

A New Struvite-Type Compound, Magnesium Sodium Phosphate Heptahydrate

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(Received 20 October 1980; accepted 28 May 1981)

Abstract

The crystal structure of $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$, a new struvite analog, has been determined by single-crystal X-ray diffraction study. The crystals are tetragonal with $a = 6.731$ (2), $c = 10.982$ (4) Å, space group $P4_2/mmc$, $Z = 2$, $V = 497.5$ Å³, $d_m = 1.77$, $d_c = 1.791$ Mg m⁻³. The structure was refined by full-matrix least-squares techniques to $R = 0.038$ and $R_w = 0.056$ for 418 reflections with $F_o > 3\sigma(F_o)$. All cations and anions are completely surrounded by water molecules. The environment of the PO_4^{3-} ion consists of 12 water molecules, all of which are hydrogen bonded to PO_4 oxygens, thus providing a model of a completely hydrated PO_4^{3-} ion in the crystalline state. The most interesting feature of the structure is the novel type of face-sharing linkage of $\text{Mg}(\text{H}_2\text{O})_6$ octahedra and PO_4 tetrahedra. All four faces of the PO_4^{3-} ion are linked to faces of four different $\text{Mg}(\text{H}_2\text{O})_6$ octahedra *via* hydrogen bonds, and each $\text{Mg}(\text{H}_2\text{O})_6$ octahedron is linked to four PO_4 faces. The linkage of $\text{Mg}(\text{H}_2\text{O})_6$ and PO_4 (along **a** and **b**) forms a cross-linked layer-type structure, leaving a relatively open channel along **c**, which is occupied by a column of alternating Na^+ ions and water molecules. Relationships with other struvite-type compounds are discussed.

Introduction

$\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ exists as the biomineral struvite. A large number of struvite-type compounds and their structural relationships have been reported by Dickens & Brown (1972). Their biological importance is dependent, in part, on their possible roles as precursors or nuclei of crystallization. Struvite-type compounds have been represented by the general formula $M^{2+}N^+XO_4 \cdot n\text{H}_2\text{O}$ where $n = 6-8$, $X = \text{P}$ or As and the ionic radius of the monovalent cation N^+ is larger than that of M^{2+} . Struvite analogs of the type $\text{Mg}N\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ($N = \text{K}, \text{Rb}, \text{Cs}, \text{Tl}$ and NH_4) have been studied by Banks, Chianelli & Korenstein (1975). Although Na^+ ions were present in most of the solutions used in these preparations, the corresponding

sodium analog was not identified as a product; it was suggested, therefore, that the struvite structure cannot accommodate univalent ions smaller than K^+ . We have, however, isolated single crystals of a sodium analog, $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$, and the crystal structure was investigated with the objective of relating it to other struvite-type compounds.

Experimental

Crystals of $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$ were obtained from a batch initially set up for the preparation of $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. Following the procedure of Kanazawa, Umegaki & Wasai (1976), crystals of $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ were allowed to stand in water and the pH was adjusted to 9.0 by the addition of Na_2CO_3 . After several weeks a sample of crystals was examined and from refractive indices appeared to be still $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$, although traces of a new phase were present. It was approximately two years later that we re-examined the sample. Large, well defined, elongated, octahedral crystals were obtained. An X-ray powder pattern showed these crystals to be different from $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ or $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$.

Preliminary precession photographs showed tetragonal symmetry, $4/mmm$. Systematic absences of hhl for $l = 2n + 1$ indicated three possible space groups, $P4_2mc$ (No. 105), $P4_2c$ (No. 112) and $P4_2/mmc$ (No. 131). The centrosymmetric space group $P4_2/mmc$, initially chosen, was confirmed by the structure analysis and refinements.

An approximately equant octahedral crystal with a mean diagonal dimension of 0.25 mm was used for the measurement of cell constants and intensity data. All measurements were made on an automatic diffractometer with graphite-monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.7093$ Å). The diffractometer-controlling programs were those of Lenhart (1975). The cell parameters were obtained by a least-squares fit of the setting angles of 15 reflections with $35 < 2\theta < 45^\circ$ by automatically centering at both positive and negative 2θ values. Crystal data are in the *Abstract*.

