

New copper selenium clusters with a sulfur functionalised ligand shell

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We introduce two new sulfur functionalised phosphines $P(C_6H_4SMe)_3$ **L1** and $PPh_2C_6H_4SMe$ **L2**. Using them as ligands, four new copper selenium clusters were synthesized. The compounds $[Cu_{15}Se_3(SePh)_9(P(C_6H_4SMe)_3)_6]$ **1**, $[Cu_{22}Se_6(SePh)_{10}(PPh_2C_6H_4SMe)_8]$ **2**, $[Cu_{20}Se(SePh)_{12}(OAc)_6(PPh_2C_6H_4SMe)_2]$ **3** and $[Cu_{38}Se_4(SePh)_{24}(OAc)_6(PPh_2C_6H_4SMe)_4]$ **4** were characterized by single crystal X-ray analysis and demonstrate the coordination of the phosphines through the phosphorus atoms. The thiomethyl groups of the ligands are not coordinated to any metal centre, but are located on the surface of the organic shell of the cluster molecules. This may provide an opportunity for further reactions between the functionalised clusters and metal atoms or surfaces. Furthermore the inner cluster cores show arrangements of copper and selenium atoms not yet found in these kinds of compounds.

Introduction

The self-assembling of chemically prepared building blocks onto pre-structured surfaces or between electrodes is one field of activity in nanotechnology. Candidates of interest are *e.g.* carbon nanotubes and fullerenes¹ or magnetic² or non-magnetic³ inorganic nanoparticles. For a surface consisting of a noble metal like gold, one can use sulfur functionalised molecules to create strongly bonded self-assembled monolayers (SAMs).⁴

In order to build electrical devices out of nanosized semiconductor materials, it is necessary to learn more about their conducting behaviour by measuring the electrical characteristics of single molecules or particles. The past decade has yielded a large variety of binary cluster compounds which are known to be semi-conductors as bulk materials.⁵ To place these well characterized clusters between gold electrodes, their organic shell should be modified in a way that allows defined bonding onto the gold metal surface. A strategy like this has recently been used to measure the conductance behaviour of single organic molecules and a platinum complex.⁶

In this article we first describe the synthesis of two sulfur functionalised phosphines, which are used to stabilise four new copper selenium clusters. All compounds were characterised by single crystal X-ray analysis.

Experimental

All reactions were carried out under an inert atmosphere of purified nitrogen using standard Schlenk techniques. Magnesium, Ph_2PCl , PCl_3 were purchased from Aldrich, *p*-bromthioanisol,⁷ copper acetate,⁸ $PhSeSiMe_3$,⁹ $Se(SiMe_3)_2$ ¹⁰ were synthesised as described in the literature. The solvents thf and dme were dried over sodium/benzophenone, *n*-hexane over $LiAlH_4$.

NMR spectra were acquired on a Bruker DPX300 spectrometer.

Syntheses

$P(C_6H_4SMe)_3$ **L1**, $PPh_2C_6H_4SMe$ **L2**. Into a Grignard solution (prepared from magnesium (3.1 g, 126 mmol) and *p*-bromthioanisol (25.3 g, 124 mmol) in 100 ml thf) PCl_3 (3.5 ml, 40 mmol) or Ph_2PCl (23.3 ml, 126 mmol) (dissolved in 80 ml

thf) is added dropwise at 0 °C. After four hours of refluxing, the reaction mixture is hydrolysed and the two phases are separated. The water phase is washed twice with 100 ml thf and then thf removed at low pressure. The remaining solid is recrystallised from ethanol/thf (10 : 1). The phosphines **L1** and **L2** are obtained as crystalline white solids. Yield **L1**: 10 g (50%) NMR: ¹H 1.95 ppm (s, 9H), 7.0–7.3 ppm (m, 12H); ³¹P{¹H} –7.70 ppm; **L2**: 30 g (78%) NMR: ¹H 2.49 ppm (s, 3H), 7.2–7.4 ppm (m, 14H); ³¹P{¹H} –5.24 ppm.

