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Electrochemical Synthesis of a New Au–Te Polyanion by the Cathodic Dissolution of an $AuTe_2$ Electrode: Structure of $Au_3Te_4^{3-}$

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In the 1930s, Zintl and co-workers investigated the synthesis and properties of the solids obtained from the reaction of alkali or alkaline earth metals with the heavier main group or post transition elements.[1] These solids, which have become known as Zintl phases, generally contain anionic main group clusters, nets, or three-dimensional frameworks and alkali/alkaline earth cations. Due to their lack of exopolyhedral ligands, they can easily form metal–metal bonds upon oxidation, making these Zintl anions ideal precursors for the preparation of conducting and semiconducting films and solids.[2a,b] Since the initial report by Kummer and Diehl[3] on the ethylenediamine (en) extraction and isolation of Sn_9^{4-} from Na_4Sn_9, many homopolyatomic[4] and heteropolyatomic[5] anions have been isolated via the solvent extraction of Zintl phases. Although there was early work on the electrochemical generation of main group polyanions in solution by Zintl and co-workers,[6] an electrochemical study of the usefulness of the Zintl ion salt $R_4N^+Hg_4^-$ to prepare new quaternary ammonium salts by Bard and co-workers,[7] and a report of the electrolytic preparation of solutions of Pb–Sn anionic clusters for NMR studies by Rudolph and co-workers,[8] utilization of electrochemically controlled cathodic dissolution of alloys to prepare structurally characterized solids appears to be uninvestigated. We have begun a study of this technique using $AuTe_2$ alloy electrodes and have demonstrated it to be useful for the synthesis of gold telluride anions by the isolation and characterization of $(TBA)_3Au_3Te_4$ ($TBA^+ = [(n\text{-}C_4H_9)_4N]^+$) (**1**) and $(TPP)_2Au_2Te_4$ ($TPP^+ = [(C_6H_5)_4P]^+$) (**2**).

Compounds containing gold and tellurium have been of interest recently as possible erasable laser recording media[9] and as indicators of the geochemical formation conditions of minerals.[10] However, the majority of publications in this field are concerned with the leaching of gold from $AuTe_2$ rather than the compounds formed from it.[11] Gold tellurides occur naturally as $AuTe_2$ in the minerals calaverite[12] krennerite,[13] as well as an Au_2Te_3 form, the thermally metastable mineral montbrayite.[14] Gold telluride materials which contain halogens, like AuTeI[15] and $AuTe_2X$ (X = Cl, Br, I),[16] are also known. Several Au–Te compounds which apparently display $K^+\cdots Au$ interactions, such as the polyanions $[KAu_9Te_7]^{4-}$,[17] $[K_2Au_4Te_4(en)_4]^{2-}$,[17] $[K_2Au_4Te_4(dmf)_2(CH_3OH)_2]^{2-}$,[17] and the solid-state material KAuTe,[18] have been structurally characterized. There is, however, apparently only one known example of an isolated Au(I)–Te polyanion, which was found in the compound $[(Ph_3P)_2N]_2Au_2Te_4$.[19] We report here a simple and facile electrochemical synthesis of Au–Te anions, which may have broad application to many other systems besides Au–Te, based on the cathodic dissolution of an element or alloy electrode. This synthetic technique is found to be advantageous when compared to the high-temperature fusion and extraction routes which have been previously used to prepare the above compounds in that it allows us to prepare single crystals of new materials at room temperature that may not be accessible by the aforementioned techniques.

The electrochemical dissolution reaction requires an $AuTe_2$ alloy, which is made by melting stoichiometric amounts of the elements under N_2 in a quartz tube. After the phase purity of the alloy is confirmed by X-ray powder diffraction, the regulus is then crushed into a fine powder and recast into cylindrical electrodes. Copper wires are then attached with 50/50 In–Sn solder, and the electrodes are sealed into glass jackets with epoxy such that only the $AuTe_2$ alloy is exposed. Under an inert atmosphere, a two-compartment, liquid junction, air-tight electrochemical cell equipped with a Pt mesh counter electrode is filled with solutions ranging from 0.3 to 0.5 M tetrabutylam-

