Synthesis, Reactivity, and Structural Characterization of the Nonclassical $[MTe_7]^{n-}$ Anions ($M = Ag, Au, n = 3; M = Hg, n = 2$)

Donna M. Smith, Lisa C. Roof, Mohammad A. Ansari, Jonathan M. McConnachie, John C. Bollinger, Michael A. Pell, Robert J. Salm, and James A. Ibers*

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

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Several tellurometalates of the general formula $[MTe_7]^{n-}$ ($n = 2, 3$) have been isolated as salts of organic cations by reaction of suitable metal sources with polytelluride solutions in DMF. The $[HgTe_7]^{2-}$ anion has the same structure in both the NEt_4^+ and the PPh_4^+ salts except for a minor change in the ligand conformation. The $[AgTe_7]^{3-}$ and $[HgTe_7]^{2-}$ anions contain metal atoms coordinated in trigonal-planar fashion to η^3-Te_7^{4-} ligands. The central Te atom of an η^3-Te_7^{4-} ligand is coordinated to the metal atom and to two Te atoms in a "T"-shaped geometry consistent with a hypervalent 10 e^- center. The planar $[AuTe_7]^{3-}$ anion may best be described as possessing a square-planar Au^{III} atom coordinated to an η^3-Te_5^{4-} ligand and to an η^1-Te_2^{2-} ligand. The reaction of $[NEt_4]_n[MTe_7]$ ($M = Hg, n = 2; M = Au, n = 3$) with the activated acetylene dimethyl acetylenedicarboxylate (DMAD) has yielded the products $[NEt_4]_n[M(Te_2C_2(COOCH_3)_2)_2]$ ($M = Hg, n = 2; M = Au, n = 1$). The metal atoms are coordinated to two $Te(COOCH_3)C{=}C(COOCH_3)Te^{2-}$ ligands, for M = Hg in a distorted tetrahedral fashion and for M = Au in a square-planar fashion.

Introduction

Over the last three decades a rich and entirely new area of coordination chemistry has resulted from reactions of main-group elements with transition metals. A large number of monomeric and oligomeric compounds containing chains, rings, and clusters have been discovered.[1−5] Most of the earlier research activity focused on pnictides and chalcogenides, and in particular on phosphides[6−9] and sulfides.[3,4,10−12] With respect to chalcogenometalates, the last decade has seen increased attention paid to selenometalates[13−16] and tellurometalates.[13−17] It turns out that there are more differences than similarities between sulfidometalates and selenometalates on the one hand and tellurometalates on the other. Most of the known tellurometalates represent distinct structural types. Examples include $[NbTe_{10}]^{3-}$,[18] $[M_4Te_{12}]^{4-}$ (M = Cd,[19,20] Hg[21]), $[Ni_4Te_{20}]^{4-}$,[22] and $[M_2Te_{12}]^{4-}$ (M = Cu, Ag).[23,24] Previously we communicated preliminary accounts of the syntheses and structures of $[AuTe_7]^{3-}$,[25] $[AgTe_7]^{3-}$,[26] and $[HgTe_7]^{2-}$;[26] all possess unusual features and nonclassical bonding modes. Here we present a detailed description of these remarkable anions as well as a discussion of their reactivity with the activated acetylene dimethyl acetylenedicarboxylate (DMAD).

Experimental Section

Syntheses. Manipulations of the complexes described below were conducted with the exclusion of air and water by the use of standard Schlenk and glovebox techniques. Anhydrous *N*,*N*-dimethylformamide (DMF), purchased from Aldrich Chemical Co., Milwaukee, WI, was vacuum-distilled off CaH_2, stored over activated molecular sieves, and degassed with dry N_2 before use. Anhydrous diethyl ether (Et_2O) was purchased from Baxter Scientific, McGaw Park, IL, and distilled off Na/benzophenone before use. Li_2Te was prepared by mixing stoichiometric amounts of freshly cut Li metal with Te powder in liquid NH_3 at −78 °C. $HgCl_2$ was purchased from Mallinckrodt Inc., Paris, KY. $Hg(xan)_2$ ($xan = EtOCS_2^-$) was prepared by a literature method.[27] $[AgI(PMe_3)]_4$ was purchased from Strem Chemical Co., Newburyport, MA, and was used as received. All other reagents were purchased from Aldrich Chemical Co. and were used without any further purification. Energy-dispersive analysis by X-rays (EDX) was performed with the use of a Hitachi 570 scanning electron microscope

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equipped with an X-ray detector. ^{125}Te (spin = $^1/_2$; 7% abundance) NMR spectra were obtained on a Varian 400 MHz Unity Plus spectrometer equipped with a 10 mm broad-band probe, a variable-temperature apparatus, and a deuterium lock. Chemical shifts are referenced to the external standard Et_2Te at 380 ppm based on $(CH_3)_2Te$ at $\delta = 0$ ppm.

$[NEt_4][PPh_4]_2[AgTe_7]$ (1). A flask was charged with Li_2Te (500 mg, 3.5 mmol), Te (1.0 g, 7.8 mmol), Na (23 mg, 1.0 mmol), and NEt_4Cl (330 mg, 2.0 mmol). DMF (15 mL) was added, and the solution was stirred for 1 h. In another flask $[AgI(PMe_3)]_4$ (622 mg, 0.5 mmol) was dissolved in DMF (10 mL), and PEt_3 (0.5 mL) was added; this solution was transferred via a canula needle to the polytelluride solution. The resultant mixture was stirred for an additional 1 h and then was filtered through a coarse-porosity sintered-glass frit. Addition of Et_2O (10 mL) to the filtrate did not produce any crystals, so the filtrate was further treated with a solution of PPh_4Br (838 mg, 2.0 mmol) dissolved in DMF (10 mL) and the mixture was then layered with Et_2O (20 mL). Over 48 h dark red needles and plates were produced. The needles were manually separated for X-ray data collection. The plates were of poor quality and were unsuitable for analysis.

$[PPh_4]_2[HgTe_7]$ (2). A flask was charged with $Hg(xan)_2$ (886 mg, 2 mmol), Li_2Te (849 mg, 6 mmol), Te (1.53 g, 12 mmol), and PPh_4Cl (1.5 g, 4 mmol). DMF (60 mL) and PEt_3 (1 mL) were added. The resultant solution was stirred for 1 h at 90 °C and then was filtered through a medium-porosity sintered-glass frit. Careful layering of Et_2O (90 mL) on top of the filtrate produced purple plates and microcrystalline powder. $[PPh_4]_2[HgTe_7]$ (**2**) and $[PPh_4]_2[Hg(Te_4)_2]$[28] crystallize as a mixture, and they were manually separated for X-ray data collection.

$[NEt_4]_2[HgTe_7]$ (3). A flask was charged with Li_2Te (283 mg, 2.0 mmol) and Te (762 mg, 6 mmol). DMF (15 mL) was added, and the solution was stirred for 1 h. In another flask $HgCl_2$ (270 mg, 1.0 mmol) was dissolved in DMF (15 mL); this solution was then transferred via a canula needle to the polytelluride solution. The resultant solution was stirred for 1 h at 25 °C and then was filtered through a medium-porosity sintered-glass frit. The filtrate was treated with a solution of NEt_4Br (420 mg, 2 mmol) dissolved in DMF (10 mL) and the resultant mixture was layered with Et_2O (50 mL). After 48 h dark red plates were obtained. Yield: 730 mg, 54% based on Hg. Anal. Calcd for $C_{16}H_{40}HgN_2Te_7$: C, 14.19; H, 2.98; N, 2.07; Hg, 14.81. Found: C, 14.97; H, 3.09; N, 2.03; Hg, 15.06.

