

CRYSTAL STRUCTURE OF MAGNESIUM POTASSIUM PHOSPHATE MONOHYDRATE (MgKPO₄·H₂O)*

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The crystal structure of MgKPO₄·H₂O has been solved by single crystal X-ray diffraction. It was shown that the compound crystallize in the orthorhombic space group *Pmm*2₁ with *Z* = 2. The crystal data are: *a* = 5.573(2), *b* = 8.231(2), *c* = 4.790(2) Å, *V* = 219.7 Å³, *D*_o = 2.63 Mg·m⁻³, *D*_c = 2.66 Mg·m⁻³, λ (CuKα) = 1.54178 Å, μ = 138.62 cm⁻¹, *F*(000) = 176, room temperature. 246 independent reflections were used for the structure determination. The coordinates of all non-hydrogen atoms were then refined to final *R* = 0.064. The structure consists of PO₄ tetrahedra, K and Mg cations and H₂O molecules. The Mg atoms are coordinated to 5 oxygens belonging to PO₄ groups and one water oxygen atom. The corresponding Mg–O distances range from 2.006(11) to 2.179(12) Å. The K atom is surrounded by eight oxygen atoms belonging to water molecule and various phosphate groups. The K–O distances vary from 2.655(12) to 3.205(6) Å. The water molecules form bifurcated hydrogen bonds being surrounded by four phosphate oxygen atoms as well as by Mg and K atom.

Key words: crystal structure; magnesium potassium phosphate monohydrate

INTRODUCTION

The unusual appearance of the infrared spectra of compounds of the type MKPO₄·H₂O (M = Mg, Mn, Co, Ni, and Cd) characterized by the existence of very low H–O–H bending frequencies (around 1500 cm⁻¹ and even lower) [1–3] led us to investigate in detail the crystal structure of the title compound. Durif and Averbuch-Pouchot [4] were the first who determined the unit cell parameters of the above mentioned compounds of type MKPO₄·H₂O as well as of the isomorphous compounds of the type MNH₄PO₄·H₂O (Cd, Co, Fe, Mg, Mn and Ni).

The unit cell parameters determined by us for MgKPO₄·H₂O [5] agree well with those found by Durif and Averbuch-Pouchot [4] while the position of the K atom in the structure of the title compound closely coincide with the position of the center of the NH₄ group in the structure of the isomorphous CoNH₄PO₄·H₂O [6]. In the meantime, the crystal

structures of phases B [7] and A [8] of CdNH₄PO₄·H₂O have been solved. The precise comparison of the structural characteristics has shown that the structures of CoNH₄PO₄·H₂O [6], phase A of CdNH₄PO₄·H₂O [8] and MgKPO₄·H₂O are isomorphous. Later the crystal structure determination of CaKPO₄·H₂O from X-ray powder diffraction data [9] has shown that, in spite of the analogue chemical formula, the calcium potassium compound crystallizes in the monoclinic system.

Here we reported the crystal structure determination of magnesium potassium phosphate monohydrate and compared its structural characteristics with those found for the analogous cobalt ammonium phosphate monohydrate [6] and phase A of cadmium ammonium phosphate monohydrate [8].

* Dedicated to professor Bojan Šoptrajanov on the occasion of his 60th birthday

EXPERIMENTAL

The compound was synthesized according to the method described by Basset and Bedwell [10] by mixing the equimolar quantities of $MgCl_2$, K_2HPO_4 and KCl . The single crystals were grown by allowing the mixture to stand for two months at 60–70 °C.

The intensity data were collected on a Philips PW1100 automatic four-circle diffractometer using graphite-monochromated $CuK\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). 20 reflections were used for determination of the accurate unit-cell parameters. The ω - 2θ scan technique was used for the intensity data collection with scan speed of $0.03^\circ \text{ s}^{-1}$. The total number of collected independent reflections was 249, while 246 reflections with $I > 3\sigma(I)$ were used in structure solution and refinement. The hkl values of the measured reflections range from 0 to 8 for h , from 0 to 12 for k and from 0 to 7 for l . Three standard reflections measured every 2 hours of exposure time showed significant (up to 10%) variations during the collection of data. The corresponding

correction for this type of variation was applied. Intensity data were also corrected for Lorentz-polarization factors but not for absorption. The atomic scattering factors and anomalous-dispersion corrections (for K and Mg) were taken from *International Tables for X-ray Crystallography* [11].