All reflections in the octant hkl with $2\theta < 60^\circ$ were measured using the θ - 2θ scan technique. The scan rate was $0.5^\circ \text{ min}^{-1}$ and the backgrounds were counted for 40 s at each end of the scan range. Three reference reflections, monitored periodically during the data collection, did not show significant variation in intensities during the data collection. The intensities were corrected for Lorentz and polarization effects and for absorption [$\mu(\text{Mo K}\alpha) = 0.41 \text{ mm}^{-1}$] using the program system XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Equivalent reflections were merged into a set of 448 independent reflections, of which 418 with $F_o \geq 3\sigma(F_o)$ were used in the structure analysis and refinements.

Solution and refinement

In the space group initially chosen, $P4_2/mmc$, all nonhydrogen atoms must be in special positions. The positions of P, Mg and Na atoms were deduced from a three-dimensional Patterson synthesis. A Fourier synthesis based on these three atoms clearly indicated the positions of the remaining nonhydrogen atoms. It was immediately obvious that O(w3) in special position $2(f)$ (site symmetry $42m$) is disordered. However, refinements indicated disorder of two more atoms, Na in special position $2(b)$ (site symmetry mmm) and O(w2) at $4(i)$ (site symmetry mm). Disorder of O(w3) was very pronounced.

Because of the disorder of Na, O(w2) and O(w3), attempts were made to refine the structure in the other two possible space groups, $P4_2c$ and $P4_2mc$. In each space group, the PO_4^{3-} ion and O(w3) molecule are at similar symmetry sites, $42m$, 4 and mm in space groups $P4_2/mmc$, $P4_2c$ and $P4_2mc$ respectively. An ordered model of Na and O(w3) is possible only in the space group $P4_2mc$. However, refinements in this space group indicated disorder of Na and O(w3) to be similar to those in space group $P4_2/mmc$. There were strong correlation coefficients between the two sets of nonequivalent O atoms of the PO_4 group and the two nonequivalent O(w2) molecules. In addition, the general positions in the space group $P4_2/mmc$ are related to those of $P4_2mc$ by the addition of a center of symmetry. The space group $P4_2mc$ was thus eliminated as a possibility.

Refinements in the space groups $P4_2/mmc$ and $P4_2c$ were carried out independently using identical conditions. In each case the PO_4 group, Mg and O(w1) had normal thermal parameters, but Na, O(w2) and O(w3) exhibited large thermal parameters indicating disorder. The magnitudes of disorder were also quite similar in the two space groups. Difference Fourier syntheses clearly indicated the positions of H atoms on O(w1) and O(w2). Their positions were also refined with fixed isotropic thermal parameters ($B = 2.5 \text{ \AA}^2$) in subsequent calculations. Attempts were made to refine a

Table 1. Final refinement parameters for $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$

Number of reflections in refinement. m : 418 ($F_o > 3\sigma(F_o)$)
Number of variables. n : 33
$R = \frac{\sum F_o - F_c }{\sum F_o }$: 0.038 (0.041 for all 448 reflections)
$R_w = \frac{(\sum w F_o - F_c ^2 / \sum w F_o ^2)^{1/2}}$: 0.056 (0.057 for all 448 reflections)
$S = \frac{ \sum w F_o - F_c ^2 / (m - n)^{1/2}}$: 2.05
Extinction parameter: $0.29 (8) \times 10^{-4} \text{ mm}$

Table 2. Final atomic parameters for $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$

Estimated standard deviations are in parentheses. Values without estimates of standard deviations are fixed by symmetry.

	x	y	z	$B_{\text{eq}} (\text{\AA}^2)^*$
P	0	0	$\frac{1}{4}$	1.19 (3)
Mg	0	$\frac{1}{2}$	0	1.41 (6)
Na	$\frac{1}{2}$	$\frac{1}{2}$	0	4.11 (12)
O	0	0.1871 (2)	0.3293 (1)	1.63 (6)
O(w1)	0.2223 (2)	0.2801 (2)	0	1.70 (6)
O(w2)	0	$\frac{1}{2}$	0.1868 (2)	3.06 (11)
O(w3)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$	10.1 (4)
H(1)	0.220 (3)	0.204 (3)	0.081 (1)	
H(2)	0	0.405 (4)	0.240 (3)	

* As defined by Hamilton (1959).

