DALTON

Syntheses and structures of four new copper(I)–selenium clusters: size dependence of the cluster on the reaction conditions

Anne Deveson, Stefanie Dehnen and Dieter Fenske *

Institut für Anorganische Chemie, Universität Karlsruhe, Engesserstr. Geb. Nr. 30.45, 76128 Karlsruhe, Germany

Reactions of copper(I) acetate with bis(trimethylsilyl)selenium in the presence of phosphine ligands produce a wide variety of cluster compounds. The formation of these compounds depends very much upon the phosphine used, the solvent and reaction conditions. The following products have been isolated and characterised by X-ray crystallography: $[Cu_{26}Se_{13}(PEt_2Ph)_{14}]$ **1**, $[Cu_{12}Se_6(PCy_3)_6]$ **2** (Cy = cyclohexyl, C_6H_{11}), $[Cu_{26}Se_{13}(PCy_3)_{10}]$ **3** and $[Cu_{59}Se_{30}(PCy_3)_{15}]$ **4**. The selenium atoms in **1** form a body-centred icosahedron, with an overall spherical cluster framework. Compound **2** also has a spherical framework with the selenium atoms forming a slightly distorted octahedron. Compounds **3** and **4** are both unsymmetrical and **4** possesses a layered structure of selenium and copper atoms.

The synthesis, structural characterisation and physical properties of large transition-metal and mixed main-group-metal clusters continues to be an active area of research for chemists, physicists and material scientists alike.[1] Molecular clusters provide a basis for the study of the change in chemical and physical properties when going from small molecules to the bulk material and therefore also provide a route into the formation of nanomaterials. These molecular cluster compounds have the advantage over most nanomaterials in that there is no particle size distribution as they have a defined size and structure. To this end Dance and Lee[2] have explored the synthesis of cadmium–chalcogenide/chalcogenolato clusters and their structural relationships to the corresponding semiconducting solid materials.

The chemistry of the heavier chalcogen–transition metal cluster complexes is also a growing area of research.[3] The synthesis and structural characterisation of a number of copper–selenide clusters has been reported,[4–7] amongst which is one of the largest known characterised clusters $[Cu_{146}Se_{73}(PPh_3)_{30}]$.[5] The compound is in itself a semiconductor and thus the isolation, characterisation and investigation of the physical properties of Cu_2Se cluster compounds could provide an insight into new nanomaterials with interesting properties. The larger clusters *e.g.* $[Cu_{70}Se_{35}(PEt_3)_{22}]$ and $[Cu_{146}Se_{73}(PPh_3)_{30}]$ show layer-type structures in the cluster framework similar to that found in the bulk material.[1] Preliminary studies show that the electrical conductivity of these cluster compounds is dependent on their size.[8]

Equation (1) (thf = tetrahydrofuran, $z = 0$ or 1) shows the

$$2x\mathrm{CuX} + y\mathrm{PR}_3 + x\mathrm{Se(SiMe_3)_2} \xrightarrow[-2x\mathrm{SiMe_3X}]{\text{thf or Et}_2\text{O}} [\mathrm{Cu}_{2x-z}\mathrm{Se}_x(\mathrm{PR}_3)_y] \quad (1)$$

general synthetic pathway for the formation of these cluster compounds. The driving force of the reaction is the elimination of $SiMe_3X$ (X = Cl or OAc, Ac = OCMe) whereby cluster formation is made possible by the shielding effect of the phosphine ligands. The ratio of Cu to PR_3, the reaction conditions and the solvents used for the syntheses play a significant role in governing the structures of the products formed. The steric demands of the phosphine ligands also influence the size and structure of the cluster.

Herein we report the structural characterisation by X-ray crystallography of four new copper selenide clusters $[Cu_{26}Se_{13}(PEt_2Ph)_{14}]$ **1**, $[Cu_{12}Se_6(PCy_3)_6]$ **2** (Cy = cyclohexyl, C_6H_{11}), $[Cu_{26}Se_{13}(PCy_3)_{10}]$ **3** and $[Cu_{59}Se_{30}(PCy_3)_{15}]$ **4**.

Experimental

Standard Schlenk-line techniques were employed throughout on a double-manifold vacuum line with high purity dried nitrogen. Solvents for reactions were distilled under nitrogen from appropriate drying agents prior to use. Diethyl ether and tetrahydrofuran were dried over sodium–benzophenone. The compounds CuOAc,[9] $Se(SiMe_3)_2$[10] and the phosphine ligands[11] were prepared according to standard literature procedures.

Syntheses

$[Cu_{26}Se_{13}(PEt_2Ph)_{14}]$ 1. Diethylphenylphosphine (1.6 ml, 6 mmol) was added to a suspension of copper(I) acetate (0.37 g, 3 mmol) in diethyl ether (27 ml). A clear colourless solution was formed which was then cooled to −80 °C. On addition of $Se(SiMe_3)_2$ (0.37 ml, 1.5 mmol) the solution gradually turned through orange to dark brown. The reaction was allowed to warm slowly to 0 °C and black crystals of the known cluster $[Cu_{44}Se_{22}(PEt_2Ph)_{18}]$[1b] were formed. When these crystals are filtered and the resulting yellow filtrate is kept at −24 °C then large red rhombuses of compound **1** crystallise within 1 week. Yield: 19% (Found: C, 33.3; H, 4.5. $C_{140}H_{210}Cu_{26}P_{14}Se_{13}$ requires: C, 33.59; H, 4.23%).

$[Cu_{12}Se_6(PCy_3)_6]$ 2. Tricyclohexylphosphine (0.5 g, 1.78 mmol) was added to a suspension of copper(I) acetate (0.1 g, 0.89 mmol) in thf (10 ml). A clear colourless solution was formed which was then cooled to −78 °C. On addition of $Se(SiMe_3)_2$ (0.11 ml, 0.445 mmol) the solution gradually turned through orange to dark brown. The reaction was allowed to warm slowly to room temperature and after 3 d red crystals of compound **2** were formed. Yield: 68% (Found: C, 44.1; H, 6.6. $C_{108}H_{198}Cu_{12}P_6Se_6$ requires: C, 44.44; H, 6.84%).

$[Cu_{26}Se_{13}(PCy_3)_{10}]$ 3. Tricyclohexylphosphine (0.56 g, 2.00 mmol) was added to a suspension of copper(I) acetate (0.24 g, 2.00 mol) in thf (20 ml). A clear colourless solution was formed which was then cooled to −78 °C. On addition of $Se(SiMe_3)_2$ (0.23 ml, 1.00 mmol) the solution gradually turned through orange to dark brown. The reaction mixture was allowed to warm slowly to 6 °C upon which 10 ml of thf was removed by condensation and 10 ml of diethyl ether was added. The reaction mixture was kept at 6 °C for 2 weeks upon which black crystalline platelets of compound **3** were formed. Yield: 46% (Found: C, 39.7; H, 5.9. $C_{180}H_{330}Cu_{26}P_{10}Se_{13}$ requires: C, 39.43; H, 6.07%).

