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X-ray Diffraction Study of Indium Phosphate Dihydrate and Isostructural Thallic Compounds

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The isostructural crystals, $InPO_4.2 H_2O$, $TlPO_4.2 H_2O$, and $TlAsO_4.2 H_2O$ have been studied by means of single crystal X-ray diffraction techniques. Structural parameters are given for the indium compound, which was chosen to represent the group. For this crystal, the cell, containing eight formula weights, has dimensions $a = 10\cdot36$, $b = 8\cdot84$, $c = 10\cdot19$ Å. The space group is $Pbca(D_{2h}^{15})$. The structure is a complex three-dimensional net, in which two sets of water oxygens are very differently situated. The framework of the net is built up of indium, phosphate groups and one set of water oxygens. The second set of water oxygens lie in otherwise unoccupied channels of the framework. The number and lengths of the bonds formed in each case strongly suggest that one has the nature of an $(OH)^-$ and the other of an $(OH_3)^+$ group. These laboratory grown crystals are isostructural with the minerals, strengite ($FePO_4.2 H_2O$) and scorodite, ($FeAsO_4.2 H_2O$).

Introduction

Under suitable conditions of preparation, the orthophosphates of indium and of trivalent thallium may be crystallized either as anhydrates or as dihydrates. The structure of $InPO_4$ and its isotype, $TlPO_4$, has been described in an earlier paper (Mooney, 1956). An X-ray analysis of the hydrated crystals was undertaken as a continuation of a series of structure studies of the phosphates of trivalent elements. Early stages in the examination of these two crystals, and also of a third, $TlAsO_4.2 H_2O$, showed, as expected, that the atomic arrangement in all three is essentially the same. The indium compound was selected as the most favorable case for detailed structure determination.

Preparation of the crystals

The addition of phosphate ion to an aqueous solution of indium nitrate results in the immediate precipitation of a voluminous white amorphous product, described in chemical literature as a basic salt of indefinite composition. It is highly insoluble except in acids. A simple method proved successful in promoting the growth of single crystals suitable for X-ray diffraction. Precipitates were dissolved in nitric acid solution and crystallized out by very slow dilution or neutralization at temperatures of about 75 °C. The crystals, of composition $InPO_4.2 H_2O$, generally appear as short, stout bipyramidal prisms, the largest of which have dimensions of a few tenth millimeters. Crystals of thallic phosphate dihydrate and thallic arsenate dihydrate were grown in the same way. The crystals of the arsenate were inferior to the other two in size and perfection of form.

X-ray diffraction methods

For $InPO_4.2 H_2O$, a complete set of diffraction data within the Cu $K\alpha$ range was collected. For the other two crystals, observations were limited to zero and first layers about the three axial directions. All of the data was photographically recorded on three-film packs by means of an integrating Weissenberg instrument. The intensities were measured by means of a

simple spot photometer, and corrected for the Lorentz-Polarization factor and for absorption. The absorption correction was applied to zero layer intensities by means of a graphical method due to Rogers & Moffat (1956). For upper layers, the correction was approximated by extrapolation from measurements of a few selected reflections.

At various stages in the progress of the analysis, the observed structure amplitudes were scaled to calculated values by the factor, $K \exp [- \beta \sin^2 \theta / \lambda^2]$, where β had a final value of 0.5 Å^2.

In the calculation of the structure amplitudes, Thomas–Fermi scattering factors, corrected for anomalous dispersion, were used for the heavy atoms, and the James & Brindley values for oxygen and phosphorus.

Unit cell and space group

The crystals are orthorhombic dipyramidal. Their cell dimensions, measured from rotation and Weissenberg photographs, are given in the following table. The densities were computed on the basis of eight formula weights per unit cell.

Table 1. *Cell dimensions and calculated densities*

Crystal	a (Å)	b (Å)	c (Å)	ϱ g.cm.$^{-3}$
InPO$_4$.2 H$_2$O	10·36	8·84	10·19	3·45
TlPO$_4$.2 H$_2$O	10·39	8·87	10·31	4·63
TlAsO$_4$.2 H$_2$O	10·48	9·16	10·49	4·93

The density of TlPO$_4$, measured from coarse crystal aggregates by means of a Berman balance, was found to be 4.64 ± 0.03 g.cm.$^{-3}$.

