

$V = 1075.2 (2) \text{ \AA}^3$
 $Z = 3$
 $D_x = 1.968 \text{ Mg m}^{-3}$

$T = 29 \pm 0.5 \text{ K}$
 Rhombic
 $1.68 \times 1.53 \times 1.23 \text{ mm}$
 Colourless

Data collection

Huber four-circle diffractometer
 $\omega/2\theta$ scans
 Absorption correction: analytical
 $T_{\min} = 0.862$, $T_{\max} = 0.903$
 790 measured reflections
 569 independent reflections

364 observed reflections
 $[I > 3\sigma(I)]$
 $R_{\text{int}} = 0.0552$
 $\theta_{\max} = 53.38^\circ$
 $h = -10 \rightarrow 9$
 $k = -10 \rightarrow 5$
 $l = -19 \rightarrow 19$
 Intensity variation of standard reflections: $< \pm 1$

Refinement

Refinement on F^2
 $R(F) = 0.0310$
 $wR(F^2) = 0.0526$
 $S = 1.122$
 364 reflections
 44 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0204P)^2 + 0.01P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 Extinction correction: SHELXL92 (Sheldrick, 1992)
 Extinction coefficient: 1.31 (6)
 Nuclear coherent scattering lengths from Koester, Rauch, Herkens & Schröder (1981)

Data collection was performed at the Studsvik Neutron Research Laboratory in Studsvik, Sweden, using the R2 reactor and a Huber four-circle diffractometer, equipped with a Cryogenics closed-circuit He₂-refrigerator cooling device. Reflections were collected with 40 steps, at an ω -step size of 0.1° , up to $\sin\theta/\lambda = 0.5290 \text{ \AA}^{-1}$ and with 50 steps above that resolution. The effective absorption coefficient, $\mu = 0.088 \text{ mm}^{-1}$, was determined experimentally. SHELXL92 (Sheldrick, 1992) was used to refine the structure. Neutron scattering lengths, b (10^{-12} cm), for the structure-factor calculation were H = -0.3741 , Si = 0.4149 and O = 0.5805 . Molecular graphics were prepared using PEANUT (Hummel, Hauser & Bürgi, 1990).

The author is grateful to Professor G. Calzaferri at the University of Berne, Switzerland, for supplying the crystals and to Mr Håkan Rundlöf at the Studsvik Neutron Research Laboratory for technical assistance during the experiment. This project is financially supported by the Swedish Natural Science Research Council.

A list of structure factors has been deposited with the IUCr (Reference: CR1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Agaskar, P. A. (1991). *Inorg. Chem.* **30**, 2702–2708.
 Auf der Heyde, T. P. E., Bürgi, H.-B., Bürgy, H. & Törnroos, K. W. (1991). *Chimia*, **45**, 38–40.
 Diamond, R. (1988). *Acta Cryst.* **A44**, 211–216.

- Hummel, W., Hauser, J. & Bürgi, H.-B. (1990). *J. Mol. Graph.* **8**, 214–220.
 Koester, L., Rauch, H., Herkens, M. & Schröder, K. (1981). KFA-Report, Jül-1755.
 Sheldrick, G. M. (1992). SHELXL92. Program for the Refinement of Crystal Structures. Univ. of Göttingen, Germany.
 Törnroos, K. W., Schwarzenbach, D., Delley, B. & Larsen, F. K. (1994). *Acta Cryst.* In preparation.
 Trueblood, K. N. (1985). THMA11. Thermal Motion Analysis. Univ. of California, Los Angeles, USA.

Acta Cryst. (1994). **C50**, 1648–1650

Cadmium Iron(III) Iron(II) Diphosphate

ALAOUI ELBELGHITTI AND ALI BOUKHARI

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

ELIZABETH M. HOLT

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

(Received 5 August 1993; accepted 17 June 1994)

Abstract

$\text{Cd}_{2.06}\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}_{0.44}(\text{P}_2\text{O}_7)_2$ crystallizes in the orthorhombic space group $C222_1$ with Fe^{III} in a distorted octahedral environment [average Fe—O 2.05 (1) Å] and Fe^{II} sharing sites with Cd atoms in two sites of sixfold coordination [average Cd/Fe—O 2.20 (1) Å]. Two further Cd atoms show sixfold coordination with average Cd—O 2.31 (1) Å.

