The Crystal Structure of TlP$_5$

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TlP$_5$ crystallizes in the orthorhombic space group $Pmc2_1$ with four formula units in a unit cell of dimensions $a = 6.465$ Å, $b = 6.925$ Å, and $c = 12.118$ Å. The detailed atomic arrangement has been determined from three-dimensional single crystal X-ray data, the anomalous scattering from thallium being used to establish the absolute configuration.

The structure is characterized as a layer structure with phosphorus atoms arranged in a way very similar to the arrangement of phosphorus atoms in Hittorf's phosphorus. The average P—P bond length is 2.208 Å, and the average P—P—P bond angle is 100.8°. The thallium atoms have a very irregular coordination with two short bonds (3.0 Å) to phosphorus atoms belonging to the same layer, and with seven additional bonds (3.3—3.7 Å), most of which are directed towards phosphorus atoms in an adjacent layer.

From a consideration of the bonding system it is proposed that TlP$_5$ is a Tl(I) compound.

According to earlier work on the thallium-phosphorus system, the phases Tl$_3$P [1] and TlP$_5$ [2,3] exist. Brown and Pramatus,[2] and Puff *et al.*[3] independently determined the orthorhombic unit cell and suggested possible space groups for TlP$_5$. The present investigation was undertaken in order to determine the crystal structure of TlP$_5$. During the attempts to prepare single crystals, X-ray powder photographs were taken of samples with compositions on the metal rich side of TlP$_5$, but no evidence was found for the existence of Tl$_3$P.

EXPERIMENTAL

Single crystals were obtained by mixing small shavings of thallium metal in various atomic proportions with red phosphorus and heating at 350°C for 4 days in sealed evacuated silica capsules. After cooling, the samples were crushed and ground to a fine powder which was pelleted and reheated at 365°C for 12 days. In a sample containing 60 at. % phosphorus, approximately cylindrical crystals of good quality were found on the surface of the pellet. These crystals may have grown from the gas phase. In some other preparations, probable gas phase reactions were observed, for instance, by slow cooling from 460°C of a sample containing about 83 at. % phosphorus, whiskers of about 1 cm length were obtained. However, they were too thin to be suitable for X-ray work.

Phase analysis of the reaction products was carried out by X-ray powder methods, using Guinier-Hägg-type focussing cameras with $CuK\alpha_1$ or $CrK\alpha_1$ radiation. Silicon ($a = 5.43054$ Å) was used as an internal calibration standard.

The single crystal investigation was performed with the equi-inclination Weissenberg method, using zirconium-filtered MoK radiation, and the multiple film technique with thin iron foils interleaved with successive films. The crystal was rotated around the b axis which was parallel with the cylinder axis of the crystal. The layer lines $0 \leqslant k \leqslant 7$ were recorded, and the intensities were estimated visually by comparison with a calibrated intensity scale. Corrections for absorption, Lorentz and polarisation effects were applied. When correcting for absorption, the crystal was assumed to have a cylindrical form with radius 0.02 mm. The linear absorption coefficient was taken to be 305 cm^{-1}. Atomic scattering factors were taken from Ref. 4, and the real and imaginary parts of the anomalous dispersion correction from Ref. 5.

All calculations were made on a CD 3600 computer, using the programs CELSIUS, DRF, LALS, DISTAN and ORTEP. The programs have been briefly presented elsewhere.[6]

UNIT CELL AND SPACE GROUP

Puff et al.[3] found the symmetry for TlP_5 crystals to be orthorhombic. In the present investigation, some X-ray reflexions were found to deviate markedly from the orthorhombic diffraction symmetry mmm, but, as will be discussed in the next section, these deviations can be accounted for by anomalous dispersion effects. Systematic absences were observed for $h0l$ reflexions with l odd and $h00$ reflexions with h odd. However, there is no diffraction symbol corresponding to these absences, and the condition for the $h00$ reflexions could later be shown to be the result of the atoms by chance being arranged in nearly identical layers spaced $a/2$ apart. Judging from the condition for $h0l$ reflexions, the space groups $Pmcm$, $P2cm$, and $Pmc2_1$ are possible. (The two first mentioned are given in a non standard setting.) If the deviations from the orthorhombic diffraction symmetry mentioned above are regarded as deviations from Friedel's law caused by anomalous dispersion, this is an indication of a noncentrosymmetric space group. A unique choice of $Pmc2_1$ could later be made from the interpretation of the Patterson projection $P(xz)$.

