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The alluaudite-like phosphate $Na_{1.79}Mg_{1.79}Fe_{1.21}(PO_4)_3$

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Mg–O) = 0.002 Å
Disorder in main residue
R factor = 0.023
wR factor = 0.071
Data-to-parameter ratio = 10.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title phosphate, $Na_{1.79}Mg_{1.79}Fe_{1.21}(PO_4)_3$ (sodium magnesium iron phosphate), has been prepared as single crystals and its structure determined from X-ray diffraction data. The structure belongs to the alluaudite structure type, characterized by the $X2X1M1M2_2(PO_4)_3$ general formula. The Na^+ ions occupy the large $X2$ and $X1$ sites, the Fe^{3+} ions partially occupy the $M2$ site and the Mg^{2+} ions are distributed over the $M1$ and $M2$ sites.

Comment

Phosphates with the alluaudite structure type (monoclinic *C*2/*c*, *Z* = 4) (Moore, 1971) are studied quite frequently. These materials have the $X2X1M1M2_2(PO_4)_3$ general formula and are known to be highly susceptible to substitution in the *X*2, *X*1, *M*1 and *M*2 sites, which can incorporate a variety of cations with different ionic radii and charges, leading to the formation of solid solutions in large composition domains (Hatert *et al.*, 2000, 2002).

During an investigation of monophosphates belonging to the Na_3PO_4–$Mg_3(PO_4)_2$–$FePO_4$ system, to establish the role of Mg^{2+} in the crystal chemistry of such materials, we have isolated the $Na_{1+x}Mg_{1+x}Fe_{2-x}(PO_4)_3$ (x from 0.5 to 1) alluaudite-like solid solution. The structure with x = 0.79 was determined by X-ray diffraction. This structure, as viewed along the [001] direction, is shown in Fig. 1. It consists of $M2_2O_{10}$ ($M2$ = 0.4Mg2 + 0.6Fe2) units of edge-sharing $M2O_6$

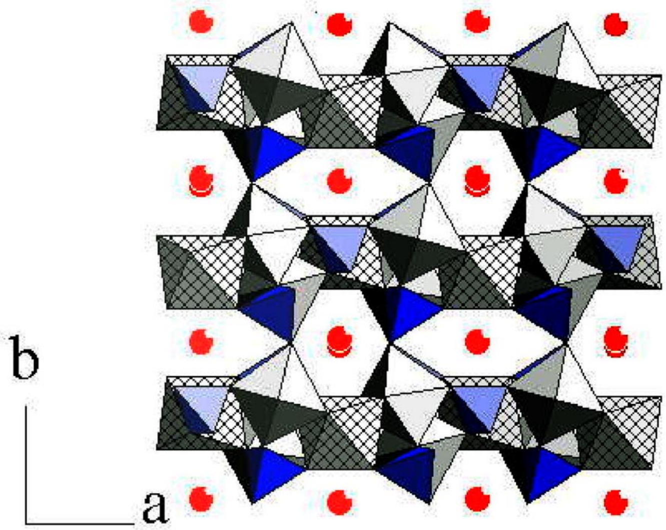

Figure 1
The structure of $Na_{1.79}Mg_{1.79}Fe_{1.21}(PO_4)_3$, viewed along the *c* direction. The $Mg1O_6$ octahedra are illustrated by cross-hatched patterns. The remaining polyhedra are the $M2O_6$ ($M2$ = Fe or Mg) octahedra and PO_4 tetrahedra. The Na^+ cations are represented by solid circles.

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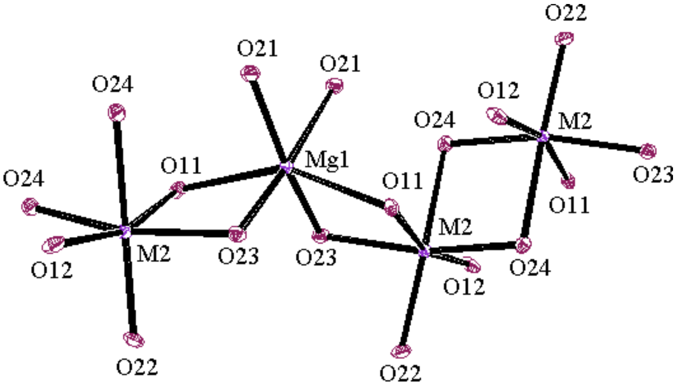

