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Synthesis and structural characterisation of new copper–tellurium clusters: $TeBu^n(SiMe_3)$ as a source of RTe^- and Te^{2-} ligands†

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Reactions of cobalt(II) and copper(I) salts with the functionalised reagents alkyl- and aryl-(trimethylsilyl)tellurium have been explored. The silylated reagents are found to be an excellent source of RTe^- and Te^{2-} ligands alike in high-nuclearity transition metal–tellurium clusters and the products isolated from the reaction mixtures have been structurally characterised by single-crystal X-ray analyses: $[Co_6(\mu_3\text{-}Te)_8(PPh_2Pr^n)_6]$ **1**, $[Cu_{11}(\mu_3\text{-}TeBu^n)_7(\mu_4\text{-}TeBu^n)_2(\mu_7\text{-}Te)(PPh_3)_5]$ **2**, $[Cu_{18}(\mu_3\text{-}TeBu^n)_6Te_6(PPr^n{}_3)_8]$ **3**, $[Cu_{58}Te_{32}(PPh_3)_{16}]$ **4** and $[Cu_{23}Te_{13}(PEt_3)_{12}]$ **5** have been synthesised. The formation of the complexes is highly dependent on the ancillary phosphine used. Cluster **1** consists of a non-bonded octahedral array of Co atoms with eight tellurium ligands capping the open Co_3 faces. Complexes **2**–**4** possess layered structures composed of Te atoms with Cu occupying peripheral and interlayer sites. The Te atoms in **5** form a body-centred icosahedron, with an overall near-spherical cluster framework.

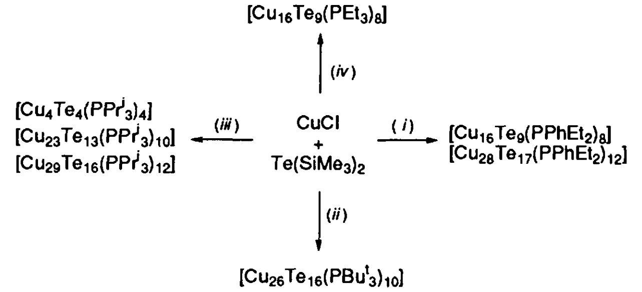
The synthesis, structural characterisation and physical properties of large transition-metal and mixed main group-metal clusters continues to be an area of active research for chemists, physicists and materials scientists alike.[1] The development of metal–chalcogenide cluster chemistry over the past 25 years has been dominated by metal–sulfur-containing complexes with much less focus on the heavier congener selenium, and even less for tellurium. Recent advances in synthetic techniques however have now enabled the chemistry to be extended to these heavier elements and two excellent and timely review articles serve to demonstrate the importance of this burgeoning area of research.[2,3]

Work in our laboratory has focussed on reactions of silylated main-group reagents [*e.g.* $AsR(SiMe_3)_2$, $SeR(SiMe_3)$, $Se(SiMe_3)_2$] with a variety of transition-metal salts in the presence of (solubilising) phosphine ligands (L).[4] The reactions are driven by the generation and elimination of $SiMe_3X$ (X = halide, O_2CMe, *etc.*) and the formation of metal–'non-metal' bonds [equation (1); E = S, Se or Te]. The reaction of

$$E(SiMe_3)_2 + MX_nL_m \longrightarrow SiMe_3X + \text{'cluster'} \quad (1)$$

bis(trimethylsilyl)selenium with copper(I) salts in particular has been extensively explored and shown to produce a variety of structural types whose nuclearities and structures are highly dependent on the reaction conditions employed. The ratio $Cu:Se:PR_3$, the steric requirements of the ancillary phosphine ligands employed and the conditions and solvents used for both the syntheses and crystallisations all play a significant role in governing the structures of the products formed.[4,5] The chemistry is dominated by the formation of molecular complexes in which the copper to selenium ratio invariably approaches 2:1 and products isolated include the complexes $[Cu_{29/30}Se_{15}(PPr^i{}_3)_{12}]$,[5a] $[Cu_{70}Se_{35}(PEt_3)_{22}]$[5b] and the mega-cluster $[Cu_{146}Se_{73}(PPh_3)_{30}]$.[5c] We have recently extended this synthetic approach to include $Te(SiMe_3)_2$ and have reported the formation of entirely different structural types.[6] The results of this latter series of reactions are summarised in Scheme 1.

In an effort to expand the general applicability of this synthetic strategy we have now turned our attention to the use of alkyl- and aryl-(trimethylsilyl)tellurium ligands. The results of some of our initial findings are presented herein.



Scheme 1 The reaction of CuCl with $Te(SiMe_3)_2$ (from ref. 6). (*i*) $PPhEt_2$, Et_2O; (*ii*) $PBu^t{}_3$, thf (tetrahydrofuran)–Et_2O; (*iii*) $PPr^i{}_3$, Et_2O; (*iv*) PEt_3, Et_2O

Experimental

Standard Schlenk-line techniques were employed throughout on a double-manifold vacuum line with high-purity dried nitrogen. Solvents for reactions and crystallisations were distilled under nitrogen from appropriate drying agents prior to use. Diethyl ether, tetrahydrofuran and diglyme (2,5,8-trioxanonane) were dried over sodium–benzophenone and hexane and heptane were collected after refluxing over $LiAlH_4$. The deuteriated solvent C_6D_6 was dried by stirring over a Na/K alloy and distilling under reduced pressure. All phosphines were prepared by standard literature procedures[7] with the exception of PPh_3 which was obtained from commercial sources. The complex $TePh(SiMe_3)$ was prepared according to the literature method.[8]

The $^{13}C\text{-}\{^1H\}$ NMR spectra were acquired on a Bruker AC 250 instrument operating at 62.9 MHz, $^{125}Te\text{-}\{^1H\}$ spectra on an AMX 300 at an operating frequency of 94.8 MHz and referenced to the external standard $TeMe_2$.

Syntheses

$TeBu^n(SiMe_3)$.[8a] In a modification of the literature procedure, Te (63 g, 0.5 mol) was suspended in thf (500 cm^3) in a three-necked round-bottom flask (2 l) equipped with a water-cooled condenser and dropping funnel. To the rapidly stirred

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† Basis of the presentation given at Dalton Discussion No. 1, 3rd–5th January 1996, University of Southampton, UK.

suspension was added $LiBu^n$ (315 cm^3, 0.5 mol; 1.6 mol dm^{-3} in hexane) in thf (250 cm^3), during which time the Te metal gradually dissolved with the formation of a red-brown solution. After complete addition, the solution was heated at reflux for 1 h and allowed to cool to room temperature. Freshly distilled $SiMe_3Cl$ (63 cm^3, 0.5 mol) was added dropwise and the mixture allowed to stir overnight. The solution was filtered to remove LiCl and Te and the solvent removed *via* distillation. Vacuum distillation afforded 82 g (*ca.* 60%) of $TeBu^n(SiMe_3)$ [b.p. 80 °C, 10 Torr (*ca.* 1333 Pa)]. The yellow liquid obtained invariably contained small amounts of $Te(SiMe_3)_2$[9] and $Bu^nTeTeBu^n$[8b] which could not be separated. NMR (C_6D_6): ^{125}Te-{^{1}H}, δ −327; ^{13}C-{^{1}H}, δ 37.2 (s, CH_2), 26.0 (s, CH_2), 14.3 (s, Me), 4.1 (s, $SiMe_3$) and −3.1 (s, CH_2Te, J_{CTe} = 132 Hz).

$[Co_6(\mu_3\text{-}Te)_8(PPh_2Pr^n)_6]$ 1. The compound $[CoCl_2(PPh_2Pr^n)_2]$[10] (0.6 g, 1 mmol) was dissolved in thf (25 cm^3) to yield a deep blue solution and $TePh(SiMe_3)$ (0.3 cm^3, 1 mmol) was added with stirring. Over the course of 1 week the colour of the solution gradually darkened to black. The homogeneous solution was layered with heptane and $[Co_6(\mu_3\text{-}Te)_8(PPh_2Pr^n)_6]$ **1** crystallised as black needles over several weeks as the only product.

$[Cu_{11}(\mu_3\text{-}TeBu^n)_7(\mu_4\text{-}TeBu^n)_2(\mu_7\text{-}Te)(PPh_3)_5]$ 2. Copper(I) acetate (0.15 g, 1.2 mmol) and PPh_3 (0.64 g, 2.4 mmol) were mixed in thf (5 cm^3) to form a white suspension. To the mixture was added $TeBu^n(SiMe_3)$ (0.37 cm^3, 1.7 mmol). The suspension dissolved almost immediately to yield a dark gold-brown homogeneous solution. The mixture was stirred for 40 min and layered with heptane. Gold coloured crystals of complex **2** grew at room temperature within 2–3 d. Yield: *ca.* 60%.

$[Cu_{18}(\mu_3\text{-}TeBu^n)_6Te_6(PPr^n_3)_8]$ 3. Copper(I) chloride (0.15 g, 1.5 mmol) was dissolved in diglyme (10 cm^3) *via* the addition of PPr^n_3 (0.60 cm^3, 3.0 mmol). To the clear, colourless solution was added $TeBu^n(SiMe_3)$ (0.30 cm^3, 1.4 mmol) yielding a dark green-brown solution. The reaction mixture was stirred for 1 h and allowed to stand. After several days small amounts of red-brown complex **3** grew as hexagonal plates at the solvent line. Cooling the mixture to 4 °C yielded 0.26 g (72%) of **3**.

$[Cu_{58}Te_{32}(PPh_3)_{16}]$ 4. To a suspension of CuCl (0.4 g, 4 mmol) in diglyme (20 cm^3) was added PPh_3 (2.1 g, 8 mmol). To the white voluminous suspension was added $TeBu^n(SiMe_3)$ (1.2 cm^3, 5.5 mmol). The mixture was stirred for 30 min to afford a dark brown homogeneous solution. This was layered with heptane and within several days black platelets of complex **4** formed in low yield in addition to black needles of an as yet unidentified product.

$[Cu_{23}Te_{13}(PEt_3)_{12}]$ 5. Copper(I) chloride (0.50 g, 5.0 mmol) was dissolved in thf (10 cm^3) by the addition of PEt_3 (1.50 cm^3, 10.1 mmol). To the clear, colourless solution was added $TeBu^n(SiMe_3)$ (1.50 cm^3, 7.0 mmol). The resultant green-black solution was stirred for 4 h and layered with heptane. Black, pseudo-octahedral crystals of complex **5** grew within several weeks. Yield: 90%.

