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Electrochemical Synthesis of New Sb–Te Zintl Anions by Cathodic Dissolution of Sb_2Te_3 Electrodes: Structures of $Sb_2Te_5^{4-}$ and $Sb_6Te_9^{4-}$

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We have recently developed a novel electrochemical synthetic method for the room-temperature generation of heteropolyatomic Zintl anion clusters from the cathodic dissolution of alloy electrodes. This technique has allowed us to synthesize compounds at room temperature from a class of materials whose synthesis previously has relied almost entirely on the high-temperature fusion of the elements.[1] Although Zintl was the first to recognize that the alkali and alkaline earth metals react with the elements of groups 14–16 to form saltlike intermetallic compounds which yielded colored polyanion solutions upon extractions,[2] he was never able to isolate crystalline derivatives from the extracts to confirm his findings. Isolation of stable solid derivatives of the more strongly reducing Zintl anions has only been accomplished recently owing in part to the cryptates which increase the solubility of alkali metal alloys of the heavier group 14–16 elements in amine solvents and hinder back electron transfer from anion to cation with concomitant reversion to the alloy phase.[3] The electrochemical synthesis of Zintl anions has not been thoroughly investigated and is limited to the early work of Zintl himself[4] and two brief communications,[5] none of which mentions the isolation of crystalline Zintl anion products. Our investigation into this area was sparked by the observation of deeply colored anion streams which are produced when a cathodic current is applied to an alloy electrode made from a post transition metal telluride or heavier main group element telluride. The constantly increasing concentration of polyanions in the presence of a concentrated supporting electrolyte of cations allows for the isolation of crystalline derivatives in as little as 3–5 days. We have found that the choice of supporting electrolyte in these syntheses greatly affects the products yielding very different anions from the same alloy electrode and that most of these anions have different stoichiometries from their parent electrodes. The versatility of this synthetic technique is demonstrated by some of the compounds we have isolated which include the gold tellurides $[(n\text{-}C_4H_9)_4N]_4Au_3Te_4$ and $[(C_6H_5)_4P]_2Au_2Te_4$,[6] the gallium telluride $[(C_6H_5)_4P]GaTe_2(en)_2$ (en = ethylenediamine),[7] the antimony tellurides $[(n\text{-}C_3H_7)_4N]_4Sb_4Te_4$ and $[(n\text{-}C_3H_7)_4N]_3Sb_9Te_6$,[8] and the indium telluride $[(n\text{-}C_4H_9)_4N]_2In_2Te_4$.[9] Here we report the synthesis of three novel antimony tellurides which we have prepared by the cathodic dissolution of Sb_2Te_3 alloy electrodes: $[(CH_3)_4N]_4Sb_2Te_5$ (**1**), $[(C_2H_5)_4N]_4Sb_2Te_5$ (**2**), and $[(C_2H_5)_4N]_4Sb_6Te_9\cdot 0.5en$ (**3**), the latter of which contains Te in an unusual square-pyramidal four-coordinate environment.

The electrode fabrication and elecrochemical cell were similar to those previously described.[6] Reactions were run at constant current using an external power supply which was connected to the leads of the Sb_2Te_3 cathode and Ni plate anode and set to run at the maximum current allowed. The current range was determined by the solubility of the tetraalkylammonium salts, and was either 100 or 300 μA in these experiments. The maximum compliance voltage of the power supply was 11 V. The solvent, ethylenediamine, was purified before use by distillation from a red solution of K_4Sn_9, and all manipulations were performed in a high-purity (<1 ppm of O_2) He atmosphere.

The synthesis of $[(CH_3)_4N]_4Sb_2Te_5$ (**1**) was accomplished in a 0.15 M ethylenediamine (en) solution of tetramethylammonium iodide ((TMA)I). Application of 100 μA of current resulted in the production of a faint light brown stream of anions which surrounded the Sb_2Te_3 cathode and then slowly sank to the bottom of the cathode chamber. The low solubility of (TMA)I in en limited the initial current to a maximum of 100 μA, which decreased over time as an insulating brown crystalline layer (the elemental microprobe analysis of which showed an Sb:Te ratio of 1:2.48) formed on the Sb_2Te_3 cathode. The reaction was stopped after 10 days when less than 1 μA current was able to pass through the cell. Dark brown hexagonal plate crystals of **1** were found growing on the Sb_2Te_3 cathode and throughout the cathode chamber but were isolated in low yield (6%),[10] presumably due to the formation of this insulating layer which prevents further dissolution of the cathode.

