Butyltellurolate ligands in cluster synthesis: molecular structures of Ag_6Te_6, $Ag_{32}Te_{25}$ and $Ag_{48}Te_{36}$ complexes

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$Bu^nTeSiMe_3$ reacts with silver(I) chloride in the presence of PEt_3 to yield the following series of cluster complexes depending on the relative amount of phosphine used: $[Ag_6(\mu_3\text{-}TeBu^n)_4(\mu\text{-}TeBu^n)_2(PEt_3)_4]$ 1, $[Ag_{32}(\mu_3\text{-}TeBu^n)_{18}Te_7(PEt_3)_6]$ 2 and $[Ag_{48}(\mu_3\text{-}TeBu^n)_{24}Te_{12}(PEt_3)_{14}]$ 3; the molecular structures of 2 and 3 are described.

The chemistry of the heavier chalcogen–transition-metal cluster complexes continues to progress at a rapid pace as highlighted by recent excellent review articles.[1] Although they represent potentially powerful tools for the synthesis of polymetallic metal–main group (cluster) compounds, to this end the chemistry of selenolate (RSe^-) and tellurolate (RTe^-) ligands remains surprisingly unexplored.[1c,2] These ligands are however fuelling widespread interest in early transition-metal-[3] and lanthanide–chalcogenolate[4] mono- and di-meric complexes. Dance and Lee have explored the synthesis of cadmium–chalcogenide/chalcogenolato clusters and their structural relationships to the corresponding semiconducting solid materials[2d] and Steigerwald *et al.* have examined this route as an entry into larger colloidal systems.[2e] Kolis and coworkers[2c] reported the synthesis of a tetranuclear silver–tellurolate complex $[Ag_4(\mu\text{-}TeC_4H_3S)_6]^{2-}$ and Grützmacher *et al.* described the preparation, structure and solution dynamics of the hexameric copper cluster $[\{Cu(SeC_6H_2Pr^i{}_3\text{-}2,4,6)\}_6]$.[2a]

Silylated group 16 elements have been shown to react readily with metal salts MX_n (X = halogen, OAc^-, *etc.*) in a general reaction sequence involving the generation and elimination of 'Me_3SiX' and the formation of metal–chalcogen bonds. If reaction conditions are tailored to ensure homogeneous solutions and controlled (slowed) growth *via* the use of solubilising ancillary ligands, crystalline materials can form from which accurate structural information may then be obtained.[5] Silver chloride is readily dissolved in ethers or hydrocarbon solvents in the presence of excess trialkylphosphine ligands. At room temperature, the addition of $Bu^nTeSiMe_3$ to such solutions proceeds with the immediate precipitation of brick-red amorphous materials. Carrying out the reactions at lower temperatures results in the formation of crystalline products suitable for single-crystal X-ray analysis. Thus the addition of $Bu^nTeSiMe_3$ to pentane solutions of $AgCl\text{–}PEt_3$ (1 : 3) at −40 °C produced a gold solution from which bright yellow crystals of $[Ag_6(\mu_3\text{-}TeBu^n)_4(\mu\text{-}TeBu^n)_2(PEt_3)_4]$ **1** grew within several days at −30 °C (yield 30%). The structure of **1** will be described elsewhere.[6]

If the ratio of phosphine to silver is reduced to 1 : 1, a completely different structural type is obtained with no evidence for the formation of **1**. The cluster $[Ag_{32}(\mu_3\text{-}TeBu^n)_{18}Te_7(PEt_3)_6]$ **2** is formed in low yield under such conditions, in addition to an as yet unidentified gold coloured product. The molecular structure of **2**, as determined by X-ray analysis,[†] is illustrated in Fig. 1. Complex **2** crystallises in the monoclinic space group $P2_1/n$ and with the two molecules in the unit cell, the central tellurium atom Te(13), located on a crystallographic inversion centre, relates the two halves of the molecule. The combination of 18 tellurolate and 7 telluride ligands suggests a +1 oxidation state for the 32 Ag atoms. The Ag–Te framework in **2** also possesses a non-crystallographic threefold rotation axis bisecting atoms Ag(10)–Te(13)–Ag(10) and the structure is clearly layered. The 'top' of the molecule consists exclusively of three $\mu_3\text{-}RTe^-$ groups whereas the second tellurium rich layer is comprised of three μ_3-tellurolate [Te(5), Te(7), Te(9)] and three μ_5-telluride ligands. The latter form a nearly planar Te_3Ag_3 ring (max. dev. 0.10 Å) which itself lies slightly above (0.61 Å) the interstitial silver atom Ag(10). The middle layer of Te is composed of six additional $\mu_3\text{-}Bu^nTe^-$ ligands and the central Te^{2-} atom which is within bonding distance to eight silver atoms. The longest contacts associated with the central tellurium are those to Ag(10) [2.938(2) *vs.* 2.789(2)–2.814(2) Å]. The distorted tetrahedral coordination geometry of these two silver atoms is unique in **2**, the remaining Ag^I centres displaying little deviation from planarity. These latter atoms all form three bonds to neighbouring Te atoms with the exception of Ag(1), Ag(3) and Ag(5) which achieve trigonal-planar coordination by bonding to two tellurolate and one phosphine ligands. Overall, the eighteen butyl chains and six trialkylphosphine ligands effectively envelop and stabilise the inner AgTe core. Although the yield of **2** is low (*ca.* 5%), the synthesis is entirely reproducible. Indeed, there appears to be some inherent stability associated with the Ag–Te framework as we have isolated analogous $[Ag_{32}(TeBu^n)_{18}Te_7(PR_3)_6]$ products using other phosphine ligands.[6]

