New Copper Chalcogenide Clusters with a Selenide Core and a Sulfide Shell

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The reaction of copper(I) acetate with mixtures of $PhSSiMe_3$ and $Se(SiMe_3)_2$ in the presence of PPh_3 leads to a series of new cluster compounds consisting of a copper selenide core surrounded by a sulfide shell: $[Cu_{17}Se(SPh)_{15}(PPh_3)_4]$, $[Cu_{20}Se(SPh)_{12}(OAc)_6(PPh_3)_4]$, $[Cu_{28}Se_6(SPh)_{16}(PPh_3)_8]$, $[Cu_{36}Se_8(SPh)_{20}(PPh_3)_8]$, $[Cu_{54}Se_8(SPh)_{30}(OAc)_8(PPh_3)_6]$, and $[Cu_{72}Se_{14}(SPh)_{36}(OAc)_8(PPh_3)_6]$. They have been structurally characterized by single-crystal X-ray analysis. The two smallest clusters have a ball-like structure with one selenium atom in the center totally enclosed by sulfur atoms. In the other clusters the inner copper–selenium core is surrounded by an incomplete sulfur shell varying between 53 and 87 % coverage.

Introduction

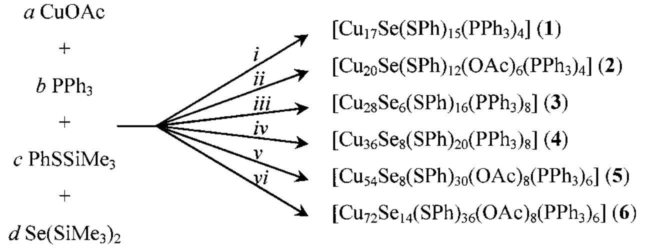
Within the last few years there has been a lot of interest in the synthesis and properties of nanoparticles consisting of binary compounds that are known to be semiconductors as bulk substances.[1–3] Investigations of their optical properties show that the quantum yield of their fluorescence can be improved enormously by surrounding them with a thin shell (one or two monolayers) of a compound that has a larger bandgap than the core material.[4–6]

In the corresponding field of binary-ligand-protected cluster compounds a large number of species have been synthesized and structurally characterized by single-crystal X-ray analysis.[7,8] In these systems the size regime of the larger clusters overlaps with the size regime of the smaller nanoparticles (having diameters of 1–3 nm). An investigation of a series of different sized cadmium selenide clusters has shown that their absorption properties are mainly dominated by the metal chalcogenide core, whereas the very weak fluorescence is due to processes in the organic ligand shell.[9–11] Further studies of clusters with the composition $[Cd_{10}E_4(E'Ph)_{12}(PEt_3)_4]$ (E, E′ = S, Se, Te) have found that the absorption is dependent upon the inner Cd_6E_4 core; the surrounding shell with its E′Ph groups has only a small influence on the absorption.[12]

In this paper we describe the synthesis and structure of six copper chalcogen clusters having a copper selenide core surrounded by a copper sulfide shell.

Results and Discussion

The reactions of copper(I) acetate with a mixture of the disilylated selenium compound $Se(SiMe_3)_2$ and the monosilylated sulfur species $PhSSiMe_3$ lead to the formation of several new copper chalcogenide clusters. As usual in the chemistry of cluster formation these reactions are highly dependent on the stoichiometry used. Scheme 1 summarizes the reactions leading to compounds **1**–**6**.



Scheme 1. Reactions leading to compounds **1**–**6**; ratios of the coefficients a:b:c:d i) 20:10:15:1, ii) 24:8:12:1, iii) 30:25:16:5, iv) 10:10:5:2, v) 60:15:30:5. iv) 40:10:18:7.

All compounds were crystallized and their structure determined by single-crystal X-ray analysis. Due to the different number of $SiMe_3$ groups in the chalcogen sources used, the selenium compound $Se(SiMe_3)_2$ reacts to give Se^{2-} ions whereas the sulfur species $PhSSiMe_3$ keeps its phenyl ring to form SPh^- groups. Therefore, all of the new compounds consist of an inner copper(I) selenide core surrounded by a sulfide shell. The phenyl groups of the SPh units and the PPh_3 ligands form an organic layer around the inorganic copper chalcogenide part. In some cases (**2**, **5**, **6**) there are additional acetate groups integrated into the ligand shell.

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The cluster [$Cu_{17}Se(SPh)_{15}(PPh_3)_4$] (**1**) crystallizes as yellow bars in the trigonal space group $R\bar{3}$ with six formula units per elemental cell. Figure 1 shows the molecular structure of the heavy atom framework and in the upper right corner the chalcogenide substructure.

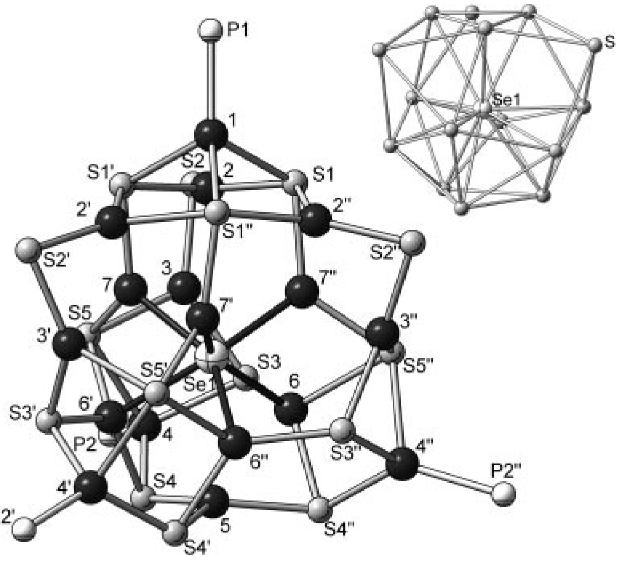

Figure 1. The molecular structure of the core of compound **1** (C and H atoms omitted for clarity); upper right: the chalcogenide substructure of **1** (same line of vision). Bond lengths [pm] in **1**: Cu–Se 239.8(3) (Cu7–Se1) and 262.8(3) (Cu6–Se1); Cu–S 221.2(7) (Cu3–S2) to 234.7(3) (Cu2–S1′); average Cu–P: 219.5.

