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FULL PAPER

Syntheses and structures of new copper(I) selenide clusters $[Cu_{32}Se_{16}(PPh_3)_{12}]$, $[Cu_{52}Se_{26}(PPh_3)_{16}]$ and $[Cu_{72}Se_{36}(PPh_3)_{20}]$ †

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The reaction of $Se(SiMe_3)_2$ with copper(I) acetate in the presence of PPh_3 yielded the new clusters $[Cu_{32}Se_{16}(PPh_3)_{12}]$ **2**, $[Cu_{52}Se_{26}(PPh_3)_{16}]$ **3** and $[Cu_{72}Se_{36}(PPh_3)_{20}]$ **4** depending on the conditions. The molecular structures of **2**, **3** and **4** have been characterised by X-ray crystallography and compared with the known cluster $[Cu_{146}Se_{73}(PPh_3)_{30}]$ **1** obtained from the same reaction under different conditions.

Introduction

The synthesis of large metal-containing clusters is of considerable interest because these compounds are good model systems for investigating the chemical and physical properties of solid state materials. This is particularly important for nanoparticulate binary metal chacogenides which show quantum effects such as size-dependent band gaps.[1]

We have been successful in preparing a large number of copper selenide clusters using the reaction of CuX (X = Cl or OAc) with $Se(SiMe_3)_2$ and PR_3 (R = organic group) outlined in eqn. (1). Some of the compounds we have structurally characterised are as follows:

$$2CuX + yPR_3 + Se(SiMe_3)_2 \xrightarrow[-2SiMe_3X]{THF\ or\ Et_2O} [Cu_2Se(PR_3)_y]_n \quad (1)$$

$[Cu_{12}Se_6(P^nPr_3)_8]$, $[Cu_{26}Se_{13}(PEt_2Ph)_{14}]$, $[Cu_{30}Se_{15}(P^iPr_3)_{12}]$, $[Cu_{36}Se_{18}(P^tBu_3)_{12}]$, $[Cu_{44}Se_{22}(PEt_2Ph)_{18}]$ and $[Cu_{70}Se_{35}(PEt_3)_{22}]$. A noteworthy example is the structure of $[Cu_{146}Se_{73}(PPh_3)_{30}]$ **1** one of the largest known structurally characterised clusters.[2b]

From the range of products listed above it can clearly be seen that the phosphine has a profound role in determining the size of the copper selenide cluster. This may be attributed both to steric effects due to the characteristic Tolman cone angle and to kinetic factors arising from stabilisation of copper/phosphine/acetate clusters. We now wish to report that other factors such as ligand concentration, temperature and solvent also influence cluster formation. For this study we have conducted a detailed investigation of the $CuOAc/Se(SiMe_3)_2/PPh_3$ system from which we have previously isolated **1**.

Experimental

Standard Schlenk techniques were employed throughout the syntheses using a double-manifold vacuum line with high purity dry nitrogen. The solvents diethyl ether, tetrahydrofuran and diglyme were dried over sodium–benzophenone and distilled under nitrogen. CuOAc[3] and $Se(SiMe_3)_2$[4] were prepared according to standard literature procedures.

Syntheses

$[Cu_{32}Se_{16}(PPh_3)_{12}]$ 2. PPh_3 (1.73 g, 6.6 mmol) was added to a suspension of copper(I) acetate (0.27 g, 2.2 mmol) in THF (40 mL). A clear colourless solution was formed. Upon the addition of $Se(SiMe_3)_2$ (0.25 mL, 1.1 mmol) the solution gradually turned yellow, and subsequently dark brown. After 1 d, 20 mL of diethyl ether were added to a solution cooled to 4 °C. After 3 d at this temperature, dark yellow crystalline plates of **2** were formed. Yield: 54% (Found: C, 39.02; H, 2.90. $C_{216}H_{180}Cu_{32}P_{12}Se_{16}$ requires C, 40.26; H, 2.80%).

$[Cu_{52}Se_{26}(PPh_3)_{16}]$ 3. PPh_3 (1.73 g, 6.6 mmol) was added to a suspension of copper(I) acetate (0.27 g, 2.2 mmol) in THF (40 mL). A clear colourless solution was formed. Upon addition of $Se(SiMe_3)_2$ (0.25 mL, 1.1 mmol), the solution gradually turned yellow, and subsequently dark brown. After 1 d, 20 mL of diethyl ether were added and the solution was kept at room temperature. After 2 d, dark yellow crystalline plates of **2** were formed in low yield, and after 2 additional days, black crystals of **3** began to grow as the major product of the reaction. Yield: 50% (Found: C, 37.1; H, 2.80. $C_{288}H_{240}Cu_{52}P_{16}Se_{26}$ requires C, 36.2; H, 2.5%).

