Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

The iron phosphate $NaZnFe_2(PO_4)_3$

Mourad Hidouri,* Besma Lajmi and Mongi Ben Amara

Département de Chimie, Faculté des Sciences, 5000 Monastir, Tunisia
Correspondence e-mail: mourad_hidouri@yahoo.fr

Received 10 June 2002
Accepted 28 August 2002
Online 11 October 2002

Crystals of sodium zinc diiron(III) triphosphate, $NaZnFe_2(PO_4)_3$, have been synthesized and structurally characterized by single-crystal X-ray diffraction. The compound features a new structural type built up from ZnO_6 octahedra, FeO_6 octahedra and FeO_4 tetrahedra, linked together *via* the corners and edges of PO_4 tetrahedra to form a three-dimensional framework, with tunnels running along [100]. Within these tunnels, Na^+ cations occupy a highly distorted cubic site.

Comment

The investigation of iron phosphates over the past two decades has led to the synthesis and characterization of numerous compounds with a variety of network structures. Most of these compounds belong to the binary A_3PO_4–$FePO_4$ system, where A is a monovalent cation. By contrast, the bibliographic data reveal only a small number of ternary iron phosphates of the A_3PO_4–$M_3(PO_4)_2$–$FePO_4$ system, where A and M are monovalent and divalent cations, respectively, namely, $Na_3Ca_{18}Fe(PO_4)_{14}$ (Strunkova *et al.*, 1997), $Na_2Fe_3(PO_4)_3$ (Yakubovich *et al.*, 1977), $NaFe_3(PO_4)_3$ (Corbin *et al.*, 1986), $Na_7Fe_4(PO_4)_6$ (Lii, 1996), $NaFe_{3.67}(PO_4)_3$ (Korznski *et al.*, 1998), $KBaFe_2(PO_4)_3$ (Battle *et al.*, 1986) and $Cu_{1.35}Fe_3(PO_4)_3$ (Warner *et al.*, 1993).

As part of our study of the crystal chemistry of ternary iron monophosphates belonging to the Na_3PO_4–$M_3(PO_4)_2$–$FePO_4$ system, we report here the synthesis and structural characterization of $NaZnFe_2(PO_4)_3$. This compound features a new type of structure (Fig. 1), comprising FeO_6, FeO_4 and ZnO_6 polyhedra connected together *via* the corners and edges of three crystallographically distinct PO_4 tetrahedra. The resulting complex three-dimensional framework contains tunnels running along the [100] direction, in which the Na^+ cations reside.

The oxygen environment around the Zn atoms in $NaZnFe_2(PO_4)_3$ approximates to a highly distorted octahedron, as indicated by the Zn—O bond lengths and O—Zn—O bond angles (Table 1). The ZnO_6 octahedron shares two corners, atoms O11 and O14, with two $P1O_4$ tetrahedra, one edge, O23–O24, with one $P2O_4$ tetrahedron, and the remaining two corners, atoms O31 and O34, with two $P3O_4$ tetrahedra.

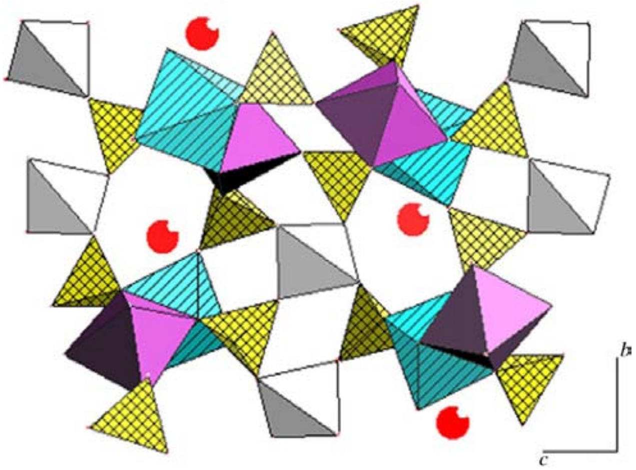

Figure 1
The structure of $NaZnFe_2(PO_4)_3$, viewed along the *a* direction. The ZnO_6 and PO_4 polyhedra are illustrated by lined and cross-hatched patterns, respectively. The remaining polyhedra are $Fe1O_6$ and $Fe2O_4$. The Na^+ cations are represented by solid circles.

