The Structure of Synthetic Dimagnesium Diphosphate(V) Dihydrate

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Abstract

The crystal structure of synthetic hydrous magnesium phosphate, $Mg_2P_2O_7.2H_2O$, $P2_1/n$, $a = 7.367$ (1), $b = 13.906$ (3), $c = 6.277$ (1) Å, $\beta = 94.37$ (3)°, $Z = 4$, $D_m = 2.60$, $D_x = 2.66$ Mg m^{-3}, μ(Mo $K\alpha$) = 0.904 mm^{-1}, has been determined. The structure was deduced from Patterson syntheses and refined by full-matrix least-squares methods to $R = 0.043$ for 1051 observed reflections. The structure consists of $P_2O_7^{4-}$ radicals, linked by two kinds of Mg atoms. The Mg atoms have six nearest neighbours of O atoms, and share edges of the coordination octahedra to form infinite chains. One of the H atoms makes an O–H···O hydrogen bond. It is proposed that the remaining three H atoms form bifurcated hydrogen bonds, but one can also be considered to occupy a position resulting from proton–cation repulsion, rather than to form hydrogen bonds.

Introduction

Structural investigations of hydrous magnesium phosphates are important from the viewpoint of the systematization of phosphate structures and also with regard to the determination of the nature of hydrogen bonds. However, very few magnesium phosphate structures have been investigated because of the difficulty of finding the chemical conditions for synthesizing single crystals large enough for structure analysis, and also because of the difficulty of finding natural specimens. Recently, the authors have succeeded in synthesizing one new phase by hydrothermal syntheses. This new phase has not previously been found either as a synthetic product or as a natural mineral. The present paper reports the crystal structure of this new phase.

Throughout the investigation, calculations were carried out at the Computer Center of Okayama University, using the modified programs of *UNICS* (Sakurai, 1971).

The intensity measurements were carried out in the Department of Earth Sciences, Kanazawa University, by the courtesy of Professor S. Sugiura.

Experimental

A solution of 5 g of $Na_2HPO_4.12H_2O$ in 500 ml of water was weakly acidified with 5 ml of a 6M solution of acetic acid. Then, a solution of 5 g of $MgSO_4.7H_2O$ in 300 ml of water was slowly added to the $Na_2HPO_4.12H_2O$ aqueous solution at room temperature. The solution was kept at 363 K for 10 d. The white precipitates formed were examined by the X-ray powder method and identified as DMP3 ($MgHPO_4.3H_2O$). These precipitated white crystals were shielded with H_3PO_4 solutions in silver tubes, and heated at a temperature ranging from 623 to 773 K for 2.5–5 d under hydrothermal environments. The single crystals obtained were analysed by EPMA and wet-chemical procedures, and their chemical formula was determined as $Mg_2P_2O_7.2H_2O$ (MPP2). These crystals are colourless and show rounded or columnar shapes about 0.1–0.5 mm in size. The hydrothermal experiments were carried out with test-tube-type apparatus made by Autoclave Engineers Company, USA, and also with autoclaves made by us.

The lattice constants and extinction rules were determined by the Weissenberg method. The intensities of the reflections were measured on an automated four-circle diffractometer using the 2θ–ω scan technique and Mo $K\alpha$ radiation ($\lambda = 0.70926$ Å) with a graphite monochromator. A crystal of approximate dimensions $0.1 \times 0.08 \times 0.05$ mm was mounted with the a axis approximately parallel to the φ axis of the diffractometer. Of a total of 1756 intensities measured up to $2\theta = 56°$, 1051 were classified as observed with $I > 3\sigma$ above background. The integrated intensities were converted to structure factors by applying Lorentz–polarization corrections. No absorption corrections were made because of the very small crystal size. The unit-cell dimensions and their standard deviations measured by the same diffractometer are shown in the *Abstract*.

The powder diffraction data were also collected ($\lambda = 1.5418$ Å) after mixing with a small amount of silicon powder as internal standard. These data are shown in Table 1.

