Element Lines: Bonding in the Ternary Gold Polyphosphides, 
\( \text{Au}_2\text{MP}_2 \) with \( M = \text{Pb}, \text{Tl}, \text{or Hg} \)

Xiao-Dong Wen,† Thomas J. Cahill,†‡ and Roald Hoffmann*,†

Department of Chemistry and Chemical Biology, Cornell University, Baker Laboratory, Ithaca, New York 14853-1301; and Department of Chemistry, Hobart and William Smith Colleges, Geneva, New York 14456

Received August 30, 2008; E-mail: rh34@cornell.edu

Abstract: We present a theoretical study of the electronic structures of \( \text{Au}_2\text{PbP}_2 \), \( \text{Au}_2\text{TlP}_2 \), and \( \text{Au}_2\text{HgP}_2 \). Structurally, these compounds contain a framework of condensed \( \text{Au}_2\text{P}_6 \) and \( \text{Au}_4\text{P}_6 \) rings forming parallel channels, which are filled by lead, thallium, or mercury atoms. Given the linear coordination of the Au atoms and the existence of zigzag \(-[\text{P}\cdots\text{P}]-\) singly-bonded chains in them, these materials present us with a rare instance of approximately linear, one-dimensional, and zerovalent element (Pb, Tl, or Hg) chains with a variable electron count. The Pb–Pb, Tl–Tl, and Hg–Hg element lines in these structures have somewhat longer bond lengths than their respective single bond lengths or their separations in (calculated) isolated chains. Yet, the zerovalent element interactions are prominent and are responsible for the metallicity of some of these materials. In the calculations, both \( \text{Au}_2\text{PbP}_2 \) and \( \text{Au}_2\text{TlP}_2 \) emerge as metallic, whereas \( \text{Au}_2\text{HgP}_2 \) is a semiconductor. The isolated element chains do not undergo a pairing (Peierls) distortion nor do the chains in the three-dimensional termanies. The small barrier for mobility of the Pb, Tl, and Hg atoms along the chain axis may explain the large thermal parameters observed in the crystal structures along the chain axis (and the need to use fractional occupations of several positions along the chain). These ternaries may show one-dimensional liquidlike behavior under some conditions.

Introduction

In 2002, the polyphosphide compounds \( \text{Au}_2\text{PbP}_2 \), \( \text{Au}_2\text{TlP}_2 \), and \( \text{Au}_2\text{HgP}_2 \) were synthesized and characterized by Eschen and Jeitschko (Figure 1).†

All three ternary structures feature one-dimensional channels built of Au and P, filled by lead (Pb), thallium (Tl), or mercury (Hg) atoms. The crystal structures of these compounds show two distinct (but as it turns out not very different) Au atoms, \( \text{Au}1 \) and \( \text{Au}2 \), one P, and one \( M \) atom (\( M = \text{Pb}, \text{Tl}, \text{or Hg} \)). The Au atoms are linearly or nearly linearly coordinated by their neighboring P atoms. The phosphorus atoms form zigzag chains of 2.194 Å; this is close to a typical P–P single bond (\( \sim 2.22 \) Å). The phosphorus atoms are approximately tetrahedrally coordinated by two gold and two phosphorus atoms.

Assuming the validity of the octet rule, as well as the electronegativity of the atoms involved, Eschen and Jeitschko suggested (and we certainly concur) that the Au atoms and the P atoms should be assigned oxidation numbers +1 and −1, respectively. Since the ternary compounds are neutral, the Pb, Tl, and Hg atoms must then be in formal oxidation state 0. The Pb–Pb, Tl–Tl, and Hg–Hg distances are 3.236, 3.241, and 3.221 Å in their respective ternary compounds, which are somewhat shorter (except for Hg) than the corresponding elemental distances (Pb: 3.50 Å (fcc); Tl: 3.41 Å (hcp)); and

Figure 1. Crystal structure of \( \text{Au}_2\text{PbP}_2 \); the illustration is reproduced with permission from ref 1.

Hg: 3.03 Å (rhombohedral). There is clearly bonding among these linearly aligned element chains. At the same time, the
The three ternary gold polyphosphides synthesized by Eschen and Jeitschko thus provide us with materials containing nearly one-dimensional $M$-atom chains, which vary in electron count. One-dimensional materials are pretty rare, and this is a good reason for exploring these compounds theoretically. We begin with a detailed analysis of the lead compound to be followed by its thallium and mercury analogues.

