

# Crystal structure of a new phosphate compound, $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$

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## Abstract

A new phosphate compound,  $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$ , formed in the laboratory by cyanobacteria, has been identified and its crystal structure studied with single-crystal X-ray diffraction and infrared spectroscopy. The crystal is orthorhombic with the space group  $Pnma$  and unit-cell parameters  $a = 25.1754(18) \text{ \AA}$ ,  $b = 6.9316(5) \text{ \AA}$ ,  $c = 11.2189(10) \text{ \AA}$ ,  $V = 1957.8(3) \text{ \AA}^3$ . Its structure can be viewed as stacking of three types of layers along the  $a$ -axis in a sequence ABCBABC... , where layer A is composed of  $\text{Mg}(\text{H}_2\text{O})_6$  octahedra and  $\text{Na}(\text{H}_2\text{O})_6$  trigonal prisms, layer B of two crystallographically distinct  $\text{PO}_4^{3-}$  tetrahedra (designated as P1 and P2), and layer C of  $\text{Mg}_2(\text{H}_2\text{O})_6$  octahedra and highly irregular K-polyhedra formed by five  $\text{H}_2\text{O}$  molecules and one  $\text{O}^{2-}$  from the P2 tetrahedron. The linkage between layers is principally achieved through hydrogen bonding, except for the K–O5 bond between layers B and C. The structure of  $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$  has many features similar to those for the struvite analogs of  $\text{MgK}(\text{PO}_4) \cdot 6\text{H}_2\text{O}$  (Acta Crystallogr. B 35 (1979) 11) or  $\text{MgNa}(\text{PO}_4) \cdot 7\text{H}_2\text{O}$  (Acta Crystallogr. B 38 (1982) 40) and represents the first struvite-type phosphate compound that contains both K and Na as univalent cations.

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**Keywords:** Structure of a new phosphate; Orthophosphate; Struvite analog

## 1. Introduction

The formation of phosphate-containing biominerals has been considered as one of the most common microbial transformations of inorganic phosphates [3,4]. Among phosphate-containing biominerals, struvite,  $\text{Mg}(\text{NH}_4)(\text{PO}_4) \cdot 6\text{H}_2\text{O}$ , has attracted considerable attention, because of its common occurrence in a wide variety of environments, such as bat droppings, decomposing foods, as a component of human infection stones, a part of biofilms that develop on the inside of pipelines in water treatment facilities, or in a range of microorganisms growing in the laboratory. Extensive evidence suggests that microorganisms play a crucial role in the formation of struvite by providing nucleation sites, phosphate ions and/or ammonia.

The crystal structure of struvite was first determined by Whitaker and Jeffery [5] and a number of struvite-

type compounds and their structural relationships were reported by Dickens and Brown [6]. A general chemical formula for struvite-type compounds can be expressed as  $X^{2+}M^+(YO_4) \cdot n\text{H}_2\text{O}$ , where  $n = 6-8$ ,  $Y = \text{P}$  or  $\text{As}$ , and the ionic radius of monovalent cations  $M^+$  is larger than that of divalent cations  $X^{2+}$ . Struvite analogs of the type  $\text{Mg}M^+(\text{PO}_4) \cdot 6\text{H}_2\text{O}$  ( $M = \text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and  $\text{Ti}^+$ ) have been examined by Banks et al. [7]. A common feature of all struvite-type structures is that  $\text{Mg}^{2+}$  cations are octahedrally coordinated by six water molecules whose H atoms are strongly bonded to oxygen atoms of  $\text{PO}_4^{3-}$  groups. No water molecules are shared between  $\text{Mg}(\text{H}_2\text{O})_6$  octahedra, which is characteristic of hydrates with  $z/xn > 1$  ( $z$  is the number of water molecules,  $x$  the number of cations, and  $n$  the coordination number of cations) classified as type “AI” by Wells [8]. Another common feature among the struvite-type phosphate compounds is the face sharing between  $\text{PO}_4$  tetrahedra and  $\text{Mg}(\text{H}_2\text{O})_6$  octahedra through hydrogen bonding, although the number of shared faces may vary from structure to structure.

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The struvite structure is thought to be unable to accommodate univalent cations smaller than  $K^+$ , but a sodium analog,  $MgNa(PO_4) \cdot 7H_2O$ , has been synthesized and its structure determined by Mathew et al. [2]. In this paper, we report a new type of phosphate-containing, biologically formed crystal, which has the chemical composition  $Mg_2KNa(PO_4)_2 \cdot 14H_2O$  and many structural features similar to those for the struvite analogs of both  $MgK(PO_4) \cdot 6H_2O$  [1] and  $MgNa(PO_4) \cdot 7H_2O$  [2]. To our knowledge, this is the first struvite-type phosphate compound that contains both K and Na as monovalent cations.

