

# Mono- and bis-silylated tellurium reagents in silver–telluride cluster synthesis: characterisation of $\text{Ag}_{30}\text{Te}_{21}$ and $\text{Ag}_{46}\text{Te}_{29}$ complexes

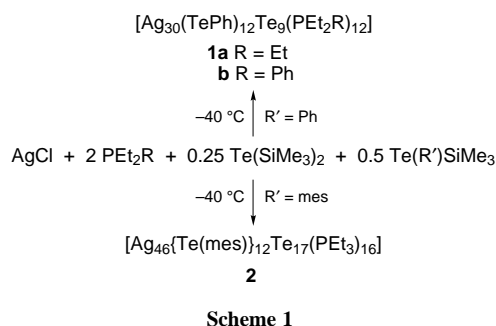
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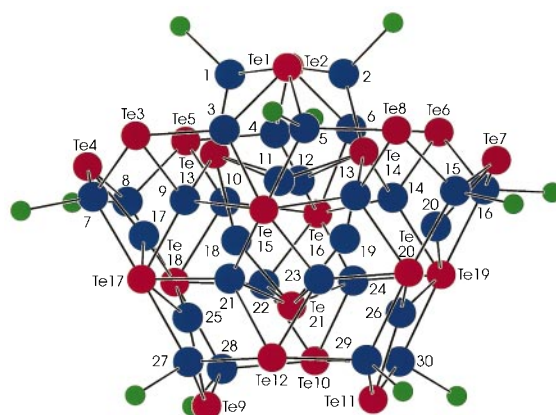
$\text{AgCl}$ , dissolved in ether solvents with tertiary phosphine ligands, reacts with a combination of the silylated reagents  $\text{Te}(\text{SiMe}_3)_2$  and  $\text{Te}(\text{R}')\text{SiMe}_3$  ( $\text{R}' = \text{Ph}, \text{mes}$ ) to yield the cluster complexes  $[\text{Ag}_{30}(\text{TePh})_{12}\text{Te}_9(\text{PEt}_2\text{R})_{12}]$  ( $\text{R} = \text{Et}$  **1a**,  $\text{Ph}$  **1b**) and  $[\text{Ag}_{46}(\text{Te}(\text{mes}))_{12}\text{Te}_{17}(\text{PEt}_3)_{16}]$  **2** in good yields; the molecular structures of **1a** and **2** are described.

The synthesis of mono-disperse, high-nuclearity metal–chalcogenide nanocluster particles represents a formidable challenge. Recent efforts in this area have led to the isolation and structural characterisation of zinc– and cadmium–sulfide complexes whose molecular structures may be viewed as fragments of the bulk semi-conducting solid materials.<sup>1</sup> Reports detailing the synthesis of high-nuclearity metal–chalcogenide clusters of the heavier congeners Se and Te are, however, still relatively rare.<sup>2</sup> Our efforts in this area have focussed on low-temperature reactions using the bis-silylated reagents  $\text{E}(\text{SiMe}_3)_2$  ( $\text{E} = \text{S}, \text{Se}, \text{Te}$ ) with copper(I) salts in the presence of solubilising and (kinetically) stabilising phosphine ligands.<sup>3</sup> Controlled reaction conditions are essential in ensuring crystalline cluster formation vs. the precipitation of amorphous, bulk phase solids and it has thus been possible to isolate and characterise a variety of copper–chalcogenide clusters. Efforts to extend this chemistry to related silver–chalcogenides using a similar synthetic strategy have however proven unsuccessful to date as the phosphine ligands are unable to sufficiently stabilise the  $\text{Ag–E}$  molecular cores.  $\text{We}$ ,<sup>4a,b</sup> and others,<sup>4c,d</sup> have however shown that silver–chalcogenolate  $[\text{Ag}_x(\text{ER})_x]$ ,  $\text{R} = \text{alkyl}, \text{aryl}$  polynuclear complexes are accessible. Using sterically demanding or functionalised chalcogenolate ligands, it has been possible to isolate homoleptic polynuclear complexes.<sup>4c,d</sup> We set out to exploit the utility of both phosphine ligands and tellurium bonded alkyl/aryl chains in order to stabilise various  $\text{AgTe}$  cores. The synthesis of these complexes offers a rich and varied structural chemistry by modification of the  $\text{PR}_3$  and  $\text{TeR}$  centres.<sup>4a,b</sup> We reasoned that the incorporation of additional Te sites within the cluster cores should be possible with the reagent  $\text{Te}(\text{SiMe}_3)_2$  leading to even larger molecular frameworks. Herein we present the initial results of our findings, detailing the synthesis and molecular structures of  $[\text{Ag}_{30}(\mu_3\text{-TePh})_{10}(\mu_4\text{-TePh})_2\text{Te}_9(\text{PREt}_2)_{12}]$  **1** ( $\text{R} = \text{Et}$  **1a**,  $\text{Ph}$  **1b**) and  $[\text{Ag}_{46}(\mu_3\text{-Te}(\text{mes}))_{12}\text{Te}_{17}(\text{PEt}_3)_{16}]$  **2** ( $\text{mes} = \text{C}_6\text{H}_2\text{Me}_3$ ).

