

GaFPO₃(C₆H₅): a new fluorinated gallium phenylphosphonate with a layered network

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Crystals of gallium fluorophenylphosphonate were synthesized hydrothermally at 453 K under autogenous pressure. The solid crystallizes in the monoclinic system and its structure is built up by the connection of zigzag chains of edge-sharing GaO₄F₂ octahedra to phenylphosphonate groups. This results in the formation of a layered structure, in which the phenyl groups point upward and downward from the inorganic sheet. The Ga atoms occupy the special positions 4*a* (inversion center) and 4*e* (twofold axis).

Comment

Metal organophosphonates are a class of materials with diverse structural varieties, displaying properties in the fields of catalysis, ion exchange and non-linear optics. Their versatility comes from the possibility of incorporating different organic groups into an inorganic matrix composed of di-, tri- or tetravalent metal phosphonate (Clearfield, 1996). More recently, these phosphonates have been used for the synthesis of molecular solids whose structures resemble the secondary building units (SBUs) encountered in the microporous phosphate family (Mason *et al.*, 1996). Despite the successful syntheses of a large number of open-framework phosphates (Cheetham *et al.*, 1999), the formation mechanisms which occur during the hydrothermal treatment are still poorly understood. For example, several reports have been devoted to the synthesis of microporous fluorinated gallium phosphates exhibiting extra-large pore systems (Estermann *et al.*, 1991; Sassoye *et al.*, 2000). The isolated clusters prepared using the phosphonate route might act as molecular precursors in the formation of three-dimensional networks. For the gallium phosphonate system, the four-ring unit Ga₂P₂O₄ (4R) and the double four-ring unit Ga₄P₄O₁₂ (D4R) have been isolated in

non-aqueous solvents (Mason *et al.*, 1997, 1998). The D4R entity is analogous to the basic building block observed in cloverite (Estermann *et al.*, 1991) or ULM-5 (Loiseau & Ferey, 1994). In this context, we studied the reactivity of organophosphonates with gallium in the presence of HF and water. Two fluorinated gallium hydroxomethylphosphonates have previously been identified utilizing methylphosphonic acid (Paulet *et al.*, 1999). The structure of GaF_{0.72}(OH)_{0.28}(H₂O)-PO₃CH₃ is similar to that of the aluminium methylphosphonate Al(OH)(H₂O)PO₃CH₃ (Sawers *et al.*, 1996) and is based on the connection, by corner-sharing, of gallium GaO₃(OH,F)(H₂O) octahedra with the tetrahedral CH₃PO₃ entity. A second solid, Ga₃(OH)₃F₃PO₃CH₃ (MIL-23), built up from the hexagonal arrangement of gallium Ga(OH,F)₄O₂ octahedra sharing corners with CH₃PO₃, was also reported. The resulting structures were lamellar. Omitting F⁻ anions, the preparation and structural characterization of layered gallium methylphosphonates and gallium phenylphosphonates have been described recently (Bujoli-Doeuff *et al.*, 2000; Morizzi *et al.*, 2000). Both compounds have a two-dimensional network formed by infinite straight chains of edge-sharing gallium GaO₂(OH)₄ octahedra linked to each other through PO₃CH₃ groups. Similar inorganic networks are observed in gallium ethylenediphosphonic acid (Bujoli-Doeuff *et al.*, 2001) and in gallium phosphate intercalated with ethylenediamine (Jones *et al.*, 1991). The present paper deals with the synthesis and structural characterization of a fluorinated gallium phenylphosphonate, which exhibits a lamellar structure (Figs. 1 and 3). The Ga atoms are octahedrally coordinated to four O and two F atoms, the F atoms occupying *trans* positions. Both Ga atoms are on special positions; Ga2 lies on an inversion center (4*a*), whereas Ga1 is located on a twofold axis (4*e*). The gallium octahedra are connected to each other by a shared edge composed of one F and one O atom, generating infinite zigzag chains running along [001] with a *cis-trans* sequence. The gallium chains are linked to each other *via* phenylphosphonate groups (Fig. 2). Two O atoms of the PO₃ species connect to two adjacent gallium octahedra belonging to the same chain, whereas the third O atom links Ga atoms from a different chain. This Ga—O—P connection mode ensures the cohesion of the inorganic sheet. One of the O atoms (O3) is

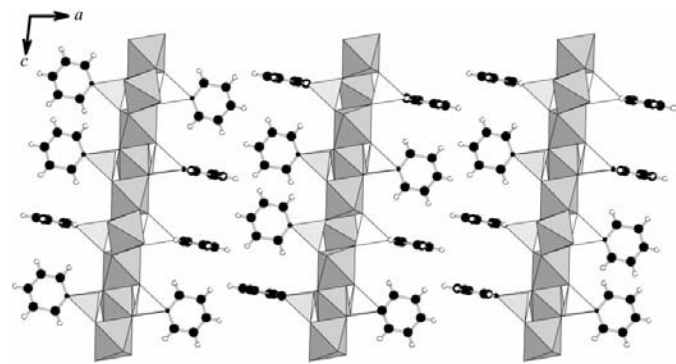


Figure 1

Projection of the structure of GaFPO₃(C₆H₅) along [010], showing the connection of the GaFPO₃C sheets to the phenyl groups. The phenyl species are statistically oriented in the (101) or (110) planes.

