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Synthesis and crystal structure of a novel pentaconta-nuclear silver anionic cluster complex $[HNEt_3]_4[Ag_{50}S_7(SC_6H_4Bu^t\text{-}4)_{40}]\cdot 2CS_2\cdot 6C_3H_6O$

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A silver 4-*tert*-butylthiophenolate complex generated *in situ* reacted with CS_2 in acetone to give an anionic cluster $[Ag_{50}S_7(SC_6H_4Bu^t\text{-}4)_{40}]^{4-}$, the core of which consists of fifty silver atoms and forty-seven sulfur atoms, shaped like a discus with a diameter of *ca.* 2.0 nm.

The study on syntheses, structures and properties of large metal clusters attracts increasing interest not only for their interesting structures but also for their potential use as new materials with unique properties.[1] A part of this interest lies in large metal chalcogenide clusters. There are a great number of reported transition metal mega-clusters with chalcogenide or chalcogenolate ligands.[2] Using the reaction of complexes of transition metal halides or carboxylates with $E(SiMe_3)_2$ or $RE(SiMe_3)$ (E = S, Se, Te) and PR_3 or bidentate phosphanes, Fenske and coworkers have successfully synthesized a series of transition metal giant clusters,[3] for instance $[Cu_{146}Se_{73}(PPh_3)_{30}]$, $[Ag_{114}Se_{34}(SenBu)_{46}(PBu^t_3)_{14}]$, $[Ag_{172}Se_{40}(SeBu^n)_{92}(dppp)_4]$, $[Ag_{48}(\mu_3\text{-}TeBu^n)_{24}Te_{12}(PEt_3)_{14}]$, $[Cu_{58}Te_{22}(PBu^t_2Bu^n)_{14}]$ and so on. However, compared with these huge Ag(Cu)–Se and Ag(Cu)–Te clusters, discrete giant Ag–S clusters are relatively rare, although a number of lower nuclearity Ag–S clusters and polymeric complexes have been found in the literature.[2] Moreover, new synthesis methods of large clusters need further development.

The insertion reaction of CS_2 into M–S bonds (M = Ag, Cu, Cd) and its application in synthesis of clusters have been reviewed by us.[4] We have found that the mononuclear insertion products $(PPh_3)_2M(S_2CSR)$ (M = Ag or Cu, R = alkyl or aryl) can react easily with various solvents to give a series of large cluster complexes, such as $Ag_{14}(\mu_6\text{-}S)(SPh)_{12}(PPh_3)_8\cdot 4CH_3OH\cdot 13H_2O$[5] and $Cu_{14}(\mu_2\text{-}S)(SPh)_{12}(PPh_3)_6$,[6] *etc.* When cadmium thiolates reacted with CS_2 in solvents in the absence of PPh_3, several large Cd–S cluster complexes, for example $[S_4Cd_{17}(SPh)_{24}(CH_3OCS_2)_{4/2}]_n \cdot nCH_3OH$[7] and $(Me_4N)_2[Cd_8S(SPh)_{12}Cl_4]$,[8] were obtained. In order to synthesize high-nuclearity clusters, we changed the size and the position of the substituents on the arylthiolate to effect steric control of ligand and increase the solubility. A silver complex with bulky sterically hindered arylthiolate ligand, $[AgSC_6H_2Pr^i_3\text{-}2,4,6]_n$, reacted with CS_2 in $CHCl_3$–C_2H_5OH to give a decanuclear silver cluster complex $[Ag(SC_6H_2Pr^i_3)]_{10}\cdot 2CHCl_3\cdot C_2H_5OH$.[9] However, with the less bulky sterically hindered ligand, 4-*tert*-butylthiophenolate, the silver anionic complex reacted with CS_2 in acetone to give a huge pentaconta-nuclear silver cluster complex. Here we present the synthesis and the X-ray crystal structure of the new complex $[HNEt_3]_4[Ag_{50}S_7(SC_6H_4Bu^t\text{-}4)_{40}]\cdot 2CS_2\cdot 6C_3H_6O$ (**1**).

