

## Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{\max} = 45^\circ$
Bisect scans	$h = -9 \rightarrow 9$
Absorption correction: none	$k = 0 \rightarrow 16$
2457 measured reflections	$l = 0 \rightarrow 14$
2457 independent reflections	3 standard reflections
1339 observed reflections	frequency: 60 min
$[I > 3\sigma(I)]$	intensity decay: <1%

## Refinement

Refinement on $F^2$	$\Delta\rho_{\max} = 0.95 \text{ e } \text{\AA}^{-3}$
$R = 0.029$	$\Delta\rho_{\min} = -0.95 \text{ e } \text{\AA}^{-3}$
$wR = 0.027$	Extinction correction: none
$S = 0.997$	Atomic scattering factors
1339 reflections	from <i>International Tables</i>
94 parameters	for <i>X-ray Crystallography</i>
$w = 1/\sigma(F)$	(1974, Vol. IV)
$(\Delta/\sigma)_{\max} < 0.001$	

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$B_{\text{iso}}/B_{\text{eq}}$
Mo	0.21270 (8)	0.5	0.22578 (6)	0.339 (6)
P(1)	0.4030 (3)	0.1806 (2)	0.0289 (2)	0.42 (2)
P(2)	0.7937 (3)	0.2851 (2)	0.4194 (2)	0.47 (2)
Li	0.797 (2)	0.364 (1)	0.821 (2)	1.8 (2)
O(1)	0.0539 (9)	0.3200 (6)	0.3608 (7)	0.96 (8)
O(2)	0.3985 (8)	0.6822 (5)	0.0963 (6)	0.80 (8)
O(3)	0.1328 (8)	0.7007 (5)	0.3807 (6)	0.72 (8)
O(4)	0.6172 (7)	0.4331 (5)	0.4226 (6)	0.96 (8)
O(5)	0.2403 (8)	0.3376 (4)	0.0069 (5)	0.56 (8)
O(6)	0.5967 (8)	0.1593 (4)	0.2607 (5)	0.80 (8)
O(7)	-0.2025 (7)	0.5375 (4)	0.0077 (5)	0.62 (7)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Mo—O(1)	2.068 (5)	P(1)—P(2)	2.915 (2)
Mo—O(2)	2.131 (4)	P(2)—O(4)	1.518 (4)
Mo—O(3)	2.112 (5)	P(2)—O(6)	1.606 (4)
Mo—O(4)	2.084 (3)	P(2)—O(1 <sup>iv</sup> )	1.493 (5)
Mo—O(5)	2.093 (4)	P(2)—O(3 <sup>iv</sup> )	1.508 (4)
Mo—O(7)	2.126 (3)	Li—O(5 <sup>v</sup> )	2.15 (1)
P(1)—O(5)	1.521 (4)	Li—O(7 <sup>v</sup> )	1.96 (1)
P(1)—O(6)	1.602 (3)	Li—O(2 <sup>iv</sup> )	1.99 (1)
P(1)—O(7 <sup>v</sup> )	1.518 (4)	Li—O(3 <sup>iv</sup> )	2.08 (1)
P(1)—O(2 <sup>ii</sup> )	1.513 (5)		
O(1)—Mo—O(2)	177.0 (1)	O(5)—P(1)—O(2 <sup>ii</sup> )	110.4 (2)
O(1)—Mo—O(3)	100.5 (2)	O(6)—P(1)—O(7 <sup>v</sup> )	102.5 (2)
O(1)—Mo—O(4)	85.3 (2)	O(6)—P(1)—O(2 <sup>ii</sup> )	108.4 (2)
O(1)—Mo—O(5)	89.3 (2)	P(1)—O(6)—P(2)	130.6 (3)
O(1)—Mo—O(7)	91.4 (1)	O(4)—P(2)—O(6)	109.5 (2)
O(2)—Mo—O(3)	80.0 (2)	O(4)—P(2)—O(1 <sup>iv</sup> )	112.7 (3)
O(2)—Mo—O(4)	91.8 (1)	O(4)—P(2)—O(3 <sup>iv</sup> )	109.4 (3)
O(2)—Mo—O(5)	90.7 (2)	O(5 <sup>v</sup> )—Li—O(7 <sup>v</sup> )	83.8 (4)
O(2)—Mo—O(7)	91.6 (1)	O(5 <sup>v</sup> )—Li—O(2 <sup>iv</sup> )	103.2 (5)
O(3)—Mo—O(4)	99.8 (1)	O(5 <sup>v</sup> )—Li—O(3 <sup>iv</sup> )	89.0 (5)
O(3)—Mo—O(5)	165.2 (1)	O(6)—P(2)—O(1 <sup>iv</sup> )	108.0 (3)
O(3)—Mo—O(7)	87.6 (1)	O(6)—P(2)—O(3 <sup>iv</sup> )	104.0 (2)
O(4)—Mo—O(5)	92.0 (1)	O(7 <sup>v</sup> )—Li—O(2 <sup>iv</sup> )	105.6 (7)
O(4)—Mo—O(7)	172.4 (1)	O(7 <sup>v</sup> )—Li—O(3 <sup>iv</sup> )	169.1 (7)
O(5)—Mo—O(7)	81.1 (1)	O(1 <sup>iv</sup> )—P(2)—O(3 <sup>iv</sup> )	112.8 (2)
O(5)—P(1)—O(6)	108.3 (2)	O(2 <sup>ii</sup> )—Li—O(3 <sup>iv</sup> )	84.0 (5)
O(5)—P(1)—O(7 <sup>v</sup> )	112.3 (2)		

