$Na_3M(OH)(HPO_4)(PO_4)$, $M=Al$, Ga: Two Phosphates with a Chain Structure

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Crystals of two phosphates, $Na_3Al(OH)(HPO_4)(PO_4)$ and $Na_3Ga(OH)(HPO_4)(PO_4)$, were grown by a high-temperature, high-pressure hydrothermal method and structurally characterized by single-crystal X-ray diffraction. $Na_3Al(OH)(HPO_4)(PO_4)$ is in the monoclinic system, space group $C2/m$ (No. 12), with $a=15.277(2)$, $b=7.0540(9)$, $c=7.0405(9)$ Å, $\beta=96.730(2)°$, $V=753.5(3)$ Å^3, $Z=4$, and $R=0.0357$; $Na_3Ga(OH)(HPO_4)(PO_4)$ is as described above except $a=15.4319(1)$, $b=7.1637(3)$, $c=7.0565(2)$ Å, $\beta=96.637(2)°$, $V=774.86(4)$ Å^3, and $R=0.0227$. The two compounds are isostructural. The structure consists of infinite chains of *trans*-corner-sharing $MO_5(OH)$ ($M=Al$, Ga) octahedra running parallel to the b axis. Adjacent octahedra are bridged by HPO_4 and PO_4 groups to form $^1_\infty[M(OH)(HPO_4)(PO_4)^{3-}]$ chains, which are linked together by 6-, 5-, and 8-coordinated Na^+ ions. Hydrogen bonding also contributes to the linkage of these chains. The composition of $Na_3Al(OH)(HPO_4)(PO_4)$ was further defined by thermogravimetric analysis. The structure is compared with that of $Na_4Al(OH)(HPO_4)(PO_4)_2$. © 1997 Academic Press

INTRODUCTION

Microporous aluminophosphates have been extensively studied because of their sorption and catalytic properties (1, 2). Numerous gallophosphates have also been synthesized to discover new open-framework materials. The replacement of aluminum by gallium yields both novel structure types (3–8) and phases that are analogous to known aluminophosphates and aluminosilicates (9–11). D'Yvoire and Pintard-Screpel reported a sodium aluminophosphate and the corresponding isotypic arsenate with the ideal formula $Na_3Al(OH)(HXO_4)(XO_4)$ (X = P, As) (12). These compounds are nonstoichiometric as a result of the presence of cation vacancies which are compensated for by protons. The formula was determined by chemical analysis, density measurements, thermogravimetry, and infrared spectroscopy. Their crystal structures were not determined because of the lack of single crystals. As part of a continuing

study on the structural chemistry of phosphates containing mixed octahedral–tetrahedral frameworks, we have examined the alkali metal–aluminum/gallium–phosphate system. In this work we describe the synthesis and crystal structures of one-dimensional alumino- and gallophosphate $Na_3M(OH)(HPO_4)(PO_4)$ (M = Al, Ga). Their structures are closely related to that of a synthetic aluminophosphate, $Na_4Al(OH)(PO_4)_2$ (13).

EXPERIMENTAL

Synthesis. High-temperature, high-pressure hydrothermal syntheses were performed in gold ampoules contained in a Leco Tem-Pres autoclave, where pressure was provided by water pumped by a compressed air intensifier. $Na_3Al(OH)(HPO_4)(PO_4)$ was synthesized from starting reagents of analytical grade or better: $Na_2HPO_4 \cdot 2H_2O$ (0.089 g), $NaH_2PO_4 \cdot 2H_2O$ (0.069 g) (Na : P molar ratio = 1.5), $Al(OH)_3$ (0.013 g), and H_2O (0.5 ml) were sealed in a gold ampoule (4.7 × 0.5 cm inside diameter) and heated to 600°C at 35,000 psi for 20 h. The autoclave was cooled at 5°C/h to 270°C and quenched to room temperature by removing the autoclave from the furnace. The product was filtered off, washed with water, rinsed with ethanol, and dried in a desiccator at ambient temperature. The product contained colorless prismatic crystals of $Na_3Al(OH)(HPO_4)(PO_4)$. Energy-dispersive X-ray fluorescence analysis of several prismatic crystals established the presence of Na, Al, and P. A suitable crystal was selected and its structure determined by single-crystal X-ray diffraction (see below). The X-ray powder pattern of the bulk product agreed well with that calculated from the single-crystal data and that reported by D'Yvoire and Pintard-Screpel (12). For the crystal growth of $Na_3Ga(OH)(HPO_4)(PO_4)$, a mixture of $Na_2HPO_4 \cdot 2H_2O$ (0.1068 g), $NaH_2PO_4 \cdot 2H_2O$ (0.0828 g) (Na : P molar ratio = 1.5), Ga_2O_3 (0.0187 g), and H_2O (0.55 ml) was heated in a gold ampoule (5.6 × 0.5 cm inside diameter) under the same reaction conditions as for the aluminum compound.

