Electrochemical Synthesis and Structural Characterization of the One-Dimensional Chain Compound $(Et_4N)_2[As_2Te_5]$ and the Tellurido Arsenate $(Me_4N)_4[As_4Te_6]\cdot 2en$

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The new arsenic telluride $(Et_4N)_2[As_2Te_5]$ (1) has been prepared by electrolytically dissolving As_2Te_3 cathodes into an ethylenediamine solution of Et_4NI. Telluride 1 crystallizes in the triclinic space group $P\bar{1}$ with lattice constants $a = 9.296(2)$, $b = 11.341(4)$, $c = 7.829(2)$ Å, $\alpha = 104.31(2)°$, $\beta = 98.60(2)°$, $\gamma = 112.54(2)°$, $V = 710.6(4)$ Å^3, $Z = 1$, and $R(R_w) = 0.064(0.058)$. The structure consists of infinite one-dimensional $As_2Te_5^{2-}$ chains running parallel to the c axis which are surrounded by Et_4N^+ cations. The structure of the unique $As_2Te_5^{2-}$ chain is built up from alternating As_2^{4+} dimers (As–As = 2.451(8) Å) and square planar Te_5^{6-} fragments with As–Te contacts of 2.587(5) and 2.598(4) Å. The Te_5^{6-} moieties contain a central square-planar tellurium atom bonded to the neighboring four Te atoms at 3.058(4) Å (2×) and 3.009(3) Å (2×). Changing the supporting electrolyte to Me_4NI allows $(Me_4N)_4[As_4Te_6]\cdot 2en$ (2) to be isolated. Telluride 2 crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.905(3)$, $b = 10.347(4)$, $c = 19.017(5)$ Å, $\beta = 100.92(2)°$, $V = 2300(1)$ Å^3, $Z = 2$ and R $(R_w) = 0.062$ (0.063). Like 1, telluride 2 contains As_2^{4+} dimers bonded to four tellurium atoms but forms an As_4Te_2 six-membered ring with an exocyclic terminal Te atom on each arsenic.

Introduction

The binary compounds formed between the chalcogenides and the pnictides span the range from molecules to three-dimensional solids. The properties of the lighter members of this class, such as the minerals orpiment (As_2S_3)[1] and realgar (As_4S_4),[2] resemble those of molecular materials, while the heavier solids, such as the mineral tellurobismuthite (Bi_2Te_3), have interesting optical and electronic properties.[3] Many of these M_2X_3 solids adopt the rhombohedral $R\bar{3}m$ tetradymite structure type. It is also possible to solubilize binary anionic clusters from neutral solids containing the group 15 and 16 elements as exemplified by the formation of As–S polyanions by the treatment of arsenic sulfides with organic amines,[4] and the work of Sheldrick and co-workers involving solvothermal reactions of arsenic sulfides and selenides with carbonates in methanol.[5] Other arsenic selenide compounds have been isolated by Kolis and co-workers.[6] In the As–Te polyanion system the clusters $As_{10}Te_3^{2-}$,[7] $As_{11}Te^{3-}$,[8] $As_2Te_6^{2-}$,[9] and $As_4Te_6^{4-}$ [10] are known. We recently reported the novel electrochemical synthesis of a wide variety of novel polyanions based on the cathodic dissolution of several different types of tellurium alloy electrodes. Examples include $Au_3Te_4^{3-}$ and $Au_2Te_4^{2-}$,[11] $GaTe_2(en)_2^{1-}$,[12] $In_2Te_4^{2-}$,[13] and $Hg_3Te_7^{4-}$.[14] This electrochemical method was also used to prepare several antimony telluride anions such as $Sb_4Te_4^{4-}$,[15] $Sb_9Te_6^{3-}$,[15] $Sb_2Te_5^{4-}$,[16] and $Sb_6Te_9^{4-}$.[16] Here we report the extension of this technique to the As–Te system with the isolation of the new one-dimensional (1-D) polymer $(Et_4N)_2[As_2Te_5]$ (1)

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and the molecular species $(Me_4N)_4[As_4Te_6]\cdot 2en$ (2), from As_2Te_3 electrodes in the presence of tetraalkylammonium halide electrolytes in ethylenediamine.

