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$Fe^{II}_3Fe^{III}_4(AsO_4)_6$, the first arsenate adopting the $Fe_7(PO_4)_6$ structure type

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Single crystals of triiron(II) tetrairon(III) hexakis[orthoarsenate(V)], $Fe_7(AsO_4)_6$, were grown by chemical transport reactions. The structure is isotypic with other $M^{II}_3M^{III}_4(XO_4)_6$ compounds (M = first row transition metals; X = P, V) which adopt the $Fe_7(PO_4)_6$ structure type. The structure includes four independent cation sites, two of which are occupied by divalent and two by trivalent iron cations. Slightly distorted [FeO_6] octahedra and [FeO_5] trigonal bipyramids share edges and form infinite chains, which are linked by corner-sharing with AsO_4 tetrahedra and with [FeO_6] octahedra into a three-dimensional network. Except for one Fe site with $\overline{1}$ symmetry occupied by a divalent iron cation, all other atoms are located in general positions.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Fe–O) = 0.002 Å
R factor = 0.021
wR factor = 0.048
Data-to-parameter ratio = 23.0

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

Comment

Since the publication of the crystal structure of $Fe_7(PO_4)_6$ (Gorbunov *et al.*, 1980), a multitude of isotypic compounds with the general formula $M^{II}_3M^{III}_4(XO_4)_6$ (where M = first row transition metal, and X = P or V) have been reported in the literature. Some mixed hydrogenphosphate/orthophosphate compounds with general formula $M^{II}_{3+n}M^{III}_{4-n}(PO_4)_{6-n}(HPO_4)_n$ and also some molybdates are also known to crys-

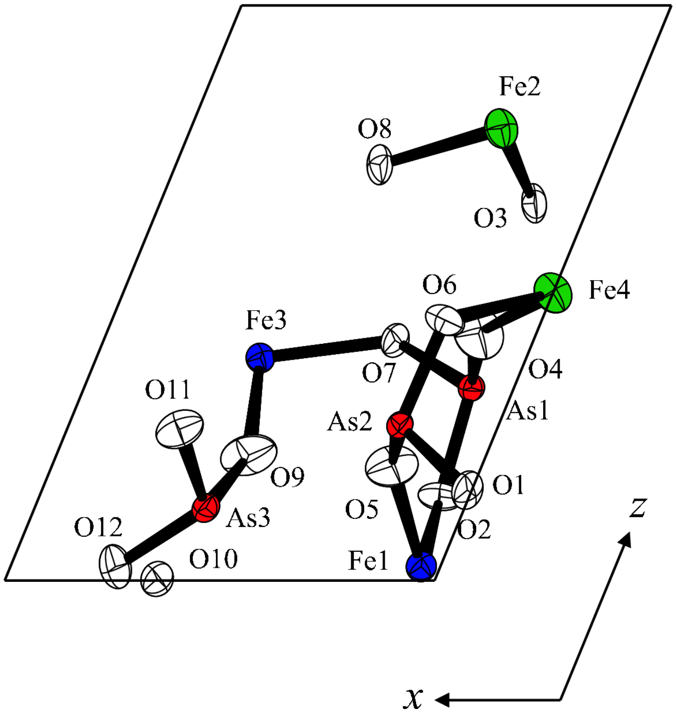

Figure 1
The asymmetric unit of $Fe_7(AsO_4)_6$, with anisotropic displacement parameters drawn at the 97% probability level.

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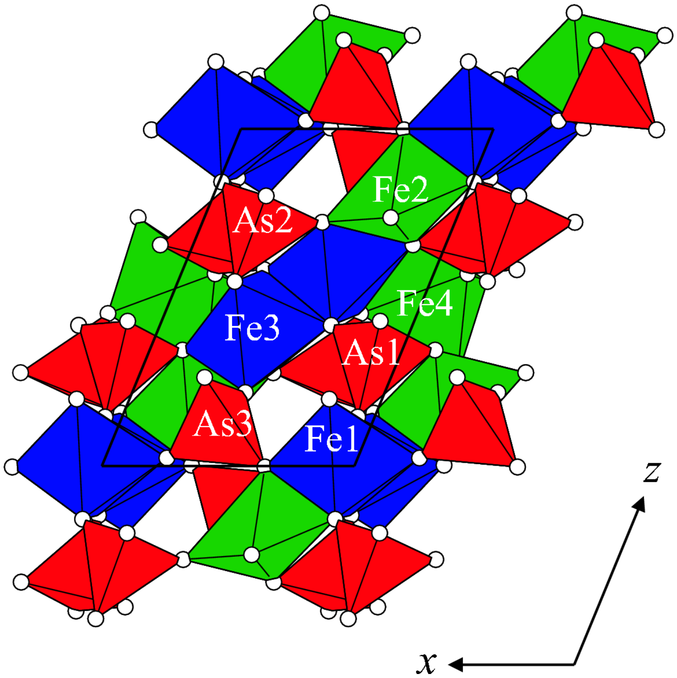

