Notes

Synthesis and Structural Characterization of $(n\text{-}Bu_4N)_3AuSn_2Te_6$

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Introduction

Considerable interest has developed in the search of soluble chalcogenides and polychalcogenides mainly related to their structural diversity and tendency toward catenation. Research on the exploration of binary chalcogenide and polychalcogenide systems, utilizing several low-temperature synthetic techniques,[1−12] has produced many compounds with unusual structures and properties. Comparatively few ternary compounds have been investigated, however, especially in the telluride system. Among these synthetic techniques, the extractive method, which was first used to study the Zintl ions, continues to yield new ternary and quaternary telluride compounds with novel structures and interesting properties. Our primary goal is to develop new types of anionic ligands and/or to use the known binary telluride anions as ligands that can be incorporated into the ternary or quaternary telluride compounds. Recently, our studies of ternary telluride systems, using the extractive method to incorporate anionic ligands of the $[As_xTe_y]^{n-}$ type, have proven to be successful. These telluride compounds include $(n\text{-}Bu_4N)_4Cu_7As_3Te_{13}$[13] and $(Et_4N)_5KAuAs_4Te_8$.[14] Meanwhile, the incorporation of the $[SnTe_4]$ tetrahedron as a building block in the construction of molecules and one-dimensional chain structures are also observed in $(Et_4N)_2HgSnTe_4$,[15] $KIn(en)_2SnTe_4{\cdot}1.5en$,[16] $(n\text{-}Pr_4N)_2K_2Cu_2SnTe_5{\cdot}2en$,[17] and in the ternary and the mixed-metal quaternary compounds, $(Et_4N)_4Au_3Sn_2Te_9$[17] and $(Et_4N)_4Au(Ag_{1-x}Au_x)_2Sn_2Te_9$,[18] respectively. During the investigation of the quaternary Au−Sn−Sb−Te system, using the extractive method, we isolated $(n\text{-}Bu_4N)_4AuSn_2Te_6$, which contains a new ternary Zintl anion that employs a $[Sn_2Te_6]$ dimer as a ligand to form a discrete cluster. Here we describe the synthesis and characterization of this new ternary telluride compound.

Experimental Section

Synthesis. Since materials described herein are sensitive to both moisture and oxygen, the operations were performed under an inert atmosphere. Elemental starting materials, K (99.95%, Cerac), Au (99.95%, Cerac), Sn (99.8%, Cerac), Sb (99.999%, Cerac), Te (99.5%, Cerac), and tetrabutylammonium bromide (99%, Aldrich), were used as received. The ethylenediamine (99.5%, Aldrich) was dried over CaH_2 and distilled, and was again distilled from a red solution of K_4Sn_9. The freshly distilled ethylenediamine was then stored in a He atmosphere.

A pentanary alloy with the nominal composition of $K_4AuSn_2Sb_2Te_{11}$ was prepared by the fusion of K_2Te, SnTe, Sb, Au, and Te in stoichiometric proportions in a silica tube under an Ar atmosphere. One gram of the alloy was treated with 10 mL of ethylenediamine and stirred for 12 h, and then the brown extract was filtered and layered with equal volume of a saturated solution of tetrabutylammonium bromide in ethylenediamine. Two weeks later, dark red chunky crystals of $(n\text{-}Bu_4N)_3AuSn_2Te_6$ were isolated in approximately 16% yield. Energy-dispersive X-ray analysis on selected crystals from the products gave an approximate ratio of 1.3:2:6.3 for Au/Sn/Te. The composition of the alloy does not seem to be crucial since the title compound could also be obtained by extracting a quaternary alloy with exact composition of $K_3AuSn_2Te_6$.

X-ray Study. A dark red crystal of $(n\text{-}Bu_4N)_3AuSn_2Te_6$ of approximate dimensions 0.20 × 0.16 × 0.10 mm was selected and mounted in a glass capillary. Single-crystal X-ray data were collected on a Rigaku AFC7R diffractometer, equipped with a rotating anode generator (50 kV and 250 mA), with graphite-monochromated Mo Kα radiation at 20 °C. Orthorhombic cell constants and an orientation matrix were obtained from a least squares refinement using 20 centered reflections in the range of $14 \le 2\theta \le 20°$. Intensity data were collected ($+h$, $+k$, $+l$) in the $\omega-2\theta$ scanning mode for reflections with $4 < 2\theta < 40°$. Three check reflections were monitored every 150 reflections and showed no significant change during the data collection process. A total of 7836 reflections were measured, of which 2837 reflections with $I \ge 3\sigma(I)$ were considered as observed. The data set was corrected for absorption using the ψ scan technique based on three reflections and decay (16%). Space group *Pbca* was determined by the systematic absences and Wilson statistics.

