

Reaction of Mercury(II) Dibromide with Tris(*n*-butyl)phosphine Telluride: Formation of an Unusual (HgTe)₃ Ring System

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ABSTRACT

Tris(*n*-butyl)phosphine telluride ($R_3P\text{Te}$) yields, with HgBr_2 from acetone solution, a very thermally and air sensitive crystalline solid. This solid has been identified as $(\text{HgBr}_2)_4 \cdot (\text{TePR}_3)_3$. X-ray diffraction analysis reveals that this compound contains a dimeric cation, $[(\text{HgTePR}_3)_3\text{Br}_2]_2^+$, in which each unit is characterized by a six-membered ring made of alternating bonds between mercury and tellurium. The counter ion is a dinuclear anion $[\text{Hg}_2\text{Br}_2]^{2-}$. The crystal belongs to the triclinic system, $P\bar{1}$ group with $a = 12.206(9)$ Å, $b = 17.613(10)$ Å, $c = 18.065(9)$ Å, and $Z = 2$. The preparation of this new heterocyclic system and its decomposition under different conditions into $\text{Hg}_3\text{Te}_2\text{Br}_2$ or HgTe are presented. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Thin films of metal chalcogenides, MX, where M is typically Pb, Cd, Cu, etc., and X = S, Se, Te are of great interest in the field of photovoltaics. One manner of depositing such films on glass, ceramic, and plastic surfaces is that of chemical deposition from homogeneous solution. In the utilization of this method, the source of the chalcogenide ion is typically a thiocarbonyl or a selenocarbonyl. Typical il-

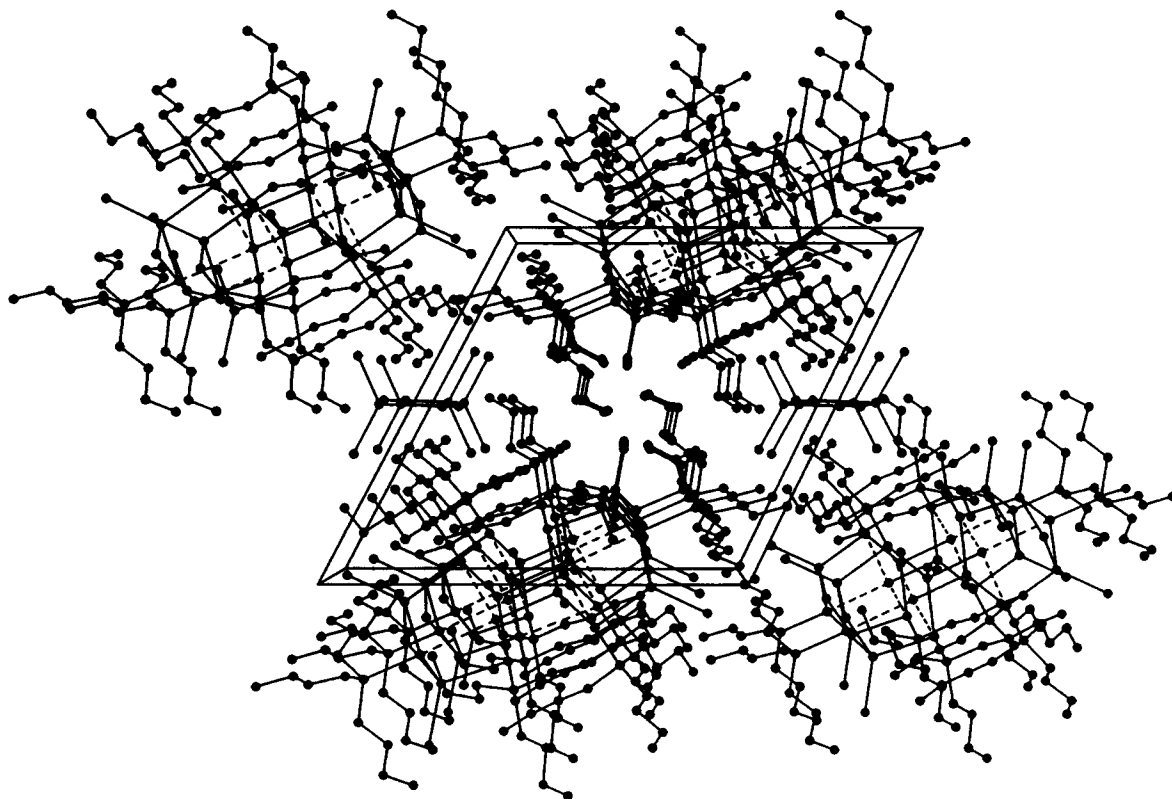
lustrative examples are the deposition of ZnSe and CuSe with the use of N,N-dimethylselenourea [1] and the reaction between cadmium ion complexed with citrate and thiourea for the deposition of photosensitive thin films of CdS [2]. Cadmium telluride is considered to be one of the prime materials for the future development of efficient photovoltaic cells. It would be desirable to be able to deposit thin films of CdTe through the use of tellurocarbonyls. The C=Te bond, however, is extremely unstable and as yet no tellurocarbonyl has successfully been used for the deposition, from homogeneous solution, of thin films of any metal telluride.