A solution of $4\text{-}Bu^tC_6H_4SH$[10] (0.38 mL, 2.3 mmol) and Et_3N (0.32 mL, 2.3 mmol) in C_2H_5OH (8 mL) was added dropwise to a solution of $AgNO_3$ (256 mg, 1.5 mmol) in CH_3CN (5 mL). After stirring overnight at room temperature under a nitrogen atmosphere, the solvents were removed. The residue was dried *in vacuo* and then recrystallized in ethanol to afford a yellow microcrystalline powder. The yellow powder (20 mg) was dissolved in CS_2 (4 ml)–acetone (4 ml) and then filtered. Red block crystals of **1** (yield 50%) suitable for X-ray diffraction analysis were obtained by evaporating the filtrate at room temperature for several days [Found: C, 39.89; H, 4.76; N, 0.399%. Calc. for $Ag_{50}S_{47}C_{424}H_{584}N_4$ (unsolvated): C, 40.30; H, 4.66; N, 0.443%]. IR (KBr): 3049w, 2946vs, 2869s, 2789w, 2671w, 2472w, 1888w, 1621w, 1589w, 1485s, 1393m, 1363m, 1298w, 1267m, 1198w, 1156w, 1116s, 1084w, 1011m, 820s, 736w, 577w, 548m, 448w cm^{-1}.

The X-ray crystal structure determination† reveals that the crystal **1** is an ionic complex composed of four cations $[HNEt_3]^+$ and an anionic cluster $[Ag_{50}S_7(SC_6H_4Bu^t\text{-}4)_{40}]^{4-}$. The structure of the anionic cluster, which possesses a twofold axis through Ag8 and Ag26, is shown in Figs. 1 and 2. The core of the anionic cluster consists of fifty silver atoms and forty-seven sulfur atoms. The shape of the core is discus-like, the inner part of which is the thickest. There is a pseudo-fivefold axis in the core. The fifty Ag atoms are organized into three parts, as shown in Fig. 2. In the inner part, there is an Ag_{15} pentagonal prismatic unit, consisting of three overlapped Ag_5 pentagonal planar

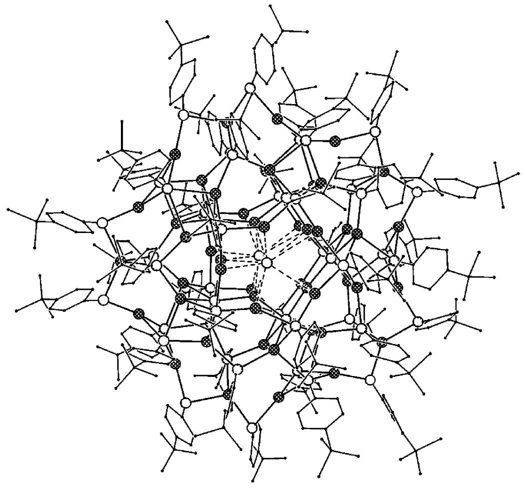

Fig. 1 The structure of anionic cluster $[Ag_{50}S_7(SC_6H_4Bu^t\text{-}4)_{40}]^{4-}$ in **1**.

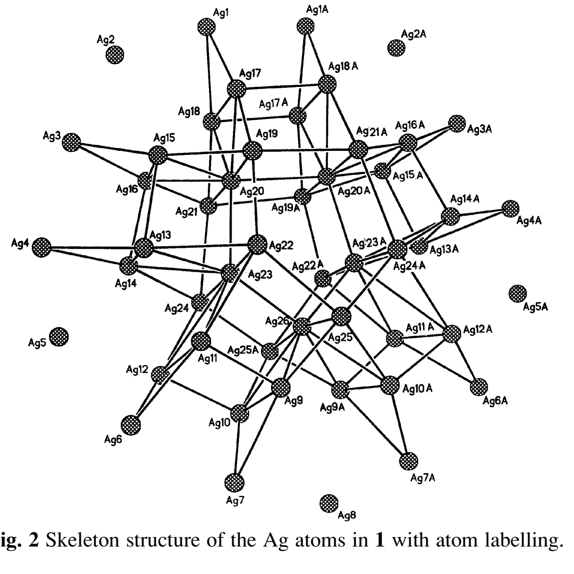

Fig. 2 Skeleton structure of the Ag atoms in **1** with atom labelling.