The structure was solved by direct methods and refined on F using *teXsan* crystallographic software package. Neutral atomic scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were obtained from standard sources.[19] Isotropic refinement of $(n\text{-}Bu_4N)_3AuSn_2Te_6$ showed reasonable thermal coefficients for all heavy atoms. All the carbon and nitrogen atoms in all three cations were refined isotropically and then fixed. Two carbon atoms in the cations were refined with disordered models. Since all the C−N and C−C bond distances in all three cations were fairly irregular, they were respectively restrained to 1.45 and 1.54 Å for the refinement. The

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Table 1. Crystallographic Data for $(n\text{-}Bu_4N)_3AuSn_2Te_6$

empirical formula	$C_{48}H_{108}N_3AuSn_2Te_6$
a, Å	25.930(6)
b, Å	35.876(9)
c, Å	16.334(5)
V, Å^3	15195(5)
Z	8
fw	1927.35
space group	*Pbca* (No. 61)
T (°C)	293
λ (Å)	0.710 73
ρ_{calcd} (g/cm^3)	1.685
μ (mm^{-1})	4.869
R^a (%)	6.2
$R_w{}^b$ (%)	8.1

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

Table 2. Important Interatomic Distances (Å) and Bond Angles (deg) for $(n\text{-}Bu_4N)_3AuSn_2Te_6$

Au1−Te1	2.550 (4)	Au1−Te6	2.546 (5)
Sn1−Te1	2.738 (5)	Sn2−Te3	2.781 (5)
Sn1−Te2	2.650 (5)	Sn2−Te4	2.782 (5)
Sn1−Te3	2.785 (5)	Sn2−Te5	2.635 (5)
Sn1−Te4	2.783 (5)	Sn2−Te6	2.743 (5)
Te1−Au1−Te6	166.6(2)	Te3−Sn1−Te4	93.9(1)
Au1−Te6−Sn2	81.8(1)	Sn1−Te3−Sn2	83.2(1)
Sn1−Te4−Sn2	83.3(1)	Te6−Sn2−Te3	108.4(2)
Au1−Te1−Sn1	82.8(1)	Te6−Sn2−Te4	109.3(2)
Te1−Sn1−Te2	115.1(2)	Te6−Sn2−Te5	116.2(2)
Te1−Sn1−Te3	108.8(2)	Te5−Sn2−Te3	116.0(2)
Te1−Sn1−Te4	107.4(2)	Te5−Sn2−Te4	110.6(2)
Te2−Sn1−Te3	116.4(2)	Te3−Sn2−Te4	94.0(1)
Te2−Sn1−Te4	113.1(2)		

hydrogen atoms were included as fixed contributors but not refined. Anisotropic refinement of all heavy atoms in $(n\text{-}Bu_4N)_3AuSn_2Te_6$ gave the final residual $R = 6.2\%$ with reasonable anisotropic thermal ellipsoids. The highest and lowest peaks in the final difference Fourier map are 1.52 and −0.58 e/Å^3, respectively. A summary of crystal and data collection parameters are listed in Table 1.

Results and Discussion

In the known binary tin telluride compounds, there exist four types of molecular structures. These include the tetrahedral $[SnTe_4]^{4-}$ anion[20] and three dimeric anions, $[Sn_2Te_3]^{2-}$,[21] $[Sn_2Te_6]^{4-}$,[22] and $[Sn_2Te_7]^{4-}$.[23] While Zintl anions of the $[As_xTe_y]^{n-}$ type act as ligands toward the synthesis of new materials, the successful incorporation of the fundamental $[SnTe_4]$ tetrahedron as a building block in many telluride compounds also suggest the applicability of using ligands of the $[Sn_xTe_y]^{n-}$ type in the construction of new structures.[15−18] The investigation of the quaternary Au−Sn−Sb−Te system has led to the isolation of the new ternary telluride compound, $(n\text{-}Bu_4N)_4AuSn_2Te_6$, which indeed uses a known dimeric $[Sn_2Te_6]^{4-}$ anion as a ligand to bind the Au atom. These results demonstrate the potential of utilizing other Zintl anionic ligands of the $[Sn_xTe_y]^{n-}$ type.