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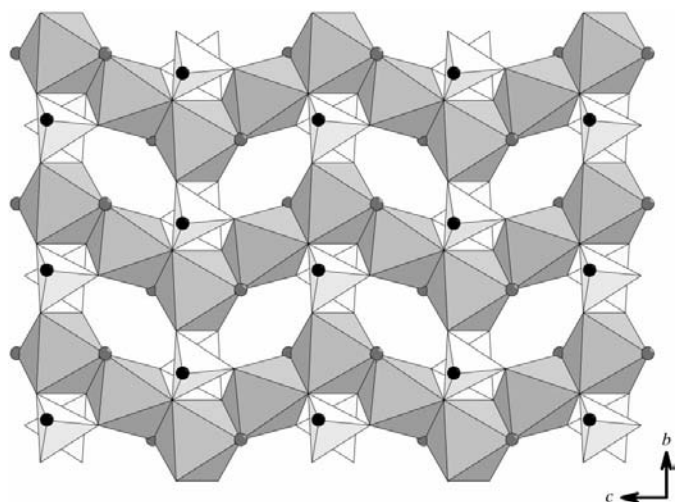


Figure 2
Polyhedral representation of a GaFPO_3C layer along $[100]$, showing the infinite zigzag chain of gallium octahedra linked with phosphonate groups (grey octahedra: GaO_4F_2 ; white tetrahedra: PO_3C ; black circles: carbon; dark-grey circles: fluorine). The O atoms and the phenyl groups have been omitted for clarity.

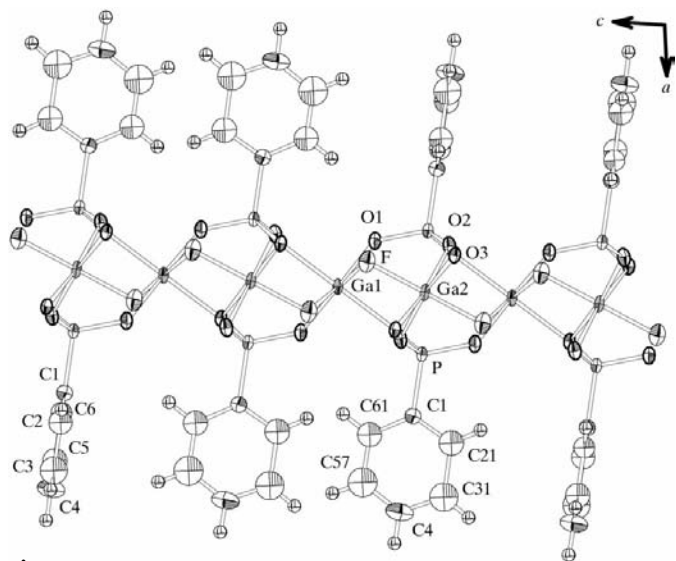


Figure 3
Displacement ellipsoid plot (50% probability) of the structure of $\text{GaFPO}_3(\text{C}_6\text{H}_5)$ viewed along $[010]$. The phenyl species are statistically oriented in the (101) or (110) planes.

threefold coordinated and is characterized by longer cation-anion distances. All the other anions are twofold coordinated, with classical P—O and Ga—(O,F) bond distances (Table 1). The inorganic arrangement of the layer is identical to that of the gallium fluorophosphate MIL-35 (Sassoye *et al.*, 2001) obtained with 1,12-diaminododecane. The phenyl substituents are oriented perpendicular to the sheet and are statistically located in two positions related by a 90° rotation around the P—C axis.

Experimental

The title compound was prepared hydrothermally from a mixture of gallium oxide, phenylphosphonic acid, hydrofluoric acid, 1,3-di-

aminopropane and deionized water in the molar ratio 1:5.3:7:2.5:290. This mixture was sealed in a teflon-lined Parr autoclave and heated for 48 h at 453 K under autogenous pressure. The pH was 4 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 for the diffraction study was selected optically and glued to a glass fibre. The presence of fluorine in the gallium bridging sites was confirmed by the chemical analysis [%F experimental = 7.4 (3); %F theoretical = 7.7]. This observation is in agreement with bond-valence calculations (O'Keeffe & Brese, 1992).

