Cluster Compounds

DOI: 10.1002/anie.200704249

Synthesis and Crystal Structures of the Ligand-Stabilized Silver Chalcogenide Clusters $[Ag_{154}Se_{77}(dppxy)_{18}]$, $[Ag_{320}(S\mathit{t}Bu)_{60}S_{130}(dppp)_{12}]$, $[Ag_{352}S_{128}(S\mathit{t}C_5H_{11})_{96}]$, and $[Ag_{490}S_{188}(S\mathit{t}C_5H_{11})_{114}]$**

Christopher E. Anson, Andreas Eichhöfer, Ibrahim Issac, Dieter Fenske, Olaf Fuhr, Paloma Sevillano, Claudia Persau, Dietmar Stalke, and Jiatao Zhang*

For the last few years we have been working on the synthesis and characterization of metal–chalcogenide clusters. For most of the transition metals, one observes the formation of relatively low-nuclearity cluster complexes,[1] such as $[Co_6E_8(PR_3)_6]$ (E = S, Se, Te; R = organic groups) und $[Ni_{34}Se_{22}(PPh_3)_{20}]$. In contrast, for clusters of copper and silver one can find a rich variety of structures.[2]

Recently, we reported the synthesis of metal-rich silver–chalcogenide clusters, such as $[Ag_{70}S_{20}(SPh)_{28}(dppm)_{20}](CF_3CO_2)_2$, $[Ag_{123}S_{35}(S\mathit{t}Bu)_{50}]$, $[Ag_{188}S_{94}(P\mathit{n}Pr_3)_{20}]$, $[Ag_{262}S_{100}(S\mathit{t}Bu)_{62}(dppb)_6]$, and $[Ag_{344}S_{124}(S\mathit{t}Bu)_{96}]$ (dppm = bis(diphenylphosphanyl)methane; dppb = 1,4-bis(diphenylphosphanyl)butane), particles with diameters in the nanometer range. The surfaces of these clusters are protected by ligands, thus preventing further reaction to form the thermodynamically stable binary silver chalcogenide salts.[3] Perhaps surprisingly, these cluster complexes could be prepared reproducibly and in high yield by the reaction at room temperature of, for example, silver carboxylates with $S(\mathit{t}Bu)SiMe_3$ in the presence of tertiary phosphanes. In contrast, at higher temperatures amorphous Ag_2S was formed. We therefore propose that these metal-rich clusters represent intermediates in the formation of solid Ag_2S. When the progress of the reaction is monitored by dynamic light scattering, initially no particles are formed that are large enough to be observed by this technique. However, after several days particles form in the size range 2–4 nm and crystallize out of solution. For example, $[Ag_{188}S_{94}(P\mathit{n}Pr_3)_{20}]$ is a spherical molecule with a diameter of approximately 1.9 nm. By contrast, molecules of $[Ag_{262}S_{100}(S\mathit{t}Bu)_{62}(dppb)_6]$ or $[Ag_{344}S_{124}(S\mathit{t}Bu)_{96}]$ are flattened ellipsoids with maximum diameters of the Ag–S cores of 2.6 and 3.2 nm, respectively.

The structural determinations of these large clusters proved problematic. With nuclearities of up to 100 metal atoms, crystals generally diffract well to up high 2θ values (50–60° with $Mo_{K\alpha}$); the atoms have low temperature factors, and no high residual electron density is observed within the clusters. However, this situation changes for larger clusters with nuclearities greater than around 120 metal atoms. For such clusters, the intensities of the reflections drop off rather sharply above $2\theta \approx 40°$, and the structure refinement results in unsatisfactorily high R factors, with high residual electron density within the cluster molecule. Satisfactory R factors can only be obtained if this electron density can be modeled during the refinement. As this electron density generally lies close to the heavy atoms, it can be difficult to interpret and thus complicates efforts to give precise estimates of the molecular formulae. These effects may result from a range of factors:

1) There is no perfect translational order in the lattice.
2) With the silver–chalcogenide clusters there is a tendency towards nonstoichiometry, as is seen for the binary phases.[4] This behavior could be a consequence of the rather similar electronegativities of silver and the chalcogenides. There is no clear distinction between Ag^+ and E^{2-} (E = S, Se, Te), and the clusters behave rather like alloys.[5]
3) The surface tension of the spherical molecules generates a Laplace pressure within the molecule, which can result in a disorder or even a phase transition.
4) Interactions between defects within the clusters can themselves lead to an increase in the defect concentration.[6]

It is therefore no longer possible, in a strict sense, to obtain precise molecular formulae of these large clusters from their structure determinations. One can only think in terms of "idealized" formulae, resulting from the assumptions that nonbonded Ag···Ag distances are larger than 280 pm and that nonbonding S···S or S···Se distances are at least 410 pm. It is conceivable that different spatial arrangements of Ag^+ and chalcogenide ions can be accommodated below the ordered