The X-ray patterns show that no special diffraction condition affects the general planes, hkl, all types of which are observed. However, for $0kl$ to reflect, k must be even; for $h0l$, l even; and for $hk0$, h even. These criteria are characteristic of the space group, $Pbca(D_{2h}^{15})$. In the absence of any evidence to the contrary, the sixty-four atoms in the cell (hydrogen excluded) were assumed to occupy the sets of eight-fold general positions required by this space group symmetry. It follows that twenty-four parameters are required to describe the structure.

Now, the atomic number is 81 for thallium and 49 for indium. Moreover, the eight cations per unit cell are geometrically equivalent. Therefore, their contributions to the intensities will dominate the diffraction patterns and so give strong evidence of their positions. On the other hand, the conditions are inauspicious for the deduction of the light atom parameters. In the more favorable case the average contribution of indium to the intensity may be expected to be about three times that of all of the light atoms together, which furthermore, are distributed in seven sets. Whether or not their contributions appreciably modify the diffracted intensities must depend on their positions relative to each other and to indium.

The diffraction patterns are characterized by an unusually large number of very weak or absent reflections. Such reflections occur with regularities which can be explained if the heavy atom set has parameters near to, but not identical with 1/8, 1/6, 1/6 for x, y, and z respectively. This results in the occurrence of many measureable reflections which have very moderate contributions from the heavy atoms. It happens that the light atoms cooperate enough, in many instances, to materially affect such reflections. Therefore, their positions could be determined directly from the X-ray data, though not to a high degree of accuracy.

Determination of the approximate structure

The Patterson projections, $F^2(0kl)$, $F^2(h0l)$ and $F^2(hk0)$ were calculated for the three crystals. The sets of diagrams differ from each other only in small details, proving the close similarity between the structures of the three compounds. They show, of course, prominent peak sets arising from heavy atom interactions, and some irregularly shaped and fairly high contours suggesting partly superposed and unresolved light-heavy atom vectors. From the heavy atom vectors, the following parameters were obtained for the cation positions in each crystal. No further information was

Table 2. *Approximate cation parameters from Patterson projections*

Crystal	x/a	y/b	z/c
InPO$_4$.2 H$_2$O	0·132	0·154	0·174
TlPO$_4$.2 H$_2$O	0·128	0·155	0·178
TlAsO$_4$.2 H$_2$O	0·126	0·154	0·183

extracted from the Patterson diagrams. Instead, the tentative parameters found for the heavy atoms were used to derive signs of the amplitudes for use in the calculation of electron density projections.

The heavy atoms, because of the particular values of their parameters, contribute very little to the intensities of a considerable number of planes, whose amplitudes thus remain indeterminate in sign. Many of these reflections are absent, and the remainder are quite low. The signs of the heavy atom contribution were attached to the observed structure amplitudes with doubtful cases omitted, and a set of two-dimensional electron density diagrams were computed for the InPO$_4$.2 H$_2$O and TlPO$_4$.2 H$_2$O crystals.

The expected number of light atom peaks were observable in the Fourier projections. However, their representation was less than ideal, in that the shapes and positions were affected by termination of series errors, by the disparity in the scattering power of the light and heavy atoms, and rather seriously by superposition. However, the superposition involved different atoms in different projections. It was possible to derive tentative sets of xy, yz, and xz parameters for the seven required positions, not very different in

the two crystals, but far less reliable in the thallic salt. A number of uncertainties were encountered in attempting to correlate the values obtained into a single consistent set of xyz's for the seven atoms. This was due to fortuitous coincidences or near coincidences among the values, and to the fact that they could not always be read with sufficient accuracy for making fine distinctions.

The uncertainties were straightforwardly resolved by using the better set of data—that of $InPO_4.2 H_2O$ —in a three-dimensional electron density calculation, prepared for sections at 12° (0·33 Å) intervals along the c-axis, from 0 to 1/8. Though all except the indium peaks were rather diffuse, their distribution in space sorted out the previously obtained parameters into a chemically reasonable trial structure. The phosphate group, oriented with a trigonal axis ap-

proximately in the c axial direction, was easily recognized, and the two remaining peaks could then be identified as water oxygens. The three-dimensional sections were computed by X-rac, through the kindness of Prof. Ray Pepinsky.