[Cu₁₅Se₃(SePh)₉(P(C₆H₄SMe)₃)₆] **1**. Copper(I) acetate (50 mg, 0.41 mmol) and **L1** (0.327 g, 0.816 mmol) are dissolved in 25 ml thf and stirred for 30 minutes at room temperature. After cooling to 0 °C $PhSeSiMe_3$ (0.19 ml, 0.41 mmol) is added to produce a yellow solution. The reaction is stored at 0 °C for one month. Red crystals of **1** are grown by layering *n*-hexane slowly onto the thf solution. Yield **1**·6thf: 25 mg (22%). Anal. calc. C, 45.12; H, 4.06; S, 10.63; Cu, 17.55. Found: C, 44.24; H, 3.75; S, 10.03; Cu, 16.83%.

[Cu₂₂Se₆(SePh)₁₀(PPh₂C₆H₄SMe)₈] **2**. Copper(I) acetate (0.42 g, 3.43 mmol) and **L2** (1.06 g, 3.43 mmol) are dissolved in 30 ml dme and stirred for one hour at room temperature. After cooling to –20 °C $PhSeSiMe_3$ (0.42 ml, 2.17 mmol) and 30 minutes later $Se(SiMe_3)_2$ (0.08 ml, 0.36 mmol) are added, giving a dark red solution. The reaction mixture is stirred for two days at room temperature. By layering with diethyl ether **2** is obtained as block-like dark red crystals. Yield **2**·2Et₂O: 0.45 g (48%). Anal. calc. C, 43.71; H, 3.40; S, 4.24; Cu, 23.12. Found: C, 43.23; H, 3.21; S, 4.46; Cu, 22.75%.

[Cu₂₀Se(SePh)₁₂(OAc)₆(PPh₂C₆H₄SMe)₂] **3**. Copper(I) acetate (1 g, 8.16 mmol) and **L2** (0.63 g, 2.04 mmol) are suspended in 100 ml dme and stirred for two hours at room temperature. First $PhSeSiMe_3$ (0.94 ml, 4.89 mmol) and after 30 minutes $Se(SiMe_3)_2$ (0.09 ml, 0.41 mmol) are added. Again after 15 minutes the bright yellow solution is separated from the remaining solid. Within a few hours, **3** crystallises from the filtrate as yellow plates. Yield **3**·6dme: 1.1 g (57%). Anal. calc. C, 37.04; H, 3.66; S, 1.35; Cu, 26.84. Found: C, 36.82; H, 3.59; S, 1.28; Cu, 26.61%.

[Cu₃₈Se₄(SePh)₂₄(OAc)₆(PPh₂C₆H₄SMe)₄] **4**. Copper(I) acetate (0.17 g, 1.37 mmol) and **L2** (0.42 g, 1.37 mmol) are

Table 1 Crystallographic data and structural refinement of **1–4**

| | | | | |
|---|---|--|---|---|
| Compound | 1 ·6thf | 2 ·2Et ₂ O | 3 ·6dme | 4 ·0.5dme |
| Empirical formula | C ₂₀₄ H ₂₁₉ Cu ₁₅ O ₆ P ₆ S ₁₈ Se ₁₂ | C ₂₂₀ H ₂₀₄ Cu ₂₂ O ₂ P ₈ S ₈ Se ₁₆ | C ₁₄₆ H ₁₇₂ Cu ₂₀ O ₂₄ P ₂ S ₂ Se ₁₃ | C ₂₃₄ H ₂₁₁ Cu ₃₈ O ₁₃ P ₄ S ₄ Se ₂₈ |
| Formula weight | 5430.7 | 6045.3 | 4734.2 | 8109.0 |
| Crystal system | Triclinic | Triclinic | Triclinic | Monoclinic |
| Space group | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ | <i>P</i> 2 ₁ / <i>c</i> |
| <i>a</i> /pm | 1858.8(4) | 1716.4(3) | 1510.5(3) | 1968.7(4) |
| <i>b</i> /pm | 1903.5(4) | 1987.1(4) | 1855.6(4) | 3710.0(7) |
| <i>c</i> /pm | 3245.4(7) | 2064.4(4) | 1880.0(4) | 3973.0(8) |
| α /° | 100.03(3) | 70.60(3) | 114.47(3) | 90 |
| β /° | 92.57(3) | 74.31(3) | 103.11(3) | 100.81(3) |
| γ /° | 109.88(3) | 66.62(3) | 101.21(3) | 90 |
| <i>V</i> /10 ⁶ pm ³ | 10566.2(3) | 6017(2) | 4416.6(15) | 28503(10) |
| <i>Z</i> | 2 | 1 | 1 | 4 |
| μ /mm ⁻¹ | 3.818 | 4.487 | 5.128 | 6.440 |
| Density/g cm ⁻³ | 1.707 | 1.668 | 1.780 | 1.890 |
| <i>F</i> (000) | 5408 | 2970 | 2324 | 15556 |
| Reflections collected | 32616 | 48180 | 35346 | 119011 |
| Independent reflections | 29174 [<i>R</i> _{int} = 0.0927] | 24480 [<i>R</i> _{int} = 0.0494] | 17951 [<i>R</i> _{int} = 0.0587] | 48942 [<i>R</i> _{int} = 0.0980] |
| <i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] | 0.0811 | 0.0647 | 0.0581 | 0.0519 |
| <i>wR</i> ₂ (all data) | 0.2260 | 0.2018 | 0.1698 | 0.1797 |
| Largest difference peak, hole/e Å ⁻³ | 1.275, -1.802 | 1.872, -1.353 | 1.568, -1.602 | 2.148, -1.140 |

