The Crystal Structure of Thallium Tetrametaphosphate, Tl₄P₄O₁₂

By J. K. Fawcett,* V. Kocman† and S. C. Nyburg

Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 1A1

The crystal structure of thallium tetrametaphosphate, $Tl_4P_4O_{12}$, has been determined from 544 reflexions collected with Zr-filtered Mo $K\alpha$ radiation. The structure was solved from the Patterson function and refined by the full-matrix least-squares method using anisotropic temperature factors to a conventional R value of 0·063 from 409 reflexions. $Tl_4P_4O_{12}$ is tetragonal, space group $P\bar{4}2_1c$, with unit-cell dimensions $a = 7·635$ (5), $c = 11·087$ (7) Å, $Z = 2$. The $P_4O_{12}^{4-}$ ring anion has symmetry $\bar{4}$ (S_4) with P–O (bridging) bond lengths of 1·63 and 1·62 Å and P–O (exocyclic) bond lengths of 1·44 and 1·51 Å. The O–P–O angles differ significantly from the tetrahedral value and vary from 100·5 to 120·0°. The P–O–P angle is 133·3°. Each of the two Tl atoms in the structure is surrounded by six oxygen atoms in distorted octahedral coordination with Tl–O distances varying from 2·70 to 3·18 Å.

Introduction

Conclusive proof of the P_4O_{12} ring structure in several tetrametaphosphates has come from X-ray structure analyses of $Al_4(P_4O_{12})_3$ (Pauling & Sherman, 1937), $(NH_4)_4P_4O_{12}$ (Romers, Ketelaar & MacGillavry, 1951; Cruickshank, 1964; Koster & Wagner, 1970), two forms of $Na_4P_4O_{12}.4H_2O$ (Ondik, Block & MacGillavry, 1961; Ondik, 1964) and, most recently, of $Cu_2P_4O_{12}$ (Laugt, Guitel, Tordjman & Bassi, 1972).

Chemical and X-ray powder studies of thallium tetrametaphosphate, $Tl_4P_4O_{12}$, and of the tetrametaarsenate, $Tl_4As_4O_{12}$, by Dostál & Kocman (1969) proved the latter to be the first known metaarsenate with an eight-membered ring system. Infrared and Raman studies have indicated that the point symmetry in both anions is $\bar{4}$ (S_4) (Kocman, 1968).

A brief report of the $Tl_4P_4O_{12}$ structure has been published (Fawcett, Kocman, Nyburg & O'Brien, 1970) and the $\bar{4}$ (S_4) symmetry of the ring was confirmed. The work presented here gives full details.

Experimental

$Tl_4P_4O_{12}$ was prepared by the method of Dostál & Kocman (1969). Suitable crystals were obtained by triple recrystallization from aqueous solution and their purity tested by paper chromatography, according to the procedure of Grunze & Thilo (1964). Crystals of $Tl_4P_4O_{12}$ are brilliant transparent colourless plates, bounded by well developed faces, of major form {001}. Preliminary examination of the crystals under polarized light indicated optical isotropy perpendicular to (001). The crystal system and space group were determined from Weissenberg and precession photographs. Cell

dimensions and their standard deviations were calculated by a least-squares program from 15 high-angle reflexions centred on a diffractometer. The density of the crystals was determined pycnometrically in toluene. Crystal data for $Tl_4P_4O_{12}$ are summarized in Table 1.

Table 1. *Crystal data*

Thallium tetrametaphosphate
$Tl_4P_4O_{12}$, F.W. 1133·24
Tetragonal; $a = 7·635$ (5), $c = 11·087$ (7) Å (22 °C)
Space group $P\bar{4}2_1c$ (No. 114); $Z = 2$
$U = 646·3$ Å³
$D_m = 5·73$, $D_x = 5·82$ g cm⁻³
Absorption coefficient μ(Mo $K\alpha$) = 504·8 cm⁻¹

A crystal with dimensions $0·3 \times 0·3 \times 0·12$ mm was selected for data collection and mounted about the X axis. Zr-filtered Mo $K\alpha$ radiation was used for the intensity measurements, a total of 544 symmetry-independent reflexions being collected at 22 °C by the θ–2θ scan technique within the range $0·03 < \sin \theta/\lambda < 0·70$ on a Picker automated four-circle diffractometer equipped with scintillation counter and pulse-height analyser. The 2θ scan rate was 0·5° min⁻¹ and two 40 s background counts were taken on each side of the peak. During data collection the intensities of three reflexions were monitored every 2 h. No changes greater than 2% were observed. After data collection was completed, four extra φ-sweeps of h00 reflexions were made at $\chi = 90°$ and their net intensities were plotted against φ for absorption corrections. Lorentz, polarization and boundary-planes absorption corrections were calculated by the *DATAP*-3 program (Coppens, Leiserowitz & Rabinovich, 1965). The minimum and maximum transmission factors applied to the data were 0·006 and 0·044. The agreement among the symmetry-related pairs of reflexions was within $\pm 3\%$ in F. 418 reflexions had $F_o > 1·5\sigma F_o$ and were considered of significant intensity.