The product contained many colorless thick tabular crystals of $Na_3Ga(OH)(HPO_4)(PO_4)$. Based on X-ray powder diffraction the bulk product contained $Na_3Ga(OH)(HPO_4)(PO_4)$ and a small amount of unidentified impurities. A single-phase product of the gallium compound was not obtained, although several different reaction conditions were tested.

Thermogravimetric analysis (TGA) for $Na_3Al(OH) \cdot (HPO_4)(PO_4)$ was performed on a DuPont thermal analyzer: the sample was heated to 950°C at 5°C/h in air.

Single-crystal X-ray diffraction. Two crystals of dimensions $0.04 \times 0.05 \times 0.33$ mm for $Na_3Al(OH)(HPO_4)(PO_4)$ (1) and $0.15 \times 0.30 \times 0.40$ mm for $Na_3Ga(OH)(HPO_4)(PO_4)$ (2) were selected for indexing and intensity data collection on a Siemens Smart-CCD diffractometer equipped with a normal-focus, 3-kW sealed tube X-ray source. Intensity data were collected in 1200 frames with increasing ω (width of 0.3° per frame). Unit cell dimensions were determined by a least-squares fit of 1291 and 1570 reflections with $2\theta > 15°$ for compounds 1 and 2, respectively. Absorption correction for 1 was not applied because $T_{min,max} = 0.849, 0.882$. Absorption correction for 2 was based on 1467 symmetry-equivalent reflections using the SHELXTL PC program package ($T_{min,max} = 0.485, 0.984$) (14). On the basis of systematic absences, statistics of intensity distribution, and successful solution and refinement of the structures, the space group for both compounds was determined to be $C2/m$ (No. 12). The structures were solved by direct methods: the metal and phosphorus atoms were first located and all the oxygen atoms were found in a difference Fourier map. Bond-valence calculations (15) indicated that O(6) and O(7) in both structures were considerably undersaturated, O(5) had a valence sum of 1.68 in 1 and 1.66 in 2, and all other oxygen atoms had values close to 2. Two hydrogen atoms must be included to balance charge. Valence sums of 1.25 and 1.12 for O(6) and O(7) in 1 and 1.24 and 1.17 for O(6) and O(7) in 2 suggest that they are hydroxo oxygens. Atom O(5) is involved in hydrogen bonding. The hydrogen atoms were located from difference Fourier maps. The multiplicities of all metal atoms were simultaneously allowed to refine. The Na(1), Na(2), Na(3), and Al/Ga positions respectively refined to multiplicities of 0.489(4), 0.485(4), 0.495(5), and 0.493(4) for 1 and 0.507(4), 0.490(3), 0.510(5), and 0.485(1) for 2. These results indicate that the Na and Al sites are fully occupied and the Ga site is slightly deficient. In subsequent least-squares refinement, the multiplicities of all metal atoms were fixed at 0.5. The final cycles of refinement including the atomic coordinates, anisotropic thermal parameters for all nonhydrogen atoms, and fixed atomic coordinates and isotropic thermal parameters for the H atoms converged at $R = 0.0357$ for 1 and $R = 0.0227$ for 2. Neutral-atom scattering factors were used for all atoms. Anomalous dispersion and secondary extinction cor-

rections were applied. Structure solution and refinement were performed on SHELXTL PC programs.

