

# One-Dimensional Mercury Telluride Polymers: Synthesis and Structure of $(\text{Et}_4\text{N})_2\text{Hg}_2\text{Te}_4$ and $(\text{Me}_4\text{N})_4\text{Hg}_3\text{Te}_7(0.5\text{en})$

Sandeep S. Dhingra,<sup>§,†</sup> Christopher J. Warren,<sup>†,‡</sup> Robert C. Haushalter,<sup>\*,†</sup> and Andrew B. Bocarsly<sup>\*,‡</sup>

NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540, and  
Department of Chemistry, Princeton University, Princeton, New Jersey 08544

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Two new one-dimensional mercury telluride polymers have been synthesized and structurally characterized by single crystal X-ray diffraction. Treatment of an ethylenediamine (en) extract of an alloy of nominal composition  $\text{K}_2\text{Hg}_2\text{Te}_3$  with  $\text{Et}_4\text{NI}$  gives a 40% yield of  $(\text{Et}_4\text{N})_2\text{Hg}_2\text{Te}_4$  (**1**). Dark hexagonal plates of (**1**) crystallize in the monoclinic space group  $P2_1/a$  with  $a = 14.869(8)$ ,  $b = 12.263(4)$ ,  $c = 15.297.6(6)$  Å,  $\beta = 97.43(4)^\circ$ ,  $Z = 4$  and  $R(R_w) = 0.057(0.069)$ . The  $\text{Hg}_2\text{Te}_4^{2-}$  chains in (**1**) are built up from five-membered  $\{\text{Hg}_2\text{Te}_3\}$  rings with the trigonally planar coordinated Hg atoms in the 1 and 3 positions of the ring. These rings are bonded into strings by Te atoms. Mercury telluride  $(\text{Me}_4\text{N})_4\text{Hg}_3\text{Te}_7(0.5\text{en})$  (**2**) is prepared by the constant current cathodic dissolution of a  $\text{Hg}_2\text{Te}_3$  electrode into an en solution of  $\text{Me}_4\text{NI}$ . Flat, black needles of (**2**), crystallize in the triclinic space group  $P\bar{1}$  with  $a = 12.080(3)$ ,  $b = 17.261(7)$ ,  $c = 9.905(1)$  Å,  $\alpha = 94.22(3)^\circ$ ,  $\beta = 92.26(1)^\circ$ ,  $\gamma = 80.12(3)^\circ$ ,  $V = 2028.2(9)$  Å<sup>3</sup>,  $Z = 2$  and  $R(R_w) = 0.041(0.038)$ . Telluride **2** contains five-membered rings similar to those found in **1** with the exception that the five-membered rings are fused at a common tetrahedrally coordinated *spiro* Hg atom. These  $\text{Hg}_3\text{Te}_6$  moieties, with two Hg possessing approximately trigonal-planar coordination and one with tetrahedral coordination are connected into one-dimensional strands via additional single Te atom bridges.

## Introduction

Many binary chalcogenides of the coinage and post transition elements have been prepared, and most are known for their very low solubilities in aqueous solution. The solubility of these materials can be increased, particularly in the case of sulfur by the addition of sulfides<sup>1</sup> or polysulfides which generate soluble binary metal complexes. Polychalcogenide complexes of the heavier chalcogenides, especially tellurium, do not readily lend themselves to similar synthetic access because of the problems associated with handling polytellurides in aqueous solutions. However, certain primary amines and other polar organic solvents have been found to be particularly suitable solvents not only for polychalcogenides but also for other main-group clusters as well.<sup>2</sup>

In the system Hg–Te, the first polyanion discovered was  $(\text{K-crypt})_2\text{HgTe}_2(\text{en})^3$  which was characterized during the pioneering studies of Corbett and co-workers on main group polyanions. The telluride  $(\text{K-crypt})_2\text{HgTe}_2(\text{en})$  was prepared by the extraction of a material of nominal composition  $\text{KHgTe}$  with 2,2,2-crypt in ethylenediamine (en). The extracts were reported to be

yellow in color, indicating that the material extracted from this alloy contained no homoatomic Te–Te bonds which characteristically give rise to colored compounds and solutions. The  $\text{HgTe}_2^{2-}$  anion was found to be linear with an Hg–Te distance of 2.5890(8) Å.

