Data collection

Enraf–Nonius CAD-4 four-circle diffractometer	$R_{int} = 0.0101$
	$\theta_{max} = 27.49°$
$\omega/2\theta$ scans	$h = -8 \rightarrow 8$
Absorption correction: empirical	$k = -8 \rightarrow 9$
	$l = 0 \rightarrow 9$
$T_{min} = 0.926$, $T_{max} = 0.999$	2 standard reflections frequency: 60 min intensity decay: none
1547 measured reflections	
1389 independent reflections	
1283 observed reflections $[I > 2\sigma(I)]$	

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.581$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.0214$	$\Delta\rho_{min} = -0.642$ e Å^{-3}
$wR(F^2) = 0.0559$	Extinction correction:
$S = 1.133$	SHELXL93 (Sheldrick,
1389 reflections	1993)
95 parameters	Extinction coefficient:
H—O distances fixed at	0.0396 (21)
0.95 (2) Å	Atomic scattering factors
$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2 + 0.1582P]$	from *International Tables for Crystallography* (1992,
where $P = (F_o^2 + 2F_c^2)/3$	Vol. C, Tables 4.2.6.8 and
$(\Delta/\sigma)_{max} < 0.001$	6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sn(1)	0.33287 (3)	0.36293 (3)	0.32999 (3)	0.03870 (12)
Ni(1)	0	0	0	0.03075 (14)
F(1)	0.2798 (4)	0.0733 (3)	0.4110 (3)	0.0513 (5)
F(2)	0.4214 (3)	0.3049 (4)	0.0397 (3)	0.0484 (5)
F(3)	0.0376 (3)	0.4248 (3)	0.2900 (4)	0.0493 (5)
O(1)	0.1695 (4)	−0.1571 (3)	−0.2308 (3)	0.0383 (5)
O(2)	0.1654 (4)	0.2311 (3)	−0.1493 (4)	0.0382 (5)
O(3)	0.2160 (4)	−0.1306 (4)	0.1574 (4)	0.0395 (5)

Table 2. *Selected geometric parameters (Å, °)*

Sn(1)—F(1)	2.040 (3)	Ni(1)—O(3)	2.050 (5)
Sn(1)—F(2)	2.047 (3)	Ni(1)—O(2)	2.054 (4)
Sn(1)—F(3)	2.057 (6)	Ni(1)—O(1)	2.069 (3)
F(1)—Sn(1)—F(2)	84.78 (12)	O(3)—Ni(1)—O(1^i)	91.3 (2)
F(1)—Sn(1)—F(3)	85.4 (2)	O(3^i)—Ni(1)—O(1^i)	88.7 (2)
F(2)—Sn(1)—F(3)	84.42 (14)	O(2)—Ni(1)—O(1^i)	91.98 (15)
O(3)—Ni(1)—O(2)	92.6 (2)	O(2^i)—Ni(1)—O(1^i)	88.02 (15)
O(3^i)—Ni(1)—O(2)	87.4 (2)		

Symmetry code: (i) $-x, -y, -z$.

Table 3. *Contact distances (Å)*

O(1)$\cdots$F(1^i)	2.653 (4)	O(2)$\cdots$F(3^{iii})	2.657 (5)
O(1)$\cdots$F(3^{ii})	2.708 (6)	O(3)$\cdots$F(1)	2.674 (7)
O(2)$\cdots$F(2)	2.660 (6)	O(3)$\cdots$F(2^{iv})	2.635 (4)

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

The structure was solved by Patterson methods using SHELXS86 (Sheldrick, 1985) and refined using SHELXL93 (Sheldrick, 1993). In the final refinement H—O distances were fixed at 0.95 (2) Å and anisotropic displacement parameters were refined for all non-H atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Molecular graphics: *SNOOPI* (Davies, 1983). Software used to prepare material for publication: *SHELXL93*.