**Computational Details. DFT Method.** DFT$^5$–$^7$ periodic calculations, as implemented in the Vienna ab initio simulation package$^8$–$^{14}$ (VASP) are carried out. For the exchange-correlation functional, the local density approximation (PAW-LDA) is employed with projector augmented wave (PAW) potentials.$^{15,16}$ In all calculations, the energy cutoff for plane waves is 400 eV using a Monkhorst Pack $k$-point grid.$^{17}$

**Extended Hückel Theory.** After the structures are optimized with DFT, extended Hückel (eH)$^{18}$ calculations are performed on each structure, utilizing the YAeHMOP program.$^{19}$ The default extended Hückel parameters are employed. The eH calculations are certainly less reliable for structures but offer a number of analytical tools for exploring the nature of bonding. With the DFT program we use, it is difficult to get reliable atomic and orbital contributions to the density of states (DOS).$^{20}$

---

**Table 1. Theoretical Unit Cell Parameters, Bond Lengths ($\text{Å}$), and Angles (deg) of $\text{Au}_2M_2P_2$ with $M = \text{Pb}, \text{Tl}, \text{or Hg}$ Calculated with DFT**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\text{Au}_2\text{PbP}_2$</th>
<th>$\text{Au}_2\text{TlP}_2$</th>
<th>$\text{Au}_2\text{HgP}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>3.20</td>
<td>3.19</td>
<td>3.16</td>
</tr>
<tr>
<td>$b$</td>
<td>11.32</td>
<td>11.31</td>
<td>11.25</td>
</tr>
<tr>
<td>$c$</td>
<td>11.16</td>
<td>11.17</td>
<td>11.16</td>
</tr>
<tr>
<td>$P$–$P$</td>
<td>2.18</td>
<td>2.18</td>
<td>2.15</td>
</tr>
<tr>
<td>$P$–$\text{Au1}$</td>
<td>2.31</td>
<td>2.32</td>
<td>2.32</td>
</tr>
<tr>
<td>$P$–$\text{Au2}$</td>
<td>2.33</td>
<td>2.33</td>
<td>2.32</td>
</tr>
<tr>
<td>$M$–$M$</td>
<td>3.20</td>
<td>3.19</td>
<td>3.16</td>
</tr>
<tr>
<td>$M$–$\text{Au1}$</td>
<td>2.86 (3.22)</td>
<td>2.89 (3.20)</td>
<td>2.88 (3.16)</td>
</tr>
<tr>
<td>$M$–$\text{Au2}$</td>
<td>3.23</td>
<td>3.23</td>
<td>3.21</td>
</tr>
<tr>
<td>$\angle P$–$\text{Au1}$–$P$</td>
<td>166.9</td>
<td>168.3</td>
<td>166.7</td>
</tr>
<tr>
<td>$\angle P$–$\text{Au2}$–$P$</td>
<td>180.0</td>
<td>180.0</td>
<td>180.0</td>
</tr>
</tbody>
</table>

$^*$ There are two $M$–$\text{Au1}$ bonds in these ternary compounds; the second is indicated in parentheses.

---

Crystal and Electronic Structure of $\text{Au}_2\text{PbP}_2$. Utilizing DFT, the unit cell parameters and the bond lengths are computed for $\text{Au}_2\text{PbP}_2$ (Table 1) and are found to be within 1.2% of experimentally determined values. For instance, the optimized $P$–$P$ (2.18 Å) and $\text{Pb}$–$\text{Pb}$ (3.20 Å) bond lengths are close to the experimental $P$–$P$ (2.194 Å) and $\text{Pb}$–$\text{Pb}$ (3.236 Å) bond lengths. The space group of this ternary compound, C$mcm$, forces the $P$–$\text{Au2}$ angle to be 180.0°. However, the computed $P$–$\text{Au1}$–$P$ angle (166.9°) is in good agreement with the experimental data (167.77°). The agreement for the Tl and Hg cases, to be discussed later, is equally good.

Let us look at the electronic structure of $\text{Au}_2\text{PbP}_2$ first, and then use the resulting analysis to understand systems containing the Tl and Hg chains. The significant total DOS (TDOS) at the Fermi level (adjusted to 0 eV for easier comparison of eH and DFT results) for $\text{Au}_2\text{PbP}_2$ (eH). The dotted vertical line indicates the adjusted Fermi level at 0 eV. The combined $(s + p + d)$ partial or projected (PDOS) of one P and Au1 atom are shown. The PDOS of Au2 is very similar to the PDOS of Au1. For one Pb atom, the s, p, and d orbital contributions to the DOS are given separately by black, red, and green lines, respectively. Note that the PDOS scales are different for each element.
The contributions to the DOS are explored utilizing partial densities of states (PDOS), with DFT (Figure 2 and Figure S1 in the Supporting Information). For Au, the d orbitals are almost completely filled (DOS between −2.5 and −8 eV), as one would expect from its [Xe]5d¹⁰ configuration (for Au⁺⁺). The 6p and 5d orbitals of the Au atoms contribute little at the Fermi level. The 3p orbital of P is partially filled (there is substantial s and p density above the window of the graph). The Fermi level falls in a region with no P density; the 3s orbital of P is found far below. For Pb, it is clear that the crystal orbitals derived from the 6s are also found far below the Fermi level. There is not much s-p mixing for Pb. However, the 6p orbital of Pb is partially filled and crosses the Fermi level. This indicates that the Pb atoms play an important role in the metallic behavior of Au₂Pb₂.

