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Trithallium(I) Phosphate, an Optical Second-Harmonic Generator

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Abstract. Tl_3PO_4, $M_r = 708{\cdot}08$, hexagonal, $P6_3$, $a = 8{\cdot}369\ (8)$, $c = 5{\cdot}111\ (5)$ Å, $V = 310{\cdot}0$ Å^3, $Z = 2$, $D_x = 7{\cdot}59$ g cm^{-3}, Mo $K\alpha$, $\lambda(\alpha_1) = 0{\cdot}70930$ Å, $\mu = 787{\cdot}6$ cm^{-1}, $F(000) = 580$, $T = 296$ K, $R = 0{\cdot}017$ for 241 reflections. The thallium(I) ion is coordinated to oxygen from three different phosphate groups at distances 2·529 (7), 2·553 (5) and 2·555 (8) Å. These distances are comparable to the shortest Tl—O distances reported for other compounds.

Introduction. In a survey of optical second-harmonic-generating materials, Tl_3PO_4 powder was found to produce a large second-harmonic intensity relative to quartz. This observation and the large birefringence observed for this material suggested that it might be a useful crystal for frequency conversion of laser light. To aid in understanding the properties of Tl_3PO_4, and to clarify the relationship of its structure to those of $LiIO_3$ and $KLiSO_4$, which are well known second-harmonic generators in the same space group (Choy, Jerphagnon & Kurtz, 1979), an accurate structure refinement was desirable. The space group of thallium(I) phosphate was proposed by Borie (1949). Powder patterns of thallium(I) phosphate (Swanson, Gilfrich & Cook, 1957) and the isomorphous thallium(I) arsenate (Swanson, Morris, Stinchfield & Evans, 1963) were reported later. Ganne & Tournoux (1973) published a brief account of the structure.

Experimental. Crystals of the title compound were grown from an aqueous solution of Tl_2CO_3 and $(NH_4)_2HPO_4$. Thin needle-shaped crystal, $0{\cdot}03 \times 0{\cdot}05 \times 0{\cdot}15$ mm; modified Picker automatic diffractometer, graphite monochromator; cell dimensions from 20 reflections, $20 < 2\theta < 36°$; analytical absorption correction, range 2·7 to 6·9; max. $(\sin\theta)/\lambda = 0{\cdot}54$ Å^{-1}, h −9 to 9, k −9 to 9, l −5 to 3; three standard reflections, $\sigma = 1{\cdot}6$, 1·8, 1·7%, data corrected for variations; 1462 data, 254 unique, $R_{\text{int}} = 0{\cdot}035$, 13 data $[(\sin\theta)/\lambda < 0{\cdot}2$ Å$^{-1}]$ given zero weight; thallium positions from Patterson function, remaining atomic positions from ΔF maps; refinement on F, 25 parameters including f'' for Tl, all atoms anisotropic; $R = 0{\cdot}019$, R(non-zero-weighted data) $= 0{\cdot}017$, $wR = 0{\cdot}016$, $S = 1{\cdot}00$; $w = [\sigma(F)]^{-2}$, derived from $\sigma^2(F^2) = \{[\sigma(F^2)$, counting statistics only$]^2 + (0{\cdot}025F^2)^2\}$; max. $\Delta/\sigma < 0{\cdot}001$; max. empirical isotropic correction for extinction 40% of F; max. and min. of ΔF synthesis 1·0 and −1·5 e Å^{-3}; atomic f for Tl^+, neutral P and O from *International Tables for X-ray Crystallography* (1974); local unpublished programs and *ORTEP* (Johnson, 1965).

The refractive indices were estimated using the Becke line criterion, and the birefringence was obtained from retardation measurements on single grains using a Zeiss microscope equipped with an Ehringhous compensator. The average index was determined to be larger than 2·0 and the birefringence approximately +0·15.

Discussion. Atomic parameters, listed in Table 1, are in agreement with and somewhat more precise than those reported by Ganne & Tournoux (1973).* The structure consists of thallous and phosphate ions connected by a three-dimensional network of Tl—O coordinations (Fig. 1). The phosphorus atom and one of the P—O bonds of the tetrahedral phosphate ion lie on the threefold axis. The thallium atom is coordinated to three oxygen atoms, each from a different phosphate group. Alternating planar triads of thallium atoms at $z = 0$ and $z = \frac{1}{2}$ form a column parallel to the c axis; each Tl atom is nearest neighbor to two Tl atoms in the layer above it and to two Tl atoms in the layer below it at distances of 3·690 Å.

