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Heptairon bis(phosphate) tetrakis(hydrogenphosphate)

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A new iron hydrogen phosphate, heptairon bis(phosphate) tetrakis(hydrogenphosphate), $Fe_7(PO_4)_2(HPO_4)_4$, has been prepared hydrothermally and characterized by single-crystal X-ray diffraction. The compound has one Fe atom on an inversion centre and is isostructural with $Mn_7(PO_4)_2(HPO_4)_4$ and $Co_7(PO_4)_2(HPO_4)_4$. The structure is based on a framework of edge- and corner-sharing FeO_6, Fe_5 and PO_4 polyhedra, isotypic with that found in the mixed-valence iron phosphate $Fe_7(PO_4)_6$. The Fe atoms in the title compound are purely in the divalent state, just like the Co atoms in $Co_7(PO_4)_2(HPO_4)_4$, the necessary charge balance being maintained by the addition of H atoms in the form of bridging Fe—OH—P groups.

Comment

Microporous materials containing transition metal elements are a focus of contemporary research due to their novel potential catalytic, electrical, optical and magnetic properties, which are not accessible to the main group elements (Cheetham *et al.*, 1999). Hydrothermal and solvothermal methods have been used to synthesize many novel transition metal phosphates with open-framework structures, such as iron (Attfield *et al.*, 1994), cobalt (Cowley & Chippindale, 1999; Feng *et al.*, 1997), nickel (Guillou *et al.*, 1999; Escobal, Pizarro, Mesa, Arriortua & Rojo, 2000), manganese (Escobal, Pizarro, Mesa, Lezama *et al.*, 2000; Fernandez *et al.*, 2001) and molybdenum phosphates (Haushalter & Mundi, 1992). The frameworks of transition metal phosphates can be controlled by introducing organic templates to form one-dimensional (chain), two-dimensional (layered) and three-dimensional structures. Among these compounds, the iron phosphates are of interest because of their rich crystal chemistry and their practical applications (Lii *et al.*, 1998).

The title iron phosphate, $Fe_7(PO_4)_2(HPO_4)_4$, was synthesized by the hydrothermal method in the presence of ethylene glycol and imidazole. It is isostructural with $Mn_7(PO_4)_2(HPO_4)_4$ (Riou *et al.*, 1987) and $Co_7(PO_4)_2(HPO_4)_4$ (Lightfoot & Cheetham, 1988). However, the method used to synthesize $Mn_7(PO_4)_2(HPO_4)_4$ and $Co_7(PO_4)_2(HPO_4)_4$, when carried out with iron-containing starting materials, gave $Fe^{II}_6Fe^{III}(PO_4)_3(HPO_4)_3$ instead of $Fe_7(PO_4)_2(HPO_4)_4$ (Lightfoot & Cheetham, 1986).

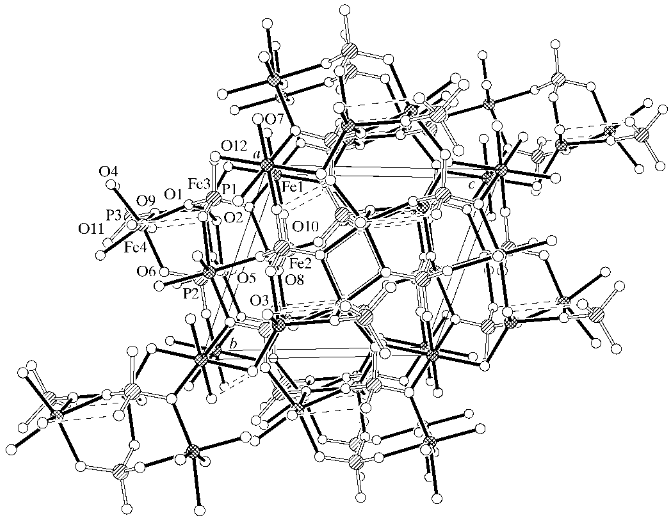

Figure 1
A view of the packing of $Fe_7(PO_4)_2(HPO_4)_4$ along the *a* direction, with dashed lines indicating hydrogen bonds.

As shown in Fig. 1, the crystal structure of the title compound consists of Fe–O polyhedra and PO_4 tetrahedra sharing edges or corners to form a three-dimensional open framework. Of the four independent Fe atoms (Fig. 2), Fe1 is located at a crystallographic inversion centre and has an almost regular octahedral coordination environment, while atoms Fe2 and Fe4 display distorted octahedral coordination environments. Atom Fe3 is surrounded by five O atoms, to give a geometry which is best described as distorted trigonal–bipyramidal. The results of a bond-strength–bond-length calculation (Brown & Shannon, 1973) suggest that all the Fe atoms should be divalent, the valence sums for the four metal sites being 1.89, 2.22, 1.94 and 2.28.