dissolved in 50 ml dme. At -20 °C PhSeSiMe₃ (0.17 ml, 0.87 mmol) and Se(SiMe₃)₂ (0.03 ml, 0.14 mmol) are added. While cooling to room temperature the colour of the reaction mixture changes from yellow to red. After one week, the volume of the solution is reduced to one third and **4** is obtained as orange crystals by layering with diethyl ether. Yield **4**·0.5dme 52 mg (18%). The Cu, Se, S, C and H analyses fit with the given formulae. Anal. calc. C, 34.66; H, 2.62; S, 1.58; Cu, 29.78. Found: C, 34.02; H, 2.89; S, 1.81; Cu, 28.81%.

X-Ray structure analyses

The selection of single crystals suitable for X-ray diffraction was carried out by immersing the air sensitive samples in perfluoropolyether oil (Riedel de Haen) and mounting the oil coated crystal on a glass pin set in a goniometer head. The oil freezes upon cooling in a flow of nitrogen protecting the crystal from oxidation. The structural analyses of **1–4** were carried out at 200 K on a STOE IPDS II (Mo-K α , λ = 0.71073 Å) equipped with an imaging plate area detector. Structure solution and refinement against *F*² were carried out using SHELXS and SHELXL software.¹¹ Molecular diagrams were prepared using the DIAMOND 2.1d program.¹² The crystallographic data of **1–4** are summarised in Table 1.

All non-hydrogen atoms were refined anisotropically with the following exceptions. In **1** O(1)–O(6), C(21), C(49), C(63), C(70), C(77) C(112), C(136), C(140)–C(144), C(184)–C(204) were refined isotropically. In **2** O(1), O(2), C(68), C(94), C(107)–C(114) were refined isotropically; O(1), O(2), C(107)–C(114) were refined with an occupation of 0.5. In **3** O(7)–O(14), C(61)–C(77) were refined isotropically; O(9)–O(12), C(66)–C(73) were refined with an occupation of 0.7, O(13), O(14), C(74)–C(77) with an occupation of 0.6. In **4** carbon atoms were refined isotropically, except of those binding directly to selenium, phosphorus or oxygen (of acetat groups) atoms; O(13), O(14), C(233)–C(235) were refined with an occupation of 0.5; one carbon atom of the non-coordinating dme molecule could not be localized during the refinement. Hydrogen atoms in all compounds were included at geometrically calculated positions and refined using a riding model.

CCDC reference numbers 186526–186529.

See <http://www.rsc.org/suppdata/dt/b2/b205057a/> for crystallographic data in CIF or other electronic format.

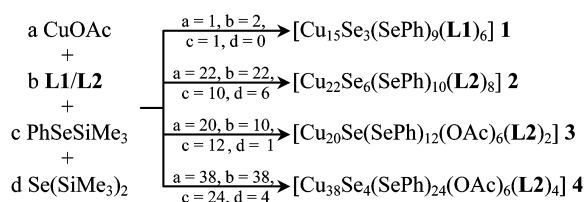
Results and discussion

To obtain cluster compounds with a sulfur containing ligand shell, the two *p*-thiomethyl substituted triphenyl phosphines, P(C₆H₄SMe)₃ **L1** and PPh₂C₆H₄SMe **L2**, were synthesised by Grignard reaction of PCl₃ or PPh₂Cl, respectively, with BrMg-

C₆H₄SMe. The phosphines can be isolated as air-stable white solids.