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layers. The Ag–Ag distances are 2.950–3.458 Å (mean 3.174 Å) in the pentagons and 3.164–3.257 Å (mean 3.214 Å) between the layers. There are twenty Ag atoms in the intermediate part forming a distorted flat Ag_{20} decagonal prism, of which the five Ag_4 rectangle fragments cap the five Ag_6 side faces of the inner pentagonal prism. Each vertex of the rectangle connects to two Ag atoms on the Ag_6 face. The Ag–Ag distances are 2.994–3.424 Å (mean 3.173 Å) in these rectangles and 2.946–4.137 Å (mean 3.486 Å) between the rectangles and the pentagonal prism. For the fifteen peripheral Ag atoms, two out of three Ag atoms add to the two opposite sides of a rectangle of the intermediate part. The Ag–Ag distances from these peripheral Ag atoms to the vertices of the rectangles are 3.102–3.522 Å (mean 3.313 Å), and the distances between two peripheral Ag atoms lie in the range 3.010–3.747 Å.

Of the forty-seven S atoms, forty S atoms are from the arylthiolate ligands 4-Bu^t $C_6H_4S^-$, and seven are S^{2-} ligands. The coordination modes of these S atoms to Ag atoms fall into several categories, as shown in Fig. 3. The arrangement of the forty-five S atoms is similar to the fifty silver atoms. In the inner region a S_{15} pentagonal prism is located between the Ag_{15} pentagonal prism and the Ag_{20} decagonal prism, and the S_{15} pentagonal prism is staggered relative to the Ag_{15} pentagonal prism. The ten S atoms at the two outer pentagonal layers of the S_{15} unit are from the arylthiolate ligands, each of which coordinates to four silver atoms. Two of the four Ag–S distances are short (2.394–2.552 Å, mean 2.452 Å) and the other two are longer (2.606–3.119 Å, mean 2.842 Å). However, the five S atoms in the middle layer of the S_{15} unit are S^{2-} ligands, each of which bonds six Ag atoms. The mean distance of the μ_6-S bridging ligands to the silver atoms is 2.545 Å (2.430–2.678 Å). The S_{20} decagonal prism of the intermediate region is larger than the Ag_{20} decagonal prism, and also staggered relative to the Ag_{20} polyhedron. The all twenty S atoms are from the arylthiolates, which coordinate to Ag atoms on both the Ag_{20} unit and peripheral Ag atoms. Ten S atoms of the S_{20} unit are μ_4-S bridges, and another ten S atoms are μ_3-S bridges. As to the mean distance of μ_3-S bridging ligands to the silver atoms, one is short [av. 2.422 Å (2.404–2.449 Å)], and two are longer [av. 2.677 Å (2.605–2.730 Å)]. The μ_4-S bridging ligands exhibit two short [av. 2.554 Å (2.470–2.668 Å)] and two long [av. 2.796 Å (2.686–3.131 Å)] distances to the silver atoms. Finally, the peripheral ten S atoms of the arylthiolates μ_2-bridge the fifteen peripheral Ag atoms, among which each three Ag atoms have two μ_2-S bridges. The mean μ_2-S–Ag distance is 2.459 Å (2.400–2.597 Å). Additionally, there are two S^{2-} ligands in the inner Ag_{15} pentagonal prism, which are located between the pentagonal layers (see Fig. 2). The distances of each S^{2-} ligand to Ag atoms are different, since the Ag20, Ag21 and Ag23 atoms are disordered, the observed Ag–S distances lie in the range 2.449–3.781 Å. Within the S polyhedrons, all the S–S distances are larger than 3.414 Å.

