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Synthesis and Structure of the New Gold Polytelluride Anion $[Au_2Te_{12}]^{4-}$

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The ethylenediamine (en) extraction of an alloy of nominal composition $KAuBiTe_3$ or $K_4Au_2Te_{12}$ followed by treatment with Et_4NBr in methanol gave $(Et_4N)_4[Au_2Te_{12}]$ (**1**) in 15% yield. Dark red crystals of **1** crystallize in the monoclinic space group $P2_1/c$ (No. 14) with unit cell dimensions $a = 14.948(2)$ Å, $b = 10.168(2)$ Å, $c = 20.591(4)$ Å, $\beta = 108.15(1)°$, $V = 2973.7(7)$ Å^3, $Z = 2$, and $d_{calc} = 2.732$ g cm^{-3} with R $(R_w) = 0.076$ (0.069) for 1914 reflections with $2\theta < 50°$ and $I \geq 3\sigma(I)$. The X-ray diffraction data revealed a novel dimeric $[Au_2Te_{12}]^{4-}$ anion which consists of square planar Au^{3+} coordinated by a η^3-Te_5^{4-} ligand forming $[AuTe_5]^-$ moieties, two of which are bridged together by a η^2-Te_2^{2-} ligand.

Introduction

The chemistry of the polytellurides has not been extensively developed and thus far has exhibited striking differences in both the bonding modes and structures obtained when compared to its lighter congeners the polysulfides and polyselenides.[1–3] Conventionally, the preparation of molecular metal polychalcogenide compounds takes place by solution-phase syntheses at ambient temperatures[1] whereas synthesis of solid-state metal chalcogenides proceed at higher temperatures.[2,3] In the past 5 years hydrothermal techniques have also been employed and have afforded several novel structures.[4] Recently, we have developed a unique method involving the cathodic dissolution of alloy electrodes which has led to tellurides such as $Au_3Te_4^{3-}$,[5] $Sb_9Te_6^{4-}$,[6] $Sb_4Te_4^{4-}$,[6] $GaTe_2(en)_2^-$,[7] and $InTe_2^-$.[8] However, synthetic efforts involving solvent extraction of intermetallic phases[9] have also shown that this method is capable of producing clusters not isolated from solution phase or flux growth methodologies. Telluride clusters exhibiting unusual and diverse structural features, as seen in $Au_2Te_4^{2-}$,[10] $Au_4Te_4^{4-}$,[11] $KAu_9Te_7^{4-}$,[11] $Hg_4Te_{12}^{4-}$,[12] $Hg_2Te_5^{2-}$,[12] $As_{10}Te_3^{2-}$,[13] and $Cu_4SbTe_{12}^{3-}$[14] have been formed. In this paper we report the extension of the extractive method of intermetallic materials which resulted in the successful isolation and structural characterization of a novel gold polytelluride complex, $(Et_4N)_4[Au_2Te_{12}]$ (**1**).

Experimental Section

All manipulations were carried out in a glovebox under a helium atmosphere with less than 1 ppm of oxygen. The ethylenediamine (en) was distilled over CaH_2 and subsequently purified by a second distillation from a red solution of K_4Sn_9. K_2Te was obtained by combining stoichiometric amounts of K metal and very fine Te powder in liquid ammonia under a nitrogen atmosphere.

Synthesis of $(Et_4N)_4[Au_2Te_{12}]$. Method A. Telluride **1** was prepared by extracting 1.000 g an alloy of nominal composition $KAuBiTe_3$, prepared from the fusion of 0.400 g of K_2Te, 0.766 g of Au, 1.556 g of Bi_2Te_3, and 0.500 g of elemental Te in a quartz ampule under N_2, with 10 mL of ethylenediamine. The homogeneous alloy thus obtained was crushed to fine black powder and stored under a He atmosphere. The red brown extract was filtered and carefully layered with a solution of 0.600 g of Et_4NBr in 10 mL of methanol, which, after 10 days, gave small dark red crystals of **1** in 14% yield. A quantitative analysis of a large number of these crystals in an electron microscope by energy-dispersive X-ray analysis gave an average composition of $Au_1Te_{6.05}$.