The reactions of copper(I) acetate with PhSeSiMe₃ or mixtures of PhSeSiMe₃ and Se(SiMe₃)₂ in the presence of one of the phosphines, **L1** or **L2**, lead to the formation of several new copper selenium clusters. These reactions show a high dependence on the stoichiometry used. In the synthesis of **1**, only PhSeSiMe₃ is used as the selenium source. Nevertheless, one finds Se²⁻ in the cluster core. Due to the long reaction time (*ca.* one month) for the formation of **1**, relatively stable Se–C bonds must be broken. There are numerous examples in the literature for similar syntheses leading to Se²⁻ and PhSe⁻ bridged clusters, using PhSeSiMe₃ as the selenium source.¹³ For the syntheses of **2–4**, PhSeSiMe₃ and Se(SiMe₃)₂ are added in the ratio for which the anions, Se²⁻ to PhSe⁻, are found in the resulting clusters.

In Scheme 1, the reactions leading to compounds **1–4** are summarized.



Scheme 1

Clusters **1–4** demonstrate phosphine coordination of the phosphorus atom only. The sulfur atoms remain free in the outer ligand shell unless otherwise stated. Fig. 1 shows space filling models of the compounds **1–4**, in which one can see the positions of the non-coordinating sulfur atoms. The shielding of the sulfur atoms by the surrounding organic groups is quite incomplete, which may give the clusters the possibility of further coordination chemistry. Such investigations will be one direction of our future work.

The clusters **1–4** also show new kinds of copper selenium cores not yet observed for cluster compounds consisting of copper atoms bridged by selenide (Se²⁻) and phenyl selenolato groups (PhSe⁻).

Compound **1** crystallises in the triclinic space group *P* $\bar{1}$ as ruby red crystals with two molecules in the unit cell and six thf molecules per formula unit. A picture of the inner core is given in Fig. 2.

The core consists of 12 selenium atoms and 15 copper atoms of which six copper atoms (Cu(1) – Cu(6)) are coordinated to

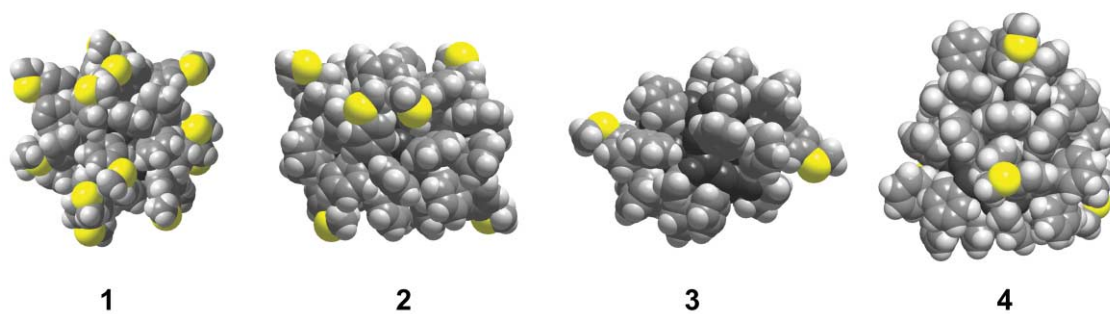


Fig. 1 Space filling models of 1–4 showing the positions of the sulfur atoms (yellow) in the ligand shell. Longest intramolecular S–S-distances: 1: 2.1 nm, 2: 2.4 nm, 3: 2.1 nm, 4: 2.5 nm.

