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Anionic Heptadecanuclear Silver(I) Cluster Constructed from in Situ Generated 2-Mercaptobenzoic Acid and a Sulfide Anion

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Supporting Information

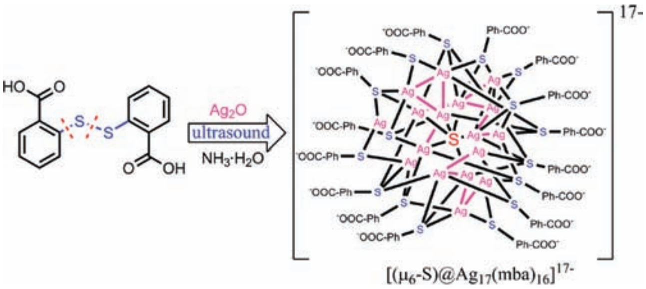
ABSTRACT: A novel anionic heptadecanuclear silver(I) cluster, $(NH_4)_{17}[(\mu_6\text{-}S)@Ag_{17}(mba)_{16}]\cdot 22H_2O$ (**1**; H_2mba = 2-mercaptobenzoic acid), was obtained by the reaction of equivalent molar silver oxide and 2,2′-dithiodibenzoic acid (H_2dtba) under ultrasonic conditions at 50 °C. Complex **1** is a discrete cluster comprised of unexpected mba ligands on the shell and a μ_6-S^{2-} ion in the core, suggesting the occurrence of in situ S−S and S−C(sp^2) bond cleavages of the H_2dtba ligand. This novel cluster displays moderate orange-red emission in the solid state at room temperature.

High-nuclear silver clusters are of special importance because of their novel structural motifs and various potential applications in catalysis, conduction, and luminescence.[1] Although huge Ag/S clusters have been documented,[2] hydrophilic silver(I) clusters have received much less attention owing to their intrinsic crystallization difficulties.[3] Recently, we successfully obtained two hydrophilic silver(I) clusters ($[Ag_6(mna)_6]^{6-}$ and $[Ag_9(mba)_9]^{9-}$) and used them as versatile metalloligands to construct two series of Ag^I−M^{II} (M = Zn and Cu) heterometallic coordination complexes (H_2mna = 2-mercaptonicotinic acid and H_2mba = 2-mercaptobenzoic acid).[4] On the other hand, flexible disulfide derivatives such as 2,2′-dipyridyl disulfide bearing −S−S− spacers can afford diverse structural motifs compared with rigid ligands because of (i) their twisted conformation with a C−S−S−C torsion angle of ca. 90°, (ii) their axial chirality, which potentially generates *M* and *P* enantiomers, and (iii) oxidative formation and reductive cleavage of the S−S bonds, which has been explored as an attractive route toward functional ligands and novel inorganic−organic hybrid materials.[5]

As far as we know, in situ ligand reactions including hydroxylation of aromatic rings, dehydrogenative carbon−carbon coupling, cycloaddition of organic nitriles with azide and ammonia, and transformation of inorganic and organic sulfur are hard to access by conventional methods unless using extreme conditions such as the solvothermal method.[6] Although in situ ligand formation by innovative synthetic procedures such as solvothermal−microwave has been observed,[7] precedents of the coordination polymer or cluster involving an in situ ligand reaction obtained by the ultrasound procedure are very scarce.[8] Compared with the ubiquitous solvothermal method in coordination chemistry, ultrasound synthesis still rarely appeared in the literature. Ultrasonic methods have found an important niche in the preparation of inorganic materials.[9] The high local temperatures and pressures, combined with extraordinarily rapid cooling, provide a unique means for driving chemical reactions. In our previous work, ultrasound techniques achieved the rapid and efficient preparation of coordination complexes.[10]

As part of our continuous work, we attempted to synthesize higher-nuclear hydrophilic silver(I) clusters as potential metalloligands and surprisingly obtained a novel anionic heptadecanuclear silver(I) mercaptobenzoate cluster, $(NH_4)_{17}[(\mu_6\text{-}S)@Ag_{17}(mba)_{16}]\cdot 22H_2O$ (**1**), which is constructed from in situ generated 2-mercaptobenzoic acid and a sulfide anion (Scheme 1).

