Synthesis and structure of Cs_2Te_{13} and Cs_4Te_{28}, tellurium-rich tellurides on the methanolothermal route to Cs_3Te_{22}

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Reaction of Cs_2CO_3 and As_2Te_3 in superheated methanol at 160 and 180 °C afford Cs_2Te_{13} and Cs_4Te_{28}, respectively, whose anionic structures contain Te_{13}^{2-} chains (Cs_2Te_{13}), Te_6^{2-} chains and Te_n rings (n = 4,8) (Cs_4Te_{28}) as building units.

Intermediate-temperature synthetic techniques including flux and solvatothermal methods have been developed in recent years to enable the incorporation of molecular building blocks such as chains X_n^{2-} and rings X_n (X = S, Se, Te) into polychalcogenides.[1–3] For instance, we have recently reported the methanolothermal preparation of $RbTe_6$[4] and Cs_3Te_{22}[5] as the first members of a new class of very tellurium-rich alkali-metal tellurides M_xTe_y with $y/x > 4$. Cs_3Te_{22} contains both isolated crown-shaped Te_8 rings and planar sheet anions† $^{2}_{\infty}[Te_6^{3-}]$ constituted of tellurium atoms with linear and T-shaped coordination geometries. Extended Hückel calculations on Cs_3Te_{22} by Hoffmann and coworkers[6] demonstrated that the geometries of the anionic Te atoms are determined by their particular electron count. These authors predicted that Cs_3Te_{22} will be metallic and have suggested two structurally related phases $[Cs(Te_8)]^+[CsTe_6]^-$ or Cs_2Te_{14}, and $[Cs(Te_8)]_3{}^{3+}[CsTe_6]^{3-}$ or Cs_4Te_{30}. Kanatzidis[7] concluded that related compounds with more than one identical layer might be possible as part of a homologous family.

The presence of two such strikingly different tellurium components in Cs_3Te_{22} can only be explained by assuming an alkali-metal directed template control of compound formation involving several reactions steps. We have now established that the reaction of Cs_2CO_3 with As_2Te_3 in superheated methanol, at temperatures lower than previously employed for Cs_3Te_{22} (195 °C),[5] leads to the formation of two related tellurium-rich tellurides with novel building units.‡ Cs_2Te_{13} may be obtained together with Cs_2Te_5[8] at 150–160 °C, Cs_4Te_{28} together with Cs_2Te_5 and Cs_3Te_{22} at 170–180 °C.

