Hydrothermal Synthesis and Crystal Structure of Na₂In₂[PO₃(OH)]₄·H₂O with a New Structure Type

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A sodium indium hydrogen phosphate hydrate, $Na_2In_2[PO_3(OH)]_4 \cdot H_2O$, was synthesized under mild hydrothermal conditions, and the crystal structure was characterized by the single-crystal X-ray diffraction method. The structure is of a new type with the following data: $M_r = 794.775$, triclinic, $aP62$, $P\text{-}1$ (No. 2), $a = 9.3013(1)$ Å, $b = 9.4976(1)$ Å, $c = 9.2685(7)$ Å, $\alpha = 98.710(4)°$, $\beta = 98.953(4)°$, $\gamma = 60.228(6)°$, $V = 699.42(5)$ Å³, $Z = 2$, $D_x = 3.217$ g cm⁻³, $\lambda = 0.71073$ Å, $\mu = 39.1$ cm⁻¹, $F(000) = 644$, $T = 293$ K, $R = 0.0551$, w$R = 0.1528$ for 245 variables and 4559 contributing unique reflections. The structure is characterized by corner-sharing InO_6 and PO_4H polyhedra forming a three-dimensional network with infinite channels along the [100] direction, where sodium cations and water molecules reside through hydrogen bonds. The topological construction of the title structure can be considered closely related to an augmented corundum network and the augmentation of the 4, 6 net has largely increased the porosity of the compound. The thermal stability investigation shows that the compound loses its water molecules around 365°C and is nonzeolitic in character. © 2001 Academic Press

Key Words: sodium indium hydrogen phosphate hydrate; hydrothermal synthesis; crystal structure.

INTRODUCTION

Materials with open-framework structure are of great interest to materials science as well as to chemistry due to their diverse industrial uses and rich structural chemistry. In contrast to the very well-known aluminophosphates and gallophosphates (1), with metallic atoms in four-, five-, or sixfold coordination, phosphate compounds containing the heavy group 13 element, indium, besides a small number of reported compounds, namely, $Li_3In_2(PO_4)_3$ (2), $LiInP_2O_7$ (3), $NaCdIn_2(PO_4)_3$ (4), $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$ (5), $RbIn(OH)PO_4$ (6), $\beta\text{-}Na_3In(PO_4)$ (7–8), $\alpha\text{-}Na_3In(PO_4)$ (8),

$KIn(OH)PO_4$ (9), $CaIn_2(PO_4)(HPO_4)$ (10), and $Na_3In_2(PO_4)_3$ (11), are still to be explored. Indium represents an interesting case since only octahedral coordination is expected. Recent interests in the organically templated structure also lead to a few compounds reported in the indium phosphate systems $[NH_3CH_2CH_2NH_3][In_2(HPO_4)_4]$ (12), $[In_8(HPO_4)_{14}(H_2O)_6](H_2O)_5(H_3O)(N_2C_3H_5)_3$ (13), $[C_5H_5NH][In(HPO_4)(H_2PO_4)_2]$ (14), $[In_4(4,4'\text{-bipy})_3(HPO_4)_4(H_2PO_4)_4] \cdot 4H_2O$, and $[In_4(4,4'\text{-bipy})_3(HPO_4)_4(H_2PO_4)_4]$ (15). Most of the compounds reported have been synthesized by either hydrothermal or solid reactions. Mild hydrothermal methods, i.e., with lower temperature and pressure, seem also suitable to synthesize indium phosphates with complex structures. Interestingly, a new indium phosphate, $Na_4[In_8(HPO_4)_{14}(H_2O)_6] \cdot 12H_2O$, has been synthesized directly in its sodium form very recently by a hydrothermal method (16). Here we report our synthesis and characterizations of a new three-dimensional indium(III) phosphate hydrate with an open-framework structure.

