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Au_2PbP_2, Au_2TlP_2, and Au_2HgP_2: Ternary Gold Polyphosphides with Lead, Thallium, and Mercury in the Oxidation State Zero

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The polyphosphide Au_2PbP_2 was prepared by reaction of the elemental components using liquid lead as a reaction medium. Well-developed crystals were obtained after dissolving the matrix in hydrochloric acid. Their crystal structure was determined from four-circle X-ray diffractometer data: *Cmcm*, $a = 323.6(1)$ pm, $b = 1137.1(2)$ pm, $c = 1121.8(1)$ pm, $Z = 4$, $R = 0.023$ for 478 structure factors and 20 variable parameters. The structure contains zigzag chains of phosphorus atoms with a typical single-bond distance of 219.4(2) pm. The two different kinds of gold atoms are both in linear phosphorus coordination with typical single-bond distances of 232.6(2) and 234.2(2) pm, and the lead atoms have only metal neighbors (7 Au and 2 Pb). Accordingly, chemical bonding of the compound may be expressed by the formula $(Au^{+1})_2Pb^{\pm 0}(P^{-1})_2$. The corresponding thallium and mercury polyphosphides Au_2TlP_2 ($a = 324.1(1)$ pm, $b = 1136.1(1)$ pm, $c = 1122.1(1)$ pm) and Au_2HgP_2 ($a = 322.1(1)$ pm, $b = 1131.4(2)$ pm, $c = 1122.6(1)$ pm) pm) were found to be almost isotypic with Au_2PbP_2. Their crystal structures were refined from single-crystal X-ray data to $R = 0.036$ (682 *F* values, 25 variables) and $R = 0.026$ (539 *F* values, 35 variables), respectively. The structure of these compounds may also be described as consisting of a three-dimensional network of condensed 8- and 10-membered Au_2P_6 and Au_4P_6 rings forming parallel channels, which are filled by the lead, thallium, and mercury atoms. The lead atoms are well localized in these channels, while the thallium and even more the mercury atoms occupy additional positions within these channels. Freshly prepared samples of Au_2HgP_2 show reproducibly slightly different axial ratios and larger cell volumes ($\Delta V = 0.5\%$) than those after exposure of the samples to air for several days. © 2002 Elsevier Science (USA)

Key Words: **flux growth; polyphosphides; crystal structure.**

INTRODUCTION

Only one binary gold phosphide, Au_2P_3 (1), one well-characterized thallium phosphide, TlP_5 (2), and no binary lead or mercury phosphides are known, although the ternary polyphosphide $HgPbP_{14}$ was prepared and characterized many years ago (3). We have recently reported on the series of rare earth gold phosphides Ln_2AuP_3 ($Ln =$ La–Nd) (4). In the course of our earlier investigations on polyphosphides with $HgPbP_{14}$-type structure (5), we tried to synthesize the as yet unknown compound $AuPbP_{14}$. So far we have had little success with this synthesis. Only small amounts of microcrystalline needles of this composition could be obtained, which easily disintegrate into very thin fibers. Instead, we obtained well-crystallized samples of the ternary gold lead polyphosphide, Au_2PbP_2, which is a subject of the present paper. A brief account of this work has already been given at a conference (6). We have also prepared the isotypic gold thallium and gold mercury compounds Au_2TlP_2 and Au_2HgP_2, and refined their crystal structures from single-crystal data.

SAMPLE PREPARATION

Samples of the new gold lead polyphosphide Au_2PbP_2 were prepared by reaction of the elements using an excess of lead as flux. Pieces of gold wire (99.9%) and lead were cold-pressed to pellets. These pellets were placed in silica tubes together with pieces of semiconductor grade red phosphorus (6N, Hoechst, Werk Knapsack). The elemental components had the atomic ratio Au:Pb:P = 1:3:1. The silica tubes were briefly heated under high vacuum to evaporate the water content of the tubes; they were then flushed with purified argon, and sealed under high vacuum. The samples were placed in a cold furnace, heated to 400°C within 20 min, held at that temperature for 16 h, heated to 800°C at a rate of 5°C/h, further annealed at that temperature for 100 h, and furnace-cooled. The silica tubes were not visibly attacked by the samples. They were crushed in air. After dissolving the lead matrix in concentrated hydrochloric acid, well-developed crystals of the new compound were obtained.

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For the preparation of the mercury compound Au_2HgP_2 we first prepared the binary intermetallic gold mercury phase Au_6Hg_5 (7). For this purpose we reacted gold powder (Degussa, $<99.9\%$) with elemental mercury (atomic ratio Au:Hg = 6:5) by mixing the compounds under water for 48 h at room temperature. The microcrystalline powder of Au_6Hg_5 was then cold-pressed to pellets. These pellets were placed in silica tubes together with pieces of semiconductor grade red phosphorus in the ratio Au_6Hg_5:P = 1:2. The sealing was carried out analogous to that described above for Au_2PbP_2.The samples were placed in a cold furnace, heated to 300°C within 15 min, held at that temperature for 5 h, heated to 500°C at a rate of 5°C/h, further annealed at that temperature for 100 h, and furnace-cooled. The silica tubes were not visibly attacked by the samples. They were crushed in air. The resulting product consisted of the desired ternary polyphosphide together with elemental mercury (corresponding to the excess mercury resulting from the nonstoichiometric starting composition). The mercury could easily be separated mechanically from the rest of the sample.