Experimental Section

General Methods. All manipulations were performed under an oxygen-free helium atmosphere. Ethylenediamine (en) was purchased from Aldrich (Gold Label, 99+%), purified by distillation from CaH_2 followed by distillation from a red solution of K_4Sn_9, and stored under He. The tetraalkylammonium salts were also purchased from Aldrich and used without further purification.

Electrode Fabrication. As_2Te_3 was prepared by the fusion of the elements (Cerac, 99.99%) in quartz under an inert atmosphere. The product was ground to a fine powder and recast in quartz tubes into 10-mm cylindrical electrodes of area ca. 1 cm^2. Copper wires were soldered onto the electrodes which were then fastened with epoxy into glass jackets leaving just the alloy exposed. The anodes were strips of Ni foil of surface area ca. 3 cm^2 sealed similarly in glass jackets.

Synthesis. The electrochemical cell was a two-compartment, liquid junction, airtight cell fitted with medium-porosity glass frits dividing the compartments. All three chambers of the electrochemical cell were filled with the electrolyte solution. The concentrations of the salts were approximately 0.30 M for the Et_4NI solution and 0.15 M for the Me_4NI solution. The assembled electrochemical cells were attached to constant current power supplies and electrolyzed at 300 μA for 5 days to produce 1 and 100 μA for 5 days to produce 2. Choice of current was determined by the solubility of the cations in the en, the values given being the maximum allowed. Yields for both compounds were greater than 30% (based on As consumed from the electrode) with electrochemically yields (mol of product/mol of e^- passed) averaging 10% or less.

Crystallography. The X-ray data for both samples was collected on crystals sealed in thin-walled glass capillaries on a Rigaku AFC7R four-circle diffractometer equipped with an 18-kW RU300 rotating anode source using graphite-monochromated Mo Kα radiation. Data collection for 1 consisted of scans of $(1.05 \pm 0.35 \tan \theta)^\circ$ in the range $5^\circ < 2\theta < 45^\circ$ which were made at a speed of 8°/min (in ω). Data collection for 2 was done at the same speed with scans of $(1.10 + 0.35 \tan \theta)^\circ$ in the range $5^\circ < 2\theta < 50^\circ$. Both data sets were collected using the ω–2θ scan technique. Weak reflections $[I < 10.0\ \sigma(I)]$ were rescanned a maximum of four times and averaged, and the intensities of three standard reflections were measured after every 150 reflections. Over the course of data collection, the standards in both samples decreased in intensity (7–26%) and polynomial correction factors were applied to account for these phenomena. Both data sets were also corrected for Lorentz and polarization effects.

The structures were solved by direct methods and refined on F by full-matrix least-squares using the TEXSAN crystallographic software package of Molecular Structure Corp.[17] All non-hydrogen atoms were refined anisotropically in 1 and either isotropically or anisotropically in 2. Hydrogen atoms in structure 1 were included in their calculated positions but not included in 2 because of the larger displacement parameters of the carbon atoms. The ethylenediamine molecule in the asymmetric unit of 2 was severely disordered and refined by assigning occupancy factors of $^1/_2$ to both of the nitrogen atoms (over four sites) and fixing their positions. One of the carbon atoms in the ethylenediamine molecule was also disordered over two sites and given a site occupancy of $^1/_2$ at each position. Further details of the X-ray structural analyses are given in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients are given in Tables 2 and 3, and some selected interatomic distances and angles for 1 are given in Table 4.

Table 1. Crystallographic Data for $(Et_4N)_2As_2Te_5$ (1) and $(Me_4N)_4As_4Te_6\cdot 2en$ (2)

	1	2
empirical formula	$C_{16}H_{40}N_2As_2Te_5$	$C_{20}H_{64}N_8As_4Te_6$
formula wt (g/mol)	1048.35	1482.07
crystal color, habit	dark red, spear	red, needle
crystal dimensions (mm)	0.07 × 0.04 × 0.03	0.15 × 0.40 × 0.20
crystal system	triclinic	monoclinic
lattice parameters		
a (Å)	9.296(2)	11.905(3)
b (Å)	11.341(4)	10.347(4)
c (Å)	7.829(2)	19.017(2)
α (deg)	104.31(2)	90.00
β (deg)	98.60(2)	100.92(2)
γ (deg)	112.54(2)	90.00
V (Å^{-3})	710.6(4)	2300(1)
Z	1	2
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
D_{calc} (g/cm^3)	2.449	2.140
radiation	Mo Kα	Mo Kα
$\mu_{Mo\ K\alpha}$ (cm^{-1})	73.88	66.33
T (°C)	20	20
reflections measured		
total	1886	4554
unique	1746 (R_{int} = 0.054)	4296 (R_{int} = 0.122)
used in refinement ($II > 3\sigma(I)$)	941	1010
$R(R_w)$[a]	0.064(0.058)	0.062(0.063)