Subsequently, we reported the synthesis and structural characterization of two polynuclear mercury tellurides, namely, tetrameric  $(\text{Bu}_4\text{N})_4\text{Hg}_4\text{Te}_{12}^{4-}$  and the one-dimensional (1-D) polymer  $(\text{Ph}_4\text{P})_2\text{Hg}_2\text{Te}_5^{4-}$ .<sup>4</sup> It is interesting to note that both  $\text{Hg}_4\text{Te}_{12}^{4-}$  and  $\text{Hg}_2\text{Te}_5^{2-}$  were prepared by the extraction of exactly the same alloy,  $\text{K}_2\text{Hg}_2\text{Te}_3$ , with only the cation used to treat the extract being different. This suggests that the species obtained from extracting  $\text{K}_2\text{Hg}_2\text{Te}_3$  must contain at least two interconvertible species. While several other mercury selenides and sulfides have been synthesized (and exist as both isolated anions and three-dimensional solids),<sup>5</sup> the only other mercury telluride anion known is the  $\text{HgTe}_2^{2-}$  anion.<sup>6</sup>

In this paper we report the synthesis and single-crystal X-ray structure determinations of the two novel 1-D mercury tellurides  $(\text{Et}_4\text{N})_2\text{Hg}_2\text{Te}_4$  (**1**) and  $(\text{Me}_4\text{N})_4\text{Hg}_3\text{Te}_7(0.5\text{en})$  (**2**). Telluride **1** was synthesized by extraction of a ternary K–Hg–Te alloy, while **2** was electrochemically synthesized from an electrode of composition  $\text{Hg}_2\text{Te}_3$ .

<sup>§</sup> Current address: Mobil Research and Development Corp., Central Research Division, PO Box 1025, Princeton, NJ 08540.

<sup>†</sup> NEC Research Institute.

<sup>‡</sup> Princeton University.

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**Table 1. Crystallographic Data for (Et<sub>4</sub>N)<sub>2</sub>[Hg<sub>2</sub>Te<sub>4</sub>] and (Me<sub>4</sub>N)<sub>4</sub>[Hg<sub>3</sub>Te<sub>7</sub>](0.5en)<sup>a</sup>**

compound	(Et <sub>4</sub> N) <sub>2</sub> [Hg <sub>2</sub> Te <sub>4</sub> ]	(Me <sub>4</sub> N) <sub>4</sub> [Hg <sub>3</sub> Te <sub>7</sub> ](0.5en)
formula	H <sub>40</sub> C <sub>16</sub> N <sub>2</sub> Hg <sub>2</sub> Te <sub>4</sub>	H <sub>52</sub> C <sub>17</sub> N <sub>5</sub> Hg <sub>3</sub> Te <sub>7</sub>
FW	1172.09	1821.60
crystal color, habit	Deep Red, Plate	Black, Plate
<i>a</i> (Å)	14.869(8)	12.080(3)
<i>b</i> (Å)	12.263(4)	17.261(7)
<i>c</i> (Å)	15.297(6)	9.905(1)
$\alpha$ (deg)	90.00	94.22(3)
$\beta$ (deg)	97.43(4)	92.26(1)
$\gamma$ (deg)	90.00	80.12(3)
<i>V</i> (Å <sup>3</sup> )	2765(1)	2028.2(9)
<i>Z</i>	4	2
space group	<i>P</i> 2 <sub>1</sub> / <i>a</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.815	2.982
$\mu$ (cm <sup>-1</sup> )	152.58	163.06
crystal size (mm)	0.025 × 0.01 × 0.025	0.110 × 0.025 × 0.010
2 $\theta$ <sub>max</sub> (deg)	40	50
no. of data collected	3119	6263
data <i>I</i> ≥ 3 $\sigma$ ( <i>I</i> )	1132	2353
no. of variables	127	199
final <i>R/R</i> <sub>w</sub>	0.057/0.069	0.041/0.038

