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Anionic Gallium Phosphate Double Four-Ring Units Containing Occluded Oxygen

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Microporous solids, such as the aluminosilicate zeolites and aluminum/gallium phosphates are important materials, with applications in catalysis, ion exchange and gas separation, and are increasingly being studied as host species for nanochemistry. The utility of all microporous solids is intimately connected with their structural architecture, and thus ability to control the structure of these types of materials is an important goal in today's chemical research. Our research focuses on attempts to understand the synthesis of gallium phosphate materials more fully, with an ultimate goal of being able to target specific architectures.

There have been recent reports that fluoride ions play a major role in specifically templating the formation of gallium phosphate materials that contain the double four-ring unit (D4R, Figure 1).[1] These D4R units are found in a number of different microporous material structures and have been described in several gallium phosphate materials such as cloverite,[2] ULM-5,[3] ULM-18,[4] MU-15,[1] and cyclam-GaPO[5] among others. The feature in common in all these gallium phosphate species is that the D4R unit has a fluoride unit occluded at its center. No empty gallium phosphate D4R units, or units containing elements other than fluoride, have yet been reported. The large number of structures containing this unit adds weight to the postulation that the fluoride acts to "template" (i.e., preferentially form) the D4R species. However, in this contribution we report the first synthesis of a gallium phosphate D4R unit containing occluded oxygen. Surprisingly, similar synthetic procedures containing fluoride failed to form materials containing the D4R unit.

The cuboidal D4R unit is an attractive unit to target because of its rigid three-dimensional shape. It is interesting to note that if a material contains only D4R units, and is linked through all eight of the corners to other D4R units, the resulting structure is geometrically limited to the ACO topology first reported by Stucky and co-workers.[6] Other topologies would only be produced when the D4R is present in association with other SBUs or the framework is interrupted (i.e., not fully condensed). Surprisingly, considering the wide range of gallium phosphates containing the D4R unit, none so far reported has the ACO structure.

The combination of "templated" D4R units and the geometrical constraints on how these units are able to condense led us to believe that this system provided an opportunity for the designed synthesis of an ACO framework with a composition that had not previously been prepared. Our goal at the beginning of this work was then to prepare gallium phosphate materials that contained only the D4R unit and identify the conditions under which this occurred. Assuming that the solid phase would be formed on full condensation, then this material would have the ACO topology. This synthetic strategy is different from the normal preparative techniques for open framework materials, which make use of organic templating molecules to direct the channel structure of the resulting solid. In this case, the pore structure is determined not by the size or shape of any guest species but by the geometric constraints of linking the cuboidal D4R units together.

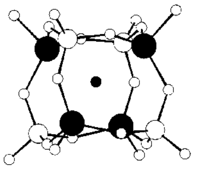

Figure 1. The D4R unit found in [pyr,O]-GaPO-4. Large shaded and open spheres are gallium and phosphorus, respectively. Small spheres are oxygen. The central oxygen is shown as a shaded sphere.

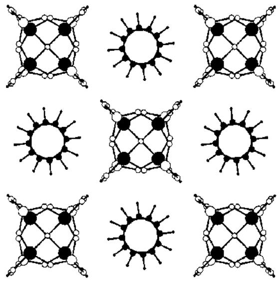

Figure 2. The structure of [pyr,O]-GaPO-4 solved from laboratory X-ray diffraction showing the arrangement of double four-ring units to form channels in the structure where pyridinium cations reside.

The oxygen occluded D4R unit, designated [pyr,O]-GaPO-4 ($[H_8Ga_4P_4O_{21}](C_6H_5NH)_2$), was prepared by a solvothermal synthesis using a mixture of pyridine and water as the solvent. Phosphoric acid (2 mL 85% weight solution in water, Aldrich) was diluted with 2 mL of distilled water, and to this 0.5 g of gallium sulfate (99.9%, Aldrich) was added with stirring, followed by 8 mL of pyridine (99%, Fischer), giving an approximate gel composition of Ga_2O_3:P_2O_5:8 pyridine:8 H_2O. The mixture (approximate pH 6) was stirred for 30 min to allow homogenization of the gel and transferred to a Teflon-lined stainless steel autoclave, which was heated at 150 °C for 72 h. The product, a crop of tiny colorless crystals, was recovered by suction filtration, washed with water and acetone, and dried at 40 °C.

Single-crystal X-ray diffraction (SCXRD) data were collected in St. Andrews using a Rigaku AFC7S four-circle diffractometer (Cu Kα radiation) and at the high-flux microcrystal diffraction facility (station 9.8) of the synchrotron radiation source (SRS), Daresbury. Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were collected by the EPSRC solid-state NMR service, Durham, UK, on a Varian Unity 300 300 MHz spectrometer.

