Synthesis and Crystal Structure of $\{[HNEt_3]_{2n}[Ag_8Ag_{4/2}(SC_6H_4tBu\text{-}4)_{12}]_n\cdot nC_2H_5OH\}$ and Its Reaction Product with CS_2

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By using an arylthiolate ligand with a substituent in the *para*-position, 4-$tBuC_6H_4S^-$, the yellow silver-thiolate complex $\{[HNEt_3]_{2n}[Ag_8Ag_{4/2}(SC_6H_4tBu\text{-}4)_{12}]_n\cdot nC_2H_5OH\}$ (**1**) has been synthesized and structurally characterized. Complex **1** is ionic composed of $[HNEt_3]^+$ cations and a polymeric $[Ag_8Ag_{4/2}(SC_6H_4tBu\text{-}4)_{12}]_n^{2n-}$ anion. Complex **1** reacts with CS_2 in acetone to give a red pentaconta-nuclear silver anionic cluster complex $\{[HNEt_3]_4[Ag_{50}S_7(SC_6H_4tBu\text{-}4)_{40}]\cdot 2CS_2\cdot 6C_3H_6O\}$ (**2**). The core of the anionic cluster of **2** consists of fifty silver atoms and forty seven sulfur atoms, shaped like a discus with a diameter of ca. 2.0 nm. The factors influencing the structure and the formation mechanism of the large cluster are discussed.

Introduction

Investigations of syntheses, structures, and properties of large metal clusters, especially nano-sized cluster complexes, continues to attract increasing interest because of their potential use as new materials with unique properties.[1] Recently Müller et al.[2] reported the largest known derivative of a heteropolyacid namely $Na_{48}[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]\cdot nH_2O$ (x = 16: n = 1000), with a diameter of ca. 6 nm. An important part of these investigations includes the remarkably large number of reported transition metal mega-clusters with chalcogenide or chalcogenolate ligands.[3] Using the reaction of transition-metal salts with group 16 silyl derivatives $E(SiMe_3)_2$ or $RESiMe_3$ (R = alkyl or aryl; E = S, Se, Te) and tertiary phosphanes, Fenske and co-workers have successfully synthesized a series of transition metal giant clusters,[4] for instance $[Cu_{146}Se_{73}(PPh_3)_{30}]$, $[Ag_{172}Se_{40}(SenBu)_{92}(dppp)_4]$, $[Ag_{38}Te_{13}(TetBu)_{12}(dppe)_6]$, $[Au_{18}Se_8(dppe)_6]Cl_2$, and $[Zn_{16}Te_{13}(TePh)_6(tmeda)_5]$. In addition to these huge M−Se and M−Te clusters, two new large Ag−S cluster complexes, $[Ag_{70}S_{16}(SPh)_{34}(PhCO_2)_4\ (triphos)_4]$ and $[Ag_{188}S_{94}(PR_3)_{30}]$ were recently synthesized by the same route.[5]

Over the last few years one of our major fields of research interest has been the synthesis of transition metal clusters with sulfur or selenium containing ligands.[6,7] We studied the insertion reaction of CS_2 into M−S bonds (M = Ag, Cu, Cd) and applied it to the synthesis of clusters.[8] It was found that the mononuclear insertion products $(PPh_3)_2M(S_2CSR)$ (M = Ag or Cu, R = alkyl or aryl) react easily with various solvents to give a series large cluster complexes, such as $[Ag_{14}(\mu_6\text{-}S)(SPh)_{12}(PPh_3)_8]\cdot 4CH_3OH\cdot 13H_2O$[9] and $[Cu_{14}(\mu_2\text{-}S)(SPh)_{12}(PPh_3)_6]$[10] etc. When cadmium thiolates were reacted with CS_2 in solvents in the absence of PPh_3, several large Cd−S cluster complexes, for example $[S_4Cd_{17}(SPh)_{24}(CH_3OCS_2)_{4/2}]_n\cdot nCH_3OH$[11] and $(Me_4N)_2[Cd_8S(SPh)_{12}Cl_4]$,[12] were obtained. In order to synthesize high-nuclearity clusters, we changed the size and the position of the substituents on the arylthiolate to affect steric control of the ligand and increase solubility. The silver complex $[AgSC_6H_2iPr_3\text{-}2,4,6]_n$ with the bulky sterically hindered arylthiolate ligand reacted with CS_2 in $CHCl_3/C_2H_5OH$ to give a deca-nuclear silver cluster complex $[Ag(SC_6H_2iPr_3\text{-}2,4,6)]_{10}\cdot 2CHCl_3\cdot C_2H_5OH$.[13] However, the less sterically hindered 4-*tert*-butylthiophenolate containing silver anionic polymeric complex $\{[HNEt_3]_{2n}[Ag_8Ag_{4/2}(SC_6H_4tBu\text{-}4)_{12}]_n\cdot nC_2H_5OH\}$ (**1**) reacted with CS_2 in acetone to give a very large pentaconta-nuclear silver cluster complex. Here we present the syntheses and the X-ray crystal structures of the silver anionic polymeric complex **1** and its reaction product with CS_2, $[HNEt_3]_4[Ag_{50}S_7(SC_6H_4tBu\text{-}4)_{40}]\cdot 2CS_2\cdot 6C_3H_6O$ (**2**). The latter compound has been reported as a communication.[14]

Results and Discussion

Structure of Complex 1

The X-ray crystal structure determination indicates that complex **1** is ionic and composed of $[HNEt_3]^+$ cations and a polymeric anion $[Ag_8Ag_{4/2}(SC_6H_4tBu\text{-}4)_{12}]_n^{2n-}$, the structure of which is displayed in Figure 1. Selected bond lengths and angles of **1** are presented in Table 1. One structural unit of the polymeric anion is $[Ag_8Ag_{4/2}(SC_6H_4tBu\text{-}4)_{12}]^{2-}$ (Fig-

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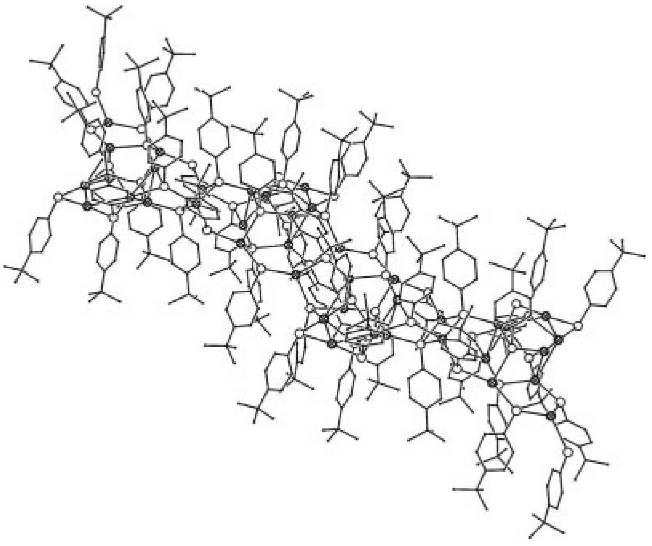