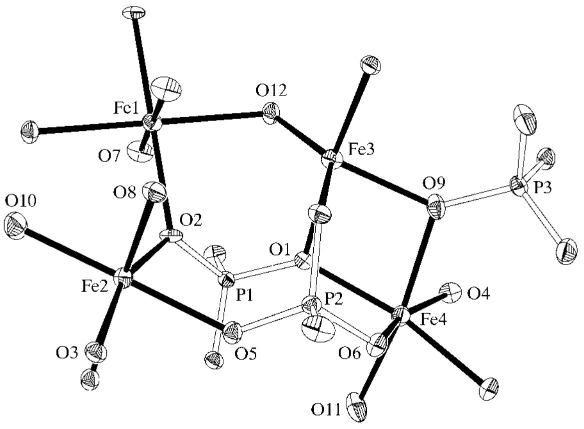

Figure 2
A view of the structure of $Fe_7(PO_4)_2(HPO_4)_4$ with 50% probability displacement ellipsoids, showing the atomic numbering scheme. H atoms have been omitted for clarity.

All the phosphate groups in the title compound are almost tetrahedral. The P—O bond lengths are in the range 1.509 (5)–1.567 (5) Å. The P1—O4 and P3—O11 bond lengths of 1.557 (4) and 1.567 (5) Å, respectively, are significantly longer than the remaining P—O bonds, which involves bridging Fe—HO—P groups. Although the shortest distance between O atoms is 2.477 Å, between O10 and O11, hydrogen bonds are expected to be formed between O11—H···O3 and O4—H···O7, if the angles between the respective atoms are considered (Table 2).

Experimental

$FeCl_2$ (0.8 g), H_2O (6 ml) and ethylene glycol (EG, 11 ml), H_3PO_4 (0.8 ml, 85% wt), and imidazole (1.0 g) were placed, successively, in a beaker with stirring; a homogeneous mixture was obtained. The mixture was treated hydrothermally in a Teflon-lined autoclave at 440 K for 6 d. The resulting single crystals were collected by filtration, washed with distilled water and dried in air at ambient temperature. Experiment proved that EG is necessary for the formation of crystals of good habit. EG has a higher viscosity than water, which may baffle the convection currents and help obtain a large good-quality single crystal (Lii *et al.*, 1998).

Crystal data

$Fe_7(PO_4)_2(HPO_4)_4$
$M_r = 964.80$
Triclinic, $P\overline{1}$
$a = 6.528$ (3) Å
$b = 7.956$ (4) Å
$c = 9.501$ (4) Å
$\alpha = 104.03$ (4)°
$\beta = 109.17$ (2)°
$\gamma = 101.66$ (3)°
$V = 430.3$ (3) Å^3
$Z = 1$
$D_x = 3.723$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 5.9$–11.4°
$\mu = 6.43$ mm^{-1}
$T = 293$ (2) K
Prism, black
0.2 × 0.1 × 0.1 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.282$, $T_{max} = 0.526$
2420 measured reflections
1921 independent reflections
1537 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 27.5°$
$h = -1 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -12 \rightarrow 12$
3 standard reflections every 100 reflections intensity decay: none

Table 1
Selected interatomic distances (Å).

Fe1—O7	2.121 (5)	Fe3—O8^{ii}	2.046 (4)
Fe1—O2	2.174 (4)	Fe3—O9	2.108 (5)
Fe1—O12	2.248 (4)	Fe3—O3^{ii}	2.126 (4)
Fe2—O10	2.047 (5)	Fe3—O1	2.187 (4)
Fe2—O5	2.085 (4)	Fe4—O1	2.069 (4)
Fe2—O2	2.121 (4)	Fe4—O4	2.087 (5)
Fe2—O8	2.125 (4)	Fe4—O6^{iii}	2.100 (4)
Fe2—O5^{i}	2.126 (5)	Fe4—O6	2.115 (5)
Fe2—O3	2.202 (4)	Fe4—O11	2.124 (5)
Fe3—O12	2.033 (4)	Fe4—O9	2.132 (5)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.106$
$S = 1.03$
1849 reflections
169 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0010P)^2 + 6.4359P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 1.22$ e Å^{-3}
$\Delta\rho_{min} = -0.94$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*A*···O7^{i}	0.85	1.71	2.539 (7)	164
O11—H11*A*···O3^{ii}	0.85	2.03	2.850 (7)	162

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

The H-atom positions were found in a difference Fourier map and the O—H bond lengths were set at 0.85 Å.

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1377). Services for accessing these data are described at the back of the journal.

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