statistically disordered model in both space groups, but the disorder was not large enough to permit resolution of their positional parameters. In general, refinements in these two space groups gave nearly identical results. The refinements were not significantly different according to Hamilton's (1965) R -factor ratio test. Therefore, the centrosymmetric space group, $P4_2/mmc$, was chosen. The results of the refinements are summarized in Table 1. Final atomic parameters are listed in Table 2.*

All refinements used the full-matrix least-squares program *RFINE4* (Finger & Prince, 1975). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(F_o) + (0.02F_o)^2$. Correction for anomalous dispersion was included. The values of f' and f'' and the scattering factors (neutral atoms) were taken from *International Tables for X-ray Crystallography* (1974). An isotropic secondary-extinction correction (Zachariasen, 1967) was applied and the parameter was refined.

Results and discussion

The structure differs from that of the typical struvite, $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (Whitaker & Jeffery, 1970), in

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36129 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

that all three ions in $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$ are completely surrounded by water molecules. The structure consists of $\text{Mg}(\text{H}_2\text{O})_6$ octahedra, hydrogen bonded to PO_4 tetrahedra with the interstitial space filled by a column of Na^+ ions and water molecules (Figs. 1 and 2).

The environment of Mg^{2+} , which is located at the intersection of three mirror planes, consists of six water molecules forming an almost ideal octahedron (Table 3). The two crystallographically non-equivalent $\text{Mg}-\text{O}(w)$ distances [$\text{Mg}-\text{O}(w1) = 2.105$, and $\text{Mg}-\text{O}(w2) = 2.051 \text{ \AA}$] agree well with those found in other hydrates (Schroeder, Mathew & Brown, 1978). The longer $\text{Mg}-\text{O}(w1)$ distance involves a water molecule sharing an edge with the Na^+ ion; thus the $\text{O}(w1) \cdots \text{Mg}$ contact is along a lone-pair orbital. The $\text{O}(w2) \cdots \text{Mg}$ contact, on the other hand, is along the bisector of the lone-pair orbitals.

The Na^+ ion is statistically disordered, in two positions separated by about 0.5 \AA , as indicated by the apparent r.m.s. amplitude of vibration. Since there is a 1:1 ratio of Na^+ ions and $\text{O}(w3)$ molecules in the

column, the average coordination of Na^+ is 5. The geometry of the Na^+ ion coordination may be described as square pyramidal or tetragonal pyramidal. A pair of edges are shared by two $\text{Mg}(\text{H}_2\text{O})_6$ octahedra, and the linkage is extended alternately along the a and b axes.

The PO_4 group is at a symmetry site $42m$ and therefore all $\text{P}-\text{O}$ distances are the same. $\text{P}-\text{O} = 1.531 \text{ \AA}$ is in good agreement with the mean value of 1.536 \AA calculated for orthophosphate groups (Baur, 1974). The $\text{O}-\text{P}-\text{O}$ angles (Table 3) show only slight variations from ideal tetrahedral angles.

The environment of the PO_4^{3-} ion consists of 12 water molecules, arranged at the vertices of a distorted cuboctahedron. Each O atom of the phosphate is the acceptor in three hydrogen bonds; $\text{O}(w) \cdots \text{O}$ distances are 2.624 and 2.669 \AA (Table 3) and are indicative of fairly strong hydrogen bonds. Similar hydration of the PO_4^{3-} ion through hydrogen bonding has been observed in $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ (Schroeder *et al.*, 1978).

$\text{O}(w1)$ is coordinated to Mg and Na, and both H atoms are involved in hydrogen bonds to phosphate O atoms. The remaining water molecules, $\text{O}(w2)$ and $\text{O}(w3)$, have large thermal parameters indicating some disorder. $\text{O}(w2)$ is coordinated to Mg and hydrogen bonded to two phosphate O atoms; all three bonds are strong, but disordering in two slightly different positions is possible in a direction perpendicular to these bonds. It would appear that the disorder of $\text{O}(w3)$ may be associated with the disorder of Na along the column. However, if this were the main cause, the amplitude of vibration of $\text{O}(w3)$ should be similar to that of Na. But the indicated disorder of $\text{O}(w3)$ is more complex. $\text{O}(w3)$ is located in a relatively large cavity (Fig. 1). The shortest intermolecular contact (except Na) is 3.44 \AA with the four $\text{O}(w2)$, indicating no significant hydrogen bonding. However, the disordering of $\text{O}(w2)$ is approximately in the direction of $\text{O}(w3)$, suggesting a shorter $\text{O}(w2) \cdots \text{O}(w3)$ separation and possible hydrogen bonding.