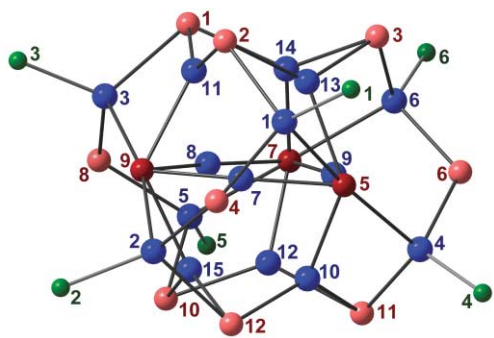


Fig. 2 Molecular structure of the core of $[\text{Cu}_{15}\text{Se}_3(\text{SePh})_9(\text{L1})_6]$ **1** (Cu, blue; Se^{2-} , dark red; PhSe^- , light red; P, green, carbon, sulfur, and hydrogen atoms are omitted). Bond lengths (pm) in **1**: Cu–Se 233.86(9) [Cu(7)–Se(5)] to 281.42(10) [Cu(2)–Se(9)], shortest Cu–Cu distance 261.9(5) [Cu(4)–Cu(10)], average Cu–P 224, average Se–C 194.

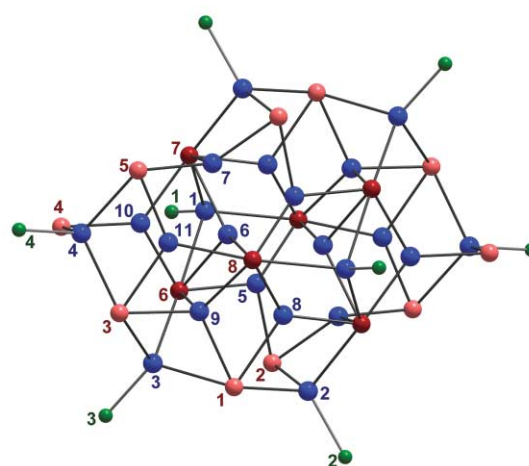


Fig. 3 Molecular structure of the core of $[\text{Cu}_{22}\text{Se}_6(\text{SePh})_{10}(\text{L2})_8]$ **2** (Cu, blue; Se^{2-} , dark red; PhSe^- , light red; P, green, carbon, sulfur, and hydrogen atoms are omitted). Bond lengths (pm) in **2**: Cu–Se 231.8(2) [Cu(10)–Se(4)] to 279.1(2) [Cu(3)–Se(3)], shortest Cu–Cu distance 245.3(2) [Cu(3)–Cu(9)], average Cu–P 223, average Se–C 193.

one phosphine each. The selenium atoms can be represented as having three layers of hexagonal ABA packing, with 3 atoms in A (Se(1)–Se(3)) and 6 atoms in B (Se(4)–Se(9)) and 3 atoms in the third layer (Se(10)–Se(12)). The copper atoms which are coordinated to the phosphine molecules act as μ_3 bridges to the selenium atom framework. The other nine copper atoms are located inside the selenium polyhedron with three atoms above (Cu(11), Cu(13), Cu(14)) and three atoms below the B plane (Cu(10), Cu(12), Cu(15)). These six atoms have trigonal planar coordination and they lie on faces of the selenium polyhedron. The last three copper atoms (Cu(7)–Cu(9)) lie in the B plane and are each linearly coordinated to two Se^{2-} ions. The angles are as follows; Se(5)–Cu(9)–Se(7) 161.05(3)°, Se(7)–Cu(8)–Se(9) 167.55(4)°, Se(5)–Cu(7)–Se(9) 170.57(5)°.

Compound **2** crystallises in the triclinic space group $P\bar{1}$ with one molecule per unit cell and two additional non-coordinating ether molecules per formula unit. In Fig. 3 one can see the cluster core of **2** which has a disc shape with an inversion centre in the middle of the molecule not occupied by any atom.

The eight copper atoms Cu(1, 2, 3, 4 and symmetry equivalent), having one coordinating phosphine, each acts by μ_3 -bridging in regard to three selenium atoms of the heavy atom framework. Cu(9) and Cu(9') are connected to four selenium atoms and have skewed tetrahedron coordination. All remaining copper atoms are trigonal coordinated by three selenium atoms having angles at the copper atoms between 99.76(2)° (Se(6)–Cu(6)–Se(7)) and 128.65(2)° (Se(4)–Cu(10)–Se(7)). The selenide ions Se(6), Se(7) and Se(8) and their symmetry equivalent are each surrounded by six copper atoms with irregular coordination polyhedras. The selenium atoms of the PhSe^- groups are bridging either four (Se(1), Se(3) and symmetry equivalent), three (Se(2), Se(5) and symmetry equivalent) or only two (Se(4), Se(4')) copper atoms. Similar variability in the coordination behaviour of PhSe^- was found in other copper selenium cluster compounds some years ago.¹³

Compound **3** crystallises as bright yellow plates in the triclinic space group $P\bar{1}$ with one formula unit per elemental cell

and with six additional dme molecules per formula unit. Fig. 4 shows the cluster core of **3**.