---

* Present address: Department of Biochemistry, University of Toronto, Ontario, Canada.
† Present address: Department of Geology, University of Toronto, Ontario, Canada.

Structure determination and refinement

From the Patterson map the eight thallium atoms per cell were found to be in two sets of special positions [(c) and (d) of *International Tables for X-ray Crystallography* (1965)] and their z parameters were immediately assignable. The residual based on these atomic positions was 0·27. The rest of the structure was found from the Tl-phased electron-density map. Scattering factors used for refinement were those for neutral Tl, P and O as given by Cromer & Mann (1968). Corrections for anomalous dispersion for Tl and for P were taken from *International Tables for X-ray Crystallography* (1962). Refinement with isotropic temperature factors lowered R to 0·10. In the last stages, anisotropic factors were used and F_o was weighted according to its observed correlation with $\Delta F/F_o$,

$$\sigma(F_o) = 0.011F_o + 4.016 + 107.24/F_o .$$

The conventional unweighted R was 0·063 and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ was 0·066. The structural parameters were considered established at this stage as the Tl and P parameter shifts were all less than 0·02σ and those of O all less than 0·1σ. Attempting further cycles of refinement resulted in a non-positive temperature factor β_{13} for O(3), possibly due to uncertainties in the absorption correction for some of the low-order reflexions. Six reflexions were not used in refinement. A further two reflexions were not correctly measured on the diffractometer and are also not included. The final electron-density map had deficiencies of about 1 e $Å^{-3}$ at the Tl sites, with ripples of order 2·5 e $Å^{-3}$. The rest of the map had no density in excess of 1·2 e $Å^{-3}$.

Final parameters are listed in Table 2; observed and calculated structure factors for all 544 reflexions are given in Table 3.*

Discussion

Table 4 lists bond lengths and angles of interest including e.s.d.'s from the *ORFFE* routine (Busing, Mar-

* Table 3 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30433 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

tin & Levy, 1964) in which estimated errors in cell dimensions have been allowed for.

Table 4. *Bond distances and angles*

P–O distances (e.s.d.'s in parentheses), P–O–P and O–P–O angles (e.s.d. 1·5°)

P(1)——O(1^i)	1·63 (3) Å
P(1)——O(1^{iii})	1·62 (3)
P(1)——O(3)	1·51 (3)
P(1)——O(2^i)	1·44 (3)

P(1)——O(1^i)——P(1^{iv})	133·3°
O(1^i)—P(1)——O(1^{iii})	100·5
O(1)—P(1)——O(3)	106·8
O(1^{iii})-P(1)——O(2^i)	114·1
O(1^{iii})-P(1)——O(3)	111·1
O(1^{iii})-P(1)——O(2^i)	102·6
O(3)——P(1)——O(2^i)	120·0

Tl–O distances

Tl(1)——O(2^{v,vi})	3·18 (3) Å
Tl(1)——O(2^{i,ii})	2·70 (3)
Tl(1)——O(3^{iii,iv})	2·70 (3)
Tl(1)——O(1^{vii,viii})	3·38 (3)
Tl(2)——O(2^{i,ii})	3·11 (3)
Tl(2)——O(2^{v,vi})	3·05 (3)
Tl(2)——O(3^{iii,iv})	2·89 (3)
Tl(2)——O(2^{i,ii})	3·39 (3)
Tl(2)——O(1^{vii,viii})	3·44 (3)

O–Tl–O angles

At Tl(1)			At Tl(2)		
O(3^{iii,iv}),	O(2^{i,ii})	73·7°	O(2^{i,ii}),	O(2^{v,vi})	91·1°
O(3^{iii,iv}),	O(2^{ii,i})	79·3	O(2^{i,v}),	O(2^{iv,ii})	92·6
O(^{iii,iv}),	O(2^{vi,v})	75·6	O(3^{iv}),	O(2^{ii,i})	65·3
O(3^{i,ii}),	O(3^{v,vi})	96·5	O(3^{iv,i}),	O(2^{i,iv})	111·7
O(2^{i,ii}),	O(3^{vi,v})	98·1	O(3^{iv,iii}),	O(2^{v,vi})	75·0
O(2^{iii}),	O(3^{iv})	79·0	O(3^{v}),	O(2^{vi})	98·0
O(2^{v}),	O(2^{vi})	130·2	O(3^{iii}),	O(2^{iv})	121·1
O(1^{vi}),	O(1^{vii})	89·1	O(3^i),	O(3^{ii})	95·8
O(1^{vii}),	O(2^{vi})	97·8	O(1^{vii}),	O(1^{viii})	53·0