Method B. Telluride **1** was also synthesized by extracting 1.000 g an alloy of nominal composition $K_4Au_2Te_{12}$,[15] prepared by the reaction of 0.500 g of K_2Te, 0.478 g of Au, and 1.550 g of elemental Te in a sealed evacuated quartz ampule at 650 °C for 12 h, with 10 mL of ethylenediamine for 12 h. The red brown extract obtained by the dissolution of the alloy was filtered and carefully layered with a solution of 0.500 g of Et_4NBr in 10 mL of en, which, after 10 days, afforded small dark red crystals of **1** in 15% yield.

Crystallography. The single crystals of the title compound were mounted in glass capillaries and flame sealed. The crystallographic data were collected on a Rigaku AFC7R four-circle diffractometer at 22 °C equipped with a RU300 18KW rotating anode using ω–2θ scans. Accurate unit cell dimensions were determined from 16 reflections in the range of $20.33 < 2\theta < 26.26°$. The intensities of three check reflections were monitored every 150 reflections, a 15.9% decay in intensities was observed, and a polynomial decay correction was applied to the data. The structure was solved by direct methods and refined using the *teXsan* crystallographic software package from Molecular Structure Corp. The atoms in the anion were refined anisotropically; the carbon and nitrogen atoms of the Et_4N^+ cations were refined isotropically while the calculated coordinates of the hydrogen atoms were kept fixed. The complete data collection parameters and details of structure solution and refinement are summarized in Table 1. Final positional parameters of all non-hydrogen atoms are given in Table 2. Selected bond distances and bond angles for the $[Au_2Te_{12}]^{4-}$ anion are given in Table 3. Further crystallographic details are available as supplementary material.

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(1) (a) Ansari, M. A.; McConnachie, J. M.; Ibers, J. A. *Acc. Chem. Res.* **1993**, *26*, 574–578. (b) Roof, L. C.; Kolis, J. W. *Chem. Rev.* **1993**, *93*, 1037–1080. (c) Kanatzidis, M. G. *Comments Inorg. Chem.* **1990**, *10*, 161–195. (d) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223–266. (e) Kolis, J. W. *Coord. Chem. Rev.* **1990**, *105*, 195–219. (f) Müller, A; Diemann, E. *Adv. Inorg. Chem. Radiochem.* **1987**, *31*, 89–122.

(2) (a) Kanatzidis, M. G. *Chem. Mater.* **1990**, *2*, 353–363. (b) Keane, P. M.; Lu, Y. -J.; Ibers, J. A. *Acc. Chem. Res.* **1991**, *24*, 223–229.

(3) Böttcher, P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 759–772.

(4) (a) Sheldrick, W. S.; Kaub J. *Z. Anorg. Allg. Chem.* **1986**, *535*, 179–185. (b) Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **1988**, *562*, 23–30. (c) Sheldrick W. S.; Hauser, H.-J. *Z. Anorg. Allg. Chem.* **1988**, *557*, 98–104. (d) Sheldrick W. S.; Hauser, H.-J. *Z. Anorg. Allg. Chem.* **1988**, *557*, 105–111. (e) Liao, J.-H.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 7400–7402. (f) Parise, J. B. *Science* **1991**, *251*, 293–294. (g) Kim, K.-W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 4878–4883.

(5) Warren, C. J.; Ho, D. M.; Bocarsly, A. B.; Haushalter, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 6416–6417.

(6) Warren, C. J.; Ho, D. M.; Haushalter, R. C.; Bocarsly, A. B. *Angew. Chem., Int. Ed. Engl* . **1993**, *32*, 1646–1648.

(7) Warren, C. J.; Ho, D. M.; Haushalter, R. C.; Bocarsly, A. B. *J. Chem. Soc., Chem. Commun.* **1994**, 361–363.