During recent years, Steigerwald and co-workers have described the use of phosphine tellurides, $R_3P\text{Te}$, for the synthesis of metal tellurides. Thus, PdTe was synthesized by the reaction between $\text{Pd}(\text{PPh}_3)_4$ and triethylphosphine telluride (Et_3PTe) [3] and the reaction between Et_3PTe and elemental mercury yielded HgTe [4]. Because of our interest in semiconducting thin films of metal chalcogenides, we have undertaken a study of the reactions between phosphine tellurides and metal salts in nonaqueous media. In the present study we describe the reactions between HgBr_2 and tris(*n*-butyl)phosphine telluride in anhydrous acetone. The reaction with HgBr_2 yields a new interesting heterocyclic system that is made up of three mercury and three tellurium atoms. The decomposition of this compound has also been investigated. Under ambient conditions and thermally under nitrogen, among other products, it decomposes to $\text{Hg}_3\text{Te}_2\text{Br}_2$. In an alkaline solution, it gives HgTe as the solid product.

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TABLE 1 Crystal Data and Structure Refinement for **1**

Empirical formula	$C_{39}H_{87}Br_8Hg_4OP_3Te_3$
Formula weight	2489.44
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 12.206(9)$ Å $\alpha = 115.94(4)^\circ$ $b = 17.613(10)$ Å $\beta = 90.72(5)^\circ$ $c = 18.065(9)$ Å $\gamma = 102.83(6)^\circ$
Volume	3379(4) Å ³
Z	2
Density (calculated)	2.447 Mg/m ³
Absorption coefficient	15.157 mm ⁻¹
$F(000)$	2260
Crystal size	0.38 × 0.23 × 0.04 mm
θ range for data collection	2.53–22.55°
Index ranges	$-13 \leq h \leq 13$, $-17 \leq k \leq 18$, $-19 \leq l \leq 0$
Reflections collected	8873
Independent reflections	8564 ($R_{int} = 0.1921$)
Absorption correction	Difabs
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8514/154/324
Goodness-of-fit on F^2	1.003
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0784$, $wR2 = 0.1497$
R indices (all data)	$R1 = 0.2443$, $wR2 = 0.2110$
Extinction coefficient	0.00030(6)
Largest diffraction peak and hole	2.267 and -3.398 eÅ ⁻³

**FIGURE 1** Stereo packing diagram for unit cells of $[Hg_3(TePR_3)_3Br_5]_2[Hg_2Br_6] \cdot 2CH_3COCH_3$.

EXPERIMENTAL

General

Mercury bromide (HgBr₂) and 97% (*n*-tributyl)phosphine were purchased from the Aldrich Chemical Co. and used as received. Toluene was sodium dried and petroleum ether was dried over molecular sieves. NMR spectra were recorded using a Varian XL-200E FT-NMR spectrometer. XRD powder patterns were recorded with the SEIFERT-SCINTAG PAD V X-ray diffractometer. Single-crystal X-ray data were collected with the Siemens R3m/V diffractometer using graphite monochromatized MoK_α radiation.

Preparation of Tris(*n*-butyl)phosphine Telluride

This compound was prepared following a previous procedure [5] with minor modification. Elemental tellurium (5 g, 0.034 mol) was suspended in toluene (45 mL) under nitrogen. After tributylphosphine (18.5 mL, 0.074 mol) was injected into the system, the mixture was heated under reflux for approximately 2 hours. During this period of time tellurium was gradually dissolved, resulting in the formation of a clear yellow solution. After the solvent was removed by evaporation under reduced pressure, petroleum ether (20 mL) chilled in dry ice was added and the mixture was allowed to cool in a dry ice bath. This gave a bright yellow crystalline solid. It was collected immediately following filtration under reduced pressure and rinsed with chilled petroleum ether (2 × 5 mL), then dried in a desiccator in vacuo. The product weighed 10.68 g and the yield was 88.7%. ¹H NMR (CDCl₃): 0.956 [m, 3H(terminal methyl group)], 1.47 [m, 4H(ethylene)], 2.01 [m, 2H(methylene bonded to phosphorus)].

Preparation of [Hg₃(TePR₃)₃Br₅]₂[Hg₂Br₄]

In spite of the fact that the material was found to be air sensitive, it was possible to prepare it under ordinary atmospheric conditions. A solution of R₃P₃Te (2.44 g, 7 mmol) (in acetone, 50 mL) was added to a stirred solution of HgBr₂ (5.04 g, 14 mmol) (in 100 mL acetone) dropwise through a filter paper. The filtration through paper was necessary so that any elemental tellurium formed during storage was removed. Upon the addition, a yellowish green precipitate formed in minutes. The mixture was stirred for approximately 5 minutes after completion of the addition of R₃P₃Te. The solid was collected by filtration under reduced pressure, and washed with acetone (about 20 mL), then dried in an evacuated desiccator over magnesium sulfate. The yield was

