Scientists reveal the inter-cluster and intra-cluster dynamics of thiolate-protected gold-silver alloys

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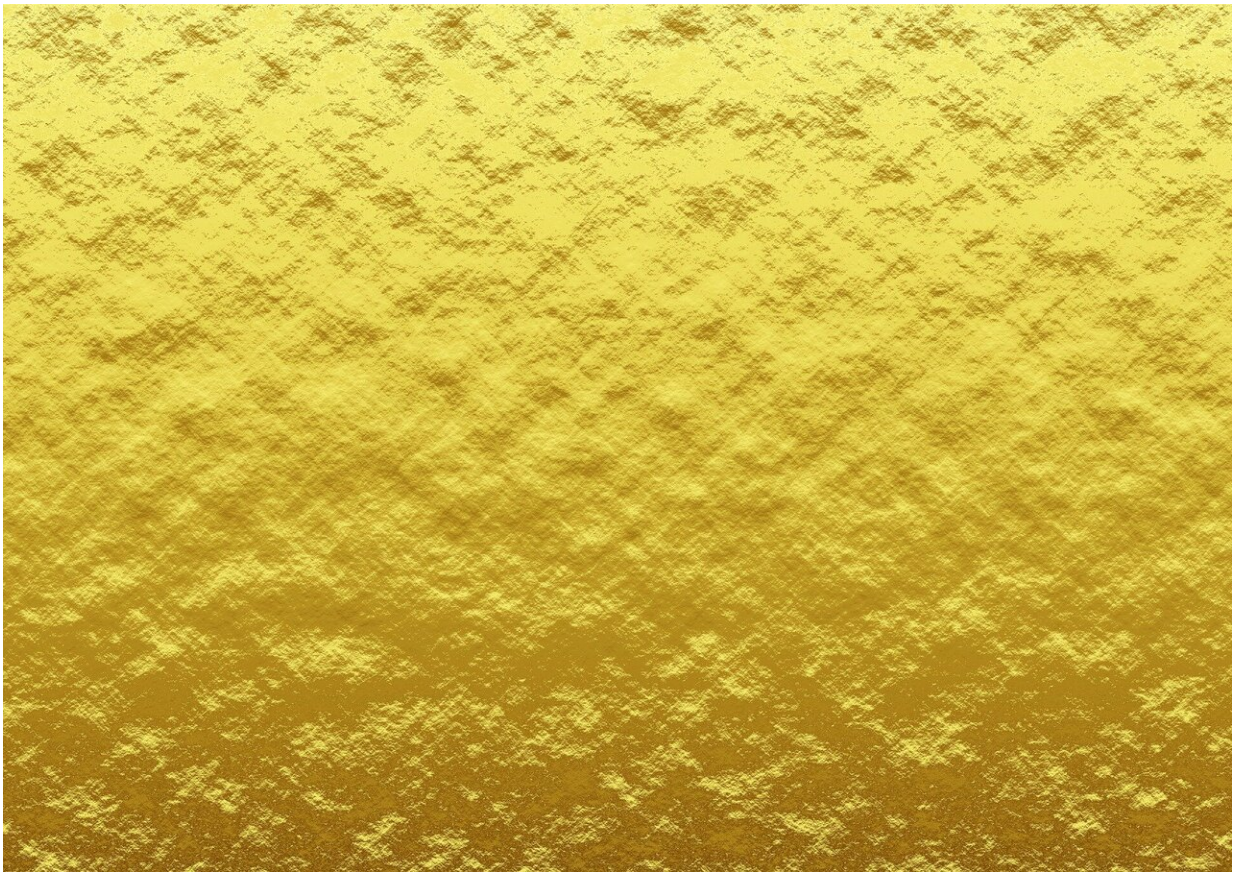

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From effective medicines to molecular sensors to fuel cells, metal

clusters are becoming fundamentally useful in the health, environment, and energy sectors. This diverse functionality of clusters arises from the variability in size and type. Now, scientists led by Professor Yuichi Negishi, of the Department of Applied Chemistry at Tokyo University of Science, add to this ongoing tale by explaining the dynamics of the metal cluster thiolate-protected gold-silver alloy in solution. This helps in understanding the stability, geometry, and tenability of these clusters for their applications.