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

Calculations were performed using a SPARC station with the *Xtal3.2* system (Hall, Flack & Stewart, 1992). The figure was obtained with *MOLVIEW* (Cense, 1993).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1147). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

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*Acta Cryst.* (1996). **C52**, 1594–1597

## Lead(II) Diiron(III) Pyrophosphate and Barium Diiron(III) Pyrophosphate

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(Received 14 August 1995; accepted 5 January 1996)

## Abstract

$\text{PbFe}_2^{\text{III}}(\text{P}_2\text{O}_7)_2$  [diiron(III) lead(II) bis(diphosphate)] crystallizes to form two types of metallic column, one containing uniquely  $\text{Fe}^{\text{III}}$  [ $\text{Fe} \cdots \text{Fe}$  7.851 (3)  $\text{\AA}$ ] and the other with alternating Pb and Fe atoms [ $\text{Pb} \cdots \text{Fe}$  3.925 (3)  $\text{\AA}$ ]. The crystalline structure of  $\text{BaFe}_2^{\text{III}}(\text{P}_2\text{O}_7)_2$  [barium diiron(III) bis(diphosphate)] is characterized by chains of Fe–O octahedra sharing faces with Ba–O decahedra and linked by corner-sharing Fe–O octahedra.

## Comment

While there are numerous structural studies of  $A^{\text{I}}B^{\text{II}}\text{P}_2\text{O}_7$  compounds, pyrophosphates of the form  $A^{\text{I}}B^{\text{III}}(\text{P}_2\text{O}_7)_2$  are relatively unknown.

$\text{SrFe}_2^{\text{III}}(\text{P}_2\text{O}_7)_2$  (Boutfessi, Boukhari & Holt, 1995) crystallizes in space group  $P\bar{1}$ , with metal atoms

distributed in two types of columns oriented along the [001] axis. The repeat unit within one column is  $\cdots\text{Sr}\cdots\text{Fe}\cdots\text{Sr}\cdots\text{Fe}\cdots$  [ $\text{Sr}\cdots\text{Fe}$  3.915 (2) Å] and within the second is  $\cdots\text{Fe}\cdots\text{Fe}\cdots$  [ $\text{Fe}\cdots\text{Fe}$  7.830 (2) Å]. Fe atoms in adjacent columns are widely separated. The Fe atoms have octahedral coordination geometry, with an average Fe—O distance of 1.996 (3) Å.

