

Ta3—Ta1	3.290 (1) × 2	Ta2—Ta1	3.298 (1)
Ta3—Ta1	3.096 (1) × 2	Ta2—Ta1	3.238 (1)
Ta3—Ta1	3.158 (1) × 2	Ta2—Ta1	3.062 (1)
Ta3—Ta2	3.046 (1) × 2	Ta2—Ta2	3.217 (1) × 2
Ta1—Ta1	2.872 (1)		
Ch1—Ta1	2.472 (2)	Ch2—Ta1	2.492 (2)
Ch1—Ta2	2.495 (2)	Ch2—Ta2	2.455 (2)
Ch1—Ta2	2.529 (2)	Ch2—Ta3	2.489 (3)
Ch1—Ta2	2.709 (2)	Ch2—Ta1	2.547 (2)

Structure refinement on the basis of intensities that had been corrected for absorption using only ψ -scan data (*SDP-Plus*; B. A. Frenz & Associates Inc., 1984) led to $R[F^2 > 3\sigma(F^2)] = 0.039$; calculations on intensities corrected only by *DIFABS* (Walker & Stuart, 1983) led to $R[F^2 > 3\sigma(F^2)] = 0.025$. In order to obtain improved structural data, intensities were corrected via ψ scans before applying the correction based on ΔF . This refinement converged at $R[F^2 > 3\sigma(F^2)] = 0.024$. The same correction procedures were applied in the refinements using the program *SHELXL93* (Sheldrick, 1993), which allowed twinning by inversion to be taken into account; this resulted in a decrease in the R values by about 0.003. Differences in the R values are due to the different $n\sigma(F^2)$ limits. The differences in the final positional parameters resulting from the different refinements were within the limits of the e.s.d.'s. The ratio T_{\max}/T_{\min} is in accord with a difference of 0.012 mm between the lengths of the two orthogonal edges perpendicular to the needle axis. Flack's absolute structure parameter (Flack, 1983) converged at 0.60 (3).

Data collection: Enraf-Nonius CAD-4 diffractometer software. Cell refinement: Enraf-Nonius CAD-4 diffractometer software. Data reduction: *SDP-Plus*. Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *SCHAKAL92* (Keller, 1992).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: SE1065). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Synthetic Magnesium Sodium Hydrogen Monophosphate: MgNa₃H(PO₄)₂

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Abstract

The structure belongs to the monophosphate group and contains one type of PO₄ tetrahedra connected to one type of MgO₆ octahedra by corner sharing. These PO₄–MgO₆ groups are connected along the two shorter a and b axes to form two-dimensional zigzag sheets. Two sheets are connected along the longer c axis by two types of Na–O polyhedra. Pairs of PO₄ tetrahedra in the sheets are connected by H atoms situated at the centres of symmetry, forming short hydrogen bonds.

Comment

This research was started with the purpose of contributing to the understanding of the structures of monophosphates. In previous structural studies of magnesium sodium monophosphates, Ghorbel, d'Yvoire & Dorémieux-Morin (1974) carried out the syntheses of three compounds: MgNa₄(PO₄)₂·H₂O and α - and γ -MgNa₄(PO₄)₂. The structural relationships of these three compounds were investigated by means of X-ray powder diffractometry. Ben Amara, Vlasse, Olazcuaga, Le Flem & Hagenmuller (1983) have determined the structure of Mg₄Na(PO₄)₃. Approximate cell dimensions of MgNa₃H(PO₄)₂ have been determined by the National Bureau of Standards (Morris & MacMundy, 1984) and the space group was described as $P1$. A study on the same compound by X-ray powder method was reported by Ben Amor & Romdhane (1992). They assigned space group $C2/m$ to this compound. No further structural studies of this compound have been reported to date. The present study describes the synthesis and the structure determination of this compound.

The mean Mg–O distance is 2.095 Å [*cf.* 2.023, 2.076 and 2.080 Å reported by Ben Amara *et al.* (1983), and 2.102, 2.026 and 2.120 Å reported by Yamakawa, Yamada & Kawahara (1994)]. The mean P–O distance is 1.537 Å, which is compatible with the P–O distances found previously [1.526, 1.538 and 1.538 Å found by Ben Amara *et al.* (1983), 1.538 and 1.535 Å by Yamakawa *et al.* (1994) and 1.536 Å by Corbridge (1971)]. The interatomic distance of the short

hydrogen bonds ($O \cdots O$ 2.442 Å) is compatible with those reported previously, including those of organic compounds [2.43–2.56 Å (Misaki, 1988)].

A stereographic view of the structure is presented in Fig. 1 (Johnson, 1971). A representation of the whole structure, including the PO_4 tetrahedra, is shown in Fig. 2 (Dowty, 1992).