The contributions to the DOS are also explored with the eH method (Figure 2b). In general, the DOS and its decompositions are similar in the two methods. The apparent discrepancy on the P states (few states above the Fermi level) is not serious; the eH calculations have a good number of unoccupied p orbital states above the energy window selected. However, eH calculations indicate substantial mixing between the 3s and 3p orbitals of P and between the 6s and 6p orbitals of Pb. In contrast to DFT, eH calculations show a significant contribution from the Au 6p orbital at the Fermi level. Clearly, there is more s-p mixing in eH than in DFT calculations. Since there are real problems with the PDOS calculations in the DFT procedure employed, we do not know which method to trust in this matter; we will continue employing both, taking advantage of the strengths of each. To be specific, we will use DFT for energetics and eH for analysis of bonding.

Where are the Bonds? The density of states only gives information about the location of electrons but not about the character of the bonds. In order to analyze the bonding in Au₂Pb₂, we employed both crystal orbital overlap populations (COOP) and crystal orbital Hamilton populations (COHP; Figure 3 for selected bonds; all bonds and respective COOP curves shown in Figure S2 in the Supporting Information). The strength of the bonds can be gauged with COOP calculations; positive and negative regions are bonding and antibonding, respectively, as measured by a Mulliken overlap population. COHP is an energy partitioning, with negative values indicating bonding.

(a) P–P. The P–P OP is 0.83, as shown in Figure 3a, but is that typical of a single bond? We computed the OP of different PP bonds in simple compounds, as a comparison standard: (1) a single bond in H₂P–PH₂; (2) a double bond in HP=PH; (3) a triple bond in P≡P (Figure 4). The OP of the P–P chain in Au₂Pb₂ indicates a single bond. The P–P single bond distance in many known compounds is around 2.19 Å to 2.26 Å.

(b) Au–Pb. Three different Au–Pb distances are observed in this ternary compound: two different Au–Pb contacts (2.86 Å and 3.22 Å) and one Au₂–Pb (3.23 Å). For the shortest bond among these, the HP value (−4.83 eV) is substantial (Figure 3b). Furthermore, the Fermi level falls into a region of Au–Pb bonding. This result is interesting, as it indicates that a simplistic model of Pb, Ti, or Hg lines sitting in an “inert” channel is only a first approximation. There are clearly some covalent interactions between the channel atoms (especially Au1) and Pb, as demonstrated by the HP value cited and the 2.86 Å Au1–Pb distance, which is similar to the sum of the atomic radii of Au (1.34 Å) and Pb (1.54 Å). The interaction of the Pb atoms with the other Au ions lining the channel is much weaker than the one shown in Figure 3b.

We probed the Au1–Pb interaction further by computing a [PH₃–Au–PH₃]⁺⁺ system (details not given here). This molecular model has a pair of nearly pure Au 6p LUMOs. It is primarily these orbitals that interact with the Pb atoms.
Figure 5. How the OP varies with Pb-Pb distance for various molecular model compounds containing Pb-Pb bonds: a Pb–Pb single bond (H,Pb=PbH₃, D₉c, solid line), a double bond (H,Pb=PbH₃, D₉a and C₉b). The solid dot marks the distance and OP of the Pb–Pb chain in Au,Pb₂.

(e) Pb–Pb. The unique characteristic of Au,Pb₂ is the element line consisting of Pb atoms. The Pb–Pb bond length is 3.20 Å, perforce the same value as the unit cell parameter a. The Pb–Pb distance in Au,Pb₂ is a little longer than the sum of atomic radii of two Pb atoms (3.08 Å). For the Pb–Pb interaction shown in Figure 3c, both the OP (0.40) and the HP (−6.25 eV) indicate Pb–Pb bonding. But, how much?

For calibration, the OP as a function of distance was computed for a prototypical Pb–Pb single bond (H,Pb,PbH₃) and a hypothetical double bond (H₂PbPbH₂) with two different geometries (Figure 5). It is apparent that the Pb–Pb OP in Au,Pb₂ falls below the single (or double); we do not want to enter here the important but vexing discussion on multiple Pb–Pb bonding) bond zone but not by much; the Pb–Pb bonding in the channels is substantial, even if it is relatively weak.