X-Ray structural analyses

The selection and mounting of single crystals suitable for X-ray diffraction were carried out by immersing the air-sensitive samples in perfluoropolyether oil (Riedel de Häen) and mounting the coated crystal on a glass pin set in a goniometer head, the oil setting upon cooling in a flow of N_2. Single-crystal X-ray structural analysis of complex **1** was performed on a Stoe Stadi IV four-circle diffractometer using graphite-monochromated Mo-Kα (λ = 0.710 73 Å) radiation, those of **2**–**5** on a Stoe IPDS instrument (Mo-Kα) equipped with an imaging plate area detector and a rotating anode. Data were corrected for Lorentz and polarisation effects and structure solution and refinements were carried out using SHELXS 86[11] and SHELXL 93[12] software using direct-methods techniques. With the exception of **1**, absorption corrections were not applied. The weighting scheme employed was of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ [a, b = refined variables, $P = \frac{1}{3}\max(F_o^2, 0) + \frac{2}{3}F_c^2$]. All calculations were performed on a MicroVAX 3500 or Silicon Graphics INDY computer. Molecular diagrams were prepared using the SCHAKAL 92 program.[13]

Complex 1. *Crystal data.* $C_{90}H_{102}Co_6P_6Te_8\cdot$thf, M = 2816.0, monoclinic, space group $C2/c$, a = 15.570(3), b = 24.567(5), c = 26.885(5) Å, β = 99.27(3)°, U = 10 149(4) Å^3 (by least-squares refinement on 25 automatically centred reflections in the 2θ range 10–25°), Z = 4, D_c = 1.843 g cm^{-3}, $F(000)$ = 5400, μ = 3.349 mm^{-1}.

Data collection and processing. Data were collected at 200 K in the θ range 1.53–25.00° using a variable scan speed in ω, 9305 measured, 8952 unique (merging R = 0.0343 after a semiempirical ψ scan absorption correction), 7045 with $I > 2\sigma(I)$.

Structure analysis and refinement. Direct methods (Co and Te) followed by normal refinement procedures. Full-matrix least-squares refinement on F^2 with all non-hydrogen atoms anisotropic and all hydrogen atoms in calculated positions gave R = 0.0346 with a goodness-of-fit value of 1.105. Table 1 contains a selection of bond lengths and angles. A thf solvent molecule was located and refined isotropically (H atoms omitted).

Complex 2. *Crystal data.* $C_{126}H_{156}Cu_{11}P_5Te_{10}$, M = 3800.3, monoclinic, space group $P2_1/n$, a = 15.755(2), b = 55.817(5), c = 17.160(2) Å, β = 155.22(1)°, U = 13 652(3) Å^3, Z = 4, D_c = 1.849 g cm^{-3}, $F(000)$ = 7304, μ = 3.873 mm^{-1}.

Data collection and processing. Data were collected at 180 K in the θ range 1.96–26.09°, using a ΔΦ value of 0.4° and a detector distance of 70 mm with 6 min irradiation time per exposure; 33 453 measured, 18 744 unique (merging R = 0.0656), 16 051 with $I > 2\sigma(I)$.

Structure analysis and refinement. Direct methods (Cu and Te) followed by normal refinement procedures. Refinement as for complex **1** gave R = 0.0584 with a goodness of fit of 1.024. Atoms C(24), C(24A) and C(36), C(36A) were found to be disordered over two sites and were refined isotropically with 50 : 50 occupancy. Table 2 contains a selection of bond lengths.

Complex 3. *Crystal data.* $C_{96}H_{204}Cu_{18}P_8Te_{12}$, M = 4281.3, monoclinic, space group $P2_1/c$, a = 29.153(6), b = 17.600(4), c = 29.116(6) Å, β = 90.60(3)°, U = 14 938(5) Å^3, Z = 4, D_c = 1.904 g cm^{-3}, $F(000)$ = 8184, μ = 4.918 mm^{-1}.

Data collection and processing. Data were collected at 200 K in the θ range 3.11–21.14°, using a ΔΦ value of 0.5° and a detector distance of 80 mm with 20 min irradiation time per exposure; 41 027 measured, 15 568 unique (merging R = 0.0920), 11 809 with $I > 2\sigma(I)$.

Structure analysis and refinement. Direct methods (Cu and Te) followed by normal refinement procedures. Full-matrix least-squares refinement on F^2 with all non-hydrogen atoms anisotropic (with the exception of disordered C atoms which were refined isotropically) gave R = 0.0788 with a goodness of fit of 1.104. Hydrogen atoms were not included in the refinement cycles. Table 3 contains a selection of bond lengths.

Complex 4. *Crystal data.* $C_{288}H_{240}Cu_{58}P_{16}Te_{32}$, M = 11 964.8, triclinic, space group $P\bar{1}$, a = 21.077(4), b = 24.053(5), c = 24.561(5) Å, α = 64.57(3), β = 67.00(3), γ = 69.97(3)°, U = 10 120(4) Å^3, Z = 1, D_c = 1.963 g cm^{-3}, $F(000)$ = 5554, μ = 5.332 mm^{-1}.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Te(1)–Co(2)	2.5023(11)	Te(3)–Co(2)	2.5291(12)	Co(2)–Te(2$^{\rm I}$)	2.5143(11)	P(1)–C(37)	1.847(7)
Te(1)–Co(1)	2.5109(11)	Te(4)–Co(2)	2.5302(11)	Co(3)–P(3)	2.143(2)	P(2)–C(22)	1.838(7)
Te(1)–Co(3$^{\rm I}$)	2.5279(11)	Te(4)–Co(1)	2.5322(11)	Co(3)–Te(2$^{\rm I}$)	2.5041(10)	P(2)–C(28)	1.837(8)
Te(2)–Co(3$^{\rm I}$)	2.5041(11)	Te(4)–Co(3)	2.5343(12)	Co(3)–Te(3$^{\rm I}$)	2.5161(11)	P(2)–C(16)	1.851(7)
Te(2)–Co(2$^{\rm I}$)	2.5143(11)	Co(1)–P(1)	2.150(2)	Co(3)–Te(1$^{\rm I}$)	2.5279(11)	P(3)–C(7)	1.843(7)
Te(2)–Co(1)	2.5247(11)	Co(1)–Te(3$^{\rm I}$)	2.5017(12)	P(1)–C(31)	1.835(7)	P(3)–C(1)	1.849(7)
Te(3)–Co(1$^{\rm I}$)	2.5017(12)	Co(2)–P(2)	2.149(2)	P(1)–C(43)	1.840(8)	P(3)–C(13)	1.850(7)
Te(3)–Co(3$^{\rm I}$)	2.5159(11)						

Co(2)–Te(1)–Co(1)	80.84(3)	P(1)–Co(1)–Te(2)	96.58(6)	Te(2$^{\rm I}$)–Co(2)–Te(4)	86.20(3)	C(31)–P(1)–Co(1)	114.0(2)
Co(2)–Te(1)–Co(3$^{\rm I}$)	79.86(3)	Te(3$^{\rm I}$)–Co(1)–Te(2)	87.40(4)	Te(3)–Co(2)–Te(4)	153.25(4)	C(43)–P(1)–Co(1)	115.5(3)
Co(1)–Te(1)–Co(3$^{\rm I}$)	79.22(4)	Te(1)–Co(1)–Te(2)	88.59(4)	P(3)–Co(3)–Te(2$^{\rm I}$)	99.12(6)	C(37)–P(1)–Co(1)	121.4(3)
Co(3$^{\rm I}$)–Te(2)–Co(2$^{\rm I}$)	81.15(4)	P(1)–Co(1)–Te(4)	109.49(6)	P(3)–Co(3)–Te(3$^{\rm I}$)	106.38(6)	C(22)–P(2)–C(28)	101.7(3)
Co(3$^{\rm I}$)–Te(2)–Co(1)	79.41(4)	Te(3$^{\rm I}$)–Co(1)–Te(4)	86.15(3)	Te(2$^{\rm I}$)–Co(3)–Te(3$^{\rm I}$)	154.50(4)	C(22)–P(2)–C(16)	100.4(3)
Co(2$^{\rm I}$)–Te(2)–Co(1)	80.42(3)	Te(1)–Co(1)–Te(4)	86.64(3)	P(3)–Co(3)–Te(1$^{\rm I}$)	96.17(7)	C(28)–P(2)–C(16)	99.5(4)
Co(1$^{\rm I}$)–Te(3)–Co(3$^{\rm I}$)	81.28(3)	Te(2)–Co(1)–Te(4)	153.85(4)	Te(2$^{\rm I}$)–Co(3)–Te(1$^{\rm I}$)	88.67(4)	C(22)–P(2)–Co(2)	113.7(2)
Co(1$^{\rm I}$)–Te(3)–Co(2)	80.57(4)	P(2)–Co(2)–Te(1)	97.34(6)	Te(3$^{\rm I}$)–Co(3)–Te(1$^{\rm I}$)	88.10(3)	C(28)–P(2)–Co(2)	116.4(3)
Co(3$^{\rm I}$)–Te(3)–Co(2)	79.58(3)	P(2)–Co(2)–Te(2$^{\rm I}$)	107.74(6)	P(3)–Co(3)–Te(4)	109.27(7)	C(16)–P(2)–Co(2)	122.0(2)
Co(2)–Te(4)–Co(1)	79.90(4)	Te(1)–Co(2)–Te(2$^{\rm I}$)	154.84(4)	Te(2$^{\rm I}$)–Co(3)–Te(4)	86.32(4)	C(7)–P(3)–C(1)	99.6(3)
Co(2)–Te(4)–Co(3)	80.26(4)	P(2)–Co(2)–Te(3)	96.17(6)	Te(3$^{\rm I}$)–Co(3)–Te(4)	85.81(3)	C(7)–P(3)–C(13)	101.5(3)
Co(1)–Te(4)–Co(3)	80.33(3)	Te(1)–Co(2)–Te(3)	88.37(3)	Te(1$^{\rm I}$)–Co(3)–Te(4)	154.55(4)	C(1)–P(3)–C(13)	101.2(3)
P(1)–Co(1)–Te(3$^{\rm I}$)	99.84(6)	Te(2$^{\rm I}$)–Co(2)–Te(3)	87.03(3)	C(31)–P(1)–C(43)	102.8(3)	C(7)–P(3)–Co(3)	115.1(2)
P(1)–Co(1)–Te(1)	105.16(6)	P(2)–Co(2)–Te(4)	110.54(6)	C(31)–P(1)–C(37)	99.9(3)	C(1)–P(3)–Co(3)	121.0(2)
Te(3$^{\rm I}$)–Co(1)–Te(1)	154.97(4)	Te(1)–Co(2)–Te(4)	86.87(3)	C(43)–P(1)–C(37)	100.5(4)	C(13)–P(3)–Co(3)	115.5(2)

