$[Cu_{24}S_{12}(PMe\mathit{i}Pr_2)_{12}]$, $[Cu_{28}S_{14}(P\mathit{t}Bu_2Me)_{12}]$, $[Cu_{50}S_{25}(P\mathit{t}Bu_2Me)_{16}]$, $[Cu_{70}Se_{35}(P\mathit{t}Bu_2Me)_{21}]$, $[Cu_{31}Se_{15}(SeSiMe_3)(P\mathit{t}Bu_2Me)_{12}]$ and $[Cu_{48}Se_{24}(PMe_2Ph)_{20}]$: New Sulfur- and Selenium-Bridged Copper Clusters

Stefanie Dehnen and Dieter Fenske*

Dedicated to Professor Hans Georg von Schnering on the occasion of his 65th birthday

Abstract: Reaction of copper(I) acetate with bis(trimethylsilyl)chalcogenides $E(SiMe_3)_2$ (E = S, Se) in the presence of tertiary phosphines in organic solvents leads to the formation of chalcogen-bridged copper clusters in crystalline form. In recent investigations, the following structures were isolated and characterised by X-ray crystallography: $[Cu_{24}S_{12}(PMe\mathit{i}Pr_2)_{12}]$ (**1**), $[Cu_{28}S_{14}(P\mathit{t}Bu_2Me)_{12}]$ (**2**), $[Cu_{50}S_{25}(P\mathit{t}Bu_2Me)_{16}]$ (**3**), $[Cu_{70}Se_{35}(P\mathit{t}Bu_2Me)_{21}]$ (**4**), $[Cu_{31}Se_{15}(SeSiMe_3)(P\mathit{t}Bu_2Me)_{12}]$ (**5**) and $[Cu_{48}Se_{24}(PMe_2Ph)_{20}]$ (**6**). The cluster cores of **1**–**6** have new structures or new structural characteristics and go some way towards providing an insight into the mechanisms of cluster formation reactions. With the help of the aforementioned compounds a number of structure principles that govern sulfur- and selenium-bridged copper clusters can be formulated.

Keywords
clusters · copper complexes · selenium compounds · structure elucidation · sulfur compounds

Introduction

Recently a large number of sulfur- and selenium-bridged copper clusters have been synthesised.[1–3] Scheme 1 shows the general synthetic pathway for the formation of these compounds. The molecular structures of these compounds could be described as fragments of the binary Cu_2E-phase materials that are protected by tertiary phosphine ligand shells. With up to 44 copper atoms, spherical cluster core formation is observed; this does not permit a direct comparison with the binary copper chalcogenides. However, with increasing cluster size, one observes a transition towards a layered Cu–E skeleton in the compounds, which clearly shows a relationship with that of the solid-state structure. It is possible that the mechanism for cluster formation and synthesis, and thus the molecular structure of the products, is strongly influenced by the reaction conditions (temperature, type of copper salt used, type and size of PR_2R'). The stabilisation of the cluster provided by the binding energy results principally from the formation of covalent copper–chalcogen bonds. The Cu–Cu bonds are dispersive in nature and have been theoretically calculated.[4]

$$CuX + PR_2R' \xrightarrow[-\,SiMe_3X]{\text{1. org. solvent} \\ \text{2. } +\,E(SiMe_3)_2} [Cu_{2n}E_n(PR_2R')_m] \qquad \begin{array}{ll} X & = Cl,\ OAc \\ R,\ R' & = \text{org. group} \\ E & = S,\ Se \end{array}$$

Scheme 1.

Through thermal treatment of the Cu–Se clusters (at 40–80 °C) under high vacuum, the PR_2R' ligands can be cleaved from the central core. This results in the formation of metastable Cu_2Se phases, which are, however, X-ray amorphous. At 210 °C these phases undergo a transition to α-Cu_2Se.[1a] Evidently we are dealing with amorphous nanocomposites, the particle size of which is approximately uniform and which are thus monodisperse particles. The first investigations show that the resulting particle size depends on the size of the cluster used in the thermal experiment.[5] It is evident that with increasing cluster size there is a transition from insulator to semiconductor. This could be confirmed by conductivity measurements.

From the reactions of copper(I) acetate with $S(SiMe_3)_2$ or $Se(SiMe_3)_2$ in the presence of $PMe\mathit{i}Pr_2$, $P\mathit{t}Bu_2Me$ or PMe_2Ph, the compounds $[Cu_{24}S_{12}(PMe\mathit{i}Pr_2)_{12}]$ (**1**), $[Cu_{28}S_{14}(P\mathit{t}Bu_2Me)_{12}]$ (**2**), $[Cu_{50}S_{25}(P\mathit{t}Bu_2Me)_{16}]$ (**3**), $[Cu_{70}Se_{35}(P\mathit{t}Bu_2Me)_{21}]$ (**4**), $[Cu_{31}Se_{15}(SeSiMe_3)(P\mathit{t}Bu_2Me)_{12}]$ (**5**) and $[Cu_{48}Se_{24}(PMe_2Ph)_{20}]$ (**6**) were synthesised and their molecular structures characterised by X-ray crystallographic analysis.[6] So far we have found no proof that other products are formed from these reactions. Scheme 2 summarises the reactions which lead to the formation of compounds **1**–**6**.

Results and Discussion

Cluster **1** possesses an inversion centre and crystallises in the triclinic space group $P\bar{1}$ with one molecule in the unit cell.

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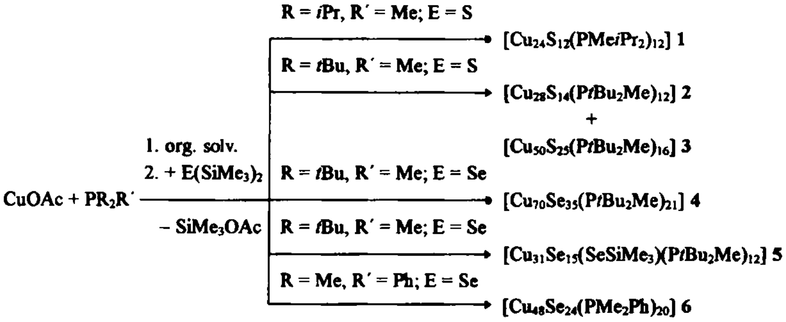

Scheme 2.

Figure 1 shows the molecular structure of **1**. The structure of the Cu–S cluster core can be formally described as a dimer of the copper sulfide skeleton of two clusters composed of $[Cu_{12}S_6(PnPr_3)_8]$,[3] which are connected through a triangular face of the copper structure (Cu1–Cu3 and their symmetry equivalents). In contrast to the molecular structure of the compound $[Cu_{20}S_{10}(PPh_3)_8]$, which can be described as the condensation product of two clusters with twelve copper atoms,[2] compound **1** results from the linking of the monomeric units with a reduction in the number of phosphine ligands, but without the loss of copper or sulfur atoms. In this hypothetical dimeric form, the six copper atoms arranged around the inversion centre of **1** (Cu1–Cu3 and their symmetry equivalents) make a slightly distorted octahedron. Because of the nature of the coordination of the chalcogen atoms in the two halves of the cluster, four of the eight faces of the octahedron are μ_3-bridged by the sulfur atoms S2, S2′, S3 and S3′. Support for dimerisation of two clusters with twelve copper atoms each—instead of cluster growth starting from a central Cu_6 octahedron—comes from the following points. Consider, for example, one of the $[Cu_{12}S_6]$ subunits, Cu1–Cu12, S1–S6 and P1–P6. The two sulfur atoms S2′ and S3′ in the other subunit take the place of what would be two phosphine ligands in a monomeric cluster precursor. The left-hand side of Figure 2 shows one subunit of **1** extended to the atoms S2′ and S3′, which serve in place of the unavailable phosphine ligands. The right-hand side of the figure shows the molecular structure of $[Cu_{12}S_6(PnPr_3)_8]$.[3] One can see that the cluster core is topologically almost identical to that of the hypothetical monomer "$[Cu_{12}S_6(PiPr_2Me)_8]$", and that both show only small differences in distortion.

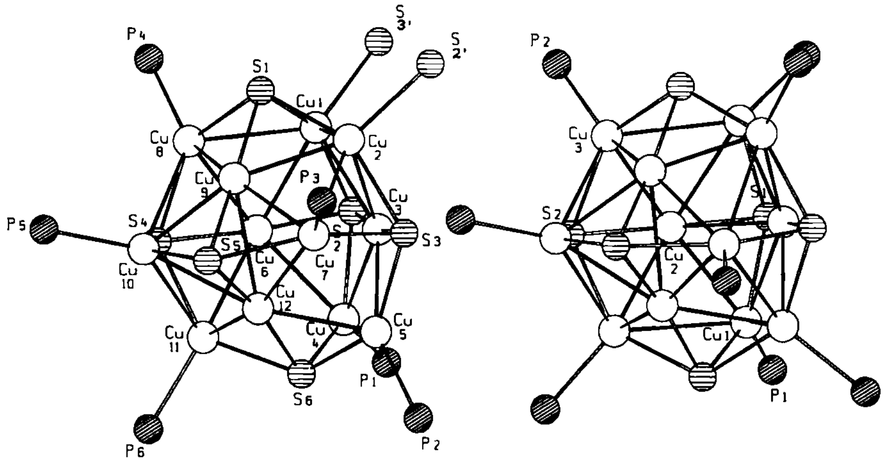

Fig. 2. Structural relationship between the Cu-S-P cores of one half of **1** (left-hand side) and $[Cu_{12}S_6(PnPr_3)_8]$[3] (right-hand side).