[*] Dr. C. E. Anson, Dr. A. Eichhöfer, Dr. I. Issac, Prof. D. Fenske, Dr. O. Fuhr, Dr. P. Sevillano, Dr. C. Persau, Dr. J. Zhang
Institut für Anorganische Chemie
Universität Karlsruhe
Engesserstrasse 15, 76131 Karlsruhe (Germany)
Fax: (+49) 721-608-8440
E-mail: dieter.fenske@aoc1.uni-karlsruhe.de
and
Institut für Nanotechnologie
Forschungszentrum Karlsruhe
Postfach 3640, 76021 Karlsruhe (Germany)
Prof. Dr. D. Stalke
Institut für Anorganische Chemie
Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)

[**] This work was supported by the DFG (Center for Functional Nanostructures) and the Fonds der Chemischen Industrie. We are grateful to Dr. H. Rösner (Institut für Nanotechnologie, Forschungszentrum Karlsruhe) for the measurement of TEM images, and to Dr. G. Buth (Institut für Synchrotronstrahung, Forschungszentrum Karlsruhe) for assistance in measuring the X-ray dataset for **4** on the SCD beamline of the ANKA synchrotron. dppxy = 1,4-bis(diphenylphosphanylmethyl)benzene; dppp = 1,3-bis(diphenylphosphanyl)propane.

surface of the cluster. This possibility is supported by the observation that datasets measured from crystals obtained from different synthetic reactions can often not be refined with the same set of coordinates for the Ag, chalcogen, and carbon atoms, even though they have the same unit cells (see below). Furthermore, one often observes a broad distribution of molecular ions in the mass spectrum. The structural determination of such large cluster molecules is thus pushing the currently available techniques to their limits, and it must be accepted that at present they may not always be able to give a satisfactory answer.

We now report the synthesis and structural determination of compounds **1**–**4**.[7]

$[Ag_{154}Se_{77}(dppxy)_{18}]$ (**1**)

$[Ag_{320}(S\mathit{t}Bu)_{60}S_{130}(dppp)_{12}]$ (**2**)

$[Ag_{352}S_{128}(S\mathit{t}C_5H_{11})_{96}]$ (**3**)

$[Ag_{490}S_{188}(S\mathit{t}C_5H_{11})_{114}]$ (**4**)

Compound **1** can be synthesized by the reaction of a suspension of Ag*S*t*Bu und 1,4-bis(diphenylphosphanylmethyl)benzene (dppxy) in a mixture of toluene and chloroform with $Se(SiMe_3)_2$. A dark solution forms after a few days, from which small platelike crystals of **1** are deposited [Eq. (1)]. The reaction of Ag*S*t*Bu, $S(SiMe_3)_2$, and 1,3-bis(diphenylphosphanyl)propane (dppp) under similar conditions results in the formation of black crystals of **2** [Eq. (2)].

$$Ag\mathit{S}t\mathit{Bu} + Se(SiMe_3)_2 \xrightarrow[\text{toluene/chloroform}]{\text{dppxy}} \mathbf{1} \quad (1)$$

$$Ag\mathit{S}t\mathit{Bu} + S(SiMe_3)_2 \xrightarrow[\text{toluene/chloroform}]{\text{dppp}} \mathbf{2} \quad (2)$$

If $Ag\mathit{S}t\mathit{C}_5H_{11}$ is now treated with $S(SiMe_3)_2$ and 4,4′-bis(diphenylphosphanyl)biphenyl (dppbp) in toluene, then either rhombic or hexagonal crystals of **4**, or occasionally needlelike crystals of **3**, are obtained from the resulting black solution. The rhombic crystals have so far only given a very unsatisfactory structure.[8] From MALDI-TOF mass spectra, however, it appears that the same compound is present in the hexagonal crystals [Eq. (3)]. In the absence of dppbp a red solution is obtained from which we have so far not obtained crystals.

$$Ag\mathit{S}t\mathit{C}_5H_{11} + S(SiMe_3)_2 \xrightarrow[\text{xylene/THF}]{\text{dppbp}} \mathbf{3} + \mathbf{4} \quad (3)$$

Compound **1** crystallizes in the space group $P2_1/n$ with $Z = 4$. Eight molecules of $CHCl_3$ per cluster molecule could be located and refined, but from the voids still present in the lattice, we assume that further chloroform molecules are present but could not be located. Figure 1 (top) shows that the cluster forms a distorted spherical molecule with 18 bidentate dppxy ligands coordinated to its surface. The Ag–P and Ag–Se distances are similar to those previously found in other Ag–Se clusters, such as $[Ag_{90}Se_{38}(Se\mathit{t}Bu)_{14}(PEt_3)_{22}]$, $[Ag_{114}Se_{32}(Se\mathit{n}Bu)_{48}(P\mathit{t}Bu)_{312}]$, and $[Ag_{172}Se_{40}(Se\mathit{n}Bu)_{92}(dppp)_4]$. We noted a structural transition in these compounds from "molecular" clusters, with no structural relationship to Ag_2Se, to ligand-protected sections of the structure of the binary phase. At that time, we suggested that this transition occurred when the nuclearity reached 112–114 Ag atoms.[9] However, the structure of **1** is completely unrelated to the Ag_2Se structure type. It appears that the ligand shell is responsible for this structure. In contrast to the clusters mentioned above, **1** is composed of a $\{(Ag_2Se)_{77}\}$ particle that is only ligated by neutral phosphane ligands. The structure determination was not straightforward, as some of the Ag atoms, and probably also some Se atoms, are disordered. The formulation as $[Ag_{154}Se_{77}(dppxy)_{18}]$ is thus only an idealized formula. If the disorder is ignored, then $R_1 = 0.107$, but by taking the disorder into account R_1 improves to 0.091. The 77 Se^{2-} ions form μ_4, μ_5, μ_6, μ_7, and μ_8 bridges.