Additional materials available from the Cambridge Crystallographic Data Centre comprise anisotropic thermal parameters.

RESULTS AND DISCUSSION

Thermogravimetric analysis. A one-step weight loss at 438°C was observed for $Na_3Al(OH)(HPO_4)(PO_4)$. The weight loss of 5.93% agrees well with that calculated for the loss of one water molecule (5.92%). The dehydration product has a nominal composition of $Na_3Al(PO_4)_2$.

Crystal structures. The crystallographic data are listed in Table 1. Atomic coordinates, interatomic distances, bond angles, and bond-valence sums are given in Tables 2 and 3, respectively. All metal atoms are at special positions. Atom Na(1) sits on a two-fold rotation axis, Na(2), P(1), and P(2) are on mirror planes, and Na(3) and Al/Ga are located at inversion centers. Most oxygen atoms are also at special positions. Both hydrogen atoms are on mirror planes. The Al/Ga and P atoms are 6- and 4-coordinated, respectively. Valence sums of Al–O, Ga–O, and P–O bonds are in good agreement with their formal oxidation states. The coordination number of Na was determined on the basis of the

TABLE 1
Crystal Data and Intensity-Collection Parameters for $Na_3Al(OH)(HPO_4)(PO_4)$ (1) and $Na_3Ga(OH)(HPO_4)(PO_4)$ (2)

	1	2
Formula weight	303.91	346.65
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$C2/m$
a (Å)	15.277(2)	15.4319(1)
b (Å)	7.0540(9)	7.1637(3)
c (Å)	7.0405(9)	7.0565(2)
β (°)	96.730(2)	96.637(2)
V (Å³)	753.5(3)	774.86(4)
Z	4	4
D_c (g cm⁻³)	2.679	2.971
F (000)	600	672
μ (MoKα) (cm⁻¹)	9.0	41.6
T (°C)	23	23
λ (MoKα) (Å)	0.71073	0.71073
$2\theta_{max}$ (°)	53.4	53.4
No. of reflections collected	3549	2999
No. of unique reflections	778	602
Observed reflections [$I > 2.5\sigma(I)$]	678	587
Parameters refined	85	85
R^a	0.0357	0.0227
$R_w{}^b$	0.0470	0.0270
$(\Delta\rho)_{max,min}$ (e Å⁻³)	0.47, −0.43	0.42, −0.55

$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$.
$^b R_w = [w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$. Weighting scheme $w^{-1} = \sigma^2(F) + g^2 \cdot F^2$, where $g = 0.00413$ for 1 and 0.00010 for 2.

TABLE 2
Atomic Coordinates and Thermal Parameters for $Na_3Al(OH)(HPO_4)(PO_4)$ (1) and $Na_3Ga(OH)(HPO_4)(PO_4)$ (2)

