Synthesis and X-Ray Structural Characterization of a Novel Oxyfluorinated Microporous Gallium Phosphate with Encapsulated 1,4-Diazabicyclo[2.2.2]octane as the Template: $Ga_3(PO_4)(HPO_4)_2F_3(OH)\cdot C_6N_2H_{14}\cdot 0.5\ H_2O$

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A gallophosphate with an open framework is synthesized; its structure consists of interconnecting $Ga_2O_7\Phi F_2$ (Φ = O or OH) bioctahedra and PO_4 tetrahedra, building up a three-dimensional network around a novel ($3^{12}6^48^8$) cage type, enclosing two 1,4-diazabicyclo[2.2.2]octane organic templates and leading to eight-membered channels along [001], six- and eight-rings along [101] and [010], the water molecule being located in the latter.

Since 1982, a new series of microporous aluminophosphates ($AlPO_4$-*n*) has been synthesised[1] by using organic molecules as templates. Replacement of aluminium by gallium in the framework led to a variety of phases,[2] some of which are analogous to aluminophosphates.[3–5] The addition of fluoride ions to the reaction medium induces mineralization[6] and leads to microporous compounds with new geometries.[7,8] We report here the synthesis in the presence of fluoride ions and the X-ray structure of a gallophosphate $Ga_3(PO_4)(HPO_4)_2F_3(OH)\cdot C_6N_2H_{14}\cdot 0.5\ H_2O$.

The title compound was synthesized hydrothermally by using 1,4-diazabicyclo[2.2.2]octane (DABCO) as the template. The aqueous mixture with the molar ratio: 2 GaO(OH) : 1 P_2O_5 : 2 HF : 2 DABCO : 80 H_2O was placed in a stainless-steel autoclave lined with Teflon and heated at 180 °C for 24 h. The pH, initially *ca.* 3–4 rises to 5–6 at the end of the reaction. An experiment carried out with a longer reaction time (7 days) led to a mixture of the title compound together with $GaPO_4$-C_7.[9] The crystalline product was filtered off, washed with water and dried at room temperature. A suitable single crystal was obtained to determine its structure† by X-ray diffraction. The corresponding phase with aluminium was also synthesized, but no single crystal has been obtained so far for a complete characterization by X-ray diffraction.

The main originality of the framework is the existence of edge shared dimeric $Ga_2O_7\Phi F_2$ (Φ = O or OH) octahedral entities, the common edge corresponding to two fluorine atoms. These dimers are linked to each other either by phosphorus tetrahedra or by hydroxy groups. The polyhedra have the following average interatomic distances: P–O: 1.53, Ga–O: 1.92 and Ga–F: 1.99 Å. The anomalously large Ga–F distances (compared with the mean distance 1.90 Å encountered in gallium fluorides[10]) correspond to the existence of O–H···F or N–H···F hydrogen bonds, which leads to an increase in the Ga–F distances from valence-bond considerations. P(2) and P(3) tetrahedra exhibit a larger P–O distance (1.596 and 1.572 Å, respectively), which corresponds to hydroxy group from valence-bond analysis.

The three-dimensional framework is built up of 2-D nets, stacked along [101]. These sheets (Fig. 1), composed of three-, six- and eight-membered rings are formed by intercon-

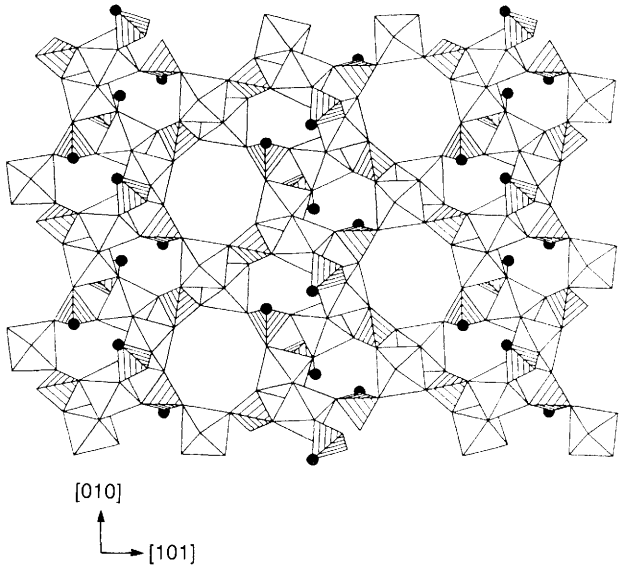

Fig. 1 Polyhedra drawing of a sheet onto (101) plane, showing the interconnection of the gallium octahedra (non-hatched polyhedra) and the phosphorus tetrahedra (hatched polyhedra) forming the three-, six- and eight-membered rings. Black circles indicate terminal oxygens (corresponding to hydroxy group) belonging to HPO_4 tetrahedra; the sheets on both sides of this layer are linked by the free remaining corner of these tetrahedra.