There is a threefold axis running through the atoms Cu1, Cu5, Se1, and P1. A selenium atom (Se1) is present at the center of the cluster, and is surrounded by six copper atoms to form a skewed trigonal prism. The trigonal faces of this prism (formed by Cu6, Cu6′, Cu6′′ and Cu7, Cu7′, Cu7′′) are twisted by 17.1° against each other. The Se–Cu distances are 239.8(3) pm (Se1–Cu7) and 262.8(3) pm (Se1–Cu6). This inner (Cu_6Se) core is surrounded by a shell of the composition [$Cu_{11}(SPh)_{15}$]; four of the outer copper atoms (Cu1, Cu4, Cu4′, Cu4′′) have additional phosphane ligands. In compound **1** the metal atoms either have a nearly trigonal planar (Cu2, Cu3, Cu5, Cu6) or a skewed tetrahedral coordination sphere (Cu1, Cu4, Cu7). The sulfur atoms within the shell bond to either two (S2), three (S3, S4), or four (S1, S5) copper atoms in addition to a phenyl group.

Compound **2** crystallizes as yellow octahedra with eight molecules per unit cell in the cubic space group *Pa*3, with a C_3 axis running through the atoms Cu1, Cu7, Se1, and P1. Figure 2 illustrates the molecular structure of **2** and the arrangement of the chalcogen atoms.

Compound **2** has a shell-like construction with the central selenium atom Se1 surrounded by copper atoms Cu6, Cu6′, Cu6′′, and Cu7 that form a slightly distorted tetrahedron with bond lengths of 237.5(3) pm (Cu7–Se1) and 239.1(1) pm (Cu6–Se1). Around this polyhedron the twelve sulfur atoms of the SPh groups form a cube octahedron, whereby the four inner copper atoms are located beneath trigonal faces of the sulfur polyhedron. The distances between the sulfur atoms and the inner metal atoms vary from 236.0(3) pm (Cu6–S2) to 246.1(3) pm (Cu6–S1). The core can also be viewed as a section of a cubic closest packing of chalcogen atoms with half of the tetrahedral holes filled with copper atoms. The outer shell of the heavy atom framework of **2** is again formed by copper atoms. The four copper atoms (Cu1, Cu8, Cu8′, Cu8′′) that are additionally bonded to phosphane ligands cap the trigonal faces of the sulfur cube octahedron that are not bridged by the inner metal atoms (average Cu–S distance: 255.7 pm). The remaining twelve copper atoms are bound by acetate ligands to form six (Cu_2OAc) units, which cap the six tetragonal faces of the sulfur polyhedron. The average Cu–Cu distance in these units is about 279 pm, which is significantly longer than the corresponding distance in copper(I) acetate (255.6 pm);[13,14] the bonds between these copper atoms and the sulfur shell are about 224.8 pm long.

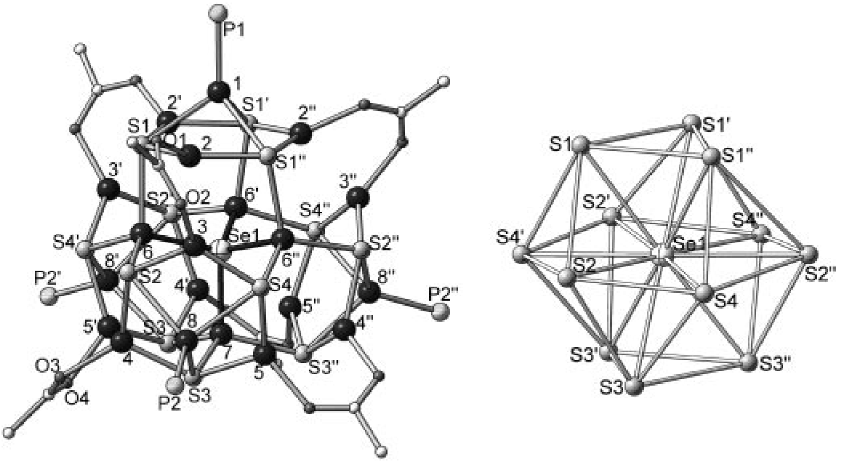

Figure 2. Left: The molecular structure of compound **2** (phenyl groups omitted for clarity); right: the chalcogenide substructure of **2** (same line of vision). Bond lengths [pm] in **2**: Cu–Se 237.5(3) (Cu7–Se1) and 2.391(2) (Cu6–Se1); Cu–S 219.5(3) (Cu2–S1′′) to 258.3(3) (Cu1–S1); average Cu–P: 222.5; average Cu–O: 195.8.

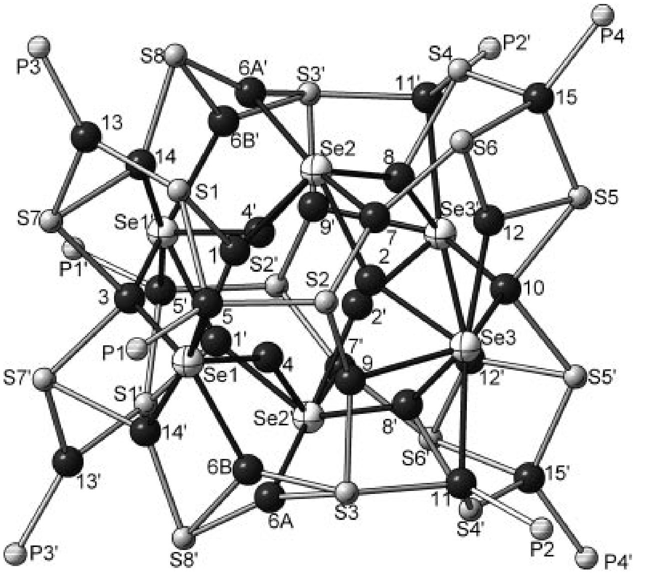

Figure 3. The molecular structure of the core of compound **3** (C and H atoms omitted for clarity). Bond lengths [pm] in **3**: Cu–Se 233.1(2) (Cu4–Se1) to 289.9(3) (Cu6A′–Se2); Cu–S 212.7(6) (Cu6A–S8′) to 2.469(9) (Cu6B–S8′); average Cu–P: 223.1.

