SHORT COMMUNICATION

Bromide-Induced Formation of a Highly Symmetric Silver Thiolate Cluster Containing 36 Silver Atoms from an Infinite Polymeric Silver Thiolate

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Owing to its good affinity with Ag^+, Br^- is able to truncate a silver thiolate polymer and induce the formation of a high-nuclearity silver thiolate nanocluster, $[Br@Ag_{36}(SC_6H_4tBu-4)_{36}]^-$. The nanocluster has a disc-like structure with one Br^- anion trapped at the center of the cluster in an octahedral coordination.

Introduction

Molecular chalcogenide nanoclusters, consisting of tens and hundreds of covalently bound atoms, represent one class of important nanoclusters.[1–5] With a size at the low limit of the size spectrum of nanoparticles and usually less than the exciton Bohr radius of their bulk counterparts, these nanoclusters exhibit a significant quantum confinement effect.[1,6–9] In addition, chalcogenide nanoclusters can be considered as truly monodispersed in size and shape. They can serve as artificial atoms for the construction of highly ordered and even functional materials (e.g. superlattices, porous materials).[6,8,10,11] The ease of crystallization of the clusters into single crystals makes it possible to determine the precise molecular structure of the clusters.

Owing to their good affinity to metals, thiolates have been widely used as capping agents in the synthesis of different chalcogenide nanoclusters (e.g. $[Cd_{54}S_{32}(SPh)_{48}(H_2O)]^{4-}$,[9] $[Ag_{352}S_{128}(St\text{-}C_5H_{11})_{96}]$,[10] $[Ag_{490}S_{188}(S\text{-}t\text{-}C_5H_{11})_{114}]$,[10] $[Ag_{70}S_{16}(SPh)_{34}(PhCO_2)_4(triphos)_4]$,[12] $[Ag_{123}S_{35}(StBu)_{50}]$,[13] $[Ag_{344}S_{124}(StBu)_{96}]$,[13] $[Ag_{262}\text{-}S_{100}(StBu)_{62}(dppb)_6]$,[14] $[Ag_{70}S_{20}(SPh)_{28}(dppm)_{10}](CF_3\text{-}CO_2)_2$,[14] $[Ag_{65}S_{13}(SC_6H_4NMe_2)_{39}(dppm)_5]$[15]). Currently, there are two approaches to prepare high-nuclearity silver thiolate nanoclusters. In one approach, silver salts (i.e. Ph_3CO_2Ag, CF_3COOAg), highly reactive thiolates [i.e. $S(Ph)SiMe_3$], and a sulfide precursor [i.e. $S(SiMe_3)_2$] were used as the reactants for the direct synthesis of the nanoclusters. The key in this approach was to prevent the facile formation of polymeric silver thiolates, which was mainly achieved by the delicate control of the reaction conditions

such as the low reaction temperature. In the other approach, polymeric silver thiolates were applied as the precursors to react with a reactive sulfide precursor, $S(SiMe_3)_2$, to yield silver thiolate clusters, which has become very effective in the synthesis of some extra-large silver thiolate nanoclusters.[10,16,17]

The possibility of using polymeric silver thiolates to prepare discrete nanoclusters arises mainly because of the strong affinity of sulfide to silver, which facilitates the break down of the polymeric chain. Similarly to sulfide, a halide anion (e.g. Cl^-, Br^-) reacts easily with a silver cation. It would be highly useful to know whether halide anions can also induce the formation of discrete nanoclusters from silver thiolate polymers. Starting from an $Ag\text{-}SC_6H_4tBu\text{-}4$ polymer, we report here the successful synthesis of $[HNEt_3]^+\text{-}[Br@Ag_{36}(SC_6H_4tBu\text{-}4)_{36}]^-$ (**1**), containing a high-nuclearity silver thiolate nanocluster, assisted by a bromide anion.

Results and Discussion

The polymeric silver thiolate compound studied in this work was prepared according to the literature method and has a composition of $\{[HNEt_3]_2[Ag_{10}(SC_6H_4tBu\text{-}4)_{12}]\}_n$.[17] This polymer is insoluble in acetonitrile. Upon addition of an aqueous solution of $(C_4H_9)_4N^+Br^-$, the acetonitrile dispersion of the polymer microcrystals quickly became a clear solution. This observation indicates that the original silver thiolate polymer is broken down by the introduction of Br^- ions. Upon heating at 60 °C, the resulting clear solution yielded **1**. As illustrated in Figure 1, single crystal structure analysis of **1** reveals the formation of $[Br@Ag_{36}(SC_6H_4tBu\text{-}4)_{36}]^-$ nanoclusters from the polymeric silver thiolate precursor. The $[Br@Ag_{36}(SC_6H_4tBu\text{-}4)_{36}]^-$ clusters crystallize with $[HNEt_3]^+$ as the counterions to form **1**. The presence of bromine in the compound was confirmed by energy dispersive X-ray analysis (see Supporting Information). The $[Br@Ag_{36}(SC_6H_4tBu\text{-}4)_{36}]^-$ cluster is highly symmetric with