TABLE 2 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for 1. $U(\text{eq})$ Is Defined as One-Third of the Trace of the Orthogonalized U_{ij} Tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
Hg(1)	3138(2)	-36(1)	4366(1)	35(1)
Hg(2)	4718(2)	176(1)	2368(1)	39(1)
Hg(3)	4671(2)	2252(1)	4095(1)	39(1)
Hg(4)	9062(2)	4982(2)	853(1)	57(1)
Te(1)	4360(3)	1671(2)	5310(2)	36(1)
Te(2)	4421(3)	-887(2)	3154(2)	35(1)
Te(3)	6483(3)	1649(2)	3282(2)	37(1)
Br(1)	3466(4)	-749(3)	5423(3)	40(1)
Br(2)	999(4)	-442(3)	4062(3)	45(1)
Br(3)	2961(4)	1053(3)	2855(3)	39(1)
Br(4)	4547(5)	3789(3)	4522(3)	56(1)
Br(5)	4412(5)	-520(4)	809(3)	56(1)
Br(6)	8770(5)	6360(4)	2007(3)	75(2)
Br(7)	8144(5)	3569(4)	886(3)	70(1)
Br(8)	11,325(5)	5093(3)	671(3)	51(1)
P(1)	2699(7)	2259(6)	5730(5)	43(2)
P(2)	2824(6)	-1963(5)	2142(5)	38(2)
P(3)	6481(8)	2289(6)	2303(5)	39(2)
O(1)	8549(29)	6416(45)	7393(21)	361(24)
C(1)	1925(8)	1776(10)	6342(9)	41(6)
C(2)	2579(11)	1617(13)	6946(11)	41(6)
C(3)	1864(15)	1155(18)	7368(15)	41(6)
C(4)	2520(19)	939(23)	7925(19)	41(6)
C(5)	3107(12)	3436(5)	6394(10)	95(9)
C(6)	4081(22)	3810(7)	7070(14)	95(9)
C(7)	4566(23)	4776(9)	7413(19)	96(9)
C(8)	5532(26)	5151(15)	8094(20)	97(9)
C(9)	1667(9)	2076(11)	4890(6)	54(7)
C(10)	568(13)	2319(21)	5097(9)	54(7)
C(11)	-229(15)	2124(16)	4361(11)	54(7)
C(12)	-421(29)	1217(18)	3670(14)	55(7)
C(13)	3315(10)	-2720(11)	1222(5)	58(7)
C(14)	4350(16)	-3007(16)	1328(8)	58(7)
C(15)	4772(17)	-3529(19)	532(10)	58(7)
C(16)	5803(22)	-3821(23)	637(14)	59(7)
C(17)	1991(8)	-2629(10)	2580(10)	72(8)
C(18)	2596(12)	-2896(13)	3119(13)	72(8)
C(19)	1839(18)	-3302(24)	3567(21)	73(8)
C(20)	2407(26)	-3712(28)	3982(26)	73(8)
C(21)	1823(9)	-1541(7)	1763(9)	68(7)
C(22)	767(14)	-2167(11)	1210(18)	68(7)
C(23)	55(19)	-1768(14)	872(19)	68(7)
C(24)	-930(21)	-2409(17)	245(19)	69(8)
C(25)	7127(17)	3450(7)	2662(10)	219(15)
C(26)	7373(27)	4041(10)	3577(11)	219(15)
C(27)	8210(31)	4899(12)	3813(16)	219(15)
C(28)	8979(41)	5237(32)	4604(29)	219(15)
C(29)	5015(7)	2099(14)	1898(11)	170(13)
C(30)	4788(11)	2300(31)	1194(24)	170(13)
C(31)	3570(16)	1996(29)	823(23)	171(13)
C(32)	3333(21)	2241(42)	151(29)	171(13)
C(33)	7174(14)	1711(12)	1409(8)	113(10)
C(34)	7907(18)	1158(14)	1475(14)	113(10)
C(35)	8660(22)	896(23)	805(15)	113(10)
C(36)	9756(27)	775(42)	1064(26)	113(10)
C(37)	9261(36)	6694(55)	7010(22)	361(24)
C(38)	9133(53)	6261(61)	6111(22)	361(24)
C(39)	10,269(63)	7383(52)	7470(41)	361(24)