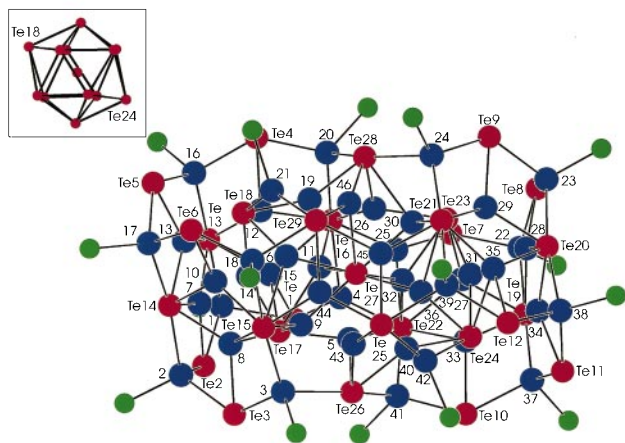
The preparations of **1** and **2**† are summarised in Scheme 1. Thus when a  $\text{AgCl–PR}_3$  (1 : 2) solution is treated with 0.5 equiv.



of  $\text{Te}(\text{Ph})\text{SiMe}_3$  and 0.25 equiv.  $\text{Te}(\text{SiMe}_3)_2$  at  $-40^\circ\text{C}$ , a dark red, homogeneous solution is produced from which crystals of **1** form within a few days at  $-30^\circ\text{C}$  (yield: **1a** = 20%; **1b** = 95%). The molecular structures of both **1a** and **1b** are essentially identical, and, owing to the better quality of the X-ray data set of the former, only it will be used in discussing the structural parameters.† The cluster core is comprised of 12 tellurolate  $[\text{Te}(\text{Ph})^-]$ ,  $\text{Te}(1)–\text{Te}(12)]$  and 9 telluride  $[\text{Te}^{2-}, \text{Te}(13)–\text{Te}(21)]$  ligands in addition to the 30 silver atoms (Fig. 1).<sup>5</sup> The order of addition of the silylated reagents does not affect the yield of product produced. The tellurolate ligands in **1a** adopt both  $\mu_3$   $[\text{Te}(1)–\text{Te}(9), \text{Te}(11)]$  and  $\mu_4$   $[\text{Te}(10)–\text{Te}(12)]$  bonding modes. The former exhibit an unsymmetrical pattern of one ‘shorter’  $[2.717(3)–2.826(3) \text{ \AA}]$ , one longer  $[2.842(3)–2.981(3) \text{ \AA}]$  and one intermediate  $\text{Ag–Te}$  bonding distances with  $\text{Te}(9)$  and  $\text{Te}(11)$  showing the least deviation  $[\text{Ag–Te } 2.817(3)–2.853(3), 2.790(3)–2.842(3) \text{ \AA}]$ , respectively. On average, the difference in length between the longest and shortest  $\text{Ag–Te}$  contacts is  $0.14 \text{ \AA}$ . The  $\mu_4\text{-Te}(\text{Ph})\text{–Ag}$  bond lengths in **1** are noticeably longer  $[2.933(8) \text{ \AA av.}]$  than their  $\mu_3$  counterparts. The nine  $\text{Te}^{2-}$  ligands  $[\text{Te}(13)–\text{Te}(21)]$  are each six coordinate  $[\text{Ag–Te } 2.703(3)–3.185(3) \text{ \AA}]$  and atoms  $\text{Te}(14)$  and  $\text{Te}(16)$  also exhibit a longer contact to a seventh metal site  $[3.260(3), 3.229(3) \text{ \AA}]$ , respectively. A +1 oxidation state can be assigned to the silver atoms and the  $\text{Ag}\cdots\text{Ag}$  contacts  $[2.849(3)–3.351(3) \text{ \AA}]$  preclude any strong bonding interactions between them. Of the twelve phosphine bonded silver sites, all exhibit tetrahedral coordination with the exception of  $\text{Ag}(1)$  and  $\text{Ag}(2)$  which are trigonal planar. Of the phosphine free silver atoms,  $\text{Ag}(18)$  and  $\text{Ag}(19)$  form but two bonds each  $[\text{Te–Ag–Te } 153.1(1) \text{ and } 153.22(9)^\circ]$ , respectively, whereas atoms  $\text{Ag}(3)$ ,  $\text{Ag}(6)$ ,  $\text{Ag}(11)$ ,  $\text{Ag}(12)$ ,  $\text{Ag}(17)$ ,  $\text{Ag}(20)$ ,  $\text{Ag}(25)$  and  $\text{Ag}(26)$  are three coordinate and  $\text{Ag}(9)$ ,  $\text{Ag}(10)$ ,  $\text{Ag}(13)$ ,  $\text{Ag}(14)$ , and  $\text{Ag}(21)–\text{Ag}(24)$  display tetrahedral coordination geometries. This varied coordination about silver contrasts with the solid state structure of the mineral



**Fig. 1** Molecular structure of  $[\text{Ag}_{30}(\text{TePh})_{12}\text{Te}_9(\text{PEt}_3)_{12}]$  **1a** (carbon atoms omitted; red: Te; blue: Ag; green: P). Silver atoms are labelled with numbers only for clarity. Tellurium atoms labelled  $\text{Te}(1)–\text{Te}(12)$  are the tellurolate ligands. Selected bond lengths ( $\text{\AA}$ ):  $\text{Te–C}$ :  $2.13(1)–2.18(2)$ ,  $\mu_3\text{-Te}(\text{Ph})\text{–Ag}$   $2.717(3)–2.981(3)$ ;  $\mu_4\text{-Te}(\text{Ph})\text{–Ag}$   $2.878(3)–3.013(3)$ ;  $\mu_{6/7}\text{-Te–Ag}$   $2.703(3)–3.229(2)$ ,  $\text{Ag}\cdots\text{Ag}$   $2.849(3)–3.351(3)$ .



**Fig. 2** The molecular structure of  $[\text{Ag}_{46}\{\text{Te}(\text{mes})\}_{12}\text{Te}_{17}(\text{PEt}_3)_{16}] \mathbf{2}$  (carbon atoms omitted; red: Te; blue: Ag; green: P). Tellurium atoms Te(1)–Te(12) are the telluroate ligands. Selected bond lengths (Å): Te–C 2.139(13)–2.179(11),  $\mu_3$ -Te(mes)–Ag 2.732(2)–2.947(2),  $\mu_6$ -Te–Ag 2.688(2)–3.338(2),  $\mu_7$ -Te–Ag 2.676(2)–3.304(2),  $\mu_8$ -Te–Ag 2.785(2)–3.294(2), Ag–Ag 2.748(9)–3.377(4).