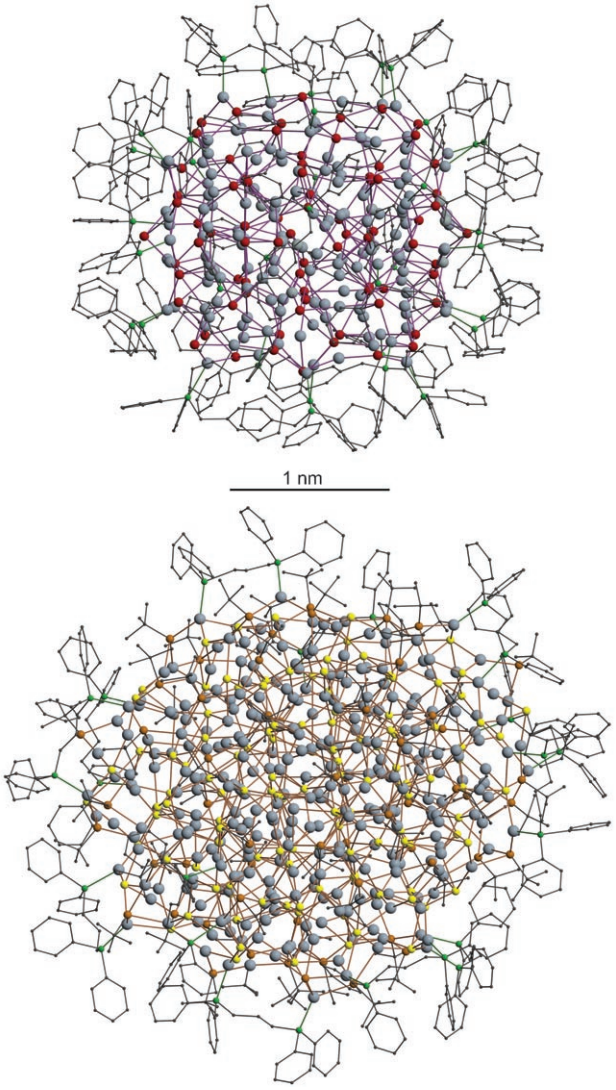

Figure 1. Structures of **1** (top) und **2** (bottom). Ag gray, Se red, S in $S\mathit{t}Bu^-$ orange, S^{2-} yellow, C gray (small spheres), P green.

As expected, the Ag–Se distances increase with increasing number of Ag centers bridged by the Se^{2-} ions. Thirty six of the 154 Ag^+ ions are bonded to phosphorus atoms of the phosphane ligands. Nineteen Ag ions have trigonal-planar geometry (Σ(bond angles) = 353–360°) with one P and two Se atoms coordinated. In contrast, 17 Ag ions are coordinated

by three Se^{2-} ions and one P atom in a distorted tetrahedral coordination sphere. All other Ag^+ ions have distorted linear, trigonal-planar, or tetrahedral coordination spheres made up of Se^{2-} ions alone.

The molecular structure of **2** (Figure 1, bottom) consists of a $\{Ag_{260}S_{130}\}$ cluster core, to which 60 Ag*S*t*Bu groups are attached; 24 Ag^+ ions are ligated by phosphorus atoms of the dppp ligands. The phosphane ligands together form a belt, which covers the equator of the spherical molecule. These P-coordinated Ag centers have either trigonal-planar (8) or tetrahedral (14) environments, and additional coordination from two or three S^{2-} ions, respectively. Only two Ag^+ ions (Ag172 and Ag188) have each one P and one S atom forming a quasi-linear coordination environment.

All the other Ag^+ ions on the surface of the cluster have either distorted linear or trigonal-planar environments about the S atoms. Only those within the cluster are bonded to four S^{2-} atoms. As expected, the mean Ag–S distance increases with increasing coordination number. For the linear S-Ag-S units, the distances lie in the range 235–252 pm. The shorter these distances, the closer the S-Ag-S angle is to 180°. For trigonal-planar coordination, the Ag–S distances are in the much wider range 240–290 pm, and in some cases it would be better to talk of 2+1 coordination. For the distorted tetrahedrally coordinated Ag^+ ions, one finds a similar range of Ag–S distances (245–298 pm).