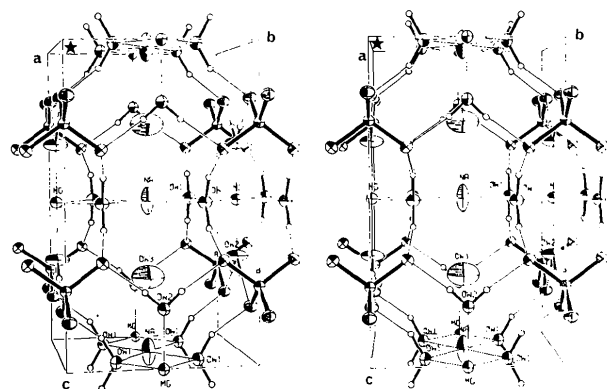


Fig. 1. A stereoscopic illustration of the unit cell of $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$. The origin is marked by a star.

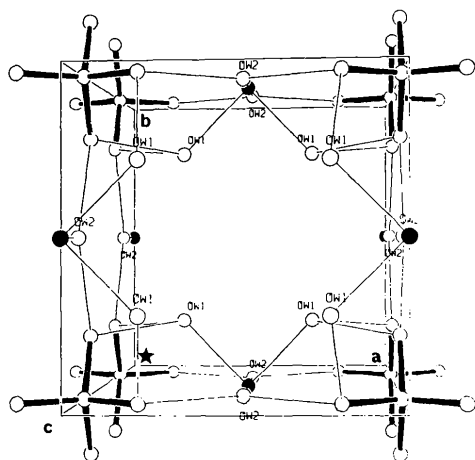


Fig. 2. The arrangement of $\text{Mg}(\text{H}_2\text{O})_6$ octahedra and PO_4 tetrahedra showing the cross-linked layer-type structure and the open channel along c . The black circles represent Mg atoms.

Table 3. Bond distances (\AA) and angles ($^\circ$) in $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$

$\text{Mg}-\text{O}(w1)$	$4 \times 2.105 (1)$	$\text{O}(w1)-\text{Mg}-\text{O}(w1)$	$89.38 (4)$
$\text{Mg}-\text{O}(w2)$	$2 \times 2.051 (2)$	$\text{O}(w1)-\text{Mg}-\text{O}(w1)$	$90.62 (4)$
		$\text{O}(w1)-\text{Mg}-\text{O}(w2)$	90.00
$\text{Na}-\text{O}(w1)$	$4 \times 2.384 (1)$	$\text{O}(w1)-\text{Na}-\text{O}(w1)$	$76.75 (4)$
$\text{Na}-\text{O}(w3)$	2×2.746	$\text{O}(w1)-\text{Na}-\text{O}(w1)$	$103.25 (4)$
		$\text{O}(w1)-\text{Na}-\text{O}(w3)$	90.0
$\text{P}-\text{O}$	$4 \times 1.531 (1)$	$\text{O}-\text{P}-\text{O}$	$108.88 (5)$
		$\text{O}-\text{P}-\text{O}$	$110.67 (5)$

Hydrogen bonds

	$\text{O}-\text{H}$	$\text{H} \cdots \text{O}$	$\text{O} \cdots \text{O}$	$\angle \text{O}-\text{H} \cdots \text{O}$
$\text{O}(w1) \cdots \text{O}[y, x, \frac{1}{2} - z]$	$1.03 (1)$	$1.70 (2)$	$2.669 (2)$	$155 (2)$
$\text{O}(w2) \cdots \text{O}[x, y, z]$	$0.87 (3)$	$1.76 (3)$	$2.624 (2)$	$171 (2)$