hessite ( $\text{Ag}_2\text{Te}$ ) in which all Ag atoms are in tetrahedral sites.<sup>6</sup>

The Ag–Te framework in **1** is less spherical in nature than those observed in related CuTe systems.<sup>7</sup> The latter crystallise with parallel  $\text{Cu}_n\text{Te}_m$  layers yielding a rather close packed arrangement. In **1**, the AgTe planes defined by Te(4)Te(18)–Te(9)Te(17)/Ag(7)Ag(8)Ag(27)Ag(28) and Te(7)Te(19)–Te(11)Te(20)/Ag(15)Ag(16)Ag(29)Ag(30) lie at an angle of  $56^\circ$  to one another.

An analogous reaction as for **1** with the bulkier reagent  $\text{Te}(\text{mes})\text{SiMe}_3$  (Scheme 1) leads to the exclusive formation of  $[\text{Ag}_{46}\text{Te}_{17}(\text{Te}(\text{mes}))_{12}(\text{PEt}_3)_{16}] \mathbf{2}$  as dark red–black crystals (yield 85%, Fig. 2). As in **1**, cluster **2** contains a mixture of telluride and telluroate ligands. There is a pseudo, non-crystallographic twofold rotation axis which bisects the central  $\text{Te}^{2-}$  [Te(27)] approximately perpendicular to the plane defined by the page (the projection is slightly rotated for clarity). About the central telluride can be found an additional 12  $\text{Te}^{2-}$  [Te(15)–Te(18), Te(21)–Te(26), Te(28), Te(29)] arranged to form a slightly distorted [non-bonded,  $\text{Te}\cdots\text{Te}$  4.523(2)–5.288(2) Å] centered icosahedron (Fig. 2, insert). Eight silver metal atoms are bonded to Te(27) [2.814(2)–3.198(2) Å] and are found within the icosahedral frame with six additional Ag atoms [Ag(4), Ag(5), Ag(25), Ag(26), Ag(44), Ag(45)] lying within its deltahedral faces. Twenty of the thirty  $\text{Te}_2$  edges of the icosahedron are spanned by Ag atoms. This central  $\text{Ag}_{36}\text{Te}_{13}$  unit is surrounded by 16 tellurium [ $12 \times \text{Te}(\text{mes})^-$ ,  $4 \times \text{Te}^{2-}$ ] and 12 Ag centres. As observed in **1**, the coordination number about the silver centres varies from two to four.

As in **1**, the metal core is stabilised with  $\text{PR}_3$  ligands and aromatic groups bonded to the outer tellurium atoms. Indeed, there is a close structural relationship between the outer fragments found in **1** and **2**. The relative arrangement in **1** of atoms Te(3)–Te(5), Te(9), Te(10), Te(12) and Te(13) and the silver atoms bonded to them is also repeated in cluster **2**. Two such fragments share a common ‘edge’ in **1** whereas in **2** they are separated by the larger inner core. This perhaps reflects the better shielding ability of the bulkier mesityl groups and the additional coordinated  $\text{PR}_3$  ligands.

The synthetic strategy outlined herein opens the doorway to accessing a variety of silver–chalcogenide clusters. We are currently actively pursuing the generation and characterisation of new and even larger molecular species.

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## Footnotes and References

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† *Preparation of 1*: a 0.16 g (1.12 mmol) sample of AgCl was dissolved in 36 ml of dried ether–thf (3 : 1) with 2.2 mmol of  $\text{PEt}_3\text{R}$  (R = Et **1a**, Ph, **1b**) and the clear, colourless solution cooled to  $-40^\circ\text{C}$ . 0.13 ml  $\text{Te}(\text{Ph})\text{SiMe}_3$  (0.6 mmol) was added followed by 0.06 ml  $\text{Te}(\text{SiMe}_3)_2$  resulting in a homogeneous yellow reaction solution. The solution was stirred for 1 h while warming to  $-30^\circ\text{C}$  gradually darkening in colour to deep red. Crystals of **1** grew within several days at this temperature. Yield: **1a**, 20%; **1b**, 95%. A similar procedure using  $\text{PEt}_3$  and  $\text{Te}(\text{mes})(\text{SiMe}_3)$  in ether yielded red–black crystals of **2** in 85% yield.