## 2. Experimental procedures

The crystal used in this study was formed in a microbiological culture containing the filamentous, photosynthetic cyanobacterium *Lyngbya* sp., which was isolated from the interior of calcareous tufa deposits collected from Mono Lake (California). The growth medium was composed of distilled water and the lake water in a 1:1 ratio, solidified with 1.2% agar. At the end of growth and as the medium in the Petri dish began to dry, tufts of elongated-tabular crystals of  $Mg_2KNa(PO_4)_2 \cdot 14H_2O$  appeared around cyanobacterial colonies (Fig. 1).

The chemical composition of the crystal was determined with an electron microprobe (JEOL superprobe) using analytical conditions of 10 kV and 5 nA with a rastered beam size of 20  $\mu m$  to minimize the possible sample damage by the electron beam. Ten analyses yielded the following average composition (wt%):  $P_2O_5$  40.3(8), MgO 22.8(6),  $K_2O$  12.4(3), and  $Na_2O$  7.9(4), with a total oxide sum of 83.4(1.2) wt%. Due to the high

hydration of the crystal, this composition was used only for the estimation of cation ratios. By assuming two P cations per formula, the relative ratio of P:Mg:K:Na is 2.00:2.00:0.93:0.90. The actual composition of the crystal,  $Mg_2KNa(PO_4)_2 \cdot 14H_2O$ , was determined by the combination of the electron microprobe and the X-ray structural data.

Based on optical examination, a nearly cube-shaped crystal was selected and mounted on a Bruker Smart CCD X-ray diffractometer equipped with graphite-monochromatized  $MoK\alpha$  radiation. A hemisphere of three-dimensional X-ray diffraction data was collected with frame widths of  $0.3^\circ$  in  $\omega$  and 30 s counting time per frame (see Table 1 for experimental details). The data were analyzed to locate peaks for the determination of the unit-cell parameters. All reflections were indexed based on an orthorhombic unit cell:  $a = 25.1754(18) \text{ \AA}$ ,  $b = 6.9316(5) \text{ \AA}$ , and  $c = 11.2189(10) \text{ \AA}$ , and space group  $Pnma$ . An empirical correction for X-ray absorption was made using the program SADABS (part of the Bruker program SAINT). Equivalent reflections were merged into a set of 2394 independent reflections, out of which 1804 ones had  $I_{obs} > 2\sigma(I_{obs})$  and were used for the structure analysis and refinements.

The crystal structure of  $Mg_2KNa(PO_4)_2 \cdot 14H_2O$  was solved using SHELX97. All non-hydrogen atoms were first located and refined with anisotropic thermal displacement parameters, resulting in  $R_1 = 0.050$  for observed reflections. The difference Fourier syntheses were then carried out, which revealed the positions of all hydrogen atoms. In the subsequent refinements, all H positions were refined with fixed isotropic thermal displacement parameters ( $U_{eq} = 0.04$ ), yielding  $R_1 = 0.033$  for the observed reflections and 0.051 for all

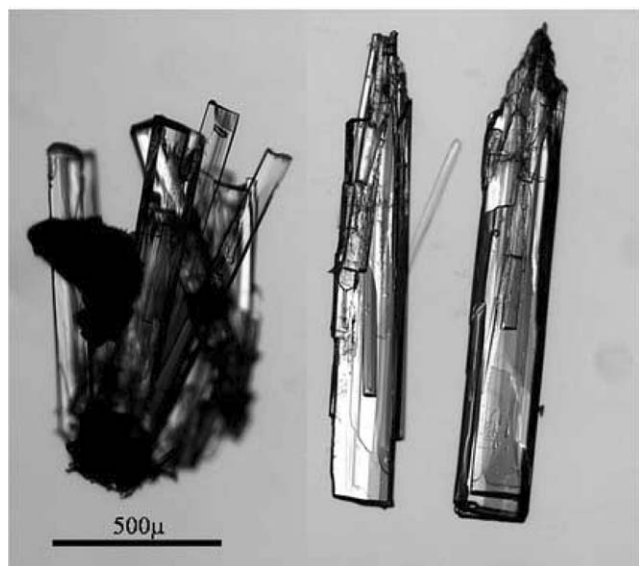


Fig. 1. Photograph of  $Mg_2KNa(PO_4)_2 \cdot 14H_2O$  crystals.

