

## Synthesis and Structural Characterization of the $[\text{AuTe}_7]^{3-}$ Anion: A Planar Species with an Unprecedented Coordination Mode

Mohammad A. Ansari, John C. Bollinger, and James A. Ibers\*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received December 14, 1992

The polychalcogenides are a fascinating class of ligands because of their structural variety and novel coordination properties.<sup>1</sup> While the coinage-metal chemistry of polysulfides<sup>2</sup> and polyselelenides<sup>3,4</sup> has been extensively investigated, that of polytellurides has not. In the last decade Haushalter has isolated gold tellurides, including  $[\text{Au}_4\text{Te}_4]^{4-}$ ,<sup>5</sup>  $[\text{Au}_9\text{Te}_7]^{5-}$ ,<sup>5</sup> and  $[\text{Au}_2\text{Te}_4]^{2-}$ ,<sup>6</sup> from the solubilization of solid-state materials, and we have recently synthesized the  $[(\text{Te}_4)\text{M}(\mu\text{-Te}_4)\text{M}(\text{Te}_4)]^{4-}$  anions,  $\text{M} = \text{Cu}, \text{Ag}$ .<sup>7</sup> None of these anions has a sulfur or selenium analogue. In this communication we report the synthesis and structural characterization of a remarkable gold anion ( $[\text{AuTe}_7]^{3-}$ ) which possesses structural features unprecedented in the metal–chalcogenide literature.

The compound  $[\text{NET}_4]_3[\text{AuTe}_7]$  was synthesized as thin black parallelepipeds by reacting  $\text{AuCN}$  with  $\text{Te}_n^{2-}$  in DMF in the presence of  $\text{PEt}_3$  and  $\text{NET}_4\text{Cl}$ .<sup>8</sup> The phosphine provides the requisite basic medium for the reaction and also solubilizes any tellurium precipitate. In contrast,  $\text{Cu(I)}$  and  $\text{Ag(I)}$  species react under the same conditions to produce the dinuclear  $[(\text{Te}_4)\text{M}(\mu\text{-Te}_4)\text{M}(\text{Te}_4)]^{4-}$  anions.<sup>7</sup> The composition of  $[\text{NET}_4]_3[\text{AuTe}_7]$  was determined by chemical analysis<sup>8</sup> and an X-ray crystal structural determination.<sup>9</sup>

The  $[\text{AuTe}_7]^{3-}$  anion is shown in Figure 1. The anion is essentially planar, the average deviation from the best least-squares plane being 0.120 Å and the maximum being 0.274 Å for atom  $\text{Te(4)}$ . An overall charge of  $-3$  on the anion is established by the presence of three independent tetraethylammonium cations per anion in the crystallographic asymmetric unit. The oxidation state of  $\text{Au(III)}$  is firmly established by three independent observations: (1) square-planar geometry about the Au center, a common coordination geometry for  $\text{Au(III)}$  but a rare one for  $\text{Au(II)}$  and an unknown one for  $\text{Au(I)}$ ; (2) the Au–Te distances,

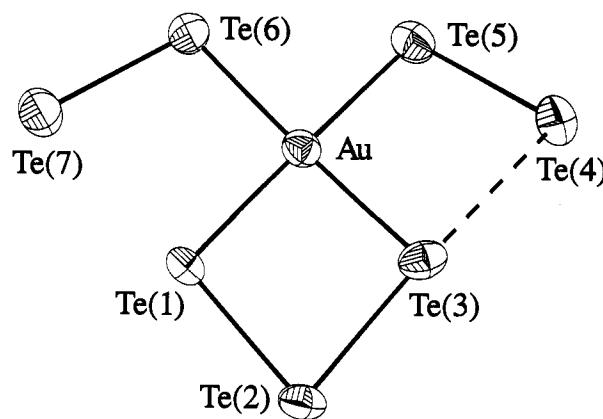


Figure 1. View of the  $[\text{AuTe}_7]^{3-}$  anion. The 90% probability ellipsoids are shown. Some selected bond distances (Å) and angles (deg) are Au–Te(1), 2.664(2); Au–Te(3), 2.638(2); Au–Te(5), 2.651(2); Au–Te(6), 2.647(2); Te(1)–Te(2), 2.809(2); Te(2)–Te(3), 2.927(2); Te(3)–Te(4), 3.120(2); Te(4)–Te(5), 2.702(2); Te(6)–Te(7), 2.719(2); Te(1)···Te(7), 3.374(2); Te(4)–Te(5)–Au, 99.90(5); Te(7)–Te(6)–Au, 102.84(5).

