

A linear DABCO templated fluorogallophosphate: synthesis and structure determination from powder diffraction data of $\text{Ga}(\text{PO}_4\text{H})_2\text{F}\cdot[\text{N}_2\text{C}_6\text{H}_{14}]$

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A new 1D fluorogallophosphate, $\text{Ga}(\text{PO}_4\text{H})_2\text{F}\cdot[\text{N}_2\text{C}_6\text{H}_{14}]$, was synthesized solvothermally using 1,4-diazabicyclo[2.2.2]octane (DABCO) as a templating agent. The structure was determined *ab initio* from X-ray powder diffraction data. It crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 14.8725(9)$ Å, $b = 12.0132(7)$ Å, $c = 7.0700(6)$ Å, $V = 1263$ Å³ and $Z = 4$. The 1D structure contains discrete inorganic chains built-up by fluorine sharing GaO_4F_2 octahedra, corner linked by bridging PO_4H tetrahedra. These chains, similar to those found in tancoite type minerals, are linked to each other *via* hydroxy groups and *via* hydrogen bonding with the ammonium groups of the doubly protonated DABCO molecules.

Introduction

The discovery of microporous aluminophosphates in the early eighties¹ spawned numerous research programs that resulted in a wealth of new inorganic open-framework materials.² In particular, many efforts have been devoted to the hydrothermal or solvothermal synthesis of new aluminophosphates (ALPOs and GAPOs). Two major breakthroughs in this field were the introduction of the fluoride ion in the synthesis medium³ and the use of non-aqueous solvents such as alcohols, glycols, amines *etc.*^{4,5} Since aluminium and gallium can be non-tetrahedrally coordinated, many ALPOs and GAPOs exhibit new framework topologies that are not encountered in classical aluminosilicate zeolites. 3D and 2D topologies have attracted the most attention because of their potential applications in catalysis or molecular sieving; comparatively few 1D phases have been reported. Among linear GAPOs, two different chain topologies have been encountered so far: in the tancoite⁶ type chain, the gallium atoms are octahedrally coordinated and share their (OH) or F vertices with each other to form the chain backbone;⁷⁻⁹ in the other type all gallium atoms are tetrahedrally coordinated.^{10,11} In both cases successive gallium centered polyhedra are connected to each other *via* PO_4 tetrahedra which leads to a gallium to phosphorus ratio of 1 to 2. The charge carried by this inorganic macroanion is compensated by alkali metal ions^{12,13} or more commonly by protonated amines.⁷⁻¹¹

Recent work⁷ has shown that a tancoite-type 1D gallophosphate can be synthesized at room temperature and can be used as a precursor for the solvothermal synthesis of a 3D phase. As a rule, high dimensionality compounds are obtained under more severe conditions than low dimensionality phases. The study of these low temperature intermediates is important in deciphering the complex reaction pathways taking place during the solvothermal synthesis of a zeotype phase.

Continuing our work on organically templated gallophosphates^{14,15} we have obtained a new 1D fluorogallophosphate using DABCO as the structure directing agent. We report here on its synthesis and *ab initio* structure determination by X-ray powder diffraction.

Experimental

Synthesis

The title compound was prepared under solvothermal conditions using a 23 mL Teflon-lined stainless steel Parr autoclave. The chemicals used in the reactions were: hydrated gallium sulfate (Alfa Aesar), phosphoric acid (Fisher, 85 wt%), hydrofluoric acid (Fisher, 49 wt%), DABCO (Aldrich), pyridine (Fisher), and deionized (D.I.) water. 0.38 g of gallium sulfate was first dissolved with stirring in a mixture of 0.70 g of D.I. water and 0.23 g of phosphoric acid. Then 0.08 g of HF, 4.00 g of pyridine and 0.30 g of DABCO were added sequentially with stirring. The starting molar ratios were thus 1 Ga : 2 P : 2 F : 2.7 DABCO : 50 H₂O : 50 pyridine. The reaction mixture was stirred for one hour at room temperature and transferred to the reactor. The autoclave was then heated to 170 °C for 4 days and cooled overnight to room temperature. The resulting product consisted of agglomerated colorless fibers up to about 100 microns in length and 5 microns in diameter. The product was separated from the dark solution by vacuum filtration, washed with D.I. water and acetone and dried in air at 50 °C.