$[NEt_4]_3[AuTe_7]$ (4). A flask was charged with AuCN (446 mg, 2.0 mmol). DMF (10 mL) was added, and the solution was kept at 90 °C until the AuCN was digested. PEt_3 (1 mL) was then added to the cloudy, orange AuCN solution; the solution turned transparent within 1 min. In another flask Li_2Te (500 mg, 3.5 mmol) and Te (1 g, 7.8 mmol) were dissolved in DMF (15 mL); the AuCN solution was added over a period of 10 min through a canula needle to the polytelluride solution. The resultant mixture was stirred for 1 h and then was filtered through a coarse-porosity sintered-glass frit. The filtrate was treated with a solution of NEt_4Cl (600 mg, 3.6 mmol) dissolved in CH_3CN (10 mL). Addition of Et_2O (70 mL) produced black needles and plates. The plates were manually separated from the needles and found to be $[NEt_4]_3[AuTe_7]$. Anal. Calcd for $C_{24}H_{60}AuN_3Te_7$: 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. From a preliminary X-ray study the needles are $[NEt_4]_3[Au_3Te_4]$; the anion has the same structure as in $[N(C_4H_9)_4]_3[Au_3Te_4]$.[29]

$[NEt_4]_2[Hg(Te_2C_2(COOCH_3)_2)_2]$ (5). In a flask $[NEt_4]_2[HgTe_7]$ (460 mg, 0.34 mmol) was dissolved in DMF (10 mL), and the solution was stirred at 25 °C for 15 min. DMAD (0.08 mL, 0.65 mmol) was added. The orange-brown solution was filtered through a coarse-porosity sintered-glass frit, and the filtrate was layered with toluene (10 mL). Overnight storage at 25 °C yielded orange needles. ^{125}Te NMR (DMF/CD_3CN; 25 °C): $\delta = 280$ ppm ($J_{Hg-Te} = 2947$ Hz). Yield: 190 mg, 45% based on Hg. Anal. Calcd for $C_{28}H_{52}HgN_2O_8Te_4$: C, 26.78; H, 4.17; N, 2.23; Te, 40.64. Found: C, 26.90; H, 4.08; N, 2.14; Te, 39.45.

$[NEt_4][Au(Te_2C_2(COOCH_3)_2)_2]$ (6). In a flask $[NEt_4]_3[AuTe_7]$ (250 mg, 0.174 mmol) was dissolved in DMF (15 mL), and the solution was stirred at 25 °C for 1 h. The solution changed immediately from a red-purple to a yellow-brown color upon the addition of DMAD (0.43 mL, 0.35 mmol). After the solution was filtered through a coarse-porosity sintered-glass frit, it was layered with diethyl ether (80 mL). Storage at 25 °C for 2 weeks yielded bright-red, rectangular rods. Yield: 30 mg, 15% yield based on Au.

Crystallographic Studies

In each instance, data collection was carried out at 113 K with the use of Mo Kα radiation; the intensities of six standard reflections, which were measured every 100 reflections, showed no significant variations throughout data collection except as noted. Data collection for compound **2** ($[PPh_4]_2[HgTe_7]$) was performed on an Enraf-Nonius CAD4 diffractometer. A Picker diffractometer was employed for the remaining compounds. Intensity data were processed by methods standard in this laboratory[30] and corrected for absorption.[31] The structures were solved by direct methods[32] and were refined anisotropically by least-squares methods.[33] Phenyl and methylene hydrogen atoms were placed at calculated positions and refined according to a riding model. Methyl hydrogen atoms were placed so that normal tetrahedral angles and C−H distances were obtained and so that the methyl-group torsion angle maximized the electron density at the three calculated hydrogen atom positions. The resultant torsion angles were then refined as additional least-squares parameters. Selected crystallographic details are provided in Table 1, and more are listed in Tables S1 and S2.[34]

$[PPh_4]_2[NEt_4][AgTe_7]$ (1). The final cycle of least-squares refinement (320 variables, 8634 observations) converged to an agreement index *R(F)* of 0.069 for those 5470 reflections having $F_o^2 > 2\sigma(F_o^2)$. Anisotropic displacement parameters were refined for P and the heavier elements. Final heavy-atom coordinates and equivalent isotropic displacement parameters are given in Table 2. Complete atomic coordinates, anisotropic displacement parameters, H atom parameters, and all bond lengths and angles are listed in Tables S3, S9, S15, and S21.[34]

$[PPh_4]_2[HgTe_7]$ (2). The anion of **2** is disordered about a center of inversion. The assignment of atom positions to the $[HgTe_7]^{2-}$ anion with inverted image was made with reference to the geometry derived from the $[AgTe_7]^{3-}$ anion. Each atom except Te(2) was assigned an occupancy of $^1/_2$. Atom Te(2) could not be resolved from the atom labeled Te(6) in the silver analogue (**1**), so it was assigned full occupancy. The final cycle of least-squares refinement for **2** (289 variables, 4292 observations) converged to an agreement index *R(F)* of 0.046 for those 3708 reflections having $F_o^2 > 2\sigma(F_o^2)$. Heavy-atom positions and equivalent isotropic displacement parameters are listed in Table 3. Complete atomic coordinates, anisotropic displacement parameters, H atom parameters, and all bond lengths and angles are given in Tables S4, S10, S16, and S22.[34]

$[NEt_4]_2[HgTe_7]$ (3). Unlike that of **2**, this anion shows no disorder. The final cycle of least-squares refinement for **3** (243 variables, 4849 observations) converged to an agreement index *R(F)* of 0.052 for those 3355 reflections having $F_o^2 > 2\sigma(F_o^2)$. Heavy-atom coordinates and equivalent isotropic displacement parameters are listed in Table 4. Complete atomic coordinates, anisotropic displacement parameters, H atom parameters, and all bond lengths and angles are given in Tables S5, S11, S17, and S23.[34]

$[NEt_4]_3[AuTe_7]$ (4). Intensity data were corrected for an average linear decline of 11% in the intensities of the standard reflections observed over the course of data collection. The final cycle of least-squares refinement (328 variables, 6867 observations) converged to an agreement index *R*(*F*) of 0.041 for those 5344 reflections having $F_o^2 > 2\sigma(F_o^2)$. Heavy-atom coordinates and equivalent isotropic

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(34) Supporting Information.

Table 1. Selected Crystallographic Details for Compounds **1**−**6**

compound	$[PPh_4]_2[NEt_4][AgTe_7]$	$[PPh_4]_2[HgTe_7]$	$[NEt_4]_2[HgTe_7]$	$[NEt_4]_3[AuTe_7]$	$[NEt_4]_2[Hg(Te_2C_2(COOCH_3)_2)_2]$	$[NEt_4][Au(Te_2C_2(COOCH_3)_2)_2]$
no.	**1**	**2**	**3**	**4**	**5**	**6**
empirical formula	$C_{56}H_{60}AgNP_2Te_7$	$C_{48}H_{40}HgP_2Te_7$	$C_{16}H_{40}HgN_2Te_7$	$C_{24}H_{60}AuN_3Te_7$	$C_{28}H_{52}HgN_2O_8Te_4$	$C_{20}H_{32}AuNO_8Te_4$
fw	1810.06	1772.53	1354.29	1480.92	1255.71	1121.83
a, Å	8.893(2)	12.755(1)	13.974(3)	10.867(4)	9.076(2)	7.132(1)
b, Å	14.663(4)	14.327(3)	9.061(2)	13.695(5)	28.632(6)	11.772(2)
c, Å	23.320(6)	13.932(2)	25.030(5)	13.741(5)	15.210(3)	17.613(4)
α, deg	87.17(1)	90	90	88.23(1)	90	90
β, deg	80.74(1)	105.58(1)	102.76(3)	75.06(1)	92.12(3)	92.26(3)
γ, deg	75.82(1)	90	90	79.42(2)	90	90
V, Å^3	2910(1)	2452(1)	3091(1)	1942(1)	3951(1)	1478(1)
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
Z	2	2	4	2	4	2
d (calc), g/cm^3	2.066	2.400	2.910	2.533	2.111	2.521
μ, cm^{-1}	38.77	73.17	114.6	89.59	68.3	88.83
T, K	113(2)	113(2)	113(2)	113(2)	113(2)	113(2)
$R(F_o)^a$	0.069	0.046	0.052	0.041	0.044	0.050
$R_w(F_o^2)$,^{b} all data	0.145	0.097	0.121	0.099	0.095	0.104

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$; $F_o^2 > 2\sigma(F_o^2)$. [b] $R_w(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$; $w^{-1} = \sigma^2(F_o^2)$, $F_o^2 < 0$.