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

**Table 2. Fractional Atomic Coordinates and *B*(eq) Values for (Et<sub>4</sub>N)<sub>2</sub>[Hg<sub>2</sub>Te<sub>4</sub>] with Their Standard Deviations in Parentheses<sup>a</sup>**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq)
Hg(1)	0.7686(2)	0.1789(2)	0.2547(1)	6.2(2)
Hg(2)	0.9940(2)	0.3654(2)	0.2558(2)	6.1(2)
Te(1)	0.6478(3)	0.0164(3)	0.2755(3)	6.0(3)
Te(2)	0.6957(3)	0.3791(4)	0.2013(3)	6.7(3)
Te(3)	0.8507(3)	0.4957(4)	0.1802(3)	7.0(3)
Te(4)	0.9510(3)	0.1593(4)	0.2922(3)	7.0(3)
N(1)	0.415(4)	0.267(5)	-0.057(3)	8(1)
N(2)	0.670(4)	0.234(5)	0.553(4)	9(1)
C(1)	0.403(4)	0.310(5)	0.036(3)	7(1)
C(2)	0.343(5)	0.409(6)	0.025(4)	10(2)
C(3)	0.467(4)	0.161(5)	-0.044(4)	7(2)
C(4)	0.561(5)	0.161(5)	0.006(4)	8(2)
C(5)	0.328(5)	0.247(6)	-0.116(4)	10(2)
C(6)	0.263(5)	0.177(6)	-0.071(4)	9(2)
C(7)	0.462(4)	0.350(5)	-0.100(4)	7(1)
C(8)	0.502(4)	0.314(6)	-0.192(4)	9(2)
C(9)	0.717(5)	0.274(5)	-0.470(4)	8(2)
C(10)	0.802(5)	0.331(6)	0.490(4)	10(2)
C(11)	0.654(5)	0.347(6)	0.603(4)	10(2)
C(12)	0.582(7)	0.405(8)	0.556(6)	14(2)
C(13)	0.584(6)	0.167(7)	0.520(5)	11(2)
C(14)	0.538(9)	0.12(1)	0.575(8)	23(1)
C(15)	0.747(5)	0.177(6)	0.620(4)	10(2)
C(16)	0.79(1)	0.10(1)	0.58(1)	29(1)

$$^a B(\text{eq}) = \frac{8}{3}\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha].$$

## Experimental Section

**General Techniques.** All reactions and manipulations were performed with the careful exclusion of the atmosphere. The en was purified first by distillation from CaH<sub>2</sub> and then from a red solution of K<sub>2</sub>Sn<sub>3</sub>, both under N<sub>2</sub>.

**X-ray Crystallography.** The data for the structures were collected at 20 °C on a Rigaku AFC7R diffractometer equipped with a RU300 18 kW rotating anode source using  $\omega$ -2 $\theta$  scans. The data was solved and the structures refined with the *teXsan* software package from Molecular Structure Corp. The crystallographic data for **1** and **2** are given in Table 1, the fractional coordinates and isotropic temperature factors for the structures are given in Tables 2 and 3, and some selected bond distances and angles given in Tables 4 and 5.

**Synthesis.** *K<sub>2</sub>Hg<sub>2</sub>Te<sub>3</sub>*. This friable, black glassy material was prepared by gently heating a mixture of 1 g of K<sub>2</sub>Te, 1.95 g of Hg, and 1.24 g of Te until it just melted in a quartz tube