Table 1  
Summary of crystal data and refinement results

Structural formula	$Mg_2KNa(PO_4)_2 \cdot 14H_2O$
Formula weight	552.93
Crystal size ( $mm^3$ )	$0.09 \times 0.09 \times 0.07$
Space group	$Pnma$ (No. 62)
$a$ ( $\text{\AA}$ )	25.1754(18)
$b$ ( $\text{\AA}$ )	6.9316(5)
$c$ ( $\text{\AA}$ )	11.2189(10)
$V$ ( $\text{\AA}^3$ )	1957.8(3)
$Z$	4
$\rho_{calc}$ ( $g/cm^3$ )	1.876
$\lambda$ ( $\text{\AA}$ )	0.71069
$\mu$ ( $mm^{-1}$ )	0.62
$\theta$ range for data collection	0–29
No. of reflections collected	12061
No. of independent reflections	2394
No. of reflections with $I > 2\sigma(I)$	1804
No. of parameters refined	198
$R(int)$	0.048
Final $R$ factors [ $I > 2\sigma(I)$ ]	$R_1 = 0.033$ , $wR_2 = 0.055$
Final $R$ factors (all data)	$R_1 = 0.051$ , $wR_2 = 0.069$
Goodness-of-fit	0.92

Table 2  
Atomic coordinates and anisotropic displacement parameters for  $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{\text{eq}}$
K	0.2214(1)	3/4	0.5022(1)	0.0308(5)	0.0542(6)	0.0353(5)	0	−0.0089(3)	0	0.0401(3)
Na	0.0003(1)	3/4	0.9260(1)	0.0406(9)	0.0270(8)	0.0355(9)	0	0.0073(6)	0	0.0344(5)
Mg1	0.9542(1)	3/4	0.6387(1)	0.0154(6)	0.0136(5)	0.0159(7)	0	0.0007(4)	0	0.0150(3)
Mg2	0.2236(1)	3/4	0.8368(1)	0.0161(6)	0.0184(6)	0.0150(6)	0	0.0006(4)	0	0.0165(3)
P1	0.1281(1)	1/4	0.7222(1)	0.0155(4)	0.0159(4)	0.0130(4)	0	−0.0006(3)	0	0.0148(3)
P2	0.1273(1)	3/4	0.2205(1)	0.0156(4)	0.0128(4)	0.0149(4)	0	0.0013(3)	0	0.0144(2)
O1	0.1360(1)	1/4	0.8584(2)	0.0318(12)	0.0272(11)	0.0164(11)	0	−0.0027(8)	0	0.0251(5)
O2	0.1829(1)	1/4	0.6610(2)	0.0220(11)	0.0284(11)	0.0243(11)	0	0.0014(8)	0	0.0249(5)
O3	0.0974(1)	0.4319(2)	0.6859(1)	0.0234(8)	0.0199(7)	0.0258(8)	0.0007(6)	−0.0017(6)	0.0007(6)	0.0230(3)
O4	0.0676(1)	3/4	0.1948(2)	0.0200(11)	0.0266(11)	0.0341(12)	0	−0.0022(9)	0	0.0269(5)
O5	0.1382(1)	3/4	0.3549(2)	0.0300(12)	0.0226(11)	0.0183(11)	0	0.0006(8)	0	0.0236(5)
O6	0.1521(1)	0.9313(2)	0.1636(1)	0.0274(8)	0.0184(7)	0.0226(7)	0.0012(6)	0.0038(6)	−0.0012(6)	0.0228(3)
Ow1	0.0096(1)	3/4	0.5065(2)	0.0312(14)	0.0227(12)	0.0409(14)	0	0.0154(10)	0	0.0316(6)
Ow2	0.8940(1)	3/4	0.7611(2)	0.0480(15)	0.0169(12)	0.0480(15)	0	0.0297(11)	0	0.0377(6)
Ow3	0.9160(1)	0.5348(2)	0.5443(1)	0.0353(9)	0.0238(8)	0.0208(8)	0.0018(6)	−0.0013(6)	−0.0082(7)	0.0266(4)
Ow4	0.9947(1)	0.9582(2)	0.7374(1)	0.0208(8)	0.0227(8)	0.0343(9)	−0.0056(7)	0.0002(6)	−0.0001(7)	0.0259(4)
Ow5	0.2494(1)	0.5358(2)	0.7232(1)	0.0224(9)	0.0300(9)	0.0400(9)	−0.0115(7)	0.0035(7)	0.0013(7)	0.0308(4)
Ow6	0.1966(1)	0.9664(2)	0.9492(1)	0.0316(9)	0.0285(9)	0.0220(9)	0.0003(7)	0.0029(7)	0.0054(7)	0.0274(4)
Ow7	0.1551(1)	3/4	0.7311(2)	0.02503	0.0220(12)	0.0478(14)	0	−0.0119(10)	0	0.0316(6)
Ow8	0.2973(1)	3/4	0.9259(2)	0.0199(12)	0.0743(18)	0.0285(13)	0	−0.0018(10)	0	0.0409(7)
Ow9	0.0597(1)	0.0098(2)	0.9826(1)	0.0314(10)	0.0435(11)	0.0319(10)	0.0084(8)	−0.0032(7)	−0.0017(8)	0.0356(4)