Table 2. Atom Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for the Anion of $[PPh_4]_2[NEt_4][AgTe_7]$ (**1**)

atom	x	y	z	$U_{eq}{}^a$
Ag	0.4926(2)	0.20576(9)	0.27713(6)	0.0206(8)
Te(1)	0.40708(14)	0.30491(9)	0.37659(5)	0.0212(7)
Te(2)	0.2657(2)	0.47714(9)	0.33296(5)	0.0245(8)
Te(3)	0.43045(14)	0.48968(8)	0.22554(5)	0.0203(7)
Te(4)	0.50887(13)	0.28384(8)	0.16852(5)	0.0184(7)
Te(5)	0.56108(14)	0.11015(8)	0.10856(5)	0.0226(7)
Te(6)	0.74284(14)	−0.01284(8)	0.17523(5)	0.0231(7)
Te(7)	0.5670(2)	0.01622(9)	0.28248(5)	0.0276(8)

[a] $U_{eq} = \sum_i\sum_j(U_{ij}a^*_i a^*_j \boldsymbol{a_i}\cdot\boldsymbol{a_j})$.

Table 3. Atom Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for the Anion of $[PPh_4]_2[HgTe_7]$ (**2**)

atom	x	y	z	U_{eq}
Hg(1)	0.05014(4)	0.52649(4)	0.53445(4)	0.01952(14)
Te(1)	0.22811(12)	0.55860(10)	0.46564(11)	0.0252(3)
Te(2)	0.12178(4)	0.53930(3)	0.26727(4)	0.02478(14)
Te(3)	0.01036(10)	0.37827(8)	0.27052(9)	0.0221(3)
Te(4)	−0.11766(7)	0.42543(6)	0.41560(7)	0.0181(2)
Te(5)	−0.26466(11)	0.46071(10)	0.55207(11)	0.0232(3)
Te(7)	0.02711(11)	0.59025(9)	0.71169(9)	0.0275(3)

Table 4. Atom Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for the Anion of $[NEt_4]_2[HgTe_7]$ (**3**)

atom	x	y	z	U_{eq}
Hg	0.31201(4)	0.10635(7)	0.01477(3)	0.0195(2)
Te(1)	0.40052(8)	0.08573(14)	0.12275(5)	0.0258(3)
Te(2)	0.24914(8)	0.21907(13)	0.15871(5)	0.0238(3)
Te(3)	0.09159(8)	0.06710(13)	0.10231(5)	0.0255(3)
Te(4)	0.11302(7)	0.11739(13)	−0.01326(5)	0.0206(3)
Te(5)	0.11126(8)	0.12479(14)	−0.13487(5)	0.0274(3)
Te(6)	0.28133(9)	0.26328(13)	−0.14088(5)	0.0258(3)
Te(7)	0.41666(8)	0.1111(2)	−0.06476(5)	0.0279(3)

displacement parameters are given in Table 5. Complete atomic coordinates, anisotropic displacement parameters, H atom parameters, and all bond lengths and angles are given in Tables S6, S12, S18, and S24.[34]

$[NEt_4]_2[Hg(Te_2C_2(COOCH_3)_2)_2]$ (5). The final cycle of least-squares refinement (388 variables, 6611 observations) converged to an agreement index $R(F)$ of 0.044 for those 4403 reflections having $F_o^2 > 2\sigma(F_o^2)$. All atoms were refined anisotropically, except for N(2). Heavy-atom coordinates and equivalent isotropic displacement parameters are given in Table 6. Complete atomic coordinates, anisotropic displacement parameters, H atom parameters, and all bond lengths and angles are given in Tables S7, S13, S19, and S25.[34]

Table 5. Atom Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for the Anion of $[NEt_4]_3[AuTe_7]$ (**4**)

atom	x	y	z	U_{eq}
Au	0.19001(4)	0.24249(3)	0.21539(3)	0.0150(2)
Te(1)	0.31457(6)	0.14211(5)	0.34140(4)	0.0143(3)
Te(2)	0.38710(6)	0.30842(5)	0.41055(5)	0.0181(3)
Te(3)	0.22697(6)	0.41010(5)	0.28305(5)	0.0180(3)
Te(4)	0.05049(7)	0.53144(5)	0.15815(5)	0.0227(4)
Te(5)	0.07433(7)	0.34537(5)	0.08678(5)	0.0231(4)
Te(6)	0.13617(6)	0.07939(5)	0.15029(5)	0.0204(4)
Te(7)	0.24204(7)	−0.06520(5)	0.26006(5)	0.0232(4)

Table 6. Atom Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for the Anion of $[NEt_4]_2[Hg(Te_2C_2(COOCH_3)_2)_2]$ (**5**)

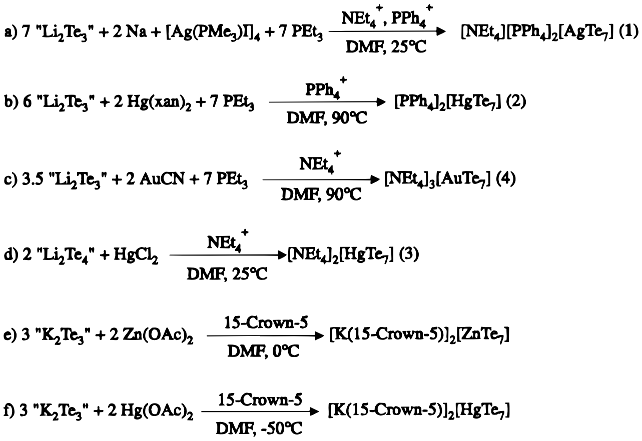
atom	x	y	z	U_{eq}
Hg(1)	0.02210(6)	0.14231(2)	0.33767(3)	0.02106(13)
Te(1)	−0.00869(9)	0.09517(3)	0.17769(5)	0.0193(2)
Te(3)	−0.17910(9)	0.19884(3)	0.41591(5)	0.0212(2)
Te(2)	0.07736(9)	0.05988(3)	0.42688(5)	0.0191(2)
Te(4)	0.21737(9)	0.21643(3)	0.31468(5)	0.0227(2)
O(1)	−0.1040(9)	−0.0156(3)	0.1239(5)	0.026(2)
O(2)	0.1395(10)	−0.0285(3)	0.1411(6)	0.033(2)
O(3)	0.2019(9)	−0.0445(3)	0.3795(5)	0.022(2)
O(4)	−0.0164(11)	−0.0638(3)	0.3136(6)	0.037(2)
O(5)	−0.1906(10)	0.2949(3)	0.5131(6)	0.033(2)
O(6)	−0.1344(11)	0.3410(3)	0.4031(6)	0.034(2)
O(7)	0.1968(10)	0.3299(3)	0.4294(6)	0.031(2)
O(8)	0.1420(10)	0.3358(3)	0.2850(5)	0.026(2)
C(1)	0.0295(12)	0.0285(4)	0.2322(8)	0.018(3)
C(2)	0.0280(14)	−0.0080(4)	0.1619(8)	0.022(3)
C(3)	−0.108(2)	−0.0501(5)	0.0540(8)	0.040(4)
C(4)	0.0603(12)	0.0165(4)	0.3165(7)	0.011(2)
C(5)	0.0756(14)	−0.0345(4)	0.3355(7)	0.019(3)
C(6)	0.227(2)	−0.0929(4)	0.3991(9)	0.033(3)
C(7)	−0.0566(12)	0.2606(4)	0.4010(7)	0.014(2)
C(8)	−0.1325(12)	0.3033(4)	0.4346(8)	0.018(3)
C(9)	−0.263(2)	0.3334(5)	0.5533(10)	0.049(4)
C(10)	0.0726(13)	0.2669(4)	0.3621(7)	0.016(3)
C(11)	0.1378(13)	0.3149(4)	0.3542(8)	0.018(3)
C(12)	0.264(2)	0.3757(5)	0.4267(9)	0.040(4)