The dimensions of the unit cell were determined from X-ray powder photographs and refined by the method of least squares (52 reflexions), giving the following result: ($\lambda = 2.28962$ Å) $a = 6.4650(7)$ Å; $b = 6.9249(6)$ Å, $c = 12.118(1)$ Å, $U = 542.54$ Å^3. The errors given are the standard deviations calculated from the least squares fit.

With four formula units of TlP_5 per unit cell, the calculated density is 4.40 g cm^{-3}, whereas an experimentally determined[3] value is 4.29 g cm^{-3}.

STRUCTURE DETERMINATION AND REFINEMENT

The positions of the thallium atoms could be determined from a three-dimensional Patterson synthesis. The large difference in scattering power between thallium and phosphorus made it easy to identify the thallium-thallium vectors. The only way to explain the largest maxima was to place the four thallium atoms on the two-fold positions $2(b)$ and $2(a)$ in space group $Pmc2_1$. The phosphorus atoms could then be located in electron density maps by successively including more and more atoms in the structure factor calcula-

tion. However, on account of the large difference in atomic number for the two types of atoms, this process had to be done very carefully in small stages. At the same time, improved positional parameters for the included atoms were obtained at each stage. All atoms were found to be situated in, or very close to, the layers with $x = 0$, $1/2$, 0.25 or 0.75, with layers spaced $a/2$ apart being occupied with the same number and types of atoms, thus explaining the extra condition for the occurrence of $h00$ reflexions.

After all atoms had been located, the refinement of the structure was continued by least squares methods. In the first cycles, the positional parameters and one scale factor for each layer line were refined. In the next stage, individual isotropic temperature factors were also refined. The discrepancy index $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was then about 0.13 for the 756 observed reflexions. A difference Fourier synthesis indicated an anisotropic thermal motion for the thallium atoms, and another least squares refinement with anisotropic temperature factors for the thallium atoms reduced the R value to about 0.11.

Up to this point, the observed structure factors were based on average values of the intensities for symmetry-related reflexions. In order to investigate the assumed effects of anomalous dispersion, further least squares refinements were undertaken, in which symmetry related reflexions were treated independently. For two refinements, both based on $F(hkl)$ but with different signs for the z coordinates, the R value differed only by a few thousandths; however, as can be seen in Table 1, the effect is quite large for some of the

Table 1. Ratios of observed and of calculated structure factors for reflexions which show the largest effect of anomalous scattering (see the text).

hkl	$\dfrac{F_c^{II}}{F_c^{I}}$	$\dfrac{F_o(hkl)}{F_o(hk\bar{l})}$	hkl	$\dfrac{F_c^{II}}{F_c^{I}}$	$\dfrac{F_o(hkl)}{F_o(hk\bar{l})}$
617	0.66	0.77	834	0.64	0.81
616	0.74	0.69	241	1.14	1.18
816	0.87	0.88	641	1.18	1.31
221	0.87	0.83	646	0.79	0.76
622	0.86	0.87	846	0.77	0.91
034	0.73	0.85	052	0.71	0.78
233	1.18	1.09	451	0.75	0.80
235	0.75	0.65	452	0.64	0.62
431	0.88	0.93	461	1.11	1.15
434	0.58	0.56	462	1.48	1.33
633	1.17	1.08	4610	0.86	0.80
634	0.78	0.91	664	0.79	0.84
635	0.66	0.91	271	1.23	1.11
6310	0.73	0.84	671	1.29	1.32

reflexions. In the table, F_c^{I} corresponds to the case with positive z coordinates, and F_c^{II} to the case with negative z coordinates. From the table is seen that there is no doubt that negative z coordinates give the correct configuration for this choice of unit cell. In the final cycles of least squares refinement, both