**Table 3. Fractional Atomic Coordinates and *B*(eq) Values for (Me<sub>4</sub>N)<sub>4</sub>[Hg<sub>3</sub>Te<sub>7</sub>](0.5en) with Their Standard Deviations in Parentheses**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq)
Hg(1)	1.24946(9)	0.27869(7)	0.6322(1)	4.31(7)
Hg(2)	0.93163(9)	0.24964(7)	0.7384(1)	4.01(7)
Hg(3)	0.5954(1)	0.26797(7)	0.6563(1)	4.59(7)
Te(1)	1.4188(1)	0.2986(1)	0.4758(2)	5.0(1)
Te(2)	1.2983(2)	0.1719(1)	0.8293(2)	6.3(1)
Te(3)	1.0914(2)	0.1391(1)	0.8823(2)	4.8(1)
Te(4)	1.0350(1)	0.3508(1)	0.6016(2)	3.9(1)
Te(5)	0.8157(2)	0.3358(1)	0.9665(2)	5.8(1)
Te(6)	0.7827(1)	0.1627(1)	0.5999(2)	4.1(1)
Te(7)	0.5969(2)	0.3738(1)	0.8807(2)	6.1(1)
N(1)	0.705(2)	0.431(1)	0.380(2)	4(1)
N(2)	0.098(2)	0.103(1)	0.330(2)	4(1)
N(3)	0.184(2)	0.394(1)	0.115(2)	4(1)
N(4)	0.644(3)	0.120(2)	0.097(3)	8(2)
N(5)	0.549(2)	0.042(2)	0.665(3)	7.7(7)
C(1)	0.742(2)	0.345(2)	0.355(3)	6.1(8)
C(2)	0.683(2)	0.451(2)	0.525(3)	6.3(8)
C(3)	0.607(2)	0.459(2)	0.292(3)	5.9(7)
C(4)	0.796(3)	0.472(2)	0.340(3)	6.2(8)
C(5)	0.109(2)	0.087(2)	0.480(3)	6.1(7)
C(6)	0.212(3)	0.105(2)	0.278(3)	6.4(8)
C(7)	0.023(2)	0.178(2)	0.314(3)	5.1(7)
C(8)	0.054(3)	0.038(2)	0.255(3)	7.1(8)
C(9)	0.164(3)	0.318(2)	0.159(4)	9(1)
C(10)	0.131(3)	0.455(2)	0.214(4)	9(1)
C(11)	0.305(3)	0.396(2)	0.117(3)	8(1)
C(12)	0.129(3)	0.408(2)	-0.021(3)	7.2(8)
C(13)	0.678(6)	0.101(5)	-0.028(8)	24.8(8)
C(14)	0.582(3)	0.204(3)	0.106(4)	12(1)
C(15)	0.728(6)	0.122(4)	0.194(7)	23(1)
C(16)	0.585(7)	0.064(5)	0.156(8)	28.3(8)
C(17)	0.515(6)	0.025(4)	0.500(8)	17(1)

**Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) of the [Hg<sub>2</sub>Te<sub>4</sub>]<sup>2-</sup> Anion in **1****

bond distances		bond angles	
Hg(1)–Te(1)	2.729(5)	Te(1)–Hg(1)–Te(2)	116.4(2)
Hg(1)–Te(2)	2.765(6)	Te(1)–Hg(1)–Te(4)	124.5(2)
Hg(1)–Te(4)	2.708(6)	Te(2)–Hg(1)–Te(4)	119.0(2)
Hg(2)–Te(1)	2.692(5)	Te(1)–Hg(2)–Te(3)	109.3(2)
Hg(2)–Te(3)	2.791(5)	Te(1)–Hg(2)–Te(4)	134.9(2)
Hg(2)–Te(4)	2.683(5)	Te(3)–Hg(2)–Te(4)	115.8(2)
Te(2)–Te(3)	2.767(7)	Hg(1)–Te(1)–Hg(2)	99.0(2)
		Hg(1)–Te(2)–Te(3)	101.1(2)
		Hg(2)–Te(3)–Te(2)	105.0(2)
		Hg(1)–Te(4)–Hg(2)	97.6(2)

under inert gas. Care has to be taken not to heat the mixture too hot as the Hg will boil out of the mixture.

*(Et<sub>4</sub>N)<sub>2</sub>Hg<sub>2</sub>Te<sub>4</sub>*. A 0.200 g portion of K<sub>2</sub>Hg<sub>2</sub>Te<sub>3</sub> was pulverized and extracted for 12 h with 4 mL of en and then filtered. This solution was then carefully layered with a solution of 0.12 g of tetraethylammonium iodide (TEA-I) in 5 mL of en. After 2 weeks, 0.112 g of **1** was isolated (40% yield) as very small, dark hexagonal platelets.

*(Me<sub>4</sub>N)<sub>4</sub>Hg<sub>3</sub>Te<sub>7</sub>(0.5en)*. Using a similar electrochemical cell to those previously described,<sup>7</sup> a cathode of nominal composition Hg<sub>2</sub>Te<sub>3</sub> was placed in an electrolyte of 0.15 M tetramethylammonium iodide (TMA-I) in en at an initial constant current of 100  $\mu$ A. After 2–3 days crystals were apparent on the cathode and a lesser number on the bottom of the cathode