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for the Non-Hydrogen Atoms of $(Et_4N)_2As_2Te_5$ (1)[a]

atom	x	y	z	B(eq)
Te(1)	0.9377(3)	0.1760(2)	0.7963(3)	3.68(7)
Te(2)	1.0000	0.0000	1.0000	3.25(9)
Te(3)	1.1032(3)	0.2322(2)	1.3590(3)	3.34(7)
As(1)	1.1110(5)	0.1094(4)	0.5974(5)	3.5(1)
N(1)	0.624(3)	0.290(2)	0.281(4)	3.2(7)
C(1)	0.724(4)	0.354(5)	0.482(4)	6(1)
C(2)	0.641(5)	0.341(4)	0.627(5)	5(1)
C(3)	0.532(4)	0.377(4)	0.256(5)	4(1)
C(4)	0.432(5)	0.326(4)	0.049(6)	5(1)
C(5)	0.734(5)	0.294(3)	0.171(5)	4(1)
C(6)	0.852(5)	0.435(4)	0.169(5)	4(1)
C(7)	0.510(5)	0.142(4)	0.242(4)	4(1)
C(8)	0.570(5)	0.050(4)	0.282(6)	5(1)

[a] $B(eq) = {}^8/_3\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12aa}{}^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

Results and Discussion

When the electrochemical cells described in the Experimental Section are fitted with an As_2Te_3 cathode and a Ni foil anode and filled with a solution of Et_4NI in en, a darkly colored red stream emanates from the cathode when a constant current of 300 μA is applied. As more current is passed, the electrode dissolves and the catholyte becomes very dark as the polyanions increase in concentration. After 5 days, two crystalline products are isolated from the cathode chamber: thin red needles having an As:Te ratio of between 1:1.2 and 1:1.5 (based on multiple EDS analyses), and black spear-shaped crystals which appear red in a thin section having an As:Te ratio of 1:2.25–1:2.58. These crystals appear to be the only solid products obtained from the cathodic dissolution process and are isolated in an approximate 50:50 ratio. The thin red needles have to date been unsuitable for single-crystal X-ray analysis, and attempts to grow more suitable ones are currently underway. Single-crystal X-ray analysis of the black spear-shaped crystals revealed the new arsenic telluride $(Et_4N)_2[As_2Te_5]$ (1). A purple powder, which has a Ni:I ratio of approximately 1:2 according EDS analysis, was deposited on and near the anode. The conversion of the anodic oxidation products into a solid is advantageous in that mixing of these anodic products

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[17] TEXSAN Single Crystal Structure Analysis Software Package, Version 1.6, 1993, Molecular Structure Corp.; The Woodlands, TX 77381.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for the Non-Hydrogen Atoms of $(Me_4N)_2As_4Te_6 \cdot 2en$ (2)[a]

atom	*x*	*y*	*z*	*B*(eq)
Te(1)	0.0163(3)	0.7219(3)	0.7981(2)	6.23(8)
Te(2)	0.1307(3)	0.4721(3)	0.9372(2)	5.58(8)
Te(3)	0.2785(3)	0.2026(3)	1.0524(2)	7.9(1)
As(1)	0.0212(4)	0.6928(4)	0.9311(2)	4.9(1)
As(2)	0.1675(4)	0.4057(4)	1.0721(2)	5.0(1)
N(1)	−0.145(3)	1.144(3)	0.834(2)	7.3(9)
N(2)	0.646(3)	0.040(4)	0.135(2)	8.2(9)
N(3)	1.050	0.142	0.436	11.1
N(3′)	0.917	0.091	0.465	5.9
N(4)	0.982	−0.037	0.296	5.9
N(4′)	0.882	−0.060	0.321	5.9
C(1)	−0.129(4)	1.251(5)	0.789(3)	9(1)
C(2)	−0.223(4)	1.193(4)	0.881(2)	8(1)
C(3)	−0.047(5)	1.096(5)	0.882(3)	9(1)
C(4)	−0.210(4)	1.040(4)	0.790(2)	6(1)
C(5)	0.541(4)	−0.039(4)	0.106(2)	7(1)
C(6)	0.691(5)	0.119(5)	0.077(3)	10(1)
C(7)	0.638(4)	0.126(5)	0.198(3)	8(1)
C(8)	0.745(4)	−0.049(4)	0.161(2)	8(1)
C(9)	0.980(5)	0.117(6)	0.397(3)	12(1)
C(10)	0.926(9)	0.01(1)	0.375(6)	8(1)
C(10′)	0.978(9)	−0.040(10)	0.359(6)	9(1)

