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Cluster Compounds

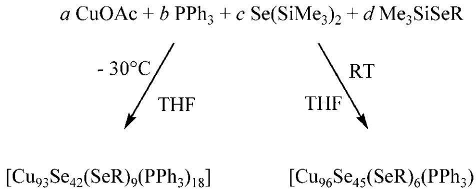
Metal-Rich Copper Chalcogenide Clusters at the Border Between Molecule and Bulk Phase: The Structures of $[Cu_{93}Se_{42}(SeC_6H_4SMe)_9(PPh_3)_{18}]$, $[Cu_{96}Se_{45}(SeC_6H_4SMe)_6(PPh_3)_{18}]$, and $[Cu_{136}S_{56}(SCH_2C_4H_3O)_{24}(dpppt)_{10}]$**

Ming-Lai Fu, Ibrahim Issac, Dieter Fenske, and Olaf Fuhr**

In memory of Herbert Schumann

For many years we have been working in the field of synthesis and characterization of ligand-shielded metal chalcogenide clusters.[1] Examples for such species are copper chalcogenide clusters stabilized by tertiary phosphanes. Compared to the binary Cu_2E phases (E: S, Se, Te) these compounds are thermodynamically instable. The phosphane ligands can be cleaved already at mild temperatures, yielding Cu_2E nanoparticles.[2]

In the case of the phosphane-stabilized Cu_2Se cluster, we were able to characterize two classes of compounds.[3] Up to a total of 50 copper atoms, these molecules are spherical and show no structural relationship to the binary bulk phase. For bigger clusters the situation changes; the selenium atoms in the compounds $[Cu_{70}Se_{35}(PR_3)_m]$ ($m = 21$, $PR_3 = PtBu_2Me$;[4] $m = 22$, $PR_3 = PEt_3$,[5] $m = 23, 24$; $PR_3 = PEt_2Ph$[6]) arrange in three trigonal layers consisting of 10, 15, and 10 selenium atoms. This arrangement corresponds to a slightly distorted section of a hexagonal closest packing of spheres. The copper atoms are either trigonal planar or tetrahedrally coordinated by selenium and phosphorus atoms. The next-largest cluster demonstrating this structural motif has the composition $[Cu_{140}Se_{70}(PR_3)_m]$, with triangular selenium layers consisting of 21, 28, and 21 selenium atoms. Again, different variations of this cluster are known: $m = 34$ or 36, $PR_3 = PEt_3$;[7] $m = 34$, $PR_3 = PEt_2Ph$.[3] These analogies in the structures hint at a topotactical growth of the clusters. Therefore there should be an intermediate copper selenide cluster having 51 selenium atoms with the sequence 15-21-15. In the case of a pure Cu_2Se cluster, its composition would be $[Cu_{102}Se_{51}(PR_3)_m]$. This compound could not be synthesized to date. Depending on the stoichiometric ratio of the starting materials, the reaction of copper(I) acetate with PPh_3 and a mixture of Me_3SiSe-C_6H_4-SMe and $Se(SiMe_3)_2$ yields the compounds $[Cu_{93}Se_{42}(Se\text{-}C_6H_4\text{-}SMe)_9(PPh_3)_{18}]$ (**1**) or $[Cu_{96}Se_{45}(Se\text{-}C_6H_4\text{-}SMe)_6(PPh_3)_{18}]$ (**2**), both having the "magic" number of 51 selenium atoms (Scheme 1).

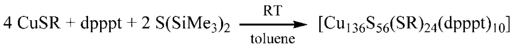


1 **2**

Scheme 1. Syntheses of **1** ($a/b/c/d = 5{:}10{:}2{:}1$) and **2** ($a/b/c/d = 95{:}95{:}42{:}9$); $R = C_6H_4$-SMe.

In the case of copper sulfide clusters, only compounds with a maximum of 50 copper atoms have been known to now; for example, $[Cu_{50}S_{25}(PtBu_2Me)_{16}]$.[4] In accordance with the selenide species of similar size, these copper sulfide clusters are spherical or ellipsoidal, and they show no structural relationship to typical binary solid-state phases. Following our work on silver chalcogenide clusters,[8,9] we investigated the reaction behavior of copper thiolates with $S(SiMe_3)_2$. Using copper 2-furanmethanthiolate, the reaction in the presence of 1,5-bis(diphenylphosphino)pentane (dpppt) yields $[Cu_{136}S_{56}(S\text{-}CH_2\text{-}C_4H_3O)_{24}(dpppt)_{10}]$ (**3**; Scheme 2). Details of the syntheses of the compounds **1**–**3** can be found in the Supporting Information.

