

Acta Crystallographica Section C

**Crystal Structure
Communications**

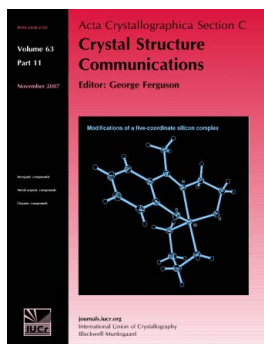
ISSN 0108-2701

Editor: **George Ferguson****Potassium gallium hydrogenphosphate fluoride,
 $K_2Ga[H(HPO_4)_2]F_2$** **Andrey Filaretov, Kurt J. Schenk, Dmitriy Rusakov and Gervais Chapuis***Acta Cryst.* (2007). **C63**, i54–i56

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site or institutional repository provided that this cover page is retained. Reproduction of this article or its storage in electronic databases other than as specified above is not permitted without prior permission in writing from the IUCr.

For further information see <http://journals.iucr.org/services/authorrights.html>



Acta Crystallographica Section C: Crystal Structure Communications specializes in the rapid dissemination of high-quality studies of crystal and molecular structures of interest in fields such as chemistry, biochemistry, mineralogy, pharmacology, physics and materials science. The numerical and text descriptions of each structure are submitted to the journal electronically as a Crystallographic Information File (CIF) and are checked and typeset automatically prior to peer review. The journal is well known for its high standards of structural reliability and presentation. *Section C* publishes approximately 1000 structures per year; readers have access to an archive that includes high-quality structural data for over 10000 compounds.

Crystallography Journals Online is available from journals.iucr.org

Potassium gallium hydrogenphosphate
fluoride, $K_2Ga[H(HPO_4)_2]F_2$ Andrey Filaretov,^{a*} Kurt J. Schenk,^{a*} Dmitriy Rusakov^b
and Gervais Chapuis^a^aLaboratoire de Cristallographie, École Polytechnique Fédérale de Lausanne, Le
Cubotron, Dorigny, CH-1015 Lausanne, Switzerland, and ^bChemistry Department,
Moscow State University, 119992 Moscow, Russian Federation
Correspondence e-mail: andrey.filaretov@epfl.ch, kurt.schenk@epfl.ch

Received 13 March 2007

Accepted 24 May 2007

Online 23 June 2007

Hydrothermally synthesized dipotassium gallium {hydrogen bis[hydrogenphosphate(V)]} difluoride, $K_2Ga[H(HPO_4)_2]F_2$, is isotypic with $K_2Fe[H(HPO_4)_2]F_2$. The main features of the structure are $[Ga\{H(HPO_4)_2\}F_2]^{2-}_n$ columns consisting of centrosymmetric $Ga(F_2O_4)$ octahedra [average $Ga-O = 1.966$ (3) Å and $Ga-F = 1.9076$ (6) Å] stacked above two HPO_4 tetrahedra [average $P-O = 1.54$ (2) Å] sharing two O-atom vertices. The charge-balancing seven-coordinate K^+ cations [average $K-O,F = 2.76$ (2) Å] lie in the intercolumn space, stabilizing a three-dimensional structure. Strong $[O \cdots O = 2.4184$ (11) Å] and medium $[O \cdots F = 2.6151$ (10) Å] hydrogen bonds further reinforce the connections between adjacent columns.

Comment

Microporous gallium phosphates have been widely studied because they find many potential applications in, for example, catalysis, ion-exchangers and adsorbents (Cheetham *et al.*, 1999). The fluoride ion has been discovered to play a major role in the gallium phosphate system, and various series of complex fluoride gallium phosphates with organic molecules substituting for the alkali cations have been synthesized by Férey and other researchers. On the other hand, the known alkali (ammonium) fluoride gallium phosphates show considerable structural variety; these include $LiGa_3F_3(OH)(H_2O)_2(PO_4)_2$ (Beitone *et al.*, 2001), $LiGa(PO_4)F_{0.74}(OH)_{0.26}$ (Beitone *et al.*, 2002), $KGaF_{1.8}(OH)_8PO_4$ (Harrison *et al.*, 1995), $K[(GaPO_4)\{F_{0.25}(GaPO_4)\}_4]$ (Sun *et al.*, 2003), $(NH_4)_{0.93}(H_3O)_{0.07}Ga(PO_4)(OH)_{0.5}F_{0.5}$ (Férey *et al.*, 1993), $(NH_4)Ga(PO_4)F$ and $(NH_4)_2Ga_2(PO_4)(HPO_4)F_3$ (Loiseau *et al.*, 2000).