Comment

Mixed-valence phosphates such as Fe₇(PO₄)₆ and Cr₇(PO₄)₆ have been reported in the literature (Gorbunov *et al.*, 1980; Glaum, 1993). Planes of bent ($-\text{M}^{\text{III}}-\text{M}^{\text{III}}-\text{M}^{\text{II}}-$) chains are found in the solid-state structures.

A number of iron diphosphates are known in the solid state. The stoichiometries of the compounds Fe^{II}P₂O₇, Fe^{III}Fe^{II}_{0.44}Cd_{2.06}(P₂O₇)₂, Fe^{II}Fe^{II}(P₂O₇)₄ and Fe^{II}Fe^{II}(P₂O₇)₂, when expressed as Fe^{II}₂P₂O₇, Fe^{III}_{0.5}(Fe^{II}, Cd)_{1.25}P₂O₇ and Fe^{III}Fe^{II}_{0.5}P₂O₇, respectively, may be seen to form a series of increasing Fe^{III}/Fe^{II} ratio. The solid-state structures of the series show a progression from planes of metal atoms with hexagonal disposition when the Fe^{II} content is high (Fe^{III}/Fe^{II} ratio low) to isolated and linear metal trimers when the Fe^{III} content is higher. The single-crystal structure of Fe^{II}₄(P₂O₇)₃ is unreported.

$\text{Fe}_2\text{P}_2\text{O}_7$ shows a coplanar array of edge-sharing metal hexagons in which adjacent pairs of pseudo-octahedral Fe atoms are bridged by two O atoms (Stefanidis & Nord, 1982; Hoggins, Swinnea & Steinfink, 1983) with $\text{Fe}^{\text{II}}-\text{Fe}^{\text{II}}$ separations of 3.236 (4)–3.590 (4) Å.

$\text{Fe}^{\text{III}}\text{Fe}_{0.44}^{\text{II}}\text{Cd}_{2.06}(\text{P}_2\text{O}_7)_2$ is isostructural with $\text{Fe}_2^{\text{III}}\text{Fe}_3^{\text{II}}(\text{P}_2\text{O}_7)_4$ [general formula $\text{Fe}_{0.5}^{\text{III}}(\text{Fe}^{\text{II}},\text{Cd})_{1.25}\text{P}_2\text{O}_7$]. Both display corrugated layers of metal atoms separated by P_2O_7 layers (Fig. 1). Closer inspection shows that the modulated layers of metal atoms consist of chains of coplanar linked metallic hexagons joined by single-atom metallic bent bridges (Fig. 2a). Both structures show octahedral Fe^{III} atoms (Fe3), positioned in the

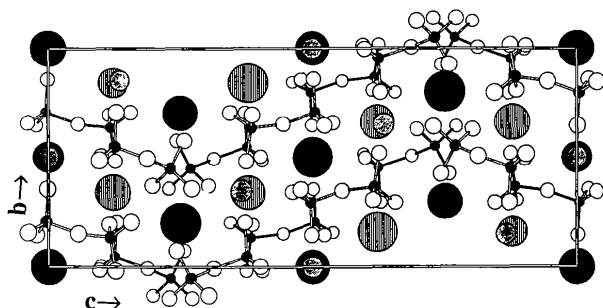


Fig. 1. Projection view of $\text{Cd}_{2.06}\text{Fe}^{\text{III}}\text{Fe}_{0.44}^{\text{II}}(\text{P}_2\text{O}_7)_2$.

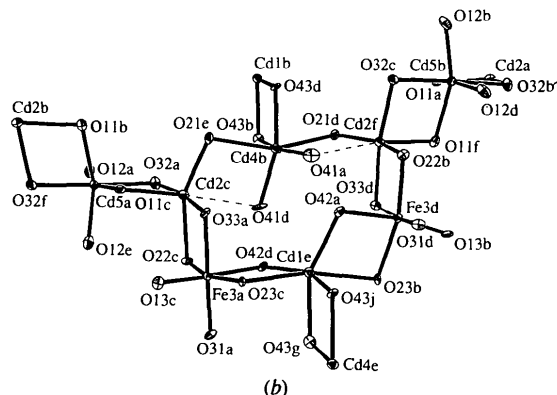
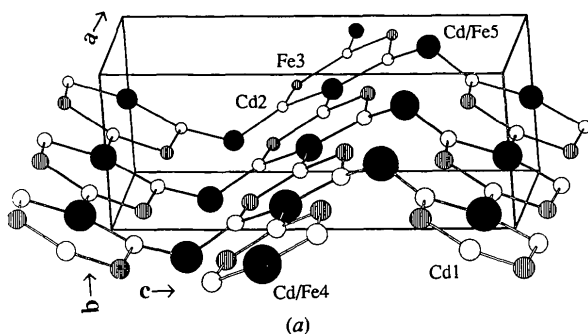