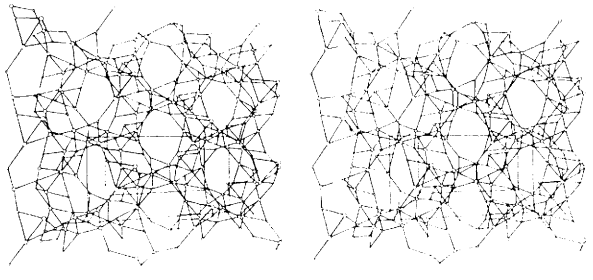

Fig. 2 Stereoview plot of $Ga_3(PO_4)(HPO_4)_2F_3(OH)\cdot C_6N_2H_{14}\cdot 0.5\ H_2O$ framework along the *c* axis. Each line represents a branch connecting two nodes occupied by either gallium atom (large circle) and phosphorus atom (small circle) or two gallium atoms (only one branch is drawn for the Ga–F–Ga bonds). Amine templates and water molecules are omitted for clarity.

† *Crystal data* for $Ga_3(PO_4)(HPO_4)_2F_3(OH)\cdot C_6N_2H_{14}\cdot 0.5H_2O$: monoclinic system, space group *C*2/*c*; a = 17.983(2), b = 9.859(2), c = 19.840(3) Å, β = 106.24(1)°, V = 3377.3(3) Å^3, Z = 8, M_r = 693.17, D_c = 2.726 g cm^{-3}, μ(Mo-Kα) = 51.1 cm^{-1}, λ = 0.71069 Å, graphite monochromator, crystal dimensions: 0.038 × 0.076 × 0.266 mm. The data were collected on a Siemens AED-2-four-circle diffractometer in the range $0 < 2\theta \leq 65°$. A total of 5905 reflections were measured of which 2846 unique reflections with $|F| \geq 6\sigma(|F|)$ were considered. The data were corrected for Lorentz-polarisation and absorption effects. The structure was solved by direct methods analysis (SHELXS-86): the gallium and phosphorus atoms were first located and all the remaining non-hydrogen atoms were found by difference Fourier map. Only one hydrogen atom was found in the final difference Fourier map and corresponds to the hydroxy group of the formula. Refinement (281 variables) was performed by full-matrix least-squares analysis (SHELX-76), with anisotropic thermal parameters for all non-hydrogen atoms. The final Fourier residue of 4.5 e Å^{-3} near the water molecule (1.70 Å) was not assigned and it might be due to the disordered localisation of the water molecule, as shown by the strong thermal parameters in the direction of the residue. The reliability factors converge to R_w = 0.051, R = 0.049. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

nection of zig-zag chains of gallium bioctahedra along [010] with isolated gallium bioctahedra *via* phosphorus tetrahedra. The eight-membered ring is a strict alternation of gallium and phosphorus atoms, while the six-membered ring shows the Ga-P-Ga*-Ga*-Ga-P alternation. The asterisks correspond to the gallium octahedra linked by fluorine edge. The three-rings contain a gallium bioctahedral entity together with a HPO_4 tetrahedron. In the chains, the bioctahedra are bound together by hydroxy groups as described above. The sheets are connected by the remaining free corner of HPO_4 tetrahedra to form the 3-D framework.

Topologically, the three-dimensional framework builds up cages limited by twelve 3-rings, four 6-rings and eight 8-rings (Fig. 2). Two organic amine templates (DABCO), which are assumed to be protonated twice to balance the excess of negative charge from the framework, are trapped in the cavities. This novel topology, with overall ($3^{12}6^{4}8^{8}$) connectivity, generates channels bounded by 8-rings along [001], 6- and 8-rings along [101] and [010]. A water molecule is at the centre of the 8-rings of the channels running along [010].

In summary, an oxyfluorinated microporous gallophosphate has been synthesized. The framework consists of dimeric $Ga_2O_7\Phi F_2$ (Φ = O or OH) octahedral entities with phosphorus tetrahedra leading to a novel ($3^{12}6^{4}8^{8}$) cage with two enclosed 1,4-diazabicyclo[2.2.2]octane organic templates, and to the interconnection of three types of 8-rings channels.

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