The S atoms of the 60 S*t*Bu$^-$ groups form μ_2, μ_3, and μ_4 bridges. All the remaining S atoms form μ_3-, μ_4-, μ_5-, μ_6-, and μ_8-bridging S^{2-} ions. There is a trend for the S^{2-} ions to bridge between a higher number of Ag atoms, the closer they are to the center of the cluster. The ellipsoidal cluster core has a diameter of 2.4–2.9 nm; if the organic ligand shell is included, this value rises to an overall particle size of 3.3–3.9 nm. This result is in agreement with TEM images of **2**, in which the clusters can be clearly seen.[10]

The bidentate ligand dppp was employed in the synthesis of **2**, and it appears to have the appropriate steric requirements to coordinate to a cluster the size of **2**. If, however, dppbp is used, no product is observed.

As already mentioned, the formation of **3** and **4** is only possible in the presence of bidentate phosphanes. At present we do not know the reason for this. The structure of **3** (Figure 2), an oblate ellipsoidal shape, shows great similarities to that of $[Ag_{344}S_{124}(StBu)_{96}]$. However, by contrast, cluster **3** has S*t*C_5H_{11} instead of S*t*Bu groups as ligands on the surface, although this seems to result in only a small structural change. It is likely that all the 96 μ_2-, μ_3-, and μ_4-S atoms on the cluster surface belong to S*t*C_5H_{11} groups, but only 84 of these 96 *t*C_5H_{11} groups could be located in the structure. However, allowing for this, we can arrive at an idealized formula $[Ag_{352}S_{128}(SC_5H_{11})_{96}]$.

It appears that **3** is only an intermediate product in the formation of the larger cluster in compound **4**. Under the reaction conditions described, **3** is only ever obtained in low yield. The principal product is always black hexagonal or rhombic crystals of **4**. The structure analysis shows that the hexagonal crystals crystallize in the trigonal space group $P3_221$ and the rhombic crystals in the monoclinic space group *Cc*. However, MALDI-TOF mass spectra indicate that the same compound is involved in both cases. In any case, we came up against substantial problems in solving and refining the crystal structures. Figure 3 shows the structure of **4** (with the *t*C_5H_{11} groups bonded to the surface S atoms omitted) viewed from two different directions. It proved to be very difficult to locate and refine many of the *t*C_5H_{11} groups, so in accordance with previous results the μ_2-, μ_3-, and μ_4-S atoms on the surface of the cluster were assumed to belong to S*t*C_5H_{11} groups, giving a total of 114 S*t*C_5H_{11} ligands. Of these 114 disordered groups, only 108 could be located.[11]

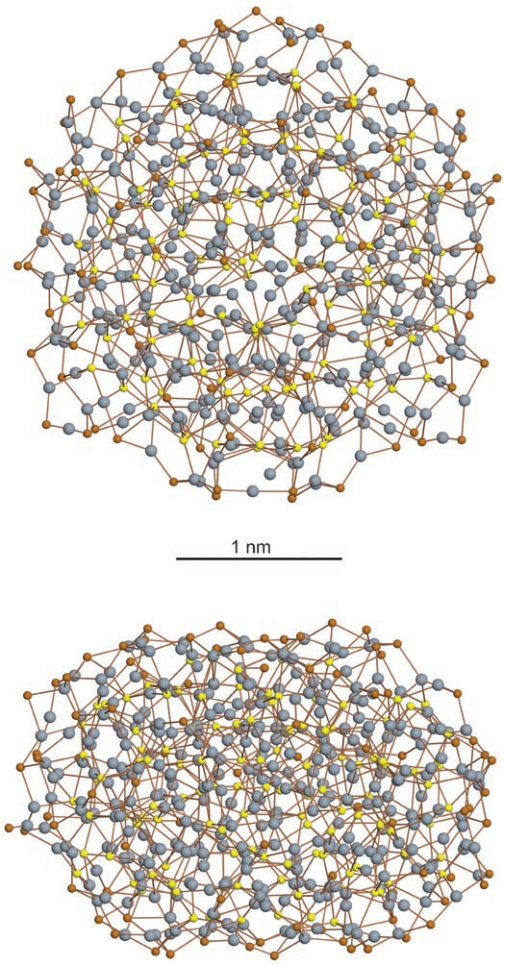

Figure 2. Top: structure of **3** (C atoms of the C_5H_{11} groups omitted); bottom: structure of **3** rotated by 90°. Ag gray, S in $SC_5H_{11}^-$ orange, S^{2-} yellow.

