

Synthesis, crystal structure and ^{71}Ga MAS NMR spectroscopy of a novel gallium phosphatooxalate: $[\text{Ga}_5(\text{OH})_2(\text{C}_{10}\text{H}_9\text{N}_2)(\text{C}_2\text{O}_4)(\text{PO}_4)_4]\cdot 2\text{H}_2\text{O}$

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The synthesis and characterization of a novel three-dimensional gallium phosphatooxalate is described; the structure consists of GaO_4 tetrahedra and GaO_6 octahedra linked by phosphate and oxalate groups to form two-dimensional sheets between which are GaO_4N square pyramids, generating tunnels in which the monoprotonated 4,4'-bipyridine molecules reside; ^{71}Ga MAS NMR confirms the presence of four-, five- and six-coordinate Ga atoms.

Open-framework materials have been the subject of intense research owing to their diverse structural chemistry and potential applications as ion-exchangers, catalysts and adsorbents.^{1–3} Many of these materials are synthesized in the presence of an organic amine as structure-directing agent.^{4–7} The organic moieties are usually accommodated in the structural voids, and in some cases can be removed by calcination or other treatments. In addition to the use of organic templates for preparing large-pore 3-D networks, the incorporation of organic multidentate ligands into the structure also creates a new route to open-framework materials. Advantages of using multidentate components can be realized by the enhancement in the thermal stability of the structure and the efficacy of rational design of crystalline solids through their coordinating propensities and geometries.⁸ Recently, many research activities have focused on the synthesis of inorganic/organic hybrid materials; we have synthesized some interesting three-dimensional organically templated iron and indium phosphates.^{9,10} There is equal interest in synthesizing 3-D GaPOs containing large apertures. Here, we report the synthesis and structural characterization of an inorganic/organic hybrid material, $[\text{Ga}_5(\text{OH})_2(\text{C}_{10}\text{H}_9\text{N}_2)(\text{C}_2\text{O}_4)(\text{PO}_4)_4]\cdot 2\text{H}_2\text{O}$ **1**. Its unique framework structure is built up from three different types of gallium–oxygen polyhedra, oxalate and phosphate groups, forming channels in which the monoprotonated 4,4'-bipyridine molecules are located. ^{71}Ga solid state NMR has been applied to study the different coordination environments for gallium.

In a typical hydrothermal synthesis, a mixture of Ga_2O_3 , 2-methylpiperazine, 4,4'-bipyridine, $\text{C}_2\text{H}_2\text{O}_4\cdot 4\text{H}_2\text{O}$, H_3PO_4 and H_2O in a molar ratio of 1 : 3 : 3 : 5 : 5 : 444 was sealed in a Teflon-lined acid digestion bomb and heated at 165 °C for 3 days under autogeneous pressure followed by slow cooling at 10 °C h⁻¹ to room temperature. The resulting product consists of pale yellow plate-shaped crystals of **1** obtained in 69% yield based on Ga. A suitable pale yellow crystal was carefully selected for structure determination by single-crystal X-ray diffraction.† The product is monophasic as judged by the total consistency of its powder X-ray diffraction pattern with that simulated from the atomic coordinates derived from the single-crystal X-ray study. Elemental analysis confirmed its stoichiometry. (Anal. Found: C, 13.89; H, 1.44; N, 2.70. Calc.: C, 13.81; H, 1.45; N, 2.68%.) We have also carried out retro-syntheses and replaced 2-methylpiperazine with tetramethylammonium hydroxide; the resulting products are either monophasic with a very low yield or a mixture of **1** and a small amount of unidentified orange side product. Thermogravimetric analysis data in air for **1** showed a broad weight loss in several overlapping steps which begins gradually at 180 °C, has a maximum rate at ca. 450 °C and is

incomplete by 975 °C. The final decomposition product is mainly GaPO_4 (JCPDS: 31-0546). The weight loss in the initial step can be attributed to the loss of water molecules in the structural channels. The framework structure is stable up to 350 °C in air, as indicated from powder X-ray diffraction.

The three-dimensional framework of **1** consists of anionic sheets made of GaO_4 tetrahedra and GaO_6 octahedra connected via coordinating PO_4^{3-} and $\text{C}_2\text{O}_4^{2-}$ anions, and bridging GaO_4N square pyramids that interlink the sheets. The layer constructed from phosphates, oxalate and two types of Ga–O polyhedra in the *bc*-plane is shown in Fig. 1. Each GaO_4 tetrahedron is coordinated to four phosphate tetrahedra of which two connect one GaO_4 and two GaO_6 polyhedra in the same sheet while the other two connect one GaO_4 , one GaO_6 and the bridging GaO_4N . Oxalate anions act as bis-bidentate ligands to two Ga(1) and form dimers of GaO_6 octahedra.

