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Novel Cu–Se clusters with Se–layer structures: $[Cu_{32}Se_7(Se\textit{n}Bu)_{18}(P\textit{i}Pr_3)_6]$, $[Cu_{50}Se_{20}(Se\textit{t}Bu)_{10}(P\textit{i}Pr_3)_{10}]$, $[Cu_{73}Se_{35}(SePh)_3(P\textit{i}Pr_3)_{21}]$, $[Cu_{140}Se_{70}(PEt_3)_{34}]$ and $[Cu_{140}Se_{70}(PEt_3)_{36}]$

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The clusters $[Cu_{32}Se_7(Se\textit{n}Bu)_{18}(P\textit{i}Pr_3)_6]$, $[Cu_{50}Se_{20}(Se\textit{t}Bu)_{10}(P\textit{i}Pr_3)_{10}]$, $[Cu_{73}Se_{35}(SePh)_3(P\textit{i}Pr_3)_{21}]$, $[Cu_{140}Se_{70}(PEt_3)_{34}]$ and $[Cu_{140}Se_{70}(PEt_3)_{36}]$ were prepared from the reactions of CuCl, $RSeSiMe_3$ and $Se(SiMe_3)_2$ (R = Ph, *n*Bu or *t*Bu) in the presence of phosphine ligands and their molecular structures were determined. The Se–Bu bond was cleaved more easily than the Se–Ph bond under the reaction conditions studied.

Introduction

The synthesis of transition-metal-containing complexes of selenium and tellurium has received[1] less attention than that of the lighter chalcogen elements oxygen and sulfur. Over the past five years there has been increasing[2] interest in this area, partly due to the discovery of selenium in some enzymes,[3] and the realisation that Se- and Te-containing compounds may have important applications, such as precursors for low-bandgap semiconductors, nanomaterials and window materials in solar cells.[4] We are interested[2a] in metal chalcogenide clusters both as potential nanoparticles and as intermediate structures between small molecules and bulk materials.

We have previously developed[5–12] a general route to copper–selenide–phosphine clusters:

$$CuX + nPR_3 + \xrightarrow[X\,=\,Cl\ or\ OAc]{\frac{1}{2}Se(SiMe_3)_2} [Cu_{2x-y}Se_x(PR_3)_m] + Me_3SiX \quad (1)$$

The driving force of the reaction is the elimination of Me_3SiX. The formation of the cluster complexes depends very much on the nature of the phosphine. The reaction conditions, the solvents used for the synthesis and the ratio of Cu : PR_3 also play a significant role in governing the structures of the products isolated, which crystallize under these conditions.

A large number of complexes have been prepared with this method that cover a range of nuclearities. In order of increasing size, these include low nuclearity clusters such as $[Cu_{12}Se_6(PR_3)_8]$ ($R_3 = Et_2Ph$[5] or *n*Pr_3 or Cy_3[6]), ranging to $[Cu_{20}Se_{13}(PEt_3)_{12}]$,[7] $[Cu_{26}Se_{13}(PCy_3)_{10}]$,[6] $[Cu_{26}Se_{13}(PEt_2Ph)_{14}]$,[6] $[Cu_{29}Se_{15}(P\textit{i}Pr_3)_{12}]$,[8] $[Cu_{30}Se_{15}(PR_3)_{12}]$ (R_3 = *i*Pr_3[8] or *t*Bu_2Me[9]), $[Cu_{31}Se_{15}(SeSiMe_3)(P\textit{t}Bu_2Me)_{12}]$,[10] $[Cu_{32}Se_{16}(PPh_3)_{12}]$,[11] $[Cu_{36}Se_{18}(P\textit{t}Bu_3)_{12}]$,[8] $[Cu_{44}Se_{22}(PEt_2Ph)_{18}]$,[12] $[Cu_{44}Se_{22}(P\textit{n}Bu\textit{t}Bu_2)_{12}]$,[12] $[Cu_{48}Se_{24}(PMe_2Ph)_{20}]$,[10] $[Cu_{52}Se_{26}(PPh_3)_{16}]$[11] and $[Cu_{59}Se_{30}(PCy_3)_{15}]$,[6] and finally to very large macromolecules such as $[Cu_{70}Se_{35}(PEt_3)_{22}]$,[7] $[Cu_{70}Se_{35}(P\textit{i}Pr_2Me)_{21}]$,[10] $[Cu_{70}Se_{35}(P\textit{t}Bu_2Me)_{21}]$,[10] $[Cu_{72}Se_{36}(PPh_3)_{20}]$[11] and $[Cu_{146}Se_{73}(PPh_3)_{30}]$.[13] The last of these is one of the largest clusters characterised so far. We observe a systematic colour change from red (Cu_{12}) through brown (Cu_{36}) and dark brown (Cu_{70}) to black (Cu_{146}). Preliminary studies also show a relationship between size and conductivity.[14]

The above synthetic method has recently been modified[15,16] to create a route to mixed seleno–selenato and telluro–tellurato clusters by employing $RESiMe_3$ or mixtures of $E(SiMe_3)_2$ and $RESiMe_3$ (E = Se, Te). In this paper we describe the synthesis and characterisation of five novel clusters synthesized by the reaction of CuX (X = Cl or SCN) with mixtures of $RSeSiMe_3$ (R = Ph or *n*Bu or *t*Bu) and $Se(SiMe_3)_2$ in the presence of alkyl phosphines PR_3 (R_3 = Et or *i*Pr).

Experimental

Standard Schlenk-line techniques were employed throughout on a double-manifold vacuum line with high purity dry nitrogen. Solvents for reactions were distilled under nitrogen from appropriate drying agents prior to use. The compounds CuCl and CuSCN were purchased and CuCl was purified prior to use. The phosphines[17] and $PhSeSiMe_3$[18] were prepared according to standard literature procedures.

Syntheses

$RSeSiMe_3$ (1a R = *n*Bu and 1b *t*Bu). In an adaptation of the preparation of *n*$BuTeSiMe_3$,[16a] grey selenium (63.0 g, 0.80 mol) was suspended in THF (700 mL) in a three-necked round-bottom flask (2 L) equipped with a water cooled condenser and dropping funnel. *n*BuLi (500 mL, 1.6 M in hexane) or *t*BuLi (500 mL, 1.6 M in pentane) was added dropwise to the rapidly stirred suspension at 0 °C, during which time the black Se gradually dissolved with the formation of a dark brown solution. After the addition was complete, stirring was continued for one hour to give a pale yellow solution. After cooling the solution to 0 °C freshly distilled $ClSiMe_3$ (100 mL, 0.80 mol) was added dropwise with vigorous stirring, during which time a white precipitate (LiCl) was formed. After complete addition, the mixture was stirred for one day at room temperature. The solution was filtered to remove LiCl and the solvent removed by distillation. Fractional vacuum distillation afforded **1a**; 80 g, 48%, bp 75–80 °C at 20 mmHg or **1b**; 94 g, 56%; bp 77–80 °C at 20 mmHg. Both yellow liquids contained about 15% each of $Se(SiMe_3)_2$ and Bu_2Se according to ^1H NMR. Attempts to remove these impurities by further fractional distillation were unsuccessful. ^1H NMR(C_6D_6): **1a** δ 2.38 (t, α-CH_2), 1.55 (m, β-CH_2), 1.29 (m, γ-CH_2), 0.80 (t, CH_3), 0.30 [s, $Si(CH_3)_3$]; **1b** δ 1.44 (s, $3CH_3$), 0.37 [s, $Si(CH_3)_3$].

