

## Crystal Structure of a Struvite Analogue, $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$

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### Abstract

The struvite analogue,  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ , crystallizes in the orthorhombic space group  $Pmn2_1$  with  $Z = 2$ . The cell of  $a = 6.873$  (2),  $b = 6.160$  (2) and  $c = 11.087$  (3) Å, obtained in this study by a least-squares fit of thirty  $\pm 2\theta$  values, is in good agreement with that reported on JCPDS powder diffraction file card 20-685. Our structure determination shows that  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  is isostructural with struvite,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , and that the substitution of  $\text{NH}_4^+$  by the smaller  $\text{K}^+$  produces only minor structural changes. The  $\text{K}^+$  ion is loosely coordinated to four water molecules at the base and more tightly to a  $\text{PO}_4$  oxygen at the apex of a tetragonal pyramid. The packing of the  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{PO}_4^{3-}$  ions occurs in planes approximately parallel to the (101) and (011) planes, which provides a structural basis for the observation that crystals grown in aqueous solutions occur as irregular tetrahedra bounded by the (101), ( $\bar{1}01$ ), (011) and (0 $\bar{1}$ 1) planes.

### Introduction

A series of orthorhombic struvite analogues ( $\text{MgMPO}_4 \cdot 6\text{H}_2\text{O}$ , with  $M = \text{K}, \text{Tl}, \text{NH}_4$  and  $\text{Rb}$ ) have been reported by Banks, Chianelli & Korenstein (1975). In terms of increasing size of  $M$  the end members are the  $\text{K}^+$  salt and the two equally sized  $\text{Rb}^+$  or  $\text{NH}_4^+$  salts. Lehr, Brown, Frazier, Smith & Thrasher (1967) reported that  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  forms an isomorphous series with struvite,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . The crystal structure of struvite has already been determined by Whitaker & Jeffery (1970). Here we report the determination of the structure of the  $\text{K}^+$  analogue. A comparison between the  $\text{K}^+$  and  $\text{NH}_4^+$  salts should reveal what effect changing the size of the larger cation has on the structure.

The sample was prepared by adding KOH solution dropwise to a solution of 5 g  $\text{MgCl}_2$  and 25 g  $\text{KH}_2\text{PO}_4$  in 100 ml of water until the pH was 7.5 (Lehr *et al.*, 1967). After a few days, crystals in the form of

irregular tetrahedra (disphenoids) appeared. In contrast, needle forms were obtained when the gel diffusion method was used (Banks *et al.*, 1975). Refractive indices, morphology, Laue symmetry and cell constants agreed with reported values (Lehr *et al.*, 1967).

The crystals are orthorhombic. The cell parameters of  $a = 6.873$  (2),  $b = 6.160$  (2) and  $c = 11.087$  (3) Å used in this study were obtained by a least-squares fit of thirty  $\pm 2\theta$  values measured on a four-circle diffractometer using  $\text{Mo } K\alpha_1$  radiation ( $\lambda = 0.70930$  Å).

The systematic absences of  $h0l$  for  $h + l = 2n + 1$  indicate the space group to be  $Pmn2_1$  or  $Pmnm$ . With only two molecules in the unit cell, the space group was assumed to be  $Pmn2_1$ , and this choice was confirmed by the successful structure analysis.

A crystal approximately tetrahedral in shape (0.13 mm on edge) and mounted in a general orientation was used for the data collection. All reflections in a quadrant ( $\pm hkl$ ) with  $2\theta \leq 45^\circ$  were measured on a four-circle diffractometer equipped with  $\text{Mo } K\alpha$  radiation ( $\lambda = 0.70930$  Å) and a graphite monochromator. The  $\theta$ - $2\theta$  scan technique (scan rate  $0.5^\circ \text{ min}^{-1}$ ) was employed with backgrounds being counted for 40 s at both ends of the scan range. The data-collection program was written by Lenhart (1975). Three standard reflections measured at intervals of every 30 reflections indicated only trivial variation in measured intensities during the data collection. The measured intensities were merged into a set of 358 independent reflections of which 328 had  $F > 2\sigma(F)$  and were therefore considered observed. No absorption correction was applied.

A three-dimensional sharpened Patterson synthesis indicated that the positions of all heavy atoms correspond to those in struvite,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  (Whitaker & Jeffery, 1970), if  $\text{K}^+$  occupies the position of the  $\text{NH}_4^+$  ion, as expected. Therefore, the coordinates of struvite (except for an origin shift along the  $z$  axis) were used as a starting point for refinement.