The pyrophosphates  $\text{BaTi}^{\text{III}}(\text{P}_2\text{O}_7)_2$  (Wang & Hwu, 1991) and  $\text{BaV}^{\text{III}}(\text{P}_2\text{O}_7)_2$  (Benhamada, Grandin, Borel, Leclaire & Raveau, 1991) crystallize in space group  $C2/c$ . Powder diffraction data have been reported for  $\text{PbFe}^{\text{II}}(\text{P}_2\text{O}_7)_2$  (Wanklyn, Wondre, Davison & Salmon, 1983) and  $\text{MgCr}^{\text{II}}(\text{P}_2\text{O}_7)_2$  (Vst'yantsev & Tretnikova, 1974).

$\text{Fe}_3(\text{P}_2\text{O}_7)_2$  ( $\text{Fe}_{0.5}^{\text{II}}\text{Fe}^{\text{III}}\text{P}_2\text{O}_7$ ) crystallizes in space group  $Pnma$  with linear  $\text{Fe}_3\text{O}^{1/2-}$  units composed of  $\text{Fe}^{\text{III}}\cdots\text{Fe}^{\text{II}}\cdots\text{Fe}^{\text{III}}$  trimers [ $\text{Fe}\cdots\text{Fe}$  2.924 (1) Å]. The central  $\text{Fe}^{\text{II}}$  atom has trigonal bipyramidal coordination geometry and shares opposite faces with octahedrally coordinated  $\text{Fe}^{\text{III}}$  atoms (Ijjaali, Venturini, Gerardin, Malaman & Gleitzer, 1991; Ijjaali, Venturini, Malaman & Gleitzer, 1990).

$\text{CuFe}^{\text{II}}(\text{P}_2\text{O}_7)_2$  is characterized by centrosymmetric  $\text{Fe}^{\text{III}}\cdots\text{Cu}^{\text{II}}\cdots\text{Fe}^{\text{III}}$  trimers in which the central Cu atoms with square-planar coordination geometry share two O atoms with each of two neighboring octahedrally coordinated Fe atoms (Boutfessi, Boukhari & Holt, 1996).

The first title compound,  $\text{PbFe}^{\text{II}}(\text{P}_2\text{O}_7)_2$ , is isotypic with  $\text{SrFe}_2(\text{P}_2\text{O}_7)_2$  (Boutfessi, Boukhari & Holt, 1995) (Fig. 1).  $\text{Fe}^{\text{III}}$  ions occupy sites of distorted octahedral geometry and are arranged in columns of two types, one with a  $\cdots\text{Pb}\cdots\text{Fe}\cdots\text{Pb}\cdots\text{Fe}\cdots$  [ $\text{Pb}\cdots\text{Fe}$  3.925 (3) Å] repeat unit and the second composed of  $\cdots\text{Fe}\cdots\text{Fe}\cdots$

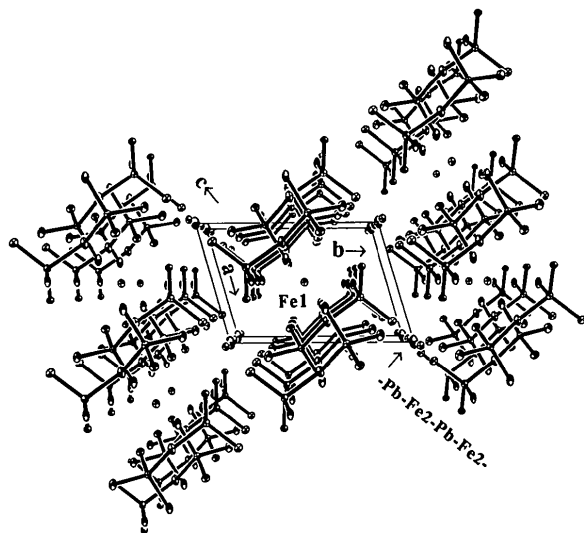


Fig. 1. A projected view of  $\text{PbFe}^{\text{II}}(\text{P}_2\text{O}_7)_2$  onto the (110) plane. Displacement ellipsoids are plotted at the 50% probability level.