Figure 2
Projection of the structure along [010]. Polyhedra around divalent iron are green, polyhedra around trivalent iron are blue and AsO_4 tetrahedra are red.

tallize in the $Fe_7(PO_4)_6$ structure type, which therefore has been described in many independent studies. Listings of the compounds investigated thus far are given in more recent publications, for example, by Gruß & Glaum (1997), Belik, Pokholok *et al.* (2000) and Belik, Malakho *et al.* (2000) for phosphates, and by Wang *et al.* (2000) and Belik *et al.* (2001) for vanadates and molybdates. To my knowledge, no arsenate compound adopting the $Fe_7(PO_4)_6$ structure type has been described previously.

Fig. 1 displays the asymmetric unit of $Fe_7(AsO_4)_6$. The three-dimensional structure contains infinite iron–oxygen chains running parallel to $[\bar{1}01]$. These chains are made up of two types of $[M_2O_{10}]$ double octahedra (metal sites Fe1 and Fe3, respectively) and trigonal–bipyramidal $[Fe2O_5]$ units by sharing common edges. The connection between neighbouring chains is achieved by intermediate AsO_4 groups and compressed $[Fe4O_6]$ octahedra which share common corners with the chains (Fig. 2).

The structure contains four independent iron cations, two of which are divalent (Fe2 and Fe4) and two of which are trivalent (Fe1 and Fe3). The bond valence sums (v.u.) for the iron cations calculated with the parameters given by Brese & O'Keeffe (1991) are in good agreement with the formal charges of +2 and +3: Fe1 3.12, Fe2 2.04, Fe3 3.09, Fe4 1.91. Sites Fe1, Fe3 and Fe4 are surrounded by six O atoms to form distorted $[FeO_6]$ octahedra, whereas Fe2 has a distorted $[FeO_5]$ trigonal bipyramid as corresponding coordination polyhedron. All Fe—O bond lengths are comparable with those of the isotypic phosphate (Gorbunov *et al.*, 1980).

The three crystallographically independent AsO_4 tetrahedra are considerably distorted from the geometry of an ideal tetrahedron. Their As—O distances range from 1.6371 (15) to 1.7046 (13) Å, with an overall mean of 1.68 Å, which is in the characteristic range observed for other orthoarsenates (Kálmán, 1971).

Experimental

The title compound was obtained during chemical transport experiments intended for the single-crystal growth of divalent transition metal diarsenates $M^{II}_2As_2O_7$, with M = Mn, Fe, Co, Ni, Cu, Zn (Weil *et al.*, 2004). For that purpose, stoichiometric amounts of iron powder (99.9%; Fluka), Fe_2O_3 (p. A.; Merck) and As_2O_5 were mixed and charged in sealed and evacuated silica tubes with an approximate reaction volume of 18 ml. As_2O_5 was prepared by oxidizing As_2O_3 (p. A.; Merck) with concentrated nitric acid and firing the product at 673 K for 12 h. Small amounts of NH_4Cl (p. A.; Merck) were added as transport agent and to maintain a slightly reducing atmosphere inside the ampoule. Application of a temperature gradient 1173 → 1073 K for one week led to the deposition of black crystals with an unspecific habit and of up to 2 mm length. Most of these crystals were deposited at the cool part of the ampoule, but some could also be found in minor amounts within the whole ampoule. In addition to $Fe_7(AsO_4)_6$, a few hexagonal-shaped single crystals of hematite, Fe_2O_3, and microcrystalline $FeAsO_4$ were observed during these experiments.