EXPERIMENTAL

Synthesis

The sample of the title compound was obtained in an attempt to synthesize main group microporous borophosphates by a mild hydrothermal method. Starting materials were of analytical grade and used without further purification. A mixture of 0.9534 g of $Na_2B_4O_7 \cdot 10H_2O$, 2.149 g of $Na_2HPO_4 \cdot 12H_2O$, and 0.115 g of indium metal dissolved in 2 ml of 18% HCl (molar ratio of Na:In:P:B = 17:1:6:10) was added to 1.0 ml of distilled water. The mixture was sealed in glass tubes about 20 cm in length. The filling of the solution were about 30% of the tube volume. The glass tubes were placed in an oven and the temperature was increased slowly to 80°C and prereacted for 1 week. The temperature was increased to 130°C and reacted for 2 weeks before cooling to room temperature. The reaction was

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under autogenous pressure. The subsequent synthesis without the boron source also led to the title compound under the same physical conditions (only with $Na_2HPO_4 \cdot 12H_2O$, In, and HCl). Attempts to synthesize a possible gallium analogue under similar reaction conditions have, eventually, led to a new borophosphate, $NaGa[BP_2O_7(OH)_3]$ (17). The colorless crystals with plate-like shape were grown from solution in a glass tube and easily isolated from the products in large quantity for powder XRD and thermal analysis.

Structure Determination

A single crystal with plate-like shape ($0.45 \times 0.20 \times 0.35$ mm^3) was mounted on an Enraf-Nonius CAD4 automatic four-circle diffractometer and exposed to MoKα radiation with graphite monochromator. Crystallographic data for the title compound are summarized in Table 1. The unit cell parameters were refined from 2θ values of 25 randomly located reflections (MoKα, $\lambda = 0.71073$ Å, $31° < 2\theta < 36°$) after indexing and normal cell reduction procedure. A total of 6616 reflections were collected out to $(\sin\theta/\lambda) = 0.700$ ($-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-1 \leq l \leq 15$) in the $\omega-2\theta$ scan mode, yielding 4559 unique observed reflections. Three standard reflections, $-1\,6\,-6$, $12\,-12$, and $5\,2\,-8$, were

TABLE 1
Crystallographic Data for $Na_2In_2[PO_3(OH)]_4 \cdot H_2O$

Formula weight (amu)	1353.74
Space group, Z	P-1, 2
a (Å)	9.3013(1)
b (Å)	9.4976(1)
c (Å)	9.2685(7)
α (°)	98.710(4)
β (°)	98.953(4)
γ (°)	60.228(6)
V (Å^3)	699.42(5)
D_x (gcm^{-3})	3.217
Temperature (K)	293(2)
Radiation, monochromator	MoKα, graphite
Crystal shape, color	Plate, colorless
Crystal size (mm^3)	$0.41 \times 0.20 \times 0.33$
Linear absorption coefficient (cm^{-1})	39.1
Scan type	$\omega-2\theta$
Two-theta range (°)	4–70
hkl range	$-15 \to 15$, $-15 \to 15$, $-1 \to 15$
Total number of collected reflections	6616
Number of observed unique reflections	4559
Number of parameters	245
$F(000)$	644
Transmission factors T_{min}, T_{max}	0.6201, 0.9899
Final $R^a(F)$, $Rw^b(F)$	0.0551, 0.1528
S	1.022
Shift/e.s.d. in the last cycle	-0.036
Residual peaks(hole), (eÅ^{-3})	3.09 (-4.40)

$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$.
$^b Rw = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(F)$.

TABLE 2
Atomic Positional and Displacement Parameters for $Na_2In_2[PO_3(OH)]_4 \cdot H_2O$ with Space Group P-1