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

Table 2 Selected bond lengths (Å) for complex **2**

Te(1)–C(1)	2.169(9)	Te(5)–Cu(7)	2.6388(10)	Te(10)–Cu(10)	2.6258(12)	Cu(7)–Cu(11)	2.800(2)
Te(1)–Cu(7)	2.6534(11)	Te(5)–Cu(11)	2.6559(11)	Te(10)–Cu(8)	2.6373(12)	Cu(8)–Cu(9)	2.6027(14)
Te(1)–Cu(2)	2.6846(10)	Te(6)–C(21)	2.179(12)	Te(10)–Cu(6)	2.7554(10)	Cu(8)–Cu(11)	2.6392(12)
Te(1)–Cu(1)	2.7159(10)	Te(6)–Cu(8)	2.6416(11)	Te(10)–Cu(11)	2.7685(11)	Cu(11)–P(5)	2.289(2)
Te(1)–Cu(3)	2.9389(11)	Te(6)–Cu(4)	2.6680(10)	Te(10)–Cu(2)	2.8966(11)	P(1)–C(49)	1.828(9)
Te(2)–C(5)	2.176(7)	Te(6)–Cu(11)	2.6838(13)	Cu(1)–P(1)	2.252(2)	P(1)–C(37)	1.831(10)
Te(2)–Cu(8)	2.6619(11)	Te(7)–C(25)	2.181(11)	Cu(1)–Cu(2)	2.5494(13)	P(1)–C(43)	1.834(8)
Te(2)–Cu(1)	2.6924(12)	Te(7)–Cu(9)	2.5192(14)	Cu(2)–Cu(7)	2.5419(11)	P(2)–C(61)	1.828(8)
Te(2)–Cu(2)	2.7220(12)	Te(7)–Cu(4)	2.6029(13)	Cu(2)–Cu(8)	2.5523(14)	P(2)–C(55)	1.833(11)
Te(2)–Cu(4)	2.7309(12)	Te(7)–Cu(8)	3.0452(12)	Cu(2)–Cu(6)	2.5549(13)	P(2)–C(67)	1.846(9)
Te(3)–C(9)	2.174(9)	Te(8)–C(29)	2.209(10)	Cu(3)–P(2)	2.229(2)	P(3)–C(85)	1.820(11)
Te(3)–Cu(6)	2.5995(11)	Te(8)–Cu(9)	2.6085(12)	Cu(3)–Cu(7)	2.4694(13)	P(3)–C(79)	1.821(10)
Te(3)–Cu(2)	2.6729(9)	Te(8)–Cu(5)	2.6227(13)	Cu(4)–P(3)	2.234(3)	P(3)–C(73)	1.836(8)
Te(3)–Cu(1)	2.6832(11)	Te(8)–Cu(6)	2.7061(11)	Cu(4)–Cu(8)	2.525(2)	P(4)–C(91)	1.811(9)
Te(4)–C(13)	2.178(8)	Te(9)–C(33)	2.204(9)	Cu(5)–P(4)	2.228(2)	P(4)–C(103)	1.813(11)
Te(4)–Cu(10)	2.5502(10)	Te(9)–Cu(5)	2.5717(11)	Cu(5)–Cu(6)	2.4789(13)	P(4)–C(97)	1.843(9)
Te(4)–Cu(3)	2.5866(13)	Te(9)–Cu(10)	2.5882(11)	Cu(6)–Cu(10)	2.5512(12)	P(5)–C(109)	1.827(9)
Te(4)–Cu(7)	3.1005(13)	Te(9)–Cu(6)	2.7610(12)	Cu(6)–Cu(9)	2.563(2)	P(5)–C(121)	1.844(10)
Te(5)–C(17)	2.177(10)	Te(10)–Cu(7)	2.5988(11)	Cu(7)–Cu(10)	2.644(2)	P(5)–C(115)	1.846(8)
Te(5)–Cu(3)	2.6119(12)	Te(10)–Cu(9)	2.6065(11)				

Data collection and processing. Data were collected at 200 K in the θ range 3.72–24.01°; 70 571 measured, 29 326 unique (merging $R = 0.1391$), 14 656 with $I > 2\sigma(I)$.

Structure analysis and refinement. Direct methods (Cu and Te) followed by normal refinement procedures. Full-matrix least-squares refinement on F^2 with all Te, Cu and P atoms anisotropic and all C atoms refined isotropically as constrained aromatic rings gave $R = 0.1008$ with a goodness of fit of 1.019. Hydrogen atoms were not included in the refinement cycles. Table 4 contains a selection of bond lengths.

Complex 5. *Crystal data.* $C_{72}H_{180}Cu_{23}P_{12}Te_{13}$, $M = 4538.0$, cubic, space group $Fm\bar{3}$, $a = 23.437(3)$ Å, $U = 12\,874(3)$ Å^3, $Z = 4$, $D_c = 2.341$ g cm^{-3}, $F(000) = 8540$, $\mu = 6.776$ mm^{-1}.

Data collection and processing. Data were collected at 180 K in the θ range 2.46–28.08°, using a ΔΦ value of 0.4° and a detector distance of 60 mm with 5 min irradiation time per exposure; 8180 measured, 1386 unique (merging $R = 0.0554$), 1298 with $I > 2\sigma(I)$.

Structure analysis and refinement. Direct methods and full-matrix least-squares refinement as for complex **2** gave $R = 0.0330$ with a goodness of fit of 1.045. Table 5 contains a selection of bond lengths and angles.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Previous work in our laboratory has demonstrated that reaction of $[CoCl_2(PR_3)_2]$ complexes with $S(SiMe_3)_2$ and $Se(SiMe_3)_2$ leads to the formation of cluster complexes of the type $[Co_6E_8(PR_3)_6]$ (E = S or Se, R = aryl or alkyl),[14] the central cobalt atoms forming an octahedral array, with each chalcogen atom capping a triangular face. Various other synthetic methods have also led to the successful preparation of this molecular structure type.[15–17] This class of complex is of course structurally related to the well known Chevrel-type extended solid phases[18] which have been the subject of intense research efforts due to their superconducting properties at low temperatures.

Table 3 Selected bond lengths (Å) for complex **3**

Te(1)–Cu(4)	2.593(3)	Te(7)–Cu(7)	2.799(3)	Cu(3)–Cu(8)	2.543(3)	Cu(15)–P(6)	2.257(8)
Te(1)–Cu(2)	2.623(3)	Te(7)–Cu(15)	2.842(3)	Cu(3)–Cu(11)	2.547(3)	Cu(16)–P(7)	2.264(7)
Te(1)–Cu(10)	2.681(3)	Te(8)–C(9)	2.15(3)	Cu(3)–Cu(7)	2.632(4)	Cu(16)–Cu(17)	2.556(4)
Te(1)–Cu(5)	2.682(3)	Te(8)–Cu(15)	2.613(4)	Cu(3)–Cu(4)	2.963(3)	Cu(17)–Cu(18)	2.980(4)
Te(1)–Cu(1)	2.709(3)	Te(8)–Cu(8)	2.637(3)	Cu(3)–Cu(6)	3.024(3)	Cu(18)–P(8)	2.347(7)
Te(2)–Cu(3)	2.566(3)	Te(8)–Cu(9)	2.643(3)	Cu(4)–Cu(10)	2.531(3)	P(1)–C(25)	1.82(2)
Te(2)–Cu(2)	2.628(3)	Te(9)–Cu(10)	2.566(3)	Cu(4)–Cu(11)	2.582(3)	P(1)–C(28)	1.83(2)
Te(2)–Cu(6)	2.651(3)	Te(9)–Cu(14)	2.632(3)	Cu(4)–Cu(9)	2.592(3)	P(1)–C(31)	1.86(2)
Te(2)–Cu(7)	2.678(3)	Te(9)–Cu(17)	2.729(3)	Cu(4)–Cu(8)	2.900(3)	P(2)–C(34)	1.84(2)
Te(2)–Cu(1)	2.789(3)	Te(9)–Cu(4)	2.769(3)	Cu(5)–P(2)	2.206(6)	P(2)–C(37)	1.81(2)
Te(3)–Cu(4)	2.565(3)	Te(9)–Cu(11)	2.812(3)	Cu(5)–Cu(10)	2.459(3)	P(2)–C(40)	1.86(3)
Te(3)–Cu(3)	2.642(3)	Te(9)–Cu(16)	2.867(3)	Cu(6)–Cu(7)	2.468(3)	P(3)–C(43)	1.98(5)
Te(3)–Cu(8)	2.666(3)	Te(9)–Cu(9)	2.889(3)	Cu(6)–Cu(12)	2.675(3)	P(3)–C(43A)	1.82(5)
Te(3)–Cu(9)	2.669(3)	Te(10)–C(13)	2.20(3)	Cu(6)–Cu(13)	2.741(3)	P(3)–C(46)	1.85(6)
Te(3)–Cu(1)	2.734(3)	Te(10)–Cu(17)	2.468(3)	Cu(6)–Cu(11)	2.774(3)	P(3)–C(46A)	1.87(6)
Te(4)–C(1)	2.21(3)	Te(10)–Cu(18)	2.695(3)	Cu(7)–P(3)	2.197(6)	P(3)–C(49)	1.96(5)
Te(4)–Cu(16)	2.572(3)	Te(10)–Cu(16)	2.743(3)	Cu(8)–Cu(9)	2.517(4)	P(3)–C(49A)	1.72(5)
Te(4)–Cu(10)	2.636(3)	Te(11)–C(17)	2.18(2)	Cu(8)–Cu(11)	2.661(3)	P(4)–C(52)	1.83(3)
Te(4)–Cu(5)	2.648(3)	Te(11)–Cu(13)	2.499(3)	Cu(8)–Cu(15)	2.699(4)	P(4)–C(55)	1.79(3)
Te(5)–Cu(6)	2.565(3)	Te(11)–Cu(12)	2.697(3)	Cu(8)–Cu(14)	2.720(4)	P(4)–C(58)	2.03(7)
Te(5)–Cu(17)	2.627(3)	Te(11)–Cu(18)	2.737(3)	Cu(9)–P(4)	2.232(7)	P(5)–C(61)	1.89(3)
Te(5)–Cu(13)	2.730(3)	Te(12)–C(21)	2.28(3)	Cu(10)–Cu(11)	2.714(3)	P(5)–C(64)	1.79(3)
Te(5)–Cu(2)	2.749(3)	Te(12)–Cu(14)	2.486(3)	Cu(10)–Cu(16)	2.716(4)	P(5)–C(67)	1.83(3)
Te(5)–Cu(11)	2.766(3)	Te(12)–Cu(15)	2.680(3)	Cu(10)–Cu(17)	2.722(4)	P(6)–C(70)	1.87(4)
Te(5)–Cu(5)	2.885(3)	Te(12)–Cu(18)	2.699(3)	Cu(11)–Cu(17)	2.472(3)	P(6)–C(73)	1.86(4)
Te(5)–Cu(12)	2.903(3)	Cu(1)–P(1)	2.230(6)	Cu(11)–Cu(13)	2.488(4)	P(6)–C(76)	1.81(3)
Te(6)–Cu(5)	2.20(2)	Cu(1)–Cu(2)	2.578(3)	Cu(11)–Cu(14)	2.496(3)	P(7)–C(79)	1.84(3)
Te(6)–Cu(12)	2.562(3)	Cu(1)–Cu(4)	2.595(3)	Cu(12)–P(5)	2.234(6)	P(7)–C(82)	1.77(3)
Te(6)–Cu(6)	2.673(3)	Cu(1)–Cu(3)	2.598(3)	Cu(12)–Cu(13)	2.581(3)	P(7)–C(85)	1.86(4)
Te(6)–Cu(7)	2.679(3)	Cu(2)–Cu(11)	2.551(3)	Cu(13)–Cu(17)	2.626(4)	P(8)–C(88)	1.78(5)
Te(7)–Cu(13)	2.609(3)	Cu(2)–Cu(6)	2.586(3)	Cu(13)–Cu(14)	2.664(4)	P(8)–C(88A)	2.01(5)
Te(7)–Cu(8)	2.617(3)	Cu(2)–Cu(5)	2.609(3)	Cu(13)–Cu(18)	2.928(4)	P(8)–C(91)	1.82(6)
Te(7)–Cu(11)	2.753(3)	Cu(2)–Cu(3)	2.925(3)	Cu(14)–Cu(15)	2.586(4)	P(8)–C(91A)	1.93(9)
Te(7)–Cu(14)	2.760(3)	Cu(2)–Cu(10)	2.946(3)	Cu(14)–Cu(17)	2.600(4)	P(8)–C(94)	1.73(5)
Te(7)–Cu(3)	2.767(3)	Cu(2)–Cu(4)	2.950(3)	Cu(14)–Cu(18)	2.946(4)	P(8)–C(94A)	1.83(9)

