Synthesis, Characterization, and Electronic Structure Analysis of $(Et_4N)_4KAuAs_4Te_8$ and Electron Counting for the Zintl Anion Containing a Square-Planar $AuTe_4$ Unit

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Received April 7, 1998

Introduction

The chemistries of soluble chalcogenides and polychalcogenides have received much attention due mainly to their structural diversity and their importance in technological applications.[1−3] The use of several convenient low-temperature synthetic techniques, for example, the extractive method,[4−7] the solventothermal method,[8−13] reactions involving fluxes,[14,15] the cathodic dissolution of intermetallic phases,[16] and the chemical reduction method,[17,18] has led to a number of new materials with unusual structures and properties. Recently, the solventothermal method using thioarsenates and selenoarsenates $[As_xQ_y]^{n-}$ (Q = S, Se) as anionic ligands has been found to be a successful route to a number of extended ternary and quaternary compounds.[10−11,19,20] These compounds have shown a great tendency of condensation of the $[AsQ_3]$ building blocks in the $[As_xQ_y]^{n-}$ (Q = S, Se) ligands. Unlike the sulfide and selenide systems, the telluride systems have not been developed progressively, partly, because the Te atom has a weaker tendency of catenation.[21] Our attempt to extend this type of chemistry into the ternary telluride system, by solvent extraction of certain ternary alloys, has yielded $(Et_4N)_3Cu_4SbTe_{12}$[22] and $(n\text{-}Bu_4N)_3Cu_7As_3Te_{13}$,[23] in which the $[SbTe(Te_2)_2]^{3-}$ and $[AsTe_2(Te_2)]^{3-}$ ligands coordinate a tetrahedral $[Cu_4]$ cluster and a cubane-like $[Cu_7Te]$ cluster, respectively. These results suggest the feasibility of preparing new telluride materials based on ligands of the $[M_xTe_y]^{n-}$ type (M = group 15 elements). During our investigations of the quaternary Au−Sn−As−Te system, by the extractive route in ethylenediamine (en), we discovered a new ternary compound $(Et_4N)_4KAuAs_4Te_8$, which contains a square-planar Au cation. In this communication, we report the synthesis and characterization of $(Et_4N)_4KAuAs_4Te_8$ by crystal and electronic structure analysis.

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), As (99.999%, Cerac), Te (99.5%, Cerac), and tetraethylammonium iodide (99%, Cerac), were used as received. The ethylenediamine 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 quaternary alloy with a nominal composition of $K_2AuSnAs_3Te_8$ was prepared by the fusion of KAs, SnTe, Au, As, and Te in stoichiometric proportions. $(Et_4N)_4KAuAs_4Te_8$ was synthesized by dissolving 1 g of the $K_2AuSnAs_3Te_8$ alloy in 10 mL of en, which was freshly distilled from a red K_4Sn_9 solution. After it was stirred for 12 h, the brown extract was filtered and layered with an equal volume of a saturated solution of tetraethylammonium iodide in en. Dark-red rhombus-like plate crystals of $(Et_4N)_4KAuAs_4Te_8$ were isolated in approximately 8% yield 3 weeks later. Energy-dispersive X-ray analysis on selected crystal samples from the products gave an approximate ratio of 1:1:4:8 for K/Au/As/Te.

X-ray Crystallography. A crystal of $(Et_4N)_4KAuAs_4Te_8$ of approximate dimensions $0.10 \times 0.07 \times 0.03$ mm^3 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. Monoclinic cell constants and an orientation matrix were obtained from a least-squares refinement using 19 centered reflections in the range of $26° < 2\theta < 40°$. Intensity data were collected ($+h$, $+k$, $\pm l$) in the $\omega-2\theta$ scanning mode for reflections with $2\theta < 60°$. Three check reflections were monitored every 150 reflections and showed no significant change during the data collection process. A total of 4356 reflections were measured, of which 1965 reflections with $I \geq 3\sigma(I)$ were considered as observed. The data set was corrected for absorption using the y-scan technique based on three reflections (transmission 1.000−0.562). The space group $C2/m$ was determined by the systematic absences and Wilson statistics.