The initial position for the K atom was determined by solution of the Patterson map, while the positional parameters of the Mg, P and O atoms were found from the subsequent Fourier synthesis. The structure was refined by full-matrix least-squares procedure on F^2 's. The final cycle of the refinement (including 28 variable parameters) assuming isotropic thermal parameters for O atoms and anisotropic thermal parameters for K, Mg and P converged to $R = 0.064$. All calculations were performed on a UNIVAC 1110 computer of the Zagreb University Computing Centre, SRCE, with program package written by Domenicano *et al.* [12].

RESULTS AND DISCUSSION

The final fractional atomic positional parameters and isotropic thermal parameters for oxygen atoms with estimated standard deviations in parentheses for the title compound are given in Table I. The final anisotropic thermal parameters with estimated standard deviations in parentheses are shown in Table II.

Table I

The final fractional atomic positional parameters and isotropic thermal parameters for oxygen atoms with estimated standard deviations in parentheses for the title compound

Atom	x	y	z	$B/\text{\AA}^2$
K	0.5	0.4616(4)	0.0180(11)	—
Mg	0.5	0.0163(5)	0.1502(12)	—
P	0.0	0.2098(4)	0.0848(11)	—
O(1)	0.0	0.1800(12)	0.4019(23)	1.8(2)
O(2)	0.0	0.3904(12)	0.0255(24)	1.9(2)
O(3)	0.2218(10)	0.1233(7)	-0.0518(17)	1.5(1)
O _w	0.5	0.2123(11)	0.4560(26)	1.7(2)

Table II

The final anisotropic thermal parameters (10^4)* with estimated standard deviations in parentheses

$$T = \exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$$

Atom	β_{11}	β_{22}	β_{33}	β_{23}
K	125(9)	82(5)	27(18)	26(13)
Mg	93(12)	49(6)	228(24)	-10(18)
P	64(9)	45(4)	171(16)	-1(10)

* $\beta_{12} = \beta_{13} = 0$

The view of the crystal structure of $MgKPO_4 \cdot H_2O$ along the b and c axis is shown in Figs. 1 and 2, respectively [13]. The structure consists of PO_4^{3-} anions, Mg^{2+} and K^+ cations and water molecules. All atoms, except O(3) atom from PO_4 group, lie on the mirror plane. The Mg atom is six coordinated, being surrounded by one water oxygen and five oxygen atoms belonging to five phosphate groups. The Mg-O distances vary from 2.006(11) to 2.210(8) Å, while the O-Mg-O angles

formed by the adjacent oxygen atoms in the distorted octahedron range from $68.0(3)$ to $99.68(3)^\circ$. The K atom is coordinated to eight oxygen atoms belonging to the water molecule and to various phosphate groups. The K-O distances range from $2.655(12)$ to $3.205(6)$ Å, see Table III. The same coordination number around the K atom has been found in the structure of $CaKPO_4 \cdot H_2O$ [9] where the K-O distances vary from $2.781(2)$ to $2.996(3)$ Å.

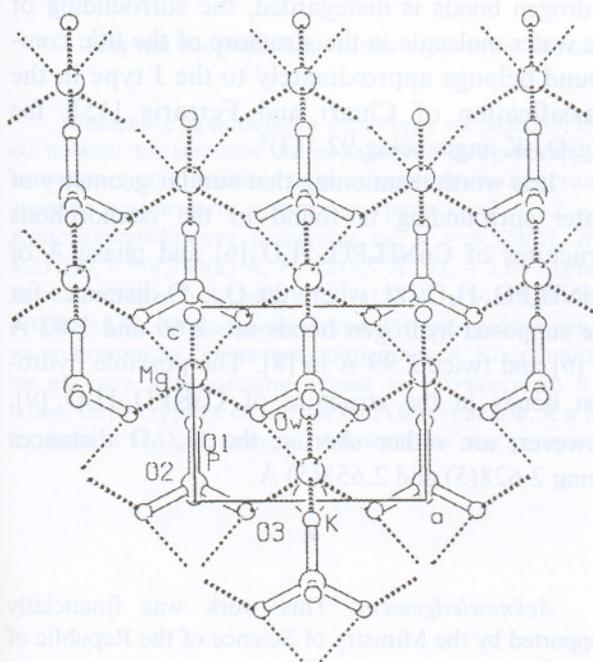


Fig. 1. The view of the structure of $MgKPO_4 \cdot H_2O$ along the b axes showing the atom-numbering scheme as well as the Mg environment

