

Silver-rich lumps: Large cluster complexes with almost 500 silver atoms

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Nanoscope “lumps” of atoms, known as clusters, are the specialty of a research team headed by Dieter Fenske from the University of Karlsruhe and the Forschungszentrum Karlsruhe.

The production and characterization of clusters made of interesting semiconductor materials are a main focus of this group. As reported in the journal *Angewandte Chemie*, the team has now been able to synthesize four new, particularly large and silver-rich clusters, and to determine their crystal structures.

Two or three-dimensional nanostructures of semiconductor materials are of interest for future nanoelectronic applications. Such structures could be built of arrays of clusters.

A cluster is an accumulation of atoms or molecules that includes hundreds or thousands of atoms. Tiny as they are, to some degree clusters have completely properties to those of “normal sized” (macroscopic) solid particles. This difference is caused by the high surface-to-volume ratio. In order to precisely interpret the measured physical properties of clusters, it is important to understand the atomic structure of these nanoparticles.

One of the things Fenske and his team are working on is the synthesis of metal-rich clusters of the elements sulfur, selenium, and tellurium (the chalcogens). For the metallic component in these systems, the coinage metals copper and silver are well suited.

By using specially developed synthetic methods, the scientists were able to make molecular cluster complexes. In this process, cluster cores made of metal and chalcogen atoms are surrounded by a protective shell of organic ligands. This protective coat prevents the tiny lumps from aggregating into larger particles or solids. This trick made it possible for the researchers to make particularly large silver-rich clusters.

The newest members of this family of clusters consist of distorted spherical silver-chalcogenide cores with diameters between two and four nanometers. Their surfaces are protected with thiolate or phosphane ligands.

Characterizing the structures of such large metal-rich cluster complexes by X-ray crystallographic studies is extremely difficult. It is actually impossible to determine the exact composition. Defects in the crystal lattice are one reason. The tendency to have defects increases as the number of silver atoms grows.

However, by using a combination of X-ray diffraction, mass spectrometry, and electron microscopy, the researchers did succeed in deriving idealized empirical formulas and idealized atomic structures for their clusters. The most silver-rich compound consists of clusters with approximately 490 silver and 188 sulfur atoms, as well as 114 sulfur-organic ligands, and an idealized composition $[\text{Ag}_{490}\text{S}_{188}(\text{StC}_5\text{H}_{11})_{114}]$.

Citation: Dieter Fenske, Synthesis and Crystal Structures of the Ligand-Stabilized Silver Chalcogenide Clusters $[\text{Ag}_{154}\text{Se}_{77}(\text{dppxy})_{18}]$, $[\text{Ag}_{320}(\text{StBu})_{60}\text{S}_{130}(\text{dppp})_{12}]$, $[\text{Ag}_{352}\text{S}_{128}(\text{StC}_5\text{H}_{11})_{96}]$ and $[\text{Ag}_{490}\text{S}_{188}(\text{StC}_5\text{H}_{11})_{114}]$, *Angewandte Chemie International Edition*, doi: 10.1002/anie.200704249

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