Atom	WP^a	X	Y	Z	U_{eq}(100 Å^2)^b
Na(1)	2i	0.2266(4)	0.2964(4)	0.6926(4)	2.69(6)
Na(2)	2i	0.0983(4)	0.8026(5)	0.2483(4)	3.62(8)
In(1)	2i	0.4593(4)	0.2924(4)	0.1305(4)	0.687(9)
In(2)	2i	0.0451(4)	0.2175(4)	0.3705(4)	0.702(9)
P(1)	2i	0.2378(2)	0.4559(2)	0.4187(2)	0.88(2)
P(2)	2i	0.3371(2)	0.0073(2)	0.1401(2)	0.96(2)
P(3)	2i	0.2381(2)	0.9109(2)	0.5960(2)	0.73(2)
P(4)	2i	0.2563(2)	0.5854(2)	$-0.1118(2)$	0.87(2)
O(1)	2i	0.6022(5)	0.1418(5)	0.3030(5)	1.40(8)
O(2)	2i	$-0.1005(5)$	0.0929(5)	0.3403(5)	1.42(7)
O(3)	2i	0.1839(5)	0.0792(5)	0.5531(5)	1.58(8)
O(4)	2i	0.3221(5)	0.1608(5)	0.0901(6)	1.31(7)
O(5)	2i	0.2930(6)	0.4674(5)	0.2765(5)	1.65(8)
O(6)	2i	$-0.0828(5)$	0.3850(5)	0.5452(5)	1.52(8)
O(7)	2i	0.6077(5)	0.4122(5)	0.1829(5)	1.42(7)
O(8)	2i	0.6421(6)	0.1205(5)	$-0.0126(5)$	1.76(9)
O(9)	2i	0.2197(5)	0.3062(5)	0.4190(6)	1.49(8)
O(10)	2i	0.3157(6)	0.4271(5)	$-0.0471(5)$	1.87(9)
O(11)	2i	0.1862(5)	0.0388(5)	0.2111(5)	1.46(8)
O(12)	2i	$-0.1125(5)$	0.3966(5)	0.2252(6)	1.56(8)
O(13)	2i	0.4968(6)	0.9304(5)	0.2507(6)	1.90(9)
O(14)	2i	0.3848(6)	0.4291(6)	0.5457(6)	2.09(9)
O(15)	2i	0.2831(6)	0.7861(5)	0.4548(5)	1.61(8)
O(16)	2i	0.1948(7)	0.7293(6)	0.0110(6)	2.3(1)
O(17)	2i	$-0.0695(8)$	0.6965(8)	0.1299(7)	3.2(1)
H(1)	2i	0.365	0.744	0.422	5.0^c
H(2)	2i	0.501	0.997	0.279	5.0^c
H(3)	2i	0.400	0.473	0.630	5.0^c
H(4)	2i	0.209	0.808	0.036	5.0^c
H(5)	2i	0.010	0.586	0.086	5.0^c
H(6)	2i	-0.190	0.783	0.035	5.0^c

^{a}Wyckoff position.
$^b U_{eq}$ were defined as one-third of the trace of the triclinic U_{ij} tensor.
^{c}The atomic positional and displacement parameters for the H atoms are fixed in the refinements.

measured 32 times with maximum variations of less than 0.1%, showing no detectable decay during the data collection. The intensity data were corrected for Lorentz and polarization effects, and absorption correction was made according to eight ψ-scan reflections with a minimum and a maximum transmission factor of 0.6201 and 0.9899, respectively. The anomalous-dispersion coefficients were taken into account in the data processing. In the triclinic system there are only two possible space groups: $P1$ and P-1 ("International Tables for Crystallography," 1983, Vol. A). The structure was solved in space group P-1 and confirmed by full-matrix least-squares structure refinement, based on F values using the SDP program package (18) and SHELXL-97 (19). The metal atoms and most of the oxygen atoms were located by the direct method and the remaining atoms were found from the successive difference Fourier

TABLE 3
Selected Important Interatomic Distances (Å), Angles, and Bond Valence Sums ($\sum$s) for Na$_2$In$_2$[PO$_3$(OH)]$_4 \cdot$ H$_2$O Structure

[NaO$_8$] polyhedra, $\sum$s[Na(1)–O] = 1.06, $\sum$s[Na(2)–O] = 1.06

Na(1)–O(17)	2.337(7)	O(3)	2.435(5)	O(13)	2.440(6)
	O(9)	2.542(6)	O(12)	2.591(5)	O(10)	2.746(6)
	O(6)	2.753(6)	O(14)	2.931(6)		

Na(2)–O(17)	2.312(7)	O(15)	2.333(6)	O(16)	2.378(6)
	O(2)	2.542(6)	O(5)	2.805(6)	O(11)	2.822(6)
	O(6)	2.870(6)	O(3)	3.080(5)		

[InO$_6$] octahedra, $\sum$s[In(1)–O] = 3.27

In(1)–O(10)	2.095(4)	O(5)	2.098(4)	O(1)	2.124(4)
	O(8)	2.146(4)	O(7)	2.149(4)	O(4)	2.150(4)

[InO$_6$] octahedra, $\sum$s[In(2)–O] = 3.22

In(2)–O(11)	2.102(4)	O(12)	2.112(4)	O(6)	2.123(4)
	O(3)	2.136(4)	O(9)	2.137(4)	O(2)	2.165(4)