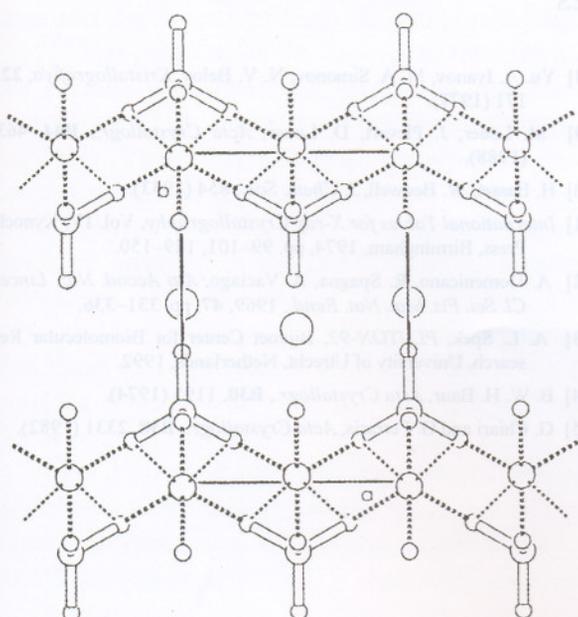


Fig. 2. The packing of the structural constituents of $MgKPO_4 \cdot H_2O$ shown along the c axes.

Table III

Selected interatomic bond distances (Å) and valence angles ($^\circ$) for $MgKPO_4 \cdot H_2O$

Mg-O distances			
Mg-O(1 ^v)	2.006(11)	Mg-O(3 ⁱ)	2.029(7)
Mg-O(3 ⁱⁱⁱ)	2.210(8)	Mg-O(3 ^{vi})	2.029(7)
Mg-O(3 ^{iv})	2.210(8)	Mg-O _w (ⁱ)	2.179(12)
O-Mg-O angles			
O(1 ^v)-Mg-O(3 ⁱ)	93.8(3)	O(3 ⁱ)-Mg-O _w (ⁱ)	89.9(3)
O(1 ^v)-Mg-O(3 ^{vi})	93.8(3)	O(3 ^{vi})-Mg-O(3 ⁱⁱⁱ)	164.0(3)
O(1 ^v)-Mg-O(3 ⁱⁱⁱ)	87.9(3)	O(3 ^{vi})-Mg-O(3 ^{iv})	96.1(3)
O(1 ^v)-Mg-O(3 ^{iv})	87.9(3)	O(3 ^{vi})-Mg-O _w (ⁱ)	89.9(3)
O(1 ^v)-Mg-O _w (ⁱ)	174.1(4)	O(3 ⁱⁱⁱ)-Mg-O(3 ^{iv})	68.0(3)
O(3 ⁱ)-Mg-O(3 ^{vi})	99.7(3)	O(3 ⁱⁱⁱ)-Mg-O _w (ⁱ)	87.2(3)
O(3 ⁱ)-Mg-O(3 ⁱⁱⁱ)	96.1(3)	O(3 ^{iv})-Mg-O _w (ⁱ)	87.2(3)
O(3 ⁱ)-Mg-O(3 ^{iv})	164.0(3)		
K-O distances			
K-O(1 ^{viii})	3.002(10)	K-O(2 ^{viii})	2.848(2)
K-O(2 ^{vii})	2.655(12)	K-O(3 ⁱ)	3.205(6)
K-O(2 ^{ix})	2.719(12)	K-O(3 ^{vi})	3.205(6)
K-O(2 ⁱ)	2.848(2)	K-O _w (ⁱ)	2.935(12)
PO₄ groups			
P-O distances			
P-O(1 ⁱ)	1.539(12)	P-O(3 ⁱ)	1.569(7)
P-O(2 ⁱ)	1.513(10)	P-O(3 ⁱⁱ)	1.569(7)
O-P-O angles			
O(1 ⁱ)-P-O(2 ⁱ)	110.0(5)	O(2 ⁱ)-P-O(3 ⁱ)	111.5(5)
O(1 ⁱ)-P-O(3 ⁱ)	109.8(4)	O(2 ⁱ)-P-O(3 ⁱⁱ)	111.5(5)
O(1 ⁱ)-P-O(3 ⁱⁱ)	109.8(4)	O(3 ⁱ)-P-O(3 ⁱⁱ)	103.9(4)
Possible bifurcated hydrogen bonds			
O _w ...O(1 ⁱ)	2.811(2)	O(1 ⁱ)...O _w ...O(1 ^{viii})	164.8(4)
O _w ...O(1 ^{viii})	2.811(2)	O(3 ^x)...O _w ...O(3 ^{xi})	64.3(3)
O _w ...O(3 ^x)	2.915(13)		
O _w ...O(3 ^{xi})	2.915(13)		

