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A layered fluorinated gallium phosphate organically templated by propane-1,3-diaminium, an analog of the aluminophosphate MIL-12: $Ga_2(PO_4)F_5 \cdot C_3H_{12}N_2$

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Crystals of the oxyfluorinated gallium phosphate MIL-12 (digallium phosphate pentafluoride propane-1,3-diaminium), $(C_3H_{12}N_2)[Ga_2(PO_4)F_5]$, were synthesized hydrothermally at 453 K under autogenous pressure using propane-1,3-diamine as the structure-directing agent. The title compound is isomorphous with the aluminium phosphate having the MIL-12 structural type. The structure is built up from a two-dimensional anionic network intercalated by the diamine species. The inorganic layer is composed of corner-linked GaO_2F_4 octahedra and PO_4 tetrahedra. The diprotonated diamine group is located on a mirror plane, between the inorganic sheets, and interacts preferentially *via* hydrogen bonding through the ammonium groups and the terminal F and bridging O atoms of the inorganic layer. One of the Ga atoms lies on an inversion centre and the other lies on a mirror plane, as does the P atom, two of the phosphate O atoms and one of the F atoms.

Comment

Microporous metal phosphates have been studied intensively because of their potential applications in diverse areas, such as catalysis, gas separation and ionic exchangers. In the past decade, the preparations of a large number of open-framework phosphates containing aluminium or gallium have been reported (Cheetham *et al.*, 1999), and structural analyses of several aluminium phosphates have shown that they possess three-dimensional networks identical to those encountered in the aluminosilicate zeolite family. The substitution of gallium for aluminium in these compounds and the use of HF as mineralizing agent have led to the discovery of novel oxyfluorinated extra-large-pore open-framework structures. In the series it was shown that different key parameters play a significant role in the formation of such three-dimensional frameworks. For instance, the reaction pH has a drastic effect on the synthesis of phases with different structures. A typical example is the study of the chemical system including gallium, phosphoric acid, hydrofluoric acid, water and propane-1,3-diamine as the structure-directing agent (Ferey, 1995).

Following this study, the concentration of the fluoride ions was considered. For high F content (*i.e.* F/Ga = 2 or 2.5), the phase called MIL-12 (MIL stands for materials of Institut Lavoisier) occurred at very low pH in this specific system. The present paper deals with the single-crystal structure characterization of the gallium phosphate MIL-12 or $Ga_2(PO_4)F_5 \cdot C_3H_{12}N_2$, prepared in the presence of propane-1,3-diamine as the templating molecule. The structure of this solid is similar to that of the layered aluminium phosphate MIL-12 (Simon *et al.*, 1999), intercalating the same diamine, and was characterized by powder X-ray diffraction techniques.

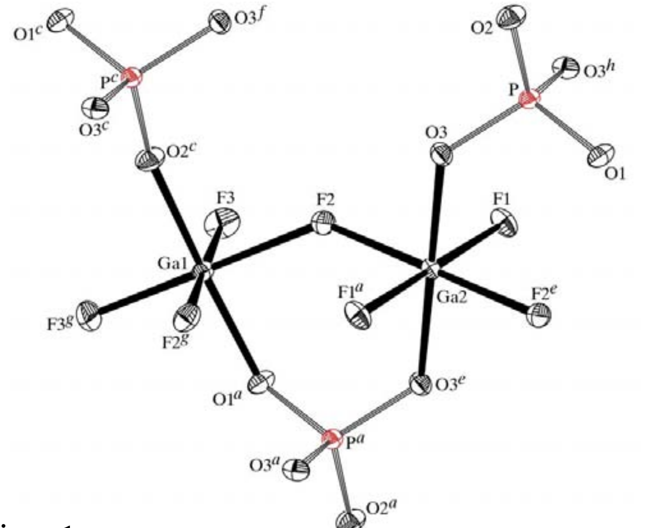

Figure 1
A displacement ellipsoid plot (50% probability level) of the structure of the cation and part of the anion in the structure of gallium phosphate MIL-12. [Symmetry codes: (*a*) $-x, -\frac{1}{2}+y, 1-z$; (*c*) $1-x, -\frac{1}{2}+y, 1-z$; (*e*) $-x, 1-y, 1-z$; (*f*) $1-x, 1-y, 1-z$; (*g*) $x, \frac{1}{2}-y, z$; (*h*) $x, \frac{3}{2}-y, z$.]