Turning to experiment, Power’s review of group 14 dimers shows trans-bent alkene congener with Pb–Pb distances of 2.990 Å in [Pb(Si(SiMe₃)₃)₂] and 3.052 Å in [Pb(Pb₂PbPb), Pb–Pb = 2.85 Å]. In the extended Ti₉P₈₈ structure, Kleinke observed one-dimensional, nonisolated Pb single bond (H₃PbPbH₃). In this extended structure, the Pb–Pb bond is noticeably shorter than the typical Pb–Pb single bond (3.10 Å).

In Au,Pb₂, two similar Au–P bonds are observed: Au₁–P (2.31 Å) and Au₂–P (2.33 Å), both of which are within the range of experimental and theoretical Au(I) phosphine complex distances (2.270–2.460 Å). In addition, the large calculated negative HP values (−15.46 eV for Au₁–P, −15.31 eV for Au₂–P) support strong Au–P bonding.

There is no Au–Au bonding to speak of, as indicated by the small OP value of 0.01. In molecular systems, at similar separations (~3.20 Å) between Au atoms, one sometimes observes weak bonding termed aurophilic.

Au₂TlP₂ and Au₂HgP₂. Au₂TlP₂ and Au₂HgP₂ are isotypic with Au₂P₂ and Au₂P₂. The DFT optimized structural parameters are shown in Table 1. They are within 2% of the observed structures. We will return later to the fractional occupancy of several sites that was needed in the Eschen and Jeitschko refinement.

Let us look at the electronic properties of Au₂TlP₂ and Au₂HgP₂. The Au and P PDOS in both compounds (not shown but, in Figures S3 and S4 in the Supporting Information) are similar to those seen in Figure 2 for Au₂P₂. The total DOS at the Fermi level for Au₂TlP₂ indicates that the compound should be metallic (Figure 6). The PDOS shows the Tl p orbitals cross the Fermi level; thus, the Tl chain is responsible for the metallicity of Au₂TlP₂.

Should we expect the same behavior for Au₂HgP₂? No, our analysis of isoelectronic Pb₃⁺ indicates a large gap at the Fermi level. For Hg, [Xe]5d¹⁰6s², the 6s and 5d bands are filled, and there is a real gap to the 6p band. To no surprise, the TDOS of Au₂HgP₂ has a pseudogap at the Fermi level (Figure 7), and the PDOS of Hg shows no significant contributions at this energy. The calculated band structure (Figure S9 in the Supporting Information) confirms the existence of a real (albeit small) energy gap at the Fermi level.

Au₂P₂ Framework, without the Element Lines. To explore the role of the M atoms in the ternary compound, the M–M element lines were removed. The optimized lattice constants a, b, and c for the resulting hypothetical Au₂P₂ complex are 3.17,
1. The interaction of the Pb line with the Au$_2$P$_2$ network changes the electron count in the chain. The eH charge on each Pb in Au$_2$PbP$_2$ is +0.70. The OP in the corresponding polymer is 0.54 (Table 2), but the Fermi level is naturally lower.

2. Pb–Au interactions spread the levels of the Pb line and weaken its bonding. We probed this in two ways: by (a) removing the 8Au$^{1+}$ from the Z = 4 [Au$_2$PbP$_2$]$_2$ ternary (i.e., calculating [PbP$_2$]$_2$), (b) adding two external Au$^{1+}$ to each Pb in a one-dimensional Pb chain, [(PbAu)$_2$]$_2$, as shown in A. The first option gives a Pb–Pb OP of 0.30, even lower than the ternary Pb–Pb OP. The second approach (several structural variants on A were also attempted) gives a Pb–Pb OP also around 0.30 (Table 2).

As Figure 8 shows, Au$_2$P$_2$ (an electron precise compound, with Au$^{1+}$ and (P$^{1+}$)$_n$ chains) is a semiconductor, with a small gap (larger with eH) at the Fermi level. Clearly, the presence of the $M$–$M$ chains in the channels of the Au$_2$P$_2$ lattice is responsible for the metallicity of Au$_2$P$_2$ with $M$ = Pb or Tl.

**Scrutinizing the Element Lines: A One-Dimensional Model for the Pb Chain.** In order to better understand the electronic structure of the element lines in the Au$_2$PbP$_2$ compound, a simple one-dimensional chain of Pb atoms (one atom per unit cell) with a length of 3.20 Å was computed and analyzed with the eH method (Figure 9). The band structure is just about what would be expected for a moderately interacting one-dimensional array of main group atoms. The bands built up by Pb 6s and 6p ($z$ is the line axis) orbitals have positive and negative slopes. The COOPs show weak, but noticeable s–p mixing. The Fermi level (for a neutral chain) passes through the p$_z$ and $\pi$ (p$_x$, p$_y$) bands.