2.638(2) Å – 2.664(2) Å, that are comparable to those in known  $\text{Au(III)}$  compounds, such as 2.642(1)–2.684(1) Å in  $\text{AuTeI}$ ,<sup>10</sup> and (3) the <sup>197</sup>Au Mössbauer spectrum.<sup>11</sup>

The formulation of this species depends upon what Te–Te distances are considered bonding. The Te–Te distances of interest (Figure 1), 3.374(2) Å for Te(1)–Te(7) and 3.120(2) Å for Te(3)–Te(4), are longer than the other Te–Te distances (2.702(2)–2.927(2) Å) but are considerably less than a van der Waals Te···Te separation of about 4 Å.<sup>12</sup> However, the Au–Te(6)–Te(7) angle of 102.84(5)° and the magnitude of the Te(1)–Te(7) separation suggest that there is no interaction between Te(1) and Te(7). Perhaps the Te(7) atom lies in the anionic plane as a result of crystal packing. In any event, an  $\eta^1\text{-Te}_2^{2-}$  ligand on a single metal is unprecedented, insofar as we know. The Au–Te(5)–Te(4) bond angle of 99.90(5)° and the presence of the Te(4) atom in the anionic plane suggest an interaction between atoms Te(3) and Te(4). The Te(3)–Te(4) distance of 3.120(2) Å, though long, is well within the recognized range for bonding. An extended Hückel molecular orbital calculation<sup>13</sup> for the geometry shown in Figure 1 shows no overlap population between atoms Te(1) and Te(7) and an overlap of 0.07 between atoms Te(3) and Te(4), compared to an average of 0.48 for the other Te–Te bonds. Consequently, we favor a description of the anion as  $[\text{Au}^{\text{III}}(\eta^3\text{-Te}_5)(\eta^1\text{-Te}_2)]^{3-}$ ; if this is accepted then the anion contains the unprecedented planar  $\eta^3\text{-Te}_5^{4-}$  ligand. Alternatively, if the Te(3)–Te(4) interaction is ignored, the anion may be formulated as  $[\text{Au}^{\text{III}}(\eta^2\text{-Te}_3)(\eta^1\text{-Te}_2)]^{3-}$ . In either case, the anion has no analogues in the literature.

The Au–Te(1)–Te(2)–Te(3) ring can be compared with  $\text{NbTe}_3$  rings in  $[\text{NbTe}_{10}]^{3-}$ .<sup>14</sup> Ligands of the type  $\eta^3\text{-Q}_n$  ( $n \geq 3$ ) occur

(1) Lee, S. C.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* 1990, 29, 840–856.

(2) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* 1987, 31, 89–122.

(3) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* 1990, 100, 223–266.

(4) Kanatzidis, M. G. *Comments Inorg. Chem.* 1990, 10, 161–195.

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

(6) Haushalter, R. C. *Inorg. Chim. Acta* 1985, 102, L37–L38.

(7) Ansari, M. A.; Bollinger, J. C.; Ibers, J. A. *Inorg. Chem.*, in press.

(8) To a polytelluride solution, generated in situ by the reaction of  $\text{Li}_2\text{Te}$  (500 mg, 3.53 mmol) with Te powder (1 g, 7.83 mmol) in DMF (15 mL), was added a solution obtained by mixing  $\text{AuCN}$  (446 mg, 2 mmol) with  $\text{PEt}_3$  (1 mL, 6.78 mmol) in DMF (10 mL). The resulting mixture so obtained was stirred at room temperature for 1 h and then filtered.  $\text{NET}_4\text{Cl}$  (600 mg, 3.63 mmol) dissolved in  $\text{CH}_3\text{CN}$  (10 mL) was added to the filtrate. Upon layering the resultant solution with ether (70 mL), needle- and platelike crystals formed. The needle-shaped crystals were not of sufficient quality for a single-crystal X-ray diffraction study. The platelike crystals were manually separated and analyzed. Yield: 560 mg, 27% based on  $\text{AuCN}$  used. Anal. Calcd for  $\text{C}_{24}\text{H}_{60}\text{AuN}_3\text{Te}_7$ : C, 19.46; H, 4.08; N, 2.84; Au, 13.30. Found: C, 18.73; H, 3.94; N, 2.72; Au, 12.89.

(9) Crystal data for  $[\text{NET}_4]_3[\text{AuTe}_7]$ :  $\text{C}_{24}\text{H}_{60}\text{AuN}_3\text{Te}_7$ ; triclinic;  $\text{C}_1$  –  $\text{P}1$ ;  $Z = 2$ ;  $a = 10.867(4)$ ,  $b = 13.695(5)$ ,  $c = 13.741(5)$  Å;  $\alpha = 88.23(1)^\circ$ ,  $\beta = 75.06(1)^\circ$ ,  $\gamma = 79.42(2)^\circ$ ;  $V = 1942$  Å<sup>3</sup> at  $-165^\circ\text{C}$ . All data ( $\pm h, \pm k, \pm l$ ) were collected out to  $50^\circ$  in  $2\theta$  ( $\text{Mo K}\alpha$ ); an analytical absorption correction was applied. Friedel pairs were averaged for structure solution. The structure was refined on  $F^2$  by full-matrix least-squares methods (Sheldrick, G. M. SHELXL-92 Unix Beta-test Version, 1992); this refinement used all the data and involved 328 variables (all non-hydrogen atoms anisotropic). This refinement converged to  $R_w(F^2) = 0.099$  for the 6867 independent reflections and to  $R(F) = 0.041$  for the 5344 reflections having  $F^2 > 2\sigma(F^2)$ .