Symmetry codes: (i) x, y, z ; (ii) $-x, y, z$; (iii) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (iv) $\frac{1}{2}+x, -y, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, -y, -\frac{1}{2}+z$; (vi) $1-x, y, z$; (vii) $\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$; (viii) $1+x, y, z$; (ix) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (x) $x, y, 1+z$; (xi) $1-x, y, 1+z$.

As seen from Figs. 1 and 2, the phosphate groups in the structure act as tridentate ligands. The P-O distances and O-P-O angles in the PO_4 group range from 1.513(10) to 1.569(7) Å and from 103.9(4) to 111.5(5) (°), respectively (see Table III). The corresponding P-O distances in the structure of the isomorphous $\text{CoNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ [6] are slightly shorter [1.49–1.57 Å], those in the phase A of the also isomorphous structure of $\text{CdNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ [8] are similar [1.53–1.55 Å] but closer to each other, while the P-O distances in the PO_4 tetrahedra of the structure of $\text{CaKPO}_4\cdot\text{H}_2\text{O}$ [9] are longer [1.561(3)–1.615(4) Å]. It is evidently that the PO_4 tetrahedron in the structure of the studied compound is rather distorted, especially concerning the P-O distances. It is confirmed by the rather large value of the deformation index $DI(TO) = 0.0140$ [2] calculated according to Baur [14], compared to the corresponding $DI(TO)$ values for the isomorphous phase A of $\text{CdNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ [$DI(TO) = 0.065$] [2] as well as for the phase B of $\text{CdNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ [$DI(TO) = 0.032$] [2]. These structural characteristics of the PO_4 group in $\text{MgKPO}_4\cdot\text{H}_2\text{O}$ agree well with the spectroscopic evidence found by Šoptrajanov [1].

The water molecule is surrounded by Mg atom [2.179(12) Å], K atom [2.935(12) Å] and four phosphate oxygen atoms (see Figs. 1 and 2). Namely, two pairs of symmetry related phosphate oxygens are found at distances 2.811(2) Å for $\text{O}_w\cdots\text{O}(1)$ and 2.915(13) Å for $\text{O}_w\cdots\text{O}(3)$. Unfortunately, the hydrogen bonding scheme is difficult to

be established with certainty, since the position of the hydrogen atom in the structure is not determined. In spite of that, the positions of the oxygen atoms around the water molecule suggests that, most probably, water protons form a bifurcated hydrogen bond. Namely, the $\text{O}(1^i)\cdots\text{O}_w\cdots\text{O}(1^{\text{viii}})$ angle is too large [164.8(4)°], while the $\text{O}(3^x)\cdots\text{O}_w\cdots\text{O}(3^{\text{xi}})$ angle is too small [64.3(3)°]. Otherwise, if the probable existence of a bifurcated hydrogen bonds is disregarded, the surrounding of the water molecule in the structure of the title compound belongs approximately to the J type in the classification of Chiari and Ferraris [15], the $\text{Mg-O}_w\text{-K}$ angle being 92.1(3)°.

It is worth mentioning that similar geometry of water surrounding is found in the isomorphous structures of $\text{CoNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ [6] and phase A of $\text{CdNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ [8], where the $\text{O}_w\cdots\text{O}$ distances for the supposed hydrogen bonds are 2.66 and 2.82 Å in [6] and twice 2.99 Å in [8]. The possible hydrogen bonds in the structure of $\text{CaKPO}_4\cdot\text{H}_2\text{O}$ [9], however, are rather shorter, the $\text{O}_w\cdots\text{O}$ distances being 2.628(5) and 2.658(5) Å.