$[Cu_{32}Se_7(Se\textit{n}Bu)_{18}(P\textit{i}Pr_3)_6]$ 2. *n*$BuSeSiMe_3$ (0.70 mL, 3.0 mmol) was added to a suspension of CuCl (0.25 g, 2.5 mmol) and P*i*Pr_3 (0.25 mL, 1.33 mmol) in Et_2O (25 mL) at 0 °C with vigorous stirring. After two hours a clear dark red solution was

Table 1 Crystallographic data

Compound	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{126}H_{288}Cu_{32}P_6Se_{25}$	$C_{69}H_{160}Cu_{25}OP_5Se_{15}$	$C_{207}H_{441}Cu_{73}P_{21}Se_{38}$	$C_{204}H_{510}Cu_{140}P_{34}Se_{70}$	$C_{226}H_{540}Cu_{140}P_{36}Se_{70}$
M	5996.66	3933.72	11234.99	18439.90	18796.30
$F(000)$	5824	7568	21688	34736	177632
Crystallized from	Diethyl ether	Diethyl ether	Diethyl ether	Diethyl ether	Pentane
Crystal size/mm	0.5 × 0.4 × 0.4	0.4 × 0.4 × 0.3	0.4 × 0.3 × 0.3	0.4 × 0.1 × 0.1	0.3 × 0.2 × 0.2
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2(1)/*n*	*C*2/*m*	*P*2(1)/*c*	*C*2/*c*	*P*2(1)/*m*
Z	2	4	4	4	2
a/Å	16.628(3)	3399.8(7)	38.460(8)	34.116(7)	31.650(6)
b/Å	29.937(6)	2016.0(4)	25.720(5)	48.433(10)	22.550(5)
c/Å	19.847(4)	1992.3(4)	36.310(7)	30.942(6)	37.840(8)
β/°	101.79(3)	119.44(3)	99.61(3)	110.47(3)	97.92(3)
V/Å^3	9671(3)	11892(4)	35414(12)	47898(17)	26749(9)
ρ (calcd.)/g cm^{-3}	2.059	2.197	2.107	2.557	2.334
T/K	203(2)	203(2)	203(2)	203(2)	203(2)
μ(Mo-Kα)/mm^{-1}	8.222	9.052	8.309	11.520	10.276
θ range/°	2.25 to 25.99	2.33 to 25.96	1.58 to 22.62	1.83 to 24.20	1.81 to 24.08
Index range	$-16 \leqslant h \leqslant 19$	$-38 \leqslant h \leqslant 39$	$-41 \leqslant h \leqslant 33$	$-25 \leqslant h \leqslant 39$	$-35 \leqslant h \leqslant 32$
	$-36 \leqslant k \leqslant 19$	$-24 \leqslant k \leqslant 24$	$-27 \leqslant k \leqslant 27$	$-53 \leqslant k \leqslant 55$	$-25 \leqslant k \leqslant 25$
	$-16 \leqslant l \leqslant 24$	$-18 \leqslant l \leqslant 24$	$-32 \leqslant l \leqslant 38$	$-34 \leqslant l \leqslant 18$	$-43 \leqslant l \leqslant 41$
Reflections collected	11978	28803	99014	48996	110121
Independent reflections	11283 ($R_{int} = 0.12$)	11157 ($R_{int} = 0.068$)	43379 ($R_{int} = 0.17$)	29499 ($R_{int} = 0.13$)	42703 ($R_{int} = 0.16$)
Reflectopms observed	8792 ($I > 2\sigma(I)$)	8990 ($I > 22\sigma(I)$)	12845 ($I > 2\sigma(I)$)	8293 ($I > 2\sigma(I)$)	12326 ($I > 2\sigma(I)$)
Parameters refined	871	430	1870	1303	1371
Reflections refined	11278	11156	40709	19169	42694
R indices (obs. refl.)	$R_1 = 0.074$,	$R_1 = 0.068$,	$R_1 = 0.095$,	$R_1 = 0.11$,	$R_1 = 0.086$,
	$wR_2 = 0.20$	$wR_2 = 0.19$	$wR_2 = 0.22$	$wR_2 = 0.27$	$wR_2 = 0.22$
Goodness of fit	1.055	1.034	1.166	1.903	1.440

formed, which was allowed to stand at room temperature. Orange crystals grew within three days. Yield 80%.

[$Cu_{52}Se_{20}(Se\mathit{t}Bu)_{10}(P\mathit{i}Pr_3)_{10}$] 3. *t*BuSeSiMe$_3$ (0.62 mL, 2.6 mmol) was added to a solution of CuCl (0.25 g, 2.5 mmol) and P*i*Pr$_3$ (0.47 mL, 2.5 mmol) in Et$_2$O (25 mL) forming a dark brown solution. The mixture was allowed to stand at room temperature. After one week a brown precipitate was filtered off. A small amount of brown crystals grew within two weeks from the filtrate. Yield 10%.

[$Cu_{73}Se_{35}(SePh)_3(P\mathit{i}Pr_3)_{21}$] 4. PhSeSiMe$_3$ (0.32 mL, 1.25 mmol) was added to a solution of CuCl (0.25 g, 2.5 mmol) and P*i*Pr$_3$ (0.94 mL, 5.00 mmol) in Et$_2$O (25 mL) to give a clear yellow solution. This was cooled to −70 °C and Se(SiMe$_3$)$_2$ (0.16 mL, 0.64 mmol) was added. The mixture was then allowed to warm slowly to room temperature, during which time the colour changed from yellow, through brown to black. On standing at room temperature black crystals grew within several weeks. Yield 40%.

[$Cu_{140}Se_{70}(PEt_3)_{34}$] 5. *Method A.* The procedure is the same as for **4**, except PEt$_3$ (0.50 mL, 3.2 mmol) was used. Black needle crystals were formed in one week together with a brown precipitate. Yield 30%.

*Method B. n*BuSeSiMe$_3$ (0.70 mL, 3.0 mmol) was added to a solution of CuSCN (0.32 g, 2.6 mmol) and PEt$_3$ (0.50 mL, 3.2 mmol) in Et$_2$O (50 mL) to give a brown solution. This was allowed to stand at room temperature. Black crystals grew within one week. Yield 90%.

[$Cu_{140}Se_{70}(PEt_3)_{36}$] 6. *n*BuSeSiMe$_3$ (0.62 mL, 2.6 mmol) was added to a solution of CuCl (0.25 g, 2.5 mmol) and PEt$_3$ (0.82 mL, 5.2 mmol) in pentane (25 mL) forming a yellow solution. The solution was allowed to stand at room temperature. A small amount of black crystals grew within several weeks. Yield 10%.

Crystal structure analyses

Single crystal X-ray structural analysis of compounds **2** to **6** were performed using a Stoe-IPDS diffractometer (Mo-Kα-radiation) equipped with an imaging plate area detector and a rotating anode. Structure solution and refinement were carried out with SHELXS-86[19] and SHELXL-93[20] software by direct methods techniques. The weighting scheme applied was of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ [a,b = refined variables, $P = 1/3$ max. $(F_o^2,0) + 2/3\ F_c^2$]. All calculations were performed on a Silicon Graphics INDY computer. Molecular diagrams were prepared using the SCHAKAL 97 program.[21] Table 1 lists the summary crystallographic data for **2** to **6**.

CCDC reference number 186/1348.

See http://www.rsc.org/suppdata/dt/1999/1067/ for crystallographic files in .cif format.

Compound 2. Data were collected at 203 K in the θ range 2.25 to 25.99° with a detector distance of 70 mm and 15 min radiation time per exposure; the φ went step by step per exposure from 0° to 80° with the scan-step $\Delta\varphi$ value of 0.5°; 11978 reflections were measured of which 11283 were independent and 8792 were considered observed with $I > 2\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. All Se, Cu P and C atoms were refined anisotropically. Hydrogen atoms (except for one disordered *n*Bu group) were placed in calculated positions. $R = 0.074$ with a goodness of fit value of 1.055. Parameters refined = 871.

