Title
TRITHALLIUM(I) PHOSPHATE

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DISCLAIMER

Trithallium(I) Phosphate

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Abstract. M_r = 708.08, hexagonal, $P6_3$, a = 8.369(8), c = 5.111(5) A, V = 310.0, Z = 2, D_x = 7.59 g cm^{-3}, Mo Kα, $\lambda(\alpha_1)$ = 0.70930, μ = 787.6 cm^{-1}, F(000)= 580, T = 296 K, R = 0.017 for 241 reflections. Thallous ion is coordinated to oxygen from three different phosphate groups at distances 2.529(7), 2.553(5) and 2.555(8) A.

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 thallous phosphate was proposed by Borie (1949). Powder patterns of thallous phosphate (Swanson et al., 1957) and the isomorphous thallous arsenate (Swanson et al., 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, 0.03 × 0.05 × 0.15 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; $\max(\sin\theta)/\lambda = 0.54$ Å^{-1}, h -9 to 9, k -9 to 9, ℓ -5 to 3; three standard reflections, σ = 1.6, 1.8, 1.7%, data corrected for variations; 1462 data, 254 unique, $R_{int} = 0.035$, 13 data ($\sin\theta/\lambda < 0.2$) 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 = 0.019, R(non-zero wtd data) = 0.017, wR = 0.016, S = 1.00; $w = [\sigma(F)]^{-2}$, derived from $\sigma^2(F^2) = \{[\sigma(F^2)$, counting statistics only$] + (0.025F^2)^2\}$; max. $\Delta/\sigma <$ 0.001; max. empirical isotropic correction for extinction 40% of F; max. and

min. of ΔF synthesis 1.0 and -1.5 e $\AA^{-3}$; atomic f for Tl^{+1}, 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, and 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 3-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 3-fold 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 = 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 A.

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 A, with a fourth oxygen atom at 3.26 A. 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, Tranquared & Pepe,1979) the Tl-O distances for four kinds of Tl atoms range from 2.51 to 3.17 A; in Tl_2WO_4 (Okada, Ossaka & Iwaii, 1979) the two shortest distances are 2.46(6) and 2.70(7) A; and in Tl(HCOO) (Oddon, Tranquard & Mentzen, 1981) the Tl-O distance is 2.56 A. In all these cases the distances less than 2.7 A involve no more than three oxygen neighbors per thallium ion.

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

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 $KLiSO_4$ are quite different. In $LiIO_3$ the 3-fold axes of pyramidal iodate ions lie parallel to the c axis (Svensson, Albertson, Liminga, Kvick & Abrahams, 1983, and references therein). In Tl_3PO_4 the pseudo-3-fold axes of the TlO_3 groups lie nearly perpendicular to the c axis. 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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Table 1. Positional and thermal Parameters with e.s.d.'s in parenthesis

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

Atom	x	y	z	B_{eq}
Tl	0.35393(5)	0.26182(5)	0	2.09(2)
P	1/3	2/3	-0.0161(26)	1.49(8)
O(1)	1/3	2/3	-0.3166(26)	2.3(3)
O(2)	0.3966(10)	0.8645(10)	0.0811(13)	2.6(3)

