Synthesis and Structure of $(PPN)_2Au_2Te_4$: A New Gold Telluride Containing Planar $Au_2Te_4^{2-}$ Rings

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There are very few examples of binary gold chalcogenide anions AuX_m^{n-} (X = S, Se, Te). Some recent structurally characterized compounds in the sulfur system include AuS_9^{1-} [1], $Au_2S_8^{2-}$ [2] and $Au_{12}S_8^{4-}$ [3]. Using a different synthetic approach than that used for the preparation of the gold sulfide anions [1–3], namely extraction of ternary K/Au/Te alloys, we have been able to prepare several novel Au–Te clusters. In addition to the title compound $(PPN)_2Au_2Te_4$, (**1**) we recently reported the structures of $[K_2Au_4Te_4 \cdot 2DMF \cdot 2MeOH^{2-}]$ [4], $[K_2Au_4Te_4 \cdot 4en^{2-}]$ [4] and $[KAu_9Te_7^{4-}]$ [4].

Compound (**1**) has been observed as a product from the treatment of several ethylenediamine (en) extracts of ternary or quaternary alloys, such as K–Au–As–Te, K–Au–Ge–Te and K–Au–Te, with en solutions of PPN·Cl ($PPN^+ = [(Ph_3P)_2N]^+$). The gold telluride (**1**) forms dark brown planes and crystallizes in the monoclinic space group $P2_1/n$ (see Table I). Cell constants for (**1**) (Table I) at 23(1) °C were obtained from 25 reflections with $2 < \theta < 16°$. For MoK_α radiation, $\mu = 64.7$ cm^{-1} and an empirical absorption correction was applied.

TABLE I. Crystal Data.

Space group	$P2_1/n$
Temperature	23(1) °C
a (pm)	1218.9(4)
b (pm)	1300.9(4)
c (pm)	2174.1(6)
β (deg)	105.16(2)°
V (10^6 pm^3)	3327.4
d_{calc} (g cm^{-3})	1.98
Z	2
Crystal color	brown
Crystal size (mm)	0.10 × 0.30 × 0.35
Radiation (pm)	71.07 (MoK_α)
$2\theta_{max}$ (deg)	45
Number of unique data	4349
Number of data with $F > 3\sigma F$	2288
Number of variable parameters	194
$R(F)$	0.058
$Rw(F)$	0.067
Largest Δ/σ	0.02

The position of the Au atom was located on a Patterson map and the remaining non-hydrogen atoms located by different methods. Hydrogen atoms on the phenyl rings were included in their calculated positions (C–H = 95 pm) but not refined. The Au, Te and P atoms were refined anisotropically and the C, N atoms isotropically.

In addition to the PPN^+ cations, (**1**) contains the novel $Au_2Te_4^{2-}$ anion which is essentially planar (max deviation 2.6 pm) and lies on a crystallographic inversion center. The structure of the anion is shown in Fig. 1 and the atomic coordinates and thermal

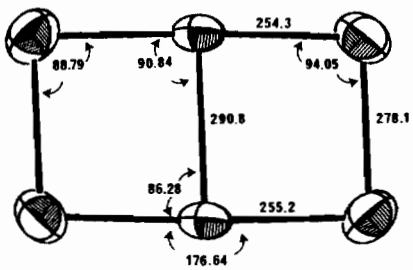

Fig. 1. Distances (pm) and angles (degrees) in the structure of the $Au_2Te_4^{2-}$ anion in $(PPN)_2Au_2Te_4$. The anion resides on a crystallographic inversion and is planar to ±2.6(1) pm.

parameters in Table II. As expected for Au(I), the Te–Au–Te angle is close to 180°. All Au–Au–Te and Au–Te–Te angles are near 90°. The Te–Te distance of 278.1(2) pm is similar to Te–Te contacts in other tellurides [5]. The Au–Au distance of 290.8(1) pm in (**1**) is slightly longer than the 288 pm observed in Au metal. In contrast to the $Au_2Te_4^{2-}$ anion, the other structurally characterized Au–Te anions [4] all have K^+ coordinated to the gold centers.

