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Azamacrocycle-Containing Gallium Phosphates: A New Class of Inorganic−Organic Hybrid Material

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The ever increasing need for new materials, and in particular new porous materials, has meant that gallium phosphate-based solids have attracted a great deal of interest over the past few years. In this paper we report the synthesis and structural characterization, using synchrotron X-ray diffraction on a very small crystal, of a novel type of inorganic−organic hybrid gallium phosphate. This material has features common to many microporous solids such as zeolites and aluminum phosphates. However, rather than having an organic templating molecule bound weakly to a wholly inorganic framework, as is normally the case, this material features an azamacrocyclic complex incorporated into the structure through covalent bonds.

Since the discovery of the aluminophosphate molecular sieves,[1] numerous new phosphate-based materials have been reported. The gallium phosphate family of solids has proved a particularly rich source of new compounds, especially since the discovery that fluoride ions are effective mineralizers in this system.[2,3] Some of these materials have structural analogues in the AlPO and zeolite families, for example, the GaPO version of zeolite-A,[4] while others have entirely new structural architecture, such as the ultra large pore cloverite.[5] The scope for the preparation of new phases in the GaPO system is exemplified by two groups; Férey et al. have prepared a series of gallium phosphates, designated ULM-*n*, which have displayed novel pore architectures and some interesting templating effects,[6] and Galen Stucky and co-workers have reported a number of new gallium phosphate-based materials with transition metals, such as cobalt, zinc, and manganese, in the frameworks.[7] Here we report the synthesis of a new type of gallium phosphate synthesized in the presence of 1,4,8,11-tetraazacyclotetradecane (CYCLAM). Rather than acting as a template, the CYCLAM is incorporated into the structure to form a novel type of inorganic−organic hybrid. Hybrids of this kind have many attractive features stemming from the possibility of using well-known organic reactions to modify the properties of the solid. Other classes of hybrid material, such as the metal phosphonates, are of increasing interest in many fields of chemistry, and their potential has been recognized in catalysis, ion exchange, charge storage and many other areas. These solids show great promise for future applications.[8,9]

A sample of CYCLAM−GaPO, $GaPO_4(OH)_2F\cdot Ga(C_{10}N_4H_{24})$, was prepared by a hydrothermal-type synthesis with pyridine as the solvent and hydrofluoric acid as the source of fluoride ions. Gallium sulfate (0.8 g) and CYCLAM (0.25 g) were slurried in pyridine and stirred vigorously. To this mixture phosphoric acid and HF (40% in pyridine, 0.2 g) were added to give a gel with the approximate composition P_2O_5:Ga_2O_3:70 pyridine:HF:0.5 CYCLAM. The pH was adjusted to 5 with trimethylamine (40% in H_2O, 3 mL), aged at 25 °C for 1 h, transferred to a Teflon-lined stainless steel autoclave, and heated at 135 °C under autogenous pressure for 72 h. The product was retrieved by suction filtration and washed with water and acetone to reveal small colorless crystals.

The crystals were too small (max. size 30 × 30 × 15 μm) for single-crystal X-ray data collection with a standard laboratory four-circle diffractometer, so diffraction data were collected at low temperature (160 K) with a Bruker AXS SMART CCD area-detector diffractometer on the high-flux single-crystal diffraction station 9.8 at CCLRC Daresbury Laboratory Synchrotron Radiation Source, Cheshire, UK.[10] The structure of CYCLAM−GaPO is closely related to that of many molecular sieve materials.[4,5,7] The structures of zeolites and aluminophosphates are described in terms of primary building units (the TO_4 tetrahedra), and secondary building units, such as four rings, six rings, and double four rings, etc., which are combinations of four, six, and eight TO_4 tetrahedra, respectively. The basic structural motif in CYCLAM−GaPO is a double four ring (D4R) unit, similar to that seen in many important molecular sieves (Figure 1).[11] As is often the case for gallium phosphates synthesized with fluoride ions as mineralizing agents, the X-ray diffraction experiment reveals a fluorine atom sited within the double four ring. This feature is present in cloverite and several of the ULM series of compounds where the fluorine atom has been reported at the exact center of the cage, or displaced toward either three or two of the gallium atoms.[5,6] In this case, the fluorine lies closer to two of the gallium atoms, making relatively long contacts of 2.286 (2) Å. The bond angles around these two gallium atoms are distorted away from the tetrahedral toward those that would be expected for trigonal bipyramidal gallium, indicating that the fluorine atoms are close enough to affect the position of the oxygen atoms. In contrast, the O−Ga−O bond angles around the other two gallium atoms remain closer to their ideal tetrahedral values.

The double four ring units are linked through the oxygens of two GaO_4 and two PO_4 tetrahedra into planar layers, which are perpendicular to the (100) direction of the unit cell (Figures 1 and 2). The sheets have 10 tetrahedral atom ring windows defined by four D4R units. This arrangement of double four ring units is reminiscent of that seen in the cobalt aluminum phosphate

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[10] Crystal data for CYCLAM−GaPO: unit cell $a = 13.2558(5)$ Å, $b = 10.4321\ (5)$ Å, $c = 18.4382(9)$ Å, $V = 2549.7(2)$ Å^3 at $T = 160$K, space group *Pbcn*, $\rho_{calcd} = 2.542$ g cm^{-3}; 14162 integrated intensities ($2.48° < \theta < 28.08°$), 2891 unique, 2693 observed [$F^2 > 2\sigma(F^2)$]; final refinement (192 least-squares parameters) converged to $wR(F^2_{obsd\ data}) = 0.1214$, $R(F_{obsd\ data}) = 0.0407$, $S(F^2_{all\ data}) = 1.066$,.

