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Cluster Compounds

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Nanoscale Molecular Silver Cluster Compounds in Gram Quantities

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silver sulfide

*Dedicated to Professor Bernt Krebs on
the occasion of his 75th birthday*

Fundamental knowledge of the intermediates between bulk materials (ionic, metallic) and molecular entities (e.g. clusters) is essential for the development of nanotechnology. The following interrelation exists between these areas, where the average oxidation number n of the metal atoms is a significant measure for the different metal-atom cluster types: "naked" metal-atom clusters ($n = 0$) stabilized with neutral ligands (PR_3), metalloid cluster compounds ($0 \leq n_{av} \leq n_{salt}$) exhibiting even conductivity and superconductivity behavior,[6] and salt-like cluster compounds[1] which are mostly semi-conducting). The nanoscience of crystalline cluster compounds connect classical inorganic chemistry (bulk metals/bulk salts) with modern inorganic physical chemistry and physics.

The silver clusters highlighted herein,[2,3] as well as the already established gold[4] and aluminum clusters,[5,6] all belong to the group of metalloid clusters of the general formulae $[M_xR_y]$ ($x > y$; M = metal such as Al,[5] Au[4], R = anionic ligands, such as $(SiMe_3)_2N^-$, $HOOC\text{-}C_6H_4\text{-}S^-$).[7] As the oxidation state of the metal atoms varies within these metalloid clusters the most complex situation within the field of metal-atom clusters results. The first compound in this field was a gold cluster compound $[Au_{55}(PPh_3)_{12}Cl_6]$;[8] its structure, however, still lacks crystallographic confirmation. Nevertheless, 26 years after the synthesis of this Au_{55} cluster compound $[Au_{55}(PPh_3)_{12}Cl_6]$ by Schmid et al.,[8] the metalloid cluster compound $[Au_{102}(S\text{-}Ar)_{44}]$ ($Ar = C_6H_4\text{-}COOH$) was obtained as a pure compound in the form of single crystals, so that it could be characterized by X-ray crystallography.[4]

Thereby the structural characterization reveals the unexpected feature of a pentagonal bipyramidal Au_7 unit in the center of the cluster, a structural motive not known for elemental gold. Therefore the simple idea that larger clusters might be seen as a cut-out of the solid-state structure is not true, even for clusters with diameters in the nanometer range; the diameter of the metal core of $[Au_{102}(S\text{-}Ar)_{44}]$ is 1.4 nm. Hence in the case of gold, a synthetic method has been established, so that definite metalloid Au cluster compounds can be synthesized and characterized—a first step for an understanding of structure–property relations in the nanometer regime on an atomic level.[9]

To date, such a synthetic method was missing for nanoscale silver clusters. However, this situation is changing as recently the group of Bigioni[2] as well as the group of Zheng[3] independently reported on the synthesis and structural characterization of anionic silver clusters of the composition $[Ag_{44}(S\text{-}R)_{30}]^{4-}$ ($R = Ar = C_6H_4COOH$ (**1**)[2] or C_6H_4F (**2**), $C_6H_3F_2$ (**3**), $C_6H_4CF_3$ (**4**))[3] exhibiting a metal–metal bonded cluster core. The metalloid clusters **1**–**4** can additionally be synthesized in an unexpected high yield in large quantities of up to 140 g per batch by a quite simple reaction sequence, thus representing a synthetic breakthrough that opens wide the door for further investigations.

For the synthesis of **1**–**4**, a silver precursor with the silver atoms in oxidation state +1 for example, Ag(S-Ar) ($Ar = C_6H_4COOH$) is reduced with $NaBH_4$. In the case of **1**, a water/ethanol mixture is used as the solvent and **1** is recrystallized from dimethylformamide (DMF) to give dark red, nearly black, rhombic crystals, which were suitable for X-ray diffraction. The molecular structure of the anionic cluster is shown in Figure 1 and might be briefly described as follows: In the center of the cluster an icosahedral Ag_{12} core is present, exhibiting average Ag-Ag distances of 282.6 pm (Ag-metal: 289 pm). Only the Ag atoms of the central Ag_{12} unit with exclusively Ag–Ag contacts and no Ag–S contacts. Thereby every triangle of the Ag_{12} icosahedron is capped by a silver atom with Ag–Ag distances of 284.1 pm, leading to a pentagonal dodecahedral arrangement of the 20 capping silver atoms. These 20 silver atoms are additionally bound to sulfur atoms of 24 S-Ar groups with average Ag–S bonds of 251 pm (248.5–252.8 pm). To these sulfur atoms a further 12 Ag atoms are bound with average Ag–S distances of 254.8 pm (253.4–256.9 pm). Finally these 12 silver atoms additionally bind to the sulfur atoms of six octahedrally arranged RS groups with the shortest Ag–S distances of 247.9 pm. The 30 S-Ar ligands in **1** are now oriented so that the COOH groups point outwards. This arrangement seems of central importance for crystallization of the anionic cluster, because the COOH groups form hydrogen-bonded dimers (Figure 1c), connecting different clusters in the solid state.[10]