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Strontium Diiron(III) Pyrophosphate

Aicha Boutfessi and Ali Boukhari

Laboratoire de Chimie du Solide Appliqué, Departement de Chimie, Faculté des Sciences, Université Mohammed V, Avenue Ibn Batouta, Rabat, Maroc

Elizabeth M. Holt

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA

Abstract

SrFe$_2^{III}$(P$_2$O$_7$)$_2$ [strontium diiron(III) bis(diphosphate)] was prepared using high-temperature fusion and was found to crystallize in the triclinic space group $P\bar{1}$.

The Fe^{III} atoms have distorted octahedral coordination geometry [average Fe—O 1.996 (3) Å] and the Sr atoms are in sites of eightfold coordination [average Sr—O 2.739 (3) Å]. Columns of alternating Sr and Fe atoms are observed at $x = \frac{1}{2}$, $y = 0$, whereas columns of widely separated Fe atoms are seen at $x = 0$, $y = \frac{1}{2}$.

Comment

Mixed divalent metal pyrophosphates $A^{II}B^{II}P_2O_7$ are well represented in the literature (Elmarzouki, Boukhari & Holt, 1994), whereas studies of mixed-valence pyrophosphates, $A^{II}B_2^{III}(P_2O_7)_2$, are much less numerous. $SrV_2^{III}(P_2O_7)_2$ (Hwu & Willis, 1991) crystallizes to form two types of tunnels, the larger of which is occupied by Sr atoms. The single-crystal X-ray structures of the isotypic pyrophosphates $BaTi_2^{III}(P_2O_7)_2$ (Wang & Hwu, 1991) and $BaV_2^{III}(P_2O_7)_2$ (Benhamada, Grandin, Borel, Leclaire & Raveau, 1991) have been reported. $PbFe_2^{III}(P_2O_7)_2$ (Wanklyn, Wondre, Davison & Salmon, 1983) and $MgCr_2^{III}(P_2O_7)_2$ (Ust'yantsev & Tretnikova, 1974) have been reported in powder form. $Fe_3(P_2O_7)_2$ ($Fe^{III}Fe_{0.5}^{II}P_2O_7$) crystallizes to form linear $Fe^{III}\cdots Fe^{II}\cdots Fe^{III}$ trimers [Fe···Fe 2.924 (1) Å] in which the Fe^{III} atoms are octahedrally coordinated but the Fe^{II} atoms have trigonal bipyramidal coordination geometry. The solid shows antiferromagnetic behavior (Ijjaali, Venturini, Gerardin, Malaman & Gleitzer, 1991; Ijjaali, Venturini, Malaman & Gleitzer, 1990). The single-crystal structure of $Fe_4^{III}(P_2O_7)_3$ is unreported.

The structure of the title compound is unlike the structures of other Fe^{III} pyrophosphates. The metal atoms are distributed between two types of columns: ···Sr···Fe1···Sr···Fe1··· [Sr···Fe1 3.915 (2) Å] and ···Fe2···Fe2··· [Fe2···Fe2 7.830 (2) Å]. These extend parallel to the [001] direction. The Fe atoms in neighboring columns are widely separated. Fe1 and Fe2 are

found in octahedral coordination geometry, each surrounded by O atoms from six different P_2O_7 groups. The octahedra are only slightly distorted from idealized geometry and the Fe—O distances are nearly equal [average 1.996 (3) Å]. The Sr atoms are surrounded by eight O atoms [average Sr—O 2.739 (3) Å]. The P_2O_7 groups display normal P—O—P angles of 132.8 (2)° and P—O distances in the range 1.491 (3)–1.606 (3) Å.

Experimental

$SrFe_2(P_2O_7)_2$ was synthesized by mixing stoichiometric amounts of $(NH_4)_2HPO_4$, $SrCO_3$ and Fe_2O_3 according to:

$$SrCO_3 + 4(NH_4)_2HPO_4 + Fe_2O_3 \rightarrow SrFe_2(P_2O_7)_2 + 8NH_3\uparrow + CO_2\uparrow + 6H_2O\uparrow.$$
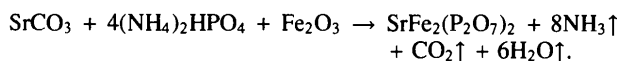
After grinding, the mixture was heated progressively to 1243 K. The final heating was followed by returning the mixture to room temperature in air. Single crystals were prepared by grinding and heating an appropriate mixture of material to 1275 K. After 24 h at this temperature, the melt was cooled (5 K h^{-1}), allowing the isolation of grey crystals.