Figure 1. Structure of the polymeric anion $[Ag_8Ag_{4/2}(SC_6H_4tBu\text{-}4)_{12}]_n^{2n-}$ in **1**

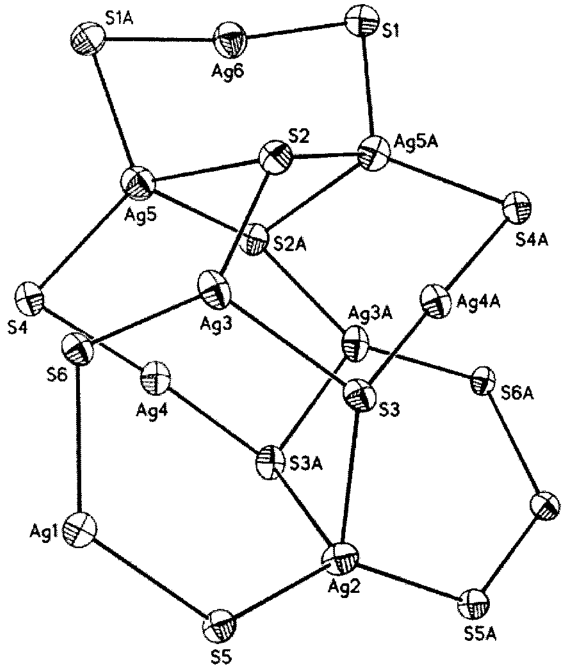

Figure 2. Structure of the $(Ag_8Ag_{4/2}S_{12})$ core of one structural unit $[Ag_8Ag_{4/2}\ (SC_6H_4tBu\text{-}4)_{12}]^{2-}$ in **1** with atom labeling

ure 2), in which there is a two-fold axis through the Ag2 and Ag6 atoms represented by $Ag_{4/2}$ in the formula. There are six Ag_3S_3 cycles fused into one unit. Another structural unit can be produced by the center of symmetry, which is

Table 1. Selected interatomic distances [Å] and angles [°] for complex **1**

Ag(1)−S(5)	2.5455(15)	Ag(5)−S(2)	2.6456(17)
Ag(1)−S(6)	2.5904(16)	Ag(5)−S(2)#2[a]	2.7348(17)
Ag(1)−S(4)#1[a]	2.6611(16)	Ag(5)−Ag(6)	3.0808(9)
Ag(1)−S(6)#1	2.6721(16)	Ag(6)−S(1)#2	2.3826(17)
Ag(2)−S(5)	2.5503(14)	Ag(6)−S(1)	2.3826(17)
Ag(2)−S(5)#2	2.5503(14)	Ag(6)−Ag(5)#2	3.0808(9)
Ag(2)−S(3)#2	2.6865(16)	S(1)−C(11)	1.766(6)
Ag(2)−S(3)	2.6865(16)	S(1)−Ag(5)#2	2.6058(18)
Ag(3)−S(6)	2.4442(14)	S(2)−C(21)	1.774(6)
Ag(3)−S(2)	2.4843(17)	S(2)−Ag(5)#2	2.7348(17)
Ag(3)−S(3)	2.6857(16)	S(3)−C(31)	1.775(5)
Ag(3)−Ag(4)	2.9641(9)	S(3)−Ag(4)#2	2.3686(16)
Ag(3)−Ag(5)	3.2920(9)	S(4)−C(41)	1.785(6)
Ag(4)−S(3)#2	2.3686(16)	S(4)−Ag(1)#1	2.6611(16)
Ag(4)−S(4)	2.3845(16)	S(5)−C(51)	1.778(6)
Ag(4)−Ag(5)	3.1720(9)	S(6)−C(61)	1.777(5)
Ag(5)−S(4)	2.5564(16)	S(6)−Ag(1)#1	2.6720(16)
Ag(5)−S(1)#2	2.6058(18)		
S(5)−Ag(1)−S(6)	124.67(5)	S(4)−Ag(5)−S(2)#2	107.66(5)
S(5)−Ag(1)−S(4)#1	114.08(5)	S(1)#2−Ag(5)−S(2)#2	112.07(5)
S(6)−Ag(1)−S(4)#1	112.13(5)	S(2)−Ag(5)−S(2)#2	80.44(6)
S(5)−Ag(1)−S(6)#1	122.90(5)	S(1)#2−Ag(6)−S(1)	170.44(9)
S(6)−Ag(1)−S(6)#1	88.13(5)	Ag(6)−S(1)−Ag(5)#2	76.14(5)
S(4)#1−Ag(1)−S(6)#1	86.60(5)	Ag(3)−S(2)−Ag(5)	79.77(5)
S(5)−Ag(2)−S(5)#2	139.75(7)	Ag(3)−S(2)−Ag(5)#2	128.70(6)
S(5)−Ag(2)−S(3)	99.94(5)	Ag(5)−S(2)−Ag(5)#2	94.24(5)
S(5)#2−Ag(2)−S(3)	111.19(5)	Ag(4)#2−S(3)−Ag(3)	94.32(6)
S(5)#2−Ag(2)−S(3)#2	99.94(5)	Ag(4)#2−S(3)−Ag(2)	116.53(6)
S(3)−Ag(2)−S(3)#2	78.17(7)	Ag(3)−S(3)−Ag(2)	119.19(6)
S(6)−Ag(3)−S(2)	142.86(5)	Ag(4)−S(4)−Ag(5)	79.80(5)
S(6)−Ag(3)−S(3)	115.15(5)	Ag(4)−S(4)−Ag(1)#1	108.46(6)
S(2)−Ag(3)−S(3)	101.08(5)	Ag(5)−S(4)−Ag(1)#1	130.20(6)
S(3)#2−Ag(4)−S(4)	172.33(5)	Ag(1)−S(5)−Ag(2)	122.42(6)
S(4)−Ag(5)−S(1)#2	119.01(6)	Ag(3)−S(6)−Ag(1)	112.71(6)
S(4)−Ag(5)−S(2)	125.60(5)	Ag(3)−S(6)−Ag(1)#1	118.25(6)
S(1)#2−Ag(5)−S(2)	105.38(6)	Ag(1)−S(6)−Ag(1)#1	91.87(5)

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[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y + 1, -z + 1$; #2 $-x, y, -z + 1/2$.