Recently, a copper–selenium structure with a similar composition and structure has been published: $[Cu_{20}Se(SePh)_{12}(OAc)_6(Ph_2PC_6H_4SMe)_2]$.[15]

Cluster **3** contains 28 copper atoms and crystallizes in the orthorhombic space group *Pnn*2 as red blocks with two formula units per elemental cell. A crystallographic C_2 axis runs through the atoms Cu3 and Cu10. Figure 3 shows the heavy atom framework and Figure 4 the arrangement of the selenium and sulfur atoms in **3**.

The selenium substructure formed by six atoms can be described as two-edge sharing tetrahedra. Except for the shared one, all edges are μ_2-bridged by copper atoms. The four atoms Cu2, Cu2′, Cu4 and Cu4′ are located inside the selenium polyhedron and do not have any further associations. The other copper atoms of this $Cu_{10}Se_6$ core are either coordinated by one additional sulfur atom in a trigonal planar way (Cu1, Cu1′, Cu8, Cu8′) or by two extra sulfur atoms (Cu3, Cu10) to form a tetrahedral sphere.

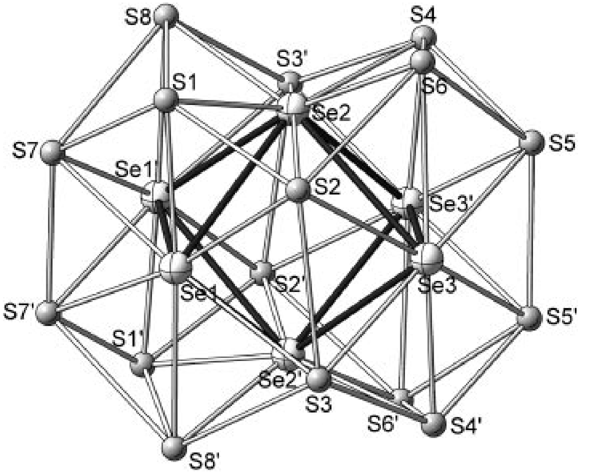

Figure 4. The chalcogenide substructure of **3**.

The sulfide shell in **3** consists of 16 sulfur atoms that form a polyhedron made out of four trigonal and six hexagonal faces (see Figure 4). Four of the hexagonal faces are nearly planar, whereas the other two are highly folded. In the center of each of these six-membered rings there is a selenium atom of the core structure. Therefore in **3**, in contrast to compounds **1** and **2**, the sulfide shell surrounding the selenium core is incomplete. Four (Cu13, Cu13′, Cu15, Cu15′) of the eight copper atoms coordinated to phosphane

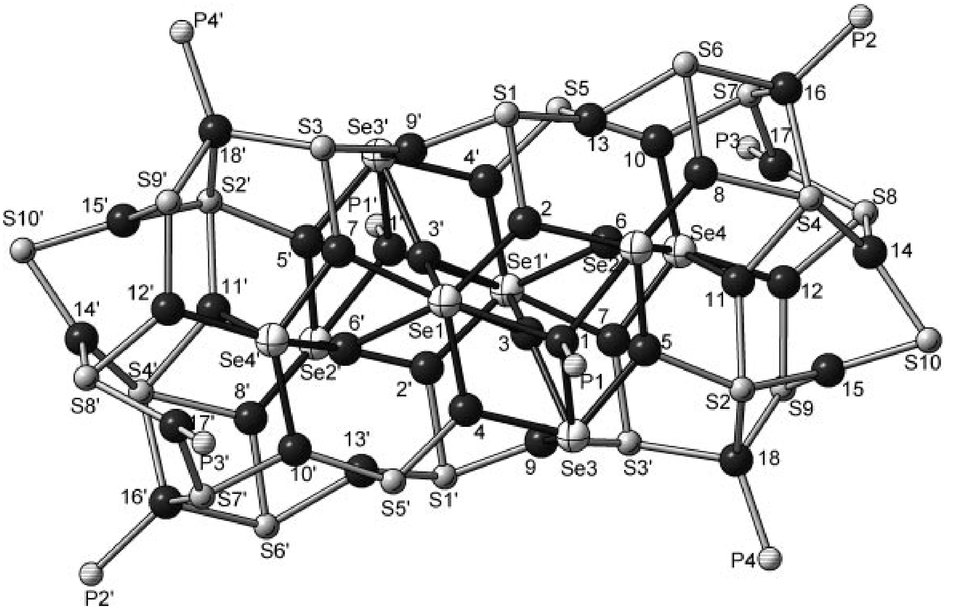

Figure 5. The molecular structure of compound **4** (C and H omitted for clarity). Bond lengths [pm] in **4**: Cu–Se 235.9(2) (Cu3–Se1′) to 281.8(2) (Cu3–Se1); Cu–S 220.6(3) (Cu4–S5′) to 246.0(3) (Cu18–S2); average Cu–P: 223.4.

ligands are located above the trigonal faces of the sulfur polyhedron. Whereas for Cu15 and Cu15′ one finds two short (about 232 pm) and one long (271 pm) Cu–S distance, for Cu13 and Cu13′ one can only speak of bonding towards two sulfur atoms (230 pm); the distance to the third sulfur atom (S8) is too long (334 pm) to be considered as a real bond. The other four copper atoms having phosphane ligands (Cu5, Cu5′, Cu11, Cu11′) are each acting as μ_3-bridges between two sulfur and one selenium atom. All other copper atoms are located inside the chalcogenide polyhedron and have (except for the already mentioned twofold and fourfold coordinated atoms) a trigonal planar sphere formed either by two sulfur and one selenium atom or by one sulfur and two selenium atoms. One copper atom (Cu6) is disordered over two positions and has been refined with an occupation of Cu6A:Cu6B of 2:1. The same phenomenon has been observed in repeated X-ray measurements of different crystals. Therefore it can be said that this disorder is a principle characteristic of compound **3** and not simply a defect of a single individual crystal.

Compound **4** crystallizes in the monoclinic space group $P2_1/n$ with two cluster molecules per unit cell. There are also noncoordinating solvent molecules (DME) in the crystal lattice which are disordered over four crystallographic positions. A symmetry center is located in the middle of the cluster (Figure 5).