The AgS core in **3** has the form of a flattened sphere of diameter 2.3 nm, or 2.5–3.5 nm if the C_5H_{11} groups are included. In **4**, the AgS cluster can be described as a narrow-waisted cylinder of dimensions 2.8–3.1 nm. If the *t*C_5H_{11} groups are included, the diameter increases to 3.3–3.6 nm. As for **3**, the Ag and S atoms within the cluster are substantially disordered, and the formula can only be idealized as $[Ag_{490}S_{188}(StC_5H_{11})_{114}]$, which would have a formula weight of 70650 Da. In fact, MALDI-TOF measurements from a number of crystals indicate that the maxima in the molecular weight vary between 65846 und 68032.6 Da,[12] even though their unit cell geometries do not vary significantly. It is also clear that the distribution of molecular

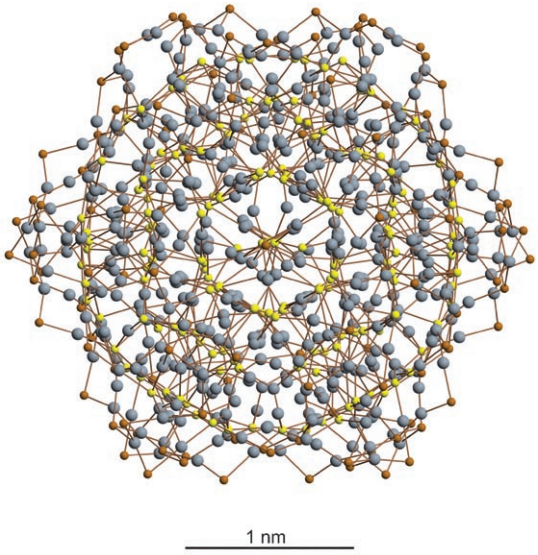

Figure 3. Top: structure of **4** (C atoms of the C_5H_{11} groups omitted); bottom: structure of **4** rotated by 90°. Ag gray, S in $SC_5H_{11}^-$ orange, S^{2-} yellow.

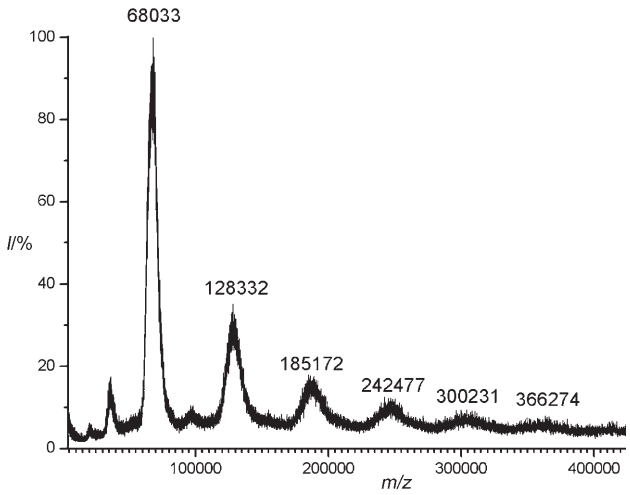

Figure 4. MALDI-TOF spectrum of **4**.

weights within a spectrum is very broad (61–74 kDa). This result is in agreement of the findings of other authors who have used MALDI-TOF methods to characterize nanoparticles.[13] From these previous results from related nanoclusters, it is clear that organic or SR groups are very easily lost by fragmentation under the conditions of MALDI-TOF experiments.[3c] For this reason, interpretation of such mass spectra is not straightforward; however, it is nonetheless striking that a broad distribution of high masses appears in the MALDI-TOF spectrum of **4** (Figure 4). In addition to the maximum at 68032 Da, there are also maxima at 128331, 185171, 242477, 300231, 366273, and 456879 Da.

This distribution evidently results from cluster aggregation, which can occur in the plasma created by laser excitation. The difference in mass between the maxima is around 57.5 kDa, which is very close to the mass of the fragment that would result from the loss of all the StC_5H_{11} groups from **4** ($\{Ag_{490}S_{188}\}$: 58.88 kDa). From samples prepared under different experimental conditions one can also observe a very narrow distribution of masses at 59.2 kDa. It is possible that a variable number of Ag_2S units could be arranged under the shell of the 114 $AgStC_5H_{11}$ groups. For this reason, a precise molecular formula cannot be obtained from the structural analyses; instead, in agreement with the MALDI-TOF results, we must be content with a range of compositions. We then arrive at $[Ag_{(474-490)}S_{(180-188)}(StC_5H_{11})_{114}]$ as the best formulation. In this case, 490 Ag atoms corresponds to full occupancy of all sites in the structure, whereas the lower number is the formula obtained from the lowest observed molecular mass. In this respect, these compounds behave in a similar manner to binary Ag_2S, for which a range of compositions is also observed.[4] The geometries and bond lengths for the Ag and S atoms of the $StC_5H_{11}^-$ and S^{2-} ligands are similar to those in **2** and **3**, but given the degree of disorder a more detailed discussion is not advisable.

Figure 5 (upper two diagrams) shows a space-filling model of the Ag, Se, and P atoms in **1**, and the Ag, S, and P atoms in **2**. The structures of the Ag–S cores in **3** and **4** are shown in the lower two diagrams in Figure 5. The crystal lattices of the distorted spheroidal molecules display the densest packing. The rather large cavities between the clusters contain disordered solvent molecules, which can be removed from the crystal in vacuo (with the exception of **1**). Characteristic bands for vibrations of the SR groups and phosphane ligands can be seen in the IR spectra of **1**–**4**.