Table 3. *Structural parameters for* $InPO_4.2 H_2O$

	x/a	y/b	z/c
In	0·1310	0·1538	0·1729
P	0·148	0·463	0·360
O_1	0·287	0·476	0·304
O_2	0·057	0·581	0·295
O_3	0·096	0·300	0·340
O_4	0·152	0·492	0·510
*O_{w1}	0·544	0·344	0·450
*O_{w2}	0·816	0·245	0·366

* (Water oxygens)

Table 4. *Observed and calculated structure factors*

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
020	(3·2)	−3·6	087	17·1	−19·4	806	24·4	23·4	410	(3·0)	−5·3
021	24·5	−27·9	088	(3·5)	−0·4	906	13·4	−13·4	420	7·6	7·3
022	(3·5)	5·8	089	10·2	9·6	10,0,6	10·0	−9·7	430	11·5	12·9
023	13·8	13·0				11,0,6	(3·0)	1·6	440	16·5	14·9
024	10·9	10·7	0,10,0	25·0	−24·3				450	(3·0)	−0·2
025	20·6	−19·6	0,10,1	9·4	10·6	008	17·8	−16·4	460	26·0	−25·1
026	(4·1)	−4·9	0,10,2	9·6	11·4	108	10·5	−11·9	470	(3·5)	3·7
027	22·3	−22·6	0,10,3	(3·5)	−1·7	208	(3·0)	−3·7	480	(3·5)	1·4
028	12·2	9·7	0,10,4	13·0	12·7	308	9·1	−8·6	490	(3·5)	0·6
029	13·8	12·9	0,10,5	7·5	−7·9	408	12·0	10·1	4,10,0	19·6	20·3
0,2,10	(3·5)	1·5	0,10,6	16·7	−17·8	508	(4·0)	7·2			
0,2,11	10·0	8·2				608	(4·0)	4·6	600	14·9	13·7
0,2,12	10·1	−8·9	002	25·5	−28·1	708	(4·0)	3·4	610	27·8	29·5
			102	15·0	−15·7	808	14·0	−12·6	620	(3·5)	4·7
040	11·1	−11·0	202	(3·5)	4·6	908	11·1	−10·9	630	10·2	11·0
041	16·2	19·4	302	13·3	−11·6	10,0,8	(3·0)	1·6	640	(3·5)	3·5
042	13·4	12·7	402	17·4	17·6				650	15·3	−13·2
043	(3·5)	−0·7	502	17·1	17·9	0,0,10	(3·0)	−7·5	660	(4·0)	6·1
044	(3·5)	1·9	602	(4·0)	1·3	1,0,10	18·3	16·6	670	14·0	14·7
045	21·8	−21·3	702	8·1	7·0	2,0,10	(3·0)	1·2	680	(4·0)	4·4
046	12·6	−11·4	802	16·5	−12·7	3,0,10	18·0	15·5	690	17·8	16·6
047	13·7	12·4	902	13·2	−13·8	4,0,10	(4·0)	7·7	6,10,0	6·9	−9·0
048	20·0	21·0	10,0,2	(3·5)	1·9	5,0,10	20·0	−19·7			
049	(4·0)	−0·8	11,0,2	9·3	−10·3	6,0,10	(4·0)	−3·6	800	21·6	21·7
0,4,10	(4·2)	1·3	12,0,2	11·5	11·4	7,0,10	8·5	−9·7	810	(4·0)	−7·0
0,4,11	8·6	−8·2				8,0,10	(4·0)	−4·3	820	(4·5)	−4·7
0,4,12	13·9	13·8	004	19·7	−19·9				830	8	−9·3
			104	8·6	11·1	0,0,12	16·0	13·7	840	17·1	−16·2
060	27·7	29·6	204	(3·5)	6·1	1,0,12	13·1	−9·8	850	(4·0)	1·8
061	18·9	21·7	304	12·5	10·7	2,0,12	(3·0)	−1·2	860	23·5	22·0
062	10·0	−8·0	404	18·1	18·7	3,0,12	8·7	−9·2	870	9·8	−11·1
063	(4·0)	0·0	504	26·2	−28·6	4,0,12	19·5	−19·7	880	(3·5)	1·2
064	(5·0)	−4·9	604	(4·0)	−7·0	5,0,12	16·0	15·2	890	12·3	−13·2
065	21·5	−19·2	704	15·4	−15·1						
066	25·2	23·6	804	12·0	−10·2	200	7·2	−5·4	10,0,0	15·2	−16·7
067	12·9	11·6	904	22·0	18·5	210	33·6	−37·7	10,1,0	19·0	−20·4
068	16·5	−15·5	10,0,4	(4·5)	3·5	220	7·0	−6·4	10,2,0	(4·5)	−6·6
069	(3·5)	0·9	11,0,4	(5·0)	8·4	230	11·0	−11·9	10,3,0	(4·5)	−4·5
0,6,10	(3·5)	−3·7	12,0,4	(5·0)	4·3	240	11·2	−11·6	10,4,0	(4·5)	5·4
0,6,11	7·1	−7·7				250	29·6	31·8	10,5,0	19·5	18·5
			006	40·5	44·8	260	(3·0)	−2·5	10,6,0	8·0	−9·1
080	(3·0)	3·1	106	(4·0)	−6·0	270	23·2	−23·9	10,7,0	(4·0)	6·7
081	13·1	−12·5	206	(4·0)	−6·4	280	(3·5)	−4·3			
082	(4·0)	1·8	306	9·2	−10·8	290	21·4	−19·2	12,0,0	20·2	−20·1
083	(4·2)	5·5	406	34·6	−35·4	2,10,0	(3·5)	2·9	12,1,0	(4·5)	8·7
084	(4·2)	1·3	506	12·3	10·9	2,11,0	14·0	13·5	12,2,0	(4·5)	5·8
085	13·7	13·7	606	9·5	8·9				12,3,0	(4·5)	3·4
086	(3·5)	2·7	706	(3·5)	3·2	400	42·7	−45·7	12,4,0	15·1	16·0