Compound 3. Data were collected at 203 K in the θ range 2.33 to 25.96° with a detector distance of 70 mm with 12 min radiation time per exposure; the φ went step by step per exposure from 0° to 72.5° with a scan-step $\Delta\varphi$ value of 0.5°; 28803 reflections were measured of which 11157 were independent and 8990 were considered observed with $I > 2\sigma\ (I)$. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. All Se, Cu and P atoms were refined anisotropically, C atoms were refined isotropically. $R = 0.068$ with a goodness of fit value of 1.034. Parameters refined = 430. The asymmetric unit contains one quarter of a molecule. Within this unit six *i*Pr groups of two phosphines and one *t*Bu group are disordered. The disorder of the *t*Bu group has been modelled using two sites related by rotation about the Se–C bond. A similar procedure involving rotation about the Cu–P bond has been used to describe the disorder of the phosphine groups. This is a good model for P(1), but is less satisfactory for P(3).

Compound 4. Data were collected at 203 K in the θ range 1.58 to 22.62° with a detector distance of 90 mm with 20 min radiation time per exposure; the φ went step by step per exposure from 0° to 105° with a scan-step $\Delta\varphi$ value of 0.3°; 99014 reflections were measured of which 43379 were independent and 12845 were considered observed with $I > 2\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. All Se, Cu and P atoms were refined anisotropically, C atoms were refined isotropically. $R = 0.095$ with a goodness of fit value of 1.166. Parameters refined = 1870. Three Cu atoms in the middle of the three face-shared octahedral holes formed by Se atoms (see structure description below) were considered to have a total population of 2 and each has a population of 0.67. Because the *i*Pr groups are quite disordered, many of the C atoms have large thermal parameters and some of them could not be found.

Compound 5. Data were collected at 203 K in the θ range 1.83 to 24.20° with a detector distance of 80 mm and 30 min radiation time per exposure; the φ went step by step per exposure from 0° to 73° with a scan-step $\Delta\varphi$ value of 0.3°; 48996 reflections were measured of which 29499 were independent and 8293 were considered observed with $I > 2\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. All Se, Cu and P atoms were refined anisotropically, C atoms were refined isotropically. $R = 0.11$ with a goodness of fit value of 1.903. Parameters refined = 1303. Many Et groups of PEt_3 and the solvent molecules could not be found.

Compound 6. Data were collected at 203 K in the θ range 1.81 to 24.08° with a detector distance of 80 mm and 20 min radiation time per exposure; the φ went step by step per exposure from 0° to 110° with a scan-step $\Delta\varphi$ value of 0.3°; 110121 reflections were measured of which 42703 were independent and 12326 were considered observed with $I > 2\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. All Se, Cu and P atoms were refined anisotropically, C atoms were refined isotropically. $R = 0.086$ with a goodness of fit value of 1.440. Parameters refined = 1371. Many Et groups of PEt_3 and the solvent molecules could not be found.

Results and discussion

Synthesis

Reactions among CuCl, $PhSeSiMe_3$ and bidentate phosphine to produce some copper–seleno–phenylselenato clusters have been reported.[14] However, the reactions of equimolar quantities of CuCl, PR_3 ($R_3 = Et_3$, *i*Pr_3, *t*Bu_3) and $PhSeSiMe_3$ in pentane produce only yellow solutions that remain unchanged over a period of a few months. This colour suggests that only low-nuclearity copper–selenium molecules are present. Evidence for this was the isolation of $[Cu_2(SePh)_2(PtBu_3)_2]$,[22] which contains doubly-bridged phenylselenolate ligands and two terminally-coordinated P*t*Bu_3. As there was clearly little hope of isolating large clusters from these solutions, this line of investigation was not continued.

We have observed that high nuclearity Cu–Se clusters often contain structural features similar to those found in copper selenide minerals. In order to facilitate the formation of similar motifs we have investigated reactions using a mixture of selenide sources. A combination of $PhSeSiMe_3$ and $Se(SiMe_3)_2$ in a ratio of 2:1 has been used with a quantity of CuX chosen so that equal amounts of X and $SiMe_3$ moieties were present. In order to avoid the formation of products containing only Se^{2-}, *i.e.* without RSe^-, we first allowed the phosphine–copper salt mixture to react with $PhSeSiMe_3$ before adding $Se(SiMe_3)_2$. Despite this most of the products we have characterised contain few or no $PhSe^-$ fragments. The reaction performed in the presence of P*t*Bu_3 yielded the cluster $[Cu_{36}Se_{18}(PtBu_3)_{12}]$,[8] which was previously isolated from reactions employing $Se(SiMe_3)_2$. When PEt_3 was used we obtained $[Cu_{140}Se_{70}(PEt_3)_{34}]$ **5**. Although this compound contains no $PhSe^-$ groups, it is different from the material obtained from similar reactions in which $Se(SiMe_3)_2$ was the only selenium source, $[Cu_{70}Se_{35}(PEt_3)_{22}]$.[7] From the reactions in which P*i*Pr_3 is present we obtain $[Cu_{73}Se_{35}(SePh)_3(PiPr_3)_{21}]$ **4**, a markedly larger cluster than that obtained from only $Se(SiMe_3)_2$, $[Cu_{30}Se_{15}(PiPr_3)_{12}]$. The presence of a relatively small number of $PhSe^-$ groups and the difference of these products from those obtained when only $Se(SiMe_3)_2$ is employed suggests that Se–C bond scission may accompany cluster growth.

For a more comprehensive insight into this, we have synthesised the silylated reagents *n*$BuSeSiMe_3$ and *t*$BuSeSiMe_3$ from which we have been unable to remove the impurities $Se(SiMe_3)_2$ and $SeBu_2$. We have used these reagents in a study of the CuX–PR_3–$BuSeSiMe_3$ system.

The reaction of CuCl, PEt_3 and *n*$BuSeSiMe_3$ in diethyl ether produces the known compound $[Cu_{70}Se_{35}(PEt_3)_{22}]$. Replacement of CuCl by CuSCN leads to the new cluster **5** in high yield. It is possible that $[Cu_{70}Se_{35}(PEt_3)_{22}]$ is an intermediate in the formation of **5** as it can be recognised as a fragment of the larger structure (see below). When pentane is used as the solvent for the reaction of CuCl, PEt_3 and *n*$BuSeSiMe_3$, cluster $[Cu_{140}Se_{70}(PEt_3)_{36}]$ **6** is produced, which differs from **5** only in the inclusion of two extra phosphine ligands. The smaller $[Cu_{70}Se_{35}(PEt_3)_{22}]$ cluster may again be an intermediate. The similar reactions with the use of *t*$BuSeSiMe_3$ lead invariably to $[Cu_{70}Se_{35}(PEt_3)_{22}]$. These reactions illustrate the profound influence of counter ion and solvent. The Se–Bu bond was cleaved in the reactions.

For reactions in the presence of P*i*Pr_3 we observe a product dependance on the Cu:PR_3 ratio in addition to the dependence on the $RSeSiMe_3$ reagent used. From the reactions of *n*$BuSeSiMe_3$ the cluster $[Cu_{32}Se_7(SenBu)_{18}(PiPr_3)_6]$ **2** is obtained when half a molar equivalent of phosphine is used. For larger amounts of phosphine no crystalline product could be isolated. Reactions with *t*$BuSeSiMe_3$ additionally show different behaviour depending on which copper salt is used. For CuCl we obtain cluster $[Cu_{50}Se_{20}(SetBu)_{10}(PiPr_3)_{10}]$ **3** when one equivalent of phosphine is used, and cluster $[Cu_{70}Se_{35}(PiPr_3)_{21}]$ when 1.5 to 4 equivalents of phosphine are used. With CuSCN as the starting material we isolate $[Cu_{70}Se_{35}(PiPr_3)_{21}]$ when 1 to 3 equivalents of phosphine are employed. When this is increased to 4 equivalents of P*i*Pr_3 the known cluster $[Cu_{30}Se_{15}(PiPr_3)_{12}]$ can be isolated.

