

(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).

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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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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 $\gamma = 94.51(2)^\circ$ 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 $\gamma = 94.69(1)^\circ$ 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.

Introduction

Struvite-type structures [named after the biomineral struvite, $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (Whitaker & Jeffery, 1970)] comprise an important class of phosphate salts (Dickens & Brown, 1972). They have been represented by the general formula $M^{2+}N^+XO_4 \cdot n\text{H}_2\text{O}$ where $n = 6-8$, $X = \text{As}$ or P and the ionic radius of the monovalent cation N^+ is larger than that of M^{2+} . Although $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$ have been listed as struvite-type compounds on the basis of composition and cell dimensions, no detailed structural studies exist. As part of a study of the structural characteristics of highly hydrated compounds we have determined the crystal structures of $\text{Mg}_2\text{KH}(\text{AsO}_4)_2 \cdot 15\text{H}_2\text{O}$ (I) and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ (II).

Experimental

Samples were prepared by a slight modification of the reported procedure (Lehr, Brown, Frazier, Smith & Thrasher, 1967). Equimolar (0.15 M) solutions of K_2HAsO_4 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ were mixed at 278 K and the pH was adjusted to 7.0 by the addition of KOH. Well defined, but very thin, platy crystals of $\text{Mg}_2\text{KH}(\text{AsO}_4)_2 \cdot 15\text{H}_2\text{O}$ (I) were obtained in a few days.

Several attempts were made to prepare $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, using different combinations of magnesium salts, concentrations (0.05–0.20 M), temperature (278–298 K) and pH (6.5–7.5). In all cases, crystals of $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ were obtained within 24 h. Most of the mixtures were subsequently discarded without realizing that $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ would be an intermediate phase. However, one mixture containing equimolar solutions (0.05 M) of $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (pH = 7.0) was left at room temperature for several weeks. Well defined, large tabular crystals of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ (II) were obtained. The X-ray powder pattern and refractive indices agree with the reported values (Lehr *et al.*, 1967).

Preliminary precession photographs confirmed the triclinic symmetry. The lattice parameters were obtained by a least-squares fit of the setting angles of 15 reflections by automatically centering at both positive and negative 2θ values. All data were measured

Table 1. Additional crystal data for $\text{Mg}_2\text{KH}(\text{AsO}_4)_2 \cdot 15\text{H}_2\text{O}$ (I) and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ (II)

	(I)	(II)
2θ range ($^\circ$)	27–35	43–52
λ (\AA)	0.7107	0.7093
V (\AA^3)	528.2	501.2
Formula weight	634.79	548.91
Z	1	1
ρ_{calc} (Mg m^{-3})	1.995	1.818
ρ_{obs} (Mg m^{-3})		1.81

Table 2. Experimental conditions and refinement parameters for $\text{Mg}_2\text{KH}(\text{AsO}_4)_2 \cdot 15\text{H}_2\text{O}$ (I) and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ (II)

	(I)	(II)
Crystal size (mm)	$0.01 \times 0.08 \times 0.09$	$0.13 \times 0.18 \times 0.28$
$2\theta_{\text{max}}$ ($^\circ$)	45	60
Scan rate ($^\circ \text{min}^{-1}$)	0.25	0.5
Background time (s)	40	40
Unique set	1377	2935
Observed ^(a)	964	2633
μ (linear absorption coefficient, mm^{-1})	3.498	0.573
Maximum absorption correction to F_o^2	1.242	1.127
Minimum absorption correction to F_o^2	1.015	1.067
Refinement ^(b)		
$R = \sum F_o - F_c / \sum F_o $	0.079 (0.121) ^(c)	0.035 (0.039) ^(c)
$R_w = (\sum w F_o - F_c ^2 / \sum w F_o ^2)^{1/2}$	0.066 (0.070) ^(c)	0.041 (0.041) ^(c)
w^{-1}	$\sigma^2(F_o) + (0.02 F_o)^2$	$\sigma^2(F_o) + (0.01 F_o)^2$
Number of variables	131	183
Goodness of fit	1.33	2.66
Average shift/error	0.01 ^(d)	0.05 ^(d)
Extinction parameter (mm)	$1.2 (3) \times 10^{-3}$	$0.27 (4) \times 10^{-3}$

(a) Only reflections with $F_o > 3\sigma(F_o)$ were used in the refinement.

(b) Values from the final cycle.