The structures of **1**–**3** could be determined by single-crystal X-ray analysis.[10] Some of the organic groups of the organic shell are disordered. For all three compounds, the bond lengths are within the typical range found for other



$$4\,CuSR + dpppt + 2\,S(SiMe_3)_2 \xrightarrow[\text{toluene}]{\text{RT}} [Cu_{136}S_{56}(SR)_{24}(dpppt)_{10}]$$

3

Scheme 2. Synthesis of **3**; $R = CH_2\text{-}C_4H_3O$.

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ligand-shielded copper(I) chalcogenide clusters.[3] As common for molecules of this size, there are huge voids in the crystal packing that are filled by disordered solvent molecules.[11,12]

Compound **1** (Figure 1, left) crystallizes in the triclinic space group $P\bar{1}$ with two cluster molecules in the unit cell; a large number of THF and diethyl ether molecules are embedded into the voids between the clusters.[13] According to the previously described stacking principle, the 51 selenium atoms in **1** are ordered in three parallel triangular layers consisting of 15, 21, and again 15 selenium atoms. In analogy to a hexagonal closest packing, these layers represent an A-B-A stacking. Those selenium atoms that bond to organic groups (-C_6H_4-SMe) are located at the corners of the triangular layers (Figure 2, top). The Se–Se distances within the layers are 355.1 to 456.8 pm (average 421 pm); between the layers the Se–Se distances are on average 10 pm longer (359.9 pm to 477.6 pm).

18 of the 93 copper atoms in **1** are coordinated to phosphane ligands and additionally bond to either two or three selenium atoms. Furthermore, one copper atom bonds to three selenium atoms and a sulfur atom of a C_6H_4-SMe