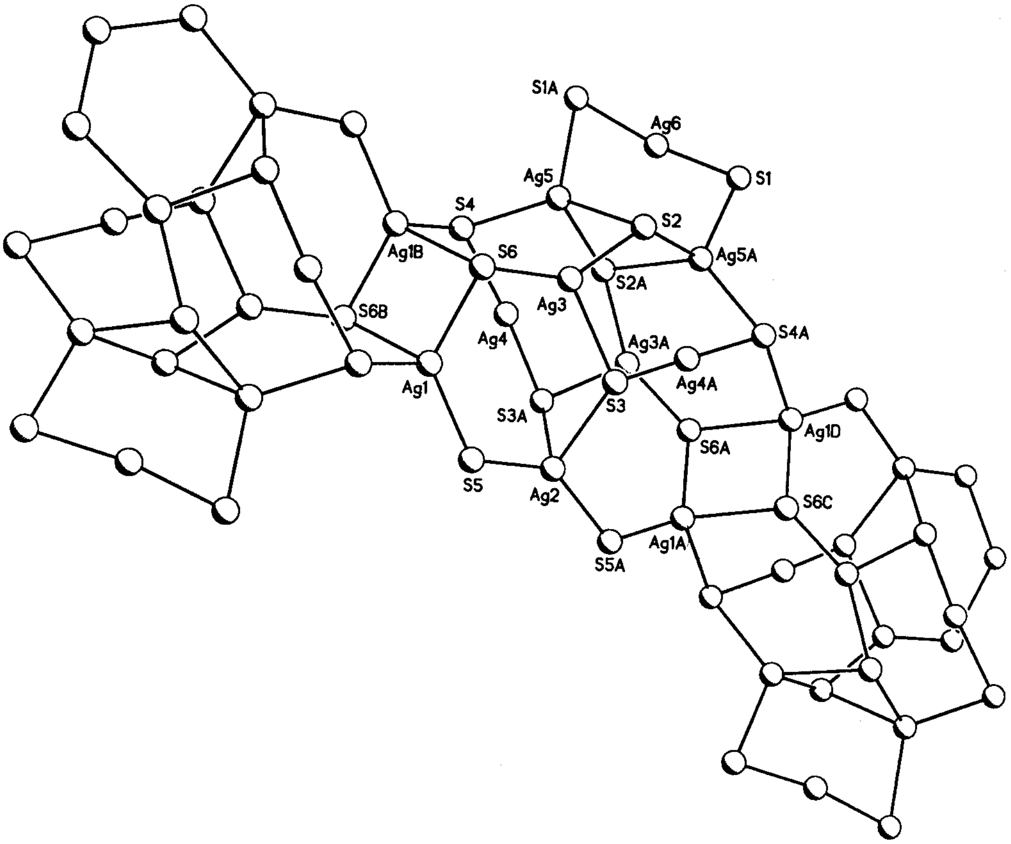

Figure 3. Structure of the $(Ag_8Ag_{4/2}S_{12})_n$ core of the polymeric anion $[Ag_8Ag_{4/2}(SC_6H_4t\text{Bu-4})_{12}]_n^{2n-}$ in **1**

at the center of the Ag_2S_2 monocycle (Ag1 S6 Ag1B S6B). Repeating the inversion symmetry operation produces a one-dimensional polymeric structure. The structure of the core of the polymeric anion of **1** is presented in Figure 3.

In the polymeric anion of **1**, all S atoms are derived from the aryl-thiolate ligands 4-tBuC$_6$H$_4$S $^-$. They are the μ_2-S (S1 and S5) and the μ_3-S (S2, S3, S4, S6) bridges to the Ag atoms. The S1 atom bridges Ag6 and Ag5A, and the angle Ag6−S1−Ag5A is 76.14 (5)°. The bond distances Ag6−S1 and Ag5A−S1 which are 2.383(2) and 2.606(2) Å, respectively are significantly different. The S5 atom bridges Ag1 and Ag2, and the angle Ag1−S5−Ag2 is 122.42(6)°. The bond distances Ag1−S5 and Ag2−S5 which are 2.546(2) and 2.550(2) Å, respectively are similar. With regards to the mean distances of the μ_3-S bridges to the Ag atoms, one is short [av. 2.449 Å (2.385−2.4845 Å)], and two are longer [av. 2.639 Å (2.556−2.735 Å)].

There are three coordination modes observed between all silver atoms and the sulfur donors: the linear, diagonally coordinated silver centers (Ag4, Ag6) exhibit an average Ag−S distance of 2.380 Å (2.383−2.369 Å), the trigonally coordinated silver centers (Ag3) exhibit an average Ag−S distance of 2.538 Å (2.444−2.686 Å) and the tetrahedrally coordinated silver centers (Ag1, Ag2, Ag5) exhibit an average Ag−S distance of 2.624 Å (2.546−2.672 Å). There are Ag−Ag interactions among the Ag atoms (Ag3, Ag4, Ag5, Ag6 Ag3A, Ag4A, Ag5A) in the unit of the polymeric anion of **1**. The Ag−Ag contacts which vary between 2.964−3.292 Å are shorter than the sum of the van der Waals radii of two Ag atoms (3.44 Å), and longer than the Ag−Ag distance in metallic Ag (2.886 Å). This may suggest they are related by so-called agentophilicity.[19] The Ag···Ag distances among those Ag atoms (Ag1, Ag2, Ag1A) are longer than 3.44 Å, which indicates that they are non-bonding and involved in very weak interactions.

Structure of Complex 2

An X-ray crystal structure determination revealed that **2** is an ionic complex composed of four $[HNEt_3]^+$ cations and an anionic cluster $[Ag_{50}S_7(SC_6H_4t\text{Bu-4})_{40}]^{4-}$. The selected bond lengths of **2** are presented in Table 2. The structure of the anionic cluster, which possesses a two-fold axis through Ag8 and Ag26, is shown in Figures 4 and . 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 five-fold axis at the core. The fifty Ag atoms are organized into three parts, as shown in Figure 5. In the inner part exists an Ag_{15} pentagonal prismatic unit, consisting of three overlapping Ag_5 pentagonal planar layers. The Ag−Ag distances are between 2.950 and 3.458 Å (mean 3.174 Å) in the pentagons and between 3.164 and 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