The most unusual feature of the structure is the extent of the face-sharing linkage between PO_4 tetrahedra and $\text{Mg}(\text{H}_2\text{O})_6$ octahedra. All four faces of the PO_4^{3-} ion are linked to faces of four different $\text{Mg}(\text{H}_2\text{O})_6$ octahedra *via* hydrogen bonds, and each $\text{Mg}(\text{H}_2\text{O})_6$ octahedron is linked to four PO_4 faces (Fig. 3). Face linkage of PO_4 tetrahedra and $\text{Mg}(\text{H}_2\text{O})_6$ octahedra occurs in other hydrates, but not as extensively as in the present structure. In $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$, three of the four PO_4 faces are linked to the faces of three $\text{Mg}(\text{H}_2\text{O})_6$ octahedra in a pseudo-trigonal arrangement (Schroeder *et al.*, 1978). In the struvites $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (Whitaker & Jeffery, 1970) and $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (Mathew & Schroeder, 1979), two of the faces of the PO_4 tetrahedron (related by a mirror) are linked to two $\text{Mg}(\text{H}_2\text{O})_6$ octahedra forming a zigzag chain along the *a* axis (6.87 Å). Additional mirror planes in $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$ repeat this pattern along the *a* and *b* axes (6.73 Å). Another result of this arrangement is that four PO_4 groups are linked together by six water molecules forming a closed cage-like arrangement with the Mg^{2+} ion at the center (Fig. 1).

The linkage of the PO_4 tetrahedra and the $\text{Mg}(\text{H}_2\text{O})_6$ octahedra acts as a cross-linked layer-type structure (along *a* and *b*), leaving a relatively large open channel at the center of the cell along *c* (Fig. 2). This open channel is occupied by a column of Na^+ ions and $\text{O}(\text{w}3)$ water molecules. Since all atoms surrounding this column are fixed by the compact assembly of PO_4 tetrahedra and $\text{Mg}(\text{H}_2\text{O})_6$ octahedra, the arrangement mimics those of a macrocyclic polyether 'crown' compound. The effective radius of this column is controlled by the $\text{O}(\text{w}1) \cdots \text{O}(\text{w}1)$ separation, which can ideally fit the Na^+ ion [ionic radii of $\text{Na}^+ = 0.99$ and $\text{O}^{2-} = 1.40$ Å (Shannon & Prewitt, 1969)]. If any cation larger than Na^+ were to be accommodated, it would be further away from the plane of water

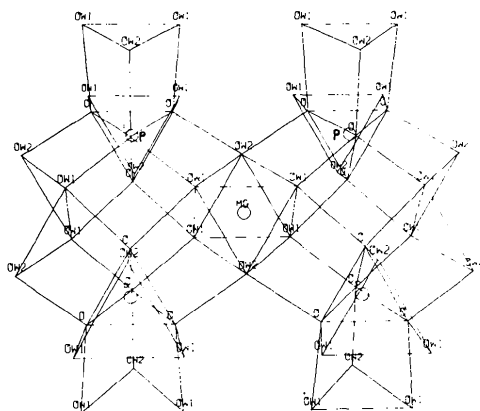


Fig. 3. The packing of $\text{Mg}(\text{H}_2\text{O})_6$ octahedra and PO_4 tetrahedra *via* face sharing within a layer. All face sharing linkages are of the type $\text{O}(\text{w})-\text{H} \cdots \text{O}$ hydrogen bonding. H atoms are omitted for clarity.

molecules $\text{O}(\text{w}1)$ and thus would not leave enough room along the column for the additional water molecule. This may be the reason why a corresponding potassium analog, $\text{MgKPO}_4 \cdot 7\text{H}_2\text{O}$, is not formed.

Struvite analogs containing Mg^{2+} can incorporate a wide range of univalent ions differing in size. $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ are isostructural (orthorhombic) and substitution of NH_4^+ by the smaller K^+ produces only minor structural changes (Mathew & Schroeder, 1979). Rb^+ and Tl^+ analogs are also orthorhombic and probably isostructural (Banks *et al.*, 1975). With the increasing size of the univalent ion, higher-symmetry forms are preferred (Banks *et al.*, 1975). For example, $\text{MgCsPO}_4 \cdot 6\text{H}_2\text{O}$ exists in hexagonal and cubic forms. This study has shown that smaller Na^+ ions also produce high-symmetry forms. The smaller ionic size of Na^+ in $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$ is effectively compensated by the $\text{Na}^+-\text{H}_2\text{O}$ pair in the column. However, due to the extensive face sharing of PO_4 tetrahedra and $\text{Mg}(\text{H}_2\text{O})_6$ octahedra in $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$, considerable strain is to be expected and therefore it may be less stable than those involving larger univalent ions. This would explain why the Na^+ ions do not enter into the crystal lattice in the presence of larger cations. A common feature of all these structures is that Mg^{2+} is surrounded by an octahedron of water molecules which are strongly hydrogen bonded to PO_4 oxygens. Thus $[\text{Mg}(\text{H}_2\text{O})_6\text{PO}_4]$ behaves as a host lattice. The wide range of symmetries observed in these compounds is a clear indication of the different types of linkages between $\text{Mg}(\text{H}_2\text{O})_6$ octahedra and PO_4 tetrahedra.