The relative weakness of the Te–C bond may account for the formation of the telluride ligands in **2**, however $Te(SiMe_3)_2$, produced in small quantities during the synthesis of $Bu^nTeSiMe_3$,[7] may also act as the source of Te^{2-}. We have however previously noted such facile Te–C bond cleavage during the synthesis of Cu–TeR clusters[7] and Arnold and coworkers

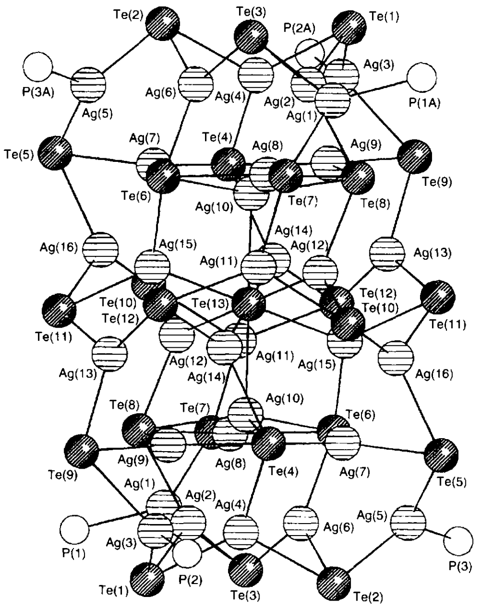

Fig. 1 The molecular structure of $[Ag_{32}(\mu_3\text{-}TeBu^n)_{18}Te_7(PEt_3)_6]$ **2** (carbon atoms omitted). Selected distances (Å): μ_3-RTe–Ag: 2.753(2)–2.848(2), μ_5-Te–Ag 2.762(2)–3.089(2), μ_8-Te(13)–Ag 2.789(2)–2.938(2). Atoms labelled Te(4), Te(6), Te(8) and Te(13) are the telluride (Te^{2-}) ligands.

isolated the remarkable telluride/tellurolate complex $[Ce_5Te_3\{TeSi(SiMe_3)_3\}_9]$[2b] from the reaction of $Ce[N(SiMe_3)_2]_3$ and $HTeSi(SiMe_3)_3$ in hexanes. In sharp contrast, Kanatzidis and Das have recently reported the solvent derived alkylation of Te^{2-} ligands during the preparation of metal carbonyl–telluride clusters.[8]

If an analogous synthetic procedure is followed with an Ag:PEt$_3$ ratio of 1:2, the complex $[Ag_{48}(\mu_3\text{-}TeBu^n)_{24}Te_{12}(PEt_3)_{14}]$ **3** is obtained as the only crystalline product from the reaction mixture, isolated as dark red crystals after several days (yield *ca.* 5–10%, Fig. 2). The cluster consists of two $Ag_{24}Te_{16}$ units linked by four μ_3-TeBu^n ligands. A crystallographic inversion centre relates the two halves of the molecule with a Te(7)···Te(7A) distance of 25.9 Å. The 24 tellurolate ligands are all of the μ_3-type although some exhibit rather long Ag–Te interactions [2.701(2)–3.404(2) Å] with the twelve telluride ligands each within bonding distances to six metal atoms [2.775(2)–3.403(2) Å] yielding a layered type structure as observed in **2**. Unlike in **2**, however, the 14 peripheral Ag-PEt$_3$ sites in **3** all exhibit tetrahedral geometries. The remaining silver atoms within the molecular frame have coordination number three (trigonal planar) or four (tetrahedral) and longer Ag···Te contacts [*cf.* Ag(13)···Te(10) 3.378(2), Ag(18)···Te(10) 3.388(2) Å] also suggest intermediate bonding descriptions. The Ag^{I}···Ag^{I} contacts vary between 2.802(2) and 3.222(2) Å. Unlike the observations by Dance and Lee where structural similarities are sometimes observed between molecular Cd/E/ER clusters and the related bulk material,[2d] the structures of **2** and **3** do not mimic those observed in the various polymorphs of the related silver(I) binary material Ag_2Te.[9] Teo *et al.* have also compared the structural properties of high-nuclearity bimetallic Ag–Au cluster complexes with those of extended solids.[10]