(c) Values in parentheses are the values for all reflections.

(d) Parameters of H were also refined in (II), whereas they were kept constant in (I).

on a four-circle diffractometer with graphite-monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.7093 \text{ \AA}$) using the $\theta-2\theta$ scan technique. The diffractometer-controlling programs were those of Lenhart (1975). The intensities were corrected for Lorentz, polarization and absorption effects (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Additional crystal data are in Table 1. Details of the data collection are given in Table 2.

Solution and refinement of the structures

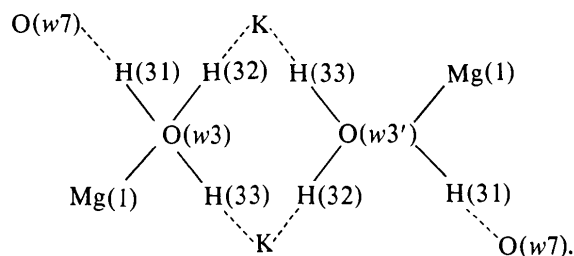
There is only one formula unit, $\text{Mg}_2\text{KH}(\text{XO}_4)_2 \cdot 15\text{H}_2\text{O}$, per unit cell. The space group was therefore assumed to be $P1$ since this does not impose any symmetry.

The structure of the arsenate analog (I) was first solved from a three-dimensional Patterson synthesis. An electron density map calculated on the basis of two As positions clearly indicated the positions of O atoms of AsO_4 and $\text{Mg}(\text{H}_2\text{O})_6$ octahedra. There were three additional peaks, approximately of the same electron density, for the three remaining atoms, K^+ and two water molecules. Therefore, the position of K^+ could not be assigned unambiguously. Subsequent Fourier syntheses or difference syntheses provided no additional clues. However, from the geometry of possible hydrogen bonding to AsO_4 , one of these three positions could be assigned to one water molecule, $\text{O}(w7)$. The remaining two positions were assigned to K^+ ions, with half occupancy, thus assuming the formula to be only $\text{Mg}_2\text{KH}(\text{AsO}_4)_2 \cdot 14\text{H}_2\text{O}$. With this model, the structure was refined to $R = 0.10$ using isotropic thermal parameters, but the correlation coefficients were very large. Closer examination of the structure revealed a center of inversion.

Transformation of the positional parameters to the centrosymmetric space group, $P\bar{1}$, indicated that the two disordered positions of the K^+ ion (in space group $P1$) were also related by a center of inversion. Refinements with anisotropic thermal parameters converged to $R = 0.088$ and $R_w = 0.082$. Most of the positive peaks in a difference Fourier synthesis were in positions that could reasonably be assigned to H atoms, the principal exception being peaks near the K^+ ion position. There were residual electron densities, approximately $2.0\text{--}2.5 \text{ e } \text{\AA}^{-3}$, around the positions of the K^+ ions and these peaks persisted even after the contributions of H were included in subsequent refinements. The apparent 'mystery' was not unraveled until a set of data on the phosphate analog was available.

When crystals of the phosphate analog (II) were obtained, a set of data was collected (Tables 1, 2). A Patterson synthesis indicated the isomorphous nature of (I) and (II). Therefore, starting values for positional parameters for (II) could have been taken from (I). However, to avoid any pitfalls which might have been overlooked in the case of (I), all parameters were obtained from reiterating Fourier syntheses. The results were nearly identical to (I) (*i.e.*, indicating statistically disordered K^+ ions and a formula with only 14 water molecules). Refinement of this model with anisotropic thermal parameters proceeded smoothly and converged to $R = 0.067$ and $R_w = 0.100$.

A difference Fourier synthesis clearly indicated the positions of all H atoms but, again, as in (I) there were residual electron densities ($1.5\text{--}1.8 \text{ e } \text{\AA}^{-3}$) around the K^+ ion positions. Another peculiarity was that the possible H atom positions on $\text{O}(w3)$ were directed towards the K^+ ion, according to the scheme:



This implied that the disordered K^+ ion position was also occupied by another atom capable of accepting a hydrogen bond. Since the X-ray powder pattern, cell parameters and refractive indices of our sample were in complete agreement with those reported, it appeared to be safe to assume the molecular formula to be $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ as originally reported (Lehr *et al.*, 1967). The measured density was also in better agreement with this formula. The hitherto undetected water molecule, $\text{O}(w8)$, was then assigned the same position as the K^+ ion (statistically disordered) and the

site is designated M . With this model, the refinements converged to $R = 0.035$ and $R_w = 0.041$. The final difference Fourier map was featureless. Final parameters are listed in Tables 3 and 4.*