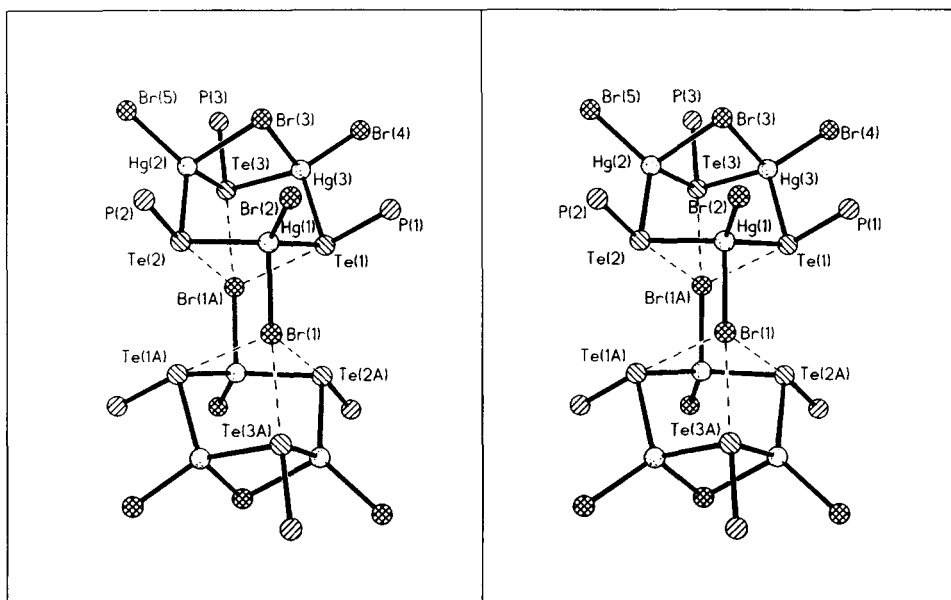
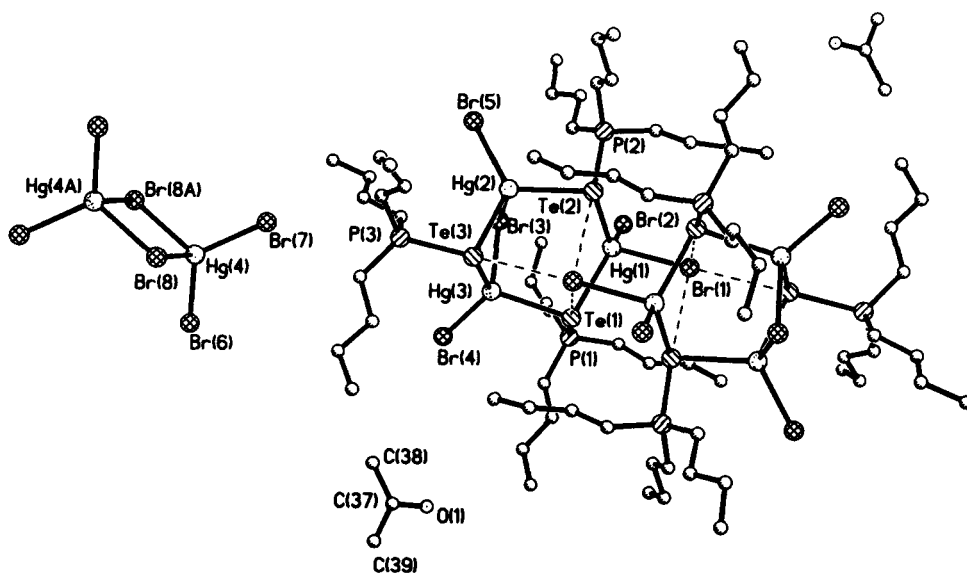
TABLE 3 Bond Lengths (Å) and Angles (°) for **1^a**