$[Cu_{59}Se_{30}(PCy_3)_{15}]$ 4. Tricyclohexylphosphine (0.44 g, 1.57 mmol) was added to a suspension of copper(I) acetate (0.19 g, 1.57 mmol) in thf (20 ml). A clear colourless solution was formed which was then cooled to −78 °C. On addition of $Se(SiMe_3)_2$ (0.18 ml, 0.785 mmol) the solution gradually turned through orange to dark brown. The reaction was allowed to warm up slowly to 0 °C and after 3 weeks small black needle-like crystals of compound **4** were formed. Yield: 12% (Found: C, 31.1; H, 4.5. $H_{495}C_{270}Cu_{59}P_{15}Se_{30}$ requires: C, 31.41; H, 4.83%).

X-Ray structural analyses

Single-crystal X-ray structural analysis of compounds **1**–**4** 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 using SHELXS 86[12] and SHELXL 93[13] 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.[14]

Compound 1. *Crystal data.* $C_{140}H_{210}Cu_{26}P_{14}Se_{13}\cdot 2Et_2O$, M = 5153.58, triclinic, space group $P\bar{1}$, a = 17.538(4), b = 18.108(4), c = 18.361(4) Å, α = 98.54(3), β = 109.40(3), γ = 118.16(3)°, U = 4510(2) Å^3, Z = 1; D_c = 1.897 cm^{-3}, F(000) = 2540, μ = 5.651 mm^{-1} for Mo-Kα radiation.

Data collection and reduction. Data were collected at 200 K in the θ range 2.35 to 25.00° using a ΔΦ value of 0.5 and a detector distance of 75 mm with 10 min radiation time per exposure; 43 097 reflections measured of which 12 097 were independent and were considered observed with $I > 2\sigma(I)$.

Structure analysis and refinement. Direct methods (Cu and Se) followed by normal refinement procedures. Full-matrix least-squares refinement on F^2 with all Se, Cu, P and C atoms anisotropic, except for those ethyl groups which were disordered and the respective atoms were refined isotropically with half occupancy and all hydrogen atoms in calculated positions gave R = 0.0529 with a goodness of fit value of 1.069. Parameters refined = 923. Table 1 contains a list of selected bond lengths. An ether solvent molecule was located and refined anisotropically.

Compound 2. *Crystal data.* $C_{108}H_{198}Cu_{12}P_6Se_6\cdot 2thf$, M = 3061.84, triclinic, space group $P\bar{1}$, a = 14.643(3), b = 17.285(4), c = 17.935(4) Å, α = 118.01(3), β = 90.12(3), γ = 114.9(3)°, U = 3518.5(12) Å^3, Z = 1; D_c = 1.438 g cm^{-3}, F(000) = 1552, μ = 3.433 mm^{-1} for Mo-Kα radiation.

Data collection and reduction. Data were collected at 200 K in the θ range 2.31 to 24.00° using a ΔΦ value of 0.5 and a detector distance of 60 mm with 10 min radiation time per exposure; 12 531 reflections measured of which 8846 were independent and 6957 were considered observed with $I > 2\sigma(I)$.

Structure analysis and refinement. Direct methods (Cu and Se) followed by normal refinement procedures. Full-matrix least-squares refinement on F^2 with all Se, Cu, P and C atoms anisotropic and all hydrogen atoms in calculated positions gave R = 0.0628 with a goodness of fit value of 1.091. Parameters refined = 635. Table 2 contains a list of selected bond lengths. A thf solvent molecule was located and refined isotropically (H atoms omitted).

Table 1 Selected bond lengths (pm) for compound **1**

Se(1)–Cu(6)	256.1(2)	Se(5)–Cu(4)	239.7(2)
Se(1)–Cu(3)	262.5(1)	Se(5)–Cu(6)	246.0(1)
Se(1)–Cu(1)	265.9(1)	Se(5)–Cu(10)	255.6(2)
Se(1)–Cu(2)	273.8(1)	Se(5)–Cu(5)	271.9(1)
Se(1)–Cu(4)	290.6(2)	Se(6)–Cu(5)	240.0(1)
Se(1)–Cu(5)	283.7(1)	Se(6)–Cu(13)	240.8(2)
Se(2)–Cu(1)	238.7(1)	Se(6)–Cu(1^{I})	246.0(1)
Se(2)–Cu(11)	241.1(1)	Se(6)–Cu(10)	254.6(1)
Se(2)–Cu(8)	246.5(2)	Se(6)–Cu(2)	264.7(1)
Se(2)–Cu(7)	250.3(2)	Se(7)–Cu(6)	237.4(1)
Se(2)–Cu(4)	259.0(1)	Se(7)–Cu(13^{I})	238.3(1)
Se(3)–Cu(2)	239.0(1)	Se(7)–Cu(9^{I})	247.4(1)
Se(3)–Cu(11)	240.2(1)	Se(7)–Cu(8)	253.1(1)
Se(3)–Cu(3)	246.4(1)	Se(7)–Cu(2^{I})	267.9(2)
Se(3)–Cu(4)	260.9(2)	Cu(7)–P(1)	226.1(2)
Se(3)–Cu(10)	261.4(2)	Cu(8)–P(2)	226.3(2)
Se(4)–Cu(3)	237.6(2)	Cu(9)–P(3)	226.0(2)
Se(4)–Cu(12^{I})	240.3(1)	Cu(10)–P(4)	225.0(2)
Se(4)–Cu(9)	248.3(1)	Cu(11)–P(5)	223.8(2)
Se(4)–Cu(7)	250.1(2)	Cu(12)–P(6)	222.7(2)
Se(4)–Cu(5^{I})	256.0(1)	Cu(13)–P(7)	223.2(2)
Se(5)–Cu(12)	238.9(1)		

Symmetry transformations used to generate equivalent atoms: I $-x + 1, -y + 1, -z + 1$.

Table 2 Selected bond lengths (pm) for compound **2**

Se(1)–Cu(4)	230.7(2)	Se(3)–Cu(5^{I})	232.2(2)
Se(1)–Cu(2)	238.0(1)	Se(3)–Cu(4)	235.3(2)
Se(1)–Cu(1)	250.8(1)	Se(3)–Cu(6)	240.3(2)
Se(1)–Cu(3)	255.1(2)	Se(3)–Cu(2^{I})	246.8(2)
Se(2)–Cu(5)	227.9(2)	Cu(1)–P(1)	228.0(2)
Se(2)–Cu(6)	235.3(2)	Cu(2)–P(2)	229.9(3)
Se(2)–Cu(3^{I})	248.2(2)	Cu(3)–P(3)	231.1(2)
Se(2)–Cu(1)	250.5(2)		

Symmetry transformations used to generate equivalent atoms: I $-x + 1, -y, -z$.

