

## Structure and $^{31}\text{P}$ NMR spectroscopy of a new phosphate, $\text{Na}_8\text{Ca}_{1.5}\text{Mg}_{12.5}(\text{PO}_4)_{12}$

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A new phosphate, sodium calcium magnesium tetrakis(phosphate),  $\text{Na}_8\text{Ca}_{1.5}\text{Mg}_{12.5}(\text{PO}_4)_{12}$ , has been synthesized by a flux method. Its novel structure consists of  $\text{MgO}_x$  ( $x = 5$  and 6) polyhedra and  $\text{MO}_7$  ( $M = \text{Mg}$  or  $\text{Na}$ ) octahedra linked directly through common corners or edges to form a rigid three-dimensional skeleton, reinforced by corner-sharing between identical  $\text{Mg}_{12}\text{MO}_{48}$  units. The connection of these units by the  $\text{PO}_4$  tetrahedra induces cavities and crossing tunnels where the  $\text{Na}^+$  and  $\text{Ca}^{2+}$  cations are located. This structural model was supported by a  $^{31}\text{P}$  NMR spectroscopy study which confirmed the existence of 12 crystallographically independent sites for the P atoms.

### Comment

Alkaline and alkaline earth monophosphates have attracted much attention for their excellent physical properties, high chemical stability and environmentally friendly attributes, offering a wide range of applications in the fields of optics, magnetism and ionic conductivity (Kanazawa & Kodansha, 1989; Blasse & Grabmaier, 1994; Goodenough *et al.*, 1976). In the Na–Mg–Ca–P–O system, only four monophosphates have been described to date. The brianite  $\text{Na}_2\text{MgCa}(\text{PO}_4)_2$  crystallizes in the monoclinic system in the space group  $P2_1/c$  (Fuchs *et al.*, 1967). An isomorphism with the mineral merwinite,  $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ , was reported by Moore (1975) and confirmed by Alkemper & Fuess (1998), who also demonstrated the existence of a reversible phase transition at 808 (5) K. The other three compounds,  $\text{Na}_{18}\text{Ca}_{13}\text{Mg}_5(\text{PO}_4)_{18}$  (Alkemper & Fuess, 1998),  $\text{Na}_4\text{Ca}_4\text{Mg}_{21}(\text{PO}_4)_{18}$  (Domanskii *et al.*, 1982) and  $\text{NaCa}_9\text{Mg}(\text{PO}_4)_7$  (Morozov *et al.*, 1997), have trigonal symmetries in the space groups  $R\bar{3}m$ ,  $R\bar{3}$  and  $R3c$ , respectively.

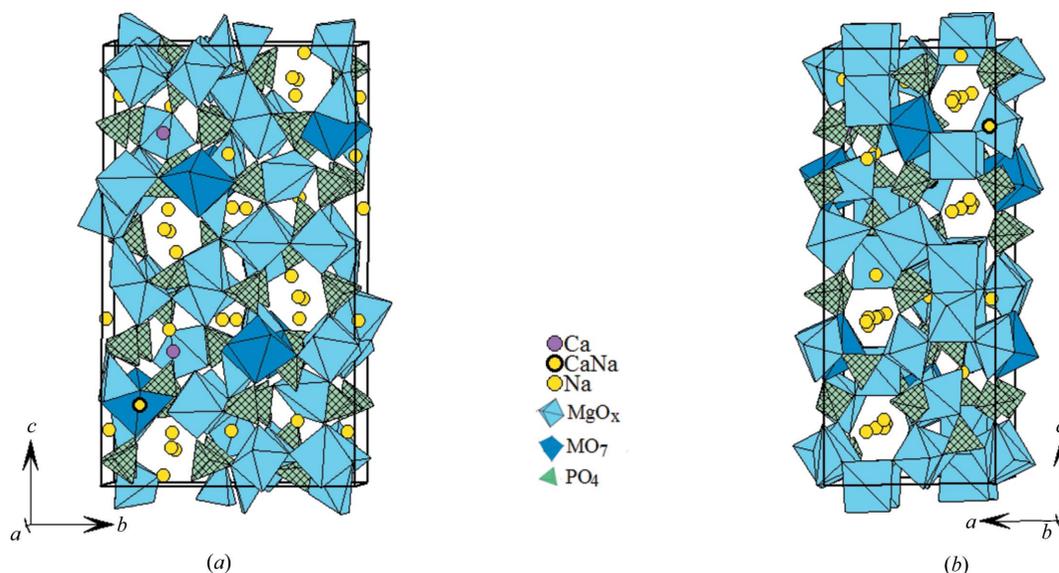
As a contribution to the investigation of the above system, we report here the structural characterization of the new title compound,  $\text{Na}_8\text{Ca}_{1.5}\text{Mg}_{12.5}(\text{PO}_4)_{12}$ , which was isolated as

