

## Crystal Structure of Anhydrous Indium Phosphate and Thallic Phosphate by X-ray Diffraction

BY ROSE C. L. MOONEY

*National Bureau of Standards, Washington 8, D.C., U.S.A.*

(Received 22 July 1955 and in revised form 24 August 1955)

The structures of anhydrous  $\text{InPO}_4$  and  $\text{TlPO}_4$  have been determined from X-ray single-crystal and powder data. The crystals are isostructural. The space group is  $Cmcm-D_{2h}^7$ . There are four stoichiometric weights of  $X\text{PO}_4$  in the orthorhombic cell, which, for  $\text{InPO}_4$ , has the dimensions  $a = 5.308$ ,  $b = 7.851$ ,  $c = 6.767$  Å; and for  $\text{TlPO}_4$ ,  $a = 5.395$ ,  $b = 8.010$ ,  $c = 7.071$  Å. The atomic positions of  $\text{InPO}_4$  were deduced from single-crystal data by means of a Patterson two-dimensional synthesis, followed by Fourier difference syntheses. Those of  $\text{TlPO}_4$  were obtained from powder diffraction data by less direct methods. The cation is coordinated to six oxygens, each the corner of a different phosphate group. The structural arrangement is closely comparable to that reported for copper chromate and vanadium chromate.

### Introduction

Very little has appeared in the literature concerning the preparation and properties of either indium phosphate or thallic phosphate. References to work done in the mid-nineteenth century (Mellor, 1924) seem to exhaust the available information, which may be briefly epitomized as follows. The compounds, highly insoluble except in acid solution, were prepared by the double decomposition of appropriate soluble salts and obtained as voluminous white gelatinous precipitates, mixtures of various hydrates. One hydrate,  $\text{TlPO}_4 \cdot 2\text{H}_2\text{O}$ , was crystallized; but no anhydrous forms of either compound were mentioned.

This work, part of a systematic investigation of the structures of the anhydrous phosphates of trivalent cations, is concerned with the preparation of the compounds in anhydrous crystalline form, possibly for the first time; and with the determination of the structures by X-ray diffraction.

### Crystal preparation and X-ray techniques

It was found that macroscopic crystals of both compounds may be grown from acidified aqueous solution by sufficiently slowing down the rate of precipitation. However, since crystals grown in this manner were invariably hydrated, it was necessary to resort to other types of crystallization processes. The method which proved successful in producing crystallized anhydrous salts consisted essentially in sealing a mixture of the appropriate oxide and dilute phosphoric acid in a hydrothermal bomb, and subjecting the system to temperatures between 350° C. and 400° C. for a week or more.

In general, the products were well crystallized powders which gave excellent diffraction patterns. Some preparations of the indium compound were relatively coarsely crystallized, appearing as feathery

masses of tiny brilliant needles. From among these, it was possible to isolate individuals which could be successfully mounted on a goniometer head to give single-crystal diffraction patterns. Samples of the thallic salt yielded occasional thin platelets of reasonable size for rotation and Weissenberg patterns, but these without exception proved to be multiply twinned aggregates. In consequence, the structural analysis of  $\text{InPO}_4$  is based primarily on integrated single-crystal intensities, while that of  $\text{TlPO}_4$  is entirely dependent on powder diffraction data.

All of the powder patterns—many used for monitoring the various chemical preparations, and a number specifically for the measurements of cell constants and intensities—were made with a geiger-counter diffractometer, using filtered copper radiation. The intensities were taken as the measured areas under the  $K\alpha_1\alpha_2$  peaks, and were subsequently scaled to the calculated intensities, which were corrected for the polarization-Lorentz factor in the usual way.

The single-crystal data was taken with a Wiebenga integrating Weissenberg camera used with filtered copper radiation. The crystal used was a thin, slightly flattened needle, which, by rough measurement under a microscope, was a tenth millimetre in length and a few hundredths of a millimetre in thickness. Because of the size and habit of the crystal, only patterns of layer lines perpendicular to the needle axis ( $z$  direction) were obtainable. The photographs of the even layers were of normal intensity, considering the small size of the crystal; those of odd layers were so faint as to be practically useless for reliable intensity measurements, though they could be indexed satisfactorily.