Compound 3. *Crystal data.* $C_{180}H_{330}Cu_{26}P_{10}Se_{13}\cdot 0.5thf$, M = 5520.68, triclinic, space group $P\bar{1}$, a = 19.715(4), b = 20.674(4), c = 34.898(7) Å, α = 90.01(3), β = 105.54(3), γ = 102.18(3)°, U = 13 366 Å^3, Z = 2, D_c = 1.372 g cm^{-3}, F(000) = 5550, μ = 3.884 mm^{-1} for Mo-Kα radiation.

Data collection and reduction. Data were collected at 193 K in the θ range 1.88 to 21.50° using a ΔΦ value of 0.3 and a detector distance of 75 mm with 8 min radiation time per exposure; 330 339 reflections measured of which 23 337 were independent and 19 804 were considered observed with $I > 2\sigma(I)$.

Structure analysis and refinement. Direct methods (Cu and Se) followed by normal refinement procedures. Full-matrix least-squares refinement on F^2 with all Se, Cu, P and C atoms anisotropic and all hydrogen atoms in calculated positions gave R = 0.0852 with a goodness of fit value of 1.165. Parameters refined = 2082. Table 3 contains a list of selected bond lengths. A thf solvent molecule was located and refined isotropically with half occupancy (H atoms omitted).

Compound 4. *Crystal data.* $C_{270}H_{495}Cu_{59}P_{15}Se_{30}\cdot 1.5thf$, M = 10 432.66, triclinic, space group $P\bar{1}$, a = 14.643(3), b = 17.285(4), c = 17.935(4) Å, α = 118.01(3), β = 90.12(3), γ = 114.94(3)°, U = 3518.5(12) Å^3, Z = 2, D_c = 1.511 g cm^{-3}, F(000) = 10 262, μ = 5.135 mm^{-1} for Mo-Kα radiation.

Data collection and reduction. Data were collected at 200 K in the θ range 1.94 to 21.50° using a ΔΦ value of 0.4 and a detector distance of 75 mm with 15 min radiation time per exposure; 87 343 reflections measured of which 50 128 were independent and 26 274 were considered observed with $I > 2\sigma(I)$.

Structure analysis and refinement. Direct methods (Cu and Se) followed by normal refinement procedures. Full-matrix least-squares refinement on F^2 with all Se, Cu and P atoms anisotropic, all C atoms isotropic (two of the cyclohexyl rings were disordered and were refined with half occupancy) and all

Table 3 Selected bond lengths (pm) for compound **3**

Se(1)–Cu(12)	237.3(2)	Se(8)–Cu(23)	267.9(2)
Se(1)–Cu(13)	239.4(2)	Se(8)–Cu(6)	292.5(2)
Se(1)–Cu(1)	246.0(3)	Se(9)–Cu(15)	231.5(2)
Se(1)–Cu(2)	256.6(2)	Se(9)–Cu(5)	247.3(2)
Se(2)–Cu(15)	233.6(2)	Se(9)–Cu(16)	253.7(2)
Se(2)–Cu(1)	244.3(2)	Se(9)–Cu(6)	257.8(2)
Se(2)–Cu(11)	248.9(2)	Se(9)–Cu(4)	270.0(2)
Se(2)–Cu(14)	252.9(2)	Se(9)–Cu(19)	276.9(2)
Se(2)–Cu(2)	271.4(2)	Se(10)–Cu(20)	233.7(2)
Se(3)–Cu(17)	234.9(2)	Se(10)–Cu(8)	248.6(2)
Se(3)–Cu(13)	243.6(2)	Se(10)–Cu(9)	254.9(2)
Se(3)–Cu(3)	249.9(2)	Se(10)–Cu(26)	275.1(2)
Se(3)–Cu(11)	255.5(2)	Cu(9)–P(9)	223.5(4)
Se(3)–Cu(2)	258.3(2)	Se(11)–Cu(22)	238.1(2)
Se(4)–Cu(4)	238.6(2)	Se(11)–Cu(26)	242.5(2)
Se(4)–Cu(3)	240.5(2)	Se(11)–Cu(9)	242.8(2)
Se(4)–Cu(16)	241.0(2)	Se(11)–Cu(24)	246.2(2)
Se(4)–Cu(11)	243.2(2)	Se(11)–Cu(7)	267.2(2)
Se(5)–Cu(20)	226.5(2)	Se(12)–Cu(23)	238.2(2)
Se(5)–Cu(22)	238.4(2)	Se(12)–Cu(8)	240.8(2)
Se(5)–Cu(12)	243.6(2)	Se(12)–Cu(26)	245.9(2)
Se(5)–Cu(10)	247.2(2)	Se(12)–Cu(25)	248.9(2)
Se(6)–Cu(21)	226.3(2)	Se(12)–Cu(7)	267.5(2)
Se(6)–Cu(23)	241.0(2)	Se(13)–Cu(25)	237.5(2)
Se(6)–Cu(18)	242.5(2)	Se(13)–Cu(5)	241.6(2)
Se(10)–Cu(21)	234.7(2)	Se(13)–Cu(24)	246.3(2)
Se(6)–Cu(13)	250.4(2)	Se(13)–Cu(7)	254.1(2)
Se(6)–Cu(10)	264.2(2)	Se(13)–Cu(6)	254.7(2)
Se(6)–Cu(17)	293.0(2)	Cu(1)–P(1)	226.1(5)
Se(7)–Cu(18)	238.5(2)	Cu(2)–P(2)	226.4(3)
Se(7)–Cu(24)	244.6(2)	Cu(3)–P(3)	223.2(4)
Se(7)–Cu(19)	244.5(2)	Cu(4)–P(4)	225.1(4)
Se(7)–Cu(14)	246.6(2)	Cu(5)–P(5)	223.7(4)
Se(7)–Cu(12)	259.9(2)	Cu(6)–P(6)	225.1(4)
Se(7)–Cu(22)	292.2(2)	Cu(7)–P(7)	224.6(3)
Se(8)–Cu(17)	233.7(2)	Cu(8)–P(8)	224.8(4)
Se(8)–Cu(25)	246.0(2)	Cu(9)–P(9)	223.5(4)
Se(8)–Cu(16)	249.8(2)	Cu(10)–P(10)	227.7(4)
Se(8)–Cu(19)	255.0(2)		

hydrogen atoms in calculated positions gave $R = 0.1019$ with a goodness of fit value of 1.188. Parameters refined = 2097. Table 4 contains a list of selected bond lengths. Three thf solvent molecules were located and refined isotropically with half occupancy (H atoms omitted).

CCDC reference number 186/745.