Table 3  
Hydrogen coordinates in  $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>
H11	0.030(1)	0.837(3)	0.485(2)
H21	0.880(1)	0.854(3)	0.792(2)
H31	0.893(1)	0.448(3)	0.575(2)
H32	0.906(1)	0.550(3)	0.465(2)
H41	0.974(1)	0.054(4)	0.757(2)
H42	0.029(1)	0.998(3)	0.728(2)
H51	0.228(1)	0.437(4)	0.708(2)
H52	0.281(1)	0.494(3)	0.714(2)
H61	0.179(1)	0.938(3)	0.020(2)
H62	0.178(1)	0.053(3)	0.920(2)
H71	0.134(1)	0.849(3)	0.721(2)
H81	0.324(1)	3/4	0.900(3)
H82	0.303(1)	3/4	0.012(3)
H91	0.082(1)	0.067(4)	0.945(2)
H92	0.078(1)	0.957(3)	0.036(2)

independent reflections. In addition, the cation occupancies at the K, Na, Mg1, and Mg2 sites were also refined, yielding 0.954(1), 0.956(2), 0.986(2), and 0.983(2), respectively. The highest residual peak after the convergence of the refinement was  $0.34 \text{ e}/\text{\AA}^3$ . The final difference Fourier map was featureless. Final atomic coordinates and anisotropic thermal displacement parameters for non-hydrogen atoms are presented in Table 2. Positions of H atoms are listed in Table 3. Selected non-hydrogen bond distances are given in Table 4 and hydrogen bond distances in Table 5.

Synchrotron infrared absorption measurements on the crystal were performed with a Bruker IFS 66 s/V

FTIR spectrometer at the U2A beam line of National Synchrotron Light Source of Brookhaven National Laboratory. To avoid saturated IR absorption, single crystals were crushed in a diamond anvil cell into a thin film sample ( $\sim 1 \mu\text{m}$  thick), which was later transferred to a KBr substrate for the IR spectrum measurements. The aperture of the spectrometer was set to  $20 \times 30 \mu\text{m}$  to ensure that only the spectra of samples were collected. The spectra of the sample and the reference were collected with a nitrogen cooled MCT detector at a resolution of  $4 \text{ cm}^{-1}$  and 1024 scans. The synchrotron IR optical system was described in detail elsewhere [9].

### 3. Results and discussion

The crystal structure of  $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$  has many features similar to those for the struvite analogs of  $\text{MgK}(\text{PO}_4) \cdot 6\text{H}_2\text{O}$  [1] or  $\text{MgNa}(\text{PO}_4) \cdot 7\text{H}_2\text{O}$  [2], and thus may be considered as a superstructure of struvite-type compounds. One of the outstanding features of this structure is that there are two crystallographically distinct  $\text{Mg}^{2+}$  cation sites, Mg1 and Mg2, both of which are octahedrally coordinated with six  $\text{H}_2\text{O}$  molecules, a characteristic of the struvite-type structures. There are also two symmetrically independent  $\text{P}^{5+}$  cations (P1 and P2), each being in a fairly regular tetrahedron formed by four  $\text{O}^{2-}$  anions (Table 4). The  $\text{Na}^+$  cation is surrounded by six  $\text{H}_2\text{O}$  molecules, whereas  $\text{K}^+$  is coordinated by five  $\text{H}_2\text{O}$  molecules and an  $\text{O}^{2-}$  anion from a P2 tetrahedron (Fig. 2). The whole crystal structure can be viewed as stacking of three types

of layers along the *a*-axis in a repeating sequence of ABCBABC... (Fig. 3), where layer A consists of Mg1 octahedra and Na trigonal prisms, layer B of P1 and P2 tetrahedra, and layer C of Mg2 octahedra and very irregular K polyhedra. These layers are linked together by hydrogen bonds, except between layers B and C, where both hydrogen bonds and K–O5 bonds contribute the linkage.