Recently, we have been systematically studying the reactivity of alkali and ammonium cations in hydrothermal synthesis and the crystal chemistry of complex gallium and indium phosphates without fluoride agents (Filaretov, Zhizhin, Komissarova *et al.*, 2002; Zhizhin *et al.*, 2000; Filaretov *et al.*, 2006; Rusakov *et al.*, 2006) and with fluoride ions as templates

(Filaretov, Zhizhin, Olenov *et al.*, 2002; Komissarova *et al.*, 2002). In this context, we report here the hydrothermal synthesis and characterization of the first potassium gallium hydrogenphosphate fluoride, $K_2Ga[H(HPO_4)_2]F_2$, (I).

The crystal structure of (I) belongs to the $K_2Fe[H(HPO_4)_2]F_2$ structure type (Mi *et al.*, 2005). The asymmetric unit contains four O, two H, one K, one Ga, one P and one F atom. The structure can be described as negatively charged infinite $[Ga\{H(HPO_4)_2\}F_2]^{2-}_n$ columns extending along [100]. The columns are built of corner-sharing $Ga(F_2O_4)$ octahedra and tetrahedral HPO_4 units fused together *via* $Ga-O-P$ bonds (Figs. 1 and 2). Each $Ga(F_2O_4)$ octahedron shares two of its four O-atom vertices with two adjacent phosphate tetrahedra, while each HPO_4 tetrahedron links two of its nonhydroxy O-atom vertices to two $Ga(F_2O_4)$ octahedra. The charge-balancing K^+ cations are located in the space between the columns, thus completing a three-dimensional structure. Additional sturdiness of the structure, *i.e.* reinforcement of the connections between adjacent columns, is provided by two hydrogen bonds.

According to the narrow range of $K-O$ and $K-F$ distances, the K^+ cation (site symmetry $\bar{1}$) adopts a sevenfold coordination comprising two F- and five O-atom nearest neighbours, with an average $K-O,F$ bond length of 2.76 (2) Å. The bond valence sum (BVS) of 1.16 for K calculated by the Brese & O'Keeffe (1991) formalism shows that its valence requirement is satisfied by this coordination. However, this coordination number is not unique because the outer O4 atom {as in $K_2Fe[H(HPO_4)_2]F_2$; Fig. 2 of Mi *et al.* (2005)} might or might not be part of the coordination environment to 3.2562 (9) Å. If it is included, the BVS value of the [7+1]-coordinate K^+ cation rises to 1.21, but this coordination still agrees with the maximum gap in the $K-O$ distance, assuming a cut-off of 3.35 Å (Donnay & Allmann, 1970). The ninth O-atom neighbour at 3.4222 (9) Å is clearly beyond this cut-off (Table 1). The coordination environment of the K^+ cation is so asymmetric that no easy polyhedral description can be proposed.

As shown by the $Ga-O$ and $Ga-F$ distances (Table 1), the Ga^{3+} cation (site symmetry $\bar{1}$) is characterized by a typical and nearly regular octahedral geometry (Harrison *et al.*, 1995; Loiseau *et al.*, 2000; Beitone *et al.*, 2002; Filaretov *et al.*, 2006;

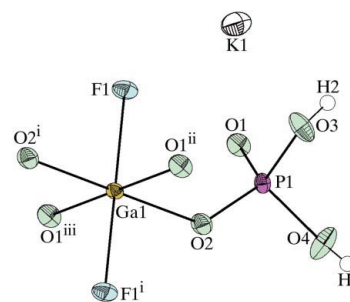


Figure 1

The main structural elements of (I) and the connectivity (displacement ellipsoids for the non-H atoms are shown at the 70% probability level). [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + 1, y, z$; (iii) $-x, -y + 1, -z + 1$.]

Rusakov *et al.*, 2006), with four long equatorial Ga—O bonds and two slightly shorter Ga—F bonds. The BVS value of 3.03 for Ga agrees with that expected for trivalent gallium. The P atom reveals its normal tetrahedral coordination [average P—O = 1.54 (2) Å] and participates in P—O1—Ga, P—O2—Ga and two terminal P—O bonds. The BVS of P is unexceptional (4.79, expected 5.00). On the basis of its length, the P—O4 bond is assumed to be protonated. The BVS values for O1 (1.96), O2 (2.03), O3 (1.54) and O4 (1.28) are all reasonably close to expected ideal valences and confirm that atoms O3 and O4 represent hydroxy groups. Atoms O4 and H1, both in general positions, participate in a moderately strong O—H···F hydrogen bond (Table 2). In contrast, the P—O3 distance (Table 1) is typical for P—O distances in PO₄ tetrahedra. This is so because atom O3 is involved in a very short symmetry-restricted hydrogen bond (Table 2).

