Discrete copper(I) clusters with $Cu_6P_6Se_6$ and $Cu_6P_4Se_6$ cores†

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The reactions of chalcogenophosphinites with copper(I) metal salts are shown to yield highly stable, multi-metallic copper–chalcogen based clusters with novel topologies.

Cluster complexes of copper chalcogenolates are of high interest due to their potential and practical applications as precursors to copper chalcogenide thin-films[1] and nanoparticles,[2] as catalysts for organic transformations,[3] and as biomimetic models to proteins and electron-transfer centres.[4] Our research has previously focussed upon the development of novel chalcogeno-phosphorus anionic ligand systems[5,6] and we were keen to see if these ligands could act as building blocks for the preparation of novel copper–chalcogen based clusters. The use of chalcogeno-phosphorus ligands for the preparation of multi-metallic copper clusters is well documented with a large number of Cu(I) dichalcogenophosph(in)ates already reported,[7] including a series of very stable cubic Cu(I) clusters of general formula $[Cu_8(\mu_8\text{-}X)\{E_2P(OR)_2\}_6]^{z-}$ (R = Me, Et, *i*Pr; E = S, Se; X = Cl, Br, I (*z* = 1) S, Se (*z* = 0)), some of which have been shown to act as highly active precatalysts for carbon–heteroatom bond-forming reactions.[3] In addition, the tripodal phosphonate homologs $[RP(O)S_2]^{2-}$ and $[RPS_3]^{2-}$ have recently been demonstrated to form cluster complexes with Cu(I) and other Group 11 metal centres.[8] Despite these recent advances there are currently, to our knowledge, no reported studies on the coordination chemistry of chalcogenophosphinite ligands $[R_2PE]^-$ (E = S, Se, Te) with any of the Group 11 metals, even though the propensity of these ligands to adopt bridging coordination modes[5,9] makes them an ideal choice for cluster forming reactions. We now report on the synthesis and solid-state structures of a new class of Cu(I) multi-metallic cluster with selenophosphinite ligands.

Addition of $Cu(CH_3CN)_4PF_6$ and NEt_3 to an acetonitrile solution of $Ph_2P(Se)H$ (prepared *in situ* from the reaction of 1.2 equiv. Ph_2PH with 1 equiv. elemental Se—a slight excess of phosphine was used to prevent formation of the diselenophosphinate[5]) gave a yellow solid which was washed with deoxygenated water, dissolved in CH_2Cl_2 and slowly diffused with pentane over several days to yield yellow crystals of $[Cu_6(SePPh_2)_6(HPPh_2)_4]\cdot 4CH_2Cl_2$ (**1**$\cdot 4CH_2Cl_2$). The structure of **1** was obtained using single-crystal X-ray diffraction‡ (Fig. 1).

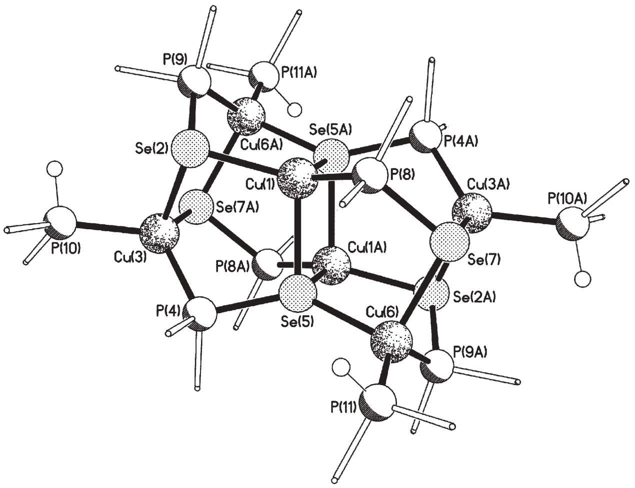
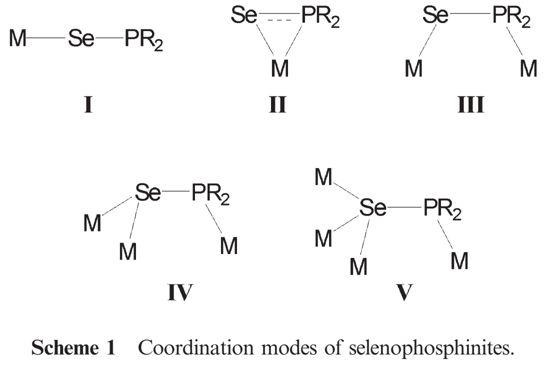


Fig. 1 The molecular structure of the C_i-symmetric complex **1**. Phenyl groups have been omitted for clarity.