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a threefold rotational axis that passes through its center. The asymmetric unit of the cluster contains only one Br⁻ ion, six Ag⁺ ions and six thiolate anions. The cluster has a core-shell structure with a flattened-cage-like core $[Br@Ag_{18}S_{12}]^-$ and a crown-like shell $[Ag_{12}S_{12}-(AgS_2)_6]$. The flattened structure is common among many reported silver thiolate clusters.

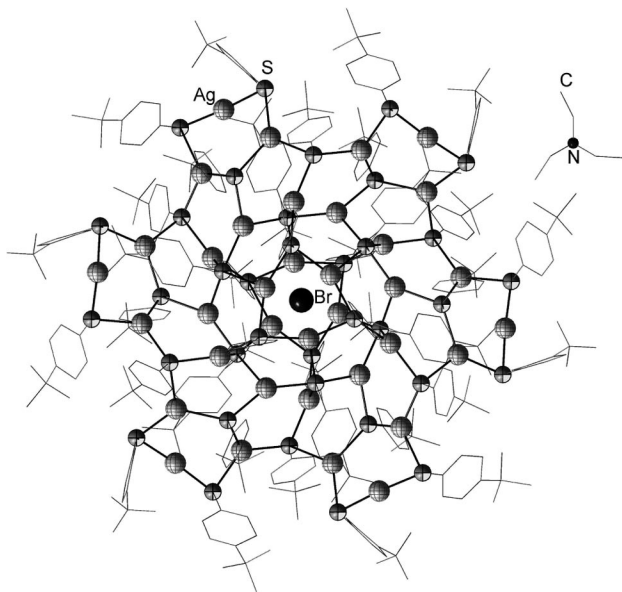Figure 1. The structure of the $[Br@Ag_{36}(SC_6H_4tBu_4)_{36}]^-$ cluster: grey globe spheres, Ag; multishaded spheres, S; black sphere, Br; grey sticks, C–C and S–C bonds.

In the core of the cluster (Figure 2), the Br⁻ ion sits in the center and is sandwiched by two Ag_3S_3 units with an Ag–Br distance of 3.0024(6) Å. This bond length is consistent with the Ag–Br lengths observed in previously reported compounds containing a Br⁻ anion with a similar coordination environment.[18] The Ag···Ag contacts in the central $Br(Ag_3S_3)_2$ sandwich unit are 3.2391(10) Å. The centers of the Ag_3S_3 units and the Br⁻ ion define the threefold rotational axis of the cluster. The $Br(Ag_3S_3)_2$ sandwich unit is then enclosed by a cyclic $Ag_{12}S_6$ to form the flattened-cage-like core. As a result, the Br⁻ anion is fully encapsulated.

In contrast to the cluster core, the shell of the cluster has a crown-like structure (Figure 3). Twelve Ag⁺ ions and twelve thiolate anions are alternatively linked together to form a cyclic structure. The $Ag_{12}S_{12}$ ring is then transformed by six additional AgS_2 units into an arrangement consisting of six S-bridged Ag_3S_3 units, $[S(Ag_3S_3)]_6$. The silver atom in the AgS_2 units is two coordinate. A linear two-coordination arrangement is a common coordination geometry for Ag^I, but has rarely been revealed in silver thiolate clusters. It should be noted that MS_2 units have recently been reported as important surface structure components in many thiolate-capped metallic gold compounds.[19–21] The presence of AgS_2 staple motifs in $[Br@Ag_{36}(SC_6H_4tBu-4)_{36}]^-$ is of the utmost significance since it implies such units might be present in thiolate-protected silver clusters. The twelve thiolate anions on the crown-like shell, $[Ag_{18}S_{24}]$, are
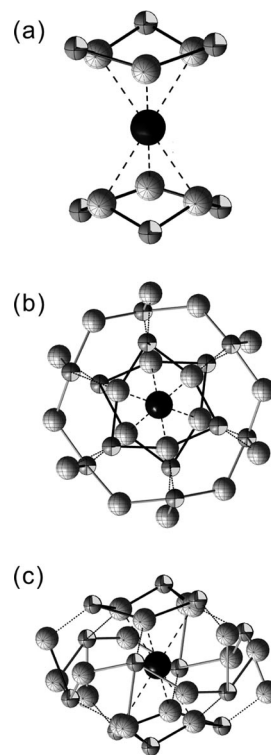