Hg(1)–Br(2)	2.534(6)	Hg(1)–Te(1)	2.761(5)
Hg(1)–Br(1)	2.772(5)	Hg(1)–Te(2)	2.784(3)
Hg(2)–Br(5)	2.514(5)	Hg(2)–Te(2)	2.772(4)
Hg(2)–Te(3)	2.790(5)	Hg(2)–Br(3)	2.845(5)
Hg(3)–Br(4)	2.511(5)	Hg(3)–Br(3)	2.760(6)
Hg(3)–Te(1)	2.797(3)	Hg(3)–Te(3)	2.817(4)
Hg(4)–Br(7)	2.518(6)	Hg(4)–Br(6)	2.519(6)
Hg(4)–Br(8)#1	2.728(5)	Hg(4)–Br(8)	2.759(6)
Te(1)–P(1)	2.458(8)	Te(2)–P(2)	2.444(9)
Te(3)–P(3)	2.479(10)	Br(8)–Hg(4)#1	2.728(5)
P(1)–C(1)	1.8266(14)	P(1)–C(9)	1.827(2)
P(1)–C(5)	1.827(2)	P(2)–C(13)	1.827(2)
P(2)–C(17)	1.827(2)	P(2)–C(21)	1.8270(14)
P(3)–C(29)	1.827(2)	P(3)–C(33)	1.827(2)
P(3)–C(25)	1.827(2)	O(1)–C(37)	1.264(13)
C(1)–C(2)	1.5001(13)	C(2)–C(3)	1.5000(13)
C(3)–C(4)	1.5000(13)	C(5)–C(6)	1.500(2)
C(6)–C(7)	1.500(2)	C(7)–C(8)	1.500(2)
C(9)–C(10)	1.500(2)	C(10)–C(11)	1.500(2)
C(11)–C(12)	1.500(2)	C(13)–C(14)	1.5000(14)
C(14)–C(15)	1.5000(14)	C(15)–C(16)	1.5000(14)
C(17)–C(18)	1.5000(13)	C(18)–C(19)	1.5000(13)
C(19)–C(20)	1.5000(12)	C(21)–C(22)	1.500(2)
C(22)–C(23)	1.5000(13)	C(23)–C(24)	1.500(2)
C(25)–C(26)	1.500(2)	C(26)–C(27)	1.500(2)
C(27)–C(28)	1.500(2)	C(29)–C(30)	1.5000(12)
C(30)–C(31)	1.500(2)	C(31)–C(32)	1.5000(12)
C(33)–C(34)	1.5000(14)	C(34)–C(35)	1.5000(14)
C(35)–C(36)	1.500(2)	C(37)–C(38)	1.4501(14)
C(37)–C(39)	1.450(2)		
Br(2)–Hg(1)–Te(1)	121.7(2)	Br(2)–Hg(1)–Br(1)	102.3(2)
Te(1)–Hg(1)–Br(1)	100.5(2)	Br(2)–Hg(1)–Te(2)	120.1(2)
Te(1)–Hg(1)–Te(2)	108.58(12)	Br(1)–Hg(1)–Te(2)	98.06(12)
Br(5)–Hg(2)–Te(2)	119.0(2)	Br(5)–Hg(2)–Te(3)	121.5(2)
Te(2)–Hg(2)–Te(3)	108.68(13)	Br(5)–Hg(2)–Br(3)	104.0(2)
Te(2)–Hg(2)–Br(3)	103.39(12)	Te(3)–Hg(2)–Br(3)	95.4(2)
Br(4)–Hg(3)–Br(3)	111.7(2)	Br(4)–Hg(3)–Te(1)	115.97(14)
Br(3)–Hg(3)–Te(1)	101.55(14)	Br(4)–Hg(3)–Te(3)	120.9(2)
Br(3)–Hg(3)–Te(3)	96.74(13)	Te(1)–Hg(3)–Te(3)	106.73(11)
Br(7)–Hg(4)–Br(6)	116.9(2)	Br(7)–Hg(4)–Br(8)#1	112.5(2)
Br(6)–Hg(4)–Br(8)#1	112.3(2)	Br(7)–Hg(4)–Br(8)	110.2(2)
Br(6)–Hg(4)–Br(8)	111.7(2)	Br(8)#1–Hg(4)–Br(8)	90.1(2)
P(1)–Te(1)–Hg(1)	95.5(2)	P(1)–Te(1)–Hg(3)	93.3(2)
Hg(1)–Te(1)–Hg(3)	100.91(13)	P(2)–Te(2)–Hg(2)	93.4(2)
P(2)–Te(2)–Hg(1)	96.5(2)	Hg(2)–Te(2)–Hg(1)	99.28(11)
P(3)–Te(3)–Hg(2)	95.8(3)	P(3)–Te(3)–Hg(3)	96.5(2)
Hg(2)–Te(3)–Hg(3)	80.89(11)	Hg(3)–Br(3)–Hg(2)	80.9(2)
Hg(4)#1–Br(8)–Hg(4)	89.9(2)	C(1)–P(1)–C(9)	106.14(10)
C(1)–P(1)–C(5)	106.13(10)	C(9)–P(1)–C(5)	106.13(10)
C(1)–P(1)–Te(1)	109.8(5)	C(9)–P(1)–Te(1)	116.2(4)
C(5)–P(1)–Te(1)	111.7(5)	C(13)–P(2)–C(17)	106.10(10)
C(13)–P(2)–C(21)	106.10(10)	C(17)–P(2)–C(21)	106.10(9)
C(13)–P(2)–Te(2)	111.0(4)	C(17)–P(2)–Te(2)	110.1(4)
C(21)–P(2)–Te(2)	116.8(4)	C(29)–P(3)–C(33)	106.11(10)
C(29)–P(3)–C(25)	106.11(10)	C(33)–P(3)–C(25)	106.10(9)
C(29)–P(3)–Te(3)	108.4(6)	C(33)–P(3)–Te(3)	109.6(5)
C(25)–P(3)–Te(3)	119.7(6)	C(2)–C(1)–P(1)	118.92(12)
C(1)–C(2)–C(3)	114.63(12)	C(4)–C(3)–C(2)	114.64(13)
C(6)–C(5)–P(1)	118.90(12)	C(7)–C(6)–C(5)	114.63(13)
C(6)–C(7)–C(8)	114.63(13)	C(10)–C(9)–P(1)	118.93(12)
C(9)–C(10)–C(11)	114.62(12)	C(12)–C(11)–C(10)	114.63(13)
C(14)–C(13)–P(2)	118.90(12)	C(13)–C(14)–C(15)	114.62(12)
C(16)–C(15)–C(14)	114.63(12)	C(18)–C(17)–P(2)	118.91(12)

TABLE 3 Continued

C(17)–C(18)–C(19)	114.63(12)	C(20)–C(19)–C(18)	114.64(12)
C(22)–C(21)–P(2)	118.90(12)	C(21)–C(22)–C(23)	114.62(12)
C(24)–C(23)–C(22)	114.63(12)	C(26)–C(25)–P(3)	118.90(12)
C(25)–C(26)–C(27)	114.6(2)	C(28)–C(27)–C(26)	114.6(2)
C(30)–C(29)–P(3)	118.92(12)	C(29)–C(30)–C(31)	114.63(12)
C(30)–C(31)–C(32)	114.63(12)	C(34)–C(33)–P(3)	118.90(12)
C(35)–C(34)–C(33)	114.64(12)	C(34)–C(35)–C(36)	114.64(12)
O(1)–C(37)–C(38)	119.8(9)	O(1)–C(37)–C(39)	119.8(10)
C(38)–C(37)–C(39)	120.0(2)		

^aSymmetry transformations used to generate equivalent atoms: #1 $-x + 2, -y + 1, -z$.