The isolated Pb–Pb chain was optimized with DFT, yielding a Pb–Pb bond distance of 2.80 Å. Note that this distance is somewhat shorter than the spacing enforced by the gold polyphosphide lattice (3.20 Å). There is some stress in the Au$_2$PbP$_2$ structures.

The Pb–Pb OP and HP for the isolated one-dimensional chain is 0.59 and $-9.69$ eV, respectively, larger in magnitude than for the corresponding element lines (0.40 and $-6.25$ eV) existing in the channels. The Fermi level in the isolated chain is lower, and the Pb–Pb bond is stronger than in the ternary. There are several possible reasons for this, which we explored:

1. The interaction of the Pb line with the Au$_2$P$_2$ network changes the electron count in the chain. The eH charge on each Pb in Au$_2$PbP$_2$ is +0.70. The OP in the corresponding polymer is 0.54 (Table 2), but the Fermi level is naturally lower.

2. Pb–Au interactions spread the levels of the Pb line and weaken its bonding. We probed this in two ways: by (a) removing the 8Au$^{1+}$ from the Z = 4 [Au$_2$PbP$_2$]$_2$ ternary (i.e., calculating [PbP$_2$]$_2$), (b) adding two external Au$^{1+}$ to each Pb in a one-dimensional Pb chain, [(PbAu)$_2$]$_2$, as shown in A. The first option gives a Pb–Pb OP of 0.30, even lower than the ternary Pb–Pb OP. The second approach (several structural variants on A were also attempted) gives a Pb–Pb OP also around 0.30 (Table 2).

**Table 2. Calculated Pb–Pb OP and Fermi Level (eV) of Au$_2$PbP$_2$ and of the Hypothetical Sublattices ([PbP$_2$]$^+$, [Pb]$^{2+}$, and [Pb]$^{3+}$)**

<table>
<thead>
<tr>
<th>Pb–Pb OP</th>
<th>Fermi level (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_2$PbP$_2$</td>
<td>0.40</td>
</tr>
<tr>
<td>[PbP$_2$]$^+$</td>
<td>0.30</td>
</tr>
<tr>
<td>[Pb]$^{2+}$</td>
<td>0.54</td>
</tr>
<tr>
<td>[Pb]$^{3+}$</td>
<td>0.59</td>
</tr>
</tbody>
</table>

The parameters and positions of the remaining atoms were not changed from those computed in Au$_2$PbP$_2$.

We conclude that both effects, interaction with Au$^{1+}$ and charging of the Pb chain, contribute, difficult as they are to take apart.

**TI and Hg Lines.** An important aspect of these structures is the electronic tuning provided by the replacement of Pb with TI or Hg. There is a change due to the inherent difference in the elements, and there is a change due to the level filling: TI has one less electron, Hg two less. In a frozen band approximation (using the Pb bands to reason about the TI and Hg structures), the $M$–$M$ bonding should weaken as one removes electrons, and the Hg line may show a band gap, as the s and d bands should be filled.

Let’s see what happens with “real” TI and Hg chains. The TI chains are similar to the Pb chains in their behavior. For example, both the computed Pb and the TI have $\pi$ contributions...
at the Fermi level. On the other hand, the computed Hg chains have a large gap at the Fermi level. (Further details in Section SB of the Supporting Information). The OPs for the one-dimensional isolated Pb, Tl, and Hg chains are computed as a function of bond distance (Figure 10). Interestingly, a decrease in $M-\cdots M$ bonding is predicted for both the Pb chains and the Tl chains upon entering into the Au$_2$P$_2$ channel, while for Hg there is a small increase in bonding. The effect is largest for Tl.

Possible Peierls Distortion of the $M-\cdots M$ Linear Chains. One-dimensional chains with partially filled bands are prone to undergo Peierls distortions, alternatively viewed as electron–phonon coupling. In general, these lower the energy of the system and create a gap at the Fermi level. Dimerization, leading to alternating long and short bonds, is the common consequence for a half-filled band. We begin by probing the potential Peierls distortions in the element lines by investigating three one-dimensional Pb chains: (a) a linear chain (1) and (b) two planar zigzag chains (2 and 3). The geometries are shown in Table 3.