$[Cu_{72}Se_{32}(PPh_3)_{20}]$ 4. PPh_3 (1.28 g, 4.9 mmol) was added to a suspension of copper(I) acetate (0.20 g, 1.63 mmol) in diglyme (30 mL). On addition of $Se(SiMe_3)_2$ (0.25 mL, 1.1 mmol) the solution gradually turned clear, changing colour from yellow to dark brown. After 3 d, black crystals of **4** were formed. Yield: 51% (Found: C, 35.49; H, 3.33. $C_{360}H_{300}Cu_{72}P_{20}Se_{36}$ requires C, 34.15; H, 2.37%). Two diglyme molecules were localised and refined in the X-ray structure analysis, but there is evidence for the existence of other highly disordered solvent molecules which may be responsible for the high carbon and hydrogen content found in the elemental analysis.

X-Ray structural analyses

Single crystal X-ray structural analyses of compounds **2**–**4** were performed using a Stoe-IPDS diffractometer (Mo-Kα radiation) equipped with an image plate area detector and a rotating anode. Structure solution and refinement were carried out using SHELXS 86[5] and SHELXL 93[6] software using direct methods techniques. The weighting scheme applied was of the form $w = 1/[\sigma^2(F^2) + (aP)^2 + bP]$ [a,b = refined variables, $P = \frac{1}{3}(F_o^2,0) + \frac{2}{3}F_c^2$]. All calculations were performed on a Silicon Graphics INDY computer. Molecular diagrams were prepared using the SCHAKAL 92 program.[7]

Compound 2. $C_{216}H_{180}Cu_{32}P_{12}Se_{16}\cdot 4C_4H_8O$, $M = 6730.6$, triclinic, space group $P\bar{1}$, $a = 19.319(4)$, $b = 21.531(4)$, $c = 33.931(7)$ Å, $\alpha = 79.58(3)$, $\beta = 80.11(3)$, $\gamma = 74.37(3)°$, $U =$

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† Dedicated to Professor Brian F. G. Johnson on the occasion of his 60th birthday.

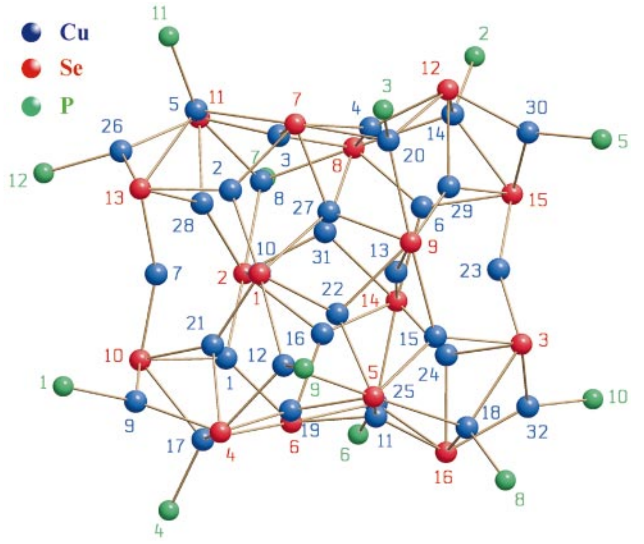

Fig. 1 Molecular structure of $[Cu_{32}Se_{16}(PPh_3)_{12}]$ **2**. Cu^{1+}: blue; Se^{2-}: red; P: green. Cu–Cu contacts and carbon atoms are omitted for clarity. Cu, Se and P atoms are labelled with blue, red and green numbers respectively.

$13254(5)$ Å^3, $T = 200$ K, $Z = 2$, $D_c = 1.675$ g cm^{-3}, $F(000) = 6496$, μ(Mo-Kα) = 4.817 mm^{-1}, $2\theta_{max} = 55°$, 31788 independent reflections measured ($R_{int} = 0.0859$) and 22364 $I > 2\sigma(I)$. The structure was solved by direct methods and refined on F^2. All Se, Cu and P atoms were refined anisotropically, all C atoms isotropically and positions for H atoms were calculated except those of THF to yield $R = 0.0823$, $wR = 0.2275$, $S = 0.991$.