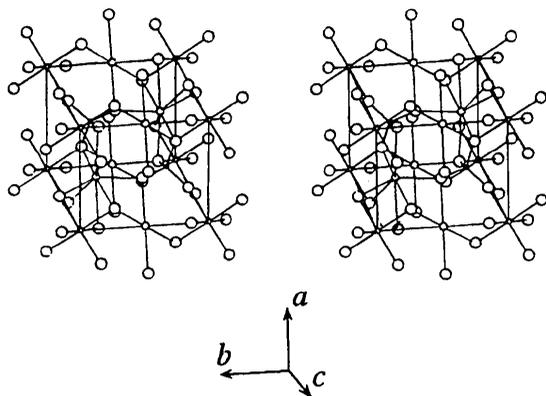


Fig. 1. Stereographic view of $MgNa_3H(PO_4)_2$. (ORTEP; Johnson, 1971).

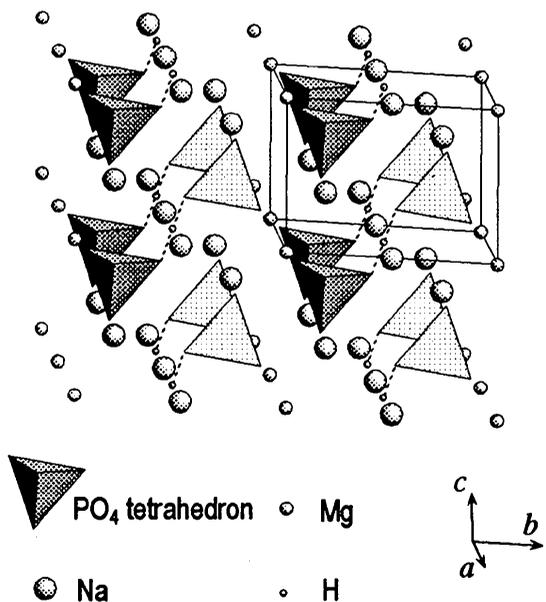


Fig. 2. Representation of the whole structure including the PO_4 tetrahedra and the positions of the H atoms. The short hydrogen bonds are drawn as dotted lines (ATOMS; Dowty, 1992).

Experimental

The synthesis of the title compound was carried out by mixing Na_2HPO_4 , $MgSO_4 \cdot 7H_2O$ and $MgCO_3$, with a molecular ratio of 1:1:2, as starting materials. 100 mg amounts of the starting materials were sealed in silver tubes of 3 mm diameter and

50 mm length. The silver tubes were put into an autoclave and heated at 673 K and 100 MPa for 72 h. After this thermal treatment, the autoclave was cooled at a rate of 1 K every 20 min. The crystals obtained were washed with pure water. The chemical composition was determined as $MgNa_3H(PO_4)_2$ by the use of electron probe microanalyses (Jeol JXA).

Crystal data

$MgNa_3H(PO_4)_2$
 $M_r = 284.23$
 Triclinic
 $P\bar{1}$
 $a = 5.230(3)$ Å
 $b = 6.822(1)$ Å
 $c = 5.175(2)$ Å
 $\alpha = 91.54(2)^\circ$
 $\beta = 117.51(3)^\circ$
 $\gamma = 90.46(3)^\circ$
 $V = 163.7(1)$ Å³
 $Z = 1$
 $D_x = 2.884$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å
 Cell parameters from 25 reflections
 $\theta = 24.53$ – 24.93°
 $\mu = 0.992$ mm⁻¹
 $T = 293$ K
 Prism
 $0.03 \times 0.02 \times 0.02$ mm
 Colourless

Data collection

Rigaku AFC-5R diffractometer
 ω -scans
 Absorption correction:
 ψ scans (ABSC; Takano, Tanaka & Kusunoki, 1973)
 $T_{min} = 0.95$, $T_{max} = 0.98$
 841 measured reflections
 841 independent reflections

779 observed reflections
 $[F > 3\sigma(F)]$
 $\theta_{max} = 27.5^\circ$
 $h = 0 \rightarrow 6$
 $k = -8 \rightarrow 8$
 $l = -6 \rightarrow 5$
 3 standard reflections monitored every 150 reflections
 intensity decay: none

Refinement

Refinement on F
 $R = 0.026$
 $wR = 0.033$
 $S = 2.34$
 779 reflections
 82 parameters
 H-atom position determined from ΔF syntheses and confirmed by calculation of the sum of electrostatic charges around connected O atoms (Brown & Wu, 1976)