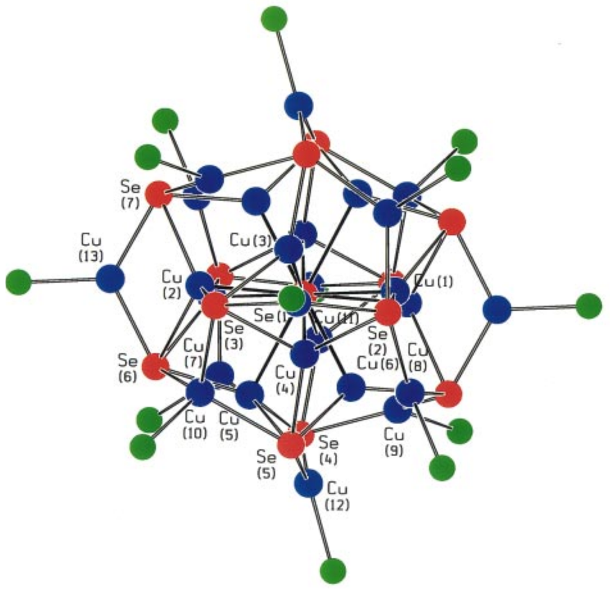

Fig. 1 Molecular structure of [$Cu_{26}Se_{13}(PEt_2Ph)_{14}$] **1** ($Cu^+$: blue; Se^{2-}: red; P: green); Cu–Cu contacts and carbon atoms are omitted for clarity

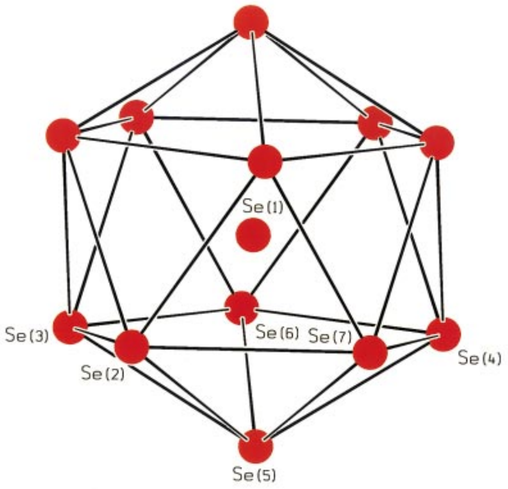

Fig. 2 The selenium cage of compound **1**. Non-bonding Se···Se contacts are shown in the range from 420 to 458 pm. For clarity, Se(1)–Se contacts [Se(1)–Se 400–432 pm] are not drawn

Results and Discussion

Fig. 1 shows the molecular structure of compound **1** which crystallises in the space group $P\bar{1}$ and contains an inversion centre [Se(1)]. The cluster framework can be described as an alternate packing of Cu and Se polyhedra respectively: the central selenium atom [Se(1)] is surrounded by a slightly distorted Cu_{12} icosahedron [Cu(1)–Cu(6) and their symmetry equivalents]. In turn, a Se_{12} icosahedron [Se(2)–Se(7) and their symmetry equivalents] is situated around the $SeCu_{12}$ core, each edge being perpendicular to a Cu–Cu edge beneath. Finally, a six-fold capped cube of the copper atoms that bind to the 14 PEt_2Ph ligands [Cu(7)–Cu(13) and their symmetry equivalents] enfolds the cluster. The 12 phosphine-free Cu atoms are located below the Se_{12} surface, each one near the centre of a deltahedral face. The remaining eight faces of the Se_{12} icosahedron co-ordinate the eight $Cu(PEt_2Ph)$ corners of the capped cube. Owing to distortions in the cluster framework, the 20 metal atoms binding to Se_3 faces only approximate tetrahedral Se_4Cu or Se_3PCu co-ordination. Twelve of them [Cu(1), Cu(3), Cu(6)–Cu(9) and their symmetry equivalents] show one longer Cu–Se contact (>315 pm; not drawn in Fig. 1) so they can better be viewed as three-co-ordinate trigonal planar. The six $Cu(PEt_2Ph)$ groups capping the Cu cube [Cu(11)–Cu(13) and their symmetry equivalents] are each situated in trigonal-planar geometry above an edge of the Se_{12} icosahedron. Compound **1** can be called a typical middle sized spherical Cu_2Se cluster[4c] containing both, trigonal planar Se_2CuP and (partially very distorted) tetrahedral Se_3CuP co-ordination. The rarely observed (partially very distorted) tetrahedral Se_3CuSe arrangement is also found in **1**. Besides the μ_{12} bridging Se(1) atom, the chalcogen atoms of **1** act as μ_5 bridges, as long as the above mentioned 'longer' Cu–Se contacts are not considered.

The selenium cage, an almost regular centred icosahedron, is shown in Fig. 2. The same substructure has been reported for [$Cu_{20}Se_{13}(PEt_3)_{12}$].[6] In contrast to the structure of **1**, the latter compound contains a Cu_8 cube around the central Se atom and a Cu_{12} icosahedron surrounding the Se_{13} cage. Accordingly, six copper atoms and two phosphine ligands are missing in the mixed-valence $Cu_{20}Se_{13}$ cluster. Both Se_{13} based compounds are minor products in the synthesis of bigger clusters and cannot be described as structural fragments of the Cu_2Se core of the major products.

The molecular structure of compound **2** is shown in Fig. 3. It crystallises in the triclinic space group $P\bar{1}$ and contains an inversion centre. This cluster differs from previously reported $Cu_{12}E_6$ cluster compounds (E = S or Se) in that it has only six shielding phosphine ligands instead of eight.[4a,d] The reason for this is probably the higher spatial demand of the phosphine