Table 2. Selected interatomic distances [Å] for complex **2**

Ag(1)−S(1)	2.400(5)	Ag(17)−Ag(18)#1[a]	3.150(2)
Ag(1)−S(15)	2.538(5)	Ag(17)−Ag(18)	3.243(2)
Ag(1)−S(15)#1	2.614(5)	Ag(17)−Ag(2D)	4.105(4)
Ag(1)−Ag(17)	3.158(2)	Ag(18)−S(14)	2.438(5)
Ag(1)−Ag(18)	3.333(2)	Ag(18)−S(22)	2.642(4)
Ag(1)−Ag(2)	3.437(2)	Ag(18)−S(15)#1	2.698(5)
Ag(1)−Ag(1)#1	3.672(3)	Ag(18)−S(23)#1	2.710(5)
Ag(2)−S(2)	2.491(6)	Ag(18)−Ag(2B)	3.074(8)
Ag(2)−S(1)	2.493(6)	Ag(18)−Ag(17)#1	3.150(2)
Ag(2)−S(13)	2.703(5)	Ag(18)−Ag(2C)	3.270(3)
Ag(2)−S(14)	2.730(5)	Ag(18)−Ag(2A)	3.721(3)
Ag(2)−Ag(3)	3.438(3)	Ag(18)−Ag(2D)	4.224(5)
Ag(3)−S(2)	2.426(6)	Ag(19)−S(19)	2.423(5)
Ag(3)−S(12)	2.563(6)	Ag(19)−S(23)	2.463(6)
Ag(3)−S(11)	2.590(5)	Ag(19)−Ag(2A)#1	2.933(4)
Ag(3)−Ag(15)	3.154(3)	Ag(19)−Ag(2C)	3.063(3)
Ag(3)−Ag(16)	3.270(3)	Ag(19)−Ag(22)	3.094(3)
Ag(3)−Ag(4)	3.665(3)	Ag(19)−Ag(2D)	3.451(4)
Ag(4)−S(3)	2.427(7)	Ag(19)−S(31)	3.574(8)
Ag(4)−S(12)	2.475(5)	Ag(19)−Ag(2B)#1	3.596(11)
Ag(4)−S(11)	2.696(6)	Ag(2A)−Ag(2B)	1.077(9)
Ag(4)−Ag(5)	3.010(2)	Ag(2A)−S(31)#1	2.349(8)
Ag(4)−Ag(13)	3.470(3)	Ag(2A)−S(23)#1	2.539(6)
Ag(4)−Ag(14)	3.522(3)	Ag(2A)−S(21)	2.706(7)
Ag(5)−S(3)	2.456(7)	Ag(2A)−Ag(19)#1	2.933(4)
Ag(5)−S(4)	2.597(5)	Ag(2A)−Ag(2D)	3.055(4)
Ag(5)−S(10)	2.605(4)	Ag(2A)−Ag(24)	3.155(4)
Ag(5)−S(9)	2.630(5)	Ag(2A)−Ag(2C)	3.260(3)
Ag(5)−Ag(6)	3.647(2)	Ag(2B)−S(21)	2.202(11)
Ag(6)−S(4)	2.406(6)	Ag(2B)−S(23)#1	2.345(10)
Ag(6)−S(7)	2.470(6)	Ag(2B)−Ag(2C)	3.222(7)
Ag(6)−S(8)	2.811(6)	Ag(2B)−Ag(2D)	3.460(9)
Ag(6)−Ag(12)	3.102(2)	Ag(2B)−Ag(24)	3.528(9)
Ag(6)−Ag(11)	3.407(3)	Ag(2B)−Ag(19)#1	3.596(10)
Ag(6)−Ag(7)	3.747(3)	Ag(2C)−Ag(2D)	1.370(5)
Ag(7)−S(5)	2.411(6)	Ag(2C)−S(20)	2.266(6)
Ag(7)−S(7)	2.492(6)	Ag(2C)−S(22)	2.275(5)
Ag(7)−S(8)	2.752(6)	Ag(2C)−Ag(2D)#1	2.826(4)
Ag(7)−Ag(9)	3.291(2)	Ag(2C)−Ag(2F)	2.919(4)
Ag(7)−Ag(8)	3.412(2)	Ag(2D)−Ag(2D)#1	1.742(8)
Ag(7)−Ag(10)	3.425(3)	Ag(2D)−Ag(2F)	2.032(5)
Ag(8)−S(5)#1	2.483(7)	Ag(2D)−S(31)	2.609(8)
Ag(8)−S(5)	2.483(7)	Ag(2D)−S(22)	2.642(7)
Ag(8)−S(6)#1	2.715(5)	Ag(2D)−S(31)#1	2.727(7)
Ag(8)−S(6)	2.715(5)	Ag(2D)−S(20)	2.776(6)
Ag(9)−S(6)	2.404(5)	Ag(2D)−Ag(2C)#1	2.826(4)
Ag(9)−S(17)	2.454(5)	Ag(2D)−Ag(2E)	2.981(5)
Ag(9)−Ag(26)	2.946(3)	Ag(2D)−Ag(2F)#1	3.143(5)
Ag(9)−S(16)	3.055(5)	Ag(22)−S(19)	2.451(6)
Ag(9)−Ag(11)	3.091(2)	Ag(22)−S(31)	2.540(6)
Ag(9)−Ag(25)	3.100(3)	Ag(22)−S(16)	2.552(6)
Ag(9)−Ag(10)	3.109(3)	Ag(22)−Ag(2E)	3.207(4)
Ag(9)−S(7)	3.131(6)	Ag(22)−Ag(2F)	3.229(4)
Ag(10)−S(6)#1	2.410(5)	Ag(22)−Ag(25)	3.458(3)
Ag(10)−S(8)	2.668(7)	Ag(2E)−Ag(2F)	1.178(4)
Ag(10)−S(17)	2.678(5)	Ag(2E)−S(17)	2.213(6)
Ag(10)−S(18)	2.790(6)	Ag(2E)−S(20)	2.279(6)
Ag(10)−Ag(12)	3.015(3)	Ag(2E)−Ag(24)	3.117(4)
Ag(10)−Ag(25)#1	3.233(4)	Ag(2E)−Ag(26)	3.288(4)
Ag(10)−Ag(26)	3.649(3)	Ag(2E)−S(31)	3.424(8)
Ag(11)−S(9)	2.445(5)	Ag(2F)−S(31)#1	2.559(6)
Ag(11)−S(17)	2.578(5)	Ag(2F)−S(20)	2.580(5)
Ag(11)−S(16)	2.627(6)	Ag(2F)−S(31)	2.582(7)
Ag(11)−S(7)	2.798(5)	Ag(2F)−S(17)	2.735(6)
Ag(11)−Ag(2E)	3.204(4)	Ag(2F)−Ag(26)	2.792(4)
Ag(11)−Ag(12)	3.424(3)	Ag(2F)−Ag(2D)#1	3.143(5)
Ag(11)−Ag(22)	3.475(3)	Ag(2F)−Ag(24)	3.211(4)
Ag(11)−Ag(2F)	4.081(4)	Ag(2F)−Ag(2F)#1	3.318(7)
Ag(12)−S(10)	2.419(5)	Ag(24)−S(18)	2.413(6)
Ag(12)−S(8)	2.509(6)	Ag(24)−S(21)	2.519(6)
Ag(12)−S(17)	2.657(5)	Ag(24)−S(31)#1	2.839(7)
Ag(12)−S(18)	3.119(5)	Ag(24)−Ag(25)#1	3.040(3)
Ag(12)−Ag(2E)	3.664(4)	Ag(25)−S(16)	2.394(6)
Ag(12)−Ag(24)	3.805(3)	Ag(25)−S(18)#1	2.409(6)
Ag(12)−Ag(2F)	4.609(4)	Ag(25)−Ag(24)#1	3.040(3)
Ag(13)−S(9)	2.414(5)	Ag(25)−S(31)	3.061(8)
Ag(13)−S(20)	2.520(5)	Ag(25)−Ag(26)	3.180(2)
Ag(13)−S(11)	2.686(5)	Ag(25)−Ag(10)#1	3.233(3)
Ag(13)−S(19)	2.980(6)	Ag(26)−S(17)	2.446(5)
Ag(13)−Ag(15)	3.079(2)	Ag(26)−S(17)#1	2.446(5)
Ag(13)−Ag(2E)	3.137(4)	Ag(26)−Ag(2F)#1	2.792(4)
Ag(13)−Ag(14)	3.348(3)	Ag(26)−Ag(9)#1	2.946(3)
Ag(13)−Ag(22)	3.622(3)	Ag(26)−S(31)	3.175(7)
Ag(13)−Ag(2F)	4.030(4)	Ag(26)−Ag(25)#1	3.180(2)
Ag(14)−S(10)	2.416(5)	Ag(26)−Ag(2E)#1	3.288(4)
Ag(14)−S(21)	2.606(5)	S(6)−Ag(10)#1	2.410(5)
Ag(14)−S(20)	2.612(6)	S(6)−S(6)#1	3.661(9)
Ag(14)−S(12)	2.765(6)	S(15)−Ag(1)#1	2.614(5)
Ag(14)−Ag(16)	2.994(2)	S(15)−Ag(18)#1	2.698(5)
Ag(14)−Ag(24)	3.168(4)	S(18)−Ag(25)#1	2.409(6)
Ag(14)−Ag(2E)	3.240(4)	S(22)−Ag(2C)#1	2.275(5)
Ag(14)−Ag(2F)	3.986(4)	S(22)−Ag(17)#1	2.545(4)
Ag(15)−S(13)	2.449(5)	S(22)−Ag(2D)#1	2.642(7)
Ag(15)−S(11)	2.624(6)	S(22)−Ag(18)#1	2.642(4)
Ag(15)−S(20)	2.659(5)	S(23)−Ag(2B)#1	2.345(10)
Ag(15)−S(19)	2.763(5)	S(23)−Ag(2A)#1	2.539(6)
Ag(15)−Ag(19)	3.047(3)	S(23)−Ag(18)#1	2.710(5)
Ag(15)−Ag(16)	3.270(2)	S(31)−Ag(2A)#1	2.349(8)
Ag(15)−Ag(2C)	3.331(3)	S(31)−Ag(2F)#1	2.559(6)
Ag(15)−Ag(2D)	4.382(4)	S(31)−Ag(2D)#1	2.727(7)
Ag(16)−S(14)	2.404(5)	S(31)−Ag(24)#1	2.839(7)
Ag(16)−S(20)	2.495(5)	S(22)−S(23)#1	3.631(5)
Ag(16)−S(21)	2.879(5)	S(22)−S(23)	3.631(5)
Ag(16)−S(12)	2.903(6)	S(19)−S(20)	3.690(6)
Ag(16)−Ag(2C)	3.001(3)	S(20)−S(21)	3.659(6)
Ag(16)−Ag(2B)	3.086(9)	S(16)−S(17)	3.809(7)
Ag(16)−Ag(2A)	3.882(4)	S(17)−S(18)	3.611(7)
Ag(16)−Ag(2D)	4.058(5)	S(15)−S(15)#1	3.414(10)
Ag(17)−S(13)	2.416(5)	S(13)−S(14)	3.640(6)
Ag(17)−S(22)	2.545(4)	S(11)−S(12)	3.418(7)
Ag(17)−S(15)	2.718(5)	S(9)−S(10)	3.731(6)
Ag(17)−S(23)	2.891(6)	S(7)−S(8)	3.531(7)
Ag(17)−Ag(2C)	3.083(3)	S(6)−S(6)#1	3.661(9)
Ag(17)−Ag(19)	3.094(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y + 1, -z + 1$; #2 $-x, y, -z + 1/2$; #3 $-x, -y, -z + 1$. Ag20, Ag21, and Ag23 (Figure 5) are disordered, corresponding to Ag2A, Ag2B, Ag2C, Ag2D, Ag2E, and Ag2F in Table 2.