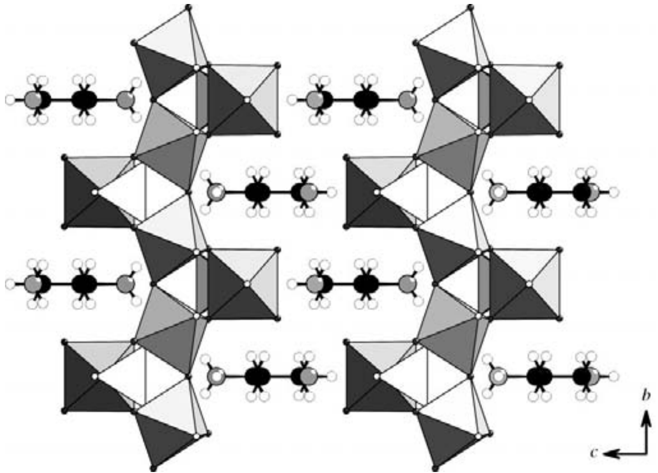

Figure 2
A polyhedral projection of the structure of $Ga_2(PO_4)F_5 \cdot C_3H_{12}N_2$ (MIL-12 type) along [100], showing the inorganic layer intercalated by the propane-1,3-diaminium molecules. Key: grey circles N; black circles C; small open circles H; grey octahedra GaO_2F_4; white tetrahedra PO_4.

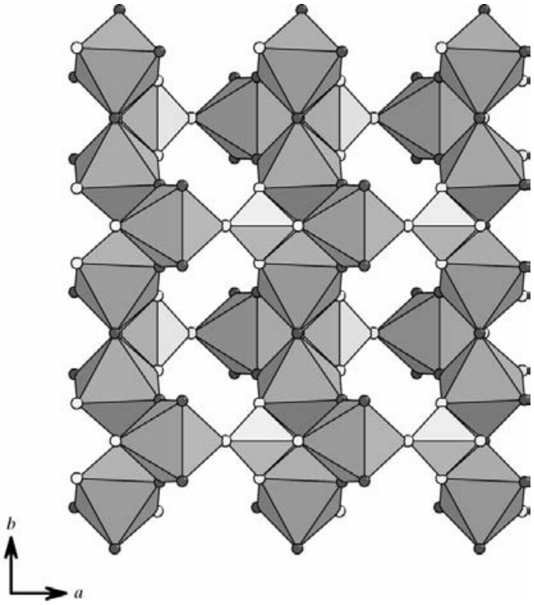

Figure 3
A polyhedral projection of the inorganic anionic $[Ga_2(PO_4)F_5]^{2-}$ sheet along [001]. Key: grey octahedra GaO_2F_4; pale-grey tetrahedra PO_4; open circles O; grey circles F.

The structure (Fig. 1) of gallium phosphate MIL-12 is built up from the connection by vertices of PO_4 tetrahedra with GaO_2F_4 octahedra (Fig. 2). The unique phosphorus crystallographic site is coordinated by four O atoms, with P—O distances ranging from 1.523 (3) to 1.550 (2) Å (Table 1), as expected for the phosphate groups. The two crystallographically inequivalent Ga atoms are octahedrally coordinated by four F and two O atoms. The Ga—O distances range from 1.897 (3) to 1.9259 (18) Å and the O atoms are in *trans* positions. The positions of the F atoms were deduced from the single-crystal X-ray diffraction and chemical analyses, and there exist two types of configuration. For atom Ga1 on special position 2*e*, two F atoms are terminal with shorter Ga—F distances [Ga1—F3 = 1.8621 (18) Å], whereas the two other bridge the Ga atoms with Ga1—F2 distances of 1.9979 (17) Å. Such a Ga—F bond difference was observed previously in another fluorinated gallium phosphate, $GaPO_4$–CJ2 (Ferey *et al.*, 1993), and in pseudo-KTP structures (Loiseau *et al.*, 2000) in which terminal and bridging F atoms occur. For atom Ga2 on special position 2*c*, four F atoms bridge the Ga atoms [Ga2—F2 = 1.9140 (16) and Ga2—F1 = 1.9425 (9) Å].