It is instructive to compare the K<sup>+</sup> coordination in the Mg<sub>2</sub>KNa(PO<sub>4</sub>)<sub>2</sub>·14H<sub>2</sub>O structure with that in the potassium struvite analog of MgK(PO<sub>4</sub>)·6H<sub>2</sub>O [1]. In both structures, the K cations are bonded to six oxygen atoms: one from a [PO<sub>4</sub>]<sup>3-</sup> tetrahedron and five from H<sub>2</sub>O molecules that are also bonded to Mg cations, forming a very irregular polyhedron. Furthermore, there is a face sharing between the K polyhedron and the Mg

octahedron in both structures. Nonetheless, the six K–O bond distances in the Mg<sub>2</sub>KNa(PO<sub>4</sub>)<sub>2</sub>·14H<sub>2</sub>O structure range from 2.668 to 3.063 Å, with an average distance of 2.918 Å, whereas they are between 2.821 and 3.363 Å, with an average of 3.034 Å in the MgK(PO<sub>4</sub>)·6H<sub>2</sub>O structure. Obviously, the K cation is more tightly packed in Mg<sub>2</sub>KNa(PO<sub>4</sub>)<sub>2</sub>·14H<sub>2</sub>O than in MgK(PO<sub>4</sub>)·6H<sub>2</sub>O.

The coordination of Na<sup>+</sup> in the Mg<sub>2</sub>KNa(PO<sub>4</sub>)<sub>2</sub>·14H<sub>2</sub>O structure, on the other hand, is significantly different from that in the sodium struvite analog of MgNa(PO<sub>4</sub>)·7H<sub>2</sub>O [2], despite the fact that the Na cations in both structures are bonded by six H<sub>2</sub>O molecules. In Mg<sub>2</sub>KNa(PO<sub>4</sub>)<sub>2</sub>·14H<sub>2</sub>O, Na is coordinated by six H<sub>2</sub>O molecules forming a slightly distorted trigonal prism; neighboring prisms share two edges to form zigzag chains running along the *b*-axis (Fig. 4a). In contrast, the six H<sub>2</sub>O molecules bonded to Na in MgNa(PO<sub>4</sub>)·7H<sub>2</sub>O form an elongated octahedron; neighboring Na(H<sub>2</sub>O)<sub>6</sub> octahedra share two apexes to form straight chains along the *c*-axis (Fig. 4b). The Na–O bond lengths in Mg<sub>2</sub>KNa(PO<sub>4</sub>)<sub>2</sub>·14H<sub>2</sub>O are between 2.425 and 2.565 Å, with an average of 2.487 Å, which is shorter than that (2.505 Å) in MgNa(PO<sub>4</sub>)·7H<sub>2</sub>O. The respective Na polyhedral volumes in the two structures are 14.58 and 20.26 Å<sup>3</sup>. This observation suggests that, as with K, Na is also more tightly bonded in Mg<sub>2</sub>KNa(PO<sub>4</sub>)<sub>2</sub>·14H<sub>2</sub>O than in MgNa(PO<sub>4</sub>)·7H<sub>2</sub>O.

Both Mg1 and Mg2 octahedra are fairly regular. The Mg1–O bonds in the Mg1 octahedra vary from 2.036 to 2.085 Å, with an average 2.064 Å, whereas those in the Mg2 octahedra range from 2.062 to 2.108, with an average of 2.079 Å. These values are in agreement with those observed in struvite and other hydrous magnesium phosphate compounds [10]. The longer Mg1–Ow4

Table 4  
Selected non-hydrogen bond distances (Å) in Mg<sub>2</sub>KNa(PO<sub>4</sub>)<sub>2</sub>·14H<sub>2</sub>O

P1–O1	1.541(2)	P2–O4	1.530(2)
P1–O2	1.541(2)	P2–O5	1.533(2)
P1–O3 (× 2)	1.534(1)	P2–O6 (× 2)	1.542(2)
Avg.	1.538	Avg.	1.537
Mg1–Ow1	2.036(2)	Mg2–Ow5 (× 2)	2.062(2)
Mg1–Ow2	2.045(2)	Mg2–Ow6 (× 2)	2.074(2)
Mg1–Ow3 (× 2)	2.067(2)	Mg2–Ow7	2.093(2)
Mg1–Ow4 (× 2)	2.085(2)	Mg2–Ow8	2.108(2)
Avg.	2.064	Avg.	2.079
K–O5	2.668(2)	Na–Ow4 (× 2)	2.565(2)
K–Ow5 (× 2)	2.975(2)	Na–Ow9 (× 2)	2.425(2)
K–Ow6 (× 2)	2.912(2)	Na–Ow9 (× 2)	2.471(2)
K–Ow7	3.063(3)		
Avg.	2.918	Avg.	2.487