The structure was solved by direct methods and refined on F using the teXsan crystallographic software package. Neutral atomic scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were obtained from standard sources.[24] Isotropic refinement of $(Et_4N)_4KAuAs_4Te_8$ showed reasonable thermal coefficients for all heavy atoms, except the two As atoms that have larger thermal coefficients. The site occupancy factors of the two crystallographically unique As atoms were refined and close to 0.5. Thus, the site

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10.1021/ic980389f CCC: $15.00
Published on Web 10/31/1998

Table 1. Crystallographic Data for $(Et_4N)_4KAuAs_4Te_8$

chemical formula	$C_{32}H_{112}N_4KAuAs_4Te_8$
a (Å)	17.556(3)
b (Å)	11.442(3)
c (Å)	14.676(4)
β (deg)	96.32(2)
V (Å^3)	2930(1)
Z	2
fw	2109.81
space group	$C2/m$ (no.12)
T (°C)	293
λ (Å)	0.710 73
ρ_{calcd} (g/cm^3)	2.391
μ (mm^{-1})	8.762
R^a (%)	6.0
$R_w{}^b$ (%)	7.1

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(Et_4N)_4KAuAs_4Te_8$

Au1–Te1	2.646(1)	As2–Te2	2.668(4)
As1–Te1	2.556(4)	As1–As2	2.427(6)
As1–Te2	2.483(4)	K1–As1	3.509(4)
As2–Te1	2.685(4)	K1–Te2	3.702(2)
Te1–Au1–Te1A	96.59(6)	Te1–As1–Te2	102.7(2)
Te1–Au1–Te1C	180.0	Te2–As1–As2	101.3(2)
Te1–Au1–Te1B	83.41(6)	Te1A-As2–As1	91.6(2)
Au1–Te1–As1	104.7(1)	Te1A-As2–Te2A	94.6(1)
Au1–Te1A-As2	100.1(1)	Te2A-As2–As1	98.1(2)
Te1–As1–As2	92.9(2)		

occupancy factors of two As atoms were fixed at 0.5 for the final refinement. The carbon atoms on one of the tetraethylammonium cations were first refined isotropically with a disordered model and then fixed. The hydrogen atoms were included as fixed contributors but not refined. Anisotropic refinement of K, Au, As, Te, and some N and C atoms in $(Et_4N)_4KAuAs_4Te_8$ gave the final residual $R = 6.0\%$ with GOF = 3.333. The highest and lowest peaks in the final difference Fourier map are 2.75 and −2.55 e/Å^3, respectively. A summary of crystal and data collection parameters is listed in Table 1.