[PO$_4$] tetrahedra, $\sum$s[P(1)–O] = 4.96

P(1)–O(9)	1.513(4)	O(6)	1.518(4)
	O(5)	1.524(5)	O(14)	1.601(5)

[PO$_4$] tetrahedra, $\sum$s[P(2)–O] = 5.00

P(2)–O(11)	1.517(4)	O(8)	1.520(5)
	O(4)	1.531(4)	O(13)	1.571(5)

[PO$_4$] tetrahedra, $\sum$s[P(3)–O] = 5.06

P(3)–O(2)	1.509(4)	O(3)	1.516(4)
	O(1)	1.517(4)	O(15)	1.582(5)

[PO$_4$] tetrahedra, $\sum$s[P(4)–O] = 5.07

P(4)–O(10)	1.507(4)	O(12)	1.521(4)
	O(7)	1.527(4)	O(16)	1.564(5)

Hydrogen bonds in the Na$_2$In$_2$[PO$_3$(OH)]$_4 \cdot$ H$_2$O structure

A	A–B	B	B–C	C	A–B–C	A–C
O(15)	0.751	H(1)	2.083	O(14)	144.5	2.73
O(13)	0.664	H(2)	1.987	O(1)	153.0	2.60
O(14)	0.852	H(3)	1.897	O(7)	169.7	2.74
O(16)	0.820	H(4)	2.545	O(8)	139.3	2.55
O(16)	0.820	H(4)	1.867	O(11)	151.2	3.20
O(17)	1.004	H(5)	2.746	O(5)	161.0	3.18
O(17)	1.303	H(6)	1.495	O(4)	165.0	2.77

maps. Attempts to refine the occupancies of the Na and In atoms did not show any significant deviation from 100% and the multiplicity was fixed at unity in the final refinements. As many as 245 variables, including anisotropic displacement parameters for nonhydrogen atoms, were refined to $R = 0.0551$ and w$R = 0.1581$ ($w = 1/\sigma^2(|F|)$, $S = 1.243$), considering 4559 contributing unique reflections with $F > 4\sigma(F)$. All the hydrogen atoms were located on the difference Fourier map but not refined. The maximum shift/e.s.d. in the last cycle was 0.036. Final residual electron density was $+3.09(-4.40)$ e Å^{-3}, all very close to the In positions (0.7 Å from In(2) and 0.91 Å from In(1), respectively). The refinement on another crystal led to even worse results. The relatively high residual electron densities and

refined R values might have been caused by a small portion of another domain grown on the crystal of investigation, although not observed under polarized microscope, or simply because there are too many weak reflections (it was noted that among the observed reflections, only 2306 are strong reflections with normalized structure factor $E > 1.2$). This will certainly cause increases in the R values. The reason for this is that the lattice could also be indexed as a subcell of a half-volume if only the strong reflections in the search list are used. The basic structure can be solved with the subcell with disorders on the Na cations and water molecules' positions. It should also be noted that the similar values of the unit cell dimensions and angles (α and β) might favor microtwining of the crystals. The atomic positional and displacement parameters are given in Table 2 and the selected important interatomic distances and bond angles in Table 3.

RESULTS AND DISCUSSION

Structure Description

All the coordination tetrahedra around the P atoms have some deformation because of the OH group. For P(1), the anionic hydrogen connected to P(1)O4 caused significant elongation of the P(1)–O(14) distance to 1.601 Å. This is 0.062 Å longer than the average value of 1.539 Å around P(1). The corresponding elongation of P–OH distances compared to the average distances for P(2), P(3), and P(4) is 0.036, 0.051, and 0.034 Å, respectively. The average bond angles for P(1), P(2), P(3), and P(4) are 109.4°, 109.4°, 109.4°, and 109.5°, respectively, which are quite normal angles. All the average P–O bond distances and bond angles are consistent with those typical values observed in phosphates. On the basis of bond strength calculations (20), the bond valence sums for P atoms are all close to 5^+ and listed in Table 3.