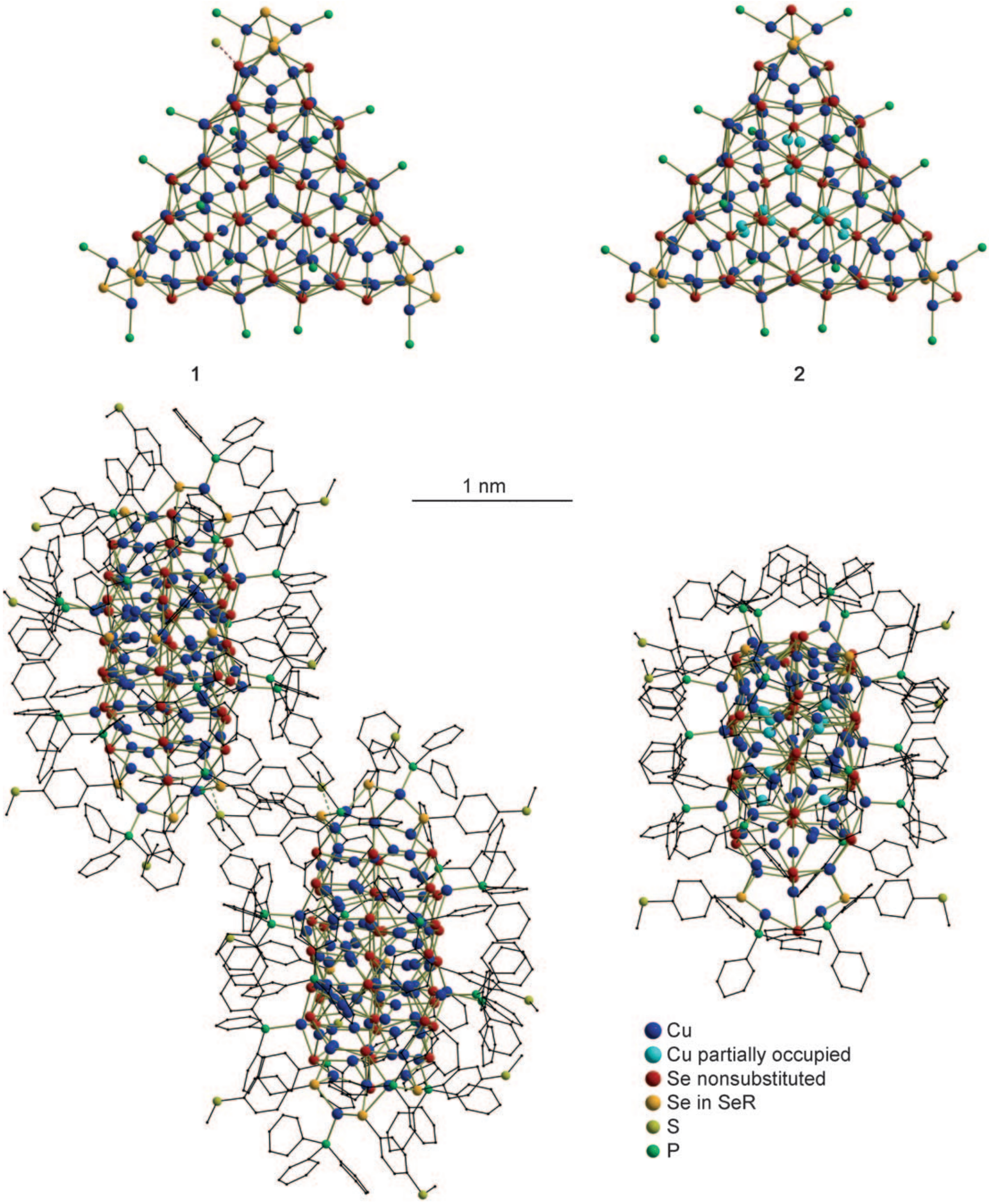

Figure 1. [$Cu_{93}Se_{42}(Se\text{-}C_6H_4\text{-}SMe)_9(PPh_3)_{18}$] (**1**, left) and [$Cu_{96}Se_{45}(Se\text{-}C_6H_4\text{-}SMe)_6(PPh_3)_{18}$] (**2**, right). Top: Structures of the cluster cores. For **1** the position of the sulfur atom of the neighboring molecule is also shown; this coordination causes dimerization in solid state. Bottom: Molecular structures with ligand shell, rotated by 90° (hydrogen atoms omitted).

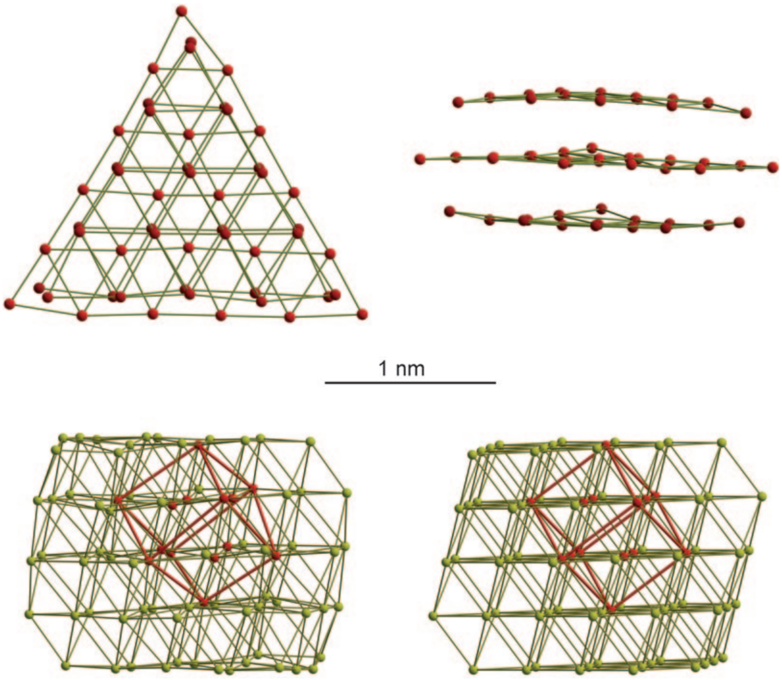

Figure 2. Top: Selenium substructure of **1** in two different projections rotated relative to another by 90°. The connecting lines between the selenium atoms are not considered as chemical bonds but demonstrate the analogy to the A-B-A stacking. Bottom left: Sulfur substructure in **3**; to demonstrate the analogy to the fcc packing, an area representing a fcc elemental cell is highlighted in red. The connecting lines between the sulfur atoms are not considered as chemical bonds but demonstrate the analogy to the fcc lattice. Bottom right: 80 atoms containing section of a fcc lattice. The elemental cell is highlighted in red.