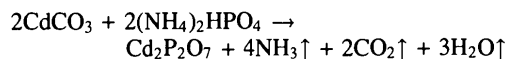
Fig. 2. (a) View of the metallic plane of $\text{Cd}_{2.06}\text{Fe}^{\text{III}}\text{Fe}_{0.44}^{\text{II}}(\text{P}_2\text{O}_7)_2$, with metal-metal separations of less than 3.6 Å indicated by lines, and (b) view (30% probability displacement ellipsoids) of a section of the metallic plane in (a) showing O atoms bridging adjacent metal atoms.

hexagonal rings with only two near metallic neighbors. In $\text{Fe}_2^{\text{III}}\text{Fe}_3^{\text{II}}(\text{P}_2\text{O}_7)_4$, all sites other than the Fe^{III} positions are occupied by Fe^{II} atoms. In $\text{Fe}^{\text{III}}\text{Fe}_{0.44}^{\text{II}}\text{Cd}_{2.06}(\text{P}_2\text{O}_7)_2$, the remaining alternate position is a mixed Cd/Fe^{II} site (Cd/Fe4) as is that of the bridging atom (Cd/Fe5). Three other ring positions are occupied by Cd atoms alone. There are no close Fe—Fe distances [average $\text{Fe}^{\text{III}}-\text{Cd}$ 3.45 (1), average Cd/Fe^{II}—Cd 3.52 (1) Å]. Adjacent metal atoms are bridged by two O atoms (Fig. 2b).

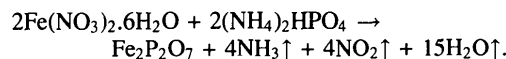
$\text{Fe}_3(\text{P}_2\text{O}_7)_2$ ($\text{Fe}^{\text{III}}\text{Fe}_{0.5}^{\text{II}}\text{P}_2\text{O}_7$) crystallizes with linear trimers of $\text{Fe}^{3+}-\text{Fe}^{2+}-\text{Fe}^{3+}$ [Fe—Fe distances 2.924 (1) Å]. Fe^{3+} atoms are octahedrally coordinated whereas the central Fe^{2+} position shows trigonal prismatic geometry. Adjacent members of the trimer are bridged by three O atoms with three P_2O_7 groups providing one bridging O atom to each of the metallic pairs. The solid shows antiferromagnetic behavior (Ijjaali, Venturini, Gerardin, Malaman & Gleitzer, 1991; Ijjaali, Venturini, Malaman & Gleitzer, 1990).

Experimental

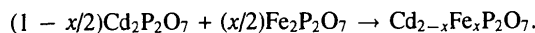
The diphosphates $\text{Cd}_2\text{P}_2\text{O}_7$ and $\text{Fe}_2\text{P}_2\text{O}_7$ were synthesized by mixing, in stoichiometric fashion, $(\text{NH}_4)_2\text{HPO}_3$ and CdCO_3 or $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ according to



or



After grinding, the mixture was treated at 393 K to avoid energetic decomposition of the ammoniacal phosphate. This mixture was then heated to 573, 773 and 1173 K. The last heating was followed by a return to room temperature in air. Materials of compositions corresponding to $\text{Cd}_{2-x}\text{Fe}_x\text{P}_2\text{O}_7$ were prepared according to



Mixtures of appropriate stoichiometries were ground together, heated to 873 K, then to 1173 K for 72 h periods with intermediate grinding. Crystals of $\text{Cd}_{2.06}\text{Fe}^{\text{III}}\text{Fe}_{0.44}^{\text{II}}(\text{P}_2\text{O}_7)_2$ were obtained by fusion in the presence of an excess of P_2O_5 and air. The mixture was heated to the fusion point (1373 K) in an open platinum crucible. Slow cooling (4 K h^{-1} to 1173 K, then 10 K h^{-1} to 473 K) followed by cessation of heating of the furnace allowed the isolation of dark brown crystals.