Crystal data

$SrFe_2(P_2O_7)_2$	Mo $K\alpha$ radiation
$M_r = 547.2$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 45
$P\bar{1}$	reflections
$a = 4.795 (1)$ Å	$\theta = 10.0–17.0°$
$b = 7.108 (1)$ Å	$\mu = 8.731$ mm^{-1}
$c = 7.830 (2)$ Å	$T = 298$ K
$\alpha = 89.83 (3)°$	Chunk
$\beta = 87.59 (3)°$	$0.3 \times 0.3 \times 0.3$ mm
$\gamma = 73.11 (3)°$	Grey
$V = 255.13 (9)$ Å^3	
$Z = 1$	
$D_x = 3.561$ Mg m^{-3}	

Data collection

Syntex $P4$ four-circle	$R_{int} = 0.018$
diffractometer	$\theta_{max} = 30°$
$\theta/2\theta$ scans	$h = -1 \rightarrow 6$
Absorption correction:	$k = -9 \rightarrow 10$
semi-empirical	$l = -11 \rightarrow 11$
$T_{min} = 0.12$, $T_{max} = 0.37$	3 standard reflections
1966 measured reflections	monitored every 97
1483 independent reflections	reflections
1247 observed reflections	intensity decay: 0.0001%
$[F > 4.0\sigma(F)]$	

Refinement

Refinement on F	$\Delta\rho_{max} = 1.41$ e Å^{-3}
$R = 0.0378$	$\Delta\rho_{min} = -0.85$ e Å^{-3}
$wR = 0.0463$	Extinction correction: none
$S = 1.13$	Atomic scattering factors
1247 reflections	from International Tables
101 parameters	for Crystallography (1992,
$w = 1/[\sigma^2(F) + 0.0008F^2]$	Vol. C, Tables 4.2.6.8 and
$(\Delta/\sigma)_{max} = 0.001$	6.1.1.4)

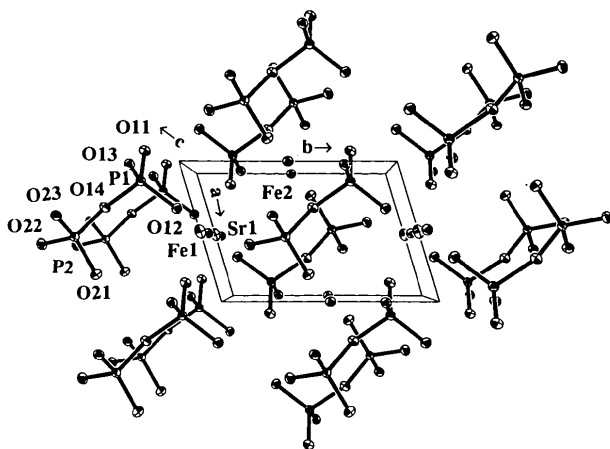
Fig. 1. A projected view of $SrFe_2^{III}(P_2O_7)_2$. Displacement ellipsoids are shown at the 50% probability level.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($\mathring{A}^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sr1	1/2	0	0	0.027 (1)
Fe1	1/2	0	1/2	0.017 (1)
Fe2	0	1/2	0	0.018 (1)
P1	0.1184 (2)	−0.2307 (2)	0.2988 (1)	0.018 (1)
P2	0.5346 (2)	−0.6203 (2)	0.2454 (1)	0.017 (1)
O11	−0.1208 (7)	−0.1804 (4)	0.4337 (4)	0.022 (1)
O12	0.3199 (7)	−0.0993 (4)	0.2933 (4)	0.021 (1)
O13	0.0124 (7)	−0.2412 (4)	0.1169 (4)	0.020 (1)
O14	0.3104 (7)	−0.4469 (4)	0.3504 (4)	0.021 (1)
O21	0.8114 (7)	−0.5653 (5)	0.2077 (4)	0.022 (1)
O22	0.5887 (7)	−0.8062 (4)	0.3457 (4)	0.024 (1)
O23	0.3844 (7)	−0.6478 (4)	0.0818 (4)	0.020 (1)