units [ $\text{Fe}\cdots\text{Fe}$  7.851 (3) Å]. The Fe—O distances within these columns are in the ranges 1.943 (6)–2.071 (6) and 1.935 (5)–2.077 (6) Å, respectively, and are similar to those observed in  $\text{SrFe}_2(\text{P}_2\text{O}_7)_2$ . Pb is eight coordinate [ $\text{Pb}\cdots\text{O}$  2.745 (6) Å] and the  $\text{P}_2\text{O}_7$  groups have an eclipsed conformation with angles and distances normal for pyrophosphate structures.

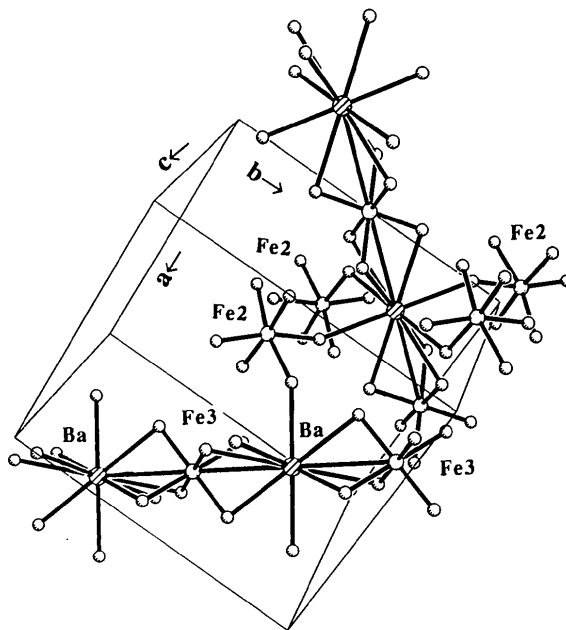
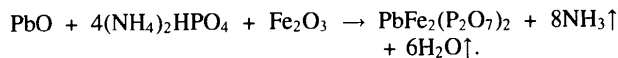


Fig. 2. A projected view of  $\text{BaFe}^{\text{II}}(\text{P}_2\text{O}_7)_2$  showing chains of Ba—O and Fe—O polyhedra linked by Fe2—O octahedra.

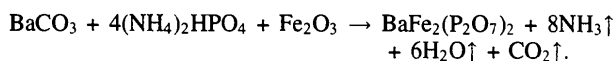
The second title compound,  $\text{BaFe}_2^{\text{II}}(\text{P}_2\text{O}_7)_2$ , is isotypic with both  $\text{BaTi}^{\text{III}}(\text{P}_2\text{O}_7)_2$  (Wang & Hwu, 1991) and  $\text{BaV}^{\text{III}}(\text{P}_2\text{O}_7)_2$  (Benhamada, Grandin, Borel, Leclaire & Raveau, 1991). Chains of  $\text{Fe}^{\text{III}}\text{—O}$  octahedra share opposite faces with each of two neighboring Ba—O decahedra (Fig. 2). These chains are aligned in parallel fashion forming layers, with the orientation of the chains altering by 90° in alternate layers. The Fe3 atom, which is situated on an inversion center, is located in these chains [average Fe3—O 1.984 (5) Å]. The crystallographically independent Fe2 atom, which is found on a twofold axis, has octahedral coordination geometry; these octahedra link the Ba—Fe chains by sharing a corner with Ba atoms of adjacent layers of chains [average Fe2—O 2.018 (5) Å]. The Ba—O distances [average Ba—O 2.918 (5) Å] are comparable to the average Ba—O distance of 2.926 (2) Å found in  $\text{BaTi}^{\text{III}}(\text{P}_2\text{O}_7)_2$ . The  $\text{P}_2\text{O}_7$  groups have a semi-eclipsed conformation.