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Резиме

КРИСТАЛНА СТРУКТУРА НА МАГНЕЗИУМ КАЛИУМ ФОСФАТ МОНОХИДРАТ,
($MgKPO_4 \cdot H_2O$)Глигор Јовановски¹, Стефан Поцев², Вранко Кайтер³¹Институт за хемија, Природно-математички факултет, Универзитет „Св. Кирил и Методиј“, 91000 Скопје, Р. Македонија²Технолошко-металушки факултет, Универзитет „Св. Кирил и Методиј“, 91000, Скопје, Република Македонија³Laboratory of General and Inorganic Chemistry, Faculty of Science, The University of Zagreb, 10000 Zagreb, Croatia**Клучни зборови:** кристална структура; магнезиум; калиум фосфат монохидрат

Решена е кристалната структура на $MgKPO_4 \cdot H_2O$ со помош на методот на рендгенска дифракција на монокристал. Најдено е дека соединението кристализира во ромбичната просторна група $Rmn2_1$ со $Z = 2$. Кристалографските податоци се: $a = 5,573(2)$, $\beta = 8,231(2)$, $c = 4,790(2)$ Å, $V = 219,7$ Å³, $D_o = 2,63$ Mg·m⁻³, $D_c = 2,66$ Mg·m⁻³, $\lambda(CuK\alpha) = 1,54178$ Å, $\mu = 138,62$ cm⁻¹, $F(000) = 176$, собна температура. Структурата е решена со помош на 246 независни рефлекси. Координатите на сите неводородни атоми се уточнети до $R = 0,064$. Структурата се состои од PO_4 тетраедри, К и Mg катјони и H_2O молекули. Атомите на магнезиум се

координирани за 5 кислородни атоми кои припаѓаат на разни PO_4 групи, како и за еден кислород од молекулата на водата. Соодветните Mg–O-растојанија се движат од 2,006(11) до 2,179(12) Å. Атомот на К е опкружен со осум кислородни атоми кои припаѓаат на молекулата на водата и на различни фосфатни групи. К–O-растојанијата варираат од 2,655(12) до 3,205(6) Å. Молекулите на водата се опкружени со четири фосфатни кислороди, како и со по еден атом на Mg и К, при што формираат бифуркирани водородни врски.

Key words: hydrogen bonds, non-statistical H/D substitution, one-dimensional crystal, Einstein model, Gibbs energy, minimisation of

INTRODUCTION

In more than 30 years, our distinguished Professor Soptrajanov has given quite a remarkable contribution in the study of hydrogen bonded systems and the aspects of the hydrogen bonding itself [2–7]. The problem of the non-equal intensities of the various OD stretchings in the IR spectra of crystallohydrates, which was briefly mentioned in his Ph.D. Thesis [2] still deserves attention. Very often, namely, the studied IR spectra of deuterated crystallohydrates, follow the same general pattern: the band intensity of the OD stretching vibrations increases with increasing the hydrogen bond strength [8, 9]. One might be inclined to conclude that these findings clearly show that deuterium atoms, for some reason, prefer the stronger hydrogen bonds.

The results of Lutz [1], suggest that this notion is probably incorrect, in the sense that it is not capable of explaining the spectral picture in the OH stretching region of the HDO molecules. One may

assume, at first, that deuterium indeed prefers stronger H-bonds. In that case, however, protium should be forced to occupy the weaker ones, and the OH stretching bands at highest frequencies should be the most intense. This not being the case [1], one is left with alternative explanations. Lutz *et al.* [10] and Corn and Strauss [11] proposed an explanation, based on the (empirical) fact of the correlation between the intensity of $\nu(X-H)$ mode and the hydrogen bond strength. According to this explanation, one would *a-priori* expect the lower frequency stretchings to give more intense bands in the IR spectra. Even this explanation is not justified in all experiments. The explanation of Lutz [1] (in the case of asymmetrically bonded water molecules) which seems to be in agreement with all experimental results, was based on the existence of non-equal normal coordinates for the stretching GH/OD vibrations of the H_2OD_2 and D_2OH_2 species present in the crystal.

¹ Dedicated to prof. Dejan Soptrajanov, on the occasion of his 60th birthday.