measured reflections, 6519 were independent and 5518 observed with $I > 2\sigma(I)$, $-25 < h < 24$, $-25 < k < 24$, $-6 < l < 10$; $R_1 = 0.0659$, $wR_2 = 0.1503$, GOF = 1.258 for 373 parameters, $\Delta\rho_{max} = 2.335\ e\,Å^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentzian and polarization corrections and absorption correction SADABS were applied, $\mu = 1.318\ mm^{-1}$, min./max. transmission 0.6627/0.8773. The coordinates of the hydrogen atoms were calculated in SHELXL using an appropriate riding model with varied thermal parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136903. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Copper Chalcogenolate Complexes as Precursors to Ternary Nanoclusters: Synthesis and Characterization of $[Hg_{15}Cu_{20}S_{25}(nPr_3P)_{18}]$[**]

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The chemistry and physics of binary semiconductor nanoclusters and colloids have been the focus of much attention due to the interesting electronic properties displayed by these nanometer sized "Q-particles".[1] The use of bis-silylated reagents $E(SiMe_3)_2$ (E = S, Se, Te) as a chalcogen source has led to the synthesis of near monodisperse XII-XVI particles [2] and a wealth of structural chemistry in copper chalcogenide complexes including the nanocluster $[Cu_{146}Se_{73}(PPh_3)_{30}]$.[3] It has also been shown that the monosilylated chalcogen reagents $RESiMe_3$ and $ArESiMe_3$ can yield mixed metal–chalcogenide–chalcogenolate complexes via subsequent chalcogen–carbon bond cleavage of the first formed metal–chalcogenolate cluster complexes.[4]

The importance of ternary semiconductor solids [5] prompts us to develop a general route into related nanometer sized ternary clusters.[1a] Brennan and co-workers have recently described the formation of ternary lanthanide-chalcogenolates [6] and Kanatzidis et al. have illustrated the utility of molecular copper–indium chalcogenolates for the generation of ternary solids.[7] We are developing suitable reagents for ternary nanocluster synthesis by targeting the reactive metal–silylchalcogenolate complexes $[L_nM{-}ESiMe_3]$, which can be used as a source of "metallachalcogenolate" (metal chalcogenide, $M{-}E^-$) fragments for the synthesis of polynuclear complexes of the type $[L_n(M'ME)_x]$.

Despite the propensity for chalcogenolate ligands to adopt bridging coordination modes, terminal coordination can be promoted by using bulky substituents about the chalcogen center [8] or by restricting the number of vacant coordination sites about the metal.[9] Herein we describe the synthesis of the tetrahedral copper–chalcogenolate complexes $[(nPr_3P)_3Cu{-}ESiMe_3]$ (**1a**, E = S; **1b**, E = Se; **1c**, E = Te) and demonstrate their utility in ternary nanocluster synthesis with the formation of $[Hg_{15}Cu_{20}S_{25}(nPr_3P)_{18}]$ **2** in high yield.

When CuOAc is treated with four equivalents of nPr_3P and one equivalent of $E(SiMe_3)_2$ at −40 °C, complexes **1a**–**c** are

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isolated in good yields as viscous oils at room temperature [Eq. (1)]. The oils readily solidify as colorless crystals when cooled slowly to $-5\,^\circ C$. Although relatively stable as neat liquids under inert atmosphere (**1c** is the least stable), the copper–chalcogenolate complexes rapidly undergo a series of condensation reactions to form copper–chalcogenide clusters if allowed to stand in solution.[10]

$$\mathrm{CuOAc} + 4\,n\mathrm{Pr_3P} + \mathrm{E(SiMe_3)_2} \longrightarrow (n\mathrm{Pr_3P})_3\mathrm{CuESiMe_3}\ (\mathbf{1}) + \mathrm{AcOSiMe_3} + n\mathrm{Pr_3P} \qquad (1)$$

The molecular structure of $[(n\mathrm{Pr_3P})_3\mathrm{Cu\text{-}SSiMe_3}]$ (**1a**, Figure 1)[11] illustrates the tetrahedral coordination geometry of the copper(I) center and the pendant $\mathrm{SiMe_3}$ moiety bonded to the sulfur atom [Cu–S = 2.397(1), S–Si = 2.078(1) Å; ∡Cu-S-Si = 129.20(5)°].