Compound 3. $C_{288}H_{240}Cu_{52}P_{16}Se_{26}\cdot 2.5C_4H_8O$, $M = 9721.53$, triclinic, space group $P\bar{1}$, $a = 22.336(5)$, $b = 23.203(5)$, $c = 37.894(8)$ Å, $\alpha = 91.00(3)$, $\beta = 106.95(3)$, $\gamma = 99.06(3)°$, $U = 18510(6)$ Å^3, $T = 200$ K, $Z = 2$, $D_c = 1.741$ g cm^{-3}, $F(000) = 9350$, μ(Mo-Kα) = 5.580 mm^{-1}, $2\theta_{max} = 51.8°$, 57286 independent reflections measured ($R_{int} = 0.0892$) and 39806 $I > 2\sigma(I)$. The structure was solved by direct methods and refined on F^2. All Se, Cu and P atoms were refined anisotropically, all C atoms isotropically and positions for H atoms were calculated except those of THF to yield $R = 0.0823$, $wR = 0.2373$, $S = 1.023$.

Compound 4. $C_{360}H_{300}Cu_{72}P_{20}Se_{36}\cdot 2C_6H_{16}O_3$, $M = 12931.18$, triclinic, space group $P\bar{1}$, $a = 25.632(5)$, $b = 33.806(7)$, $c = 34.904(7)$ Å, $\alpha = 72.69(2)$, $\beta = 87.16(2)$, $\gamma = 72.64(2)°$, $U = 27534(1)$ Å^3, $T = 190$ K, $Z = 2$, $D_c = 1.560$ g cm^{-3}, $F(000) = 12440$, μ(Mo-Kα) = 5.185 mm^{-1}, $2\theta_{max} = 45°$, 66463 independent reflections measured ($R_{int} = 0.073$) and 45921 $I > 2\sigma(I)$. The structure was solved by direct methods and refined on F^2. All Se, Cu and P atoms were refined anisotropically, all C atoms isotropically to yield $R = 0.0829$, $wR = 0.2271$, $S = 0.939$.

CCDC reference number 186/1098.

See http://www.rsc.org/suppdata/dt/1998/2969/ for crystallographic files in .cif format.

Results and discussion

We have previously shown that copper(I) acetate reacts with 5 equivalents of PPh_3 and 0.5 equivalent of $Se(SiMe_3)_2$ in THF at room temperature to yield $[Cu_{146}Se_{73}(PPh_3)_{30}]$ **1**,[2b] after a number of days. We now find that similar reactions with only 3 equivalents of PPh_3 produce dark coloured solutions. Addition of diethyl ether and cooling to 4 °C leads to the crystallisation of $[Cu_{32}Se_{16}(PPh_3)_{12}]$ **2.** Keeping these mixed solvent solutions at room temperature leads to the formation of $[Cu_{52}Se_{26}(PPh_3)_{16}]$ **3**. $[Cu_{72}Se_{36}(PPh_3)_{20}]$ **4** crystallises from the same reactions if diglyme is used instead of THF as a solvent.

Compound **2** crystallises as dark yellow plates in the triclinic space group $P\bar{1}$. Fig. 1 shows the structure with the exception of the carbon atoms. The selenium atoms Se1–Se16 form a flattened polyhedron compromising of non-bonded Se_3 triangles (Se–Se 3.984 to 4.645 Å). There are four distinct copper environments. Twenty-four of the copper atoms cap the selenium triangles, of these sixteen (Cu1, Cu2, Cu3, Cu4, Cu6, Cu11, Cu15, Cu16, Cu19, Cu21, Cu22, Cu24, Cu27, Cu28, Cu29, Cu31) are bonded only to selenium producing a distorted trigonal coordination geometry. These copper atoms lie below the plane formed by the selenium atoms to which they are coordinated such that they are within the selenium polygon. A further eight (Cu5, Cu8, Cu12, Cu14, Cu17, Cu18, Cu20, Cu25) are also bonded to a phosphine ligand (P2, P3, P4, P6, P7, P8, P9, P11) giving a tetrahedral environment with the copper atoms situated on the exterior of the selenium faces. Four copper atoms (Cu7, Cu10, Cu13, Cu23) are coordinated in a quasi-linear fashion to two selenium atoms (Se3–Cu23–Se15 156.13, Se13–Cu7–Se10 159.28, Se1–Cu10–Se2 170.2, Se9–Cu13–Se14 170.52°). The four remaining copper atoms Cu9, Cu26, Cu30 and Cu32 are bonded in a distorted trigonal environment to two selenium atoms and one phosphorus atom from PPh_3. The Cu–Se distances range from 2.295 to 2.930 Å. For the selenium atoms, the coordination numbers five (Se3, Se4, Se10, Se11, Se12, Se13) and six (Se1, Se2, Se5, Se6, Se7, Se8, Se9, Se14) are found.