Symmetry code

i	x y z	v	$\frac{1}{2}-x$ $\frac{1}{2}+y$ $\frac{1}{2}-z$
ii	$\bar{x}$ $\bar{y}$ z	vi	$\frac{1}{2}+x$ $\frac{1}{2}-y$ $\frac{1}{2}-z$
iii	$\bar{y}$ x $\bar{z}$	vii	$\frac{1}{2}+y$ $\frac{1}{2}+x$ $\frac{1}{2}+z$
iv	y $\bar{x}$ $\bar{z}$	viii	$\frac{1}{2}-y$ $\frac{1}{2}-x$ $\frac{1}{2}+z$

The space group fixes the symmetry of the $P_4O_{12}^{4-}$ anion as $\bar{4}$ (S_4), see Fig. 1(a). This symmetry contrasts with the 2/m and $\bar{1}$ symmetry of the anion found in

Table 2. *Atomic positional parameters* ($\times 10^4$ for Tl, $\times 10^3$ for remainder), *isotropic temperature factors, B* ($Å^2$), *and anisotropic temperature factors* ($\times 10^4$ for Tl, $\times 10^3$ for remainder) *in the form*

$$exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right]$$

E.s.d.'s are in parentheses.

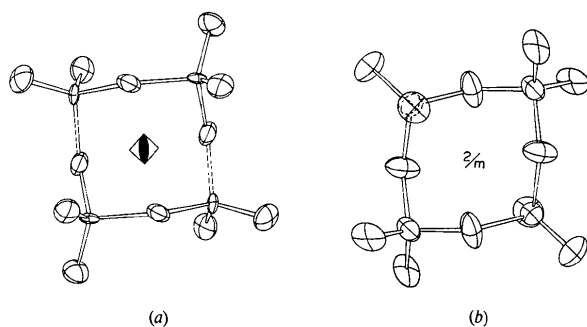|	x	y	z	B	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tl(1)	0	5000	−2266 (1)	1·7	71 (4)	92 (4)	29 (1)	15 (5)	0	0
Tl(2)	0	0	−1666 (2)	2·5	138 (4)	105 (4)	43 (1)	50 (10)	0	0
P(1)	345 (1)	282 (1)	−33 (1)	1·2	5 (1)	1 (1)	3 (1)	0 (1)	0 (1)	−1 (1)
O(1)	306 (3)	447 (3)	56 (2)	2·0	4 (4)	7 (4)	4 (2)	1 (3)	0 (2)	0 (2)
O(2)	273 (4)	301 (4)	−153 (3)	2·4	8 (5)	6 (4)	5 (2)	1 (4)	−1 (3)	−3 (3)
O(3)	308 (4)	118 (4)	38 (2)	1·7	9 (5)	7 (4)	4 (2)	−2 (4)	0 (3)	2 (3)

Fig. 1. Best molecular fit of two $P_4O_{12}^{4-}$ anions: (a) $P_4O_{12}^{4-}$ anion in $Tl_4P_4O_{12}$, symmetry $\bar{4}$ (S_4). Thermal ellipsoids are drawn with 70% probability. (b) $P_4O_{12}^{4-}$ anion in $(NH)_4P_4O_{12}$, symmetry $2/m$ (Koster & Wagner, 1970). Thermal ellipsoids enclose 20% probability. Both drawings were produced by ORTEP (Johnson, 1965).

other tetrametaphosphates (see Table 5). These results illustrate the fact that the $P_4O_{12}^{4-}$ anion is flexible and adopts a conformation to suit the cationic environment.