Table 5  
Hydrogen bonds with H...A < 2.0 Å and ∠D–H...A > 110°

D–H	d(D–H) (Å)	d(H...A) (Å)	∠D–H...A (deg)	d(D...A) (Å)	A
Ow1–H11	0.828	1.959	171.59	2.780	W3
Ow2–H21	0.874	1.765	172.65	2.635	O6
Ow3–H31	0.903	1.766	166.54	2.653	O5
Ow3–H32	0.931	1.700	166.95	2.615	O3
Ow4–H41	0.872	1.799	177.07	2.670	O4
Ow4–H42	0.913	1.851	171.62	2.757	O3
Ow5–H51	0.888	1.802	173.37	2.686	O2
Ow5–H52	0.853	1.829	167.69	2.669	O6
Ow6–H61	0.931	1.748	167.59	2.665	O6
Ow6–H62	0.829	1.860	178.52	2.689	O1
Ow7–H71	0.875	1.820	171.84	2.689	O3
Ow8–H81	0.732	2.524	157.65	3.214	W2
Ow8–H82	0.977	1.709	176.46	2.684	O2
Ow9–H91	0.806	2.098	172.16	2.899	O1
Ow9–H92	0.840	2.303	139.58	2.992	O4
Ow9–H92	0.840	2.358	154.16	3.135	O6

Note: D = donor atom; A = acceptor atom.

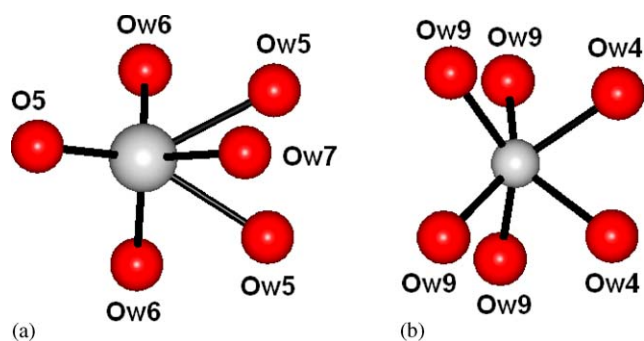


Fig. 2. Atomic coordination for (a) K and (b) Na in  $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$ .

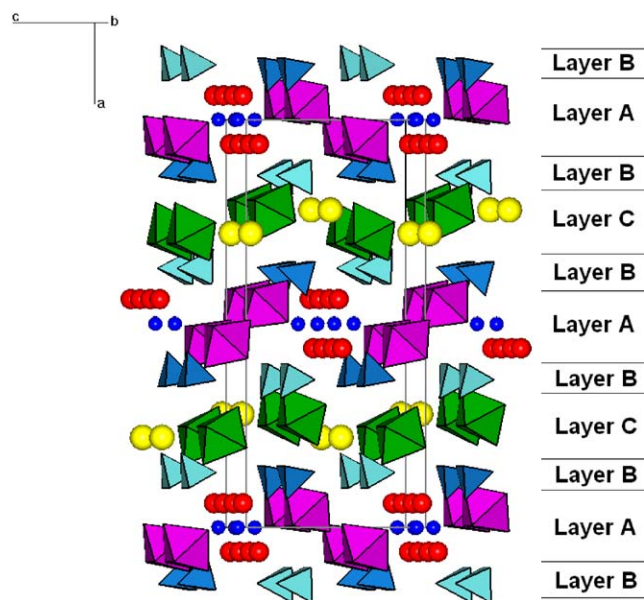


Fig. 3. Crystal structure of  $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$ . Tetrahedra =  $\text{PO}_4^{3-}$  groups and octahedra =  $\text{Mg}(\text{H}_2\text{O})_6$ . Layer A consists of Mg1 octahedra and Na trigonal prisms, layer B of P1 and P2 tetrahedra, and layer C of Mg2 octahedra and very irregular K polyhedra. For clarity of viewing, the Na and K polyhedra were not drawn. Instead, they were represented by spheres. The largest spheres stand for K, the medium for a water molecule (Ow9), and the smallest for Na.

distance in the Mg1 octahedron (Table 4) is due to the sharing of its Ow4–Ow4 edge with the Na polyhedron.