Unit weights applied
 $(\Delta/\sigma)_{max} = 0.41$
 $\Delta\rho_{max} = 0.45$ e Å⁻³
 $\Delta\rho_{min} = -0.61$ e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	x	y	z	B_{eq}
Na(1)	0.7000 (3)	0.2086 (2)	0.3355 (2)	1.29 (2)
Na(2)	0	1/2	0	1.35 (1)
Mg	0	0	0	1.33 (7)
P	0.6469 (1)	0.7562 (1)	0.3396 (1)	0.31 (4)
O(1)	0.7854 (4)	0.8943 (3)	0.2127 (4)	0.90 (14)
O(2)	0.3226 (4)	0.7919 (3)	0.2125 (4)	0.69 (13)
O(3)	0.6834 (4)	0.5415 (3)	0.2487 (4)	0.80 (14)
O(4)	0.2039 (4)	0.2247 (3)	0.3277 (4)	0.63 (13)
H	1/2	1/2	0	

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

Table 2. Selected geometric parameters (Å, °)

Na(1)—O(1 ⁱ)	2.325 (4)	Na(2)—O(4 ^{vi})	2.464 (1)
Na(1)—O(1 ⁱⁱ)	2.863 (3)	Mg—O(1 ⁱⁱ)	2.040 (3)
Na(1)—O(1 ⁱⁱⁱ)	2.740 (4)	Mg—O(1 ^{viii})	2.040 (3)
Na(1)—O(2 ⁱⁱ)	2.782 (4)	Mg—O(2 ⁱ)	2.117 (3)
Na(1)—O(2 ^{iv})	2.395 (3)	Mg—O(2 ^{vi})	2.117 (3)
Na(1)—O(3)	2.321 (4)	Mg—O(4)	2.127 (2)
Na(1)—O(4)	2.579 (3)	Mg—O(4 ^{ix})	2.127 (2)
Na(1)—O(4 ^v)	2.656 (3)	P—O(1)	1.518 (3)
Na(2)—O(2)	2.477 (1)	P—O(2)	1.534 (2)
Na(2)—O(2 ^{vi})	2.477 (1)	P—O(3)	1.566 (2)
Na(2)—O(3 ⁱⁱ)	2.537 (2)	P—O(4 ^{iv})	1.528 (2)
Na(2)—O(3 ^{vii})	2.537 (2)	H—O(3)	1.221 (2)
Na(2)—O(4)	2.464 (1)		
O(1 ⁱⁱ)—Mg—O(2 ^{vi})	88.5 (1)	O(1)—P—O(4 ^{iv})	111.0 (3)
O(1 ^{viii})—Mg—O(4 ^{ix})	88.8 (1)	O(2)—P—O(3)	107.6 (3)
O(2 ^{vi})—Mg—O(4)	85.4 (1)	O(2)—P—O(4 ^{iv})	111.2 (1)
O(1)—P—O(2)	110.9 (3)	O(3)—P—O(4 ^{iv})	108.4 (3)
O(1)—P—O(3)	107.7 (2)		

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

The intensities of the reflections were measured at the X-ray laboratory of Okayama University, Japan. Data collection, cell refinement and data reduction: *AFC/MSD Diffractometer Control Program* (Rigaku Corporation, 1991). Structure solution: *TEXSAN* (Molecular Structure Corporation, 1985). Structure refinement: *RSFLS4* (Sakurai, 1971). Geometric calculations: *CCPC* (Kawamura & Kawahara, 1980). Molecular graphics: *ORTEP* (Johnson, 1971), *ATOMS* (Dowty, 1992). Preparation of material for archive: *LISTHKL* (Yamakawa & Kawahara, 1994).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: OH1084). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Caesium Lithium Borate: a New Nonlinear Optical Crystal

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Abstract

The structure of the title compound, CsLiB₆O₁₀, comprises eight-coordinate Cs atoms and four-coordinate Li atoms, and an anion network of chains formed from B₃O₇ groups. The Cs and Li atoms occupy alternate sites in the channel along the *c* axis.

Comment

Borate crystals are of interest for the generation of coherent UV light because of their superior nonlinear optical properties. Various nonlinear optical borate crystals [β -BaB₂O₄ (BBO) (Chen, Wu, Jiang & You, 1985), LiB₃O₅ (LBO) (Chen *et al.*, 1989) and CsB₃O₅ (CBO) (Wu *et al.*, 1993)] have been found to date. Recently, we discovered a new borate crystal, CsLiB₆O₁₀ (CLBO) (Sasaki *et al.*, 1995; Mori, Kuroda, Nakajima, Sasaki & Nakai, 1995), which has a different space group (*I*42*d*) compared with LBO (*Pna*2₁) and CBO (*P2*₁2₁2₁). CLBO, LBO and CBO contain the same basic unit in the borate network. It consists of a six-membered ring in which two of the B atoms are threefold coordinated and the third B atom is fourfold coordinated by O atoms. The borate network of CLBO surrounds eight-coordinate Cs atoms and four-coordinate Li atoms.