Since an ordered model (Fig. 1*a* or *b*) is possible in space group $P1$, attempts were made to refine both structures in $P1$. However, in each case, the atom assumed to be a K^+ ion (fully occupied) had large thermal parameters ($B \approx 4.0 \text{ \AA}^2$) while that assumed to be $\text{O}(w8)$ had very low values ($B \approx 0.5 \text{ \AA}^2$). Moreover, correlation coefficients were large for the remaining atoms. Therefore, an ordered model in space group $P1$ was discarded.

* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36130 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Final positional ($\times 10^4$) and equivalent isotropic thermal parameters of the non-hydrogen atoms in $\text{Mg}_2\text{KH}(\text{AsO}_4)_2 \cdot 15\text{H}_2\text{O}$ (I) and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ (II)

The two entries for each atom, except As and P, correspond to values for (I) and (II), respectively.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}} (\text{\AA}^2)^\dagger$
Mg(1)	0	5000	5000	1.9 (4)
	0	5000	5000	1.43(3)
Mg(2)	5000	0	5000	1.8 (4)
	5000	0	5000	1.23 (3)
As	1195 (3)	1933 (1)	472 (3)	1.1 (1)
P	1144 (1)	1913 (3)	434 (1)	0.94 (1)
M^*	4741 (10)	3116 (5)	5724 (11)	4.3 (3)
	4668 (1)	3101 (1)	5598 (1)	3.36 (3)
O(1)	301 (15)	1828 (8)	2865 (14)	1.7 (5)
	322 (2)	1819 (1)	2635 (2)	1.50 (4)
O(2)	394 (14)	3053 (8)	-486 (14)	1.6 (5)
	383 (2)	2931 (1)	-470 (2)	1.52 (4)
O(3)	132 (15)	852 (8)	-926 (15)	2.0 (5)
	160 (2)	881 (1)	-883 (2)	1.37 (4)
O(4)	3820 (15)	1939 (8)	328 (16)	2.6 (5)
	3575 (2)	1933 (1)	331 (2)	1.71 (4)
O(<i>w</i> 1)	232 (24)	6579 (9)	4349 (17)	4.8 (7)
	336 (3)	6628 (1)	4391 (2)	2.77 (6)
O(<i>w</i> 2)	1596 (17)	4636 (9)	2304 (16)	2.7 (6)
	1593 (2)	4614 (1)	2289 (2)	2.25 (5)
O(<i>w</i> 3)	2900 (17)	5220 (10)	6375 (18)	3.6 (7)
	2949 (2)	5192 (1)	6448 (2)	2.51 (6)
O(<i>w</i> 4)	2211 (16)	713 (9)	5449 (16)	2.9 (6)
	2212 (2)	728 (1)	5360 (2)	2.41 (6)
O(<i>w</i> 5)	3901 (16)	-1246 (10)	6735 (16)	3.0 (6)
	3914 (2)	-1200 (1)	6902 (2)	2.69 (6)
O(<i>w</i> 6)	3819 (14)	-926 (9)	2523 (15)	2.8 (6)
	3835 (2)	-1014 (1)	2538 (2)	2.49 (6)
O(<i>w</i> 7)	3533 (15)	6297 (8)	53 (17)	2.5 (6)
	3520 (2)	6331 (1)	120 (2)	2.34 (5)

* M represents the site containing statistically disordered K and $\text{O}(w8)$. See text for details.

† Defined according to Hamilton (1959).

The arsenate analog (I) was then refined, with the correct formula $\text{Mg}_2\text{KH}(\text{AsO}_4)_2 \cdot 15\text{H}_2\text{O}$ and with a statistically disordered K/O(w8) model in space group $P\bar{1}$. The final difference Fourier map was now better and had very little residual electron density around the K/O(w8) position. Final parameters reported (Tables 2, 3, and 4) are for this model.