The integrated single-crystal reflections were measured by means of a simple densitometer, corrected for the Lorentz-polarization factor by a graphical method (Lu, 1943), and subsequently scaled to the calculated values by an appropriate factor. Absorption

Table 1. Possible atomic distributions

Space group	Equivalent positions	Atomic distribution
$Cmc2_1$ $\left\{ \begin{array}{l} 4 \ a \ m \\ 8 \ b \ 1 \end{array} \right.$	$0, y, z; 0, \bar{y}, \frac{1}{2}+z$ $x, y, z; \bar{x}, y, z; \bar{x}, \bar{y}, \frac{1}{2}+z; x, \bar{y}, \frac{1}{2}+z$	$4X, 4P, 4O_2, 4O_3$ $8O_1$
$Cmcm$ $\left\{ \begin{array}{l} 4 \ a \ 2/m \\ 4 \ c \ mm \\ 8 \ f \ m \\ 8 \ g \ m \end{array} \right.$	$0, 0, 0; 0, 0, \frac{1}{2}$ $0, y, \frac{1}{2}; 0, \bar{y}, \frac{3}{2}$ $0, y, z; 0, \bar{y}, \bar{z}; 0, y, \frac{1}{2}-z; 0, \bar{y}, \frac{1}{2}+z$ $x, y, \frac{1}{2}; \bar{x}, y, \frac{1}{2}; x, \bar{y}, \frac{3}{2}; \bar{x}, \bar{y}, \frac{3}{2}$	$4X$ $4P$ $8O_2$ $8O_1$

effects were neglected, since the crystal used was close to the optimum size for copper radiation. No corrections were made for either temperature or extinction. The former was apparently negligibly small; the latter may be held responsible for the somewhat low observed intensities of a few strong, low-order planes. For want of definite information, the states of ionization of the constituents were assumed to be  $O^{2-}$ ,  $P^{5+}$ ,  $Tl^{+3}$ ,  $In^{+3}$ . The scattering factors were obtained from the *International Tables* (1935), those for Tl and In being slightly modified at low orders to fit the assumed state.

### Crystallographic data

It was immediately obvious, from the similarity of the powder patterns, that  $TIPO_4$  and  $InPO_4$  are isostructural. With the aid of approximate constants obtained from  $InPO_4$  rotation and Weissenberg data, the two patterns were indexed and the cell dimensions were calculated from a selection of moderately high-angle lines. The crystals are orthorhombic. Their axial ratios differ sufficiently so that the order of succession of the reflections is not quite the same on the two patterns, that is, the  $TIPO_4$  cell is the larger by about 2% in the  $x$  and  $y$  directions, and by about 5% in the  $z$  direction. The cell constants are:

	$TIPO_4$	$InPO_4$
$a$ (Å)	$5.395 \pm 0.005$	$5.308 \pm 0.005$
$b$ (Å)	$8.010 \pm 0.008$	$7.851 \pm 0.008$
$c$ (Å)	$7.071 \pm 0.007$	$6.767 \pm 0.007$
$a : b : c$	$0.674 : 1 : 0.880$	$0.675 : 1 : 0.862$

On the assumption that the cell contains four stoichiometric weights of the compound, the calculated densities of  $TIPO_4$  and  $InPO_4$  are, respectively,  $6.47 \text{ g.cm.}^{-3}$  and  $4.91 \text{ g.cm.}^{-3}$ .

Inspection of the indices of reflection shows, in both cases, that planes  $hkl$  are absent when  $h+k$  is odd; that all reflections  $hkl$  where  $l$  is odd are either absent or very weak; and that no reflection  $h0l$ , with  $l$  odd, gives an observable intensity. It follows that the structure is based on a  $C$ -centered lattice; and that the cations (whose scattering power in the case of  $InPO_4$  is equal to, and in the case of  $TIPO_4$  greatly exceeds, the sum of the scattering power of the phosphate group) must lie in planes at separations of  $\frac{1}{2}c$ , thus making no contribution to the intensities of planes  $hkl$ ,  $l$  odd. Because of this condition, the observed  $h0l$  absence ( $l$  odd) may not, without some question, be attributed to space-group symmetry.