Figure 2
A view of the infinite chains in the title compound. Displacement ellipsoids are drawn at the 50% probability level.

octahedra. These units share opposite edges with $Mg1O_6$ octahedra to form infinite —*M*2—*M*2—Mg1— chains running along the $[10\overline{1}]$ direction (Fig. 2). These chains are linked to similar neighboring chains *via* common corners of $P1O_4$ and $P2O_4$ tetrahedra. The $P1O_4$ tetrahedron connects two chains by sharing each pair of its O atoms with one chain. The $P2O_4$ tetrahedron connects three adjacent chains by sharing two of its O atoms with one chain and the remaining two O atoms with two different chains.

The three-dimensional framework constructed in this way generates two crystallographically independent tunnels running along the *c* axis. These tunnels, located at 0,0,*z* and at $\frac{1}{2}$,0,*z*, respectively, are available for the Na^+ cations.

Table 1 lists the principal bond distances and angles in $Na_{1.79}Mg_{1.79}Fe_{1.21}(PO_4)_3$. The $M2O_6$ octahedron is distorted, as indicated by the *M*2—O bond lengths and O—*M*2—O bond angles. Such distortion can be correlated to the rigidity of the phosphate groups which connect the chains. The $Mg1O_6$ octahedron is more distorted than $M2O_6$. However, the average Mg1—O distance is consistent with those observed in other phosphates containing Mg^{2+} in an octahedral environment (Alkemper & Fuess, 1998).

The interatomic distances in the phosphate tetrahedra are similar to those observed in phosphates without hydrogen bonding (Corbin *et al.*, 1986; Korzenski *et al.*, 1998; Warner *et al.*, 1993). The $P1O_4$ tetrahedron is slightly more regular than $P2O_4$, which is in accordance with the fact that the P1 atom sits on a twofold axis, while atom P2 is located in a general position.

The coordination environment of each sodium ion was determined using Na—O distances less than 3.0 Å. Na1 has a very distorted cubic environment. Each $Na1O_8$ polyhedron shares faces with equivalent polyhedra that form chains in the *c* direction. The Na2 site is partially filled, with an occupation number of 0.79. This site has a strongly irregular environment which consists of four O atoms at short distances and four others at rather long distances.

The structure of $Na_{1.79}Mg_{1.79}Fe_{1.21}(PO_4)_3$ was compared to that of the natural alluaudite from the Buragna pegmatite of Central Africa (Moore, 1971). In spite of numerous similarities, the two compounds are not isostructural, since the cation distribution within the sites in the tunnels is not exactly the same. In fact, in the title compound, the *X*2 site (at 0,~0,0) is partially occupied, while the *X*1 site (at $\frac{1}{2}$,0,0) is totally filled with Na^+ cations. By contrast, the natural alluaudite of Buragna features an *X*1 site partially occupied by Na^+ and Ca^{2+} cations and an empty *X*2 site.

Experimental

Crystals of $Na_{1.79}Mg_{1.79}Fe_{1.21}(PO_4)_3$ were grown in a flux of sodium dimolybdate. Amounts of starting products corresponding to the stoichiometry of the crystals studied [$Fe(NO_3)_3{\cdot}9H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, NaH_2PO_4, $(NH_4)_2HPO_4$ and MoO_3] were mixed and gradually heated up to 873 K to allow the production of ammonia, water and carbon dioxide. After final grinding, the sample was melted for 1 h at 1173 K and then cooled down to room temperature at a rate of 10 K h^{-1}. The crystals, obtained after washing with hot water to remove the flux, were yellow and existed in two forms, parallelepipeds and more elongated crystals.

Crystal data

$Fe_{1.21}Mg_{1.79}Na_{1.79}O_{12}P_3$
$M_r = 437.5$
Monoclinic, $C2/c$
$a = 11.791$ (3) Å
$b = 12.489$ (3) Å
$c = 6.4191$ (10) Å
$\beta = 113.82$ (2)°
$V = 864.7$ (4) Å^3
$Z = 4$
$D_x = 3.36$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 10$–12°
$\mu = 2.93$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, yellow
0.25 × 0.15 × 0.10 mm

Table 1
Selected geometric parameters (Å, °).