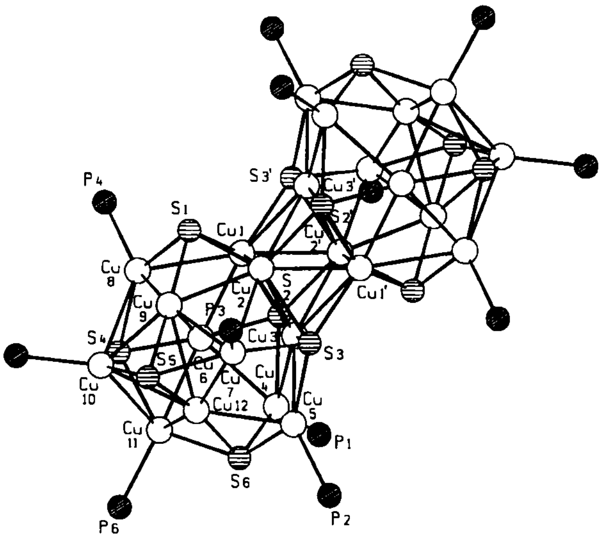

Fig. 1. Molecular structure of **1** in the crystal (organic groups omitted). Cu: empty circles; S: horizontal hatching; P: sloping hatching. Cu–Cu contacts are included up to 299 pm. Most important distances [pm] and angles [°] (±0.6 pm or ±0.3°): Cu–Cu 255.5–298.7, Cu(1,2,3)–Cu(2,3,1) 265.4–268.3, Cu1–Cu2′ 263.6, Cu2–Cu3′ 276.8, Cu1–Cu3′ 282.2, Cu–S (one asymmetric unit) 215.9–237.8, Cu1–S3′ 248.5, Cu2–S2′ 250.9, Cu–(S3, S3′) 219.6–248.5, Cu–(S2, S2′) 221.4–250.9, Cu–P 227.1–229.9; S–Cu(3,6,9,12)–S (approx. linear environment) 169.5–171.7, sum of angles around Cu(4,5,7,8,10,11) (approx. trigonal planar environment of two S and one P) 359.6–360.0, sum of angles around Cu(1,2) (central Cu_6 octahedron; approx. trigonal planar environment of three S) 359.6 and 359.8.

The copper atoms Cu1 and Cu2 in the central Cu_6 octahedron in **1** have trigonal planar coordination to three neighbouring chalcogen atoms. This is previously unknown for copper sulfide clusters; in the other CuS clusters known, the copper atoms are always either linearly coordinated to two sulfur atoms or have trigonal planar coordination to two sulfur atoms and the phosphorus atom of a PR_2R' ligand. The S2 and S3 atoms (and their symmetry equivalents) act as μ_5 bridges; this, too, is not normally observed in copper sulfide clusters. This higher bridging factor is reflected in the larger Cu–S distances of the chalcogen atoms concerned in comparison with normal Cu–S distances. The Cu–S distances between the subunits are 248.1 pm (Cu2–S2′, Cu2′–S2) and 251.1 pm (Cu1–S3′, Cu1′–S3), which are more than 10 pm longer than the normal Cu–S distances in **1**. Unusual coordination numbers are not necessarily an indication of a preceding dimerisation, as the bonds within a newly formed cluster can relax. However, from the observation of **1**, it would appear that the molecule has indeed been formed out of two monomeric molecules.

As a result of the unusual coordination number of the sulfur atoms, the cluster skeleton can be assigned 344 valence electrons. In spite of the reduced number of phosphine ligands, this is exactly double that for the monomeric "Cu_{12}" clusters. The resulting electronic situation of **1** is probably very similar to that of the smaller clusters and **1** is also evidently the preferred product with respect to the hypothetical "$[Cu_{12}S_6(PiPr_2Me)_6]$" cluster, which is only partially shielded.

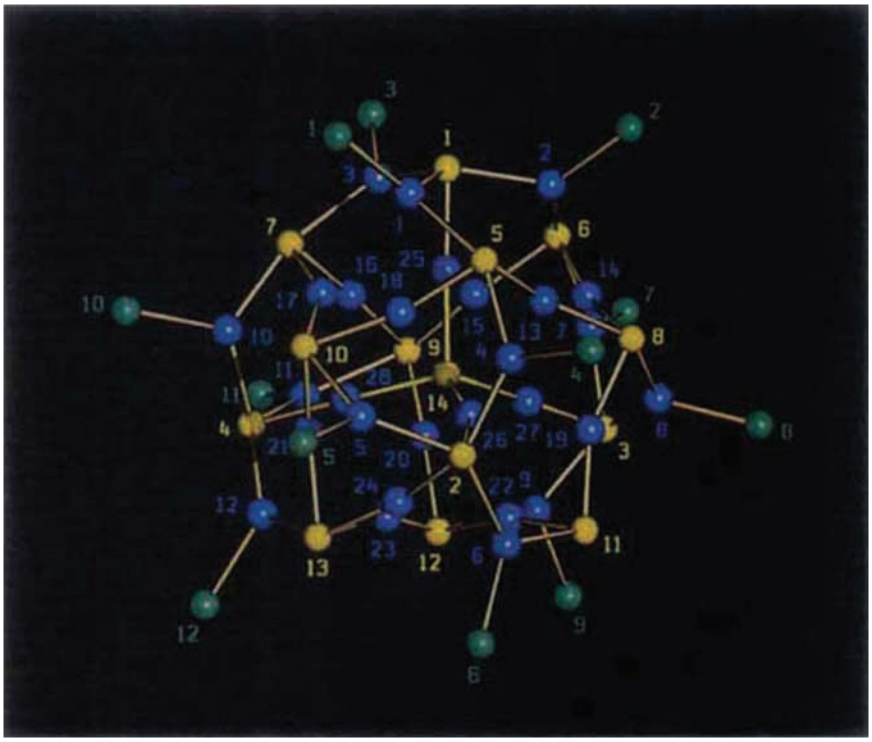

Fig. 3. Molecular structure of one of the two independent molecules of **2** in the crystal (organic groups omitted). Cu: blue; S: yellow; P: green. For clarity Cu–Cu contacts have not been drawn. Most important distances [pm] and angles [°] (without decimal places) [6]: Cu–Cu 247–295, Cu–S 211–251, Cu–S2 (S: μ_5-bridging) 217–251, Cu–S11 (S: μ_3-bridging) 211–225, Cu–P 224–232; Cu-S14-Cu 104–117, S14-Cu(25–28)-S (approx. linear environment) 163–179, S-Cu(13–24)-S (approx. linear environment) 153–173, sum of angles around Cu(1–12) (approx. trigonal planar environment of two S and one P) 355–360.

The twelve phosphine ligands in **1** are organised in a regular pattern around the copper sulfide core. These ligands form a P_{12} polyhedron that can be described as a tetragonal antiprism capped with two P_2 units. The surrounding dodecahedron of the $[Cu_{12}S_6(PnPr_3)_8]$[3] cluster core has basically been extended in this case by two P_4 rings. The nonbonding P–P distances in this polyhedron range from 552.3 to 886.9 pm.

The spatial requirements of the P*i*Pr$_2$Me groups in **1** (Tolman angle 146°[7]) are larger than the steric demands of all other phosphine ligands with which "Cu$_{12}$" sulfide clusters can be isolated. As in the case of $[Cu_{20}S_{10}(PPh_3)_8]$[2] and $[Cu_{20}S_{10}(PtBu_2nBu)_8]$,[3] it is conceivable that restricted space makes it impossible to arrange the eight phosphine ligands normally observed around the $[Cu_{12}S_6]$ unit so that sufficiently short (and strong) Cu–P bonds are formed with acceptable ligand–ligand interactions.

From ab initio calculations for $[Cu_{2n}S_n(PH_3)_m]$ clusters,[9] one finds that with increasing cluster size the Cu–P binding energy decreases (the Cu–P distances increase). With the removal of some ligands (to give $[Cu_{12}S_6(Ph_3)_8]$ instead of $[Cu_{12}S_6(PH_3)_{12}]$) this effect is hindered and therefore the cluster can be stabilised.[8, 9] However, it is evident from this result that an even smaller phosphine ligand shell around **1** is unable to protect the cluster sufficiently and so might lead to a further reaction. The density functional theory (DFT) approximation is currently being used to investigate the influence of the spatial requirements of the different PR$_2$R′ groups on the stability of the ligand shell of "Cu$_{12}$" clusters.