The reaction of $[CoCl_2(PPh_2Pr^n)_2]$, dissolved in thf, with the reagent $TePh(SiMe_3)$ led to gradual darkening of the reaction solution and the isolation of $[Co_6(\mu_3\text{-}Te)_8(PPh_2Pr^n)_6]$ **1** as the only crystalline product from the reaction mixture. The molecular structure of **1** is illustrated in Fig. 1. The cluster crystallises in the monoclinic space group *C*2/*c* and, with four molecules in the unit cell, a crystallographic inversion centre relates the two halves of the molecule. The central cobalt atoms form a non-bonded octahedral array with each Te atom capping an open Co_3 face. Each Co atom forms four bonds to unique tellurium atoms and a fifth interaction to the phosphine ligand at the apex of a square-pyramidal co-ordination geometry. The reaction has thus proceeded with cleavage of the tellurium–carbon bonds. The formation of this structural type using this general synthetic method has been repeatedly observed with a wide variety of phosphine ligands, essentially insensitive to solvent and reaction conditions, reflecting the relative stability of this cluster type.[19] An analogous complex has also previously been described by Steigerwald *et al.*[17] *via* the reaction of $[Co_2(CO)_8]$ with PEt_3Te and PEt_3.[17]

Complex **1** possesses 98 cluster valence electrons, with each μ_3-Te ligand donating four electrons to the cluster framework and the six phosphine ligands contributing a total of 12 electrons to the valence count. Thus, within the formalism of the effective atomic number rule, the complex is electron deficient assuming the absence of Co–Co bonding interactions [Co–Co 3.212(1)–3.268(1) Å]. An alternative description would be an electron *rich* central octahedron with the (14) excess valence electrons occupying delocalised Co–Co antibonding orbitals, resulting in overall cluster expansion.[20]

The increasing number of $[Co_6E_8(PR_3)_6]$ complexes[15–17,20] displaying similar core geometries to that observed in **1** allows for some general features to be noted (Table 6). The cobalt–cobalt contacts observed in the sulfur-bridged complexes are significantly shorter *versus* their selenium counterparts which are in turn much shorter than those observed in **1**. These elongated distances suggest that the cluster is best described as being electron rich, the occupation of Co–Co antibonding orbitals resulting in a delocalised weakening of the metal–metal bonds. Support for this argument is provided by noting the contraction of the Co–Co distances observed for the 93-valence-electron cationic complexes $[Co_6S_8(PR_3)_6]^+$ *versus* their neutral counterparts $[Co_6S_8(PR_3)_6]$ (R = Ph or Et).[15] Amongst early studies, Dahl and co-workers[21] clearly illustrated these ideas

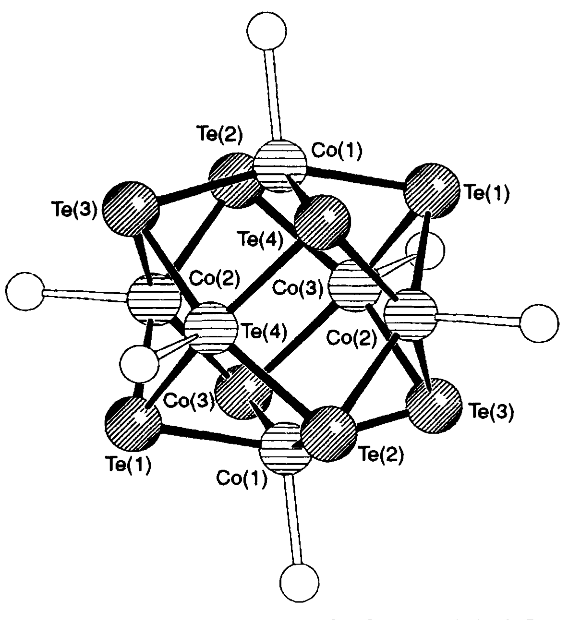


Fig. 1 The molecular structure of $[Co_6(\mu_3\text{-}Te)_8(PPh_2Pr^n)_6]$ **1** emphasising the geometry of the central Co_6Te_8 core. Carbon atoms are omitted for clarity