Scheme 1. Schematic Presentation of the Synthesis of 1 Involving in Situ S−S and C−S Bond Cleavages of the H_2dtba Ligand



In a typical synthesis, complex **1** was synthesized by the reaction of equivalent molar silver oxide and 2,2′-dithiodibenzoic acid (H_2dtba) in the presence of 1 mL of aqueous ammonia (25%) under ultrasonic conditions (160 W, 40 kHz, 30 min, 50 °C; see the Supporting Information, SI). The yellow crystals of **1** were obtained using an evaporation method at room temperature. The crystals of **1** are stable in mother liquor and become brittle once exposed to air. The compositions of **1** were further deduced from single-crystal X-ray diffraction (XRD), elemental analysis, and IR spectrometry. The solid-state IR spectrum of complex **1** shows (i) an intense broad band around 3400 cm^{-1} attributed to the existence of water

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molecules, (ii) the disappearance of the S−H stretching band around 2560 cm^{-1} due to the SH group in the "free" H_2mba, suggesting formation of the Ag−S bond in **1**, and (iii) the absence of a band in the region of 1690−1730 cm^{-1}, indicating complete deprotonation of the carboxyl groups (Figure S1 in the SI).[11] The phase purity of **1** is sustained by its powder XRD pattern, which is consistent with that simulated on the basis of the single-crystal XRD data (Figure S2 in the SI). The differences in intensity may be due to the preferred orientation of the crystalline powder samples. These results are in good agreement with the crystal structure of **1**.

X-ray structural analysis (Table S1 in the SI) of a single crystal of **1** reveals that it is a ball-shaped skeleton comprised of 17 Ag^I ions, 16 mba^{2-} ligands, and 1 μ_6-S^{2-} ion sitting inside the silver cluster. Owing to the size of the cluster, there is a significant interstitial space of 31.0% (calculated using the *PLATON/VOID* routine[12]), accommodating the countercation NH_4^+ and the additional water molecules in a severely disordered fashion. Bond-valence sum calculations with Ag−O and Ag−S bond-valence parameters taken from the literature[13] confirm that the Ag centers are unambiguous Ag^I, with values ranging from 0.94 to 1.17 (Table S2 in the SI). As shown in Figure 1, 17 Ag^I ions have linear, trigonal-planar, and tetrahedral coordination geometries without consideration of Ag···Ag interactions. In detail, only one Ag^I ion (Ag17) is linearly coordinated by two S atoms with a S−Ag−S angle of 156.82(14)°, nine Ag^I ions have trigonal-planar geometry, and seven Ag^I ions adopt two kinds of tetrahedral geometries (five S_3O and two S_4) with τ_4 parameters[14] ranging from 0.621 to 0.798 (for perfect tetrahedral geometry, $\tau_4 = 1$; Table S3 in the SI). Only 5 of 16 carboxyl groups participate in coordination to the Ag^I centers (three μ_1-O and two μ_2-O). The whole silver cluster is protected by 16 peripheral mba^{2-} ligands through Ag−S and Ag−O bonds (Table S4 in the SI), with distances in the ranges of 2.389(3)−2.665(4) and 2.376(10)−2.587(8) Å, respectively, both of which fall within the reported ranges.[15] The Ag···Ag contacts in **1** are in the range of 2.9014(16)−3.3015(13) Å, which are comparable to those observed, for example, in the silver alkynyl clusters reported by Xie and Mak,[16] and are attributed to significant argentophilic Ag···Ag interactions.[17] The anionic cluster **1** is novel and quite different from another anionic octanuclear silver mercaptobenzoate cluster, $K_{12}[Ag_8(mba)_{10}]\cdot 12H_2O$,[15a] but without an endohedral S^{2-} ion.

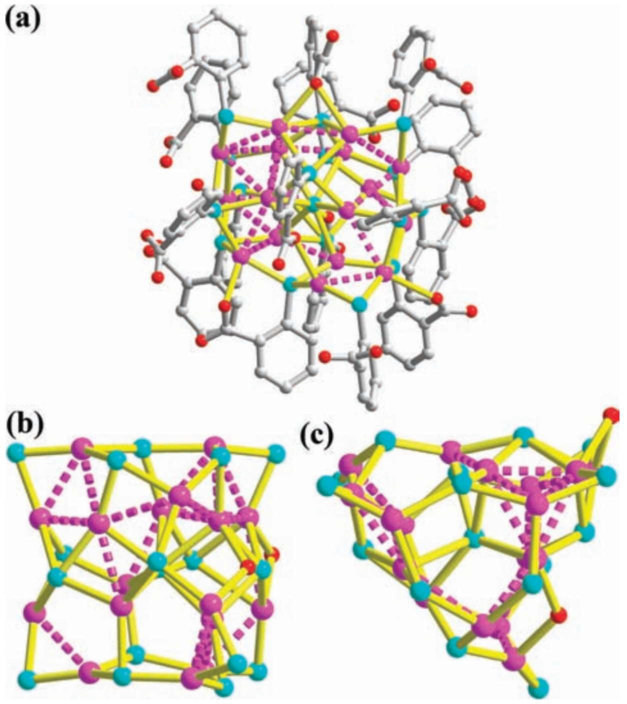

Figure 1. (a) Representation of the molecule structure of the $[(\mu_6\text{-S})@Ag_{17}(mba)_{16}]^{17-}$ cluster. (b and c) Views of the core structure along different directions. Color legend: purple, Ag; cyan, S; red, O; gray, C.