FIGURE 2 Stereographic views of the dimeric cation $[\text{Hg}_3(\text{TePR}_3)_3\text{Br}_5]_2^+$.

FIGURE 3 Molecular drawing of $[\text{Hg}_3(\text{TePR}_3)_3\text{Br}_5]_2[\text{Hg}_2\text{Br}_6] \cdot \text{CH}_3\text{COCH}_3$.

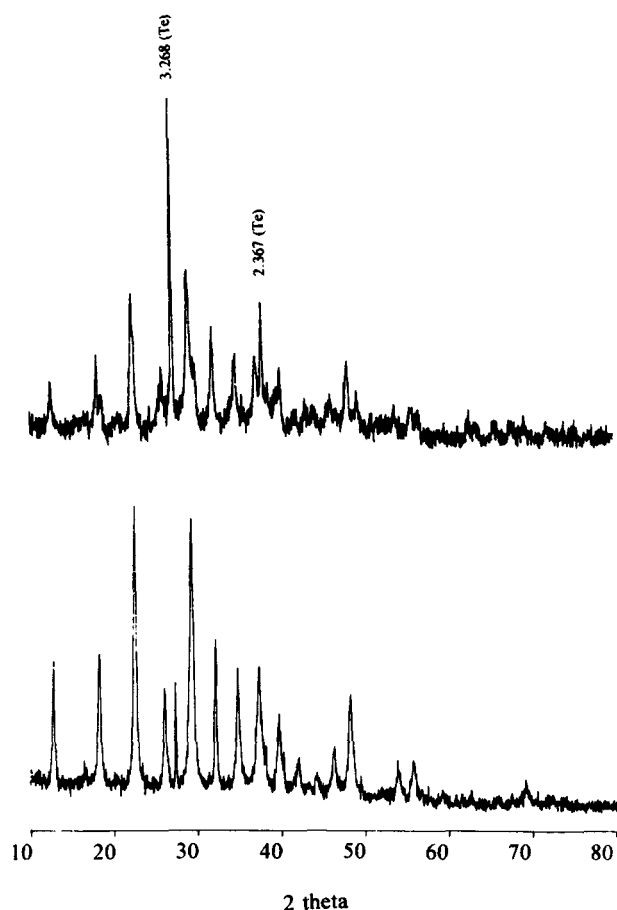


FIGURE 4 XRD powder pattern on the mixture formed by the decomposition under ambient condition for 2 weeks (top), indicating the formation of $\text{Hg}_3\text{Te}_2\text{Br}_2$ (JCPDS 18-824) and Te (JCPD 36-1452), and on the product formed by the decomposition under nitrogen at 120°C for 2 hours (bottom), indicating the formation of $\text{Hg}_3\text{Te}_2\text{Br}_2$ (JCPDS 18-825).

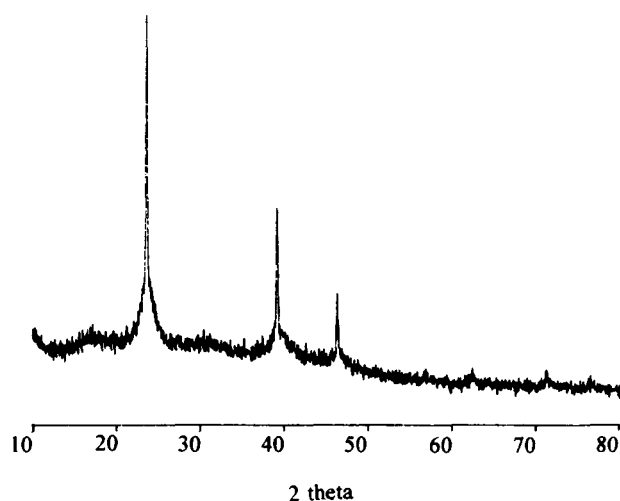


FIGURE 5 XRD powder pattern on the decomposition product in 0.5 M NaOH solution, indicating the formation of HgTe (JCPDS 32-665).

58.4% based on the tris(*n*-butyl)phosphine telluride. Elemental analysis gave C(16.65), H(3.18), Br(25.70), P(4.04), Hg(36.13), calculated for $[\text{Hg}_3(\text{TePR}_3)_3\text{Br}_5]_2[\text{Hg}_2\text{Br}_6]$: C(17.78), H(3.36), Br(26.29), P(3.82), Hg(33.00). The melting point was at 108°C with decomposition.

Decomposition of $[\text{Hg}_3(\text{TePR}_3)_3\text{Br}_5]_2[\text{Hg}_2\text{Br}_6]$ under N_2

The solid compound (0.24 g, 1 mmol) was placed in a 250 mL flask and heated to 120°C under nitrogen for 2 hours, then cooled to room temperature. Acetone (10 mL) was added to this mixture, followed by filtration. The solid product was rinsed with acetone (3×5 mL) and dried in air. This gave a green product identified as $\text{Hg}_3\text{Te}_2\text{Br}_2$ (0.12 g) by its XRD powder pattern.