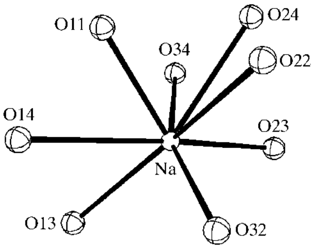

Figure 2
The coordination environment of the Na^+ cations. Displacement ellipsoids are drawn at the 50% probability level.

The Fe1 atoms also exhibit a distorted octahedral environment. The $Fe1O_6$ octahedron shares one edge, O13–O14, with one $P1O_4$ tetrahedron, and three corners, atoms O21, O23 and O24, with three $P2O_4$ tetrahedra. The sixth vertex, atom O34, is shared with the $P3O_4$ group.

The Fe2 atoms exhibit an unusual tetrahedral environment. The corresponding bond distances are close to those observed in $FePO_4$ (Calvo, 1975). The $Fe2O_4$ tetrahedron shares the corners O12 and O22 with $P1O_4$ and $P2O_4$ tetrahedra, respectively, and the other two corners, atoms O32 and O33, with two $P3O_4$ groups.

Na^+ cations are located within tunnels running along [100]. Their environment (Fig. 2) was determined assuming Na—O distances of less than 3.0 Å. They then have an irregular eight-coordinate site, with Na—O bond distances similar to those frequently observed for Na atoms with coordination number 8.

Experimental

Crystals of $NaZnFe_2(PO_4)_3$ were prepared from a stoichiometric mixture of $Fe(NO_3)_3{\cdot}9H_2O$, ZnO, NaH_2PO_4 and $(NH_4)_2HPO_4$. The mixture was initially heated for 12 h at 873 K to evacuate the decomposition products (H_2O, NH_3, *etc.*), then melted for 1 h at 1253 K and finally cooled to room temperature at a rate of 10 K h^{-1}.

DOI: 10.1107/S010827010201541X

Elemental analysis of crystal samples *via* electron microprobe analysis indicated the presence of Zn, Fe, P and Na in the atomic ratio 1:2:3:1.

Crystal data

$\mathrm{NaZnFe_2(PO_4)_3}$
$M_r = 484.97$
Orthorhombic, $P2_12_12_1$
$a = 5.1240$ (10) Å
$b = 12.213$ (5) Å
$c = 15.072$ (9) Å
$V = 943.2$ (7) Å^3
$Z = 4$
$D_x = 3.415$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 6.18$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, brown
0.22 × 0.10 × 0.06 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min} = 0.529$, $T_{\rm max} = 0.690$
1314 measured reflections
1293 independent reflections
1184 reflections with $I > 2\sigma{\rm i}(I)$

$R_{\rm int} = 0.020$
$\theta_{\rm max} = 27°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 15$
$l = -1 \rightarrow 19$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.078$
$S = 1.24$
1293 reflections
173 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.4314P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.006$
$\Delta\rho_{\rm max} = 0.64$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.05$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0038 (8)
Absolute structure: Flack (1983), 70 Friedel pairs
Flack parameter = 0.02 (3)

Table 1
Selected geometric parameters (Å, °).