Both halves of the cluster **1** have 22 short Cu–Cu contacts (Cu–Cu distances 255.5–298.7 pm), four fewer than the formal underlying cluster with twelve copper atoms. Through the linking of the two subunits, a total of six new Cu–Cu interactions are formed. These interactions are dispersive in nature and it is therefore likely that the formation of four new Cu–S bonds is of more importance for the formation and stabilisation of the cluster as a whole. With the exception of the μ_5-bridging sulfur atoms in the central unit (S2, S2′, S3 and S3′), the chalcogen atoms in **1** act as μ_4-bridges, as observed in the other copper sulfide clusters isolated to date. Together they form a polyhedron made up of three face-sharing distorted octahedra (nonbonding S–S distances 366.6–449.6 pm).

Cluster **2** crystallises in the monoclinic space group $P2_1$ with two independent molecules in the asymmetric unit, which are related to each other as enantiomers. Some problems occurred with the refinement of the second enantiomer during the structure analysis. The temperature factor coefficients for most of the heavy atoms were very high in certain directions. Therefore it made sense to refine these in split positions.[6] The heavy-atom skeleton of the molecule, which showed no disorder in the Cu–S core, is depicted in Figure 3. The cluster core of **2** only approximately possesses C_3 symmetry. Perfect symmetry is prevented by the position of Cu24. If one disregards this and other minor distortions and the position of the organic groups attached to the phosphorus atoms, there would be a C_3 rotation axis through the atoms S1 and S14 (this will be explained later). The description of the cluster skeleton construction can be based on the partial sulfur structure, which can be likened to a distorted S_{13} deltahedron centred around S14. Four of the 28 metal atoms (Cu25–Cu28) are in almost ideal tetrahedral positions around the central S14 and are linearly coordinated by S14 and a further chalcogen atom at the surface of the polyhedron (S1–S4). The remaining 24 copper atoms are coordinated along the edges of the polyhedron in a typical fashion for sulfur-bridged copper clusters. Cu13 to Cu24 show approximately linear coordination to two chalcogen atoms and Cu1 to Cu12 have an almost trigonal planar environment as a result of further coordination to one each of the phosphorus atoms of the twelve P*t*Bu$_2$Me ligands. The phosphine-free metal atoms are slightly shifted towards the centre of the cluster, explaining the deviation of the S-Cu-S angle from 180°. The twelve metal atoms bound to the phosphine ligands always bind in threefold fashion to one of the sulfur atoms (S1–S4), which in turn bind to the inner copper atoms. These chalcogen atoms (with the exception of the μ_5-bridging atom S2) are surrounded in a trigonal pyramidal environment by copper atoms.

The distribution of the 24 metal atoms on the 36 edges of the polyhedron occurs such that the chalcogen atoms act as μ_4 bridges, which is likewise typical for copper sulfide clusters. The exceptions are S2 (μ_5 bridging) and S11 (μ_3 bridging). This is a result of the irregular position of Cu24 in the cluster framework. If this metal atom were bound to S11 and S13 and not, as is actually the case, to S2 and S13, then S2 and S11 would also act as μ_4 bridges. Also the threefold symmetry of the molecular structure, previously mentioned, would then be realised. Finally, the phosphorus atoms of the P*t*Bu$_2$Me molecules surround the approximately spherical core of the cluster in the form of a distorted icosahedron.

Besides **2**, compound **3** is also formed from the same reaction solution in the form of thin, dark red-brown crystals. It has been shown that the decrease in the HOMO–LUMO gap and therefore the convergence[10, 11] towards the band gap of the semiconductor solid-state compound Cu_2E (ca. 0.5–3 eV)[12, 13] can be qualitatively derived from the colour of the compound. Compared with the red crystals of the Cu–S clusters isolated to date, the much darker colour of this reaction product indicates a larger number of $Cu_{2n}S_n$ units in **3**, as long as one disregards the possibility of mixed valences.

Cluster **3** (Fig. 4) crystallises in the triclinic space group $P\bar{1}$ and possesses an inversion centre at the atom S13. In addition, **3** has approximate mirror symmetry, with a mirror plane through the atoms S1, S1′, Cu18 and Cu18′, which altogether approximates to C_{2h} symmetry. The cylindrical skeleton of the cluster of **3** shows both known and new structural characteristics of the coordination geometry of the copper and sulfur atoms. The chalcogen part of the structure (nonbonding S–S distances 374.4–448.3 pm) is made up of four parallel, slightly corrugated, five-membered rings (S2–S6, S7–S11 and their symmetry equivalents). These rings alternate with five other sulfur atoms (S1, S1′, S12, S12′ and S13) arranged on an imaginary axis along the length of the molecule. The two S_5 rings that lie in the same asymmetric unit are elliptically arranged, while the two rings which are positioned around the inversion centre of the cluster are staggered with respect to each other. Thus, these two S_5 rings together form a pentagonal antiprism, which is connected to the outer S_5 rings to form a further pentagonal prism. All (anti)prisms are all slightly distorted and centred around one of the sulfur atoms S12, S12′ or S13. The two remaining sulfur atoms, S1 and S1′, cap the two outer surfaces of the polyhedron, which has a total length of 1713.7 pm. In Figure 4, the mirror plane referred to above lies roughly parallel to the plane of the paper. All sixteen metal atoms bound to $PtBu_2Me$ (Cu1–Cu8 and their symmetry equivalents) have trigonal planar coordination, and a further 24 copper atoms (Cu9–Cu17, Cu19, Cu21, Cu22 and their symmetry equivalents) show linear coordination to two sulfur atoms as is usual for a Cu–S cluster.

If, however, one gets closer to the inversion centre, one comes across some unusual coordination geometry. The coordination of a copper atom to three sulfur atoms, as has previously been noted for **1**, is unusual. In this manner, Cu18 and Cu18′ are bound in a trigonal planar environment to S7, S10′ and S11′ and their symmetry equivalents, and are found at the triangular surfaces of the chalcogen polyhedron instead of along the edges. Cu20 and Cu23 to Cu25 (and their symmetry equivalents) bind to sulfur atoms at the cluster surface as well as to one or two of the inner sulfur atoms S12, S12′ or S13, and thus also have an approximately trigonal planar environment. This leads to an almost hexagonal planar arrangement of six copper atoms (Cu23–Cu25 and their symmetry equivalents) around the sulfur atom S13, which is the first of its kind to be reported. The corresponding Cu–S bond lengths are unusually large, 263.3–267.3 pm, on average 30–50 pm longer than the other Cu–S distances found in the cluster. Cu–S distances of this extent are clearly longer than the average of those found in the different Cu_2S phases.[14] There are, however, examples of similarly long bonds in the structures of ternary copper sulfides such as $K_3Cu_8S_6$ or $RbCu_8S_6$ (Cu–S distance 223–284 pm).[15] One of the Cu–S distances for monoclinic chalcocite (Cu_2S) amounts to 288 pm, although this is uncertain owing to twinning problems.[16] The oscillation ellipsoids of the atoms Cu24 and Cu25 show extensive elongation along the binding axis to S13. Cu24