For the linear Pb chain, all simple pairing distortions led back to the linear polymer geometry. The absence of a Peierls distortion was at first sight surprising. When a one-dimensional congenic C chain is modeled, the expected Peierls distortion

![Figure 9. Band structure, TDOS and COOP of a one-dimensional Pb–Pb chain (Pb–Pb = 3.20 Å) calculated with the eH method. The dotted horizontal line indicates the Fermi level.](image)

![Figure 10. Overlap population of isolated M chains (Pb, Tl, or Hg) as a function of varying bond lengths (eH): The dot marks the location of the OP for the Pb, Tl, and Hg chains in their ternary compounds.](image)

![Figure 11. Band structures (DFT) of the optimized C linear chain (1.27 Å) and the Pb linear chain (2.80 Å) with one atom per unit cell. The main orbital contributions are shown.](image)

![Table 3. Structures, Geometrical Parameters, and Energies of Isolated Pb Chains (DFT) are Shown](image)

### Table 3. Structures, Geometrical Parameters, and Energies of Isolated Pb Chains (DFT) are Shown

<table>
<thead>
<tr>
<th>Structure</th>
<th>Distances and Angles</th>
<th>$E_f$ (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$a=b=2.80$ Å</td>
<td>-2.25</td>
</tr>
<tr>
<td>2</td>
<td>$a=b=2.82$, $a=114^\circ$</td>
<td>-2.47</td>
</tr>
<tr>
<td>3</td>
<td>$a=b=3.10$, $a=60^\circ$</td>
<td>-2.92</td>
</tr>
</tbody>
</table>

The formation energy ($E_f$) per Pb atom in the unit cell is calculated: $E_f = 1/2[\text{energy of Pb chain for 2 atoms in unit cell} - (2 \times \text{energy of Pb atom})]$.

(35) Note the difference in these curves for the Pb single and double bond models of the structures, inset in Figure 5; the isolated line for Pb features some multiple bonding.
The Fermi level does not half-fill either the $\pi$ or the $\sigma_p$ band, so the simplest Peierls distortion does not occur.

However, we found more complicated stabilizing distortions with $Z = 2$, two atoms per unit cell. Two different zigzag structures, 2 and 3, were obtained when the optimization is performed from a nonlinear starting geometry. The Pb atoms in 2 are coordinated by two Pb atoms with a Pb–Pb distance of 2.82 Å and a Pb–Pb–Pb angle of 114°. However, the Pb atoms in 3 are coordinated by four Pb atoms with a Pb–Pb distance of 3.10 Å and a Pb–Pb–Pb angle of 60°. Both structures are metallic.

An interesting question is whether there exists a barrier to this increase in dimensionality. We have probed this by building a potential energy surface relating 1, 2, and 3 (Figure 12). There is essentially no barrier (<0.01 eV) between linear chain 1 and ribbon 2 and only a small barrier (~0.06 eV) between the two ribbon geometries. Such barriers, conferring metastability and possible kinetic persistence on lower dimensional materials, are likely to be highest for C.

Though we do not find a Peierls distortion for an isolated Pb chain, could the tension occasioned by fitting that chain into the Au$_2$Pb$_2$ “box” (with its stretched repeat distance of 3.20 Å) activate the pairing distortion? Calculations utilizing a 2 × 1 × 1 super cell of Au$_2$Pb$_2$ indicate no tendency toward distortion in the Pb chains. We have not explored deviations from stoichiometry that might accommodate such distortions (e.g., y Au per x Pb, where y/x = 2).

Returning to simple, isolated Pb chains, there are other, still more stable structures than 2 or 3. The Pb chain may coil up in a helix, make a ladder, and build more complicated structures. It turns out that all of the other computed structures (see Figure S14 in the Supporting Information) are preferred over the linear chain.

Is this a surprise? It should not be, as such ribbons, helices, and ladders are essentially ways of increasing dimensionality; they are stages in moving from a one-dimensional to a two-dimensional and eventually to a three-dimensional structure. In the case at hand, elemental Pb, in the face centered cubic (fcc) lattice, is the expected limit of these distortions. Its computed (DFT) formation energy is ~−3.83 eV on the scale shown. To put it another way, the Pb atoms desire more neighbors than a linear geometry provides. They can get them within a one-dimensional constraint by bending, kinking, and/or curling up in a variety of ways.

Pb dimer chains have been observed experimentally on a Si(100) surface with STM. Theoretical work also describes Pb dimer chains on Si(100). Chan et al. suggested that these Pb dimer chains form near step edges of the Si(100) substrate.