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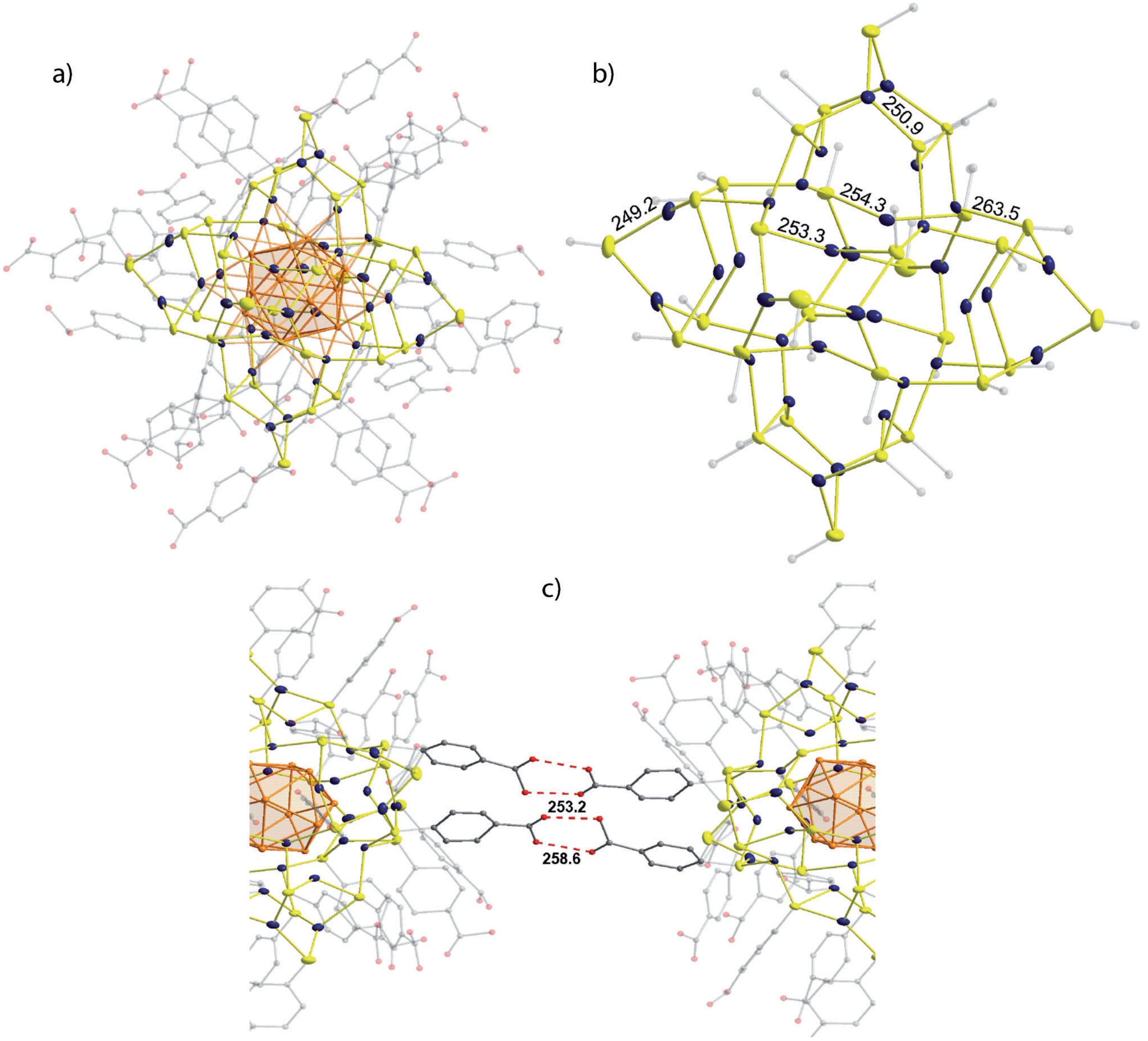

Figure 1. a) Molecular structure of $[Ag_{44}(S\text{-}Ar)_{30}]^{4-}$ (**1**) (Ar = C_6H_4-COOH), hydrogen atoms omitted for clarity. The central Ag_{12} icosahedron is emphasized by a polyhedral presentation. b) Outer $[Ag_{32}(S\text{-}Ar)_{30}]$ shell (silver atoms in blue); from the Ar ligand only the directly bound C atoms are presented and selected Ag–S separations [pm] are given. c) Section of the solid-state structure of $[Ag_{44}(S\text{-}Ar)_{30}]^{4-}$ (**1**; Ar = C_6H_4-COOH), without hydrogen atoms, indicating the connection of the clusters in the solid state. The O–O separations of oxygen atoms in the carboxylic groups of different clusters are given and emphasized by dashed bonds.