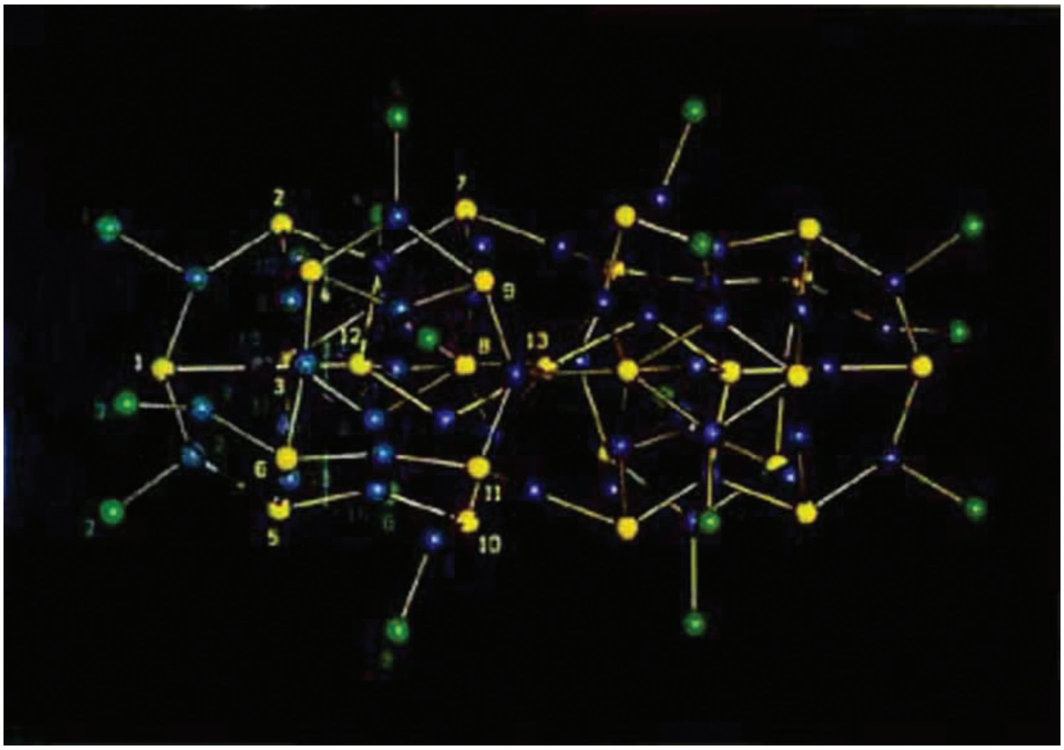

Fig. 4. Molecular structure of **3** in the crystal (organic groups omitted). Cu: blue; S: yellow; P: green. For clarity Cu–Cu contacts have not been drawn. Most important distances [pm] and angles [°] (±0.7 pm or ±0.4°): Cu–Cu 251.9–299.5, Cu–S 217.1–251.2, Cu(23,24,25)–S13 263.3–267.3, Cu18–S(7,10,11) 229.0–244.0, Cu–P 220.8–230.8; S–Cu(9–17, 19, 21, 22)–S (approx. linear environment) 148.9–178.4, sum of angles around Cu(1–8) (approx. trigonal planar environment of two S and one P) 354.2–359.9, sum of angles around Cu(18,20,23–25) (approx. trigonal planar environment of three S) 341.4–360.0, Cu-S13-Cu 59.8–60.9.

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can be refined at half occupancy with a Cu–Cu distance of 70.5 pm and a Cu-S-Cu angle of 5.3°, which results in a shorter Cu 24A–S 13 distance (232.8 pm) and a longer Cu 24B–S 13 distance (299.0 pm). If one does not take this disorder into account, then the arrangement of the SCu_6 unit is very regular. The seven atoms lie approximately in one plane that cuts the imaginary axis S 1–S 1′ with an angle of 29.2°. The deviation of the copper atoms from the least-square plane is ± 18 pm and thus tends towards a slightly corrugated Cu_6 ring in chair conformation around S 13. All the Cu-S 13-Cu angles are approximately 60° (59.8–60.9°). Such an SCu_6 unit has not been observed to date in any copper(I)- and sulfur-containing compounds, whereas other common coordination polyhedrons have been observed. In the metastable tetragonal form of Djurleit ($Cu_{1.96}S$), for example, six copper atoms always form a trigonal prism around a central sulfur atom.[14] It is not possible to explain the bonding of the central sulfur atom S 13 in terms of the simple orbital viewpoint. It makes more sense to assume that an interstitial S^{2-} ion exists at the centre of **3**. From an ionic point of view, one ought to take the electrostatic interactions with the next-but-one neighbour into consideration. These are the atoms Cu 16–Cu 18, Cu 21, Cu 22 and their symmetry equivalents, which lie at 289.6–381.6 pm from S 13.

Sixteen chalcogen atoms in **3** act as μ_4 bridges (S 1–S 7, S 11 and their symmetry equivalents), eight adopt μ_5 bridging (S 8, S 9, S 11, S 12 and their symmetry equivalents) and one acts as a μ_6-bridging ligand (S 13). This unusual coordination geometry for sulfur atoms in Cu–S clusters could be attributed to preceding cluster dimerisation, as was discussed for **1**. The investigations of the molecular structures of **2** and **3** provide three indications for this.

The linking of the two symmetrically equivalent cluster halves in **3** around an inversion centre is unusual and appears to be very loose-packed in comparison with the rest of the cluster skeleton. Besides the central S^{2-} ion only two further copper atoms, Cu 18 and Cu 18′, act as bridges between the two middle Cu_5S_5 heterocycles (S 7–S 11, Cu 8, Cu 16, Cu 17, Cu 24, Cu 25 and their symmetry equivalents). Both terminal fragments of **3**, consisting of S 1–S 6, Cu 1–Cu 3, P 1–P 3, Cu 9–Cu 13, Cu 19 and their symmetry equivalents, are sections also found in the molecular structure of **2**. The relationship between the two structures is shown in Figure 5. The view of the cluster skeleton of **2** has been so chosen that the section common to both structures can be easily recognised. As a result of the approximate threefold symmetry in **2** there are three such fragments to be found. The sixteen phosphorus atoms of the terminal ligands in **3** form a polyhedron that can be described as a pentagonal antiprism, capped with two P_3 units. This arrangement of the phosphorus atoms can also be interpreted as an expanded icosahedron, which is therefore geometrically related to the ligand shell of **2** (c.f. the relationship of the ligand shells of **1** and $[Cu_{12}S_6(PnPr_3)_8]$[3]).

It is possible that in **3** there is a transition to the characteristics of the Cu_2E phases. This is borne out by the higher coordination numbers of the chalcogen atoms, but not however by the long bond lengths of S 13.[14]

Clusters **2** and **3** are the largest known copper sulfide clusters as well as being the first examples of sulfur-bridged copper clusters with interstitially bound Cu–S structure fragments. While the tetrahedral Cu_4S fragment in the cluster core of **2** shows typical coordination numbers for copper sulfide clusters (four for sulfur and two for copper), one finds that the central structural unit of **3** deviates considerably from the normal coordination pattern. Here, instead of several SCu_4 tetrahedra being linked together, three μ_5- or μ_6-bridging sulfur atoms are coordinated to inner and outer copper atoms, respectively.

The reactions of CuOAc corresponding to those which yield **1**, **2** and **3** were carried out with $Se(SiMe_3)_2$ instead of $S(SiMe_3)_2$ (c.f. Scheme 2). Depending on the reaction conditions the following compounds were formed: the cluster compound **4**, a compound analogous to **4** with $PiPr_2Me$ as ligand,[17] a cluster with the same Cu–Se skeleton as $[Cu_{30}Se_{15}(PiPr_3)_{12}]$[1a] but with $PtBu_2Me$ as the ligand,[17] and the cluster compound **5**. None of these four compounds show any topological relationship to **1**, **2** or **3**. The reactions with $PtBu_2Me$ were conducted at −78 °C and the resulting reaction mixtures were kept at +2 °C. Small differences in the amount of phosphine used (c.f. Experimental Procedure) resulted in the formation and crystallisation of **4**, **5** and $[Cu_{30}Se_{15}(PtBu_2\text{-}Me)_{12}]$ (the structure of which will not be discussed here in detail).[17] Variation of the amount of phosphine as an influence on the formation and crystallisation of clusters of different sizes has also been postulated for other systems, for example the synthesis of phosphorus-bridged silver clusters.[18] Figure 6 shows the molecular structure of **4**, which crystallises in the triclinic space group $P\bar{1}$. The composition is different in comparison with other known copper selenide structures containing seventy metal atoms, $[Cu_{70}Se_{35}(PEt_2Ph)_{23}]$ and $[Cu_{70}Se_{35}(PEt_3)_{22}]$,[1a] not only in

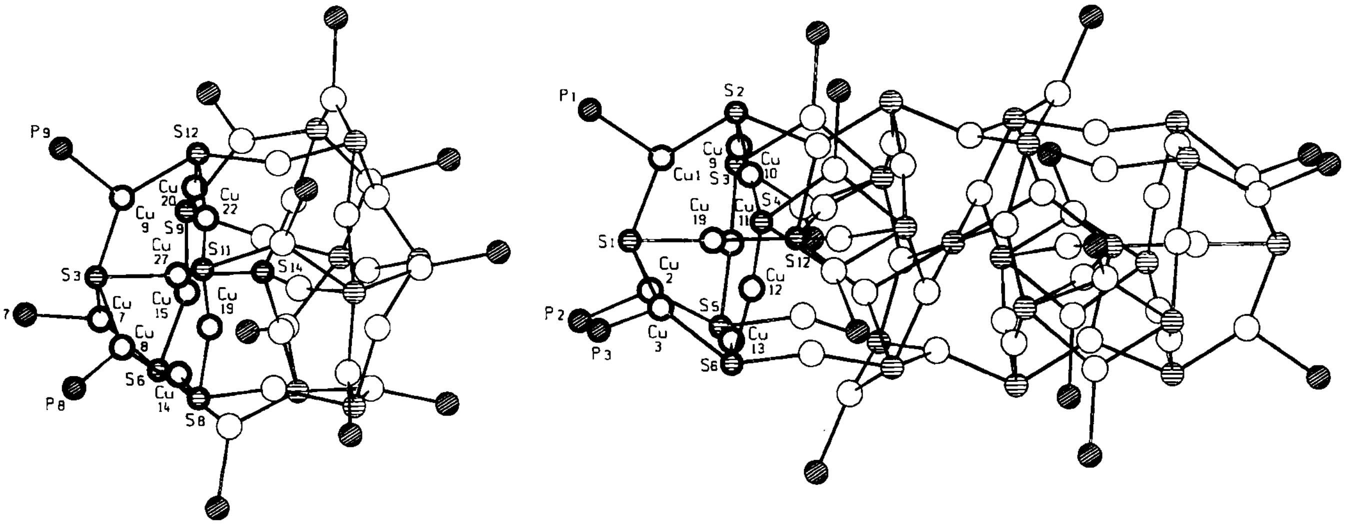

Fig. 5. Structural relationship between **2** (left) and **3** (right); the related fragments are emphasised in bold.