The coordination environments around the sodium cations are shown in Fig. 1. The coordination number of each
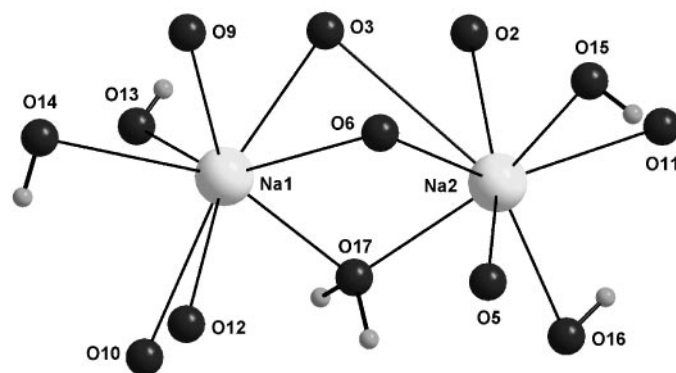
FIG. 1. The coordination environment of the two sodium cations in Na$_2$In$_2$[PO$_3$(OH)]$_4 \cdot$ H$_2$O.
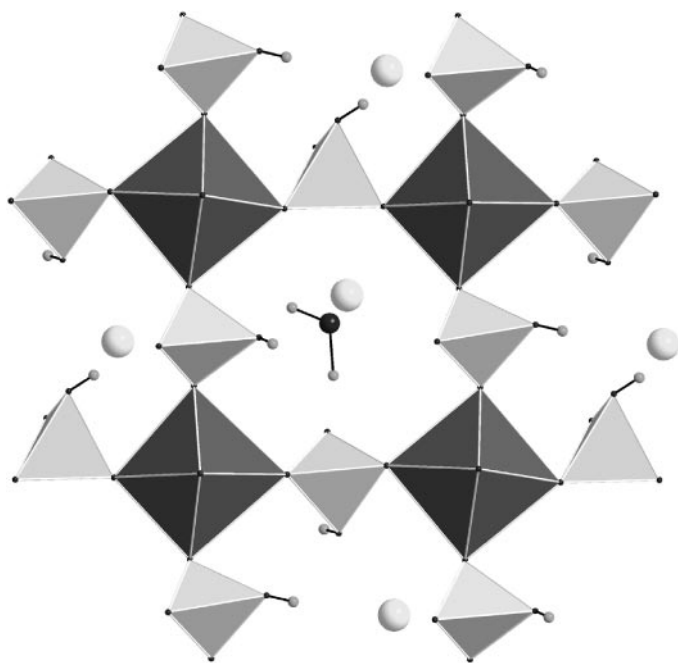
FIG. 2. Polyhedral representation of a slice of the $Na_2In_2[PO_3(OH)]_4 \cdot H_2O$ structure cut parallel to the (100) plane, showing the 8-member ring formed by four InO_6 and four PO_4H polyhedra.

Na atom was determined on the basis of the clear coordination gap (3.080 to 3.580 Å) in the Na–O distance distribution histogram. Both Na atoms have a clear separation of inner and outer coordination sphere. For Na(1), the inner coordination sphere consists of five oxygen atoms (distance ranging from 2.337 to 2.591 Å) and the outer shell of three

oxygen atoms (distances ranging from 2.746 to 2.931 Å). For Na(2), the inner shell has four oxygen atoms (distance ranging from 2.312 to 2.542 Å) and the outer shell four oxygen atoms (distance ranging from 2.805 to 3.080 Å). Therefore both Na atoms are coordinated by eight oxygen atoms. The average Na–O distances for Na(1) and Na(2) are 2.597 and 2.643 Å, respectively. The calculated valence sums for Na(1) and Na(2) atoms are 1.06 and 1.06, respectively. The maximum Na–O distances of 2.931 and 3.080 Å for each Na atom are smaller than the L_{max} of 3.250 Å obtained by using the ionic radii of Shannon (21) with the method described by Donnay and Allmann (22). The coordination environments for the two Na atoms are so asymmetric that no easy polyhedral descriptions could be rationalized.

Two indium atoms have quite regular octahedral coordination with average bond distances of 2.127 and 2.129 Å for In(1) and In(2), respectively. These values are close to the single-bond value of 2.150 Å (21) and also close to values observed in other indium phosphates. For In(1)O_6, the *cis* ∠O–In(1)–O bond angles range from 88.1° to 92.0°. The *trans* ∠O–In(1)–O angles along the pseudo-tetragonal axis range from 175.7° to 175.9°. For In(2)O_6, the *cis* ∠O—In(2)–O bond angles range from 84.7° to 95.7°. The *trans* ∠O–In(2)–O angles along the pseudo-tetragonal axis range from 167.6° to 175.2°. The bond valence sum calculations show both indium atoms are trivalent. The calculated valence sums are listed in Table 3.