Characterization

Elemental analysis was performed by Galbraith Laboratories Inc. (Knoxville, TN). The methods used are inductively coupled plasma-optical emission spectroscopy for gallium and phosphorus, an ion-selective electrode for fluorine and combustion analysis for carbon, nitrogen and hydrogen. Thermogravimetric analysis was carried out on a TA Instruments SDT 2960 simultaneous Thermo Gravimetric Analyzer–Differential Thermal Analyzer (TGA–DTA) under flowing oxygen (50 cm³ min⁻¹) and a heating rate of 5 °C min⁻¹. The X-ray powder diffraction patterns were measured with a Siemens D500 diffractometer, in Bragg–Brentano geometry, with Ni filtered Cu–K α radiation.

Results and discussion

Since no suitable single crystals were obtained, an *ab initio* structure determination from powder diffraction data was

carried out. The positions of the first twenty peaks were refined with the program XFIT¹⁶ using a split Pearson VII function for the more asymmetric low angle peaks and a pseudo-Voigt function for the peaks above 15°. The pattern was then indexed with good figures of merit¹⁷ ($M_{20}=58$, $F_{20}=128$) by the program TREOR90¹⁸ with a primitive orthorhombic cell of approximate cell parameters $a=14.87$ Å, $b=12.01$ Å and $c=7.07$ Å. The refined lattice constants (program LATCON¹⁹) are given in Table 1. A structureless whole pattern profile refinement by the Le Bail method²⁰ (program FULLPROF98²¹) confirmed the adequacy of this cell and showed that the systematic absences are consistent with the space group²² $P2_12_12_1$. The needle-like character of the crystallites required trying to minimize the preferred orientation. The sample was thus thoroughly ground under ethanol, mixed with an equal volume of an amorphous filler (namely, instant coffee²³) and back loaded in the sample holder which was rotated during the measurement. The data collection conditions are summarized in Table 1.

The structure determination was performed using the EXPO²⁴ package, which combines an integrated intensities extraction routine (EXTRA²⁵) and a direct method program (SIRPOW²⁶) optimized for powder diffraction data. The elemental chemical analysis gave the following atomic ratio: Ga/P=0.55 and Ga/F=1.11. The organic fraction had composition $C_6N_2H_{16.2}$, showing that the DABCO molecule was very likely intact and gave a Ga/DABCO ratio close to 1. Based on the elemental analysis, the mean atomic volume in similar phases (about 16 Å³ per non-hydrogen atom) and the multiplicity of the only site in $P2_12_12_1$ ($4a; x, y, z$) we expected the idealized composition $Ga(PO_4H)_2F \cdot [C_6N_2H_{14}]$ with $Z=4$. This would correspond to 20 independent non-hydrogen atoms

Table 1 Crystal data and structure refinement parameters

Compound	Ga(PO ₄ H) ₂ F·[N ₂ C ₆ H ₁₄]
Chemical formula	GaP ₂ FO ₈ N ₂ C ₆ H ₁₆
Formula weight/g mol ⁻¹	394.9
Temperature/K	298(2)
Radiation source	Cu-K _{α1,α2}
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)
Unit cell dimensions; <i>a, b, c</i> /Å	14.8725(9), 12.0132(7), 7.0700(6)
Volume/Å ³	1263.2(1)
<i>Z</i>	4
<i>D_c</i> /g cm ⁻³	2.06
<i>F</i> (000)	800
2θ range/°	8.5–85.0
Step size 2θ /°	0.04
Time per step/s	30
Min FWHM/°	0.12
No. of free parameters ^a	81
No. of structural parameters ^a	63
No. of ‘independent’ reflections	549
No. of soft constraints	23 distances and 12 angles constrained: P–O=1.53(2) Å (8 ×); Ga–O=1.95(5) Å (4 ×); Ga–F=1.95(5) Å (2 ×); N–C=1.48(1) Å (6 ×); C–C=1.50(1) Å (3 ×); O–P–O=109(2.5)° (12 ×)
Final <i>R</i> indices (background subtracted)	$R_p=12.30\%$; $R_{wp}=13.38\%$; $R_{exp}=4.13\%$; $\chi^2=10.52$; $R_{Bragg}=4.92\%$