Table 2. Observed and calculated structure factors. Reflexions not included in the refinement are marked with an asterisk. Reflexions too weak to be measured are not included in the table. Of these, the calculated intensity in no case exceeded the limits of observation.

h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$

Table 2. Continued.

h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$	h	k	l	$|F_o|$	$|F_c|$
3	7	9	42.4	49.1	4	7	3	107.3	126.2●	4	7	10	97.4	96.6	5	7	4	28.9	25.7	6	7	3	37.5	37.3
3	7	10	31.1	32.1	4	7	5	38.2	25.0●	4	7	11	44.4	42.2	5	7	6	57.6	69.0	6	7	5	93.2	98.1
3	7	11	42.5	32.5	4	7	6	73.9	80.5	4	7	13	57.9	64.2	5	7	11	49.1	50.3	6	7	6	67.1	59.3
3	7	13	79.2	79.2	4	7	7	69.7	62.4	4	7	14	37.9	32.0	6	7	1	53.3	55.5	6	7	7	46.4	43.2
3	7	14	43.9	50.2	4	7	8	41.8	35.3	5	7	0	61.6	72.0	6	7	2	44.6	50.8	6	7	8	60.3	58.5
4	7	0	45.8	44.9	4	7	8	62.6	68.7	5	7	2	40.1	40.2						8	7	2	58.2	58.8
4	7	1	70.7	67.8	4	7	9	37.6	40.0	5	7	3	40.8	33.3										

$F(hkl)$ and $F(hkl)$ were used with some of the strongest reflexions excluded on account of secondary extinction. The final R value based on the 1197 reflexions used in the refinement was 0.095. For all 1224 reflexions, $R = 0.102$. The number of parameters refined was 45. The data were weighted according to $w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$. The values $a = 100.0$, $c = 0.01$, and $d = 0.001$ finally used were suitable, as was shown by a weighting analysis. The highest maximum found in a final difference Fourier synthesis was about 10 % of a phosphorus maximum in the electron density synthesis.

The observed and calculated structure factors are listed in Table 2, and the results of the structure determination and refinement are summarized in

Table 3. Atomic coordinates and isotropic temperature factors with standard deviations.

Atom	x	y	z	B Å²
Tl(1) in 2(a)	0	0.2214 (3)	0[a]	—
Tl(2) in 2(b)	0.5	−0.0141 (3)	−0.1591 (2)	—
P(1) in 4(c)	0.2511 (10)	0.2146 (10)	−0.3871 (5)	0.43 (8)
P(2) in 4(c)	0.2510 (12)	0.4037 (10)	−0.2382 (5)	0.37 (8)
P(3) in 2(a)	0	0.6146 (13)	−0.2722 (7)	0.22 (11)
P(4) in 2(a)	0	0.8286 (17)	−0.1460 (9)	0.94 (15)
P(5) in 2(a)	0	0.6565 (12)	0.0087 (6)	−0.38 (9)
P(6) in 2(b)	0.5	0.3372 (13)	−0.4911 (9)	0.54 (12)
P(7) in 2(b)	0.5	0.6120 (15)	−0.2818 (8)	0.64 (13)
P(8) in 2(b)	0.5	0.6452 (14)	−0.4562 (8)	0.60 (13)

[a] Arbitrarily.

Table 4. Anisotropic temperature factor parameters with standard deviations, each multiplied by 10^4. The expression used is: $\exp|-(h^2\beta_{11} + hk\beta_{12} + ...)|$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tl(1)	157 (4)	22 (8)	18 (1)	0	0	3 (2)
Tl(2)	197 (5)	25 (9)	18 (1)	0	0	−25 (3)

Tables 3 and 4. As is seen in Table 3, the isotropic temperature factor for P(5) is negative and deviates about ten standard deviations from the mean value of the others. It is probable that this is the result of systematic errors associated with the fact that P(5) lies almost directly above Tl(1) in the [010] direction, which also was the direction used as rotation axis when the intensity data were collected. The series termination effects around the

thallium atoms were particularly marked in this direction. Another source of error which might produce a negative temperature factor value could be the presence of foreign atoms heavier than phosphorus in the structure. This explanation seems very unlikely in this case, because the P(5) atom has the same surrounding as P(3), P(6), and P(7), with almost the same distances to its neighbours as the others mentioned. Moreover, in order to check this possibility, an emission spectrographic analysis of the thallium metal used in the syntheses was undertaken. The thallium metal was considered to be the most likely source of contaminating heavy atom species. However, only traces of silicon, copper, and lead were found, and a quantitative determination using atomic absorption showed the copper content to be only 0.001 %.