Structure determination and refinement

Systematic absences in the diffraction pattern show that the space group of MPP2 is $P2_1/n$. The positions of two kinds of P atoms were found from a three-dimensional Patterson map. The positions of the Mg and O atoms were found from successive Fourier syntheses. After diagonal least-squares refinements, five cycles of full-matrix least-squares refinement with isotropic temperature factors were carried out and the R value reduced to 0·046. The positions of four H atoms were determined by difference Fourier syntheses. Three further cycles of refinement including the H atoms with fixed isotropic temperature factors converged to $R = 0·043$.

The atomic scattering factors of neutral atoms used in *International Tables for X-ray Crystallography* (1974) were used throughout the calculation.

Final atomic parameters are listed in Table 2.*

Table 1. *Powder diffraction data*

D_o	I_o	$h\,k\,l$	D_c	D_o	I_o	$h\,k\,l$	D_c
7·02 Å	70	0 2 0	6·953 Å	2·89 Å	90	2 3 0	2·879 Å
6·55	35	1 1 0	6·495	2·87	5	0 2 2	2·854
5·06	100	1 2 0	5·049	2·61	20	1 5 0	2·601
3·93	30	1 3 0	3·920	2·57	5	2 3 1	2·558
3·74	5	0 3 1	3·725	2·53	15	2 4 0	2·525
3·57	3	2 1 0	3·551	2·39	4	2 4 1	2·385
3·49	8	0 4 0	3·476	2·35	3	3 0 1	2·342
3·26	7	2 2 0	3·248	2·32	5	3 2 0	2·310
3·16	3	1 4 0	3·142	2·22	10	2 5 0	2·217

Table 2. *Atomic positional parameters* ($\times 10^4$ *for* P, Mg *and* O, $\times 10^3$ *for* H *atoms*) *and isotropic thermal parameters, with standard deviations in parentheses*

For nonhydrogen atoms $B_{eq} = \frac{4}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

	x	y	z	B_{eq}/B_{iso} (Å^2)
P(1)	4324 (2)	1881 (1)	5622 (2)	0·44 (2)
P(2)	1522 (2)	852 (1)	7570 (2)	0·43 (2)
Mg(1)	3537 (2)	2512 (1)	474 (2)	0·65 (3)
Mg(2)	831 (2)	1122 (1)	2627 (2)	0·59 (3)
O(1)	2734 (5)	37 (3)	2599 (6)	1·24 (8)
O(2)	8771 (4)	192 (2)	2095 (5)	0·73 (7)
O(3)	3493 (4)	933 (2)	6642 (5)	0·61 (7)
O(4)	1645 (4)	1423 (2)	9635 (5)	0·64 (7)
O(5)	5656 (5)	1478 (3)	625 (7)	1·49 (9)
O(6)	6266 (4)	1618 (2)	5275 (5)	0·79 (7)
O(7)	3150 (4)	2089 (2)	3580 (5)	0·74 (7)
O(8)	9144 (4)	2322 (2)	2263 (5)	0·70 (7)
O(9)	239 (4)	1311 (2)	5852 (5)	0·63 (7)
H(1)	586 (13)	118 (7)	146 (15)	5·0
H(2)	658 (12)	165 (7)	39 (16)	5·0
H(3)	703 (10)	11 (5)	842 (12)	2·0
H(4)	697 (9)	50 (5)	626 (11)	2·0

Description of the structure and discussion

The structure of $Mg_2P_2O_7.2H_2O$ is shown in Fig. 1. Both P(1) and P(2) are tetrahedrally coordinated. As in α- and β-$Mg_2P_2O_7$ (Calvo, 1965, 1967), these two tetrahedra are linked to each other by sharing O(3), to make the pyrophosphate $P_2O_7^{4-}$ radicals.