## Experimental

$\text{PbFe}^{\text{II}}(\text{P}_2\text{O}_7)_2$  was synthesized according to:



BaFe<sub>2</sub><sup>III</sup>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub> was synthesized by mixing stoichiometric quantities of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, BaCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> according to:



For both compounds, the reaction mixture was ground together and heated progressively to 1273 K. After 24 h at this temperature, the molten mixture was cooled slowly (5 K h<sup>-1</sup>) to 573 K and then in an uncontrolled manner to room temperature in air.

### PbFe<sub>2</sub><sup>III</sup>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>

#### Crystal data

PbFe<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>

*M<sub>r</sub>* = 666.8

Triclinic

*P*1̄

*a* = 4.785 (2) Å

*b* = 7.097 (2) Å

*c* = 7.851 (3) Å

α = 89.71 (2)°

β = 87.53 (3)°

γ = 73.54 (2)°

*V* = 255.5 (2) Å<sup>3</sup>

*Z* = 1

*D<sub>x</sub>* = 4.334 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

#### Data collection

Syntex *P4* four-circle diffractometer

θ/2θ scans

Absorption correction:

semi-empirical *via* ψ

scans (*XEMP*; Siemens, 1991*b*)

*T<sub>min</sub>* = 0.27, *T<sub>max</sub>* = 0.49

2352 measured reflections

1176 independent reflections

#### Refinement

Refinement on *F*

*R* = 0.0421

*wR* = 0.0534

*S* = 1.22

1026 reflections

100 parameters

*w* = 1/[σ<sup>2</sup>(*F*) + 0.0008*F*<sup>2</sup>]

(Δ/σ)<sub>max</sub> = 0.035

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 45 reflections

θ = 8.7–16.4°

μ = 19.954 mm<sup>-1</sup>

*T* = 298 K

Chunk

0.15 × 0.15 × 0.15 mm

Colorless

1026 observed reflections

[*F* > 5.0σ(*F*)]

*R<sub>int</sub>* = 0.0767

θ<sub>max</sub> = 30.0°

*h* = -6 → 6

*k* = -9 → 9

*l* = 0 → 10

3 standard reflections

monitored every 97

reflections

intensity decay: negligible

Δρ<sub>max</sub> = 1.41 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -1.77 e Å<sup>-3</sup>

Extinction correction: none

Atomic scattering factors

from *International Tables for Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for PbFe<sub>2</sub><sup>III</sup>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Pb1	0	0	0	0.027 (1)
Fe1	1/2	1/2	0	0.011 (1)
Fe2	0	0	1/2	0.010 (1)
P1	0.0332 (4)	0.3810 (3)	0.2475 (2)	0.009 (1)
O11	0.3062 (14)	0.4372 (9)	0.2062 (7)	0.016 (2)
O12	-0.1225 (13)	0.3524 (9)	0.0850 (7)	0.015 (2)

O13	0.0891 (14)	0.1971 (10)	0.3513 (7)	0.018 (2)
O14	-0.1875 (14)	0.5547 (9)	0.3501 (6)	0.015 (2)
P2	-0.3813 (5)	0.7695 (3)	0.2989 (2)	0.011 (1)
O21	-0.6269 (12)	0.8198 (8)	0.4312 (6)	0.011 (2)
O22	-0.1839 (13)	0.9021 (9)	0.2955 (6)	0.014 (2)
O23	-0.4818 (14)	0.7573 (9)	0.1161 (7)	0.015 (2)

Table 2. Selected geometric parameters (Å) for PbFe<sub>2</sub><sup>III</sup>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>