^a60 positional parameters and 3 isotropic atomic displacement parameters. 18 profile parameters: scale factor; 3 cell parameters; zero-point; 3 variable pseudo-Voigt parameters; *U*, *V*, *W* for the Cagliotti function;³⁴ 2 asymmetry parameters;³⁵ 1 preferred orientation correction factor³³ and 4 polynomial background coefficients.

per unit cell, a structure of moderate complexity by current standards in conventional X-ray powder diffraction.²⁷

The first E-map revealed the location of the gallium site, one of the two phosphorus sites, and several possible sites for oxygen or fluorine atoms. The completion of the structure by successive difference Fourier maps was hampered by the preferred orientation effects that had not been completely eliminated by the specimen preparation, and cannot be properly taken into account in the initial stage of a structure determination. The overall 1D character of the structure was nevertheless clearly defined. The distance between adjacent gallium atoms within a chain was $d_{Ga-Ga}=3.54$ Å, very similar to those encountered in ‘tancoite type’ phases ($d_{Ga-Ga}=c/2=3.56$ Å for GaF(HPO₄)₂·N₂C₃H₁₂,⁸ $d_{Ga-Ga}=3.58$ Å = $c/2$ for [*trans*-1,2-C₆H₁₀(NH₃)₂][Ga(OH)(HPO₄)₂]·H₂O⁹ and $d_{Ga-Ga}=b/2=3.58$ Å for Na₃Ga(OH)(HPO₄).¹² By analogy to those phases, the present compound should therefore contain a zigzag chain of fluorine sharing PO₄F₂ octahedra, corner linked to each other by bridging PO₄ tetrahedra. The free Rietveld refinement (program WinMprof²⁸) of this manually built partial model converged to $R_{Bragg}=20\%$ but this led to unreasonable bond distances and angles and furthermore did not allow the location of the DABCO template. The use of soft distance and angular constraints to regularize this starting structural model increased R_{Bragg} to about 28% but gave a slightly clearer difference electron density map. It was then possible to identify five sites sensibly belonging to the DABCO molecule. Their inclusion in the model lowered the agreement factor to $R_{Bragg}=18\%$. Further alternate cycles of refinement and difference Fourier maps allowed the completion of the template molecule and of the structure. The refinement eventually converged to a satisfactory agreement factor $R_{Bragg}=4.9\%$. The observed and difference Rietveld plots are given in Fig. 1.

The DABCO molecule was refined from the start using bond distance constraints corresponding to typical values encountered in DABCO-templated zeotypes.²⁹ The constraints applied to the inorganic chain could not be fully relaxed as this led to two (and only two) unreasonable bond distances (P1–O2=1.70 Å and P1–O3=1.43 Å). The final values of the soft constraints are given in Table 1. The template molecules are assumed to be doubly protonated and their hydrogen positions were geometrically calculated using SHELX97³⁰ within the WinGX system.³¹ These 14 hydrogen sites were included in the final stages of the refinement and kept fixed at their idealized positions. No other guest molecules, such as water or pyridine, were detected and no voids were present in the structure.³² The preferred orientation (fiber axis (001)) was corrected using the March function.³³ The summary of crystallographic data, including the values of the geometrical constraints is given in Table 1. Non-hydrogen atom coordinates are presented in Table 2 and selected distances and bond angles given in Table 3. Although the structure was solved and refined in the non-centrosymmetric space group $P2_12_12_1$, no increase in symmetry was evidenced afterwards (option ADDSYM in PLATON³²). In order to balance the charges, two oxygen atoms per formula unit have to correspond to hydroxy groups but the accuracy of the P–O bond distances is too low to further precisely define their assignments. The complete ionic formula of the phase should therefore be given as $[Ga(PO_4H)_2F]^{2-} \cdot [N_2C_6H_{14}]^{2+}$.