Crystal data

$Fe_7(AsO_4)_6$
$M_r = 1224.47$
Triclinic, $P\bar{1}$
$a = 6.5738$ (6) Å
$b = 8.0973$ (9) Å
$c = 9.6190$ (6) Å
$\alpha = 104.843$ (7)°
$\beta = 107.936$ (6)°
$\gamma = 101.842$ (9)°
$V = 447.85$ (8) Å^3

$Z = 1$
$D_x = 4.540$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 13.7$–17.9°
$\mu = 16.64$ mm^{-1}
$T = 293$ (2) K
Block, black
0.40 × 0.29 × 0.14 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical (*HABITUS*; Herrendorf, 1993–1997)
$T_{min} = 0.022$, $T_{max} = 0.266$
7836 measured reflections
3918 independent reflections

3589 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 35.0$°
$h = -10 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 300 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.048$
$S = 1.16$
3918 reflections
170 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0213P)^2 + 0.3318P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.05$ e Å^{-3}
$\Delta\rho_{min} = -1.12$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0387 (8)

Table 1
Selected geometric parameters (Å, °).

Fe1—O12^{i}	1.8896 (14)	Fe4—O4^{vi}	2.0107 (14)
Fe1—O5	1.9191 (15)	Fe4—O6^{vi}	2.2087 (14)
Fe1—O1^{ii}	1.9867 (14)	Fe4—O6	2.2087 (14)
Fe1—O2	2.0147 (14)	Fe4—O11^{v}	2.3194 (15)
Fe1—O10^{iii}	2.0950 (13)	Fe4—O11^{i}	2.3194 (15)
Fe1—O2^{iv}	2.1768 (14)	As1—O4	1.6371 (15)
Fe2—O11^{v}	1.9808 (16)	As1—O2	1.6977 (13)
Fe2—O8	2.0693 (13)	As1—O3^{viii}	1.7007 (13)
Fe2—O3	2.0744 (15)	As1—O7	1.7037 (13)
Fe2—O10^{v}	2.0987 (14)	As2—O5	1.6519 (15)
Fe2—O1^{vi}	2.1251 (13)	As2—O8^{v}	1.6842 (13)
Fe3—O9	1.8514 (15)	As2—O1	1.6965 (13)
Fe3—O3^{vii}	2.0166 (13)	As2—O6	1.7046 (13)
Fe3—O6^{v}	2.0332 (14)	As3—O12	1.6575 (14)
Fe3—O7	2.0432 (12)	As3—O9	1.6624 (16)
Fe3—O8^{vii}	2.0510 (14)	As3—O11	1.6860 (15)
Fe3—O7^{vii}	2.0863 (14)	As3—O10^{iii}	1.6924 (13)
Fe4—O4	2.0107 (14)		
O4—As1—O2	115.81 (8)	O5—As2—O6	110.91 (7)
O4—As1—O3^{viii}	108.82 (7)	O8^{v}—As2—O6	109.94 (7)
O2—As1—O3^{viii}	108.57 (7)	O1—As2—O6	107.49 (7)
O4—As1—O7	111.60 (8)	O12—As3—O9	112.76 (9)
O2—As1—O7	104.82 (7)	O12—As3—O11	109.58 (8)
O3^{viii}—As1—O7	106.81 (7)	O9—As3—O11	107.08 (8)
O5—As2—O8^{v}	107.68 (7)	O12—As3—O10^{iii}	106.38 (7)
O5—As2—O1	110.42 (7)	O9—As3—O10^{iii}	108.54 (7)
O8^{v}—As2—O1	110.42 (7)	O11—As3—O10^{iii}	112.59 (7)

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

The atomic coordinates of the isotypic compound $Fe_7(PO_4)_6$ (Gorbunov *et al.*, 1980) were taken as starting values for the least-squares refinement. The refined coordinates were then standardized with the program *STRUCTURE-TIDY* (Gelato & Parthé, 1987). The highest peak and the deepest hole are located 0.87 and 0.72 Å, respectively, from As2.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *HELENA* implemented in *PLATON* (Spek, 2003); method used to solve structure: from the coordinates of Gorbunov *et al.* (1980); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *SHELXL*97.

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