Table 4. Parameters of the hydrogen atoms

All positional parameters are multiplied by 10^3 . Parameters in (I) were not refined. Their contributions were calculated with a fixed isotropic thermal parameter ($B = 2.5 \text{ \AA}^2$). The two entries for each atom correspond to the values in (I) and (II), respectively.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)	O—H (\AA)
H(11)	0	675	292		1.00
	3 (4)	687 (2)	330 (5)	4.1 (6)	0.82 (3)
H(12)	0	725	485		0.90
	14 (4)	712 (2)	532 (4)	3.3 (5)	0.84 (3)
H(21)	167	395	125		1.08
	133 (4)	412 (2)	133 (4)	3.7 (6)	0.85 (3)
H(22)	235	533	179		1.03
	233 (4)	505 (2)	164 (4)	3.3 (5)	0.81 (3)
H(31)	354	575	750		1.04
	313 (6)	550 (3)	750 (6)	6.2 (9)	0.77 (4)
H(32)*	313	450	660		0.94
	333	456	646	2.5	0.83
H(33)*	345	560	537		0.89
	375	575	563	2.5	0.99
H(41)	188	75	688		0.97
	153 (4)	73 (2)	629 (4)	3.2 (6)	0.74 (3)
H(42)	192	137	458		1.06
	155 (4)	108 (2)	444 (4)	3.0 (5)	0.89 (3)
H(51)	458	-138	812		1.06
	465 (6)	-136 (3)	785 (5)	5.7 (8)	0.82 (3)
H(52)	250	-150	700		0.94
	256 (5)	-141 (2)	705 (4)	4.3 (6)	0.87 (3)
H(61)	218	-100	215		1.08
	269 (5)	-98 (2)	209 (4)	4.1 (6)	0.79 (3)
H(62)	500	-137	188		1.04
	475 (5)	-133 (2)	162 (4)	3.9 (6)	0.92 (3)
H(71)	221	663	42		0.99
	240 (4)	670 (2)	23 (4)	3.4 (5)	0.87 (3)
H(72)	478	682	-21		1.01
	451 (5)	676 (2)	-15 (4)	4.5 (7)	0.81 (3)
H(O3)	0	0	0		1.26
	0	0	0	3.0	1.25

* Parameters for these possibly disordered hydrogen atoms were not refined in both (I) and (II).

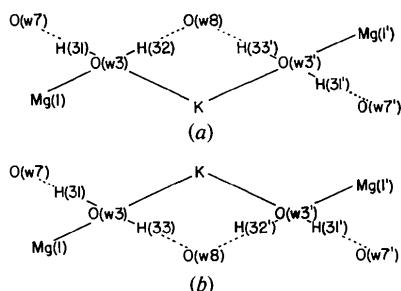


Fig. 1. Idealized view of the two possible ordered models in the noncentrosymmetric space group $P\bar{1}$.

All refinements were by the full-matrix least-squares program *RFINE4* (Finger & Prince, 1975). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where w was calculated as shown in Table 2. The scattering factors for neutral atoms and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). An isotropic secondary-extinction correction (Zachariasen, 1967) was applied.

Results and discussion

$\text{Mg}_2\text{KH}(\text{AsO}_4)_2 \cdot 15\text{H}_2\text{O}$ (I) and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ (II) are isostructural. The structure consists of $\text{Mg}(\text{H}_2\text{O})_6$ octahedra (for simplicity hereafter referred to as Mg octahedra), dimeric units of $[\text{H}(\text{XO}_4)_2]$ and a 'loose' water molecule, O(w7), all linked together by a three-dimensional network of hydrogen bonds (Fig. 2). The remaining water molecule, O(w8), and the K^+ ion are statistically disordered on the site designated *M* (Fig. 2).

A layer consisting of $[\text{H}(\text{XO}_4)_2]$ units and Mg(1) octahedra (layer A1) is interleaved with a layer containing Mg(2) octahedra, O(w7) and K/O(w8) (layer B1). These layers, A1 and B1, are approximately perpendicular to *a*. Another way of describing the structure is to consider a layer consisting of $[\text{H}(\text{XO}_4)_2]$ dimers and Mg(2) octahedra (layer A2) which alternates with a layer consisting of Mg(1) octahedra, O(w7) and K/O(w8) (layer B2). These layers A2 and B2 are approximately perpendicular to the layers A1 and B1. In either description, the layer containing $[\text{H}(\text{XO}_4)_2]$ dimers and Mg octahedra, A1 or A2, dominates the structure and these intersect along lines parallel to *c*. This arrangement of $[\text{H}(\text{XO}_4)_2]$ dimers and Mg octahedra produces two open channels (along *c*) which would allow free movement of O(w7), O(w8) and K^+ . However, a pair of O(w7) closes each channel at the top and bottom by linking $[\text{H}(\text{XO}_4)_2]$