[a] Atoms N(3), N(3′), N(4), N(4′), C(10), and C(10′) have occupancy factors of $^1/_2$.

with the highly reducing catholytic polyanion solution is thus prevented, allowing the reactions to run for longer periods of time.

The arsenic and tellurium in **1** are present as novel 1-D $As_2Te_5^{2-}$ infinite chains which are separated in the solid state by Et_4N^+ cations. These chains run parallel to the crystallographic *c* axis and have the structure shown in Figure 1. A unit cell view of the $(Et_4N)_2[As_2Te_5]$ compound showing the one-dimensional chains separated by the Et_4N^+ cations is shown in Figure 2. The polyanions that make up these chains can be considered in a formal sense to be built up from As–As bonded As_2^{4+} dimers and planar Te_5^{6-} squares. The arsenic–arsenic bond length of the As_2^{4+} dimer, which lies astride the $\bar{1}$ site at 0, 0, $^1/_2$, is 2.451(8) Å and can be compared to As–As distances of 2.517 Å in the α form of elemental arsenic[18] or the contacts in the range of 2.357–2.498 Å as found in the As_7^{3-} [19] or As_{11}^{3-} [20] polyanions. The As_2^{4+} dimers are bonded to four neighboring Te atoms at 2.587(5) and 2.598(4) Å. These As–Te distances are similar to the As–Te distances of 2.604–2.614 Å for μ^3 bridging tellurium atoms in previously characterized arsenic tellurides.[7,9,10]

The tellurium portion of the polyanion can be considered to be present as 36-electron $TeTe_4^{6-}$ units that are topologically similar to XeF_4 molecules.[21] Similar Te moieties can be recognized in Ga_2Te_5.[22] However, the closest structural analogs to the 1-D chains in **1**, in terms of the $TeTe_4^{6-}$ units, are found in the 1-D chains present in K_2SnTe_4[23] and isotypic Rb_2SnTe_5.[24] In all of these materials containing the $TeTe_4^{6-}$, the distance of the central Te to the remaining Te atoms falls in a surprisingly narrow range around 3.05 Å. The polymeric anions present in K_2SnTe_5 and Rb_2SnTe_5 are shown in Figure 3b, where it can be seen that an Sn^{4+} cation and As_2^{4+} dimers occupy similar positions within the chains with respect to the $TeTe_4^{6-}$ units. The distances per comparable repeat unit along the $SnTe_5^{2-}$ and $As_2Te_5^{2-}$ chains are very similar with values of 7.795 and 7.829 Å for $SnTe_5^{2-}$ and $As_2Te_5^{2-}$, respectively. The similarity of charge and connectivity requirements of the Sn^{4+} cations and As_2^{4+} dimers suggest it may be possible to prepare materials with a solid solution of different cations at the metal sites within the telluride chain as was recently found for the 1-D chains in $K_2HgSnTe_4$.[25] In fact, the 1-D telluride chains in $K_2HgSnTe_4$ (Figure 3c) are related to the chains in $SnTe_5^{2-}$ by simply replacing the square-planar Te with a tetrahedral Sn/Hg site which results in a halving of the *c* axis in $HgSnTe_4^{2-}$ (or $As_2Te_5^{2-}$) relative to $SnTe_5^{2-}$. The compound K_2SnTe_5,[23] which was reported to crystallize in the polar space group *I*4*cm* actually appears to be centric and, like $K_2HgSnTe_4$, crystallizes in the space group *I*4/*mcm*.[25]