Zn—O31	1.908 (5)	Na—O32$^{\rm viii}$	2.476 (6)
Zn—O11	2.006 (5)	Na—O13$^{\rm iv}$	2.497 (6)
Zn—O34$^{\rm i}$	2.024 (5)	Na—O24$^{\rm ix}$	2.705 (6)
Zn—O24$^{\rm ii}$	2.181 (5)	Na—O34$^{\rm vii}$	2.705 (6)
Zn—O14$^{\rm ii}$	2.279 (5)	Na—O14$^{\rm vii}$	2.922 (6)
Zn—O23$^{\rm ii}$	2.369 (5)	Na—O22$^{\rm ix}$	2.987 (6)
Fe1—O21$^{\rm iii}$	1.882 (5)	P1—O11	1.521 (5)
Fe1—O13	1.942 (5)	P1—O12	1.544 (5)
Fe1—O24	1.991 (5)	P1—O13	1.549 (5)
Fe1—O14$^{\rm i}$	2.026 (5)	P1—O14	1.552 (5)
Fe1—O23$^{\rm i}$	2.054 (5)	P2—O21	1.511 (5)
Fe1—O34$^{\rm iv}$	2.340 (5)	P2—O22	1.541 (5)
Fe2—O22$^{\rm v}$	1.852 (5)	P2—O23	1.543 (5)
Fe2—O33$^{\rm vi}$	1.851 (5)	P2—O24	1.563 (5)
Fe2—O12$^{\rm vi}$	1.872 (5)	P3—O31	1.522 (5)
Fe2—O32$^{\rm i}$	1.881 (5)	P3—O32	1.544 (5)
Na—O11$^{\rm vii}$	2.401 (7)	P3—O33	1.545 (5)
Na—O23	2.444 (6)	P3—O34	1.559 (5)
O31—Zn—O11	100.0 (2)	O34$^{\rm i}$—Zn—O14$^{\rm ii}$	77.84 (19)
O31—Zn—O34$^{\rm i}$	109.1 (2)	O24$^{\rm ii}$—Zn—O14$^{\rm ii}$	79.40 (18)
O11—Zn—O34$^{\rm i}$	109.1 (2)	O31—Zn—O23$^{\rm ii}$	168.10 (19)
O31—Zn—O24$^{\rm ii}$	109.0 (2)	O11—Zn—O23$^{\rm ii}$	89.45 (19)
O11—Zn—O24$^{\rm ii}$	82.5 (2)	O34$^{\rm i}$—Zn—O23$^{\rm ii}$	73.97 (19)
O34$^{\rm i}$—Zn—O24$^{\rm ii}$	137.1 (2)	O24$^{\rm ii}$—Zn—O23$^{\rm ii}$	64.82 (17)
O31—Zn—O14$^{\rm ii}$	96.1 (2)	O14$^{\rm ii}$—Zn—O23$^{\rm ii}$	73.03 (17)
O11—Zn—O14$^{\rm ii}$	158.9 (2)		

Symmetry codes: (i) $1+x, y, z$; (ii) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$; (iv) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (v) $x, y-1, z$; (vi) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (vii) $-1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (viii) $x, 1+y, z$; (ix) $x-1, y, z$.

The Zn and Fe atoms were located by direct methods, and the remaining atoms were found by successive difference Fourier maps.

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: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97.

The authors thank Professor A. Driss from F. S. Tunis for the X-ray diffraction measurements.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1022). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Battle, P. D., Cheetham, A. K., Harrison, W. T. A. & Long, G. J. (1986). *J. Solid State Chem.* **62**, 16–25.

Brandenburg, K. (1998). *DIAMOND*. Version 2.0. University of Bonn, Germany.

Calvo, C. (1975). *Can. J. Chem.* **53**, 2064–2067.

Corbin, R. D., Whiteny, J. F., Fluz, W. C., Stucky, G. D., Edly, M. M. & Cheetham, A. K. (1986). *Inorg. Chem.* **25**, 2279–2280.

Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.

Korznski, M. B., Shimek, G. L., Kolis, J. W. & Long, G. J. (1998). *J. Solid State Chem.* **139**, 152–160.

Lii, K.-H. (1996). *J. Chem. Soc.* **96**, 819–822.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Strunkova, T. V., Morozov, V. A., Kasanov, S. S., Pokhlok, K. V., Zhdanova, A. N. & Lazoryak, B. I. (1997). *Kristallographia*, **42**, 64–67. (In Russian.)

Warner, T. E., Milius, W. & Mayer, J. (1993). *J. Solid State Chem.* **106**, 301–309.

Yakubovich, O. V., Simonov, M. A., Ergov, T. & Belov, N. V. (1977). *Dokl. Acad. Nauk SSSR*, **236**, 1123–1126. (In Russian.)