A difference electron-density map calculated after full-matrix least-squares refinement including all non-H atoms with anisotropic displacement parameters clearly shows a maximum near atom O4 between atoms O4 and F1 (interpreted as atom H1), and two maxima close to the inversion centre at $(0, \frac{1}{2}, 0)$ between two O3 atoms related by inversion (Fig. 3). These two maxima were suggestive of disordered hydrogen positions and were therefore refined with a fixed isotropic displacement parameter and a half occupancy. This kind of disordered hydrogen is characteristic of the K₂Fe-[H(HPO₄)₂]F₂ and Li₂Fe[(PO₄)(HPO₄)] structures (Mi *et al.*, 2004). One might suspect that the structural formula Li₂Fe-[(PO₄)(HPO₄)] does not take into account the fact that the H atom is shared between two structurally identical P sites.

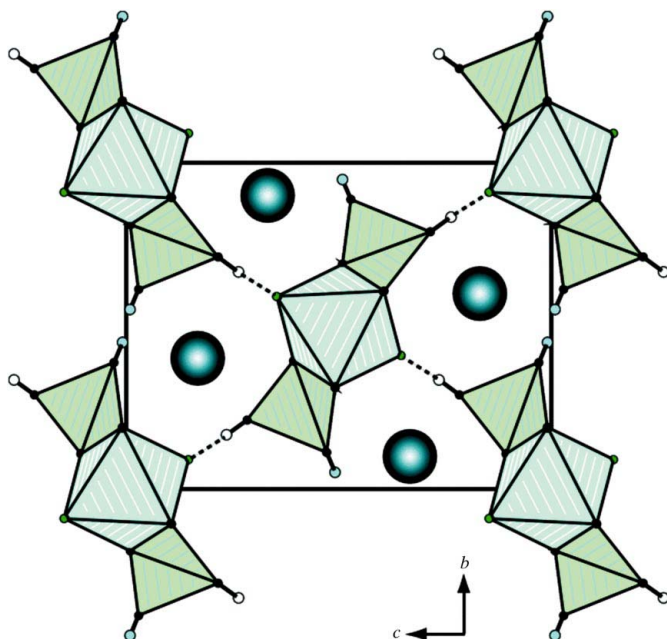
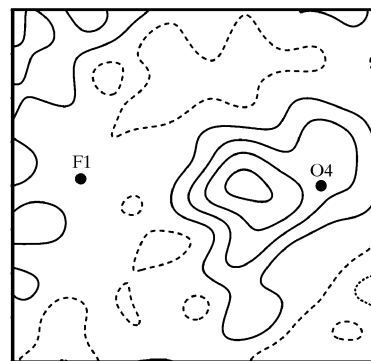
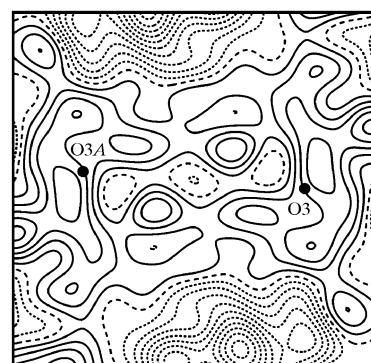


Figure 2

A view of K₂Ga[H(HPO₄)₂]F₂ along [100]. The K atoms (large spheres) separate the $([\text{Ga}\{\text{H}(\text{HPO}_4)_2\}\text{F}_2]^{2-})_n$ columns. *trans*-Oriented F atoms in Ga(F₂O₂) octahedra and the positions of the split H2 atom are drawn as small shaded and nonshaded circles, respectively. The medium-strength O—H···F hydrogen bonds are shown as dashed lines.



(a)



(b)

Figure 3

Difference maps around the H-atom positions. Full, dashed and stippled lines correspond to positive, zero and negative values of the electron density with (a) 0.1 e Å⁻³ and (b) 0.025 e Å⁻³ steps. [Symmetry code: (A) $-x, -y, -z + 1$.]

Probably, a more correct formula should read Li₂Fe[H(PO₄)₂], or as a new Sc analogue, Li₂Sc[H(PO₄)₂], according to recent results of ours. The crystal chemical function of the H2 atoms is to interconnect the $([\text{Ga}\{\text{H}(\text{HPO}_4)_2\}\text{F}_2]^{2-})_n$ columns in the *ab* plane (Fig. 3). Similarly, very short symmetry-restricted hydrogen bonds are well known and have recently been reported for structures of hydrogenphosphates, arsenates and borates (Mi *et al.*, 2004; Schwendtner & Kolitsch, 2005; Massa *et al.*, 2006). They were also found in the novel hydrogenphosphates Li₂Sc[H(PO₄)₂] and Ba₄Sc₂[H(PO₄)₂](HPO₄)₄·(H₂PO₄)₂·2H₂O (Filaretov, unpublished results).