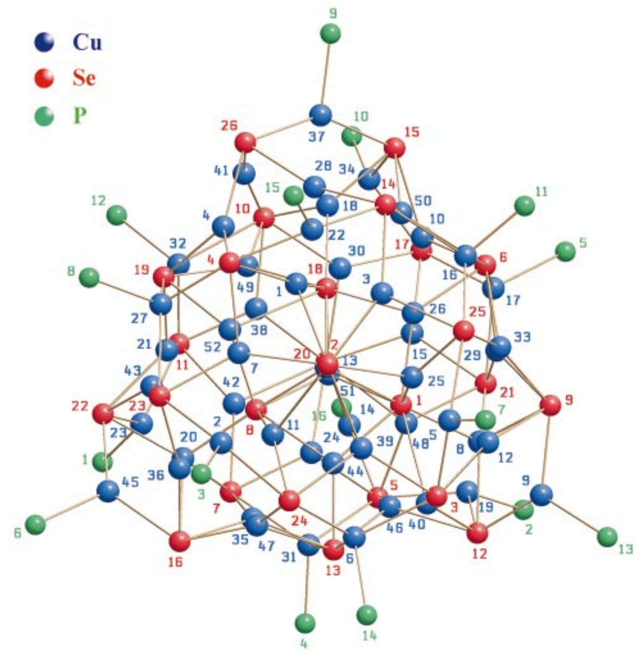

Fig. 2 Molecular structure of $[Cu_{52}Se_{26}(PPh_3)_{16}]$ **3**. Cu^{1+}: blue; Se^{2-}: red; P: green. Cu–Cu contacts and carbon atoms are omitted for clarity. Cu, Se and P atoms are labelled with blue, red and green numbers respectively.

Compound **3** forms large black or smaller brown crystals which crystallise in the triclinic space group $P\bar{1}$ (Fig. 2). By analogy with **2**, the framework in **3** can also be seen to be made up from edge-sharing Se_3 triangles. The selenium atoms form an approximately spherical polyhedron with three additional atoms (Se1, Se8, Se18) located within the cavity. The Se–Se distances range from 3.803 to 4.707 Å and are essentially non-bonding. Thirty-six of the fifty-two copper atoms are bonded only to the selenium atoms (Cu–Se 2.19–2.91 Å) and are located within the lattice, exhibiting either a linear (Cu12, Cu28, Cu36, Cu41, Cu43), distorted trigonal (Cu1, Cu3, Cu4, Cu7, Cu10, Cu11, Cu15, Cu18, Cu21, Cu24, Cu25, Cu26, Cu29, Cu30, Cu33, Cu35, Cu38, Cu39, Cu40, Cu42, Cu44, Cu46, Cu47, Cu48, Cu49, Cu50, Cu52) or a distorted tetrahedral structure (Cu8, Cu13, Cu20, Cu51). Coordination numbers for the selenium atoms vary from four (Se26) to five (Se3, Se4, Se7, Se9,