‡ *Crystal data*: for **1a**:  $\text{C}_{144}\text{H}_{240}\text{Ag}_{30}\text{P}_{12}\text{Te}_{21}\cdot\text{OC}_4\text{H}_{10}$ , red plate fragment,  $0.15 \times 0.19 \times 0.23$  mm,  $M = 8332.8$ , monoclinic, space group  $P2_1/n$ ,  $a = 28.614(6)$ ,  $b = 28.163(6)$ ,  $c = 29.296(6)$  Å,  $\beta = 93.56(3)^\circ$ ,  $U = 23580(8)$  Å<sup>3</sup>, at 200 K,  $Z = 4$ ,  $D_c = 2.347$  g cm<sup>-3</sup>,  $\mu = 5.089$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 52.2^\circ$ , 40888 independent reflections measured ( $R_{\text{int}} = 0.1266$ ) on a STOE IPDS diffractometer. 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  $R = 0.0900$ ,  $wR_2 = 0.2345$ , GOF = 1.073 for 18883 data [ $F_o > 4\sigma F_o$ ]. Phenyl rings were refined as rigid groups, the bond distances of the solvent molecule and the P–C distances about P(1) and P(2) were each refined with common values.

**1b**:  $\text{C}_{192}\text{H}_{372}\text{Ag}_{30}\text{P}_{12}\text{Te}_{21}$ , red plate fragment,  $0.06 \times 0.15 \times 0.20$  mm,  $M = 835.2$ , monoclinic, space group  $P2_1/n$ ,  $a = 24.052(5)$ ,  $b = 31.045(6)$ ,  $c = 37.611(8)$  Å,  $\beta = 103.33(3)^\circ$ ,  $U = 27327(9)$  Å<sup>3</sup>, at 180 K,  $Z = 4$ ,  $D_c = 2.147$  g cm<sup>-3</sup>,  $\mu = 4.398$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 44.5^\circ$ , 18826 independent reflections measured ( $R_{\text{int}} = 0.1544$ ) on a STOE IPDS diffractometer. The structure was solved by direct methods and refined as for **1a** to yield  $R = 0.1392$ ,  $wR_2 = 0.3698$ , GOF = 1.050 for 12081 data [ $F_o > 4\sigma F_o$ ]. Phenyl rings were refined as rigid groups and not all C atoms could be located in the difference Fourier map.

**2**:  $\text{C}_{204}\text{H}_{372}\text{Ag}_{46}\text{P}_{16}\text{Te}_{29}\cdot 3\text{OC}_4\text{H}_{10}$ , dark red block,  $0.7 \times 0.7 \times 0.7$  mm,  $M = 12205.3$ , triclinic, space group  $P\bar{1}$ ,  $a = 19.894(4)$ ,  $b = 25.672(3)$ ,  $c = 37.771(3)$  Å,  $\alpha = 72.94(1)$ ,  $\beta = 81.17(2)$ ,  $\gamma = 68.37(2)^\circ$ ,  $U = 17121(4)$  Å<sup>3</sup>, at 180 K,  $Z = 2$ ,  $D_c = 2.368$  g cm<sup>-3</sup>,  $\mu = 5.093$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 44.5^\circ$ , 42728 independent reflections measured ( $R_{\text{int}} = 0.0905$ ) on a STOE IPDS diffractometer. The structure was solved by direct methods and refined as for **1** to yield  $R = 0.0663$ ,  $wR_2 = 0.1771$ , GOF = 1.057 for 33664 data [ $F_o > 4\sigma F_o$ ]. Atoms Ag(21) and Ag(42) were disordered over two sites and each refined satisfactorily with 70 : 30 and 65 : 35 relative occupancies, respectively. CCDC 182/558.

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