The corresponding thallium compound Au_2TlP_2 was prepared by reaction of the elemental components: gold wire (Degussa, 99.9%, 1 mm diameter), pieces of thallium (Chempur, 99.999%), and ultrapure red phosphorus. A pellet of cold-pressed gold and thallium (2:1) was reacted with the stoichiometric amount of red phosphorus in an evacuated silica tube. The sealing and annealing were carried out as described above for Au_2HgP_2.

PROPERTIES AND LATTICE CONSTANTS

Freshly prepared samples of the three ternary polyphosphides crystallize in the form of elongated prisms. They are dark with some metallic luster, like elemental silicon. The powders are black. They deteriorate slowly in air, as was investigated with Au_2PbP_2 using a scanning electron microscope. In the upper part of Fig. 1 we show a crystal of Au_2PbP_2, which had been isolated from a sample stored in air for several weeks. It can be seen that the crystal has sharp edges, thus indicating little attack by the hydrochloric acid, which had been used to dissolve the lead matrix right after opening the sample tube. Nevertheless, the surface shows some sign of deterioration. This can be better seen in the scanning electron micrograph in the lower part of Fig. 1. The material for this micrograph was taken from a sample of Au_2PbP_2 that had been kept in air for more than a year after the treatment with hydrochloric acid. This sample had a brownish color. The energy dispersive X-ray (EDX) fluorescence analysis of position **1** resulted in an Au:Pb:P ratio of 50(10):10(2):40(8) at.%, indicating the remainder of an original crystal. The analysis of position **2** showed a high oxygen content and no gold. However, small crystals of gold were observed in other positions of the sample. In this context we should mention that already the diffraction patterns of freshly prepared samples contain diffuse diffraction lines of elemental gold. The EDX analysis of position **2** resulted in a Pb:P:oxygen ratio of 12(3):9(2):79(20) at.%. This ratio is similar to the ideal ratio of 24:14:62 for lead hydroxy apatite $Pb_5(PO_4)_3OH$, and indeed the Guinier X-ray powder pattern of this deteriorated sample contained—besides the expected diffraction lines of Au_2PbP_2 and diffuse lines of fcc gold—as strongest peaks those reported for lead hydroxy apatite (8, 9).

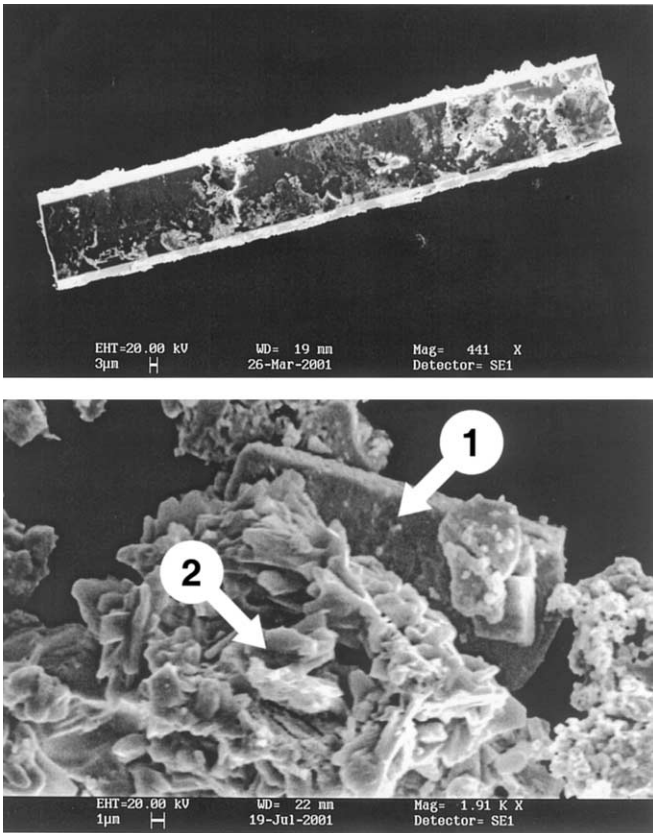


FIG. 1. Scanning electron micrographs of two samples of Au_2PbP_2. The upper micrograph shows a single crystal as obtained after dissolving the lead matrix in concentrated hydrochloric acid and storage on air for several weeks. The elongated dimension corresponds to the *a* axis; it has a length of approximately 0.25 mm. The lower part of the figure shows a sample of Au_2PbP_2 after treatment in hydrochloric acid and subsequent storage of the resulting Au_2PbP_2 crystals on air for more than one year. The EDX analysis of position **1** is compatible with the composition Au_2PbP_2; apparently it identifies the remainder of such a crystal. Position **2** gives an EDX analysis compatible with the composition $Pb_5(PO_4)_3OH$; apparently the plate-like crystallites are decomposition products after reaction of the Au_2PbP_2 crystals with moist air.

All samples were characterized through their Guinier patterns, recorded with monochromated Cu$K\alpha_1$ radiation using α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. To assure the proper assignement of indices the observed powder patterns were compared with those calculated (10), eventually using the positional parameters as obtained from the single-crystal investigation of Au_2PbP_2. The lattice constants were refined by least-squares fits (Table 1).