(7) Some examples of anions include (a) [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>4</sub>Au<sub>3</sub>Te<sub>4</sub> and [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P]<sub>2</sub>Au<sub>2</sub>Te<sub>4</sub>: Warren, C. J.; Ho, D. M.; Bocarsly, A. B.; Haushalter, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 6416. (b) [(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N]<sub>4</sub>Sb<sub>4</sub>Te<sub>4</sub> and [(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N]<sub>3</sub>Sb<sub>3</sub>Te<sub>6</sub>: Warren, C. J.; Ho, D. M.; Haushalter, R. C.; Bocarsly, A. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1646. (c) [(CH<sub>3</sub>)<sub>4</sub>N]<sub>4</sub>Sb<sub>2</sub>Te<sub>5</sub>, [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>4</sub>Sb<sub>2</sub>Te<sub>5</sub>, and [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>4</sub>Sb<sub>2</sub>Te<sub>5</sub>(0.5en): Warren, C. J.; Dhingra, S. S.; Ho, D. M.; Haushalter, R. C.; Bocarsly, A. B. *Inorg. Chem.* **1994**, *33*, 2709. (d) [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub>As<sub>2</sub>Te<sub>5</sub> and [(CH<sub>3</sub>)<sub>4</sub>N]<sub>4</sub>As<sub>4</sub>Te<sub>6</sub>(2en): Warren, C. J.; Haushalter, R. C.; Bocarsly, A. B. *Chem. Mater.* **1994**, *6*, 780. (e) [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>In<sub>2</sub>Te<sub>4</sub>: Warren, C. J.; Dhingra, S. S.; Haushalter, R. C.; Bocarsly, A. B. *J. Solid-State Chem.* **1994**, *112*, 340.

**Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) of the  $[\text{Hg}_3\text{Te}_7]^{4-}$  Anion in **2****

bond distances		bond angles	
Hg(1)–Te(1)	2.697(2)	Te(1)–Hg(1)–Te(2)	117.56(7)
Hg(1)–Te(2)	2.761(3)	Te(1)–Hg(1)–Te(4)	124.43(7)
Hg(1)–Te(4)	2.691(2)	Te(2)–Hg(1)–Te(4)	117.95(7)
Hg(2)–Te(3)	2.883(2)	Te(3)–Hg(2)–Te(4)	112.25(7)
Hg(2)–Te(4)	2.770(2)	Te(3)–Hg(2)–Te(5)	98.99(7)
Hg(2)–Te(5)	2.884(2)	Te(3)–Hg(2)–Te(6)	106.61(7)
Hg(2)–Te(6)	2.792(2)	Te(4)–Hg(2)–Te(5)	109.31(7)
Hg(3)–Te(1)	2.735(2)	Te(4)–Hg(2)–Te(6)	120.00(7)
Hg(3)–Te(6)	2.697(2)	Te(5)–Hg(2)–Te(6)	107.55(7)
Hg(3)–Te(7)	2.773(3)	Te(1)–Hg(3)–Te(6)	123.06(7)
Te(2)–Te(3)	2.734(3)	Te(1)–Hg(3)–Te(7)	116.41(7)
Te(5)–Te(7)	2.729(3)	Te(6)–Hg(3)–Te(7)	119.14(7)
		Hg(1)–Te(1)–Hg(3)	99.63(7)
		Hg(1)–Te(2)–Te(3)	102.70(8)
		Hg(2)–Te(3)–Te(2)	105.69(8)
		Hg(1)–Te(4)–Hg(2)	98.65(7)
		Hg(2)–Te(5)–Te(7)	105.44(8)
		Hg(2)–Te(6)–Hg(3)	95.80(7)
		Hg(3)–Te(7)–Te(5)	100.10(8)

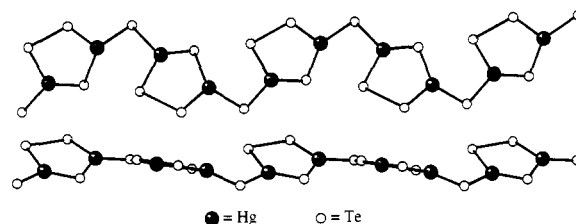
chamber. The experiment was run for 10 days over which time the current had dropped to ca. 10  $\mu\text{A}$  as the crystals of **2** built up on the cathode. At this point, 59.2 mg of **2** was removed from the electrode which corresponded to an approximately 48% yield based on the amount of the cathode that was consumed during the experiment (electrochemical yield = 14%).<sup>8</sup>

## Results and Discussion

Employing the methods similar to those originally employed by Zintl to generate polyanions, namely, the solvent extraction of intermetallic phases and the electrolysis of main-group metal electrodes, we have isolated a large number of telluride materials.