Comparisons of the conformation of $P_4O_{12}^{4-}$ ions of symmetry $\bar{4}$, $\bar{1}$ and $2/m$ (see Table 5) are conveniently made by a best-molecular-fit routine (Nyburg, 1974). This routine superimposes two rigid molecules such that all, or a specified list of, atoms of the second molecule give the best mean-squares fit with corresponding atoms of the first molecule. We found that $P_4O_{12}^{4-}$ ions of symmetry $\bar{1}$ and $2/m$ fitted almost exactly, whereas, as might be expected, those of $\bar{4}$ and $2/m$ did not (see Fig. 1(b); only ring phosphorus and oxygen atoms were compared). As can be seen from Table 5, the differences in conformation have no obvious effect on bond lengths or on the bond angles subtended at the phosphorus atoms.
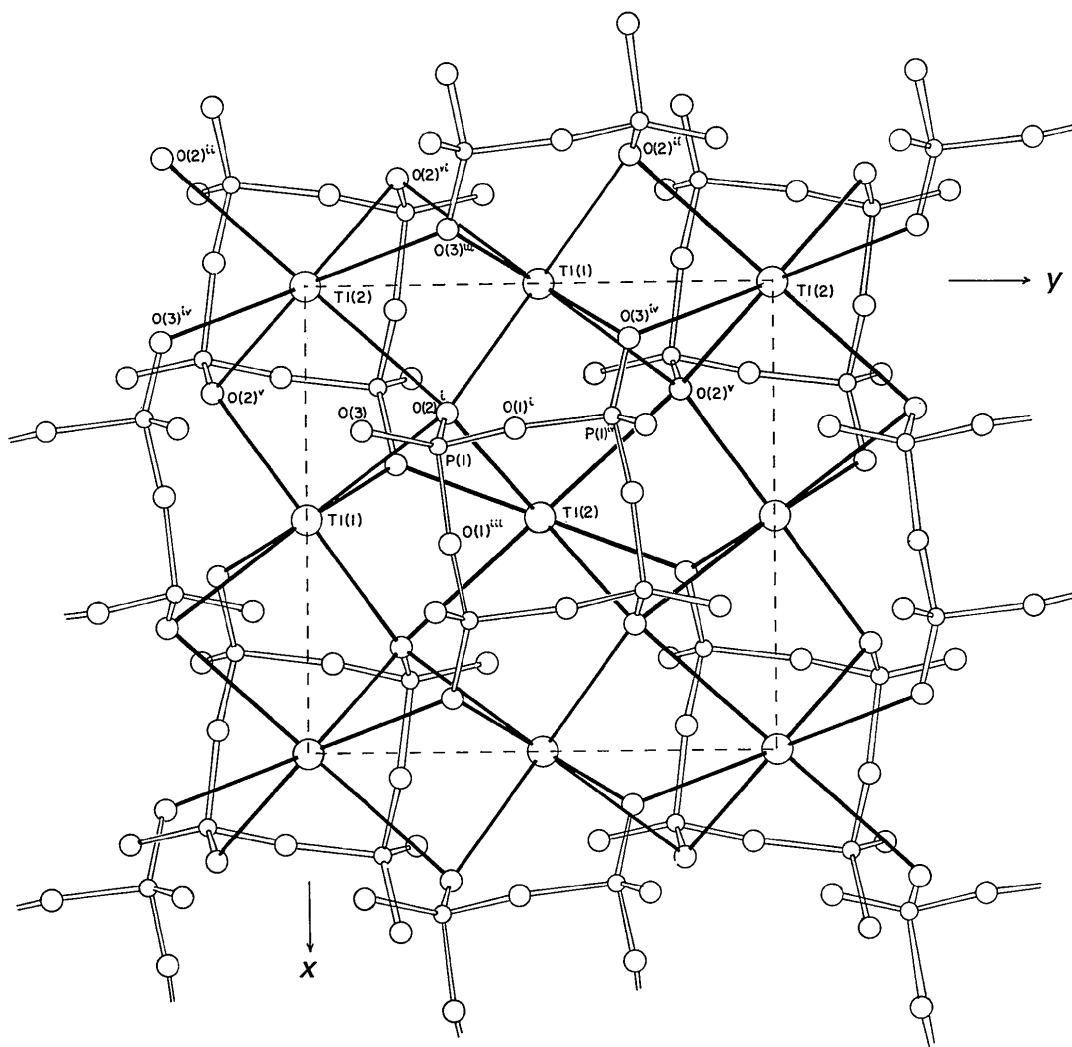

Fig. 2. Structure in z projection. Full lines show octahedra of oxygen atoms about Tl(1) and Tl(2). Unfilled lines show $P_4O_{12}^{4-}$ anions of $\bar{4}$ symmetry.