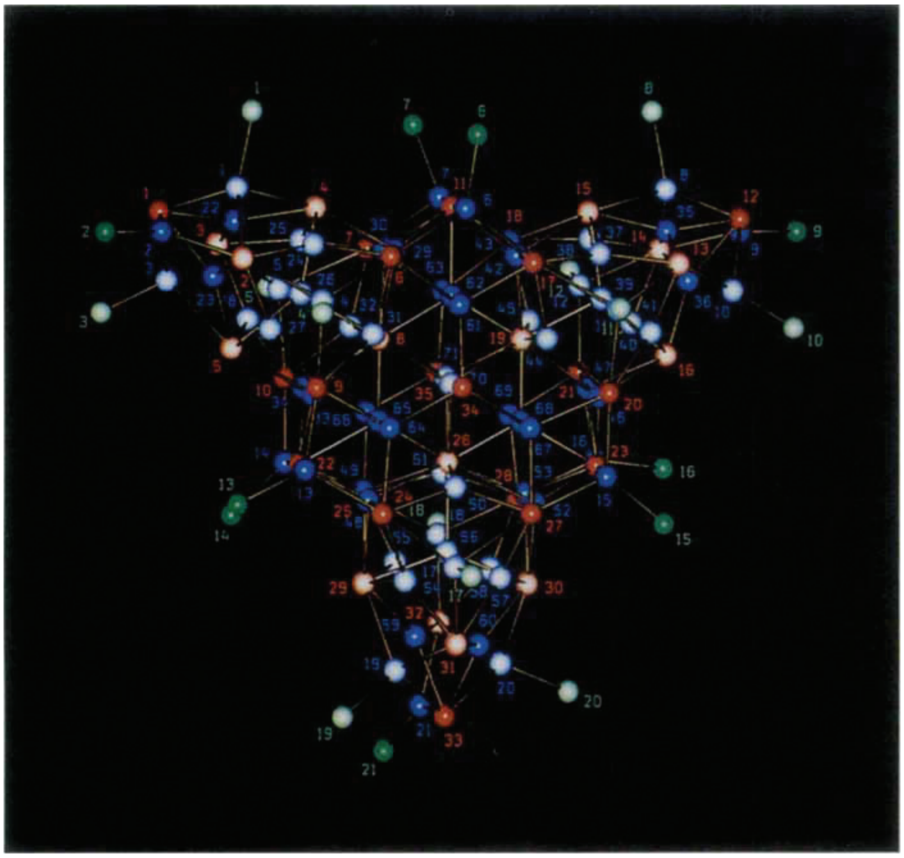

Fig. 6. Molecular structure of **4** in the crystal (organic groups omitted). Cu: blue; Se: red; P: green. For clarity Cu–Cu contacts have not been drawn. Highlighted atoms show topological relationships to a corresponding fragment in **5** (Fig. 7). Most important distances [pm] (±8 pm): Cu–Cu 244.3–298.7, Cu–Se 230.1–292.3, Cu–P 217.9–225.8.

$(PEt_3)_{22}]$,[1a] not only in the nature, but also in the number of phosphine molecules per formula unit. In **4**, twenty-one ligand molecules are sufficient to coat the cluster core of 105 metal and chalcogen atoms. The reason for this could lie in the fact that $PtBu_2Me$ has a much larger Tolman angle, 161°, than those of PEt_2Ph or PEt_3, 136° and 132° respectively.[7] A similar, even stronger reduction in the number of ligands is observed for the recently reported clusters $[Cu_{44}Se_{22}(PEt_2Ph)_{18}]$ and $[Cu_{44}Se_{22}(PtBu_2nBu)_{12}]$.[1b] As one can see for the diverse Cu–S clusters containing 12 or 20 copper atoms[2, 3] as well as for the Cu–Se clusters containing 44 copper atoms,[1b] in order to achieve the preferred cluster size and the optimum number and arrangement of phosphine ligands, a looser packing array of the ligand shell on the cluster surface is accepted. As long as the possible energetically preferred cluster sizes or ligand-sphere types can be realised and as long as the cluster formed does not react further, then the corresponding parameters do not change. If not, then obviously cluster growth will continue until another energy minimum on the energy hypersurface has been reached.

The copper selenide core of **4** correlates quite well with the Cu–Se skeleton of $[Cu_{70}Se_{35}(PEt_2Ph)_{23}]$ and differs more markedly from the molecular structure of $[Cu_{70}Se_{35}(PEt_3)_{22}]$ (c.f. ref. [1a]). The small differences between the structure of **4** and that of $[Cu_{70}Se_{35}(PEt_2Ph)_{23}]$ can be put down to the fact that in **4**, the two extra, ligand-free copper atoms are shifted slightly towards the cluster core. An approximate threefold axis, if one disregards small distortions and the disorder of Cu62, Cu65 and Cu68,[6] is hindered by the position of the copper atom Cu2 and the phosphorus atom P2 bound to it. This also prevents the existence of mirror planes or twofold axes in **4**. The Cu–Cu and Cu–Se distances in **4** and in the related clusters[1a] are essentially the same.

Compound **5**, shown in Figure 7, also crystallises in the triclinic space group $P\bar{1}$ with two molecules per unit cell.

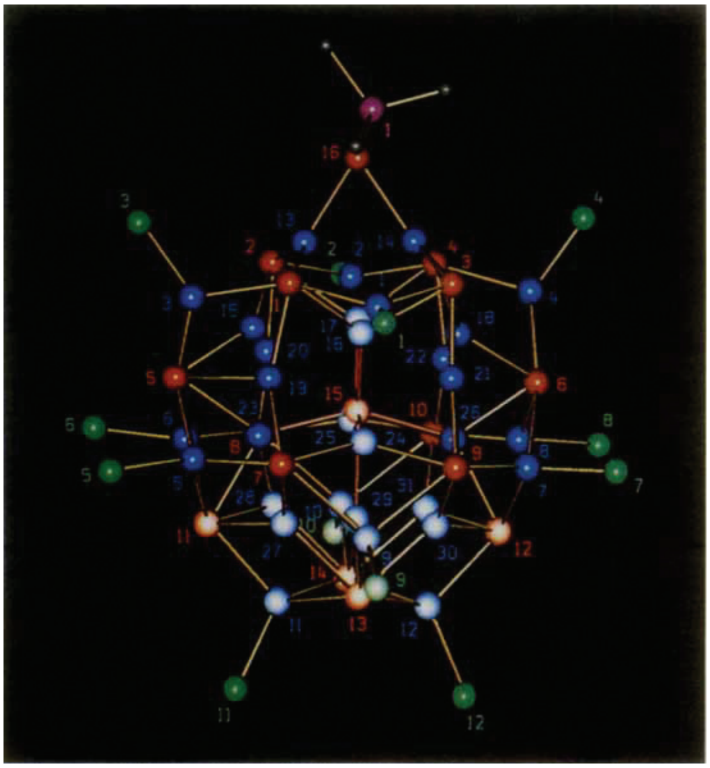

Fig. 7. Molecular structure of **5** in the crystal (organic groups omitted). Cu: blue; Se: red; P: green; Si: violet; C: grey. For clarity Cu–Cu contacts have not been drawn. Highlighted atoms show topological relationships to three corresponding fragments in **4** (Fig. 6). Most important distances [pm] and angles [°] (±0.9 pm and ±0.5°): Cu–Cu 250.7–298.5, Cu–Se 227.1–289.4, Cu19–Se5 280.1, Cu15–Se1 311.4, Cu–P 221.4–228.3; Se-Cu(20–22)-Se 147.6–169.7, Se1-Cu19-Se7 140.3, Se2-Cu15-Se5 138.4, sum of angles around Cu19 (three bonds to Se) 356.2, sum of angles around Cu(1–4) (approx. trigonal planar environment of two Se and one P) 356.4–358.7, sum of angles around Cu(13,14,16,17,23–31) (approx. trigonal planar environment of three Se) 358.6–360.0, sum of angles around Cu15 (with regard to Cu15–Se1) 344.1, sum of angles around Cu18 (highly distorted trigonal planar environment) 338.62, Cu13-Se16-Cu14 66.1, Cu(13, 14)-Se16-Si1 108.9 and 113.6.