The chalcogenide substructure, which is shown in two different projections in Figure 6, can be described as a stack of two skewed hexagonal layers that are shifted against each other like inside a closest packing. The eight selenium atoms are located in the middle of the chalcogenide substructure and, similar to **3**, six of them (Se1, Se2, Se3 and their symmetry equivalents) form two edge-sharing tetrahedra. The remaining two (Se4, Se4′) are found above the edges formed by Se1 and Se2, and Se1′ and Se2′, respectively. As in **3** the sulfide shell surrounding the selenide core is incomplete.

All copper atoms that do not have phosphane ligands are coordinated to three chalcogen atoms in all different combinations ranging from three selenium through to three sulfur atoms. The Cu–Se distances are found to be between 239.2(2) and 281.9(2) pm, and the Cu–S distances are between 220.7(3) and 245.9(4) pm. The copper atoms Cu17 and Cu17′ also form a trigonal planar sphere by acting as a μ_2-bridge over one S–S edge of the chalcogenide frame [Cu17–S7 229.1(3) pm, Cu17–S8 228.4(4) pm]; they also have an additional bond to a phosphane ligand. Only the copper atoms Cu1, Cu16, and Cu18, and their symmetry equivalents, show a skewed tetrahedral coordination sphere: Cu1 binds to Se1, Se2, Se3 and the phosphorus atom P1, whereas Cu16 and Cu18 bind to three sulfur and one phosphorus atom each. The copper–chalcogen distances of these atoms are, on average, about 16 (Cu–Se) and 9 pm (Cu–S) longer than those of the triply coordinated copper atoms. The remaining electron density found in the refinement (largest peak 2.095 eÅ^{-3}) is located in the area between the cluster molecules, thus indicating that the additional DME molecule might be disordered over more than the refined positions.

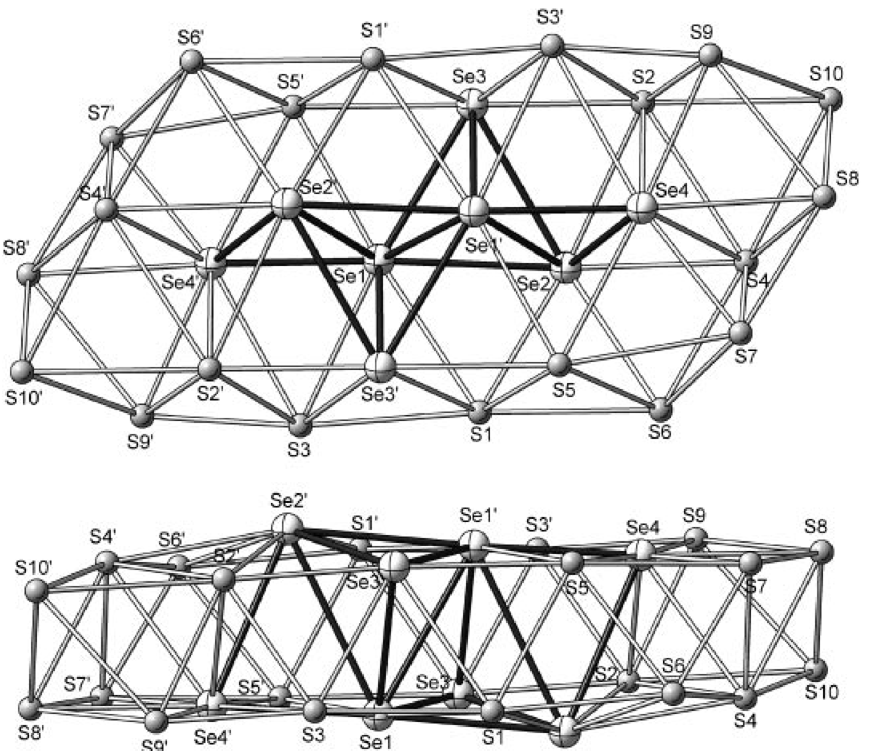

Figure 6. Two different views of the chalcogenide layer structure of **4**.

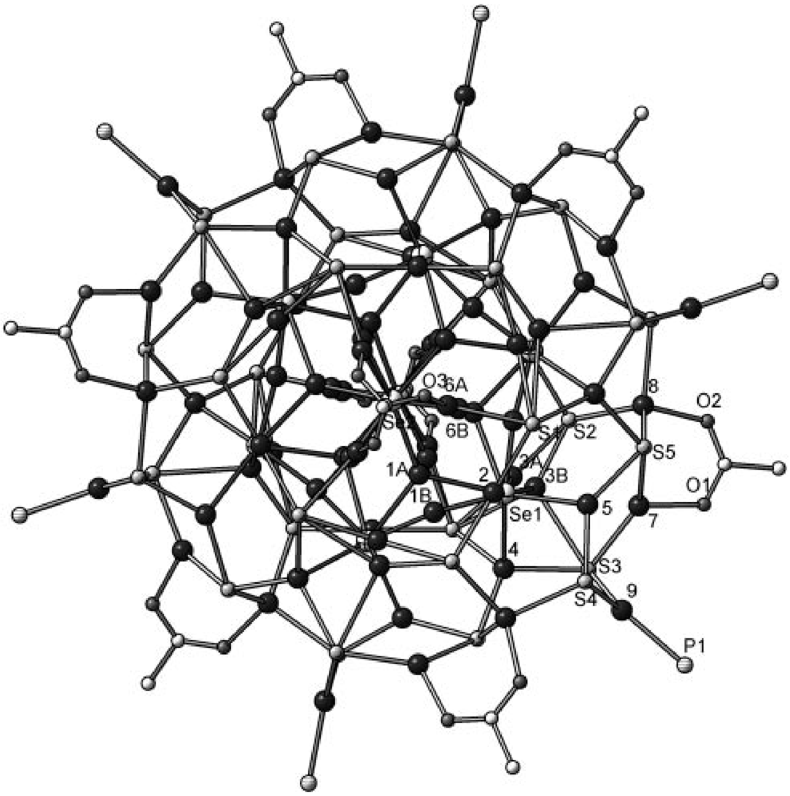

Figure 7. The molecular structure of compound **5** (phenyl groups omitted for clarity; only the atoms of the asymmetric unit are labeled). Bond lengths [pm] in **5**: Cu–Se 195.4(6) (Cu1B–Se1′) to 248.4(2) (Cu3A–Se1); Cu–S 213.3(8) (Cu6B–S1) to 266.8(8) (Cu3B–S1′); Cu–P 223.5(3); average Cu–O: 196.1.