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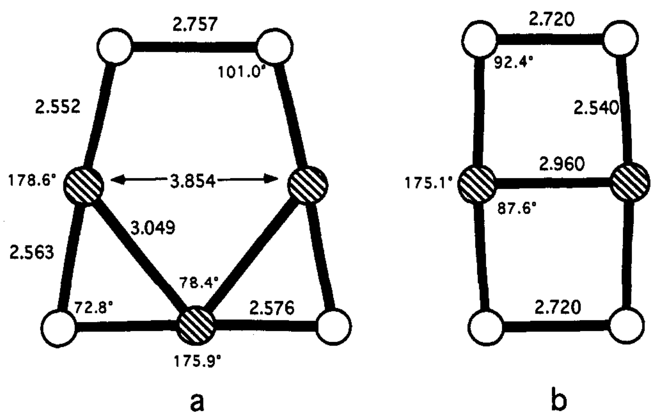


Figure 1. (a) Some distances (Å) and angles (deg) in the structure of one of the two crystallographically independent $[Au_3Te_4]^{3-}$ anions in $(TBA)_3Au_3Te_4$. (b) Some distances and angles in the structure of the $[Au_2Te_4]^{2-}$ anion in $(TPP)_2Au_2Te_4$. The shaded circles represent Au atoms.

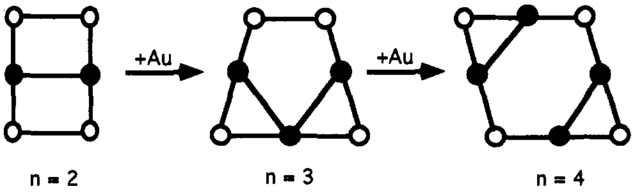
monium iodide (TBA·I) or tetraphenylphosphonium bromide (TPP·Br) in en, which serve both as a source of cations required for crystallization and as the supporting electrolyte.

The cathodic dissolution of a $AuTe_2$ alloy electrode (surface area ≈ 1 cm²) in 20 mL of a 0.4 M solution of TBA·I in en (which was distilled from a red solution of K_4Sn_9 under an inert atmosphere) that ran at a constant current of 300 μA immediately gave rise to a deep purple/brown stream of polyanion and after 2 days yielded dark brown rectangular crystals of **1** in greater than 60% yield (electrochemical yield = 26%).[20] Crystals of **1** were found growing on the $AuTe_2$ cathode and throughout the cathode chamber. A control experiment of powdered $AuTe_2$ and TBA·I in en did not give rise to any color (no polyanions), and varying the current from 100 μA to 1 mA in the above experiment had no effect on the product, yielding **1** in all cases.

X-ray structural analysis of **1**[21] at 235 K revealed the novel $[Au_3Te_4]^{3-}$ anion, which is shown in Figure 1a. There are two slightly puckered, crystallographically independent $[Au_3Te_4]^{3-}$ anions in the unit cell, each possessing crystallographic 2-fold symmetry in the solid state. The central Au atom in a given $[Au_3Te_4]^{3-}$ anion resides on the Wyckoff 4e special position in space group $C2/c$, lying on a c-glide plane. Each $[Au_3Te_4]^{3-}$ anion contains three Au(I) atoms joined together by Au–Au bonds of 3.049(3) or 3.015(3) Å and making Au–Au–Au angles of 78.4(1)° or 81.1(1)°, respectively. These Au–Au distances are somewhat longer than the 2.88-Å Au–Au distances observed in gold metal.[22] The transannular nonbonded Au–Au distance is either 3.854(4) or 3.922(4) Å. As expected for Au(I), the Te–Au–Te angles are all close to 180°, varying from 172.5(2)° to 178.9(1)°. Au–Te bonds range from 2.549(4) to 2.589(3) Å, and the Te–Te distances of 2.757(8) and 2.760(7) Å are similar to the Te–Te contacts observed in other structurally characterized tellurides.[23]

Changing the cation has a profound effect on the course of the reaction. If, for instance, the cation is changed to TPP·Br, an intense deep red color streams from the cathode, and after 3 days in 20 mL of a solution of 0.5 M TPP·Br in en at a current density of ca. 300 μA cm^{-2}, dark red needles of **2** are isolated in approximately 40% yield (electrochemical yield = 10%).[24] X-ray structural analysis of **2** revealed the $[Au_2Te_4]^{2-}$ anion, which had been previously synthesized by the $[(Ph_3P)_2N]\cdot Cl$/en extraction of $KAuTe_2$, $K_2AuAsTe_3$, and $K_3AuGeTe_3$.[19] The $[Au_2Te_4]^{2-}$ anion is shown in Figure 1b. This anion is planar (to within 0.026 Å) and lies on a crystallographic inversion center. It has essentially the same Te–Te distances and Te–Au–Te angles as those observed in $[Au_3Te_4]^{3-}$.