The heavy-atom skeleton of the cluster has approximate C_2 symmetry, if one disregards the $SiMe_3$ group, with a rotation axis through Se 15 and Se 16. The existence of the trimethylsilyl fragment makes **5** stand out from all the other known copper sulfide and copper selenide clusters. The unusual, odd, number of copper atoms and the charge-balancing $SeSiMe_3$ group are the two most obvious differences between **5** and the compound $[Cu_{30}Se_{15}(PiPr_3)_{12}]$.[1a] As well as these, it can clearly be seen that, apart from the hint of five parallel layers (in **5** parallel to an imaginary plane through Se 16, Cu 9 and Cu 10), there is no structural correlation or topological relationship between the two compounds. Therefore, the compound with 31 copper atoms cannot be described as the product of the uptake of a further copper atom and an $SeSiMe_3$ unit by $[Cu_{30}Se_{15}(PiPr_3)_{12}]$,[1a] but is a completely independent structure. The presence of the trimethylsilyl group attached to the cluster core leads to the assumption that this compound could rather be an intermediate product for the synthesis of larger clusters, for example, **4**. The $SeSiMe_3$ fragment could react further with CuOAc through the loss of $SiMe_3OAc$. Besides the fact that the courses of the reactions that lead to the formation of **4** and **5** are at least not inconsistent with a connection between the two clusters, there is also a fragment of the cluster skeleton of **5** which appears three times in the molecular structure of **4**. In Figures 6 and 7, the topologically related $Cu_{13}Se_5P_4$ fragments are highlighted. It can therefore not be excluded that from three of these structure fragments, instead of three molecules of **5**, one molecule of compound **4** could be produced through a slightly different reaction path.

The arrangement of the selenium atoms in **5** leads to an unusual Se_{14} polyhedron centred around Se 15. This is additionally capped through Se 16 ($SeSiMe_3$ group). Apart from Se 16 all the selenium atoms are at a similar distance from the central selenium atom, Se 15 (Se 15–Se(1–14) 428.7–463.0 pm, Se 15–Se 16 616.7 pm). The Cu–P fragments and other copper atoms bind to the selenium atoms both along the edges, typical for small Cu–Se clusters, and at the faces of the polyhedron, typical for larger Cu–Se clusters. This compound unifies in its cluster core the different structural characteristics that one finds separately in the other Cu–Se clusters. The copper atoms that occupy the edges of the polyhedron (Cu 19–Cu 22) are approximately linearly coordinated by two selenium atoms or else are almost trigonal planar through coordination to two selenium and one phosphorus atom (Cu 1–Cu 4). In addition, Cu 19 has a third very long Cu–Se bond (280.1 pm) to Se 5, which leads to a T-shaped geometry with the sum of the angles around the copper atom being 356.2°. The coordination geometry of the copper atoms that bind on the faces of the polyhedron is almost trigonal planar, in the case of the phosphine-ligand-free atoms (Cu 13–Cu 15,[19] Cu 18, Cu 23–Cu 31), or approximately tetrahedral with an additional bond to phosphorus. The metal atoms Cu 16, Cu 17, Cu 23–Cu 26 and Cu 29 are arranged below the faces of the polyhedron and have almost trigonal planar environments. The third coordination partner is found to be the central Se 15 atom. This chalcogen atom acts as a μ_7 bridge, which is clearly in contrast to the μ_4-bridging S 14 in the similarly sized cluster core of **2**, in which sulfur is the bridging ligand. The rest of the selenium atoms in **5** act as μ_6-bridging (Se 4–Se 6, Se 11–Se 14), μ_5-bridging (Se 1–Se 3, Se 7–Se 10) or μ_3-bridging ligands (S 16); this differs considerably from the coordination mode of the sulfur atoms in **2**, in which most of the chalcogen atoms are μ_4-bridging. The $SiMe_3$ group lies at an angle of 116.3° to the plane defined by the atoms Cu 13, Se 16 and Cu 14, which shows the steric effect of the free electron pair of the μ_3-selenium atom.

To find out more about the influence of phosphine ligands on the structure of selenium-bridged copper clusters, we investigated the reaction of CuOAc with $Se(SiMe_3)_2$ in the presence of PMe_2Ph. This phosphine ligand with a Tolman angle of 127°[7] has a smaller spatial requirement than the other PR_2R' ligands that have been used so far in the stabilisation and isolation of sulfur- and selenium-bridged copper clusters. The product **6** (the heavy-atom skeleton of which is shown in Fig. 8) crystallizes in the monoclinic space group $C2/c$ and has C_2 symmetry with a twofold rotation axis through the atoms Se 11 and Se 13. With an approximate C_2 axis through Se 12 and Se 12′ and a further one perpendicular to these two, the compound approaches D_2 symmetry. If one compares the empirical formula of **6** with those of other Cu–Se clusters, one finds a resemblance to the composition of the compounds $[Cu_{44}Se_{22}(PEt_2Ph)_{18}]$ and $[Cu_{44}Se_{22}(PnBu{\it t}Bu_2)_{12}]$.[1b] Actually the cluster core of **6** can be described in a fully analogous way. In **6** one can start with an Se_{22} deltahedron (Se 1–Se 11, Se 13 and their symmetry equivalents) which has 40 triangular faces in its overall surface

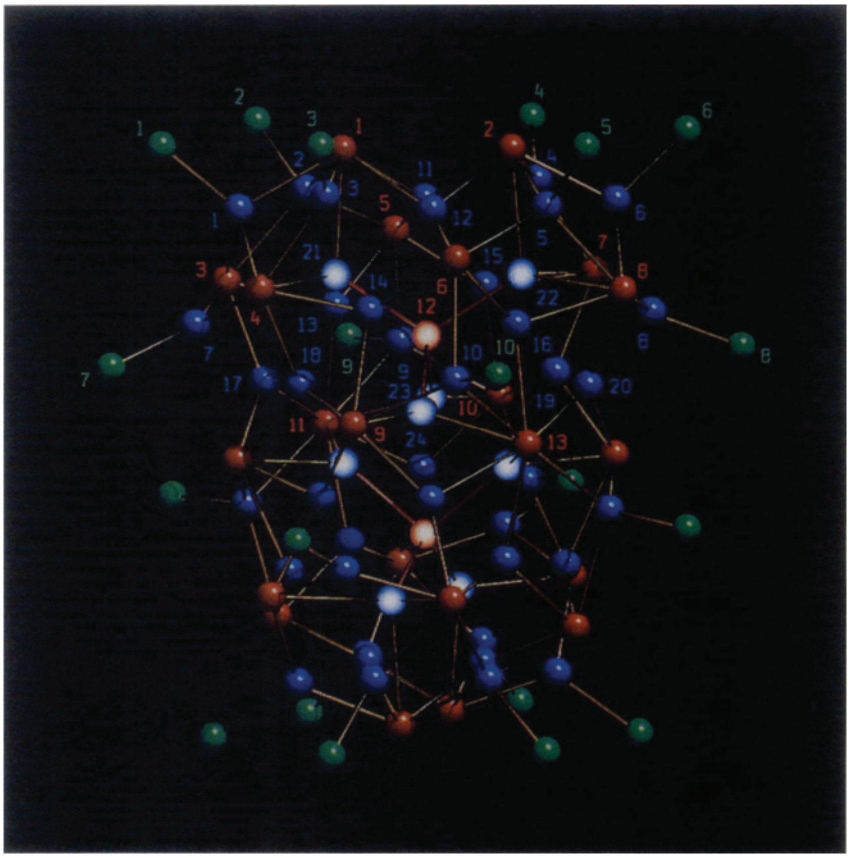

Fig. 8. Molecular structure of **6** in the crystal (organic groups omitted). Cu: blue; Se: red; P: green. For clarity Cu–Cu contacts have not been drawn. The atoms of the inner Cu_8Se_2 fragment are highlighted. Most important distances [pm] and angles [°] (±0.7 pm and ±0.3°): Cu–Cu 249.3–299.3, Cu–Se 233.6–298.1, Cu 3–Se 6 330.4, Cu 4–Se 5 350.3, Cu 7–Se 10 314.9, Cu 8–Se 10 327.0, Cu–P 220.1–227.4; sum of angles around Cu(3,4,7,8) (approx. trigonal planar environment of two Se and one P) 352.8–358.3, sum of angles around Cu(11–21, 23, 24) (distorted or regular trigonal planar environment of three Se) 335.6–357.4.