$[NEt_4][Au(Te_2C_2(COOCH_3)_2)_2]$ (6). The NEt_4^+ cation is disordered, with atom N(1) residing on an inversion center at full occupancy and with the remaining atoms at half-occupancy. The anion has a crystallographically imposed center of symmetry. The final cycle of least-squares refinement (144 variables, 3242 observations) converged to an agreement index $R(F)$ of 0.050 for those 2297 reflections having $F_o^2 > 2\sigma(F_o^2)$. Only the heavy atoms were refined anisotropically. Heavy-atom coordinates and equivalent isotropic displacement parameters are given in Table 7. Complete atomic coordinates, anisotropic displacement parameters, H atom parameters, and all bond lengths and angles are given in Tables S8, S14, S20, and S26.[34]

Table 7. Atom Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for the Anion of $[NEt_4][Au(Te_2C_2(COOCH_3)_2)_2]$ (**6**)

atom	*x*	*y*	*z*	U_{eq}
Au(1)	0	1	$^1/_2$	0.0158(2)
Te(1)	−0.30921(10)	0.88335(6)	0.48087(4)	0.0209(2)
Te(2)	0.14555(10)	0.90215(6)	0.38384(4)	0.0190(2)
O(1)	−0.4527(12)	0.7463(7)	0.2772(5)	0.031(2)
O(2)	−0.4852(11)	0.6580(7)	0.3884(5)	0.032(2)
O(3)	−0.1003(11)	0.6439(6)	0.2700(4)	0.027(2)
O(4)	−0.0037(12)	0.8020(7)	0.2138(5)	0.034(2)
C(1)	−0.2487(13)	0.8012(8)	0.3791(6)	0.014(2)
C(2)	−0.4065(14)	0.7265(9)	0.3505(6)	0.018(2)
C(3)	−0.581(2)	0.6643(11)	0.2422(8)	0.039(3)
C(4)	−0.0899(14)	0.8099(8)	0.3426(6)	0.016(2)
C(5)	−0.059(2)	0.7539(9)	0.2680(6)	0.019(2)
C(6)	−0.094(2)	0.5842(11)	0.1973(8)	0.042(3)

Scheme 1. Syntheses for the Various $[MTe_7]^{n-}$ Anions



a) $7\ \text{"}Li_2Te_3\text{"} + 2\ Na + [Ag(PMe_3)I]_4 + 7\ PEt_3 \xrightarrow[\text{DMF, 25°C}]{NEt_4^+,\ PPh_4^+} [NEt_4][PPh_4]_2[AgTe_7]$ (1)

b) $6\ \text{"}Li_2Te_3\text{"} + 2\ Hg(xan)_2 + 7\ PEt_3 \xrightarrow[\text{DMF, 90°C}]{PPh_4^+} [PPh_4]_2[HgTe_7]$ (2)

c) $3.5\ \text{"}Li_2Te_3\text{"} + 2\ AuCN + 7\ PEt_3 \xrightarrow[\text{DMF, 90°C}]{NEt_4^+} [NEt_4]_3[AuTe_7]$ (4)

d) $2\ \text{"}Li_2Te_4\text{"} + HgCl_2 \xrightarrow[\text{DMF, 25°C}]{NEt_4^+} [NEt_4]_2[HgTe_7]$ (3)

e) $3\ \text{"}K_2Te_3\text{"} + 2\ Zn(OAc)_2 \xrightarrow[\text{DMF, 0°C}]{\text{15-Crown-5}} [K(\text{15-Crown-5})]_2[ZnTe_7]$

f) $3\ \text{"}K_2Te_3\text{"} + 2\ Hg(OAc)_2 \xrightarrow[\text{DMF, -50°C}]{\text{15-Crown-5}} [K(\text{15-Crown-5})]_2[HgTe_7]$

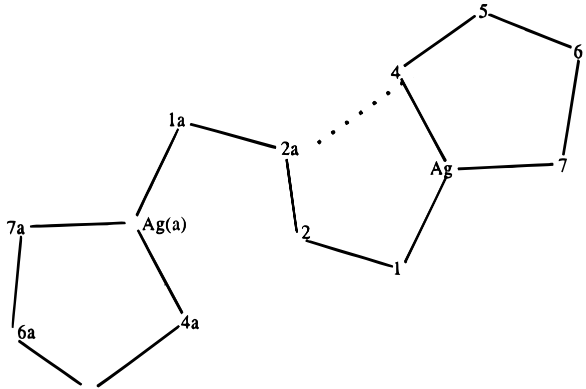
Results and Discussion

Synthesis. Preparation of tellurometalates has proven to be very challenging because of their sensitivity to air and moisture and because of their low solubility in most organic solvents. Several measures were taken to meet and overcome this challenge. Careful Schlenk and drybox techniques exclude nearly all air and moisture, and a small amount of PEt_3 added to the reaction mixtures reacts with any remaining traces. The solubility of the tellurometalate products is fair in highly polar organic solvents and is improved by the use of appropriate quaternary ammonium and phosphonium countercations.[14] Whereas Haushalter has used ethylenediamine to extract telluroaurates and telluromercurates from solid-state materials,[35,36] we have used polytelluride solutions containing BH_4^- [37] or PEt_3 to produce tellurometalates by reaction with soluble metal salts. Three of the anions discussed here, $[AgTe_7]^{3-}$, $[HgTe_7]^{2-}$ (PPh_4^+ salt), and $[AuTe_7]^{3-}$, were synthesized by reacting suitable metal precursors with excess neat PEt_3, followed by addition of polytelluride in DMF at or above room temperature (Scheme 1a−c). The NEt_4^+ salt of $[HgTe_7]^{2-}$ was prepared in the same way except without PEt_3 (Scheme 1d). The $[K(\text{15-Crown-5})_2]_2[MTe_7]$ (M = Zn, Hg) compounds were also synthesized without addition of base by reaction of polytelluride with zinc or mercury salts in DMF at low temperatures.[38] (Scheme 1e,f).

