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Synthesis and Structure of $KIn(OH)PO_4$: Chains of Hydroxide-Bridged $InO_4(OH)_2$ Octahedra

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The new compound $KIn(OH)PO_4$ was prepared by hydrothermal reaction of In_2O_3 and K_2HPO_4 at 900°C and 3 kbar pressure with subsequent slow cooling. Single-crystal X-ray data for $KIn(OH)PO_4$: orthorhombic, $a = 9.277(2)$ Å, $b = 9.339(2)$ Å, $c = 11.245(2)$ Å, space group $P2_12_12_1$, $Z = 8$, $R = 2.64$, $R_w = 2.92\%$. The compound is built of *cis*-$InO_4(OH)_2$ octahedra that form spiral chains, parallel to the c axis, by corner-sharing of the OH groups. The chains are interconnected by phosphate tetrahedra in a manner that creates tunnels along the z direction containing the K ions. $KIn(OH)PO_4$ is related in structure to the γ phase of $NaTiOPO_4$. The title compound does not generate an SHG signal. TGA and Guinier X-ray powder diffraction data are also reported.

INTRODUCTION

For several years, our laboratories have been studying the synthesis and structures of phosphate compounds, searching for new materials that may have interesting and useful physical, electronic, magnetic, or structural properties. In the course of this work, we synthesized a new phase, $KIn(OH)PO_4$, having a structural formula similar to that of the important nonlinear optical (NLO) material $KTiOPO_4$ (KTP) (1). However, the title compound has a different structure, and does not demonstrate an NLO effect even though it possesses an acentric space group. It does, nevertheless, exhibit an interesting structure, containing chains of hydroxide-bridged indium-oxide octahedra, which we describe in this paper.

EXPERIMENTAL

Synthesis, TGA

In_2O_3 (1.0 g), K_2HPO_4 (1.0 g), and saturated aqueous K_2HPO_4 solution (12.0 g) (66.5% by wt. K_2HPO_4) were sealed in a gold tube (6″ in length × 3/8″ in diameter). The tube was heated to 900°C under 3 kbar pressure over a period of 3 h, held for 12 h, slowly cooled over 32 h to 500°C, and then quenched to room temperature. X-ray powder diffraction showed the solid products to be In_2O_3 and clear crystals of $KIn(OH)PO_4$ up to 2 mm in length.

TGA analysis of the mixed product, in air to 1100°C, indicated onset of weight loss at approximately 560°C.

X-Ray Powder Diffraction

A Guinier–Hägg focusing camera ($r = 40$ mm) was used to obtain X-ray powder diffraction data at room temperature. The radiation was monochromatic Cu$K\alpha_1$ ($\lambda = 1.5405$ Å). Silicon powder ($a = 5.4305$ Å) was used as an internal standard. Lattice parameters for $KIn(OH)PO_4$ were obtained by least-squares treatment of the data. The single-crystal X-ray parameters were used to initiate the refinement. Because it was not possible to completely separate $KIn(OH)PO_4$ and In_2O_3, the few observed lines of In_2O_3 were removed from the list. The indexed X-ray powder diffraction pattern is given in Table 1. It was indexed as orthorhombic with $a = 9.286(1)$ Å, $b = 9.341(1)$ Å, and $c = 11.250(1)$ Å.

Single Crystal X-Ray Structure Determination

A crystal of $KIn(OH)PO_4$ was glued onto the end of a glass fiber and placed on an Enraf-Nonius CAD4-F diffrac-

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TABLE 1
X-Ray Powder Diffraction Data for $KIn(OH)PO_4$[a]