Using the extractive techniques, we have isolated  $\text{Au}_2\text{Te}_4^{2-}$ ,<sup>9</sup>  $\text{Au}_4\text{Te}_4^{4-}$ ,<sup>10</sup>  $\text{KAu}_9\text{Te}_7^{4-}$ ,<sup>10</sup>  $\text{Au}_2\text{Te}_{12}^{4-}$ ,<sup>11</sup>  $\text{Hg}_4\text{Te}_{12}^{4-}$ ,<sup>4</sup>  $\text{Hg}_2\text{Te}_5^{2-}$ ,<sup>4</sup>  $\text{As}_{10}\text{Te}_3^{2-}$ ,<sup>12</sup> and  $\text{Cu}_4\text{SbTe}_{12}^{3-}$ .<sup>13</sup> Employing the electrochemical methods, we have characterized several novel clusters and polymers such as  $\text{Au}_3\text{Te}_4^{3-}$ ,  $\text{Sb}_2\text{Te}_5^{4-}$ ,  $\text{Sb}_4\text{Te}_4^{4-}$ ,  $\text{Sb}_6\text{Te}_9^{4-}$ ,  $\text{Sb}_6\text{Te}_9^{4-}$ ,  $\text{As}_2\text{Te}_5^{2-}$ ,  $\text{GaTe}_2(\text{en})_2$ , and  $\text{In}_2\text{Te}_4^{2-}$ .<sup>7</sup> We have now used these procedures to produce two new 1-D mercury telluride polymers.

The polymer  $(\text{Et}_4\text{N})_2\text{Hg}_2\text{Te}_4$  was isolated in moderate yield via the extraction of the intermetallic material of nominal composition  $\text{K}_2\text{Hg}_2\text{Te}_3$ . The alloy  $\text{K}_2\text{Hg}_2\text{Te}_3$  appears visually to be homogeneous and can be easily crushed to a powder which is very soluble in en. The crystals which slowly formed upon treatment of the en extracts of  $\text{K}_2\text{Hg}_2\text{Te}_3$  with  $\text{Et}_4\text{N-I}$  were very small and did not increase in size even upon prolonged standing in the reaction mixture. We determined the structure on the largest crystal available which was only approximately  $25 \times 25 \times 10 \mu\text{m}^3$ . Despite the small size



**Figure 1.** Two views (rotated approximately 90° about an axis that lies in the plane of the page) of the one dimensional  $\text{Hg}_2\text{Te}_4^{2-}$  polyanion present in (**1**).

of this crystal, we were able to achieve a data to parameter ratio of about 9:1 due to the intensity of the rotating anode X-ray source coupled with the adequate crystal quality and the abundance of heavy atoms in the structure.

The structure of mercury telluride polymer **1** was solved in the monoclinic space group  $P2_1/a$  and consists of one-dimensional chains of composition  $\text{Hg}_2\text{Te}_4^{2-}$  separated by tetraethylammonium cations. Two views of the chain are shown in Figure 1. The chain is built up from  $\text{Hg}_2\text{Te}_3$  five-membered rings (Figure 4a) with the Hg atoms in the 1 and 3 positions of the ring. The Hg1 atom has approximately trigonal-planar coordination with Te–Hg1–Te angles of 116°, 119°, and 124°, while those of Hg2 are somewhat less regular with Te–Hg2–Te angles of 135°, 109°, and 116°. The distances of Hg1 and Hg2 from the least-square planes of the three surrounding tellurium atoms are 0.05 and 0.18 Å, respectively. The six crystallographically independent Hg–Te distances range from 2.683 to 2.791 Å with an average distance of 2.728 Å. These are similar to the average Hg–Te distances of 2.737 and 2.742 Å for Hg to two coordinate Te in  $\text{Hg}_4\text{Te}_{12}^{4-}$  and  $\text{Hg}_2\text{Te}_5^{2-}$ .<sup>4</sup> The five-membered  $\text{Hg}_2\text{Te}_3$  rings are connected together into the infinite 1-D chains by two coordinate Te. The five-membered rings themselves are quite planar, but the planes of these rings are tilted relative to one another such that the mercury telluride chain is somewhat buckled as shown in Figure 1.