Table 5. *Interatomic distances in the* $P_4O_{12}^{4-}$ *ion in various crystal structures*

Compound	Crystal system	$P_4O_{12}^{4-}$ symmetry	P–O bridge (Å)	P–O terminal (Å)	P–O–P ring angle (°)	O–P–O ring angle (°)	Reference
$(NH_4)_4P_4O_{12}$	Orthorhombic	$2/m$	1·613 1·600 } (4)	1·483 1·481 1·472 } (4)	131·2 (2)	98·7 104·5 } (2)	Koster & Wagner (1970)
$Na_4P_4O_{12}.4H_2O$	Monoclinic	$\bar{1}$	1·639 1·631 1·587 1·579 } (16)	1·498 1·488 1·484 1·476 } (16)	133·2 133·2 } (9)	102·4 97·4 } (9)	Ondik, Block & MacGillavry (1961)
$Na_4P_4O_{12}.4H_2O$	Triclinic	$\bar{1}$	1·614 1·602 1·596 1·592 } (6)	1·475 1·473 1·469 1·468 } (6)	137·6 129·9 } (3)	103·6 98·9 } (3)	Ondik (1964)
$Cu_2P_4O_{12}$	Monoclinic	$\bar{1}$	1·600 1·593 1·590 1·578 } (6)	1·508 1·493 1·473 1·471 } (6)	137·7 136·3 } (6)	104·4 101·1 } (6)	Laügt, Guitel, Tordjman & Bassi (1972)
$Tl_4P_4O_{12}$	Tetragonal	$\bar{4}$	1·63 1·62 } (3)	1·51 1·44 } (3)	133·3 (2·0)	100·5 (2·0)	This study

With choice of origin as in *International Tables for X-ray Crystallography* (1965) for this space group, the $P_4O_{12}^{4-}$ anions are centred at $\frac{1}{2},\frac{1}{2},0$ and $0,0,\frac{1}{2}$. Thus the anions form two layers extending through the crystal structure, one at $z=0$, the other at $z=\frac{1}{2}$. Because the eight Tl ions per cell are in two different sets of special positions the spatial relation between the cations and anions at $z=0$ is different from that at $z=\frac{1}{2}$. Fig. 2 shows the structure in z projection.

Thallium to oxygen distances in the structure fall into two groups, short (2·70–3·18 Å) and long (3·38–3·44 Å). If only the shorter distances are taken into account, both Tl atoms in the structure have distorted octahedral coordination (Fig. 2) with the Tl(1) octahedron slightly more distorted than the Tl(2) octahedron. Similar distances (2·57–3·19 Å) have been observed in thallous fluoride carbonate Tl_3FCO_3 in which all three crystallographically independent Tl atoms are seven-coordinated (Alcock, 1973). However if we include the longer Tl–O distances (3·38–3·44 Å) the coordination of Tl(1) will increase to eight and Tl(2) will be ten-coordinated. It is difficult to decide if these longer coordination bonds are of chemical significance since the sum of ionic radii for Tl^+ and O^{2-} is about 2·80 Å (Pauling, 1960) and all the shorter octahedral bonds are clustered within 7% of this value. Accurate data on Tl^+ coordination are scarce (Hughes & Truter, 1972; Alcock, 1973).

References

Alcock, N. W. (1973). *Acta Cryst.* B29, 498–502.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306, Oak Ridge National Laboratory, Tennessee.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* 18, 1035–1038.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A24, 321–324.

Cruickshank, D. W. J. (1964). *Acta Cryst.* 17, 675–676.

Dostál, K. & Kocman, V. (1969). *Z. anorg. allgem. Chem.* 367, 92–101.

Fawcett, J. K., Kocman, V., Nyburg, S. C. & O'Brien, R. J. (1970). *Chem. Commun.* p. 1213.

Grunze, I. & Thilo, E. (1964). *Z. anorg. allgem. Chem.* 331, 102–110.

Hughes, D. L. & Truter, M. R. (1972). *J. Chem. Soc.* pp. 2214–2219.

International Tables for X-ray Crystallography (1962). Vol. III, p. 216. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1965). Vol. I, p. 204. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Kocman, V. (1968). Ph. D. Thesis, Univ. J. E. Purkyne, Brno, Czechoslovakia.

Koster, D. A. & Wagner, A. J. (1970). *J. Chem. Soc.* (A), pp. 435–441.

Laügt, M., Guitel, J. C., Tordjman, I. & Bassi, G. (1972). *Acta Cryst.* B28, 201–208.

Nyburg, S. C. (1974). *Acta Cryst.* B30, 251–253.

Ondik, H. M. (1964). *Acta Cryst.* 17, 1139–1145.

Ondik, H. M., Block, S. & MacGillavry, C. H. (1961). *Acta Cryst.* 14, 555–561.

Pauling, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.

Pauling, L. & Sherman, J. (1937). *Z. Kristallogr.* 96, 481–487.

Romers, C., Ketelaar, J. A. A. & MacGillavry, C. H. (1951). *Acta Cryst.* 4, 114–120.