Crystal data

$\text{Cd}_{2.06}\text{Fe}^{\text{III}}\text{Fe}_{0.44}^{\text{II}}(\text{P}_2\text{O}_7)_2$
 $M_r = 659.9$
 Orthorhombic
 $C22_1$
 $a = 8.702$ (1) Å
 $b = 9.889$ (1) Å
 $c = 23.968$ (3) Å
 $V = 2062.5$ (3) Å³
 $Z = 8$
 $D_x = 4.250\text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 10.0-17.0^\circ$
 $\mu = 6.902\text{ mm}^{-1}$
 $T = 298\text{ K}$
 Chunk
 $0.1 \times 0.1 \times 0.1\text{ mm}$
 Dark brown

Data collection

Syntex P4 four-circle
diffractometer
 $\theta/2\theta$ scans
Absorption correction:
semi-empirical
 $T_{\min} = 0.12$, $T_{\max} = 0.37$
2174 measured reflections
2056 independent reflections
1470 observed reflections
[$I > 4.0\sigma(F)$]

Refinement

Refinement on F
 $R = 0.0489$
 $wR = 0.0525$
 $S = 0.95$
1470 reflections
207 parameters
 $w = 1/[\sigma^2(F) + 0.0008F^2]$
 $(\Delta/\sigma)_{\max} = 0.012$

$\theta_{\max} = 22.5^\circ$
 $h = -1 \rightarrow 12$
 $k = -1 \rightarrow 13$
 $l = -1 \rightarrow 33$
3 standard reflections
monitored every 97
reflections
intensity variation: none

$\Delta\rho_{\max} = 1.38 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.67 \text{ e } \text{\AA}^{-3}$
Atomic scattering factors
from *International Tables*
for *Crystallography* (1992),
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Fe3—O42 ⁱⁱ	2.027 (10)	P3—O31	1.496 (13)
Fe3—O33 ^{iv}	2.131 (12)	P3—O32	1.502 (13)
Fe3—O22 ^{vi}	2.098 (12)	P3—O33	1.530 (12)
Cd/Fe4—O43	2.172 (11)	P4—O41	1.502 (14)
Cd/Fe4—O41 ^{ix}	2.125 (14)	P4—O42	1.533 (11)
Cd/Fe4—O21 ^v	2.408 (10)	P4—O43	1.524 (11)
Cd/Fe4—O43 ⁱ	2.172 (11)	P4—O34	1.603 (11)
Cd/Fe4—O41 ^x	2.125 (14)		
O43—P4—O41	111.6 (7)	P1—O14—P2	134.5 (8)
O43—P4—O34	107.2 (7)	O34—P3—O33	104.0 (6)
O41—P4—O34	113.9 (7)	O33—P3—P32	110.8 (7)
O43—P4—O42	112.7 (7)	O33—P3—O31	114.9 (7)
O42—P4—O41	112.5 (7)	O34—P3—O32	106.4 (7)
O42—P4—O34	98.1 (6)	O34—P3—O31	105.5 (7)
O11—P1—O14	102.0 (6)	O32—P3—O31	114.3 (7)
O11—P1—O12	111.7 (7)	O14—P2—O23	106.3 (6)
O12—P1—O14	107.9 (7)	O23—P2—O22	112.7 (7)
O11—P1—O13	113.2 (7)	O23—P2—O21	112.8 (7)
O14—P1—O13	107.3 (6)	O14—P2—O22	105.7 (7)
O12—P1—O13	113.8 (8)	O14—P2—O21	105.4 (6)
P4—O34—P3	137.8 (8)	O22—P2—O21	113.1 (7)