single crystals during an attempt to crystallize  $\text{Na}_2\text{CaMg}_7(\text{PO}_4)_6$  using the flux method. The cell parameters resemble those reported for the mineral panethite,  $(\text{Na,K,Ca})_{1.76}(\text{Mg,Fe,Mn})_{1.98}(\text{PO}_4)_2$  (Fuchs *et al.*, 1967), and the so-called ‘X phase’ of Hatert *et al.* (2006). Nevertheless, the existence of structural relationships with these phases cannot be proved because their structures have not yet been described.

Projections of the structure of  $\text{Na}_8\text{Ca}_{1.5}\text{Mg}_{12.5}(\text{PO}_4)_{12}$  along  $a$  and  $b$  (Figs. 1*a* and 1*b*) show that the three-dimensional framework is constructed by  $\text{MgO}_x$  ( $x = 5$  or 6) and  $\text{MO}_7$  ( $M = \text{Na}$  or  $\text{Mg}$ ) octahedra and  $\text{PO}_4$  tetrahedra, which form cavities and intersecting tunnels occupied by  $\text{Na}^+$  cations. Although the framework is highly complex, it can be easily envisaged by considering that all the Mg and  $M$  polyhedra are linked directly by sharing either corners or edges to form a rigid skeleton, which can be described as formed by the connection of identical  $\text{Mg}_{12}\text{MO}_{48}$  units. Each of these units (Fig. 2) consists of two segments of four edge-sharing polyhedra. The first is made up of three  $\text{MgO}_6$  octahedra and one  $\text{MgO}_5$  trigonal bipyramid, while the second is formed by two  $\text{MgO}_5$  trigonal bipyramids, one  $\text{MgO}_6$  octahedron and one  $\text{MO}_7$  polyhedron. Adjacent segments are coupled through common corners of their polyhedra, giving rise to an  $\text{Mg}_7\text{MO}_{32}$  octanuclear cycle. This cycle is bridged on one side by an  $\text{Mg}_2\text{O}_9$  unit of edge-sharing  $\text{MgO}_5$  and  $\text{MgO}_6$  polyhedra, and on the opposite side is connected to one  $\text{Mg}_3\text{O}_{15}$  unit consisting of one  $\text{MgO}_6$  and two  $\text{MgO}_5$  polyhedra, linked by corner-sharing with a Y shape. The space formed by the Mg/ $M$ /O network is filled by the  $\text{PO}_4$  tetrahedra, and the resulting framework delimits both cavities and intersecting tunnels, containing a distribution of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  cations.

There are 12 distinct Mg sites, labelled  $\text{Mg}_i$  ( $i = 1\text{--}11, 13$ ). Site  $\text{Mg}_1$  is [4+1]-coordinated, with four short  $\text{Mg}_1\text{--O}$  distances [1.934 (3)–1.991 (3) Å] and a fifth longer distance of 2.588 (3) Å. The average value of 1.963 (3) Å calculated from the four short distances is consistent with 1.93 (2) Å reported for the tetrahedral  $\text{Mg}^{2+}$  cation in  $\text{KMgPO}_4$  (Wallez *et al.*, 1998). Sites  $\text{Mg}_2\text{--Mg}_6$  are five-coordinated, with  $\text{Mg}\text{--O}$  distances in the range 1.915 (6)–2.143 (3) Å. The corresponding average values are close to those reported by Jaulmes *et al.* (1997) for the same cation with similar coordination. Sites  $\text{Mg}_7$  and  $\text{Mg}_8$  are [5+1]-coordinated, with  $\text{Mg}\text{--O}$  distances in the range 1.993 (3)–2.707 (4) Å for  $\text{Mg}_7$  and 2.043 (3)–2.504 (4) Å for  $\text{Mg}_8$ . Sites  $\text{Mg}_9\text{--Mg}_{11}$  and  $\text{Mg}_{13}$  are six-coordinated, with  $\text{Mg}\text{--O}$  distances in the range 2.002 (3)–2.299 (3) Å, leading to average values consistent with those observed for octahedral  $\text{Mg}^{2+}$  cations (Jaulmes *et al.*, 1997). The  $M_{12}$  site is statistically occupied by Mg and Na, with partial occupancy 0.5:0.5. This site has a [6+1] coordination, with six short distances between 2.045 (3) and 2.291 (3) Å and a long distance of 2.647 (4) Å. The mean distance of 2.266 (4) Å agrees with that of 2.23 (3) Å reported for the disordered octahedral (Mg,Na) site in the molybdate  $\text{Na}_2\text{Mg}_5(\text{MoO}_4)_6$  (Klevtsova *et al.*, 1980).