Results and Discussion

The single-crystal diffraction data reveal that $(Et_4N)_4KAuAs_4Te_8$ contains an unprecedented $AuAs_4Te_8^{5-}$ anion. The selected bond distances and angles of $(Et_4N)_4KAuAs_4Te_8$ are listed in Table 2. A projection view of the crystal structure on the *ac* plane is shown in Figure 1a. There is only one crystallographically unique K^+ cation, which makes close contacts with two $AuAs_4Te_8^{5-}$ anions [K···Te = 3.702(2) Å, K···As = 3.509(4) Å]. Formally, an isolated $AuAs_4Te_8^{5-}$ anion can be viewed in terms of two $As_2Te_4^{4-}$ anions coordinating to an Au^{3+} cation to form a square-planar $AuTe_4$ unit (Figure 1b). The discrete $As_2Te_4^{4-}$ anion was previously reported in $Rb_4As_2Te_4$•en.[25] In the $AuAs_4Te_8^{5-}$ anion, there are four terminal [2.483 Å × 2 and 2.668 Å × 2] and four bridging [2.556 Å × 2 and 2.685 Å × 2] As–Te bonds. Each of the terminal As–Te bond distances is slightly shorter or longer than those of $(Ph_4P)_2As_{10}Te_3$ [2.534–2.550 Å (terminal) and 2.605–2.611 Å (bridging), respectively][26] and $(Et_4N)_4As_4Te_6$ [2.541–2.552 Å (terminal) and 2.610–2.614 Å (bridging), respectively],[27] as well as the bridging ones. The average As–As bond distance of 2.427(6) Å in the $AuAs_4Te_8^{5-}$ anion is close to those of $Rb_4As_2Te_4$•en [2.47(1) Å][25] and $(Et_4N)_4As_4Te_6$ [2.440(4) Å].[27] The two crystallographically unique As atoms are disordered, via pyramidal inversion, and have an occupancy of one-half at each site. Thus, when viewed approximately along the *c* direction, the two As–As bonds of an $AuAs_4Te_8^{5-}$ anion are either eclipsed or staggered. Note that the As–As bonds in both $(Et_4N)_4As_4Te_6$[27] and $(Et_4N)_2As_2Te_5$[28] adopt only the eclipsed geometry, which is probably the thermodynamically stable form. Although we do not tend to exclude the staggered geometry of the two As–As bonds in the $AuAs_4Te_8^{5-}$ anion, the eclipsed geometry shall also be favorable in the present ternary anion. (Figure 1b shows the eclipsed arrangement.) The Au–Te bonds of 2.646(1) Å are comparable to those observed for the square-planar $AuTe_4$ units in $(Et_4N)_3AuTe_7$ [2.638–2.664 Å][29] and $(Et_4N)_4Au_2Te_{12}$ [2.625–2.661 Å],[30] both of which have the polytelluride ligand Te_5. (Namely, Te_7 consists of one Te_5 unit and one Te_2 unit, while Te_{12} consists of two Te_5 units and one Te_2 unit.) $(Et_4N)_4KAuAs_4Te_8$ is the first ternary telluride Zintl anion containing a square-planar $AuTe_4$ unit not surrounded by a homoleptic polytelluride ligand environment.

The Au cation of the $AuAs_4Te_8^{5-}$ anion would be trivalent Au^{3+} from the viewpoint that it has two $As_2Te_4^{4-}$ anions. In the square-planar $AuTe_4$ units of $(Et_4N)_3AuTe_7$[29] and $(Et_4N)_4Au_2Te_{12}$[30] as well, the Au cation was regarded to be trivalent. However, this assignment is inconsistent with experimental and theoretical results of Au compounds containing square-planar Au cations. For example, in $AuTe_2$, which has both two-coordinate and four-coordinate Au atoms at the extremes of its structural modulation, all Au atoms are monovalent.[31,32] Likewise, in $Cs_2Au_2I_6$, which consists of two-coordinate and four-coordinate Au atoms, all Au atoms are monovalent.[33,34] Therefore, it is possible that the Au atoms of $(Et_4N)_4KAuAs_4Te_8$, $(Et_4N)_3AuTe_7$, and $(Et_4N)_4Au_2Te_{12}$ should also be considered to be monovalent.

To examine this question, we carried out extended Hückel molecular orbital (EHMO)[35] calculations for the $AuAs_4Te_8^{5-}$ anion and the $(As_2Te_4^{4-})_2$ system resulting from $AuAs_4Te_8^{5-}$ by simply removing the Au cation in the form of Au^{3+}. Analysis of the calculated charge distributions in the two systems shows that once the Au^{3+} and $(As_2Te_4^{4-})$ ions are combined to form $AuAs_4Te_8^{5-}$, the Au cation receives a significant amount of electron density mainly from the four Te atoms coordinating the Au cation (about 2.8 electrons in terms of gross population). We also carried out EHMO calculations for the $Au_2Te_{12}^{4-}$ anion and the $(Te_5)(Te_2)(Te_5)^{10-}$ system, resulting from $Au_2Te_{12}^{4-}$ by removing the two "Au^{3+}" cations. This calculation also shows that when two Au^{3+} ions are combined with the $(Te_5)(Te_2)(Te_5)^{10-}$ system to form $Au_2Te_{12}^{4-}$; each Au cation receives a significant amount of electron density from the four Te atoms coordinating the Au (about 2.8 electrons in terms of gross population). Therefore, the Au cation in the square-planar $AuTe_4$ units of $(Et_4N)_4KAuAs_4Te_8$, $(Et_4N)_3AuTe_7$, and $(Et_4N)_4Au_2Te_{12}$ should be regarded as monovalent.