In summary, these results show that the extraction binary and ternary potassium containing alloys provide a route to $AuTe_x^{n-}$ anions which does not depend on the use of inconvenient and unstable H_2Te.

Experimental

All manipulations were performed in a high purity (<1 ppm O_2) argon atmosphere. Ethylenediamine (en) was purified by distillation from CaH_2 onto K_4Sn_9 followed by a second distillation from the red K_4Sn_9 solution.

Compound (**1**) has been observed as a product from the treatment of en extracts of alloys of

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TABLE II. Table of Positional and Thermal Parameters and Their Estimated Standard Deviations.[a]

Atom	x	y	z	$\beta_{1,1}$	$\beta_{2,2}$	$\beta_{3,3}$	$\beta_{1,2}$	$\beta_{1,3}$	$\beta_{2,3}$
Au1	0.06891(7)	0.08332(7)	−0.01431(4)	0.00815(6)	0.00456(5)	0.00298(2)	−0.0016(1)	0.00552(5)	−0.00019(6)
Te1	−0.0205(2)	0.0420(1)	−0.13101(7)	0.0176(2)	0.0066(1)	0.00265(4)	−0.0008(3)	0.0060(1)	0.0004(1)
Te2	0.1479(1)	0.1214(1)	0.10435(8)	0.0086(1)	0.0098(1)	0.00342(4)	−0.0048(2)	0.0030(1)	−0.0028(1)
P1	0.4231(4)	0.0896(4)	−0.2774(2)	0.0040(3)	0.0040(3)	0.0012(1)	−0.0008(7)	0.0011(3)	−0.0008(3)
P2	0.2040(4)	0.1005(4)	−0.3730(2)	0.0031(3)	0.0036(3)	0.0014(1)	0.0003(6)	0.0019(3)	−0.0002(3)