Our conclusion is that no physical meaning is to be attached to the fact that the temperature factor for P(5) is significantly less than those for the other phosphorus atoms but instead is a result of systematic errors.

DESCRIPTION AND DISCUSSION OF THE TlP$_5$ STRUCTURE

1. The phosphorus network. The crystal structure is shown in Fig. 1. The phosphorus atoms are connected to each other in a two-dimensional network
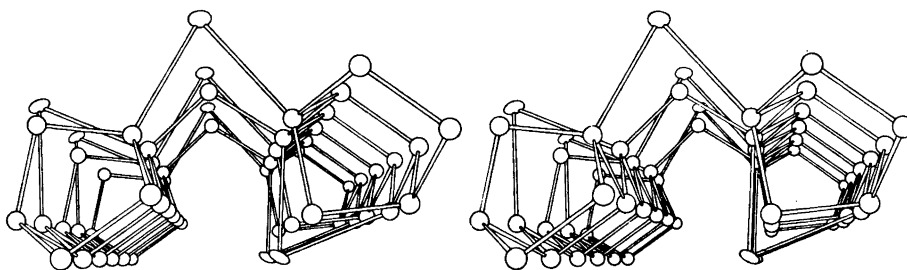

Fig. 1. A stereoscopic pair, showing part of a layer in the structure of TlP$_5$, viewed in a direction just off the *a* axis. The *b* axis is vertical in the figure. The atoms shown with anisotropic thermal motion are thallium atoms.

which is parallel to the (010) plane and extends as a molecular layer throughout the crystal. The distances between the closest neighbours within these layers are all close to the expected 2.20 Å for single bond distances, while the shortest distance between phosphorus atoms belonging to different layers is 4.3 Å. The phosphorus network is very similar to the network observed in the monoclinic modification of red phosphorus, the so-called Hittorf's phosphorus.[7] In this modification of phosphorus it is possible to discern tubes with pentagonal cross-sections as a very characteristic structural element. Tubes very similar in nature to those in Hittorf's phosphorus can also be found in the phosphorus arrangement in TlP$_5$. In Fig. 2, these structural elements are compared and it can be seen that the phosphorus network in TlP$_5$ can be regarded as being formed by a partial breaking down of the network in Hittorf's phosphorus.
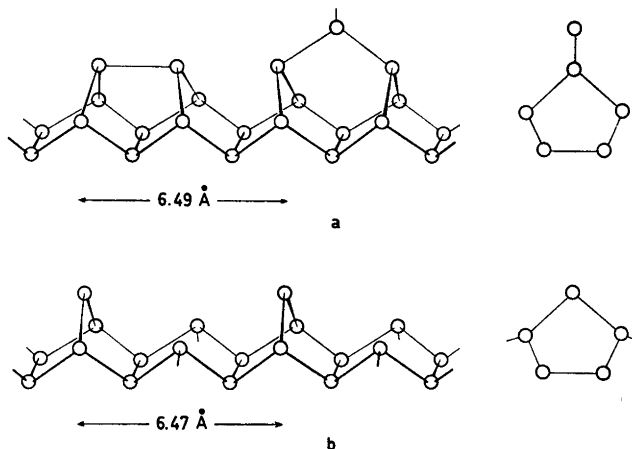
Fig. 2. Comparison of the pentagonal tubes found in the phosphorus network of Hittorf's phosphorus (a) and in TlP₅. Left: viewed at right angles to the tube axis. Right: Viewed along the tube axis.