The key structural feature of **1** is the $Cu_6P_6Se_6$ core which is constructed from the aggregation of six Cu(I) centres and six $[Ph_2PSe]^-$ ligands. In the centre of the cluster is a four membered Cu_2Se_2 ring containing two distorted tetrahedral Cu centres, each coordinated to four different selenophosphinite units. The remaining four Cu centres within the cluster also adopt close to tetrahedral geometries, each coordinating to three selenophosphinite ligands and a Ph_2PH secondary phosphine unit. Cu–Se bond distances in **1** are in the range 2.4421(14) to 2.5510(14) Å (mean 2.494 Å) and Cu–P bonds in the range 2.225(3) to 2.283(2) Å (mean 2.256 Å). Previously reported coordination modes for selenophosphinites are shown in Scheme 1 (modes **I**, **II** and **III**).[5,10,11] Therefore in **1** two new bonding geometries for selenophosphinites are observed—coordination modes **IV** and **V**. Four of the selenophosphinite ligands in **1** adopt coordination mode **IV**, bridging three copper centres: μ_1 from P and μ_2 from Se (P–Se = 2.233(2), 2.255(2) Å). The remaining two selenophosphinites are present in coordination mode **V**, bridging four metal centres: μ_1 from P and μ_3 from Se (P–Se = 2.336(2) Å). In both coordination modes the P–Se bond is close in length to that expected for a P–Se single bond (2.26 Å),[5] indicating that the



Scheme 1 Coordination modes of selenophosphinites.

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negative charge is predominately localised on the Se atom to give the $Ph_2P–Se^-$ tautomer with negligible contribution from the $Ph_2P(=Se)^-$ tautomer.

Since it was unclear whether the terminal secondary phosphine units in **1** arose due to the excess secondary phosphine used in the synthetic protocol or alternatively from P=Se bond scission[12] of the selenophosphinite, the experimental procedure for **1** was repeated except this time using a stoichiometric amount of secondary phosphine (*i.e.*, 1 equiv.). The reaction again proceeded to initially give a yellow solid which was washed with water, dissolved in CH_2Cl_2, filtered and slowed diffused with pentane to give yellow crystals. These crystals were identified using single-crystal X-ray diffraction‡ to be a mixture of $\mathbf{1}\cdot 4CH_2Cl_2$ and the new cluster $[Cu_6(SePPh_2)_6(HPPh_2)_3]$ (**2**). Similar to **1**, **2** contains a $Cu_6P_6Se_6$ core comprising six bridging selenophosphinite ligands and six Cu(I) centres (Fig. 2). The P–Se bond lengths in **2** are in the range 2.239(3) to 2.244(2) Å, again indicative of P–Se single bonds. However **2** differs from **1** in having on average one less $HPPh_2$ ligand per cluster. The complex is disordered over a centre of symmetry, and can best be considered with the P(10) $P(H)Ph_2$ unit being only on one "side" of the complex (see the supporting information† for a fuller explanation of the disorder present). Therefore in **2** Cu(3) is four coordinate to three selenophosphinite ligands and a secondary phosphine unit, whereas Cu(3′) is just three coordinate to three selenophosphinite ligands and adopts a close to planar geometry (sum of angles around Cu(3′) = 358.8°). Concomitant with the decrease in coordination number, there is an observed shortening of the bond lengths to this atom: Cu(3′)–Se(2A) = 2.364(6), Cu(3′)–Se(7) = 2.362(6) and Cu(3′)–P(4A) = 2.169(6) Å. The change in geometry about the Cu(3′) centre *cf.* Cu(3) also results in the copper centre being drawn more towards the centre of the cluster, thus generating a Cu···Cu contact distance with Cu(1A) of 3.026(5) Å (*cf.* Cu(1)···Cu(3) = 3.580(5) Å). This short Cu···Cu distance is comparable in length to previously reported Cu···Cu contacts within cubic copper(I) dichalcogenophosph(in)ate clusters (which typically lie in the range 2.9 to 3.4 Å).[7] There has been much debate concerning the nature and significance of the $d^{10}\cdots d^{10}$ interactions between the metal centres in these dichalcogenophosph(in)ate and related Cu(I) cubic clusters. Recently, theoretical studies have demonstrated that these Cu···Cu interactions are likely to be weak, with the chelating effect of the ligands playing a far more important role in the overall stability of the clusters.[7a,13] On the basis of these previous studies it seems highly probable that the Cu–Se and Cu–P bonds, rather than any Cu···Cu interactions, are responsible for the cluster topology observed in **2**.