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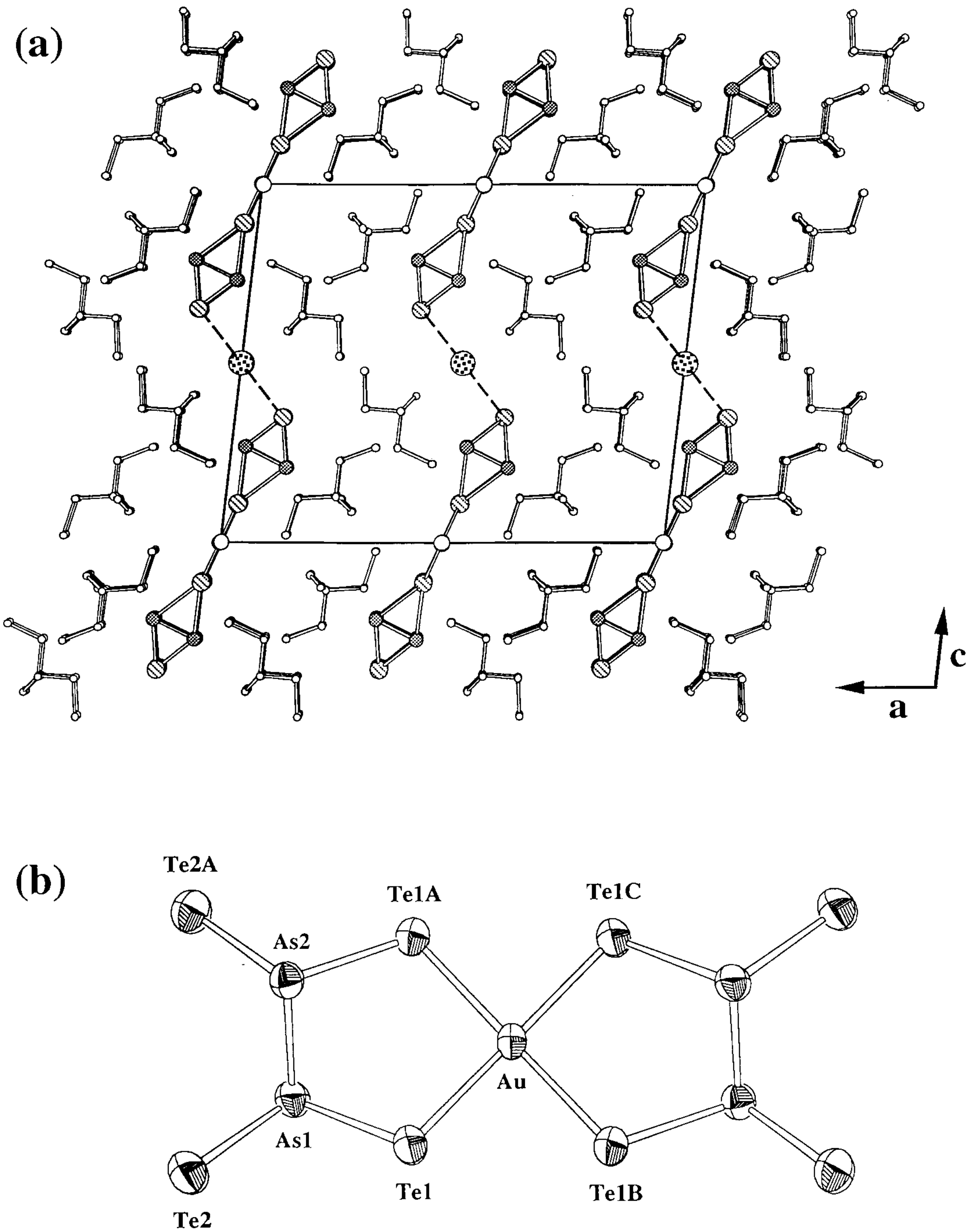

Figure 1. (a) Structure of $(Et_4N)_4KAuAs_4Te_8$ projected down [010]. The K^+ cations and $AuAs_4Te_8^{5-}$ anions form a pseudo-one-dimensional chain running approximately along the *c* axis. The contacts between K and Te atoms are shown with dashed lines. The K, Au, Te, and As atoms are shown as patched, open, hatched, and gray circles, respectively. (b) Perspective view of the $AuAs_4Te_8^{5-}$ anion (50% probability ellipsoids), which is composed of two $As_2Te_4^{4-}$ anions and a square-planar $AuTe_4$. Two crystallographically unique As atoms are all disordered; therefore, two As−As bonds can be arranged in an eclipsed and/or a staggered fashion. The two $[As_2Te_4]$ units in the $AuAs_4Te_8^{5-}$ anion are shown here in an eclipsed fashion.