$[PPh_4]_2[Hg(Te_4)_2]$ was previously synthesized as a mixture with $[PPh_4]_2[HgTe_7]$ by the reaction of polytelluride with $Hg(xan)_2$ or $HgCl_2$ in DMF with or without the addition of PEt_3.[28] Interestingly, under the same conditions but with a change of cation, we isolate pure $[NEt_4]_2[HgTe_7]$ (**3**), as judged by a satisfactory chemical analysis and by an X-ray powder pattern. ^{125}Te NMR spectroscopy suggests $[PPh_4]_2[HgTe_7]$ (**2**) and $[NEt_4]_2[HgTe_7]$ (**3**) do not retain their solid-state structure in solution. Three unique ^{125}Te resonances would be expected for the $[HgTe_7]^{2-}$ anion. However, within the +4000 to −3000 ppm region, only two resonances appear in the ^{125}Te NMR spectra of both compounds at 208 ppm (J_{Te-Te} 1263 Hz) and −386 ppm (J_{Hg-Te} 3696 Hz; J_{Te-Te} 1293 Hz). These correspond to the resonances for $[PPh_4]_2[Hg(Te_4)_2]$.[28]

The compounds $[PPh_4]_2[NEt_4][AgTe_7]$ (**1**), $[PPh_4]_2[HgTe_7]$ (**2**), and $[NEt_4]_3[AuTe_7]$ (**4**) may form via initial coordination of PEt_3 to the metal to form intermediates that then react with polytelluride to yield the final products. In general, phosphines are not good leaving groups, but the opposite appears to be true for late-transition-metal complexes in the presence of selenides.[39,40] We used $Hg(xan)_2$ as a Hg^{II} source in the synthesis of $[PPh_4]_2[HgTe_7]$ (**2**) because xanthate is known to be a good leaving group,[41,42] but we used $HgCl_2$ in the preparation of $[NEt_4]_2[HgTe_7]$ (**3**) because it gave a cleaner reaction. The acetate group is shown to be an effective leaving group in the syntheses of $[K(\text{15-Crown-5})_2]_2[MTe_7]$ (M = Zn, Hg).[38]

Cation dependence does not appear to be relevant in the mercury system; the $[HgTe_7]^{2-}$ anion has been isolated as three different salts. However, cation size has been demonstrated to affect profoundly the nature of the isolable products in the Ag/Se system,[15] and such effects might be expected to extend to the Cu/Te, Ag/Te, and Au/Te systems as well. Indeed, Au forms $[Au_2Te_4]^{2-}$ with the PPN^+,[35] PPh_4^+,[29] or NPr_4^+ [43] cations, but it forms $[AuTe_7]^{3-}$ with the smaller and more soluble NEt_4^+ cation. Likewise, the compound $[NEt_4]_4[Ag_2Te_{12}]$ was obtained under conditions similar to those that led to $[AgTe_7]^{3-}$, except for the omission of PPh_4Br and Na.[23] Formation of $[AgTe_7]^{3-}$ when PPh_4^+ and NEt_4^+ are used together is probably a solubility effect, but it may also be the result of the Na metal in the reaction mixture. Conceptually, the $[AgTe_7]^{3-}$ anion can arise from the fragmentation of $[Ag_2Te_{12}]^{4-}$ by the formation of a bond between two weakly interacting Te atoms, Te(4) and Te(2a), separated by only 3.456(4) Å, with concomitant loss of an "$[AgTe_5]^{n-}$" fragment. A reasonable pathway would involve



$[Ag_2Te_{12}]^{4-}$

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Table 8. Selected Bond Distances (Å) and Angles (deg) for the $[MTe_7]^{3-}$ and $[M_2Te_{12}]^{4-}$ (M = Au, Ag) Anions

bond/angle	$[AuTe_7]^{3-}$ (**4**)	$[Au_2Te_{12}]^{4-}$ [a]	bond/angle	$[AgTe_7]^{3-}$ (**1**)	$[Ag_2Te_{12}]^{4-}$ [b]
M−Te(1)	2.664(2)	2.650(4)	M−Te(1)	2.702(2)	2.680(1)
M−Te(3)	2.638(2)	2.625(4)	M−Te(4)	2.725(2)	2.710(1)
M−Te(5)	2.651(2)	2.661(4)	M−Te(7)	2.695(2)	2.709(1)
M−Te(6)	2.647(2)	2.629(4)	Te(1)−Te(2)	2.756(2)	2.731(1)
Te(1)−Te(2)	2.809(2)	2.745(5)	Te(2)−Te(3)	2.714(2)	2.735(1)
Te(2)−Te(3)	2.927(2)	2.982(5)	Te(3)−Te(4)	3.230(2)	3.456(4)
Te(3)−Te(4)	3.120(2)	3.044(5)	Te(4)−Te(5)	2.866(2)	2.774(1)
Te(4)−Te(5)	2.702(2)	2.741(5)	Te(5)−Te(6)	2.720(2)	2.730(1)
Te(6)−Te(7)	2.719(2)	2.748(7)	Te(6)−Te(7)	2.721(2)	2.732(1)
Te(7)−Te(1)	3.374(2)				
Te(1)−M−Te(3)	89.56(4)	90.2(1)	Te(1)−M−Te(4)	124.48(6)	126.25(3)
Te(1)−M−Te(5)	177.75(2)	177.1(1)	Te(1)−M−Te(7)	119.45(6)	117.89(3)
Te(1)−M−Te(6)	92.70(4)	97.6(1)	Te(4)−M−Te(7)	116.07(6)	115.86(3)
Te(3)−M−Te(5)	89.25(4)	88.5(1)	M−Te(1)−Te(2)	99.48(5)	99.23(3)
Te(3)−M−Te(6)	176.16(3)	170.7(1)	M−Te(4)−Te(3)	89.41(5)	
Te(5)−M−Te(6)	88.59(4)	84.0(1)	M−Te(4)−Te(5)	95.52(5)	97.19(3)
M−Te(1)−Te(2)	95.47(4)	96.6(1)	M−Te(7)−Te(6)	96.89(6)	99.41(3)
M−Te(3)−Te(2)	93.30(4)	91.7(1)	Te(1)−Te(2)−Te(3)	105.21(5)	97.72(3)
M−Te(3)−Te(4)	90.36(4)	92.0(1)	Te(2)−Te(3)−Te(4)	106.69(5)	
M−Te(5)−Te(4)	99.90(5)	98.4(1)	Te(3)−Te(4)−Te(5)	174.12(5)	
M−Te(6)−Te(7)	102.84(5)	103.1(2)	Te(4)−Te(5)−Te(6)	102.15(5)	104.76(3)
Te(1)−Te(2)−Te(3)	81.22(4)	81.3(1)	Te(5)−Te(6)−Te(7)	101.84(5)	104.60(3)
Te(2)−Te(3)−Te(4)	175.85(3)	173.8(2)			
Te(3)−Te(4)−Te(5)	78.94(4)	79.0(1)			

[a] Reference 53. The atoms are renumbered to facilitate direct comparison. Te(1) is now Te(6), Te(2) is Te(1), Te(3) is Te(2), Te(4) is Te(3), Te(5) is Te(4), Te(6) is Te(5), and Te(1a) is Te(7). [b] Reference 23. Te(3) is Te(2a). Te(1) is now Te(7), Te(2) is Te(6), Te(3) is Te(5), Te(5) is Te(1), and Te(6) is Te(2).

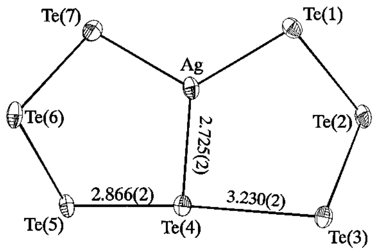

Figure 1. View of the $[AgTe_7]^{3-}$ anion. In this and succeeding figures the 50% probability displacement ellipsoids are shown. Distances are given in angstroms.

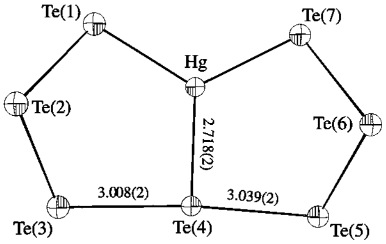

Figure 2. View of the anion in $[NEt_4]_2[HgTe_7]$.

reduction by Na of the Te(1a)−Te(2a) bond. Metrical features of $[AgTe_7]^{3-}$ and of the appropriate fragment of $[Ag_2Te_{12}]^{4-}$ bear a remarkable resemblance to each other (Table 8). However, our attempts to convert $[Ag_2Te_{12}]^{4-}$ to $[AgTe_7]^{3-}$ with the use of reducing agents and to crystallize $[AgTe_7]^{3-}$ with other cations have not been successful.