five Ag_4 rectangle fragments cap the five Ag_6 side faces of the inner pentagonal prism. Each vertex of the rectangle is connected two Ag atoms on the Ag_6 face. The Ag−Ag distances are between 2.994 and 3.424 Å (mean 3.173 Å) in these rectangles and range from 2.946 to 4.137 Å (mean 3.486 Å) between the rectangles and the pentagonal prism. For the fifteen peripheral Ag centers, two out of three Ag atoms are located at the two opposite sides of a rectangle of the intermediate part. The mean Ag−Ag distance from

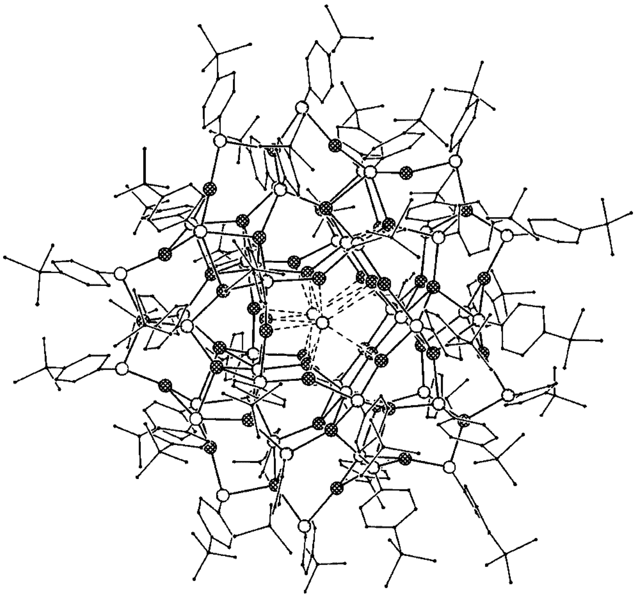

Figure 4. Structure of anionic cluster $[Ag_{50}S_7(SC_6H_4tBu\text{-}4)_{40}]^{4-}$ in **2**

