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}
Y	4 (*i*)	0.6202 (1)	0	0.3230 (2)	0.0082 (4)
Al(1)	4 (*i*)	0.3058 (4)	0	0.1342 (7)	0.014 (1)
Al(2)	2 (*a*)	0	0	0	0.016 (2)
Si	4 (*i*)	0.0931 (3)	0	0.6403 (6)	0.011 (1)

Table 2. *Selected interatomic distances* (Å)

Y—Si		2.892 (4)
Y—Si	× 2	2.964 (3)
Y—Si	× 2	3.015 (3)
Y—Al(2)	× 2	3.019 (1)
Y—Al(1)	× 2	3.188 (4)
Y—Al(1)		3.209 (4)
Y—Al(1)		3.260 (5)
Y—Al(1)		3.521 (5)
Y—Y		3.713 (2)
Y—Y	× 2	3.761 (2)
[Y—Y	× 2	4.035 (1)]
Al(1)—Si	× 2	2.599 (3)
Al(1)—Al(1)	× 2	2.780 (4)
Al(1)—Al(2)		3.076 (4)
Al(1)—Al(2)	× 2	3.081 (4)
Al(1)—Y	× 2	3.188 (4)
Al(1)—Y		3.209 (4)
Al(1)—Y		3.260 (5)
Al(1)—Y		3.521 (5)
Al(1)—Si		3.551 (5)
Al(2)—Si	× 2	2.732 (4)
Al(2)—Y	× 4	3.019 (1)
Al(2)—Al(1)	× 2	3.076 (4)
Al(2)—Al(1)	× 4	3.081 (4)
Si—Si		2.382 (5)
Si—Al(1)	× 2	2.599 (3)
Si—Al(2)		2.732 (4)
Si—Y		2.892 (4)
Si—Y	× 2	2.964 (3)
Si—Y	× 2	3.015 (3)
Si—Al(1)		3.551 (5)

Structure solution was performed using *MULTAN*87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). Least-squares refinement included varying a scale factor, isotropic extinction, atomic positional and anisotropic displacement parameters. Programs used for data reduction and structure refinement were from the *Xtal*3.2 system (Hall, Flack & Stewart, 1992).

Lists of structure factors, anisotropic displacement parameters and bond distances have been deposited with the IUCr (Reference: DU1080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Synthetic Spheniscidite

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Abstract

Spheniscidite, ammonium hydroxide iron phosphate dihydrate, $[Fe_2(NH_4)(OH)(PO_4)_2].2H_2O$, is known as a mineral isotypic with leucophosphite. Crystals were obtained by hydrothermal synthesis at medium temperature. The crystal structure determination confirms the leucophosphite structure type and provides detailed localization of the water molecules and ammonium cations inside the cavities of the framework.

Comment

With a view to synthesizing some oxyfluorinated phosphates of iron which have microporous frameworks, we investigated the system $FeO(OH)–H_3PO_4–HF–1,3$-diaminopropane (hereafter 1,3-DAP)–H_2O through the synthetic route described by Tapp, Milestone & Bibby (1988), which uses an organic amine as a template. Under our reaction conditions, 1,3-DAP decomposed and $[Fe_2(NH_4)(OH)(PO_4)_2].2H_2O$, which corresponds to the formula of spheniscidite (Wilson & Bain, 1986), was formed. The structure of mineral spheniscidite has not yet been described, but is claimed to be isotypic with leucophosphite $[KFe_2(PO_4)_2(OH)].2H_2O$ (Moore, 1972). Related substances with this well known structure type, but different chemical compositions, can be found in the literature: $GaPO_4.2H_2O$ (Mooney-Slater, 1966), also labelled $GaPO_4–C_7$ by Wang, Yang, Feng, Shang & Xu (1989), and $RbMo_2P_2O_{10}.1-xH_2O$ (Leclaire, Borel, Grandin & Raveau, 1994). The detailed structure determination of spheniscidite is presented here.