(10) Fenner, J.; Mootz, D. *J. Solid State Chem.* 1978, 24, 367–369.

(11) The correlation between isomer shift and quadrupole splitting for  $[\text{NET}_4]_3[\text{AuTe}_7]$  nicely accommodates it in the range of  $\text{Au(III)}$ –tellurides. An isomer shift of 1.86 mm/s and a quadrupole splitting of 2.92 mm/s found for  $[\text{NET}_4]_3[\text{AuTe}_7]$  are comparable to those for known square-planar  $\text{Au(III)}$  tellurides, such as  $\text{AuTe}_2$  (1.97, 2.43 mm/s) and  $\text{AuAgTe}_4$  (1.71, 2.64 mm/s) (Friedl, J.; Wagner, F. E.; Sawicki, J. A.; Harris, D. C.; Mandarino, J. A.; Marion, P. *Hyperfine Interact.* 1992, 70, 945–948).

(12) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Crystallogr.* 1976, 32, 751–767.

(13) Calculations were performed with the EHMCC extended Hückel program originally written by M.-H. Whangbo at Cornell University in the laboratory of R. Hoffmann and later modified by others in Hoffmann's laboratory and also in Whangbo's laboratory at North Carolina State University. Crystallographic coordinates were used. Built-in parameters for the gold d-orbitals (double- $\zeta$ ) and Te s- and p-orbitals (both single- $\zeta$ ) were used. More detailed calculations are currently being made by R. Hoffmann and co-workers.

(14) Flomer, W. A.; Kolis, J. W. *J. Am. Chem. Soc.* 1988, 110, 3682–3683.

in  $(\text{Cp}^*\text{Sm})_2\text{Se}_3\cdot\text{THF}$ ,<sup>15</sup>  $(\text{PMe}_3)_3\text{OsS}_7$ ,<sup>16</sup>  $[(\text{CO})_4\text{Mo}(\text{Te}_3)]^{2+}$ ,<sup>17</sup> and  $[(\text{CO})_4\text{W}(\text{Te}_3)]^{2+}$ ,<sup>18</sup> but the  $\text{MQ}_n$  arrangement in these compounds is anything but planar, quite unlike the ligands in  $[\text{AuTe}_7]^{3-}$ . A number of gold sulfide and gold selenide anions are known, including  $[\text{AuS}_9]^-$ ,<sup>19</sup>  $[\text{Au}_2\text{S}_8]^{2-}$ ,<sup>20</sup>  $[\text{Au}_2\text{Se}_5]^{2-}$ ,<sup>21</sup>  $[\text{Au}_2\text{Se}_6]^{2-}$ ,<sup>21</sup> and  $[\text{Au}_2\text{Se}_{10}]^{2-}$ ,<sup>22</sup> but none of them has features similar to those found in  $[\text{AuTe}_7]^{3-}$ . Again one sees the greater

(15) Rabe, G. W.; Ziller, J. W.; Doedens, R. J.; Evans, W. J. *Abstracts of Papers*; 204th National Meeting of the American Chemical Society, Aug. 23–28, 1992, Washington, DC; American Chemical Society: Washington, DC, 1992; INOR 62.

(16) Gotzig, J.; Rheingold, A. L.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 814–815.

(17) Seigneurin, A.; Makani, T.; Jones, D. J.; Rozière, J. *J. Chem. Soc., Dalton Trans.* **1987**, 2111–2116.

(18) Faggiani, R.; Gillespie, R. J.; Campana, C.; Kolis, J. W. *Chem. Commun.* **1987**, *7*, 485–486.

(19) Marbach, G.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 246.

(20) Müller, A.; Römer, M.; Bögge, H.; Krickemeyer, E.; Schmitz, K. *Inorg. Chim. Acta* **1984**, *85*, L39–L41.

propensity of tellurium, compared to sulfur and selenium, to participate in unusual coordination, to be involved in partial bonding, and to assume intermediate oxidation states.

**Acknowledgment.** This research was supported by the National Science Foundation, Grant No. CHE-8922754. We are especially indebted to Prof. Dr. F. E. Wagner of the Technische Universität, München, for the measurement and interpretation of the  $^{197}\text{Au}$  Mössbauer spectrum.

**Supplementary Material Available:** Crystallographic details (Table SI), positional parameters (Table SII), thermal displacements (Table SIII), bond distances and angles (Tables SIV and SV), and hydrogen atom parameters (Table SVI) (8 pages). Ordering information is given on any current masthead page.

(21) Huang, S.-P.; Kanatzidis, M. G. *Inorg. Chem.* **1991**, *30*, 3572–3575.

(22) Kanatzidis, M. G.; Huang, S.-P. *Inorg. Chem.* **1989**, *28*, 4667–4669.