Refinement and estimated accuracy

The trial structure derived from the two and three-dimensional electron density calculations had a residual factor, $R = \Sigma|F_o - F_c|/\Sigma|F_o|$ of about 0·19, while R calculated for the partial structure, that is, on the basis of indium alone, was 0·31. The trial structure was then refined by means of two-dimensional difference Fouriers along each axial direction. The diagrams rapidly improved in quality, and after several reiterations, showed only low background ripples, as illustrated in Fig. 1. During the process, all of the parameters shifted to some extent. The R factor, which, for monitoring purposes, was calculated for observed reflections only, steadily decreased to the end values, 0·082, 0·083 and 0·078 for the $0kl$, $h0l$, and $hk0$ zones respectively. When the unobserved planes, rated as $\frac{1}{2}F_o$ (minimum) are included in the calculation, the values become 0·12 for $0kl$, and 0·13 for $h0l$ and $hk0$ zones.
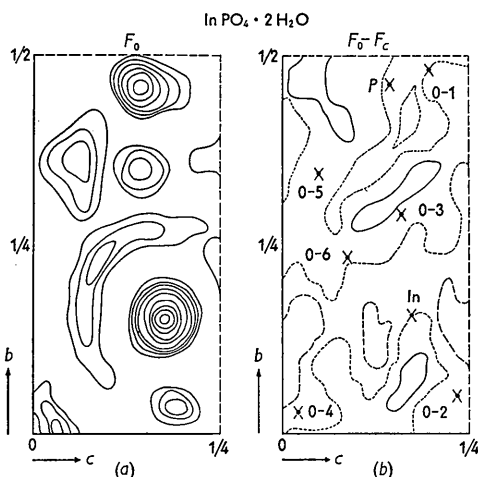
In PO$_4$ · 2 H$_2$O

Fig. 1. (a) Initial Fourier projection on (100) for InPO$_4$.2H$_2$O with phases based on the indium position alone. The contour intervals are equal and arbitrary. (b) Final $(F_o - F_c)$ Fourier synthesis derived from the same data, with F_c including all atoms. Zero contours are indicated by broken lines, positive contours by solid lines.

The final parameters, given in Table 3, are mean values of the two measurements obtained from different projections. The structure amplitudes calculated from these parameters are compared with experimentally measured values in Table 4. As has been mentioned, the number of absent planes is very high. Actually, about 33% of the possible reflections could not be measured, despite experimental efforts to do so. However, the calculated amplitudes of such planes are agreeably low. More than half of them are less than $\frac{1}{2}F_o$(min.), and very few exceed F_o(min.).