Refinement was carried out using the least-squares technique in the program *RFINE4* (Finger & Prince, 1975). The quantity minimized was  $\sum w(F_o - F_c)^2$ , where  $w = [\sigma(F_o)^2 + 0.0004(F_o)^2]^{-2}$ . The scattering factors, including  $f'$  and  $f''$  terms, were those for the neutral atoms (*International Tables for X-ray Crystallography*, 1974). Refinements with anisotropic

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thermal parameters reduced  $R$  ( $= \sum |F_o| - |F_c| / \sum |F_o|$ ) to 0.065. The positions of all H atoms were located in a difference Fourier synthesis. Further refinements which included the H atoms with fixed temperature factors converged to  $R = 0.033$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2} = 0.020$  for the 328 observed reflections ( $R = 0.037$  for all reflections). Final atomic parameters are listed in Tables 1 and 2.\*

### Results and discussion

Inasmuch as the struvite structure itself has been amply discussed by Whitaker & Jeffery (1970), we will focus here on a comparison of the  $\text{K}^+$  and  $\text{NH}_4^+$  salts. Fig. 1 shows that the structure consists of  $\text{Mg} \cdot 6\text{H}_2\text{O}$  octahedra and  $\text{PO}_4$  groups held together by a network of

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33865 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ( $\times 10^4$ ) of the non-hydrogen atoms in  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$

Estimated standard deviations are given in parentheses.

	x	y	z
K	0*	3681 (6)	0†
Mg	0*	3830 (7)	6487 (4)
P	0*	-69 (6)	2744 (4)
O(1)	0*	-186 (14)	1363 (8)
O(2)	0*	-2386 (11)	3285 (9)
O(3)	1827 (7)	1120 (8)	3181 (6)
O(w1)	5000*	3124 (15)	631 (11)
O(w2)	5000*	9144 (13)	2404 (9)
O(w3)	2223 (10)	2737 (9)	5382 (6)
O(w4)	2912 (8)	5105 (11)	2656 (7)

\* Fixed by symmetry.

† Fixed as origin.

Table 2. The final positional parameters ( $\times 10^3$ ) of the hydrogen atoms

A fixed isotropic temperature factor ( $3.0 \text{ \AA}^2$ ) was used in all calculations.

	x	y	z
H(1)	0*	717 (20)	503 (11)
H(2)	500*	197 (20)	84 (9)
H(3)	382 (9)	-13 (12)	255 (7)
H(4)	185 (12)	228 (12)	462 (8)
H(5)	198 (11)	802 (14)	88 (5)
H(6)	246 (11)	408 (12)	266 (7)
H(7)	199 (10)	593 (12)	273 (8)

\* Fixed by symmetry.

hydrogen bonds. In Fig. 1 it can also be seen that the packing of  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{PO}_4^{3-}$  ions occurs in planes approximately parallel to the (101) and (011) planes, which provides a structural basis for the morphological forms {101} and {011} exhibited by these orthorhombic crystals.

The  $\text{K}^+$  ion is bonded to five O atoms: O(1) from the  $\text{PO}_4^{3-}$  ion and four water molecules (Table 3). The next-nearest water molecules are more than 3.3 Å away. The overall geometry of the  $\text{K}^+$  ion coordination may be described as tetragonal pyramidal with the four water molecules at the base and the  $\text{PO}_4$  oxygen at the axial position. All the  $\text{K} \cdots \text{O}$  contacts involving water molecules are at least 0.16 Å longer than the sum of the ionic radii (Shannon & Prewitt, 1969). This implies unusually weak  $\text{K} \cdots \text{O}$  bonding. In contrast, the geometry of the  $\text{Mg} \cdot 6\text{H}_2\text{O}$  octahedra in the struvite structures shows that the  $\text{Mg} \cdots \text{O}$  bonding is not affected by the size of the substituted larger cation. The  $\text{Mg} \cdots \text{O}$  distances vary from 2.042 to 2.103 Å, which is in excellent agreement ( $\leq 1\sigma$ ) with the isomorphous ammonium salt (Whitaker & Jeffery, 1970).

The O atoms of the water molecules bound to the  $\text{K}^+$  ions have their largest amplitude of vibration parallel to the  $\text{K} \cdots \text{O}$  bond, while those coordinated to Mg ions have their smallest amplitude of vibration parallel to the  $\text{Mg} \cdots \text{O}$  bond. These observations confirm the observation, made from  $\text{K} \cdots \text{O}$  distances, that the  $\text{K} \cdots \text{O}$  interactions are much weaker than those of  $\text{Mg} \cdots \text{O}$ . Strong  $\text{Mg} \cdots \text{O}$  water bonds are probably responsible for the weak  $\text{NH}_4 \cdots \text{O}(w)$  or  $\text{K} \cdots \text{O}(w)$  interactions. The fact that interactions between the larger cation and the O atoms are weak in struvite-type structures is the reason why the substitution of  $\text{K}^+$  for  $\text{NH}_4^+$  has little effect on the structure.

On the basis of the splitting of the  $\nu_3$  asymmetric-stretch absorption band in the infrared spectrum, Banks *et al.* (1975) suggested the  $\text{PO}_4^{3-}$  ion might be more distorted in the  $\text{K}^+$  salt than in other struvite analogues. However, our crystallographic results (Table 3) do not indicate any significant increase in distortion of  $\text{PO}_4^{3-}$  in the  $\text{K}^+$  salt from that found in the  $\text{NH}_4^+$  salt.