(8) Warren, C. J.; Dhingra, S. S.; Haushalter, R. C.; Bocarsly, A. B. *J. Solid State Chem.*, in press.

(9) (a) Kummer, D.; Diehl, L. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 895. (b) Corbett, J. D. *Chem. Rev.* **1985**, *85*, 383.

(10) Haushalter, R. C. *Inorg. Chim. Acta* **1985**, *102*, L37-L38.

(11) Haushalter, R. C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 432–433.

(12) Haushalter, R. C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 434–435.

(13) Haushalter, R. C. *J. Chem. Soc., Chem. Commun.* **1987**, 196–197.

(14) Dhingra, S. S.; Haushalter, R. C. *J. Am. Chem. Soc.* **1994**, *116*, 3651–3652.

(15) The intermetallic alloy of the nominal composition of $K_4Au_2Te_{12}$ is actually a mixture of K_2Te_3 and $AuTe_2$, two known phases identified by their powder X-ray diffraction patterns.

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Table 1. Crystallographic Data for $(Et_4N)_4[Au_2Te_{12}]$

compd	$(Et_4N)_4[Au_2Te_{12}]$
formula	$H_{80}C_{32}N_4Au_2Te_{12}$
fw	2446.14
cryst color, habit	deep red, hexagonal plate
a (Å)	14.948(2)
b (Å)	10.168(2)
c (Å)	20.591(4)
β (deg)	108.15(1)
V (Å^3)	2973.7(7)
Z	2
space group	$P2_1/c$ (No. 14)
D_{cal} (g cm^{-3}))	2.732
μ (cm^{-1})	107.40
cryst size (mm)	0.10 × 0.05 × 0.10
$2\theta_{max}$ (deg)	50
no. of data collcd	5784
no. of data with $I \geq 3\sigma(I)$	1914
no. of variables	136
final R/R_w	0.076/0.069

Table 2. Fractional Atomic Coordinates and B(eq) Values (Å^2) for $(Et_4N)_4[Au_2Te_{12}]$ with their Standard Deviations in Parentheses

atom	x	y	z	B(eq)^a
Au(1)	0.7862(1)	0.0567(2)	0.4974(1)	4.62(5)
Te(1)	0.9293(2)	0.0581(4)	0.4487(2)	8.4(2)
Te(2)	0.8564(2)	–0.1127(3)	0.5982(2)	6.0(1)
Te(3)	0.7035(2)	–0.1165(4)	0.6452(2)	7.2(1)
Te(4)	0.6266(2)	0.0610(3)	0.5254(2)	5.0(1)
Te(5)	0.5306(2)	0.2212(3)	0.3978(2)	6.1(1)
Te(6)	0.7149(2)	0.2356(3)	0.4008(2)	5.9(1)
N(1)	0.893(3)	0.130(4)	0.158(2)	7(1)
N(2)	0.394(3)	0.228(4)	0.138(2)	7(1)
C(1)	0.885(6)	0.124(10)	0.221(5)	17(2)
C(2)	0.843(4)	0.253(7)	0.243(3)	11(2)
C(3)	0.968(8)	0.24(1)	0.146(6)	20(2)
C(4)	1.055(5)	0.248(7)	0.199(4)	12(1)
C(5)	0.966(8)	0.03(1)	0.164(7)	24(1)
C(6)	0.950(5)	0.005(8)	0.081(4)	14(2)
C(7)	0.817(7)	0.13(1)	0.105(6)	18(2)
C(8)	0.733(4)	0.033(7)	0.113(3)	10(1)
C(9)	0.487(4)	0.191(6)	0.193(3)	10(1)
C(10)	0.562(4)	0.299(6)	0.200(3)	10(1)
C(11)	0.400(3)	0.228(5)	0.069(3)	6(1)
C(12)	0.450(4)	0.102(6)	0.052(3)	8(1)
C(13)	0.322(4)	0.117(6)	0.148(3)	9(1)
C(14)	0.224(4)	0.138(6)	0.096(3)	9(1)
C(15)	0.358(4)	0.362(6)	0.156(3)	9(1)
C(16)	0.340(3)	0.386(5)	0.222(3)	7(1)