2θ(obs)	I(obs)	hkl	d(obs)	d(calc)
13.423	17	1 1 0	6.591	6.586
15.568	100	1 1 1	5.687	5.684
18.979	2	0 2 0	4.672	4.670
19.108	3	2 0 0	4.641	4.643
20.555	30	0 2 1	4.317	4.313
20.662	19	2 0 1	4.295	4.292
		1 1 2		4.277
22.733	8	1 2 1	3.908	3.912
		2 1 1		3.900
26.624	23	2 1 2	3.345	3.344
		1 2 2		3.351
27.038	2	2 2 0	3.295	3.293
27.340	51	1 1 3	3.259	3.259
28.216	4	2 2 1	3.160	3.160
29.745	3	0 3 1	3.001	3.001
30.572	12	0 2 3	2.922	2.924
		2 0 3		2.917
31.301	18	1 3 1	2.855	2.855
31.452	70	2 2 2	2.842	2.842
		3 1 1		2.843
31.784	14	0 0 4	2.813	2.813
32.061	8	1 2 3	2.789	2.789
		2 1 3		2.785
33.250	2	1 0 4	2.692	2.692
		0 1 4		2.693
34.267	9	1 3 2	2.615	2.614
34.414	7	3 1 2	2.604	2.605
34.657	2	2 3 0	2.586	2.586
		1 1 4		2.586
34.725	1	3 2 0	2.581	2.580
35.603	1	2 3 1	2.520	2.520
		3 2 1		2.515
37.515	1	0 3 3	2.395	2.395
38.284	3	2 3 2	2.349	2.350
38.350	2	3 2 2	2.345	2.345
38.541	3	0 4 0	2.334	2.335
		1 2 4		2.332
		2 1 4		2.330
38.786	5	1 3 3	2.320	2.320
		4 0 0		2.322
38.911	4	3 1 3	2.313	2.313
40.588	1	1 4 1	2.221	2.220
40.814	1	4 1 1	2.209	2.209
41.089	5	3 3 0	2.195	2.195
41.905	2	3 3 1	2.154	2.155
		0 4 2		2.157
42.228	5	2 2 4	2.138	2.139
42.428	8	2 3 3	2.129	2.129
		1 1 5		2.129
		3 2 3		2.126
43.330	1	2 4 0	2.087	2.086
		0 3 4		2.087
		3 0 4		2.082
		4 1 2		2.092
44.108	6	2 4 1	2.052	2.051
44.277	7	4 2 1	2.044	2.044
		3 3 2		2.045
44.453	2	1 3 4	2.036	2.036
44.570	2	3 1 4	2.031	2.032
44.674	5	0 2 5	2.027	2.027
		2 0 5		2.025
46.377	2	2 4 2	1.956	1.956
46.819	2	1 4 3	1.939	1.939
47.036	3	4 1 3	1.930	1.931
47.764	3	2 3 4	1.903	1.904
47.814	2	3 2 4	1.901	1.901
47.984	2	3 3 3	1.894	1.894
48.804	2	3 4 0	1.865	1.864
48.908	2	4 3 0	1.861	1.861
		2 2 5		1.858
49.622	1	4 3 1	1.836	1.836
		1 0 6		1.838
		0 1 6		1.838
		3 4 1		1.839
49.726	1	5 0 1	1.832	1.833
		1 5 0		1.831
49.998	9	2 4 3	1.823	1.823
		0 3 5		1.824
		5 1 0		1.822
50.150	5	4 2 3	1.818	1.818
		3 0 5		1.820
50.579	4	1 1 6	1.803	1.803
50.779	8	0 4 4	1.797	1.797
		5 1 1		1.798
50.992	15	1 3 5	1.790	1.789
		4 0 4		1.790
51.081	4	3 1 5	1.787	1.786
51.505	2	0 5 2	1.773	1.773
		3 4 2		1.770
51.721	2	4 3 2	1.766	1.767
51.801	2	5 0 2	1.763	1.764
		1 4 4		1.764
51.966	2	4 1 4	1.758	1.758
52.810	4	2 5 0	1.732	1.733
		5 1 2		1.733
		3 3 4		1.731
53.465	2	2 5 1	1.712	1.713
53.559	2	2 1 6	1.710	1.709
		1 2 6		1.710
53.705	2	5 2 1	1.705	1.706
54.046	1	3 2 5	1.695	1.696
		2 3 5		1.697
54.962	3	3 4 3	1.669	1.669
		4 3 3		1.667
		4 2 4		1.672
		0 5 3		1.672
55.806	5	1 5 3	1.646	1.646
		4 4 0		1.646
56.433	21	4 4 1	1.629	1.629
		2 2 6		1.629
58.228	4	3 5 1	1.583	1.583
		1 0 7		1.584
		1 3 6		1.583
		0 1 7		1.584
58.374	5	5 3 1	1.580	1.579
		4 4 2		1.580
		3 1 6		1.581
58.637	2	2 5 3	1.573	1.573
		3 3 5		1.571
58.881	1	5 2 3	1.567	1.568
59.122	6	1 1 7	1.561	1.561

[a] Orthorhombic with a = 9.286(1) Å, b = 9.341(1) Å, and c = 11.250(1) Å.