Table 4. Relative Total Energy per Unit Cell (eV) for the Three Ternary Compounds as the Metal Atom Chains (Four M Chains/Unit Cell) are Slid through the Channel

<table>
<thead>
<tr>
<th></th>
<th>initial (P0)</th>
<th>step 1</th>
<th>step 2</th>
<th>step 3</th>
<th>step 4 (Pf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_2$Pb$_2$</td>
<td>[0]</td>
<td>0.11</td>
<td>0.43</td>
<td>0.84</td>
<td>1.07</td>
</tr>
<tr>
<td>Au$_2$TIP$_2$</td>
<td>[0]</td>
<td>0.10</td>
<td>0.40</td>
<td>0.79</td>
<td>1.08</td>
</tr>
<tr>
<td>Au$_2$Hg$_2$</td>
<td>[0]</td>
<td>0.09</td>
<td>0.32</td>
<td>0.62</td>
<td>0.74</td>
</tr>
</tbody>
</table>

*The energies are referred relative to that for P$_0$.

Recently, coupled Pb chains were found experimentally by Tegenkamp et al. on a Si(557) surface. Recently, Höhn et al. reported a study of the ternary nitrides Ga$_3$N$_x$M$_{3-x}$, which contain one-dimensional chains similar to the Au$_2$M$_2$ compounds ($M = \text{Pb, Tl, or Hg}$). These linear chains are referred to as “guests in a subnitride host.” Höhn et al. suggested that the interaction between the $M$ chain and the channel inhibits a Peierls distortion.

Sliding the Chains through the Lattice. Could the metal atoms occupy different positions along the chain in these ternary compounds, and if so, might this cause the metal chains to buckle slightly? A small potential energy surface was probed to locate other energy minima (Table 4). The $M$ chain atoms were gradually moved a total distance of 1.6 Å in the $a$ direction (along the channel, in four 0.4 Å steps from $P_0$ to $P_4$) in single point calculations without changing the optimized $M$–$M$ distances in Au$_2$MP$_2$ (displayed in Scheme 1). Note that there are four $M$ atoms (thus, four $M$ chains) per unit cell; all chains were shifted in the same direction and by the same amount. As the metal chain atoms (Pb, Tl, or Hg) were shifted further from their optimized positions, the total energy increased.

To put it another way, we have calculated here an approximate barrier to the Pb chains sliding along the channel axis of 1.07 eV per 4 Pb atoms (~6 kcal/Pb atom). This energy is small, comparable with the typical activation barriers observed for ionic conduction (~11 kcal, under elevated pressure and...
temperature).\(^{44,45}\) The possibility of chain mobility (or liquid-like behavior at slightly elevated temperatures) is fascinating. The small barrier for Pb motion along the chain axis (and the still smaller barrier for Hg) may also explain the large thermal parameters along the chain axis observed in the crystal structures and the refinement that required alternative sites for Hg (and Tl).

Next, optimizations were performed to determine if any of these single point geometries (Steps 1, 2, 3, or 4 as shown in Table 4) might "activate" buckling of the chain. The symmetry was not constrained in these optimizations. Depending on the initial point of the chain in the channel, two different energy minima were found for each ternary compound. Optimizations beginning in Step 1 or 2 geometries, all (for all three ternary compounds) reverted back to their initial P0 structures, labeled OPT P0. But, optimizations starting from the Step 3 or 4 geometries converged to new structures, with the same Cmcm group, labeled OPT P1 (as the M chains most closely resembled the geometries utilized in Step 4 of the single point calculations).

In what way are the OPT P1 structures different from the OPT P0 ones? Overall, the answer is "not much." The differences in unit cell parameters and distances are less than 2%. However, there is an essential and obvious change in Pb (and Au2) coordination as indicated in Structures C and D with Pb = black, Au1 = 1, and Au2 = 2. Note that the four 4-fold coordination of Pb by Au2 in OPT P0 is now 2-fold in OPT P1.

If the barrier to sliding the lines through the lattice is taken as \([E_{\text{OPT P1}}] - E_{\text{OPT P0}}\), we are led to an activation barrier per four chains in a unit cell of 0.25 eV (Pb), 0.12 eV (Tl), and 0.06 eV (Hg). Per chain, this energy comes to less than 0.07 eV = 1.6 kcal/atom of M. That is a really small energy, which helps us understand the large anisotropic displacement parameters and the need for alternative sites in the structural refinement.

There are some interesting differences among the three polyphosphides, to which we alluded. The structural refinement by Eschen and Jeitschko for the Tl and Hg cases indicates fractional occupation of several M positions along a line. There is also a large \(U_{ii}\) (anisotropic displacement parameters) for the atoms in the channel. The position of the Hg atoms is the least well determined followed by Tl and then Pb. The indication in the mercury and thallium compounds is of disorder or atom mobility along the chain. Other than the clear finding that such mobility is theoretically easy, we have not investigated theoretically (it would be difficult to do so) the potential of fractional site occupation.

We suggest that one look experimentally for the indicated high mobility of these element chains.