The twelve selenium atoms of the SePh^- groups form a highly skewed cube octahedron with the 13th selenium atom (Se(7), not bonded to a phenyl ring) occupying the crystallographic inversion centre in the middle of the molecule. Two opposite triangular faces of the selenium polyhedron (formed by Se(1), Se(2), Se(3) and Se(1'), Se(2'), Se(3')) are capped by two copper atoms Cu(1) and Cu(1'), which are both coordinated to one phosphine each. Above all six square faces of the cube octahedron there are Cu_2OAc -units, whereas every copper atom is coordinated by two selenium atoms and one oxygen atom. In these units the Cu–Cu distances between 275.5(6) pm and 282.2(7) pm are found to be significantly longer than the intermetal distance in copper(i) acetate (255.6 pm).¹⁴ The remaining six copper atoms are located inside the selenium polyhedron, each coordinated by two selenium atoms from SePh^- groups and the central selenium atom in a trigonal planar manner. This leads to a coordination number of six for the inner selenium atom Se(7), with the copper atoms forming a highly screwed octahedron. Again as in **2** the SePh^- groups are either bound to three or four copper atoms; coordination to only two metal atoms is not found in **3**.

Because of their position at opposite ends of the cluster molecule, the distance of the two sulfur atoms is 2.1 nm (Fig. 1).

Compound **4** crystallises in the monoclinic space group $P2_1/c$ with four cluster molecules and two additional dme molecules per elemental cell. The structure of the cluster core is shown in Fig. 5.

Cluster **4** is structurally related to **3**. Starting with Cu(1), which has one coordinating phosphine, the same sequence of atoms is found as in **3**: Cu(1) is located above a triangle formed by Se(1), Se(2) and Se(3). These selenium atoms are again part

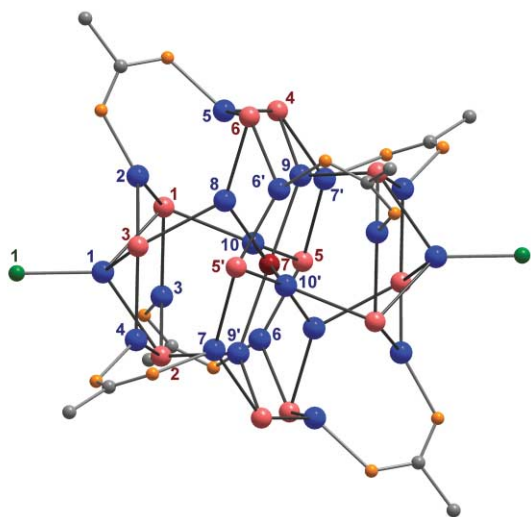


Fig. 4 Molecular structure of the core of $[\text{Cu}_{20}\text{Se}(\text{SePh})_{12}(\text{OAc})_6(\text{L2})_2]$ **3** (Cu, blue; Se^{2-} , dark red; PhSe^- , light red; P, green; O, orange; C, grey, phenyl rings are omitted). Bond lengths (pm) in **3**: Cu–Se 235.6(1) [Cu(8)–Se(6)] to 265.5(1) [Cu(1)–Se(1)], shortest Cu–Cu distance 257.6(1) [Cu(7)–Cu(10')], Cu(1)–P(1) 224.4(2), average Cu–O 196, average Se–C 195.