group of a neighboring cluster (S−Cu: 279.3(7) pm). This leads to the formation of dimers in solid state (Figure 1 left, bottom). The remaining 74 copper atoms in **1** occupy different voids within the selenium network. Ten copper atoms are linearly, 61 trigonal planar, and three tetrahedrally coordinated. However it is not possible to give unequivocal coordination numbers in all cases, as most of the copper atoms do not occupy the ideal position of the coordination polyhedra. In general, the linearly coordinated atoms show a shift towards a third copper atom; the trigonal planar coordinated atoms either have a tendency to a linear coordination with two short and one long Cu−Se bond or they are shifted out of the trigonal plane in direction of a fourth selenium atom; for tetrahedral coordination there is a tendency towards a trigonal surrounding. The Cu−Se bond distances are between 227 pm and 288 pm; the additional interactions leading to the distortion of the coordination polyhedra have a range up to approximately 310 pm.

This flexibility of the copper atoms with respect to their positions in the lattice is typical for binary copper(I) selenide and sulfide phases.[14] As a result of this structural feature, these compounds normally have remarkable ionic conductivities at higher temperatures.[15] In the literature, two copper(I) selenide phases $Cu_{2-\delta}Se$ ($\delta = 0$–0.25) are described (the low-temperature phase α and the high-temperature phase β). The exact structures of these phases are still under discussion.[16,17] These phases can be approximately described on the basis of the anti-fluorite type ($Fm\bar{3}m$), which consists of an immobile cubic face-centred (fcc) lattice of selenium atoms, with the copper atoms occupying the tetrahedral voids with a tendency towards trigonal coordination. In contrast to the binary phases, the selenium sublattice in **1** follows the principle of a hexagonal closest packing. Therefore this cluster can be taken as a section of a hypothetical (up to now) unknown hexagonal modification of copper(I) selenide. The prismatic cluster core in **1** has a thickness of approximately 0.7 nm and an edge length of the trigonal faces of about 2.0 nm. The selenium atoms in **1** have different bridging modes: the selenium atoms of the Se-C_6H_4-SMe groups are μ_3-bridging; the non-substituted selenium atoms show bridging from μ_4 to μ_7.

Compound **2** (Figure 1, right) crystallizes in the trigonal space group $R\bar{3}c$ with six formula units in the unit cell. Again, the voids between the clusters are filled by a high number of solvent molecules (THF).[18] The structure of the individual molecules of **2** is very similar to those of **1**. The 51 selenium atoms are again arranged in three layers staggered A-B-A (with only small deformations of the individual layers). However there is no additional coordination between the cluster molecules. In **2**, the trigonal symmetry of the individual molecules is maintained; there is one threefold and three orthogonal twofold axes running through each cluster. In contrast to **1**, only six selenium atoms are bond to organic groups (-C_6H_4-SMe) in **2**. The corner atoms of the middle selenium layer are non-substituted. Therefore, it can be calculated that the selenium sublattice should have an overall charge of −96. Altogether, the positions of 98 copper atoms can be refined in **2**. Comparing the structures of **1** and **2** (Figure 1, top), it can be seen that most of the copper atoms are located on identical positions inside the selenium lattices. An exception are those copper atoms in **2** that are highlighted in light blue color in Figure 1. These twelve atoms were refined with occupation factors of 0.6 or 0.4, respectively, due to large vibration factors compared to the other copper atoms. This deficiency in occupation leads to a content of 92 copper atoms per cluster. Therefore, the composition of $[Cu_{96}Se_{45}(SeC_6H_4SMe)_6(PPh_3)_{18}]$ should be understood as an idealized formulation assuming that all copper atoms are in the oxidation state +I. This uncertainty in the content of copper is in agreement with the phase width found for binary copper(I) selenide phases, which normally show an deficiency in the copper content.[16–20]