Atom	x	y	z	U_{eq}^a ($Å^2 \times 100$)
Compound 1				
Na(1)	0	0.2347(2)	0	2.54(5)
Na(2)	0.1101(1)	0.5	−0.2908(2)	2.69(6)
Na(3)	0.25	0.25	0.5	3.78(7)
Al	0.25	0.25	0	1.76(4)
P(1)	0.37703(6)	0	−0.2259(1)	1.75(4)
P(2)	0.11949(6)	0	−0.2912(1)	1.76(4)
O(1)	0.4761(2)	0	−0.2127(4)	2.06(8)
O(2)	0.3333(2)	0	−0.4299(4)	2.28(9)
O(3)	0.3477(1)	0.1789(3)	−0.1187(3)	2.12(6)
O(4)	0.1703(1)	0.1788(3)	−0.2244(3)	2.14(6)
O(5)	0.0258(2)	0	−0.2401(4)	2.18(8)
O(6)	0.1194(2)	0	−0.5183(4)	2.43(9)
O(7)	0.2423(1)	0	0.1067(4)	1.94(8)
H(6)	0.0659	0	−0.5877	5.0
H(7)	0.1960	0	0.1705	5.0
Compound 2				
Na(1)	0	0.2352(2)	0	1.62(6)
Na(2)	0.1103(1)	0.5	−0.2933(2)	1.94(6)
Na(3)	0.25	0.25	0.5	3.32(9)
Ga	0.25	0.25	0	0.85(3)
P(1)	0.37870(6)	0	−0.2271(1)	0.84(3)
P(2)	0.11842(7)	0	−0.2966(1)	0.83(4)
O(1)	0.4768(2)	0	−0.2184(4)	1.33(8)
O(2)	0.3325(2)	0	−0.4277(3)	1.38(8)
O(3)	0.3517(1)	0.1759(2)	−0.1171(2)	1.22(6)
O(4)	0.1692(1)	0.1769(2)	−0.2326(2)	1.15(6)
O(5)	0.0269(2)	0	−0.2387(4)	1.36(8)
O(6)	0.1163(2)	0	−0.5225(3)	1.52(8)
O(7)	0.2413(1)	0	0.1175(3)	1.04(8)
H(6)	0.0602	0	−0.6004	5.0
H(7)	0.1887	0	0.1748	5.0

$^a U_{eq}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

maximum gap in the Na–O distances ranked in increasing order. The limiting value for Na–O, 3.19 Å, of Donnay and Allmann was also considered (16). Therefore, Na(1), Na(2), and Na(3) are coordinated by 6, 5, and 8 oxygen atoms with the 7th Na(1)–O, 6th Na(2)–O, and 9th Na(3)–O distances at 3.22, 3.14, and 3.27 Å in **1** and 3.27, 3.15, and 3.23 Å in **2**, respectively. The valence sums of Na(3)–O bonds in both compounds are significantly greater than 1, indicating that they are tightly bound. In the following, only the structure of $Na_3Al(OH)(HPO_4)(PO_4)$ is discussed because the two compounds are isostructural.

The structure of $Na_3Al(OH)(HPO_4)(PO_4)$ is shown in Fig. 1. It consists of infinite chains of *trans*-corner-sharing $AlO_5(OH)$ octahedra running parallel to the *b* axis. The metal atoms are linked together by means of single bridges of hydroxo groups. The hydrogen atom of the hydroxo

bridge is not involved in hydrogen bonding. There are two octahedra per chain of unit cell length along the *b* axis. The central axis of each chain is a two-fold rotation axis. Adjacent octahedra within a chain are bridged by HPO_4 and PO_4 groups to form the $\frac{1}{\infty}[Al(OH)(HPO_4)(PO_4)^{3-}]$ chain as shown in Fig. 2. These infinite chains are held together primarily by the interaction between oxygen and sodium atoms. All oxygen atoms are involved in Na–O bonds. Further interchain linkages are provided by hydrogen bonds. Atom O(5) of a HPO_4 group is a hydrogen bond acceptor from a HPO_4 group belonging to an adjacent infinite chain. Na(1) and Na(2) lie in the channels between the infinite chains. Na(3) lies between two HPO_4 groups of a chain.

The AlO_6 octahedron is distorted as shown by the Al–O bond lengths and $O \cdots O$ distances. In contrast, the O–Al–O bond angle distortion is quite small. The mean Al–O distance is 1.911 Å, which is close to the sum of the effective ionic radii, 1.915 Å, for 6-coordinated Al^{3+} and 4-coordinated O^{2-} ions (17). The $P(1)O_4$ tetrahedron is also distorted. The longer P(1)–O bonds involve the oxygens that form the shortest Al–O bonds. The average value of the P(1)–O distances, 1.536 Å, agrees well with the value for $Na_4Al(OH)(PO_4)_2$, 1.537 Å. The P(2)–O distances do not differ significantly from those found for HPO_4 groups in other compounds. The P(2)–O(6) distance is the longest because O(6) is the hydroxo oxygen. The Na atoms show irregular coordination polyhedra. Na(1) and Na(2) are 6- and 5-coordinated, respectively, with a narrow range of Na–O distances. $Na(3)O_8$ forms a distorted cube with a wide range of bond lengths: four short bond distances at 2.196 and 2.461 Å, two medium distances at 2.654 Å, and two long bonds to oxygen at 2.957 Å.