The  $\text{PO}_4$  tetrahedra are rather regular, with classical P–O distances (Baur, 1974) except for  $\text{P9O}_4$ , for which the

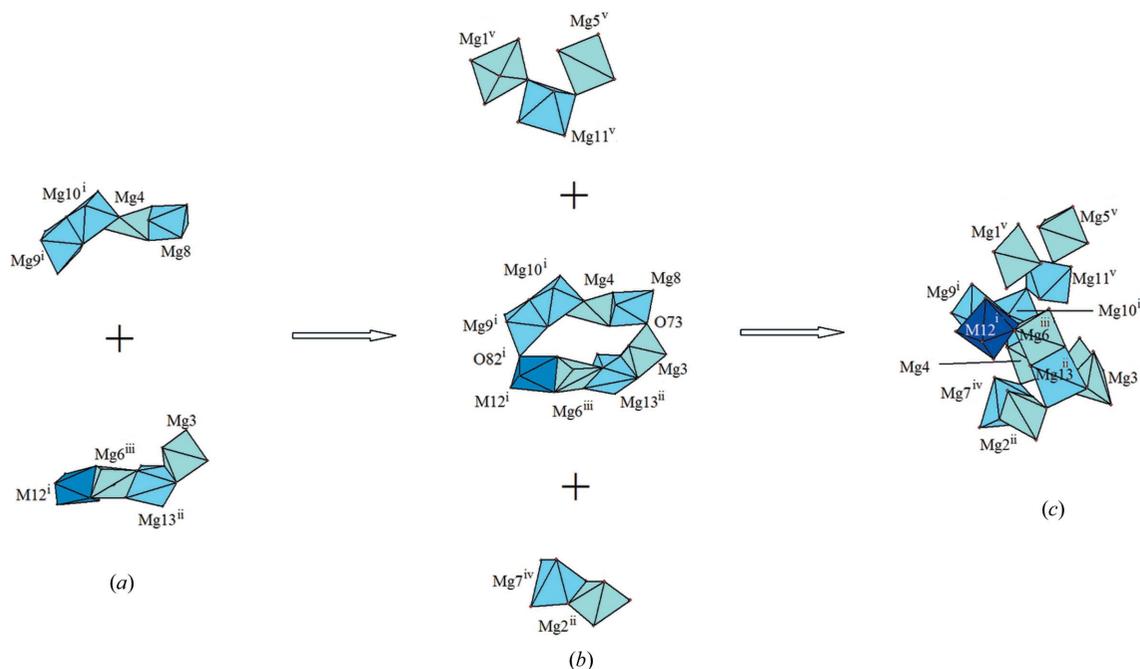


**Figure 1**  
Projections of the  $\text{Na}_8\text{Ca}_{1.5}\text{Mg}_{12.5}(\text{PO}_4)_{12}$  structure (a) along *a* and (b) along *b*.