Compound **3** (Figure 3) crystallizes in the monoclinic space group $C2/c$ with four inversion symmetrical cluster molecules per unit cell. The void between the clusters is filled with a great number of toluene molecules. The sulfur substructure of **3** can be described as a distorted section of a cubic closest packing (fcc; stacking A-B-C). The left side of the bottom part of Figure 2 shows the arrangement of the sulfur atoms in **2**; the distorted red cube represents the

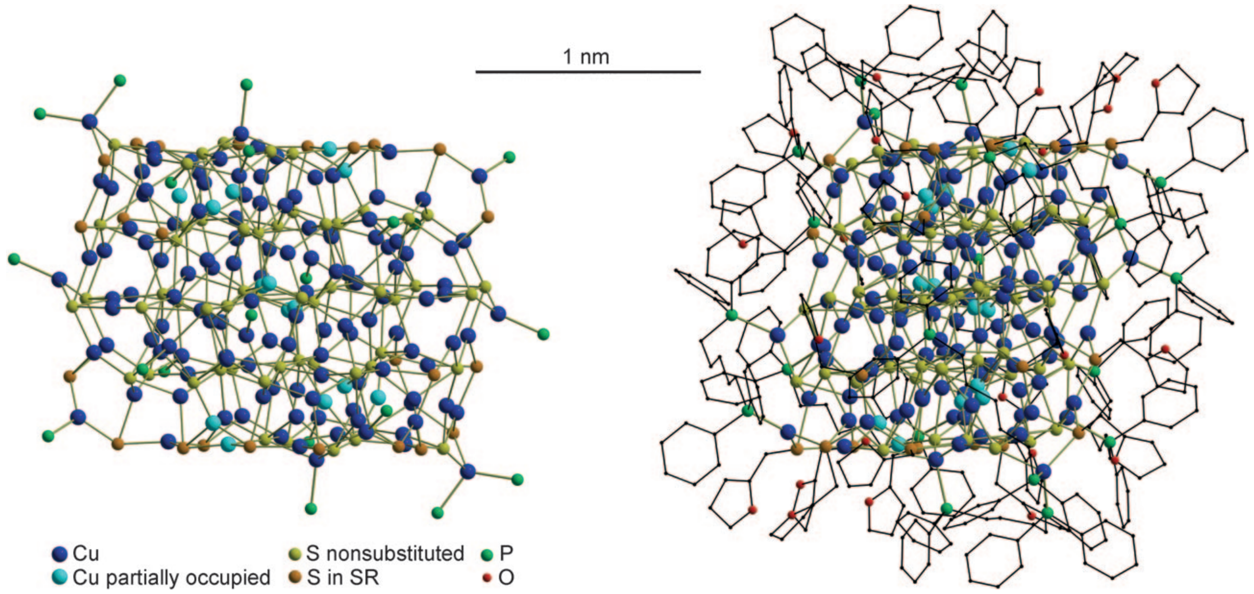

Figure 3. Molecular structure of $[Cu_{136}S_{56}(SCH_2C_4H_3O)_{24}(dpppt)_{10}]$ (**3**). Left: Cluster core consisting of copper, sulfur, and phosphorus atoms. Right: Structure of the complete molecules with ligand shell, rotated by 90° (H atoms omitted).

elemental cell of a cubic closest packing. To demonstrate the analogy, the right part shows an 80-atom section of a fcc lattice (space group $Fm\bar{3}m$) and also its elemental cell. The copper atoms also have different coordination modes in this cluster. Two out of 18 peripheral copper atoms bind to two phosphorus and two sulfur atoms each, eight bind to one phosphorus and two sulfur atoms, and the last eight copper atoms bind to one phosphorus and three sulfur atoms. Inside the sulfur lattice, 124 positions for copper atoms could be refined. As in **1** and **2**, these atoms bind to two, three, or four sulfur atoms in different distorted coordination polyhedra. The sulfur atoms of the S-CH_2-C_4H_3O groups are either μ_3- or μ_4-bridging; the non-substituted sulfur atoms have bridging modes of between μ_5 and μ_7. The Cu−S distances are between 216 pm and 287 pm. As in the previous compound, some of the copper positions in **3** are only partly occupied (light blue in Figure 3). To compensate the negative charges of the sulfur lattice, 136 copper atoms are needed, which was considered in the occupation factors of the copper atoms during the refinement.

