Acta Cryst. (1998). C**54**, 702–703

$Mg(H_2PO_4)_2.4H_2O$

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(*Received 4 August 1997; accepted 6 January 1998*)

Abstract

Magnesium bis(dihydrogenorthophosphate) tetrahydrate contains four-membered rings made up of two $[PO_4]$ tetrahedra and two $[MgO_6]$ octahedra sharing corners. These rings are joined through the $[MgO_6]$ octahedra and are alternately twisted by approximately 90° to form an infinite linear chain.

Comment

The crystal structure and dehydration of magnesium bis(dihydrogenorthophosphate) dihydrate, $Mg(H_2PO_4)_2.2H_2O$, have been reported in several papers (Shpunt *et al.*, 1950; Kinoshita *et al.*, 1981). In contrast, although the dehydration process of the title compound, magnesium bis(dihydrogenorthophosphate) tetrahydrate, has been investigated by X-ray diffraction (Itatani *et al.*, 1986), its crystal structure has not been clarified.

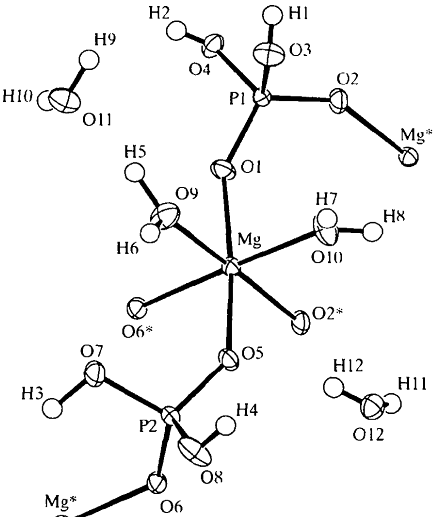

Fig. 1. *ORTEP*II (Johnson, 1976) illustration of the molecular geometry of the title compound indicating the atom labeling. Displacement ellipsoids are drawn at the 50% probability level. Starred (*) atoms have symmetry codes as shown in Table 1.

The basic unit of the title compound is shown in Fig. 1. The structure consists of one $[MgO_6]$ octahedron, two $[PO_4]$ tetrahedra, and two bonding and non-bonding water molecules. The $[MgO_6]$ octahedra are constructed by four corner-sharing $[PO_4]$ tetrahedra and two water molecules, which are in *cis* positions, and are slightly distorted [Mg—O 2.0359 (9)–2.1346 (7) Å and O—Mg—O 85.46 (4)–96.97 (4)°]. Two O atoms of the $[PO_4]$ tetrahedra are bonded to H atoms and the others are bonded to the Mg atoms. The P—O(H) bond lengths [1.5653 (10)–1.5783 (9) Å] are longer than the P—O(Mg) bond lengths [1.4904 (7)–1.5077 (8) Å]. Consequently, the $[PO_4]$ tetrahedra are distorted [O—P—O 105.04 (4)–117.44 (5)°].

The packing is shown in Fig. 2. The $[MgO_6]$ octahedra and $[PO_4]$ tetrahedra are linked by the apical O atoms, forming four-membered rings [O···O 2.551 (1)–2.986 (1) Å]. These rings are joined through the $[MgO_6]$ octahedra and are alternately twisted by approximately 90° to form an infinite linear chain. The non-bonding water molecules are situated between these chains.

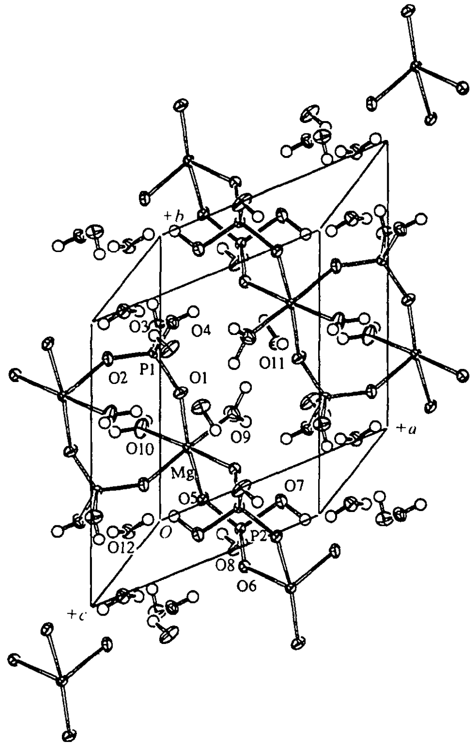

Fig. 2. *ORTEP*II (Johnson, 1976) illustration of the unit cell. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The synthesis and thermal condensation reaction of the title compound have been reported previously (Matsuda *et al.*, 1994). Colorless single crystals of $Mg(H_2PO_4)_2.4H_2O$ were grown from a saturated aqueous solution of H_3PO_4/MgO in the molar ratio 2.3:1.