The structure of $Na_3Al(OH)(HPO_4)(PO_4)$ is very similar to that of $Na_4Al(OH)(PO_4)_2$. The latter is orthorhombic with a unit cell volume nearly twice that of the former. The title compound contains fewer sodium atoms. In $Na_3Al(OH)(HPO_4)(PO_4)$ the hydroxyl groups of HPO_4 point into the open channel, which is located at $0, y, \frac{1}{2}$. In contrast, in $Na_4Al(OH)(PO_4)_2$ the corresponding channel is filled with Na atoms. The infinite chains in both compounds have the same connectivity as those $[M(TO_4)_2\phi]$ chains (ϕ, unspecified ligand) in many phosphate, sulfate, and silicate minerals (18).

D'Yvoire and Pintard-Screpel reported the preparation of $Na_3Al(OH)(HPO_4)(PO_4)$ under mild hydrothermal conditions. Its X-ray powder pattern, which agreed well with ours, was indexed in the same unit cell as that described in this work. They also concluded that the compound was nonstoichiometric because of metal cation vacancies. In contrast, our $Na_3Al(OH)(HPO_4)(PO_4)$ samples do not show any cation vacancies, as indicated from the results of a single-crystal X-ray diffraction study and thermogravimetric analysis.

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TABLE 3
Selected Bond Lengths (Å), Bond Valence Sums ($\sum s$), and Bond Angles (°) for Na$_3$Al(OH)(HPO$_4$)(PO$_4$) (1) and Na$_3$Ga(OH)(HPO$_4$)(PO$_4$) (2)

Compound 1
AlO$_6$ octahedron[a]

Al	O(3)	O(4)	O(7)	O(3)′	O(4)′	O(7)′
O(3)	**1.862(2)**	2.725(2)	2.703(3)		2.659(3)	2.656(2)
O(4)	91.4(1)	**1.944(2)**	2.763(3)	2.659(3)		2.709(3)
O(7)	91.0(1)	91.1(1)	**1.926(1)**	2.656(2)	2.709(2)	
O(3)′	180	88.6(1)	89.0(1)	**1.862(2)**	2.725(2)	2.703(3)
O(4)′	88.6(1)	180	88.9(1)	91.4(1)	**1.944(2)**	2.763(3)
O(7)′	89.0(1)	88.9(1)	180	91.0(1)	91.1(1)	**1.926(1)**

$\sum s$(Al–O) = 2.99

The P(1)O$_4$ tetrahedron

P(1)	O(1)	O(2)	O(3)	O(3)′
O(1)	**1.505(3)**	2.514(3)	2.486(3)	2.486(3)
O(2)	112.8(2)	**1.512(3)**	2.516(3)	2.516(3)
O(3)	108.3(1)	109.8(1)	**1.563(2)**	2.524(4)
O(3)′	108.3(1)	109.8(1)	107.7(2)	**1.563(2)**

$\sum s$(P(1)–O) = 5.00

P(2)O$_4$ tetrahedron

P(2)	O(4)	O(5)	O(6)	O(4)′
O(4)	**1.527(2)**	2.534(3)	2.470(3)	2.523(4)
O(5)	112.8(1)	**1.516(3)**	2.557(4)	2.534(3)
O(6)	104.4(1)	110.3(1)	**1.599(3)**	2.470(3)
O(4)′	111.5(1)	112.8(1)	104.4(1)	**1.527(2)**

$\sum s$(P(2)–O) = 4.91

Na(1)–O(1)	2.398(2) (2×)	Na(1)–O(3)	2.455(2) (2×)
Na(1)–O(5)	2.431(2) (2×)		