In conclusion, we must emphasize that the structures we have obtained for these large nanoclusters are by no means a perfect solution to the problem, but this is perhaps to be expected, as we are at the very edge of molecular chemistry. Clusters **1**–**4** can be obtained in high yields, and future work will investigate the spectroscopic and electronic properties of compounds of this type.

Experimental Section

1: A suspension of Ag*St*Bu (0.1 g, 0.5 mmol) and dppxy (0.12 g, 0.25 mmol) in a mixture of 15 mL chloroform and 5 mL toluene was

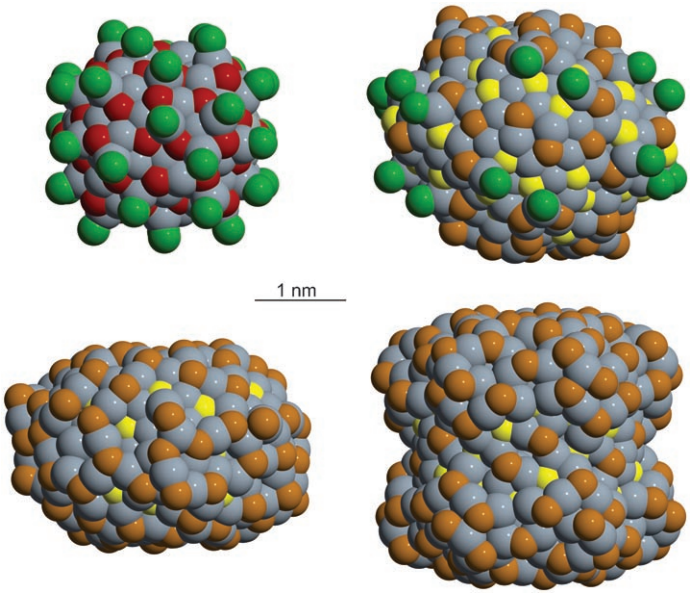

Figure 5. Space-filling structures of the Ag-Se-P core of **1** (top left), the Ag-S-P core of **2** (top right), the Ag-S core of **3** (bottom left) and the Ag-S core of **4** (bottom right). Ag gray, Se red, S in S*t*Bu$^-$ orange, S^{2-} yellow, P green.

treated at −55 °C with $Se(SiMe_3)_2$ (0.064 mL), and the resulting solution was allowed to warm with stirring to −25 °C. After one week at −25 °C, one week at 0 °C, and a further week at room temperature, black crystals of **1** were obtained in 30–50 % yield.

2: AgS*t*Bu (0.1 g, 0.5 mmol) and dppp (0.1 g, 0.25 mmol) were suspended in 25 mL toluene and 15 mL chloroform, and treated with $S(SiMe_3)_2$ (0.04 mL, 0.25 mmol) at ambient temperature (20–23 °C) with stirring. The initial white suspension turned yellow and then bright orange. After 10 minutes, the solid had dissolved, and a clear deep red solution formed, which turned dark brown on standing. After 2–3 weeks, large black crystals of **2** began to form, but the yield increased to 80–90 % if the solution was left undisturbed for 6 weeks.

3: AgS*t*C_5H_{11} (0.105 g, 0.5 mmol) and dppbp (0.1 g, 0.25 mmol) in 20 mL tetrahydrofuran were treated with $S(SiMe_3)_2$ (0.04 mL, 0.25 mmol) at −25 °C with stirring and allowed to warm to room temperature. After standing for 3–4 weeks, crystals of **4** were obtained, together with a low yield (10–20 %) of black needlelike crystals of **3**.

4: A suspension of AgS*t*C_5H_{11} (0.105 g, 0.5 mmol) and dppbp (0.1 g, 0.25 mmol) in a mixture of 15 mL *p*-xylene und 10 mL tetrahydrofuran was treated with $S(SiMe_3)_2$ (0.04 mL, 0.25 mmol) at 15 °C with stirring. The initial white suspension turned yellow and then bright orange. After 10 minutes, the solid had dissolved, and a clear deep red solution formed, which turned dark brown on standing. After 2–3 weeks, black rhombic and hexagonal crystals of **4** were obtained in 40–60 % yield.

Received: September 14, 2007
Published online: January 4, 2008

Keywords: chalcogenides · cluster compounds · mass spectrometry · silver · structure elucidation

[1] a) D. Fenske, J. Ohmer, J. Hachgenei, *Angew. Chem.* **1985**, *97*, 993 – 995; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 993 – 995; b) D. Fenske, J. Ohmer, J. Hachgenei, K. Merzweiler, *Angew. Chem.* **1988**, *100*, 1300 – 1320; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1277 – 1296; c) D. Fenske in *Clusters and Colloids, From Theory to Applications* (Ed.: G. Schmid), VCH, Weinheim, **1994**.