The coordination by the oxalate leads to a distorted octahedron for Ga(1), as indicated by the wide range of Ga–O bond lengths [1.887(3)–2.057(4) Å] and the O–Ga–O bond angle [81.5(1)°] subtended by the oxalate group. Connectivity between the dimers is via $\text{P}(1)\text{O}_4^{3-}$ and GaO_4N . Bond-valence calculations indicate that the bridging atom, O(11), between GaO_6 and GaO_4N is a hydroxo oxygen. The Ga(1)–O(11)–Ga(3) bond angle is 134.9(2)°. GaO_4N square pyramids, positioned in between the layers, join the GaO_6 and $\text{P}(2)\text{O}_4^{3-}$ from different layers, generating two types of tunnels parallel to the [001] direction (Fig. 2). Monoprotonated 4,4'-bipyridine cations are accommodated in the 12-membered void while the water molecules are located in the 8-membered channel. Ga(3) sits on a twofold axis and is bonded to four oxygens in the basal plane [Ga–O 1.869(4) Å (2×), 1.943(4) Å (2×)] and one nitrogen at the vertex [Ga–N 2.024(7) Å]. The two rings of 4,4'-bipy are twisted at an angle of 35.1°.

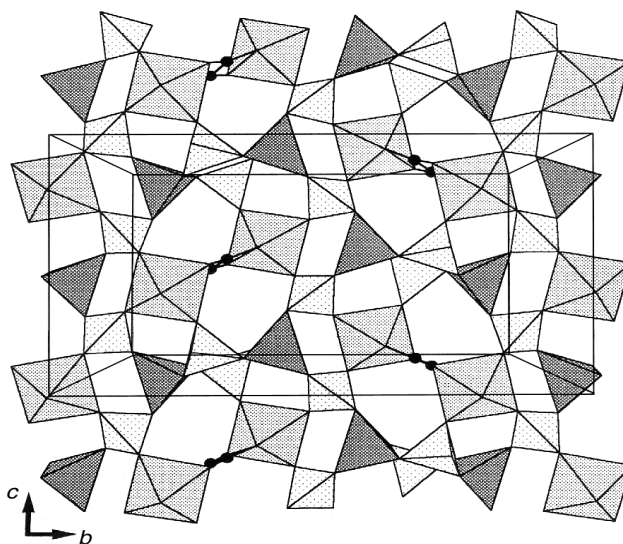


Fig. 1 Section of a sheet in **1** showing the connectivity among the Ga–O polyhedra, phosphate and oxalate anions. GaO_6 octahedra are medium grey, GaO_4 tetrahedra are dark grey and PO_4 tetrahedra are light grey. Solid circles are the carbon atoms of oxalate groups.

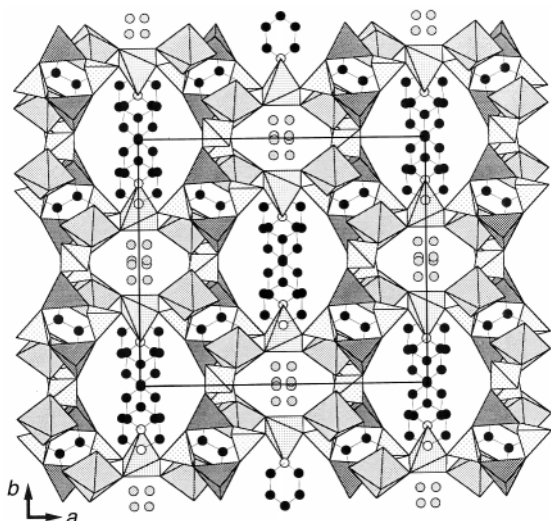


Fig. 2 Structure of **1** viewed along the [001] direction. Polyhedra with decreasing shading: GaO₄ tetrahedra, GaO₆ octahedra, GaO₄N square pyramids and PO₄ tetrahedra. Solid circles, C atoms; open circles, N atoms; stippled circles, water oxygen atoms.

The most interesting structural feature of **1** is the presence of GaO₆ octahedra, GaO₄N square pyramids and GaO₄ tetrahedra. In other microporous gallium phosphates, most frameworks are composed of some combinations of four-, five- or six-coordinate gallium atoms and PO₄ tetrahedra. Rb₂[Ga₄(HPO₄)₄·0.5H₂O] and GaPO₄-14 are the other two examples in which gallium atoms have mixed four-, five- and six-coordination.^{11,12} Because there is little known on solid state Ga NMR owing to intrinsic experimental difficulties,¹³ it would be of great interest to investigate the correlation between the ⁷¹Ga NMR of **1** and the structure. Fig. 3 shows the ⁷¹Ga NMR spectrum (*I* = 3/2, *ν* = 121.84 MHz) with spinning rate of 12000 Hz and a single 45° pulse (a hard *B*₁ = 120 kHz is used). Chemical shifts were measured relative to the [Ga(H₂O)₆]³⁺ ion in a gallium nitrate solution. Because there is a linear correlation between ²⁷Al and ⁷¹Ga NMR chemical shifts in isostructural Al and Ga compounds,¹⁴ the resonances at δ 116.4 and 94.0 correspond to tetrahedrally and octahedrally coordinated gallium, respectively. Interestingly, an additional resolved band at δ 66.8 is evident. We can compare the NMR spectrum of **1** with the ⁷¹Ga MAS NMR of [Ga₄(C₁₀H₉N₂)₂(PO₄)(H_{0.5}PO₄)₂(HPO₄)₂(H₂PO₄)₂(H₂O)₂·H₂O **2**,¹⁵ where X-ray structure analysis shows only octahedral and tetrahedral gallium. Two bands at δ 94.0 and 116.4 were observed for **2**, while no band below δ 90 is evident. Therefore, we conclude that the resonance at δ 66.8 corresponds to the five-coordinate gallium (GaO₄N square pyramid). To our knowledge solid state NMR of five-coordinate gallium has not been documented previously. The splitting in the band at δ 116.4 reflects the residual line shape originated