Employing a different and unrelated synthetic technique, we have been able to isolate another example of a 1-D mercury telluride polymer with a different structure. The telluride  $(\text{Me}_4\text{N})_4\text{Hg}_3\text{Te}_7(0.5\text{en})$  was prepared via electrolysis of an  $\text{Hg}_2\text{Te}_3$  electrode. We have recently employed this technique of the cathodic dissolution of tellurium alloy electrodes, which was inspired by the original electrolytic experiments of Zintl, to prepare several novel anionic clusters and 1-D tellurides from the gold, arsenic, antimony, indium, and gallium telluride systems.<sup>7</sup> The  $\text{Hg}_2\text{Te}_3$  electrode was prepared by the fusion of 2 equiv of Hg with 3 equiv of tellurium in a quartz tube under an inert gas. Although the binary compound  $\text{Hg}_2\text{Te}_3$  does not appear on the Hg–Te phase diagram, this material appeared to be visually homogeneous. The resulting shiny metallic mass was crushed to a powder and recast into cylindrical electrodes with an area of approximately 1  $\text{cm}^2$ . The electrodes were placed into an electrochemical cell as previously described,<sup>7</sup> and an initial current of 100  $\mu\text{A}$  was applied. Unlike the majority of our other electrochemical telluride syntheses, the solution did not become very dark as most of the reacted material apparently precipitated rapidly onto or near the electrode. The deposition of **2** onto the  $\text{Hg}_2\text{Te}_3$  increased the resistance

(8) A yield of 48.5% was based on 0.0788 g (0.1005 mmol) of  $\text{Hg}_2\text{Te}_3$  electrode dissolved after 10 days which gave rise to 0.0592 g (0.0325 mmol) of  $[(\text{CH}_3)_4\text{N}]_4\text{Hg}_3\text{Te}_7(0.5\text{en})$  crystals that were collected from the cathode chamber. The percent yield was calculated on the basis of moles of Hg. Electrochemical yield = moles of product/moles of e<sup>−</sup> passed (where it was assumed that an average of 100  $\mu\text{A}$  current was passed for 10 days).

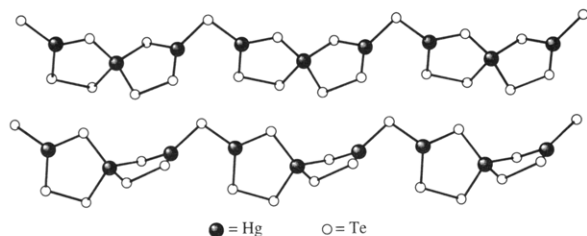
(9) Haushalter, R. C. *Inorg. Chim. Acta* **1985**, 102, L37.

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

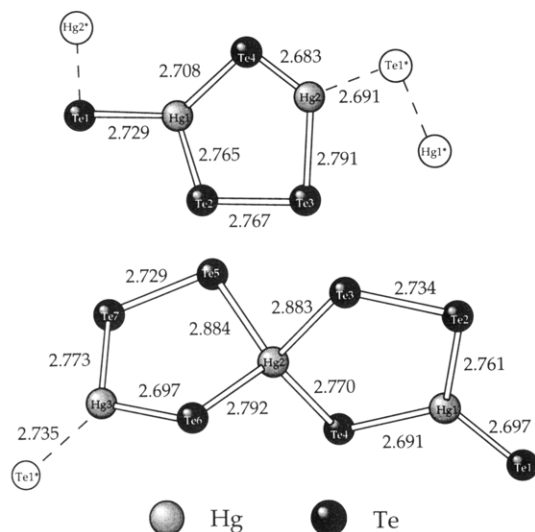
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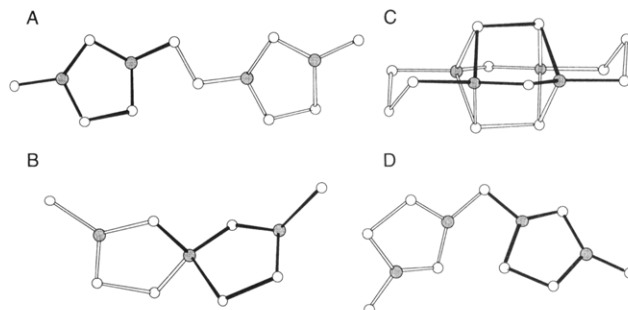
**Figure 2.** Projections of the structure of the  $\text{Hg}_3\text{Te}_7^{4-}$  anion present in **(2)**.