The selected bond distances and angles of $(n\text{-}Bu_4N)_4AuSn_2Te_6$ are listed in Table 2. The single-crystal diffraction data revealed that $(n\text{-}Bu_4N)_4AuSn_2Te_6$ consists of an unprecendented $[AuSn_2Te_6]^{3-}$ anion and tetrabutylammonium cations. The unit cell contains eight $[AuSn_2Te_6]^{3-}$ anions with each completely separated by tetrabutylammonium cations. The structure of the $[AuSn_2Te_6]^{3-}$ anion (Figure 1) is composed of a slightly bent $[AuTe_2]$ unit and a dimeric $[Sn_2Te_6]^{4-}$ anion. The discrete dimeric $[Sn_2Te_6]^{4-}$ anion, built up from an edge sharing of two $[SnTe_4]^{4-}$ tetrahedra, was reported in $(Me_4N)_4Sn_2Te_6$.[22] The average terminal and bridging Sn−Te bond distances (2.64(1) and 2.77(2) Å) in the $[AuSn_2Te_6]^{3-}$ anion are close to those of $(Me_4N)_4Sn_2Te_6$ (2.695(8) and 2.799(7) Å),[22] $KIn(en)_2SnTe_4\cdot 1.5en$ (2.691(2) and 2.766(2) Å)[16] and $Cs_4Sn_2Te_7$ (2.683(4) and 2.804(6) Å).[23] Although the $[Sn_2Te_6]^{4-}$ anion occurs in both $(n\text{-}Bu_4N)_4AuSn_2Te_6$ and $(Me_4N)_4Sn_2Te_6$, the most distinctive difference of two $[Sn_2Te_6]^{4-}$ anions is that the four-membered ring of $[Sn_2Te_2]$ in the former forms a butterfly shape in which each Sn atom is bent inward by 18°, while in the latter, all four atoms are coplanar. This is also evidenced by a shorter Sn−Sn distance, 3.696 Å ($[AuSn_2Te_6]^{3-}$) vs 3.783 Å ($[Sn_2Te_6]^{4-}$) and by the much longer $Te_{terminal}-Te_{terminal}$ distance, 7.74 vs 6.70 Å. This bending restraint is resulted from the bonding between the Au and two terminal Te atoms from the dimeric $[Sn_2Te_6]^{4-}$ anion. The $[AuTe_2]$ unit in the $[AuSn_2Te_6]^{3-}$ anion also exhibits a bent geometry with an angle of 166.6(2)°. To our knowledge this is the most distorted angle of the linear $[AuQ_2]$ unit (Q = chalcogens) and obviously results from the incorporation of a putative linear $[AuTe_2]$ unit into the five-membered $[AuSnTe_3]$ ring. The average Au−Te bond of 2.548(3) Å is comparable to those observed in $(Ph_4P)_2[K_2Au_4Te_4(en)_4]$ (2.576(4) Å)[7] and $(PPN)_2Au_2Te_4$ (2.548(6) Å).[24] Thus, the $[AuSn_2Te_6]^{3-}$ anion, formed by sharing Te atoms between the $[AuTe_2]$ unit and the dimeric $[Sn_2Te_6]^{4-}$ anion, displays a highly strained geometry. The distances between the Au and Sn atoms are 3.446 and 3.500 Å, which indicate no significant interactions compared to the Au−Sn bond of 2.852 Å in the alloy AuSn.[25] Given the oxidation state I for Au and IV for Sn, and −II for Te, the charge of $AuSn_2Te_6$ is −3 which is in agreement with the charge of −3 established from the single-crystal structure determination. The bond valence sum calculations resulted in sums of 4.00 and 4.05 for the Sn1 and Sn2 atoms, respectively, and 1.02 for the Au1 atom.[26] These results also confirm the charge assignment of each atom in $(n\text{-}Bu_4N)_3AuSn_2Te_6$.

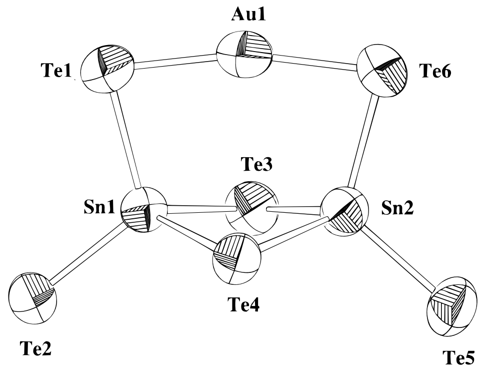

Figure 1. Perspective view of the $[AuSn_2Te_6]^{3-}$ anion (50% probability ellipsoids) with the labeling scheme. The bending of both the $[Sn_2Te_6]^{4-}$ anion and the linear $[AuTe_2]$ unit results in a highly strained $[AuSn_2Te_6]^{3-}$ anion.

The telluride $(n\text{-}Bu_4N)_3AuSn_2Te_6$ represents the first compound that uses a dimeric $[Sn_2Te_6]^{4-}$ anion to construct the

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structure. Also, the 9-atom anionic cluster is the smallest ternary Zintl telluride anion that has been synthesized to date. The research of Zintl compounds, incorporating ligands of both $[As_xTe_y]^{n-}$ and $[Sn_xTe_y]^{n-}$ types, has proven to be very successful by using the extractive technique. To further our investigation of ligands of this $[Sn_xTe_y]^{n-}$ type, we isolated another ternary silver tin telluride compound whose complexed structure is also built up by an unusual polytelluride Zintl anion of the $[Sn_xTe_y]^{n-}$ type.[27] Owing to the successful use of binary or, perhaps, ternary Zintl anions to bind metal atoms, this strategy can be extended to other types of anionic ligands, for example, $[M_xQ_y]^{n-}$ (M = group 13 elements and Q = chalcogens) in the synthesis of Zintl compounds with novel structures and unusual properties. We are currently investigating ternary and quaternary systems incorporating ligands of either $[Sn_xTe_y]^{n-}$ or $[In_xTe_y]^{n-}$ type and characterizing the compounds thus formed.

Supporting Information Available: Four X-ray crystallographic files, in CIF format, are available free of charge via the Internet at http://pubs.acs.org.

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