Ga(PO₄H)₂F·[N₂C₆H₁₄] is a 1D compound that consists of the infinite macroanions $[Ga(PO_4H)_2F]^{2-}$ (shown in Fig. 2), whose charges are balanced by doubly protonated DABCO molecules. The backbone of the chain consists of GaO₄F₂ octahedra connected by their F vertices. The octahedron is fairly regular, with Ga–O distances ranging from 1.95(2) to 2.00(2) Å and the two nonequivalent Ga–F distances being both equal to 1.97(2) Å. It should be noted that the bond and angle constraints used are sufficiently relaxed to allow

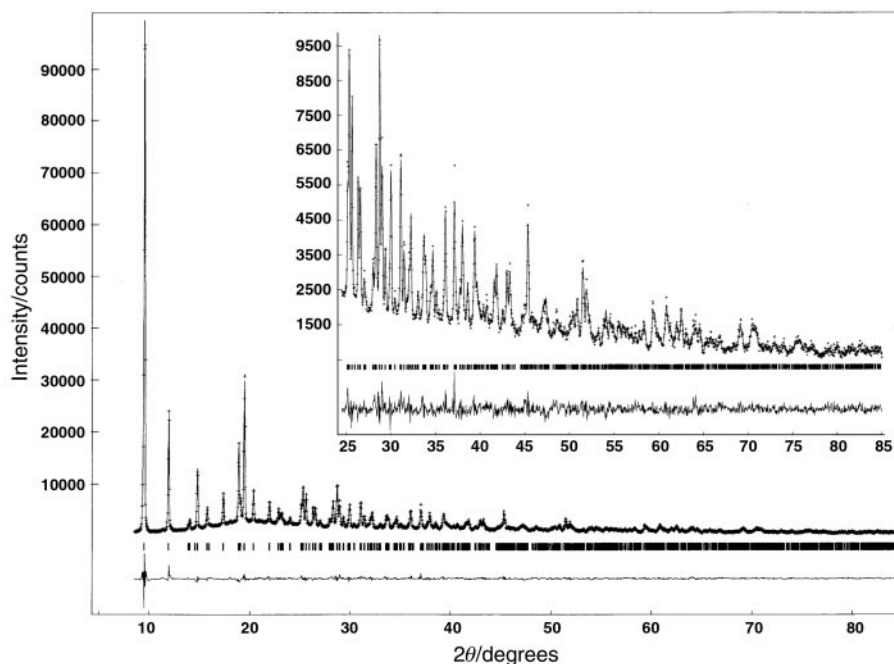


Fig. 1 Observed, calculated and difference powder X-ray diffraction pattern of $\text{Ga}(\text{PO}_4\text{H})_2\text{F}\cdot[\text{N}_2\text{C}_6\text{H}_{14}]$ (Cu- K_α radiation). Insert: high-angle part of the patterns, magnified $6\times$.

significant excursion from the prescribed values. For example, constraining the Ga–O distance to be 1.90 Å instead of 1.95 Å does not change the observed bond lengths. The observed regularity of the gallium coordination sphere is therefore not strictly imposed *a priori*. The resulting Ga–F chain is not linear, with Ga–F–Ga = $129.3(7)^\circ$ and F–Ga–F = $169.2(4)^\circ$. Successive octahedra are thus tilted in opposite directions and are linked together by two PO_4 tetrahedra. The equatorial oxygen atoms of the octahedra are thus all bonded to phosphorus atoms (see Fig. 2). The resulting chains run along the *c* axis and are roughly packed in a pseudo-hexagonal manner, as $b/a = 0.93$ [$(\sqrt{3})/2$] (see Fig. 3).