For the mercury compound Au_2HgP_2 we observed slightly different lattice constants for freshly prepared samples directly after the sample tubes were crushed and after the samples had been kept in air for several days or weeks. This was observed for two samples. As can be seen from the densitometer scans of the Guinier films (Fig. 2), there is not only a shrinking of the cell volume by about 0.5% (Table 2), but also a change in the axial ratios, resulting in a different appearence of certain groups of diffraction maxima. The scanning electron micrographs of such crystals of Au_2HgP_2 showed no signs of serious deterioration. Thus, the reason for this change in the lattice constants is not clear. It may be that the compound reacts with air. It could also be that a small fraction of the mercury atoms evaporates. For that reason we have kept one sample in an open vacuum of <0.01 Torr for one week at 70°C. After that treatment a fraction of the sample possibly had decomposed as could be judged from a visible gold content. The remainder of the sample gave a perfect diffraction pattern of the compound with the same lattice constants as were obtained previously for a sample exposed to air.

SINGLE-CRYSTAL INVESTIGATIONS

Fragments of crushed single crystals of the lead compound Au_2PbP_2 were investigated with an Enraf-Nonius four-circle diffractometer. The intensity data were recorded with graphite-monochromated Mo$K\alpha$ radiation, using a scintillation counter with pulse-height discrimination and $\theta/2\theta$ scans with background counts at both ends of each scan. An empirical absorption correction was applied on the basis of psi scan data. Further details are listed in Table 1.

The centrosymmetric space group *Cmcm* (No. 63) suggested by the program system SHELXTL PLUS (12) turned out to be correct during the structure refinement. For the structure determination and refinement the SHELX-97 program package (13) was used. The atomic positions obtained by Patterson and difference Fourier methods were refined by a full-matrix least-squares program using atomic scattering factors, corrected for anomalous dispersion as supplied by the program. The weighting scheme accounted for the counting statistics, and a parameter correcting for isotropic secondary exctinction was optimized as a least-squares variable. To check the composition we fixed the occupancy of the lead position, and we refined the occupancy parameters of the other atomic positions together with their displacement parameters. As can be seen from Table 3 all occupancy parameters of the lead compound Au_2PbP_2 were very

TABLE 1
Crystallographic Data for the Compounds Au_2PbP_2, Au_2TlP_2, and Au_2HgP_2

Compound	Au_2PbP_2	Au_2TlP_2	Au_2HgP_2
Formula mass	663.08	660.25	656.47
Space group	*Cmcm* (No. 63)	*Cmcm* (No. 63)	*Cmcm* (No. 63)
Cell parameters from Guinier powder [and single-crystal] data			
a (pm)	323.64(4) [323.73(3)]	324.07(6) [323.70(5)]	322.05(6) [322.04(5)]
b (pm)	1137.1(2) [1137.3(2)]	1136.1(2) [1135.0(2)]	1131.4(2) [1130.1(2)]
c (pm)	1121.8(1) [1121.6(1)]	1122.1(1) [1121.3(1)]	1122.6(1) [1122.3(2)]
V (nm^3)	0.4128(2) [0.4129(1)]	0.4131(2) [0.4120(1)]	0.4091(2) [0.4085(1)]
Formula units/cell, Z	4	4	4
Pearson symbol[a]	*oS*20	*oS*28–8	*oS*36–16
Calculated density (g/cm^3)	10.67	10.62	10.66
Crystal size (μm^3)	25 × 25 × 50	18 × 32 × 50	25 × 25 × 25
2θ range up to (°)	70	85	80
Range in h, k, l	0–4, ±16, ±16	±6, ±21, ±21	±5, ±20, ±20
Total number of reflections	2847	5922	4700
Independent reflections	541	857	713
Internal residual R_i (F^2)	0.050	0.104	0.080
Reflections with $F_o > 2\sigma$ (F_o)	478	682	539
Max./min. transmission	2.53	2.11	2.95
Variables	20	25	35
R ($F > 2\sigma$)[b]	0.022	0.036	0.026
R_w (all F^2)[c]	0.051	0.089	0.058
Highest/lowest residual peak (e/Å^3)	2.3/−2.9	8.8/−7.5	4.8/−2.9

[a] For definitions concerning the Pearson symbol see Ref. (11).

[b] $R = \sum||F_o| - |F_c|| / \sum|F_o|$.

[c] $R_w = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1\backslash 2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and P is $[2F_c^2 + \mathrm{Max}(F_o^2,\ 0)]/3$.

close to the ideal values, and we resumed with the latter in the final refinement cycles.

The structures of the corresponding thallium and mercury compounds were refined from single-crystal X-ray data essentially analogous to those described above for the lead compound. The only differences concerned the positions of the thallium and mercury atoms, as discussed below. In view of the fact that the mercury compound shows some change of the lattice constants on air, we should emphasize that the single-crystal of this compound used for the structure determination was isolated from a sample, which had been exposed to air for two weeks. The highest residual electron densities of the final difference Fourier syntheses were all in the vicinity of fully occupied gold positions and for that reason they were unsuited for additional atomic sites. The results of the structure refinements are summarized in Tables 1, 3, and 4. The crystal structure and the near-neighbor coordinations, as drawn with the program DIAMOND (15), are shown in Figs. 3 and 4.

The crystal data have been deposited. They may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the registry numbers CSD-412224 for Au_2PbP_2, CSD-412225 for Au_2TlP_2, and CSD-412226 for Au_2HgP_2.