Structure description

Compound $[Cu_{32}Se_7(SenBu)_{18}(PiPr_3)_6]$ **2** crystallizes from a diethyl ether solution in the monoclinic space group $P2(1)/n$ and contains an inversion center at Se(10). Fig. 1 shows the molecular structure which consists of Cu^I, Se^{2-}, Se*n*Bu^- and P*i*Pr_3 ligands. The heavy atoms Cu and Se form the $Cu_{32}Se_{25}$ framework of the molecule.

The six phosphine ligands are terminally linked to copper atoms [Cu(4), Cu(8), Cu(14) and their symmetry equivalents], each of which is doubly bridged by two Se*n*Bu^- ligands to give a trigonal-planar coordination. The corresponding Cu–Se bond lengths of Cu(4), Cu(8) and Cu(14) are similar to the other Cu–Se*n*Bu bonds, within a narrow range from 2.439(2) to 2.500(2) Å.

24 Cu atoms have trigonal-planar coordination geometry, of which six copper atoms [Cu(10), Cu(13) and Cu(15) and their symmetry equivalents] are each coordinated by three Se*n*Bu^-

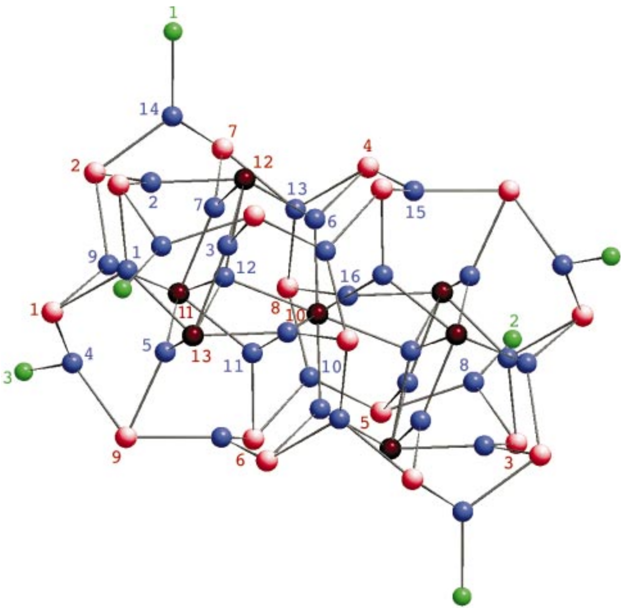

Fig. 1 Molecular structure of $Cu_{32}Se_7(SenBu)_{18}(PiPr_3)_6$ **2** (Cu: purple; Se^{2-}: dark red; Se–*n*Bu^-: light red; P green); Cu–Cu contacts and carbon atoms are omitted for clarity. Selected bond lengths (Å) in **2**: Cu(4)–Se(1) 2.439(2), Cu(8)–Se(5) 2.500(2); Cu(9)–Se(1) 2.388(2), Cu(1)–Se(1) 2.489(2), Cu(1)–Se(13) 2.381(2); Cu(12)–Se(10) 2.600(2), Cu(12)–Se(11) 2.600(2), Cu(12)–Se(12) 2.622(2), Cu(12)–Se(13) 2.605(2), average Se–C 1.98(2); average Cu–P 2.240(4).

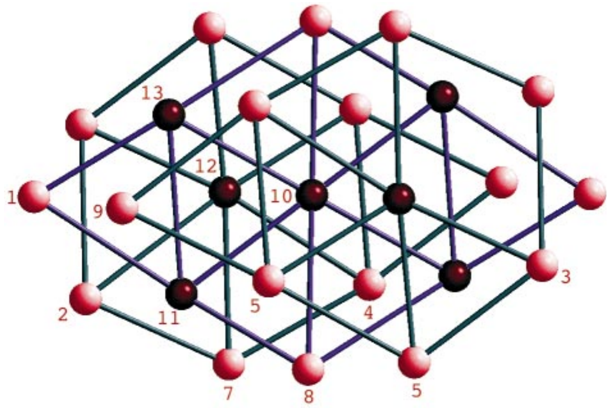

Fig. 2 The Se packing of **2** (Se^{2-}: dark red; Se–*n*Bu^-: light red); non-bonding Se···Se contacts are shown within 5.5 Å and the lines between Se atoms in the middle Se layer are drawn in violet (Se···Se contacts between layers are omitted for clarity).

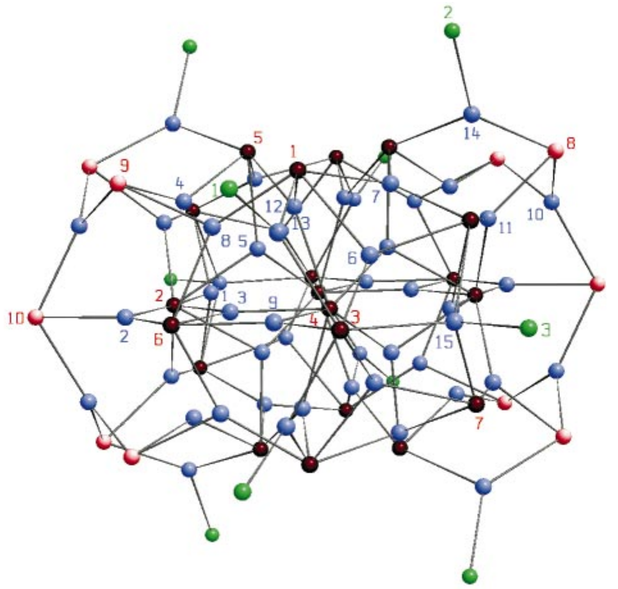

Fig. 3 Molecular structure of $Cu_{50}Se_{20}(SetBu)_{10}(PiPr_3)_{10}$ **3** (Cu: purple; Se^{2-}: dark red; Se–*t*Bu^-: light red; P: green); Cu–Cu contacts and carbon atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) in **3**: Cu(4)–Se(5) 2.347(2), Cu(4)–Se(9) 2.370(2); Cu(10)–Se(8) 2.394(2); Cu(8)–Se(1) 2.386(2), Cu(2)–Se(2) 2.517(2), Cu(2)–Se(6) 2.353(2), Cu(2)–Se(10) 2.379(2); Cu(6)–Se(1) 2.573(2), Cu(1)–Se(2) 2.875(2), Cu(9)–Se(4) 2.718(2), Cu(12)–Se(4) 2.595(1), Cu(15)–Se(7) 2.715(2); average Se–C 2.03(2); average Cu–P 2.230(4); Se(5)–Cu(4)–Se(9) 136.67(7).