In order to differentiate between oxygen atoms and hydroxy groups, we employed bond valence sum³⁸ (BVS) calculations. BVS are of limited accuracy when applied to a structure determined from powder diffraction data because of the inherent imprecision of bond distances. Nevertheless, BVS calculations

Table 2 Atomic coordinates for non-hydrogen atoms for $\text{Ga}(\text{PO}_4\text{H})_2\text{F}\cdot[\text{N}_2\text{C}_6\text{H}_{14}]$

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ga1	0.7483(4)	0.9854(3)	0.5783(7)
P1	0.6819(5)	0.7921(7)	0.852(2)
P2	0.8917(5)	0.8712(6)	0.300(2)
F1	0.702(1)	0.963(1)	0.321(3)
O1	0.578(1)	0.792(1)	0.862(3)
O2	0.714(1)	0.835(1)	0.652(3)
O3	0.705(1)	0.674(1)	0.875(3)
O4	0.716(1)	0.861(1)	0.026(3)
O5	0.861(1)	0.921(1)	0.490(3)
O6	0.873(1)	0.956(1)	0.145(3)
O7	0.832(1)	0.767(1)	0.258(3)
O8	0.993(1)	0.842(1)	0.307(4)
N1	0.854(2)	0.608(2)	0.765(5)
N2	0.992(2)	0.543(3)	0.583(5)
C1	0.832(2)	0.584(3)	0.564(6)
C2	0.915(2)	0.561(2)	0.451(4)
C3	0.018(2)	0.643(3)	0.693(6)
C4	0.929(2)	0.689(2)	0.764(6)
C5	0.964(2)	0.455(3)	0.718(5)
C6	0.884(2)	0.497(3)	0.831(5)

Isotropic atomic displacement parameters: $B(\text{Ga}) = B(\text{P}) = 1.9(1) \text{ \AA}^2$; $B(\text{F}) = B(\text{O}) = 1.6(2) \text{ \AA}^2$; $B(\text{C}) = B(\text{N}) = 6.2(5) \text{ \AA}^2$.

confirm here that the gallium, phosphorus and non-terminal oxygen atoms have essentially expected valences. Hence, the two protons necessary to balance the charges are likely to be bonded to the terminal oxygen atoms O1, O3, O7 or O8. We can assume that those two hydroxy groups are not bonded to the same phosphorus atom. Since O3 is hydrogen bonded to N1, and O1 and O8 interact with each other with $\text{O1}\cdots\text{O8} = 2.38(2) \text{ \AA}$, we can postulate that the two protons are bonded to O1 and O7 (see Fig. 4). An extensive network of

Table 3 Selected bond lengths (Å) and angles ($^\circ$) for $\text{Ga}(\text{PO}_4\text{H})_2\text{F}\cdot[\text{N}_2\text{C}_6\text{H}_{14}]$