Reactions of crystals of $[NEt_4]_2[HgTe_7]$ (**3**) and $[NEt_4]_3[AuTe_7]$ (**4**) with DMAD afford the compounds $[NEt_4]_2[Hg(Te_2C_2(COOCH_3)_2)_2]$ (**5**) and $[NEt_4][Au(Te_2C_2(COOCH_3)_2)_2]$ (**6**), respectively. The most likely mechanism proposed for the reaction of the activated acetylenes with MQ_4 rings involves as a rate-determining step an associative nucleophilic attack of the metal-bound chalcogen on the acetylene.[44,45] The ^{125}Te NMR data discussed above suggest that in solution the $[HgTe_7]^{2-}$ anion is in equilibrium with $[Hg(Te_4)_2]^{2-}$. The formation of $[NEt_4]_2[Hg(Te_2C_2(COOCH_3)_2)_2]$ (**5**) strengthens this suggestion. The reaction of $[Hg(Te_4)_2]^{2-}$ with DMAD could easily follow the proposed mechanism for the other MQ_4 rings whereas the formation of **5** from $[NEt_4]_2[HgTe_7]$ (**3**) would require considerable bond cleavage and bond formation. The formation of $[NEt_4][Au(Te_2C_2(COOCH_3)_2)_2]$ (**6**) would require the cleavage of the MQ_3 ring and two Te−Te bonds. Since the $AuTe_4$ core essentially remains intact with similar bond angles and distances for $[NEt_4]_3[AuTe_7]$ (**4**) and $[NEt_4][Au(Te_2C_2(COOCH_3)_2)_2]$ (**6**), the reaction also most likely follows the proposed mechanism.

Structural Characterization. The tellurometalates reported here do not exhibit characteristic infrared or ultraviolet spectra. As mentioned previously, only for $[NEt_4]_2[Hg(Te_2C_2(COOCH_3)_2)_2]$ (**5**) were we successful in obtaining a characteristic ^{125}Te NMR spectrum. Consequently, characterization is mainly restricted to chemical analyses and solid-state structures as established by single-crystal X-ray diffraction techniques.

The structure of $[PPh_4]_2[NEt_4][AgTe_7]$ consists of well-separated cations and anions. The $[AgTe_7]^{3-}$ anion (Figure 1) features an Ag^{I} center coordinated in a trigonal-planar fashion to the central and the two terminal atoms of a Te_7^{4-} moiety. Except for atoms Te(2) and Te(6), the anion is planar, the average deviation from the least-squares plane being 0.108 Å. The Te(3), Te(4), and Te(5) atoms are nearly collinear, the angle around Te(4) being 174.12(5)°. The Te(3)−Te(4) distance of 3.230(2) Å is longer than a typical Te−Te bond, but it is significantly shorter than the van der Waals Te−Te interaction of 4 Å; the Te(4)−Te(5) distance is 2.866(2) Å. If the Te(3)−Te(4) interaction is not considered to be a bond, then the anion must be described as $[Ag(\eta^1\text{-}Te_3)(\eta^2\text{-}Te_4)]^{3-}$ and it would possess the unlikely η^1-Te_3^{2-} ligand. If the interaction is considered to be a bond, then atom Te(4) is coordinated in a "T"-like planar arrangement, consistent with its possessing a hypervalent 10 e$^-$ configuration. As we note below, the $[HgTe_7]^{2-}$ ion possesses a similar T-like arrangement, but in

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Table 9. Selected Bond Distances (Å) and Angles (deg) for $[MTe_7]^{n-}$ (M = Ag, *n* = 3; M = Hg, Zn, *n* = 2)

	$[PPh_4]_2[NEt_4][AgTe_7]^a$ (**1**)	$[PPh_4]_2[HgTe_7]^a$ (**2**)	$[NEt_4]_2[HgTe_7]^a$ (**3**)	$[K(15\text{-Crown-}5)_2]_2$-$[HgTe_7]^{b,c}$	$[K(15\text{-Crown-}5)_2]_2$-$[ZnTe_7]^{b,d}$
M−Te(1)	2.702(2)	2.730(2)	2.715(2)	2.710(3)	2.542(2)
M−Te(4)	2.725(2)	2.742(1)	2.718(2)	2.681(3)	2.518(3)
M−Te(7)	2.695(2)	2.722(2)	2.719(2)	2.681(3)	2.518(3)
Te(1)−Te(2)	2.756(2)	2.746(2)	2.754(2)	2.588(5)	2.811(7)
Te(2)−Te(3)	2.714(2)	2.716(2)	2.713(2)	2.657(9)	2.688(3)
Te(3)−Te(4)	3.230(2)	2.997(2)	3.008(2)	3.258(8)	3.253(3)
Te(4)−Te(5)	2.866(2)	3.050(2)	3.039(2)	2.962(4)	2.931(3)
Te(5)−Te(6)[e]	2.720(2)	2.682(2)	2.721(2)	2.666(3)	2.684(4)
Te(6)−Te(7)	2.721(2)	2.727(2)	2.742(2)	2.962(4)	2.931(3)
Te(1)−M−Te(4)	124.48(6)	117.70(5)	118.32(5)	117.8(1)	124.7(2)
Te(1)−M−Te(7)	119.45(6)	124.37(5)	121.93(4)	117.8(1)	124.7(2)
Te(4)−M−Te(7)	116.07(6)	117.92(4)	119.74(5)	124.3(1)	128.8(2)
M−Te(1)−Te(2)	99.48(5)	95.97(5)	94.65(5)	101.9(1)	89.4(2)
M−Te(4)−Te(3)	89.41(5)	92.75(4)	93.43(5)	90.3(1)	80.4(2)
M−Te(4)−Te(5)	95.52(5)	90.53(6)	92.34(5)	96.4(1)	95.6(1)
M−Te(7)−Te(6)	96.89(6)	96.72(4)	96.71(5)	96.4(1)	95.6(1)
Te(1)−Te(2)−Te(3)	105.21(5)	100.83(4)	101.59(5)	101.7(3)	106.8(2)
Te(2)−Te(3)−Te(4)	106.69(5)	101.66(5)	100.47(5)	101.9(1)	98.9(1)
Te(3)−Te(4)−Te(5)	174.12(5)	174.52(5)	170.40(5)	173.3(2)	175.1(1)
Te(4)−Te(5)−Te(6)	102.15(5)	102.04(5)	104.57(5)	109.2(1)	106.4(1)
Te(5)−Te(6)−Te(7)	101.84(5)	102.50(5)	101.91(6)	109.2(1)	106.4(1)

[a] This work. [b] Reference 38. [c] To facilitate comparisons, the original atom-numbering scheme[38] has been changed. The original Te(2) is now Te(3), Te(3) is Te(4), Te(4) is Te(5), Te(4a) is Te(6), Te(3a) is Te(7), and Te(5) is Te(2). [d] The original numbering scheme[38] has been changed. Te(3) is now Te(7), Te(4) is Te(6), Te(2b) is Te(3), Te(3a) is Te(4), and Te(4a) is Te(5). [e] For Compound **2**, Te(6) is the symmetry equivalent of Te(2) according to the operation −*x*, 1 −*y* 1 − *z*.

this instance the two Te−Te bonds are the same length. Such unsymmetric and symmetric hypervalent configurations are found in trihalide systems, particularly in the I_3^- anion.[46] Thus, in CsI_3[47] the linear I_3^- anion is unsymmetric (I−I = 2.83(1) and 3.03(1) Å) whereas in $[AsPh_4]I_3$[48] it is symmetric (I−I = 2.90(2) Å).