A comparison of the series $[Au_nTe_4]^{n-}$ (n = 2–4) reveals an interesting arrangement of Au and Te atoms. The addition of a Au atom between two Te atoms in $[Au_2Te_4]^{2-}$ increases the initial Au–Au contact of 2.960(3) Å to a nonbonded distance of 3.854(4) Å while at the same time creating two new Au–Au bonds of 3.049(3) Å and twisting the anion out of its planar arrangement. The addition of still another Au atom, into the Te–Te bond of the $[Au_3Te_4]^{3-}$ ring, restores the anion back to a planar arrangement, giving rise to the rhombohedrally distorted $[Au_4Te_4]^{4-}$ species found in the anions $[KAu_9Te_7]^{4-}$,[17] $[K_2Au_4Te_4(en)_4]^{2-}$,[17] and $[K_2Au_4Te_4(dmf)_2(CH_3OH)_2]^{2-}$.[17] These latter anions have two shorter Au–Au contacts of 3.054 and 3.259 Å and two longer nonbonded Au–Au contacts of 3.988 and 4.134 Å.



The electrochemical cathodic dissolution technique presented here should be widely applicable to the synthesis of a variety of new and interesting materials. It is an ideal crystal growth technique, relying on the constantly increasing concentration of anion, which is easily adjusted by the current applied to the alloy electrode. The seemingly endless choice of both alloys and cations makes this technique very appealing as a route to the design and synthesis of anions, molecular compounds, and even three-dimensional materials. We have recently isolated the compounds $(TPP)GaTe_2(en)_2$, $(TBA)_2In_2Te_4$, $(TPA)_3Sb_9Te_6$ ($TPA^+ = [(n\text{-}C_3H_7)_4N]^+$), and $(TPA)_4Sb_4Te_4$ using this technique and have obtained crystals from other telluride systems that are currently under investigation in our laboratory.

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Supplementary Material Available: Tables of crystal data, data collection, solution and refinement parameters, atomic coordinates, bond lengths and angles, anisotropic displacement coefficients and torsion angles for **1** (16 pages); table of observed and calculated structure factors for **1** (40 pages). Ordering information is given on any current masthead page.

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(20) The yield of ~60% was based on 0.1008 g (0.2229 mmol) of $AuTe_2$ electrode dissolved after 2 days, which gave rise to 0.0864 g (0.0472 mmol) of $(TBA)_3Au_3Te_4$ crystals that were collected from the cathode chamber. The % yield was based on the assumption that the electrode dissolved as $AuTe_2^{1-}$ and was calculated on the basis of moles of Au. Electrochemical yield = moles product/moles e⁻ passed. The deep brown/red color of the catholyte solution suggests that some fraction of the polyanions produced are soluble and remain in solution. The difference in stoichiometry of the product and reactant requires the existance of excess Te, which could be present in the catholyte solution in the form of soluble polytellurides.

(21) **1**: monoclinic space group $C2/c$ (No. 15) with a = 22.407(4) Å, b = 27.553(7) Å, c = 21.382(4) Å, β = 101.12(2)°, V = 12953(4) Å³, and Z = 8. Data were collected on a Siemens P4 diffractometer at 235 K. The structure was solved by heavy-atom methods and refined on F by full-matrix least-squares using Siemens SHELXTL PLUS program package. The Au and Te atoms were refined with anisotropic displacement coefficients, while the C and N atoms were refined isotropically. The n-butylammonium cations in the structure are severely disordered, and multiple site models were attempted. Unfortunately, the models gave only unrealistic geometries and were sequentially abandoned. The n-butylammonium cations were therefore refined with all C–C and C–N bonds constrainedto 1.51 Å and all angles idealized to 109.5°. No hydrogen atoms were included. The refinement converged to $R(F)$ = 0.0710, $R_w(F)$ = 0.0684, and S = 1.17, with 269 variables and 9.9 reflections per refined parameter.

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(24) The yield of ~40% was based on 0.0781 g (0.1727 mmol) of $AuTe_2$ electrode dissolved after 3 days, which gave rise to 0.0622 g (0.0393 mmol) of $(TPP)_2Au_2Te_4$ crystals that were collected from the cathode chamber. The assumptions in ref 20 are also valid here.