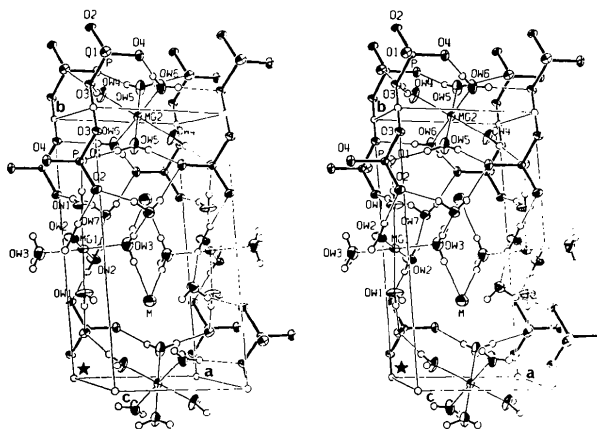


Fig. 2. A stereoscopic illustration of the unit cell of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$. The origin is labeled with a star.

units in adjacent A1 layers (Fig. 2). K/O(w8) is thus trapped in the relatively large cavity, allowing statistical disorder.

The two independent Mg^{2+} ions in (I) and (II) are at crystallographic centers of inversion. Each Mg^{2+} is coordinated to six water molecules forming a slightly distorted octahedron. Mg—O(w) distances in (II) vary from 2.035 to 2.085 Å (Table 5), with a mean value of 2.062 Å in good agreement with those in other hydrates (Mathew & Schroeder, 1979; Schroeder, Mathew & Brown, 1978; Whitaker, 1973). The 'right' angles for the $\text{Mg}(\text{H}_2\text{O})_6$ octahedra in (II) range from 87.6 to 92.4° (Table 5). The corresponding values of bond distances and angles in (I) are not significantly different, indicating that the substitution of PO_4^{3-} by the larger AsO_4^{3-} anion has not affected the Mg^{2+} coordination. All O(w)···Mg coordinations except O(w3) are along the bisectors of the lone-pair orbitals and therefore neither act as acceptors in hydrogen bonds nor are involved in any significant bonding to the K^+ ion.

Dimensions of the XO_4 groups are given in Table 5. The P—O(3) bond length of 1.571 Å is significantly longer than the remaining P—O bonds supporting the assignment of a covalently bonded H atom on O(3).

Table 5. Bond lengths (Å) and bond angles (°) in $\text{Mg}_2\text{KH}(\text{AsO}_4)_2 \cdot 15\text{H}_2\text{O}$ (I) and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ (II)

Estimated standard deviations are given in parentheses.

	(I)	(II)
Mg(1)—O(w1,w1')	2.04 (1)	2.048 (1)
Mg(1)—O(w2,w2')	2.09 (1)	2.074 (1)
Mg(1)—O(w3,w3')	2.08 (1)	2.085 (1)
Mg(2)—O(w4,w4')	2.06 (1)	2.035 (1)
Mg(2)—O(w5,w5')	2.06 (1)	2.054 (1)
Mg(2)—O(w6,w6')	2.08 (1)	2.076 (1)
P,As—O(1)	1.69 (1)	1.533 (1)
P,As—O(2)	1.69 (1)	1.527 (1)
P,As—O(3)	1.70 (1)	1.571 (1)
P,As—O(4)	1.68 (1)	1.527 (1)
O(w1)—Mg(1)—O(w2)	89.0 (5)	89.64 (6)
O(w1)—Mg(1)—O(w3)	89.9 (5)	89.28 (6)
O(w1)—Mg(1)—O(w2')	91.0 (5)	90.36 (6)
O(w1)—Mg(1)—O(w3')	90.1 (5)	90.72 (6)
O(w2)—Mg(1)—O(w3)	87.8 (4)	88.22 (5)
O(w2)—Mg(1)—O(w3')	92.2 (4)	91.78 (5)
O(w4)—Mg(2)—O(w5)	90.5 (4)	90.81 (5)
O(w4)—Mg(2)—O(w6)	91.5 (4)	92.41 (5)
O(w4)—Mg(2)—O(w5')	89.5 (4)	89.19 (5)
O(w4)—Mg(2)—O(w6')	88.5 (4)	87.59 (5)
O(w5)—Mg(2)—O(w6)	87.4 (4)	88.64 (5)
O(w5)—Mg(2)—O(w6')	92.6 (4)	91.36 (5)
O(1)—P,As—O(2)	110.5 (5)	110.66 (7)
O(1)—P,As—O(3)	107.8 (5)	107.83 (7)
O(1)—P,As—O(4)	111.4 (5)	111.17 (7)
O(2)—P,As—O(3)	107.8 (5)	107.41 (7)
O(2)—P,As—O(4)	110.3 (5)	110.61 (7)
O(3)—P,As—O(4)	108.9 (5)	109.02 (7)