Table 4 Selected bond lengths (pm) for compound **4**

Se(1)–Cu(16)	230.3(4)	Se(9)–Cu(59)	251.3(4)	Se(19)–Cu(14)	246.7(4)	Se(30)–Cu(58)	246.3(4)
Se(1)–Cu(29)	237.9(4)	Se(9)–Cu(37)	262.9(4)	Se(19)–Cu(46)	246.7(5)	Se(30)–Cu(13)	250.5(5)
Se(1)–Cu(31)	244.7(4)	Se(12)–Cu(39)	236.7(4)	Se(19)–Cu(36)	251.1(4)	Se(30)–Cu(9)	260.6(5)
Se(1)–Cu(3)	248.2(4)	Se(12)–Cu(52)	243.0(4)	Se(19)–Cu(34)	254.4(4)	Cu(1)–P(1)	226.2(7)
Se(1)–Cu(39)	271.8(4)	Se(12)–Cu(42)	249.2(4)	Se(22)–Cu(48)	247.9(4)	Cu(2)–P(2)	227.1(7)
Se(2)–Cu(28)	237.9(4)	Se(12)–Cu(55)	254.8(4)	Se(22)–Cu(4)	249.3(4)	Cu(3)–P(3)	225.6(7)
Se(2)–Cu(30)	238.6(4)	Se(12)–Cu(48)	267.8(4)	Se(23)–Cu(53)	241.9(4)	Se(10)–Cu(28)	235.0(4)
Se(2)–Cu(27)	238.7(5)	Se(12)–Cu(3)	275.2(4)	Se(23)–Cu(56)	244.0(4)	Se(10)–Cu(38)	243.5(4)
Se(2)–Cu(29)	241.8(4)	Se(13)–Cu(17)	234.1(4)	Se(23)–Cu(52)	244.1(4)	Se(10)–Cu(37)	243.7(4)
Se(3)–Cu(43)	239.9(4)	Se(13)–Cu(41)	241.3(4)	Se(23)–Cu(55)	244.3(4)	Se(10)–Cu(12)	245.4(4)
Se(3)–Cu(42)	240.9(4)	Se(13)–Cu(38)	253.6(4)	Se(23)–Cu(5)	272.4(4)	Se(10)–Cu(10)	265.1(5)
Se(3)–Cu(31)	245.3(4)	Se(13)–Cu(30)	255.6(4)	Se(23)–Cu(7)	273.7(4)	Se(11)–Cu(17)	232.4(4)
Se(3)–Cu(33)	247.3(4)	Se(13)–Cu(32)	261.9(4)	Se(24)–Cu(51)	235.6(4)	Se(11)–Cu(39)	242.7(4)
Se(3)–Cu(1)	269.9(4)	Se(13)–Cu(6)	289.3(4)	Se(24)–Cu(53)	240.4(4)	Se(11)–Cu(51)	224.0(4)
Se(3)–Cu(3)	272.4(4)	Se(13)–Cu(28)	294.8(4)	Se(24)–Cu(50)	244.4(4)	Se(11)–Cu(40)	268.5(4)
Se(4)–Cu(32)	243.8(4)	Se(14)–Cu(19)	232.3(4)	Se(24)–Cu(49)	248.7(4)	Se(11)–Cu(29)	283.5(5)
Se(4)–Cu(40)	248.5(4)	Se(14)–Cu(40)	245.6(4)	Se(24)–Cu(5)	260.2(4)	Se(11)–Cu(27)	285.0(5)
Se(4)–Cu(30)	248.6(4)	Se(14)–Cu(51)	249.5(4)	Se(25)–Cu(18)	239.1(4)	Se(11)–Cu(59)	286.8(5)
Se(4)–Cu(31)	251.3(4)	Se(14)–Cu(45)	249.7(4)	Se(25)–Cu(38)	242.5(4)	Se(20)–Cu(23)	225.8(7)
Se(4)–Cu(2)	257.3(4)	Se(14)–Cu(42)	256.4(4)	Se(25)–Cu(50)	243.5(4)	Se(20)–Cu(22)	231.3(5)
Se(4)–Cu(33)	257.5(4)	Se(14)–Cu(54)	260.0(4)	Se(25)–Cu(12)	248.0(4)	Se(20)–Cu(24)	233.2(5)
Se(5)–Cu(25)	228.7(4)	Se(15)–Cu(55)	237.8(4)	Se(25)–Cu(6)	253.0(4)	Se(20)–Cu(13)	246.7(5)
Se(5)–Cu(43)	245.2(4)	Se(15)–Cu(45)	239.5(4)	Se(26)–Cu(57)	239.9(4)	Se(21)–Cu(18)	236.7(4)
Se(5)–Cu(47)	246.0(5)	Se(15)–Cu(43)	244.4(4)	Se(26)–Cu(56)	240.5(4)	Se(21)–Cu(49)	246.3(4)
Se(5)–Cu(1)	253.1(4)	Se(15)–Cu(57)	249.8(4)	Se(26)–Cu(58)	247.6(4)	Se(21)–Cu(37)	246.7(4)
Se(5)–Cu(15)	260.7(5)	Se(15)–Cu(7)	262.5(4)	Se(26)–Cu(7)	250.2(4)	Se(21)–Cu(59)	250.6(4)
Se(5)–Cu(35)	291.3(4)	Se(16)–Cu(19)	234.3(4)	Se(26)–Cu(9)	251.4(5)	Se(21)–Cu(4)	264.7(4)
Se(6)–Cu(35)	238.0(4)	Se(16)–Cu(32)	240.6(4)	Se(27)–Cu(20)	232.1(4)	Se(22)–Cu(52)	237.9(4)
Se(6)–Cu(2)	247.7(4)	Se(16)–Cu(34)	241.4(4)	Se(27)–Cu(56)	246.4(4)	Se(22)–Cu(49)	243.8(4)
Se(6)–Cu(33)	248.1(4)	Se(16)–Cu(44)	249.4(4)	Se(27)–Cu(54)	253.9(4)	Se(22)–Cu(5)	247.7(4)
Se(6)–Cu(34)	249.4(4)	Se(16)–Cu(41)	283.2(4)	Se(27)–Cu(53)	254.6(4)	Cu(4)–P(4)	225.9(8)
Se(6)–Cu(36)	254.1(4)	Se(16)–Cu(2)	286.3(4)	Se(27)–Cu(58)	254.6(4)	Cu(5)–P(5)	225.5(8)
Se(6)–Cu(1)	267.5(4)	Se(17)–Cu(20)	233.4(4)	Se(27)–Cu(8)	259.3(4)	Cu(6)–P(6)	223.6(7)
Se(7)–Cu(24)	226.2(5)	Se(17)–Cu(26)	239.3(6)	Se(28)–Cu(41)	235.5(4)	Cu(7)–P(7)	223.1(7)
Se(7)–Cu(25)	229.5(5)	Se(17)–Cu(35)	239.3(4)	Se(28)–Cu(54)	243.0(4)	Cu(8)–P(8)	228.5(7)
Se(7)–Cu(36)	243.3(4)	Se(17)–Cu(45)	247.8(4)	Se(28)–Cu(50)	246.2(4)	Cu(9)–P(9)	225.7(8)
Se(7)–Cu(14)	257.0(5)	Se(17)–Cu(46)	261.1(5)	Se(28)–Cu(44)	251.2(4)	Cu(10)–P(10)	221.7(8)
Se(8)–Cu(16)	228.9(4)	Se(17)–Cu(47)	264.3(5)	Se(28)–Cu(6)	259.3(4)	Cu(11)–P(11)	226.7(7)
Se(8)–Cu(59)	243.5(4)	Se(18)–Cu(23)	221.5(7)	Se(28)–Cu(8)	273.4(4)	Cu(12)–P(12)	222.1(8)
Se(8)–Cu(48)	244.7(4)	Se(18)–Cu(47)	244.3(5)	Se(29)–Cu(21)	228.1(4)	Cu(13)–P(13)	227.4(8)
Se(8)–Cu(11)	256.3(4)	Se(18)–Cu(57)	247.8(5)	Se(29)–Cu(46)	234.5(4)	Cu(14)–P(14)	222.5(9)
Se(8)–Cu(4)	271.5(4)	Se(18)–Cu(15)	253.1(5)	Se(29)–Cu(44)	241.5(4)	Cu(15)–P(15)	222.2(8)
Se(9)–Cu(27)	238.4(5)	Se(18)–Cu(9)	279.9(5)	Se(29)–Cu(8)	246.1(4)		
Se(9)–Cu(10)	241.8(5)	Se(18)–Cu(26)	291.1(7)	Se(30)–Cu(21)	230.1(4)		
Se(9)–Cu(11)	241.9(4)	Se(19)–Cu(22)	232.0(4)	Se(30)–Cu(26)	236.0(5)		