However, thorough inspection of powder photographs and of the row lines on long-exposure first- and third-layer Weissenberg patterns failed to discover a single example of this class of reflections, while all other possible types are represented. On the basis of these extinctions, it was concluded that the space group is either  $Cmc2_1-C_{2v}^{12}$  or  $Cmcm-D_{2h}^{17}$ .

Assuming only that phosphorus must have a tetrahedral oxygen coordination of four, the possible atomic distribution of four formula weights of  $XPO_4$  is given for  $Cmc2_1$  and  $Cmcm$  by the sets of equivalent positions (*International Tables*, 1935) shown in Table 1, to which must be added the additional points generated by face centering.

Since the phosphorus must lie in a mirror plane if the space group is  $Cmc2_1$ , or in the intersection of two mirror planes if the space group is  $Cmcm$ , the space-group symmetry of the crystal depends solely on the orientation of the oxygens about phosphorus.

### Structure determination of $InPO_4$

Parameters for a structure as simple as is indicated by the foregoing considerations might be obtained in a variety of ways. In order to eliminate any preliminary assumptions concerning the space group or In-O distances in the structure, the following procedure was adopted.

From the observed intensities, the Patterson projection,  $\sum |F(hk0)|^2 \cos 2\pi hU \cos 2\pi kV$ , was calculated. The resulting diagram is shown in Fig. 1. Since all of

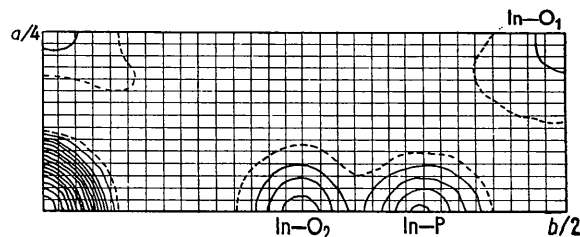


Fig. 1. Patterson projection on (001) for  $InPO_4$  structure.

the peaks which emerge clearly from background are unquestionably due to vectors involving indium, and since the indium lies at the origin, the vector map gives directly a picture of the structure projected on [001], and furnishes at least approximate values of the required parameters in the  $xy$  plane. The two well-defined peaks on the line,  $x = 0$ , (In-O<sub>2</sub> and In-P), together with the more diffuse peak in the neighbor-

hood of  $x = \frac{1}{4}$ ,  $y = \frac{1}{2}(\text{In}-\text{O}_1)$ , outline the projection of the phosphate tetrahedron. The single, quite symmetrical peak representing the In-O vector in the  $x$  mirror plane shows that these oxygens are in the eight-fold set of  $Cmcm$  rather than in two fourfold sets of  $Cmc2_1$ . Though the maxima of the second set of oxygens are not well defined, their positions are consistent with an orientation such that the planes of symmetry of the tetrahedron are parallel and perpendicular to the crystal axes. It may be concluded then, that the absences,  $h0l$ , where  $l$  is odd, are due to space-group symmetry; and that the structure has the symmetry of  $Cmcm$  rather than  $Cmc2_1$ .

The structure amplitudes,  $F_c$ , were calculated for  $hk0$  reflections by means of approximate parameters obtained from the vector map; the observed amplitudes,  $F_o$ , were put on roughly the same scale as the  $F_c$  values by a factor derived from their ratios, and a Fourier series was calculated with the differences,  $F_o - F_c$ , as coefficients (Cochran, 1951). There were no ambiguities involving signs since the indium contribution is always larger than that of all the light atoms combined.

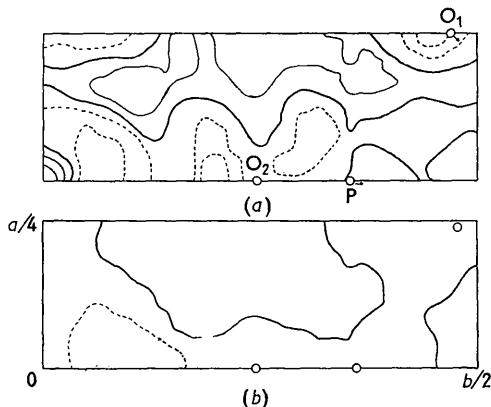


Fig. 2.  $(F_o - F_c)$  synthesis projected on (001): (a) first diagram; (b) final diagram. Heavy lines: zero contours; light lines: positive contours; broken lines: negative contours.