However, the P—O(3) distance, 1.571 Å, is unusually long, considering the fact that only a 'half' H is associated with O(3). On the other hand, analysis of the distortion indices (Baur, 1974) indicates a more symmetrical nature. The distortion indices for P—O and O···O distances and O—P—O angles, 0.010, 0.003 and 0.012 respectively, are clearly closer to the corresponding values for orthophosphates (0.005, 0.006 and 0.009) than to acidic orthophosphates (0.017, 0.011 and 0.025).

The As—O distances vary from 1.68 to 1.70 Å with a mean value 1.69 Å in good agreement with those in other arsenates (Whitaker, 1973). The assignment of the covalently bonded H on O(3) is consistent with the overall isomorphism with (II), the hydrogen bonding and the O—As—O angles.

Two XO_4 groups related by a center of inversion are linked together through an apparently 'symmetric' hydrogen bond (H at the center of inversion) forming an $[\text{H}(\text{XO}_4)_2]$ dimer. The O(3)···O(3') distances, 2.520 Å in (I) and 2.502 Å in (II), are in the range of values, 2.40–2.55 Å, quoted for symmetric hydrogen bonds (Hamilton & Ibers, 1968). Although linkage through symmetric hydrogen bonds is known in several phosphates (Dickens, Bowen & Brown, 1972; Takagi, Mathew & Brown, 1980) and arsenates (Ferraris, Jones & Yerkess, 1972; Ferraris & Franchini-Angela, 1973), neutron diffraction studies have shown that some of these are disordered structures and the hydrogen bonds are only apparently symmetrical (Catti, Ferraris & Filhol, 1977). Since disordering and possible deviations from the centrosymmetric space group exist in the present structures it is likely that these hydrogen bonds, O(3)···O(3'), are also only apparently symmetric, representing the average structure. In any case, regardless of the symmetry restrictions, the hydrogen bond O(3)···O(3') is strong in both (I) and (II) and is involved in the formation of the dimeric unit $[\text{H}(\text{XO}_4)_2]$.

Every O atom except O(3) of the XO_4^{3-} ion is the acceptor in three hydrogen bonds from water molecules. O(3) is also involved in three hydrogen bonds, two from water molecules and the third with the symmetry-related O(3). Thus the immediate environment of XO_4 consists of 11 water molecules and O(3'), distributed approximately at the vertices of a very distorted cuboctahedron (Fig. 3). Similar hydrogen bonding and hydration of PO_4 has been observed in other water-rich hydrates (Schroeder *et al.*, 1978; Mathew, Kingsbury, Takagi & Brown, 1982). All O(w)···O(PO_4) distances are in the range 2.646–2.771 Å (Table 6) indicating fairly strong hydrogen bonds. O(w)···O(AsO_4) bonds are very similar to those of (II) (range 2.65–2.77 Å).

Of the eight water molecules in the asymmetric unit [O(w8) is only half occupied] six are strongly coordinated to Mg^{2+} . All 14 of the available H atoms [H

on O(*w*8) not included] are involved in hydrogen-bond formation, 11 of them to XO_4^{3-} ions. O(*w*7) serves as a vital link in the structure even though it is not bonded to Mg^{2+} . It acts as a donor in two hydrogen bonds to two XO_4 groups linking adjacent Al layers. O(*w*7) is also the acceptor in two additional hydrogen bonds which are the only links between Mg(1) octahedra. All four hydrogen bonds involving O(*w*7) are strong. All O(*w*)—H distances involving the refined H positions in (II) are in the range 0.074–0.92 Å, and the corresponding H—O(*w*)—H angles are in the range 98–113°.