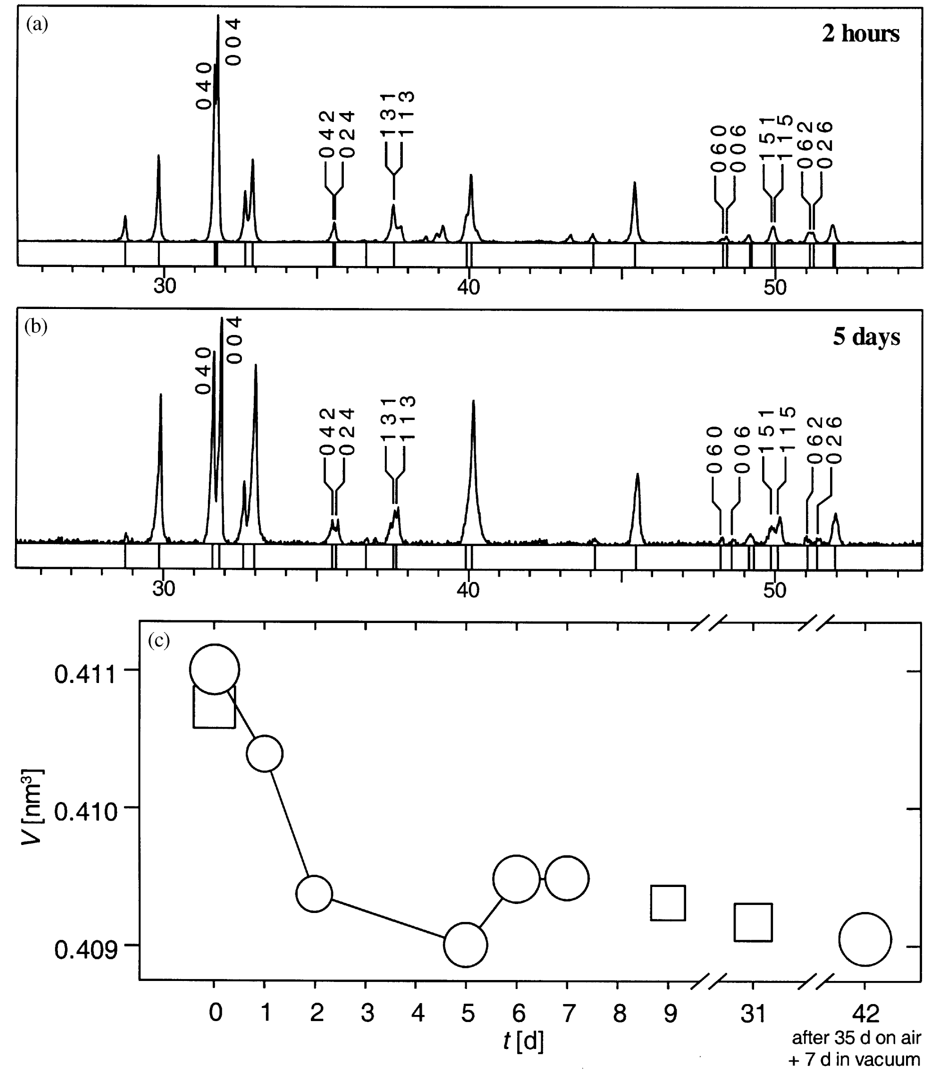


FIG. 2. Changes in the lattice constants of the mercury compound Au_2HgP_2. The top diagram (a) shows a cutout of a Guinier powder diffractogram of Au_2HgP_2 recorded with Cu$K\alpha_1$ radiation ca. 2 h after the sample had been taken out of the sample tube. The second diagram (b) has been recorded under exactly the same conditions (same sample window) five days later. The *hkl* values of some reflections with noticeable changes in their positions are indicated. The third diagram (c) shows the cell volumes of the compound for two samples. For one sample (squares) the lattice constants were measured directly after the sample tubes were opened and subsequently after 9 and 31 days. For the other sample (circles) the lattice constants were determined for the first 7 days and again after the sample had been exposed to air for another 28 days and kept subsequently at 70°C under vacuum for another 7 days. The size of the symbols approximately corresponds to the standard deviations.

TABLE 2
Lattice Constants of the Mercury Compound Au_2HgP_2 Directly after Opening the Sample Tubes and after Several Days[a]

Days	*a* (pm)	*b* (pm)	*c* (pm)	*V* (nm^3)
		Sample 1		
0	323.04(6)	1129.4(1)	1125.8(1)	0.4107(1)
9	322.38(4)	1131.0(1)	1122.6(1)	0.4093(1)
31	322.27(5)	1131.0(1)	1122.6(1)	0.4092(1)
		Sample 2		
0	323.04(5)	1129.5(2)	1126.4(1)	0.4110(2)
1	322.86(4)	1130.1(1)	1124.8(1)	0.4104(1)
2	322.52(5)	1130.2(1)	1123.0(1)	0.4094(1)
5	322.30(5)	1130.3(1)	1122.7(1)	0.4090(2)
6	322.33(4)	1131.1(1)	1123.2(2)	0.4095(2)
7	322.36(5)	1131.2(1)	1122.9(2)	0.4095(2)
35+7[b]	322.06(6)	1131.4(2)	1122.6(1)	0.4091(2)

[a] Standard deviations in the place values of the last listed digits are given in parentheses throughout the paper.
[b] The last seven days this sample had been kept at 70°C in an open vacuum of 0.01 Torr.