The structure was initially solved using a laboratory single-crystal X-ray diffractometer.[7] It shows an ionic structure containing discrete $[H_8Ga_4P_4O_{21}]^{2-}$ anions (Figure 1) hydrogen-bonded into an open structure (Figure 2) with the charge balanced by pyridinium cations. The oxygen atom at the center of the D4R was found using difference Fourier techniques. The model is consistent with the MAS NMR reported below. However, close inspection of the structural model indicated quite large thermal displacement parameters on a number of the oxygens, which indicated possible disorder/twinning. Subsequent X-ray diffraction experiments carried out using the high flux single-crystal X-ray

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(7) Crystal data for [pyr,O]-GaPO-4 ($[H_8Ga_4P_4O_{21}](C_6H_5NH)_2$. Unit cell a = 13.016 (3) Å, c = 7.356 (4) Å, V = 1246.2 (8) Å^3 at T = 293K, Z = 2, tetragonal spacegroup $I\text{-}42m$, ρ_{calcd} = 2.48 g cm^{-3}. 562 integrated intensities (4.8° < θ < 60.14°, λ = 1.54178 Å), 302 unique, 265 observed [$F^2 > 2\sigma(F^2)$]. Final refinement (59 least-squares parameters) converged to $wR(F^2_{\text{observed data}})$ = 0.195, $R(F_{\text{observed data}})$ = 0.070, $S(F^2_{\text{all data}})$ = 1.089.

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diffraction station 9.8 at the synchrotron Radiation Source, Daresbury, UK, indicated that the structure could be described using a larger unit cell,[8] indicated by the presence of weak super cell reflections. The structure solution using this unit cell gave a disordered model, with two D4R units of different orientations present. This model is not consistent with the NMR as it requires more than one phosphorus environment, and therefore, the correct description of the structure is probably a complicated twin of several domains, each having different orientation with respect to the others. However, no simple twin law could be resolved, and the final refinement was carried out using the original model. Despite the twinning of the structure, the presence of D4R units is clearly illustrated by the experiments.

The ^{31}P MAS NMR experiments show one resonance at 4.0 ppm (together with a small amount of impurity, which is due to the berlinite $GaPO_4$ phase). The resonance for the fluoride-encapsulated D4R anions prepared by Patarin and co-workers is around −4.0 ppm; no such resonance is visible in this spectrum. To ensure that no fluoride was present from accidental contamination a ^{19}F spectrum was taken, which confirmed no fluorine was present.

An interesting feature of this type of anion is the location of the protons. For fluoride-encapsulated D4R units in the layered material ULM-18, it has been shown very elegantly by NMR[4] and by recent quantum chemical modeling[9] that there is a proton associated with the fluoride inside the D4R. In the case of the structure reported here, the ^{15}N MAS NMR spectrum shows only one resonance at −182 ppm, indicating that all of the pyridine molecules in the material are protonated, as would be expected given the synthesis conditions used. There are two pyridinium cations per D4R unit, and thus each D4R must have an overall charge of −2. This can be fulfilled by either eight protons on the external oxygen atoms of the D4R, or seven on the exterior and one inside, or six on the exterior and two inside. Fluoride and hydroxide have been shown to occupy the same crystallographic sites in the same structure,[10] and thus one might expect there to be an equivalence between the two inside the D4R units. This would mean that OH^- or OH_2 would be the most likely species to be encapsulated. Taulelle and co-workers have also postulated that the presence of protons inside the D4R units plays an important part in the nucleation and crystal growth of these types of materials.[9] Further experiments, are ongoing to differentiate between the possible models.

The structure itself shows a quite clear relationship to the ACO framework that is the target structure in this work in that each D4R unit is bonded to eight other D4Rs. In this case however, they are connected to each other purely by hydrogen bonds, leading to a more open structure, but one that has essentially the same connectivity. Because of the geometry of the hydrogen bonds, however, the spatial orientation of the D4R units with respect to each other is different, leading to a one-dimensional structure rather than a three-dimensional one. Unsurprisingly, the solid is not thermally stable, the structure collapsing at temperatures as low as 200 °C. The structure is also closely related to a number of materials containing the fluoride-occluded D4R unit[11] and to an iron phosphate D4R material.[12] Interestingly, the ^{31}P NMR spectra reported in one of these papers[11a] shows an unidentified resonance at about ∼3.9 ppm, indicating that there may possibly be some of the oxygen-occluded D4R present in this material.

Attempts to dissolve [pyr,O]-GaPO-4 in water were unsuccessful. However, the solid does dissolve in basic media (aqueous KOH). ^{31}P NMR of the resulting solution showed one peak, shifted only slightly downfield from that seen in the solid, indicating that the D4R units are probably still intact. This species can then be regarded as a soluble analogue of the D4R unit, similar to the phosphonate cages reported by Roesky.[13]

The synthetic procedure was repeated, but this time fluoride ions were added to the mixture, and a number of synthetic conditions (pH, temperature, water content, crystallization time) were varied over a wide range. The preparations produced three different fluoride-containing gallium phosphate materials, including an analogue of UT-6[14] a closely related phase,[15] and a known structure previously published by Weigel et al.[16] None of these phases, however, contained the D4R building unit. This raises some questions over the causal nature of the occluded atom in forming the D4R units. The results would tend to imply, completely against the conventional wisdom that has grown up surrounding these materials, that fluoride ions do not template the D4R unit and may even preferentially form other subunits at the expense of the D4R, at least under the conditions reported here.

This work reports the first example of a gallium phosphate D4R containing occluded oxygen. The fact that in the presence of fluoride this material cannot be prepared has important implications regarding the role of the occluded atom in forming the D4R unit. This may be useful in the future design of materials from such molecular precursors.

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Supporting Information Available: Listings of refinement and structural details in CIF format. This material is available free of charge at http://pubs.acs.org.

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[8] The supercell was $a = 18.3247$ (8) Å, $c = 14.6191$ (9) Å, $V = 4909.01$(4) Å^3 at $T = 150$ K. The structure could be solved in spacegroup I-4*c*2, with two disordered orientations of the D4R unit.

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