The three-dimensional network of spheniscidite is built up from octahedrally coordinated Fe^{III} and PO_4 tetrahedra. It can also be described as the corner sharing of octameric building units (Fig. 1*a*). This octamer consists of an edge-sharing bioctahedron of Fe^{III}, whose common edge is delimited by two OH groups which are also shared with the satellite octahedra. One vertex of each satellite octahedron is occupied by a terminal water molecule. The octamer is completed by four PO_4 tetrahedra, each sharing either two or three corners with the Fe octahedra of the octamer. After their linkage, these octamers adopt a quasi-cc lattice within the unit

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cell, forming eight-membered tunnels running along the three axes of the cell. NH_4^+ cations and water molecules are inserted in these tunnels (Fig. 1*b*).

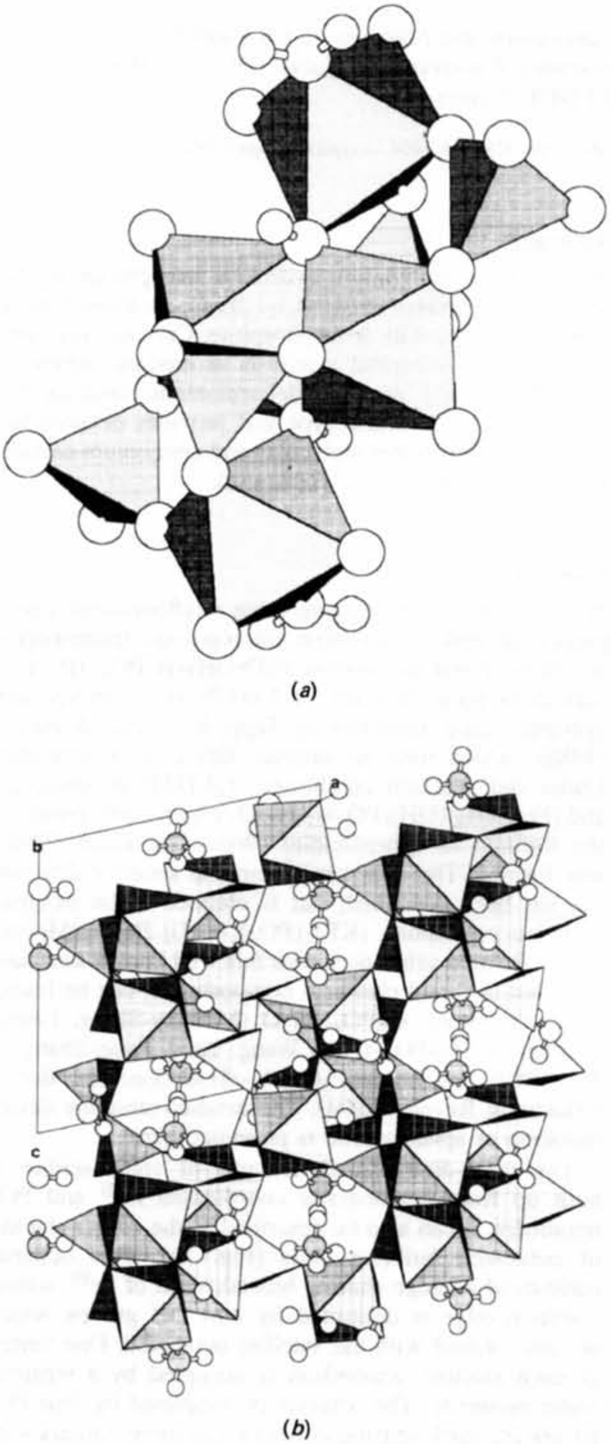

Fig. 1. (a) Perspective view of the octameric building units of the title structure. (*b*) Projection along [010].

Experimental

The title compound was prepared hydrothermally from a mixture of FeO(OH), H_3PO_4, HF, 1,3-DAP and water in a molar ratio 2:2:2:3:80. The resulting product was heated at 473 K for 24 h in an autoclave under autogenous pressure, then filtered, washed and finally dried in air. A brownish green crystal with rhombohedral faces was isolated and its quality tested by Laue photography. The chemical composition, first determined by energy-dispersive X-ray (EDX) analysis performed with a Jeol-2010 TEM equipped with a KEVEX energy dispersive X-ray spectrometer, was improved by the crystal structure determination. The ammonium cations probably come from the decomposition of the organic compound during synthesis at 473 K.