The resulting diagram is shown in Fig. 2(a). The  $\text{O}_2$  atom seems to be correctly placed, or nearly so, since it lies in a fairly uniform region. The gradients on which P and  $\text{O}_1$  lie—fairly steep for the latter—suggest shifts of the parameters in the directions shown by the arrows, that is, in the direction of rising gradient. Fig. 2(b) shows the graph of a second difference series, calculated after the parameters were corrected as indicated, and the scale factor improved. The background is low, and all of the atoms lie in regions of uniform density, so that no further refinement of the  $xy$  parameters is indicated.

Only one more parameter,  $z$  for  $\text{O}_2$ , is required. This was calculated directly from the dimensions of the phosphate group, which, from its projection in the  $xy$  plane, appears to be of regular tetrahedral form in this crystal. The complete set of parameters required to describe the structure is as follows:

	$x/a$	$y/b$	$z/c$
In	0	0	0
P	0	0.360	0.25
$\text{O}_1$	0.240	0.475	0.25
$\text{O}_2$	0	0.246	0.062

Table 2 shows the observed and calculated structure amplitudes for the single-crystal data; Table 3 gives

Table 2.  $\text{InPO}_4$  single-crystal data

$hk$	(Copper radiation)					
	$l = 0$		$l = 2$		$l = 4$	
	$F_o$	$F_c$	$F_o$	$F_c$	$F_o$	$F_c$
11	27	34	38	44	23	24
02	33	39	21	19	34	35
20	37	46	35	41	29	30
13	40	42	26	25	32	34
22	16	14	35	36	21	20
04	41	41	37	38	26	24
31	28	28	32	34	21	22
24	26	24	43	46	14	15
15	31	31	26	26	28	27
33	36	36	20	19	29	32
06	30	29	18	15	30	30
40	42	46	18	17	33	35
42	27	25	19	19	27	26
26	24	21	21	20	23	24
35	29	29	25	22	26	25
17	17	17	31	30	18	16
44	26	26	28	30	22	19
51	17	18	27	29	17	17
08	32	33	21	19	25	27
53	27	27	19	18	23	25
37	17	16	28	27	15	16
46	24	24	13	14	25	26
28	29	29	19	21	22	24
60	28	28	22	21	18	22
55	23	23	21	21	18	21
19	24	23	19	21	18	20
62	14	13	22	23		
64	12	16	28	30		
0,10	10	13				

part of the powder-pattern observations compared with calculated intensities, in order to include data for planes  $hkl$ ,  $l$  odd, which were not satisfactorily measured from the single crystal.

The value of the factor,  $R = \sum |F_o - F_c| \div \sum |F_o|$ , calculated for the single-crystal data is 0.066. It should be remembered, however, that the values of the structure amplitudes are highly dependent on the heavy atoms which are in special positions.

#### Crystal structure of $\text{TIPO}_4$

Only powder data were available for the structure analysis of thallic phosphate. The diffraction pattern, strongly similar to that of indium phosphate in spacing and relative intensities, indicated clearly that the structural parameters of the two crystals could not be far different. Owing to the disparity in the scattering powers of thallium, phosphorus and oxygen, the calculated intensities could not be expected to be sensitive to small changes in the positions of the lighter