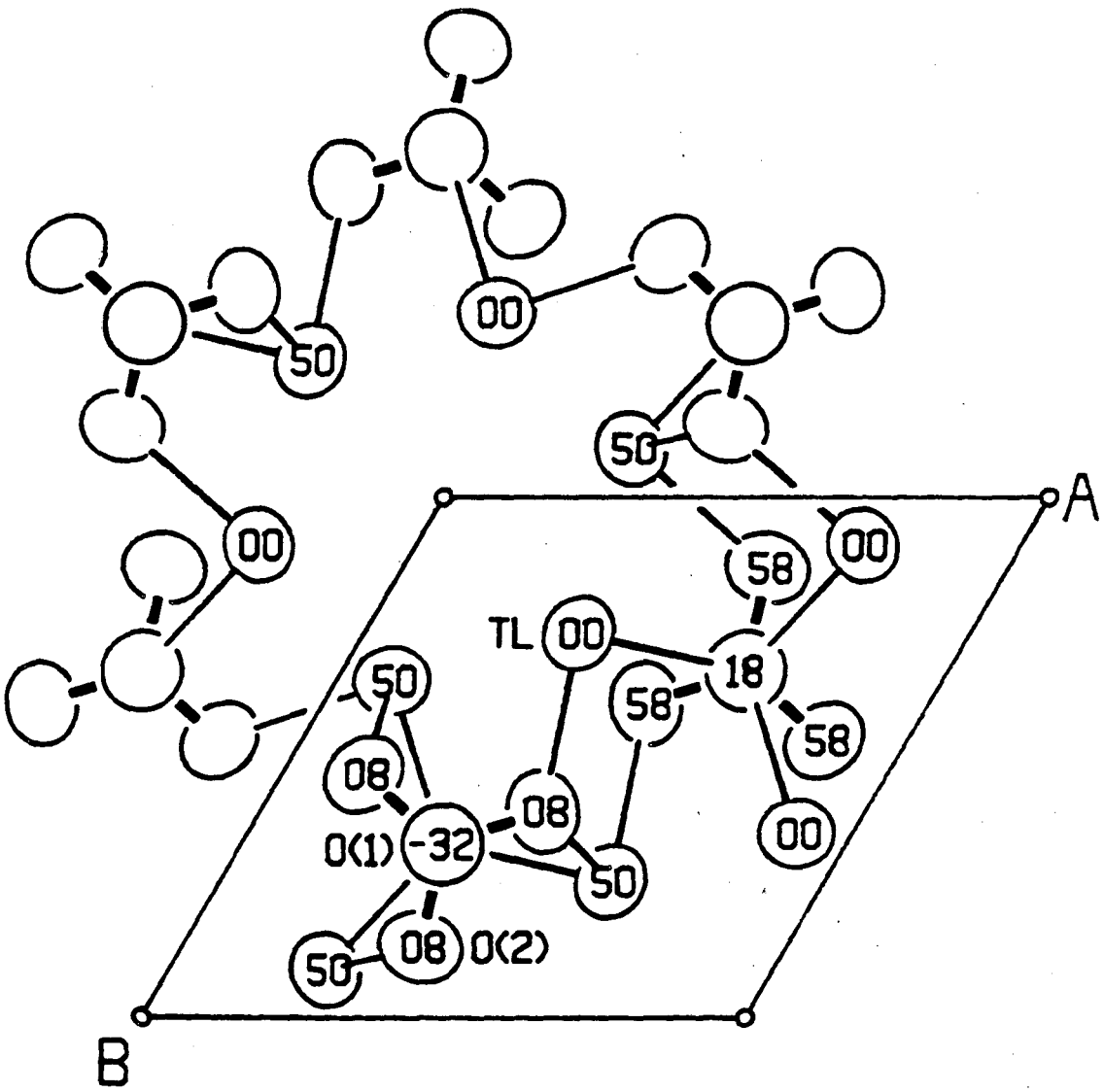
Table 2. Interatomic distances (Å) and angles (°) with e.s.d.'s in parenthesis*

Tl	-	$O(1)^{iv}$	2.553(5)
Tl	-	$O(2)^{vi}$	2.529(7)
Tl	-	$O(2)^{iii}$	2.555(8)
P	-	$O(1)^{i}$	1.536(18)
P	-3	$O(2)^{i,ii,iii}$	1.547(8)
Tl^{i}	-4	$Tl^{v,vii,viii,ix}$	3.690(3)

$O(1)^{iv}$	-Tl	$-O(2)^{iii}$	84.98(15)
$O(1)^{iv}$	-Tl	$-O(2)^{vi}$	84.24(32)
$O(2)^{iii}$	-Tl	$-O(2)^{vi}$	80.28(18)
$O(1)^{i}$	-P	$-O(2)^{i}$	108.7(6)
$O(2)^{i}$	-P	$-O(2)^{ii}$	110.2(5)
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,1/2+z; (v) y,y-x,1/2+z; (vi) 1+x-y,x,z-1/2; (vii) y, y-x,z-1/2; (viii) x-y,x,z-1/2; (ix) x-y,x,1/2+z; (x) y,1-y+x,z-1/2; (xi) 1-x,1-y,1/2-z.

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 x 100. The P atom is hidden under the O(1) atom. 97% probability ellipsoids are shown..