Table 4 Selected bond lengths (Å) for complex **4**

Te(1)–Cu(2)	2.588(4)	Te(8)–Cu(11)	2.664(4)	Te(15)–Cu(7)	2.842(5)	Cu(10)–Cu(14)	2.703(5)
Te(1)–Cu(1)	2.620(4)	Te(8)–Cu(3)	2.720(4)	Te(15)–Cu(18)	2.885(5)	Cu(10)–Cu(17)	2.727(5)
Te(1)–Cu(5)	2.630(4)	Te(9)–Cu(6)	2.554(4)	Te(15)–Cu(15$^{\mathrm{I}}$)	3.034(4)	Cu(10)–Cu(17$^{\mathrm{I}}$)	2.907(5)
Te(1)–Cu(3)	2.661(5)	Te(9)–Cu(15)	2.588(4)	Te(15)–Cu(17$^{\mathrm{I}}$)	3.064(4)	Cu(11)–P(4)	2.284(9)
Te(1)–Cu(4)	2.673(4)	Te(9)–Cu(5)	2.596(4)	Te(16)–Cu(17)	2.675(4)	Cu(11)–Cu(13$^{\mathrm{I}}$)	2.633(5)
Te(2)–Cu(6)	2.542(4)	Te(9)–Cu(10)	2.694(4)	Te(16)–Cu(29)	2.710(4)	Cu(11)–Cu(15)	2.727(5)
Te(2)–Cu(28)	2.603(4)	Te(9)–Cu(11)	2.697(4)	Te(16)–Cu(4)	2.754(4)	Cu(12)–P(5)	2.280(9)
Te(2)–Cu(4)	2.627(4)	Te(9)–Cu(4)	2.844(4)	Te(16)–Cu(10)	2.759(4)	Cu(12)–Cu(16)	2.582(5)
Te(2)–Cu(27)	2.722(4)	Te(9)–Cu(14)	3.100(5)	Te(16)–Cu(22$^{\mathrm{I}}$)	2.815(4)	Cu(12)–Cu(14)	2.588(5)
Te(2)–Cu(29)	2.741(4)	Te(10)–Cu(14)	2.624(4)	Te(16)–Cu(25)	2.918(4)	Cu(12)–Cu(21)	2.663(6)
Te(2)–Cu(1)	2.783(4)	Te(10)–Cu(17$^{\mathrm{I}}$)	2.638(4)	Te(16)–Cu(21$^{\mathrm{I}}$)	2.982(5)	Cu(13)–Cu(18)	2.541(5)
Te(2)–Cu(7)	2.846(4)	Te(10)–Cu(21)	2.673(5)	Te(16)–Cu(2)	2.990(4)	Cu(14)–Cu(17$^{\mathrm{I}}$)	2.542(5)
Te(3)–Cu(16)	2.597(4)	Te(10)–Cu(15)	2.706(4)	Cu(1)–P(1)	2.278(9)	Cu(14)–Cu(16)	2.952(6)
Te(3)–Cu(6)	2.632(4)	Te(10)–Cu(12)	2.735(4)	Cu(1)–Cu(2)	2.661(6)	Cu(15)–Cu(20$^{\mathrm{I}}$)	2.518(5)
Te(3)–Cu(14)	2.638(4)	Te(10)–Cu(22)	2.813(4)	Cu(1)–Cu(4)	2.675(5)	Cu(15)–Cu(17$^{\mathrm{I}}$)	2.644(5)
Te(3)–Cu(7)	2.647(4)	Te(10)–Cu(20$^{\mathrm{I}}$)	2.990(5)	Cu(1)–Cu(27)	2.685(6)	Cu(16)–Cu(19)	2.594(5)
Te(3)–Cu(12)	2.728(4)	Te(11)–Cu(8$^{\mathrm{I}}$)	2.613(4)	Cu(2)–Cu(25)	2.460(5)	Cu(17)–Cu(29)	2.583(5)
Te(3)–Cu(9)	2.816(5)	Te(11)–Cu(19$^{\mathrm{I}}$)	2.680(4)	Cu(2)–Cu(3)	2.590(5)	Cu(17)–Cu(20)	2.695(5)
Te(4)–Cu(19$^{\mathrm{I}}$)	2.560(4)	Te(11)–Cu(2)	2.688(5)	Cu(2)–Cu(4)	2.817(5)	Cu(17)–Cu(22$^{\mathrm{I}}$)	2.837(4)
Te(4)–Cu(21$^{\mathrm{I}}$)	2.597(5)	Te(11)–Cu(23)	2.760(4)	Cu(3)–P(2)	2.258(9)	Cu(18)–Cu(24)	2.729(5)
Te(4)–Cu(16$^{\mathrm{I}}$)	2.627(4)	Te(11)–Cu(25)	2.766(5)	Cu(3)–Cu(5)	2.563(5)	Cu(19)–Cu(23$^{\mathrm{I}}$)	2.603(5)
Te(4)–Cu(12$^{\mathrm{I}}$)	2.646(4)	Te(11)–Cu(3)	2.787(4)	Cu(3)–Cu(8$^{\mathrm{I}}$)	2.632(5)	Cu(19)–Cu(21)	2.748(6)
Te(4)–Cu(23)	2.654(4)	Te(12)–Cu(1)	2.605(4)	Cu(4)–Cu(5)	2.518(5)	Cu(20)–Cu(22$^{\mathrm{I}}$)	2.648(5)
Te(5)–Cu(25)	2.573(4)	Te(12)–Cu(26)	2.632(5)	Cu(4)–Cu(6)	2.609(5)	Cu(20)–Cu(24)	2.668(6)
Te(5)–Cu(26)	2.620(5)	Te(12)–Cu(27)	2.637(4)	Cu(4)–Cu(29)	2.715(5)	Cu(20)–Cu(29)	2.809(6)
Te(5)–Cu(21$^{\mathrm{I}}$)	2.654(4)	Te(12)–Cu(25)	2.657(5)	Cu(4)–Cu(10)	3.007(5)	Cu(20)–Cu(28)	3.034(6)
Te(5)–Cu(23)	2.656(5)	Te(12)–Cu(2)	2.666(4)	Cu(5)–Cu(11)	2.613(5)	Cu(21)–Cu(22)	2.544(6)
Te(5)–Cu(22$^{\mathrm{I}}$)	2.746(4)	Te(13)–Cu(28)	2.596(4)	Cu(5)–Cu(8$^{\mathrm{I}}$)	2.897(6)	Cu(21)–Cu(23$^{\mathrm{I}}$)	2.647(5)
Te(6)–Cu(28)	2.514(4)	Te(13)–Cu(7)	2.601(4)	Cu(6)–Cu(7)	2.487(5)	Cu(22)–Cu(26$^{\mathrm{I}}$)	2.737(5)
Te(6)–Cu(20)	2.568(4)	Te(13)–Cu(24)	2.620(5)	Cu(6)–Cu(14)	2.492(5)	Cu(22)–Cu(27$^{\mathrm{I}}$)	2.742(6)
Te(6)–Cu(22$^{\mathrm{I}}$)	2.638(4)	Te(13)–Cu(18)	2.621(5)	Cu(6)–Cu(29)	2.772(5)	Cu(22)–Cu(25$^{\mathrm{I}}$)	2.866(6)
Te(6)–Cu(27)	2.745(5)	Te(13)–Cu(9)	2.683(4)	Cu(6)–Cu(10)	2.794(6)	Cu(22)–Cu(29$^{\mathrm{I}}$)	2.976(5)
Te(6)–Cu(26)	2.805(4)	Te(14)–Cu(13)	2.598(4)	Cu(7)–Cu(28)	2.529(4)	Cu(23)–P(6)	2.263(8)
Te(6)–Cu(24)	2.851(5)	Te(14)–Cu(16)	2.599(4)	Cu(7)–Cu(9)	2.540(5)	Cu(23)–Cu(25)	2.578(6)
Te(7)–Cu(13$^{\mathrm{I}}$)	2.583(4)	Te(14)–Cu(19)	2.676(4)	Cu(7)–Cu(29)	2.768(5)	Cu(24)–P(7)	2.272(10)
Te(7)–Cu(15)	2.594(4)	Te(14)–Cu(18)	2.717(4)	Cu(7)–Cu(18)	2.777(6)	Cu(24)–Cu(28)	2.593(6)
Te(7)–Cu(20$^{\mathrm{I}}$)	2.633(5)	Te(14)–Cu(9)	2.757(5)	Cu(8)–Cu(19)	2.448(5)	Cu(25)–Cu(26)	2.670(5)
Te(7)–Cu(24$^{\mathrm{I}}$)	2.713(5)	Te(14)–Cu(8)	2.800(4)	Cu(8)–Cu(13)	2.574(5)	Cu(26)–P(8)	2.275(8)
Te(7)–Cu(11)	2.725(4)	Te(15)–Cu(17)	2.655(4)	Cu(9)–P(3)	2.250(10)	Cu(26)–Cu(27)	2.651(5)
Te(7)–Cu(18$^{\mathrm{I}}$)	2.725(4)	Te(15)–Cu(29)	2.702(4)	Cu(9)–Cu(16)	2.592(5)	Cu(27)–Cu(29)	2.587(5)
Te(8)–Cu(8$^{\mathrm{I}}$)	2.536(4)	Te(15)–Cu(10)	2.766(4)	Cu(9)–Cu(18)	2.745(6)	Cu(27)–Cu(28)	2.779(6)
Te(8)–Cu(5)	2.551(4)	Te(15)–Cu(10$^{\mathrm{I}}$)	2.796(4)	Cu(10)–Cu(15)	2.563(5)	Cu(28)–Cu(29)	2.608(5)
Te(8)–Cu(13$^{\mathrm{I}}$)	2.598(4)	Te(15)–Cu(14)	2.820(4)	Cu(10)–Cu(29)	2.616(5)		

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

when they investigated the correlation between electron population and molecular structure for a series of tetranuclear sulfidocyclopentadienyl cluster complexes, which included an elegant study of the tetrahedral cubane-like systems $[Fe_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]^{n+}$ ($n = 0$–2). X-Ray analysis of the neutral 68-valence-electron cluster shows four long Fe–Fe contacts and two normal metal–metal bonds whilst the 66-electron dication displays a marked shortening of two of the four elongated Fe–Fe bonds. Recent studies of $[Co_6Se_8(PR_3)_6]$ have also shown that two-electron oxidations of these electron-rich systems are also possible.[16a]

The marked elongation of the Co–Co bonds contrasts with the relatively small lengthening of the Co–E contacts observed on going from sulfur through to tellurium. The Te···Te contacts in complex **1** [3.447(1)–3.517(1) Å] may reflect the presence of weak bonding interactions. Such a description would then have the (Ph_2Pr^nPCo) units symmetrically [2.502(1)–2.534(1) Å] capping the six Te_4 faces of a distorted Te_8 cube. Steigerwald and co-workers[17] have shown that the complex $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6]$ can be considered as a molecular intermediate in the formation of the binary-phase material β-CoTe. Indeed, their studies have shown that the formation of these premixed intermediates allows for general low-temperature routes to the corresponding bulk materials.[22] Structural relationships between molecular complexes of type **1** and β-CoTe, which has the NiAs type structure, were also described.

The synthesis of numerous metal-rich copper–selenium clusters has been extensively developed in different laboratories.[2,3] Through careful control of reagent ratios, temperature and solvent conditions, various cluster types have been isolated and characterised. Although the nuclearity and geometries are varied, one common characteristic of these systems is that reaction of copper(I) salts with $Se(SiMe_3)_2$ invariably leads to complexes in which the copper to selenium ratio approaches 2:1.[4,5] Our initial findings with the tellurium analogue $Te(SiMe_3)_2$ suggest that the formation of different cluster complexes with non-stoichiometric Cu:Te ratios is equally possible.[6] These findings, combined with the possibility of facile tellurium–carbon bond cleavage to provide a source of RTe^- and Te^{2-} ligands, prompted us to explore the chemistry of the alkyltellurium reagent $TeBu^n(SiMe_3)$.

The molecule $[Cu_{11}(\mu_3\text{-}TeBu^n)_7(\mu_4\text{-}TeBu^n)_2(\mu_7\text{-}Te)(PPh_3)_5]$ **2** is formed in high yield from the reaction of CuO_2CMe and $TeBu^n(SiMe_3)$ in the presence of 2 equivalents of PPh_3 (Scheme 2). The molecular geometry is illustrated in Fig. 2 and Fig. 3 shows the packing arrangement of the Te atoms. The 10 tellurium atoms form one half of a cubeoctahedron, capped on one side by the unique Te atom [Te(10)], yielding a distorted 'close-packed' array. The Te···Te contacts are in fact all greater than 4 (4.009–4.626 Å) thus precluding any significant bonding interactions. Seven of the nine $TeBu^n$ ligands are bonded in μ_3 fashion whilst Te(1) and Te(2) bond to four copper atoms. The bridging of a fourth metal atom does not

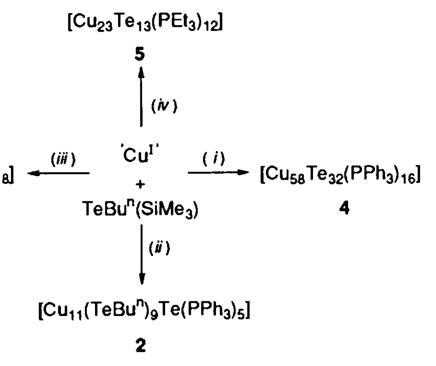
Table 5 Selected bond lengths (Å) and angles (°) for complex **5**