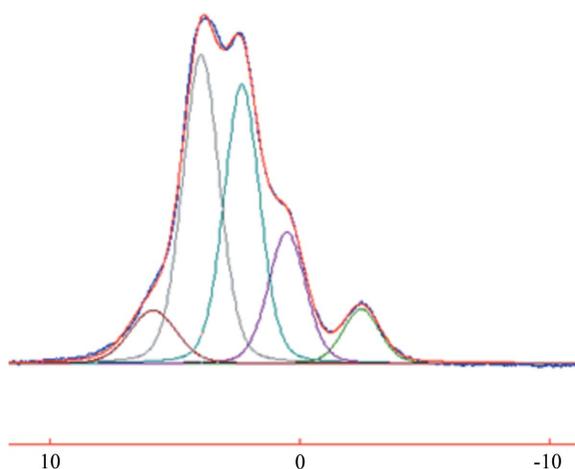
observed strong distortion can be explained by the disordered of atoms O93 and O94 over two positions (O93A and O93B, and O94A and O94B) which cannot be occupied simultaneously due to their short distance. This disorder leads to four different orientations of the  $\text{P9O}_4$  tetrahedron which occur statistically.

The environments of the seven crystallographically distinct pure Na sites were determined assuming a maximum cation–oxygen distance  $L_{\text{max}} = 3.13 \text{ \AA}$ , as suggested by Donnay & Allmann (1970). The Na1 environment then consists of five O atoms, with Na–O distances varying from 2.186 (3) to 2.499 (3)  $\text{ \AA}$ . That of Na2 is formed by eight O atoms, with

Na–O distances in the range 2.270 (8)–3.001 (4)  $\text{ \AA}$ . Sites Na4, Na5 and Na7 are bonded to seven O atoms, with Na–O distances between 2.245 (7) and 2.861 (4)  $\text{ \AA}$ . Each of the Na3 and Na6 atoms is distributed over two sites (Na3A and Na3B, and Na6A and Na6B) having a sum occupancy of 1. Most of the Na atoms are found in the *A*-type positions, with a [7] coordination and Na–O distances in the range 2.211 (3)–2.988 (4)  $\text{ \AA}$  for Na3A and 2.455 (3)–2.963 (3)  $\text{ \AA}$  for Na6A. The *B* positions, containing small fractions of Na, have sevenfold coordination for Na3B and sixfold coordination for Na6B, with Na–O distances in the ranges 2.234 (8)–2.992 (8) and 2.34 (2)–2.92 (2)  $\text{ \AA}$ , respectively.



**Figure 2**  
A depiction of the construction of the structure: (a) the two segments of four edge-sharing polyhedra; (b) the  $\text{Mg}_7\text{MO}_{32}$  octanuclear loop; (c) the entire  $\text{Mg}_{12}\text{MO}_{48}$  unit. [Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$ ; (ii)  $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-x, -y + 2, -z$ ; (iv)  $x - 1, y, z$ ; (v)  $-x, -y + 1, -z$ .]



**Figure 3**  
The observed  $^{31}\text{P}$  NMR spectrum and its deconvolution.

The  $\text{Ca}^{2+}$  cations are distributed over two distinct sites. Site Ca1 is exclusively occupied by  $\text{Ca}^{2+}$ , being coordinated by eight O atoms with Ca–O distances in the range 2.373 (3)–2.792 (3) Å. The (Ca8,Na8) site is statistically occupied by  $\text{Na}^+$  and  $\text{Ca}^{2+}$ . These cations have identical occupancies of 0.5:0.5 and slightly different positions. Both are seven-coordinated, with cation–oxygen distances in the range 2.245 (4)–2.536 (4) Å for Ca and 2.268 (11)–2.616 (11) Å for Na.

A bond-valence sum (BVS) calculation was performed using the empirical values of Brown & Altermatt (1985). The calculated BVS for all the anionic and cationic sites are consistent with their formal charges. In particular, the values obtained for the (Ca8,Na8) and M12 sites (1.65 and 1.63, respectively) confirm the disorder within these sites.

The  $^{31}\text{P}$  NMR spectrum (Fig. 3) consists of a dissymmetric and too-broad signal arising from the overlap of many sites. It could be fitted by five resonance peaks with chemical shifts of 5.86, 3.39, 2.29, 0.49 and  $-2.48$  p.p.m., in agreement with the values found in other monophosphates (Benmokhtar *et al.*, 2007; Turner *et al.*, 1986). These peaks could be integrated in a ratio of 1:4:4:2:1, leading to 12 resonances, in accordance with the 12 crystallographically distinct P sites in the structure.

