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Study on the structural evolution of thiolate-protected gold clusters by means of ^{197}Au Mössbauer spectroscopy

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

Biography

Norimichi Kojima has completed his PhD from Kyoto University, Japan. In 1994, he was appointed as a full Professor, and the Vice-President between 2009 and 2011, the University of Tokyo, and became the Emeritus Professor in 2015. After retiring from the University of Tokyo, he moved to Toyota Physical and Chemical Research Institute, as a fellow. His current interests include the electronic and structural properties of nanoparticles by means of Mössbauer Spectroscopy.

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