Te(1)–Cu(3)	2.468(2)	Te(2)–Cu(1)	2.6855(8)	Cu(1)–Cu(3)	2.3822(14)	Cu(2)–Cu(3)	2.5491(7)
Te(2)–Cu(3)	2.6546(11)	Te(2$^{\mathrm{VI}}$)–Cu(1)	2.6978(6)	Cu(1)–Cu(2)	2.7249(6)	Cu(2)–Te(1)	2.9607(10)
Te(2)–Cu(2)	2.6580(4)	Cu(1)–P(1)	2.2374(14)				
Cu(3)–Te(1)–Cu(3$^{\mathrm{VIII}}$)	106.57(6)	P(1)–Cu(1)–Te(2$^{\mathrm{XIII}}$)	110.89(2)	Te(1)–Cu(2)–Te(2)	96.13(2)	Cu(1)–Cu(2)–Te(1$^{\mathrm{I}}$)	100.31(4)
Cu(3)–Te(1)–Cu(3$^{\mathrm{X}}$)	86.67(3)	Cu(3$^{\mathrm{IX}}$)–Cu(1)–Te(2$^{\mathrm{XIII}}$)	62.65(2)	Te(2)–Cu(2)–Te(2$^{\mathrm{XII}}$)	118.876(7)	Te(1)–Cu(3)–Cu(1$^{\mathrm{XIV}}$)	144.07(5)
Cu(3$^{\mathrm{IX}}$)–Te(1)–Cu(3$^{\mathrm{X}}$)	157.09(9)	Te(2)–Cu(1)–Te(2$^{\mathrm{XI}}$)	116.49(2)	Cu(3)–Cu(2)–Cu(1$^{\mathrm{XII}}$)	94.32(2)	Te(1$^{\mathrm{V}}$)–Cu(3)–Cu(1$^{\mathrm{XIV}}$)	125.99(5)
Cu(3$^{\mathrm{X}}$)–Te(1)–Cu(3$^{\mathrm{XI}}$)	75.29(5)	Te(2$^{\mathrm{XIII}}$)–Cu(1)–Te(2$^{\mathrm{XI}}$)	103.81(3)	Cu(3$^{\mathrm{VIII}}$)–Cu(2)–Cu(1$^{\mathrm{XII}}$)	53.58(3)	Cu(1$^{\mathrm{XIV}}$)–Cu(3)–Cu(1$^{\mathrm{XI}}$)	88.37(6)
Cu(3$^{\mathrm{VIII}}$)–Te(2)–Cu(2)	57.35(2)	P(1)–Cu(1)–Cu(2)	128.31(3)	Cu(3)–Cu(2)–Cu(1)	125.80(4)	Cu(1$^{\mathrm{XIV}}$)–Cu(3)–Te(1$^{\mathrm{VII}}$)	128.45(4)
Cu(2)–Te(2)–Cu(2$^{\mathrm{III}}$)	84.42(3)	Cu(3$^{\mathrm{IX}}$)–Cu(1)–Cu(2)	59.43(3)	Te(2)–Cu(2)–Cu(1$^{\mathrm{XII}}$)	60.140(13)	Cu(1$^{\mathrm{XI}}$)–Cu(3)–Te(1$^{\mathrm{VII}}$)	142.28(4)
Cu(3$^{\mathrm{VIII}}$)–Te(2)–Cu(1)	92.85(3)	Te(2)–Cu(1)–Cu(2)	58.843(12)	Te(2$^{\mathrm{XI}}$)–Cu(2)–Cu(1$^{\mathrm{XII}}$)	172.13(4)	Te(1)–Cu(3)–Cu(2$^{\mathrm{I}}$)	82.40(4)
Cu(2)–Te(2)–Cu(1)	61.319(11)	Te(2$^{\mathrm{XI}}$)–Cu(1)–Cu(2)	58.700(9)	Cu(1$^{\mathrm{XII}}$)–Cu(2)–Cu(1$^{\mathrm{XI}}$)	119.909(2)	Te(1$^{\mathrm{I}}$)–Cu(3)–Cu(2$^{\mathrm{I}}$)	69.17(6)
Cu(3$^{\mathrm{VIII}}$)–Te(2)–Cu(1$^{\mathrm{XII}}$)	52.85(2)	Te(2$^{\mathrm{XIII}}$)–Cu(1)–Cu(2)	120.80(3)	Te(1)–Cu(2)–Cu(1)	91.74(2)	Te(1$^{\mathrm{II}}$)–Cu(3)–Cu(2$^{\mathrm{I}}$)	95.22(8)
Cu(2)–Te(2)–Cu(1$^{\mathrm{XII}}$)	61.160(13)	Cu(2$^{\mathrm{III}}$)–Cu(1)–Cu(2)	81.89(3)	Te(2)–Cu(2)–Cu(1)	59.839(14)	Cu(1$^{\mathrm{XIV}}$)–Cu(3)–Cu(2$^{\mathrm{I}}$)	66.99(2)
Cu(2)–Te(2)–Cu(1$^{\mathrm{IX}}$)	110.16(2)	Cu(3)–Cu(2)–Cu(3$^{\mathrm{VIII}}$)	72.51(6)	Te(2)–Cu(2)–Te(1$^{\mathrm{I}}$)	96.80(2)	Cu(1$^{\mathrm{XI}}$)–Cu(3)–Cu(2$^{\mathrm{I}}$)	125.85(4)
Cu(1)–Te(2)–Cu(1$^{\mathrm{IX}}$)	122.40(2)	Cu(3)–Cu(2)–Te(1)	43.07(4)	Te(2$^{\mathrm{XII}}$)–Cu(2)–Te(1$^{\mathrm{I}}$)	87.52(4)	Te(1$^{\mathrm{IV}}$)–Cu(3)–Cu(2$^{\mathrm{I}}$)	72.31(5)
Cu(1$^{\mathrm{XII}}$)–Te(2)–Cu(1$^{\mathrm{IX}}$)	75.97(3)	Cu(3)–Cu(2)–Te(2)	133.74(4)	Te(2$^{\mathrm{XI}}$)–Cu(2)–Te(1$^{\mathrm{I}}$)	103.92(4)	Te(1$^{\mathrm{VI}}$)–Cu(3)–Cu(2$^{\mathrm{I}}$)	92.08(6)
P(1)–Cu(1)–Cu(3$^{\mathrm{IX}}$)	167.17(5)	Cu(3$^{\mathrm{VIII}}$)–Cu(2)–Te(2)	61.26(3)	Cu(1$^{\mathrm{XII}}$)–Cu(2)–Te(1$^{\mathrm{I}}$)	83.90(4)	Cu(2$^{\mathrm{I}}$)–Cu(3)–Cu(2$^{\mathrm{V}}$)	88.944(11)
P(1)–Cu(1)–Te(2)	98.39(4)	Cu(3$^{\mathrm{IX}}$)–Cu(2)–Te(2)	91.336(13)	Cu(1$^{\mathrm{XI}}$)–Cu(2)–Te(1$^{\mathrm{I}}$)	90.98(2)	C(3)–P(1)–C(1$^{\mathrm{III}}$)	104.9(2)
Cu(3$^{\mathrm{IX}}$)–Cu(1)–Te(2)	94.44(3)						

Symmetry transformations used to generate equivalent atoms: I $x, -y + 1, z$; II $-x, y, z$; III $x, y, -z$; IV $x, -y + 1, -z$; V $-x, -y + 1, z$; VI $-x, y, -z$; VII $-x, -y + 1, -z$; VIII $z, x + \frac{1}{2}, y - \frac{1}{2}$; IX $-y + \frac{1}{2}; -z + \frac{1}{2}, -x$; X $y - \frac{1}{2}, z + \frac{1}{2}, x$; XI $-z, -x + \frac{1}{2}, -y + \frac{1}{2}$; XII $-y + \frac{1}{2}, z + \frac{1}{2}, x$; XIII $-z, -x + \frac{1}{2}, y - \frac{1}{2}$; XIV $z, x + \frac{1}{2}, -y + \frac{1}{2}$.

Table 6 Average bond distances (Å) for $[Co_6(\mu_3\text{-}E)_8(PR_3)_6]$ complexes

Complex	Co–Co	Co–E	E···E	Ref.
$[Co_6S_6(PEt_3)_6]$	2.817	2.233	3.095	15(*b*)
$[Co_6S_6(PEt_3)_6]^+$	2.794	2.234	3.101	15(*b*)
$[Co_6Se_6(PEt_2Ph)_6]$	2.935	2.351	3.245	14
$[Co_6Se_6(PPh_3)_6]$	3.009	2.351	3.220	14
$[Co_6Te_6(PEt_3)_6]$	3.253	2.525	3.483	17
$[Co_6Te_8(PPh_2Pr^n)_6]$	3.246	2.519	3.474	This work



Scheme 2 (*i*) PPh_3, diglyme; (*ii*) PPh_3, thf; (*iii*) $PPr^n{}_3$, diglyme; (*iv*) PEt_3, thf

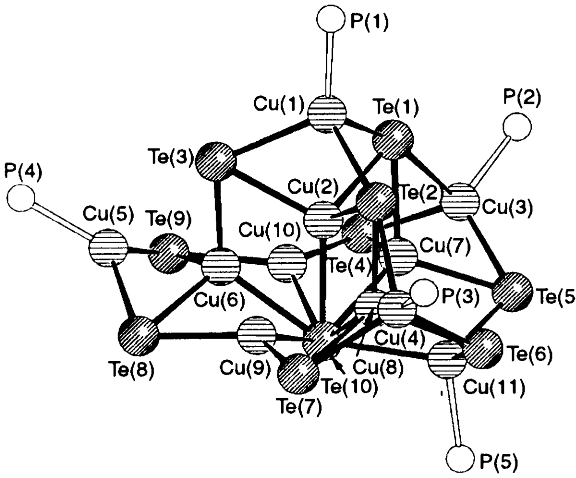


Fig. 2 The molecular structure of $[Cu_{11}(\mu_3\text{-}TeBu^n)_7(\mu_4\text{-}TeBu^n)_2(\mu_7\text{-}Te)(PPh_3)_5]$ **2**. The Cu–Cu contacts and C atoms have been omitted for clarity. Atoms labelled Te(1)–Te(9) are those present as Bu^nTe ligands

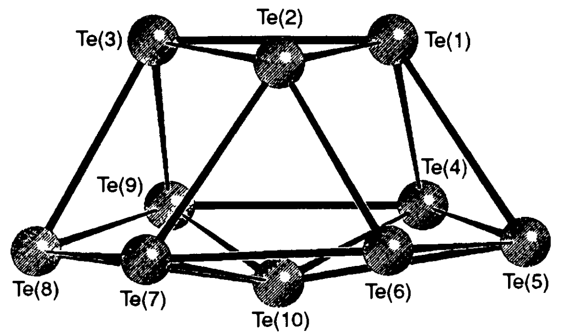


Fig. 3 The geometry of the Te atoms in complex **2**

result in any general lengthening of the Cu–Te distances. Indeed, the longest Cu–Te contacts [3.045(1) and 3.101(1) Å] are associated with the μ_3 ligands Te(7) and Te(4) respectively. The tellurium–carbon bond distances span a relatively narrow range [2.169(9)–2.209(19) Å] and the nine Bu^n groups and 15 phenyl rings serve effectively to envelope and thus solubilise the copper–tellurium core. At the 'base' of the cluster a naked Te atom is found within bonding distance to seven copper atoms [2.599(1)–2.897(1) Å]. The formation of this ligand may have arisen from Te–C bond cleavage although trace quantities of $Te(SiMe_3)_2$ present in the reaction solution (see above) may also act as the source of Te^{2-}. Analogous reactions with an excess (2 equivalents) of $TeBu^n(SiMe_3)$ did not result in the formation of products other than **2**.