Two independent Mg atoms, Mg(1) and Mg(2), octahedrally coordinated, share edges to form infinite chains in the $|10\bar{1}|$ directions. These infinite MgO_4 chains are not directly linked to other chains but four MgO_4 chains are linked to one P_2O_7 radical to form three-dimensional networks.

Interatomic distances and angles are shown in Table 3. The mean P—O distances are 1·540 and 1·533 Å, respectively. The bridging P—O(3) distances (1·607 and 1·609 Å) are significantly longer than the non-bridging bonds (mean values, 1·517 and 1·507 Å) (Cruickshank, 1961; Calvo, 1965, 1967). The correlation between the P—O—P angles and the difference in the mean values of the bridging and non-bridging bonds (125·7° and 0·096 Å) are approximately in line with those pointed out by Robertson & Calvo (1968).

Both MgO_6 octahedra are slightly distorted. The mean MgO distances are 2·088 and 2·091 Å, respectively. These agree with those in $MgHPO_4$ (Sutor, 1967), $Mg_3(PO_4)_2$ (Nord & Kierkegaard, 1968), $MgNH_4PO_4.6H_2O$ (Whitaker & Jeffery, 1970), $MgKPO_4.6H_2O$ (Mathew & Schroeder, 1979), and $MgHPO_4.3H_2O$ (Abbona, Boistelle & Haser, 1979). The shared edges (2·793, 2·725 Å) are much shorter than the unshared edges (mean 2·956, 2·986 Å).

O(1) and O(5) are present in the form of water molecules and are coordinated only to Mg(2) and Mg(1) atoms.

The angles H—O—H are 111 and 101°, while the O—H distances vary from 0·71 to 1·05 Å. The distance O(1)···O(6) is 2·733 Å, corresponding to a hydrogen
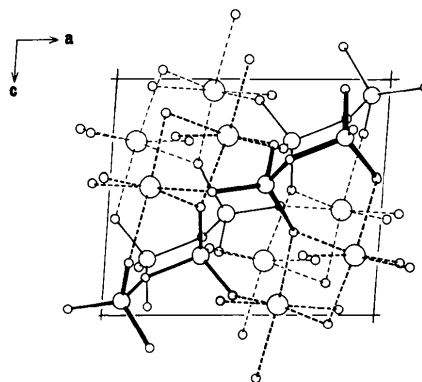

Fig. 1. The schema of the structure of $Mg_2P_2O_7.2H_2O$ viewed along $|010|$. The large, intermediate and small circles correspond to Mg, P and O atoms, respectively. The P_2O_7 radicals are shown by bold lines.

Table 3. *Interatomic distances (Å) and angles (°)*
with standard deviations in parentheses

P polyhedra

P(1)–O(3)	1·607 (3)		P(2)–O(2)	1·485 (3)
O(6)	1·508 (3)		O(3)	1·609 (3)
O(7)	1·518 (3)		O(4)	1·517 (3)
O(8)	1·526 (3)		O(9)	1·519 (3)

O(3)–P(1)–O(6)	104·7 (2)		O(3)–O(6)	2·467 (4)
O(7)	106·4 (2)		O(7)	2·504 (4)
O(8)	105·8 (2)		O(8)	2·498 (4)
O(6) O(7)	114·2 (2)		O(6)–O(7)	2·541 (4)
O(8)	113·9 (2)		O(8)	2·544 (4)
O(7) O(8)	111·0 (2)		O(7)–O(8)	2·509 (4)
O(2)–P(2)–O(3)	105·3 (2)		O(2)–O(3)	2·462 (4)
O(4)	113·0 (2)		–O(4)	2·503 (4)
O(9)	115·0 (2)		–O(9)	2·533 (4)
O(3) O(4)	106·0 (2)		O(3)–O(4)	2·497 (4)
O(9)	104·1 (2)		–O(9)	2·467 (4)
O(4) O(9)	112·3 (2)		O(4)–O(9)	2·522 (4)
P(1)–O(3)–P(2)	125·7 (2)			