The standard deviation of the indium position, estimated by Cruickshank's method (1949) is 0·0035 Å. For the light atom positions, the standard deviation appears to be in the neighborhood of 0·04 Å.

Description of the structure

The structure, shown in projection in Fig. 2, is a three-dimensional net of some complexity. Its oxygen framework is built up of interconnected tetrahedra and octahedra; that is, of phosphate groups and six-coordinated In^{3+} ions arranged in such a way that no atoms are shared between octahedra. One edge of the oxygen octahedron enclosing indium is a pair of waters; the other four points are corners of different phosphate groups. Each phosphate oxygen is linked to one In^{3+} ion, and, excepting the four oxygens in its own indium coordination ring, has only one close neighbor, a water oxygen of an adjacent octahedron.

The water corners of successive octahedra, together with indium, form a continuous zig-zag twisted chain configuration, $\cdots O_{w1}-In-O_{w2} \cdots O_{w1}-In-O_{w2} \cdots$ which serves to distribute positive charge so that each phosphate oxygen can have at least two-fold coordination. This contrasts with the condition in the anhydrate, InPO$_4$, where half the oxygens have a coordination number of only one. However, the two waters are dissimilar in their oxygen environment. O_{w1} forms a short bond to only one phosphate oxygen, while O_{w2}, which lies in an otherwise unoccupied channel in the network, has three close phosphate oxygen neighbors.

Interatomic distances and discussion

All of the interatomic distances less than 3·4 Å are listed in Table 5. The standard deviation of the lengths is estimated as 0·04 Å for distances involving indium, and about 0·06 Å for those between light atoms.

The phosphate group is a regular tetrahedron with dimensions P–O = 1·55 Å, and O–O = 2·54 Å. In the coordination octahedron, the O–O separations average 3·06 Å, and range between 2·86 Å and 3·19 Å. The In–O distances average 2·17 Å, and lie between 2·08 and 2·28 Å. Actually, the indium–oxygen distances fall into two groups, four very near to 2·12 Å, and the other two close to 2·25 Å. The difference, 0·13 Å, may be significant. The longer distances occur for a phosphate oxygen, O$_1$, and for a water oxygen, O$_{w1}$, which are at opposite ends of a diagonal of the octahedron. If accepted as real, the difference in the coordination distances may indicate a relatively higher degree of covalency in four of the bonds; on the other hand, it may be a consequence of the particular structural geometry. An inequality has been observed between the six-oxygen coordination distances in the anhydrous salt, InPO$_4$, where four of the distances are 2·19 Å, and two are 1·97 Å. In this case, however, the difference can be attributed to the fact that the shorter distances occur for oxygens which are coordinated only to a single indium, while the longer bonds are to oxygens which are doubly coordinated.