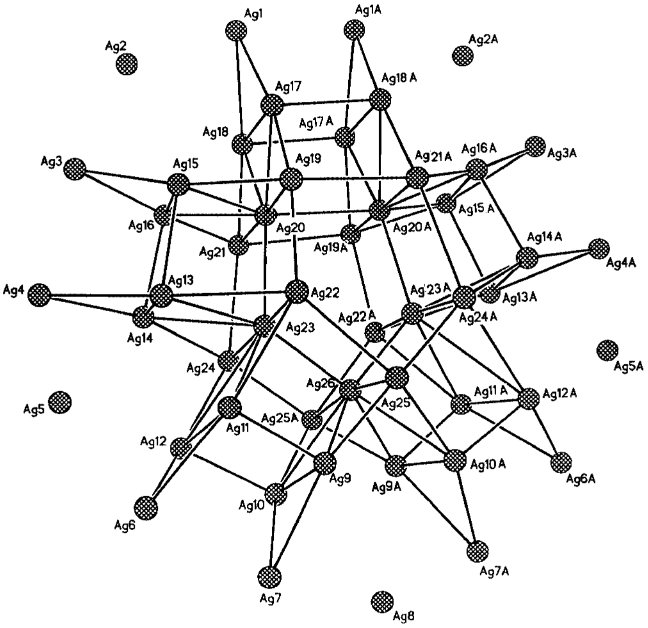

Figure 5. Skeleton structure of the Ag atoms in **2** with atom labeling

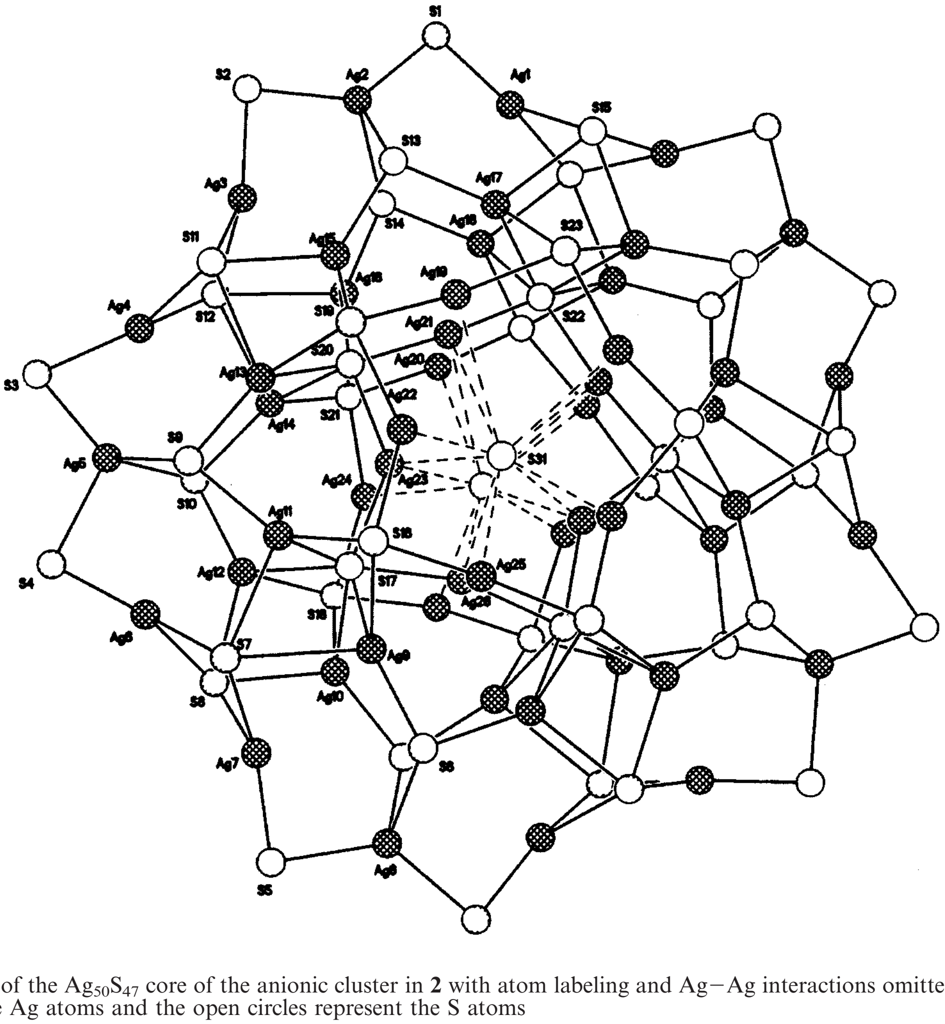

Figure 6. Structure of the $Ag_{50}S_{47}$ core of the anionic cluster in **2** with atom labeling and Ag−Ag interactions omitted; the cross-hatched circles represent the Ag atoms and the open circles represent the S atoms

these peripheral Ag atoms to the vertices of the rectangles is 3.313 Å (3.102−3.522 Å), and the distances between two peripheral Ag atoms lie in the range of 3.010−3.747 Å.

Of the forty seven S atoms, forty of them are derived from the arylthiolate ligands 4-tBuC$_6$H$_4$S$^-$, and seven constitute the S^{2-} ligands. The coordination modes of these S atoms to the Ag atoms fall into several categories, as shown in Figure 6. The arrangement of the fortyfive 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 (2.394−2.552Å, mean 2.452 Å) and the other two are longer (2.606−3.119Å, mean 2.842 Å). However, the five S atoms in the middle layer of the S$_{15}$ unit exist as 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 in the intermediate region is larger than the Ag$_{20}$ decagonal prism, and also staggered relative to the Ag$_{20}$ polyhedron. All twenty S atoms are from the arylthiolates, which coordinate to the peripheral Ag atoms and the Ag centers of the Ag$_{20}$ unit. Ten S atoms of the S$_{20}$ unit are μ$_4$-S bridges and another ten S atoms are μ$_3$-S bridges. With regards to the mean distance of the μ$_3$-S bridging ligands to the silver atoms, one is short (2.404−2.449 Å, mean 2.422 Å), and two are longer (2.605−2.730 Å, mean 2.677 Å). The μ$_4$-S bridging ligands exhibit two short (2.470−2.668 Å, mean 2.554 Å) and two long (2.686−3.131 Å, mean 2.796 Å) distances to the silver atoms. Finally, the peripheral ten S atoms of the arylthiolates μ$_2$- bridge the fifteen peripheral Ag atoms three of which 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 (Figure 6). The distances between each S^{2-} ligand and the Ag atoms are different, since the Ag20, Ag21 and Ag23 atoms are disordered. The observed Ag−S distances lie in the range of 2.449−3.781 Å. Within the S polyhedra, all the S−S distances are larger than 3.414 Å.

The core of the discus-shaped cluster, which is a nanocluster, has a diameter of ca. 2.0 nm. The core of the Ag−S cluster 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 in the channel-like cavities formed by the thiophenolates (Figure 7). The six acetone solvent molecules and four [HNEt$_3$]$^+$ cations are located in the bigger cavities formed by the clusters. The solvent molecules are easy to remove so that the unsolvated compound was used for elemental analysis.