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

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^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_{eq}
Cd1	0.1911 (2)	0	1/2	0.019 (1)
Cd2	-0.3154 (2)	0.1497 (1)	0.3650 (1)	0.021 (1)
Fe3	0.0739 (2)	0.1597 (2)	0.3774 (1)	0.013 (1)
Cd/Fe4	0.5810 (2)	0	1/2	0.021 (1)
Cd/Fe5	1/2	0.2992 (2)	1/4	0.018 (1)
P1	-0.2456 (6)	0.0502 (5)	0.2310 (2)	0.017 (1)
P2	-0.3780 (5)	-0.0488 (4)	0.1248 (2)	0.014 (1)
P3	0.3866 (5)	0.3655 (4)	0.3831 (2)	0.016 (1)
P4	0.4002 (5)	0.2956 (4)	0.5046 (2)	0.015 (1)
O11	-0.3335 (12)	0.1389 (13)	0.2710 (5)	0.022 (3)
O12	-0.1878 (18)	-0.0749 (11)	0.2588 (5)	0.033 (4)
O13	-0.1243 (14)	0.1256 (12)	0.1986 (5)	0.023 (3)
O14	-0.3780 (13)	0.0061 (12)	0.1873 (4)	0.021 (3)
O21	-0.5157 (14)	0.0152 (14)	0.0974 (4)	0.022 (3)
O22	-0.3908 (14)	-0.2033 (12)	0.1294 (5)	0.020 (3)
O23	-0.2260 (12)	-0.0032 (12)	0.0989 (4)	0.016 (3)
O31	0.2296 (14)	0.3043 (12)	0.3856 (5)	0.021 (3)
O32	0.4952 (16)	0.2947 (12)	0.3441 (5)	0.026 (4)
O33	0.3894 (14)	0.5183 (11)	0.3733 (4)	0.018 (3)
O34	0.4568 (13)	0.3480 (12)	0.4447 (4)	0.023 (3)
O41	0.2512 (15)	0.3568 (14)	0.5235 (5)	0.032 (4)
O42	0.5376 (12)	0.3450 (13)	0.5390 (4)	0.017 (3)
O43	0.3906 (13)	0.1419 (11)	0.5015 (5)	0.019 (3)

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

Cd1—O43 ⁱ	2.232 (11)	Cd/Fe4—O21 ⁱⁱⁱ	2.408 (10)
Cd1—O42 ⁱⁱ	2.239 (11)	Cd/Fe5—O32	2.257 (11)
Cd1—O23 ⁱⁱⁱ	2.391 (10)	Cd/Fe5—O11 ⁱⁱⁱ	2.206 (12)
Cd1—O43	2.232 (11)	Cd/Fe5—O12 ^{xi}	2.065 (14)
Cd1—O42 ^{iv}	2.239 (11)	Cd/Fe5—O11 ^{xii}	2.206 (12)
Cd1—O23 ^v	2.391 (10)	Cd/Fe5—O12 ^{xiii}	2.065 (14)
Cd2—O41	2.736 (11)	Cd/Fe5—O32 ^{xiv}	2.257 (11)
Cd2—O33 ^{iv}	2.214 (12)	P1—O11	1.507 (13)
Cd2—O22 ^{vi}	2.314 (12)	P1—O12	1.492 (13)
Cd2—O11	2.260 (11)	P1—O13	1.509 (12)
Cd2—O32 ^{vii}	2.241 (13)	P1—O14	1.618 (12)
Cd2—O21 ^{viii}	2.177 (12)	P2—O14	1.593 (11)
Fe3—O31	1.979 (12)	P2—O21	1.505 (13)
Fe3—O13 ⁱⁱⁱ	1.904 (11)	P2—O22	1.536 (12)
Fe3—O23 ⁱⁱⁱ	2.161 (12)	P2—O23	1.528 (12)

Data were collected using a variable scan rate, in a θ - 2θ scan mode with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$ to a maximum 2θ value of 45° . Data collection, cell refinement and data reduction were performed using *XSCANS* (Fait, 1991). The structure was solved and refined using *SHELXS86* (Sheldrick, 1990). Refinement was completed using full-matrix least-squares methods. Molecular graphics were produced using *CHEM3D* (Rubenstein & Rubenstein, 1987).

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: BR1058). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Fait, J. (1991). *XSCANS Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Glaum, R. (1993). *Z. Kristallogr.* **205**, 69–83.
- Gorbunov, Y., Maksimov, B., Kabalov, Y., Ivachenko, A. N., Melnikov, O. & Belov, N. (1980). *Dokl. Akad. Nauk SSSR*, **154**, 873–877.
- Hoggins, J. T., Swinnea, J. S. & Steinfink, H. (1983). *J. Solid State Chem.* **47**, 278–283.
- Ijjaali, M., Venturini, G., Gerardin, R., Malaman, B. & Gleitzer, C. (1991). *Eur. J. Solid State Inorg. Chem.* **28**, 983–998.
- Ijjaali, M., Venturini, G., Malaman, B. & Gleitzer, C. (1990). *C. R. Acad. Sci. Paris*, **310**, 1419–1423.
- Rubenstein, M. & Rubenstein, S. (1987). *Chem3D, The Molecular Modeling System*. Cambridge Scientific Computing Inc., Cambridge, Massachusetts, USA.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Stefanidis, T. & Nord, A. G. (1982). *Z. Kristallogr.* **159**, 255–264.