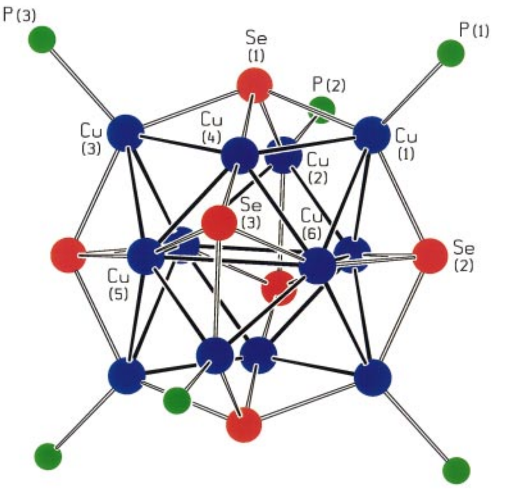

Fig. 3 Molecular structure of [$Cu_{12}Se_6(PCy_3)_6$] **2** (Cu^+: blue; Se^{2-}: red; P: green), Cu–Cu contacts are shown in black. Carbon atoms are omitted for clarity

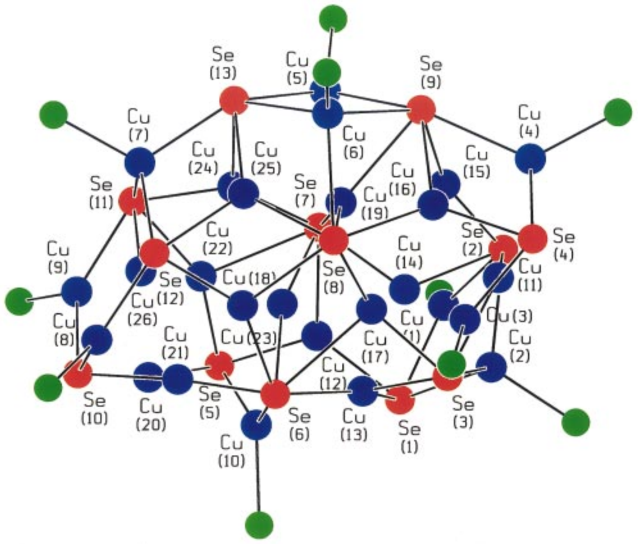

Fig. 4 Molecular structure of [$Cu_{26}Se_{13}(PCy_3)_{10}$] **3** ($Cu^+$: blue; Se^{2-}: red; P: green); Cu–Cu contacts and carbon atoms omitted for clarity

ligand. In turn, the Cu_{12} cuboctahedron that forms the base of all $Cu_{12}Se_6$ clusters is distorted in a new, very irregular manner.[4a,d] The selenium atoms act as μ_4 bridges and form a slightly distorted octahedron. All copper atoms bind to two selenium atoms along the edges of this octahedron. Accordingly, the copper atoms [Cu(1), Cu(2), Cu(3) and their symmetry equivalents] which are also co-ordinated to the phosphine ligands are almost trigonal planar and are shifted away from the cluster core whereas the remaining copper atoms [Cu(4), Cu(5), Cu(6) and their symmetry equivalents] are distorted out of the ideal linear co-ordination towards the centre of the cluster [Se–Cu–Se bond angle 154.7(7)–176.8(5)°]. The Cu–Cu distances range from 253.3(2) to 302.6(3) pm and are, in the main, too long to have any significant bonding interactions.[15]

The molecular structure of compound **3** is shown in Fig. 4. It crystallises in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit. In contrast to **1** this compound contains no symmetry and is much more oval in shape. The Se atoms form a Se_{13} polyhedron, Fig. 5, with triangular faces, and with the selenium atoms roughly arranged in three layers. Such polyhedral Se cages are observed in all other CuSe spherical clusters.[4,6,7] Apart from Cu(2), Cu(6) and Cu(7) which are bound almost tetrahedrally to three selenium atoms and one phosphorus atom, Se_3CuP, the CuP fragments are bound in almost trigonal-planar fashion to two selenium atoms and a phosphorus atom, Se_2CuP. The rest of the copper atoms bind in one of two ways, either trigonal planar (sometimes distorted) to three selenium atoms, Se_2CuSe [Cu(11)–Cu(13), Cu(16), Cu(17), Cu(19), Cu(22)–Cu(26)] or almost linear to two selenium atoms, SeCuSe [Cu(15), Cu(18), Cu(20), Cu(21)] (Se–Cu–Se bond angle 159.6–172.4°). The atom Cu(14) is however very distorted from linearity (Se–Cu–Se bond angle 112.8°) and has a long contact 296.4 pm to a third selenium atom, Se(3), so it can be better described as having almost trigonal-planar co-ordination. The selenium atoms act either as μ_4 [Se(1), Se(4), Se(5)], μ_5 [Se(2), Se(3), Se(10)–Se(13)] or μ_6 [Se(6)–Se(9)] bridges.

The different co-ordination modes of the copper and selenium atoms in various sizes of such clusters has previously been discussed.[4c] Smaller clusters {*e.g.* $[Cu_{12}Se_6(PEtPh_2)_8]$}[4a] tend to contain linear Se–Cu–Se and trigonal planar Se_2CuP fragments, as is observed in compound **2**, whereas larger clusters tend towards trigonal Se_2CuSe and Se_3CuP arrangements {*e.g.* $[Cu_{44}Se_{22}(PEt_2Ph)_{18}]$,[4b] $[Cu_{70}Se_{35}(PEt_3)_{22}]$,[6] $[Cu_{146}Se_{73}(PPh_3)_{30}]$[5]}. In this cluster one observes co-ordination modes common to both large and small clusters, as is also the case in **1**. However no other similarities can be drawn between the two structures, indicating again the high structural influence of the phosphine used. One could possibly also claim an effect on the reaction pathway that results in different structural details of a particular cluster size. The Cu–Cu contacts in **3** range between 251.0 and 305.1 pm. Similar Cu–Cu distances are found in other multinuclear copper compounds, again indicating only weak interactions.[15]

The cluster framework of compound **4** as determined by X-ray analysis is shown in Fig. 6. It crystallises in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The cluster is oblong in shape and is the largest known 'spherical' copper selenide cluster. The Se atoms form a Se_{27} polyhedron around three inner Se atoms [Se(11), Se(14) and Se(17)], Fig. 7, with the selenium atoms roughly arranged in three layers. There are no bonding interactions between the selenium atoms. This Se_{27}

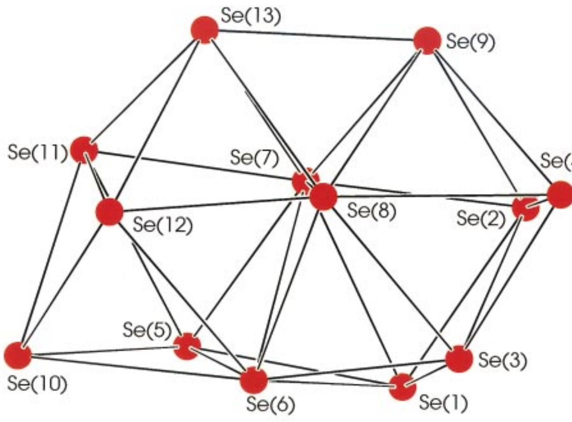

Fig. 5 The selenium cage of compound **3**. Non-bonding Se···Se contacts are shown in the range from 388 to 474 pm