It is of note that in the formation of the cluster complex **2**, the S^{2-} ligands were not added via a reagent. However, the S^{2-} ligands are essential for the formation of large clusters, since they bind the metal ions together. We have also found that in our previously reported large complexes, [Ag$_{14}$(μ$_6$-S)(SPh)$_{12}$(PPh$_3$)$_8$]·4CH$_3$OH·13H$_2$O,[9] [Cu$_{14}$(μ$_2$-S)(SPh)$_{12}$(PPh$_3$)$_6$],[10] and [S$_4$Cd$_{17}$(SPh)$_{24}$(CH$_3$OCS$_2$)$_{4/2}$]$_n$·

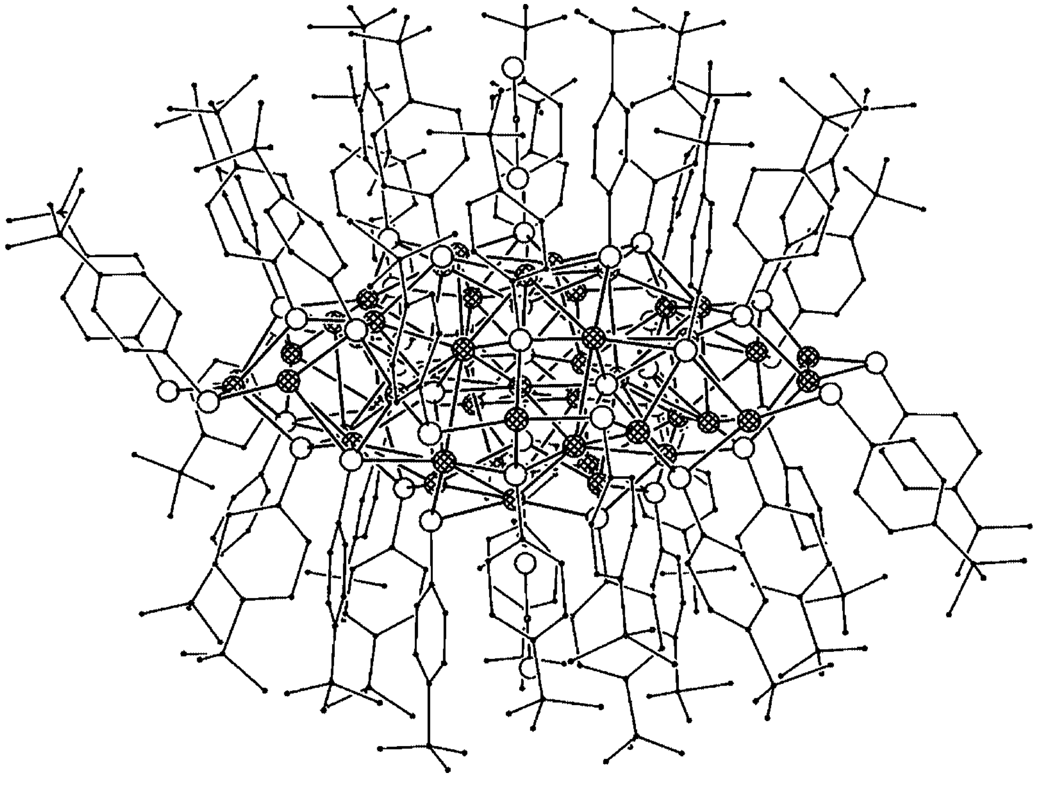

Figure 7. Structure of anionic cluster [Ag$_{50}$S$_7$(SC$_6$H$_4$$t$Bu-4)$_{40}$]$^{4-}$ in **2** with CS$_2$ solvent molecules in the channel-like cavities formed by the thiophenolates

nCH$_3$OH[11] etc., the S^{2-} ligands are formed from the reaction of CS_2 with RS^- in solution. We suggest that when the metal thiolate compound is dissolved, the solvent causes it to dissociate into various "active fragments", including RS^-, which reacts with CS_2 resulting in the formation of S^{2-} ions, as shown in Equation (1).[8]

$$RS^- + CS_2 \longrightarrow RS\text{-}CSS \underset{}{\overset{RS^-}{\rightleftharpoons}} RS\text{-}CS\text{-}SR + S^{2-} \qquad (1)$$

The new product is formed by the optimum "self-assembly" of these active fragments and then crystallizes from the solution. This new method for the synthesis of large M-S clusters has many advantages compared with other methods. The S^{2-} anions result from the equilibrium reaction. When large clusters are formed, the S^{2-} anions are used and the position of equilibrium shifts to right and the formation 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 the **2**, the reaction conditions are mild (room temperature) and easy to control and a moderate yield of 67% was observed. This result suggests that this is a promising method although further investigations are needed.

We have found that silver thiolate complexes, $(AgSR)_n$, such as $(AgS\textit{t}Bu)_n$, $(AgSC_6H_5)_n$, or $(AgSC_6H_2Me_3\text{-}2,4,6)_n$ with less bulky substituents hardly react with CS_2 and are insoluble in inert solvents. However, by increasing the size of the substituents, the polymeric complex $(AgSC_6H_2\textit{i}Pr_3\text{-}2,4,6)_n$ with sterically hindered arylthiolate ligands reacts readily with CS_2 in solution to give a decanuclear silver cluster complex $[Ag(SC_6H_2\textit{i}Pr_3\text{-}2,4,6)]_{10}$.[13] The arylthiolates with bulky substituents in the *ortho*-positions are more sterically congested than those with substituents in the *para*-position and this limits the cluster size. In this study, by the use of an arylthiolate ligand, $4\text{-}\textit{t}BuC_6H_4S^-$, with a substituent in the *para*-position, we obtained a large pentaconta-nuclear silver cluster complex **2**. However, using the arylthiolate ligand, $4\text{-}\textit{i}PrC_6H_4S^-$, with a less bulky substituent in the *para*-position, a larger hexaconta-nuclear silver cluster complex $[HNEt_3]_4[Ag_{60}S_7(SC_6H_4\textit{i}Pr\text{-}4)_{50}]$ (**3**) has been recently synthesized by the same method.[20] Complex **3** is also ionic composed of four $[HNEt_3]^+$ cations and an anionic cluster $[Ag_{60}S_7(SC_6H_4\textit{i}Pr\text{-}4)_{50}]^{4-}$, the structure of which is very similar to that of $[Ag_{50}S_7(SC_6H_4\textit{t}Bu\text{-}4)_{40}]^{4-}$, as shown in Figure 8. The core of the anionic cluster **3** consists of sixty silver atoms and fifty seven sulfur atoms. The shape of the core is discus-like, the inner part of which is the thickest. This fact once again demonstrates the rule we have observed that the less bulky the R group in $(AgSR)_n$, the more the degree of the association, n.[6] Clearly, however, the factors influencing the formation and structures of large clusters need to be further investigated.