Crystal data

[$Fe_2(NH_4)(OH)(PO_4)_2$].$2H_2O$
$M_r = 372.72$
Monoclinic
$P2_1/n$
$a = 9.8232$ (6) Å
$b = 9.7376$ (8) Å
$c = 9.8716$ (8) Å
$\beta = 102.803$ (8)°
$V = 920.8$ (1) Å^3
$Z = 4$
$D_x = 2.689$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 34 reflections
$\theta = 14$–16°
$\mu = 3.642$ mm^{-1}
$T = 293$ K
Rhombohedral
0.418 × 0.380 × 0.228 mm
Brownish green

Data collection

Stoe Siemens AED-2 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.222$, $T_{\max} = 0.459$
2582 measured reflections

2582 independent reflections
2582 observed reflections
$\theta_{\max} = 30.01°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity variation: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0258$
$wR(F^2) = 0.0734$
$S = 1.240$
2582 reflections
182 parameters
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0298P)^2 + 2.4280P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.007$

$\Delta\rho_{\max} = 0.720$ e Å^{-3}
$\Delta\rho_{\min} = -0.514$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0075 (8)
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^2)

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

	x	y	z	$U_{\rm eq}$
Fe1	0.60167 (3)	0.23175 (3)	0.31330 (3)	0.0070 (1)
Fe2	0.88696 (3)	−0.04489 (3)	−0.12997 (3)	0.0071 (1)
P1	0.79641 (6)	0.03494 (6)	0.14807 (6)	0.0070 (1)
P2	0.79230 (6)	0.18304 (6)	−0.36871 (6)	0.0070 (1)

O1	0.7814 (2)	0.0406 (2)	−0.3014 (2)	0.0109 (3)
O2	0.6877 (2)	0.1309 (2)	0.1833 (2)	0.0122 (3)
O3	0.7135 (2)	0.3934 (2)	0.2846 (2)	0.0110 (3)
O4	0.7623 (2)	0.0184 (2)	−0.0121 (2)	0.0101 (3)
O5	1.0549 (2)	−0.0931 (2)	−0.1988 (2)	0.0105 (3)
O6	0.7375 (2)	0.1688 (2)	0.4751 (2)	0.0121 (3)
O7	0.5007 (2)	0.3587 (2)	0.4403 (2)	0.0087 (3)
O8	0.4451 (2)	0.2718 (2)	0.1578 (2)	0.0126 (3)
O9	0.7952 (2)	−0.2160 (2)	−0.1955 (2)	0.0124 (3)
O*W*1	0.4941 (2)	0.0534 (2)	0.3443 (2)	0.0203 (4)
O*W*2	0.6809 (3)	−0.1468 (2)	0.4654 (2)	0.0253 (4)
N	0.5103 (3)	0.1894 (3)	−0.1031 (3)	0.0210 (5)