A polyhedral representation of a slice of the $Na_2In_2[PO_3(OH)]_4 \cdot H_2O$ structure parallel to the (100) plane is shown in Fig. 2. The projection direction is approximately along one of the pseudo-tetragonal axes of the In
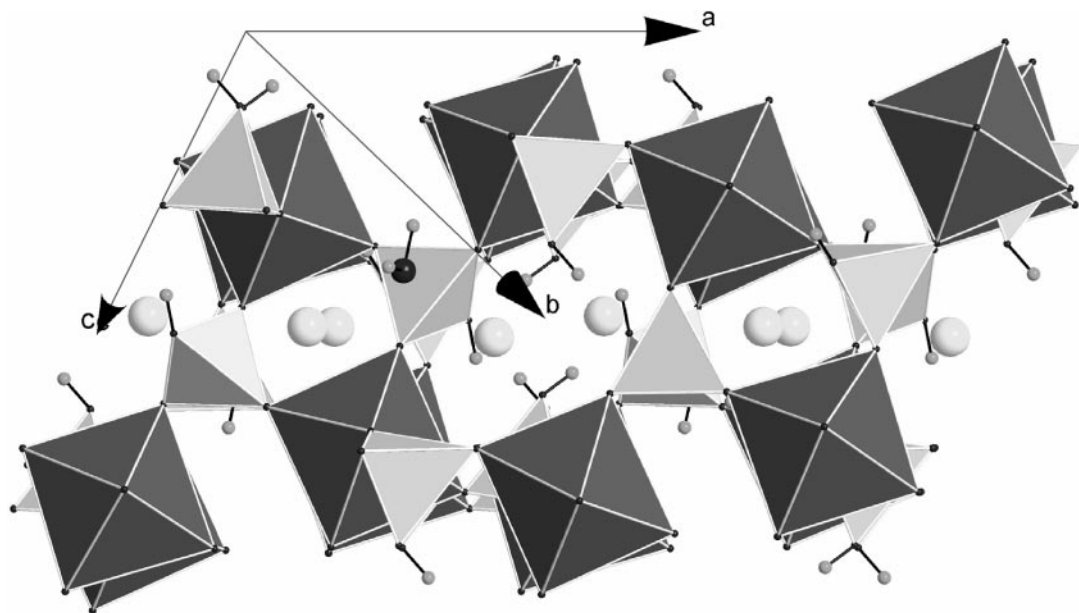
FIG. 3. Packing of the layers, shown in Fig. 2, parallel to the (100) plane.

coordination octahedron. The four oxoligands on the basal plane of the In octahedron are in contact with four PO$_4$H tetrahedra. All the four unique phosphorus sites are presented as (PO$_4$H)$^{2-}$ units that share two oxygen atoms with each of the two adjacent indium atoms in the plane. The condensation of four InO$_6$ and four PO$_4$H polyhedra results in an 8-membered ring, while the structure reported in (16) contains 12-membered rings. The expansion of the ring in the (100) plane leads to a polyhedral layer. The layers are packed parallel to the (100) plane, sharing two In octahedron vertices and oxo-ligand vertices in the PO$_4$H group with adjacent layers as shown in Fig. 3. This construction leads to infinite channels along the [100] direction where the sodium cations and water molecules reside. A polyhedral representation of the whole Na$_2$In$_2$[PO$_3$(OH)]$_4 \cdot$ H$_2$O structure is shown in Fig. 4. The OH ligands in the PO$_4$H groups are also arranged toward the channels and contribute to hydrogen bonds that hold the Na cations and H$_2$O. The O–H $\cdots$ O bond angles range from 139.3° to 169.7° and the oxygen distances range from 2.55 to 2.77 Å, which are quite normal for hydrogen bonds. The O(16)–H(4) $\cdots$ O(11) and O(17)–H(5) $\cdots$ O(5) distances of 3.20 and 3.18 Å may be too long to be considered as bonds but the angles (151.2° and 161.0°) indicate right positions for hydrogen bonds.