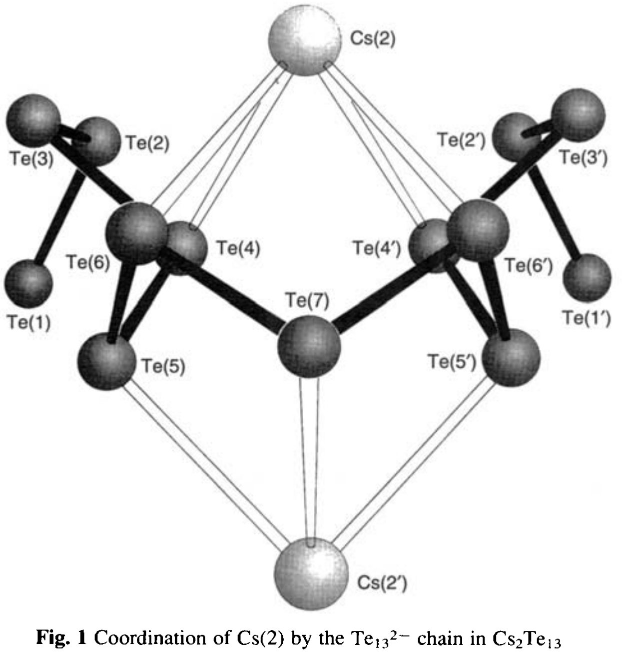

Fig. 1 Coordination of Cs(2) by the Te_{13}^{2-} chain in Cs_2Te_{13}

The crystal structures§ of Cs_2Te_{13} and Cs_4Te_{28} provide a fascinating mechanistic insight into the formation of separated Te_8 rings and $^{2}_{\infty}[Te_6^{3-}]$ sheet anions in Cs_3Te_{22}. On ignoring secondary Te···Te interactions longer than 3.17 Å in Cs_2Te_{13}, the anion structure can be described as an isolated Te_{13}^{2-} chain that is stabilised by its coordination of the caesium atom Cs(2) (Fig. 1). The largest previously known Te_n^{2-} anions were provided for n = 8 by an isolated spirobicyclic species $[Te(Te_3)(Te_4)]^{2-}$ with $[K([15]\text{-crown-}5)_2]^+$ as counter cation[9] and by chainlike building units in the sheet anions $^{2}_{\infty}[Te_4]$ of $CsTe_4$.[10] Characteristic for the novel chain anion Te_{13}^{2-} with its C_s symmetry is the central Te_7 unit [atoms Te(4) to Te(4)′] that can be regarded as an incomplete crown. Bond lengths [2.755(2)–2.808(2) Å], bond angles [99.4(1)–100.4(1) °] and

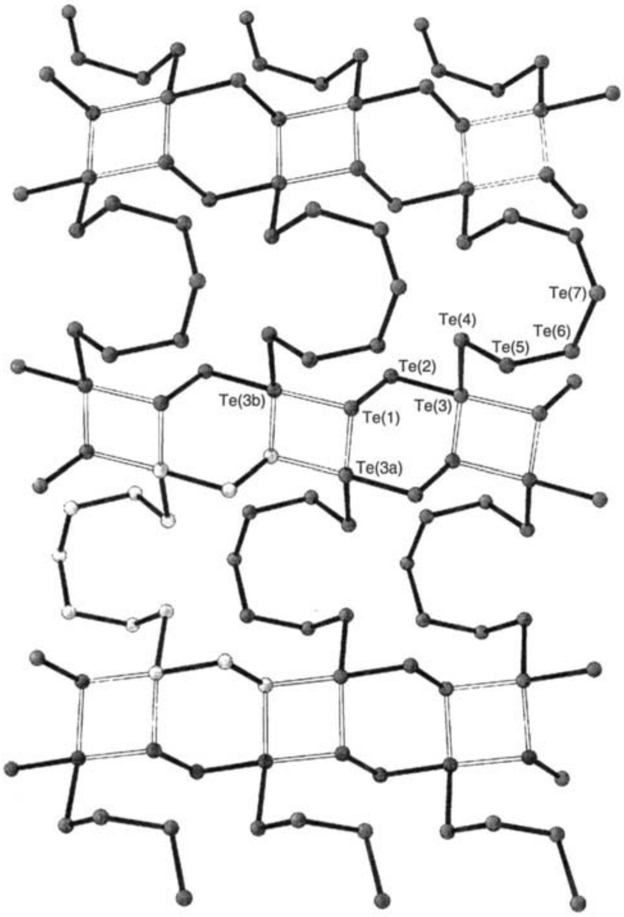

Fig. 2 Structure of the sheet anion $^{2}_{\infty}[Te_{13}^{2-}]$ perpendicular to [010] on inclusion of the secondary Te(1)···Te(3) interactions. Selected bond distances: Te(1)–Te(2) 2.763(2), Te(2)–Te(3) 2.896(2), Te(3)–Te(4) 2.910(2) Å.