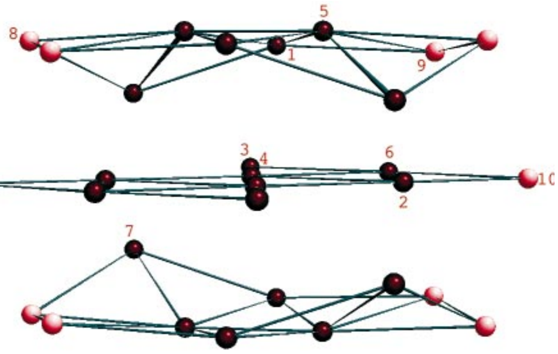

Fig. 4 The Se packing of **3** (Se^{2-}: dark red; Se–*t*Bu^-: light red); non-bonding Se···Se contacts are shown within 5.5 Å and Se···Se contacts between layers are omitted for clarity.

ligands, six Cu atoms [Cu(1), Cu(2) and Cu(9) and symmetry equivalents] by two Se*n*Bu^- and one Se^{2-} ligand and the other twelve by one Se*n*Bu^- and two Se^{2-} ligands. The related Cu–Se bond lengths for Se^{2-} and Se*n*Bu^- ligands are in the range 2.381(2)–2.489(2) Å. The remaining two Cu atoms [Cu(12) and its symmetry equivalent] have ideal tetrahedral coordination formed by four selenide ligands. Accordingly the Cu–Se bond lengths are relatively long [2.600(2)–2.622(2) Å] in comparison to the other Cu–Se bonds.

In contrast to the 18 Se*n*Bu^- ligands that are μ_3-bridging, the seven selenide ligands have greater connectivity. The selenide ligand Se(10) on the inversion centre coordinates to eight copper atoms with two long and six short Cu–Se bonds. The other six selenide ligands act as μ_5-bridges. The 25 Se atoms together form a regular triple-layer structure which corresponds to a cubic close packed arrangement as shown in Fig. 2. The middle layer has 9 Se atoms in a 3 × 3 rhombohedral arrangement. The other two layers each have one Se atom less.

The location of the copper atoms can be explained with reference to this selenium grid. The six phosphine-bound copper atoms bind to two Se atoms of Se*n*Bu^- ligands and are located on the periphery. Six copper atoms [Cu(2), Cu(15) and Cu(16) and their symmetry equivalents] are located approximately within the Se-layers and have trigonal-planar coordination geometry with normal Cu–Se bond lengths of 2.406(2)–2.483(2) Å. The other 20 Cu atoms are located between the Se layers. Two of these [Cu(12) and its symmetry equivalent] have ideal tetrahedral geometry, while the others are shifted away from the centre of tetrahedral holes. Hence each of them has only three normal Cu–Se bonds with the fourth Cu–Se distance being relatively long (3.18 Å to 3.35 Å).

The structure of the Se lattice in **2** is similar to that in the bulk material Cu_2Se;[23] however, most Se atoms in **2** come from Se*n*Bu^- ligands. Despite this, the similarity between the structure of **2** and the non-molecular Cu_2Se suggests that a fragment of a bulk structure may be stabilised to nanosize by coating the surface with suitable groups. This tendency is also observed in three silver–seleno–selenolate clusters,[24] $[Ag_{112}Se_{48}(SenBu)_{32}(PtBu_3)_{12}]$, $[Ag_{114}Se_{46}(SenBu)_{34}(PtBu_3)_{14}]$ and $[Ag_{172}Se_{40}(SenBu)_{92}\{Ph_2P(CH_2)_3PPh_2\}_4]$.

Compound $[Cu_{50}Se_{20}(SetBu)_{10}(PiPr_3)_{10}]$ **3** (Fig. 3) crystallises in the monoclinic space group *C*2/*m*. The molecule contains an inversion centre and a mirror plane, so that the asymmetric unit consists of only a quarter of the cluster.

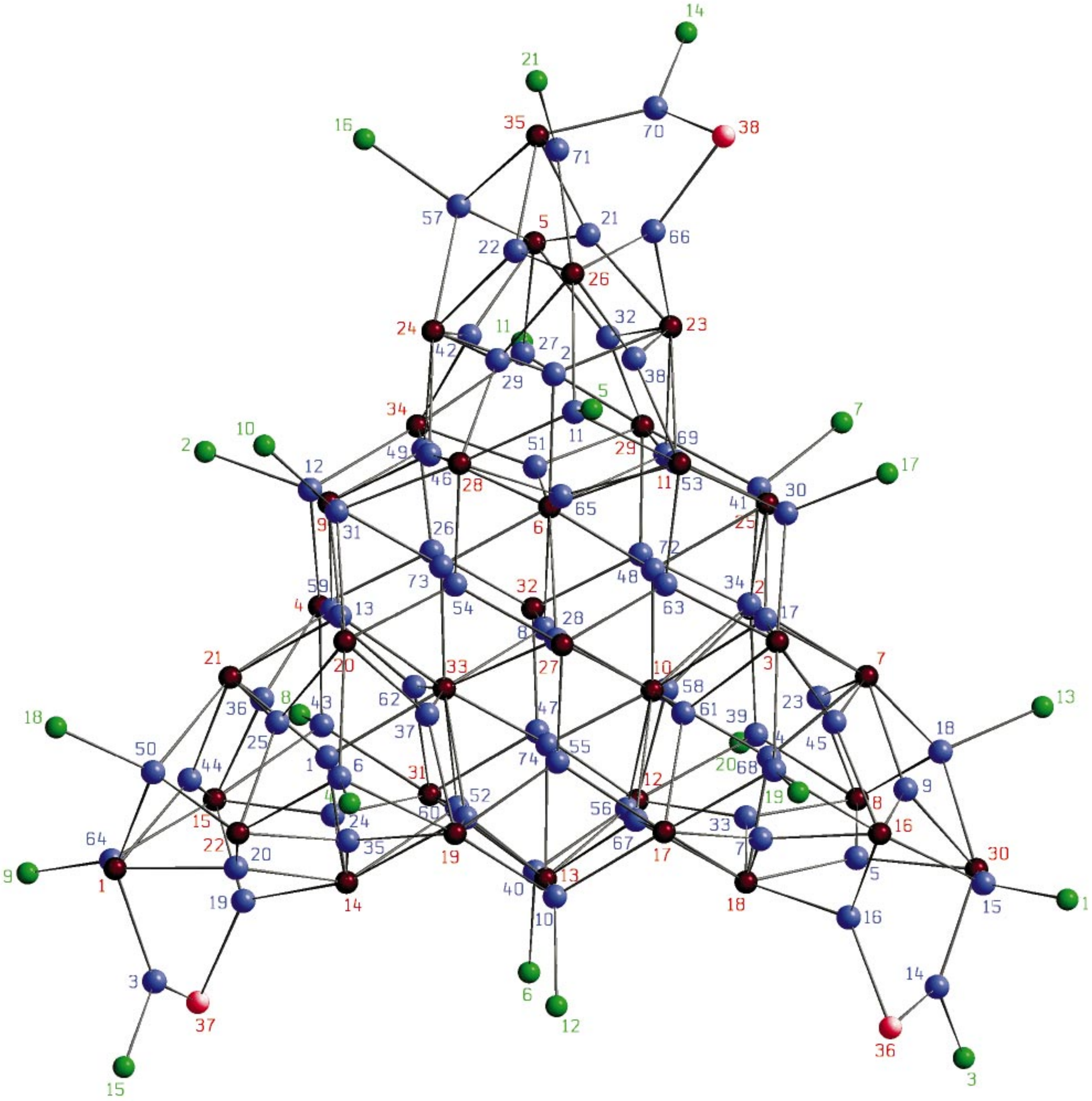

Fig. 5 Molecular structure of $Cu_{73}Se_{35}(SePh)_3(PiPr_3)_{21}$ **4** (Cu: purple; Se^{2-}: dark red; $Se–Ph^-$: light red; P: green); Cu–Cu contacts and carbon atoms are omitted for clarity. Selected bond lengths (Å) in **4**: Cu(8)–Se(6) 2.783(7), Cu(8)–Se(10) 2.628(7), Cu(8)–Se(32) 2.338(8), Cu(8)–Se(33) 2.674(8); Cu(51)–Se(6) 2.726(7), Cu(51)–Se(29) 2.458(6), Cu(51)–Se(34) 2.489(6); Cu(54)–Se(20) 2.480(6), Cu(54)–Se(27) 2.396(6), Cu(54)–Se(28) 2.473(5); Cu(73)–Se(6) 2.407(6), Cu(73)–Se(9) 2.498(6), Cu(73)–Se(33) 2.391(5); Se(36)–Cu(14) 2.401(8), Se(36)–Cu(16) 2.372(5), Se(37)–Cu(3) 2.398(9), Se(37)–Cu(19) 2.378(6), Se(38)–Cu(66) 2.357(6), Se(38)–Cu(70) 2.390(10); average Se–C 1.91(2).