In TlP₅ these tubes run parallel with the [100] direction and are connected in the [001] direction *via* bridging phosphorus and thallium atoms. This similarity in the arrangement of phosphorus atoms is also reflected in the dimensions of the unit cells. The a-axis for TlP₅, 6.47 Å in length, nearly equals half the diagonal in the ab plane in the unit cell of Hittorf's phosphorus, which is 6.49 Å. The tubes run in the [110] direction in the latter case. These two distances are also given in Fig. 2. Fragments of similar pentagonal tubes can also be found in other very phosphorus rich polyphosphides, for instance KP₁₅ [8] and HgPbP₁₄.[9]

Considering the coordination, three different types of phosphorus atoms can be distinguished in TlP₅:

(a) Pyramidal three-fold coordination with all three neighbours being phosphorus atoms (P(1) and P(2) in Table 5).

(b) Tetrahedral four-fold coordination consisting of one thallium neighbour at a distance of 3.0 Å and three phosphorus neighbours (P(3), P(5), P(6) and P(7)).

(c) Two-fold coordination, both neighbours being phosphorus atoms (P(4) and P(8)).
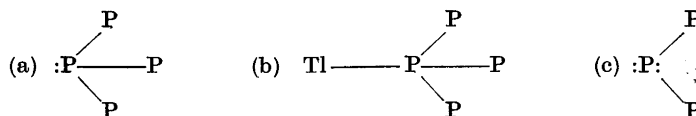
From Table 5 is clear that this division comes out quite naturally from the nearest neighbour coordination. The phosphorus atoms of types (a) and (c) have a low coordination, and it seems reasonable to assume that these atoms

Table 5. Interatomic distances (Å units) with standard deviations in TlP_5. $Tl-P$ distances up to 4.2 Å and $P-P$ distances up to 3.5 Å are included.

Tl(1)−	P(3)	2.985 (9)		P(4)−	P(3)	2.130 (14)
	P(5)	3.014 (9)			P(5)	2.221 (13)
	P(4)	3.245 (12)			Tl(1)	3.245 (12)
	2P(8)	3.403 (3)			2Tl(2)	3.415 (4)
	2P(2)	3.543 (6)				
	2P(1)	3.691 (7)				
	P(5)	3.914 (9)				
	2Tl(2)	4.102 (2)				
Tl(2)−	P(7)	2.986 (10)		P(5)−	P(4)	2.221 (13)
	P(6)	3.025 (10)			2P(1)	2.242 (8)
	2P(4)	3.415 (4)			Tl(1)	3.014 (9)
	2P(2)	3.447 (7)			2P(6)	3.233 (0)
	P(8)	3.545 (10)			P(3)	3.251 (12)
	2P(1)	3.568 (7)			P(3)	3.417 (11)
	2P(1)	3.921 (7)			2P(2)	3.495 (9)
	2Tl(1)	4.102 (2)			Tl(1)	3.914 (9)
P(1)−	P(6)	2.213 (9)		P(6)−	P(8)	2.174 (14)
	P(2)	2.230 (9)			2P(1)	2.213 (9)
	P(5)	2.242 (8)			Tl(2)	3.025 (10)
	P(1)	3.218 (13)			P(7)	3.171 (14)
	P(1)	3.247 (13)			2P(5)	3.233 (0)
	P(7)	3.434 (11)			2P(2)	3.493 (11)
	P(8)	3.491 (11)				
	Tl(2)	3.568 (7)				
	Tl(1)	3.691 (7)				
	Tl(2)	3.921 (7)				
P(2)−	P(3)	2.222 (10)		P(7)−	P(8)	2.127 (14)
	P(7)	2.225 (10)			2P(2)	2.225 (10)
	P(1)	2.230 (9)			Tl(2)	2.986 (10)
	P(2)	3.219 (16)			P(6)	3.171 (14)
	P(2)	3.246 (16)			2P(3)	3.235 (1)
	Tl(2)	3.447 (7)			2P(1)	3.434 (11)
	P(6)	3.493 (11)				
	P(5)	3.495 (9)				
	Tl(1)	3.543 (6)				
P(3)−	P(4)	2.130 (14)		P(8)−	P(7)	2.127 (14)
	2P(2)	2.222 (10)			P(6)	2.174 (14)
	Tl(1)	2.985 (9)			2Tl(1)	3.403 (3)
	2P(7)	3.235 (1)			2P(1)	3.491 (11)
	P(5)	3.251 (12)			Tl(2)	3.545 (10)
	P(5)	3.417 (11)				
	2P(1)	3.500 (10)				