Table 2. *Selected geometric parameters* ($\mathring{A}$, °)

Sr1—O12	2.588 (3)	Fe2—O23ⁱ	1.970 (3)
Sr1—O13ⁱ	2.747 (3)	P1—O11	1.491 (3)
Sr1—O22ⁱⁱ	3.141 (3)	P1—O12	1.526 (4)
Sr1—O23ⁱⁱ	2.481 (3)	P1—O13	1.541 (3)
Fe1—O11ⁱⁱⁱ	1.947 (3)	P1—O14	1.606 (3)
Fe1—O12ⁱᵛ	2.084 (3)	P2—O14	1.585 (3)
Fe1—O22ᵛ	1.956 (3)	P2—O21	1.507 (4)
Fe2—O13ⁱⁱ	2.074 (3)	P2—O22	1.497 (3)
Fe2—O21ᵛⁱ	1.948 (3)	P2—O23	1.536 (3)
O12—P1—O11	115.6 (2)	O14—P2—O21	108.9 (2)
O14—P1—O12	107.3 (2)	O22—P2—O21	111.9 (2)
O14—P1—O11	103.4 (2)	O14—P2—O23	106.5 (2)
O14—P1—O13	108.4 (2)	O23—P2—O22	107.9 (2)
O11—P1—O13	113.9 (2)	O23—P2—O21	112.2 (2)
O12—P1—O13	107.8 (2)	P1—O14—P2	132.8 (2)
O14—P2—O22	109.3 (2)		

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

A variable scan rate with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$ was used for data collection. Refinement was completed using full-matrix least-squares methods. Data collection, cell refinement and data reduction: *XSCANS* (Siemens, 1991). Structure solution and refinement: *SHELXS*86 (Sheldrick, 1990). Molecular graphics: *XP* (Siemens, 1991).

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Eu₂(PO₃H)₃

Jean-D. Foulon, Jean Durand et Louis Cot

Laboratoire de Physicochimie des Matériaux (URA 1312 du CNRS), Ecole Nationale Supérieure de Chimie de Montpellier, 8 Rue de l'Ecole Normale, 34053 Montpellier CEDEX 1, France

Najib Tijani et Mohamed Rafiq

Laboratoire de Chimie Minérale Appliquée, Faculté des Sciences, Fès, Maroc

Abstract

The structure of dieuropium tris(hydrogen phosphite), Eu₂(PO₃H)₃, contains three independent phosphite anions. One Eu³⁺ cation is eight-coordinate whereas the other is only seven-coordinate. One [EuO₈] dodecahedron and one monocapped [EuO₇] trigonal prism alternate so that, by sharing one vertex, infinite layers are formed parallel to the [101] direction. The layers are held together by Eu—O interlayer bonds.

Commentaire

A partir de la phase Ln₂(PO₃H)₃.2,5H₂O on obtient par déshydratation progressive à l'état solide la phase monohydratée Ln₂(PO₃H)₃.H₂O puis la phase anhydre Ln₂(PO₃H)₃ avec Ln = Pr, Nd, Gd ou Eu. Dans le cadre de notre étude générale visant à mieux connaître les différents arrangements structuraux possibles dans la famille des phosphites neutres de terres rares, les structures cristallines des deux phases hydratées ont déjà été mises en évidence (Foulon, Tijani, Durand, Rafiq & Cot, 1993*a,b*). La détermination structurale de Eu₂(PO₃H)₃ complète notre étude en permettant la caractérisation structurale de la phase anhydre.

La structure de Eu₂(PO₃H)₃ peut être décrite à partir de trois tétraèdres PO₃H²⁻ indépendants centrés en