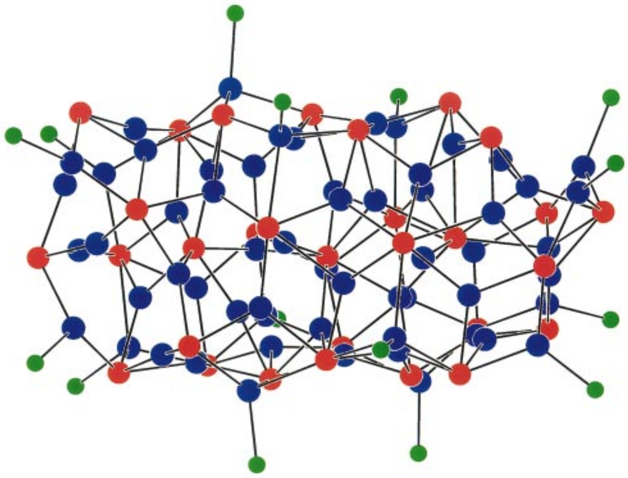

Fig. 6 Molecular structure of $[Cu_{59}Se_{30}(PCy_3)_{15}]$ **4** (Cu^+: blue; Se^{2-}: red; P: green); Cu–Cu contacts and carbon atoms are omitted for clarity

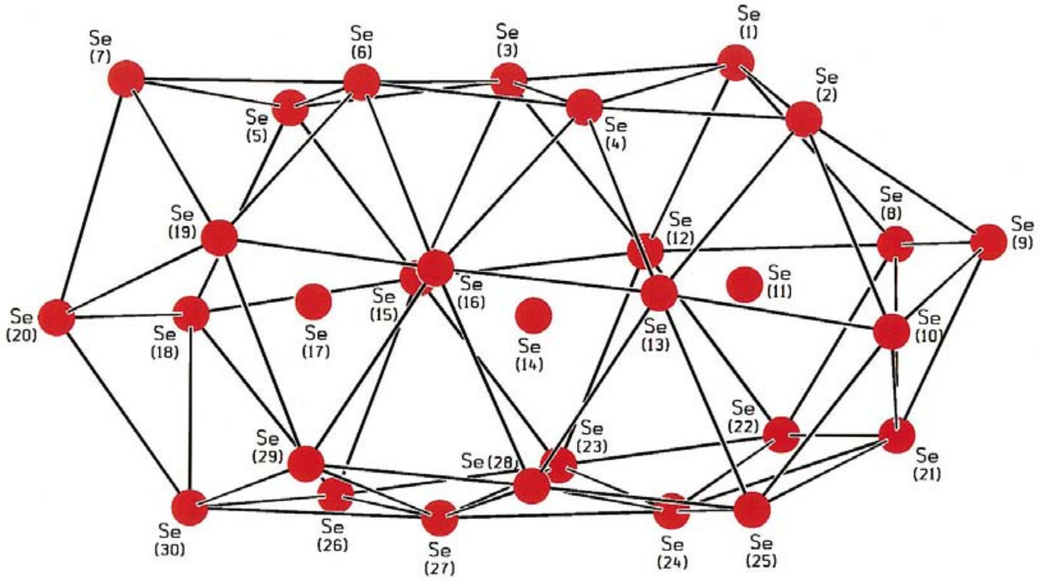

Fig. 7 The selenium cage of compound **4**. Non-bonding Se···Se contacts are shown in the range from 396 to 467 pm. For clarity, Se···Se contacts concerning the central Se atoms [Se(11), Se(14), Se(17)] are not drawn

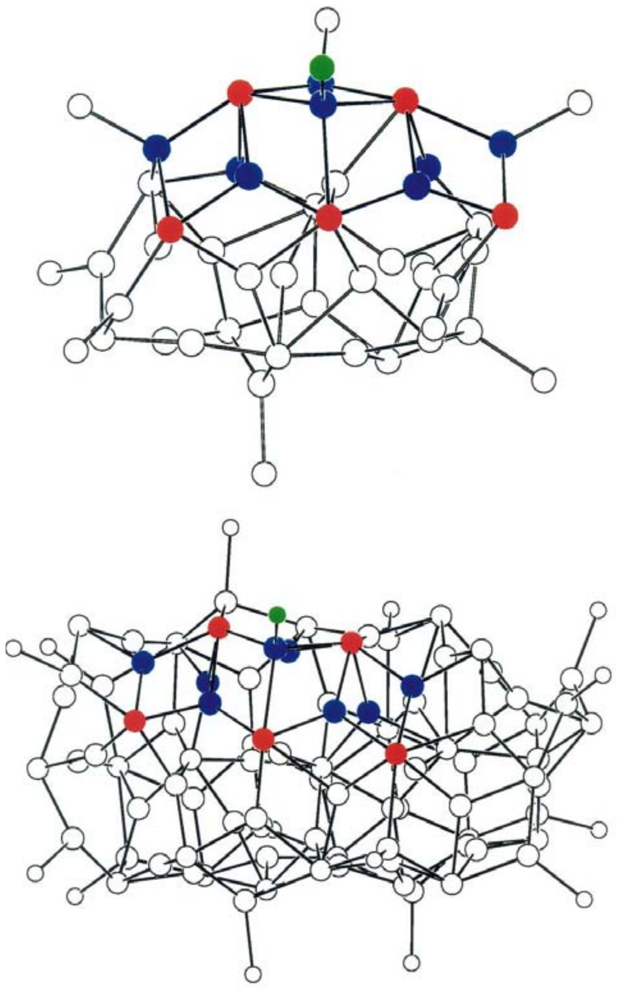

Fig. 8 Common motif [Cu_8Se_5P] found in both compounds **3** and **4** highlighted in both structures (Cu^+: blue; Se^{2-}: red; P: green)

polyhedron is made up of triangular faces with three square faces [Se(1), Se(2), Se(8), Se(9); Se(5), Se(7), Se(18), Se(20); Se(19), Se(20), Se(29), Se(30)] which are situated two at one end of the oblong and one at the other end.