In both P1 and P2 tetrahedra, the average P–O bond distance is 1.537 Å, in accord with the mean value of 1.536 Å given by Baur [11] for orthophosphate groups. The O–P–O angles show only slight deviations from the value for an ideal tetrahedron. It is interesting to note that both P1 and P2 tetrahedra have a configuration comparable to that in the potassium struvite analog  $\text{MgK}(\text{PO}_4) \cdot 6\text{H}_2\text{O}$ . In both structures, every  $\text{PO}_4^{3-}$  tetrahedron has two faces shared with two different  $\text{Mg}(\text{H}_2\text{O})_6$  octahedra via hydrogen bonds and vice versa. Such an arrangement differs from that in the sodium analog  $\text{MgNa}(\text{PO}_4) \cdot 7\text{H}_2\text{O}$ , where all four faces of a  $\text{PO}_4^{3-}$  tetrahedron are shared, each with a different

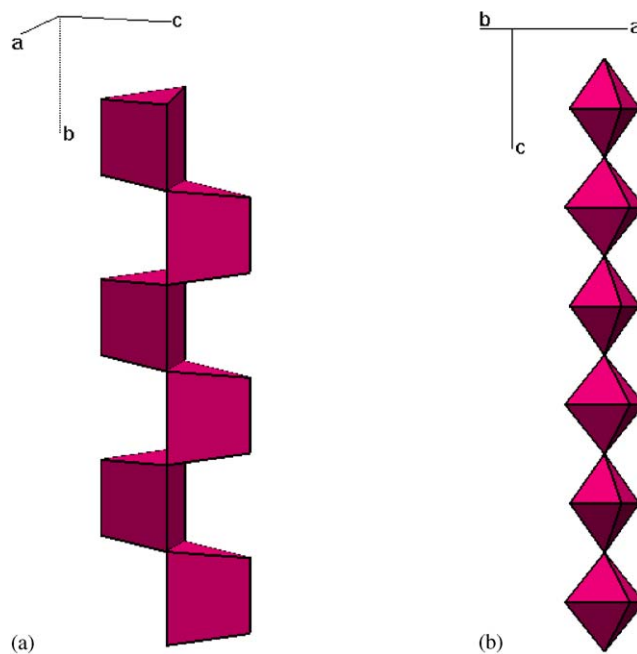


Fig. 4. Comparison of the configuration and linkage of Na polyhedra in (a)  $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$  and (b)  $\text{MgNa}(\text{PO}_4) \cdot 7\text{H}_2\text{O}$ .

$\text{Mg}(\text{H}_2\text{O})_6$  octahedron through hydrogen bonds, and each  $\text{Mg}(\text{H}_2\text{O})_6$  octahedron has four faces shared with different tetrahedra.

All H atoms of water molecules in  $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$  are engaged in hydrogen bonds of various strengths. The O–H...O contacts range from 2.615 to 2.899 Å, corresponding to medium–strong hydrogen bonds. Of the only two Ow–Ow contacts in the structure, Ow1–Ow3 at a distance of 2.784 Å is far shorter, and thus stronger than Ow2–Ow8 (3.214 Å). The latter, in fact, corresponds to insignificant hydrogen bonding from the cut-off value obtained from the histogram by Ferraris and Franchini-Angela [12]. A similar situation has been observed in struvite. This result suggests that the location of H81 has more to do with minimizing cation–proton repulsion than with maximizing the hydrogen bonding.

The infrared spectrum of  $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$  is shown in Fig. 5. For the purpose of comparison, spectrum assignments for both  $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$  and  $\text{MgK}(\text{PO}_4) \cdot 6\text{H}_2\text{O}$  [7] are listed in Table 6. Major features of the two spectra are remarkably similar, due to the fact that they primarily reflect the bonding environments of  $\text{Mg}(\text{H}_2\text{O})_6$  and  $\text{PO}_4^{3-}$ , a common feature shared by the two compounds. The relative shifts in the positions of some modes between two spectra are attributable to differences in the interaction between the univalent ions and the  $\text{PO}_4^{3-}$  groups. According to Banks et al. [7], the splitting of the  $\nu_3$  anti-symmetric stretching bands, which occurs near

$1000\text{ cm}^{-1}$ , is a quantitative measure of the deviation of the  $\text{PO}_4^{3-}$  group from ideal tetrahedral symmetry. This band is triply degenerate if the  $\text{PO}_4^{3-}$  tetrahedron is perfect and the degeneracy will lift if the tetrahedron is distorted. Our data appear to support this statement. A severe distortion of the  $\text{PO}_4^{3-}$  tetrahedron will cause the infrared-inactive  $\nu_1$  symmetric stretch to appear weakly at  $\sim 990\text{ cm}^{-1}$ , as observed for the struvite analog  $\text{MgRb}(\text{PO}_4) \cdot 6\text{H}_2\text{O}$  [7].