DISCUSSION

The crystal structure of Au_2PbP_2 is of a new, rather simple type with only four different atomic positions and four variable positional parameters. Both of the two different gold atoms have two phosphorus neighbors in linear arrangement as is frequently observed for Au(I) and isoelectronic Hg(II) compounds. The P–Au1–P angle is 167.28(9)°. The relatively small deviation from the ideal 180° can readily be ascribed to packing effects. The P–Au2–P angle is exactly 180° because of the site symmetry of the Au2 position. The Au1–P and Au2–P distances of 232.6(2) and 234.2(2) pm compare well with the Au–P distances of 233.1(1) and 233.9(1) pm in Au_2P_3 (1), 232.1(1) and 233.5(1) pm for the Au2 and Au1 atoms in $Au_7P_{10}I$ (1), and 232.6(3) pm in AuSiP (16). In all of these compounds the gold atoms have two close phosphorus neighbors, with the exception of AuSiP, where the gold atoms are in linear coordination of one silicon and one phosphorus atom (16). In addition to the two tightly bound phosphorus neighbors

TABLE 3
Atomic Parameters of the Three Polyphosphides Au_2PbP_2, Au_2TlP_2, and Au_2HgP_2[a]

Atom	*Cmcm*	Occupancy	*x*	*y*	*z*
Au1	4*c*	1.00(1)/1.00(1)/1.00(1)	0	0.22403(3)/0.22184(4)/0.22507(4)	$\frac{1}{4}$
Au2	4*a*	1.00(1)/1.01(1)/1.00(1)	0	0	0
Pb/Tl1/Hg1	4*c*	0.99(1)/0.92(1)/0.76(1)	0	0.47665(4)/0.47595(6)/0.4821(4)	$\frac{1}{4}$
Tl2/Hg2	8*g*	0.03(1)/0.10(1)	0.19(1)/0.11(3)	0.466(2)/0.472(3)	$\frac{1}{4}$
Hg3	8*g*	0.030(7)	0.42(1)	0.446(3)	$\frac{1}{4}$
P	8*f*	1.02(1)/0.98(1)/0.95(1)	0	0.2014(1)/0.2013(2)/0.2024(2)	0.0439(2)/0.0435(2)/0.0435(2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq} or U
Au1	205(2)/164(2)/163(2)	100(2)/137(2)/179(2)	36(2)/96(2)/73(2)	0	0	0	114(1)/132(1)/138(1)
Au2	195(2)/161(2)/159(2)	59(2)/77(2)/100(2)	92(2)/165(2)/182(2)	0	0	−3(1)/−3(1)/2(1)	115(1)/134(1)/147(1)
Pb/Tl1/Hg1	262(2)/238(7)/314(15)	137(2)/161(3)/203(10)	231(3)/309(4)/266(6)	0	0	0	210(1)/236(3)/261(5)
Tl2/Hg2	—/2311(891)	—/167(39)	—/201(29)	—/ −473(180)	—/0	—/0	217(48)/893(300)
Hg3	491(278)	356(101)	171(48)	94(116)	0	0	339(92)
P	113(7)/62(8)/65(8)	60(6)/83(7)/105(8)	37(6)/91(7)/71(6)	0	0	4(5)/ −3(6)/10(6)	70(3)/78(3)/80(3)

[a] Only one atomic position has been observed for the lead atoms. In the thallium and in the mercury compounds two thallium and three mercury positions were found, respectively. The occupancy values listed for the gold and phosphorus positions were obtained in previous least-squares cycles. In the final cycles the ideal occupancy values were assumed for these positions. For the lead compound the ideal occupancy values were used for all positions in the final least-squares cycles. Thus, in the final least-squares cycles only the occupancy values of the thallium and mercury positions were allowed to vary. The total occupancies for the thallium and the mercury compounds add up to the formulas $Au_2Tl_{0.98(1)}P_2$ and $Au_2Hg_{1.02(1)}P_2$, respectively. Whenever three values are listed for a variable, separated by slashes, the first one corresponds to the lead compound and the last one to the mercury compound. The positional parameters were standardized using the program STRUCTURE TIDY (14). The displacement parameters are listed in pm^2 units. The Tl2 position was refined only with isotropic displacement parameters.

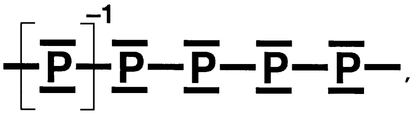
TABLE 4
Interatomic Distances in the Structures of the Ternary Polyphosphides Au_2MP_2 ($M = Pb/Tl/Hg$)[a]

Distances between fully or almost fully occupied atomic sites								
Au1:	2P	232.6(2)/232.9(2)/233.2(2)	Pb/Tl1/Hg1:	1Au1	287.3(1)/288.7(1)/290.8(4)	P:	2P	219.4(2)/219.1(3)/217.0(3)
	1Pb/Tl1/Hg1	287.3(1)/288.7(1)/290.8(4)		2Pb/Tl1/Hg1	323.6(1)/324.1(1)/322.1(1)		1Au1	232.6(2)/232.9(2)/233.2(2)
	2Au1	323.6(1)/324.1(1)/322.1(1)		2Au1	324.5(1)/322.9(1)/318.6(4)		1Au2	234.2(2)/233.9(2)/234.1(2)
	2Pb/Tl1/Hg1	324.5(1)/322.9(1)/318.6(4)		4Au2	324.9(1)/325.1(1)/324.2(1)		2P1	323.6(1)/324.1(1)/322.1(1)
Au2:	2P	234.2(2)/233.9(2)/234.1(2)						
	2Au2	323.6(1)/324.1(1)/322.1(1)						
	4Pb/Tl1/Hg1	324.9(1)/325.1(1)/324.2(1)						
Distances for the partially occupied sites Tl2, Hg2, and Hg3								
Tl2:	Tl2	61(3)	Hg2:	1Hg2	71(17)	Hg3:	1Hg3	51(7)
	Tl2	121(7)		1Hg3	104(7)		1Hg2	104(7)
	Tl2	203(7)		1Hg3	154(10)		1Hg1	142(4)
	Tl1	264(3)		1Hg3	174(11)		1Hg2	154(10)
	1Au1	284(2)		1Hg3	224(8)		1Hg2	174(11)
	2Au2	301(1)		1Hg2	251(17)		1Hg1	191(3)
	1Au1	307(2)		1Au1	282(3)		1Hg2	224(8)
	Tl2	324.1(1)		1Hg1	287(9)		1Hg3	271(7)
	2Au2	360(2)		2Au2	309(3)		1Au1	284(3)
	1Au1	366(3)		1Au1	313(3)		2Au2	288.4(6)
	2P	368(1)		2Hg2	322.1(1)		1Au1	312(4)
				2Au2	344(5)		1Au1	317(3)
				1Au1	347(7)		2Hg3	322.1(1)
				1Hg1	358(9)			