The CuP fragments bind in one of two ways. Either along an Se–Se edge forming bonds to two selenium atoms and therefore roughly in trigonal-planar co-ordination [Cu(1)–Cu(9)] or at a Se triangular face and therefore almost tetrahedrally co-ordinated [Cu(10)–Cu(15)]. The other copper atoms bind in one of three ways. The atoms Cu(16)–Cu(25) have two Se neighbours and are very distorted from the ideal linear co-ordination [Se–Cu–Se bond angle 144.3(2)–170.2(3)°]. The atoms Cu(26)–Cu(58) bind to three Se atoms and have approximately trigonal-planar co-ordination. The atom Cu(59) is bound to four selenium atoms in a slightly distorted tetrahedron. The selenium atoms act as μ_4 [Se(2), Se(7), Se(20), Se(29)], μ_5 [Se(1), Se(8)–Se(10), Se(15), Se(19), Se(21), Se(22), Se(24)–Se(26), Se(30)], μ_6 [Se(3)–Se(6), Se(12), Se(14), Se(16)–Se(18), Se(23), Se(27), Se(28)] or as μ_7 [Se(11), Se(13)] bridges.

Considering the size of this cluster it is interesting to note that we observe co-ordination modes found in both the small and large clusters even though it is larger than [$Cu_{44}Se_{22}(PEt_2Ph)_{18}$], in which only Se_2CuSe and Se_3CuP co-ordination occurs. Moreover, **4** (in common with **1**) exhibits a Se_3CuSe arrangement [Cu(59)] which is more rarely observed {*e.g.* in [$Cu_{48}Se_{24}(PMe_2Ph)_{20}$][4c]}. The variable co-ordination numbers of the selenium atoms is in keeping with the other known Cu_2Se clusters of this size. However no obvious topological similarity with that of the bulk material Cu_2Se is observed except for the range of the co-ordination numbers and the interatomic distances.

Another slightly unusual feature of **4** is that the Cu : Se ratio is not 2 : 1 which indicates a mixed-valence compound. There are however two other examples of Cu_2Se clusters, [$Cu_{20}Se_{13}(PEt_3)_{12}$][6] and [$Cu_{29}Se_{15}(PPr^i_3)_{12}$],[7] and also a few CuTe clusters[16] in which this is also the case. Also copper selenide itself is known to have phases $Cu_{2-x}Se$ in which the Cu : Se ratio is less than 2 : 1.[17] The Cu–Cu contacts in **4** range between 241.7(7) and 305.6(5) pm.

The results presented herein extend the series of known copper selenium clusters, showing how changing the nature of the phosphine ligand and slight variation of the reaction conditions provides access to new clusters. Yet it is not certain whether **1** and **2** should be discussed as isolated intermediates during the growth of bigger clusters. There is no evidence for close topological relationships between **1** and [$Cu_{44}Se_{22}(PEt_2Ph)_{18}$] or **2** and **4**, respectively. Therefore it is more likely that **1** and **2** are products of separate cluster formation pathways. If, however, one compares the structures of **3** and **4** one finds a motif of 14 atoms (Cu_8Se_5P) which occurs in both compounds. In Fig. 8 the common motif is highlighted in both molecules, but for the sake of clarity it is only shown once in **4** although it occurs four times altogether in this compound. It is therefore possible that **3** is an intermediate in the reaction pathway for the formation of **4**. At the very least similar reaction pathways are followed in the formation of these compounds. This shows once more than one has to consider a complex equilibrium for a given system CuOAc–$E(SiMe_3)_2$–PR_3, providing several possible cluster compounds on a flat energy hyperface.[4c,15d]

Ab intio calculations on the new $Cu_{12}Se_6$ structure, for comparison purposes to those already known, and density functional calculations (DFT) for the two $Cu_{26}Se_{13}$ structures, **1** and **3**, are currently being undertaken. Furthermore the family of clusters formed with the tricyclohexylphosphine ligand provide a good starting point for the investigation of the physical properties of such compounds and their dependence on the size of the cluster.

References

1 (*a*) G. Schmid (Editor), *Clusters and Colloids, From Theory to Applications*, VCH, Weinheim, 1994; (*b*) L. J. de Jongh (Editor), *Physics and Chemistry of Metal Cluster Compounds*, Kluwer, Dordrecht, 1994.

2 I. Dance and G. Lee, *Spec. Publ. R. Soc. Chem.*, 1993, 131.

3 I. Dance and K. Fischer, *Prog. Inorg. Chem.*, 1994, **41**, 637; L. C. Roof and J. W. Kolis, *Chem. Rev.*, 1993, **93**, 1037; J. Arnold, *Prog. Inorg. Chem.*, 1995, **43**, 353.

4 (*a*) S. Dehnen, A. Schäfer, D. Fenske and R. Ahlrichs, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 764; (*b*) S. Dehnen and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2287; (*c*) S. Dehnen and D. Fenske, *Chem. Eur. J.*, 1996, **2**, 1407; (*d*) D. Fenske, A. C. Deveson and S. Dehnen, *J. Clust. Sci.*, 1996, **7**, 351.

5 H. Krautscheid, D. Fenske, G. Baum and M. Semmelmann, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1303.

6 D. Fenske and H. Kraustscheid, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1452.

7 D. Fenske, H. Krautscheid and S. Balter, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 796.

8 D. van der Putten, D. Olevano, R. Zanoni, H. Krautscheid and D. Fenske, *J. Electron Spectrosc. Relat. Phenom.*, 1995, **76**, 207.

9 D. A. Edwards and R. Richards, *J. Chem. Soc., Dalton Trans.*, 1973, 2463.

10 H. Krautscheid, Ph.D. Thesis, Universität Karlsruhe, 1991.

11 *Anorganische Synthesechemie*, ed. B. Heyn, Springer Verlag, Berlin, 1990; M. Müller, Ph.D. Thesis, Universität Karlsruhe, 1990.

12 G. Sheldrick, SHELXS 86, Program for the solution of Crystal Structures, University of Göttingen, 1986.

13 G. Sheldrick, SHELXL 93, Program for Crystal Structure Determination, University of Göttingen, 1993.

14 E. Keller, SCHAKAL 92, A Computer Program for the Graphic Representation of Molecular and Crystallographic Models, Universität Freiburg, 1992.

15 (*a*) F. A. Cotton, X. Feng, M. Matusz and R. Poli, *J. Am. Chem. Soc.*, 1988, **110**, 7077; (*b*) C. Kölmel and R. Ahlrichs, *J. Phys. Chem.*, 1990, **94**, 5536; (*c*) A. Schäfer and R. Ahlrichs, *J. Am. Chem. Soc.*, 1994, **116**, 10 686; (*d*) P. K. Mehrotra and R. Hoffmann, *Inorg. Chem.*, 1978, **17**, 2187; (*e*) R. Mason and D. M. P. Mingos, *J. Organomet. Chem.*, 1973, **50**, 53; (*f*) K. M. Merz, jun. and R. Hoffmann, *Inorg. Chem.*, 1988, **27**, 2120.

16 J. F. Corrigan, S. Balter and D. Fenske, *J. Chem. Soc., Dalton Trans.*, 1996, 729; D. Fenske and J. Steck, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 238.

17 A. L. N. Stevens and F. Jellinek, *Recl. Trav. Chim. Pays-Bas*, 1971, **90**, 273; R. MacLaren Murray and R. D. Heyding, *Can. J. Chem.*, 1975, **53**, 878.

Received 6*th August* 1997; *Paper* 7/05750D