In conclusion, the K₂Ga[H(HPO₄)₂]F₂ structure reveals an original arrangement which had not yet been found amongst well known complex gallium phosphates.

Experimental

Compound (I) was prepared hydrothermally from a mixture of Ga₂O₃ (0.607 g), KH₂PO₄ (3.081 g), H₃PO₄ (2.13 ml of an 85% solution), HF (0.65 ml of a 19% solution) and deionized water, corresponding to a K:Ga:P:F starting ratio of 3.5:1:5:2. These components were sealed in a 15 ml Teflon-lined autoclave filled to approximately 75% of its capacity and then heated to 473 K for 96 h under autogenous pressure. The pH was roughly equal to 1.0 during the synthesis. After cooling to room temperature, the solid product was filtered off, washed with water, rinsed with ethanol and then

dried in air. It consisted of colourless transparent needle-like crystals of (I) and some polycrystalline material. The presence of K, Ga, P and F in the crystals was confirmed by quantitative energy-dispersive X-ray analysis. Powder X-ray diffraction analysis of the reaction products revealed the cocrystallization of two phases, viz. $K_2\text{-Ga}[\text{H}(\text{HPO}_4)_2]\text{F}_2$ (~40 vol%) and $\text{KGaF}_{1-x}(\text{OH})_x\text{PO}_4$ (~60 vol%). The selected crystal of (I) was bounded by a {011} prism, an incomplete $\{3\bar{1}1\}$ prism and a $(\bar{1}12)$ bevel face.

Crystal data

$K_2\text{Ga}[\text{H}(\text{HPO}_4)_2]\text{F}_2$	$V = 425.20$ (8) Å ³
$M_r = 378.9$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 4.7449$ (6) Å	$\mu = 4.65$ mm ⁻¹
$b = 8.2814$ (8) Å	$T = 293$ (2) K
$c = 10.8351$ (13) Å	$0.13 \times 0.13 \times 0.12$ mm
$\beta = 92.941$ (10)°	

Data collection

Stoe IPD5II diffractometer	11412 measured reflections
Absorption correction: integration (<i>X-RED</i> ; Stoe & Cie, 2005)	1824 independent reflections
$T_{\min} = 0.468$, $T_{\max} = 0.644$	1768 reflections with $I > 3\sigma(I)$
	$R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.033$	$\Delta\rho_{\text{max}} = 0.35$ e Å ⁻³
$S = 1.23$	$\Delta\rho_{\text{min}} = -0.33$ e Å ⁻³
1824 reflections	
77 parameters	

Table 1

Selected geometric parameters (Å, °).

Ga1—F1	1.9079 (6)	K1—O4 ^{vii}	3.2562 (9)
Ga1—O1 ⁱⁱ	1.9712 (7)	K1—O4 ^{viii}	2.8163 (9)
Ga1—O2	1.9604 (7)	P1—F1	3.2073 (7)
K1—F1	2.7197 (7)	P1—F1 ⁱⁱⁱ	3.2398 (7)
K1—F1 ^{iv}	2.7172 (7)	P1—O1	1.5121 (7)
K1—O1 ⁱⁱ	2.8070 (8)	P1—O2	1.5133 (7)
K1—O2 ^v	2.6996 (8)	P1—O3	1.5419 (8)
K1—O3	2.7770 (9)	P1—O4	1.5889 (9)
K1—O3 ^{vi}	2.7858 (8)		
F1—Ga1—O1 ⁱⁱ	88.26 (3)	O1—P1—O4	105.01 (4)
F1—Ga1—O2	92.53 (3)	O2—P1—O3	109.39 (4)
O1 ⁱⁱ —Ga1—O2	90.77 (3)	O2—P1—O4	107.83 (5)
O1—P1—O2	116.22 (4)	O3—P1—O4	107.44 (5)
O1—P1—O3	110.50 (4)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H1 ^{ix} ···F1 ^{ix}	0.84 (3)	1.79 (3)	2.6151 (10)	170 (3)
O3—H2 ^{ix} ···O3 ^{vii}	0.70 (6)	1.72 (6)	2.4185 (11)	174 (7)

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

The atomic coordinates of isotypic $K_2\text{Fe}[\text{H}(\text{HPO}_4)_2]\text{F}_2$ (Mi *et al.*, 2005) were used as starting parameters in the final refinement. The H atoms were refined with fixed isotropic displacement parameters. The highest electron-density peak is 1.92 Å from the H1 site.