In struvite analogs  $\text{Mg}M^+(\text{PO}_4) \cdot 6\text{H}_2\text{O}$ , where  $M^+ = \text{K}^+$  or  $\text{NH}_4^+$ , the structure assumes the orthorhombic symmetry with the space group  $Pmn2_1$  [1,5]. The  $\text{Rb}^+$  and  $\text{Tl}^+$  analogs are also orthorhombic and probably isostructural with struvite, whereas the  $\text{Cs}^+$  analog exists in hexagonal and cubic forms [7]. Thus, it appears that higher-symmetry structures are preferred as the size of the univalent cation increases in the struvite

analog. Nonetheless, Mathew et al. [2] reported a tetragonal symmetry ( $P4_2/mmc$ ) for  $\text{MgNa}(\text{PO}_4) \cdot 7\text{H}_2\text{O}$ . One explanation for this is that the smaller ionic size of  $\text{Na}^+$  in  $\text{MgNa}(\text{PO}_4) \cdot 7\text{H}_2\text{O}$  is effectively compensated by the  $\text{Na}^+ - \text{H}_2\text{O}$  pair. Mathew et al. [2] speculated that  $\text{MgNa}(\text{PO}_4) \cdot 7\text{H}_2\text{O}$  may be less stable than other struvite-type compounds containing larger univalent cations, due to the possible strain stemming from the extensive face sharing between  $\text{PO}_4$  tetrahedra and  $\text{Mg}(\text{H}_2\text{O})_6$  octahedra in the structure. They further suggested that this could be the reason “why the  $\text{Na}^+$  ions do not enter into the crystal lattice in the presence of larger cations”. Apparently, the finding of the  $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$  structure invalidates this hypothesis.

Struvite minerals are known to form inside living bacteria, as a diagenetic byproduct of bird feces, in kidney stones, or in association with decaying organisms. One common feature shared by these environments is high alkalinity, suggesting that high pH conditions are required for the formation of struvite-type phosphate minerals. However, our growth medium is not particularly rich in inorganic phosphate. This raises an intriguing question regarding the source of phosphate, given the high phosphate content in  $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$ . Conceivably, phosphate metabolism or phosphate-containing organic compounds could be a good source of inorganic phosphate. In the cytoplasm of a living bacterium, much of phosphate in a cell occurs in the form of phospholipids in the membranes. Presumably, following the cell death, the slow breakdown of phosphorus-containing organic compounds would become the steady supply for phosphate. In addition, the cell membranes may be energetically favored for nucleation of crystals. While these conditions could be simulated in the laboratory, they may be most handily achieved with the existence of organisms, living or dead in natural environments.

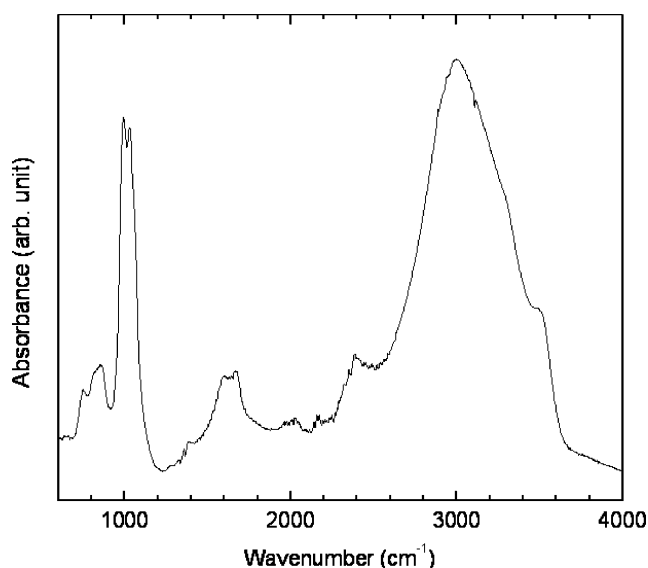


Fig. 5. Infrared spectrum of  $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$ .

Table 6  
Infrared spectra of the struvite analogs ( $\text{cm}^{-1}$ )

$\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$	$\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$	Intensity	Assignment
3700–2500	3700–2500	Strong, broad	Water $\nu_1 - \nu_3$ sym- and antisymmetric stretching
3450	3500	Shoulder	
2950	3000		
2350	2380	Weak	Water–phosphate hydrogen bonding
1630	1630	Weak, broad	Water bending
1070		Shoulder	
1040	1040	Strong, sharp	$\nu_3$ ( $\text{PO}_4$ ) P–O antisymmetric stretching
1015	990	Strong, sharp	
900	860	Weak	
	820		
730	750	Weak	Water–water H bonding

Note: Data for  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  were taken from Banks et al. (1975).

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