Synthesis and *X*-Ray Structure of a Chiral, Arsenic-rich Telluride, $As_{10}Te_3^{2-}$

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Oxidation of polyarsenides with elemental Te or reduction of As_2Te_3 with potassium both yield large arsenic telluride anions, one of which, $As_{10}Te_3^{2-}$, has been structurally characterized.

The homopolyatomic anions of the Group 15 elements like arsenic display a wide range of structures and stoicheiometries such as As_4^{2-}, As_6^{4-}, As_7^{3-}, and As_{11}^{3-}.[1] Examples of heteropolyanions containing arsenic and the chalcogens are known, such as $As_8S_{13}^{2-}$,[2] $As_4S_6^{2-}$,[3] and $As_2Te_6^{2-}$,[4] but their structures do not resemble the homopolyatomic anions, *i.e.* they do not usually contain As–As bonds, as they are predominantly chalcogen rich with arsenic : chalcogen ratios of less than one. We report here the synthesis and structure of the first example of an arsenic rich, chalcogen containing polyanion, $As_{10}Te_3^{2-}$, which is chiral.

Two synthetic routes to the As–Te clusters have been investigated, one involving the oxidation of arsenic polyanions with elemental Te and the other reduction of As_2Te_3 with potassium. Stirring of solid As_2Te_3 with potassium in ethylenediamine (en) followed by treatment of the filtrate with PPh_4Br in en gives two products: a major product of poorly diffracting brown plates, the elemental analysis of which showed it to contain As/Te anions, and a minor product (<10%) of dark rods which a single crystal structure determination showed to be the title compound.

The structure[†] of $(PPh_4)_2As_{10}Te_3$ was solved in the triclinic

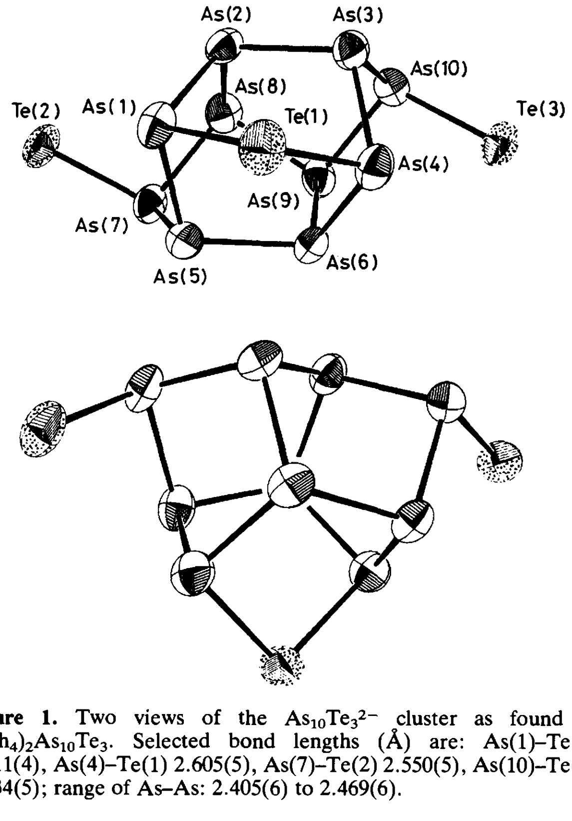

Figure 1. Two views of the $As_{10}Te_3^{2-}$ cluster as found in $(PPh_4)_2As_{10}Te_3$. Selected bond lengths (Å) are: As(1)–Te(1) 2.611(4), As(4)–Te(1) 2.605(5), As(7)–Te(2) 2.550(5), As(10)–Te(3) 2.534(5); range of As–As: 2.405(6) to 2.469(6).

[†] *Crystal data* for $(PPh_4)_2As_{10}Te_3$: space group $P\bar{1}$, $a = 10.536(4)$, $b = 26.84(1)$, $c = 9.574(2)$ Å, $\alpha = 91.15(3)$, $\beta = 90.51(3)$, $\gamma = 90.63(4)°$, $U = 2707(3)$ Å^3, $Z = 2$, $D_c = 2.22$ g cm^{-3}. For 3424 reflections with $(I) > 3\sigma(I)$, $R = 7.6\%$. For Mo-K_α radiation, $\mu = 218$ cm^{-1} and an empirical absorption correction was applied. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

space group $P\bar{1}$ and consists of six five-membered rings sharing edges as shown in Figure 1. The basic eleven atom cluster is related to the P_{11}^{3-} [5] or As_{11}^{3-} [6] structure type but with one of the two co-ordinate phosphorus atoms in P_{11}^{3-} replaced by a bridging Te atom and with two additional Te atoms bonded in an exopolyhedral fashion to As(10) and As(7). Like P_{11}^{3-}, $As_{10}Te_3^{2-}$ is chiral but the crystals do not display optical activity as both enantiomers are present in the unit cell and are related by an inversion centre. The As–As distances in $(PPh_4)_2As_{10}Te_3$ [range: 2.405(6) to 2.469(6) Å] are similar to the corresponding distance in As_{11}^{3-} [range: 2.357(7) to 2.474(7) Å][6] and slightly shorter than the As–As contacts of 2.517 Å in α-As. As in the anion $As_2Te_6^{2-}$ [4] which has As to bridging Te distances of 2.601(2) and 2.604(2) Å and an As to terminal Te distance of 2.506(2) Å, the anion $As_{10}Te_3^{2-}$ also contains shorter As–Te bonds for the terminal Te compared to the bridging Te (see Figure 1).

When a melt of nominal composition K_3As_7 is powdered, stirred with dry ethylenediamine, filtered, and stirred with six equivalents of Te powder per As_7^{3-} for 12 h under anaerobic conditions, the Te dissolves and the solution turns from orange to dark orange–brown. Filtration and treatment of the solution with PPh_4Br in en gives good yields of very thin, orange–brown needles which have As/Te ratios of *ca.* 2.8 : 1 from elemental analysis. The crystals obtained in this fashion *via* the oxidation of As_7^{3-} with elemental Te using the cations PPh_4^+, Et_3NMe^+, or $EtPPh_3^+$ all showed the presence of As/Te anions from elemental analysis but it was not possible to obtain satisfactory *X*-ray diffraction data on any of the compounds.

The mechanism of formation of $As_{10}Te_3^{2-}$ from As_2Te_3 is not clear at this time, but probably involves the formation of polytellurides in addition to the arsenic containing anions.

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