TABLE 2
Data Collection and Refinement Parameters for $KIn(OH)PO_4$

Empirical formula	$KIn(OH)PO_4$
Formula weight	265.90
Crystal size (mm)	$0.15 \times 0.15 \times 0.30$
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	9.277(2)
b (Å)	9.339(2)
c (Å)	11.245(2)
V (Å^3)	974.2
Z	8
ρ_{calc} (g cm^{-3})	3.624
$F(000)$	992
X-radiation	Mo$K\alpha$
λ (Å)	0.71069
Linear abs. coeff. (cm^{-1})	58.80
θ range (°)	1–26
ω-scan width (°)	$0.8 + 0.35 \tan \theta$
Scan speed range (° min^{-1})	1.6–5.5
Total data	1437
Total unique data	1331
Observed data ($I > 3\sigma(I)$)	1327
Data collected	$-1, 11\ -1, 11\ -1, 13$
R_{merge}, %	3.68
Abs. correction range	1.00–1.22
No. of refined parameters	149
Weights	351.6, 505.7, 272.4, 48.8
Extinction parameter	110(7)
Final rms shift/error	0.08
Max, residual electron density (e Å^{-3})	1.6
Final R, R_w (%)	2.64, 2.92

tometer. Automatic search, indexing, and centering routines were used to obtain the unit cell and orientation matrix. The final cell was obtained by centering 24 high angle reflections. Data were collected using the scan parameters shown in Table 2. Intensities of 3 standard reflections were monitored every hour and indicated no crystal decay. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied (2).

The systematic absences uniquely defined the space group as $P2_12_12_1$. The heavy atom positions were deduced from inspection of a Patterson map and the light atoms were located from subsequent difference-Fourier syntheses. The hydrogen atom could be refined to a chemically sensible position only by imposing distance (O–H = 1.0 ± 0.05 Å) and angle (In–O–H = 120 ± 10°) restraints. The refinement converged, using unit weights, to an R factor of 2.68%. Application of a modified four-term Chebyschev polynomial weighting scheme after Tukey and Prince (3) followed by final refinement of positional parameters, anisotropic temperature factors, and an extinction parameter yielded a weighted R factor of 2.92%. The correct enantiomer was chosen by refining an enantiopole parameter. The results are summarized in Table 2, with final fractional atomic coordinates and anisotropic temperature factors presented in Tables 3a and 3b and selected distances and angles listed in Table 4.

The computer programs RC85 (4) and CRYSTALS (5) were used throughout. Neutral atom scattering factors (6) and anomalous scattering terms were included for the non-hydrogen atoms. Structural diagrams were drawn with SNOOPI (7), and polyhedral representations with STRUPLOT (8). Bond-length valence calculations were performed with the program VALENCE (9), which uses the method of Brown and Altermatt (10).

RESULTS AND DISCUSSION

$KIn(OH)PO_4$ crystallizes in the noncentrosymmetric space group $P2_12_12_1$ with two independent groupings in the unit cell. Only one of the two hydrogen atoms required to give charge balance could be located. Bond-length valence calculations (10) clearly indicate that two of the oxygen atoms, O(5) and O(6), are hydroxide rather than oxide ions (see Table 5). The hydrogen atom which was located from a difference-Fourier map is bonded to O(5), and was successfully refined using distance and angle restraints. Close inspection of difference-Fourier maps around O(6) indicated excess electron density in a geometrically sensible place, but the position was too close to K(1) to be physically reasonable (2.1 Å). The temperature factors for both potassium atoms are higher than expected (see Table 3b), but attempts to model this as partial occupanies failed.

The overall structure of this material is shown in Fig. 1. This can best be described as composed of spiral chains of *cis*-corner-shared $InO_4(OH)_2$ octahedra which run along

TABLE 3a
Atomic Positional Parameters for $KIn(OH)PO_4$

Atom	x	y	z
In(1)	0.14813(5)	0.10651(6)	0.12268(6)
In(2)	0.39842(6)	0.15400(6)	0.37663(6)
P(1)	−0.0669(2)	0.1599(2)	−0.1222(2)
P(2)	0.0795(2)	0.3124(2)	0.3692(2)
K(1)	0.0196(4)	0.4687(3)	0.0984(2)
K(2)	−0.2584(3)	0.1378(4)	0.1649(3)
O(1)	0.0299(9)	0.2064(9)	−0.0176(7)
O(2)	0.499(1)	0.2729(9)	0.2362(8)
O(3)	0.5713(6)	0.0030(7)	0.3657(7)
O(4)	0.2444(6)	0.3218(7)	0.3806(7)
O(5)	0.2885(9)	0.0194(8)	0.2531(6)
O(6)	0.2416(8)	−0.0386(9)	0.0007(6)
O(7)	0.511(1)	0.255(1)	0.5195(7)
O(8)	0.0351(9)	0.2188(8)	0.2615(7)
O(9)	−0.0266(6)	−0.0339(7)	0.1536(5)
O(10)	0.2799(7)	0.2908(7)	0.0962(6)
H(1)	0.31(1)	−0.07(1)	0.24(1)