The dark-red compound **5** crystallizes with three formula units per elemental cell in the trigonal space group $R\bar{3}$. The crystallographic $\bar{3}$ axis runs through the atoms Se2, Se2′, C3, C3′, C4, and C4′. The heavy-atom framework of **5** is shown in Figure 7 and the chalcogenide substructure in Figure 8.

Compound **5** appears to be discus-like in shape with the copper chalcogenide core having a diameter of 1.6 nm and a height of 0.7 nm. In the middle of the cluster eight selenium atoms form a highly compressed hexagonal bipyramid in which six copper atoms are embedded. These are disordered and were refined over two positions where they are either occupying a face of the bipyramid (pos. A), where they are coordinated by three selenium atoms, or an edge, with two neighboring selenium atoms (pos. B). The inner Cu_6Se_8 core is surrounded by a copper–sulfur shell consisting of 30 copper atoms and the 30 sulfur atoms from the SPh groups. In this shell the coordination spheres of the copper atoms vary. The tetrahedral copper atoms are bonded to three sulfur and one selenium atom (Cu–Se: av. 242.2 pm; Cu–S: av. 245.3 pm), whilst the trigonal copper atoms are bonded to one selenium and two sulfur atoms (Cu–Se: av. 245.1 pm; Cu–S: av. 225.4 pm). The remaining copper atoms are either bonded to one phosphane ligand and two sulfur atoms or form Cu_2OAc groups, as in compound **2**. At the top and bottom of the discus-like copper chalcogenide core are two acetate units whose two oxygen atoms are disordered over three positions, consistent with

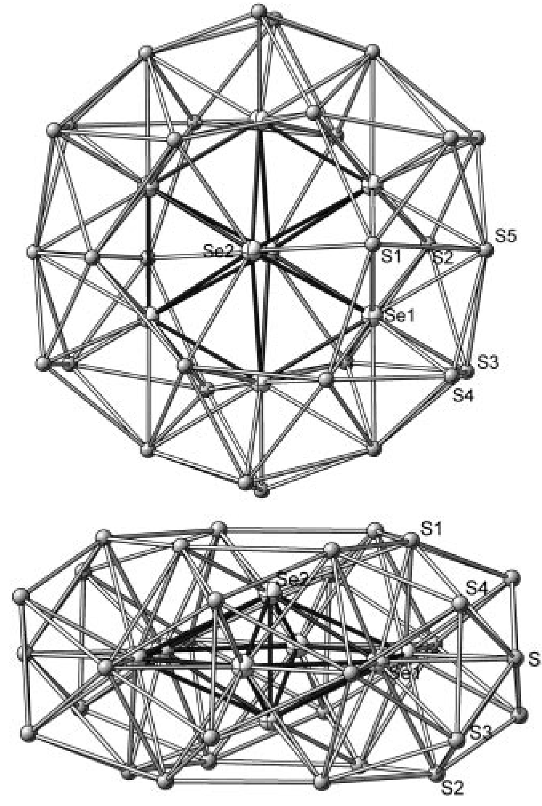

Figure 8. Two different views of the chalcogenide substructure of **5**.

the threefold symmetry of the cluster. The copper atoms binding to these ligands are also disordered and occupy one position (Cu6A), with coordination to a sulfur, a selenium, and an oxygen atom, or are coordinated linearly (Cu6B) to only the two chalcogen atoms. Due to all of these disordering phenomena, all of which were observed in several crystals, the structure solution ends up with poor quality factors and additional electron density near to the disordered copper atoms [distance between largest peak (2.329 e Å^{-3}) and Cu3B: 0.75 Å].

Compound **6**, which contains 72 copper atoms, crystallizes in the monoclinic space group $P2_1/n$ with four formula units per elemental cell as large black blocks. Figure 9 shows the heavy-atom framework.

The whole cluster has pseudo-C_3 symmetry with a (pseudo) axis running through the atoms Cu54, Cu56, Cu72, Se13, and Se14. The selenide core in **6** has the shape of a hexagonal antiprism (hexagonal faces formed by Se1–Se6 and Se7–Se12) with one additional selenium atom at the center of each hexagonal face (Se13 and Se14, respectively). Thus, the mantle as well as the top and the bottom faces of the selenium polyhedron consist of nearly equilateral triangles. At the center of the selenide core there is a linearly coordinated copper atom (Cu72); further doubly coordinated copper atoms are located on the edges of the mantle faces of the selenium prism (Cu39 between Se2 and Se8; Cu43 between Se4 and Se10; Cu47 between Se6 and Se12). Another twelve copper atoms (Cu60–Cu71) are located inside the selenium polyhedra, with each being coordinated by three selenium atoms. These copper atoms form an icosahedron which is highly compressed in the direction of the (pseudo)-C_3 axis. The $Cu_{16}Se_{14}$ core described above is shown in Figure 10, and the chalcogenide substructure is shown in Figure 11.

The first copper shell surrounding the selenium core consists of eight atoms (Cu13, Cu15, Cu17, Cu19, Cu21, and Cu23) which each bonded to one sulfur and two selenium atoms. Furthermore, there are 44 copper atoms bonded to only one selenium atom. Three different coordination