[a] These distances were computed with the lattice constants obtained from the Guinier powder data as listed in Table 1. All distances shorter than 370 pm are listed.

the gold atoms of Au_2PbP_2 have lead and gold atoms in their coordination shells (Table 4, Fig. 4). The Au–Pb distances vary between 287.3(1) and 324.9(1) pm. They may be considered as weakly bonding in view of the fact that the sum of the metallic radii for the coordination number (CN) 12 for gold (144.2 pm) and lead (175.0 pm) is of similar length (17) with 319.2 pm. The Au1–Au1 and Au2–Au2 distances of 323.6(1) pm (corresponding to the lattice constant *a*) are distinctly greater than the Au–Au distance of 288.4 pm in the cubic close-packed structure of gold (18). Hence, the Au–Au distances in Au_2PbP_2 can be considered as only very weakly bonding, especially also since the CN values of the Au1 (2P + 2Au + 3Pb) and Au2 atoms (2P + 2Au + 4Pb) are lower than that in the fcc structure of elemental gold with CN 12.

The phosphorus atoms are tetrahedrally coordinated by two gold and two phosphorus atoms. They form zigzag chains with a P–P distance of 219.4(2) pm. This distance is within the range of the single-bond P–P distances of 222 ± 4 pm found in many polyphosphides (19) and also in the various modifications of elemental phosphorus (18). In counting two electrons for each P–P bond, and assuming the octet rule to be valid for the phosphorus atoms (phosphorus is the most electronegative component and therefore the 3*s* and 3*p* states of phosphorus should be completely filled), we obtain the oxidation number (formal charge) −1 for the phosphorus atoms as can be seen from the corresponding Lewis formula



where each heavy line represents two electrons and the electrons shown as lone pairs form the bonds with the gold atoms.

Together the gold and phosphorus atoms form a three-dimensional infinite network of condensed eight-membered Au_2P_6 and 10-membered Au_4P_6 rings. As can be seen in the upper part of Fig. 3, these rings form channels that extend along the *x* direction. The channels contain the lead atoms, which are coordinated only by metal atoms: seven gold and two lead atoms. Of the seven gold neighbors, only one is at the relatively short Pb–Au distance of 287.3 pm, which is shorter than the sum of the CN 12 radii of 319.2 pm, as already discussed above. The other gold neighbors are at the weakly bonding distances of 324.5 (2 ×) and 324.9 pm (4 ×). The two lead neighbors of a lead atom are at the distance of 323.6 pm, which is shorter than the Pb–Pb distance of 350.0 pm, computed by us from the lattice constant of the cubic close-packed structure (CN 12) of elemental lead (18). Hence, a lead atom in Au_2PbP_2 has only three relatively strongly bonded neighbors: one Au1 atom and the two Pb neighbors within the same channel.

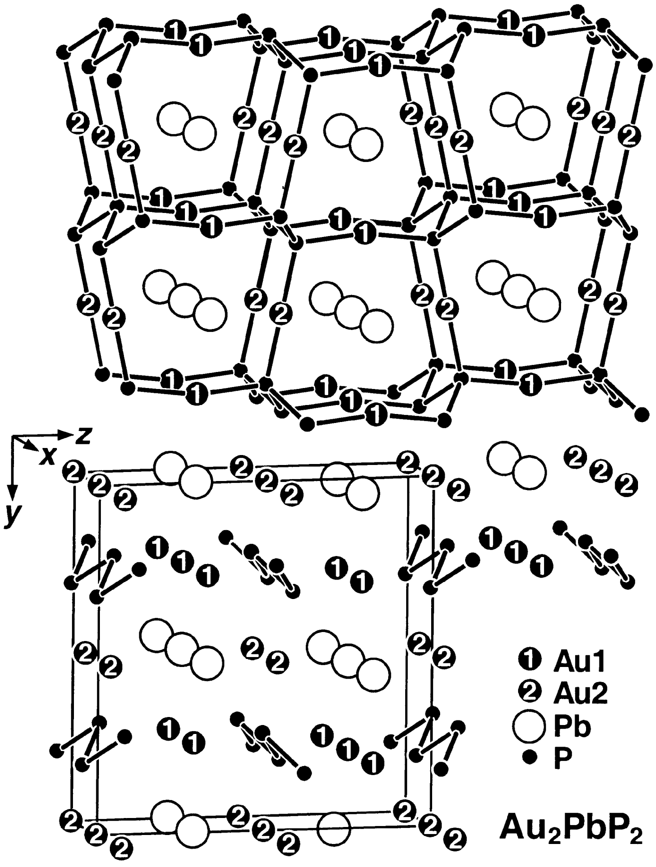


FIG. 3. Projection of the structure of Au_2PbP_2 emphasizing the three-dimensional network of gold and phosphorus atoms (top of the drawing) and the zigzag chains of phosphorus atoms (bottom).