Interestingly, this Ag_{17} cluster entrapped an in situ generated S^{2-} ion in the middle without it being added purposely. The S^{2-} ion is in an irregular octahedral environment completed by six Ag^I ions through the Ag−S bond with an average bond length of 2.833(3) Å and acts as an anionic template to some extent.[18] A similar μ_6-S^{2-} ion was also found in $[Ag_{28}(\mu_6\text{-}S)_2\{ArP(O)S_2\}_{12}(PPh_3)_{12}]$ (Ar = 4-anisyl) where the S^{2-} ion originated from in situ decomposition of Lawesson's reagent (S−P bond cleavage) in an organic solvent.[19] In many giant silver sulfide clusters, there are also S^{2-} ions in the core formed by in situ S−C(sp^3) or S−Si bond cleavage.[20] Compared to the relatively easy cleavages of the S−P, S−Si, and S−C(sp^3) bonds, the S−C(sp^2) bond cleavage is more difficult to achieve.[18c]

It is noteworthy that H_2dtba not only in situ affords the H_2mba ligand to construct a protective shell around the Ag_{17} core but also acts as the source of S^{2-} ions. Although no ammonia was observed in the resulting cluster, ammonia plays important roles in the formation of **1**. First, it acts not only as a base to deprotonate the carboxyl groups but also as a ligand to form certain $[Ag^INH_3]$ intermediates, which may reduce the reaction rate and facilitate the growth of single crystals. Second, it is also a reductive reagent that promotes scission of the S−S and S−C(sp^2) bond of H_2dtba. The only S−S bond cleavage of H_2dtba at room temperature (25 °C) has been observed in a coordination polymer $[Ag_4(mba)_2\cdot(H_2O)_2]_n$ without S−C(sp^2) bond cleavage,[8b] but in **1**, we observe simultaneous S−S and S−C(sp^2) bond cleavages of the same ligand at 50 °C, which suggests that the energy barrier of the S−C(sp^2) bond cleavage is higher than that of the S−S bond cleavage and the temperature plays a critical role in the formation of the final product.

Thermogravimetric analysis (TGA) for complex **1** is measured under a N_2 atmosphere (Figure S3 in the SI). Before 170 °C, the preliminary weight loss of about 9.89% is attributed to the loss of solvent molecules and countercations (calculated, 11.65%) contained in the void spaces. Then, above that temperature, the crystal undergoes rapid decomposition through loss of the mba^{2-} ligand. The residual weight of 36.65% is consistent with that of 37.85% calculated for metallic silver.

The electronic absorption spectrum of **1** exhibits one broad peak in the UV region and a weak absorption in the visible region (Figure S4 in the SI). The high-energy absorption band centered at ca. 300 nm can be ascribed to the intraligand $\pi-\pi^*$ transition of the mba moiety. The weak low-energy band can reasonably be assigned to an electronic transition from the σ(Ag−S) orbital to an empty π^*-antibonding orbital located at the phenyl group of the mba ligand.[4] The excitation spectrum of **1** in the solid state shows a high-energy band in the UV region (364 nm) and one lower-energy band (460 nm). As shown in Figure 2, complex **1** exhibits orange-red emission

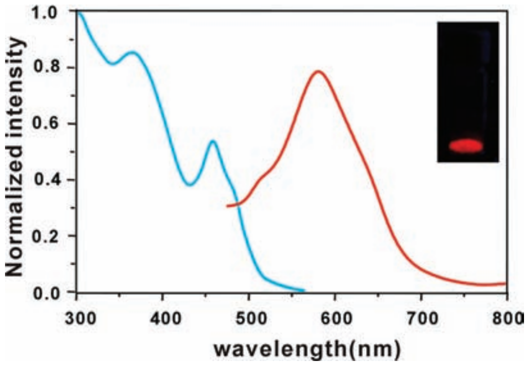

Figure 2. Excitation (cyan trace) and emission (red trace) spectra of **1** in the solid state. Inset: photograph of the emission from **1** in the solid state at room temperature under 365 nm excitation.

(λ_{em} = 577 nm) upon exposure to 365 nm UV radiation. Compared with the emission of free H_2mba (λ_{em} = 383 nm and λ_{ex} = 300 nm),[4b] the emission band of **1** is red-shifted by nearly 200 nm and can be assigned to a ligand-to-metal charge-transfer excited state, which is probably mixed with a cluster-based metal-centered (4d-5s/5p) excited state perturbed by Ag···Ag interactions.[21]

In summary, this work demonstrated that an anionic heptadecanuclear silver(I) cluster was constructed by in situ generated mba ligands and a μ_6-S^{2-} ion, indicating the occurrence of in situ S−S and S−C(sp^2) bond cleavages of the H_2dtba ligand. Moreover, the UV−vis absorption and luminescent property of **1** were discussed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis of complex **1**, selected bond lengths and angles, powder XRD patterns, IR and TGA curves, and X-ray crystallographic files in CIF format for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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