Crystal data

$\text{GaFPO}_3(\text{C}_6\text{H}_5)$
 $M_r = 244.79$
Monoclinic, $C2/c$
 $a = 29.7810(4) \text{ \AA}$
 $b = 5.42200(10) \text{ \AA}$
 $c = 9.8768(2) \text{ \AA}$
 $\beta = 96.6180(10)^\circ$
 $V = 1584.21(5) \text{ \AA}^3$
 $Z = 8$

$D_x = 2.053 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 4648 reflections
 $\theta = 1.4\text{--}29.9^\circ$
 $\mu = 3.65 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
Needle, colourless
 $0.80 \times 0.08 \times 0.01 \text{ mm}$

Data collection

Siemens SMART diffractometer
 ω scans
Absorption correction: empirical (Blessing; 1995)
 $T_{\min} = 0.606$, $T_{\max} = 0.807$
5433 measured reflections
2111 independent reflections

1797 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\text{max}} = 29.9^\circ$
 $h = -40 \rightarrow 37$
 $k = -6 \rightarrow 7$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.104$
 $S = 1.14$
2111 reflections
96 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 6.8305P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.12 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.99 \text{ e \AA}^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0007 (2)

Table 1

Selected interatomic distances (\AA).

| | | | |
|-----------------------|-----------|---------|------------|
| Ga1—F | 1.877 (2) | P—C1 | 1.784 (4) |
| Ga1—O2 ⁱ | 1.929 (3) | C1—C2 | 1.377 (11) |
| Ga1—O3 | 2.175 (2) | C1—C6 | 1.394 (7) |
| Ga2—F | 1.900 (2) | C4—C5 | 1.334 (13) |
| Ga2—O1 ⁱⁱ | 1.963 (2) | C4—C3 | 1.368 (15) |
| Ga2—O3 ⁱⁱⁱ | 2.034 (2) | C2—C3 | 1.38 (2) |
| P—O1 | 1.521 (2) | C5—C6 | 1.377 (13) |
| P—O2 ^{iv} | 1.527 (3) | C21—C31 | 1.559 (10) |
| P—O3 | 1.556 (2) | C51—C61 | 1.381 (10) |

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

Data collection: *SMART* (Siemens, 1994); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1373). Services for accessing these data are described at the back of the journal.

References

- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Brandenburg, K. (1996). *DIAMOND*. Gerhard-Domagk-Straße 1, Bonn, Germany.
- Bujoli-Doeuff, M., Evain, M., Fayon, F., Alonso, B., Massiot, D. & Bujoli, B. (2000). *Eur. J. Inorg. Chem.* pp. 2497–2499.
- Bujoli-Doeuff, M., Evain, M., Janvier, P., Massiot, D., Clearfield, A., Gan, Z. & Bujoli, B. (2001). *Inorg. Chem.* **40**, 6694–6698.
- Cheetham, A. K., Ferey, G. & Loiseau, T. (1999). *Angew. Chem. Int. Ed.* **38**, 3268–3292.
- Clearfield, A. (1996). *Curr. Opin. Solid State Mater. Sci.* **1**, 268–278.
- Estermann, M., McCusker, L. B., Baerlocher, C., Merrouche, A. & Kessler, H. (1991). *Nature*, **352**, 320–323.
- Jones, R. H., Thomas, J. M., Huo, Q., Xu, R. & Husthouse, M. B. (1991). *J. Chem. Soc. Chem. Commun.* pp. 1520–1522.
- Loiseau, T. & Ferey, G. (1994). *J. Solid State Chem.* **111**, 416–421.
- Mason, M. R., Mashuta, M. S. & Richardson, J. F. (1997). *Angew. Chem. Int. Ed.* **36**, 239–241.
- Mason, M. R., Matthews, R. M., Mashuta, M. S. & Richardson, J. F. (1996). *Inorg. Chem.* **35**, 5756–5757.
- Mason, M. R., Perkins, A. M., Matthews, R. M., Fisher, J. D., Mashuta, M. S. & Vij, A. (1998). *Inorg. Chem.* **37**, 3734–3746.
- Morizzi, J., Hobday, M. & Rix, C. (2000). *J. Mater. Chem.* pp. 1693–1697.
- O'Keeffe, M. & Brese, N. (1992). *Acta Cryst.* **B48**, 152–154.
- Paulet, C., Serre, C., Loiseau, T., Riou, D. & Ferey, G. (1999). *C. R. Acad. Sci. Paris Ser. IIC 2*, pp. 631–636.
- Sassoye, C., Loiseau, T. & Ferey, G. (2001). *J. Fluorine Chem.* **107**, 187–192.
- Sassoye, C., Loiseau, T., Taulelle, F. & Ferey, G. (2000). *Chem. Commun.* pp. 943–944.
- Sawers, L. J., Carter, V. J., Armstrong, A. R., Bruce, P. G., Wright, P. A. & Gore, B. E. (1996). *J. Chem. Soc. Dalton Trans.* pp. 3159–3161.
- Sheldrick, G. M. (1993). *SHELXL93*. University of Göttingen, Germany.
- Sheldrick, G. M. (1994). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1994). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.