The $[HgTe_7]^{2-}$ anions in the structures of $[PPh_4]_2[HgTe_7]$ (**2**), $[NEt_4]_2[HgTe_7]$ (**3**) (Figure 2), and $[K(15\text{-Crown-}5)]_2[HgTe_7]$[38] resemble the $[AgTe_7]^{3-}$ anion (Figure 1) and are also well separated from the cations. However, only in **3** is the anion ordered. Also known is the related $[ZnTe_7]^{2-}$ ion, which has been isolated as the [K(15-Crown-5)] salt.[38] But the average structure of $[ZnTe_7]^{2-}$, which also exhibits two-dimensional disorder, is apparently different and is described as consisting of a Zn^{2+} cation coordinated in a bidentate manner to a Te_4^{2-} anion and in a monodentate manner to a Te_3^{2-} anion. Table 9 compares selected bond distances for the $[MTe_7]^{n-}$ (M = Ag, Hg, Zn) anions. Similar to the Ag^I center in $[AgTe_7]^{3-}$, the Hg^{II} center in $[HgTe_7]^{2-}$ is also coordinated in a trigonal planar fashion. The Te(4) atoms in these structures are again bonded in a T-like arrangement, and the Te(3)−Te(4) and Te(4)−Te(5) distances are 2.997(2) and 3.050(2) Å for $[PPh_4]_2[HgTe_7]$ (**2**), 3.008(2) and 3.039(2) Å for $[NEt_4]_2[HgTe_7]$ (**3**), and 2.962(4) and 3.258(8) Å for $[K(15\text{-Crown-}5)]_2[HgTe_7]$. Note that some of the differences exhibited in Table 9 may be the result of disorder in some of the structures. It is interesting that although both five-membered rings in $[PPh_4]_2[HgTe_7]$ (**2**) and $[NEt_4]_2[HgTe_7]$ (**3**) have an envelope conformation, the flaps are located on opposite sides of the MTe_5 plane in **2** and on the same side in **3**.

The $[AuTe_7]^{3-}$ anion of **4** (Figure 3) consists of a square-planar Au^{III} center coordinated by an η^3-Te_5^{4-} ligand and an η^1-Te_2^{2-} ligand.[49] The overall 3− charge of the $[AuTe_7]^{3-}$ anion is required by the presence of three NEt_4^+ cations per anion in the unit cell. The oxidation state Au^{III} is firmly established by three independent properties: square-planar geometry about the Au atom, the ^{197}Au Mössbauer spectrum, and the Au−Te distances. Square-planar Au^I is unknown, and square-planar Au^{II} is very uncommon. The ^{197}Au Mössbauer spectrum shows an isomer shift of +1.86 mm/s (referenced to the source of gold in platinum metal) and a quadrupole splitting of 2.92 mm/s; these data compare favorably with those found for other square-planar Au^{III} tellurides, such as $AuTe_2$ (1.97, 2.43 mm/s) and $AuAgTe_4$ (1.71, 2.64 mm/s).[50,51] The Au−Te distances, ranging from 2.638(2) to 2.664(2) Å, are comparable to those in Au^{III} compounds such as AuTeI (2.642(1)−2.684(1) Å)[52] and are longer than the range 2.543(2)−2.582(2) Å found in the Au^I anions $[Au_3Te_4]^{3-}$,[29] $[Au_2Te_4]^{2-}$,[35] and $[Au_4Te_4]^{4-}$.[36] In the $[AuTe_7]^{3-}$ anion the geometry about the central atom of the η^3-Te_5^{4-} ligand (Te(3)) is again T-like and the Te(2)−Te(3) and Te(3)−Te(4) distances are 2.927(2) and 3.120(2) Å (Table 8). The $[Au_2Te_{12}]^{4-}$ anion in $[NEt_4]_4[Au_2Te_{12}]$ also contains

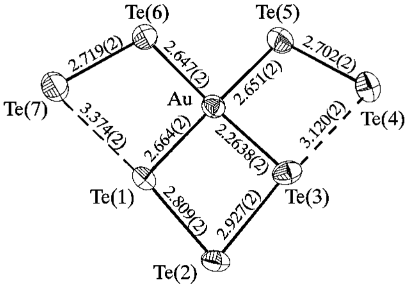

Figure 3. View of the $[AuTe_7]^{3-}$ anion.

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(49) An alternative description of $[AuTe_7]^{3-}$ suggested by a reviewer is that of a square-planar Au^{III} center coordinated by a η^4-Te_7^{6-} ligand. The Te(1)···Te(7) interaction of 3.374(2) Å is considered to be a bond and each of the two T-shaped atoms, Te(1) and Te(3), possesses a trigonal-bipyramidal electron-pair arrangement via the VSEPR model.

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Table 10. Average Bond Distances (Å) and Angles (deg) for $M(Q_2C_2)$ Rings in Selected Ditellurolene (Q = Te) and Diselenolene (Q = Se) Compounds

	Hg[a] (**5**)	Au[a] (**6**)	Mo[b]	W[c]	W_2[d]	Fe_2[e]
C═C	1.35(1)	1.328(13)	1.317(10)	1.339(25)	1.340(8)	1.342(6)
$C-COOCH_3$	1.50(1)	1.497(10)	1.480(20)	1.491(21)	1.489(20)	1.491(6)
C═O	1.210(7)	1.196(9)	1.202(9)	1.198(17)	1.199(8)	1.201(5)
$C-OCH_3$	1.332(7)	1.334(9)	1.310(15)	1.348(19)	1.332(15)	1.324(5)
$O-CH_3$	1.441(8)	1.455(10)	1.444(7)	1.440(19)	1.453(8)	1.453(9)
C═C−C	118.7(5)	122.5(7)	123.3(10)	122.2(15)	122.2(16)	123.5(14)
C−C═O	124.2(6)	124.3(7)	124.5(13)	124.6(16)	123.7(10)	124.6(8)
$C-C-OCH_3$	112.4(5)	111.7(6)	113.2(9)	112.5(13)	111.8(9)	112.6(11)
$O-C-OCH_3$	123.3(6)	123.9(7)	122.3(13)	122.8(19)	124.5(17)	122.8(9)
$C-O-CH_3$	115.8(5)	115.1(7)	117.1(14)	115.3(14)	114.5(6)	116.4(9)
M−Q−C	95.03(15)	99.1(2)	103.2(8)	107.8(6)	107.6(10)	105.2(7)

[a] $[Hg(Te_2C_2R_2)_2]^{2-}$ and $[Au(Te_2C_2R_2)_2]^{2-}$; this work. [b] $[MoO(Te_2C_2(COOCH_3)_2)_3]^{2-}$; ref 60. [c] $[W(Se_2C_2(COOCH_3)_2)_3]^{2-}$; ref 58. [d] $[W_2Se_2(Se_2C_2(COOCH_3)_2)_4]^{2-}$; ref 58. [e] $[Fe_2(S_2C_2(COOCH_3)_2)_4]^{2-}$; ref 59.

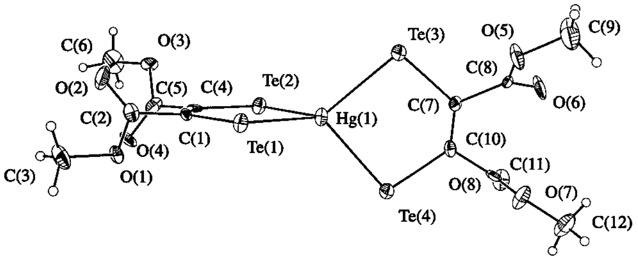

Figure 4. View of the $[Hg(Te_2C_2(COOCH_3)_2)_2]^{2-}$ anion.

square-planar Au^{III} centers coordinated by η^3-Te_5^{4-} ligands; two such $AuTe_5^-$ fragments are linked by a Te_2^{2-} chain.[53] The conformation of the present η^3-Te_5^{4-} ligand in $[NEt_4]_3[AuTe_7]$ (**4**) is planar whereas in $[Au_2Te_{12}]^{4-}$ it is puckered to provide a distorted envelope conformation. The metrical features (Table 8), however, are very similar.