Table 3.  $\text{InPO}_4$  powder diffraction data

(Copper radiation)				
$hkl$	$\sin^2 \theta$ (obs.)	$I_o$	$I_c \times 10^{-3}$	
110	0.0302	143	150	
020	0.0372	70	76	
111	0.0431	31	29	
021	0.0501	37	13	
002	0.0515			23
112	0.0817	150	164	
200	0.0837	47	44	
022	0.0887	16	14	
130	0.1046	55	57	
131	0.1175	0	0	
220	0.1209	5	5	
221	0.1338	0	2	
202	0.1352	41	41	
113	0.1461	0	0	
040	0.1488	18	19	
023	0.1531	3	3	
132	0.1561	26	26	
041	0.1617	0	0	
222	0.1724	46	46	
310	0.1977	13	12	
203	0.1996	24	0	
042	0.2003			22
004	0.2061	17	16	
311	0.2106	2	2	
133	0.2205	3	3	
240	0.2325	8	7	
114	0.2363	15	14	
223	0.2368			1
024	0.2433	16	14	
241	0.2454	0	1	
312	0.2492	27	26	
150	0.2534	10	11	
043	0.2647	0	0	
151	0.2663			1
330	0.2721	16	14	
242	0.2840	39	41	
331	0.2850			0
204	0.2898	8	8	
152	0.3049	11	12	
134	0.3107	20	21	
313	0.3136	0	0	
332	0.3236	6	6	
224	0.3270	6	7	
060	0.3348	14	3	
400	0.3349			9
061	0.3477			0
401	0.3478	0	0	
243	0.3484			1
115	0.3522	2	2	
044	0.3549	3	4	
025	0.3592	0	1	
153	0.3693	0	2	
420	0.3721	3	4	
421	0.3850	5	1	
062	0.3863			2
402	0.3864			2
333	0.3880	0	1	
314	0.4038	5	7	
205	0.4057	0	0	
260	0.4185	2	3	
350	0.4209	6	5	
422	0.4236	5	4	
135	0.4266	0	0	

Table 4.  $\text{TIPO}_4$  powder diffraction data

(Copper radiation)				
$hkl$	$\sin^2 \theta$ (obs.)	$I_o$	$I_c \times 10^{-3}$	
110	0.0295	473	515	
020	0.0369	262	232	
111	0.0414	40	34	
002	0.0472	110	117	
021	0.0486	13	15	
112	0.0768	480	496	
200	0.0812	122	122	
022	0.0841	111	101	
130	0.1031	184	162	
131	—	0	0	
220	0.1184	50	48	
202	0.1284	129	120	
221	0.1290	0	1	
113	—	0	0	
023	0.1431	4	4	
040	0.1473	51	50	
132	0.1505	121	115	
041	—	0	0	
222	0.1654	160	152	
004	0.1890	52	42	
310	0.1918	45	46	
042	0.1947	68	64	
311	0.2036	2	3	
133	0.2098	2	4	
114	0.2185	77	67	
223	0.2259	50	1	
024				50
240	0.2286	31	32	
312	0.2394	85	82	
241				2
150	0.2506	32	37	
043	—	0	0	
151	—	0	0	
330	0.2656	45	40	
204	0.2704	31	29	
242	0.2758	96	96	
331				0
134	0.2923	60	66	
152	0.2978	38	48	
313				0
224	0.3071	31	36	
332	0.3129	28	31	
400	0.3249	21	21	
115				2
060	0.3316	8	11	
025				1
243	0.3364	16	1	
044				17
061	—	0	0	
153	0.3615	11	2	
420				17
333	0.3721	1	1	
421				1
062	0.3792	7	10	
314	0.3811	22	28	
135	—	0	0	
422	0.4087	17	23	
260	0.4128	29	17	
350				0
225				0
244	0.4177	12	17	
261	—	0	1	
351	0.4250	1	0	
006				3
063	0.4397	22	0	
154				28

atoms. Therefore the phosphate group was assumed to be of regular tetrahedral form, with P-O distances of 1.56 Å, as found in the indium compound. On the other hand, the intensities of a number of reflections

were quite measurably affected by the position of the phosphate group taken as a unit. These reflections,

along with the very few which are free of thallium contribution, were used as criteria for the location of the center of the phosphate group. The parameter values found to give the best agreement between calculated and observed intensities are very close to those determined for indium phosphate. The complete set is as follows:

	$x/a$	$y/b$	$z/c$
Tl	0	0	0
P	0	0.358	0.25
O <sub>1</sub>	0.236	0.470	0.25
O <sub>2</sub>	0	0.245	0.070

Table 4 shows a list of observed and calculated intensities. The value of the ratio  $\sum |F_o - F_c| \div \sum |F_o|$  is 0.065. Since the predominant scatterer, thallium, is in positions fixed by the space group, this is no doubt an optimistic evaluation of the accuracy of the structure as a whole.