On the mirror plane lie ten Se atoms [Se(2), Se(3), Se(4), Se(6), Se(10) and their symmetry equivalents], ten Cu atoms [Cu(1), Cu(2), Cu(3), Cu(9), Cu(15) and their symmetry equivalents] and two P atoms [P(3) and its symmetry equivalent]. The other Cu, Se and P atoms each have three symmetry-equivalent atoms within the molecule.

The ten phosphine-bound Cu atoms [Cu(13), Cu(14) and Cu(15) and equivalents] are located on the periphery of the $Cu_{50}Se_{30}$ cluster core with two different types of coordination. Cu(13), Cu(14) and their symmetry equivalents have a trigonal-planar coordination mode, and Cu(15) and its symmetry equivalent are tetrahedrally coordinated. As expeted, the Cu–Se bond lengths for Cu(13), Cu(14) and their symmetry equivalents [2.435(2)–2.584(2) Å] are significantly shorter than those for Cu(15) and its equivalent [2.630(2) and 2.715(2) Å], but the Cu–P bonds have a very small range [2.227(2)–2.233(2) Å].

The other 40 Cu atoms are coordinated exclusively by Se atoms with two types of coordination geometries. Four Cu atoms [Cu(4) and its symmetry equivalents] are bound by two Se atoms, one Se^{2-} [Se(5)] and one $SetBu^-$ [Se(9)]. They have short Cu–Se bond lengths [2.347(2) and 2.370(2) Å] and a bent Se–Cu–Se bond angle [136.67(7)°]. The remaining 36 Cu atoms are located in a distorted trigonal-planar coordination geometry. Four of them [Cu(10) and its equivalents] bind purely to $SetBu^-$ ligands, ten [Cu(2), Cu(8), Cu(11) and their symmetry equivalents] are each coordinated by two Se^{2-} and one $SetBu^-$ ligand, and the other 22 Cu atoms [Cu(1), Cu(3), Cu(5), Cu(6), Cu(7), Cu(9), Cu(12) and their symmetry equivalents] are bound only to Se^{2-} ligands. The Cu–Se bond lengths for Se^{2-} and $SetBu^-$ are similar and lie within the range of 2.353(2) to 2.595(2) Å. One exception is the bond Cu(1)–Se(2) 2.875(2) Å, which is relatively long and indicates that Cu(1) tends to be only doubly coordinated by Se atoms in a similar fashion to Cu(4).

The ten $SetBu^-$ ligands [Se(8), Se(9) and Se(10) and their symmetry equivalents] are located on the sides of the molecule and act as μ_3-bridging ligands, while the 20 Se^{2-} ligands have

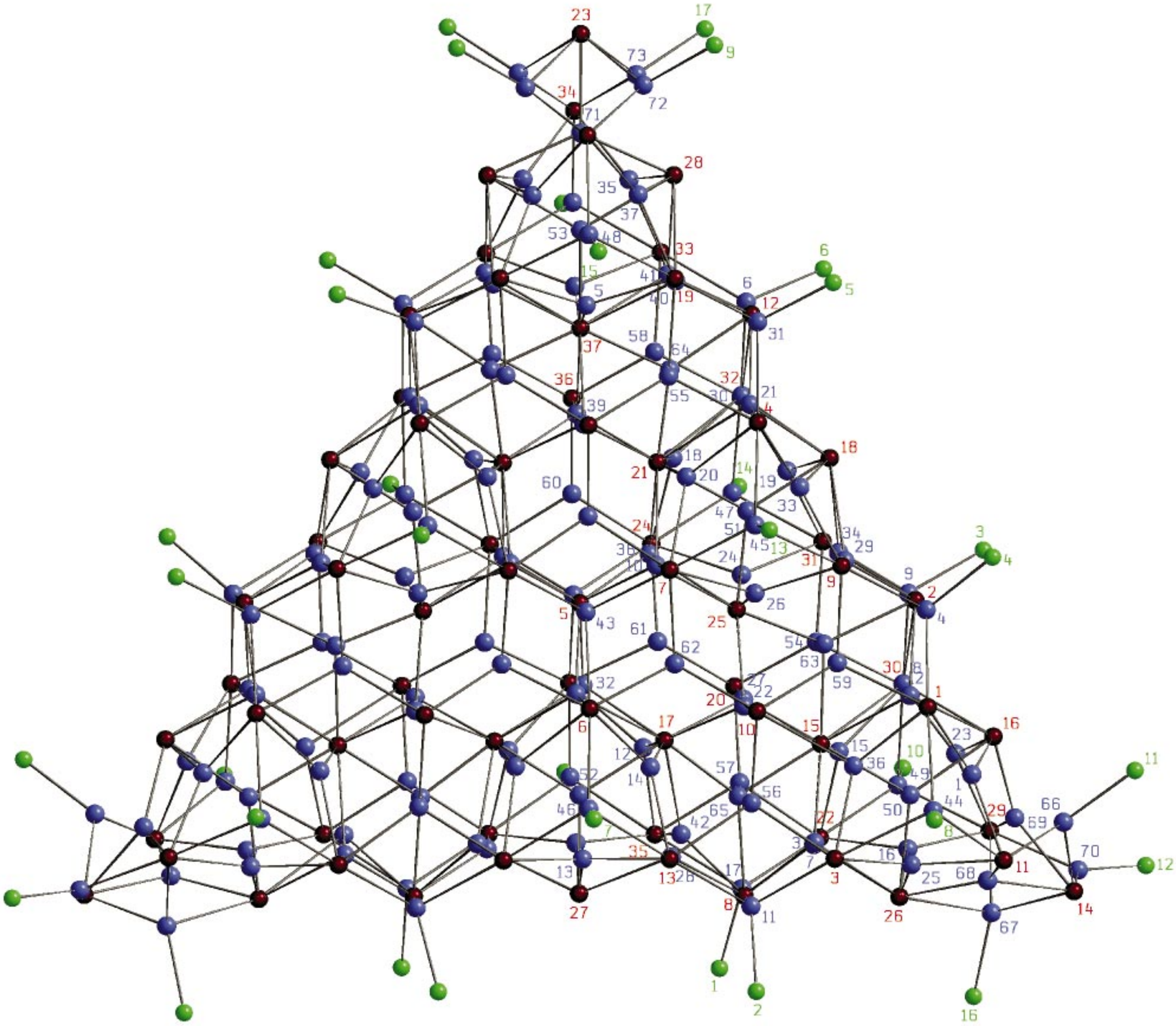

Fig. 6 Molecular structure of $Cu_{140}Se_{70}(PEt_3)_{34}$ **5** (Cu: purple; Se^{2-}: dark red); Cu–Cu contacts and carbon atoms are omitted for clarity. Selected bond lengths (Å) in **5**: Cu(60)–Se(24) 2.426(6), Cu(60)–Se(36) 2.383(5); Cu(10)–Se(5) 2.456(6), Cu(10)–Se(7) 2.380(8), Cu(10)–Se(21) 2.756(7), Cu(10)–Se(25) 2.739(10); Cu(26)–Se(7) 2.577(8), Cu(26)–Se(9) 2.467(6), Cu(26)–Se(25) 2.577(8); Cu(59)–Se(1) 2.485, Cu(59)–Se(9) 2.462(5), Cu(59)–Se(10) 2.379(7); Cu(63)–Se(2) 2.489(9), Cu(63)–Se(15) 2.464(5), Cu(63)–Se(25) 2.310(9); average Cu–P 2.20(1).

more neighbouring Cu atoms. 14 Se^{2-} ligands [Se(1), Se(5), Se(6) and Se(7) and their symmetry equivalents] are each bound to five copper atoms, four [Se(3) and Se(4) and their symmetry equivalents] bridge between five Cu atoms and two Se atoms [Se(2) and its equivalent] act as μ_7 ligands. This variation in the bonding ability of the Se^{2-} ligand is also demonstrated by the series of Cu–Se–cluster complexes mentioned above.