Supplemental Material

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Table of Thermal Parameters[a] with Estimated Standard Deviations for Trithallous Phosphate

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Tl	1.890(19)	2.208(20)	2.088(26)	0.959(12)	0.10(6)	0.19(6)
P[b]	1.47(8)	1.47	1.54(20)	0.734	0	0
O(1)[b]	2.6(3)	2.6	1.6(7)	1.3	0	0
O(2)	2.8(3)	2.08(27)	2.9(6)	1.26(26)	0.47(24)	-0.09(26)

[a] The temperature factor has the form $-1/4\sum h_i h_j B_{ij} a_i \cdot a_j$

[b] $B_{22} = B_{11}$; $B_{12} = 1/2\ B_{11}$; $B_{13} = B_{23} = 0$.

OBSERVED STRUCTURE FACTORS, STANDARD DEVIATIONS, AND DIFFERENCES (ALL X 4.0)
THALLOUS PHOSPHATE F(0,0,0) = 2226

SG = Estimated standard deviation of Fob. DEL = /Fob/- /Fca/, where Fob and Fca are the observed and calculated structure factors.
* indicates zero weighted data.

K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL
H,L=	0,	-4		0	388	6	3	H,L=	3,	-3		-1	812	11	12	-2	777	10	-13
0	921	14	-7	H,L=	2,	-4		-2	45	14	-17	0	238	3	-2	-1	444	6	9
H,L=	0,	-2		-1	345	31	40	-1	138	3	-3	H,L=	4,	-1		0	776	10	7
0	1494	0	-77*	0	279	4	5	0	123	3	1	-3	1023	13	1	H,L=	5,	0	
H,L=	0,	2		H,L=	2,	-3		H,L=	3,	-2		-2	374	5	-5	0	439	6	-9
0	1562	0	-44*	-1	699	9	5	-2	408	5	-1	-1	57	8	-6	1	491	6	0
H,L=	1,	-5		0	697	9	-1	-1	789	10	3	0	191	3	1	2	283	4	0
0	155	4	-4	H,L=	2,	-2		0	421	6	-3	H,L=	4,	0		3	266	4	-3
H,L=	1,	-4		-1	513	7	7	H,L=	3,	-1		0	318	4	-8	4	371	5	6
0	32	25	0	0	389	5	1	-2	204	3	8	1	177	3	-2	H,L=	5,	1	
H,L=	1,	-3		H,L=	2,	-1		-1	140	2	-1	2	760	19	-3	0	756	10	-6
0	227	3	2	-1	1027	0	56*	0	237	3	6	3	155	3	1	1	78	6	-4
H,L=	1,	-2		0	1028	0	55*	H,L=	3,	0		4	229	3	3	2	174	3	-3
0	69	5	5	H,L=	2,	0		0	535	7	-3	5	59	9	-2	3	107	4	4
H,L=	1,	-1		0	487	0	6*	1	591	12	-12	H,L=	4,	1		H,L=	5,	2	
0	295	0	14*	1	558	0	-3*	2	316	4	-4	0	204	3	-2	0	367	5	-8
H,L=	1,	0		2	235	3	-5	3	205	3	-1	1	145	3	3	1	425	6	-6
0	67	0	5*	3	410	5	-6	4	168	3	3	2	57	9	-5	2	237	4	2
1	529	0	18*	4	148	3	5	5	59	9	-5	3	436	6	-10	3	236	4	7
2	920	0	-2*	5	865	11	-4	H,L=	3,	1		4	471	6	-6	H,L=	5,	3	
3	911	12	-24	6	42	17	-13	0	241	3	2	H,L=	4,	2		0	609	8	14
4	281	4	1	H,L=	2,	1		11	040	13	8	0	245	4	-3	1	61	13	-16
5	91	4	-4	0	1009	0	46*	2	80	5	-6	1	132	3	1	2	132	4	8
6	181	3	0	1	222	3	6	3	519	7	-5	2	689	9	10	H,L=	6,	-4	
7	228	4	2	2	378	5	-7	4	244	4	-3	3	129	3	2	-4	462	6	-3
H,L=	1,	1		3	776	10	-11	5	66	8	5	4	217	4	1	-3	156	4	-1
0	293	0	8*	4	306	4	1	H,L=	3,	2		H,L=	4,	3		-2	44	25	-14
11	009	0	42*	5	27	30	20	0	414	5	-3	0	117	4	2	H,L=	6,	-3	
2	125	2	-3	6	27	35	10	1	529	7	3	1	84	9	-11	-5	83	4	3
3	66	3	5	H,L=	2,	2		2	250	4	0	2	63	9	-4	-4	70	5	1
4	432	6	-1	0	384	5	4	3	199	21	-19	3	359	5	8	-3	394	5	-6
5	196	3	-1	1	420	6	1	4	128	3	-2	H,L=	5,	-4		-2	248	4	-5
6	90	5	-1	2	170	3	-1	5	41	25	-7	-4	122	4	6	-1	157	3	-5
7	386	5	3	3	341	5	2	H,L=	3,	3		-3	159	4	0	0	316	4	1
H,L=	1,	2		4	107	3	5	0	139	3	3	-2	229	4	-2	H,L=	6,	-2	
0	51	6	6	5	741	10	7	1	762	10	27	-1	196	4	-1	-5	415	6	-8
1	509	7	11	6	63	9	3	2	95	5	0	0	261	4	0	-4	691	9	10
2	794	10	5	H,L=	2,	3		3	402	5	2	H,L=	5,	-3		-3	230	3	1
3	821	11	17	0	703	9	5	4	202	4	7	-4	88	4	-1	-2	100	4	4
4	282	4	1	1	87	3	-2	H,L=	4,	-4		-3	97	6	-2	-1	104	3	2
5	100	3	2	2	259	4	1	-3	406	6	2	-2	597	8	4	0	234	4	-1
6	174	3	3	3	610	8	14	-2	145	4	-3	-1	335	5	-2	H,L=	6,	-1	
H,L=	1,	3		4	240	4	-2	-1	504	7	-6	0	599	8	2	-5	92	3	5
0	212	3	2	5	21	33	16	0	151	4	-1	H,L=	5,	-2		-4	65	7	-2
1	688	9	-1	H,L=	3,	-5		H,L=	4,	-3		-4	138	3	3	-3	519	7	-5
2	137	3	1	-2	35	40	-5	-3	756	10	24	-3	242	3	-2	-2	306	4	1
3	67	7	1	-1	68	12	0	-2	243	4	-5	-2	337	5	0	-1	196	3	0
4	338	5	4	0	57	18	0	-1	58	10	-7	-1	294	4	2	0	385	5	-3
5	154	4	1	H,L=	3,	-4		0	98	4	2	0	368	5	-6	H,L=	6,	0	
6	70	11	6	-2	252	4	-1	H,L=	4,	-2		H,L=	5,	-1		0	242	4	-2
H,L=	2,	-5		-1	480	6	-8	-3	553	7	7	-4	141	3	3	1	275	4	0
-1	393	5	-15	0	308	4	-5	-2	171	3	-3	-3	100	3	5	2	309	4	-1