Decomposition of $[\text{Hg}_3(\text{TePR}_3)_3\text{Br}_5]_2[\text{Hg}_2\text{Br}_6]$ in NaOH solution

The solid compound (0.24 g, 1 mmol) was placed in a 100 mL beaker, followed by the addition of an aqueous solution of NaOH (0.5 N, 20 mL). The compound was not soluble in NaOH solution and this mixture was stirred at room temperature for 10 hours. The color of the suspended solid converted to black. The solid was collected by filtration, followed by rinsing with distilled water (100 mL), then with acetone (20 mL), and dried in air. This gave a crystalline solid of HgTe (0.075 g).

X-ray Diffraction

Crystals suitable for X-ray diffraction were prepared by mixing 2 mmol of HgBr_2 and 1 mmol of R_3PTe in 150 mL acetone, and the cloudy solution was maintained at 8°C for a week. Pale green platelets were formed and separated physically from the yellow powder that was formed simultaneously. The best looking crystal in the sample was selected and attached at room temperature to a glass fiber with epoxy cement. The crystal was mounted on a Siemens R3m/V diffractometer and cooled to -78°C in a nitrogen stream. Inspection of axial photographs showed the crystal to be of triclinic symmetry. The crystal gave reflections of low intensity and seemed to be of only fair quality. However, the material is unstable in air as well as when exposed to room light, so data collection was begun immediately [6]. Details of the data collection are given in Table 1. Data reduction [7] which included peak profiling [8] was carried out. Absorption was expected to be severe. The empirical absorption correction routine DI-

FABS was employed [9]. The structure was solved by direct methods [10]. Refinement of the heavy atom parameters proceeded satisfactorily using least squares and Fourier methods [11], but only 26 carbon atoms could be located and $R = 0.12$. A different approach to the data analysis was required. The remaining carbon atoms were subsequently located by phase expansion techniques [12] and restraints to idealized values. All atoms were refined isotropically to convergence. An isolated acetone molecule was identified in the difference Fourier map and was included, with restraints, in the overall structural model. Large unusual residual electron density peaks were seen to be symmetrically arranged about the large metal atom positions, suggesting that an error had occurred in the absorption correction procedure. The corrected data were replaced by the raw data and the structure was again refined isotropically while the carbon and oxygen atoms were refined isotropically to convergence. Hydrogen atoms were placed in idealized position with their individual isotropic parameters allowed to ride on the adjacent carbon atoms. The crystal data and structure refinement are listed in Table 1.

RESULTS AND DISCUSSION

Reaction between $HgBr_2$ and R_3PTe

A series of reactions have been reported between alkylphosphine tellurides R_3PTe and organometallic compounds ML_n ($M = Fe, Mn, Co,$ and Ni ; $L =$ neutral ligands, such as $CO, Cp,$ etc.), in which the central metal is in the oxidation state of zero [13,14,15,16]. In these reactions, one thing in common is that R_3PTe dissociates and furnishes "soluble" elemental tellurium and alkylphosphine, resulting in clusters containing a fragment of $R_3P-M-Te$. These reactions were usually carried out at the temperature of refluxing toluene. The relative stoichiometries of the reagents and the length of the reaction time are important variables in these reactions. For example, for the reaction between $Co_2(CO)_8$ and Et_3PTe , prolonged heating gives $L_6Co_6Te_8$ ($L = Et_3P, CO$) while either a deficiency of Et_3PTe or a large excess of Et_3P gives $L_{10}Co_4Te_2$ [15]. In our experiment, the reaction between mercury(II) bromide and tributylphosphine telluride was carried out at room temperature in acetone. Under these conditions, the $P-Te$ bond remains intact and R_3PTe acts as an adduct. Consequently, a new type of compound containing the fragment $R_3P-Te-Hg$ was generated. It was found that the changing of the relative stoichiometry of reactants had no effect on the product, except the yield. When the ratio of mercury(II) bromide and tributylphosphine telluride was changed

from 2:1 to 1:1, the yield decreased from 58.4 to 38.9%.

Structure of $[Hg_3(TePR_3)_3Br_5]_2[Hg_2Br_6] \cdot 2CH_3COCH_3$

The packing diagram of this molecule is shown in Figure 1 and illustrates that no close molecular contacts exist between distinct molecules. The unit cell contains the dimetric cation, $[Hg_3(TePR_3)_3Br_5]_2^+$, positioned on the center of symmetry at $(1, 1/2, 0)$. The anion, $[Hg_2Br_6]^{2-}$, is located on the center of symmetry at $(1/2, 0, 1/2)$. In addition, the unit cell contains two molecules of acetone of solvation in general positions. Atomic coordinates and equivalent isotropic displacement parameters are provided in Table 2.