The 30 Se atoms in **3** form approximately three layers (Fig. 4). The middle layer lies on the mirror plane and consists of ten Se atoms. The other two layers are symmetry equivalent and also contain ten Se atoms each. In contrast to the central layer these atoms do not form a strictly planar array. Not considering the eight out-of-plane Se atoms [Se(7) and Se(8) and their equivalents], the other 22 Se atoms show hexagonal close packing. This type of packing has been found in other Cu–Se macromolecules. The Cu atoms are positioned in the tetrahedral holes or sites relating to the octahedral holes of the Se lattice. Eight Cu atoms [Cu(5) and Cu(12) and their equivalents] are located in the tetrahedral holes with long Cu–Se distances, while ten Cu atoms [Cu(3), Cu(4) and Cu(7) and their equivalents] are not in the octahedral holes, but shifted strongly from the centre of the holes with only three Cu–Se bonds. This fragment of the structure is present in larger Cu–Se macromolecules indicating that **3** could be an intermediate in the formation of $[Cu_{70}Se_{35}(PiPr_3)_{21}]$,[25] which is obtained by changing the ratio of Cu to $PiPr_3$.

Compound $[Cu_{73}Se_{35}(SePh)_3(PiPr_3)_{21}]$ **4** crystallizes in the monoclinic space group $P2(1)/c$ with four molecules in the unit cell. Fig. 5 shows the molecular structure and the Se_{38}-lattice, which is based on $[Cu_{70}Se_{35}(PiPr_3)_{21}]$ with three additional CuSePh groups on the three corners. The structure of the $[Cu_{70}Se_{35}(PiPr_3)_{21}]$ fragment is almost the same as that seen in the other Cu_{70} clusters.[7,9,10] The structure of the new $[Cu_{70}Se_{35}(PiPr_3)_{21}]$ compound, also synthesised in this work, has not yet been completely solved.

The Cu_{70} clusters have the common feature that the 35 Se atoms build a layer type structure. It contains three Se layers with 10, 15 and 10 Se atoms, respectively that form a hexagonal close packing. The copper atoms are positioned according to the Se lattice. The detailed structure of **4** is not given here due to the similarity to the known Cu_{70} clusters.[7,10]

Two of the three CuSePh groups are located on the same edge of the molecule, so that no symmetry is present. The linkage of the three CuSePh groups at corners indicates that the corners of the Cu_{70} clusters are capable of being altered. Another type of corner structure has been found in the very large cluster Cu_{146},[13] which has four Se and six Cu atoms at each corner.

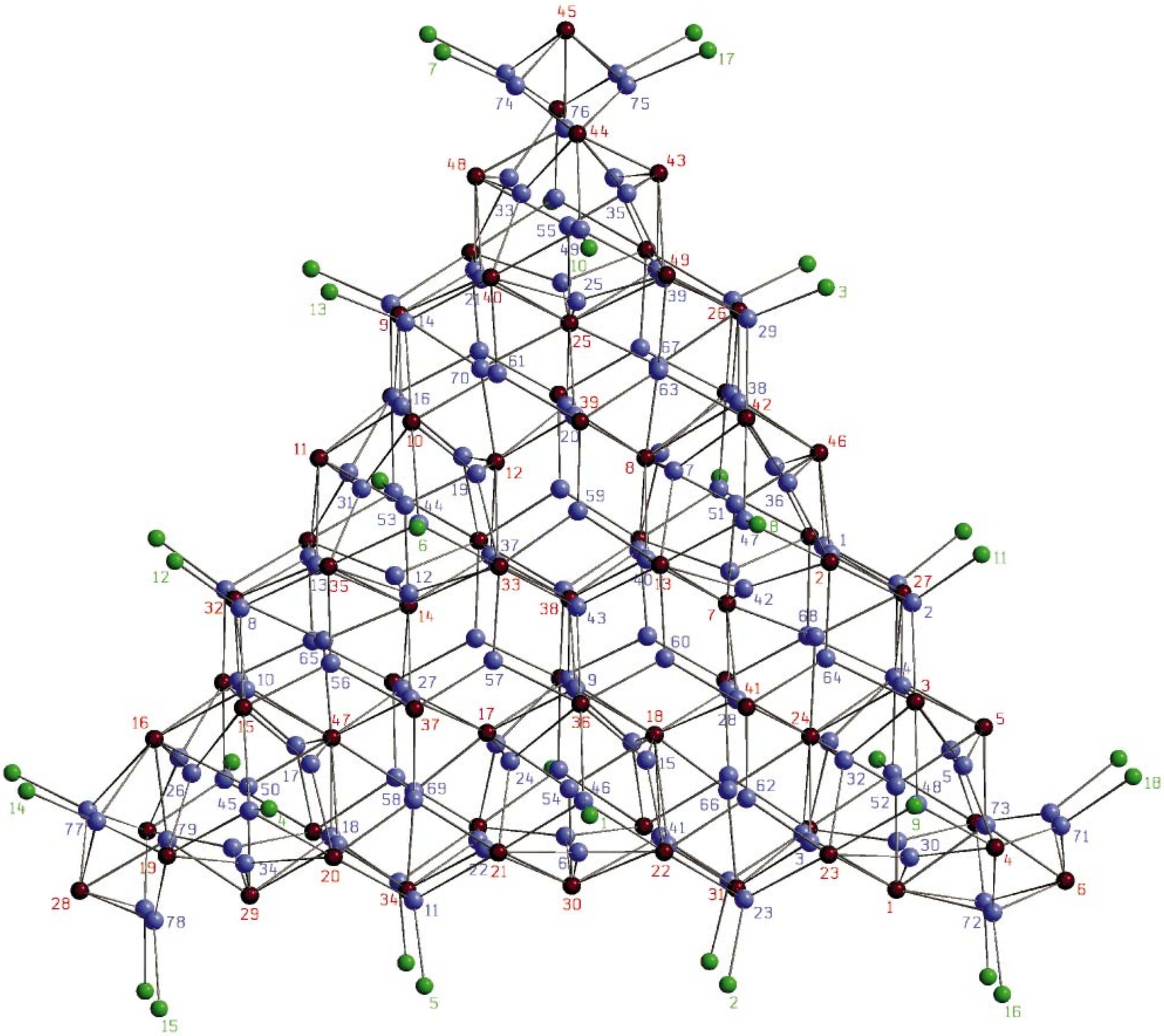

Fig. 7 Molecular structure of $Cu_{140}Se_{70}(PEt_3)_{36}$ **6** (Cu: purple; Se^{2-}: dark red); Cu–Cu contacts and carbon atoms are omitted for clarity. Selected bond lengths (Å) in **6**: Cu(43)–Se(13) 2.588(9), Cu(43)–Se(33) 2.632(9), Cu(43)–Se(36) 2.617(9); Cu(60)–Se(13) 2.419(4), Cu(60)–Se(36) 2.435(4), Cu(60)–Se(41) 2.380(4); Cu(15)–Se(18) 2.585(4), Cu(15)–Se(22) 2.468(4), Cu(15)–Se(36) 2.531(4); Cu(62)–Se(22) 2.464(4), Cu(62)–Se(23) 2.457(4), Cu(62)–Se(41) 2.390(4); average Cu–P 2.20(1).