torsion angles [108.3(1), 98.2(1) °] in the Te_7 fragment are reminiscent of those observed for isolated Te_8 rings in Cs_3Te_{22} and Cs_4Te_{28}. The Te_{13}^{2-} chains in the crystal lattice of Cs_2Te_{13} are connected into an undulating sheet through secondary Te(1)···Te(3) interactions [distances 3.181(2) and 3.261(2) Å] leading thereby to a ladder of Te_4 rectangles and chair-shaped Te_6 rings (Fig. 2). Te(1) exhibits a pyramidal geometry, Te(3) a distorted square-planar geometry. The template controlled formation of separated Te_8 crowns and ${}^{2}_{\infty}[Te_6]$ sheets can now be readily explained on the basis of the Cs_2Te_{13} structure. Cleavage of the symmetry-related Te(3)–Te(4) bonds and addition of a Te atom to the liberated Te_7 fragment affords the isolated Te_8 rings. Rearrangement of the remaining ${}^{1}_{\infty}[Te_6^{2-}]$ chains into a thinned 4^4 net with Te_4 and Te_{12} squares as observed in Cs_3Te_{22} can be achieved by cleavage of the old Te(1)–Te(2) bonds and formation of new Te(1)–Te(2) bonds between the remaining Te_4 rings of originally adjacent ladders.

A phase of the stoichiometry (Cs_2Te_{14}) proposed by Hoffmann and coworkers[6] can indeed be synthesised in superheated methanol at a temperature elevated by 20 °C in comparison to the preparation conditions for Cs_2Te_{13}. However, whereas the isolated polytelluride Cs_4Te_{28} does contain isolated Te_8 crowns, the formation of a ${}^{2}_{\infty}[Te_6^{2-}]$ sheet anion remains incomplete (Fig. 3). The discrete Te_8 rings [Te(1), Te(2)] exhibit C_4 symmetry and display molecular dimensions similar to those of the analogous crowns in Cs_3Te_{22}. When Te···Te secondary bonds longer than 3.15 Å are ignored, both Te_6^{2-} chains and isolated Te_4 square rings can be identified in the lattice of Cs_4Te_{28}. These molecular building units are linked through longer Te(5)···Te(6) and Te(5)···Te(7) interactions [lengths 3.153(2) and 3.194(2) Å] into a network structure ${}^{3}_{\infty}[Te_{20}^{4-}]$. The all-*trans* configured Te_6^{2-} chains [Te(5) to Te(5)′ with C_2 symmetry], which can be regarded as a fragment of the helix structure of elemental tellurium, connect the individual sheets of Te_4 rings [Te(6), Te(7)] with C_i symmetry. A consequence of the above interpretation of the Cs_4Te_{28} structure will be a partial localisation of negative charge on the terminal atoms Te(5) of the bridging Te_6 chains. Addition of two electrons to the ${}^{3}_{\infty}[Te_{20}^{4-}]$ unit in Cs_4Te_{28} must lead to cleavage of the Te(4)–Te(5) bonds and formation of two planar ${}^{2}_{\infty}[Te_6^{3-}]$ sheet anions (as in Cs_3Te_{22}) and a further Te_8 ring [from atoms Te(3) and Te(4)]. Extended Hückel calculations[6] have yielded atomic charges of −1.065 for the linear Te atoms and −0.87 for the Te_4 rings in Cs_3Te_{22}. Inspection of the ${}^{2}_{\infty}[Te_6]$ sheets in Cs_4Te_{28} indicates that charge must have been removed mainly from the now effectively isolated Te_4 rings, which exhibit Te–Te distances of 2.911(2) and 2.955(2) Å, markedly shorter than in Cs_3Te_{22} [3.003(1) Å]. At the same time, the secondary bonds to the bridging atom Te(5) are on average 0.097 Å longer than in Cs_3Te_{22} [3.077(1) Å]. These atoms are displaced from the plane of the Te_4 squares [Te(6)–Te(5)–Te(7) 166.57(4) °].