The most intriguing structural feature of these anions is the presence of η^3-Te_7^{4-} or η^3-Te_5^{4-} anions, both previously unknown in the chalcogenometalates. The sulfur ligands in the compounds $[M(S_7)(PMe_3)_3]$ (M = Ru, Os)[54] are most convincingly formulated as η^3-S_7^{2-}, as these compounds are diamagnetic, expected for a d^6-metal configuration (S_7^{2-} ligand) but unexpected for a d^4-metal configuration (S_7^{4-} ligand). The three-coordinate S atom is not T-shaped but exhibits normal bond angles and lengths. Comparisons with halogens suggest the increased size and polarizability and decreased p-to-d promotional energy in Te versus S may account for such bonding differences. The VSEPR model would describe the orbitals around the central Te(4) atom as sp^3d hybridized, but this model is known to overestimate the d-orbital contributions to bonding. The molecular orbital approach of a three-centered four-electron bond around atom Te(4) may be preferable. Application of delocalized orbitals to the isoelectronic species I_3^- and XeF_2 indicates p orbitals dominate the bonding with only minor contributions from s and d orbitals.[46,55] The bonding description with Te(4) being part of a three-centered four-electron system implies this atom is hypervalent and that it donates electrons to the metal center. The T-shaped portions of these anions are unsymmetrical in $[PPh_4]_2[NEt_4][AgTe_7]$ (**1**) and $[NEt_4]_3[AuTe_7]$ (**4**) but symmetrical in $[PPh_4]_2[HgTe_7]$ (**2**) and $[NEt_4]_2[HgTe_7]$ (**3**). The unsymmetrical bonds in the I_3^- system may originate from the effect on the anion of the unsymmetrical field of the surrounding cations. Hückel MO calculations show that an unsymmetrical perturbation of the symmetrical ion would cause qualitative changes in bond orders in directions consistent with the observed changes in bond lengths.[46,55] Clearly, a theoretical study of these unusual chalcogenometalates is badly needed.

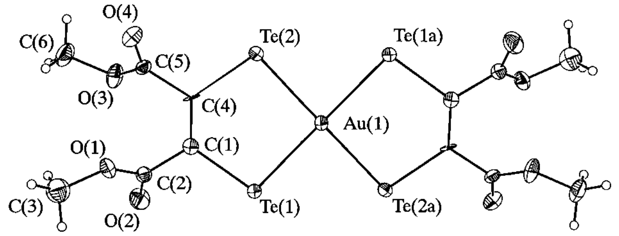

Figure 5. View of the $[Au(Te_2C_2(COOCH_3)_2)_2]^-$ anion.

Table 11. Bond Distances (Å) and Angles (deg) for $[M(Te_2C_2(COOCH_3)_2)_2]^{n-}$ (M = Hg, Au, MoO) Species

	Hg (**5**)	Au (**6**)[a]	MoO[b]
M−Te(1)	2.788(1)	2.608(1)	2.686(1)
M−Te(2)	2.759(1)	2.599(1)	2.682(1)
M−Te(3)	2.745(1)	2.600(1)	2.678(1)
M−Te(4)	2.795(1)	2.608(1)	2.681(1)
Te(1)−C(1)	2.105(12)	2.105(10)	2.142(7)
Te(2)−C(4)	2.090(10)	2.096(10)	2.154(8)
Te(3)−C(7)	2.107(11)	2.096(10)	2.164(7)
Te(4)−C(10)	2.100(11)	2.105(10)	2.122(8)
M−Te(1)−C(1)	94.9(3)	98.7(3)	102.5(2)
M−Te(2)−C(4)	96.1(3)	99.4(3)	103.0(2)
M−Te(3)−C(7)	95.0(3)	99.4(3)	103.1(2)
M−Te(4)−C(10)	94.1(3)	98.7(3)	104.3(2)
Te(1)−M−Te(2)	91.49(3)	91.54(3)	85.0(1)
Te(1)−M−Te(4)	107.56(3)	88.46(3)	83.4(1)
Te(2)−M−Te(3)	113.75(3)	88.46(3)	85.6(1)
Te(3)−M−Te(4)	92.39(3)	91.54(3)	85.0(1)

[a] Te(3) is Te(1a) and Te(4) is Te(2a). [b] $[MoO(Te_2C_2(COOCH_3)_2)_2]^{2-}$; ref 60. Atoms have been renumbered. Te(4) is now Te(3), Te(3) is Te(4), C(2) is C(4), C(5) is C(10), and C(6) is C(7).

The $[Hg(Te_2C_2(COOCH_3)_2)_2]^{2-}$ anion of **5** (Figure 4) consists of a Hg^{II} center in a distorted tetrahedral environment coordinated to two bidentate ditellurolene ligands. The $HgTe_2C_2$ rings are essentially planar, the mean deviations from the best least-squares planes being 0.039 and 0.004 Å, respectively. The Hg−Te distances range from 2.745(1) to 2.795(1) Å, slightly longer than the distances found in **2** or **3** but shorter than the average Hg−Te distance of 2.806(9) Å in $[PPh_4]_2[Hg(Te_4)_2]$.[28] The Te(1)−Hg−Te(2) and Te(3)−Hg−Te(4) angles are 92.39(3) and 91.49(3)°, respectively. Bond distances and angles for the ring system are comparable to those seen in other chalcogenide ring systems (Table 10).

The $[Au(Te_2C_2(COOCH_3)_2)_2]^-$ anion of **6** (Figure 5), which has a crystallographically imposed center of symmetry, consists of a square-planar Au^{III} center coordinated to two bidentate ditellurolene ligands. The Au−Te distances are 2.600(1) and

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2.608(1) Å, slightly shorter than those observed in the $[AuTe_7]^{3-}$ anion. The Te(1)−Au−Te(2) angle is 91.54(3)°. The $AuTe_2C_2$ five-membered ring is planar, with the mean deviation from the best least-squares plane being 0.053 Å.

Although it is well-known that sulfidometalates and selenometalates react with activated acetylenes to form coordinated dithiolenes and diselenolenes,[44,56−59] only one example of an analogous reaction with a tellurometalate, namely $[PPh_4]_2[MoOTe_8]$, is known.[60] The metal center in $[PPh_4]_2[MoO(Te_2C_2(COOCH_3)_2)_2]$ retains its coordination with some flattening of the metal ring. The C−Te bond lengths are similar to those seen in $[NEt_4]_2[Hg(Te_2C_2(COOCH_3)_2)_2]$ (**5**) and $[NEt_4][Au(Te_2C_2(COOCH_3)_2)_2]$ (**6**) (Table 11). Note the relative positions of the ester groups. For M = Mo, the two ester groups on the same ligand are cis to each other but trans to the two ester groups on the opposing ligand. In **5**, the ester groups on one ligand are trans to each other while cis on the other ligand; in **6**, they are trans to each other on both ligands. ^{125}Te NMR data for the Mo anion and **5** suggest that the esters are equivalent on the NMR time scale.

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Supporting Information Available: Crystallographic details (Tables S1 and S2), complete atomic coordinates (Tables S4−S9), anisotropic displacement parameters (Tables S10−S15), hydrogen atom parameters (Tables S16−S21), and complete bond lengths and angles (Tables S22−S26) for compounds **1**−**6** (40 pages). Ordering information is given on any current masthead page.

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