[2] a) H. Krautscheid, D. Fenske, G. Baum, M. Semmelmann, *Angew. Chem.* **1993**, *105*, 1364 – 1367; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1303 – 1305; b) D. Fenske, H. Krautscheid, *Angew. Chem.* **1990**, *102*, 799 – 801; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 796 – 799; c) S. Dehnen, A. Schäfer, R. Ahlrichs, D. Fenske, *Chem. Eur. J.* **1996**, *2*, 429 – 435; d) S. Dehnen, A. Schäfer, D. Fenske, R. Ahlrichs, *Angew. Chem.* **1994**, *106*, 786 – 790; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 746 – 749; e) S. Dehnen, A. Eichhöfer, D. Fenske, *Eur. J. Inorg. Chem.* **2002**, 279 – 317; f) D. Fenske, *Nanoparticles, From Theory to Application* (Ed.: G. Schmid), VCH, Weinheim, **2004**.

[3] a) X. J. Wang, T. Langetepe, C. Persau, B. S. Kang, G. S. Sheldrick, D. Fenske, *Angew. Chem.* **2002**, *114*, 3972 – 3977; *Angew. Chem. Int. Ed.* **2002**, *41*, 3818 – 3822; b) D. Fenske, C. Persau, S. Dehnen, C. E. Anson, *Angew. Chem.* **2004**, *116*, 309 – 313; *Angew. Chem. Int. Ed.* **2004**, *43*, 305 – 309; c) D. Fenske, C. E. Anson, A. Eichhöfer, O. Fuhr. A. Ingendoh, C. Persau, C. Richert, *Angew. Chem.* **2005**, *117*, 5376 – 5381; *Angew. Chem. Int. Ed.* **2005**, *44*, 5242 – 5246.

[4] a) G. A. Wiggers, *Am. Mineral.* **1971**, *56*, 1882 – 1888; b) Z. G. Pinsker, C. Chiang Ling, R. M. Imamov, E. L. Lapidus, *Sov. Phys. Cristallogr. (Engl. Transl.)* **1965**, *7*, 225 – 233; c) F. C. Kracek, *Trans. Am. Geophys. Union* **1946**, *27*, 364; d) S. Djurle, *Acta Chem. Scand.* **1958**, *12*, 1427; e) P. Rahlfs, *Z. Phys. Chem. Abt. B* **1936**, *31*, 157 – 194; f) E. Rickert, *Z. Phys. Chem.* **1960**, *24*, 418 – 421; g) A. Böttcher, G. Haase, H. Treupel, *Z. Angew. Phys.* **1955**, *7*, 478 – 487; h) P. Junod, *Helv. Phys. Acta* **1959**, *32*, 567 – 600; i) A. J. Früh, *Z. Kristallogr.* **1958**, *110*, 136 – 144.

[5] a) R. Ahlrichs, D. Fenske, A. Rothenberger, S. Wieber, C. Schrodt, *Eur. J. Inorg. Chem.* **2006**, 112 – 1129; b) R. Ahlrichs, D. Fenske, M. McPartlin, A. Rothenberger, C. Schrodt, S. Wieber, *Angew. Chem.* **2005**, *117*, 4002 – 4005; *Angew. Chem. Int. Ed.* **2005**, *44*, 3932 – 3936; c) R. Ahlrichs, C. E. Anson, R. Clérac, D. Fenske, A. Rothenberger, M. Sierka, S. Wieber, *Eur. J. Inorg. Chem.* **2004**, 2933 – 2936.

[6] J. Maier, *Solid State Ionics* **2002**, *154–155*, 291 – 301; J. Maier, *Solid State Ionics* **2002**, *148*, 367 – 374; W. Münch, *Z. Anorg. Allg. Chem.* **2000**, *626*, 264 – 269.