Pb1—O12	2.489 (6)	P1—O11	1.493 (8)
Pb1—O22 <sup>i</sup>	2.607 (6)	P1—O14	1.576 (6)
Pb1—O12 <sup>ii</sup>	2.489 (6)	P1—O13	1.500 (7)
Pb1—O22 <sup>iii</sup>	2.607 (6)	P1—O12	1.547 (6)
Pb1—O23 <sup>iv</sup>	2.776 (6)	P2—O14	1.603 (6)
Pb1—O23 <sup>v</sup>	2.776 (6)	P2—O21	1.500 (5)
Pb1—O13	3.197 (6)	P2—O22	1.510 (8)
Pb1—O13 <sup>vi</sup>	3.197 (6)	P2—O23	1.544 (6)
Fe1—O11	1.943 (6)	Fe2—O13	1.944 (7)
Fe1—O11 <sup>vii</sup>	1.943 (6)	Fe2—O13 <sup>viii</sup>	1.944 (7)
Fe1—O12 <sup>ix</sup>	1.957 (6)	Fe2—O21 <sup>x</sup>	1.935 (5)
Fe1—O12 <sup>x</sup>	1.957 (6)	Fe2—O21 <sup>xi</sup>	1.935 (5)
Fe1—O23 <sup>xii</sup>	2.071 (6)	Fe2—O22 <sup>xii</sup>	2.077 (6)
Fe1—O23 <sup>xiii</sup>	2.071 (6)	Fe2—O22 <sup>xiii</sup>	2.077 (6)

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

### BaFe<sub>2</sub><sup>III</sup>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>

#### Crystal data

BaFe<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>

*M<sub>r</sub>* = 596.9

Monoclinic

*C2/c*

*a* = 10.586 (2) Å

*b* = 10.463 (2) Å

*c* = 9.685 (2) Å

β = 103.16 (3)°

*V* = 1044.5 (4) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 3.796 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

#### Data collection

Syntex *P4* four-circle

diffractometer

θ/2θ scans

Absorption correction:

semi-empirical *via* ψ

scans (*XEMP*; Siemens,

1991*b*)

*T<sub>min</sub>* = 0.142, *T<sub>max</sub>* =

0.448

1930 measured reflections

1528 independent reflections

#### Refinement

Refinement on *F*

*R* = 0.0421

*wR* = 0.0534

*S* = 1.22

1528 reflections

100 parameters

*w* = 1/[σ<sup>2</sup>(*F*) + 0.0008*F*<sup>2</sup>]

(Δ/σ)<sub>max</sub> = 0.035

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 45

reflections

θ = 10.0–17.6°

μ = 7.171 mm<sup>-1</sup>

*T* = 298 K

Chunk

0.215 × 0.15 × 0.15 mm

Colorless

1024 observed reflections

[*F* > 9.0σ(*F*)]

*R<sub>int</sub>* = 0.0668

θ<sub>max</sub> = 30.0°

*h* = -1 → 14

*k* = -1 → 14

*l* = -13 → 13

3 standard reflections

monitored every 97

reflections

intensity decay: negligible

Δρ<sub>max</sub> = 1.41 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -1.77 e Å<sup>-3</sup>

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for  $\text{BaFe}_2^{\text{III}}(\text{P}_2\text{O}_7)_2$

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{\text{eq}}$
Ba1	1/4	3/4	0	0.024 (1)
Fe2	1/2	0.4521 (1)	1/4	0.014 (1)
Fe3	0	1/2	0	0.014 (1)
P1	0.5606 (2)	0.6910 (2)	0.0561 (2)	0.014 (1)
O11	0.4663 (5)	0.6003 (5)	0.1058 (5)	0.017 (1)
O12	0.5243 (5)	0.8273 (5)	0.0832 (6)	0.019 (1)
O13	0.5648 (5)	0.6677 (5)	-0.0946 (6)	0.020 (2)
O14	0.7009 (5)	0.6736 (5)	0.1565 (5)	0.016 (1)
P2	0.7810 (2)	0.5435 (2)	0.2015 (2)	0.014 (1)
O21	0.6822 (5)	0.4428 (5)	0.2153 (5)	0.018 (1)
O22	0.8472 (5)	0.5059 (5)	0.0861 (6)	0.020 (2)
O23	0.8736 (5)	0.5820 (5)	0.3395 (5)	0.019 (2)

Table 4. Selected geometric parameters ( $\text{\AA}$ ) for  $\text{BaFe}_2^{\text{III}}(\text{P}_2\text{O}_7)_2$