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

Fe1—O6	1.940 (2)	Fe2—O7^{i}	2.162 (2)
Fe1—O2	1.951 (2)	Fe2—O7^{ii}	2.165 (2)
Fe1—O8	1.957 (2)	P1—O2	1.517 (2)
Fe1—O3	1.976 (2)	P1—O5^{iii}	1.543 (2)
Fe1—O*W*1	2.091 (2)	P1—O3^{ii}	1.543 (2)
Fe1—O7	2.153 (2)	P1—O4	1.551 (2)
Fe2—O9	1.936 (2)	P2—O6^{iv}	1.522 (2)
Fe2—O1	1.963 (2)	P2—O8^{i}	1.530 (2)
Fe2—O4	1.966 (2)	P2—O9^{v}	1.532 (2)
Fe2—O5	1.975 (2)	P2—O1	1.552 (2)
O6—Fe1—O2	93.64 (7)	O9—Fe2—O7^{i}	176.58 (7)
O6—Fe1—O8	170.68 (8)	O1—Fe2—O7^{i}	93.32 (7)
O2—Fe1—O8	87.94 (7)	O4—Fe2—O7^{i}	83.84 (7)
O6—Fe1—O3	93.83 (8)	O5—Fe2—O7^{i}	84.14 (7)
O2—Fe1—O3	88.33 (7)	O9—Fe2—O7^{ii}	91.49 (7)
O8—Fe1—O3	95.40 (8)	O1—Fe2—O7^{ii}	178.76 (7)
O6—Fe1—O*W*1	83.97 (8)	O4—Fe2—O7^{ii}	83.64 (7)
O2—Fe1—O*W*1	89.13 (9)	O5—Fe2—O7^{ii}	83.69 (7)
O8—Fe1—O*W*1	86.87 (8)	O7^{i}—Fe2—O7^{ii}	87.59 (7)
O3—Fe1—O*W*1	176.54 (8)	O2—P1—O5^{iii}	111.32 (10)
O6—Fe1—O7	91.34 (7)	O2—P1—O3^{ii}	109.68 (10)
O2—Fe1—O7	174.12 (7)	O5^{iii}—P1—O3^{ii}	109.48 (10)
O8—Fe1—O7	87.64 (7)	O2—P1—O4	107.09 (10)
O3—Fe1—O7	88.21 (7)	O5^{iii}—P1—O4	110.15 (10)
O*W*1—Fe1—O7	94.51 (8)	O3^{ii}—P1—O4	109.08 (10)
O9—Fe2—O1	87.65 (7)	O6^{iv}—P2—O8^{i}	108.20 (10)
O9—Fe2—O4	99.34 (8)	O6^{iv}—P2—O9^{v}	111.86 (10)
O1—Fe2—O4	95.62 (7)	O8^{i}—P2—O9^{v}	111.33 (11)
O9—Fe2—O5	92.49 (8)	O6^{iv}—P2—O1	108.04 (10)
O1—Fe2—O5	97.23 (7)	O8^{i}—P2—O1	109.98 (10)
O4—Fe2—O5	162.86 (7)	O9^{v}—P2—O1	107.37 (10)

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

Data collection and cell refinement: *DIF*4 (Stoe & Cie, 1988*a*). Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990), option *TREF*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

The authors thank Dr R. Retoux, Université du Maine, for his help in data collection and microprobe analysis.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1089). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cadmium Diselenite and Cadmium Hydrogenselenite Selenite

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Abstract

Cadmium diselenite, $CdSe_2O_5$, consists of an octahedrally coordinated Cd atom and a diselenite group that acts as a bidentate ligand. Cadmium hydrogenselenite selenite, $Cd_3(HSeO_3)_2(SeO_3)_2$, has seven- and six-coordinated Cd atoms and two different selenite groups: hydrogenselenite and selenite.

Comment

The crystal structures of cadmium selenites are almost unknown. Before this year the only published structure was that of cadmium hydrogenselenite nitrate (Leskelä, Valkonen & Leskelä, 1984). We have now synthesized and solved the structures of seven different cadmium selenites: $CdSeO_3$(*oP*20), $CdSeO_3$(*mP*40), $4CdSeO_3.3H_2O$, $CdSe_2O_5$, $Cd_3(HSeO_3)_2(SeO_3)_2$, $(NH_4)_2Cd(SeO_3)_2$ and $Cd(NH_3)SeO_3$. [The Pearson notation is used for phase nomenclature: *oP*20 and *mP*40 (IUPAC, 1990)]. The structures of the first three of these compounds have been published recently (Valkonen, 1994), the next two are discussed in this paper and the final two structures will be reported shortly.

The structures of both of the title compounds comprise three-dimensional networks in which cadmium polyhedra are connected together. In $CdSe_2O_5$, the octahedra share edges only [O(2)—O(2)] but in $Cd_3(HSeO_3)_2(SeO_3)_2$ there are common edges and corners. Unit cells are shown in Figs. 1 and 2 together with the atomic numbering.

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