The presence of secondary phosphines in the products (**1**, **2**) of the reaction employing a phosphine : Se 1 : 1 ratio suggests either the selenophosphinite was not fully formed in solution prior to reaction with the copper salt or alternatively that the lability of the P=Se bond[12] leads to bond scission thus regenerating the secondary phosphine, possibly with simultaneous generation of copper selenide clusters or nanoclusters.[14] ^{31}P NMR spectroscopic studies on the reaction mixture prior to addition of the copper salt suggest the latter of these explanations to be the more likely since $Ph_2P(Se)H$ (δ = 7.99 ppm, $^1J_{PSe} = -757$ Hz) was identified as by far the predominate species in solution with only trace amounts of Ph_2PH ($\delta = -35.47$ ppm) observable.

In an alternative procedure the yellow solid obtained from the reaction of $Cu(CH_3CN)_4PF_6$, NEt_3 and $Ph_2P(Se)H$ was washed with water then heated at reflux for 30 mins in CH_2Cl_2. On cooling orange crystals of $[Cu_6(SePPh_2)_4(SeCH_2SePPh_2)_2(HPPh_2)_2]$ (**3**) grew slowly over several days. X-ray crystallographic studies‡ reveal the structure of **3** (Fig. 3) to exhibit some similar features to the structures of **1** and **2**: all lie on a crystallographic centre of symmetry and contain six Cu(I) centres and four selenophosphinite ligands with coordination mode **IV** (P–Se = 2.226(3), 2.230(2) Å).

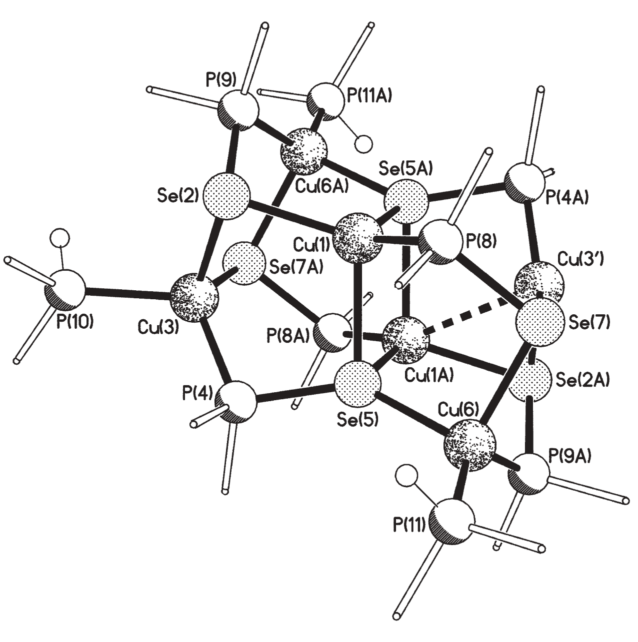

Fig. 2 The molecular structure of **2**. Phenyl groups have been omitted for clarity.

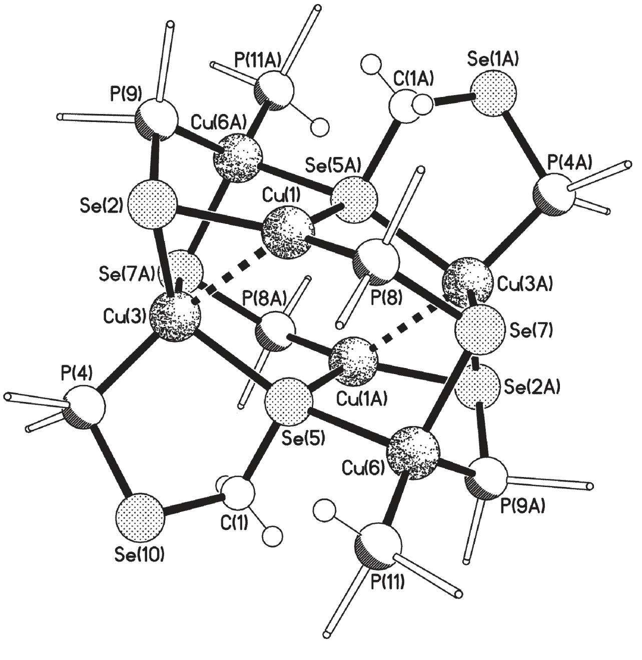

Fig. 3 The molecular structure of the C_i-symmetric complex **3**. Phenyl groups have been omitted for clarity.