STRUCTURE FACTORS continued for
THALLOUS PHOSPHATE

K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL
H,L=		6,	1																
0	378	5	-7																
1	264	4	-8																
2	497	7	-2																
H,L=		6,	2																
0	234	4	0																
1	228	3	-1																
2	275	4	0																
H,L=		6,	3																
0	313	5	3																
1	185	4	-3																
H,L=		7,	-3																
-6	175	4	1																
-5	120	4	5																
-4	350	5	0																
-3	196	3	-4																
-2	22	37	16																
-1	76	6	8																
H,L=		7,	-2																
-6	220	3	-4																
-5	239	4	0																
-4	123	3	-7																
-3	122	3	-3																
-2	728	10	5																
-1	168	3	-6																
0	247	4	-1																
H,L=		7,	-1																
-6	259	4	-1																
-5	171	3	-1																
-4	449	6	1																
-3	248	4	3																
-2	18	32	11																
-1	82	5	-5																
0	420	6	-3																
H,L=		7,	0																
0	277	4	-2																
1	211	3	2																
H,L=		7,	1																
0	408	5	-9																
1	37	20	9																
H,L=		7,	2																
0	246	4	2																
H,L=		8,	-2																
-6	288	4	5																
-5	233	4	6																
-4	218	4	0																
-3	44	13	-4																
-2	61	10	-3																
H,L=		8,	-1																
-7	34	28	9																
-6	496	7	3																
-5	112	3	3																
-4	476	6	0																
-3	64	6	7																
-2	28	34	23																
-1	394	5	8																

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