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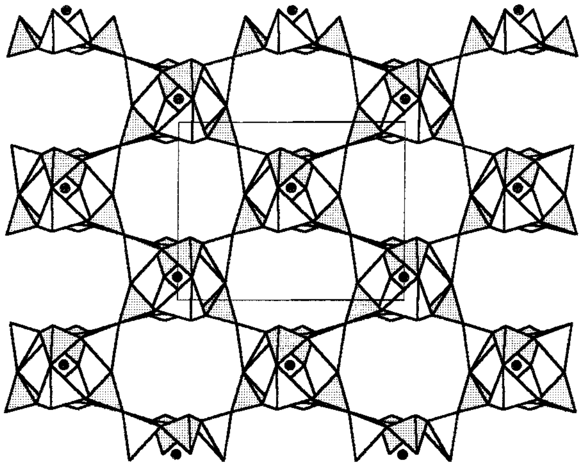

Figure 1. One layer of D4R units viewed parallel to the (100) direction. The 10-ring windows in the layers, defined by four D4Rs, can be clearly seen. The fluorine atom present inside the D4R is shown as a dark sphere. GaO_4 and PO_4 tetrahedra are shown as shaded and unshaded polyhedra, respectively.

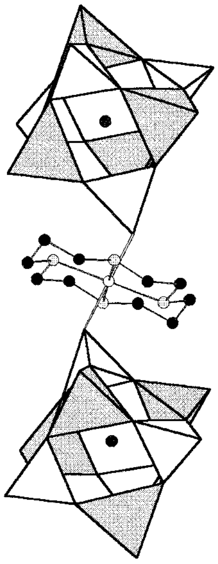

Figure 2. The gallium−CYCLAM complex links two D4R units from adjacent layers. For clarity, the hydrogen atoms on the macrocycle ligand have been omitted. The polyhedra are depicted as in Figure 1.

structure, ACP-1, recently reported by Stucky and co-workers.[7] However, rather than the double four rings being linked together into a three-dimensional zeolite-like structure, the layers in CYCLAM−GaPO are joined together by a six-coordinate gallium CYCLAM complex, four of the six coordination sites around the gallium are taken by the four nitrogen atoms from the macrocycle, while the other two are taken by oxygen atoms from PO_4 tetrahedra of D4R units in adjacent layers (Figures 2 and 3). Two of the oxygen atoms connected to gallium atoms in the D4R units do not coordinate to any other atom, and from bond valence and charge balancing considerations these have been assigned as hydroxyl groups. The CYCLAM complex adopts the Trans III conformation, which is the most thermodynamically favored for this system.

On heating in nitrogen, CYCLAM−GaPO is stable up to ∼500 °C when it undergoes a substantial weight loss, presumably caused by removal of the organic part of the material. The residue is amorphous when studied with X-ray diffraction. The structure of CYCLAM−GaPO can be considered similar to many of the other gallium phosphate materials in the literature, where the organic part, in this case the azamacrocycle, of the structure effectively fills any void space in the solid while being impossible to remove without causing collapse of the inorganic framework. Laboratory powder X-ray diffraction (XRD) on the CYCLAM−GaPO sample indicates that there is a small amount of impurity phase present in the bulk. However, the thermogravimetric analysis cannot be quantified exactly in terms of the expected weight loss for this material, because of the presence of a larger amount of impurity than that seen from the XRD. Elemental analysis (C, H, N) indicates the presence of carbon, hydrogen, and nitrogen in the correct ratios, but as a smaller absolute weight percentage, for the CYCLAM−GaPO materials, indicating that the impurities are probably a mixture of crystalline and amorphous $GaPO_4$ phases.

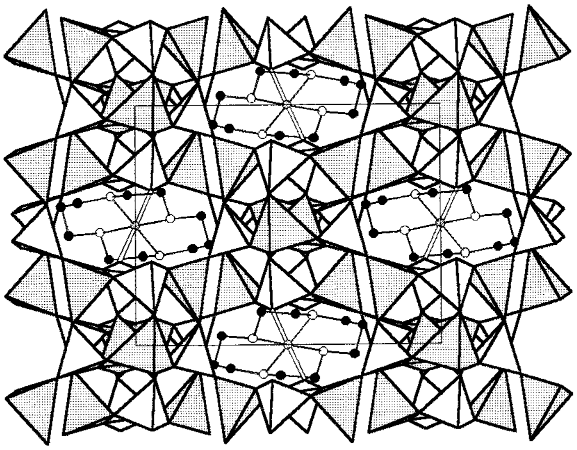

Figure 3. A view of CYCLAM−GaPO parallel to the (100) direction. The polyhedra are depicted as in Figure 1.

The unusual nature of this structure opens up many possibilities for the chemical modification of this type of material in order to target specific applications. The synthesis of CYCLAM−GaPO was accomplished in “one-pot” with use of the free macrocycle. However, preparation of metal−azamacrocycle complexes prior to the synthesis would enable, for example, transition metals to be incorporated into these materials, with possible consequences for catalysis and other applications. The versatility in the azamacrocycle ligand, in terms of the possibility of functionalizing the ring, could also be used to prepare solids of different compositions and structural architectures.

In conclusion, this work reports the synthesis and characterization of a new inorganic-hybrid material incorporating features similar to important molecular sieve materials as well as an azamacrocycle complex. The work illustrates the possibility of preparing new types of solid that combine the attractive features of inorganic frameworks with the versatility of organic functional groups.

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Supporting Information Available: A listing of refinement details, atomic coordinates, thermal displacement parameters, and bond lengths and angles (11 pages, print/PDF). See any current masthead page for ordering information and Web access instructions. Supporting information is also available in CIF format.

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