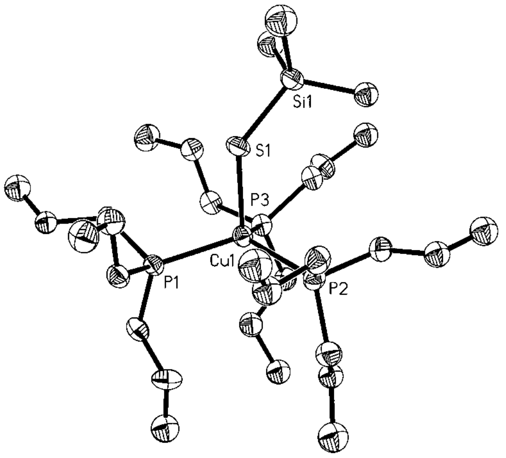

Figure 1. The molecular structure of $[(n\mathrm{Pr_3P})_3\mathrm{Cu\text{-}SSiMe_3}]$ (**1a**, hydrogen atoms omitted, thermal ellipsoids are drawn at the 40% probability level). Selected interatomic distances [Å] and angles [°]: Cu–P 2.284(1)–2.3011(9), Cu1–S1 2.397(1), S1–Si1 2.078(1); P-Cu1-P 111.77(4)–119.87, P-Cu1-S1 100.06(3)–109.77(4), Si1-S1-Cu1 129.20(5). Each carbon atom around Si1 was disordered over two sites.

Due to the labile nature of the phosphine ligands bonded to the copper center, in conjunction with the expected reactivity of the S–SiMe$_3$ moiety,[12] we reasoned that **1a** would serve as a good source of "metallathiolate" Cu–S$^-$ when reacted with a second metal salt. Thus, when **1a** is treated with 0.5 equivalents of $[(n\mathrm{Pr_3P})_2\mathrm{Hg(OAc)_2}]$ at $-30\,^\circ C$, orange crystals of $[\mathrm{Hg_{15}Cu_{20}S_{25}}(n\mathrm{Pr_3P})_{18}]$ (**2**) form in good yields within a few hours [Eq. (2)].

$$(n\mathrm{Pr_3P})_3\mathrm{CuSSiMe_3} + 2\,n\mathrm{Pr_3P} + 0.5\,\mathrm{Hg(OAc)_2} \longrightarrow [\mathrm{Hg_{15}Cu_{20}S_{25}}(n\mathrm{Pr_3P})_{18}]\ (\mathbf{2}) \qquad (2)$$

An X-ray analysis [11] provided full structural details (Figure 2) and illustrates the intimate mixing of the three core elements. The molecule resides on a crystallographic $\bar{3}$ site with the three-fold axis along the Hg2–S5 vector. There is some disorder about the central sulfide ion S5 where atoms Hg3 and Cu3 are each statistically distributed over six equivalent centers (see supplementary material). Twenty-five sulfide (S^{2-}) ions bridge the Cu and Hg centers. There are no unusually short Cu–Hg contacts. The Hg atoms adopt either near linear (Hg1; ∡S1-Hg1-S2 = 177.0(3)°) or trigonal coordination (Hg2–5; sum of the angles = 352.5–358.5°), although for atoms Hg3–5, the third Hg–S contact is markedly longer (2.73–2.98 Å) than the other two (2.22(1)–2.45(1) Å). The copper centers have coordination numbers three (Cu2–3) and four (Cu1, 4–5). None of the fifteen Hg atoms is bonded to a phosphine ligand, whereas metal centers Cu1 and its symmetry equivalents are each bonded to two phosphorus centers and sites Cu4 and Cu5 also form single Cu–P bonds. Cu–Cu and Hg–Hg contacts are 2.54 and 3.35 Å, respectively, which is consistent with oxidation states +1 (Cu) and +2 (Hg) for the d^{10} metal centers. The 25 sulfur ligands bridge either three (S3, S5) or four (S1, S2, and S4) metal centers. The molecule contains a 0.7 × 1.2 nm CuHgS core that is enveloped in a tri-*n*-propylphosphine ligand shell.