Also in the copper–sulfur system, phases with different compositions are known, which again have remarkable electrical conductivity.[14,21–23] For Cu_2S (chalcocite), a monoclinic (pseudo-hexagonal) low-temperature phase and a hexagonal high-temperature phase are known. A further monoclinic (also pseudo-hexagonal) phase is the mineral djurleite ($Cu_{31}S_{16} \approx Cu_{1.94}S$). In approximation, these three phases can be described as a hexagonal closest packing of sulfur atoms with embedded copper atoms showing different coordination modes (linear to tetrahedral). At higher temperatures, these compounds undergo a phase transition towards a cubic phase with approximate antifluorite structure. Furthermore, another sub-stoichiometric phase with the composition $Cu_{1.8}S$ ($=Cu_9S_5$, digenite) is known, which crystallizes in the cubic system, even at room temperature. According to this, **3** can be described as a small distorted octahedral section (edge lengths ca. 1.2, 1.4, 1.9 nm) of the cubic copper(I) sulfide phases.

From the absorption spectrum of **3**, a HOMO–LUMO gap of approximately 1.87 eV (664 nm) can be determined (Figure S4 in the Supporting Information). As expected due to the quantum confinement effect, this energy difference is significantly larger than the band gaps of the different copper(I) sulfide phases (chalcocite 1.2 eV,[24] djurleite 1.3 eV,[25] digenite 1.75 eV[26]).

The MALDI-TOF mass spectrum of **3** (see Figure S5 in the Supporting Information) shows very broad signals for m/z 14400, 26200, 38100, 49900, 61500, and 73200 Da. The first signal can be assigned to the cluster itself, indicating a stepwise loss of the organic shell in the gas phase. The signals at higher masses indicate the formation of agglomerates of clusters in the gas phase. The average distance between the signals (11760 Da) can be interpreted as a cluster that has nearly completely lost its organic shell ($[Cu_{136}S_{80}]$: 11208 Da). Similar observations were found in mass spectrometric investigations of the silver sulfide clusters $[Ag_{344}S_{124}(StBu)_{96}]$[8] and $[Ag_{490}S_{188}(StC_5H_{11})_{114}]$.[9]

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[11] For all three compounds it was impossible to locate all solvent molecules embedded in the lattice voids. Using the program PLATON[12] it is possible to calculate the dimension of the remaining voids. Approximating that THF and diethyl ether molecules have a volume of 100×10^6 pm^3 and toluene molecules have a volume of 120×10^6 pm^3, it is possible to estimate the additional number of solvent molecules per cluster. **1**: calcd void 1228×10^6 pm^3, ca. 6 additional solvent molecules (THF or Et_2O); **2**: calcd void $11\,087\times10^6$ pm^3, ca. 18 additional THF molecules; **3**: calcd void 8214×10^6 pm^3, ca. 17 additional toluene molecules.

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[13] For compound **1**, different crystals obtained from various reaction samples were subjected to X-ray diffraction. The refined lattice constants deviate significantly. For the longest axis, deviations up to 4.4 % and for the angles up to 3.4 % were found. A reason for this range of fluctuation could be that different amounts of solvent molecules are embedded into the lattice, yielding different expanding of the packing of cluster molecules. Due to this phenomenon, the signals in the powder diffraction are considerably broadened (Figure S1 in the Supporting Information). In some rare cases, very thin black needles of a second modification of cluster **1** was obtained. A refinement of this modification with satisfying quality factors was not as yet possible. The major difference of this modification is that it does not show dimerization via the thioether function of the ligands. (Lattice parameters of the second modification of **1**: triclinic, $P\bar{1}$, $a=2548.8$, $b=3355.0$, $c=3534.1$ pm, $\alpha=88.40$, $\beta=70.00$, $\gamma=80.61°$, $V=28\,005\cdot10^6$ pm^3.)

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[18] Compound **2** sometimes also crystallizes in small amounts of a second packing as very small, black, cuboctahedral crystals. An exact determination of the structure was not possible as yet, owing to the small number and poor quality of the available crystals. Only the atoms of the cluster core could be refined; their alignment corresponds with the structure shown in Figure 2 (top, right). (Lattice parameters of the second modification of **2**: trigonal primitive, space group not clearly determinable, $a=b=3802.2$, $c=2325.7$ pm; $V=29\,118\times10^6$ pm^3.)

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