When the reaction conditions used to prepare **1** are changed by substituting Me_4NI for the Et_4NI electrolyte, a maximum current of 100 μA is allowed to pass, and a new arsenic telluride compound, $(Me_4N)_4[As_4Te_6] \cdot 2en$ (**2**), is isolated as the only solid product from the cathode chamber. Dark red needles of telluride **2** contain the $As_4Te_6^{4-}$ anion which is shown in Figure 4b. This anion consists of a six-membered As_4Te_2 ring with an exocyclic Te atom bonded to each As atom in the ring. The $As_4Te_6^{4-}$ polyanion was previously identified by Eisenmann et al. in the material $[Ba(en)_4]_2As_4Te_6$.[10] The As–As distances in **2** of 2.457(6) Å, along with the bridging As–Te distances of 2.611(5)–2.623(5) Å and terminal As–Te contacts of 2.537(5)–2.544(5) Å, are all very similar to those reported in the $[Ba(en)_4]_2^{4+}$ compound. While ethylenediamine molecules in **2** do not have the same chelating role as in the $[Ba(en)_4]_2^{4+}$ compound, they may be involved in hydrogen-bonding interactions with the Te atoms in the $As_4Te_6^{4-}$ anions. The nearest Te–N distances of between 3.325(3)–3.719(3) Å are within the range expected for these hydrogen-bonding interactions,[12] but the large thermal motion of the ethylenediamine nitrogen atoms and the extreme disorder of these molecules in the crystal structure make it difficult to say if this hydrogen bonding actually exists.

Both $(Et_4N)_2[As_2Te_5]$ (**1**) and $(Me_4N)_4[As_4Te_6] \cdot 2en$ (**2**) are soluble in DMF and acetonitrile and are only slightly soluble in ethylenediamine. Neither are soluble in methanol, and they decompose into silver metallic-looking solids when dissolved in water. They are also both extremely air sensitive, decomposing into black solids on exposure to the atmosphere.

It is interesting to note that while both **1** and **2** contain As–As bonds, neither the monoclinic[26] nor rhombohedral[27] modifications of As_2Te_3, the starting electrode material, have any direct As–As interactions. However, the As–As interaction forms the basis of a common building block

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Table 4. Selected Bond Distances (angstroms) and Angles (degrees) for $(Et_4N)_2As_2Te_5$ (1)

bond distances		bond angles			
As(1)–As(1)*	2.451(8)	As(1)–Te(1)–Te(2)	85.3(1)	Te(1)–Te(2)–Te(3)	88.80(7)
Te(1)–As(1)	2.587(5)	Te(1)–As(1)–Te(3)	102.7(1)	Te(1)–Te(2)–Te(3)*	91.20(7)
Te(3)–As(1)	2.598(4)	Te(2)–Te(3)–As(1)	101.2(1)	Te(1)–Te(2)–Te(1)*	180.00
Te(1)–Te(2)	3.009(3)	Te(3)–As(1)–As(1)	95.8(2)	Te(3)–Te(2)–Te(3)*	180.00
Te(2)–Te(3)	3.058(2)	Te(1)–As(1)–As(1)*	94.6(2)		

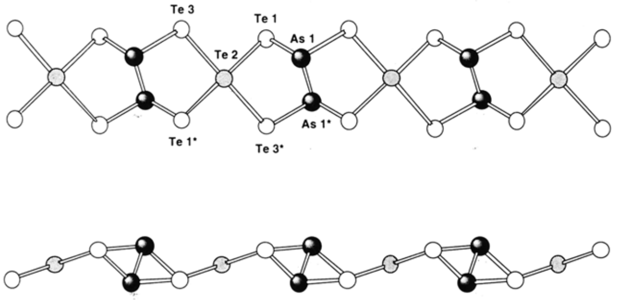

Figure 1. Top: structure of the polymeric $As_2Te_5^{2-}$ chains in 1. Bottom: An edge-on view, 90° from the top view, of the same structural unit. Selected bond lengths and angles for this compound are given in Table 4.