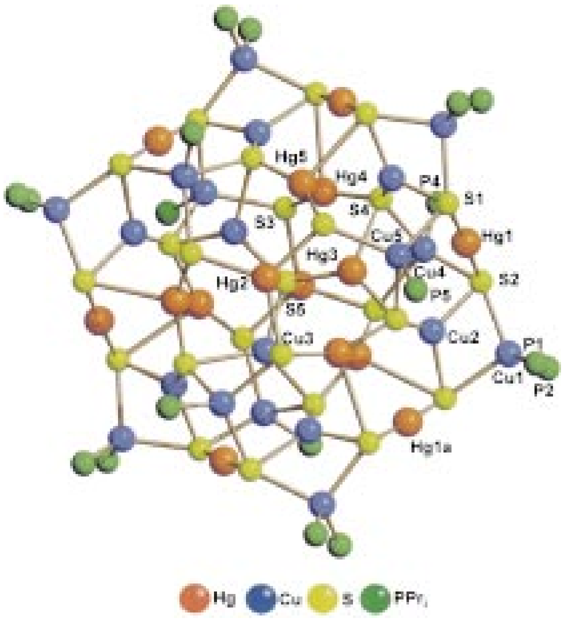

Figure 2. The molecular structure of $[\mathrm{Hg_{15}Cu_{20}S_{25}}(n\mathrm{Pr_3P})_{18}]$ (**2**, carbon atoms omitted for clarity). Selected bond lengths and angles are discussed in the text.

Using this strategy we have now isolated several CuHgE (E = S, Se, Te) nanoclusters and these findings will be reported shortly.[10] Interestingly, varying the ratio of **1a**:Hg(OAc)$_2$:nPr$_3$P has yet to afford polynuclear HgCuS complexes other than **2**. The approach of using a silylated "CuE" precursor has allowed the intimate mixing of the three core elements at low temperatures, with a general distribution of the metal centers within the (nonbonded) S25 polyhedron. The strategy outlined above for the synthesis of phosphane-stabilized copper-mercury sulfide clusters offers a powerful route into a variety of ternary clusters and colloids.

Experimental Section

Synthesis of **1**: CuOAc (1.84 g, 14.5 mmol) was dissolved in ether (25 mL) with four equivalents of nPr$_3$P to give a colorless solution. The solution was cooled to $-40\,^\circ C$ and one equivalent of E(SiMe$_3$)$_2$ was added to give a clear pale yellow solution after stirring. The reaction mixture was allowed to warm up slowly to $-5\,^\circ C$, with stirring. After three hours at this temperature, the solvent was removed in vacuo to leave a white solid. The solid was redissolved in cold ether (5 mL) and cooled to $-30\,^\circ C$. Colorless crystals of **1** formed within a few hours in high yield. Crystals of **1** are low melting solids (≈5 °C). Whilst **1a** and **1b** are stable at room temperature, **1c** decomposes rapidly to yield elemental tellurium. X-ray quality crystals of **1a–c** were obtained in each case, although only the structure of **1a** is reported here. Satisfactory elemental analyses were obtained for **1a**, **1b**, and **2**. **1a**: Yield >90%; $^{31}P\{^1H\}$ NMR (−50°C, [D$_8$]toluene) −21.5(s). **1b**: Yield 80%; $^{31}P\{^1H\}$ NMR (−50°C, [D$_8$]toluene) −27.0(s). **1c**: Yield >90%; $^{31}P\{^1H\}$ NMR (−50°C, [D$_8$]toluene) −29.9(br.s). Synthesis of **2**: Mercuric acetate (0.63 g, 1.98 mmol) was dissolved with nPr$_3$P (0.64 mL, 4 mmol) in THF (15 mL) and cooled to −65°C. This clear solution was added to a freshly prepared solution of **1a** with excess nPr$_3$P. Upon warming to −30°C, the solution became bright orange and, within several hours at this temperature, orange crystals (0.62 g, 60%) of **2** appeared.