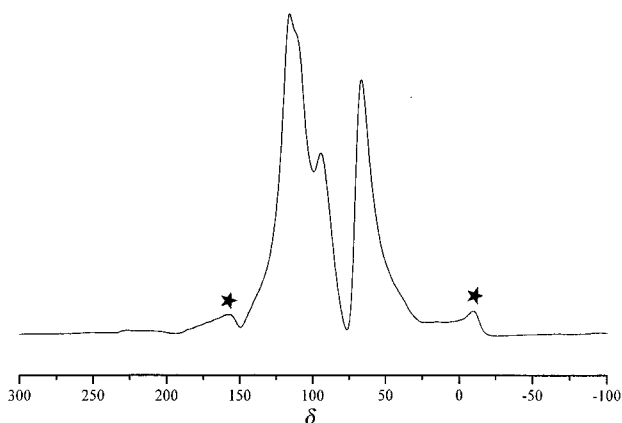


Fig. 3 ⁷¹Ga MAS NMR spectrum for **1**. Asterisks denote spinning side bands.

from the second order quadrupolar interaction associated with the large electric field gradient (efg) in the GaO₄ unit. By contrast, both GaO₆ and GaO₄N moieties show relatively smaller efg values. The large upfield shift for five-coordinate gallium is believed to be due to the strong shielding by directly bonded nitrogen.

In summary, this work illustrates that a novel gallium phosphatooxalate with a framework structure is synthesized hydrothermally and structurally characterized by single-crystal X-ray diffraction and ⁷¹Ga MAS NMR spectroscopy. There is a good correspondence between the NMR spectrum and the structure.

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Notes and references

† X-Ray intensity data were collected on a Siemens SMART CCD diffractometer in 1271 frames with ω scans (width 0.30° and exposure time of 20 s per frame).

Crystal data for [Ga₅(OH)₂(C₁₀H₉N₂)(C₂O₄)(PO₄)₄]·2H₂O: monoclinic, space group *C2/c*, *a* = 18.3430(2), *b* = 15.9372(4), *c* = 9.1019(2) Å, β = 90.867(1)°, *U* = 2660.5(1) Å³, *Z* = 4, *M_r* = 1043.74, *D_c* = 2.606 g cm⁻³, μ (Mo-K α) = 53.5 cm⁻¹, λ = 0.71073 Å, graphite monochromator, crystal dimensions 0.135 × 0.045 × 0.009 mm. Of the 2902 unique reflections collected ($2\theta_{\max}$ = 56°, *R*_{int} = 0.0466), 2187 reflections were considered observed [*F*_o > 4 σ (*F*_o)] after empirical absorption correction (*T*_{min/max} = 0.826/0.942). Bond-valence calculations indicated that both Ga atoms are trivalent, O(11) had a valence sum of 1.24, and all other phosphate oxygens had values close to 2. The value for O(11) indicates that it is a hydroxo oxygen. The H atom was found in difference Fourier maps. Two lattice water sites, O(w1) and O(w2), were located in the structural tunnel. Both water oxygens initially showed very large thermal parameters. If the occupancy of O(w) is refined, the site occupancy factors obtained are 0.56(2) for O(w1) and 0.45(2) for O(w2), indicative of a half occupancy of the water of crystallization. The water hydrogens were not located. The 4,4'-bipyridine ligand acts as a monodentate ligand to Ga. To balance charge, the N atom which is not coordinated to Ga is protonated. The H atom which appears to be disordered over two positions, which are symmetry related by a twofold axis, is not included in the refinement. All other H atoms in 4,4'-bipyridine were located. Least-squares refinement (240 parameters) was performed with anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic thermal parameters (*U* = 0.05 Å²) for all H atoms. ($\Delta\rho$)_{max,min} = 0.79, -0.97 e Å⁻³. The reliability factors converged to *R*₁ = 0.0410, *wR*₂ = 0.0921 and *S* = 1.072.

CCDC 182/1316. See <http://www.rsc.org/suppdata/cc/1999/1473/> for crystallographic files in .cif format.

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