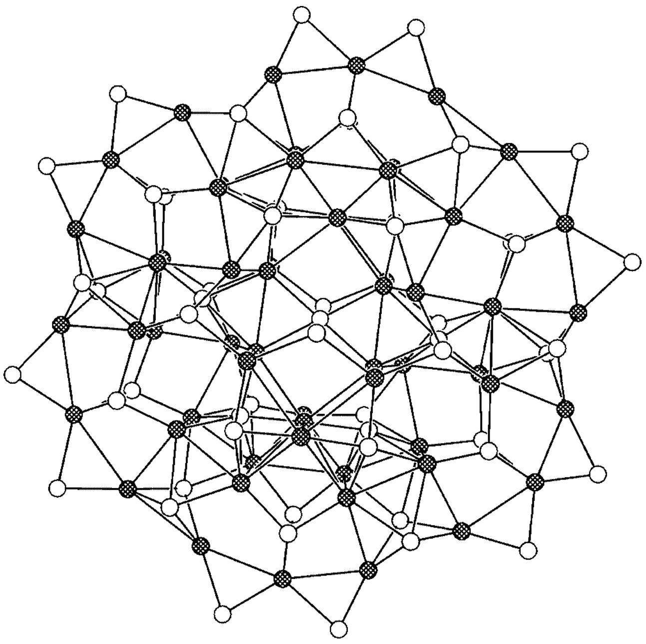

Figure 8. Structure of the $Ag_{60}S_{57}$ core of the anionic cluster $[Ag_{60}S_7\ (SC_6H_4\textit{i}Pr\text{-}4)_{50}]^{4-}$ in **3**; the cross-hatched circles represent the Ag atoms and the open circles represent the S atoms

Experimental Section

Reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled under nitrogen. Infrared spectra were recorded in KBr discs with a Nicolet-550 spectrometer. Elemental analyses were carried out using an Elemantar Vario EL analyzer. Melting points were measured with an X_6 microscopic melting point apparatus.

Complex 1: A solution of $4\text{-}\textit{t}BuC_6H_2SH$[15] (0.38 cm^3, 2.3 mmol) and Et_3N (0.32 cm^3, 2.3 mmol) in C_2H_5OH (8 cm^3) was added dropwise with stirring to a solution of $AgNO_3$ (274 mg, 1.6 mmol) in CH_3CN (5 cm^3). After stirring overnight at room temperature under a nitrogen atmosphere, the solvents were removed. The residue was dried in vacuo and then recrystallized from ethanol to afford a yellow powder (470 mg, yield 89.1%). Yellow crystals of **1** suitable for X-ray diffraction analysis were obtained by slow evaporation of the solvent from the ethanol solution of the crude product at room temperature over two days. m.p. 244.2−246.1 °C. $\{[HNEt_3]_{2n}[Ag_8Ag_{4/2}(SC_6H_4\textit{t}Bu\text{-}4)_{12}]_n\cdot nC_2H_5OH\}$: calcd. C 48.64, H 6.00, N 0.833; found C 48.40, H 5.676, N 0.790%. IR: $\tilde{\nu}$ = 3057 w, 3019 vw, 2958 vs, 2915 m, 2869 m, 2789 w, 2656 w, 2468 w, 1900 w, 1629 m, 1560 vw, 1483 s, 1465 m, 1393 m, 1361 m, 1268 m, 1190 w, 1159 w, 1118 s, 1080 w, 1018 m, 821 s, 732 w, 588 w, 546 m, 465 w cm^{-1}.

Complex 2: Carbon disulfide (4 cm^3) was added to a yellow-green solution of **1** (20 mg) in acetone (4 cm^3). The solution became golden-yellow and was then filtered. The filtrate gradually became red upon standing. Red block crystals of **2** (yield 67%) suitable for X-ray diffraction analysis were obtained by evaporating the filtrate at room temperature over several days. The crystals of **2** break into pieces and desolvate in a few minutes upon removal of the mother liquor and become black very easily when exposed to light. This necessitates storage with the mother liquor and with the exclusion of light. $Ag_{50}S_{47}C_{424}H_{584}N_4$ (unsolvated): calcd. C 40.30, H 4.66, N 0.443; found C 39.89, H 4.76, N 0.399%. IR: $\tilde{\nu}$ = 3049 w, 2946 vs, 2869 s, 2789 w, 2671 w, 2472 w, 1888 w, 1621 w, 1589 w, 1485

Table 3. Crystal data and refinement for **1** and **2**

	1	**2**
Empirical formula	$C_{68}H_{100}Ag_5NOS_6$	$C_{444}H_{620}Ag_{50}N_4O_6S_{51}$
M	1679.20	13138.00
T [K]	123(2)	123(2)
Color	yellow	red
Crystal size [mm]	0.50 × 0.20 × 0.20	0.80 × 0.60 × 0.40
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a [Å]	38.314(8)	36.486(7)
b [Å]	18.605(4)	36.666(7)
c [Å]	20.288(4)	40.702(8)
α [°]	90.0	90.0
β [°]	103.25(3)	95.21(3)
γ [°]	90.0	90.0
V [Å^3]	14077(5)	54226(16)
Z	8	4
D_c [g·cm^{-3}]	1.585	1.609
F(000)	6832	26104
μ [mm^{-1}]	1.585	1.998
θ range [°]	2.17−27.48	0.79−25.00
No.of reflections collected/unique	56953/16058	148864/44541
R_{int}	0.0494	0.0993
Data/restraints/ parameters	16058/9/806	44541/111/1751
Goodness of fit on F^2	0.773	0.813
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0433$ $wR2 = 0.0916$	$R1 = 0.0969$ $wR2 = 0.2331$
R indices (all data)	$R1 = 0.1083$ $wR2 = 0.1002$	$R1 = 0.2694$ $wR2 = 0.2907$
Largest difference peak and hole [e·Å^{-3}]	1.136, −0.743	3.102, −1.596

s, 1393 m, 1363 m, 1298 w, 1267 m, 1198 w, 1156 w, 1116 s, 1084 w, 1011 m, 820 s, 736 w, 577 w, 548 m, 448 w cm^{-1}.

X-ray Crystal Structure Determination of Complexes 1 and 2: Crystallographic measurements of complexes **1** and **2** were made on a Rigaku R-AXIS RAPID Image Plate diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) operating at 50Kv and 40 mA. Absorption corrections were applied by correction of symmetry-equivalent reflections using the ABSCOR program.[16] The structures were solved by direct methods and successive difference map (SHELXS-97)[17] and refined using full-matrix least-squares on F^2 for all unique data (SHELXL-97).[18] For complex **1**, all non-hydrogen atoms except the C and O atoms in the solvent molecule C_2H_5OH were refined anisotropically. The hydrogen atoms in the benzene groups and the three ordered *t*Bu groups were included in their calculated positions with the rigid model. Other hydrogen atoms were excluded from the refinement. The carbon atoms of the three *t*Bu groups are disordered. The occupancy of the solvent molecules C_2H_5OH were fixed at 0.7. For complex **2**, the Ag, S, and 72 C atoms are anisotropic whilst the N, O, and 150 C atoms are isotropic. Three Ag atoms and six C atoms are disordered. No hydrogen 3atoms were included in the refinement. There are 20 residual peaks (1.00−3.10 e·Å^{-3}) near the Ag atoms.

CCDC-199451 (for **1**) and -178360 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Crystal data and structure refinements for **1** and **2** are presented in Table 3.

Acknowledgments

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