at the core surface, each of which is bound to a single thiolate (**Au2**; blue balls in Figure 1A); and 12 Au atoms on the outermost layer, each of which is bound to two thiolates (**Au3**; red balls in Figure 1A).[10–12] These three sites have different *IS* and quadrupole splittings (*QS*) reflecting the different densities of s electrons at the nucleus and the different symmetries of the charge distribution around the nucleus, respectively.[16] Based on symmetry considerations, **Au1** and **Au2**/**Au3** atoms will produce a singlet peak ($QS = 0$) and doublet peaks, respectively. Thus, the spectrum was fitted by a superposition of a single Lorentzian and two sets of Lorentzian doublets; all the components were assumed to have the same full width at half-maximum. Even under such constrained conditions, there were several possible fits (data not shown). However, only a single fit gave reasonable *IS* and *QS* values that satisfy the empirical correlation for various Au^{I} compounds.[16] Figure 1B shows the best fitting result, which reproduces the experimental data by superposing the three components **c1**–**c3**. Table 1 lists the optimized Mössbauer parameters for each component. The singlet component **c1** is assigned to **Au1**. The *IS* value of **Au1** (0.94 mm s^{-1}) is much larger than those of bulk gold ($IS =$ 0 mm s^{-1}) and of the Au_{13} core of $Au_{55}(PPh_3)_{12}Cl_6$ ($IS = -0.22$ mm s^{-1}).[17] This suggests that the 6s electron density increases in the vicinity of the central atom, which is consistent with two s electrons being accommodated in 1S superatom orbitals.[12,15] The

Table 1. Mössbauer parameters for each component

Component	*IS* /mm s^{-1}	*QS* /mm s^{-1}	*P* /%	*FWHM* /mm s^{-1}
c1	0.94	0.00[a]	9.1	2.11
c2	0.34	4.14	44.8	2.11
c3	2.78	6.35	46.1	2.11

[a]This value is constrained in the fitting.

doublets **c3** are assigned to **Au3** because their *IS* and *QS* values are similar to those ($IS = 3.04\,\mathrm{mm\,s^{-1}}$; $QS = 6.67\,\mathrm{mm\,s^{-1}}$) of $Au_{10}(SG)_{10}$ in which Au is bound to two thiolates.[18] The remaining doublets **c2** are assigned to **Au2**. **c2** has smaller *IS* and *QS* values than **c3**, which suggests that **Au2** is less cationic than **Au3**. From the spectral areas, the numbers of Au atoms for **c1**, **c2**, and **c3** were estimated to be 2.3, 11.2, and 11.5, respectively. These numbers agree well with the numbers of Au atoms of **Au1**, **Au2**, and **Au3** determined by XRD analysis (1, 12, and 12, respectively; see Figure 1A). The slight overestimation of the **Au1** population is ascribed to the larger recoilless fraction of the central atom due to it being more strongly bound to the lattice framework than **Au2** and **Au3**.

Single-crystal XRD analysis of $Au_{38}(SR)_{24}$ and $Au_{102}(SR)_{44}$ has revealed that the Au atoms of stable $Au_n(SR)_m$ can be classified into three substructures (**Au1**–**Au3**) as in the case of $Au_{25}(SR)_{18}$ although the lengths of the oligomer –S(R)–[Au–S(R)–]$_2$ depend on the cluster size.[19,20] Successful analysis of $Au_{25}(SG)_{18}^-$ encourages us to estimate the numbers of Au atoms in each substructure by ^{197}Au Mössbauer spectroscopy. Such information in conjunction with the empirical building-up principle[21,22] will provide important data for developing structural models of stable $Au_n(SR)_m$ clusters.

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