Single-crystal X-ray analysis of the brown hexagonal plate crystals revealed the compound $[(CH_3)_4N]_4Sb_2Te_5$ (**1**) which crystallizes in the space group $P2_1/c$ with four $Sb_2Te_5^{4-}$ anions in the unit cell.[11] The structure of the $Sb_2Te_5^{4-}$ anion is shown in Figure 1. The anion consists of two distorted $SbTe_3$ trigonal pyramids that share a corner Te atom, making an Sb–Te–Sb angle of 87.4(2)°. Although it appears highly symmetric, the anion displays only an approximate *2mm* point group symmetry in the solid state. The geometry of the Sb in the $Sb_2Te_5^{4-}$ anion is similar to that observed in the Zintl phase compound K_3SbTe_3,[12] which consists of discrete $SbTe_3^{3-}$ trigonal pyramids. This latter

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(10) The percent yield was based on 0.1156 g (0.1845 mmol) of Sb_2Te_3 electrode dissolved after 10 days which gave rise to 0.0132 g (0.0112 mmol) of $[(CH_3)_4N]_4Sb_2Te_5$ (**1**) crystals that were collected from the cathode chamber and was calculated on the basis of moles of Sb. The electrochemical yield, which is estimated to be much less than 1%, was not calculated due to multiple reductions in the applied current which resulted in this current not remaining constant throughout the synthesis.

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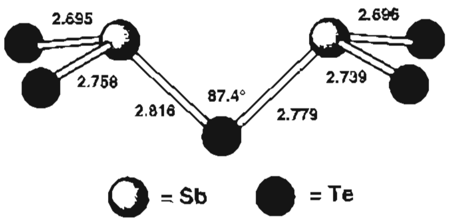

Figure 1. Some bond distances (Å) and angles in the $Sb_2Te_5^{4-}$ anion in $[(CH_3)_4N]_4Sb_2Te_5$ (**1**).

compound has three equivalent Te–Sb–Te bond angles of 101.86(2)° and Sb–Te bond distances of 2.7831(7) Å. In **1**, terminal Sb–Te bond distances range from 2.695(7) to 2.758(6) Å with internal Sb–Te bond distances of 2.779(6) and 2.816(7) Å. Angles within the $SbTe_3$ pyramids are more obtuse than those in K_3SbTe_3, ranging from 102.0(2) to 107.8(2)°.

When the supporting electrolyte is changed to a 0.30 M ethylenediamine solution of tetraethylammonium iodide ((TEA)I), an initial current of 300 μA can be applied. This results in the generation of a deep red-brown stream of anions which surrounds the Sb_2Te_3 cathode and then slowly sinks to the bottom of the cathode chamber. After approximately 5 days, the dissolution reaction results in the formation of two solid products: black diamond shaped crystals of $[(C_2H_5)_4N]_4Sb_2Te_5$ (**2**) and dark brown prismatic crystals of $[(C_2H_5)_4N]_4Sb_6Te_9{\cdot}0.5en$ (**3**), which are observed in an approximate 90:10 ratio. Chemical and electrochemical yields for these two products were 17% and 33% for **2** and 3% and 2% for **3**.[13] These two compounds appear to be the only solid products from the cathodic dissolution process and are not obtained from a control experiment of powdered Sb_2Te_3 and (TEA)I in en.

A single crystal X-ray analysis of **2** revealed the $Sb_2Te_5^{4-}$ anion found in **1**, and further details of its structural analysis will not be reported here. The single-crystal X-ray analysis of the dark brown prismatic crystals of **3** revealed the novel antimony telluride $[(C_2H_5)_4N]_4Sb_6Te_9{\cdot}0.5en$, which crystallizes in the space group $P2_1/n$ with four $Sb_6Te_9^{4-}$ anions in the unit cell. The structure of the $Sb_6Te_9^{4-}$ anion with some of its Sb–Te bond distances is shown in Figure 2. This anion also displays approximate, but not crystallographically imposed, *2mm* point group symmetry in the solid state.

The assignment of Sb and Te atoms in the $Sb_6Te_9^{4-}$ anion was based on their chemically reasonable connectivities and multiple elemental microprobe analyses on different crystals, which yielded Sb:Te ratios of 1:1.45 to 1:1.52. The overall charge of 4– on the anion is established by the presence of four crystallographically independent tetraethylammonium cations per anion in the asymmetric unit. The distribution of charge in this anion can be rationalized in the following manner: Terminal tellurium atoms Te(1) and Te(9), each having only one bond, have an expected charge of 1–. The capped Te(5) atom, which is weakly coordinated to antimony atoms Sb(2–5), exists as a dianion (2– charge). All of the other Te atoms in the anion are two-coordinate and, along with all of the antimony atoms in the anion which are three-coordinate, have no charge. Another equally valid way of looking at the bonding in the $Sb_6Te_9^{4-}$ anion would be to adopt an ionic model which would assume that the two Sb dimers (each containing a homonuclear Sb–Sb bond) in the anion each have a charge of 4+, and that the two isolated Sb atoms, Sb(1) and Sb(6), are present as 3+. All of the Te atoms must then have a formal 2– charge, including the capped Te(5) atom. This unusual capped Te species has been seen in the solid-state chalcogenide compound $K_4Cu_8Te_{11}$,[14] but to our knowledge is unprecedented in antimony tellurides. This geometry results in unusually long Sb–Te interactions of between 3.133(5)–3.229(5) Å, which are longer than any previously reported Sb–Te bond. The other Sb–Te bond distances of 2.702(5) and 2.717(5) Å for the two terminal Sb–Te bonds, and 2.765(6)–2.984(5) Å for internal Sb–Te bonds, as well as the Sb–Sb bond distances of 2.814(5) and 2.841(5) Å in this anion, are all within the values expected for these interactions.