Structural relationships between several struvite-type compounds have been described by Dickens & Brown (1972) and in the following paper (Takagi, Mathew & Brown, 1982). The structure of $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ is related to $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$, but the structures differ considerably in detail (Dickens & Brown, 1972). The present compound, $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$, is intermediate in the degree of hydration and accordingly has some characteristics of both. A face-sharing linkage of PO_4 tetrahedra and $\text{Mg}(\text{H}_2\text{O})_6$ octahedra is a common feature of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$. However, the AsO_4 tetrahedra in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ are not involved in any face sharing with cation polyhedra. On the other hand, in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ and $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$ all ions are completely surrounded by water molecules, whereas in $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ there is a direct contact of one phosphate O and a K^+ ion. Cell dimensions of $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ (orthorhombic, $a = 7.146$, $b = 7.100$ and $c = 11.696$ Å, rearranging the axes) resemble a tetragonal system and the atomic arrangements clearly indicate a pseudo fourfold axis along *c*. These similarities may be related to the fact that the radius ratios of the cations are the same in these two compounds, $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ and $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$

(Ca/K = 0.72, Mg/Na = 0.72). This ratio, 0.72, appears to be the optimum value for the higher hydration numbers since the substitution of the K⁺ ion in CaKAsO₄·8H₂O by the slightly larger NH₄⁺ ion (radius 1.48 Å, ratio Ca/NH₄ = 0.68) results in a lower hydrate, Ca(NH₄)AsO₄·7H₂O, which is unstable (Lehr, Brown, Frazier, Smith & Thrasher, 1967).

The figures were drawn with a local version of the ORTEP program (Johnson, 1965). This investigation was supported by Research Grant DE 05030-2 to the American Dental Association Health Foundation Research Unit by the National Institute for Dental Research and is part of the Dental Research Program conducted by the National Bureau of Standards in cooperation with the American Dental Association Health Foundation.

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Water-Rich Hydrates. The Structures of Dimagnesium Potassium Hydrogenbis(arsenate) 15-Hydrate and Dimagnesium Potassium Hydrogenbis(phosphate) 15-Hydrate

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(Received 20 October 1980; accepted 28 May 1981)

Abstract

The crystal structures of two isomorphous salts of the type Mg₂KH(XO₄)₂·15H₂O, where X = As (I) and X = P (II), have been determined by single-crystal X-ray diffraction. The crystals are triclinic, space group P $\bar{1}$, with cell dimensions $a = 6.390$ (2), $b = 12.477$ (3), $c = 6.659$ (2) Å, $\alpha = 93.54$ (2), $\beta = 88.71$ (2) and $\gamma = 94.51$ (2)° for (I) and $a = 6.288$ (1), $b = 12.228$ (1), $c = 6.554$ (1) Å, $\alpha = 93.64$ (1), $\beta = 89.18$ (1) and $\gamma = 94.69$ (1)° for (II). The structures were refined by full-matrix least-squares techniques to $R = 0.079$ and 0.035 using 964 and 2633 non-zero

reflections for (I) and (II) respectively. The two crystallographically independent Mg²⁺ ions are coordinated to six water molecules. The acidic H atom appears to be involved in a symmetrical hydrogen bond forming a dimeric [H(XO₄)₂] unit. The [H(XO₄)₂] unit is completely surrounded by water molecules. Each O atom of XO₄ is involved in three hydrogen bonds. The structure can be described in terms of interpenetrating layers with two open channels. These channels are randomly occupied by a K⁺ ion and a water molecule. Relationships with other struvite-type compounds are discussed.