^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B(eq) = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) in the $[Au_2Te_{12}]^{4-}$ Anion

Bond Distances			
Au(1)–Te(1)	2.629(4)	Te(2)–Te(3)	2.745(5)
Au(1)–Te(2)	2.650(4)	Te(3)–Te(4)	2.982(5)
Au(1)–Te(4)	2.625(4)	Te(4)–Te(5)	3.044(5)
Au(1)–Te(6)	2.661(4)	Te(5)–Te(6)	2.741(5)
Te(1)–Te(1)	2.748(7)		
Bond Angles			
Te(1)–Au(1)–Te(2)	97.6(1)	Au(1)–Te(2)–Te(3)	96.6(1)
Te(1)–Au(1)–Te(4)	170.7(1)	Te(2)–Te(3)–Te(4)	81.3(1)
Te(1)–Au(1)–Te(6)	84.0(1)	Au(1)–Te(4)–Te(3)	91.7(1)
Te(2)–Au(1)–Te(4)	90.2(1)	Au(1)–Te(4)–Te(5)	92.0(1)
Te(2)–Au(1)–Te(6)	177.1(1)	Te(3)–Te(4)–Te(5)	173.8(2)
Te(4)–Au(1)–Te(6)	88.5(1)	Te(4)–Te(5)–Te(6)	79.0(1)
Au(1)–Te(1)–Te(1)	103.1(2)	Au(1)–Te(6)–Te(5)	98.4(1)

Results and Discussions

During our investigation of quartenary K–Au–Bi–Te alloys, we prepared a brown-black material of nominal composition of $KAuBiTe_3$. The extraction of this alloy with en and subsequent treatment of the extract, at ambient temperature, with different quartenary ammonium or phosphonium salts dissolved in en or methanol, afforded dark red crystals in all the reactions. The reaction with tetrapropylammonium iodide (Pr_4NI), tetraphenylphosphonium bromide (Ph_4PBr), and bis(triphenylphosphine)-nitrogen(1+) chloride ($(Ph_3P)_2NCl$) gave red brown crystals of $(R_4A)_2[Au_2Te_4]$ (where $R_4A = Pr_4N$,[16] Ph_4P,[17] and $(Ph_3P)_2N$[10]). However , if the extract is treated with tetraethylammonium bromide (Et_4NBr) in methanol, dark red crystals of **1** are obtained. Subsequently **1** was prepared by the extraction of an alloy of the composition $K_4Au_2Te_{12}$.

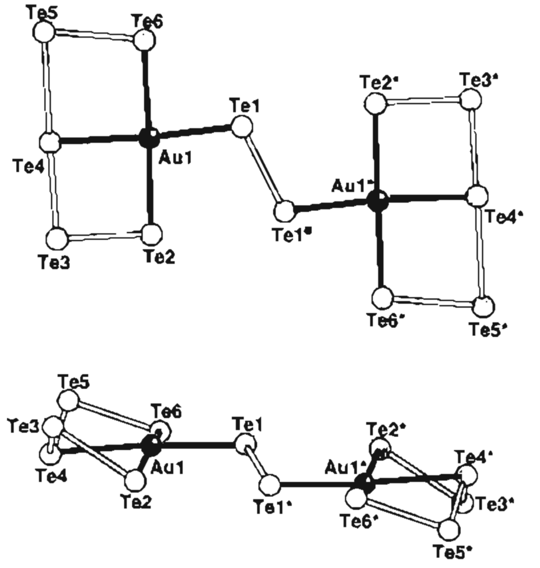

Figure 1. Two views of the anion $[Au_2Te_{12}]^{4-}$ in $(Et_4N)_4[Au_2Te_{12}]$ (**1**).