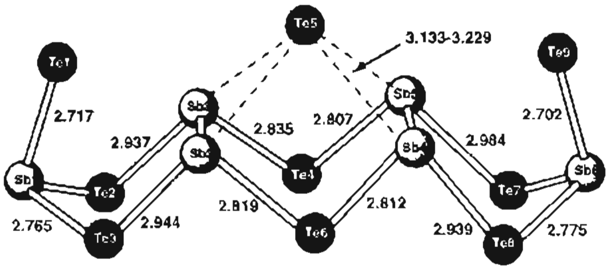

Figure 2. Structure of the $Sb_6Te_9^{4-}$ anion in $[(C_2H_5)_4N]_4Sb_6Te_9{\cdot}(0.5\,en)$ (**3**) showing the unusual capped Te(5) atom. The Sb–Te interactions (Å) involving Te(5) are Sb(2)–Te(5) = 3.179(5), Sb(3)–Te(5) = 3.188(5), Sb(4)–Te(5) = 3.229(5) and Sb(5)–Te(5) = 3.133(5). The Sb–Sb bond distances (Å) are Sb(2)–Sb(3) = 2.814(5) and Sb(4)–Sb(5) = 2.841(5). Some other Sb–Te bond distances are shown.

Comparison of the above Sb–Te bond distances with those of the few other known antimony tellurides, K_3SbTe_3,[12] $LiSbTe_2$,[15] $BaSbTe_3$,[16] and $AgSbTe_2$[17] (all of which have been prepared by the high-temperature fusion of the elements) reveals no significant differences in Sb–Te bond lengths. We have also recently isolated the antimony tellurides $[(n\text{-}C_3H_7)_4N]_4Sb_4Te_4$ and $[(n\text{-}C_3H_7)_4N]_3Sb_9Te_6$ from the cathodic dissolution of Sb_2Te_3 electrodes in a tetrapropylammonium iodide supporting electrolyte,[8] the latter of which has a backbone structure similar to that of **3**.

Our investigation into the electrochemically controlled cathodic dissolution of alloy electrodes to produce Zintl anions has resulted in the synthesis of a variety of novel structures. The technique that we have developed provides a convenient route to the syntheses of these materials and should be amenable to a wide variety of systems.[18]

Supplementary Material Available: Text describing the structure determination, tables of crystal data, data collection, solution and refinement parameters, atomic coordinates, anisotropic displacement coefficients, bond distances and angles, and torsion angles, and nonbonding contacts, and ORTEP diagrams for **1** and **3** (42 pages). Ordering information is given on any current masthead page.

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(11) Crystal data for **1**: $C_{16}H_{48}N_4Sb_2Te5$, monoclinic, space group $P2_1/c$ (No. 14) with a = 12.500(3) Å, b = 13.704(3) Å, c = 20.281(4) Å, β = 98.02(2)°, and V = 3440(1) Å³. For Z = 4, and fw = 1178.08, D_c = 2.274 g/cm³. A total of 6328 unique reflections were collected in the range $5° \le 2\theta \le 50°$ for which 1404 with $I > 3\sigma(I)$ were considered observed. R (R_w) = 0.073 (0.082). Crystal data for **3**: $C_{33}H_{84}N_5Sb_6Te_9$, monoclinic, space group $P2_1/n$ (No. 14), with a = 15.173(2) Å, b = 22.914(4) Å, c = 18.937(2) Å, β = 92.15(1)°, and V = 6579.3(15) Å³. For Z = 4 and fw = 2430.0, D_c = 2.453 g/cm³. A total of 8650 unique reflections were collected in the range $4° \le 2\theta \le 45°$ for which 2447 with $F > 3\sigma(F)$ were considered observed. R (R_w) = 0.0647 (0.0623). Both structures were solved by direct methods using a combination of the *teXsan* crystallographic software package of Molecular Structure Corp. and the SHELXTL PLUS crystallographic software package of Siemens.

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(13) The yield calculations were based on 0.4116 g (0.6572 mmol) of Sb_2Te_3 electrode dissolved after 5 days which gave rise to 0.1736 g of crystals that were collected from the cathode chamber. The percent yields were based on the assumption that the product was 90% $[(C_2H_5)_4N]_4Sb_2Te_5$ (**2**) [0.1562 g, 0.1114 mmol] and 10% $[(C_2H_5)_4N]_4Sb_6Te_9$ (**3**) [0.0174 g, 0.0073 mmol], and were calculated on the basis of moles of Sb. Electrochemical yield = moles of product/moles of electrons passed.

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