For intercomparison, the average In–O bond length in the hydrate is 2·17 Å, and in the anhydrate, 2·12 Å. The four-bond sets average 2·12 Å in the hydrate,
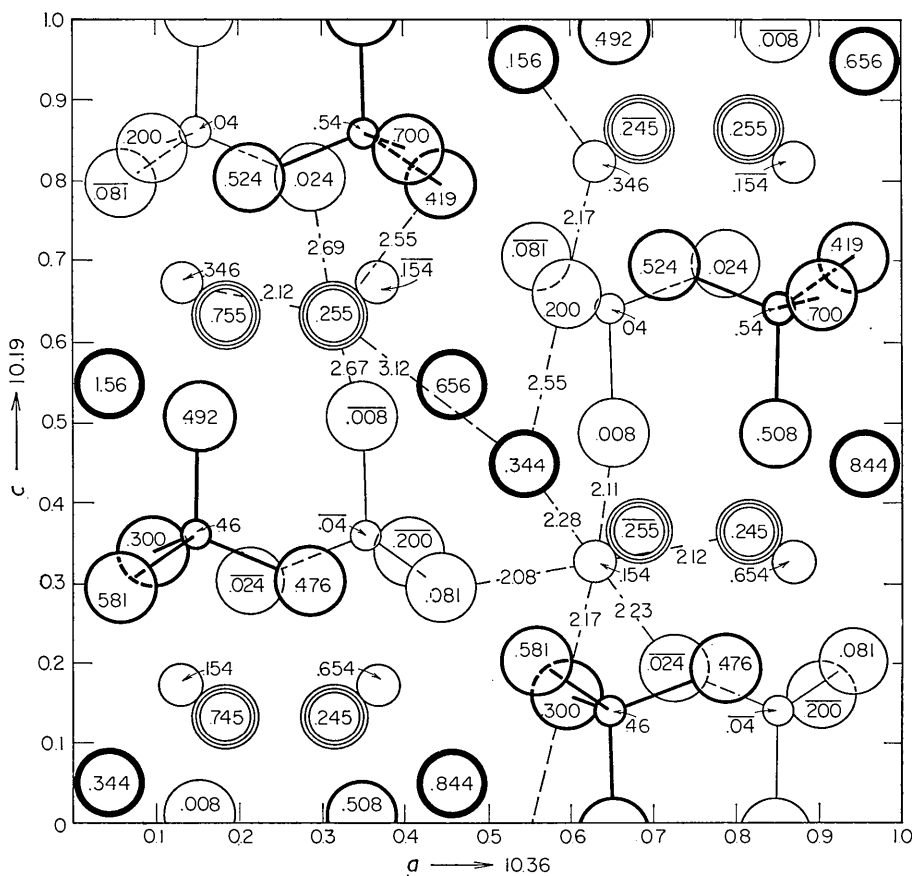
Fig. 2. A unit cell of the $InPO_4.2H_2O$ structure projected on (010). The circles, in decreasing order of size, represent O, In and P, with attached numerical values of y/b. The water oxygen, O_{w1}, is distinguished by a solid ring, and O_{w2} by a striped one. Interatomic distances are indicated by broken lines, and their values given in Å units.

Table 5. *Interatomic distances in* $InPO_4.2H_2O$

(A) Within coordination ring				(B) Phosphate ion		(C) Neighbors (< 3.5 Å)	
$In-O_1$	2·23 Å	O_1-O_{w2}	3·13 Å	$P-O_1$	1·55 Å	$O_{w1}-O_3$	2·55 Å
$In-O_2$	2·08	O_2-O_3	2·86	$P-O_2$	1·56	$O_{w1}-O_{w1}$	3·08
$In-O_3$	2·17	O_2-O_4	3·01	$P-O_3$	1·55	$O_{w1}-O_{w2}$	3·12
$In-O_4$	2·11	O_2-O_{w1}	3·00	$P-O_4$	1·54	$O_{w1}-O_2$	3·26
$In-O_{w1}$	2·28	O_3-O_{w1}	3·03	O_1-O_2	2·56	$O_{w1}-O_1$	3·27
$In-O_{w2}$	2·12	O_3-O_{w2}	3·14	O_1-O_3	2·54	$O_{w2}-O_1$	2·69
O_1-O_2	3·11	O_4-O_{w1}	3·19	O_1-O_4	2·53	$O_{w2}-O_2$	2·55
O_1-O_3	3·13	O_4-O_{w2}	2·98	O_2-O_3	2·56	$O_{w2}-O_4$	2·67
O_1-O_4	3·08	O_5-O_{w2}	3·07	O_2-O_4	2·53	$O_{w2}-O_3$	2·95
				O_3-O_4	2·49		

and 2·19 Å in the anhydrate. The sum of the Pauling crystal radii is 2·21 Å. The only measured In–O distance listed in Sutton's *Table of Interatomic Distances in Molecules and Ions* (1958) is the In–H₂O distance in $(NH_4)_2InCl_5$, which is 2·23 Å.

The distances between successive waters in neighboring octahedra, between two in the same octahedron, and also between two O_{w1} waters across symmetry centers, are the same within experimental error, and have the average value, 3·09 Å. Only the first of these are possible water–water binding distances, the others

being highly improbable on chemical grounds in one case, and on symmetry grounds in the other.