The single-crystal diffraction data revealed that **1** contains the unprecedented $[Au_2Te_{12}]^{4-}$ anion (Figure 1) and tetraethylammonium cations. The anion in the title compound has a crystallographically imposed center of symmetry and consists of square planar Au^{3+} atoms coordinated by a η^3-Te_5^{4-} ligand forming $[AuTe_5]^-$ moieties, which are bridged together by a η^2-Te_2^{2-} ligand to form $[(Te_5)Au(\mu\text{-}Te_2)Au(Te_5)]^{4-}$ dimers. The –4 charge on the anion was established by the presence of two crystallographically independent Et_4N^+ cations in the asymmetric unit. Gold is in the +3 oxidation state, validated by the square planar coordination environment as well as longer Au–Te bond distances, 2.625(4)–2.661(4) Å, in contrast to the average Au–Te distance in the Au(I) complexes[5,10,11,16,17] of 2.57 Å.

This anion does not have a sulfur or selenium analog, although the geometry of the $AuTe_5$ moiety is quite similar to that found in the recently reported $[AuTe_7]^{3-}$[18] anion. The coordination environment of the $AuTe_5$ moiety is unusual, exhibiting a η^3-Te_5^{4-} ligand as shown in Figure 1. The Te–Te distances of the central Te atom of the Te_5 chain are 2.982(5) and 3.044(5) Å, which are longer than the Te–Te contacts of 2.7–2.8 Å typically observed in other polytellurides that are uncoordinated to metal centers. In contrast to the planar η^3-Te_5^{4-} ligand found in $[AuTe_7]^{3-}$, the Te_5^{4-} ligand in **1** is puckered and exhibits a slightly distorted envelope conformation. Similar lengthening of the Te–Te bonds to the central Te atom of polytelluride chains are observed in $Cu_4SbTe_{12}^{3-}$[14] and MTe_7^{2-} (M = Hg,[19,20] Ag[20])

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(16) Dark brown crystals of $(Pr_4N)_2[Au_2Te_4]$ crystallize in the triclinic space group $P1$ (No. 2) with unit cell parameters a = 9.726(3) Å, b = 11.062(3) Å, c = 9.526(5) Å, α = 105.88(3)°, β = 109.18(3)°, γ = 69.994(2)°, V = 894.4(6) Å^3, Z = 2, and d_{calc} = 2.37 g cm^{-3} with R (R_w) = 0.068 (0.073) at 22 °C.

(17) (a) Warren, C. J.; Ho, D. M., Bocarsly, A. B.; Haushalter, R. C. *J. Am. Chem. Soc.* 1993, *115*, 6416–6417. (b) Kanatzidis, M. G.; Huang S.-P. *Phosphorus, Sulfur, Silicon* 1992, *64*, 153–160.

(18) Ansari, M. A.; Bollinger, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* 1993, *115*, 3838–3839.

resulting in another rather unusual η^3-Te_7^{4-} ligand. The other Te–Te bonds in **1** are in the range 2.741(5)–2.747(5) Å within the expected and typical range for polytellurides.

The synthesis and structural characterization of this new polytelluride anion $[Au_2Te_{12}]^{4-}$ demonstrates that extraction of ternary and quaternary intermetallic phases is a promising pathway to novel metal tellurides. Thus far the chemistry of polytellurides has afforded a large number of unusual and unconventional coordination modes and attests that a rich structural chemistry remains to be discovered. In addition to the $[Au_2Te_{12}]^{4-}$ reported here, we have successfully synthesized and characterized, via this route, other binary and ternary as well as quartenary polyanions.

Supplementary Material Available: Text describing the X-ray procedures and tables of crystal data, data collection, solution, and refinement parameters, complete atomic coordinates and thermal parameters, anisotropic displacement coefficients, and bond lengths and bond angles (14 pages). Ordering information is given on any current masthead page.

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(19) Müller, U.; Grebe, C.; Neumüller, B.; Schreiner, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1993**, *619*, 500–506.

(20) McConnachie, J. M.; Ansari, M. A.; Bollinger, J. C.; Salm, R. J.; Ibers, J. A. *Inorg. Chem.* **1993**, *32*, 3201–3202.