Figure 2. The structure of the core cage of the $[Br@Ag_{36}(SC_6H_4tBu_4)_{36}]^-$ cluster: (a) the $Br(Ag_3S_3)_2$ sandwich unit at the center of the cluster. (b) top and (c) side view of the flattened cage in the core of the $[Br@Ag_{36}(SC_6H_4tBu_4)_{36}]^-$ cluster.

connected to the twelve outer Ag⁺ ions in the core unit $[Br@Ag_{18}S_{12}]^-$ to form the overall structure of the Ag_{36} cluster.

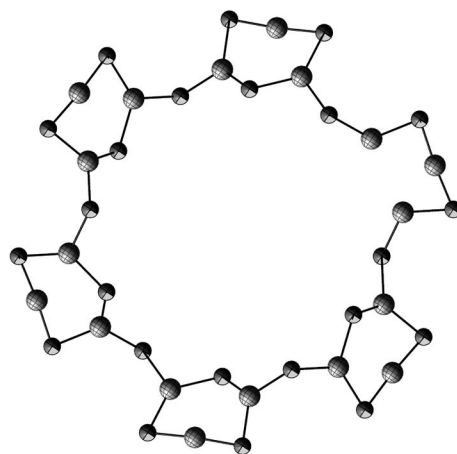

Figure 3. The structure of the crown-like shell of the $[Br@Ag_{36}(SC_6H_4tBu_4)_{36}]^-$ cluster. All carbon atoms are omitted for clarity.

The use of Br⁻ anions is important for the transformation of silver thiolate polymers into discrete $[Br@Ag_{36}(SC_6H_4tBu-4)_{36}]^-$ clusters. In the polymeric precursor, half of the Ag⁺ sites are fourfold coordinated to the thiolate anions. Each thiolate is shared by either two or three Ag⁺ ions, which means that the bond valence contributed to Ag⁺

by each thiolate anion is either 1/2 or 1/3. According to Pauling's electrostatic valence rule, the four-coordinate silver sites in the polymeric precursor are not structurally stable. Indeed, with the introduction of Br^- ions, all of these four-coordinate Ag^+ ions, the structurally least-stable sites, break down, which results in the formation of high-nuclearity clusters in which all silver cations are either two- or threefold coordinated to the thiolate groups.

Experimentally, when Br^- was replaced by Cl^- or I^-, we failed to obtain the Ag_{36} cluster. We did not obtain a clear solution from the polymeric silver thiolate precursor when Br^- was substituted by I^-. Upon addition of Cl^-, we observed the formation of a clear solution from the polymer. Single crystals with a space group of $P2_1/n$ were successfully grown from the solution. Although the precise structure determination of the single crystals was hampered by the lack of quality, the preliminary structural analysis reveals that the yielded cluster contains chloride anions and its structure is significantly different from that of the Ag_{36} cluster discussed above (see Supporting Information).

In **1**, the highly symmetric $[Br@Ag_{36}(SC_6H_4tBu-4)_{36}]^-$ clusters crystallize in the R-3 space group, and pack in a hexagonal pattern in the ab plane with a intercluster distance of 26.151(4) Å (center to center). Along the c axis, the hexagonal layers of the clusters have an ABC arrangement with a layer-to-layer distance of 17.913(4) Å. The intercluster space is occupied by charge balancing cations, triethylammonium. The shortest distance between the proton on the triethylammonium cation and the sulfur on the Ag_{36} clusters is 6.2105(20) Å, which indicates no strong interaction between the clusters and cations.