Ba1—O11	2.771 (5)	Fe3—O23 <sup>viii</sup>	1.999 (5)
Ba1—O12	2.944 (5)	P1—O11	1.531 (6)
Ba1—O11 <sup>i</sup>	2.771 (5)	P1—O12	1.516 (5)
Ba1—O12 <sup>i</sup>	2.944 (5)	P1—O13	1.491 (6)
Ba1—O22 <sup>ii</sup>	2.921 (6)	P1—O14	1.590 (5)
Ba1—O22 <sup>iii</sup>	2.921 (6)	P2—O14	1.611 (5)
Ba1—O21 <sup>ii</sup>	3.101 (6)	P2—O22	1.501 (6)
Ba1—O21 <sup>iii</sup>	3.101 (6)	P2—O21	1.511 (6)
Ba1—O23 <sup>iv</sup>	2.854 (6)	P2—O23	1.521 (5)
Ba1—O23 <sup>v</sup>	2.854 (6)	Fe2—O11 <sup>v</sup>	2.063 (5)
Fe3—O12 <sup>vi</sup>	1.971 (5)	Fe2—O11	2.063 (5)
Fe3—O12 <sup>vii</sup>	1.971 (5)	Fe2—O13 <sup>iii</sup>	1.958 (5)
Fe3—O22 <sup>viii</sup>	1.982 (6)	Fe2—O13 <sup>ix</sup>	1.958 (5)
Fe3—O22 <sup>vii</sup>	1.982 (6)	Fe2—O21	2.034 (6)
Fe3—O23 <sup>v</sup>	1.999 (5)	Fe2—O21 <sup>v</sup>	2.034 (6)

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

A variable scan rate was used, with a scan width of  $0.6^\circ$  below  $K\alpha_1$  and  $0.6^\circ$  above  $K\alpha_2$ . Refinement was completed using full-matrix least-squares methods.

For both compounds, data collection: XSCANS (Siemens, 1991a); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SHELXS86 (Sheldrick, 1990); program(s) used to refine structures: SHELXS86; molecular graphics: XP (Siemens, 1990).

The authors express their thanks to the National Science Foundation for assistance in the form of a grant to permit collaborative investigation and to the Moroccan-American Commission for a Fulbright grant to EMH.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1996). **C52**, 1597–1599

## Copper(II) Diiron(III) Pyrophosphate

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(Received 23 November 1995; accepted 16 January 1996)

## Abstract

The crystalline structure of  $\text{CuFe}_2^{\text{II}}(\text{P}_2\text{O}_7)_2$  [copper(II) diiron(III) bis(diphosphate)] is characterized by isolated and centrosymmetric  $\text{Fe} \cdots \text{Cu} \cdots \text{Fe}$  trimers. The  $\text{Cu}^{\text{II}}$  atom has square-planar coordination geometry, with Cu—O distances in the range 1.920(3)–1.934(3) Å, while the  $\text{Fe}^{\text{III}}$  atom is octahedrally coordinated, with an average Fe—O distance of 2.000(3) Å.

## Comment

Studies of mixed-valence pyrophosphates of the type  $A^{\text{II}}B^{\text{III}}\text{P}_2\text{O}_7$  are limited in the literature.  $\text{Fe}_3(\text{P}_2\text{O}_7)_2$  ( $\text{Fe}_{0.5}^{\text{II}}\text{Fe}_{2.5}^{\text{III}}\text{P}_2\text{O}_7$ ) crystallizes in space group *Pnma*, with linear  $\text{Fe}_3\text{O}_{12}^{6-}$  trimers composed of  $\text{Fe}^{\text{III}} \cdots \text{Fe}^{\text{II}} \cdots \text{Fe}^{\text{III}}$  units [Fe<sup>II</sup>—Fe distances 2.924(1) Å]. The central  $\text{Fe}^{\text{II}}$  atom has trigonal bipyramidal coordination geometry, sharing opposite faces with octahedrally coordinated  $\text{Fe}^{\text{III}}$  atoms. The solid shows antiferromagnetic behavior