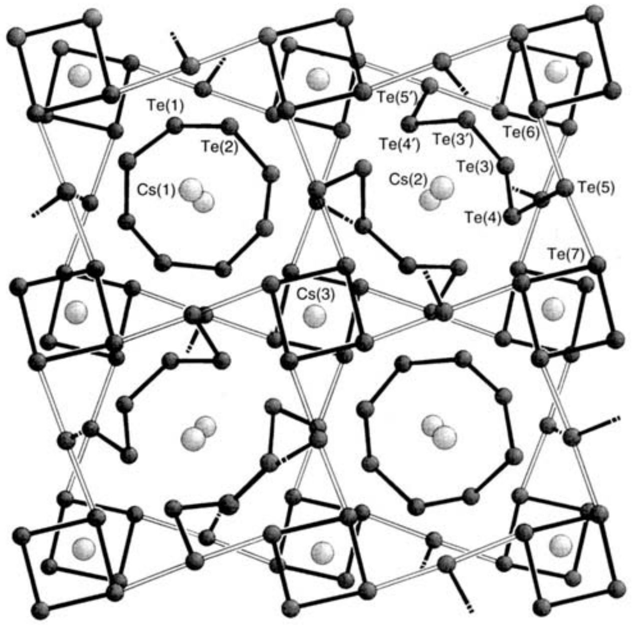

Fig. 3 Network structure of ${}^{3}_{\infty}[(Te_8)(Te_4)_2(Te_6^{2-})_2]$ in Cs_4Te_{28} depicted perpendicular to [001]. Selected bond distances and angles: Te_8 ring, Te(1)–Te(2) 2.778(2), Te(1)–Te(2′) 2.829(2) Å, Te(1)–Te(2)–Te(1′) 100.63(7), Te(2)–Te(1)–Te(2′) 97.91(6) °; Te_6^{2-} chain, Te(3)–Te(3′) 2.788(3), Te(3)–Te(4) 2.774(2), Te(4)–Te(5) 2.797(2) Å.

The present work demonstrates how controlled variation of methanolothermal reaction conditions can allow the synthesis of designed solid-state structures. It also provides a unique mechanistic insight into template directed structural pre-assembly in solid-state synthesis in superheated fluids.

Footnotes

† In the notation for infinite anions ${}^{n}_{\infty}[\ ]$ the index *n* refers to the dimensionality of the structure

‡ Cs_2CO_3 and As_2Te_3 were heated in 0.5 ml MeOH in a sealed glass tube to the required temperature. After tempering the contents were cooled to 20 °C at 1.5 °C h^{-1}. The phases were separated manually and characterised by their crystal data. Cs_2Te_{13}: Cs_2CO_3 (0.200 g), As_2Te_3 (0.296 g), T = 160 °C, 100 h; yields Cs_2Te_5 (27%), Cs_2Te_{13} (5%). Cs_4Te_{28}: Cs_2CO_3 (0.148 g), As_2Te_3 (0.309 g), T = 180 °C, 10 h; yields Cs_2Te_5 (30%), Cs_3Te_{22} (8%), Cs_4Te_{28} (3%).

§ *Crystal data* for Cs_2Te_{13}: Siemens P4 diffractometer, Mo-Kα radiation, orthorhombic, space group *Pbcm*, a = 7.341(1), b = 13.593(3), c = 22.652(5) Å, U = 2320.2(8) Å^3, $F(000)$ = 3144, Z = 4, D_c = 5.51 g cm^{-3}, R = 0.052 [for 1604 data with $I > 2\sigma(I)$], wR_2 = 0.128 for 2647 unique reflections. Absorption corrections were based on ψ-scan data (max/min transmission 0.022/0.003). The structure was solved with SHELXS and refined with SHELXL. For Cs_4Te_{28}: tetragonal, space group *P4/ncc*, a = b = 18.885(2), c = 13.517(2) Å, U = 4821(2) Å^3, $F(000)$ = 6704, Z = 4, D_c = 5.65 g cm^{-3}, R = 0.033 [for 1148 data with $I > 2\sigma(I)$], wR_2 = 0.074 for 3566 unique reflections. Absorption corrections were based on ψ-scan data (max/min transmission 0.032/0.008). Diffractometer and refinement as above. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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