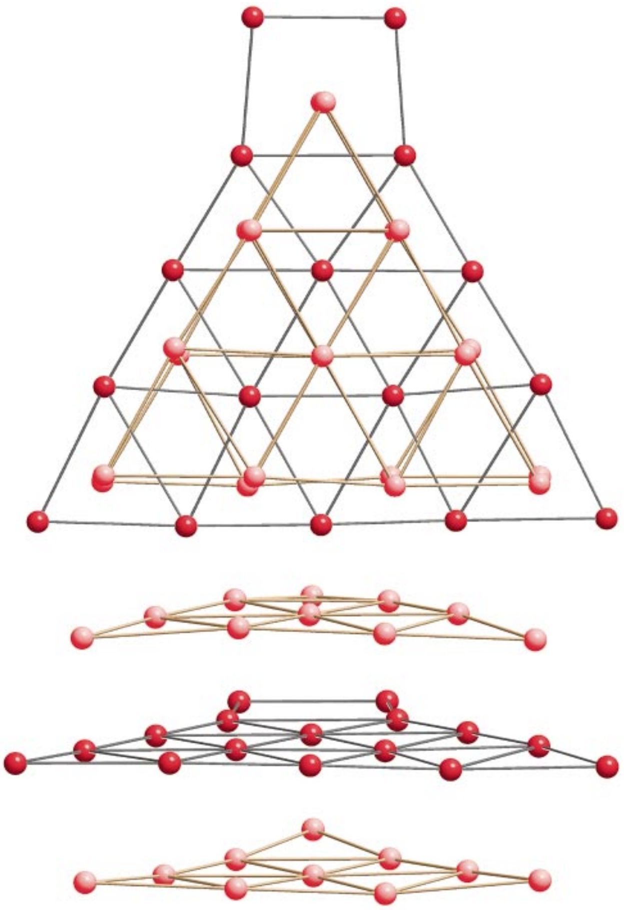

Fig. 3 View perpendicular (above) and parallel (below) to the hexagonal ABA layering of the selenium atoms in **4**. Non-bonding Se–Se contacts are shown only in the layers. Distance between the layers *ca.* 3.61 Å.

Se11, Se12, Se14, Se15, Se16, Se17, Se21, Se22, Se23, Se24, Se25), six (Se5, Se8, Se10, Se13, Se19), seven (Se1, Se2, Se6, Se18) and eight (Se20). Those copper atoms which are bonded to the sixteen phosphine ligands are either coordinated in a nearly trigonal planar fashion, for those that are bonded to one phosphorus atom and two selenium atoms (Cu2, Cu5, Cu9, Cu14, Cu22, Cu23, Cu34, Cu37, Cu45), or in a distorted tetrahedral way for those that are coordinated by three selenium atoms and one phosphorus atom (Cu6, Cu16, Cu17, Cu19, Cu27, Cu31, Cu32). As in structure **2** copper atoms which are coordinated by three selenium atoms only are shifted to the interior of the cluster cage. Copper atoms additionally bonded to one phosphorus atom are located on the cluster surface. In contrast to the wide range of Cu–Se distances, the Cu–P bonds all lie within a narrow range (2.215–2.284 Å).

Compound **4** forms black crystals in the triclinic space group $P\bar{1}$. The thirty-six selenium atoms build up a nearly trigonal prismatic polyhedron with trigonal selenium faces (Fig. 3). In contrast to **2** and **3**, **4** possesses a symmetrical layer-type structure with three layers each containing ten, sixteen and ten selenium atoms. The packing of the layers is nearly hexagonal, of the type ABA. Only Se30 and Se32 do not follow this trend. The non-bonding Se–Se distances range from 3.81 to 4.71 Å, and the distance between the layers is approximately 3.6 Å. The holes in the selenium lattice are filled with seventy-two copper atoms (Fig. 4). As in **2** and **3**, there are three coordination environments for the copper atoms bonded only to selenium. Cu4 is linearly coordinated, forty copper atoms (Cu1, Cu2, Cu3, Cu7, Cu8, Cu9, Cu11, Cu12, Cu13, Cu14, Cu15, Cu17, Cu19, Cu20, Cu21, Cu22, Cu23, Cu24, Cu25, Cu27, Cu29, Cu30, Cu34, Cu38, Cu41, Cu42, Cu43, Cu46, Cu47, Cu49, Cu50, Cu54, Cu55, Cu58, Cu59, Cu61, Cu63, Cu65, Cu71, Cu72) exhibit a distorted trigonal environment and eleven copper atoms (Cu6, Cu16, Cu33, Cu36, Cu37, Cu39, Cu44, Cu51, Cu52, Cu57, Cu70) are coordinated in a distorted tetrahedral fashion (Cu–Se 2.354–2.921 Å). For those copper atoms bonded to selenium and phosphorus atoms, six copper atoms (Cu5, Cu18, Cu31, Cu32, Cu35, Cu69) exhibit the coordination number three (2 Se, 1 P atom), and fourteen copper atoms (Cu10, Cu26, Cu28, Cu40, Cu45, Cu48, Cu53, Cu56, Cu60, Cu62, Cu64, Cu66, Cu67, Cu68) are coordinated in a distorted tetrahedral geometry by three selenium atoms and one phosphorus atom of the PPh_3 ligands (Cu–P 2.211–2.242 Å). The copper atoms coordinated to phosphine ligands are shifted to the surface of the cluster in contrast to pure trigonal coordinated ones, as was also observed for **2** and **3**. If we assume a maximum Cu–Se distance for a bonding interaction of 2.92 Å we find a wide spread of selenium coordination numbers ranging from four to ten: four (Se11, Se4), five (Se1, Se5, Se7, Se10, Se22, Se26, Se27, Se31, Se36), six (Se2, Se3, Se4, Se6, Se8, Se9, Se24, Se28, Se29, Se30, Se32, Se33, Se34, Se35), seven (Se13, Se14, Se15, Se17, Se18, Se21, Se23, Se25), eight (Se16), nine (Se19) and ten (Se19). We have also previously observed a large range of selenium coordination numbers in other copper selenide clusters. The larger the cluster size the higher the average coordination numbers for selenium atoms leading to more dense copper selenium packing. The $[Cu_{70}Se_{35}(PEt_3)_{21}]$[2a] structure is related to **4** simply by removal of a Cu_2Se unit (Cu18, Cu35, Se30) which caps one of the corners of the CuSe polyhedron. Furthermore the two selenium atoms (Se30 and Se32) in this fragment are not part of the close-packed selenium array. This structural motif, in which a rectangular selenium frame is grafted onto one edge of the triangle is also present in **1** therefore **4** is in fact a fragment of the larger cluster.