Combined, the nine formally RTe^- and lone Te^{2-} ligands require a +1 charge and a d^{10} configuration on the eleven copper atoms. Five of the eleven metal atoms [Cu(1), Cu(3), Cu(4), Cu(5), Cu(11)] are bonded to triphenylphosphine ligands. With the exception of Cu(5), these five copper atoms exhibit distorted-tetrahedral co-ordination geometries, each bonded to three tellurium and one phosphorus atoms. Atom Cu(5) displays a near trigonal-planar co-ordination, bonded to P(4), Te(8) and Te(9) (sum of the corresponding angles = 357.3°). Atom Cu(3) may be regarded as intermediate between the two bonding descriptions, as it exhibits an unusually long Cu–Te contact of 2.939(1) Å. It is also interesting that the two shortest Cu···Cu contacts [Cu(3)···Cu(7) 2.469(1); Cu(5)···Cu(6) 2.479(1) Å] are associated with these metal centres. Theoretical investigations on polynuclear copper(I) systems displaying short metal–metal contacts suggest that these are dictated primarily by the nature of the geometric restraints of the surrounding ligands and that metal–ligand bonding may simply serve to reduce $Cu^+ \cdots Cu^+$ Coulombic repulsive forces by effectively shielding the metal centres.[23] Overall, the long copper–copper contacts however (2.469–2.800 Å) do not suggest any strong metal–metal interactions. Of the six interstitial copper atoms, all exhibit tetrahedral co-ordination environments with the exception of Cu(9) and Cu(10) which have only three bonding contacts and near trigonal-planar co-ordination geometries. Presumably it is the presence of the four shielding Bu^n ligands associated with the open face defined by Te(4), Te(7), Te(8) and Te(9) which prohibit additional sterically demanding[24] PPh_3 ligands from bonding to the co-ordinatively unsaturated metal centres.

The ratio of copper to tellurium in complex **2** approaches 1 : 1. The structure of CuTe[25] consists of a distorted cubic close-packed array of Te atoms with the Cu occupying one half of the tetrahedral sites, the octahedral positions being unoccupied. Unlike in **2**, the stoichiometry of the bulk material requires the copper atoms be in a +2 oxidation state, and thus a d^9 electron configuration. The tellurium–tellurium distances in the extended solid are much shorter (3.16 Å) than those observed in the more open structure **1**. Nonetheless, we note that atoms Cu(6)–Cu(8) and Cu(2) occupy the available tetrahedral sites between the two layers of Te atoms. Although there exist many non-stoichiometric $Cu_{2-x}Te$ phases, the basic geometric arrangement of atoms in the binary material Cu_2Te has Te forming trihedral prisms with the Cu^I within these sites.[26]

If the analogous reaction between CuCl and $TeBu^n(SiMe_3)$ is carried out in the presence of $PPr^n{}_3$ a different structural type is obtained in high yield. Red-brown pseudo-hexagonal plates of $[Cu_{18}(\mu_3\text{-}TeBu^n)_6Te_6(PPr^n{}_3)_8]$ **3** are obtained from cooling diglyme solutions. Crystals of **3** are soluble in hydrocarbon solvents. The molecular structure is illustrated in Fig. 4 and the packing arrangement of the tellurium framework is shown in Fig. 5. The layering of the tellurium atoms is clearly evident, and the 12 atoms adopt a distorted hexagonal-packed (ABA) type geometry, although neither the inter- nor intra-layer Te···Te contacts (3.947–4.737 Å) suggest any strong bonding interactions. The cluster possesses a non-crystallographic three-fold rotation axis along atoms P(1)–Cu(1)–Cu(18)–P(8). Complex **3** contains six Bu^nTe ligands, each bonded in μ_3 fashion to the copper atoms and the remaining Te atoms are each within bonding distances to five or seven copper atoms (Table 3). The three layers of tellurium ligands consist of a 'top' layer of three naked Te atoms, a second layer of three Bu^{n}Te and three which alternate positions around the edges of the triangular array and, finally, a basal triangle consisting of three additional Bu^{n}Te groups. The tellurium–carbon bond lengths of the Bu^n ligands are close to 2.2 Å. Simplistically, one may envisage this arrangement creating two different interlayer environments with, formally, a more negative charge associated with the top half (*i.e.* 4.5 Te^{2-} + 1.5 Bu^nTe^-) *versus* the bottom half of the molecule (1.5 Te^{2-} + 4.5 Bu^nTe^-). Indeed, close examination of the molecular structure of **3** reveals a 'copper-rich' phase associated with the top half of the cluster with 11 Cu atoms, and a 'copper-deficient' lower half, with only seven copper atoms present. The overall combination of 6 Te^{2-} and 6 Bu^nTe^- ligands again suggests a +1 oxidation state for all 18 copper atoms.

Eight of the copper atoms 'cap' open Te_3 triangular faces, with a fourth bonding interaction to a $PPr^n{}_3$ ligand. The long Cu–P contact [2.347(7) Å] associated with Cu(18) is noteworthy however and may reflect the steric crowding associated with this unique metal centre which is bonded to three Bu^{n}Te ligands. The C_4 hydrocarbyl chains appear to bend away from this cavity in the solid-state structure, perhaps in order to accommodate the phosphine ligand. Indeed, the metal centre shows but little deviation from a trigonal-planar type Te_3Cu co-ordination geometry (sum of the angles = 354.7°). Of the interstitial copper atoms, Cu(2)–Cu(4), Cu(13), Cu(14) and Cu(17) display only three bonding contacts each to their neighbouring Te atoms. These six copper atoms are arranged in a highly distorted octahedral geometry around the central copper atom, Cu(11), with somewhat short Cu–Cu contacts [2.472(1)–2.582(1) Å]. Atom Cu(11) also forms but three bonding contacts to the surrounding tellurium ligands.

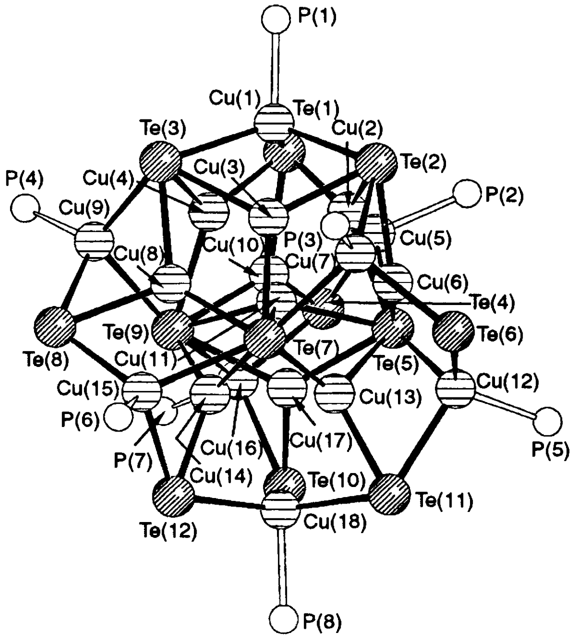


Fig. 4 The molecular structure of $[Cu_{18}(\mu_3\text{-}TeBu^n)_6Te_6(PPr^n{}_3)_8]$ **3** (Cu–Cu contacts and C atoms omitted for clarity). Atoms labelled Te(4), Te(6), Te(8), Te(10)–Te(12) are those of the TeBu^n groups

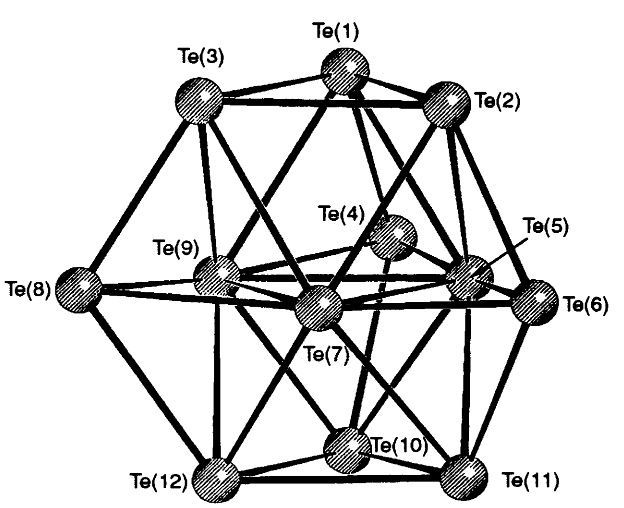


Fig. 5 The tellurium framework in complex **3**

Unlike the reaction of $TeBu^n(SiMe_3)$ with CuO_2CMe, the use of CuCl as a starting reagent in the presence of PPh_3 results in an entirely different cluster complex, $[Cu_{58}Te_{32}(PPh_3)_{16}]$ **4**, being isolated, albeit in low yield. Cluster **4** (Fig. 6) crystallises in the triclinic space group $P\bar{1}$ with only one molecule in the unit cell. The two halves of the cluster are related by a crystallographic inversion centre between atoms Te(15) and Te(15′). There was no evidence for the formation of **4** from the reaction with CuO_2CMe.

The 32 tellurium atoms are arranged in a layered type structure, the most significant deviation being atoms Te(2) which lie between the sheets composed of nine and twelve tellurium atoms. All of the tellurium ligands in this complex are exclusively of the Te^{2-} type, none of the Te–C bonds having been retained, with little bonding interactions between the tellurium atoms (Te $\cdots$ Te 3.733–4.944 Å).

The periphery of the cluster is defined by 28 Te atoms and 16 copper atoms, with the latter each bonded to a PPh_3 ligand and capping open Te_3 faces. The Cu–Te distances of these Ph_3PCu centres span a relatively narrow range [2.588(4)–2.851(4) Å] relative to their interstitial counterparts [2.514(4)–3.100(5) Å]. About the centre of complex **4** are the Te atoms with the highest co-ordination numbers (nine) observed in the cluster, with distances varying from 2.655(4) to 3.064(4) Å. Unlike in complexes **2** and **3**, the presence of 32 discrete Te^{2-} ligands in **4** does not allow for a formal charge of +1 to be assigned to the 58 copper centres and mixed-valence conditions must be assumed. Cluster **4** represents the largest structurally characterised transition metal–tellurium cluster reported to date.