As shown in Figure 2, the dimeric cation $[Hg_3(TePR_3)_3Br_5]_2^+$ consists of two six-membered rings, in the chair conformation, made up of alternating bonds between mercury and tellurium. It may be thought of as made up of two $[Hg_3(TePR_3)_3Br_5]^{1+}$ units, coupled across the center of symmetry through these weak bonds with a corresponding lengthening of the $Hg-Br$ distance. The average $Te-P$ distance is 2.46 Å, compared with the sum of covalent single-bond radii, $(1.37 + 1.10) \text{ Å} = 2.47 \text{ Å}$. Four bromine atoms act as terminal groups and one as a bridging group between two mercury atoms. The average terminal $Hg-Br$ distance is 2.52 Å (excluding $Hg-Br$, vide infra) and the average bridging $Hg-Br$ distance is 2.80 Å. The terminal distance $Hg-Br = 2.771 \text{ Å}$ is longer than normal, but Br has three short contacts to $Te1', Te2',$ and $Te3'$ of length 3.40, 3.41, and 3.36 Å, respectively. All the important bond lengths and bond angles are listed in Table 3.

As discussed previously, this structure is entirely different from that of those formed by the reaction between alkylphosphine telluride and the organometallic compounds in which the metal atom possesses the oxidation state of zero. A typical example of those types of compounds is $(Et_3P)_4Fe_4Te_4$ [13]. It is an oligomer in a polyhedron structure. The bonds among iron atoms and tellurium atoms form as the frame and phosphine coordinate with iron atoms as terminal groups. The compound is also unique compared with those known to form between mercury(II) and the other members of the chalcogenide family. The reaction of mercury halides HgX_2 ($X = Cl, Br,$ and I) with Ph_3PS and Ph_3PSe resulted in isomorphous 1:1 adducts HgX_2SPPPh_3 and HgX_2SePPh_3 [17]. Later crystal structure analysis revealed that the adduct with the formula of $HgCl_2SePPh_3$ is actually a dimer [18]. It consists of discrete dimeric chlorine-bridged molecules with two chlorine atoms

and two SePPh_3 molecules coordinated in a centrosymmetric fashion as terminal groups.

Ten structures that have Te–Hg bonds were found in the Cambridge Structural Database, none of which resembled the present ring structure. For bent units of the type Hg–Te–Hg, two-coordinate tellurium, the Hg–Te distance observed varied from 2.706 to 2.776 Å, while for three-coordinate units, Te–TeHg₂, it varied from 2.925 to 2.954 Å [19], compared with the average value of 2.79 Å for the Hg–Te distance in the three-coordinate unit, P–TeHg₂, of the present structure, and distances 2.728 [20], 2.818, and 2.753 Å [21] in the three-coordinate unit, Hg–TeC₂.

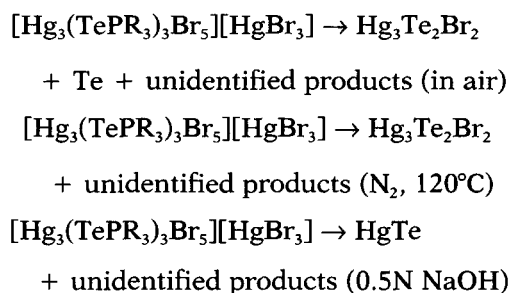
The anion $[\text{Hg}_2\text{Br}_6]^{2-}$ (shown in Figure 3) consists of two mercury atoms coordinated to two bridging bromine atoms and four terminal bromine atoms. Ten structures that contain $[\text{Hg}_2\text{Br}_6]^{2-}$ were found in the Cambridge Structural Database [22]. Excluding one case in which $[\text{HgBr}_3]^{1-}$ units are loosely coupled, the terminal Hg–Br distances in these structures vary from 2.47 to 2.56 Å and the bridging Hg–Br distances from 2.69 to 2.86 Å [23] compared with the corresponding average values found here of 2.52 Å for terminals and 2.74 Å for bridges.

Decomposition of $[\text{Hg}_3(\text{TePR}_3)_3\text{Br}_5][\text{Hg}_2\text{Br}_6]$

The compound is not soluble in nonpolar solvents, and barely soluble in acetone, acetonitrile, and chloroform. In the ambient atmosphere, the compound in the solid state decomposes gradually and the color converts to a dark grayish green. The XRD powder pattern of the product matches those of $\text{Hg}_3\text{Te}_2\text{Br}_2$ (JCPDS 18-824) and synthesized Te (JCPDS 36-1452) (see Figure 4). Heating in air speeds up the decomposition process and increases the proportion of tellurium in the product. When the compound is heated under nitrogen, it has been found that the acetone-insoluble product is $\text{Hg}_3\text{Te}_2\text{Br}_2$ (see Figure 4), although the presence of a trace amount of tellurium can be observed, indicated by the peak at 3.268. However, it is considered to arise from the decomposition during storage based on the intensity of the peak.

Because of our interest in developing compounds to serve as precursors for the chemical deposition of thin films of metal telluride, the decomposition reaction was also tested in alkaline solution. The XRD powder pattern of the solid product formed by the decomposition in NaOH solution (0.5N) matches that of coloradoite, synthesized HgTe (JCPDS 32-665) (see Figure 5). It is evident that the compound undergoes a different process in so-

lution compared with the decomposition in solid state.



The decomposition of this compound under different conditions can be summarized as shown in the preceding. In addition to the interesting structure of this compound itself, the manner of its decomposition in alkaline solution into HgTe is encouraging from the point of view of thin film deposition.

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