TABLE 3b
Anisotropic Thermal Parameters for $KIn(OH)PO_4$[a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
In(1)	0.0069(3)	0.0064(3)	0.0089(3)	−0.0002(3)	−0.0007(3)	−0.0009(2)
In(2)	0.0077(3)	0.0066(3)	0.0084(3)	0.0005(3)	−0.0007(3)	0.0003(2)
P(1)	0.0070(9)	0.0073(9)	0.0093(8)	0.000(1)	0.000(1)	0.0007(7)
P(2)	0.0082(9)	0.0067(9)	0.0092(9)	0.000(1)	0.002(1)	0.0003(7)
K(1)	0.078(2)	0.022(1)	0.023(1)	−0.006(1)	−0.014(1)	0.023(1)
K(2)	0.026(1)	0.058(2)	0.043(1)	0.006(1)	0.003(1)	0.024(1)
O(1)	0.020(4)	0.017(4)	0.008(3)	0.000(3)	−0.006(3)	−0.003(3)
O(2)	0.012(3)	0.015(4)	0.021(4)	0.008(3)	−0.002(3)	0.002(3)
O(3)	0.012(3)	0.012(3)	0.016(3)	0.005(3)	−0.002(3)	−0.001(2)
O(4)	0.010(3)	0.012(3)	0.020(3)	−0.003(4)	0.003(3)	0.002(2)
O(5)	0.016(3)	0.010(4)	0.019(4)	−0.008(3)	−0.004(3)	0.000(3)
O(6)	0.008(3)	0.010(3)	0.021(4)	0.000(3)	−0.001(2)	0.002(3)
O(7)	0.016(4)	0.010(3)	0.013(4)	−0.001(3)	−0.007(3)	0.000(3)
O(8)	0.012(4)	0.012(4)	0.021(4)	−0.011(3)	0.004(3)	0.000(3)
O(9)	0.009(3)	0.009(3)	0.018(3)	−0.003(3)	0.003(2)	−0.007(2)
O(10)	0.011(3)	0.011(3)	0.021(4)	0.004(3)	−0.004(3)	−0.004(2)

[a] Anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)]$.

TABLE 4
Selected Interatomic Distances (Å) for $KIn(OH)PO_4$

In(1)–O(1)	2.136(8)	In(2)–O(2)	2.144(8)
In(1)–O(5)	2.123(7)	In(2)–O(3)	2.140(6)
In(1)–O(6)	2.114(7)	In(2)–O(4)	2.122(6)
In(1)–O(8)	2.154(8)	In(2)–O(5)	2.134(7)
In(1)–O(9)	2.114(6)	In(2)–O(6)	2.190(8)
In(1)–O(10)	2.132(6)	In(2)–O(7)	2.136(8)
P(1)–O(1)	1.542(8)	P(2)–O(4)	1.538(6)
P(1)–O(2)	1.553(9)	P(2)–O(7)	1.536(8)
P(1)–O(3)	1.528(6)	P(2)–O(8)	1.550(8)
P(1)–O(10)	1.523(6)	P(2)–O(9)	1.539(6)
K(1)–O(1)	2.777(8)	K(2)–O(1)	2.954(9)
K(1)–O(6)	2.885(8)	K(2)–O(2)	2.700(10)
K(1)–O(7)	2.746(9)	K(2)–O(3)	3.030(7)
K(1)–O(8)	2.972(9)	K(2)–O(4)	2.997(7)
K(1)–O(8)	2.862(9)	K(2)–O(8)	3.028(9)
K(1)–O(9)	2.790(7)	K(2)–O(9)	2.686(7)
K(1)–O(10)	2.933(7)	K(2)–O(10)	3.031(7)
O(5)–H(1)	0.84(8)		

TABLE 5
Calculated Bond Valence Sums

Cation	In(1)	In(2)	P(1)	P(2)	K(1)	K(2)
Valence	3.25	3.13	4.98	4.92	1.03	0.91

Anion	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	O(9)	O(10)
Valence	−2.04	−1.92	−1.89	−1.88	−1.09	−1.15	−1.96	−2.04	−2.20	−2.03