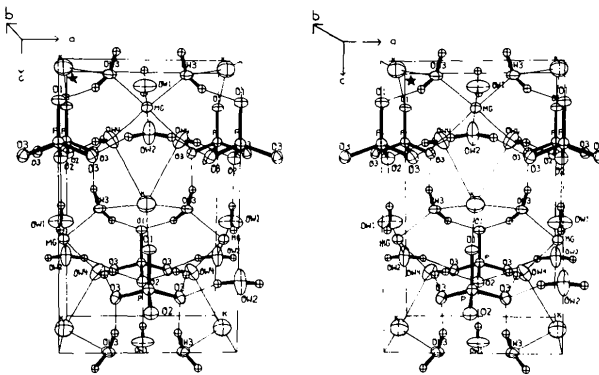


Fig. 1. A stereoscopic pair showing the three-dimensional structure of the unit cell of  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ .

Table 3. Selected interatomic distances (Å) and angles (°) in MgKPO<sub>4</sub>·6H<sub>2</sub>O

K—O(1)	2.821 (9)	P—O(1)	1.533 (10)	Mg—O(w1)	2.103 (11)	O(1)—P—O(2)	110.1 (4)
K—O(w3,w3')	2.948 (7)	P—O(2)	1.549 (9)	Mg—O(w2)	2.095 (10)	O(1)—P—O(3)	109.8 (4)
K—O(w4,w4')	3.062 (8)	P—O(3)	1.533 (6)	Mg—O(w3,w3')	2.071 (8)	O(2)—P—O(3)	108.6 (4)
				Mg—O(w4,w4')	2.042 (8)	O(3)—P—O(3)	110.0 (4)
O(1)—K—O(w3,w3')	123.7 (2)	O(w3,w3')—K—O(w4',w4)	104.0 (2)			H(1)—O(w1)—H(2)	93 (10)
O(1)—K—O(w4,w4')	131.4 (2)	O(w4)—K—O(w4')	55.9 (2)			H(3)—O(w2)—H(3')	119 (6)
O(w3,w3')—K—O(w4,w4')	68.6 (2)	O(w3)—K—O(w3')	80.7 (2)			H(4)—O(w3)—H(5)	124 (7)
						H(6)—O(w4)—H(7)	103 (8)

Table 4. Probable hydrogen bonds

D—H...A*	D—H	H...A	D...A	∠D—H...A
O(w1)—H(1)...O(2)	0.69 (12) Å	1.96 (12) Å	2.640 (15) Å	172 (11)°
O(w1)—H(2)...O(w2)	0.75 (12)	2.45 (11)	3.142 (14)	154 (9)
O(w2)—H(3)...O(3)	0.94 (6)	1.72 (7)	2.642 (7)	166 (7)
O(w3)—H(4)...O(3)	0.93 (9)	1.75 (9)	2.649 (9)	163 (8)
O(w3)—H(5)...O(1)	0.90 (7)	1.83 (8)	2.701 (9)	160 (7)
O(w4)—H(6)...O(3)	0.70 (8)	1.97 (8)	2.631 (9)	159 (8)
O(w4)—H(7)...O(2)	0.82 (7)	1.82 (7)	2.623 (8)	166 (8)

\* D: donor atom; A: acceptor atom.

The hydrogen bonds between water molecules and PO<sub>4</sub> groups in general (Table 4) are very similar to those observed in struvite. The O(w)···O(w) distance of 3.142 Å between water molecules O(w1) and O(w2) can be seen from the cut-off value obtained from the histogram given by Ferraris & Franchini-Angela (1972) to correspond to insignificant hydrogen bonding. A similar situation has been observed in struvite. This result also suggests that the location of H(2) is chosen to minimize cation-proton repulsion (Fig. 1) rather than to maximize hydrogen bonding.

In summary, the substitution of K<sup>+</sup> for NH<sub>4</sub><sup>+</sup> in the struvite structure produces insignificant effects. Thus solid solutions of the type MgM<sub>x</sub>N<sub>1-x</sub>PO<sub>4</sub>·6H<sub>2</sub>O, where M and N are K<sup>+</sup>, Tl<sup>+</sup> or NH<sub>4</sub><sup>+</sup>, may be easily formed. Ordering in such solutions would depend mainly on entropy and ionic interactions among the substituents.

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#### References

- BANKS, E., CHIANELLI, R. & KORENSTEIN, K. (1975). *Inorg. Chem.* **14**, 1634–1639.
- FERRARIS, G. & FRANCHINI-ANGELA, M. (1972). *Acta Cryst.* **B28**, 3572–3583.
- FINGER, L. W. & PRINCE, E. (1975). *Natl Bur. Stand. (US) Tech. Note* 854.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99–102. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LEHR, J. R., BROWN, E. H., FRAZIER, A. W., SMITH, J. P. & THRASHER, R. P. (1967). *Tenn. Val. Auth. Chem. Eng. Bull.* No. 6.
- LENHERT, P. G. (1975). *J. Appl. Cryst.* **8**, 568–570.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–946.
- WHITAKER, A. & JEFFERY, J. W. (1970). *Acta Cryst.* **B26**, 1429–1444.