However, the structures differ in that the remaining two selenophosphinites which exhibited coordination mode **V** in **1** and **2** are no longer present in **3** and can be considered to have been replaced by two unique $Ph_2PSeCH_2Se^-$ ligands. These $Ph_2PSeCH_2Se^-$ ligands coordinate μ_1 to Cu(3) from the phosphorus centre and μ_3 to Cu(1A), Cu(3) and Cu(6) from the selenolate atom Se(5), hence forming a five membered chelate with Cu(3). The P–Se and C–Se bonds within this chelate are all single bonds: P(4)–Se(10) = 2.236(3), Se(10)–C(1) = 1.991(10), C(1)–Se(5) = 1.937(10) Å. Formation of the chelate ring also results in the extrusion of the phosphorus P(4) from the central core of the cluster to yield a new $Cu_6P_4Se_6$ core. There is also a significant elongation of the Cu(1)–Se(5) distance, presumably due to the steric requirements of the new 5-membered chelate ring. As a consequence of this the central Cu_2Se_2 ring observed in **1** and **2** is not present in **3**, and the copper centres Cu(1) and Cu(1A) now adopt approximately trigonal-planar coordination geometries (sum of angles about Cu(1) = 358.24°). Analogously to Cu(3) in **2** (*vide supra*), these three coordinate copper centres form shorter bonds with the selenophosphinite ligands when compared to the four coordinate copper centres: Cu(1)–P(8) = 2.212(2), Cu(1)–Se(2) = 2.3471(16), Cu(1)–Se(5A) = 2.4027(15) Å. In addition they exhibit close Cu···Cu contacts (2.8043(18) Å) with a neighbouring tetrahedral copper centre (Fig. 3).

The formation of the novel $Ph_2PSeCH_2Se^-$ ligand in the synthesis of **3** can be rationalised as arising from the reaction of CH_2Cl_2 solvent with a selenophosphinite anion to give $Ph_2PSeCH_2^-$ followed by subsequent reaction with Se (derived from P=Se bond scission of $Ph_2P(Se)H$). In related reactions Liu *et al.*[15] have shown copper(I) dithiophosphates can abstract Cl^- from CH_2Cl_2 under certain conditions, and several groups have reported on metal thiolates undergoing alkylation in dichloromethane solvent whereby a methylene group derived from CH_2Cl_2 inserts directly into the metal–thiolate bond to yield a thioether.[16]

All three new clusters presented here (**1–3**) are air, moisture and temperature stable. Although the low solubility of **1–3** in virtually all solvents has prohibited their full characterisation using ^{31}P and ^{77}Se NMR spectroscopy, all show satisfactory elemental analyses and characteristic ν(P–H) stretches at 2309 cm^{-1} in the IR spectra of their nujol mulls.

In conclusion, the clusters **1**, **2** and **3** represent the first examples of a new class of multi-metallic copper cluster synthesised from the reaction of Cu(I) salts with chalcogenophosphinite ligands. The ability to in effect remove a secondary phosphine from **1** to give **2** without significantly altering the topology of the cluster-core is of interest as it suggests these clusters maybe of utility for catalytic applications, an area of interest we are currently investigating. The structure of **3** is also of particular note due to the unusual selenolate ligand present, formed as a result of incorporation of a methylene group derived from CH_2Cl_2. Routes to the thio and telluro homologs of these clusters are currently under investigation.

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Notes and references

‡ Crystal data for **1**: $C_{120}H_{104}Cu_6P_{10}Se_6\cdot 4CH_2Cl_2$, M = 3050.44, triclinic, $P\bar{1}$ (no. 2), a = 15.440(2), b = 15.973(4), c = 16.656(3) Å, α = 62.152(13), β = 64.756(10), γ = 89.518(13)°, V = 3190.4(10) $Å^3$, Z = 1 (C_i symmetry), D_c = 1.588 g cm^{-3}, μ(Mo-Kα) = 3.033 mm^{-1}, T = 183 K, yellow plates; 7770 independent measured reflections, F^2 refinement, R_1 = 0.054, wR_2 = 0.097, 5039 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 45°], 634 parameters. **2**: $C_{108}H_{93}Cu_6P_9Se_6$, M = 2524.55, monoclinic, $P2_1/n$ (no. 14), a = 16.776(2), b = 14.959(3), c = 20.173(6) Å, β = 99.657(19)°, V = 4990.6(19) $Å^3$, Z = 2 (C_i symmetry, see text), D_c = 1.680 g cm^{-3}, μ(Cu-Kα) = 5.631 mm^{-1}, T = 293 K, yellow plates; 7398 independent measured reflections, F^2 refinement, R_1 = 0.061, wR_2 = 0.146, 4589 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 120°], 667 parameters. **3**: $C_{98}H_{86}Cu_6P_8Se_8$, M = 2524.35, monoclinic, $P2_1/n$ (no. 14), a = 13.1362(12), b = 22.2016(14), c = 17.6252(14) Å, β = 106.850(7)°, V = 4919.6(7) $Å^3$, Z = 2 (C_i symmetry), D_c = 1.704 g cm^{-3}, μ(Cu-Kα) = 6.372 mm^{-1}, T = 203 K, orange/yellow blocks; 7269 independent measured reflections, F^2 refinement, R_1 = 0.060, wR_2 = 0.135, 5605 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 120°], 445 parameters. CCDC 604049 to 604051. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605191j

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