**Threading Other Chains through Au\(^2\)P\(_2\).** To the best of our knowledge, only Au\(_2\)MP\(_2\) with \(M = \text{Pb}, \text{Tl}, \text{or Hg}\) have been prepared. In the hope that other ternary gold polyphosphides will be investigated, we modeled a series of Au\(_2\)MP\(_2\) compounds with \(M = \text{Zn}, \text{Cd}, \text{In}, \text{Sn}, \text{Sb}, \text{Te}, \text{I, Bi, or Au}\) (Table 5; unit cell parameters shown in Table S8 of the Supporting Information). Some of these are congeners of the known ternary compounds, others are quite hypothetical. We did not study structural alternatives for any of these compounds. Once the geometries of the compounds were optimized (DFT), \(\epsilon\)H computations were carried out. The OP and HP of these hypothetical element lines are smaller than those of the corresponding isolated one-dimensional chains (except in Hg and Cd). HP analysis, unlike OP, can be utilized to compare the bonding properties of different atoms. There is clear indication of bonding in the chains for all these hypothetical phases (Sb–Sb chains have been studied extensively in the literature).\(^{46}\)

Iodine is especially interesting, as infinite I—I chains only exist in organic complexes. The 3.25 Å I—I distance computed for Au\(_2\)IP\(_2\) is significantly shorter than the van der Waals I—I interaction (3.30 Å) and longer than the molecular I2 bond length (2.67 Å). Is the predicted I—I distance in Au\(_2\)IP\(_2\) realistic? It would seem so, based on the only well-studied infinite polyiodide chain, in the starch-iodine complex.\(^{47}\) The starch-iodine complex has an average I—I separation of 3.1 Å, similar to the 3.25 Å I—I distance in Au\(_2\)IP\(_2\). Although the I—I OP in Au\(_2\)IP\(_2\) (0.15) seems small, the molecular I2 OP is only 0.49 at the much shorter separation of 2.67 Å.

As mentioned earlier, only one binary Au–P compound is known to date, Au\(_3\)P\(_3\). One obvious idea for generating an alternative is to fill the Au\(_3\)P\(_3\) channel structure with a Au line (i.e., Au\(_3\)P\(_3\) listed in Table 5). This structure turns out to be metallic. We also computed the known Au\(_3\)P\(_3\) structure and found it to have a large pseudogap. The \(\Delta E\) computed (8Au(fcc)

---

+ 8Au₂P₃ → 8P(black phosphorus) + 8Au₃P₃) a hypothetical reaction relating Au₃P₂ and Au₂P₃ is 7.47 eV.

**Conclusion**

In this work, the electronic structure and chemical bonding of three ternary gold polyphosphides were analyzed. The DOS predicts that Au₃PbP₂ and Au₃TlP₂ should be metallic, Au₃HgP₂ a semiconductor. The metal element lines play an important role in determining metallic behavior in these unusual compounds. The Pb, Tl, and Hg chains do not undergo a pairing (Peierls) distortion, for good reasons. The small barrier for Pb motion along the chain axis and the still smaller barrier for Tl and Hg may also explain the large thermal parameters observed in the crystal structures along the chain axis and the refinement that required alternative sites for Hg (and Tl).

Liquidlike behavior of the metal chains is expected for any M in Au₂MP₂. To guide future work, some hypothetical compounds (containing other atoms inserted into the Au₂P₂ channel) were also studied. The likely distances between atoms in these chains ranged from 3.05 Å (Au₂AuP₂) to 3.25 Å (Au₂IP₂). The results suggest that one could synthesize other ternary compounds based on the Au₂P₂ framework.

**Acknowledgment.** Calculations were performed in part at the Cornell NanoScale Facility, a member of the National Nanotechnology Infrastructure Network, which is supported by the National Science Foundation. Our work at Cornell was supported by the National Science Foundation through Grant No. CHE-0613306. This research was also supported in part by the National Science Foundation through TeraGrid resources provided by [NCSA].

**Supporting Information Available:** Details of all the COOP curves, OP and HP values of the three ternaries; the band structures, COOP curves, and TDOS of the Tl and Hg isolated chains; the TDOS, PDOS, COOP curves with OP and HP values of the Au₂P₂ lattice; a frozen band approximation of the Tl and Hg chains using isoelectronic Pb; further analysis of the Tl and Hg lines with corresponding structure geometries and band structures; the different one- and three-dimensional Pb structures predicted with DFT and corresponding energies of formation; the computed parameters (and corresponding figures) compared to the experimental parameters of the different ternary compounds predicted; the computed parameters obtained when threading other elements through the Au₂P₂ lattice, and their corresponding OP and HP values. This material is available free of charge via the Internet at http://pubs.acs.org.