Similar three-dimensional topological constructions can be also found in the recently reported mixed-valence titanium phosphates Ti^{III}Ti^{IV}(HPO$_4$)$_4 \cdot$ C$_2$N$_2$H$_9 \cdot$ H$_2$O and Ti^{IV}Ti^{IV}(HPO$_4$)$_4$ (23). In these structures, eight-membered rings can also be identified and the condensations are similar to those of the indium compound, except that in the titanium phosphate structures, there are disorders in the phosphate groups that make the structure lack channels. The P–OH terminals in the titanium phosphates are also pointed into the channels. Instead of all the Ti atoms occupying the same crystallographic position in a high symmetry space group, the In atoms in the title compound occupy two different positions in an ordered fashion and the symmetry is lowered to triclinic. The corresponding disordered ethylenediamine molecule positions in the channel are now occupied by two Na cations also in an ordered way. Therefore the title compound possesses crystallograghically a new structure type.

Furthermore, the topology of the connection of the InO$_6$ and PO$_4$H groups is similar to the topology of the connection in the corundum form of Al$_2$O$_3$. Figure 5 shows a comparison of both structures. It should be noted that the motifs in Fig. 5a represent both the InO$_6$ and PO$_4$H groups instead of a single atom like Al or O in Fig. 5b. If one replaces the Al atoms by the InO$_6$ octahedra and the O atoms by the HPO$_4$ tetrahedra in the corundum structure, it result to a decoration of the Al$_2$O$_3$ network. Therefore the topological construction of the Na$_2$In$_2$[PO$_3$(OH)]$_4 \cdot$ H$_2$O structure can be considered closely related to an augmented corundum network. The augmentation of the
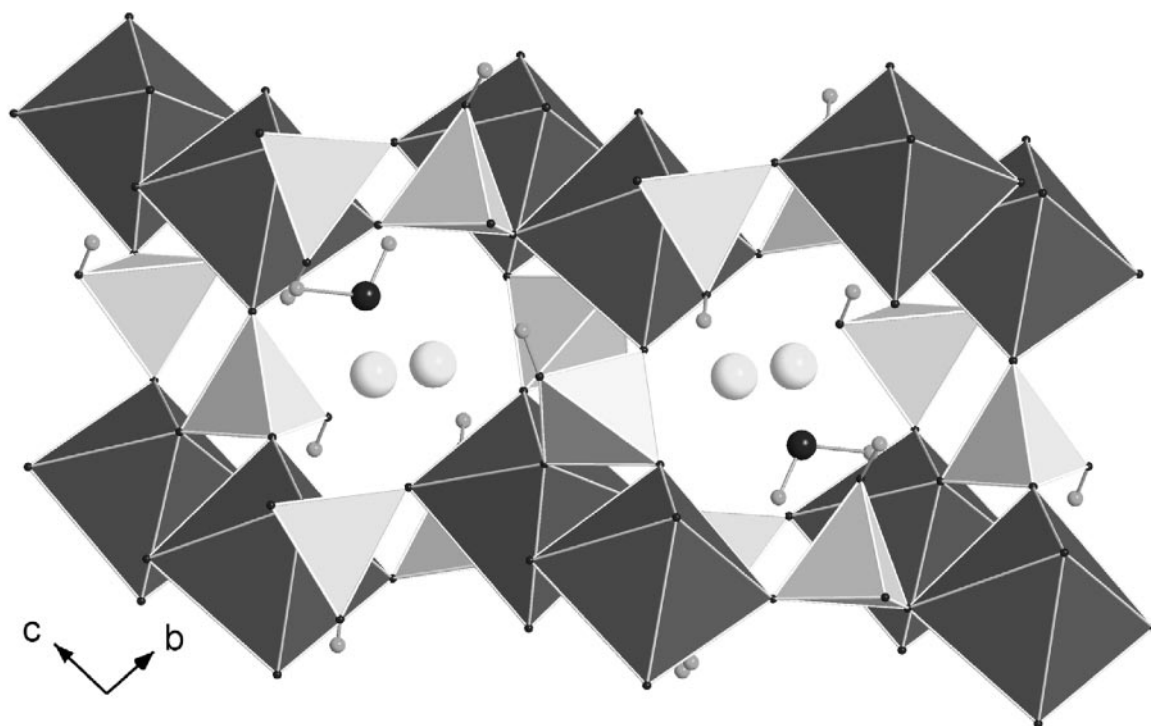