have a rather strong interaction also with the thallium atoms which are at distances of $3.25-3.69$ Å. This will be further discussed when the thallium coordination is considered.

In conclusion, the phosphorus network in TlP_5 is very similar in nature to those observed in some other polyphosphides as well as in the crystalline modifications of elemental phosphorus.[7],[10] The average value for $P-P$ distances is 2.208 Å, and the average value for bond angles $P-P-P$ is 100.8°. There

are two rather short P−P distances of 2.13 Å in TlP₅. Distances as short as these are unusual, but in NiP_2 and SiP_2 of the pyrite structure type, distances of 2.12 Å and 2.13 Å, respectively, have been reported.[11,12] It must also be kept in mind that the large difference in atomic number for the atomic species in TlP₅ makes it an unfavourable case for the accurate determination of P−P distances.

2. The thallium coordination. The two non-equivalent thallium atoms have both a very irregular coordination with two phosphorus neighbours at rather short distance of about 3.0 Å and seven additional phosphorus neighbours at distances ranging between 3.25 Å and 3.69 Å. The bond angles P−Tl−P between the two Tl−P bonds are 72.2° and 65.6°, respectively. For both thallium atoms, these short Tl−P bonds are to phosphorus atoms within the same phosphorus layer, one of them serving as a bridging atom between different phosphorus tubes, while most of the longer Tl−P contacts are to phosphorus atoms in an adjacent layer. As has already been mentioned, the shortest P−P distance between different layers is as long as 4.3 Å, which means that the main part of the cohesion between the layers is due to Tl−P interaction. In Fig. 1 is seen that from structural point of view, the thallium atoms act in a way similar to the phosphorus atoms which have only two close neighbours.

The two different types of Tl−P distances indicate different types of interaction. It will be shown later that TlP₅ can conveniently be regarded as a Tl(I) compound. Unfortunately, there does not seem to exist any covalent radius value for Tl(I) in the literature. For Tl(III), a covalent radius of about 1.5 Å is often given, and the radius for Tl(I) can accordingly be expected to be at least 1.7 Å. From a collection of different Tl(I)−S distances reported for sulphides and various complexes containing sulphur as ligand atoms,[13−16] two groups of Tl(I)−S distances are found. One group contains bonds which are characterized as being primarily of a covalent nature and having lengths in the range 2.9−3.1 Å. The second group consists of bonds in the range 3.3−3.6 Å, which generally are considered as being of an ionic type or as an ion-dipole interaction. Adopting this classification, the Tl−P bonds of 3.0 Å in length should be regarded as being of covalent nature, while the longer Tl−P bonds are of the ionic type.

Besides the Tl−P interactions discussed, it can also be mentioned that each thallium atom has two other thallium neighbours at distances of 4.10 Å. These distances are about 20 % longer than in elemental thallium, and consequently a weak Tl−Tl interaction cannot be completely neglected. The Tl−Tl contacts are between atoms belonging to different layers, resulting in zigzag chains running between the layers in the [100] direction.

3. The oxidation number for thallium. It was mentioned above, that TlP₅ should be regarded as being a Tl(I) compound. The reasons for this will be set foreward in the following.

By considering the number and type of crystallographic positions for the independent phosphorus atoms it is possible to calculate an average value for the number of P−P bonds per phosphorus atom. This average value is 2.8 in this case. As the corresponding number is 3 in elemental phosphorus, it means that on the average 0.2 P−P bonds are broken per phosphorus atom

when TlP_5 is formed. For each $P-P$ bond broken, there needs to be one electron supplied from the electropositive constituent to each phosphorus

Table 6. Bond angles with standard deviations in TlP_5.