Mg polyhedra

Mg(1)–O(4)	2·098 (3)		Mg(2)–O(1)	2·061 (4)
O(5)	2·119 (4)		O(2)	2·002 (3)
O(6)	2·061 (3)		O(4)	2·058 (3)
O(7)	2·077 (3)		O(7)	2·220 (3)
O(8)	2·110 (3)		O(8)	2·083 (3)
O(9)	2·064 (3)		O(9)	2·119 (3)

O(4)–Mg(1)–O(5)	89·7 (1)		O(4)–O(5)	2·974 (5)
O(6)	83·6 (1)		O(6)	2·771 (4)
O(7)	84·0 (1)		O(7)	2·793 (4)
O(8)	91·4 (1)		O(8)	3·012 (5)
O(5) O(7)	85·4 (2)		O(5)–O(7)	2·845 (5)
O(8)	84·7 (2)		O(8)	2·850 (5)
O(9)	95·4 (1)		O(9)	3·094 (5)
O(6) O(7)	93·1 (1)		O(6)–O(7)	3·004 (4)
O(8)	96·2 (1)		O(8)	3·105 (4)
O(9)	91·4 (1)		O(9)	2·953 (4)
O(8) O(9)	81·5 (1)		O(8)–O(9)	2·725 (4)

O(1)–Mg(2)–O(2)	91·9 (1)		O(1)–O(2)	2·921 (5)
O(4)	84·0 (1)		O(4)	2·755 (5)
O(7)	86·3 (1)		O(7)	2·930 (5)
O(9)	106·8 (1)		O(9)	3·355 (5)
O(2) O(4)	104·4 (1)		O(2)–O(4)	3·209 (4)
O(8)	93·5 (1)		O(8)	2·976 (4)
O(9)	91·8 (1)		O(9)	2·960 (4)
O(4) O(7)	81·4 (1)		O(4)–O(7)	2·793 (4)
O(8)	87·1 (1)		O(8)	2·853 (4)
O(7) O(8)	89·1 (1)		O(7)–O(8)	3·021 (4)
O(9)	83·0 (1)		O(9)	2·876 (4)
O(8) O(9)	80·8 (1)		O(8)–O(9)	2·725 (4)

H(1)–O(5)	0·68 (9)		O(5)···O(2)	2·999 (5)
···O(2)	2·55 (10)		···O(6)	2·926 (5)
···O(6)	2·47 (9)		O(5)···O(7)	3·058 (5)
			···O(8)	2·939 (5)

Table 3 (*cont.*)

H(2)–O(5)	0·75 (9)			
···O(7)	2·43 (10)		O(5)–H(1)···O(2)	125 (10)
···O(8)	2·34 (9)		···O(6)	127 (10)
			O(5)–H(2)···O(7)	143 (9)
			···O(8)	138 (10)
H(3)–O(1)	0·71 (8)		O(1)···O(2)	3·085 (5)
···O(2)	2·56 (7)		···O(5)	3·210 (6)
···O(5)	2·60 (7)		O(1)···O(6)	2·733 (5)
H(4)–O(1)	1·05 (7)		O(1)–H(3)···O(2)	134 (7)
···O(6)	1·74 (7)		···O(5)	146 (7)
			O(1)–H(4)···O(6)	157 (6)

bond. Also, the distances O(5)···O(7) and O(5)···O(8) are 3·058 and 2·939 Å, O(5)···O(2) and O(5)···O(6) are 2·999 and 2·926 Å, and O(1)···O(2) and O(1)···O(5) are 3·085 and 3·210 Å, indicating the existence of bifurcated hydrogen bonds (Abbona *et al.*, 1979). However, the O(1)···O(2) and O(1)···O(5) distances are somewhat too long for hydrogen bonds, and H(3) may be located at a position to minimize the cation–proton repulsion rather than to form hydrogen bonds (Mathew & Schroeder, 1979).

The values of bond strengths around all the atoms (except H atoms) were calculated according to the method of Brown & Wu (1976). The results are satisfactory for P and Mg atoms.

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