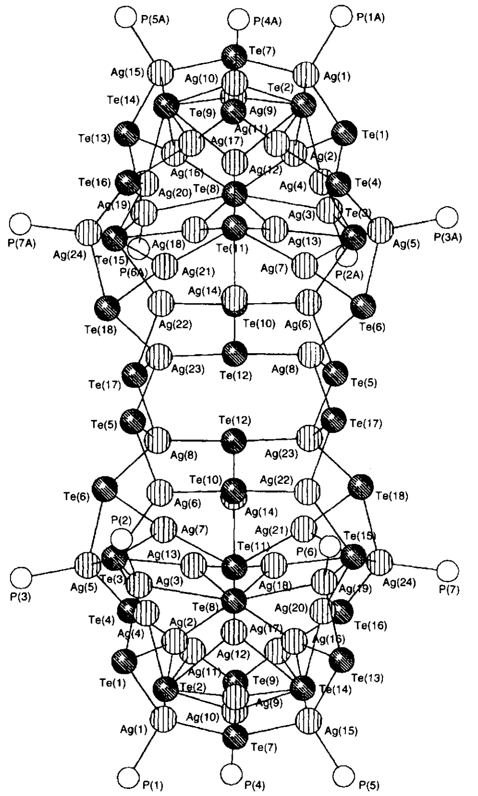

Fig. 2 The molecular structure of $[Ag_{48}(\mu_3\text{-}TeBu^n)_{24}Te_{12}(PEt_3)_{14}]$ **3** (carbon atoms omitted). Selected distances (Å): μ_3-RTe–Ag 2.701(2)–3.404(2), μ_5-Te–Ag 2.802(2)–3.280(2), μ_6-Te–Ag 2.793(2)–3.403(2), μ_7-Te–Ag 2.775(2)–3.292(2). Atoms labelled Te(2), Te(3), Te(8), Te(11), Te(14) and Te(15) are the telluride (Te^{2-}) ligands.

The results presented herein suggest a rich and diverse structural chemistry using tellurolate ligands under low-temperature conditions. Furthermore, the incorporation of additional telluride ligands within the cluster framework [*i.e.* with $Te(SiMe_3)_2$] in conjunction with peripheral RTe$^-$ and PR$_3$ ligands should lead to complexes with even larger molecular frameworks. We are actively exploring these possibilities.

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Footnotes

† *Crystal data* for **1**: $C_{48}H_{114}Ag_6P_4Te_6$, M = 2228.9, monoclinic, space group Cc, a = 20.312(2), b = 24.881(4), c = 14.769(2) Å, β = 92.440(9)°, U = 7457(2) Å^3, at 200 K, Z = 4, D_c = 1.985 g cm^{-3}, μ = 3.958 mm^{-1}, $2\theta_{max}$ = 56.4°, 15445 independent reflections measured (R_{int} = 0.0359). The structure was solved by direct methods and refined on F^2 using SHELXTL software. All P, Ag and Te atoms were refined anisotropically, all C atoms isotropically to yield R = 0.0561, wR = 0.1432, GOF = 1.073 and an absolute structure parameter = −0.02(5) for 10707 data [$F_o > 4\sigma F_o$] (no absorption corrections were applied). The ethyl groups about atoms P(1)–P(3) were disordered over two sites; these were satisfactorily refined with 50:50 occupancy with equivalent P–C distances. For **2**: $C_{108}H_{252}Ag_{32}P_6Te_{25}\cdot 2C_5H_{12}$, M = 8523.1, monoclinic, space group $P2_1/n$, a = 16.453(3), b = 26.060(5), c = 24.666(5) Å, β = 100.82(3)°, U = 10388(4) Å^3, at 200 K, Z = 2, D_c = 2.725 g cm^{-3}, μ = 6.456 mm^{-1}, $2\theta_{max}$ = 52°, 18326 independent reflections measured (R_{int} = 0.0778). The structure was solved and refined as for **1** to yield R = 0.0733, wR = 0.2057 and GOF = 1.038 for 13093 data [$F_o > 4\sigma F_o$]. For **3**: $C_{180}H_{426}Ag_{48}P_{14}Te_{36}$, M = 12796.2, orthorhombic, space group $Pbca$, a = 22.170(4), b = 27.898(6), c = 54.67(1) Å, U = 33815(12) Å^3, at 200 K, Z = 4, D_c = 2.513 g cm^{-3}, μ = 5.847 mm^{-1}, $2\theta_{max}$ = 48.4°, 25105 independent reflections measured (R_{int} = 0.0839). The structure was solved and refined as for **1** to yield R = 0.0727, wR = 0.1893 and GOF = 0.991 for 12184 data [$F_o > 4\sigma F_o$]. Not all C atoms could be located in the difference Fourier map and P–C distances were blocked together and refined with common values. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/20.

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