O(*w*3), shown with three H atoms (Fig. 2, Tables 4 and 6), is not to be considered an oxonium ion. Two of the three H-atom sites, H(32) and H(33), are dis-

ordered and only half occupied. Since the two *M* sites are randomly occupied by one O(*w*8) and one K^+ , only the proton site directed towards O(*w*8) can be present (Fig. 1). Although it was not possible to locate the H atoms on this disordered water molecule O(*w*8), from the geometry and the $M \cdots O(w)$ distances it is unlikely that O(*w*8) would be involved as a donor in any significant hydrogen bonding.

Chemically it is tempting to speculate that the *M* sites are occupied by K^+ and H_3O^+ ions since there would be no restrictions placed on site occupancy by electrostatic repulsion. However, the results of the present analysis do not support this view since the proton has been identified as being bonded to XO_4^{3-} ions.

Structural relationship with struvite

On the basis of the molecular formulae and unit-cell dimensions it has been proposed that the structures of $Mg_2KH(PO_4)_2 \cdot 15H_2O$ and $MgHPO_4 \cdot 7H_2O$ are related to struvite, $Mg(NH_4)PO_4 \cdot 6H_2O$ (Dickens & Brown, 1972). Although the structure of $MgHPO_4 \cdot 7H_2O$ is still unknown, we can make some valid comparisons on the basis of the probably isostructural $MgHASO_4 \cdot 7H_2O$ (Whitaker, 1973; Ferraris & Franchini-Angela, 1973). Since $Mg(NH_4)PO_4 \cdot 6H_2O$ (struvite) and $MgKPO_4 \cdot 6H_2O$ are isomorphous and the substitution of NH_4^+ by K^+ produces only minor structural changes (Mathew & Schroeder, 1979), $MgKPO_4 \cdot 6H_2O$ can be used as a model. Inasmuch as the relationship of $CaKAsO_4 \cdot 8H_2O$ with struvite has been amply discussed by Dickens & Brown (1972), we will focus on the remaining members.

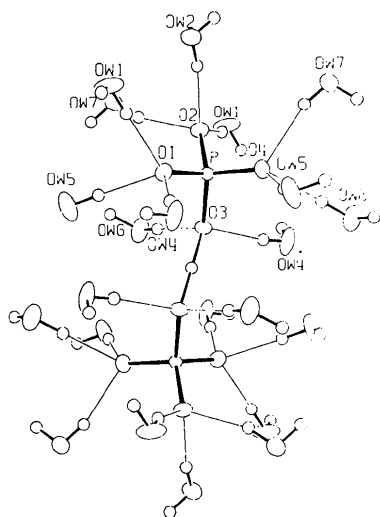


Fig. 3. The configuration of water molecules around the $[H(PO_4)_2]^{5-}$ ion in $Mg_2KH(PO_4)_2 \cdot 15H_2O$.

Table 6. Probable hydrogen bonds in $Mg_2KH(AsO_4)_2 \cdot 15H_2O$ (I) and $Mg_2KH(PO_4)_2 \cdot 15H_2O$ (II)

Estimated standard deviations are given in parentheses.