$P(3)-Tl(1)-P(5)$	65.6 (2)°	$P(6)-Tl(2)-P(7)$	72.2 (3)°
$P(2)-P(1)-P(5)$	102.8 (4)	$P(1)-P(2)-P(3)$	103.7 (4)
$P(2)-P(1)-P(6)$	103.6 (4)	$P(1)-P(2)-P(7)$	100.9 (4)
$P(5)-P(1)-P(6)$	93.0 (3)	$P(3)-P(2)-P(7)$	93.3 (4)
$P(2)-P(3)-P(2)$	93.8 (5)	$P(1)-P(6)-P(1)$	93.3 (5)
$P(2)-P(3)-P(4)$	108.9 (4)	$P(1)-P(6)-P(8)$	105.4 (4)
$P(2)-P(3)-P(4)$	108.9 (4)	$P(1)-P(6)-P(8)$	105.4 (4)
$Tl(1)-P(3)-P(2)$	114.9 (3)	$Tl(2)-P(6)-P(1)$	95.7 (3)
$Tl(1)-P(3)-P(2)$	114.9 (3)	$Tl(2)-P(6)-P(1)$	95.7 (3)
$Tl(1)-P(3)-P(4)$	113.6 (5)	$Tl(2)-P(6)-P(8)$	148.9 (5)
$P(3)-P(4)-P(5)$	103.5 (6)	$P(6)-P(8)-P(7)$	95.0 (6)
$P(1)-P(5)-P(1)$	92.8 (4)	$P(2)-P(7)-P(2)$	92.7 (5)
$P(1)-P(5)-P(4)$	105.2 (4)	$P(2)-P(7)-P(8)$	107.8 (4)
$P(1)-P(5)-P(4)$	105.2 (4)	$P(2)-P(7)-P(8)$	107.8 (4)
$Tl(1)-P(5)-P(1)$	114.7 (3)	$Tl(2)-P(7)-P(2)$	116.4 (3)
$Tl(1)-P(5)-P(1)$	114.7 (3)	$Tl(2)-P(7)-P(2)$	116.4 (3)
$Tl(1)-P(5)-P(4)$	120.4 (4)	$Tl(2)-P(7)-P(8)$	113.7 (5)

atom in the bond, in order to retain a complete octet for each phosphorus atom. That is, if 0.2 bonds have been broken per phosphorus atom, 0.2 electrons are needed per atom or 1 electron per formula unit TlP_5. One electron per thallium atom is accordingly supplied to the electronegative phosphorus atoms, and as there are no $Tl-Tl$ bonds of covalent nature, this electron is the only electron from thallium entering into the bonding system. The $Tl-P$ bonds are then considered to arise through the lone pairs on the phosphorus atoms. *

The formal way to account for the bonding electrons given above is in principle very similar to the type of reasoning resulting in the generalised $(8-N)$ rule, as discussed by Kjekshus [17] and others (see further Refs. in Ref. 17).

In polyphosphides of the s and p metals, the metal usually has an oxidation number, defined as above, equal to the group number. However, it is not particularly surprising to find that thallium deviates from this rule. From the chemical behaviour of these metals it is known that an extra stability of oxidation numbers two units less than the group number is found for the heaviest elements in the third, fourth, and fifth groups. In connection with this it is interesting to find that a calculation along the lines outlined above for $HgPbP_{14}$ gives an average oxidation number of two for the metal atoms. The most reasonable combination is then with the oxidation number two for both mercury and lead.

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* *Note ad 'ed in proof.* For a more thorough discussion of calculations of oxidation numbers of metal atoms in polyphosphides, see Ref. 18.

All elements in the third group, except thallium, form monophosphides of the zincblende type. In the Tl $-$ P system, the equilibrium situation at the equimolar composition is a two-phase mixture of thallium metal (perhaps with small amounts of dissolved phosphorus) and the Tl(I) compound TlP_5. This indicates that the non-existence of a thallium monophosphide may be attributed to the lower stability of Tl(III) compounds as compared with Tl(I) compounds.

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