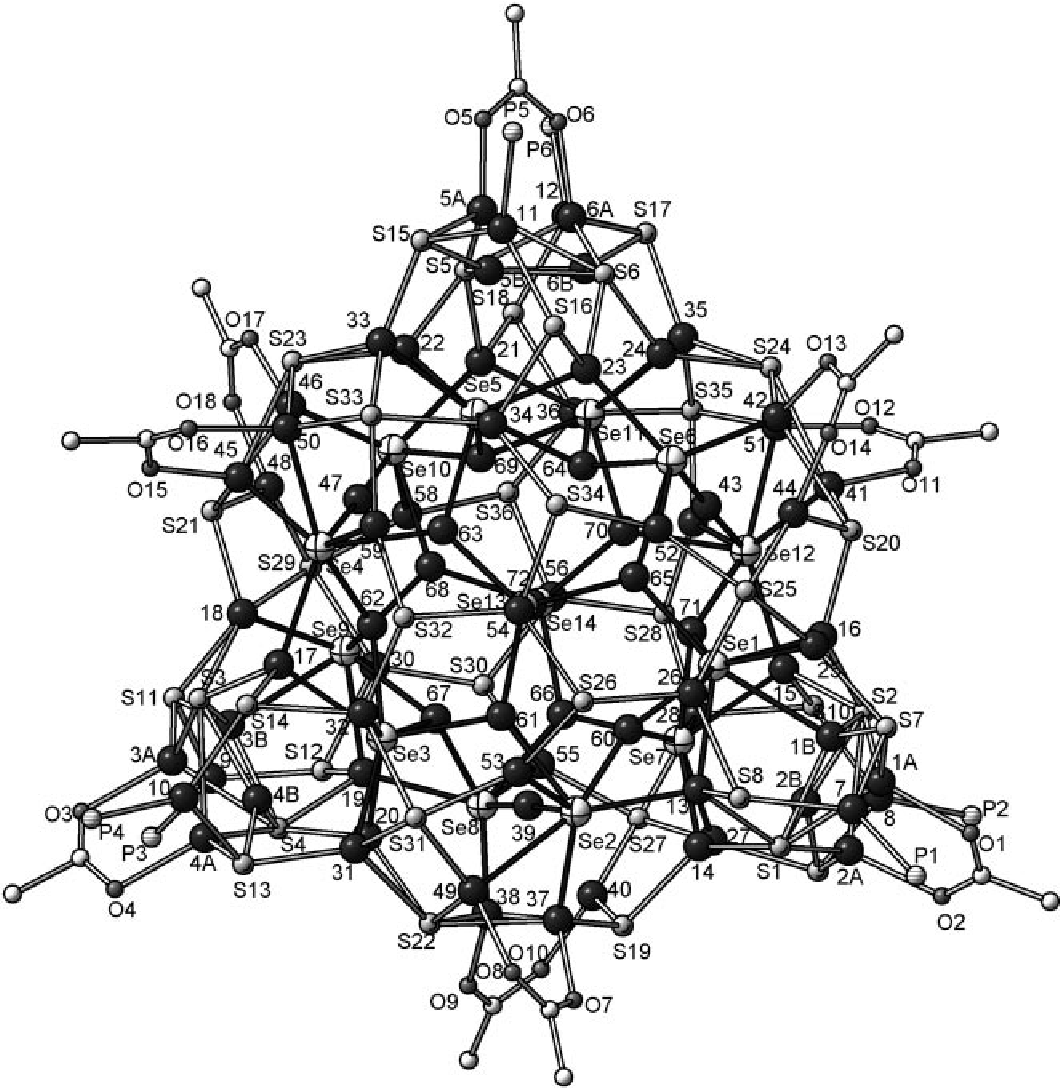

Figure 9. The molecular structure of compound **6** (phenyl groups omitted for clarity). Bond lengths (pm) in **6**: Cu–Se 232.7(4) (Cu72–Se13) to 291.4(7) (Cu44–Se6); Cu–S 192(3) (Cu1B–S7) to 276(1) (Cu2A–S2); average Cu–P 220; average: Cu–O 201.

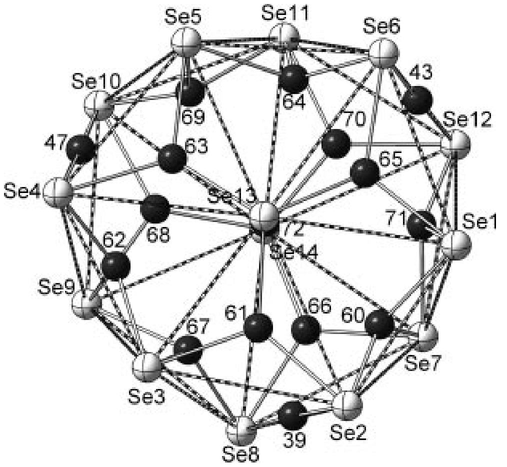

Figure 10. The inner $Cu_{16}Se_{14}$ core of **6**.

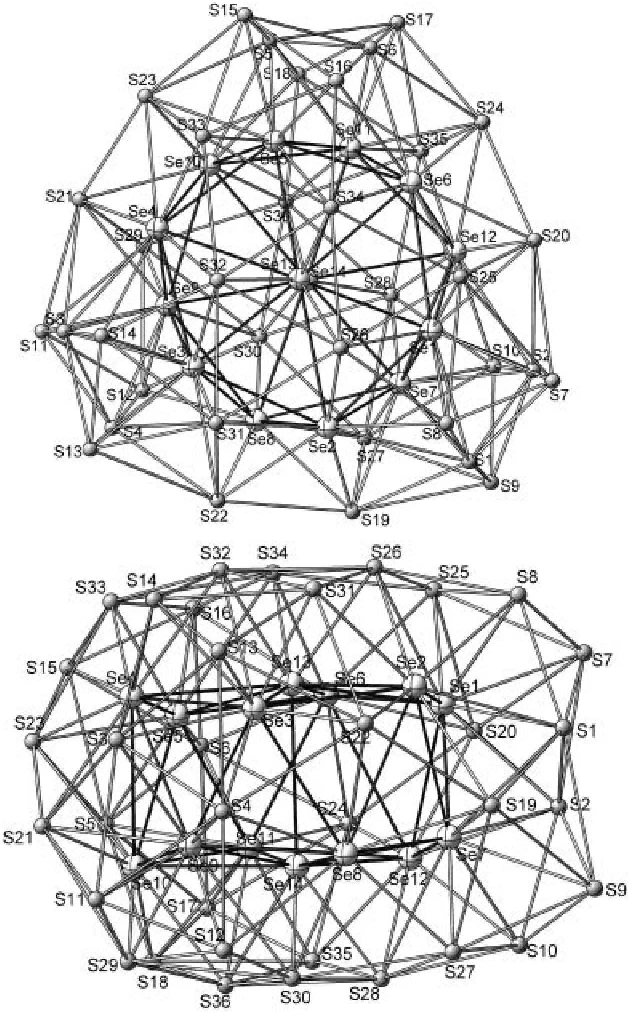

Figure 11. Two different views of the chalcogenide substructure of **6**.