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å^2)
N1	0.300(1)	0.130(1)	−0.3120(6)	2.9(3)	C34	0.221(2)	−0.238(2)	−0.4240(9)	4.2(5)
C1	0.420(1)	0.018(1)	−0.2046(8)	3.0(4)	C35	0.192(2)	−0.210(2)	−0.3701(9)	4.4(5)
C2	0.315(2)	0.015(1)	−0.1894(8)	3.4(4)	C36	0.184(1)	−0.107(1)	−0.3558(8)	3.0(4)
C3	0.319(2)	−0.032(2)	−0.1291(9)	4.7(5)	H1	0.2471	0.0413	−0.2168	5.0000
C4	0.415(2)	−0.066(2)	−0.0917(10)	4.9(5)	H2	0.2508	−0.0379	−0.1158	5.0000
C5	0.517(2)	−0.064(2)	−0.1073(11)	6.0(6)	H3	0.4136	−0.0946	−0.0516	5.0000
C6	0.514(2)	−0.020(2)	−0.1660(9)	4.2(5)	H4	0.5845	−0.0908	−0.0800	5.0000
C7	0.488(1)	0.013(1)	−0.3276(8)	2.6(4)	H5	0.5829	−0.0161	−0.1788	5.0000
C8	0.481(2)	−0.093(2)	−0.3279(9)	4.1(4)	H6	0.4526	−0.1281	−0.2968	5.0000
C9	0.516(2)	−0.149(2)	−0.3744(10)	5.2(5)	H7	0.5105	−0.2217	−0.3755	5.0000
C10	0.558(2)	−0.101(2)	−0.4162(10)	5.3(5)	H8	0.5827	−0.1409	−0.4467	5.0000
C11	0.566(2)	0.002(2)	−0.4179(9)	4.3(5)	H9	0.5961	0.0333	−0.4494	5.0000
C12	0.530(2)	0.065(1)	−0.3728(8)	3.3(4)	H10	0.5342	0.1378	−0.3736	5.0000
C13	0.519(1)	0.195(1)	−0.2520(7)	2.6(4)	H11	0.6645	0.1103	−0.2279	5.0000
C14	0.635(2)	0.178(1)	−0.2295(8)	3.3(4)	H12	0.7861	0.2481	−0.1953	5.0000
C15	0.707(2)	0.261(2)	−0.2095(9)	4.0(5)	H13	0.7206	0.4120	−0.1940	5.0000
C16	0.669(2)	0.357(2)	−0.2093(9)	4.0(5)	H14	0.5273	0.4451	−0.2321	5.0000
C17	0.555(2)	0.377(2)	−0.2315(9)	3.9(5)	H15	0.3992	0.3076	−0.2693	5.0000
C18	0.478(2)	0.294(1)	−0.2535(8)	3.1(4)	H16	0.0599	0.1337	−0.4971	5.0000
C19	0.208(1)	0.180(1)	−0.4394(7)	2.0(3)	H17	0.0628	0.2356	−0.5863	5.0000
C20	0.122(2)	0.178(1)	−0.4948(8)	3.3(4)	H18	0.2191	0.3486	−0.5767	5.0000
C21	0.122(2)	0.239(2)	−0.5481(10)	5.1(5)	H19	0.3646	0.3563	−0.4830	5.0000
C22	0.216(2)	0.306(2)	−0.5419(9)	4.4(5)	H20	0.3567	0.2450	−0.3986	5.0000
C23	0.303(2)	0.310(1)	−0.4869(8)	3.5(4)	H21	−0.0193	0.0163	−0.4209	5.0000
C24	0.296(1)	0.244(1)	−0.4364(8)	2.8(4)	H22	−0.1965	0.0423	−0.4003	5.0000
C25	0.068(1)	0.117(1)	−0.3568(7)	1.8(3)	H23	−0.2165	0.1604	−0.3258	5.0000
C26	−0.026(2)	0.065(1)	−0.3893(8)	3.4(4)	H24	−0.0612	0.2474	−0.2683	5.0000
C27	−0.132(2)	0.080(2)	−0.3771(8)	3.7(4)	H25	0.1211	0.2233	−0.2855	5.0000
C28	−0.144(2)	0.149(2)	−0.3333(9)	4.3(5)	H26	0.2527	−0.0118	−0.4780	5.0000
C29	−0.052(2)	0.200(2)	−0.2999(10)	5.5(6)	H27	0.2631	−0.1882	−0.5020	5.0000
C30	0.057(2)	0.186(2)	−0.3100(9)	4.0(5)	H28	0.2257	−0.3085	−0.4333	5.0000
C31	0.208(1)	−0.033(1)	−0.3966(7)	2.2(3)	H29	0.1779	−0.2610	−0.3421	5.0000
C32	0.237(1)	−0.062(1)	−0.4500(8)	3.1(4)	H30	0.1613	−0.0876	−0.3188	5.0000
C33	0.243(2)	−0.167(2)	−0.4644(9)	4.2(5)					

[a]The form of the anisotropic thermal parameter is: $\exp[-(\beta_{1,1} \times h^2 + \beta_{2,2} \times k^2 + \beta_{3,3} \times l^2 + \beta_{1,2} \times hk + \beta_{1,3} \times hl + \beta_{2,3} \times kl)]$. Estimated standard deviations in the least significant digits are shown in parentheses. Hydrogens were included in calculated positions (assuming idealized geometries with C–H = 0.95 Å) and were not refined.

nominal composition $KAuTe_2$, $K_2AuAsTe_3$ and $K_3AuGeTe_3$ (which were prepared from fusion of the elements under helium in quartz ampoules) with PPN·Cl in en. The aforementioned alloys did not appear homogeneous in all cases nor were they completely soluble in en.

To isolate (**1**), the filtered brown en extracts were carefully layered with PPN·Cl in en and the products filtered off after standing for 1 or 2 days.

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