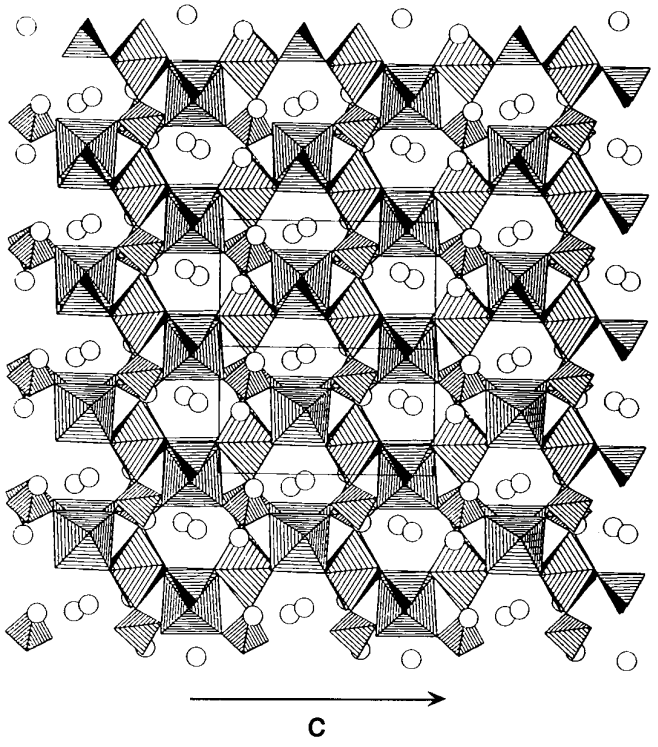

FIG. 1. A polyhedral representation of the structure of $KIn(OH)PO_4$ as viewed down (110). Indium, phosphorus, and potassium are represented by octahedra, tetrahedra, and open circles, respectively.

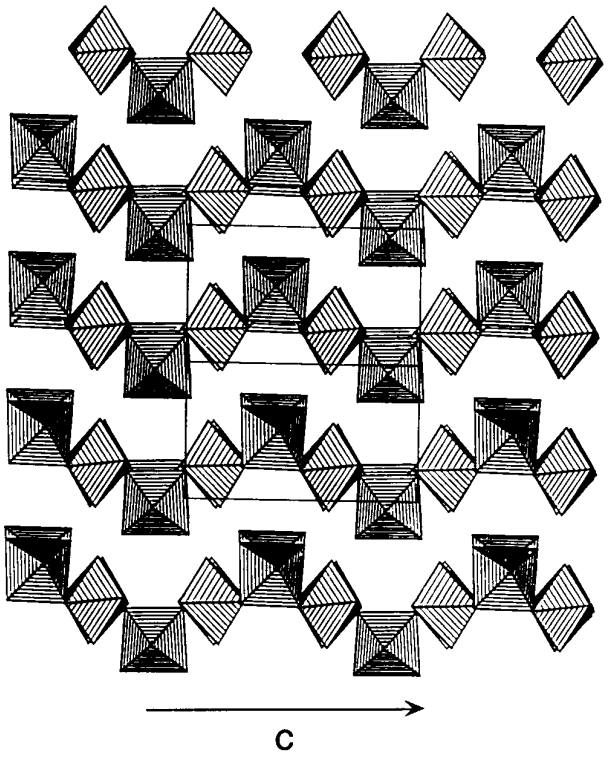

FIG. 2. A view down (110) showing only the chains of indium–oxygen octahedra in $KIn(OH)PO_4$.

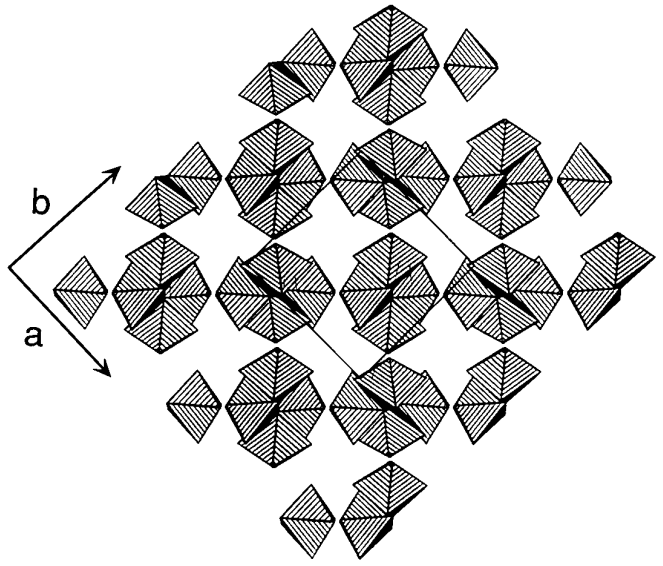

FIG. 3. A view down (001) showing only the chains of indium–oxygen octahedra and the tunnels (without potassium) parallel to the *c* axis in $KIn(OH)PO_4$.