The structures of $[Cu_{140}Se_{70}(PEt_3)_{34}]$ **5** and $[Cu_{140}Se_{70}(PEt_3)_{36}]$ **6** are very similar and differ only by the presence of two extra phosphine ligands at the periphery (Figs. 6 and 7). In **6,** all three corners have the same $[Cu_5Se_2(PEt_3)_4]$ fragment. The corner with four PEt_3 has approximate twofold symmetry as found in $[Cu_{70}Se_{35}(PEt_3)_{22}]$.[7] In **5** two of the corners only have three phosphine ligands. Owing to the similarities of the structures, only **5** is discussed below.

The 70 Se atoms in **5** build a layer-type structure with 21, 28 and 21 Se atoms in the three layers. They are arranged in a hexagonal close packing structure (Fig. 8), which is characteristic for the Cu–Se macromolecules previously characterised. Except for the corner Se atoms, 36 Se atoms of both outer Se layers construct 36 tetrahedral holes together with the Se atoms of the middle layer. 25 Se atoms of the middle Se layer, excepting the three corner Se atoms, build 50 tetrahedral holes with the Se atoms of the outer ones. Some of these holes are open at the edges and become completed with the help of phosphine ligands. Thus, there are 86 tetrahedral holes in the Se_{70} lattice and 30 octahedral holes. One finds 15 pairs of octahedral holes sharing an Se triangular face.

Besides the 15 Cu atoms at the three corners, the remaining 125 copper atoms are positioned according to the 86 tetrahedral holes and 15 pairs of octahedral holes of the Se lattice. The 86 tetrahedral holes are each found to be occupied by one Cu atom, although many copper atoms deviate from the center of the holes. However, the two positions in the middle of the molecule are actually found to be only partly occupied. These two positions are treated as one disordered copper atom [Cu(43)]. Hence there are 85 Cu atoms in the tetrahedral holes. The remaining 40 Cu atoms are found in the 15 pairs of octahedral holes. Six of these 15 pairs are bi-capped by two $CuPEt_3$ groups and have the third Cu atom in the middle. The other nine pairs contain two or three Cu atoms.

The structure of $[Cu_{70}Se_{35}(PEt_3)_{22}]$[7] can be seen as a substructure of **5** and they feature similar structural properties. The structure of **5** is also very similar to $[Cu_{146}Se_{73}(PPh_3)_{30}]$,[13] the difference between them being found in the corner regions.

Conclusion

This paper presents the synthesis and crystal structures of novel Cu–Se and Cu–Se–SeR clusters that are synthesized by employing mixtures of $RSeSiMe_3$ (R = Ph or *n*Bu or *t*Bu) and $Se(SiMe_3)_2$ in the presence of alkyl phosphines PR_3 (R_3 = Et or *i*Pr). The formation of the products is strongly influenced by the

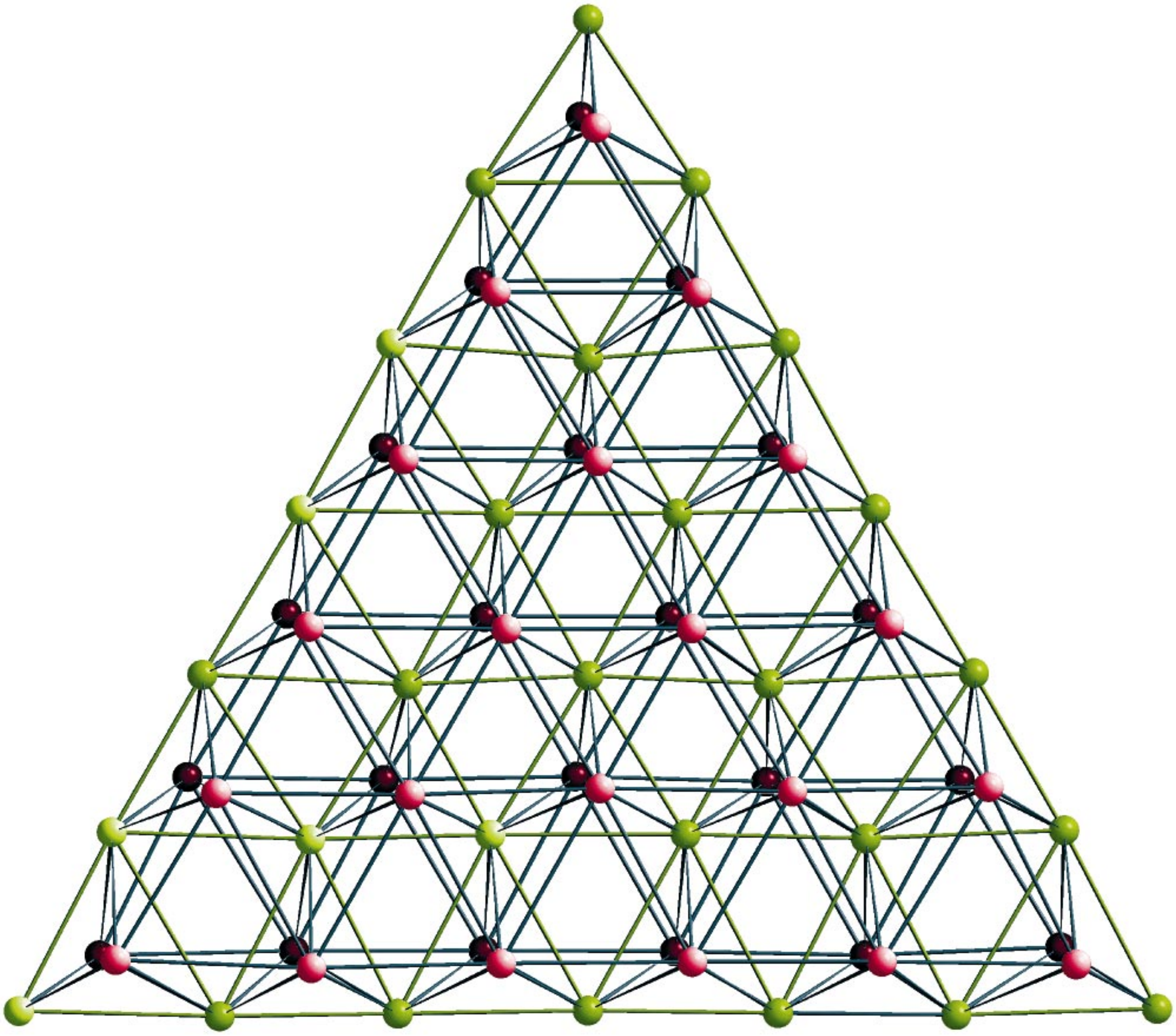

Fig. 8 The selenium lattice of **5** (first layer: light red; second layer and the related Se–Se lines in the same layer: green; third layer: dark red); nonbonding Se · · · Se contacts are shown within 5.5 Å.

reaction conditions and the starting materials, mainly by the phosphine ligand itself. However, for the same phosphine ligand, products of different cluster size and structure can be isolated through the variation of other conditions. It is not yet possible to predict the structure of the possible products when using a new phosphine ligand.

The clusters presented herein show a layer-type structure of Se atoms as their common structural feature, which is often found in the non-molecular binary bulk materials. The Se substructure in **2** is cubic close packed, while the Se lattices in **3**–**6** are hexagonal close packed. The synthetic method employed in this work provides a route by which fragments of a bulk structure may be stabilised by coating the surface with suitable groups.

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