Ga(1)–O(2)	1.95(2)	Ga(1)–O(5)	1.95(2)
Ga(1)–O(4)	1.96(2)	Ga(1)–O(6)	2.00(2)
Ga(1)–F(1)	1.97(2)	Ga(1)–F(1)'	1.97(2)
P(1)–O(1)	1.55(1)	P(1)–O(2)	1.59(1)
P(1)–O(3)	1.47(1)	P(1)–O(4)	1.56(1)
P(2)–O(5)	1.54(1)	P(2)–O(6)	1.52(1)
P(2)–O(7)	1.57(1)	P(2)–O(8)	1.55(1)
N(1)–C(1)	1.49(1)	N(1)–C(4)	1.48(1)
N(1)–C(6)	1.49(1)	N(2)–C(2)	1.49(1)
N(2)–C(5)	1.48(1)	N(2)–C(3)	1.48(1)
C(1)–C(2)	1.50(1)	C(3)–C(4)	1.51(1)
C(5)–C(6)	1.51(1)		
F(1)–Ga(1)–O(2)	91.8(8)	F(1)–Ga(1)–O(5)	87.4(8)
F(1)–Ga(1)–F(1)'	169.2(4)	F(1)–Ga(1)–O(4)	92.7(7)
F(1)–Ga(1)–O(6)	87.0(7)	O(2)–Ga(1)–O(5)	86.7(7)
O(2)–Ga(1)–F(1)'	99.9(8)	O(2)–Ga(1)–O(4)	175(1)
O(2)–Ga(1)–O(6)	91.4(7)	O(5)–Ga(1)–F(1)'	94.4(8)
O(5)–Ga(1)–O(4)	94.4(8)	O(5)–Ga(1)–O(6)	174.0(9)
F(1)–Ga(1)–O(4)	76.6(7)	F(1)–Ga(1)–O(6)	91.4(6)
O(4)–Ga(1)–O(6)	87.9(7)	Ga(1)–F(1)–Ga(1)'	129.3(7)
O(1)–P(1)–O(2)	110(1)	O(1)–P(1)–O(3)	103.6(9)
O(1)–P(1)–O(4)	106(1)	O(2)–P(1)–O(3)	110(1)
O(2)–P(1)–O(4)	115.7(9)	O(3)–P(1)–O(4)	110(1)
O(5)–P(2)–O(6)	108.1(9)	O(5)–P(2)–O(7)	108(1)
O(5)–P(2)–O(8)	110(1)	O(6)–P(2)–O(7)	107(1)
O(6)–P(2)–O(8)	110(1)	O(7)–P(2)–O(8)	112.3(9)
C(1)–N(1)–C(4)	107(3)	C(1)–N(1)–C(6)	101(3)
C(4)–N(1)–C(6)	111(2)	C(2)–N(2)–C(5)	107(2)
C(2)–N(2)–C(3)	114(3)	C(3)–N(2)–C(5)	108(3)
N(1)–C(1)–C(2)	111(3)	N(1)–C(4)–C(3)	115(2)
N(1)–C(6)–C(5)	112(2)	N(2)–C(3)–C(4)	104(3)
N(2)–C(2)–C(1)	109(3)	N(2)–C(5)–C(6)	109(2)

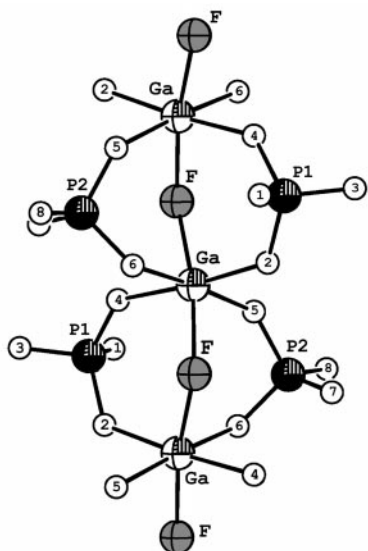


Fig. 2 Representation and atom numbering of the $[\text{Ga}(\text{PO}_4\text{H})_2\text{F}]^{2-}$ tancoite-type macroanion (small numbered spheres: oxygen atoms). Drawing software: ORTEP3 for Windows.³⁶

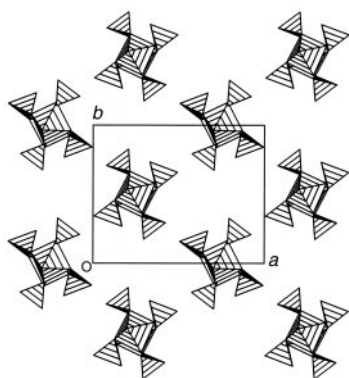


Fig. 3 Polyhedral representation of the inorganic chains down the *c* axis. Drawing software: STRUPLO.³⁷