The $Ga2O_2F_4$ species are linked *via* atom F1 in such a way as to form infinite straight chains of *trans*-connected octahedra running along the *b* axis. These chains are connected together through the phosphate groups (*via* O atoms) and the $Ga1O_2F_4$ species (*via* F atoms), and this type of connection results in the formation of an inorganic sheet, $[Ga_2(PO_4)F_5]^{2-}$, in the *ab* plane (Fig. 3). The terminal F3 atoms point alternately downward and upward in the layer, toward the intercalated organic propane-1,3-diamine molecules, which lie perpendicular to the inorganic sheet (in the mirror plane). The diamine species is diprotonated and the resulting positive charges balance the negative ones of the anionic layer. One of the diamine atoms (N2) is linked to terminal atom F3 through a very strong hydrogen-bond interaction and is weakly linked to atom O2 (Table 2). The other ammonium N atom (N1) mainly interacts with atom O3 (Table 2). An identical layer-like atomic arrangement was reported previously in aluminium phosphate MIL-12 (Simon *et al.*, 1999), which is isomorphous with the present structure and in which Al atoms replace the Ga atoms.

Experimental

The title compound was prepared hydrothermally from a mixture of gallium oxide (Ga_2O_3, 99.999%), phosphoric acid (H_3PO_4, 85%), hydrofluoric acid (HF, 40%), propane-1,3-diamine ($C_3H_{10}N_2$, 98%) and deionized water in the molar ratio 0.5:1:2(or 2.5):0.4:40. This mixture was sealed in a Teflon-lined Parr autoclave and then heated for 26 h at 453 K under autogenous pressure. The pH was 1–2 during the synthesis. After cooling to room temperature, the solid was separated from the liquid phase by filtration, washed with water and then dried in air. A single crystal was selected optically for the diffraction study and glued to a glass fibre. The presence of fluorine was deduced from the consideration of the thermal parameter analysis. It was confirmed by bond-valence calculations (O'Keeffe & Brese, 1992) and was in agreement with the chemical analysis (observed: 23.0 wt%; calculated: 23.4 wt% for 5F/2Ga).

Crystal data

$(C_3H_{12}N_2)[Ga_2(PO_4)F_5]$
$M_r = 405.56$
Monoclinic, $P2_1/m$
$a = 6.2082$ (1) Å
$b = 7.2183$ (1) Å
$c = 11.2335$ (3) Å
$\beta = 100.477$ (2)°
$V = 495.01$ (2) Å^3
$Z = 2$
$D_x = 2.721$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2320 reflections
$\theta = 1.8$–29.5°
$\mu = 5.69$ mm^{-1}
$T = 293$ (2) K
Platelet, colourless
0.12 × 0.03 × 0.01 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical [using intensity measurements (*SADABS*; Blessing, 1995, 1997)]
$T_{min} = 0.549$, $T_{max} = 0.945$
3501 measured reflections
1374 independent reflections
1160 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 29.5°$
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 7$
$l = -13 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.072$
$S = 0.90$
1374 reflections
109 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.1108P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0112 (18)

Table 1
Selected interatomic distances (Å).

Ga1—F3	1.8621 (18)	Ga2—O3	1.9259 (18)
Ga1—O1^{ii}	1.897 (3)	Ga2—F1	1.9425 (9)
Ga1—O2^{iii}	1.918 (3)	P—O2	1.523 (3)
Ga1—F2	1.9979 (17)	P—O1	1.532 (3)
Ga2—F2	1.9140 (16)	P—O3	1.550 (2)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N1···O3^{i}	0.85 (3)	2.06 (3)	2.866 (3)	157 (4)
N2—H1N2···F3^{iv}	0.93 (3)	1.84 (3)	2.764 (3)	174 (4)
N2—H2N2···O2^{v}	0.92 (4)	2.14 (4)	3.062 (5)	178 (6)

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

H atoms bonded to C atoms were included as riding atoms, with C—H distances of 0.97 Å.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *SHELXTL* (Siemens, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1243). Services for accessing these data are described at the back of the journal.

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