$\sum s$(Na(1)–O) = 1.11

Na(2)–O(1)	2.181(3)	Na(2)–O(2)	2.239(3)
Na(2)–O(4)	2.469(2) (2×)	Na(2)–O(7)	2.465(3)

$\sum s$(Na(2)–O) = 1.16

Na(3)–O(2)	2.196(1) (2×)	Na(3)–O(3)	2.957(2) (2×)
Na(3)–O(4)	2.461(2) (2×)	Na(3)–O(6)	2.654(2) (2×)

$\sum s$(Na(3)–O) = 1.32

O(6)–H(6)	0.902	O(7)–H(7)	0.881
O(5)···H(6)	1.742		

Al–O(7)–Al′	132.6	P(2)–O(6)–H(6)	115.8
Al–O(7)–H(7)	106.8	O(6)–H(6)···O(5)	168.8

Compound 2
GaO$_6$ octahedron[a]

Ga	O(3)	O(4)	O(7)	O(3)′	O(4)′	O(7)′
O(3)	**1.931(2)**	2.840(1)	2.808(3)		2.737(2)	2.729(2)
O(4)	92.1(1)	**2.013(2)**	2.883(3)	2.737(2)		2.769(2)
O(7)	91.6(1)	92.3(1)	**1.985(1)**	2.729(2)	2.769(2)	
O(3)′	180	87.9(1)	88.4(1)	**1.931(2)**	2.840(1)	2.808(3)
O(4)′	87.9(1)	180	87.7(1)	92.1(1)	**2.013(2)**	2.883(3)
O(7)′	88.4(1)	87.7(1)	180	91.6(1)	92.3(1)	**1.985(1)**

$\sum s$(Ga–O) = 3.10

P(1)O$_4$ tetrahedron

P(1)	O(1)	O(2)	O(3)	O(3)′
O(1)	**1.508(3)**	2.526(3)	2.479(3)	2.479(3)
O(2)	113.7(2)	**1.510(2)**	2.516(3)	2.516(3)
O(3)	107.7(1)	110.0(1)	**1.562(2)**	2.521(3)
O(3)′	107.7(1)	110.0(1)	107.6(1)	**1.562(2)**

$\sum s$(P(1)–O) = 5.00

Table 3—*Continued*

P(2)O$_4$ tetrahedron

P(2)	O(4)	O(5)	O(6)	O(4)′
O(4)	**1.530(2)**	2.532(3)	2.464(3)	2.534(3)
O(5)	112.5(1)	**1.516(3)**	2.560(4)	2.532(3)
O(6)	104.3(1)	111.0(1)	**1.590(3)**	2.464(3)
O(4)′	111.8(1)	112.5(1)	104.3(1)	**1.530(2)**

$\sum s$(P(2)–O) = 4.92

Na(1)–O(1)	2.444(2) (2×)	Na(1)–O(3)	2.426(2) (2×)
Na(1)–O(5)	2.452(2) (2×)		

$\sum s$(Na(1)–O) = 1.07

Na(2)–O(1)	2.186(3)	Na(2)–O(2)	2.249(3)
Na(2)–O(4)	2.505(2) (2×)	Na(2)–O(7)	2.475(3)

$\sum s$(Na(2)–O) = 1.12

Na(3)–O(2)	2.222(1) (2×)	Na(3)–O(3)	3.011(2) (2×)
Na(3)–O(4)	2.436(2) (2×)	Na(3)–O(6)	2.723(2) (2×)