FIG. 4. Polyhedral representation of the three-dimensional structure in Na$_2$In$_2$[PO$_3$(OH)]$_4 \cdot$ H$_2$O viewed along the [100] direction, showing the channels occupied by the sodium cations and water molecules.
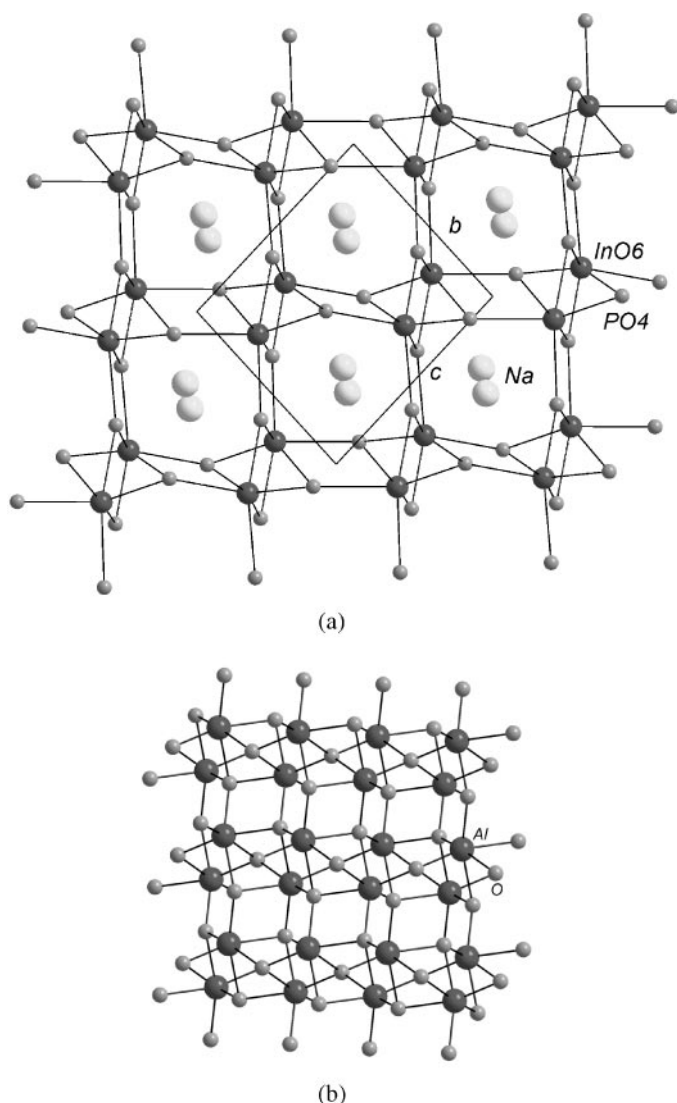
(a)

(b)

FIG. 5. Comparison of (a) the topological connectivity of $Na_2In_2[PO_3(OH)]_4 \cdot H_2O$ with (b) the α-Al_2O_3 structure.

4, 6 net in the corundum structure has largely increased the porosity of the structure and caused it to accept sodium cations and water molecules in the channels. The methods of producing open-framework structures by decoration and expansion of simple networks have drawn much attention recently (24).

The thermal stability of the compound was investigated by DTA-TG analysis using a NETZSCH STA 409EP equipment. The sample has a step weight loss around 365°C (DTG peak value) of about 3.2% compared with 3.8% water molecules in the compound. So it may be concluded that this weight loss corresponds to the loss of water molecules residing in the tunnels. The X-ray powder result for the dehydrated sample shows a pattern with a relatively bad crystallization and different from that of the title compound.

One may conclude that the water molecules in the compound are nonzeolitic. The dehydrated compound has a melting point of 1208°C.

CONCLUSIONS

The title compound has been synthesized under mild hydrothermal conditions and its crystal structure has shown to possess a new type. The structure is characterized by corner-sharing InO_6 and PO_4H polyhedra, forming a three-dimensional network with infinite channels along the [100] direction, where sodium cations and water molecules reside through hydrogen bonds. The topological construction of the title structure can be considered closely related to an augmented corundum network and the augmentation of the 4, 6 net has largely increased the porosity of the compound. The thermal stability investigation shows that the compound loses its water molecules around 365°C and is nonzeolitic in character. To our knowledge, no aluminum and gallium analogues of the title compound have been reported.

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