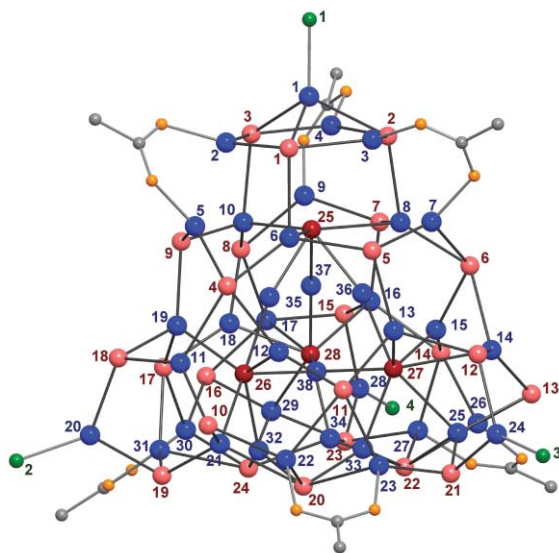


Fig. 5 Molecular structure of the core of $[\text{Cu}_{38}\text{Se}_4(\text{SePh})_{24}(\text{OAc})_6(\text{L2})_4]$ **4** (Cu, blue; Se^{2-} , dark red; PhSe^- , light red; P, green; O, orange; C, grey, phenyl rings are omitted). Bond lengths (pm) in **4**: Cu–Se 230.0(2) [Cu(35)–Se(26)] to 293.2(2) [Cu(17)–Se(28)], shortest Cu–Cu distance 252.8(2) [Cu(21)–Cu(22)], average Cu–P 221, average Cu–O 198, average Se–C 193.

of three highly skewed squares (Se(1, 2, 5, 6); Se(2, 3, 7, 8); Se(1, 3, 4, 9)), each of which are capped by Cu_2OAc -units. Inside this part of the molecule there is a triangle of copper atoms (Cu(6, 8, 10)) with Se(25) at the centre. The latter is also equivalent to the central selenium atom Se(7) in **3**. As in **3**, the previously described structure according to the central symmetry is repeated and enclosed forming a ball-like molecule, whereas **4**, forms a more expanded cluster. Se(25) is part of an inner slightly stretched tetrahedron formed by the four selenium atoms not connected to phenyl rings ((Se(25, 26, 27, 28)). These selenium atoms are all connected to six copper atoms each. Three edges of the tetrahedron are μ -bridged by Cu(35), Cu(36) and Cu(37) with Se–Cu–Se angles of about 163.4° . The base of the tetrahedron is μ_3 -bridged by Cu(38). The motif of the tetrahedron is repeated in the shape of the whole cluster core of **4**. The four copper atoms connected to the phosphine ligands form a skewed tetrahedron (Cu(1, 20, 24, 28)) with an edge length between 1.14 and 1.19 nm. Over each edge one of the six Cu_2OAc -units is found with Cu–Cu distances between 262.8(5)

pm (Cu(30)–Cu(31)) and 288.8(3) pm (Cu(3)–Cu(7)) again longer than in copper(i) acetate. In contrast to Cu(1) which acts as μ_3 -bridging (average Cu(1)–Se distance 261.3 pm) the other three phosphine coordinated copper atoms (Cu(20, 24, 28)) are only connected to two additional selenium atoms each resulting in a trigonal planar coordination sphere with Cu–Se distances of about 237.5 pm. As for the copper atoms also for the PhSe^- groups different coordination numbers are found starting with three metal atoms (Se (5, 7, 9–13, 15, 16, 18, 19, 21)) going on with μ_3 -bridging (Se (1–4, 6, 8, 14, 17, 23)) up to selenium atoms acting as μ_5 -bridges (Se(20, 22, 24)). The whole cluster core has a pseudo C_3 symmetry with the axes passing through atoms P(1), Cu(1), Se(25), and Cu(38).

Conclusion

This paper presents the synthesis of two new sulfur functionalised phosphines which were thereupon used to stabilize four new copper selenium cluster compounds. The formation of these compounds is strongly influenced by the reaction conditions, mainly small changes in the used starting stoichiometry of the educts leads to noticeably different products. Although lots of copper selenium species have been reported in the literature so far the structures of the presented clusters have not been observed before. As shown, the sulfur atoms of the phosphine ligands are all at the outer part of the ligand shell which should provide the possibility of linking these compounds with metals such as gold. First attempts have been made to deposit the cluster $[\text{Cu}_{20}\text{Se}(\text{SePh})_{12}(\text{OAc})_6(\text{PPh}_2\text{C}_6\text{H}_4\text{SMe})_2]$ **3**, having only two sulfur atoms at opposite sides of the molecule, and will be published later.

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