	H...O (Å)		O...O (Å)		$\angle O-H \cdots O$ (°)	
	(I)	(II)	(I)	(II)	(I)	(II)
O(<i>w</i> 1)—H(11) ... O(2)	1.68	1.91 (3)	2.68 (1)	2.711 (2)	176	164 (3)
O(<i>w</i> 1)—H(12) ... O(1)	1.87	1.84 (3)	2.67 (1)	2.685 (2)	147	179 (3)
O(<i>w</i> 2)—H(21) ... O(2)	1.73	1.88 (3)	2.70 (1)	2.719 (2)	148	170 (2)
O(<i>w</i> 2)—H(22) ... O(<i>w</i> 7)	1.83	2.00 (3)	2.82 (2)	2.795 (2)	160	166 (2)
O(<i>w</i> 3)—H(31) ... O(<i>w</i> 7)	1.79	1.95 (4)	2.74 (2)	2.716 (2)	150	177 (4)
O(<i>w</i> 3)—H(32) ... <i>M</i> *	2.12	2.08	2.96 (1)	2.876 (1)	148	162
O(<i>w</i> 3)—H(33) ... <i>M</i> *	2.06	1.87	2.88 (1)	2.862 (2)	152	173
O(<i>w</i> 4)—H(41) ... O(3)	1.82	2.04 (3)	2.73 (1)	2.766 (2)	155	169 (3)
O(<i>w</i> 4)—H(42) ... O(1)	1.71	1.76 (3)	2.65 (1)	2.646 (2)	145	178 (2)
O(<i>w</i> 5)—H(51) ... O(4)	1.69	1.85 (4)	2.69 (2)	2.666 (2)	156	170 (4)
O(<i>w</i> 5)—H(52) ... O(1)	1.81	1.85 (3)	2.74 (1)	2.727 (2)	169	179 (3)
O(<i>w</i> 6)—H(61) ... O(3)	1.73	1.99 (3)	2.77 (1)	2.771 (2)	161	178 (3)
O(<i>w</i> 6)—H(62) ... O(4)	1.77	1.80 (3)	2.71 (1)	2.719 (2)	148	176 (3)
O(<i>w</i> 7)—H(71) ... O(2)	1.74	1.84 (3)	2.70 (1)	2.685 (2)	163	163 (2)
O(<i>w</i> 7)—H(72) ... O(4)	1.73	1.93 (3)	2.69 (1)	2.713 (2)	157	164 (3)
O(3)—H(O3)—O(3)	1.26	1.25	2.52 (1)	2.502 (2)	180	180

* *M* represents the site containing statistically disordered K and O(*w*8) but the hydrogen bond involves O(*w*8).

A common feature of the struvite analogs, $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and $\text{MgHAsO}_4 \cdot 7\text{H}_2\text{O}$, is the complete hydration of the Mg^{2+} cations without sharing of water molecules between $\text{Mg}(\text{H}_2\text{O})_6$ octahedra. This is characteristic of hydrates with $z/xn \geq 1$ (z = number of water molecules, x = number of cations and n = coordination number of cation) classified as type 'AI' by Wells (1975). K—O(w) interactions were weak and can therefore be ignored. When the monovalent cation—water interactions are significant as in $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ (Dickens & Brown, 1972) and $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$ (Mathew *et al.*, 1982), the ratio z/xn is less than one and results in a sharing of the coordination polyhedra of the different cations.

Another characteristic feature of the struvites, $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgHAsO}_4 \cdot 7\text{H}_2\text{O}$, is the interpenetrating layer-type structure with open channels at the center (Fig. 4), although those channels are not as prominent in $\text{MgHAsO}_4 \cdot 7\text{H}_2\text{O}$. The open channel in $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ is occupied by K^+ . In $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, the apparently rectangular channel (Fig. 4b) is divided into two approximately square channels by the Mg(1) octahedra, separated by only 6.3 Å. The two channels are then randomly occupied by K^+ ions and water molecules. Both Na^+ and a water molecule occupy the open column in $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$ (Fig. 4c) (Mathew *et al.*, 1982). The stability of all these struvite-type compounds may be related to the ionic radius of the larger monovalent cation which can be accommodated in these channels even though it is involved in comparatively weak bonds.

In the light of these crystal-chemical relationships, the probable transformation reactions of these struvite-type compounds in aqueous solutions can be discussed. $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ has been identified in this work as an intermediate product during the formation of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$. It is interesting to note that this intermediate product, $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$, also has a layer-type structure with open channels (Schroeder *et al.*, 1978). In aqueous solution $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ hydrolyzes slowly and incongruently (Lehr *et al.*, 1967) to $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, possibly forming the latter through the unstable intermediate

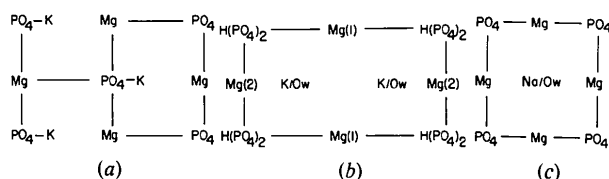


Fig. 4. Idealized view of the linkage of $\text{Mg}(\text{H}_2\text{O})_6$ octahedra and PO_4 tetrahedra showing the open channels in (a) $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$, (b) $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and (c) $\text{MgNaPO}_4 \cdot 7\text{H}_2\text{O}$.

$\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$. $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ also undergoes incongruent hydrolysis to form $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ (Lehr *et al.*, 1967). The relative ease of interconversion of these struvite-type compounds may be related to the close similarities in structure.

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