## Experimental

$\text{Na}_8\text{Ca}_{1.5}\text{Mg}_{12.5}(\text{PO}_4)_{12}$  was extracted from a mixture of nominal composition  $\text{Na}_2\text{CaMg}_7(\text{PO}_4)_6$ , prepared in a flux of sodium molybdate,  $\text{Na}_2\text{MoO}_4$ , with a P:Mo atomic ratio of 2:1. Appropriate amounts of the starting reactants  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$  and  $\text{Na}_2\text{MoO}_4$  were homogenized by grinding in an agate mortar, and subsequently heated in a platinum crucible for 24 h at 673 K and then for 12 h at 873 K. After being reground, the sample was melted for 2 h at 1273 K and then cooled slowly to 773 K at  $10\text{ K h}^{-1}$ , after which time the furnace was turned off. The solidified melt was washed with boiling water to dissolve the flux. From the mixture, colourless and irregularly shaped crystals were extracted. ICP analysis indicated the presence of Na, Ca, Mg and P in an approximate atomic ratio of 7.9 (2):1.5 (1):13.5 (3):12.0 (2), in accordance with the  $\text{Na}_8\text{Ca}_{1.5}\text{Mg}_{12.5}(\text{PO}_4)_{12}$  composition.

## Crystal data

$\text{Na}_8\text{Ca}_{1.5}\text{Mg}_{12.5}(\text{PO}_4)_{12}$	$V = 3876 (4) \text{ \AA}^3$
$M_r = 1687.56$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 10.185 (8) \text{ \AA}$	$\mu = 1.18 \text{ mm}^{-1}$
$b = 14.860 (8) \text{ \AA}$	$T = 293 \text{ K}$
$c = 25.610 (9) \text{ \AA}$	$0.40 \times 0.11 \times 0.10 \text{ mm}$
$\beta = 90.87 (2)^\circ$	

## Data collection

Enraf–Nonius TurboCAD-4 diffractometer	11269 independent reflections
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	8933 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.75$ , $T_{\max} = 0.89$	$R_{\text{int}} = 0.065$
13798 measured reflections	2 standard reflections every 120 min
	intensity decay: 1%

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$	761 parameters
$wR(F^2) = 0.133$	11 restraints
$S = 1.04$	$\Delta\rho_{\max} = 1.85 \text{ e \AA}^{-3}$
11269 reflections	$\Delta\rho_{\min} = -1.69 \text{ e \AA}^{-3}$

The structure was solved by direct methods (Altomare *et al.*, 1993), which gave one position for the Ca atoms. Subsequent inspection of the difference electron-density maps revealed a second position for the Ca atoms, 13 for Mg, seven for Na, 12 for P and 48 for O. However, three anomalies were revealed: (i) large displacement parameters for the Ca2 atoms; (ii) very long Mg–O distances within the M12 polyhedra; (iii) significant residual electron densities at unusually short distances of 0.813 Å from Na3 and 2.55 Å from Na6.

Taking into account the electrical neutrality of the compound and the result of the ICP analysis, statistical distributions of (0.5Na8 + 0.5Ca8) within the second Ca site and of (0.5Na + 0.5Mg) within the M12 sites were considered. Each of the Na3 and Na6 sites was disordered over two positions, labelled *A* and *B*, having the sum of their occupancies restrained to be equal to 1. These positions cannot be filled simultaneously due to their proximity. The refined site-occupation factors were 0.728 (3), 0.272 (3), 0.913 (3) and 0.087 (3) for atoms Na3A, Na3B, Na6A and Na6B, respectively. Furthermore, disorder of the O atoms around P9 was indicated by the existence of significant residual electron density near atoms O93 and O94. Two positions, labelled *A* and *B*, were modelled for atoms O93 and O94, and the sum of the occupancies of each disordered pair were restrained to be equal to 1. These disordered atoms were refined isotropically and the refined site-occupation factors were 0.647 (3), 0.353 (3), 0.572 (3) and 0.428 (3) for atoms O93A, O93B, O94A and O94B, respectively. In addition, the P9–O92, P9–O93A, P9–O93B, P9–O94A and P9–O94B distances were restrained using a target value of 1.540 (2) Å. Several significant peaks ( $1.11$ – $1.85 \text{ e \AA}^{-3}$ ) of residual electron density remain in the plane of the O92, O93A/B, O94A/B atoms, which suggests that the P9O<sub>4</sub> group is highly disordered by rotation about the P9–O91 bond, but further attempts to model the disorder were not fruitful.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3038). Services for accessing these data are described at the back of the journal.

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