Crystal data

$Mg(H_2PO_4)_2.4H_2O$
$M_r = 290.3$
Triclinic
$P\bar{1}$
$a = 7.791\,(1)$ Å
$b = 9.197\,(1)$ Å
$c = 7.688\,(1)$ Å
$\alpha = 95.31\,(1)^\circ$
$\beta = 107.04\,(1)^\circ$
$\gamma = 66.98\,(1)^\circ$
$V = 484.6\,(1)$ Å^3
$Z = 2$
$D_x = 1.990$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 22.3$–22.5°
$\mu = 0.570$ mm^{-1}
$T = 300$ K
Spherical
0.175 mm (radius)
Colorless

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: spherical (*TEXSAN*; Molecular Structure Corporation, 1992)
$T_{\rm min} = 0.862$, $T_{\rm max} = 0.862$
4544 measured reflections
4287 independent reflections

3629 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.012$
$\theta_{\rm max} = 35^\circ$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -12 \rightarrow 0$
4 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.022$
$wR = 0.033$
$S = 1.88$
3629 reflections
185 parameters
All H atoms refined
$w = 4F_o^2/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\rm max} = 0.12$ (see below)

$\Delta\rho_{\rm max} = 0.49$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.39$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 3.0386×10^{-5}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Mg—O1	2.0359 (9)	P1—O2	1.5041 (9)
Mg—O2$^{\rm i}$	2.0669 (10)	P1—O3	1.5748 (9)
Mg—O5	2.0782 (8)	P1—O4	1.5783 (9)
Mg—O6$^{\rm ii}$	2.1346 (7)	P2—O5	1.4987 (7)
Mg—O9	2.0748 (10)	P2—O6	1.5077 (8)
Mg—O10	2.0977 (8)	P2—O7	1.5653 (10)
P1—O1	1.4904 (7)	P2—O8	1.5752 (8)
O1—Mg—O2$^{\rm i}$	96.97 (4)	O1—P1—O2	116.81 (5)
O1—Mg—O6$^{\rm ii}$	88.84 (3)	O1—P1—O3	108.48 (4)
O1—Mg—O9	87.28 (4)	O1—P1—O4	110.71 (4)
O1—Mg—O10	92.23 (4)	O2—P1—O3	109.46 (4)
O2$^{\rm i}$—Mg—O5	90.33 (4)	O2—P1—O4	105.04 (4)
O2$^{\rm i}$—Mg—O6$^{\rm ii}$	88.49 (3)	O3—P1—O4	105.78 (5)
O2$^{\rm i}$—Mg—O10	90.27 (4)	O5—P2—O6	117.44 (5)
O5—Mg—O6$^{\rm ii}$	90.27 (3)	O5—P2—O7	108.77 (5)
O5—Mg—O9	85.46 (4)	O5—P2—O8	108.41 (4)
O5—Mg—O10	88.81 (3)	O6—P2—O7	109.03 (4)
O6$^{\rm ii}$—Mg—O9	93.36 (3)	O6—P2 O8	106.40 (5)
O9—Mg—O10	87.81 (4)	O7—P2—O8	106.23 (5)

Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $1 - x, -y, 1 - z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H1$\cdots$O12$^{\rm i}$	0.73 (3)	1.98 (3)	2.695 (1)	170 (3)
O4—H2$\cdots$O6$^{\rm i}$	0.74 (2)	1.91 (3)	2.648 (1)	175 (2)
O7—H3$\cdots$O2$^{\rm ii}$	1.00 (2)	1.65 (2)	2.623 (1)	165 (2)
O8—H4$\cdots$O12$^{\rm iii}$	0.79 (2)	1.83 (2)	2.602 (1)	165 (2)
O9—H5$\cdots$O11	0.97 (2)	1.80 (3)	2.760 (1)	170 (1)
O9—H6	0.79 (2)			
O10—H7$\cdots$O3$^{\rm iv}$	0.93 (3)	1.99 (2)	2.864 (1)	158 (2)
O10—H8$\cdots$O11$^{\rm v}$	0.85 (3)	2.03 (3)	2.874 (1)	174 (3)
O11—H9$\cdots$O8$^{\rm i}$	0.85 (2)	1.99 (2)	2.813 (1)	163 (2)
O11—H10$\cdots$O1$^{\rm vi}$	0.87 (2)	1.92 (2)	2.773 (1)	166 (2)
O12—H11$\cdots$O4$^{\rm vii}$	0.78 (2)	2.03 (2)	2.800 (1)	169 (2)
O12—H12$\cdots$O5	0.77 (3)	1.94 (2)	2.700 (1)	168 (2)

Symmetry codes: (i) $x, 1 + y, z$; (ii) $1 + x, y - 1, z$; (iii) $-x, -y, -z$; (iv) $-x, 1 - y, -z$; (v) $x - 1, y, z$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $-x, 1 - y, 1 - z$.

The non-H atoms were refined with anisotropic displacement parameters. H atoms, located by difference Fourier synthesis, were refined with isotropic displacement parameters. The ratios of the refinement shift to s.u. of the H atoms in the final cycle were larger than those of the non-H atoms; the maximum was 0.12 for the y parameter of the H10 atom. These were not considered to be attributable to unaccounted-for disorder or correlation between parameters, because the s.u.'s of the H atoms were small; moreover, the ratios of the refinement shift to s.u. of the non-H atoms in the final cycle were found to be less than 0.001.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *DIRDIF*92 (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

We are grateful to Dr Masanobu Izaki of Osaka Municipal Technical Research Institute, Japan, for enlightening discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OH1110). Services for accessing these data are described at the back of the journal.

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