hydrogen bonds thus contributes to the cohesion of the compound through chain–chain and chain–template interactions. The shortest interchains distance is $\text{O}1\cdots\text{O}8 = 2.38(2) \text{ \AA}$ and shows that every chain is directly linked to its four nearest neighbors by $(\text{O}-\text{H})\cdots\text{O}$ bonds. The ammonium groups of the template also interact strongly with the chains, with $\text{N}1\cdots\text{O}3 = 2.48(3) \text{ \AA}$ and $\text{N}2\cdots\text{O}6 = 2.77(3) \text{ \AA}$; the DABCO molecules therefore also link adjacent chains together. The interactions between the chains and with the template molecules are schematically shown in Fig. 4. The fluorine atoms are marginally involved in hydrogen bonding with the amine, with $\text{F}\cdots\text{N}2 = 3.18(3) \text{ \AA}$; similar distances $\text{F}\cdots\text{N} = 3.0 \text{ \AA}$ are found in $\text{GaF}(\text{HPO}_4)_2\cdot\text{N}_2\text{C}_3\text{H}_{12}$.⁸

$\text{Ga}(\text{PO}_4\text{H})_2\text{F}\cdot[\text{N}_2\text{C}_6\text{H}_{14}]$ has moderate thermal stability. TGA–DTA measurements under flowing oxygen show an abrupt weight loss of about 10 wt% with an onset at 250 °C, which likely corresponds to the loss of the hydroxy groups and the beginning of decomposition of the template. This first step is followed by a continuous weight loss until a plateau is reached around 1000 °C. The total loss is 44 wt% whereas the DABCO molecules represent only 29 wt% of the compound mass, which indicates that part of the inorganic moiety has also evolved. The end-product at 1100 °C is a glass which was not further characterized.

Only three other organically templated GAPOs of the tancoite type have been reported so far and they were all

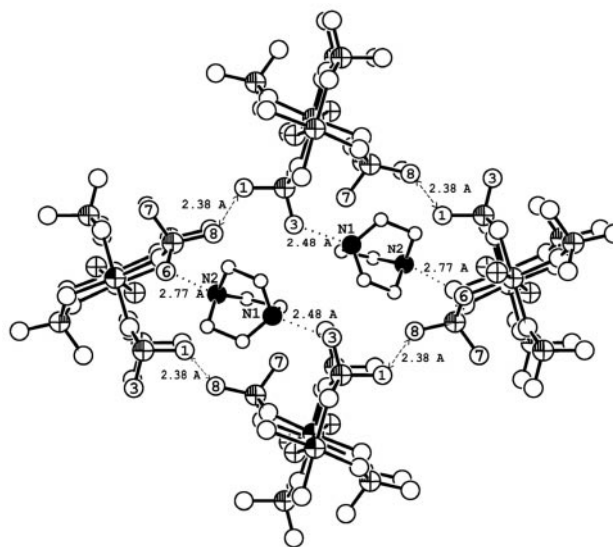


Fig. 4 Hydrogen bonding in $\text{Ga}(\text{PO}_4\text{H})_2\text{F}\cdot[\text{N}_2\text{C}_6\text{H}_{14}]$. Hydrogen atoms omitted for clarity.

synthesized under milder conditions than those employed here (120 °C^{8,9} or even room temperature⁷). The use of distinctly different reaction conditions to synthesize compounds with essentially the same structure type is somewhat surprising and warrants further exploration of the phases of phosphate based zeotypes.