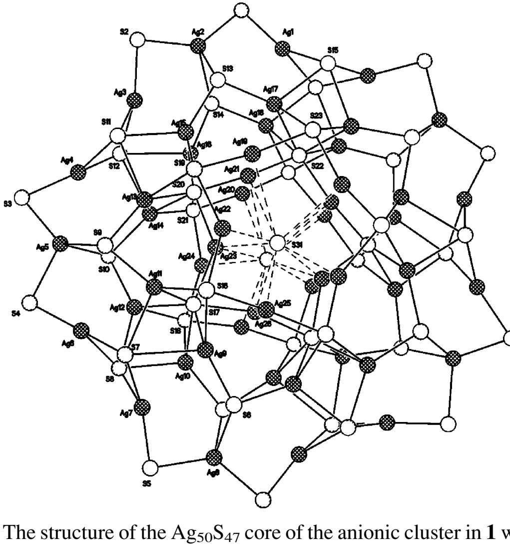

Fig. 3 The structure of the $Ag_{50}S_{47}$ core of the anionic cluster in **1** with atom labelling and Ag–Ag interactions omitted. The cross-hatched circles represent the Ag atoms and the open circles represent the S atoms.

The core of the discus-shaped cluster, which is a nanocluster, has a diameter of *ca.* 2.0 nm and is surrounded by 4-*tert*-butylthiophenolate ligands leading to a diameter of *ca.* 2.9 nm and a maximum depth of *ca.* 2.2 nm. Two CS_2 solvent molecules fill the channel-like cavities formed by the thiophenolates. The six acetone solvent molecules and four cations $[HNEt_3]^+$ are located in the larger cavities formed by the clusters, and the solvent molecules are easy to remove, so that the unsolvated compound was used for the elemental analysis. Crystals of **1** break into pieces and effloresce in a few minutes upon removal of the mother liquor.

It is of note that in the formation of the cluster complex **1**, the ligands S^{2-} were not added as a reagent. However, the S^{2-} ligands are essential for the formation of large clusters, since they cement the metal ions together. We have also found that in our previously reported large complexes, $Ag_{14}(\mu_6\text{-}S)(SPh)_{12}(PPh_3)_8\cdot 4CH_3OH\cdot 13H_2O$,[5] $Cu_{14}(\mu_2\text{-}S)(SPh)_{12}(PPh_3)_6$[6] and $[S_4Cd_{17}(SPh)_{24}(CH_3OCS_2)_{4/2}]_n\cdot nCH_3OH$[7] *etc.*, the ligands S^{2-} are formed in the reaction of CS_2 with solvents, and the production process of S^{2-} is slow. However, the direct addition of reagents, such as Na_2S, S, NaHS or $S(SiMe_3)_2$, may cause M_xS_y precipitation, because the reaction is rapid and difficult to control. In the formation of cluster complex **1**, the reaction conditions are mild (room temperature) and easy to operate, and a moderate yield is observed. The result has shown that this is a promising method although further investigation is needed.

We expect the new nanocluster complex **1** to have special properties. Investigations on these, including nonlinear optical and fluorescence behavior, are currently being carried out and efforts will be continued to explore applications.

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Notes and references

† Data were collected (crystal size 0.80 × 0.60 × 0.40 mm) on a Rigaku R-AXIS RAPID Image Plate diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) operating at 50 kV and 40 mA. Absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program. The structure was solved by direct methods and successive difference maps (SHELX-97) and refined by full-matrix least-squares on F^2 using all unique data (SHELXL-97). *Crystal data* for **1**: $Ag_{50}S_{47}C_{424}H_{584}N_4\cdot 2CS_2\cdot 6C_3H_6O$, M = 13138.00, monoclinic, $C2/c$, a = 36.486(7) , b = 36.666(7) , c = 40.702(8) , β = 95.21(3), V = 54226(16) Å^3, D_c = 1.609 Mg m^{-3}, Z = 4, T = 123(2) K, μ(Mo-Kα) = 1.998 mm^{-1}, $F(000)$ = 26104. 148864 reflections collected, θ range 0.79–25.00°, 44541 unique reflections (R_{int} = 0.0993), final R indices [$I > 2\sigma(I)$], R_1 = 0.0969, wR_2 = 0. 2331; GOF = 0.813; 1751 parameters (Ag, S anisotropic; N, O isotropic; 72 C anisotropic, 150 C isotropic); three Ag atoms and six C atoms are disordered; no hydrogen atoms were included in the refinement; 20 residual peaks (1.00–3.10 e Å^{-3}) are near the Ag atoms. CCDC reference number 178360. See http://www.rsc.org/suppdata/cc/b2/b201116f/ for crystallographic data in CIF or other electronic format.

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