Metal clusters are formed when metal atoms come together to form clumps, somewhere between the size of a molecule and that of a bulk solid. Recently, these clusters have gained a lot of attention owing to their diverse chemical capabilities that depend on their size and composition. Unlike the closed, set, and stable packing observed in bulk metal lattices, the geometry of these clusters, which often governs their chemical reactivity too, is based on special atomic arrangements that minimize energy. Furthermore, their functionalities vary depending on the number of constituent atoms in the cluster. Because these micro-level factors govern the ultimate macro-level activity of the clusters, understanding cluster dynamics at the atomic scale is essential. Recent exploration in the field of such metal clusters has enabled the cataloging of these clumps as compounds of defined chemical compositions.

One such interesting metal cluster with catalytic properties and luminescence is the thiolate-protected gold-silver alloy cluster. These metal clusters are formed when thiolate-protected individual gold and silver clusters are kept together in a solution. The individual pure clusters undergo metal exchange, like a chemical "barter": a gold for a silver atom. While the cluster-metal complex reaction (CMCR) method is widely used, the actual dynamics of it and the energy incentive driving such processes are not understood. This became the seed of curiosity for Prof. Negishi's team, as they state, "the dynamic behavior of these clusters in solution must be taken into consideration to understand the

origins of the catalytic activity and luminescence properties of gold-silver alloy clusters in addition to the geometric structure."

To illuminate the metal exchange behavior between the pure clusters after synthesis, the team devised an experiment based on reverse-phase chromatography. They focused on this setup because it differentiates molecules based on electronic features, i.e., whether the molecule is polar (with a simultaneous positive and negative center) or non-polar (without separation of charge).

Using this setup proved worthwhile as the team reported that, in fact, the individual structural isomers (different spatial and geometrical distribution for a given cluster) change in solution even though the mass of the cluster remains unchanged. This indicated that there was intra-cluster exchange of metal atoms, which changed the electronic state of the cluster even though the mass remained the same. They also reported that after the synthesis, with the passage of time, the concentration of different structural types of gold-silver alloys in the solution changed. This indicated that there was also an inter-cluster metal exchange at play. Lastly, the researchers also observed that the inter-cluster metal exchange occurs much more frequently after synthesis and eventually slows down after holding for a long time. They assigned this to the difference in stability and energy among the different structures. "The metastable geometries formed initially likely convert to thermodynamically stable geometries through inter-cluster (and intra-cluster) metal exchange in solution," explains Prof. Negishi.

The scientists verified their claims about the observed dynamics of the cluster-metal complex reaction (CMCR) by carrying out a comparative study with the alternate synthesis procedure. Since, traditional procedures (Co-Reduction of Metal Ions) produces alloys under severe conditions, only the thermodynamically and energetically favorable structures see the light of day. Thus, predominantly stable structures are

formed, indicating that metal exchange is relatively suppressed. This stood in opposition to the clusters formed by the CMCR where signatures for various species are initially observed. As time passes, like all things in nature, the unstable species try to rearrange themselves into stable ones. How? Through metal exchange, of course!

To summarize, Prof. Negishi states, "These results demonstrate that gold-silver alloy clusters have different geometric structures (and distributions) immediately after synthesis, depending on the synthesis method. Thereby, their dynamic behavior in solution also depends on the synthesis method."

The study of clusters with varying core sizes and compositions is exciting as it offers exciting opportunities to harness novel physical and chemical properties. But that's not all: it also provides an insight into their structure-property relationships, almost like peeping into the "social life" of atoms.

More information: Yoshiki Niihori et al, Dynamic Behavior of Thiolate-Protected Gold–Silver 38-Atom Alloy Clusters in Solution, *The Journal of Physical Chemistry C* (2019). DOI: 10.1021/acs.jpcc.9b02644

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