When the electron-counting scheme is used too literally, conceptual problems can arise. The square-planar $AuTe_4$ unit of $AuAs_4Te_8^{5-}$ is similar in structure to the square-planar $TeTe_4$ unit of the $As_2Te_5^{2-}$ anion chain in $(Et_4N)_2As_2Te_5$ (parts a and b of Figure 2).[28] The square-planar $TeTe_4$ unit is also found in the $SnTe_5^{2-}$ anion chain of M_2SnTe_5 (M = K, Rb),[36,37] in which the $TeTe_4$ unit is considered to be isoelectronic with XeF_4 so that the formal charge on the central Te atom is −2. In this picture, the central Te atom is hypervalent and is isoelectronic with the Au^+ cation in that the Te^{2-} and Au^+ ions both have 10 valence electrons. Alternatively, the $As_2Te_5^{2-}$ chain of $(Et_4N)_2As_2Te_5$ can be regarded to consist of $As_2Te_4^{4-}$ anions. Then the formula unit $As_2Te_5^{2-}$ is written as $(As_2Te_4^{4-})(Te^{2+})$ so that the central Te atom of each $TeTe_4$ unit in the $As_2Te_5^{2-}$ chain has the charge +2. This picture is certainly at odds with the hypervalency of the central Te atom in the $TeTe_4$ unit. Obviously, what happens is that when the $As_2Te_4^{4-}$ and Te^{2+} ions are combined to form the $As_2Te_5^{2-}$ chain, a significant charge transfer takes place from $As_2Te_4^{4-}$ to make the central Te atom hypervalent.

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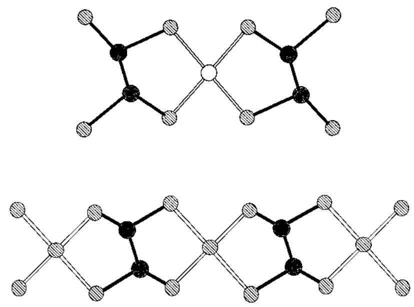

Figure 2. Structural relationships between the discrete $AuAs_4Te_8^{5-}$ anion (a) and the 1-D chain $As_2Te_5^{2-}$ anion (b). A similar $MAs_4Te_8^{5-}$ (M = Au and Te) geometry is observed in both anions. The Au, Te, and As atoms are shown as open, hatched, and gray circles, respectively.

Extraction reactions of ternary and quaternary alloys have led to new ternary and quaternary Zintl anions. Using this synthetic technique, we obtained a ternary Zintl anion, $AuAs_4Te_8^{5-}$, which is the first Zintl anion in the Au−As−Te system. Formally, the $AuAs_4Te_8^{5-}$ anion consists of binary Zintl $As_2Te_4^{4-}$ anions. The preparation of the $AuAs_4Te_8^{5-}$ anion suggests possibilities of finding new ternary or quaternary Zintl anions with binary Zintl anions as building blocks. Our molecular orbital calculations strongly suggest that the Au cations of the square-planar $AuTe_4$ units in $(Et_4N)_4KAuAs_4Te_8$, $(Et_4N)_3AuTe_7$, and $(Et_4N)_4Au_2Te_{12}$ are monovalent.

Acknowledgment. The work at North Carolina State University was supported by the U.S. Department of Energy, Office of Basic Sciences, Division of Materials Sciences, under Grant DE-FG05-86ER45259.

Supporting Information Available: Tables of crystal data, atomic coordinates, thermal parameters, anisotropic displacement parameters, and bond distances and angles for $(Et_4N)_4KAuAs_4Te_8$ (14 pages). Ordering information is given on any current masthead page.

IC980389F