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[11] X-ray structure analyses: Enraf-Nonius Kappa CCD diffractometer (Mo$_{K\alpha}$ radiation). Crystal data for $C_{30}H_{72}P_3CuSSi$ **1a**: colorless polyhedron, $M_r = 649.48$, triclinic, space group $P\bar{1}$, $a = 10.9010(2)$, $b = 11.1233(2)$, $c = 17.3734(2)$ Å, $\alpha = 92.8890(11)$, $\beta = 97.3160(11)$, $\gamma = 105.1140(7)°$, $V = 2009.48(6)$ Å^3, at 200 K, $Z = 2$, $\rho_{calcd} = 1.073\ \mathrm{g\,cm^{-3}}$, $\mu = 0.761\ \mathrm{mm^{-1}}$, $2\theta_{max} = 41.6°$, 11440 reflections collected, 4058 independent ($R_{int} = 0.037$). The structure was solved by direct methods and refined on F^2 using SHELXTL software. Data were corrected for Lorentz and polarization effects. No absorption corrections were performed. All atoms (with the exception of disordered carbon sites, see supplementary material) were refined anisotropically and hydrogen atoms were included as riding on their respective carbon atoms, 307 parameters). Final $R = 0.0357$ ($wR_2 = 0.0851$) and GoF = 1.058. Largest difference peak and hole = 0.34 and −0.25 e Å^{-3}, respectively. For $C_{162}H_{378}P_{18}Cu_{20}S_{25}Hg_{15}$ **2**: orange polyhedron, $M_r = 7965.25$, rhombohedral, space group $R\bar{3}$, $a = 23.5814(9)$, $c = 43.376(2)$ Å, $V = 20889.1(15)$ Å^3, at 200 K, $Z = 3$, $\rho_{calcd} = 1.900\ \mathrm{g\,cm^{-3}}$, $\mu = 10.044\ \mathrm{mm^{-1}}$, $2\theta_{max} = 40.0°$, 8646 reflections collected, 4339 independent ($R_{int} = 0.0744$). The structure was solved and refined as for **1a** except C atoms were refined isotropically, P–C and C–C distances were each refined with common values, and H atoms were not included. Final $R = 0.0709$ ($wR_2 = 0.2167$) and GOF = 1.102. Largest difference peak and hole = 1.11 and −1.21 e Å^{-3}, respectively. Atoms Cu3 and Hg3 were statistically distributed over the six equivalent positions ($\bar{3}$) around S5. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135160 and -135161. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Stereocontrol in Pinacol Ring-Contraction of Cyclopeptidyl Glycols: The Diazonamide C_{10} Problem[**]

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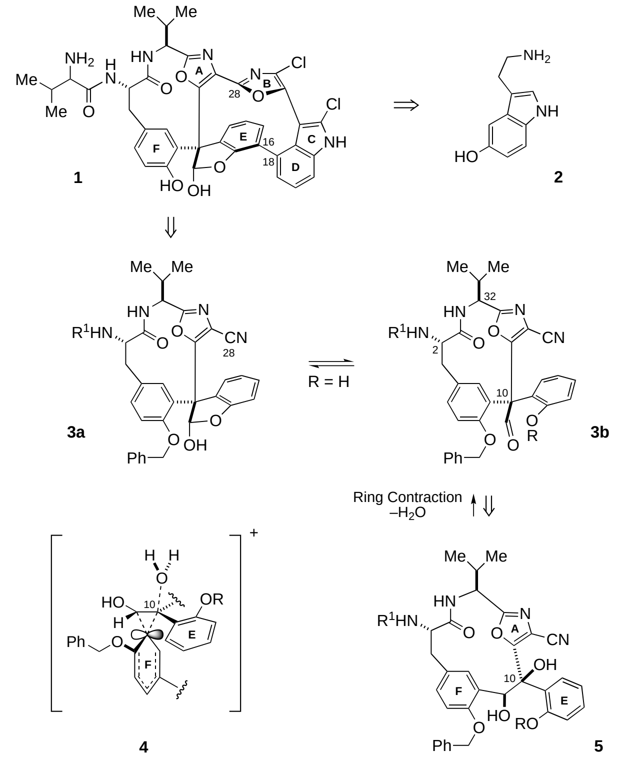
Diazonamide A (**1**) is a unique product of marine invertebrate secondary metabolism reported to inhibit the growth of a human colorectal carcinoma ($IC_{50} < 15\ \mathrm{ng\,mL^{-1}}$ against HCT-116) in vitro.[1] Nearly a decade after this discovery, the biochemical events mediating this activity, as well as the effects of the molecule on other cell types and tissues, remain unknown. Mode of action studies have been limited by a shortage of natural material[2] and the difficulties inherent in efforts to reconstitute the structure through synthesis.[3] The diazonamide network of linked aromatic/heteroaromatic rings maintains elements of axial chirality (constrained to a single atropisomeric form) around a densely functionalized triarylacetaldehyde core **3b** (Scheme 1). Recently, we



Scheme 1. Diazonamide synthesis: primary disconnections and strategy for control of stereochemistry at C_{10}.

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