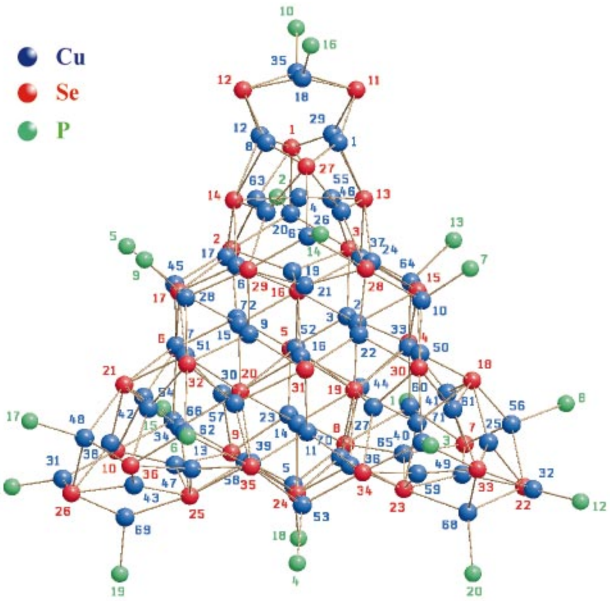

Fig. 4 Molecular structure of $[Cu_{72}Se_{36}(PPh_3)_{20}]$ **4**. Cu^{1+}: blue; Se^{2-}: red; P: green. Cu–Cu contacts and carbon atoms are omitted for clarity. Cu, Se and P atoms are labelled with blue, red and green numbers respectively.

Conclusion

In summary the Se cages for **2** and **3** differ significantly from the symmetrical ones found in **4** and **1**. This suggests that **2** and **3** cannot be intermediate structures in the formation of the layered clusters **4** and **1**. Whilst there is a clear similarity between the structures of **4** and **1** no relationship between **2** and **3** is evident. Further, one can find analogies between all of the clusters in the coordination modes of the copper atoms. In common with other copper selenide clusters, the copper atoms prefer a distorted trigonal planar coordination of selenium atoms. At the cluster surfaces the copper atoms coordinate the selenium atoms in a slightly distorted triangular fashion, with some shifts towards the interior of the selenium polyhedron. Copper atoms that are linked to a phosphine ligand adopt the predicted tetrahedral geometry and are located well outside the Se lattice. The preference of trigonal coordination can also be seen from the fact that copper atoms in β-Cu_2Se leave their ideal tetrahedral sites in the transition from a cubic high temperature phase to the lower symmetry α-Cu_2Se phase to take up a more trigonal coordination.[8] Although the final structure determination of the low temperature α-Cu_2Se phase is still a point of discussion the best refinement of the data is achieved by assuming a cubic lattice of selenium atoms with the copper atoms occupying the tetrahedral and trigonal holes in a ratio 0.37 to 0.63.[9] In contrast, **4** and **1** possess a hexagonal lattice of selenium atoms, a structure type known for the low temperature phase of Cu_2S.[10] Therefore it is possible that these cluster molecules display a new structure type of an as yet unknown Cu_2Se polymorph. Hence cluster formation of **2** and **3** can be seen to be more like an unordered spontaneous aggregation process whereas the crystallisation of **4** and **1** is comparable to the formation of an ordered solid state structure.

The results presented herein show the complex dependence of these reactions on a range of parameters. This knowledge will assist us in the design of rational syntheses for even larger clusters.

Acknowledgements

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