This low coordination of the lead atoms is evidenced by their large thermal parameters, which are considerably greater than those of the (slightly lighter) gold atoms. Considering that the near-neighbor environments of the gold atoms are typical for gold in the oxidation state +1, and the phosphorus atoms of the phosphorus chains obtain the oxidation number −1, the lead atoms are assigned the oxidation number zero, according to the formula $(Au^{+1})_2Pb^{\pm 0}(P^{-1})_2$. In this context it is worth mentioning that lead does not form any binary lead phosphide, as was clearly demonstrated by growing Hittorf's modification of phosphorus from a flux of elemental lead (20).

To prevent frequently occurring misunderstandings we should make two remarks. One remark concerns the oxidation number. Ascribing the oxidation number zero to the lead atoms does not mean that they do not form chemical bonds with their neighbors. The lead atoms in elemental lead have by definition the oxidation number zero; yet they are well bonded to their neighbors. The carbon atoms in formaldehyde (H_2CO) or in sugar ($C_{12}H_{22}O_{11}$) have the oxidation number zero, although they form more or less polar bonds with the hydrogen and oxygen atoms (21). Two electrons are transferred in an electrochemical reaction oxidizing the carbon atoms in formaldehyde (oxidation number zero) to the carbon atoms in formic acid (HCOOH), where they have the oxidation number +2. The other remark concerns the concept of the two-electron bond in transition metal polyphosphides with low CN values, e.g., octahedral phosphorus coordination of the rhenium atoms in Re_6P_{13} (22) and Re_2P_5 (23). When two electrons are counted for each of the Re–Re, Re–P, and P–P interactions in Re_2P_5, the number of available valence electrons and the number of bonds exactly match, and consequently the compound is a diamagnetic semiconductor. In contrast, Re_6P_{13} is a paramagnetic (32) metallic conductor. Its structure is slightly electron deficient. Per formula unit 109 electrons would be needed to saturate all short near-neighbor interactions. The compound, however, has only $6 \times 7 + 13 \times 5 = 107$ electrons per formula unit. Thus, an electron deficiency of less than 2% is responsible for the paramagnetism and the metallic conductivity of this compound, or, vice versa, exactly (not nearly) two electrons need to be counted for each near-neighbor

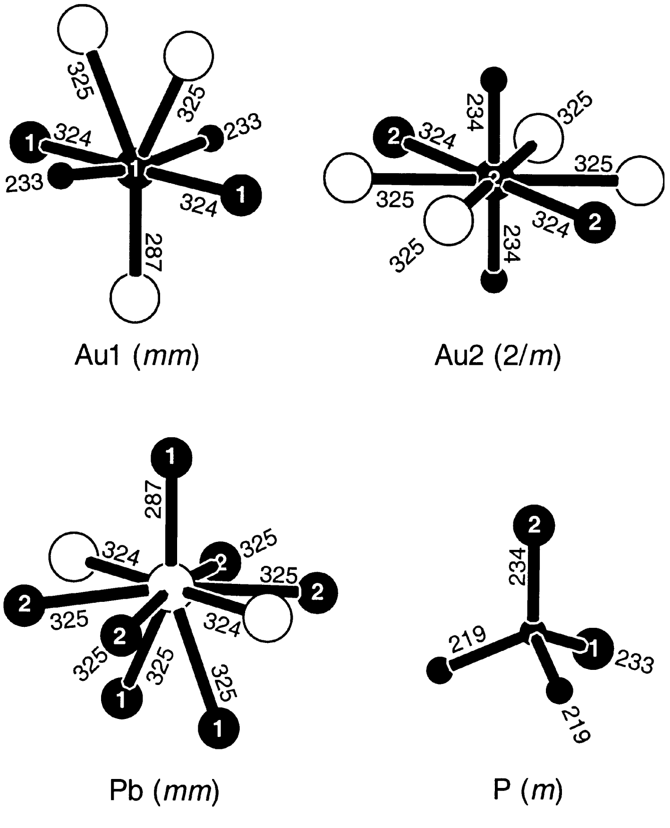


FIG. 4. Near-neighbor coordinations in the structure of Au_2PbP_2. The site symmetries are indicated in parentheses. Interatomic distances are in pm units.

interaction in Re_2P_5 to rationalize the diamagnetism and the semiconductivity of this compound. This example is so impressive because both compounds have been prepared the same way and their electrical conductivities have been measured by the same procedure (23).

The other two compounds Au_2TlP_2 and Au_2HgP_2 are essentially isotypic with the lead compound Au_2PbP_2. The gold and phosphorus atoms form parallel channels with practically the same Au–P distances in the three compounds. Thus, in analogy we can also assign the oxidation number zero to the thallium and mercury atoms corresponding to the formulas $(Au^{+1})_2Tl^{\pm 0}(P^{-1})_2$ and $(Au^{+1})_2Hg^{\pm 0}(P^{-1})_2$.