The striking difference in the environments of the two waters is illustrated in Fig. 3. Indium, the phosphate group and O_{w1} together form a framework which has wide channels running through the structure parallel to the *c*-axial direction. The water oxygens, O_{w2}, stacked one above the other at intervals of $\frac{1}{2}c$, span the open space by linking to indium, to O_{w1} at a distance of 3·12 Å, and to three phosphate oxygens at an average distance of 2·64 Å, a length indicating
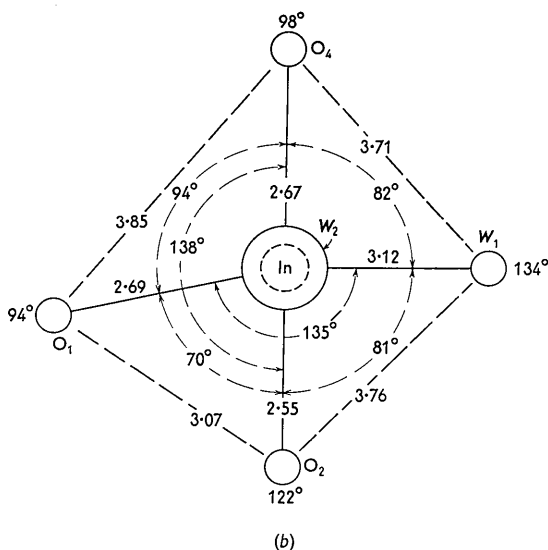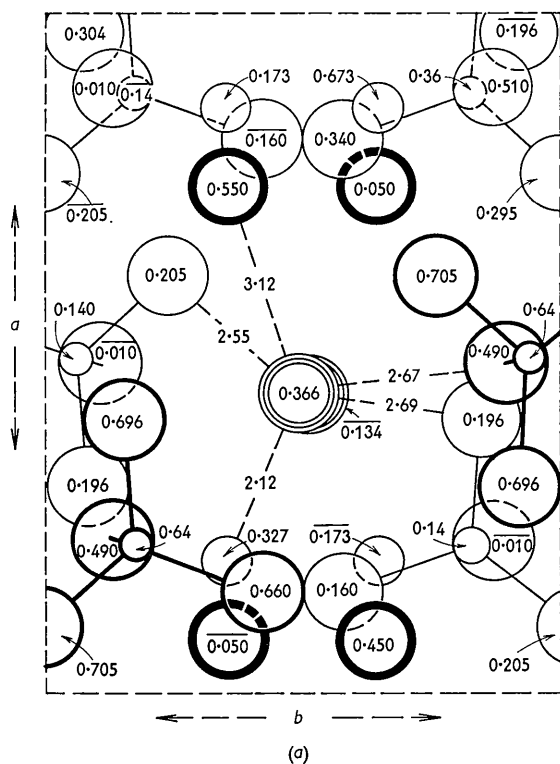
(a)

(b)

Fig. 3. (a) Detail of $InPO_4.2H_2O$ structure, projected on (001), showing the sites of O_{w2} in channels of the network. (b) Diagrammatic representation of the configuration about O_{w2}, with the $In-O_{w2}$ vector taken perpendicular to the plane of the diagram. Angles between this bond and each of the other bonds are given at the periphery of the figure. Distances are in Å units.

hydrogen or hydroxyl bonds. The bonds from the water to the phosphate oxygens are inclined away from the $In-O_{w2}$ bond at angles of 90° or more, so as to lie at three corners of a distorted 'square', the

fourth corner of which, considerably displaced, is supplied by O_{w1}. The distances and bond angles of this configuration are given in Fig. 3(b).

The water oxygen, O_{w1}, in addition to its connection with indium and O_{w2}, forms only one short bond, 2·55 Å, to a phosphate oxygen. The bond angle, $In-O_{w1}-O_3$, is 91°. The next nearest neighbors, always excepting those in the same octahedron, are two phosphate oxygens at 3·26 Å. The system of bonds, $\cdots O_3-In-O_{w1} \cdots O_3-In-O_{w1} \cdots$ zig-zag in the c-axial direction, connecting successive phosphate groups through the O_3 corner.

Since no direct information concerning the location of the hydrogen atoms is available, the fundamental nature of the two 'waters' in the crystal can only be surmised from the structural data. It is obvious that they are different, and that neither shows evidence of the tetrahedral charge distribution expected and repeatedly observed in the crystals of true hydrates. Instead, the number of the water–oxygen bonds, their lengths and their configuration lead to the premise that O_{w1} is an $(OH)^-$ group, and that O_{w2} is an $(OH_3)^+$ group, both forming directed bonds under the polarizing influence of the small and highly charged indium. No distinction can be made between hydrogen or hydroxyl bonds since the difference between the bond lengths are not significant within the estimated error of measurement.