[7] Crystal structure determinations: Data collection: Stoe IPDS 2 diffractometers with $Mo_{K\alpha}$ radiation (**1**–**3**) or Bruker SMART Apex diffractometer with synchrotron radiation ($\lambda = 0.8000$ Å) on the SCD beamline at ANKA, Forschungszentrum Karlsruhe; absorption correction, structure solution, and refinement with SHELXD and SHELX97. CCDC-660926, CCDC-660927, CCDC-660928, and CCDC-660929 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. **1**: $C_{584}H_{512}Ag_{154}Cl_{24}P_{36}Se_{77}$, 32006.12 g mol^{-1}, $T = 150$ K, monoclinic, $P2_1/n$ (No. 14), $Z = 4$, $a = 5270.4(6)$, $b = 3270.1(2)$, $c = 5421.9(5)$ pm, $\beta = 98.85(1)°$, $V = 92332.5 \times 10^6$ pm, $F(000) = 58560$, $\mu(Mo_{K\alpha}) = 6.38$ mm^{-1}, $2\theta_{max} = 38°$, 269926 reflections, of which 72624 unique and 47986 with $I > 2\sigma(I)$, $R_{int} = 0.1171$, $R\sigma = 0.091$. 3674 parameters (Ag, Se, P: anisotropic, C: isotropic; phenyl groups refined as rigid groups; Ag1–Ag152 refined with full occupancy, Ag153–Ag164 as partial Ag atoms; residual electron density peaks near Ag atoms of ca. 5 e Å^{-3} were refined as partially occupied Ag atoms.). $R_1 = 0.098$, $wR_2 = 0.2592$. **2**: $C_{578}H_{868}Ag_{320}P_{24}S_{190}$, 48953.48 g mol^{-1}, $T = 100$ K, orthorhombic, $P2_12_12_1$ (No. 19), $Z = 4$, $a = 4769.7(9)$, $b = 5025.2(10)$, $c = 5665.3(11)$ pm, $V = 135789.8 \times 10^6$ pm^3, $F(000) = 90640$, μ-$(Mo_{K\alpha}) = 4.83$ mm^{-1}, $2\theta_{max} = 41.6°$, 299136 reflections, of which 142157 unique, and 103936 with $I > 2\sigma(I)$, $R_{int.} = 0.1582$, $R\sigma = 0.1228$. 6538 parameters (Ag, P, S: anisotropic, C: isotropic), some *t*Bu and Ph groups refined as rigid groups. $R_1 = 0.0786$,

$wR_2 = 0.2230$, Flack χ parameter = 0.03(3). Residual density peaks near the Ag atoms were refined as disordered partial S atoms (S189–S196). **3**: $C_{480}H_{1056}Ag_{352}S_{224}$, 52176.30 g mol^{-1}, T = 140 K, monoclinic, *Cc* (No. 9), $Z = 4$, $a = 2875.4(6)$, $b = 6572.9(13)$, $c = 5848.9(12)$ pm, $\beta = 96.89(3)°$, $V = 109743.4 \times 10^6$ pm^3, $F(000) = 96564$, $\mu(Mo_{K\alpha}) = 6.61$ mm^{-1}, $2\theta_{max} = 37°$, 56074 reflections, of which 48592 unique and 30580 with $I > 2\sigma(I)$, $R_{int} = 0.0943$, $R\sigma = 0.0595$. 5086 parameters (Ag, S: anisotropic, C: isotropic). $R_1 = 0.1069$, $wR_2 = 0.2947$. S1–S96 are S atoms of the S*t*C$_5$H$_{11}$ groups, S97–S220 are the S^{2-} ions, S300–S311 are disordered S positions. Ag1–Ag342 were refined with full occupancy, Ag343–Ag355 as disordered partially occupied Ag atoms. **4**: $C_{570}H_{1254}Ag_{490}S_{302}$, $T = 100$ K, trigonal, $P3_221$ (No. 154), $Z = 3$, $a = 3525.36(12)$, $c = 9789.4(6)$ pm, $V = 105364.4 \times 10^6$ pm^3, $F(000) = 97608$, $\lambda = 0.8000$ Å, $\mu = 7.12$ mm^{-1}, $2\theta_{max} = 36°$, 142128 reflections, of which 41927 unique and 34549 with $I > 2\sigma(I)$, $R_{int} = 0.121$, $R\sigma = 0.095$, 3622 parameters (Ag, S: anisotropic, C: isotropic), $R_1 = 0.110$, $wR_2 = 0.275$. Ag1–Ag226 were refined with full occupancy, Ag227–Ag253 with partial occupancy, S1–S57 are the S atoms of the S*t*C$_5$H$_{11}^-$ groups, S58–S149 the S^{2-} ions. If the disordered partial S atoms S200–S227 are not included in the refinement, R_1 increases to 0.115.

[8] Unit cell parameters (100 K): $a = 3677.5(2)$, $b = 5953.9(2)$, $c = 6239.9(3)$ pm, $\beta = 93.93(2)°$, $V = 136300 \times 10^6$ pm^3, space group *Cc* (No. 7). So far we have only been able to refine the structure to $R_1 = 0.17$.

[9] D. Fenske, N. Zhu, T. Langetepe, *Angew. Chem.* **1998**, *110*, 2783 – 2788; *Angew. Chem. Int. Ed.* **1998**, *37*, 2639 – 2644.

[10] A carbon grid was dipped into a dilute solution of the cluster and transferred into the microscope under a protective atmosphere.

[11] Solvent molecules were removed from the crystals by pumping under vacuum before analysis. Elemental analysis for the dried crystals (%): calcd for $[Ag_{490}S_{188}(StC_5H_{11})_{114}]$: C 9.69, H 1.79, Ag 74.81, S 13.21; found: C 9.76, H 1.01, S 12.82.

[12] MALDI-TOF spectra were recorded on an Applied Biosystems Voyager System 6059, with 2-hydroxybenzoic acid as matrix. A more or less broad distribution of masses for the molecular ions is observed, depending on the precise settings of the instrument parameters.

[13] G. A. Khitrov, G. F. Strouse, *J. Am. Chem. Soc.* **2003**, *125*, 10465 – 10469.