Some differences in the three structures concern the metal atoms within the channels. In Fig. 5 we show the displacement ellipsoids of the lead, thallium, and mercury atoms in views perpendicular to the channels that extend horizontally. The lead atoms have their largest displacement parameters U_{ii} in the x direction, the channel axis. This was also the case for the thallium and the mercury atoms as long as only one position for these atoms was offered in the least-squares refinements. However, the U_{11} parameters for the thallium and mercury atoms were that large that we preferred to refine these two structures with additional split positions for these metal atoms. The additional positions could clearly be located in the difference Fourier analyses. One additional position was found for the thallium atoms and two additional positions were found for the mercury atoms. The occupancy parameters of the two thallium and the three mercury atoms were then refined independently, and it can be seen from the results listed in Table 3 that they add up to the ideal composition within the error limits. The occupancy value of 0.030(7) for the Hg3 position seems to be almost insignificant in view of the relatively large standard deviation. However, the large standard deviation is a consequence of refining this position together with the thermal parameters. If an equivalent isotropic thermal parameter for the Hg3 position is fixed during the least-squares refinement, an occupancy parameter of 0.029 is obtained for the Hg3 position with the much smaller standard deviation of 0.003.

The unusual behavior of the thallium and especially of the mercury atoms in their respective host structures suggests a high mobility for these atoms in the direction of the channels, as is known for solid electrolytes, e.g., the mobility of alkali ions A^+ in the channels of various tungsten and vanadium bronzes, e.g., A_xWO_3 and $A_xV_2O_5$ (24), of barium ions in the structure of hollandite $Ba_x(Ti_{8-x}Mg_x)O_{16}$ (25, 26), of lithium ions in β-eucryptite $LiAlSiO_4$ (27, 28), or of the copper and silver ions in $Cu_2P_3I_2$ and $Ag_2P_3I_2$ (29). It seems possible that the shrinking of the lattice of the mercury compound Au_2HgP_2 during exposure to air—as described above (Table 2, Fig. 2)—is associated with a slight loss of mercury. Considerable more experimental work would be required to investigate the potential ionic conductivity behavior of Au_2HgP_2. Finally, we relate the remark of one reviewer, who pointed out that the crystal structure of Hg_3AsF_6 (30, 31) has—like Au_2HgP_2—infinite chains of partially occupied mercury atoms. In Au_2HgP_2 these chains are all parallel to each other, whereas in the

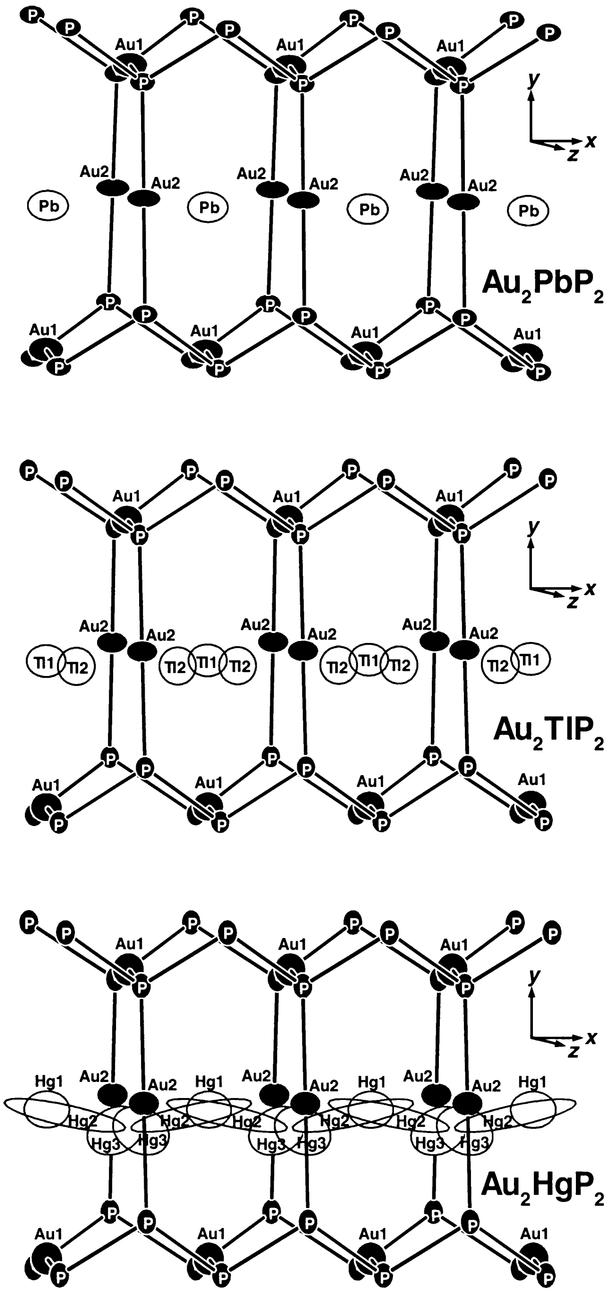


FIG. 5. Anisotropic displacement parameters in the structures of the three polyphosphides Au_2MP_2 (M = Hg, Tl, Pb) as viewed approximately perpendicular to the channel (x) direction. The thermal ellipsoids are drawn at the 90% probability limit.

tetragonal compound Hg_3AsF_6 the chains extend perpendicular to the 4_1 axis along the *a* and *b* directions. Another difference concerns the oxidation numbers. In the gold compound the mercury atoms have the oxidation number zero, whereas in the fluoroarsenate their oxidation number is 0.33.

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