spheres are observed within this group. The first contains trigonal-planar copper atoms coordinated by two additional sulfur atoms, whilst in the second the copper atoms have a tetrahedral geometry, binding to three more sulfur atoms. The remaining twelve copper atoms form six Cu_2OAc units with coordination spheres comprising one selenium, two sulfur, and one oxygen atom each. Not all of the copper atoms in the sulfide shell bond to the core selenium atoms. On the one hand Cu7–Cu12 are coordinated by two sulfur atoms and one phosphorus atom, while on the other hand Cu1A–Cu6A bond to two sulfur atoms and one oxygen atom of an acetate group. As in clusters **3** and **5** it is found that some of the copper atoms present in **6** are disordered. In this case, it is the atoms Cu1–Cu6, which have been refined using occupations between 0.1 and 0.9 for positions A and B. Position A has already been described above. Those copper atoms in position B are located further inside the cluster and again interact with two sulfur atoms along with a core selenium atom. Assuming that the corresponding positions A and B have a total occupancy of one copper atom, the total number of copper atoms for the whole cluster is 72. Considering **6** to be electrically neutral there must be eight acetate units; six of these were refined with satisfying vibration factors. The remaining two acetate groups are split over three possible positions, with bonds to the partially occupied copper positions A.

Due to disordering the refinement has poor R values (R_1 = 0.141, wR_2 = 0.393), with additional electron density near to the areas of disordered copper atoms [distance between largest peak (3.772 $e\,Å^{-3}$) and Cu2A: 0.78 Å]. Similar results were obtained with crystals from other reactions.

Conclusions

We have described six new cluster compounds. All of them have a selenide core consisting of 1 to 14 selenium atoms. In compound **2** the one selenium atom in the center is surrounded by twelve sulfur atoms to form a cube octahedron. Compared with the corresponding fcc lattice, this means that there is one complete shell formed around the central atom. In **1** there are 15 sulfur atoms in more than one layer. In the other compounds the covering of the interior selenide core is less than one layer of sulfur atoms. The approximate completeness of the covering in all compounds is summarized in Table 1.

Table 1. Comparison of the completeness of the sulfide shell covering the selenide core in **1**–**6**.

Compound	Se in core	S in shell	Coverage [%]
1	1	15	>100
2	1	12	100
3	6	16	53
4	8	20	53
5	8	30	83
6	14	36	67

The colors of the compounds vary from yellow (**1**, **2**) to different shades of red (**3**–**5**), and black (**6**). Investigations into the optical properties of these compounds are an area of current work.

Experimental Section

Due to the high oxygen and moisture sensitivity of the compounds used, all reactions were performed under a dry, oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried with sodium/benzophenone and freshly distilled. Copper(I) acetate (CuOAc),[16] $Se(SiMe_3)_2$,[17]and $PhSSiMe_3$[18] were synthesized according to literature procedures. All reactions described below are very sensitive to small variations of the starting material ratio such that in some cases mixtures of different compounds were obtained.

Synthesis of $[Cu_{17}Se(SPh)_{15}(PPh_3)_4]$ (1): At room temperature, copper(I) acetate (0.365 g, 2.98 mmol) and PPh_3 (0.39 g, 1.49 mmol) were suspended in DME (100 mL). $PhSSiMe_3$ (0.42 mL, 2.23 mmol) and $Se(SiMe_3)_2$ (0.034 mL, 0.15 mmol) were then added. The bright yellow solution was stirred for 24 h and then its volume was reduced. After some hours **1** crystallized as yellow rods. Yield: 0.23 g (40%). $C_{162}H_{135}Cu_{17}P_4S_{15}Se$ (3845.6): calcd. C 50.59, H 3.54, S 12.51; found C 51.32, H 3.78, S 12.59.

Synthesis of $[Cu_{20}Se(SPh)_{12}(OAc)_6(PPh_3)_4]$ (2): $PhSSiMe_3$ (0.54 mL, 2.87 mmol) and $Se(SiMe_3)_2$ (0.057 mL, 0.24 mmol) were dissolved in DME (10 mL) and added to a suspension of CuOAc (0.703 g, 5.73 mmol) and PPh_3 (0.50 g, 1.91 mmol) in DME (100 mL) at –30 °C. After stirring for five minutes the mixture was filtered and allowed to warm up to 4 °C. Within several hours **2** crystallized as small, yellow octahedra. Yield: 0.35 g (36%). found C 46.87, H 3.98, S 9.14; $C_{156}H_{138}Cu_{20}O_{12}P_4S_{12}Se$ (4063.2): calcd. C 46.11, H 3.42, S 9.47%).

Synthesis of $[Cu_{28}Se_6(SPh)_{16}(PPh_3)_8]$ (3): CuOAc (0.329 g, 2.68 mmol) and PPh_3 (0.59 g, 2.22 mmol) were suspended in DME (50 mL). After adding $PhSSiMe_3$ (0.27 mL, 1.43 mmol) and $Se(SiMe_3)_2$ (0.11 mL, 0.45 mmol) all solids were dissolved resulting a dark red solution. Within several days one got **3** as red coffin shaped crystals. Yield: 0.19 g (41%). $C_{244}H_{208}Cu_{28}O_2P_8S_{16}Se_6$ (**3**·DME) (6185.7): calcd. C 47.37, H 3.39, S 8.29; found C 46.61, H 3.50, S 8.42.

Synthesis of $[Cu_{36}Se_8(SPh)_{20}(PPh_3)_8]$ (4): CuOAc (0.342 g, 2.79 mmol) and PPh_3 (0.73 g, 2.79 mmol) were dissolved in DME (100 mL). Addition of $PhSSiMe_3$ (0.26 mL, 1.39 mmol) led to a yellow solution, which turned dark red after addition of $Se(SiMe_3)_2$ (0.13 mL, 0,56 mmol). Within some days **4** crystallized directly from the reaction mixture as red plates. Yield: 0.15 g (30%). $C_{268}H_{230}Cu_{36}O_2P_8S_{20}Se_8$ (**4**·DME) (7290.6): calcd. C 44.15, H 3.18, S 8.80; found C 44.43, H 3.25, S 8.79 .