### Discussion of the structure

Fig. 3 is a projection of the indium phosphate structure on the plane perpendicular to the  $c$  axis. Indium

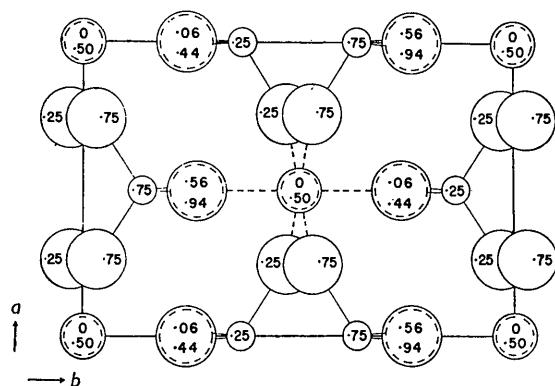


Fig. 3. Structure of  $\text{InPO}_4$  projected on (001). The circles, in descending order of size, represent oxygen, indium and phosphorus. The numbers give the height of each atom in fractions of the  $c$  translation. The coordination is shown for the central indium.

is coordinated to six oxygens, two O<sub>2</sub> and four O<sub>1</sub>, each of which is the corner of a different phosphate group. The coordination distances are unequal. The two oxygens O<sub>1</sub>, each associated with only one indium, are at distances of  $1.97_6$  Å. The four oxygens O<sub>2</sub>, each of which is shared by two indiums, are at distances of  $2.19_2$  Å. The resulting configuration is such

that each indium atom is surrounded by six oxygens at the corners of a somewhat distorted octahedron, two edges of which are shared between nearest indium neighbors, lying at intervals of  $\frac{1}{2}c$  along the  $z$ -axis direction. The closest approach between oxygens in different phosphate groups is  $2.76$  Å.

The structure of thallic phosphate may be described in similar fashion. The coordination ring consists of two oxygens at a distance of  $2.02$  Å, and four oxygens at distances of  $2.28$  Å. The nearest O–O approach of different phosphate groups is  $2.85$  Å.

Though no other phosphate having this structure has previously been reported, the structure type is not new. The chromates of cadmium, cobalt, copper, nickel, vanadium and zinc are known to crystallize with this arrangement. The two for which structures have been determined (Brandt, 1943),  $\text{VCrO}_4$  and  $\text{CuCrO}_4$ , have parameters which are very similar to those found for  $\text{TlPO}_4$  and  $\text{InPO}_4$ .

In a search among the phosphates of trivalent cations for other possible members of this structural group, one more example of the type was found. This is an unstable form of  $\text{CrPO}_4$ , for which  $d$  values have been published by Sullivan & McMurdie (1952). Their data can be indexed in conformity with an orthorhombic cell of dimensions:

$$a = 5.15, b = 7.77, c = 6.11 \text{ \AA}.$$

The relative intensities, recorded as peak heights, differ from those of indium phosphate only in ways that can be explained by the difference in scattering power of the cations.

The assistance of Mr Alvin Perloff in crystal-growing experiments, of Mr Homer Kissinger in X-ray techniques, and of Mr Gordon Burley in a number of the calculations is gratefully acknowledged. Thanks are also due to Mr George Ugrinic for the careful preparation of the powder diffraction patterns.

### References

- BRANDT, K. (1943). *Ark. Kemi Min. Geol.* **17** A, No. 6.  
 COCHRAN, W. (1951). *Acta Cryst.* **4**, 81.  
*International Tables for the Determination of Crystal Structures* (1935). Berlin: Borntraeger.  
 LU, C.-S. (1943). *Rev. Sci. Instrum.* **14**, 331.  
 MELLOR, J. W. (1924). *Comprehensive Treatise on Inorganic and Theoretical Chemistry*. London: Longmans, Green.  
 SULLIVAN, B. M. & McMURDIE, H. F. (1952). *J. Res. Nat. Bur. Stand.* **48**, 159.