In view of the chemical properties of indium, and the method of preparation of the phosphate as previously described, it is highly probable that the components entering into the crystallization process are $(In.OH)^{2+}$, $(HPO_4)^{2-}$, and H_2O. If this is so, the resulting crystal has the constitution of a mono-hydrated hydroxy-acid phosphate rather than a dihydrated orthophosphate; an assumption which is supported by the structural results.

The $(OH)^-$ group as a structural component of hydroxy compounds such as $Cu_2(OH)PO_4$ (libthenite), $Cu_2(OH)AsO_4$ (olivenite), $Zn_2(OH)AsO_4$ (adamine), and many others, is well known. The (OH_3) configuration in solids is far less familiar. It has been observed only for a few cases, in the structures of hydrated crystalline acids and acid salts, where the acidic hydrogen is associated with an H_2O. An excellent discussion of both types of compounds is given by Wells (1950). The literature seems to provide no established example of a structure in which both the $(OH)^-$ and the $(OH_3)^+$ groups function. Such examples will probably not be particularly uncommon when more structures such as hydrated basic salts are studied in detail.

Some structural relationships

There is no close resemblance between the structural arrangement in $InPO_4$ and $InPO_4.2H_2O$, and the dehydration process must involve a breakdown of the hydrate, followed by a recrystallization into the anhydrous structure. Simple experiments made on the

dehydration of crystalline powders of the hydrate showed, as expected, that the water content of the crystal is strongly bound. Several hours of heating at a temperature of about 750 °C. were required to entirely convert a sample to the anhydrous form, which was identified by means of powder diffraction patterns. Additional information was obtained from a differential thermal analysis experiment, which gave evidence that the water content is lost in two stages, the first in the range of temperature between 200 and 300 °C., and the second between 600 and 700 °C. Further data are required for an understanding of the process. However, an explanation is suggested by the structural arrangement. It may be that, at the lower temperature, O_{w2} is expelled from its channels as H$_2$O, leaving a framework structure of In(OH)HPO$_4$. At the higher temperature, the framework collapses to free the second H$_2$O, and to recrystallize as InPO$_4$.

It is of interest to recall that InPO$_4$ and TlPO$_4$ are isostructural with VCrO$_4$ and CuCrO$_4$ (Brandt, 1943) and also with an unstable form of CrPO$_4$ (Sullivan & McMurdie, 1952), this on the basis of comparisons with their published d-values. The anhydrous structure type is unrelated to the known forms of AlPO$_4$ or FePO$_4$. However, the only crystals which could be found to be identifiable as isotypes of InPO$_4$.2 H$_2$O, TlPO$_4$.2 H$_2$O and TlAsO$_4$.2 H$_2$O proved to be three minerals, phosphates and arsenates of Fe and Al. They are scorodite, FeAsO$_4$.2 H$_2$O (Hiriyama & Sakurai, 1949); strengite, FePO$_4$.2 H$_2$O (Kokkorros,

1938) and very probably mansfieldite, Al$_2$O$_3$.As$_2$O$_5$. 4 H$_2$O (Allen, Fahey & Axelrod, 1948).

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The Crystal Structure of 2-Amino-Ethanol Phosphate

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The crystal structure of 2-amino-ethanol phosphate has been solved by Patterson superpositions and refined in three dimensions by difference syntheses and least-squares. The refined parameters include hydrogen positions and isotropic temperature factors, as well as heavy atom positions and anisotropic temperature factors. The refinement was based on 1239 reflections, and was taken to a final R factor of 0·065 for 1000 observed reflections.

Bond lengths and angles are normal. An extensive system of hydrogen bonds is found, the arrangement of which further supports the belief that at least two of the oxygens of the phosphate group are attached by double bonds.

Introduction

2-amino-ethanol phosphate,

$$NH_3^+-CH_2-CH_2-O-PO_3H^-,$$
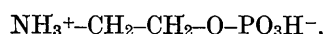
is a moiety of the brain lipid phosphatidyl ethanolamine, and is also found free in brain tissue. This

study of its structure was undertaken for several reasons. First, it provided a conveniently small, though biochemically important molecule with which to acquire initial experience in the application of automated vector-coincidence methods. A long range study of the possibility of using vector coincidence as an essentially automatic structure-solving tool is