Synthesis of $[Cu_{54}Se_8(SPh)_{30}(OAc)_8(PPh_3)_6]$ (5): CuOAc (0.55 g, 4.49 mmol) and PPh_3 (0.29 g, 1.12 mmol) were suspended in DME (75 mL) and stirred for two hours. $PhSSiMe_3$ (0.42 mL, 2.24 mmol) and $Se(SiMe_3)_2$ (0.089 mL, 0.37 mmol) were added within two minutes resulting a dark-red solution with no solids left. Within a few minutes a yellow precipitate had formed. After five hours the mixture was filtered and within one day square, red plates of **5** crystallized. Yield: 0.11 g (25%). $C_{304}H_{264}Cu_{54}O_{16}P_6S_{30}Se_8$ (9383.6): calcd. C 38.91, H 2.84, S 10.25; found C 38.43, H 2.81, S 10.49).

Synthesis of $[Cu_{72}Se_{14}(SPh)_{36}(OAc)_8(PPh_3)_6]$ (6): $PhSSiMe_3$ (0.24 mL, 1.28 mmol) and $Se(SiMe_3)_2$ (0.12 mL, 0.50 mmol) were dissolved in DME (10 mL) and added to a suspension of CuOAc (0.347 g, 2.83 mmol) and PPh_3 (0.19 g, 0.71 mmol) in DME (50 mL) at 0 °C. After one hour the resulting dark solution was allowed to warm up to room temperature. Within some days **6** crystallized as big black blocks. Yield: 0.11 g (26%). $C_{344}H_{304}Cu_{72}O_{18}P_6S_{36}Se_{14}$ (**6**·DME) (11747.1): calcd. C 35.17, H 2.61, S 9.83; found C 35.19, H 2.67, S 9.69.

X-ray Structure Determination: Crystals were removed from the reaction flask under a stream of N_2 gas and immediately covered with a layer of perfluoropolyether oil (Riedel-de Haën). A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream. The data were collected with a STOE IPDS II diffractometer using Mo-K_α (λ = 0.71073 Å) radiation, either from a common X-ray tube at 2 kW (compounds **1**–**3**, **5**) or a rotating anode run at 4.8 kW (**4**, **6**). Structure solution and refinement against F^2 were carried out using shelxs and shelxl software.[19] Molecular drawings were prepared with Diamond 2.1[20] and PaintShopPro 7AE;[21] in the figures cop-

Table 2. Crystallographic data for **1**–**3**.

	1	2	3·DME
Formula	$C_{162}H_{135}Cu_{17}P_4S_{15}Se$	$C_{156}H_{138}Cu_{20}O_{12}P_4S_{12}Se$	$C_{244}H_{208}Cu_{28}O_2P_8S_{16}Se_6$
Formula mass	3845.62	4063.02	6185.7
Temperature [K]	200	200	200
Crystal system	trigonal	cubic	orthorhombic
Space group	$R\bar{3}$	*Pa*3	*Pnn*2
a [pm]	1873.5(3)	3189.4(4)	3298.7(7)
b [pm]	1873.5(3)	3189.4(4)	1916.3(4)
c [pm]	8318.3(17)	3189.4(4)	2025.1(4)
α [°]	90	90	90
β [°]	90	90	90
γ [°]	120	90	90
Volume [10^6 pm^3]	25286(7)	32444(7)	12801(4)
Z	6	8	2
Density [g cm^{-3}]	1.515	1.664	1.605
μ [mm^{-1}]	2.580	3.033	3.351
$2\theta_{max}$ [°]	48	50	54.4
F(000)	11604	16288	6160
Reflections collected	9218	65717	40096
Indep. reflections	4063 [R_{int} = 0.0457]	9507 [R_{int} = 0.1717]	19915 [R_{int} = 0.1691]
Indep. refl. with $F_o > 4\sigma(F_o)$	2612	4076	13909
Restraints/parameters	0/535	0/618	1/1669
GooF on F^2	1.020	0.842	1.038
R_1 [$I > 2\sigma(I)$]	0.0599	0.0558	0.0690
wR_2 (all data)	0.1969	0.1648	0.2079
Largest diff. peak and hole (e Å^{-3})	0.936/–0.527	1.454/–0.771	1.117/–1.278
Flack parameter			0.001(17)

Table 3. Crystallographic data for **4**–**6**.

	4·DME	**5**	**6**·DME
Formula	$C_{268}H_{230}Cu_{36}O_2P_8S_{20}Se_8$	$C_{304}H_{264}Cu_{54}O_{16}P_6S_{30}Se_8$	$C_{344}H_{304}Cu_{72}O_{18}P_6S_{36}Se_{14}$
Formula mass	7290.60	9383.61	11747.05
Temperature [K]	200	200	100
Crystal system	monoclinic	trigonal	monoclinic
Space group	$P2_1/n$	$R\bar{3}$	$P2_1/n$
a [pm]	2177.0(4)	2946.9(4)	2660.4(5)
b [pm]	2975.2(6)	2946.9(4)	4445.7(9)
c [pm]	2412.6(5)	3964.7(8)	3820.4(8)
α [°]	90	90	90
β [°]	106.05(3)	90	98.49(3)
γ [°]	90	120	90
Volume [10^6 pm^3]	15017(5)	29818(8)	44690(15)
Z	2	3	4
Density [g cm^{-3}]	1.612	1.568	2.629
μ [mm^{-1}]	3.683	3.775	4.714
$2\theta_{max}$ [°]	48	50	48
$F(000)$	7220	13872	22592
Reflections collected	48076	35133	197207
Independent reflections	24151 [R_{int} = 0.0743]	11519 [R_{int} = 0.0663]	68063 [R_{int} = 0.1467]
Indep. refl. with $F_o > 4\sigma(F_o)$	11358	6581	38849
Restraints/parameters	0/1537	0/743	11/2518
GooF on F^2	0.906	0.987	0.978
R_1 [$I > 2\sigma(I)$]	0.0598	0.0846	0.1413
wR_2 (all data)	0.1922	0.2917	0.3928
Largest diff. peak and hole (e Å^{-3})	2.095/–0.787	2.329/–2.076	3.772/–1.758

per atoms are represented only by their numbers, other elements are named with symbols and numbers. In the figures showing the chalcogenide substructures the lines between neighboring atoms do not represent bonds. The crystal and refinement data of **1**–**6** are summarized in Tables 2 and 3.

CCDC-260742 (for **1**), -260743 (for **2**), -260744 (for **3**), -260745 (for **4**), -260746 (for **5**), and -260747 (for **6**) 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.

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