and two further selenium atoms within (Se 12 and Se 12′). The selenium structure is shown in Figure 9. There are no bonding interactions between the selenium atoms. Exactly as observed for the Se_{22} substructures of the clusters with 44 copper atoms, one also observes in **6** three almost parallel six-membered rings of selenium atoms (Se 3–Se 8, Se 9–Se 11, Se 13 and their symmetry equivalents). While these rings are planar in $[Cu_{44}Se_{22}(PEt_2Ph)_{18}]$ and distorted in $[Cu_{44}Se_{22}(P\textit{n}Bu\textit{t}Bu_2)_{12}]$, in **6** the rings can be described with the terminology used for cyclohexane as a boat conformation (for the outer Se_6 rings) or a twist conformation (for the middle Se_6 ring). If one disregards the corrugation of the three hexagons, one discovers two face-linked hexagonal antiprisms in **6**, as also found for the clusters with 44 copper atoms. These antiprisms are centred around Se 12 and Se 12′. Unlike the Se_{22} polyhedron in the Cu 44 clusters, the outer Se_6 rings are capped by two selenium atoms each (Se 1 and Se 2 or Se 1′ and Se 2′). 40 of the 48 metal atoms (Cu 1–Cu 20 and their symmetry equivalents) bind at the cluster surface to three atoms each of the selenium Se_{22} polyhedron, so that all the triangular faces are occupied by a copper atom or a Cu–P fragment. Eight further metal atoms (Cu 21–Cu 24 and their symmetry equivalents) are arranged below the $Cu_{40}Se_{22}$ surface and form an inner Cu_8Se_2 structural unit, which is different from the construction of the inner units in the compounds with 44 copper atoms. The Cu_8Se_2 fragment is formed from three edge-linked Cu_4 tetrahedra, of which the outer two are centred around Se 12 and Se 12′. The atoms concerned are highlighted in Figure 8. The twenty outer copper atoms without phosphine ligands (Cu 11–Cu 20 and their symmetry equivalents) show typical trigonal coordination to their neighbouring selenium atoms. They shift slightly under the Se_{22} deltahedral surface towards the centre of the cluster, resulting in different deviations from the trigonal planar environment. The sum of the angles around the copper atoms lies in the region 335.6–357.4°. Furthermore, six of the eight copper atoms in the middle of the cluster (Cu 21, Cu 23, Cu 24 and their symmetry equivalents) have distorted trigonal planar environments (the sum of the angles is 343.5–349.3°), surrounded by two outer and one of the two inner selenium atoms. Cu 22 and Cu 22′ each bind to a fourth selenium atom with bond lengths of 288.8 pm (Se 8 and Se 8′, respectively) so that they have almost tetrahedral coordination.

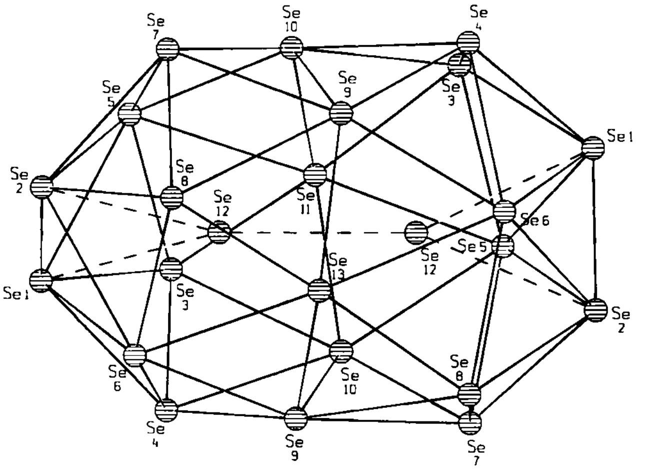

Fig. 9. Selenium substructure in **6** (rotated 90° with respect to the projection in Fig. 8). Nonbonding Se–Se distances: 370.2–466.1 pm; for clarity, only selected Se–Se connections are drawn inside the polyhedron.

For a Cu–Se cluster of this size the almost tetrahedral environment of the copper atoms bound to the phosphine ligands (Cu 1–Cu 10 and their symmetry equivalents) is typical. The atoms Cu 3, Cu 4, Cu 7, Cu 8 and their symmetry equivalents, however, have a bond length too great for a covalent bond to the fourth potential selenium neighbour (Se 6, Se 5, Se 9′, Se 10′ and their symmetry equivalents); this is reflected in their approximate trigonal planar environments (the sums of the angles for these copper atoms are 352.8°, 358.3°, 357.1° and 357.9°, respectively).

Besides having basically the same construction principles as the Cu_{44} clusters, the cluster skeleton of **6** again shows how the influence of the ligand shell coordinated to the cluster core acts on the structure of the cluster, or how comparable routes to cluster formation can show differences in detail if different phosphine ligands are available. One can also conclude that either the influence of the ligands on the structure extends to the structural unit in the centre of the cluster or that different inner-molecule fragments indicate different situations at the beginning of the cluster growth.

Conclusions

The compounds **1**–**6** reported here, together with the results of earlier investigations, can be used to identify certain basic principles governing the structures of sulfur- and selenium-bridged copper clusters. Thus, in sulfur-containing clusters with up to 28 copper atoms one always finds almost linear S-Cu-S or trigonal planar S_2-Cu-P arrangements (with the exception of the central unit of **1**). The selenium-containing copper clusters, however, only show this coordination pattern in $[Cu_{12}Se_6(PR_2R')_8]$ (R = Ph, R′ = Et or R = R′ = *n*Pr).[2, 3] Larger cluster structures tend increasingly towards trigonal Se_2-Cu-Se or tetrahedral Se_3-Cu-P arrangements. In the medium-sized clusters (for example, **5**) all these coordination geometries, from linear through to tetrahedral, can be found. Conversely, the chalcogen atoms in the copper sulfide clusters almost always act as μ_4 bridges between copper atoms in more-or-less regular four-membered rings (planar or butterfly-shaped). The exceptions to this are the μ_5-bridging atoms S 2, S 2′, S 3 and S 3′ in the central cluster fragment in **1** and the atoms S 2 (μ_5) and S 11 (μ_3) in **2**. On the other hand the coordination number of the selenium atoms in such clusters vary considerably. In the central fragments of **5**, $[Cu_{44}Se_{22}(PEt_2Ph)_8]$ or $[Cu_{44}Se_{22}(P\textit{t}Bu_2\textit{n}Bu)_{12}]$[1b] and in the larger copper selenide clusters with 70 or 146 metal atoms, the chalcogen atoms can also be seven- or eight-fold coordinating; this establishes a relationship to the Cu_2Se phases.[20] The first obvious deviation from these principles is found in **3** and can be put down to an unusual dimerisation. It is possibly also an indication that this larger copper sulfide cluster marks a transition to the structural characteristics of the binary-phase solid compound.[14, 16] This can also be assumed for the copper–selenium clusters; indeed these hints occur at smaller cluster sizes in the case of the Cu–Se system.

The structure "rules" are attributed to the different properties of sulfur and selenium as ligands. Thus it is probable that they are the main cause of the differences in the chemistry of the copper clusters, which are characterised by a tendency to form smaller clusters with sulfur as the bridging ligand, on the one hand, and the preferred formation of larger selenium-bridged clusters, on the other hand. Only when both systems obey the same principles, in the skeletons of the clusters with twelve copper atoms, can a relationship between the structures be seen. Additional effects support these tendencies, such as better coverage of the more compact Cu–S system through the phosphine ligands in comparison with the Cu–Se analogues, or kinetic effects, through which the removal of the ligand shell is made more difficult by stronger bonding in the Cu–S clusters in contrast to the Cu–Se clusters.[9]

The spatial requirements of the phosphine ligand used play an important role in the "choice" of cluster size in both copper cluster systems. For cluster cores of the same size, different structural details may occur when different numbers of phosphine ligands PR_2R' are required to shield the cluster core sufficiently. If a reduction in the number of ligands for the same cluster size is not sufficient to protect the cluster core, further reaction and cluster growth may occur, as one can accept from the formation of **1**. It is, however, not yet possible to predict the cluster size with new phosphine ligands in the sense of product design. The cluster structures tolerate (within certain limits) gaps in their phosphine shells, and the difference in Cu:P ratio of the different copper clusters is not big enough to permit a clear correlation of the two free parameters, spatial requirement and the number of phosphine ligands, with the cluster size.

Experimental Procedure

All steps in the following reaction procedures were carried out under nitrogen and with pure absolute solvents. Details of the X-ray crystal structure determinations are given in ref. [6].

Preparation of compound 1: To a suspension of CuOAc (0.37 g, 3 mmol) in diethylether (30 mL), P*i*Pr$_2$Me (0.74 mL, 4.5 mmol) was added, causing the CuOAc to dissolve. The reaction mixture was cooled to −78 °C, and $S(SiMe_3)_2$ (0.31 mL, 1.5 mmol) was added. After three days the solution was a red-orange colour. The solution was slowly warmed to −24 °C, whereby the colour deepened. After 7 d, red rhombohedral crystals of **1** were formed (yield 70%).

Preparation of compounds 2 and 3: To a suspension of CuOAc (0.37 g, 3 mmol) in diethylether (30 mL) P*t*Bu$_2$Me (1.2 mL, 6 mmol) was added, causing the CuOAc to dissolve. The reaction mixture was cooled to −78 °C, $S(SiMe_3)_2$ (0.31 mL, 1.5 mmol) was added, and the mixture was warmed to 2 °C, at which the solution turned a deep orange. After three days, red rhombohedral crystals of **2** and black hexagonal crystals of **3** were formed (yields 85% and 10%, respectively).