The arrangement of the $[Ag_{44}(S\text{-}Ar)_{30}]^{4-}$ anions **1** within the crystal leads to large voids (50% of the crystal volume) where solvent molecules and cations are localized in a disordered fashion so that they could not be refined during structure solution. However, in the case of $[Ag_{44}(S\text{-}C_6H_4F)_{30}]^{4-}$ (**2**), four countercations PPh_4^+ could be resolved during crystal structure analysis underlining the charge of −4, which was assigned in the case of **1** with the aid of mass-spectrometric investigations.

Nevertheless, the arrangement in the solid state does not explain why the cluster compounds **1**–**4** are obtained in such excellent yields of up to 95%, which will open the way for a plethora of further investigations! To get a first idea about this issue, the electronic structure of the cluster was analyzed by both groups, revealing a shell closure of 18 electrons $[1S^2/1P^6/1D^{10}/..]$, indicating that the cluster can be described by the super-atom model. Thereby the authors of both publications[2,3] have made high computational–theoretical efforts on the analysis of frontier orbitals and their rigorous projections on the super-atom model. The calculations are thereby helpful to understand the structure and bonding of the novel silver clusters, especially with respect to their optical spectra. The calculated local charges of the metal atoms also give an indication that helps to understand the atomic structure: The Ag atoms of the central Ag_{12} core exhibit a slightly negative charge, while all the other Ag atoms are significantly positive charged. These computational results showing 32 positively charged Ag atoms that are all bound to sulfur atoms is in line with structural details of many silver sulfide clusters made by Fenske and co-workers,[1] where an outer $[Ag^+(SR^-)]$ shell is shielding a $(Ag_2S)_n$ core. Especially in the case of the $[Ag_{50}S_7(SC_6H_4tBu)_{40}]^{4-}$ cluster anion[11] with its $[Ag_2S]_7[Ag_{36}(SC_6H_4tBu)_{40}]^{4-}$ structure; the $Ag^+(SC_6H_4tBu)^-$ shell shows a similar arrangement of the Ag^+ and $(SC_6H_4tBu)^-$ groups as realized in the $Ag_{32}(SR)_{30}$ unit in **1**. This structural similarity, together with the calculated atomic charges, give a strong indication that the outer shell of **1** exhibits Ag^+ and $(SR)^-$ units, leading to a $[Ag_{32}(SR)_{30}]^{2+}$ moiety. Consequently, a Zintl-like $Ag_{12}{}^{6-}$ core results, also representing an 18 electron system. This alternative description of **1** as an $Ag_{12}{}^{6-}$ core and an $[Ag_{32}(SR)_{30}]^{2+}$ shell, which has to be carefully examined in further calculations, is corroborated by the structure of the $[Au_{12}Ag_{32}(S\text{-}R)_{30}]^{4-}$ clusters ($R = C_6H_4F$ (**5**), $S\text{-}C_6H_3F_2$ (**6**), $S\text{-}C_6H_4CF_3$ (**7**)).[3] They are synthesized under the same reaction conditions as **2**–**4**, however a mixture of $Ag(NO_3)$ and $[(PPh_3)AuCl]$ as the metal source is used. Thereby the metal with the higher redox potential (Au) is reduced and the other one (Ag^+) builds the $Ag_{32}(SR)_{30}$ shell, leading to a complete separation, that is, all the silver and gold positions in the solid state show an occupation factor of 100%, leading to an icosahedral Au_{12} core.

The synthetic breakthrough by the groups of Bigioni and Zheng, giving a high amount of the substances, opens a plethora of future applications of these definite nanoscale silver cluster compounds. Additionally the results hint at a new synthetic principle, where an oxidized shell encloses an anionic metal core, which might be broadened also to more reactive metals, such as cobalt or iron, or other noble metals such as palladium. This result will further help to understand the area of nanoscale metals where often only the molecular composition is known, but no information about the atomic arrangement is available.

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[10] The O–O distance of the hydrogen bond can thereby be quite short (253–259 pm), indicating that strong hydrogen bonds are present. Thus, assuming an average bond energy for one hydrogen bond of 20 $kJ\,mol^{-1}$, the overall energy is 600 $kJ\,mol^{-1}$, being an essential feature for the formation of single crystals. The influence of hydrogen-bonding in **2**, **3**, and **4** (e.g. between C–H bonds in $[PPh_4]^+$ and the negatively polarized F atoms of the anionic clusters) for the crystallization is less clear and might be the task of future work.

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