Fe2—O12	1.9599 (19)	Na1—O12^{viii}	2.9030 (19)
Fe2—O22^{i}	1.9715 (19)	Na2—O22	2.451 (2)
Fe2—O23	2.0415 (18)	Na2—O22^{i}	2.5816 (19)
Fe2—O24^{ii}	2.0506 (18)	Na2—O23	2.827 (3)
Fe2—O11^{iii}	2.0579 (18)	Na2—O11^{ix}	2.889 (3)
Fe2—O24^{iv}	2.1825 (19)	P1—O12^{vi}	1.5398 (18)
Mg1—O21^{iv}	2.113 (2)	P1—O11^{vi}	1.5547 (17)
Mg1—O11^{iii}	2.1436 (17)	P2—O21	1.5283 (18)
Mg1—O23^{v}	2.1628 (19)	P2—O22	1.5414 (18)
Na1—O12^{vi}	2.3041 (18)	P2—O24	1.5546 (18)
Na1—O21^{vii}	2.3898 (19)	P2—O23	1.5601 (18)
Na1—O21^{i}	2.5424 (18)		
O12—Fe2—O22^{i}	94.56 (8)	O11^{iii}—Mg1—O11^{xi}	148.33 (11)
O12—Fe2—O23	109.33 (8)	O21^{iv}—Mg1—O23^{v}	163.53 (8)
O22^{i}—Fe2—O23	87.05 (7)	O21^{x}—Mg1—O23^{v}	86.08 (7)
O12—Fe2—O24^{ii}	87.27 (8)	O11^{iii}—Mg1—O23^{v}	87.36 (7)
O22^{i}—Fe2—O24^{ii}	101.23 (8)	O11^{xi}—Mg1—O23^{v}	74.35 (7)
O23—Fe2—O24^{ii}	160.97 (7)	O21^{x}—Mg1—O23	163.53 (8)
O12—Fe2—O11^{iii}	162.93 (7)	O23^{v}—Mg1—O23	109.29 (11)
O22^{i}—Fe2—O11^{iii}	100.95 (7)	O12^{vi}—P1—O12	103.82 (14)
O23—Fe2—O11^{iii}	78.80 (7)	O12^{vi}—P1—O11^{vi}	112.49 (9)
O24^{ii}—Fe2—O11^{iii}	82.78 (7)	O12—P1—O11^{vi}	108.48 (9)
O12—Fe2—O24^{iv}	80.16 (7)	O11^{vi}—P1—O11	110.92 (14)
O22^{i}—Fe2—O24^{iv}	172.65 (7)	O21—P2—O22	112.70 (10)
O23—Fe2—O24^{iv}	89.88 (7)	O21—P2—O24	108.36 (10)
O24^{ii}—Fe2—O24^{iv}	83.72 (7)	O22—P2—O24	109.31 (10)
O11^{iii}—Fe2—O24^{iv}	84.97 (7)	O21—P2—O23	111.09 (10)
O21^{iv}—Mg1—O21^{x}	79.36 (10)	O22—P2—O23	107.08 (10)
O21^{iv}—Mg1—O11^{iii}	91.34 (7)	O24—P2—O23	108.21 (10)
O21^{x}—Mg1—O11^{iii}	113.37 (7)		

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

Data collection

Enraf–Nonius TurboCAD4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: analytical (Alcock, 1970)
$T_{\min} = 0.59$, $T_{\max} = 0.73$
1138 measured reflections
1048 independent reflections
982 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.014$
$\theta_{\max} = 28.0^\circ$
$h = -15 \rightarrow 14$
$k = -16 \rightarrow 0$
$l = 0 \rightarrow 8$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.071$
$S = 1.15$
1048 reflections
98 parameters
$(\Delta/\sigma)_{\max} = 0.033$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.75$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0037 (6)

The Fe atoms were located by direct methods, and the remaining atoms were found by successive difference Fourier maps. The occupation number of the *M*2 site was constrained to 1.0 and the occupation number of the Na2 site was set equal to the partial occupation of Mg2 in the *M*2 site, in accordance with the $\mathrm{Na}_{1+x}\mathrm{Mg}_{1+x}\mathrm{Fe}_{2-x}(\mathrm{PO}_4)_3$ formula.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1998).

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