Preparation of compound 4: To a suspension of CuOAc (0.37 g, 3 mmol) in diethylether (30 mL) P*t*Bu$_2$Me (0.6 mL, 3 mmol) was added, causing the CuOAc to dissolve. The reaction mixture was cooled to −78 °C, $Se(SiMe_3)_2$ (0.37 mL, 1.5 mmol) was added, and the mixture was allowed to warm to −24 °C. In the space of three weeks the solution was gradually warmed to 2 °C, at which a deep brown colour was observed. After a further day at −24 °C, black rhombohedral crystals of **4** were formed (yield 80%).

Preparation of compound 5: To a suspension of CuOAc (0.37 g, 3 mmol) in diethylether (30 mL) P*t*Bu$_2$Me (0.84 mL, 4.2 mmol) was added, causing the CuOAc to dissolve. The reaction mixture was cooled to −78 °C, $Se(SiMe_3)_2$ (0.37 mL, 1.5 mmol) was added, and the mixture was warmed to 2 °C, whereby it turned a dark brown colour. After one day, black needles of **5** were formed (yield 80%).

Preparation of compound 6: To a suspension of CuOAc (0.37 g, 3 mmol) in diethylether (30 mL) PMe_2Ph (1.55 mL, 9 mmol) was added, causing the CuOAc to dissolve. The reaction mixture was cooled to −78 °C, and the phosphine complex formed a white precipitate. $Se(SiMe_3)_2$ (0.37 mL, 1.5 mmol) was added and the reaction mixture was slowly warmed to 2 °C over a period of four days, whereby the precipitate dissolved and the solution turned orange in colour. After seven weeks, besides a lot of red powder, a small quantity of black rectangular crystals of **6** was formed (yield 15%).

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[6] X-ray structural analysis of **1**–**6**: STOE IPDS with SIEMENS rotating anode, $Mo_{K\alpha}$, 200 K, data collection and refinement:
1: Cell parameters: $a = 1524.9(7)$, $b = 1578.2(11)$, $c = 1627.5(7)$ pm, $\alpha = 109.12(4)$, $\beta = 92.47(4)$, $\gamma = 111.87(5)°$, $V = 3373(3) \times 10^6$ pm^3; space group $P\bar{1}$ (no. 2), $Z = 1$, μ ($Mo_{K\alpha}$) = 3.97 mm^{-1}, $2\theta_{max} = 48°$; 12336 reflections, 8644 independent reflections, 7829 with $I > 2\sigma(I)$, 625 parameters (Se, Cu, P, C anisotropically refined); the positions of the H atoms have been calculated; $R = 0.056$.
2: Cell parameters **2**·0.5 Et$_2$O: $a = 2889.3(3)$, $b = 2086.7(7)$, $c = 2949.8(7)$ pm, $\beta = 98.83(2)°$, $V = 17574(7) \times 10^6$ pm^3; space group $P2_1$ (no. 4), $Z = 4$, μ ($Mo_{K\alpha}$) = 3.62 mm^{-1}, $2\theta_{max} = 40°$; 55371 reflections, 30209 independent reflections, 19484 with $I > 3\sigma(I)$, 1886 parameters (Cu, P, S anisotropically refined as far as possible and not disordered; C isotropically refined; five C atoms could not be localised); the positions of the H atoms have not been calculated; $R = 0.094$. Problems occurred during the refinement; it has not been possible, even from the data of several crystals from different reactions, to localise all the heavy atoms of the second enantiomer unambiguously. A transition to $P2_1/m$, $P2_1/a$, $P2_1/c$ or $P2_1/n$ is not possible. This might result from twinning. Owing to the structure problem, distances and angles are presented without decimal places.
3: Cell parameters **3**·3 Et$_2$O: $a = 1887.0(8)$, $b = 1918.9(8)$, $c = 2015.9(5)$ pm, $\alpha = 70.81(2)$, $\beta = 82.12(2)$, $\gamma = 67.53(3)°$, $V = 6370(4) \times 10^6$ pm^3; space group $P\bar{1}$ (no. 2), $Z = 1$, μ ($Mo_{K\alpha}$) = 4.41 mm^{-1}, $2\theta_{max} = 46°$; 40995 reflections, 16815 independent reflections, 11832 with $I > 2\sigma(I)$, 845 parameters (Se, Cu, P anisotropically refined; some of the C atoms of the phosphine ligands are disordered, therefore the coordinates were refined isotropically); the positions of the H atoms have not been calculated; $R = 0.083$.
4: Cell parameters **4**·1.5 Et$_2$O: $a = 2347.8(4)$, $b = 2473.4(9)$, $c = 3392.8(7)$ pm, $\alpha = 90.30(3)$, $\beta = 102.79(2)$, $\gamma = 94.50(3)°$, $V = 19149(6) \times 10^6$ pm^3; space group $P\bar{1}$ (no. 2), $Z = 2$, μ ($Mo_{K\alpha}$) = 7.23 mm^{-1}, $2\theta_{max} = 38°$; 57272 reflections, 29570 independent reflections, 19234 with $I > 3\sigma(I)$, 2009 parameters (Se, Cu, P anisotropically refined; the positions of the atoms Cu62, Cu65 and Cu68 show usual sizes of the oscillation ellipsoids if one assumes a $^2/_3$ occupancy, leading to $[Cu_{68}(Cu_{2/3})_3Se_{35}(PtBu_2Me)_{21}]$; some of the C atoms of the phosphine ligands are disordered, therefore the coordinates were refined isotropically); the positions of the H atoms have not been calculated; $R = 0.093$.
5: Cell parameters **5**·Et$_2$O: $a = 1760.8(4)$, $b = 1899.3(6)$, $c = 3126.3(14)$ pm, $\alpha = 96.19(3)$, $\beta = 93.95(3)$, $\gamma = 106.89(2)°$, $V = 9890(6) \times 10^6$ pm^3; space group $P\bar{1}$ (no. 2), $Z = 2$, μ ($Mo_{K\alpha}$) = 6.33 mm^{-1}, $2\theta_{max} = 41°$; 41758 reflections, 19006 independent reflections, 11048 with $I > 4\sigma(I)$, 1108 parameters (Se, Cu, P anisotropically refined; some of the C atoms of the phosphine ligands are disordered, therefore the coordinates were refined isotropically; one C atom could not be localised); the positions of the H atoms have been calculated; $R = 0.090$.
6: Cell parameters **6**·Et$_2$O: $a = 2749.7(10)$, $b = 3069.1(14)$, $c = 2777.6(9)$ pm, $\beta = 97.03(3)°$, $V = 23264(16) \times 10^6$ pm^3; space group $C2/c$ (no. 15), $Z = 4$, μ ($Mo_{K\alpha}$) = 8.21 mm^{-1}, $2\theta_{max} = 38°$; 21933 reflections, 9239 independent reflections, 8248 with $I > 2\sigma(I)$, 643 parameters (Se, Cu, P anisotropically refined; some of the C atoms of the phosphine ligands are disordered, therefore the coordinates were refined isotropically); the positions of the C atoms have been calculated; $R = 0.078$.
Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-404875, -404876, -404877, -404878, -404879 and -404880.

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[17] Reaction of CuOAc with $Se(SiMe_3)_2$ in the presence of $PMe\mathit{i}Pr_2$ (molar ratio 1:0.5:1.2) at −78 °C in diethylether leads to the formation of big black crystalline rhombuses. By means of X-ray crystallography ($R = 0.085$) a compound $[Cu_{70}Se_{35}(PMe\mathit{i}Pr_2)_{21}]$ can be identified. The skeleton of this cluster is exactly like the cluster framework of **4**. Therefore it is not presented or discussed in this report.
From a reaction analogous to the synthesis of **4**, but after keeping the reaction solution for 6 weeks at 2 °C, we obtained black rhombohedral crystals which were analysed by X-ray crystallography ($R = 0.080$). The structure $[Cu_{30}Se_{15}(P\mathit{t}Bu_2Me)_{12}]$ can be determined, the molecular structure of which is similar to $[Cu_{30}Se_{15}(P\mathit{i}Pr_3)_{12}]$ [1a]. We will not discuss further details of this known cluster core here. However, it should be mentioned that the formation of this compound, in contrast to the formation of **4** and **5**, was not surprising, since $P\mathit{t}Bu_2Me$ and $P\mathit{i}Pr_3$ have similar Tolman angles (161 and 160°) [7] and consist of the same numbers of atoms.

[18] F. Simon, *Dissertation*, Karlsruhe, **1995**.

[19] The third potential bond, Cu15–Se1, 311.4 pm, is too long for a covalent bond. Cu15 is, strictly speaking, twofold coordinated with an Se2-Cu15-Se5 angle of 138.4°. The sum of the angles around this metal atom, taking the Cu15–Se1, into account is 338.6 (and thus clearly deviates from planarity). Also the Cu18 trigonal environment is no longer planar. The sum of the Se-Cu-Se angles around copper is 338.6°.

[20] W. Borchert, *Z. Kristall.* **1945**, *106*, 5; R. M. Murray, R. D. Heyding, *Can. J. Chem.* **1975**, *53*, 878; N. Frangis, C. Monolikas, S. Amelinckx, *Phys. Stat. Solidi* **1991**, *A126*, 9.