When copper(I) chloride is dissolved in thf with 2 equivalents of triethylphosphine a clear, colourless solution is obtained which immediately turns dark green-black upon the addition of $TeBu^n(SiMe_3)$. Crystals of $[Cu_{23}Te_{13}(PEt_3)_{12}]$ **5** form in near-quantitative yield as black pseudo-octahedra within a few days. They are cubic, and successful solution and refinement of the molecular structure was achieved in the centric space group $Fm\bar{3}$. The molecular structure is shown in Fig. 7. At the centre of a distorted icosahedron of Te atoms is a central tellurium atom Te(1) (Fig. 8). Satisfactory refinement and the elimination of excessive electron density about the central Te was achieved if this atom was refined in a position slightly removed from the crystallographic $m\bar{3}$ site (x = 0.012 79, y = 0.487 21, z = 0.012 79 *versus* 0, $\frac{1}{2}$, 0). The surrounding six copper atoms [Cu(3)] refined with satisfactory thermal parameters when the occupancy was reduced by $\frac{1}{2}$ for the positions at (0, $\frac{1}{2}$, z). Chemically, this has the consequence of eliminating the nonsensical, short (< 2.0 Å) Cu–Te contacts which would have otherwise arisen.

The spherical structure of complex **5** consists of four CuTe layers at the centre of which is the unique Te atom. The cluster core is effectively shielded by the twelve equivalent phosphine ligands bonded to Cu(1). The stoichiometry $Cu_{23}Te_{13}$ has previously been observed in the cluster $[Cu_{23}Te_{13}(PPr^i{}_3)_{10}]$ **6**[6] obtained from the reaction of CuCl with $Te(SiMe_3)_2$. Although clusters **5** and **6** exhibit structural similarities, the more sterically demanding[24] $PPr^i{}_3$ ligand more effectively envelops the latter, requiring only 10 phosphine ligands to do so. Unlike in **6**, the generation of the tellerium ligands in **5** has

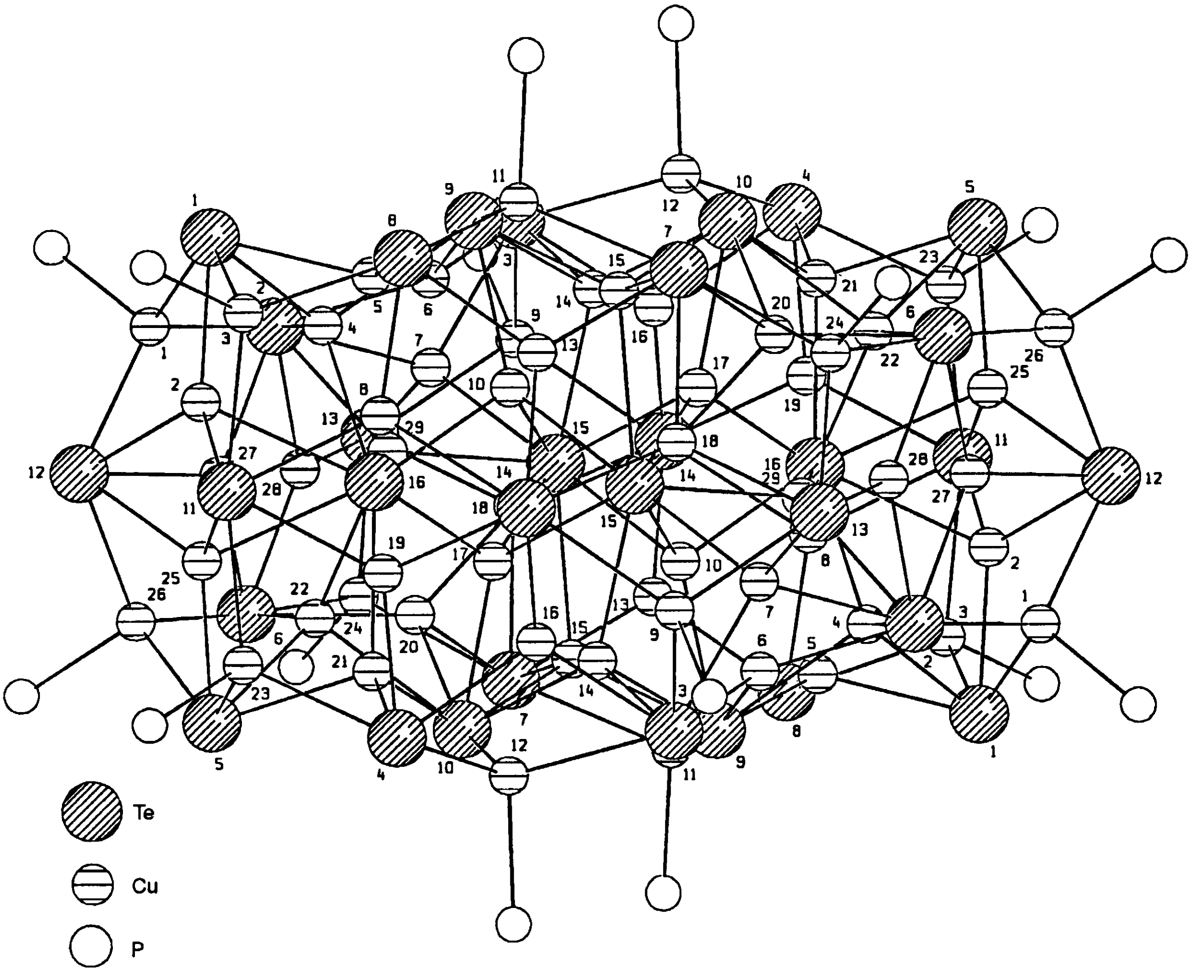


Fig. 6 The molecular structure of $[Cu_{58}Te_{32}(PPh_3)_{16}]$ **4**. The phenyl rings of the phosphine ligands have been omitted and the covalent radii of the Cu atoms reduced for clarity

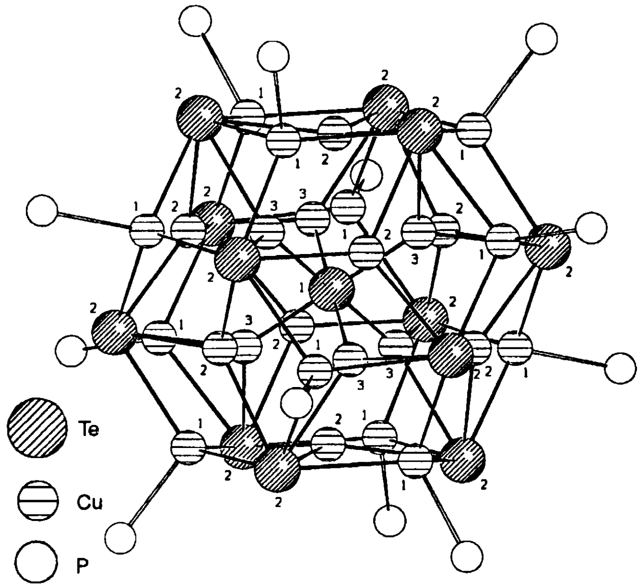


Fig. 7 The molecular structure of $[Cu_{23}Te_{13}(PEt_3)_{12}]$ **5** (Cu–Cu contacts and C atoms omitted). Atoms labelled Cu(3) were satisfactorally refined with only half occupancy

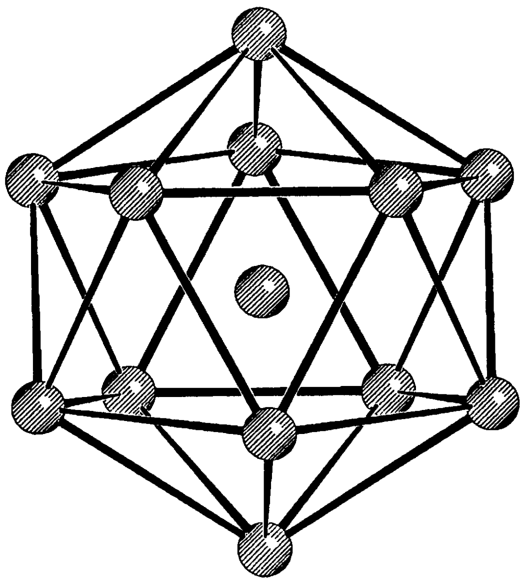


Fig. 8 The Te_{13} polyhedron in complex **5**

occurred from cleavage of the tellurium–carbon bond of the starting reagent $TeBu^n(SiMe_3)$.

In addition to the six contacts to Te(1) [Te(1)–Cu(3) 2.468(2) Å], there are an additional eight weaker Te(1)···Cu interactions [Te(1)···Cu(2) 2.961(1) Å]. The angles about these three-co-ordinate copper sites however suggest little deviation from planarity [Te(2)–Cu(2) 2.658(1) Å, sum of the angles = 356.6°]. The remaining 12 Te atoms are each symmetrically bonded in μ_6 fashion to both the peripheral and interstitial copper centres [Te(2)–Cu 2.655(1)–2.6978(6) Å]. An alternative description of complex **5** is as a body-centred tellurium icosahedron with 12 of the 20 triangular faces capped by $CuPEt_3$ groups, the remaining eight faces spanned by atoms Cu(2). The remaining interstitial atoms, Cu(3), form markedly short contacts to atoms Cu(1) [Cu(1)–Cu(3) 2.382(1) Å], perhaps a consequence of the mixed-valence bonding description which must be associated with **5**. We are currently pursuing the electronic make-up of **5** and related non-stoichiometric clusters and their potential to serve as precursors to related, non-stoichiometric bulk CuTe materials.

The results presented herein suggest that the synthesis of new Cu–Te clusters using $TeR(SiMe_3)$ reagents offers new and unexplored avenues of research for accessing crystalline samples of high-nuclearity cluster complexes. Clearly there is a delicate balance between the choice of phosphine ligand, the method of preparation and crystallisation and the choice of copper(I) salt *versus* the final product formed. We anticipate many new novel and interesting structural types from this generally applicable synthetic method.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft (SFB 195), to the Fonds der Chemischen Industrie and the EU through the HCM program for support of this work. J. F. C. thanks the Natural Sciences and Engineering Research Council (Canada) for a postdoctoral fellowship.

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Received 18*th September* 1995; *Paper* 5/06726J