$\sum s$(Na(3)–O) = 1.25

O(6)–H(6)	0.970	O(7)–H(7)	0.948
O(6)···H(6)	1.656		

Ga–O(7)–Ga′	129.0	P(2)–O(6)–H(6)	118.8
Ga–O(7)–H(7)	106.3	O(6)–H(6)···O(5)	171.3

[a] The distances between *trans* oxygen atoms are not shown.
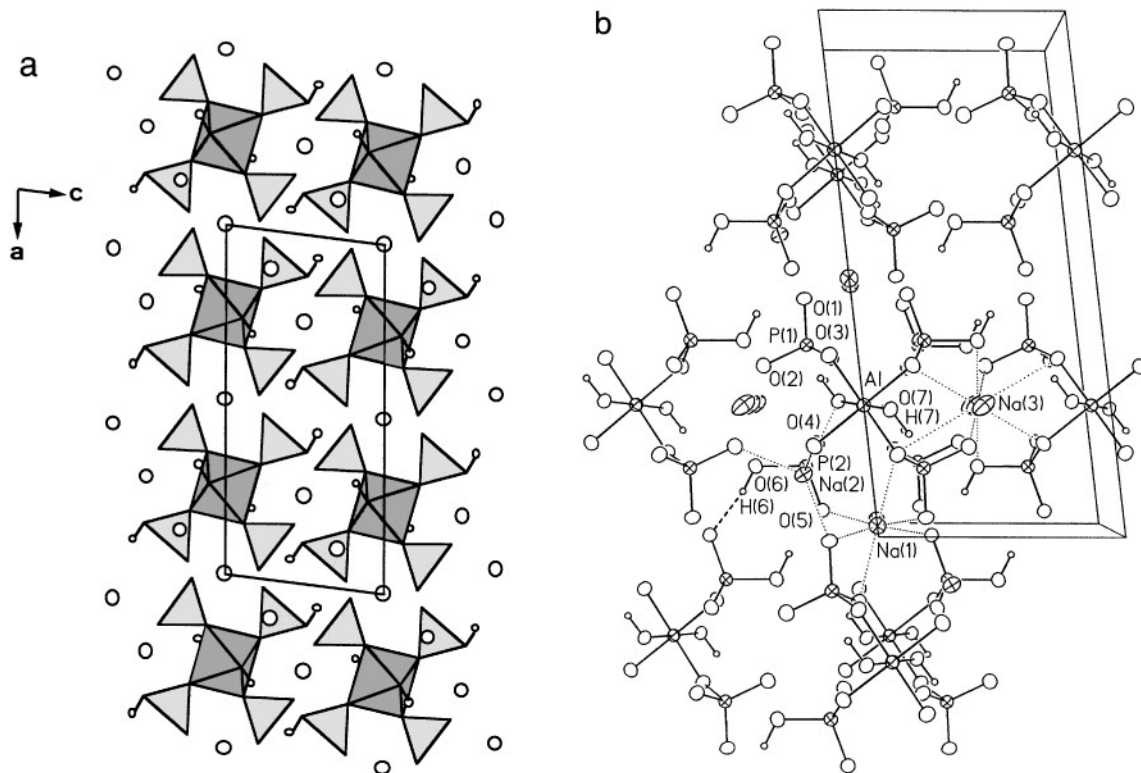
FIG. 1. (a) Polyhedral view of the Na$_3$Al(OH)(HPO$_4$)(PO$_4$) structure along the b axis. Large open circles, Na atoms; small open circles, H atoms. (b) Ball-and-stick representation of the structure. Na–O bonds are represented by dotted lines. A hydrogen bond is shown by the dashed line.
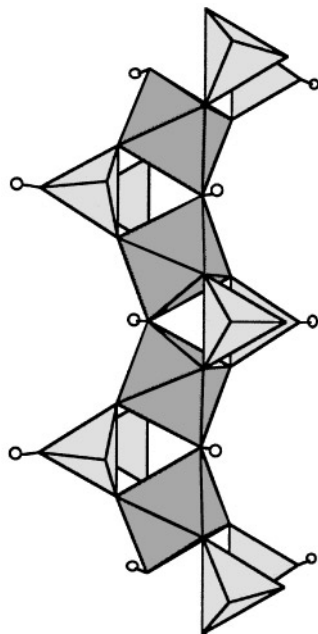
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FIG. 2. Section of the $\frac{1}{\infty}[\text{Al(OH)(HPO}_4\text{)(PO}_4\text{)}^{3-}]$ chain in $\text{Na}_3\text{Al(OH)(HPO}_4\text{)(PO}_4\text{)}$, viewed in a direction perpendicular to the *b* axis. Small open circles represent H atoms.