the *c* axis (Figs. 2 and 3). The hydroxide oxygen atoms, O(5) and O(6), bridge between the indium atoms. The phosphate groups link together the indium–oxide–hydroxide chains. There are no contacts between the tetrahedral phosphate groups. This bonding arrangement creates tunnels (Fig. 3), along the *z* direction, containing the K ions. The framework structure of $KIn(OH)PO_4$, consisting of the interconnected $InO_4(OH)_2$ and PO_4 units, is essentially the same as that of γ-$NaTiOPO_4$ (1, 11). The major difference lies in the positions of the alkali metal cations in the tunnels of the structure.

The metal–oxygen distances and angles are presented in Table 4, and thermal ellipsoid plots are shown in Fig. 4. These clearly show that the indium atoms are in nearly octahedral coordination, with average indium–oxygen distances of 2.129 and 2.144 Å for In(1) and In(2), respectively. The distortions from ideal symmetry are more obvious from inspection of the angles rather than distances. Both phosphorus atoms are tetrahedrally coordinated by oxygen atoms and have average bonding distances of 1.536 and 1.541 Å. The potassium atoms are seven-coordinate, and the geometry around K(1) can be described as a distorted edge-capped trigonal antiprism. In this description (see Fig. 4), one face is defined by O(1), O(8), and O(10), the other by O(6), O(7), and O(8), and O(9) bridges the O(8)–O(8) edge. For K(2), the coordination environment

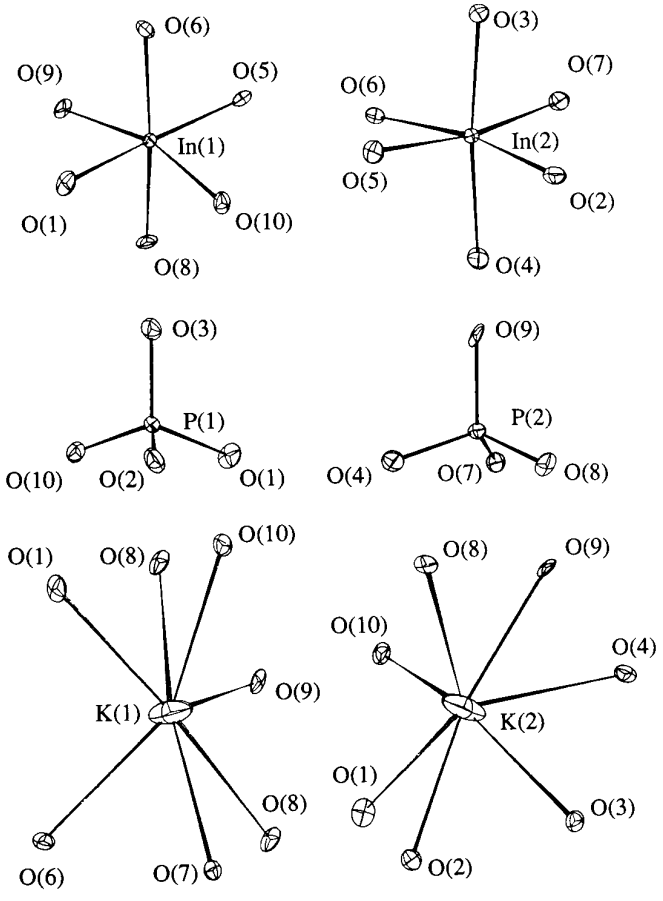

FIG. 4. Thermal ellipsoid plots (50% probability) of $KIn(OH)PO_4$ showing the metal and phosphorus coordination spheres.

is so asymmetric that no easy description based on a polyhedron could be found.

A survey of the literature shows that only a few indium phosphate based crystal structures have been reported. The synthesis of $KIn(OH)PO_4$ suggests that many more indium phosphate phases are waiting to be discovered.

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