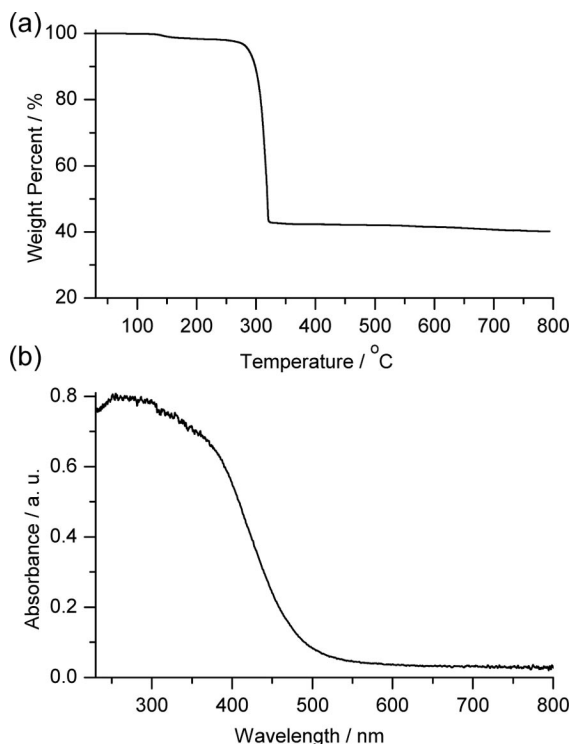To investigate the thermal stability of the as-prepared Ag_{36} clusters, thermal gravimetric analysis of vacuum-dried **1** was carried out under nitrogen. As shown in Figure 4a, the analysis reveals a weight loss of 2.1% between 110 and 220 °C, which corresponds to the removal of the counterion and Br^- (calcd.: 1.8%). The major weight loss of about 57.0% occurs between 220 and 400 °C. At this stage, $Ag_{36}(SC_6H_4tBu-4)_{36}$ decomposes into Ag with the loss of $(SC_6H_4tBu-4)_{36}$ (calcd.: 57.2%). The final product was also confirmed by X-ray powder diffraction measurement. Optical absorption data derived from the reflectance shows that **1** absorbs light with an onset at 487 nm (Figure 4b), which corresponds to an optical band gap of 2.5 eV.

Experimental Section

General: The polymeric anionic silver thiolate, $[HNEt_3]_n[Ag_{10}(SC_6H_4tBu-4)_{12}]_n$, was first prepared according to the literature method.[17]

1: In a glass vial, the polymeric silver thiolate (60 mg) was dispersed in acetonitrile (3 mL). A solution containing $(C_4H_9)_4NBr$ (10 mg) in water (0.1 mL) was then added into the polymer dispersion. After being stirred for 30 min at room temperature, the mixture became clear. The clear solution was sealed and heated at 60 °C for 1 d. **1** (18 mg) was obtained in the form of pale-yellow crystals with a yield of 35%. IR: $\tilde{v}$ = 2958 (s), 2915 (m), 2869 (m), 2784 (vw), 2698 (w), 1614 (s), 1384 (vs), 1268 (m), 1190 (w), 1159 (w), 1118 (s), 1080 (w), 1010 (m), 821 (s), 732 (w), 588 (w), 546 (m), 478 (w) cm^{-1}.

Structure Determination: Intensities were collected at 173 K with an Oxford Gemini S ultra diffractometer. The structures were solved by direct methods and refined by using SHELXL-97, all non-hydrogen atoms were refined anisotropically. Selected refinement results are summarized in Table 1. CCDC-684173 contains the supplementary crystallographic data for the structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Selected details of the data collection and structure refinement of **1**.

	$HN(C_2H_5)_3[Br@Ag_{36}-(SC_6H_4tBu-4)_{36}]^-$
Color	pale yellow
Crystal size [mm]	$0.25 \times 0.20 \times 0.20$
Crystal system	rhombohedral
Space group	R-3
a [Å]	26.151(4)
c [Å]	53.740(11)
V [Å^3]	31829 (9)
Z	3
$\rho_{calcd.}$ [g cm^{-3}]	1.583
$F(000)$	15147
μ [mm^{-1}]	1.955
θ range [°]	3.04–25.00
Reflections collected	12432
Data/restraints/parameters	5810/2/672
R_{int}	0.1034
Goodness-of-fit on F^2	1.014
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0772$, $wR2 = 0.2210$
Largest difference peak and hole [e Å^{-3}]	1.773, –1.306

Figure 4. (a) Thermal gravimetric analysis (TGA) curve and (b) UV/Vis absorption spectrum of **1**.

Thermal Gravimetric Analysis: Thermoanalytical measurements were performed with a DTA-TG device SDT Q600 from TA. All measurements were performed under a nitrogen atmosphere (flow rate: 100 mL min^{-1}) with Al_2O_3 crucibles. The heating rate was 10 K min^{-1}.

Supporting Information (see footnote on the first page of this article): XRD patterns of **1** and the sample after TGA measurement, the EDX spectrum of **1**, and the preliminary structure of the Cl$^-$-templated silver thiolate cluster with an elongated shape are presented.

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