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References

- 1 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146.
- 2 A. K. Cheetham, G. Férey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268.
- 3 J. L. Guth, H. Kessler and R. Wey, *Stud. Surf. Sci. Catal.*, 1986, **28**, 121.
- 4 Q. Kan, P. Glasser and R. Xu, *J. Mater. Chem.*, 1993, **3**, 983.
- 5 R. E. Morris and S. J. Weigel, *Chem. Soc. Rev.*, 1997, **26**, 309.
- 6 F. C. Hawthorne, *Tschermaks Mineral. Petrogr. Mitt.*, 1983, **31**, 121.
- 7 R. I. Walton, F. Millange, A. Le Bail, T. Loiseau, C. Serre, D. O'Hare and G. Férey, *Chem. Commun.*, 2000, 203.
- 8 R. I. Walton, F. Millange, D. O'Hare, C. Paulet, T. Loiseau and G. Férey, *Chem. Mater.*, 2000, **12**, 1977.
- 9 H.-M. Lin and K.-H. Lii, *Inorg. Chem.*, 1998, **37**, 4220.
- 10 T. Loiseau, F. Serpaggi and G. Férey, *Chem. Commun.*, 1997, 1093.
- 11 A. M. Chippindale, A. D. Bond, A. D. Law and A. R. Cowley, *J. Solid State Chem.*, 1998, **136**, 226.
- 12 K.-H. Lii and S.-L. Wang, *J. Solid State Chem.*, 1997, **128**, 21.
- 13 F. Bonhomme, R. Maxwell and T. M. Nenoff, 2001, manuscript in preparation.
- 14 F. Bonhomme, S. G. Thoma, M. A. Rodriguez and T. M. Nenoff, *Chem. Mater.*, 2001, **13**, 2112.
- 15 F. Bonhomme, S. G. Thoma, M. A. Rodriguez and T. M. Nenoff, *Microporous Mesoporous Mater.*, 2001, in press.
- 16 R. W. Cheary and A. A. Coelho, *J. Appl. Crystallogr.*, 1992, **25**, 109.
- 17 P. M. de Wolff, *J. Appl. Crystallogr.*, 1972, **5**, 243.
- 18 P. E. Werner, L. Eriksson and M. Westdahl, *J. Appl. Crystallogr.*, 1985, **18**, 367.
- 19 D. Schwartzbach, [LATCON] Xtal3.7 System, ed. S.R. Hall, D.J. du Boulay and R. Olthof-Hazekamp, University of Western Australia, 2000.

- 20 A. Le Bail, H. Duroy and J. Fourquet, *Mater. Res. Bull.*, 1988, **23**, 447.
- 21 J. A. Rodriguez-Carvajal, in *Collected Abstracts of Powder Diffraction Meeting*, Toulouse, France, 1990, p.127.
- 22 *International Tables for Crystallography, Volume A*, ed. T. Hahn, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1995.
- 23 J. Krumhansl, personal communication, 2000.
- 24 A. Altomare, M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Rizzi, *J. Appl. Crystallogr.*, 1999, **32**, 339.
- 25 A. Altomare, M. C. Burla, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni and G. Polidori, *J. Appl. Crystallogr.*, 1995, **28**, 842.
- 26 A. Altomare, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
- 27 A. Le Bail, Structure Determination from Powder Diffraction-Database, 1994-2001; <http://www.cristal.org/iniref.html>
- 28 A. Jouanneaux, *CPD Newslett.*, 1999, **21**, 13.
- 29 A. V. Chavez, T. M. Nenoff, L. Hannooman and W. T. Harrison, *J. Solid State Chem.*, 1999, **147**, 584.
- 30 G. M. Sheldrick, *SHELX97 Programs for Crystal Structure Analysis (Release 97-2)*, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
- 31 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
- 32 (a) A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34; PLATON, A Multipurpose Crystallographic Tool, A. L. Spek, 1998, Utrecht University, Utrecht, The Netherlands.
- 33 W. A. Dollase, *J. Appl. Crystallogr.*, 1986, **19**, 267.
- 34 G. Cagliotti, A. Paoletti and F. P. Ricci, *Nucl. Instrum.*, 1958, **3**, 223.
- 35 J. F. Bézar and G. Baldinozzi, *J. Appl. Crystallogr.*, 1993, **26**, 128.
- 36 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.
- 37 R. X. Fischer, *J. Appl. Crystallogr.*, 1985, **18**, 258.
- 38 N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B*, 1991, **47**, 192.