**Figure 3.** Some selected distances and angles found in the two five-membered rings present in **1** and **2**.

of the cell and by the end of the experiment in 10 days, it was possible to pass only about 10  $\mu\text{A}$  of current through the cell.

The structure of mercury telluride **(2)** was solved and refined in the triclinic space group  $P\bar{1}$  and is comprised of tetramethylammonium cations which separate infinite one-dimensional mercury telluride chains of composition  $\text{Hg}_3\text{Te}_7^{4-}$ . The structure of this chain is shown in Figure 2. The structure of the chains in **2** are also built up from five-membered rings as are the chains in **1**. Unlike the rings in **1**, however, the five-membered rings in  $\text{Hg}_3\text{Te}_7^{4-}$  share a common mercury atom as shown in Figures 3 and 4b. The two Hg atoms in each ring in **2** occupy the 1 and 3 positions as found in **1**. The common mercury atom shared between the two rings is tetrahedrally coordinated. As expected, the  $\text{Te}-\text{Hg}_{\text{tet}}$  contacts are significantly longer than the  $\text{Te}-\text{Hg}_{\text{trig}}$  distances. The six  $\text{Te}-\text{Hg}_{\text{trig}}$  distances range from 2.691(2) to 2.773(3) Å with an average of 2.726 Å, while the four  $\text{Te}-\text{Hg}_{\text{tet}}$  contacts range from 2.770(2) to 2.884-



**Figure 4.** Common structural motif of the five-membered  $\text{Hg}_2\text{-Te}_5$  rings present in (A)  $\text{Hg}_2\text{Te}_5^{2-}$ , (B)  $\text{Hg}_3\text{Te}_7^{4-}$ , (C)  $\text{Hg}_4\text{Te}_{12}^{4-}$ , and (D)  $\text{Hg}_2\text{Te}_4^{2-}$ .

(2) Å with an average of 2.832 Å. The  $\text{Te}-\text{Te}$  distances of 2.734(3) and 2.729(3) Å are typical of many polytellurides. The six  $\text{Te}-\text{Hg}_{\text{tet}}-\text{Te}$  bond angles range from 99° to 120° with an average of 109.5°, while the six  $\text{Te}-\text{Hg}_{\text{trig}}-\text{Te}$  bond angles fall between 116° and 124° with an average angle of 120°. A comparison of the bond distances found in the two 1-D mercury telluride polymers is shown in Figure 3. The complete listing of bond distances and angles in these two polymers is given in Tables 4 and 5.

The  $\text{Hg}-\text{Te}$  rings in tellurides **1** and **2** share a common structural feature. Both contain a five-membered  $\text{Hg}_2\text{Te}_3$  ring, with mercury atoms in the 1 and 3 positions, with an exocyclic Te atom attached to each Hg atom. In the case of **1**, these five-membered rings are connected into 1-D strings via two-coordinate Te atoms, while in **(2)** the rings share a common Hg atom. In fact, this very same five-membered ring is found in two of our earlier mercury telluride structures, namely,  $(\text{Bu}_4\text{N})_4\text{Hg}_4\text{Te}_{12}^{4-}$  and  $(\text{Ph}_4\text{P})_2\text{Hg}_2\text{Te}_5^{4-}$ .<sup>4</sup> The common structural element in all four of our mercury telluride anions is shown in Figure 4.

In summary, two novel 1-D mercury telluride polyanions have been synthesized and structurally characterized. Telluride **1** was prepared by an alloy extraction method, while telluride **2** was prepared by a constant-current cathodic dissolution of an  $\text{Hg}_2\text{Te}_3$  electrode. Both compounds display a five-membered  $\text{Hg}_2\text{Te}_3$  ring which resembles those found in the previously characterized  $\text{Hg}_2\text{Te}_5^{2-}$  and  $\text{Hg}_4\text{Te}_{12}^{4-}$  polyanions.

**Supplementary Material Available:** Complete tables of experimental crystallographic details, atomic coordinates, bond distances and angles, and anisotropic displacement parameters for **1** and **2** (43 pages); calculated and observed structure factors (24 pages). Ordering information is given on any current masthead page.