Data collection: *X-AREA* (Stoe & Cie, 2006); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2005); program(s) used to solve structure: *SIR02* (Burla *et al.*, 2003); program(s) used to refine structure: *JANA2000* (Petříček *et al.*, 2000); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *JANA2000*.

Financial support by the Swiss National Science Foundation (grant No. 20-105325/1) is gratefully acknowledged. We thank Alla Arakcheeva (Laboratoire de Cristallographie, École Polytechnique Fédérale de Lausanne, Switzerland) and Lydia Komissarova (Chemistry Department, Moscow State University, Russian Federation) for fruitful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3042). Services for accessing these data are described at the back of the journal.

References

Beitone, L., Guillou, N., Millange, F., Loiseau, T. & Férey, G. (2002). *Solid State Sci.* **4**, 1061–1065.

Beitone, L., Marrot, J., Lorentz, C., Taulelle, F., Loiseau, T. & Férey, G. (2001). *Solid State Sci.* **3**, 641–647.

Brandenburg, K. (1999). *DIAMOND*. Version. 2.1c. Crystal Impact GbR, Bonn, Germany.

Brese, N. E. & O’Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.

Burla, M. C., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Polidori, G. & Spagna, R. (2003). *J. Appl. Cryst.* **36**, 1103.

Cheetham, A. K., Férey, G. C. & Loiseau, T. (1999). *Angew. Chem. Int. Ed.* **38**, 3268–3292.

Donnay, G. & Allmann, R. (1970). *Am. Mineral.* **55**, 1003–1015.

Férey, G., Loiseau, T., Lacorre, P. & Taulelle, F. (1993). *J. Solid State Chem.* **105**, 179–190.

Filaretov, A. A., Zhizhin, M. G., Khasanov, S. S., Bobylev, A. P., Danilov, V. P. & Komissarova, L. N. (2006). *Russ. J. Inorg. Chem.* **51**, 155–165.

Filaretov, A. A., Zhizhin, M. G., Komissarova, L. N., Danilov, V. P., Chernyshev, V. V. & Lazoryak, B. I. (2002). *J. Solid State Chem.* **166**, 362–368.

Filaretov, A. A., Zhizhin, M. G., Olenev, A. V., Gurkin, A. A., Bobylev, A. P., Lazoryak, B. I., Danilov, V. P. & Komissarova, L. N. (2002). *Russ. J. Inorg. Chem.* **47**, 1773–1789.

Harrison, W. T. A., Phillips, M. L. F. & Stucky, G. D. (1995). *Chem. Mater.* **7**, 1849–1856.

Komissarova, L. N., Zhizhin, M. G. & Filaretov, A. A. (2002). *Russ. Chem. Rev.* **71**, 619–650.

Loiseau, T., Paulet, C., Simon, N., Munch, V., Taulelle, F. & Férey, G. (2000). *Chem. Mater.* **12**, 1393–1399.

Massa, W., Yakubovich, O. V. & Dimitrova, O. V. (2006). *Acta Cryst.* **C62**, i106–i108.

Mi, J.-X., Borrmann, H., Zhang, H., Huang, Y.-X., Schnelle, W., Zhao, J.-T. & Kniep, R. (2004). *Z. Anorg. Allg. Chem.* **630**, 1632–1636.

Mi, J.-X., Wang, C.-X., Wei, Z.-B., Chen, F.-J., Xu, C.-Y. & Mao, S.-Y. (2005). *Acta Cryst.* **E61**, i143–i145.

Petříček, V., Dušek, M. & Palatinus, L. (2000). *JANA2000*. Institute of Physics, Prague, Czech Republic.

Rusakov, D. A., Filaretov, A. A., Bubentsova, M. N., Danilov, V. P. & Komissarova, L. N. (2006). *Russ. J. Inorg. Chem.* **51**, 852–861.

Schwendtner, K. & Kolitsch, U. (2005). *Acta Cryst.* **C61**, i90–i93.

Stoe & Cie (2005). *X-RED*. Version 1.31. Stoe & Cie GmbH, Darmstadt, Germany.

Stoe & Cie (2006). *X-AREA*. Version 1.36. Stoe & Cie GmbH, Darmstadt, Germany.

Sun, D., Cao, R., Sun, Y., Bi, W. & Hong, M. (2003). *Eur. J. Inorg. Chem.* pp. 1303–1305.

Zhizhin, M. G., Morozov, V. A., Bobylev, A. P., Popov, A. M., Spiridonov, F. M., Komissarova, L. N. & Lazoryak, B. I. (2000). *J. Solid State Chem.* **149**, 99–106.