The nearest neighbors to the Tl ion (Table 2) are three oxygen atoms at the base of a trigonal pyramid at distances ranging from 2·53 to 2·56 Å, with a fourth

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43159 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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oxygen atom at 3·26 Å. Thallium and oxygen exhibit a variety of coordination numbers in other compounds with a range of distances; the shortest values are comparable to those reported here. In Tl_2HPO_4 (Oddon, Vignalou, Transquard & Pèpe, 1979) the Tl—O distances for four kinds of Tl atoms range from 2·51 to 3·17 Å; in Tl_2WO_4 (Okada, Ossaka & Iwaii, 1979) the two shortest distances are 2·46 (6) and 2·70 (7) Å; and in Tl(HCOO) (Oddon, Tranquard & Mentzen, 1981) the Tl—O distance is 2·56 Å. In all these cases the distances less than 2·7 Å involve no more than three oxygen neighbors per thallium ion.

The f'' of Tl refined to a value of 10·3 (8) electrons and is statistically equivalent to the 9·66 electron value from *International Tables* (1974). The sign of this f'' shows that the configuration chosen for the structure is correct, and its magnitude indicates no significant inversion twinning in the specimen.

The structures of Tl_3PO_4, $LiIO_3$ and $LKiSO_4$ are quite different. In $LiIO_3$ the threefold axes of pyramidal iodate ions lie parallel to the *c* axis (Svensson, Albertsson, Liminga, Kvick & Abrahams, 1983, and references therein). In Tl_3PO_4 the pseudo-threefold axes of the TlO_3 groups lie nearly perpendicular to the *c* axis.

Table 1. *Positional and thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \sum B_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j / 3.$$

	x	y	z	B_{eq}(Å^2)
Tl	0·35393 (5)	0·26182 (5)	0	2·09 (2)
P	$\frac{1}{3}$	$\frac{2}{3}$	−0·0161 (26)	1·49 (8)
O(1)	$\frac{1}{3}$	$\frac{2}{3}$	−0·3166 (26)	2·3 (3)
O(2)	0·3966 (10)	0·8645 (10)	0·0811 (13)	2·6 (3)

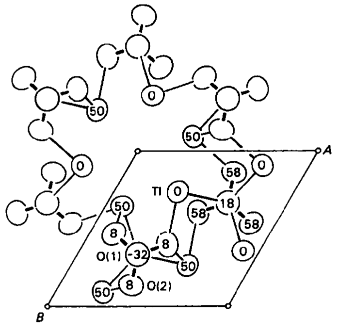

Fig. 1. Schematic *ORTEP* showing the contents of a unit cell and the disposition of the Tl ions about the *c* axis. Numbers inside the atom boundaries are *z* coordinate ×100. The P atom is hidden under the O(1) atom. 97% probability ellipsoids are shown.

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Tl—O(1)^{iv}	2·553 (5)	O(1)^{iv}—Tl—O(2)^{iii}	84·98 (15)
Tl—O(2)^{vi}	2·529 (7)	O(1)^{iv}—Tl—O(2)^{vi}	84·24 (32)
Tl—O(2)^{iii}	2·555 (8)	O(2)^{iii}—Tl—O(2)^{vi}	80·28 (18)
P—O(1)^{i}	1·536 (18)	O(1)^{i}—P—O(2)^{i}	108·7 (6)
P—3O(2)^{i,ii,iii}	1·547 (8)	O(2)^{i}—P—O(2)^{ii}	110·2 (5)
Tl^{i}—4Tl^{v,vii,viii,ix}	3·690 (3)	Tl^{xi}—O(1)—Tl^{x}	107·3 (3)
		Tl^{xi}—O(1)—P^{i}	111·5 (3)

Symmetry code: (i) x, y, z; (ii) $1-y, 1+x-y, z$; (iii) $y-x, 1-x, z$; (iv) $1-x, 1-y, \frac{1}{2}+z$; (v) $y, y-x, \frac{1}{2}+z$; (vi) $1+x-y, x, z-\frac{1}{2}$; (vii) $y, y-x, z-\frac{1}{2}$; (viii) $x-y, x, z-\frac{1}{2}$; (ix) $x-y, x, \frac{1}{2}+z$; (x) $y, 1-y+x, z-\frac{1}{2}$; (xi) $1-x, 1-y, \frac{1}{2}-z$.

There are no atomic groups in $KLiSO_4$ (Bradley, 1925) which are analogous to the highly-polarizable pyramids in the other two structures. The very large positive birefringence in Tl_3PO_4 is opposite in sign from that in $LiIO_3$ and much larger than that of $KLiSO_4$ (Cook & Jaffe, 1979).

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