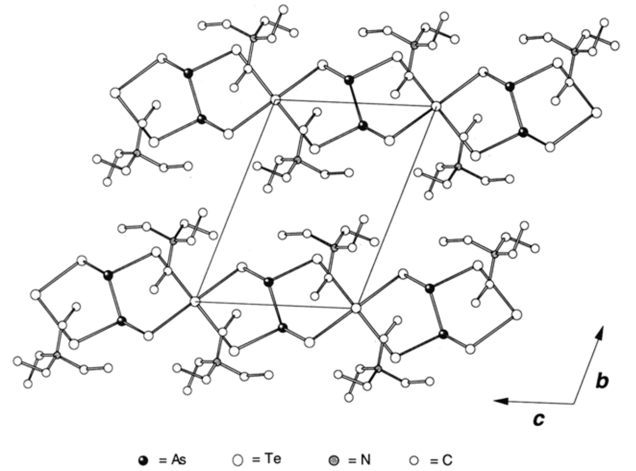

Figure 2. Unit-cell view of the structure of $(Et_4N)_2[As_2Te_5]$ (1) showing the one-dimensional $As_2Te_5^{2-}$ chains which are separated by tetraethylammonium cations.

that is found in both 1 and 2. As shown in Figure 4A, an arsenic–arsenic bonded As_2Te_4 moiety (A) is found in both tellurides 1 and 2. In fact, we have isolated and structurally characterized this $As_2Te_4^{4-}$ unit (from a high-temperature fusion/extraction synthesis) and will report its structure shortly. Figure 4B shows how the As_2Te_4 units combine, with the loss of two Te atoms to form the $As_4Te_6^{4-}$ anion, while Figure 4C shows the As_2Te_4 unit present in each repeat unit of the infinite 1-D $As_2Te_5^{2-}$ polymer.

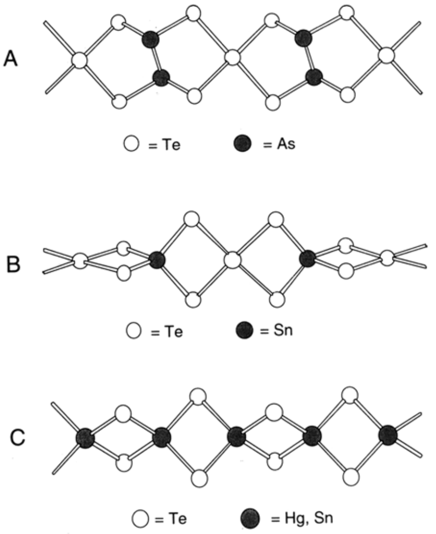

Figure 3. Comparison of the Te environment in structurally similar one-dimensional chain fragments: (A) $As_2Te_5^{2-}$, (B) $Sn_2Te_5^{2-}$,[23,24] (C) $HgSnTe_4^{2-}$.[25]

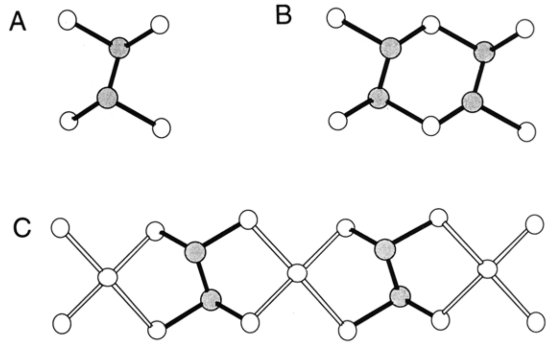

Figure 4. As_2Te_4 structural unit (A) and its incorporation into the tellurido arsenates $As_4Te_6^{4-}$ (B) and $As_2Te_5^{2-}$ (C). Shaded circles = As in this figure.

Conclusions

Our recently developed synthetic technique for the preparation of Zintl anions by cathodically dissolving tellurium alloy electrodes in the presence of tetraalkylammonium electrolytes in ethylenediamine has been extended to the arsenic tellurium system. In the presence of Et_4NI, the electrodes dissolve to give good yields of the novel 1-D polymer $(Et_4N)_2As_2Te_5$ (1), which contains As_2^{4+} and Te_5^{6-} units with a square-planar central tellurium atom. By changing the electrolyte to Me_4NI, the tellurido–arsenate $(Me_4N)_4[As_4Te_6]\cdot 2en$ (2), can be isolated. These compounds, along with others from the Au, Ga, In, Sn and Sb telluride systems help to demonstrate the broad applicability of this versatile synthetic technique.

Supplementary Material Available: Complete tables of experimental crystallographic details, atomic coordinates, bond distances and angles, and anisotropic displacement parameters for 1 and 2 (35 pages); tables of calculated and observed structure factors (28 pages). Ordering information is given on any current masthead page.